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Australasian Polymer Symposium **33**

12-15 February 2012
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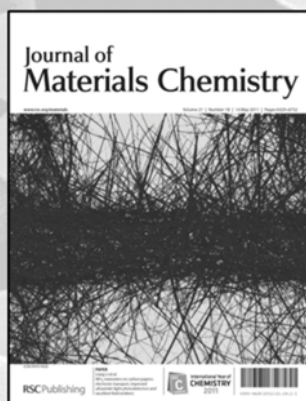
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33APS Organisation

33APS Chair	Sébastien Perrier
33APS Organising Committee	The Polymer Division of the Royal Australian Chemical Institute (RACI), Ramon Tozer IP/C Program
33APS Secretariat	Leishman Associates, Hobart
33APS Sponsorship	Natasha Stagg, Leishman Associates
Treloar Prize	Kevin Jack



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Julian Curwen and Ramon Tozer will be attending the Symposium, and they look forward to seeing you in Hobart.

Please feel free to drop by the **Intellectual Property Café** to ask them any questions about intellectual property or simply to have a complimentary coffee and a chat.



**Julian
Curwen**

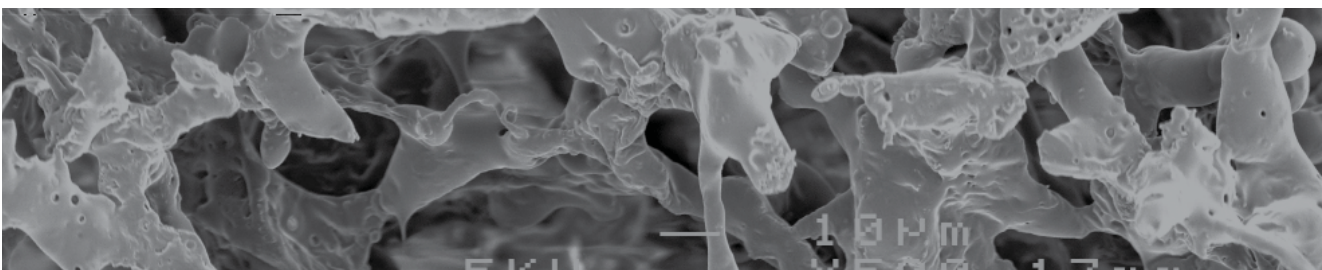


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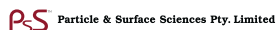
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Dear colleagues,

On behalf of the Royal Australian Chemical Institute (RACI) Polymer Division, I welcome you to the 33rd Australasian Polymer Symposium (33APS) here at Wrest Point Convention Centre in Hobart.

We have compiled an exciting program covering all areas of polymer science and engineering, including synthesis, characterisation, processing, modeling and materials. A large number of sessions will also cover topics at the interface between polymer science and other disciplines that address a range of important issues faced by our modern society, for instance in medicine, energy and the environment. Such a varied programme shows how multidisciplinary polymer science has become, and how collaborations across fields are the best approach to tackle today's challenges. I am very impressed by the large number of collaborative papers that will be presented over the next few days.

Over the years, the APS has developed a strong reputation for bringing together the latest polymer research from top international and Australian polymer scientists. This year, we will again welcome a number of leading Plenary and Keynote Speakers from around the world, and also a very large number of contributors, over 300, to what promises to be another exciting forum. The programme also includes a number of special sessions. In addition to our now regular Early Career Researchers session on Tuesday morning, we have introduced a new session on Innovation in the afternoon. It will cover the very dynamic topic of knowledge transfer from academia to industry, with talks from experts from both academia and the private sectors. In addition to a packed programme of oral presentations, I am very much looking forward to the poster session on Monday night. This year again, the posters are of great quality, and the session is an excellent opportunity for networking.

I would like to extend a particular welcome to our invited speakers and to our delegates who contribute to the success of 33APS through their presentations and posters. An especially warm welcome goes to our delegates from overseas, who have travelled long distances to take part in the meeting. This year again, the ratio of international delegates is nearly a third of our total delegate number, which shows that APS is now truly an international event.

Traditionally, APS has always focused on early career researchers, and in particular students and postdocs. I would like to welcome you all to the meeting. Young researchers are key to our discipline, and I am very pleased to see that students are making more than the third of our total delegate numbers. Despite becoming a large international event, APS has clearly not lost its original focus!

The reputation of APS goes further than great science; it is also famous for its warm and convivial atmosphere. This year again, we have a busy social schedule, with a welcome reception on Sunday night in one of the best wineries in Tasmania, a special Student Night on Tuesday following the Polymer Division AGM, and the Symposium Dinner on Wednesday night, organised at Wrest Point.

Contributing to the success of 33APS are also all our sponsors, whose details you can find in these pages. We are very grateful to them for their support. You will have plenty of opportunities to meet with our trade exhibitors in the main meeting room throughout the conference.

For those who do not formally belong to the RACI and / or the Polymer Division, I encourage you to join, become active and especially get on the Polymer Division mailing list, so you can keep up with the goings on in our community. Come and find out more about the Polymer Division at the AGM on Tuesday night! The Polymer Division champions our discipline in Australia and internationally through conferences, regular meetings, lecture tours, etc. We also have a number of awards for early career and established researchers, for which I strongly encourage nominations; statistics show that 100% of the winners were nominated! Please also visit our website for further information (<http://www.polymer.org.au>).

Finally, 33APS is focusing on being environmentally friendly in 2012. For instance, the conference bag you are using is made from bamboo, one of the world's fastest growing plants, a renewable resource and biodegradable material. In addition, unless if you pre-ordered a hard copy of the book of abstracts, proceedings will be supplied to each delegate on a USB stick.

Welcome to Hobart and to the 33rd Australasian Polymer Symposium. I hope you enjoy the meeting and find it a great opportunity to discuss science, strengthen existing collaborations and start new ones.

Sébastien Perrier

33APS Convenor
Chair of the
Polymer Division
of the RACI



The host organization for 33APS is the Polymer Division of the Royal Australian Chemical Institute. Unprofessional conduct breaches the inherent principle of the RACI Code of Ethics (By-Law 26, in particular section 26.2). It has no place at any time, especially at conferences or other meetings of the RACI. Unprofessional conduct includes sexual harassment and discrimination in respect to sex, race, creed and sexual preference or status. The unprofessional conduct may be verbal, written or implied.

The Polymer Division of the RACI expect delegates and members to conduct themselves in a professional manner at all times. The Organising Committee in turn is committed to present and manage 33APS in a professional way.

Substantive complaints against RACI members and other professional organisations will be referred to the RACI Executive Council for action under By-Law 26 or for other recommended action as appropriate.

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- Competitive advantages by providing the new polymeric materials required for sustainability and high technology developments and growth in manufacturing, biotechnology, agriculture, mining and energy.
- Significant overseas exports and licensing income from the Centre's global exploitation of technologies, aided by the global market reach of some industrial participants.
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RACI Polymer Division - an Outline

Website: <http://www.polymer.org.au/>

The Royal Australian Chemical Institute maintains a strong involvement in polymer science and technology through the national Polymer Division, as well as through the RACI State Branches (which in NSW, Queensland, South Australia and Victoria have active Polymer Groups), and a special liaison with the New Zealand Institute of Chemistry Polymer Group. The Polymer Division concentrates on national and international activities, whilst the Polymer Groups focus on local activities. The Polymer Division is coordinated by a standing committee – it is elected at the General Meeting held at each Australasian Polymer Symposium; the Chairpersons of the State Polymer Groups are ex-officio members of the Polymer Division Committee.

The RACI Polymer Division was formed in 1964 with the objective of advancing the theory and practice of polymer science in Australia. Prior to this, the Polymer Group of the Victorian Branch took the initiative, with a National focus, and was responsible for organising the first three Polymer symposia in Australia. As a result, there is some debate as to which was the “first” APS, with legitimate claims by the 1957 Adelaide, 1964 Mildura and the 1966 Canberra conferences. Since the latter was the first conference following the formation of the Polymer Division, it has been designated 1APS and used to number all subsequent Symposia. More information on the history of the Polymer Division can be found at the Division web site (<http://www.polymer.org.au/index.php/home/history>).

Even though the Polymer Division is part of a Chemical Institute, the Division has always looked beyond the chemistry of polymers and takes a broader view to encompass chemical, physical and engineering aspects of polymers. This is reflected in the name Polymer Division, which does not include the word “chemistry” and was chosen to demonstrate the dedication to polymer science. A feature of the Polymer Division’s activities has been the participation of chemists, physicists, engineers, mathematicians and biologists with an interest in polymers. Polymer Division meetings bring together industrialists and academic and government polymer scientists and technologists from all over Australasia and from overseas.

While the most visible activity of the Polymer Division are the Australasian Polymer Symposia (APS), which are held every 12–18 months, the Division is also the focal point for international interactions and was a foundation member of the Pacific Polymer Federation, which brings together scientists from Japan, Australia, New Zealand, United States of America, South East Asia and many other Pacific nations. The first Pacific Polymer Congress was held in Hawaii in 1989, followed by Japan in 1991, Brisbane, Australia in 1993, Hawaii in 1995, Korea in 1997, China in 1999, Mexico in 2001, Thailand in 2003, Hawaii again in 2005, Kobe in 2007, and Cairns, Australia in 2009 and organized by the Australian RACI Polymer Division. The leadership demonstrated in this area has resulted in the Polymer Division remaining a key entity in world polymer science and has resulted in the cosponsorship of many conferences held around the world and the encouragement of polymer science in developing Pacific Rim countries.

The Division is also a strong supporter of student development, the future of the Division, through the subsidised attendance and participation at national conferences from early stages of degrees. As a means of achieving this objective, the Division provides financial assistance to postgraduate students to allow them to attend Polymer Division symposia and provides the Treloar prizes at each APS for the best paper and poster presented by a polymer scientist under the age of thirty.

Additionally, the Division is a sponsor and supporter of the Polymer Summer School (in conjunction with the CRC for Polymers and the Key Centre for Polymer Colloids). It also fosters student development by subsidising travel to related conferences and specialist symposia, usually in collaboration with the State Polymer Groups.

The Division also sponsors the Australian Polymer Students' Forum, attended by young polymer scientists from around the country. The format includes students giving overviews of their own and of their group's research, along with talks by representatives of industry, academia and government. This forum enables research students to interact scientifically and to start the networking that is an essential part of effective science and technology. The absence of supervisors is a vital component for the success of these meetings!

The Polymer Division provides a range of other services for the Australasian polymer community, including a directory of Polymer Science and Engineering in Australasia, which lists scientists and research establishments, and web pages providing information on polymer science activities in Australia and New Zealand.

The RACI Polymer Division has a number of prestigious awards – see <http://www.polymer.org.au/index.php/home/awards>. The most distinguished is the Australian Polymer Medal for eminence in Australian Polymer Science. In 1992 the Australian Polymer Science & Technology Achievement Award, now called the David Sangster Polymer Science & Technology Achievement Award, was created to recognize the achievement of Australian polymer scientists while their careers are still developing (age limit of 40). Citations are also awarded at Australasian Polymer Symposia for significant service and contributions in any aspect of polymer science, technology or education.

There are also awards to encourage young polymer scientists. As already mentioned, Treloar Prizes are awarded for the best presentations at each APS by scientists under the age of 30. The inaugural O'Donnell Young Scientist Award was made at 21APS. This is for a PhD student to undertake a short attachment to another University to perform research towards the PhD, and is given in recognition of the longstanding support and encouragement of young polymer scientists by the late Prof James O'Donnell of the University of Queensland. Prof O'Donnell's vision for polymer scientists in Australia provided many tangible benefits to young Australian polymer scientists, such as reduced conference registration fees, travel subsidies and prizes. This has resulted in increased student participation in the Division at all levels, and consequently in an increased profile in the national and international polymer community.

In 2000 the Division initiated a lecture series aimed at bringing a prominent scientist to the major polymer centres in Australia between APS meetings. It was decided to name the series after David Solomon, recently of the University of Melbourne, in recognition of his long-standing and continuing leadership in the Polymer Division. It was also deemed appropriate that he should also be the inaugural lecturer of the series named after him.

A complete list of the activities and services is included in the Division's webpage (www.polymer.org.au). The Polymer Division welcomes suggestions of new initiatives and participation in the organisation of them. Of greatest importance, at all of its meetings the Polymer Division provides an excellent means by which professionals in the field of polymer science can extend their scientific experience and interact with a large group of their professional colleagues.

RACI Polymer Division

Standing Committee 2011 - 2012

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Student Representative

Nathan Boase University of Queensland
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Dr Marion Gaborieau
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School of Biomedical and Health Science
University of Western Sydney
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Queensland State Representative

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Centre for Advanced Imaging/
Australian Institute for Bioengineering
and Nanotechnology
University of Queensland
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Fax: +61 7 3365 3833
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Victoria State Representative

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Department of Chemical and Biomolecular
Engineering
The University of Melbourne
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Fax: +61 3 8344 4153
gregghq@unimelb.edu.au

South Australia State Representative

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Flinders University
Bedford Park
SA 5041
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Fax: +61 8 8201 5571
milena.ginic-markovic@flinders.edu.au

NZIC Polymer Group

Professor Greg Russell
University of Canterbury
Christchurch, NZ
Phone: +64 3 364 2458
Fax: +64 3 364 2110
greg.russell@canterbury.ac.nz

RACI Polymer Division Meetings

Australasian Polymer Symposia

APS YEAR	VENUE	DIVISION CHAIR
	1957 Adelaide	D O Jordan
	1963 Mildura	D H Solomon
	1964 Mildura	B S Harrup
1	1966 Canberra	F W Ayscough (with 3rd Nat. Conv.)
2	1968 Canberra	D H Solomon (with Aust. Biochem. Soc.)
3	1969 Sydney	H J Battaerd (with 22nd IUPAC Conf.)
4	1970 Canberra	D O Jordan (with 4th Nat. Conv.)
5	1971 Mildura	M J Jordan
6	1973 Broadbeach	J H O'Donnell
7	1974 Canberra	J H Bradbury (with 5th Nat. Conv.)
8	1975 Terrigal	I C Watt
9	1977 Tanunda	P E M Allen
10	1978 Surfers Paradise	B A Bolto (with 6th Nat. Conv.)
11	1980 Lorne	C E M Morris
12	1981 Blackheath	D F Sangster
13	1982 Canberra	D R G Williams (with 7th Nat. Conv.)
14	1984 Ballarat	G B Guise
15	1986 Leura	D H Napper
16	1987 Philip Island	R A Shanks
17	1989 Brisbane	D J T Hill
18	1990 Bendigo	E Rizzardo
19	1992 Perth	G M Ferguson
20	1995 Adelaide	H K Toh
21	1996 Wollongong	M Binns (Division Chair); G Spinks (Conf. Chair)
22	1997 Auckland (NZ)	R Gilbert (Division Chair); R Cooney (Conf. Chair)
23	1999 Geelong	W D Cook
24	2001 Beechworth	G Moad
25	2002 Armidale	T P Davis
26	2003 Noosa	A K Whittaker
27	2004 Adelaide	D A Lewis
28	2006 Rotorua (NZ)	G T Russell
29	2007 Hobart	C Barner-Kowollik
30	2008 Melbourne	G P Simon
31	2009 Cairns	(with PPC11) M Stenzel (Division Chair); A Whittaker (Conf. Chair)
32	2011 Coffs Harbour	M Stenzel

YEAR	VENUE	TITLE
1968	Melbourne	Australian Polymer Workshop
1969	Sydney	Residential Polymer Studies School
1971	Adelaide	Tailor Made Molecules
1973	Sydney	Natural and Synthetic Fibres
1975	Melbourne	Polymer Degradation
1976	Warburton	Polymer Degradation
1977	Warburton	Ion Radicals in Growth and Development
1978	Sydney	Polymer Identification and Characterisation
1979	Warburton	Adhesion and Adhesives
	Leura	Polymer Education
1980	Melbourne	Adhesion Science and Technology
1981	Melbourne	Polymer Materials Science
1983	Melbourne	Structure Property Relationships in Synthetic Polymers
	Melbourne	Transitions and Relaxations in Synthetic Polymers
	Melbourne	Poly(Vinyl Chloride)
	Melbourne	Patents in Chemical Industry and Research (with Institute of Patent Attorneys)
	Canberra	Aust. Polymer Discussion Group: Free Radical Polymerization
1984	Sydney	Polymers as Materials
	Melbourne	Polymers as Materials
	Melbourne	Deformation, Failure and Strengthening of Polymers (with Materials Engineering, Monash University)
	Sydney	Chemistry and Physics of Elastomers
	Canberra	Polymerization: Polymer Degradation (Australian Polymer Discussion Group)
1985	Melbourne	POLYMER 85: Characterisation and Analysis of Polymers (with IUPAC, AAA, AATS)
	Melbourne	Characterisation and Flow of Rheologically Complex Liquids (with Chemical Engineering, Melbourne University)
	Sydney	Electrical, Optical and Acoustic Properties of Polymers (with Physics, Macquarie University)
	Canberra	Polymerization: Mechanical Properties (Australian Polymer Discussion Group)
1986	Sydney	Emulsion Polymers and Latexes
		Brisbane Controlled Release Technology (with Australian Pharmaceutical Science Association)
	Canberra	Polymerization: Kinetics & Mechanism (Australian Polymer Discussion Group)

1987	Philip Island Noosa	Thermal Characterisation of Polymeric Materials Radiation Effects on Polymeric Materials (with ACS Polymer Chemistry Division)
	Sydney	Copolymerisation (with 8th Nat. Conv.)
	Canberra	Polymer Spectroscopy (Australian Polymer Discussion Group)
1988	Melbourne	Controlled Release: Science and Technology
1989	Brisbane	Modern Methods for Characterisation of Polymers (with Division of Analytical Chemistry)
	Maui	Pacific Polymer Congress (organised by the Pacific Polymer Federation)
	Honolulu	Pacificchem
1991	Melbourne	Polymer Materials Preparation, Characterisation, Properties (at POLYMER 91; with IUPAC, AAS, AATS)
	Japan	Third Pacific Polymer Congress
1992	Melbourne	RACI 9th National Convention
	Perth	Polymers in Medicine
1993	Canberra	Aust. Polymer Discussion Group: Polymer Networks
	Brisbane	4th Pacific Polymer Congress
1994	Canberra	Aust. Polymer Discussion Group: Adhesion and Advanced Adhesives
1995	Adelaide	RACI 10th National Convention (Thermal Analysis)
	Kauai	5th Pacific Polymer Congress
1996	Wollongong	Polymer Reaction Engineering Workshop
	Canberra	Aust. Polymer Discussion Group: Polymer Toughening
1997	Canberra	Aust. Polymer Discussion Group: Polymer Dynamics
	Seoul	6th Pacific Polymer Congress
1998	Gold Coast	Macro 98 (IUPAC World Polymer Congress)
1999	Coburn	Thermal Characterisation of Polymers
2001	Beechworth	Biomaterials (with Aust Society of Biomaterials)
2002	Armidale	Living Polymer Radical Polymerisation

In addition, the Polymer Division has part sponsored the Radiation Chemistry Conferences organised by the Australian Institute for Nuclear Science and Engineering, held at Lucas Heights every two years from 1972.

Australasian Polymer Students' Forums

(<http://www.polymer.org.au/index.php/home/activities/student-forum>)

YEAR	VENUE	ORGANISING INSTITUTION
1990	Mt Tambourine, QLD	University of Queensland
1994	Cunningham's Gap, QLD	University of Queensland
1996	Stradbroke Island, QLD	University of Queensland
1997	Avoca Beach, NSW	University of New South Wales
1999	Old Clarendon Winery, SA	University of South Australia
2001	Lake Hume Resort, NSW	University of Sydney

Australasian Polymer Summer Schools

(<http://www.polymer.org.au/index.php/home/activities/polymer-summer-school>)

APS	YEAR	VENUE	ORGANISING INSTITUTION
1	2000	Thredbo, NSW	CRC for Polymers/Key Centre for Polymer Colloids
2	2001	Albury, NSW	CRC for Polymers/Key Centre for Polymer Colloids
3	2002	Armidale, NSW	CRC for Polymers/Key Centre for Polymer Colloids
4	2003	Albury, NSW	CRC for Polymers/Key Centre for Polymer Colloids
5	2004	Wamberal, NSW	CRC for Polymers/Key Centre for Polymer Colloids
6	2004	Sunset Cove, SA	CRC for Polymers/Key Centre for Polymer Colloids
7	2006	Ballarat, VIC	CRC for Polymers/Key Centre for Polymer Colloids
8	2007	Geelong, VIC.	CRC for Polymers/Key Centre for Polymer Colloids
9	2008	Brisbane, QLD.	CRC for Polymers
10	2009	Blue Mountains, NSW	CRC for Polymers
11	2010	Melbourne, VIC	CRC for Polymers
12	2010	Wollongong, NSW	CRC for Polymers
13	2011	Brisbane, QLD	CRC for Polymers

Sponsored International Scientists

- 1968 **K F O'Driscoll**, State University of New York, Buffalo, USA
S Okamura, University of Kyoto, JAPAN
- 1970 **P Plesch**, University of Keele, UK
- 1971 **P J Flory**, Stanford University, USA
- 1972 **M B Huglin**, University of Salford, UK
- 1973 **H Morawetz**, Polytechnic Institute of New York, USA
- 1974 **M Nagasawa**, Nagoya University, JAPAN
H F Mark, Polytechnic Institute of New York, USA
R L Whistler, Purdue University, USA
V T Stannett, North Carolina State University, USA
- 1975 **F W Billmeyer**, Rensselaer Polytechnic Institute, USA
A M North, Strathclyde University, UK
R Takemoto, Osaka University, JAPAN
- 1976 **J Silverman**, University of Maryland, USA
F R Mayo, Stanford Research Institute, USA
- 1977 **H Benoit**, Centre de Recherches sur la Macromolecules, FRANCE
WO Statton, University of Utah, USA
M Swarc, State University of New York, Syracuse, USA
R B Seymour, University of Southern Mississippi, USA
- 1978 **Y Tabata**, University of Tokyo, JAPAN
J P Kennedy, University of Akron, USA
D M Wiles, Canadian National Research Council, CANADA
R A Hochschwender, American Hoechst Corporation, USA
P D Calvert, University of Sussex, UK
- 1980 **W D Woolley**, Building Research Establishment, Boreham Wood, UK
T T Tsuruta, University of Tokyo, JAPAN
G B Butler, University of Florida, USA
A N Gent, University of Akron, USA
W Schnabel, HahnMeitner Institut fuer Kernforschung, Berlin, GERMANY
D H Richards, Waltham Abbey, UK
C E Carraher, Wright State University, Dayton, USA
J E Guillet, University of Toronto, CANADA
C H Bamford, Liverpool University, UK
R D Haward, Birmingham University, UK
D Hull, Birmingham University, UK

- 1982 **R J Irvin**, Queen's University, Belfast, IRELAND
D O Hummell, University of Koln, GERMANY
G Kraus, Phillips Petroleum, USA
D B Wetlaufer, University of Delaware, USA
R Wuthrick, ETH, Zurich, SWITZERLAND
H Ruterjans, Goethe University, Frankfurt, GERMANY
- 1983 **A M North**, Strathclyde University, UK
G Williams, University College of Wales, UK
R A Wetton, Loughborough University, UK
- 1984 **T Otsu**, Osaka City University, JAPAN
G L Wilkes, Virginia Polytechnic, USA
T C Ward, Virginia Polytechnic, USA
J E McGrath, Virginia Polytechnic, USA
C B Bucknall, Cranfield Institute of Technology, UK
A Chapiro, CNRS, Paris, FRANCE
A Peterlin, National Bureau of Standards, USA
H Brown, Case Western Reserve University, USA
- 1985 **G Williams**, Aberystwyth University College, UK
R J Young, Queen Mary College, UK
R A Pethrick, Strathclyde University, UK
J E Mark, University of Cincinnati, USA
C Berry, Carnegie Mellon University, USA
B Billingham, University of Sussex, UK
F Ciardelli, Universita di Pisa, ITALY
D T Clark, ICI Runcorn, UK
A E Hamielec, McMaster University, USA
H J Harwood, University of Akron, USA
R W Lenz, University of Massachusetts, USA
J L Koenig, Case Western Reserve University, USA
N Plate, USSR Academy of Science, USSR
J C Randall, Phillips Petroleum, USA
W H Stranes, Bell Laboratories, USA
- 1986 **T Saegusa**, Kyoto University, JAPAN
J Economy, 113M, San Jose, USA
R Qian, Academia Sinica, CHINA
D Bassett, Union Carbide, USA
J R Robinson, University of Wisconsin, USA
J Heller, SRI International, California, USA
J Sohma, Hokkaido University, JAPAN

- 1987 **E A Turi**, New York Polytechnic Institute, USA
K F O'Driscoll, University of Waterloo, CANADA
V Crescenzi, University of Rome, ITALY
P J Lemstra, Eindhoven University of Technology, NETHERLANDS
W F Maddams, BP Research and University of Southampton, UK
O Vogl, Polytechnic Institute of New York, USA
G N Foster, Union Carbide, USA
J K Gillham, Princeton University, USA
J E McGrath, Virginia Polytechnic Institute and State University, USA
J M C Frechet, Cornell University, USA
H K Hall, University of Arizona, USA
V Percec, Case Western Reserve University, USA
D Y Sogah, Du Pont, USA
R Asami, Nagoya Institute of Technology, JAPAN
G B Butler, University of Florida, USA
R E Cais, A T & T Bell Laboratories, USA
W M Culbertson, Ashland Chemical Company, USA
B Gordon, Pennsylvania State University, USA
H J Harwood, University of Akron, USA
D A Tirrell, University of Massachusetts, USA
J F Rabek, Royal Institute of Technology, SWEDEN
- 1988 **R Duncan**, University of Keele, UK
D Williams, University of Liverpool, UK
E Tomlinson, CIBA Geigy, UK
Lord F S Dainton, Oxford, UK
W Schnabel, HahnMeitner Institute, GERMANY
V T Stannett, North Carolina State University, USA
- 1989 **J E Cardotte**, Film Tec Corporation, USA
I M Ward, University of Leeds, UK
I Mita, RCAST, University of Tokyo, JAPAN
A F Johnson, University of Bradford, UK
D C Sundberg, University of New Hampshire, UK
C Y Kim, Advanced Institute of Science and Technology, KOREA
S A McDonald, IBM Almaden Research Centre, USA
B Tighe, Aston University, UK
- 1990 **H R Brown**, IBM, USA
M Fryd, Du Pont, USA

- D O Hummel**, University of Koln, GERMANY
M Kamachi, Osaka University, JAPAN
Z Li, Academia Sinica, CHINA
W J MacKnight, University of Massachusetts, USA
W F Maddams, University of Southampton, UK
G Percival, Rohm and Haas, NZ
E Tsuchida, Waseda University, JAPAN
J M Vergnaud, University of SaintEtienne, FRANCE
1991 **A Abe**, Tokyo Institute of Technology, JAPAN
J M G Cowie, HeriotWatt University, UK
F Candau, Institute Charles Sadron, FRANCE
A Eisenberg, McGill University, CANADA
W J Feast, Durham University, UK
A D Jenkins, University of Sussex, UK
E T Kana, National University of Singapore, SINGAPORE
H H Kausch, EPFL, Lausanne, SWITZERLAND
C Y Kim, KIST, KOREA
J E McGrath, Virginia Polytechnic and State University, USA
T R Manley, Newcastleon Tyne, UK
E F Oleynik, USSR Academy of Science, Moscow, USSR
E M Pearce, Polytechnic University of New York, USA
R Qian, Academia Sinica, CHINA
R P Quirk, University of Akron, USA
I Soutar, Lancaster University, UK
N Spassky, University Pierre et Marie Curie, Paris, FRANCE
HW Spiess, Max Planck Institut, Mainz, GERMANY
M A Winnik, University of Toronto, CANADA
1992 **D R Williams**, University of Wales, UK
K Friedrich, University of Kaiserslautern, GERMANY
H B Feng, Academia Sinica, CHINA
1995 **J Gerlock**, Ford Motor Company, USA
J Gillham, Princeton University, USA
C Hoyle, University of Southern Mississippi, USA
T Jacobine, Loctite Corporation, USA
A Ledwith, Pilkington Technology Centre, UK
C C Ho, University of Malaya Kuala Lumpur, MALAYSIA
1996 **M El Aasser**, Lehigh University, USA
A German, Eindhoven University, NETHERLANDS

- A Holmes**, Cambridge University, UK
B O'Shaughnessy, Columbia University, USA
J Scrivens, ICI, UK
A Balazs, University of Pittsburgh, U.S.A. (with Polymer Blends CRC)
M Xanthos, Stevens Institute of Technology, U.S.A. (with Polymer Blends CRC)
1997 **M Sawamoto**, Kyoto University, JAPAN
K Friedrich, Kaiserslautern University, GERMANY
D Bassett, UCAR Emulsion Systems, North Carolina, USA
A Halperin
J Vlachopoulos, McMaster University, Ontario, CANADA
J Ebdon, University of Liverpool, UK
K Dusek, Institute of Macromolecular Chemistry, CZECH REPUBLIC
W Mormann, University Siegen, GERMANY
1998 **T Aida**, The University of Tokyo, JAPAN
A C Albertsson, Royal Institute of Technology, SWEDEN
T Asakura, Tokyo University of Agriculture and Technology, JAPAN
D C Bassett, University of Reading, UK
A Bhowmick, Indian Institute of Technology, INDIA
N Billingham, University of Sussex, UK
M Bowden, R & D Olin Microelectronic Materials, USA
C Decker, Université de Haute Alsace – 3, FRANCE
J Economy, University of Illinois, USA
E T Denisov, Institute of Problems of Physical Chemistry RAS, RUSSIA
W J Feast, University of Durham, UK
J M Frechet, University of California Berkeley, USA
T Fukuda, Kyoto University, JAPAN
J L Gardette, Université Blaise Pascal, FRANCE
K Hatada, Osaka University, JAPAN
J N Hay, University of Birmingham, UK
A S Hoffman, University of Washington, USA
K Horie, University of Tokyo, JAPAN
T Kajiyama, Kyushu University, JAPAN
J Karger-Kocsis, Universität Kaiserslautern, GERMANY
A R Khokhlov, Moscow State University, Moscow, RUSSIA
C Y Kim, Polymer Materials LabKIST, KOREA
A J Kinloch, Imperial College of Science, Technology and Medicine, UK
P J Lemstra, Eindhoven University of Technology, THE NETHERLANDS
O Long, Malaysian Rubber Board, MALAYSIA

- P A Lovell**, University of Manchester and UMIST, UK
A G MacDiarmid, University of Pennsylvania, USA
C Macosko, University of Minnesota, USA
R H Marchessault, McGill University, CANADA
K Matyjaszewski, Carnegie Mellon University, USA
C K Ober, Cornell University, USA
N Ogata, Sophia University, JAPAN
Y Osada, Hokkaido University, JAPAN
J M Piau, Université de Grenoble, FRANCE
M F Refojo, Harvard Medical School, USA
E Rizzardo, CSIRO Division of Chemicals and Polymers
T Russell, University of Massachusetts, USA
S Russo, Università di Genova, ITALY
J Schultz, University of Mulhouse, FRANCE
V P Shibaev, Moscow State University, RUSSIA
H W Siesler, University of Essen, GERMANY
R F T Stepto, UMIST and University of Manchester, UK
S Stupp, University of Illinois at Urbana-Champaign, USA
J Sun, Changchun Institute of Applied Chemistry, CHINA
D N Theodorou, University of Patras, GREECE
Y Tabata, Japan Atomic Energy Commission, JAPAN
S E Webber, University of Texas, USA
R Weiss, University of Connecticut, USA
A Windle, Cambridge University, UK
H Winter, University of Massachusetts, USA
M Wulkow, Computing in Technology GmbH (CiT), GERMANY
 1999 **W Mormann**, University of Siegen, Siegen, GERMANY
G Mitchell, University of Reading, UK
D Attwood, British Aerospace (Operations) Ltd, UK
C N Bowman, University of Colorado, USA
P Hodge, University of Manchester, Manchester, UK
F Horii, Kyoto University, JAPAN
M Jianbio, Nankai University, CHINA
D E. Kranbuehl, University of William & Mary, Virginia, USA
M Patel, IRC in Biomedical Materials, London, UK
G Russell, University of Canterbury, Christchurch, NEW ZEALAND
H Sautereau, Laboratoire des Matériaux Macromoléculaires, Lyon, FRANCE
 2000 **U Suter**, ETH Zurich, SWITZERLAND
D N Theodorou, University of Patris, GREECE

- A Windle**, Cambridge University, UK
C Holm, Johannes Gutenberg University, Mainz, GERMANY
- 2001 **A Balazs**, University of Pittsburg, USA
J Gerlock, Ford Motor Company, Dearborn, MI, USA
E Malmstrom, Royal Inzstitute of Technology, SWEDEN
R Metheson, DuPont Performance Coatings, Troy, MI USA
A Matsumoto, Osake City University, JAPAN
W van Ooij, University of Cincinnati, USA
H Pasch, Deutsches Kunststoff-Institut, Darmstadt, GERMANY
S Pascual, Warwick University, UK
M Reading, Loughborough University, UK
S Rimmer, Sheffield University, UK
S Sheiko, University of North Carolina, USA
R Ruchards, Durham University, UK
- 2002 **M Buback**, University of Gottingen, GERMANY
S Brocchini, London University, UK
D Haddleton, Warwick University, UK
C McCormick, University of Southern Mississippi, USA
S Holdcroft, Simon Fraser University, CANADA
C Hawker, IBM, USA
M Monteiro, Eindhoven University of Technology, NETHERLANDS
C Bowman, University of Colorado, USA
- 2003 **K Anseth**, University of Colorado, USA
C Bowman, University of Colorado, USA
J M Fréchet, University of California, USA
JF Gerard, INSA-Lyon, FRANCE
C Hawker, IBM, USA
J-I Jin, Korea University, KOREA
J Lacoste, Universite Blaise Pascal, Aubiere, FRANCE
M Mackay, Michigan State University, USA
T McNally, Queens University, Belfast, UK
R Segal, University of Minnesota, USA
U Schelre, Institute fur Polymforschung, Dresden, GERMANY
M Terano, Japan Advanced Institute for Science and Technology, JAPAN
K Wooley, Washington University, St. Louis, USA
- 2004 **J Hedrick**, IBM, Almaden Research Center, USA
A Hoffman, University of Washington, USA

- J Mark**, University of Cincinnati, USA
V Percec, University of Pennsylvania, USA
L Averous, University Louis Pascal, Strasburg, FRANCE
W Conley, Sematech, USA
D Graiver, Michigan State University, USA
F Groehn, Max Planck Institute for Polymer Research, GERMANY
A Adam Hitchcock, McMaster University, CANADA
M Owen, MMI / Dow, USA
V Schadler, BASF-ISIS Team, Strasbourg, FRANCE
M Textor, ETH Zurich, SWITZERLAND
D Tomasko, Ohio State University, USA
Y-Y Yang, University of Singapore, SINGAPORE
- 2006 **P Callaghan**, VICToria University of Wellington, NEW ZEALAND
B Charleux, Université Pierre et Marie Curie, FRANCE
D Haddleton, University of Warwick, UK
R Laine, University of Michigan, USA
G Parker, Wayne State University, USA
K Woodhouse, University of Toronto, CANADA
C Bowman, University of Colorado, USA
Prof. Mike Coleman, Pennsylvania State University, USA
S Fakirov, University of Auckland, New Zealand, and University of Sofia, BULGARIA
R French, DuPont Co., USA
T Fukuda, Kyoto University, JAPAN
E Harth, Vanderbilt University, USA
P Vana, University of Göttingen, GERMANY
K. Anseth, University of Colorado, USA
D. Hutmacher, National University of Singapore, SINGAPORE
I. Lacik, Slovak Academy of Sciences, SLOVAKIA
J van Hest, University of Nijmegen, NETHERLANDS
J Barralet, McGill University, CANADA
- 2007 **AH E Müller**, University of Bayreuth, GERMANY
CJ Hawker, University of California Santa Barbara, USA
A Ryan, University of Sheffield, UK
K Matyjaszewski, Carnegie Mellon University, USA
E Malmström, Royal Technical Institute Stockholm, SWEDEN
HD Maynard, University of California Los Angeles, USA
J Torkelson, Northwestern University, USA

- M Buback**, University of Göttingen, GERMANY
D Taton, University of Bordeaux, FRANCE
A Buleon, National Inst. of Agronomic Research, FRANCE
J Wendorff, University of Marburg, GERMANY
S Perrier, University of Leeds, UK
G Russell, University of Canterbury, NEW ZEALAND
R Waymouth, Stanford University, USA
- 2008 **V Abetz**, Max-Planck-Strasse, GERMANY
A Balazs, University of Pittsburgh, USA
C Beatty, University of Florida, USA
C Bowman, University of Colorado, USA
P Coates, University of Bradford, UK
J Dorgan, Colorado School of Mines, USA
K Haupt, Compiègne University of Technology, FRANCE
W Hayes, The University of Reading, UK
S Howdle, University of Nottingham, UK
M Leeson, IMEC Center, BELGIUM
K Loos, University of Groningen, NETHERLANDS
T McNally, Queens University, UK
T Nagamura, Kyushu University, JAPAN
B Ratner, University of Washington, USA
J Runt, Penn State University, USA
H. W. Spiess, Max-Planck-Strasse, GERMANY
M Stamm, Leibniz-Institut fuer Polymerforschung Dresden, GERMANY
- 2009 **J M Fréchet**, University of California, USA
T Ikeda, Tokyo Institute of Technology, JAPAN
S Chul Kim, National Academy of Engineering, KOREA
J Ying, Institute of Bioengineering and Nanotechnology, SINGAPORE
M Sawamoto, Kyoto University, JAPAN
and **120 invited keynote speakers**
- 2011 **T Aida**, University of Tokyo, Japan
D Castner, University of Washington, USA
R Kaner, University of California, USA
K Landfester, Max-Planck-Institute Germany
C Ober, Cornell University, USA
T Russell, University of Massachusetts, USA
and **18 invited keynote speakers**

BATTEARD-JORDAN Australian Polymer Medallists

(<http://www.polymer.org.au/index.php/home/awards/batteard-jordan-medal>)

- 1974 **Prof D O Jordan**, University of Adelaide
- Dr J A J Battaerd**, ICI Australia, Central Research Laboratory
- 1978 **Dr D H Solomon**, CSIRO, Division of Applied Organic Chemistry
- 1982 **Prof J H O'Donnell**, University of Queensland
- 1987 **Prof D H Napper**, University of Sydney
- 1992 **Dr E Rizzardo**, CSIRO, Chemicals and Polymers Division
- 1995 **Prof R G Gilbert**, University of Sydney
- 2000 **Prof K Ghiggino**, University of Melbourne
- 2006 **Prof G George**, Technical University of Queensland

David Sangster Polymer Science and Technology Achievement Award (formerly Australian Polymer Science and Technology Achievement Award)

(<http://www.polymer.org.au/index.php/home/awards/sangster-award>)

- 1992 **Prof G Wallace**, University of Wollongong
- 1995 **Dr G Meijs**, CSIRO Division of Chemicals & Polymers
- 1997 **Dr G Spinks**, University of Wollongong
- 2000 **Dr A Whittaker**, University of Queensland
- 2006 **Prof F Caruso**, University of Melbourne
- 2008 **A/Prof M Stenzel**, University of New South Wales
- 2009 **A/Prof S Perrier**, University of Sydney
- 2011 **Prof M. Coote**, Australian National University

TRELOAR Prize Recipients

(<http://www.polymer.org.au/index.php/home/awards/treloar-prize>)

The Treloar Prize was established in 1980 in recognition of the contributions to polymer research and teaching by the late Dr F E (Ted) Treloar. The Prize is awarded for the best scientific presentation(s) at an Australasian Polymer Symposium by a person less than 30 years of age; usually there are separate awards for best oral presentation and best poster presentation.

- 1981 12 APS **G Lichti**, University of Sydney
- 1982 13 APS **M Cuthbertson**, CSIRO, Div. of Applied Organic Chemistry; jointly
 P O'Sullivan, University of Queensland
- 1984 14 APS **P J Feeney**, University of Sydney; jointly
 M R Hatswell, Albright and Wilson
- 1986 15 APS **A Whittaker**, University of Queensland

1987	16APS	M E Adams , University of Sydney
1987	8NC	A P Lang , University of Queensland
1989	17APS	G M Spinks , University of Melbourne
1990	18APS	H A Willis , University of Queensland B R Morrison , University of Sydney
1991	Polymer 91	C Hawker , University of Queensland P Pascal , University of Sydney
1992	19APS	H A Willis , University of Queensland
1992	9 NC	M Monteiro , University of Queensland
1993	PPC 3	B Fox , CSIRO Chemicals and Polymers J Forsythe , University of Queensland
1995	20APS	R Evans , CSIRO Chemicals and Polymers P Dokolas , University of Melbourne
1996	21APS	A Bishop , Monash University C Fellows , James Cook University M Zammit , University of New South Wales
1997	22APS	E Furness , University of New South Wales D Kukulj , University of New South Wales
1998	Macro98	H Heuts , University of New South Wales P Ghi , University of Queensland
1999	23APS	L Yee , University of New South Wales N Grigg , Queensland University of Technology
2001	24APS	S Harrison , University of New South Wales J Hutchinson , University of Melbourne
2002	25APS	L Stanton , University of New South Wales T Dargaville , University of Queensland
2003	26APS	A Ah Toy , University of New South Wales B Muir , Monash University A Botella , INSA, Lyon
2004	27APS	J Quinn , University of Melbourne G Such , University of New South Wales/C.S.I.R.O. R Joso , University of New South Wales
2006	28APS	E Prime , University of Melbourne G Smith , University of Canterbury K Wong , University of New South Wales
2007	29APS	J Wiltshire , University of Melbourne L Connal , University of Melbourne

2008	30APS	T. K. Goh , University of Melbourne D. Konkolowicz , University of Sydney G. Johnston-Hall , University of Queensland
2009	31APS/PPC11	J Kulis , University of Queensland R Chapman , University of Sydney
2011	32APS	John Moares , The University of Sydney Vien T. Huynh , The University of New South Wales

O'Donnell Young Scientist Award

(<http://www.polymer.org.au/index.php/home/awards/odonnell-prize>)

1996	J Campbell	Monash University
1997	E Coen	University of Sydney
1998	K Lenghaus	University of Melbourne
1999	B Haupt	Australian National University
2000	S Prescott	University of Sydney / CSIRO Molecular Science
2004	L Connal	University of Melbourne
2007	T Schiller	Queensland University of Technology
2008	J Hodgson	Australian National University
2011	John Moraes	University of Sydney

Polymer Citation Recipients

(<http://www.polymer.org.au/index.php/home/awards/polymer-citations>)

The Polymer Division Citations were awarded for the first time at 16 APS. Up to three Citations may be presented in any year at a national meeting of the Polymer Division. They are awarded for significant contributions and service in any area of polymer science and/or technology.

1986	16 APS	G B Guise , CSIRO, Division of Textile Industry H J Ruddell , Telecom Australia D F Sangster , CSIRO, Division of Chemical Physics
1987	8 NC	D Oldfield , DSTO, Materials Research Laboratory I C Watt , CSIRO, Division of Textile Physics
1989	17 APS	D R G Williams , University of Adelaide C E M Morris , DSTO, Materials Research Laboratory
1990	18 APS	B A Bolto , CSIRO, Division of Chemicals and Polymers R A Shanks , RMIT

1991	Polymer 91	D J T Hill , University of Queensland P E M Allen , University of Adelaide
1992	19APS	E Rizzardo , CSIRO, Division of Chemicals and Polymers P Pomery , University of Queensland
1992	9NC R	P Burford , University of New South Wales W D Cook , Commonwealth Department of Health
1993	PPC3	Z H Stachurski , Australian National University T Chirila , Lions Eye Institute
1995	20APS	K Busfield , Griffith University G Moad , CSIRO Chemicals and Polymers G M Ferguson , SCM Chemicals
1996	21APS	J G Matisons , University of South Australia
1997	22APS	G A George , Queensland University of Technology Special Citation: B Guise , CSIRO
1998	Macro98	Special Citation: D Hill , University of Queensland Special Citation: P Pomery , University of Queensland Special Citation: D Oldfield , DSTO A Whittaker , University of Queensland
1999	23APS	N Edmonds , University of Auckland H Toh , Sola Optics
2001	24APS	G P Simon , Monash University I Dagley , CRC Polymers
2002	25APS	J Hodgkin , CSIRO Molecular Science E Senogles , James Cook University
2003	26APS	T Davis , University of New South Wales G Russell , University of Canterbury
2004	27APS	J P A Heuts , University of New South Wales/University of Murcia H Brown , University of Wollongong Special Citation: D F Sangster , University of Sydney
2006	28APS	B Hawke , University of Sydney D Lewis , Carl Zeiss Optical
2007	29APS	C M Fellows , University of New England
2008	30APS	C Barner-Kowollik , University of New South Wales/Karlsruhe Institute of Technology G. Spinks , University of Wollongong

CRC for Polymers Prize

(<http://www.polymer.org.au/index.php/home/awards/crc-prize>)

- 1994 **M Singer**, Monash University
- 1995 **A Mayr**, Monash University
- 1996 **M Griffiths**, Sydney University
- 1997 **J McNicol**, Australian National University
- 1998 **B Muir**, Monash University
- 1999 **E Dymke**, University of Wollongong
- 2000 **J Castro**, University of Sydney
- 2001 **S Angus**, University of New South Wales
- 2002 **K George**, Queensland University of Technology
- 2003 **H Chaffey-Miller**, University of New South Wales
- 2004 **K Varcoe**, University of Queensland
- 2006 **J Hodgson**, Australian National University
- 2007 **A J Inglis**, University of New South Wales
K Tsang, Monash University
- 2008 **J van Hensbergen**, University of New South Wales
J M Ren, University of Melbourne
- 2009 **J Tom**, University of Sydney
A Widjaya, University of Melbourne
- 2010 **S Passmore**, University of Queensland 2010
R Brooke, Flinders University

Solomon Lecturers

- 2000 **Prof David Solomon**, University of Melbourne
- 2001 **Prof Julia Higgins**, DBE, Imperial College, UK
- 2005 **Prof Gerhard Wegner**, MPI für Polymerforschung, Germany
- 2006 **Prof David Tirrell**, California Institute of Technology, USA
- 2007 **Prof Mitsuo Sawamoto**, Kyoto University

Bruce Guise Award

- 2011 **H Toh**, Carl Zeiss

The International Award for Promotion of Australasian Polymer Science and Technology

- 2011 **C Bowman**, University of Colorado

Speakers at 33APS

PLENARY SPEAKERS AT 33APS

Prof Harm-Anton Klok, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Prof Heather Maynard, University of California, USA

Prof Gordon Wallace, University of Wollongong, Australia

Prof David Haddleton, University of Warwick, England

Prof Ludwick Leibler, ESPCI, France

Prof Xi Zhang, Tsinghua University, China

Prof David Solomon, University of Melbourne

Dr Ezio Rizzardo, CSIRO

KEYNOTE SPEAKERS AT 33APS

Prof Stuart Rowan, Case Western Reserve University

Dr Remzi Becer, University of Warwick

Prof Thomas Junkers, Universiteit Hasselt

Prof Steven Holdcroft, Simon Fraser University

A/Prof Brian Hawke, The University Of Sydney

Prof Laurent Fontaine, LCOM - Chimie Des Polymères

Prof Feihe Huang, Zhejiang University

Prof Martina Stenzel, University of New South Wales

Prof Junpo He, Fudan University

Prof Ulrich Wiesner, Cornell University

Prof Theresa Reineke, University of Minnesota

Prof Jas Pal Badyal, Durham University

Prof Bert Klumperman, Stellenbosch University

Dr Eduardo Vivaldo-Lima, Universidad Nacional Autonoma De Mexico (UNAM)

Prof Brent Sumerlin, Southern Methodist University

Prof Filip DuPrez, Ghent University

Prof Richard Kaner, University Of California, Los Angeles

Prof Philippe Guégan, Université D'Evry Val D'Essonne

Prof Michael Monteiro, The University of Queensland

Prof Nicolas Voelcker, University of South Australia

EARLY CAREER RESEARCHERS AND LECTURERS IN AUSTRALIA AT 33APS

Dr Patrice Castignolles, University Of Western Sydney

Dr Kristopher Thurecht, University of Queensland

Dr Anthony Granville, University of New South Wales

Dr Daniel Keddie, CSIRO Materials Science And Engineering

Sunday 12 February

- 1200 – 1800 Registration Open
- 1600 – 1750 Conference Opening and Plenary Session
- 1800 Transfers depart Wrest Point for Welcome Reception
- 1830 – 2030 Welcome Reception at Meadowbank Winery

Monday 13 February

- 0800 – 1830 Registration Desk Opens
- 0900 – 0950 Plenary Session
- 0950 – 1010 Morning Refreshments
- 1010 – 1225 Concurrent Sessions
- 1225 – 1325 Lunch
- 1325 – 1525 Concurrent Sessions
- 1525 – 1545 Afternoon Refreshments
- 1545 – 1830 Concurrent Sessions
- 1830 – 2030 Symposium Poster Session

Tuesday 14 February

- 0800 – 1900 Registration Desk Open
- 0900 – 0950 Plenary Session
- 0950 – 1010 Morning Refreshments
- 1010 – 1225 Concurrent Sessions
- 1225 – 1325 Lunch
- 1325 – 1525 Concurrent Sessions
- 1525 – 1545 Afternoon Refreshments
- 1545 – 1830 Concurrent Sessions
- 1840 – 1940 Annual General Meeting – RACI Polymer Division
- 2030 Student Night

Wednesday 15 February

- 0800 – 1700 Registration Desk Open
- 0900 – 0950 Plenary Session
- 0950 – 1010 Morning Refreshments
- 1010 – 1225 Concurrent Sessions
- 1225 – 1325 Lunch
- 1325 – 1415 Plenary Session
- 1425 – 1610 Concurrent Sessions
- 1610 – 1630 Afternoon Refreshments
- 1630 – 1810 Plenary Session
- 1810 – 1830 Symposium Conclusion
- 1930 – 2330 Symposium Dinner at Wrest Point Convention Centre

Information for Presenters and Session Chairs

All Speakers will be asked to report to the Speakers Preparation Room to load their presentations onto the symposium laptop. This must be done AT LEAST four hours before you are due to present – this may mean the day before your presentation. An audio visual technician will be available throughout the symposium. Please see the staff at the Registration Desk for further assistance or directions.

Speakers are asked to introduce themselves to their session Chair during the break – at least ten minutes before the session, if possible, to familiarise themselves with the room and equipment and check that presentations are working.

Oral Presentations

Invited Plenary Presentations

Will be allocated 50 minutes presentation time, which includes 5 minutes for questions and answers.

Invited Keynote Presentations

Will be allocated 30 minutes presentation time, which includes 5 minutes for questions and answers.

Submitted Oral Presentations

Will be allocated 15 minutes presentation time which includes 3 minutes for questions and answers to be held at the conclusion of each presentation.

To aid in the smooth running of the sessions, a bell will ring once – indicating the time for questions is approaching. At the second ring you should stop for questions.

Total Presentation Time	Warning Bell	Second Bell – Question Time
15 Minutes	10 Minutes	12 Minutes
30 Minutes	20 Minutes	25 Minutes
50 Minutes	40 Minutes	45 Minutes

In order that the concurrent sessions remain aligned, all sessions must run according to the program. Speakers who run overtime will be cut off by the session chair. It is the responsibility of the session chairs to ensure that all speakers remain within their allocated presentation time.

Poster Presentations

Posters will be displayed in the Trade Exhibition Area during the symposium. There will be a poster session on Monday 13 February from 1830 to 2030. At least one of the poster authors is expected to be present adjacent to their posters to answer questions.

Treloar Prize Applicants must be present in person to answer questions during the poster sessions.

Welcome Reception

DATE: Sunday 12 February 2012

TIME: 1830 – 2030

ASSEMBLY TIME: 1800

VENUE: Meadowbank Winery

This event will be held at Meadowbank Estate's vineyard which is situated on the base of the foothills at the end of the Coal River Valley, which overlooks the picturesque Barilla Bay.

This will be the first opportunity of the symposium to meet with colleagues and friends from around the world, for drinks and canapés as well as a wine tasting.

The cost of the Welcome Reception is included in each full registration. Additional bookings can be made for accompanying persons at a cost of \$70 per person.

Coach transfers to the Welcome Reception are available for all delegates. You are required to assemble at the Wrest Point Convention Centre entrance (outside Wellington Rooms) for a 6.00pm sharp departure.

Symposium Poster Session

DATE: Monday 13 February 2012

TIME: 1830 – 2030

VENUE: Wrest Point Convention Centre, Tasman Room

Poster authors will be available for questions and answers during this session. Cocktail food and beverages will be served. The cost of the Poster Session is included in each full registration. Additional bookings can be made for accompanying persons at a cost of \$55 per person.

Student Night

DATE: Tuesday 14 February 2012

TIME: 2030 – late

VENUE: The Squires Bounty, 55 Salamanca Place

All students are welcome to The Squires Bounty for Happy Hour and nibbles from 8.30pm - 9.30pm. After this time students will have access to drink specials. The Squires Bounty is located in Salamanca Square which is tucked away behind the main Salamanca strip.

Please note students must bring their name badges to receive drink specials.

Symposium Dinner

DATE: Wednesday 15 February 2012

TIME: 1930 – 2330

VENUE: Wrest Point Convention Centre, Tasman Room

Join us on the last night of the Symposium program for another chance to network and meet with colleagues whilst enjoying a night of great food, wine and entertainment at Wrest Point Convention Centre. The cost of the Symposium Dinner is included in each full registration.

Additional bookings can be made for accompanying persons at a cost of \$120.

General Information

Registration Desk Opening Times	Sunday 12 February	1200 – 1800
	Monday 13 February	0800 – 1830
	Tuesday 14 February	0800 – 1900
	Wednesday 15 February	0800 – 1700

Accommodation: If you have any queries relating to your accommodation booking, first please see the staff at your hotel. Your one night deposit has been transferred to the hotel you have selected – please confirm this on check in with your hotel. If you arrive 24 hours later than your indicated arrival day you may find that you have forfeited your deposit.

Symposium Handbook & Name Badge: At the Symposium you will receive the handbook on USB, plus hard copy pocket program. If you have pre-ordered a hard copy handbook you will also receive this when you register. Each delegate will also receive a name badge upon arrival to the Symposium. The name badge will be your official pass and must be worn to obtain entry to all sessions and to social functions. Additional bookings for day registrants and partners is required.

Social Program Additional Guests: The welcome reception, poster session and symposium dinner are included in the cost of each full symposium registration. Social events ARE NOT included in the cost of day registrations or for accompanying partners. Places for day registrants and additional guests for these events may still be available at an additional cost. Bookings can be made at the symposium registration desk subject to availability. You will not be provided with an actual printed ticket, additional guests will be included on the event guest lists.

Entry to Conference Sessions: It is suggested that delegates arrive at preferred sessions promptly to ensure a seat. If sessions become full then delegates will not be allowed entry.

Messages: Messages can be left on the message board located near the registration desk. Please check this board regularly as no responsibility can be taken to deliver messages personally.

Mobile Phones: As a courtesy to other delegates, please ensure that all mobile phones and pagers are turned off or in a silent mode during all sessions and social functions.

Photographs, videos, recording of sessions: Delegates are not permitted to use any type of camera or recording device at any of the sessions unless written permission has been obtained from the relevant speaker.

Smoking: All venues are non smoking - no rooms are designated smoking rooms however guests are allowed to smoke outside the venue.

Speakers: Speakers will be asked to bring their presentations with them on a CD or USB stick, then load their presentations onto the conference laptop. This must be done AT LEAST four hours before you are due to present – this may mean the day before your presentation. Please see the staff at the registration desk for further information.

Speakers Preparation: Computer and audio visual equipment will be available for speakers wishing to review or change their presentations.

Special Diets: All catering venues have been advised of any special diet preferences you have indicated on your registration form. Please identify yourself to venue staff as they come to serve you and they will be pleased to provide you with all pre-ordered food. For day catering, there may be a specific area where special food is brought out, please check with catering or Symposium staff.

Prayer Room: A prayer room will be located in the Tasman Green Room for the duration of the conference. Please see staff at the registration desk for directions.

Disclaimer: The 33APS reserves the right to amend or alter any advertised details relating to dates, program and speakers if necessary, without notice, as a result of circumstances beyond their control. All attempts have been made to keep any changes to an absolute minimum.



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intellectual property

Our passion is science. We believe that good science is worth protecting and worth rewarding.

Phillips Ormonde Fitzpatrick specialises in helping clients identify, protect and defend their intellectual property through patents, trade marks, designs and copyright in Australia and overseas. We assist clients across a range of industries using polymer chemistry including cosmetics, agrochemicals, drug delivery, medical devices, packaging, building technology, nanotechnology and green technology.

Our attorneys have a wealth of industrial and academic experience in scientific research so we understand and appreciate both the complexities and subtleties of your invention – after all, we are scientists too.

To find out more, visit our website or speak to our polymer specialists Sarah Whitehead, Ray Evans and Grace Chan attending the 33rd Australasian Polymer Symposium.

pof.com.au



Ray Evans
Partner



Grace Chan
Associate



Sarah Whitehead
Trainee Patent Attorney

Melbourne
Sydney
Adelaide

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Symposium Program

SUNDAY 12 February 2012

Plenary Session Plenary Hall

Chair: Kevin Jack

1600 – 1610 **Welcome to the 33rd Australasian Polymer Symposium**

1610 - 1700 PL 1 - **Vitrimers**. Prof Ludwik Leibler, ESPCI

1700 - 1750 PL 2 - **Organic (Nano) Bionics**. Prof Gordon Wallace, University of Wollongong

1800 Coach transfers depart Wrest Point Convention Centre (Wellington Room Entrance)

1830 – 2030 **Welcome Reception, Meadowbank Winery**



INNOVATIVE POLYMERIC MATERIALS AT CSIRO

CSIRO is developing creative polymeric solutions in areas as diverse as aerospace, renewable energy and packaging.

Our research in polymer science includes world-leading capabilities in controlled free-radical polymerisation, reactive extrusion, condensation polymerisation, biomedical polymer synthesis and polymer processing.

We are currently addressing challenges in the areas of organic photovoltaics, polymeric photochromic materials; biomedical implants; and degradable biomaterials.

For more information:

Polymeric and molecular materials: www.csiro.au/science/Polymer-and-molecular-science

Sustainable materials: www.csiro.au/science/Sustainable-materials

RAFT technology: www.csiro.au/products/RAFT

Flexible electronics: www.csiro.au/science/Flexible-Electronics

or contact:

Mr Phil Casey: Phil.Casey@csiro.au
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Dr Stuart Bateman: Stuart.Bateman@csiro.au
Ph: (03) 9545 8410

Dr Greg Simpson: Greg.Simpson@csiro.au
Ph: (03) 9545 2519

Dr Gerry Wilson: Gerry.Wilson@csiro.au
Ph: (03) 9545 2205



Plenary Session Plenary Hall

Chair: Amanda Ellis

0900 – 0950 PL 3 - **Stimuli-responsive Polymeric Superamphiphiles for Controlled Self-assembly.** Prof Xi Zhang, Tsinghua University

0950 – 1010 Morning Refreshments and Trade Exhibition

Advanced Materials Plenary Hall

Chair: Jas Pal Badyal

1010 - 1040 M1.1 - **Utilizing Supramolecular Interactions to Access Dynamic Materials.** Stuart Rowan*

1040 - 1055 M1.2 - **Using Hyperbranched Polymers for Surface Modification: Towards the Facile Self Assembly of Sensing Devices.** Idriss Blakey*, Kristofer J. Thurecht

1055 - 1110 M1.3 - **Self-assembly by hierarchical information transfer.** Rueben Pfukwa*, Alan E. Rowan, Paul Kouwer, Bert Klumperman

1110 - 1125 M1.4 - **Molecularly Imprinted Microgels.** Clovia Z. Holdsworth*, Edwin F. Romano Jr., Regina C. So

1125 - 1140 M1.5 - **Control of Poly(vinyl alcohol) fibre deposition during electrospinning via electric field Manipulation.** A. H. Nurfaizey*, J. Stanger, N. Tucker, N. Buunk, A. Wallace, A. R. Wood, M. P. Staiger

1140 - 1155 M1.6 - **Cellulose Acetate Polymeric Membranes with Varying Amounts of Covalently Attached POSS Nanoparticle Fillers.** Clare Worthley*, Kristina Constantopoulos, Elda Markovic, Milena Ginic-Markovic, Stephen Clarke

1155 - 1210 M1.7 - **Fabrication and *In Vitro* Testing of Chitosan-ECM Bandages for Photochemical Tissue Bonding.** Antonio Lauto*, Leonardo Longo, Damia Mawad

1210 - 1225 M1.8 - **Macroporous monolithic polymers containing embedded nanoparticles for high performance chromatography, sample preparation and catalysis.** Emily F. Hilder*, Dario Arrua, Mark E. Thomas, Roderick C. Jones, Paul R. Haddad

Polymers for Health Wellington Room

Chair: Brian Hawke

1010 - 1040 M2.1 - **Smart glycopolymers and their interactions with lectins.** Remzi Becer*

1040 - 1055 M2.2 - **Mapping the Binding Efficiency between Concanavalin A and Star-Shaped Glycopolymers with Varying Degrees of Glycosylation.** Yong Chen*, Martina H. Stenzel

1055 - 1110 M2.3 - **Poly(glycidyl methacrylate) as a “polymeric building block” through post-polymerization processes.** Massimo Benaglia*

Symposium Program

MONDAY 13 February 2012

- 1110 - 1125 **M2.4 - Improving the performance of micelles as drug delivery carriers by shell-crosslinking.** Yoseop Kim*, Mohammad Pourgholami, David Morris, Martina H. Stenzel
- 1125 - 1140 **M2.5 - Controlling Properties of Polymeric Drug Capsules Using Charge-Shifting Polymers.** Sher Leen Ng*, Georgina K. Such, Angus P. R. Johnston, Frank Caruso
- 1140 - 1155 **M2.6 - Targeted Drug Delivery: Understanding cellular binding and uptake of nanoengineered capsules.** Angus P. R. Johnston*, Marloes M. J. Kamphuis, Georgina K. Such, Frank Caruso
- 1155 - 1210 **M2.7 - Synthesis of Amphiphilic Block Copolymers for Study of Cellular Interaction and Uptake.** Ted Chang*, Megan Lord, Martina Stenzel
- 1210 - 1225 **M2.8 - Modular Charge-Shifting Capsules for Therapeutic Delivery.** Georgina K. Such*, Kang Liang, Zhiyuan Zhu, Yan Yan, Hannah Lomas, Angus. P. R. Johnston, Frank Caruso

Latest Development in Polymer Synthesis Boardwalk Gallery

Chair: Laurent Fontaine

- 1010 - 1040 **M3.1 - Living *p*-quinodimethane polymerization for the synthesis of well-defined PPV materials: Is it even possible?** Thomas Junkers*
- 1040 - 1055 **M3.2 - Recent Travels in k_t -Land.** Johannes Barth, Sabine Beuermann, Michael Buback, Gregory T. Russell*, Rebekka Siegmann
- 1055 - 1110 **M3.3 - Recent Macromolecular Design and Application of Catalytic Chain Transfer Polymerization.** Alexander Soeriyadi*, Michael Whittaker, Cyrille Boyer, Thomas Davis
- 1110 - 1125 **M3.4 - CCT-derived Macromonomers as Macroinitiators for Anionic Polymerisation.** Gemma Sanders*, Rob Duchateau, Hans Heuts
- 1125 - 1140 **M3.5 - Predicting Polymer Tacticity in Radical Polymerization.** Michelle L. Coote*, İsa Değirmenci, Benjamin Noble
- 1140 - 1155 **M3.6 - Rapid, Selective and Reversible Nitroxide Radical Coupling (NRC) Reactions at Room Temperature.** Jakov Kulis*, Craig A. Bell, Aaron S. Micallef, Zhongfan Jia, Michael J. Monteiro
- 1155 - 1210 **M3.7 - PolyBank: Development of a bank of advanced polymeric materials via RAFT technology and high throughput experimentation.** Carlos Guerrero-Sanchez*, Daniel Keddie, Christian H. Hornung, Simon Harrisson, Simon Saubern, San H. Thang, Graeme Moad, Ezio Rizzardo, and John Chiefari
- 1210 - 1225 **M3.8 - Molecular Imprinting Using Biaryl Monomers: Comparison of Thermal and Microwave-assisted Approaches.** Hazit A. Zayas, Michael Bowyer, Adam McCluskey, Clovia Holdsworth*
- 1225 - 1325 Lunch and Trade Exhibition

Advanced Materials Plenary Hall

Chair: Feihe Huang

- 1325 - 1355 M1.9 - **Functional Nanocoatings.** Jas Pal Badyal*
- 1355 - 1410 M1.10 - **Controlled Synthesis of Block Copolymer for Proton Exchange Membrane Application.** S. X. Zhao*, J. M. Ren, P. A. Gurr, Y. X. Wang, G.G. Qiao
- 1410 - 1425 M1.11 - **New Fluorinated Polymers bearing Pendant Phosphonic Groups for Proton Conducting Membranes.** G. David*, R. Tayouo, B. Améduri, J. Rozière, S. Roualdès
- 1425 - 1440 M1.12 - **Porous PDMS Membranes Fabricated from Polymerizable Microemulsion Templates.** Shuhua Peng*, Patrick G. Hartley, Timothy C. Hughes, Qipeng Guo
- 1440 - 1455 M1.13 - **Use of the *Breath Figures* technique to form ordered microporous thin films from Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate).** M. Huh, M. Jung, Y. S. Park, T. Kang, R.A. Russell, P.J. Holden*, S.I. Yun
- 1455 - 1510 M1.14 - **Non-cracking honeycomb formation on nonplanar surface driven by polymer intrinsic properties.** Zhou Zhang*, Timothy C. Hughes, Paul Gurr, Xiaojuan Hao, Greg Qiao
- 1510 - 1525 M1.15 - **Nanocomposite gels with extraordinary properties: Formation and characteristics of unique organic / inorganic network structures.** Kazutoshi Haraguchi*

Polymers for Health Wellington Room

Chair: Marion Gaborieau

- 1325 - 1355 M2.9 - **Applications for RAFT in Disperse Phase Systems.** Brian S. Hawkett*
- 1355 - 1410 M2.10 - **Development of core-crosslinked micelles for the delivery of albendazole.** Yue Zhao*, Yoseop Kim, Ling Zhang, Xin Tan, Martina H. Stenzel
- 1410 - 1425 M2.11 - **CPP-decorated polymeric micelles from arginine-based monomers: An efficient tool for drug delivery?** Yoseop Kim, Yoon Ji Kim, Sandra Binauld*, Martina H. Stenzel
- 1425 - 1440 M2.12 - **Synthesis, self-assembly and evaluation of cholesterol-containing biodegradable block copolymers for drug delivery applications.** Shrinivas Venkataraman*, Ashlynn L.Z. Lee, James L. Hedrick, Yi Yan Yang
- 1440 - 1455 M2.13 - **Biocompatible Patterned Polymer Surface Coatings to Control Protein Adsorption and Endothelial Cell Behaviour.** Stuart C. Thickett*, Joshua Moses, Jennifer Gamble, Chiara Neto
- 1455 - 1510 M2.14 - **Stabilization of Peptide- Based Vesicles via *In Situ* Oxygen-Mediated Cross-Linking.** Adrian Sulistio*, Anton Blencowe, Jiapeli Wang, Gary Bryant, Xiaoqing Zhang, Greg Qiao

Symposium Program

MONDAY 13 February 2012

1510 - 1525 M2.15 - **Macromolecular Ruthenium Complexes as Anticancer Agents.** Bianca Blunden*, Donald Thomas, Martina Stenzel

Latest Developments in Polymer Synthesis Boardwalk Gallery **Chair: Junpo He**

1325 - 1355 M3.9 - **Controlled Radical Polymerization, Metathesis, and “Click” Chemistry: A Versatile Combination to Target New Reactive Polymers.** L. Fontaine*, S. Pascual, V. Montembault, M. Levere, D. Le

1355 - 1410 M3.10 - **Investigation of Ring-Opening Metathesis Polymerisation with Hoveyda-Grubbs Catalysts.** Anton Blencowe*, Greg G. Qiao

1410 - 1425 M3.11 - **Block Copolymers via Macromercaptan Initiated Ring Opening Polymerization.** Catherine Lefay*, David Glé, Marion Rollet, Jérôme Mazzolini, Denis Bertin, Stéphane Viel, Christina Schmid, Christophe Boisson, Franck D'Agosto, Didier Gigmes, Christopher Barner-Kowollik

1425 - 1440 M3.12 - **Organic Catalyst-Mediated Ring Opening Polymerization Towards the Near-quantitative Synthesis of Star Polymers.** J. M. Ren*, Q. Fu, A. Blencowe, G.G. Qiao

1440 - 1455 M3.13 - **Renewal of Allyl Polymerization Mechanism.** Akira Matsumoto*

1455 - 1510 M3.14 - **A Simple, Efficient and Novel Methodology in Forming Complex Macromolecular Architecture Films via Continuous Assembly of Polymers (CAP).** Edgar H. H. Wong*, Stefanie N. Guntari, Georgina K. Such, Anton Blencowe, Frank Caruso, Greg G. Qiao

1510 - 1525 M3.15 - **Synthesis of new bisallylic dithioether monomers for photoplastic polymers.** Cornelis Moorhoff*, Wayne Cook, Tara Schiller, Carl Braybrook, San Thang

1525 – 1545 Afternoon Refreshments and Trade Exhibition

Advanced Materials Plenary Hall **Chair: Stephen Clarke**

1545 - 1615 M1.16 - **Supramolecular Polymers Based on Threaded Structure Connections.** Feihe Huang*

1615 - 1630 M1.17 - **Accessing Supramolecular Structures with (N-Methylated Cyclic Peptide)-Polymer Conjugates.** Ming Liang Koh*, Katrina A. Jolliffe, Sébastien Perrier

1630 - 1645 M1.18 - **Dually Thermo-sensitive Block-copolymers: Self-assembly into Micelles based on Aqueous LCST and into Inverted Micelles based on UCST in Alcohols.** Peter J. Roth*, Thomas P. Davis, Andrew B. Lowe

1645 - 1700 M1.19 - **Advanced Polymer Nanoparticles.** Luke A. Connal*, Eric D. Pressley, Craig J. Hawker

- 1700 - 1715 M1.20 - **Shear Induced Orientation and Structure Development in α -Isotactic Polypropylene Containing Particles.** Amita Bhatia*, Terence Turney, Graham Edward, Peng-Wei Zhu
- 1715 - 1730 M1.21 - **Supramolecular assembly as a route to organic nanotubes of tunable dimensions.** Robert Chapman*, Katrina A. Jolliffe, Sébastien Perrier
- 1730 - 1745 M1.22 - **Advanced fluorescence methods as a tool for studying polymer self-assembly.** Karel Procházka*, Miroslav Štěpánek, Pavel Matějček, Mariusz Uchman, Zuzana Limpouchová, Peter Košovan, Filip Uhlík, Jana Humpolíčková, Martin Hof, Joerg Schroeder
- 1745 - 1800 M1.23 - **Processable Star Polymers.** Azrinawati Mohd. Zin*, Erica Wanless, Clovia Holdsworth
- 1800 - 1815 M1.24 - **Vesicle-Templated pH-Responsive Polymeric Nanocapsules.** Syed Imran Ali*, Johan P.A. Heuts, Brian S. Hawkett, Alex M. van Herk
- 1815 - 1830 M1.25 - **A Facile Approach to Chemically Modified Graphene and its Polymer Nanocomposites.** Jun Ma*, Izzuddin Zaman, Hsu-Chiang Kuan

Polymers for Health Wellington Room

Chair: Heather Maynard

- 1545 - 1615 M2.16 - **Nanoparticles with pendant cyclodextrins as drug delivery carrier.** Martina Stenzel*, Firdaus Yhaya, Manuela Callari
- 1615 - 1630 M2.17 - **Stimuli-responsive polymers for MRI imaging.** Mariana Beija*, Yang (Daniel) Li, Andrew B. Lowe, Thomas P. Davis, Cyrille A. Boyer
- 1630 - 1645 M2.18 - **Polymeric micelles with pendant pair-wise carboxylato groups afforded via Michael addition for sufficient cis-platinum drug delivery.** Vien T. Huynh*, Paul de Souza, Martina H. Stenzel
- 1645 - 1700 M2.19 - **Development of a PET-MRI Hyperbranched Polymer Imaging Agent.** Nathan Boase*, Kristofer Thurecht, Eskender Mume, Suzanne Smith, Cameron Alexander, Idriss Blakey
- 1700 - 1715 M2.20 - **Multifunctional Star and Hyperbranched polymer for cancer targeted drug delivery and MR imaging.** Yang Li*, Hien Duong, Mariana Beija, Andrew Lowe, Tom Davis, Cyrille Boyer
- 1715 - 1730 M2.21 - **Novel lanthanide(III) hyperbranched polymers as advanced targeting imaging agents.** Sabrina Dehn*, Sébastien Perrier
- 1730 - 1745 M2.22 - **Hydrophobically modified OSA starches: a fluorescence probe study of the influence of macromolecular architecture on the critical micelle concentration.** Morgan J. Tizzotti*, Michael C. Sweedman, Christian Schaefer, Robert G. Gilbert
- 1745 - 1800 M2.23 - **Enzymatic Degradation of Poly(Polyol Sebacte).** Qizhi Chen*, Shuling Liang

Symposium Program

MONDAY 13 February 2012

1800 - 1815 M2.24 - **Synthesis and Physico-Mechanical Characterization of Reinforced Microcellular Polyurethane-Sisal Biocomposites.** M. Bassyouni*, Shereen M.-S. Abdel-hamid

Latest Developments in Polymer Synthesis Boardwalk Gallery Chair: Kristopher Thurecht

- 1545 - 1615 M3.16 - **Small Molecular Kinetic Model for the RAFT Process.** Junpo He*
- 1615 - 1630 M3.17 - **Synthesis and Characterization of "Glycopolymers".** Christina Ott*, Christopher D. Easton, Thomas R. Gengenbach, Sally L. McArthur, Pathiraja A. Gunatillake
- 1630 - 1645 M3.18 - **Catalytic Cycle of Nitroxide Activation and Regeneration.** Ganna Gryn'ova*, Keith U. Ingold and Michelle L. Coote
- 1645 - 1700 M3.19 - **NMP and ATRP in nanoreactors: Factors influencing compartmentalization effects on bimolecular termination.** Per B. Zetterlund*
- 1700 - 1715 M3.20 - **Towards Nitroxide Mediated Photo-Polymerization.** Yohann Guillauneuf*, Davy-Louis Versace, Denis Bertin, Jean-Pierre Fouassier, Jacques Lalevée, Didier Gigmes
- 1715 - 1730 M3.21 - **Miniemulsion polymerization based on in situ surfactant formation and ultrasonication: A novel synthetic route to nano-sized (< 20 nm) polymer particles.** Yi Guo*, Per B. Zetterlund
- 1730 - 1745 M3.22 - **Well-defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization.** Emilie Groison*, Ségolène Brusseau, Franck D'Agosto, Stéphanie Magnet, Rabi Inoubli, Laurence Couvreur, Bernadette Charleux
- 1745 - 1800 M3.23 - **Controlled/living radical polymerization in CO₂-induced miniemulsions.** Siqing Cheng*, Per B. Zetterlund
- 1800 - 1815 M3.24 - **Polymeric nanoparticle synthesis in CO₂-induced emulsions.** Da Wei Pu*, Frank P. Lucien, Per B. Zetterlund
- 1815 - 1830 M3.25 - **Corrosion resistant double stranded conducting polymer nanocomposite coating for aircraft applications.** Gunjan Gupta*, Nick Birbilis & A.S.Khanna

Poster Session Tasman Room

1830 – 2030 Refreshments will be served during the Poster Session

Plenary Session Plenary Hall

Chair: Lachlan Yee

0900 – 0950 PL 4 - **Combating Diseases with Peptide - Synthetic Polymer Conjugates.**

Prof Harm-Anton Klok, Ecole Polytechnique Federale de Lausanne

0950 – 1010 Morning Refreshments and Trade Exhibition

Advanced Materials Plenary Hall

Chair: Xi Zhang

1010 - 1040 T1.1 - **Functional Nanomaterials from Block Copolymer Self-Assembly.** Ulrich Wiesner*

1040 - 1055 T1.2 - **Synthesis and Functionalization of Ordered Macromolecular Architectures Using a Combination of RAFT Polymerization and Click Chemistry.** John Moraes*, Thomas Maschmeyer, Sébastien Perrier

1055 - 1110 T1.3 - **Use of plasma polymerisation to facilitate new growth possibilities for surface-initiated polymerisation.** Bryan R. Coad*, Yi Lu, Katie E. Styan, Laurence Meagher

1110 - 1125 T1.4 - **Simultaneous photoinduced silver nanoparticles formation and cationic polymerization of divinyl ethers.** Wayne D. Cook*, Phoi Boon, Quoc Dat Nghiem, Qizhi Chen, Tara Schiller, Bjorn Winther-Jensen, Kei Saito, Marco Sangermano

1125 - 1140 T1.5 - **Photoclick chemistry for spatially and temporally functionalized materials.** G. Delaittre*, T. Paulöhr, M. Dietrich, M. Glassner, K. Öhlenschläger, M. Bastmeyer, C. Barner-Kowollik

1140 - 1155 T1.6 - **Interactions of Charged Block Copolymers with Surfaces: a Tunable Roughness.** Ya-Mi Chuang*, Idriss Blakey, Kevin Jack, Michael Leeson, Todd Younkin, Andrew K. Whittaker

1155 - 1210 T1.7 - **Carbon nanotube strain sensors for paint degradation monitoring.** Michael K. Njuguna, Nicholas Tilley, Cheng Yan, Geoffrey D. Will, John M. Colwell*

1210 - 1225 T1.8 - **New Fluorescent Nanocomposites for Fingerprint Detection.** Jessiré Dilag*, Hilton Kobus, Amanda Ellis

Polymers for Health Wellington Room

Chair: Bert Klumperman

1010 - 1040 T2.1 - **Delivery Agents Designed from Core-Shell Carbohydrate-Based Block Copolycations.** Theresa Reineke*

1040 - 1055 T2.2 - **Self-Catalyzed Degradable Polycation for DNA Release.** Nghia P. Truong*, Zhongfan Jia, Melinda Burgess, Liz Payne, Nigel A. J. McMillan, Michael J. Monteiro

1055 - 1110 T2.3 - **siRNA Delivery with ABA Triblock Copolymers and Star Block Copolymers.** Bill Chong, Carlos Guerrero-Sanchez, Thilak Gunatillake, Tam Le, San H. Thang*, Tracey Hinton, and Shuning Shi, Mark Tizard

Symposium Program

TUESDAY 14 February 2012

- 1110 - 1125 **T2.4 - Hyperbranched Polymer/siRNA Conjugates as Targeted Cancer Therapeutics.** Daniel J. Coles*, Nigel A.J. McMillan, Andrew K. Whittaker, and Kristofer J. Thurecht
- 1125 - 1140 **T2.5 - Reducible multiblock poly(lysine)-PEG for siRNA delivery.** Warren Knower*, Pete Cass, Thilak Gunatillake, Tracey Hinton, Shuning Shi, Mark Tizard
- 1140 - 1155 **T2.6 - Polydimethylsiloxane microchannel modifications for DNA detection in microfluidics.** Dmitriy Khodakov, Claire E. Lenehan, Gunther Andersson, Hilton Kobus, Amanda V. Ellis*
- 1155 - 1210 **T2.7 - A novel approach towards dynamic cross-linked hydrogels.** Shereen Tan*, Anton Blencowe, Greg Qiao
- 1210 - 1225 **T2.8 - Hybrid Hydrogel Sponges with Controlled Pore Sizes.** Berkay Ozcelik*, Anton Blencowe, Geoff Stevens, Greg Qiao

Early Career Researchers Boardwalk Gallery

Chair: David Lewis

- 1010 - 1040 **T3.1 - Separation of copolymers, conjugates and supramolecular architectures of polysaccharides, thermoresponsive and pH-responsive polymers by capillary electrophoresis in the critical conditions.** Patrice Castignolles*, Mariam Mnatsakanyan, Pierre Guiglion, Rozet Roi, Angel Medina-Oliva, Joel Thevarajah, Danielle Taylor, Jerikho Bulanadi, Cameron Ferris, Marc in Het Panhuis, Matthias Destarac, Francois Ganachaud, Christopher Jones, Manfred Schmidt, Antonio Lauto, Marion Gaborieau
- 1040 - 1110 **T3.2 Polymeric Theranostics: Hyperbranched Polymers for Treating Disease.** Kristofer J Thurecht*, Idriss Blakey, Hui Peng, Barbara Rolfe, Cameron Alexander, Andrew K Whittaker
- 1110 - 1140 **T3.3 - Biosensor and Drug Delivery Technology through Surface Modification.** Anthony Michael Granville*, Solomon Le-Masurier, Yan Jin, Kok Hou Wong
- 1140 - 1210 **T3.4 - Acid/Base "Switchable" Chain-Transfer Agents for RAFT Polymerization.** Daniel J. Keddie*, Carlos Guerrero-Sanchez, Roger Mulder, Graeme Moad, Ezio Rizzardo, San H. Thang
- 1225 - 1325 Lunch and Trade Exhibition

Advanced Materials Plenary Hall

Chair: Eduardo Vivaldo-Lima

- 1325 - 1355 **T1.9 - Acid-Bearing Polymer Membranes for PEM Fuel Cells.** E.M.W. Tsang, A. Yang, Z. Shi, T. Weissbach, S. Holdcroft*
- 1355 - 1410 **T1.10 - Polymer nanocomposites: is it worth the effort?** Theo J. Dingemans*, Maruti Hegde, Y. Si, Edward T. Samulski
- 1410 - 1425 **T1.11 - Continuous Assembly of Polymers (CAP): A Versatile Approach for Surface-Driven Nanocoatings.** Stefanie Nina Guntari*, Tor Kit Goh, Anton Blencowe, Edgar H. H. Wong, Frank Caruso, Greg G. Qiao

- 1425 - 1440 T1.12 - **Structure/Property Relationships in Sulphur containing Epoxy Resins for High Performance Applications.** Wouter Vogel, Theo Dingemans, Russell J. Varley*, Buu Dao, Wendy Tian, Stephen Christensen
- 1440 - 1455 T1.13 - **Synthesis of Core Cross-linked Star (CCS) Polypseudorotaxane via Inclusion Complexation of CCS PCL Polymers and α -Cyclodextrins.** Q. Fu*, J. M. Ren, S. Tan, G.G. Qiao
- 1455 - 1510 T1.14 - **Functionalization of Well-Defined Star Polymers Built from Biodegradable Microgel/Nanogel Cores via Click Chemistry.** Jinna Liu*, Thomas P. Davis, Cyrille Boyer
- 1510 - 1525 T1.15 - **Effect of Lateral Fluorine Substituent on Mesophase behavior of Bent-shaped Molecules with Asymmetric Central Naphthalene Core.** Xiaodong Li*, Mao-sheng Zhan, Kai Wang

Polymers for Health Wellington Room
Chair: Per Zetterlund

- 1325 - 1355 T2.9 - **Synthesis and application of drug delivery systems.** Nathalie Bailly, Hamilton Kakwere, Mark Thomas, Gwenaelle Pound-Lana, Bert Klumperman*
- 1355 - 1410 T2.10 **Nitric Oxide: A New Hope for the Treatment of Multidrug Resistant Cancers.** Cyrille Boyer*
- 1410 - 1425 T2.11 - **Various preparation methods of highly porous hydroxyapatite/polymer nanoscale biocomposites for bone regeneration.** Fangfang Sun, Hongjian Zhou, Jaewook, Jaebeom Lee*
- 1425 - 1440 T2.12 - **Biocompatible Polyurethanes for Spinal Cord Regeneration.** Aaron S. Micallef*, Bronwin Dargaville, Fiona F. Filardo, Florian H. M. Graichen, Mike S. O'Shea, Firas Rasoul, David K. Wang, Andrew K. Whittaker
- 1440 - 1455 T2.13 - **Polyurethane Nanocomposites as Biomaterials – Mechanical Performance, Morphology and Biocompatibility.** Darren Martin*, Azlin Fazlina Osman, Yosephine Andriani, Ajay Padsalgikar, Martin Svehla, Peter Halley, Rodney Minchin
- 1455 - 1510 T2.14 - **Development of Bioactive 3D Block Copolymer Scaffolds for Repair of Bone Tissue.** Chunli Liu*, Hui Peng, Yin Xiao, Andrew K. Whittaker
- 1510 - 1525 T2.15 - **Optimal Design of Polymer Artificial Muscles.** Geoffrey M. Spinks*, Gordon G. Wallace, Philip G. Whitten and Wen Zheng

Innovation Session Boardwalk Gallery
Chair: Ramon Tozer

- 1325 - 1345 T3.9 - **Setting up and starting a spin off company: The story of Warwick Effect Polymers.** David Haddleton*
- 1345 - 1405 T3.10 - **Intellectual Property and Science – an overview.** Ramon Tozer*

Symposium Program

TUESDAY 14 February 2012

- 1405 - 1425 T3.11 - **Collaborative Industry Driven Polymer Research in Australia.** Ian Dagley*
- 1425 - 1445 T3.12 - **Beyond patents – forms of intellectual property protection.** Richard Grant*
- 1445 - 1505 T3.13 - **The Materials Accelerator: A National Network In Manufacturing Materials.** Ralph P.Cooney*
- 1505 - 1525 T3.14 - **When and How to Patent an Invention.** Sarah Whitehead*, Grace Chan
- 1525 – 1545 Afternoon Refreshments and Trade Exhibition

Opto- and Electro-active Polymers Plenary Hall

Chair: Richard Kaner

- 1545 - 1615 T1.16 - **Stimulus-Responsive Polymers Interfaced with Porous Semiconductors.** Roshan Vasani, Stéphanie Pace, Amanda V. Ellis, Nicolas H. Voelcker*
- 1615 - 1630 T1.18 - **Synthesis and Characterization of Thiophene Polymer Brushes.** Robert Brooke*, Anirudh Sharma, Marie-Claire Hermant, David Lewis
- 1630 - 1645 T1.19 - **Recent Development of Charge Transport Materials and Donor Materials for Organic Solar Cells.** Xiwen Chen*, Zhitao(Tom) Jiang, Yu Chen, Deng Hong, Scott Watkins, Mei Gao, Ping Lu, Haiqiao Wang, Yanguang Wang
- 1645 - 1700 T1.20 - **Influences of Functional Groups on the Orientation Birefringence of Uniaxially Drawn Cellulose Ester Films.** Mohd Edeerozey Abd Manaf*, Shogo Nobukawa, Masayuki Yamaguchi
- 1700 - 1715 T1.21 - **Linear expansion of electrochemically actuating gels.** S. C. Moratti*, L.R. Hanton, C.J. MacAdam, S.K. Goswami
- 1715 - 1730 T1.22 - **Bacterial Cellulose Electro Active Polymer for Biomimetic Robot.** Si-Seup Kim*, Chang-Doo Kee
- 1730 - 1745 T1.23 - **Self-assembled Electrically Active Multilayers for the Functionalization of 2D and 3D Neural Scaffolds.** Kun Zhou*, David R. Nisbet, George A. Thouas, Claude C. Bernard, John S. Forsythe
- 1745 - 1800 T1.24 - **Conducting Polymer Anti-Microbial Agents.** Ralph Cooney*, Simon Swift, James Wu, Adeline Le Cocq, Sudip Ray, Marija Gizdavic-Nikolaidis, Karnika de Silva
- 1800 - 1815 T1.25 **One Single Component Conducting Polymer Hydrogel as a Scaffold for Tissue Engineering.** Damia Mawad*, Elise Stewart, David L. Officer, Gordon G. Wallace
- 1815 - 1830 T1.26 - **Charge Loss in the Electrospinning System.** Jonathan Stanger*, Nick Tucker, Mathieu Sellier, Mark Staiger, Alan Wood

Polymer Characterisation Wellington Room

Chair: Patrice Castignolles

- 1545 - 1600 T2.16 - **Two-dimensional distributions of complex branched polymers.** Francisco Vilaplana, Jovin Hasjim, Robert G Gilbert*
- 1600 - 1615 T2.17 - **Study on the Mechanical Model of Double Network Hydrogel.** Isamu Riku*, Koji Mimura
- 1615 - 1630 T2.18 - **Characterization of polysaccharides for medical applications and bioplastics with solid-state NMR and capillary electrophoresis.** Marion Gaborieau*, Gino Mangiante, Julien Bernard, Aurelia Charlot, Etienne Fleury, Joel Thevarajah, Rozet Sallom Roi, Mariam Mnatsakanyan, Antonio Lauto, Patrice Castignolles
- 1630 - 1645 T2.19 - **Production and characterization of deuterated cellulose.** Christopher Garvey*, Michael Gidley, Deirdre Mikkelsen, Charles Hocart, Marion Gaborieau, Marie Gillon, Peter Holden
- 1645 - 1700 T2.20 - **Investigating the Cooking of Starch – Simultaneous Small-Angle Neutron Scattering and Rapid Visco-Analysis.** James Douth, Mark Bason, Ferdi Franceschini, Douglas Clowes, Kevin James, Elliot P. Gilbert*
- 1700 - 1715 T2.21 - **Injection Molding Studied by Flash DSC Experiments.** Franz Reisinger, Craig Gordon*
- 1715 - 1730 T2.22 - **Investigating the Self-Assembly of Block Copolymer Films by Grazing-Incidence Small-Angle X-Ray Scattering.** Kevin S. Jack*, Imelda Keen, Anguang Yu, Han-Hao Cheng, Idriss Blakey, Michael J. Leeson, Todd R. Younkin, Andrew K. Whittaker
- 1730 - 1745 T2.23 - **Versatile X-ray solutions for polymer screening, characterization, quality control and compliance testing.** T. van der Maten*, Scott Gilroy
- 1745 - 1800 T2.24 - **Topological Assessment of Novel Polymers Subjected to Photoinduced Creep and Stress Relaxation.** Tara Schiller*, Wayne Cook, Cornelis Moorhoff
- 1800 - 1815 T2.25 - **Mapping phase separation of deuterated/hydrogenated polymer blends using Infrared microspectroscopy.** R.A. Russell*, P.J. Holden, L. John R. Foster
- 1815 - 1830 T2.26 - **Characterization of polymers using high resolution impedance spectroscopy.** M. Darestani*, H. Coster, V. Gomes, M. Abtahi

Polymers and the Environment Boardwalk Gallery

Chair: Daniel Keddie

- 1545 - 1600 T3.16 - **Polymer 'tools' for probing ecological questions in the marine environment.** Lachlan H Yee*, Tilmann Harder, Shaun Neilsen, Peter D Steinberg, Symon Dworjanyan, Peter L Harrison
- 1600 - 1615 T3.17 - **Investigation of Native Spinifex Plant Resin and Fibers as Renewable Building Blocks for Composite.** N.Amiralian*, P.Memmott, D.Martin

Symposium Program

TUESDAY 14 February 2012

- 1615 - 1630 T3.18 - **Influence of Soils Type on the Above-Ground Degradation of Polyethylene Thin Films.** Emilie Gauthier *, Melissa Nikolic, Bronwyn Laycock, Jennifer Maia , Gregory Cash, Peter Halley, Graeme George
- 1630 - 1645 T3.19 - **Dielectric investigation of novel reprocessable ionomers based on Natural rubber.** Georgekutty Joseph*, Thommachan Xavier
- 1645 - 1700 T3.20 - **Wholly Printed Polypyrrole-based Biosensors on Flexible Substrate.** Bo Weng*, Aoife Morrin, Roderick Sheppard, Karl Crowley, Anthony J. Killard, Gordon G. Wallace
- 1700 - 1715 T3.21 - **Thermal Degradation Study of a Polyimide Foam.** Xiao-Yan Liu*, Mao-Sheng Zhan, Kai Wang
- 1715 - 1730 T3.22 **Using SAXS to make real-space models of photo-oxo-degradable LLDPE as it ages.** Michael P. Weir*, Yu-Chieh Hsu, Christopher J. Garvey, Peter Halley, Rowan Truss, Timothy Nicholson
- 1730 - 1745 T3.23 - **Improving the Interfacial Properties of Polylactide/Jute Biocomposites by Application of Amphiphilic PEG-PLLA Block Copolymers.** Kevin Magniez*, Andreea S. Voda, Audrey Fichini, Abdullah A. Kafi, Bronwyn Fox, Qipeng Guo
- 1745 - 1800 T3.24 - **New opportunities in renewable polymer and functional materials.** M. S. O'Shea*, F. H.M. Graichen, B. A. Leita, G. Peeters
- 1800 - 1815 T3.25 - **Antagonism Between Transition Metal Prodegradants In Accelerated Photo- and Thermo-Oxidation of Polyethylene Films.** Melissa Nikolić*, Emilie Gauthier, Bronwyn Laycock, Karina George, Gregory Cash, Peter Halley, Graeme George
- 1815 - 1830 T3.26 - **Determination of Monosaccharides from Chemically Hydrolysed Polysaccharides for the Biofuel Industry.** James Oliver*, Michael Phillips, Mark Williams, Patrice Castignolles

Annual General Meeting Plenary Hall

1840 – 1940 RACI Polymer Division

Student Night The Squires Bounty, Salamanca

2030 – late Happy Hour and drink specials available to students

Plenary Session Plenary Hall

Chair: Greg Qiao

0900 – 0950 PL 5 - **Semi-Telechelic and Telechelic Polymers for Conjugation to Biomolecules: From Smart Nanocapsules to Reversible Surface Modification.**
A/Prof Heather Maynard, University of California

0950 – 1010 Morning Refreshments and Trade Exhibition

Advanced Materials Plenary Hall

Chair: Greg Russell

- 1010 - 1040 W1.1 - **Modeling of polymer network formation by nitroxide-mediated radical copolymerization of vinyl/divinyl monomers using a multifunctional polymer molecule approach.** Julio C. Hernández-Ortiz, Eduardo Vivaldo-Lima*
- 1040 - 1055 W1.2 - **Poly(o-methoxyaniline)-Lignosulfonic Acid Composite.** Xiao Wang*, Sudip Ray, Ralph Cooney, Paul Kilmartin
- 1055 - 1110 W1.3 - **Electrically Conductive, Tough Hydrogels with pH Sensitivity.** Sina Naficy*, Geoffrey M Spinks, Gordon G Wallace
- 1110 - 1125 W1.4 - **Supported Hydrogel Polyacrylamide Membranes for the Size-Selective Separation of Gold Nanoparticles.** David Valade*, Yujung Jeon, Lawrence K. Wong, Michael J. Monteiro
- 1125 - 1140 W1.5 - **The Effect of the First Network Heterogeneity on the Mechanical Properties of PNVP-PAAc Double Network Hydrogels.** Hai Xin*, Hugh R. Brown, Sureyya Saricilar, Geoffrey M. Spinks, Philip G. Whitten
- 1140 - 1155 W1.6 - **The influence of hydrophobic modification on the structural alteration of granular branched polysaccharides by β -amylase enzyme treatment.** Michael Sweedman*, Morgan Tizzotti, Robert Gilbert
- 1155 - 1210 W1.7 - **Toughening of PLA: Routes towards Improvement in Mechanical Properties.** Mojtaba Abtahi*, Avinash Baji, Yiu-Wing Mai
- 1210 - 1225 W1.8 - **Thermomechanical Behavior of Conducting Polymer Blends.** J. A. Campbell*, A. Sharma, D. A. Lewis

Polymers for Health Wellington Room

Chair: Michael Whittaker

- 1010 - 1040 W2.1 - **Making Proteins Smarter by Conjugation with Responsive Polymers.** Brent S. Sumerlin*, Ming Li, Hongmei Li, Priyadarsi De
- 1040 - 1055 W2.2 - **Versatile Multi-functionalization of Magnetic Nanoparticles for Biomedical Applications.** Johan Sebastian Basuki*, Thomas Paul Davis, Cyrille Boyer
- 1055 - 1110 W2.3 - **Novel Crosslinked Polymeric Vesicles Conjugated with *cis*-Platinum Drug.** Jiangtao Xu*, Jing M. Ren, Qiang Fu, Greg G. Qiao

Symposium Program

WEDNESDAY 15 February 2012

- 1110 - 1125 W2.4 - **Micelles: NO delivery.** Hien T.T. Duong*, Tom P. Davis, Cyrille Boyer
- 1125 - 1140 W2.5 - **Electrospinning Writing of Scaffolds for Enhanced Cellular Infiltration.** Brooke Farrugia*, Rebecca Dawson, Toby Brown, Paul Dalton, Dietmar Hutmacher, Tim Dargaville
- 1140 - 1155 W2.6 - **Tailoring Layer-by-Layer Films to Reduce Protein Fouling.** Sarah J. Dodds*, Angus P. R. Johnston, Georgina K. Such, Robert de Rose, Frank Caruso
- 1155 - 1210 W2.7 - **Optimizing interfaces to regulate neural progenitor cells using polyelectrolyte multilayers and BDNF.** Kun Zhou, David R. Nisbet, George A. Thouas, Claude C. Bernard, John S. Forsythe*
- 1210 - 1225 W2.8 - **Optimization of Polysiloxane Ophthalmic Biomaterials Used as Accommodating Intraocular Lens Using Factorial Design.** Timothy C. Hughes*, David L.J. Alexander, Tam Le, Asitha Balachandra, Fei Huang, Lisa P.T. Hong, Xiaojuan Hao

Latest Development in Polymer Synthesis Boardwalk Gallery

Chair: Thomas Junkers

- 1010 - 1040 W3.1 - **Novel and Powerful Polymeric Platforms for Conjugation and Postpolymerization Functionalization.** Filip Du Prez*, Pieter Espeel, Milan M. Stamenović, Fabienne Goethals, Claire F. Hansell, Rachel K. O'Reilly
- 1040 - 1055 W3.2 - **Tuning Macromolecular Functionality via Efficient Radical Exchange Reaction.** Kathryn Fairfull-Smith*, Steven Bottle, Aaron Micallef, James Blinco
- 1055 - 1110 W3.3 - **ROMP and Click Modification of Acetylene Functionalised Random and Block Copolymers.** Johann v. Hensbergen*, Andrew B. Lowe, Robert P. Burford
- 1110 - 1125 W3.4 - **The Fabrication of Star Polymer-based Films via ROMP-mediated Continuous Assembly of Polymers (CAP-ROMP).** Steven Harris Wibowo*, Stefanie Nina Guntari, Edgar H. H. Wong, Anton Blencowe, Frank Caruso, Greg G. Qiao
- 1125 - 1140 W3.5 - **Facile Route to Functional Hyperbranched Polymers by Combining RAFT Polymerization and Thiol-Yne Chemistry.** Raphael Barbey*, Sébastien Perrier
- 1140 - 1155 W3.6 - **RAFT polymerization and post-processing using a multi-stage continuous flow approach.** Christian H. Hornung*, Karin von Känel, Stella Kyi, Xuan Nguyen, Almar Postma, Simon Saubern, John Chiefari
- 1155 - 1210 W3.7 - **Rapid and Highly Efficient Functionalization of Polymer Bromide End-Groups by SET-NRC.** Zhongfan Jia*, Craig A. Bell, Michael J. Monteiro
- 1210 - 1225 W3.8 - **Self-Assembly of Porphyrin-Polymer Conjugates obtained via CuAAC Chemistry.** Derrick A. Roberts*, Maxwell J. Crossley, Sébastien Perrier
- 1225 - 1325 Lunch and Trade Exhibition

Plenary Session Plenary Hall

Chair: Martina Stenzel

- 1325 - 1415 PL 6 - **Bioconjugates and glycopolymers from living radical polymerisation.** Prof David Haddleton, University of Warwick

Living Radical Polymerisation Plenary Hall

Chair: Tom Davis

- 1425 - 1455 W1.9 - **Polymer Architectures and Nanostructures Generated via Living Radical Polymerization.** Michael J. Monteiro*
- 1455 - 1510 W1.10 - **Efficient synthesis of α -isocyanate end-functional polymers.** Guillaume Gody*, Thomas Maschmeyer, Sébastien Perrier
- 1510 - 1525 W1.11 - **Syntheses of Polyacrylates by SET-LRP for use in Adhesives and Sealants.** John Woods*, Tony Jacobine, David Dworak
- 1525 - 1540 W1.12 - **Living Free Radical Polymerisation in the Presence of Cu(0): Towards Biological Precision.** Alexander H. Soeriyadi, Cyrille Boyer, Fredrik Nystrom, Per Zetterlund, Michael R. Whittaker*

The Batteard-Jordan Australian Polymer Medal

- 1540 - 1610 W1.13 - **End Group Transformation and RAFT Polymerization.** Graeme Moad*, Ming Chen, Yen K. Chong, Matthias Haeussler, Shadi Houshyar, Daniel Keddie, Ezio Rizzardo, San H. Thang, John Tsanaktsidis

Polymers for Health Wellington Room

Chair: Remzi Becer

- 1425 - 1455 W2.9 - **Star-Shaped PEO-Based Polymers as Artificial Channels : Correlation between Chemical Structure and Channel Activity.** Zahra Eskandani, Nezha Badi, Véronique Bennevault-Celton, Cécile Huin, Philippe Guégan*
- 1455 - 1510 W2.10 - **Study of Diffusion of Model Drugs in Well-Defined Thermo-responsive Poly(*N*-isopropylacrylamide)-Based Hydrogels.** Huey Wen Ooi*, Kevin Jack, Hui Peng, Kristi Anseth, Andrew Whittaker
- 1510 - 1525 W2.11 - **Folate-mediated cancer targeting polymeric micelles as a drug carrier for platinum anticancer agents.** Wei Scarano*, Hien T.T Duong, Paul De Souza, Martina Stenzel
- 1525 - 1540 W2.12 - **Antiviral polymer therapeutics: polymer prodrug design for hepatitis C.** Anton A. A. Smith*, Mille Kryger, Kasper F. Rasmussen, Alexander N. Zelikin
- 1540 - 1555 W2.13 - **Development of wireless and highly sensitive sensor devices for biomedical applications.** Solomon P. Le-Masurier*, Anthony M. Granville
- 1555 - 1610 W2.14 - **New Synthesis of Biodegradable Nanoparticles based on Dextran.** Felicity J. Hughes*, Hien Duong, Tom P. Davis, James M. Hook, Cyrille Boyer

Symposium Program

WEDNESDAY 15 February 2012

Advanced Composite Materials Boardwalk Gallery

Chair: Filip Du Prez

- 1425 - 1455 W3.9 - **Exploring the synthesis and applications of grapheme.** Jonathan Wassei, Sergey Dubin, Jaime Torres, Richard B. Kaner*
- 1455 - 1510 W3.10 - **Imparting Polymer Properties to Graphene Composites via π - π Stacking Surface Modification.** Jingquan Liu*, Tom Davis
- 1510 - 1525 W3.11 - **Using Copolymer Micro-domains to Control the Orientation of Multi-Walled Carbon Nanotubes in a Uniformly Distributed Thin Film.** Tony Aitchison*, Milena Ginic-Markovic, Stephen Clarke
- 1525 - 1540 W3.12 - **Surface Modification of Carbon Nanotubes Using RAFT Polymer Coatings.** Xiaojuan Hao*, Marcio Pasotto, Xuan Nguyen, Yue (Luna) Liu, Jieshan Qiu, Timothy C. Hughes
- 1540 - 1555 W3.13 - **Polymer Coating of Multiple-Walled Carbon Nanotubes via RAFT Mediated Emulsion Polymerisation.** Duc Nguyen*, Chris Such, Brian Hawke
- 1555 - 1610 W3.14 - **Electrospun Polystyrene Short Fibres from Ultrasonication Method.** Marini Sawawi*, George P. Simon, David Nisbet
- 1610 - 1630 Afternoon Refreshments and Trade Exhibition

Plenary Session Plenary Hall

Chair: Sébastien Perrier

- 1630 - 1720 PL 7 - **The Origins of Living Radical Polymerization (LRP) in CSIRO.** Prof David Solomon, University of Melbourne
- 1720 - 1810 PL 8 - **RAFT polymerization: past, present and future.** Dr Ezio Rizzardo, CSIRO
- 1810 - 1830 Symposium Conclusion

Symposium Dinner Tasman Room

1930 - 2330 Enjoy a 3 course dinner with beverages and entertainment from Rum Jungle

Vitrimers

Damien Montarnal, Mathieu Capelot, François Tournilhac, Ludwik Leibler

Matière Molle et Chimie (UMR 76167 ESPCI-CNRS), ESPCI, 10 rue Vauquelin, 75005 Paris, France

We will discuss a concept and practical realizations of a glass transition by reversible topology freezing of a molecular network. Permanently cross-linked materials, like thermosets or rubbers, have outstanding mechanical properties and solvent resistance, but they cannot be processed and reshaped once synthesized. Non-cross-linked polymers and those with reversible cross-links are processable, but they are soluble. We design epoxy networks able to rearrange their topology by exchange reactions without depolymerization and show that they are insoluble and processable¹. Unlike organic compounds and polymers whose viscosity varies abruptly near glass transition, these networks, vitrimers, show Arrhenius-like gradual viscosity variations just like vitreous silica. Like silica, the vitrimers can be wrought and welded to make complex objects by local heating without the use of molds. The concept of a glass, made by reversible topology freezing in epoxy networks can be readily scaled up for applications and generalized to other chemistries. Vitrimers constitute thus a new class of materials that are processable, repairable, and recyclable like thermoplastics yet insoluble like thermosets or elastomers, their behavior resembles that of amorphous silica, but they are organic materials and therefore much lighter and less breakable than silica.

Dr. Leibler, Director of Research (Exceptional Class) at Centre National de la Recherche Scientifique (CNRS) and adjunct professor at Ecole Supérieure de Physique et Chimie Industrielles (ESPCI) in Paris is the director of Soft Matter and Chemistry Laboratory at ESPCI.



Organic (Nano) Bionics

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Medical bionic devices such as the cochlear ear implant that restores hearing to the deaf and vagus nerve stimulators that provides control over a range of neurological conditions have a profound impact on quality of life.

A number of other bionic implants such as the bionic eye, devices that connect the brain to prosthetics or conduits for nerve/muscle regeneration are under development. The performance of each of these devices is ultimately dependent on the effectiveness of the electrode- cellular interface.

In our work we have been concerned with the development of polymeric organic conductor systems to create an appropriate interface. Here we describe how the dynamic properties of inherently conducting polymers can be used to facilitate nerve and muscle growth. The effect of polymer composition, both the conducting polymer backbone and the molecular dopant, has been investigated. The ability to incorporate a range of biologically active molecules as an integral component of the structure provides some exciting opportunities. Accessibility to these biomolecules is achieved *in-situ* by electrical stimulation. In order to control the direction of nerve and muscle growth we have used topographical cues with either micron or nano dimensions.

In addition we are concerned with two parallel streams of activity that are critical to the realization of clinically relevant devices based on organic conducting polymers. The first is the development of new characterization tools that enable us to “visualize” events in the nanodomain. Bio Atomic Force Microscopy provides some fascinating insights. The techniques developed allow us to obtain topographical information under cell culturing conditions. Bio AFM also allows mechanical data on the organic conducting polymer bioplatfoms to be obtained with nanodimensional resolution.

The other parallel activity involves the development of novel nanofabrication tools to create platforms with spatial control over the distribution of functionality. In this area we have been involved in the development of fiber spinning techniques and in particular coaxial electrospinning and printing using Dip Pen Nanolithography.

Success in this challenging area will be judged on our ability to meet real clinical needs. We have targeted applications in nerve and muscle regeneration as well as epilepsy detection and control. Here we will update on our progress in these areas.

Selected Publications in Organic Bionics:

¹ B. Weng, X. Liu, M.J. Higgins, R. Shepherd, G. Wallace, *Small* In Press.

² E.M. Stewart, X. Liu, G.M. Clark, R.M.I. Kapsa, G.G. Wallace, *Acta Biomaterialia* In Press.

³ B.C. Thompson, S.E. Moulton, R.T. Richardson, G.G. Wallace, *Biomaterials* **2011**, 32, 3822-3831.

⁴ Z. Yue, X. Liu, P. Molino, G.G. Wallace, *Biomaterials* **2011**, 32, 4714-4724.

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Stimuli-responsive Polymeric Superamphiphiles for Controlled Self-assembly

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Superamphiphiles refer to amphiphiles that are formed by non-covalent interactions, including host-guest interactions, hydrogen bonds, and charge transfer interactions or combined interaction of different intermolecular forces.¹⁻⁶ The superamphiphiles can be low-molecule-weight molecules as well as polymers. The advance of superamphiphiles can enrich the family of conventional amphiphiles that are formed on the basis of covalent bond; in the mean time it opens a new avenue of controlled self-assembly and disassembly for functional supramolecular materials.

One of the advantages of superamphiphiles is incorporation of stimuli-responsive moieties easily, due to the dynamic nature of noncovalent bonds. In this presentation, we will discuss two methods for fabricating stimuli-responsive polymeric superamphiphiles. One method is to employ the electrostatic attraction between adenosine 5-triphosphate (ATP) and polyethyleneglycol-b-polylysine (PEG-b-PLKC).⁷ In this way, an enzyme-responsive polymeric superamphiphile has been successfully prepared. This superamphiphiles self-assemble in water to form spherical aggregates, which disassemble in response to enzymatic stimulus and subsequently release the loaded molecules. The other method to fabricate polymeric superamphiphile is driven by dynamic covalent bond. A toothbrush-type polymeric superamphiphiles has been constructed on the basis of dynamic benzoic imine bonds by using a double-hydrophilic PEG-b-PLKC and α -(decyloxy)benzaldehyde (DBA). The superamphiphile can self-assemble into spherical aggregates under physiological conditions. Due to the pH-responsive nature of the benzoic imine bond, the superamphiphile can be formed and disassociated reversibly in response to small pH fluctuations in the physiologically accessible range, and this leads to self-assembly and disassembly of the aggregates.⁸

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Combating Diseases with Peptide – Synthetic Polymer Conjugates

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Peptides and proteins often combine unique self-assembly properties with very specific biological activity. From a therapeutic point of view, peptides and proteins are of interest, not only because of the possibilities to act as inhibitors or antagonists of biological processes (i.e. to act as therapeutics), but also because they provide opportunities e.g. for targeted delivery or to guide intracellular trafficking. Judiciously combining biologically active peptides or proteins provides opportunities to overcome problems related to the limited stability and plasma half life of peptides and proteins, to enhance the efficacy of polymer-drug conjugates and to augment the activity of peptide based therapeutics. This presentation will consist of three parts which will successively discuss: (i) non-covalent polymer – drug conjugates in which the peptide-based linker not only acts to bind and release cargo but also is involved in directing intracellular trafficking; (ii) polymer-modified HIV fusion inhibitors that show increased stabilities as compared to the unmodified peptides while maintaining activity and (iii) multivalent HIV entry inhibitors based on side-chain peptide – polymer conjugates which allow to augment the activity of the peptide. In all three cases, precision polymer synthesis is essential in the successful design of the final conjugates. Amongst others, the examples will highlight the importance of controlling molecular weight, the site of polymer – peptide conjugation as well as polymer architecture on the final properties and activity of the peptide – synthetic polymer conjugates.

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Semi-Telechelic and Telechelic Polymers for Conjugation to Biomolecules: From Smart Nanocapsules to Reversible Surface Modification

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Conjugation of polymers to proteins results in materials with enhanced properties compared to the native biomolecules. Controlled radical polymerizations, such as atom transfer radical polymerization (ATRP)^{1,2} and reversible addition-fragmentation chain transfer (RAFT) polymerization^{3,4} can be utilized to prepare protein-polymer conjugates. CRPs enable synthesis of semi-telechelic, protein-reactive polymers and polymerization directly from biomolecules.^{5,6} Cysteine-reactive activated disulfides, maleimides, and vinyl sulfones have been installed by our laboratory. Aminoxy moieties that react with aldehydes or ketones have been prepared. Ligand binding sites such as biotin have been targeted. In Nature, proteins often self assemble into multimers of specific stoichiometry in order to induce biological processes. Thus, conjugate designs that control the number and presentation of proteins should be advantageous to both study these interactions and to prepare therapeutics preorganized into the active state. Indeed, telechelic polymers⁷ which can have the same or different end groups to prepare homo-dimeric or hetero-dimeric proteins, respectfully, have been prepared by CRP techniques.⁸⁻¹⁵ One strategy we have employed involves radical reaction of thiocarbonyl end groups produced by RAFT polymerization with specially designed protein-reactive azo initiators. Homotelechelic and heterotelechelic polymers were prepared for conjugation to the same or different protein, respectively. We also showed that atom transfer radical polymerization using protein-reactive initiators with atom transfer coupling in the final step produces the desired polymers. This talk will focus on the synthetic approaches, characterization, and conjugation of biomolecules. In addition use of the polymers to prepare biomedical biohybrid materials will be discussed. For example, modification of a protein nanocapsule called a vault with polymers (**Fig.1**) will be discussed. Vaults are 42 x 42 x 75 nm and non-immunogenic.¹⁶ These conjugates have a lot of promise for drug delivery applications, and this will be discussed.

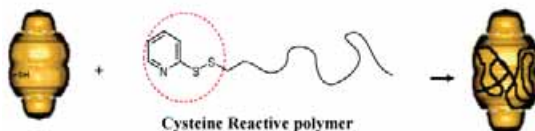


Fig.1 Preparation of vault-polymer nanocapsule for drug delivery

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Bioconjugates and glycopolymers from living radical polymerisation*David M Haddleton*

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Non-covalent interactions between complex carbohydrates and proteins drive many fundamental processes within biological systems, including human immunity. DC-SIGN (dendritic cell specific ICAM-3 grabbing nonintegrin) is a C-type lectin of significant medical interest that is expressed on the surface of dendritic cells: highly specialized cells that govern immune responses. DC-SIGN recognizes oligosaccharide structures on host glycoproteins and regulates immune functions such as cytokine production and antigen presentation. Importantly, DC-SIGN also binds to carbohydrates on the surfaces of lethal opportunistic pathogens, notably HIV-1, enhancing their adhesion, infectivity and persistence in patients. Solid phase competition assays have demonstrated monosaccharide mannose binding to DC-SIGN with millimolar affinity, and that affinity for oligosaccharide ligands such as $\text{Man}_6\text{GlcNAc}_2$ is greatly enhanced. High-resolution structural studies have shown that DC-SIGN binds preferentially to complex mannose oligosaccharide structures and the primary carbohydrate-binding site selectively accommodates the equatorial stereochemistry of the C3 and C4 hydroxyls found in the mannopyranosides.

The well-defined clickable polymer backbone was synthesized by copper-mediated living radical polymerization of trimethylsilyl propargyl methacrylate to give a polymer with a range of number average degree of polymerization. Following the removal of the trimethylsilyl group, copper(I) catalyzed click was used to synthesise glycopolymer species containing varying densities of α -D-mannose and β -D-galactose and fucose as well as control polymers with glucose. We have been investigating range of different architecture polymers from living radical polymerisation. In particular we have found that star shaped polymers have high affinity and compete with GP120 at therapeutic concentrations. This talk will present our latest results in this area.

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The Origins of Living Radical Polymerization (LRP) in CSIRO

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The lecture will review the many factors that led to the establishment of Polymer Research in CSIRO and the discovery of Living Radical Polymerization (LRP). These include experience with Balm Paints Pty. Ltd. where acrylic lacquers were synthesized and supplied to the automotive industry, and the importance of contacts formed via the Polymer Division in progressing work on polymers in CSIRO.

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Research interests: Radical polymerization, water evaporation control



RAFT polymerization: past, present and future

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Radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization) is a form of living radical polymerization that was first introduced in 1998 (1). It is conducted by the addition of an appropriate thiocarbonylthio compound (RAFT agent) to a conventional free radical polymerization. The overall process is as follows:



Its experimental simplicity, its close relationship to conventional free radical polymerization and its applicability to a wide range of monomers are particularly attractive characteristics of the RAFT process. Since its introduction thousands of papers have appeared on studies of its mechanism and on its application to the synthesis of narrow polydispersity polymers of various architectures, including gradient, block, and star polymers (2).

Our interest in recent times has focused on extending the utility of RAFT polymerization. To this end we have devised scalable procedures for the removal or modification of the thiocarbonylthio polymer end group, and developed switchable RAFT agents that give us the ability to synthesise block copolymers from ‘more activated monomers’ (e.g. methyl acrylate) with ‘less activated monomers’ (e.g. N-vinyl carbazole) (3).

The commercial future of RAFT appears to be bright. Some 60 of the major chemical companies around the world have filed more than 500 patents/patent applications covering a wide range of products including polymer therapeutics, drug delivery, contact lenses, plastic solar cells, integrated circuits, desalination membranes, cosmetics, lubricants, elastomers, paints, inks and adhesives.

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Research interests: Radical polymerization, polymer synthesis



Utilizing Supramolecular Interactions to Access Dynamic Materials

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Utilizing non-covalent interactions to access controlled molecular assemblies as well as to influence communication between different components is a critical concept in most biological processes and natural biomaterials. Transferring this approach to designed synthetic polymer systems potentially opens the door to materials that exhibit unusual structural, mechanical and functional properties. The reversible nature of the non-covalent bond allows, when molecules are designed correctly, to access thermodynamically stable, complex self-assembled architectures, as well as to a new generation of adaptive, stimuli-responsive materials.¹ As such the designed utilization of supramolecular chemistry in the field of polymer science has seen a dramatic growth in the last decade or so. We have been interested in the potential of such systems to access new material platforms and have developed a range of new mechanically stable, supramolecular polymer films that change their properties in response to a given stimulus, such as temperature, light or specific chemicals. Such supramolecular materials have been targeted toward applications that range from new implantable adaptive nanocomposites² (**Fig. 1a**) and healable plastics³ to sensors for chemical warfare agents⁴ (**Fig. 1b**), thermally responsive hydrogels⁵ and shape memory materials.⁶ Our latest result in this area will be discussed.

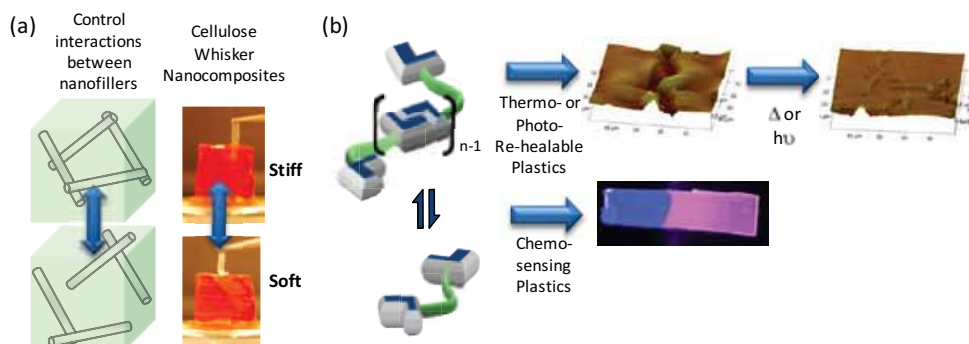


Figure 1. Two different approaches to stimuli-responsive materials where equilibrium (dynamic) chemistry is used to control the responsiveness of the material. (a) Controlling filler-filler interactions in nanocomposites and (b) main-chain supramolecular polymers,

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Research interests: supramolecular polymers, stimuli-responsive materials, metal-containing polymers, nanocomposites, gels, biomaterials



Stuart Rowan is currently the Kent H. Smith Professor of Engineering in the Department of Macromolecular Science and Engineering at Case Western Reserve University. He received his B.Sc. (Hons.) in Chemistry in 1991 from the University of Glasgow and stayed there for his Ph.D. where he worked on Supramolecular Crystal Engineering of Inclusion Compounds. In 1994 he moved to the Chemistry Department at the University of Cambridge and carried out research on the development of Dynamic Combinatorial Libraries in the labs of Prof Jeremy Sanders, FRS. In 1998 he continued his postdoctoral studies at the University of California, Los Angeles with Sir Fraser Stoddart FRS, where he developed new methods for the construction of interlocked molecules. In 1999 he was appointed as an Assistant Professor in the Department of Macromolecular Science and Engineering at CWRU in Cleveland, Ohio and became Full Professor in 2008. He is also the director of CWRU's Institute for Advanced Materials (IAM). He is a NSF CAREER awardee and received the CWRU School of Engineering Research Award in 2008. His research interests focus on the potential of dynamic chemistry (covalent and non-covalent) in the construction and properties of polymeric materials. His group works on supramolecular polymers, self-healing materials, metal-containing polymers, gels, biomaterials, and developing new synthetic methods for the construction of complex polymeric architectures. He is the Deputy Editor of the new *ACS Macro Letters* journal and a Fellow of the Royal Society of Chemistry. He has published over 95 scientific papers and reviews.

Smart glycopolymers and their interactions with lectins

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Tailor-made macromolecules have been attracting more and more attention to deliver the desired properties to the advanced materials by the use of their controlled compositions and architectures. Development of various controlled radical polymerization techniques and “click” reactions provide a sufficient platform to prepare functional polymers.¹⁻³ Various combinations of these techniques yield functional polymers. For instance, one of the most widely used combinations is the metal-mediated living radical polymerization and Cu catalyzed Huisgen cycloaddition reaction between azide and alkyne. Alternatively, thiol-ene click reaction can be employed for the thiol terminated or vinyl terminated polymers where thiol terminated polymers can be achieved simply by RAFT polymerization and a subsequent reducing reaction of the chain transfer agent. Similarly, vinyl terminated polymers are also very easy to obtain, *i.e.* by catalytic chain transfer (CCT) polymerization. CCT polymerization provides vinyl-terminated methacrylate polymers with high fidelity of end groups.

In this study, we have prepared glycopolymers in various architectures using atom transfer radical polymerization and copper catalyzed azide-alkyne click reaction. As illustrated in Figure 1, we have prepared linear polymers that can be a homopolymer, block copolymer, and random copolymer. For the preparation of block copolymers, we first polymerized either di(ethyleneglycol) methacrylate (DEGMA) or trimethylsilyl propargyl methacrylate (TMSMA) using Cu(I)Br and *N*-(ethyl)-2-pyridylmethanimine catalyst system and disulfide functional bisinitiator. Using these as macroinitiators, ABA block copolymers were prepared with TMSMA or DEGMA.

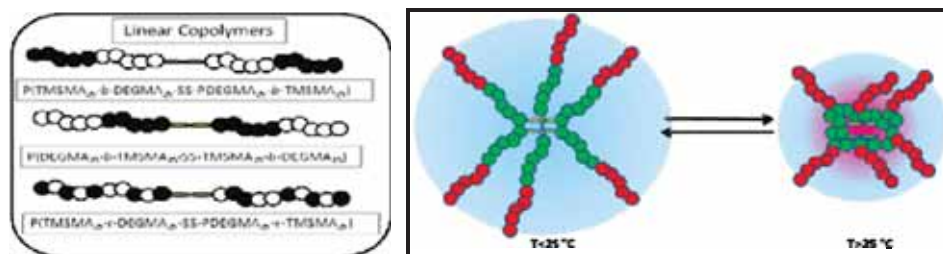


Figure 1. Composition of responsive glycopolymers (left), and their thermoresponsive behavior (right).

Moreover, we have investigated the affinity of poly(mannose-methacrylate) with a selected mannose binding lectin using SPR technique.⁴ Selected members of a glycopolymer library were used to demonstrate the interactions between DC-SIGN and mannose rich polymers. We extend this study to a broader set of polymers to examine the effect of chain length, end group, architecture, thermoresponsive block, and number of arms in the star shaped polymers on the lectin binding.

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Living *p*-quinodimethane polymerization for the synthesis of well-defined PPV materials: Is it even possible?

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One of the most prominent synthesis strategies for conjugated polymer systems is the so-called *p*-quinodimethane polymerization, which is also often referred to as the precursor routes to obtain poly(*p*-phenylene vinylene) materials.¹ Thereby, a monomer precursor is used that upon reaction with a strong base forms an active quinodimethane system that can undergo radical polymerization. Due to its radical mechanism, quinodimethane polymerization is an attractive synthesis route since it allows for relatively mild reaction conditions and high tolerance towards functional groups. To date, however, no control methodologies that allows to synthesize poly(phenylvinylene)s or other poly(arylene vinylene)s in a precise manner comparable to controlled/living radical polymerization techniques in the realm of conventional radical polymerization are known. Only materials with high dispersity, insufficient control over the average molecular weight and functionality are thus available. If an efficient control is achieved, conjugated polymers with narrow molecular weight distribution, exactly pre-determinable molecular weight and high endgroup fidelity will become available. With such material at hand, block copolymers of various types become available, either in sequential or in modular design approaches by using *Click*-type chemistries.



First advances towards controlled quinodimethane polymerization have been made by carrying out successful chain-transfer polymerizations or anionic polymerizations, hence enabling the synthesis of well-structured, however still not immaculate PPVs materials.²⁻⁴ The state of the art of controlled PPV synthesis will be outlined and outstanding problems are summarized and pathways to overcome these challenges discussed.

¹ T. Junkers, J. Vandenberg, L. Lutsen, P. Adriaenssens, D. Vanderzande, *Polym. Chem.* **2012**, *in press*.

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Functional Nanocoatings

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The worldwide market for functional surfaces exceeds \$50 billion per annum (US Department of Energy). A key driver is the added value that can be imparted to commercial products by tailoring their surface properties. For example, the cleanliness of optical lenses, the feel of fabrics, the resistance of biomedical devices to bacteria, the speed of computer hard disks, and even the wear of car brake pads are all governed by their surface functionality. In order to generate such surfaces incorporating specific chemical groups, there exists no shortage of methods including: self-assembled monolayers (SAMs), Langmuir-Blodgett films, grafting, chemical vapour deposition, to name just a few. However such techniques suffer from drawbacks including substrate-specificity (cannot be easily adapted to different materials or geometries) and environmental concerns associated with the utilization of solvents, strong acid / base media, and heat. Non-isothermal plasmachemical functionalization is a promising alternative which offers many potential benefits including low energy consumption, absence of solvents, minimal waste, rapid treatment times, and ambient temperatures. Earlier attempts to control surface functionality using this approach experienced only limited success due to the difficulty associated with controlling secondary reaction pathways within the electrical discharge. An innovative solution will be described for molecularly tailoring solid surfaces with high levels of structural definition so as to make them super-repellent, rewritable, bioactive, thermoresponsive, adhesive, gas impermeable, non-fouling, opto-chiral, catalytic, antibacterial, or nano-actuated. This fundamental research has led to the filing of 29 patent families and the establishment of 3 start-up companies.

Jas Pal Badyal was awarded BA/MA (1985) and PhD (1988) degrees from Cambridge University; where he subsequently held a King's College Fellowship and the Oppenheimer Fellowship. In 1989 he moved to Durham University to take up a lectureship and was promoted to Professor in 1996. He is named as the primary author / inventor on 152 refereed research publications / 29 patents, and has presented 54 plenary / invited lectures at international conferences. He has been recipient of the *Harrison Prize* from The Royal Society of Chemistry; *Burch Prize* from The British Vacuum Council; and an *EPSRC Advanced Research Fellowship*. International journal editorial board membership has included: *Plasmas and Polymers*; *Journal of Adhesion Science and Technology*; *Plasma Chemistry and Plasma Processing*; and *ACS Applied Materials & Interfaces*. His research has led to 3 start-up companies: *Dow Corning Plasma Ltd* (atmospheric plasma processing), *P2i Ltd* (super-repellent surfaces), and *Surface Innovations Ltd* (bioactive coatings).



Applications for RAFT in Disperse Phase Systems

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The advent of controlled radical polymerisation has revolutionised the scope for free radical polymerisation. Of the various controlled radical techniques now available Reversible Addition Fragmentation chain Transfer (RAFT) would seem to be the most versatile, with applicability to a wide range of monomers at readily accessible temperatures¹. The adaptation of RAFT for use in dispersed phase systems² has further enhanced the capability of the technique and paved the way for a fine control of the morphology of latex and composite nanoparticles that was not possible by conventional free radical polymerisation techniques. These include the ability to coat a wide range of solid particles with polymer, provide very monodisperse latex particles of less than 20 nm diameter and prepare titanium dioxide nanorattles with very high light scattering efficiency for paint applications.

The capacity of RAFT to provide short chain block copolymers has enabled the preparation of a wide range of sterically stabilised nanoparticles that exhibit a diverse range of behaviors in biological media, including penetration of solid tumor models. Changing nano particle functionality radically affects the fate of particles both in solid tumor models and in vivo. The block copolymer stabilised particles have obvious potential in many biomedical applications such as drug deliver and imaging.

We have applied the new technology of controlled radical polymerisation to synthesize particles with particular sizes and surface properties for biomedical applications.

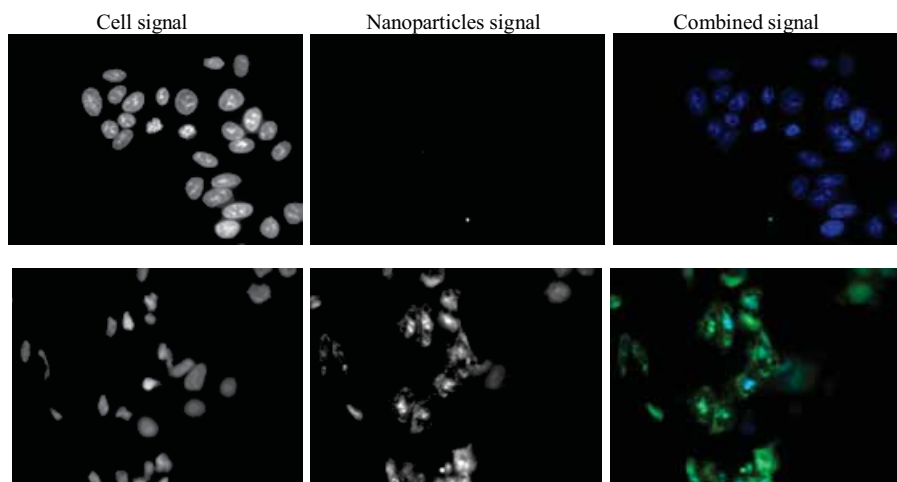


Figure 1: Confocal microscopy images for the uptake of iron oxide nanoparticles into the DLD-1 colon cancer cells. Top row: Folate-free nanoparticles; Bottom row: folate functionalized nanoparticles.

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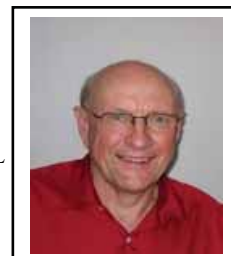
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- Research interests: Disperse phase polymerisation, particularly RAFT mediated.



Controlled Radical Polymerization, Metathesis, and “Click” Chemistry: A Versatile Combination to Target New Reactive Polymers

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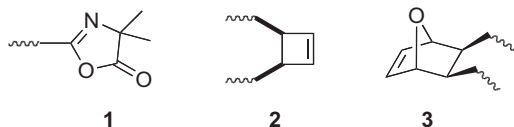
The design and the synthesis of well-defined polymers with multiple pendent functionalities have attracted considerable interest in modern polymer chemistry. Because properties and performances of polymers greatly depend on the nature and number of functional groups, new synthetic strategies have been developed that exert excellent control over functionalities through highly efficient orthogonal chemical reactions. Controlled/living radical polymerization, ring-opening metathesis polymerization (ROMP), and “click” chemistry can now afford such a high degree of control over polymer topology, composition, and functionality.ⁱ

Complex functional polymers such as reactive polymers, macromonomers and functionalized oligomers are required for the precise synthesis of various macromolecular architectures: block, graft, and hyperbranched (co)polymers.ⁱⁱ To prepare new functional materials, we have investigated synthetic strategies to incorporate highly reactive functionalities using orthogonal chemical processes.

The talk will present results related to the manipulation of such orthogonal chemistries in order to prepare new well-defined reactive polymers: macromonomers, block, and graft copolymers. Atom-transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT), ROMP, and “click” chemistries (thiol-ene Michael addition and Huisgen 1,3-dipolar cycloaddition) have been used in combination with highly reactive functionalities (Scheme 1):

- The azlactone ring (**1**) of 2-vinyl-4,4-dimethyl-5-oxazolone (VDM) that reacts with nucleophiles without the formation of by-product, to prepare reactive and thermoresponsive polymers;ⁱⁱⁱ
- The cyclobutenyl group (**2**) to synthesize well-defined grafted copolymers based on a strictly linear 1,4-polybutadiene trunk;^{iv}
- The bicyclic oxanorbornenyl group (**3**) to prepare poly(ethylene oxide) macromonomers and graft copolymers *via* “click” chemistry and ROMP.^v

Those strategies provide excellent control over all synthetic steps, leading to polymers that are useful for the synthesis of various functional materials.



Scheme 1

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Research interests: Macromolecular engineering using controlled / « living » polymerization and application to the synthesis of functional and reactive homopolymers, block and graft copolymers (Ring-Opening Metathesis Polymerization [ROMP], controlled radical polymerization [ATRP, RAFT]); Biomedical applications of polymers; Polymers for optics.

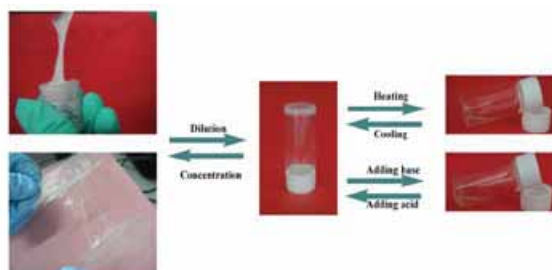


Supramolecular Polymers Based on Threaded Structure Connections

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Threaded structures, such as rotaxanes and catenanes, have attracted much attention not only because of their topological importance but also due to their application in the preparation of artificial molecular machines. Supramolecular polymers, assembled from low molecular weight monomers via noncovalent interactions, such as hydrogen bonding, metal coordination as well as host-guest interactions, have demonstrated traditional polymeric properties and become an important source for the development of stimuli-responsive dynamic materials. We are interested in the fabrication of supramolecular polymers based on threaded structure connections.¹⁻⁵ Self-sorting organization of two AB-type heteroditopic monomers led to the formation of linear supramolecular alternating copolymers driven by host-guest noncovalent interactions based on the bis(p-phenylene)-34-crown-10/paraquat derivative and dibenzo-24-crown-8/dibenzylammonium salt recognition motifs. By utilization of host-guest and metal-ligand noncovalent recognitions motifs, different topologies of supramolecular polymers, such as linear and crosslinked species, can be reversibly interconverted by external stimuli. Based on the dibenzo-24-crown-8/1,2-bis(pyridinium)ethane recognition motif, a hyperbranched mechanically interlocked polymer was prepared by polyesterification of an easily available dynamic trifunctional AB₂ pseudorotaxane monomer. By utilization of a crown ether-based host-guest recognitions motif, a supramolecular polymer gel constructed from a low molecular weight A-B monomer shows thermo- and pH-induced reversible gel-sol transitions. The thermal- and pH-responsive gel-sol transitions were successfully employed in the controlled release of Rhodamine B.



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Nanoparticles with pendant cyclodextrins as drug delivery carrier

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The advantage of polymers with pendant cyclodextrin over the amorphous “cyclodextrin polymer” are their well-defined structures and their controlled solution properties. Interestingly, not much attention has been drawn yet to the combination of controlled polymer architectures with cyclodextrin.¹ Reversible Addition Fragmentation chain Transfer (RAFT) polymerization opened the door to a range of polymer architectures with precise control over the molecular weight.² Linear polymer chains with well-defined endfunctionality are as easily accessible as block copolymers or starpolymers.

Attractive is also ability of cyclodextrin to act as a carrier for drugs. While a single cyclodextrin molecule might enhance the solubility of often insoluble drugs, a polymeric structure can enhance drug delivery by better accumulating in the tumour. Micelles are attractive drug delivery carriers due to their small size and their water-soluble shell.³ We therefore decorate amphiphilic block copolymers with pendant cyclodextrin molecules. These molecules can then undergo self-assembly into polymeric micelles.

There are potentially two pathways to polymers with pendant cyclodextrins, either via the postfunctionalization of reactive polymers or via the polymerization of cyclodextrins with vinyl functionality.¹ We employed various click reaction to functionalize block copolymers with cyclodextrins. Thermo-responsive block copolymers with β -CD (Fig. 1), but also various other block copolymers were generated. We studied the encapsulation of various drugs including albendazole, curcumin and platinum drugs, but also the simultaneous crosslinking of micelles using a supramolecular approach based on the host-guest chemistry between cyclodextrin and adamantane derivatives were investigated.

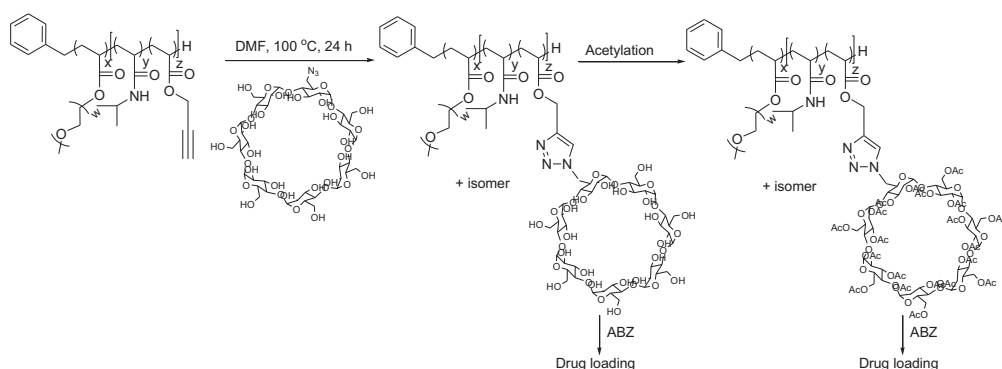


Figure 1. Synthesis of block copolymers with pendant cyclodextrin for encapsulation of drugs

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Research interests: Block copolymer micelles, drug delivery, macromolecular metal drugs

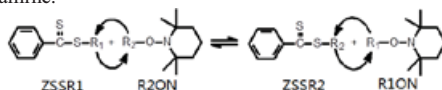


Small Molecular Kinetic Model for the RAFT Process

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The fundamental study on kinetics and mechanism of the RAFT-based polymerization, with the aim of determining the rate coefficients of chain transfer reactions, is an ongoing topic in scientific community. A number of approaches have been applied to determine the chain transfer coefficient¹, particularly, the individual rate coefficients of addition (k_{add}) and fragmentation (k_{frg}). In the present work, we have studied the mechanism and kinetics of a pure RAFT process, e.g., without polymerization, using a small molecular model reaction between dithioester and alkoxyamine.²



The purpose of using alkoxyamine is because it generates carbon-centered radicals at a rate regulated by the persistent radical effect (PRE). Thus the radical R_2 from homolysis of alkoxyamine R_2ON adds to dithioester $ZSSR_1$, forming the intermediate radical possessing two leaving groups, R_1 and R_2 . When fragmentation occurs at R_1 side, a chain transfer process is fulfilled and the released R_1 is trapped by the persistent nitroxyl radical to form a new alkoxyamine, R_1ON . An equilibrium between alkoxyamine and dithioester is built through the RAFT process. The kinetics of the RAFT process closely relates to the macroscopic kinetics of the exchange reaction, which can be easily measured by HPLC and ESR.

Fig. 1 shows the computer simulated concentration of nitroxyl radical, TEMPO, as a function of reaction time. It is clear that the free TEMPO concentration depends on the rate coefficients of the RAFT process. **Fig. 2** shows the concentration of the starting dithioester decrease along with the reaction proceeds. The time for building a dynamic balance between the reverse reactions strongly relates to the rate of the RAFT process. These results allows reasonable fitting of kinetic parameters to the macroscopic kinetics.

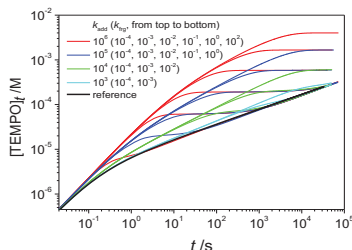


Figure 1. Monte Carlo simulated TEMPO concentration as a function of reaction time for various k_{add} and k_{frg} .

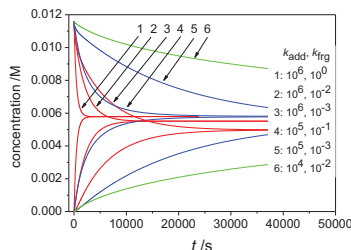


Figure 2. Monte Carlo simulated concentrations of starting and the resulting dithioesters as functions of reaction time for various k_{add} and k_{frg} .

The comparison between theoretical and the experimental results, the side reactions that interfere the kinetic model, as well as the successful determination of k_{add} and k_{frg} , will be discussed.

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Functional Nanomaterials from Block Copolymer Self-Assembly

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This talk will describe the synthesis and characterization of functional nanostructured materials from the self-assembly of blocked macromolecules with inorganic materials.¹⁻⁶ It is structured according to the degree of order achieved in the resulting materials, moving from amorphous to polycrystalline to single crystal-type materials. By using thermodynamic principles established for block copolymers and mixtures with inorganic species (e.g. nanoparticles) well-defined nanostructured morphologies are obtained at all these levels of structural order. Thermal processing of the polymer-inorganic hybrids results in nanoporous materials with uniform pores and hexagonal as well as bicontinuous cubic pore structures. These concepts are applied to amorphous nanostructured aluminosilicates and non-oxide type ceramics stable up to 1500°C, polycrystalline nanostructured transition metal oxides and metals, as well as nanostructured, porous single crystal silicon and metal thin films (~10-100nm) with epitaxial growth relation to the substrate. The various chemical approaches will be discussed. Perspectives will be given in the context of nanomaterials for applications ranging from microelectronics to energy generation and storage, i.e. materials for solar cell, fuel cell and battery applications

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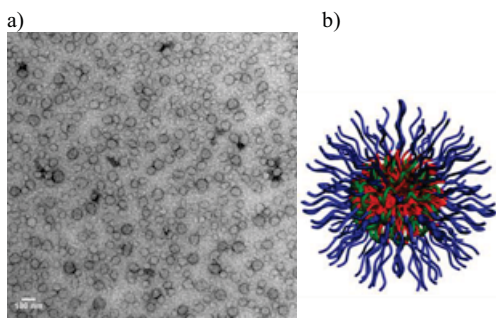
Delivery Agents Designed from Core-Shell Carbohydrate-Based Block Copolyations

Nilesh Ingle, Antons Sizovs, Giovanna Grandinetti, Lian Xue, Adam E. Smith, Theresa M. Reineke¹

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The intracellular delivery of nucleic acids offers unprecedented promise for revolutionizing biomedical research and novel drug development. However, the nucleic acid delivery vehicle plays a central yet elusive role in dictating the efficacy, safety, mechanisms, and kinetics of gene regulation in a spatial and temporal manner. To this end, we have developed several novel carbohydrate-containing polymers that have shown outstanding affinity to encapsulate polynucleotides into nanoparticles termed polyplexes and facilitate highly efficient intracellular delivery without toxicity. We have utilized step growth polymerization techniques to yield a comprehensive series of polycations that contain various mono-, di-, and oligosaccharide moieties copolymerized with ethyleneamine units. In addition, we have recently created analogs of these polymers via RAFT polymerization methods, allowing us to create a variety of block copolymer architectures with saccharides and a variety of cationic units in a highly controlled manner. A number of these polymer systems have revealed high efficacy for both pDNA and siRNA delivery. To examine the intracellular mechanisms of delivery, we have utilized live cell confocal microscopy imaging techniques to examine the intracellular trafficking of the polyplexes with Hela cells, which allows us to observe polyplex movement within the cells. We have also developed three dimensional data processing techniques to surface render confocal images, allowing us to visualize the spatial and temporal distribution of polyplexes within the cellular environment.

Figure 1. a) TEM image of polyplexes formed with carbohydrate-polycation block copolymers that have encapsulated pDNA. b) Depiction of the core-shell structure of the polyplexes (polymerized pendant carbohydrates form the shell).



1. A. E. Smith, A. Sizovs, G. Grandinetti, and T. M. Reineke, *Biomacromolecules* **2011**, 12, 3015-3022

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Personal History

2000	PhD, University of Michigan
2000-2002	NIH Postdoctoral Scholar, California Institute of Technology
2002-2008	Assistant Professor of Chemistry, University of Cincinnati
2008-2011	Associate Professor of Chemistry, Virginia Tech
2011-present	Lloyd H. Reyerson Professor of Chemistry University of Minnesota



Research interests: polymer synthesis, nucleic acids, drug delivery, cell and tissue imaging

Acid-Bearing Polymer Membranes for PEM Fuel Cells

*E.M.W. Tsang, A. Yang, Z. Shi, T. Weissbach, **S. Holdcroft***

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This presentation is intended to highlight structure-property relationships that lead to a better understanding of proton conducting polymers. This necessarily requires the undertaking of rigorous, systematic studies of representative materials that possess known and controllable structures and morphologies. Proton conductivity and related properties of solid polymer electrolytes possessing unique variations in ionic phase segregation networks will be described. Emphasis is placed on obtaining an understanding of the physical processes that give rise to proton conductivity. In this presentation the synthesis and properties of series of novel ionic copolymers of controlled structure will be described. Emphasis will be placed on controlling the crystallinity of the polymers and its role on influencing ionic cluster size, water sorption, and proton conductivity. The effect of introducing organized ionic networks on the anisotropy of proton conductivity will also be discussed and comparisons of graft versus block copolymer systems will be drawn using model polymer systems.

Steven Holdcroft

Professor

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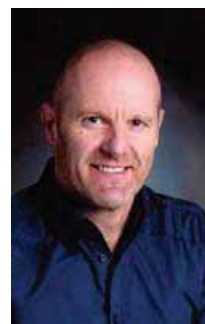
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Personal History

1990-present Simon Fraser University

2001 –present (KTH) Secondment (50%) to Institute for Fuel Cell Innovation,
National Research Council of Canada, Vancouver

Research interests: Design, synthesis and implementation of functional polymers and polymeric microstructures for electronic and electrochemical applications: electrochemistry; electrocatalysis; design, synthesis and characterization of ion conducting polymers; fuel cells. Organic photovoltaics. Nanostructured morphologies of functional polymers



Synthesis and application of drug delivery systems.

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Poly(*N*-vinyl pyrrolidone)-*b*-poly(vinyl acetate) (PVP-*b*-PVAc) block copolymers of varying molecular weight and hydrophobic block lengths were synthesized via controlled radical polymerization and investigated as micellar carriers for the solubilization of highly hydrophobic riminophenazine compounds. These compounds have recently shown to exhibit a strong activity against a variety of cancer types. PVP-*b*-PVAc self-assembles into polymer micelles in aqueous media, and the dialysis method was used to load the water-insoluble drugs (clofazimine) into these polymer micelles. The polymer micelles were characterized by ¹H NMR spectroscopy to confirm micelle formation and the incorporation of the anticancer drugs into the polymeric micelles. Dynamic light scattering was used to determine the particle size and particle size distribution of the drug-loaded micelles as well as the stability of the micelles under physiological conditions. The size of the polymer micelles did not increase upon loading with clofazimine, and the particle size of 180–200 nm and the narrow particle size distribution were maintained. The morphology of the micelles was examined by transmission electron microscopy. The drug loading capacity and the encapsulation efficiency of the polymer micelles were determined by UV/Vis spectroscopy. The polymer micelles had a relatively high drug loading capacity of more than 20 %. *In vitro* cytotoxicity assessment was carried out using the PVP-*b*-PVAc micelles against MDA-MB-231 multi-drug resistant breast epithelial cancer cell lines and MCF12A normal breast epithelial cell lines. The acute toxicity studies confirmed the biocompatibility of the PVP-*b*-PVAc block copolymer. The results indicate that the present PVP-*b*-PVAc diblock copolymer micelles system could be a potential candidate as a drug delivery carrier for clofazimine.

In a second approach, polymeric prodrugs were synthesized via the reversible attachment of a clofazimine derivative to one block of a double hydrophilic block copolymer. The attachment of the hydrophobic drug introduces amphiphilicity to the polymer. This causes the polymer to form micelles in aqueous media. Hydrolysis rates of the linker between polymer and drug are measured as a function of pH. The hydrolysis leads to disintegration of the micelles and concomitant release of the drug. The polymeric prodrugs are compared with the drug-loaded micelles in *in vitro* studies.

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Personal History

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- 1994-2001 Assistant Professor, Eindhoven University of Technology
- 2002-present Associate Professor, Eindhoven University of Technology
- 2007-present Research Chair, Stellenbosch University, South Africa

Research interests: living radical polymerization, polymers for biomedical applications



Stimulus-Responsive Polymers Interfaced with Porous Semiconductors

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Stimulus-responsive polymers are synthetic macromolecules that undergo changes in their properties in response to a defined external stimulus¹. The responsiveness of these systems is being exploited for manifold applications in life sciences such as controlled drug release², cell and tissue culture³, actuators, and sensors⁴. Interfacing stimulus-responsive polymers with nanostructured materials such as porous semiconductors allows the construction of novel functional materials. Our research efforts in grafting temperature and pH stimulus-responsive polymer brushes from porous semiconductor surfaces and in fabricating stimulus-sensitive hydrogels filling the pores will be reviewed here (**Figure 1A**). The talk will also highlight recent developments in our laboratory in terms of applying these hybrid materials in drug delivery for wound healing (**Figure 1B**) and biosensors of wound healing status.

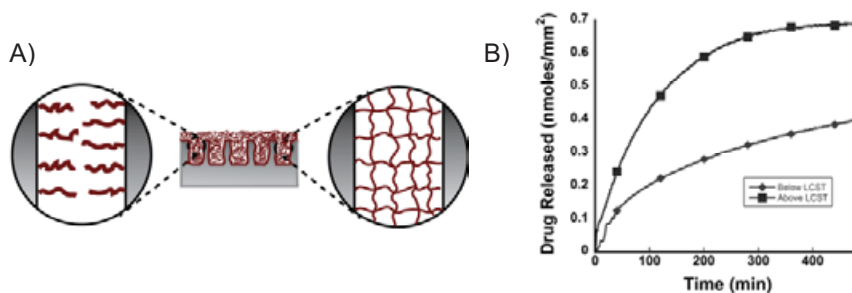


Figure 1: Schematic illustration of polymer chains grafted from porous silicon membrane (left) and crosslinked hydrogels within porous silicon membrane (right); B) camptothecin release from porous silicon membrane coated with poly(N-isopropylacrylamide) brushes above (□) and below (■) the LCST.

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- ³ R. Vasani, S. McInnes, M. Cole, A. Jani, A. Ellis, N.H. Voelcker, *Langmuir*, **2011**, *27*, 7843-7853.
- ⁴ M. Cole, N.H. Voelcker, H. Thissen, R. Horn, H.J. Griesser, *Soft Matter*, **2010**, *6*, 2657-2667.

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Research interests: Nanoporous materials, biosensors, drug delivery, biointerfaces



Modeling of polymer network formation by nitroxide-mediated radical copolymerization of vinyl/divinyl monomers using a multifunctional polymer molecule approach

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A new mathematical model for the kinetics of nitroxide-mediated radical copolymerization with crosslinking of vinyl/divinyl monomers has been developed. Polymerization rate, molecular weight development, gelation point, gel content, crosslink density, copolymer composition and concentrations of the different species involved in the polymerization mechanism can be calculated with the model. With the aim of describing the kinetics of network formation, a reaction scheme considering multifunctional polymer molecules was proposed. In order to simplify the mathematical treatment of the copolymerization reaction, the “pseudo-kinetic rate constants method” was employed. The method of moments was used to obtain average properties of the multidimensional distribution. Flory-Stockmayer’s theory was used for the post-gelation period. Two approaches were used for calculation of average crosslink and cyclization densities. The first method represents a history-dependant approach similar to the one used by Tobita and Hamielec¹ for the conventional case. In the second method the rate of crosslink and cyclization reactions is calculated using a kinetic approach.² The model was validated using experimental data reported in the literature. Several conditions were examined, showing good agreement in all cases as shown in Fig.1. It was found that the presence of NMRP controllers has an important effect on the kinetics of network formation, delaying gelation. According to our results, overall monomer concentration, controller/initiator ratio and crosslinker initial concentration are the governing factors for the development of average crosslink and cyclization densities and, therefore, for the homogeneity of the resulting polymer network.

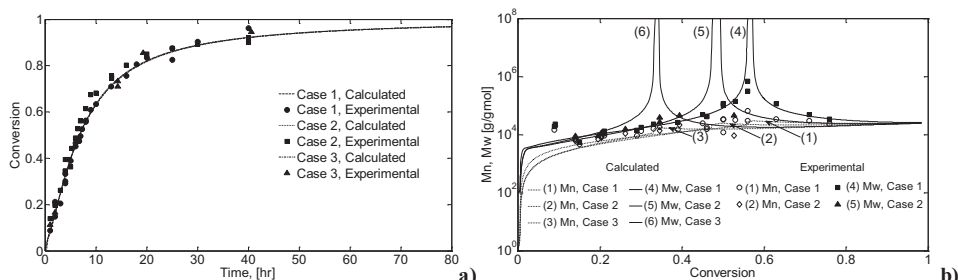


Figure 1. Comparison of experimental and calculated profiles of a) Conversion versus time and b) number and weight-molecular weight (M_n , M_w) versus conversion for the free-radical copolymerization of styrene/divinylbenzene in the presence of TEMPO as controller and BPO as chemical initiator. Experimental conditions (reported by Tuinman et al.³): $[BPO]_0=0.036$ M, $[TEMPO]_0/[BPO]_0=1.1$, temperature=393.15 K, $[DVB]_0=1$ wt% (Case 1), 1.5 wt% (Case 2), 3% (Case 3).

¹ H. Tobita, H. E. Hamielec, in *Polymer Reaction Engineering*, K.-H. Reichert and W. Geiseler, Eds., VCH Publishers, New York, **1989**, p. 43-83

² R. Wang, Y. Luo, B. Li, S. Zhu, *Macromolecules* **2000**, 42, 85-94

³ E. Tuinman, N. T. McManus, M. Roa-Luna, E. Vivaldo-Lima, L.M.F. Lona, A. Penlidis, *J. Macromol. Sci., Part A: Pure Appl. Chem* **2006**, 43, 995-1011

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Research interests: CRP, polymerization in compressed fluids, modeling



Making Proteins Smarter by Conjugation with Responsive Polymers

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Conjugation to synthetic polymers is a viable means to modify the solubility, activity, and potential utility of proteins. For applications in vivo, functionalization of a protein therapeutic with an appropriate high molecular weight polymer can substantially reduce immunogenicity and rates of renal clearance/proteolysis. Similarly, conjugation of stimuli-responsive polymers to proteins can significantly improve catalyst performance and recyclability during enzymatic catalysis. Accordingly, many diverse routes of polymer-protein conjugation have been reported. Generally, these approaches can be classified as either grafting-to, which involves conjugation of a preformed polymer with a protein by reactive coupling, or grafting-from, which describes the polymerization of monomer from a protein capable of initiation (Fig. 1).

The end group retention, molecular weight control, and functional group tolerance of controlled radical polymerization (CRP) facilitates the preparation of well-defined polymer-protein conjugates and allows the facile synthesis of conjugates that contain stimuli-responsive polymer components. Of the various CRP techniques reported, reversible addition-fragmentation chain transfer (RAFT) polymerization offers perhaps the most promise in this area because of its ready amenability to aqueous media, high degree of functional group tolerance, and lack of a transition metal catalyst that can potentially interact unfavorably with the protein.

By exploiting functional chain transfer agents (CTAs) or the sulfur chemistry inherent to the RAFT process, we have immobilized thermoresponsive polymers to model proteins via thiol-maleimide Michael addition, copper(I) catalyzed azide-alkyne cycloaddition, or amidation of activated esters. Additionally, functionalization of proteins with a RAFT CTA prior to polymerization has allowed high molecular weight conjugates to be formed by the grafting-from process. The grafted polymers are well-defined, as observed by successful block copolymerization with a second monomer and by molecular weight analysis after cleavage from the protein. The thermoresponsive nature of the immobilized polymers has allowed thermal tuning of the conjugate self-assembly process and reversible modulation of protein bioactivity.

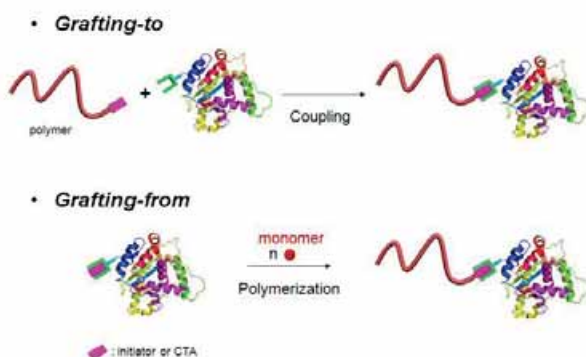


Figure 1. Polymer-protein conjugation strategies by RAFT

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1998 B.S., North Carolina State University, Raleigh, NC

Research interests: stimuli-responsive polymers, polymer synthesis, controlled/living radical polymerization, RAFT polymerization, polymer bioconjugates



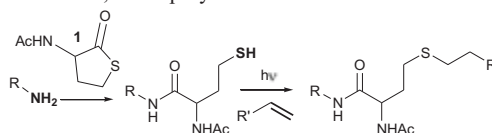
Novel and Powerful Polymeric Platforms for Conjugation and Postpolymerization Functionalization

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Claire F. Hansell,² Rachel K. O'Reilly²

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Metal-free conjugation reactions based on thiol-ene and (hetero)-Diels-Alder (HDA) chemistries have recently gained much attention in synthetic polymer groups as they were introduced as an alternative 'click' reaction for the widely exploited copper(I) assisted azide-alkyne 1,3-dipolar-cycloaddition (CuAAC). Consequently, the number of related publications in polymer journals has increased dramatically, demonstrating the eagerness of the field to evaluate these metal-free approaches and compare it to other, more established conjugation methods. However, as was recently demonstrated,¹ some serious limitations should be taken into account when considering radical thiol-ene chemistry as a ligation tool for polymer-polymer conjugation. The complexity of the (inseparable) reaction mixture is a violation to the set of 'click' requirements.² Consequently, radical thiol-ene is only reliable as a method for the conjugation of a polymer with a small molecule counterpart, although excess of the low-molecular-weight compound is necessary to achieve high conversion. In order to circumvent thiol-related issues (sensitivity to oxidation and limited availability), a thiolactone entity can serve as a precursor for thiols in a one-pot amine-thiol-ene reaction. This amine-thiol-ene conjugation (Scheme 1) as a simple, efficient, and modular linking process is considered to be a relevant extension of the thiol-ene chemistry, especially in polymer science. Functional, linear polymers and networks were obtained using this methodology.³



Scheme 1 – General concept of the Investigated Metal-Free One-Pot Reaction: Nucleophilic Opening of a Thiolactone (Aminolysis), Followed by a Radical Thiol-Ene Conjugation

The inverse-electron demand Diels-Alder cycloaddition (DA_{inv}) between norbornenes (Nb) and 1,2,4,5-tetrazines has recently been employed in some bioconjugation studies. However, this additive-free mild approach has not yet been applied to the ligation or end group modification of polymers. Nb functional α -semi-telechelic polymers provide a basis upon which this conjugation strategy was evaluated in macromolecular systems. Solvent screening and a kinetic study using low-MW model compounds revealed the remarkable scope of this methodology: the reaction proceeds in water and in a range of organic solvents, depending on which is the most appropriate for the system chosen. When applied to polymer-polymer coupling of Nb-PS and a tetrazine-functionalized polyethylene glycol (PEG), the conjugation efficiently reaches very high conversion within 2 hours, expanding the toolbox for the preparation of advanced polymer structures.⁴

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Personal History

Since 1999 head of Polymer Chemistry Research Group (full professor)

Research interests: self-healing polymers, novel 'click' chemistries, porous polymer

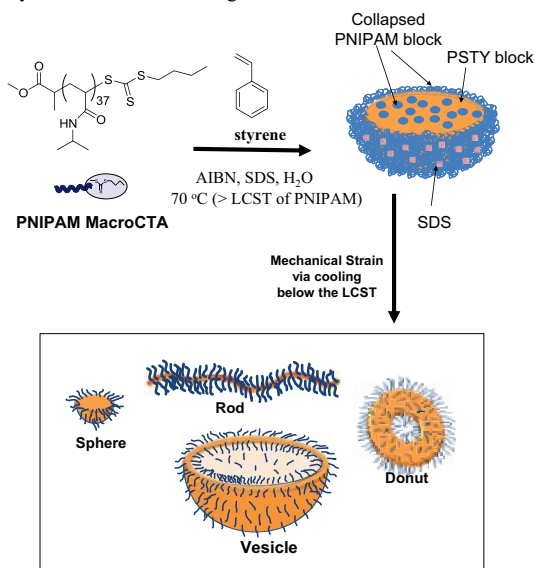
Particles, highly branched copolymer structures, controlled polymerizations



Polymer Architectures and Nanostructures Generated via Living Radical Polymerization

Prof. Michael J. Monteiro, ARC Future Fellow
Australian Institute of Bioengineering and Nanotechnology
The University of Queensland, Brisbane, Australia

The seminar will present work on the synthesis of complex polymer architectures using LRP and 'click' coupling reactions and their self-aggregation in water. Examples will be given for the use of such nanostructures in biological applications. We will also report a new approach to control the formation of a variety of 3D structures at high weight fractions of polymer in water from a single diblock.



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Personal History

2009 ARC Future Fellow

2004-2008 ARC QEII Fellow

Research interests: Living radical polymerization, nanostructures, biomedical applications.



Star-Shaped PEO-Based Polymers as Artificial Channels : Correlation between Chemical Structure and Channel Activity

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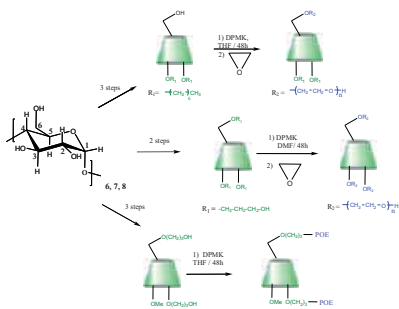
The design of synthetic pores has been addressed through various pathways including the synthesis of star polymers with a cyclodextrin core. The convergent strategy is often convenient but suffers of a lack of versatility¹. We will present the synthesis of star polymer using cyclodextrins (CD) derivatives as new initiators for anionic ethylene oxide polymerization. The first part of the work is devoted to the selective modification of the CD in order to generate hydroxyl functions of similar class^{2,3}. Selective modification appends to control the number of branches per star-molecules as well as their pore formation properties. The polymerization of ethylene oxide is conducted with a default of diphenylmethylpotassium and demonstration of the livingness of the system is carried out³. Star polymers having a number of branches ranging from 7 to 21 have been synthesized (Fig 1). Demonstration of pore formation is conducted with electrophysiological experiments. The cyclodextrin-based initiators are difficult to insert in the lipid bilayer due to their poor water solubility. Depending on the architecture of the star-molecules, permanent or transient pores have been observed. The relevant selective modifications of the cyclodextrins stabilize the amphiphilic pore within the bilayer and the PEO segments ensure the water solubility. Seminal results concerning translocation will be provided..

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² N. Badi, N. Jarroux, P. Guégan, *Tetrahedron Lett.* **2006**, 47, 8925.

³ Z. Eskandani, C. Huin, P. Guégan, *Car. Res.* **2011**, 2014-2020.

⁴ N. Badi, L. Auvray, P. Guégan *Adv. Mater.* **2009**, 21, 4054–4057



Scheme 1

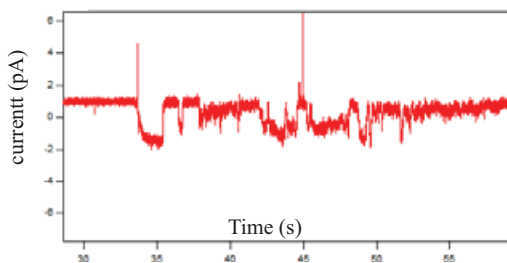


Figure 1 :I-V curve of a CD-based polymer inserted in a lipid bilayer

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Personal History

2002-: Professor, the university of Evry, France

2000: Habilitation à Diriger des Recherches

1994-2002: Maître de conférences at the University of Evry, France

1992-1994: research fellow at the university of Minnesota,



Research interests: Cyclodextrin modification, Biomimetic nanopores, Polymers from renewable resources, Anionic polymerization.

Exploring the synthesis and applications of graphene

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Graphene is the ultimate two-dimensional polymer consisting of a single layer of sp^2 hybridized carbon. Here we explore different approaches to synthesize this carbon allotrope, ranging from chemical conversion to vapor phase deposition. Briefly, graphite can be converted into graphene oxide (GO) sheets, which readily disperse in water, and then can be reduced by various methods.¹⁻³ Due to its unique ability to be solution processed and patterned, GO and chemically converted graphene (CCG) hold promise for applications ranging from distributed ignition to transparent conducting electrodes for flexible solar cells, touch screens, etc.⁴⁻⁸ Chemical vapor deposition of graphene onto metal substrates enables the growth of continuous, large-area graphene (**Fig. 1**).⁹ The challenges of growing graphene, controlling the number of layers, transferring graphene and some exciting new uses such as flash memory will be discussed.¹⁰ Characterization includes optical microscopy, AFM, SEM, TEM, STM and Raman spectroscopy.

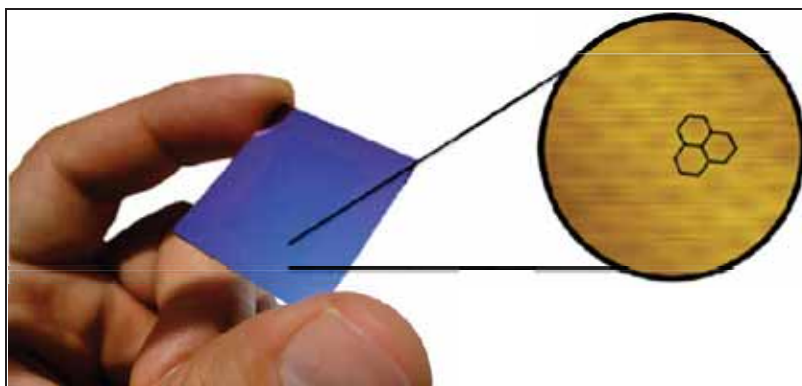


Figure 1. Large-area single layer graphene transferred onto a silicon substrate with a 300 nm oxide can be seen with the naked eye, while STM imaging allows us to see the honeycomb network of carbon that makes this material so robust.

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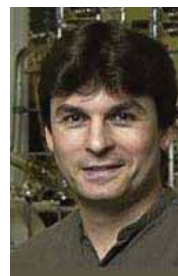
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1987 – 1991	Assistant Professor of Chemistry, UCLA
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2002 – present	Professor of Material Science and Engineering, UCLA
2010 – present	Adjunct Professor, Computer Science and Engineering, RMIT



Research interests:

Professor Kaner and his research group concentrate on the synthesis and characterization of new materials. Four important research areas are targeted: 1) the development of conducting polymer nanofibers with applications in flash welding, sensors, artificial muscles and memory devices; 2) the synthesis and characterization of ultra-incompressible, superhard materials; 3) nanostructured thermoelectric materials and devices; and 4) new synthetic routes to carbon based materials and composites.

Utilizing Supramolecular Interactions to Access Dynamic Materials

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Utilizing non-covalent interactions to access controlled molecular assemblies as well as to influence communication between different components is a critical concept in most biological processes and natural biomaterials. Transferring this approach to designed synthetic polymer systems potentially opens the door to materials that exhibit unusual structural, mechanical and functional properties. The reversible nature of the non-covalent bond allows, when molecules are designed correctly, to access thermodynamically stable, complex self-assembled architectures, as well as to a new generation of adaptive, stimuli-responsive materials.¹ As such the designed utilization of supramolecular chemistry in the field of polymer science has seen a dramatic growth in the last decade or so. We have been interested in the potential of such systems to access new material platforms and have developed a range of new mechanically stable, supramolecular polymer films that change their properties in response to a given stimulus, such as temperature, light or specific chemicals. Such supramolecular materials have been targeted toward applications that range from new implantable adaptive nanocomposites² (Fig. 1a) and healable plastics³ to sensors for chemical warfare agents⁴ (Fig. 1b), thermally responsive hydrogels⁵ and shape memory materials.⁶ Our latest result in this area will be discussed.

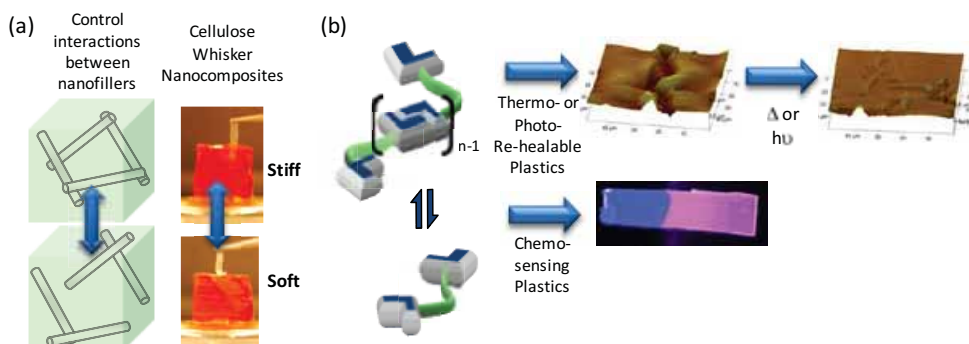


Figure 1. Two different approaches to stimuli-responsive materials where equilibrium (dynamic) chemistry is used to control the responsiveness of the material. (a) Controlling filler-filler interactions in nanocomposites and (b) main-chain supramolecular polymers,

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Stuart Rowan is currently the Kent H. Smith Professor of Engineering in the Department of Macromolecular Science and Engineering at Case Western Reserve University. He received his B.Sc. (Hons.) in Chemistry in 1991 from the University of Glasgow and stayed there for his Ph.D. where he worked on Supramolecular Crystal Engineering of Inclusion Compounds. In 1994 he moved to the Chemistry Department at the University of Cambridge and carried out research on the development of Dynamic Combinatorial Libraries in the labs of Prof Jeremy Sanders, FRS. In 1998 he continued his postdoctoral studies at the University of California, Los Angeles with Sir Fraser Stoddart FRS, where he developed new methods for the construction of interlocked molecules. In 1999 he was appointed as an Assistant Professor in the Department of Macromolecular Science and Engineering at CWRU in Cleveland, Ohio and became Full Professor in 2008. He is also the director of CWRU's Institute for Advanced Materials (IAM). He is a NSF CAREER awardee and received the CWRU School of Engineering Research Award in 2008. His research interests focus on the potential of dynamic chemistry (covalent and non-covalent) in the construction and properties of polymeric materials. His group works on supramolecular polymers, self-healing materials, metal-containing polymers, gels, biomaterials, and developing new synthetic methods for the construction of complex polymeric architectures. He is the Deputy Editor of the new *ACS Macro Letters* journal and a Fellow of the Royal Society of Chemistry. He has published over 95 scientific papers and reviews.

Using Hyperbranched Polymers for Surface Modification: Towards the Facile Self Assembly of Sensing Devices

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The ability to control the surface chemistry of materials is crucial for scientific fields where interfacial properties are important. Some of these include protein binding, cell adhesion and orientation of phase separated domains in block copolymers. Hence, surface chemistry has a significant impact on a range of applications ranging from biomedical devices to computer chip manufacture. Polymers prepared by controlled synthetic methods are an ideal platform to use for modification of surfaces due to their multi-functionality that can arise through controlled end group chemistry and/or the nature of different pendant functional groups. In this presentation we report on the use of hyperbranched polymers prepared using the RAFT methodology to modify surfaces using a 'grafting to' approach. The hyperbranched architecture is attractive due to the increased number of end group functionalities compared to linear architectures and the comparatively easier synthesis (i.e. multi-functional control agents not required) compared to stars. Hyperbranched polymers were prepared and then chain extended with linear arms. With appropriate choice of monomers used for the synthesis of the core blocks it was possible to modify the surface of common materials such as glass (See Fig. 1). When the linear arms that result from chain extension do not interact with the substrate then it is expected that they are free to present at the surface.

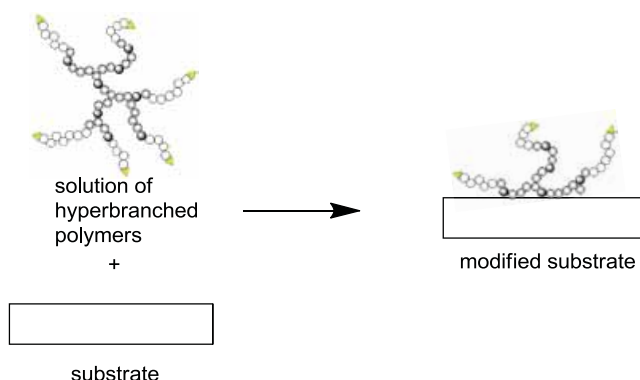


Figure 1. Schematic showing the modification of a substrate with hyperbranched polymers

The modification of surfaces such as glass, silicon wafers and PMMA has been followed using a range of techniques, including x-ray photoelectron spectroscopy and grazing angle attenuated total reflectance FTIR. Through the end functionality of the arms in the hyperbranched polymers it was possible to use these surfaces for self assembly of gold nanoparticles for spectroscopic based sensors (e.g. surface enhanced Raman scattering based sensor arrays), or for conjugation of biomolecules for application in microarray based sensors that use fluorescence as a detection strategy.

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Self-assembly by hierarchical information transfer**Rueben Pfukwa¹, Alan E. Rowan^{*2} and Bert Klumperman^{*1}**¹ Stellenbosch University, Department of Chemistry and Polymer Science, Private Bag X1, Matieland 7602, South Africa² Institute for Molecules and Materials, Radboud University Nijmegen
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Molecular association is central to all life forms. Scientists have been looking into understanding driving forces behind molecular association in natural biological processes as a way to understand how nature operates. The ultimate goal is to design and create synthetic systems that assemble in the same fashion possibly leading to new functional materials. Viruses offer good lessons on self-assembly from the bottom up, i.e. hierarchical self-assembly. In particular, the tobacco mosaic virus (TMV) is one of the best understood self-assembled biological structures. Hence it is an excellent model for the design, synthesis and self-assembly of abiotic structures. Native TMV is made up of identical protein subunits assembled around an RNA helix in a helical fashion, forming a helical structure 300 nm long, 18 nm wide, with a cylindrical cavity 4 nm wide.¹ The length of the TMV complex is fixed by length of the RNA template.¹ The TMV complex is inherently asymmetric and chiral. Some important lessons are drawn from here, i.e. (1) the use of a template to introduce asymmetry and regulate length of the self-assembly and (2) the use a few subunits that all make the same type of contacts thereby reducing the requisite genetic information programming, to direct the assembly process.^{2,3} Also, stable subunits are assembled first, e.g. helices, and these are then brought together into the final structure.^{2,3} In this work we describe a system mimicking TMV in the elegance of the self-assembly. Firstly, we design a polytriazole foldamer, which folds into a regular helical conformation. The helix possesses a well-defined cylindrical cavity, and its folding is driven by solvophobic forces, in a water/DMF solvent system. The exterior of the folded conformation is amphiphilic and the interior is hydrophobic. The conformational transitions of the foldamer can be controlled by varying DMF/water ratio. The addition of a hydrophobic poly(γ -benzyl-L-glutamate) (PBLG) template to this system elicits the stacking/assembly of the helical foldamer disks with the PBLG template entrapped inside, driven by solvophobic forces. The PBLG template regulates the length and the chirality of the system

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Molecularly Imprinted Microgels

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Microgels are crosslinked polymers with particle size ranging from 0.1 to 100 μm which are capable of swelling in an appropriate solvent¹. Most recently, microgels have become the material of interest in molecular imprinting². Molecular imprinting is a process of making a mould on a polymer material using a molecule of interest as the template. The process is carried out by polymerizing the monomers together with the template molecule. Subsequently, the template is removed leaving behind cavities in the polymer matrix which are complementary in size, shape, and functionality of the template.

Molecularly imprinted microgels (MIMs) are believed to exhibit enhanced binding performance because of the improved accessibility of the binding sites compared to the conventional highly crosslinked monolith. In addition, these materials are solution processable which make them ideal for thin film application especially when integrated in sensing devices.

This project investigates different methods of preparing MIMs for histamine (Figure 1) via solution radical polymerization. MIMs obtained are spherical and with particle size range approximately 60 -700 nm. Among the polymerisation methods employed, RAFT polymerisation gives the most consistent particle size and distribution for both MIMs and NIMs. Preliminary rebinding experiments showed a binding capacity ranging from 0.243 to 0.363 μmol histamine per mg of MIM.

The fluorescent MIMs prepared by adding ZnPP as co-monomer will potentially be used as recognition material in optical fiber sensor.

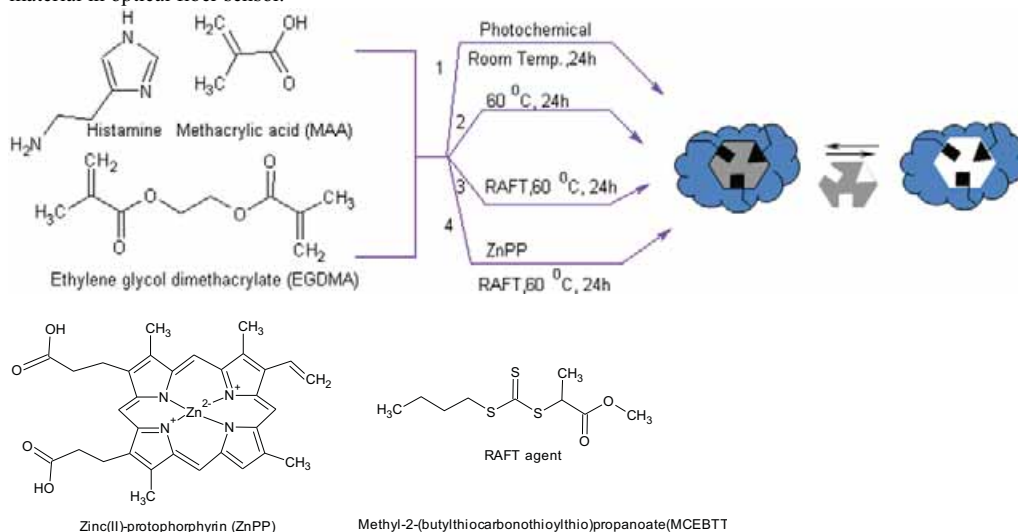


Figure 1. Synthesis of molecularly imprinted microgels using histamine as template molecule.

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Control of Poly(vinyl alcohol) fibre deposition during electrospinning *via* electric field manipulation

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Electrospinning is a process for producing polymeric fibres with diameters in the nano- to micro-metre range.

Typically, the fibre is produced by drawing out the polymer from a solution or melt that is supplied *via* an electrically charged needle or nozzle.¹ Due to the inherently low production rate of the single nozzle process, a multiple nozzle or jet setup, combined with moving collectors, is used to upscale the production rate of fibres.²⁻³

However, multiple jet electrospinning results in repulsive Coulombic forces of like charges within adjacent jets that act to push the fibres away from each other during their flight to the collector.⁴ The fibre repulsion results in

inhomogeneous deposition of the fibre forming ‘tram line’ appearance on the collector. It was reported that control of the deposition can be obtained using collectors or spinning heads that move back and forth perpendicular to the axis of spinning.³ In such mechanical systems complicated setups are required and the efficiency of the system is limited by moving components. The use of electric field manipulation has been studied to control the deposition area of electrospun fibres.⁵⁻⁶ In this technique, the flight path of the fibres is influenced by changing the electric field in the system. The advantage of this technique is that it has no moving components and therefore the technique can be used for high speed applications.⁶ In this study, the effects of auxiliary electric field on the magnitude of deflection of electrospun fibres was investigated. The auxiliary field was generated by charging two pairs of rod electrodes using two independent high voltage power supplies. The electrodes were positioned adjacent and parallel to the spinning axis. It was observed that by varying the electrodes’ voltage, the location of deposition area on the collector can be moved in a control fashion. The changes of deposition location were quantified using optical scanning and image analysis. From the data, graphs of magnitude of deflection were plotted as a function of voltage difference. A linear correlation was observed between the magnitude of deflection and voltage difference between the electrodes. It is possible to “squeeze” the area of fibre deposition to alter the aspect ratio of the deposition area. Statistical analysis showed that the movement and squeezing responses can be thought of as independent control actions. Correlations between the experimental results and multiphysics modeling (COMSOL) are presented. The results presented are useful as the basis of understanding the use of electric field manipulation as a control method in electrospinning. It is envisaged that electric field manipulation could be used for producing more homogeneous electrospun mats during multiple jet electrospinning by the elimination of ‘tram lines’.

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Cellulose Acetate Polymeric Membranes with Varying Amounts of Covalently Attached POSS Nanoparticle Fillers

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Asymmetric cellulose acetate (CA) membranes are commonly used in the reverse osmosis (RO) desalination of brackish waters. They have an asymmetric structure formed by phase inversion, resulting in a thin, dense, salt-rejecting layer at the surface, and a more porous underlying support structure. Physical compaction of the porous support layer can occur due to the high feed pressures intrinsic to RO membrane processes. Compaction is irreversible and leads to reduced water output¹.

Polymer mechanical properties can be tailored by the addition of reinforcing molecules. Cellulose acetate membranes have historically been reinforced with mineral fillers. In recent years there has been a move towards low concentrations of nanoparticles as membrane fillers². Examples of currently used nanofillers include TiO₂², silver nanoparticle², carbon nanotubes³, and zeolites¹. Aggregation, sedimentation and leaching of nanoparticles, however, are a critical problem².

Polyhedral oligomeric silsesquioxane (POSS) molecules are attractive as nanofillers because their rigid Si-O cage structures have monodisperse size, low density, and the corner groups are easily modified to attach groups to tether the molecule in the polymer matrix (Figure 1). In fact, POSS has already been incorporated into several polymers, including polystyrene, polyurethane, polysiloxanes and polyacrylics⁴.

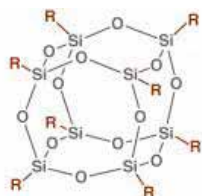


Figure 1: The Si-O cage structure of POSS nanoparticles.

Agglomeration and sedimentation of nanoparticles is avoided by their modification. In addition, this allows for a homogeneous dispersion of POSS within the CA matrix. Furthermore, covalently linking POSS to CA reduces leaching of the POSS nanoparticles. Therefore, a modified CA polymer additive with pendant POSS groups (CA-POSS) has been prepared by chemical modification of commercially available CA, with POSS, via an isocyanate linking group. The stable carbamate-cellulose acetate linkage formed is strongly resistant to both acid and alkaline hydrolysis. The chemical composition of the CA-POSS additive has been confirmed by ¹H NMR and ATR-FTIR spectroscopies, and the thermal properties investigated using thermogravimetric analysis (TGA).

The main purpose of this work was to investigate the effects of varying the concentration of the CA-POSS additive in the casting solution on the morphology and performance of CA membranes, prepared via the phase inversion method. The morphology of the nanocomposite CA membranes was studied by SEM. The compaction behaviour and permeation characteristics of the prepared membranes were evaluated using stirred-cell filtration of 2000 ppm NaCl solution. The changes in membrane morphology due to compaction were determined using dynamic mechanical analysis (DMA), and by analysing SEM cross-sectional images.

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Fabrication and *In Vitro* Testing of Chitosan-ECM Bandages for Photochemical Tissue Bonding

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Extracellular matrices (ECMs) are currently applied in reconstructive surgery to enhance wound healing and tissue remodeling.^{1,2} Sutures and staples are usually employed to stabilize ECM on tissue although they may damage the matrix structure. In this investigation, a novel biocompatible bandage was developed as an alternative to sutures for fixing ECM on tissue.

An adhesive film, based on chitosan and rose bengal (RB), was integrated with small intestine submucosa (SIS) in a single bandage strip (**Fig.1A**). This bandage was bonded photochemically to sheep small intestine (**Fig.1B**) using a green laser ($\lambda=635$ nm, $P=0.18$ W, Fluence ~ 110 J/cm², Irradiance ~ 0.9 W/cm²). K-type thermocouples were used to estimate temperatures under the chitosan-RB film and SIS during laser irradiation.³ Bandage strips were also mechanically tested to evaluate their tensile strength before and after laser irradiation.

The bandages successfully bonded to the intestine tissue achieving an adhesion strength of 16.3 ± 3.2 kPa (mean $\pm$ SD, $n=20$). The estimated chitosan-RB film and ECM temperatures remained below 33 °C and 25 °C respectively during laser irradiation. These low temperatures are thus safe for the host tissue and the matrix embedded growth factors. The bandages withstood a tensile strength of 3249 ± 524 kPa ($n=10$) and 3155 ± 497 kPa ($n=10$, $p=0.4$ t-test) before and after irradiation respectively. The bandage bonded firmly to tissue without sutures and preserved the ECM structure avoiding irreversible thermal denaturation of embedded bioactive proteins.

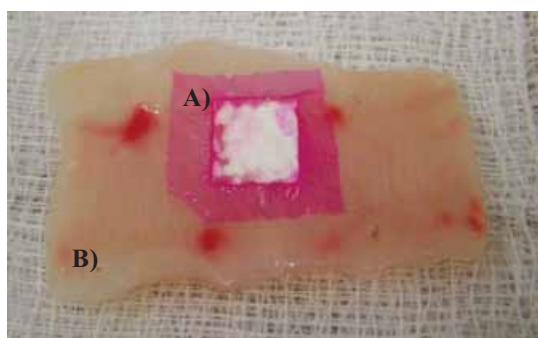


Figure 1: **A)** The bandage comprises a central SIS part that is integrated with the RB-chitosan film. **B)** the bandage bonded to sheep small intestine after laser irradiation.

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Macroporous monolithic polymers containing embedded nanoparticles for high performance chromatography, sample preparation and catalysis

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Monolithic polymers were introduced more than 20 years ago¹ and have become increasingly popular as a new generation of stationary phases to be used in separation science. The best-known advantage they present is a rigid structure with high permeability due to the presence of large through pores, which permit the use of high liquid flow rates at low backpressures. Generally they are prepared by free radical initiated polymerization from a homogeneous polymerization mixture, which consists of mono- and divinyl- monomers, porogenic mixture and free radical initiator. It is well known that the different reactions parameters (such as polymerization temperature, monomer concentration, porogenic composition, etc) have a direct influence over the porous properties of the polymer synthesized². Specific selectivity (e.g. hydrophobic, ion-exchange, affinity etc) for applications in separation science and flow chemistry can be imparted through addition of monomers bearing different functional groups. However, the reaction conditions that are optimized for a specific monomer system cannot easily be transferred directly to another system. Therefore, alternative approaches that use the same polymeric scaffold as stationary phase in different interaction modes could eliminate the need of re-optimization of the polymerization conditions according to the monomers used. One approach which allows this is the incorporation of functional nanoparticles to introduce the desired functionality into a generic scaffold.

In this work we present the preparation of nanocomposite monolithic polymers incorporating a range of functional nanoparticles. In one example poly(butyl methacrylate-*co*-ethyleneglycol dimethacrylate) [polyBuMA-*co*-EDMA)] is used as a monolithic scaffold to which functionality was imparted through the addition of polymer nanoparticles bearing different functionality (e.g. amine, sulfonate, boronate and phenyl). This presentation will describe the effect of the addition of a range of different nanoparticles on both the polymer morphology and also on the separation performance in chromatographic applications. In addition to introducing the desired selectivity, addition of nanoparticles also generally resulted in marked improvements in separation performance for the separation of both large and small molecules. The monolithic polymers obtained were successfully used as stationary phases and separations of a range of analytes from small molecules to proteins, under different chromatographic modes will be presented. In a second example the application of nanocomposite monolithic polymers containing Pd or other metal nanoparticles is demonstrated for heterogeneous catalysis. For example, in hydrogenation reactions using this material 100% conversion of trans-ethylcinnamate to the saturated product was achieved with no loss of activity over more than 5 cycles.

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Functional Nanocoatings*J. P. S. Badyal*

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The worldwide market for functional surfaces exceeds \$50 billion per annum (US Department of Energy). A key driver is the added value that can be imparted to commercial products by tailoring their surface properties. For example, the cleanliness of optical lenses, the feel of fabrics, the resistance of biomedical devices to bacteria, the speed of computer hard disks, and even the wear of car brake pads are all governed by their surface functionality. In order to generate such surfaces incorporating specific chemical groups, there exists no shortage of methods including: self-assembled monolayers (SAMs), Langmuir-Blodgett films, grafting, chemical vapour deposition, to name just a few. However such techniques suffer from drawbacks including substrate-specificity (cannot be easily adapted to different materials or geometries) and environmental concerns associated with the utilization of solvents, strong acid / base media, and heat. Non-isothermal plasmachemical functionalization is a promising alternative which offers many potential benefits including low energy consumption, absence of solvents, minimal waste, rapid treatment times, and ambient temperatures. Earlier attempts to control surface functionality using this approach experienced only limited success due to the difficulty associated with controlling secondary reaction pathways within the electrical discharge. An innovative solution will be described for molecularly tailoring solid surfaces with high levels of structural definition so as to make them super-repellent, rewritable, bioactive, thermoresponsive, adhesive, gas impermeable, non-fouling, opto-chiral, catalytic, antibacterial, or nano-actuated. This fundamental research has led to the filing of 29 patent families and the establishment of 3 start-up companies.

Jas Pal Badyal was awarded BA/MA (1985) and PhD (1988) degrees from Cambridge University; where he subsequently held a King's College Fellowship and the Oppenheimer Fellowship. In 1989 he moved to Durham University to take up a lectureship and was promoted to Professor in 1996. He is named as the primary author / inventor on 152 refereed research publications / 29 patents, and has presented 54 plenary / invited lectures at international conferences. He has been recipient of the *Harrison Prize* from The Royal Society of Chemistry; *Burch Prize* from The British Vacuum Council; and an *EPSRC Advanced Research Fellowship*. International journal editorial board membership has included: *Plasmas and Polymers*; *Journal of Adhesion Science and Technology*; *Plasma Chemistry and Plasma Processing*; and *ACS Applied Materials & Interfaces*. His research has led to 3 start-up companies: *Dow Corning Plasma Ltd* (atmospheric plasma processing), *P2i Ltd* (super-repellent surfaces), and *Surface Innovations Ltd* (bioactive coatings).



Controlled Synthesis of Block Copolymer for Proton Exchange Membrane Application

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To enhance the conductivity of proton exchange membranes (PEM), researchers have attempted numerous methods to modify the polymers¹ or to optimise the methods for membrane preparation².

Controlled polymerization method could precisely control the polymer molecular structure which could be applied to achieve a structure controlled PEM.

A diblock copolymer with structure shown in Figure 1 is synthesised by RAFT controlled polymerization. The first block is hydrophilic, designed for proton conductivity, and the second block is hydrophobic, for phase separation and minimising solubility in water. The key advantage afforded by using block copolymers for PEM, is that precise membrane morphology can be formed via self-assembly with hydrophilic proton channels in the membrane's trans-plane direction. In this way straight proton exchange channels and improved PEM efficiency can be achieved.

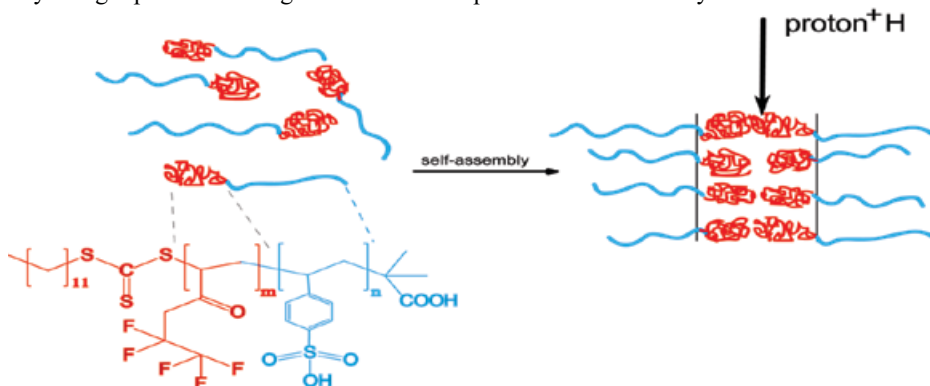


Figure 1. Amphiphilic diblock copolymer self-assembly for PEM preparation.

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New Fluorinated Polymers bearing Pendant Phosphonic Groups for Proton Conducting Membranes

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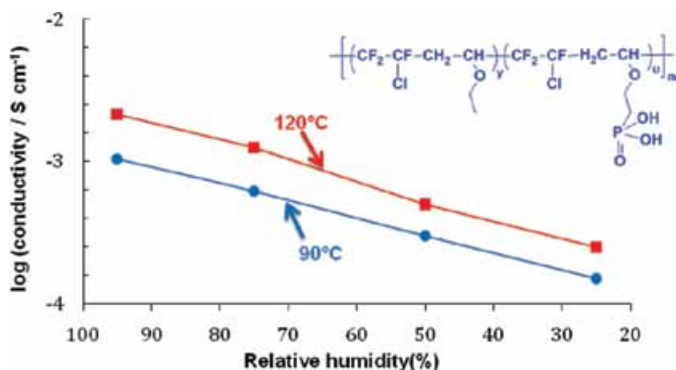
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The synthesis and characterizations of original fluorinated copolymers bearing phosphonic acid side functions for novel membranes for further fuel cell applications are presented. These copolymers were achieved by chemical modifications of various poly(CTFE-*alt*-CEVE) and poly[(CTFE-*alt*-IEVE)-*co*-(CTFE-EVE)] terpolymers (where CTFE, CEVE and EVE stand for chlorotrifluoroethylene, 2-iodo ethylvinyl ether and ethylvinyl ether) via Arbuzov reaction. The hydrolysis of the phosphonate moieties into phosphonic acid groups was carried out quantitatively in the presence of bromotrimethylsilane. The Ionic Exchange Capacities (IECs) values were determined by potentiometric titration from 2.9 to 6.8 meq/g. The thermal and electrochemical properties of the resulting membranes (processed by casting) were investigated. Whatever the phosphonic acid content, the main degradation started from 250°C, showing a high thermo-oxidative stability of these copolymers. At 25°C and 100 % relative humidity, the level of conductivity was found in the range of 0.02 to 20 mS/cm and highly dependent on the IEC. Finally, moderate to good conductivity values (about 0.25 mS/cm) at higher temperature (120 °C) and lower RH (25 %) were observed, which demonstrated a limited dependence towards both temperature and RH (**Fig. 1**).

Figures should be cited in the text (**Fig.x**). Each Figure should have captions in Times New Roman, 10pt. Schemes are not required to have caption, but can be included (**Scheme x**)

Figure 1. Proton conductivity vs RH at 90 and 120 °C of fluorinated membranes bearing phosphonic acid pendant groups



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Porous PDMS Membranes Fabricated from Polymerizable Microemulsion Templates

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Porous polymeric materials with well-defined pore size have been drawing increasing attention in recent years because of their numerous potential applications such as membranes for filtration and separation, catalyst supports, fuel cells, photovoltaics, and controlled release media.¹ Since the utility of these materials is largely dependent on the structure and size of their pores, several techniques associated with controlling the size, pore distribution, and connectivity of the porous materials have been developed. Microemulsion templating offers an appealing complementary route to fabricate porous polymeric materials. Microemulsions exhibit rich nanostructural diversity, and they have been extensively applied for the production of nanoporous materials *via* organic and inorganic polymerization reactions. The variety of these template structures in microemulsions offers novel reaction media for the fabrication of materials grown at nanometer to microns length scales. Porous polymeric solids have been prepared by polymerization of MMA or styrene in W/O microemulsion.² Porous polymer membranes with interconnected and open-cell pores can be obtained from polymerization of monomers located in the sponge phases of bicontinuous microemulsion.³

The aim of the work presented here is to fabricate porous PDMS membranes by templating polymerizable microemulsions. PDMS has received considerable attention as a membrane material for gas separation due to its high intrinsic permeability to gas and vapours. In our previous study, a polymerizable microemulsion based on siloxane macromonomer has been prepared and the time-evolution of nanostructural changes during the course of polymerization were directly investigated by *in situ* synchrotron small angle X-ray scattering (SAXS).⁴ A fundamental understanding of the structural rearrangements which occur during the microemulsion polymerization process has been developed. In this work, a dynamic rheological technique was used to monitor in real time the evolving rheological properties during the course of microemulsion polymerization (Fig. 1). The morphology of the obtained porous PDMS membrane was investigated by SEM (Fig. 2). This study illustrates the ability of employing microemulsion template to fabricate porous PDMS membranes incorporating good mechanical properties and tunable pore sizes.

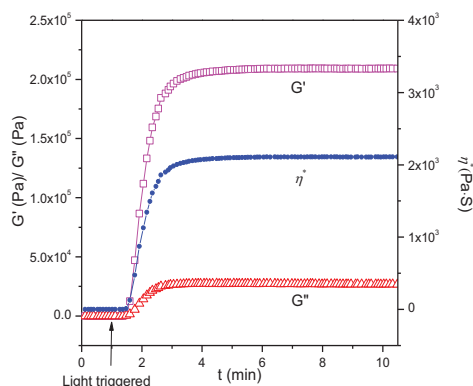


Figure 1. Photo-rheology profile of cure process for a microemulsion formulation.

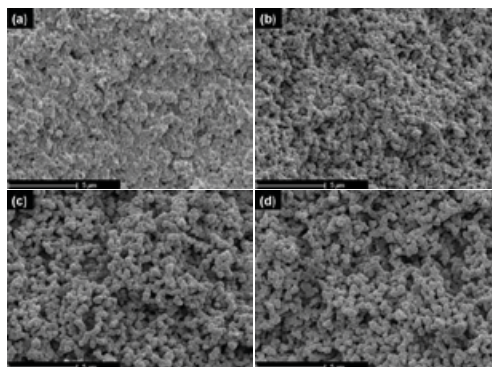


Figure 2. SEM images of the porous polymer samples with increasing water content.

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⁴ Peng, S.; Guo, Q.; Hughes, T. C.; Hartley, P. G.; *Macromolecules* **2011**, 44, 3007.

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Use of the *Breath Figures* technique to form ordered microporous thin films from Poly(3-hydroxybutyrate) and Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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There is considerable recent interest in polymer templating for formation of ordered thin films with potential application in enzymic catalysis, membranes, voltaic and electrochemical devices and tissue engineering. The “breath figures” method (BF) can be used to form monodisperse hexagonal microporous arrays of a range of polymers through templating on water droplets when humid conditions are used during solvent casting of thin films. This technique has been successfully applied to microporous film formation for branched polystyrenes and amphiphilic polymers¹.

Polyhydroxyalkanoates are biopolyesters produced by bacteria as carbon storage products under growth limiting conditions. Poly-3-hydroxybutyrate (PHB) and poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV) in particular are the subject of development of a range of biomedical and consumer plastic applications due to their biocompatibility and biodegradability. Formation of porous films from these polymers using the breath figures (BF) method was investigated by solvent casting chloroform solutions in humid air. Film structure was examined using optical and scanning electron microscopy, thermal characteristics by differential scanning calorimetry and crystallinity by WAXS. BF films displaying hexagonal arrays of pores were successfully fabricated from PHB ($M_w = 486,000$) solutions with pore diameter decreasing from 7.3 to 2.7 μm as solution concentration increased over the range 0.5 to 2.00 %. SEM of fractured films also showed subsurface closed nanopores ($D = 600 \pm 100$ nm). BF film formation did not occur under non-humid conditions or when low molecular weight PHB was used (M_w 10,000). BF films cast from PHBV (5% HV) also formed BF hexagonal arrays with smaller pores and apparent surface defects. Again, pore size decreased from 3.5 ± 0.3 to 1.8 ± 0.2 μm with increasing solution concentration (0.5 ~ 2 %). PHBV with 12% HV content failed to produce BF arrays. DSC and WAXS showed that BF films of PHB were more crystalline than non-porous films cast under dry conditions. Crystallinity calculated from enthalpy of fusion (DSC) was 63 ± 5 % and 54 ± 5 % respectively and crystalline peak area was 30-40% smaller in non-porous film. A similar trend was observed with PHBV.

This represents the first successful application of the BF technique to short chain length polyhydroxyalkanoate homopolymers or copolymers, and the first success with any member of this class of biopolyester without the use of molecular tailoring or addition of amphiphiles to increase the hydrophilicity for the purposes of array formation. The fact that PHB and PHBV are highly crystalline, linear polymers contrasts with the branched, amphiphilic nature of polymers for which BF formation has previously been reported. The ability to produce microporous arrays of high surface area using the simple process described above is likely to increase the range of possible environmental and biomedical applications – particularly in fields such as tissue engineering.

¹ U.H.F. Bunz, *Adv. Mater.* **2006**, *18*, 973–989

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Non-cracking honeycomb formation on nonplanar surface driven by polymer intrinsic properties

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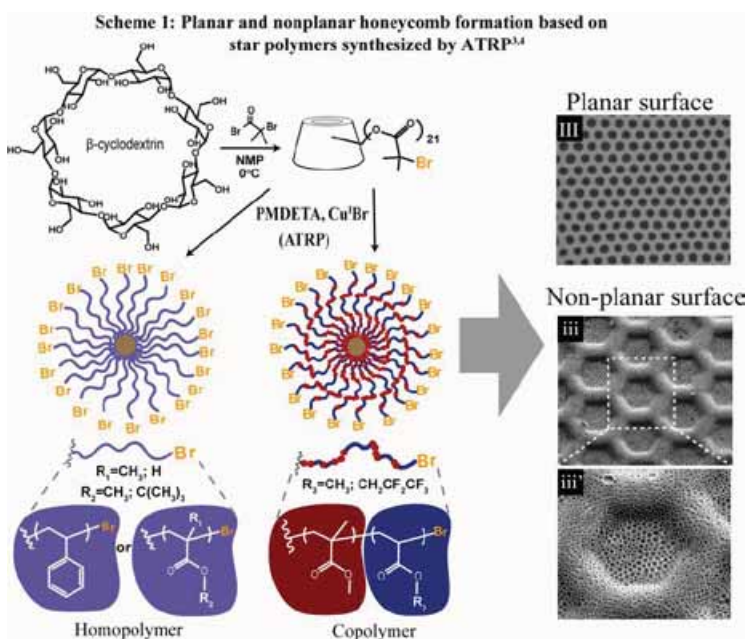
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'Breath Figures' (BFs) technique is well known as a robust and highly efficient technique for the preparation of highly ordered porous films.¹ BF technique was first introduced by Francios and co-workers whereby water droplets were utilized as templates for polymers to form self-assembled highly ordered honeycomb (HC) films.² Highly ordered HC patterned films are of great interest due to the wide range of potential applications in specialized and highly technological applications including biosensors, membranes, scaffolds for tissue engineering, microreactors, photonic band gap, and optoelectronic devices.

However, the poor repeatability and the difficulty of scaling up have limited HC films from many promising industrial-scale applications. 'Cracking' of films is a very common issue which occurs during the formation of films on different materials, especially on a nonplanar surface. Therefore, the development of strategies for the fabrication of ordered patterned films on rough surfaces will significantly expand their suitability in a real application. Here we report on the investigation of a key factor, the modulus of the casting materials, which has major influences on the formation of non-cracking honeycomb film on a nonplanar surface.

After full characterization, the star polymers with varies Young's modulus were used to demonstrate the formation of nonplanar HC as shown in Scheme 1.



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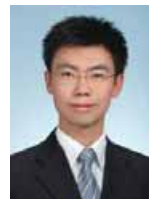
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Nanocomposite gels with extraordinary properties: Formation and characteristics of unique organic / inorganic network structures

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We have fabricated a novel class of nanocomposite gels (NC gels) with a unique organic / inorganic network structure. The NC gels were synthesized by *in-situ* free radical polymerization of N-isopropylacrylamide (NIPA) or N,N-dimethylacrylamide (DMAA) in the presence of inorganic clay (hectorite) in aqueous system. NC gels exhibit high transparency (~90%~) (**Fig.1A(ii)**), high degrees of swelling, and superb mechanical properties with extraordinarily large deformations (1,000% or more) (**Fig.1A(i)**). Also, NC gels formed from thermo-sensitive polymers (PNIPA), exhibit rapid temperature-response in transparency and gel volume (deswelling) at the lower critical solution temperature (LCST). These mechanical and functional properties can be controlled over a wide range by altering the gel compositions. All the properties of NC gels are very different from those of conventional chemically crosslinked hydrogels (OR gels). OR gels were mechanically very weak and brittle (**Fig.1B**) regardless of the concentration of crosslinking agents. The formation of unique organic / inorganic network structure of NC gels (**Fig.2**), which consists of exfoliated clay platelets (1nm² × 30nmφ) uniformly dispersed in an aqueous medium with a number of flexible polymer chains linking them together, was confirmed by TEM, DSC, TG, XRD, DLS, SANS etc. The formation mechanism of organic/inorganic network during the *in-situ* polymerization was also elucidated. Further, NC gels exhibit a number of new characteristics relating to optical anisotropy, polymer/clay morphology, bio- compatibility, stimuli-sensitive surfaces, micropatterning and so on. These results indicate that NC gels are promising soft material for various applications.

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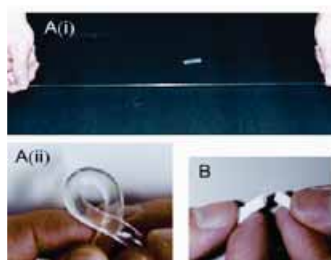


Fig.1

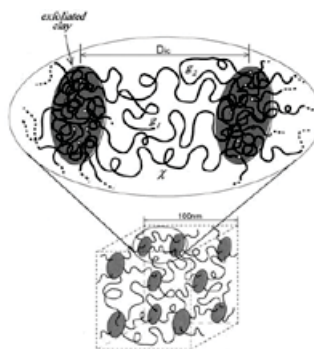


Fig.2

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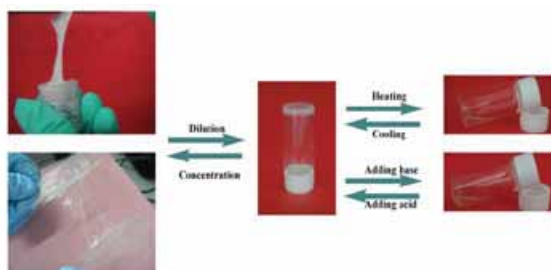


Supramolecular Polymers Based on Threaded Structure Connections

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Threaded structures, such as rotaxanes and catenanes, have attracted much attention not only because of their topological importance but also due to their application in the preparation of artificial molecular machines. Supramolecular polymers, assembled from low molecular weight monomers via noncovalent interactions, such as hydrogen bonding, metal coordination as well as host-guest interactions, have demonstrated traditional polymeric properties and become an important source for the development of stimuli-responsive dynamic materials. We are interested in the fabrication of supramolecular polymers based on threaded structure connections.¹⁻⁵ Self-sorting organization of two AB-type heteroditopic monomers led to the formation of linear supramolecular alternating copolymers driven by host-guest noncovalent interactions based on the bis(p-phenylene)-34-crown-10/paraquat derivative and dibenzo-24-crown-8/dibenzylammonium salt recognition motifs. By utilization of host-guest and metal-ligand noncovalent recognitions motifs, different topologies of supramolecular polymers, such as linear and crosslinked species, can be reversibly interconverted by external stimuli. Based on the dibenzo-24-crown-8/1,2-bis(pyridinium)ethane recognition motif, a hyperbranched mechanically interlocked polymer was prepared by polyesterification of an easily available dynamic trifunctional AB₂ pseudorotaxane monomer. By utilization of a crown ether-based host-guest recognitions motif, a supramolecular polymer gel constructed from a low molecular weight A-B monomer shows thermo- and pH-induced reversible gel-sol transitions. The thermal- and pH-responsive gel-sol transitions were successfully employed in the controlled release of Rhodamine B.



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Accessing Supramolecular Structures with (*N*-Methylated Cyclic Peptide)-Polymer Conjugates

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Supramolecular polymers are structures with reversible intermolecular interactions between repeating units. These non-covalent interactions give rise to novel and useful properties. For example, materials that can be stimuli-responsive and/or self-healing.¹ The versatility and functionality (in particular, directed H-bonding) of peptides have been increasingly exploited in supramolecular chemistry.²

Thoroughly explored in the 1990s by Ghadiri *et al.* and Lorenzi *et al.* cyclic peptides made from alternating L and D residues were found to self-assemble into cylindrical beta-sheets (i.e. tubes).³⁻⁴ The ability for these cyclic peptides to self-assemble into tubular structures has gained interest as a template for complex nanostructures.⁵⁻⁸ By selectively introducing *N*-methylated residues, the self-assembly of the cyclic peptides is restricted to one face.⁹

Using microwave assisted copper(I) catalysed azide-alkyne cycloaddition (CuAAC) chemistry we have synthesised peptide-polymer conjugates in which each polymer is conjugated to either one (**Fig. 1a**) or two (**Fig. 1b**) *N*-methylated cyclic peptide(s) at their end-group(s). These *N*-methylated cyclic peptides are then used as linkers to form supramolecular polymers, either as dimers from the mono-conjugated polymer (**Fig. 2a**), or as multimers from the di-conjugated polymers (**Fig. 2b**). The resulting supramolecular polymers exhibit interesting solution and physical properties that will be discussed.

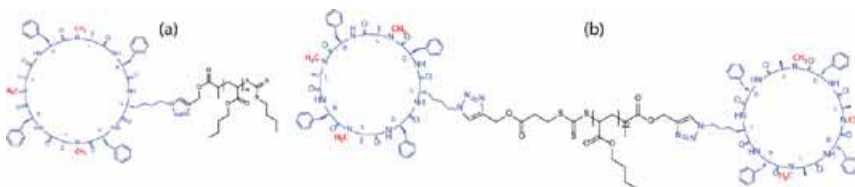


Figure 1. The two *N*-methylated cyclic peptide polymer conjugates used in this work: (a) Monofunctional and (b) difunctional (telechelic).

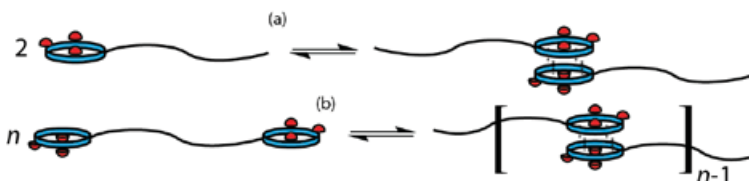


Figure 2. Self-assembly of (a) monofunctional conjugate and (b) difunctional conjugate.

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Dually Thermo-sensitive Block-copolymers: Self-assembly into Micelles based on Aqueous LCST and into Inverted Micelles based on UCST in Alcohols

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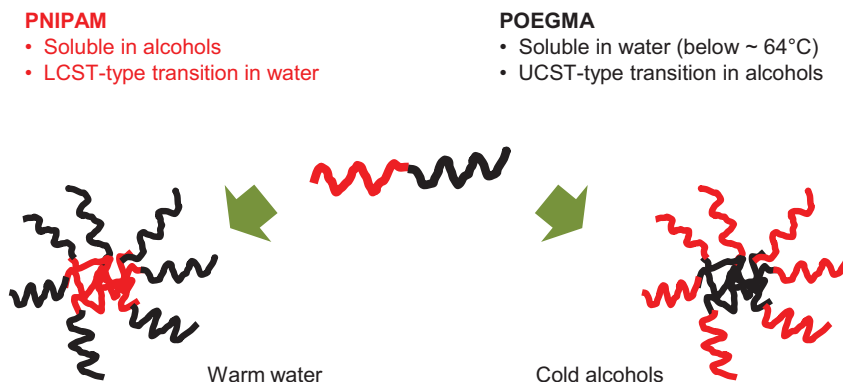
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Poly[oligo(ethylene glycol) methyl ether methacrylate] (POEGMA) is well known to show soluble-insoluble (LCST-type) phase transitions in water and – being biocompatible – has proven a very potential platform for a wide range of applications.¹

Here, the UCST-type behaviour of POEGMA in aliphatic alcohols is presented. POEGMA shows sharp, completely reversible and reproducible insoluble-soluble transitions upon heating in alcohols with very low hystereses between heating and cooling cycles.² Firstly, the influences of molecular weight, concentration, chemical nature of end groups, alcohol structure and co-solvents onto the cloud points were analysed. In the next step, the thermal behaviour of POEGMA in diblock copolymers was investigated. POEGMA was found to undergo a chain collapse upon cooling a solution in isopropanol, 1-butanol, or 1-octanol, causing the diblock copolymer to reversibly self-assemble into micelles. The dependences on concentration, water impurity and alcohol chain length were similar to those found for homopolymers, making POEGMA a predictable system for UCST-based self-assembly applications.

A copolymer of POEGMA and poly(*N*-isopropyl acrylamide) (PNIPAM) was found to form PNIPAM-core micelles in water above ~40°C and POEGMA-core (“inverted”) micelles in 1-octanol below ~25°C. Crosslinking experiments based on activated esters and diamines were carried out on self-assembled POEGMA-*block*-[PNIPAM-*co*-poly(pentafluorophenyl acrylate)].

The successful formation and crosslinking of POEGMA-core / PNIPAM-shell particles in cold alcohols highlights the usefulness of the UCST behaviour of POEGMA for the preparation of novel complex thermoresponsive nanomaterials.



¹ J.-F. Lutz, *Advanced Materials* **2011**, 23, 2237-2243

² P. J. Roth, F. D. Jochum, P. Theato, *Soft Matter* **2011**, 7, 2484-2492

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Advanced Polymer Nanoparticles

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The ability to engineer molecules that self-assemble into highly ordered nanostructures will lead to the next generation of advanced materials. Nature has already mastered these processes, for instance cells consist of lipid membranes that enclose different sub-compartments with specific environments and functions. The key to these processes is very specific interactions between lipids and proteins that form well controlled nanostructures.

Synthetic chemists are continually striving to develop facile chemistries and procedures to mimic nature. With the advent of living polymerization strategies and hence the ability to control polymer topography and architecture,¹ polymer chemists now have an extensive tool box to design macromolecules for specific interactions and therefore control self-assembly.²

This presentation will describe our latest efforts in the controlled polymerization of functional materials and their application in catalysis. For example, functional block copolymers can be self assembled into nanoparticles that contain discrete mesostructured regimes (**Figure 1**). Utilizing orthogonal and efficient chemistries, sites for catalysis can be embedded inside these particles controlling the chemistry and the local environment – approaching the complexities of nature.

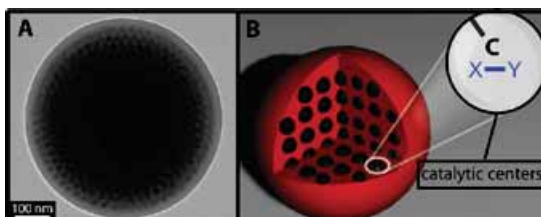


Figure 1. A) TEM micrograph of self assembled polymer with discrete phase separated mesostructure. B) polymer particles with discrete areas for catalysis.

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Shear Induced Orientation and Structure Development in α -Isotactic Polypropylene Containing Particles

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One of the major goals of nucleation is to modify the crystallization kinetics and the crystallization temperature which is quite important in processing as it shortens the processing cycle time. The specific structural α - and/or β -form modification of iPP may lead to significant changes in the end-use properties. Enhancement of the impact strength and lower of stiffness can be achieved in β -nucleated iPP. It is well established that the microstructure of thermoplastic semi-crystalline polymers depends on the processing route leading to the final article, and that in processes such as injection moulding the microstructure shows large structural gradients within a particular moulding, particularly in the form of layers through the thickness of the articles. Study on the nucleation and growth processes by in-situ synchrotron wide-angle scattering (WAXS) and small-angle X-ray scattering (SAXS) techniques were the main focus in this work. The project develops an understanding of how the properties of a polymer depend on microstructure, taking into account orientation and crystallinity. Optical microscopy has been used to characterise the microstructure and Izod impact test was carried on the samples. WAXS/SAXS studies indicated that zinc monoglycerolate (ZMG) is not a β -phase nucleating agent. However, decrease in $t_{1/2}$ from these results showed that ZMG is a very good α -nucleating agent. At 80 shear rate for 0.1 wt% of ZMG in iPP, strong scattering maxima on the meridian indicated parent lamellae and daughter lamellae was shown by the weak bimodal scattering distribution on the both sides of the equator. Spherulites size of iPP decreased with the presence of ZMG. Samples having 0.1 and 1 wt% of ZMG afford a typical “shish-kebab” structure at 80 shear rate. Remarkable improvement in the impact strength was observed at lower loadings of ZMG.

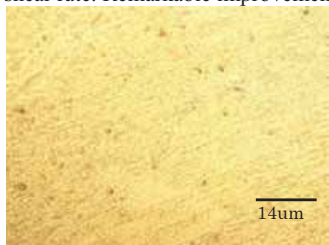


Figure 1: Spherulite morphology of iPP with having 1 wt% of ZMG at shear rate 80s⁻¹

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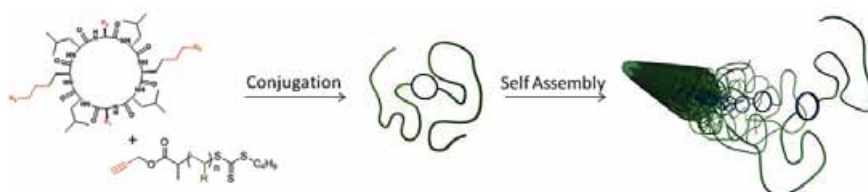


Supramolecular assembly as a route to organic nanotubes of tunable dimensions

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The synthesis of well defined organic nanotubes is a current challenge of polymer chemistry. Such materials offer tremendous potential for applications as sensors, antimicrobials, transmembrane channels, electronic devices, nanoporous membranes, drug carriers and catalysts, but are difficult to prepare due to their complexity.¹ Supramolecular assembly offers a versatile approach to the synthesis of such structures.² We are interested in assembling organic nanotubes through a class of cyclic peptides of alternating D and L chirality which are known to stack into tubes through β -sheet hydrogen bonding, even when large substituents are attached.³⁻⁶ By conjugating polymers to the peptide we are able to use this interaction to drive the self assembly of a rigid polymeric nanotube. (Scheme 1)



Scheme 1: Synthesis and self assembly of cyclic peptide polymer conjugates

Using this approach, we prepared well defined peptide polymer conjugates from a range of functional monomers, and assembled them into soluble nanotubes.³⁻⁴ The tubes were characterized by a variety of methods including transmission electron microscopy (TEM), light scattering, and small angle neutron scattering (SANS). The convergent approach we have employed has allowed us to investigate the effect that the polymer and the self assembly conditions have on the resulting nanotube. For example, by varying the molecular weight of the polymer, and by mixing conjugates with different polymer chain lengths we have been able to tune the dimensions of the assembled tube.⁴ This approach to the preparation of nanotubes is quite versatile, and so by preparing conjugates of different functionalities we have been able to investigate the preparation of cross-linked, and core shell nanotubes.

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Advanced fluorescence methods as a tool for studying polymer self-assembly

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Advanced fluorescence techniques, such as fluorescence correlation spectroscopy (FCS), solvent relaxation method (SRM), etc. are suitable tools for studying the behavior of self-assembled polymeric particles in aqueous media. They are indirect and have to be combined with other techniques (light scattering, SANS, etc.) and their results have to be interpreted with care (sometimes with help of computer simulations), but they provide unique pieces of information inaccessible by other experimental methods.

Fluorescence correlation spectroscopy monitors the fluctuations of emission intensity from a very small volume of a solution containing fluorescent particles and provides information on their translational diffusion.¹ As compared with dynamic light scattering (DLS) which also yields information on diffusion of scattering particles, the main difference (sometimes disadvantage, but often a strong advantage) consists in the fact that only fluorescent and fluorescently labeled particles can be studied. This condition restricts the choice of studied systems, but it (i) allows to study a fraction of fluorescent particles in an excess of other highly scattering particles and (ii) yields number average data on the studied systems. We present new results of Monte Carlo computer simulation study aimed at interpretation of possible complications arising in FCS studies of large fluorescently labeled nanoparticles, particularly the effects of multiple labeling and rotational diffusion.

Solvent relaxation method is an advanced time-resolved fluorescence technique which monitors the reorientation of solvent molecules in the solvation shell upon the change of dipole moment of the fluorophore connected with the absorption of a photon and transition to the excited state.¹ It can be used to study the micropolarity and microviscosity of nanodomains in heterogeneous materials. We report new results on the behavior of self-assembled polymeric core-shell micelles formed by a three block copolymer: polystyrene-poly(4-vinylpyridine)-poly(ethylene oxide) and on the solvation of their water-soluble shells.

As an example of self-assembles we have been studying recently by a combination of fluorescence, scattering and other techniques, we describe the formation and behavior of core shell micelles with cores formed by an insoluble complex of polyethylene oxide (PEO) and metallacarborane COSAN and water-soluble shells of poly(methacrylic acid). Some data have already been published²⁻⁴, but the study of similar systems is in progress. The studied system offers potential applications in medicine (i) as a potent inhibitor of HIV protease and (ii) in anticancer treatment (neutron-boron capture therapy).

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Processable Star Polymers

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Star polymers have attracted much attention over the years due to their various functions and properties as a result of their unique three-dimensional globular structures.¹ The recent development in the controlled radical polymerization (CRP) such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), nitroxide mediated polymerization (NMP) and iniferter has made it possible to synthesise star polymers with well defined molecular weights, structural and compositional homogeneity.^{2,3}

In this work, star polymers have been synthesised by CRP process with a benzyl N,N-diethyldithiocarbamate (BDDC) iniferter via the arm-first method as shown in Figure 1. Firstly, linear polystyrene (PS) arms were photochemically synthesised in the presence of BDDC, according to the procedure developed by Otsu *et al.*⁴ The synthesised PS arms were then subsequently cross-linked with ethylene glycol dimethylmethacrylate (EGDMA) to form the star polymers. The effect of varying several experimental parameters, such as the PS arm length, the amount of cross-linker and the concentration of the linear arms on the structure of the star polymers was investigated.

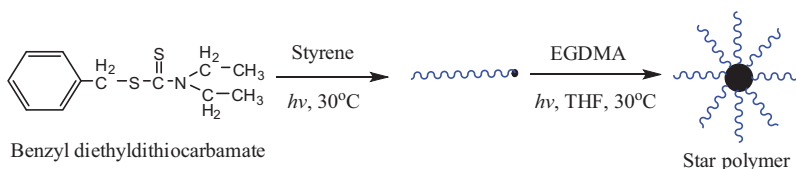


Figure 1. Synthesis of PS star polymers

The structural composition of the star polymers were determined by fourier transform infrared (FTIR) and proton nuclear magnetic resonance (¹H NMR). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to study the morphology of the star polymers. The particle size of the star polymers was measured by dynamic light scattering (DLS) whilst their molecular weight was determined by gel permeation chromatography (GPC).

Subsequent syntheses have focused on inclusion of a molecularly imprinted core within the star polymer using benzyloxyethylamine (BZE) as the template.⁵ The goal is to include these imprinted star polymers in thin film organic field-effect transistors (OFET) devices. Our latest results in this area will be presented.

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Vesicle-Templated pH-Responsive Polymeric Nanocapsules

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Abstract: We report the synthesis of pH responsive polymeric nanocapsules by templating unilamellar vesicles of dimethyldioctadecyl ammonium bromide (DODAB) using a RAFT-based templating approach¹. A short-chain living anionic copolymer containing randomly distributed acrylic acid and butyl acrylate units was first synthesized by RAFT in solution using dibenzyl trithiocarbonate (DBTTC) as the RAFT agent². The anionic copolymer chains were subsequently adsorbed onto the surface of cationic DODAB vesicles and were further chain extended to form a thick polymeric shell by feeding a monomer mixture comprising methyl methacrylate (MMA), tertiary butyl acrylate (*t*-BA) in combination with the divinyl cross linker ethylene glycol dimethacrylate (EGDMA) under starved feed conditions. CryoTEM characterization demonstrated successful formation of a thick crosslinked polymeric shell around the vesicles. Subsequent acid hydrolysis of the tertiary butyl ester groups of the crosslinked polymeric shell resulted in the formation of pH-responsive nanocapsules².

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² S. I. Ali, J. P. A. Heuts, A. M. van Herk, *Soft Matter*, **2011**, *7*, 5382-5390

A Facile Approach to Chemically Modified Graphene and its Polymer Nanocomposites

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A scalable approach for mass production of chemically modified graphene has yet to be developed, which holds the key to large-scale production of stable graphene colloid for optical electronics, energy conversion and storage materials, catalysis, sensors, composites, etc. Here, we present a facile approach to fabricating graphene and its polymer composite, which involves (i) employing a common furnace, rather than a furnace installed with a quartz tube or operating in inert gas as required in previous reports, to treat a commercial graphite intercalation compound (Asbury 3494, at 3–4 US\$/lb) with thermal shocking and ultrasonication to fabricate graphene platelets (GnPs) of 2.51 ± 0.39 nm in thickness which contain only 7 atomic % oxygen (Fig. 1), (ii) grafting these platelets with a commercial long-chain surfactant (5–6 US\$/lb) that is able to create molecular entanglement with polymer matrixes, by taking advantage of the reaction between the epoxide group of the platelets and the amine-terminated group of the surfactant, to produce chemically modified graphene platelets (*m*-GnPs) (Fig. 1), and (iii) solution-mixing *m*-GnPs with a commonly used polymer to fabricate composites. These *m*-GnPs are well dispersed in a polymer matrix, leading to a 110 % improved toughness and a low percolation threshold of electrical conductivity at around 0.25 vol%. This novel approach could lead to future scalable production of graphene and its composites.

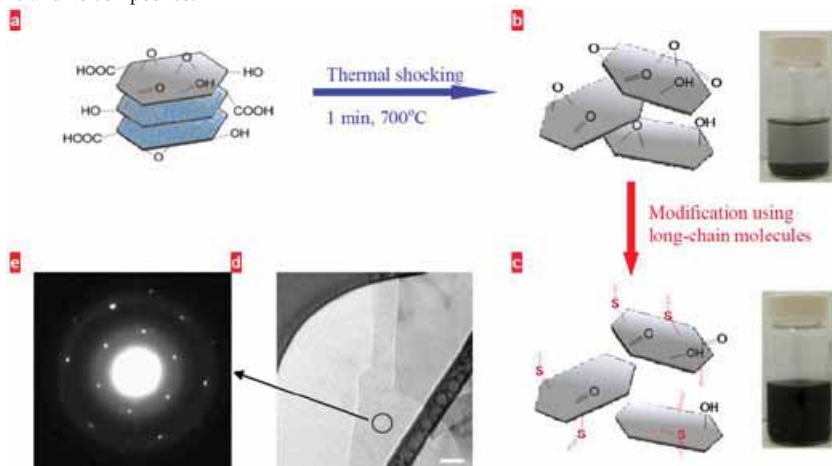


Figure 1 Chemically modified graphene platelets (*m*-GnPs) from a graphite intercalation compound. a, Schematic of graphite intercalation compound, “ $\sim$ ” represents intercalated molecules. b, Schematic of thermal shocking to produce GnPs. c, Schematic of long-chain molecules grafting into GnPs, “ $\sim$ ” represents a long-chain molecule. d, TEM image of a typical GnP suspended on a lacey carbon film-coated grid. The scale bar is 50 nm. e, Electron diffraction pattern of *m*-GnPs as in d, showing high crystallization.

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Smart glycopolymers and their interactions with lectins

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Tailor-made macromolecules have been attracting more and more attention to deliver the desired properties to the advanced materials by the use of their controlled compositions and architectures. Development of various controlled radical polymerization techniques and “click” reactions provide a sufficient platform to prepare functional polymers.¹⁻³ Various combinations of these techniques yield functional polymers. For instance, one of the most widely used combinations is the metal-mediated living radical polymerization and Cu catalyzed Huisgen cycloaddition reaction between azide and alkyne. Alternatively, thiol-ene click reaction can be employed for the thiol terminated or vinyl terminated polymers where thiol terminated polymers can be achieved simply by RAFT polymerization and a subsequent reducing reaction of the chain transfer agent. Similarly, vinyl terminated polymers are also very easy to obtain, *i.e.* by catalytic chain transfer (CCT) polymerization. CCT polymerization provides vinyl-terminated methacrylate polymers with high fidelity of end groups.

In this study, we have prepared glycopolymers in various architectures using atom transfer radical polymerization and copper catalyzed azide-alkyne click reaction. As illustrated in Figure 1, we have prepared linear polymers that can be a homopolymer, block copolymer, and random copolymer. For the preparation of block copolymers, we first polymerized either di(ethyleneglycol) methacrylate (DEGMA) or trimethylsilyl propargyl methacrylate (TMSMA) using Cu(I)Br and *N*-(ethyl)-2-pyridylmethanimine catalyst system and disulfide functional bisinitiator. Using these as macroinitiators, ABA block copolymers were prepared with TMSMA or DEGMA.

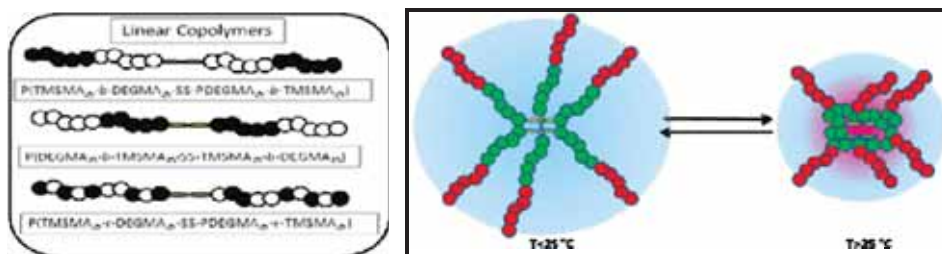


Figure 1. Composition of responsive glycopolymers (left), and their thermoresponsive behavior (right).

Moreover, we have investigated the affinity of poly(mannose-methacrylate) with a selected mannose binding lectin using SPR technique.⁴ Selected members of a glycopolymer library were used to demonstrate the interactions between DC-SIGN and mannose rich polymers. We extend this study to a broader set of polymers to examine the effect of chain length, end group, architecture, thermoresponsive block, and number of arms in the star shaped polymers on the lectin binding.

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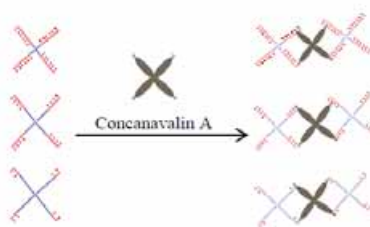
Mapping the Binding Efficiency between Concanavalin A and Star-Shaped Glycopolymers with Varing Degrees of Glycosylation

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Carbohydrates play an important role in many biological recognition events such as cell-cell adhesion, development of new tissues and infectious behaviour of virus and bacteria. The key is the ability of carbohydrates to bind selectively to carbohydrate binding. The interaction between a single sugar molecule and the protein is rather weak, but the simultaneous binding of numerous sugar molecules can result in strong conjugation. This “glycoside cluster effect”^[1] or multivalency effect is determined not only by the thermodynamics between the two participants but also by the architecture.^[2] Our group previously synthesized a series of star-shaped glycopolymers (molecular weight 6,000-53,000Da) and tested their binding ability with Concanavalin A, a lectin that binds specifically to mannose and glucose.^[3] Results show that although slight differences in binding affinity are found between these glycopolymers, all of them bind to con A with a molar ratio of approximately 1:1, which means, it is difficult for one glycopolymer molecule to simultaneously bind to multiple con A molecules. Then arise the questions that what will the cause of this be; whether it is possible that the core of the star-shaped glycopolymer molecule lacks accessibility to con A molecules, making the sugar pendants near the core unable to contribute to the binding at all.

In this experiment, our group synthesized a series of star-shaped glycopolymers with similar tether lengths, while the tethers are different in term of the length of unmodified core. The binding efficiency of these glycopolymers is then tested in the interest of any correlation between the distribution of sugar pendants and the efficiency of lectin binding.



Scheme 1 Testing the binding efficiency of concanavalin A and a series of glycopolymers with varying distribution of carbohydrate pendants. From top to bottom, the size of the un-decorated core of polymer increases while the whole molecule remains the same size.

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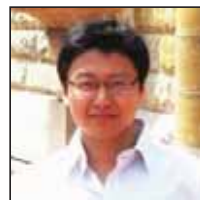
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Synthesis of Glycopolymers using RAFT Polymerization and click reaction



Poly(glycidyl methacrylate) as a “polymeric building block” through post-polymerization processes

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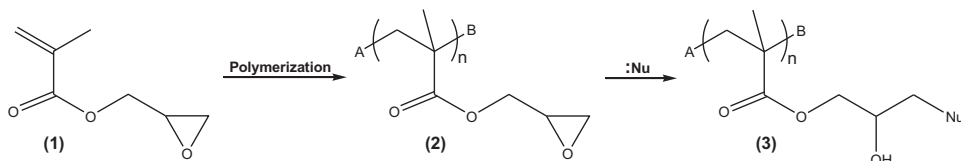
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Glycidyl methacrylate (**1**, **Fig. 1**) is a monomer widely employed for the production of acrylic epoxy-functionalized resins. The reactive side group, constituted by the strained three atoms cyclic ether, allows for further functionalization like grafting and/or hyperbranching.

S_N2 ring opening of oxiranes by nucleophiles is a well known reaction in terms of versatility and selectivity. This reaction, which is performed on the repeating epoxidic function units of poly(glycidyl methacrylate) (PGMA) (**2**, **Fig. 1**), have been the object of the present study.

The treatment of PGMA with various nucleophiles by using the appropriate conditions leads to the formation of new kind of polymers that are characterized by completely different properties from the starting material. It is possible to obtain polymers soluble in water or with a wide solubility that ranges from aqueous to organic solvents. The nucleophilic group that is inserted in each repeating unit can be selected in order to give peculiar functions to the obtained polymer. Furthermore, the nucleophilic substitution carried out into the ring leads to the formation of a hydroxyl group (**3**, **Fig. 1**) that, besides helping the solubility in water, can be exploited for supplementary functionalization *i.e.* addition reactions or ring-opening polymerization.

Figure 1. PGMA synthesis and epoxide ring opening by nucleophiles



The treatment of PGMA with nucleophiles has to be performed in carefully controlled conditions in order to avoid the formation of hyperbranched polymers.

PGMA can also be synthesized under RAFT conditions to obtain polymeric material characterized by a determined molecular weight with narrow distribution. Moreover, the use of RAFT technique allows for the introduction of different functionalities on the extremities of the polymeric chain for obtaining highly functionalized materials and in a very specific way.

The versatility of the post-polymerization process of PGMA combined with the flexibility of the RAFT technique permits the formation of a myriad of different kind of functional materials that can be also capable of self-assembling into supramolecular structures like micelles.

The applications of the material obtained reside in the nano-biomedical field such as drug delivery, gene delivery, diagnostics, etc.

For other fields of applications it is possible to develop photoactive materials or materials capable of electron and proton transport to be employed in photovoltaic and fuel cells technology.

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Improving the performance of micelles as drug delivery carriers by shell-crosslinking

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Poly(poly(ethylene glycol) methyl ether methacrylate-co-methacrylic acid)-block-poly(methyl methacrylate) P(PEGMEMA-co-MAA)-b-PMMA block copolymer were prepared via RAFT (reversible addition fragmentation chain transfer) polymerization and subsequently self-assembled into micelles as a drug delivery carrier for albendazole (ABZ). For comparison, the micelles were additionally crosslinked to study the effect of shell-crosslinking on the biological activity. The hydrodynamic diameter of crosslinked and uncrosslinked micelles was with approximately 40 nm similar in both cases. While the crosslinked micelle was stable even in good solvents for both blocks, the uncrosslinked micelle was found to lose its integrity in cell growth media. Crosslinking had a major effect on the rate of drug release with around four times more drugs released after 24 hours.¹ Both drug delivery systems were tested on human prostate cancer cells (PC-3, DU-145) and human ovarian cancer cells (OVCAR-3, A-2780). No toxic effects were measured with the unloaded micelle while the ABZ loaded uncrosslinked micelle lead to IC₅₀ values between 0.2 and 0.9 μ M depending on the cell line. The

IC₅₀ dropped below 0.1 μ M once the micelles were stabilized by crosslinking. Three treatment cycles with ABZ for one day, followed by two days incubation in media using ABZ loaded drug carriers led to complete cell death even at low concentrations in the case of the crosslinked micelle only. Cellular uptake has been studied using fluorescently labelled micelles and Nile red as model drug, showing cell uptake above the CMC but no micelle uptake below the CMC. Additional biological studies such as colony formation assay and tubulin disorganisation tests were also performed to gain more insight into the effect of micelle crosslinking.

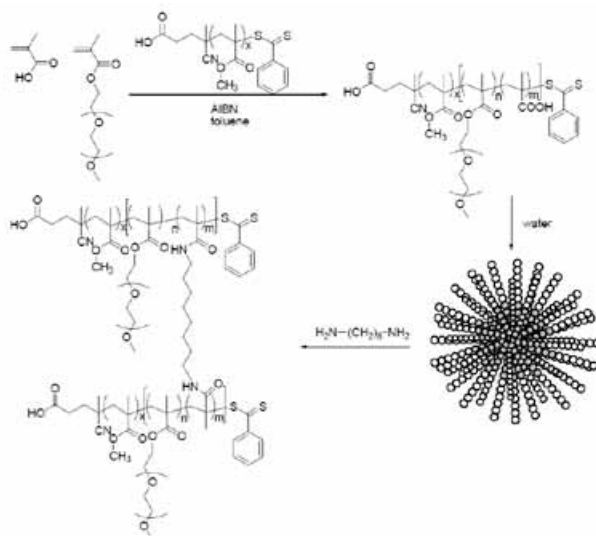


Figure 1. P(PEGMEMA-co-MAA)-b-PMMA block copolymer synthesis using PMMA macroRAFT agent via RAFT polymerization technique, followed by self-assembly and shell-crosslinking using 1,8- diaminooctane

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Controlling Properties of Polymeric Drug Capsules Using Charge-Shifting Polymers

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The development of therapeutic delivery systems to improve drug efficacy requires efficient drug loading, improved blood circulation, targeted delivery and controlled release inside the target cells. A wide range of drug delivery systems, such as micelles, liposomes, polymersomes, polymeric capsules, nanoparticles and dendrimers, have been developed to address these challenges. The layer-by-layer (LbL) technique for the synthesis of polymeric drug carriers is a highly versatile approach that allows specific properties to be engineered into the delivery carriers.¹ Recently, we reported the loading and release of DNA from covalently crosslinked poly(*N*-vinyl pyrrolidone) (PVPON) capsules.^{2,3} This polymer is known to be biocompatible and has low fouling properties. In a related study, we also developed charge-shifting capsules using poly[2-(diisopropylamino)ethyl methacrylate] (PDPA) which respond to specific pH changes when the polymer capsules enter an acidic compartment of a cell.⁴ This system shows high fouling when at physiological pH. Therefore, the current study involves the design of hybrid capsules by combining these materials and the advantages of both the PVPON and PDPA-based systems. We anticipate that these hybrid capsules can potentially find applications in drug or gene delivery.

The synthesis of covalently crosslinked hybrid PDPA/PVPON capsules involves material assembly using a combination of electrostatic and hydrogen-bond interactions, followed by film stabilisation using a click functional crosslinker to produce hollow capsules. The crosslinker contains a disulphide bond which can be triggered in an intracellular reducing environment to degrade specifically.^{2,3} At physiological pH, PDPA is expected to become hydrophobic, forming a more compact capsule interior as compared to capsules containing PVPON only, and hence affecting capsule properties, such as cargo retention and degradability. Hybrid systems with different percentages of each component were synthesised and the effects of different components on material properties were investigated.

We also report the successful encapsulation of small interfering RNA (siRNA) and investigate the effects of the film components on properties, such as cargo retention and the release from these hybrid carriers. In addition, disulphide degradation of films coupled with the morphological change of the PDPA component in an acidic environment (lysosomal compartment) is expected to aid therapeutic cargo release, enhancing drug efficacy. These capsules can also be post-functionalised to display surface properties, such as targeting and fluorescent labeling. Hence, these biocompatible, low-fouling carriers are expected to have improved blood circulation and carrier properties, making them potential candidates for drug delivery applications.

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³ S. L. Ng, G. K. Such, A. P. R. Angus, G. Antequera-Garcia, F. Caruso, *Biomaterials* **2011**, 32, 6277.

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Targeted Drug Delivery:
Understanding cellular binding and uptake of nanoengineered capsules

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Targeted delivery of drugs to specific cells in the body has the potential to revolutionise the treatment of many diseases. An emerging technique to deliver drugs is to immobilise the drug inside a nanocapsule, whereby the body is protected from potentially harmful side effects of a drug, while also preventing the drug from being degraded by the body. This technique has potential to treat a range of diseases, from HIV to cancer.

To achieve this goal a number of key areas must be addressed in the design of the drug carrier, including the loading and release of drugs, as well as functionalisation with targeting molecules. Such nanoengineered capsules can be assembled using the layer-by-layer (LbL) deposition of interacting polymers onto a sacrificial template particle. This technique allows for fine control over the properties of the capsule by altering the number of layers deposited, the material deposited at each layer, and also by controlling the assembly conditions. We have demonstrated that a number of therapeutics, such as DNA, proteins, peptides and anti-cancer drugs, can be encapsulated within the LbL polymer shell and released in an active form, both in vitro and in vivo.

One major challenge in this field is understanding how the nanoengineered capsules interact with cells. We have recently developed a 'click' chemistry approach to functionalise capsules with targeting molecules, such as antibodies (Ab). Using these capsules we have demonstrated that Ab-functionalised capsules specifically bind to cancer cells, even when the target cells are less than 0.1% of the total cell population.

This precise targeting and control over capsule internalisation offers significant promise for drug delivery applications.

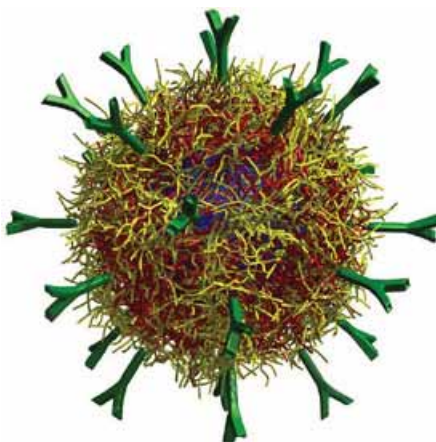


Figure 1. Schematic of an antibody-functionalised LbL capsule.

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Synthesis of Amphilic Block Copolymers for Study of Cellular Interaction and Uptake

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Polymers can play important role in biomedical applications by acting as a vehicle for more effective drug delivery. Current treatments for various forms of cancer include therapeutics that are either hydrophobic or have harmful side effects. Amphilic block copolymers can provide a compatible hydrophobic environment or a protective shell for delivery of the drugs. An important aspect of drug delivery is the process of the uptake of the polymers by the cell. Cellular uptake can occur through various paths of the cell membrane. Depending on the size and shape of the aggregate will greatly affect the type of uptake. Smaller particles and micelles are able to simply diffuse through the lipid bilayer of cell membrane while larger micelles as well as other aggregates are processed by various types of endocytosis. By studying the various size and shapes of the polymer with their respective cellular uptake mechanism we are able to find the most beneficial and efficient type of drug delivery.

Diblock copolymers were prepared via reversible addition fragmentation chain transfer (RAFT) polymerization with poly((ethylene glycol) methyl ether methacrylate) (PEGMEMA, 300) as the hydrophilic block and polystyrene as the hydrophobic block. Once polymerized the block copolymers were self-assembled to form aggregates of various shapes and sizes. The sizes of the respective blocks were controlled through the monomer ratios during polymerization as well as the time of polymerization. By increasing the size of the hydrophobic component while decreasing the size of the hydrophilic component we are able to form micelles of varying sizes as well as rod shaped aggregates. These aggregates were then seeded with colon cancer cells (WiDr cell line) and incubated over a period of time. The polymers were tagged with a fluorescence to view their uptake into the cells for comparison (Figure 1). Plotted against a control of only cells the increase in intensity signifies an increase in uptake of the polymers. From the graph the shift in the fluorescent intensity of the polymers indicate that the size of the aggregate plays a key role in the uptake abilities of the cells.

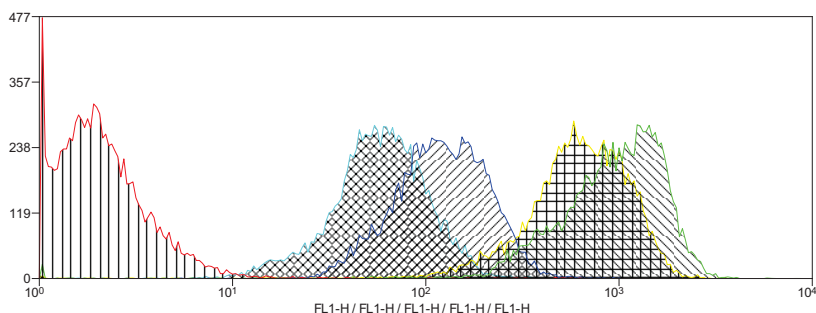


Figure 1. Cell Count vs. FITC intensity. Red: Control of Cells, Green: Micelle 34nm, Blue: Micelle 59 nm, Yellow: Micelle 68nm, Turquoise: Micelle 99nm

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Modular Charge-Shifting Capsules for Therapeutic Delivery.

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The design of functional delivery systems with finely controlled and intelligent properties is important for the generation of new biomedical approaches in areas such as delivery or sensing. A range of polymer systems have been developed including micelles, polymersomes and polymer capsules.¹ One technique that has generated interest for synthesis of polymer capsules is the layer-by-layer (LbL) technique due to the simple and versatile nature of this approach. The LbL technique is based on the serial adsorption of species with complementary interactions and can be performed on a diverse range of templates. LbL assembly on particles and subsequent template removal to form polymer capsules has generated particular interest for use as polymer carriers. Recently, we developed a new method to assemble LbL capsules allowing enhanced control over film characteristics such as stealth capabilities, drug loading and degradability. The technique is based on combining LbL assembly with click chemistry to allow the synthesis of single-component capsules with tailored properties.²

Click chemistry refers to reactions that have high yields, minimal byproducts and can proceed under mild conditions. A well studied example is the copper catalyzed alkyne and azide cycloaddition to form a 1,3 triazole. In this work we used hydrogen bonding to assemble an alkyne-modified polymer with a corresponding hydrogen-bonding partner. After assembly, the alkyne groups are used to covalently stabilize the film by reaction with a bifunctional azide crosslinker tailored with specific degradation characteristics. When these materials were incubated at physiological pH, the hydrogen bonding was disrupted, allowing the non-functionalized polymer to be removed. In this way click stabilised single-component films and capsules could be engineered.

The application of this technique to synthesise charge-shifting capsules and films based on poly(2-diisopropylaminoethyl methacrylate) (PDPA) will be presented.² The properties of these capsules are attractive for delivery applications as the material is non-charged at physiological pH allowing good stability of cargo yet becomes highly charged at endosomal pH, thus allowing cargo to be released. It will be demonstrated these capsules responded reversibly to pH stimuli, shrinking to 60% of their original size at physiological pH. In addition, we demonstrate these systems could be loaded with model cargo, which was released only at endosomal pH based on a synergistic response to pH and redox potential. This degradation could also be readily tuned by varying either crosslinker properties or concentration.

The responsive and modular nature of these materials provides exciting new opportunities for the design of nanoengineered materials with customised properties for application in drug and gene delivery.

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Applications for RAFT in Disperse Phase Systems

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The advent of controlled radical polymerisation has revolutionised the scope for free radical polymerisation. Of the various controlled radical techniques now available Reversible Addition Fragmentation chain Transfer (RAFT) would seem to be the most versatile, with applicability to a wide range of monomers at readily accessible temperatures¹. The adaptation of RAFT for use in dispersed phase systems² has further enhanced the capability of the technique and paved the way for a fine control of the morphology of latex and composite nanoparticles that was not possible by conventional free radical polymerisation techniques. These include the ability to coat a wide range of solid particles with polymer, provide very monodisperse latex particles of less than 20 nm diameter and prepare titanium dioxide nanorattles with very high light scattering efficiency for paint applications.

The capacity of RAFT to provide short chain block copolymers has enabled the preparation of a wide range of sterically stabilised nanoparticles that exhibit a diverse range of behaviors in biological media, including penetration of solid tumor models. Changing nano particle functionality radically affects the fate of particles both in solid tumor models and in vivo. The block copolymer stabilised particles have obvious potential in many biomedical applications such as drug deliver and imaging.

We have applied the new technology of controlled radical polymerisation to synthesize particles with particular sizes and surface properties for biomedical applications.

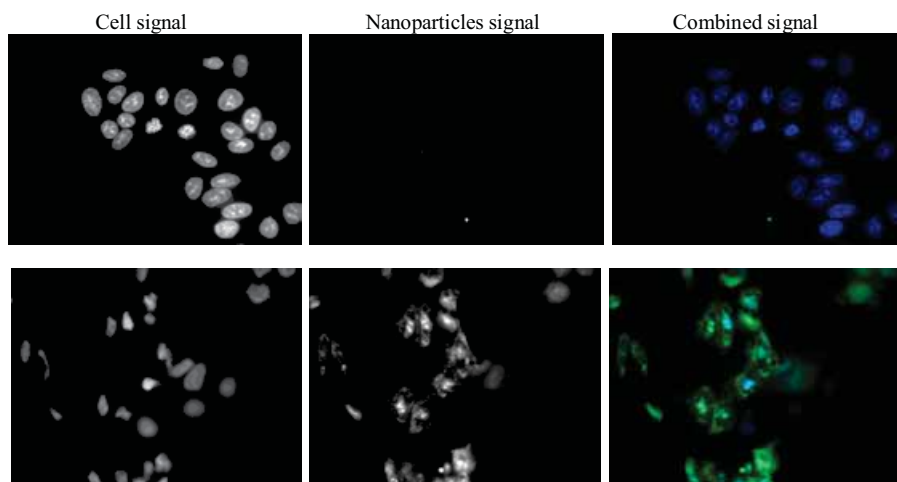


Figure 1: Confocal microscopy images for the uptake of iron oxide nanoparticles into the DLD-1 colon cancer cells. Top row: Folate-free nanoparticles; Bottom row: folate functionalized nanoparticles.

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Development of core-crosslinked micelles for the delivery of albendazole

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Living / controlled radical polymerization opened up the pathway to an easy access to well-defined complex macromolecules. Among these techniques, RAFT polymerization is relatively versatile and robust since it can be applied to a broad range of monomers and experimental conditions.

Over the past decades, numerous block copolymers were successfully generated using RAFT polymerization.¹ Amphiphilic block copolymers can self-assemble into micelles, which have gained much interest as a delivery system for drugs, genes and imaging agents. However, due to the nature of dynamic structure, polymeric micelles tend to disintegrate into unimers at low concentration or upon environment change such as temperature, pH or ionic strength. This disassembly will cause the undesired release of the drug from the micellar nanocontainer before it reaches the targeted disease sites.² In order to prevent the premature release of drug, it has been proposed to crosslink the polymer chains to reinforce the micellar structure.

In this research, we investigated novel core crosslinked micelles as potential nanocarriers for albendazole. These micelles were self-assembled from block copolymers composed of a water-soluble block poly(ethylene glycol) methyl ether methacrylate(PEGMEMA) and a core-forming block poly(methyl methacrylate)-co-poly(3-isopropenyl-a,a-dimethylbenzyl isocyanate (PMMA-co-TMI). These block copolymers were synthesized via RAFT polymerization.

The hydrophilic PEGMEMA shell can enable the nanocarriers to evade rapid clearance by immune system and impart additional functions such as protecting the therapeutic payload against enzymatic degradation and providing better stability in vivo. The proposed micelles have hydrophobic cores composed of a random copolymer of methyl methacrylate and TMI, which can not only take part in free radical polymerization but also polyadditions to form polyurea (with amines) or polythiocarbamates (with thiols) to crosslink micelles. The hydrophobic core of the micelles can physically entrap albendazole with a high loading capacity.

¹ Graeme Moad, Ezio Rizzardo, and San H. Thang. *Aust. J. Chem.* **2009**, 62, 1402

² L. Barner, C. Barner-Kowollik and T. P. Davis, *J. Polym. Sci., PartA: Polym. Chem.*, **2002**, 40, 1064

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CPP-decorated polymeric micelles from arginine-based monomers: An efficient tool for drug delivery ?

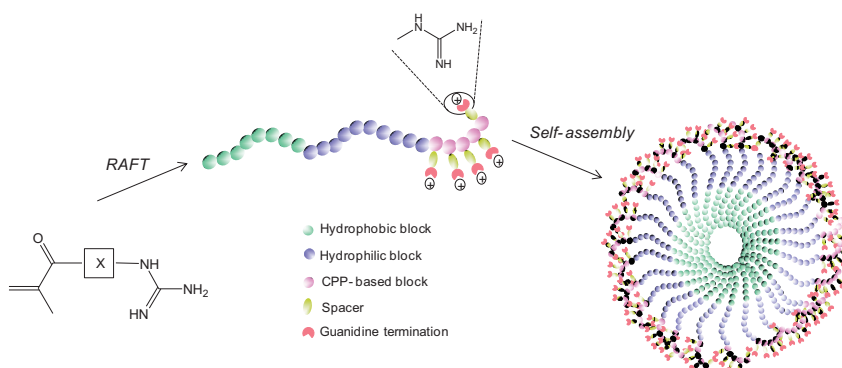
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The efficient passage of macromolecular therapeutics through the plasma membrane remains a major challenge for drug delivery. Cell-penetrating peptides (CPPs) are a class of molecules that exhibit the ability to cross biological barriers to enter cells efficiently, and can bring with them different covalently attached cargoes with molecular weights significantly greater than their own.

If the main classes of CPPs can differ from one another in structure, they are generally composed of large fractions of basic amino acids and in particular often contain a high concentration of guanidinium moieties. Since almost all native and synthetic CPPs are highly positively charged, they attach rapidly and strongly to cell surfaces, via non-specific interactions with the negative phospholipids and glycosaminoglycans.¹

While a lot of studies has focused on the conjugation of CCP with biological molecules such as peptides, proteins, oligonucleotides, pDNA, or liposomes, only few studies have been conducted so far on the use of CCP in combination with complex polymeric systems.²⁻⁴ In that case, the CCP are usually incorporated via post-modification of the polymeric scaffolds, with the major drawback of poor conjugation efficiencies.



In the present work, we propose to develop micelles presenting a high functionality in guanidinium moieties, by chain extension of an amphiphilic copolymer with novel arginine-based monomers using RAFT polymerization. The self-assembly of the triblock copolymers in water leads to the obtention of CCP-decorated micellar systems. To this purpose, different methacrylate cationic monomers have been synthesized, to study notably the influence of the polymer charge on the cellular uptake. The efficiency of these micelles as drug delivery system will also be determined by in vitro studies on different cell lines.

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Synthesis, self-assembly and evaluation of cholesterol-containing biodegradable block copolymers for drug delivery applications

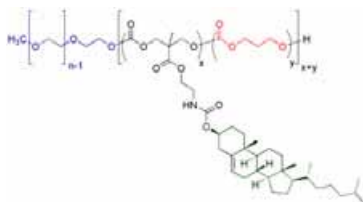
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Ability to incorporate diverse functionalities on to biodegradable polymers would pave way for the synthesis of novel functional materials for biomedical applications. Amongst different classes of monomers, aliphatic cyclic carbonates are excellent platform for the facile introduction of desired functionalities onto degradable materials. In our group we have developed cholesterol-containing cyclic carbonate monomer, cholesteryl 2-(5-methyl-2-oxo-1,3-dioxane-5-carboxyloxyloxy)ethyl carbamate (MTC-Chol). By using organo-catalysis, MTC-Chol can be readily polymerized and also co-polymerized with other carbonate monomers such as trimethylene carbonate (TMC) to result in well-defined polymers, with relatively low polydispersity index (PDI, generally ≤ 1.2). A series of amphiphilic block copolymers were synthesized by initiating from monomethoxy polyethylene glycol (mPEG-OH) with either TMC or MTC-Chol or a combination of both the monomers (TMC and MTC-Chol) to result in mPEG_n-b-PTMC_m, mPEG_n-b-P(MTC-Chol)_m and mPEG_n-b-P(MTC-Chol_x-co-TMC_y)_{x+y}, respectively. Effects of molecular weight and composition of the hydrophobic block of these polymers on aqueous self-assembly of these block copolymers to form nanostructures and the drug-loading capacities of these nanostructures were explored. Paclitaxel, an extremely hydrophobic anticancer drug could be encapsulated into the self-assembled nanostructures by simple self-assembly without any need for sonication or homogenization procedures. The presence of both MTC-Chol and TMC units in the hydrophobic block significantly increased paclitaxel loading levels, and the nanostructures formed from the polymer with the optimal composition (i.e., mPEG₁₁₃-b-P(MTC-Chol₁₁-co-TMC₃₀)) were relatively small in size (~ 36 nm), with low poly dispersity (~ 0.07), with high paclitaxel loading capacity (~ 15 wt.%) and also had excellent kinetic stability. *In vitro* experiments demonstrated that compared to free drug, the paclitaxel loaded micelles killed tumour cells much more effectively, whilst the blank nanostructures had almost no toxicity. In this presentation, syntheses and characterization of cholesterol-functional polycarbonates, their self-assembly behaviors will be discussed. Also the application of these materials as a versatile drug delivery vehicle for other hydrophobic drugs will also be presented.

Figure 1. General structure of cholesterol-functionalized biodegradable block copolymers mPEG_n-b-P(MTC-Chol_x-co-TMC_y)_{x+y}



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Biocompatible Patterned Polymer Surface Coatings to Control Protein Adsorption and Endothelial Cell Behaviour

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Cardiovascular disease is a leading cause of death in first-world countries, with up to 40 % of patients with an acute cardiovascular condition requiring stent implantation.¹ Stent failure and restenosis however occurs in up to 60 % of these patients, primarily caused by either vascular injury or poor biocompatibility of the implant.² Numerous methods have been proposed to enhance the compatibility between a stent surface and the endothelium by minimizing activation and inflammation of endothelial cells; such methods include drug eluting stents, and coatings which induce a particular density and topography of cells on the microscopic scale.

In this work, we have prepared patterned polymer surface coatings via the dewetting of polymer films to be used to control the location of extra-cellular matrix (ECM) protein adsorption and ultimately endothelial cell (EC) adhesion and behaviour. These surfaces consist of two immiscible polymers, one of which is protein-adhesive (e.g. polystyrene, PS) and the other protein-repellent (e.g. poly(*N*-vinylpyrrolidone), PNVP), which enables a typical ECM protein such as collagen to be readily adsorbed in specific locations on the surface (**Fig. 1**). Surface patterning occurs by simply annealing a pre-formed polymer bilayer above the glass transition temperature T_g of the top layer; due to unfavourable intermolecular forces at the interface the top polymeric layer dewets,³⁻⁶ forming a series of monodisperse holes of controllable size. We have shown that by Type 1 Collagen can be readily adsorbed into the interior of the formed pattern with minimal adsorption on the surrounding phase, and the resultant protein surface morphology can be readily controlled (e.g. varying adsorption time, drying conditions, surface oxidation⁷). Human umbilical vein endothelial cell (HUVEC) adhesion can then occur on these collagen-rich domains, showing good cell health and minimal activation.

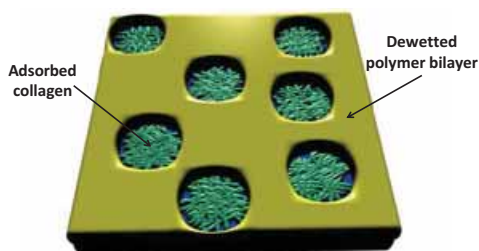


Figure 1. Cartoon depiction of collagen adhesion on a patterned polymer bilayer film.

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Stabilization of Peptide- Based Vesicles via *In Situ* Oxygen-Mediated Cross-Linking

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Polymeric micelles (and vesicles) represent a class of nanoparticles that are formed by self-assembly of block copolymers in selective solvents, whereby the non-soluble component self-assembles to form the core of the micelle and the soluble component forms the solvated shell.¹ In this study, the formation of pH sensitive reversible cross-linked vesicles composed entirely from amino acid building blocks was investigated via the formation of block copolymers having acidic groups on one block and basic groups on the other. To avoid the use of additional cross-linkers and strong oxidizing agents, such as sodium periodate (NaIO₄), DOPA monomers were incorporated into the basic block, which could then cross-link the vesicle *in situ* using oxygen as the oxidizing agent at basic pH.^{2,3} This provides a facile and novel approach to synthesize cross-linked reversible vesicles composed entirely from amino acid building blocks under very mild conditions.

Poly(L-glutamic acid)₆₅-*b*-poly(L-lysine-*r*-dihydroxyphenylalanine)₇₅ (PLGA₆₅-*b*-P(LL-*r*-DOPA)₇₅) block copolymers formed vesicles at pH 12 as determined from SLS, DLS, AFM and TEM. ¹H NMR spectroscopic analysis also revealed that the PLGA block formed the solvated shell, whereas the P(LL-*r*-DOPA) block formed the inner layer of the vesicle shell. Subsequent stabilization of the vesicles was achieved using oxygen to oxidize the DOPA phenolic side groups into quinone intermediates, which underwent intermolecular dimerization, ultimately generating covalent cross-links between polymer chains within the internal layer of the vesicle's shell (Figure 1). The resulting cross-linked vesicles were capable of maintaining their structure even when the pH was reduced to 3, whereas the uncross-linked vesicles underwent reversible of their configuration to form ellipsoidal aggregates. These results demonstrate that oxygen-mediated *in situ* phenolic oxidation and dimerisation provides a facile and environmentally 'green' approach to the stabilization of reversible vesicles.

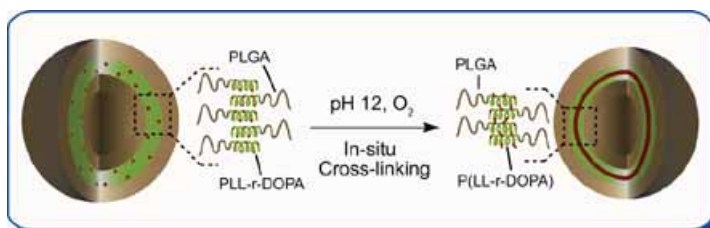


Figure 1. Vesicle stabilization via *in situ* core cross-linking at pH 12 using oxygen as the oxidizing agent.

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Research interests: hybrid polymers, polymer therapeutics, star-polymer synthesis



Macromolecular Ruthenium Complexes as Anticancer Agents

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Ruthenium forms complexes that are useful for a wide variety of applications including catalysis, electronics, photochemistry, biosensors and anticancer drugs.¹ NAMI-A and KP1019 are two anticancer ruthenium drugs that have already entered clinical trials.² However, these low molecular weight drugs have a number of disadvantages. They are unprotected, degrade easily through a variety of mechanisms and do not have targeting capabilities. Many of these problems can be addressed by incorporating complexes, having anti-cancer activity, into macromolecular polymer structures (**Figure 1**).

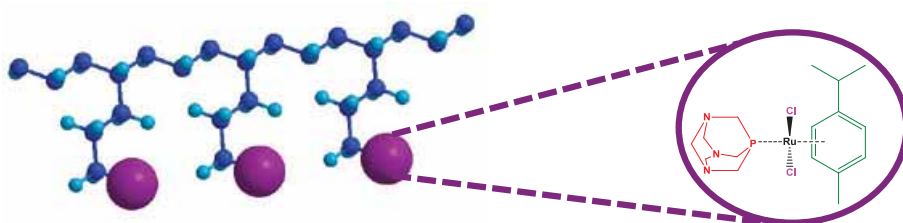
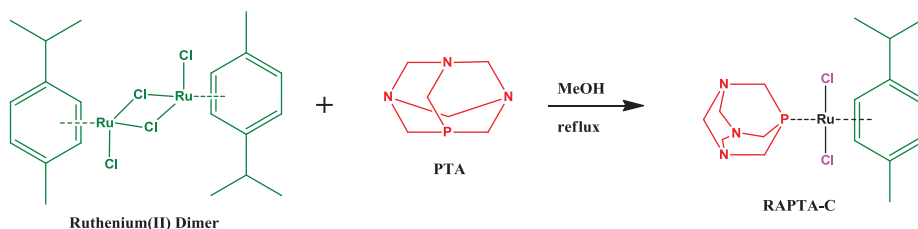


Figure 1. Ruthenium Complex attached to Polymer.

The RAPTA (ruthenium – arene - 1,3,5-Triaza-7-phosphaadamantane(PTA)) series of complexes have shown potential for the further development of anticancer remedies.^{3,4} They were chosen for initial investigation as they provide a site of attachment, through the nitrogen ligand group of the PTA ligand, to the polymer. A synthesis scheme of one such complex is shown (**Scheme 1**). The attachment of this complex to polymer moieties will be discussed.



Scheme 1. Synthesis of RAPTA-C.

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Nanoparticles with pendant cyclodextrins as drug delivery carrier

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The advantage of polymers with pendant cyclodextrin over the amorphous “cyclodextrin polymer” are their well-defined structures and their controlled solution properties. Interestingly, not much attention has been drawn yet to the combination of controlled polymer architectures with cyclodextrin.¹ Reversible Addition Fragmentation chain Transfer (RAFT) polymerization opened the door to a range of polymer architectures with precise control over the molecular weight.² Linear polymer chains with well-defined endfunctionality are as easily accessible as block copolymers or starpolymers.

Attractive is also ability of cyclodextrin to act as a carrier for drugs. While a single cyclodextrin molecule might enhance the solubility of often insoluble drugs, a polymeric structure can enhance drug delivery by better accumulating in the tumour. Micelles are attractive drug delivery carriers due to their small size and their water-soluble shell.³ We therefore decorate amphiphilic block copolymers with pendant cyclodextrin molecules. These molecules can then undergo self-assembly into polymeric micelles.

There are potentially two pathways to polymers with pendant cyclodextrins, either via the postfunctionalization of reactive polymers or via the polymerization of cyclodextrins with vinyl functionality.¹ We employed various click reaction to functionalize block copolymers with cyclodextrins. Thermo-responsive block copolymers with β -CD (**Fig. 1**), but also various other block copolymers were generated. We studied the encapsulation of various drugs including albendazole, curcumin and platinum drugs, but also the simultaneous crosslinking of micelles using a supramolecular approach based on the host-guest chemistry between cyclodextrin and adamantane derivatives were investigated.

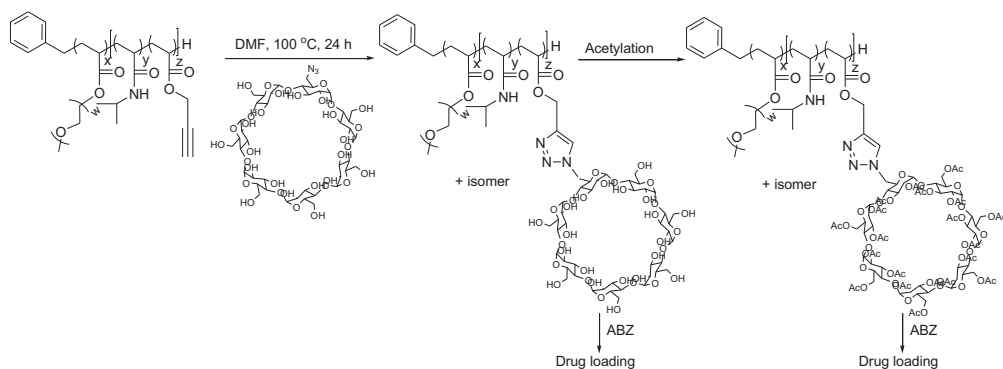


Figure 1. Synthesis of block copolymers with pendant cyclodextrin for encapsulation of drugs

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- (2) J. Chiefari, Y. K. Chong, F. Ercole, *et al. Macromolecules* **1998**, 31, 5559.
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Stimuli-responsive polymers for MRI imaging

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Magnetic Resonance Imaging (MRI) is unarguably one of the most employed imaging technique in clinical radiology. It is a non-invasive technique, which exhibits excellent spatial and temporal resolution whilst obviating exposure to harmful radiation. To improve the contrast, Gadolinium(III) complexes such as Gd(III)-DTPA (diethylene triamine pentaacetic acid) or Gd(III)-DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) are used as contrast agents (CAs) in approximately one third of MRI scans.¹ In spite of their efficiency, the short circulation time of these CAs and some recent concern about gadolinium leakage, causing nephrogenic systemic fibrosis in some patients, had propelled the search for better alternatives.

Biocompatible, water-soluble polymers are outstanding candidates for MRI imaging. By attaching CAs to the polymer backbone not only improvement of the pharmacokinetics properties (by increasing the blood circulation time and promoting specific accumulation in tumours through the enhanced permeability and retention effect) but also higher relaxivities, and thus better contrast, can be achieved. Poly(ethylene oxide)-based polymers are particularly interesting for this application due to its anti-fouling properties.³

In this work, we explore the use of stimuli-responsive polymers to tune the relaxivity of Gd(III) CAs. The exchange rate of the Gd(III)-bound water with the bulk water molecules of the body determines the enhancement of the relaxation (T_1 and T_2) of the water protons and, consequently, the contrast of the images. By using stimuli-responsive polymers, we can control the Gd(III) environment and thus design the contrast agent in a way the MRI signal will be increased specifically under certain conditions. For example, we demonstrate the use of thermoresponsive polymers based on poly(oligoethyleneglycol acrylate) derivatives as platforms for MRI CAs (Fig. 1). These polymers present an adjustable lower critical solution temperature (LCST) in the range of 20 °C to 90 °C without loss of anti-fouling property.⁴ So, by increasing the temperature, we modify the hydrophobicity of the polymer, leading to a control of the accessibility of water molecules to Gd and, consequently, of its relaxivity properties. In addition, we also investigate the use of polymers responding to pH or small biomolecules as sugars.

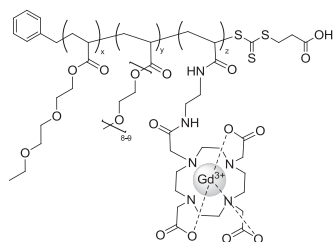


Figure 1. Structure of thermoresponsive polymers for MRI imaging.

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Polymeric micelles with pendant pair-wise carboxylate groups afforded via Michael addition for sufficient *cis*-platinum drug delivery

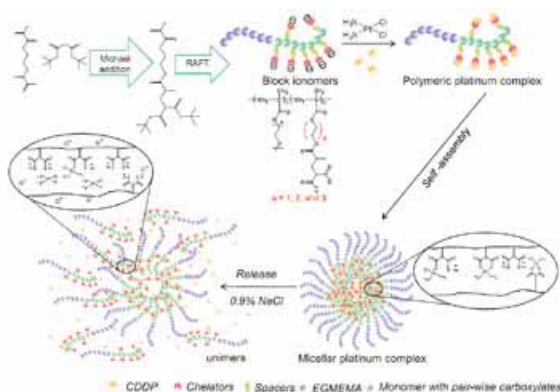
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Cis-platin [*cis*-dichlorodiamineplatinum(II); CDDP] has become an important class of antitumor agents and is widely used for the treatment of a number of solid malignancies. However, its clinical use is limited due to side effects and drug resistance.¹ The use of macromolecular such as water-soluble polymers and polymeric micelles can potentially improve the therapeutic indices of this drug. There are two different ways for covalently attaching CDDP to polymer backbone. While the formation of the leaving ligands leads to the release of platinum inside the cell, permanent ligand attachment generates a polymeric platinum drug (prodrug).

Herein, the drug was conjugated to the polymer backbones via the leaving ligands. The resulting block copolymers showed clearly amphiphilic character in aqueous solution leading to the self-assembly of micelles. The resulting nanoparticles allow then passive targeting of the tumour.² Polymers incorporated CDDP was prepared through the metal-polymer complex formation of CDDP with poly(ethylene glycol methyl ether methacrylate)-block- poly(*tert*-Bu malonic ethylene glycol methacrylate) (POEGMEMA-*b*-PMAETC). Different spacer-length monomers with neighboring carboxylate groups were synthesized via Michael addition between di-*tert*-butyl malonate and different dimethacrylates. The monomers were prepared with about 60% yield. A range of block copolymers were prepared through chain extension of macroRAFT POEGMEMA agent, $M_n = 15000 \text{ g mol}^{-1}$) with the monomers synthesized. Micelle formation was ultimately driven by enhancement of hydrophobicity of PMAETC blocks conjugated to CDDP (as noted in **Scheme 1**). An increase in length of spacer led to a significant increase in the micellar size and even tends to form rod-like micelles with the presence of the longest spacer. The toxicity of polymers was ignored while their platinum conjugates showed high activity against A549, OVCAR3, and SKOV3. The longest spacer appeared to be the most effective to above cell lines. This interesting result was directly attributed to cellular uptake observed. The colonogenic assay confirmed that the platinum polymeric micelles enable to limit the reproducibility of A549.



Scheme 1. Platinum polymer conjugates and subsequently self-assembled into micelles.

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Development of a PET-MRI Hyperbranched Polymer Imaging Agent

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Chronic diseases such as cancer can be highly debilitating for the patient, have a high financial burden on the Australian health-care system and in many cases result in death. Despite substantial research being directed towards cancer diagnosis and therapies, cancer was the underlying cause of 30% deaths in Australia in 2008.¹ It is clear that there is a need for a radical improvement in the way cancer is detected and treated. Medical devices need to be capable of delivering a therapeutic dose to the tumour site within the body, but must also possess mechanisms for *in-vivo* real-time diagnosis, monitoring of tumour progression and efficacy of treatment.

A single imaging modality that has high sensitivity, high resolution and is capable of imaging all disease states is not available. Therefore, development of a molecular imaging agent that combines existing modalities into one device and can be measured on a single machine is a priority goal in the area of imaging for diseases. In our group we are aiming to develop PET-MRI imaging agents, as they combine the sensitivity of Positron Emission Tomography (PET) with the detailed anatomical images available from Magnetic Resonance Imaging (MRI).

Here we report on the development of PET-MRI imaging agents, building upon the hyperbranched polymer ^{19}F MRI agents previously developed in our lab.² These hyperbranched nanoparticles are synthesised by RAFT polymerisation methods.³ A dodecyl trithiocarbonate RAFT agent has been functionalised with an alkyne leaving group. This allows for the attachment of a $\text{N}_3\text{-(PEG)}_3\text{-NH}_2$ linker by a 1,3-dipolar cycloaddition reaction. A copper free method was utilised, so as to prevent contamination of the cage ligands with cold copper. This reaction was characterised by end group analysis by ^1H NMR and UV-Vis analysis of formation of the triazole ring.

The SarAr-NCS cages from ANSTO⁴ are then attached by reaction of the isothiocyanate group with the amine of the PEG linker to form a stable thiourea bond. Attachment of the cage was then characterised by ¹H NMR analysis, Gel Permeation Chromatography (GPC) and UV-Vis spectroscopy. Radio-labelling of the polymer was performed with carrier-free ⁶⁴Cu²⁺. Characterisation by SE-HPLC and ITLC-SG showed that the final ⁶⁴Cu radio-labelled polymers were radio-chemically pure.

In conclusion we have shown the successful synthesis of hyperbranched polymer nanoparticles that have been functionalised with ^{64}Cu cage ligands. It is hoped that these materials will prove to be successful PET-MRI multimodal imaging agents in the future.

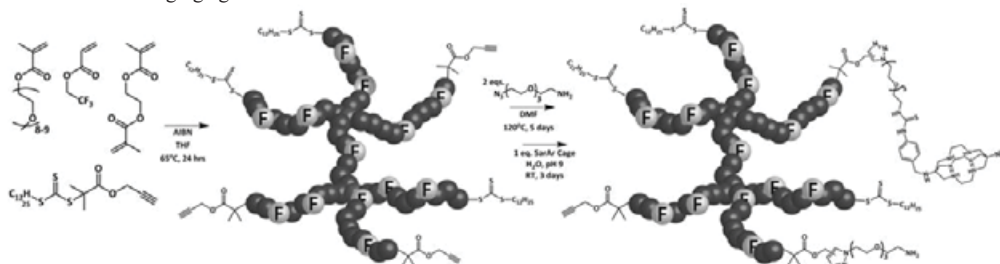


Figure 1. Synthesis of a hyperbranched polymer via RAFT polymerisation and functionalisation with a SarAr cage⁴, to produce a PET-MRI multimodal imaging agent.

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Multifunctional Star and Hyperbranched polymer for cancer targeted drug delivery and MR imaging

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Magnetic Resonance Imaging (MRI) is one of the most widely used imaging technologies to obtain images of pathological areas in contemporary medical science. The use of Gadolinium (Gd) as contrast agent provided enhanced positive contrast and great improvement of imaging quality. In our work, we use poly(ethylene glycol) methyl ether acrylate (PEG-A) to build compact nanostructure, such as star polymer and hyperbranched polymers via reversible addition fragmentation transfer polymerization. We have incorporated penta-fluorophenyl acrylate (PFPA) in the polymer structures. Then, we successfully introduced gadolinium (Gd) chelating agents (DOTA) into the nanostructures by reaction between amine-modified DOTA and pentafluoro ester groups. (Fig. 1)

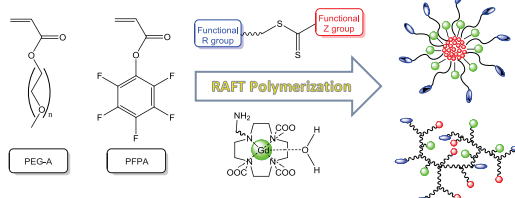


Figure 1. Use RAFT polymerization building nanostructures.

The formation and specification of the nanostructures was confirmed by gel permeation chromatography (GPC), transmission electron microscopy (TEM), and dynamic light scattering (DLS). It was found that the nanostructures were obtained with very narrow size distributions (Fig. 2), with the size under 100 nm, suggesting their passive targeting potential to tumour tissue and possible EPR effect.

In addition, the nanostructures were functionalized with different targeting moieties via thiol-ene and click chemistry reactions. The use of RAFT polymerization offers the opportunity for utilising thiol Z groups.¹ This thiol group opens up the possibilities of thiol-ene, thiol-yne, thiol-isocyanate, thio-epoxide or thiol-disulfide exchange chemistry for the attachment of targeting moieties.^{2,3} The stability of Gd was studied using inductively coupled plasma mass spectrometry (ICP-MS), while MRI properties were evaluated by nuclear magnetic resonance (NMR). The toxicity and targeting properties were tested in-vitro studies, (Fig. 3) and revealed the absence of toxicity at high concentration.

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³ A. B. Lowe, *Polym. Chem.* **2010**, 1, 17-36

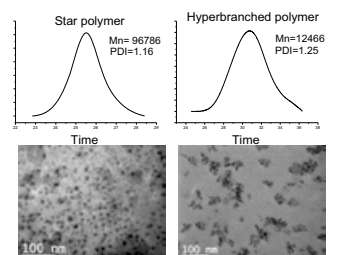


Figure 2. GPC spectra and TEM image of Star polymer (left) and Hyperbranched polymers (right)

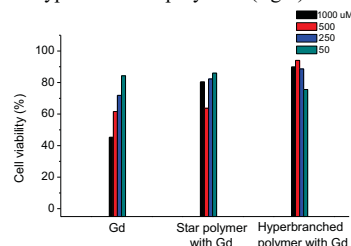


Figure 3. Toxicity tests in-vitro studies.

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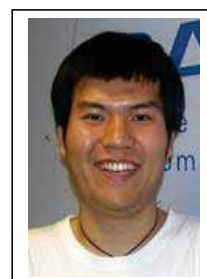
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Novel lanthanide(III) hyperbranched polymers as advanced targeting imaging agents

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The early and exact identification of infected or tumor tissue is one of the major challenges in medical imaging. The key aspect of luminescent molecular probes is a fast and highly contrasted real-time imaging. Conventional luminescent probes have a number of limitations such as short lived excited states, small stoke shifts, photobleaching, interference from light scattering and autofluorescence.¹ These restriction can be overcome by lanthanide(III) based materials. The main advantages are their long lived excited states which allow time-resolved signal detection thus eliminate autofluorescence, little sensitivity to photobleaching and a high sensitivity for *in vitro* imaging².

Another application for lanthanide(III) complexes is in Magnetic Resonance Imaging (MRI), a routine diagnostic with a high anatomical resolution but a poor sensitivity.³ MRI is particularly useful for tissues with little density contrast, such as brain or tumor. Contrast agents are injected intravenously to enhance the appearance of blood vessels, tumors or inflammation. Gadolinium(III) complexes are widely used as contrast agents in MRI⁴ and as all lanthanide complexes require coordination by ligands suitable for energy transfer.⁵ Chromophoric hyperbranched polymers generated *via* RAFT polymerization technique will be a novel class of organic ligands for this purpose. These highly branched structures are of particular interest because they provide multiple and highly concentrated functionalities which allow for application in targeting⁶ or drug delivery⁷. Hyperbranched polymer Gadolinium(III) complexes provide a revolutionary way for the development of materials for targeted magnetic resonance imaging. Other lanthanide(III) ions such as Europium(III) or Erbium(III) coordinated by hyperbranched polymers will generated new bioprobes for targeted cell imaging (figure 1).

The ultimative aim is the combination of optical and magnetic resonance imaging properties to provide high sensitivity and specificity to enable an early detection of diseases.⁸

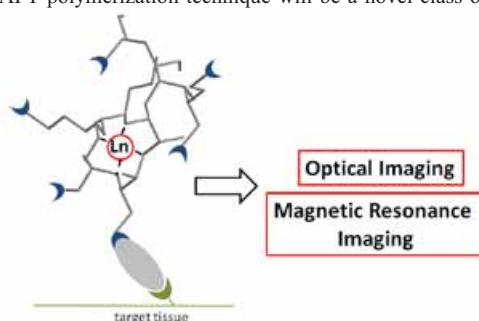


Figure 1. Lanthanide(III) hyperbranched polymers as targeting imaging agents.

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⁸ C. S. Bonnet, E. Toth, *C. R. Hebd. Séances Acad. Sci.* **2010**, 13.

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Hydrophobically modified OSA starches: a fluorescence probe study of the influence of macromolecular architecture on the critical micelle concentration

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Hydrophobically modified starches have a wide range of uses as dispersing agents in aqueous media for nutritional ingredients in the food industry. As an example, modification with octenyl succinic anhydride (OSA) in basic medium leads to amphiphilic starch derivatives composed of a hydrophilic starch backbone and hydrophobic OSA short side chains (**Fig. 1a**). Despite such products being widely used for 60 years, the choice of an OSA modified starch for a given application remains empirical.

OSA starches fall into the category of electrosteric colloidal stabilizers for which the colloidal particles formed are kept apart by both electrostatic and steric repulsion forces. The emulsifying properties of OSA modified starches are strongly related to the extent of chemical modification, *i.e.* the average number of OSA side chains per monosaccharide unit (degree of substitution, *DS*). Due to the complex highly branched macromolecular architecture of starch (**Fig. 1b**), the degree of branching (*DB*) and the size of starch chains must also exert a key role on end-use properties.

Despite a plethora of papers describing the optimization of the OSA grafting reaction, only very few involving the emulsifying properties of the formed products can be found, none of which has considered any correlation between the structural parameters of OSA starches and their critical micelle concentration (CMC), which is the most important parameter for such amphiphilic products (**Fig. 1c**).

We report herein the first structure / CMC study for OSA modified starches for the food and related industries. A range of well-defined OSA-modified starches has been prepared and their various structural and compositional characteristics have been characterized by NMR¹ and SEC.² CMCs have been determined by the measurement of fluorescence intensity ratio of pyrene. Influences of the degree of substitution of OSA side chains, the degree of branching of the starch backbone and the macromolecule size are reported and these results aim to provide the platform to develop the first means of choosing and/or synthesizing modified starches best suited as stabilizers for particular applications.

The support of the Australian Research Council (LP100100225) is gratefully acknowledged.

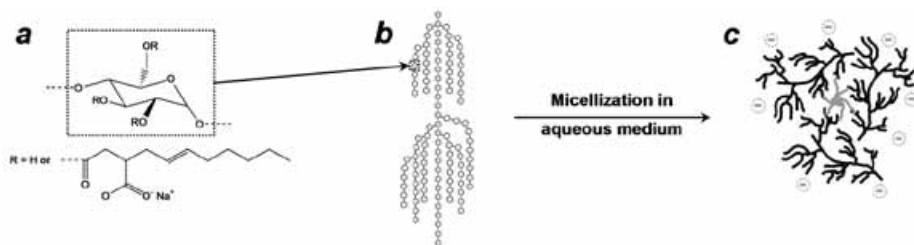


Figure 1. OSA grafting onto starch glucose units (**a**) ; schematic representation of hyperbranched starch macromolecules (**b**) ; schematic representation of OSA modified starch micelle in aqueous medium (**c**).

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Enzymatic Degradation of Poly(Polyol Sebacate)

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Poly (polyol sebacate) (PPS) is a new family of biodegradable elastomers recently developed for application to soft tissue engineering^{1,2,3}. However, in vitro studies indicated that the degradation of PPS results in an acidic environment as with other polyesters (e.g. PGA). Such acidic degradation products would launch an inflammatory responses and limits PPS's application in most organ systems. To address this issue, alkaline bioceramic (e.g. Bioglass® and hydroxylapatite) particles could be used as fillers in the PPS-based composites, as the degradation products of bioceramics could buffer the acidic environment.

In this work, one of PPS, poly(xylytol sebacate) (PXS) and Bioglass® were used. Various percentages (up to 15 wt%) of Bioglass® were added to PXS pre-polymer in THF solution. This was followed by casting the above slurry onto glass slides to produce sheet materials. Finally the cast was treated for PXS to crosslink under vacuum to make the final composites.

Preliminary results showed that PXS with 10 wt% and 15 wt% Bioglass® buffered culture medium successfully, with pH value remaining at the normal physiological level. In vitro degradation assessment in DMEM culture medium demonstrated that the composite materials retained their structural integrity and form stability after 2 months' degradation. The Young's Modulus of the composites with 10 wt% and 15 wt% Bioglass® remained in a stable state after an initial drop. This is of great importance to tissue engineering which demands a stable mechanical support. The excellent mechanical properties, desirable degradation profile and improved biocompatibility (less cytotoxicity) make this family of composites a very promising candidate in the application of soft tissue engineering, such as blood vessel, heart muscle and valves, cartilage, tendon and bladder.

¹ D. Motlagh , J. Yang , K.Y. Lui, A.R. Webb, G.A. Ameer. *Biomaterials* 2006;27(24):4315-4324.

² Q.Z. Chen, H. Ishii, G. Thouas G, J.S.Wright, A.R. Lyon AR, S.E. Harding. *Biomaterials* 2010;31:3885-3893.

³ C.A. Sundback, J.Y. Shyu, Y. Wang, W.C. Faquin, R.S. Langer, J.P. Vacanti, *Biomaterials* 2005;26(27):5454-5464

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Synthesis and Physico-Mechanical Characterization of Reinforced Microcellular Polyurethane-Sisal Biocomposites.

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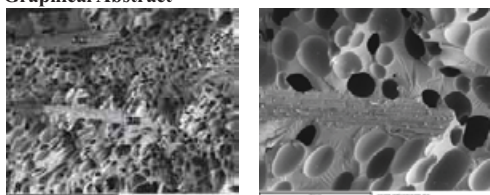
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Abstract

This study aims to develop and characterize reinforced microcellular polyurethane biomass composite to meet high performance as well as environmental sustainability requirements. Microcellular polyurethane (PU) - natural fiber (NF) composites were synthesized based on castor oil and sisal fibers. Biocomposites were prepared at different sisal fiber loading. The effect of natural fiber treatment using water and alkaline solution (1.5% NaOH) were investigated. The synthesized reinforced biocomposites were characterized mechanically and physically under tension load, viscoelasticity, and water absorption tests. The interfacial adhesion between PU and sisal fibers was investigated using SEM technique. In general the short NF loads (3% wt/wt) showed an obvious improvement in the mechanical properties of the PU-Sisal biocomposites. Values of modulus of elasticity were increased up to 133% higher than obtained microcellular PU. While the yield and tensile strengths were enhanced up to 14.35 % and 36.7% respectively. The NaOH treatment showed a lower improvement in the mechanical properties. Viscoelastic measurements showed that the real compliance J' is always above the imaginary compliance J'' , which means that J' is the dominant factor for showing the characteristics of the composite thus, the material is showing an elastic behavior rather than a viscous one. Moreover, increasing NF loads resulted in decreasing in J' . Applying variant temperature (80-120 °C) caused an increase in stiffness at different frequencies. PU- treated and untreated sisal biocomposites showed around 2.5% water uptake at room temperature for 24 hrs.

Graphical Abstract



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Living *p*-quinodimethane polymerization for the synthesis of well-defined PPV materials: Is it even possible?

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One of the most prominent synthesis strategies for conjugated polymer systems is the so-called *p*-quinodimethane polymerization, which is also often referred to as the precursor routes to obtain poly(*p*-phenylene vinylene) materials.¹ Thereby, a monomer precursor is used that upon reaction with a strong base forms an active quinodimethane system that can undergo radical polymerization. Due to its radical mechanism, quinodimethane polymerization is an attractive synthesis route since it allows for relatively mild reaction conditions and high tolerance towards functional groups. To date, however, no control methodologies that allows to synthesize poly(phenylvinylene)s or other poly(arylene vinylene)s in a precise manner comparable to controlled/living radical polymerization techniques in the realm of conventional radical polymerization are known. Only materials with high dispersity, insufficient control over the average molecular weight and functionality are thus available. If an efficient control is achieved, conjugated polymers with narrow molecular weight distribution, exactly pre-determinable molecular weight and high endgroup fidelity will become available. With such material at hand, block copolymers of various types become available, either in sequential or in modular design approaches by using *Click*-type chemistries.



First advances towards controlled quinodimethane polymerization have been made by carrying out successful chain-transfer polymerizations or anionic polymerizations, hence enabling the synthesis of well-structured, however still not immaculate PPVs materials.²⁻⁴ The state of the art of controlled PPV synthesis will be outlined and outstanding problems are summarized and pathways to overcome these challenges discussed.

¹ T. Junkers, J. Vandenbergh, L. Lutsen, P. Adriaenssens, D. Vanderzande, *Polym. Chem.* **2012**, *in press*.

² I. Cosemans, L. Hontis, D. Van Den Berghe, A. Palmaerts, J. Wouters, W. Maes, T. J. Cleij, L. Lutsen, T. Junkers, D. J. M. Vanderzande, *Macromolecules* **2011**, *44*, 7610–7616.

³ I. Cosemans, J. Wouters, W. Maes, T. J. Cleij, L. Lutsen, T. Junkers, D. J. M. Vanderzande, *Macromol. Rapid Commun.* **2012**, *in press*.

⁴ J. Vandenbergh, I. Cosemans, L. Lutsen, D. Vanderzande, T. Junkers, *Polym. Chem.* **2012**, *submitted*.

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Recent Travels in k_t -LandJohannes Barth,¹ Sabine Beuermann,² Michael Buback,¹ Gregory T. Russell,³ Rebekka Siegmann²¹ Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 6, D-37077 Göttingen, Germany² Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam/Golm, Germany³ Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Until a few years ago, a presentation such as this would instead have been entitled “Recent *Travails* in k_t -Land”. What has changed in the last half-decade is the advent of the SP-PLP-EPR technique. It couples single-pulse pulsed-laser polymerization (SP PLP) with highly time-resolved EPR spectroscopy. The result is unrivalled access to chain-length-dependent termination rate coefficients, $k_t^{i,i}$, in radical polymerization.¹ Where once it was a constant source of exasperation to measure termination rate coefficients, k_t , now one may obtain highly satisfying results using SP PLP EPR. In particular this is the case for small chain lengths, as illustrated in **Fig. 1**. This shows radical concentration, c_R , in the milliseconds immediately after a laser pulse induces polymerization. By fitting these results, one obtains $k_t^{1,1}$, the rate coefficient for termination between radicals of unity degree of polymerization, and α_s , the power-law exponent in the variation of $k_t^{i,i}$ with chain length, i , at small i . No other currently available technique can deliver these highly important parameters with such authority.

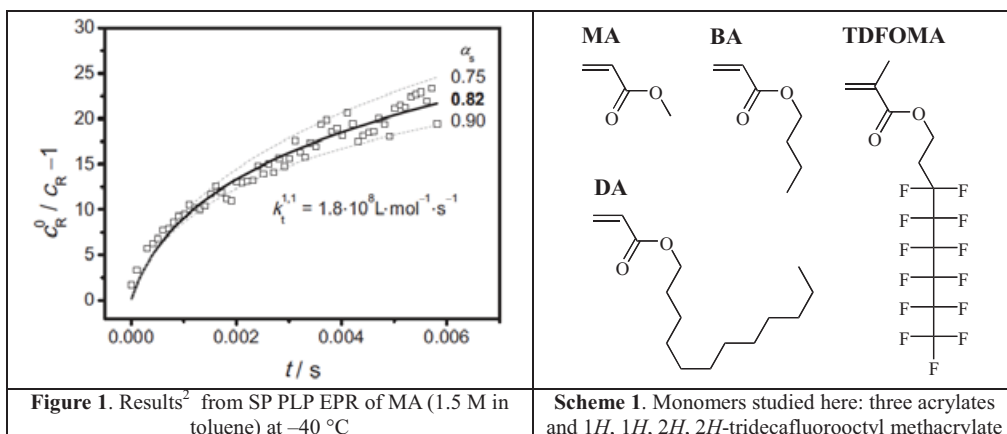


Figure 1. Results² from SP PLP EPR of MA (1.5 M in toluene) at $-40\text{ }^{\circ}\text{C}$

Scheme 1. Monomers studied here: three acrylates and 1H, 1H, 2H, 2H-tridecafluorooctyl methacrylate

This presentation will report on results from a recent sabbatical year in Göttingen, where the only SP-PLP-EPR setup¹ is located. The monomers studied are shown in **Scheme 1**. They are (1) a series of n -alkyl acrylates,² and (2) a fluorinated methacrylate. These were of interest in that: (1) Previous $k_t^{i,i}$ results for acrylates were ambiguous due to the likelihood of mid-chain radicals being present. In the current study this uncertainty was eliminated by working at temperatures too low for backbiting to occur; and (2) Previously only ‘standard’ methacrylates had been studied, and so the effect of fluorination – which is known to alter miscibility and conformation – remained to be established.

¹ J. Barth, M. Buback, *Macromol. React. Eng.* **2010**, *4*, 288-301

² J. Barth, M. Buback, G. T. Russell, S. Smolne, *Macromol. Chem. Phys.* **2011**, *212*, 1366-1378

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Recent Macromolecular Design and Application of Catalytic Chain Transfer Polymerization

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Catalytic chain transfer polymerization (CCTP) is a free radical polymerization technique that has been shown to control both molecular weight and chain end functionality. Polymer synthesized by CCTP display a terminal vinylic group in almost quantitative yield.¹ While CCTP is a relatively old technique; there has been renewed interest with the recent wide-spread application of Thiolene “click” chemistry²: reaction between thiols and –enes.

In this project, we demonstrate the homo- and co-polymerization of biocompatible polymers via CCTP and their post-synthetic modification using thiolene chemistry to synthesize ethylene glycol base polymers with tunable lower critical solution temperature (LCST).³ Furthermore we have also utilized the combination of CCTP and thiolene to create nanoparticle-polymer hybrids via a grafting-to approach. Modification of nanoTiO₂ with a linker such as (3-Mercapto)propyl trimethoxysilane will give TiO₂ with thiol groups on the outer layer. This synthetic handle facilitates the attachment of CCT synthesized polymers to the surface of the nanoparticles via Thiolene chemistry (Figure 1). After modification the nanoparticles showed improved size distribution and a reduction in particle aggregation. In fact, the nanoparticles modified with these biorelevant polymers stabilized at around 300nm in various biological media. Biological toxicity studies carried out both before and after modification found that the polymer modification significantly reduced the nanotoxicity of the nanoparticles

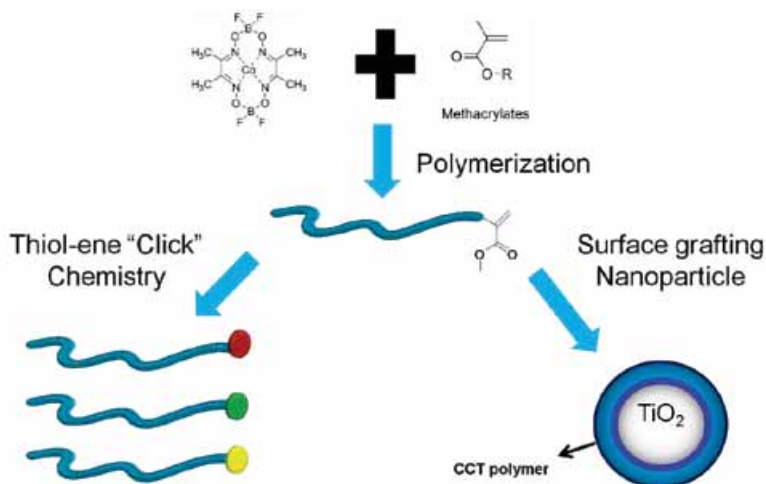


Figure 1. Catalytic Chain transfer polymerization (CCTP) as a technique to synthesize polymer with vinylic end group and its combination with Thiolene chemistry for end group modification and nanoparticle grafting.

1. Davis, T.P., Kukul,D., Haddleton,D.M., Maloney, D.R., *Trends in Polym. Sci.*, **1995**, 11, 365.
2. Kolb, H.C., Finn, M.G., Sharpless, K.B., *Angewandte Chemie Int. Ed.*, **2001**, 40, 2004.
3. Soeriyadi, A.H, Li, G.Z., Slavin, S., Amos, C., Becer, C.R., Whittaker, M.R., Boyer, C., Haddleton, D.M., Davis, T.P., *Polym. Chem.*, **2011**, 2, 815

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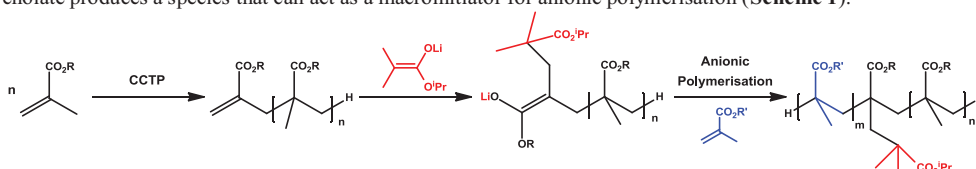
Research interests: Controlled/Living FRP, Polymer Degradation, ESI-MS



CCT-derived Macromonomers as Macroinitiators for Anionic Polymerisation

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The concept of combining multiple polymerisation mechanisms is of significant interest as it allows the synthesis of functional polymers with a controlled architecture. Thus enabling the combination of physical properties in a single polymeric material, which may not otherwise be possible. Terminal vinylic groups of macromonomers can be coupled to a simple lithium enolate to generate a macroinitiator. This in turn can be employed to anionically polymerise methacrylic monomers to form a block copolymer. Methacrylate polymers synthesised via catalytic chain transfer polymerisation (CCTP) result in macromonomers with vinylic end groups. During a post-polymerisation step, a Michael addition between the vinylic end group and *iso*-propoxy lithium enolate produces a species that can act as a macroinitiator for anionic polymerisation (Scheme 1).



Scheme 1. Reaction scheme for macromonomer synthesis, post-polymerisation functionalisation using a lithium enolate and anionic polymerization from a macroinitiator. R = Me, Bz; R' = Me, Bz.

Two methods of anionic polymerisation have been investigated. Firstly, lithium chloride and a toluene/THF solvent mixture was used to synthesis an isotactic second block. Although block copolymers could be made, the process was inefficient (Figure 1). A second route, involving the use of MeAl(BHT)₂, produced a second block which was syndiotactic in nature. This method was much more efficient (Figure 2) and has been shown to be versatile towards macromonomers of different methacrylates and chain lengths. The compositions of the resultant polymers were determined using multiple analytical techniques, and the tacticities investigated. The resultant polymer consists of an atactic block (originating from CCTP) and an isotactic or syndiotactic block (originating from the anionic polymerisation).

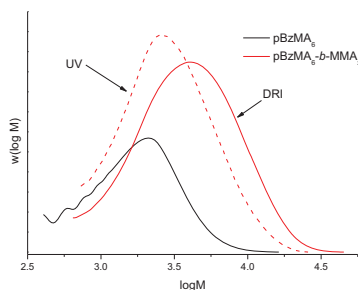


Figure 1. Molecular weight distribution (relative to PS, measured in THF) of pBzMA₆ (made via CCTP) and p(BzMA₆-*b*-MMA_x) (made via CCTP followed by anionic polymerisation in the presence of LiCl). Chromatograms normalised to the amount of polymer.

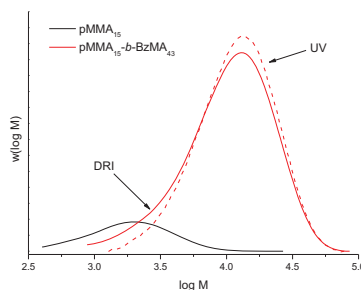


Figure 2. Molecular weight distribution (relative to PS, measured in THF) of pMMA₁₅ (made via CCTP) and p(MMA₁₅-*b*-BzMA₄₃) (made via CCTP followed by anionic polymerisation in the presence of MeAl(BHT)₂). Chromatograms normalised to the amount of polymer.

This work is part of the Research programme of the Dutch Polymer Institute DPI, Eindhoven, The Netherlands, Project No. 651

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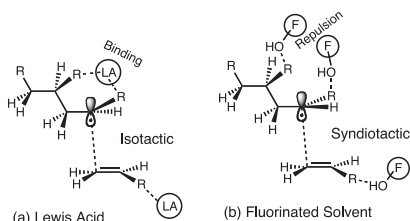


Predicting Polymer Tacticity in Radical Polymerization

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Controlling the stereochemistry of a polymer is highly desirable as this can affect its physical properties, such as its crystallinity, melting point, solubility and mechanical strength. Stereoregular polymers are normally prepared using expensive transition metal catalysts, which typically require demanding reaction conditions (such as high purity, low temperatures and/or high pressures). Extending stereochemical control to free radical polymerisation has been a long sought goal, as free-radical processes tend to require less expensive reagents, less demanding reaction conditions, are applicable to a wider range of monomers, and are therefore often preferred industrially.¹ For monomers containing carbonyl groups (such as vinyl acetate, methacrylates, and (meth)acrylamides) some degree of control has been achieved by carrying out the polymerisation in the presence of certain Lewis acids² or using fluorinated alcohols as solvents.³ As shown in Scheme 1, it is thought that they alter the stereochemistry by binding to the carbonyl groups on the monomer and propagating radical, thereby constraining the configuration of the transition structure.¹ Depending on whether the additives coordinate simultaneously with both the terminal and penultimate carbonyl groups as in Scheme 1(a), or merely at a single site as in (b), a preference for isotactic or syndiotactic transition structures can be induced. However, specific mechanistic details have yet to be clarified, and optimisation of these methods has yet to be achieved, particularly for isotactic polymers where maximum reported ratios of isotactic to non-isotactic triads are around 70:30, and are often much lower. Not surprisingly, the degree of stereochemical control achieved is highly temperature and solvent dependent, and this can raise a problem when attempting to combine these techniques with methods for controlling the molecular weight distribution in free-radical polymerisation, as optimal conditions for these processes are not always compatible.⁴ Moreover the extension of significant stereochemical control to the free-radical polymerisation of important monomers that do not contain carbonyl groups, such as styrene, has yet to be achieved. As a first step toward this goal, we have been using computational chemistry to study the mechanism of stereocontrol in a variety of free-radical polymerization processes, and to predict the effect of solvents and novel control agents on polymer tacticity. In this presentation we will outline some of our recent work.



Scheme 1

¹ For a review, see for example: Kamigaito, M.; Satoh, K. *Macromolecules*, **2008**, *41*, 269.

² See for example: (a) Okamoto, Y.; Habaue, S.; Isobe, Y.; Suito, Y.; *Macromol. Symp.* **2003**, *195*, 75; (c) Isobe, Y.; Suito, Y.; Habaue, S.; Okamoto, Y. *J. Polym. Sci. A* **2003**, *41*, 1027. (c) Isobe, Y.; Nakano, T.; Okamoto, Y. *J. Polym. Sci. A Polym. Chem.* **2001**, *39*, 1463.

³ See for example: (a) Yamada, K.; Nakano, T.; Okamoto, Y. *Macromolecules*, **1998**, *31*, 7598; (b) Isobe, Y.; Yamada, K.; Nakano, T.; Okamoto, Y. *J. Polym. Sci. A* **2000**, *38*, 4693; (c) Koumura, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules*, **2006**, *39*, 4054.

⁴ Chong, Y. K.; Moad, G.; Rizzardo, E.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2007**, *40*, 9262.

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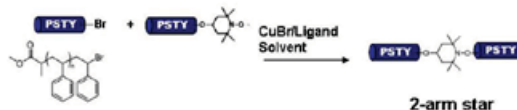


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Conditions were chosen to facilitate the disproportionation of Cu(I)Br to the highly activating nascent Cu(0) and deactivating Cu(II)Br₂ in the presence of DMSO solvent and Me₆TREN ligand. SET-NRC reactions at room temperature gave near quantitative yields of macromolecular coupling of low molecular weight polystyrene with bromine chain-ends (PSTY-Br) and a tri-nitroxide core in under 7 min even in the presence of functional groups to form 3-arm stars² (e.g. -OH, -COOH, -NH₂, =O). Utilization of the reversibility of the NRC reaction at elevated temperatures allowed the exchange of chain-end groups with a variety of functional nitroxide derivatives. The robustness and orthogonality of this SET-NRC reaction was further demonstrated using the Cu-catalyzed azide/alkyne ‘click’ (CuAAC) reaction, in which yields greater than 95% were observed for coupling between PSTY-N3 and a PSTY chain first trapped with an alkyne functional TEMPO (PSTY-TEMPO≡) (Scheme 1):



Scheme 2:



⁴ Kulis, J.; Bell, C. A.; Micallef, A. S.; Monteiro, M. J. *Aust J Chem* **2010**, 63, 1127-1236.

Research Interests: Living radical polymerisation, single electron transfer, nitroxide radical coupling

PolyBank: Development of a bank of advanced polymeric materials via RAFT technology and high throughput experimentation

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Thang, Graeme Moad, Ezio Rizzardo, and John Chiefari

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There is an increasing need by industry and academia to screen a range of polymer materials to evaluate their performance for diverse applications. However, researchers interested in testing such materials in their areas of expertise generally do not have the synthetic skills or infrastructure to prepare them. Consequently, they have to rely on collaborations or commercial suppliers to obtain the materials and often the desired products are not available. This approach can considerably slow the discovery and development process. The development of a bank of advanced polymeric materials (PolyBank) is currently seeking to address this need. PolyBank makes use of high-throughput synthetic techniques currently available at CSIRO and the powerful controlled radical polymerization method developed at CSIRO known as the Reversible Addition Fragmentation chain Transfer (RAFT) Technology (see Fig. 1). This strategy allows for the systematic, rapid generation and characterization of polymer libraries encompassing a broad range of properties. The RAFT process allows for the preparation of well-defined polymers with predefined molecular weight, chemical composition and architecture. The use of high-throughput synthetic protocols available at CSIRO for RAFT technology can expedite the production of these polymer materials. Many scientific projects would benefit from such a reserve of materials because their researchers could systematically plan their activities based on the polymer resource of PolyBank. This would speed up their investigations and thus accelerate the generation of knowledge and lower the costs of research. This contribution addresses the current status towards the full establishment of PolyBank.

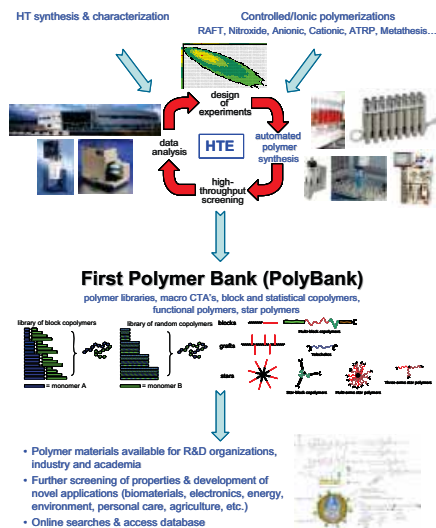


Fig. 1: Schematic representation of the development of the first bank of advanced polymer materials (PolyBank).

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Research interests: Controlled radical and ionic polymerizations, self-assembled materials, composite materials based on ionic liquids, and high-throughput experimentation



Molecular Imprinting Using Biaryl Monomers: Comparison of Thermal and Microwave-assisted Approaches

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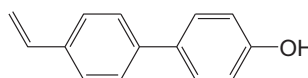
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A number of novel biaryl monomers, synthesized by Suzuki coupling¹, were evaluated as functional monomers for the preparation of molecularly imprinted polymers (MIPs).

In molecular imprinting, a group of polymerisable functional monomers forms a three-dimensional assembly around a template and the resulting adduct formed is maintained by copolymerisation with a crosslinker. Subsequent extraction of the template from the polymer generates a cavity with spatial arrangements and functional groups complementary to the template molecule.

The MIPs were prepared by conventional thermal and microwave-assisted (MW) polymerization for test targets theophylline (THP) and phenylphosphonic acid (PPA). Recently, our group has shown that microwave-induced polymerisation enhanced the selectivity of the MIPs towards the template caffeine.²

Results of semi-empirical molecular modelling and ¹H and ³¹P NMR titrations for theophylline and PPA, respectively, have shown 4'-vinyl-biphenyl-4-ol to interact most favourably with THP and PPA and deemed the best monomer, among the biaryls tested, to use for the synthesis of both theophylline and PPA MIPs.



4'-vinyl-biphenyl-4-ol

Both thermal and MW THP and PPA MIP systems prepared using 4'-vinyl-biphenyl-4-ol as functional monomer showed significant imprinting effect as confirmed by the analysis of their binding properties. The MW MIPs, however, exhibited higher template uptake than their thermal counterparts, attributed to its high microporosity and lower surface charge. Cross-reactivity and selectivity tests with caffeine also showed the MW MIP to be more selective, than the thermal MIP, towards the template THP.

The mode of polymerisation and nature of the porogen were observed to affect the physical properties of the polymers. MW polymers showed higher porosity, lower surface charge and lower surface area than their thermal equivalents.

¹ H.A. Zayas, C.I. Holdsworth, M.C. Bowyer, A. C.P. Gordon, C.I. Holdsworth, A. McCluskey, *Tetrahedron Letters* **2009**, 50, 5894-5895.

² N.W. Turner, C.I. Holdsworth, S.W. Donne, A. McCluskey, M.C. Bowyer, *New Journal of Chemistry* **2010**, 34 (4), 686-692.

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Controlled Radical Polymerization, Metathesis, and “Click” Chemistry: A Versatile Combination to Target New Reactive Polymers

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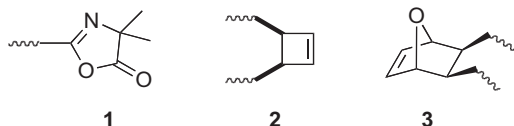
The design and the synthesis of well-defined polymers with multiple pendent functionalities have attracted considerable interest in modern polymer chemistry. Because properties and performances of polymers greatly depend on the nature and number of functional groups, new synthetic strategies have been developed that exert excellent control over functionalities through highly efficient orthogonal chemical reactions. Controlled/living radical polymerization, ring-opening metathesis polymerization (ROMP), and “click” chemistry can now afford such a high degree of control over polymer topology, composition, and functionality.ⁱ

Complex functional polymers such as reactive polymers, macromonomers and functionalized oligomers are required for the precise synthesis of various macromolecular architectures: block, graft, and hyperbranched (co)polymers.ⁱⁱ To prepare new functional materials, we have investigated synthetic strategies to incorporate highly reactive functionalities using orthogonal chemical processes.

The talk will present results related to the manipulation of such orthogonal chemistries in order to prepare new well-defined reactive polymers: macromonomers, block, and graft copolymers. Atom-transfer radical polymerization (ATRP), reversible addition-fragmentation transfer (RAFT), ROMP, and “click” chemistries (thiol-ene Michael addition and Huisgen 1,3-dipolar cycloaddition) have been used in combination with highly reactive functionalities (Scheme 1):

- The azlactone ring (**1**) of 2-vinyl-4,4-dimethyl-5-oxazolone (VDM) that reacts with nucleophiles without the formation of by-product, to prepare reactive and thermoresponsive polymers;ⁱⁱⁱ
- The cyclobutenyl group (**2**) to synthesize well-defined grafted copolymers based on a strictly linear 1,4-polybutadiene trunk;^{iv}
- The bicyclic oxanorbornenyl group (**3**) to prepare poly(ethylene oxide) macromonomers and graft copolymers *via* “click” chemistry and ROMP.^v

Those strategies provide excellent control over all synthetic steps, leading to polymers that are useful for the synthesis of various functional materials.



Scheme 1

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Research interests: Macromolecular engineering using controlled / « living » polymerization and application to the synthesis of functional and reactive homopolymers, block and graft copolymers (Ring-Opening Metathesis Polymerization [ROMP], controlled radical polymerization [ATRP, RAFT]); Biomedical applications of polymers; Polymers for optics.



Investigation of Ring-Opening Metathesis Polymerisation with Hoveyda-Grubbs Catalysts

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Cyclic polymers exhibit a number of unique properties compared to their linear counterparts including, thermodynamic, optical, physical and biophysical properties.¹ For example, the pharmacokinetics of cyclic polymers over their linear counterparts offers several advantages, with reduced clearance rates, extended plasma circulation times and greater tumour accumulation, which has been attributed to enhanced permeation and retention effects.

In recent years a wide variety of synthetic approaches have been investigated for the preparation of cyclic polymers, and can be divided into two main categories, either ring-closure techniques or ring-expansion techniques.² In particular, the development of ring-expansion metathesis polymerisation has enabled the synthesis of high molecular weight and high purity cyclic polymers. However, the cyclic catalysts employed are custom made and are not commercially available.³ In contrast, Song *et al.* have demonstrated that the commercially available Hoveyda-Grubbs catalysts **1** (Figure 1a) also allows access to cyclic copolymers via cyclic alternating ring-opening metathesis polymerisation (ROMP) (Figure 1b).⁴

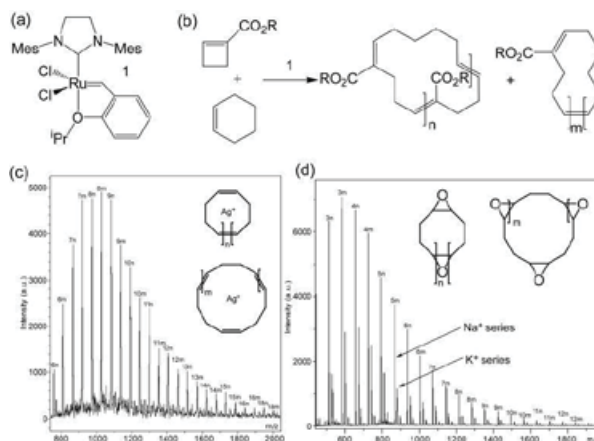


Figure 1. (a) 2nd Generation Hoveyda-Grubbs catalyst **1**. (b) Synthesis of cyclic polymers via cyclic alternating ROMP. MALDI ToF MS spectra of (b) cyclic poly(cyclooctadiene) and (c) cyclic poly(cyclooctadiene epoxide).

In the current study the application of Hoveyda-Grubbs catalysts for the ROMP of cyclooctadiene and cyclooctene derivatives was investigated for the preparation of functionalised cyclic polymers (Figure 1c and d). The synthesis, characterisation and properties of the resulting cyclic polymers will be presented.

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Block Copolymers via Macromercaptan Initiated Ring Opening Polymerization

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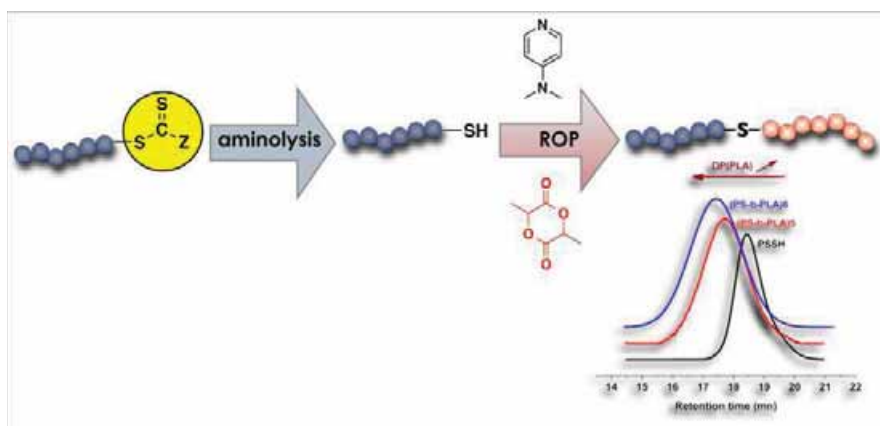
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To combine ROP and RAFT techniques, several main approaches exist. One of the most employed is based on a dual initiator, such as a RAFT agent bearing a functional group that is capable of initiating the ROP of lactides (LA). Alternative strategies have been developed as well, such as introducing the RAFT agent after the ROP or combining simultaneous RAFT and ROP to produce grafted copolymers. However all those methods keep the RAFT agent intact either at the end or in the middle of the polymer chain, introducing potential problems with regard to block stability and/or toxicity. The present work details our efforts in preparing diblock copolymers based on PLA and polystyrene (PS) where the two blocks are linked by a covalent sulfur bond. The key idea is to transform the dithioester/trithiocarbonate end group into a thiol function by aminolysis and to subsequently use it as the initiator of the ROP of lactide (Scheme 1). The analyses of the polymeric material via multiple detector Size Exclusion Chromatography (SEC) and Liquid Chromatography under Critical Conditions (LCCC) as well as Diffusion Ordered NMR Spectroscopy (DOSY-NMR) evidences the formation of the desired block copolymer structures alongside residual macromercaptane and homopoly(lactide) in minor quantities.



Scheme 1. Synthesis of PLA-based diblock copolymers via thiol-initiated ROP

In addition, it was possible to prepare a thiol-capped poly(ethylene), which was subsequently employed to initiate the ROP of a lactide and to prepare a polyethylene-*block*-poly(lactide) copolymer, which formation was evidenced via NMR as well as SEC.

The current study has demonstrated that it is possible to employ RAFT derived macromercaptanes as initiating species in the organo-catalyzed ROP of lactides, thus providing an alternative platform for the generation of block copolymers with degradable and nondegradable strands.¹

¹ Lefay, C.; Gle, D.; Rollet, M.; Mazzolini, J.; Bertin, D.; Viel, S.; Schmid, C.; Boisson, C.; D'Agosto, F.; Gigmes, D.; Barner-Kowollik, C. *J. Polym. Sci. Pol. Chem.* **2011**, *49*, 803.

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Organic Catalyst-Mediated Ring Opening Polymerization Towards the Near-quantitative Synthesis of Star Polymers

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Core cross-linked star (CCS) polymers possess a unique 3-D molecular architecture, which consists of a cross-linked core surrounded by a number of radiating arms.¹ Currently a diverse spectrum of potential applications for CCS polymers have arisen, which includes drug delivery, cascade reaction catalysis, membrane formation and paint additives.² Recent advances in the synthesis of CCS polymers *via* the ‘arm first’ approach and ring opening polymerization³ (ROP) of cyclic esters has enabled the development of biocompatible and degradable stars, making them suitable candidates for *in vivo* drug delivery devices.⁴ However, the previous reported synthetic protocols *via* ROP suffer from low yields resulting from a low arm-to-star conversion, and often tedious and costly purification processes are required to isolate the star polymers from the unconverted ‘arm’ macroinitiators.^{4,5} Therefore, large scale production of these CCS polymers is infeasible. This creates a shortage of materials for research and development of polyester-based degradable CCS polymer and hinders their potential commercialization.

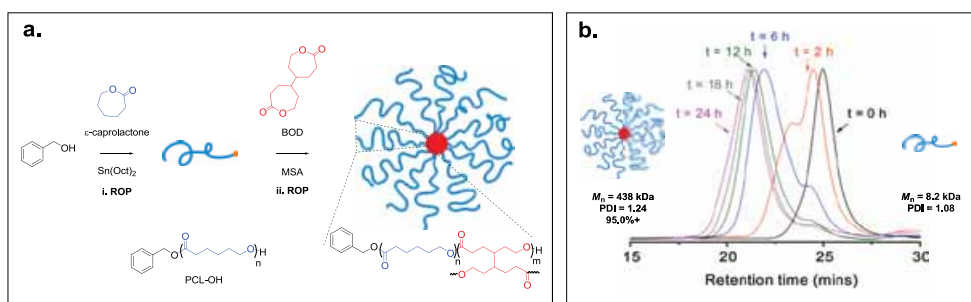


Figure 1. a. Synthesis of polyester-based CCS polymers *via* ring opening polymerization (ROP) of i. ϵ -caprolactone (CL) and ii. 4,4'-bioxipanyl-7,7'-dione (BOD). b. Gel permeation chromatography (GPC) refractive index (RI) chromatograms of the star formation reaction mixture at different reaction time.

Herein we report the synthesis of polyester-based degradable CCS polymers *via* methyl sulphonic acid-mediated ROP of 4,4'-bioxipanyl-7,7'-dione (BOD) using poly(ϵ -caprolactone) (PCL-OH) macroinitiators with various molecular weights (Figure 1a). The reaction kinetic profiles as exemplified in Figure 1b displayed fast reaction rates and near-quantitative arm-to-star conversion (> 95 %). Optimization of the reaction conditions to achieve quantitative arm-to-star conversion and development of functionalized star polymers will be presented.

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Renewal of Allyl Polymerization Mechanism

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The free-radical polymerization of allyl monomers, generally referred to as “allyl polymerization”, has received much less attention than the corresponding vinyl polymerization of common vinyl monomers. The low tendency to polymerize and the obtainment of products with a low degree of polymerization were characteristic of allyl polymerization, so that a large amount of initiator was required, i.e., reaching up to almost 10^2 times when compared with common vinyl polymerization. These results are attributable to “degradative monomer chain transfer”. However, the well-known allyl polymerization mechanism is based on only the kinetic data; thus far any structural identification has not been given. Thus, we carried out the free-radical polymerization of allyl acetate (AAc) as a most typical allyl monomer¹ and the resulting oligomeric poly(AAc)s were characterized using MALDI-TOF-MS in order to reassess the AAc polymerization mechanism proposed by Litt and Eirich² as a summary of the results reported in the period of 1940'-1960. Conclusively, we have proposed a renewal of the well-known reaction scheme for the free-radical polymerization of AAc. Based on the renewed reaction mechanism yielding oligomer, the fate of resonance-stabilized monomeric allyl radical was pursued as follows: The coupling termination of monomeric allyl radical with growing polymer radical leading to a shortening of oligomeric poly(AAc) chain length was significant under a common allyl polymerization condition where a remarkably large amount of initiator was used. Under a completely opposite condition where the polymerization would be carried out at a low initiator concentration, the reinitiation reaction of monomeric allyl radical occurred predominantly compared to the common initiation through the primary radical. Concurrently, the contribution of monomeric allyl radical to the coupling termination reaction with growing polymer radical was reduced greatly, leading to an enlargement of polymer chain length.

Then, the latter reinitiation reaction of monomeric allyl radical was discussed in more detail, especially focused on the temperature dependency of reinitiation efficiency of resonance-stabilized allyl radical.³ The reinitiation efficiencies of monomeric allyl radical were pursued by the dead-end polymerizations of allyl benzoate (ABz) at 80, 105, and 130 °C using a small amount of initiators; they increased remarkably with raised temperature. Thus, the enhanced reinitiation reactivity of allyl radical at an elevated temperature could bias the well-known “degradative monomer chain transfer” characteristic of allyl polymerization toward the chain transfer in common vinyl polymerization.

On the course of our investigation,³ especially focused on the polymerization behavior at elevated temperatures, we found by chance that any direct contribution of cumyloxy radical to initiation reaction was not observed at all in the polymerization of ABz with dicumyl peroxide as a typical peroxide initiator at elevated temperatures but the methyl radical initiation preceded by β -scission of cumyloxy radical occurred predominantly. This finding was then extended to the generalization of initiation reaction mechanism in allyl polymerization with organic peroxide initiators at elevated temperatures.⁴

Finally, we referred to an alternative chain termination involving β -scission of growing polymer radical through addition-fragmentation chain transfer, in addition to a well-known degradative monomer chain transfer; this could be significant at elevated temperatures.

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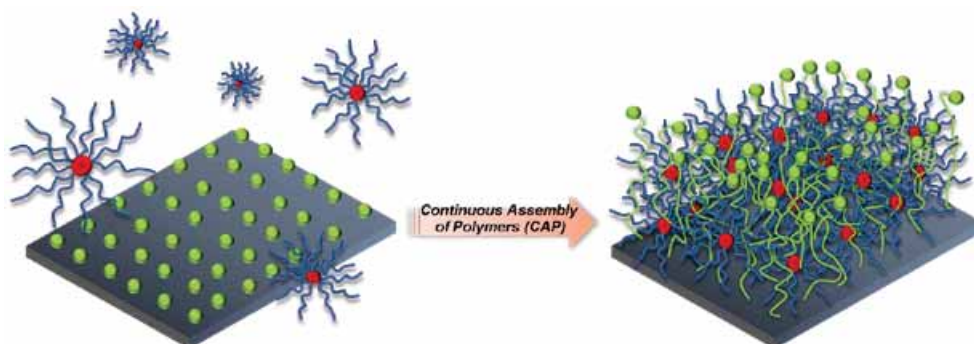


A Simple, Efficient and Novel Methodology in Forming Complex Macromolecular Architecture Films via Continuous Assembly of Polymers (CAP)

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Polymeric thin films have found a diverse range of applications including biomaterials and optoelectronics. Over the years, the fabrication of these materials has been successfully achieved using techniques such as layer-by-layer (LbL),¹ grafting 'from',² or grafting 'to' approaches. However, in most cases, only polymer precursors of linear architectures are used (or derived) in film formation and examples on applying more complex architectures such as star polymers³ or dendrimers are scarce, which is not surprising given that the number of approaches that actually allow the 'growing' of such macromolecular films are indeed limited. Thus, it would be highly advantageous if new and efficient methods can be developed to permit the formation of complex macromolecular films – hence potentially leading to novel (bio)applications.



Scheme 1. The generation of surface-confined polymer films made up of complex macromolecular architectures (e.g. star polymers).

Recently, Goh et. al. have developed a new strategy, term continuous assembly of polymers (CAP),⁴ in forming surface-confined polymer films. By polymerizing premade polymer precursors functionalized with (a minimal amount of) polymerizable moieties from surface-anchored initiators via controlled polymerization techniques, cross-linked films can be generated efficiently and continuously in one-step as well as in a controlled manner. The fundamental concept behind CAP – although simple – is extremely versatile and robust in forming thin films and as will be shown in this work, can easily be extended to different complex polymer architectures including star polymers. The work in here will serve as a stepping stone towards developing the next generation of the materials of tomorrow.

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4. T. K. Goh, S. N. Guntari, C. J. Ochs, A. Blencowe, D. Mertz, L. A. Connal, G. K. Such, G. G. Qiao, F. Caruso, *Small* **2011**, DOI: 10.1002/smll.201101368

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Synthesis of new bisallylic dithioether monomers for photoplastic polymers

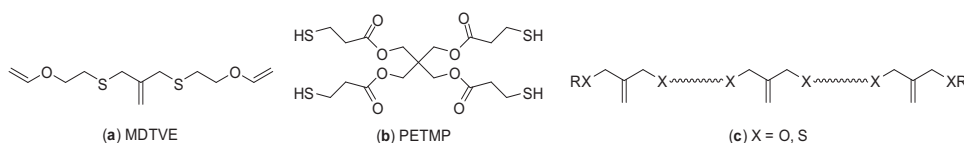
Cornelis Moorhoff,¹ Wayne Cook,¹ Tara Schiller,¹ Carl Braybrook,² San Thang.²

¹ Department of Materials Engineering, Monash University, Clayton, VIC, Australia.

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Photoplastic polymers, such as those formed from MDTVE (**a**) and PETMP (**b**) (Scheme 1), undergo creep and stress relaxation on irradiation with UV or visible light.¹ We are in the process of synthesizing new monomers based on our recent synthetic successes² and to extend the range and speed of these systems. We now have made tris-allylic compounds having the structure (**c**) with R polymerizable groups which allow us to investigate how the position of the allylic thioether group in the monomer affects the photoplasticity. We will be discussing the synthesis and photoplasticity of networks formed from these new monomers, such as those in **1** to **3** (Scheme 2).

Scheme 1



Scheme 2

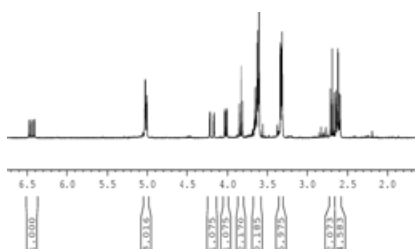
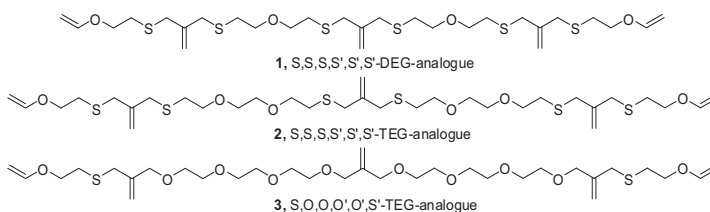


Fig. 1. ¹H-NMR of **2** and

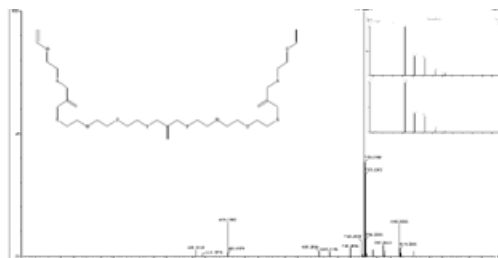


Fig 2. ESI-MS of **2**, S,S,S,S',S',S'-TEG-analogue

Supported by ARC DP0877382

¹ W.D. Cook, F. Chen, Q.D. Nghiem, T. F. Scott, C.N. Bowman, S. Chausson, L. Le Pluart, *Macromol. Symp.* **2010**, 291–292, 50.

² C.M. Moorhoff, W.D. Cook, F. Chen, D. Nghiem, C. Braybrook, S.H. Thang, J. Sun, T.F. Scott, C.N. Bowman. *Aust. J. Chem.* **2011**, 64, 1083–1093

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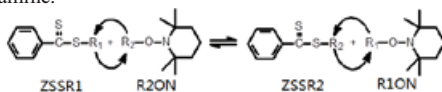


Small Molecular Kinetic Model for the RAFT Process

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The fundamental study on kinetics and mechanism of the RAFT-based polymerization, with the aim of determining the rate coefficients of chain transfer reactions, is an ongoing topic in scientific community. A number of approaches have been applied to determine the chain transfer coefficient¹, particularly, the individual rate coefficients of addition (k_{add}) and fragmentation (k_{frag}). In the present work, we have studied the mechanism and kinetics of a pure RAFT process, e.g., without polymerization, using a small molecular model reaction between dithioester and alkoxyamine.²



The purpose of using alkoxyamine is because it generates carbon-centered radicals at a rate regulated by the persistent radical effect (PRE). Thus the radical $\text{R}_2\cdot$ from homolysis of alkoxyamine R_2ON adds to dithioester ZSSR1 , forming the intermediate radical possessing two leaving groups, R_1 and R_2 . When fragmentation occurs at R_1 side, a chain transfer process is fulfilled and the released R_1 is trapped by the persistent nitroxyl radical to form a new alkoxyamine, R_1ON . An equilibrium between alkoxyamine and dithioester is built through the RAFT process. The kinetics of the RAFT process closely relates to the macroscopic kinetics of the exchange reaction, which can be easily measured by HPLC and ESR.

Fig. 1 shows the computer simulated concentration of nitroxyl radical, TEMPO, as a function of reaction time. It is clear that the free TEMPO concentration depends on the rate coefficients of the RAFT process. **Fig. 2** shows the concentration of the starting dithioester decrease along with the reaction proceeds. The time for building a dynamic balance between the reverse reactions strongly relates to the rate of the RAFT process. These results allow reasonable fitting of kinetic parameters to the macroscopic kinetics.

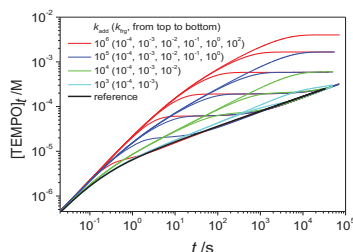


Figure 1. Monte Carlo simulated TEMPO concentration as a function of reaction time for various k_{add} and k_{frag} .

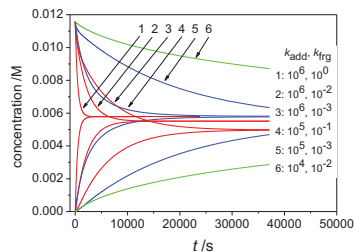


Figure 2. Monte Carlo simulated concentrations of starting and the resulting dithioesters as functions of reaction time for various k_{add} and k_{frag} .

The comparison between theoretical and the experimental results, the side reactions that interfere the kinetic model, as well as the successful determination of k_{add} and k_{frag} , will be discussed.

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- Y. Ao, J. He, X. Han, Y. Liu, X. Wang, D. Fan, J. Xu, Y. Yang, *J. Polym. Sci.: Part A: Polym. Chem.* **2007**, *45*, 374-387.

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Synthesis and Characterization of “Glycopolyurethanes”

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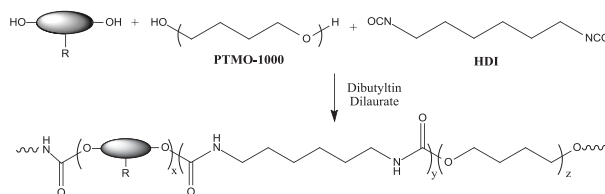
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Polyurethanes (PU's) have proven to be an essential class of synthetic polymers due to their versatility and ability to tune the material properties by the choice and composition of the starting materials. Areas of application include, for example, automotive, electrical/electronics and construction industries. Tremendous progress has been made in the field of biomaterials where PU's play an important role in the development of medical devices and implants due to their favorable bio- and blood-compatibility properties. Nowadays, research has focused more and more on the elaboration of synthetic strategies to attach biorecognizable groups *e.g.* carbohydrates to polymeric materials because of their ability to specifically interact with cell surface receptor proteins.¹ For instance, Davis *et al.* described the functionalization of RAFT²-derived copolymers using a thio-halogen click reaction as well as a nucleophilic substitution based on a *para*-toluenesulfonyl precursor.³

This contribution will address an efficient synthetic route towards the preparation of novel glycopolymers by combining polyurethane chemistry and subsequent functionalization of the synthesized materials via “click” procedures. For this purpose, carefully chosen chain extenders possessing alkene and alkyne functionalities, respectively, were applied for step-growth polymerization processes (**Scheme 1**). Depending on the utilized chain extender, modification of the polymers was achieved by performing either copper catalyzed Huisgen 1,3-dipolar cycloaddition or thiol-ene click reactions. Polyurethanes with glucose and galactose moieties have been prepared and characterized by means of nuclear magnetic resonance spectroscopy, gel permeation chromatography, infrared spectroscopy, X-ray photoelectron spectroscopy and water contact angle measurements. Preliminary cell viability tests have shown that these polymers are non cytotoxic.



Scheme 1: Schematic representation of the polyurethanes synthesized using differently functionalized chain extenders.

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Research interests: Controlled free radical and “living” polymerization methods, self-assembled materials, free radical polymerization, biomaterials, polyurethanes, glycopolymers



Catalytic Cycle of Nitroxide Activation and Regeneration

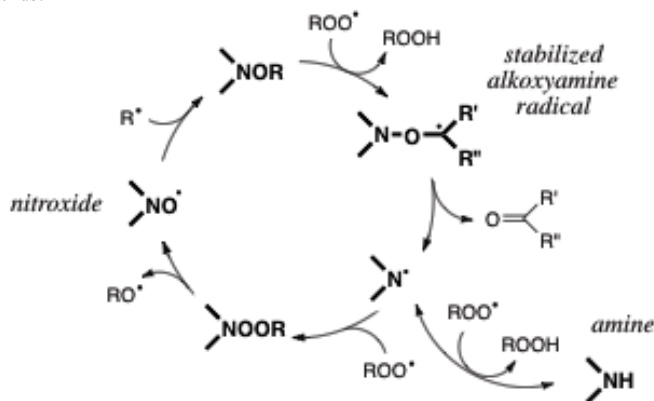
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Hindered Amine Light Stabilizers (HALS) are remarkably effective antioxidants used to protect organic materials against oxidative degradation. However, despite their widespread use, the mechanism underlying the Denisov cycle¹ of their activation and regeneration, and the nature of the side-reactions that disrupt this process, remains a topic of debate. Not only is the commonly accepted Klemchuk's pathway² kinetically unfeasible under service conditions,³ but it also fails to explain the experimentally detected formation of secondary piperidine analogues in the thermal decomposition of HALS.⁴ There thus appears to be an important gap in our knowledge of the reactions of nitroxide radicals with organic materials, and this has implications not only for designing effective HALS, but for many of the other important applications of this class of aliphatic nitroxide radicals.

In the present study we apply high-level *ab initio* calculations (G3(MP2)-RAD theory) to discriminate between the various literature mechanisms of nitroxide activation/regeneration and of side reactions involving amine formation. We also investigate the relevance of the catalytic cycle⁵ that successfully describes protective action of diarylamines, and accompanying direct N–OR bond homolysis as a route to secondary piperidine analogues. Finally, we suggest a new catalytic cycle of HALS (see below) that accounts for both nitroxide activation/regeneration and amine formation. We show that this new cycle is the most kinetically and thermodynamically favored amongst all other considered mechanisms, and allows the explanation of a number of experimental trends.



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NMP and ATRP in nanoreactors: Factors influencing compartmentalization effects on bimolecular termination

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Controlled/living radical polymerization (CLRP) in dispersed systems¹ enables synthesis of polymeric nanoparticles of various morphologies comprising well-defined polymer with a number of potential applications. The intrinsic characteristics associated with CLRP in dispersed systems, *e.g.* compartmentalization, may dramatically influence the progression of the polymerization. Compartmentalization refers to the physical isolation of reactant species in confined spaces, *i.e.* the monomer droplets or polymer particles. Compartmentalization effects offer the potential of improving the level of control over the molecular weight distribution and the livingness (end-functionality) using droplet/particle size as a tool. In CLRP based on the persistent radical effect (*e.g.* NMP and ATRP), compartmentalization may manifest itself in two different ways: (i) the segregation effect and (ii) the confined space effect.² We here focus on the segregation effect, which refers to how two propagating radicals in different particles cannot terminate, thus leading to an increase in livingness.

The extent of the segregation effect on termination depends strongly on the particular CLRP system. Consider NMP of styrene (125 °C) mediated by TEMPO and TIPNO, respectively, in the absence of spontaneous initiation of styrene. If one compares the compartmentalized termination rate (R_t^c) with that of a bulk system (R_t^{nc}) with the same overall propagating radical concentration for [alkoxyamine]₀ = 0.02 M at $d = 50$ nm, the segregation effect is almost two orders of magnitude stronger for TIPNO (Fig. 1).³

In the present work, theoretical investigations have been carried out based on simulations using two-dimensional Smith-Ewart equations to elucidate what factors govern the extent of the segregation effect. The reduction in termination rate due to segregation cannot be predicted merely based on the average number of propagating radicals per particle. This is because the magnitude of the segregation effect is also governed by the distribution of propagating radicals between particles, which is influenced by both the termination and the deactivation rate coefficients in NMP and ATRP.^{3,4}

The results have implications with regards to improvement of livingness by exploitation of particle size, and apply also to other controlled/living systems based on the persistent radical effect.

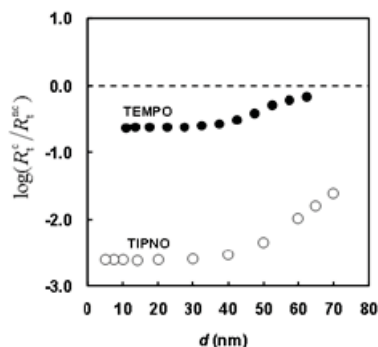


Figure 1. Ratios of simulated “compartmentalized” (R_t^c) and “non-compartmentalized” (R_t^{nc}) termination rates for TEMPO- and TIPNO-mediated polymerizations of styrene in dispersed system at 125 °C at 1% conv.

¹ P. B. Zetterlund, Y. Kagawa, M. Okubo, *Chem. Rev.* **2008**, *108*, 3747-3794

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Towards Nitroxide Mediated Photo-Polymerization

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New alkoxyamines bearing a chromophore group linked to the aminoxyl function are proposed as photoinitiators. These original compounds decompose under UV irradiation to generate the corresponding alkyl and nitroxide radicals (Figure 1). Laser Flash Photolysis experiments showed an efficient shortening of the excited state lifetimes suggesting a C-O bond homolytic dissociation under UV irradiation. ESR study evidences that a C-O homolysis occurs under UV irradiation.¹ When these compounds are used as photoinitiators in Nitroxide Mediated PhotoPolymerization (NMP2), a linear growth of the polymer chain, reaching 80 % of conversion in less than 500 s, is observed combined with a reinitiation of the photopolymerization after the end of the irradiation: this is the first report showing a at least partial NMP2 process.¹⁻³

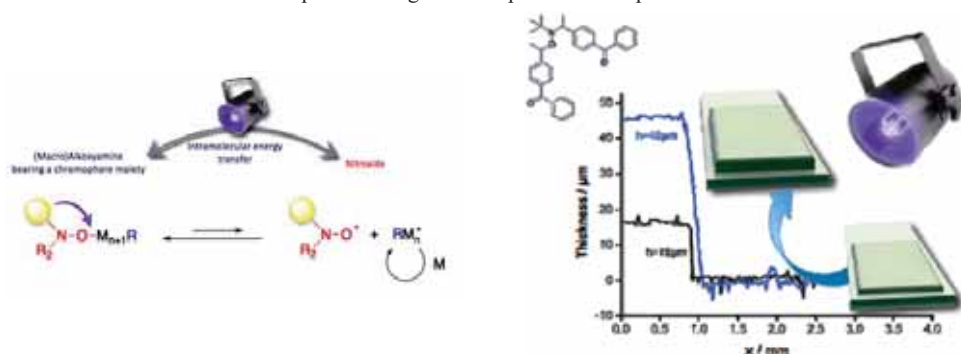


Figure 1. a) Mechanism of the NMP2 process. b) Micropatterning experiments (Ebecryl 605 matrix). Thickness before and after reinitiation determined by an altimeter.

As the main application of this kind of compound is for micro-patterning, the ability of the macroalkoxyamine derived from the alkoxyamine described in Figure 1b to reinitiate a second polymerization process was investigated. By this approach, multi-layered film polymerization was successfully obtained (Figure 1b).⁴

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Miniemulsion polymerization based on *in situ* surfactant formation and ultrasonication: A novel synthetic route to nano-sized (< 20 nm) polymer particles

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The heterogeneous polymerization technique known as miniemulsion polymerization is associated with a number of advantages, most notably its applicability to synthesis of organic/inorganic hybrid and hollow polymeric nanoparticles in the particle diameter range 50-1000 nm, as well as for implementation of controlled/living radical polymerization (CLRP) in dispersed systems.¹ Miniemulsion polymerization is distinct from the more common emulsion polymerization technique with respect to the mechanism of particle formation. In miniemulsion polymerization, particles are formed via monomer droplet nucleation, whereas in emulsion polymerization, particle formation occurs in the aqueous phase via micellar and/or homogeneous nucleation. This difference has important implications, because it means that in miniemulsion polymerization, there is no requirement for species to diffuse across the aqueous phase from monomer droplets to polymer particles, and hence the synthetic advantages highlighted above. In general, it is difficult to access polymer particles of diameters less than 50 nm via miniemulsion polymerization.

We here describe a novel polymeric nanoparticle preparation technique by combination of *in situ* surfactant generation^{2,3} at the oil/water interface (using oleic acid and potassium hydroxide) and ultrasonication at relatively high surfactant content (**Figure 1**).⁴ This technique enables synthesis of nanoparticles of diameters less than 20 nm in a one step process (no monomer feed technique) using considerably less surfactant (60-120 wt% surfactant relative to monomer) than in a microemulsion polymerization (normally 250-350 wt% surfactant relative to monomer). The method is applicable to both non-living (conventional) radical polymerization and CLRP. Using nitroxide-mediated radical polymerization, the molecular weight distributions were narrow and the number average molecular weights were in agreement with theory, indicating good control/livingness.

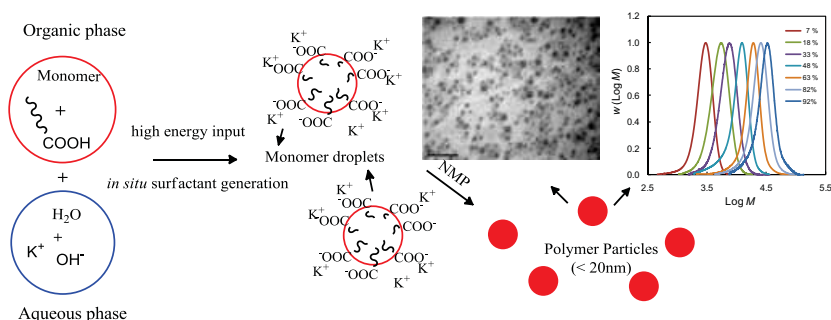


Figure 1. Synthesis of nano-sized polymer particles by nitroxide-mediated polymerization in miniemulsion based on *in situ* surfactant formation and ultrasonication.

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Nanoparticle synthesis; Miniemulsion polymerization



Well-defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization

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This work will describe surfactant-free and nitroxide-mediated controlled free-radical polymerization (NMP) in aqueous dispersed systems.

Water-soluble polymers with a reactive alkoxyamine end-group are used as macroinitiators for the polymerization of hydrophobic monomers in water. These polymerization systems operate via *in-situ* chain extension of the hydrophilic living precursor by addition of hydrophobic monomers, and concomitant self-assembly of the so-formed amphiphilic block copolymers. The selected system is based on methacrylate type main monomers (methacrylic acid (MAA), for the hydrophilic segment and methyl methacrylate (MMA), for the hydrophobic one). These monomers were copolymerized with a low percentage of a styrenic monomer (sodium 4-styrene sulfonate (SS), and styrene (St), respectively) to turn the non-living NMP of methacrylate monomers into a living NMP performed at low temperature^{1,2}. After the polymerization of the hydrophobic monomers, the resulting nanoobjects are thus formed by a polymerization induced micellization mechanism. The method has all the advantages associated with the conventional emulsion polymerization process and leads to concentrated aqueous suspensions, obtained in the absence of both organic co-solvent and particular emulsification techniques.

The morphologies of the amphiphilic block copolymer nanoobjects depend on the length of the hydrophobic blocks. Expected morphologies such as spherical micelles were observed^{3,4,5} but other morphologies like nanofibers and vesicles were also formed (Fig. 1).

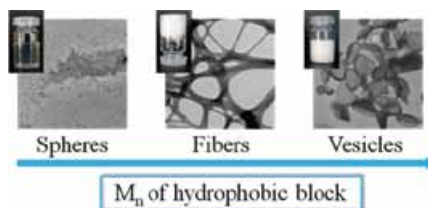


Figure 1. Latex and TEM images of block copolymer particles with different hydrophobic block molar masses and obtained with same macroinitiator

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Well-defined Amphiphilic Block Copolymer Nanoobjects via Nitroxide-Mediated Emulsion Polymerization

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Controlled/living radical polymerization in CO₂-induced miniemulsions

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The miniemulsion polymerization technique has attracted much attention due to its suitability for synthesis of hybrid polymer particles, hollow polymer particles, as well as for implementation of controlled/living radical polymerization (CLRP).¹ These synthetic advantages are all related to the monomer droplet nucleation mechanism, whereby diffusion across the aqueous phase is not a requirement. However, the high energy demand for miniemulsion preparation by traditional methods (e.g. ultrasonification) has precluded widespread industrial application. Various low energy emulsification techniques have been developed for the preparation of polymeric nanoparticles.²⁻⁶ Nevertheless, CLRP has rarely been carried out in miniemulsion based on low energy emulsification, the exception being our work on miniemulsion NMP using *in situ* surfactant formation.⁷

In this presentation, we introduce a novel method⁶ for low energy generation of miniemulsions by use of compressed CO₂. This method has been employed in tandem with RAFT chemistry to prepare well-defined polymeric nanoparticles. Gentle stirring of styrene/hexadecane/Dowfax 8390/water generates a macroemulsion of low stability. Pressurization with CO₂ results in reversible formation of an emulsion with much greater stability (Fig. 1), and within a certain pressure window (close to 7.50 MPa), a transparent emulsion is obtained. RAFT polymerizations of styrene using benzyl dodecyl trithiocarbonate and the initiator VA-044 at 50 °C were carried out in the CO₂-induced miniemulsions. Excellent colloidal stability as well as good control/livingness were observed. Interestingly, the particle size could be tuned by adjusting the CO₂ pressure without altering the recipe (Fig. 1). Therefore, in addition to the benefits of a low energy process, this environmentally benign technique offers reversible control over monomer droplet and nanoparticle size by pressurization and depressurization with CO₂.

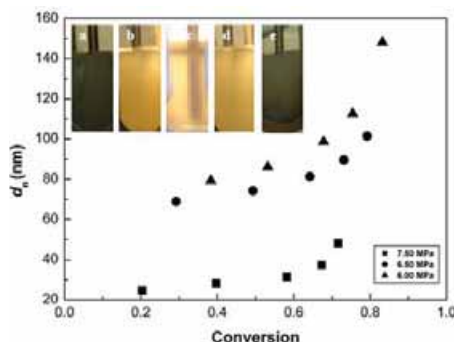


Figure 1. Particle diameter (d_n) vs conversion for RAFT miniemulsion polymerization of styrene at 50°C at different CO₂ pressures. Insert: a) 3.00, b) 7.13, c) 7.50, d) 7.86, e) 8.00 MPa.

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Research Interests: Controlled/living radical polymerization in miniemulsion; CO₂-related dispersed systems; Mixed surfactant vesicles etc.

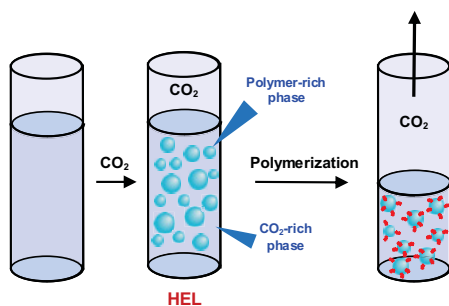
Polymeric nanoparticle synthesis in CO₂-induced emulsions

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CO₂-expanded liquids (CXLs) are a relatively new class of solvent that have considerable potential for the development of sustainable processes. CXLs combine the tunability and transport properties of supercritical CO₂ (scCO₂) with the solvating power of organic solvents to generate a continuum of reaction media.¹ When a monomer/polymer solution is equilibrated with compressed CO₂, the system comprises two phases: the CO₂-expanded liquid phase, and a CO₂ gas phase. At sufficiently high pressures, the dissolved CO₂ induces a phase separation in the liquid phase at the point known as the homogeneous expansion limit (HEL).² In the case of CO₂-expanded vinyl monomer/polymer systems, this phase separation can generate a fine emulsion where the continuous phase comprises CO₂/monomer, and the dispersed phase comprises CO₂/monomer/polymer. The physical appearance of the emulsion is “milky”/translucent, indicative of a submicron-sized dispersed phase.

We have recently developed a novel type of heterogeneous polymerization that relies on CO₂-assisted particle formation exploiting the HEL.³ In the absence of CO₂, this system is a dispersion polymerization. However, in the presence of CO₂, the proposed mechanism is entirely different from that of a traditional dispersion polymerization (in organic solvent or scCO₂). The key aspect of this technique is to exploit CO₂ in the particle formation process, and to stabilize the emulsion formed at the HEL via an *in situ* generated or preformed block copolymer stabilizer as the system is depressurized. This approach, along with the benefits of using a benign medium at a much reduced pressure than scCO₂, has the potential of allowing exceptional control over the particle size and is also anticipated to be applicable to controlled/living radical polymerization techniques, which are difficult to implement in normal dispersion polymerizations.⁴



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Corrosion resistant double stranded conducting polymer nanocomposite coating for aircraft applications

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Epoxy based double stranded conducting polymer nanocomposite (DSCPN) coating was formulated and applied uniformly over aluminium AA2024 alloys. The resulting films were characterized using electrochemical impedance spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy and salt spray test. Electrochemical impedance spectroscopy data showed that the DSCPN in epoxy matrix caused a noticeable increase in the impedance of the film. DSCPN coating showed excellent corrosion resistance compared to single stranded system. It also solves the problem of dopant loss due to heat, rain water and etc. in long term exposure. Coating was stable up to 1200 hrs in salt spray chamber and adhesion was found excellent.

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Corrosion resistant double stranded conducting polymer nanocomposite coating for aircraft applications

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Functional Nanomaterials from Block Copolymer Self-Assembly

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This talk will describe the synthesis and characterization of functional nanostructured materials from the self-assembly of blocked macromolecules with inorganic materials.¹⁻⁶ It is structured according to the degree of order achieved in the resulting materials, moving from amorphous to polycrystalline to single crystal-type materials. By using thermodynamic principles established for block copolymers and mixtures with inorganic species (e.g. nanoparticles) well-defined nanostructured morphologies are obtained at all these levels of structural order. Thermal processing of the polymer-inorganic hybrids results in nanoporous materials with uniform pores and hexagonal as well as bicontinuous cubic pore structures. These concepts are applied to amorphous nanostructured aluminosilicates and non-oxide type ceramics stable up to 1500°C, polycrystalline nanostructured transition metal oxides and metals, as well as nanostructured, porous single crystal silicon and metal thin films (~10-100nm) with epitaxial growth relation to the substrate. The various chemical approaches will be discussed. Perspectives will be given in the context of nanomaterials for applications ranging from microelectronics to energy generation and storage, i.e. materials for solar cell, fuel cell and battery applications

¹ H. Arora, P. Du, K. W. Tan, J. Hyun, J. Gratzul, H. L. Xin, D. Muller, M. Thompson, U. Wiesner, *Block Copolymer Self-Assembly Directed Single-Crystal Homo- and Heteroepitaxial Nanostructures*, Science **2010**, 330, 214-219.

² S. C. Warren, L. C. Messina, L. S. Slaughter, M. Kamperman, Q. Zhou, S. M. Gruner, F. J. DiSalvo, U. Wiesner, *Ordered mesoporous materials from metal nanoparticle-block copolymer self-assembly*, Science **2008**, 320, 1748-1752.

³ J. Lee, M. C. Orilall, S. C. Warren, M. Kamperman, F. J. DiSalvo, U. Wiesner, *Direct Access to Thermally Stable and Highly Crystalline Mesoporous Transition Metal Oxides with Uniform Pores*, Nature Mater. **2008**, 7, 222-228.

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Synthesis and Functionalization of Ordered Macromolecular Architectures Using a Combination of RAFT Polymerization and Click Chemistry

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Reversible addition-fragmentation chain transfer (RAFT) polymerization is an extremely versatile technique of living radical polymerization that has proven itself tolerant to a range of functionalities.¹ Consequently, the range of macromolecular architectures accessible *via* RAFT lend themselves to ready post-polymerization modification using highly efficient click reactions.² We herein present the preparation and modification of such architectures, either by solvent-driven self-assembly or by solid-supported RAFT polymerization.

RAFT polymerization has proven useful in the synthesis of hydrophobic block co-polymers bearing “clickable” moieties. Post-polymerization functionalization of these materials with hydrophilic polymers allows us to access amphiphilic block copolymers, which are capable of self-assembly in aqueous conditions (Figure 1). Alternatively, anchoring the RAFT agent on a silica particle, allows us to graft polymers onto a solid support to obtain hybrid nanoparticles. Subsequent aminolysis of the RAFT agent then offers free thiols on the surface of the hybrid particles. The clickability of these thiols are demonstrated to induce further post-polymerization of the hybrid particles.

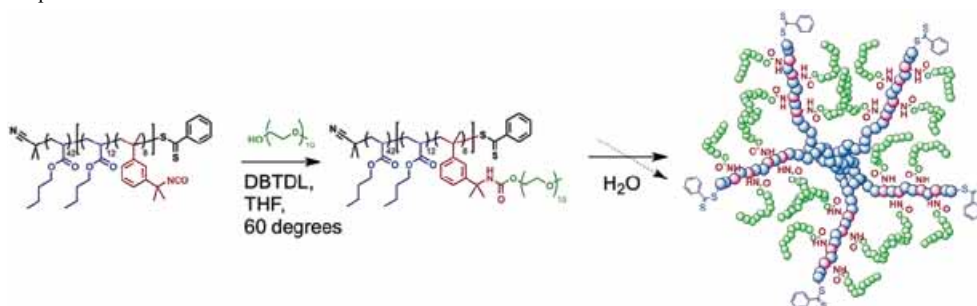


Figure 1. Click functionalization of a block copolymer followed by solvent-driven self-assembly.

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2. Barner L., Davis T. P., Stenzel M. H., Barner-Kowollik C., *Macromol. Rapid Comm.* **2007**, 28 (5), 539; Moraes J., Maschmeyer T., Perrier S., *Aust. J. Chem.* **2011**, 64(8) 1047-1053; Moraes J., Maschmeyer T., Perrier S., *J. Polym. Sci., Part A: Polym. Chem.* **2011**, 49 (13), 2771.

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Use of plasma polymerisation to facilitate new growth possibilities for surface-initiated polymerisation

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This presentation describes the use of plasma polymerisation to deposit polymer interlayers on substrates that allow for the growth of polymer chains from the surface with desired thickness and density. The technique is advantageous in eliminating substrate-specific linking chemistries providing for controlled radical polymerisation of different polymer chains from various substrate materials (inorganic and organic, hard and soft, and on substrates of complex geometry).

One barrier preventing wide-spread application of SI-ATRP (surface initiated atom transfer radical polymerisation) as a coating methodology is that surfaces must first be functionalised with ATRP initiators and this functionalisation depends upon complementary linking chemistries between the surface and initiator. Since different substrate materials present different potential anchoring groups, a universal method allowing the same ATRP brush coating on, for example, organic and inorganic substrates is lacking.

In this work plasma polymerisation approaches are presented allowing for controlled density and thickness graft coatings to be manufactured on different substrates using two approaches. First, plasma polymerisation was used to form a covalently attached surface-bound interlayer to which an ATRP macro-initiator was coupled. The macro-initiator is a novel polymer itself having a tunable and quantifiable composition of ATRP initiators. This allowed both low and high density polymer brushes to be grafted from surfaces. High density “brushes” of poly(poly(ethylene glycol) methyl ether methacrylate) (PEGMA475) showed a highly repulsive force profile when probed hydrodynamically with an AFM colloid probe. By contrast, polymer “mushrooms” were grown from the low density initiator. Good control of the graft thickness was also provided for by the nature of the ATRP mechanism and gave low-polydispersity chains. The end-grafted polymer chains presented an entropic barrier preventing protein adsorption compared to ungrafted surfaces. Here, the plasma-based, substrate independent coating methodology was advantageous because it allowed protein adsorption assays to be run in parallel in conventional soaking experiments as well as on QCM-D (quartz crystal microbalance with dissipation) sensors. This is an important insight because we observed that protein partitioning into polymer brushes is diminished (i.e. lower protein fouling) when evaluated by QCM-D because the polymer chains are stretched under the influence of flow. Conversely, using a classical static-equilibrium soaking experiment, we observed higher protein fouling because protein partitioning into polymer brushes occurs to a greater degree.

A second use of plasma polymerisation allowed one-step initiator functionalisation of surfaces. Using volatile, simple halogenated organic ATRP compounds, vapour was introduced in to the reaction chamber and plasma polymerisation was generated on substrates. The resulting surfaces possessed high amounts of immobilised halogen atoms. Significant retention of the parent compound’s structure in the plasma polymer resulted and this allowed surface-initiated ATRP to take place. We conclude by showing the utility of this approach in a moving-stage plasma reactor allowing for a continuously-varying concentration of ATRP initiators to be polymerised across the surface. This approach can be used to fabricate terminally-attached polymer chain gradient surfaces on any substrate.

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Simultaneous photoinduced silver nanoparticles formation and cationic polymerization of divinyl ethers

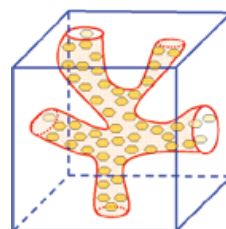
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We have recently developed ¹ a photo-induced mechanism for simultaneous photo-generation of radicals, reduction of silver ions by the radicals to the nano-metal particles and cationically polymerizing TEGDVE divinyl ether (Fig 1). This induced rapid photopolymerization (Fig 2) is very rapid and increases with increased concentration of benzoin ethyl ether (BEE). The formation of the nanoparticles can be monitored by the UV-vis plasmon absorption resonance near 410nm caused by the collective oscillation of the particle's electrons (Fig 3). In an attempt to control the morphology of the silver nano-particles (e.g. Scheme 1), we have performed the silver salt photo-reduction in a solution of polyvinyl acetate (PVAc) and TEGDVE. The plasmon resonance exhibits a dramatic increase during the polymerization reaction-induced phase separation (RIPS) of the PVAc from the crosslinking matrix (see Fig 4). Unfortunately no increase in the bulk electrical conductivity of the elastomer-thermoplastic-nanoparticle composite was observed.



Scheme 1 Schematic of directed nano-particle formation by RIPS

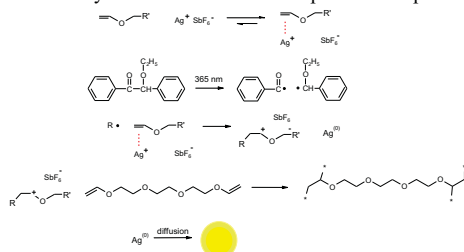


Fig 1 Proposed mechanism of simultaneous photo silver ion reduction and cationic polymerization of vinyl ether.

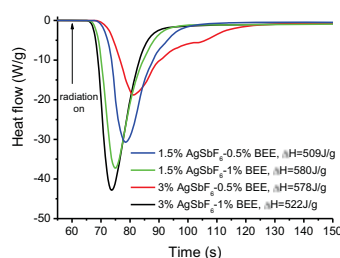


Fig 2 Photo-DSC of cure of TEGDVE monomer with varying amounts of initiator system.

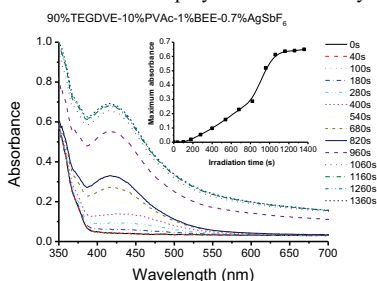


Fig 3 Development of Ag plasmon resonance during 365nm irradiation of TEGDVE/PVAc/BEE/AgSbF₆

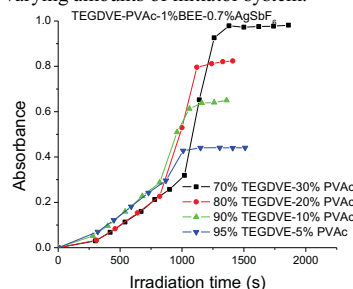


Fig 4 Ag plasmon resonance absorbance during 365nm irradiation of TEGDVE/PVAc/BEE/AgSbF₆

1. W D. Cook, Q D Nghiem, Q Chen, F Chen, M Sangermano: *Macromolecules*, **44**, 4065–4071 (2011)

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Photoclick chemistry for spatially and temporally functionalized materials

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To gain temporal and spatial control over materials functionalization, we have recently developed a range of phototriggered modular ligations applied to polymeric materials. Three different pathways were explored: (i) classic protecting group chemistry on thiols followed by thiol-ene chemistry, (ii) photoisomerization of *o*-methylphenyl aldehydes and ketones and subsequent Diels–Alder [4+2] cycloaddition, and (iii) photolysis of diaryl tetrazoles to nitrile imines reactive in 1,3-dipolar cycloadditions.

Firstly, the introduction of *o*-nitrobenzyl thioether moieties into polymeric chains was carried out, either at the chain terminus or in the repeating unit. In the latter case, novel monomers were synthesized and their polymerization was studied via conventional free-radical polymerization, ATRP, or RAFT-mediated polymerization.¹ As expected, it was observed that the *o*-nitrobenzyl groups disturb the radical polymerization process. Nevertheless, well-defined homo- and copolymers could be obtained. Subsequently, the masked thiol groups were released by UV irradiation and addressed by thiol-ene chemistry. Although a fully simultaneous process could not be achieved due to undesired parallel photoinduced reactions, a stepwise in-situ method was established to perform thiol-ene coupling on the non-purified deprotected polymers.

Secondly, *o*-methylphenyl aldehydes and ketones were introduced at the chain end of variable polymers by polymer analog modification or ATRP prepared macromolecules using a functional initiator.² Under UV irradiation, the photoreactive groups isomerize to *o*-quinodimethanes, i.e., dienes highly reactive in Diels–Alder cycloaddition. In presence of maleimide derivatives, Diels–Alder cycloadducts are quantitatively obtained within few minutes to few hours. Diblock copolymers could be produced by this method, as well as triblock copolymers using non-light activated Diels–Alder cycloaddition or orthogonal azide-alkyne cycloaddition in parallel. Furthermore, the method proved to be efficient for the precise patterning of (macro)molecules on surfaces.

Finally, macromolecules and surfaces were functionalized with diaryl tetrazoles. Under UV light, these compounds release molecular nitrogen to yield reactive nitrile imine intermediates. In presence of alkenes (maleimides, (meth)acrylates, non-activated enes), these species rapidly undergo a 1,3-dipolar cycloaddition to form stable and highly fluorescent pyrazoline linkages. Within minutes, block copolymers can be obtained from homopolymer precursors.³ This route was also employed to graft polymethacrylates onto silicon or cellulose substrates. In particular, this method provided an easy access route to surface patterning (Fig. 1).



Figure 1. Pattern of PMMA on cellulose obtained by light-induced 1,3-dipolar cycloaddition

¹ T. Paulöhr, G. Delaittre, M. Bastmeyer, C. Barner-Kowollik, *Polym Chem.* **2011**, submitted; G. Delaittre, T. Paulöhr, M. Bastmeyer, C. Barner-Kowollik, *in preparation*.

² T. Gründling, K. K. Öhlenschläger, E. Frick, M. Glassner, C. Schmid, C. Barner-Kowollik, *Macromol. Rapid Commun.* **2011**, *32*, 807.; M. Glassner, K. K. Öhlenschläger, T. Gründling, C. Barner-Kowollik, *Macromolecules* **2011**, *44*, 4681.

³ M. Dietrich, G. Delaittre, J. P. Blinco, A. J. Inglis, M. Bruns, C. Barner-Kowollik, *Adv. Funct. Mat.* **2011**, submitted.

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Interactions of Charged Block Copolymers with Surfaces: a Tunable Roughness

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Today's integrated circuits (IC) have features sizes as small as 32 nm and this will continue to decrease into the future. ICs are generally produced by optical lithography, which is a process that relies on photo-generated acids catalyzing a cascade of chemical reactions in a polymer film that allows selective removal of areas exposed to light, leaving behind the desired features.¹ However, these features always inherit some roughness. Nanoscale surface roughness has become a key factor in determining the performance and reliability of ICs and also in dictating the adhesion of surfaces, which is crucial for applications in micro/nanoelectro mechanical systems (M/NEMS) and biomaterials.

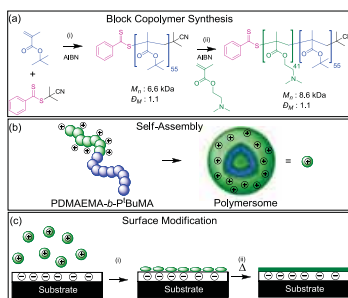


Fig.1. (a) Synthesis of PtBuMA-*b*-PDMAEMA using RAFT (b) Self assembly to vesicles (c) Schematic representation of the reduction of roughness through surface modification and annealing

In our approach to reduce nanoscale surface roughness, we adopt a bottom-up process driven by electrostatic forces that involves surface modification with polymeric vesicles. The side-walls of patterned features prepared from conventional photoresists inherits a negative charge as a result of the deprotection reaction,¹ so for this application we have prepared positively-charged polymeric vesicles. Here we used poly(dimethylaminoethyl methacrylate)-*block*-poly(*t*-butyl methacrylate) prepared by RAFT polymerization (Fig 1(a)) as the building block for the vesicles. To gain an understanding of the process, the polymersomes formed from these polymers were deposited onto negatively-charged flat surfaces through electrostatic attraction followed by annealing. (Fig 1(c)). An AFM image of the flat substrate is shown in Figure 2(a). The adhesion of the polymersomes on that surface initially roughened the surface (Fig 2(b)), while by annealing the surfaces, the surface roughness decreased (Fig 2(c)), where it was observed that the roughness could be tuned as a function of temperature. A similar outcome was also obtained by applying the same treatment to rough surfaces. However, in this case it was possible to significantly decrease the degree of roughness. The ability to decrease surface roughness is likely to have a significant impact on processes used in the manufacture of integrated circuits, while the ability to tune the roughness of surfaces may find uses in M/NEMS and microfluidic applications.

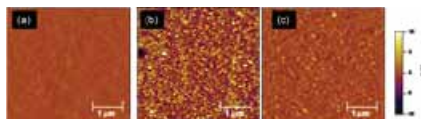


Fig.2. AFM images showing (a) the unmodified substrate, (b) after deposition of vesicles and (c) after annealing of the treated surface

¹ J.H.Hah; S.Mayya,S.; M. Hata; Y.K. Jang,; *J.Vac.Sci.Technol.,B*, **2006**, 24, 2209-2213

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Carbon nanotube strain sensors for paint degradation monitoring

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Paints play a pivotal role in preventing corrosion of structures by providing a barrier to moisture, oxygen and salts. Loss of barrier properties due to paint degradation leads to corrosion of underlying metallic structures, which can ultimately cause structural failure. Understanding and predicting paint degradation is therefore key to corrosion prevention.

The loss of paint properties during degradation may arise from polymer chain scission or embrittlement due to further crosslinking reactions. These processes alter the Glass Transition Temperature (T_g), leading to shrinkage at the paint surface. This localised shrinkage can result in micro-crack formation and loss of paint barrier properties. During shrinkage, changes in paint strain occur. Recording this paint strain change as a function of paint age is one possible method for determining paint health, with the development of sensitive, paint-compatible strain sensors being an important step toward the implementation of this methodology.

Carbon nanotube strain sensors may be suitable for such applications, where high strain sensitivity is desirable, as they have shown greater strain sensitivity than conventional sensors.¹ Further to this; carbon nanotube strain sensors can be prepared in paint-compatible materials such as epoxy resins, making them even more desirable for paint-related applications.

Here, we will describe the development of carbon nanotube/polymer composite strain sensors with suitable properties for application as paint degradation monitors. The chemistry of these sensors will be discussed and their characterisation by infrared and Raman spectroscopies will be described. The relationship between strain sensing and sensor chemistry as well as their ultimate application as strain sensors during paint degradation will be assessed.

The authors acknowledge the financial support of DSTO, Melbourne.

¹ N. Hu, Y. Karube, M. Arai, T. Watanabe, C. Yan, Y. Li, Y. Liu, H. Fukunaga, *Carbon* **2010**, 48, 680-687

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New Fluorescent Nanocomposites for Fingerprint Detection

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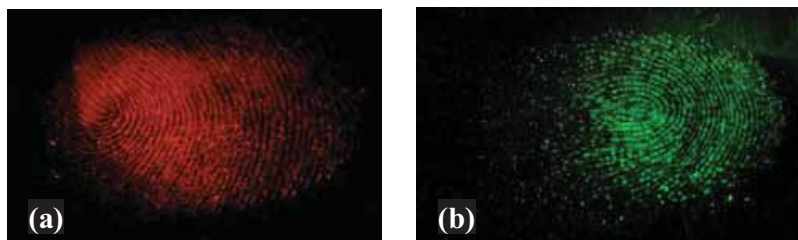
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In recent years Reverse Addition Fragmentation Chain Transfer (RAFT) polymerisation has emerged as an attractive method for polymer synthesis, providing control of molecular weight and molecular weight distributions with narrow polydispersity indexes¹. There has also been a unique twist in fingerprint research which has involved the implementation of nanotechnology into the function of novel fluorescent fingerprint reagents, based on Quantum Dots (QDs)². QDs are semi-conducting nanostructures that possess unique intrinsic luminescent properties that are size dependent at the nanoscale³. Here we combine advantages of RAFT polymerisation with nanotechnology using QDs in the synthesis of fluorescent nanocomposites for fingerprint detection. The polymeric surface modifications provide stability and solubility of the QDs. QDs investigated in this study were Cadmium Sulphide (CdS) and Carbon QDs in various polymers, in particular, polydimethylacrylamide (PDMA) based polymers. The polymers also play a role in the adherence to latent fingerprints (produced by sweat excretions on the palmer of the hand).

Size tuneable CdS QDs capped with 2-mercaptoethanol were first synthesised, with the appropriate amounts of sodium sulphide and cadmium chloride in DMF. The 2-mercaptoethanol on the surface of CdS was coupled, with an ester link, to a C12-carboxyl-terminated RAFT agent. From then RAFT polymerisation of a chosen monomer was performed via a grafting-from mechanism. Similar chemistry was applied to Carbon QDs; synthesised via acid treatment of activated carbon. Fingerprint subjects were prepared by depositing fingerprints onto non-porous surfaces such as glass, and aluminum foil. Aqueous solutions and powder-form of each nanocomposite (CdS/Polymer and Carbon QDs/Polymer) were applied onto the fingerprint substrate. Fluorescently developed fingerprints by these nanocomposites were visualised and photographed under UV light, using lens filters (Fig. 1).

Figure 1. Latent Fingermarks deposited on Aluminium Foil, developed by (a) CdS/P(DMA-co-Sty) and (b) CdS/P(DMA-co-MMA) powders. Using the appropriate lens filters; 610 ± 40 nm and 555 ± 24 nm, respectively.



¹ Moad, G., Y.K. Chong, A. Postma, E. Rizzardo, and S.H. Thang, Advances in RAFT Polymerization: the synthesis of polymers with defined end-groups. *Polymer* **2005**, 46(19), p. 8458-8468..

² Dilag, J.; Kobus, H.; Ellis, A. V., Nanotechnology as a New Tool for Fingerprint Detection: A review, *Current Nanoscience*, **2011**, 7, p. 153-159

³ Jorge, P.; Martins, M. A.; Trindade, T.; Santos, J. L.; Farahi, F., Optical Fiber Sensing Using Quantum Dots, *Sensors* **2007**, 7, p. 3489-3534.

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Personal History

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Acid-Bearing Polymer Membranes for PEM Fuel Cells

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This presentation is intended to highlight structure-property relationships that lead to a better understanding of proton conducting polymers. This necessarily requires the undertaking of rigorous, systematic studies of representative materials that possess known and controllable structures and morphologies. Proton conductivity and related properties of solid polymer electrolytes possessing unique variations in ionic phase segregation networks will be described. Emphasis is placed on obtaining an understanding of the physical processes that give rise to proton conductivity. In this presentation the synthesis and properties of series of novel ionic copolymers of controlled structure will be described. Emphasis will be placed on controlling the crystallinity of the polymers and its role on influencing ionic cluster size, water sorption, and proton conductivity. The effect of introducing organized ionic networks on the anisotropy of proton conductivity will also be discussed and comparisons of graft versus block copolymer systems will be drawn using model polymer systems.

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Personal History

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Research interests: Design, synthesis and implementation of functional polymers and polymeric microstructures for electronic and electrochemical applications: electrochemistry; electrocatalysis; design, synthesis and characterization of ion conducting polymers; fuel cells. Organic photovoltaics. Nanostructured morphologies of functional polymers



Polymer nanocomposites: is it worth the effort?*Theo J. Dingemans¹, Maruti Hegde¹, Y. Si², Edward T. Samulski²*¹Delft University of Technology, Faculty of Aerospace Engineering, Kluyverweg 1, 2629 HS Delft, The Netherlands²University of North Carolina at Chapel Hill, Department of Chemistry CB#3290, Chapel Hill, NC 27599-3290 (USA)

Single-walled Carbon Nanotubes (SWCNTs) are under investigation as one-dimensional (1-D) reinforcing nanofillers in a wide variety of polymers.[1] In an attempt to explore highly aligned polymer-SWCNT nanocomposites we have dispersed SWCNTs in an all-aromatic thermotropic liquid crystal polyetherimide (PEI) matrix. The mesomorphic nature of the matrix is expected to enable the formation of highly aligned films and fibers by stretching the nanocomposites in the liquid crystalline (LC) state.[2] Dispersion by *in-situ* polymerisation in the presence of aromatic diamine precursor, along with sonication, enabled us to prepare polymer nanocomposites with high SWCNT loadings of up to 6.0 vol%.[3] Optical microscopy, scanning electron microscopy, and dynamic light scattering were employed to analyze the bundle size and the uniformity of the dispersion in the fully imidized LC matrix at different length scales. The storage modulus increased by a factor of 2.5, *i.e.* from 3.2 GPa to 8 GPa and this modulus could be increased to 14 GPa for an aligned LC film at 2.4 vol% SWCNT loading. The glass-transition temperature (T_g) increased from 209 °C for the neat polymer, to 229 °C for the 2.4 vol% modification, which is an increase of 20 °C. DSC measurements also showed that the presence of SWCNT induced crystallinity in the polymer matrix and the degree of crystallinity was found to be proportional to the SWCNT concentration. In order to understand which factors govern polymer crystallization we prepared carbon nanocomposites based on C60 (0-D) and graphene (2-D). In the case of C60 the polymer is exposed to a strained all- sp^2 carbon surface whereas in the case of graphene the polymer is exposed to both sides of the sp^2 carbon network. Both C60 and graphene induce crystallization in BPDA-P3 and a direct correlation was found between surface area and degree of crystallinity. The graphene-based composites are highly crystalline (>60%), extremely brittle and therefore difficult to handle. The SWCNT nanocomposites (2.4 vol% loading) on the other hand show a tensile strength of 208 MPa and a strain of 8%. The neat polymer shows a tensile strength of 90 MPa and a strain of 80%.

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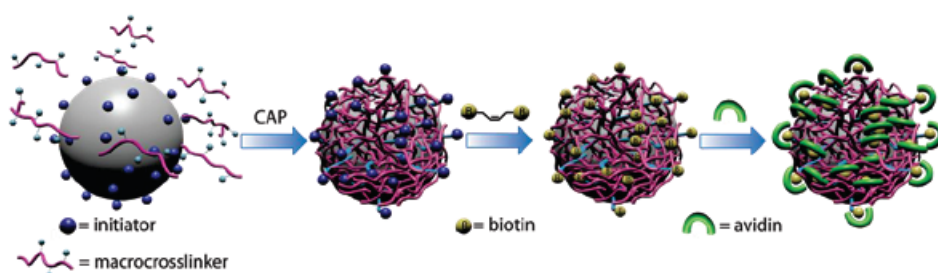
Continuous Assembly of Polymers (CAP): A Versatile Approach for Surface-Driven Nanocoatings

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Nanoscale polymeric films and interfaces are integral to a wide range of advanced materials and emerging nanotechnologies. Continuous assembly of polymers (CAP) is a novel nanoengineering strategy that utilizes surface-initiated controlled polymerization in the “bottom up” single-step assembly of macrocrosslinker (macromolecules with pendent polymerizable moieties) onto surfaces with simultaneous control over internal functionality and film thickness.¹ This approach combines the advantages of current fabrication strategies including polymer grafting² and layer-by-layer,³ by providing excellent compositional flexibility, direct cross-linking and fine control over film parameters. The simplicity of preparing thin films with a broad range of polymer precursors makes this system attractive for many applications such as biomaterials⁴ and chromatography stationary phases.⁵

In this study, we demonstrate the versatility of the CAP approach via ring-opening metathesis polymerization (ROMP), where fine control over film thickness can be obtained with polymerization time. The ability of this strategy to engineer coating composition and surface functionality of the CAP films will be presented and discussed. These features allow for the preparation of materials for advanced bio-functionalization as shown in **Scheme 1**, using biotin-avidin interaction.



Scheme 1. CAP film formation and surface bio-functionalization.

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Structure/Property Relationships in Sulphur containing Epoxy Resins for High Performance Applications.

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The advent of the Boeing 787 Dreamliner is revolutionising the use of composite materials for primary structural applications in commercial aircraft. The reduction in weight caused by the increase in composite materials has a profound effect upon the weight of the aircraft and therefore fuel consumption. Along with the large improvement in environmental impact, composite materials provide new challenges in the area of processing and final properties. Composite materials for primary structural applications in aircraft are typically based upon epoxy amine resin systems which are known to lack toughness, but more importantly have low distortional von Mises strain (yield strain). Molecular dynamic computational predictions have indicated that if new resin systems with enhanced von Mises strain can be produced, an entirely new generation of composite components with enhanced performance at reduced weight can be introduced into these aircraft. Unfortunately, polymer matrices with enhanced von Mises strain tend to have poor solvent resistance, so the search for matrix resins with an optimum balance of solvent resistance and von Mises strain is required.

Sulphur containing epoxy resins are a new approach to this, combining their advantageous solvent resistance, (as evidenced by their use as fuel tank sealants), with the excellent mechanical properties afforded by largely aromatic epoxy resins. To explore this further, two sulphur based epoxy resins, analogous to the traditional epoxy resin, diglycidyl ether of bis-phenol A (DGEBA), have been synthesised and are shown in Figure 1 and compared with DGEBA. As can be seen, in one example, the glycidyl ether linkages are replaced with two sulphurs (DGTEBA) while in the other the iso-propylidene group is replaced with a single sulphur element (DGETD).

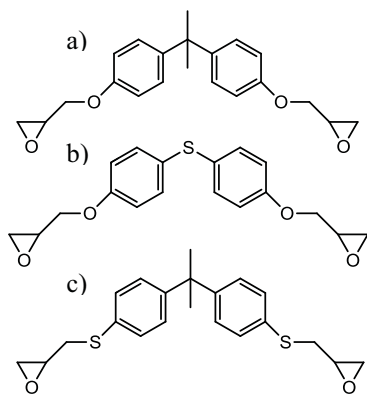


Figure 1. Epoxy resins used in this study, a) DGEBA, b) DGETD, c) DGTEBA

The study will present a comprehensive investigation of the structure/property relationships of these three epoxy resins during and after cure with 4, 4, di-amino di-phenyl sulphone (4,4 DDS), focusing upon cure kinetics, mechanical properties, fluid (MEK) resistance and thermal resistance. The positional changes of the sulphur on the epoxy monomer have enabled important new insights into the structure/property relationships of epoxy resin systems. The impact of the location of the sulphur species has been shown to play a critical role in determining properties and their usefulness in aerospace applications. An example of this is the large reduction in glass transition temperature and thermal stability caused by the thio-ether linkages compared with the di-phenyl sulphur. The sulphur atom is much larger and less electronegative than oxygen and therefore would be expected to significantly impact network properties. In addition to this, the DGETD resin significantly reduced the level of MEK absorption compared with DGEBA while having similar mechanical and thermal properties warranting further investigation as a candidate resin system.

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Synthesis of Core Cross-linked Star (CCS) Polypseudorotaxane *via* Inclusion Complexation of CCS PCL Polymers and α -Cyclodextrins

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In 1990, Harada *et al.*^[1] firstly demonstrated the formation of polypseudorotaxane - a supramolecular complex consisted of cyclodextrins (CDs) as the host and a linear polymer as the guest molecule. Various types of polypseudorotaxanes with novel supramolecular architectures provide a diverse spectrum of potential applications in drug delivery,^[3] gene delivery^[4] and tissue engineering.^[5] However, to our knowledge there has been no study dealing with synthesis of core cross-linked star (CCS) polypseudorotaxanes *via* inclusion complexation of CCS polymers and CDs. Furthermore, little investigation has been done on the morphologic change of the guest macromolecules before and after the formation of inclusion complexes with CD host molecules.

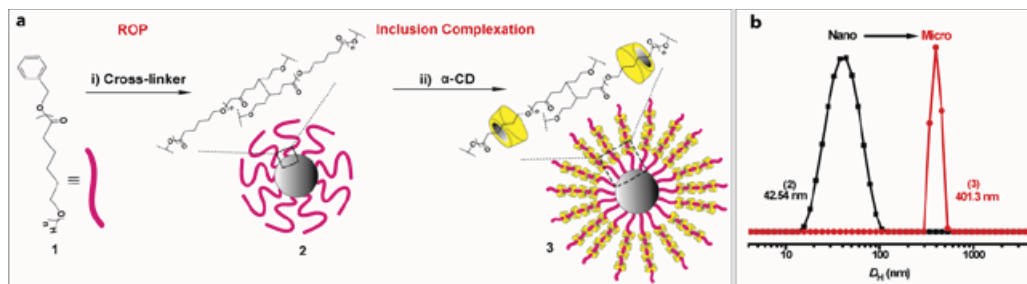


Figure 1. Synthesis of core cross-linked star (CCS) polypseudorotaxane (a) and volume-average hydrodynamic diameter distribution of CCS PCL polymer and CCS polypseudorotaxane (b).

In this study, an improved star formation *via* arm-first approach, through ring-opening polymerization (ROP) of 4,4'-bioxepanyl-7,7'-dione (BOD) as a cross-linker with poly(ϵ -caprolactone) (PCL) macroinitiator (**1** in **Figure 1a**) and methanesulfonic acid as catalyst was achieved. A series of CCS PCL polymers were then synthesized with different side-chain lengths with conversions of macroinitiators close to 95 %. The obtained CCS PCL polymers (**2** in **Figure 1a**) were subsequently used directly without further purification to form inclusion complexation with α -CDs, affording the novel CCS polypseudorotaxanes (**3** in **Figure 1a**). These polypseudorotaxanes were characterized by ¹H-NMR, 2D ROSEY NMR and XRD. The thermal properties of the CCS polypseudorotaxanes were further investigated *via* TGA and DSC. The DLS analysis revealed a dramatic morphologic change of CCS PCL polymers before and after the formation of inclusion complexes, with the hydrodynamic diameters of the CCS polypseudorotaxane increased approximately 10 times (**Figure 1b**).

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Functionalization of Well-Defined Star Polymers Built from Biodegradable Microgel/Nanogel Cores via Click Chemistry

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The design of star/hyperbranched polymers and nanogels has attracted recent interests, especially since the development of controlled/living radical polymerisation (C/LRP) techniques. Star (and related) architectures can be applied to a large range of applications, ranging from engine oils, to coatings and drug delivery systems. Star polymers have previously been synthesized by all three principal LRP techniques (ATRP, RAFT and NMP) by either growing a linear polymer chain and adding a cross-linking agent (arm first, microgel (nanogel) cores), or by synthesising a multifunctional initiator and growing the arms from this initiator (core first) or by attaching arms onto a core.^{1,2} The core first strategy requires several preparation steps, whereas, in contrast, the arm first strategy offers an easier route to functional stars. Microgels (or nanogels) can be designed with functional groups and with potential for biodegradability. Descriptions of the synthesis of star polymers using an arm first methodology via RAFT polymerization are relatively rare. Typically, the star obtained by RAFT presents a high PDI (>1.5) with low incorporation of arms. Recently, we have optimized the star synthesis to yield star with a low PDI (<1.10).³

In this talk, we exploit this technology to obtain a library of functional and biodegradable star. The synthesis of biodegradable stars was achieved by chain extension of alkyne or alkene terminated poly(OEG-A) polymers in the presence of different biodegradable cross-linkers (containing a ketal and disulfide group) and functional monomers, e.g. pentafluorophenyl acrylate. In subsequent work, the alkyne group was modified via thiol-yne or azide-alkyne click chemistry to introduce functional groups, such as peptide and folic acid (**Figure 1**). The core was finally exploited to encapsulate and to attach drugs using biodegradable linker. The star polymers were characterized by DLS, TEM and NMR. The functional star polymers do not show any toxicity (until 10 mg/mL for 3T3 cell line) and can release therapeutic agents.

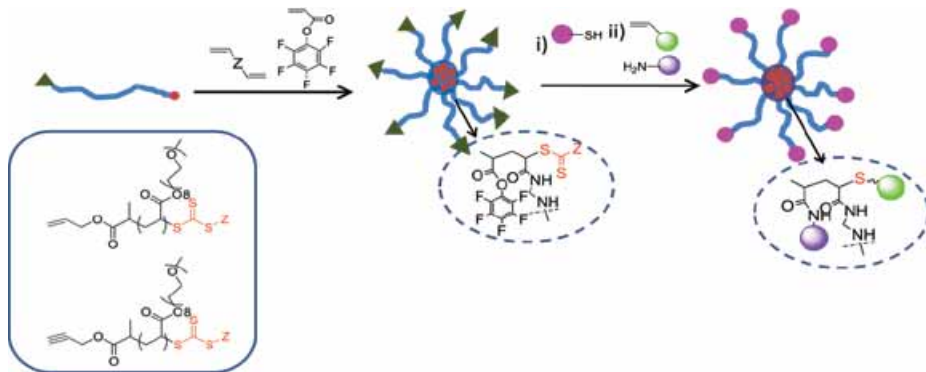


Figure 1. General scheme for the synthesis and functionalization of the star polymers obtained in this study.

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Effect of Lateral Fluorine Substituent on Mesophase behavior of Bent-shaped Molecules with Asymmetric Central Naphthalene Core

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Bent-shaped liquid crystals have attracted considerable attention over the past few years since its first discovery by Watanabe et al in 1996. Generally, a bent-shaped molecule consists of three parts: the angular central core, side arms and terminal chains. Outstanding works where modifications on different parts of the molecule have been analyzed and reported. It is of particular interest to note that the introduction of a fluorine atom to the external phenyl ring has a great effect on the mesomorphic behavior in molecules based on symmetric central core such as 1,3-benzene or 2,7-naphthalene unit. However, the effect of the lateral fluorine substituent on mesomorphic behaviors of bent-shaped molecules with asymmetric central core has been rarely reported.

Thus, we have synthesized bent-shape molecules with asymmetric central core based on 1,7- or 1,6-naphthalene units and side arms containing Schiff base moieties, designated as N(1,7)-F12 and N(1,6)-F12 (Scheme 1). For molecules based on 1,7-naphthalene unit with an acute-angle, the presence of the electron-withdrawing group leads to form a specific hexagonal columnar phase and a dark B4 phase. The column phase has a hexagonal lattice with edges of 66.9 Å and exhibits polar switching with spontaneous polarization along the column axis. By assuming a density of $\rho = 1 \text{ g cm}^{-3}$ and a height of the columnar slice of $h = 4.5 \text{ Å}$, the number of molecules calculated in each column slice is about 10~11. A tube-like assembly of molecules and cylindrically symmetric deformation of layers were assumed. The alkyl tails of molecules are protruding outside of the column wall and inside of the enclosed mesogenic layer respectively.

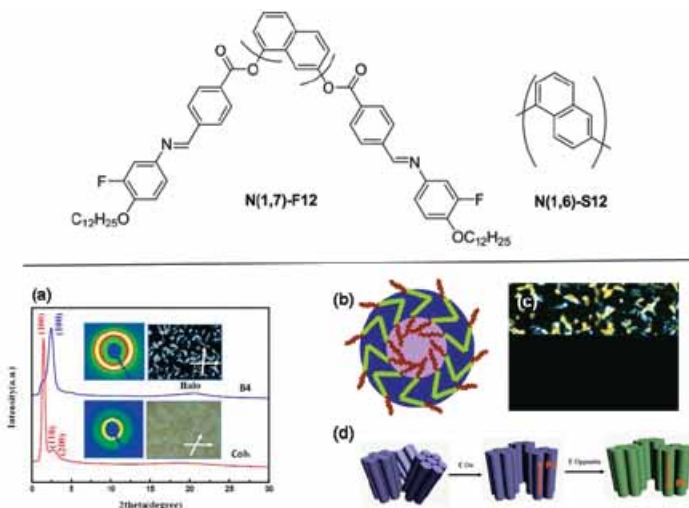


Figure 1. (a) X-ray diffractions and microphotographs observed in N(1,7)-F12, (b) molecular assembly in the cross section of one column slice, (c) switching behavior of N(1,7)-F12 (135°C, 400Vpp, 30 Hz), the upper part is the fan texture of Col_h phase exhibited in cell area without electrode part, the downer part is the dark texture under electric field, (d) switching model

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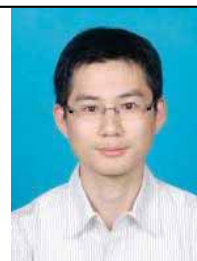
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Stimulus-Responsive Polymers Interfaced with Porous Semiconductors

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Stimulus-responsive polymers are synthetic macromolecules that undergo changes in their properties in response to a defined external stimulus¹. The responsiveness of these systems is being exploited for manifold applications in life sciences such as controlled drug release², cell and tissue culture³, actuators, and sensors⁴. Interfacing stimulus-responsive polymers with nanostructured materials such as porous semiconductors allows the construction of novel functional materials. Our research efforts in grafting temperature and pH stimulus-responsive polymer brushes from porous semiconductor surfaces and in fabricating stimulus-sensitive hydrogels filling the pores will be reviewed here (**Figure 1A**). The talk will also highlight recent developments in our laboratory in terms of applying these hybrid materials in drug delivery for wound healing (**Figure 1B**) and biosensors of wound healing status.

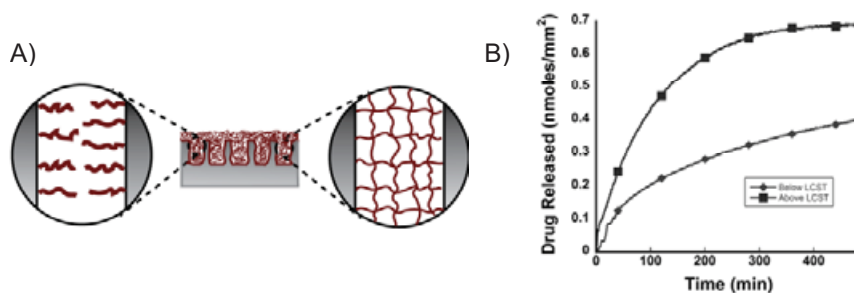


Figure 1: Schematic illustration of polymer chains grafted from porous silicon membrane (left) and crosslinked hydrogels within porous silicon membrane (right); B) camptothecin release from porous silicon membrane coated with poly(N-isopropylacrylamide) brushes above (□) and below (○) the LCST.

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Synthesis and Characterization of Thiophene Polymer Brushes

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Conjugated polymers have been receiving a large amount of interest recently due to their interesting conductive properties and applications in organic electronics, including organic photovoltaic cells. However, since these polymers conduct along the chain¹, the bulk electrical properties and performance of the devices they are used in are limited by polymer conformation. Therefore our research aims at aligning the polymers perpendicular to the electrodes via chemical attachment which should reduce the resistance and improve efficiency.

Polythiophenes are a particularly useful class of conjugated polymers as they are soluble and have good electrical properties. The Kumada Catalyst-Transfer Polycondensation reaction has been used by various groups to produce moderate molecular weight, regioregular and low polydispersity poly(3-hexylthiophene).^{2,3} This approach is also applicable to the formation of brushes through a grafting-from approach.⁴

We have successfully synthesised P3HT using a variety of initiators with differing functional groups to find an optimal initiating and attachment group in solution as a control. The nature of the initiator was also investigated; in particular whether it is necessary to include an aromatic-halide bond for catalyst insertion and whether any control is maintained throughout the polymerisation. Preliminary results using benzyl bromide as an initiator have produced moderate molecular weight P3HT. Further investigation and optimization are necessary for determination of control.

Polymer brushes have also been created using a various nickel catalysts formed through an oxyphenyl bromide initiator. X-ray photoelectron spectroscopy analysis shows sulphur present and atomic force microscopy images show structures of up to 150nm high with a high density.

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Recent Development of Charge Transport Materials and Donor Materials for Organic Solar Cells

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Organic solar cells (OPV) are now attracting wide interests both in academic and industry because of its potential low cost for green energy from the Sun.¹ A typical OPV includes an active layer sandwiched between two electrodes. Light irradiates through a transparency ITO electrode and photo-induced electron transfer takes place in the active layer from conjugated polymer (donor) to fullerene derivative (acceptor), the charges dissociate at the donor-acceptor interface and move to the respective electrodes, i.e. the hole moves to ITO anode and electron moves to the aluminum cathode. One of the most extensive studied areas at present is the donor materials. The state-of-art solar cells based on organic conjugated materials with fullerene blends reach a power conversion efficiency of 8.3 % from photon to electricity.² With a ternary blend consisting of one extra donor, we got a power conversion efficiency of 3.0 % with more broad photo-responses, an average value of the two individual donor-acceptor binary blends. This is useful for making tandem cells where multi-cells can be made together to absorb broad light and deliver higher current.

For high efficient solar cells, the donor materials need to have high mobility, low bandgap, suitable energy levels and solubility that are compatible with the acceptors. We will report our progress on a series of novel donor polymer based on dithienopyrrole by tuning the energy level and bandgaps in order to get higher open circuit voltage and higher efficiency in the OPV devices.

While most people work on new materials for photoactive layer, there are problems associated with interfaces. Between active layer and the cathode aluminium, people insert an electron collection/transport layer recently. One of the promising electron transport materials is conjugated polymer electrolytes (CPE), which was originally discovered in the area of polymer light emitting diodes.³ It is now applied not only to organic light emitting diodes and organic field effect transistors but also to OPVs for the improvement of the power conversion efficiency very recently. With this layer in between the active layer and cathode, no reactive metals such as Ca, Ba and Mg are needed and inert cathodes such as Cu, Al, Ag and Au could be used for printable organic electronics. The mechanism of the CPE in PLED operation are not well understood yet, but it is believed that the charge redistribution contributes to the reduced electron injection barrier between cathode and light-emitting materials, along with the dipole moment formed at the interface. Recently we developed some novel electron collection materials and we will report their application in OPV devices and the mechanism behind for the improvement of the OPV performance.

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Influences of Functional Groups on the Orientation Birefringence of Uniaxially Drawn Cellulose Ester Films

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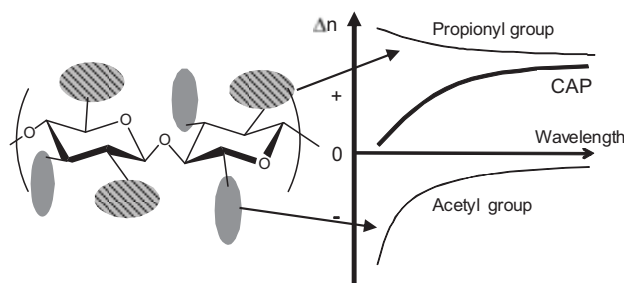
The growing interest in sustainable materials has motivated studies on cellulose-based materials for various applications. In particular, cellulose ester films have been actively studied as optical films such as protective films and retardation films in liquid crystal display (LCD) assembly.¹ For such applications, it is necessary for the materials to show birefringence that is suitable for different roles in LCD assembly. For example, films showing extraordinary wavelength dispersion, i.e., the absolute value of birefringence increases with increasing wavelength, are needed for retardation films.²

In this study, the wavelength dispersion of orientation birefringence for hot-drawn films of various celluloses esters such as cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and cellulose triacetate (CTA) are studied. Hot drawings are performed at a temperature where the tensile storage modulus is 10 MPa at 10 Hz which is determined from their respective dynamic mechanical analysis results. CABs having different degrees of substitution are used to investigate the effect of the ester group content on orientation birefringence.

CAP and CAB show positive orientation birefringence that increases with increasing wavelength while CTA shows negative birefringence that decreases with increasing wavelength. Infrared dichroic measurements suggest that the orientation birefringence of cellulose esters is not proportional to the orientation function, indicating that the orientation of the main chains is not responsible for the orientation birefringence. Moreover, orientation birefringence is also found to increase with increasing butyryl content. Acetyl group contributes to polarizability anisotropy perpendicular to the stretching direction as reflected by the negative value of birefringence in CTA.

On the other hand, propionyl and butyryl groups contribute to polarizability anisotropy parallel to the stretching direction as demonstrated by their positive orientation birefringence. The summation of the birefringence arising from the acetyl group and that from propionyl or butyryl groups results in the extraordinary wavelength dispersion, due to the combination of strong wavelength dependence of the acetyl group with weak wavelength dependence of the propionyl or butyryl groups as shown in **Fig. 1** below.

Figure 1. Schematic illustration of contributions of polarizability anisotropy of acetyl and propionyl groups that produce the extraordinary wavelength dispersion of CAP



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Linear expansion of electrochemically actuating gels

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Conducting polymers have been used extensively in actuating systems. However, due to the low strains found they have been typically employed in bending modes. Gels offer the possibility of large volume changes, but to date they have not been easy to address electrically. They also expand isotropically, which is less useful for actuation. We have incorporated a series of electroactive monomers, including ferrocene and quinones, into gels (Figure 1). These units can be oxidized or reduced, resulting in passage of counterions to and from the gel which controls the expansion.

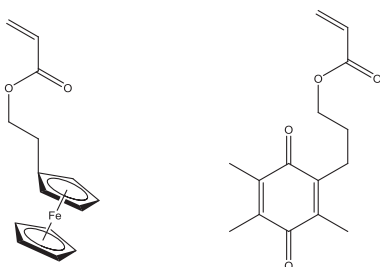


Figure 1. Typical ferrocene and quinone monomers used for gel construction

Larger bulk samples of the gels were too insulating to electrochemically switch, so carbon nanotubes were incorporated which increased the conductivity by several orders of magnitude. A spring electrode was incorporated, which biased the mechanical response and produced linear actuation of up to 50% (Figure 2). In this way, the redox state and the expansion of the gel could be cycled scores of times without degradation. The gel was also capable of real force, with a 0.15 g sample being able to lift 50 g reversibly.

Many challenges lie ahead, including decreasing the response time (30 minutes to 1 h), and encapsulating the device. However we hope that this concept may prove useful in real devices such as a lab on a chip or drug release.

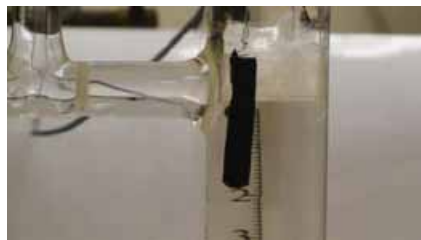
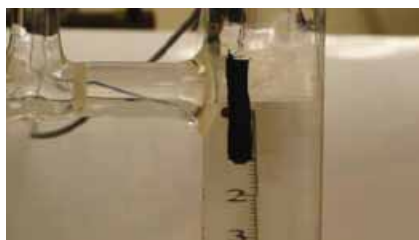


Figure 2. Expansion of the gel (black) after reduction at -1.0 V.

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Bacterial Cellulose Electro Active Polymer for Biomimetic Robot

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Electro active polymer changes the size and shape by electrical stimulus. Among the various polymers, cellulose is most abundant all of the earth. Especially, several bacteria are produced the cellulose that is bacterial cellulose¹. In this research, electro active bacterial cellulose actuator was developed using freeze dried bacterial cellulose membrane. The bacterial cellulose actuator was fabricated by very simple dipping and drying method. The freeze dried bacterial cellulose was immersed in the ionic liquid and conducting polymer as PEDOT:PSS solution. Ionic liquid was used to increase the performance of actuator and PEDOT:PSS was used for the electrode instead of the gold electrode². The FT-IR was conducted to confirm the electrochemical change that the bacterial cellulose has native cellulose I crystal structures³ but it was transformed into amorphous of cellulose II structures after ionic liquid treatment⁴. And the XRD was conducted to investigate the variations of crystallinity index⁵. The crystallinity index was decreased by ionic liquid treatment and the TGA was conducted for thermal analysis. Besides, the step and harmonic response were measured to confirm actuation performance of developed bacterial cellulose actuator. Developed actuator was improved the performance almost five times than previous reported bacterial cellulose actuator⁶. Through the actuation performance test, the developed bacterial cellulose actuator was expected to use the actuator for biomimetic robots.

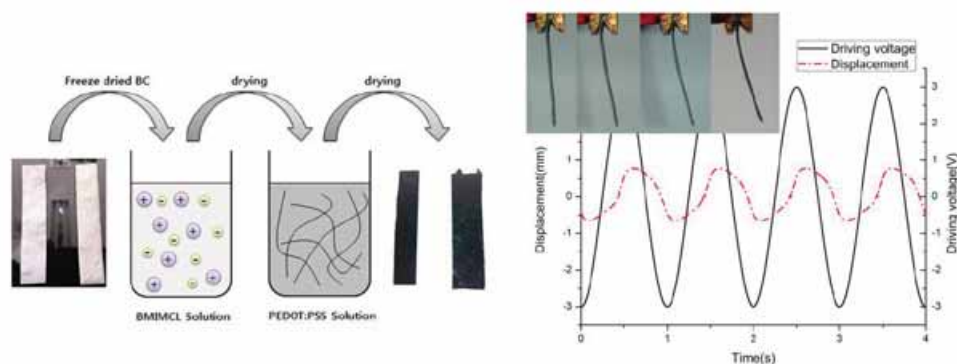


Figure 1. Fabrication method and performance of bacterial cellulose actuator

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Self-assembled Electrically Active Multilayers for the Functionalization of 2D and 3D Neural Scaffolds

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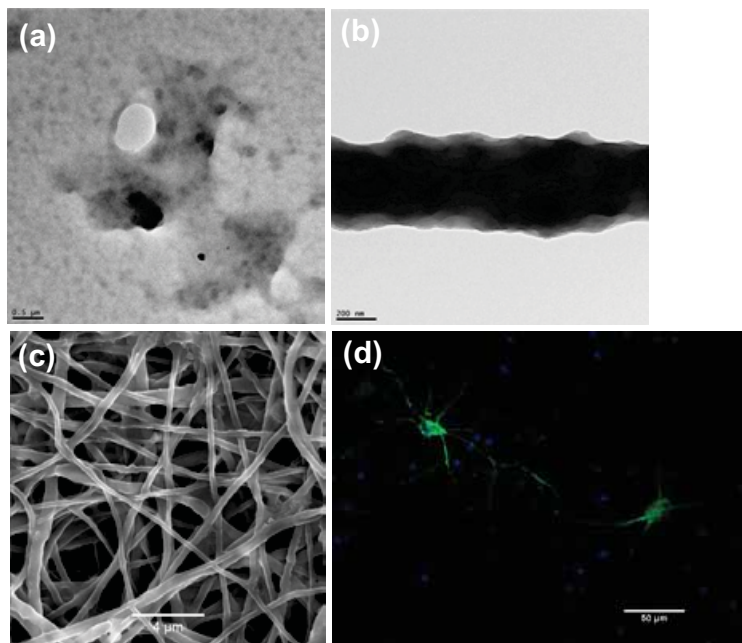
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Electrical conductive polymer composites play an important role in various fields. One example is signal recording and stimulation in tissue engineering. Layer-by-Layer (LbL) self-assembled conductive multilayers shows a versatile approach to functionalize devices with complex geometry with nanometer scale precision.

In the current work, nanosized colloidal graphene/heparin mixture and poly-L-lysine were used as polyanions and polycations respectively for LbL deposition onto 2D surfaces and 3D electrospun polycaprolactone nanofibres. Utilising this strategy, an electrical active multilayer coating with a thickness of a couple hundred nanometers was achieved on both 2D surface and nanofibres. The surface chemistry of PEMs after each LbL deposition process under various conditions was characterized by water contact angle measurements, showing an alternating step change in contact angle values, which reflected the new polyelectrolyte adsorption. The dispersion of graphene in the PEMs (Figure 1a, b) and surface morphology (Figure 1c) of graphene-LbL functionalized surface/nanofibres was characterized by SEM and TEM. By varying the size and concentration of the colloidal graphene, a range of conductivities of up to 3.5 S/cm was obtained on these scaffolds. Biocompatibility was tested by culturing E14 cortical neurons on these functionalized surfaces for up to 1 month, and the resulting immunostaining images (Figure 1d) showed no cytotoxic effect to the cultured cells.

Figure 1 shows the
(a) TEM image of graphene-PEMs on a 2D surface and (b) graphene-LbL functionalized PCL nanofibres,
(c) SEM image of graphene-LbL functionalized PCL nanofiber network,
(d) primary cortical neurons cultured on functionalized 2D PCL substrate, where neurons (green) were stained by SMI-32, and nuclear (blue) stained by DAPI.



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CONDUCTING POLYMER ANTI-MICROBIAL AGENTS

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The global market for anti-microbial agents is receptive to novel technologies free from the health concerns and limitations of existing agents. The current global market for industrial anti-microbial agents encompasses many diverse types of compounds and materials. One new technology that is attracting commercial interest is based on a family of polyaniline-related polymers. The Hybrid Polymers team has developed a series of potent conducting polymers that exhibit anti-oxidant and anti-microbial properties¹. This programme has involved consultation with >100 NZ and international companies and has attracted \$2.5M of industry co-funding. During consultations with companies, and subsequent joint planning meetings with several of these companies, a range of applications have been identified which are being developed across a range of sectors including construction, packaging, coatings, marine and hearing technologies.

A 1% w/v suspension of key polymeric biocides will reduce *S. aureus* populations by 99.9% within 2 hours. We have applied the active polymers as solutions, blends, films, powders, electrospun nano-fibres, colloids and composites (see Figure). The hybrid substrates include thermoplastics, elastomers, metals, paper and oxides including zeolites. We have demonstrated that the potent polymers are non-cytotoxic and so are applicable in medical and health applications. The competitive advantages of the new active polymers include, in many cases, their insolubility in water, non-leaching property, thermal stability in most cases to c.300C, ability to be combined with porous substrates, and their support for the growth of mammalian cells.

Overall, these advantages make the active polymers readily applicable across the range of sectors listed above. The anti-bacterial mechanism of action of these agents has been investigated using transcriptomics and the analysis of super-sensitive mutant bacteria. Our data supports a hypothesis where an antimicrobial polymer challenge leads to bacterial cell death through iron dysregulation, oxidative stress and a loss of membrane integrity.

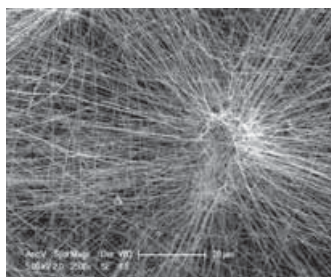


Figure: Electrospun biocompatible fibres with 10% anti-microbial conducting polymer

Acknowledgements. The materials are covered by the patent PCT/NZ2008/000254 (WO 2009/04837) extended to national phase filings in New Zealand, Australia, USA, Canada, Europe, Japan and China. Funding for this 6 year Research for Industry (RFI) programme is from NZ Ministry of Science and Innovation (Hybrid Plastics, UOAX0812). We are grateful to our research partners VUW, IRL and Scion Research

¹M.Gizdavic-Nikolaidis, S. Ray, J. Bennett, A.J. Eastale, R.P. Cooney, *Macromolecular Bioscience*, **2010** 10, 1424,

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One Single Component Conducting Polymer Hydrogel as a Scaffold for Tissue Engineering

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Processable electroactive materials such as soluble conducting polymers (CPs) are impacting on a wide variety of bioapplications. In particular, CPs have exciting potential as scaffolds for tissue engineering, typically applied in regenerative medicine applications.¹ The optimal physical and biological characteristics of a scaffold for tissue engineering include tissue-like mechanical properties, a hydrated environment, biocompatibility and biodegradability. Many of these characteristics are found in hydrogels rendering them excellent candidates for tissue scaffolds.² However, scaffolds for muscle and nerve cell regeneration would also benefit from electrical conductivity, which has been shown to provide enhanced cell growth and differentiation.^{3,4} Electrically conductive hydrogels (ECHs) could fulfill this role. Largely, however, ECHs are polymeric composites fabricated from two components; a hydrogel component that provides a highly hydrated environment and a CP component that provides electrical conductivity. One of the limitations these ECHs have is the leaching of the physically entrapped CP as the hydrogel swells leading to a drop in conductivity as well as possible toxic effect. Herein we report for the first time the development of a chemically crosslinked single component CP hydrogel that was fully characterized for potential use as a scaffold for tissue engineering.

Poly(3-thiophene acetic acid) (P3TAA) CP was chosen as the polymeric backbone for hydrogel fabrication. Networks of three different crosslinking densities were prepared. Their swelling behavior, mechanical properties, conductivity and electroactivity were all assessed at physiological pH and temperature. The internal structure of the network was characterized by scanning electron microscope (SEM). Adhesion and proliferation of two cell lines, fibroblast L929 and C2C12 muscle cells, were investigated.

Fabrication of chemically crosslinked P3TAA hydrogels was successful (Fig.1A). All hydrogels swelled and reached equilibrium within 1 day incubation. Hydrogels displayed remarkable swelling capabilities despite the hydrophobic nature of the polymer backbone. By decreasing the crosslinking density, % swelling ratios could be varied from 343.36 ± 27.88 to 878.55 ± 61.04 and the compressive modulus from 17.88 to 1.22 kPa. SEM cross-sectional micrographs of the hydrogel networks showed a

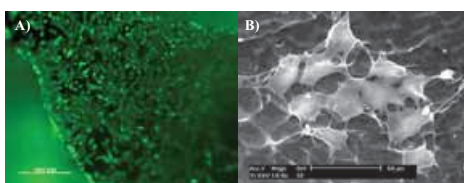


Figure 2: A) Cells on the hydrogel surface stained with Calcein-AM to visualise metabolically active cells. B) CryoSEM images of C2C12 cells adhered to the hydrogel substrates following 72h incubation.

This is the first report of a single component CP hydrogel that has controlled structural properties and its potential use as a scaffold has been demonstrated for cell growth, opening the way for the development of new tissue engineering scaffolds with inherently electroactive properties.

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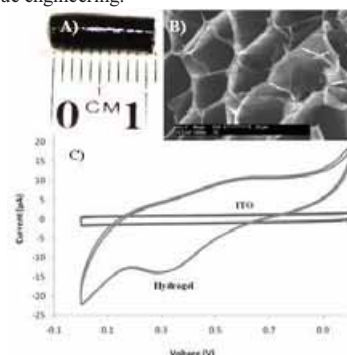


Figure 1: A) P3TAA hydrogel. B) SEM micrograph. C) Cyclic voltammograms (100 mV s⁻¹) of ITO bare electrode and hydrogel in 0.1 M PBS.

porous internal structure with interconnected

pores (Fig.1B). Hydrogels were electroactive in phosphate buffer solution (PBS, pH=7.4, Fig.1C) and conductivities of 1.4×10^{-3} S/cm were achieved. Fully hydrated hydrogels supported attachment and growth of C2C12 muscle cells (Fig.2A). CryoSEM imaging (Fig.2B) also showed the undulating surface topography of the hydrogel with cells showing good interaction and an adherent morphology on the surface.

Charge Loss in the Electrospinning System

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Electrospinning has been established as a valuable method of producing micro- and nano-scale continuous fibres¹. Electrospinning uses high strength electric fields ($> 1 \text{ kV/cm}$) to form jets of fluid polymer and then draw them into nanometre diameter fibres². The application of high voltage causes charging of the droplet formed at the tip of the spinneret. The accumulated charge results in the droplet deforming into a Taylor cone from which mass is ejected in the form of a fluid jet³.

It has been shown that electric current observed at the collector has a power law relationship to the applied voltage⁴⁻⁶. Existing reports have only varied the applied voltage to study the effect of different magnitude electric fields on the electric current at the collector electrode. Hence it is impossible to distinguish between an effect due to applied voltage and an effect due to applied electric field. Existing reports have also focused exclusively on electric current measured at the collector electrode. This work aims to present results showing the electric current response at a range of applied electric fields by varying the applied voltage and the inter-electrode distance. Additionally this work will present results showing the electric current simultaneously measured at the high voltage electrode and the collector electrode (**Fig 1**).

It is generally assumed that charge is conserved in the electrospinning process^{3,7,8}. When numerical simulations are being constructed this conservation applies to a closed system containing only the two electrodes and the polymer jet in a vacuum. Kalayci et. al. explain that “*solvent evaporation does not remove charge from the system in electrospinning or electrospinning; charged droplets evaporate losing mass without losing charge*”⁹. It is a physical requirement that there is a system that encompasses a sufficient portion of the environment that charge is conserved. Therefore any discrepancy between the electric current at the high voltage electrode and the collector electrode must be accounted for by charge being lost into the surrounding environment. This paper examines a number of such cases and it was found that such a discrepancy existed implying that charge was lost in flight. This has important implications for simulation of the electrospinning process and for understanding the mechanisms by which fibres are formed.

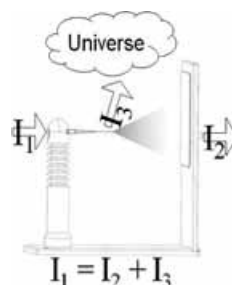


Figure 1: Electric current measurement points and charge conservation equation

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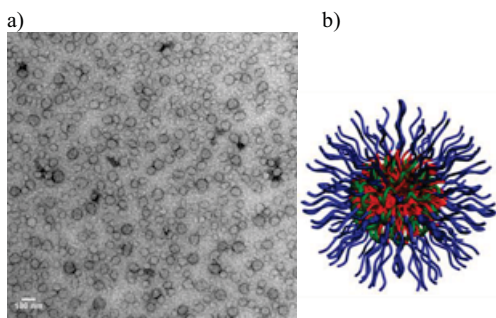
Delivery Agents Designed from Core-Shell Carbohydrate-Based Block Copolymers

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The intracellular delivery of nucleic acids offers unprecedented promise for revolutionizing biomedical research and novel drug development. However, the nucleic acid delivery vehicle plays a central yet elusive role in dictating the efficacy, safety, mechanisms, and kinetics of gene regulation in a spatial and temporal manner. To this end, we have developed several novel carbohydrate-containing polymers that have shown outstanding affinity to encapsulate polynucleotides into nanoparticles termed polyplexes and facilitate highly efficient intracellular delivery without toxicity. We have utilized step growth polymerization techniques to yield a comprehensive series of polycations that contain various mono-, di-, and oligosaccharide moieties copolymerized with ethyleneamine units. In addition, we have recently created analogs of these polymers via RAFT polymerization methods, allowing us to create a variety of block copolymer architectures with saccharides and a variety of cationic units in a highly controlled manner. A number of these polymer systems have revealed high efficacy for both pDNA and siRNA delivery. To examine the intracellular mechanisms of delivery, we have utilized live cell confocal microscopy imaging techniques to examine the intracellular trafficking of the polyplexes with Hela cells, which allows us to observe polyplex movement within the cells. We have also developed three dimensional data processing techniques to surface render confocal images, allowing us to visualize the spatial and temporal distribution of polyplexes within the cellular environment.

Figure 1. a) TEM image of polyplexes formed with carbohydrate-polycation block copolymers that have encapsulated pDNA. b) Depiction of the core-shell structure of the polyplexes (polymerized pendant carbohydrates form the shell).



1. A. E. Smith, A. Sizovs, G. Grandinetti, and T. M. Reineke, *Biomacromolecules* **2011**, 12, 3015-3022

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Self-Catalyzed Degradable Polycation for DNA Release

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The controlled release of siRNA or DNA complexes from cationic polymers is an important parameter design in polymer-based delivery carriers.^{1,2} In this work, we use the selfcatalyzed degradable poly(2-dimethylaminoethyl acrylate) (PDMAEA) to strongly bind, protect, and then release oligo DNA (a mimic for siRNA) without the need for a cellular or external trigger whereas quaternized PDMAEA cannot release DNA (**Fig.1**). This self-catalyzed hydrolysis process of PDMAEA forms poly(acrylic acid) and *N,N*-dimethylamino ethyl ethanol, both of which have little or no toxicity to cells, and offers the advantage of little or no toxicity to off-target cells and tissues. We found that PDMAEA makes an ideal component of a delivery carrier by protecting the oligoDNA for a sufficiently long period of time to transfect most cells (80% transfection after 4 h) and then has the capacity to release the DNA inside the cells after ~10 h. The PDMAEA formed large nanoparticle complexes with oligo DNA of ~400 nm that protected the oligo DNA from DNase in serum. The nanoparticle complexes showed no toxicity for all molecular weights at a nitrogen/phosphorus (N/P) ratio of 10. Only the higher molecular weight polymers at very high N/P ratios of 200 showed significant levels of cytotoxicity. These attributes make PDMAEA a promising candidate as a component in the design of a gene delivery carrier without the concern about accumulated toxicity of nanoparticles in the human body after multadministration, an issue that has become increasingly more important.

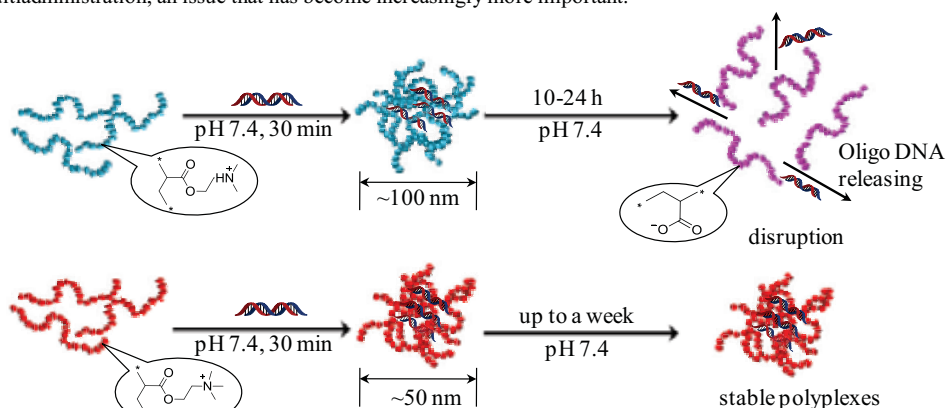


Figure 1. The controlled release of siRNA or DNA from degradable and undegradable cationic polymers.

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² Kurreck, J. *Angew. Chem., Int. Ed.* **2009**, 48, 1378-1398.

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siRNA Delivery with ABA Triblock Copolymers and Star Block Copolymers

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RAFT polymerization, a reversible deactivation radical polymerization (RDRP), is arguably the most versatile method for providing living characteristics to radical polymerization. The method, developed at CSIRO laboratories, is now well-established in providing polymers with exceptional control over molecular weight, molar mass distribution, composition and architecture. The process can be applied to most monomers polymerizable by radical polymerization and offers a convenient route to well-defined homo-, gradient, diblock, triblock and star polymers as well as more complex architectures that include microgels and polymer brushes. Moreover, RAFT polymerization, like conventional radical polymerization, is tolerant of functionality in monomer, solvent (it can be carried out in aqueous media), it is compatible with bulk, solution, suspension and emulsion processes.

Ribonucleic acid (RNA) is a bio-macromolecule used by cells for defense and to regulate gene expression. The RNAi process is occurred by the incorporation of specific siRNA to the specific target messenger RNA (mRNA) as a means of inhibiting the synthesis of the encoded protein. Small interfering RNAs (siRNAs), 19-23 mer double-strand oligonucleotides, play a fundamental role in RNA interference, and are a very powerful tool for reducing the expression of genes which are specifically targeted. Despite the significant potency of siRNAs to treat gene-related diseases, their poor *in vivo* delivery remains a major challenge for medical therapies. Thus, the therapeutic value of siRNAs under *in vivo* conditions is still controversial due to their fast degradation in physiological media (e.g., low stability against enzymatic digestion in the blood stream), poor cellular uptake, inefficient translocation into the cytoplasm, rapid renal clearance after systematic administration, and lack of targeting activity.

The RAFT process is well placed to meet these challenges due to its robustness, high flexibility, mild experimental conditions and ability to insert functional groups within the polymer chain. This produces well defined polymers needed to construct well-defined polymer-therapeutic conjugates. This talk will focus on our recent study using RAFT polymerization with specific RAFT agents to produce a series of ABA triblock copolymers, star block copolymers with neutral and cationic blocks, and explores the ability of these polymers to bind, and deliver siRNA into cells to allow silencing of target genes.

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1987	PhD
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Hyperbranched Polymer/siRNA Conjugates as Targeted Cancer Therapeutics

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siRNA is a powerful therapeutic which has the potential to treat numerous diseases including cancer. However, it is not an effective drug without a carrier system due to degradation by enzymes in serum. In this project we investigated the use of hyperbranched polymers (HBPs) as carrier vehicles for siRNA. The HBP will provide protection for the siRNA from degradation, as well as facilitate targeted delivery of the siRNA to cancer cells by incorporating folate. In addition, the HBP includes fluorinated moieties to enable ¹⁹F MRI and FITC for fluorescence microscopy studies. The siRNA was conjugated through a disulfide linkage which is degraded by glutathione once the conjugate reaches the cytosol.

The HBPs were synthesized by RAFT polymerisation using an alkyne-functional trithiocarbonate and subsequently characterized by NMR and GPC. Alkyne end-groups were reacted with a PEG-azide linker by click chemistry and subsequently coupled with folic acid and FITC. The amount of folate and FITC coupled to the HBP was quantified using UV-vis spectroscopy. The trithiocarbonate end-groups were then reduced using ethanolamine and the resulting thiol was protected using Ellman's reagent. This was assessed using NMR and UV-vis spectroscopy. Finally, the siRNA was coupled through a thiol-disulfide exchange reaction and the resulting HBP/siRNA conjugates were analysed by PAGE. Figure 1 shows a schematic of the synthesis of the HBP/siRNA conjugate.

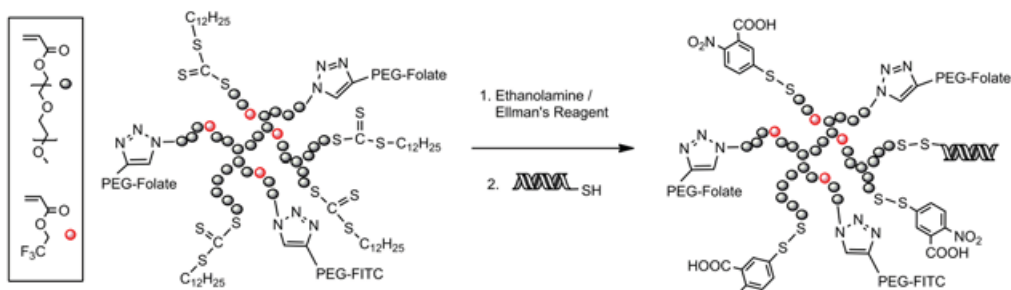


Figure 1. Reaction scheme for the conjugation of one siRNA to the HBP including folate and FITC.

In conclusion, we have successfully synthesized a multifunctional HBP/siRNA conjugate. Future studies will examine cell uptake and silencing of the target gene. ¹⁹F MRI will be used to determine the targeting ability of the conjugate in an animal model.

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Polydimethylsiloxane microchannel modifications for DNA detection in microfluidics

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Poly(dimethylsiloxane) (PDMS) is a popular material for microfluidic devices due to its relatively low cost, ease of fabrication, oxygen permeability and optical transmission characteristics. However, its highly hydrophobic surface is still the main factor limiting its wide application, in particular as a material for biointerfaces. Furthermore, it is prone to hydrophobic recovery even after preliminarily surface oxidation techniques. Modern microfluidic PCR/CE devices made from PDMS offer a solution to simpler and faster front-end DNA profiling devices and this is particularly true when they also include nanoscale architectures for analyte differentiation.

Here we describe the fabrication of a PDMS microfluidic device and the subsequent *in-situ* surface modification of the PDMS with synthetic oligonucleotide capture probes. Several approaches will be highlighted including, (1) a 2-step plasma modification of PDMS with Ar and then acrylic acid (AAc), after which 5'-amino-terminated oligonucleotides are attached to the PAAc modified PDMS surface and (2) plasma oxidising, silanisation with 3-aminopropyltriethoxysilane (APTES) then thiourea coupling with *p*-phenylene diisothiocyanate, finally an amine modified oligonucleotides (capture probe) is attached to the activated PDMS.

The latter approach will be further described by the novel development of a primer system (using stem-looped primers) that allows us to perform hybridisation of a double-stranded PCR product on capture probes immobilised on the PDMS surface. Subsequent release of the PCR product can be carried out using a method of choice - thermal denaturation or photocleavable detachment. Surface modification and immobilisation of capture probes on the PDMS surfaces is monitored by Fourier transform infrared spectroscopy, water contact angle, zeta potential and fluorescent microscopy. Results show successful surface modification and subsequent hybridisation with a fluorescently labeled fully complementary DNA sequence to the immobilised capture probe in a PDMS microchannel (Figure 1a). To show selectivity of the modified surface two differently labeled complementary strands were combined and passed over a capture probe surface (Fig 1b and c (fluorescence emission data)). This technique combined with analysis of short tandem repeats (STRs) will improve both forensic human identification and medical diagnostics of any genetic alteration linked with mutation in STR regions.

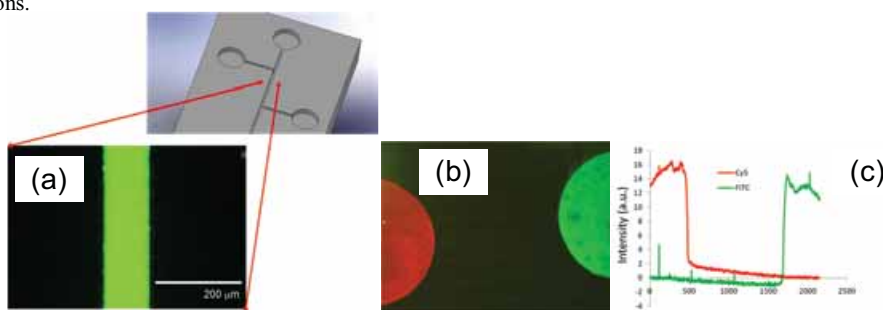


Figure 1. (a) Fluorescently labelled (FITC) oligonucleotide captured on a PDMS microchannel, (b) isolation of 2 fluorescently labelled (Cy5 and FITC) oligonucleotides captured on a PDMS microchannel and (c) corresponding fluorescent emission plot.

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A novel approach towards dynamic cross-linked hydrogels

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Cyclodextrins (CDs) are cyclic organic compounds linked together by α -(1,4) glucose units (**Figure 1**). The three naturally occurring forms of cyclodextrin are α , β , γ ; each having 6, 7, and 8 glucose repeat units. CDs are often conveyed as a truncated cone with a hydrophilic exterior and a hydrophobic interior.¹ This interior cavity allows CDs to form tight non-covalent interactions, with various complementary molecules and macromolecules like poly (ethylene glycol) (PEG). This is commonly referred to as an inclusion complex.² The interaction of CD with PEG has been widely explored for a diverse range of applications.²

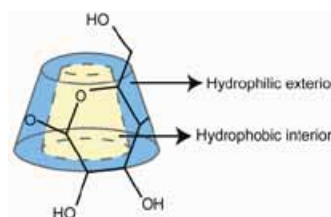


Figure 1. Schematic representation of cyclodextrin (CD).

Previously freely movable (dynamic) hydrogels have been synthesised via linking CDs together to create 'figure-of-eight' like cross-links from pre-prepared and isolated polyrotaxanes.³ The advantage of these moveable cross-link points is that when force is imparted on the network the cross-link points can freely move along the PEG chain to dissipate the tension imparted (**Figure 2**). This feature allows the networks to stretch and swell to levels not seen in conventional covalently cross-linked networks.³ In this study we demonstrate that dynamically cross-linked hydrogels can be prepared in one-pot using click chemistry and polypseudorotaxanes, eliminating the need to prepare discrete polyrotaxanes. The synthesis and characterization of these hydrogels will be discussed.

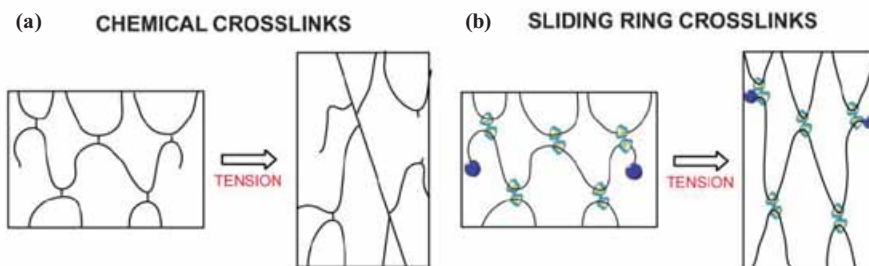


Figure 2. Schematic representation of the difference between (a) conventional and (b) sliding-ring networks under tension.³

¹ F. Manakker, *Biomacromolecules* **2009**, 12, 3157

² E. M.M. Valle, *Process Biochemistry* **2003**, 39, 13

³ Y. Okumura, *Advanced Materials* **2001**, 13, 485

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Hybrid Hydrogel Sponges with Controlled Pore Sizes

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Scaffolds are required to allow the target tissue to grow within their structure to be suitable for tissue engineering applications. To achieve this, such scaffolds need to have an interconnected porous structure for tissue to penetrate, vascularise and grow as well as maintain their integrity when implanted *in vivo*. Therefore hybrid hydrogel sponges with desired porous and elastic properties have been developed using a chitosan biopolymer which was modified with poly(ethylene glycol) (PEG) to provide improved stability and mechanical properties.

Initially, a 3-dimensional biopolymer network was produced using a freeze templating technique. Various porogens were incorporated during the freeze templating method to control the pore sizes. Two types of porogens, n-butanol and lactide particles were used to produce small or large pores respectively. Lactide in its crystal form was ground and sieved to produce particles ranging from 100-600 μm prior to incorporation. To a homogenous solution of the biopolymer was added porogen and the biopolymer-porogen mixture was frozen at -20°C . Subsequently water and the porogen were removed by leeching in chilled acetone (-20°C). The dried biopolymer network was subsequently modified with functionalized PEG solutions to provide hydrogel sponges with improved stability and mechanical properties. Various concentrations of PEG were used to determine the effect on the mechanical properties of the newly fabricated hydrogel sponges. Enviro-Scanning Electron Microscopy (E-SEM) was used to determine the pore structure and the effect of porogen on wall thickness. Mechanical characterization using an Instron Microtester 5848 was carried out to determine the effect of modification with PEG.

Analysis of the sponges via E-SEM (**Figure 1**) revealed that n-butanol resulted in the formation of small pores whereas lactide particles led to large pores. Furthermore, the different porogens also affected the thickness and surface of the walls with n-butanol providing thinner walls with a 'pitted' topology while lactide particles produced smooth and thicker walls. An interconnected porous structure was observed for all hydrogel sponges, which is ideal for tissue penetration and vascularisation. Mechanical characterization of the hydrogel sponges revealed excellent elastic properties with repetitive compressive testing showing identical compressive tangent moduli thus demonstrating their spongy character. Using various concentrations of PEG for the modification process demonstrated a trend whereby the compressive modulus of the sponges can be tailored for specific tissue or implantation sites. These properties demonstrate that the hybrid hydrogels are suitable for tissue engineering applications where such scaffolds are required to maintain an interconnected porous structure without collapsing or fracturing under physical forces *in vivo*.

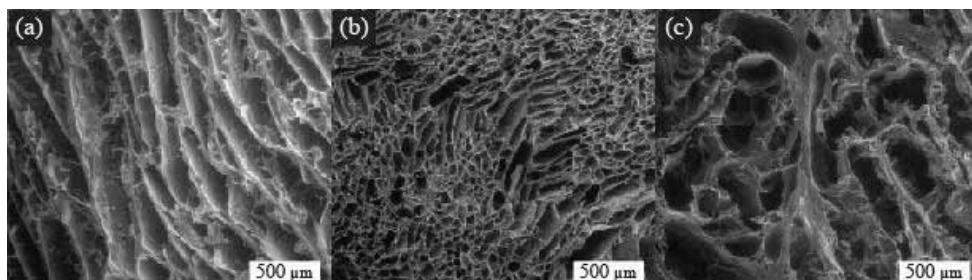


Figure 1: E-SEM images of hydrogel sponges with a) no porogen b) n-butanol c) lactide particles

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Synthesis and application of drug delivery systems.

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Poly(*N*-vinyl pyrrolidone)-*b*-poly(vinyl acetate) (PVP-*b*-PVAc) block copolymers of varying molecular weight and hydrophobic block lengths were synthesized via controlled radical polymerization and investigated as micellar carriers for the solubilization of highly hydrophobic riminophenazine compounds. These compounds have recently shown to exhibit a strong activity against a variety of cancer types. PVP-*b*-PVAc self-assembles into polymer micelles in aqueous media, and the dialysis method was used to load the water-insoluble drugs (clofazimine) into these polymer micelles. The polymer micelles were characterized by ¹H NMR spectroscopy to confirm micelle formation and the incorporation of the anticancer drugs into the polymeric micelles. Dynamic light scattering was used to determine the particle size and particle size distribution of the drug-loaded micelles as well as the stability of the micelles under physiological conditions. The size of the polymer micelles did not increase upon loading with clofazimine, and the particle size of 180–200 nm and the narrow particle size distribution were maintained. The morphology of the micelles was examined by transmission electron microscopy. The drug loading capacity and the encapsulation efficiency of the polymer micelles were determined by UV/Vis spectroscopy. The polymer micelles had a relatively high drug loading capacity of more than 20 %. *In vitro* cytotoxicity assessment was carried out using the PVP-*b*-PVAc micelles against MDA-MB-231 multi-drug resistant breast epithelial cancer cell lines and MCF12A normal breast epithelial cell lines. The acute toxicity studies confirmed the biocompatibility of the PVP-*b*-PVAc block copolymer. The results indicate that the present PVP-*b*-PVAc diblock copolymer micelles system could be a potential candidate as a drug delivery carrier for clofazimine.

In a second approach, polymeric prodrugs were synthesized via the reversible attachment of a clofazimine derivative to one block of a double hydrophilic block copolymer. The attachment of the hydrophobic drug introduces amphiphilicity to the polymer. This causes the polymer to form micelles in aqueous media. Hydrolysis rates of the linker between polymer and drug are measured as a function of pH. The hydrolysis leads to disintegration of the micelles and concomitant release of the drug. The polymeric prodrugs are compared with the drug-loaded micelles in *in vitro* studies.

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Nitric Oxide: A New Hope for the Treatment of Multidrug Resistant Cancers

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Soft core-shell polymeric nanoparticles have been widely investigated as potential vectors for the sustained delivery of therapeutic payloads, such as drugs, proteins, genes, and for the transport of imaging agents.¹ It is known that polymeric nanoparticles have prolonged circulation times in the bloodstream and allow effective accumulation in vascularised solid tumors due to the enhanced permeability and retention (EPR) effect.² Polymeric nanoparticles can be assembled from a range of polymer architectures, including dendrimers, micelles, star polymers, and vesicles, combs, brushes, and so on, to yield polymeric nanoparticles (eg micelle, liposome, etc). To improve their stability, these nanoparticles can be cross-linked. However, these materials are usually based on synthetic polymers, and therefore are non-biodegradable. One of the major concerns of these synthetic nanoparticles is their potential accumulation in the body, resulting in potential side effects. For this reason, the design biodegradable polymeric nanoparticles are of great interest.

In a first part of this presentation, a sample approach to prepare pH-responsive or redox-sensitive biodegradable nanoparticles based on dextran and on poly(ethylene glycol) (PEG) is presented. Dextran was chosen because of its biocompatibility, biodegradability, wide availability, and ease of modification, while PEG base polymer was used because it is biocompatible and hydrophilic. First, dextran was modified with 2-methoxypropene to yield acetalated-dextran (soluble in organic solvents, such as dichloromethane).³ Subsequent, the unreacted hydroxyl groups were reacted with a carboxylic acid RAFT agent to yield RAFT modified acetalated-dextran. RAFT modified dextran was used to control the polymerization of oligo(ethylene glycol methyl ether) methacrylate (OEG-MA) to yield dextran-g-POEG-MA copolymers. These graft copolymers were self-assembled in water to yield spherical and tubular nanoparticles with a tuneable size range from 20-100nm (assessed by TEM and DLS). Doxorubicin was loaded into the nanoparticles and released at low pH due to the cleavage of acetal bond. *In-vitro* data shows that these nanoparticles can successfully treat neuroblastoma cancer cells.

In a second part of this talk, the synthesis of responsive nanoparticles will be shown to deliver consecutively nitric oxide (NO) and the therapeutic agent (doxorubicin) is used for the treatment of multidrug resistant cancers (MDR). Multidrug resistance is one of the major reasons for the failure of chemotherapy treatment due to the production of MDR and P-glycoprotein reducing the chemotherapy drug's activity. Recently, it has been demonstrated that the treatment of MDR cells using NO allows for the reduction of the production of these proteins. To demonstrate this approach, the author has designed biodegradable nanoparticles able to store NO and doxorubicin. Finally, these nanoparticles were tested to treat multidrug resistant neuroblastoma cells. *In-vitro* data show promising synergetic effects when NO is combined with an anti-cancer drug.

1. K. Kataoka and co-workers, *Angew. Chem.Int. Ed.*, 2009, **48**, 5309-5312.
2. O. C. Farokhzad and R. Langer, *ACS Nano*, 2009, **3**, 16-20.
3. *J. Am. Chem. Soc.*, 2008, **130**, 10494-10495.

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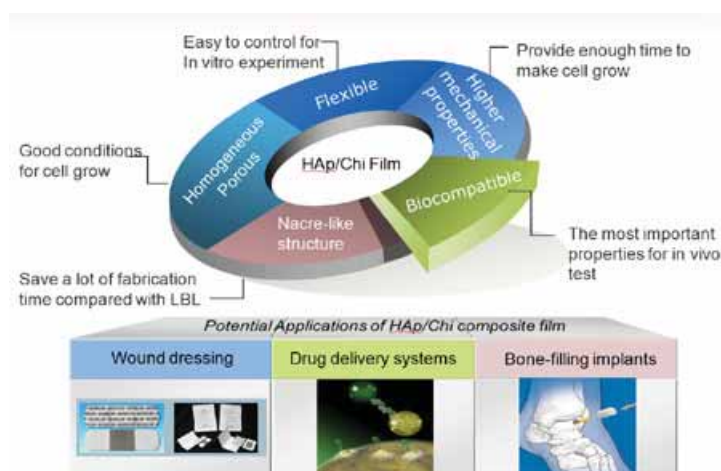
Research interests: Iron oxide nanoparticles, imaging, RAFT, end group modification, protein conjugates.

Various preparation methods of highly porous hydroxyapatite/polymer nanoscale biocomposites for bone regeneration

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Main text: Tissue engineering utilizes expertise in the fields of materials science, biology, chemistry, transplantation medicine, and engineering to design materials that can temporarily serve in a structural and/or functional capacity during regeneration of a defect. Hydroxyapatite (HAp) scaffolds are among the most extensively studied materials for this application. However, HAp has been reported to be too weak to treat such defects and, therefore, has been limited to non-load-bearing applications. To capitalize the advantages of HAp and at the same time overcome the drawbacks nanocrystalline HAp (nHAp) is combined with various types of bioactive polymers to generate highly porous biocomposite materials that are used for osteoconduction in the field of orthopedic surgery. In this study we reviewed current results on nanosized HAp-based highly porous composite materials used for bone tissue engineering using various fabrication methods to prepare nHAp/polymer composite scaffolds. Then, these films are characterized these scaffolds on the basis of their biodegradability and biocompatibility through in vitro and in vivo tests.



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Biocompatible Polyurethanes for Spinal Cord Regeneration

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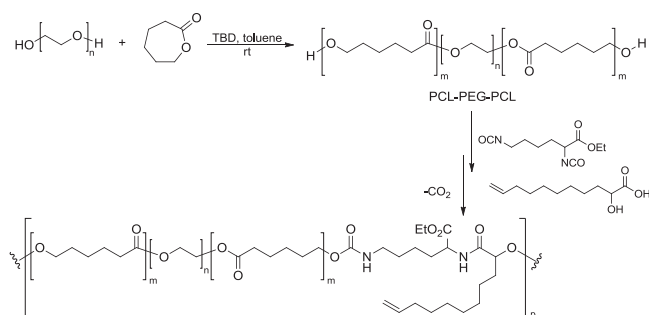
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The personal, social and economic effects of spinal cord injury (SCI) on the victims, their families and society at large are enormous. In humans, the severed nerve tracts fail to regenerate across the injured site and there is currently no effective treatment for these injuries. Consequently, there has been a major push to develop strategies for SCI repair in recent years, using biomolecular-, cellular- and biomaterial-based approaches. Considering the complexity of SCI, it is most likely that a successful strategy will require of a combination of these approaches.

One aspect of our strategy is the development of a 3-dimensional scaffold, based on biocompatible and biodegradable polymers, to bridge the SCI lesion and promote the regeneration of severed nerve tracts. This scaffold will fulfill several roles; aligned nanofibres will promote axonal growth to allow realignment of nerve tracts and an external conduit will provide mechanical protection and prevent ingress of scar tissue (fibroblasts, extracellular matrix etc).

Here, we report the first stages of our materials development and characterisation program. We have prepared and characterised a range of biocompatible and biodegradable polyurethanes based on well-defined PCL-PEG-PCL tri-block co-polymer building blocks (soft segments) and lysine-based isocyanates. Modifying the size of each block allows us to tune its hydrophobicity and alter its mechanical and biological characteristics. Novel functionalised α -hydroxy acids, derived from renewable sources, have also been utilized in chain extension segments (**Scheme 1**). Functionalisation on these residues allows the conjugation of signaling molecules. The biological compatibility of both bulk and electrospun polyurethane samples has been investigated in cell culture.



Scheme 1. Synthesis of functionalised biocompatible polyurethanes

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Research interests: polymer-based biomaterials for tissue regeneration, nitroxide radical chemistry, contrast agents for biomedical imaging



Polyurethane Nanocomposites as Biomaterials – Mechanical Performance, Morphology and Biocompatibility

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Polyurethanes are excellent potential materials for the construction of implantable medical components due to their very good mechanical properties and biocompatibility. Currently, soft silicone materials are employed as insulation for implantable Cochlear electrode arrays. Siloxane-based thermoplastic polyurethane (TPU) nanocomposites containing synthetic layered silicates are being investigated as new insulation materials with superior tensile/tear strength and reduced surface tack, potentially allowing a thinner insulation and more intricate electrode designs.

In this project, ElastEon™ E5-325 (Aortech Ltd) TPU nanocomposites reinforced with 2 and 4 wt% low aspect ratio organo-hectorite and high aspect ratio organo-fluoromica (Lucentite SWN, Somasif ME100, both modified with octadecyltrimethyl ammonium (ODTMA)) were prepared by a solvent casting technique. The mechanical properties of the resulting nanocomposites were measured and they were characterised mechanically by tensile, tear and creep testing, and morphologically by DSC, DMTA, XRD, TEM, dielectric spectroscopy and strained in-situ synchrotron SAXS. In general, the hydrophobic low aspect ratio nanofiller acts as a very potent interfacial compatibiliser. At 4% loading, gross morphological changes in the TPU microdomain texture are observed causing adverse effects on the mechanical properties of the TPU. However at 2% loading, the resulting nanocomposites display an increased hard domain melting temperature and a broadly enhanced property profile, with appreciable enhancements in tensile and tear strength, creep resistance, and toughness. In addition to providing 25nm x 1nm synthetic clay reinforcing elements which are readily capable of orientation and reinforcement¹, shown in the 2D SAXS patterns Fig 1 below, these nanofillers also serve to provide more cohesive hard microdomains, and thus creep

resistance and dimensional stability.

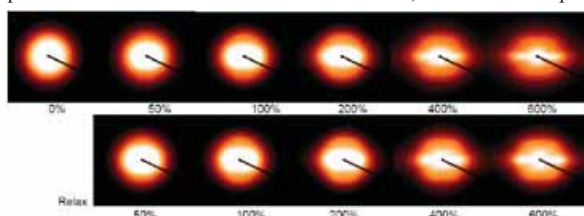


Fig 1 2D strained synchrotron SAXS patterns and TEM image of best performing nanocomposite (100nm scale bar)

In parallel, we have performed exhaustive *in-vitro* toxicology studies on the nanofillers, pristine synthetic clays and organic modifiers, as well as nanofiller release studies on fatigued and non-fatigued nanocomposites. These results will be presented.

1. Granted International patent application AU 2005279677 entitled "Polymer Composite"

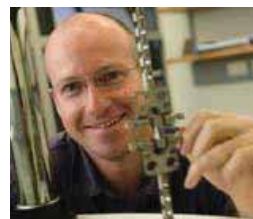
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Development of Bioactive 3D Block Copolymer Scaffolds for Repair of Bone Tissue

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Biodegradable polymers have been used extensively as scaffolding materials to regenerate tissue. These scaffolds should possess certain physical characteristics including a three-dimensional structure, high porosity with an interconnected pore structure, and a suitable surface structure to encourage cell attachment, proliferation, and differentiation.

Solvent casting combined with particle leaching is one of the most widely used methods to fabricate polymeric 3D scaffolds. The advantages of this technique include a large range of pore sizes, high porosity and independent control of the porosity and pore size. However, conventional solvent casting techniques use salt, sugar or paraffin as the porogen, which are either nonspherical or polydisperse. In this work, a microfluidic device has been utilized to prepare monodisperse calcium-alginate beads (Figure 1). The average diameter of the beads increased with increase of the dispersed phase flow rate and decrease of the continuous phase flow rate. The beads were then used as the porogen to fabricate 3D polymeric scaffolds. By controlling the diameter of the beads, the pore size of the scaffold can be adjusted. This can help us better understand the effect of the scaffold parameters on the cell adhesion, proliferation and differentiation (Figure 2).

We have synthesized amphiphilic triblock copolymers of methoxy-poly(ethylene glycol)-*b*-poly(L-lactide)-*b*-poly(L-lysine) (MPEG-*b*-PLLA-*b*-PLL) as surface active biopolymers. The films were fabricated by casting PLLA blended with the triblock copolymers. No cytotoxicity was detected on the films and the triblock copolymers MPEG-*b*-PLLA-*b*-PLL showed better surface properties in promoting osteoblast adhesion and proliferation compared with pure PLLA and PLLA modified with MPEG-*b*-PLLA diblock copolymers.¹ This triblock copolymer will be blended with PLLA as the scaffold material to further optimize the biological properties of the polymeric scaffold.

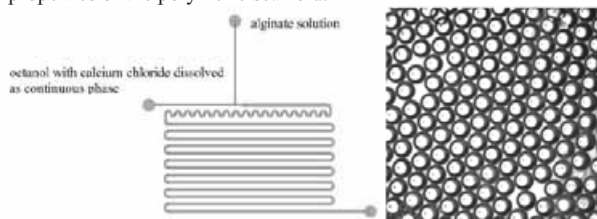


Figure 1 The microfluidic device design and the monodisperse calcium-alginate beads.

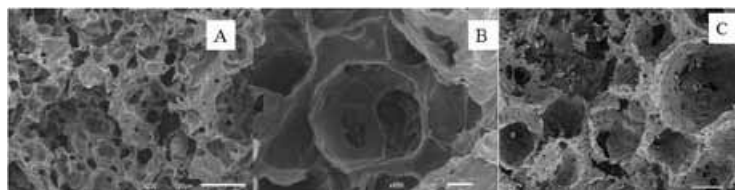


Figure 2 The morphology of the porous scaffold using different sizes of porogen (a) 50 μm calcium-alginate beads as porogen; (b) high magnification of (a); (c) 100 μm calcium-alginate beads as porogen

¹Peng, H.; Xiao, Y.; Mao, X.; Chen, L.; Crawford, R.; Whittaker, A. K. *Biomacromolecules* **2009**, *10*, 95.

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Optimal Design of Polymer Artificial Muscles

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Polymer based artificial muscles are of interest for a variety of applications in areas such as robotics, machine parts, medical prostheses and tools. This presentation concentrates on low-voltage electromechanical actuators based on conducting polymers or hydrogels and including carbon nanotubes or graphene as a reinforcing phase. Since the key performance metric is often the power generated by the actuator material, we are interested in maximizing the stroke and force and minimizing the speed of response. Studies of polypyrrole films prepared to different thicknesses and tested under isotonic conditions (Fig. 1a) show several important features. Firstly, the actuator response is strongly influenced by the rate at which the voltage is scanned and this effect is related to the slowness of the mass transfer that occurs between the polymer and the surrounding electrolyte solution. Secondly, the actuator strain tends to decrease with increasing isotonic stress applied and this effect has been attributed to the change in elastic modulus of the polymer that accompanies the volume change. Thirdly, the maximum stress that can be sustained (ie. strength) is quite low when the polymer is immersed in electrolyte.

This presentation reviews some of our work designed to both understand and overcome these problems. We show, for example, that the inclusion of carbon nanotubes to form a laminate type composite with polypyrrole greatly increases the work-per-cycle¹.

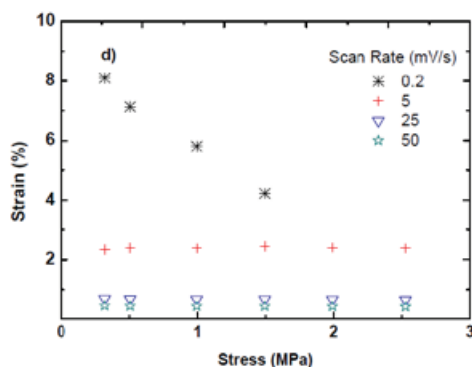


Figure 1. Actuator strain obtained for a polypyrrole film tested at the 4 different scan rates shown and at increasing isotonic stress.

1. W. Zheng, J.M. Razal, P.G. Whitten, Artificial Muscles Based on Polypyrrole/Carbon Nanotube Laminates, *Advanced Materials*, 23, 2011, 2966-2970.

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Two-dimensional distributions of complex branched polymers

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A method has recently been developed^{1,2} to obtain two-dimensional distributions to characterize complex branched polymers. The first dimension is the total molecular size. For separation by size-exclusion chromatography (SEC, also termed GPC), this size is the hydrodynamic volume, or equivalently the hydrodynamic radius of the branched polymer $R_{h,br}$. The second dimension is the DP of individual branches, X_{de} , or equivalently the corresponding debranched size $R_{h,de}$. These 2D distributions are obtained by first separating by $R_{h,br}$ using preparative SEC columns, collecting the fractions, and then debranching these fractions (which for starch and glycogen is done with debranching enzyme) and carrying out a second separation in $R_{h,de}$ using small-pore SEC columns.

Starch is a complex branched polymer of glucose, with two components having the same basic structure: amylose, with molecular weight $\sim 10^6$ and a few long-chain branches, and amylopectin, with much larger molecular weight and many short-chain branches. Examples of starch 2D distributions are given in **Fig. 1**, for two varieties of starch: normal ('native') maize, and a genetically modified maize, Gelose 80, where there is a greater proportion of smaller molecules with longer chains. These 2D distributions reveal much more than can conventional (1D) SEC. In the present case, normal maize shows the expected structure: two "mountains", the one on the upper left being smaller molecules with longer branches, i.e. amylose, and that on the lower right being larger molecules with smaller branches, i.e. amylopectin. There has been debate about the nature of these Gelose 80 mutants: whether they create more amylose molecules which also have slightly longer branches, or whether they create amylopectin molecules with much longer branches. These 2D distributions show that it is clearly the former, as the upper left mountain looks like an augmented form of the amylose mountain in the native variety. Moreover, the appearance of multiple peaks in each mountain can be interpreted in terms of changes in the different types of branching enzymes that are always present in wild-type plants. In addition, these plots will be shown to provide a definitive answer to long-ongoing arguments in the literature about which of various methods for measuring amylose content is better.

- (1) Vilaplana, F.; Gilbert, R. G. *Macromolecules* **2010**, *43*, 7321.
- (2) Vilaplana, F.; Gilbert, R. G. *J. Chromatography A* **2011**, *1218*, 4434.

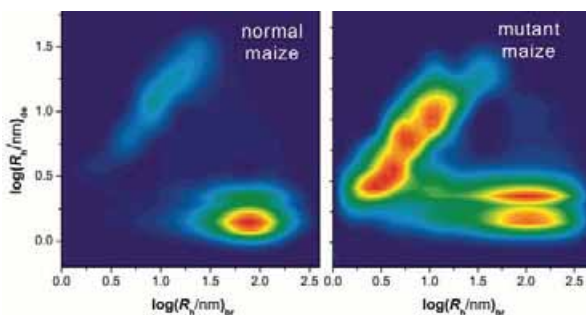


Figure 1. 2D weight distributions of starch from normal maize and from Gelose 870, a GM maize with increased numbers of long branches. The subscripts *br* and *de* refer to fully branched and debranched hydrodynamic radii, respectively.

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Study on the Mechanical Model of Double Network Hydrogel

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Double network (DN) hydrogels have drawn much attention as an innovative material having both high water content and high mechanical strength and toughness. DN gels are characterized by a special network structure consisting of two types of polymer components with opposite physical natures: the minor component is abundantly cross-linked polyelectrolytes (rigid skeleton) and the major component comprises of poorly cross-linked natural polymers (ductile substance). The former and the latter components are referred to as the first network and the second network, respectively. Extensive experimental studies have shown that the rigid, brittle first network serves as a sacrificial bond that fractures at a relatively low stress, while the soft, ductile second network serves as hidden length that sustains stress by large extension afterwards¹. To take advantage of the toughness mechanism of DN gels and explore the possibility for engineering application as the structural member, the information on the mechanical behaviour of DN gels under various loading conditions is indispensable. Therefore, in this study, a computational model of DN gel is firstly constituted based on the nonaffine molecular chain network model. And then, the parameters of the model are identified to reproduce the propagation of the necking of DN gel under simple tension. Finally, the model is employed to clarify the mechanical behaviour of DN gel under different triaxiality loading conditions.

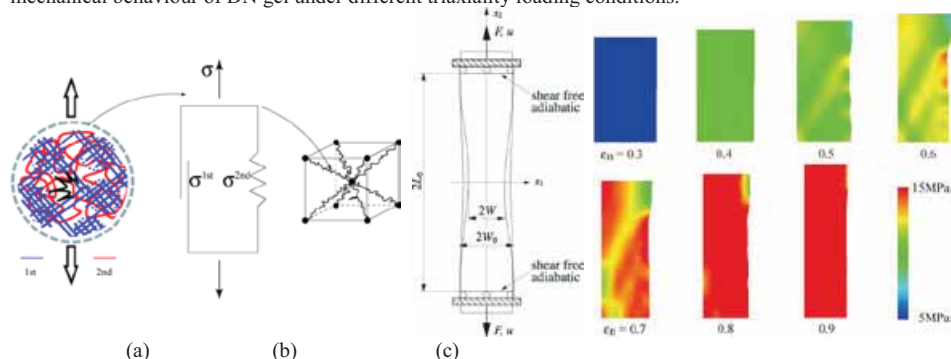


Figure (a) Hierarchy model of DN gel; (b) Computational model of DN gel under plane-strain tensional loading; (c) Distribution of tensional stress at different deformation stages.

To account for the resistance from both the first and the second network of DN gel, the model requires two elements: a slider element used to characterize the first network's response as rigid and brittle; and a nonlinear rubber elasticity spring element that accounts for an anisotropic resistance to molecular chain alignment. Both elements operate in parallel to deliver the total response of the material, σ , given by $\sigma = \sigma^{1st} + \sigma^{2nd}$, where σ^{1st} and σ^{2nd} are the stresses on the elements as shown in **Fig.(a)**. Continuously, this one-dimensional model is implemented into each chain of the network of eight non-Gaussian molecular chains as sketched in **Fig.(a)** for isotropic and deformed, anisotropic configurations. On the other hand, to account for the re-division of the cluster of the first network after fracture, which playing a role of cross-linker, the number of entangled points of the second network is proposed to evolve according to the value of local principal stretch, i.e. nonaffine movement of the entangle points² is considered. **Fig.(b)** shows the computational model of DN gel. Employing this model, the propagation of the necking of DN gel under simple tension can be reproduced at some level, as shown in **Fig.(c)**. At the deformation stage $\epsilon_n = 0.4$, the first network fractures at the lateral face of the central part, which leads to the onset of the necking. After it, due to the strain hardening of the second network inside the necking area, the localized deformation turns to evolve outside the necking area, i.e. the necking propagates.

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Characterization of polysaccharides for medical applications and bioplastics with solid-state NMR and capillary electrophoresis

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Polysaccharides are renewable, cheap, biodegradable and biocompatible. Their natural variability is the main restriction in their use, it will only be overcome with proper characterization. Cellulose is the most abundant polysaccharide, and it is increasingly used in bioplastics. Solid-state Nuclear Magnetic Resonance is an invaluable tool in the study of polysaccharides: it yields local information on their structure and dynamics.^{1,2} We are investigating the structural changes undergone by cellulose fibers during conjugation carried out to modify their macroscopic properties.

Chitin is the second most abundant natural polysaccharide, as main component of crab and shrimp shells, also a major waste product of the seafood industry. Its partial deacetylation yields chitosan, a copolymer of glucosamine and N-acetylglucosamine. Chitosan is widely and increasingly used in biomedical applications such as tissue engineering and drug delivery, owing to its biocompatibility, biodegradability, and non-toxicity.³

Solid-state NMR, combined with X-ray diffraction, revealed the molecular origin of the difference in mechanical properties of self-associated chitosan films.⁴ One-dimensional and two-dimensional solid-state NMR spectra revealed the interplay between local molecular structure and molecular dynamics. Films cast from acidic aqueous solutions were compared before and after neutralization; the role of the counter was investigated.

The composition of the chitosan (degree of acetylation) also influences materials properties. Chitosan is successfully separated according to its degree of acetylation with capillary electrophoresis in the critical conditions (CE-CC), allowing the determination of distributions of degrees of acetylation.

For surgical applications⁵, it is crucial to evaluate the toxicity of the enzymatic degradation products of chitosan. Their molecular structure is investigated with capillary electrophoresis and NMR.

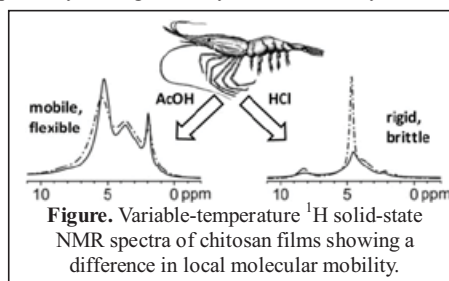


Figure. Variable-temperature ¹H solid-state NMR spectra of chitosan films showing a difference in local molecular mobility.

¹ M. Gaborieau, R. Graf, S. Kahle, T. Pakula, H.W. Spiess, *Macromolecules* **2007**, *40*, 6249-6256

² P. Castignolles, R. Graf, M. Parkinson, M. Wilhelm, M. Gaborieau, *Polymer* **2009**, *50*, 2373-2383

³ A. Lauto, D. Mawad, M. Barton, A. Gupta, S.C. Pillar, J. Hook, *BioMedical Engineering OnLine* **2010**, *9*, 47

⁴ C. Gartner, B.L. Lopez, L. Sierra, R. Graf, H.W. Spiess, M. Gaborieau, *Biomacromolecules* **2011**, *12*, 1380-1386

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Research interests: structure and dynamics in polymers, polysaccharides, synthetic polymers, solid-state Nuclear Magnetic Resonance (NMR), size-exclusion chromatography, capillary electrophoresis



Production and characterization of deuterated cellulose.

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Deuteration is an established contrast tool to study the structure and dynamics of polymers with techniques such as vibrational spectroscopy, NMR or neutron scattering. In polymer science it has been usual to use chemical synthesis to produce monomers with the desired labeling of H's with ²H, from site specific labeling to per-deuteration. Biosynthesis of polymers relies on the incorporation of ²H into molecules via biochemical pathways, and so the challenges in producing the desired deuteration, both in terms of site and levels, are quite different. Here we demonstrate selective ²H labeling of sites in cellulose produced by the bacterium *Gluconacetobacter xylinus*, and characterization of this material. Cellulose and its higher level organization are unique, in that both nanostructure (unitary crystallites) and the polymer chain are simultaneously synthesized. As a consequence although -OH groups are normally exchangeable, in the case of cellulose intra-crystalline -OH groups are not normally exchangeable. In this study we demonstrate the selective labeling of various sites around glucose ring using different substrates and manipulation of the isotopic mix in growth media's water. Bacterial cellulose (BC) production which takes place in D₂O will label the -OH groups. BC production from cultures of *Gluconacetobacter xylinus* in deuterated glycerol and glucose in H₂O media allow us to label any or most of the C-H groups.

The deuteration pattern of C-H in cellulose was analysed using mass spectrometry on the glucitol hexa-acetate derivative. Partial and selective deuteration of the C-H groups is consistent with the current knowledge of the biosynthesis of cellulose which is to say that use of deuterated glucose with all C-D's (or selective deuteration), and all exchangeable H's remaining in the ¹H form; and in the case of using glycerol as a substrate results in 3 C-D's in the glucose ring. Solid state ²H NMR measurements are consistent with ²H in a relatively rigid environment. Because it is carried out in H₂O MS analysis does not give information on the relative intra-crystalline deuteration of -OH groups. IR measurements do not show any isotopic shift of hydroxyl stretch. Synchrotron wide angle x-ray scattering measurements on dried BC films do not show any major changes to either the crystal structure or the nanostructure (as evident from line broadening) due to the inclusion of ²H.

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Research interests: polymer physics, neutron and x-ray scattering, polysaccharides

Investigating the Cooking of Starch – Simultaneous Small-Angle Neutron Scattering and Rapid Visco-Analysis

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Small angle neutron scattering (SANS) is a valuable technique to characterise structure on the one to several hundred nanometre size range and has been widely applied to polymers. One of the most ubiquitous forms of polymers with which we come into daily contact is in food and, within the Bragg Institute at ANSTO, we have a research programme specifically focussed on food structure and dynamics. As a structural probe, Neutrons are particularly attractive as they are able to penetrate dense samples, complex sample environments with no sample damage.

The technique of Rapid Viscoanalysis (RVA) is widely used in the grain industry as a standard method for determining the pasting properties of starches – one of the most common naturally occurring polymers; however little is known about structural changes that occur during standard temperature-ramping protocols.

In this presentation, we describe one of our recent studies that explores the structural changes taking place in a series of commercial starches during and after cooking by simultaneously measuring the SANS and RVA on the SANS instrument, Quokka, at ANSTO.

A commercial RVA instrument was modified to include suitable apertures for the neutron beam through the heating block and a modified paddle assembly. A standard profile was used taking the sample from 30 to 95 and back to 30 degrees C over a 13 minute period. SANS measurements were made at 1 minute intervals throughout the RVA process across a q range of $0.018 - 0.2 \text{ \AA}^{-1}$. In each of the starches, the well-known lamellar structure is observed up to the point at which the viscosity begins to increase markedly. At this stage, the lamellar structure transforms almost instantaneously, the scattering patterns changing to that of a large scale structure with no apparent semi-crystalline properties and whose structure is analysed in terms of a fractal like gel. The basic building blocks of this gel, under the assumption that they are spheroids, appear to have dimensions of ca. 1 nm across all the starches tested. The sizes of the clusters they form are several times larger, vary across the time course of the experiment and have aggregate sizes showing considerable botanical variation.

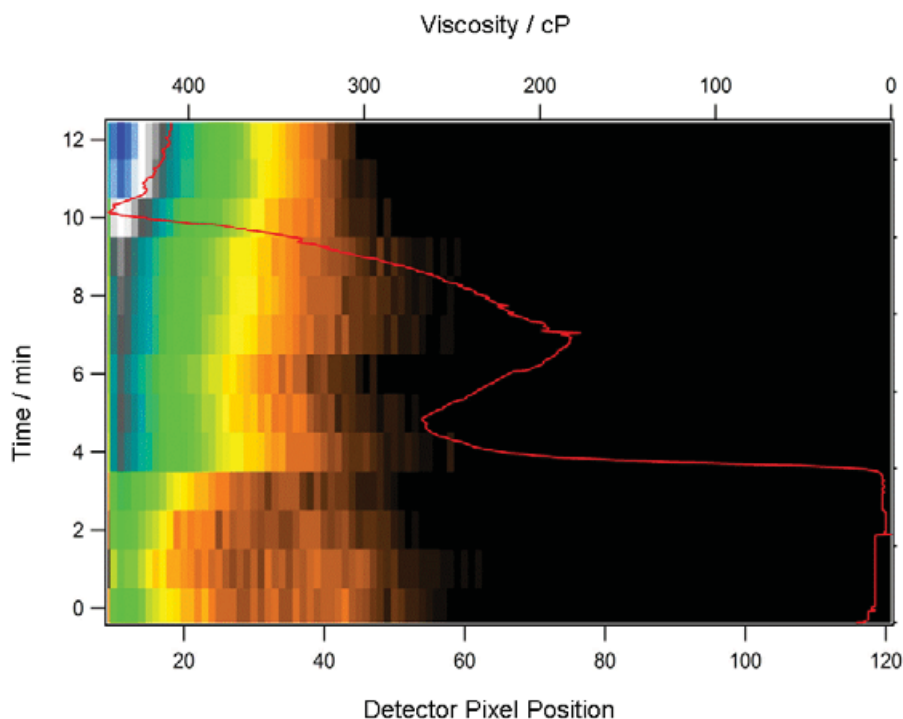


Figure 1-Simultaneous Small-Angle Neutron Scattering and Rapid Visco-Analysis from Tapioca Starch.

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Personal History

2012	Chair, International Small-Angle Scattering Conference
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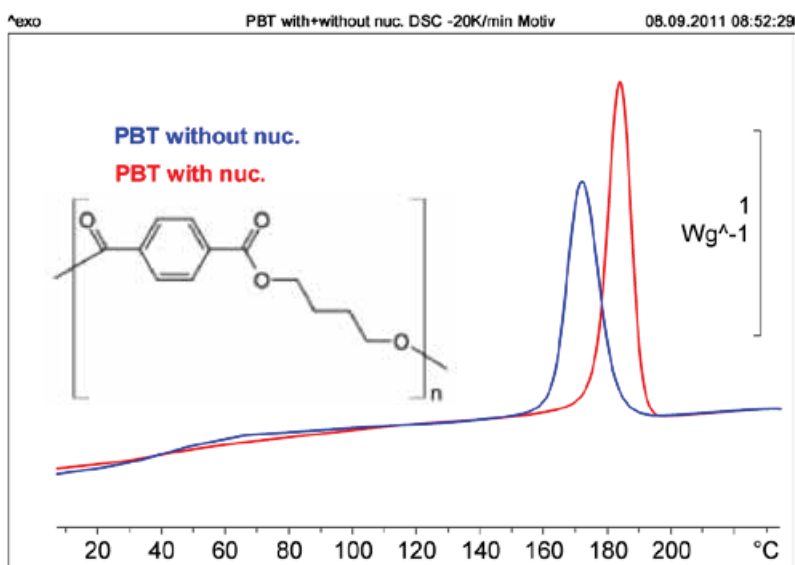
Franz Reisinger¹, Craig Gordon²

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The new Flash DSC 1 with possible scanning rates between 10 K/min and 2,400,000 K/min presents new opportunities to study materials under their technically relevant processing conditions.

This study investigates the effectiveness of a nucleating additive on the crystallization of polybutylene terephthalate (PBT) under real processing conditions compared to the usual DSC cooling rates of 20K/min (**Fig.1**) and shows how conventional DSC often does not show the whole picture.



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Investigating the Self-Assembly of Block Copolymer Films by Grazing-Incidence Small-Angle X-Ray Scattering

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Grazing-incidence small-angle scattering is a powerful technique for investigating the nano-scale structure of thin films from a few to a few hundred nm in thickness¹. Indeed the technique offers the potential to investigate the morphology in polymeric films both laterally (in-plane) and normal to the film surface simultaneously. Moreover, it is sensitive to long-range ordering and therefore provides information about the nano-scale structure over a macro-scale and is, therefore, highly complementary to direct imaging techniques such as electron microscopy or atomic force microscopy. With the recent commissioning of the SAXS/WAXS beamline at the Australian Synchrotron, Grazing-Incidence Small-Angle X-Ray Scattering (GISAXS) and Diffraction can now be routinely accessed within Australia.

Recently our group has established a program of research, which aims to design, synthesise and investigate a range of block copolymers for applications in directed self assembly and in the healing of lithographic defects. In this work we present the results from a recent GISAXS investigation of the morphology of thin films (*ca.* 30 – 100 nm) of poly(styrene)-*b*-poly(lactide) (PS-PLA) on silicon substrates. The lateral ordering within the films was studied as a function of the film thickness and thermal annealing conditions and also after modification of the surface energy of the substrate via underlayers of varying compositions. These experiments have provided information on the composition of the neutral surface and annealing conditions for the PS-PLA thin films. Moreover, the results of in-situ annealing experiments are discussed in which anisotropic long-range ordering could be induced through directed-self assembly within the x-ray beam.

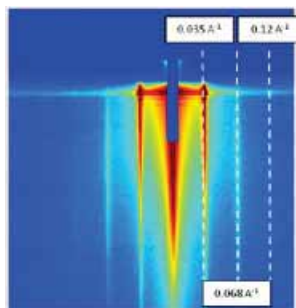


Figure 1. A GISAXS measurement taken from an aligned 50% PS-PLA block-copolymer on a neutral substrate.

¹ P. Busch, M. Rauscher, D-M. Smilgies, D. Posselt, and C. M. Papadakis, *J. Appl. Cryst.*, **2006**, 39, 433-442.

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Research interests: Structure-Property Relations, NMR, Small-angle Scattering



Versatile X-ray solutions for polymer screening, characterization, quality control and compliance testing.

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Basic concepts of X-ray Fluorescence and X-ray diffraction are explained by several applications. The examples cover applications ranging from screening for and quantification of relevant additive and environmental elements, to ASTM compliance testing. Also simple identification of polymer types for quality and recycling purposes are discussed. Finally particle sizing of nano-particle and core-shell polymers by Small Angle X-ray Scattering (SAXS) is covered demonstrating latest advancements in this field.

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Topological Assessment of Novel Polymers Subjected to Photoinduced Creep and Stress Relaxation

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Stimuli responsive polymers can undergo changes to their shape in response to a stimulus, such as light; this rearrangement of polymer strands is termed photoplasticity. Previous researchers used a radiation source of a particular UV wavelength to induce creep and stress relaxation which has the limitation where a single photon can rearrange only one bond. Our approach [1-3] uses crosslinked polymers where allyl dithioether functionalities are embedded within the polymer strands (see Fig. 1). Here, a photon produces a sulphur-centred radical

that can attack the terminal carbon of the alkene of the allylic dithioether with the simultaneous β -scission of one of the C-S thioether bonds producing another sulphur-centred radical and a new terminal alkene, thus causing topological rearrangement of the network strands. The new sulphur-centred radical can subsequently attack another allylic dithioether in a different strand continuing the bond rearrangement process, and thus giving rise to a high quantum efficiency. This process is not restricted to UV irradiation of a particular wavelength - in fact UV, visible radiation or heat can be used to generate the initial radicals. In addition, any crosslinkable monomer containing an allylic dithio (or monothio) ether group can also be used so this process is applicable to a wider range of network polymers than previous photoplastic systems.

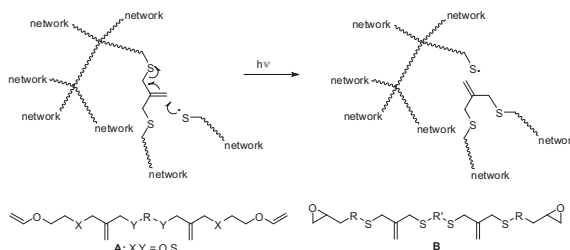


Fig 1. Photoplasticity mechanism for networks containing allylic thioether groups

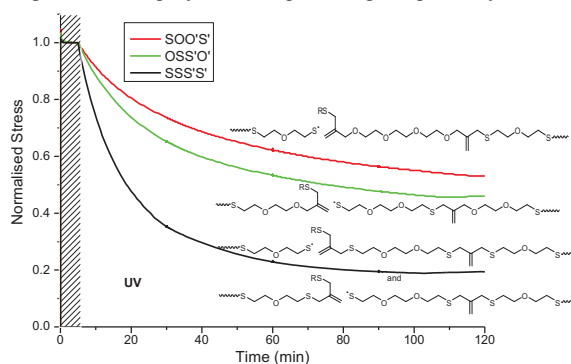


Fig 2. Photoplasticity of networks containing varying allylic thioether groups

1. Cook, W.D., *et al.*, Polym. Int., 2008. 57(3): p. 469-478.
2. Cook, W.D., *et al.*, Macromol. Symp., 2010. 291-292(Polymer Networks): p. 50-65.
3. Scott, T.F., *et al.* Science (Washington, DC, U. S.), 2005. 308(5728): p. 1615-1617.

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Mapping phase separation of deuterated/hydrogenated polymer blends using Infrared microspectroscopy

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Blending of polymers is a commonly used strategy to modify the thermal and mechanical properties of the final product. Biopolyesters, of which poly(3-hydroxybutyrate) (PHB) is the most widely studied, have been blended with many different polymers but with varying degrees of miscibility.¹ The brittle nature of PHB should be moderated by blending with more elastomeric members of this class such as poly(3-hydroxyoctanoate) (PHO), while maintaining the desirable biodegradable and biocompatible properties. This blend has received little attention because the polymers have been reported as completely immiscible and the partially crystalline nature of the two components has made determination of miscibility difficult. This study aimed to map the phase separation between these two polyhydroxyalkanoates (PHAs) using infrared (IR) microspectroscopy, and determine the effect of nanoparticle addition on their miscibility.

Conventional spatial techniques are unable to distinguish between two similar polyesters, consequently we have developed a biosynthetic route to deuterate one component of the blend allowing the observation of C-H and C-D signatures.² Deuterated octanoic acid precursor was synthesised at the National Deuteration Facility, ANSTO, and fed to cultures of *Pseudomonas oleovorans* under oxygen limiting conditions. The acid was converted to PHO and stored in inclusions within the microbial cells, which were harvested and lyophilised prior to solvent extraction and purification of the biopolymer. Solutions of dPHO and PHB (Sigma Aldrich) dissolved in chloroform were mixed at different ratios and formed into solvent cast and spin-coated films.

Regions of spin-coated films were subjected to Infrared Microspectroscopy at the Australian Synchrotron, Melbourne. IR maps (ca. 30 x 30 μm) of dPHO/PHB blends showed localised intensity of C-D signal (ca. 2000 – 2200 cm^{-1}), which corresponded to regions of low C-H intensity (ca. 2800 – 3000 cm^{-1}), indicating phase separation between the components. These results are in agreement with other investigations showing phase separation in SEM images of PHO/PHB solvent cast films.¹

Addition of single wall carbon nanotubes (SWCNTs) to PHO/PHB blend solutions at 0.5 wt% of polymer mass to determine any effect on miscibility of spin-coated films. High intensities of C-D and C-H were observed in the same regions of IR maps of these films, indicating improved miscibility of dPHO with PHB. The addition of conductive nanoscale fillers to polymer blends may therefore expand the range of applications of these biodegradable and biocompatible polymers. The chemical and biological deuteration employed in this study may be applied to investigate miscibility of various polymer combinations.

¹ A. Dufresne, M. Vincendon, *Macromolecules*. **2000**, *33*, 2298

² L.J.R. Foster, R. Russell, V. Sanguanhaipaiwong, D.J.M. Stone, J. Hook and P.J. Holden, *Biomacromolecules*. **2006**, *7*, 1344

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Characterization of polymers using high resolution impedance spectroscopy

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Introduction: Electrical impedance spectroscopy (EIS) has become a widely applied, non destructive and powerful tool to investigate the properties of the polymer electrolytes¹, films²⁻³ and membranes⁴. EIS has also been successfully used in the evaluation of the properties of polymer-coated metals and their changes during exposure to corrosive environments⁵ and to polymer degradation⁶. The fundamental principle of EIS was established in the 19th century but the precision by which the electrical properties can be monitored has been significantly improved during the last decade. High resolution EIS has been recently used for analysis of surface interaction in micro and nano-scales for various systems⁷. Electrical modelling of the accurately performed measurements has also provided useful information on the molecular and micro-structure of the samples. The case study data presented here are examples of using high resolution impedance spectroscopy for analysing various polymeric samples.

Piezoelectric polymers: Poly (vinylidene fluoride) (PVDF) is the most common piezoelectric polymer that has four known crystalline structures. Three (α , γ and π) are not piezoelectrically active, whereas the all-trans (β) phase is piezoelectric. Piezoelectric properties in PVDF can be induced using various preparation techniques such as poling in an intense electric field. We have shown that a strong electric field can impart piezoelectric properties to PVDF porous films⁸. Here, we present the electrical impedance properties of PVDF films before and after poling in an intense electrical field.

The EIS measurements show that applying pressure does not change the conductance or the impedance of an un-poled sample. But when pressure is applied to a poled membrane there is an increase in the conductance, and this correlates to an even larger decrease in the impedance. Also, the higher conductivity of the poled PVDF membrane under pressure correlates with a piezoelectric potential generated for this sample under pressure. Modelling the impedance results shows that a constant phase element (CPE) can describe the piezoelectric response of the PVDF membrane.

Polymer thin films: Polystyrene thin films were prepared by spin coating a PS/Toluene solution onto silicon wafers. High-resolution impedance identified a hydrophobic sub-layer in the polystyrene film and a series of sub-layers with electrochemical and geometrical properties consistent with a transition region in which the density of polystyrene tapers towards the film surface. The sum of the thicknesses of these sub-layers is comparable to measurement using ellipsometry⁹.

Polymer nano-composite emulsions: A dual step fictionalization method was used to pre-treat the carbon nanotubes (CNT) and in-situ emulsion polymerisation was used to synthesise PS/CNT composites. The nanocomposites showed enhanced electrical behaviour in high resolution EIS over pure PS. EIS was also able to detect the variations of electrical behaviour when different chemical species were added to the same emulsion.

EIS was also used to characterize *polymer nano-composite films, biodegradable polymer films, polymeric membranes and polymer films with different crystalline structures.*

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Separation of copolymers, conjugates and supramolecular architectures of polysaccharides, thermoresponsive and pH-responsive polymers by capillary electrophoresis in the critical conditions

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New methods for separation and characterization of complex (bio)polymers are needed to follow on breakthrough in macromolecular engineering (e.g. RAFT)¹ and polymer applications (e.g. conducting materials² or chitosan as bioadhesive³). Size-exclusion chromatography (SEC/GPC) is not used to its full potential, but its accuracy is limited for some copolymers or branched polymers.⁴⁻⁶ Liquid chromatography in the critical conditions show some powerful separations,⁷ but it is tedious and mostly limited to organosoluble polymers.⁸⁻⁹

Capillary electrophoresis (CE) is a method widely used to separate DNA and proteins but barely used for other polymers. CE can be performed with a gel as separating media, but also without gel, then named free solution CE. Free solution CE separate oligomers with a higher resolution than SEC.^{10,11} For degrees of polymerization typically above 10, there is no separation according to degree of polymerization (/molecular weight). This corresponds to the type of separation sought in liquid chromatography in the critical conditions. We apply capillary electrophoresis in the critical conditions (CE-CC) to separate copolymers according to their composition, branched polymers according to branching and polyelectrolytes according to end-groups.

CE-CC separates polysaccharides according to their composition, namely the degree of acetylation in the case of **chitosan** and the degree of acylation for **gellan gums**. Synthetic **block copolymers** can also be separated including **pH-responsive** and **temperature-responsive** ones. Hybrid copolymers, such as DNA **conjugates**, can be separated as well as branched **polypeptides**. Moreover, polyelectrolytes such as functionalized DNA can be separated according to their end-groups (i.e. their functionalization). Supramolecular assemblies, such as aggregates of **amyloid peptides**, **DNA complexes** or **silicones**, can also be separated.

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Polymeric Theranostics: Hyperbranched Polymers for Treating Disease

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Recent synthetic advances that facilitate control over polymer structure and functionality have led to the advent of polymer theranostics; devices capable of both diagnosing disease and providing a treatment. While the potential application of such devices is tremendous, *in vivo* monitoring remains a significant scientific challenge. In this report we present recent work on the synthesis of hyperbranched (meth)acrylates¹ for imaging and cancer therapy.

While the ultimate aim in polymer theranostics is the development of a multi-modal, multi-functional, biodegradable delivery device with the possibility of facile conjugation of therapeutics, imaging agents and targeting moieties, current methodologies are plagued by poor drug loading, inefficient cell uptake, targeting inefficiencies, synthetic complexities or a combination of all of these factors. Here, we discuss the properties of hyperbranched polymers and show how they offer a unique solution to many of these problems: they are ideal for this technology because they have the potential to combine many different functionalities (and hence chemistries) into a single molecule; their structural non-uniformity, yet highly controlled size, volume and intramolecular dynamics facilitates structural rearrangements not possible in many other theranostic analogues.

Here we demonstrate how RAFT chemistry can be used to introduce multiple functionalities within a molecule that can subsequently be utilized for drug conjugation or application in magnetic resonance imaging (MRI) by correct choice and placement of monomers. In this report we present the synthesis and characterisation of such polymers and describe both *in vitro* and *in vivo* data on the application of these molecules as drug delivery devices (both siRNA and chemotherapies) and as multimodal imaging agents (MRI and fluorescence). Fig. 1 depicts a cartoon of a hyperbranched polymer that contains ¹⁹F MRI and fluorescence modalities for imaging and folate ligands for targeted therapies; *in vivo* images demonstrate the efficacy of both multimodal-imaging and tumour targeting.

In conclusion, hyperbranched polymers for drug delivery and imaging have been synthesised by a controlled free radical technique with the overall aim of developing the field of polymer theranostics. Various ligation technologies have been used to attach cell-targeting moieties, drug molecules and other markers to the molecule.

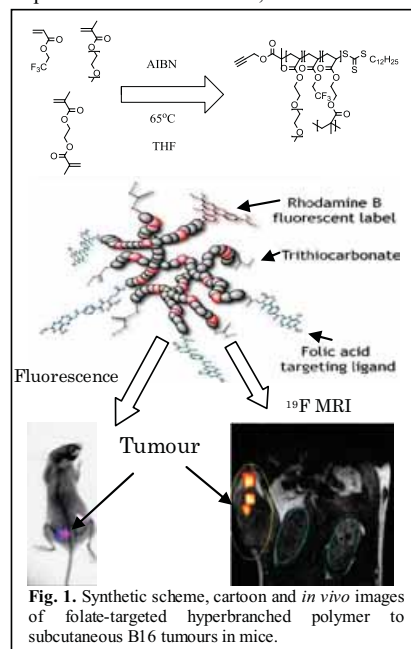


Fig. 1. Synthetic scheme, cartoon and *in vivo* images of folate-targeted hyperbranched polymer to subcutaneous B16 tumours in mice.

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Biosensor and Drug Delivery Technology through Surface Modification

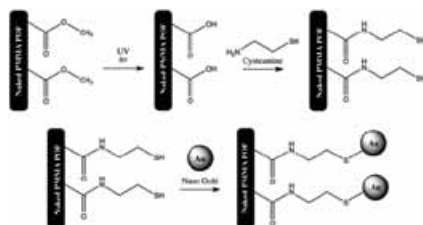
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The surface modification of substrate materials to alter environmental interactions and binding/fouling properties has been a typical chemical procedure for several decades.¹⁻² The use of polymer brushes, through techniques such as “grafting from” and “grafting to”, have been a popular approach to alter both the functionality of the surface in question as well as the density of the binding sites. The synthesis of modified surfaces by grafting polymer brushes has led to unique properties and applications, such as colloidal stabilization, surface property tailoring, “chemical gates”, and microlithographic patterning. These techniques allow for high polymer grafting densities with specific and regular functional groups, which is a key component of biological and chemical binding.

Currently, we are investigating these, and other, surface modification techniques from various substrate materials and configurations for their potential in the biotechnology arena. Polymeric nano- and microspheres are attractive devices for use in the fields of bioseparation and drug/enzyme carriers.¹ Using silica particles as removable cores to develop hollow materials, we’ve begun to use polydopamine³ and polydopamine derivative coatings to act as scaffolds for drug carriers. By coupling these materials with protein specific glycopolymers and degradable cross-linking agents, these polymeric particles can also be used for targeted drug delivery applications. This simple, mussel-inspired scaffold technique has also been the basis of encapsulating quantum dots into these same devices, for generating simple image contrast agents with biorecognition moieties as well as coating magnetoelastic substrates for biosensors devices. Magnetoelastic materials are typically amorphous, ferromagnetic compounds which are capable of undergoing elastic deformation in response to a time-varying magnetic field. Furthermore, these materials are also magnetostrictive, that is as the materials mechanically deform, they will induce a magnetic field which is related to the mass of, and on, the material. Thereby, simple wireless biosensors can be designed with an appropriate analyte recognition functionality on the surface. Finally, we have made biological sensors from optical fibres utilising the surface modification of PMMA fibres with gold nanoparticles. The gold acts as a cladding layer which can also be further modified with RAFT generated polymers using a “grafting to” approach. As analyte materials bind to the functional sites on the polymer brushes, the intensity and wavelength of the light traveling through the fibre is altered, thus allowing for attenuation and it’s usage as a photonic sensing device.



Scheme 1. Modification of PMMA optical fibres with gold particles.

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2004-2007	Research Associate, CAMD, University of New South Wales
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Research interests: surface modification, controlled radical polymerisation systems, novel biosensor devices

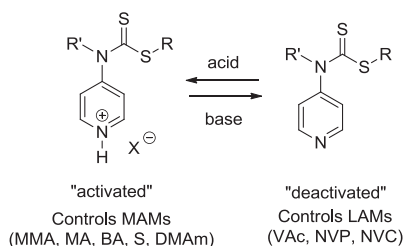


Acid/Base “Switchable” Chain-Transfer Agents for RAFT Polymerization

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Unlike conventional reversible addition-fragmentation chain transfer (RAFT) agents, acid/base “switchable” dithiocarbamates (**Scheme 1**) offer a high level of control over polymerization of both “more-activated monomers” (MAMs, i.e. (meth)acrylates, (meth)acrylamides, styrenics) and “less-activated monomers” (LAMs, i.e. vinyl esters, vinyl amides).^{1, 2} This is accomplished by using the “switchable” RAFT agent in either its protonated (activated to control MAM polymerization) or neutral (deactivated to control LAM polymerization) form. This new class of RAFT agent allows access to polyMAM-*block*-polyLAM copolymers, with narrow molecular weight distributions, which are unobtainable using standard RAFT techniques.

Recently, we demonstrated that this methodology is compatible with aqueous reaction media by preparation of low dispersity poly(dimethylacrylamide).³ In this presentation some recent developments in the area of “switchable” RAFT polymerization, including the effect of RAFT agent structure on chain-transfer kinetics, will be discussed.



Scheme 1: Acid/Base “Switchable” Dithiocarbamate RAFT Agents

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Research interests: Free radical polymerization, Organic synthesis



Setting up and starting a spin off company: The story of Warwick Effect Polymers

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Following work in the mid 1990's and filing of key Intellectual Property by the University of Warwick I had to make a decision on what on earth we should do with this. The decision was to spin off a company and see if we could successfully exploit the research. This started a journey of raising capital from individuals (so called Business Angels) and seed corn Venture Capital organisations. The journey included finding a premises, building a fully equipped laboratory, recruiting scientific and non scientific staff. In turn the organisation had to be run and we had to learn how to pay people, taxes and suppliers as well as dealing with our customers. Along the way we raised, and spent a few million (pounds) and have dealt with small and major organisations. As well as exploring exploiting the science it has involved meeting many people from different walks of life including lawyers, business development people, accountants and CEO's. Thus many challenges have been met with some overcome and some providing difficult obstacles. This talk will describe this journey and the learning points that have arisen along the way.

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Intellectual Property and Science – an overview

Ramon Tozer

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With increasing awareness amongst scientists of the potential value in their intellectual property, in order to effectively capture that value it is important to have an appreciation of a number of fundamental issues. This presentation will provide an overview on what exactly is "intellectual property", when should you consider seeking protection for it, and the process involved in seeking that protection.

The presentation will have a particular emphasis on protecting intellectual property by way of filing a patent application. In that regard, a practical overview of the patenting process will be provided, together with a discussion on pitfalls to avoid along the way.

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Collaborative Industry Driven Polymer Research in Australia

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Since 1992 the Cooperative Research Centre for Polymers (CRC-P) has been conducting collaborative polymer research projects with companies to develop products that provide economic and environmental benefits to Australia. It is the largest collaborative polymer research centre in Australia, linking Australian polymer scientists with scientists from other areas of economic and research strength to address problems of global importance that include health, sustainability, water and energy. Some examples of research undertaken by the Centre will be discussed against the background of the evolving nature of industrial research in Australia and the pursuit of clean technologies.

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Beyond patents – forms of intellectual property protection*Richard Grant*

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This paper will describe a range of different forms of intellectual property protection and will discuss the different uses for each. These include:

- Patents – for protecting an invention
- Trademarks – for protecting a means for identifying the origin of a product
- Design registration – for protecting the appearance of a product
- Copyright – for protecting an original work
- Trade secrets – for protecting confidential information
- Domain names – for protecting web addresses
- Plant breeders' rights – for protecting varieties of plants and fungi

Ways in which these various forms of protection may be used in combination to provide more effective protection will also be discussed

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THE MATERIALS ACCELERATOR: A NATIONAL NETWORK IN MANUFACTURING MATERIALS

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The Materials Accelerator is a New Zealand national capability network which seeks to develop transformational multi-material products in cooperative R&D partnership with innovative high-technology companies. The programme has a mandate to operate from basic research to commercial products. It has demanding commercial contractual targets including numbers of engaged companies, co-funding and revenue enhancements.

The Materials Accelerator has multi-disciplinary teams of researchers drawn from various organisations with multi-materials expertise in composites, plastics, conducting polymers, nanotechnology, light metals and steel. It also has network of members with expertise in prototyping, virtual manufacturing, industrial design, materials analysis, modelling, interfacial analysis and materials testing. The network also has access to micro-fabrication facilities. The Materials Accelerator Network which is hosted by the University of Auckland (UA) includes contributions from 5 Universities and 3 Government Laboratories (Crown Research Institutes). These partners include Scion, IRL, GNS, AUT, VUW and more recently U Canterbury and U Waikato. It also includes contributions from 10 research centres within the University of Auckland. The number of applied researchers associated with the network is approximately 100. There are approximately equal numbers of engineers and scientists contributing to the overall list of commercial projects.

The Materials Accelerator programme has involved interviews with 230 companies across several sectors, discovering their pain points, materials strategies, platform themes and identifying lead companies. Each of the shortlisted companies contributes to a confidential brainstorming process (Joint Technology Planning or JTP) with a selected team of researchers drawn from the network. The Materials Accelerator has already developed technology platforms in aerospace, construction, agri-tech, air-quality and telecommunications which involve innovative high-technology companies. Each of these combinations of platforms and lead companies are generating joint technology projects which have major commercial impact. The joint commercial projects with lead companies involve Project Managers, Principal Investigators (selected from the network) and Masters students.

To fill capability gaps across the various technology platforms several PhD projects have been launched in basic research. These PhD students are supervised by inter-materials multi-provider teams of Principal Investigators drawn from the network.

As an international extension to this programme, a study leave survey was conducted which involved 8 countries (EU and North America), which involved identifying international best practice in researcher-industry partnership, and in cooperative research. This survey included visits to 40 research or innovation centres, and it included approximately 100 interviews with research leaders, agencies and funders.

Acknowledgements. *Funding is from Ministry of Science and Innovation TRST The Materials Accelerator UOAX0819*

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When and How to Patent an Invention

Sarah Whitehead and Grace Chan

Phillips Ormonde Fitzpatrick

When a project has potential applications in industry, one of the considerations for researchers will be what should be done with the results? Should they be made freely available to others, for example by publishing in a journal? Should they be kept confidential to try and prevent others from exploiting the findings? Or should they be protected by filing a patent application? This presentation will discuss these options and particularly focus on factors that should be taken into account when deciding whether or not to file a patent application.

If a patent application is then filed, there will be certain stages throughout the application process where further decisions need to be made. For example, will we want to add more experimental findings to the application? Should we file this application in a number of countries or just 1 or 2? Is it important for the patent to be granted quickly, or do we want to try and delay incurring costs for as long as possible? This presentation will discuss various options for how a patent application can proceed and factors that will determine which option is the most suitable.

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Research interests: Polymer chemistry, organic synthesis, biochemistry



Polymer 'tools' for probing ecological questions in the marine environment

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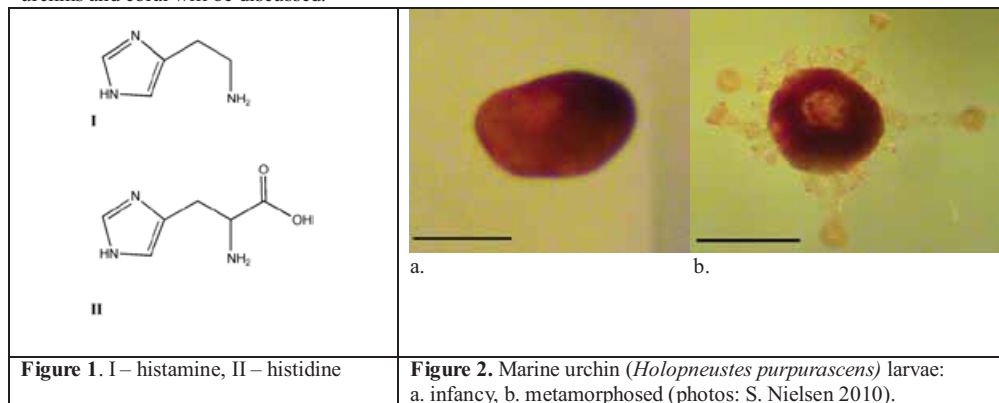
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Traditionally, technical applications of polymers toward biofouling (e.g. living paints¹) and potential biodegradable marine polymers (polyhydroxyalkanoates²) are notable examples of how polymers can be applied in the marine environment. However, importantly, polymers assist experimental designs to test ecological based enquiries in the marine environment. Underwood et. al. reported on how "sticky plastic polymers" were used to prevent insect larvae from crawling into intertidal treatment plots.³ Our research group's ability to produce polymer products capable of delivering bioactive cues provides material to perform comprehensive ecological field studies. For example, examining the ecological impact of a polymer substrates with histamine or histidine endgroups (**Fig. 1**) as well as the role of primary and / or secondary amines in the metamorphosis of urchin larvae (**Fig. 2**)⁴. This ability to induce metamorphosis and settlement of urchin larvae on a synthetic surface enables aquaculture enhancement as well as ecological studies into the juvenile phase of urchin lifecycles.

A further example of ecologically applied polymer science examines how copper (and possibly other metal ions) chelated into organic cyclens on the surface of polyvinyl chloride (PVC) could be used to study the settlement and inhibition of settlement of coral species such as *Acropora tenuis* on to these PVC surfaces.⁵

This paper will discuss examples of polymer chemistry constructs used to investigate ecologically relevant challenges in the marine environment. In particular, settlement and metamorphosis of marine species such as urchins and coral will be discussed.



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Investigation of Native Spinifex Plant Resin and Fibers as Renewable Building Blocks for Composite

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Spinifex grasses are the predominant species in Australian grassland habitats, and in fact cover approximately 27% of the Australian landmass. Threshed spinifex fibers and resin could potentially be used as reinforcement and Matrix components respectively, for natural fiber composites ¹. Spinifex resin is a thermoplastic bioorganic polymer, which is a mixture of volatile and non-volatile compounds and secondary metabolites ². Current research efforts are focused on spinifex resin extraction with different organic solvents. We have characterized the resin derived from native Australian *Triodia Pungens* grass and investigated the effect of different extraction parameters on the resin's glass transition temperature, functional groups, thermal degradation properties and extraction yield. Different extraction methods gave Rise to different property profiles and functional groups. Extraction using acetone produced resin with the highest T_g (Fig.1) and yield. It is important to choose an appropriate solvent to grass ratio for obtaining the high yield and low solvent consumption. The solvent removal process involved oven drying for 72 hours in order to evaporate volatile components effectively (Fig.2). Furthermore, higher drying temperatures resulted in higher resin T_g values and thermal degradation properties, in part due to the removal of more low molecular weight volatile components, and also due to the interaction of functional groups to form 3D networks (Fig.3). Moreover, producing nano cellulose form spinifex grass for making nano paper was successfully attempted. The delignification of spinifex grass with ethanol solution, followed by bleaching with sodium chlorite acidic solution caused the removal of lignin and the other waxy compounds from the surface of the fibres, and nano paper samples were subsequently prepared from a micronized cellulose product.

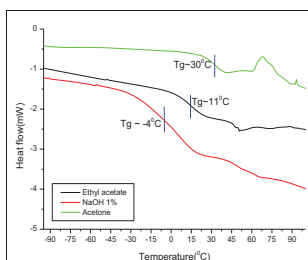


Figure 1. DSC spectra of extracted resin with different solvents

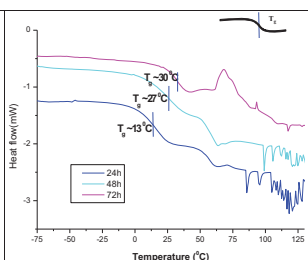


Figure 2. DSC spectra of resin at different drying time

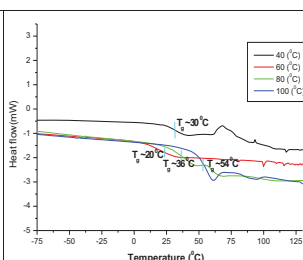


Figure 3. DSC spectra of resin at different drying temperature

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Since 2010 PhD in Bioengineering and Nanotechnology, University of Queensland, Australia

Research interests: Biomaterial, Fibers Nanotechnology, polymer nanocomposite



Influence of Soils Type on the Above-Ground Degradation of Polyethylene Thin Films

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Polyethylene is widely used for various applications, such as food packaging and agricultural applications (greenhouses and mulch films), which leads to the accumulation of large quantities of plastic waste in the environment. To increase the rate of polyethylene (PE) degradation in the environment, it is necessary to add prodegradants to enhance the photo- and/or thermo-oxidation of the plastic

Several studies have investigated the photo- and/or thermo-oxidation of PE buried in soil or compost^{1,2}. However, limited literature is available on the above-ground degradation of PE on soil, which is a result of the photo-thermal oxidation combined with the biodegradation induced by the soil. The rate of PE degradation can be influenced by the type & concentration of prodegradants and also by the environmental factors, such as type of soil³, UV spectral irradiance and dose, air temperature and humidity. Evaluation of the impact of these environmental factors in addition to the effect of soil type on the above-ground degradation of PE needs to be defined, to allow for the development of PE films with predictable and reliable above-ground degradation.

This study evaluates the above-ground degradation of PE films on different soil types using accelerated weathering device, referred to as a Q-Sun. This device simulates day & night cycles, whilst controlling the air temperature and humidity. The characteristics of the soils used in the study are shown in **Tab. 1**.

Table 1. Soil Characteristics.

Soil	Krasnozern	Commercial soil
texture	Medium Clay	Coarse sandy clay loam
colour	Red Brown	Grey
pH (water)	7.1	7.2
% organic matter	6	4.5

The impact of these environmental factors and soil type on the above-ground degradation has been investigated for PE films containing combinations of TiO₂ & Fe (II) stearate prodegradants. FTIR-ATR was used to measure the extent of oxidation by characterisation of the carbonyl index, followed by UV-Vis spectroscopy and SEM to monitor changes in film opacity and topology during oxidation. **Fig. 1** presents the time to embrittlement for a film containing TiO₂ over different soils. Preliminary results suggest that organic matter within the soil may impact upon the rate of above-ground degradation of PE.

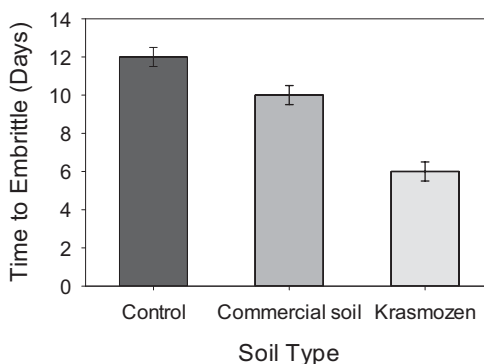


Figure 1. The effect of soil type on the rate of above-ground degradation of an oxo-degradable PE.

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Research interests: from Polymer processing to its degradation.



Dielectric investigation of novel reprocessable ionomers based on Natural rubber*Georgekutty Joseph¹ Thommachan Xavier²*¹Department of Physics, Sacred Heart College, Thevara, Kochi- 13, Kerala, India.²Department of Chemistry, Sacred Heart College, Thevara, Kochi- 13, Kerala, India.

Novel reprocessable ionic polymers based on Natural rubber¹ are synthesized by the sulphonation of natural rubber, followed by its neutralization with zinc salt. The oven dried samples of ionomers are characterized spectroscopically. The electrical properties of ionomers are probed by complex impedance spectroscopy. The ionomers are cut into blocks having thickness of 1mm. The electrical investigation is made in the frequency range 500Hz – 4MHz. The variation of AC conductivity with frequency revealed that the electrical conductivity is an increasing function of frequency, obeys Jonscher's universal power law. The power law parameters are also found out. The value of the frequency exponents is found to be less than 1. The cole-cole plots revealed the ionic conducting nature of these ionomers. The bulk resistance, bulk capacitance and relaxation time has been found out from the cole-cole plot. The loss tangent decreases with increase in frequency and the value of loss tangent proved that the samples are medium loss materials.

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Wholly Printed Polypyrrole-based Biosensors on Flexible Substrate

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Trends including aging populations in western countries, increasing environmental legislation, the rise of genetic technology, and the emergence of such ubiquitous computing become growth drivers for the development of sensor applications. The increasing demands for low cost, mass-producible sensor products promise a vast and rapidly evolving market to the sensor manufactures. Printed chemical- and bio-sensors represent distinct opportunities in specific key area of this market such as point-of-care medical diagnostics and smart packaging. Among all the printing techniques, inkjet printing shows great potential to revolutionize the production of the sensor interface for its speed, cost and automation. Inkjet printing is a non-contact and non-impact printing technique which does not need a plate and surface contact during printing. It is also a “drop on demand” system that can transfer designed patterns onto various conductive and non-conductive substrates. These unique advantages illustrated the potential of inkjet printing as a technique for new sensor production in the future.

Conducting polymers have been utilized as electrode materials in biosensing applications as electrons can transfer between conducting polymers and biomolecules (hydrogen peroxidase (H_2O_2), glucose, et al.) during redox procedure. This electron movement can be monitored by electrochemical methods such as CV and amperometry. The obtained results have been found to be related to the concentration of biomolecules thus conducting polymers were suitable for sensor materials. PPy was the first conducting polymer that has been utilized as biosensor. However, the fabrication of PPy biosensors was seriously limited by the poor process ability of PPy. Recently, an inkjet printable PPy nanoformulation¹ was developed in our lab and examined suitable for sensor application.

In this work, we look into developing wholly printable electrochemical sensor chips, using printable conducting polymers inks and enzymes to impart functionality and selectivity. This, we believe, is a truly viable, low-cost route to mass producing devices for commercially relevant sensing applications. Enzymes were incorporated into inkjet printable PPy nanoformulation synthesized in our lab as previously reported to introduce biosensing functionality into the ink. HRP or GoD was simply mixed into the PPy formulation and the resulted ink was inkjet printed to screen printed carbon electrodes (SPCEs) then encapsulated by ethyl cellulose (EC) membrane which was also deposited by inkjet printing. CV and amperometry was used to characterize the printed sensors. Current response varied when the loading of PPy and enzyme changed. The linear range of detection of H_2O_2 was found to be $10\mu\text{M}$ - 10 mM and for glucose was 1 - 5 mM .

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Thermal Degradation Study of a Polyimide Foam

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Main text: A type of polyimide foam (PIF) was prepared successfully based on a one-pot process by the reaction of a first solution and a second solution. The first solution was mainly comprised of pyromellitic dianhydride (PMDA), and polyethylene glycol. And the second one contained polyaryl polymethylene isocyanate (PAPI). In the present study, the polyimide foam possessed excellent thermal stability with the decomposition-starting temperature of 280 °C and the 5% weight loss temperature of 320 °C. Meanwhile, it showed a two-stage degradation process during the whole decomposition process with the residual weight retention value at 750 °C of 61.2%. When the pyrolysis temperature rose up to 550 °C, ten kinds of pyrolysis products were identified including the major products of O₂, CO₂ and methyl formate. According to the degradation behaviors and the structure and relative content of pyrolysis products, the pyrolysis process and mechanism of polyimide foam can be described as follows. The carbon-oxygen and carbon-carbon bonds in the polyethylene glycol segment can break into radicals easily because of their low bond energy. So the methane, ethylene, methyl, vinyl and ethoxyl are derived from the cleavage of the polyethylene glycol segment. The carbon-nitrogen and carbon-carbon bonds in the imide rings can break at higher temperature, producing CO, O₂, benzamide and radicals. Oxygen radicals derived from the cleavage of carbonyl group (C=O) in the imide rings can combine with CO and form CO₂. Cyanophenyl is produced when H₂O is separated from benzamide at higher temperature. *M-dicyanobenzene* is generated by the cleavage of CO₂ from the imide radicals. The carbon-carbon and carbon-nitrogen bonds in the isocyanate segment break at higher temperature, producing hydrogen cyanide, phenylamine and phenyl through hydrogen transfer reactions. Styrene can be generated by the combination of vinyl and phenyl through radical reactions and hydrogen transfer reactions. The phenylamine groups generated by isocyanate groups and H₂O are cleaved from the main chain, which forms phenylamine. Methyl formate is pyrolyzed from part of the ester derived from the esterification of pyromellitic dianhydride and methanol. Propionaldehyde, butanone, acetol and other compounds are produced by a series of radical coupling/disproportionation termination reactions, mono-radical termination reactions, chain transfer reactions, hydrogen transfer reactions, isomerization reactions and secondary reactions.

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Using SAXS to make real-space models of photo-oxo-degradable LLDPE as it ages

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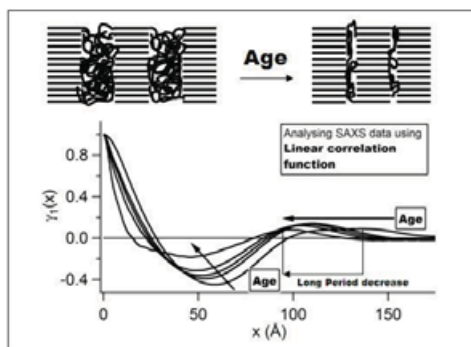
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The use of polyethylene (PE) films for agricultural applications is a well known technique used to improve crop growing conditions. Agricultural PE films are used on broad acre crops and their stability, which aids their application, actually poses a waste problem after the film's useful life. This has led to the development of time-controlled photo-oxo-degradable PE films, where with oxidation the film loses its ductility and becomes brittle after use in the 6-9 months crop cycle.

The development of these time-controlled photo-oxo-degradable PE films have been a challenge as the PE degradation process is complex and is governed by many factors: film composition (molecular properties and additives), processing methods (affects the crystal morphology & physical properties) and methods of ageing¹. A better understanding of the relationships between these factors will improve the development of time-controlled photo-oxo-degradable PE films with the desired lifespan.



Top: a lamellar semicrystalline system with decreasing long period and increasing crystallinity. Bottom: Linear Correlation Function² data calculated from SAXS, from which real space parameters are extracted

In this paper, the crystal morphology of a commercial grade *linear low density polyethylene* (LLDPE), Dowlex 2045G, with Ampacet 30091 pro-degradant (Ampacet) system was studied using small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS). We show and explain use of the Linear Correlation Function² to extract real-space parameters from SAXS, watching long period, lamellar thickness and the interfacial width evolving with the UV age of the films. Data show that long period and interfacial width decrease with age alongside only small increases in the lamellar thickness. Importantly, the degree of crystallinity may be extracted quantitatively from SAXS and is higher than that estimated from WAXS.

¹ S. Fatahi, et al., *Journal of Plastic Films and Sheeting*. **2005**, 21, 281-305

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Research interests: responsive/functional polymers, nanostructured polymers, polymer physic, polymers at surfaces and interfaces



Improving the Interfacial Properties of Polylactide/Jute Biocomposites by Application of Amphiphilic PEG-PLLA Block Copolymers

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Government regulations and growing environmental awareness throughout the world, requires moving towards the design of composite materials which are more and more eco-friendly. In this frame of mind, the combination of natural biodegradable fibres and biodegradable, renewable polymers is particularly attractive. The focus on the use of natural fibres in conjunction with biopolymers to produce eco-friendly composites has increased considerably over the past few years. Nevertheless, their application has been somewhat set back because of the quality of the interfacial adhesion between the fibre and host matrix, substantial for the mechanical properties of the resulting biocomposite, can be limited. This study investigated various methods to improve the interfacial properties between the hydrophilic jute and hydrophobic polylactide matrix. Two chemical surface modifications were carried out using alkali treatment with sodium hydroxyl or esterification of the pendant hydroxyl group of cellulose with stearic acid. Surface adsorption of amphiphilic PEG-PLLA block copolymers having various hydrophobic/hydrophilic ratios was also investigated. Jute/polylactide bio-composites having a fibre volume fraction over 43% were produced by compression moulding and their flexural, thermo-mechanical and impact properties were tested. The strength, stiffness and storage modulus of the bio-composites showed a reasonable increase after PEG-PLLA treatment while their impact properties remained comparable. The findings of the study showed that the compatibility and interfacial properties in this system can be improved using surface adsorption of biodegradable amphiphilic block copolymers. It is believed that strong interfacial interactions such as hydrogen bonds are formed across the interface between the two components and account for the improved adhesion in the system.

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New opportunities in renewable polymer and functional materials

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There is significant global momentum around the (re)emergence of bio-derived feedstock for the chemicals and polymer industries. Many of the current renewable polymer modifiers are normally unsuitable due to reliability of cost and / or supply or their relative performance to incumbent technologies. CSIRO's research in the areas of woody biomass, industrial oils and complex monomers is aimed at the production, evaluation and modification of novel oil, fatty acid and woody biomass building blocks for a range of industrial applications including:

- renewable chemical intermediates
- renewable polymers
- oligomers
- cross-linkable polymers
- bioactive compounds
- fuel additives
- thermo/mechano-chromic devices

CSIRO believes that there are significant opportunities in the production of woody biomass based polymer modifier and oils/fatty acids with novel/improved functionality. We have investigated the synthetic and biological production of a range of structures and their utility in the chemicals and polymers industries (replacement of petrochemical derived monomers and polymers, novel multifunctional materials, biobased/biodegradable polymers).

Alpha-hydroxy fatty acids for example have a range of interesting properties, some of which are strongly influenced by the self assembly properties of the 2-hydroxy fatty acids. Uses for these novel fatty acids include:

- monomer/modifier for commodity polymers (polyurethanes, polyesters and polyamides)
- adhesives
- materials to produce optoelectronic devices

Cineol diol – an example for a woody biomass derived polymer modifier – has the potential to improve the thermo- and barrier properties of a range of polymers – regardless of bio- or petrochemical derived.

This paper will cover synthesis methods for the functionalization of fatty acids, fatty acid derivatives and cineol diol derivatives as well as their applications. CSIRO's research activities in these areas offer a shift in novel polymer modifiers and opens up access to new and sustainable product platforms for the chemical industry.

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Personal History

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Since year	Industry (Petroleum, Composites, Coal)

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Antagonism Between Transition Metal Prodegradants

In Accelerated Photo- and Thermo-Oxidation of Polyethylene Films

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The photo- and thermo-oxidation of polyethylene thin films containing combinations of Titanium (IV) Dioxide (TiO₂), Cobalt (II) Stearate (CoSt) & Iron (II) Stearate (FeSt) has been evaluated under accelerated laboratory and real outdoor weathering conditions. The impact of these prodegradant combinations on the rate and degree of polyethylene degradation has not been previously investigated and elucidating an understanding of the effectiveness of this combination is important for the effective design and use of oxo-degradable plastics. The accelerated laboratory thermo-oxidative results have shown that the presence of TiO₂ in combination with CoSt or FeSt, did not significantly impact on the rate of polyethylene degradation compared with TiO₂ alone, but was controlled by the type and concentration of transition metal stearate. However, under accelerated laboratory photo-oxidative conditions, the rate of polyethylene oxidation was significantly decreased for TiO₂/CoSt combinations and to a lesser extent TiO₂/FeSt compared to TiO₂, CoSt or FeSt alone at identical metal ion concentrations. Real outdoor weathering results confirmed the photo-induced antagonism effects for TiO₂/CoSt combinations by a significant decrease in the rate of polyethylene photo-oxidation.

Further investigations revealed that the redox potential of the metal ion from the transition metal stearate and their interaction with the photo-induced band edge potentials of the TiO₂ nanoparticle, dominate the influence on polyethylene film photo-oxidation rate (Fig.1).¹

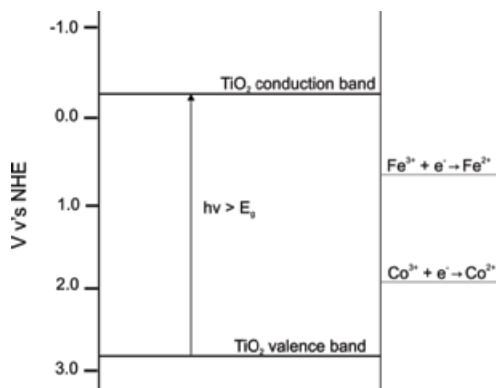


Figure 1. Schematic illustration of the valence and conduction bands of Degussa P25 Titania (80% anatase) at pH 7.0 with corresponding reduction (e⁻) and oxidised (h⁺) sites along with standard reduction potential of Fe³⁺ & Co³⁺ metal ions. Adapted from Brezová et al.¹

¹V, Brezova, A. Blazkova, E. Borosova, M. Ceppan, R. Fiala, R. *J. Mol. Catal. A: Chem.* **1995**, 98, 109.

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Determination of Monosaccharides from Chemically Hydrolysed Polysaccharides for the Biofuel Industry.

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The search for alternate substrates continues as the current biofuel industry is based on food crops or on land suitable for food crops. Research into alternative feedstock for the bioethanol industry is being lead into natural non-food based substrates. The polysaccharides of these feedstock range in complexity of the monosaccharides composition and bonds. Currently there are very few methods that can breakdown carbohydrates and analyse the monosaccharide compositions of these materials without interference from other compounds. The popular methods of analysis are based on Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC)¹. When the sample composition is qualitatively known, these methods are unmatched. Free Solution Capillary Electrophoresis (CE) can qualify and quantify unknown samples with little to no sample preparation or interference due to salts, pH levels, acids, bases, solvents etc.² The separation is achievable in the case of monosaccharide's by using a buffer pH above the pKa of the analytes³⁻⁴.

The presentation focuses on the comparison of current HPLC and CE techniques used for monosaccharide determination derived from polysaccharide hydrolysis as well as the development of a CE method that is robust when applied to 'real' sample analysis.

¹M. Suárez, A. Redondo-Cuenca, M. Rodríguez-Sevilla, M. Martínez, *J. Agric. Food Chem.*, **2003**, 51, 5950–5955

² M. Gaborieau, T. J. Causon, Y. Guillaneuf, E. F. Hilder, P. Castignolles, *Aust J Chem.* **2010**, 63, 1219-26

³S. Rovio, J. Yli-Kauhaluoma, H. Sirén, *Electrophoresis*, **2007**, 28, 3129-3135

⁴S. Rovio, H. Simolin, K. Koljonen, H. Sirén, *J. Chromatogr. A*, **2008**, 1185, 139–144

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Personal History

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Since 2010 PhD student, University of Western Sydney (UWS)

Research interests: Fermentation Science, Biotechnology, Microbiology,
Analytical Chemistry, HPLC, Capillary Electrophoresis.



Modeling of polymer network formation by nitroxide-mediated radical copolymerization of vinyl/divinyl monomers using a multifunctional polymer molecule approach

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A new mathematical model for the kinetics of nitroxide-mediated radical copolymerization with crosslinking of vinyl/divinyl monomers has been developed. Polymerization rate, molecular weight development, gelation point, gel content, crosslink density, copolymer composition and concentrations of the different species involved in the polymerization mechanism can be calculated with the model. With the aim of describing the kinetics of network formation, a reaction scheme considering multifunctional polymer molecules was proposed. In order to simplify the mathematical treatment of the copolymerization reaction, the “pseudo-kinetic rate constants method” was employed. The method of moments was used to obtain average properties of the multidimensional distribution. Flory-Stockmayer’s theory was used for the post-gelation period. Two approaches were used for calculation of average crosslink and cyclization densities. The first method represents a history-dependant approach similar to the one used by Tobita and Hamielec¹ for the conventional case. In the second method the rate of crosslink and cyclization reactions is calculated using a kinetic approach.² The model was validated using experimental data reported in the literature. Several conditions were examined, showing good agreement in all cases as shown in Fig.1. It was found that the presence of NMRP controllers has an important effect on the kinetics of network formation, delaying gelation. According to our results, overall monomer concentration, controller/initiator ratio and crosslinker initial concentration are the governing factors for the development of average crosslink and cyclization densities and, therefore, for the homogeneity of the resulting polymer network.

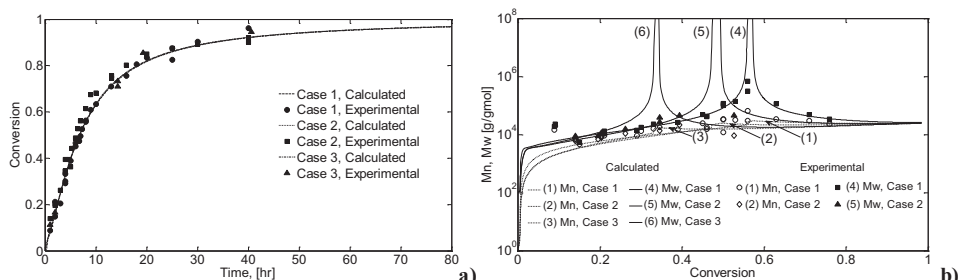


Figure 1. Comparison of experimental and calculated profiles of a) Conversion versus time and b) number and weight-molecular weight (M_n , M_w) versus conversion for the free-radical copolymerization of styrene/divinylbenzene in the presence of TEMPO as controller and BPO as chemical initiator. Experimental conditions (reported by Tuinman et al.³): $[BPO]_0=0.036$ M, $[TEMPO]_0/[BPO]_0=1.1$, temperature=393.15 K, $[DVB]_0=1$ wt% (Case 1), 1.5 wt% (Case 2), 3% (Case 3).

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Poly(*o*-methoxyaniline)-Lignosulfonic Acid Composite

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Polyaniline (PANI) is one of the most extensively explored conducting polymers due to its excellent properties and a range of potential applications. However, PANI has poor processability due to its insolubility and infusibility, which greatly limits its commercial application. Poly(*o*-methoxyaniline) (POMA) is, in this context, attractive because of its improved solubility in a range of solvents and its own specific reactivity compared with the parent PANI.

In this study, POMA was, for the first time, synthesized through oxidative chemical polymerization in the presence of lignosulfonic acid sodium salt (LSNa, Mw ~52,000, water soluble), which is derived from the inexpensive by-product of the pulp processing industry. Due to the structural complexity of LSNa molecules, the quantitative determination of the molar ratio of LSNa to monomer was not feasible, thus samples with different empirical weight ratios of LSNa to the monomer (*o*-methoxyaniline, or OMA) were prepared. The structure and property of the as-synthesized conducting polymer complex were explored by FTIR, UV-vis spectra, SEM, elemental analysis, surface area characterization, AC conductivity and free radical scavenging capacity. It was found that the LSNa/OMA weight ratio had a significant effect on the structure and properties of the composite. As expected, elemental analysis showed that more LSNa was present in the final product with an increased LSNa/OMA weight ratio, however, LSNa was found to be more efficiently incorporated with a lower LSNa/OMA weight ratio.

Analysis of the benzenoid to quinoid peak ratio in FTIR indicated that the degree of oxidation of POMA decreased with an increase in LSNa content, while the AC conductivity increased with LSNa content. These suggested that LSNa, even though not in the acid form, showed some degree of doping effect, similar as PANI-LSNa¹. The doping effect might come from the ionic strength induced in the reaction medium, together with the “falling pH” effect and the proton released from the monomer². The spatial relationship between the two large polymeric components (POMA and LSA) is not yet elucidated. One hypothesis might involve a composite particle consisting of a POMA coated LSA core, with the outer POMA formed from surface polymerization of adsorbed positively charged OMA monomers³. A morphological study showed that the LSNa/OMA weight ratio appeared to influence the composite nano-structure, as well as the surface area of the final product. This in turn affected the anti-oxidant property of the composite as evidenced by the DPPH assay. With more LSNa in the reaction medium, POMA-LSNa composite with higher porosity and BET surface area was obtained, which demonstrated strong free radical scavenging ability, indicating its potential in antioxidant applications. All of the POMA composites synthesized in the presence of LSNa had AC conductivity from 10⁻⁹ to 10⁻⁷ S/cm, using a frequency range from 1 to 10,000 Hz, suggesting that these products can be potentially used as anti-static/electrostatic discharge (ESD) materials⁴.

Acknowledgement: The authors gratefully acknowledge the funding for this project from the NZ Ministry of Science and Innovation (Hybrid Plastics, UOAX0812)

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Electrically Conductive, Tough Hydrogels with pH Sensitivity

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Electrically conductive, mechanically tough, pH sensitive hydrogels were fabricated based on an interpenetrating polymer network (IPN) structure comprised of a pH sensitive polyelectrolyte (poly(acrylic acid), (PAA)) and a neutral polymer network (poly(ethylene glycol) methyl ether methacrylate, (PPEGMA)). Poly(3,4-ethylenedioxythiophene) (PEDOT) was chemically polymerised within the IPN hydrogel to introduce the electrical conductivity, with repeated EDOT polymerisation used to increase the loading of PEDOT. The mechanical and electrical properties were evaluated at different pH. The conductivity of hydrogels at all pH increased significantly by repeating the PEDOT polymerisation step (**Fig. 1**). The achieved conductivity could reach as high as ~ 4.3 S/cm in a fully swollen pH sensitive hydrogel when PEDOT polymerisation was performed three times. As pH rises from pH 2 to pH 6 the swelling ratio increases almost 10 times around pH ~ 4.5 while the conductivity drops more than 5 times. The effect of pH on tensile and compression mechanical properties was also studied with typical stress-elongation curves given in **Fig. 2**. The PEDOT containing gel clearly shows a higher modulus and strength compared with the IPN gel. A sudden drop in both compression and tensile strengths was observed when pH increased above 4. These strong, pH sensitive conducting hydrogels may be useful for controlled release or artificial muscle applications.

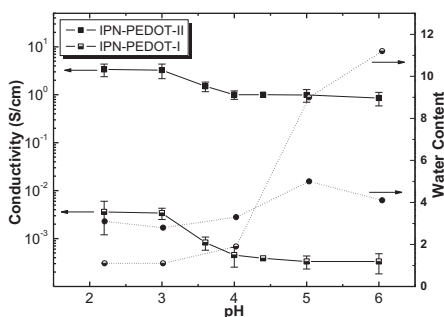


Figure 1. Conductivity and water content of IPN-PEDOT-*i* hydrogels vs. pH, at constant ionic strength ($I = 0.5$ M): $i = I$ (half-filled symbols), II (filled symbols) indicates number of PEDOT polymerisation.

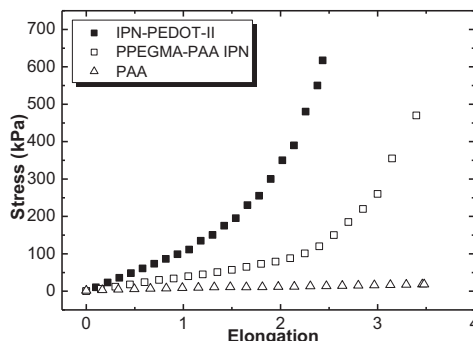


Figure 2. Tensile behaviour of fully swollen (pH 3) IPN-PEDOT hydrogel compared with the starting IPN hydrogel and the corresponding single network.

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Supported Hydrogel Polyacrylamide Membranes for the Size-Selective Separation of Gold Nanoparticles

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Polyacrylamide hydrogel membranes¹ have been widely used for biological² processes, water desalination³ or for separation of protein⁴, macromolecules⁵ or molecules⁶. Because of their poor mechanical properties, hydrogel membranes need to be supported (i.e. poly(vinylidene fluoride) or poly(ethylene) support). The hydrogel polymer is not a porous material; its crosslink swollen structure behaves like a sieve, filtering particles, ions, proteins or molecules according to the molecular weight of the polymer and to the mesh size and the charge of the hydrogel.⁷ Therefore, the filtration capacity of a supported hydrogel membrane depends on the volume fraction of the gel polymer in the hydrogel layer and on the tortuosity of the support.

In this study, the separation properties of PVDF-supported polyacrylamide hydrogel membranes towards gold nanoparticles are presented. First, several polyacrylamide hydrogel membranes were prepared using different monomer and crosslinker concentrations. These conditions have led to a series of membranes presenting a large range of hydrodynamic hydraulic permeability and of swelling properties. Then, their capability to reject gold nanoparticles according to their size has been tested with polymer-coated gold nanoparticles, using transmission electron microscopy, dynamic light scattering and UV-vis spectroscopy to analyze permeate and retentate solutions. Finally, mixtures of various sizes of gold nanoparticles have been filtered under pressure through these supported polyacrylamide membranes (**Figure 1**). These membranes have shown a high efficiency for purification and separation of gold nanoparticles based on their size.

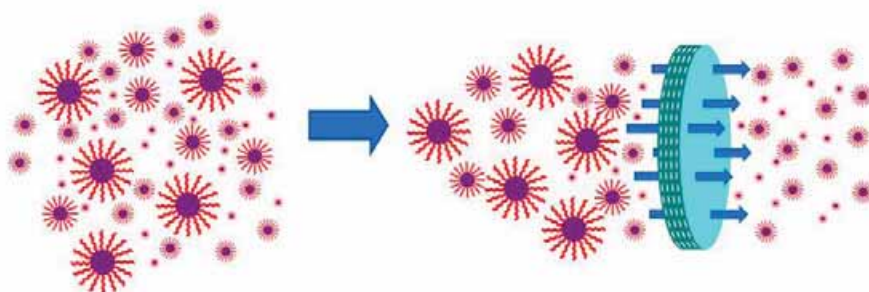


Figure 1. Separation of gold nanoparticles through polyacrylamide hydrogel membranes.

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The Effect of the First Network Heterogeneity on the Mechanical Properties of PNVP-PAAc Double Network Hydrogels

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The heterogeneity of the first network has been identified as an important factor for the improvement in mechanical properties of Double Network hydrogels (DN gels)¹⁻⁴. In the present research, poly(N-vinyl pyrrolidinone) (PNVP) - poly(acrylic acid) (PAAc) DN gels were prepared. The first network heterogeneity was adjusted by systematically changing the crosslinker concentration and monomer concentration separately. Tensile and tearing tests showed that with increasing crosslinker and monomer concentration of the 1st network, the mechanical strength and toughness of gels increased. Tensile loading-unloading tests were carried out on the gels to investigate the toughening mechanism. The test consisted of a series of loading-unloading cycles with increasing maximum extension ratio (λ). When the sample returned to its original length, the subsequent cycle was performed on it immediately. Large hysteresis between loading and unloading curves was observed for each gel for cycles with λ greater than 1.6. The test results indicated that with increase in the crosslinker and monomer concentration of 1st network, PNVP-PAAc DN gels exhibited increased hysteresis for cycles with the same λ (Figure 1). Since the viscoelastic dissipation mechanism can be ignored in DN system during crack propagation, the observed hysteresis was attributed to the energy dissipated by the breakage of covalent bonds⁴⁻⁵. Thus, the test results provided new clues for toughening mechanism of DN gels based on classic Lake-Thomas theory.

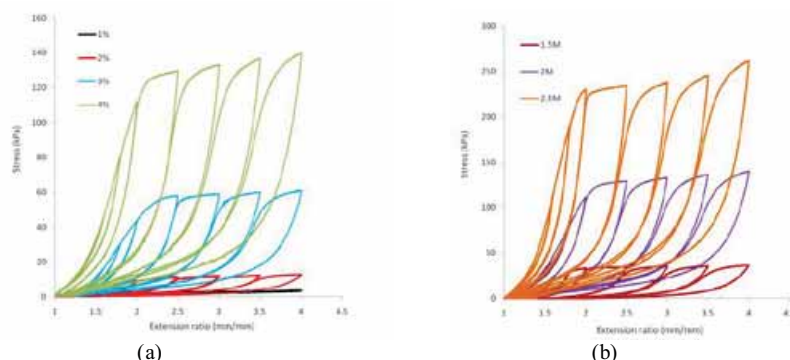


Figure 1. The loading-unloading curves for PNVP-PAAc DN gels with various crosslinker concentration (a) and monomer concentration of 1st network (b) over a series of cycles with increasing maximum extension ratio (λ).

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The influence of hydrophobic modification on the structural alteration of granular branched polysaccharides by β -amylase enzyme treatment.

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Highly branched polysaccharides are routinely modified to create functional products for consumption as food ingredient and applications in the materials industry. Their biological origins mean great opportunity for structural control by the use of highly specialised enzymes. Working with the polysaccharides in granular form, β -amylase specifically cleaves dimers from the non-reducing end of glucose polymer chains and is obstructed by branching points and substituted group introduced by chemical modification. This is complicated by differences in the access of solvents and reagents to molecules in the polysaccharide granule containing semi-crystalline structure.

Superior products are produced by taking advantage of the optimal conditions for modification and β -amylase treatment; however, the mechanisms for these structural changes require investigation. Removal of unmodified linear sections by this method artificially inflates the measurable degrees of branching and substitution of the polymer, perhaps without much real change to the real underlying structure. Modifications that affect the action of β -amylase have significant effect on the outcome. This study includes enzyme kinetics of the treatment with substrates modified to varying degrees, as well as advanced structural analysis of the resulting products.

Enzyme kinetics used to derive Michaelis-Menten parameters for samples give an indication of the challenge posed to β -amylase by the presence of modified groups. This supports the inhibition provided inherent to the substrate by branch points.

Structural characterisation of the samples utilised breakthrough techniques in size exclusion chromatography, nuclear magnetic resonance and electron microscopy. These data sets converge to provide a robust picture of the progression of enzyme hydrolysis in the context of varying levels of hydrophobic modification with octenyl succinic anhydride.

The results of this study indicate significant influence of chemical modification on enzyme susceptibility. As increases in the level of chemical modification can result in decreases to enzyme function, therefore a corresponding decrease in the measurable degree of branching of the final product. As both the levels of chemical and enzymatic modification and the branch structure are important to functional properties, the knowledge developed in this study represents a step towards highly tailored and significantly useful specialty materials.

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Personal History

2010 - Michael is broadly working to understand the relationship between structure and function in OSA starches. His work is supervised by Professor Robert Gilbert at the University of Queensland.

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Toughening of PLA: Routes towards Improvement in Mechanical Properties

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Poly(lactide) (PLA) is linear aliphatic thermoplastic polyester, has been received lots of interest as one of most promising polymer among other biodegradable polymers¹. Following this interest, there has been major focus to overcome on some drawbacks of this polymer such as processability, small elongation at break and low impact strength. Different approaches have been employed to modify brittleness of PLA by synthesis route^{2,3} and melt blending with other polymers⁴⁻⁶.

Nanocomposites of polylactide (PLA) and nanofiller and impact modifier were prepared by melt blending. Two different nanofillers Halloysite and Closite93A and impact modifier copolymer (EGMA) were used in Nanocomposites. The structural properties of Nanocomposites were characterized with x-ray diffraction and transmission electron microscopy. Results showed that EGMA particles are highly compatible with Halloysite and Closite 93A. It is found that two kinds of morphology were formed. EGMA and Halloysite showed separation whereas; 93A nanofiller particles remained mostly inside the EGMA droplets in the form of intercalation and exfoliation. These different morphologies affect on the tensile test and fracture mechanics were studied.

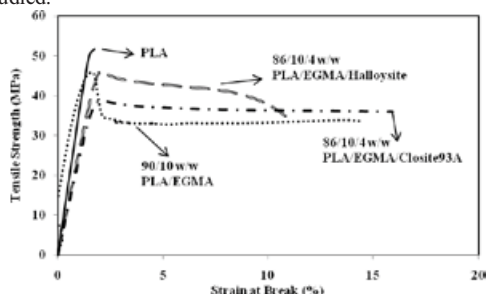


Figure 1. Stress-strain curves of: (a) neat PLA, (b) 90/10 w/w PLA/EGMA, (c) 86/10/4 w/w PLA/EGMA/Halloysite and (d) 86/10/4 w/w PLA/EGMA/Closite93A

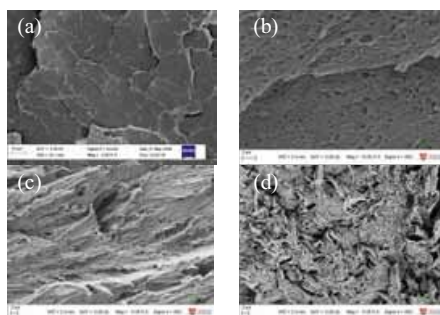


Figure 2. SEM micrographs of fracture surfaces of nanocomposites.

The effect of using EGMA varied between the different nanofillers because of dissimilar mechanism. Tensile testing showed improvement in strain at break (%) in binary (PLA/EGMA) and ternary (PLA/EGMA/nanofiller) blends (**Fig.1**). In this study, the composites with separate dispersion structure (PLA/EGMA/Halloysite) showed higher modulus and tensile strength, while PLA/EGMA/Closite 93A showed more improvement in elongation at break. Fracture energy is improved dramatically due to EGMA addition and showed synergistic results in ternary composites. The surface morphology (**Fig.2**) was characterized with optical microscopy and scanning electron microscopy.

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Thermomechanical Behavior of Conducting Polymer Blends

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Polymer solar cells containing poly(3-hexyl thiophene) (P3HT) as donor and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) as acceptor have recently become important devices in the quest for all-polymer photovoltaics [1], and offer the potential for high speed roll-to-roll manufacturing and therefore low cost devices.

Optimisation of these materials to obtain high efficiencies requires a co-continuous network of the two materials with maximum interfacial area and domain sizes of the order of 5-10 nm [2]. Both thermodynamic and kinetic parameters influence this microstructure formation.

In high throughput roll-to-roll manufacturing the thermo-mechanical properties of the polymers are critical, particularly when heat is used to laminate layers of the device. Control of the level of adhesion between the layers and the deformation of the films, and therefore thickness of final device, will have a strong influence on device performance. The thermal properties of these materials, such as glass transition and crystallisation, have been found to depend on heating rate and solvents used for casting, for example [3]. For lamination processing, the temperature at which these materials plastically deform is important.

The processability of these materials has been investigated by the dynamic mechanical thermal analysis (DMTA) technique. For example, the $\tan\delta$ behaviour of a P3HT/PCBM blend cast on a polyimide carrier film (Fig. 1) shows two relaxations, related to the softening (glass transition) processes of the two components. Characterisation of the thermo-mechanical behaviour of films of these polymer blends will enable the understanding of the level of inter-mixing of the components, and the effect of processing on this complex microstructure.

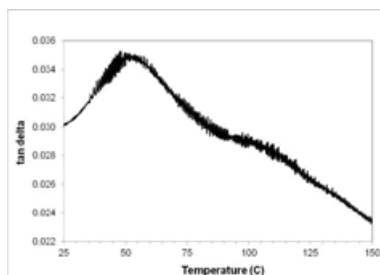


Figure 1. DMTA $\tan\delta$ spectra for P3HT/PCBM blend cast onto polyimide film.

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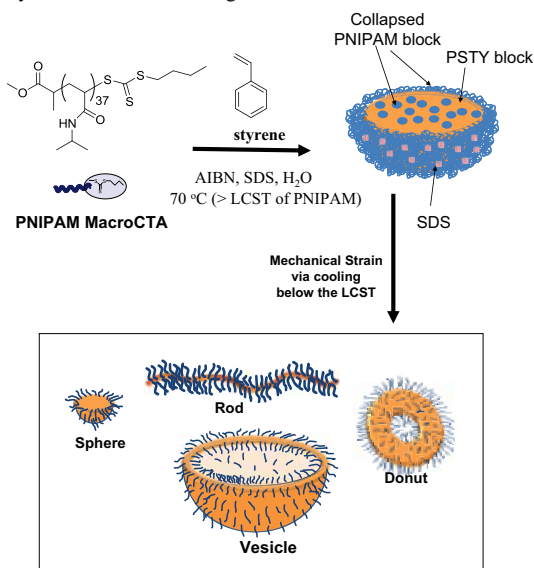
Research interests: polymer engineering and processing, structure-property relationships, nanomaterials, composites, solar cells, optical polymers, hybrid materials.



Polymer Architectures and Nanostructures Generated via Living Radical Polymerization

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The seminar will present work on the synthesis of complex polymer architectures using LRP and 'click' coupling reactions and their self-aggregation in water. Examples will be given for the use of such nanostructures in biological applications. We will also report a new approach to control the formation of a variety of 3D structures at high weight fractions of polymer in water from a single diblock.



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Efficient synthesis of α -isocyanate end-functional polymers

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In the field of polymer synthesis, one of the ultimate challenges is to prepare functional polymers with complex architectures. The advent of controlled radical polymerisation (CRP) along with the raise of efficient organic chemistry methodologies, i.e. “click” reactions provides today a great opportunity to design and to obtain a large variety of well-defined polymeric materials.

Azide-alkyne, thiol-ene/yne and Diels-Alder reactions are amongst the most used “click” reactions.¹ Another very interesting reaction of this type is the addition of nucleophiles to an isocyanate group. Indeed, isocyanate is the only functionality that can react rapidly and completely with alcohols, thiols and amines. Moreover, its stability in radical polymerisation has already been demonstrated in the literature. However, only a few articles mention the use of isocyanate-modified monomers in CRP² and, until now, the synthesis of an α -isocyanate end-functional polymer by CRP has not been reported, possibly because of the difficulty in handling such a reactive functionality.

In this work, we present for the first time the synthesis of a polymer bearing an isocyanate at the α chain end using a straightforward method, which does not require a post-modification step. The carboxylic acid of a commercial RAFT agent, S-dodecyl-S'-(α,α' -dimethyl- α'' -acetic acid) trithiocarbonate (DDMAT), was first transformed into a carbonyl azide. Then, new chain transfer agent **1** was used directly for the RAFT polymerisation of monomers of different nature ((meth)acrylates, acrylamides and styrenics) (Figure 1). The Curtius rearrangement occurred during the polymerization, yielding α -isocyanate end-functional polymers. It is noteworthy that the Curtius rearrangement could not be obtained before polymerization, as degradation of the RAFT agent occurs.

Such efficient way to introduce an isocyanate will pave the way for the preparation of complex architectures and nanostructures whilst expanding the current “toolbox” available to polymer chemists.

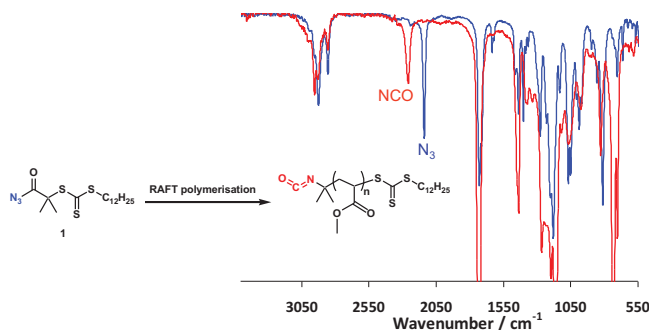


Figure 1. Comparison of the IR analysis of the initial RAFT agent (carbonyl azide in blue) with the polymer obtained after RAFT polymerisation (isocyanate in red)

¹ U. Mansfeld, C. Pietsch, R. Hoogenboom, R. Becer, U. Schubert, *Polymer Chem.* **2010**, *1*, 1560-1598.

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Syntheses of Polyacrylates by SET-LRP for use in Adhesives and Sealants

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The development of techniques for the controlled radical polymerization (CRP) of vinyl monomers presents the adhesives industry with an unprecedented opportunity to access materials with properties tailored for specific function and performance. A recent report has valued this opportunity in the region of \$20 billion.¹ CRP, and certain related ionic living polymerizations, permit the syntheses of polymers with structures that are controlled at both the molecular (molecular weight, monomer sequence, branching, microstructure, end-functionality) and supramolecular levels (micelles, vesicles, lamellae).²⁻⁴ Such control provides a practical means by which the structures of adhesive resins can be tuned to provide a balance of adhesive and cohesive properties required of high performing adhesive products.

CRP offers many benefits over ionic living polymerizations in particular its tolerance for functional groups and impurities.⁵ In this paper, we describe the syntheses of polyacrylates by copper-catalyzed single-electron transfer living radical polymerization (SET-LRP).⁶ This method has several distinguishing features over other CRP techniques that make it particularly amenable for large-scale industrial production. Polymers were prepared in a simple one-pot, two-step processes, in which the monomers and polymerizing solutions were continuously pumped through a catalytic amount of copper mesh contained in an external tubular reactor. In this way, acrylate-terminated polyacrylates, having high degrees of end-functionality (Figure I) and acrylate block copolymers with low levels of cross-block contamination were synthesized. The telechelic polymers are suitable for production of chemically resistant elastomeric sealants *via* photo or other radical-initiated polymerizations and the amphiphilic block copolymers are useful for toughening of epoxy resins. The properties and applications of these polymers will be outlined in more detail.

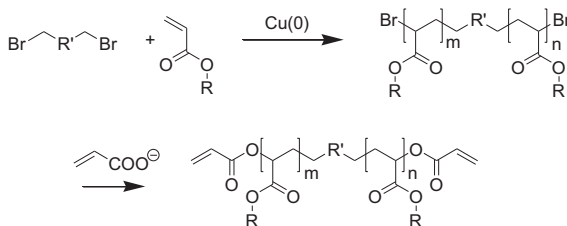


Figure I. Synthesis and end-functionalization of telechelic polyacrylate by sequential SET-LRP and substitution reactions.

¹ J. Spanswick and B. Pike in *Controlled/Living Radical Polymerization: Progress in ATRP*, Ed. K. Matyjaszewski, ACS Symp. Series 1023; Am. Chem. Soc.: Washington, DC, 2009, pp.385-396

² B. Grubbs, J. Dean, M. Broz, and F. Bates, *Macromolecules* **2000**, *33*, 9522-9534

³ N. Lynd and M. Hillmyer, *Macromolecules* **2005**, *38*, 8803-8810

⁴ D. Konkolewicz, M. Monteiro and S. Perrier, *Macromolecules* **2011**, *44*, 7067-7087

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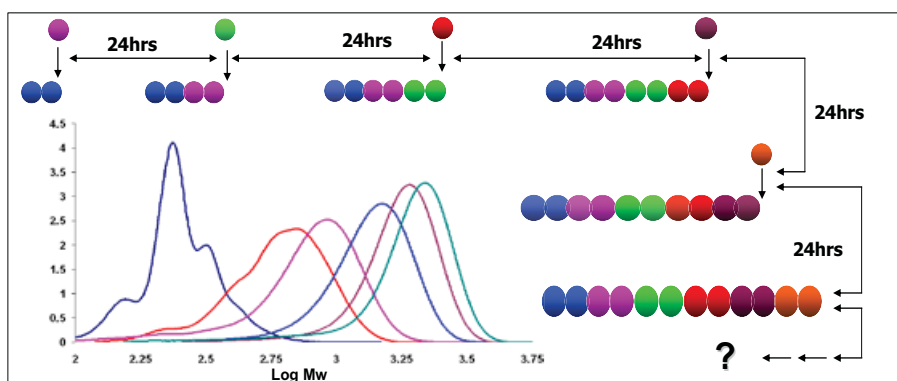


Living Free Radical Polymerisation in the Presence of Cu(0): Towards Biological Precision

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Natural biopolymers comprise well-defined and highly controlled sequence distributions of different monomers, e.g. amino acids in proteins. This specific distribution/placement of monomer units along the chain confers their remarkable biological, structural and chemical properties. Matching this structural control in synthetic polymers is an important goal of macromolecular scientists. Here we report a novel strategy for the synthesis of multiblock copolymers, which comprise very short blocks (on average two monomers units), in high yield, narrow polydispersity and controlled structural complexity.¹ To achieve this breakthrough we have applied recent advances in living free radical polymerization in the presence of zero valent copper (SET-LRP), to the iterative synthesis of block polymers. Unlike previous block polymer syntheses, this method involves no purification between the successive block formation steps, because each step is taken to full monomer conversion. This is only possible due to the high maintenance of “livingness” under high conversion/post-polymerization conditions. The approach is general, facile and offers the opportunity to synthesize new macromolecular materials with unprecedented control of block lengths, providing materials that could find application in a diverse range of disciplines, from materials science to biotechnology.



Scheme 1: Synthesis of Poly(MA-b-nBuA-b-EA-b-2EHA-b-EA-b-nBuA)

1. Soeriyadi A.H., Boyer C., Nystrom F., Zetterlund P.B. Whittaker M.R., *J. Am. Chem. Soc.*, 2011, **133**, 11128–31

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End Group Transformation and RAFT Polymerization

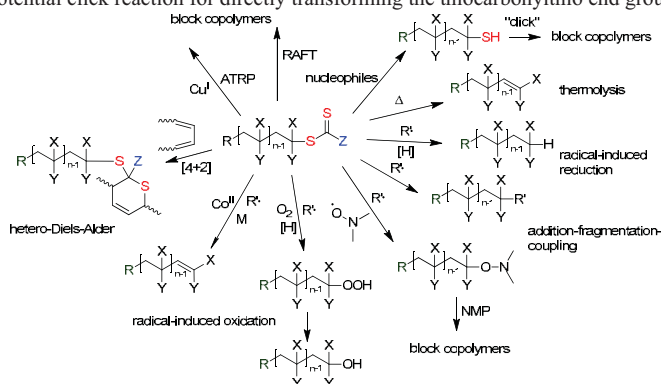
Graeme Moad, Ming Chen, Yen K. Chong, Matthias Haeussler, Shadi Houshyar, Daniel Keddie, Ezio Rizzardo, San H. Thang, John Tsanaktisidis

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Processes for thiocarbonylthio end group removal or transformation post RAFT polymerization attract significant interest.^[1] A wide variety of methods are now available for removing or transforming the thiocarbonylthio-groups in RAFT-synthesized polymers. All have advantages and limitations depending on the intended application. The thiocarbonyl functionality present in RAFT-synthesized polymers, once seen as a limitation to the wide-spread adoption of RAFT polymerization can now be seen as an enabling functionality in addressing the needs of the biomedical, optoelectronic, nanotechnology and other sectors. Some of the possibilities are shown in **Error! Reference source not found..**

We have recently reported

- A new class of “switchable” RAFT agents. Simple protonation/deprotonation of the end group allows synthesis of block copolymers based on more activated (styrene, (meth)acrylates, (meth)acrylamides) and less activated monomers (vinyl acetate, N-vinyl pyrrolidone).^[2-5]
- A more efficient method for end group removal by radical-induced coupling.^[6]
- A Single unit monomer insertion process that provides a route to block copolymers based on fully conjugated backbones.^[7]
- A new potential click reaction for directly transforming the thiocarbonylthio end group.^[8]



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Making Proteins Smarter by Conjugation with Responsive Polymers

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Conjugation to synthetic polymers is a viable means to modify the solubility, activity, and potential utility of proteins. For applications in vivo, functionalization of a protein therapeutic with an appropriate high molecular weight polymer can substantially reduce immunogenicity and rates of renal clearance/proteolysis. Similarly, conjugation of stimuli-responsive polymers to proteins can significantly improve catalyst performance and recyclability during enzymatic catalysis. Accordingly, many diverse routes of polymer-protein conjugation have been reported. Generally, these approaches can be classified as either grafting-to, which involves conjugation of a preformed polymer with a protein by reactive coupling, or grafting-from, which describes the polymerization of monomer from a protein capable of initiation (Fig. 1).

The end group retention, molecular weight control, and functional group tolerance of controlled radical polymerization (CRP) facilitates the preparation of well-defined polymer-protein conjugates and allows the facile synthesis of conjugates that contain stimuli-responsive polymer components. Of the various CRP techniques reported, reversible addition-fragmentation chain transfer (RAFT) polymerization offers perhaps the most promise in this area because of its ready amenability to aqueous media, high degree of functional group tolerance, and lack of a transition metal catalyst that can potentially interact unfavorably with the protein.

By exploiting functional chain transfer agents (CTAs) or the sulfur chemistry inherent to the RAFT process, we have immobilized thermoresponsive polymers to model proteins via thiol-maleimide Michael addition, copper(I) catalyzed azide-alkyne cycloaddition, or amidation of activated esters. Additionally, functionalization of proteins with a RAFT CTA prior to polymerization has allowed high molecular weight conjugates to be formed by the grafting-from process. The grafted polymers are well-defined, as observed by successful block copolymerization with a second monomer and by molecular weight analysis after cleavage from the protein. The thermoresponsive nature of the immobilized polymers has allowed thermal tuning of the conjugate self-assembly process and reversible modulation of protein bioactivity.

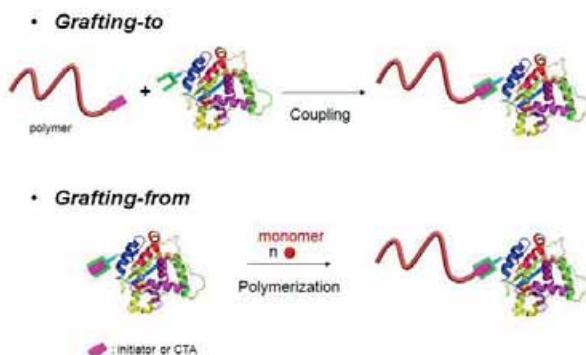


Figure 1. Polymer-protein conjugation strategies by RAFT

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Versatile Multi-functionalization of Magnetic Nanoparticles for Biomedical Applications

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Advancements in controlled polymer synthesis like RAFT¹ (reversible addition fragmentation chain transfer) and surface functionalization of nanoparticles have lead to a fabrication of multifunctional hybrid nanomaterials. In particular, iron oxide nanoparticles (IONP) due to their superparamagnetic properties have been exploited as contrast agent in magnetic resonance imaging (MRI) and diagnostic probes for multimodal tracking.² The interactions between the magnetic nanoparticles with their physiological environment strongly depend upon the size of the nanoparticles but also on the individual surface characteristics, like charge, morphology and surface chemistry.²

In order to improve the colloidal stability of IONP and prolong their blood circulation times, biocompatible polymers with anti-fouling properties such as polyethylene glycol (PEG) can be grafted chemically onto the outer surface of IONP core via terminal silane or phosphonic acid groups.² Nevertheless, in order to achieve high grafting density and stability, yet retaining the T_2 relaxivity of the IONP core, the chemical functionalities and chain length of the polymeric layer must be controlled. In this communication, we have prepared IONPs/polymer hybrid nanomaterials via RAFT polymerization (Fig. 1).³

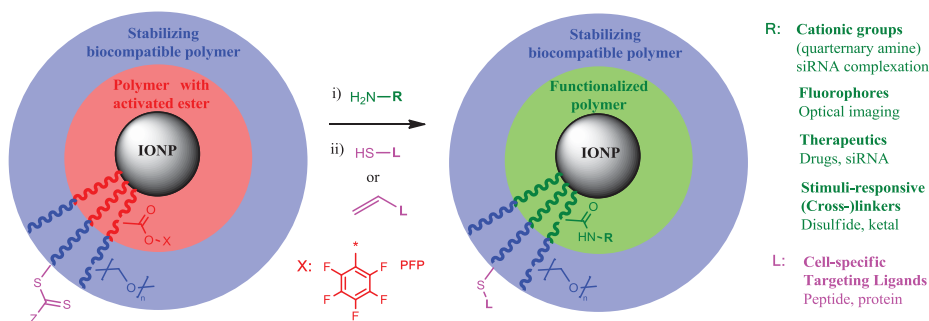


Figure 1.: Versatile polymer functionalization of magnetic nanoparticles via amine substitution.

Polymeric activated esters (**X**) like pentafluorophenyl (PFP) were assembled on the surface of IONP. This 'reactive' layer can undergo amidation in the presence of various primary amines to yield a library of (**R**) functionalized nanoparticles. Using this approach, the nanoparticles can be functionalized with chemotherapeutic drug (eg. doxorubicin) and siRNA through a stimuli-responsive linker (eg. disulfide, ketal) and cationic pendant groups (eg. quarternary amine). This offers an opportunity to utilize IONP as drug/siRNA delivery system. In addition, fluorophore (eg. fluoresceinamine) can be incorporated into the nanoparticles as well, in order to complement the MRI 'tracking' capabilities of the IONP via optical imaging. Cell-specific targeting ligands (**L**) such as RGD peptide or folic acid can be conjugated to the external surface of the polymer layer by conversion and further functionalization of the terminal RAFT thiocarbonylthio group via thiol-ene chemistry.³

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³ C. Boyer, M. H. Stenzel, T. P. Davis, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, 49, 551.

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Novel Crosslinked Polymeric Vesicles Conjugated with *cis*-Platinum Drug

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Chemotherapy is one of widely used cancer treatments, which kills micro-organisms or cancerous cells by chemicals or drugs. However, it has had limited success over the years due to limited aqueous solubility and *in vivo* stability, and serious side effects to healthy cells. Nanoparticles, including polymer drug conjugates, micelles, lipid vesicles, dendrimers and hydrogels, have long been sought as promising candidates for drug delivery systems,^{1,2,3} in order to improve the water solubility and *in vivo* stability of the drugs, prolong their circulation in blood compartments. Despite of these extensive researches, there are only a few FDA approved nanoparticle drug delivery systems on the market. Lipid vesicles (liposomes) are one of the most successful drug delivery systems in commercialized formulation since 1990's. However, lipid vesicles have a number of inherent drawbacks of relatively low stability due to lack of mechanical strength, low drug contents (not greater than 10%), and free drug premature burst release.³ These drugs were commonly not covalently attached to the carriers. Polymer vesicles, compared to lipid vesicles, prepared by synthetic polymers have the capability of designable and robust architectures, with great diversity of functionalities, which can facilitate the conjugation of drugs as well as other useful reagents.

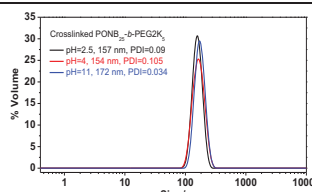
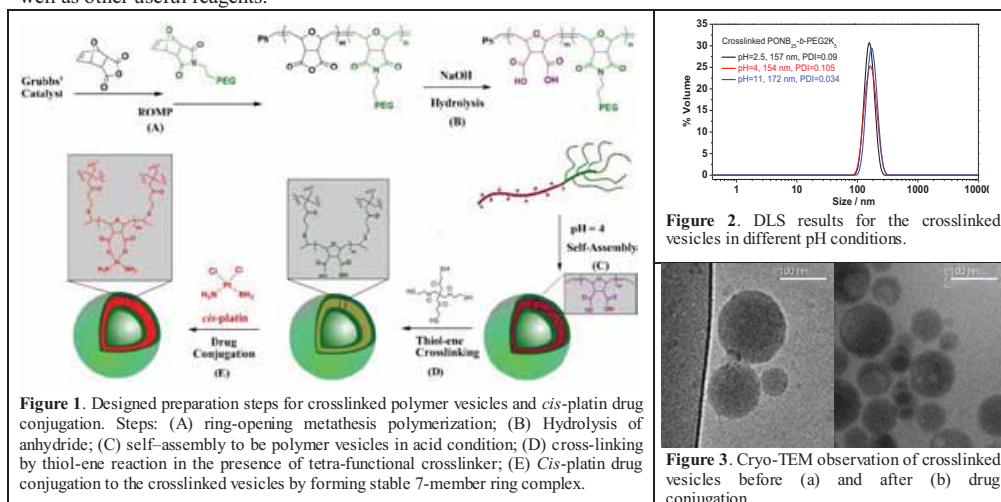


Figure 2. DLS results for the crosslinked vesicles in different pH conditions.

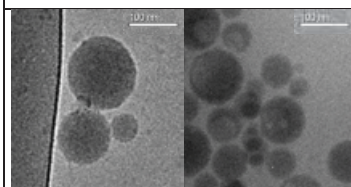


Figure 3. Cryo-TEM observation of crosslinked vesicles before (a) and after (b) drug conjugation.

In this work, we developed a straightforward strategy to prepare crosslinked polymer vesicles with idealized particle sizes using ring-opening metathesis polymerization (ROMP) and thiol-ene “click” chemistry (See the synthetic route in Figure 1). These novel polymer vesicles were characterized by DLS (Figure 2) and cryo-TEM (Figure 3), which gave the particle size at 150 nm. The hollow ‘open-mouth’ structure was confirmed by the conjugation of *cis*-platin drug, which also enhanced the contrast during TEM measurement compared to that before conjugation.

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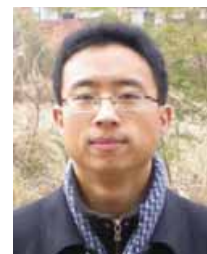
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Micelles: NO delivery

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Nitric oxide (NO), which is produced by many cell types in the body, has been shown to be involved in many physiological and pathophysiological processes. NO has been proven to play a vital role in the relaxation of blood vessels, immune regulation, neurotransmission, and the inhibition of platelet aggregation. Many diseases such as hypertension, atherosclerosis, and restenosis were found to involve the NO deficiency.¹ The introduction of NO into the biological systems is, however, challenging because of its gaseous state and high reactivity. Thus, the development of compounds that can release NO *in situ* the cells, known as NO donors, is very essential. In fact, there are two main classes of NO donors, namely diazeniumdiolates (NONOates) and *S*-nitrosothiols have been extensively studied.^{2,3} However, the clinical application of NONOates has been limited by the potential toxicity of the parent compounds and carcinogenic secondary nitrosamines by-product of NONOate metabolism. On the other hand, *S*-nitrosothiols (RSNOs) have been considered as a more desirable class of NO donors because they occur endogenously such as *S*-nitrosoglutathione (GSNO) or *S*-nitroso-L-cysteine. However, the stability of these RSNOs is often less than desirable.

In this study, we reported the first time the use of polymeric micelles to improve the stability of the RSNO. Micelles were built from amphiphilic copolymers consisting of poly(OEG-A) homopolymers chain extended with vinyl benzyl chloride (VBC) and pentafluorophenyl acrylate (PFP-A) comonomers. The RAFT process has been demonstrated to be a versatile technique, suitable for the generation of well-defined complex macromolecules. In this system, the core domain is composed of random copolymer of vinyl benzyl chloride (VBC) and pentafluorophenyl acrylate (PFP-A). GSNO endogenous precursor was then covalently conjugated to hydrophobic core, which can restrict the access of the agents that are required for NO release (such as metal ions, heat, reducing agents, and light) as well as the limit the mobility of polymeric NO donor resulting the reduced rate of decomposition compared with that of free GSNO. The conjugation of NO donor to the polymeric platform and the release of NO were confirmed by FTIR, UV-Vis spectroscopy. The results revealed the significant increase in stability of macromolecular GSNO donor (more than 14 days) compared to free GSNO (2 days) in water. The NO release rate catalysed by a reducing agent (ascorbic acid) of GSNO-polymer conjugate was found slower than free GSNO. Preliminary *in vitro* testing for the synergistic effect of NO and an anticancer drug revealed that NO enhanced the its cytotoxicity. Further studies will focus on the optimization the NO storage and release at desirable rate for specific biomedical application such as wound healing, vasodilation, cancer therapy.

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² Li, Y., Lee, P.I *Mol. Pharmaceutics*, **2010**, *7*, 254.

³ Jo, Y.S. *et al.*, *J. Am. Chem. Soc.* **2009**, *131*, 14413.

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Electrospinning Writing of Scaffolds for Enhanced Cellular Infiltration

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Electrospinning is continuously growing in popularity as a fabrication method for producing scaffolds within the field of tissue engineering. The ability to fabricate scaffolds with this technique is attractive due the number of materials able to be utilised; both natural and synthetic, relatively low costs involved, and the capability to optimise scaffold characteristics, for example fibre diameter, pore size, and porosity by altering key fabrication parameters. However, solution electrospinning, in general, produces nanofibre scaffolds with small pore sizes, < 1µm, which are smaller than the size of a cell. While this closely mimics features of the extra cellular matrix, from a tissue engineering point of view this is a major drawback, due to the limitation in cellular infiltration that is able to be achieved.^{1,2}

An emerging alternative to solution electrospinning is melt electrospinning, a technique with the ability to produce microfibrillar scaffolds with pore sizes ranging from 10 – 100µm, characteristics essential to allow adequate cellular infiltration within the fabricated scaffolds.³ Our work has focused on the melt electrospinning writing of polycaprolactone (PCL), to make scaffolds with a proposed application as artificial full thickness skin substitutes.

Scaffolds for *in vitro* cell culture studies were 8mm diameter, sterilised by exposure to UV, pre-wet with a graded EtOH series, washed in PBS and placed in serum containing (10%) culture medium overnight. Human dermal fibroblasts were seeded onto the scaffolds. After 7 days, keratinocytes were then seeded onto scaffolds pre-seeded with fibroblasts, cultured for 2 days, and brought to the air-liquid interface for an additional 7 days. On completion, scaffolds were fixed and prepared for SEM and histological (H&E) analysis, to assess cellular infiltration. SEM analysis of melt electrospun written scaffolds (**Fig. 1**) showed an average distance between fibres and fibre diameter of 54.6 ± 21.3 µm and 16.3 ± 1.1 µm respectively. SEM (**Fig. 2**) and histological (**Fig. 3**) assessment of the melt electrospun scaffolds following cell seeding and *in vitro* tissue culture revealed complete cell infiltration through the entire thickness (0.15 – 0.2 mm) of the scaffold.

These results highlight the potential of electrospinning writing to fabricate polymer scaffolds for use in tissue engineering applications where controlled pore size and porosity are important.

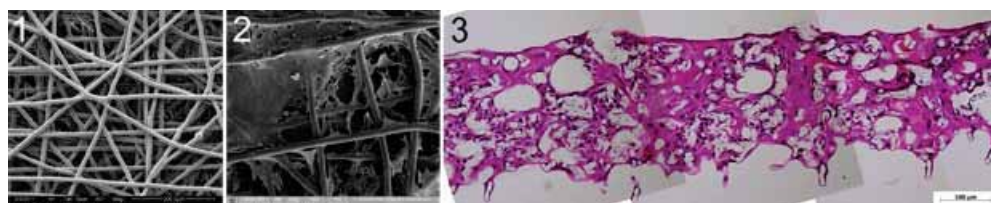


Figure 1: SEM analysis of melt electrospun PCL scaffolds, **Figure 2:** SEM analysis of PCL scaffolds following *in vitro* culture **Figure 3:** Histological analysis of PCL scaffolds following *in vitro* culture, H&E staining.

¹ A. S. Badami, M. R. Kreke, M. S. Thompson, J. S. Riffle, A. S. Goldstein, *Biomaterials* **2006**, 27, 596.

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³ K. Tuzlakoglu, N. Bolgen, A. Salgado, M. Gomes, E. Piskin, R. Reis, *J. Mater. Sci.: Mater. Med.* **2005**, **16**, 1099.

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Tailoring Layer-by-Layer Films to Reduce Protein Fouling

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The field of nanomedicine is a rapidly expanding area of research, which draws on the properties of polymeric materials to act as functional therapeutic carriers. Polymer drug conjugates, polymersomes, dendrimers and layer-by-layer (LbL)-assembled capsules are all examples of materials which have shown potential.¹ In particular, LbL capsules show a high degree of versatility, which makes them attractive candidates in this area. The range of assembly and template materials which have been demonstrated gives rise to capsules which can provide a wide array of responsive properties. Capsules can also be functionalised to achieve targeting to particular cells. The ability of capsules to circulate in the bloodstream is of utmost importance. Evading the body's immune system begins with the ability to resist the adsorption of plasma proteins. For effective drug delivery it is therefore necessary to investigate how capsule surfaces can be engineered to be low fouling in the presence of proteins. Poly(ethylene glycol) (PEG) is a hydrophilic polymer which is widely used to impart materials with stealth properties. The packing of PEG chains at a particle's surface plays an important role in the effectiveness of a PEG coating; therefore, gaining a clear understanding of PEG functionalisation is crucial.

Poly(2-diisopropylaminoethyl methacrylate) (PDPA) is a pH responsive polymer (pK_a 6.4) which can be used to assemble click-stabilised capsules that demonstrate release properties over a physiologically relevant pH range.² At the pH of the bloodstream (7.4), the material is hydrophobic and capsules shrink to approximately 40% of the template particle size. Below pH 6.4, for example in endosomal compartments where the typical pH is more acidic, PDPA becomes charged and swells, providing a cargo release mechanism. To exploit these interesting properties, the hydrophobic, high fouling nature of the capsules at pH 7.4 must be screened to prevent protein fouling and eventual clearance.

This work examines the modification of PDPA-based LbL films to improve their resistance to plasma proteins. Post-functionalisation of PDPA films with hydrophilic materials, such as linear PEG, was achieved by clicking azide-functionalised molecules to residual alkyne click groups within the films. The use of block copolymers of materials, such as PDPA and PEG for the assembly of LbL materials, was also addressed. Following functionalisation or film assembly, the amount of blood serum protein adsorbed by each surface was investigated. The planar study was extended to LbL capsules which were analysed both in blood serum and in white blood cell uptake assays which provided insights into ultimate behaviour *in vivo*. Addressing the challenge of sustaining LbL capsule availability in the blood for prolonged periods is fundamental to the eventual application of LbL capsules as delivery vehicles.

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Optimizing interfaces to regulate neural progenitor cells using polyelectrolyte multilayers and BDNF

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Development of biomaterials with controllable interfacial features, which have the capability to instruct cellular behaviour are required to produce functional scaffolds.

In this work, polycaprolactone (PCL) surfaces were biofunctionalized via Layer-by-Layer (LbL) deposition for neural tissue engineering applications. The polyelectrolytes employed were heparin and poly-L-lysine (PLL), the latter being chosen to improve cell adhesion and subsequent cellular function of in vitro cultured neural progenitor cells (NPCs). Material characterization results confirmed the deposition of well structured multilayers. Polyelectrolyte multilayer (PEM) surfaces with PLL as the terminating layer dramatically improved neurite outgrowth. The PEM coating was used to present brain derived neurotrophic factor (BDNF) and was found to be superior to soluble BDNF (Figure 1). In Figure 2, the no BDNF group showed significant differences to all adsorbed groups and the 50 ng/mL soluble group ($p < 0.001$), 2.81 ng/cm² adsorbed BDNF group also had a significant difference to its counterpart where biological activity was blocked ($p < 0.001$). Significant differences were observed between the adsorbed and soluble BDNF groups. The coating strategy was also applied to electrospun PCL nanofibres. These findings highlight the potential of using PEMs to present neurotrophic factors to stem cells in order to assist stem cell treatments for brain and spinal cord repair.

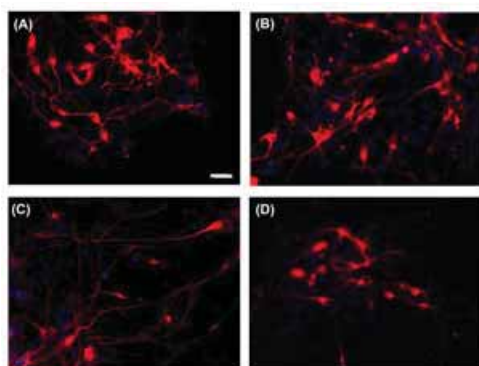


Figure 1

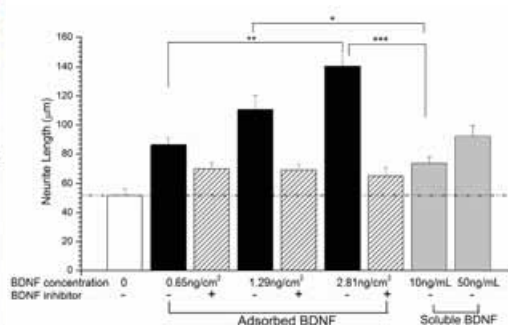


Figure 2

Figure 1 Images correspond to NPCs cultured on P6 surfaces with (A) No BDNF, (B) 50ng/mL soluble BDNF, (C) 2.81ng/cm² adsorbed BDNF and (D) 2.81ng/cm² BDNF inhibited groups. Neurons (red) stained by betaIII-tubulin, nuclear (blue) stained by DAPI.

Figure 2 Neurite length (day 5) of NPCs cultured on P6 surfaces with either adsorbed or soluble BDNF of different concentrations and their control groups (no BDNF and BDNF inhibited groups). Error bars shown as standard error of the mean. Significance represented at (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$).

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Optimization of Polysiloxane Ophthalmic Biomaterials Used as Accommodating Intraocular Lens Using Factorial Design

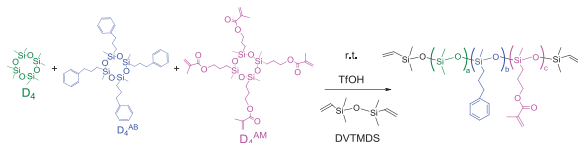
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Presbyopia is a condition in which the aging eye loses its ability to focus on close objects (accommodation), due to hardening of the natural lens. An attractive potential solution to presbyopia involves replacing the hardened natural lens with a gel soft enough to allow accommodation. For clinical success, this requires a biostable and biocompatible material to be injected into the capsular bag in a liquid form and cured *in situ* to form a soft gel (i.e. injectable *in situ* curable accommodation intraocular lens (A-IOL)).¹ In this study, functional polysiloxane macromonomers have been investigated as possible candidate materials to replace the hardened natural lens for correction of presbyopia. This application has very challenging material requirements as the polymers need to mimic the optical and mechanical properties of a young person's natural lens. In order to optimize the materials in the minimum number of experiments, a factorial design² was used to simultaneously investigate multiple factors that affect the properties of the materials and determine how a combination of manipulated factors (and their interactions) impact on a particular monitored response. Here we report on the outcome of the factorial experimental design conducted to optimize siloxane macromonomers for application as injectable *in situ* curable A-IOLs.

A factorial design containing 4 factors (feed ratio of D₄^{AB}, D₄^{AM}, DVTMDS and initiator concentration in the ROP) and 5 levels for each factor (very low, low, medium, high, very high) was used to model the relationship between feed ratios and material properties (RI, precure viscosity and postcure modulus). Initially 27 experimental macromonomer syntheses were conducted in blocks of 6 or 5 with random order. Following the syntheses of the macromonomers (Scheme 1) and the addition of photoinitiator, the RI and precure viscosity of the macromonomer and postcure modulus of the resulting gel were measured. Mathematical models were then constructed to relate the measured properties to the feed ratios. In all cases the generated mathematical quadratic models closely matched the measured data and had low residual standard errors (see table 1). From these relationships, optimal feed ratios were predicted and the resulting polymers were found to have promising properties for A-IOL.



Scheme 1: Synthesis of high RI polysiloxanes

	RI	Precure Viscosity	Post Cure Modulus
residual standard errors	0.00008	0.2754 (Pa.s)	250.6 (Pa)
R ² (%)	99.98%	96.83%	98.82%

Table 1: Residual standard errors and coefficient of determination for the measured responses

Acknowledgements

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Star-Shaped PEO-Based Polymers as Artificial Channels : Correlation between Chemical Structure and Channel Activity

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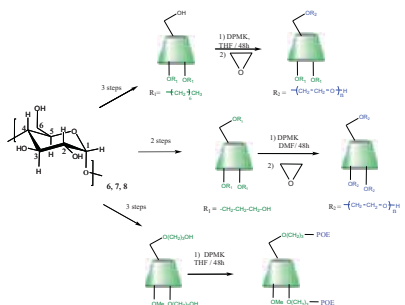
The design of synthetic pores has been addressed through various pathways including the synthesis of star polymers with a cyclodextrin core. The convergent strategy is often convenient but suffers of a lack of versatility¹. We will present the synthesis of star polymer using cyclodextrins (CD) derivatives as new initiators for anionic ethylene oxide polymerization. The first part of the work is devoted to the selective modification of the CD in order to generate hydroxyl functions of similar class^{2,3}. Selective modification appends to control the number of branches per star-molecules as well as their pore formation properties. The polymerization of ethylene oxide is conducted with a default of diphenylmethylpotassium and demonstration of the livingness of the system is carried out³. Star polymers having a number of branches ranging from 7 to 21 have been synthesized (Fig 1). Demonstration of pore formation is conducted with electrophysiological experiments. The cyclodextrin-based initiators are difficult to insert in the lipid bilayer due to their poor water solubility. Depending on the architecture of the star-molecules, permanent or transient pores have been observed. The relevant selective modifications of the cyclodextrins stabilize the amphiphilic pore within the bilayer and the PEO segments ensure the water solubility. Seminal results concerning translocation will be provided..

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⁴ N. Badi, L. Auvray, P. Guégan *Adv. Mater.* **2009**, 21, 4054-4057



Scheme 1

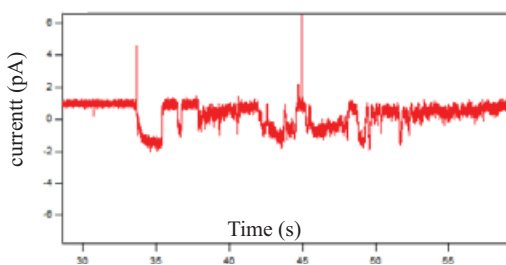


Figure 1 :I-V curve of a CD-based polymer inserted in a lipid bilayer

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Study of Diffusion of Model Drugs in Well-Defined Thermo-responsive Poly(*N*-isopropylacrylamide)-Based Hydrogels

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Due to the many properties of hydrogels which resemble natural tissue, these materials have been researched extensively for various biomaterial applications including in potential drug delivery devices.¹ However, the homogeneity of drug loading and length of drug release often do not meet the requirements of an effective drug delivery system. It is important to study release profiles extensively and this is usually carried out via release experiments. However, drug release experiments are time consuming and their reliability is often limited.² Fluorescence recovery after photobleaching (FRAP) involves briefly bleaching a small area of interest which contains mobile fluorescent molecules and recording the recovery of the fluorescence via an optical microscope (Figure 1).³ This technique has been used extensively to study translational diffusion of molecules and often diffusion of molecules in hydrogel systems.² Another technique of interest for studying diffusion of molecules is pulsed-gradient spin echo nuclear magnetic resonance (PGSE-NMR) which can observe self-diffusion coefficients down to the $10^{-12} \text{ m}^2 \text{ s}^{-1}$.

The conventional method for preparing hydrogels is using free radical polymerisation, whereby the final structure of the network is determined by statistical processes. For these networks, the properties are always described in terms of average properties and can never be defined precisely. However, it is now possible to synthesise hydrogels with networks of higher homogeneity with the combination of living radical polymerisation techniques and coupling reactions such as Click chemistry. These well-defined networks can be considered a model system for understanding and predicting the diffusion properties of molecules within gels more accurately.

In this study, poly(*N*-isopropylacrylamide) hydrogels of different mesh sizes were synthesised via the Cu(I) catalysed Click reaction. The rates of diffusion of fluorescein isothiocyanate-labelled dextran (FITC-dextran) of different molecular weights in these hydrogels were measured. In addition, PGSE-NMR was also carried out on the same set of samples. From these experiments, a complete description of the release kinetics of these models drugs was obtained.

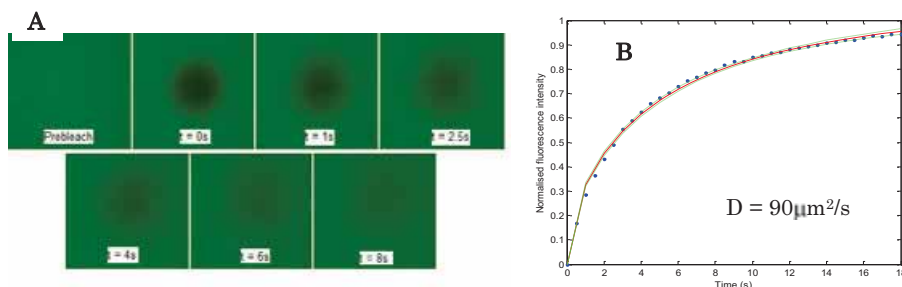


Figure 1. (A) Image stack of a FRAP experiment (5k P(NIPAAm) hydrogel, FITC-dextran 70k). (B) Recovery curve extracted from image stack with the experimental data represented by symbols (•) and least-square fits by a solid line.

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³ D. Axelrod, D.E. Koppel, J. Schlessinger, E. Elson, W.W. Webb *Biophys. J.* **1976**, 16, 1055-1069

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Folate-mediated cancer targeting polymeric micelles as a drug carrier for platinum anticancer agents

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Polymeric micelles synthesised from amphiphilic block copolymers have been studied extensively for their drug delivery abilities in the recent years. One major advantage of these polymeric micelles is that its critical characteristics including particle size, stability and loading capacity can be altered to suit its need, simply by modifying the structures and physiochemical properties of the fundamental block copolymers.¹

These polymeric micelles are currently used to deliver a wide range of drugs which include chemotherapeutic agents. To date, there are many platinum complexes which have shown cytotoxic properties but only a few are clinically proven. However Pt(IV) complexes provide an attractive alternative to Pt(II) compounds because of their inertness which results in fewer side effects compared to Pt(II) based drugs which has higher reactivity and thus lower biological stability. In addition, the axial ligands of Pt(IV) complexes can be used to adjust properties such as redox potential, aqueous solubility and lipophilicity therefore affecting the mechanism and the rate of drug uptake.²

To further enhance the therapeutic index of these platinum complexes, an active targeting approach may be employed. It is well known that folate-binding proteins (FBP) are selectively overexpressed on the surface of cancer cells; hence it is desired to design an appropriate drug delivery system which guides the carriers directly to targeting cells and then internalised via receptor-mediated endocytosis.³ This research focuses on the synthesis of polymeric micelles which consist of amphiphilic block copolymers via reversible addition fragmentation chain transfer (RAFT) process. The active targeting mechanism is achieved through a surface modification of these polymeric micelles with a reversible linker for the conjugation of folate itself. The cytotoxicity of these folate decorated micelles is tested against folate receptor positive and negative cell lines.

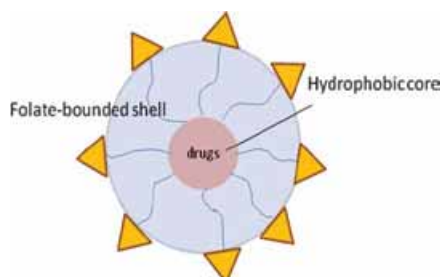


Figure 1 Folic acid decorated polymeric micelle

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Antiviral polymer therapeutics: polymer prodrug design for hepatitis C*Anton A. A. Smith, Mille Kryger, Kasper F. Rasmussen, Alexander N. Zelikin*¹Department of Chemistry and Interdisciplinary Nanoscience Centre (iNano), Aarhus University, Denmark

Viruses have remained a source of pathogenic wonder since their discovery. The shared molecular machinery of the host and the virus makes them an elusive target, and effective drugs often have adverse effects. Hepatitis C (HCV) is with more than 170 million people infected worldwide, a very successful virus. It antagonizes the immune response in 85% of acute infected individuals, and persists as a chronic infection. Chronic HCV is closely associated with hepatic cirrhosis and hepatocellular carcinoma. The current treatment for HCV consists of a combination treatment with PEG-interferon and ribavirin, a nucleoside analogue. However, a major drawback to this therapy is a dose dependent hemolytic anemia caused by ribavirin, which can lead to cessation of treatment¹. A transporter mediated uptake of ribavirin by the erythrocytes results in a hundred-fold higher concentration of the drug in the cytosol, compared to the plasma concentration². Moreover, this treatment is only 50% effective in achieving a sustained response against the virus; however, high dose ribavirin therapy has proven to be more effective, though not applicable as a widespread treatment due to the resulting hemolytic anemia³. An improved treatment of HCV requires a drug delivery system for reaching an optimal concentration of ribavirin in hepatocytes, while removing the severe side effects in non-targeted tissues. Ribavirin conjugated to a polymer prodrug is not likely to be subject to an erythrocyte specific uptake, removing a major limiting factor in HCV treatment. This, combined with hepatocyte targeting functionalities, can provide a target tissue specific release of an otherwise toxic drug.

While polymer therapeutics is well established in anticancer therapy, it is surprisingly un-explored in the field of antivirals. The preceding decades have yielded successful research into combining anticancer drugs with polymers through appropriate linkers, for both drug delivery and controlled release. Similar research with antiviral drugs remains to be performed.

In our work, we address these shortcomings in an effort to pair drug molecules with polymer carriers through appropriate linkers, towards well controlled macromolecular characteristics in specific drug delivery applications. The synthesized polymers are screened for cellular internalization and cytotoxicity, the latter being a convenient measure of both internalization and drug release. This research should provide widely applicable insight into the required properties of both polymer carriers and the nature of the drug conjugation site for polymer prodrugs, towards a more effective antiviral therapy

The presentation will cover the up-to-date results of this ongoing research project

¹ Fried, MW, *Hepatology*. **2002**, 34, 237-44

² Inoue, Y, *Hepatology Research*. **2006**, 34, 23-27

³ Schvarcz, R. *Hepatology*. **2005**, 41, 275-279

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Development of wireless and highly sensitive sensor devices for biomedical applications

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Effective biochemical detection technologies play an important role in the quality of life we (can) have today. Pregnancy test kits and drug and alcohol testing are common examples of the benefits of biochemical detection, not forgetting of course the suite of pathological testing that are used to diagnose disease and illnesses. While this paints a rather rosy picture of biochemical detection, there is always room for improvement – for example in the accuracy, sensitivity, speed and cost of biochemical detection. Furthermore there is still one area of biochemical detection that is currently still off limits to our existing technologies. Biochemical detection inside sealed and opaque containers currently cannot happen, as the best instruments we have require either wired access to the containers or the removal of a sample¹.

Here we report the development of a solution to the aforementioned problem – a wireless biosensing device with accuracy and speed that rivals the existing technologies, a drastically lowered cost of production and most importantly – operation free from wires and without the need for any internalised mechanics and electronics.

A special Fe-Ni-Mo alloy is used as the substrate for our biosensing devices. This substrate vibrates and produces a magnetic signal when the substrate is placed in an alternating magnetic field (Figure 1).

The biosensing is facilitated by exploiting the mass-dependence of the generated magnetic signal.² The substrate on its own cannot sustain any useful biochemical detection due to the absence of functional groups required for attracting and binding biochemicals and also requires a protective coating to prevent degradation when placed in buffered test

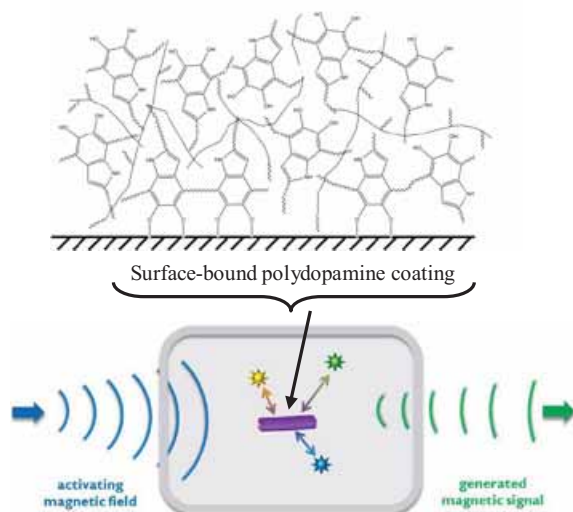


Figure 1. Depiction of equipment setup and polymer coating.

solutions. We use a polydopamine³ coating to provide both a surface for binding the biochemicals of interest and also to protect the metal alloy substrate. Initial work has shown the successful development of a biosensor that is easy to use, cheap to produce and most importantly – completely wireless.

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New Synthesis of Biodegradable Nanoparticles based on Dextran

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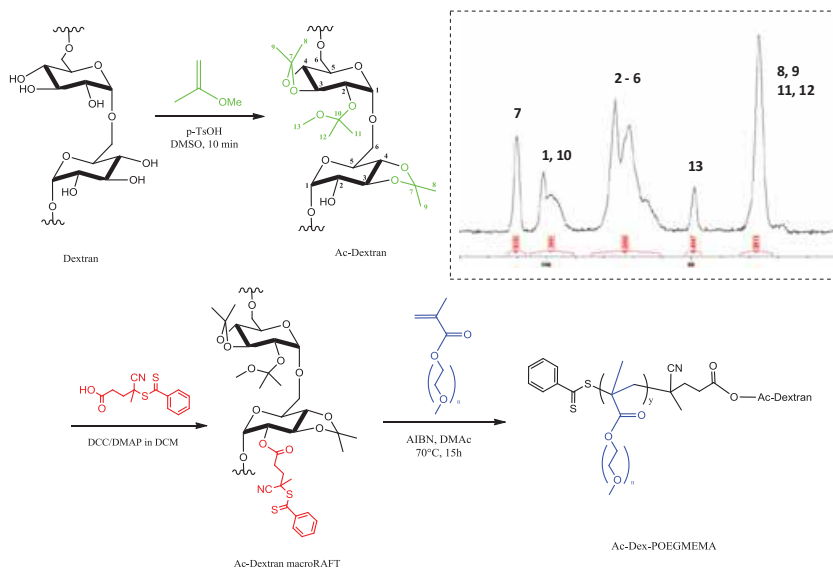
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Soft core-shell polymeric nanoparticles are an area of great research interest, due to their potential advantages in the sustained and targeted delivery of therapeutic payloads including drugs, proteins and imaging agents. While these systems can offer significant improvements in the temporal and spatial control of drug delivery, they often consist of synthetic polymers which are non-biodegradable. This limits the possible dosage due to damaging accumulation of polymers in the body. For this reason, increasing effort has been directed toward developing biodegradable polymeric nanoparticles.

Acetalated dextran is an interesting material described recently by the Fréchet group^{1,2} – a modified version of native dextran, which is known to be biodegradable and is used clinically as a plasma expander. The acid-labile acetal groups introduce pH sensitivity, as they degrade in acidic environments.

The present study prepared an amphiphilic block copolymer via the steps shown in **Scheme 1** below. The acetalated dextran backbone was prepared using a revised method, with PEG-based side-chains attached via a “grafting from” RAFT polymerisation. The resulting copolymer self-assembled in water to yield structures such as micelles, which can encapsulate a variety of hydrophobic payloads.

An important aspect of the work centred on characterising and optimising the acetalation reaction. Solid state and solution NMR techniques were developed to provide information about the degree and type of acetalation. This information was then used to tune the reaction conditions, giving control over the degradation time and grafting density of the PEG side-chains.



Scheme 1. Synthesis of nanoparticles from dextran

Figure 1. (inset) Solid state ¹³C CP/MAS spectrum of acetalated dextran.

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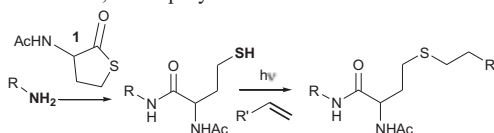
Novel and Powerful Polymeric Platforms for Conjugation and Postpolymerization Functionalization

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Metal-free conjugation reactions based on thiol-ene and (hetero)-Diels-Alder (HDA) chemistries have recently gained much attention in synthetic polymer groups as they were introduced as an alternative 'click' reaction for the widely exploited copper(I) assisted azide-alkyne 1,3-dipolar-cycloaddition (CuAAC). Consequently, the number of related publications in polymer journals has increased dramatically, demonstrating the eagerness of the field to evaluate these metal-free approaches and compare it to other, more established conjugation methods. However, as was recently demonstrated,¹ some serious limitations should be taken into account when considering radical thiol-ene chemistry as a ligation tool for polymer-polymer conjugation. The complexity of the (inseparable) reaction mixture is a violation to the set of 'click' requirements.² Consequently, radical thiol-ene is only reliable as a method for the conjugation of a polymer with a small molecule counterpart, although excess of the low-molecular-weight compound is necessary to achieve high conversion. In order to circumvent thiol-related issues (sensitivity to oxidation and limited availability), a thiolactone entity can serve as a precursor for thiols in a one-pot amine-thiol-ene reaction. This amine-thiol-ene conjugation (Scheme 1) as a simple, efficient, and modular linking process is considered to be a relevant extension of the thiol-ene chemistry, especially in polymer science. Functional, linear polymers and networks were obtained using this methodology.³



Scheme 1 – General concept of the Investigated Metal-Free One-Pot Reaction: Nucleophilic Opening of a Thiolactone (Aminolysis), Followed by a Radical Thiol-Ene Conjugation

The inverse-electron demand Diels-Alder cycloaddition (DA_{inv}) between norbornenes (Nb) and 1,2,4,5-tetrazines has recently been employed in some bioconjugation studies. However, this additive-free mild approach has not yet been applied to the ligation or end group modification of polymers. Nb functional α -semi-telechelic polymers provide a basis upon which this conjugation strategy was evaluated in macromolecular systems. Solvent screening and a kinetic study using low-MW model compounds revealed the remarkable scope of this methodology: the reaction proceeds in water and in a range of organic solvents, depending on which is the most appropriate for the system chosen. When applied to polymer-polymer coupling of Nb-PS and a tetrazine-functionalized polyethylene glycol (PEG), the conjugation efficiently reaches very high conversion within 2 hours, expanding the toolbox for the preparation of advanced polymer structures.⁴

¹ Koo, S. P. S.; Stamenovic, M. M.; Prasath, R. A.; Inglis, A. J.; Du Prez, F. E.; Barner-Kowollik, C.; Camp, W. V.; Junkers, T. J. *Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1699-1713. ² Barner-Kowollik, C.; Du Prez, F. E.; Espeel, P.; Hawker, C. J.; Junkers, T.; Schlaad, H.; Van Camp, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 60-62. ³ Espeel, P.; Goethals, F.; Du Prez, F. E. *J. Am. Chem. Soc.* **2011**, *133*(6), 1678-1681. ⁴ Hansell, C.F.; Stamenovic, M.M.; Espeel, P.; Du Prez, F. E.; O'Reilly, R.K. *J. Am. Chem. Soc.*, submitted.

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Personal History

Since 1999 head of Polymer Chemistry Research Group (full professor)

Research interests: self-healing polymers, novel 'click' chemistries, porous polymer

Particles, highly branched copolymer structures, controlled polymerizations



Tuning Macromolecular Functionality via Efficient Radical Exchange Reaction

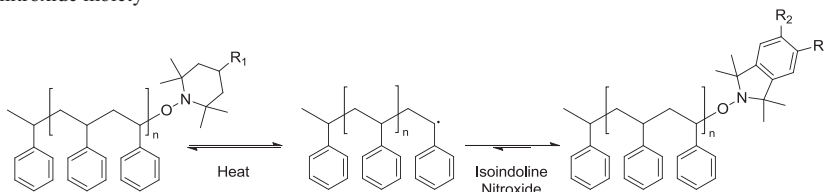
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The combination of efficient conjugation chemistry with controlled free radical polymerization has increasingly proven to be an important tool in the synthesis of novel polymeric materials. Polymerisation techniques such as Nitroxide Mediated Polymerisation (NMP), Atom Transfer Radical Polymerisation (ATRP) and Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerisation have successfully been combined with conjugation reactions such as the “click” chemistry of copper(I) azide-alkyne cycloaddition (CuAAC) to achieve a wide variety of structures ranging from complex, multi-arm architectures through to the attachment of polymers to fluorescent markers or biologically important molecules with a high degree of selectivity and efficiency.^{1–4}

The nitroxide exchange reaction⁵ is a similar conjugation technique involving the trapping of free radicals generated from a small molecule or macromolecular precursor. In this process, a polymer chain with an alkoxyamine cap (usually prepared via NMP) is heated in solution in the presence of a conjugation partner which features a nitroxide moiety



Scheme 1 Conjugate exchange of nitroxides in polymer systems where piperidine nitroxides may be statistically exchanged or swapped with a more strongly binding isoindoline nitroxide.

In this study⁶, the inherent stability of the isoindoline nitroxide derived alkoxyamine is exploited in order to introduce functionality at a polymer's terminus (see Scheme 1). This concept was demonstrated through radical exchange reactions between the isoindoline profluorescent nitroxide 1,1,3,3-tetramethyldibenzo[*e,g*]isoindolin-2-yloxy (TMD BIO) and a TEMPO-terminated polystyrene. High conversions to isoindoline terminated polymers were achieved using only stoichiometric ratios of the exchange nitroxide relative to polymer. The scope of this study was expanded by exploiting the di-nitroxide 9,10-bis[5-[1,1,3,3-tetramethylisoindolin-2-yloxy]]anthracene (BTMIOA) as a connector between two polymer chains forming an AA' block copolymer system with a fluorescent mid-chain linkage.

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⁶ J. P. Blinco, K. E. Fairfull-Smith, A. S. Micallef and S. E. Bottle, *Polym. Chem.*, **2010**, 1, 1009–1012.

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Personal History

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2009–present Vice-Chancellor's Research Fellow, QUT

Research interests: free radical chemistry, nitroxides, polymer ligation



ROMP and Click Modification of Acetylene Functionalised Random and Block Copolymers

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Ring-opening metathesis polymerisation (ROMP) is a living technique that facilitates the synthesis of well-defined polymers. Further versatility and topological control may be achieved by combining ROMP with Sharpless 'click' chemistry, as a route to a library of highly functional materials.

In this work we report the successful syntheses, (co)polymerisation and accompanying kinetic data for monomers A and B. After removal of the TMS group, the acetylene functionality enables three different click chemistries (copper catalysed cycloaddition,¹ alkyne hydrothiolation, and Diels Alder²) to be conducted independently or sequentially upon a single copolymer substrate (**Fig. 1**). Finally, by preparing block and statistical copolymers with varying monomer feed ratios, we were able to quantify the effect of acetylene concentration on the clicking efficacy of each technique.

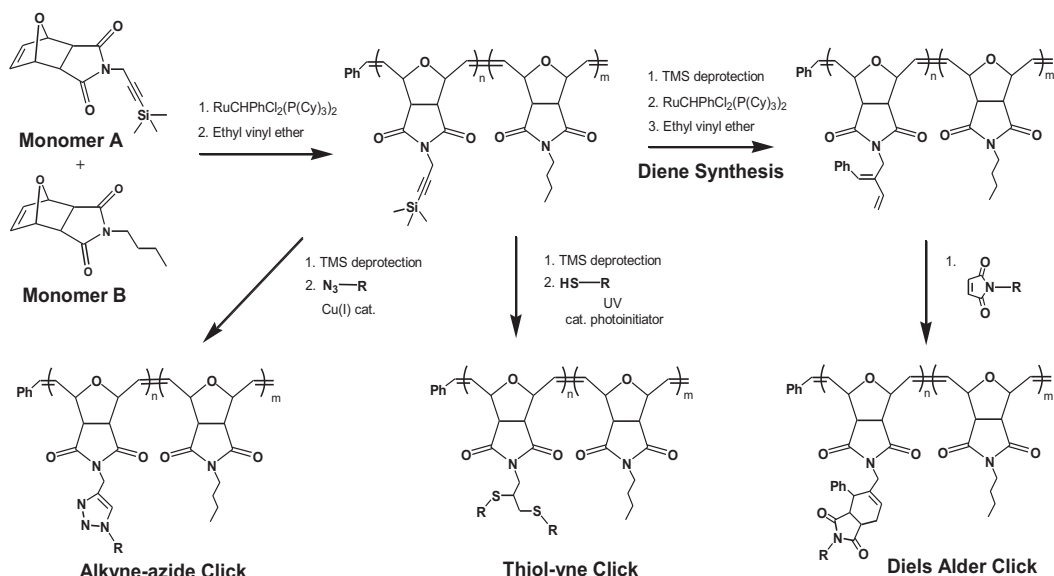


Figure 1. ROMP copolymerisation with CuAAC, thiol-yne and Diels Alder click modification.

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Personal History

2008 BE Industrial Chemistry, UNSW (Hons 1, University Medal)

Since 2010 PhD Candidate, CAMD, UNSW.

Research interests: ROMP, click chemistry, stimuli responsive materials, thermal & mechanical characterisation



The Fabrication of Star-Polymeric Film via ROMP-mediated Continuous Assembly of Polymer (CAP-ROMP)

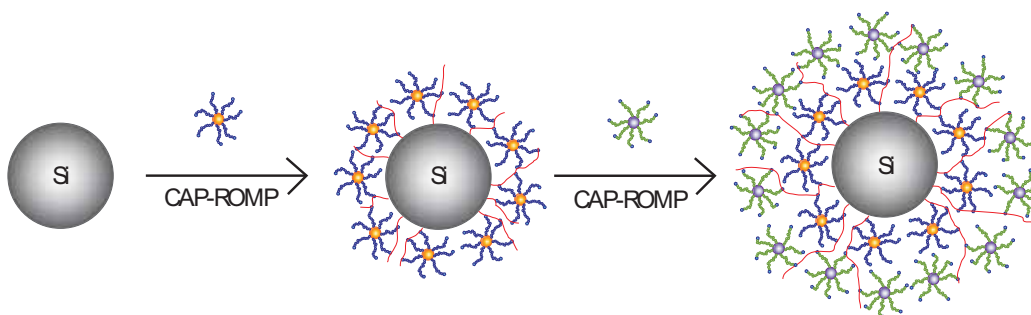
Steven Harris Wibowo, Stefanie Nina Guntari, Edgar H. H. Wong, Anton Blencow¹, Greg G. Qiao¹

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Star polymers show immense potential for applications in drug delivery, advanced coatings, encapsulation and novel polymeric film. In particular, the unique rheological properties and the tuneable functionality of star polymers appeal the utilization of star polymers as building blocks for fabricating nanostructured thin polymeric films.

An emerging novel method of fabricating polymeric film, namely the continuous assembly of polymers (CAP), combines the direct cross-linking as well as compositional flexibility of the surface grafting approach and the fine control of Layer-by-Layer (LbL) system¹. This CAP method polymerises preformed pendant-functionalised macrocross-linkers by employing living polymerisation mechanism such as ring-opening metathesis polymerisation (ROMP). This establishes a one-pot and surface-confined system which facilitates continuous fabrication of polymeric ultrathin film. The characteristics of this fabrication method also eliminate the time-consuming sequential incubation and washing in LbL and opens the opportunity of constructing tailored thin films with a broad range of polymer architectures.

In the presented study, we demonstrate the fabrication star polymer-based polymeric films via CAP-ROMP. The use of star polymers add greater versatility due to the reduced number of synthetic steps required to achieve a specific film thickness while allowing easy functionalisation and morphological tuning.² **Scheme 1** below shows a general route to the fabrication of the aforementioned film.



Scheme 1. Fabrication of CCS polymeric film *via* CAP-ROMP. Through reinitiation, different star polymers can be introduced into the ultrathin polymeric film.

¹ T. K. Goh, S. N. Guntari, C. J. Ochs, A. Blencowe, D. Mertz, L. A. Connal, G. K. Such, G. G. Qiao, F. Caruso, *Small* **2011**, DOI: 10.1002/sml.201101368.

² L.A. Connal, Q.Li, J.F., Quinn, E. Tjpto, F.caruso and G.Qiao, *Macromolecules* **2008**, 42, p.2620-2626.

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A Facile Route to Functional Hyperbranched Polymers by Combining RAFT Polymerization and Thiol–Yne Chemistry

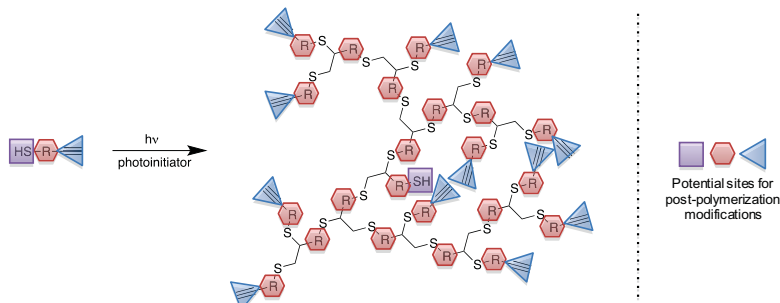
Raphael Barbey and Sébastien Perrier

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Dendritic polymers such as dendrimers or hyperbranched polymers are globular macromolecules that are characterized by a highly branched structure and a high density of functional chain-ends.^{1,2} These specific characteristics, which give those structures markedly different properties in comparison to their linear analogues, render them very attractive candidates for a wide range of applications in the (bio)medical sector or the coating industry, among others.³ In contrast to dendrimers, which are defined by a strictly regular generational structure and which preparation requires tedious, sequential syntheses and intermediate purification steps, hyperbranched polymers can be prepared via an easier (and, from an industrial point of view, more affordable) synthetic route.² Despite having randomly distributed branches, hyperbranched polymers are promising alternatives to dendrimers since they also possess a high branching density and a large number of functional terminal groups.⁴

Recently our group developed a strategy for the synthesis of hyperbranched polymers based on the UV irradiation of molecules bearing a thiol moiety at one end and an alkyne group at the other in the presence of trace amount of photoinitiator.⁵ Such molecules act as an AB₂ monomer where the thiol is the A unit and each of the π bond of the alkyne is the B unit. This method was successfully transferred to macromolecules. Combining the versatility of reversible addition–fragmentation chain transfer (RAFT) polymerizations and the robustness of thiol–yne chemistry allows the synthesis of a wide variety of functional hyperbranched structures with well-defined, polymeric building blocks.^{5,6}

Here we will discuss strategies to obtain a better control over the structure of the synthesized hyperbranched polymers and we will show how we can exploit these structures to introduce functionalities via (orthogonal) post-polymerization modifications.



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Personal History

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Research interests: controlled radical polymerization, polymer brushes, post-polymerization modification strategies.



RAFT polymerization and post-processing using a multi-stage continuous flow approach

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Herein, we describe a controlled radical polymerization process using the RAFT approach (Reversible Addition-Fragmentation Chain Transfer) under continuous flow conditions. A series of different monomers, **2**, including acrylates, acrylamides, styrene and vinyl acetate were polymerized in flow to high conversions (between 80 and 100 %) at temperatures between 70 and 110 °C and in comparatively short reaction times of the order of 2 h, provided that steel tubing is used to prevent quenching of the radical process by oxygen. For these polymerisations, several different RAFT agents, **1**, including trithiocarbonates, dithiobenzoates and dithiocarbamates and different solvents and radical initiators were used. The synthesised polymers, **3**, exhibited low dispersities, typically between 1.15–1.20, and average molecular weights similar to those prepared in a conventional batch process. The herein presented continuous approach provides a facile alternative scale-up route to conventional batch polymerization.

By using sequential processing flow technology, the polymeric product can be processed further in a second continuous reactor, usually without isolation of the intermediate. In this second stage, various different post-processing operations can be performed, such as inline purification, the synthesis of a second polymer block, **4**, using a monomer with different chemical or physical properties, and other procedures. Sequential processing can eliminate the need for isolation of hazardous, reactive or odorous intermediates which is a significant improvement on the safety of a chemical process.

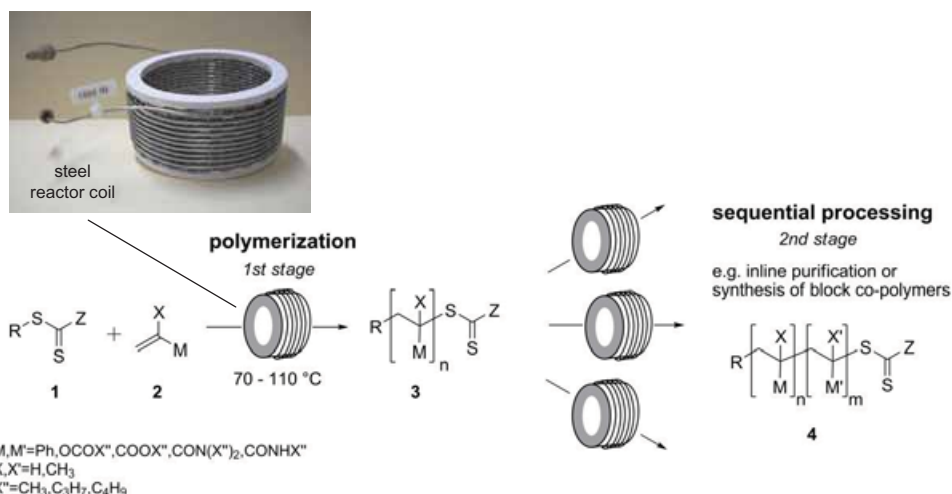


Figure 1. RAFT polymerisation using continuous flow processing; synthesis of polymers, **3**, and post processing, e.g. inline purification or synthesis of block-copolymers, **4**.

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Research interests: microreactor technology, flow chemistry, RAFT polymerization, reaction engineering



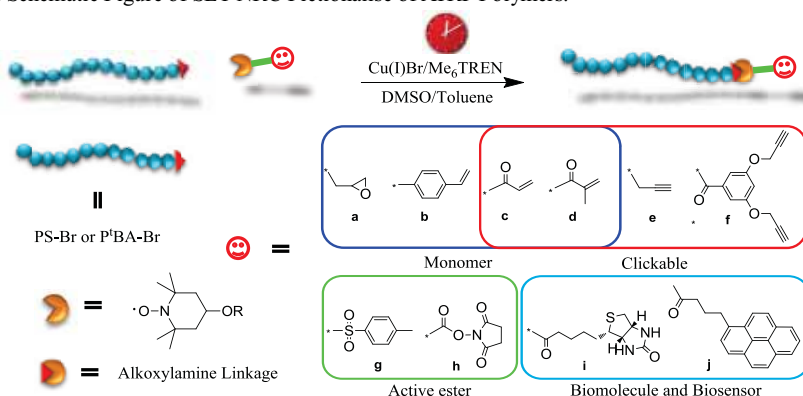
Rapid and Highly Efficient Functionalization of Polymer Bromide End-Groups by SET-NRC

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Synthetic polymers with chemical and biological functional end-groups have attracted considerable attention in recent years due to their broad applications in the construction of complex polymer architectures,¹ macromonomers, bioconjugates, polymeric therapy, functional surfaces, inorganic-organic hybrid materials and nanotechnology.¹⁻⁵ In this work, we report a rapid and highly effective method to functionalize polymers with bromine end-groups by single electron transfer – nitroxide radical coupling (SET-NRC). A library of functional nitroxide radicals synthesized from the parent molecule, 2,2,6,6-tetramethyl-4-hydroxyl-piperidin-1-oxyl (HTEMPO), included glycidyl ether, styryl, acrylate, methacrylate, succinimide carbonate, tosylate, alkyne, dialkyne, biotin and pyrene groups. These groups were chosen for their diverse functional characteristics, and were attached at 25 °C with high efficiency (> 95%) in just 10 min and with little or no side reactions to either polystyrene or poly(*t*-butyl acrylate). This synthetic methodology demonstrates the unique orthogonal and ‘click’-type attributes of the NRC approach.

Figure 1. Schematic Figure of SET-NRC Fictionalise of ATRP Polymers.



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Personal History

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2009- UQ Postdoc Research Fellow: Australian Institute for Bioengineering and Nanotechnology (AIBN) UQ

Research interests: Living radical polymerization, polymer structure design, functional polymers for biomedical application.



Self-Assembly of Porphyrin-Polymer Conjugates obtained via CuAAC Chemistry

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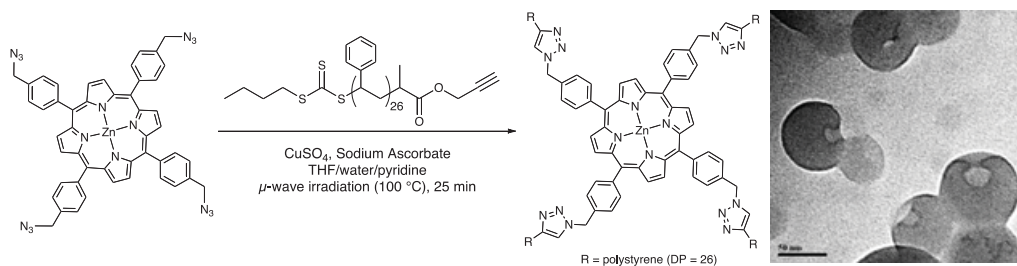
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Porphyrins and related macrocycles are fundamentally important molecules in biology, being chiefly responsible for photosynthetic light-harvesting, oxidation catalysis in cytochrome P450 enzymes, and for the gas-transport capabilities of hemoglobin.^{1, 2} The diverse synthetic and physical chemistry of porphyrins has consequently inspired many attempts to emulate these incredibly complex natural systems in the pursuit of a deeper understanding of their inherent function as well as the promise of developing exciting technologies ranging from molecular electronics and organic solar cells to novel drug vehicles and molecular sensors.^{3, 4}

Alongside their chemical functionality, porphyrins can also serve as stable, stackable square-planar scaffolds, obtainable on multi-gram scales, around which nanostructured materials can be assembled.^{5, 6} Our research group is currently investigating porphyrin-polymer conjugates, prepared by the copper(I)-catalysed alkyne-azide cycloaddition reaction (**Scheme 1**), as building blocks for supramolecular structures such as polymersome stomatocytes⁷ (**Scheme 1, inset**). This convergent ‘click’ strategy rapidly affords a variety of porphyrin-polymer conjugates from a library of RAFT-based polymers, while also providing an opportunity for post-conjugation modification through the use of functionalisable polymers, e.g., trithiocarbonate RAFT agents as masked thiols.

By tuning the interplay between the unique self-assembly properties of both the porphyrin (e.g., π - π stacking, metal-ligand interactions, electrostatic forces) and the polymer (e.g., phase separation, chain folding and inter-chain bonding) moieties, nanostructures such as rigid nanoparticles, stomatocytes, polymer thin-films and linear rod-like stacks can be obtained.



Scheme 1. Reaction scheme for the synthesis of a 4-arm porphyrin-polystyrene (DP 26) conjugate. (*Inset*) Polymersome stomatocytes from a mixture of 2, 3 and 4-arm porphyrin-polystyrene conjugates (scale bar: 50 nm)

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7. Kim, K. T., *et al.*, *J. Am. Chem. Soc.* **2010**, 132, 12522-12524.

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Personal History

2007 - 2010	Bachelor of Science (Advanced), Honours Class 1 & The University Medal, The University of Sydney, Australia
2011	PhD candidate, Key Centre for Polymer Colloids, School of Chemistry, The University of Sydney, Australia



Exploring the synthesis and applications of graphene

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Graphene is the ultimate two-dimensional polymer consisting of a single layer of sp^2 hybridized carbon. Here we explore different approaches to synthesize this carbon allotrope, ranging from chemical conversion to vapor phase deposition. Briefly, graphite can be converted into graphene oxide (GO) sheets, which readily disperse in water, and then can be reduced by various methods.¹⁻³ Due to its unique ability to be solution processed and patterned, GO and chemically converted graphene (CCG) hold promise for applications ranging from distributed ignition to transparent conducting electrodes for flexible solar cells, touch screens, etc.⁴⁻⁸ Chemical vapor deposition of graphene onto metal substrates enables the growth of continuous, large-area graphene (**Fig. 1**).⁹ The challenges of growing graphene, controlling the number of layers, transferring graphene and some exciting new uses such as flash memory will be discussed.¹⁰ Characterization includes optical microscopy, AFM, SEM, TEM, STM and Raman spectroscopy.

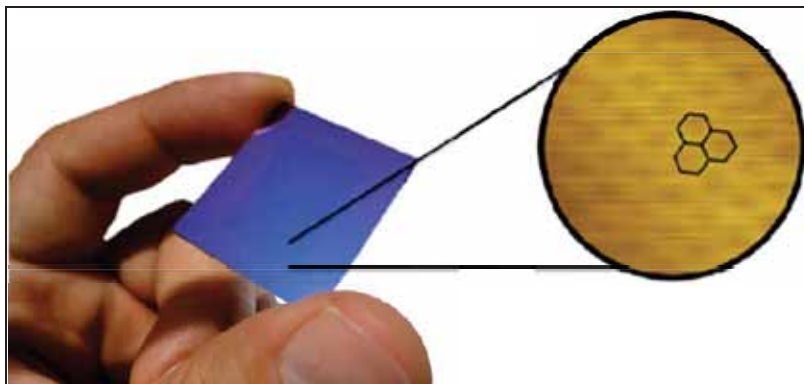


Figure 1. Large-area single layer graphene transferred onto a silicon substrate with a 300 nm oxide can be seen with the naked eye, while STM imaging allows us to see the honeycomb network of carbon that makes this material so robust.

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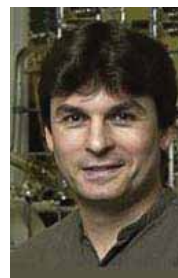
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Personal History

1984	Ph.D., University of Pennsylvania
1984 – 1987	Post-Doctoral Scholar, UC Berkeley
1987 – 1991	Assistant Professor of Chemistry, UCLA
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1993 – present	Professor of Chemistry, UCLA
2002 – present	Professor of Material Science and Engineering, UCLA
2010 – present	Adjunct Professor, Computer Science and Engineering, RMIT



Research interests:

Professor Kaner and his research group concentrate on the synthesis and characterization of new materials. Four important research areas are targeted: 1) the development of conducting polymer nanofibers with applications in flash welding, sensors, artificial muscles and memory devices; 2) the synthesis and characterization of ultra-incompressible, superhard materials; 3) nanostructured thermoelectric materials and devices; and 4) new synthetic routes to carbon based materials and composites.

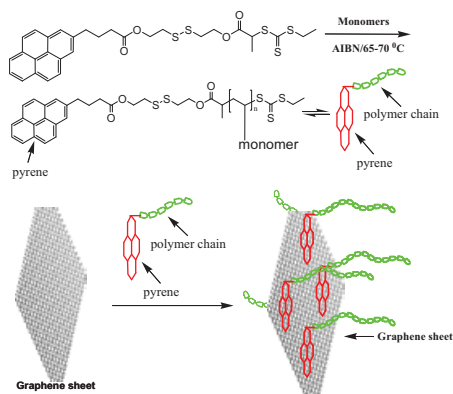
Imparting Polymer Properties to Graphene Composites via π - π Stacking Surface Modification

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Graphene sheets have envisioned extensive applications in super-computer, novel materials, nano-electronics and sensors etc, due to their excellent two dimensional mechanical, structural, thermal and electrical properties.^{1,2} The graphene sheets are quite hydrophobic and tend to aggregate irreversibly via van der Waals interaction. Therefore, modification of graphene via varied methods to making it stable, functional would be of great importance for practical applications. Comparing with the covalent modification methods, non-covalent ones will not destroy the conjugated structure of graphene, thus maximally protect its electrical conductivity. π - π stacking interaction has exhibited incomparable advantages over other methods for graphene modification, particularly in the protection of graphene conductivity. In this presentation a number of thermal sensitive polymers with controlled low critical solution temperatures (LCSTs) from 31 to 82 °C and pH sensitive polymers with different charges and also with pyrene termini were synthesized using reversible addition fragmentation chain transfer (RAFT) polymerization technique and utilized to modify the graphene surface to afford graphene-polymer nanocomposites with polymer properties. (Scheme 1) These functional graphene composites were characterized using AFM, SEM, TGA, FTIR, QCM etc and may envisioned more extensive commercializations.^{3,4}



Scheme 1. Synthesis of pyrene terminated functional polymers for modification of graphene via π - π stacking surface.

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Using Copolymer Micro-domains to Control the Orientation of Multi-Walled Carbon Nanotubes in a Uniformly Distributed Thin Film

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Forming a uniformly dispersed carbon nanotube material has long been sought after to increase the mechanical properties of the resulting nanocomposite.^{1,2} Many chemical techniques have been employed to increase such dispersions,³ however the orientation of carbon nanotubes in a polymer matrix has not been greatly studied and is often ignored.

In this work, homopolymer brushes of polystyrene on multi-walled carbon nanotubes are produced by activators regenerated by electron transfer in atom-transfer radical polymerization (ARGET ATRP)(see **Fig. 1a**).⁴ As the brushes are living polymers, the chain lengths are controlled by reaction time and hence, tailor made polystyrene coverage on carbon nanotubes has been achieved. This surface treatment increased the architectural similarity between a polymer matrix and the carbon nanotube, which upon loadings of 0 to 1w/w% demonstrated a uniform dispersion in the bulk.

As the surface treated nanotubes now have an affinity for polystyrene, a 30/70 block copolymer melt of P(S-b-MMA) was used in an attempt to align the carbon nanotubes perpendicularly to a substrate surface. Using the segregation forces of the block copolymer melt the hexagonal cylindrical melt has the same structure as the tubular carbon nanotube, and due to the nanotubes affinity for the polystyrene phase, the nanotubes orientate themselves to lie within the cylindrical phase (see **Fig. 1b and c**).

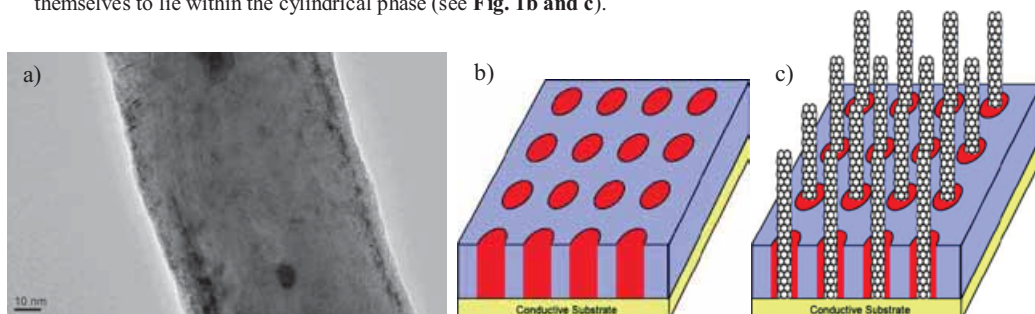


Figure 1. a) HRTEM image of an ARGET ATRP polymer brushes on a multi-walled carbon nanotube,⁴ b) a 30/70 cylindrical copolymer melt and c) the 30/70 cylindrical nanotube copolymer melt (right)

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Surface Modification of Carbon Nanotubes Using RAFT Polymer Coatings

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Carbon nanotubes (CNTs) are generally hydrophobic and tend to aggregate in aqueous media. In addition, they do not have functional groups unless treated with strong acids. Treatment of MWCNTs with strong acids not only provides them functional groups such as $-\text{COOH}$ and $-\text{OH}$ but also makes them hydrophilic. The charged functional groups on the surface of CNTs attract oppositely charged polyelectrolytes to form a layer of polymer on the surface via electrostatic interaction. Through this interaction multiple layers of polymers can be deposited on the surface by using alternatively charged polymers. In this study, a pair of two polyelectrolytes, poly[2-methacryloxyethyl trimethyl (ammonium chloride)] (1), a positively charged polymer, and poly(3-sulfopropylacrylate potassium) (2), a negatively charged polymer, were prepared by RAFT polymerisation (Fig. 1) and used for layer-by-layer (LbL) deposition (up to six layers) on the surface of MWCNTs. The advantage of using RAFT process to prepare polyelectrolytes is to be able to control the molecular weight and polydispersity of the synthesised polymers, thus, it is possible to control the surface properties of MWCNTs. Evidence of the alternate deposition of oppositely charged polyelectrolytes was investigated by zeta potential measurement which was found to reverse from positive to negative as a function of the number of deposited layers (Fig. 2). The inclusion of superparamagnetic Fe_3O_4 nanoparticles resulted in aqueously dispersible magnetic nanoparticle and MWCNT hybrid materials which may have application as MRI contrast agents. Furthermore, as the polymer layers carry RAFT end groups the polymer coated MWCNTs can be further used as macroRAFT agent to grow polymer brushes from the surface, providing more opportunities for biomedical applications.

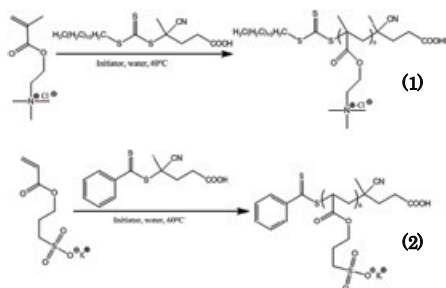


Figure 1. Synthesis of polyelectrolytes via RAFT polymerisation

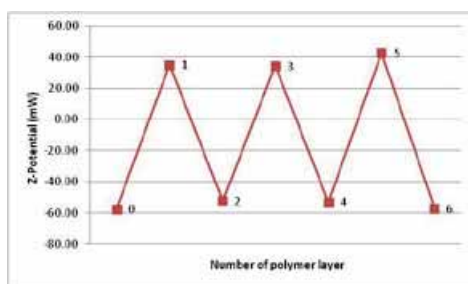


Figure 2. Zeta potential of treated MWCNTs (zero layer) and 1–6 layers of polymers (1) and (2).

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Polymer Coating of Multiple-Walled Carbon Nanotubes via RAFT Mediated Emulsion Polymerisation

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Since first reported by Iijima in 1991,¹ carbon nanotubes have fascinated researchers all over the world due to their excellent mechanical properties and high electrical and thermal conductivities. However, difficulties encountered in dispersing carbon nanotubes in useful media, such as solvents or polymers have continued to be the factor limiting their use in a range of applications.² This is because carbon nanotubes are very small in diameter and their surface properties are often incompatible with the materials in which we would like to disperse them. Recent studies have shown that RAFT mediated polymerisation can be successfully utilised to modify the surface of COOH functionalized multi-walled carbon nanotubes (MWCNTs).³⁻⁵ The method involves covalent bond attachment of RAFT groups onto the surface of carbon nanotubes.³⁻⁵ Subsequent free radical growth of the RAFT groups produces a uniform polymer coating. The thus modified MWCNTs displayed good dispersion in either hydrophobic solvents or water depending on the nature of the grafted polymers. However, chemical attachment of RAFT groups onto carbon nanotubes is cumbersome, time consuming and not suitable for large scale production. Furthermore, the free radical polymerisation is carried out in a way that generates a lot of homopolymer, which is not associated with the carbon nanotubes.

In this study, a method to efficiently disperse and uniformly coat COOH functionalized MWCNTs with polymer by RAFT mediated emulsion polymerisation was explored. Amphiphilic Macro-RAFT copolymers were first physically adsorbed onto the surface of carbon nanotubes. The copolymers were found to provide the nanotubes with excellent stability after ultrasonic dispersion. Chain extension of the adsorbed living copolymers by emulsion polymerisation was found to successfully coat MWCNTs with uniform polymer layers (**Figure 1**).

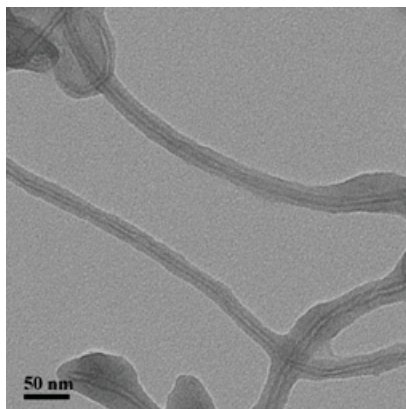


Figure 1. Polymer coated MW carbon nanotubes

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Electrospun Polystyrene Short Fibres from Ultrasonication Method

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Electrospun nanofibre membranes have been widely used in areas such as membrane technologies, biomedical, sensors and in tissue engineering applications^{1,2}. The fibres produced from electrospinning are in the form of non-woven fibre webs. However, limited research has been carried out to convert these electrospun webs to short nanofibres. In this research, ultrasonication method will be used as a novel means for the scission of electrospun fibres by ultrasonic radiation propagating through a liquid (solvent) medium. The concept is based on a method that has previously been used to reduce and control the size of carbon nanotubes and improve their dispersion³. The scission effect is created when ultrasound energy provided creates cavitation bubbles that generate high strain rate upon implosion⁴. It was found that sonication of electrospun polystyrene fibre mat in water media manage to shorten the long continuous fibre down to about 3 μm at sonication run time of 8 minutes. The SEM images of electrospun PS fibre before and after 8 minutes of sonication is shown in **Fig. 1**, whilst **Fig. 2** shows the average short fibre length after sonication run time of 2, 3, 4 and 8 minutes.

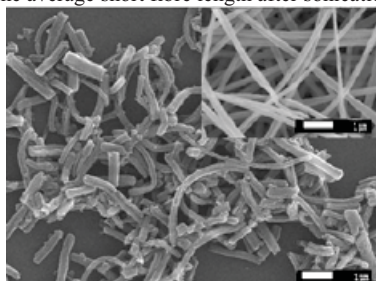


Figure 1 Electrospun PS fibre before (inset) and after sonication run time of 8 minutes (scale bar = 1 μm)

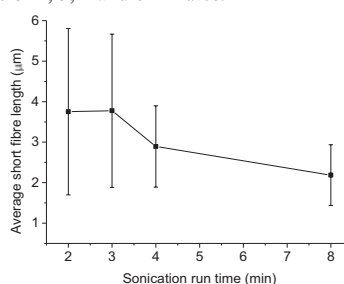


Figure 2 Average PS short fibre length after sonication of 2, 3, 4 and 8 minutes.

Both infrared spectroscopy and thermal calorimetry were used to determine if the sonication caused a change to the chemical properties of the bulk or surface post scission. The result shows that the absorption peaks for electrospun fibres before and after sonication are similar to that for neat PS (see **Fig. 3**). It was also found from the Differential Scanning Calorimetry (DSC) that the bulk properties remained the same (see **Fig. 4**), where the glass transition temperature (T_g) for all the samples was approximately 100 $^{\circ}\text{C}$.

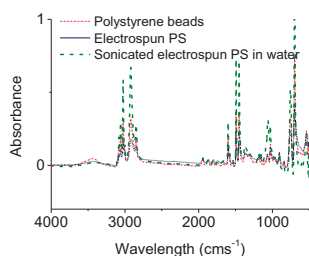


Figure 3 FTIR Spectra of Polystyrene

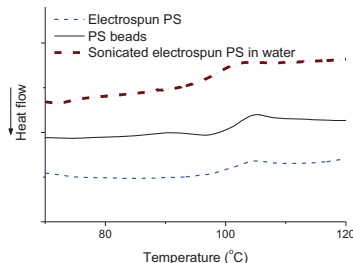


Figure 4 DSC results showing the glass transition temperature, T_g for various polystyrene samples, including electrospun fibres

Therefore, ultrasonication method is suitable for shortening of polystyrene nanofibres in a short time whilst maintaining its chemical and polymer architecture.

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- P 1 **En Route to Polymeric Janus Nano Particles**
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- P 2 **Photoinduced “Melting” of Sugar Alcohols Having Mesogenic Azobenzene Multiarms**
Haruhisa Akiyama, Masaru Yoshida
National Institute of Advanced Industrial Science and Technology
- P 3 **Novel monolithic cryopolymers containing embedded nanoparticles with different functionality**
Dario Arrua, Roderick Jones, Paul Haddad, Emily Hilder
Australian Centre for Research on Separation Science, School of Chemistry, UTAS
- P 4 **Characterization of PAN-based carbon fibers having flame retardant treated nano-cellulose**
Jee-Woo Yang¹, Jong Sung Won¹, Jae Jung Yoo¹, Yong-Sik Chung², Seung Goo Lee^{1,*}
BK21 FTIT, ¹Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon, South Korea, ²Department of Organic Materials & Fiber Engineering, Chonbuk National University, South Korea
- P 5 **Electron Beam Cross-linked Halogen Free Flame Retardant (HFFR) Shape Memory Polymers**
Ahmed Basfar
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- P 6 **Novel Thermo-responsive Polymers for Biomedical Applications**
Thomas Bennett, Andrew Whittaker, Idriss Blakey, Kris Thurecht
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- P 7 **Hetero-Diels-Adler Chemistry for Nano-Structured Materials Design**
James Blinco^{1,2}, Michael Bruns³, Peter Gerstel¹, Mathias Glassner¹, Hartmut Gliemann⁴, Vanessa Trouillet³, Christopher Barner-Kowollik¹
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- P 8 **An easy way to introduce activated disulfide groups in the hyperbranched polymer structure using sodium methanethiosulfonate**
Cyrille Boyer, Tom Davis
Centre for Advanced Macromolecular Design (CAMD), UNSW, Sydney, Australia
- P 9 **Synthesis of Glucose Decorated Nanocapsules using a Layer by Layer Approach and Gold Nanoparticle as Sacrificial Templates**
Cyrille Boyer, Xikai Li, Tom Davis
Centre for Advanced Macromolecular Design (CAMD), UNSW, Sydney, Australia
- P 10 **Self-organization of magnesium nanoparticles at the molecular level to store hydrogen using functional polymer**
Cyrille Boyer^a, Kondo-Francois Aguey-Zinsou^b
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- P 11 **Preparation of 2-N, 6-O- sulfated chitosan based nanoparticle and its application in a photopolymerisable hydrogel system for BMP-2 delivery**
Lingyan Cao^{1,2,3}, Jerome Werkmeister¹, Jing Wang^{2,3}, Veronica Glattauer¹, Yen Truong¹, John Ramshaw¹, Keith McLean¹, Changsheng Liu^{2,3}
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- P 12 **A Large PCE Enhancement for Organic Solar Cells via Incorporation of a Novel Alcohol-soluble Conjugated Polyelectrolyte interlayer**
 Yu Chen^{1,2}, Zhitao Jiang^{2,3}, Scott Watkins², Mei Gao², Ping Lu³, Haiqiao Wang¹, Xiwen Chen²
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- P 13 **Preparation and Characterization of the PAR/PET Composite System**
Tae-Min Hong¹, Han Na Choi¹, Jee-Woo Yang¹, Seung Goo Lee¹
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- P 14 **Functionality of proteins bound to plasma polymer surfaces**
Bryan R Coad^{1,2}, Tanja Scholz¹, Krasimir Vasilev², Robert D Short², Hans J Griesser¹
¹Ian Wark Research Institute, ²Mawson Institute
- P 15 **Janus Cyclic Peptide-Hybrid Polymer Nanotubes**
Maarten Danial¹, Kate Jolliffe², Sébastien Perrier¹
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- P 16 **Investigation of the mechanism of urethane formation in the presence of organotin(IV) carboxylate catalysts using computational and experimental methods for selected isocyanates**
Ransi Devendra¹, Tilo Söhnle¹ and Neil Edmonds¹,
¹School of Chemical Sciences, The University of Auckland, New Zealand
- P 17 **Self-Assembly of Gold Nanoparticles Mediated by Hyperbranched Polymers for Making Spectroscopically Barcoded Particles**
Priyanka Dey¹, Idriss Blakey², Kristofer Thurecht², Peter Fredericks¹
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- P 18 **Functional Thiophene-Based Conductive Polymers for Organic Electronics**
Anang WM Diah^{1,2}, Warwick Belcher¹, Clovia Holdsworth¹
¹Chemistry, School of Environmental and Life Sciences, University of Newcastle, Australia, ²Department of Chemistry, Tadulako University, Palu, Indonesia
- P 19 **Synthesis and Analysis of Photodegradable Polymers and Hydrogels for Biological Applications**
Francesca Ercole¹, Richard Evans², John S. Forsythe¹
¹Monash University, Department of Materials Engineering, ²CSIRO, Materials and Science Engineering

- P 20 **Poly(2-oxazoline): An alternative to PEG?**
Brooke Farrugia^{1,2}, Rebecca Forster^{1,2}, Kristian Kempe³, Richard Hoogenboom⁴, Ulrich Schubert³, Tim Dargaville^{1,2}
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- P 21 **PGS-co-LA Nanofibers Scaffolds by Core/Shell Electrospinning**
Bing Xu¹, Qizhi Chen¹
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- P 22 **Amphiphilic Biodegradable PCL-g-Amylose Synthesized in scCO₂ and its Self-assembly Behaviour**
Wanli Fu, Kristofer Thurecht, Peter Halley, Andrew Whittaker
 Australian Institute for Bioengineering and Nanotechnology, UQ, Brisbane, Queensland
- P 23 **Thermal properties of self-healing nanocomposite polymer**
Gigi George, Qipeng Guo
 Institute for Technology Research and Innovation, Deakin University, Australia
- P 24 **Validity Limits for the Zero-1 Approximation in Styrene Emulsion Polymerisation**
Brian S Hawkett¹
¹ Key Centre for Polymers and Colloids, The University of Sydney
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Wan-Gyu Hahm¹, Seung Goo Lee²
¹ Korea Institute of Industrial Technology (KITECH), KOREA, ² Chungnam National University, KOREA
- P 26 **Functionalized Nanodiamonds for platinum drug delivery**
Vien Huynh^{1,2}, Samuel Pearson¹, Janina Noy¹, Wei Scarano^{1,2}, Paul de Souza², Martina Stenzel¹
¹ Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, ² St. George Clinical School, University of New South Wales, Sydney, NSW
- P 27 **The Effects of Surface Modifications of Polyketone Fibers on the Interfacial Adhesion of Silicone Rubber Composites**
Jong Sung Won¹, Tae Min Hong¹, Jae Jung Yoo¹, Han Na Choi¹, and Seung Goo Lee¹
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- P 28 **Towards Supramolecular Actuation in Polymer Gels**
Lyall Hanton, Stephen Moratti, Daniel Hutchinson
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- P 29 **Methacrylic Macromonomers and Thiol-Isocyanate Chemistry: Synthesis and Copolymerization**
Alyse Harvison, Andrew Lowe
 UNSW- CAMD

- P 30 **Poly(arylene ether ketone)s composed of non-coplanarly accumulated aromatic-rings repeating unit**
Daichi Hijikata, Natsumi Sakai, Hideaki Oike, Akiko Okamoto, Noriyuki Yonezawa
Tokyo University of Agriculture and Technology
- P 31 **Click chemistry approaches towards the synthesis of daisy chain click polyrotaxanes**
Asif Noor, James Crowley, Stephen Moratti
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- P 32 **The effect of polymer molecular weight on P3HT:PCBM Nanoparticulate organic photovoltaic device performance**
Natalie Holmes¹, Syahrul Ulum¹, Mitchell G. Wilson¹, Prakash Sista², Kerry B. Burke¹, Mihaela C. Stefan², Glenn Bryant¹, Xiaojing Zhou¹, Warwick J. Belcher¹, Paul C. Dastoor¹
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- P 33 **Tandem Synthesis of N-heterocycles and monomers**
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- P 34 **Sequential self-repetitive reaction toward full polyimides featuring linear or hyperbranched structures with stable optical nonlinearity.**
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- P 35 **All-cellulose composite laminates via solvent infusion processing**
Tim Huber¹, Simon Bickerton², Jörg Müssig³, Mark P. Staiger¹
¹Department of Mechanical Engineering, University of Canterbury. ²Centre for Advanced Composite Materials, Department of Mechanical Engineering, University of Auckland. ³Hochschule Bremen - University of Applied Sciences, Germany.
- P 36 **CCT-derived Macromonomers as Macroinitiators for Anionic Polymerisation**
Gemma Sanders^{1,2}, Robbert Duchateau^{1,2}, Hans Heuts^{1,2}
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- P 37 **The high dielectric and energy density composites with block copolymer hybridized nanoparticles**
Hyun Min Jung, Sunwoo Lee, Jong Chan Won
- P 38 **PGS-co-LA Nanofibers Scaffolds by Core/Shell Electrospinning**
Bing Xu¹, Qizhi Chen¹
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- P 39 **Bio-based Adhesive Resins - Their Characteristics and Applications**
Daisaku Kaneko¹, Noriko Hiraishi², Tomohito Shimada¹, Tatsuo Kaneko¹
¹School of Materials Science, Japan Advanced Institute of Science and Technology, ²Graduate School, Department of Restorative Sciences, Tokyo Medical and Dental University

- P 40 **Development of ultra-hydrophobic non -fluorine sol-gel films for aluminum alloy**
Ruchi GroverWankhede¹, Nick Birbilis³ & A.S.Khanna²
¹ IITB-Monash Research Academy, IIT Bombay ²Department of Metallurgical Engineering and Materials Science, IIT Bombay, Mumbai, Maharashtra, 400076, India, ³Department of Materials Engineering, Monash University
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 Chungju National University
- P 42 **Bio-inspired Polymers and Gels based on Dopamine-Modified Polyaspartamides For Versatile Coating and Adhesive Applications**
Ji Heung Kim^{1,2}, Jung Hyun An¹, Seong-beom Heo¹, Young Sil Jeon²
¹ Department of Chemical Engineering, Sungkyunkwan University, ² Polymer Technology Institute, Sungkyunkwan University
- P 43 **Effect of Heterostructure of Metallic Nanoparticles and Carbon Nanotubes on the Mechanical Properties of Polymer Composite Films**
Soo Hyung Kim, Ji Young Ahn, Jae Beom Lee, Suckwon Hong, Dongyun Lee, Jongman Kim
 Pusan National University
- P 44 **Natural antioxidants for polyolefin elastomer**
Anna Masek, Marian Zaborski
 Institute of Polymer and Dye Technology, Technical University of Lodz
- P 45 **Elastomer composites containing layered fillers and hydroxyapatites**
Magdalena Lipinska, Joanna Pietrasik, Marian Zaborski
 Institute of Polymer and Dye Technology, Technical University of Lodz
- P 46 **Degradable composites containing modified cellulose**
Magdalena Lipinska, Anna Masek, Marian Zaborski
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- P 47 **Cellulose fibre as natural filler for epoxidized natural rubber**
Marian Zaborski¹, Anna Masek¹
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- P 48 **Green tea extracts as antiageing substances for rubber**
Anna Kosmalka, Marian Zaborski
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- P 49 **Chitosan-based nanofibrous mats as anti-adhesion barriers**
Oh Hyeong Kwon¹, Mr Jae Eok Ko¹, Mr Won Il Kim^{1,2}
¹ Kumoh National Institute of Technology, ² Wonbiogen Ltd.
- P 50 **A Study of Nano Size Standard Material Validation by the Photon Correlation Spectroscopy (PCS) method**
John Arthur, Gavin Soon
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- P 51 **A Study of Low Volume Cell for Zeta Potential and Size Distribution of Submicron Particles**
John Arthur, Gavin Soon
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- P 52 **Characterization of Nanoparticles by Light Scattering**
John Arthur, Gavin Soon
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Yuan Li, Wenchao Huang, Wayen Cook, Qizhi Chen
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Shin-Chih Liu¹, Shi-Min Shau, Shenghong A. Dai, Professor Ru-Jong Jeng
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LiHui Liu, Cheryl Taylor, Brad Woonton, Kirthi De Silva
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John Arthur, Gary Deger
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Elda Markovic¹, Kristina Constantopoulos², Milena Ginic-Markovic³, Stephen Clarke⁴
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- P 61 **Selective Deposition of Silica-Polymer Hybrid Nanoparticles on Gold Surfaces**
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- P 62 **RAFT Polymerisation in Continuous Flow Microreactors**
Xuan Nguyen, Christian H. Hornung, Stella Kyi, Geoff Dumsday, Simon Saubern and John Chiefari
CSIRO Materials Science and Engineering
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Kewei Wang, Hui Peng, Kristofer J. Thurecht, Andrew K. Whittaker
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- P 64 **Synthesis of Structurally Regulated Polymers with Five- and Six-Membered Rings via Isomerization Polymerization**
Kohtaro Osakada, Daisuke Takeuchi, Taksehi Okada
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- P 65 **Functional Hyperbranched Polymers for Prostate Cancer Theranostics**
Amanda Pearce,¹ Kristofer J. Thurecht,¹ Idriss Blakey¹ and Andrew K. Whittaker¹
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- P 66 **Copper(I)-mediated azide-alkyne cycloaddition for cyclic peptide-polymer conjugation**
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- P 68 **Photo-initiation for the Formation of Hybrid Silica-Vinyl Network Systems**
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- P 69 **Increasing the Swelling- and Deswelling Kinetics of HEA/PEG Diacrylate Hydrogels by Incorporating Well Defined PMMA-PLMA Block Copolymers and n-alkanes as Sacrificial Templates**
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- P 70 **Dissolution behaviour of regenerated cellulose fibre**
Jeremias Schuermann¹, Tim Huber¹, Mathieu Sellier¹, David Collings² and Mark P. Staiger¹
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- P 71 **Thermo- and Thermooxidative Stability of Modified Pectins**
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- P 72 **Cholesterol Conjugated Polymers as siRNA Delivery Vehicles: Correlation between Physicochemical and Biological Properties**
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- P 74 **High Resolution Electrospray Ionization Mass Spectrometry (ESI-MS) Investigation of Cu(0) - Mediated Radical Polymerization**
Alexander Soeriyadi, Fredrik Nystrom, Cyrille Boyer, Per Zetterlund, Michael Whittaker
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- P 75 **Mathematical modeling of linear and non-linear RAFT polymerization using a multifunctional polymer molecule approach**
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- P 76 **Insights into the power law relationships that describe mass deposition rates during electrospinning**
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- P 77 **Synthesis of Polydimethylsiloxane-Containing Block Copolymers via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization and their Self Assembly in Water**
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- P 78 **Effect of Annealing on Physical Properties of Polypropylene Slit Film Yarn**
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- P 79 **The history of electrospinning from 1600 to 1995**
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- P 80 **Characterization of Gellan Gum by Capillary Electrophoresis**
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- P 82 **A generalised small scale synthesis of polymer nanoparticles by RAFT in mini-emulsion polymerization for applications in separation science.**
Mark Thomas, Roderick Jones, Emily Hilder
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- P 84 **Employing A Liquid, Model Polyolefin For The Evaluation Of Profluorescent Nitroxides As Probes For Polymer Degradation**
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- P 85 **Employment of mixed host for performance enhancement in blue phosphorescent organic light emitting devices**
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- P 86 **Study on Fabrication of Functionalized Polymer with Patterned Nano-scale Silver Metal using Radiation Reduction Technique**
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- P 87 **hMSC behaviors on electrospun fibrous PCL/BG composite scaffold via the sol-gel process**
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- P 88 **Functionalised HIPE Polymers via ROMP & Gamma Initiated Thiol-ene Click**
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- P 89 **Dynamic Mechanical Analysis of Functionalised ROMP Polymers**
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- P 90 **Bioactivity of electrospun PCL-Bioactive glass fiber preparation via blending and sol-gel process**
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- P 91 **Biocompatible PCL scaffold fabrication using electrospinning and forcespinning method for bone tissue engineering application**
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- P 92 **The use of cationic polymers at bubble interfaces for water reclamation**
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- P 93 **On the Electrospinning of Monosaccharides**
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- P 94 **Preparation of Chitosan Electrospun Nanofibers Membrane and its Characterization**
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En Route to Polymeric Janus Nano Particles

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The method developed by Ferguson et al.¹ to conduct ab initio emulsion polymerization using macro-RAFT agents as sole stabilizers has been used to synthesize monodisperse seed nano particles which in turn are used as building blocks to produce polymeric Janus nano particles. Compared to the work done by Geneva et al.² which used frozen micelles as seed particles in ab initio emulsion polymerization, this work focuses on labile micelles made up of acrylic acid and *n*-butyl acrylate block copolymers. The labile micelles are further polymerized with styrene and crosslinked with divinyl benzene and subsequently swollen with styrene and polymerized to form the second face of the Janus particles. The morphology and properties of Janus particle formation has been optimized by varying the type of initiator used and its amount. The amount of crosslinker needed to facilitate Janus particle formation has also been quantified.

¹ Ferguson, Hughes; Nguyen, Pham; Gilbert; Serelis; Such and Hawke, B. S. *Macromolecules* 2005, 38, 2191-2204

² Geneva, Sprong, de Bruyn, Warr, Such and Hawke *Macromolecules* 2007, 40, 6181

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Photoinduced "Melting" of Sugar Alcohols Having Mesogenic Azobenzene Multiarms

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Sugar alcohols are useful materials for synthesis of comb-like liquid crystals, because they can be considered as an oligomer of hydroxymethylene units and some of the naturally derived compounds are commercially available at low cost. We have already reported substitution of the hydroxyl groups of several kinds of sugar alcohols with multiple azobenzene-mesogenic side chains and thermotropic liquid crystal properties of tetramer, hexamer and octamer analogues.¹ In this study, we further investigated the photoresponsivity of the oligomeric materials based on azo-functional sugar alcohols in the solid state. As a result, a unique photoinduced isothermal and reversible solid-liquid phase transition (melting) of the multi-azo liquid crystalline compounds at room temperature was observed.

All of compounds including monomer, dimer, tetramer, hexamer and octamer, were obtained as powdered solid at room temperature. Under ultra violet (UV) light ($\lambda_{\max}=365$ nm), the tetramer, hexamer and octamer analogues with liquid crystalline property at higher temperature than room temperature gradually melted even at room temperature, although the monomer and dimer with no mesophase kept their shapes under an identical condition. Figure 1a-d shows the photoinduced-melting behaviour of the hexamer analogue. The powders slowly transferred to liquid droplets under UV light. The resultant liquid has no birefringence confirmed by polarization microscopy, suggesting the isotropic nature as a liquid. Absorption spectroscopy for the compounds before and after UV light irradiation revealed that the phase transition was accompanied with *E* to *Z* isomerisation of azobenzene moieties. After the photoinduced-melting, the orange liquid was irradiated with visible light (Figure 1e-f). Then the colour was changed from orange to yellow, corresponding to *Z* to *E* isomerisation of the azobenzene moieties confirmed by UV spectroscopy (Figure 1f). As shown in Figure 1g-h, the resultant yellow materials were able to be peeled off from the plate using micro spatula with keeping their shape, which meant a liquid transferred to a solid again by visible light irradiation.

In conclusion, the reversible phase transition of the sugar alcohols with the mesogenic azobenzene multiarms between liquid and solid was controlled by UV and visible light irradiation. The relationship between liquid crystalline properties and photo reactivity in the solid state will be also discussed.

¹ H. Akiyama et al., *J. Mater. Chem.*, 2009, **19**, 5956–5963.

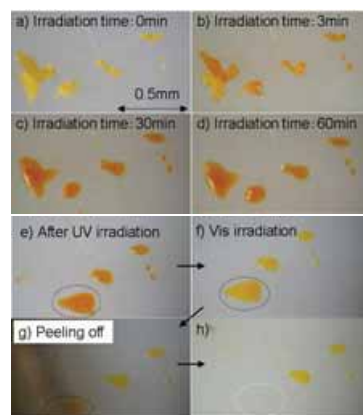
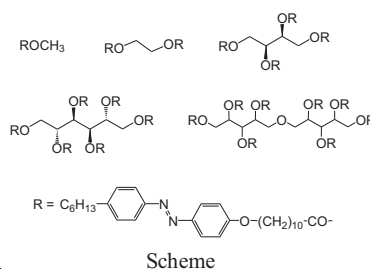


Fig. 1 Photoinduced-melting of a hexamer analogue: a) before and b) after UV light irradiation ($\lambda_{\max}=365$ nm, 40 mW/cm²) for 3 min, c) 30 min and d) 60 min. Recovering solid state: e) after UV light irradiation, f) after visible light irradiation for 10 min ($\lambda_{\max}=510$ nm, 20 mW/cm²), and g) during and h) after peeling off a piece of the solid.

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Photoinduced "Melting" of Sugar Alcohols Having Mesogenic Azobenzene Multiarms

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Novel monolithic cryopolymers containing embedded nanoparticles with different functionality

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Macroporous cryogels are a novel generation of chromatographic supports used in separation science. They are characterized by having a high porosity (up to 90%) and very high pore sizes (0.1 to 200 μm). Due to these porous properties, these materials have been extensively used in the capture of target molecules from complex mixtures such as crude cell homogenates and particulate systems. However, cryogels generally present a low specific surface area and consequently there are few reports in the use of these supports as stationary phases for the highly efficient separation of biomolecules by adsorption modes. Therefore, new approaches to increase the specific area of these polymers could broaden the application of them in separation science. In this study we present the preparation of rigid macroporous poly(ethyleneglycoldimethacrylate) cryopolymers in capillary format and their evaluation as chromatography supports for the separation of a protein mixture by hydrophobic interaction chromatography. The optimization of the polymerization reaction was carried out by studying the influence of different reaction parameters (temperature of reaction, monomer concentration and solvent) over the porous properties of the polymers obtained. Moreover, to improve the performance of the synthesized materials, we prepared composite cryopolymers with embedded nanoparticles in their structure. These cryopolymers present a regular, open porous structure unlike that described previously for cryopolymers and also a considerable specific surface area that makes them particularly interesting materials to be used in the separation of both biomolecules and small molecules. Cryopolymers formed using a range of nanoparticles with different core and surface functionality will be presented, demonstrating that this also offers an excellent approach to controlling both the structure and chemical functionality of monolithic materials, whilst also providing high separation efficiencies.

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Characterization of PAN-based carbon fibers having flame retardant treated nano-cellulose

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Carbon fibers having excellent mechanical properties and thermal stability have been used for reinforcement of high performance polymer composites including special applications. However, high thermal conductivity of the PAN based carbon fibers limited their applications for the high temperature insulating materials, such as rocket propulsion parts and nozzles etc. Recently, nano-cellulose has generated a great deal of interest as a source of nano-meter sized reinforcement having excellent mechanical properties.¹ In this study, we prepared the nano-cellulose filled PAN based carbon fibers to reduce the thermal conductivity of them. Because the low char yield of nano-cellulose after the high temperature carbonization, flame retardant treatment of the nano-cellulose was conducted to improve its char yield.² The char yield of cellulose has been improved by a proper flame retardant treatment. Dispersion condition of nano-cellulose particles in the PAN solution was studied for the PAN/nano-cellulose mixture. Optimum conditions for stabilization and carbonization of PAN/nano-cellulose fibers were investigated. Consequently, thermal conductivity of the carbon fibers filled with flame retardant treated and carbonized nano-cellulose was reduced. Physical, mechanical and thermal properties of the carbon fibers filled with flame retardant and heat treated nano-cellulose particles were examined utilizing X-ray diffractometer, field emission scanning electron microscopy, tensile tester and thermal analyzer.

¹ M. Samir, F. Alloin, J. Sanchez, and A. Dufresne, *J. Polymer*. **2004**, *45*, 4149-4157

² S. B. Yoon, D. Cho, and J. K. Park, *J. Korea, Polymer*. **2005**, *29*, 211-215

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Electron Beam Cross-linked Halogen Free Flame Retardant (HFFR) Shape Memory Polymers

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Abstract

Halogen free flame retardant (HFFR) shape memory polymers were prepared using blends of ethylene vinyl acetate (EVA), ethylene propylene diene monomer (EPDM) and linear low density polyethylene (LLDPE) in the presence of flame retardants and other additives. The HFFR compounds were cross-linked by electron beam (EB) up to an absorbed dose of 150 kGy and were characterized in terms of mechanical, thermal and electrical properties. Both tensile strength (TS) and elongation at break (Eb) were found to increase with increase of irradiation dose in contrast to the fact that generally, TS increases and Eb decreases with radiation cross-linking in polymers. However, both TS and Eb decreased with increase of total flame retardant contents. Optimum mechanical properties were 11MPa for TS and 200 – 350% for Eb. Limiting oxygen index (LOI) was found to increase as total flame retardant contents increased with values over the range of 30 – 35%. Shore A hardness was about 92 and retentions of TS and Eb after thermal ageing at 136°C for 168 hours were between 93% - 112% and 75% - 93%, respectively. UL94 rating of V-0 and volume resistivity of $3.21\text{E}+15$ to $3.49\text{E}+15$ were obtained with these HFFR compounds. The developed blends are of particular importance for heat shrinkable tubing applications.

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Novel Thermo-responsive Copolymers for Biomedical Applications

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Synthetic polymers capable of exhibiting a sharp change in their physical properties upon experiencing a small change in their environmental conditions have received significant interest in recent years. One of the primary reasons for the increased popularity of these so called 'intelligent polymers' is their ability to mimic biological response behaviour, and thus potentially deliver drugs in a highly selective manner.¹

In this work, we have been investigating the thermal transitions of novel copolymers, focusing in particular on the relatively under-explored upper critical solution temperature (UCST) transition, which results in the polymers swelling or becoming soluble upon an increase in temperature. It is thought that this transition could be exploited to release a payload at a target site upon heating from an external source. In particular we are investigating systems that exhibit this transition in an aqueous environment.

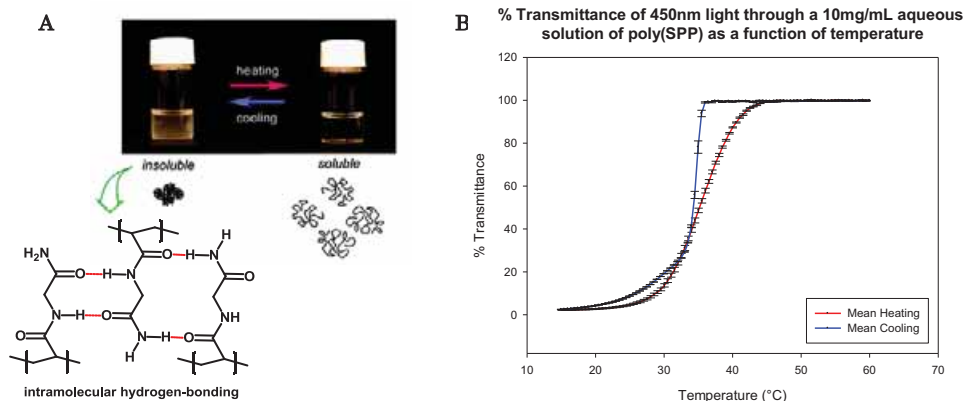


Figure 1: A. Demonstration of the cloud points for an I-S transition of poly(N-acryloyl glycineamide) and the hydrogen bonding interactions that occur during the insoluble phase. B. The Transmittance versus Temperature curve of an aqueous poly(SPP) solution.

We aimed to create copolymers which undergo an UCST transition close to physiological temperature by building upon the work of both Arotcarena et al.² and Seuring et al.³ Using RAFT polymerisation, the monomers N-acryloyl glycineamide (NAGA) and 3-[N-(3-methacrylamidopropyl)-N,N-dimethyl]ammonio propane sulfonate (SPP) were copolymerised with the monomers solketal methacrylate (SMA) and dimethylaminopropyl methacrylamide (DMPMA) respectively, in various mole ratios. These increasing changes in the hydrophilicity of the polymers were theorised to allow the UCST transitions to be tuned to a desired temperature. Additional changes to the NAGA copolymers could be induced through a simple deprotection of the SMA groups with 1:1 THF:1N HCl, resulting in polymers with a marked increase in their hydrophilicity.

¹ Schmaljohann, D., *Advanced Drug Delivery Reviews*, 2006, 58, 1655-1670

² Arotcarena, M., et al., *Journal of the American Chemical Society*, 2002, 124, 3787-3793

³ Seuring, J., et al., *Macromolecular Chemistry and Physics*, 2011, 19, 2109-2117

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HETERO-DIELS-ALDER CHEMISTRY FOR NANO-STRUCTURED MATERIALS DESIGN

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Tuning the properties of surfaces and functional polymeric materials is a key focus in materials science. One of the major scientific challenges is to achieve well-defined properties and structural order on the surface of materials in an efficient and selective fashion. Thus, the fine control of surface properties is a field of intense research. Concomitantly, the design of polymeric materials with reversible linkages continues to be a highly investigated area in materials research, with a need for simple and convenient methods to covalently conjugate a specific molecule to a surface or to obtain materials of varying properties from facile conjugation methods. A range of efficient reactions, some of which adhere to the criteria defined for *Click* chemistries,¹ (e.g. copper catalyzed Huisgen [2+3] cycloadditions, Michael additions as well as (hetero) Diels-Alder (DA) cycloadditions), fulfill the criterion of reaching (ideally) quantitative conversions, thus making them a particularly attractive reaction class to be employed for orthogonal surface design. Among these mild ligation strategies, the reversible addition fragmentation chain transfer (RAFT)-HDA concept for macromolecular conjugation chemistry is one of our methods of choice for the design of functional materials.² As well as acting as an (ultra)rapid conjugation technique, RAFT-HDA reaction sequence also has the advantage of containing a cycloadduct linkage that is completely reversible (via a retro-Diels-Alder (rDA) reaction) at elevated temperatures.

The application of the RAFT-HDA/rDA reactions to produce functional materials is demonstrated in two examples. In the first, the reversibility of the rDA reaction is utilized for the preparation of nanoporous films from poly(styrene)-*block*-poly(ethylene oxide) synthesized via the combination of RAFT polymerization and HDA cycloaddition. The copolymers can be cleaved in the solid state by a retro DA reaction occurring at 90°C.³ A simple heating and washing procedure allows the formation of the nanoporous films. In the second example silicon substrates coated with a highly reactive, cyclopentadienyl analogue were shown to undergo rapid RAFT-HDA reactions with a variety of polymers, both hydrophobic and hydrophilic. Mild heating of the substrates causes the rDA reaction to occur, thus reforming the reactive cyclopentadiene surface, generating an efficiently switchable surface.⁴

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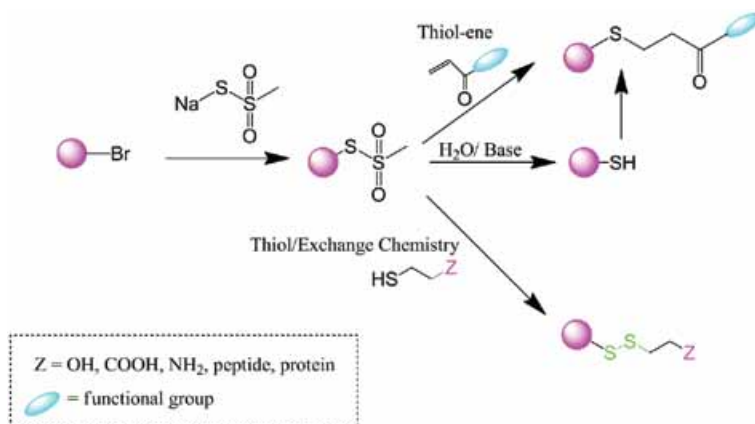
An easy way to introduce 'activated disulfide' groups in the hyperbranched polymer structure using sodium methanethiosulfonate

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Atom transfer radical polymerization (ATRP) is one of the major living radical polymerization methods together with reversible addition transfer fragmentation and nitroxide mediated polymerization. ATRP is a powerful approach allowing the synthesis of polymers with excellent control over architecture (diblock, gradient and co polymers for example) and end-groups. ATRP has been applied to the syntheses of complex architectures, such as star, microgels, hyperbranched polymers, protein-polymer conjugates and hybrid organic/inorganic nanoparticles. The introduction of functional end-groups using the halide atom as the synthetic starting point, has been achieved using click chemistry reactions, such as the azide alkyne click reaction, the thio-bromo nucleophilic reaction and radical addition in the presence of allyl compounds.

In this communication, we present a straightforward method to introduce activated disulfide as end group or as side group to polymer obtained by ATRP using a nucleophilic substitution of halide atom in the presence of sodium methanethiosulfonate. Sodium methanethiosulfonate is a powerful nucleophilic agent able to substitute at room temperature halide atom to yield activated disulfide (methane thiosulfonate group). This functional disulfide groups can then be reacted with free thiols to incorporate functional polymer endgroups via disulfide bonds (**Scheme 1**) or the functional disulfide can be cleaved into thiol terminii by hydrolysis in the presence of trace of water. This thiol can then participate in thiol ene reactions (**Scheme 1**), via two steps or in a one pot reaction without the formation of byproducts. This reaction was successfully exploited for the end group-functionalization of library of poly(vinyl benzyl chloride) hyperbranched polymers obtained by ATRP using a variety of compounds, such as functional thiols, peptides, proteins, and oligonucleotides, to yield functional hyperbranched polymers..



Scheme 1. An original route to obtain functional polymers exploiting either thiol/disulfide exchange chemistry or thiol/ene reactions from ATRP polymers.

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Synthesis of Glucose Decorated Nanocapsules using a Layer by Layer Approach and Gold Nanoparticle as Sacrificial Templates

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Hybrid organic/inorganic nano-structures are of great interest for application in numerous medical and nanotechnology fields.¹ Gold and iron oxide nanoparticles are two of the most promising materials for sensing, imaging applications, gene and drug delivery as their intrinsic properties (magnetism for IONPs and plasmon resonance for gold) and their low toxicity favor in vivo medical applications.² However, to maintain colloidal stability in aqueous media, the nanoparticles require modification by low or high molecular weight organic compounds. The utilization of polymers to coat inorganic nanoparticles can result in beneficial properties imparted to the resultant hybrid nanoparticles including the provision of functional groups on the nanoparticle surfaces. In addition, a polymer layer can be used to encapsulate therapeutic agents. Two different synthetic strategies are widely used to attach polymers; 'grafting-from' or '-onto' or a layer-by-layer (LbL) assembly approach.

In this presentation, we propose an efficient route to prepare glycopolymer-functionalized nanocapsules using gold nanoparticles as sacrificial templates. First, we describe the post-modification of poly(acrylic acid-co-2-bromoethyl acrylate) (PAA-co-PBrEtA) or poly(acrylic acid-*block*-2-bromoethyl acrylate) (PAA-*b*-PVBC) using thiol-glucose compounds via thio-bromo nucleophilic reaction. The reaction is quantitative, and allows the synthesis of well defined glycopolymer polymers. The amount of glucose moieties can be controlled according the [R-SH]/[Br-] ratio. In a second part, these glycopolymers were self-assembled onto gold nanoparticles surfaces via a layer-by-layer methodology exploiting electrostatic interactions to yield a thin polymer film. The polymer was crosslinked using the presence of residual bromide group and by the addition of a difunctional thiol compound (dithiol poly(ethylene glycol)). Finally, the gold core was removed by treatment with Aqua Regia to yield nano-capsule with a size around 40-60 nm by DLS and dispersity around 0.1-0.2.³ These nano-capsules can interact with the specific lectine.

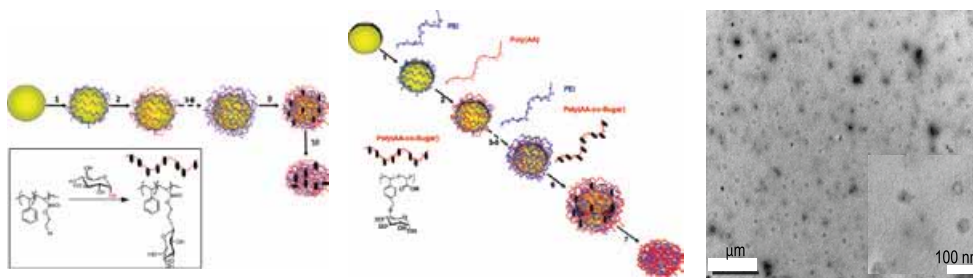


Figure 1. Left- Synthesis of glycopolymer decorated nanocapsule using gold nanoparticles as sacrificial template; Right- TEM picture of nanocapsules.

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Self-organization of magnesium nanoparticles at the molecular level to store hydrogen using functional polymer

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The so-called fossil fuels have powered our industrial revolution. Unfortunately, a heavy reliance on finite resources and the adverse effects of fossil fuels on global climate are now threatening further development. Alternative energy carriers, such as hydrogen, are required to power our society and sustain future generations. Indeed, in its purest form hydrogen has a high energy content (142 MJ.Kg^{-1}), and therefore hydrogen has naturally emerged as the only possible synthetic energy carrier with sufficient versatility to replace oil. Hydrogen is already central to our current energy systems. However the use of hydrogen in its purest form still relies on the finding of methods for the effective storage of hydrogen in a dense and compact manner. Efforts over the last decades have targeted a range of materials capable of storing hydrogen with high density. For example, light metals can absorb hydrogen to form of hydride materials, e.g. MgH_2 , NaAlH_4 , H_3BNH_3 and LiBH_4 , but the realization of successful strategies to control the properties of these materials for the practical storage of hydrogen remains unanswered. Indeed, these materials can be easily oxidized by water or oxygen. It is important to protect these materials to avoid their oxidation.

Herein, we report a bottom-up method for the facile production of magnesium hydride (MgH_2) nanoparticles and their assembly using functional polymers into a stable tertiary structure. The approach proposed is based on the in-situ synthesis of MgH_2 nanoparticles in the presence of functional polymers. The functional group allows to anchor the polymer onto the MgH_2 nanoparticle surfaces. According to the nature of this functional group, the morphology and the size of the MgH_2 nanoparticles is affected. In addition, the polymers allow to self-organize the nanoparticles into tridimensional structure (tubular structure and microparticles). This material presents exceptional properties compared to bulk magnesium. i) It can release hydrogen, according to the following equation: $\text{MgH}_2 \leftrightarrow \text{Mg} + \text{H}_2 (\text{g})$, at room temperature. ii) The material is less sensitive to trace of oxidizing agents, such water.

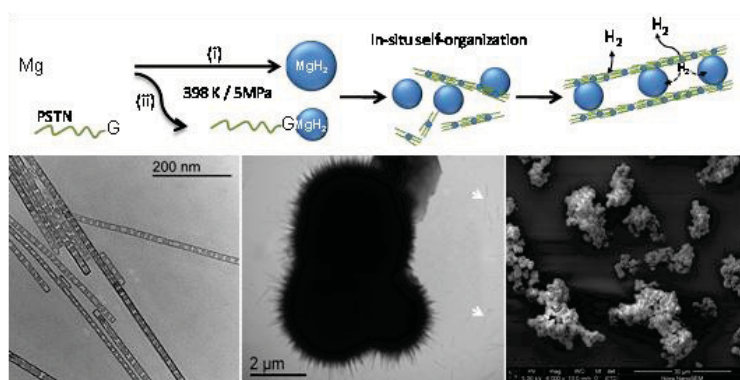


Figure 1. (top) General scheme for the synthesis and functionalization of MgH_2 ; (bottom) MgH_2 nanoparticles self-organized into tubular structure and tube organized into microparticles.

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Preparation of 2-N, 6-O- sulfated chitosan based nanoparticle and its application in a photopolymerisable hydrogel system for BMP-2 delivery

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We have previously shown that 2-N,6-O sulfated chitosan (2,6SCS) can enhance the bioactivity of Bone Morphogenic Protein-2 (BMP-2)¹. In the present study, we have synthesized 2,6SCS and loaded BMP-2 within 2,6SCS nanoparticles embedded in a photopolymerisable gelatin hydrogel² to form a composite biodegradable delivery system that allows prolonged release of active BMP-2.

2-N,6-O-sulfated chitosan was synthesized as described². BMP-2 loaded 2-N,6-O-sulfated chitosan based nanoparticles (BMP-2/2,6SCS-NPs) were prepared using a modified complex coacervation method³. To prepare the composite systems, 10% gelatin solutions containing 1 mM [RuII(bpy)₃]²⁺ and 20 mM sodium persulfate (SPS) were mixed with BMP-2/2,6SCS-NPs and hydrogels were formed by irradiation from a quartz tungsten halogen lamp for 30s². FTIR and ¹³C NMR spectra were used to confirm structure of synthesized 2-N,6-O-sulfated chitosan. Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) were used to determine the mean particle size of the 2,6SCS-NPs as well as the zeta potential. Scanning Electron Microscopy (SEM) was used to observe the distribution of 2,6SCS-NPs in the hydrogel. *In vitro* release of BMP-2 from BMP-2/2,6SCS-NPs-embedded hydrogels was quantified using a QuantiPro BCA Assay Kit (Sigma, USA).

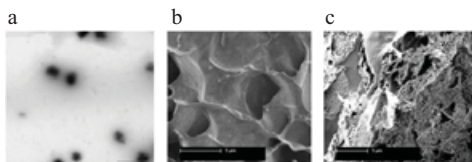


Figure 1. (a) TEM image of 2,6SCS-based nanoparticles. Scale bar = 1 μ m. SEM image of photopolymerised gelatin hydrogel without (b) and with (c) 2,6SCS-NPs.

FTIR and ¹³CNMR were used to characterize the SCS and in particular the substitution positions. In the FTIR spectrum, two absorption peaks at ~1230 cm⁻¹ derived from S=O and ~800 cm⁻¹ for C–O–S bond stretching, respectively were observed. In the ¹³C NMR spectrum, the peak shift after chitosan sulfonation indicated that the C-6 hydroxyl group and C-2 amido group were both completely sulphated. 2,6SCS-NPs had a negative zeta potential (-22.5±0.8 mV) and were observed to be approximately 700 nm in diameter using DLS and approximately 300-500 nm by TEM (Fig. 1a), presumably due to dehydration effects. The photopolymerised hydrogel containing the 2,6SCS-NPs showed a relatively even distribution of the NPs within the hydrogel (Fig. 1b, 1c). *In vitro* rate of release of BMP-2 from 10% gelatin hydrogels and from hydrogels containing the BMP-2/2,6SCS-NPs were investigated. Incorporation of BMP-2/2,6SCS-NPs slowed the cumulative release of BMP-2 with 30% detected at 24 hrs and around 50% at 150 hrs. BMP-2 release from hydrogels alone was rapid with 50% detected within the first 60 hrs and over 80% release detected at 150 hrs.

We have synthesized 2,6SCS and fabricated a composite photopolymerisable hydrogel incorporating BMP-2-loaded 2-N,6-O-sulfated chitosan based nanoparticles with controlled slow release of active BMP-2.

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A Large PCE Enhancement for Organic Solar Cells via Incorporation of a Novel Alcohol-soluble Conjugated Polyelectrolyte interlayer

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Organic solar cells have attracted considerable attentions in recent years because of their unique advantages of low costs, light weight, flexible processing and great potential for printing. Bulk heterojunction (BHJ) solar cell was discovered as a promising device configuration for high power conversion efficiency (PCE), which involves a phase-separated blend of an electron-rich donor and an electron-deficient acceptor. So far, the efficiency of BHJ solar cells have achieved over 7% by a number of methods, such as adding additive in photoactive material solution to optimise the film morphology and inserting a cathode interfacial layer etc.^{1,2}

In this work, we demonstrate that by inserting a layer of novel conjugated material as the electron-injection layer the PCE of our organic solar cells increases by 89%. A typical donor polymer, Poly [9, 9-dioctyl- 2,7-fluorene – alt -5,5- (4',7'-di-2'-thienyl-2',1',3'- benzothiadiazole)](PFOTBT), is blended with a typical acceptor phenyl-C61 butyric acid methyl ester (PCBM) to construct the active layer, and then Al, Ca/Al and CPE/Al were used as cathodes respectively (**Fig.1**). The performance of reference cells are as follows: for Al cathode device, Voc=0.82V, Jsc=7.41mA/cm², FF=39.64% and PCE=2.41%; for Ca/Al cathode device, Voc=0.9V, Jsc=7.52 mA/cm², FF=42.62% and PCE=2.89%. When our conjugated electrolyte is simply inserted between the active layer and the Al cathode as an interfacial layer via spin-coating, the Voc, Jsc, FF and PCE are increased dramatically, which performs as follows: Voc=1.05V, Jsc=8.86mA/cm², FF=48.93% and PCE=4.55%. This result is very promising as our material is even better than active metal cathode (Calcium) and could be applicable for printing solar cells.

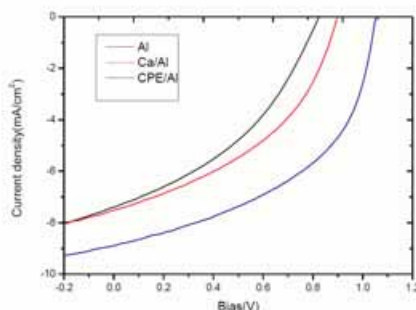


Figure 1. I-V curves of photovoltaic cells under AM1.5, 1kW/cm²

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Preparation and Characterization of the PAR/PET Composite System

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Various polymer composites, reinforced with high performance fibers, have been developed as the engineering structural materials. In this study, a manufacturing process is studied to develop a polyarylate(PAR) nanofiber reinforced polyethylene terephthalate(PET) composite system. Generally, PAR has excellent mechanical properties of high strength and modulus, three times higher than PET, comparable with polyphenylene terephthalic acid(PPTA, so called para-aramid). To prepare the PAR/PET composite, firstly, a PET bulk conjugated fiber, having multi nanofilaments of PAR, was melt spun by a conjugate spinning process, as shown in Fig.1. Then the conjugated PAR/PET fibers were aligned uni-directionally and molded in a hot press under proper conditions of temperature and pressure. In this molding process, PET phase was melted and became as a matrix material, while PAR nanofilament became a reinforcement of the composite. Thus, we can obtain a PAR nanofiber reinforced PET composite. Mechanical, thermal and morphological properties of the prepared PAR/PET composite were characterized with a tensile tester, DSC(Differential Scanning Calorimeter) and SEM(Scanning Electron Microscopy), etc. The PAR/PET composites can be used in the various application fields of the lightweight membrane structure, parts of electronic devices, high pressure pipes etc.

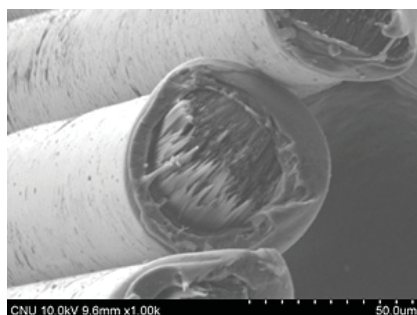


Figure 1. SEM image of the PET conjugated fiber having PAR multi-filament

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Functionality of proteins bound to plasma polymer surfaces

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Polymerisation of organic vapours on surfaces by radio-frequency glow discharge (plasma polymerisation) allows for functional polymer surface coatings to be manufactured in a substrate-independent fashion.¹ Already well-established as a passive coating technology for biomaterials and in the automotive industry, our aim is to further research into bioconjugation platforms.² Although our goal is to *specifically* immobilise functional proteins to surfaces, others have shown that this may prove difficult since adsorption of some proteins onto different plasma polymer surfaces can lead to loss of protein function (denaturation).^{3,4}

We present results of a study attempting to understand how the structure of the polymer layer potentially affects specific or non-specific protein binding. Organic vapours from oxygen-containing organic compounds (ethanol and propionaldehyde) were plasma polymerized onto surfaces at different powers to give example surfaces decorated with different compositions of hydroxyl and aldehyde functional groups respectively. Our hypothesis was that plasma polymerisation at decreasing power would lead to greater retention of alcohol or aldehyde groups on the surface of the plasma polymer. When comparing results from both surfaces, we discovered that at the lowest power studied (5 W) there was a strong preference for aldehyde surfaces to bind proteins through imine bond formation and for alcohol surfaces to reduce protein adsorption. At higher power, both surfaces bound protein equally well but it was clear that the mechanism of binding was different. Streptavidin on aldehyde surfaces was *specifically* bound leading to the surface-bound protein retaining its biotin-binding ability. On ethanol surfaces, *non-specific* adsorption led to a protein denaturation. We know that this binding event must be related to the primary or secondary amino-acid sequence of the protein since linear, primary amine containing synthetic polymers did not bind to ethanol surfaces. We believe that understanding the polymeric structure of the surface layer, how to use plasma power to control the functionality thereof, and understanding factors contributing to protein denaturation will be of importance as we continue to develop plasma polymer-derived bioconjugation platforms.

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Janus Cyclic Peptide-Hybrid Polymer Nanotubes

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Nanotubes in Nature such as transmembrane channel proteins and microtubules, provide a pool of inspiration for novel, functional, self-assembled, (bio)materials. As opposed to carbon nanotubes, the self-assembly of cyclic peptides, which are based on alternating D- and L-amino acids, provide facile alternative methods for functionalization using mild coupling strategies. Although promising work in the 1990s lead to antibacterial agents, cyclic peptide nanotubes have limited solubility and leave little room for fine control over the self-assembly and length and thus have little prospect of finding applications.¹⁻³ Recent developments have shown that the attachment of polymers to the periphery of the cyclic peptide nanotubes permits control over the length and increase solubility.⁴⁻⁷ One of the synthetic approaches that have lead to cyclic peptide-polymer nanotubes includes grafting the polymer from the preformed cyclic peptide nanotubes.⁵ However, conjugates synthesized by this approach are not easily characterized and do not provide quantitative control over the number of polymers as well as the molecular weight of the polymers attached to the cyclic peptide core. On the other hand, grafting polymers of well-defined degrees of polymerization to the cyclic peptide core provides an elegant, distinct alternative that allows fine control over chemical structure and number of polymers attached.^{6,7}

Here we present new synthetic strategies that permit orthogonal coupling of well-defined polymers that contain different functionalities and degrees of polymerization to the cyclic peptide core and following self-assembly leads to multifunctional cyclic peptide-polymer nanotubes. Through the judicious choice of orthogonally attaching phase separating polymers, Janus nanotubes can be envisioned (**Fig. 1**). In addition, this fresh approach to controlling the self-assembly process may lead to multifunctional polymer therapeutics as well as provide innovative insights to current (bio)applications.

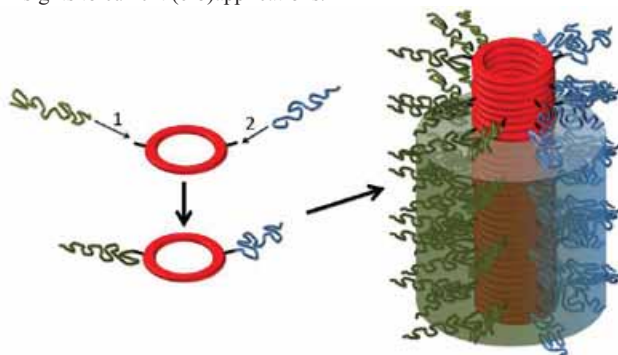


Figure 1. Concept of orthogonal polymer conjugation to cyclic peptide followed by self-assembly into cyclic peptide-polymer Janus nanotubes.

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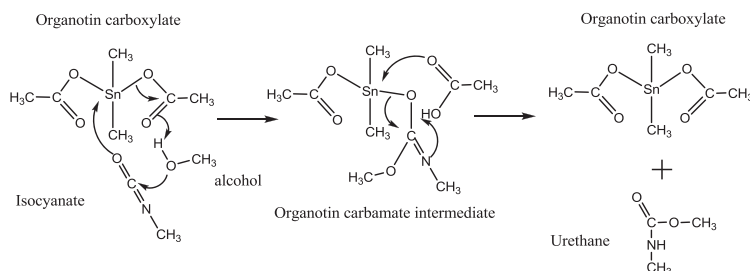
Investigation of the mechanism of urethane formation in the presence of organotin(IV) carboxylate catalysts using computational and experimental methods for selected isocyanates

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Organotin carboxylate compounds are widely used as catalysts in the polyurethane industry¹. However in spite of numerous investigations²⁻⁷ the exact mechanism of the catalysed reaction is still not clear. The computational approach outlined below is used to investigate this reaction. Urethane formation between isocyanate and alcohol groups in the presence of organotin carboxylate⁷ for both aliphatic and aromatic isocyanates are simulated using DFT and *ab-initio* computational methods and the results are compared with experimental findings. Our results reveal that organotin carboxylate catalysis of the reaction between aromatic or aliphatic isocyanate and n-butanol in less polar media follows two routes depending on the isocyanate used. Both types of isocyanate initially form a ternary complex which then form an organotin carbamate² intermediate. Thereafter there is a change in the route depending on the proton affinity of the nitrogen atom of the intermediate. The reactivity of aliphatic isocyanate shows a significant dependence on the carboxylate ligand content in the catalyst, while the effect is much less with the aromatic isocyanate. Based on experimental and computational results a mechanism is proposed for organotin carboxylate catalysis of urethane formation (**Scheme 1**).



Scheme 1: Proposed mechanism for organotin carboxylate catalysis of aliphatic isocyanate in urethane formation.

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Personal history

After graduation from University of Colombo in 1977 Ransi started his professional career as a research chemist in the surface coatings industry in Sri Lanka. In 1980 he obtained a M.Sc. degree in Polymer Science and Technology from the University of Sri Jayawardanapura and has continued to work in the surface coatings industry. In 1983 he joined the Ceylon Institute of Scientific and Industrial Research as a research officer in the Material Technology Division.



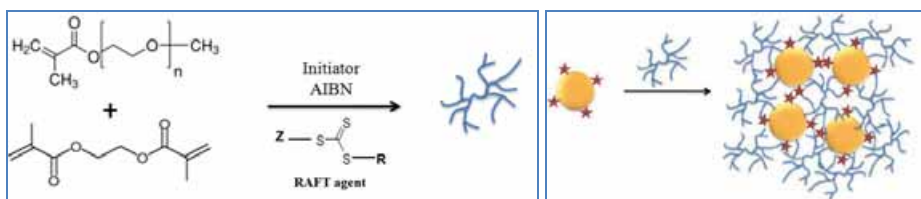
Self-Assembly of Gold Nanoparticles Mediated by Hyperbranched Polymers for Making Spectroscopically Barcoded Particles

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Encoded particles have potential applications in diagnostic devices and as multi-modal biomedical imaging probes. Commonly, different levels of fluorescence dyes can be used to encode polymer based or inorganic particles. However, there are a number of issues associated with fluorescence, such as photobleaching and lack of multiplexing ability that limit its use in this area. Depending on the configuration, Surface enhanced Raman Spectroscopy (SERS) constructs can overcome the problems associated with fluorescence. Novel methodologies are required to prepare stable gold nanoparticle (AuNP) aggregates that have high SERS intensities and good physiochemical stability. Recently, a few studies have suggested the use of linear¹ or dendritic² polymers to mediate AuNP aggregation and control inter-particle spacing. Self-assembly of polymers around AuNPs can be directed by sulfur containing end-groups. RAFT polymerisation is an obvious route to polymers with sulfur end-group functionality with the additional benefits of end-group chemistry, pendant group functionality and polymer architecture. The interaction of hyperbranched RAFT polymers (HBP) (Synthesis according to Scheme 1 (left)) with gold and its use as a controlled aggregating agent for AuNPs, providing for an efficient SERS probe, has been explored here (Schematically shown in Scheme 1 (right)). We focus on the synthesis of hybrid AuNP/HBP aggregates and investigate the parameters that alter the inter-particle spacing thus affecting the SERS “hot spots” and SERS enhancement. The AuNP/HBP size ratio and the AuNP/HBP molar ratio are the two major controlling factors for the hybrid construct morphology. The aggregation behavior of these constructs has been studied by UV-Vis spectroscopy, TEM, DLS and its imaging capability studied with Raman spectroscopy. These constructs will also have application in other areas of nanomedicine such as electron microscopy immuno-stains, *in vivo* SERS imaging, x-ray contrast, radiation sensitisers.



Scheme 1. (left) Schematic diagram demonstrating the synthesis of Hyperbranched RAFT polymers (left) Schematic diagram demonstrating the controlled self assembly of AuNP mediated by HBP (right).

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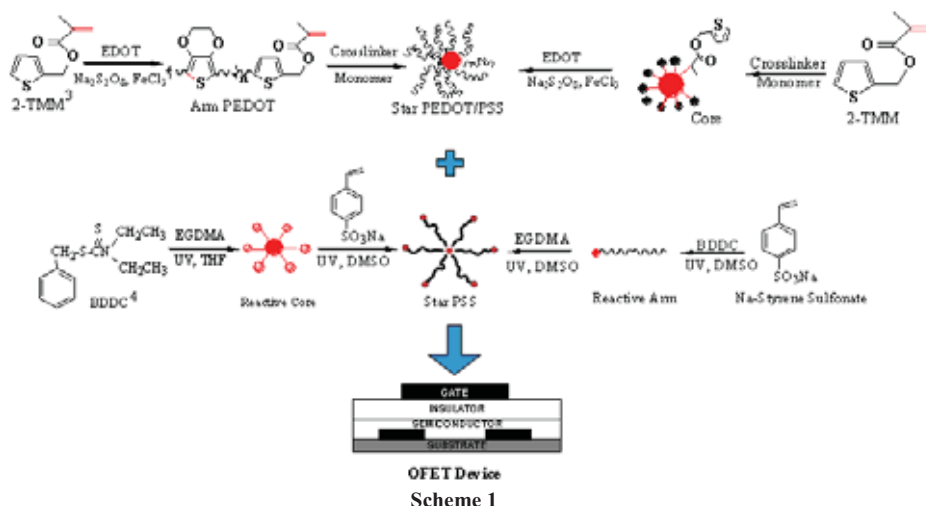
Functional Thiophene-Based Conductive Polymers for Organic Electronics

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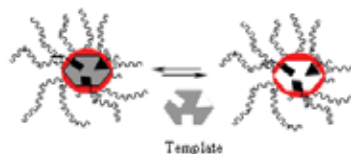
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Poly(3,4-ethylenedioxythiophene) (PEDOT) is commonly used as a gate electrode for organic field effect transistor (OFET) devices. It has several advantageous properties such as a low oxidation potential, moderate band gap with very good stability in the doped state, and excellent environmental stability.^{1,2} PEDOT is an insoluble polymer, but in the presence of polystyrene sulfonic acid (PSS), it will form a stable dispersion in water. This work deals with the synthesis of star PEDOT and star PSS polymers for potential molecular imprinting application. Both star PEDOT and star PSS were synthesized, according to **Scheme 1**, via arm first and core first methods.¹⁻⁴



Scheme 1

The synthesized star polymers were characterized by FTIR, ¹H NMR, UV VIS, SEM/TEM and conductivity. The conductivity data show the films of the star PEDOT/PSS to be one to two orders of magnitude higher than the commercial PEDOT/PSS. The current focus of this work is the incorporation of molecularly imprinted cores in these star PEDOT/PSS systems (**Scheme 2**). Thus, the molecular imprinted star PEDOT/PSS can be used as recognition gate in OFET devices.



Scheme 2

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Synthesis and Analysis of Photodegradable Polymers and Hydrogels for Biological Applications

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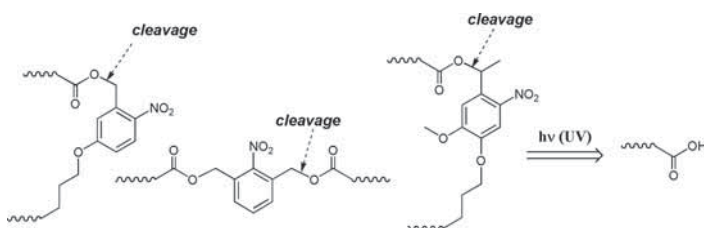
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Polymers that are able to respond and change on demand using an external stimulus have attracted interest in many scientific disciplines. Among the stimuli available, light is particularly useful since it can be localized both in time and space and can be triggered externally. Light-induced reactions therefore have the potential to offer both temporal and spatial control of material properties. In biological domains, however, these features can be offset by the limited penetration depth that the irradiation beam can achieve in biological tissue and the potential for UV irradiation to cause cell damage at high doses. Hence a methodology that encompasses efficient photosensitive chemistry is important. One such system which has been successfully applied is the *o*-nitrobenzyl functionality. Traditionally it has been used as a photosensitive protective group for carboxylic acids in the synthesis of peptides, polysaccharides and nucleotides. Cell biology and neurosciences have used 'caged compounds' to study events that follow chemical signalling. A photolabile protective group allows a biochemist to control the release of bioactive compounds to target sites in living tissue.

An *o*-nitrobenzyl ester cleaves irreversibly with UV light (365 nm) to liberate a carboxylic acid (Scheme 1). A notable application of this photolabile chemistry in polymer science is a hydrogel whose properties can be manipulated externally using UV light. When used as a cell culture platform, changes in the properties in a PEG hydrogel, such as crosslinking density and modulus can be externally manipulated using light, to target important cellular functions such as migration and differentiation.²⁻³ Such hydrogel networks can also be applied as photolithographic resists.⁴ As reviewed recently, the photosensitive moieties have also been incorporated into block copolymer structures.⁵ This has provided a means to dissociate formed assemblies with light due to the changes in the copolymer hydrophobicity/hydrophilicity balance as a result of the photo reaction. As a chemical junction in between separate blocks of a polymer, UV irradiation has also been used to cause chain cleavage to bring about changes in nano and micro-scale properties of polymer films.

In this poster we will highlight some of the strategies that we have used to incorporate *o*-nitrobenzyl esters into polymers and the motivations underpinning the work. This will include their synthesis, analysis of their photo-degradation properties and suitability for those biological applications of interest to us.



Scheme 1. Photocleavable linkers which liberate carboxylic acid.

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Poly(2-oxazoline): An Alternative to PEG?

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Poly(ethylene glycol) hydrogels are extensively used in tissue engineering applications due to their non-fouling properties.¹ These hydrogels are frequently prepared by crosslinking modified PEG, through acrylate functionalization of the hydroxyl end groups.² However, any functionalization of PEG, whether for co-polymerization or incorporation of biofunctionality, is limited to the hydroxyl end groups. Therefore, there is great interest in the development of new polymers that can easily be functionalized, preferably within the monomer repeating unit, and exhibit similar non-fouling properties as PEG possesses. One polymer class that meets these requirements are poly(2-oxazoline)s (POX), whose biocompatibility has long since been demonstrated.^{3,4} POX have been shown to have protein repellent properties comparable to PEG,⁵ and contain a tailorable side chain within the repeating monomer unit (**Fig. 1**). Our work has focused on preparing POX hydrogels by cross-linking alkene functionalized POX using thiol-ene chemistry, for the potential use in biological applications.

POX hydrogels were prepared using various copoly(2-oxazoline)s consisting of 2-decenyl-2-oxazoline (DecOx) and either 2-methyl-2-oxazoline (MeOx) or 2-ethyl-2-oxazoline (EtOx). The copoly(2-oxazoline)s were cross-linked with UV irradiation using the dithiol 2,2'-(ethylenedioxy)diethanethiol (EDDET) in the presence of the photo initiator 2,2-dimethoxy-2-phenylacetophenone. The reaction between p(EtOx-co-DecOx)-OH and EDDT is shown in **Fig. 2** which resulted in the formation of a transparent hydrogel (**Fig. 3**).

The ability to alter the side chain of the POX monomer lends this family of polymers to a variety of opportunities for co-polymerization or bio-functionalization. This, in addition to its protein repellent properties, suggests that POX is a highly potent alternative material to PEG for use in biological applications.

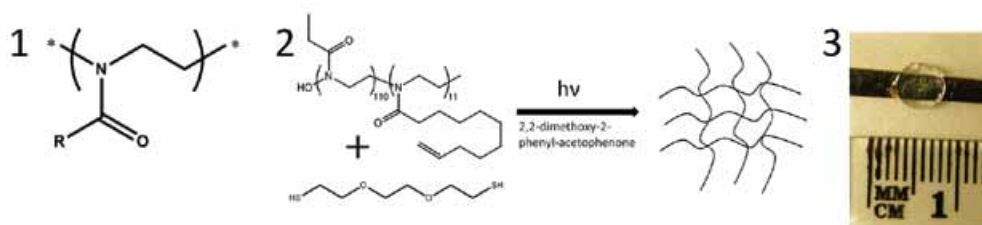


Figure 1: POX structure, containing a tailorable side chain. **Figure 2:** Synthesis of POX hydrogels via thiol-ene 'click' reaction **Figure 3:** Prepared POX hydrogel

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PGS-co-LA Nanofibers Scaffolds by Core/Shell Electrospinning

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Abstract

Poly(glycerol sebacate) (PGS) is a novel degradable elastomer. Its super elasticity makes this polymer more suitable for use as a tissue engineering scaffold material compared to thermoplastic polyesters. Unlike thermoplastics that can be easily processed into many shapes by melting or dissolving in solvents, elastomers cannot be shaped by melting or solution casting due to their chemically crosslinked network. In this project we successfully fabricated PGS nanofibers scaffolds (**Figure 1**) by core/shell electrospinning as shown in **Figure 2**. Thermoplastic poly (lactic acid) (PLA) was proved to be a good polymer as a shell material because it has a low miscibility with PGS. PGS and lactic acid (LA) copolymer was synthesized and proved to have good elasticity as pure PGS. Lactic acid was reported to reduce the toxicity and slow down the degradation speed of PGS. Moreover, PGS with different molar ratios of glycerol and sebacate was used to make copolymer and the mechanical test results showed that PGS with molar ratio of glycerol and sebacate 1:1 based copolymer were more compliant than PGS with ratio 2:3.

The core/shell spun fibers demonstrated J-shaped nonlinear elastic deformation behavior, resembling that of muscle tissues. Hence, the muscle-like PGS/PLLA fibrous sheet materials have potentials for application of muscular tissue engineering.

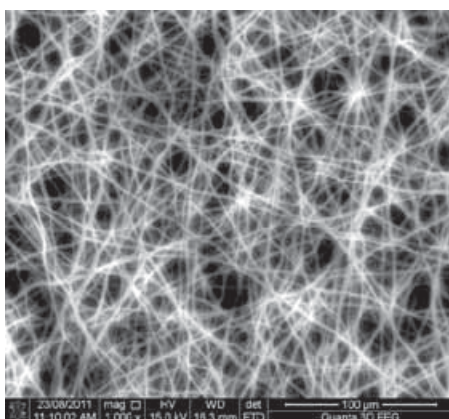


Figure 1. SEM photographs of PGS/PLLA scaffolds



Figure 2. SEM of PGS/PLLA core/shell fiber

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Research interests: Bone tissue engineering, Muscle-like biomaterials, Surgical sealants



Amphiphilic Biodegradable PCL-g-Amylose Synthesized in scCO₂ and its Self-assembly Behaviour

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As a typical biopolymer, poly(ϵ -caprolactone) (PCL) has shown immense applications in the biomedical field, specifically in drug delivery and in tissue scaffolds. However, its hydrophobicity and slow rate of degradation are major disadvantages.¹ On the other hand, amylose separated from starch is a hydrophilic biopolymer and is abundant in nature. It has a fast degradation rate and been used as a carrier for drug release for many years due to its ability to form inclusion complexes with low-molecular weight organic drug molecules.² The combination of such two biopolymers via graft copolymerization will provide a novel material with great potential applications in drug release and tissue engineering.³

In this project, supercritical fluid technology, which is environmentally friendly, will be adopted to synthesize the graft copolymer PCL-g-amylose. The effects of reactant ratios, reaction temperature, reaction pressure and reaction time on the monomer conversion, graft efficiency, graft percentage, graft density and branched-chain length will be studied systematically by using ¹H NMR, ¹³C NMR and FTIR. Also, the influence of the graft density and branched-chain length on the chain configuration of the graft copolymer will be examined by solid-state NMR and AFM. Moreover, the self-assembly behaviour of the graft copolymer with different graft density and branched-chain length in selective solvent like H₂O or DMSO will be explored by DLS, TEM and AFM.

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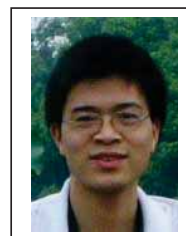
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Thermal properties of self-healing nanocomposite polymer

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Recently a large part of scientific community is focusing its attention towards the research on self-healing polymeric materials [1]. Also a lot of interest in polymer technology is being given to nanocomposites [2] due to their superior properties and high commercial interest. This project is focused on the study of nanostructure and thermal properties of self-healing nanocomposites. The influence of different montmorillonite nanoclays on the thermal stability of self healing nanocomposites is largely investigated.

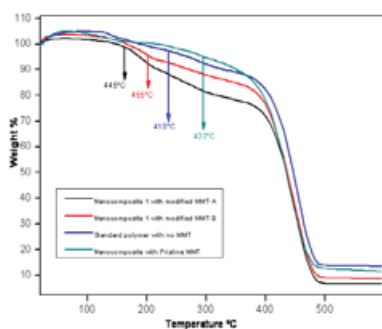


Fig 1. TGA curves of self-healing polymer nanocomposites

The approach employed for the synthesis of nanocomposites was in-situ polymerisation. These polymers can be easily synthesised from relatively inexpensive and commercially available starting materials using a simple two step synthetic approach. With moderately small quantity of pristine or organic modified montmorillonite nanoclays, nanocomposites prepared can demonstrate superior thermal properties compared to the host polymer in the absence of any reinforcing particles [3, 4].

The optimum percentage of 3 wt% nanoclay added to the nanocomposite matrix has been found to influence the temperature stability of nanocomposites. The local dynamics confined within the pristine and organically modified montmorillonite nanoclays were analysed using various characterisation techniques such as DSC, TGA, XRD, SEM and ATR-FTIR spectroscopy.

It has been proven from this study that that pristine and organically modified montmorillonite nanoclay have different effects on the thermal stability of the self-healing polymer and the careful control of the hydrogen bonding functional groups have various effects on the thermal properties. Our investigation also evidenced that the presence of hydrogen bonding groups (hydroxyl groups) in the nanocomposite 2 with modified MMT-B nanoclay matrix increases the matrix-filler interaction and thus facilitates the dispersion of the fillers to improve its thermal stability(**Fig 1**). This method can be used to produce structure responsive self-healing materials with improved thermal and mechanical properties which can have potential applications in adhesives, coating and health care technologies. The further improvements in thermal, physical and mechanical properties are under exploration.

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Validity Limits for the Zero-1 Approximation in Styrene Emulsion Polymerisation

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It is now more than 30 years since the kinetics of the emulsion polymerisation of styrene were first resolved and the parameters governing the entry of free radicals into particles (ρ), their exit from particles (k) and their reduced bimolecular termination rate coefficient (c) were first measured¹⁻³. The most important factor leading to this success was that a very large number of meticulous kinetic experiments were carried out on a single seed latex that was rigorously characterised regarding particle size. This rigorous determination of particle size enabled an accurate determination of the average number of free radicals per particle $\langle n \rangle$ and hence the propagation rate coefficient (k_p), allowing other parameters to also be accurately determined. In the light of developments in emulsion polymerisation since that time there are a number of areas that can profit from revisiting some of the original data. One of the areas where statements can be made, based on the original data, is the validity of the zero-1 approximation in styrene emulsion polymerisation.

For styrene emulsion polymerisation, a system in which no particle contains more than 1 free radical for a kinetically significant period of time is referred to as a zero-1 system. The simplest zero-1 system is one in which k can be neglected and $c \gg \rho$. In such a system, on average, a particle contains a radical for half of the time and $\langle n \rangle = 0.5$. The point in the polymerisation where the zero-1 approximation breaks down can be detected kinetically because the number of free radicals per particle, and hence the polymerisation rate, begins to creep above the value dictated by $\langle n \rangle = 0.5^{2,3}$. In systems where k is significant and $\langle n \rangle$ is less than 0.5 the breakdown can also be detected when $\langle n \rangle$ creeps above its steady state value.

Theoretical studies^{4,5,6} have suggested that the zero-1 approximation is valid only for particles with a radius of less than 90 nm⁵ or even less than 70 nm⁶. However, initial calculations, based on the original work suggested that the zero-1 approximation would be valid for monomer droplets as large as 850 nm in radius. However, solids constraints that govern any emulsion polymerisation system restrict the total number of particles of this size that can be contained in the system, which imposes further constraints on the validity of the zero-1 approximation. A further finding of the original work³ is that pure styrene in pure water generates about 1.3×10^{13} radicals per litre per second at 50 °C, and that these radicals enter the particles singly with approximately 100% capture efficiency. In systems with low particle number these thermal background radicals can lead to very high values of radical entry rates into particles that are much larger than termination rates, allowing $\langle n \rangle$ values that are greater than 0.5. When these background radicals are taken into account the limiting particle size for the zero-1 approximation, suggested by the original work, is approximately 400 nm in radius for systems of moderate solids content.

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Evaluation of Spinnability and Thermo-Mechanical Behaviors of Chemically Recycled PET Fibers by using High-Speed Melt Spinning Process

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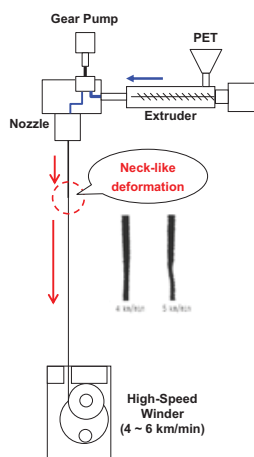
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Poly(ethylene terephthalate) (PET) is one of the most commercial thermoplastic polymer which is used to manufacture textiles and packaging materials. However, enormous consumption of PET has generated a large amount of the plastic wastes, and PET recycling technology has been attracted the attention of manufacturer and researchers to solve the environmental problems and conserve raw petrochemical products, energy, and CO₂ emission. In this study, to investigate spinnability and thermo-mechanical properties of chemically recycled PET, high-speed melt spinning for the recycled PET was conducted at various spinning velocities.

Chemically recycled PET (C-PET) of I.V. 0.634 dl/g, reproduced by using glycolysis processes, and commercial virgin PET (PET) of I.V. 0.645 dl/g were supplied by Huvis Co. Ltd.. The polymers were melted using a single screw extruder and extruded from a spinneret with a single hole of 1 mm diameter by gear pump. The throughput rate and spinning temperature were controlled to 7.0 g/min and 285 °C, respectively. High-speed melt spinning for C-PET and PET was executed by varying the take-up velocity from 1 to 6 km/min (Scheme 1). Thermo-mechanical properties of as-spun PET fibers were analyzed by DSC, birefringence, and tensile test, etc.

High-speed spinning of PET could be conducted up to 6 km/min, while C-PET could be only spun up to spinning velocity of 5 km/min. DSC thermograms showed that the crystallization peak (T_c) of as-spun PET fiber shifted toward lower temperature with increasing spinning velocity, and then disappeared at 4 km/min. These



Scheme. 1. High-speed spinning process and neck-like deformation¹

results indicated that the molecular orientation of PET increased with spinning velocity. Melting temperature (T_m) of as-spun PET fibers started to shift toward higher temperature at 5 km/min by high-speed strain-induced crystallization¹. As-spun C-PET fibers showed relatively higher T_c and lower T_m values than those of PET, respectively, at every spinning velocity. Birefringence of as-spun PET fibers increased with spinning velocity, and maximum birefringence value reached around 0.125 at the spinning velocity of 6 km/min. Slope of curve more steepened from 4 km/min, where the crystallization peak (T_c) started to disappear in DSC thermograms. As-spun C-PET fibers showed also similar curve, but birefringence at the spinning velocity of 5 km/min showed lower values than that of PET as-spun fibers. The tensile strength increased and the elongation at break point decreased as the spinning speed increased. The typical region of constant load elongation in the stress-strain curves disappeared at 5 km/min, at which strain-induced crystallization of PET started to occur. Thus, C-PET showed relatively lower spinnability and structure development than those of PET in the high-speed spinning process.

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Functionalized Nanodiamonds for platinum drug delivery

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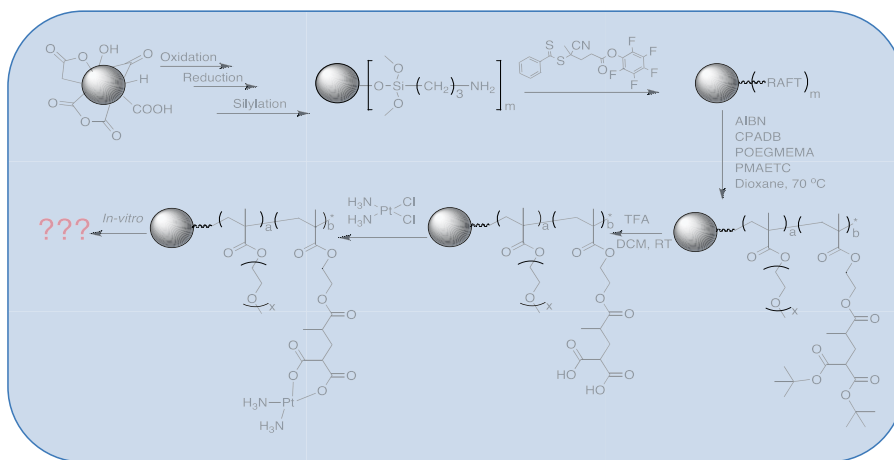
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Nanodiamonds (NDs) have currently gained world-wide attention due to their inexpensive large scale synthesis based on the detonation of carbon-containing explosives. Recent studies have also shown that NDs have emerged as new and very promising candidates for medical imaging research and drug delivery systems as a result of non-cytotoxic, superior fluorescence with no sign of fading because of photobleaching, and surface modification with ease.¹

Cis-platin [*cis*-dichlorodiamineplatinum(II); CDDP] has become an important class of antitumor agents and is widely used for the treatment of a number of solid malignancies. However, its clinical use is limited due to side effects and drug resistance.² Using NDs as biocompatible materials can potentially overcome the drawbacks and therefore improve the therapeutic indices of this drug.

In this study, detonation NDs were first oxidized and followed by reduction to yield NDs with hydroxyl groups on the surface. These NDs were amino functionalized by aminosilane agents, and then the dithiocarbonate chain transfer agent (CTA) was anchored via activated R-group to the amino-functionalized surface of NDs. This surface layer of CTA groups was then employed to grow linear statistical copolymer of ethylene glycol methyl ether methacrylate (OEGMEMA) and *tert*-Bu malonic ethylene glycol methacrylate (MAETC) via RAFT polymerization (**Scheme 1**). Deprotection of *tert*-butyl groups results in ND-polymer containing pendant dicarboxylate groups, which can conjugate to platinum drugs via metal-polymer complex formation.³ These conjugates expect to increase the drug efficiency in comparison to free ones.



Scheme 1. Synthetic route of nanodiamond containing platinum drug

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The Effects of Surface Modifications of Polyketone Fibers on the Interfacial Adhesion of Silicone Rubber Composites

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The term of super fibers refer to a fiber having high tensile strength over 1GPa and high modulus over 50GPa, respectively. One of the super fibers, the polyketone fiber is recently developed which has excellent mechanical properties and relatively low price compared with other super fibers. Polyketone fiber is composed of ethylene and carbon dioxide and thus it can be completely decomposed into water and carbon dioxide by combustion. Polyketone fiber has various applications including tire reinforcements and high performance polymer composites. Especially, polyketone fiber reinforced rubber composites have wide application fields of mechanical rubber goods(MRG) such as automobile hoses and belts, membrane structure and awnings. In order to apply for these purposes, the interfacial property between polyketone fiber and rubber is very important.

In this study, physical and chemical surface treatments, such as the UV irradiation and the acid treatment, were conducted to modify the surface morphological and chemical properties of the polyketone fiber. The effects of surface treatments of polyketone fiber on the interfacial adhesion with silicone rubber matrix were investigated. Changes of surface morphologies and chemical composition were observed with a scanning electron microscope (SEM) or an atomic force microscope (AFM) and a XPS(X-ray photoelectron spectroscopy), respectively. Finally, interfacial shear strength between polyketone fiber and silicone rubber was tested and estimated with a microdroplet debonding method.

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2. T. Matsuo, Fibre materials for advanced technical textiles, *Textile Progress*, 40, 87-121(2008)

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Towards Supramolecular Actuation in Polymer Gels

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In recent years polymer gels have emerged as a new “wetware” actuating technology due to their characteristically large volume changes that can be triggered by a range of external stimuli. We are currently working towards creating a polymer gel which exhibits expansion and contraction due to dynamic changes in the ligand component of the gel upon coordination with metal ions.

To this end we have synthesised a series of pyrimidine-hydrazone (pym-hyz) strands that have terminal hydroxymethyl or acryloyl groups. These functional groups allow the pym-hyz strands to be incorporated into a co-polymer gel network. X-ray crystallographic studies have shown that the strands are coiled in their free state, with the pym-hyz linkages in a transoid conformation. Upon coordination with suitable metal ions the strands uncoil into a linear arrangement as the pym-hyz linkages rotate to a cisoid conformation (Figure 1). Copper(II), lead(II), zinc(II) and silver(I) ions have all been shown to cause this dynamic change, resulting in expanded linear complexes when an excess of the metal ion is used.

Two of the pym-hyz strands have been successfully polymerised with methyl acrylate to form co-polymer gels, which swell in solvent upon coordination of metal ions. Our hypothesis is that the extent of swelling will be dependent on the length of the pym-hyz strand used as a cross-linking unit in the gel. A variety of the metal complexes obtained from our pym-hyz ligands will be presented along with the preliminary gel studies.

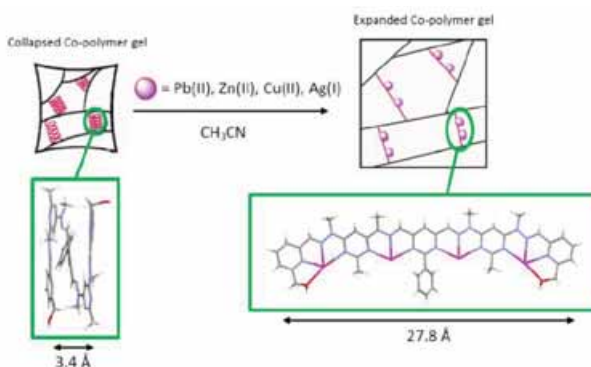


Figure 1. Schematic view of pyrimidine-hydrazone strands incorporated into a polymer gel and the expansion caused by upon metal coordination

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Methacrylic Macromonomers and Thiol-Isocyanate Chemistry: Synthesis and Copolymerization

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The application of click chemistry has grown exponentially since Sharpless et al.¹ noted in 2001 that chemists should take advantage of the progress that has been made during the past century in organic chemistry and focus on reactions that are high yielding and simple to perform in the preparation of complex (macro)molecules.

Reversible addition-fragmentation chain transfer (RAFT) radical polymerization² is a controlled polymerization method that affords (co)polymers with thiocarbonylthio functional groups at the ω -terminus. This functionality can be cleaved from the chain end using a variety of methods³ to afford thiol-terminated (co)polymers in which the mercapto group serves as a functional handle for further chemical modifications.

In this work, we have utilized the click-like reaction between polymeric thiols and isocyanates as a route to make novel (co)polymers. Polystyrene homopolymers of varying molecular weights were cleaved to have thiol functionality which was further reacted with 2-isocyanatoethyl methacrylate in near quantitative yields. The macromolecular thiol selectively reacted at the isocyanate end of the monomer giving a methacrylate end terminated macromonomer. This methacrylic macromonomer was then used in the copolymerization with various (meth)acrylates such as methyl methacrylate, furfuryl methacrylate and lauryl methacrylate. The copolymer was then used in the preparation of block copolymers with PEGMA, NIPAM and DEA. (Figure 1)

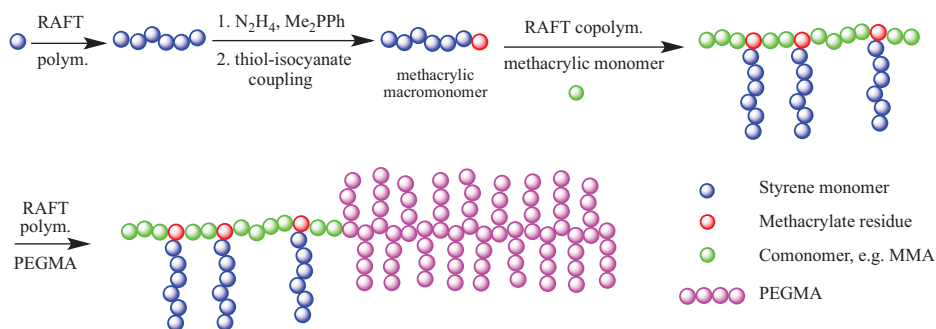


Figure 1. Synthetic route to PS-MMA-block-PEGMA

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Poly(arylene ether ketone)s composed of non-coplanarly accumulated aromatic-rings repeating unit

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Recently, highly susceptible and selective mono- and diarylation of 2,7-dimethoxynaphthalene at 1- and 1,8-positions has been revealed.¹ The 1-mono and 1,8-diarylated naphthalene homologues having several kinds of substituents on the aryl group have proved to bear structures of almost perpendicular accumulation of aromatic rings by X-ray crystal analyses.² In the crystal, the aryl groups of 1,8-diarylnaphthalene derivatives attach to the naphthalene ring in the opposite directions. **Fig. 1** displays the crystal structure of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**), exemplifying the non-coplanarly accumulated aromatic-rings structure of series of 1,8-diarylnaphthalene homologues.³

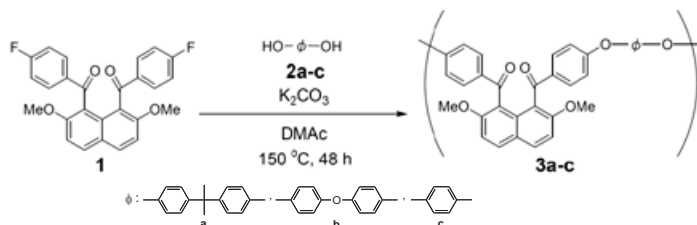


Fig. 1. X-ray crystal structure of 1,8-diarylnaphthalene **1**

The characteristic congested shapes of these molecules prompted the authors to trigger the incorporation of 1,8-diarylated 2,7-dimethoxynaphthylidene moiety into poly(arylene ether ketone) backbone. The 1,8-diaryl-2,7-dimethoxynaphthylidene unit incorporated in polymer molecule is expected to have unique topology of non-coplanarly accumulated aromatic-rings spatial structure as well as that in the crystal of the relating diarylnaphthalene molecules.

The nucleophilic aromatic substitution polycondensation of 1,8-diarylnaphthalene **1** with bisphenol A (**2a**) smoothly proceeded in the presence of K_2CO_3 at rather low temperature in aprotic polar solvents such as DMF, NMP, and DMAc. Resulting polymer (**3a**) proves insoluble not only in conventional organic solvents but also in conc. H_2SO_4 . On the other hand, the transparent flexible film is easily obtained by heat casting. Referring to the optimized polymerization condensations for 1,8-diarylnaphthalene **1** and diol **2a**, that of compound **1** with other diols (**2b** and **2c**) was also carried out to afford high-molecular-weight poly(ether ketone)s **3**. The detailed investigation on polymerization behavior and structure of 1,8-diarylnaphthylidene moiety in the polymer chain was undertaken on the basis of model reaction with oligomeric arylnaphthalenes.

In this presentation, the authors briefly report and discuss the polymerization reaction behaviour of 1,8-bis(4-fluorobenzoyl)-2,7-dimethoxynaphthalene (**1**) in nucleophilic aromatic substitution polycondensation with fundamental thermal properties of the resulting polyketones and the structural studies⁴ of oligomeric molecules.



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Click chemistry approaches towards the synthesis of daisy chain click polyrotaxanes

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A synthetic approach utilizing Catalytic “CuAAC” Active-Metal template strategy to develop a new type of mechanically linked polyrotaxanes was conducted. A [2]rotaxane was synthesized using CuAAC “click” reaction between a monopyridine macrocycle bearing an alcohol functionality and two different blocking groups consisting of trityl derivatives with terminal azide and alkyne. The [2]rotaxane was then polymerized to give a ‘Daisy-chain’ polymer. Only two other examples of this type of polymer have been described to date. The presence of metal-coordinating sites on the polymer should have a dramatic effect on its properties and ability to slide the subunits.

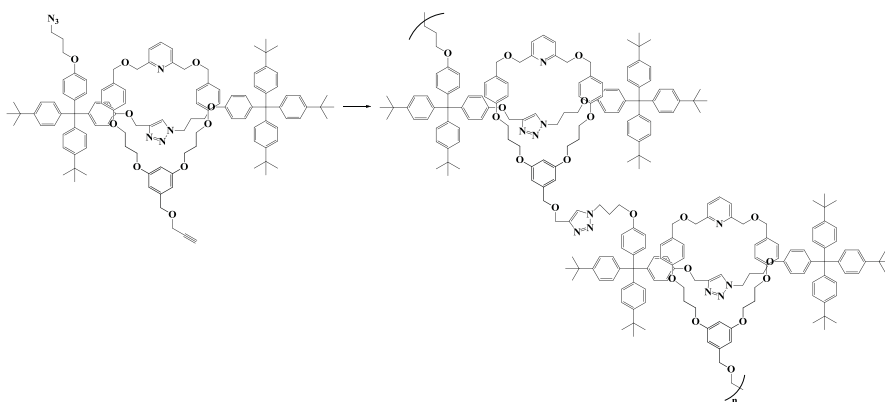


Figure 1 The structures of monomer and polyrotaxane

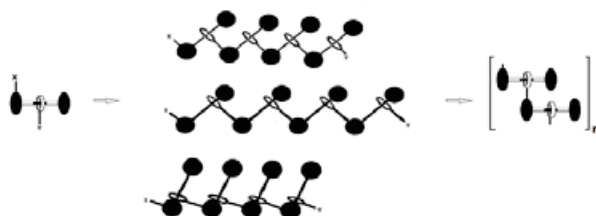


Figure 2 The sliding action of a polyrotaxane showing the “monomer”, and free, extended and collapsed states

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The effect of polymer molecular weight on P3HT:PCBM Nanoparticulate organic photovoltaic device performance

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It is commonly known that the conjugated polymers and fullerenes utilised in organic photovoltaics (OPVs) are generally limited in solubility to organic solvents, such as chloroform, chlorobenzene and dichloromethane. With future energy demand, and the intention to print OPVs on a large scale to meet electricity needs, printing large area OPVs from these toxic, volatile solvents poses substantial health, safety and environmental issues. In response to this motivation we have commenced fabricating OPV devices from surfactant stabilised aqueous dispersions of polymer nanoparticles. Here we describe the effect of fundamental polymer material properties, such as molecular weight, on nanoparticle synthesis and nanoparticulate device fabrication. We have found that while large molecular weight polymers are optimal for P3HT (poly(3-hexylthiophene):PCBM (phenyl-C61-butyric acid methyl ester) bulk heterojunction OPV device performance, this is not necessarily the case for nanoparticulate OPV devices.

Nanoparticles were prepared using the miniemulsion method as described by Landfester and co-workers¹⁻³. Nanoparticles prepared from 14 kDa (M_n) P3HT (**Figure 1**) were found to give the best performing OPV devices, this was the mid-range of polymer molecular weights tested. Whilst still unoptimised, P3HT:PCBM nanoparticulate devices prepared from aqueous dispersions have resulted in surprisingly high device efficiencies and we anticipate significant improvements as optimisation occurs.

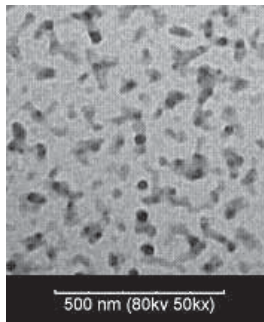


Figure 1. TEM image of nanoparticles prepared from 14 kDa 1:1 P3HT:PCBM.

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³T. Kietzke, D. Neher, M. Kumke, R. Montenegro, K. Landfester, U. Scherf, *Macromolecules*. **2004**, *37*, 4882-4890

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Tandem Synthesis of *N*-heterocycles and monomers

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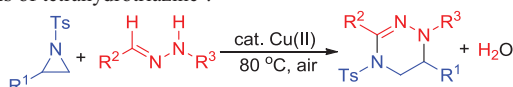
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Nitrogen is a key atom in nature, found in several well known natural product families. Moreover, nitrogen is ubiquitous in biology and material sciences¹. Carbon-nitrogen bond formation is one of the most useful and fundamental reactions in both academic and industrial chemistry, due to the high prevalent subunits of nitrogen-containing heterocycles in a variety of biologically active natural products and pharmaceuticals. Herein, some of our recent works that synthesis of *N*-heterocycles and monomers are displayed.

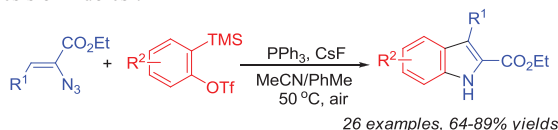
We have developed a single step approach to tetrahydrotriazines *via* the Cu(II)-catalyzed tandem reaction of *N*-tosylaziridines and hydrazones under aerobic conditions (**Figure 1**). The use of inexpensive Cu catalyst and air as the ideal oxidant is a significant practical advantage. The synthetic applications of this new methodology are under investigation.

Figure 1. Tandem synthesis of tetrahydrotriazine².



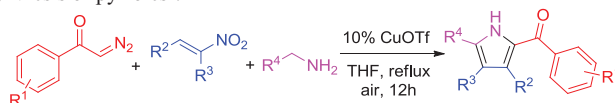
Indoles constitute an important class of alkaloids and are common building blocks for a number of bioactive natural products and marketed drugs. we demonstrated a mild and efficient procedure for the synthesis of substituted indoles (**Figure 2**). In the presence of CsF and PPh₃, 2-azidoacrylates reacted with *ortho*-silyl aryltriflates to afford the corresponding indole derivatives in good yields. Furthermore, the indole products could be easily converted into 10*H*-indolo[1,2-*a*]indol-10-ones.

Figure 2. Tandem synthesis of indoles³.



Pyrroles represent an important class of heterocycles in organic chemistry. They are structural units in many natural products and pharmaceuticals and are key intermediates for the synthesis of a variety of biologically active molecules and functional materials. we synthesized polysubstituted pyrroles *via* a copper-catalyzed three-component reaction of α -diazoketones, nitroalkenes and amines under aerobic conditions (**Figure 3**). Due to the easy availability of the starting materials and potential utilities of products, this method might be useful in organic synthesis and medicinal chemistry.

Figure 3. Tandem synthesis of pyrroles⁴.



Dithieno[3,2-*b*:2',3'-*d*]pyrroles have attracted much more attention as appealing fused bithiophene member with a bridge nitrogen having strong electron-donating ability, which might lead to the development of a low band gap polymer. We also focus on synthesize some polymers based on the dithieno[3,2-*b*:2',3'-*d*]pyrroles. The further synthetic application of this *N*-heterocycles in more complex settings is currently in progress.

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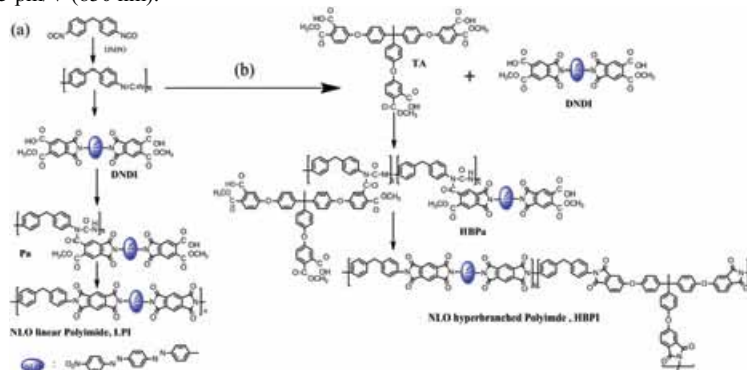
Sequential self-repetitive reaction toward full polyimides featuring linear or hyperbranched structures with stable optical nonlinearity.

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A sequential self-repetitive reaction (SSRR)^{1, 2, 3} based on carbodiimide (CDI) chemistry was utilized for preparing a high-yield wholly aromatic nonlinear optical (NLO) polyimide (Scheme 1 (a)). The polyimide was synthesized with 4,4'-methylenediphenylisocyanate (MDI) and a di(acid-ester) compound, 2,4-diamino-4'-(4-nitrophenyl-diazenyl)-azobenzene derivative containing diimide-di(ester-acid)(DNNDI). Poly-CDI was first synthesized from MDI. The di(acid-ester) compound was then reacted with poly-CDI to form poly(N-acylurea). After curing process, N-acylurea moiety was converted to di(ester-amide) structure via SSRR and further subjected to a ring-closure reaction to form the wholly aromatic NLO polyimide with a T_g of 208 °C. After *in situ* poling and curing processes, the wholly aromatic NLO polyimide was formed with an electro-optical coefficient, r_{33} of 25 pm/V (830 nm). Excellent temporal stability at elevated temperatures (200 °C) and a waveguide optical loss of 2.5 dB cm⁻¹ at 1310 nm were also obtained. Base on this approach, we introduce the concept of the three-dimensional spatial separation of the chromophores endowing the polymers with favorable site-isolation effects⁴ and further to synthesize the hyperbranched polyimide (Scheme 1(b)) via SSRR. The resulting hyperbranched polymer exhibited excellent organosolubility with a T_g of 168 °C, which enabled the fabrication of high quality optical thin films, and an enhancement of electro-optical coefficient, r_{33} of 35 pm/V (830 nm).



Scheme 1 Synthetic routes for (a) LPI, (b) HBPI.

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All-cellulose composite laminates *via* solvent infusion processing

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Cellulose is the most abundant biopolymer on earth, providing a sustainable and biodegradable source of polymeric material. The specific strength of cellulose has been ranked as the highest among all natural materials although the mechanical properties of cellulose-reinforced polymer composites fall short of expectations due to insufficient bonding between the cellulose and polymer matrix.

In a new type of monocomponent composite, so-called all-cellulose composites (ACCs), interfacial bonding problems are negated by using cellulose for both the reinforcement and the matrix. Strong hydrogen bonds are hypothesised to yield strong adhesion between the cellulosic matrix and fibres, thereby improving the mechanical properties and providing an “interfaceless” composite material¹.

Cellulose does not exhibit a melting point and must therefore be dissolved to aid processing. In this work, a new solvent infusion process (Figure 1) is developed in which an ionic liquid (1-butyl-3-methylimidazolium acetate) is used to process a rayon fabric into an ACC laminate based on the principle of partial fibre surface dissolution after Gindl *et al*². Different inlet and vent positions as well as different pressures for laminate consolidation were used to produce ACC laminates. The resulting ACCs made using this technique exhibited tensile strengths and Young's moduli of up to ~100 MPa and ~5 GPa, respectively. The fibre microstructure, void content and fracture surfaces of the ACC composites were analyzed *via* scanning electron microscopy (*e.g.* see Figure 2).

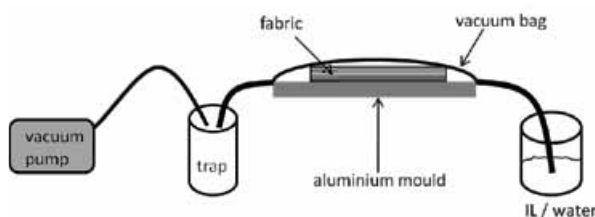


Figure 1: Schematic of the solvent infusion process.

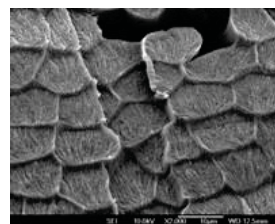


Figure 2: Scanning electron micrograph of a typical fracture surface of an ACC laminate.

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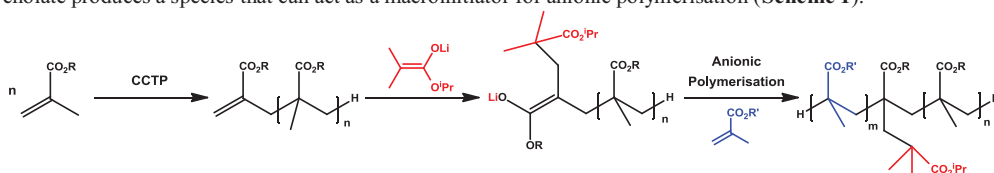
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CCT-derived Macromonomers as Macroinitiators for Anionic Polymerisation

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The concept of combining multiple polymerisation mechanisms is of significant interest as it allows the synthesis of functional polymers with a controlled architecture. Thus enabling the combination of physical properties in a single polymeric material, which may not otherwise be possible. Terminal vinylic groups of macromonomers can be coupled to a simple lithium enolate to generate a macroinitiator. This in turn can be employed to anionically polymerise methacrylic monomers to form a block copolymer. Methacrylate polymers synthesised via catalytic chain transfer polymerisation (CCTP) result in macromonomers with vinylic end groups. During a post-polymerisation step, a Michael addition between the vinylic end group and *iso*-propano lithium enolate produces a species that can act as a macroinitiator for anionic polymerisation (Scheme 1).



Scheme 1. Reaction scheme for macromonomer synthesis, post-polymerisation functionalisation using a lithium enolate and anionic polymerization from a macroinitiator. R = Me, Bz; R' = Me, Bz.

Two methods of anionic polymerisation have been investigated. Firstly, lithium chloride and a toluene/THF solvent mixture was used to synthesis an isotactic second block. Although block copolymers could be made, the process was inefficient (Figure 1). A second route, involving the use of MeAl(BHT)₂, produced a second block which was syndiotactic in nature. This method was much more efficient (Figure 2) and has been shown to be versatile towards macromonomers of different methacrylates and chain lengths. The compositions of the resultant polymers were determined using multiple analytical techniques, and the tacticities investigated. The resultant polymer consists of an atactic block (originating from CCTP) and an isotactic or syndiotactic block (originating from the anionic polymerisation).

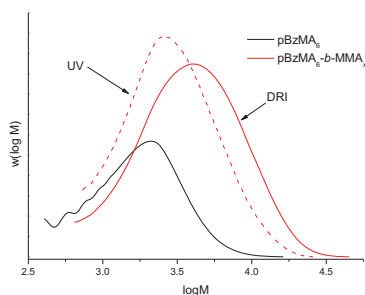


Figure 1. Molecular weight distribution (relative to PS, measured in THF) of pBzMA₆ (made via CCTP) and p(BzMA₆-b-MMA_x) (made via CCTP followed by anionic polymerisation in the presence of LiCl). Chromatograms normalised to the amount of polymer.

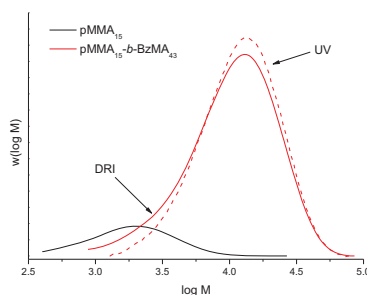


Figure 2. Molecular weight distribution (relative to PS, measured in THF) of pMMA₁₅ (made via CCTP) and p(MMA₁₅-b-BzMA₄₃) (made via CCTP followed by anionic polymerisation in the presence of MeAl(BHT)₂). Chromatograms normalised to the amount of polymer.

This work is part of the Research programme of the Dutch Polymer Institute DPI, Eindhoven, The Netherlands, Project No. 651

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The high dielectric and high energy density composites with block copolymer hybridized nanoparticles

Professor Hyun Min Jung, Professor Sunwoo Lee, Dr. Jong Chan Won

The applications of dielectric materials in electric components, especially in power storage capacitors, are usually required to afford large energy density with a high breakdown strength and low current leakage. The incorporation of high dielectric inorganic particles in the polymer matrix has been intensively investigated as a way of obtaining high dielectric permittivity. However, it is still remaining to overcome the limitation that high proportion of inorganic particles increase the particles-matrix interface area, giving a breakdown path and resulting in reduced dielectric strength and energy density.

In order to obtain the important dielectric characteristics of high dielectric permittivity and large dielectric strength, in this work, we developed block copolymer-shielded BT nanoparticles composited in polystyrene matrix, showing high dielectric permittivity and dielectric strength with a low leakage current. The 5~7 nm thick core-shell particle structure forming the stable polymer layer on BT nanoparticles prevented close connections between the charged interfaces of the BT particles, which become a route of electric leakage and dielectric breakdown. Thus, the resulting composite films containing core-shell particles well meet the universally desirable properties of dielectric materials for use in energy storage devices—high permittivity and large dielectric strength with low leakage current resulting in a large energy density—the ideal features of controlled interface: 1) robust, stable, and physically thick insulating layers to prevent direct particle-particle contact, 2) a shielded and buried polar and charged interface between the inorganic particles and the organic layers under the nonpolar shielding layers, and 3) increase the dispersability of the hybrid particles by matching the solubility parameters of outer surface of the particles with matrix polymers.

To obtain a robust polymer shell that acts as an insulating layer and as a surface modifier for good dispersability in non polar polymer matrix, we performed a fabrication of core-shell BT-polymer particles, where polystyrene-*block*-poly(styrene-*co*-vinylbenzylchloride) was introduced as a stable organic shell for the complete wrapping of the BT nanoparticles. The chloromethyl group functionalized copolymer played a significant role in the formation of the core-shell BT-polymer particles for dispersability and for obtaining good dielectric insulating properties. Our strategy to obtain a stable organic layer was to employ an in situ transformation of the non-polar chloromethyl functional blocks to the polar ammonium blocks which form a self-assembled layer and interact strongly with the BT particle surface. This layer was directly observed by TEM and showed a polymer layer with a uniform thickness of 5~7 nm without any non-covered sites.

The dielectric properties of the nanocomposite film of core-shell particles were investigated on a parallel plate type capacitor fabricated from composite films. The high permittivity value $\epsilon_r = 44$ (at 10 kHz) was obtained, which is comparable to the highest reported values. Significantly, the core-shell composites afforded high dielectric permittivity with a very low leakage current density of 0.76 nA/cm^2 (at 0.2 MV/cm) and the quite large breakdown strength, $222 \pm 14 \text{ V/}\mu\text{m}$. The energy density of composite film was calculated to be 9.7 J/cm^3 due to the resulting high breakdown strength and dielectric permittivity, which is comparable to the highest reported values for polymer-bound particles and exceeds the conventional BT-polymer composites.

PGS-co-LA Nanofibers Scaffolds by Core/Shell Electrospinning

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Abstract

Poly(glycerol sebacate) (PGS) is a novel degradable elastomer. Its super elasticity makes this polymer more suitable for use as a tissue engineering scaffold material compared to thermoplastic polyesters. Unlike thermoplastics that can be easily processed into many shapes by melting or dissolving in solvents, elastomers cannot be shaped by melting or solution casting due to their chemically crosslinked net work. In this project we successfully fabricated PGS nanofibers scaffolds by core/shell electrospinning as shown in **Figure 1**. Thermoplastic poly (lactic acid) (PLA) was proved to be a good polymer as a shell material because it has a low miscibility with PGS. PGS and lactic acid (LA) copolymer was synthesized and proved to have good elasticity as pure PGS. Lactic acid was reported to reduce the toxicity and slow down the degradation speed of PGS. Moreover, PGS with different molar ratios of glycerol and sebacate was used to make copolymer and the mechanical test results showed that PGS with molar ratio of glycerol and sebacate 1:1 based copolymer were more compliant than PGS with ratio 2:3.

The core/shell spun fibers demonstrated J-shaped nonlinear elastic deformation behavior, resembling that of muscle tissues. Hence, the muscle-like PGS-Co-LA/PLLA fibrous sheet materials have potentials for application of muscular tissue engineering.



Figure 1. SEM photographs of PGS/PLLA core/shell fiber

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Bio-based Adhesive Resins - Their Characteristics and Applications -

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It is well known that Mussels can adhere strongly to rocks (on organic or inorganic surfaces) by producing 3,4-dihydroxyphenyl-L-alanine (DOPA), which contains the catechol group. The catechol group can play a role to adhere strongly and reversibly to both organic and inorganic surfaces. Although many attempts have been made to clarify the adhesion mechanism, the details are not completely understood. However, potential applications of this adhesive function have fascinated many researchers. For example, the group of Messersmith and Miller has demonstrated to mimic a material that mimics the behavior of mussel adhesive in the form of adhesive sheets by using DOPA.

We have synthesized novel Mussel-mimetic adhesive resin from various kinds of biomass monomers (Caffeic acid, Hydrocaffeic acid, *p*-coumaric acid, *m*-hydrocoumaric acid, etc.) by ester exchanging reaction. Because those of resins contain catechol groups at their chain ends, which is similar to the chemical structure of protein containing DOPA of Mussel, it demonstrates strong adhesive characteristics onto organic and/or inorganic surfaces. For example, copolymerization of hydrocaffeic acid (10%) and *m*-hydrocoumaric acid (90%), shown in **Figure 1** demonstrated over 20MPa of adhesive strength even onto very flat optics glasses (**Figure. 2**), which is equivalent value to epoxy resins. Positive control in **Figure 2** was conventional instant super glue.

We have supposed that an origin of this strong adhesive characteristic was attributed to strong hydrogen bond interaction between -OH group of our resins and oxidized and/or -OH on the substrates. In my presentation, we will report the potential of our Bio-base adhesive resins and their applications.

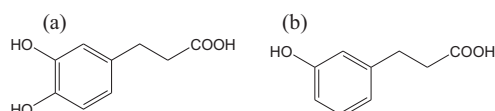


Fig. 1 : Chemical structure of (a) hydrocaffeic acid and (b) *m*-hydrocoumaric acid

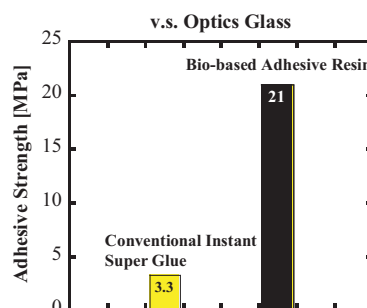


Fig. 2: Adhesive strength onto optics glass

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*Development of Ultra-Hydrophobic Non fluorine Sol-Gel films for Aluminium Alloy**Ruchi GroverWankhede¹, Nick Birbilis³ & A.S.Khanna²*¹ IITB-Monash Research Academy, IIT Bombay²Department of Metallurgical Engineering and Materials Science, IIT Bombay,
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Super hydrophobic coatings represent an important and interesting field of research. This report begins with a brief discussion about the causes of super hydrophobicity and characterization of super hydrophobic surfaces. Some recent synthesis techniques and several applications of these surfaces and coatings are then described. The present work aims at development of ultra-hydrophobic organic-inorganic hybrid sol-gel coatings with contact angle $>120^\circ$ for aluminum substrate for better oil and water repellent, anti graffiti, stain resistant and corrosion resistant properties. This can be achieved by synergistic effect of lowering of surface energy and increase in surface roughness. Lowering of surface energy can be achieved by use of both fluoroalkyl silane precursors and non fluoro silane precursors leading to initial hydrophobicity which could be further enhanced by further incorporation of nano-particles to sol-gel or by modifying the surface finish of aluminum surface using various mechanical, chemical and advance surface roughening methods.

Low energy hydrophobic sol-gel coatings are developed on aluminum substrates by using combination of non fluoro C-16 HDTMS, GPTMS and TEOS silanes in different ratios to develop an organic-inorganic hybrid coating network. In this approach increase in surface roughness was achieved by etching aluminium substrate with various dislocation reagents. Coatings were applied on aluminum by dipping technique and cured at 120°C for 30 minutes. Surface morphology of the coating was characterized using SEM and AFM and its hydrophobicity was evaluated by using contact angle measurements.

It was found that sol-gel formulation with HDTMS: GPTMS: TEOS ratio of 2:2:6 had optimum gel time and hydrophobicity and were found to be ultra hydrophobic with water contact angle values ranging from 110° to 130° when applied on differentially etched aluminium specimens.

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Development of Ultra-Hydrophobic Non fluorine Sol-Gel films for Aluminium Alloy

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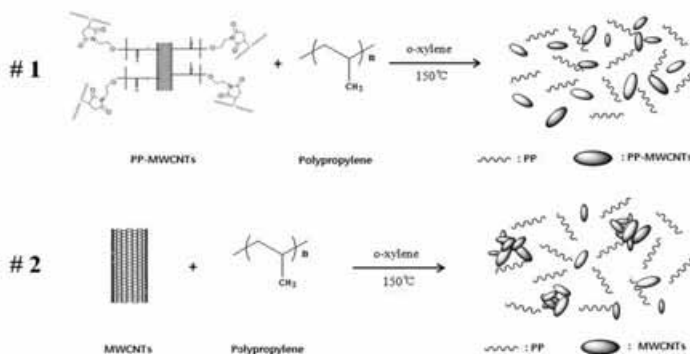
Fabrication of Homogeneous Composites of Polypropylene and Multiwalled Carbon Nanotubes by Solution Mixing

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Carbon nanotubes (CNTs) are noted for their outstanding electrical, mechanical, and thermal properties. However, the practical uses of pristine CNTs are impeded by their aggregation properties and their insolubilities in organic solvents or water. In order to increase solubility and reduce the tendency of aggregation, CNTs are often functionalized with organic moieties and polymers.¹⁻³ Polypropylene/CNT composites have previously been prepared by melt processing with CNT concentration ranging from 5% to 20% to the polypropylene. This approach is the simplest method to fabricate polypropylene/CNT composites without any modification of the surface of CNTs. However, it usually results in the unfavorable effect on improvement in thermal and electrical properties of the polypropylene/CNT composites even with high CNTs concentration because of the low compatibility between CNTs and polymer.

In this study, the polypropylene-grafted multiwalled carbon nanotubes (PP-MWCNTs) were produced from the reaction of PP containing the hydroxyl groups and MWCNTs having 2-bromoisobutryl groups. The PP-MWCNTs had a significantly rougher surface than the original MWCNTs. PP-MWCNTs had PP layers of thickness 10-15 nm on the outer walls of the MWCNTs. PP/PP-MWCNT composites and PP/MWCNT composites were prepared by solution mixing in *o*-xylene (Scheme 1). Unlike PP/MWCNT composites, PP-MWCNTs were homogeneously dispersed in the PP matrix. As a consequence, the thermal stability and thermal conductivity of PP/PP-MWCNT composites were dramatically improved even if only 1 wt% of PP-MWCNTs was added to the PP matrix. The good miscibility of PP and PP-MWCNTs plays a critical role in the formation of the homogeneous composites and leads the high thermal stability and thermal conductivity.



Scheme 1

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² D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* **2006**, 106, 1105.

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Bio-inspired Polymers and Gels based on Dopamine-Modified Polyaspartamides For Versatile Coating and Adhesive Applications

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Novel adhesive polymers based on dopamine(DOP)-conjugated poly(amino acid) were synthesized and characterized. The catechol group of DOP has been known for the ability to form strong adhesion onto both inorganic and organic surfaces in aqueous environments.^{1,2} Adhesion and subsequent oxidative crosslinking of DOP-conjugated polymers can provide a way to modify various material surfaces including synthetic polymers, metals, metal oxides, and ceramics in wet environment. Here a versatile coating was demonstrated for material-independent surface modification using biocompatible polyaspartamides conjugated with DOP (**Fig. 1**). The modified surface was characterized by XPS, contact angle measurement, and FTIR. Cytotoxicity of the materials was also elucidated from the cell viability by MTT assay. Further modification of polymer with PEG chains and the subsequent coatings therefrom was also attempted to verify the anti-fouling characteristics of the modified surfaces. These novel functional polymers have potential for use in broad technological fields including industrial and medical adhesives, surface modification of biomaterials, DDS, etc.

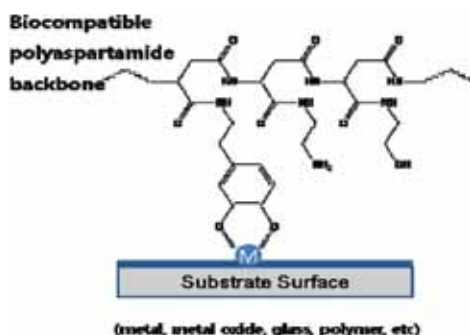


Figure 1. Dopamine-modified polyaspartamide derivatives for versatile coating on various substrates

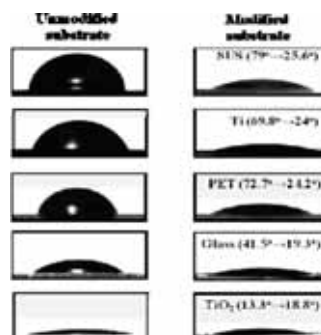


Figure 2. Contact angle measurement

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Effect of Heterostructure of Metallic Nanoparticles and Carbon Nanotubes on the Mechanical Properties of Polymer Composite Films

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The effect of dimensionality of metallic nanoparticles- and carbon nanotubes-based filler on the mechanical properties of an acrylonitrile butadiene styrene (ABS) polymer matrix was examined. ABS composite films, reinforced with low-dimensional metallic nanoparticles (MNPs, 0-D) and carbon nanotubes (CNTs, 1-D) as nanofillers were fabricated by a combination of wet phase inversion and hot pressing. The tensile strength and elongation of the ABS composite were increased by 39% and 6%, respectively, by adding a mixture of MNPs and CNTs with a total concentration of 2 wt%. However, the tensile strength and elongation of the ABS composite were found to be significantly increased by 62% and 55%, respectively, upon addition of 3-D heterostructures with a total concentration of 2 wt%. The 3-D heterostructures were composed of multiple CNTs grown radially on the surface of MNP cores, resembling a sea urchin. The mechanical properties of the ABS/3-D heterostructured nanofiller composite films were much improved compared to those of an ABS/mixture of 0-D and 1-D nanofillers composite films at various filler concentrations. This suggests that the 3-D heterostructure of the MNPs and CNTs plays a key role as a strong reinforcing agent in supporting the polymer matrix and simultaneously serves as a discrete force-transfer medium to transfer the loaded tension throughout the polymer matrix.

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Natural antioxidants for polyolefin elastomer

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Ageing processes of materials bring about irreversible changes in structural properties, which is undoubtedly an undesirable effect. In order to establish a specified working life of a product it is indispensable to properly select effective stabilizers, whose basic task will be its protection against oxidation processes. Usually, the industry uses amines with steric hindrance and substituted phenols as anti-ageing substances, what can bring about the hazardous effect to the environment and human health. In our studies, we propose the use of natural proecological substances, such as flavonoides, to protect elastomers against ageing. Flavonoids are natural vegetable dyes synthesized from phenylalanine.

An object of the study was morinhydrate obtained from Aldrich. Compositions of the rubber blends were as follows: Engage (Dow Chemical Company) was used as an elastomer matrix (100 phr), dicumyl peroxide (DCP, Fluka) used as a cross-linking agent (2 phr) and fumed silica Aerosil 380 (Degussa) was used as a filler (30 phr). The rubber blends were prepared by means of a laboratory mixing mill with rolls and the vulcanization was carried out with the use of steel vulcanization molds placed between the shelves of electrically heated hydraulic press. Samples for study were vulcanized at a temperature of 160°C, under a pressure of 15 MPa for 30 min.

Density of crosslinks in the rubber network of obtained vulcanizates was determined by a method of equilibrium swelling. Tensile strength of the vulcanizates was tested according to standard PN-ISO 37:1998 by means of a ZWICK tester, model 1435, for dumbbell w-3. Ageing characteristics were determined according to standard PN-82/C-04216. UV ageing was performed by means of an UV 2000 apparatus from Atlas. The measurement lasted for 120 h and consisted of two alternately repeating segments with the following parameters: daily segment (radiation intensity 0.7 W m⁻², temperature 60° C, duration 8h), night segment (no UV radiation, temperature 50° C, duration 4 h). Climatic ageing was carried out using a Weather-Ometer (Atlas; Ci4000). The test was based on two variable segments simulating day (irradiation, condensation, 70°C) and night (condensation, 50°C) conditions.

The results showed that morinhydrate provided high protection of the studied polyolefin elastomer against UV and climatic ageing. The additional advantage is the proecological character of the applied antioxidant. The results are shown in Table 1.

Table 1. Effect of morinhydrate on tensile strength of EPM vulcanizates (SE300 – stress at 300 % of elongation, TS – tensile strength, Eb – elongation at break).

	SE300, (MPa)	TS, (MPa)	Eb, (%)	(TS*EB) _{after ageing} / (TS*EB) _{before ageing}
Engage	5,86	22,90	524	-
Engage/ morinhydrate	5,61	26,20	557	-
After UV (50h)				
Engage	2,11	2,03	293	0,05
Engage/ morinhydrate	5,15	23,80	570	0,93
After weathering (150h)				
EPM	2,70	3,51	383	0,11
EPM/ morinhydrate	4,73	18,70	562	0,72

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Elastomer composites containing layered fillers and hydroxyapatites

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Traditionally, as a filler of rubber carbon black is used. It is an active filler able to reinforce and improve the properties of finished rubber products. For ecological and economic reasons the research activity is focused on looking for new methods of surface modification of inactive fillers to enhance their strengthening performance in elastomers.

In our work as a filler of elastomeric compounds a cation-exchangeable aluminosilicates-type montmorillonites with nanometric thickness of the tiles were used. can be used to obtain nanocomposites due to produce nanoscopic structures „in-situ” in polimer matrix by intercalation and exfoliation of single layers of filler.

Montmorillonites are incompatible with most polymers and therefore is necessary to modify them in order to increase layer-spacing and to facilitate the penetration of polymer chains. The modification involves introducing various organic cations in place of sodium cation present between layers. Most commonly used for this purpose are ammonium or phosphonium salts. Modification increases the distance between the packages in the filler, and also due to adsorption of modifier on the surface increases the affinity to elastomeric matrix. In our study as a elastomer fillers also hydroxyapatites were used.

Surface properties of modified fillers, the zeta potential of suspended solids in the water, the oil absorption number, the impact of modifications on the tendency to agglomerate in the non-polar and polar medium were investigated.

The modified fillers were used in elastomer matrix with different polarity: the ethylene-propylene copolymer EPM and acrylonitrile-butadiene rubber NBR. The effect of the application of fillers on the cross-linking density of the vulcanizates, rheometric and mechanical properties of filled systems was investigated. The ageing studies (thermal, atmospheric and under UV radiations) were conducted.

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Degradable composites containing modified cellulose

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There are several research activities focusing on obtaining environmental friendly polymer materials¹⁻³. One of them refers to the polymers with an increased degree of degradability which can be obtained through the addition of natural biodegradable supplements to the synthetic polymers⁴⁻⁶. The aim of our study was to obtain an composites with a good mechanical properties and determined time of degradability. In the investigation as a matrix degradable polymers as aliphatic-aromatic co-polyesters PEAA and polycaprolactone PCL were used. As a fillers the modified and unmodified montmorillonites MMT have been applied to improve the mechanical properties of composites. It is well known that layered silicates have several advantages when compared to traditionally used fillers i.e. they improve the mechanical strength of composites, increase barrier properties and reduce flammability⁷. To improve the properties of final composite to the mixtures modified cellulose was added. In our work for the composites preparation we used surface modified with different ionic liquid cellulose. The mixtures were prepared with the Brabender micro-mixer connected to the computer. The mixture components were weighted on a laboratory balance to obtain values calculated in advance. The PEAA and PCL mixtures were prepared with the Brabender micro-mixer at different stirring speeds and at temperatures of 80 or 100°C (PEAA) and 120°C (PCL). After pressing, samples were obtained in the form of 1 mm thick foil. Mechanical properties of the moulded pieces were examined. Mechanical properties of polyester moulded pieces after ageing at different temperatures, under UV radiation and in ozone also were examined. Tensile strength and relative break at elongation values were measured after ageing in controlled conditions. The application of cellulose modified by ionic liquid resulted in an increased susceptibility for degradation of composites during the ageing and storage on land and composting.

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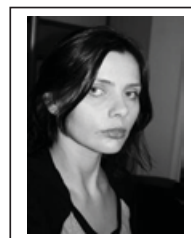
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Cellulose fibre as natural filler for epoxidized natural rubber

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An upward tendency in manufacture and consumption of elastomeric materials has been still observed during the several dozen years. An increasing knowledge of ecological and environmental problems has a real and considerable influence on the requirements and demands toward modern technologies. One of the most important subject in this matter is the production of environmentally friendly materials. To meet the aim, much investigations focus on the use of natural and pro-ecological materials as additives for synthetic materials.

Our work concerns studies on new non-sulphur cross-linking system for epoxidized natural rubber. The presence of oxirane ring in epoxidized natural rubber allows for the application of various compounds as the cross-linking agents [1-3]. We assume that new cross-linking system provides the elastomeric composites with good mechanical properties and enables their hydrolysis in natural environment due to the presence of amide groups in the resulting network of the composite. As a filler, pro-ecological cellulose as well as silica with OH groups on the surface has been used.

The initial results of the study show that elastomeric vulcanizate filled with cellulose has higher elongation at break (EB) in comparison with the sample filled with silica. While, the tensile strength for both vulcanizates of ENR(50) is comparable. The results are shown in Table 1.

Further measurements, with the object of better dispersion degree and improvement of mechanical properties and degradability, are planned.

Table 1. Effect of cellulose on the tensile strength of ENR(50) vulcanizates (SE300% – stress at 300% of elongation, TS – tensile strength, Eb – elongation at break.

Vulcanizate	SE300, (MPa)	TS, (MPa)	Eb, (%)
ENR(50) /adypic acid(1phr)	1,33	1,86	432
ENR(50) /adypic acid(1phr)/ imidazole(1phr)/Cellulose fibre (10phr)	2,38	2,56	367
ENR(50) /adypic acid(1phr)/ imidazole(1phr)/ Silica(10phr)	2,40	2,64	314

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Green tea extracts as antiageing substances for rubber

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A permanent increase in the demand for polymers is closely connected with the issue of their degradation. Nowadays aromatic amines or phenol derivatives are used to protect materials against ageing.

In our studies, we propose the use of natural pro-ecological substances such as polyphenols from green tea to protect elastomers against ageing. Several extracts from Sencha and Gun Powder green tea were incorporated into ethylene-propylene rubber (EPM, Dutral CO-054) and then the vulcanizates of EPM containing the anti-oxidants under investigation were subjected to UV, climatic and thermal ageing processes.

The changes in deformation energy, color and cross-linking density of the EPM vulcanizates were then measured before and after each ageing process. Based on the investigations performed, it has been found that both extracts of Sencha and Gun Powder green tea show anti-oxidative properties that can protect EPM rubbers against the action of climatic factors.

The extracts tested by us and characterized in the study show their capability to scavenging free radicals and impeding oxidation processes. The protective action of these extracts in elastomers is comparable to that of the commercial stabilizer. This indicates that in the future the pro-ecological anti-oxidants in the form of natural plant extracts proposed by us can be an attractive alternative to the HALS type stabilizers.

Table 1. UV and climatic ageing coefficients (S_{UV} , S_C) of EPM vulcanizates containing different compounds as anti-ageing substances.

Vulcanizates	S_{UV}	S_C
EPM	0,22	0,45
EPM/chimassorb81	0,83	0,99
EPM/Gun polder green tea	0,31	0,85
EPM/Sencha green tea	0,94	0,94

S_{UV} , S_C – ageing coefficients, calculated on the basis of mechanical parameters (tensile strength and elongation at break) changes, caused as a result of ageing.

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Chitosan-based nanofibrous mats as anti-adhesion barriers

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The field of surgical research has been paying a lot of attention to find the way of preventing the formation of post-operative adhesions and the history of preventive strategies goes back over 100 years. Despite much interest in the prevention of post-operative adhesions, the formation of peritoneal adhesions persistently appears and carries common serious complications such as post-operative pain, bowel obstruction and infertility after surgery.^{1,2} Chitosan is the deacetylated derivative of chitin, which is the second most abundant polysaccharide found on earth next to cellulose. It comprises copolymers of glucosamine and N-acetyl glucosamine has a combination of many unique properties such as nontoxicity, biocompatibility and biodegradability. The living body affinity, antibacterial properties and wound recovering effect of chitosan have drawn a lot of interest in recent years. Poly(lactide-co-glycolide)(PLGA), the random copolymer of poly(lactide)(PLA) and poly(glycolide)(PGA), has been widely used for medical applications such as surgical suture, temporary scaffolds for tissue engineering, and drug carriers because of the complementary nature of PLA and PGA.

In this study, chitosan and PLGA with a small quantity of poly(ethylene oxide)(PEO) blend nanofibers were produced by electrospinning. The effects of solution and processing parameters on the morphology of electrospun nanofibers were investigated. The average diameter of fabricated Chitosan/PLGA/PEO nanofibers were controllable from 900 nm to 600.

Various ratios of the Chitosan/PLGA/PEO nanofibrous membranes were characterized by SEM, ATR-FTIR and antimicrobial test. Rheological study combined with SEM characterization revealed that the spinnability of Chitosan/PLGA solution was substantially improved when the solution viscosity was optimized. A small portion of PEO into Chitosan/PLGA solution allowed the solution to be spinnable with few beads on mat, and considerably improved the spinnability of the solution. ATR-FTIR spectroscopy was suited for investigating the presence of specific C=O, C-O and N-H vibration peaks at the surface of Chitosan/PLGA/PEO nanofibrous membrane. The antimicrobial activity of chitosan-based nanofibers was studied. As the amount of chitosan was increased, the antimicrobial effect was enhanced. Cell culture results showed that Chitosan/PLGA/PEO nanofibrous membrane tended to reduce cell proliferation by increasing their hydrophilicity and biodegradability. From *in vivo* animal test, it was observed that Chitosan/PLGA/PEO nanofibrous membranes were significantly effective in preventing post-operative adhesion and wound healing, due to the appropriate hydrophilicity preventing shrinkage of the membrane and increasing biocompatibility. Electrospinning of Chitosan/PLGA/PEO nanofibrous membrane may give the possibility of producing new materials for potential biomedical applications such as a post-operative anti-adhesion barrier.

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A Study of Nano Size Standard Material Validation by the Photon Correlation Spectroscopy (PCS) method

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In the field of particle size measurements using the PCS method, the most popular standard material is polystyrene latex beads. The standard material of polystyrene latex for the PCS method is held in a suspended condition. Care is taken so that there is no aggregation. The PCS principle is based on a diluted sample condition at an order of 0.001 weight %. Hence the spherical material should be diluted for the measurement.

A validation condition is defined by ISO 13321:1996. The narrow distribution polystyrene latex, about (PSL) 100 nm, is used for the validation in a diluted condition. The accuracy of particle size should be within 2 % of the standard size. The PSL is diluted by deionized water, whereas the result of particle size is always a few % bigger than certified diameter. The PSL standard should be diluted by 0.01 mol/L NaCl aqueous solution for the validation procedure. Real samples were used for the measurement of particle size across a wide concentration and ion strength.

The purpose of this study is to validate diluted process for the PSL standard by the PCS method. From verifiable results, Horiba propose optimized condition of concentration by PCS method.



Figure 1. The Horiba SZ-100 NanoPartica

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A Study of Low Volume Cell for Zeta Potential and Size Distribution of Submicron Particles

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When the stability of particles in solution is discussed amongst researchers, zeta potential can be a good indicator for characterization. Controlling the quality of the sample solution is one of the most important factors for good products. Also, the sample is often very precious and some users want to make an evaluation using a very small amount of sample. Thus a small volume cell was designed and the performance was evaluated. Detrimental processes such as electrolysis and polarization resistance can prevent correct answers. To avoid those influences, some examinations were made in this study. For the evaluation, two different kinds of sample cells were prototyped. One electrode was made from carbon and the other electrode from gold. The evaluation results are discussed for designing a better small volume cell for zeta potential measurement.

Zeta potential relates to interfacial electric phenomena like electrophoresis, electroosmosis and streaming potential. Especially for colloids, zeta potential is a reliable index for dispersibility evaluation.

The principle of measurement: Mobility of particles in aqueous solution can be obtained by observing the frequency shift of the scattered light from electrophoresis. The mobility was mathematically converted to zeta potential.

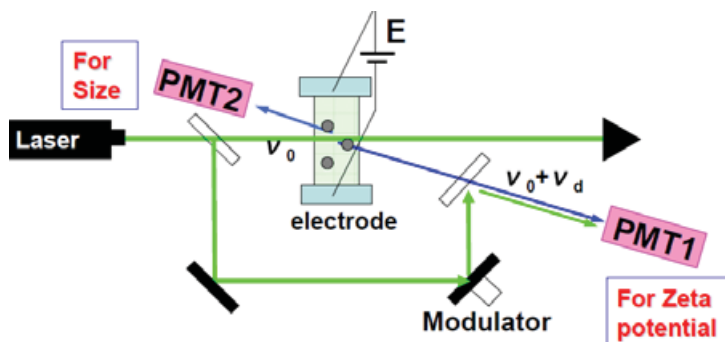


Figure 1. An optical design for Zeta potential and PCS. Signal of Doppler shift and PCS method.

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Characterization of Nanoparticles by Light Scattering*John K Arthur¹, Gavin Soon²*¹DKSH Australia Pty Ltd, Australia²Horiba, Japan

Characterization of nanoparticles is of main importance for many activities like material research, pharmaceutical research and industrial developments. Light scattering techniques offer many advantages like simplicity of use, compactness and sample preservation.

Characterization of nanoparticles by light scattering can be achieved in many ways. The two main approaches can be distinguished as follows: Static (SLS) and Dynamic (DLS) light scattering.

SLS use the averaged intensity scattered by particles. DLS use the time dependence of the fluctuations of intensity.

The SZ-100 combines the principles of SLS and DLS to make characterization of several nanoparticle properties available in one machine. The SZ-100 can measure Size, Zeta potential and Molecular weight.

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Latest Trends in Particle Size Characterization of Polymers*John K Arthur¹, Mick Pohl²*¹DKSH Australia Pty Ltd, Australia²Horiba, USA

Polymers and many other materials now represent the growing class of nano-materials being manufactured. As these new materials are used in final products, it is increasingly important to be able to properly characterize them after production. One of the key physical properties is the Particle Size Distribution. An emerging technology to perform this measurement is Dynamic Light Scattering. In order to use this technology it is necessary to develop primary reference standards. As would be expected over in the United States, NIST is playing a key role in this effort. The development of nano-gold reference materials, as well as polymers such as dendrimers and other lattices, will be presented. Real samples have been evaluated and statistical data has been produced for this new and growing technique.

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Improving the reproducibility of synthesis and properties of poly(polyol sebacate)

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Biodegradable soft elastomers have gained much recent attention in the field of soft tissue engineering because these polymers mechanically resemble soft tissues. Poly (polyol sebacate) (PPS) is a new family of crosslinked elastomers which are elastic, biocompatible and degradable. They have already shown potential applications in nerve, vascular and myocardial tissue engineering. However, a number of issues remain with these novel polymers, which include poor repeatability and reproducibility of PPS properties, the toxicity of very soft version of PPS members and fast degradation kinetics.

In this study, two PPS versions, poly (glycerol sebacate (PGS) and poly (xylitol sebacate) (PXS), have been synthesized under various conditions from the polyol (glycerol or xylitol) and sebacic acid. Two methods were used to quantify the reaction kinetics, namely, measurement of the mass loss during the polycondensation reaction and titration of the unreacted carboxylic groups. It was found that during the polycondensation process glycerol as well as water evaporated and this loss of glycerol was a major cause of poor reproducibility, of the synthesized PGS polymer. Glycerol loss was lower at 130°C than 150°C, and thus PGS synthesised at 120-130°C was more repeatable. PXS can achieve a higher break strain and lower Young's modulus than PGS, and demonstrates better biocompatibility than PGS. Finally, the biocompatibility of both PGS and PXS materials can be improved through a longer curing time (**Fig.1**).

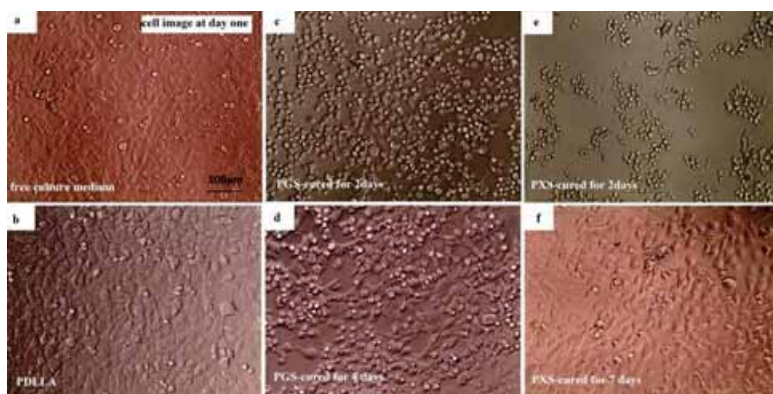


Figure 1. Images of SNL cells cultured in extracts prepared by different samples at day one (a-e): (a) free culture medium, (b) PDLLA, (c-d) PGS was treated for same pre-conditioning at 150 °C for 8 hours, but crosslinked at 130 °C for different days (c) 2days, (d) 4days, (f-e) PXS was treated for same pre-conditioning at 150 °C for 24h, but crosslinked at 130 °C for different days (f) 2days, (e) 7days.

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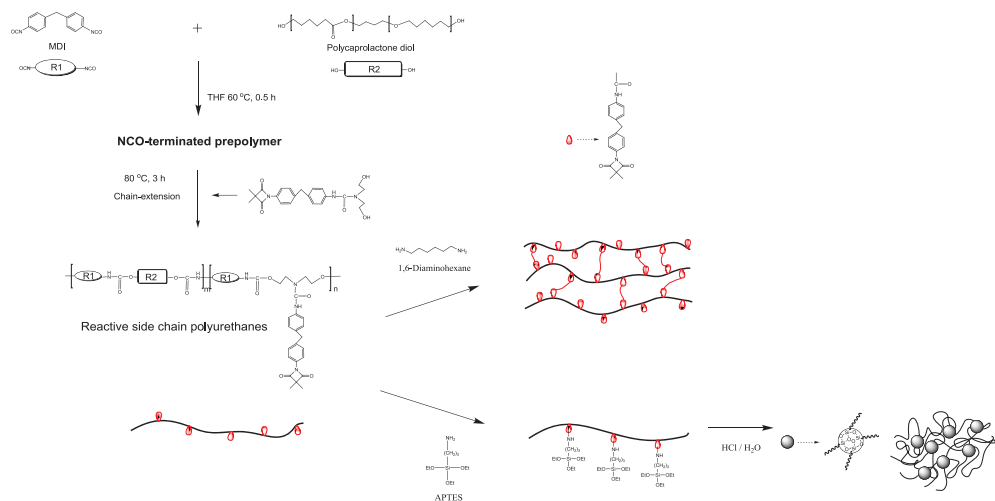
Side-chain Crosslinked Polyurethane with Shaped Memory Effect

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A short-chain diol with reactive azetidine-2,4-dione group¹ was prepared and introduced into polyurethane backbone. The side-chain² polyurethane with reactive pendent azetidine-2,4-dione group was further crosslinked by short-chain aliphatic diamine and modified by silane coupling agent (APTES)³. The structure of the polyurethane was characterized by Fourier transform infrared spectrometer (FTIR), X-ray diffraction (XRD) and differential scanning calorimeter (DSC). FT-IR indicates that APTES reacted with pendent azetidine-2,4-dione resulting in a grafted alkoxy silane polyurethane⁴. XRD and DSC shows that crystallinity of polyurethane decreased with the increase of crosslinking density. Tensile strength of films increases with increasing crosslinking density and hydrolysis degree of pendent alkoxy silane. The maximum tensile strength of crosslinking polyurethane increased up to 50.6 MPa and the strain remained at 481%. During cyclic shape memory tests, high crosslinking density series could effortlessly achieve complete recovery in less than 10 second without any deficiency. The shape recovery went up to an amazing 99.5% and did not decrease below 97.5% after cycle three while showing no significant drop in the shape recovery speed.



Scheme 1 Synthetic routes of crosslinked polyurethane

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Dynamic studies to investigate the effect of phosphate buffer concentrations on lactoferrin adsorption and desorption using a novel temperature-responsive ion-exchange chromatographic resin

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A temperature-responsive cation-exchange resin has been developed by grafting poly(N-isopropylacrylamide-co-acrylic acid-co-tert-butylacrylamide, ItBA) onto cross-linked agarose beads was developed. The new resin can reduce the use of salt (NaCl) in eluting protein during ion exchange chromatography by using temperature as the trigger for the release of adsorbed molecules.

Lactoferrin is commercially manufactured from cheese whey using ion-exchange chromatography. This process involves desorption of adsorbed LF using salt, which requires the additional salt removal and disposal steps. These additional steps increase the cost of production due to the energy required to de-salt the product and further economic and environmental cost associated with the disposal of the residual salt. The new temperature-responsive resin could be used to separate LF from crude whey proteins with a significantly reduced amount of salt.

Stimuli-responsive polymers undergo conformational changes in response to any changes in the environment, such as: temperature, pH, ionic strength, UV irradiation, magnetic or electric field¹. One of the most widely studied stimuli-responsive polymers is a temperature-responsive polymer, which by altering the temperature of the system, undergoes an abrupt reversible change in structure. This reversible phase transition of the polymer takes place at the lower critical solution temperature (LCST). The polymer on heating above its LCST is converted into more hydrophobic globular particles and upon cooling below the LCST is converted into a more hydrophilic extended coil, resulting in reversible dehydration and rehydration of the polymer². This research was conducted to further understand the dynamic response of the temperature-responsive resin to phosphate buffer concentrations using LF as a model protein.

The dynamic adsorption and desorption behaviour of temperature-responsive cation exchange resin (containing 5% of acrylic acid) with LF in MilliQ water (MQW, 0 mM), 10 mM and 50 mM phosphate buffers at pH 6.5 and temperatures of 20°C and 50°C were examined. The resin demonstrated temperature responsive LF adsorption characteristics between 20 and 50°C in all three buffers at pH 6.5. With MQW, the amount of LF adsorbed at 50°C was 2 fold greater than that at 20°C. The resin demonstrated the greatest LF adsorption capacity in MQW at 50°C, followed by LF in 10 mM buffer, and LF in 50 mM phosphate buffer respectively.

After adsorption of LF in MQW or 10mM phosphate buffer at 50°C, the column was washed using the same loading buffer at 50°C, followed by eluting with either MQW, 10mM or 50mM phosphate buffers at a temperature of 20°C and pH 6.5. Most of the LF was eluted with 50mM phosphate buffer and only a portion of LF was eluted with 10mM phosphate buffer. However, MQW water was unable to elute any LF from the resin at 20°C after adsorption of LF in MQW; a portion of LF was eluted from the resin at 20°C after adsorption of LF in 10mM buffer. In contrast, when LF in 50mM phosphate buffer was adsorbed, elution of LF was achieved by all three, MQW, 10mM and 50mM phosphate buffer at a temperature of 20°C. These trials demonstrated that high salt concentrations are not required to elute the adsorbed LF from the resin.

The resin with 5% acrylic acid demonstrated varying LF adsorption capacities at temperatures of 20 and 50°C. There were also significant differences in LF adsorption and desorption characteristics when different buffer concentrations were used at 20 and 50°C. The combined effects of temperature-responsiveness and the buffer concentrations on the adsorption and desorption of LF provides a way to optimise the performance of temperature responsive resins to achieve a significant reduction in the use of salt in the separation of LF from dairy streams. This will result in reducing the need for additional processing steps, reducing costs and making the process more environmental friendly.

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Multi-Step Thermal Characterization of Polymers by GCMS*John K Arthur¹, Gary Deger²*¹DKSH Australia Pty Ltd, Australia²CDS Analytical, USA

The composition of a polymeric product, especially a finished manufactured good, is a complex combination of materials formulated to meet the specific requirements and functions of that product. The polymer matrix itself may be a blend, copolymer, laminate, reinforced or multilayered system. The physical properties are then modified by the addition of plasticizers, tackifiers, antioxidants, light stabilizers and other additives, making the finished product an analytical challenge. In addition, there are residuals such as unreacted monomers and solvents which are rarely completely removed in drying steps.

Although some of the smaller molecules may be removed by solvent extraction, this may complicate the analysis if the analytes themselves are trace levels of solvents, which become diluted in the extraction.

The organic materials in such a system, even the polymers, may be sampled without solvents by careful selection of the sample temperature. Small molecules, including solvents and residual monomers, are desorbed from the polymer at relatively low temperatures. Larger molecules, such as antioxidants and plasticizers, are removed at intermediate temperatures. The polymer itself may be pyrolyzed at high temperature to enable analysis by GC/MS, showing not only the monomer content, but copolymer information and even microstructure. This paper shows the analysis of complex polymeric materials such as packaging and rubber deformed using temperature as the sample preparation step.

**The Use of Pyrolysis Gas Chromatography Mass Spectrometry
to Characterize Synthetic Degradable Polymers**

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The recent growing concern for our ecosystem quality as well as limits of natural resources, such as petroleum, has lead to development of disposable plastics that decompose quickly. Some degradable plastics are simply our old standbys such as petroleum-based polyethylene, but with additives to encourage decomposition. Other degradable plastics are made from plant starch; still others are blends of starch and synthetic polymers. Each of these polymers looks different from each other when pyrolyzed. Analytical pyrolysis extends the applications of a gas chromatograph to nonvolatile materials such as polymers. In this presentation, we will discuss the use of analytical pyrolysis coupled with gas chromatography/mass spectroscopy to investigate pyrolysis products and locate additives in manmade biodegradable polymers, mainly plastics. Investigations will include polymers that have been in existence for some time as well as newer formulations. This method produces a repeatable fingerprint, and so allows it to be useful for determining polymer type. Because there is a renewed interest in creating biodegradable plastics, and analytical pyrolysis can be a useful tool for investigating polymer structure, pyrolysis results can be used by manufacturers to de-formulate a competitor's product.

A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting POSS-Polymers

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Thin film Composite (TFC) membranes are now one of the most important and popular technologies for water separation such as brackish and ocean water desalination, waste water reclamation and ultrapure water production. However, improved membrane materials are still required to make TFC membranes last longer and function more effectively in these challenging applications (Figure 1).

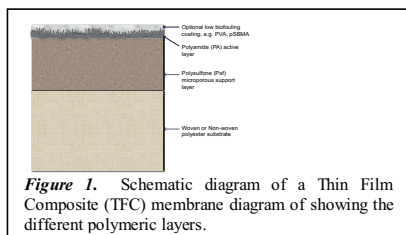


Figure 1. Schematic diagram of a Thin Film Composite (TFC) membrane diagram of showing the different polymeric layers.

Asymmetric polysulfone (PSf) membranes are an important substrate used in water separation technologies. A thin, dense skin layer on top of a porous sublayer, which includes macrovoids, pores and micropores, is characteristic of the cross-sectional morphology of PSf membranes used for microfiltration (MF) and ultrafiltration (UF) purposes. In Reverse Osmosis (RO) seawater desalination membranes, the microporous PSf layer cast onto a non-retentive substrate, functions as a support for a non-porous polyamide (PA) skin. Macrovoids in RO membranes can lead to membrane collapse after extended operation at high (>5500 kPa) pressures that in turn leads to a decline in permeate flux. However, the improvements in membrane resistance to compaction must be balanced against the need to maintain an open PSf support layer structure to facilitate efficient permeate transport through the membrane. Many researchers have studied the effect of casting conditions (solution composition, additives and temperature) on the cross-sectional morphology of PSf membranes.^{1,2} Recently, the inclusion of nanofillers in membrane materials is developing, with the aim of not only producing membranes with enhanced mechanical properties but also improving the permeation properties.^{3,4}

The main purpose of this work was to develop an efficient process for preparing POSS endcapped Polysulfones. Covalently linking the POSS^{5,6} nanoparticles to PSf will anchor the nanoparticles within the polymer matrix, thus reducing precipitation and/or sedimentation of the nanoparticles; it will allow for a homogeneous dispersion of POSS within the PSf matrix, and inhibit or reduce surface migration of the POSS nanoparticles. In addition to this POSS nanohybrids were incorporated into the polyamide layer and the properties and performance of these membranes were studied

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New Techniques for the Production of Acrylate Monomers From Waste Biofuels

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With increasing concern for climate change caused by greenhouse gases, the cost of oil, and the energy crisis, biofuels, which are fuels derived from vegetable oils and animal fats, are thought to be a renewable carbon neutral substitute for the finite source, carbon polluting crude oil.

Biofuels are produced from fats and oils using transesterification to form fatty acid methyl esters, however the by-product of this mechanism is glycerol. As the demand for biofuels has increased so has the production of glycerol, which has in-turn significantly lowered the market prices and made glycerol a waste product (**Fig.1**).

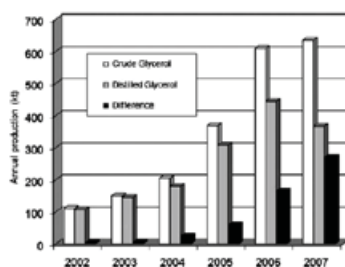
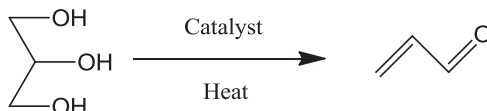


Figure 1. Increasing production of Glycerol over a five year period. The difference is often burned.¹

To combat this ever increasing issue, the waste glycerol can be chemically altered to form value-added products. Many products can be formed,² however acrolein is typically made from propene, which also comes from the finite source, carbon polluting crude oil. An alternative synthesis technique is needed as acrolein is produced in several million tonnes a year.



Scheme 1. The typical dehydration reaction for acrolein synthesis.

A simple technique of heating glycerol with an acid catalyst can produce acrolein, which can subsequently be treated to form a variety of acrylate monomers. However, the instability of acrolein at high heat reduces the yield to below 40%. Many techniques have arisen to increase the yield and selectivity. In particular, supercritical water has had much attention, producing high yields, but the process is energy intensive, the catalyst is short lived and is a batch type system, which slows down the rate of production. A new system has been explored that is a continuous flow setup, and has the capacity to rejuvenate the inert media and catalyst. This technique has shown great promise and is a suitable design for industry.

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Selective Deposition of Silica-Polymer Hybrid Nanoparticles on Gold Surfaces

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Monodisperse silica nanoparticles provide an ideal scaffold onto which polymeric materials may be grafted in order to design composite materials with a range of interesting properties.¹ Varying the size of the initial silica particle as well as the length, nature and density of the grafted chains affords further control over the range of properties the composite material exhibits.² Reversible addition-fragmentation chain transfer (RAFT) polymerization allows access to polymers of a tunable molecular weight and low polydispersity. We have previously demonstrated that RAFT agents anchored on to silica nanoparticles allows us to grow polymers from these surfaces yielding silica-polymer hybrid nanomaterial.³

Facile aminolysis of the RAFT agent affords thiolated chains that can be post-functionalised using a variety of high-yielding reactions. Alternatively, the thiols can be used to localise the hybrid nanoparticles on gold surfaces (**Figure 1**). This allows us to modify the gold surface in a highly-efficient, manner yielding confined domains of polymeric material on gold.

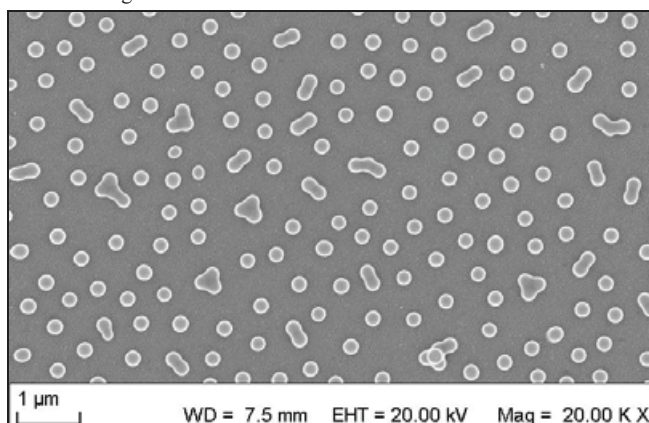


Figure 1. Silica-polymer hybrid nanoparticles deposited onto gold

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RAFT Polymerisation in Continuous Flow Microreactors

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In recent years, Reversible Addition Fragmentation Chain Transfer (RAFT) polymerisation has been extensively explored by academic and industry researchers due its ability to control the molecular weights, compositions and architectures of the resulting polymers. RAFT polymerisation is usually conducted in batch process where the solution containing chain transfer agent, monomer(s) and initiator is carefully deoxygenated by either freeze-pump-thaw or nitrogen bubbling prior to heating in a sealed vessel. Although it is a convenient and versatile process, the steps involved are laborious, time consuming and may require specialised glassware. In addition, scaling up is limited due to uneven heat transfer within the reaction vessel and oxygen sensitivity. Here we report a new processing method where RAFT polymerisation is performed under continuous flow conditions using a laboratory scale tubular flow reactor system.

The flow reactor system is a modular unit consisting of a series of microtubular reactors that use fluidic pumping systems. Starting materials are injected through precision manufactured reactor coils with controlled mixing and temperature. This process enables multi-step synthesis such as polymerisation of block or multi-block copolymers to be obtained sequentially. A series of different acrylates, acrylamides and vinyl acetate based homopolymers and block copolymers were obtained via the flow process in high conversion (80%-100%) at temperature between 70°C and 100°C using various chain transfer agents, initiators and solvents with average molecular weights and dispersity (1.1-1.2) comparable to that of batch process.

The applicability of RAFT polymerisation in continuous flow systems represents an effective method to access high quality polymers in large scale without the need for isolation of hazardous, reactive or odorous intermediates. By using multistep processing, the system can readily be modified to include an in-line degasser, multiple reactors, in-line analysis systems such as a UV detector as well as in-line purification.

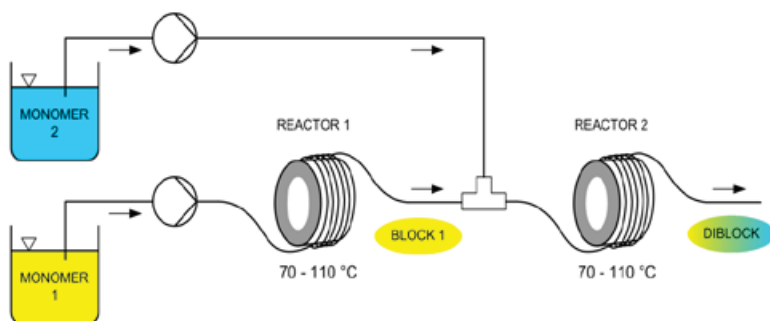


Figure 1. Continuous flow system of RAFT polymerisation in microreactors. Starting materials are pumped directly into the reactors as a continuous stream and polymer solution is collected at the outlet

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Synthesis of pH-Responsive Hyperbranched Polymers and Their Application as ^{19}F MRI Contrast Agents

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Early and accurate diagnosis is of essential importance in fighting against cancer related diseases, which are becoming increasingly problematic for society. During the past few decades, magnetic resonance imaging (MRI) has been proven to be a noninvasive, nondestructive and effective diagnostic modality. At present, ^1H MRI is popular in clinical applications. However, because of the background signals that arise from the abundance of ^1H in human tissue, it is often difficult for ^1H MRI to generate unambiguous images and discriminate tumor tissue from normal tissue.¹ Since its first appearance in 1977,² ^{19}F MRI has been considered as a promising alternative because the ^{19}F contrast agents possess considerable advantages, e.g., zero ^{19}F background in living body, high gyromagnetic ratio, favorable sensitivity and the natural abundance of ^{19}F .^{3,4} Therefore, as a novel diagnosis modality, ^{19}F MRI has great potential in cancer treatment by highly sensitive images.

In recent years, fluorinated polymers have attracted increasing attention as a potentially new generation of ^{19}F MRI contrast agents. Compared to their counterparts, polymers have some intrinsic advantages, such as small sizes (usually less than 100 nm in aqueous solution), myriad designable molecular structures to satisfy various demands, and abundant possibilities for further functionalisation. Recently, statistical copolymers, amphiphilic block copolymers and hyperbranched polymers have been studied by the Whittaker group as ^{19}F MRI contrast agents, and a list of design criteria for ^{19}F polymer contrast agents have also been pointed out, such as high ^{19}F content with a single resonance, highly mobile and flexible ^{19}F segments, small particle size, etc.⁵⁻⁷

In this work, multifunctional hyperbranched polymeric agents have been designed for ^{19}F MRI. First, a series of ^{19}F -containing and pH-responsive hyperbranched polymers were synthesized via atom transfer radical polymerization (ATRP), in which 2,2,2-trifluoroethyl acrylate (TFEA) was used to provide the ^{19}F resonance and 2-(dimethylamino)methyl methacrylate (DMAEMA) was introduced for its pH-responsive property. The structure and composition of hyperbranched polymers were characterized by ^1H NMR, FTIR and GPC, and the particle size and pH-responsive behavior were studied through DLS analysis. Finally, the ^{19}F NMR and MRI properties under different pH conditions were also examined and discussed. The results indicate that these hyperbranched polymers are promising ^{19}F MRI contrast agents and may find application in cancer diagnosis.

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Synthesis of Structurally Regulated Polymers with Five- and Six-Membered Rings via Isomerization Polymerization

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Ethylene polymerization catalyzed by the Pd-diimine complexes yields the polymer with rich branching owing to isomerization of the growing polymer chain named as chain-walking.¹ Recently, we applied the catalysis to cyclopolymerization of functionalized terminal dienes and trienes and of alkylcycloalkenes and obtained the polymers composed of five- and six-membered rings and alkylene spacers in high selectivity.² The polymers of 4-alkyl- cyclopentene prepared by this catalysis contained *trans*-cyclopentane-1,3-diyl groups in every repeating unit and exhibited liquid crystalline properties (eq 1). The obtained polymers exhibit liquid crystalline properties as revealed by DSC and polarizing optical measurement (Fig. 1).

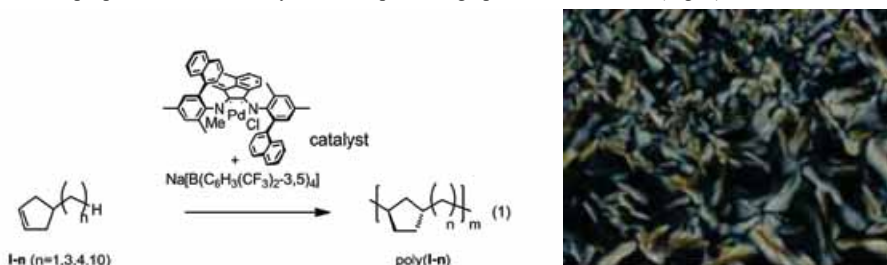
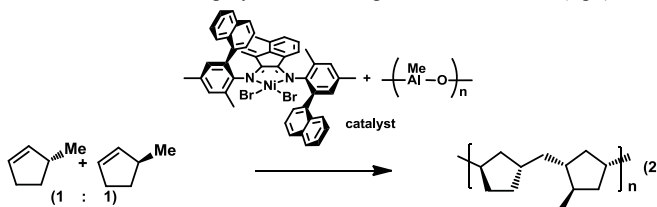


Figure 1 Polarizing Optical Image
of Poly (I-4)_n

The polymerization of 3-alkylcyclopentene was catalyzed by the Ni complex with C2 type diimine ligand. The enantiomerically pure monomer yields the polymer composed of 1,3-cyclopentane repeating units, while use of the racemic monomer results in the polymer containing two structural units (eq 2).



The Pd complex with C2-symmetrical structure also promotes the polymerization to form the products with different structural units depending on the optical purity of the monomer. Insertion of the monomer and further chain-walking fixes stereochemical inversion of the ligand of the catalyst precursor.

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Functional Hyperbranched Polymers for Prostate Cancer Theranostics

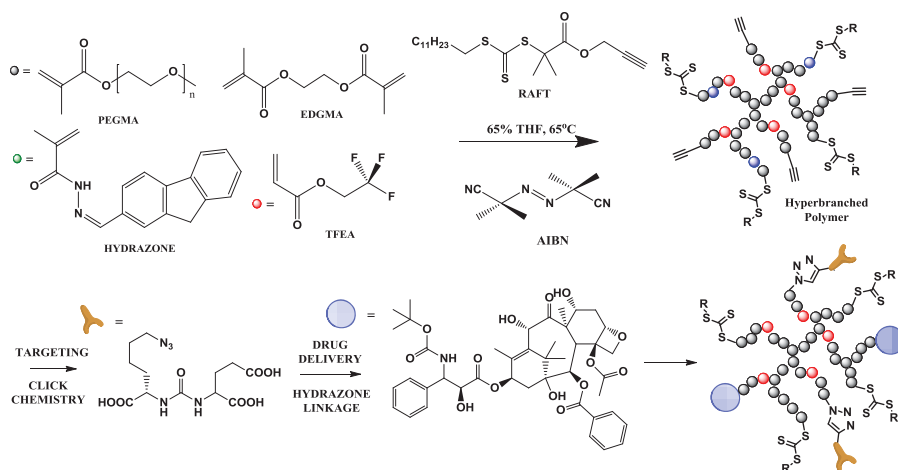
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Prostate cancer is the most common neoplasm in men over 50, causing 3000 deaths each year in Australia.¹ Current imaging technologies are generally not sensitive enough, and thus there is great need for new technologies, in particular, those which allow simultaneous targeting of cancer cells, in conjunction with drug delivery and imaging – this concept is often termed “theranostics”. Previous attempts have largely been unsuccessful *in vivo*, due to issues such as poor drug loading, poor imaging, and inefficient targeting.



Prostate Specific Membrane Antigen (PSMA) is a protein that is highly overexpressed on the surface of prostate cancer cells. Literature has shown that PSMA can be targeted with small molecules, such as the glutamate ureas.² We therefore aim to synthesise a hyperbranched polymer that combines a number of attributes: it is biocompatible; it can be imaged using conventional scanners *in vivo*, it can target PSMA and be internalised within the cancer cells and; it can ultimately deliver a chemotherapeutic drug (e.g. docetaxel) to the tumour site in a controlled manner.

We demonstrate the use of RAFT polymerisation in the synthesis of a hyperbranched polymer comprised of polyethylene glycol methacrylate, with ethylene glycol dimethacrylate as the branching agent, and 20 mol% trifluoroethyl acrylate to allow for ¹⁹F MRI *in vivo*.³ An alkyne-terminated trithiocarbonate was used as the chain transfer agent, providing alkyne endgroups for facile attachment of glutamate urea-based compounds using click chemistry. Additionally, a hydrazide-methacrylate monomer was incorporated into the polymer, allowing attachment of docetaxel through a hydrolytically-degradable hydrazone linkage. The general methodology is outlined in Figure 1.

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Copper(I)-mediated azide-alkyne cycloaddition for cyclic peptide-polymer conjugation

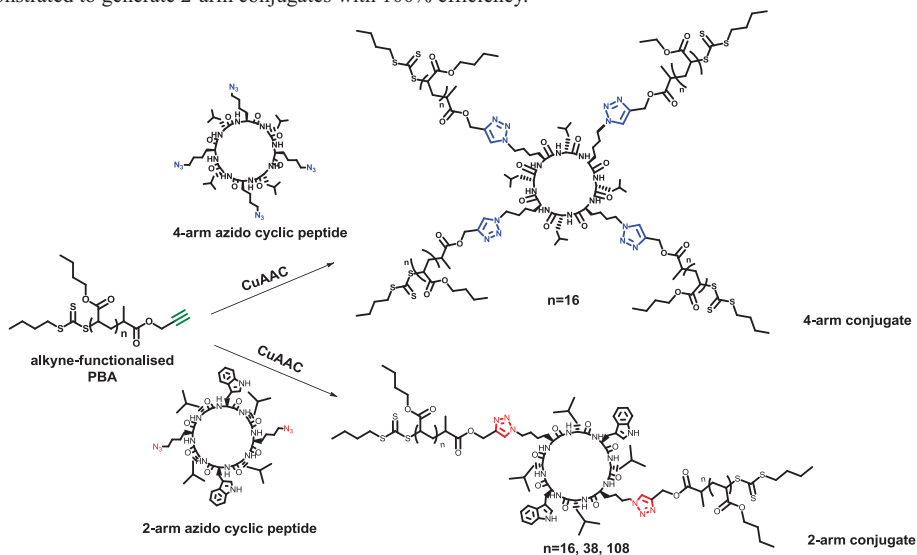
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“Click” chemistry¹ is a versatile approach for the construction of macromolecules with tailored architectures from different molecular subunits. We have employed the copper(I)-mediated azide-alkyne 1,3 dipolar cycloaddition (CuAAC) “click” reaction to prepare cyclic peptide-polymer conjugates.²⁻⁴ This involved grafting a pre-made alkyne-containing polymer, poly(butyl acrylate) (PBA), to an azido cyclic peptide to generate triazole-linked conjugates under microwave irradiation (**Scheme 1**).

The efficiency of “clicking” the polymer (DP 16) to a 4-arm azido cyclic peptide was investigated by varying the number of equivalents of copper (2, 4, 6, 8, and 10 relative to the cyclic peptide), the solvents [dimethylformamide (DMF), trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP)] and the duration of microwave irradiation (15 and 2×15 minutes). A maximum conjugation efficiency of 50% was achieved when the reaction was performed under optimal conditions in co-solvent DMF/TFE (1:1), mediated by 4 equivalents of copper and under microwave irradiation for 15 minutes. The conjugation efficiency of grafting alkyne-functionalised PBA of different chain lengths (DP 16, 38 and 108) to a diazido cyclic peptide was also investigated. The reaction was carried out with either 2 or 4 equivalents of copper, relative to the diazido cyclic peptide) in DMF/TFE (1:1) under microwave irradiation for 15 minutes. Conjugation to the long polymer was found to be more efficient than to the short polymer. Reactions performed with 4 copper equivalents were demonstrated to generate 2-arm conjugates with 100% efficiency.



Scheme 1. CuAAC between alkyne-functionalised PBA and azido cyclic peptides.

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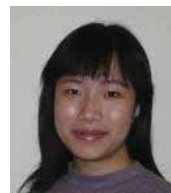
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Research interests: peptide-polymer conjugates, “click” chemistry, polymer architecture



The links between chemiluminescence and thermal analysis in characterization of degradation of polyether and polyester polyurethane foams

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The behavior of both the polyester urethane and polyether urethanes in thermal and photo oxidation is compared and quantitatively estimated by non-isothermal chemiluminescence, DSC and thermogravimetry methods. The foams of the polyurethanes were aged under different conditions and the subsequent changes of the material quality were assessed.

Two different PUR ether- and ester- based foams considered as reference samples have been used. Reference foam has been subjected to artificial ageing: light ageing (day light 1000Wm⁻², 25°C/50% RH) as well as to thermal ageing in dry (90°C, <10%RH) or humid (90°C, 50%RH) conditions. All measurements were performed under nonisothermal conditions in nitrogen and oxygen at the rate of heating 5 °C/min.

The principal differences in polyether urethane and polyester urethanes are following. Polyether urethanes give a considerably stronger light emission (CL) when oxidized than polyester urethanes. This corresponds to a strong exothermic peak of polyether urethanes on DSC record in oxygen while in the case of polyester urethane the degradation process starts by endotherm and exotherm may be observed at considerably higher temperatures. On the other hand, TG pattern of polyester urethane shows that a strong crosslinking of the sample occurs during thermal and light initiated ageing which ends by strong decay of the mass due the sample glowing. The aged samples were also compared from the viewpoint of the amount of carbon residue remaining on the thermogravimetry pan which is the highest for the samples aged by light and in humid atmosphere.

Acknowledgements

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Photo-initiation for the formation of hybrid silica-vinyl network systems

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Silane based UV-curable monomers are widely used as weather resistant coatings due to their low surface energy, low polarity, chemical inertness, and long-term weather resistance. Two new silane monomers have been investigated in this work (**Fig. 1**) - TetMESi which contains four hydrolysable, polymerizable methacrylate units¹ and TriMEMPSi which has three hydrolysable, polymerizable methacrylate units and one non-hydrolysable unit. **Fig. 2** shows that these monomers photopolymerize readily at room temperature. The DMTA of the resultant polymers (**Figs. 3&4**) indicate that these polymers have high temperature resistance. The simultaneous or sequential curing and hydrolysis of these materials have been investigated by FTIR revealing a replacement of the water peak by an alcohol peak, loss of the methacrylate peak and replacement of the Si-O-R peak by the Si-O-Si peak, and the formation of silica in the polymers has been studied by SEM and NMR.

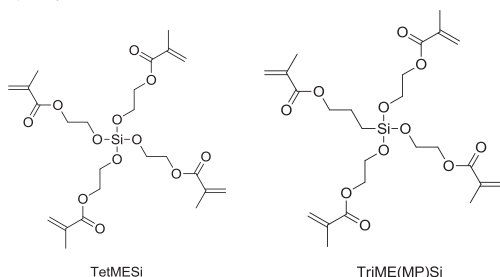


Fig 1. Monomers synthesised for this work

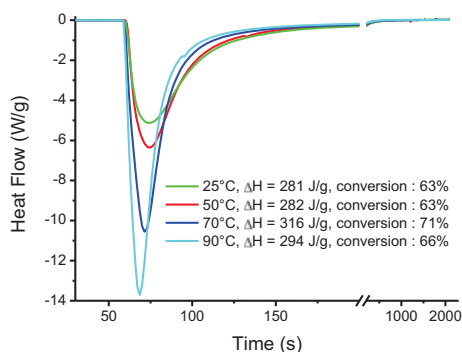


Fig 2. PhotoDSC of the cure of TriMEMPSi

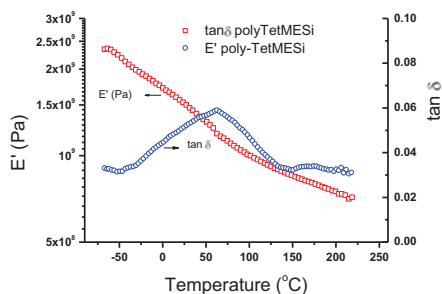


Fig 3. DMTA of the cure of TetMESi

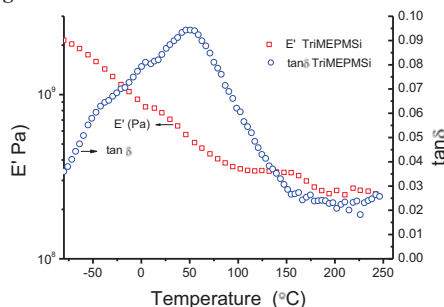


Fig 4. DMTA of poly(TriMEMPSi)

¹ M. Uygun, W. D. Cook, Y. Yagci, C. Moorhoff, F. Chen, C. Vallo, M. Sangermano, *Macromolecules*, **2011**, 44, 1792–1800

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Increasing the Swelling- and Deswelling Kinetics of HEA/PEG Diacrylate Hydrogels by Incorporating Well Defined PMMA-PLMA Block-Copolymers and n-alkanes as Sacrificial Templates

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Due to their chemical and mechanical behavior, polymer hydrogels show promising applications in areas such as actuators or in the field of tissue engineering. However, the extent of application is sometimes limited due to the slow kinetics of the swelling process, which is determined by the diffusion coefficient of the solvent and the dimensions of the gel. By incorporating sacrificial templates into the hydrogel network and subsequent removal thereof, porous hydrogel structures are obtained leading to a distinct increase of the swelling rate of the gels.

This project focuses on the use of n-alkane/DMSO emulsions stabilized by PMMA-PLMA diblock-copolymers to generate porous 2-hydroxyethyl acrylate (HEA) hydrogels by post-polymerization removal of the n-alkane phase and the surfactant. The advantage of using polymer surfactants compared to low molecular weight surfactants is the greater stability of the emulsions as well as the possibility to control the resulting microstructure.

The surfactants are synthesized under ATRP conditions to generate block-copolymers with predictable chain length and narrow molecular weight distributions. By using a system of Ethyl-2-bromo-isobutyrate (EiBBr), N,N,N',N'',N'''-Pentamethyl-diethylenetriamine (PMDETA), Copper(I) and Copper(II) chloride block copolymers of PMMA and PLMA are obtained and characterized by ¹H-NMR, GPC, TGA and DSC techniques. These amphiphilic block-copolymers were tested on their ability to stabilize n-alkane/DMSO emulsions and the best systems were then selected for subsequent gel formation. After removal of the template the structural properties of the hydrogels were evaluated using scanning electron microscopy (SEM) and the swelling and deswelling behavior of the gels are presented.

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Dissolution behaviour of regenerated cellulose fibre

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Cellulose is the most abundant naturally occurring polymer on Earth, providing a readily available resource of sustainable, biodegradable, carbon neutral polymeric material. Cellulose possesses excellent mechanical properties and provides the structural support within plants. Cellulose has been extensively used as reinforcement for polymeric composite materials.¹ However, chemical incompatibility between the cellulose reinforcement and polymer matrix causes inefficient load transfer within the composite, leading to mechanical properties that fall short of expectations.² Recently, the concept of all-cellulose composites (ACCs) has been explored, wherein both the matrix and reinforcement consist of cellulose.³ Chemical incompatibility issues are negated and this has enabled fabrication of composites with impressive mechanical properties. In one possible processing route, the synthesis of an ACC requires the partially dissolution of powdered or fibrous cellulose *via* a suitable solvent. Following solvent removal, the regenerated cellulose then acts as a matrix phase that surrounds the original, undissolved cellulose. Despite a multitude of solvents that can facilitate cellulose dissolution, a group of molten salts called ionic liquids (ILs) have been proven to be the most successful.⁴ ILs provide a non-toxic, recyclable medium for cellulose dissolution. Regeneration of cellulose is performed using an anti-solvent such as water or alcohol, which precipitates the cellulose from the ionic liquid. The regenerated cellulose is subsequently dried and the ACC is formed.

In this study, the cellulose dissolution process is investigated in detail to gain an understanding of the chemical interaction between an IL and a regenerated cellulose fibre (Cordenka). This work provided new insights into how the ionic liquid penetrates through the regenerated fibre and the rate of dissolution as a function of time and temperature. For the first time, the dissolution process was tracked in real time using Confocal microscopy, allowing fluorescent mapping of the dissolution process. Increased optical accuracy using fluorescent probes is also investigated. This facilitates direct observation of changes in the diameter of the fibre as the ionic liquid dissolves the fibre surface. The knowledge gained is used for improving process control in the synthesis and optimization of ACCs *via* a partial dissolution route. The effect of dissolution time and temperature on the final volume fraction of cellulose reinforcement and matrix phases is also reported.

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Thermo- and Thermooxidative Stability of Modified Pectins

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Pectins, as important components of the cell wall of higher plants, have a linear 1, 4-linked α -D-galacturonate backbone, with its galacturonic acid units that are partially methylesterified. They are widely used as gelling and thickening agents in food industry and are known as valuable dietary fiber components^{1, 2}. Pectins can be structurally modified in order to change their physicochemical properties so that their functional properties can be improved as well. In this way, they found an application in pharmacy and medicine³.

Besides the types of substitution, the degree of esterification (DE) affects properties of the derivatives as well. Different types of chemically modified derivatives (pectinates) from citrus pectin were prepared by the de-esterification of commercial pectin followed by controlled esterification (alkylation, acetylation, amidation and alkylamidation). For determination of DE of pectinates Fourier transform infrared (FTIR), ¹H- and ¹³C-NMR spectroscopy techniques were used.

For the new applications of modified pectin it is of importance to know – among other factors – the impact of changes in the structure on their stability. Their thermo- and thermooxidative characteristics were determined by chemiluminescence (CL) measurements, differential scanning calorimetry and thermogravimetry.

Fig.1a and **1b** are the examples of CL emission accompanying thermooxidative- and thermal degradation of deesterified pectin (potassium pectate - PK) and methyl esters of pectin with different DE

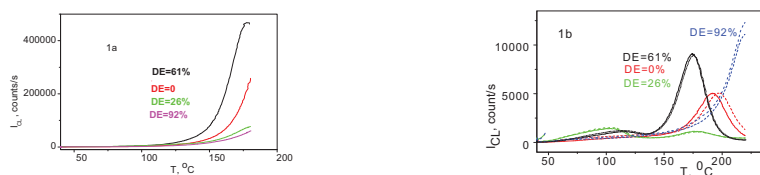


Figure.1a and 1b. Temperature dependences of chemiluminescence intensity for pectin esters in oxygen (1a) and in nitrogen (1b) (Spectroluminometer LUMIPOL-3, product of Polymer Institute Bratislava, rate of heating 2.5°C/min).

As one can see from these figures, low and very high degrees of substitution enhance the thermo-oxidative stability of pectin methyl esters; DE around 50 % has a negative effect on this property. Thermal stability decreases proportionally to the increasing value of DE, but 92% again leads to more stable PE. Thermal analysis TG and DSC of esters proved this trend

Conclusions

- Two series of citrus pectin methyl and benzyl esters with the degree of esterification DE (0 - 92 %) were prepared and characterized by chemiluminescence and by thermal analysis.
- Thermal and thermo-oxidative stability of pectin esters strongly depend on degree of substitution; this relation is not straightforward; in most cases, the optimal values of DE are below 30% and higher than 70-80 %

¹ B.R. Thakur, R. K. Singh, A.K. Handa, *Crit. Rev. Food Sci. Nutr.* **1997**, 37, 47

² W.G.T. Willats, J.P. Knox, J.D. Mikkelsen, *Trends Food Sci. Techn.* **2006**, 7, 97

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Cholesterol Conjugated Polymers as siRNA Delivery Vehicles: Correlation between Physicochemical and Biological Properties

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The use of nano-sized synthetic polymers, comprised of therapeutic entities like drugs or peptides, into clinical development has established *polymer therapeutics* as a credible option for nanomedicine.^{1,2} These nanoscale delivery vehicles offer significant advantages as they enhance therapeutic efficiency by prolonging drug half-life, improving solubility of hydrophobic drugs, reducing potential immunogenicity, and/or releasing drugs in a sustained or stimuli-triggered manner.³

Short interfering RNAs (siRNA) offer an extremely selective, endogenous method of gene silencing that has great potential for application as a therapeutic for numerous diseases including cancer and AIDS.⁴ Whilst the siRNA silencing mechanism is very efficient and specific, its use as a therapeutic is somewhat hindered by several factors including its low *in vivo* stability and poor cell uptake. The enhancement of cell-membrane transport of therapeutics can be achieved by using lipid structures, such as cholesterol, that can interact with cell membrane.⁵ Cholesterol conjugation to siRNA has been described by others to enhance the cytoplasmic delivery of siRNA.⁶ The incorporation of cholesterol units to pH-sensitive synthetic polymers, allows the cell-membrane activity of cholesterol to be tuned in a pH-dependent manner.

The reversible addition fragmentation chain transfer (RAFT) technique was used to generate well-defined statistical copolymers of cholesteryl methacrylate and methacrylic acid as potential carriers for siRNA. The copolymerization kinetic studies revealed a linear pseudo-first order kinetic plot and narrow poly-dispersity profile, indicating a successful RAFT-controlled polymerization. Aqueous solution properties were investigated by turbidity and light scattering revealing the physicochemical behavior underlying pH-dependent phase transition and shift in hydrodynamic diameter for poly(methacrylic acid-co-cholesteryl methacrylate) (P(MAA-co-CMA)) respectively. Both negatively charged siRNA and P(MAA-co-CMA) were conjugated thru the addition of positively charged oligolysine molecules that help trigger an instantaneous electrostatic interaction, consequently forming polymer shielded therapeutic delivery vehicles. The complexation ratios between siRNA, oligolysine, and P(MAA-co-CMA) were investigated by a gel retardation assay. Using *in vitro* cell viability assays, it was shown that these copolymers display no toxicity up to 30 μ M over a period of 72 hours.

The preliminary results obtained thus far highlight the potential of these well-defined P(MMA-co-CMA) copolymers as siRNA delivery vehicles.

¹ M.E. Davis, Z. Chen, D.M. Shin, *Nature Reviews Drug Discovery*, **2008**, 7, 771

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⁵ V. Incani, A. Lavasanifar, H. Uludag, *Soft Matter*, **2010**, 6, 2124-2138

⁶ C. Wolftrum, S. Shi, K.N. Jayaprakash, M. Jayaraman, G. Wang, R.K. Pandey et al. *Nature Biotechnology*, **2007**, 25, 1149-1157

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Submitted Abstracts:

- ✓ **Sevimli, S.**; Gunasekaran, K.; Bulmus, V. (accepted, 2009) 'Biohybrid Polymers for Intracellular Delivery of siRNA', 11th Pacific Polymer Conference, Cairns Australia, 6-10 December 2009.
- ✓ **Sevimli, S.**; Gunasekaran, K.; Bulmus, V. (accepted, 2009) 'Polymeric Hybrid Nanostructures for Intracellular Delivery of siRNA', International Conference on Advanced Nanomaterials and Nanotechnology (ICANN-2009), Guwahati India, 9-11 December 2009.

Poster Presentations:

- ✓ **Sevimli, S.**; Inci, F.; Ismuil Z.A.; Bulmus, V. (accepted, 2010) 'Designer Transporters: A Biosynthetic Hybrid Polymer for Intracellular Drug Delivery', Sydney 2010 International Nanomedicine Conference, Sydney Australia, 30 June - 2 July 2010.
- ✓ **Sevimli, S.**; Inci, F.; Bulmus, V. (accepted, 2011) 'RAFT-Synthesis of Cholesterol Conjugated Polymers as Potential Therapeutic Carriers', Fall 2011 ACS National Meeting & Exposition, Denver, Colorado, USA, 28 August – 1 September 2011.

Oral Presentations:

- ✓ **Sevimli, S.**; Sagnella, S.; Bulmus, V.; Kavallaris, M.; Davis, T.P., (accepted, 2011) 'Biomimetic Cholesterol Conjugated Polymers for Intracellular Delivery of siRNA', Sydney 2011 International Nanomedicine Conference, Sydney Australia, 14 - 16 July 2011.

Publications:

- ✓ Wong, L.J.; **Sevimli, S.**; Zareie, H.M.; Davis, T.P.; Bulmus, V., 'PEGylated Functional Nanoparticles from a Reactive Homopolymer Scaffold Modified by Thiol Addition Chemistry', *Macromolecules*, **2010**, 43 (12), 5365-5375.

Research interests: nanomedicine; drug delivery; siRNA; polymer science

Synthesis and characterisation of Polysulfone-POSS additives for water filtration membranes

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Polymers such as polysulfone and polyvinylidene fluoride are often used to form membranes for use in applications such as water pretreatment, reverse-osmosis and porous filtration, owing to their long term chemical and oxidative stability. However, a significant problem plaguing such polymeric membranes is compaction, which significantly reduces membrane performance and life time, as increased pressures (and hence energy requirements) are needed in order to compensate for reduced flow rate through the membrane.

Polyhedral Oligomeric Silsequioxanes (POSS) are cube-shaped cage structures comprised of silicon and oxygen, where each silicon atom possesses an additional organic group (R). All of these groups may be identical (octa-functionalised) or one group may be different to the others (mono-functionalised) (Fig. 1);

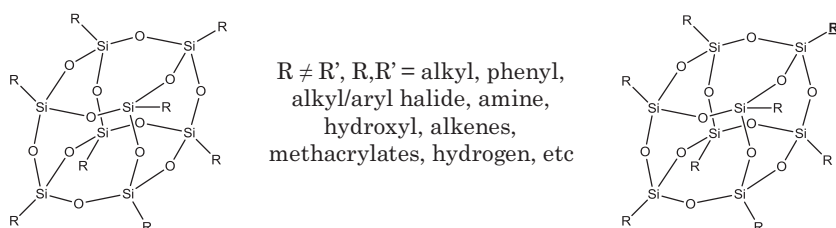


Figure 1. Diagram of symmetrical octa-functionalised POSS (left) and the asymmetrical mono-functionalised POSS (right)

The presence of these organic groups allows POSS molecules to be used as a cross-linking agents, dendrimer cores, or grafting agents to covalently attach to polymers. The resulting molecules may be used as additives for polymers, often resulting in improved mechanical properties as well as thermal and chemical stability.

Here, we present the results of the first stage in creating a polymer-POSS additive to improve the mechanical properties of polymeric membranes. A POSS-endcapped polysulfone as well as an octafunctionalised POSS-Psf star have been synthesised, and these molecules were structurally characterised by ¹H, ¹³C, ²⁹Si NMR and ATR-FTIR, with the thermal stability and transitions being characterised by thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC). The properties of these two POSS molecules were compared in order to elucidate the effect these different POSS-types may have on the properties of the polymer.

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High Resolution Electrospray Ionization Mass Spectrometry (ESI-MS) Investigation of Cu(0)–Mediated Radical Polymerization

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One of the most important features of any Living / Controlled Free Radical Polymerization is the preservation of chain-end functionality. One of the techniques that has been widely reported to give excellent chain end fidelity is living free radical polymerization in the presence of copper (0); single electron transfer-living radical polymerization (SET-LRP).¹ It is an efficient technique which can be used to polymerize acrylates, vinyl chloride, and other monomers yielding bromide terminated polymer in high yield. While other living polymerization technique are widely used (RAFT, ATRP, NMP etc) they have difficulty in preserving end group fidelity at high conversion (above 70%) due to termination side reactions, the Cu(0) approach has shown to have good end group fidelity in the high conversion regime.

In this study we have investigated the evolution of the chain-end fidelity at very high monomer conversion both in the presence and in the absence of initially added Cu(II) bromide (CuBr₂). We have employed a high resolution LTQ-Orbitrap mass spectrometer to be able to confidently identify both “living” and “dead” polymers. Based on the monitoring of the polymerization reaction by ESI-MS, there were two different regions that can be assigned, in consideration of the termination reactions that occur, during polymerization; up to 100% conversion and post-polymerization. During polymerization, the mode of termination was mainly via disproportionation while in the post-polymerization region, after 100% conversion had been reached, dead polymers were generated by chain transfer reactions (presumably to ligand). In conclusion, addition of Cu(II) to the polymerization reduced significantly the termination reactions, especially the chain transfer reaction to ligand, giving a simple approach to the preservation of end group fidelity.² This method gives a simple technique for achieving further macromolecular design especially for preparation of complex block copolymers.

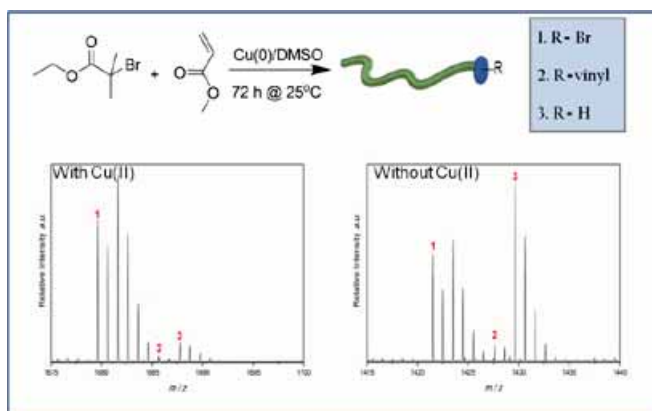


Figure 1. The utilization of High Resolution Electrospray Ionization Mass Spectrometry to investigate the end-group fidelity of Cu(0)-mediated radical polymerization.

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2. Nystrom, F., Soeriyadi, A.H., Boyer, C., Zetterlund, P.B., Whittaker, M.R., *J. Polym. Sci. Part A: Polym. Chem.* **2011**, accepted

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Mathematical modeling of linear and non-linear RAFT polymerization using a multifunctional polymer molecule approach

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A new mathematical model for linear and non-linear reversible addition-fragmentation chain transfer (RAFT) polymerizations, based on a multidimensional polymer molecule approach, has been developed. A single type of multifunctional macromolecule was considered and therefore, a single mass balance equation for polymer species was required. The reactions taken into account were chemical initiation, dimer formation, thermal initiation, monomer propagation, reversible chain transfer to RAFT agent, reinitiation by the RAFT agent leaving group, addition-fragmentation chain equilibration, propagation through pendant double bonds (crosslinking and cyclization in the non-linear polymerization), bimolecular termination and cross-termination. The method of moments was used for calculation of average properties of the resultant multidimensional distribution. A generalized stoichiometric kernel was used to model the breakage of chains during the reversible fragmentation step, following the work by McCoy and Wang.¹ For non-linear polymerization, molecular weight development during the pre-gelation period was calculated by using the method of moments, while Flory-Stockmayer's theory was used for the post-gelation period. Polymerization rate, molecular weight development, gelation point, evolution of sol and gel weight fractions, crosslink density, and copolymer composition, as well as concentrations of all the species participating in the reaction mechanism can be calculated with the model. Under the assumption of midpoint chain scission for the fragmentation step, low polydispersities are predicted. It was found that the RAFT process has considerable effect on the kinetics of copolymerization with crosslinking. Polymerization rate is reduced and the gelation point is delayed when the initial concentration of the RAFT agent is increased, as shown in Fig.1.

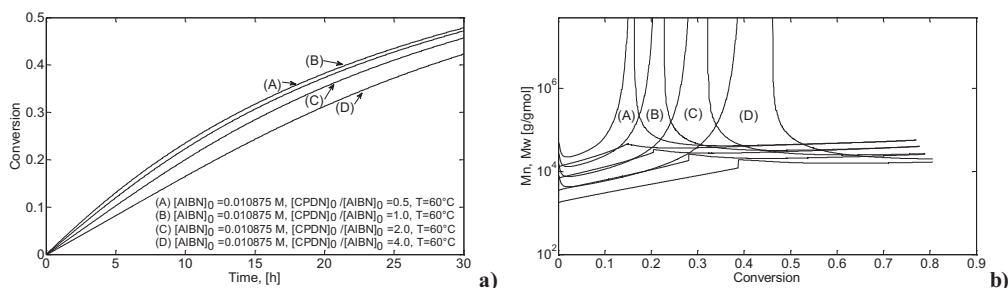


Figure 1. Predicted profiles of a) conversion versus time, and b) average molecular weight versus conversion for the RAFT copolymerization of styrene/divinylbenzene in the presence of 2-cyanoprop-2-yl 1-dithionaphthalate (CPDN) as RAFT agent, and azobisisobutyronitrile (AIBN) as chemical initiator.

¹ B. J. McCoy, M. Wang, *Chem. Eng.* **1994**, 49, 3773–3785

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Insights into the power law relationships that describe mass deposition rates during electrospinning

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Electrospinning has been established as a valuable method of producing micro- and nano-scale continuous fibres¹. Electrospinning uses high strength electric fields (> 1 kV/cm) to form jets of fluid polymer and then draw them into nanometre diameter fibres². The application of high voltage causes charging of the droplet formed at the tip of the spinneret. The accumulated charge results in the droplet deforming into a Taylor cone from which mass is ejected in the form of a fluid jet³.

Typically, the fibre or mass deposition (or production) rate or flow (or feed) rate has been treated as a parameter that can be varied independently^{4,5}. However, a constant internal pressure within the Taylor cone must be maintained to allow stable electrospinning from the Taylor cone that in turn establishes a constant flow rate⁶. It is possible, when studying the process in a quasi-stable state, to treat the mass deposition rate as a response variable related to processing conditions (such as voltage, electrode distance, humidity, polymer concentration, conductivity...)⁷. Treating mass deposition rate as a response variable, it has been shown that both the mass deposition rate and electric current observed at the collector have a power law relationship to the applied voltage⁷⁻⁹. Existing reports have only varied the applied voltage to study the effect of different magnitude electric fields on the electric current at the collector electrode and the mass deposition rate. Hence it is impossible to distinguish between an effect due to applied voltage and an effect due to applied electric field.

This work aims to relate variation in mass deposition rate and electric current at the high voltage electrode to corresponding variation in distance between the spinneret and the collector plate in addition to applied voltage. In addition this work attempts to determine if there is a relationship between mass deposition rate and electric current flow. This relationship could be used to determine valid charge densities for use in theoretical modelling of the process. Mass deposition rate is measured as the amount of dry material deposited on the collector plate over a given time. When stable electrospinning is occurring this mass is entirely in the form of a nano-fibre. If the process is unstable, then spots of liquid polymer or sprayed particulates may also be deposited. Electric current was measured using a current feedback from the high voltage supply.

The deposition of fibre was observed to occur at a constant rate for deposition times of up to 30 min. Both the mass deposition rate and electric current were found to vary with the applied voltage according to a power law. The relationship between the electric current and mass deposition rate was found to be linear for all combinations of applied voltage and electrode separation. This means that for all combinations of applied voltage and electrode separation, hence for all applied electric field conditions, there is a constant charge density of 96.1 C/kg for PVOH.

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Synthesis of Polydimethylsiloxane-Containing Block Copolymers via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization and their Self Assembly in Water

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Synthesis of amphiphilic polydimethylsiloxane(PDMS)-containing copolymers have received much attention^{1,2} due to the unique properties of PDMS, such as its very low-glass transition temperature, low surface tension and good gas permeability, nontoxic and biocompatibility. In addition, self-assemblies of polymeric amphiphiles into micelles and vesicles have allowed access to a wide range of functionalized nanoscale structures that are of great use in biomedical and material science.³

In this work, a series of PDMS-containing diblock copolymers were synthesized by reversible addition-fragmentation chain transfer polymerization (RAFT), a powerful technique for the synthesis of polymeric architectures with narrow molecular weight distribution. The RAFT polymerization of dimethylamino ethyl acrylate was mediated by a PDMS macro-RAFT agent to yield block copolymers of controlled molecular weight distribution. The aqueous self-assembly of these block copolymers and the resulting morphologies were studied and characterized via transmission electron microscopy (TEM) and dynamic light scattering (DLS).

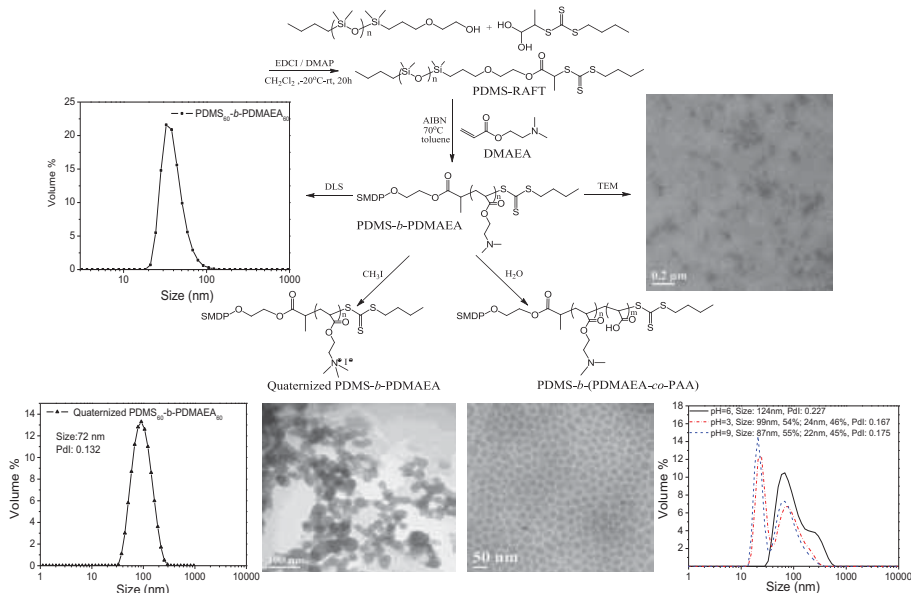


Figure 1: Synthesis and self assembly of PDMS-containing diblock polymers

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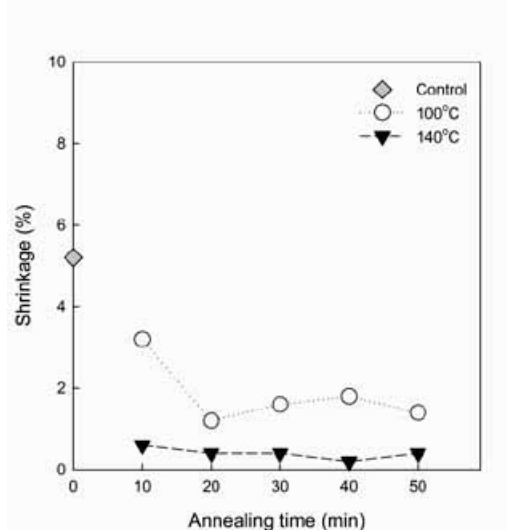
Effect of Annealing on Physical Properties of Polypropylene Slit Film Yarn

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Most fibers materials are produced by extruding polymer melts or solutions through spinneret holes. However, fibers can also be made from slitting polymer film into film yarns and tape yarns¹. Annealing effects of polypropylene slit film yarns on physical properties and structural changes were investigated. Two annealing temperature of 100 and 140°C and annealing time of 10 to 50 minutes were selected as annealing conditions. Tenacity increased and thermal shrinkage decreased with increasing annealing time and temperature. Structural changes due to annealing led to development of oriented crystal structure and the amorphous orientation revealed by infrared spectroscopy was not affected by the annealing. Crystal thickness obtained wide angle x-ray scattering (WAXS) peak increased with increasing annealing time. Annealing affected crystal structure such as crystal size and orientation, however, amorphous region had little changed by the heat treatment. To obtain low thermal shrinkage of less than 1% (Fig.1), the annealing at least for 10 minutes at 140 °C was necessary.

Figure 1. Thermal shrinkage versus annealing time for different annealing temperatures



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A history of electrospinning 1600-1995

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The science behind the technology of electrospinning has a history that stretches back to the earliest days of scientific investigation. Current interest in the process is due to the ease with which nano-scale fibres can be produced in the laboratory. The history of the prior art in the process should be of great interest to the research and development community as it provides a rich vein of ingenious mechanisms to solve the problems of the manufacturer, and access to the theoretical considerations of several generations of scientists.

The first record of the electrostatic attraction of a liquid observed in the time of Queen Elizabeth 1 of England by William Gilbert¹. This is the first record of the deformation of a drop of liquid into what would become known as the Taylor cone.

John Francis Cooley filed the first electrospinning patent² in which he proposed three types of indirectly charged spinning heads – a conventional head, a coaxial head, an air assisted model, and a spinneret featuring a rotating emitter. He also proposed the recovery of solvent and the use of a dielectric liquid instead of a gas as the medium.

Dipl. Ing Ludwig Rudolph Anton Formhals was born in Mainz on 24 Aug 1877. He worked for the Verein fur Chemische Industrie AG.. His contribution to electrospinning is marked by at least 18 patents.

In 1938 N.D Rozenblum and I.V Petryanov-Sokolov at the Aerosol Laboratory of the L. Ya Karpov Institute in the USSR, generated electrospun fibres, which they developed into filter materials that became known as “Petryanov filters”. By 1939, this work had led to the establishment of a factory in Tver’ for the manufacture of electrospun smoke filter elements for gas masks. The material, dubbed BF (Battlefield Filter) was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol. By the 1960s output of spun filtration material was claimed as 20 million m² per annum³

Between 1964 and 1969 Sir Geoffrey Ingram Taylor produced the beginnings of a theoretical underpinning of electrospinning. Taylor’s work contributed to electrospinning by mathematically modelling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone.

In the early 1990s several research groups (notably that of Reneker who popularised the name electrospinning for the process) demonstrated that many organic polymers could be electrospun into nanofibres. Since then, the number of publications about electrospinning has been increasing exponentially every year.

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Characterization of Gellan Gum by Capillary Electrophoresis

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There is a need for the development of new methods to characterize natural polymers that are not experimentally tedious or limited to some branched polymers.¹ Free solution Capillary Electrophoresis, FSCE, is a method of separating ionic species in regards to their composition. There is very little application of FSCE to polysaccharides, although the method has been proven successful in separating chitosan in regards to its composition and short oligoacrylates according to their molar mass and their tacticity.^{2,3} FSCE is a promising method of characterizing gellan gum in terms of its composition. In particular the separation is in terms of gellan gum's average degree of acylation and distribution of degrees of acylation independently of molecular weight.

Gellan gum is of great interest in current research due to its many unique and its wide variety of potential applications as a multifunctional gelling, stabilizing and suspending agent with uses in food, pharmaceutical, medical and chemical industries.^{1, 4-6} Gellan gum is a natural exopolysaccharide produced by the bacterium *Spingomonas paucimobilis* which is widely distributed throughout nature. With gellan gum's increasingly widespread use its importance has become apparent with its unique properties showing advantages over other naturally occurring polysaccharides. These advantageous properties are its excellent thermal and acid stability, adjustable gel elasticity and rigidity, high transparency and good flavor release.⁵

Currently there is no definitive method available to produce identical gellan gum samples with the same degree of acyl substituents and equal distribution of molecular weights.⁵ It is therefore important to determine the degree of acylation and the distribution of the degrees of acylation within a gellan gum sample.

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Enhanced Bioconjugation Methods for Polymer Particles Used in Highly Multiplexed Bio-Assays

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The traditional use of fluorescent chromophores in multiplexed biological assays (such as particle-based assays) is severely limited by spectral overlap, which reduces the number of unique species that can be resolved in one experiment. The development of mass cytometry,¹ which couples individual cytometric delivery with high resolution mass spectrometric (ICP-MS) detection, has allowed for a significantly increased multiplexed capability by using heavy metal (lanthanide, Ln) tags. Ln-encoded polystyrene particles synthesized by dispersion polymerization have shown to be excellent candidates for mass cytometry based immunoassays,^{2,3} however, they have lacked the ability to successfully conjugate biomolecules to the particle surface.

In this work, we present three approaches to post-functionalize Ln-encoded polystyrene particles with the aim of enhancing the covalent attachment of proteins to the particle surface. Two approaches involved increasing the surface carboxylic acid (-COOH) content of the particles, namely i) using partially hydrolyzed PNVP as a dispersion polymerization stabilizer and ii) performing seeded emulsion polymerization with poly(methacrylic acid). These approaches however gave little to no improvement in the extent of bioconjugation. In our third approach, we used seeded emulsion polymerization to grow a functional polymer shell of poly(glycidyl methacrylate) (PGMA) onto the surface (Fig. 1), which proved highly successful.⁴ The epoxide-rich PGMA shell permitted extensive surface bioconjugation of NeutrAvidin ($\sim 7 \times 10^5$ binding events per particle, with a very low amount of nonspecific binding). Traditional coupling agents such as EDC were not needed, such was the reactivity of the particle surface. These particles were stable, and the addition of a polymeric shell did not affect the narrow lanthanide ion distribution within the particle interior as analyzed by mass cytometry. These particles represent the most promising candidates for the development of a highly multiplexed bioassay based on lanthanide-labeled particles to date.

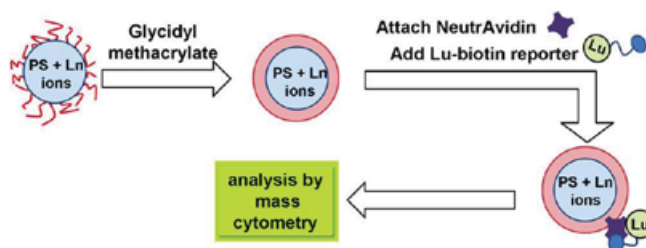


Figure 1. Formation of reactive poly(glycidyl methacrylate) shell by seeded emulsion polymerization.

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A generalised small scale synthesis of polymer nanoparticles by RAFT in mini-emulsion polymerization for applications in separation science.

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The use of polymer nanoparticles has been demonstrated in many applications in separation science, with the ability to accurately control both the particle size distribution and also the surface functionality critical for optimising both separation efficiency and separation selectivity respectively. We have previously shown in our group that polymer nanoparticles can be used both as effective pseudo-stationary phases for electrokinetic chromatography [1,2] and also in the synthesis of high performance latex agglomerated monolithic stationary phases [3,4]. Typically these polymeric nanoparticles have been synthesised using traditional free radical emulsion polymerisation methods, often leading to a relatively broad distribution of particle size. In addition the reaction conditions of traditional emulsion methodologies often dictate the addition of stabilisers that need to be removed post-synthesis so as not to interfere with the final use of the nanoparticles in chromatographic applications. Our previous work in this area has demonstrated that the use of a RAFT in emulsion approach enabled the synthesis of nanoparticles that perform well in applications such as electrokinetic chromatography without these drawbacks. In this current work we investigate the development of a stepwise method that will allow the formation of a suite of complex nanoparticles on a small scale for use in applications such as separation science. This was done by modification of standard previously reported methods of synthesis [5,6], to allow synthesis on a smaller scale in a stepwise procedure. By doing this it allows the use of a variety of different monomers to suit the need of the desired application. Examples of a range of functionalities will be shown including ion-exchange (sulfonic acid, quaternary amine), boronate affinity with varying hydrophobicity. Application of these nanoparticles in separation science will also be shown.

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6. B. T. T. Pham, H. Zondanos, C. H. Such, G. G. Warr, B. S. Hawkett, *Macromolecules* (2010) 7950–7957.

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Research interests: Well controlled synthesis of polymers for applications in separation science and organic catalysis.



Quokka: an advanced small angle neutron scattering instrument suitable for polymer science

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Small angle neutron scattering (SANS) is an experimental technique suitable for elucidating average structural aspects of polymer organisation in bulk samples¹. The SANS instrument at ANSTO's OPAL reactor, Quokka (Figure 1)^{2,3}, is a conventional pin-hole reactor based instrument. After interacting with a sample neutrons are collected on a two-dimensional as a function of scattering vector, q (where $q = 4\pi \sin(\theta)/\lambda$, 2θ is the angle between the incident beam and the scattered intensity, and λ is the wavelength of the neutrons). Neutrons enter the instrument from a neutron guide via a velocity selector which can provide a variable average wavelength, λ , and spread of wavelengths, $\Delta\lambda$. The velocity selector may provide a balance of neutron flux on the sample and q resolution, optimisation of the former being suitable for weakly scattering samples, and the latter for investigations of periodicity in highly ordered systems. The available range of scattering vectors is $6 \times 10^{-4} \text{ \AA}^{-1} < q < 0.7 \text{ \AA}^{-1}$ which is achieved with a range of sample to detector distances in combination with suitable collimation, variable wavelength and in the case of the lowest scattering vector focussing optics. Careful calibration of the instrument allows for expression of scattered intensity on an absolute scale. In this way the technique is quantitative, allowing, with a suitable model, quantification of the volume fraction of scattering structures. For isotropic scatterers, where the scattering is radially averaged around the beam-stop, the area detector allows an improvement of signal to noise. The improved signal to noise enhances the investigation of kinetic phenomena over a range of time-scales. Neutron flux on the sample may also be optimised with relaxation of $\Delta\lambda$ to further extend the time-scales which may be investigated. The area detector also allows the analysis of molecular and nanoscale orientation in samples under an external stimulus such as shear, tensile stress or electric and magnetic fields. Polymeric samples may include solutions, complex fluids and solid phases at equilibrium in the presence of an external perturbation, the possibilities being limited by the size of the sample required for SANS measurements, access to the sample by the incident beam, the free measurement of the scattered beam and the ability to analyse data meaningfully. Access to the instrument by the polymer scientist is by a peer reviewed process⁴, with two proposal rounds a year. A local contact may provide assistance for preparation of proposals.

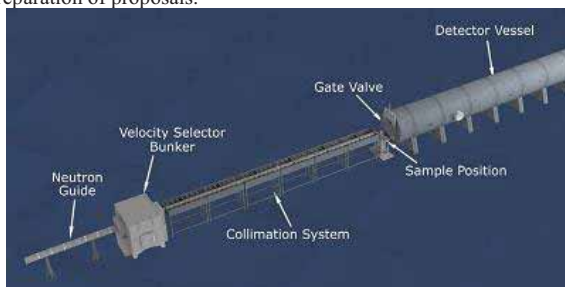


Figure 1. A schematic view of the Quokka instrument.

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4. http://www.ansto.gov.au/research/bragg_institute/users/call_for_proposals.

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Employing A Liquid, Model Polyolefin For The Evaluation Of Profluorescent Nitroxides As Probes For Polymer Degradation

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Profluorescent Nitroxides (PFNs) have been shown to be sensitive probes for the early detection and analysis of thermo-oxidative degradation in polyolefins.¹ The radical scavenging action of the nitroxide moiety in PFNs leads to the formation of highly fluorescent species that can be detected at low concentration in a degrading polymer matrix. Previously, we have employed polypropylene (PP) as a standard polymer for exploring the application of PFNs in studying polymer degradation due to PP's well understood thermo-oxidative degradation processes.²

To be effective polymer degradation sensors, PFN probes should display an efficient nitroxide-dependent fluorescence switch-off/switch-on capability, as well as possess sufficient chemical stability to survive within a degrading polymer matrix. Comparing the library of existing and novel PFNs is crucial in determining which PFNs make effective degradation probes. Issues that affect these comparisons include: the determination of probe concentration within solid polymer samples, the variation in achievable doping concentration of PFNs, as well as the differences in crystallinity and light scattering in PP from sample to sample. Currently, semi-quantitative methods are employed to determine PFN concentration but total quantitation cannot be confirmed in the solid state without lengthy sample preparation.

A liquid model system can circumvent the problems arising from a solid polymer matrix. Using a polyolefin liquid that follows a similar degradation profile to polyolefins, such as PP, allows the determination of PFN concentrations to be readily achieved using spectroscopic techniques. It also reduces the impact of sampling issues that arise at later stages of degradation where cracking and crazing can interfere with spectroscopic analysis. Using a liquid model also decreases the sample preparation required by techniques used for analysing the degradation process. Such techniques include NMR, GPC, GC-MS and LC-MS.³

Paraffin oil is a simple, saturated hydrocarbon liquid that is inexpensive and readily available. In this study, we chose this liquid as a model polyolefin and investigated whether solutions containing PFNs show similar degradation sensing and stabilisation to that previously observed for PP under the same oxidative conditions. This study will present results from paraffin oil liquid model experiments that may be used to evaluate existing and novel PFNs under uniform conditions and concentrations.

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Employment of mixed host for performance enhancement in blue phosphorescent organic light emitting devices

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Phosphorescent organic light emitting devices (PHOLEDs) are desirable as it has potential to achieve high internal quantum efficiency up to 100 %. Before they meet the realistic requirements for commercial applications, great efforts are still needed on improving the efficiency of blue PHOLEDs. In order to improve the performance, the choice of host material is important in which one of the prerequisites is the triple energies of host materials must be higher than those of blue phosphorescent dopants. Unfortunately, there are only few suitable host materials that have both high triplet energies and good charge-carrier mobilities.

As electron- or hole-transporting triplet host materials, specifically 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) or 4,4',4''-tris(*N*-carbazolyl)triphenylamine (TCTA) is commonly used in PHOLEDs, they were doped into emissive layer to form mixed host structures. It is found that the performance of blue PHOLEDs is directly correlated to the composition of mixed host. In particular, a superior device performance with high current and power efficiencies of 47.4 cd/A and 37.3 lm/W, respectively, and more importantly, a theoretical maximum of external quantum efficiency of 21.9 %, can be achieved for an optimized TCTA-doped device. However, as TAZ concentration increases from 0 to 100 %, both current and external quantum efficiencies of the devices decrease from 8.1 cd/A and 3.9 % to 2.1 and 1.0 %, respectively. The difference in triplet energies and the highest occupied molecular orbital (HOMO) levels of the host materials may be the reason for the performance discrepancies, in which a lower triplet energy and a larger HOMO level of TAZ would detrimentally decrease the device efficiencies. As confirmed by the transient phosphorescence decays studies, the lifetime of FIrpic is strongly dependent on the use of triplet host materials and a shorter lifetime of triplet excitons in TAZ-doped films is the origin of low electroluminescence efficiency of all TAZ-doped devices.

Study on Fabrication of Functionalized Polymer with Patterned Nano-scale Silver Metal using Radiation Reduction Technique

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Recently, the demands for the nano / micro-fabricated metals have been growing in industrial fields, such as metallic catalysts, micro machines, and so on. In our previous work, nano / micro silver metals (Ag) had been made by direct solid state reduction technique on functionalized polymer. Ag particles dispersed on the polymer matrix have been successfully synthesized using functionalized polymers with Ag⁺ ions by plasma exposure and ion beam irradiation^{1,2}. In this study, it is attempted to fabricate the controlled nano / micro-scale patterned Ag metals using Ar plasma exposure. The polymeric materials with controlled nano- / micro-scale patterned functionalizing were fabricated by ion beam induced grafting technique. The localized functionalizing polymer which has Ag⁺ ions on patterned area was exposed to plasma for metal reduction.

Poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films were irradiated with C⁶⁺ ion beam (Medium energy experimental port of Heavy Ion Medical Accelerator in Chiba [HIMAC], installed at NIRS, 6 MeV/u) under vacuum at room temperature. The FEP was covered with nickel mesh (size: 72 μm square) before ion beam irradiation. The trapped free radicals were induced in the uncovered area of the films by the irradiation (Fluence: $1.0\text{E}+10$ ions cm^{-2}). That is, the radicals were produced as the transfer shape of the mesh. The irradiated samples were immersed in styrene monomer at 80 $^{\circ}\text{C}$ for 2 h for the grafting reaction using pre-irradiation method using peroxy radicals. Since the grafting was carried out with induced the radicals in patterned area, polystyrene grafted FEP films with micro-pattern shape (PS-g-FEP) could be fabricated. Then the PS-g-FEP was functionalized by chlorosulfonic acid. The sulfonated PS-g-FEP (s-FEP) was immersed in the AgNO₃ solution for 24 h under the ambient conditions, and then Ag⁺ ions were put into only the area with the mesh micro-pattern. The s-FEP with patterned Ag⁺ ions (Ag-formed s-FEP) was exposed to Ar plasma (RIE-10NOU, SAMCO, installed at ISIR, Osaka University) to carry out the direct reduction reaction. The exposed Ag-formed s-FEPs were observed with a scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (SEM-EDX).

Figure 1 shows the SEM image of plasma exposed Ag-formed s-FEP. After the exposure, the nano-scale particles were appeared on the mesh-patterned functionalized area of the Ag-formed s-FEP, as seen in Figure 1(b). EDX spectra of un-exposed and exposed Ag-formed s-FEP were evaluated. In the case of exposed sample, although the peak of F atom (F-K α) decreased with increasing the exposure time, the peak intensity of Ag atom (Ag-L α) increased. It is indicated that the patterned nano-scale metal structure would be fabricated using both of the ion beam induced patterning and the plasma induced direct reduction techniques in solid state. Thus, the obtained samples have the electric insulated polymer and conducted metal phase, it would be expected to be widely used for various industrial applications such as micro-electronics and micro reactor.

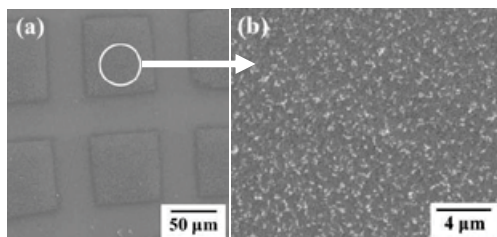


Figure 1. SEM image of Ag-formed s-FEP exposed to Ar plasma, (a) wide-view (b) magnification of the circle area of (a)

¹ H. Tsubokura, T. Takahashi, H. Fujita, T. G. Oyama, H. Yamamoto, A. Oshima, S. Tagawa, M. Washio, *Abstract of PACIFICHEM-2010*, 2010

² H. Tsubokura, A. Oshima, T. G. Oyama, H. Yamamoto, T. Murakami, S. Tagawa, M. Washio, *J. Photopolym. Sci. Technol.*, 2011, 24 No.5 513-516

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Study on Nano-scale Patterning of Silver Metal with Functionalized Polymer using Radiation Reduction Technique

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hMSC behaviors on electrospun fibrous PCL/BG composite scaffold via the sol-gel process

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Bioactive glass (BG) is known for its excellent biocompatibility, osteoconductivity, and ability to form a bonelike mineral phase at the interface when in contact with living tissues. Poly(ϵ -caprolactone) (PCL) / Bioglass powders nano-fibers prepared by electrospinning process have attracted significant interest in bone tissue engineering applications¹. Recently, the sol-gel synthesis route has been used to combine organic-inorganic components. In this study, 2D film and 3D electrospun PCL-BG fiber scaffolds were constructed via the sol-gel method². PCL and tertiary bioactive glass with a glass composition of 70 mol % SiO₂, 25 mol % CaO, and 5 mol% of P₂O₅ were used as the polymer and inorganic phases, respectively. The morphology of 2D film and 3D electrospun fiber scaffolds were investigated by scanning electron microscopy (SEM) and EDX. Human MSCs were cultured to show cell behaviors in terms of the attachment, morphology (Fig. 1), and proliferation.

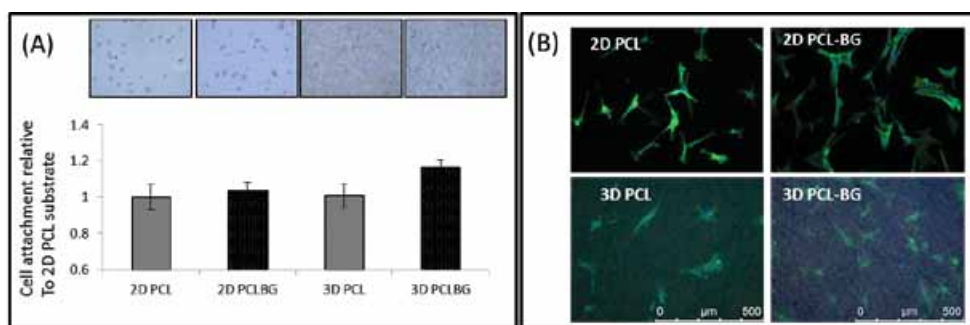


Fig 1. Static 1 hr assays of hMSC adhesion to different substrates (A). Adherent cells were stained with crystal violet, then solubilized and absorbance determined at 500 nm. Values represent means $\pm$ standard deviation ($n=3$). Human MSC cell spreading and morphology, actin (green), nucleus (DAPI) after 24 h on various substrates (B).

¹ H. Lee, H. Yu, J. Jang, H. Kim, *Acta Biomaterialia*. **2008**, 4, 622

² B. Allo, A. Rizkalla, K. Mequanint, *Langmuir*. **2010**, 26, 18340

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Functionalised HIPE Polymers via ROMP & Gamma Initiated Thiol-ene Click

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High Internal Phase Emulsion (HIPE) polymers, are highly porous crosslinked monoliths characterised by large (micrometer dimension) cavities interconnected by a series of smaller pores (**Fig. 1**). They can possess void volumes in excess of 90%, and find application in adsorption, chromatography, and catalyst support.

HIPE polymers are prepared from an inverse emulsion of monomer and crosslinking agent (e.g. a styrene-divinylbenzene system in water), such that the minority polymeric component forms the continuous phase. This confers exceptional surface area to the material, but at the expense of mechanical strength.

To address this, Slugovc et al.¹ have prepared HIPE polymers via the ring-opening metathesis polymerisation (ROMP) of dicyclopentadiene (DCPD). As a bicyclic olefin, DCPD is able to crosslink with itself under metathesis conditions, to yield a robust high density network.

All ROMP polymers retain double bonds between each repeat unit. These are reactive towards 'Thiol-ene Click' chemistry (radical mediated hydrothiolation), and may be targeted for post-polymerisation modification. In the current work, we employ gamma radiation to generate radicals in situ, and efficiently functionalise DCPD HIPE materials with a suite of thiols.

The penetrative nature of gamma radiation permits all internal HIPE surfaces to be accessed, while the abundance of double bonds allows for an extremely high density of functionalisation. A further advantage is the wealth of different and inexpensive thiols that are commercially available (**Fig. 2**). Finally, many biologically active compounds bear thiol moieties, and this technique could be extended to the creation of solid supports for immobilised enzymes and therapeutic drugs.

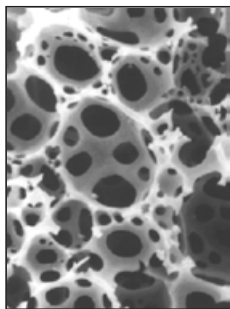


Figure 1. SEM of HIPE Polymer

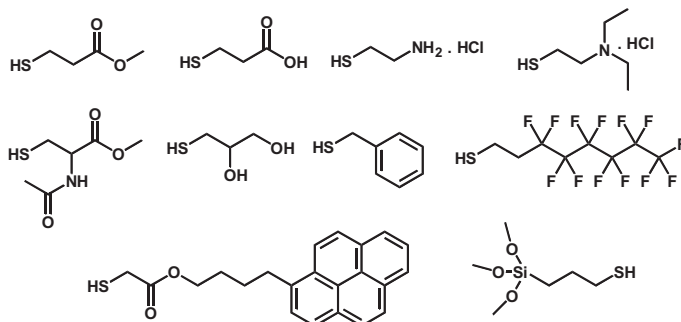


Figure 2. Suite of commercially available thiols.

¹ S. Kovačič, P. Krajnc, C. Slugovc, *Chem. Commun.* **2010**, 46, 7504

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Dynamic Mechanical Analysis of Functionalised ROMP Polymers

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Ring-opening metathesis polymerisation (ROMP) is a living technique that yields well-defined polymers bearing carbon-carbon double bonds between each repeat unit. This structural feature is analogous to natural and synthetic rubber compounds, and as a result, ROMP polymers tend to exhibit broad viscoelastic properties and superior performance in damping applications.

Although simple norbornene-based polymers have been recently commercialised and characterised (e.g. Norsorex®), the majority of literature on functionalised ROMP polymers has neglected to examine the unique thermal and mechanical properties of these materials.

In this work, we have synthesised various functionalised oxo-norbornene adducts, and polymerised them to form novel homopolymers and statistical and block copolymers (**Fig. 1**). A hot-press and custom mould was then used to shape these into rectangular test bars for testing on a Dynamic Mechanical Analysis (DMA) instrument. Properties such as glass transition temperature, melting point, modulus, tan delta and damping coefficients, resistance to creep, and crystallinity have been compared and correlated with pendant group structure.

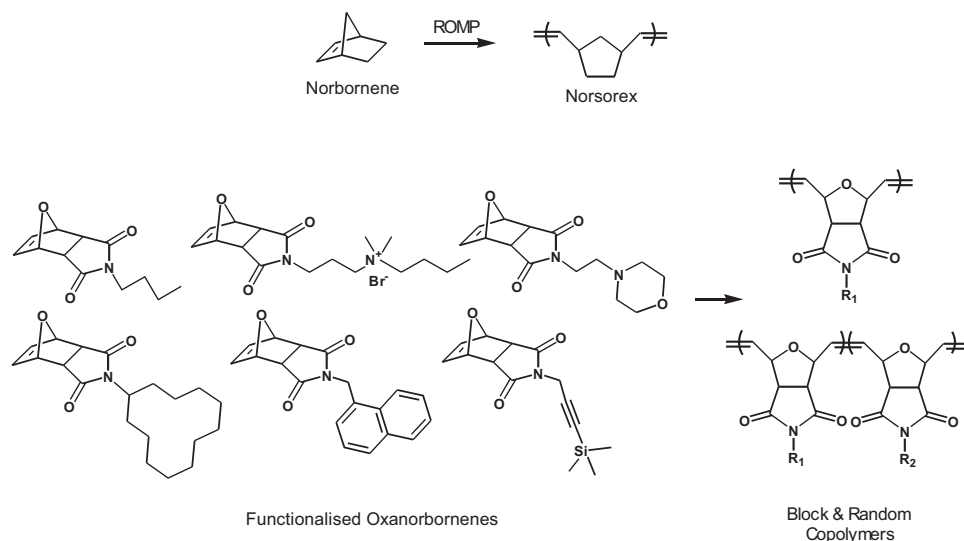


Figure 1. Suite of functionalised oxanorbornenes.

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Bioactivity of electrospun PCL-Bioactive glass fiber preparation via blending and sol-gel process

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Poly(ϵ -caprolactone) (PCL) / Bioglass powders nano-fibers prepared by electrospinning process have attracted significant interest when functioning as scaffold in tissue engineering such as bone repair techniques¹. In this study, PCL-Bioactive glass (BG) scaffolds with 15% and 30% of bioglass content were constructed by blending with bioglass powder and using the Sol-Gel method² with bioglass precursors, and both were compared with pure PCL scaffold (**Fig 1**). The scaffold was made by adding bioglass precursors into PCL solution to achieve a clear gel and then electrospinning. They were investigated in terms of the morphology, chemical and mechanical properties, as well as bioactivity. The bioactivity and bone bonding ability of the scaffolds were examined in a simulated body fluid (SBF) and Human MSCs were cultured on them. Tensile testing was employed to test the mechanical properties while the morphology and chemical properties were investigated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), respectively.

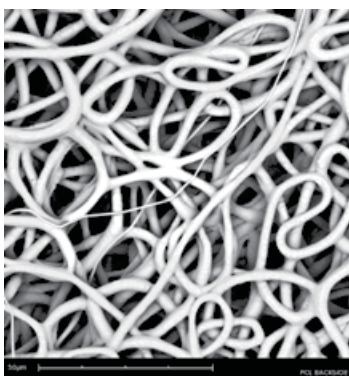


Fig 1. The SEM image of PCL electrospun scaffold.

¹ H. Lee, H. Yu, J. Jang, H. Kim, *Acta Biomaterialia*. **2008**, 4, 622

² B. Allo, A. Rizkalla, K. Mequanint, *Langmuir*. **2010**, 26, 18340

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Biocompatible PCL scaffold fabrication using electrospinning and forcespinning method for bone tissue engineering application

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Electrospun PCL has been shown to be a suitable material for bone engineering due to its biocompatible nature.¹ Forcespinning² is a new technique also able to produce nanofibres by centrifugal force, and likewise has the possibility to produce PCL scaffolds (Fig 1). In this study, HA nanoparticles were blended into scaffolds simultaneously during the force-spinning procedure, to produce a scaffold that mimics ECM native bone tissue. SEM and EDX were performed to examine the microstructure and surface chemistry of force-spun of PCL-HA scaffolds. Tensile tests were conducted to obtain the mechanical properties of those scaffolds. MSCs will be cultured, expanded and seeded on the PCL-HA fiber scaffolds and then cultured to determine the biocompatibility of PCL-HA fiber scaffolds produced by such a force-spinning procedure.

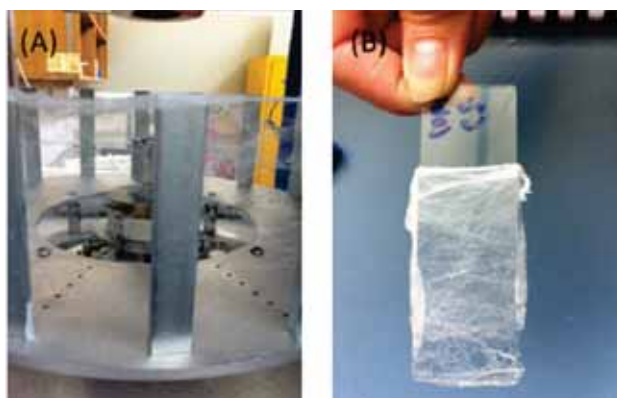


Fig 1. Photographic images of PCL fibers produced by the forcespinning method. (A) PCL nanofiber webs , (B) PCL fiber on glass coverslip.

¹ Y. Zhang, J.R. Venugopal, A. El-Turki, S. Ramakrishna, B. Su, C.T. Lim, *Biomaterials*. **2008**, 29, 4314

² K. Sarkar, C. Gomez, S. Zambrano, M. Ramirez, E. de Hoyos, H. Vasquez, K. Lozano, *Mater Today*. **2010**, 13, 12

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The use of cationic polymers at bubble interfaces for water reclamation

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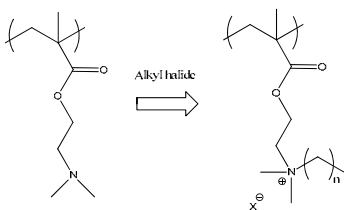
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Algal contamination in surface waters can be a challenge to remediate for consumption. Ineffective clarification of algal laden waters can lead to the formation of disinfection by products (DBPs) from downstream chlorine treatment. To effectively remove algal cells from the water dissolved air flotation (DAF) is typically employed. In this process, micro bubbles are attached to flocculated particles to remove them via flotation, however, during algal blooms, a large quantity of algae can remain in the DAF effluent. Algal cells carry a negative charge and when not flocculated experience an electrostatic repulsion from bubbles which also carry a negative charge. Increasing the attachment forces between algal cells and bubbles would thus increase the effectiveness of DAF in remediating algae contaminated water.

Conventionally, cationic polymers are used as a flocculant aid after water conditioning with hydrolysing metal salts such as aluminium sulphate¹. The result is an increased floc size which is more easily intersected by the rising bubbles in DAF. Most untreated contaminants from natural sources and bubbles carry a negative surface charge. Thus modifying bubble surfaces with cationic polymers allows an increased electrostatic attraction between bubbles and algae cells, thereby improving removal efficiency.

Bubble modification with poly(diallyl dimethyl ammonium chloride) (pDADMAC) in DAF has been demonstrated to be effective on *Microcystis aeruginosa*, however varying species of algae could not be removed as effectively². Continuing this research, an Australian *Microcystis aeruginosa* was used to simulate raw waters for bubble surface modification studies. In addition to pDADMAC, poly(dimethyl amino ethyl methacrylate) (pDMAEMA) and alkylhalide- quaternerised, variations of pDMAEMA were used to functionalise bubble surfaces. A variety of molecular weight pDMAEMA was synthesised both by conventional free radical polymerisation, and atom transfer radical polymerisation (ARTP)³. The pDMAEMA homopolymers were then functionalised using iodomethane, 1-bromopentane, 1-bromodecane and 1-bromopentadecane via quaternerisation of the amino group shown in **Scheme 1**. Polymers were characterised using ATR, NMR and DLS.



Scheme 1. Quaternerisation of pDMAEMA; n=0, 4, 9 or 14

Select polymers were tested at bench scale using a DAF jar test. The initial findings show that elevated molecular weights result in improved algal cell removal. The elevation of polymer charge due to quaternerisation did not influence bubble-particle interactions, though poly-surfactant properties were apparent.

¹ B. Bolto, J. Gregory, *Water Res.*, **2007**, *41*, 2301-2324

² R.K. Henderson, S.A. Parsons, B. Jefferson, *Sep. Sci. Tech.*, **2008**, *44*, 1923-1940

³ Mao, 2006, B.W. Mao, L.H. Gan, Y.Y. Gan, *Polymer*. **2006**, *47*, 3010-3040

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ON THE ELECTROSPINNING OF MONOSACCHARIDES

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Electrospinning of glucose, fructose and sucrose composite nanofibres was successfully achieved for the first time (see fig. 1). The successful electrospinning of these materials challenges current electrospinnability mechanisms proposed by other research groups[1, 2]; establishing the need for a new re-evaluation of the physical principles underlying the electrospinning process and the need to describe a new electrospinnability mechanism for short carbohydrate molecules.

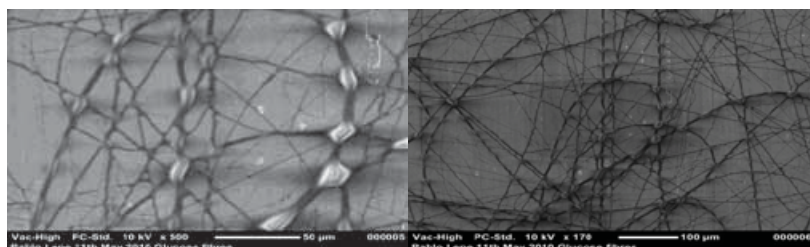


Figure 1; SEM pictures of electrospun D-glucose microfibers.

Saturated aqueous solutions of D-glucose present molecular structural fluctuations (temperature and H₂O concentration dependant) between its furanose and pyranose isomeric structures at all times. Due to this constant changes in its crystalline (ring) and linear positions; D-glucose solutions stabilize by glycoside bonds between the anomeric C1- carbon and nearby water molecules. Producing in this way high concentrations of HO³⁺, free HO², HO⁻, and H⁺. because it is constantly seeking equilibrium between its two isomeric forms, this induces a natural de-protonation of the chain structure, especially in saturated solutions. This, coupled with the high voltages and fast charge transfer typically seen in electrospinning; might help promoting the creation of long range hydrogen bond networks, stabilizing in this way the “poly-glucose” molecules during the process, hence forming fibers.

How much electrospinning changes its crystalline configuration and what effects electrospinning have on the formation of glycoside and hydrogen bond in this and other monosaccharide solutions? Are still questions that need to be answered in order to experimentally proof or disproof the proposed electrospinnability mechanism.

1. Suresh L. Shenoy, W.D.B., Harry L. Frisch and Gary E. Wneck, *Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer-polymer interaction limit*. Polymer, 2005. **46**: p. 3372 - 3384.
2. Suresh L. Shenoy, W.D.B.a.G.E.W., *Correlations between electrospinnability and physical gelation*. Polymer, 2005. **46**: p. 8990 - 9004.

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Preparation of Chitosan Electrospun Nanofibers Membrane and its Characterization

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Abstract; Nanotechnology is the study and development of materials at nano-levels. Nanofibers membranes are new form of nanomaterials, which possesses fine diameter (from nano to submicron), large surface area per unit mass, high porosity, high gas permeability, and interfibrous pore size¹. Several processing techniques such as drawing², template synthesis³, phase separation⁴ etc. have been used to prepare nanofibers from polymer or biopolymer. However, electrospinning was found an efficient fabrication technique as compared to the above mentioned processes because it is cost effective, utilize simple equipment, produces dry fibers (solvent is evaporated allowing the production), creates fiber with diameters in the range 10 and 500 nm, have very high specific surface area and mechanically superior properties. In the present work, we undertake the preparation chitosan (biopolymer) nanofibers *via* electrospinning by varying solution concentration (1, 2, 3, 4, 6 and 8 wt % (w/v)), applied voltage (14, 18 and 22 kV), flow rate (0.4 mL/h and 0.8 mL/h), needle diameter (0.2 mm and 0.8 mm) and distance between needle tip and collector (100 mm and 140 mm). The chitosan solutions for electrospinning were prepared in trifluoroacetic acid (TFA) and the morphologies of the electrospun nanofibers were studied by using field emission scanning electron microscope (FE-SEM). The optimized conditions (e.g. concentration of solution 6 w%, applied electrical potential 22 kV, flow rate 0.4 mL/h, needle diameter 0.8 mm and needle to collector distance 100 mm) were used for producing nanofibers sheets/membranes (**Fig. 1**). The membranes were then functionalized by treating those with anhydrous potassium carbonate (K_2CO_3) and glutaraldehyde ($(C_5H_8O_2)$ GTA vapors). The chemical structure, morphology and thermal behavior of the nanofibers membranes after treatment with K_2CO_3 and GTA were studied by using fourier transform infrared (FT-IR), FE-SEM and thermal gravimetric analysis (TGA), respectively. FT-IR confirmed the introduction of the new functional groups into the primary structure of chitosan. FE-SEM showed no deterioration of the nanofibers morphology and TGA showed variation in thermal behavior of the nanofibers membranes after functionalization.

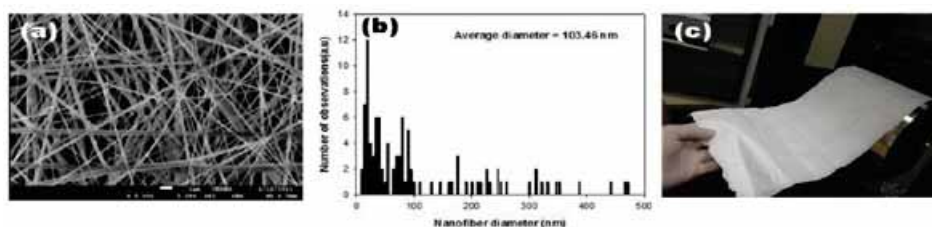


Fig.1. (a) FE-SEM micrograph of the chitosan at concentration 6w%, flow rate 0.4 mL/h, needle tip to collector distance 100 mm, needle diameter 0.8 mm and at applied voltage 22 kV, (b) nanofibers diameter histogram and (c) digital image of the nanofibers membrane.

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- [4] P. X Ma, R. Zhang, J. Biomed Mat. Res. 1999, 46, 60-72.

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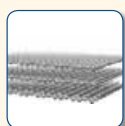
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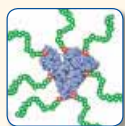
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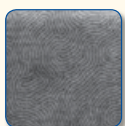
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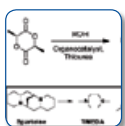
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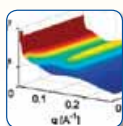
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