DARWIN CONVENTION CENTRE
NORTHERN TERRITORY
7–10 JULY 2013

WWW.34APS.ORG.AU

SYMPOSIUM HANDBOOK

Contents

34APS

34APS Organisation

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The firm continues to proudly sponsor, and to be actively involved with the Australasian Polymer Symposium. Please visit us at the 'IP Café' located in the trade display area where you can relax and enjoy a complimentary real coffee! Some of our polymer specialist patent attorneys will also be on hand to answer any IP questions that you may have. Please also be sure to attend the "Polymers in Industry and Translational Research" session being held in conjunction with the scientific program.

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The Centre's goal is to further strengthen Australia's leading role in the field of free radical chemistry, expand the frontiers of free radical chemistry and biotechnology at a fundamental level, and develop advanced materials and technologies that will build and transform our industries.

The Centre is home to over 180 researchers, drawing together a unique grouping of fundamental chemists, medicinal chemists, biochemists, biologists and materials scientists dedicated to the understanding and application of free radical chemistry.

Organisations that are affiliated with the Centre include: BlueScope Steel, Dulux Australia, PPG Industries Australia Pty Ltd, the Centre for Cultural Materials Conservation, the Environmental Biotechnology Co-operative Research Centre and the CSIRO, along with a range of international partners.

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For over 20 years, the Cooperative Research Centre for Polymers (CRC-P) has been carrying out collaborative polymer research in Australia. It has developed new materials and processes that have uses in a wide range of industrial applications. The organisations that participate in the current CRC-P research activities work collaboratively to address the CRC-P's major challenge: establishing Australian manufacturing as a leading provider and exporter of products that meet emerging global needs in three areas – health therapies and delivery, water and food security, and low-cost solar energy – using enabling and sustainable advanced polymer technology

www.crcp.com.au

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Our Materials Science and Engineering division is host to a diverse range of scientific capabilities ranging from stem cells to superconductivity. As an international leader in advanced materials and engineering, we combine the scientific disciplines of biology, chemistry and physics with electronic, mechanical and software engineering to provide advanced materials-based technologies to Australian and international industries.

www.csiro.au/cmse

Refreshment Break Sponsor – American Chemical Society

The American Chemical Society, the world's largest scientific society, publishes three leading journals in Polymer Science. Macromolecules is the most cited journal in polymer science and has a 2011 Impact Factor of 5.167 and Total Citations of 93,776. Biomacromolecules is a high impact journal focusing on the intersection of polymer and biological systems with a 2011 Impact Factor of 5.479 and Total Citations of 21, 280. ACS Macro Letters was introduced in 2012 as an all-Letters-format journal and has the fastest time to publication in polymer science.

www.pubs.acs.org

Lanyard Sponsor - Australian Microscopy & Microanalysis Research Facility (AMMRF)

The AMMRF is a national network of equipment, advanced instrumentation and expertise in microscopy and microanalysis. It is a joint venture between Australian university-based microscopy and microanalysis centres providing nanostructural characterisation capabilities and services to the Australian research community, thereby enabling scientific discovery and innovation. It operates as a collaborative facility accessible to all Australian researchers and provides specialised online tools for improved training. It offers its suite of sophisticated instruments to publicly funded researchers on the basis of merit for a nominal fee and to industry-based researchers for proprietary research at commercial rates.

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www.davies.com.au

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Trade Booth 2 – Agilent Technologies

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www.shimadzu.com.au

Trade Booth 5 – TA Instruments

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www.tainstruments.com

Trade Booth 6 – Sigma Aldrich

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Bestech Australia was founded in 2002 in Melbourne and is now one of the fastest growing companies in Australia and New Zealand; distributing world leading NETZSCH Analysing & Testing instruments, providing quality customer service to local customers.

Bestech Australia also carries a full range of teaching aids and programmes for electrical and mechanical engineering training alongside with sensors, transducers, signal conditioners and test systems for measurement of physical parameters like Leak, Displacement, Tilt, Pressure, Temperature, Strain, Force, Torque, Vibration, Viscosity, Level, Flow, Material Properties and Thermal Analysis.

www.bestech.com.au

Welcome

Dear Colleagues,

On behalf of the Royal Australian Chemical Institute (RACI) Polymer Division, I welcome you to the 34th Australasian Polymer Symposium (34APS) here at Darwin Convention Centre in the Northern Territory.

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, to what promises to be another exciting forum.

I would like to extend a particular welcome to our invited speakers and to our delegates who contribute to the success of 34APS 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. Your participation and continuing support makes the annual symposium the premier forum for the presentation and exchange of ideas on polymer research in Australasia.

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.

This year again, we have a busy social schedule, with a welcome reception on Sunday night at the Darwin Convention Centre, the poster session on Monday night, a special student night on Tuesday, ending with the symposium dinner on Wednesday night, being held at SkyCity Darwin.

Contributing to the success of 34APS are also all our sponsors and exhibitors, whose details you can find in these pages. We are very grateful to them for their support. Please take the time to visit and talk to all of our sponsors and exhibitors in the trade exhibition room throughout the symposium.

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. 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. Please also visit our website for further information www.polymer.org.au.

It is wonderful that you have all joined us to contribute to the exploration of ideas and exchange of information in Darwin. I hope you enjoy the meeting and find it a great opportunity to discuss science, build valuable relationships and start new ones.

We welcome you and look forward to your participation during the 34th Australasian Polymer Symposium.

Dr Kevin Jack

34APS Convenor
Chair of the Polymer Division of the RACI

Unprofessional Conduct Declaration

The host organization for 34APS 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 34APS 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.

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 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, engineering and industrial aspects of polymers. 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). 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 a series of forums which are for and organised by Polymer Students. 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. These forums enable 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 2012 - 2013

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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**
33	2012	Hobart	**S Perrier**

Other Symposia and Courses

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	Thermal Characterisation of Polymeric Materials
	Noosa	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	Pacifichem
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	olymer 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 Charcterisaton 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 INSTITUION
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

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 Cincinatti, 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 Southhampton, 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 Southhampton, 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 Khokhlokov, 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 Materiaux Macromoleculaires, Lyon, FRANCE

2000 **U Suter**, ETH Zurich, SWITZERLAND
D N Theodorou, University of Patris, GREECE
A Windle, Cambridge University, UK
C Holm, Johannes Gutenburg University, Mainz, GERMANY

2001 **A Balazs**, University of Pittsburg, USA
J Gerlock, Ford Motor Company, Deerborn, 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, Pennysylvania 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

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
P Vana, University of Göttingen, GERMANY
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**

2012 **H Klok**, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
H Maynard, University of California, USA
G Wallace, University of Wollongong, Australia
D Haddleton, University of Warwick, England
L Leibler, ESPCI, France
X Zhang, Tsinghua University, China
D Solomon, University of Melbourne, Australia
E Rizzardo, CSIRO, Australia
and **20 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
2012	**Dr G Moad**, CSIRO

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
2012	33APS	**Zhou Zhang**, University of Melbourne
		Adrian Sulistio, University of Melbourne
		Wei Zhao, The University of Sydney

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 Hawkett**, 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
2012	33APS	**Prof G Qiao**, University of Melbourne
	33APS	**A/Prof M Stenzel**, University of New South Wale

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
2011 **S Harris Wibowo**, University of Melbourne
A Pearce, University of Queensland
2012 **S J Lam**, University of Melbourne
Y Tang, Monash 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
2012 **Prof Krzysztof Matyjaszewski**

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

PLENARY SPEAKERS AT 34APS

Professor Cameron Alexander, University of Nottingham
Professor Kristi Anseth, University of Colorado
Dr Anna Balazs, University of Pittsburgh
Professor Maria Forsyth, Deakin University
Professor Axel Muller, Universität Bayreuth
Professor Mitsuo Sawamoto, Kyoto University

KEYNOTE SPEAKERS AT 34APS

Professor Luc Averous, Université de Strasbourg
Professor Christopher Bowman, University Of Colorado
Professor Paul Burn, University of Queensland
Professor Neil Cameron, Durham University
Professor Paul Dastoor, University of Newcastle
Dr Cecile Dreiss, Kings College London
Professor Bob (Robert) Gilbert, University of Queensland
Leo Hyde, DuPont
Dr Derek Irvine, University Of Nottingham
Professor Masami Kamigaito, Nagoya University
Professor David Lewis, Flinders University
Professor Zi-Chen Li, Peking University
Dr Jean-Francois Lutz, Université de Strasbourg
Associate Professor Shigeru Okamoto, Nagoya Institue of Technology
Professor Sebastien Perrier, Univesrity of Sydney
Dr Theresa Reineke, University of Minnesota
Professor Dr Holger Schönherr, Universität Siegen
Professor Brent Sumerlin, Southern Methodist University
Associate Professor Erica Wanless, University of Newcastle
Professor Yanlei Yu, Fudan University

EMERGING TALENT PRESENTATIONS AT 34APS

Dr James Blinco, Queensland University Of Technology
Dr Cyrille Boyer, University of New South Wales
Dr David Huang, University of Adelaide
Dr Jianyong Jin, University of Auckland
Dr Georgina Such, University Of Melbourne

INVITED SPEAKERS AT 34APS

Prof Steven Bottle, Queensland University Of Technology
Dr Toen Castle, ANU
Dr Grace Chan, Phillips Ormonde Fitzpatrick
Prof Suwabun Chirachanchai, The Petroleum And Petrochemical College, Chulalongkorn University
Dr Stephen Clarke, Mawson InsUniversity Of South Australia
Prof Wayne Cook, Monash University
Dr Simon Corrie, The University Of Queensland
Dr Annette Dexter, The University Of Queensland
Prof John Dorgan, CSM
Prof John Drennan, Centre For Microscopy And Microanalysis, University Of Queensland
Prof Naba Dutta, University Of South Australia
Dr Natasha Evans, Victoria University Of Wellington
A/Prof Bronwyn Fox, Deakin University
David Francis, Qenos
Dr Christopher Garvey, Ansto
Dr Didier Gigmes, Aix-Marseille University
Dr Anja Goldmann, Karlsruhe Institute Of Technology
Dr Anthony Granville, Centre For Advanced Macromolecular Design
Prof Hans Griesser, University Of South Australia
Prof Qipeng Guo, Deakin University
Dr Angus Johnston, The University Of Melbourne
Dr Geoffrey Johnston-Hall, Siemens Ltd Memcor Products
Prof Peter Kingshott, Swinburne University of Technology
Dr Bronwyn Laycock, University Of Queensland
Dr Shih-Chun (Lawrence) Lo, University of Queensland
Dr David Nisbet, The Australian National University
Dr Simon Puttick, The University Of Queensland
Prof Namita Roy Choudhury, University Of South Australia
Dr Kei Saito, Monash University
Dr Greg Simpson, CSIRO
Dr Jim Thackery, Dow Chemical Company
Dr Lars Thomsen, Australian Synchrotron
Dr Kevin Thomson, Enterprise Connect
Dr George Vamvounis, The University Of Queensland
A/Prof Jeff Wiggins, University Of Southern Mississippi

Sunday 7 July

1200 – 1830	Registration Open
1330 - 1500	Annual General Meeting – RACI Polymer Division
1600 – 1825	Conference Opening and Plenary Session
1830 - 2030	Welcome Reception at Darwin Convention Centre

Monday 8 July

0800 - 1700	Registration Desk Open
0820 – 0930	Plenary Session
0930 – 1000	Morning Refreshments
1000 – 1215	Concurrent Sessions
1215 – 1315	Lunch
1315 – 1530	Concurrent Sessions
1530 – 1600	Afternoon Refreshments
1600 – 1815	Concurrent Sessions
1815 – 1945	Symposium Poster Session

Tuesday 9 July

0800 – 1700	Registration Desk Open
0820 – 0930	Plenary Session
0930 – 1000	Morning Refreshments
1000 – 1215	Concurrent Sessions
1215 – 1315	Lunch
1315 – 1530	Concurrent Sessions
1530 – 1600	Afternoon Refreshments
1600 – 1830	Concurrent Sessions
1930 - 2030	Student Night

Wednesday 10 July

0800 – 1600	Registration Desk Open
0820 – 0930	Plenary Session
0930 – 1000	Morning Refreshments
1000 – 1215	Concurrent Sessions
1215 – 1315	Lunch
1315 – 1430	Concurrent Sessions
1430 - 1450	Afternoon Refreshments
1450 - 1550	Plenary Session
1550 - 1600	Symposium Conclusion
1830 - 1100	Symposium Dinner at SkyCity Darwin

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 60 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
60 Minutes	50 Minutes	55 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 8 July from 1815 – 1945. 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 7 July 2013
TIME: 1830 - 2030
VENUE: Darwin Convention Centre – Exhibition Concourse

Held at the symposium venue, the welcome reception will be held in the Exhibition Concourse, with a beautiful waterfront setting. This is quite befitting, as to the Larrakia people the harbour is a place of connection where, for centuries, they have welcomed visitors while trading with other indigenous tribes and Southeast Asian neighbours.

Symposium Poster Session

DATE: Monday 8 July 2013
TIME: 1815 – 1945
VENUE: Darwin Convention Centre – Hall 1

Poster authors will be available for questions and answers during this session and beverages will be served.

Student Night

DATE: Tuesday 9 July 2013
TIME: 1930 - 2030
VENUE: The Precinct Tavern
ADDRESS: 7 Kitchener Dr, Darwin Waterfront

All students are welcome to The Precinct Tavern for Happy Hour and nibbles from 7.30pm – 8.30pm. After this time students will have access to "Trade out Tuesday" drink specials. This special will give all students the opportunity to try different flavours of beer & cider at half the price! Please note students must make their own way to the venue and bring their name badges to receive drink specials.

Symposium Dinner

DATE: Wednesday 10 July 2013
TIME: 1830 - 2300
VENUE: SkyCity Darwin

The Symposium Dinner will be an open air event, with delegates enjoying dinner under the stars! Become immersed in the natural beauty of the property and enjoy the surrounding tropical gardens and spectacular ocean views.

TRANSFERS: Coaches have been arranged to transfer delegates to SkyCity. Please assemble out the front of one of the below hotels by 1800. Coaches will depart by 1810 sharp.
Adina Apartment Hotel Darwin Waterfront- 7 Kitchener Dr, Darwin
Mantra On The Esplanade - 88 The Esplanade, Darwin
Mantra Pandanas - 43 Knuckey St, Darwin
Travelodge Mirambeena Resort - 64 Cavenagh St, Darwin

Return transfers back to your hotel will also be provided at the end of the dinner.

General Information

Registration Desk Opening Times:	Sunday 7 July	1200 - 1800
	Monday 8 July	0800 - 1700
	Tuesday 9 July	0800 - 1700
	Wednesday 10 July	0800 - 1600

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.

Social Program: 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.

Conference Dinner Entry: All delegates who are registered to attend the symposium dinner will receive a named sticker at registration. You MUST place your sticker on a table located on poster boards at the registration desk. **You must allocate yourself to a table no later than 10.00am on Wednesday 10 July 2013.**

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 in the speakers preparation room. 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 directions.

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 available for the duration of the symposium. Please see staff at the registration desk for directions.

Disclaimer: The 34APS 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.

1100 - 1300 **Polymer Division Standing Committee Meeting**

1330 - 1500 **Annual General Meeting - RACI Polymer Division**

Plenary Session Waterfront Room 2/3
Chair: A/Prof Amanda Ellis

1600 – 1620 **Welcome to the 34th Australasian Polymer Symposium**

1620 – 1720 PL 1 - **Synthetic polymers for pharmaceutical applications.** Cameron Alexander*, Francisco Fernandez-Trillo, Johannes Magnusson, Aram Saeed, Sebastian Spain

1720 – 1820 PL 2 - **Reconfigurable assemblies of active, auto-chemotactic gels.** Pratyush Dayal, Olga Kuksenok, Anna C. Balazs*

1820 – 1825 **Closing remarks**

Welcome Reception Darwin Convention Centre

1830 – 2030 **Assemble in the Exhibition Concourse for canapés and beverages**

Plenary Session Waterfront Room 2/3
Chair: Dr Lachlan Yee

0820 - 0830 **Welcome and housekeeping**

0830 - 0930 PL 3 - **Dynamically Tunable Hydrogels and Their Biological Application**. Mark Tibbitt, Cole DeForest, Dan McKinnon, Kristi Anseth*

0930 – 1000 **Morning Refreshments and Trade Exhibition** - Hall 1

Advanced Characterisation Waterfront Room 2/3
Chairs: Dr Marianne Gaborieau & A/Prof Shigeru Okamoto

1000 – 1030 M1.1 / KN 1 - **High Speed Video Observation of Giant Pickering Emulsion and Colloidosome Droplet Interaction and Stability.** Erica J. Wanless*, Kate Thompson, Andrew Morse, Emma Giakoumatos, Grant B. Webber, Steven P. Armes, Seher Ata

1030 – 1045 M1.2 - **Distribution of "smartness" of copolymers: Composition of block and statistical copolymers by capillary electrophoresis.** Patrice Castignolles*, Adam Sutton, Emilie Groison, Akashdeep Singh, Joel Thevarajah, Maryanne Selim, Emmanuelle Read, Valentina Naumovski, Kelvin Chan, Jean-Daniel Marty, Mathias Destarac, Bernadette Charleux, Marion Gaborieau

1045 – 1100 M1.3 - **Complex structures in branched polymers.** Toen Castle*, Myfanwy E. Evans, S.T. Hyde, Vanessa Robins

1100 - 1115 M1.4 - **Novel Applications of Nitroxides in Polymer and Materials Science.** James Blinco, John Colwell, James Allen, Kathryn Fairfull-Smith, Steven Bottle*

1115 - 1130 M1.5 - **Imaging light emitting polymer films at high spatial and temporal resolution.** Xiao-Tao Hao*, Trevor A. Smith

1130 - 1145 M1.6 - **A comprehensive comparison of nanoparticle characterisation instrumentation.** Åsa K. Jämting*, Victoria A. Coleman, Heather J. Catchpoole, Maitreyee Roy, Jan Herrmann

1145 - 1200 M1.7 - **Developing Profluorescent Nitroxide Additives as Probes for Polymer Degradation: The Use of a Liquid Model for Polyolefins.** Liam A. Walsh*, James P. Blinco, John M. Colwell, Kathryn E. Fairfull-Smith, Graeme A. George, Steven E. Bottle

1200 – 1215 M1.8 - **Development of fluorescent nanothermometers.** Kai-Anders Hansen*, Kathryn E. Fairfull-Smith, Steven E. Bottle and James P. Blinco

Polymers in Therapy and Imaging Meeting Room 2
Chair: Dr Kristofer Thurecht

1000 – 1030 M2.1 / KN 2 - **Block Copolymer Drug Delivery Vehicles from a Combination of RAFT and Anionic Polymerization Routes.** Zachary Tolstyka, Swapnil Tale, Molly Dalsin, Nilesh Ingle, Theresa M. Reineke*

1030 – 1045 M2.2 - **Preparation of Polymeric Nanoparticles for Therapeutic Applications.** Cheuk Ka Poon*, Owen Tang, Xin-Ming Chen, Carol Pollock, Brian S. Hawkett, Sébastien Perrier

1045 – 1100 M2.3 - **Size-exclusion chromatography of healthy and diabetic glycogen reveals differences in their biosynthesis and biodegradation.** Mitchell A. Sullivan*, Torsten Witt, Prudence O. Powell, Eugeni Roura, David I. Stapleton, Robert G. Gilbert

1100 – 1115 M2.4 – **Synchrotron X-ray imaging of gold loaded alginate microcapsules in ex vivo rodents for cellular based therapeutic treatments.** Xiaojuan Hao*, Fengxiang Qie, Alberto Astolfo, Astrid Kibleur, Tianwei Tan, Tim Hughes

1115 – 1130 M2.5 - **Hyperbranched Polymer-siRNA Conjugates: Advanced Polymeric Carriers for Cancer Therapy.** Aditya Ardana*, Andrew K Whittaker, Nigel McMillan, Kristofer J Thurecht

1130 – 1200 M2.6 / ET 1 - **Engineering Polymeric NanoParticles for Advanced Applications.** Cyrille Boyer*, Hien Duong, Jinna Liu, Michael Whittaker, Thomas P. Davis

1200 – 1215 **Additional Question Time**

Polyelectrolytes and Semiconducting Polymers Meeting Room 3
Chairs: Prof Maria Forsyth & Prof Yanlei Yu

1000 – 1030 M3.1 / KN 3 - **Solution processable poly(dendrimers) for organic light-emitting diodes.** Paul Burn*, Wen-Yong Lai, Shih-Chun Lo

1030 – 1045 M3.2 - **Advanced Branched Macromolecules for Opto-Electronics.** Shih-Chun Lo*

1045 – 1100 M3.3 - **Synthesis and Properties Triphenylamine-cored Dendrimer Semiconductors.** George Vamvounis*, Paul Burn

1100 – 1115 M3.4 - **Polymeric Ionic Liquids (PILS): Synthesis and characterisation of solid polyelectrolytes for advanced energy applications.** Thomas Bennett*, Kristofer Thurecht, Idriss Blakey

1115 – 1130 M3.5 - **Well defined water-soluble conjugated polyelectrolyte with high hole transport mobility.** Johannes Brendel*, Gunter Hagen, Ralf Moos, Mukundan Thelakkat

1130 – 1145 M3.6 - **Highly conducting yet processable graphene for polymers.** Jun Ma*, Qingshi Meng

1145 – 1200 M3.7 - **Novel electrospun polymer nanofibre/Organic Ionic Plastic Crystal Composite electrolytes.** Patrick C. Howlett*, Nahid Iranipour, Florian Ponzio, Jim Efthimiadis, Jian Fang, Cara Doherty, Anthony F. Hollenkamp, and Maria Forsyth

1200 – 1215 **Additional Question Time**

Symposium Program
MONDAY 8 July 2013

Polymers in Industry and Translational Research Meeting Room 1
Chairs: Dr Ramon Tozer & Prof Peter Halley

1000 – 1030 M4.1 / KN 4 - **Research Collaborations in Polymer Industry.** Leo Hyde*

1030 – 1045 M4.2 - **NanoConnect: Providing a Bridge between Industry and University.** Jonathan A. Campbell, David A. Lewis*

1045 – 1100 M4.3 - **The Power of Collaboration - Commercialisation of a World First Polymer Technology.** David Francis*, Predrag Micic, Brian Egan

1100 – 1115 M4.4 - **New Zealand Industry-Researcher Partnerships: The Materials Accelerator Model.** Ralph P. Cooney*, Mark P. Taylor

1115 – 1130 M4.5 - **Industry Collaboration – why it's important and how to do it.** Kevin Thomson

1130 – 1145 M4.6 - **IP Reform: How will it affect you?** Matthew Fisher*

1145 – 1215 M4.7 - **Commercialisation of Industrial Polymer Research.** Chris Such*

1215 – 1315 **Lunch and Trade Exhibition** - Hall 1

Advanced Characterisation Waterfront Room 2/3
Chairs: Prof Andrew Whittaker & Dr Kevin Jack

1315 - 1345 M1.9 / KN 5 - **Photonic Crystals Formed in Semi-Dilute Solutions of Block Copolymers and Application to Non-Linear Optical Devices.** Shigeru Okamoto*

1345 - 1400 M1.10 - **Chitosan and its conjugates for medical applications.** Joel J. Thevarajah, Danielle L. Taylor, Catherine Lefay, Patrice Castignolles, Marianne Gaborieau*

1400 - 1415 M1.11 - **Dynamic Nuclear Polarization solid-state NMR spectroscopy : A valuable tool for functional polymer characterization.** O. Ouari, T. Phan, F. Ziarelli, G. Casano, F. Aussenac, P. Thureau, Didier Gigmes*, P. Tordo, S. Viel

1415 - 1430 M1.12 - **Characterisation of Polymers using Modern Methods in Electron Microscopy.** John Drennan*, Ron Rasch

1430 - 1445 M1.13 - **Solid State Deuterium NMR Study of Phenylene Ring Motions in Glassy Epoxy Networks.** Jianwei Tu, Luke O'Dell, Bronwyn Fox, Jeffrey S. Wiggins*

1445 - 1500 M1.14 - **Analysis of lamellar morphology of semi-crystalline polymers using small angle scattering and the linear correlation function.** M.P. Weir, Christopher Garvey*

1500 - 1515 M1.15 - **Longitudinal and Transverse properties and molecular motions in single aramid fibers.** Judith Wollbrett-Blitz*, Alba Marcellan, Sébastien Joannès, Anthony Bunsell

1515 - 1530 M1.16 - **NEXAFS measurements of a high mobility semiconducting polymer on the soft X-ray beamline at the Australian Synchrotron.** Lars Thomsen*, Christopher R. McNeill

Polymers in Therapy and Imaging Meeting Room 2
Chair: Prof Martina Stenzel

1315 – 1345 M2.9 - **Targeted Drug Delivery: Understanding Internalisation and Processing of Nanoparticles.** Angus P. R. Johnston*, Haiyin Liu

1345 – 1400 M2.10 - **Oral delivery of nanoparticles to the colon for targeting colorectal cancer cells.** Yiming Ma*, Allan GA Coombes, Kristofer J Thurecht

1400 – 1415 M2.11 - **Guanylated Polymethacrylates as Potent Antibacterials with Low Toxicity.** Katherine Locock*, Michl T, Griesser HJ, Meagher L, Haeussler M

1415 – 1430 M2.12 - **New chemotherapeutics via efficient complexation of gold(I) compounds to glycopolymers.** Samuel Pearson*, Hongxu Lu, Martina H. Stenzel

1430 – 1445 M2.13 – **Functional Hyperbranched Polymers for Prostate Cancer Theranostics.** Amanda Pearce*, Andrew K. Whittaker, Kristofer J. Thurecht

1445 – 1500 M2.14 - **Development of a Multimodal Hyperbranched Polymer Imaging Agent.** Nathan Boase*, Idriss Blakey, Karine Mardon, Kristofer Thurecht

1500 – 1530 **Additional Question Time**

Photovoltaics and Energy Storage Meeting Room 3
Chair: Prof Paul Burn

1315 – 1345 M3.9 / KN 6 - **Water-based Nanoparticulate Organic Photovoltaics.** Paul C Dastoor*

1345 – 1400 M3.10 - **Nanoparticle organic photovoltaics (OPVs): the effect of fabrication method on nanoparticle morphology and device performance.** Natalie P. Holmes*, Matthew Barr, Syahrul Ulum, Prakash Sista, Kerry B. Burke, A.L. David Kilcoyne, Mihaela C. Stefan, Xiaojing Zhou, Paul C. Dastoor, Warwick J. Belcher

1400 – 1415 M3.11 - **Alcohol Soluble Conjugated Interface Materials for Organic Solar Cells** Menglan Lv*, Xiwen Chen, Ming Lei, Scott Watkins, Jin Zhu

1415 - 1430 M3.12 - **Revealing the Nanomorphology of Organic Photovoltaic Polymer Blends through Selective Dissolution.** Yaqi Tang*, Christopher McNeill

1430 – 1445 M3.13 - **Self-assembled of MgH2 Nanoparticles @ MgH2 Nanotubes Linking Architecture to Hydrogen Storage.** Cyrille Boyer*, Eki J. Setijadi, Kondo-Francois, Aguey-Zinsou

1445 – 1515 M3.14 / KN 8 - **Role of Polymer Morphology in Organic Photovoltaics.** David Lewis*

1515 – 1530 **Additional Question Time**

Symposium Program
MONDAY 8 July 2013

Polymers in Industry and Translational Research Meeting Room 1
Chair: Chris Such

1315 – 1345 M4.9 / KN 7 - **Investigation into the Mechanism of Microwave Induced Rate Enhancements in Chain Growth Polymerisation.** Nam Nguyen, Jaouad El Harfi, Kamaruddin Mohd, Ed Greenhalgh, Georgios Dimitrakis, Sam W. Kingman, John P. Robinson, Derek J. Irvine*

1345 – 1400 M4.10 - **Challenges in the Development of MF/UF Membranes for the Global Water Treatment Market.** Geoffrey Johnston-Hall*

1400 – 1415 M4.11 - **Engineering Thermoplastics for Improved Self-Contained Breathing Apparatus.** Peter Trask, Sam Miller, John R. Dorgan*, Jay Hotchkiss, Clay Perbix, Laura Hollingsworth, Christopher Thellen, Joann Ratto

1415 – 1430 M4.12 - **Silicon and Polymer Microprojection Arrays for Circulating Biomarker Capture from Skin.** Simon R Corrie*, Mark AF Kendall

1430 – 1445 M4.13 - **How Can You Patent When You Have Published?** Grace Y N Chan*

1445 – 1500 M4.14 - **Academic Research in Collaboration with Industry.** Stephen Clarke*

1500 – 1530 M4.15 - **Carbon nexus: opportunities for translational research in carbon fibres and composites.** Bronwyn Fox*

1530 - 1600 **Afternoon Refreshments and Trade Exhibition** - Hall 1

Bio-functional and Responsive Polymers Waterfront Room 2/3
Chairs: Prof Holger Schönherr & Dr Kei Saito

1600 – 1630 M1.17 / KN 9 - **Precision Macromolecular Chemistry: Building Nanostructured Materials One Molecule at a Time.** Sebastien Perrier*

1630 – 1645 M1.18 - **Azide-functionalized Poly-2-Oxazoline Brushes for Biomedical Applications.** Jasmin Bühler*, Sabine Gietzen, Karl Fischer, Manfred Schmidt

1645 – 1700 M1.19 - **Polymers for Inorganic Scale Control: On the Edge of Glory.** Christopher M. Fellows*, Ali A. Alhamzah, Erica J. Smith

1700 – 1715 M1.20 - **Influence of the architecture of thermosensitive copolymers bearing phosphonated moieties on their physical properties in water.** Alain Graillot*, Sophie Monge, Denis Bouyer, Catherine Faur, Jean-Jacques Robin

1715 – 1730 M1.21 - **Incorporating Indazoles into the Dopamine Self-Polymerisation System.** Anthony Michael Granville*, Matthew Peterson, Solomon Le-Masurier, Khoon Lim, Penny Martens

1730 – 1745 M1.22 - **Responsive macromolecular assemblies: sol / gel transition under pH and temperature control.** Elodie Siband, Yvette Tran, Dominique Hourdet*

1745 – 1800 M1.23 - **Functional polymers for the design of nanoengineered polymer capsules.** Kristian Kempe*, Ka Fung Noi, Sher Leen Ng, Frank Caruso

1800 – 1815 M1.24 - **Diffusion in Precisely-Structured Hydrogels of NIPAM.** Huey Wen Ooi, Hui Peng, Kevin S. Jack, Andrew K. Whittaker*

Polymers in Therapy and Imaging Meeting Room 2
Chair: Dr Angus Johnston

1600 – 1630 M2.17 / KN 10 - **Smart polymer-protein hybrids and sugar-responsive micelles.** Jennifer N. Cambre, Debashish Roy, Abhijeet P. Bapat, Hongmei Li, Ming Li, Priyadarsi De, Brent S. Sumerlin*

1630 – 1645 M2.18 - **Macromolecular Ruthenium(III) Chemotherapeutics.** Bianca M. Blunden*, Hongxu Lu, Aditya Rawal, Martina H. Stenzel

1645 – 1700 M2.19 - **Polymers for Imaging and Therapy.** Kristofer J Thurecht*, Cameron Alexander, Andrew K Whittaker, Nathan RB Boase, Daniel Coles

1700 – 1715 M2.20 - **Intracellular Nitric Oxide Delivery From Stable NO-Polymeric Nanoparticle Carriers.** Hien T.T. Duong, Zulkamal M. Kamarudin, Rafael B. Erlich, Yang Li*, Mathew W. Jones, Maria Kavallaris, Cyrille Boyer, Thomas P. Davis

1715 – 1730 M2.21 - **Study Of The Responsive Properties of Porous Silicon – Responsive Polymer Composites With Applications in Drug Delivery.** Roshan Vasani*, Nicolas H. Voelcker

1730 – 1745 M2.22 - **Enhanced cellular uptake of nanoparticles by synthetic peptides and proteins.** Martina Stenzel*, Yoseop Kim, Hongxu Lu, Yanyan Jiang

1745 – 1800 M2.23 - **pH–Responsive Star Polymer Nanoparticles as Selective 19F MRI Contrast Agents.** Kewei Wang*, Kristofer J. Thurecht, Hui Peng, Andrew K. Whittaker

1800 – 1815 M2.24 - **Magnetic Nanoparticles as Dual Chemotherapeutic Delivery and MRI Contrast Agent.** Johan Sebastian Basuki*, Hien Duong, Lars Esser, Maria Kavallaris, Thomas Paul Davis, Cyrille Boyer

Patterning and Photosensitive Polymers Meeting Room 3
Chair: Prof Paul Dastoor

1600 – 1630 M3.17 / KN 11 - **Photocontrollable Liquid Crystalline Polymer Actuators.** Zhen Jiang, Jiu-an Lv, Ming Xu, Fuyou Li, and Yanlei Yu*

1630 – 1645 M3.18 - **Bottom Up / Top Down High Resolution Lithography Utilizing Block Bottle Brush Polymers.** James W. Thackeray*, Peter Trefonas, Guorong Sun, Sangho Cho, Corrie Clark, Stanislav V. Verkhoturov, Michael J. Eller, Ang Lee, Adriana Pavía-Jiménez, Emile A. Schweikert, Karen L. Wooley

1645 – 1700 M3.19 - **Behaviour of Lamellae Forming Block Copolymers Under Nanoconfinement: Implications for Topologically Guided Self Assembly of sub-10 nm Features.** Idriss Blakey*, Imelda Keen, Han-Hao Cheng, Anguang Yu, Kevin S. Jack, Andrew K. Whittaker

1700 – 1715 M3.20 - **Light Responsive Lyotropic Liquid Crystals.** Shuhua Peng, Qipeng Guo, Patrick G. Hartley, Timothy C. Hughes*

1715 – 1745 M3.21 / ET 2 - **Modelling Nano-scale Structure and Energy Transfer in Conjugated Polymers.** David M. Huang*, Kyra N. Schwarz, Ming Chiu, Patrick C. Tapping, Scott N. Clafton, Tak W. Kee

1745 – 1815 **Additional Question Time**

Polymers in Industry and Translational Research Meeting Room 1
Chair: A/Prof Derek Irvine

1600 – 1630 M4.17 - **RAFT – the development of a Polymer Platform Technology for National Development and International Impact.** Megan L. Fisher, Gregory W Simpson*

1630 – 1645 M4.18 - **TenasiTech - Development of a nanotech platform for medical and industrial applications.** Céline Chaléat*, Darren J Martin

1645 – 1700 M4.19 - **Exemptions to infringement : experimental use and regulatory approvals.** Richard Grant*

1700 – 1715 M4.20 - **Polyhydroxyalkanoates from industrial wastes and mixed cultures: Experience moving from the laboratory to technology prototyping.** Bronwyn Laycock*, Alan Werker, Monica Arcos, Steven Pratt, Peter Halley, Paul Lant

1715 – 1730 M4.21 - **Leahy-Smith America Invents Act: Implications for Australian Inventors.** Donald Lewis*

1730 – 1745 M4.22 - **Rapid Translation of Next Generation Composite Materials Through Multi-Scale Modeling.** Jeffrey S Wiggins*

1745 – 1815 M4.23 - **Industrial Polymer Research: A 20 year journey from SME's to Multinationals to Spinouts, developing Packaging, Scaffolds, Drug Polymer Conjugates and Renewable Chemicals and Polymers.** Mike O'Shea*, Gary Peeters, Graeme Moad, Louis Kyaratzis, Yen Truong, Mark Hickey, Florian Graichen, Heng Taing, Justine Jeffery, Ben Leita, Ramon Tozer, Simona Lavric

Poster Session Hall 1

1815 – 1945 **Refreshments will be served during the Poster Session**

Plenary Session Waterfront Room 2/3
Chair: A/Prof Idriss Blakey

0820 – 0830 **Welcome and housekeeping**

0830 - 0930 PL 4 - **Novel solid state electrolytes - enabling future energy technologies.** Maria Forsyth*, Patrick C Howlett, Jenny Pringle, Wren Greene, Douglas R. Macfarlane

0930 - 1000 **Morning Refreshments and Trade Exhibition** - Hall 1

Bio-functional and Responsive Polymers Waterfront Room 2/3
Chairs: Prof Mitsuo Sawamoto & Prof Anna Balazs

1000 – 1030 T1.1 /KN 12 - **Tailor-made Polymers for Bacteria-Responsive Wound Dressings: Fabrication, Characterization and Enzyme-Triggered Release.** Simon Haas, Katrin-Stephanie Tücking, Stephan Handschuh, Holger Schönherr*

1030 – 1045 T1.2 - **Enzyme mimics.** Luke A. Connal*, Ashley Davalos, Eric Pressly, Craig J. Hawker

1045 – 1100 T1.3 - **Well-defined Synthetic Transmembrane Pores using Cyclic Peptide–Polymer Nanotubes.** Maarten Danial*, Sébastien Perrier, Katrina A. Jolliffe

1100 – 1115 T1.4 - **Gelling of a short designed α-helical peptide under physiological conditions.** Annette F. Dexter*, Nicholas L. Fletcher, Kevin S. Jack

1115 – 1130 T1.5 - **Multi stimuli-responsive bio-mimetic protein-polymers and their functional conjugates.** Naba K. Dutta*, Rajkamal Balu, Namita R. Choudhury, Christopher M. Elvin, Anita J. Hill

1130 – 1145 T1.6 - **Peptide-Based Complex Macromolecular Architectures: A Platform Technology in Polymer Therapeutics.** Shu Jie Lam*, Adrian Sulistio, Anton Blencowe, Greg G Qiao

1145 – 1200 T1.7 - **Photo-responsive reversible polymeric materials using dynamic covalent bonds.** Priscilla Johnston, Kei Saito*

1200 – 1215 T1.8 - **Role of Environment on the Secondary Structure of a Biomimetic Protein-based Elastomer.** Jasmin Whittaker*,Namita R. Choudhury, Naba Dutta, C. M. Elvin, A. J. Hill

Platforms for Enhanced Biological Interactions Meeting Room 2
Chair: Prof Kristi Anseth

1000 – 1030 T2.1 / KN 13 - **Hybrid gelation processes in enzymatically gelled gelatin: impact on nanostructure, macroscopic properties and cellular response.** Cécile A Dreiss*

1030 – 1045 T2.2 - **Photodegradable microsphere templates for creating model alveoli in PEG hydrogels.** Katherine J. R. Lewis*, Mark W. Tibbitt, Kristi S. Anseth

1045 – 1100 T2.3 - **Nano-bottlebrush Electrospun Scaffolds: Decoupling Cellular Cues in 3D.** Andrew E. Rodda*, Francesca Ercole, Laurence Meagher, David R. Nisbet, Kevin E. Healy, John S. Forsythe

Symposium Program
TUESDAY 9 July 2013

1100 – 1115 T2.4 - **Synthesis, characterization and properties of biocompatible poly(glycerol sebacate) pre-polymer and gel.** Yuan Li*, Wayne D Cook, Cornelis Moorhoff, Wen-Chao Huang, Qi-Zhi Chen

1115 – 1130 T2.5 - **Presentation of bioactive signals to cells via self-assembling peptides.** Alexandra L. Rodriguez*, Richard J. Williams, Clare L. Parish, David R. Nisbet

1130 – 1145 T2.6 - **Preparation of Superabsorbent Cross-linked Chitosan Hydrogels by Various Type of Aldehyde Crosslinkers and Their Swelling Behaviour.** Emil Budianto*, Siti Prilia Muthoharoh, Noverra M. Nizardo

1145 – 1215 T2.7 - **Surface Patterning for Biointerface Applications based on Colloidal Crystals.** Peter Kingshott*

Latest Developments In Polymer Synthesis Meeting Room 3
Chairs: Prof Per Zetterlund & Dr James Blinco

1000 – 1030 T3.1 / KN 14 - **Novel Developments in Controlled Radical and Cationic Polymerizations via Dual Mechanisms.** Masami Kamigaito*, Kotaro Satoh

1030 – 1045 T3.2 - **Synthesis of Novel Trithiocarbonate and Allyl Sulfides and their Application into the Advances in Covalent Adaptable Networks.** Christopher R. Fenoli*, Christopher N. Bowman

1045 – 1100 T3.3 - **Quasi-block copolymer libraries on demand via sequential RAFT polymerization in an automated parallel synthesizer.** Carlos Guerrero-Sanchez*, Lisa O'Brien, Colin Brackley, Daniel Keddie, Simon Saubern, John Chiefari, Graeme Moad

1100 – 1115 T3.4 - **The influence of domain segregation in ionic liquids upon RAFT polymerisation mechanism.** Simon Puttick*, Adrienne L. Davis, Kevin Butler, Derek J. Irvine, Peter Licence, Kristofer J. Thurecht

1115 – 1130 T3.5 - **RAFT polymerization of phosphonated-based monomers: synthesis of innovative (co)polymers and applications.** Sophie Monge*, Alain Graillot, Benjamin Canniccioni, Ghislain David, Jean-Jacques Robin

1130 – 1145 T3.6 - **RAFT Polymerization of N-Vinyl Carbazole – An Intermediate Reactivity Monomer.** Graeme Moad*, Daniel Keddie, Carlos Guerreo-Sanchez

1145 – 1200 T3.7 - **Tackling the Cross-termination Challenge in Radical Polymerization Through the RAFT-CLD-T Technique.** Pieter Derboven*, D. R. D'hooge, M.-F. Reyniers, G. B. Marin, C. Barner-Kowollik

1200 – 1215 T3.8 - **Novel RAFT-derived poly(fluorovinyl esters): Controlled synthesis and enhanced CO2-philicity.** Mathias Destarac*, Etienne Girard, Jean-Daniel Marty, Thierry Tassaing

1215 – 1315 **Lunch and Trade Exhibition** - Hall 1

Networks, Blends and Physical Properties Waterfront Room 2/3
Chairs: A/Prof Bronwyn Fox & Prof Rob Burford

1315 – 1345 T1.9 / KN 15 - **Using Chemical Reactions to Control Polymer Network Shape, Topography, and Behavior.** Christopher N. Bowman*, Christopher J. Kloxin, Timothy F. Scott, Devatha P. Nair, Neil B. Cramer, Wayne D. Cook

1345 – 1400 T1.10 - **Blends of thermoplastics and thermosetting monomers.** Wayne D. Cook*, Arjulizan Rusli, George G. Liang

1400 – 1415 T1.11 - **Block Ionomer-Toughened Epoxy Thermosets.** Qipeng Guo*, Shuying Wu, Yiu-Wing Mai

1415 - 1430 T1.12 - **Preparation of ordered monolithic structures by unidirectional freezing and radical polymerisation.** Emily F. Hilder*, R. Dario Arrua, Katharina Dihm

1430 – 1445 T1.13 - **Dissipation and recovery of Nano-hybrid hydrogels.** Severine Rose, G. Agoda-Tandjawa, Testuharu Narita, Dominique Hourdet, Alba Marcellan*

1445 – 1500 T1.14 - **The Effect of Matrix Polarity on the Properties of Poly(o-methoxyaniline) – EVA Blends.** Xiao Wang*, Ralph P. Cooney, Sudip Ray, Paul A. Kilmartin and Jianyong Jin

1500 – 1515 T1.15 - **Tough and self repairing ionic-covalent entanglement network hydrogels of gellan gum and gelatin.** Damian M. Kirchmajer*, Marc in het Panhuis

1515 – 1530 T1.16 - **Behaviour of pH-responsive sterically-stabilised latex particles at the air-water interface.** Olivier J. Cayre*, Peter Renvoize, Mark D'Souza Mathew, M. Soyeb Manga, Timothy N. Hunter, Simon Biggs

Platforms for Enhanced Biological Interactions Meeting Room 2
Chair: A/Prof Cyrille Boyer

1315 – 1345 T2.9 / KN 16 - **Emulsion-templated Scaffolds for Tissue Engineering and 3D Cell Culture.** Neil R Cameron*

1345 – 1400 T2.10 - **Photodegradable gelatin methacrylate hydrogels for improved cardiomyocyte alignment.** KM Tsang, N Annabi, F Ercole, RA Evans, H Thissen, A Khademhosseini, John Forsythe*

1400 – 1415 T2.11 - **An Injectable Hydrogel System Incorporating Free or Covalently-Bound Sulphated Polysaccharide for Intervertebral Disc Regeneration.** Jessica Frith*, Donna Menzies, Andrew Cameron, Darryl Whitehead, Stan Gronthos, Andrew Zannettino, Peter Ghosh, Justin Cooper-White

1415 - 1430 T2.12 - **Characterisation of polyelectrolyte complexes and their distribution in an alginate matrix.** Robyn Aston*, Gwen Lawrie, Lisbeth GrØndahl

1430 – 1445 T2.13 - **Osteoblast Cytotoxicity Study of Plant-Derived Bio-Adhesive Polymer.** Shougo Kinugawa*, Siqian Wang, Shu Taira, Noriko Hiraishi, Daisaku Kaneko

1445 – 1500 T2.14 - **Synthesis and characterization of biodegradable graft copolymer PCL-g-Amylose.** Wanli Fu*, Peter J. Halley, Andrew K. Whittaker and Kristofer J. Thurecht

1500 – 1530 **Additional Question Time**

Latest Developments In Polymer Synthesis Meeting Room 3
Chairs: Prof Masami Kamigaito & Dr Grace Chan

1315 – 1345 T3.9 / KN 17 - **Sequence-controlled Polymers: Recent Progress and Promise.** Jean-François Lutz*

1345 – 1400 T3.10 - **Preparation of Amphiphilic Block Copolymers with Various Morphologies in one Pot Polymerization Reaction.** Bunyamin Karagoz*, Lars Essera, Cyrille Boyera, Tom Davisa

1400 – 1415 T3.11 - **Using Orbital Conversion to pH Switch Nitroxide Mediated Polymerization.** Michelle L. Coote*, Ganna Gryn'ova

1415 - 1430 T3.12 - **Equilibration of Trithiocarbonates During RAFT Polymerization.** Algi Serelis*

1430 – 1445 T3.13 - **One-Pot RAFT/"Click" Chemistry via Isocyanates.** Guillaume Gody*, Thomas Maschmeyer, Sébastien Perrier

1445 – 1500 T3.14 - **Thermally and Photochemically Induced Living Radical Polymerization with Organic Catalysts.** Atsushi Goto*

1500 – 1530 T3.15 / ET 3 - **Modular Design of Profluorescent Nitroxide-Based Sensor Materials.** Emily Simpson, Kathryn Fairfull-Smith, Steven Bottle, James Blinco*

1530 – 1600 **Afternoon Refreshments and Trade Exhibition** - Hall 1

Polymeric Composites and Nanocomposites Waterfront Room 2/3
Chairs: Prof Wayne Cook & Prof Chris Bowman

1600 – 1630 T1.17 - **Void reduction mechanisms in vibration assisted consolidation of fibre reinforced polymer composites.** Zbigniew H Stachurski*

1630 – 1645 T1.19 - **Graphene Oxide as a Novel Surfactant for the Preparation of Hybrid Polymer Nanoparticles.** Stuart C Thickett*, Siti Hajjar Che Man, Nur Yasmin Mohd Yusof, Michael R. Whittaker, Per B. Zetterlund

1645 – 1700 T1.20 - **Plasma polymers, nanocomposites and their applications.** Kostya Ostrikov*

1700 – 1715 T1.21 - **Hollow Polymer Particles by Nano-Templating.** Duc Nguyen*, Chris Such, Brian Hawkett

1715 – 1730 T1.22 - **One-Dimensional Hybrid Silica Nanowires and Nanotubes.** Markus Müllner*,Thomas Lunkenbein, Josef Breu, Frank Caruso, Axel H.E. Müller

1730 – 1745 T1.23 - **New surface treatments for carbon fibres to enhance fibre matrix adhesion in composites.** Claudia Creighton, Abdullah Kafi, Luke Henderson, Linden Servinis, Xiujuan Jane Dai, Zhiqiang Chen, Mickey Huson, Thomas Gengenbach, Jeff Wiggins, Bronwyn Fox*

1745 – 1800 T1.24 - **Preparation and characterisation of poly(2-hydroxyethyl methacrylate)-zeolite composite hydrogels.** Rohan Holmes, Ivan Yordanov, Robert Burford*, Tracey Hanley

1800 – 1815 T1.25 - **Hybrid Conducting Polymer-Carbon Nanotube Yarns.** Javad Foroughi*, G. M. Spinks, G. G. Wallace, R. H. Baughman

1815 – 1830 T1.26 - **Supramolecular coBioNanocomposites Incorporating Stereocomplexation.** John R Dorgan*, Birgit Braun, Rodolfo Sosa, Laura Hollingsworth

Platforms for Enhanced Biological Interactions Meeting Room 2
Chair: Prof Brent Sumerlin

1600 – 1615 T2.17 - **Anti-Bacterial Conducting Polymers in Blends, Fibres, Colloids and Layers.** Ralph Cooney*, Simon Swift, Jianyong Jin, Paul Kilmartin, Adeline Le Cocq, Sudip Ray, Marija Gizdavic-Nikolaidis, Karnika de Silva

1615 – 1630 T2.18 - **Promoting engraftment of transplanted neural stem cells in the brain using biofunctionalised scaffolds.** David R Nisbet*

1630 – 1645 T2.19 - **Using chitosan hydrogels to form biomimetic composites for artificial bone.** Natasha H Evans*, Kathryn McGrath

1645 – 1700 T2.20 - **On the importance of detailed surface characterisation of bioactive coatings.** Marek Jasieniak, Hardi Ys, Htwe Mon, Hans J Griesser*

1700 – 1715 T2.21 - **A facile approach to assemble PEG hydrogel particles.** Qiang Fu*, Jiwei Cui, Frank Caruso, Greg G. Qiao

1715 – 1730 T2.22 - **Macromolecular Ligands for Gadolinium MRI Contrast Agents: Effect of Polymer Architecture.** Yang Li*, Mariana Beija, Sophie Laurent, Luce vander Elst, Robert N. Muller, Hien T. T. Duong, Andrew B. Lowe, Thomas P. Davis, Cyrille Boyer

1730 – 1745 T2.23 - **Chitosan films grafted with peptides for stem cell culture.** Danielle Taylor*, Joel Thevarajah, Diksha Narayan, Catherine Lefay, Michael O'Connor, Patrice Castignolles, Marianne Gaborieau

1745 – 1800 T2.24 - **New antibacterial surfaces: biomimetic black-silicon with dragonfly wing nanostructures.** J Hasan, HK Webb, G Gervinskas, S Juodkazis, VK Truong, DE Mainwaring, X Duan, RN Lamb, V Baulin, GS Watson, JA Watson, Russell J Crawford*, EP Ivanova

1800 – 1815 T2.25 - **Bioinspired Phosphorylcholine Containing Polymer Flms with Silver Nanoparticles Combining Antifouling and Antibacterial Properties.** Adrian V. Fuchs*, Sandra Ritz, Constanze Walter, Sabine Pütz, Volker Mailänder, Katharina Landfester, Ulrich Ziener

1815 – 1830 **Additional Question Time**

Symposium Program
TUESDAY 9 July 2013

Latest Developments In Polymer Synthesis Meeting Room 3
Chairs: Prof Zi Chen Li & Dr Jean-Francois Lutz

1600 – 1630 T3.17 / ET 4 - **A Versatile Polymer Building Block Based On Trifluorovinyl Ethers Chemistry.** Jianyong Jin*

1630 – 1645 T3.19 - **Assembly of free-standing polypeptide films via the synergistic combination of hyperbranched macroinitiator, the grafting-from approach and intermolecular cross-chain termination.** Steven Harris-Wibowo*, Edgar H. H. Wong, Adrian Sulistio, Stefanie N. Guntari, Anton Blencowe, Frank Caruso, Greg G. Qiao

1645 – 1700 T3.20 - **Stereoregular cyclic poly(methyl methacrylate)s: synthesis, characterization and their unique supramolecular assemblies.** Jing Ming Ren*, Kotaro Satoh, Tor Kit Goh, Anton Blencowe, Kanji Nagai, Kenji Ishitake, Masami Kamigaito, Greg Guanghua Qiao

1700 – 1715 T3.21 - **Amphiphilic Micellar Films via ATRP-Mediated Continuous Assembly of Polymers.** Dr Edgar H H Wong*, Eun Hyung Nam, Martin P. van Koeverden, Stefanie N. Guntari, Steven Harris Wibowo, Anton Blencowe, Frank Caruso, Greg G. Qiao

1715 – 1730 T3.22 - **Conducting polymer macroinitiators for surface-initiated ATRP.** Lisa Strover*, Jenny Malmström, Olivia Laita,Nihan Aydemir, Jóhannes Reynisson, David E. Williams, Margaret Brimble, P. Rod Dunbar, Jadranka Travas-Sejdic

1730 – 1745 T3.23 - **Polypseudorotaxanes Made from Self-Assembly of γ-Cyclodextrins with Poly(N -isopropylacrylamide) End-capped Block Copolymers.** Lan Jiang, Lin Ye, Ai-ying Zhang, Zeng-guo Feng*

1745 - 1830 **Additional Question Time**

Student Night The Precinct Tavern

1930 – 2030 **Happy hour and drink specials available for students**

Plenary Session Waterfront Room 2/3
Chair: Prof Sébastien Perrier

0820 – 0830 **Welcome and housekeeping**

0830 - 0930 PL 5 - **Self-Organized Multicompartment Nanostructures From New Triblock Terpolymers.** Axel H E Müller*

0930 – 1000 **Morning Refreshments and Trade Exhibition** - Hall 1

Surfaces and Interfaces Waterfront Room 2/3
Chairs: Dr Georgina Such & A/Prof Erica Wanless

1000 – 1030 W1.1 / ET 5 - **Smart Polymer Capsules with Synergistic Response to Biological Stimuli.** Georgina K Such*, Kang Liang, Sylvia T. Gunawan, Sarah J. Dodds, Angus. P. R. Johnston and Frank Caruso

1030 – 1045 W1.2 - **Substrate-Independent Thermal Nanoimprint Lithography by Using Mussel-Inspired Adhesive Polymer Layers.** Hiroshi Yabu*, Yuta Saito, Masatsugu Shimomura, Yasutaka Matsuo

1045 – 1100 W1.3 - **Adhesion Improvement Of Poly(Dimethylsiloxane) Surface By Grafting Of Poly(Butyl Acrylate) Chains.** Omer Javed Chaudhary*, Jadranka Travas-Sejdic, Emilio Calius, John Kennedy

1100 – 1115 W1.4 - **A Universal Approach to Growing Biological Fouling Resistant Coatings from Polymeric Membrane Surfaces Using an Adhesive Polydopamine-Mimetic Initiator.** Amanda Ellis*, Kristina T Constantopoulos, Tawfiq Alghamdi, Dmitriy Khodakov, Elda Markovic, Milena Ginic-Markovic

1115 – 1130 W1.5 - **Chlorinated plasma polymers: "one-step" non-fouling polymer coatings.** Thomas D Michl*, Doran M, Valentin J, Vasilev K, Griesser HJ

1130 – 1145 W1.6 - **PDMS for Ethanol Pervaporation – A hydrophilic material?** Rowan Prangley*, Tony Vancov, Erica Smith, Chris Fellows

1145 – 1200 W1.7 - **Stimuli-responsive materials from genetically engineered Protein-polymer AN16.** Rajkamal Balu*, N. K. Dutta, N. R. Choudhury, R. E. Lyons, C. M. Elvin, R. Knott, A. J. Hill

1200 – 1215 **Additional Question Time**

Bio and Natural Polymers and the Environment Meeting Room 2
Chairs: Prof Bob Gilbert & Prof Neil Cameron

1000 – 1030 W2.1 / KN 18 - **Elaboration and properties of multiphase systems based on thermoplastic chitosan.** Prof Luc Avérous

1030 – 1045 W2.2 - **Biobased polymer processing.** Peter J Halley*, M Li, W-C Liu, RG Gilbert, F Xie, S Mateyawa, TM Nicholson, RW Truss

1045 – 1100 W2.3 - **Synthesis of glycerol-based oligomers: new materials and new applications.** Sophie Monge*, Phuoc Dien Pham, Vincent Lapinte, Sophie Monge, Yann Raoul, Jean-Jacques Robin

1100 – 1115 W2.4 - **Understanding starch degradation mechanism at multiple structural levels during extrusion.** Ming Li*, Jovin Hasjim, Fengwei Xie, Peter J. Halley, Robert G. Gilbert

1115 – 1130 W2.5 - **A Parameterized Model of Amylopectin Synthesis provides key insights into the Synthesis of Starch.** Alex Chi Wu*, Matthew K Morell, Robert G Gilbert

1130 – 1145 W2.6 - **The influence of starch amylopectin molecular structure on the native crystalline-amorphous lamellar structure.** Torsten Witt*, James Doutch, Elliot P. Gilbert, Robert G. Gilbert

1145 – 1215 W2.7 - **Hybridization of Chitosan and Inorganic Nanoparticles via Water-based and Mild Reaction Conditions.** Suwabun Chirachanchai*, Sutima Chatrabhuti, Jatesuda Jirawutthiwongchai

Latest Developments In Polymer Synthesis Meeting Room 3
Chairs: Dr Jianyong Jin

1000 – 1030 W3.1 / KN 19 - **Multicomponent Polymerization for New Polymer Synthesis.** Xin-Xing Deng, Lei Li, Yao-Zong Wang, An Lv, Fu-Sheng Du, Zi-Chen Li*

1030 – 1045 W3.2 - **Biomimetic radical polymerization in nanoreactors: Exploiting templating and compartmentalization.** Per B Zetterlund*, Ronan McHale, Stuart C. Thickett, Joseph P. Patterson, Rachel O'Reilly

1045 – 1100 W3.3 - **Synthesis of Hyperbranched Polymers via Thiol–Yne Photopolymerization.** Raphael Barbey*, Sébastien Perrier

1100 – 1115 W3.4 - **Nano Emulsion Polymerization of Acrylamide at Phase Inversion Point.** Zohreh Abdollahi*, M. Darestani, B. Hawkett, V. Gomes

1115 – 1130 W3.5 - **Inverse Miniemulsion Periphery RAFT Polymerization as a Versatile Tool to Synthesize Hollow and Loaded Polymeric Nanoparticles.** Martina Stenzel*, Robert H. Utama, Per B. Zetterlund

1130 – 1145 W3.6 - **Synthesis of Cyclic Polysulfides: Controlled Ring-Expansion Polymerization of Cyclic Tetrathioester with Thiirane.** Hiroto Kudo*, Yuki Takeshi

1145 – 1200 W3.7 - **RAFT Synthesis of CO2-responsive (Co)Polymers.** Jing Yang Quek*, Peter J. Roth, Thomas P. Davis, Andrew B. Lowe

1200 - 1215 **Additional Question Time**

1215 – 1315 **Lunch and Trade Exhibition** - Hall 1

Surfaces and Interfaces and Polymeric Composites
Waterfront Room 2/3
Chairs: Prof Naba Dutta & Dr Stuart Thickett

1315 – 1330 W1.9 - **"Click" Chemistry – a novel fabrication method for fabricating microfluidic devices using thiol-ene polymers.** Simon J M C Bou*, Amanda V. Ellis

1330 – 1345 W1.10 - **Modification of Carboneaous Nanomaterials using RAFT.** Jessirie Dilag, Amanda V Ellis*

1345 – 1400 W1.11 - **Coating Graphene Oxide via RAFT-Mediated Emulsion Polymerization.** Vien T. Huynh*, Duc Nguyen, Brian Hawkett

1400 – 1415 W1.12 - **Functional (Bio)Surfaces for Reversible Coatings.** Anja S. Goldmann*, Corinna Preuß, Thomas Tischer, Andreas Walther, Leonie Barner, Michael Bruns, Hans G. Börner, Christopher Barner-Kowollik

1415 -1430 W1.13 - **Self Healing Hybrid Coating for Harsh Environment.** Jason Yu, Adrian Guo, Ravindra Potrekar, Namita Roy Choudhury*, Naba Dutta

Bio and Natural Polymers and the Environment Meeting Room 2
Chair: A/Prof John Forsythe & Prof Suwabun Chirachanchai

1315 – 1345 W2.9 / KN 20 - **Biosynthesis-structure-property relations of hyperbranched glucose polymers.** Shang Chu, Robert G Gilbert*, Cheng Li, EnPeng Li, Seila Sar, Mitchell A Sullivan, Torsten Witt, Alex C Wu

1345 – 1400 W2.11 - **Stimuli responsive Elastin based Polymer Brushes as Biocompatible Nano Carriers.** Désirée Weller*, Jonathan R. McDaniel, Karl Fischer, Ashutosh Chilkoti, Manfred Schmidt

1400 – 1415 W2.12 - **A marine antifouling surface from bacterially biodegraded paraffin wax.** Anisul Asfar, Lachlan H. Yee*, Tim Charlton, Peter D. Steinberg

1415 -1430 W2.13 - **Novel renewable architectural coating.** Cameron Tristram*, Jenny Mason, Ian Sims, Bradley Williams and Simon Hinkley

1430 - 1450 **Afternoon Refreshments and Trade Exhibition** - Hall 1

Plenary Session Waterfront Room 2/3
Chair: Prof Greg Qiao

1450 - 1550 PL 6 - **Precision Radical Polymerization: Catalysis and Functional Polymers.** Mitsuo Sawamoto*

1550 – 1600 **Symposium Conclusion**

Symposium Dinner Skycity Darwin

1830 – 1100 **Dinner and beverages served**

Synthetic polymers for pharmaceutical applications

Cameron Alexander,*[,a] Francisco Fernandez-Trillo,[a] Johannes Magnusson,[a] Aram Saeed and Sebastian Spain.[a]

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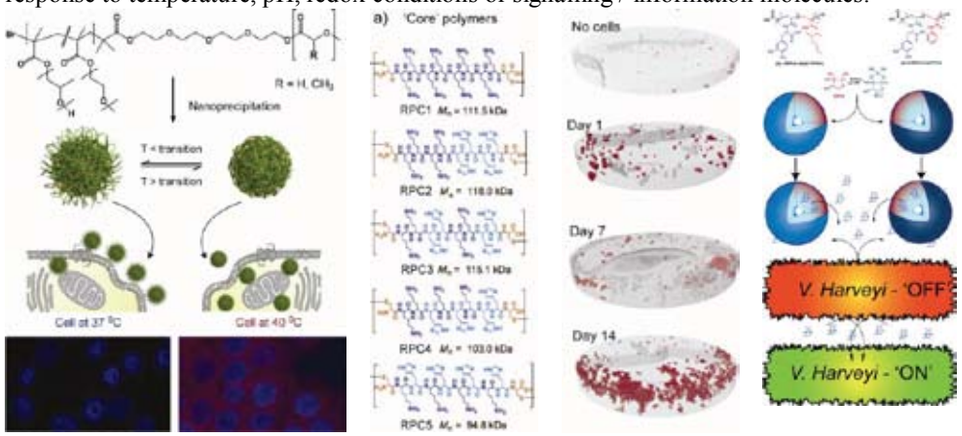
Synthetic polymers have found a variety of uses in the biomedical context, ranging from implant materials following surgery, through to carriers for therapeutic agents. Our interests in polymers for pharmaceutical applications include synthesising new materials as drug, gene and cell delivery agents,[1-3] and also polymers which can interfere in cell signalling processes.[4]

A common feature for these polymers is their ability to exhibit different conformations or architectures, either through specific synthetic constructions, or response to an external stimulus. As a consequence, the polymers can bind a drug or cell under one set of conditions, then release their cargo when the external environment changes or a stimulus is applied. A key focus is the tuning of polymer behaviour to changes in biological surroundings which are manifest in disease. Accordingly we have prepared polymers that alter their function in response to temperature, pH, redox conditions or signalling / information molecules.



a) Thermoresponsive nanoparticles b) Bioreducible polypeptides c) Cell growth in thermogelling polymer colloids d) Control of bacterial Quorum Sensing

The talk will feature our recent data on a range of polymers designed for biomedical applications.

References

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2. Soliman, M.; Nasanit, R.; Abulateefeh, S. R.; Allen, S.; Davies, M. C.; Briggs, S. S.; Seymour, L. W.; Preece, J. A.; Grabowska, A. M.; Watson, S. A.; Alexander, C., *Molecular Pharmaceutics* **2012,** *9* (1), 1-13.
3. Wang, W.; Liang, H.; Cheikh Al Ghanami, R.; Hamilton, L.; Fraylich, M.; Shakesheff, K. M.; Saunders, B.; Alexander, C., *Advanced Materials* **2009,** *21* (18), 1809-1813.
4. Xue, X.; Pasparakis, G.; Halliday, N.; Winzer, K.; Howdle, S. M.; Cramphorn, C. J.; Cameron, N. R.; Gardner, P. M.; Davis, B. G.; Fernandez-Trillo, F.; Alexander, C., *Angewandte Chemie-International Edition* **2011,** *50* (42), 9852-9856.

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Personal History:

Professor Alexander received degrees (BSc and PhD) in Chemistry from the University of Durham, UK and carried out post-doctoral research at the Melville Laboratory for Polymer Synthesis, University of Cambridge. He is a Fellow of the Royal Society of Chemistry and has published more than 120 refereed articles. Research in his group centres on the synthesis of responsive/'smart' materials for biomedical applications. Recent papers have focused on cell signal recognition, diagnostics and cell targeting (*Angew Chem Int Ed*. **2011** *50, 9852 –9856. J. Am. Chem. Soc.* **2010**, *132 (*15), 5336–5337*; Adv. Mater* **2009** *21*(18), 1809-1813, *Angew Chem Int Ed*. **2008** *47* (*26)*, 4847-4850, *J. Am. Chem. Soc.* **2008**, *130* (33), 10852 - 10853), drug and gene delivery (*Mol. Pharmaceutics* **2012**, *9 (1),* 1–13.*J. Control. Release* **2012** *158,* (3), 479–486. *Bioconjugate Chem.* **2011,** *22* (2), 156-168)., and polymer-biopolymer conjugates (*Polymer Chem.* **2011** *2,* 1567-1578, *Bioconjugate Chem.* **2010** *21,* 671–678).

Professor Alexander is the Director of the £2.5 million EPSRC Centre for Doctoral Training in Targeted Therapeutics and Formulation Sciences, a partnership between the University of Nottingham, University College London and seven leading pharmaceutical companies. He also is Principal Investigator for the UK component of the Erasmus Mundus Joint Doctorate (NanoFar) in Nanomedicine

Reconfigurable assemblies of active, auto-chemotactic gels

Pratyush Dayal [1], *Olga Kuksenok* [1] *and Anna C. Balazs* [1]

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Species ranging from single-cell organisms to social insects can undergo auto-chemotaxis, where the entities move towards a chemo-attractant that they themselves emit. This mode of signaling allows the organisms to form large-scale structures, with amoebas and *E* coli self-organizing into extensive multi-cellular clusters and termites constructing macroscopic mounds. Notably there are few equivalents of such auto-chemotactic driven assembly in the synthetic world. While researchers have devised a range of nano- and micro-scopic self-propelled particles, hardly any exhibit auto-chemotaxis that leads to the formation of extended structures. Though recent theoretical models provide insight into the auto-chemotaxis of a self-propelled walker and active Brownian particles, these studies provide few guidelines for synthesizing specific materials that display auto-chemotactic self-organization. The latter materials would open new routes for dynamic, reconfigurable self-assembly, where self-propelled elements communicate with neighboring units and thereby actively participate in constructing the final structure. Herein, we use computational modeling to show that millimeter-sized polymer gels can display such self-sustained, auto-chemotatic behavior. In particular, we demonstrate that gels undergoing the self-oscillating Belousov-Zhabotinsky (BZ) reaction not only respond to a chemical signal from the surrounding solution, but also emit this signal and thus, multiple neighboring gel pieces can spontaneously self-aggregate into macroscopic objects. These findings indicate that BZ gels can undergo a form of "self-recombining": if a BZ gel is cut into distinct pieces and the pieces are moved relatively far apart, then their auto-chemotactic behavior drives the parts to move autonomously and recombine into a structure resembling the original, uncut sample. We also show that the gels' coordinated motion can be regulated by light, allowing us to achieve selective self-aggregation and control over the shape of the gel aggregates, as well as reconfiguration of the entire structure.

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Dynamically Tunable Hydrogels and Their Biological Application

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Methods for culturing mammalian cells in a biologically relevant context are increasingly needed to study cell and tissue physiology, expand and differentiate progenitor cells, and to grow replacement tissues for regenerative medicine. Two-dimensional culture has been the paradigm for *in vitro* cell culture; however, evidence and intuition suggest that cells behave differently when they are isolated from the complex architecture of their native tissues and constrained to petri dishes or material surfaces with unnaturally high stiffness, polarity, and surface to volume ratio. As a result, biologists are often faced with the need for a more physiologically relevant 3D culture environment, and many researchers are realizing the advantages of hydrogels as a means of creating custom 3D microenvironments with highly controlled chemical, biological and physical cues. Further, the native ECM is far from static, so ECM mimics must also be dynamic to direct complex cellular behavior. In general, there is an un-met need for materials that allow user-defined control over the spatio-temporal presentation of important signals, such as integrin-binding ligands, growth factor release, and biomechanical signals. Developing such hydrogel mimics of the ECM for 3D cell culture is an archetypal materials engineering problem, requiring control of numerous properties on multiple time and length scales important for cellular functions. New materials systems have the potential to significantly improve our understanding of how cells receive information from their microenvironment and the role that these dynamic processes may play in controlling the stem cell niche to cancer metastasis. This talk will illustrate our recent efforts to advance hydrogel chemistries for 3D cell culture and dynamically control biochemical and biophysical properties through orthogonal, photochemical reaction mechanisms[1-4]. These photoactive hydrogels afford unique user-defined manipulation of the extracellular microenvironment in real time, allowing dynamic for the study and manipulation of cell behavior (**Fig. 1**).

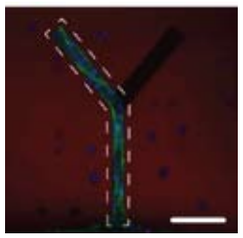

Fig. 1 Directed cell motility within patterned hydrogels. A fibrin clot containing NIH3T3 fibroblasts was encapsulated within a click hydrogel formulation. Chemical channels of RGD, a cell-adhesive fibronectin motif, as well as physical channels of arbitrary shape were created radially from the clot. The combination of having physical space to spread, as well as chemical moieties to attach, were found to be required to direct cell motility. By day 10, cells were found to migrate only down physical channels that were functionalized with RGD. In particular, the cell outgrowth was controlled in the presence of encapsulated human mesenchymal stem cells and confined to branched photodegraded channels that were functionalized with RGD. The regions of RGD-functionalization are depicted by dashed polygons. The hydrogel is shown in red, F-actin green, and cell nuclei blue. Scale bars = 100 μm. [modified from (1)].

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Novel solid state electrolytes - enabling future energy technologies

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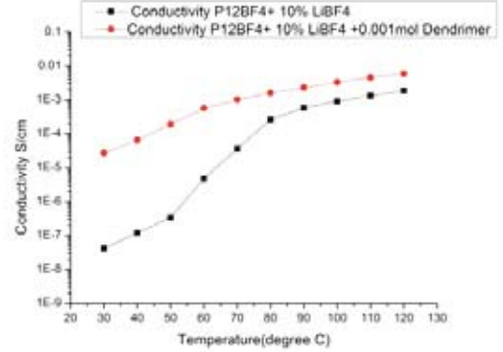
Significant progress has been made, in recent years, in the development of solid state ionic conductors based on polymer electrolytes, polymer gels, organic ionic plastic crystal materials and composites, driven by a continued need for high conductivity solid state electrolytes for a range of electrochemical devices. The research in this field covers many aspects including synthesis of new materials, fundamental understanding of the structural and transport properties in these materials in both the pure state and as gels or composites, and the development of these materials as electrolytes in devices such as lithium batteries, sodium batteries, dye sensitised solar cells and fuel cells. We will discuss the history and the advances of a number of novel solid electrolytes and their future prospects in solid state device applications.

Some examples will include the design of new sodium ion conducting polymer electrolytes based on polyelectrolyte copolymers and their self-plasticization by quaternary ammonium cations, new composite materials based on organic ionic plastic crystals (OIPC) and dendrimers (Figure 1) as well as OIPC/ polymer fiber electrospun mats. These latter composite electrolytes are easily formed into thin, flexible and mechanically robust films which can have desirable properties for device applications.

Figure 1 An SEM image (upper) of an organic ionic plastic crystal composite based on ethyl, methyl pyrrolidinium tetrafluoroborate and a dendrimer (hyperbranched bis MPA polyester-64-hydroxyl, generation 4) composite and ionic conductivity (below) of the composite material compared with the pure OIPC. A significant enhancement in conductivity can be observed.



Self-Organized Multicompartment Nanostructures From New Triblock Terpolymers

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Compartmentalization of nanostructures is an important issue since different compartments can have different functions, e.g. loading of different payloads, such as drugs or inorganic nanoparticles. The self-assembly of triblock terpolymers (also known as ABC triblock copolymers) in solution and in the bulk are ideally suited for such a task. A typical example is polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate). Compartmentalization can occur either in the corona or in the core.

We have prepared corona-compartmentalized nanoparticles (Janus spheres, cylinders, or disks) by crosslinking domains in the bulk nanostructures of triblock terpolymers. These Janus micelles have superior properties as interfacial agents, as stabilizers in emulsion polymerization, or as compatibilizers of polymer blends.[1]

We present a flexible route for the directed self-assembly of triblock terpolymers into multicompartment micelles (MCMs) of different shapes and sizes, simply by choosing the right solvent conditions and solvent sequences. These MCMs can have spherical shapes, like hamburgers, clovers, or footballs. However, we can also trigger the shapes in a way that they form worm-like structures with alternating compartments of, e.g. polystyrene and polybutadiene, with a corona of PMMA. The different compartments can be loaded with various nanoparticles.[2]

We also demonstrate a novel, solution-based approach to Janus micelles by crosslinking the patches on a spherical MCM. In contrast to our former bulk morphology approach this new approach for the first time provides soft Janus micelles with adjustable Janus balance, i.e. adjustable fraction of polymer chains forming one face.[3] This balance is important, e.g., for their use as dispersants of carbon nanotubes.

A new miktoarm-star triblock terpolymer, having one arm each of polybutadiene, quaternized poly(2-vinylpyridine) and poly(*tert*-butyl methacrylate (μ-BVT) forms unusual assemblies in water. Depending on the nature of the counterion of the quaternized 2-vinylpyridine units, a multitude of assemblies is formed, starting from micelles over cylinders to woodlouse-shaped assemblies of lamellae (**Fig. 1**).[4]

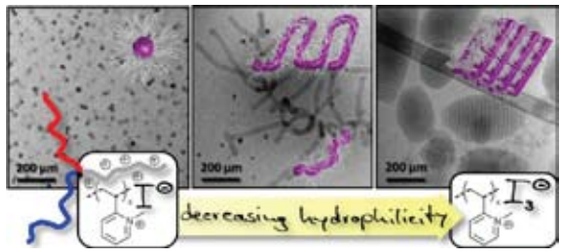

Figure 1. Self-assembeld structures of a μ-BVT miktoarm star terpolymers in water in dependence of the counterion

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Precision Radical Polymerization: Catalysis and Functional Polymers

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Precision or living radical polymerization has been finding a steady and productive progress, to provide versatile and user-friendly methodologies of polymer synthesis open to a wide range of scientists working beyond polymer chemistry. Metal-catalyzed living radical polymerization (LRP) is not an exception (**Fig.1**),[1] and this lecture will highlight some of the recent developments in our laboratories:

(A) Generalization of "dormant species" in precision control of chain-growth polymerization;
(B) "Green" catalysts based on Ru(II) and Fe(II): super-active, abundant, and functionality-tolerant (**Fig.2**);[1]
(C) "Core-functionalized" star polymers: synthesis, catalysis, and molecular recognition (**Fig.3**);[2]
(D) "Sequence-controlled" multifunctional macromolecules: new strategies for sequence regulation (**Fig.4**).[3]

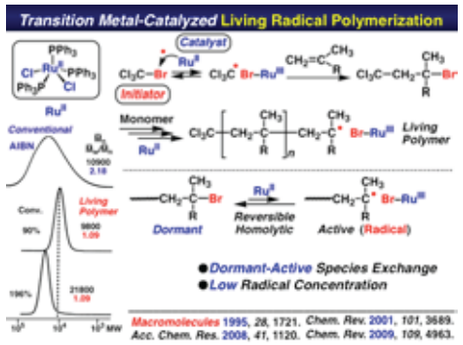

Figure 1. Metal-catalyzed LRP.

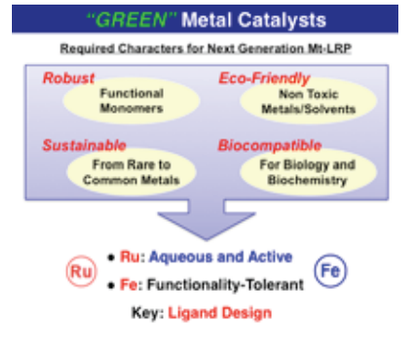

Figure 2. "Green" catalysts for future LRP.

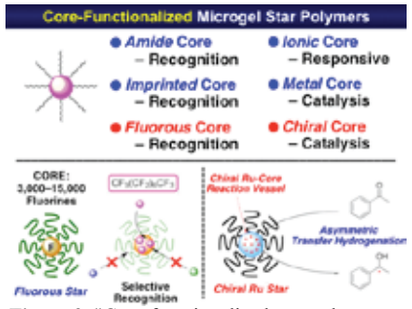

Figure 3. "Core-functionalized star polymers.

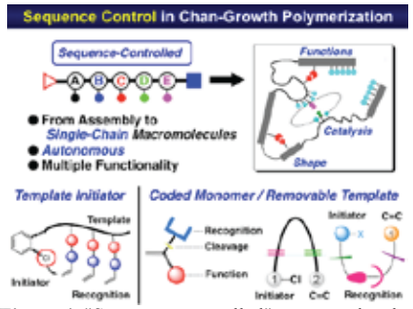

Figure 4. "Sequence-controlled" macromolecules.

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High Speed Video Observation of Giant Pickering Emulsion and Colloidosome Droplet Interaction and Stability

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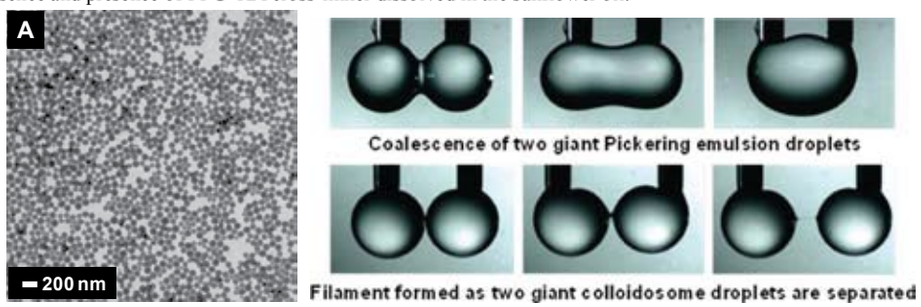
The interactions of two 2-mm pendant oil droplets grown in the presence of an aqueous solution of latex particles was observed using a high-speed video camera on a homebuilt coalescence rig.[1] The coalescence behaviour was monitored as a function of oil type (n-dodecane versus sunflower oil) and adsorbed latex type (poly(glycerol monomethacrylate)-stabilised polystyrene (**Fig.1A**)[2] versus lightly cross-linked 2-(tert-butylamino)ethyl methacrylate)[3]. Both latexes had previously been reported to be effective Pickering emulsifiers, with the pH-responsive microgel character of the latter leading to rapid demulsification upon exposure to acid. This pH response has been characterised here on giant Pickering emulsion droplets using the coalescence rig. Colloidosomes had been reported as formed by both latexes in the presence of an oil-soluble cross-linker [tolylene 2,4-diisocyanate-terminated poly(propylene glycol)]. The impact of this cross-linking reaction on droplet stability was also followed on the coalescence rig (**Fig.1B**).

The damping coefficient of the coalescing n-dodecane droplets was found to increase in the presence of the latex, confirming particle adsorption.[4] Coalescence times increased when the oil phase was changed from n-dodecane to sunflower oil, because of the much higher viscosity of the latter oil. In addition, increasing the adsorbed $PGMA_{50}$-PS latex particle size led to longer coalescence times because of the greater distance separating the oil droplets. Addition of PPG-TDI to the oil phase reduced the interfacial elasticity and ultimately prevented coalescence through the formation of giant colloidosomes which were found to be stable in contact for several hours without undergoing coalescence. Finally, evidence for cross-linker diffusion from one pendant droplet to another was indicated by a visible filament connecting the two droplets upon retraction.

Figure 1. (A) Transmission electron microscopy image of 135 nm $PGMA_{50}$-PS latex particles prepared by aqueous emulsion. (B) High speed video images of latex coated sunflower oil droplets in aqueous solution in the absence and presence of PPG-TDI cross-linker dissolved in the sunflower oil.



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Block Copolymer Drug Delivery Vehicles from a Combination of RAFT and Anionic Polymerization Routes

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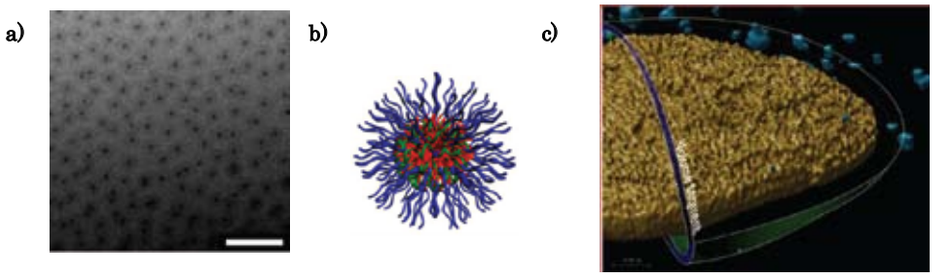
My research group is focused on the development of polymers for the delivery of drugs, nucleic acids, and peptides. The intracellular delivery of nucleic acids offers unprecedented promise for revolutionizing biomedical research and novel drug development. Likewise, small molecule drug and vaccine development could significantly benefit from new materials that aid targeted delivery. However, the polymeric delivery vehicle plays a central yet elusive role in dictating the efficacy, safety, mechanisms, and kinetics of transport 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, drugs, and peptides into nanocomplexes 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 and anionic polymerization methods, allowing us to create a variety of block copolymer architectures with saccharides and functional groups of diverse chemistries (hydrophobic, cationic, and anionic units) in a highly controlled manner. To examine the intracellular mechanisms of delivery, we have utilized live cell confocal microscopy imaging techniques to examine the intracellular trafficking of the vehicles, which allows us to observe nanocomplex movement in a spatial and temporal manner.

Figure 1. a) CryoTEM image of polymeric micelles formed with carbohydrate-based block copolymers (scale bar = 100nm). b) Depiction of the core-shell structure of the nanocomplexes (polymerized pendant carbohydrates form the shell in blue). c) 3D image of the polymeric nanocomplexes (blue) trafficking near the nucleus (yellow) in a HeLa cell.



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Solution processable poly(dendrimers) for organic light-emitting diodes

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The discovery that phosphorescent materials can give rise to efficient organic light-emitting diodes (OLEDs)[1] has caused an explosion of interest in the development of new materials. The majority of the effort has focused on small molecule emitters, which are processed by evaporation under high vacuum. Although this has been highly successful there are now concerns that the evaporation process might lead in some cases to the deposition of degraded materials. In addition, processing by evaporation is best suited to small devices.

To take phosphorescent materials into the realm of large area displays and lighting it would be advantageous to have solution processable materials. Phosphorescent dendrimers in which the phosphorescent emitter is encapsulated within a dendritic architecture has proved to be a very effective method for forming thin films for monochrome emission. Simple devices containing two layers, the emissive dendrimer layer and an electron transport layer, have been reported to have external quantum efficiencies of 13% at usable brightnesses.[2] However, the viscosity of such materials is not sufficient for them to be processed by methods such as ink-jet printing.

To overcome this limitation we have been developing phosphorescent poly(dendrimers). We have found that unlike previously reported copolymers containing small phosphorescent complexes it is possible to form homopolymers in which every 'monomer unit' has a phosphorescent moiety attached (e.g., **1**[3] and **2** in **Fig. 1**). In the homopolymers with simple side-chain complexes the close proximity of the phosphorescent emitters was found not to quench the luminescence in solution significantly, although in the solid state the intermolecular interactions do lead to a dramatic reduction in the photoluminescence quantum yield. By using dendritic emitters attached to the polymer backbone (e.g., **2** in Fig. 1) it was found that the homopolymer could be easily solution processed to give devices with good performance.[4] In this presentation I will discuss the design principles for and synthesis of poly(dendrimers), as well as their photophysical and device performance.

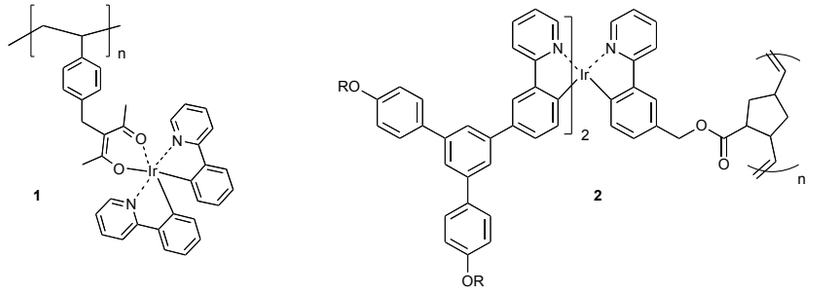

Figure 1: Structures of solution processable phosphorescent homopolymers, **1)** a polymer containing side chains comprised of a small molecule iridium(III) complex and **2)** a poly(dendrimer) with side-chains comprised of iridium(III)-cored dendrimers; R = 2-ethylhexyl.

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Burn is a Fellow of the Australian Academy of Science, Fellow of the Royal Society of Chemistry, and Honorary Professor at the Nanjing University of Posts and Telecommunications (China). He has published ≈250 papers and has an H-factor of 51. Burn has been involved in significant commercialization activities, developing technologies for five start-up entities including Cambridge Display Technology Ltd, Opsys Ltd, Arborescent2 Ltd, OZCOPE, and Scaffvac Therapeutics.

Research Collaborations in Polymer Industry

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The discussion around research is a great one but if this research has no utility in the world of business then of what use is it.

A good question in my many years working with researchers in Australia and overseas this question has been asked and in many instances and it often takes a person of vision to see the industrial utility of this research or where it might lead in the industrial world.

In one project working with CSIRO a technology that allows the precise control of the molecular structure of a chosen polymer was discovered by a team working with the industrial partner but the initial response was we can't use this technology because of the smell and colour, but over the next few years these issues were solved and the technology is now being used in commercial applications from photoresists to house paint. It's the collaboration and knowledge from both sides each with their unique perspectives that really allows commercial success. Its true one plus one is greater than two.

So it's not just the research but the collaboration between researcher and commercial partner that leads to the final positive result for all concerned.

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Photonic Crystals Formed in Semi-Dilute Solutions of Block Copolymers and Application to Non-Linear Optical Devices

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The publication on the optical properties of three-dimensionally arrayed dielectric materials by Yablonovitch and John in 1987 has stimulated many researches and inventions of optical materials for these decades. The optical materials allow us to control light propagation that provide a new technology of optical devices[1], such as low-energy consumption laser, high-speed computers, and so on. We have succeeded in fabrication of a photonic crystal (PhC), representing a novel class of optical materials, via self-assembly of block copolymers (BCP) that generally form one-, two-, three-dimensional periodic nanostructures, i.e., lamellar, cylindrical, spherical, gyroids microdomains, etc[2]. Lattice spacings of the microdomain structures are dependent on molecular sizes of BCPs. In order to obtain a large spacing on the order of wavelength of visible light, we should utilize BCPs with ultra-high-molecular weight (UHMW) such as 10^6 g/mol. They, however, are highly entangled and hence too viscous in bulk to attain structural equilibrium. In contrast, we have found that microphase separation is strongly induced by solvent selectivity even in a semi-dilute solution on the order of several percent[3] (Fig. 1). In these solutions, BCP's can easily reach structural equilibrium with high order because of their high mobility at such low concentrations. In the vicinity of the boundary of lyotropic order-disorder transition, large grains with the size of centimeters (Fig. 2) were obtained. The large grain gives a spot-like ultra-small-angle x-ray scattering pattern (Fig. 3). These phenomena was successfully analyzed by computer simulation using "SUSHI"[4].

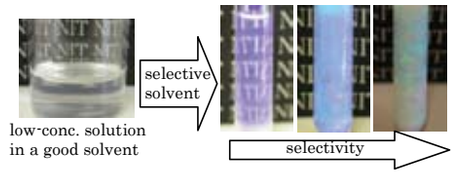

Fig. 1 Microphase separation induced by selective solvent.

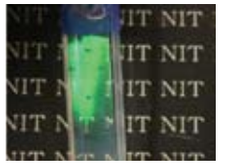

Fig. 2 a giant grain in a BCP solution.

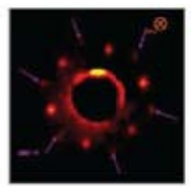

Fig. 3 2D USAXS of gyroid single grain

On the basis of this idea, we fabricated a laser resonator by mixing rhodamin to the block copolymer solution with THF and water described above. The block copolymers successfully inhibit the spontaneous emission of dyes induced in the microdomain structures, and laser emission was generated as seen in Fig. 4 when the green laser with the wavelength of 532 nm as a pumping light stimulated the sample. Three-dimensional emission was observed because the sample have gyroid structures with the trisoctahedral symmetry.

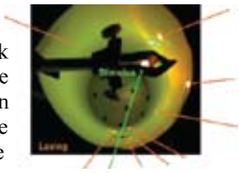

Fig. 4 Laser emission from microdomain sturctures

[1] "Photonic Crystals" ed. by J. D. Joannopoulos etc, Princeton University Press, 1995.
[2] S. Sakurai, S. Okamoto, K. Sakurai, ed. by I. W. Hamley, Wiley & Sons Ltd , 2004, pp. 127-158.
[3] K. Tsuchiya, S. Okamoto et al., OPTICS EXPRESS,2008, vol. 16, No. 8, pp. 5362-5371.
[4] developed by the group of Professor Doi (http://www.octa.jp/OCTA/sushi_jp.html).

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Water-based Nanoparticulate Organic Photovoltaics

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Recently, the fabrication of organic solar cells from water-dispersed nanoparticulate materials (solar paint) has attracted increasing interest since it offers the potential of morphological control coupled with device processing in the absence of an organic solvent. In this talk I will present our recent work on developing optimized nanoparticulate organic photovoltaic (NP-OPV) devices from water-based polymer nanoparticle dispersions.

Our initial studies were focussed on blends of poly(9,9-dioctylfluorene-co-N,N-bis(4-butylphenyl)-N,Ndiphenyl-1,4-phenylenediamine) (PFB) and poly(9,9-dioctylfluorene-co-benzothiadiazole (F8BT). By controlling both nanoparticle morphology[1] and inter-particle interactions it is now possible to build polyfluorene NP-OPV devices that are more efficient than the corresponding bulk heterojunction devices. In particular: (1) the polyfluorene nanoparticle morphology is suited to effective charge separation, (2) thermal treatment of the deposited layers results in improved interparticle connectivity and effective charge transport, and (3) the optimal device thickness is a delicate balance between the repair of layer defects and the creation of stress cracking in the nanoparticulate film[2]. Moreover, the addition of calcium into the cathode structure results in a dramatic increase in open circuit voltage and power conversion efficiencies (PCE) approaching 1% for water-based polyfluorene NP-OPV devices are now possible[3].

Poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blends are the most studied organic photovoltaic materials system and conventionally are processed into thin films via organic solvent based routes. We have recently probed directly the structural motif of P3HT:PCBM NP-OPV devices and have shown how NP morphology determines device function. For this system, the unannealed NP-OPV devices exhibit the highest efficiencies, with PCEs of 1.3 %. Scanning transmission X-ray microscopy (STXM) studies show that annealing these devices leads to gross phase segregation and reduced device performance[4]. Finally, the performance of nanoparticulate organic photovoltaic (NP-OPV) devices fabricated from poly(3-hexylthiophene) (P3HT):indene-C60-bisadduct (ICBA) blends. These devices exhibit power conversion efficiencies of 2.5 %, which is the highest so far reported for NP-OPV cells. Using STXM and thermodynamic modelling we show that the improved performance is driven by the enhanced miscibility of ICBA in P3HT, which results in a more efficient intermixed structure in the annealed devices[5].

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5. S. Ulum et al., The Role of Miscibility in Polymer:Fullerene Nanoparticulate Organic Photovoltaic Devices, *Nano Energy*, submitted, (2013).

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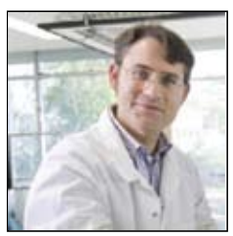

Investigation into the Mechanism of Microwave Induced Rate Enhancements in Chain Growth Polymerisation

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Abstract

This presentation will report new work that builds on our initial studies concerned with defining the influence that microwave energy has upon the mechanisms of chain growth polymerisations. This presentation will present data from recent studies which were dedicated toward broadening the investigating into how the dielectric properties of chain growth polymerisation systems produce significant rate enhancements for the polymerisation. Furthermore, this dielectric property assessment will then be compared and contrasted to these materials actual performance in polymerisation reactions conducted using microwave energy as a heating source.

The use of microwave energy as a heating source to drive chemical reactions has been well documented in recent years, along with the numerous potential advantages offered by its use. These include rapid bulk heating, good temperature homogeneity and selective heating. However, in many cases these reports have detailed the outcomes of conducting the test chemistry in less than rigorous conditions, for example in commercially available domestic multi-mode microwave apparatus. Unfortunately, processing in this way does not allow for the true scientific/engineering effects that have lead to this observation to be identified, because the true influence of the factors that can influence the reaction, cannot be decoupled from one another. In the particular case of chain growth polymerization chemistry, the "high level" microwave effects that have been reported thus far include accelerated polymerization rate, molecular weight differences and changes to reaction selectivity. However, little work has been done to further investigate the exact microwave effects that are the root cause of these observed phenomena. Many literature publications have simply claimed the influence of "non-thermal microwave effects" to explain empirical results, without any further postulation on a possible mechanistic explanation of the effects detailed. Thus it is still not completely clear, on a scientific basis, where in the overall process the microwave energy is generating the changes observed.

This paper will report the results of our latest work targeted at defining the actual effects of applying microwave energy to both free radical and ring opening based polymerization systems. Data from these reactions will be presented that not only demonstrates the key benefits of applying microwaves to these systems but also proposes the mechanistic aspects that are responsible for these observations. Furthermore, the conclusions from these results will be supported by being cross-referenced to;

(a) the dielectric property predictions to assess if this method is correctly predicting the effects that microwaves are having over the active species present in the polymerization.
(b) real time spectroscopic assessment of the progression of the key reactions that are involved in the polymerisation mechanism.

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Role of Polymer Morphology in Organic Photovoltaics

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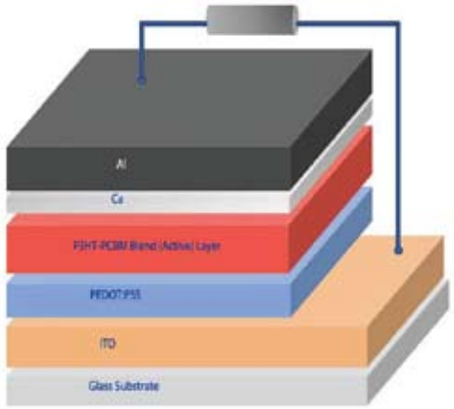
Organic Photovoltaics (OPVs) offer a number of interesting commercial opportunities around their ability to be incorporated into buildings in an architecturally attractive way. However, before this opportunity becomes reality, there are many challenges to be overcome including efficiency, cost and lifetime.

While the structure shown below appears simple, it is in fact an idealised cartoon suggesting sharp interfaces which are potentially ideal for electron transport, but of course is not the reality. More importantly, diffusion across these interfaces can destroy the device properties.



The most complex and studied layer is the active layer, shown below using a blend of poly(3-hexyl thioophene (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM). This layer partially phase separates to form a bulk heterojunction (BHJ) which has a complex morphology with a very high surface area promoting charge separation and transport to electrodes.

This presentation will describe a number of initiatives being investigated to control the structure of these devices and better understand the factors limiting device lifetime.

One such approach is to effectively polymerise the small molecule PCBM by attaching the active part, a fullerene, to a polymer chain. The resulting polymer has significantly less solubility in P3HT, providing alternate avenues to phase development of this layer.

In a second approach, while the structure can be created by a sequential series of processing steps, a hierarchy of solvents and temperature profiles inherently limits the structure and performance of each layer. Lamination offers the potential to optimise the structural development of each layer independently and then bring them together to create the final device. Results of lamination at various interfaces will be presented.

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Precision Macromolecular Chemistry: Building Nanostructured Materials One Molecule at a Time.

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Chemists are remarkably proficient at directing the synthesis of small molecules, but fine-tuning the structures of large molecules, such as those found in polymers, is far more taxing. Despite many years of research, the field of macromolecular engineering i.e. the preparation of large molecules with strict control over their size and chemical groups has many mountainous challenges yet to overcome. Nature provides endless examples of precisely engineered macromolecules; proteins, for instance, which contain amino-acid side-chains that are accurately positioned, often in a way that determines the proteins' roles. Synthetic chemists have tried to recreate nature's exceptional control over macromolecules, and in so doing they have designed new materials with precisely defined structures, for use in applications ranging from materials to medicine.

The lecture will describe new synthetic paths to design macromolecules showing excellent control over their topology and functionality. These synthetic macromolecules are then exploited to directly form functional materials, or associated to biopolymers such as peptides to form natural / synthetic polymer conjugates. The exploitation of these well-defined macromolecules for the design of functional nanostructured materials via molecular self-assembly and self-organization will be discussed, with examples of applications in the material and biomedical fields.

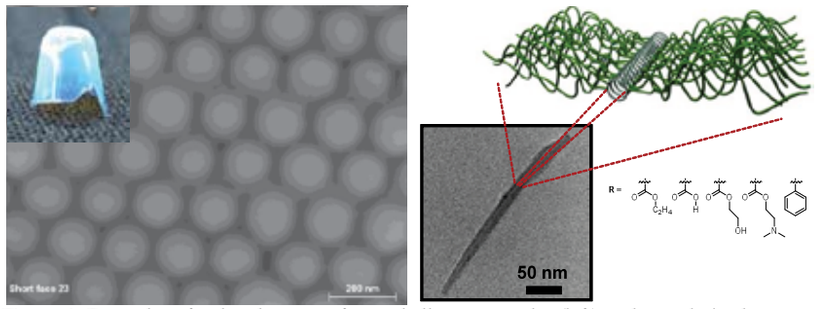

Figure 1. *Examples of ordered arrays of core shell nanoparticles (left) and peptide / polymer conjugates nanotubes (right).*

Selected Recent Publications

- Gody, G.; Rossner, C.; Moraes, J.; Vana, P.; Maschmeyer, T. ; Perrier, S. *J. Am. Chem. Soc.*, **2012**, 134 (30), 12596–12603
- Chapman, R.; Jolliffe, K.A.; Perrier, S. *Polym. Chem.*, **2011**, 2011, 2 (9), 1956-1963
- Konkolewicz, D.; Gaillard, S.; West, A.G; Cheng, Y.Y; Gray-Weale, A.; Schmidt, T.W., Nolan, S.P.; Perrier, S. *Organometallics*, **2011**, 30 (6), 1315-1318.
- Kakwere, H.; K.Y. Chun, C.; Jolliffe. K.A.; Payne, R.J., Perrier, S. *Chem. Commun.*, **2010**, 46, 2188-2190
- Semsarilar, M.; Perrier, S. *Nature Chem*, **2010**, 2, 811-820
- Konkolewicz, D.; Gray-Weale, A.; Perrier, S. *J. Am. Chem. Soc.*, **2009**, 131 (50), 18075-18077
- Kakwere, H.; Perrier, S. *J. Am. Chem. Soc.* **2009**, 131(5), 1889-1895

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Smart polymer-protein hybrids and sugar-responsive micelles

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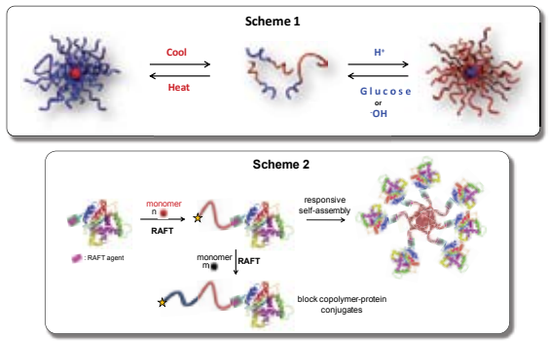
This presentation will discuss our results in two areas of responsive polymeric nanomaterials. The first topic of the presentation will discuss glucose-responsive polymers and their potential to be employed in the area of sugar-induced release of diabetes therapeutics (Scheme 1). Boronic acid-containing block copolymers were shown to be both pH- and glucose-responsive in aqueous media, which led to unique adaptive self-assembly behavior. Polymeric micelles and vesicles constructed from these block copolymers were capable of encapsulating model therapeutics and allowing their release upon an increase in the surrounding glucose concentration.

The second topic of the presentation will describe the synthesis and characterization of polymer-protein conjugates (Scheme 2). Specifically, block copolymer-protein bioconjugates were prepared by grafting from proteins modified with reversible addition-fragmentation chain transfer (RAFT) agents. Both maleimide-functional and activated ester-functional RAFT agents were reacted with cysteine or amine residues, respectively, on model proteins to afford protein macro-chain transfer agents that contained the RAFT agents immobilized via their R-groups. Polymerization of *N*,*N*-dimethylacrylamide (DMA) led to poly(DMA)-protein conjugates that retained the thiocarbonylthio functionality necessary for addition of a second block of poly(*N*-isopropylacrylamide). The resulting block copolymer conjugates contained an outer hydrophilic block and an inner thermoresponsive block. Cleavage of the block copolymers from the proteins and subsequent analysis suggested the homopolymerizations and subsequent block copolymerizations were efficient and well-controlled. Preliminary solution studies of the resulting block copolymer-conjugates indicated the self-assembly behavior and bioactivity could be controlled by temperature modulation.



Photocontrollable Liquid Crystalline Polymer Actuators

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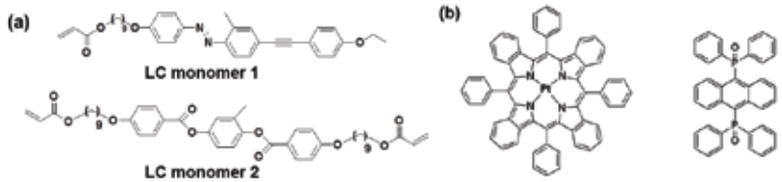
By incorporating azobenzene groups into the crosslinked liquid crystal polymers (CLCPs), large deformations such as contraction and bending have been induced by light due to the photoisomerization of the azobenzene chromophores. [1-4] Since light is an ideal stimulus for it can be localized (in time and space), selective, and allows for remote delivery of energy, photodeformable CLCPs present an interesting opportunity to realize soft actuators in microscope applications, such as full-light-driven motor, oscillators, and microrobots.[5-8] However, most of the photocontrollable CLCP systems were controlled by ultraviolet light which is not idea for practical application, due to considerations of safety, power consumption and cost. Therefore, it would be interesting and significant to develop photodeformable CLCPs which could be photo-regulated by a low energy light, because it is more environment-friendly and causes less damage.[9,10] Upconversion materials, which are capable of the conversion of optical radiation into light of a shorter wavelength, could be potentially utilized in this regard. Recently, we incorporated upconversion nanophosphors which absorb near-infrared (NIR) light and convert it to higher-energy photons in the UV and visible regions, into the azotolane-containing CLCP film and succeeded in generating fast bending of the resulting composite film upon exposure to continuous-wave (CW) NIR light at 980 nm.[11] Most lately, by the integration of platinum(II) tetraphenyl-tetrabenzoporphyrin (PtTPBP)/ 9,10-bis(diphenylphosphoryl) anthracene (YN2)-containing upconverting rubbery polymer film with an azotolane CLCP film (**Scheme 1**), we achieved a new photodeformable composite film driven by triplet-triplet annihilation based upconversion luminescence (TTA-UCL). This composite film bent towards the light source when irradiated with 635 nm light, because the generated upconverted blue YN2 fluorescence released from the rubbery upconverting film triggered trans-cis photoisomerization of the azotolane units and an alignment change of the mesogens in the CLCP film.



Scheme 1. (a) Chemical structures and properties of LC compounds 1 and 2 used in this study. (b) TTA multi-chromophore systems consisting of a sensitizer PtTPBP and an annihilator YN2.

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Tailor-made Polymers for Bacteria-Responsive Wound Dressings: Fabrication, Characterization and Enzyme-Triggered Release

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In this contribution our recent efforts to exploit supramolecular assemblies of tailor-made polymers for application in advanced wound dressings will be discussed. Nanocapsules obtained by the self-organization of tailor-made enzyme-responsive block copolymers provide dual functionality in currently developed advanced wound dressings as (*i*) indicator for wound infection with pathogenic bacteria and (*ii*) *in situ* on demand treatment against those pathogens.[1,2]

In general, the self-organization of amphiphilic block copolymers represents an interesting pathway to obtain functional nanoscale structures, which can be controlled regarding size distributions and dimensions. Vesicles of amphiphilic block copolymers belong to the class of polymeric, stimuli-responsive nanocarriers that are widely discussed in the literature as promising drug delivery systems (**Fig. 1**). Due to their stable nature and versatile properties, they can also be used as storage compartments of active compounds in other biomedical applications, such as advanced wound dressings, where the release of antimicrobials and/or fluorescent markers as part of an indicator system of bacterial infection represents a central mode of action.[1] The *in situ* detection and treatment of infections in scald or burn wounds is not only essential for proper healing as well as the prevention of scarring, but may contribute to reduce the spread of antibiotic resistance stemming from prophylactic administration of broadband antibiotics. In this context we synthesized and investigated assemblies of novel amphiphilic block copolymers, e.g. hyaluronic acid-*block*-ε-polycaprolactone and hyaluronic acid-*block*-poly(lactic acid) copolymers.[2] Hyaluronic acid is the target for the enzyme hyaluronidase that is excreted by the bacterium *staphylococcus aureus*. Hence in an infected wound covered with a capsule-containing dressing, the capsules are opened by the bacterial enzymes, which signals selectively the infection and may allow the on demand-only administration of potent antimicrobials. The synthesis, the detailed characterization and finally application of these novel block copolymer vesicles in the detection of bacteria will be discussed. In addition, bacteria-responsive biopolymer thin film systems will received attention.

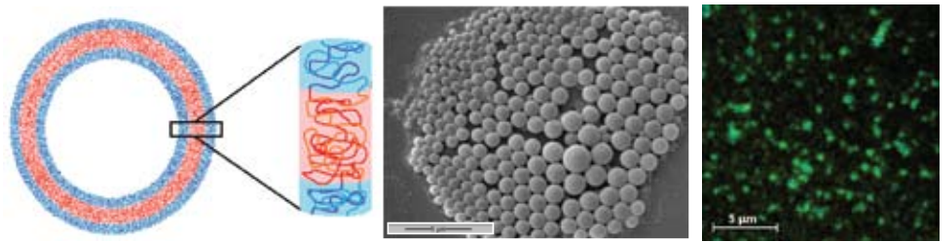

Figure 1. (Left) Scheme of block copolymer vesicle, (middle) SEM and (right) fluorescence lifetime imaging microscopy image of dye filled hyaluronic acid-*block*-poly(lactic acid) vesicles.

[1] J. Zhou, A. L. Loftus, G. Mulley G., A. T. A. Jenkins, *J. Am. Chem. Soc.* **2010**, *132*, 6566-6570.
[2] S. Haas, Y. Chen, C. Fuchs, S. Handschuh, M. Steuber, H. Schönherr, *Macromol. Symposia* **2013**, *in press.*

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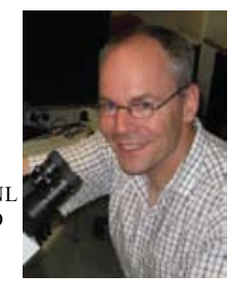

Hybrid gelation processes in enzymatically gelled gelatin: impact on nanostructure, macroscopic properties and cellular response

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Hydrogels obtained from the chemical or physical association of macromolecules are an important subject of materials science as they offer an ample array of design possibilities and have found in particular numerous applications in biomedicine; they serve for instance as skin substitutes, adhesives, or drug delivery matrices. Through the careful selection of macromolecules, the associations that maintain the hydrogels 3D network can be selected and tuned. We report on hydrogels made from fish gelatin in the presence and absence of the enzymatic cross-linker microbial transglutaminase (mTGase)[1,2].

Different types of networks were fabricated: *physical gels*, thermally-triggered and reversible, resulting from the single-strand to triple-helices transition of gelatin; *chemical gels*, where gelatin strands are cross-linked by mTGase, and *hybrid gels*, obtained from the combination of both processes, either contemporaneous or sequential.

An array of techniques - rheology, small-angle neutron scattering, optical rotation and molecular dynamics - was employed to connect the bulk properties with the nanoscale morphology of the gels, both as a function of gelation time and at equilibrium. The study provides new insight into the synergism between mixed gelation processes in hybrid gels. For instance, we find that triple-helices are able to guide covalent cross-linking, thus resulting in more homogeneous networks, which reflects in stronger mechanical properties and, subsequently, a higher metabolic activity in cell culture studies.

The systems reported here, based on a sustainable material and an enzymatic cross-linking process, are attractive for biomedical applications, in particular tissue engineering. The type of multi-disciplinary approach proposed here, where the architecture of the gels on the nanoscale, their mechanical behaviour on the macroscale and their biological performance for cell regeneration are examined and correlated, is paramount to achieve a comprehensive understanding of networks properties and rationalise the design of hydrogels with controlled functional properties.

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Novel Developments in Controlled Radical and Cationic Polymerizations via Dual Mechanisms

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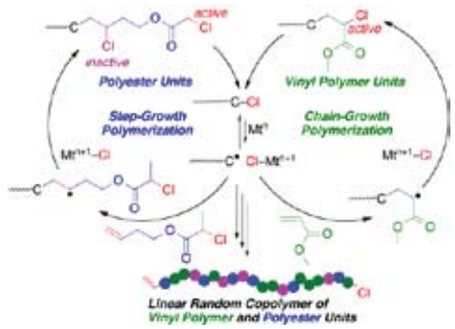
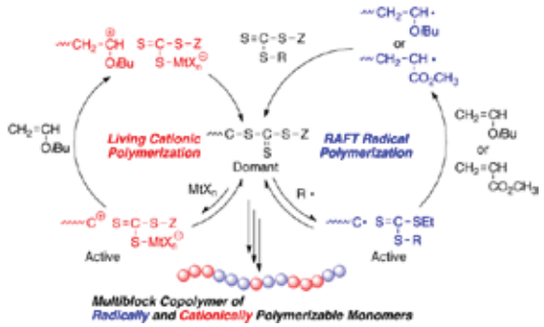
Controlled or precision polymerization is a powerful tool for the synthesis of well-defined polymers, which would work as high-performance and/or functional materials based on their controlled structures. Recent progresses in controlled/living polymerizations via various mechanisms, including radical, ionic, coordination, and condensation polymerizations, have enabled the precision synthesis of various polymers with controlled architectures. However, there are still limitations in monomers prone to each polymerization mechanism.

We have been investigating precision polymerization proceeding via radical or cationic mechanism in terms of control of molecular weight, stereochemistry, and monomer sequence. Recently, we found that novel metal-catalyzed step-growth radical polymerizations, in which monomers possessing unconjugated C=C and reactive C–Cl bonds are polymerized via radical polyaddition mechanism to give polyesters, polyamides, and sequence-regulated vinyl copolymers.[1,2] Furthermore, we combined the radical step-growth polymerizations with the metal-catalyzed living radical chain-growth polymerizations of conjugated vinyl monomers such as acrylates and acrylamides to synthesize novel random and block copolymers consisting of the polyesters or polyamides and the vinyl monomer units (**Scheme 1**).[3]



Scheme 1

Another dual but different simultaneous precision polymerization has also been developed via concurrent activation of C–S terminal by a radical species and a Lewis acid, which induces simultaneous controlled/living radical and cationic polymerizations of acrylate and vinyl ether to give the novel multiblock copolymers with unprecedented monomer sequences of both monomer units (**Scheme 2**).[4] In my presentation, I will present our current work on such precision polymerizations proceeding via dual mechanisms and more recent related topics.



Scheme 2

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Using Chemical Reactions to Control Polymer Network Shape, Topography, and Behavior

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The ability to induce adaptive network behavior in traditional thermoset polymer networks in response to a specific external stimuli in the immediate material environment has enabled simultaneous shape and topography control within a covalently crosslinked polymer system. Here, two approaches to transform the shape, topography and behavior of thermoset polymer network are investigated. In the first approach, a Covalent Adaptable Network (CAN) thermoset thiol-acrylate polymer with exchangeable bonds upon exposure to light can undergo cleavage and reformation in a manner that enables the crosslinked network structure to respond chemically to an applied stimulus by continuously and locally deforming via polymer network connectivity rearrangement, which enables 3D control of its geometry. [1] In a second approach, a thiol-acrylate shape memory dual-cure polymer system is demonstrated to have the ability to go from a temporary shape configuration to a permanent shape configuration on being exposed to a specific temperature range.[2] Additionally, this network is demonstrated to simultaneously maintain the ability to react further and achieve a second and final set of material properties via a photoinduced reaction. Such a two-stage reactive polymer system that enables the achievement of two distinct and largely independent sets of properties might be necessary for multiple stages in the life-cycle of applications such as shape memory polymers (SMP) based sensors and actuators.

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Emulsion-templated Scaffolds for Tissue Engineering and 3D Cell Culture

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There are numerous routes described in the literature for the production of highly porous and permeable polymer materials for use as, for example, catalyst supports, tissue engineering scaffolds and separation media. However, many of these methods result in poorly defined materials with void sizes that are difficult to control and limited connectivity. One method that has the ability to create well-defined porous polymers (foams) is the so-called emulsion templating process, whereby a high internal phase emulsion (HIPE) is used as a precursor to a porous material (**Fig.1**)[1]. The presentation will describe the preparation of HIPEs and the resulting porous polymers (polyHIPEs) together with methods by which the morphology, properties and surface chemistry can be varied. In particular, the use of photopolymerization methods as a means to prepare porous materials from relatively unstable HIPEs will be presented[2]. Subsequently, the application of these materials as matrices for tissue engineering and in vitro cell culture will be discussed.

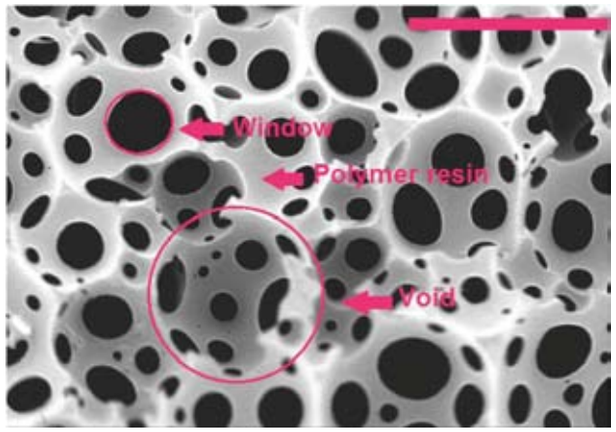

Figure 1. SEM of typical polyHIPE material illustrating the key structural features.

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Sequence-controlled Polymers: Recent Progress and Promise.

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Synthetic polymers do not exhibit controlled sequences of monomers as biological macromolecules do (**Fig. 1**). However, ordered comonomer sequences could open interesting technological avenues in synthetic polymer science.[1, 2, 3] Surprisingly, very little research has been carried out during the last part of the 20th century for developing sequence-specific polymerization methods. Yet, for about five years, a renewed interest in the subject has emerged. This growing field of research will be described in my presentation.

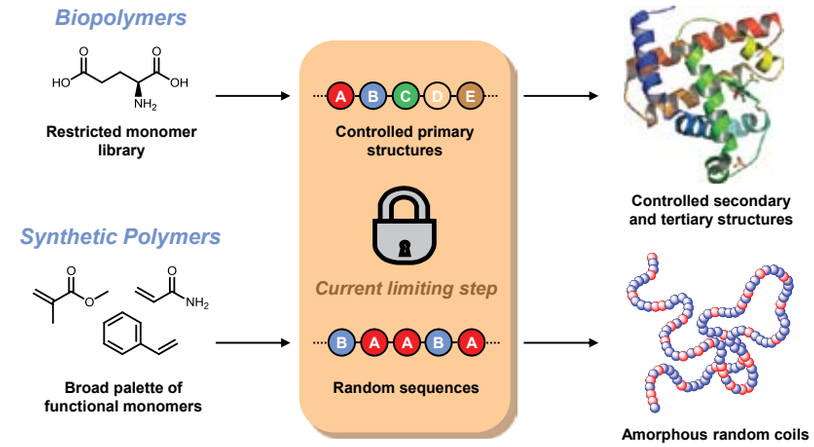

Figure 1. Sequence-controlled macromolecules: a new level of complexity in synthetic polymer science.

Recent sequence-controlled approaches developed in our laboratory will be discussed.[4, 5] Moreover, the advantages of the formed sequence-controlled polymers will be highlighted. For instance, the preparation of complex macromolecular structures such as encoded chains, 1D macromolecular arrays or folded polymer origamis will be presented.[6, 7, 8] Ultimately, challenges and future directions in the field will be analyzed.

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Elaboration and properties of multiphase systems based on thermoplastic chitosan

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In the last years, biopolymers have attracted great attention due to their large availability, renewability, biocompatibility, and biodegradability[1]. It is for instance the case of chitosan, a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-β-D-glucan. It is a deacetylated derivative of chitin, which is the second most abundant polysaccharide found in nature after cellulose. Chitosan has been found to be nontoxic, biodegradable, biofunctional, and biocompatible in addition to having antimicrobial and antifungal properties, and thus has a great potential for environmental (e.g., packaging) or biomedical applications. It is worth noting that, for preparing chitosan-based materials, only solution casting or similar methods have been used in all the past studies. Solution casting is known to have the disadvantage in low efficiency and difficulty in scaling-up towards industrial applications. In addition, a great amount of environmentally unfriendly chemical solvents are used and released to the environment in this method. The reason for not using a melt processing method like extrusion or kneading in the past studies is that chitosan, like many other polysaccharides such as starch, has very low thermal stability and degrade prior to melting. Therefore, even if the melt processing method is more convenient and highly preferred for industrial production, its adaptation for polysaccharide-based materials remains very difficult. While the processing issues of starch has been emphasised to some extent[2-4], there has been very limited focus on the melt processing of chitosan-based materials.
However, our recently published study[5] has demonstrated the successful use of an innovative melt processing method (internal mixer) as an alternative route to solution casting, for preparing materials based on thermoplastic chitosan.
These promising thermoplastic materials, obtained by melt processing, have been the main topic of recent international projects, with partners from different countries (see below[*]). For instance, multiphase systems based on various renewable plasticizers have been elaborated and studied[6]. More recently, different nano-biocomposites based on montmorillonite have been processed and analysed. The effects of nanoclay content, organomodification, preparation method on the structure, properties, and biodegradation of the plasticised chitosan-based nano-biocomposites have been examined.

(*) **International partners:** (i) **CSIRO (Clayton-Australia):** Dr. K. Dean, Dr. P. Sangwan, Dr. C. Way, Dr. X. Zhang; (ii) **Ecole Polytechnique de Montréal (Canada):** Pr. M.C. Heuzey, Pr. A. Ajji, M. Matet; (iii) **University of Queensland (Brisbane-Australia):** Pr. P. Halley, Dr. F. Xie; (iv) **University of Strasbourg (France):** Pr. L. Avérous, A/Pr. E. Pollet, Dr. V. Martino

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Multicomponent Polymerization for New Polymer Synthesis

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Isocyanide based multicomponent reactions (IMCRs) are very efficient atom-economical reactions that can assemble three or more different components into one molecule in a one-pot process, and have therefore been playing important roles in many fields.[1,2] Among the IMCRs, Passerini reaction, a three component reaction first described in 1921, has been proved to be a powerful synthetic method that can yield an ester-amide linkage from a carboxylic acid, an aldehyde and an isocyanide (**Figure 1**).[1,2] It is thus quite advantageous to use this reaction to prepare polymers with different architectures and functional groups in a very efficient and straightforward way. Unfortunately, this highly efficient reaction has been overlooked for a long time in polymer synthesis; only until quite recently, synthesis of polyesters by this reaction has been reported.[3] We extended the scope of Passerini reaction in polymer science as a multicomponent polymerization method. In this talk, I will describe several synthetic approaches to different functional polymers based on Passerini reaction. This will include linear poly(ester-amide),[4] polyamides,[5] star polymers,[6] graft copolymers, and photo-degradable polymers.

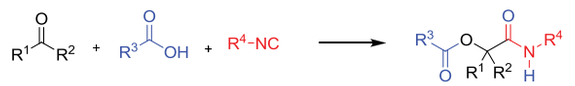

Figure 1. General Passerini reaction

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Biosynthesis-structure-property relations of hyperbranched glucose polymers

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Glycogen and starch are hyperbranched glucose polymers with multiple structural levels, and are of major importance for humanity. Our bodies synthesize glycogen as a glucose (blood-sugar) buffer. Starch, synthesized by plants for glucose storage, supplies 50% of our food energy and is a renewable polymer with significant current and potential uses in biomaterials. Both polymers have complex multi-level structures, the first three of which are: Level 1, the molecular weight distributions of individual branches; Level 2, the multiple-dimensional distribution describing the full branching structure of isolated molecules, and Level 3, which for starch comprises the spatial arrangements of crystalline and amorphous regions in lamellae, and, for glycogen, the distributions of smaller clusters of hyperbranched glucose polymer molecules (β particles) into larger agglomerates (α particles, where the binding is probably through the protein glycogenin[1]). Starch comprises (1) amylose, which is of moderate molecular weight and contains a few long branches, and (2) amylopectin, a hyperbranched component of very high molecular weight; glycogen is similar to amylopectin except it is randomly branched. Structural characterization involves diverse techniques: for Level 1, finding the molecular weight distribution of the individual branches by enzymatic debranching followed by either fluorophore-assisted carbohydrate electrophoresis or SEC; for Level 2, multiple-detector SEC and, for the larger molecules (amylopectin and glycogen) where shear scission cannot be avoided[2], multiple-angle laser light scattering without size separation; and, for Level 3, X-ray and neutron scattering. Interpretation of the data so obtained in turn requires new theoretical advances. Level 1 data for starch is fitted by a new theory[3] which also shows that there are genetic constraints on the enzymatic rate coefficients which can result in the crystalline starch necessary for survival of the plant. This theory also provides a new means of parameterizing *Level 1 data* which has provided a greatly improved way of understanding the relations between data such as (1) how Level 1 structure controls that of Level 3[4], and also (2) properties such as digestibility rate[5], which is important for human health, and (3) the suitability of barley varieties for making beer. It also shows how new crops can be developed, either by conventional plant breeding or GM methods, which have starches with significantly improved digestibility, of importance in prevention and management of obesity, diabetes and colo-rectal cancers. L*evel 2 data* for plants grown at different temperatures has suggested what constraints stop starch molecules growing indefinitely: as with any branched polymer, while there are events which control the lengths of individual branches, there are no obvious candidates for the whole molecule, but these new data suggest a steric crowding mechanism. *Level 3 data* for glycogen has revealed new insights into the role of this molecule in diabetes[1,6], and suggests new types of drug targets for managing diabetes.

There are major challenges for polymer scientists in developing characterization techniques for Level 2, and in developing quantitative theories for this complex, infinite-dimensional[7] structural level which relate biosynthesis and biodegradation to structure, and structure to properties. The same challenges exist for complex branched synthetic polymers.

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Engineering Polymeric NanoParticles for Advanced Applications

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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. These systems can offer significant improvements in the temporal and spatial control of drug delivery. In this talk different polymeric nanoparticles that have been specifically designed to deliver anti-cancer drugs and to image specific tissue, will be discussed. The first system presented will be based on pH- and redox- responsive nanoparticles which are able to deliver different payloads in different cellular compartments. The synthesis and the characterization of these nano-objects will be outlined in detailed. As an example, the delivery of nitric oxide will be presented using these nanoparticles for the treatment of liver fibrosis and neuroblastoma. We have also demonstrated synergistic effect when we combine nitric oxide (NO) with chemotherapy drugs for the treatment in multi-drugs resistance in cancer. In a second part of this talk, the synthesis of new hybrid organic/inorganic nanomaterials, based on iron oxide, gold and gadolinium, will be reported for use as MRI contrast agents. The effect of the architecture and the nature of polymers will be correlated with the magnetic properties of these nano-objects. In addition, the polymeric shell of these nanomaterials can be designed to conjugate with anti-cancer drugs. Finally, I will rapidly mention the use of hybrid inorganic polymeric nanoparticles for the storage of hydrogen. In this part, I will present and discuss on the synthesis of magnesium hydride (MgH_2) nanoparticles stabilized and assembled using functional polymer to yield a new generation of nanomaterials with remarkable hydrogen storage properties.

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Modelling Nano-scale Structure and Energy Transfer in Conjugated Polymers

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The performance of organic electronic devices made from conjugated polymers is sensitive to the nano-scale morphology of the polymers. But modelling the structural and electronic properties of conjugated polymers on length scales that are relevant to device performance is challenging. This talk will discuss coarse-grained computational models that we have developed to study the self-assembly (**Fig. 1**) of the nano-scale structure of conjugated polymers and the impact of polymer structure on functional properties such as energy transport that are important in devices like organic solar cells. The talk will focus on our studies of two widely used conjugated polymers, poly(3-hexylthiophene) (P3HT)[1] and poly(2-methoxy-5-(2'-ethylexyloxy)-1,4-phenylenevinylene) (MEH-PPV)[2], and will compare the computational results obtained with ultrafast time-resolved spectroscopic measurements.

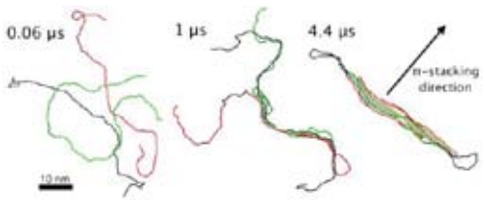

Figure 1. Self-assembly of ordered P3HT nanostructures in anisole from coarse-grained molecular dynamics simulations (different chains are coloured differently and only polymer backbones are shown for clarity).

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Modular Design of Profluorescent Nitroxide-Based Sensor Materials

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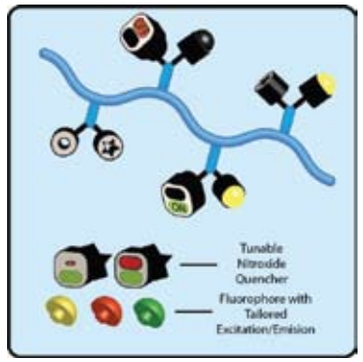
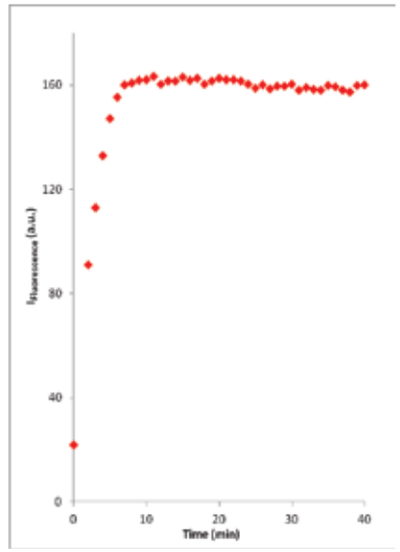
Nitroxides are stable, kinetically persistent free radicals with a number of unique properties. One of their recent applications is to be covalently linked to a fluorescent moiety giving them the ability to function as a switchable fluorometric probe.[1] The capability of the nitroxide/fluorophore couple to act as a probe arises from the nitroxide moiety's capacity to efficiently quench excited states both inter- and intra-molecularly. This presentation will demonstrate the synthesis of polymeric scaffolds containing multiple reactive functionalities that can be transformed orthogonally to yield a polymer adorned with profluorescent nitroxides. These materials can be utilised, in turn, to function as fluorescent sensors for both chemical and physical changes.





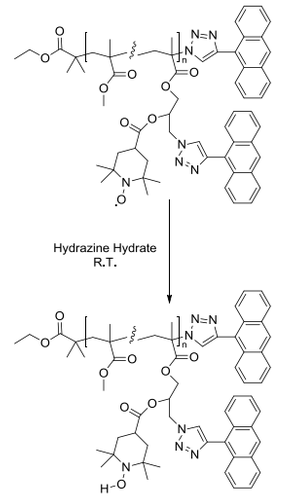


Figure 1. Representative example of the construction of profluorescent nitroxide-containing polymers (top right) and a plot of fluorescence intensity at emission maximum over time when a profluorescent nitroxide containing polymer is exposed to hydrazine hydrate as a model reductant (bottom).

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A Versatile Polymer Building Block Based On Trifluorovinyl Ethers Chemistry

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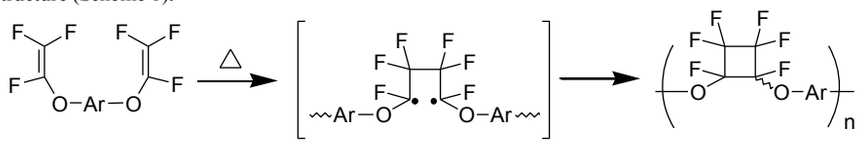
Fluorine-containing polymers are one of the new and exciting research directions within the polymer science programme at The University of Auckland. In the plastics world, fluorine- containing polymers represent a rather specialised group of polymeric materials.[1] Their many attributes include remarkable thermal and chemical attack inertness, solvent resistance and outstanding electrical properties. These properties offset their higher cost and greater difficulty in processing than is the case for most other non-fluorinated thermoplastics.

Fluoropolymers are typically made from the free radical polymerization of fluorinated alkenes. Unlike those, this talk introduces a unique kind of fluorinated olefin – aryl trifluorovinyl ethers- as building block to deliver high performance polymers.[2] Polymers are prepared via thermally activated [2+2] cycloaddition of aryl trifluorovinyl ether monomers.[2] The resulting semi-fluorinated polymer contains perfluorocyclobutane (PFCB) ring structure (Scheme 1).



Scheme 1. [2+2] Cyclo-polymerization of aromatic trifluorovinyl ether monomers.

Various macromolecular architectures such as linear, branched and cross-linked as well as a range of functional groups can be prepared and incorporated by [2+2] cycloaddition of functional monomers containing multiple aryl trifluorovinyl ether groups.[3] Initially developed for aerospace and microelectronics applications at Dow Chemical, PFCB polymer technology can serve as a versatile materials platform for many industrial applications, such as microphotonic[4], optoelectronics[5] and membranes[6-8].

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Smart Polymer Capsules with Synergistic Response to Biological Stimuli.

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The design of 'smart' delivery systems with precisely tuned response to their environment is integral to advances in areas such as biomedicine and energy. Self-assembled polymeric carriers have generated significant interest for such advanced applications due to the ease and versatility of these approaches. One important technique to design such carriers is the layer-by-layer (LbL) 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. Polymer capsules can be readily synthesised using this technique by assembly on a sacrificial template and have demonstrated significant potential for use as delivery systems.[1] Recently, we developed a new method to assemble LbL capsules based on combining LbL assembly with click chemistry to allow the synthesis of single-component capsules with tailored properties.

Polymeric carriers that respond to pH are of significant interest for biomedical applications as the internalization of such carriers typically occurs through acidic compartments of the cell, which have lower pH then the blood stream (pH 7.4). One interesting pH responsive polymer is poly(2-diisopropylaminoethyl methacrylate) (PDPA) as it has charge-shifting capabilities which correspond specifically within this pH range. Herein the synthesis of charge-shifting carriers based on poly(2-diisopropylaminoethyl methacrylate) (PDPA) will be presented.[2] The PDPA carriers have interesting properties for biomedical applications as they shrink at physiological pH enabling efficient loading of a range of therapeutic cargo but swell again below 6.4 when internalized into a cell. It will be demonstrated that PDPA carriers can be designed to respond synergistically to multiple cargo eg. pH and redox, thus optimizing degradation efficiency once at the targeted site. The degradation rate of these carriers can also be tuned by systematic changes in crosslinking degree[3] and by using specific enzyme cleavable components. This study provides important fundamental insights into the use of responsive crosslinkers in such nanoengineered carriers.[3]

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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High Speed Video Observation of Giant Pickering Emulsion and Colloidosome Droplet Interaction and Stability

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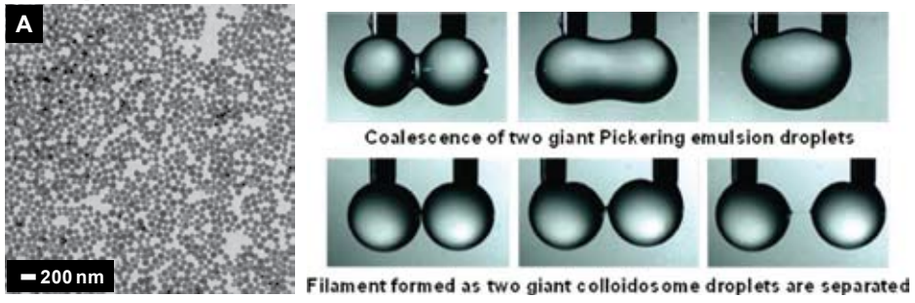
The interactions of two 2-mm pendant oil droplets grown in the presence of an aqueous solution of latex particles was observed using a high-speed video camera on a homebuilt coalescence rig.[1] The coalescence behaviour was monitored as a function of oil type (n-dodecane versus sunflower oil) and adsorbed latex type (poly(glycerol monomethacrylate)-stabilised polystyrene (**Fig.1A**)[2] versus lightly cross-linked 2-(tert-butylamino)ethyl methacrylate)[3]. Both latexes had previously been reported to be effective Pickering emulsifiers, with the pH-responsive microgel character of the latter leading to rapid demulsification upon exposure to acid. This pH response has been characterised here on giant Pickering emulsion droplets using the coalescence rig. Colloidosomes had been reported as formed by both latexes in the presence of an oil-soluble cross-linker [tolylene 2,4-diisocyanate-terminated poly(propylene glycol)]. The impact of this cross-linking reaction on droplet stability was also followed on the coalescence rig (**Fig.1B**).

The damping coefficient of the coalescing n-dodecane droplets was found to increase in the presence of the latex, confirming particle adsorption.[4] Coalescence times increased when the oil phase was changed from n-dodecane to sunflower oil, because of the much higher viscosity of the latter oil. In addition, increasing the adsorbed $PGMA_{50}$-PS latex particle size led to longer coalescence times because of the greater distance separating the oil droplets. Addition of PPG-TDI to the oil phase reduced the interfacial elasticity and ultimately prevented coalescence through the formation of giant colloidosomes which were found to be stable in contact for several hours without undergoing coalescence. Finally, evidence for cross-linker diffusion from one pendant droplet to another was indicated by a visible filament connecting the two droplets upon retraction.

Figure 1. (A) Transmission electron microscopy image of 135 nm $PGMA_{50}$-PS latex particles prepared by aqueous emulsion. (B) High speed video images of latex coated sunflower oil droplets in aqueous solution in the absence and presence of PPG-TDI cross-linker dissolved in the sunflower oil.



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Distribution of "smartness" of copolymers: Composition of block and statistical copolymers by capillary electrophoresis

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Most industrial (synthetic) and natural polymers are copolymers. Their composition plays a key role in their properties: stability of emulsions, adhesion, degradability, digestibility etc. These copolymers do not have a given composition for a given sample, but a distribution of compositions. The distributions of molecular weights are commonly determined by SEC and used to understand polymer properties. This is not the case for the distributions of compositions since no reliable and easy method allows this determination as a routine analysis. We propose free-solution capillary electrophoresis (CE) as the method of choice for the determination of distributions of composition. This CE method does not separate by molecular weight, in a way similar to liquid chromatography in the critical conditions.[1] We name the method capillary electrophoresis in the critical conditions (CE-CC).

We successfully applied CE-CC to the characterisation of gellan gums[2] and grafting on chitosan[3]. We have applied the method to various copolymers to determine their distributions of compositions. Copolymers of methacrylic acid and styrene sulfonate were synthesized by nitroxide-mediated polymerisation[4] and the evolution of the distribution of compositions with monomer conversion was monitored using CE-CC. The CE-CC methodology developed with these "well-behaved" copolymers was applied to copolymers: polysaccharides, whose solubility is a challenge for SEC. The distribution of degree of acetylation is studied in chitosan, whose films and gels have a variety of biomedical applications[5]. The distribution of glucose-to-mannose ratio is investigated in glucomannans by CE-CC to relate it to its digestibility properties[6]. Finally CE-CC was applied to double hydrophilic block copolymers[7] whereby the unreacted homopolymer is quantified, and the distribution of molecular weights of each block is determined.

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Complex structures in branched polymers

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Structure is an important determinator of material properties, on all length scales. However on small length scales and in materials resistant to clear 3D experimental imaging - such as polymers - very little is known about the complexities and subtleties of structures. Part of the problem is experimental, but a large contributor is the lack of a firm theoretical foundation to provide a 'library' of structures for experimentalists to identify. I aim to fill some of these theoretical gaps by describing, illustrating and categorising different modes of entanglement.

Polymers are composed of molecular chains which have the form of long and flexible filaments. A natural language to describe the entanglement of the filaments comes from the mathematical discipline of knot theory. Using these ideas, the topological linking of filaments with themselves and other filaments can be described as knots and links. Unfortunately these ideas get a bit over-stretched when the filaments are anything except simple loops or threads, *i.e.* if they branch or are fused to other filaments. So it's more appropriate to describe such structures as 'embedded graphs', which means that they are curves connecting the points where filaments branch, or where two filaments attach.

A 'ravel' is an entanglement mode in embedded graphs such as those formed by branching and connecting filaments. It doesn't actually contain any knots or links, but nevertheless it is entangled. My coauthors and I introduced ravels in 2008 [1] (**Fig.1a**), and a ravelled chemical system was found soon after in a metal-ligand complex (**Fig.1b**) [2]. Other structures do contain knots or links, and form simple entangled conformations (**Fig.1c**).

To my knowledge these entanglements have not yet been discovered in polymer systems. I will present these ravels and several other new entanglement modes related to ravels, and explain why they almost certainly exist within polymeric systems. These entangling modes are valid for all sorts of polymers from biopolymers like DNA to processed synthetic materials.

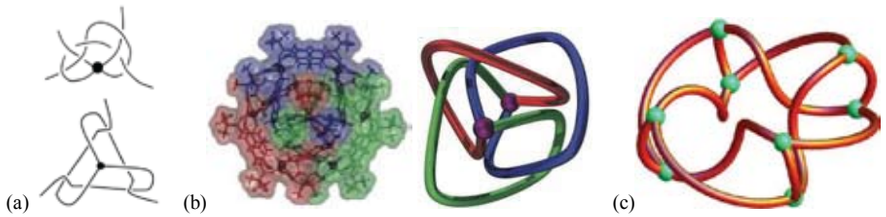

Figure 1. (a) Ravels with three and four strands. However you join up the dangling ends, there will be no knot or link, but there will still be entanglement. (b) A ravelled metal-ligand complex, together with its simplified structure, both from [2]. (c) A tangled cube (note the 8 corners and 12 edges) containing two interlinked cycles. This structure is a reasonable synthesis target using DNA self-assembly methods.

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Novel Applications of Nitroxides in Polymer and Materials Science

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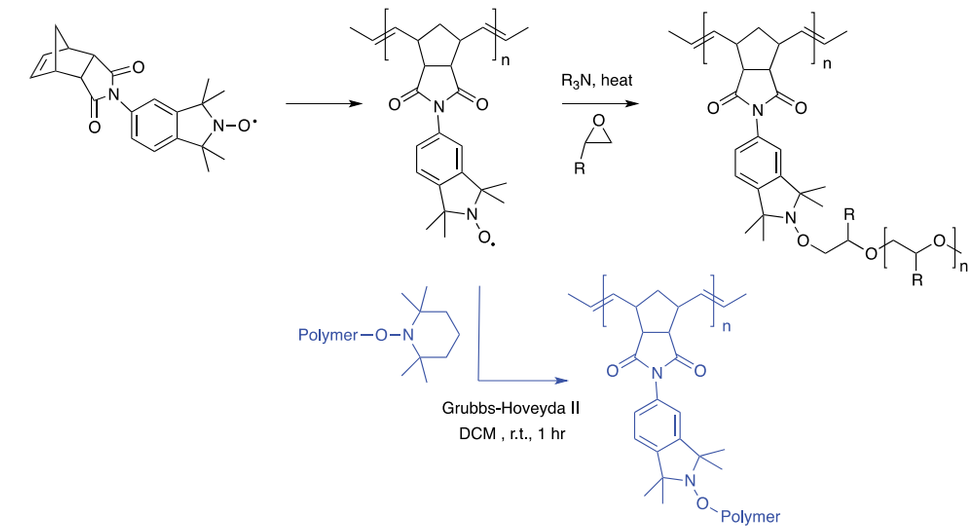
Polymer scientists will be familiar with nitroxides through their role in nitroxide-mediated controlled polymerisation. Industrially however, another important use of nitroxides involves their critical contribution as stabilisers to prolong the service-life of a range of polymeric materials. Most recently nitroxides have been exploited as charge carrying agents in polymer batteries and dye sensitised solar cells. This presentation will introduce some new applications of nitroxides in polymer and materials science and will describe our development of polymeric poly-nitroxides, polymer synthesis through nitroxide exchange reactions and the use of fluorescence and nitroxides as analytical tools to monitor polymer degradation.

Of particular interest is the use of nitroxides as additives in coatings, composite materials and epoxy resins. We have shown that nitroxides incorporating fluorescent components (profluorescent nitroxides, or PFN's), when present in coatings, act as a monitor of the polymer's degradation through exposure to environmental stresses. This can be used to predict lifetime as well as highlight impact damage in composite materials. The presence of PFN's in epoxy resins on cure leads to significant incorporation of the nitroxide into the polymer resin. This may be balanced through structural modifications of the nitroxide, but equally may be of value in facilitating the synthesis of new hybrid polymeric architectures (**Scheme 1**) or as an indicator of cure completion.



Scheme 1. ROMP Poly-nitroxide reaction with epoxy resins or nitroxide-capped polymers to generate new polymer brush structures

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Imaging light emitting polymer films at high spatial and temporal resolution

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The solid-state characteristics of light emitting polymers are the key factors that often govern the performance of organic electroluminescence devices. Aggregates are readily formed in most conjugated polymer films resulting in good charge transport via strongly interacting π-electron systems, but these aggregates also likely induce inhomogeneous morphologies and emission quenching, and thereby affect device efficiency.[1,2] Determining the spatial scale of these inhomogeneities in conjugated polymer films on different spatial scales from nanometres to many microns, and their effect on the dynamics of electron/hole transport, is necessary to develop more efficient injection processes for high performance devices. Coupling ultrafast spectroscopic methods with high spatial resolution optical techniques makes it possible to map the dynamics of the photo-induced charge transfer/transport processes as a function of location in the film. We report here the inhomogeneities in the morphology and fluorescence dynamics of thin films of the light emitting conjugated polymers, on the sub-micrometre spatial and picosecond temporal scales using time-resolved scanning confocal fluorescence imaging measurements.[3, 4]

Time-resolved scanning confocal fluorescence imaging measurements were performed on MEH-PPV films deposited from solutions of various solvents. Fig.1 shows a fluorescence lifetime map and fluorescence decay profiles corresponding to three representative locations on the map for a MEH-PPV film. The morphology of the films, in particular, the presence of inhomogeneities in fluorescence decay behaviour on micro- and sub-micrometre scales, is clear. These inhomogenieites are attributed to regions of various degrees of polymer aggregation that contribute to, but are unresolvable in, the overall bulk spectral properties of the films. The images were collected from typical regions in films containing what appear to be distributions of larger aggregates, smaller aggregates, and largely nonaggregated regions, and the decay profiles shown are from points that correspond to these differently sized aggregates (points A-C, respectively). The decays are clearly nonexponential, and we have analyzed them in terms of multiexponential decay functions. The spatiotemporal spectral behaviour observed resembles that of varying degrees of aggregation, from a level of "single-chain like" regions (emitting to the blue with approximately nanosecond emission decay components) to highly aggregated (short-lived, red emitting) regions, within the film morphology. The overall time-resolved behaviour was sensitive to the degree of aggregation, which in turn was dependent on the solvent from which the film was cast.

Thin films of a water-soluble DPS-PPV, formed on silica substrates by a solvent-free friction transfer technique, were highly aggregated producing "rods" of polymer aligned perpendicular to the drawing direction. This "log-rolling" is in contrast with the reported behaviour of most comparable polymers, which tend to align along the drawing direction. The photophysical behaviour of the friction-transferred film is also different compared with other film formation techniques of the same polymer. Friction transfer films would be expected to be more favorable to aggregate formation within the polymer "rods" and therefore contain more short-lived fluorescence species that enhance the fluorescence quenching, resulting in weaker emission in the films.

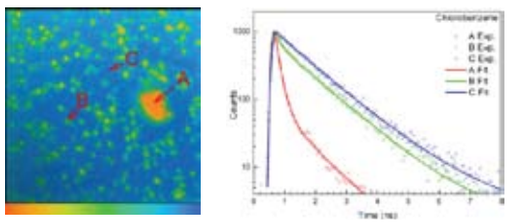

Fig. 1 Time resolved fluorescence image (left) for MEH-PPV thin films and the fluorescence decay profiles (right) recovered from the time resolved images.

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A comprehensive comparison of nanoparticle characterisation instrumentation

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Accurate and reliable characterisation of nanoparticles is crucial for both industrial applications and understanding their toxicological and environmental impacts. The most relevant material properties for such studies include the number and/or mass concentration, chemical composition, particle size distribution, agglomeration/aggregation state, surface charge and surface chemistry. Characterisation of these parameters in nanoscale systems presents numerous challenges, including determining the appropriate quantities to be measured for a given application, measurement of particle systems with complex size distributions, accounting for matrix effects, and distinguishing naturally occurring material from engineered nanomaterials. No single instrument is capable of addressing all of these requirements, so a combination of different measurement techniques should be applied.

Here, a wide range of instrumentation for the characterisation of particle size and size distribution are compared, including electron microscopy, dynamic light scattering, differential centrifugal sedimentation, particle tracking analysis, asymmetric flow-field flow fractionation, micro-channel resonator, and electrical zone sensing. The advantages and limitations of the various methods are discussed together with experimental results highlighting the comparability of these techniques.

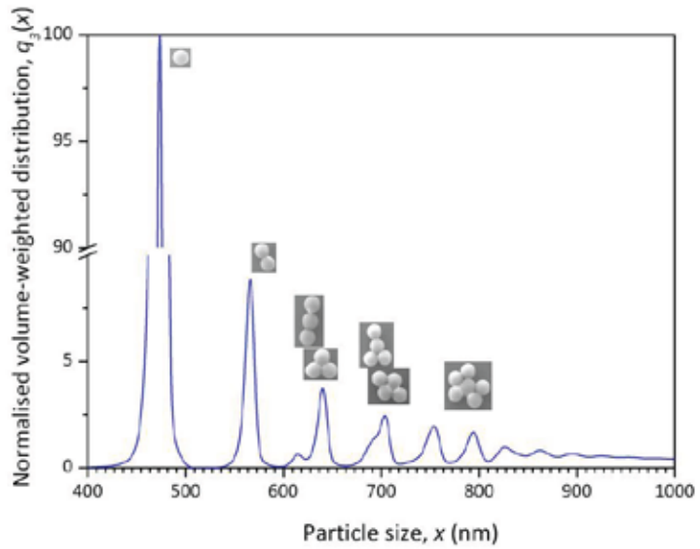

Figure 1: Volume-weighted particle size distribution $q_3(x)$ of an aggregated polystyrene sample, highlighting the size discrimination of differential centrifugal sedimentation. The insets show scanning electron microscopy images of monomers, dimers, trimers, etc. of primary particles next to the corresponding features in $q_3(x)$.

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Developing Profluorescent Nitroxide Additives as Probes for Polymer Degradation: The Use of a Liquid Model for Polyolefins

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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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[2] G. Grynova, J. L. Hodgson, M. L. Coote, *Org. Biomol. Chem.* **2011**, *9*, 480.
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Development of fluorescent nanothermometers

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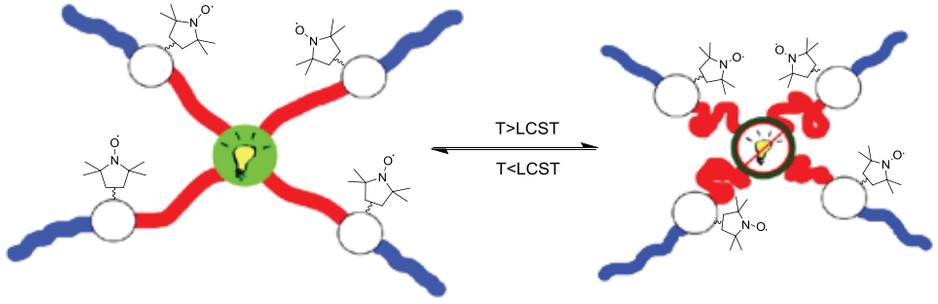
Research on stimuli-responsive materials, a field prominently featuring polymers, has seen tremendous growth over the last few decades.[1-3] These smart materials respond to changes in their external environment, with reversible changes in their physical structure. Such stimuli can be physical (e.g. light, temperature), chemical (e.g. ionic, pH) or biological (e.g. enzymes, receptors) in nature. The ability to respond to stimuli in this way (and ultimately tailor the response through synthetic design) makes such polymeric materials desirable for a wide range of applications, many of them in the fields of bioengineering and biotechnology. One such application is in the field of sensory materials. Developing new means of assessing temperature changes has been a focal point of research for a long time with increased interest from the biomedical field.[3] Certain diseases, such as cancer, manifest temperature changes, resulting in an increased demand for diagnostic tools.

This project aims to develop a new class of thermal sensor materials based on the switching of fluorescence. For this purpose fluorophores are being tethered to fluorescence-quenching nitroxides *via* thermo-responsive polymer linkage. The highly efficient fluorescence-quenching properties of nitroxides, which are persistent free radicals, are well documented in the development of profluorescent nitroxides (PFN) as probes for redox states and radical formation.[4]

This presentation will demonstrate that by combining controlled free radical polymerisation with orthogonal "click reaction" it is possible to produce first generation thermal sensor materials that exhibit a fluorescence change with changing temperature. It will also show the pathway being explored for next generation materials that include other important features such as solubilising groups, reference fluorophore and cell-targeting moieties.



Scheme 1. Cartoon representation of fluorescence switching by the polymeric nanothermometers.

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[4] J.P. Blinco, K.E. Fairfull-Smith, B.J. Morrow, S.E. Bottle, *Australian Journal of Chemistry* **2011**, *64*, 373.

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Photonic Crystals Formed in Semi-Dilute Solutions of Block Copolymers and Application to Non-Linear Optical Devices

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The publication on the optical properties of three-dimensionally arrayed dielectric materials by Yablonovitch and John in 1987 has stimulated many researches and inventions of optical materials for these decades. The optical materials allow us to control light propagation that provide a new technology of optical devices[1], such as low-energy consumption laser, high-speed computers, and so on. We have succeeded in fabrication of a photonic crystal (PhC), representing a novel class of optical materials, via self-assembly of block copolymers (BCP) that generally form one-, two-, three-dimensional periodic nanostructures, i.e., lamellar, cylindrical, spherical, gyroids microdomains, etc[2]. Lattice spacings of the microdomain structures are dependent on molecular sizes of BCPs. In order to obtain a large spacing on the order of wavelength of visible light, we should utilize BCPs with ultra-high-molecular weight (UHMW) such as 10^6 g/mol. They, however, are highly entangled and hence too viscous in bulk to attain structural equilibrium. In contrast, we have found that microphase separation is strongly induced by solvent selectivity even in a semi-dilute solution on the order of several percent[3] (Fig. 1). In these solutions, BCP's can easily reach structural equilibrium with high order because of their high mobility at such low concentrations. In the vicinity of the boundary of lyotropic order-disorder transition, large grains with the size of centimeters (Fig. 2) were obtained. The large grain gives a spot-like ultra-small-angle x-ray scattering pattern (Fig. 3). These phenomena was successfully analyzed by computer simulation using "SUSHI"[4].

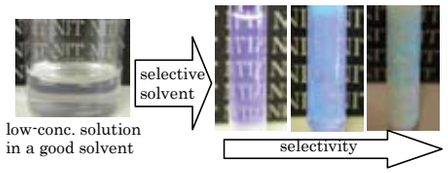

Fig. 1 Microphase separation induced by selective solvent.

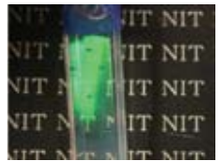

Fig. 2 a giant grain in a BCP solution.

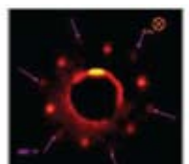

Fig. 3 2D USAXS of gyroid single grain

On the basis of this idea, we fabricated a laser resonator by mixing rhodamin to the block copolymer solution with THF and water described above. The block copolymers successfully inhibit the spontaneous emission of dyes induced in the microdomain structures, and laser emission was generated as seen in Fig. 4 when the green laser with the wavelength of 532 nm as a pumping light stimulated the sample. Three-dimensional emission was observed because the sample have gyroid structures with the trisoctahedral symmetry.

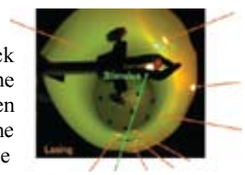

Fig. 4 Laser emission from microdomain sturctures

[1] "Photonic Crystals" ed. by J. D. Joannopoulos etc, Princeton University Press, 1995.
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[4] developed by the group of Professor Doi (http://www.octa.jp/OCTA/sushi_jp.html).

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Chitosan and its conjugates for medical applications

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Chitosan is a biopolymer of increasing significance, as well as a renewable and sustainable material. It is obtained from the partial deacetylation of chitin. 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. Chitosan is increasingly used in biomedical applications such as tissue engineering and drug delivery, owing to its biocompatibility, biodegradability, and non-toxicity. Its natural variability is the main restriction to its use, it will only be overcome with proper characterization and possible chemical modification.

Solid-state NMR yields local information on their structure and dynamics of polysaccharides. Combined with X-ray diffraction, revealed the molecular origin of the difference in mechanical properties of self-associated chitosan films.[1] 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 ion was investigated.

Chitosan is a copolymer of glucosamine and N-acetylglucosamine (Figure). Precise average degrees of acetylation were measured by quantitative ^{1}H solution-state NMR spectroscopy. To characterize the heterogeneity of the chitosan polymer chains in terms of degree of acetylation, a separation method is needed. We report the first separation of chitosan according to its degree of acetylation using capillary electrophoresis in the critical conditions. The heterogeneity of chitosan samples in terms of composition (distribution of degrees of acetylation) cannot be neglected contrary to an assumption commonly done in the literature.

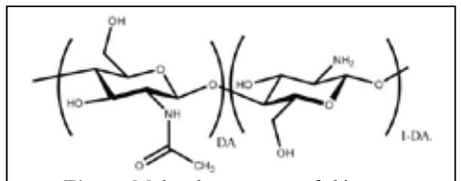

Figure. Molecular structure of chitosan. DA is the degree of acetylation (DA=1 for chitin).

The poor mechanical properties of chitosan compared to synthetic polymers is a drawback for some applications. To overcome this problem, chitosan was modified by SG1-based nitroxide-mediated polymerization (NMP) under heterogeneous conditions of methyl methacrylate or sodium 4-styrenesulfonate.[2] ESR and free-solution capillary electrophoresis confirmed the synthesis of chitosan covalently modified with SG1. The successful synthesis of the grafted copolymers was evidenced by solid-state NMR spectroscopy.

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Dynamic Nuclear Polarization solid-state NMR spectroscopy : A valuable tool for functional polymer characterization

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Thanks to the spectacular take off of the so-called macromolecular engineering, advanced polymeric materials are about to play critical roles in areas of major importance for society, such as energy, health, environment and advanced technologies. Typically, comprehensive description of microstructure/properties relationships in polymeric materials appears essential to better understand their macroscopic behavior. Such description ideally requires exhaustive structural elucidation of the analyzed macromolecules. Unfortunately, to date, no direct method is available to unambiguously characterize structural details in polymers of high (or even moderate) molecular weight. In this context, NMR is typically regarded as one of the techniques of choice, but its intrinsically low sensitivity precludes the elucidation of subtle structural or dynamic features in polymers. Several methods have been proposed to enhance the NMR sensitivity, including Dynamic Nuclear Polarization (DNP).[1] Recently, continuous technological and theoretical DNP developments have resulted in remarkable solid-state NMR advances, which would have been totally difficult to achieve a few years earlier without DNP.[2] In this communication, we will present that, by capitalizing on recent advances in DNP polarizing agent design,[3] high-resolution solid-state DNP NMR can considerably improve the characterization of functionalized high-molecular weight polymers. Typically, we will show that by choosing appropriate polarizing agent and sample preparation, polymer chain-end signals of both, living polystyrene samples (**Fig. 1**) obtained *via* Nitroxide Mediated Polymerization (NMP) in presence of MAMA-SG1 and a poly(ethylene oxide) (PEO) diacrylate sample, while hardly observable in conventional SSNMR, could be clearly identified in the DNP SSNMR spectrum due to the increase in sensitivity afforded by the DNP setup (a factor ~10 was achieved here). Obviously this gain in sensitivity opens up new avenues for the characterization of macromolecules and molecular compounds dispersed in polymer matrix.

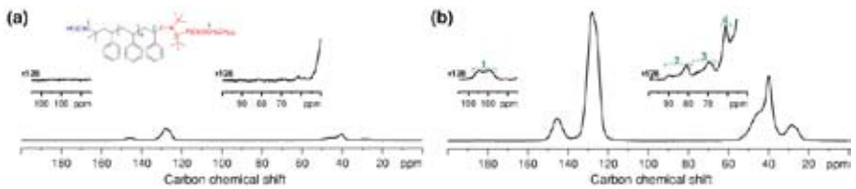

Figure 1. ^{13}C CPMAS SSNMR spectra of a living PS sample (M_n 13500 g mol^{-1}) obtained (a) without and (b) with DNP (at 285 and 105 K, resp.). The sample in (b) was doped with 0.5 wt% bCTbK. In both cases 26624 scans were used and intensity scales are identical.

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Characterisation of Polymers using Modern Methods in Electron Microscopy

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Electron microscopy characterisation of polymer based materials has been developing through improvements in sample preparation and handling, and new means of manipulating the image production by controlling the energy of the incident electrons and the energy of the electrons used to produce the image. These combined developments have opened up the characterisation of soft materials to resolution limits that have not been previously possible.

Sample preparation techniques have been mostly borrowed from the biological science. Applying microtome technologies, cryopreparation techniques such cryosectioning and rapid freezing to polymer samples, has allowed a range of materials to be prepared and examined. In addition microscope technology has developed. More sensitive camera systems allow examination at low dose, restricting beam damage. The microscopes can also examine materials under cryogenic conditions which further preserves the structure during examination.

The modern in-lens scanning electron microscope can further expand the range of materials that can be examined. Taking advantage of lowering the accelerating voltage with minimal loss in resolution and forming the image by controlling the means of extracting the emitted electrons is providing a new dimension in information available from polymer materials. Non-conducting materials can also be examined without having to coat them. This opens the possibility on a wide range of materials which until know have not been able to be examined. For example, subtle phase differences can now be visualised where the difference in composition is minimal.

This paper will outline some of the latest developments in both sample preparation and imaging, by providing examples of how the new techniques are improving our ability to understand the fine structure of polymer and polymer composite materials.

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Solid State Deuterium NMR Study of Phenylene Ring Motions in Glassy Epoxy Networks

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Network architectures in crosslinked glassy epoxy matrices control engineering properties such as modulus, yield strength, fluid sensitivity, and etc. Epoxy materials containing bisphenol A units exhibit pronounced sub-T_g relaxations as observed by various techniques including dynamic mechanical analysis, dielectric spectroscopy, neutron scattering, and solid state nuclear magnetic resonance spectroscopy (NMR). In dynamic mechanical analysis, the principle loss peak typically spans over 100 degrees with maximum lying between -80 °C and -40 °C under a testing frequency of 1 Hz. The interpretation of the molecular origin of this principle sub-T_g relaxation has been an interesting area of research in polymer physics. While some earlier work attributed this relaxation to either the motions of the phenylene rings[1] or the motions of the hydroxypropyl ether groups[2] Jones and Inglefield have definitively shown through solid state deuterium NMR spectroscopy that both motions contribute to the principle sub-T_g relaxation process, with the phenylene ring π-flips occurring at lower temperatures and the trans-gauche isomerization of the hydroxypropyl ether groups at higher temperatures[3]. Although there has been clear evidence on the correlation between the ring motions and the sub-T_g relaxation, there have been debates over how phenylene ring π-flips induce mechanical relaxation, considering the symmetry of ring flips which seem to involve no other atoms and cause no volume change[4].

In this work, phenylene ring motions were studied by means of solid state deuterium NMR spectroscopy and quadrupolar echo lineshape simulation in two crosslinked DGEBA epoxy networks cured with isomeric DDS. Four samples with different deuterated sites were synthesized and the phenylene ring motions were interpreted as a combination of π-flips and small amplitude fast vibrations via simulation using a four-site jump model. Lineshape simulation gave the rates and vibrational amplitudes of motion as well as their distributions. The amine rings in the 3,3'-DDS system do not exhibit large amplitude motions. The other three ring motions all contribute to the sub-T_g relaxations. The apparent activation energies for epoxy ring motions in 3,3'-DDS and 4,4'-DDS systems are 55.2 kJ/mol and 53.8 kJ/mol, respectively, and that for 4,4'-DDS amine ring motion is 62.3 kJ/mol. The cooperativity of the motions was calculated using Starkweather method and the mechanical relaxation mechanism will be discussed. The apparent activation energies for the ring flip motions were determined using the main correlation times from simulations according to the Arrhenius relationship and the plot is shown in Figure 1 shows how the slopes of linear fitting the activation energies E_a of ring motions can be obtained using this technique.

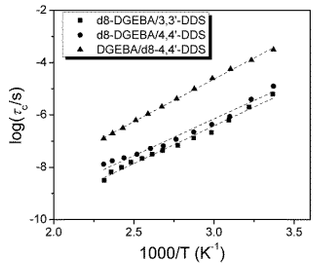

Figure 1: Phenylene motions

[1] A.N. Garroway, W.N. Ritchey, W.B. Moniz, *Macromolecules* **1982**, *15*, 1051-1063
[2] G. Williams, D.C. Watts, *Trans. Faraday Soc.* **1970**, *66*, 80-85
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Analysis of lamellar morphology of semi-crystalline polymers using small angle scattering and the linear correlation function

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The linear correlation function (LCF) is a well-established tool for extracting structural parameters from small angle scattering data from pseudo-one-dimensional systems such as lamellar semi-crystalline polymers. Here we present a simple LCF routine to for small-angle-scattering data, useful for both small-angle x-ray (SAXS) and small-angle neutron scattering (SANS) data, with a focus on simplicity of data formatting and ease of use. We will present a short review of the use of LCF applied to SAXS and SANS data, covering issues of optimum Q-range, interfacial models, background subtraction and possible artefacts using a case study of UV-radiation-induced degradation in linear low-density polyethylene (LLDPE) films. Films of Dowlex 2045 G LLDPE were aged for different periods in an accelerated UV aging environment and imaged on the Australian Synchrotron SAXS/WAXS beamline[1]. The correlation function from the SAXS data was calculated as a function of film age and shows that the lamellar long period decreases with age, while the lamellar thickness remains roughly constant. Furthermore the interfacial width between the crystalline and amorphous regions decreases with increasing age. The analysis is, provided that certain limitations are observed, suitable for the rapid analysis of large amounts of data, for example as the result of synchrotron measurements.

1. Hsu, Y-C., Weir, M. P., Truss, R. W., Garvey, C. J., Nicholson, T. M. and Halley, P. J. A fundamental study on photo-oxidative degradation of linear low density polyethylene films at embrittlement. Polymer, 53 (12), 2012, 2385–2393.

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Since 2002	Research Scientist and co-responsible SANS instrument Quokka, ANSTO

Research interests: biopolymers, cellulose, polymer physics, small angle scattering

Longitudinal and Transverse properties and molecular motions in single aramid fibers

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The para-aramid fibre is a high performance fibre mostly used in bullet-proof vest, wires or wheels because of its good mechanical properties such as its high modulus (85 GPa), its good transverse resistance conferred by its anisotropy or its high temperature resistance. The mechanical performance of an aramid fibre is due to its different scales organisation: the primary (molecular structure held by covalent bonds), the secondary (pleated sheets held by interactions) and the tertiary structure (sheets stacked together). The longitudinal mechanical properties of a single para-aramid fibre are far better known than its transverse ones and even though the molecular structure is well understood, the molecular motions are not[1]. The transverse compression (called Brazilian test) has been done experimentally by different authors[2,3], but they sometimes consider more than one fibre and did some assumptions such as isotropy or not considering the elasticity limit. This study is based on investigating the single fibre mechanical properties (mean diameter of 14 µm), coupling longitudinal and transversal testings. Particular attention has been paid on the transverse properties, focusing on dissipation processes. Developing an experimental setup [4] (ordinary used for soft adhesives called the Micro-Tack), it has been possible to follow a compression test; either one cycle load/unload or a cyclic solicitation; and look at it from an upside camera (**Figure 1**). The mechanical transverse behaviour obtained from this experiment show, for instance, a first cycle highly dissipative, similar along a fibre (**Figure 2**) and leads to a softening in subsequent cycles.

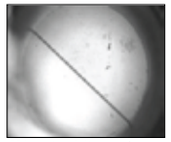

Fig. 1: View from the camera of the fiber compression.

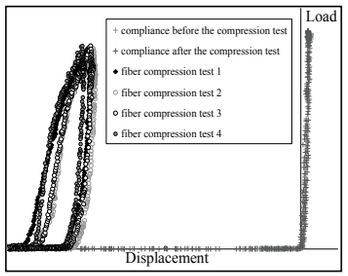

Fig. 2 : Compression test on four points on a single fiber.

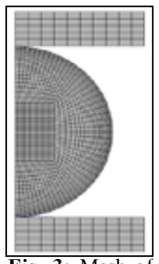

Fig. 3: Mesh of the compression test on the fibre.

Finite element modelling (ZéBuLoN code) was used in support to this experimental investigation to give a relevant quantification of the transverse elastic modulus and of the yielding stress. Compression tests were calculated assuming an anisotropic behaviour (**Figure 3**). The elasticity domain is well represented but the plasticity domain is much more complex with the contact area changing, the irreversible molecular motions and the disparity of the experimental results.

This experimental study will be used to develop a multi-scale structural characterization in order to reveal the transverse structure/properties relationship and further understand the structural parameters controlling the dissipative mechanism.

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[2] S. L. Phoenix, J. Skelton, *Textile Research Journal*, **1974**, *44,* 934-940
[3] J. Singletary, H. Davies, *Journal of Materials Science*, **2000**, *35*, 573-592

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Research interests: single fibre, polymers, mechanical properties, molecular behavior, material characterization.

NEXAFS measurements of a high mobility semiconducting polymer on the soft X-ray beamline at the Australian Synchrotron

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Being able to combine the optoelectronic properties of inorganic semiconductors with the processibility and flexibility of polymers and small molecules makes organic electronics a highly attractive technology.[1] OFETs (organic field effect transistors) in particular are one such area within organic electronics which exploits carbon-based organic semiconductors like conjugated polymers as the active electronic medium. OFETs are currently being developed for a variety of applications including low-cost, flexible electronic devices through the use of high-throughput printed flexible thin film transistors. A key issue for the development and exploitation of this technology is to understand the interplay between film microstructure and charge transport in order to control interfacial molecular structure in solution-processed organic semiconductor films.[2] Organic semiconductors tend to be significantly more disordered than their inorganic counterparts, with most semiconducting polymers exhibiting complex, semicrystalline or liquid crystalline structure. Nevertheless, highly-ordered solution-processable polymers with charge transport mobilities similar to amorphous silicon have successfully been developed.[3] It is well-known that charge transport in an OFET occurs within the thin accumulation layer that forms within the first few nanometres from the dielectric/semiconductor interface making sensitivity to near-surface structure paramount. In this presentation results will be discussed where synchrotron radiation, in particular Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy, was used to probe the degree of order and measure the molecular orientation at the interfaces of P(NDI2OD-T2), a high mobility semiconducting polymer. An update of the current status of the Soft X-ray beamline at the Australian Synchrotron will also be given.

[1] S.R. Forrest, *Nature,* **2004**, *428*, 911-918
[2] H. Sirringhaus, *Adv. Mater.,* **2005**, *17*, 2411-2425
[3] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M.L. Chabinyc, R.J. Kline, M.D. McGehee, M.F. Toney, *Nat. Mater.,* **2006**, *5*, 328-333

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Research interests: My research interest is based around organic electronics especially with regards to understanding the orientation and morphology of organic molecules in organic photovoltaic devices using synchrotron based techniques.

Precision Macromolecular Chemistry: Building Nanostructured Materials One Molecule at a Time.

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Chemists are remarkably proficient at directing the synthesis of small molecules, but fine-tuning the structures of large molecules, such as those found in polymers, is far more taxing. Despite many years of research, the field of macromolecular engineering i.e. the preparation of large molecules with strict control over their size and chemical groups has many mountainous challenges yet to overcome. Nature provides endless examples of precisely engineered macromolecules; proteins, for instance, which contain amino-acid side-chains that are accurately positioned, often in a way that determines the proteins' roles. Synthetic chemists have tried to recreate nature's exceptional control over macromolecules, and in so doing they have designed new materials with precisely defined structures, for use in applications ranging from materials to medicine.

The lecture will describe new synthetic paths to design macromolecules showing excellent control over their topology and functionality. These synthetic macromolecules are then exploited to directly form functional materials, or associated to biopolymers such as peptides to form natural / synthetic polymer conjugates. The exploitation of these well-defined macromolecules for the design of functional nanostructured materials via molecular self-assembly and self-organization will be discussed, with examples of applications in the material and biomedical fields.

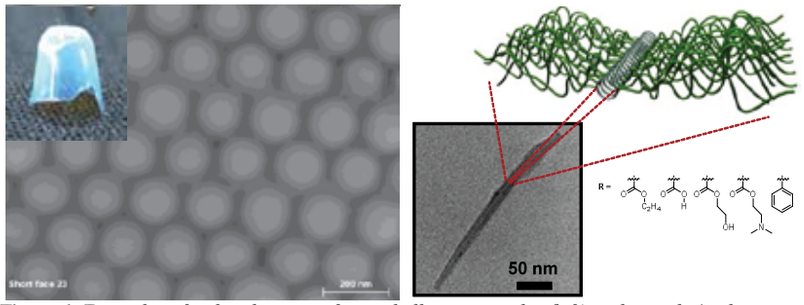

Figure 1. *Examples of ordered arrays of core shell nanoparticles (left) and peptide / polymer conjugates nanotubes (right).*

Selected Recent Publications

- Gody, G.; Rossner, C.; Moraes, J.; Vana, P.; Maschmeyer, T. ; Perrier, S. *J. Am. Chem. Soc.*, **2012**, 134 (30), 12596–12603
- Chapman, R.; Jolliffe, K.A.; Perrier, S. *Polym. Chem.*, **2011**, 2011, 2 (9), 1956-1963
- Konkolewicz, D.; Gaillard, S.; West, A.G.; Cheng, Y.Y; Gray-Weale, A.; Schmidt, T.W., Nolan, S.P.; Perrier, S. *Organometallics*, **2011**, 30 (6), 1315-1318.
- Kakwere, H.; K.Y. Chun, C.; Jolliffe. K.A.; Payne, R.J., Perrier, S. *Chem. Commun.*, **2010**, 46, 2188-2190
- Semsarilar, M.; Perrier, S. *Nature Chem*, **2010**, 2, 811-820
- Konkolewicz, D.; Gray-Weale, A.; Perrier, S. *J. Am. Chem. Soc.*, **2009**, 131 (50), 18075-18077
- Kakwere, H.; Perrier, S. *J. Am. Chem. Soc.* **2009**, 131(5), 1889-1895

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Azide-functionalized Poly-2-Oxazoline Brushes for Biomedical Applications

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The controlled delivery of genes and drug therapeutics are a vital aspect of modern medicine. Inspired by naturally occurring polypeptides, poly-(2-oxazoline)s are excellent candidates for applications in the field of drug and gene delivery as their structure is similar to natural polypeptides. These synthetic polymers thus offer potential advantages to overcome current obstacles in drug and gene therapeutics in terms of cytotoxicity and efficiency. Cylindrical polymer brushes have become increasingly popular because of their anisotropic character and the recent results on the shape dependent endocytosis.

The synthesis of azide functionalized poly-(2-oxazoline) brushes offers a simple opportunity for further modifications as conjugation of biologically active molecules like proteins, peptides or carbohydrates. Reduction of the azide groups leads to amine groups at the end of each side chain, which offers another versatile route for conjugation reactions and provides cationic charges for complex formation with DNA and siRNA.

In this work different N_3-functionalized poly-(2-oxazoline) brushes consisting of ethyl- and/or isopropyloxazoline units were synthesized. According to literature 2-isopropyloxazoline offers a lower critical solution temperature of around 37°C and 2-ethyloxazoline a transition temperature of around 70°C, depending on the molecular weight, concentration and salt content. We choose these two monomers as they offer the possibility to access control of the lower critical solution temperature in the range of 30°C to 70°C which might be advantageous for applications in the biomedical field. The synthesized brushes were characterized by static and dynamic light scattering as well as by AFM. The molecular weight of the different brushes lies in the range of $3.6 \cdot 10^6$ g/mol and $6.8 \cdot 10^5$ g/mol. The hydrodynamic radius ranks from 42 nm to 25 nm. Figure 1 shows AFM images of different N_3-functionalized poly-(2-oxazoline) brushes. Recently our group developed a new method based on dynamic light scattering to determine the aggregation behavior of nanoparticles in human blood serum.[1] First experiments with the azide functionalized brushes show no protein absorption in human blood serum. Hence cylindrical poly-2(-oxazoline) brushes may be promising candidates for various biomedical applications.

Further experiments focus on the reduction of the azide-groups. Two different reduction methods were tested and the results will be presented. Finally the obtained amine functionalized brushes will be used in DNA or siRNA complexation experiments.

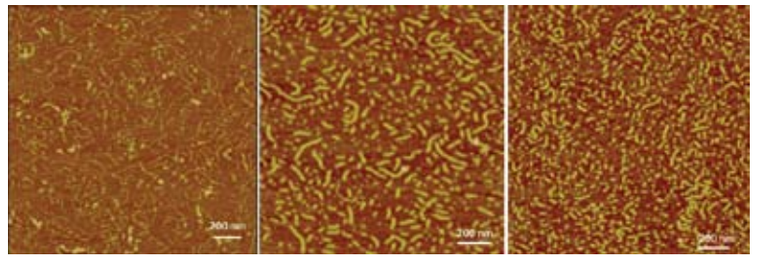

Figure 1. AFM pictures (height) of poly-(2-oxazoline) brushes of different size and composition spin cast from aqueous solution onto mica.

[1] K. Rausch, A. Reuter, K. Fischer and M. Schmidt , Biomacromolecules **2010**, *11*, 2836-2839

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Polymers for Inorganic Scale Control: On the Edge of Glory

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Scale formation from aqueous solution is a significant problem in many industrial processes, impairing efficiency and necessitating costly shut-downs in processes as diverse as sugar milling and seawater desalination. For many years low molecular-weight polyelectrolytes, such as poly(acrylic acid), have been used to inhibit scale formation in aqueous solution. Three mechanisms that have been observed are chelation of scale-forming cations, adsorbing to crystallites to act as dispersants, and adsorbing to crystallites to block growth sites. We have found that the extent of inhibition of bulk crystallisation by poly(acrylic acid) in the calcium oxalate and calcium carbonate scaling systems can be increased by incorporating end-groups of moderate hydrophobicity.[1]

We have been using Atom Transfer Radical Polymerisation (ATRP)[2] to prepare poly(acrylic acid) scale inhibitors of known molecular weight and end-group functionality and applying them to investigation of calcium carbonate, magnesium hydroxide, calcium sulfate and calcium oxalate scaling. In these systems we have found dramatic effects on inhibition time,[1] crystal morphology and speciation,[3] and the balance between heterogeneous and homogeneous nucleation.

This presentation will survey our current experimental work and molecular dynamics modelling on these systems being carried out to investigate the hypothesis that polymers with structure encouraging them to be **edge-active** under conditions where different charge densities are exhibited by different crystal surfaces will be most effective in inhibiting scale formation (**Fig. i**).

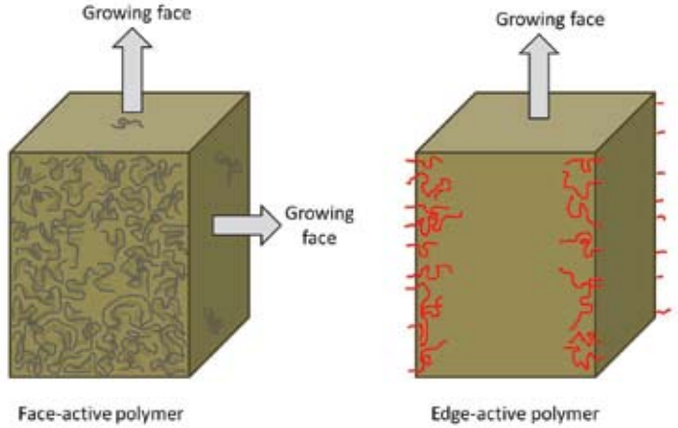

Figure I. The Edge-Active Polymer Model for crystal growth inhibition

[1] A. D. Wallace, A. Al-Hamzah, C. P. East, W. O. S. Doherty, C. M. Fellows, *J. Appl. Polym. Sci.* **2010**, *116*, 1165-1171
[2] Q. Ma, K. L. Wooley, *J. Polym. Sci., Polym. Chem*. **2000**, *38*, 4805-4820
[3] C. P. East, A. D. Wallace, A. Al-Hamzah, W. O. S. Doherty, C. M. Fellows, *J. Appl. Polym. Sci.*, **2010**, *115*, 2127-2135.

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Influence of the architecture of thermosensitive copolymers bearing phosphonated moieties on their physical properties in water

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The synthesis of thermosensitive copolymers bearing phosphonic acids moieties with different architecture is described here. All copolymers have been synthesized from N-*n*-propylacrylamide (N*n*PAAm) as acrylamide monomer leading to the thermosensitive properties of the copolymers. The incorporation of phosphonated moieties was obtained by the copolymerization of the N*n*PAAm monomer with different phosphonated co-monomers, the (dimethoxyphosphoryl)methyl 2-methylacrylate (MAPC1) and the diethyl 2-(acrylamido)ethylphosphonate (DAAmEP). From theses monomers, three different copolymers have been synthesized. Two of them, P(N*n*PAAm-*stat*-MAPC1) and P(N*n*PAAm-*stat*-DAAmEP) have been obtained by free radical copolymerization. P(N*n*PAAm-*block*-DAAmEP) was obtained by a two-step RAFT polymerizations process as already described in a previous paper[1]. Theoretical architectures of both statistical copolymers were determined by measuring the reactivity ratios of both monomers couples, *i.e.* NnPAAm/MAPC1 and NnPAAm/DAAmEP. The diblock architecture of P(N*n*PAAm-*b*-DAAmEP) obtained by RAFT polymerization have also been verified. For all copolymers, an additional hydrolysis step of the phoshonated esters into phosphonic acid was achieved leading to three thermosensitive copolymers bearing phophonic acid moieties, the P(NnPAAm-*stat*-$_h$MAPC1) and P(NnPAAm-*stat*-AAmEPA) for the statistical copolymers and the P(NnPAAm-*b*-AAmEPA) for the diblocks copolymer. The thermosensitive behaviour of these three copolymers was evaluated (Fig.1). All three copolymers, characterized by the same amount of phosphonic acid moieties, showed different thermosensitive properties which was linked to the copolymers architecture.

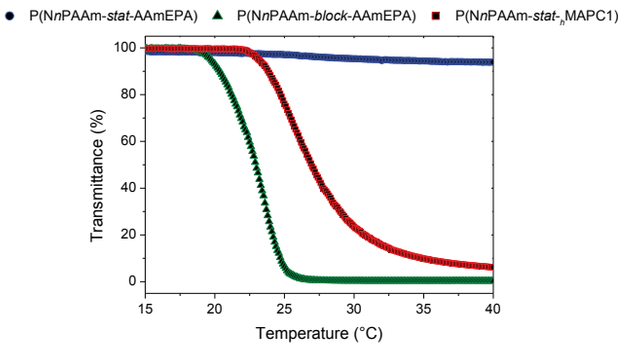

Figure 1. Thermosensitive behaviour of copolymers aqueous solutions (5 g.L^{-1}).

Finally, the sorption properties of all three copolymers for Ni^{2+} metallic pollution were evaluated in different conditions which brought important information on the sorption mechanisms involved between the phosphonic acid groups and Ni metallic pollution.

[1] A. Graillot, S. Monge, C. Faur, D. Bouyer, J.J. Robin, *Polymer Chemistry*. **2013**, DOI:10.1039c2py20720f.

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Incorporating Indazoles into the Dopamine Self-Polymerisation System

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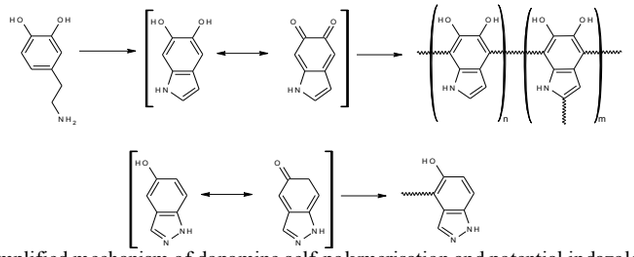
Since the seminal work of Messersmith and coworkers[1] into the mussel-inspired self-polymerization of dopamine, research into this area of biomimetic polymers has ballooned. In this short five year span, over 100 articles relating to this dopamine polymerization and use can be found. Messersmith and coworkers were able to show that a pH-buffered aqueous solution of dopamine would result in the spontaneous formation of a thin and robust cross-linked polymer coating on an array of flat materials dipped into the solution.[1] Furthermore, the surfaces were capable of cell adhesion, multi-layer reactions through latent amine and hydroxyl groups on the polydopamine coating, as well as microlithography imprinting. This work led to increased research efforts into this area, where polydopamine coatings have been investigated for hollow nanocapsule generation[2], biomimetic surfaces[3], and even living-cell encapsulation[4].

However, it should also be noted that even though the mechanism for this reaction has been investigated, the agreed upon system is still relatively illusive. One of the main commonalities between the proposed mechanisms for this base catalyzed self-polymerization is the conversion of the catechol functional groups into quinone structures, and thereby activating the adjacent aromatic carbon atoms for the polymerization process (Scheme 1). It would appear that the nature of the fused indole ring plays very little into the formation of the quinone structure, as derivatives in the 2 position of the indole have also been shown to abide by this mechanism. With this in mind, we have begun to extrapolate this polymerization scheme to other compounds of similar structure to the 5,6-dihydroxyindole formed from the dopamine cyclization. If the driving force for this self-polymerization mechanism is the base-catalyzed formation of the quinone structure, then this mechanism could be useful for the aqueous polymerization of a wide range of compounds. One compound of particular interest is indazole compounds, where the carbon in the 2 position of the indole (where crossliking occurs in Scheme 1) is replaced with nitrogen. These indazole compounds have been shown to exhibit a large range of biological activities as well as medical properties such as antimicrobial agents, anti-HIV agents, and ligands for ruthenium-based chemotherapy agents. We've characterised their incorporation using solid state NMR techniques as well as cytotoxicity evaluations.



Scheme 1. Simplified mechanism of dopamine self-polymerisation and potential indazole incorporation.

1 H. Lee, S.H. Dellatore, W.M. Miller, P.H. Messersmith, *Science* **2007**, *318*, 426.
2 A. Postma, Y. Yan, Y. Wang, A.N. Zelikin, E Tjipto, F. Caruso, *Chem. Mater.* **2009**, *21*, 3042.
3 Q. Ye, F. Zhou, W. Liu, *Chem. Soc. Rev.* **2011**, *40*, 4244.
4 S.H. Yang, S.M. Kang, K.-B. Lee, T.K. Chung, H. Lee, In.S. Choi, *J. Am. Chem. Soc.* **2011**, *133*, 2795.

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Responsive macromolecular assemblies: sol / gel transition under pH and temperature control.

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Responsive polymers were prepared by copolymerizing a small amount of ionisable monomers, acrylic acid (**A**) or N,N-dimethylaminopropylmethacrylamide (**M**), with N-isopropylacrylamide (**NIPA**). From differential scanning calorimetry experiments, it is shown that the pH strongly influences the phase separation of these copolymers (**PNIPA-A** and **PNIPA-M**) in water (temperature and enthalpy). At pH 7, when ionisable groups are charged, both PNIPA-A and PNIPA-M remain soluble in water at all temperatures but their mixtures show a phase separation above a critical temperature due to the formation of a reversible inter polyelectrolyte complex.

When PNIPA-A stickers are introduced as side-chains within a poly(acrylamide) backbone (**PAM**), pH and temperature are still able to drive the association process at a local scale, giving rise to a sol/gel transition of semi-dilute solutions (see **Fig.1**). At pH 7, while the graft copolymer PAM-g-PNIPA-A cannot self-assemble in water, even at high temperature, the introduction of oppositely charged PNIPA-M is able to trigger the self-assembling process in a very specific way (**Fig.1**).

The structure and the viscoelastic properties of these complex macromolecular assemblies are investigated by small angle neutron scattering, DSC and rheology and their responsivity is discussed as a function of environmental conditions.

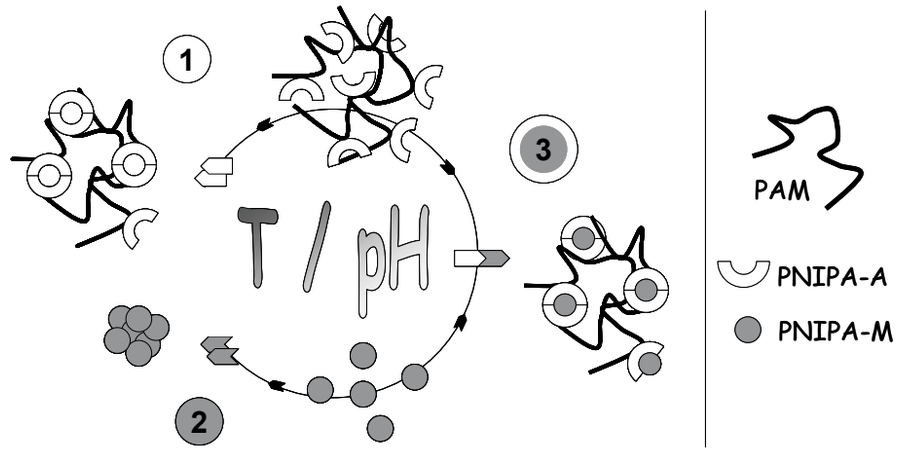

Figure 1. Responsive macromolecular assemblies in aqueous solutions.

[1] E. Siband, Y. Tran, D. Hourdet, *Progress in Colloid and Polymer Science* **2010**, *137*, 19-22.
[2] E. Siband, Y. Tran, D. Hourdet *Macromolecules* **2011**, *44*, 8185-8194.

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Functional polymers for the design of nanoengineered polymer capsules

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The layer-by-layer (LbL) technique has found widespread use for the nanoscale engineered assembly of materials, as it is simple, versatile and allows precise control over film properties such as thickness and morphology. Recently, there has been emphasis on the development of biocompatible LbL capsules specifically engineered to respond to specific stimuli for therapeutic delivery applications or as microreactors.

The preparation of LbL polymer capsules stabilized by "click chemistry" and/or highly efficient cross-linking reactions is reported. For this purpose polymers with different side and end group functionalities were synthesized and utilized for the design of responsive polymer capsules. The choice of the polymerization technique or post-polymerization modification allowed the introduction of diverse functionalities, which allowed the stabilization of the capsules using different approaches. The polymers obtained rendered the capsules responsive to external stimuli such as pH, temperature and redox. This responsive behavior was exploited, e.g. for the preparation of dual stabilized capsules with gateable permeability.

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Diffusion in Precisely-Structured Hydrogels of NIPAM

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Polymeric hydrogels have myriad applications many of which depend on an understanding of how molecules diffuse through their structure. Diffusion is a complex phenomenon, and the observed rate of diffusion critically depends on both the method and the time scale of observation. In the limit of infinitely short times the solute/drug molecules diffuse in an unhindered manner, similar to Brownian motion is a pure solvent. At progressively longer times there is an increasing probability that a solute molecule encounters an obstacle (e.g. polymer chains), thus decreasing its overall rate of translational motion. The dependence of the rate of diffusion of the solute on the diffusion (observation) time yields important information on the structure of the diffusive medium, in this case the polymeric hydrogel. This has obvious implications for studies of drug release from hydrogels, to give but one important example.

In this work we have examined diffusion of water and water-soluble probe molecules in hydrogels prepared by a combination of reversible-deactivation radical polymerisation and 1,3-dipolar cycloaddition click chemistry. A series of telechelic macromers of N-isopropylacrylamide were prepared using RAFT polymerisation and these were crosslinked into three-dimensional polymers of infinite molecular weight using the copper-catalysed azide-alkyne coupling reaction. The polymers were rigorously characterised by conventional and advanced spectroscopic techniques to confirm a highly regular structure largely free of defects usually found in conventional hydrogels.

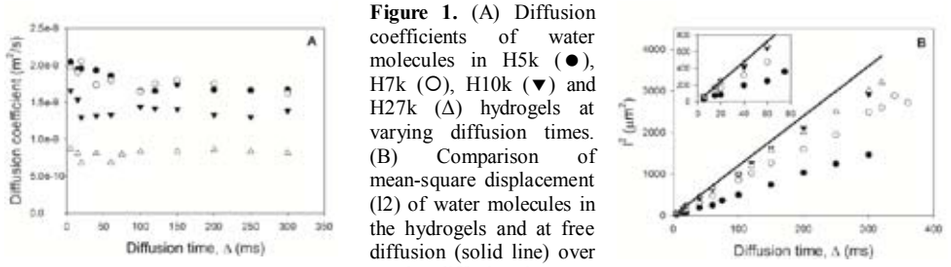

Figure 1. (A) Diffusion coefficients of water molecules in H5k (●), H7k (○), H10k (▼) and H27k (Δ) hydrogels at varying diffusion times. (B) Comparison of mean-square displacement (l2) of water molecules in the hydrogels and at free diffusion (solid line) over varying diffusion times.

The structure of the hydrogels was further characterised by measurement of the coefficients of diffusion of water molecules within the hydrogels using pulsed-gradient spin echo NMR. The rate of diffusion was found to depend on the observation time, indicative of restricted diffusion; the polymer chains act as barriers to diffusion and the observation of a plateau in the diffusion coefficient (Figure 1(A)) with increasing observation time demonstrates the presence in the gel of an effective diffusive volume. The size of this diffusive volume is several orders of magnitude larger than the polymeric mesh size, suggesting that the water molecules pass through a large number of interconnected spaces defined by the hydrogel structure. Hydrogels of PNIPAM experience a volume change close to the temperature of the lower critical solution temperature of equivalent linear chains. Measurements of the diffusion coefficient as a function of temperature confirm a dramatic decrease in the diffusive volume as the temperature is increased.

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Block Copolymer Drug Delivery Vehicles from a Combination of RAFT and Anionic Polymerization Routes

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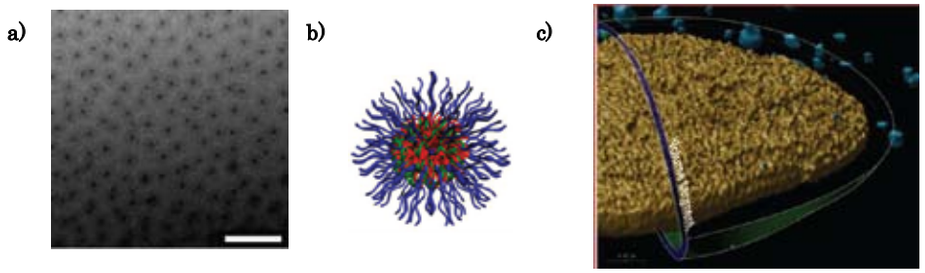
My research group is focused on the development of polymers for the delivery of drugs, nucleic acids, and peptides. The intracellular delivery of nucleic acids offers unprecedented promise for revolutionizing biomedical research and novel drug development. Likewise, small molecule drug and vaccine development could significantly benefit from new materials that aid targeted delivery. However, the polymeric delivery vehicle plays a central yet elusive role in dictating the efficacy, safety, mechanisms, and kinetics of transport 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, drugs, and peptides into nanocomplexes 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 and anionic polymerization methods, allowing us to create a variety of block copolymer architectures with saccharides and functional groups of diverse chemistries (hydrophobic, cationic, and anionic units) in a highly controlled manner. To examine the intracellular mechanisms of delivery, we have utilized live cell confocal microscopy imaging techniques to examine the intracellular trafficking of the vehicles, which allows us to observe nanocomplex movement in a spatial and temporal manner.

Figure 1. a) CryoTEM image of polymeric micelles formed with carbohydrate-based block copolymers (scale bar = 100nm). b) Depiction of the core-shell structure of the nanocomplexes (polymerized pendant carbohydrates form the shell in blue). c) 3D image of the polymeric nanocomplexes (blue) trafficking near the nucleus (yellow) in a HeLa cell.



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Preparation of Polymeric Nanoparticles for Therapeutic Applications

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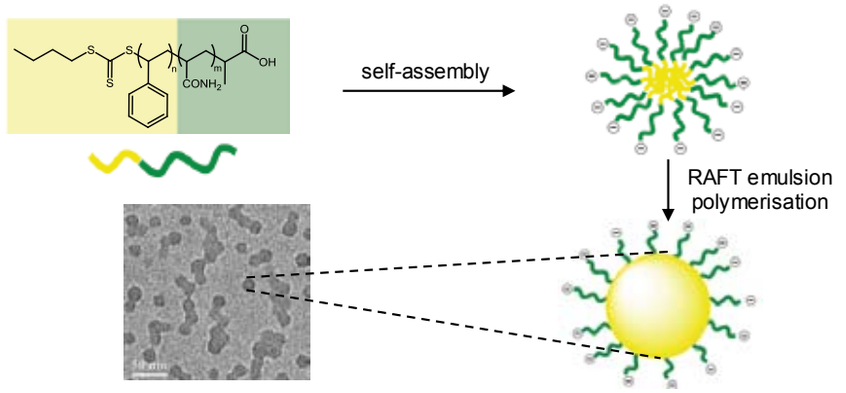
Polymeric nanoparticle drug carriers have attracted great interest in therapeutics for their potential applications in gene and drug delivery. The incorporation of polymers in therapeutics offers a promising route to improve function and properties, such as enhancing cellular uptake of drugs across biological barriers, improving solubility, pH and charges in cellular environment and therefore improving the drug biocompatibility and control of drug release.[1]

By employing surfactant-free RAFT emulsion polymerisation,[2-5] we have prepared 20-30 nm polystyrene (PS) latex particles with narrow dispersities. The PS nanoparticles were stabilised by an amphiphilic diblock copolymer, polyacrylamide$_m$-*block*-polystyrene$_n$ (PAAm$_m$-*b*-PS$_n$), which synthesis was mediated by the amphiphilic chain transfer agent 2-propanoyl butyl trithiocarbonate (PABTC). The resulting amphiphilic diblock copolymer self-assembled in water and formed micelles, which were evolved into PS particles *via* RAFT emulsion polymerisation of styrene (**Scheme 1**). The surface of these polystyrene nanoparticles was functionalised with Rhodamine B (RhB) to allow for tagging of the particles for *in vivo* tests on a mouse model. The RhB-labelled PS nanoparticles were shown to be present in the blood circulation system and accumulated in heart, lungs, liver and kidneys following intravenous injection.



Scheme 1. Preparation of polystyrene latex particles stabilised by amphiphilic diblock copolymer.

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Size-exclusion chromatography of healthy and diabetic glycogen reveals differences in their biosynthesis and biodegradation.

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Glycogen is a hyperbranched glucose polymer with an assembly of linear chains of α-(1⟶4)-linked D-glucose residues connected via α-(1⟶6) branching linkages. Glycogen comprises smaller glycogen β particles (~ 10^{6-7} Da) which can also form much larger rosettes denoted α particles[1,2].
The recent discovery[3] that these α particles are smaller and fewer in diabetic, compared to healthy, mouse liver highlights the need to elucidate the nature of α-particle formation. It is postulated that the larger and denser α particles are slower to degrade back to glucose, and thus would have a slower blood-sugar release than do β particles; this has ramifications for diabetes, which is uncontrolled release of blood glucose. Here we optimized the conditions of size-exclusion chromatography by comparing glycogen dissolved in the different solvents, aqueous and dimethyl sulfoxide, run through different column materials and pore sizes. This has resulted, for the first time, in the separation of β– and α–particle peaks. This now allows much more detailed analysis of the differences between healthy and diabetic liver glycogen. Also, by analysing mouse-liver glycogen at different times in the feeding cycle, we were able to gain a much better understanding of the process of α-particle formation.
Given the recent finding that α particles are most likely connected via proteinaceous linkages[4], potential drug targets may be explored that allow diabetic glycogen to form the larger α particles found in healthy liver.

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(1) Sullivan, M. A.; Vilaplana, F.; Cave, R. A.; Stapleton, D. I.; Gray-Weale, A. A.; Gilbert, R. G. *Biomacromolecules* **2010**, *11*, 1094.
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Synchrotron X-ray imaging of gold loaded alginate microcapsules in *ex vivo* rodents for cellular based therapeutic treatments

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Cell based therapy has the potential to treat a wide range of diseases. One potential solution to enable immuno-isolation of the transplanted cells is to encapsulate the cells in alginate matrixes (called microcapsules - MCs). The aim of this project is to develop a non-invasive and simple technique that permits the tracking of the position and integrity of the MCs when placed in laboratory animals. Information obtained from tracking the MCs will help guide best practice as encapsulated cells are being contemplated as clinical therapies, for example, for treatment of insulin-dependent diabetes. The results of our preliminary experiments conducted at the IMBL (Australian Synchrotron, Melbourne, Australia) and at SYRMEP (Elettra, Trieste, Italy) beamlines have shown that gold nanoparticles (GNPs) are an attractive solution for capsules tracking if combined with X-ray computed tomography (CT).
This work focuses on the preparation of GNPs modified with polymers synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. Poly((2-methacryloyloxyethyl) trimethyl ammonium chloride)), a positively charged polymer, and poly (ethylene glycol), a non-charged polymer were used as prepared, i.e. containing dithioester end groups. Alternatively, the RAFT end groups were cleaved off affording the corresponding thiol-capped polymers. The various polymers were used to modify GNPs via either electrostatic interaction or chemical assembly (thiol group absorbed to GNPs) (Figure 1). These polymer-modified GNPs were then encapsulated in alginate MCs (~500 µm) (Figure 2) in order to test their ability to track alginate MCs within the body by X-ray imaging (Figure 3). X-ray imaging of encapsulated GNPs modified with RAFT polymers is a promising methodology to track alginate capsules *in situ* that may be used as drug delivery devices [1] or to encapsulate cells for cell therapy (diabetes treatment) [2].

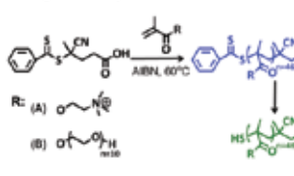

Figure 1. RAFT polymer synthesis and modification of GNPs

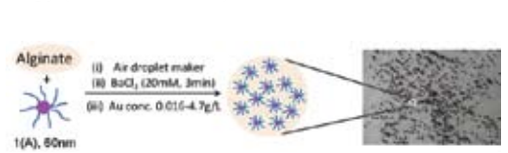

Figure 2. Synthetic route of GNPs loaded alginate MCs

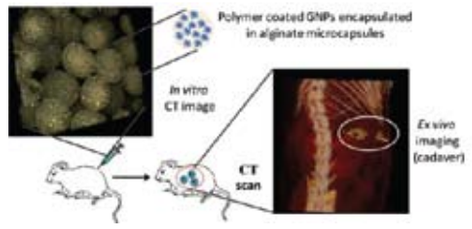

Figure 3. 3D rendering based on X-ray CT imaging of GNPs loaded alginate MCs.

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Hyperbranched Polymer-siRNA Conjugates: Advanced Polymeric Carriers for Cancer Therapy

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The discovery of RNA interference which leads to efficient silencing of specific genes by double-stranded RNA (siRNA) has opened up a revolutionary way of treating cancer-related diseases[1]. Nonetheless, in order for it to be a viable and universal therapeutic option, a number of important issues must be first addressed. Of particular importance is the poor *in vivo* stability of siRNA due to the presence of degrading enzymes (RNAse and DNAse) within the blood plasma. Additionally, efficacy of cell transfection is often compromised due to poorly-designed carrier vehicles (or in the case of free siRNA, electrostatic repulsion from the cell membrane)[2,3].

To overcome all these difficulties, we wish to develop a wide reaching and broadly applicable platform technology for the effective delivery of siRNA and complementary chemotherapeutics to cell-specific tissues using charge-neutral hyperbranched polymers (HBPs). Due to large functional-group availability on hyperbranched molecules, it is possible to covalently integrate all the modalities needed (therapeutic agents, targeting ligands, imaging moieties etc.) in one molecule. This will make our non-viral delivery system an ideal theranostic device (Figure 1).

In this presentation, a comprehensive structural analysis of our RAFT polymerised HBPs will be discussed. We would also like to communicate various strategies for covalent attachment of siRNA to polymers, along with other approaches that we have been developing in our group. This will include the development of efficient intracellular release of the therapeutics (based on various linker chemistry). Our current work has demonstrated that radical-induced reduction of trithiocarbonate end groups by using excess amount of 4,4'-Azobis(4-cyanovaleric acid) is the best method for introducing well-defined functional groups on our HBPs. We have also successfully chain extended the polymers with pyridyl disulphide (PDS)-terminated PEG linkers. We envisage that by extending the length of PDS groups away from the core of HBP, not only we can get higher siRNA-HBP coupling efficiency via thiol-disulfide exchange reactions but also better extracellular protection for the siRNA.

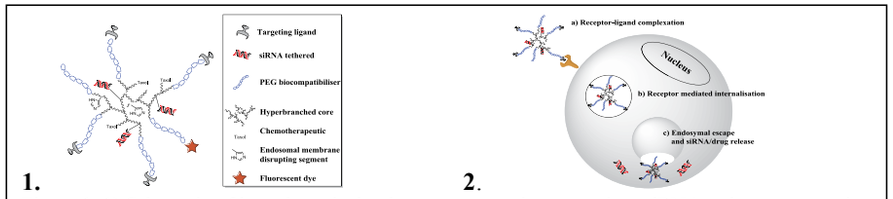

Figure 1. 1) Schematic of hyperbranched polymer structure incorporating: siRNA and a representative drug (taxols) tethered via cleavable linkages; imidazole-containing groups to facilitate endosomal escape; segments for ^{19}F MRI and; targeting ligands on the particle periphery – all of these are protected within a PEG shell. 2) Cellular processes required for effective release of siRNA and chemotherapeutic drug intracellularly

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Engineering Polymeric NanoParticles for Advanced Applications

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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. These systems can offer significant improvements in the temporal and spatial control of drug delivery. In this talk different polymeric nanoparticles that have been specifically designed to deliver anti-cancer drugs and to image specific tissue, will be discussed. The first system presented will be based on pH- and redox- responsive nanoparticles which are able to deliver different payloads in different cellular compartments. The synthesis and the characterization of these nano-objects will be outlined in detailed. As an example, the delivery of nitric oxide will be presented using these nanoparticles for the treatment of liver fibrosis and neuroblastoma. We have also demonstrated synergistic effect when we combine nitric oxide (NO) with chemotherapy drugs for the treatment in multi-drugs resistance in cancer. In a second part of this talk, the synthesis of new hybrid organic/inorganic nanomaterials, based on iron oxide, gold and gadolinium, will be reported for use as MRI contrast agents. The effect of the architecture and the nature of polymers will be correlated with the magnetic properties of these nano-objects. In addition, the polymeric shell of these nanomaterials can be designed to conjugate with anti-cancer drugs. Finally, I will rapidly mention the use of hybrid inorganic polymeric nanoparticles for the storage of hydrogen. In this part, I will present and discuss on the synthesis of magnesium hydride (MgH_2) nanoparticles stabilized and assembled using functional polymer to yield a new generation of nanomaterials with remarkable hydrogen storage properties.

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Targeted Drug Delivery: Understanding Internalisation and Processing of Nanoparticles

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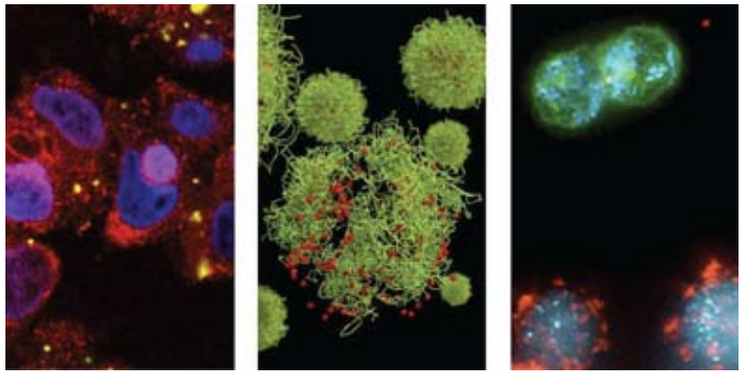
Targeted delivery of drugs to specific cells in the body has the potential to revolutionise the treatment of many diseases.[1] An emerging technique to deliver drugs is to immobilise the therapeutic inside a nanoparticle, whereby the body is protected from potentially harmful side effects of the drug, while also preventing the drug from being degraded by the body.

To engineer these 'smart', responsive materials, it is essential to understand how the nanoparticles interact with cells. In particular, internalisation and processing of nanoparticles inside the cell plays a critical role the effectiveness of the therapeutic response. Our current methods for evaluating internalisation have a number of limitations. We present here a simple, high throughput method for determining the cellular uptake of a range of materials that is independent of pH, compatible with a range of fluorophores, and does not interfere with cell phenotyping or cellular processes. Using this technique, we have demonstrated that we can specifically examine the internalisation of proteins and nanoparticles. We have demonstrated that the antibodies used to target nanoparticles to specific cells play an important role in internalisation.[2,3] To design effective nanoparticle therapies the mechanism of nanoparticle internalisation must be understood to ensure the particles are internalised and processed in the correct way.

By understanding how these materials interact with cells, we can precisely engineer the properties of nanomaterials to help improve the treatment of diseases like cancer[2] and HIV.[4]



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Oral delivery of nanoparticles to the colon for targeting colorectal cancer cells

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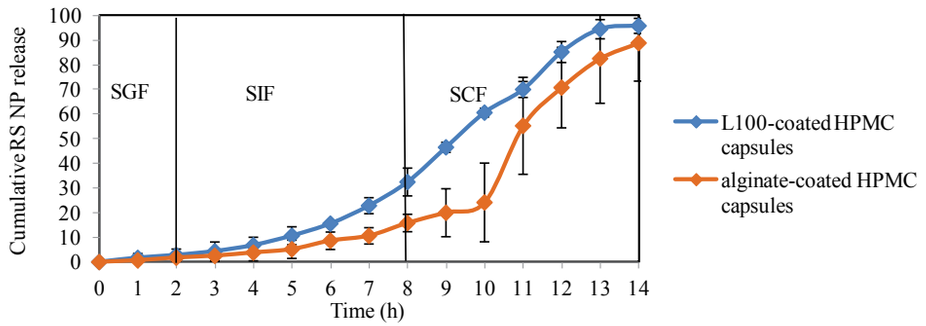
According to WHO, colorectal cancer has ranked the fourth leading cause of cancer-related death worldwide in 2008, with 1.2 million new cases diagnosed and causing 0.6 million deaths[1]. Colorectal cancer is curable at early stage during which cancer cells have not spread through the colon wall. But for patients diagnosed with cancer metastasis, their 5-year relative survival rate is only 11.9%[2]. The conventional chemotherapy has been widely used to kill cancer cells and thus prevent cancer development. Anti-cancer drugs are often administered via intravenous injection at high doses for a long time to maintain therapeutic concentration at tumor site. However, its efficacy on colorectal cancer is far from satisfactory. Blood circulation transports drug to major organs (e.g. liver, lung, heart and kidney), resulting in widespread distribution and consequently decreased drug concentration in the colon with diverse side effects. Moreover, the colonic mucosa presents a barrier for drug absorption and molecular efflux pumps in cancer cells decreases drug accumulation in cancer cells.

The problem of insufficient drug delivery to the colon tumor site could be improved by targeted delivery of nanoparticle (NP) to the colorectal region for absorption by cancer cells. The specific delivery of small molecule drugs to the colon has been widely investigated for topical treatment of local diseases. Various nanoparticles have been studied for cancer treatment due to their ability to controlled drug release and ease of surface modification to target cancer cells. Hence, the aim of our study is to protect NP release in the upper gastrointestinal tract and deliver individual NPs to the colon for cellular uptake by cancer cells.

Hydroxypropyl methylcellulose (HPMC) is extensively used in the pharmaceutical science as a controlled release agent. We investigated HPMC capsules as NP carriers to the colon, using Eudragit RS nanoparticles (130 nm in diameter) as model NPs. Eudragit L100 or alginate coating was applied to HPMC capsules, aiming to improve capsule resistance to the upper gastrointestinal fluids. In vitro NP release studies in simulated fluids indicated that Eudragit L100-coated capsules released 65% of the NP load in simulated colonic fluid (SCF). In contrast, alginate-coated capsules showed more specific NP delivery, for releasing 75% of the NP load in SCF (**Figure 1**). In collected colonic release samples, individual NPs could be detected by laser light scattering.

In conclusion, our results have shown that HPMC capsules could be a promising carrier for colon targeted NP delivery.

Figure 1. In vitro RS NP release from coated HPMC capsules



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Guanylated Polymethacrylates as Potent Antibacterials with Low Toxicity

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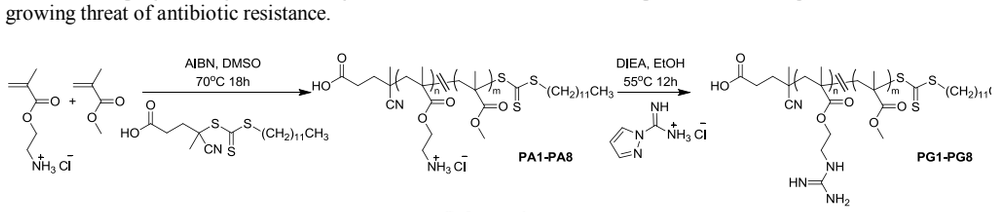
Host defence antimicrobial peptides (AMPs) are a promising lead in the search for novel antibiotics. Many of these peptides have been shown to exhibit broad spectrum antibacterial ability, low toxicity toward human cells and little susceptibility to currently known mechanisms of bacterial resistance[1,2]. Their use has been somewhat limited, however, as proteins are typically pharmacokinetically unstable and large scale production costs expensive.

Several AMP-mimicking polymers have been developed to overcome such issues. These polymers are able to retain the essential facially amphiphilic secondary structure of AMPs, while being cheaper and easier produced and chemically manipulated.

This study describes a novel class of AMP-mimicking polymers, guanylated polymethacrylates. The synthesis of these polymers was achieved using Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization, followed by a base-catalyzed guanylation (**Scheme 1**). A range of random copolymers of methylmethacrylate (MMA) and 2-guanidinoethyl methacrylate (2-GEMA) were produced, varying monomer ratio (hydrophobic character) and polymer length. A number of these poly(MMA-GEMA) copolymers exhibited potent antimicrobial effects (MIC = 10 μg/ml) against gram-positive strains of bacteria (eg. *S. epidermidis*) and low toxicity towards human blood cells.

Data produced from this study will not only help to elucidate the structure-activity relationships governing antimicrobial polymethacylates but may also reveal a lead for the development of novel agents to combat the growing threat of antibiotic resistance.



Scheme 1

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New chemotherapeutics via efficient complexation of gold(I) compounds to glycopolymers

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Auranofin is a gold(I) complex which exhibits potent toxicity to several cancer cell types conferred by strong and selective binding to the mitochondrial protein thioredoxin reductase.[1] However, the pronounced anti-cancer activity *in vitro* does not translate into *in vivo* potency due to rapid ligand displacement reactions with serum proteins.[2] We propose that amphiphilic micelles with pendant auranofin analogues in the core will shield the drug from serum proteins and improve delivery to cancer cells. Our previous studies have demonstrated that a block copolymer system containing deacetylated auranofin complexed to the core displays comparable potency to the free drug itself against ovarian cancer cells.[3] In our most recent work, auranofin has been complexed to a new glycopolymer block in a highly efficient reaction which generates very narrowly defined gold-polymer complexes (**Fig. 1a**).

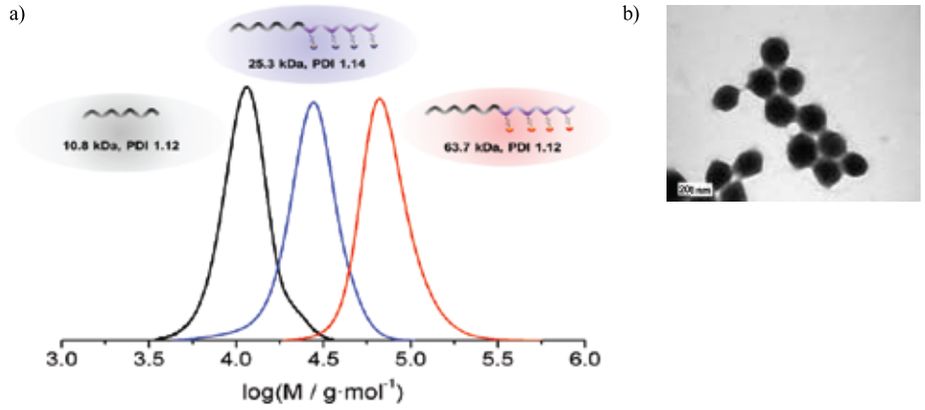

Figure 1. a) SEC traces of macroRAFT agent, block copolymer, and block copolymer-gold complex (l to r); b) Unstained TEM image of the self-assembled block copolymer containing gold(I) in the core.

A new glycomonomer containing a protected thiol was synthesised from glucose and polymerised in a well-controlled fashion via RAFT polymerisation, indicating that the protecting group successfully eliminated transfer reactions. Selective deprotection and attachment of an auranofin precursor to the exposed thiols introduced auranofin analogues along the polymer chain with high complexation efficiency and no evidence of cross-linking. Self-assembly of the block copolymers produced highly uniform spherical structures (**Fig 1b**) with promising anti-cancer activity. Toxicity against an ovarian cancer cell line and its cisplatin-resistant variant was found to depend on the hydrophobic (drug-containing) block length.

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Functional Hyperbranched Polymers for Prostate Cancer Theranostics

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Prostate cancer (PC) is the most common neoplasm in men over 50, causing 3000 deaths each year in Australia.[1] Current imaging technologies for early detection of PC are generally not sensitive enough, and thus there is great need for new technologies which allow simultaneous targeting of cancer cells, in conjunction with drug delivery and enhanced imaging – this concept is often termed "theranostics". Previous attempts to design molecules that achieve all of these functions have largely been unsuccessful *in vivo*, due to issues such as poor drug loading, poor imaging, and inefficient targeting.

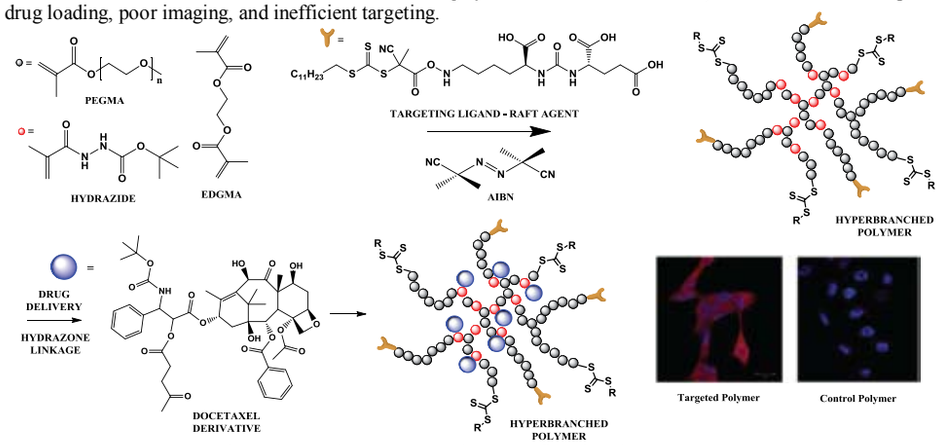

Figure 1. Reaction scheme leading to the final functional polymer.

Prostate Specific Membrane Antigen, (PSMA), is a protein that is highly overexpressed on the surface of prostate cancer cells and 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 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 and 10mol% Boc-protected hydrazide methacrylate monomer, with ethylene glycol dimethacrylate as the branching agent. The PSMA targeting molecule is attached through a glutamate urea-functionalised trithiocarbonate chain transfer agent. Following polymerisation the hydrazide monomer can be deprotected to allow attachment of a docetaxel-derivative through a hydrolytically-degradable hydrazone linkage.[3] The general methodology is outlined in Figure 1.

Preliminary results show that the PSMA targeting ligand has a high affinity for prostate cancer cells expressing PSMA, as shown in Figure 1, and that the degradation of the hydrazone linkage in an acidic environment occurs over 2 hours.

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Development of a Multimodal Hyperbranched Polymer Imaging Agent

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With the development of polymers for nanomedicine, it is important to be able to study and detect these materials *in vivo* in order to fully understand their biological fate. While one single imaging modality that combines the various attributes of high sensitivity, high resolution and high through-put is not yet clinically available, it is possible to develop multimodal devices which combine the advantages of numerous modalities into a single device.

Our group has recently developed hyperbranched polymer ^{19}F MRI devices, which are able to provide high resolution images, with high signal to noise ratio *in vivo*.[1] Here we report on the further development of these hyperbranched polymers to include fluorescent dyes for optical imaging and radioisotopic ligands for Positron Emission Tomography (PET). *In vivo* optical imaging is a commonly used pre-clinical technique, due to its relative low cost and high throughput capacity, but has drawbacks when moving to larger animal models or ultimately into a clinical setting. PET imaging is highly sensitive (10^{-11} M), but increases the radiation burden on patients and is also an expensive technique which requires access to a cyclotron. By combining these two latter imaging modalities, we are able to undertake preliminary screenings on the targeting ability of our materials with optical imaging, and then delve into more detailed experiments surrounding biodistribution of the polymer using PET.

The hyperbranched nanoparticles in this work were synthesised using RAFT polymerisation.[2] A trithiocarbonate RAFT agent was functionalised with an alkyne leaving group. This allowed for the attachment of a N_3-$(PEG)_3$-NH_2 linker-group by 1,3-dipolar cycloaddition to the periphery of the polymer. A commercially available DOTA-NCS ligand was then coupled to the amine of the PEG linker. DOTA is a macrocyclic chelator, which is commonly used in the literature for the attachment of Copper-64 for PET imaging.[3] Cu^{64} was chosen for this work as it has a longer half life (12.7 hours), in comparison to other commonly used isotopes (^{18}F: 110 mins, ^{11}C: 20 mins), which better matches the reported biological half life of polymers. Attachment of the ligands was initially characterised by ^{1}H NMR analysis and preliminary studies of copper loading were performed using cold Cu^{2+} and analysed by atomic absorption spectroscopy. *IR Dye 750* (LI-COR Biosciences) and folate targeting ligands were introduced via coupling activated NHS-esters to the remaining amines on the PEG spacer.

Preliminary *in vivo* PET and optical imaging experiments have been performed using a subcutaneous melanoma mouse model. Optical imaging experiments were performed on a Carestream MS-FX Pro imaging station and were able to show uptake of the folate labelled polymers by the tumours. These results have been corroborated with Cu^{64} imaging experiments on an Inveon PET/CT scanner demonstrating the potential of these materials as multimodal imaging devices.

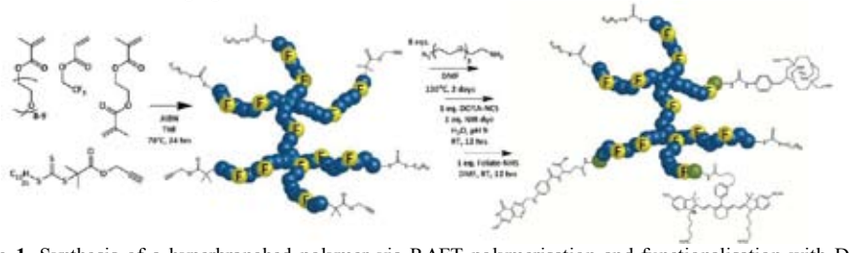

Figure 1. Synthesis of a hyperbranched polymer via RAFT polymerisation and functionalisation with DOTA ligands, NIR dyes and folic acid, to produce a targeted multimodal imaging agent.

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Smart polymer-protein hybrids and sugar-responsive micelles

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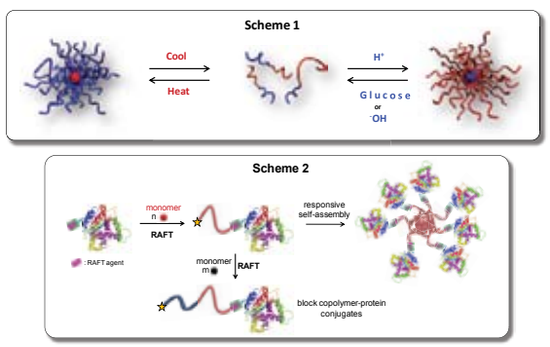
This presentation will discuss our results in two areas of responsive polymeric nanomaterials. The first topic of the presentation will discuss glucose-responsive polymers and their potential to be employed in the area of sugar-induced release of diabetes therapeutics (Scheme 1). Boronic acid-containing block copolymers were shown to be both pH- and glucose-responsive in aqueous media, which led to unique adaptive self-assembly behavior. Polymeric micelles and vesicles constructed from these block copolymers were capable of encapsulating model therapeutics and allowing their release upon an increase in the surrounding glucose concentration.

The second topic of the presentation will describe the synthesis and characterization of polymer-protein conjugates (Scheme 2). Specifically, block copolymer-protein bioconjugates were prepared by grafting from proteins modified with reversible addition-fragmentation chain transfer (RAFT) agents. Both maleimide-functional and activated ester-functional RAFT agents were reacted with cysteine or amine residues, respectively, on model proteins to afford protein macro-chain transfer agents that contained the RAFT agents immobilized via their R-groups. Polymerization of *N*,*N*-dimethylacrylamide (DMA) led to poly(DMA)-protein conjugates that retained the thiocarbonylthio functionality necessary for addition of a second block of poly(*N*-isopropylacrylamide). The resulting block copolymer conjugates contained an outer hydrophilic block and an inner thermoresponsive block. Cleavage of the block copolymers from the proteins and subsequent analysis suggested the homopolymerizations and subsequent block copolymerizations were efficient and well-controlled. Preliminary solution studies of the resulting block copolymer-conjugates indicated the self-assembly behavior and bioactivity could be controlled by temperature modulation.



Macromolecular Ruthenium(III) Chemotherapeutics

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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.

NAMI-A has completed Phase I trials and shown high selectivity for tumour metastases,[3] and is thus a very promising candidate for chemotherapy. We designed a macromolecular drug based on NAMI-A by synthesising a polymer backbone containing imidazole units.[4] The rest of the complex could then be attached in a similar fashion to the synthesis of the small molecule NAMI-A.[5] **Figure 1** shows the proposed homopolymer structure.

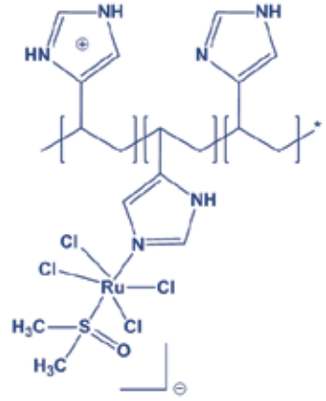

Figure 1. NAMI-A Macromolecule.

Initial cytotoxicity results were promising but difficulties with solubility arose. The polymeric candidate was further improved by synthesising an amphiphilic polymer that could form micelles. Poly(ethylene glycol) methyl ether acrylate was chosen as a suitable water-soluble block due to its biocompatibility and hydrophilicity, while poly(vinyl imidazole) was used to form the core and drug component (**Figure 2**).

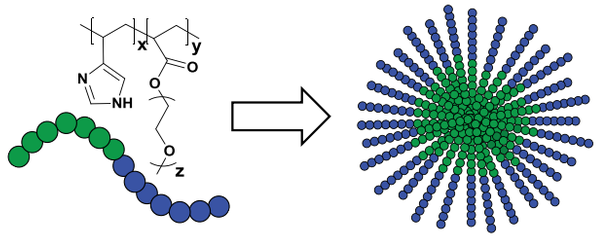

Figure 2. Self-assembly of the Amphiphilic Block Copolymer.

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Polymers for Imaging and Therapy

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The manipulation of the physicochemical properties of materials has long been used to tailor devices towards a particular application. This is particularly true for applications in nanomedicine,[1] since the material must ultimately be effective in the harsh physiological environment that is the human body – not to mention be resilient to the stringent tests that it must be subjected to along the pipeline to clinical approval. Thus, the key to designing an effective nanomaterial lies in the early stages of development where the role of chemistry is paramount in determining the fundamental properties of the material. One area of nanomedicine where this holds particular import is theranostics – these are materials that can provide a diagnostic response to targeted drug delivery *in vivo* – since the two separate components (imaging[2] and therapy) must ultimately be complementary in order to elicit a measurable "theranostic" response. This requires both a fundamental understanding of the mechanisms that drive a certain physical response in a material, as well as the ability to generate the material through efficient synthetic methodology to control the chemical properties.[3] 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, PET and fluorescence).

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.

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Intracellular Nitric Oxide Delivery From Stable NO-Polymeric Nanoparticle Carriers

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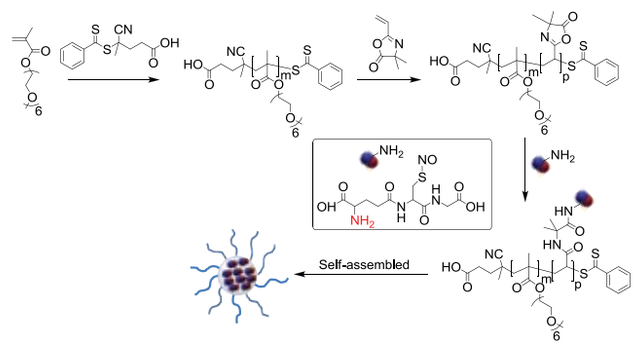
Nitric oxide (NO), which is produced by many cell types in the body, has been shown to be involved in many physiological and pathophysiological processes. NO has been proven to play a vital role in the relaxation of blood vessels, immune regulation, neurotransmission, and the inhibition of platelet aggregation. 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.

In this study, we report for the first time a straightforward and versatile method to conjugate nitroso-glutathione (GSNO) to polymeric nanoparticles with enhanced NO donor stability in aqueous media. The NO-release half-life time was extended by a factor of 5. The NO-nanoparticles were non-toxic and could efficiently release NO intracellularly. The application of NO-nanoparticles, in combination with cisplatin resulted in a synergistic cytotoxicity to neuroblastoma cancer cells (by a factor of 5 over cisplatin application alone). In contrast, no enhanced cytotoxicity was observed when dual NO/cisplatin administration was tested on a non-cancer cell line.



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Study Of The Responsive Properties of Porous Silicon – Responsive Polymer Composites With Applications in Drug Delivery

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Porous silicon (pSi) is a large surface area, biocompatible and biodegradeable form of silicon. The material possesses a host of useful properties such as optical and photonic effects, which allow for detection of changes within the porous layer. It is easy to functionalise and it is also possible to tune the pore diameters and porous layer depth. As a result, this material has been extensively studied for application in several different fields such as drug delivery, sensing, cell and tissue engineering, etc. pSi is of interest in the field of drug delivery, as the ability to tune the thickness of the porous layer allows to optimise the loading while the ability to control the pore size provides control over the release of the payload. Additionally, interfacing polymers with pSi provides a good means to further control the release of the therapeutics. As an example, using responsive polymers can impart stimulus-responsive behaviour to the release kinetics of the drug molecules, where the polymers act as actuators to control the release.

Ethylene glycol methyl ether methacrylates (EGMA) are monomers that possess thermo-responsive behaviour. The transition temperature of the monomer is dependent upon its molecular weight. For example, diethylene glycol methyl ether methacrylate has a transition around 26°C while oligo(EGMA) (Mn = 300) undergoes a transition at 65°C. Above the transition temperature the hydrated monomers collapse to form more hydrophobic globules, which precipitate out of solution. An interesting property of EGMA monomers is that, when randomly co-polymerised, the transition temperature of the resultant co-polymer, is dependent upon the ratio of the two monomers incorporated into the polymer chain.

Herein, we describe the fabrication of pSi microparticles grafted with EGMA copolymers and the application of these composites as drug delivery vehicles for use in wound dressings. We first use aqueous activators regenerated by electron transfer-atom transfer radical polymerisation to produce EGMA copolymers with physiologically relevant transition temperature (37°C) and a narrow transition range (**Fig. 1**). We then demonstrate a method of grafting the poly(EGMA) based co-polymers with tuned transition temperature from the pSi particle surface. The particles are characterised using infrared spectroscopy, x-ray photoelectron spectroscopy and scanning electron microscopy. Following this, we demonstrate temperature-controlled release of the fluorescent antibiotic levofloxacin, from these composites.

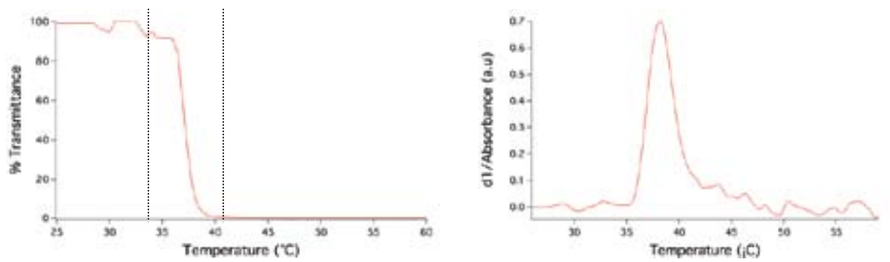

Figure 1. A) Percentage transmittance of a solution of poly(EGMA) copolymer with 20/80% ratio of oligo(EGMA) monomer and diethylene glycol methyl ether methacrylate with narrow transition temperature range. B) First derivative spectrum illustrating the transition temperature of 37 °C of the copolymer.

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Enhanced cellular uptake of nanoparticles by synthetic peptides and proteins

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Micelles are widely proposed for the controlled delivery of drug due to their core-shell structure and their nanoscopic size.[1] The delivery of drug-loaded micelles into the cell has always been a topic of interest[2] and the enhancement of cell uptake was found to translate directly to enhanced drug toxicity.[3] The ability of several peptides, called cell penetrating peptides (CCPs) or protein transduction domains (PTDs), to translocate across the cell membrane into the cytoplasm and nucleus in an energy independent or receptor-independent manner has been described vividly in literature. The improvement of cell uptake has been reported to be dependent on the presence of arginine and not on the secondary structure. Although many peptides are easily available, we are aiming at exploring synthetic alternatives, which are probably commercially more viable. A range of studies have shown that polymers with guanidine functionalities can indeed enhance cellular uptake. This approach holds great promise, although the potential toxicity of these cationic groups needs to be considered.

In this work, we investigated a range of block copolymer micelles using three different types of cationic oligomers as potential cell penetrating moieties. Among them, two of these oligomers are based on the guanidine carrying amino acid arginine, but while one has a cationic charge, the other oligomer has a zwitterionic structure (Figure 1).[2]

Furthermore, we looked into alternatives to simple PEG-based polymers coated with peptides. Albumin, which is abundant in the blood stream has recently been tested as small-sized drug carriers. Although the results were promising, the real breakthrough was achieved when albumin was processed into nanoparticles. Recently, a new nano-formulation based on paclitaxel and albumin was approved in the hunt for cancer. Inspired by this work, we developed micelles coated with albumin. The surface coated particles were found to enhance the cellular uptake and leading to an increased activity of the anti-cancer drug.

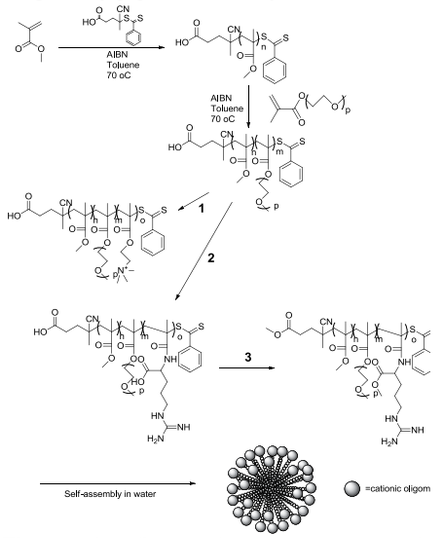

Figure 1. Streptavidin microarray with immobilization of protein in the pores

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pH–Responsive Star Polymer Nanoparticles as Selective ^{19}F MRI Contrast Agents

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Magnetic resonance imaging (MRI), a key diagnosis modality, has attracted considerable attention because of its non-invasive and non-destructive properties as well as its capability to provide high resolution images including three-dimensional images with intrinsic anatomic contrast.[1,2] So far, ^{1}H MRI has been the dominant imaging modality in routine clinical MRI. However, due to the large background signal arising from the abundance of ^{1}H in human tissue, it is often difficult for ^{1}H MRI to generate unambiguous images and discriminate tumour tissue from the surrounding normal tissues, especially in the early stages of disease.[3] In the past few decades, ^{19}F MRI has been considered as a promising alternative because of the advantages of negligible ^{19}F background in the living body, high gyromagnetic ratio, favourable sensitivity and high natural abundance of ^{19}F.[4,5] A particular aim in the field is the development of imaging agents "responsive" to the in vivo environment, for example changes in pH.

In this work, star polymers with a branched core and hydrophilic arms were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerisation as responsive ^{19}F MRI contrast agents. The branched core consists of 2,2,2-trifluoroethyl acrylate (TFEA, providing ^{19}F NMR signal) and 2-(dimethylamino)ethyl methacrylate (DMAEMA, offering pH-responsive properties). The arms are comprised of poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA) brushes that form hydrophilic and biocompatible shells around the cores. The structure and composition of the star polymers were characterised in detail. Unimolecular nanoparticles were fabricated by direct dissolution of the star polymers in aqueous solution. As shown in **Fig.1**, cryo-transmission electron microscopy (cryo-TEM) confirmed the pH-responsiveness of particle size (25 nm at pH 6 and 5 nm at pH 9). ^{19}F nuclear magnetic resonance (^{19}F NMR) also revealed that the ^{19}F signal intensity and spin-spin relaxation time (T_2) were significantly dependent on the pH of polymer solution, while the ^{19}F spin-lattice (T_1) relaxation time remained constantly low at ~450 ms upon increasing the pH above the p*K*a of the DMAEMA groups. These results indicate that these ^{19}F detectable and pH-sensitive star polymer nanoparticles are promising as ^{19}F MRI 'smart' contrast agents for selective imaging.

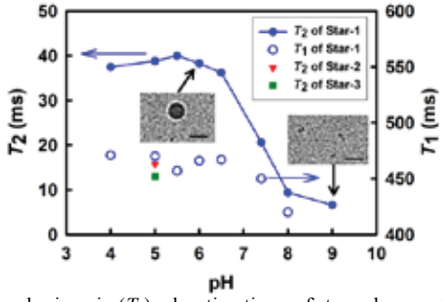

Figure 1 Spin-lattice (T_1) and spin-spin (T_2) relaxation times of star polymer nanoparticles in PBS. (Inset: cryo-TEM images of the nanoparticles, scale bar = 25 nm)

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Magnetic Nanoparticles as Dual Chemotherapeutic Delivery and MRI Contrast Agent

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Over the past 20 years, superparamagnetic iron oxide nanoparticles (IONPs) have been studied extensively as contrast agent in MRI.[1] It is well known that high magnetic susceptibility of IONPs core provides strong enhancement of transverse (T_2 and T_2^*) relaxation in tissue regions where nanoparticles are localized. Although there are several IONPs that have been clinically approved (e.g. Ferridex and Resovist) as negative contrast agent in T_2-weighted MRI, the colloidal stability of the nanoparticles remains a challenge, particularly in biologically relevant media. Biocompatible polymers with anti-fouling properties such as polyethylene glycol (PEG) or dextran have been coated on the surface of IONPs, in order to prevent aggregation and prolong their blood circulation times.[1]

The application of IONPs in MRI has generated considerable interest in their use as drug delivery vehicles. Limiting the small particle size of IONPs core (< 200 nm) would be appropriate for cell internalization and the integration of a chemotherapeutic agent on the surface of IONPs can be achieved by different strategies, such as physical (electrostatic or hydrophobic) interactions and chemical linkage.[2] It is essential that the drug remains encapsulated in the nanoparticles during blood circulation and after cell internalization the drug has to be released via e.g. pH-responsive cleavable linkage. Polymers with specific chemical functionalities could be utilized to conjugate or complex chemotherapeutics on the surface of IONPs, while at the same time impart higher colloidal stability on IONPs. Main advantages of IONPs as dual chemotherapeutic delivery and MRI contrast agent are that they can be used to track the distribution of the drugs in the body and they can be guided to target sites using an external magnetic field.

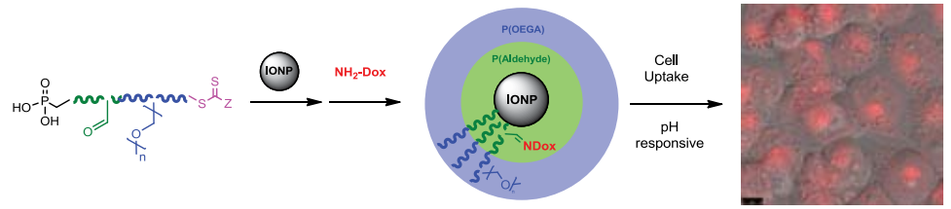

Fig. 1.: Doxorubicine functionalized magnetic nanoparticles as dual drug delivery and MRI contrast agents.

In this communication, we have prepared phosphonic acid bearing block co-polymers via RAFT polymerization followed by the grafting 'to' IONPs and the conjugation of anti-cancer drug doxorubicin. (**Fig. 1**.).[3] These IONP coatings comprise of an inner layer of polymer with aldehyde pendent groups and an outer layer of poly(oligo ethylene glycol acrylate).[3] Ultimately doxorubicin was conjugated via a cleavable imine bond to the inner layer of these hybrid IONP/polymer nanoparticles. Different assays such as colloidal stability, T_2 relaxivity, cytotoxicity, cell internalization (uptake) were performed on these doxorubicin functionalized magnetic nanoparticles. Cell uptake and intracellular release of doxorubicin were demonstrated using FLIM and confocal microscopy.

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[3] J. Liu, H. Duong, M.R. Whittaker, T.P. Davis, C. Boyer *Macro. Rapid Comm.* **2012**, *33*, 76.

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Solution processable poly(dendrimers) for organic light-emitting diodes

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The discovery that phosphorescent materials can give rise to efficient organic light-emitting diodes (OLEDs)[1] has caused an explosion of interest in the development of new materials. The majority of the effort has focused on small molecule emitters, which are processed by evaporation under high vacuum. Although this has been highly successful there are now concerns that the evaporation process might lead in some cases to the deposition of degraded materials. In addition, processing by evaporation is best suited to small devices.

To take phosphorescent materials into the realm of large area displays and lighting it would be advantageous to have solution processable materials. Phosphorescent dendrimers in which the phosphorescent emitter is encapsulated within a dendritic architecture has proved to be a very effective method for forming thin films for monochrome emission. Simple devices containing two layers, the emissive dendrimer layer and an electron transport layer, have been reported to have external quantum efficiencies of 13% at usable brightnesses.[2] However, the viscosity of such materials is not sufficient for them to be processed by methods such as ink-jet printing.

To overcome this limitation we have been developing phosphorescent poly(dendrimers). We have found that unlike previously reported copolymers containing small phosphorescent complexes it is possible to form homopolymers in which every 'monomer unit' has a phosphorescent moiety attached (e.g., **1**[3] and **2** in **Fig. 1**). In the homopolymers with simple side-chain complexes the close proximity of the phosphorescent emitters was found not to quench the luminescence in solution significantly, although in the solid state the intermolecular interactions do lead to a dramatic reduction in the photoluminescence quantum yield. By using dendritic emitters attached to the polymer backbone (e.g., **2** in Fig. 1) it was found that the homopolymer could be easily solution processed to give devices with good performance.[4] In this presentation I will discuss the design principles for and synthesis of poly(dendrimers), as well as their photophysical and device performance.

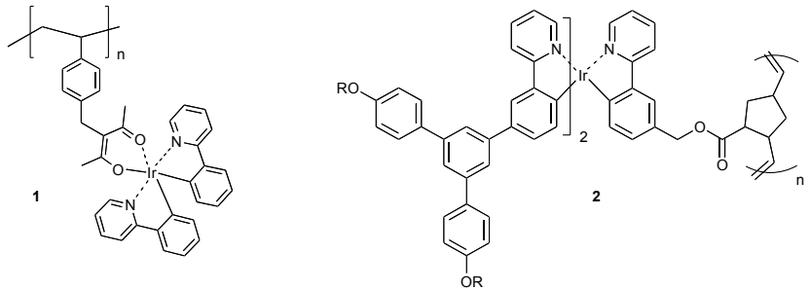

Figure 1: Structures of solution processable phosphorescent homopolymers, **1)** a polymer containing side chains comprised of a small molecule iridium(III) complex and **2)** a poly(dendrimer) with side-chains comprised of iridium(III)-cored dendrimers; R = 2-ethylhexyl.

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Advanced Branched Macromolecules for Opto-Electronics

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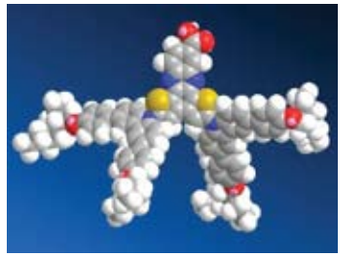
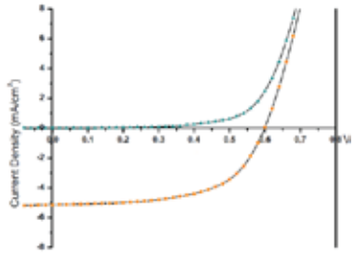
Organic semiconducting materials have been playing a vital role in opto-electronics such as light emitting diodes, solar cells, field effect transistors and photodiodes, which have been mainly dominated by inorganic semiconductors (silicon, gallium arsenide, tellurium, *etc*). Unlike such environmental unfriendly inorganic semiconductors, organic materials also offer many other advantageous such as lighter weight, cheaper in synthesis and device fabrication, showing the great potential in replacing the inorganic counterparts, in particular for disposable and flexible opto-electronic devices as well as critical components for next-generation high-end organic electronics in such as Saumsung "*Youm*", Apple "*iWatch*".

To facilitate fast, low-cost, room-temperature manufacturing purposes as well as large-size patterning by using such as blade-coating or ink-jet printing, it is important that organic semiconductors will be solution processable. In this presentation, we will describe our material design strategies for solution processable organic semiconductors based on branched macromolecules that lead to optimised photo-electronic properties. We will detail our synthesis methodology for these organic semiconductors, and preliminary device characteristics will be also discussed.





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Synthesis and Properties Triphenylamine-cored Dendrimer Semiconductors

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Optical and electronic devices containing a solution-processable organic semiconductor active layer have shown rapid progress in terms of their charge mobility, light emission, and sensing properties. Organic semiconductors have been primarily limited to molecular and polymeric based materials. One class of organic semiconductor that has received little attention in electronics and sensing applications are electroactive dendrimers. Dendrimers are branched macromolecules that are solution-processable (like polymers) and monodisperse (like molecular materials), and can range in shape from being planar to spherical. In this presentation, synthetic strategies to, characterization of, and device performance of electroactive dendrimers (Fig. 1) will be discussed. The effect of varying the dendrons, and surface functionality on the charge transport[1] and explosives sensing[2-3] properties will be discussed.

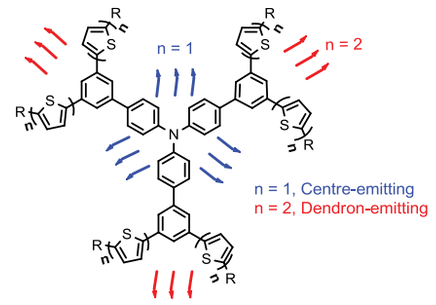

Figure 1. First-generation triarylamine-cored dendrimers studied

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Polymeric Ionic Liquids (PILS): Synthesis and characterisation of solid polyelectrolytes for advanced energy applications.

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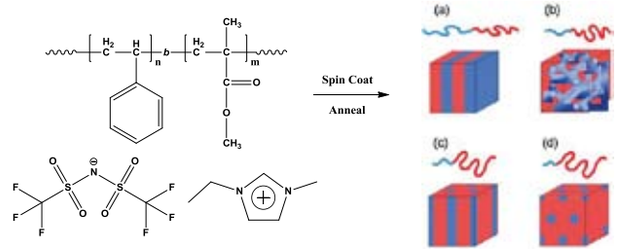
Ionic liquids (ILs) are a family of low melting point organic salts with a diverse range of chemical structures that possess many interesting physico-chemical properties; they have minute vapour pressure, high ion conductivity, high thermal and chemical stability, as well as being non-flammable.[1] The idea of incorporating an IL into a solid polymer matrix has received much interest of late, because the gels that are formed combine the unique properties of ILs with the physical and mechanical properties of a polymer.[2, 3] This is typically achieved by either adding an IL to a pre-existing polymer matrix to form a polymer ionogel or by polymerising an IL monomer into a polymeric ionic liquid (PIL). Unfortunately, the high cross-link densities or crystalline domains which provide the mechanical support in these polymer matrices are inherently deleterious to the ability of the material to transport ion or gas molecules at a high rate.[4] A promising solution to this issue is the incorporation of these polymer/polymeric IL materials into block copolymer architectures with other non-ionic polymer species. Through phase separation, the mechanical and transport properties of each block can be largely retained and potentially tuned further by targeting different morphologies.[5, 6]

We have taken several PS-b-PMMA block copolymers (BCPs) and added the ionic liquid EMIM NTf2 in varying volume fractions to create a series of polymer ionogels. Each material was then cast into films and the phase separation morphology was studied in depth with small-angle X-ray scattering (SAXS), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) (Scheme 1). From this we have successfully demonstrated that both the overall BCP morphology and the domain size of the phase separation can be controlled by simply varying the volume of IL added. The ability to achieve various morphologies and domain sizes from a single block copolymer has huge potential for application in systems ranging from ion transport to templating.



Scheme 1. Illustration of the BCP/IL ionogels we have synthesised and the morphologies we were targeting by varying the block lengths and the volume of IL incorporated into the polymers.

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Well defined water-soluble conjugated polyelectrolyte with high hole transport mobility

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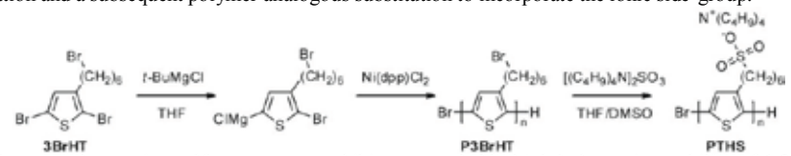
Water-soluble conjugated polyelectrolytes (CPE) find widespread applications in biosensors and interface modifications for electronic devices, due to their solubility in aqueous systems or other highly polar solvents. Furthermore, these properties make them of great interest for an environmentally benign processing of solar cells. However, in most cases ion reorganization under applied fields and low charge carrier mobility impede the use as active component in electronic systems. Here we present a new class of CPEs, which resemble the structure of highly regioregular and narrowly dispersed poly(3-hexyl thiophene) (P3HT) in its backbone, but comprising ionic groups attached to the side-chains. The synthesis comprises a controlled Kumada catalyst transfer polymerization and a subsequent polymer analogous substitution to incorporate the ionic side-group.



The polymer with negative sulfonate groups exhibits a remarkably high hole carrier mobility of 1.3 ± 0.5 x 10^{-2} cm^2/Vs calculated from the space charge limited current, which is superior to P3HT and among the highest values reported so far. The underlying transport mechanism was examined by current (J) –voltage (V) measurements and impedance spectroscopy. The former shows a quadratic dependence of J vs. V and a temporal response of the current within microseconds, which does not alter with continuing measurement time. Furthermore, no hysteresis was observed in the J-V plots, indicating the suppression of ion motion. The impedance measurements result in one semicircle in the Nyquist plot, which is characteristic for a pure semiconductor. UV-Vis absorption spectroscopy clearly reveals the formation of very small aggregates in aqueous solution similar to crystalline poly(3-hexylthiophene), which are stabilized by electrostatic interaction. This conformation can be maintained in the thin film enabling charge transport pathways. Thus we assume that the regioregular chain conformation and the narrow molecular weight distribution promote the formation of aggregates enhancing the charge transport throughout the whole material. In contrast to other CPEs, the combination of the aggregated structure and sterical demanding counter ions suppress the ion motion and reorganization, resulting in a pure semiconducting material.

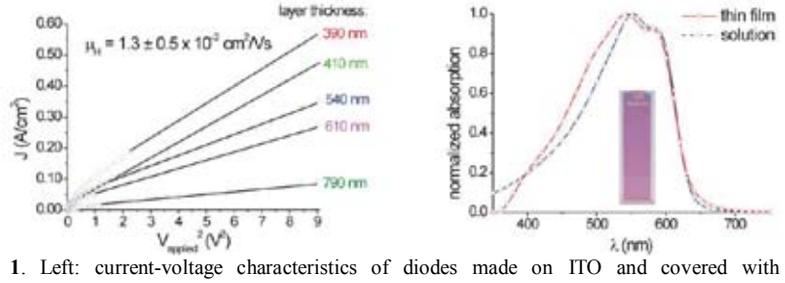


Figure 1. Left: current-voltage characteristics of diodes made on ITO and covered with gold as counterelectrode. The thickness of the active layer was varied from 390 nm to 790 nm. Right: normalized absorbtion spectra of the polymer in aqueous solution and in thin film (inset: image of the aqueous solution).

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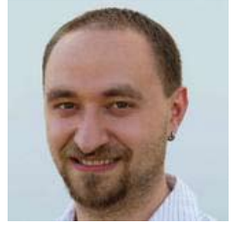

Highly conducting yet processable graphene for polymers

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Since graphene fabricated by micromechanical exfoliation and chemical vapor deposition cannot suspend in solvent, a graphene derivative–graphene oxide–has been developed and extensively studied for a wide variety of applications [1–3]. Graphene oxide has to be reduced in most applications. For example, the thermal reduction of graphene oxide in Ar/H_2 at 900°C for 0.5 h removed oxygen completely, producing an electric conductivity of 400 S/cm [4], far below 2000 S/cm — the electric conductivity of graphene produced by CVD [5].

Cost-effective fabrication plays a critical role in promoting the applications of graphene. Recently we have developed graphene platelets (GnPs) by combining the thermal expansion of a commercial graphite intercalation compound (GIC) in a common-purpose furnace with the sonication of the expanded product in solvent [6,7]. GnPs features (i) low cost at 10–20 US$/kg, (ii) covalently modifiable interface, which plays a critical role in developing processable graphene in solution and matrixes, and (iii) a low thickness at 2–4 nm, far lower than previous efforts which only achieved over 10-nm thick platelets [8–10]. Graphene has an in-plane conductivity higher than copper but its through-plane conductivity is exceptionally poor, and this explains why graphite is only a semiconductor. Therefore, it is indispensable to keep GnPs as thin as possible.

Urgent fundamental questions unresolved for GnPs include: (i) since the starting material in the fabrication of GnPs is not highly oxidied, whether GnPs demonstrate a far higher electric conductity than the thermally reduced graphene oxide, and (ii) it is not clear the exact effect of surface modification on the GnP conductivity . Surface modification is inevitable in making GnPs processable in solvent or matrixes, but it coates an organic layer on GnPs reducing the conductivity.

We in this study modified GnPs with two types of polyoxyalkyleneamine (M_w = 2000 g mol^{-1}): reactive J2000 and non-reactive B200. A high electrical conductivity 1460 S/cm was found for GnPs. The modification by J2000 increased the platelet thickness, because the two end-amine groups of each J2000 molecule can react with the epoxide groups of adjacent platelets. Depending on the ratio of GnPs to solvent, the modified platelet thickness ranged from 5 nm to over 20 nm. Thicker platelets showed a lower conductivity of 694 S/cm due to the damaging effect of the poor through-plane conductivity. By contrast, the 5-nm thick GnPs demonstrate a conductivity of 972 S/cm. The B200 modification made no change of the thickness and thus the modified GnPs showed a similar conductivity to the unmodified platelets.

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Novel electrospun polymer nanofibre/Organic Ionic Plastic Crystal Composite electrolytes

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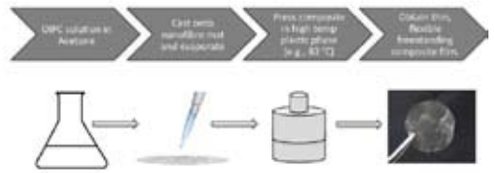
Organic ionic plastic crystal (OIPC) solid-state electrolytes are promising materials for electrochemical applications, particularly high energy density Lithium batteries. The OIPC ions exhibit long range order but also possess orientational and/or rotational disorder which leads to relatively high ionic conductivity and plasticity. They support fast Li ion transport inside their crystal structure and it has been reported that Li salt doping enhances their conductivity. Importantly, their excellent electrochemical and thermal stability makes them ideal candidates for improving safety aspects of high energy density Lithium batteries[1-3]. However, in most cases the ionic conductivity of OIPCs is too low for application on devices at ambient temperatures. It has been reported that addition of nanoparticles to OIPCs could enhance the ionic conductivity depending on the type of the nanoparticle and OIPC[4,5]. In the current work, the use of an electrospun polymer nanofibre network as an additive and mechanical support matrix has been investigated.

A general procedure for the preparation of the composites is shown in **Scheme 1**. Where the melting point of the OIPC is sufficiently low, i.e., at temperatures where the polymer nanofibres do not melt or decompose, the composite can also be formed by melting and wetting of the nanofibre network. The different preparative procedures result in starkly different morphologies as shown in **Fig. 1.**



Scheme 2 General procedure for the preparation of polymer nanofibre/OIPC composites

The new composite materials are easily formed and are thin, flexible, mechanically robust and optically transparent. Initial studies investigating the phase behavior and ionic transport properties of the composites has revealed that the presence of the nanofibres can enhance the ionic conductivity by up to an order of magnitude compared to the bulk materials.

We will describe our current efforts to understand the mechanism of conductivity enhancement and to control the interactions of various polymer fibres and OIPC matrices to achieve improved composites for membrane applications, including rechargeable lithium batteries.

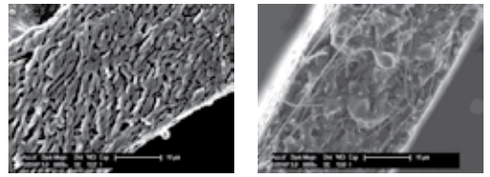


Figure 2 SEM images of sample cross-sections,
a) *N*-methyl-*N*-ethylpyrrolidinium bis(trifluoromethane sulfonyl)amide/polyacrylonitrile composite ($[C_2mpyr][NTf_2]$/PAN) prepared by melt wetting,
b) *N*-methyl-*N*-ethylpyrrolidinium tetrafluoroborate polyacrylonitrile ($[C_1mpyr][BF_4]$/PAN) composite prepared by solvent casting from acetone.

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Water-based Nanoparticulate Organic Photovoltaics

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Recently, the fabrication of organic solar cells from water-dispersed nanoparticulate materials (solar paint) has attracted increasing interest since it offers the potential of morphological control coupled with device processing in the absence of an organic solvent. In this talk I will present our recent work on developing optimized nanoparticulate organic photovoltaic (NP-OPV) devices from water-based polymer nanoparticle dispersions.

Our initial studies were focussed on blends of poly(9,9-dioctylfluorene-co-N,N-bis(4-butylphenyl)-N,Ndiphenyl-1,4-phenylenediamine) (PFB) and poly(9,9-dioctylfluorene-co-benzothiadiazole (F8BT). By controlling both nanoparticle morphology[1] and inter-particle interactions it is now possible to build polyfluorene NP-OPV devices that are more efficient than the corresponding bulk heterojunction devices. In particular: (1) the polyfluorene nanoparticle morphology is suited to effective charge separation, (2) thermal treatment of the deposited layers results in improved interparticle connectivity and effective charge transport, and (3) the optimal device thickness is a delicate balance between the repair of layer defects and the creation of stress cracking in the nanoparticulate film[2]. Moreover, the addition of calcium into the cathode structure results in a dramatic increase in open circuit voltage and power conversion efficiencies (PCE) approaching 1% for water-based polyfluorene NP-OPV devices are now possible[3].

Poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blends are the most studied organic photovoltaic materials system and conventionally are processed into thin films via organic solvent based routes. We have recently probed directly the structural motif of P3HT:PCBM NP-OPV devices and have shown how NP morphology determines device function. For this system, the unannealed NP-OPV devices exhibit the highest efficiencies, with PCEs of 1.3 %. Scanning transmission X-ray microscopy (STXM) studies show that annealing these devices leads to gross phase segregation and reduced device performance[4]. Finally, the performance of nanoparticulate organic photovoltaic (NP-OPV) devices fabricated from poly(3-hexylthiophene) (P3HT):indene-C60-bisadduct (ICBA) blends. These devices exhibit power conversion efficiencies of 2.5 %, which is the highest so far reported for NP-OPV cells. Using STXM and thermodynamic modelling we show that the improved performance is driven by the enhanced miscibility of ICBA in P3HT, which results in a more efficient intermixed structure in the annealed devices[5].

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Nanoparticle organic photovoltaics (OPVs): the effect of fabrication method on nanoparticle morphology and device performance

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Nanoparticle organic photovoltaics (OPVs) offer a low cost, renewable energy alternative that can be manufactured from water-based inks. A disadvantage associated with conventional organic photovoltaics is that the semiconducting polymers are limited in solubility to toxic, non-polar, organic solvents, such as chloroform, meaning the printing step of OPV manufacture has associated occupational health, safety and environmental hazards. Emerging developments in nanotechnology have presented a solution to this problem whereby the polymer materials can be suspended in a non-solvent, such as water, by generating nanoparticles of the materials via a miniemulsion process.

An added advantage of this process is that we are able to gain a superior level of control over the morphology of the organic photovoltaic active layer, that is, a nano-scale level of control. Our research to date has shown that this morphology is highly dependent upon the nanoparticle fabrication conditions in addition to post-film deposition annealing treatments and polymer material properties.

We have fabricated nanoparticles from poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) via the Landfester[1] miniemulsion process. Once a miniemulsion is generated, chloroform is driven off from the dispersed oil phase, the method and rate by which the chloroform is driven off affects the morphology of the nanoparticles, which are commonly core-shell (**Figure 1**). This in turn affects the performance of the nanoparticle organic photovoltaic devices due to charge transport mechanisms within the active layer, and thus is a significant area of investigation for optimisation of device performance.

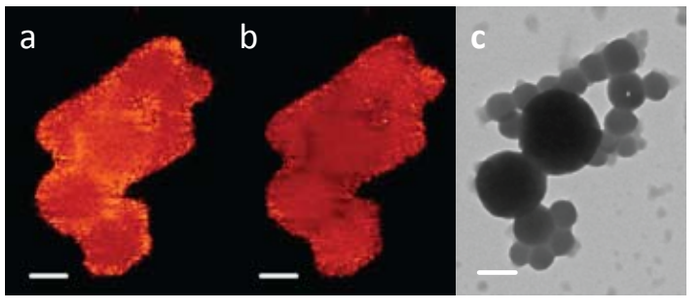

Figure 1. Scanning transmission X-ray microscopy (STXM) percentage composition maps showing P3HT concentration (a) and PCBM concentration (b) and matching transmission electron microscopy (TEM) image (c) for unannealed P3HT:PCBM nanoparticles prepared by a fast chloroform evaporation method. All scale bars are 200 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. Minima and maxima for the colour scale are black = 0 and white = 100%.

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Alcohol Soluble Conjugated Interface Materials for Organic Solar Cells

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Combined with low cost, low weight and flexibility, organic solar cells (OPVs) are getting more and more attractive as an independent energy source.[1] A conventional OPV includes an active layer sandwiched between two electrodes. Light irradiates through a transparency tin-doped indium oxide (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. The improvements in device performances are strongly depending on the improved processing conditions, and use of active materials and interface materials as well. One of the most extensive studied areas at present is the donor materials. Polymer solar cells based on conjugated polymer as donor blended with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as acceptor have achieved 9.2% power conversion efficiencies (PCE).[2]

Besides, the engineering of improved interface materials are of importance for highly efficient and stable OPV devices and modules, since unadjusted interfaces limit or even drastically reduce the PCE. With the linear polyfluorene bearing pendant amine as the cathode interfacial layer, Cao et al. obtained a high PCE, and Voc, Jsc, FF and PCE are improved significantly.[2] The reasons behind are attributed to increased built-in potential due to the interfacial dipole, improved charge mobilities, avoiding of Fermi level pinning between the metal cathode and the acceptor in the active layer. Since three dimensional polymers have different densities of the pedant functional groups on the polymer surfaces and thus the surface property may be different from the linear analogues either in solutions or in condensed states,[4] we developed the 3D analogues with a spiro-fluorene unit as cathode interfacial layers for OPVs. The performances are as good as with the linear ones or even better.[5] Because of crosslinking, 3D spiro-fluorene polymers are very difficult to dissolve (in any solvent). So we change the structure of it in order to resolve this problem, and we design a novel hyperbranched polymer.

At the same time, two PCBM derivatives with side chain attaching amine end group, PCBDAN and PCBDANI, were designed and synthesized for the application of cathode buffer layer in PSCs. In comparison with the traditional low workfunction active metal Ca cathode, both PCBDAN and PCBDANI cathode buffer layer demonstrated identical or slight improved photovoltaic performance in the PSCs based on P3HT/PCBM, P3HT/ICBA and PBDTTT-C-T/$PC_{70}BM$. Due to remarkable improvement in efficiency, it encourages us to explore further optimization of the materials and detailed updated results will be reported in the conference.

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Revealing the Nanomorphology of Organic Photovoltaic Polymer Blends through Selective Dissolution

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A significant fraction of the cost of commercial Silicon Solar panels comes from the photoactive materials and sophisticated, energy-intensive processing technologies[1]. Therefore, in order to further develop the use of sustainable energy, it is urgent to search for new photovoltaic materials with a cost-effective manufacturing procedure. The huge potential of solution-processed bulk-heterojunction photovoltaic cells was first realised in the mid to late 1990s[2]. This solar cells system utilizes a blend of semiconducting polymers or blend of a semiconducting polymer with fullerene derivative as the photoactive layer. Such blend films are simply processed by dissolving the two components in solution and depositing via solution-based processes such as spin-coating or printing, greatly diminishing the cost of industrial manufacture[3].

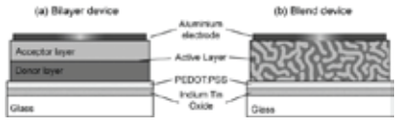

Fig. 1 Schematic diagram of the structure of a typical bilayer **(a)** and blend **(b)** organic photovoltaic devices

When light is shone on a polymer solar cell, an electron-hole pair is generated within the blend active layer. For effective charge collection, the electron-hole pair – or exciton, has to be dissociated in to charges, a process that is efficient at a heterojunction between the two blended materials. Subsequent to exciton dissociation the charges then collected accordingly. A bilayer structure (**Fig. 1a**) allows unhindered movement of separated charges; however the small exciton diffusion length (~ 10 nm) limits the efficiency of exciton dissociation. A blended structure (**Fig.1b**) however provides combines a high interfacial with smaller domain size facilitating efficient exciton dissociation and charge collection.

Exciton dissociation efficiency and charge carrier mobility are therefore two important processes influencing the power conversion efficiency of organic photovoltaic devices. These factors are also strongly dependent on the bulk morphology of active layer in OPVs. However, there still lacks a simple and effective method to characterize the nanoscale bulk morphology due to the high chemical similarity of the components, especially for polymer/polymer configurations. In this project we apply a technique named Temperature-Controlled Selective Dissolution[4] (**Fig.2**) to reveal the nanostructure of two prominent photovoltaic blends – P3HT/PCBM and P3HT/N2200, spin-coated from various organic solvents. Optical absorption results show that both N2200 and PCBM phases can be effectively extracted from their respective blends, leaving a P3HT-rich scaffold on the substrate as imaged by atomic force microscopy. The use of different casting solvents is found to produce large variations in the morphology of P3HT/N2200 layers while P3HT/PCBM films exhibit a good consistency.

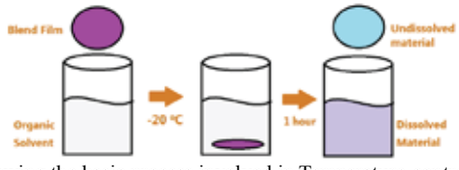

Fig. 2 Schematic diagram showing the basic process involved in Temperature-controlled Selective Dissolution.

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SELF-ASSEMBLED OF MgH_2 NANOPARTICLES @ MgH2 NANOTUBES LINKING ARCHITECTURE TO HYDROGEN STORAGE

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Hydrogen could be the ultimate energy carrier enabling energy security and global sustainability in this 21st century. Hydrogen is already central to our current energy systems. Indeed, hydrogen bonded to carbon provides us with the so-called fossil fuels that 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. 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. However, the effective storage of hydrogen in a compact manner remains the central difficulty for its widespread use. Efforts over the last decades have targeted a range of materials capable of storing hydrogen with high density in the form of a hydride, e.g. MgH_2, $NaAlH_4$, H_3BNH_3 and $LiBH_4$,[1] but the realization of successful strategies to control and balance competitive thermodynamics/kinetics requirements for the effective storage of hydrogen remains unanswered. Effective molecular control would only be feasible by manipulating the atomic arrangements, i.e. building new storage materials from the bottom-up. However, the challenge with such an approach is the lack of methods for: a) the controlled synthesis of nanosized hydrides and b) their controlled assembly into larger functional systems providing efficient networks for hydrogen diffusion as well as stability against nanoparticles sintering (to ensure long life cycling). Herein, we report a bottom-up method for the facile production of MgH_2 nanoparticles and their assembly into a stable tertiary structure via confinement within MgH_2 nanotubes (Figure 1A).

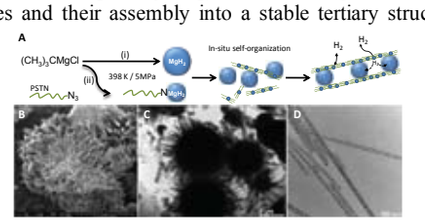

Figure 1. (**A**) Schematic showing the approach for the synthesis and stabilization of nanosized MgH_2 through self-assembly within MgH_2 nanotubes. (**B**) SEM image of PSTN-MgH_2. (**C**) TEM micrograph of PSTN-MgH_2 showing similar fibers assembled into larger particles. (**D**) High-resolution TEM micrograph of the fibers revealing particles nanoconfined within tubes closed at both ends.

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Role of Polymer Morphology in Organic Photovoltaics

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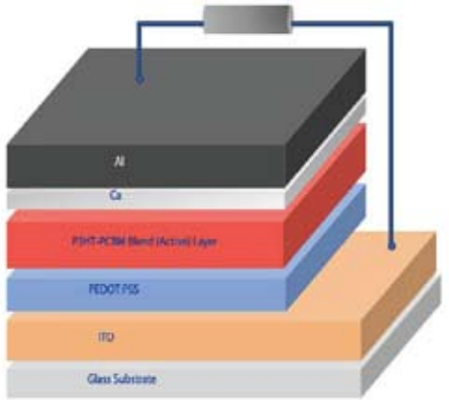
Organic Photovoltaics (OPVs) offer a number of interesting commercial opportunities around their ability to be incorporated into buildings in an architecturally attractive way. However, before this opportunity becomes reality, there are many challenges to be overcome including efficiency, cost and lifetime.

While the structure shown below appears simple, it is in fact an idealised cartoon suggesting sharp interfaces which are potentially ideal for electron transport, but of course is not the reality. More importantly, diffusion across these interfaces can destroy the device properties.



The most complex and studied layer is the active layer, shown below using a blend of poly(3-hexyl thioophene (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM). This layer partially phase separates to form a bulk heterojunction (BHJ) which has a complex morphology with a very high surface area promoting charge separation and transport to electrodes.

This presentation will describe a number of initiatives being investigated to control the structure of these devices and better understand the factors limiting device lifetime.

One such approach is to effectively polymerise the small molecule PCBM by attaching the active part, a fullerene, to a polymer chain. The resulting polymer has significantly less solubility in P3HT, providing alternate avenues to phase development of this layer.

In a second approach, while the structure can be created by a sequential series of processing steps, a hierarchy of solvents and temperature profiles inherently limits the structure and performance of each layer. Lamination offers the potential to optimise the structural development of each layer independently and then bring them together to create the final device. Results of lamination at various interfaces will be presented.

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Photocontrollable Liquid Crystalline Polymer Actuators

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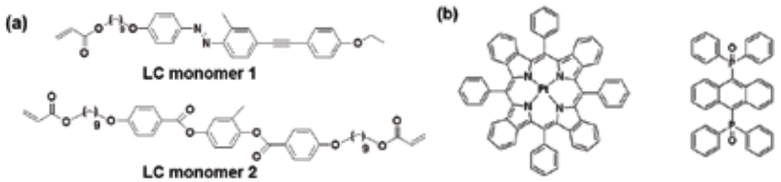
By incorporating azobenzene groups into the crosslinked liquid crystal polymers (CLCPs), large deformations such as contraction and bending have been induced by light due to the photoisomerization of the azobenzene chromophores. [1-4] Since light is an ideal stimulus for it can be localized (in time and space), selective, and allows for remote delivery of energy, photodeformable CLCPs present an interesting opportunity to realize soft actuators in microscope applications, such as full-light-driven motor, oscillators, and microrobots.[5-8] However, most of the photocontrollable CLCP systems were controlled by ultraviolet light which is not idea for practical application, due to considerations of safety, power consumption and cost. Therefore, it would be interesting and significant to develop photodeformable CLCPs which could be photo-regulated by a low energy light, because it is more environment-friendly and causes less damage.[9,10] Upconversion materials, which are capable of the conversion of optical radiation into light of a shorter wavelength, could be potentially utilized in this regard. Recently, we incorporated upconversion nanophosphors which absorb near-infrared (NIR) light and convert it to higher-energy photons in the UV and visible regions, into the azotolane-containing CLCP film and succeeded in generating fast bending of the resulting composite film upon exposure to continuous-wave (CW) NIR light at 980 nm.[11] Most lately, by the integration of platinum(II) tetraphenyl-tetrabenzoporphyrin (PtTPBP)/ 9,10-bis(diphenylphosphoryl) anthracene (YN2)-containing upconverting rubbery polymer film with an azotolane CLCP film (**Scheme 1**), we achieved a new photodeformable composite film driven by triplet-triplet annihilation based upconversion luminescence (TTA-UCL). This composite film bent towards the light source when irradiated with 635 nm light, because the generated upconverted blue YN2 fluorescence released from the rubbery upconverting film triggered trans-cis photoisomerization of the azotolane units and an alignment change of the mesogens in the CLCP film.



Scheme 1. (a) Chemical structures and properties of LC compounds 1 and 2 used in this study. (b) TTA multi-chromophore systems consisting of a sensitizer PtTPBP and an annihilator YN2.

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Bottom Up / Top Down High Resolution Lithography Utilizing Block Bottle Brush Polymers

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ABSTRACT

This presentation covers a novel deterministic bottom-up / top-down approach to sub-30 nm photolithography using a film composed of assembled block brush polymers of highly uniform composition and chain length. The polymer architecture consists of a rigid backbone of polymerized norbornene, each linked to flexible short side brush chains. The resultant 'bottle brush' topology has a cylindrical shape with short brush chains arranged concentrically around the backbone, in which the cylinder radius is determined by the number of monomers within the brush fragment, while the cylinder length is determined by the degree of backbone polymerization. The modularity of the synthetic system allows a wide diversity of lithographically useful monomers, sequencing, dimension and property variation. Sequential grafting of pre-synthesized blocks allows for facile formation of either concentric or lengthwise block copolymers. Placement of brush chains of different compositions along different regions of the cylinder, along with variation of the relative concentric and lengthwise dimensions, provides mechanisms to align and control placement of the cylinders. These polymers are compatible with photoacid generators (PAGs) and crosslinker functionality.

Our results are consistent with a model that the bottle brush polymers assemble (bottom-up) in the film to yield a 'forest' of vertically arranged cylindrical block brush polymers, with the film thickness determined by the coherence lengths of the cylinders. Subsequent imaging via ebeam or optical radiation yields a (top-down) mechanism for acid catalyzed crosslinking of adjacent cylinders. Uncrosslinked cylinders are removed in developer to yield negative photoresist patterns. Exposure doses are very low and throughputs are amenable to the requirements of EUV lithography. The imaging scheme is shown in Figure 1. The limiting resolution with ebeam exposure is potentially about two cylinder diameters width (< 8 nm), with the smallest observed patterns approaching 10 nm. This presentation will show the impressive negative-tone resist results. It will also cover key factors in optimizing performance such as resist thickness, film morphology and variation in bottle brush dimensionality.

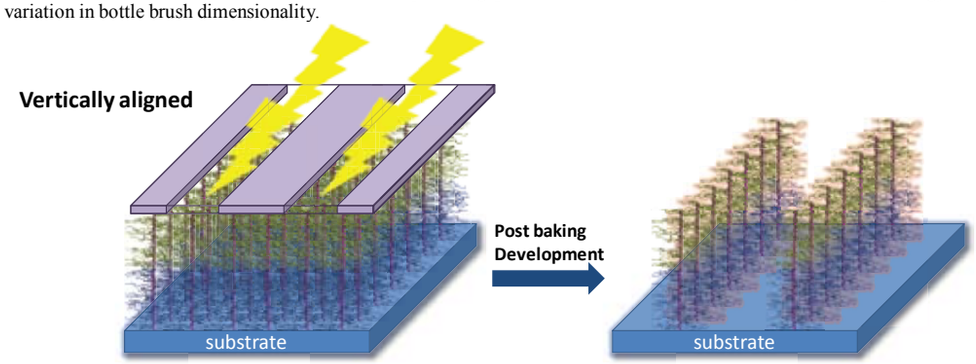

Figure 1. Vertically-aligned bottle brush polymers imaged using negative-tone chemically amplified resist technology.

Behaviour of Lamellae Forming Block Copolymers Under Nanoconfinement: Implications for Topologically Guided Self Assembly of sub-10 nm Features.

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Block copolymers (BCPs) consist of at least two chemically distinct polymer chains that are covalently linked. In an analogous fashion to immiscible solvents, the distinct functional polymers can undergo phase separation into discrete phases, when the chains are immiscible, but because the blocks are covalently linked this phase separation occurs on the nanoscale. The precise size and morphology of phase separated domains depends primarily on the relative degree of polymerisation of each block, as well as the degree to which the blocks are immiscible.

Without an external influence the morphology of BCPs is isotropic over large scales. However, when BCPs are confined in thin films the interactions with the polymer-substrate and polymer-air interfaces strongly dictate alignment of the morphology. By understanding the interactions of BCPs with surfaces and then tuning those interactions, researchers are increasingly becoming able to control the orientation of phase separated domains with respect to a substrate in thin films of BCP. Fig. 1 a) shows a SEM micrograph where lamellae are oriented perpendicular to the substrate. In this case the BCP is polystyrene-*block*-polylactic acid (PS-*b*-PLA) and the chemistry of the substrate has been tuned to be non-preferential with either of the blocks. This results in control of morphology perpendicular to the substrate, but laterally the arrangement is random. This fundamental advance, originally pioneered by Russell and co-workers, has paved the way for the development of directed self assembly (DSA) of block copolymers, whereby patterns generated by top-down lithography techniques are used to control the lateral orientation and/or placement of the phase separated domains.

An example of the DSA of PS-*b*-PLA is shown in Fig. 1 (b) and (c), where the lithographic features prepared by extreme UV lithography (EUVL) direct the self assembly of PS-*b*-PLA lamella to be parallel to the printed features. Depending on the degree of polymerisation of the block copolymers, the size of the phase separated domains can be much smaller than what can be printed via optical lithography. For the example shown in Fig 1c) the domains have a width of approximately 9 nm. This ability to improve the hierarchical control of the phase separated domains allows the creation of templates with densely patterned arrays, which are desirable for a number of nanofabrication based applications, including pattern multiplication, magnetic storage media, formation of nanowires, and contact hole shrinking/repair.

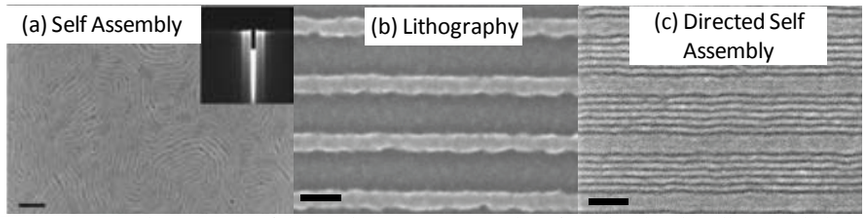

Figure X. Top down SEMs of (a) PS-*b*-PLA on a neutral surface showing lamellar morphology oriented perpendicular to the substrate, which was confirmed by the GISAXS shown in the inset, where characteristic Bragg rods can be observed.[19] (b) Line-space patterns (spaces = 120 nm) printed by extreme UV lithography (c) Directed self assembly of PS-*b*-PLA in lithographically printed features. Scale bars are 100 nm.

This presentation will present results showing the behaviour of BCPs confined between topographical features that are 2-4 times the long period (L_0) of the BCP. Furthermore, the implications that this behaviour has on the use of these ordered materials as templates will be discussed

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Light Responsive Lyotropic Liquid Crystals

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Triggerable transitions in the nanostructure of self assembled materials can be harnessed in biomedical and mechanical applications such as localized drug delivery, brakes, valves, and actuable armor. Both physical and chemical stimuli can be employed. Amongst these, light triggering is particularly attractive, since it offers a broad range of tunable parameters, e.g., wavelength, intensity, and duration.[1] Moreover, light stimulation can be localized, enabling both spatial and temporal control.[2]

Lyotropic liquid crystals (LLC) are a class of soft matter characterized by diverse nanostructures which arise spontaneously through the self assembly of natural and synthetic amphiphiles in water.[3] They have been successfully exploited in therapeutic delivery applications as liposomes, and other dispersed LLC forms such as cubosomes and hexasomes are currently under development by a number of groups.

We present preliminary studies of a photoresponsive LLC system which we have developed, based on light switchable lipid-like amphiphiles and water (Figure 1A). The system exhibits rapid reversible phase transitions through the cis/trans- isomerism of an intramolecular azobenzene moiety under exposure to UV or visible light (rates up to 13,500 Pa/s). We have explored the dynamics of the structural reorganization which occurs during switching using synchrotron X-ray scattering, and correlated this with spectroscopic measurements of azobenzene conformation. Rheological measurements revealed changes in material properties of unprecedented magnitude (20,000 Pa to 50 Pa) which occur between phase states (Figure 1B). Significantly, the rapid and reversible photorheological responses of large magnitude observed for transitions between different phases may open a door to new applications for photorheological materials.

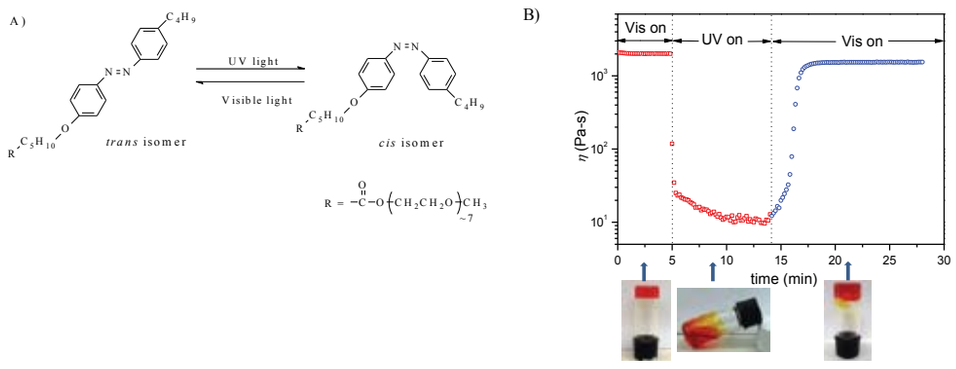

Figure 1. (A) Photoisomerization of the azosurfactant; (B) Photorheological change of the azosurfactant azosurfactant/water (50/50 w/w)

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Modelling Nano-scale Structure and Energy Transfer in Conjugated Polymers

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The performance of organic electronic devices made from conjugated polymers is sensitive to the nano-scale morphology of the polymers. But modelling the structural and electronic properties of conjugated polymers on length scales that are relevant to device performance is challenging. This talk will discuss coarse-grained computational models that we have developed to study the self-assembly (**Fig. 1**) of the nano-scale structure of conjugated polymers and the impact of polymer structure on functional properties such as energy transport that are important in devices like organic solar cells. The talk will focus on our studies of two widely used conjugated polymers, poly(3-hexylthiophene) (P3HT)[1] and poly(2-methoxy-5-(2'-ethylexyloxy)-1,4-phenylenevinylene) (MEH-PPV)[2], and will compare the computational results obtained with ultrafast time-resolved spectroscopic measurements.

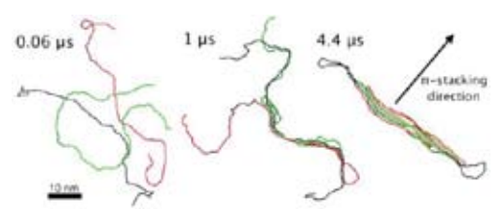

Figure 1. Self-assembly of ordered P3HT nanostructures in anisole from coarse-grained molecular dynamics simulations (different chains are coloured differently and only polymer backbones are shown for clarity).

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Research Collaborations in Polymer Industry

Leo Hyde[1]

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The discussion around research is a great one but if this research has no utility in the world of business then of what use is it.

A good question in my many years working with researchers in Australia and overseas this question has been asked and in many instances and it often takes a person of vision to see the industrial utility of this research or where it might lead in the industrial world.

In one project working with CSIRO a technology that allows the precise control of the molecular structure of a chosen polymer was discovered by a team working with the industrial partner but the initial response was we can't use this technology because of the smell and colour, but over the next few years these issues were solved and the technology is now being used in commercial applications from photoresists to house paint. It's the collaboration and knowledge from both sides each with their unique perspectives that really allows commercial success. Its true one plus one is greater than two.

So it's not just the research but the collaboration between researcher and commercial partner that leads to the final positive result for all concerned.

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NanoConnect: Providing a Bridge between Industry and University

Jonathan A. Campbell and David A. Lewis

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No country can afford to ignore the role of nanotechnology in social, economic and technological change. Estimates of the amount of products that will incorporate emerging nanotechnologies is as high as 15% of global manufacturing output[1] and its application in key sectors has the means to provide highly skilled jobs and contribute to a prosperous future for Australia[2,3]. Australia has a reputation for scientific and technological creativity and is renowned for its strong R&D credentials, innovative and highly skilled scientists, and enterprising Australia was recently ranked tenth in the world for the number of nanotechnology research papers[4], well above expectations based on population.

However, Australia is primarily a small to medium enterprise (SME) based economy with few large vertically integrated companies, with the result that most nanotechnology developments are being driven by academic research and the benefits are not being captured commercially. To address this, Flinders University's Centre for Nanoscale Science and Technology launched "NanoConnect", a pilot program to demonstrate to businesses how nanotechnology can help improve their products and processes. It is primarily aimed at smaller firms that don't have the knowledge base to understand emerging technologies and how they could apply to their products and technologies. Key aspects of the program include a single point of contact and a simple, low-risk engagement mechanism to provide access to advanced equipment and know-how to solve product or process issues of any size.

In the first year, NanoConnect has completed technology reviews for 10 companies and progressed to stage 2 proof-of-concept studies to with four of those. The companies that have been involved in the 2012 pilot program have come from a range of industry sectors and most have never engaged with a University before.

This presentation will describe the program in more detail and discuss the key learnings from the pilot program.

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The Power of Collaboration - Commercialisation of a World First Polymer Technology

David Francis, Predrag Micic, Brian Egan

Qenos Pty Ltd

Polyethylene is widely used in the manufacture of pipes for pressure applications. On a global basis, the market for polyethylene in pipe applications is amongst the highest growth areas. This is particularly true in Australia, where the importance of water management, growth of the mining sector, and the development of coal seam gas projects, has created exceptionally strong demand for polyethylene (PE) pipes.

The growing demand for PE pipes is driven by the benefits they offer in long term performance and ease of installation. Over the past 50 years the R&D activities of both universities and polyethylene technology companies has resulted in several generations of PE for pipe, leading to the current high performance PE100 resins. These advances have been achieved through enhanced understanding of structure-property-performance relationships, and the application of catalyst and process know-how to modify the molecular structure and deliver enhanced pipe performance.

PE100 performance is achieved by leveraging the strength and processing balance possible from a bimodal molecular weight distribution. This is typically achieved by the use of dual reactor systems (Fig 1). The challenge for Qenos was to utilise existing single Unipol reactor asset (Fig 2) to produce a bimodal PE100 resin.

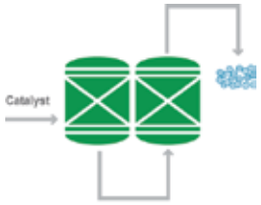

Figure 1: Dual Slurry Reactor System

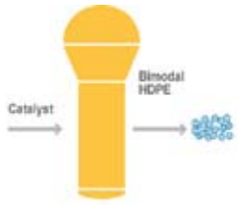

Figure 2: Single Unipol reactor system

Qenos is exceptionally strong in understanding market needs and translating them into polymer structure to deliver the required performance. However, the challenge facing Qenos required a break through catalyst technology, and was outside the scope of in-house R&D capability. Qenos called on its research partner, Univation, for the specific scientific input to develop a catalyst that could assist Qenos to create the required molecular architecture in a single Unipol gas phase reactor (Fig 2).

The resultant collaboration has been an extraordinary success for both parties. This paper will describe the significant challenges encountered from initial concept through to commercialisation, along with the critical elements that made the collaboration successful. Qenos' new PE100, HDF145B, is a world leading resin allowing new applications for polyethylene pipes. Our customers have been able to produce pipes up to 2 metres in diameter, and with wall thickness up to 110 mm. These are dimensions not previously possible with existing resins. Qenos is manufacturing tens of thousands of tonnes of PE100 using this technology each year, and Univation is licensing the catalyst technology to a global client base. This is truly a win-win outcome for both the industrial partner and the research provider, and of significant benefit to Australian industry.

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New Zealand Industry-Researcher Partnerships: The Materials Accelerator Model

Ralph P. Cooney* and Mark P. Taylor

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The Materials Accelerator is a national capability network which seeks to develop multi-material products in cooperative R&D partnership with innovative high-technology companies. It represents the next step in open innovation. It has recently been commended in NZ Cabinet documents as an effective means of producing economic benefits.

The Materials Accelerator has inter-disciplinary teams of engineers and scientists drawn from several New Zealand research organizations with multi-materials expertise in composites, plastics, conducting polymers, nanotechnology and metals. It also has a network of members with expertise in prototyping, virtual manufacturing, industrial design, materials analysis, modeling, interfacial analysis and materials testing.

The Materials Accelerator Network which is hosted by the University of Auckland (UA) includes contributions from several Universities and Government Laboratories including Scion, IRL, GNS, AUT, VUW, U Canterbury and U Waikato. It also includes contributions from several research centres within the University of Auckland. The number of applied researchers associated with the network is approximately 100.

The programme has involved interviews with 230 NZ companies. Each short-listed company contributes to a confidential brainstorming process (Joint Technology Planning) with a selected team of researchers drawn from the network. The Materials Accelerator has already developed platforms in aerospace, construction, agri-tech, air-quality and coatings all of which involve lead companies. 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 basic research projects have been launched.

An extension to this programme with a view to identifying international best practice in Industry-University partnership was conducted which involved 8 countries (mainly EU and North America). This survey included visits to 40 research or innovation centres, and it included approximately 100 interviews with research leaders, agencies and funders. This will be reported during the presentation.

We **acknowledge** the contributions of the Project Managers involved with the Materials Accelerator (Dr Chuong Nguyen, Dr Robert Blache, Dr Karnika de Silva and Anthony Meyer) and the Business Development Manager (Brian McMath). We also acknowledge our various industry network and research provider partners (above).

Funding: The New Zealand Ministry of Business, Innovation and Employment (MBIE) Contract UOAX0819

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2001-2009	Pro Vice Chancellor
2009-present:	Director of Hybrid Polymers; Director & Deputy Director of Materials Accelerator

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Industry Collaboration – why it's important and how to do it

Dr Kevin Thomson

Enterprise Connect/Ai Group

Although Australia has a strong public research sector, our performance in translating research to commercial outcomes is poor in comparison to other industrialised countries. Many companies are facing declining competitiveness due to slowing productivity growth, increasing labour costs and the high Australian dollar. They need the skills, knowledge and capabilities that researchers can offer, to help improve productivity and innovation.

Increasing collaboration between researchers and industry has become an important priority for both Commonwealth and State governments. It is being addressed through grant programs, voucher schemes and initiatives such as Industry Innovation Precincts and Enterprise Connect's successful Researchers in Business program.

But few companies use public sector research organisations as a source of innovation. This is particularly true for the small and medium enterprises that comprise 99.7% of all Australian businesses and contribute 58% of industry value add.

Making connections between researchers and industry is difficult. Researchers need to understand the industries they seek to collaborate with and develop strategies for engagement at an early stage in the innovation process. Some aspects to be considered are:

- Understanding industry – what companies are out there?
- How to connect with companies
- The role of Industry Associations and Professional Societies such as Ai Group and SPE
- What grants are available?
- Factors for successful collaboration

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Kevin started his career in research with a B.Sc (hons) in Physics, an M.Eng.Sci and a Ph.D. in materials engineering from Monash University in 1981, followed by a post-doctoral appointment at the Illinois Institute of Technology in Chicago working on carbon fibre composites. He then moved into the plastics industry, working for ICI, PolyPacific, Terumo Medical Devices and Nylex, where he held a number of technical positions including General Manager for Technical Development. He became a consultant in 2001, working with a series of polymer based start-up companies, as well as completing projects on plastic materials, recycling, sustainability and energy efficiency. He has been involved in many research collaborations with Universities and CSIRO, including ARC Linkage, CRC, and Victorian Government funded MVP projects. He currently delivers the Researchers in Business program for Enterprise Connect and is employed by the Australian Industry Group (Ai Group). He is also a current committee member and past President of the Society of Plastics Engineers (Australia – New Zealand Section).

IP Reform: How will it affect you?

Matthew Fisher

IP Australia, Canberra, ACT

The polymer art remains a very active area of academic and industrial research and as such, IP Australia continues to receive many patent applications per year for inventions relating to new polymers, their use and synthesis.

Last year the *Intellectual Property Amendment (Raising the Bar) Act* was signed into law, part of which will see major amendments to the *Patents Act 1990* that come into effect on 15 April 2013.[1] This presentation will highlight some of the major changes that are likely to affect examination of patent applications and subsequently what these changes will mean for applicants.

[1] http://www.ipaustralia.gov.au/about-us/ip-reforms/

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Commercialisation of Industrial Polymer Research

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DuluxGroup (DG) is a standalone company that can trace its history through the demerger of ICI (Aust) from ICI UK in the late 1990s and more recently demerger from Orica. DG has always maintained a strong position in industrial polymer research. In-house research can allow the design of new products with performance features outside those achievable with commercially available raw materials. When successful, the patent portfolio that flows from in-house research can assist in the development of international business networks. This talk will present case studies where in-house polymer research has progressed through into commercial product, in some cases earning significant international royalty income. One such technology is the use of suspension polymerization to form synthetic extender particles. This technology, know as Spindrift, is used commercially and is patented widely. It is undergoing a new level of interest through the application of controlled polymerization such as RAFT to a well established process. Other areas where modern polymer science can impact on a very familiar product such as paint will be touched on.

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Research interests: waterborne polymer science, materials science applicable to coatings.

Investigation into the Mechanism of Microwave Induced Rate Enhancements in Chain Growth Polymerisation

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Abstract

This presentation will report new work that builds on our initial studies concerned with defining the influence that microwave energy has upon the mechanisms of chain growth polymerisations. This presentation will present data from recent studies which were dedicated toward broadening the investigating into how the dielectric properties of chain growth polymerisation systems produce significant rate enhancements for the polymerisation. Furthermore, this dielectric property assessment will then be compared and contrasted to these materials actual performance in polymerisation reactions conducted using microwave energy as a heating source.

The use of microwave energy as a heating source to drive chemical reactions has been well documented in recent years, along with the numerous potential advantages offered by its use. These include rapid bulk heating, good temperature homogeneity and selective heating. However, in many cases these reports have detailed the outcomes of conducting the test chemistry in less than rigorous conditions, for example in commercially available domestic multi-mode microwave apparatus. Unfortunately, processing in this way does not allow for the true scientific/engineering effects that have lead to this observation to be identified, because the true influence of the factors that can influence the reaction, cannot be decoupled from one another. In the particular case of chain growth polymerization chemistry, the "high level" microwave effects that have been reported thus far include accelerated polymerization rate, molecular weight differences and changes to reaction selectivity. However, little work has been done to further investigate the exact microwave effects that are the root cause of these observed phenomena. Many literature publications have simply claimed the influence of "non-thermal microwave effects" to explain empirical results, without any further postulation on a possible mechanistic explanation of the effects detailed. Thus it is still not completely clear, on a scientific basis, where in the overall process the microwave energy is generating the changes observed.

This paper will report the results of our latest work targeted at defining the actual effects of applying microwave energy to both free radical and ring opening based polymerization systems. Data from these reactions will be presented that not only demonstrates the key benefits of applying microwaves to these systems but also proposes the mechanistic aspects that are responsible for these observations. Furthermore, the conclusions from these results will be supported by being cross-referenced to;

(a) the dielectric property predictions to assess if this method is correctly predicting the effects that microwaves are having over the active species present in the polymerization.
(b) real time spectroscopic assessment of the progression of the key reactions that are involved in the polymerisation mechanism.

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Challenges in the Development of MF/UF Membranes for the Global Water Treatment Market

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It is estimated that there is enough fresh water on the planet for 6 billion people, yet the world's population stands at around 7 billion. With continuing population growth, and increasing water scarcity there is increasing demand for clean drinking water sources. Not surprisingly, demand for microfiltration (MF) and ultrafiltration (UF) membranes in water purification, wastewater treatment and seawater desalination pre-treatment has grown significantly in the past 20 years and is only expected to rise with continued global industrialization and sustained population growth.

MEMCOR Products pioneered the use of MF in water treatment during the 1980's, with the introduction of a porous polypropylene hollow fibre membrane. More recently, our hydrophilic poly vinylidene fluoride (PvdF) hollow fibre MF and UF membrane technology provides low-cost, low energy water treatment with excellent water quality security for many applications, including drinking water, water re-use, wastewater, desalination pre-treatment and industrial process water applications (**Figure 1**).

Figure 1. A 160 ML/day installation in Perth (left) uses MEMCOR's hollow fibre membrane technology (middle and right).

Increasing demand for clean water has also driven increased competition in the MF/UF market. In looking to the future, the marketplace is looking to the next generation of higher performance, higher quality, and lower cost products. Along with feed water quality and operating process, the physical and chemical make-up of the MF/UF membrane technology is fundamental to performance and operating costs. The development of membranes with higher flow, which are able to resist flux decline through fouling is a real challenge.

Careful design and selection of the chemical make-up along with microstructural control are critical to performance. Hollow fibre membranes are synthesized via any mixture of polymer/polymer, polymer/non-solvent or polymer/diluent phase separation processes; whether thermally or diffusion driven. In either case, controlling the equilibria between dissolution, demixing (ie precipitation) and gelation/solidification are critical to the final membrane composition, microstructure, pore size, and porosity.

In this paper, we will discuss some of the membrane technology developments MEMCOR Products have been pursuing to address the challenges facing MF/UF membrane technology. In particular, we will discuss aspects of MEMCOR Product's membrane technology and membrane development activities, challenges associated with scale-up and product validation for the global low-pressure membrane market.

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Engineering Thermoplastics for Improved Self-Contained Breathing Apparatus

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"Turnout Gear" refers to the outer layer of protective clothing used by firefighters. Figure 1 shows a first responder in turnout gear, which is a subset of the larger classification of personal protective equipment (PPE). PPE refers to protective clothing, helmets, goggles, or other garments designed to protect the wearer's body from injury by blunt impacts, electrical hazards, chemical exposure, heat, and fire. An integral part of modern turnout gear is the self-contained breathing apparatus (SCBA). A SCBA consists of a pressure tank (2200 psi to 4500 psi), a pressure regulator, a support frame, an inhalation connection and an integrated Personal Alert Safety System (PASS). In Figure 1, the face shield is comprised of scratch resistant (outer) and fog resistant (inner) coated polycarbonate.

Polycarbonate (PC) is used due to its excellent clarity and very good impact properties; however, its resistance to heat is increasingly recognized as an inherent limitation.[1] Also, it has been known for some time that the thermal history of polycarbonate can lead to a phenomenon known as physical aging which results in a dramatic decrease in its mechanical properties.[2] Several deaths have been attributed to PC faceshield failures. This study was funded by the U.S. Department of Homeland Security (DHS) to investigate several candidate commercial polymers for applicability in the SCBA faceshield application.

A number of technical issues must be addressed to provide face shields that can meet both NFPA 1981 and NIOSH certification. Several commercially available high glass transition (Tg) engineering thermoplastics were investigated. Comprehensive thermomechanical properties were measured and compared; Figure 2 shows the shear modulus for the candidate polymers measured in 3-point bending as a function of temperature. Flame and ignition data were also collected along with optical property data. The key finding is that polyethersulfone (PES) is a promising replacement for polycarbonate (PC) with respect to thermal and optical properties. The results of the study were shared with Honeywell international, a major manufacturer of SCBA equipment resulting in a new product development effort. This successful translational research program represents an excellent example of what can be accomplished when government, academia, and industry work together in cooperative teams.

Figure 1. A first responder in turnout gear.

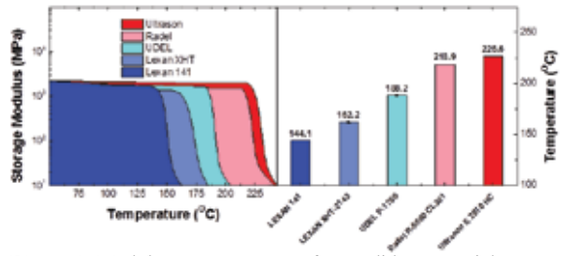

Figure 2. Modulus vs. temperature for candidate materials.

1. Mensch, A.; Bryner, N. *NIST Special Publication 1123 - Emergency First Responder Respirator Thermal Characteristics: Workshop Proceedings*; Engineering Laboratory, National Institute of Standards and Technology, United States Department of Commerce: Gaithersburg, MD 20899, 2011.
2. Allen, G.; Morley, D. C. W.; Williams, T., The impact strength of polycarbonate. *Journal of Materials Science* **1973,** 8, (10), 1449-1452.

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Research interests: polymers from renewable resources, nanocomposites, polymer membranes for biorefining, polymer rheology, polymer morphology.

Silicon and Polymer Microprojection Arrays for Circulating Biomarker Capture from Skin

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Blood is the sample most often collected for diagnostic purposes,[1] but needle/lancet-based extraction of blood samples is an important bottleneck to widespread, low-cost biomarker detection. We have recently developed a new method for biomarker-selective capture of proteins and antibodies directly from the skin, using Microprojection arrays coated with biomarker-selective probes.[2-4] Polymers play a key role in these devices – both as fabrication materials and as anti-fouling surface coatings.

Key challenges in developing diagnostic Microprojection array devices include (a) developing capture surfaces that maximize binding for enhanced assay sensitivity, and (b) fabricating devices from materials that have the right mixture of chemical and mechanical properties, and also can be fabricated using scalable technologies. Starting with silicon devices, we have targeted several parameters to investigate for improving capture efficiency, including surface chemistry (polymer composition and functionality), projection size and shape (extended surface area), application time on skin and site of application - all tested in mouse models of vaccination or pseudo-infection. More recently we have used these silicon devices to make polymer copies, using solvent casting or micromolding approaches. In this presentation we present our latest results in (a) improving assay sensitivity and (b) developing polymer surface modification strategies to develop bioassays for comparison with our standard silicon-based devices.

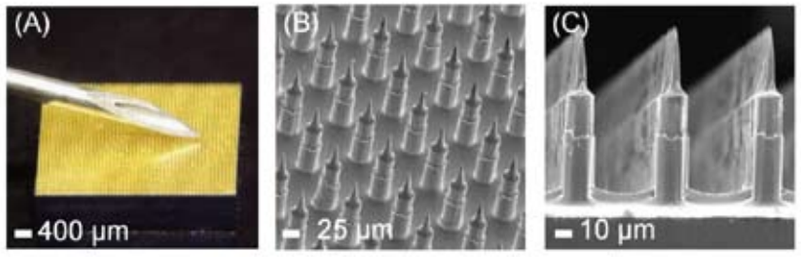

Figure X. Microprojection arrays (A) in comparison to standard 18 gauge needles and (B/C) scanning electron micrographs showing individual projection morphology

[1] N. L. Anderson, N. G. Anderson, *Mol. Cell. Proteomics.* **2002**, *1*, 845-867.
[2] A. Bhargav, D. Muller, M. Kendall, S. Corrie. *ACS Applied Materials and Interfaces.* **2012**, *4*, 2483-2489.
[3] D. Muller, S. R. Corrie, J. Coffey, P. Young, M. Kendall. *Analytical Chemistry* **2012**, *84*, 3262-3268.
[4] S. Corrie, G. Fernando, M. Crichton, M. Brunck, C. Anderson, M. Kendall. *Lab on a Chip* **2010**, *10*, 2655-2658.

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How Can You Patent When You Have Published?

Grace Y. N. Chan[1]

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A problem that can be encountered in the research environment is that the commercial value of a new development is not realised at an early stage, so that steps required to protect the development are not taken until it is almost too late. This problem usually presents itself when researchers publish research findings, which only later attract commercial interest after their initial publication.

For research work that has commercial potential, the protection of that work by a patent can be vital to its commercial success. Otherwise, without patent protection, it is likely that a commercial partner will see little benefit in investing funds to develop the research.

A general rule of the patent system is that an invention must be new in order to be entitled to patent protection. This usually means that an invention cannot have been publicly disclosed anywhere in the world before a patent application for the invention is filed. Publications made by anyone (including an inventor) which occur prior to filing could render an invention no longer new. As a result, a valid patent for the invention could not be obtained.

However, in limited circumstances some countries will still allow inventors to apply for and obtain a patent for an invention despite an earlier disclosure. To gain patent protection in these circumstances "grace period" provisions that are available in these countries must be relied on. The grace period can be therefore used to as an avenue of last resort to obtain some protection for a commercially useful development that has been published and disclosed.

This presentation will provide an overview of the grace period provisions that are available in some countries and outline the requirements that need to be satisfied in order to for an inventor to invoke the grace period.

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ACADEMIC RESEARCH IN COLLABORATION WITH INDUSTRY

Stephen Clarke [1]

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The Australian Government has progressively encouraged the academic community to move toward research having some level of community impact. Funding bodies, like the Australian Research Council (ARC), are expanding the range of funding programs for academic research, linked with industry, with schemes like the *ARC Linkage* program and more recently a new *Industrial Research Transformation Program*, designed to forge stronger links with industry. This industry/academic research already happens in Europe, and in the USA, where academics with strong links to industry are highly regarded by their academic institutions and peers.

We also see the ARC expanding the way it assesses *Academic Research Excellence* (ERA), apparently moving away from previous simplistic academic, assessment protocols, and from 2015 onwards, moving toward more complex, but realistic, assessment procedures that will take into account community impact. No longer will the academic community be able to simply assess research excellence from an unrealistic assessment of numbers of peer reviewed papers published in scientific journals. Hopefully, reducing the reliance on unrepresentative performance metrics, such as the *'h-index'*, which limit the funding opportunities for Australian scientists working with industry, will result. For example, the author has knowledge of a world recognised, and international leading polymer scientist, who has strong links with industry and was largely responsible for introducing dendrimer polymers to the world, but apparently may not be eligible for a prestigious ARC Laureate Fellowship application, because this person's *'h-index'* does not exceed a nominal value of 40 ?

The author came to academia in 1996 following 17 years of experience in industry, reaching the levels of National Technical Services Manager for Building Products and Polyurethanes Divisions at ICI Australia. He was also National Technical Manager of the Coloro Division of Glenn Industries, Technical Consultant for Australia's largest cement company – the Adelaide Brighton Cement, and proprietor of his own small business. In 1996 the author re-entered academia, and by 2000, completed his PhD, funded by an ARC SPIRT grant in collaboration with Dow Corning Corporation. In 2002, the author became an 'official' academic and subsequently procured $18.6 million (cash + in-kind), equating to $10.4 million (in cash) predominantly from industry related research; a number of these being ARC Linkage projects, until mid-2012.

Recognising Dr Clarke's expertise in polymer science, the Kansas Polymer Research Center at Pittsburg State University, at the end of 2011, offered Dr Clarke the position of Research Director of its Centre, to manage research activities. However, Dr Clarke eventually refused this position, electing to remain in Australia, having a desire to build polymer research excellence in Australia. Recognizing the importance to Australia, of Dr Clarke's research, a commercial partner then negotiated with the Mawson Institute at the University of South Australia (UniSA), for Dr Clarke and his research team to transfer to UniSA. In mid-2012 this transfer began, and was finalised by early-2013, with a team of eight highly qualified Research Fellows established at UniSA.

Dr Clarke also established, at UniSA, five new industry research projects having a cash value of $2.7 million, demonstrating Dr Clarke's ability to undertake collaborative research with industry. In addition, Dr Clarke, was part of a consortium across the three South Australian universities, obtaining $1,983,800 in cash, from ARC LE130100168 (LIEF grant) for new NMR facilities. $1,235,000 (cash) was provided by the Government.
The five new industry projects established at UniSA by Dr Clarke and his team at the Mawson Institute are:

1. Polymers, for use as accommodating gels, in the intraocular lens of the eye (CRC project).
2. Polymer, insulating foams to reduce energy consumption (Researcher in Business (RIB) project).
3. Low fouling, reverse osmosis membranes for dairy applications (Researcher in Business (RIB) project).
4. Epoxy resins synthesised from waste glycerol, obtained from biodiesel manufacture, as a waste by-product. ARC Linkage LP100200616 in partnership with Adelaide University and industry partner SQC.
5. Safe, polymer based adjuvants, in modern anti-viral vaccines. (Researcher in Business (RIB) project).

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Carbon nexus: opportunities for translational research in carbon fibres and composites.

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Environmentally sustainable transport solutions for the future demand innovation in vehicle mass reduction to improve fuel efficiency and reduce CO_2 emissions. Carbon fibre composites, materials where carbon fibre is embedded in a polymer matrix, are a key element in helping realise these demands—as evidenced by the remarkable increase in the commercial applications of these materials as a substitution for heavier, traditional materials such as steel. For example, carbon fibre composites make up 50% of the structural materials of Boeing's Dreamliner passenger aircraft resulting in a 20% improvement in fuel economy. As a result of this increasing use, carbon fibre production is projected to more than treble in the next 10 years.

An Australian facility with the capacity to produce aerospace quality carbon fibre, Carbon Nexus (www.carbon.nexus.com.au) will facilitate world leading, industrially relevant research on all aspects of carbon fibre including structure-property relationships. Carbon Nexus represents a partnership between Deakin University and the Victorian Centre for Advanced Materials Manufacturing (VCAMM) and has been supported by both the Victorian State and Australian Federal Governments. It is the world's first university based multiscale carbon fibre research facility capable of producing industrially relevant, high quality fibre. Both a laboratory scale single tow line and a larger 20 ton pilot line will be capable of converting a range of precursors to carbon fibre and is due to be completed in June 2013. The research in this facility will build on Deakin and VCAMM's existing partnerships with companies such as Quickstep, Futuris, Boeing, Ford, Despatch and Furnace Engineering. Extensive consultation with the major industrial suppliers and end users of carbon fibre has led to the identification of the grand challenges to be solved by conducting targeted research. This presentation will describe the vision and research themes for Carbon Nexus, how the outcomes from this research will be translated to industry as well as highlighting opportunities for research collaboration.

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RAFT – the development of a Polymer Platform Technology for National Development and International Impact

Megan L. Fisher[1], Gregory W. Simpson[2],

1. CSIRO Intellectual Property and Licensing
2. CSIRO Materials Science and Engineering

The invention of the RAFT technology by Rizzardo and co- workers in 1998 has transformed the field of radical polymerisation, making available a new process for the synthesis of a wide range of polymers with potential commercial application in diverse fields – from industrial polymers to medical applications, from commodity chemicals to speciality additives.

The technology was developed by CSIRO, Australia's largest publically funded research agency, in partnership with DuPont, one of the world's leading chemical companies. There are significant challenges and issues in commercialising platform technologies such as RAFT where the interests of companies must be balanced with need to deliver benefit to the nation in return for the public investment in CSIRO.

This presentation will provide some history on the "discovery" of RAFT, challenges faced with taking the technology from the laboratory into the commercial world, industry involvement/collaborations, the relevance of protecting the IP, licensing the IP, where the technology is currently placed and where CSIRO is hoping to take it in the future.

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From a career beginning as a researcher Greg quickly progressed to managing large translational research portfolios focussing on benefits for the chemicals and plastics industry. His career developed into business development, commercialisation and technology transfer where he was responsible for various large transactions including the establishment of a number of start-up chemical and biotechnological companies. He has developed strategic responses to major national challenges such as national security and counter-terrorism, manufacturing and health; leading major cross-disciplinary research portfolios in these diverse areas.

Currently Deputy Chief Industry, CSIRO Materials Science and Engineering

TenasiTech – Development of a nanotech platform for medical and industrial applications

Céline M Chaléat, Darren J Martin

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This talk will describe the development of TenasiTech [1], a startup company originating from nanotechnology research of Professor Darren Martin at The University of Queensland. This technology was licensed by UniQuest, the main technology transfer company at The University of Queensland, to TenasiTech. The company has since received seed funding from Uniseed and has been the recipient of grant funding from COMET, Commercialization Australia and the Queensland Government.

TenasiTech's additive technology – Adaptive Polyol™ – is a new way of incorporating its proprietary nanotechnology additives [2] into a polyol precursor. This 'drop-in' nanotech solution can be used in a broad range of PU types (eg thermoplastics, castables, foams and solvent-based systems) without the need for any additional investment in processing infrastructure by the customers. In thermoplastic polyurethanes, TenasiTech delivers: super strength and toughness; excellent thermo-stability and dimensional-stability gains; increased resistance to oils/ethanol; enhanced film barrier properties.

TenasiTech is actively involved in multiple polymer families including acrylics and silicones. When these patented additives are incorporated to acrylics via an Adaptive Masterbatch™, scratch resistance can be doubled without degrading the impact strength or affecting clarity of the final product. This technology also enables multilayer extrusion along with other secondary processing such as thermo-forming, unlike post-manufacture coating treatments such as "silane flood coating".

TenasiTech is currently developing products with "lighthouse" customers in a number of fields. TenasiTech is at industrial-scale production (tonnage) and now supplying to molders or formulators.

This talk will follow the transfer of technology from university lab bench to industrial scale-up via a blend of fundamental and applied research [3-5] supported by continuous industry feedback.

1. www.tenasitech.com
2. Granted International patent application AU 2005279677 entitled "Polymer Composite"
3. A.F. Osman, G. A. Edwards, T. L. Schiller, Y. Andriani, K. S. Jack, I. C. Morrow, P. J. Halley and D. J. Martin, Structure-Property Relationships in Biomedical Thermoplastic Polyurethane Nanocomposites, Macromolecules, (2012), 45, 198-210
4. B Finnigan, K Jack, K Campbell, P Halley, R Truss, P Casey, D Cookson, S King, and D Martin, Segmented Polyurethane Nanocomposites: Impact of Controlled Size Nanofillers on the Morphological Response to Uniaxial Deformation, Macromolecules, (2005) 38(17), 7386-7396
5. Martin D.J., Osman A.F., Andriani Y., Edwards G., Advances in Polymer Nanocoposites:Types and Applications. Vol 1 Chapter 16. Thermoplastic Polyurethane Nanocomposites : Processing, Properties and Applications edited by F.Gao (Woodhead Publishing, January 28, 2013)

Exemptions to infringement : experimental use and regulatory approvals

Richard Grant

Spruson & Ferguson Intellectual Property

Recent changes to the Patents Act and Regulations have significant implications for researchers in academia and in industry, IP managers and patent attorneys. These changes have resulted, amongst other things, in a clearer experimental use exemption and an expanded exemption for activities connected with obtaining regulatory approvals.

One of the stated intentions[1] of the changes to the Patents Act is to provide free access to patented inventions for regulatory approvals and research: ensuring experimentation and approval for generic manufacturers is not delayed or negatively impacted by patents. This is intended to provide certainty to researchers and manufacturers and to allow them to work without worrying about patent litigation.

Details of the changes and their implications for researchers and other users of the IP system will be discussed.

1 IP Australia, "Intellectual Property Reform in Australia, January 2013: A summary of important legislative changes." http://www.ipaustralia.gov.au/about-us/ip-reforms/

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Since 2011 Principal, Spruson & Ferguson
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Polyhydroxyalkanoates from industrial wastes and mixed cultures: Experience moving from the laboratory to technology prototyping

Bronwyn Laycock[1, 2], *Alan Werker*[3], *Monica Arcos*[3], *Steven Pratt*[1], *Peter Halley*[1, 2], *Paul Lant*[1]

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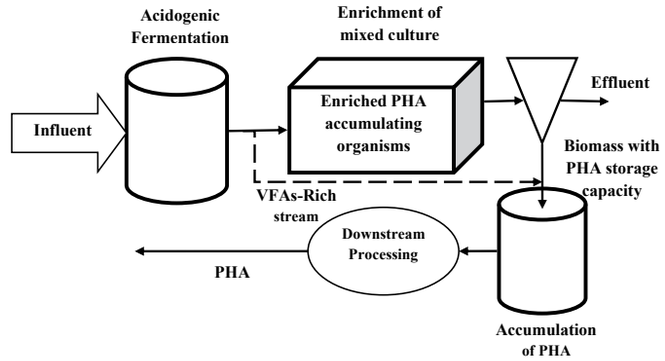
[3]AnoxKaldnes AB, Lund, Sweden

Polyhydroxyalkanoates (PHAs) are a family of fully biodegradable polyesters that are produced by a wide variety of bacteria as carbon/energy storage materials. They have attractive material properties, comparable with polyolefins, and have been intensively investigated since the 1980's[1]. However, they have not yet attained a mainstream commercial presence. Current PHA production methods at the industrial scale are based on pure cultures fed with pure carbon sources, requiring complex and costly equipment and processing procedures[2]. New, more cost-effective processes are being developed that involve the use of renewable carbon resources derived from agriculture or industrial wastes as substrates, with excess activated sludge from wastewater treatment plants as a source of mixed cultures for PHA accumulation[3].

At the University of Queensland, we have been working in close collaboration with AnoxKaldnes (Sweden), who are advancing to commercialize the production of PHA using mixed cultures in Europe. From an initial DIISR-ISL project through to the current ARC Linkage, we have been involved in analyzing the full process train from biological characterization and manipulation through to PHA isolation, analysis and processing. We have investigated the potential for direct accumulation of PHA in waste activated sludge sourced from local waste water treatment plants, without the need for enrichment of the biomass, but have also been able to undertake larger-scale PHA production in enriched mixed cultures at the pilot plant facilities in Lund (Figure 1). This initiative gave direct access to PHA in sufficient quantities so as to be able for the first time evaluate the mechanical, thermal and crystallization properties of the polymer produced under varying feeding conditions, and to explore the properties of the subfractions of differing composition. This work is helping to inform the further developments that AnoxKaldnes is undertaking towards commercialization of Cella™ technologies with benchmarking in prototype facilities operating in Sweden and Belgium for industrial and municipal wastewater management scenarios.

Figure 1. Schematic of pilot plant for production of PHA (AnoxKaldnes, Lund, Sweden)



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Leahy-Smith America Invents Act: Implications for Australian Inventors

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The recently implemented Leahy-Smith America Invents Act (AIA) was the most significant legislative overhaul of the American patent system in sixty years. The IP ground rules in the US have been radically altered. Successful IP procurement and exploitation in the US by Australian entities requires an understanding of these new ground rules. The present talk will focus on changes relevant to Australian patentees in the chemical arts, both in industry and academia, for successfully navigating the new US IP regime.

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Rapid Translation of Next Generation Composite Materials Through Multi-Scale Modeling

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Despite extensive material research and development, high-modulus matrix resins used in advanced aerospace composites are relatively brittle, glassy polymers and limit carbon fiber ultimate performance in applications. Limitations in understanding how the interface and interphase develop between the matrix and fiber have hindered the ability to fully extract strength and modulus capabilities of fibers within composites. And finally, a lack of fundamental knowledge associated with the evolution of carbon fiber morphology and surface chemistry from white-fiber precursor chemistry through carbonization has limited next generation fiber development. Collectively, these constraints have hindered the rapid translation for next generation materials in this field. The scientific experimentation methodology, next generation material development strategies and application development science within the composites field has been delayed by a lack of historical performance data and increased regulations leading to conservative insertion decisions leading to an inability to rapidly employ advancements. As a result, the current approach for insertion of new materials cannot keep up with advancement and radical changes in translation methods are necessary to assure the benefits new materials.

Our research is focusing upon improving the accuracy of multiscale models that will expedite the development of high performance aerospace matrices into application. Our collaboration with major corporations and defense agencies is focused upon the development and implementation of computational simulations for predicting the performance of glassy polymer networks, down-selecting high performance matrix network chemistries for experimental synthesis and analysis through computational simulation, maintaining a pilot scale development infrastructure which provides rapid fabrication of next generation composite test coupons from new chemistries and fibers, the ability to assess physical performance and continuously improve multiscale modeling frameworks. This iterative development cycle is proving to be an effective approach to expedite the development of new matrices and fiber materials into composites and has been refined through global research programs with leading institutions. This research model and will significantly enhance the ability to expedite new matrices materials with optimized capabilities by providing the necessary simulation, synthesis, fabrication and testing which provide "***decision making confidence***". The prediction of failures utilizing traditional methods is complicated by the fact that fracture initiation and progression in fiber-reinforced composites is multifaceted involving numerous failure modes associated with interfacial delamination, fiber-matrix interfaces, fiber-breakage, matrix cracking, etc. The development of these calculations depends upon the specific physics for each laminate construction and contingent upon matrix chemistries, fiber lay-up packages, fiber orientations, and modes of deflection; this becomes cumbersome for broad utility in structural analysis for cost-effective macroscale predictions.

This presentation will review our approach and discuss critical computational and experimental data necessary to advance multiscale computational models which link length and time scales from the molecular level through continuum level structural failure. These multi-scale modeling frameworks are specifically designed to expedite development time, reduce cost and minimize qualification testing for inserting new materials into complex structures and applications. The ultimate goal of the multiscale approach is to calculate the properties and behavior of complex materials across all relevant length and time scales through computational techniques, and rapidly produce new materials which have been guided by simulation methods.

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Industrial Polymer Research: A 20 year journey from SME's to Multinationals to Spinouts, developing Packaging, Scaffolds, Drug Polymer Conjugates and Renewable Chemicals and Polymers

Mike O'Shea[1, 2], Gary Peeters[1], Graeme Moad[1], Louis Kyaratzis[1], Yen Truong[1], Mark Hickey[1], Florian Graichen[1], Heng Taing[1], Justine Jeffery[1], Ben Leita[2], Ramon Tozer[3], Simona Lavric[1].

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This presentation will cover the process of "Research"-turning money into knowledge and "Innovation" – "turning knowledge into money" as has been applied to a range of technologies developed from the core capability of polymer science.

What will be covered breifly includes:

- Upgrading PET through Reactive Extrusion and masterbatches: (Visy -Dual Ovenable trays, Ciba - Masterbatch to upgrade recycled PET etc)
- Branched Foamable PP – (Lyondell Basell – Target: Foamable Food packaging)
- Transesterification Resistant High Barrier Polyester Block Copolymers for Packaging
- Guides for Peripheral Nerve Repair
- Thermochromic Fibres for Wound Care
- Degradable Controlled Release Drug Polymer Conjugates for Wound care and Opthalmic applications (PolyActiva).
- Renewable Chemicals and Polymers – Fatty acid polymer modifiers, Bioaromatic and New Monomers from Terpenes.

Case studies will include what worked, almost worked and things that failed.

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Tailor-made Polymers for Bacteria-Responsive Wound Dressings: Fabrication, Characterization and Enzyme-Triggered Release

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In this contribution our recent efforts to exploit supramolecular assemblies of tailor-made polymers for application in advanced wound dressings will be discussed. Nanocapsules obtained by the self-organization of tailor-made enzyme-responsive block copolymers provide dual functionality in currently developed advanced wound dressings as (*i*) indicator for wound infection with pathogenic bacteria and (*ii*) *in situ* on demand treatment against those pathogens.[1,2]

In general, the self-organization of amphiphilic block copolymers represents an interesting pathway to obtain functional nanoscale structures, which can be controlled regarding size distributions and dimensions. Vesicles of amphiphilic block copolymers belong to the class of polymeric, stimuli-responsive nanocarriers that are widely discussed in the literature as promising drug delivery systems (**Fig. 1**). Due to their stable nature and versatile properties, they can also be used as storage compartments of active compounds in other biomedical applications, such as advanced wound dressings, where the release of antimicrobials and/or fluorescent markers as part of an indicator system of bacterial infection represents a central mode of action.[1] The *in situ* detection and treatment of infections in scald or burn wounds is not only essential for proper healing as well as the prevention of scarring, but may contribute to reduce the spread of antibiotic resistance stemming from prophylactic administration of broadband antibiotics. In this context we synthesized and investigated assemblies of novel amphiphilic block copolymers, e.g. hyaluronic acid-*block*-ε-polycaprolactone and hyaluronic acid-*block*-poly(lactic acid) copolymers.[2] Hyaluronic acid is the target for the enzyme hyaluronidase that is excreted by the bacterium *staphylococcus aureus*. Hence in an infected wound covered with a capsule-containing dressing, the capsules are opened by the bacterial enzymes, which signals selectively the infection and may allow the on demand-only administration of potent antimicrobials. The synthesis, the detailed characterization and finally application of these novel block copolymer vesicles in the detection of bacteria will be discussed. In addition, bacteria-responsive biopolymer thin film systems will received attention.

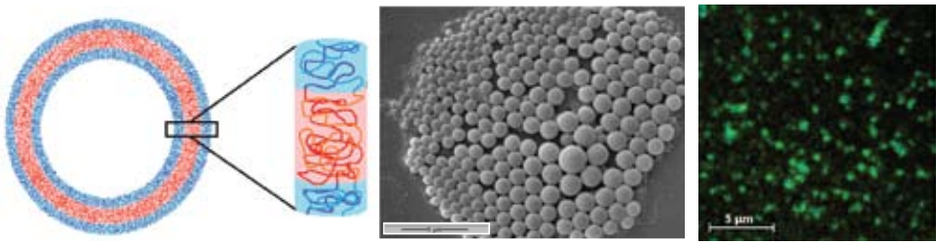

Figure 1. (Left) Scheme of block copolymer vesicle, (middle) SEM and (right) fluorescence lifetime imaging microscopy image of dye filled hyaluronic acid-*block*-poly(lactic acid) vesicles.

[1] J. Zhou, A. L. Loftus, G. Mulley G., A. T. A. Jenkins, *J. Am. Chem. Soc.* **2010**, *132*, 6566-6570.
[2] S. Haas, Y. Chen, C. Fuchs, S. Handschuh, M. Steuber, H. Schönherr, *Macromol. Symposia* **2013**, *in press.*

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Enzyme mimics

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Currently enzymes are being explored for a variety of applications. In fact, enzymes are already well established in common technologies, for example; active ingredients in detergents, food additives, and paper and pulp processing.[1] Recently, enzymes have also been developed as useful catalysts in pharmaceutical and specialty chemical synthesis. [2] Enzymes have also attracted attention for the renewable preparation of bioethanol[3] and biodiesel.[4] The downfall in the majority of these applications is the small operating range, limited stability, and the cost of enzymes. Enzyme mimics could address all of these issues and create new, high-value products for a range of industries. This presentation will develop platform chemistries to mimic some of the complex mechanisms of enzymes. Specifically, this work will develop self-assembled macromolecular mimics of hydrolytic enzymes.

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3. H. Shahsavarani, M. Sugiyama, Y. Kaneko, B. Chuenchit, S. Harashima *Biotechnology Advances* **2012**, *30*, 1289.
4. C-H. Liu, C-C.Huang, Y-W. Wang, D-J. Lee, J-S. Chang, *Applied Energy* **2012**, *100,* 41.

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Well-defined Synthetic Transmembrane Pores using Cyclic Peptide–Polymer Nanotubes

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In Nature, transmembrane protein channels function as homeostatic regulators that facilitate the transport of polar molecules and ions across lipid bilayer membranes.[1] While the lipophilic nature of membranes acts as a barrier, it also permits hydrophobic peptide regions of the transmembrane proteins to anchor in the lipid bilayer. Here, synthetic channel mimics based on nanotubes obtained from the self-assembly of cyclic peptide – polymer conjugates (**Fig. 1a**)[2] were created to mediate transbilayer solute transfer. The hydrophobic interactions between the lipids and the polymer periphery of the nanotubes were exploited to anchor the nanotubes into the bilayer, mimicking the hydrophobic anchoring of transmembrane proteins in membranes. As depicted in **Fig. 1b**, a convergent synthesis methodology based on active ester reactive groups was used to synthesize the cyclic peptide–polymer conjugates from well-defined cyclic peptide and polymer precursors. In this study, the type of transbilayer channels formed was assessed using large unilamellar vesicles. The types of channels that can be envisioned include (i) a pore defined by the internal diameter of a single cyclic peptide–polymer nanotube, (ii) a macropore defined by the space between a bundle of cyclic peptide–polymer nanotubes and (iii) disruption of the lipid bilayer (**Fig. 1c**). Examination of a library of cyclic peptide – polymer conjugates revealed that the type of transbilayer channels formed strongly depends on the type of polymer that is ligated to the cyclic peptide.

The self-assembly methodologies of the channels described here could prove extremely useful in membrane technologies[3] and biosensors.[4] The channels can also be applied in therapeutics, as antibacterials,[5] defective channel replacement[6,7] and as drug delivery vehicles where the synthetic channels could be used to deliver non-lipophilic drugs effectively into cells without relying on an endosomal escape.

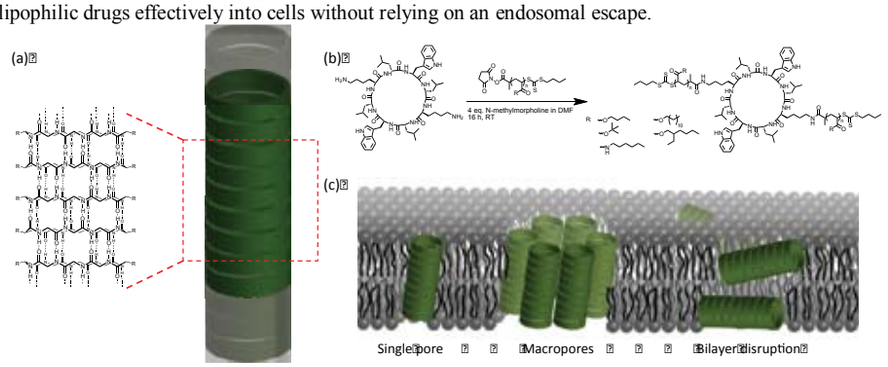

Figure 1. (a) Side view and schematic of the cyclic peptide upon assembly into nanotubes. (b) Synthesis of the cyclic peptide – polymer conjugates. (c) Self-assembly of the nanotubes in lipid bilayers forming channels as single pores, macropores, or 'carpet-like' bilayer disruptions.

[1] E. Gouaux, R. MacKinnon *Science* **2005**, *310*, 1461-1465.
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[6] J. Sánchez-Quesada, M. P. Isler, M. R. Ghadiri *J. Am. Chem. Soc.* **2002**, *124*, 10004-10005.
[7] B. Shen, X. Li, F. Wang, X. Yao, D. Yang, *PLoS ONE* **2012**, *7*, e34694.

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Gelling of a short designed α-helical peptide under physiological conditions

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Hydrogels are soft solids that represent potentially useful matrices for tissue engineering, wound healing and drug delivery. We have recently developed alpha-helical peptides that self-assemble to form fibrils and molecular gels in a pH-responsive fashion.[1] Rational modification of the first-generation sequence, AFD19, which gels at pH 6.0 but precipitates at pH 7.5, was used to obtain a new 21-residue peptide, AFD36, which gels at neutral pH (**Fig. 1**). Small-angle X-ray scattering shows that AFD36 self-assembles to form fibrils with a diameter of 3.5 nm and a persistence length of 10-14 nm between pH 4.0 and 7.0, while macroscopic gels form at pH 7.4 and 0.5% (w/v) peptide. Gelling occurs rapidly at a permissive pH, which can create mixing difficulties, leading to the formation of non-uniform gels. We found that a controlled rate of pH change, allowing for uniform gelation, can be achieved by titrating the peptide solution with sodium bicarbonate, followed by gradual loss of carbonic acid from solution as carbon dioxide. The peptide hydrogels were stable to 90 °C when prepared in physiological salt solutions, and were able to support the growth and proliferation of mouse 3T3 cells over >6 days. Studies of the biomedical applications of the gels are ongoing.

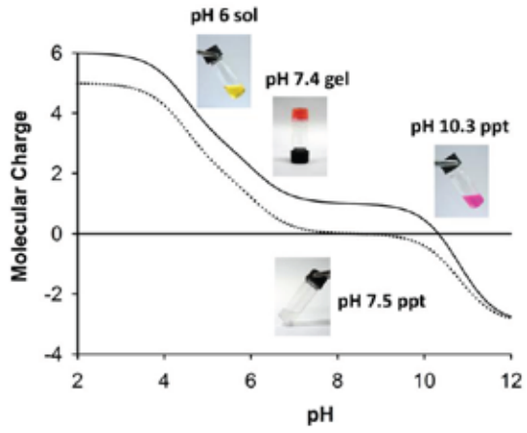

Figure 1. Phase diagram for gelation of AFD36 and parent sequence AFD19. Calculated charge curves are given for AFD36 (solid line) and AFD19 (dotted line). Inset: photographs of sol, gel and aggregate states for AFD36 (top) and aggregate state for AFD19 (bottom). Phenol red has been included in the AFD36 samples as a visual indicator of pH.

[1] N.L. Fletcher, C.V. Lockett, A.F. Dexter, *Soft Matter* **2011**, *7*, 10210-10218

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Multi stimuli-responsive bio-mimetic protein-polymers and their functional conjugates

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Responsive nanostructured materials, whose characteristics can be modulated on demand is an exciting area of research with potential applications in the areas of material science, nanotechnology, nano-biotechnology and medicine. Currently, such advanced materials are prepared from a very limited number of synthetic polymers and biopolymers.[1] Recent progress and emerging breakthroughs in synthetic biology has generated unprecedented opportunities, and offer powerful strategies to exercise exquisite control over molecular architecture, size organization and functionality using protein based polymers. The protein-polymers so synthesized are superior to synthetic polymers in many ways including: (i) multi-functionality/tunability, (ii) adaptability/stimulus-responsiveness, (iii) ambient and aqueous synthesis and processing, (iv) recyclability and biodegradability. Biomimetic stimuli-responsive proteins including highly elastic elastin, elastin-mimetic polymers and green fluorescent protein (GFP) have revolutionized controlled drug delivery, cell culture, biological assay, and targeted sensing.[1] In this presentation we highlight and discuss the advanced responsive behaviour and functionality of hydrogels, solid-liquid interfaces, nanoparticles and nanohybrids derived from resilin-mimetic protein-polymer rec1-resilin[2] and AN-16.[3] Resilin is a member of the family of elastic proteins that includes elastin, gluten, gliadin, abductin and spider silks and occurs as a highly elastic extracellular skeletal component in insects. It is purported to be the most resilient elastic material known with resilience of 97%. Resilin-mimetic recombinant protein *rec1-resilin* was first synthezied from the repeat sequences of the first exon of the Drosophila melanogaster CG15920 gene.[2] The composition of this polypeptide is dominated by 18 copies of a 15-residue repeat sequence: GGRPSDSYGAPGGGN. In view of studying resilin from various sources, recently through homology searching, we[3] have identified another resilin gene belonging to *Anopheles Gambiae* (African Malaria mosquito). The consensus sequence from Anopheles (AQTSSQYGAP) contains a slightly different combination of amino acid to the *Drosophila* sequence. Recursive cloning strategy was employed for generating synthetic genes encoding multiple copies of consensus polypeptides, based on the repetitive domains within resilin-like genes from bloodsucking mosquito *Anopheles Gambiae*. The resulting protein An16 that was successively expressed and purified from the synthetic construct is dominated by 16 copies of a 11-residue repeat sequence: GAPAQTPSSQY.[3]

We have demonstrated that resilin-mimetic elastic proteins are responsive to multiple environmental stimuli, including displaying both a lower and a tunable upper critical solution temperature (LCST and UCST).[4] This is for the first time such dual responsiveness has been displayed by a single polymer molecule. Moreover, this bio-mimetic protein-polymers are also pH responsive, photo-responsive and exhibit tunable photophysical properties.[4,5] It has been identified that in swollen crosslinked state resilin-mimetic proteins exhibit extraordinary resilience (>94%), and perfect rubber like elasticity.[6] We have successfully used the environment induced tuning of the self-assembling of *rec1-resilin* for constrained synthesis and stabilization of nanostructured metal nanoparticles and nano-hybrids of controlled size, photophysical properties and electrochemical activities.[7] These observations reveal the opportunities and challenges for development of other *rec1-resilin* mutants for novel biomaterials design—an exciting finding for protein engineering and materials science. We reveal the potential of these multi-responsive protein-polymers to pave the way for the design of novel biologically inspired materials for nanotechnology, nanobiotechnology, medicine and tissue engineering applications.

[1] D.G. Maskarinec, D.A. Tirrell, Curr. Opin. in Biotechnol. 2005, 16, 422. [2]C. M. Elvin, et al., Nature 2005, 437, 999-1002; [3]R. E. Lyons et al., Protein Eng. Design and Select. 2007, 20, 25-32. [4]N. K. Dutta et al., Angew. Chem. Int. Ed. 2011, 50, 4428-4431, [5]M. Y. Truong et al, Biomaterials 2010, 31, 4434-4446. [6]M. Y. Truong et al. Biomaterials et al. 2011, 32, 8462-8473. [7] S. Mayavan et al., Biomaterials 2011, 32, 2786-2796.

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Peptide-Based Complex Macromolecular Architectures: A Platform Technology in Polymer Therapeutics

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The ability to incorporate amino acid building blocks into synthetic precursors and the creation of hybrid polymers in a highly controlled manner are significant steps forward in polymer therapeutics as they lead to improved biodegradability and biocompatibility of the polymer construct.[1] Recently, researchers have begun to further increase the macromolecular complexity of peptide-containing polymers by exploring complex architectures, such as star-shaped polymers.[2-5]

In this work, a star polymer platform technology which could potentially cater for a broad range of novel applications was successfully developed in the form of well-defined 16- and 32-arm hybrid star polymers based on the core-first approach and a one-pot strategy *via* ring opening polymerisation (ROP) of ε-Z-L-lysine *N*-carboxyanhydrides (Lys NCA) from second and third generation poly(amido amine) (PAMAM) dendrimers initiators, respectively. Further functionalisation of these generic star polymers yielded three other distinctive types of star polymers. The first type of stars was obtained from PEGylation followed by deprotection to afford water soluble poly(PEG-*b*-L-lysine)$_{arm}$PAMAM$_{core}$ stars with positively-charged amino groups along the arms (Fig. 1A). The second type of star polymers consisted of poly(L-lysine) arms, decorated with allyl groups around the periphery (Fig. 1B). Lastly, poly(L-lysine-*b*-DL-valine)$_{arm}$PAMAM-$(NH_2)_{16,core}$ star polymers having a cationic outer component and a hydrophobic inner component on the arms were successfully synthesised (Fig. 1C).

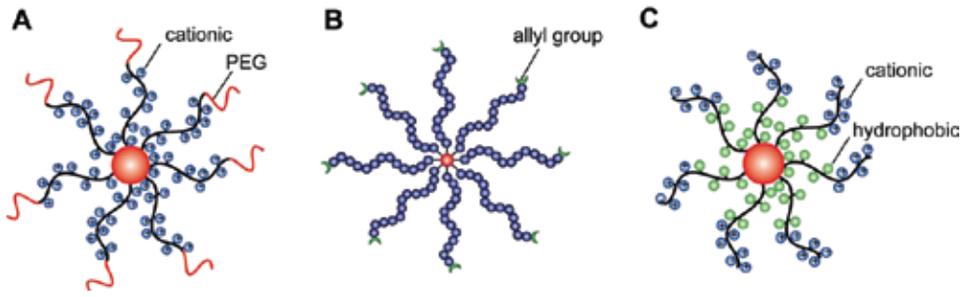

Figure 1. Structure of (A) cationic PEGylated star polymers. (B) allyl-functionalised star polymers. (C) star polymers with a cationic outer component and a hydrophic inner component on the arms.

The results presented herein based on the star polymer platform technology will inevitably open up new opportunities in the development of novel polymer therapeutics applications such as siRNA and antimicrobial peptide (AMP) delivery as well as the fabrication of amphiphilic antimicrobial stars.

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Photo-responsive reversible polymeric materials using dynamic covalent bonds

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Reversible polymers represent a relatively new class of materials that possess bonds capable of reversibly connecting and disconnecting monomers in response to stimuli such as heat or light. These reversible bonds can be used to construct a recyclable polymer via material polymerization and depolymerization, on demand (**Fig. 1**).

Thymine, one of the nucleic bases in DNA, exhibits both the ability to form relatively strong hydrogen bonds, as well as the ability to photo-crosslink. The hydrogen bonding of thymine is well known to contribute to the stabilization of the double helix structure of DNA. The photo-dimerisation of thymine, a UV induced 2π + 2π photo-cyclisation, results in the covalent dimerisation of adjacent thymines and disrupts the helical structure of DNA. This process has been linked with the development of certain forms of skin cancer. Photo-crosslinking of thymine occurs with irradiation at wavelengths above 270 nm. Crosslinking is reversed either by irradiation below 249 nm or enzymatically. Our research exploits this reversible dimerization to develop a novel, photo-responsive reversible polymer system using di-thymine monomers.

We have used the reversible [2π + 2π]-cycloaddition of a bioinspired bis-thymine monomer to topochemically synthesize a polymer. The polymer can be fully photo-depolymerized to the monomer, and then reversibly and repeatedly photo-polymerized and photo-depolymerized (**Fig. 2**). This is the first demonstration of complete photo-depolymerization and subsequent monomer recycling using this mechanism. The design and synthesis of various di-thymine monomers, determination of monomer crystal structures, and characterization of the photoproducts using Nuclear Magnetic Resonance, UV-Visible Spectroscopy, Gel-Permeation Chromatography, and other polymer characterization techniques will be discussed in the presentation.

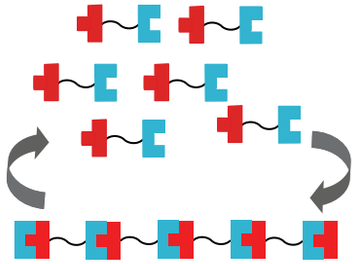

Figure 1. Schematic of a Reversible

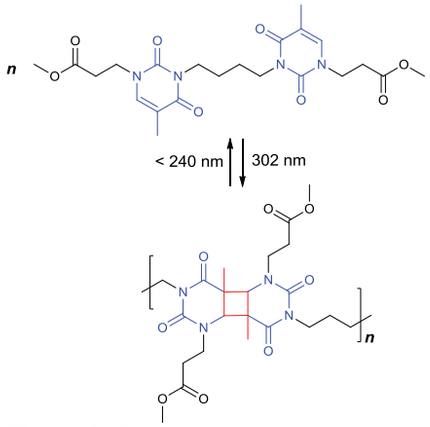

Figure 2 Photoreversible polymerisation of *n*-butyl-linked-bis(thymine propanoate).

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Role of Environment on the Secondary Structure of a Biomimetic Protein-based Elastomer

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Resilin is an elastomeric, structural protein that is found in the cuticle region of many arthropods1. Resilin mimetic protein-polymer rec1-resilin has recently been identified as a promising material for a range of applications as it is biocompatible, displays remarkable elasticity, and responds to multiple stimuli. Our recent work1-3 has demonstrated significant potential for developing resilin as a new biomimetic material. However, the elevated LCST and lack of strength displayed by the material limits its suitability for many applications. The presence of very high content of Gly (~34.5 mol %) and Pro (~14 mol %) amino acid residues with very different backbone rigidity may contribute to the disorder in resilin also and answer our question "where does the multi stimuli responsiveness of an elastic reslin come from?"**.** Therefore, the aim is to develop an understanding of the role of environment and effect of molecular architecture of a few sequence specific residues on rec1-resilin's structure-property relationship. We have selected various macromolecules including, a synthetic stimuli-responsive polymer, a rigid and a flexible peptide, and a rigid naturally occurring polymer. Hybrid materials formed through physical and chemical interactions of rec1-resilin with these materials have been investigated in details using circular dichroism (CD). Hydrodynamic radius and global charge of the protein solution have been determined from dynamic light scattering using Nanozetasizer. CD results reveal that the addition of the rigid peptide, poly-L-proline, resulted in a conformational change of the rec1-resilin structure. The circular dichroism spectra demonstrate that the rec1-resilin structure changes from random coil to predominantly polyproline-II helical with increasing proportion of poly-L-proline (Fig.1). In most of the disordered protein, PPII is the major conformation with a left-handed helix structure with three residues per turn and no intramolecular hydrogen bonds. However, PPII conformation is always in equilibrium with β-sheet, β turn, and unordered conformations. Such geometrical flexibility of PPII conformation may allow the protein to progress from random conformation to an ordered β -sheet conformation through intermolecular interaction as seen in elastin and a number of proteins/polypeptides under a wide variety of conditions and plays a pivotal role in the elasticity. The study thus confirms that the self-assembly behavior of this protein can be tailored as needed. This will enable us to tune the elasticity and other responsive properties through macromolecular modification making it suitable for a wide range of applications, e.g dermal tissue engineering and cell sheet engineering.

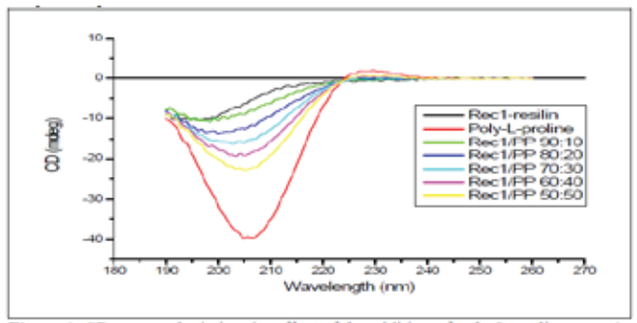

Figure 1. CD spectra depicting the effect of the addition of poly-L-proline to rec1-resilin

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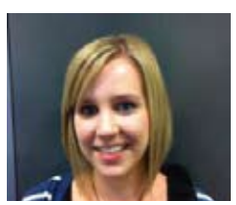

Using Chemical Reactions to Control Polymer Network Shape, Topography, and Behavior

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The ability to induce adaptive network behavior in traditional thermoset polymer networks in response to a specific external stimuli in the immediate material environment has enabled simultaneous shape and topography control within a covalently crosslinked polymer system. Here, two approaches to transform the shape, topography and behavior of thermoset polymer network are investigated. In the first approach, a Covalent Adaptable Network (CAN) thermoset thiol-acrylate polymer with exchangeable bonds upon exposure to light can undergo cleavage and reformation in a manner that enables the crosslinked network structure to respond chemically to an applied stimulus by continuously and locally deforming via polymer network connectivity rearrangement, which enables 3D control of its geometry. [1] In a second approach, a thiol-acrylate shape memory dual-cure polymer system is demonstrated to have the ability to go from a temporary shape configuration to a permanent shape configuration on being exposed to a specific temperature range.[2] Additionally, this network is demonstrated to simultaneously maintain the ability to react further and achieve a second and final set of material properties via a photoinduced reaction. Such a two-stage reactive polymer system that enables the achievement of two distinct and largely independent sets of properties might be necessary for multiple stages in the life-cycle of applications such as shape memory polymers (SMP) based sensors and actuators.

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Blends of thermoplastics and thermosetting monomers

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High performance thermoplastic polymers often have good properties such as toughness and recyclability but tend to be difficult to process, whereas thermosets offer ease of processibility and thermal resistance but are brittle. Therefore, blends of thermosets and thermoplastics have been used recently to toughen the thermoset (for low thermoplastic levels) or to enhance thermoplastic processability (at low concentrations of the thermosetting monomers). Usually in both cases, the initially miscible blend undergoes phase separation into thermoplastic-rich and thermoset-rich domains due to the reduction in the entropy of mixing during the reaction, resulting in either a co-continuous phase structure or a matrix with dispersed domains (either thermoplastic-rich or thermoset-rich, depending on the initial composition).

In this work[1-6] we have used radical-cured diallylic (e.g. DAOP) and dimethacrylate monomers or amine-cured di-epoxies (e.g DGEBA/MCDEA) to form blends with polyvinylacetate (PVAc), polyvinylchloride (PVC), polymethylmethacrylate (PMMA), bisphenol-A polycarbonate (PC), and polydimethylphenylene oxide (PPO), some with nanofillers (e.g. organo-modified Cloisite clay), over the whole range of compositions by solvent blending, batch mixing or extrusion. These systems have been studied by rheology, hot-stage microscopy and DMTA of the uncured blends, their curing kinetics by FTIR and dynamic DSC, their chemorheology during cure, the DMTA of the cured products, their morphology by SEM and their mechanical properties.

In most cases, addition of the thermoplastic to the thermosetting resin retarded the polymerization kinetics due to dilutional effects but for the cure of an allylic with a hydroperoxide, the trace metal impurities in PPO actually accelerated the polymerization. Addition of plasticizing monomer markedly decreased the blend viscosity as illustrated in Fig. 1 and resulted in a reduction of the lowest processing temperature by as much as 100°C. Additionally, the T_g of the blends is significantly reduced by the uncured thermomosetting resin but after polymerization, good thermomechanical behaviour is restored (see Fig. 2). Fig. 3 illustrates the micron-scaled island morphologies formed in thermoplastic-rich cured blends. The use of reactive monomers as plasticizers also enhances dispersion and partial exfoliation of clay nano-layers in the thermoplastic-rich matrix (Fig. 4).

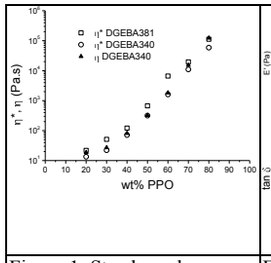

Figure 1. Steady and dynamic viscosity of PPO:DGEBA blends

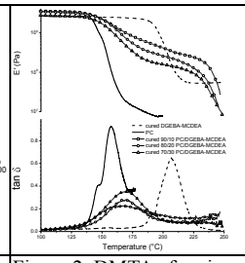

Figure 2. DMTA of various cured blends of PC:DGEBA/MCDEA

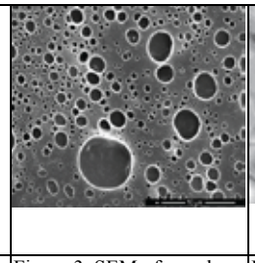

Figure 3. SEM of cured 60PPO:40DAOP/DCP blend (etched)

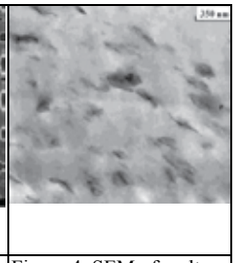

Figure 4. SEM of melt blended PVC:DAOP with 5 wt% Cloisite10A

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5. GG Liang, WD Cook, HJ Sautereau, A Tcharkhtchi, Polymer **48**, 7291 (2007); **50**, 2635, 2655 (2009)
6. GG Liang, W D. Cook, HJ Sautereau , A Tcharkhtchi, Euro Polym J **44**, 366 (2008)

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Block Ionomer-Toughened Epoxy Thermosets

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Toughening thermosets by amphiphilic and reactive block copolymers has been extensively studied during the past decade.[1] Recently, we have employed block ionomer complexes to modify epoxy thermosets by achieving nanostructures in thermoset blends.[2,3] Here we report a novel approach to toughen epoxy thermosets using a block ionomer, i.e., sulfonated polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene (SSEBS). SSEBS was synthesized by sulfonation of SEBS with 67 wt.% polystyrene. In the present epoxy system, phase structure can be controlled at either nano-scale or micron-scale by simply adjusting sulfonation degree of the SSEBS. It has been found that there exists a critical threshold of sulfonation degree (10.8 mol%) to form nanostructures in the epoxy/SSEBS blends. Above this threshold, macro-phase separation can be avoided and only micro-phase separation takes place, resulting in transparent nanostructured materials. **Fig. 1** shows a TEM image of the typical morphology of the nanostructured SSEBS/epoxy blends. **Fig. 2** presents the variations of stress intensity factor K_{IC} and critical strain release energy rate G_{IC} of the SSEBS/epoxy blends as a function of sulfonation degree of SSEBS. The epoxy/SSEBS blends show morphological transformation from the micron scale (Regime I) to the submicron scale (Regime II) and the nanoscale (Regime III); the fracture mechanical properties are correlated with the phase structure over a broad range of length scales from nanometers to tens of microns. All the epoxy blends with SSEBS display improved fracture toughness. In the nanostructured blends (Regime III) corresponding to the high sulfonation degrees of SSEBS, the fracture toughness decreases with deacreasing the size of microdomains. In the largely macrophase-separated blends (Regime I), only slight improvement in fracture toughness can be obtained with SSEBS of low sulfonation degree. The epoxy blend with submicron phase structure of 0.05-1.1 μm (Regime II) with SSEBS of moderate sulfonation degree (5.8 mol%) displays maximum fracture toughness.

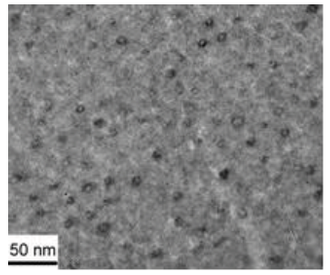

Fig. 1. TEM image of epoxy blend containing 10 wt.% SSEBS with 21.9 mol% sulfonation degree.

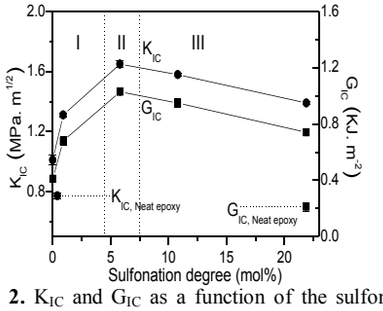

Fig. 2. K_{IC} and G_{IC} as a function of the sulfonation degree of SSEBS.

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Preparation of ordered monolithic structures by unidirectional freezing and radical polymerisation

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Polymer based monoliths were introduced about 20 years ago as a new generation of stationary phases in separation science with recognised advantages over traditional particle packed columns. To date the majority of monolithic structures explored for analytical applications have been based on the same synthetic approach first described by Svec and Fréchet[1]. However, as new chromatographic systems challenge the theoretical limits of high performance chromatography, it is now clear that one of the limiting factors in preparing reproducible polymer monoliths with good chromatographic performance is the degree of bed heterogeneity. Novel polymerisation methods are needed to improve the structural homogeneity, reducing the contribution of eddy dispersion to band broadening and allowing polymer monoliths to reach their true potential for analytical applications.

We have recently demonstrated that by using a cryopolymerisation approach and incorporating suitable polymer nanoparticles during the polymerisation process it is possible to significantly improve the structural homogeneity and thus the chromatographic performance of polymer monoliths[2]. In this presentation we extend this work to demonstrate the preparation of homogenous monolithic polymers by unidirectional freezing. In this technique a mixture of monomers/polymers and solvent is unidirectionally frozen at subzero temperatures. During this process, the solvent ice crystals grow in the freezing direction and the solidified monomer phase is structured around the aligned crystals which act as template. The monomer phase is then polymerised in its solid state and subsequently the ice crystals are easily removed after the polymerisation reaction. This process leads to the preparation of highly ordered monolithic structures with porous properties that can be easily tuned according to the freezing/polymerisation conditions.

In this work, we present the preparation of a range (hydrophilic, hydrophobic and reactive) monolithic cryopolymers by unidirectional freezing and we evaluate these novel porous materials as stationary phases in liquid chromatography. The influence of the freezing/polymerisation conditions (freezing rate, monomer concentration, etc.) over the porous properties will be also presented. These cryopolymers present a regular, open porous structure unlike that described previously for other monolithic columns what makes them particularly interesting materials to be used in separation science.

[1] Q.C. Wang, F. Svec, J.M.J. Fréchet, *Anal. Chem.* **1993**, *65*, 2243-2248

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Dissipation and recovery of Nano-hybrid hydrogels

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The simplest sketch of a synthetic hydrogel consists of a 3D organic network, using hydrophilic polymer chains with chemical cross-linker to make inter-chains covalent bonds. Evidently, the resulting macromolecular architecture is a swollen network that mechanically performs poorly, that combines a very low modulus with high fragility. Over the past ten years, research has evolved from the simple idealization of a classical chemical gel, to envisaging diverse designs for tough gels, i.e. introducing additional dissipative mechanisms at the molecular level. For instance, Gong et al.[1] have developed double network (DN) gels which demonstrated dramatic improvements of the fracture toughness. These DN gels are however permanently damaged upon deformation. In contrast to this quite sophisticated macromolecular architecture, Haraguchi et al.[2] developed initial highly extensible nano-composite gels (NC gels) in which clay platelets play the role of reversible cross-linker.

In order to better understand the mechanical properties of such NC gels and taking advantage of the DN strategy, our group developed a parent system[3] using spherical silica nanoparticles (i.e. to avoid any effects of strain induced filler orientation) as physical crosslinker and introducing a chemical crosslinker to ensure a full strain recovery after mechanical loading. Interestingly, these hybrid hydrogels (i.e. mixing physical and chemical inter-chains junctions) appeared to possess a very unusual combination of properties: modulus, dissipation, strength and strain at failure were seen to be enhanced simultaneously, keeping a full strain recovery, (Fig. 1).

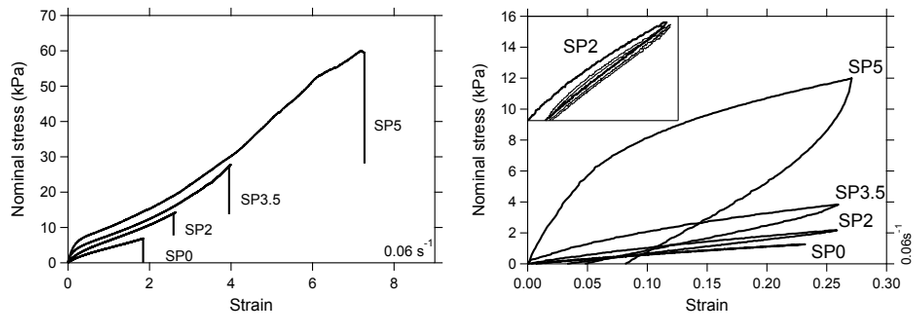

Figure 1: (a) Tensile mechanical behavior at 0.06 s^{-1}: effect of nano-particle content for SP0 (without silica), SP2, SP3.5 and SP5; and (b) effect of silica volume fraction on dissipation (within 30 seconds of rest SP5 behaviour is seen to be fully recovered).

The process implied by transient polymer/nano-silica interactions seems to govern the dynamic of the hydrogel. The physical "interactions" induced by polymer/nano-silica interactions may that way delay irreversible damage of the network but may also get the potential to reform, allowing the network to accommodate its connectivity during deformation.

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[3] Carlsson, L., Rose, S., Hourdet, D., Marcellan, A., *Soft Matter* **2010**, *6*, 3619.

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The Effect of Matrix Polarity on the Properties of Poly(*o*-methoxyaniline) – EVA Blends

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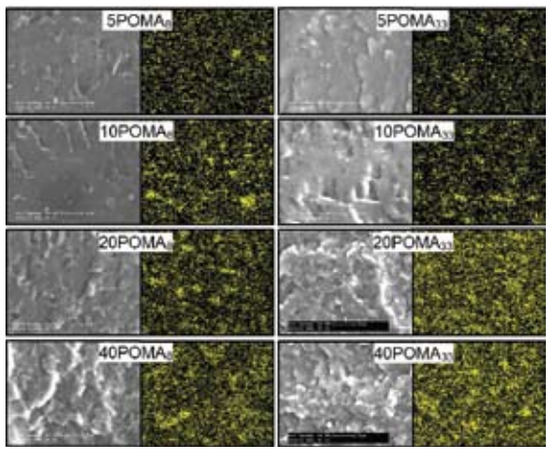
Dispersion of conducting polymers in thermoplastic matrix is one of the most promising approaches to overcome the processability issue of conducting polymers; melt blending is industrially favourable over solution blending as it avoids the usage of any solvent and enables the utilization of already existing machinery in the polymer industries. Poly(*o*-methoxyaniline) (POMA) doped with *p*-toluene sulfonic acid (TSA) was successfully melt blended with ethylene – vinyl acetate copolymer (EVA). The effect of the matrix polarity as well as the blend composition on the properties of the blends was investigated using two grades of EVA as matrix. The lower polarity EVA contains 8% vinyl acetate (VA) (EVA_8) and the higher polarity EVA contains 33% VA (EVA_{33}). The surface resistivity of the POMA-EVA blends was found to decrease with an increase of POMA loading. The POMA-EVA_8 blends had a lower surface resistivity than POMA-EVA_{33} blends which is attributed to the presence of a higher proportion of conductive POMA particles in the surface region resulting from the larger polarity difference between the POMA and the EVA8 matrix. More uniform dispersion is observed from scanning electron microscopy (energy-dispersive X-ray spectroscopy) for POMA in EVA_{33} compared to POMA in EVA_8 (as presented in Fig. 1) and this has been interpreted as being a consequence of the similar polarities between POMA and EVA_{33}. The mechanical properties of the blends were found to be affected by both POMA loading and matrix polarity. The oxygen barrier property of the POMA-EVA blends was found to increase with POMA loading in both high and low polarity EVA matrices, suggesting that POMA can be used as oxygen barrier agent in the packaging industry.

Figure 1. Cross-section Morphology of POMA-EVA blends (SEM images and EDX sulfur mapping)



Acknowledgement

The authors acknowledge the financial support for this project (Hybrid Plastics, UOAX0812) from the New Zealand Ministry of Business, Innovation and Employment.

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Tough and self repairing ionic-covalent entanglement network hydrogels of gellan gum and gelatin

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Hydrogels are a class of polymeric materials characterised by high water content (up to approximately 99%) and generally weak mechanical properties. Hydrogels have many applications including foods, cosmetics, creams, ointments, pastes and in particular as a scaffold material for tissue engineering. However, not all types of tissue can be supported by typical hydrogels, for example cartilage which is tougher than most hydrogels and must be able to withstand repetitive shocks without deteriorating. A relatively recent innovation in hydrogel materials are inter-penetrating network (IPN) [1-2] hydrogels which possess superior mechanical properties but are unable to mend after plastic deformation. Ionic-covalent entanglement (ICE) network hydrogels have recently emerged and been demonstrated to be both tough and self healing materials but much about them is still unknown[3].

A thorough investigation of ICE network hydrogels comprised of Ca^{2+} cross-linked gellan gum and genipin cross-linked gelatin is presented. The effects of polymer ratio, polymer molecular weight, total polymer content, Ca^{2+} and genipin cross-linker concentrations are investigated through compressive mechanical analysis (**Fig.1**). The toughness and self-healing nature of the gels are demonstrated as is their dimensional stability when immersed in simulated body fluid.

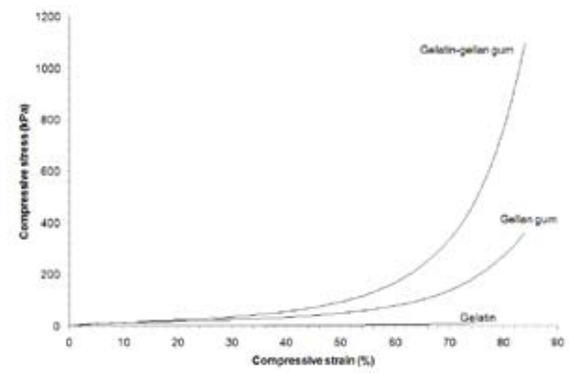

Figure 1. Compressive stress-strain curves for gelatin-gellan gum ICE network hydrogel and constituent gelatin and gellan gum individual networks reveal a significant increase in mechanical performance.

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Behaviour of pH-responsive sterically-stabilised latex particles at the air-water interface

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Particle adsorption at interfaces is a phenomenon widely studied for its practical applications in product formulation including emulsion technology, mineral processing, petroleum engineering. Control over the adsorption properties of engineered particles can be achieved through the use of steric polymer coatings on the particles.[1,2]

Here, we study the interfacial behaviour of core-shell latex particles, where the steric stabilizer changes its configuration in response to variation in pH. We investigate the adsorption properties of these particles at the air-water interface using a Langmuir trough. The behaviour of the particles at the interface is found to be strongly dependent on the water pH. Additionally, we study the particle desorption properties when the pH of the aqueous subphase is varied after compression of the particle monolayers.[3]

We first produce latex particles stabilized by diblock copolymers of poly[2-(dimethylamino)ethyl methacrylate]-b-poly[methyl methacrylate] (PMMA-*b*-PDMAEMA), where the PMMA block serves as an anchor into the particle core and the PDMAEMA block provides steric stabilization in aqueous suspensions. The hydrodynamic diameter and electrophoretic mobility of the core-shell particles are systematically characterized by light scattering. Subsequently, particle monolayers spread at the air-water interface are compressed on the Langmuir trough and corresponding isotherms are recorded for different pHs of the aqueous subphase. Upon compression, high surface pressures are reached for pHs above the stabilizing polymer pKa (~7) when the particles are strongly adsorbed to the air-water interface. This is shown in Figure 1.

We also study particle desorption characteristics by decreasing the pH of the aqueous subphase after compression of strongly adsorbed particles. Protonation of the PDMAEMA block increases the affinity of the particles for the water and their subsequent desorption is followed as a function of time.

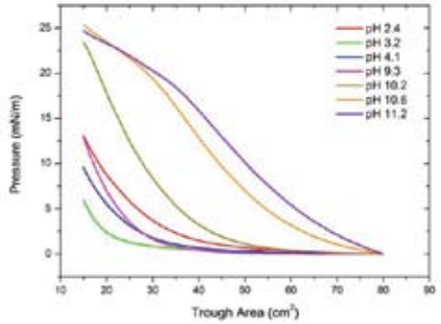

Figure 1. Air-water interface compression isotherms of latex particles with a pH responsive polymer shell.

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Void reduction mechanisms in vibration assisted consolidation of fibre reinforced polymer composites

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We have experimented with glass fibre and epoxy resin composites. Manufacturing of the laminates is achieved in two stages, (i) the impregnation of resin into the fibre mat laminates, and curing of the final component. In the first stage voids (gas bubbles) are introduced into the resin in the laminate. In the second stage the component is cured at elevated temperature. In so-called Quickstep method, void minimization can be achieved by applying mechanical vibrations and vacuum to the encapsulated component.

Analysis of the process shows that voids escape from the stationary resin by floatation only, governed by Stoke's law. Application of vibrations during the curing stage of frequency close to the resonance frequency of the curing system resulted in significant lowering of the void content (from 5% to 1%). Several phenomena contribute to this effect. Diffusion of gas, aided by the Thomson-Freundlich effect, allows growth of bubbles. The oscillations of a bubble are non-linear under the applied acoustic vibrations of the resin, also aiding growth of bubbles. Dynamic resonance effects amplify these effects, further causing bubbles to grow. Since the escape velocity of a bubble in a stationary fluid is proportional to the square of its radius, judicious choice of vibration frequency during curing results in significant improvement in the quality of the final laminate.

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Graphene Oxide as a Novel Surfactant for the Preparation of Hybrid Polymer Nanoparticles

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Since the discovery of graphene in 2004,[1] there has been intense research devoted to the creation of graphene-polymer composite materials, aimed at exploiting graphene's extraordinary mechanical, electrical and thermal properties.[2] Graphene however is incompatible with most polymers and homogeneous composites are difficult to realize. An attractive route to the creation of such composites is the use of graphene oxide (GO), prepared by the treatment of graphite with strong oxidizing agents and acids.[3] GO possesses numerous functional groups for further reaction, and can be readily dispersed in aqueous media. Additionally, GO can be reduced back to graphene post-functionalization using a variety of techniques.

It was recently reported that GO can act as a 'surfactant' to stabilize oil in water (o/w) emulsions,[4,5] which was attributed to the amphiphilic nature of GO (consisting of hydrophobic graphitic regions and hydrophilic and charged oxygen containing functional groups). These Pickering emulsions are extremely stable and are also pH dependent, raising the possibility of switchable systems. Our research focusses on utilizing these surfactant-like properties of GO to create polymer nanoparticles that are 'armoured' with GO sheets, in particular by miniemulsion polymerization. Using precursor graphite nanofibres to ensure a narrow distribution in GO sheet size, miniemulsions of styrene (with 5 % w/w hexadecane) in water have successfully been polymerized with GO as a sole surfactant, the first time that this has been reported (**Fig 1.**).[6] Highly textured particles with an average diameter of approximately 500 nm were formed, the surface morphology due to GO sheets at the particle interface. This approach can also be used to polymerize various (meth)acrylates and cross-linkers such as divinylbenzene. We are also currently investigating the use of GO in emulsion polymerization systems and the ability to create polymer-graphene composites using aqueous-phase reducing agents. We consider these methods to be convenient routes towards the creation of polymer-graphene composites for a variety of different applications.

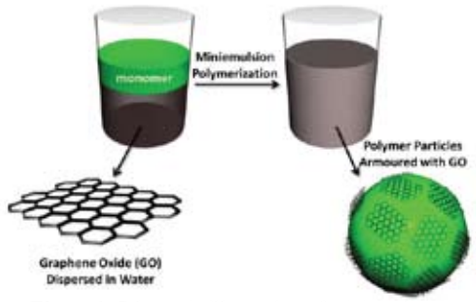

Figure 1. Schematic illustration of miniemulsion polymerization using dispersed graphene oxide (GO) sheets as a surfactant.

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Plasma polymers, nanocomposites and their applications

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This presentation introduces numerous low-temperature plasma-specific effects that enable many interesting features in the synthesis, surface structuring, and processing of nanostructured polymeric materials. This class of materials is highly-promising in many fields such as health care (e.g., biomedical implants or drug/gene delivery systems), organic optoelectronics (organic light emitting diodes), photovoltaics, and nanoelectronics. The common issues in the synthesis, processing, and device integration of such materials are high temperature sensitivity (due to low melting temperatures), structural and morphological control at micro- and nanoscales, modification of surface energy to enable a certain functionality, gas-phase control of cross-linking and macromolecular building units, conformity of ultra-thin polymer layers to nanometer-sized surface features, and several others. Importantly, unique physical and chemical effects due to low-temperature plasmas in many cases help resolving these issues. The two most common examples include plasma polymers for surface coatings with nanometer dimensions as well as precise control of surface energy by nanoscale surface texturing and/or functionalization. Owing to the very high reactivity of the plasma, these effects can be achieved even at room temperature. Examples of low-temperature plasma-assisted nano-structuring of polymer surfaces and conformal deposition of ultra-thin plasma polymers on nanometer-sized features are presented. The plasma polymerization is unique because of the large variety of reactive species produced through the plasma-assisted fragmentation and remodelling of monomer precursors. As a result, a cocktail of original precursors, reactive radicals, non-radical neutrals, macromolecules, ions, electrons and photons is generated. The large species produced have different structures (e.g., linear or aromatic) and charging states (cations, anions, or neutral). For many years it was commonly assumed that merely neutral radical and molecular species play a role in the plasma polymerization. However, recent advances have revealed a crucial role of the plasma ions which was commonly overlooked. Specifically, this role is evidenced by the recent demonstration of very large ions whose masses are several times larger than the masses of original precursors. Moreover, the plasma ions can supply a large fraction of the mass of the deposited polymeric films. This is supported by calculations and direct measurements showing that the ion fluxes during the synthesis of plasma polymers can be comparable to or even larger than the fluxes of neutrals. The numerical modelling results also confirm that ion-neutral reactions trigger plasma polymerization and lead to the production of macromolecules and nanoclusters of various structures including chains and aromatic rings. Low-temperature reactive plasmas are also very effective for the precise control of the surface energy through the nanoscale polymer surface texturing and/or functionalization. The surface texturing can be implemented in two ways, namely by using the bottom-up and top-down approaches. The top-down approach is implemented by using the plasma etching (e.g., in oxygen plasmas) and nanopattern transfer by using pre-fabricated or self-organized masks to produce a variety of ordered nanopatterns and arrays. Nanoscale etching in oxygen plasmas was also effective in thickening and branching of single-crystalline organic (e.g., metalloporphyrin, metallophtalocyanine, and perylene) nanowires. Recently, it also became possible to produce self-organized polymer nanopatterns without using any etching masks. Surface functionalization of soft organic matter also benefits from plasma effects. A combination of the effective production of the relevant functional groups (e.g., OH-, COOH-, NHx, CFx, etc.) and activation of the dangling bonds on the surface makes the plasma-assisted polymer surface functionalization particularly versatile. Since these surfaces are usually tailored to enable specific functionalities the plasma surface processing should have deterministic features. Recent application of cold atmospheric-pressure plasmas to modify silica nanoparticles to enhance their compatibility with polymer matrices is also discussed. Compared to the pure polymer and the polymer nanocomposites with untreated SiO_2, the plasma-treated SiO_2-polymer nanocomposites show higher dielectric breakdown strength and extended endurance under a constant electrical stress. These improvements are attributed to the stronger interactions between the SiO_2 nanoparticles and the surrounding polymer matrix after the plasma treatment. This plasma-enabled method is generic and can be used in the production of high-performance organic−inorganic functional nanocomposites. These examples discussed in this presentation are based on the recent results in our research group and numerous results of other researchers.

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Hollow Polymer Particles by Nano-Templating

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Hollow polymer particles have raised a lot of interest due to their potential applications in biomedicine.[1] They are nano-sized particles consisting of a polymer shell encapsulating an empty void which can be utilised to accommodate drugs for sustained release.[1] Currently, they can be synthesized by a number of techniques such as layer by layer deposition, self assembly, emulsion or using sacrificial templates.[1-3] However, these methods suffer from their complexity or lack of control which may limit their commercial applications.[1-3]

In recent work on polymer encapsulation using macro-RAFT copolymers as stabilizers,[4] we demonstrated the ability to synthesize nanostructures of titanium dioxide nanorattles which were found to significantly improve the pigment opacity. These structures are essentially hollow polymer particles containing an individual pigment particle in the air void. The synthesis method involves multiple polymer coating of different hydrophobicity onto the pigment surface. This is to be followed by subsequent swelling of the inner hydrophilic polymer layer at high pH and temperature to expand the hydrophobic hard polymer shell. The method has been found to be simple, scalable where the air void size can be readily controlled by adjusting the thickness of the inner hydrophilic polymer layer.

In this work, we explored the possibility of applying the method on a number of templates to synthesize rattle-typed hollow particles. Materials such as carboxylic functionalized MWCNTs offer a great opportunity to form novel hollow tubes (Figure 1a) with extremely high specific surface area. On the other hand, paramagnetic iron oxide nanorattles (Figure 1b) have magnetic properties which can be useful in certain biomedical applications.

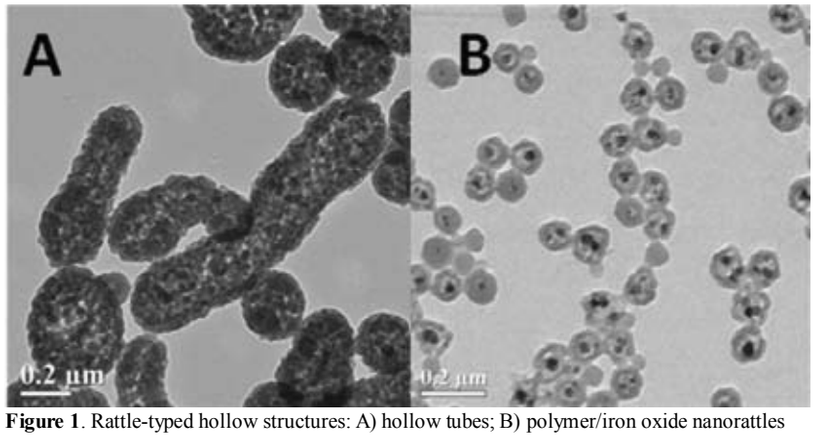

Figure 1. Rattle-typed hollow structures: A) hollow tubes; B) polymer/iron oxide nanorattles

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One-Dimensional Hybrid Silica Nanowires and Nanotubes

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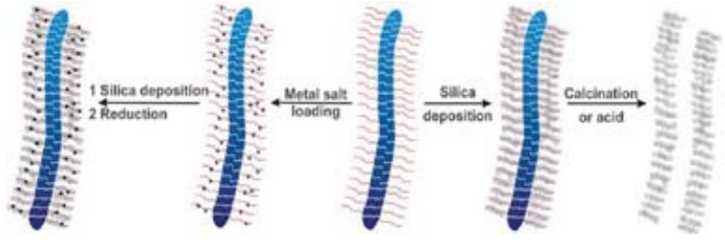
One-dimensional (1D) nanomaterials, such as nanowires and nanotubes, have attracted immense interest, as these anisotropic nanostructures are expected to play an important role as building blocks, interconnects and functional units in the fabrication of electronic, optoelectronic, electrochemical and electromechanical nanoscale devices. The interest and demand for 1D hybrid nanomaterials increased dramatically after their production became much more feasible through various templating techniques.[1-3] Template-directed or template-assisted production of 1D hybrid nanomaterials became even more facile when polymeric soft templates were used. The large scale production of well-defined polymers and polymeric templates in all kinds of compositions became rather simple due to the many improvements in controlled/living polymerisation techniques.

Herein, we use core–shell CPBs, consisting of poly(ε-caprolactone) (PCL) as a core and poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) as a polycationic shell, as a molecular soft template for the fabrication of silica nanowires and nanotubes (**Scheme 1**).[4] The applied polymerization techniques permitted excellent control over the synthesis of the template brushes and allowed precise adjustment of the aspect ratio and morphology of the 1D silica nanostructures. Ring-opening polymerization (ROP) of ε-caprolactone (CL) increased the grafting efficiency and allowed the removal of the core-forming block. The production of silica nanomaterials with different lengths and different core and shell diameters was achieved by loading the amine-containing shell with a silica precursor, namely tetramethyl orthosilicate (TMOS), and the subsequent hydrolysis and condensation. TMOS has already been used for the synthesis of various silica nanostructures.[5,6] Acid treatment or calcination of the PCL-filled nanowires led to hollow silica nanotubes. Calcined nanotubes were microporous and exhibited high pore volumes and high specific surface areas. Furthermore, we loaded the polyelectrolyte shell with metal ions (e.g., $PtCl_4^{2-}$ or $AuCl_4^-$) and embedded the corresponding Pt or Au nanoparticles into the silica shell, giving catalytically active silica nanomaterials.

Scheme 1. Cylindrical polymer brush templates were used to produce silica hybrid nanowires and nanotubes.



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2 M. Müllner, et al., *Macromolecules* **2012**, *45*, 6981
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New surface treatments for carbon fibres to enhance fibre matrix adhesion in composites.

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The use of carbon fibre composites in aerospace and automotive applications has risen exponentially as a result of the high specific strength and stiffness of these materials. Concurrently, there has been an increasing demand for the development of new carbon fibre surface treatments to improve fibre wetting and optimise the micromechanics of composites. Carbon fibre can only be sourced commercially, and comes as-received covered in a polymer coating of unknown composition (due to commercial secrecy), referred to as a sizing agent. This sizing is an essential protective agent for enabling the handling of the fibres in the composite fabrication process. However, it is often not optimised for the formation of a strong interfacial bond between the fibre and the polymer matrix in the finished composite as most commercial sizing is specific to epoxy based resins. As a result, most of the literature in this field relies on attempts to remove the sizing from the commercial fibre prior to the application of new treatments. Both thermal and chemical de-sizing of fibres results in the degradation of the properties of the fibre and does not accurately reflect commercial surface treatments.

An Australian facility with the capacity to produce aerospace quality carbon fibre, Carbon Nexus (www.carbon.nexus.com.au), has enabled a new approach to this problem. Access to untreated and electrolytically oxidised fibre prior to sizing has supported the development and evaluation of new fibre surface treatments. Fibres have been functionalised using both organic chemistry and plasma polymer methodologies. Functionalised fibres were characterised by Atomic Force Microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Surface Energy Analysis (SEA). The role of the fibre matrix interface in inferring composite properties has been interrogated by measuring the fibre matrix adhesion by micromechanical methods as well as by measuring the interfacial shear strength of laminates. Figure 1 compares the interlaminar shear strength (ILSS) of laminates from fibres taken from three different stages of the manufacturing process highlighting an increase in ILSS with an increasing degree of surface treatment. This paper will describe the vision for research at Carbon Nexus as well as describing the progress of research aimed to develop new commercial fibre surface treatments.

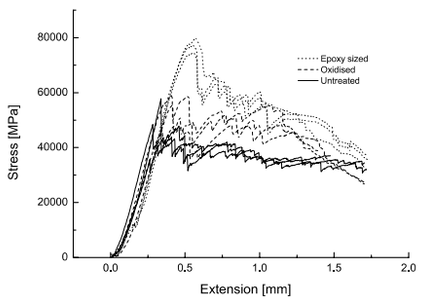

Figure 1. Interlaminar Shear Strength (ILSS) of composites made from fibers with different surface treatments; epoxy sized fibers, electrolytically oxidized fibers and unoxidized fibers. The epoxy sized fibers resulted in laminates with the highest ILSS.

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Preparation and characterisation of poly(2-hydroxyethyl methacrylate)-zeolite composite hydrogels.

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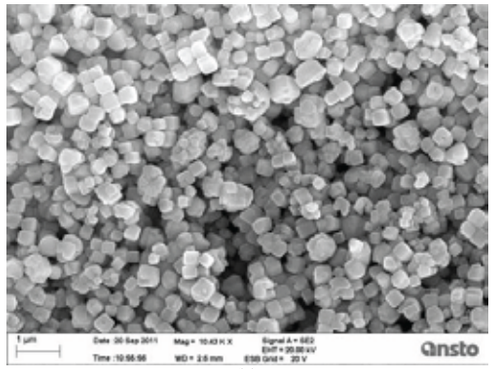
In this work, the preparation and characterisation of composites of poly(2-hydroxyethyl methacrylate) (pHEMA) and LTA type zeolites was explored, with the aim of preparing materials applicable to separations science for the adsorption of metallic species. Previously, hybrids of pHEMA and titania were prepared via an in situ sol-gel and polymerisation reaction[1]. Initiation of the polymerisation process using gamma-radiation was found to be a suitable method that resulted in monoliths with high monomer to polymer conversion; which is typically challenging when using traditional chemical initiators. The preparation of composite hydrogels and the characterisation of these materials are presented; the preparation of the zeolite component is also briefly discussed.

The composite materials were prepared by mixing the required amount of zeolite (**Fig.** 1a), water, and monomer to polyethylene vials, which were irradiated using the GATRI ^{60}Co source at ANSTO using a dose-rate of 4.1kGy/h and a total dose of 10kGy. This resulted in solid monoliths forming (**Fig.** 1b). The zeolite content for the composites was determined on vacuum dried samples using thermogravimatric analysis, which showed loadings of up to 40wt.% could be routinely achieved. A general trend on increasing glass transition temperature was observed with increasing zeolite content. The chemical structure of the composite was probed using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and solid state nuclear magnetic resonance spectroscopy (SSNMR). Modest shifts in the carbonyl peaks for the FTIR and the SSNMR (0.5ppm) were observed showing that there is a weak coordination between the polymer and the zeolite. The equilibrium swelling based on dry weight increased with zeolite addition from ~60% for the unfilled polymer up to ~200% for a composite containing 10wt.% zeolites and even higher (~300%) for a material containing 40wt.% zeolites..



(a)

unfilled 30wt.% zeolite 50wt.% zeolite
(b)

Figure 1 (a) SEM of LTA-type zeolites used in composite preparation; (b) optical images of the composites.

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Hybrid Conducting Polymer-Carbon Nanotube Yarns

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Keywords: Carbon nanotube, Conducting polymer, Polypyrrole

Hybrid polypyrrole (PPy)–multi walled carbon nanotube (MWNT) yarns were obtained by chemical and electrochemical polymerization of pyrrole on the yarn surface (Fig. 1). The material was characterized by SEM imaging, electrochemical, mechanical and electrical measurements. It was found that the hybrid PPy-MWNT yarns possess significantly higher mechanical strength (over 740 MPa) and Young's modulus (over 54 GPa) and than the pristine MWNT yarn. The material also exhibited substantially higher electrical conductivity (over 23500 S/m). Specific capacitance for PPy-MWNT yarn was found over 60 F/g. Measurements of temperature dependences of electrical conductivity revealed metallic behaviour at high temperature and semiconducting behaviour at low temperature with the metal-to- insulator transition near 100 K. The collected low temperature data are in the good agreement with variable range hopping model (3D-VRH). The improved durability of the yarns is important for electrical applications. The composite yarns can be produced in commercial quantities and used for the applications where the electrical conductivity is of primary importance.

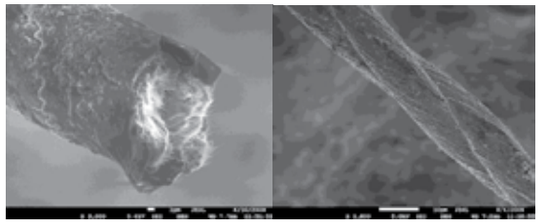

Fig.1: SEM micrographs of electrochemically prepared CNT-PPy yarn (L) and surface morphology two-ply CNT-PPy yarn(R)

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Supramolecular EcoBioNanocomposites Incorporating Stereocomplexation

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Green materials can be produced through ecologically responsible conversion of renewable resources using industrial biotechnology and enhanced by nanotechnology. This approach represents a *triple technological convergence* that results in an emerging class of bioplastics that can be referred to as ecobionanocomposites.[1] It is essential that non‐food resources such as those depicted in Figure 1 be identified and developed. Utilizing crops with low inputs of water and fertilizer that can be grown on marginal lands reduces deforestation and pressures on food supplies.[2] Similarly, the recent rapid developments in Industrial Biotechnology are making the conversion of biomass into useful chemicals and fuels increasingly feasible.[3, 4] This approach expands the use of renewable feedstocks thereby reducing petroleum dependence and improving industrial sustainability.

The present work describes the development of a better understanding of a novel "buried" interface in a new class of nanocomposites. As shown in Figure 1, these novel materials consist of biobased polylactides (PLA) grafted to cellulosic nanowhiskers (CNW) embedded in a stereocomplexing matrix. The approach has also been utilized to graft inorganic particles including fumed silica. The dramatic property changes associated with this new paradigm in polymeric nanocomposites are reported.

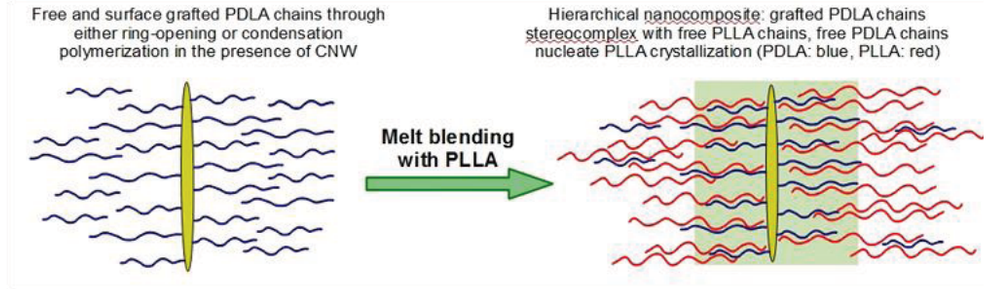

Figure 1. Ecobionanocomposite incorporating stereocomplexation; this represents a new paradigm in the supramolecular ordering of polymers.

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Hybrid gelation processes in enzymatically gelled gelatin: impact on nanostructure, macroscopic properties and cellular response

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Hydrogels obtained from the chemical or physical association of macromolecules are an important subject of materials science as they offer an ample array of design possibilities and have found in particular numerous applications in biomedicine; they serve for instance as skin substitutes, adhesives, or drug delivery matrices. Through the careful selection of macromolecules, the associations that maintain the hydrogels 3D network can be selected and tuned. We report on hydrogels made from fish gelatin in the presence and absence of the enzymatic cross-linker microbial transglutaminase (mTGase)[1,2].
Different types of networks were fabricated: *physical gels*, thermally-triggered and reversible, resulting from the single-strand to triple-helices transition of gelatin; *chemical gels*, where gelatin strands are cross-linked by mTGase, and *hybrid gels*, obtained from the combination of both processes, either contemporaneous or sequential.
An array of techniques - rheology, small-angle neutron scattering, optical rotation and molecular dynamics - was employed to connect the bulk properties with the nanoscale morphology of the gels, both as a function of gelation time and at equilibrium. The study provides new insight into the synergism between mixed gelation processes in hybrid gels. For instance, we find that triple-helices are able to guide covalent cross-linking, thus resulting in more homogeneous networks, which reflects in stronger mechanical properties and, subsequently, a higher metabolic activity in cell culture studies.
The systems reported here, based on a sustainable material and an enzymatic cross-linking process, are attractive for biomedical applications, in particular tissue engineering. The type of multi-disciplinary approach proposed here, where the architecture of the gels on the nanoscale, their mechanical behaviour on the macroscale and their biological performance for cell regeneration are examined and correlated, is paramount to achieve a comprehensive understanding of networks properties and rationalise the design of hydrogels with controlled functional properties.

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Photodegradable microsphere templates for creating model alveoli in PEG hydrogels

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A major challenge in tissue engineering is recreating native tissue architecture, such as tubules and cysts, in *in vitro* cultures. With lung epithelial cells, researchers have relied on spontaneous structure formation of varying sizes within natural gels, a process which has not been replicated in synthetic scaffolds. However, a molecular-level understanding of synthetic materials enables design of macroscale properties. Therefore, bioinert and tailorable synthetic hydrogels are desirable for *in vitro* models given that user control of biochemical and mechanical signals can facilitate discovery of important cues for tissue morphogenesis and pathology. Towards this end, we have developed a procedure for the formation of cystic structures within biofunctionalized poly(ethylene glycol) (PEG) hydrogels using photodegradable microspheres[1] as templates for the spherical cysts (**Fig. 1**).
Specifically, PEG-based microspheres were polymerized containing a photo-cleavable moiety[2] as part of the network crosslink and entrapping extracellular matrix proteins (e.g. laminin) to render the microspheres adhesive to cells. Next, alveolar epithelial cells were incubated with the microspheres for enough time to facilitate cell attachment and proliferation to coat the microsphere surface. Then, these "pre-cysts" were encapsulated within a second PEG-based hydrogel[3] containing pendant integrin binding peptide sequences and enzymatically cleavable crosslinks to allow for cell attachment and remodeling of the surrounding scaffold. Finally, cytocompatible light was used to cleave the microsphere network crosslinks and completely erode the template, leaving a hollow shell of epithelial cells anchored to the encapsulating hydrogel.
Microsphere degradation was determined by tracking micron-scale particles embedded within the microsphere that exhibit Brownian motion once reverse gelation is achieved. Degradation product fate was visualized by fluorescent tagging one of the monomers. Basic biologic function was confirmed through immunostaining for epithelial junctional proteins and secreted mucin proteins. This photodegradable template technique is an effective method for creating stable model alveoli within synthetic, tuneable hydrogel scaffolds. This platform offers new opportunities to study lung development and disease, and could easily be expanded to allow co-culture with other cell types in the surrounding gel.

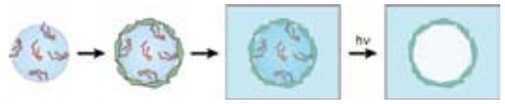

Figure 1. Schematic of cyst-forming procedure. ECM proteins (red) were entrapped within microspheres (blue sphere), which were seeded with cells (green), entrapped within a second hydrogel (blue rectangle), and degraded with light.

Acknowledgements: HHMI, NSF (DMR 1006711), and the Teets Family Endowed Fellowship (MWT).
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Nano-bottlebrush Electrospun Scaffolds: Decoupling Cellular Cues in 3D

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Cells in the body reside in a complex three-dimensional environment. Here they respond to many types of environmental signal, including biological signals (such as extracellular matrix proteins and growth factors) and physical features such as dimensionality, topography and mechanical properties. Cells often respond in unpredictable ways to environments that contain multiple variable stimuli, due to interactions between intracellular signalling cascades. Investigation of these non-linear responses requires a culture platform where stimuli are closely controlled and can be varied independently of each other.

We have developed a platform that utilises electrospun fibres, whose fibrous morphology can mimic that of the native extracellular matrix (ECM) and is of interest in cell transplantation as a supportive scaffold. These fibres are produced from poly(styrene-co-chloromethyl styrene), where the CMS monomer subunits allow for the subsequent grafting of polymer brushes onto the fibres via atom transfer radical polymerisation (ATRP) without requiring further chemical activation. This creates a bottlebrush-like core-shell structure.

Surface-initiated ATRP grafting of PEG-based monomers can provide a low protein-fouling background, preventing interactions between cells and proteins that often non-specifically adsorb to surfaces during culture[1]. Co-grafting of other monomers can provide reactive groups such as alkynes that, when combined with azide-modified peptides, allow for oriented, highly specific and chemically orthogonal covalent attachment of these peptides via click chemistry (**Fig. 1**). This system is designed to ensure, as much as possible, consistent and optimal bioactivity of the attached peptide while preventing other unwanted interactions.

At the same time, the physical properties of the material can be altered independently of changes in peptide attachment, by changing electrospinning conditions. In this way, biological and physical cues can be independently modulated. Here we will discuss the fabrication and biofunctionalisation of the fibre scaffold and the advantages of this structure in investigating cell-substrate interactions.

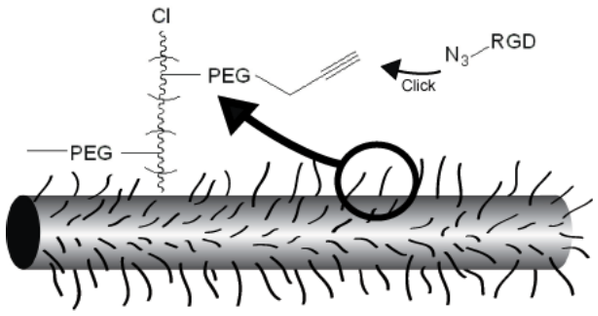

Figure 1. Simplified structure of nano-bottlebrush electrospun fibre (not to scale), with clickable brush layer for peptide conjugation

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Synthesis, characterization and properties of biocompatible poly(glycerol sebacate) pre-polymer and gel

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Poly(glycerol sebacate) (PGS) is an elastomer with potential biomedical applications but it suffers from problems with irreproducible synthesis and the unacceptable toxicity of very soft PGS elastomers[1,2]. To establish the reason for these problems, PGS has been synthesized at 150 ºC/8 hours or 130 ºC/24h, but crosslinked at 130 ºC under vacuum for 24, 48, 72, 96, 144 or 168 hours, and the reaction monitored by titration of the unreacted carboxylic groups and measurement of the mass loss during synthesis. It was found that evaporation of glycerol was a major cause of irreproducibility of the elastomer synthesis and this was more significant at higher reaction temperatures. The polymer microstructure was analyzed by NMR and all twelve acylglyceride ^{13}C-signals as well as two small extra peaks of the residual glycerol were observed in the prepolymer and for the PGS gel (**Fig.1a,b**), the glyceride moieties were characterized by NMR for the first time, providing information on the crosslinked nature of the polymers. The modulus and ultimate tensile strength of the gel increased with longer cure times (**Fig.1c**) and at higher cure temperatures while the elongation to break decreased and this was interpreted in terms of network theory. The cell viability of mouse fibroblasts was better for PGS samples with a higher conversion[3].

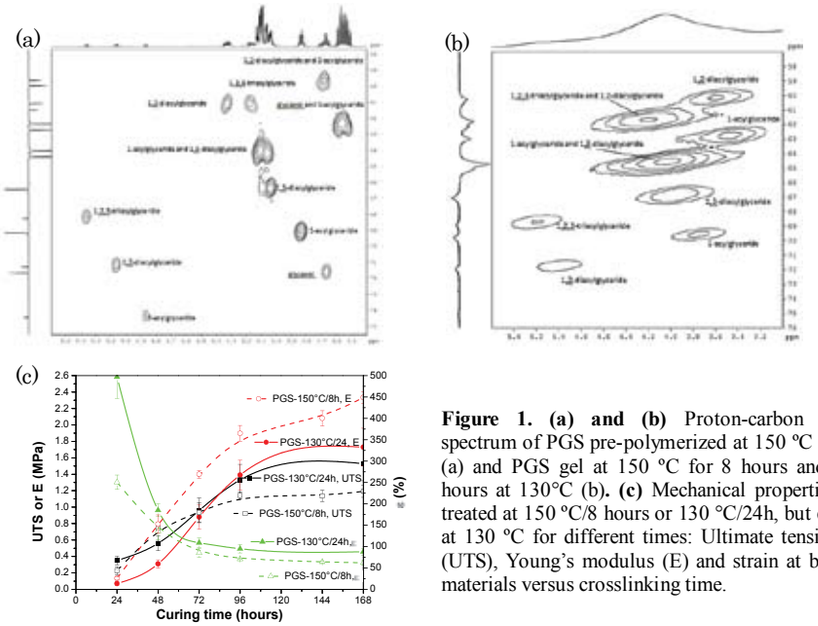

Figure 1. (a) and (b) Proton-carbon correlation spectrum of PGS pre-polymerized at 150 ºC for 8 hours (a) and PGS gel at 150 ºC for 8 hours and cured 48 hours at 130°C (b)**. (c)** Mechanical properties of PGS treated at 150 ºC/8 hours or 130 ºC/24h, but crosslinked at 130 ºC for different times: Ultimate tensile strength (UTS), Young's modulus (E) and strain at break (ε) of materials versus crosslinking time.

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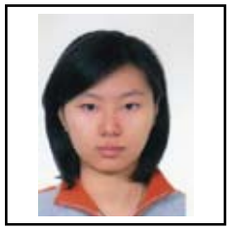

Presentation of bioactive signals to cells via self-assembling peptides

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Biochemical and physical cues that mimic the extracellular matrix (ECM) environment are integral in the design of novel biomaterials for promoting cell survival, proliferation and directing cell fate[1]. Fmoc self-assembling peptides (SAPs) exploit simple concepts to form more complex structures similar to that seen in biology[1]. SAPs self-assemble via non-covalent interactions between Fmoc-aromatic groups (π-stacking) resulting in a nanofibrous hydrogel network **(Fig1)**. These fibres are further stabilised by the peptide sequences themselves that go on to form secondary protein structures such as β-sheets and α-helices through hydrogen bonding[2]. The self-assembly process is based on step-by-step reduction of pH that modulates the charge on the peptide resulting in a shift in pK_a[2]. At an optimal pH (7.4 for physiological conditions), the charge on the SAP will be such that it will self-assemble through these π-β interactions into its most thermodynamically stable conformation, nanofibres with peptides presented on the external surface.

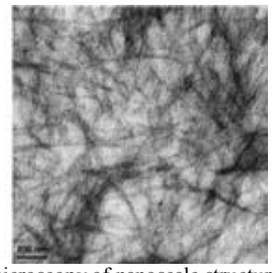

Figure 1. Transmission electron microscopy of nanoscale structures that underpin the formation of the peptide hydrogels. The sample was negative stained and imaged using a Hitachi HA7100 TEM at 75kV.

We have developed three different injectable hydrogels, based on Fmoc self-assembly, with the capacity to present different bioactive signals based on known peptide sequences in laminin and fibronectin, key proteins of the ECM. These peptide sequences bind to specific integrins on the cell surface to promote adhesion, migration and differentiation[3]. As a result, our SAP hydrogels have the capacity to present physical cues to cells in a 3D culture, in terms of the nanofibrous structure similar to that seen in the ECM, as well as a variety of bioactive cues to potentially direct cell fate[1]. With three different signals, control on the signal composition of the hydrogel is possible, allowing us to mimic more closely the extracellular environment *in vitro*.

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Preparation of Superabsorbent Cross-linked Chitosan Hydrogels by Various Type of Aldehyde Crosslinkers and Their Swelling Behaviour

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Superabsorbent cross-linked chitosan hydrogels were synthesized by varying reaction time, crosslinking agent (formaldehyde, acetaldehyde, and glutaraldehyde), and volume of crosslinker. The percentage of swelling and degree of crosslinking were measured to get information about the absorption capability. Moreover, it was also observed the percentage of swelling and the degree of crosslinking in various pH (4, 7, 10) and temperature (35, 45, 55°C). As results, the crosslinker of acetaldehyde gave the highest percentage of swelling, but the lowest degree of crosslinking of around 345% and 25% respectively. On the other hand, glutaraldehyde showed the lowest percentage of swelling with 28% and the highest degree of crosslinking with around 91%. It was also observed that the more volume of crosslinker was, the lower percentage of swelling was, but the higher degree of crosslinking can be obtained. In the variation of pH, the percentage of swelling decreased with increasing pH. In addition, just like the previous observation, acetaldehyde got the highest percentage of swelling of 303% at pH 4, while glutaraldehyde only had 36% at the same pH. When temperature was varied, the inverse trend was also observed. The higher temperature applied, the higher percentage of swelling could be obtained. Acetaldehyde still had the highest percentage of swelling with 384% at 55°C, while glutaraldehyde had only 25% at 55°C. Fourier Transform Infrared Spectroscopy (FTIR) confirmed the formation of chitosan hydrogels.

Keywords: Superabsorbent hydrogels; Cross-linked Chitosan; Swelling properties; Aldehyde crosslinker.

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Surface Patterning for Biointerface Applications based on Colloidal Crystals

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Nano- and micrometer site-specific chemical surface patterning has become important to the field of biology and medicine.[1] Precise spatial control of chemistry on surfaces provides an essential platform for the directed attachment of bioactive molecules,[2] relevant for numerous applications such as biosensors, tissue engineering and fundamental studies of molecular and cell and micro-biology. New patterning methods based on colloidal crystals will be presented, in which colloids of one size or binary colloids are generated on surfaces over large areas. The crystal layers are used as masks against deposition of plasma polymers[3] and/or metals such as gold[4] to create complex patterns of dimensions ranging from μms to sub 100nms and are useful for post-modification with different chemistries for site-specific immobilisation of biomolecules. This includes using chemistries for preventing non-specific adsorption of proteins and attachment of cells, including new ways of generating high graft density polymer brushes. The presentation will also demonstrate the importance of using surface sensitive analytical tools to prove the presence of the different surface chemistries. These include x-ray photoelectron spectroscopy (XPS), and high resolution time-of-flight secondary mass spectrometry (ToF-SIMS) imaging.[5,6] Finally, the presentation will discuss broader aspects of chemical patterning in biomaterials.

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Emulsion-templated Scaffolds for Tissue Engineering and 3D Cell Culture

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There are numerous routes described in the literature for the production of highly porous and permeable polymer materials for use as, for example, catalyst supports, tissue engineering scaffolds and separation media. However, many of these methods result in poorly defined materials with void sizes that are difficult to control and limited connectivity. One method that has the ability to create well-defined porous polymers (foams) is the so-called emulsion templating process, whereby a high internal phase emulsion (HIPE) is used as a precursor to a porous material (**Fig.1**)[1]. The presentation will describe the preparation of HIPEs and the resulting porous polymers (polyHIPEs) together with methods by which the morphology, properties and surface chemistry can be varied. In particular, the use of photopolymerization methods as a means to prepare porous materials from relatively unstable HIPEs will be presented[2]. Subsequently, the application of these materials as matrices for tissue engineering and in vitro cell culture will be discussed.

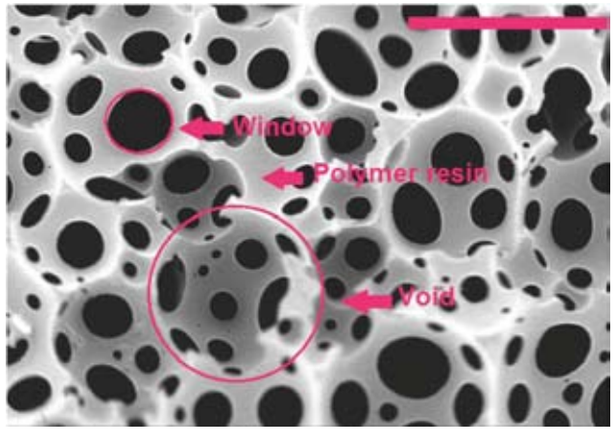

Figure 1. SEM of typical polyHIPE material illustrating the key structural features.

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Photodegradable gelatin methacrylate hydrogels for improved cardiomyocyte alignment

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Hydrogel biomaterials are often employed as temporary platforms for cell proliferation and organisation. The ability to exert control and manipulation of the hydrogel's properties during this fledging period remains an important but elusive development to provide the necessary temporal cues to developing cells. Hydrogels incorporating photodegradable moieties have been reported[1] as a means of engineering spatiotemporal control over material properties with synthetic polymers. Here we have developed a version of photodegradable hydrogels made of gelatin methacrylate (GelMA) with custom synthesised photodegradable crosslinkers. The hydrogels degrade rapidly and specifically in response to UV light and can be photopatterned to a variety of shapes and dimensions.

Hydrogels were photopatterned using UV light to create 20 μm sized channels and mounted on glass substrates. Neonatal cardiomyocyte were isolated from 2 day old Sprague-Dawley rats and cultured on patterned and unpatterned hydrogels (**Fig. 1**). Cells seeded on photopatterned substrates showed an improvement in uniformity and cell alignment as well as improvements in achieving regular, synchronous beating compared to unpatterned controls. Overall this work introduces a class of photodegradable natural-based polymeric hydrogels with tuneable acute and long term degradability as cell culture substrates for encouraging cellular organisation and regeneration.

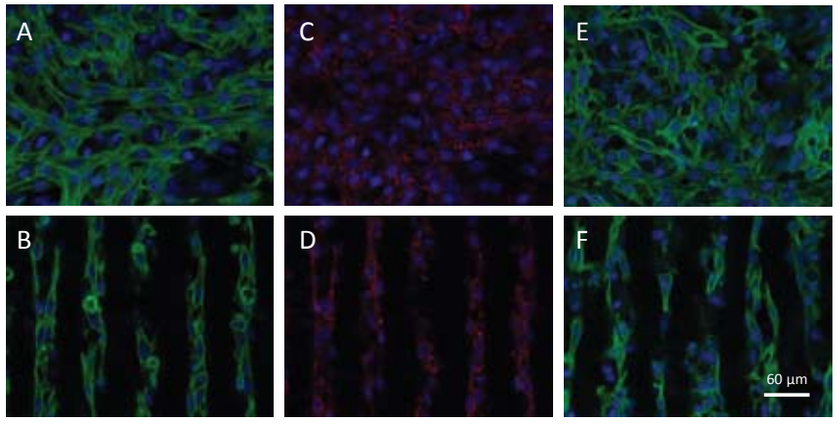

Figure 1. Confocal images of immunostained day 7 neonatal rat cardiomyocytes with DAPI nuclei counterstain (blue) on unpatterned (A,C,E) and patterned (B,D,F) photodegradable hydrogels. Immunostaining with sarcomeric alpha actinin (green, A & B) showed the presence of organised contractile sarcomeres. Connexin 43 (red, C&D) shows local gap junction density. Calcium sensitivity and contractility is confirmed by the presence of Troponin I (green, E & F). Hydrogel patterning can be observed to show improved organisation and alignment of cells and contractile units.

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An Injectable Hydrogel System Incorporating Free or Covalently-Bound Sulphated Polysaccharide for Intervertebral Disc Regeneration

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Hydrogels show significant promise for regenerative medicine as they are highly hydrated and have good permeability to both oxygen and nutrients, making them an ideal material both for cell delivery and to promote tissue regeneration. In addition, hydrogels may be loaded with bioactive molecules (drugs and growth factors) to promote cell viability and differentiation. We have previously developed an injectable hydrogel system for encapsulation and delivery of mesenchymal progenitor cells (MPCs) to the intervertebral disc (IVD). Particularly, when loaded with a sulphated polysaccharide (SP), these MPC/hydrogel composites showed good cell viability and induction of a chondrogenic phenotype, appropriate for regeneration of the IVD. In this study we aimed to increase the availability of the SP and optimise these outcomes by covalently binding the SP to the hydrogel matrix.

In soluble form, SP is known to increase the viability and chondrogenic differentiation of MPCs (even in the absence of inductive factors) and so we first investigated the activity of the bound-SP, comparing it to free-SP when added to culture media. Cell proliferation, as determined by CCK8 and EdU assay, was decreased by both bound and free SP whilst chondrogenic differentiation, as determined by DMMB assay and histology, was also enhanced. In all cases the effect of the bound-SP was more potent than that of the unbound form. Interestingly, although free-SP does not promote osteogenesis, differentiation was significantly increased by the bound-SP in the presence of osteogenic factors. This suggests applications of this new molecule in enhancing both osteogenic and chondrogenic outcomes when combined with the appropriate differentiation cues.

We then investigated the use of the bound-SP as a component of our hydrogel system. Rheological testing confirmed that incorporation of bound and free SP did not significantly affect gelation kinetics or final hydrogel modulus. Addition of both bound and free SP had a small but significant effect on swelling but did not influence the degradation properties. When encapsulated in the hydrogels, MPCs retained good viability and a rounded morphology. Histological analysis of both GAG and collagen deposition showed increased matrix formation in the presence of SP, which was enhanced by tethering the SP to the matrix. Overall these hydrogels incorporating covalently bound-SP show significant potential for IVD regeneration. Furthermore, bound-SP may be used as a factor to enhance osteo- and chondrogenic differentiation outcomes in a wider range of tissue engineering applications.

Characterisation of polyelectrolyte complexes and their distribution in an alginate matrix

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Polyelectrolyte complexes (PECs) have been receiving an increasing interest in biomaterials science over the past years; mainly in the area of drug delivery.[1] In this study, PECs are being investigated for their potential to increase mechanical strength of a hydrogel scaffold. One requirement is optimal distribution of the PECs throughout the hydrogel matrix; another the interfacial interactions between the PEC and the matrix.

PECs formed from alginate or alginate dialdehyde (5, 10, 20 and 40 %; ADA) with chitosan (Chi) have been synthesised. The effect of pH (3.8, 4.2 and 5.5) on PEC formation has been investigated with the resulting PECs characterised by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS) and elemental microanalysis. Results from XPS indicated the presence of amine and protonated amine species in the PECs (**Fig.1**). The PECs were dispersed in an alginate matrix at equivalent pH and dried to a film. The films were then cross-linked by immersion in a calcium chloride solution and the morphological structure of the cross-section of the resulting gels characterised by scanning electron microscopy (SEM). Various techniques (including cryo-SEM, **Fig.2**) are being investigated to more accurately elucidate the pore architecture and PEC distribution in the scaffolds. Specifically, due to the potential of formation of pore structure artefacts in freezing preparations used for cryo-SEM imaging,[2] a variety of preparation techniques are being investigated.

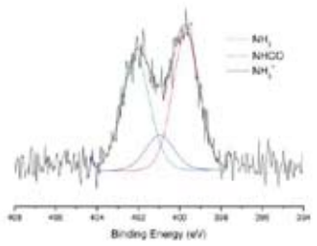

Figure 1. XPS of N1s narrow scan of PEC sample 40ADA_Chi_4.2

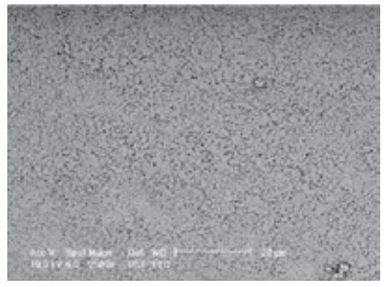

Figure 2. Cryo-SEM of cross-linked gel incorporating PEC sample 40ADA_Chi_4.2

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Osteoblast Cytotoxicity Study of Plant-Derived Bio-Adhesive Polymer

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Abstract

Usually we hardly aware that we send useful life benefited from adhesives. But using adhesives is not limited to our daily needs, it is active in many fields, architecture, automobile industry, medical, electronics, and so on. Suffice to say, we can't make a useful life without adhesives. Type of adhesives is a wide variety according to the use. We must choose an adhesive that is suitable for target material.

On the other hand, there is some organism that is inhabited by adhering to the rocks in the water. Mussel is one of them. Protein that secreted when mussel adheres to rocks contains unusual amino acid 3,4-dihydroxyphenyl-L-alanine (DOPA). DOPA contains the cathechol group. The catechol group can play a role to adhere strongly and reversibly onto both organic and inorganic surfaces in water.

We succeeded to synthesize Mussel-mimicking polyester which is copolymer of 3,4-hydrocinnamic acid (DHHCA,**Fig.1**) and 3-(3-Hydroxyphenyl) propionic acid(3HPPA, **Fig.2**). This copolymer is synthesized from natural products and has a catechol group at the end. For that reason, this copolymer has the capacity for adhesion and may also be expected to adhesive in water. This adhered strongly to bovine teeth (**Fig.3**). So, we are aiming for the application of the adhesive to the teeth or bones using their properties.

At present, we confirmed that this copolymer has no cytotoxicity for pulp cell using MTT assay (**Fig.4**) and has no effluent in water. However we still do not know Cytotoxicity of this copolymer for Osteoblast. So we investigated about Cytotoxicity of this copolymer for Osteoblast.

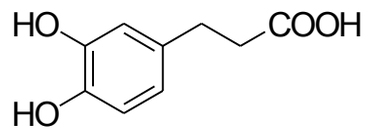

Figure1. The structure of DHHCA

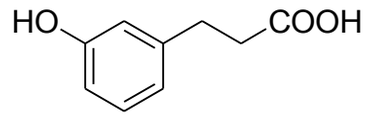

Figure2. The structure of 3HPPA

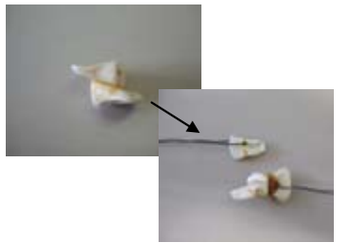

Figure3. Adhesion of bovine teeth

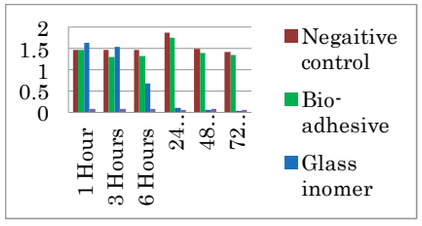

Figure4. MTT assay using pulp cell

Acknowledgement
This research was financially supported by a New Energy and Industrial Technology Development Organization (NEDO, Project ID: 11B16002d) and Grants-in-Aid for Scientific Research (Wakate B).

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Synthesis and characterization of biodegradable graft copolymer PCL-g-Amylose

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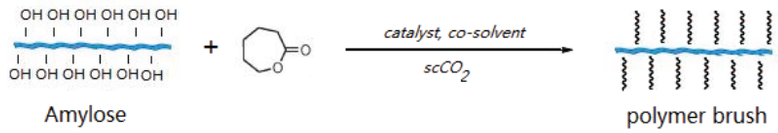
In recent years, biopolymers such as polylactide (PLA), polyglycolide(PGA) and polycaprolactone (PCL), starch, etc., have been used extensively in the medical field, specifically controlled drug delivery and tissue engineering[1]. However, new materials with improved properties that are synthesized using environmentally-friendly methods are still in great demand[2,3]. The combination of PCL and starch polymers to form completely biodegradable amphiphibic PCL-g-amylose in $scCO_2$ may offer an opportunity to meet the growing requirements in the biomaterials field.

In this project, a biodegradable graft copolymer brush of PCL-g-amylose was successfully synthesized in the green solvent, supercritical CO_2 ($scCO_2$), by using the linear starch component (amylose) as the starting material and $Sn(Oct)_2$ as the catalyst (*Scheme 1*). The $scCO_2$ was chosen because of its "liquid-like" density and "gas-like" viscosity, which enabled us to tailor the solvent properties (by changing the temperature and pressure) and undertake grafting reactions on the CO_2-swollen amylose; typically amylose shows very low solubility in most organic solvents. The effect of concentration of catalyst, monomer and amylose on the graft copolymerization was investigated and the microstructure of the graft copolymers was characterized with FTIR, ^1H NMR, ^{13}C NMR and 2D NMR (HSQC and HMBC). Contact angle testing shows that the hydrophobicity of the graft copolymers increased with graft percentage as compared to that of pure amylose, indicating successful chemical modification of amylose by graft copolymerization with PCL. TEM analysis suggested that the amphiphilic copolymers self-assembled into globular aggregates ca. 20nm in size. The application of these polymers as drug delivery devices is proposed, and so degradation behaviour and drug loading and release behaviour were also examined.



Scheme 1

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Anti-Bacterial Conducting Polymers in Blends, Fibres, Colloids and Layers

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The 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 functionalized polyaniline-related (fPANI) oligomers and polymers.

The interdisciplinary Hybrid Polymers team (Materials Chemistry and Microbiology) have developed a series of potent conducting polymers that exhibit anti-oxidant and anti-microbial properties. A range of applications have been identified which are being developed across a range of sectors including construction, packaging, coatings, marine and health 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, electro-spun fibres, colloids, layers on oxide and zeolite surfaces and composites. Various modes of presentation of these materials are pursued in several PhD theses projects.

The hybrid substrates include thermoplastics, elastomers, metals, cellulose, paper and oxides including zeolites. We have demonstrated that the potent polymers are non-cytotoxic and so are applicable in medical and health applications. Molecular contact between bacteria and the anti-microbial agents appears to be essential for potency. The advantages of the active polymers include, insolubility in water, non-leaching property, thermal stability, incorporation in porous substrates, and their support for the growth of mammalian cells (see Fig.1).

Overall, these advantages make the active polymers 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.

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Funding is from New Zealand Ministry of Business, Innovation and Employment (Hybrid Polymers, UOAX0812). Selected materials are covered by provisional patents.

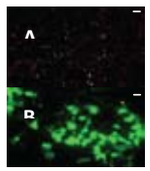

Fig.1. PCL nanofibres containing fPANi are antimicrobial, but not cytotoxic. A) S. aureus dying, B) Murine fibroblasts (L929) growing on fPANI containing nanofibres. Dead cells stain red, Live cells stain green. Bar 10 mm.

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Promoting engraftment of transplanted neural stem cells in the brain using biofunctionalised scaffolds

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Extracellular matrix (ECM) mimicry is important in tissue engineering for neural regeneration in order to provide physical and chemical cues that will promote cell survival. Biomaterials such as nanofibrous scaffolds and hydrogels have played an important role in providing physical support to cells both *in vitro* and *in vivo*. Providing chemical support is equally important as the presentation of proteins at varying concentrations could allow us to direct cell behavior, including migration and differentiation.

Previously, we tethered brain derived neurotrophic factor (BDNF) to poly-caprolactone nanofibrous scaffolds using a succinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SMCC) crosslinker[1]. We found that these functionalized scaffolds promoted neural stem cell proliferation and directed cell differentiation. In addition, we showed that immobilizing BDNF to the scaffold improved cell survival compared to cells cultured on scaffolds with soluble BDNF. More recently, we used this same immobilization method for attachment of glial cell derived neurotrophic factor (GNDF) and assessed its biofunctionality in the brain parenchyma[2]. With such convincing results, this crosslinking technique can now be transferred to short electrospun polymer nanofibers as an immobilized growth factor delivery mechanism.

We have developed methods to cut the electrospun scaffolds into short fibres. These short fibres (5-10 μm) are of interest as they could allow the presentation of proteins in an insoluble form, similar to the work previously described, without the limitations of scaffold geometry and void formation *in vivo*. Neurotrophic factors can be attached to these fibres using the same method demonstrated previously. The potential exists for these biologically active fibres to create protein gradients with spatial and temporal control in order to direct cell differentiation and migration.

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[2] T. Y. Wang, J. S. Forsythe, C. L. Parish, D. R. Nisbet, *Biomaterials*. **2012**.

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Using chitosan hydrogels to form biomimetic composites for artificial bone

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Tissue engineering is an exciting field aimed at augmenting the natural processes in the body to repair and replace damaged tissue. The polysaccharide chitosan is commonly used in tissue engineering as it is soluble, biocompatible and can stop bleeding. It can also be controllably biodegradable in the human body allowing for regenerative healing of wounds.

In addition to use in soft-tissue healing, hard composite materials based on chitosan with inorganic crystals have been proposed as artificial bone replacement materials. Chitosan hydrogels have been used as a biomimetic scaffold for composite materials[1] based on the material nacre (mother-of-pearl). Nacre is formed of inorganic calcium carbonate crystals within an organic matrix of the polysaccharide chitin and acid-rich proteins. The remarkable structure and strength of nacre means biomimetic materials may be suitable for use as artificial bone and teeth. With time, it is possible that the material is remodelled and replaced by the native tissue, allowing these materials to be used in hard-tissue engineering.

We are interested in understanding the principles of how nacre forms, and utilising a biomimetic method to form synthetic analogues as potential implant materials. We have developed a method to mimic the mineralisation of the hydrogel *in vitro*, which allows the formation of composite materials similar in structure to nacre[2]. The reaction of chitosan or chitin with the polymer poly(acrylic acid) to form a poly(electrolyte) complex is important in controlling the crystal sizes and shapes (**Fig.1**). Manipulation of the chitosan hydrogel by chemical and physical modification is possible, and leads to changes in the final composite structures of these advanced materials.

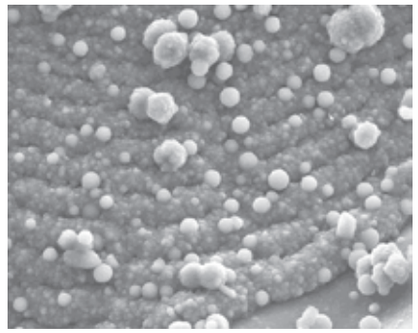

Figure 1. Ordered ribbons and spheres of calcium carbonate crystals in a composite material. These complex crystal morphologies arise due to the interaction of the two polymers poly(acrylic acid) and chitin.

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On the importance of detailed surface characterisation of bioactive coatings

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An alternative title could be "How to slow down your rate of publication by looking closely at thorough surface analysis data rather than jumping to expected but erroneous conclusions in terms of simple single effects". Accordingly, I will report in this contribution how we have used detailed surface characterisation data, particularly by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), to study antibacterial coatings and elucidate reasons for observations that upon a closer second look were not consistent with simple expectations. This talk will also show how easily one might have jumped to erroneous simplistic explanations that in some cases would have totally missed the real reason why the observed effects occurred. We also aim to show that the unrivalled sensitivity and the rich chemical information in ToF-SIMS analyses offer biomaterials scientists a powerful way to ensure that they understand the biomaterials surfaces that are subjected to biological testing.

Much of the recent research efforts in the Griesser group have focused on the development of antibacterial coatings employing covalently surface-grafted bioactive molecules. The covalent grafting is intended to provide long-term protection against bacterial colonisation as well as lead to easier regulatory approval compared with release strategies. One class of molecules we are interested in is serrulatane class diterpenes isolated from Australian plants; some have pendent groups suitable for covalent interfacial bonding.[1] When immobilising a carboxylated serrulatane onto amine surfaces via carbodiimide catalysis, we observed that the resultant surface coating afforded excellent antibacterial activity, with no colonisation, including by multidrug-resistant *Staphylococcus aureus* (Golden Staph "superbugs"). XPS and ToF-SIMS spectra at first glance seemed to confirm the intended amide coupling, but on closer examination some peaks did not fit expectations. They could eventually be assigned to a side reaction product, an acylurea, that had precipitated onto the surface. The side product could be removed by ethanol washing, and this led to ToF-SIMS spectra assignable only to amide-immobilised serrulatane.

We then used levofloxacin, a commercial antibiotic that also has a carboxyl group, to optimise the carbodiimide-mediated surface coupling onto a heptylamine plasma polymer interlayer. With its higher water solubility, the side product should not precipitate, and indeed XPS and ToF-SIMS data were in accord with a surface-coupled levofloxacin layer. Polymer samples thus coated showed excellent resistance to bacterial colonisation. However, levofloxacin was chosen for a second reason: its mode of action is reported to be the inhibition of gyrase (topoisomerase) enzymes, which exist in the bacterial cytoplasm. How could an antibacterial molecule tightly attached (without a flexible PEG linker) to a solid biomaterial surface act intracellularly? Or were the biologists wrong and we had data for a Nature paper on our hands? One clue arose by measuring the number of bacteria in solution versus a control. As the *Staphylococcus epidermidis* strain chosen for this study doubles in less than 1 hr, contact with a killing surface is not capable of killing bacteria fast enough. Yet, the samples killed bacteria in solution very effectively, indicating that levofloxacin molecules diffused into solution. Absorbance measurements confirmed this, and showed that after 5 days the amount in solution was above the bactericidal concentration. But this amount would correspond to more than 100 adsorbed layers, yet ToF-SIMS spectra showed substrate signals consistent with less than full monolayer coverage. Hence, levofloxacin molecules must have diffused to appreciable amounts into the plasma polymer matrix - bypassing the carbodiimide catalyst - and diffused out again. This was confirmed by a) soaking samples in saline and re-testing, and b) leaving out the carbodiimide catalyst. Indeed, samples comprising in-diffused levofloxacin gave excellent resistance to bacterial colonisation. After 5 days of soaking, however, samples were much less resistant to bacterial colonisation, yet the ToF-SIMS spectra were identical, showing that the covalently coupled molecules were still on the surface but inactive, in accord with their presumed mechanism of action which requires intracellular uptake. Thus, the antibacterial activity was not due to surface-grafted antibiotic mlecules, as had been concluded erroneously in some earlier studies. We conclude that incomplete reaction and diffusive release should be considered when fabricating grafted coatings of bioactive molecules that are sufficiently small and soluble inside polymer matrices.

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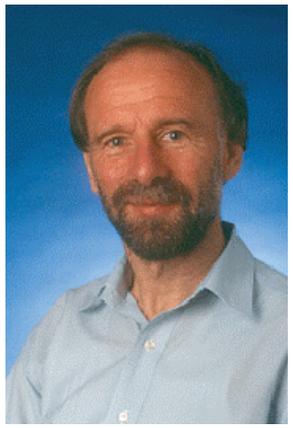

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A facile approach to assemble PEG hydrogel particles

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The design and preparation of hydrogel particles have drawn a lot of interest in biomedical engineering, pharmaceutical applications and biomaterials science because of their tunable chemical and three-dimensional (3D) physical structure, high water content and biocompatibility.[1] These desirable properties offer great potential for the utilization of hydrogel particles in drug delivery and bionanotechnology.[2] Studies have shown that poly(ethylene glycol) (PEG) has low fouling property and high biocompatibility, which has been widely used in bio-applications.[3] Recently, we have developed a facile and robust approach to prepare PEG replica particles via templating mesoporous silica (MS) particles.[4] These antifouling monodisperse PEG hydrogel particles are promising to be used in biomedical applications.

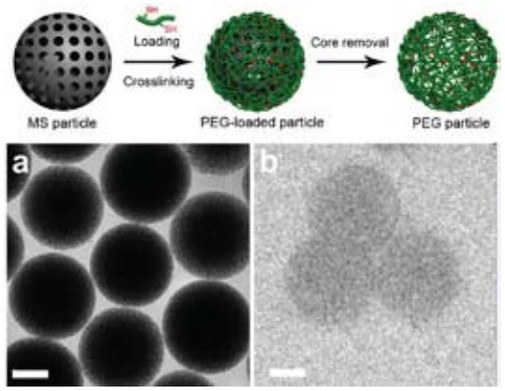

Figure 1. (Top) Schematic illustration for the fabrication of PEG hydrogel particles from MS particle templates. (Bottom) TEM images of MS templates (a) and PEG hydrogel particles (b). All scale bars represent 200 nm.

In this study, we report the assembly of antifouling monodisperse PEG particles based on the MS templating method. Briefly, MS particles were used as templates and thiolated PEG (PEG_{SH}) was synthesized and infiltrated into MS particles, followed by cross-linking the PEG chains and subsequent removal of the template, resulting in PEG hydrogel particles (Figure 1). This approach offers a number of distinct advantages. Firstly, monodisperse PEG particles are obtained by a single-step macromolecular assembly step. Secondly, this facile method is also versatile and applicable to systems with PEG-drug conjugates. Thirdly, this approach offers great chance to assemble low-fouling PEG particles for further biological applications.

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Macromolecular Ligands for Gadolinium MRI Contrast Agents: Effect of Polymer Architecture

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Macromolecular ligands for Gadolinium contrast agents (CAs) with various architectures were prepared via a "grafting to" strategy. (**Fig. 1**) Copolymers of oligoethyleneglycol methyl ether acrylate (OEGA) and an activated ester monomer, pentafluorophenyl acrylate (PFPA), were synthesized and modified with a 1-(5-amino-3-aza-2-oxypentyl)-4,7,10-tris(t-butoxycarbonylmethyl)-1,4,7,10-tetraaza-cyclododecane (DO3A-tBu-NH2) chelate for the complexation of Gd(III).

The relaxivity properties of the ligated Gd(III) agents were then studied to evaluate the effect of macromolecular architecture on their behavior as magnetic resonance imaging (MRI) CAs.(**Fig. 2**) Ligands made from linear and hyperbranched macromolecules showed a substantially increased relaxivity in comparison to existing commercial Gd(III) MRI contrast agents. In contrast, star polymers exhibited a slightly lower relaxivity per Gd(III) ion (but still substantially higher relaxivity than existing low molecular weight commercial CAs). This work shows that macromolecular ligands have the potential to serve as components of Gd MRI agents as there are enhanced effects on relaxivity, allowing for lower Gd concentrations to achieve contrast, whilst potentially imparting control over pharmacokinetics.

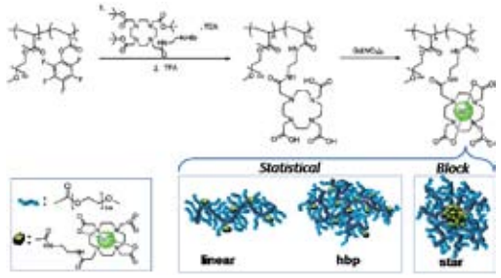

Figure 1. General procedure for the preparation of macromolecular CAs with various architectures via a grafting-to strategy

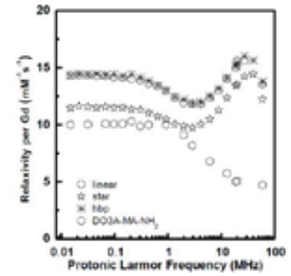

Figure 2. 1H NMRD profiles of P(OEGA-co-DO3A-MA-Gd(III)) with various architectures.

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Chitosan films grafted with peptides for stem cell culture

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Chitosan is a natural polysaccharide that is produced predominantly by the N-deacetylation of chitin[1], the main component extracted from discarded crustacean and molluscs' shells[2]. Chitosan has antifungal, antimicrobial, biocompatibility and biodegradability properties which make it very attractive for biomedical applications[3]. Solid-state NMR (ssNMR) is shown to be a versatile tool for the characterisation of both structure and dynamics of chitosan films[4].

Chitosan can be cast into fibres, gels, scaffolds, beads and films[4]. Chitosan films have great potential as bioadhesives to replace sutures[5], or as a growth substrate for stem cells and their differentiated derivatives[6]. The controlled grafting of synthetic polymers through nitroxide-mediated polymerization was used to improve elasticity and mechanical properties for bioadhesives[7]. Peptide grafting is expected to increase adhesion of stem cells and their differentiated derivatives to the chitosan film substrate by better mimicking the molecular features of extracellular matrices found in vivo. Film synthesis and pre-grafting treatment was analysed by solid-state NMR to increase cell adhesion, growth and survival. The grafting of peptide onto chitosan films was monitored in real-time using free-solution capillary electrophoresis (CE) while the films were characterized using ssNMR, Fourier transform infrared spectroscopy (FTIR), CE and scanning electron microscopy (SEM).

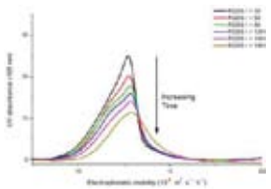

Figure 1. Electropherograms showing the consumption of RGDS from the reaction media over time.

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New antibacterial surfaces: biomimetic black-silicon with dragonfly wing nanostructures

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Cicada wings were recently reported as the first example of a novel class of antibacterial surfaces, which are selectively lethal to Gram-negative bacterial cells. The bactericidal effect was found to be a function of the wing surface physical nanoarchitecture.

Surfaces such as these insect wings represent an exciting opportunity for the development of a wide range of antibacterial biomaterials for industrial and biomedical applications. Here, we assessed the bactericidal potential of *Diplacodes bipunctata* dragonfly wings and black silicon, a nano-structurally similar surface fabricated using a simple and fast reactive-ion etching technique compatible with large-scale production.

We conclusively demonstrate that both the dragonfly wings and the black silicon surfaces are lethal for tested types of bacterial cells, despite their differences in surface chemistry and wettability. Insect wings and black silicon surfaces were lethal to the Gram-negative *Pseudomonas aeruginosa,* Gram-positive *Staphylococcus aureus* and *Bacillus subtilis* bacterial cells. Both surfaces were also effective against *B. subtilis* spores, which are highly resistant to most forms of sterilisation. The bactericidal efficiencies of both the wing and silicon surfaces were very similar in most cases, with each square centimetre killing in excess of 100000 cells per minute in the case of *S. aureus*, however the black silicon was almost twice as effective as dragonfly wings at killing *Pseudomonas aeruginosa* cells; inactivating > 70000 cells cm^{-2} min^{-1}. Our results demonstrated that (i) *D. bipunctata* wings are highly effective bactericidal surfaces, (ii) a simple ion etching technique can be used to produce antibacterial nanomaterials from silicon wafers based on dragonfly wing structures and (iii) these bio-inspired black silicon surfaces have enhanced activity relative to their natural counterparts.

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Bioinspired Phosphorylcholine Containing Polymer Flms with Silver Nanoparticles Combining Antifouling and Antibacterial Properties

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The synthesis, antibacterial (bioactive) and antifouling (biopassive) properties of stable, uniform, high surface coverage films of poly(hydroxyethyl methacrylate-co-2-methacryloyloxyethyl phosphorylcholine) (p(HEMA-co-MPC)) with embedded, non-leaching silver nanoparticles (AgNPs) are reported. Films were prepared from hybrid colloids obtained by an inverse miniemulsion polymerization which were drop cast and solvent annealed and extensively characterized.[1] Based on the experimental findings, a mechanism of action of AgNPs in antibacterial activity in combination with antifouling characteristics is discussed.[2] Long-term antifouling studies of E. coli determine little to no adhesion on p(HEMA-co-MPC)/Ag films at 2.5×10^6 CFU mL^{-1} for 7 d, measured using live/dead staining assays. Agar diffusion tests indicate that there is no leaching of Ag from the films and SEM and EDX analyses of the films before and after incubation with E. coli show no attachment of E. coli and no visible change in film morphology or AgNP dispersal. Antibacterial studies are investigated using E. coli K-12 as a model bacterial strain and are tested in static (CFUs) and dynamic contact assays. Antibacterial efficacy of the films containing extremely low AgNP concentration (3.8 ng cm^{-2}) is shown with growth suppression of E. coli in culture medium for 4 h at 1.35×10^5 CFU mL^{-1} and killing greater than 99% of E. coli in only 1 h of exposure to concentrations up to 1×10^5 CFU mL^{-1}. These hybrid films may propose an exciting direction to long-term antibacterial and antifouling films in clinical applications.

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Novel Developments in Controlled Radical and Cationic Polymerizations via Dual Mechanisms

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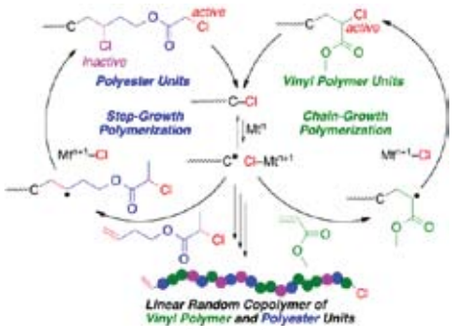
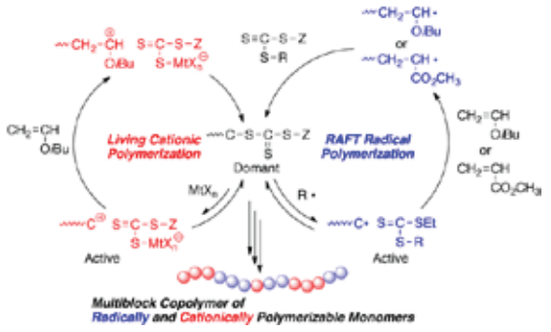
Controlled or precision polymerization is a powerful tool for the synthesis of well-defined polymers, which would work as high-performance and/or functional materials based on their controlled structures. Recent progresses in controlled/living polymerizations via various mechanisms, including radical, ionic, coordination, and condensation polymerizations, have enabled the precision synthesis of various polymers with controlled architectures. However, there are still limitations in monomers prone to each polymerization mechanism.

We have been investigating precision polymerization proceeding via radical or cationic mechanism in terms of control of molecular weight, stereochemistry, and monomer sequence. Recently, we found that novel metal-catalyzed step-growth radical polymerizations, in which monomers possessing unconjugated C=C and reactive C–Cl bonds are polymerized via radical polyaddition mechanism to give polyesters, polyamides, and sequence-regulated vinyl copolymers.[1,2] Furthermore, we combined the radical step-growth polymerizations with the metal-catalyzed living radical chain-growth polymerizations of conjugated vinyl monomers such as acrylates and acrylamides to synthesize novel random and block copolymers consisting of the polyesters or polyamides and the vinyl monomer units (**Scheme 1**).[3]



Scheme 1

Another dual but different simultaneous precision polymerization has also been developed via concurrent activation of C–S terminal by a radical species and a Lewis acid, which induces simultaneous controlled/living radical and cationic polymerizations of acrylate and vinyl ether to give the novel multiblock copolymers with unprecedented monomer sequences of both monomer units (**Scheme 2**).[4] In my presentation, I will present our current work on such precision polymerizations proceeding via dual mechanisms and more recent related topics.



Scheme 2

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Synthesis of Novel Trithiocarbonate and Allyl Sulfides and their Application into the Advances in Covalent Adaptable Networks

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There are a number of important applications and benefits for the type of network rearrangement implemented in photochemical Covalent Adaptable Networks (CAN's). In this study, we focus on CANs -based materials that can be designed to reduce the shrinkage stress that arises during polymerization when weak intermolecular interactions are replaced by covalent bonds. CANs-based networks with different reversible addition-fragmentation termination (RAFT) moieties present within the polymer have been shown to reduce the external stresses applied post-polymerization via photo-induced creep with differing efficiencies. The differences in the RAFT-induced rearrangement of the network in a polymer formed by a radical-mediated thiol-ene reaction versus a thiol-ene `click` Michael addition reaction has also been studied and characterized. Additionally, a mild and efficient synthesis of acrylate functionalized trithiocarbonates and allyl sulfides RAFT monomers are described and their efficiency in photo-stress relaxation during and post polymerization is demonstrated. The RAFT monomers designed in this study have been shown to have highly efficient stress relaxation properties. In post-polymerization relaxation studies of thin films using the trithiocarbonates, stress reduction of up to 55% has been observed whereas in stress reduction observed during polymerization RAFT monomers present within the network at 1.5% by weight was shown to reduce up to 70% of the stress in a traditional dental monomer system.

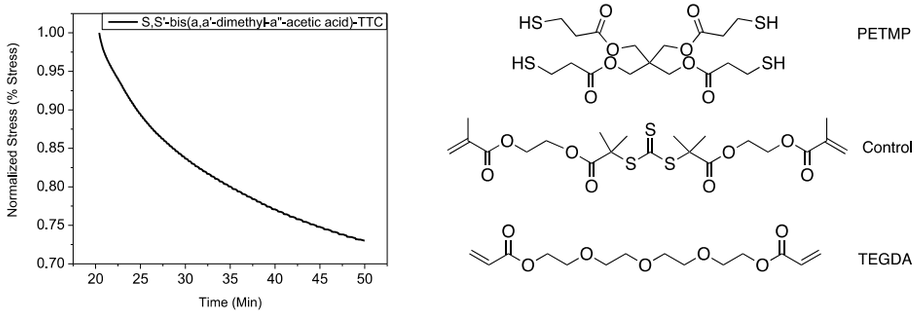

Figure 1 . Photoresponsive formulation and stress relaxation properties. a) The resins were formulated with a 1:1:1 stoichiometric ratio based on functional groups of pentaerytheritol tetrakis(3-mercaptopropionate) (PETMP) and tetraethylene glycol diacrylate (TEGDA) and the RAFT trithiocarbonate. The RAFT component incorporates trithiocarbonate functional groups into the network strands. b) Photoinduced stress relaxation (normalized), owing to the RAFT mechanism was performed at 20 mW/cm^2 using 1% by weight DMPA at 365 nm for 30 minutes.

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Research interests: Synthesis and Development of New RAFT Agents

Quasi-block copolymer libraries on demand via sequential RAFT polymerization in an automated parallel synthesizer

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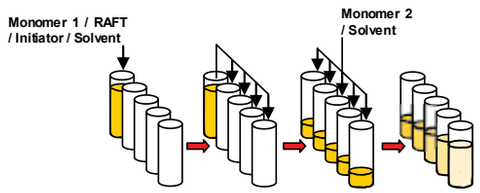
A fully unattended synthetic method for the parallel and systematic synthesis of quasi-block copolymers via sequential RAFT polymerization in a commercially available automated synthesizer[1] will be presented. This method is very convenient as systematic quasi-block copolymer libraries can be prepared on demand in an and in a short period of time.[2] The method consists of two consecutive RAFT polymerizations. In the first, several macroRAFT agents are synthesized reaching at least 80% of monomer conversion (**Scheme 1**). The reaction mixtures obtained are subsequently divided equally amongst the reactors of the apparatus and different amounts of a second monomer are added to each (**Scheme 1**). A second polymerization reaction is then performed to yield a systematic library of quasi-diblock copolymers (**Scheme 1**). The sequential RAFT polymerizations showed a good control in providing low dispersity macroRAFT agents and derived quasi-diblock copolymers. The residual monomer from the first reaction that was copolymerized into the second block during the second RAFT polymerization was determined to be <15% by proton nuclear magnetic resonance. In accord with this finding differential scanning calorimetry showed the quasi-blocks to possess properties similar to those expected for "pure" diblock copolymers. Further investigations in this direction currently focus on the detailed characterization of these quasi-block copolymer libraries by 2-dimensional gel permeation chromatography and well on the development of applications.[3,4] Overall, the described method is more convenient, more rapid, and much less expensive, alternative than the conventional route for the preparation and screening of block copolymer libraries.



Scheme 1. Representation of the automated parallel and systematic synthesis of a quasi-diblock copolymer library via sequential RAFT polymerization.

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The influence of domain segregation in ionic liquids upon RAFT polymerisation mechanism

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Recent evidence has suggested that the solvent environment in ionic liquids is dynamic and composed of polar and non-polar domains governed by the summation of weak interactions and self-assembly.[1-3] Consequently, the effect of a nano-structured solvent environment on chemistries conducted in ionic liquids is coming under increased scrutiny.

In this work we investigate how the domain-like structure of ionic liquids affects the kinetics and products of the reversible addition fragmentation chain transfer (RAFT) controlled free radical polymerisation (FRP) of methyl methacrylate in a number of room temperature ionic liquids. By utilising rotating frame Overhauser effect spectroscopy (ROESY) to probe the solvation environment of the 2-cyano prop-2-yl dithiobenzoate (CPDB) RAFT agent, we show that in almost all cases preferential partitioning of the dithiobenzoate-moiety of the RAFT agent into the ionic domain of the ionic liquid occurs.

We suggest that directed interactions between the imidazolium cation of the ionic liquid and the RAFT agent in combination with previously observed interactions between the ionic liquid and the monomer and polymer species in the reaction[4] can explain the unique kinetics of RAFT polymerisations in ionic liquids.[5]

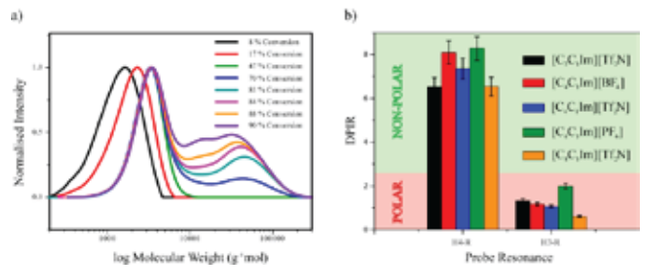

Figure 1. a) Sequential GPC traces for the RAFT controlled polymerisation of MMA in $[C_4C_1Im][BF_4]$, it can be seen that the reaction proceeds in a controlled manner up to 50 % conversion at which point the growth of a high molecular weight polymer can be observed. b) The DPIR partition coefficient calculated from ROESY spectra of the CPDB RAFT agent in 5 ionic liquids. It can be seen that the H3-R resonance, the aromatic ring protons of the RAFT agent, are preferentially dissolved in the polar domain of the ionic liquids.

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RAFT polymerization of phosphonated-based monomers: synthesis of innovative (co)polymers and applications

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Phosphorus containing polymers are very promising compounds as their range of applications is broad.[1] For example, they can improve flame resistance and are used as adhesion promoters for paints, and adhesives. They are also employed in the composition of glasses fibers and films with high mechanical resistance. More recently, these materials were involved for applications in the biomedical field, especially as agents for controlled drug release. They also proved to be useful for wastewater treatment due for their metal sorption abilities.[2] This multiple and specific applications explain the growing interest in the research of new phosphorus containing monomers and polymers. Additionally, another important benefit of phosphonated ester groups is the possibility to easily achieve their hydrolysis to produce phosphonic diacid ones, able to enhance properties already mentioned. For such purpose, polymer structures have to be well-known, notably in terms of molecular weight, and architecture. In that context, Reversible Addition Fragmentation Transfer (RAFT) polymerization appears as an interesting tool as it allows the synthesis of polymers with well-controlled architecture, predictable molecular weight, and narrow polydispersity without using such drastic conditions as in ionic polymerizations.

In this contribution, we report on the controlled polymerization of two different phosphonated monomers, namely dimethyl(methacryloyloxy)methyl phosphonate ($MAPC_1$), and diethyl 2-(acrylamido)ethylphosphonate (DAAmEP). RAFT polymerization allowed us to prepare homo or diblock copolymers. In the latter case, the second block was poly(methyl methacrylate) (PMMA), poly(ethylene glycol methacrylate) (PEGMA) or thermosensitive poly(N-*n*-propylacrylamide) (PN*n*PAAm)) (Figure 1). Copolymers proved to be useful for two different purposes (wastewater treatment and biomedical applications) after hydrolysis of the phosphonated ester groups.

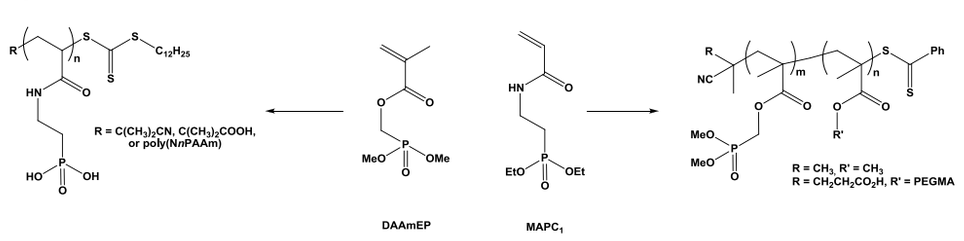

Figure 1. RAFT polymerization of phosphonated monomers and resulting homo and diblock copolymers.

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RAFT Polymerization of *N*-Vinyl Carbazole – An Intermediate Reactivity Monomer

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Since the first report of photoconductive properties, polymers comprising poly(*N*-vinylcarbazole) (PNVC) segments have drawn attention for their potential optoelectronic applications.[1,2] *N*-vinylcarbazole (NVC) can be polymerized by cationic or radical mechanisms, however, radical polymerization is simpler to implement and generally provides better outcomes.[1] There have been a number of reports on controlling NVC polymerization using reversible deactivation radical polymerization (RDRP). This work is summarized in the review by Nakabayashi and Mori.[3] Mori et al reported on RAFT polymerization of NVC with different RAFT agents. They used benzyl dithiobenzoate and benzyl pyrrolocarbodithioate (Z only suitable for controlling the polymerization of more activated monomers or MAMs), and benzyl and 1-phenylethyl xanthate (Z suitable for controlling the polymerization of less activated monomers or LAMs). Of these agents only 1-phenylethyl xanthate provided good control and afforded a low dispersity polymer. Based on these findings Nakabayashi and Mori proposed that NVC should be considered a less activated monomer (LAM). However they also noted that benzyl was a poor initiating radical for NVC polymerization.

In our recent work describing switchable RAFT agents we found that NVC polymerization was well-controlled with the non-protonated form of *N*-methyl-[4] and N- aryl-*N*-(4-pyridyl)dithiocarbamates.[5] The protonated form of the RAFT agent could not be used in NVC polymerization due to the instability of the monomer and the PNVC macro-RAFT agents in the presence of even trace amounts of acid.

The use of RAFT agents $Z(C{=}S)S{-}CH_2CN$ including the dithiobenzoate (Z=Ph), trithiocarbonate (Z=SR'), xanthate (Z=OR), and conventional and switchable dithiocarbamates ($Z{=}NR'_2$) in RAFT polymerization of *N*-vinylcarbazole (NVC). The xanthates and dithiocarbamates were found to give adequate control ($Đ$<1.3), contrary to the literature, we find the polymerization is best controlled with the trithiocarbonate RAFT agents (minimal retardation and $Đ$<1.1); a RAFT agent usually only suited for controlling MAM polymerization. NVC has reactivity intermediate between that of the traditional MAMs and LAMs such that the polymerization can be controlled by both active and less active RAFT agents. The key to good control is the selection of R to be both a good leaving group and a good initiating radical. Benzyl is a poor R group because it is slow to reinitiate polymerization, cyanomethyl is a good R group that meets these criteria.

An important ramification of this is that it is possible to prepare block copolymers with both MAMs and LAMs and the block order is not important. Thus we have successfully prepared poly(butyl acrylate)-block-PNVC and PNVC-block-poly(butyl acrylate) using a trithiocarbonate RAFT agent and used two-dimensional SEC HPLC to demonstrate block purity. the corresponding styrene-based block have also been synthesized, however, the reinitiation of NVC polymerization by the polystyryl radical constrains the purity of poly(styrene)-block-PNVC.

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Tackling the Cross-termination Challenge in Radical Polymerization Through the RAFT-CLD-T Technique

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So far, many efforts have been devoted to the determination of absolute values for apparent termination rate coefficients throughout radical polymerizations, i.e. as a function of chain length and conversion. Despite the significant progress made in this field,[1-3] the accurate measurement of the chain length and conversion dependency of apparent cross-termination rate coefficients still remains an outstanding challenge. Nevertheless, cross-termination is the most important termination pathway in most radical polymerization processes, in particular for the free radical polymerizations which are dominated by "short-long" terminations. Hence, the precise assessment of the dependency of the apparent cross-termination rate coefficient on the polymer size and composition of the reaction mixture is an absolute necessity for the accurate prediction of the evolution of the polymerization rate and molar mass distribution. It is clear that this will enable a further optimization of existing industrial radical polymerization processes on the one hand and aid the development of new functional polymeric materials on the other hand.

In this contribution, it is explored whether the so-called RAFT – chain length dependent – termination (RAFT-CLD-T) technique, which has shown to provide a simple and model independent way to measure the apparent homotermination rate coefficients,[4-6] can be extended for the first time to measure the cross-termination rate coefficients for methyl methacrylate (MMA) and styrene (STY) homopolymerizations for different chain length and conversion regimes.

Experiments are being currently performed at the KIT and the results of this assessment will be presented. The experimental procedure being used is based on the theoretical evaluation of Lovestead et al.,[7] involving differential scanning calorimetry, size exclusion chromatography and on-line ^{1}H-NMR analysis of RAFT polymerization mixtures containing both a RAFT chain transfer agent (RAFT CTA; cyano isopropyl dithiobenzoate for MMA; cyano isopropyl dodecyl trithiocarbonate for STY) and a macro- RAFT CTA. The experimental conditions are selected based on model screening and each experimental response is being measured at two different DSC instruments to exclude any ambiguity in the obtained data. In addition, experiments will be performed both in solution (methyl isobutyrate for MMA; toluene for styrene) and in bulk to assess the application scope of the obtained results and its concomitant impact on currently accepted theories to describe diffusional limitations on termination.

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Novel RAFT-derived poly(fluorovinyl esters): Controlled synthesis and enhanced CO_2-philicity

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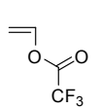
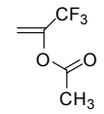
In the development of green chemistry solutions, the replacement of conventional organic solvents by "greener" ones has been identified as a key criterion to address the environmental challenges imposed by chemical synthesis, processing and separations.[1] In this perspective, supercritical carbon dioxide (sc-CO_2) has been considered a solvent of high potential to reduce environmental damage due to its low inflammability, cost, toxicity, reactivity and critical temperature and pressure (31.1 °C, 73 bar). However, its use in chemical processes has been limited until now, mainly because its feeble solvating power which results in the low or non solubility of a large variety of polar or ionic reactants, catalysts and macromolecules. Therefore, the seek for novel generations of hydrophilic/CO_2-philic (macro)molecular species for the stabilization of water/sc-CO_2 emulsions is highly topical and relevant.

Most commodity polymers possess limited solubilities in sc-CO_2 under mild conditions (P < 350 bar, T < 100 °C). The only examples of highly CO_2-soluble polymers include high molecular weight (i.e. higher than 10000 g.mol^{-1}) fluorinated polyacrylates, perfluoroalkyl ethers and polysiloxanes. To a lesser extent, poly(vinyl esters)[2,3]are another promising family of CO_2-philic polymers that present practical advantages of favorable price and toxicology compared with the habitual polyfluoroolefins and poly(siloxane) CO_2-philic polymers.

In this communication, we report the first controlled radical polymerization of two fluorinated vinyl esters, namely vinyl trifluoroacetate (VTFAc)[4] and (1-trifluoromethyl)vinyl acetate (CF_3VAc),[5] by means of RAFT. Their statistical copolymerization with vinyl acetate (VAc) and amphiphilic block copolymers derived therefrom are presented. Some unprecedented increase in solubility and distinctive features compared to previously reported poly(vinyl alkylates)[2,3] are demonstrated, based on cloud point pressure and surface tension measurements.



VTFAc



CF_3VAc

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Sequence-controlled Polymers: Recent Progress and Promise.

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Synthetic polymers do not exhibit controlled sequences of monomers as biological macromolecules do (**Fig. 1**). However, ordered comonomer sequences could open interesting technological avenues in synthetic polymer science.[1, 2, 3] Surprisingly, very little research has been carried out during the last part of the 20th century for developing sequence-specific polymerization methods. Yet, for about five years, a renewed interest in the subject has emerged. This growing field of research will be described in my presentation.

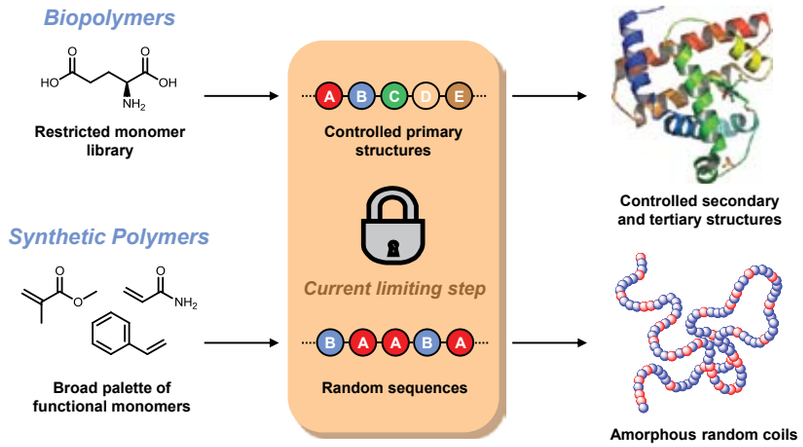

Figure 1. Sequence-controlled macromolecules: a new level of complexity in synthetic polymer science.

Recent sequence-controlled approaches developed in our laboratory will be discussed.[4, 5] Moreover, the advantages of the formed sequence-controlled polymers will be highlighted. For instance, the preparation of complex macromolecular structures such as encoded chains, 1D macromolecular arrays or folded polymer origamis will be presented.[6, 7, 8] Ultimately, challenges and future directions in the field will be analyzed.

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PREPARATION OF AMPHIPHILIC BLOCK COPOLYMERS WITH VARIOUS MORPHOLOGIES IN ONE POT POLYMERIZATION REACTION

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ABSTRACT

In the present work, various morphologies (micelles, worm-like, rod-like and vesicles) were obtained by polymerization self-assembly approach in one-pot RAFT dispersion polymerization. For this purpose, well defined amphiphilic block copolymers, poly[oligo(ethyleneglycol) methacrylate]-*block*-poly(styrene) (POEGMA-*b*-PST) and core functional poly[oligo(ethyleneglycol) methacrylate]-*block*-poly(styrene)-*co*-poly(vinyl benzaldehyde) (POEGMA-*b*-PST-*co*-PVBA) were synthesized starting from dithiobenzoate functional POEGMA as macro-CTA in methanol in the presence of AIBN as a radical source with 1:5000 molar feed ratio of POEGMA:ST or ST(% 95)-VBA (% 5). Simultaneous morphology transitions were easily achieved by gradually increase of number-average degree of polymerization (DPn) of the core forming polymer with polymerization time. Continously increasing DPn of the core polymer led to block copolymer assemblies and consecutive morphology transitions in the following order spherical micelles, worm-like, rod-like and vesicles, respectively. Furthermore permanent stable nanoparticles were obtained by crosslinking the core polymer by reaction aldehyde groups on the core with 1-3 propylenediamine in methanol. Whole morphologies and number average particle size characterized by transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements. Structures and average molecular weight of the resulting polymers were determined by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and size exclusion chromatography (SEC).

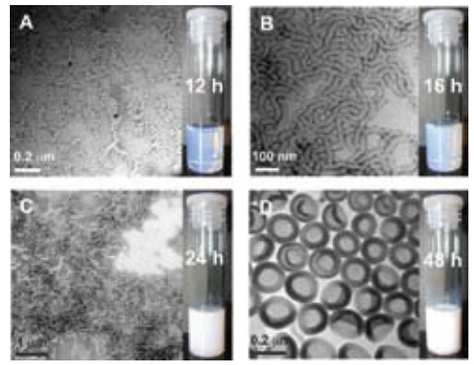

Figure 1: TEM images of RAFT dispersion polymerization solution of POEGMA-*b*-PS amphiphilic block copolymer at different polymerization time.

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Using Orbital Conversion to pH Switch Nitroxide Mediated Polymerization

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The electronic configuration of an atom or a molecule is normally defined according to the Aufbau principle: '*a maximum of two electrons are put into orbitals in the order of increasing orbital energy*'.[1] However, a limited number of recent publications have reported non-aufbau occupation of molecular orbitals in radicals, where the molecular orbital accommodating the unpaired electron (the singly-occupied molecular orbital, or SOMO) is no longer energetically the highest occupied molecular orbital (HOMO).[2] Recently, we have discovered a brand new class of fully organic SOMO-HOMO converted compounds, and the first such species capable of being manipulated by pH.[3] Using quantum-chemical calculations, validated by gas-phase thermochemistry experiments, we have shown that distonic radical anions comprising a stabilized radical (such as an aminoxyl, peroxyl or aminyl functionality) that is *not* conjugated (or hyperconjugated) with a remote negatively charged functional group (such as a carboxylate, phosphate, sulphate, alkoxide anion) undergo SOMO-HOMO conversion. When the negatively charged group is protonated the Aufbau orbital configuration is restored (see **Fig. 1**). Intriguingly, we also found that SOMO-HOMO orbital conversion is associated with a dramatic and unprecedented effect on the stability of the radical, significantly weakening the bonds it forms with hydrogen and with carbon-centred radicals. This long-range substituent effect on radical stability appears to defy explanation using traditional physical organic chemistry concepts (i.e., steric, polar, resonance, hydrogen bonding effects), and is likewise switched off by protonation, suggesting that it may be utilized to design a new class of pH-switchable polymerization control agents, capable of operating under mild conditions. This talk will outline the practical applications of orbital switching for nitroxide-mediated polymerization.

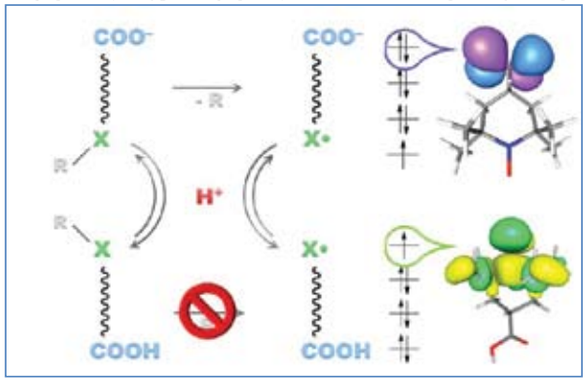

Figure 1. Deprotonation of carboxy-TEMPO results in both SOMO-HOMO orbital conversion and an increase in radical stability by nearly 4 orders of magnitude at room temperature

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Equilibration of Trithiocarbonates During RAFT Polymerization

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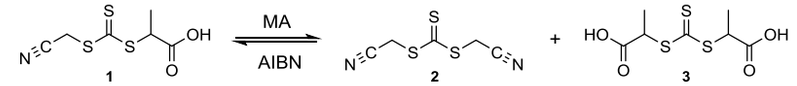
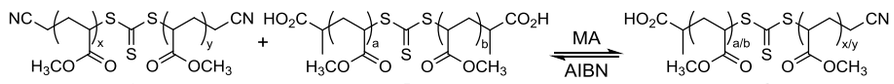
The existence of equilibrating species in RAFT polymerizations is beyond dispute, and many fundamental rate constants for the component radical additions and fragmentations of these equilibria have been determined, yet as recently as 2012, it was stated that "*debate continues....on the rapidity with which the various equilibria are established....*"[1]. The exchange processes that occur during typical RAFT polymerizations, at initialization, chain growth, and (if required) thiocarbonyl end group removal by radicolysis, are only visible as one-directional reactions characterized by the non-radical starting species and end products, so that any intervening equilibration or reversibility is normally not seen and cannot be measured. Here we present the idea of a suitably designed RAFT agent which permits easily monitored diversionary pathways that allow such intervening equilibria to be observed and measured.

In this talk we describe how the *quasi*-symmetrical[2] trithiocarbonate **1** used in the RAFT polymerization of methyl acrylate undergoes rapid, complete, and reversible scrambling of its two radicofuges to produce a statistical mixture with the two symmetrical trithiocarbonates **2** and **3**. (**Scheme 1**) The changes in composition can be quantitatively monitored by ^{1}H nmr and clocked against monomer conversion.



Scheme 1

In a similar vein, the two symmetrically-ended polymers **4** and **5**, synthesized by RAFT polymerization of methyl acrylate mediated by the two symmetrical RAFT agents **2** and **3**, respectively, when combined and re-subjected to the original polymerization conditions, undergo equilibration to produce a mixture now containing the unsymmetrically-ended polymer **6**. (**Scheme 2**) In this case, the progress of the equilibration can be monitored by ESI mass spectrometry.



Scheme 2

[1] G. Moad, E. Rizzardo, S.H. Thang, *Aust. J. Chem.* **2012**, *65*, 985–1076

[2] We use the term *quasi*-symmetrical to mean the compound is non-symmetric in structure but behaves symmetrically (or nearly so) in terms of bifunctional reactivity.

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One-Pot RAFT/“Click” Chemistry via Isocyanates

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Over the past decade, a growing number of tools has been developed and combined to access controlled and functionalized architectures. Among these tools the discovery of reversible-deactivation radical polymerization (RDRP), coupled to the use of highly efficient coupling chemistries (e.g. “click chemistry”), enables polymer chemists to overcome one of the central difficulties in functionalizing macromolecules and it allows the preparation of new nanomaterials with improved properties.
Azide-alkyne, thiol-ene/yne and Diels-Alder reactions are amongst the most used “click” reactions.[1] However, all these approaches suffer from two major drawbacks: (1) the necessity to modify the substrate, as none of these functional groups exist in natural compounds; (2) their non compatibility in radical polymerization, which requires protection/deprotection steps.

In this context, it would be highly advantageous to employ a functionality that is readily synthesized, is stable in radical polymerizations, and is capable of reacting efficiently with a wide range of (naturally occurring) functional groups like amines, alcohols and thiols. Within this framework the isocyanate group is a very promising candidate. Our group recently developed an original and highly efficient strategy based on the use of a carbonyl-azide RAFT agent precursor **1** (**Fig. 1**) that rearranges into an isocyanate *in-situ* during the RAFT process.[2] The concept of using a stable prereactive group appears very powerful and circumvents numerous difficulties associated with the synthesis, purification, and storage of a highly reactive functionality. This strategy can be used either to produce α-isocyanate end-functional polymers or to produce α-end-functionalized polymers in a one-pot RAFT polymerization/“click” alcohol or amine isocyanate coupling approach (**Fig. 1**). This approach is rapid, very versatile, and offers important new perspectives in the quest for a fast, simple synthesis of α-end-functionalized polymers. We present here our latest developments in the use of this technology for macromolecular engineering.

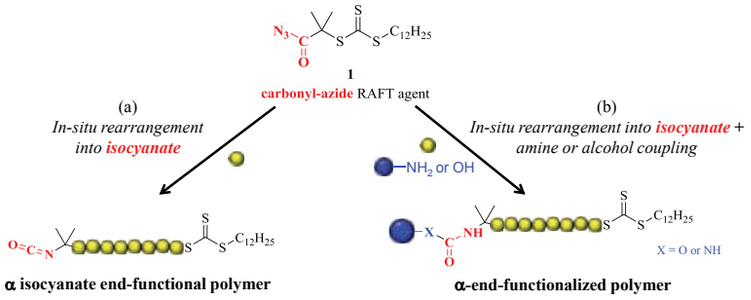

Figure 1. (a) Simultaneous RAFT polymerization and rearrangement into isocyanate; and (b) one-pot RAFT polymerization/“click” alcohol/amine-isocyanate via in-situ rearrangement into isocyanate.

[1] U. Mansfeld, C. Pietsch, R. Hoogenboom, R. Becer, U. Shubert, *Polymer Chem.* **2010**, *1*, 1560-1598.
[2] G. Gody, C Rossner, J. Moraes, P. Vana, T. Maschmeyer, S. Perrier *J. Am. Chem. Soc.* **2012**, *134*, 12596-12603.

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Thermally and Photochemically Induced Living Radical Polymerization with Organic Catalysts

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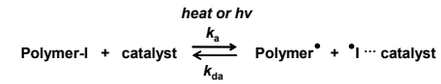
We developed new families of living radical polymerization, which use organic catalysts. They are based on reversible formation of the propagating radical (Polymer•) from polymer-iodide (Polymer-I) using organic catalysts. We developed two systems with different mechanisms. This presentation introduces the newer system, reversible complexation mediated polymerization (RCMP).

Figure 1 shows examples of RCMP catalysts. They include such common amines as triethylamine (TEA). Mechanistically, the catalyst coordinates iodine of Polymer-I and reversibly gives Polymer• and the complex of iodine and catalyst:



As shown in Figure 2 (filled circles), TEA effectively controlled the polymerization of methyl methacrylate (MMA) at 90 °C, yielding low-polydispersity polymers up to high conversions.

Instead of neutral tertiary amines such as TEA, quaternary ammonium and phosphonium salts (Figure 1) were also successfully used as catalysts. The ammonium and phosphonium salts were more active catalysts than TEA, allowing us to synthesize relatively high molecular weight polymers (M_n up to 140,000) for methacrylates (Figure 2 (triangles and squares)) and widening the monomer versatility to acrylates and styrene as well as methacrylates. Because of the good tolerance to functional groups, the organic salt catalysts were also applicable to several hydrophobic and hydrophilic functional monomers, e.g., with epoxy and hydroxyl groups.

RCMP was induced by visible light irradiation as well as thermal heating. With tributylamine (TBA) as a catalyst, the polymerization of MMA successfully proceeded under xenon lamp irradiation at a wavelength of 350-600 nm at room temperature (Figure 2 (open circles)). Polymer• was generated by the photo-dissociation of Polymer-I itself and the complex of Polymer-I and TBA. Perfectly no polymerization took place without photo-irradiation (Figure 3), meaning that the system is an ideal polymerization switched “on” and “off” by external photo-stimulus. The polymerization rate was also finely tunable by the external irradiation power (Figure 3). The uses of inexpensive compounds and visible light, good polydispersity control, and fine response to external photo-irradiation may be useful features of this system.

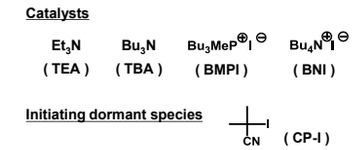


Figure 1. Examples of catalysts and initiating dormant species (low-mass alkyl iodide).

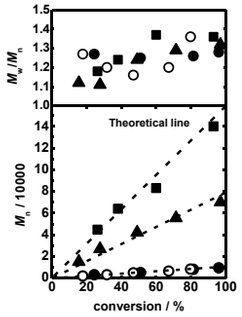


Figure 2. Plots of M_n and M_w/M_n vs conversion for the MMA/CP-I/catalyst systems. The catalyst was TEA (90 °C) (filled circles), BMPI (60 °C) (triangles and squares), and TBA (under xenon lamp irradiation at r.t.) (open circles).

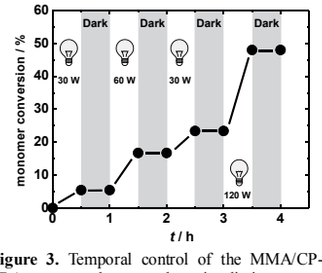


Figure 3. Temporal control of the MMA/CP-I/TBA system under xenon lamp irradiation at r.t.

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Modular Design of Profluorescent Nitroxide-Based Sensor Materials

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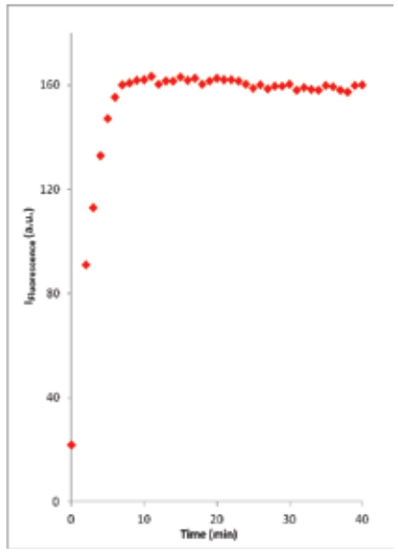
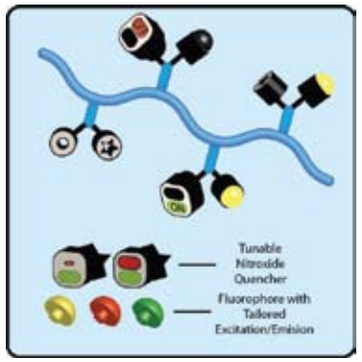
Nitroxides are stable, kinetically persistent free radicals with a number of unique properties. One of their recent applications is to be covalently linked to a fluorescent moiety giving them the ability to function as a switchable fluorometric probe.[1] The capability of the nitroxide/fluorophore couple to act as a probe arises from the nitroxide moiety's capacity to efficiently quench excited states both inter- and intra-molecularly. This presentation will demonstrate the synthesis of polymeric scaffolds containing multiple reactive functionalities that can be transformed orthogonally to yield a polymer adorned with profluorescent nitroxides. These materials can be utilised, in turn, to function as fluorescent sensors for both chemical and physical changes.





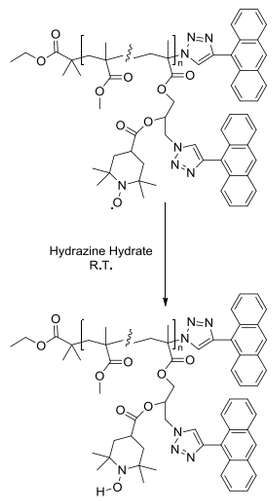


Figure 1. Representative example of the construction of profluorescent nitroxide-containing polymers (top right) and a plot of fluorescence intensity at emission maximum over time when a profluorescent nitroxide containing polymer is exposed to hydrazine hydrate as a model reductant (bottom).

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A Versatile Polymer Building Block Based On Trifluorovinyl Ethers Chemistry

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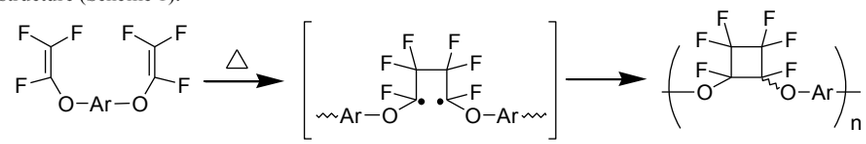
Fluorine-containing polymers are one of the new and exciting research directions within the polymer science programme at The University of Auckland. In the plastics world, fluorine- containing polymers represent a rather specialised group of polymeric materials.[1] Their many attributes include remarkable thermal and chemical attack inertness, solvent resistance and outstanding electrical properties. These properties offset their higher cost and greater difficulty in processing than is the case for most other non-fluorinated thermoplastics.

Fluoropolymers are typically made from the free radical polymerization of fluorinated alkenes. Unlike those, this talk introduces a unique kind of fluorinated olefin – aryl trifluorovinyl ethers- as building block to deliver high performance polymers.[2] Polymers are prepared via thermally activated [2+2] cycloaddition of aryl trifluorovinyl ether monomers.[2] The resulting semi-fluorinated polymer contains perfluorocyclobutane (PFCB) ring structure (Scheme 1).



Scheme 1. [2+2] Cyclo-polymerization of aromatic trifluorovinyl ether monomers.

Various macromolecular architectures such as linear, branched and cross-linked as well as a range of functional groups can be prepared and incorporated by [2+2] cycloaddition of functional monomers containing multiple aryl trifluorovinyl ether groups.[3] Initially developed for aerospace and microelectronics applications at Dow Chemical, PFCB polymer technology can serve as a versatile materials platform for many industrial applications, such as microphotonic[4], optoelectronics[5] and membranes[6-8].

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Assembly of free-standing polypeptide films via the synergistic combination of hyperbranched macroinitiators, the grafting-from approach and intermolecular cross-chain termination

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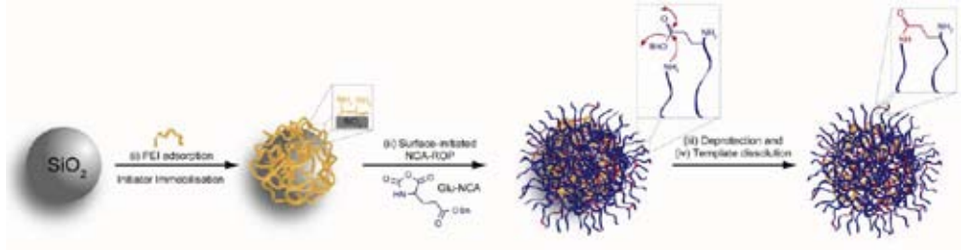
Synthetic peptide-based materials having various macromolecular architectures is of great interest due to their tunable functionalities, specific stereochemistries as well as their biocompatibility and (bio)degradability. In particular, hollow polymeric capsules – i.e. coreless free-standing cross-linked films capable of cargo encapsulation – when comprised of such amino acid constituents, are therefore highly attractive as biomolecular devices.[1] To date, the fabrication of peptide-based capsules have utilised techniques driven by self-assembly, namely the layer-by-layer (LbL) method.[2] Although this approach allows for fine control over the capsule film properties, the synthesis of pre-functionalised polypeptides (or proteins) often involves multi-step processing. Thus, given the numerous beneficial properties of polypeptides coatings and free-standing films, and the current synthetic limitations, it was the aim of this study to develop a new and versatile approach towards cross-linked polypeptide capsules for various targeted bioapplications.

Recently, studies reported the occurrence of side-reactions during the ring-opening polymerisation (ROP) of amino acid *N*-carboxyanhydride (NCA) derivatives leading to the formation of 'dead' polymer chains as a result of intramolecular cyclisation.[3] Based upon these reports, we herein demonstrate the possibility of utilising this side reaction as a cross-linking mechanism to form free-standing nanoscale polypeptide films in a single-step. In the present study, we also establish the synergistic combination of hyperbranched macroinitiators, the grafting-from approach and cross-chain termination reactions in the assembly of peptide-based capsules with tunable properties (**Scheme 1**).



Scheme 1. Formation of cross-linked peptide-based capsules by the synergistic contribution of hyperbranched macroinitiator, surface-initiated NCA-ROP and cross-chain termination reactions.

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Stereoregular cyclic poly(methyl methacrylate)s: synthesis, characterization and their unique supramolecular assemblies

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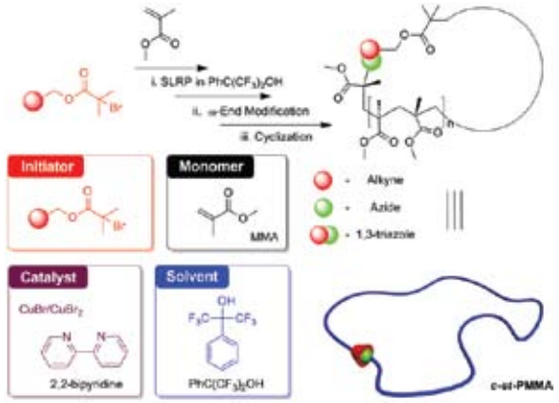
Naturally occurring macromolecules have highly controlled microstructures, e.g., precisely-regulated molecular weight, monomer composition, sequence, and stereochemistry (i.e., tacticity). The meticulous control exerted by nature renders them unique structure, distinct properties and the ability to form intricate and exquisite supramolecular assemblies (e.g., DNA and glycogens). The ultimate goal for polymer chemists is to emulate and match nature in devising synthetic routes to macromolecules with precisely controlled primary structure, and to use those to assemble advanced nanostructured materials with novel properties and functions.[1]



Scheme 1: Schematic illustration for the preparation of stereospecific cyclic PMMA.

In this work, we report a synthetic route for preparation of an unprecedented stereospecific cyclic polymer that is constructed from achiral monomer building block methyl methacrylate (MMA). The devised synthetic protocol uses a combination of stereospecific living radical polymerization[2] and 'click' end-to-end cyclization techniques[3] (**Scheme 1**), to generate a cyclic syndiotactic poly(methyl methacrylate) (*st*-PMMA) with simultaneous control over molecular weight, tacticity and topology. The resultant cyclic *st*-PMMA was characterized via gel permeation chromatography (GPC), matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry, and ^{1}H NMR spectroscopy, and found to have high cyclic purity (> 93%).

The regulated primary structure enable the cyclic polymers to form unique supramolecular assemblies with the complementary linear stereoregular polymers (i.e., linear isotactic (*it*-)PMMA) through stereocomplexation. Compared to the conventional linear *st*-/*it*-PMMA stereocomplex,[4] the resultant stereocomplex prepared from cyclic *st*-PMMA and linear *it*-PMMA displayed an exclusive crystallization behaviour.

The self-assembly system presented in this study demonstrates hierarchical control over the primary structure of the polymeric precursors, their supramolecular assembly and the morphology of crystalline superstructures. The hierarchical control resulting from the tethering of chain ends of the macromolecular building blocks will set new directions of supramolecular chemistry. The reported synthetic strategy might pave the way for the development of advanced nanomaterials for molecular recognition, separation, and electronic applications.

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Amphiphilic Micellar Films via ATRP-Mediated Continuous Assembly of Polymers

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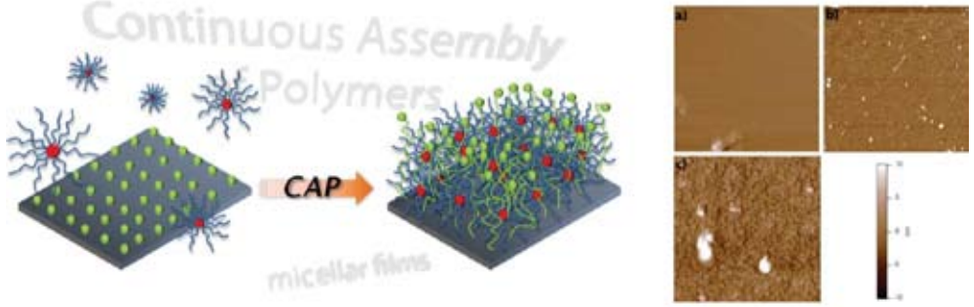
The development of highly efficient film fabrication technologies has enabled the generation of advanced materials for a diverse range of applications. Techniques including layer-by-layer[1] and surface grafting approaches[2] are among some of the commonly used methods in the production of such materials. Recently, the labs of Qiao and Caruso have developed a novel film fabrication technique, termed continuous assembly of polymers, CAP.[3–6] By polymerizing through pre-formed macrocross-linkers – defined as (bio)macromolecules functionalized with polymerizable moieties – from surface-anchored initiators, highly robust and versatile cross-linked films are formed via the CAP method. Thus far, the CAP approach has mainly employed linear homopolymers in film assembly processes and the use of sophisticated macromolecular architectures that could potentially lead to novel (bio)applications has yet to be fully explored.

In this work, the assembly of amphiphilic micellar films via the CAP approach is demonstrated (Scheme 1). Macrocross-linkers derived from polystyrene and poly(2-hydroxypropyl methacrylamide) block ccopolymers that form micelles are subjected to ATRP-mediated CAP reactions, generating films with unique surface morphologies and thicker films compared to linear homopolymers.



Scheme 1. Graphical representation of the assembly of micellar films via CAP and the difference in surface morphologies between linear and micellar films.

The use of micellar macrocross-linkers could open up many new and interesting biomedical applications given that the hydrophobic cores/pockets in the film allow for effective encapsulation of therapeutic molecules. These micellar films will lead towards the development of highly engineered multicompartment films as drug delivery vehicles as well as for catalysis and electronics applications.

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Research interests: controlled polymerization, click chemistry, radical spin traps, surface-initiated polymerization, star polymers, biomaterials, organic solar cells

Conducting polymer macroinitiators for surface-initiated ATRP

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Conducting polymer (CP)-based molecular brushes are a promising class of materials for stimuli-responsive or "smart" surfaces due the reversible transitions in chemical, electrical and mechanical properties that accompany their electrochemically-stimulated oxidation and reduction.[i] Brush-type structures are particularly suited to smart surface applications as desired properties may be introduced by functionalising a suitable substrate with polymeric sidechains. We have recently developed CP-based molecular brushes where the conformation of sidechains is influenced by applied electrical potential[ii] or salt concentration[iii]. We present here work on a new macroinitiatior for electrically conductive and electrochemically-active CP-based molecular brushes: poly(2-(2,5-di(pyrrol-2-yl)thiophen-3-yl)ethyl 2-bromopropanoate)) (PPyThon). The CP and its derivative brushes can be reversibly oxidised and reduced electrochemically in both acetonitrile and aqueous solution. Initial characterisations suggest that these systems possess a rich electrochemistry with the redox state of the CP backbone affecting surface conformation of the brushes.[iv] In our current work, PPyThon is grown directly on conductive substrates suitable for use as electrodes, which can then be used as macroinitiators for surface-initiated ATRP (SI-ATRP) techniques. **(Fig. 1)** The precursor monomer (PyThon) is very readily electropolymerised at low monomer concentrations and low applied potentials, and conductivity of the CP is superior to that of the well-characterised CP polypyrrole (PPy). PPyThon can also be copolymerised with PPy to influence conductivity and space out initiating sites. With careful control over parameters such as sidechain composition and grafting density, which are readily moderated via ATRP and CP structure respectively, PPyThon-based polymer brushes could allow reversible modulation of surface properties including wettability and interaction with molecules of significance for biomedical applications.

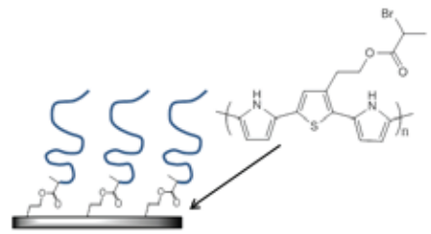

Figure 1. Scheme of PPyThon-based molecular brush, comprising conductive PPyThon backbone and grafted sidechains, on Au-coated substrate.

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[iv] Strover, L. et al. *Polymer.* **2013,** *54*, 1305-1317.

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Polypseudorotaxanes Made from Self-Assembly of γ -Cyclodextrins with Poly(*N* -isopropylacrylamide) End-capped Block Copolymers

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Cyclodextrins (CDs) constitute a series of cyclic oligosaccharides composed of 6, 7 and 8 D-glucose units linked by α-1,4 bonds (α-, β- and γ-CDs). The geometry of CDs is like a hollow truncated cone enabling to form a hydrophobic cavity, and as a result they can include not only small molecules but also polymers to give rise to polypseudorotaxanes (PPRs) and polyrotaxanes (PRs) after end-capping with bulky stoppers. Poly(*N*-isopropyl-acrylamide) (PNIPAAM) is a unique thermo-responsive polymer showing a lower critical solution temperature (LCST) at around 32 °C in aqueous solution. As previously reported[1], PNIPAAM is too bulky to pass through the cavity of α- and β-CDs so that it was used as end-capping polymer blocks in the preparation of PR-based block copolymers *via* atom transfer radical polymerization (ATRP). Attaching PNIPAM not only inhibits the slipping of α- and β-CDs off the polymer chain, but also imparts the thermo-responsibility to the copolymers.

Recently we have carried out ATRP of NIPAM initiated with PPRs self-assembled from 2-bromopropionyl end-capped Pluronic F127 with γ-CDs. Surprisingly those entrapped γ-CDs in the resulting PRs were found to be capable of moving over and slipping off the end-capping PNIPAAM blocks in DMF eluent during GPC analysis. To get further insight into whether those γ-CDs could encompass the PNIPAAM blocks, PNIPAAM end-capped block copolymers of PEG and Pluronic F68 were synthesized via ATRP, and then mixed with γ-CDs in aqueous solution to form PPRs. They were characterized by means of XRD, ^{1}H and ^{13}C CP/MAS NMR, TGA, FTIR and DSC analyses. For PNIPAAM homopolymer, γ-CDs could include it to form PPRs in very low rate and yield[2]. As for PNIPAAM-PEG-PNIPAAM, γ-CDs enabled to move over PNIPAAM to be entrapped on the PEG block to give loose-fit PPRs[3]. In the case of PNIPAAM-Pluronic F68-PNIPAAM, those γ-CDs tended to be resided on the PPO block showing the characteristic channel-type crystal structure. The WXRD and ^{13}C CP/MAS NMR spectra of PPRs created from the self-assembly of PNIPAAM-Pluronic F68-PNIPAAM with γ-CDs are shown in **Fig. 1**. It indicated that γ-CDs could encompass and move over the PNIPAAM blocks. A study on the conversion of these PPRs into the corresponding PRs and the dynamical simulation of γ-CDs encompassing PNIPAM process in DMF and aqueous solution using AMBER are under way in our laboratory.

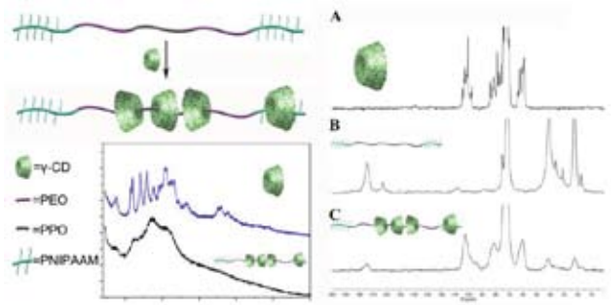

Figure 1. WXRD (left) and ^{13}C CP/MAS NMR (right) spectra of the self-assembly of PNIPAAM-Pluronic F68-PNIPAAM with γ-CDs.

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Smart Polymer Capsules with Synergistic Response to Biological Stimuli.

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The design of 'smart' delivery systems with precisely tuned response to their environment is integral to advances in areas such as biomedicine and energy. Self-assembled polymeric carriers have generated significant interest for such advanced applications due to the ease and versatility of these approaches. One important technique to design such carriers is the layer-by-layer (LbL) 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. Polymer capsules can be readily synthesised using this technique by assembly on a sacrificial template and have demonstrated significant potential for use as delivery systems.[1] Recently, we developed a new method to assemble LbL capsules based on combining LbL assembly with click chemistry to allow the synthesis of single-component capsules with tailored properties.

Polymeric carriers that respond to pH are of significant interest for biomedical applications as the internalization of such carriers typically occurs through acidic compartments of the cell, which have lower pH then the blood stream (pH 7.4). One interesting pH responsive polymer is poly(2-diisopropylaminoethyl methacrylate) (PDPA) as it has charge-shifting capabilities which correspond specifically within this pH range. Herein the synthesis of charge-shifting carriers based on poly(2-diisopropylaminoethyl methacrylate) (PDPA) will be presented.[2] The PDPA carriers have interesting properties for biomedical applications as they shrink at physiological pH enabling efficient loading of a range of therapeutic cargo but swell again below 6.4 when internalized into a cell. It will be demonstrated that PDPA carriers can be designed to respond synergistically to multiple cargo eg. pH and redox, thus optimizing degradation efficiency once at the targeted site. The degradation rate of these carriers can also be tuned by systematic changes in crosslinking degree[3] and by using specific enzyme cleavable components. This study provides important fundamental insights into the use of responsive crosslinkers in such nanoengineered carriers.[3]

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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Substrate-Independent Thermal Nanoimprint Lithography by Using Mussel-Inspired Adhesive Polymer Layers

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Requirements for nanoscale structures have forced researchers to develop novel fabrication techniques. Nanoimprint lithography (NIL) is one of the state-of-art microfabrication technologies realizing nanoscale two-dimensional features by simple embossing of a surface template mold onto polymeric resins. In any NIL processes, there are two important interfaces affecting quality and throughput of NIL processes; one is the mold–resin interface and the other is the resin–substrate interface. There are a few studies about the resin–substrate interface, nevertheless low adhesion of the interface induces exfoliation of polymeric resin layers from the substrate during the mold removal process. Due to the exfoliation, imprinting of hydrophobic polymeric resins on hydrophilic substrates or inverted hydrophobicity combinations is difficult. Moreover, there are no obvious pathways in the NIL technologies to form polymeric patterns on low surface energy substrates such as poly(tetrafluoroethylene) (PTFE). In this paper, we show the first demonstration of a substrate-independent thermal nanoimprint lithography (T-NIL) process by using a mussel-inspired amphiphilic polymer as an adhesive layer (Figure 1(a)). Since the thin adhesive layer comprised of the mussel-inspired amphiphilic polymer (Figure 1 (b)) strongly bound substrates and polymer layers, surface patterns successfully transferred onto polymer layers by T-NIL process without any exfoliation even at near the glass transition temperature of the polymer. By using this biomimetic T-NIL process, surface patterns successfully transferred even onto a PTFE substrate, which is one of the most non-adhesive materials (Figure 1 (c))[1].

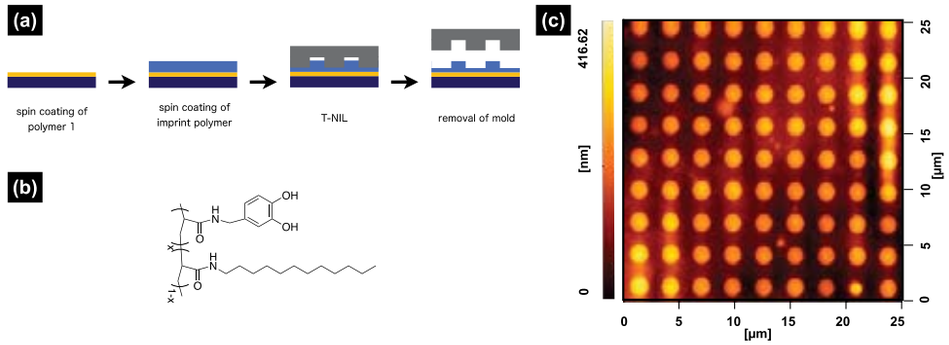

Figure 1. Schematic illustration of T-NIL process (a), chemical structure of amphiphilic copolymer (b), and atomic force microscope image of surface patterns formed on a polystyrene and amphiphilic copolymer coated glass substrate (c), respectively.

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Adhesion Improvement Of Poly(Dimethylsiloxane) Surface By Grafting Of Poly(Butyl Acrylate) Chains

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The structure of Gecko's feet is extensively microstructured, enabling Geckos to adhere strongly to most surfaces and perform various maneuvers, even upside down. Inspired by the structure of Gecko's feet, a large number of biomimetic dry adhesives have been reported[1,2]. Biomimetic polymer-brush modified surfaces can offer a large number of attachment points to surfaces and this could result in improvement in adhesion[3]. ATRP is a convenient tool for producing well-defined biomimetic dry adhesive surfaces: the ease of polymerization procedure, ability to process large surface areas, a large choice of monomers and control over the polymerization allow production of modified surfaces on large scale with properties tailored to target applications[4].
To study the effect of polymer brushes on adhesion, Atom Transfer Radical Polymerization (ATRP) was used to graft polymer brushes on a poly(dimethylsiloxane) (PDMS) surface. Poly(butylacrylate) chains were chosen as grafts. PDMS samples with grafted poly(butylacrylate) chains were obtained with varying degree of polymerization. Growth of polymer brushes was verified by ATR-FTIR spectroscopy. Ellipsometric measurements were made on Silicon wafer modified with poly(butylacrylate) using same surface immobilized initiator and under similar conditions. To establish relationship between polymer brush thickness and the adhesion strength, all samples were tested for pull off adhesion. In general, polymer-brush modified samples showed an increase in adhesion compared to unmodified samples. In modified PDMS samples, adhesion strength increased generally with polymer brush thickness. In future such modification of biomimetic structure by polymer chains can offer a low-cost solution for improvement of adhesion in such systems, by avoiding use of highly expensive nano-fabrication techniques.

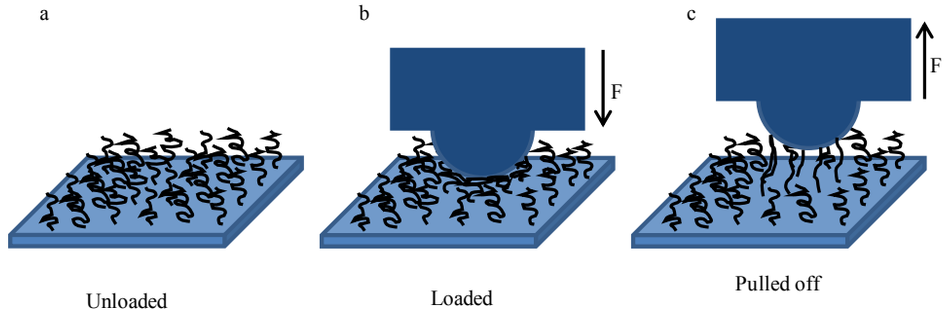

Figure 1. Schematic representation: (a) polymer-brush modified surface; (b) behavior of polymer brush under loading; (c) behavior of polymer brush under unloading.

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A Universal Approach to Growing Biological Fouling Resistant Coatings from Polymeric Membrane Surfaces Using an Adhesive Polydopamine-Mimetic Initiator

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Biofouling is caused by the attachment of microorganisms to membrane surfaces and the subsequent growth of colonies on the surface. The microorganisms and their secretions of adhesins, exopolysaccharides and proteins form a biofilm that is stabilised by weak physico-chemical interactions including electrostatic, hydrophobic and van der Waal's interactions. Biofilms lead to negative effects, such as a reduction in water flux, and the need for intensive cleaning processes and degradation of the membrane surface. Indeed, mature biofilms have been shown to be resistant to harsh antimicrobial treatments, and therefore it is more desirable to seek approaches that mitigate biofilm formation. In this work we report on a study conducted to examine the biofouling resistance of a zwitterionic, polysulfobetaine (p3SBMA) coating applied to polyamide Reverse Osmosis (RO) membranes at varying thicknesses, and its effect on membrane permeation properties.

To improve improve biofouling resistance, polyamide membranes were modified by first depositing an adhesive polydopamine-initiator primer coating (PDOPA-initiator), followed by polymeric grafting of zwitterionic sulfobetaine monomer (SBMA) using ARGET (activators regenerated by electron transfer) ATRP to achieve a PDOPA-g-pSBMA coating. The thickness of the polymer coating was tuned by varying the polymerisation growth time. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopic analysis confirmed the coating deposition, and Water Contact Angle (WCA) measurements showed that there was a significant increase in the hydrophilicity of all coated membrane surfaces relative to the uncoated membrane surface. Results showed that after grafting p3SBMA for 1, 3, 6 and 24 hr on the initiator-modified RO membranes that the WCA measurements were 11 ± 4°, 11 ± 3°, 11 ± 1° and 9 ± 1°, respectively, whereas the WCA for the uncoated membrane was 39 ± 2°.

Permeation tests carried out at 400 psi revealed that a reduction in pure water flux (20-37%) was observed for pDOPA-g-p3SBMA modified membranes with longer polymerisation times (3, 6 and 24 hr) compared to the unmodified membranes. However, this reduction was less than reported in the literature for polyethylene glycol modified RO membranes and polysulfobetaine modified RO membranes prepared by Initiated Chemical Vapor Deposition.[1,2] Furthermore, the coatings did not impair the salt rejection properties of the modified membranes.

Bacterial growth on both pDOPA-g-p3SBMA coated and uncoated membranes exposed to a nutrient solution were compared to probe the effect of pDOPA-g-p3SBMA on their biofouling resistance. A greater resistance to bacterial deposition was found for pDOPA-g-p3SBMA modified membranes with respect to uncoated membranes. In addition, there was a decrease in the number of bacteria on the pDOPA-g-p3SBMA modified membranes with increasing coating thickness; however, the difference was not statistically significant. Similarly, protein adhesion tests using a fluorescently tagged Bovine Serum Albumin (BSA) solution showed a significant decrease in the amount of adsorbed BSA protein on pDOPA-g-p3SBMA coated RO membranes compared with the uncoated RO membranes.

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Chlorinated plasma polymers: "one-step" non-fouling polymer coatings

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Surface fouling due to adhesion of bacteria and/or other microorganisms causes substantial technological problems and financial losses in various areas of modern society. Therefore there is a demand for cost-effective and reliable surface treatment or coating methods that can achieve resistance to bio-adhesion without changing the mechanical properties of materials and devices [1].

Plasma polymerisation offers unique advantages for producing thin coatings on a wide range of substrate materials, and plasma methods have been used for a variety of purposes in the area of biomedical coatings [2]. However, so far plasma polymers have not demonstrated good resistance to bacterial colonisation; while for example a heptylamine plasma polymer does reduce bacterial attachment to some extent, the reduction is not sufficient, and good results have only been achieved when coupling antibacterial molecules onto plasma polymer surfaces [3]

We here report the "one-step" fabrication of highly effective antibacterial coatings, by the plasma deposition of highly chlorinated polymers, using the appropriate monomers. Such coatings resist the attachment and biofilm formation of bacteria such as *Staphylococcus epidermidis* and *E. coli*. They also resist the attachment of eukaryote cell lines such as m3T3 and KG1a.

The exact mechanism of this biofouling resistance is as yet unknown and is a major focus of ongoing research.

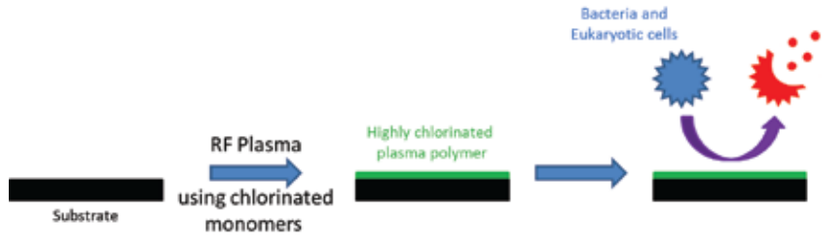

Figure 1. General scheme of "one-step" non-fouling polymer coatings

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(3) Vasilev, K.; Griesser, S. S.; Griesser, H. J. *Plasma Processes and Polymers* **2011**, *8*, 1010.

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PDMS for Ethanol Pervaporation – A hydrophilic material?

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Membranes for pervaporation have come a long way in recent years, but for an emerging biofuels market the use of organophilic materials for separation of residual water obtained by ethanol/water distillation is visibly evolving as a preferred choice for purification[1]. While pervaporation for the removal of an ethanol-rich fraction from water-rich water/ethanol mixtures has not been commercially applied, the benefits of this technique regarding cost and energy efficiencies are apparent, and the possibility of achieving continual fermentation should not be overlooked.

Polydimethylsiloxane (PDMS) is an extremely resilient and versatile material used in many industrial, domestic and scientific applications. Our goal is to extend the useful range of this elegant material for pervaporation by modifying hydrophobic character without compromising its desirable properties (i.e. structural integrity, elasticity and chemical resistance). This research is directed towards developing an improved model for pervaporation of water/ethanol mixtures and a proof-of-concept illustration that selectivity and flux can be improved by incorporating a grafted layer of hydrophilic polymer on a hydrophobic pervaporation membrane.

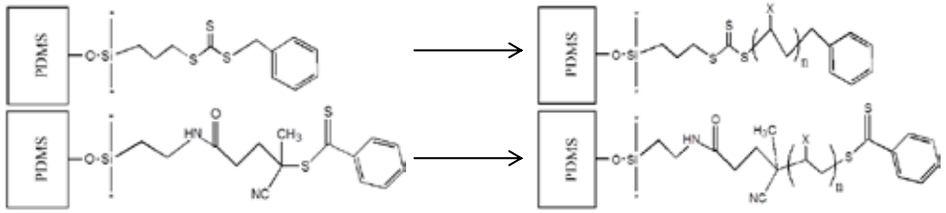

Figure 1: Reaction schemes for RAFT grafting

By disrupting the strong hydrogen bonded network between ethanol and water, we hope to encourage the formation of water clusters at the liquid-membrane interface reducing rates of water diffusion.

Our previous work has shown[2-4] robust techniques for controlled surface grafting using RAFT (Reversible Addition Fragmentation Chain Transfer) and ATRP (Atom Transfer Radical Polymerisation) in the presence of oxygen. Currently, Z- and R-supported RAFT polymerisation from the PDMS surface (**Fig. 1**) have been applied to increase surface-graft densities.

Polyacrylic acid (PAA), polyacrylamide (PAM), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), and poly(glucose acrylate) have been grafted to PDMS substrates **(Fig. 2)**. The properties of these hydrophilic layers are in each case to a degree 'tunable' through addition of salts and changing pH.

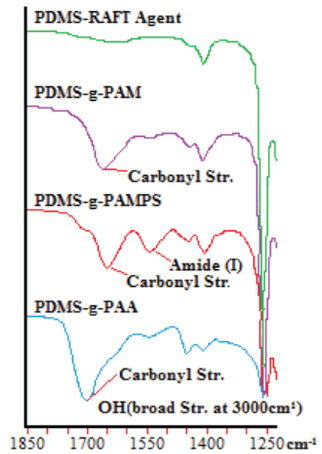

Figure 2: PDMS FT-IR analysis

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[2] R. P. Prangley, A. D. Wallace, E. J. Smith, C. M. Fellows, 12th Pacific Polymer Conference, Abstract **(2011)**
[3] R. P. Prangley, A. D. Wallace. C. M. Fellows, 11th Pacific Polymer Conference, Abstract, Cains **(2009)**
[4] A. D. Wallace, C. M. Fellows, 30th Australasian Polymer Symposium, Abstract 33, Melbourne **(2008)**

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Stimuli-responsive materials from genetically engineered Protein-polymer AN16

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Engineering stimuli-responsive polymers through supramolecular self-assembly has been a major focus of recent research. Recent advancement in cloning techniques including concatemerization and more efficient overlap-extension rolling circle amplification (OERCA) have stimulated rational protein engineering approach in molecular design and development of biomimetic protein-polymers of controlled size and molecular architecture.[1] Resilin is a member of the family of elastic protein, which has been recognized long for its unique role in jumping, flying, and sound production mechanism in insects. Elvin *et al*.[2] first reported an elastomeric protein *rec*1-resilin using the *Drosophila melanogaster* gene encoding resilin. Dutta *et al*.[3-5] identified the protein to be multi-stimuli responsive, exhibiting uncommon dual-phase behavior (DPB, occurrence of both UCST and LCST) and unusual resilence characteristics >94% upon cross linking. The protein also potentially served as a functional template in synthesis of optically coupled hybrid architectures of gold nanoparticles[6]. Recently, Lyons *et al*.[7] employed a recursive cloning strategy to synthesize a consensus polypeptide *An*16-resilin from genes encoding resilin of blood sucking mosquito *Anopheles gambiae*. The resulted protein represented a periodic polypeptide consisting 16 copies of a 11-residue repeat sequence: GlyAlaProAlaGlnThrProSerSerGlnTyr, almost entirely of perfect repeats unlike *rec*1-resilin. With a view to understand its physico-chemical characteristics, we have examined, for the first time, the effects of pH, temperature, photon, ions, and humidity on its conformation, self-assembly, photophysical property, stability and molecular chain dynamics and report its distinctive stimuli-responsive characteristics.

Using discrimination of secondary structure class routine (DSC) we predict that the secondary structure of An16 is completely devoid of α-helices/β-sheets and exhibits random-coil configurations. This prediction was well supported by the experimental evidence from circular dichroism (CD) spectroscopy. Furthermore, the corresponding degree of compactness of the protein was derived using Kratky plot from small angle scattering experiments and identified to be unfolded, random coil. Experimental zeta potential measurement as a function of pH delineates the surface of *An*16 to be negative at neural pH and positive at acidic pH with isoelectric point (IEP) at pH ~4.8.

*An*16 exhibits distinctive photophysical properties that arise from the tyrosine amino acid residues in the structure. The optical density spectrum showed red-shifting of the peak absorbance from 275 to 295 nm suggesting ionization of the Tyr residue at basic pH (≥10). No shift was observed in acidic pH. This distinctive optical responsiveness of *An*16 is similar to that of *rec*1-*resilin* mutant and can be compared to GFP-based chromophores, representing a structural basis for functioning as molecular sensors. We also demonstrate that self-assembly pathway (@ pH 7.4) of An16 as a function of temperature exhibit occurrence of the uncommon DPB. However, this prototype is observed to be highly concentration dependent -with UCST clearly appearing for protein solutions of concentration ≥ 3% w/v and is concentration dependent. Nonetheless, LCST does not depend on concentration. Further, thermoresponsiveness of *An*16 was tested for change in UCST with SO_4^{2-} (kosmotrope) following Hofmeister series to illustrate the mechanism of transformation behaviour as interaction between the anions and adjacent hydration shells.

In summary, genetically engineered *An*16-resilin is identified to be multi-stimuli-responsive, unfolded, random-coil protein with complex organization and exhibiting tunable phase behavior and photophysical properties, whichhas the potential applications as intelligent bio/nanomaterials

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"Click" Chemistry – a novel fabrication method for fabricating microfluidic devices using thiol-ene polymers

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Off stoichiometric thiol-enes (OSTEs) which exhibit rapid UV curing, low volume shrinkage and optical transparency have been recently developed for use in a new polymeric microfluidic platform.[1] The OSTE pre-polymer can be cast onto standard SU-8/ silicon masters and polymerised using a UV-lamp, making it ideal for rapid prototyping.[1] Due to the off stoichiometric ratios, the mechanical properties of the OSTE polymer can be modified allowing for the tuning of the polymers physical properties for fabrication of microfluidic devices.[1] Here, we investigate the bulk and surface characteristics of 90% excess thiol (OSTE-90), and 30 % excess allyl (OSTE Allyl-30) fabricated OSTE polymers (**Fig. 1**). We report on the development of a novel colorimetric test for thiol functionality on the surface of the OSTE polymers and also subsequent surface modifications using gold nanoparticles and thiolated DNA. Evidence of modification of the OSTE platform is shown by UV-Vis spectroscopy, atomic force microscopy and fluorescence microscopy. The results show the versatility of the OSTE polymers and highlight their potential for future microfluidic diagnostic platforms.

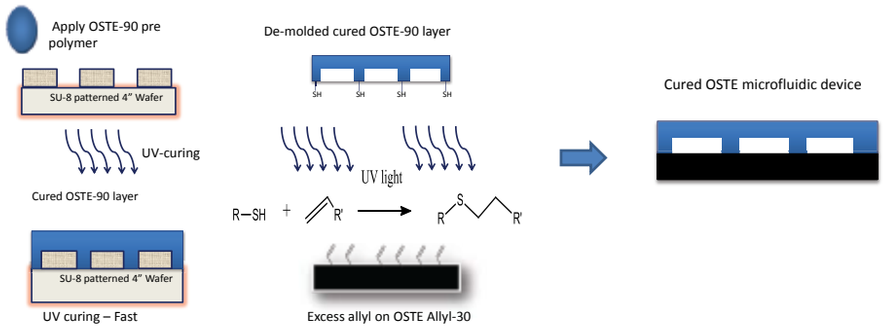

Figure 1. UV–curing of an OSTE-90 polymer and UV-initiated bonding of the OSTE-90 and OSTE Allyl-30 polymers.

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Modification of Carboneaous Nanomaterials using RAFT

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Carbon nanotubes (CNTs) and carbon nanodots have many potential uses in applications such as water treatment membranes and fingerprinting. To make carboneaous materials useful for these applications there is often a need to modify them, or embed them, into a polymer matrix. Given that these materials are reasonably chemically inert their surface chemistry is often limited. Here we report on the modification of carbon nanotubes (Fig. 1(a)) and fluorescent carbon dots (Fig. 1(b)) with RAFT agents and their use in surface initiated reversible addition fragmentation chain transfer (RAFT) polymerisation to graft polymer from the surfaces. We demonstrate the covalent attachment of vertically aligned (VA) acid treated CNTs onto a silicon substrate via dicyclohexylcarbodiimide (DCC) coupling chemistry. The CNTs were then modified with bis(dithioester) moieties which acted as a chain transfer agent (CTA) in the polymerisation of styrene from the surface. Atomic force microscopy (AFM) verified vertical alignment of the SWCNTs and the maintenance thereof throughout the synthesis process. Finally, Raman scattering spectroscopy and AFM confirmed polystyrene functionalisation.

In a separate approach we fabricate fluorescent carbon dots modified with a CTA and graft polydimethylacrylamide from the surface. We then demonstrate their use in a powder as a fingermark developing agent.

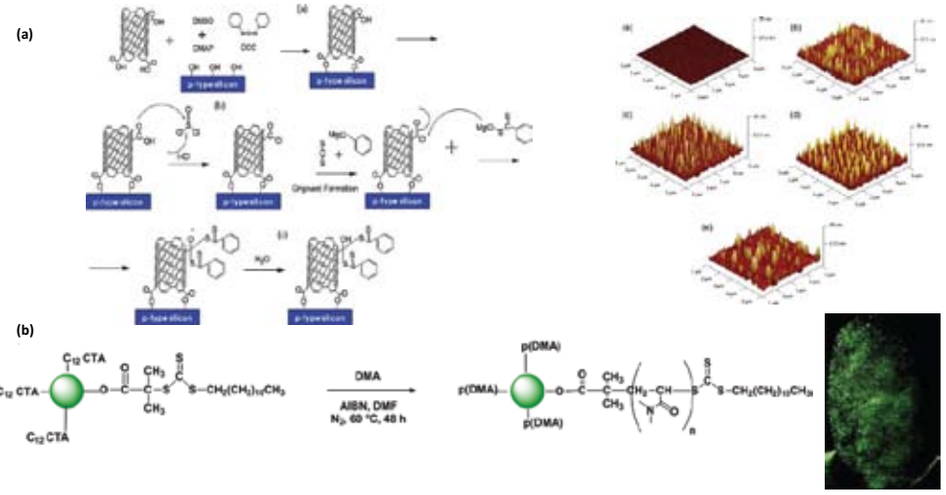

Figure 1. (a) Left: Schematic of the fabrication of VA-bis(dithioester) SWCNTs, Right: 3D AFM images of vertically aligned modified CNTs (b) Left: Carbon dots modified with a CTA and PDMA, Right: Fingermark developed using the fluorescent PDMA/carbon dots.

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Coating Graphene Oxide via RAFT-Mediated Emulsion Polymerization

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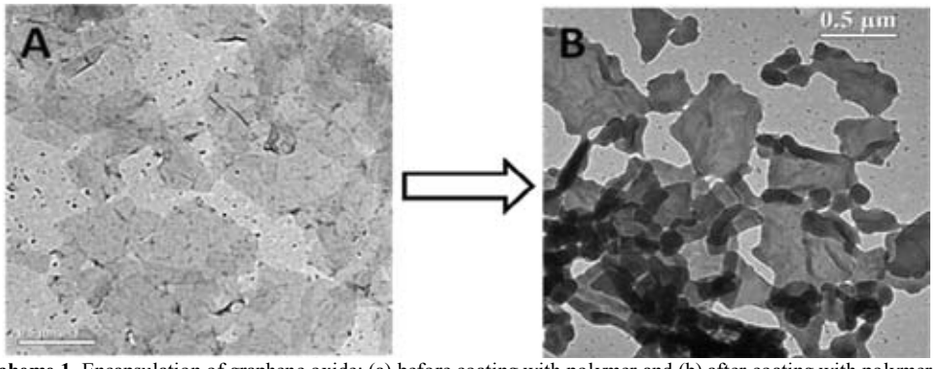
Graphene has currently gained world-wide attention due to its extraordinary mechanical, optical, thermal, and electrical properties. These unique characteristics of the two-dimensional (2D) material make it possible for numerous applications in electronics, novel composites, biosensors, and a range of biological applications including drug delivery and medical imaging. However, the strong tendency of single-layer graphene nanosheets to undergo agglomeration into multilayered graphene because of strong π-π and Van der Waals interactions can have a significant effect on final material properties.[1]

Graphene oxide (GO), a product of graphene oxidation, has been recently employed as an alternative option because it can be easily convert back to graphene and be readily dispersed in water and polar solvent. Various strategies consisting of chemical and physical surface modification have been developed to control the dispersion of GO, limit reaggregation, and enhance compatibility with a receiving host matrix. One of the promising approaches involved covalent bond attachment of RAFT groups onto the surface of GO and subsequent growth polymer via RAFT polymerization. This is, however, time-consuming and not suitable for large-scale production. A possible solution to all such problems is a robust coating method using RAFT-mediated polymerization, which has recently evidenced to successfully modify the surface of various materials such as pigments and carbon nanotubes.[2]

In this study, polymeric encapsulation of GO via RAFT-mediated emulsion polymerization was successfully reported. Poly(allylamine hydrochloride) was initially used to alter the charge on the surface of GO to enhance the adsorption of negatively charged macro-RAFT copolymer onto the surface via electrostatic interactions. Macro-RAFT copolymer stabilized GO was coated by starve feed a mixture of methyl methacrylate and butyl acrylate. The resulting latex containing uniform polymer-coated GO where polymer layer thickness can be tailored by the amount of monomer fed into the system. This method also allowed to encapsulate GO with a temperature responsive polymer, poly(N-isopropylacrylamide). The encapsulated GO appeared to be dispersible in both polar and nonpolar solvents.



Scheme 1. Encapsulation of graphene oxide: (a) before coating with polymer and (b) after coating with polymer

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Functional (Bio)Surfaces for Reversible Coatings

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The present contribution will describe how modular synthetic strategies in polymer chemistry can be employed to obtain functional, structured and reversibly coated bio- and bioinspired surfaces. The specific protocols to be addressed include fast and mild thermally driven as well as photo-induced Diels-Alder based ligation chemistries. It will be demonstrated how such conjugation chemistries can be employed to alter the chemical and physical properties of biosubstrates. For instance, an access route to peptide and polymer modified cellulose will be highlighted, where the peptide segments allow for the excecution of specific functions. The light driven polymer modification of cellulose materials will additionally be highlighted. Further, the lecture will introduce a universal bioinspired mussel adhesive based surface coating technique able to provide the reversible attachment and detachment of tailor made polymer strands via reversible Diels-Alder chemistry.

The synthetic efforts will be underpinned by the in-depth characterization of the obtained modified materials via surface sensitive characterization techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Tof-SIMS, Fourier transform infrared (FT-IR) spectroscopy as well as Fourier transform infrared microscopy.

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Self Healing Hybrid Coating for Harsh Environment

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Self-healing material can repair itself in response to failure in an autonomous manner. Self-healing is a desirable property of a coating on a metallic substrate to help arrest the development of micro-cracks and the propagation of corrosive species to the interfacial layer and eventually to the substrate. The majority of the metallic materials particularly active metals such as carbon steel on exposure to environmental conditions during their applications deteriorate and fail prematurely. Such items may become corroded over relatively short period of time in salt water environment. Recently, many approaches[1-4] to self-healing have emerged, which are primarily based on liquid phase and phase separated healing agent; however, they have the limitation to supply the healing agents repeatedly at the damaged area. The use of hollow tube or capsule with controlled release active ingredient offers a novel approach to deliver sustainably the anticorrosive agents at the crack plane. With a view to achieve such self-healing characteristics, nanotubes and capsules have been employed as nanocontainers for active ingredients in a new generation of protective coating. The potential of active ionic liquid entrapped nanotube and microcapsules in coating layer has been explored as protective self-healing layer on metal. Polymerizable ionic liquid (PIL) with different alkyl chain lengths was also synthesised and employed as corrosion inhibitors for their strong physical adsorption characteristics on metal surfaces and ability to form polymeric barrier. Characterisation of these coatings was performed by thermal, spectroscopy, microscopy and electrochemical experiments[5-7]. The release results of the anticorrosion agent from the nano/micro-containers demonstrate a sustained release behavior efficient for corrosion protection and self healing characteristics. The spectroscopic, microscopic and electrochemical evaluations demonstrate strong adhesion properties of such coatings compared to the conventional silane based systems and confirm the increased barrier protection of the coating system. The details of the structure property relationship of the self-healing coating developed and their mechanism of action will be discussed.

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Elaboration and properties of multiphase systems based on thermoplastic chitosan

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In the last years, biopolymers have attracted great attention due to their large availability, renewability, biocompatibility, and biodegradability[1]. It is for instance the case of chitosan, a linear polysaccharide consisting of (1,4)-linked 2-amino-deoxy-β-D-glucan. It is a deacetylated derivative of chitin, which is the second most abundant polysaccharide found in nature after cellulose. Chitosan has been found to be nontoxic, biodegradable, biofunctional, and biocompatible in addition to having antimicrobial and antifungal properties, and thus has a great potential for environmental (e.g., packaging) or biomedical applications. It is worth noting that, for preparing chitosan-based materials, only solution casting or similar methods have been used in all the past studies. Solution casting is known to have the disadvantage in low efficiency and difficulty in scaling-up towards industrial applications. In addition, a great amount of environmentally unfriendly chemical solvents are used and released to the environment in this method. The reason for not using a melt processing method like extrusion or kneading in the past studies is that chitosan, like many other polysaccharides such as starch, has very low thermal stability and degrade prior to melting. Therefore, even if the melt processing method is more convenient and highly preferred for industrial production, its adaptation for polysaccharide-based materials remains very difficult. While the processing issues of starch has been emphasised to some extent[2-4], there has been very limited focus on the melt processing of chitosan-based materials.
However, our recently published study[5] has demonstrated the successful use of an innovative melt processing method (internal mixer) as an alternative route to solution casting, for preparing materials based on thermoplastic chitosan.
These promising thermoplastic materials, obtained by melt processing, have been the main topic of recent international projects, with partners from different countries (see below[*]). For instance, multiphase systems based on various renewable plasticizers have been elaborated and studied[6]. More recently, different nano-biocomposites based on montmorillonite have been processed and analysed. The effects of nanoclay content, organomodification, preparation method on the structure, properties, and biodegradation of the plasticised chitosan-based nano-biocomposites have been examined.

(*) **International partners:** (i) **CSIRO (Clayton-Australia):** Dr. K. Dean, Dr. P. Sangwan, Dr. C. Way, Dr. X. Zhang; (ii) **Ecole Polytechnique de Montréal (Canada):** Pr. M.C. Heuzey, Pr. A. Ajji, M. Matet; (iii) **University of Queensland (Brisbane-Australia):** Pr. P. Halley, Dr. F. Xie; (iv) **University of Strasbourg (France):** Pr. L. Avérous, A/Pr. E. Pollet, Dr. V. Martino

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Biobased polymer processing

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Our labs have focused on many areas of bio-based polymer processing including the structure-property-processing-biodegradation relationships of thermoplastic starch polymers [1-3], highlights of rheological and processing understanding for scale-up [4] and novel fundamental work on the genetics-molecular structure-property relationships of model starch polymers [5,6]. Extensions of this work to recent ionic liquid plasticisation of thermoplastic starch and effect of extrusion processing parameters on thermoplastic starch extrusion will be specifically highlighted in this paper.

Clearly thermoplastic starch based polymers offer a very attractive low cost base for new biodegradable polymers due to their low material cost and ability to be processed on conventional plastic processing equipment. The engineering of more advanced properties into this low cost base materials will continue to be the main technological drive into the future. This development will most probably be in the form of integrating research already being developed in parallel from (a) thermoplastic starch polymer formulation (alike blending, alternative plasticisation, nanocomposites and reactive modification) and (b) better understanding of processing conditions on extruded starch structure and properties (gelatinization, plasticization, retrogradation (molecular weight loss) final material structure and properties). This paper will examine recent results of ionic liquid plasticization (aim: reduce temperatures required for gelatinization, achieve better plasticization, reduce plasticizer loss) and statistical design of experiment (DOE) analyses of thermoplastic starch extrusion parameters on starch properties.

Acknowledgements to over 40 researchers who have worked on this work since 1995 and to funding from the CRC for International Food Manufacture and Packaging Science, the Australian Research Council, The University of Queensland, Plantic Technologies and CRC Polymers.

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Synthesis of glycerol-based oligomers: new materials and new applications

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Glycerol is a one of the most important feedstock in the modern oleochemical industry[1] obtained by saponification of fats or as a coproduct in the production of biodiesel by transesterification of vegetable oils. Due to its competitive cost, worldwide availability, and built-in functionality, the glycerin and its derivatives are useful for numerous commercial applications. As glycerin demand is nowadays exceeding supply, the emerging trend is on the development of higher-added value applications of the latter. As a result, glycerol is increasingly being used in industry in the synthesis of numerous chemical intermediates (epichlorhydrin, propylene glycol, glycerin carbonate (GC), solketal (Sol), acrylic acid …). We focused on glycerin carbonate acrylate (GCA) and solketal acrylate (SolA) which can be synthesized from glycerol.[2] We report here the synthesis of low mass polymers (oligomers) such as oligoGC and oligoSol by radical telomerization process. Furthermore, to avoid the poor solubility of polyGC, we develop the copolymerization of GCA with SolA as the latter proved to be soluble in various solvents and could lead to an enhancement of the GCA-based polymers solubility. The resulting oligomers (oligoGC, oligoSol, and oligo(GC-*stat*-Sol)s) were characterized by NMR and FTIR spectroscopies, size exclusion chromatography (SEC) and MALDI-Tof. It appeared that low molar mass cotelomers permitted to modulate the properties of the resulting glycerol-based oligomers, which will probably lead to further developments, for rechargeable lithium batteries for instance.

The free-radical telomerization of GCA and SolA monomers was achieved in acetonitrile with AIBN and 2-mercaptoethanol (ME) as telogen at 80 °C for 8 hours with different molar ratios R_0 ($R_0 = n_{telogen}/n_{monomer}$) ranging from 0.05 to 0.3. The structure of oligoGC and oligoSol were confirmed by MALDI-Tof mass spectroscopy. The oligoGC was easily precipitated in cold ethanol whilst the oligoSol was miscible in common organic solvents except diethylether. As a consequence, precipitation of oligoSol was difficult for high R_0 (0.1, 0.2 and 0.3). These results prompted us to investigate the cotelomerization between GCA and SolA in order to enhance the solubility of oligoGC and the precipitation of oligoSolA. As a result, several oligo(GC-*stat*-Sol)s bearing various GCA/SolA ratios were synthesized (Figure 1). Whatever the co-oligomer, its experimental GCA/SolA ratio was consistent with the theoretical one. We evaluated the solubility of the oligo(GC-*stat*-Sol)s with different compositions. Interestingly, the solubility of oligo(GC-*stat*-Sol)s with various GCA/SolA ratios was intermediate between the one of oligoGC and the one of oligoSol. The solubility of oligo(GC-*stat*-Sol)s increased with SolA/GCA ratio. In summary, the incorporation of SolA in GCA structure by cotelomerization solved GCA problem of solubility.

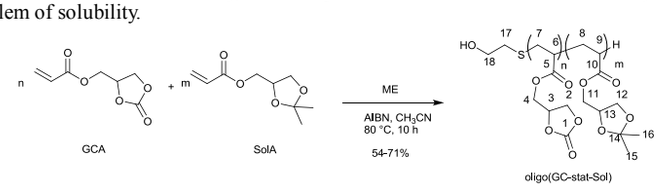

Figure 1. Cotelomerization of GCA and SolA in the presence of ME, achieved with different GCA/SolA ratios.

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Understanding starch degradation mechanism at multiple structural levels during extrusion

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The degradation mechanism of starch during extrusion was investigated by examining multiple levels of starch structures. Three types of starches with different amylose contents (0 - 63 %) were extruded, with extrusion conditions—temperature, screw speed, and plasticizer content—being varied. Analysis using size-exclusion chromatography of whole (fully branched) starch molecules showed that amylopectin molecules of all three types of starches were degraded, whereas amylose molecules remained relatively unchanged. Regardless of starch type, more intact (less degraded) amylopectin molecules or a lower amount of degraded starch (small amylopectin molecules) was observed with the starch was extruded at lower temperature (105 °C), higher plasticizer content (40%), and lower specific mechanical energy (SME, 220 - 390 kW h t^{-1}). The presence of granular structure and the residual A- or B- type of crystallinity in the starch extrudate, as revealed by light microscopic images and X-ray diffractograms, respectively, suggested that the remaining intact amylopectin molecules in the starch extrudate were from the ungelatinized or partially gelatinized starch granules being protected from shear and thermal degradation. Starch is more gelatinized when it is processed at higher temperature and/or higher energy, such as SME. The molecules in starch melt are not protected by the granular and crystalline structures against shear and thermal degradation, thus leading to higher molecular degradation.

Keywords: amylose, degradation, structure characterization, specific mechanical energy

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A Parameterized Model of Amylopectin Synthesis provides key insights into the Synthesis of Starch

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Starch is the dominant component of our daily calorie intake. It is a complex branched polymer of glucose, synthesized by the biosynthetic pathway in living plants. Its properties are largely determined by its branching structure. For example, the semi-crystalline structure formed by the branches of the amylopectin fraction of starch is of critical biological and economic importance, as this structure allows plants to store carbon at high density in an osmotically inert form. Understanding the formation of the structure is important for manipulating starch structure and functionality.

The modelling of starch structure presented here, based on our previous work,[1] adopts a battery of techniques for modelling the molecular weight distribution (MWD) of linear polymers in synthetic polymer science. The MWD of the branches in starch is termed the chain-length distribution (CLD), experimentally obtained by the enzymatic debranching of starch followed by characterization of the resulting linear chains by techniques such as SEC. The model of the CLD is based on the core enzymatic mechanisms defined by genetic and biochemical studies. The core enzymes are starch synthases (SSs) which cause chain propagation, starch branching enzymes (SBEs) which create branches, and debranching enzymes (DBEs) which remove branches; all have analogies to, but are more complex than, corresponding processes in synthetic polymers. It is assumed that one of each of SS, SBE and DBE forms an enzyme set, and the CLD is governed by the actions of multiple enzyme sets. Quantitative agreement between the modelled and experimentally obtained CLDs for various botanical backgrounds supports the precepts of the model.

This model is the first tool allowing the amylopectin CLD to be parameterized by a small number of meaningful mechanistically-based parameters, which proves useful in understanding higher-level structure.[2] The model also gives new in-depth understanding of several aspects of starch biosynthesis and structures. (1) To generate crystalline starch, defined restrictions on particular ratios of enzymatic activities apply. (2) An independent confirmation of the conclusion, previously reached solely from genetic studies, of the absolute requirement for debranching enzyme in semi-crystalline amylopectin synthesis. (3) The model provides a mechanistic basis for understanding how successive arrays of crystalline lamellae are formed based on the identification of two independent types of long amylopectin chains, one type remaining in the amorphous lamella, while the other propagates into, and is integral to the formation of, an adjacent crystalline lamella.

Quantitative understanding of the structure of starch can potentially accelerate efforts in understanding starch biosynthesis using a series of testable predictions based on a robust mechanistic framework as set out by the model. It also shows new ways to alter the structure of starch by tuning the actions of SBEs to produce starch with improved properties such as slower digestibility, which is of major importance in the prevention of diabetes and obesity.

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The influence of starch amylopectin molecular structure on the native crystalline-amorphous lamellar structure.

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Starch is a highly branched polymer of glucose, with multiple scales of structural levels. The molecular and crystalline-amorphous lamellar structures of starch are important to many important starch properties such as the gelatinization, gelling, viscosity and digestion. There is, however, a significant knowledge gap about the influence that varying amylopectin (the hyperbranched component of starch which is responsible for the creation of the crystalline-amorphous lamellae) structures exert on the lamellar structures. A series of 11 waxy starches were examined and the following data was produced: the chain length distribution (CLD) of the molecular structure using size exclusion chromatography, and the scattering pattern of the lamellar structure using small angle X-ray scattering. The experimental data was parameterised using a new biosynthesis-based model[1] for statistical analyses and strong correlations between molecular and lamellar parameters were observed. The distribution of the average size of the crystalline-amorphous lamellar repeats was directly linked to increases in the number of larger lamellar repeats.[2] An increase in the number of the shortest starch chains was found to decrease the number of larger lamellae present. Increases to the size of the lamellae were produced by increasing the steepness slope of the chain length distribution, showing that fewer long chains in the linear areas of the CLD produce fewer chains which are capable of forming longer crystalline portions in the crystalline region of the lamellae. Increases in the length of the shoulder region of the CLD was also responsible for increases in the size of the crystalline-amorphous repeats, it is proposed that this increase in the size of the lamellae is due to increases in the size of the amorphous lamella region. This can be understood in terms of the effects of the CLD on the way these branches arrange themselves into microcrystalline structures. It also suggests that the lowest level of starch structure, that of the individual branches, heavily influences a higher level of structure, the arrangement of these branches in space.

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Hybridization of Chitosan and Inorganic Nanoparticles via Water-based and Mild Reaction Conditions

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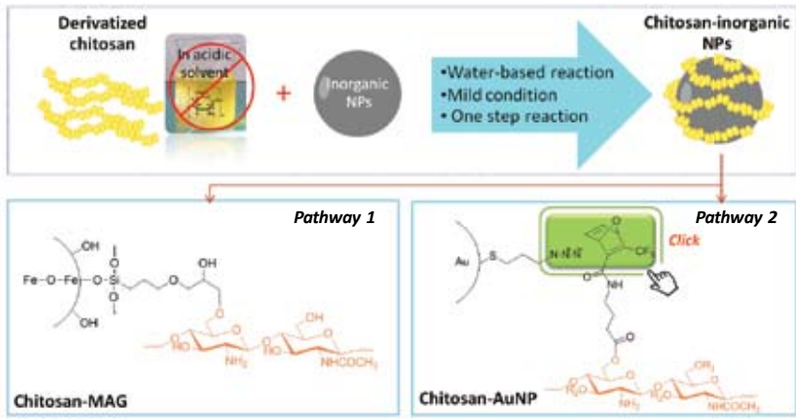
Surface functionalization of inorganic nanoparticles with biopolymers that can response to external stimuli has biological and biomedical applications. Chitin/chitosan, a naturally abundant aminopolysaccharide polymer, is well known as a potential biomaterial due to its bio-related properties and reactive functional groups for targeted derivatization. Hybridization of chitin/chitosan with inorganic nanoparticles has the potential to lead to practical materials. However, as chitosan is soluble only in acidic solvents, the reaction conditions and efficiency, including bio-safety require investigation.

The present work examines the conjugation of chitin/chitosan onto inorganic nanoparticles using a water-based system without using organic solvents, mild and simple condition, particularly at room temperature (Scheme I). Here, the model inorganic nanoparticles, i.e. magnetic nanoparticles (MAG) and gold nanoparticles (AuNPs), are selected for their model application, i.e. sensors.

The use of chitosan complexation with hydroxybenzotriazole[1, 2] leads to a water-soluble chitosan whereas epoxy silane favors a single step coupling with chitosan and magnetic nanoparticles (Chitosan-MAG) (Pathway 1). Chitosan-oxanorbornadiene[3] as reactive species enables the use of "Click" chemistry with AuNPs at room temperature without any metal catalyst (Pathway 2). The presentation will cover extensive developments in using chitosan-MAG for entrapment of the microbes in food and on chitosan-AuNPs as a material for a quick diagnosis system.

Scheme I



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Biosynthesis-structure-property relations of hyperbranched glucose polymers

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Glycogen and starch are hyperbranched glucose polymers with multiple structural levels, and are of major importance for humanity. Our bodies synthesize glycogen as a glucose (blood-sugar) buffer. Starch, synthesized by plants for glucose storage, supplies 50% of our food energy and is a renewable polymer with significant current and potential uses in biomaterials. Both polymers have complex multi-level structures, the first three of which are: Level 1, the molecular weight distributions of individual branches; Level 2, the multiple-dimensional distribution describing the full branching structure of isolated molecules, and Level 3, which for starch comprises the spatial arrangements of crystalline and amorphous regions in lamellae, and, for glycogen, the distributions of smaller clusters of hyperbranched glucose polymer molecules (β particles) into larger agglomerates (α particles, where the binding is probably through the protein glycogenin[1]). Starch comprises (1) amylose, which is of moderate molecular weight and contains a few long branches, and (2) amylopectin, a hyperbranched component of very high molecular weight; glycogen is similar to amylopectin except it is randomly branched. Structural characterization involves diverse techniques: for Level 1, finding the molecular weight distribution of the individual branches by enzymatic debranching followed by either fluorophore-assisted carbohydrate electrophoresis or SEC; for Level 2, multiple-detector SEC and, for the larger molecules (amylopectin and glycogen) where shear scission cannot be avoided[2], multiple-angle laser light scattering without size separation; and, for Level 3, X-ray and neutron scattering. Interpretation of the data so obtained in turn requires new theoretical advances. Level 1 data for starch is fitted by a new theory[3] which also shows that there are genetic constraints on the enzymatic rate coefficients which can result in the crystalline starch necessary for survival of the plant. This theory also provides a new means of parameterizing *Level 1 data* which has provided a greatly improved way of understanding the relations between data such as (1) how Level 1 structure controls that of Level 3[4], and also (2) properties such as digestibility rate[5], which is important for human health, and (3) the suitability of barley varieties for making beer. It also shows how new crops can be developed, either by conventional plant breeding or GM methods, which have starches with significantly improved digestibility, of importance in prevention and management of obesity, diabetes and colo-rectal cancers. L*evel 2 data* for plants grown at different temperatures has suggested what constraints stop starch molecules growing indefinitely: as with any branched polymer, while there are events which control the lengths of individual branches, there are no obvious candidates for the whole molecule, but these new data suggest a steric crowding mechanism. *Level 3 data* for glycogen has revealed new insights into the role of this molecule in diabetes[1,6], and suggests new types of drug targets for managing diabetes.

There are major challenges for polymer scientists in developing characterization techniques for Level 2, and in developing quantitative theories for this complex, infinite-dimensional[7] structural level which relate biosynthesis and biodegradation to structure, and structure to properties. The same challenges exist for complex branched synthetic polymers.

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Stimuli responsive Elastin based Polymer Brushes as Biocompatible Nano Carriers

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The prominent role of brush like molecular structures in nature and responsibility of cylindrical brush polymers for various functions in living organisms have encouraged several synthetic approaches for the preparation of artificial brush polymers. Combination of the cylindrical polymer topology with the stimulus responsive behavior of amino acids and peptides may generate polymer brushes with unique polypeptide architecture[1] and possible application as highly biocompatible nano carriers with sensitivity to environmental triggers.

Primary polymeric model systems on the basis of peptides are designed to get a general idea of the synthesis and properties of cylindrical polymer brushes with elastin-based side chains. Elastin-like polypeptides (ELPs), consisting of VPGXG pentapeptide repeats, are derived from the natural protein tropoelastin. Exhibiting an inverse solubility phase transition, they are soluble in water below their inverse transition temperature (T_t), but become insoluble above their T_t. The T_t can be tuned by variations in pH, salt and polymer concentration and is in addition dependent upon the amino acid X and the molecular weight of the ELP.

We are able to introduce a methacrylate moiety at the ELPs and afford via free radical polymerization high molecular weight elastin-based side chain polymer brushes (**Fig. 1**). Circular dichroism is performed to study the effect of salt and temperature on the brush conformation, the brush collaps is investigated by dynamic light scattering measurements. ELP polymer brushes are demonstrated to exhibit a high chain stiffness as revealed by static and dynamic light scattering and AFM.

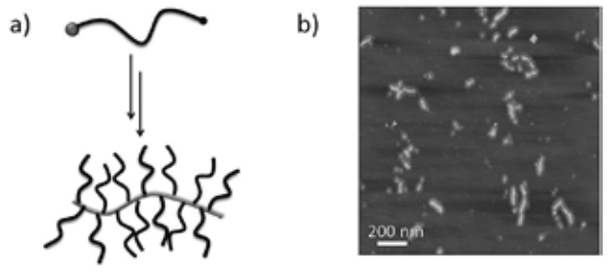

Figure 1. a) Schematics of methacryloyl-ELP macromonomer and elastin-based side chain polymer brush; b) AFM image of ELP polymer brushes spin-cast from aqueous solution on mica.

Such complex peptide based molecular structures with tunable physical properties may constitute a versatile platform for conjugation of various biologically active substrates. Furthermore cylindrical core shell structures with possible application in drug encapsulation or gene transfection may be achieved using macromonomers comprising (positively charged) ELP-block copolymers.

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A marine antifouling surface from bacterially biodegraded paraffin wax

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This study represents the first reporting of a bacterially induced paraffin wax surface capable of antifouling in a submerged marine environment. We investigated the marine antifouling properties and mechanisms of wax coatings, focusing on paraffin waxes. In field trials for 6 months, paraffin waxes were substantially less fouled than a microcrystalline wax (Figure 1).

Observation of the paraffin waxes after several weeks of immersion in seawater suggested modification of the surface of the wax, and "aging" (immersion) of the waxes in seawater (in the field or in recirculating seawater aquaria) for 4-8 weeks enhanced antifouling activity relative to non-aged wax against the settlement of invertebrate larvae and algal spores. This aging effect was hypothesized to be due to microbial activity, and consistent with this the addition of antibiotics to aging treatments significantly diminished or eliminated the inhibitory effect of the waxes. Confocal microscopy confirmed changes in the surface microtopography following aging of the paraffin waxes and physical properties of the surfaces were further explored. Aging resulted in a significant increase in crystallinity and contact angle (i.e. decreased surface wettability), as well as a decrease in elastic modulus of the paraffin wax surfaces, all of which were correlated to significant settlement inhibition of marine fouling organisms in laboratory assays. We suggest that in marine environments bacteria preferentially degraded the amorphous phase of these wax surfaces, increasing the proportion of the crystalline phase that is exposed at the surface. This affects the microtopography, wettability and other physical properties of the surface, resulting in increased antifouling. The proposed *in situ* establishment of a complex microtopographic surface is of particular interest, given the challenges in commercial application of current manufactured micro- or nano- topographies.

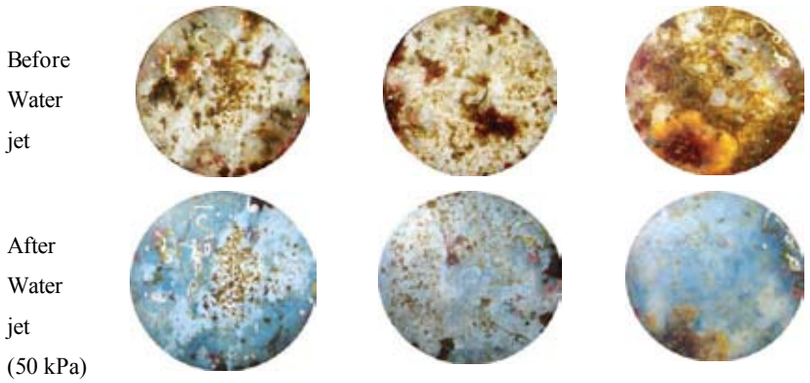

Figure 1. Photos of the Paraffin plates with biofouling both before and after application of the water jet (50kPa) after six months exposure in the field.

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Novel renewable architectural coating

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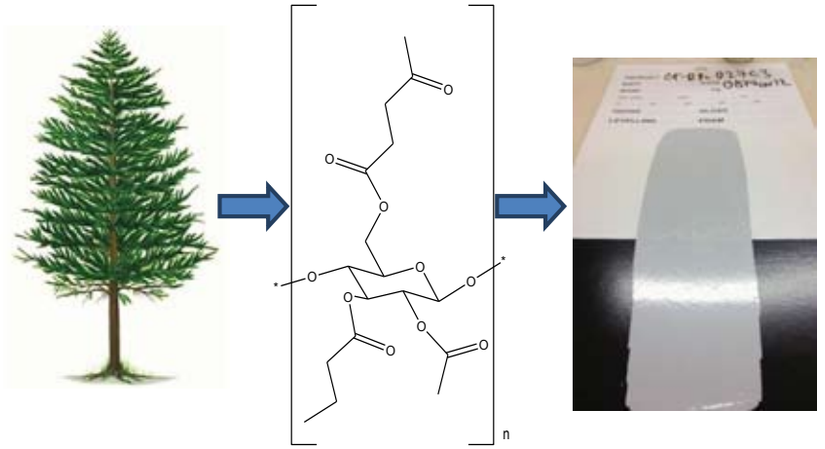
A novel polymeric binder has been formulated into a water based, low volatile organic compound (VOC), interior architectural coating.

We chose to esterify cellulose with levulinic acid as it provides a pendant reactive ketone moiety that permits additional derivation of the cellulosic polymer. Furthermore, the unexpected acetylation chemistry that levulinic acid displays in the esterification of cellulose incorporates this group at an accelerated rate compared to comparable alkyl-esters.

A series of levulinyl-cellulose mixed esters were produced that are constituted of largely renewable materials culminating in the production of the optimum material butyryl-levulinyl-acetyl cellulose (BLAC). The cellulosic polymer BLAC was chemically modified utilising the levulinyl keto-group, plasticized and dispersed with the acetone process ultimately generating a "VOC-free" 25wt% polymer dispersion. The dispersed polymer was capable of casting films at room temperature and a low sheen interior coating was formulated.

Levulinyl cellulose mixed-ester synthesis, characterisation and the novel reaction chemistry used as well as the dispersion technology developed to formulate this water based coating will be presented.



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Multicomponent Polymerization for New Polymer Synthesis

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Isocyanide based multicomponent reactions (IMCRs) are very efficient atom-economical reactions that can assemble three or more different components into one molecule in a one-pot process, and have therefore been playing important roles in many fields.[1,2] Among the IMCRs, Passerini reaction, a three component reaction first described in 1921, has been proved to be a powerful synthetic method that can yield an ester-amide linkage from a carboxylic acid, an aldehyde and an isocyanide (**Figure 1**).[1,2] It is thus quite advantageous to use this reaction to prepare polymers with different architectures and functional groups in a very efficient and straightforward way. Unfortunately, this highly efficient reaction has been overlooked for a long time in polymer synthesis; only until quite recently, synthesis of polyesters by this reaction has been reported.[3] We extended the scope of Passerini reaction in polymer science as a multicomponent polymerization method. In this talk, I will describe several synthetic approaches to different functional polymers based on Passerini reaction. This will include linear poly(ester-amide),[4] polyamides,[5] star polymers,[6] graft copolymers, and photo-degradable polymers.

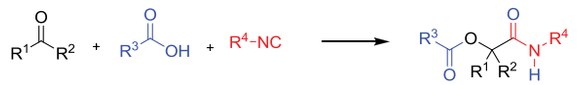

Figure 1. General Passerini reaction

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Biomimetic radical polymerization in nanoreactors: Exploiting templating and compartmentalization

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One of the primary long-standing goals in polymer chemistry is to be able to synthesize a (co)polymer with "perfect" tailor-made structure in terms of molecular weight, molecular weight distribution (MWD), monomer sequence distribution, end functionality and tacticity. The attainable level of control over polymer microstructure has increased dramatically with the advent of controlled/living radical polymerization (CLRP). However, it remains a difficult challenge to manipulate single chains and control the order of monomer units,[1] and synthesis of well-defined polymer of ultrahigh molecular weight (above ~150,000 g/mol) is also generally challenging.

In recent years, the use of so called nanoreactors (reactors in the form of *e.g.* droplets/particles/micelles) for both polymerizations and small molecule organic reactions has been expanding. In an emulsion polymerization, the termination rate is reduced due to segregation (compartmentalization), leading to high polymerization rates and high molecular weights. Compartmentalization can also lead to improved control over the MWD and end-group fidelity in CLRP.[2]

The realization that the concept of nanoreactors may be exploited in tandem with template polymerization led us to develop a biomimetic approach based on template polymerization involving nucleobase containing vinyl monomers in a segregated environment (nanoreactors) achieved via self-assembly of template diblock copolymers (**Fig. 1**).[3] The template is a synthetic nucleic acid analogue, namely poly(styrene-*b*-vinylbenzyl thymine (VBT)), and the monomer is vinylbenzyl adenine (VBA). The template polymer self-assembles in chloroform, with the template segments of the block copolymers forming the core. Subsequent addition of vinylbenzyl adenine leads to templating via hydrogen bonding within the core of the micelles. Finally, initiation using a conventional radical initiator yields template polymerization within the core of the micelles, resulting in very high molecular weight polymer (up to ~ 400,000 g/mol) with very low polydispersity (≤ 1.08). Radical template polymerization within such a confined environment thus affords significant benefits over traditional solution based templating approaches, both in the form of markedly reduced bimolecular termination due to segregation in nanoreactors and controlled propagation along a defined number of templates.

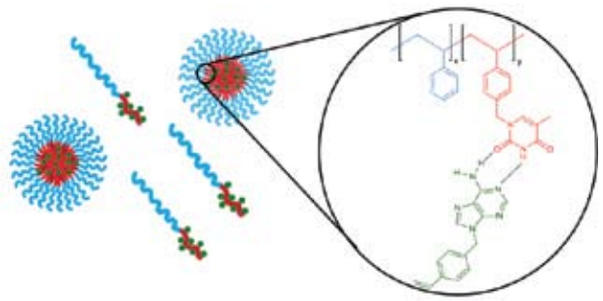

Figure 1. Schematic illustration of template radical polymerization in self-assembled micelles (nanoreactors); styrene, VBT, VBA.

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Synthesis of Hyperbranched Polymers via Thiol–Yne Photopolymerization

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Dendritic polymers such as dendrimers or hyperbranched polymers are globular structures that are characterized by a highly branched skeleton and a high density of functional chain ends.[1] Unlike the regular branching in dendrimers, the branch points in a hyperbranched polymer are randomly distributed. Although hyperbranched polymers are not as perfectly defined as dendrimers, they possess the clear advantage that their synthesis typically follows a much easier, often one-pot, synthetic pathway.[2,3] This relative ease in preparation, in addition with the specific characteristics obtained with such structures, renders hyperbranched polymers interesting alternatives to dendrimers for a wide variety of applications.[4,5]

The thiol–yne reaction is inherently an ideal strategy for the design of branched structures, as it readily yields a branch point upon the addition of two thiol moieties to one alkyne functional group. This reaction has been exploited in traditional dendrimer divergent synthesis,[6] and, as pioneered by our group, in the one-pot modular synthesis of hyperbranched polymers.[7,8] This second approach uses RAFT polymerization to produce linear polymeric chains with alkyne and thiol functionalities as α- and ω-end-groups, respectively. UV irradiation of these thiol/yne macromonomers in presence of trace amounts of photoinitiator allows the production of dendritic structures in which each branching unit is linked to the other by the polymeric chain.

In this presentation, we will discuss the use of this Thiol–Yne Photopolymerization (TYP) approach (**Fig. 1**) to prepare a wide range of hyperbranched polymeric materials as well as the parameters that influence the structure of the final products.

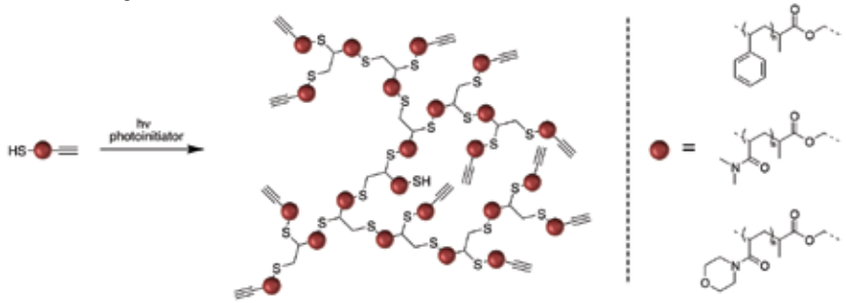

Figure 1. Schematic representation of the TYP strategy for the preparation of hyperbranched polystyrene, poly(*N*,*N*-dimethyl acrylamide) and poly(4-acryloyl morpholine).

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Nano Emulsion Polymerization of Acrylamide at Phase Inversion Point

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High molecular weight polyacrylamide (PAAM) and its copolymers have been demanded by many industries as water soluble polymers for their viscosifying characteristics. Various methods are applied by industry for synthesis of high molecular weight PAAM such as solution and inverse emulsion polymerization[1]. The problem with solution polymerizations for synthesis of high molecular weight PAAM is that the synthesized polymer is soluble in the medium which increases its viscosity and causes a) limitations in mixing due to the Weissenberg effect b) limitation in heat transfer followed by hot spots which makes the synthesized polymer insoluble in water c) limitation in conversion and molecular weight for inefficient removal of generated heat of polymerization. That's why inverse emulsion polymerization gained interest. In inverse emulsion polymerization, aqueous monomer phase is dispersed in an oil medium and polymerization proceeds in droplets[2] or micelles[3] of emulsifier. Therefore, the heat of polymerization can be easily removed to oil medium and helps in synthesis of high molecular weight PAAM.

Based on what mentioned, as small droplet size as possible, the heat of polymerization is expected to be removed easier followed by better controllability of system and higher molecular weight. Smaller droplet size can be achieved mechanically by applying higher mechanical energy input that is achievable using high shear rate, high pressure homogenizer or ultrasound generator[4]. However, recently another method for producing nano-scale droplet gained interest called catastrophic phase inversion (CPI). In CPI, the two phases change their place as a dispersed and continuous phase. During this complex procedure the nano droplets can be formed. CPI can be induced by increasing the dispersed phase or by any other factor which causes coalescence of droplets[5]. As long as our knowledge goes, there is no report for synthesis of acrylamide polymer via inverse emulsion polymerization at inversion point. However, some other polymers such as high impact polystyrene (HIPS), methyl methacrylate[6] were synthesized at CPI point.

In this study, it was tried to synthesize inverse emulsion PAAM at CPI point by decreasing agitation speed which can lead coalescence of droplets. The synthesized polymers were characterized using Transmission Electron Microscopy (TEM) and the inversion point was followed by optical microscope. The results show that the method is successful in synthesis of nano scale particles of PAAM in emulsion form.

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Inverse Miniemulsion Periphery RAFT Polymerization as a Versatile Tool to Synthesize Hollow and Loaded Polymeric Nanoparticles

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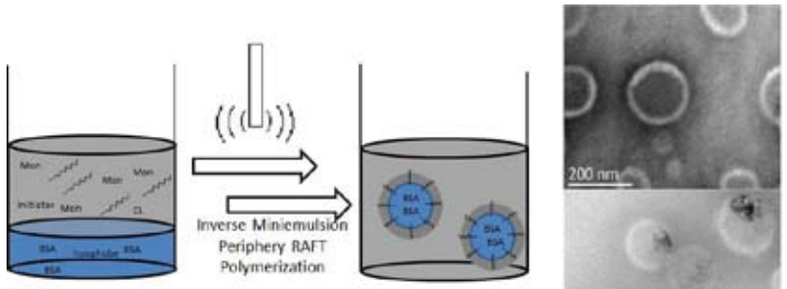
The administration of therapeutically active proteins has shown great potential in the treatment of many diseases. However, the delivery of protein is still limited by its rapid degradation. Even the utilization of polymeric nanoparticles is often challenged by denaturation of the protein.[1] The recently developed inverse miniemulsion periphery RAFT polymerization[2] alleviates this problem and provides a facile avenue to the synthesis of hollow or loaded nanoparticles. It utilizes an amphiphilic macroRAFT agent acting as stabilizer of water droplets in an organic continuous phase while also mediating crosslinking chain growth in a controlled/living manner on the outer periphery of the droplets.



Scheme 1. A schematic representation of the IMEPP process, with TEM images of synthesized hollow nanoparticles (top) and BSA-loaded nanoparticles (bottom)

The macroRAFT agent comprised a hydrophilic block of poly(N-(2-hydroxypropyl) methacrylamide and a hydrophobic block of either polystyrene or poly(methyl methacrylate), and the crosslinked shell was formed on polymerization of styrene/divinyl benzene or methyl methacrylate/ethylene glycol dimethacrylate, respectively. The effects of various reaction parameters on the resulting hollow nanoparticles have been systematically investigated, and it has been demonstrated that the shell thickness can be tuned based on initial stoichiometry and monomer conversion. Successful encapsulation and release of the model protein was also presented. The absence of protein denaturation throughout the polymerization process was confirmed *via* Trp measurement. The release of the protein was achieved though diffusion and the structure and activity of the released protein were confirmed to be identical to that of the native protein.

In conclusion, a novel, one-pot synthetic route has been successfully designed, developed and applied to create nanocapsules with aqueous core, with encapsulation and release of sensitive protein molecules demonstrated as a potential application.

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Synthesis of Cyclic Polysulfides: Controlled Ring-Expansion Polymerization of Cyclic Tetrathioester with Thiirane

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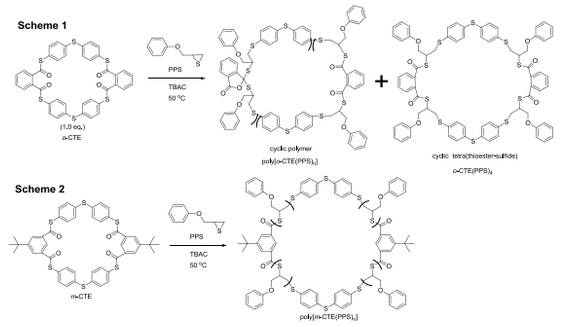
The synthetic strategies of polymers are usually classified into two categories: chain-growth and step-growth polymerization. However, the synthetic strategies of cyclic polymers cannot belong to either of these categories, because cyclic polymers have no end-group. Although the physical properties, such as thermal stability, glass transition temperature, and viscoelastic behavior of cyclic polymers have attractived much attention compared to linear polymers, their detailed examinations have been restricted by the synthetic limitations. Three strategies for the synthesis of cyclic polymers are well-known: (1) ring-closure reaction of linear polymers, (2) ring-expansion polymerization of cyclic monomers, and (3) ring-crossover polymerization (ring-ring equilibration) of cyclic monomers. We also reported that the insertion of thiirane into cyclic dithioester or monothiocarbanate was performed, selectively yielding cyclic polysulfides.[1, 2] Furthermore, ring-crossover polymerization is due to the thioester bond as a dynamic covalent bond,; i.e., the ring size of the cyclic polysulfides is related their skeletons.[3] In this paper, we focused on the ring-expansion polymerization behavior of thiirane using cyclic tetrathioester compounds for the synthesis of cyclic polysulfides.

We examined the reaction on the insertion of phenoxy propylenesulfide (PPS) into the cyclic tetrathioesters containing thioester moieties at the *o*-position (*o*-CTE) and *m*-position (*m*-CTE) of an aromatic skeleton. When the insertion of PPS into *o*-CTE was performed using tetrabutylammonium chloride (TBAC) as a catalyst in NMP at 50 °C for 24 h, both the intra-cyclization of thioester groups and ring-crossover polymerization proceeded, and cyclic polysulfides poly[*o*-CTE(PPS)$_n$] containing cyclic lactone moieties with M_n's = 37,000 ~ 540,00 were synthesized at 34 ~ 61 % yields, and their molecular weights could not be controlled (Scheme 1). In the case of the insertion of PPS and *m*-CTE, no intra-cyclization of thioester groups proceeded. With the supply of PPS and *m*-CTE, the molecular weight of the corresponding polysulfides could be controlled, yielding poly[*m*-CTE(PPS)$_n$] with M_n's = 46,600 ~ 107,200 in 63 ~ >99% yields(Scheme 2). The absolute molecular weights ($M_{w(MALLS)}$) of the cyclic polysulfides (poly[*m*-CTE(PPS)$_{4.4}$], M_n = 46,700, poly[*m*-CTE(PPS)$_{30.8}$], M_n =107,200) and linear polysulfide (polyPPS, M_n = 102,600) were also determined by MALLS, and the ratio of $M_{w(SEC)}$ /$M_{w(MALLS)}$ of poly[*m*-CTE(PPS)$_{4.4}$] was larger than for any other polymer. The glass transition temperature (T_g) and initial decomposition temperature (T_d^i) of poly[*m*-CTE(PPS)$_{4.4}$] were also the largest, i.e., a lower molecular weight cyclic polymer could show a characteristic physical property due to its cyclic skeleton.



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RAFT Synthesis of CO_2-responsive (Co)Polymers

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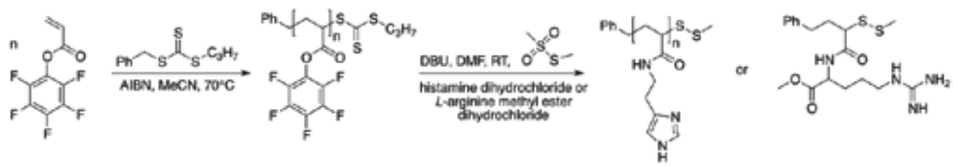
RAFT polymerization is a versatile reversible deactivation radical polymerization method for the synthesis of polymers with defined architectures and diverse functionality.[1] A homopolymer of pentafluorophenyl acrylate (PFPA) was synthesized using RAFT polymerization before it was modified into a polymer containing an amidine or guanidine functional group. **Scheme 1** demonstrates how amidine or guanidine containing polymers were synthesized.



Amidines and guanidines are responsive to carbon dioxide. A polymer with amidine or guanidine functionality would be useful in biological applications such as drug delivery and gene transport systems.[2] The CO_2 responsive nature of such polymers is demonstrated in **Figure 1**. The histamine homopolymer was initially dispersed in water and observed to be completely insoluble (left). After bubbling CO_2 through the solution, the polymer dissolved giving a homogeneous solution (middle). Subsequent sparging with N_2 induced a further phase separation (right). The tunable solubility is due to the reversible formation of carbonate salts involving the amidine functionality.

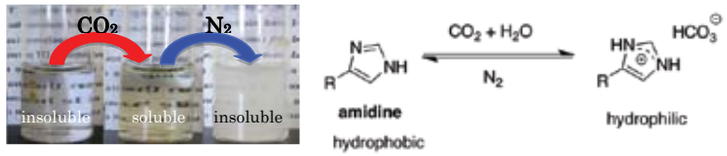


Figure 1: Pictures demonstrating the reversible solubility of histamine homopolymers and a scheme highlighting reversible salt formation.

This approach has been extended to AB diblock copolymers which gives access to CO_2-responsive block copolymers where reversible self-directed assembly is possible.

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P1 **Comparison Study of P(OEGA) functionalized Magnetic Nanoparticles Synthesized via Grafting 'from' and 'to' Approaches for MRI Applications**
Johan Sebastian Basuki[1], Lars Esser[1], Per B. Zetterlund[2], Michael R. Whittaker[1,2], Thomas Paul Davis[1,2] and Cyrille Boyer[1,2]
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P2 **Diels-Alder Networks and Acrylates: A Powerful Combination for Layer-by-Layer Stereolithography**
Gayla J. Berg[1], Tao Gong[1], Christopher R. Fenoli[1], and Christopher N. Bowman[1]
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P3 **Synthesis and Functionalization of pH-responsive Dextran-g-P(OEG-A) Nanoparticles via RAFT polymerization for Drug and Gene Delivery**
Cyrille Boyer[1]*, Thomas P. Davis[1] Hien Duong[1], Sharon Sagnella[1], and Maria Kavallaris[1]
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P4 **ROMP Titania Organic/ Inorganic Hybrids**
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P5 **Functionalized HIPE's via ROMP & Gamma Thiol-ene Click Chemistry**
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P6 **Hierarchical Nanostructures of Liquid Crystal Block Copolymers Bearing Side-attached Natural Cholesterol Mesogen**
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P7 **Immune response to polymeric nanoparticles**
Liyu Chen, Barbara E Rolfe and Kristofer J Thurecht
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P8 **Ligation of biomacromolecules to α-functionalized RAFT polymers**
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P9 **Controlled self assembly of gold nanoparticles mediated by tailored hyperbranched polymers with potential in diagnostics**
Priyanka Dey[1], Idriss Blakey[2], Kristofer J. Thurecht[2] and Peter M. Fredericks[1]
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P10 **Rapid biomineralization of hydroxyapatite-g-PDLLA hybrid microspheres**
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P11 **Surface modification with RAFT polymers via Thiol Click Reactions**
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P12 **Multiresponsive Organogels from Block Ionomer via Charge-Induced Assembly**
Tao Zhang and Qipeng Guo
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P13 **Self-Assembly and Nanomechanical Properties of Block Ionomer Complexes**
Shuying Wu[1], Qipeng Guo[1], Taiye Zhang[2], Yiu-Wing Mai[3]
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P14 **Tuning Surface Wettability via Ring Opening Polymerisation of Naturally-Occurring Hydrophobic Amino Acid**
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P15 **Plant-Derived Bio-Adhesive Polymer**
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P16 **Modification of PLA with e-caprolactone by reactive processing – The effect of modifier loading, temperature, time and catalyst level upon the polymer structure, mechanical, thermal properties and the rate of degradation.**
Simona Lavric [1, 2], Mike O'Shea[1], Gary Peeters, Roger Mulder, Carl Braybrook, Lance Nichols and Jo Cosgriff
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P17 **Investigating New Architectures of Natural Rubber and Silicon Based Polymers**
Gaelle Leveque[1, 2], Jean-François Pilard[2], Pamela Pasetto[2], Tony Aitchison[1], Stephen Clarke[1]
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P18 **The enzymatic hydrolysis and oxidation of poly(glycerol sebacate) and poly(xylitol sebacate)**
Yuan Li[1], Hanning Shi[1], Wayne Cook[1], Qizhi Chen[1]
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P19 **Si3N4 Coating For Polymethl Methyacrylate Intraocular Lens To Prevent Posterior Capsule Opacification**
Lingli Li[1,2], Xu Xu[1], Xiaona Liu[1], Hao Chen[1*]
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P20 **High-Efficiency Inverted Polymer Solar Cells based on P3HT/PC61BM Blend and Cathode Interlayer**
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P21 **Separation of hydrophilic polyacrylates according to the topology using capillary electrophoresis in critical conditions**
Alison R. Maniego[1, 2], Dale Ang[1, 2], Yohann Guillaneuf[3], Catherine Lefay[3], Didier Gigmes[3], Janice R. Aldrich-Wright[1], Marianne Gaborieau[1], Patrice Castignolles[2]
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P22 **Synthesis and Property of Noria (Water-Wheel Like Macrocycle) Derivatives with Pendant Alkoxyl and Adamantyl Ester Groups, and Their Application for Extreme Ultraviolet Resist**
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P23 **Well-defined polyoxazoline-based amphiphilic copolymers: from synthesis by polymer-polymer coupling to self organization in water**
Brieuc Guillerm[1], Vincent Darcos[2], Vincent Lapinte[1], Sophie Monge[1], Jean-Jacques Robin[1]
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P24 **Solid Li+-carrying Membranes**
Mathieu Meyer[1], André Vioux[1], Ahmad Medhi[1], Sophie Monge[2], Lydie Viau[1]
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P25 **The Utilization of Two Recycled Polymers and Bagasse Fibers in Wood Plastics Composites Nano / Clay**
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P26 **Synthesis of glycopolymer–gold(I) complexes**
Samuel Pearson, Wei Scarano, Hongxu Lu, Martina H. Stenzel
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P27 **Study of Well-Defined Poly(N-isopropylacrylamide) Hydrogels via Thiol-ene Chemistry**
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P28 **In-situ Monitoring of Microwave Polymerisations for Increased Activity**
Samuel J Richardson[1], Idriss Blakey[1], Kristofer J Thurecht[1], Kevin Adlington[2,3], Sam Kingman[3], Derek J Irvine[2,3], Andrew K Whittaker[1]
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P29 **Coating of Inorganic Nanoparticles with Mussel-Inspired Amphiphilic Copolymers and Fabrication of Hierarchic Porous Films**
Yuta Saito[1], Masatsugu Shimomura[2,3], Hiroshi Yabu[3,4]
[1]Graduate School of Engineering, Tohoku Univ., [2]WPI-AIMR, Tohoku Univ., [3]IMRAM, Tohoku Univ., [4]PRESTO-JST

P30 **Multi-layered Polymersome Formed by Amphiphilic Asymmetric Macromolecular Brushes**
Hung-Yu Chang[1], Yu-Jane Sheng[1], and Heng-Kwong Tsao[2]
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[2]Department of Chemical and Materials Engineering, Department of Physics, National Central University, Jhongli, Taiwan, R.O.C.*

P31 **Termini-modified mPEG5k-Dendritic Poly-(l)-lysine Cationic Copolymers for Low toxic and Efficient Gene Delivery**
Ruilong Sheng[1], Kejia Xia[1, 2],Jian Chen[2], Ting Luo[1], Hui Li[1], Jingjing Sun[1], Zhao Wang[1], and Amin Cao[*1]
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P32 **Amino acid-based star polymers for cancer therapy**
Steven Josef Shirbin[1], Adrian Sulistio[1], Anton Blencowe[1], Xiaoqing Zhang[2], Wei Duan[3], and Greg G. Qiao[1]
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P33 **Reducible Polymer DNA-Hydrogel as a Dual Switchable Release Gate**
Giovanna Sicilia[1], Christine Grainger-Boultby[1], Nora Francini[1], Johannes P. Magnusson[1], Aram O. Saeed[1], Francisco Trillo-Fernandez[1], Sebastian Spain[1] and Cameron Alexander[1]
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P34 **Effect of Lithium bistrifluoromethanesulfonimidate on the Propagation rate of Methyl Methacrylate**
Leesa M. Smith[1], Benjamin B. Noble[1] and Michelle L. Coote[1]
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P35 **Synthesis of Noria-like Macrocycle Containing Methoxy Groups based on the Dynamic Covalent Chemistry (DCC) System by the A2 + B4 type Condensation Reactions**
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P36 **Separation of DNA bound with Cisplatin, Hoechst33258 and Ethidium Bromide by Capillary Electrophoresis in the critical conditions**
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P37 **Characterizing chitosan and its conjugates for biomedical applications**
Joel Thevarajah[1,2,3,4], Danielle Taylor[1,2,3], Catherine Lefay[4], Yohann Guillaneuf[4], Michael O'Connor[5], Patrice Castignolles[1,2] and Marianne Gaborieau[1,4]
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P38 **Novel Epoxy Resins From an Unlikely By-Product**
Neil A. Trout[1], Stephen R. Clarke[1]
[1]University of South Australia, Mawson Institute, SA

P39 **Self-assembly of Solvophilic Nanoparticles in a Polymer Matrix: Depletion Interactions**
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P40 **Concentration of bio-ethanol through porous hydrophobic polymer membranes**
Tadashi Uragami
Kansai University

P41 **Synthesis and Optical Properties of Dithienylethenes**
George Vamvounis,* David Gendron, Nic Sandery and Evan G. Moore
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P 43 **Crosslink of graphene for energy applications**
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P44 **Novel microcavitary hydrogel system for 3D culture and hepatogenic differentiation of murine induced pluripotent stem (iPS) cells**
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P45 **Redox-Cleavable Mikto-arm Star Polymers Synthesized by RAFT Polymerization**
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P46 **Preparation of Superabsorbent Polymers from Starches with Different Amylose/ Amylopectin Ratios**
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Comparison Study of P(OEGA) functionalized Magnetic Nanoparticles Synthesized via Grafting 'from' and 'to' Approaches for MRI Applications

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Surface modification through surface grafting of polymers is becoming increasingly important for biotechnology, medical and electronic applications.[1] Recent successful applications of living radical polymerization (LRP) have made it possible to graft various low-polydispersity functional polymers to a wide range of materials. This surface grafting 'from' technique has resulted in an increase of grafting density of polymer chains. Surfaces such as silicon wafer, gold or iron oxide nanoparticles can be decorated with suitable LRP initiators, which allow a controlled growth of polymer chains from the surfaces. Recently it has been demonstrated that Cu(0) mediated LRP provides high chain fidelity even at high monomer conversion.[2]

Superparamagnetic iron oxide nanoparticles (IONPs) have been studied extensively as contrast agents in MRI.[3] For effective clinical use, it is essential that the T_2 relaxation (r_2) should be maximized in tissue where the IONPs are localized, and T_1 relaxation (r_1) should be minimized. When these conditions are met, higher contrast is achieved. Nevertheless, since colloidal stability of IONPs needs to be improved in biologically relevant media, biocompatible polymers with anti-fouling properties such as polyethylene glycol (PEG) have been coated on the surface of IONPs for longer blood circulation times.[3] In order to achieve high grafting density, stability and retaining T_2 relaxivity of the IONP core, the chemical functionalities and chain length of the polymeric layer must be controlled.

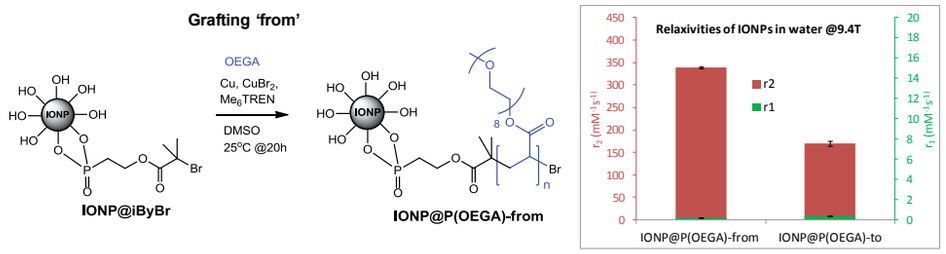

Fig. 1.: P(OEGA) functionalized magnetic IONPs synthesized via grafting 'from' and its MRI relaxivity .

In this work we have synthesized poly(oligoethylene glycol acrylate) functionalized magnetic iron oxide nanoparticles (IONP) using the grafting 'from' approach (**Fig. 1**). Cu(0) mediated LRP has been applied to grow polymer chains of predetermined length. The polymer can be further extended through an iterative addition of the same monomer demonstrating high fidelity of the system. IONPs with different lengths of the P(OEGA) layer were also synthesized using the grafting 'to' approach for a comparison study. Colloidal stability and MRI relaxivity of these functionalized IONPs were investigated in water, as well as in fetal calf serum (FCS). In comparison with the grafting 'to' approach, the IONPs synthesized using grafting 'from' approach exhibited higher T_2 relaxivity in water. This value is comparable with a commercial MRI contrast agent Resovist® [3].

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Diels-Alder Networks and Acrylates: A Powerful Combination for Layer-by-Layer Stereolithography

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Microstereolithography (μSL), the fabrication of 3D microstructures through photopolymerization, is an impressive and potent tool used in many emerging technologies, such as photonic crystals[1], micromachines[2], and cell scaffolds for tissue engineering[3,4]. One of the challenges faced by μSL is accurate fabrication of overhanging, high aspect ratio, or freely-moving parts. Feature collapse or sedimentation can occur without the use of temporary support materials, which can be costly or difficult to remove for certain geometries. Here, a Diels-Alder (DA) network encapsulating acrylate-containing monomers is demonstrated as a solid, crosslinked photoresist for layer-by-layer fabrication of 2D and 3D objects (**Fig. 1**). The thermoreversible network provides inherent support for all structures being formed, while simultaneously allowing facile removal of unexposed regions. When a polymer film is selectively photopatterned, both acrylate and unreacted maleimide will polymerize, rendering a permanent network structure. Removal of unexposed material during the development step was achieved at 120°C, where the retro-Diels-Alder reaction dominates. Free acrylate and maleimide groups were shown to tolerate these development temperatures, with no evidence of side reactions in unexposed regions. Because the network reverts to a low-viscosity liquid at this temperature, solventless development was achieved solely through gravity for larger macrostructures, and the authors underscore the potential for solventless development of microstructures simply by added force (e.g. pressured gas streams) at development temperature. A robust, reliable process was developed for the fabrication of 3D microstructures using a mask alignment system. Finally, in perhaps the clearest sign of the system's versatility, mechanical properties were easily tailored by adjusting the choice of monomers and weight percentage of added acrylates.

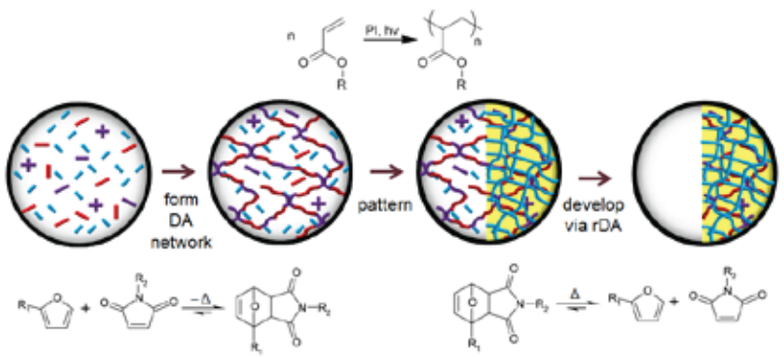

Figure 1. Photopatterning and development process for Diels-Alder networks containing liquid acrylate monomer.

[1] S. Kirihara, Y. Miyamoto, *J. Am. Ceram. Soc.* **2002**, *85*, 1369-71
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Synthesis and Functionalization of pH-responsive Dextran-*g*-P(OEG-A) Nanoparticles via RAFT polymerization for Drug and Gene Delivery

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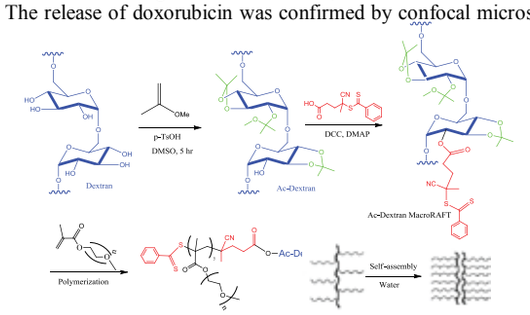
Soft core-shell polymeric nanoparticles have been widely investigated as potential vectors for the sustained delivery of therapeutic payloads, such as drugs, proteins, genes, and imaging agents.[1] It is known that polymeric nanoparticles have prolonged circulation times in the bloodstream and allow 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 nanoparicles (e.g. micelle, liposome, etc). However, these materials are usually based on synthetic polymers, and there are no-biodegradable. One of the major concerns of these synthetic nanoparticles is their potential accumulations in the body, resulting potential side effects. For this reason, the design biodegradable polymeric nanoparticle presents a great interest.

In this communication, we design a sample approach to prepare pH-responsive biodegradable nanoparticles based on dextran and on poly(ethylene glycol) (PEG). 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 (**Scheme 1**). 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 20-100 nm (assessed by TEM and DLS). Interestingly, different morphologies were obtained from spherical to tubular structures according the grafting density of PEG. Finally, doxorubicine was loaded into the nanoparticles and released in acidic media due to the cleavage of acetal bond. These nanoparticles were tested using different cell lines, such as MRC5 (fibroblast cell line) and SY5Y (neuroblastoma cell line). The release of doxorubicin was confirmed by confocal microscopy, flow cytometry and toxicity study.



Scheme 1. Chemical modification of dextran to yield nanoparticles.

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ROMP Titania Organic/ Inorganic Hybrids

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Composite materials are attracting increasing interest. Synergy between their organic and inorganic phases can lead to significantly improved mechanical, thermal, electrical, and magnetic properties. While most research efforts have been on macro and micro scale hybrids, the field is now moving towards higher interfacial area nano composites.[1]

In this work we report the synthesis of organic/ inorganic materials via the first in situ Ring-opening Metathesis Polymerization (ROMP) of norbornene in an acetyl acetone stabilized titania sol. The result is a novel composite comprising nano scale TiO_2 particles evenly dispersed throughout a solid polynorbornene matrix.

Titania loadings (as well as silica, although this aspect will not be detailed here) of 0, 10, 20 and 50 weight percent were investigated, and verified by thermal gravimetric analysis. Importantly, no aggregation of the TiO_2 particles was detected. The material retains its optical clarity (**Fig. 1**), and a scanning electron micrograph of the titania char remaining after pyrolysis shows discrete nanometer sized particles (**Fig 2**).

Characterisation of these hybrids (TGA, DSC, and DMA) has identified broad trends relating thermal and mechanical properties to overall titania loading and particle size. We are currently performing small angle X-ray (SAX) analysis to further corroborate homogeneity of dispersion, and also to investigate the possible formation of interpenetrating networks when an unstabilized TiO_2 sol-gel and ROMP are allowed to proceed simultaneously.

Finally, we highlight that this system is not limited to norbornene. Several other monomers have been used successfully, including cross-linkable dicyclopentadiene and an oxanorbornene based monomer bearing a simple butyl pendant. In this way, specific chemical functionality may be imparted to any hybrid. For example, we have previously synthesised a wide range of functional oxanorbornenes[2] including alcohol, alkyne, sugar, ester, thiazoline, perfluoro, triethoxysilane and POSS variants. These last two undergo strong covalent-like interactions with the inorganic phase, potentially leading to even greater property enhancement.

Figure 1. 20 wt% TiO_2 hybrid.

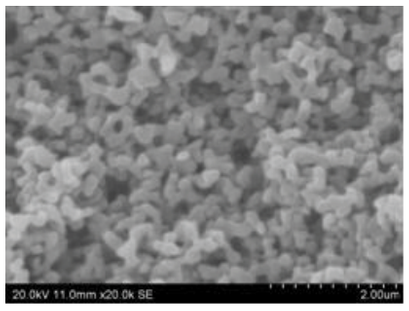

Figure 2. SEM of TiO_2 char after pyrolysis.

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Functionalized HIPE's via ROMP & Gamma Thiol-ene Click Chemistry

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High Internal Phase Emulsion (HIPE) polymers, are highly porous crosslinked monoliths characterized by large (micrometer dimension) cavities interconnected by a series of smaller pores. They possess void volumes in excess of 90%, making them lightweight materials with moderate to high surface area and excellent flux. Example applications include adsorption and catalyst support.[1]

HIPE's have been constructed from various polymers, including styrenic and acrylic systems. More recently, Slugovc et al.[2] prepared a more mechanically robust HIPE via the Ring-opening Metathesis Polymerisation (ROMP) of dicyclopentadiene (DCPD).

In our research, we extend Slugovc's work and show how the surface area, pore size and morphology of a DCPD HIPE may be controlled by varying stirrer speed and mixing energy (**Fig. 1**). Furthermore, we disclose a method of chemically modifying these HIPE's with a wide range of functional groups.

All ROMP polymers retain double bonds between each repeat unit. These sites are reactive towards thiol-ene 'Click' chemistry (radical mediated hydrothiolation), and allow virtually any thiol to be conjugated to the HIPE. While thiol-ene chemistry is typically conducted via photochemical means, we instead employ gamma radiation to generate radicals in situ.

Importantly, the penetrative nature of gamma radiation permits us to access all internal surfaces of the HIPE, while the abundance of double bonds allows for an extremely high density of functionalization. A further advantage is the wealth of inexpensive thiols that are commercially available (**Fig. 2**), and the great range of biologically active compounds that bear mercaptan moieties. We envisage this technique as a convenient and efficient method for creating heterogeneous catalytic and enzymatic supports.

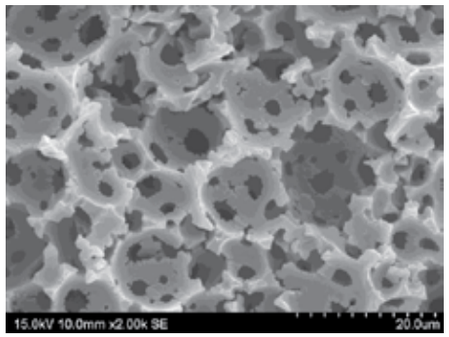

Figure 1. SEM of HIPE stirred at 400rpm.

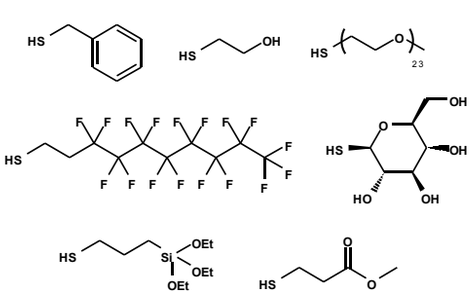

Figure 2. Examples of available thiols.

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Hierarchical Nanostructures of Liquid Crystal Block Copolymers Bearing Side-attached Natural Cholesterol Mesogen

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Cholesterol is one of the well-known natural based steroidal compounds involved in many important biological processes of plants and animals, and the cholesterol as an important material has also already been wildly applied for preparation of structurally stable liposome capable of encapsulating diverse therapeutic drugs for integrated controlled drug delivery system in pharmaceutical industry. Alternatively, more than 100 hundred years ago, natural cholesterol has been known as a thermotropic liquid crystalline mesogen with chiral nematic phase, and can be exploited as a biologically reactive and rod structural building block for construction of new nanostructured and functional polymer materials. In this poster, we would like to present our recent works on utilizing the natural cholesterol to build amphiphilic Rod-Coil block structural liquid crystal copolymers as shown in figure 1 and the structure dependence of hydrophilic block on self-assembly in solid and selective solvents was also discussed[1-6].

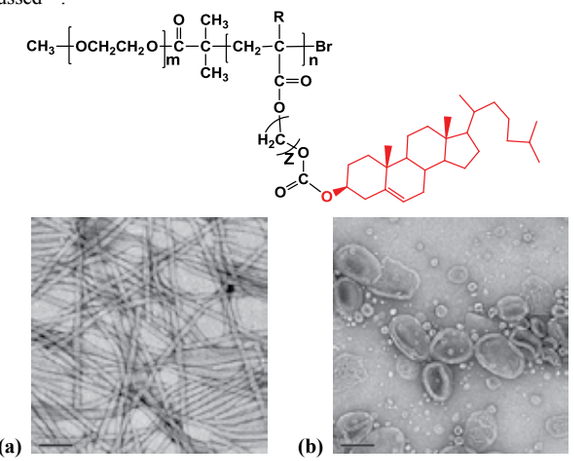

Figure 1 TEM images of self-assemblies of block copolymers in dioxane/water (a) MPEG5000-*b*-PAChol (14/86). (b) MPEG2000-*b*-PAChol (28/742). The scale bars are 200 nm

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Immune response to polymeric nanoparticles

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It was predicted the nanomedicine market would be valued at around 12 billion dollars in the year 2012, driven mainly by the twenty-three approved nanoscale drug delivery systems. The big three polymer nanoparticle (NPs) therapetuics (Neulasta, Pegasys, and PEG-Intron) alone account for 3.2 billion dollars[1].The tremendous economical and social benefits, together with the benefits associated with improved standard of living for patients, will inevitably facilitate increased research into multi-component and multi-functional polymeric nanomaterials which allow for drug delivery, molecular imaging and/or diagnostics, stimultaneous disease monitoring and many others.

As extraneous particles, NPs will experience numerous environmental changes upon intravenous (i.v.) administration, including dramatic blood dilution, exposure to pH and salt variations, interaction with a myriad of proteins (e.g., opsonins, IgG or complement fragments) and cells in blood (e.g., monocyte, neutrophils) or tissues (e.g.,Kupffer cells, marcrophages)[2]. However, only those with optimised particle parameters, including composition, particle size, surface properties (e.g. surface charges, hydrophobicity and others), will avoid rapid clearance from blood by the reticuloendothelial system (RES) or subsequent immunological responses. Thus, only appropriately designed molecules will overcome the multiple biological barriers and take effect at the targeted site.

Here we report on the observed immune response to various hyperbranched polymers (HBP) synthesised using RAFT chemistry [3]. The immunotoxicity experiments (e.g. cell viability, time-course for uptake by RAW macrophages, influence of complement) were carried out to evaluate how the physico-chemical properties of the HBP affected these response. Endotoxin and haemolysis tests showed that typically these polymers and NPs were endotoxin-free and could be i.v. administrated. Additionally, *in vivo* experiments in rats were also carried out to monitor the biodistribution of the polymers in living animals.

In summary, we have carried out a systemic investigation of the complicated physiological response to HBP through in vitro, in vivo and ex vivo analyses. We envisage that these studies will provide us with strategies to predict and evaluate the fate of polymers even on the subcellular level, making the application of polymeric material in healthcare more promising and time and cost effective, as moderate modifications (e.g. size, surface charge, or composition) might potentially enhance their physiological response.

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Ligation of biomacromolecules to α-functionalized RAFT polymers

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With the recent advances of macromolecular chemistry, techniques of bioconjugation, *i.e.* the attachment of synthetic polymers to biomacromolecules such as proteins and peptides, have dramatically improved.[1, 2] In general, polymers are chosen to increase the solubility and/or stability of the resulting bioconjugate due to the shielding effects provided by the polymeric chain, and typical examples can be found in the technique of pegylation, the attachment of a PEG chain to a protein.[3-5] Recent advances in polymer chemistry now makes it possible to couple stimuli-responsive polymers to biomacromolecules, an exciting option since the application of an external stimulus (e.g., change in temperature, light or pH, etc.) may tune the solubility, stability and/or bioactivity of the resulting smart bioconjugate.[6]

Modern Living Radical Polymerization (LRP) techniques provide control over the molecular weight and the molecular weight distribution of a polymeric material. In addition, the better LRP techniques incorporate many desirable features, such as compatibility with a wide range of monomers, facile reaction conditions, tolerance of many functionalities, which may be employed subsequently as a coupling point to biomacromolecules. Hence, LRP has enabled access to complex architectures and site-specific functionality that were previously impossible to achieve via free radical polymerizations.[7]

In this work, a family of conveniently α-functionalized polymers (**Fig. 1**) were prepared through Reversible Addition–Fragmentation chain Transfer (RAFT) polymerization then ligated to peptides and/or proteins using a mild and highly chemoselective procedure.

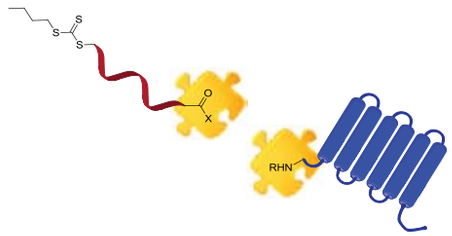

Figure 1. Schematic showing of the concept of ligating an α-functionalized RAFT polymer to a protein

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Controlled self assembly of gold nanoparticles mediated by tailored hyperbranched polymers with potential in diagnostics

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The development of new types of surface-enhanced Raman scattering (SERS) substrates has extended the applicability of this technique to medical diagnosis.[1] It is well established that NP assemblies perform better as SERS substrates compared with single NPs. This is because Raman signals are dramatically enhanced when Raman-active molecules are adsorbed in the interstitial gaps between NP assemblies, often referred to as "hot spots". Stable colloidal gold NP assemblies with optimized size, morphology and high "hot spot" density may be an ideal candidate for diagnostics. We have previously demonstrated[2] that by employing tailored RAFT synthesized hyperbranched polymers (HBP) as a linker, we can self-assemble gold NPs into hybrid nano-assemblies (Fig. 1A). We have been successful in achieving a degree of control over the "hot-spot" density of gold NP assemblies. With careful selection of the two different end-groups of the RAFT agent and water soluble, biocompatible monomers, together with optimization of the reaction parameters, we were able to synthesize varying architectures of HBP with different numbers of branches. Recent work has shown that by manipulating N_e, the number of anchoring end-groups to gold NPs, it is possible to control the morphology of the nano-assemblies. As we increase N_e, from 2 to 18, the morphology changes from linear to a 3D random morphology (Fig. 1B&C). This in turn changes the number of "hot-spots" and thus the SERS performance.

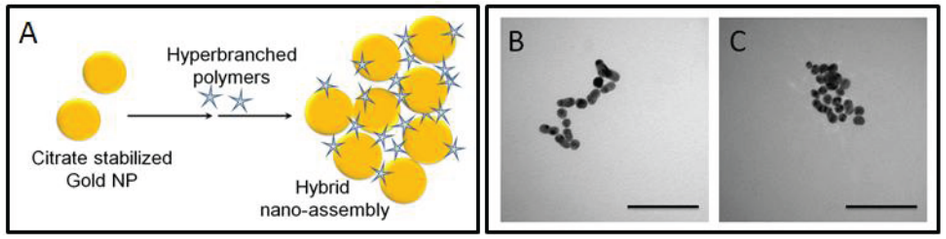

Figure 1: (A) Scheme of formation of hybrid nano-assemblies mediated by HBP; (B & C) Linear and 3D morphologies of hybrid nano-assemblies (TEM scale = 100 nm) as an effect of N_e, N_e= 2 and 18 respectively.

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Rapid biomineralization of hydroxyapatite-g-PDLLA hybrid microspheres

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Biodegradable polymeric microspheres have been widely investigated as cell-loading scaffolds to be used for bone defect repair purpose. Especially the development of injectable scaffolds for bone tissue engineering boosts the investigation on biodegradable polymeric microspheres as temporary cell-loading microcarriers. The cell-loaded microspheres can localize and control delivery of cells with a high viability, this offering an attractive strategy to fill in bone defects[1]. However, a desirable artificial substitute for bone defects healing should be capable of mimicking the natural properties of bone and provide a temporary scaffold for tissue regeneration[2].

In this study, poly(DL-lactide) grafted from hydroxyapatite (HA) nanoparticles as synthesized to fabricate hybrid microspheres with diameters in the range of 150-200 μm by single and double emulsion solvent evaporation techniques. The as-obtained microspheres were treated by alkaline solution in order to selectively degrade the PDLLA component from the surface of hybrid microspheres and subsequently to produce a dense coating of hydroxyapatite nanoparticles. The hybrid microspheres with enriched HA nanoparticles on the surface after alkaline treatments were further immersed in simulated body fluid (SBF) solution to evaluate the bone-forming ability of the bioactive hybrid microspheres via in vitro biomineralization (**Fig.1**). The resultant microspheres were analyzed by using X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) to understand the nucleation and growth of bioactive calcium phosphate (Ca-P) crystals as a function of surface treatments. This work clearly demonstrates that the existing HA nanoparticles on the surface of hybrid microspheres following alkaline treatment affect greatly the growth behavior of the bone-like Ca-P crystals in SBF solutions. The biomimetic hybrid microspheres are promising candidates for injectable scaffolds in bone tissue engineering.

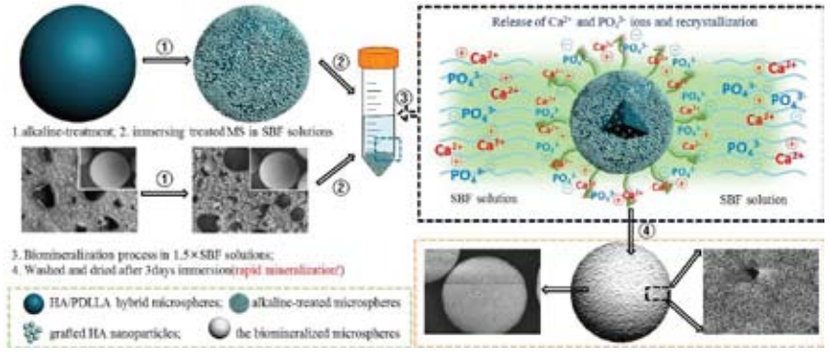

Fig.1 Schematic depiction of rapid mineralization process of alkaline-treated hybrid microspheres

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Surface modification with RAFT polymers via Thiol Click Reactions

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Polymer coating of surfaces is of particular importance for biomedical materials development where desirable bulk properties and desirable surface properties are often not found in one material. While RAFT mediated polymerization has been employed extensively to graft polymers from a variety of surfaces, direct attachment of a presynthesized polymer to a surface is sometimes advantageous.

One of the recently explored advantages of RAFT mediated polymerization is the ability to generate thiol terminated polymers, by aminolysis of the RAFT group, thus providing a means to attach polymers to a surface with thiol-reactive substituents. This feature of RAFT-polymerized macromolecules has been exploited in the surface coating of materials via nucleophilic Michael addition and thiol-gold reactions.

Here we explore the attachment of various RAFT generated, thiol-terminated polymers to both norbornene and dopamine coated surfaces. Polymers prepared from novel monomers, are tested for cell attachment and protein adsorption. Surfaces are characterized by contact angle measurements and x-ray photoelectron spectroscopy (XPS).

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Multiresponsive Organogels from Block Ionomer via Charge-Induced Assembly

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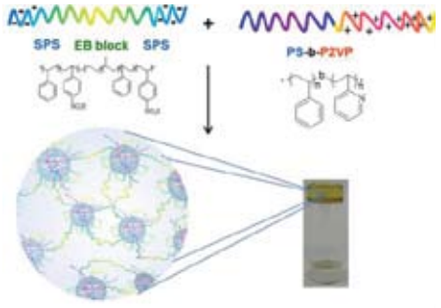
Multiresponsive organogels have recently attracted much attention since they are able to respond to external triggers. A promising class of responsive organogels is physically crosslinked polymer networks, but the transient networks reported usually are either only responsive to temperature or time-consuming to form.

Here we report a novel approach to prepare multiresponsive physically crosslinked organogels through charge-driven assembly between a triblock ionomer, namely sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) and a diblock copolymer polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) (**Scheme 1**). Acidic groups on the sulfonated polystyrene (SPS) blocks of triblock ionomer SSEBS can react with opposite charged polymers to form insoluble complexes in organic solvents.[1,2] The two SPS blocks of a triblock ionomer chain may enter two different solvophobic cores stabilized by the middle soluble block. The cores can be connected by the middle block, resulting in formation of gels. The organogels were observed to form in 20~30 seconds upon mixing the two separated solutions. FT-IR study demonstrates that the formation of gels is induced by ionic interaction between SO_3H groups on SPS blocks and pyridine groups on PS-*b*-P2VP diblock copolymer. SAXS investigation shows that nanophase separation occurs in organogels (**Fig. 1**). By theoretical fitting with a hard sphere model, it can be calculated that averagely about 5 protonated poly(2-vinylpyridine) blocks and 50 SPS blocks assemble to form spherical cores and poly(ethylene-*ran*-butylene) blocks bridge the cores to form gels in organic solvents. The dynamic moduli decrease when 0.5v/v% of acid, amine and melt salt are added to pre-formed organogels, and the preformed gels turn into solutions with 2v/v% of acid, amine or melt salt added. The fast formation, multiresponsiveness and the structural tunability endow a variety of properties of these novel charge-induced organogels.



Scheme 1. Formation of organogels from SSEBS and PS-*b*-P2VP.

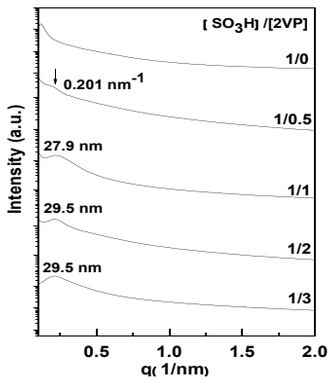


Fig. 1. SAXS profiles of SSEBS/ PS-*b*-P2VP organogels.

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Self-Assembly and Nanomechanical Properties of Block Ionomer Complexes

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Block ionomer complexes exhibit many attractive properties in solid state and in solution. Much attention, in recent times, is focused on block ionomer complexes based on block copolymers containing ionic and non-ionic chains blocks ("block ionomers") with oppositely charged molecules such as polyions, surfactants or metal ions. Recently, we reported the preparation of a class of new block ionomer complexes, namely SSEBS-*c*-PCL, based on sulfonated polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SSEBS) and tertiary amine terminated poly(ε-caprolactone), i.e., 3-dimethylaminopropylamine-terminated poly(ε-caprolactone) (APCL). The formation of these complexes is a result of the protonation from the sulfonic acid groups to the tertiary amine end group. The resultant block ionomer complexes have been successfully used as a template to prepare tough nanostructured epoxy thermosets.[1,2] However, to-date, little work has been done on the phase structure and properties of these novel block ionomer complexes.

In the present work, we report a detailed study of the self-assembly, phase behavior and nanomechanical properties of these new block ionomer complexes. Small-angle X-ray scattering study revealed that SSEBS-*c* -PCL displays less ordered micro-phase structure compared to SSEBS. Quantitative mapping of mechanical properties at the nanoscale was achieved using peak force mode atomic force microscopy. **Fig 1** shows the elastic modulus maps of SEBS, SSEBS and SSEBS-*c*-PCL as well as the corresponding histograms of elastic modulus. It is found that the block ionomer complex possesses higher average elastic modulus after complexation with crystallizable APCL. The moduli for both hard and soft phases increase and the phase with the higher modulus assignable to the hard SPS component shows much more pronounced changes after complexation, confirming that APCL interacts mainly with the SPS blocks. This provides an understanding of the composition and nanomechanical properties of these new block ionomer complexes and an alternative insight into the micro-phase structures of these chemically and mechanically heterogeneous materials at the nanoscale.

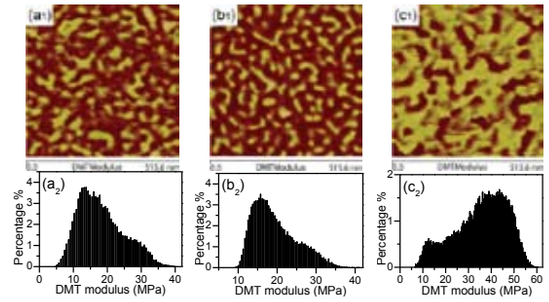

Figure 1. Elastic modulus maps of (a_1) SEBS, (b_1) SSEBS and (c_1) SSEBS-*c*-PCL and the corresponding elastic modulus histograms.

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Tuning Surface Wettability via Ring Opening Polymerisation of Naturally-Occurring Hydrophobic Amino Acid

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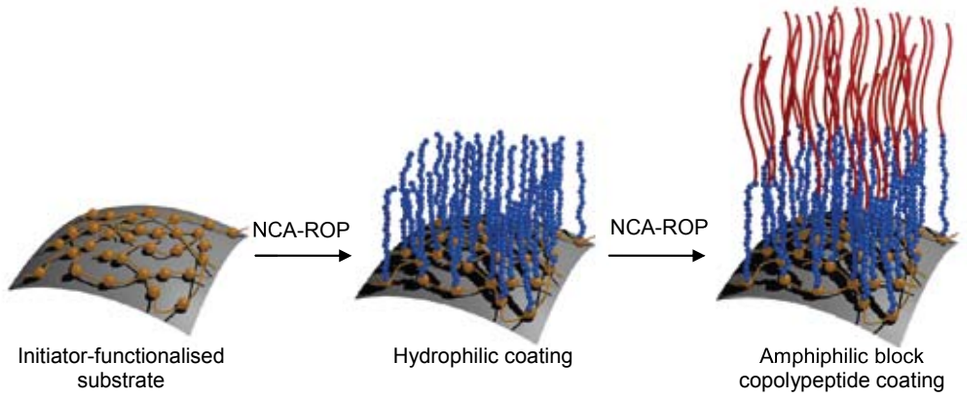
The application of synthetic polypeptide as coating materials is of great interests due to the specific stereochemistry, biocompatibility and (bio)degradability. In particular, the ability to alter surface wetting characteristic by simply tuning the hydrophobic-hydrophilic composition in polypeptide films is highly attractive for engineering non-biofouling surfaces, (bio)chemosensors and other functional materials.[1-3] In this study, we demonstrate the assembly of hydrophobic and amphiphilic peptide-based coatings with tuneable wetting characteristics through surface-initiated ring-opening polymerisation of naturally-occurring hydrophobic amino acid *N*-carboxyanhydrides (NCA-ROP) (**Scheme 1**). To the best of our knowledge, this is one of the first examples of a grafting-from approach with hydrophobic amino acids *N*-carboxyanhydrides from amine-functionalized surfaces.



Scheme 1. Formation of amphiphilic peptide-based coatings by metal-free surface-initiated ring opening polymerisation of of naturally-occurring amino acids.

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Plant-Derived Bio-Adhesive Polymer

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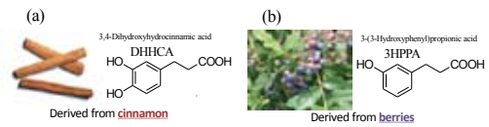
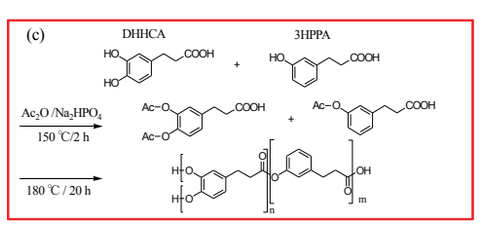
Abstract

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 onto both organic and inorganic surfaces. Although many attempts have been made to clarify the adhesion mechanism, the details are not completely understood. However, potential of the mechanism have fascinated many researchers. For example, the group of Messersmith and Miller has demonstrated to make a practical adhesive sheet using DOPA. Based on preceding studies of DOPA, we have found the adhesive functions plant-derived monomers of cinnamic acids with catechol groups and succeeded to synthesize Mussel-mimicking polyester adhesives biomass monomers which can substitute petroleum materials. In our presentation we will demonstrate novel super Plant-Derived Bio-Adhesives.

Experimental

The monomers composing adhesives were selected under a conception of safeness to environment and human body. Based on this conception, 3,4-Dihydroxyhydrocinnamic acid (DHHCA, Scheme 1a) and 3-(3-Hydroxyphenyl)propionic acid acid (3HPPA, scheme 1b) which can be respectively derived from cinnamon and berries were selected. The copolymer of poly(DHHCA-*co*-3HPPA)s were prepared in the presence of catalyst of Na_2HPO_4 (Scheme 1c). The reaction mixture was treated by acetic anhydride at 150°C and was polymerized for 180°C in vacuo for 20h. The excess acetic anhydride was evaporated during polymerization, and gradually increased its viscosity to finally solidify and not allow further agitation. After cooling down to room temperature, the solid was taken out from flask and milled to powder state of adhesives.





Results

Figure 2 shows the results of shear adhesion test on various engineering materials using molar ration of DHHCA : 3HPPA = 20:80. For positive and negative control, we have respectively compared to results of same test using conventional instant super glue and epoxy resin. It is confirmed that adhesion force of poly(DHHCA-*co*-3HPPA) is superior to that of epoxy resin, which is said to be the strongest glue in engineering field, at every adherent.

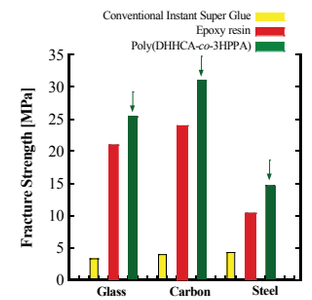


Fig. 2 Adhesion tests

Acknowledgement

This research was financially supported by a New Energy and Industrial Technology Development Organization (NEDO, Project ID: 11B16002d) and Grants-in-Aid for Scientific Research (Wakate B).

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Modification of PLA with e-caprolactone by reactive processing – The effect of modifier loading, temperature, time and catalyst level upon the polymer structure, mechanical, thermal properties and the rate of degradation.

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This poster covers the reactive processing modification of PLA with e-caprolactone. The e-caprolactone modified PLA show significantly improved softness, flexibility and the ability to be processed into films.

It was found that the modified PLA-Caprolactone polymer produced by the in-situ ring opening / trans-esterification process is significantly different to the polymer produced by the melt transesterification of PLA with polycarpolactone. The differences are shown in mechanical, thermal (DSC) as well as chemical structure (NMR, GPC) of the resulting copolymers.

Kinetic data will be presented for the effect of reaction time, catalyst level as well as loading of e-caprolactone. The data for PLA and melt blends of PLA with polycaprolactone are presented for comparison.

The PLA-Caprolactone copolymer also was found to degrade significantly faster in ambient conditions as well as when the polymer is exposed to elevated temperature and humidity compared to PLA, polycaprolactone or blends of PLA and polycaprolactone.

These differences in the chemical structure, morphology and presence of residual catalysts can be used to explain the mechanical, thermal and degradability of the modified PLA copolymer.

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Investigating New Architectures of Natural Rubber and Silicon Based Polymers

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Natural rubber is widely used in many applications for its elasticity, flexibility and waterproofing properties. Produced by some plants, natural rubber is also susceptible to vulcanisation and ozone cracking. However, the downside to natural rubber is that it loses its elasticity as the temperature is lowered and can eventually become brittle/hard.

Silicones are also widely used for their unique thermal and chemical properties. Applications exist in the fields of coatings, electronics, lubricants, medicine to name a few. However, they cannot biodegrade like natural rubber can due to their high level of microbial resistance and UV resistance.

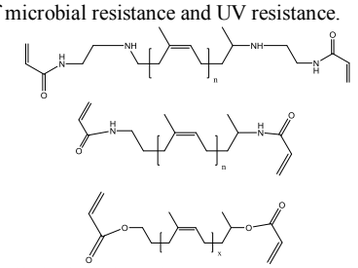

Figure 1. The well-controlled telechelic polyisoprene oligomers that were used in this study.

By chemically combining natural rubbers and silicones, a hybrid material was synthesized. This was achieved by firstly synthesizing three well-controlled telechelic polyisoprene oligomers (Fig.1) that were formed by an oxidative cleavage with successive modifications of the chain ends to obtain acrylate or acrylamide groups. Secondly, these well-controlled telechelic polyisoprene oligomers were covalently attached to many different silicone chemicals to form several structural variations (Fig. 2). Characterized by GPC, NMR, and rheology, each hybrid structure exhibited enhanced properties that the pure materials could not.

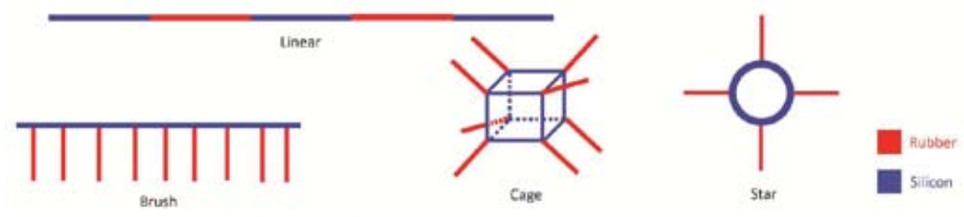

Figure 2. Some of the hybrid architectures investigated.

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The enzymatic hydrolysis and oxidation of poly(glycerol sebacate) and poly(xylitol sebacate)

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Poly (glycerol sebacate) (PGS) and poly (xylitol sebacate) (PXS) are biodegradable elastomers showing potential in implant applications of soft tissue engineering[1, 2, 3]. However, the drawbacks of these two elastomers are the fast *in vivo* degradation rate and the toxicity consequences. Moreover, knowledge on the mechanisms of *in vivo* degradation is limited. In this study the degradation mechanisms of PGS and PXS were explored *in vitro* using tissue culture medium containing an ester hydrolyzing enzyme (esterase), an enzyme (xanthine oxidase) which produce the superoxide anion in an ischemic heart, and/or Fenton's reagent ($FeSO_4/H_2O_2$) which mimics the inflammation response to foreign implants. PGS and PXS prepolymers were crosslinked to two different levels[4] by polyesterification at 130°C for 2 days to produce low crosslink density elastomers, or at 130°C for 7 days (PGS)/12 days (PXS) to give high crosslink density elastomers. These were soaked in culture medium with 1) esterase enzyme, 2) $FeSO_4$/1 vol% H_2O_2 with a molar ratio of Fe^{2+}/H_2O_2, 3) xanthine and xanthine oxidase, 4) $FeSO_4/H_2O_2$ and esterase, or 5) xanthine/xanthine oxidase and esterase to test the comparative rates of de-esterification, oxidation and their combination. These studies were conducted for 35 days, and the extent of degradation was followed by the changes in the sample's mass loss (see **Fig. 1**) and thickness after thorough drying in a vacuum oven prior, and changes in the culture medium's pH. The degradation kinetics of both PGS and PXS materials were found to be primarily determined by the degree of crosslink density, with high crosslink density of the materials demonstrating a slower degradation rate. $FeSO_4/H_2O_2$ and esterase were found to accelerate the degradation of PGS and PXS, whereas the presence of xanthine oxidase/xanthine had no significant influence on the degradation kinetics of the polymers. The results of this work indicate that hydrolysis of ester bonds mediated by the esterase enzyme and oxidation of the polymer chains by free radicals are the dominant degradation mechanisms of PGS and PXS.

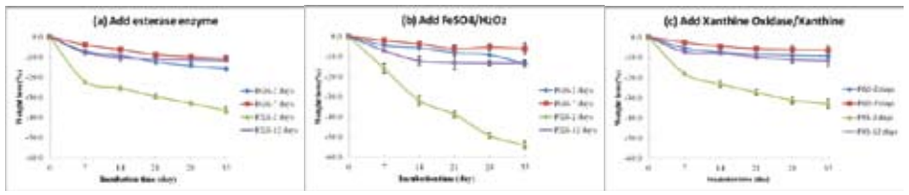

Figure 1. (a)-(c) Weight loss profiles of PGS and PXS during the 5 weeks incubation at 37°C in esterase enzyme, $FeSO_4/H_2O_2$ and Xanthine oxidase/Xanthine, respectively.

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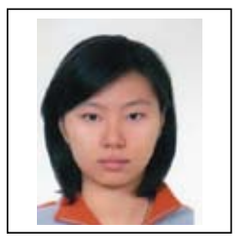

Si_3N_4 COATING FOR POLYMETHL METHYACRYLATE INTRAOCULAR LENS TO PREVENT POSTERIOR CAPSULE OPACIFICATION

Lingli Li[1,2], *Xu Xu*[1], *Xiaona Liu*[1], *Hao Chen*[1*]

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Purpose The purposes of the study was surface modification of polymethyl methyacrylate (PMMA) intraocular lens (IOL) with Si_3N_4 coating to improve its hydrophilicity and biocompatibility, thus potentially reducing the incidence of posterior capsular opacification (PCO) and provide a new surface modification technology for the development of hard intraocular lenses.

Background Posterior capsular opacification (PCO) is the most common complication of extracapsular cataract extraction by phacoemulsification[1]. Many methods are used to prevent PCO including the design of IOLs[2], drug loaded IOLs[3] and surface modification of IOLs[4]. In this study, sputter coating of biocompatible Si_3N_4 was adopted to modify the surface of PMMA IOLs and the effect of coating thickness on the surface properties was studied.

Methods Different thicknesses (10nm, 25nm and 50nm) of Si_3N_4coatings were sputtered onto the surface of PMMA IOLs to improve its surface hydrophilicity. Atomic force microscope (AFM) was used to observe the surface morphology. Hydrophilicity was assessed by static contact angle. Cellular adhesion was performed by human lens epithelial cells (HLECs) onto the surface of the materials to evaluate the effect of surface modification.

Results Surface modification of PMMA IOLs by Si_3N_4 coatings could improve hydrophilicity of IOLs (Fig 1) without etching effect (Fig 2). 10 and 25nm coating of Si_3N_4 can effectively affect the hydrophilicity of PMMA IOLs and greatly reduce the adhesion and HLECs (Fig 3).

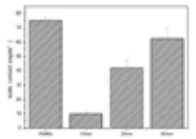

Fig 1. Changes in water contact angle with different thickness of coating

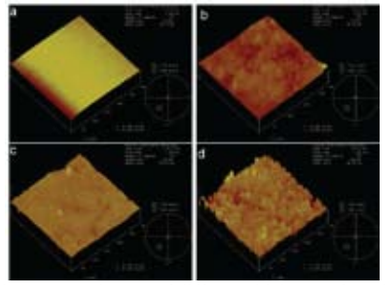

Fig 2. AFM pictures of different thickness of coating: a. pristine; b. 10nm; c. 25nm; d. 50nm

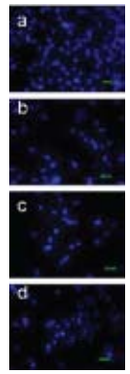

Fig 3. Fluorescence microscope photos of HLEC on different thickness of coating. a. pristine; b. 10nm; c. 25nm; d. 50nm

Conclusions

Surface modification of PMMA IOLs by Si_3N_4 coatings could improve the surface hydrophilicity without affecting bulk material properties. The results of cellular assay show that surface modification of PMMA IOLs by Si_3N_4 coatings results good anti-fouling ability and have some potential in the application of prevention of posterior capsular opacification.

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High-Efficiency Inverted Polymer Solar Cells based on P3HT/$PC_{61}BM$ Blend and Cathode Interlayer

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Polymeric solar cells have attracted considerable attention as a promising alternative for producing clean and renewable energy because of their advantages in low-cost, light weight, flexible and large-area solar devices.[1,2] Bulk hetero-junction(BHJ) is the structure that growing fast in nowadays researches.[3] In a typical conventional BHJ solar cell, which has a structure of ITO/hole selective layer/active layer/electron selective layer/Al, the incident light will go through the glass substrate and the indium tin oxide(ITO) layer then absorbed by the active layer resulting in geminate charges. Then charges will be collected at different electrodes. The ITO works as the anode and aluminium works as the cathode. Cathode buffer layers are inserted between the active layer and metal cathode which may give one or several good effects like dipole effect, better electron transporting, optical spacer, hole blocking and better work function alignment.[4] Up to now research groups have reported conventional BHJ devices with efficiency over 8 percents. Cao's group reported a device structure ITO/PEDOT: PSS/active layer/PFN/Al using low band gap donor material poly[N -9´´-hepta-decanyl-2,7-carbazole-alt-5,5-(4´,7´-di-2-thienyl-2´,1´,3´-benzothiadiazole) (PCDTBT) and novel cathode interlayer of poly [(9,9-bis(3´-(N,N -dimethylamino) propyl)-2,7-fluorene)- alt -2,7-(9,9–dioctylfluorene)](PFN) to achieve efficiency of 8.4 %.[5]

Usually low work function metal used as top cathode is easy to get oxidized, the active layer could degrade and overall performance of the device will drop quickly when being used in ambient environment.[6] A new device structure was introduced into this field, the inverted cells. The typical structure is ITO/electron selective layer/active layer/hole selective layer/Ag (or Al). Compared with the conventional structure, the inverted solar cells can give same good efficiencies and have better long-term stability by using inert metal as top anode.[1] Cathode buffer layers are also introduced into the inverted devices. Researchers have tried both organic and inorganic materials that used as cathode interlayer.[5,7] Wu etc reported the enhanced power-conversion efficiency of 9.2% in inverted polymer solar cells using PFN as the cathode interlayer.[5] Our group has reported enhancement of the performance of the conventional solar cells with three dimensional conjugated inter layers which show 5 to 10% higher efficiency than that with the linear analogues.[8] In this study we synthesize some novel cathode interlayer materials and tested in inverted cells based on poly(3-hexylthiophene)(P3HT) and phenyl-C_{61}-butyric acid methyl ester($PC_{61}BM$) BHJ. Promising results have been achieved and details will be presented in the conference.

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8 Y. Chen, Z. Jiang, M. Gao, S. E. Watkins, P. Lu, H. Wang, and X. Chen, *Appl. Phys. Lett. 100*, 203304 (**2012**)

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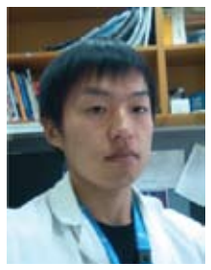

Separation of hydrophilic polyacrylates according to the topology using capillary electrophoresis in critical conditions

Alison R. Maniego,[1, 2] *Dale Ang,*[1, 2] *Yohann Guillaneuf,*[3] *Catherine Lefay,*[3] *Didier Gigmes,*[3] *Janice R. Aldrich-Wright,*[1] *Marianne Gaborieau,*[1] *Patrice Castignolles*[2]

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Branching was observed in polyacrylates when synthesised through radical polymerization.[1] Hydrophilic polyacrylates have shown a potential for drug delivery applications.[2] However, their characterization has encountered difficulties. Lacik *et al*. have observed inconsistencies for the determination of the molecular weight of hydrophilic polyacrylates between two SEC methods (aqueous-phase and organic-phase SEC).[3]

In this work, poly(sodium acrylate), PNaA, was separated for the first time using Capillary Electrophoresis in Critical Conditions (CE-CC). The use of CE-CC enables the characterization of polyacrylates according to their various topologies instead of molecular weight.[4] PNaAs with different branching structures (linear, star branched and hyperbranched) were separated using CE-CC. The PNaAs exhibit an increase in electrophoretic mobility as the degree of branching decreases (**Fig. 1**). The branching topologies of these PNaAs were qualitatively confirmed via solution-state NMR. Separation of several PNaAs according to their end chain were also investigated through CE-CC. The replacement of a relatively bulky nitroxide end group with hydrogen yielded a lower electrophoretic mobility. The novel CE-CC method enabled the characterization of hydrophilic polyacrylates according to their degree of branching and their chain ends for the first time. This will enable the scientific design of polyacrylates and increase their potential for advanced applications.

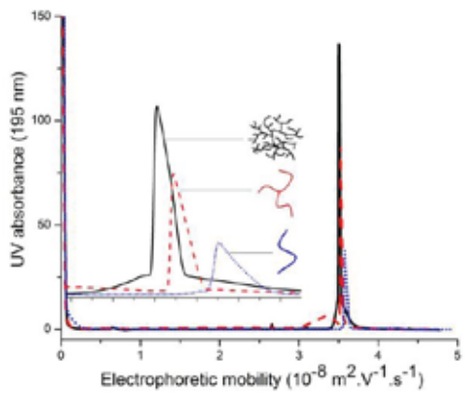

Figure 1. Electropherogram of hyperbranched (solid black line), 3-arm star (dashed red line) and linear (dotted blue line) PNaA with capillary electrophoresis in critical conditions.

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Synthesis and Property of Noria (Water-Wheel Like Macrocycle) Derivatives with Pendant Alkoxyl and Adamantyl Ester Groups, and Their Application for Extreme Ultraviolet Resist

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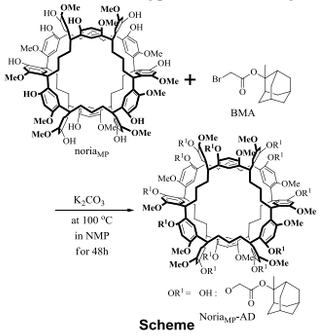
Photolithography system employing electron beam (EB) and shorter wavelength lasers, such as KrF (λ = 248 nm), ArF (λ = 193 nm), and extreme ultraviolet (EUV, λ = 13.5 nm) have been expected to offer higher resolution pattern. Very recently, extreme ultraviolet (EUV) laser has been expected to offer higher resolution pattern with less than about 20 nm resolution. Recently, we could design a ladder type cyclic oligomer "noria" (noria = water wheel in Latin),[1] and examined the synthesis, physical properties, and patterning properties of noria derivatives with pendant *t*-butyl ester groups, *t*-butyloxycarbonyl groups, adamantyl ester groups, cyclohexyl acetal moiety, and oxetanyl groups using electron beam (EB) or EUV exposure systems.[2] Meanwhile, noria analogues with pendant twelve alkoxyl groups could be synthesized by the condensation reaction of 1,5-pentanedial with 3-methoxyphenol or 3-ethoxyphenol under dynamic covalent chemistry (DCC) system.[3] In DCC system, noria derivatives with pendant twelve methoxy groups ($noria_{MP}$) and twelve ethoxy groups ($noria_{EP}$) could be obtained selectively and their solubility and film-forming ability are superior to those of noria. In this paper, synthesis, physical properties, and patterning properties of $noria_{MP}$ derivatives ($noria_{MP}$-AD) with pendant adamantyl ester moieties were examined.



Scheme

Figure EUV-resist pattern at 32 nm-hp obtained with $noria_{MP}$-Ad_{18}. Exposure dose = 9.0 mJ, LER = 10.5 nm.

$Noria_{MP}$-AD_n was synthesized by the substitution reaction of $noria_{MP}$ and 2-bromoacetyloxy-2-methyladamantane, and the degrees of adamantate moieties (DI) could be controlled by the their feeds ratios(Scheme). We prepared $noria_{MP}$-AD_n with DI values of 11, 18, 45, 54, and 75%. The physical properties such as solubility, film-forming ability, and thermal stability of $noria_{MP}$-AD_n with more than DI = 18% were very good for the application of positive resist material. $Noria_{MP}$-AD_{18} (DI = 18%) provided a clear line and space pattern with a resolution of 32 nm and a line-width roughness (LWR) of 10.5 nm with exposure dose = 9.0 mJ/cm^2 in an EUV resist system (Figure). The synthesized $noria_{MP}$-AD showed high sensitivity in an EUV system and have high potential to offer higher resolution pattern as next-generation EUV-resist materials in near future.

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Well-defined polyoxazoline-based amphiphilic copolymers: from synthesis by polymer-polymer coupling to self organization in water

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The increasing interest of amphiphilic copolymers mainly arose from their self-organization in water leading to the formation of micelles where hydrophobic core is surrounded by a hydrophilic corona. This property was employed for the encapsulation of chemicals using polymeric drug carriers, for instance. Among all the possible synthesis pathways, the polymer-polymer coupling appeared to be an attractive approach to get block copolymers. Over the last few years, polymer-polymer coupling using "click" chemistry showed enormous potential for material science. One of the great advantages of this concept was for example the possibility to combine homopolymers preliminary prepared by various living/controlled polymerization techniques. Huisgen's cycloaddition catalyzed by copper (CuAAC) was notably investigated to produce block copolymers but less examples of CuAAC polymer-polymer coupling dealt with the synthesis of amphiphilic copolymers.

We report here the synthesis and self-assembly of original amphiphilic block copolymers based on poly(2-methyl-2-oxazoline) (P(MOx)) and (i) poly(tert-butyl acrylate) (P(t-BA)),[1] or (ii) poly(ε-caprolactone) (PCL)[2] to get P(MOx)-*b*-PCL diblock copolymers or PCL-*g*-P(MOx) graft copolymers, respectively. The P(MOx), PCL and P(t-BA) building blocks were synthesized either by ROP or ATRP processes. The alkyne and azide terminal functionalizations were carefully characterized by MALDI-Tof spectroscopy and polymer-polymer coupling was then achieved using Huisgen's cycloaddition reaction. Self-assembly of resulting amphiphilic diblock copolymers in water was studied by AFM, TEM, DLS and fluorescence spectroscopy.

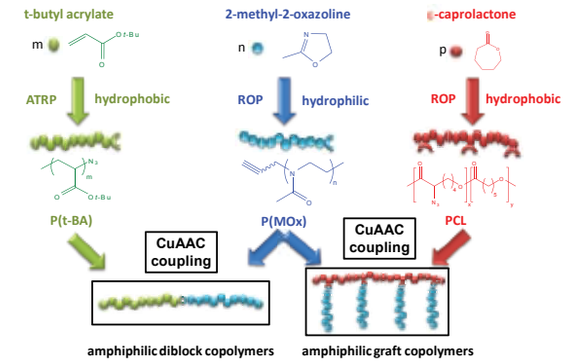

Figure 1. Reactional pathway for the synthesis of poly(2-methyl-2-oxazoline)-based amphiphilic copolymers.

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Solid Li^+-carrying Membranes

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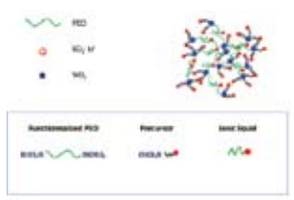
There is currently a strong industrial demand for all-solid-state lithium batteries. Especially, solid electrolytes offer crucial advantages in terms of safety. This demand has prompted the recent development of polymer electrolyte membranes (PEMs), which are particularly attractive because they can be flexible and shaped in different geometries. However there are some important limitations to their industrial development. As a matter of fact ion conductivity in solid state up to now remains significantly below that observed in liquid, especially at low temperature.

There is currently a burst in using room-temperature ionic liquids (liquids consisting of only ions) in polymer-in-salt systems, due to their unique properties (high ionic conductivity, negligible vapor pressure, thermal stability, non-flammability and wide electrochemical stability window). However, the simple dissolution of a lithium salt in ionic liquids always results in electrolytes in which only a fraction of the current is actually carried by Li^+ ions. Moreover, extensive loadings of ionic liquid entail a loss of mechanical resistance of PEMs in relation to plasticizing effects, and some release of the ionic liquid may affect their long-term stability.

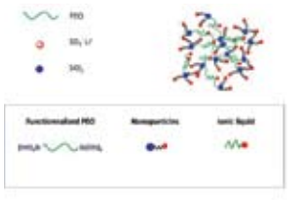
SLiM project proposes to address these issues by designing new ionic liquid lithium salts and by incorporating them into nanocomposite polymer-silica membranes. PEO chains are chosen for their outstanding ability to solvate lithium cation. We are currently developing two methods to obtain these polymer-silica membranes. The first one arises from the end-bonding of polyethylene oxide (PEO) chains to silica-like nanofillers (**Scheme 1**). These nanofillers are produced *in situ* by sol-gel. The second method consists in the incorporation of silica nanoparticles into the polymer chains. The incorporation of silica component provides mechanical strength, thus allowing high loadings of ionic liquid. The surface of these silica-nanofillers or nanoparticles are functionalized with lithium salt groups (sulfonates or bis(sulfonyl)imides), which afford lithium cations as charge carriers, while minimizing the contribution of anions, which are bonded to the surface, to the ionic conduction (**Scheme 2**).

In PEMs for lithium battery, ionic liquids (ILs) are usually quaternary aliphatic ammonium salts, in which a lithium salt is dissolved. In the present project, the ionic liquids will be themselves lithium salts. Moreover their sulfonate (or bis(sulfonyl)imide) anions will be tagged with ethylene oxide units. Accordingly, they are expected both to act as plasticizers of PEO chains and to contribute to the solvation of Li^+. Actually, all the components (the ionic liquids as well as the functional groups in nanofillers) are built from original aromatic perfluorosulfonate and perfluorobis(sulfonyl)imide synthons.

In this presentation we will describe the results obtained for the synthesis of our sol-gel precursors bearing lithium salt groups and for the functionnalisation of silica nanoparticles. Our synthesis methods imply thiol-ene reaction as well as click-chemistry. The first results concerning the formation of polymer-silica membranes will be discussed in term of mechanical stability, mechanical properties and ionic conductivities.



Scheme 1: Nanofiller produce by sol-gel method



Scheme 2: Incorporation of silica nanoparticles

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The Utilization of Two Recycled Polymers and Bagasse Fibers in Wood Plastics Composites Nano / Clay

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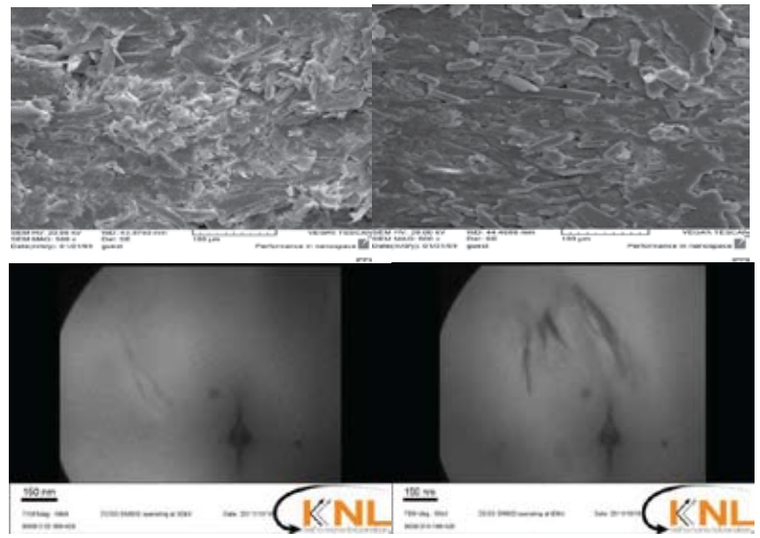
In this study, to improve the mechanical properties of wood plastics nano-composites, baggase is used as a reinforcing material. The amount of baggase fibers at different levels (25, 35and, 45 percent) on the performance of wood plastics composites was considered. Two recycled polymers (rPP and rHDPE) were used as a polymer matrix. Tensile, flexural and impact properties were measured according to ASTM standard regulations. To interpret the results of scanning electron imaging (SEM) and X-Ray Diffraction (XRD) was performed. The use of 35 percent of bagasse compared with 25 and 45 percent has increased strength of wood plastics composites.When using rHDPE nano-clay particles strength properties is the maximum. Imaging the morphology of nano-clay by x-ray diffraction and electron microscopy showed that the distribution of nano-clay particles on polymer in the structure of intercalation that with rHDPE of nano-clay in 2 percent increased the distance between layers.



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Synthesis of glycopolymer–gold(I) complexes

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Gold(I) complexes such as auranofin are promising therapeutic agents against several types of cancer,[1] but ligand displacement reactions with serum proteins limit their potency *in vivo*. We have developed several block copolymer micelle systems in which gold(I) drugs are complexed to the core block with the aim of limiting drug exposure to serum proteins and promoting delivery into cancer cells (Fig. 1).

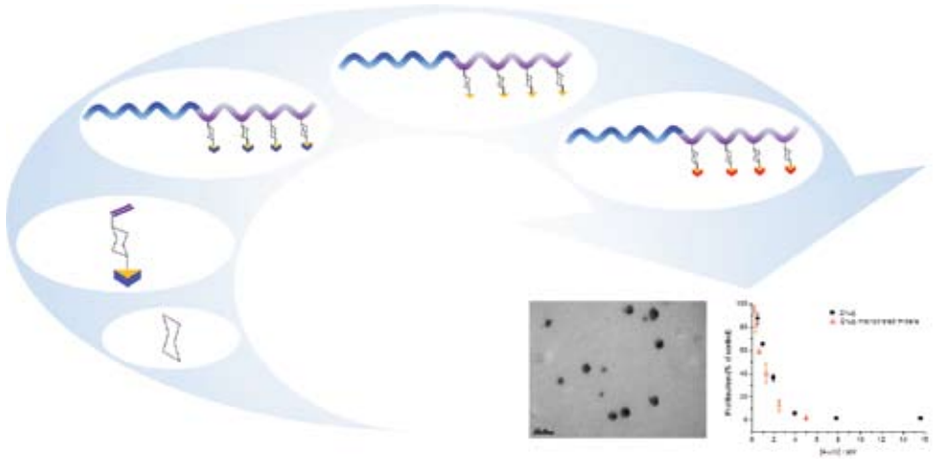

Figure 1. Schematic of monomer synthesis, polymerisation, deprotection, complexation of gold(I), and micellisation to form drug carries whose cytotoxicity matches that of the free drug.

We have designed glycomonomers displaying protected thiols in the anomeric position, which can be polymerised via RAFT to generate well-defined block copolymers. Deprotection yields free thiols to which gold(I) can be complexed, introducing auranofin-like pendant groups along the polymer chains. The resulting glycopolymer–gold(I) conjugates self-assemble into spherical structures under aqueous conditions, with the gold-containing block forming the hydrophobic core.

Our initial work utilised a disulfide-protected glycomonomer to generate block copolymer micelles containing deacetylated auranofin units in the core. The cytotoxicity of this system rivalled that of the free drug in ovarian cancer cells (inset, Fig. 1).[2] Recently we have developed a more robust and hydrophobic glycomonomer which undergoes a remarkably efficient deprotection and complexation sequence to generate narrowly defined block copolymers containing gold(I) units analogous to auranofin itself. The resulting particles have shown high cytotoxicity in both normal and cisplatin-resistant ovarian cancer cells. Finally, a post-polymerisation approach proved an effective alternative for introducing protected thiol groups into glycopolymers.

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Study of Well-Defined Poly(*N*-isopropylacrylamide) Hydrogels via Thiol-ene Chemistry

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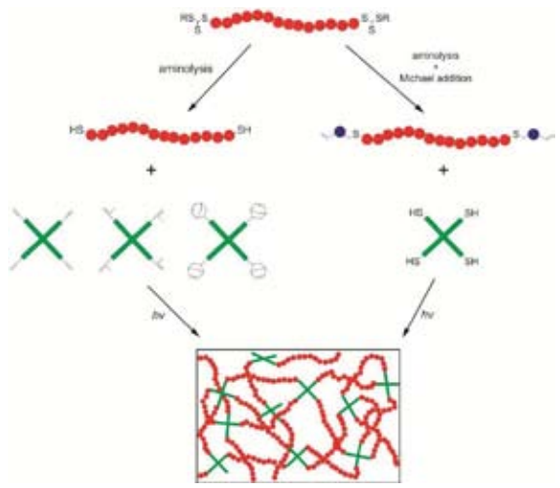
Since the emergence of the "click" chemistry concept,[1] there has been tremendous interest in studying many other classical organic reactions that may potentially be qualified as "click" chemistry. The most widely used "click" reaction to-date is the Cu-catalysed azide-alkyne Huisgen cycloaddition. However, one of the biggest drawbacks of this reaction is the use of copper as catalyst, which is cytotoxic at low concentrations[2] and nearly impossible to remove completely, hence rendering this reaction unsuitable for synthesising biomaterials. Therefore, many efforts have been put forth to improve this reaction so that the use of copper as a catalyst can be avoided while still being consistent with the concept of "click" chemistry.

The use of thiol-ene free radical chemistry to prepare crosslinked networks was first reported in the 1970s.[3] Among the advantages of using thiol-ene radical reactions to form networks over traditional methods (i.e. acrylates) are the rapid formation of crosslinks quantitatively under ambient conditions and fewer defects typically found in conventional radical photopolymerisation reactions. Thiol-ene chemistry has proven to be a versatile, mild and rapid technique to prepare crosslinking networks. The use of light as an initiation source allows spatial and temporal control of the reaction sites. When used with biocompatible materials, this reaction does not form side products, if any, that are toxic and harmful to biological systems. The step-growth mechanism involved in radical thiol-ene reactions enables formation of more homogeneous hydrogel networks compared to conventional free radical polymerisation techniques.



In this study, well-defined poly(N-isopropylacrylamide) P(NIPAAm) networks were synthesised using a Cu-free "click" reaction via photoinitiated thiol-ene "click". Scheme 1 depicts the overall reaction plan to prepare the hydrogels. RAFT polymerised P(NIPAAm) with trithiocarbonate end-groups are synthesised and modified via two proposed reaction routes: The thiol functionalised P(NIPAAm) chains were then reacted with three, four-arm crosslinkers, which were conjugated with acrylate, methacrylate and norbornene groups; at the same time the methylene end functionalised P(NIPAAm) chains are used to crosslink to form networks with a four-arm crosslinker with conjugated thiol groups.

Scheme 1: Synthetic plan to prepare P(NIPAAm) "model networks" via photoinitiated thiol-ene reaction.

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In-situ Monitoring of Microwave Polymerisations for Increased Activity

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Microwave chemistry has shown great promise for industrial processes, so considerable research has been focussed on observing the effects on chemical reactions for applying microwave heating. A number of these studies have proposed the existence of non-thermal effects to explain the practical observations made. Consequently, there has been much debate over the existence of such effects. In many of the more recent studies into microwave chemistry, these conclusions have been shown to arise from poor temperature comparisons between the microwave experiments and their conventional counterparts due to the use of IR temperature probes. The use of fibre-optic temperature probes have led to more accurate measurements which allow the bulk temperature of reactions to be closely matched using both heating methods. As a result, the existence of novel non-thermal effects has been questioned, in favour of hypotheses which centre upon as the existence of thermal effects such as selective heating and activation of key species in the system. Increased yield observed in rapid, high temperature microwave polymerisations suggest an increase in the kinetics of propagation in radical polymerisations, induced by selective heating. As such, it is proposed that selective heating rates of radical species are promoting propagation effects in polymerisation.[1]

This study details investigations into such selective heating effects in catalytic chain transfer polymerisation (CCTP). Recently, we have developed a method for CCTP which utilises *in-situ* formation of the chain transfer catalyst. $CoBr_2(dpgH_2)_2$ (**Fig.1**) is synthesized in a one-pot polymerisation method by addition of cobalt(II) bromide and *anti*-diphenylglyoxime.[2] The resulting complex has very similar activity to existing benchmark CCTP catalysts such as CoPhBF and whilst air-sensitive once complexed, the two reagents are stable at standard conditions, making the catalyst very suitable for industrial applications. The formation of the complex was monitored using an *in-situ* fibre-optic Raman spectroscopy system in both microwave and conventional heating systems (**Fig.2**). Electron Spin Resonance (ESR) spectroscopy was also used to monitor the formation of the complex. Polymerisations of methyl methacrylate were performed using the $CoBr_2(dpgH_2)_2$ catalyst in both conventional heating and microwave heating environments to ensure the existence of both increased rate of complex formation and radical activity due to microwave heating. The polymerisations were also monitored with an *in-situ* Raman spectroscopy system and ESR spectroscopy to measure increased radical activity.

Figure 1. Structure of catalyst

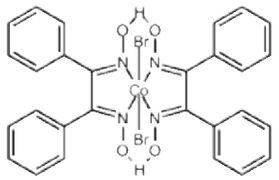
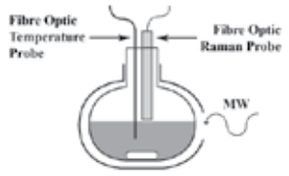


Figure 2. *In-situ* Raman spectroscopic monitoring of microwave reactions



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[2] K. Adlington, A. Green, W. Wang, S. Howdle, D.J. Irvine, *Dalton Trans.* **2012**, *42*, 127-136

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Coating of Inorganic Nanoparticles with Mussel-Inspired Amphiphilic Copolymers and Fabrication of Hierarchic Porous Films

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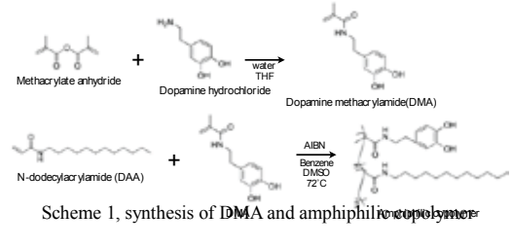
Inorganic porous structures attract much interest due to their high potentials for improving photocatalitic activities, increasing surface areas, and so on. Especially, hierarchic porous structures enhance these activities further. The breath-figure technique is one of the preparation methods to prepare porous films by using condensed water droplets on polymer solution as templates. To employ this method to fabrication of porous films comprised of inorganic nanoparticles, nanoparticles should be dispersed in organic solvents. Catechol groups, which are involved in foot proteins of mussels, strongly adhere onto inorganic surfaces including noble metals, oxides, and ceramics. In this study, we synthesized an amphiphilic copolymer containing catechol groups and prepared hierarchic porous structures of inorganic nanoparticles covered with the polymer by using the breath-figure methods.

N-(3,4-Dihydroxyphenthyl)methacrylamide (DMA) was prepared from dopamine hydrochloride and methacrylamide anhydride in water with sodium borate as protecting group. Amphiphilic copolymers containing catechol groups were synthesized from DMA and N-dodecylacrylamide(DAA) in benzene and DMSO(Scheme 1). The ratio of DMA and DAA was one to eight respectively. The amphiphilic copolymer having catechol groups were successfully synthesized. A yield of the amphiphilic copolymer was 55 %. From the SEC measurements, a number average molecular weight and polydispersity index(Mw/Mn) of the amphiphilic copolymer were 1.0 x 10^4 and 2.42, respectively. Titanium dioxide (TiO_2) nanoparticles were ultrasonicated in chloroform for 5 min. A chloroform solution of the amphiphilic copolymer was added into the TiO_2 nanoparticle dispersion, and then mixed solution was ultrasonicated for 5 min. The resulting solution was washed with mixture of chloroform and acetone, and corrected by centrifugation three times. Stabilized nanoparticles were re-dispersed in chloroform and then the chloroform solution was cast on a glass substrate under highly humid condition and dried. Finally, the obtained film was heated at 600˚C for 5 min in air.



Scheme 1, synthesis of DMA and amphiphilic copolymer

Due to stabilization of TiO_2 nanoparticles with the amphiphilic copolymer, the stabilized nanoparticles were well dispersed in chloroform. Dispersed size of TiO_2 nanoparticles in chloroform was ca. 210 nm determined by dynamic light scattering measurements. Hierarchic porous structures comprised of TiO_2 nanoparticles were successfully prepared by using water droplets as templates. The porous materials had hexagonally arranged pore and three-dimensional structures. The top and bottom layers were connected with pillars. To remove the amphiphilic copolymers, the porous structures were heated at 600˚C. After heating, the porous structures kept their three-diminsional structures, and nano-sized pores were observed among nanoparticles (Fig. 1). These results suggested that hierarchic porous structures were successfully prepared. Hierarchic porous structures composed of other kinds of nanoparticles also will be discussed.

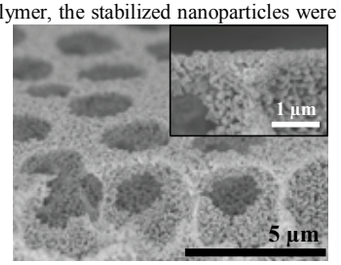


Fig. 1, a tilted SEM image of hierarchic porous structure after annealing. The inset shows a magnified image.

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Multi-layered Polymersome Formed by Amphiphilic Asymmetric Macromolecular Brushes

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Well-defined amphiphilic asymmetric macromolecular brushes were synthesized recently and were able to self-assemble into vesicles in selective solvents.[1] The self-assembly of polymer brushes consisting of a solvophobic backbone attached with two different side-chains, solvophilic and amphiphilic diblock, is explored by dissipative particle dynamics.[2] Dependent on the block length, molecular architecture, and grafting density, the multi-compartment aggregate exhibits a rich variety of morphological conformations, including five types of vesicles, porous aggregates, worm-like micelles, donut micelles, hamburger micelles and unimolecular micelles (Figure 1). For certain polymer brushes, atypical polymersomes with asymmetric multi-layered membranes are spontaneously formed. In addition, temperature variation induced morphological transformation from an asymmetric four-layered polymersome to a symmetric seven-layered polymersome is observed for polymer brushes containing a thermoresponsive block (Figure 2). Consequently, the resulting polymersome decreases in size quite sharply as temperature exceeds lower critical solution temperature. These simulation findings are consistent with experimental observations. By varying the lengths of various blocks, the morphological phase diagram and internal structures of the resulting aggregates are obtained. At a fixed composition of polymer brushes, the aggregate morphology varies with the structural arrangement of the two solvophilic blocks in the molecule. Asymmetric polymersomes are formed when the two solvophilic blocks are separately attached to the backbone and side-chain. Although asymmetric vesicles are observed at moderate grafting density, unique donut aggregates are formed for high density but hamburger micelles develop at low density.

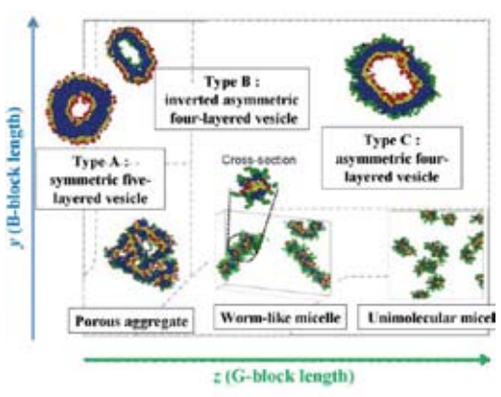

Figure 1. The characteristic morphological snapshots are illustrated for various B-block lengths (y) and G-block lengths (z).

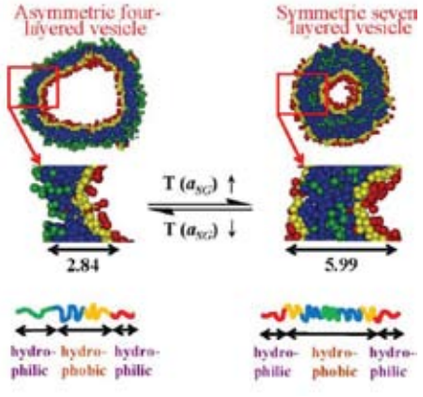

Figure 2. The structure comparison between the membranes of polymersomes at temperatures higher than LCST and lower than LCST.

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Termini-modified mPEG5k-Dendritic Poly-(*l*)-lysine Cationic Copolymers for Low toxic and Efficient Gene Delivery

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Gene therapy has been rapidly developed as a new approach to treat inherited human diseases and recently also other diseases. However, most of the synthetic polymeric gene carriers such as PEI, PAMAM etc were constructed from synthetic products with low biocompatibility, which leads to high cytotoxicity, limiting their application[1]. As the solution of the dilemma between the safety and efficiency, new synthetic polymeric vectors with biocompatible natural product building blocks have attracted increasing attention in recent years[2].

In this work, we developed a series of termini-modified mPEG5k-dendritic poly-(*l*)-lysine cationic copolymers (mPEG5k-DPL4-CG) by coupling of various cationic moieties onto mPEG5k-G4-dendritic poly-(*l*)-lysine (mPEG5k-DPL4) skeleton[3]. The cytotoxicity and *in vitro* gene transfection was evaluated in COS-7 cell line in the presence and absence of serum by MTT assay and luciferase expression assay(Figure1), respectively.The results suggest that low molecular weight PEI800 termini-modified cationic copolymer mPEG5k-DPL4-PEI800 might be utilized as a low toxic and high efficient carrier for gene delivery applications.

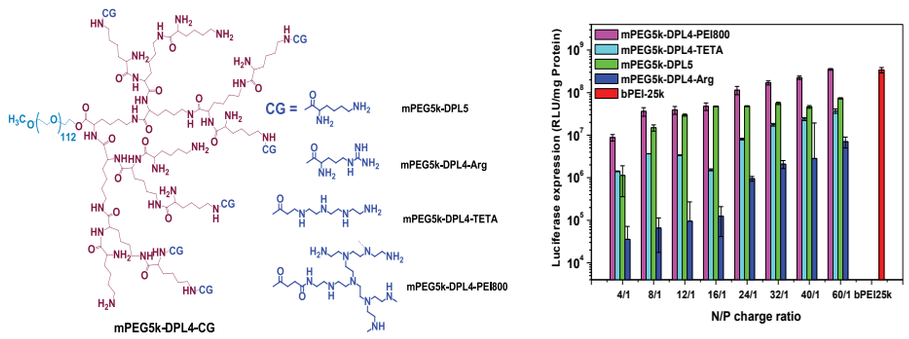

Figure 1. Molecular structure of the cationic copolymer mPEG5k-DPL4-CG (left) and their luciferase gene transfection efficiencies in COS-7 cells (right).

Key word: cationic copolymer, dendritic-(*l*)-lysine, termini-modification, gene delivery.

Acknowledgements: The authors thank the National Science Foundation of China (21174160, 20874114, 21002116 and 81001406) for their financial support.

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Amino acid-based star polymers for cancer therapy

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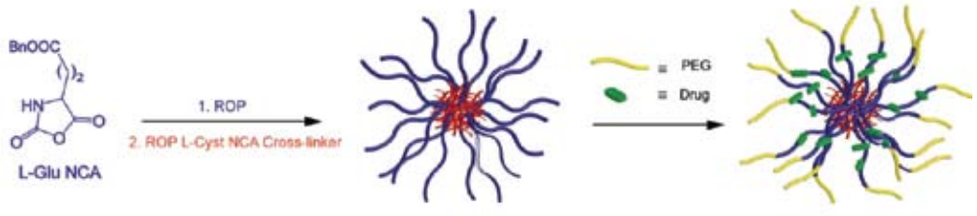
Polymer-drug conjugates have demonstrated to be a viable approach to combating the shortfalls of free drug molecules in cancer therapy by functioning as effective drug nano-carriers that increase local drug concentrations at the desired site of therapeutic need.[1] The conjugates alter the biodistribution of the free drugs, and enable tumour-specific targeting, and release of drug payloads to tumor sites, thus reducing toxicity issues. Overcoming the biocompatibility and biodegradability issues that hamper many existing synthetically derived polymer-drug conjugates has necessitated the use of natural building blocks, such as amino acids.[2]

Recently, amino acid-based core cross-linked star (CCS) polymers as drug delivery vehicles have been synthesized by ring-opening polymerisation (ROP) of amino acid *N*-carboxyanhydride (NCA) derivatives.[3] These star polymers have demonstrated a wide range of core functionalities, effective encapsulation of hydrophobic drugs in the core, core degradation and active targeting towards cancer cells.[3, 4] However no studies have been reported on polypeptide-based CCS concerning covalent drug attachment and more importantly, controlled drug release from the CCS arms. The labile attachment of drugs to the CCS through pH sensitive hydrazone linkages on the arms presents a viable approach to the controlled release of drug inside the tumour cell endosome.

It is the aim of this project to extend and improve the synthesis and functionalisation of amino acid-based CCS polymers composed of poly-L-glutamic acid arms and poly-L-cystine core for effective acid-labile conjugation of drugs to the CCS arms (**Scheme 1**). Drug conjugation, drug release and cell studies will be reported. Functionalisation of the arms for advanced CCS targeting of cancer cells will also be investigated.



Scheme 1: Formation of functionalised amino acid-based CCS for covalent conjugation of drugs to star arms

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Reducible Polymer DNA-Hydrogel as a Dual Switchable Release Gate

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Recently the concept of DNA assembly has been expanded to construct biocompatible stimuli-responsive DNA hydrogels. The ability of DNA hybrid networks to undergo conformational changes based on DNA hybridization and strand displacement mechanisms has been widely analysed at the macroscopic level. However, in order to develop dynamic DNA based hydrogels capable of performing programmable logic operations, a better understanding of the switching capabilities at the microscopic scale is required to generate more flexibility to further applications as biosensors and/or drug/gene delivery devices.

In the present study, we explore in more detail both the macroscopic and the microscopic phase transitions of a novel dual stimuli responsive polymer-DNA hydrogel that is cross-linked *via* DNA base pairing and disulphide bonds. By tailoring the swelling properties on disulfide bond disruption and toehold-mediated DNA strand displacement, the hydrogel can function as a programmable logic gate for multiplex detection and sensing or controlled release applications depending on the number of cross-linking units and on the selectivity of the DNA strands.

The hydrogel was synthesised *via* free radical polymerization. Gel formation and its capabilities to switch between mechanically distinct conformational states in response to a target DNA sequence and/or a reducing agent were evaluated by rheological studies. Microscopic morphological changes of the gel inner structure consequent to the exposure to the dual stimuli were analysed by cryo-scanning electron microscopy. Controllable release properties were investigated by fluorescence spectroscopy following the diffusion rates of FITC-Dextran 150 KDa from the gel matrix. Sensing and signalling abilities were evaluated by fluorescence microscopy. Fluorescent microparticles were chosen as signalling agents and their translocation through gels following exposure to different stimuli was examined.

In all cases breaking of the inter-chain cross-links caused by the addition of either a target DNA sequence or a reducing agent, allows control over pore sizes in the gel, enabling programmable release and transport of objects of different length scale.

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Effect of Lithium bistrifluoromethanesulfonimidate on the Propagation rate of Methyl Methacrylate

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The ability of Lewis acids to afford a degree of stereocontrol in the radical polymerization of acrylate and acrylamide polymers has been well studied[1]. In some systems it has also has been observed there is an enhancement of the rate of polymerization[2,3]. Stereocontrol and rate enhancement is thought to be due to the ability of the Lewis acid to coordinate to the carbonyl group but the actual mechanisms for these effects are not clear. Whilst overall polymerization rate enhancement has been observed, investigations of the individual rate constants have not been carried out. Pulsed laser polymerization (PLP) provides an efficient and accurate route to k_p which will give us clues to whether the propagation step is involved in the coordination.

In this work we have carried out a detailed study on the effect of a lithium based Lewis acid, lithium bistrifluoromethanesulfonimidate (LiBTFMS) on the propagation rate constant, k_p. We have also measured the tacticity of the resulting polymers. Whilst a definite enhancement of k_p was observed during PLP (**Fig**. 1), there was is no effect of the LiBTFMS on the tacticity of the resulting poly(methyl methacrylate). This indicates that the coordination of the lithium ion favours either the polymer chain end and/or the monomer.

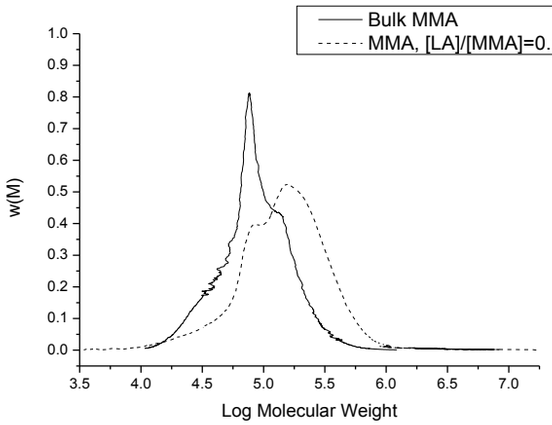

Figure 1. Plot of w(M) vs logM for the PLP of MMA with and without LiBTFMS at 25°C and 5Hz

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Synthesis of Noria-like Macrocycle Containing Methoxy Groups based on the Dynamic Covalent Chemistry (DCC) System by the $A_2 + B_4$ type Condensation Reactions

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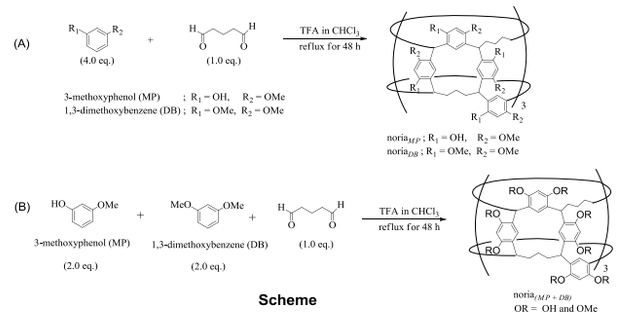
Dynamic covalent chemistry (DCC) has more attractive attention, because the final products are depending on thermodynamic stability under equilibrium control, and a one pot method can be used. DCC can become a powerful tool for the synthesis of non linear products selectively. Certain dynamic covalent bonds are well known such as acetal, disulfide, ester, and imine. Gutsche[1] reported that calixarene was successfully synthesized in high yield based on a DCC system. We[2] succeeded the synthesis of ladder cyclic oligomer (noria; water-wheel in Latin) based on a DCC system by the condensation reaction of resorcinol and 1,5-pentanedial, which is similar to the way for the synthesis of calixarene. The noria had 24 hydroxyl groups, 6 cavities in the side, and a large hydrophobic central hole, i.e., a water-wheel-like structure with ladder-type cyclic rings. Furthermore, noria derivatives containing acid labile groups were good candidates for next-generation electron beam (EB)- and extreme ultraviolet (EUV)-resist materials,[3] because their photo-sensitivity and structural stability were excellent. However, the solubility and film forming property of noria were insufficient. If hydroxyl groups of noria converted to methoxy groups in part, the resulting noria derivatives can have better solubility and film forming ability compared to those of noria, and are applicable to novel next generation resist materials. In this paper, we therefore considered the synthesis of new noria-like macrocyle by the condensation reaction of 3-methoxyphenol or 1,3-dimethoxybenzene with 1,5-pentanedial (Scheme).[4]



Scheme

The condensation reaction of 3-methoxyphenol and/or 1,3-dimethoxybenzene with 1.5-pentanedial using certain acids (HCl, CF_3COOH, CH_3COOH, H_3PO_4, $BF_3{\cdot}Et_2O$) as catalysts in ethanol and $CHCl_3$. It was found that these reactions proceeded based on dynamic covalent chemistry system to afford the soluble polymers, oligomers, and noria-like ladder macrocyles. As the result, the selective synthesis of the noria-like macrocycles could be achieved in high yields under the conditions using CF_3COOH as a catalyst in $CHCl_3$ at reflux for 48h. This reaction proceeded under DCC, yielding noria-like macrocycles containing alokoxy groups such as $noria_{MP}$, $noria_{DB}$, [Scheme (A)]and $noria_{MP+DB}$ [Scheme (B)] in 82 ~ 87% yields. The thermal stabilities and solubilities of the synthesized these macrocycles were consistent with the ratios of hydroxyl and methoxy groups. This means that the physical property of $noria_{MP+DB}$ can be controlled by the feeds ratios of 3-methoxyphenol and/or 1,3-dimethoxybenzene. The applications of $noria_{MP+DB}$ are under now investigation for EB and EUV resist materials.

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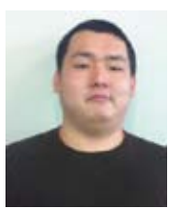

Separation of DNA bound with Cisplatin, Hoechst33258 and Ethidium Bromide by Capillary Electrophoresis in the critical conditions

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According to the Australian Cancer Council, cancer is the leading cause of deaths in Australia claiming approximately 30% of all deaths. Extensive research has been carried out to develop new anticancer drugs since the discovery of cisplatin currently used in cancer treatment[1, 2]. The interaction of the drugs with DNA is one key in understanding their mechanism of action. It is known that interactions are complex and can occur by many modes[3]. The characterisation of these complexes is important as it would reveal information on the effect and mechanism of the drug.

The current work separates the drug - DNA complex using capillary electrophoresis in the critical conditions: the separation is independent of molecular weight (number of base pairs) and by the DNA structure only[4]. Capillary Electrophoresis allows for the analysis of large sections of DNA in solution which is limited in other techniques such as X-ray diffraction and Mass spectrometry. Through CE changes in electrophoretic mobilities are monitored as a function of the drug or model compound bound to DNA. The method is also relatively quick and simple compared to others such as NMR spectroscopy and viscosity measurements.

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Characterizing chitosan and its conjugates for biomedical applications

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Chitosan is a promising material for biomedical applications: it is antifungal, antimicrobial, biocompatible, biodegradable and additionally exhibits good mechanical and thermal properties[1]. This study aims at properly characterizing pure chitosan and modified chitosan samples using free-solution capillary electrophoresis (CE) for the first time, as well as solid-state nuclear magnetic resonance (NMR) spectroscopy [2].

The controlled grafting by nitroxide-mediated polymerization of synthetic polymers such as poly(methyl methacrylate), PMMA, and poly(styrene sulfonate), PSS, was used to improve elasticity and mechanical properties[3]. Electron-spin resonance (ESR) and free-solution CE were used to confirm the synthesis of intermediates in the grafting process, such as BlocBuilder covalently grafted onto chitosan. Solid-state NMR and thermogravimetric analysis (TGA) allowed the analysis and direct observation of the grafting of PSS and PMMA onto the chitosan powder and also allowed a comparison of methods of grafting and adsorption. The grafting method used was proven to successfully graft the polymers onto chitosan at a significantly higher amount.

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Novel Epoxy Resins From an Unlikely By-Product

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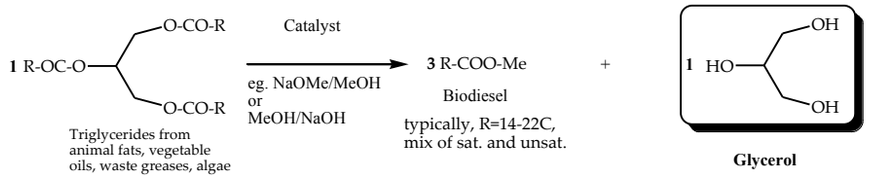
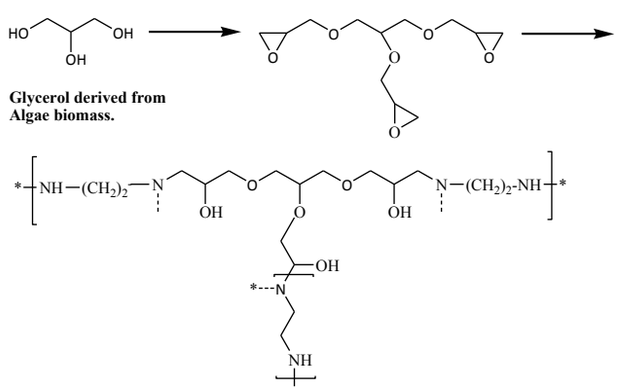
Over the last 20 years there has been a huge interest in alternative fuels coupled with climate change and the cost of oil. This has resulted in the exponential increase of biodiesel producers worldwide with the core starting material ranging from canola crops (food vs fuel debate) to the more elaborate of fresh and salt water algae.

Consequently, as seen from scheme 1 below, this huge increase in biodiesel manufacturing has led to an over-supply of the by-product glycerol (mega tonnes) after the usual refinement for pharmaceutical products and the like.



In order to make use of this over supplied by-product, we have developed new methods for producing an epoxy starting material from glycerol and the production of a variety of cured epoxy resins as seen below in Scheme 2.



The results described in the poster will highlight significant advances in this project with the possibility of new epoxy resins produced from an unlikely by-product.

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Self-assembly of Solvophilic Nanoparticles in a Polymer Matrix: Depletion Interactions

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The property improvement of polymer materials can be achieved by the incorporation of nanoparticles into polymer matrices. However, the dispersion of nanoparticles in a polymer matrix has been proven a challenge. Recently, an approach based on the control of the relative size of the nanoparticle and matrix polymer has been proposed and the experimental observations[1] reveal that for appropriate relative size, solvophilic nanoparticles can cluster together while solvophobic nanoparticles are able to disperse in a polymer matrix. The consequence is contradictory to the general belief that solvophilic particles tend to spread in a solvent while solvophobic particles are liable to aggregate. Dissipative particle dynamics simulations are thus employed to investigate self-assembly of solvophilic nanoparticles and dispersion of solvophobic nanoparticles.[2] The degree of aggregation in terms of the mean aggregation number is evaluated to explore the aggregation kinetics of nanocubes and nanoplatelets (Figure 1). The influence of the length of the matrix polymer on the aggregation behavior is studied as well (Figure 2). It is found that the depletion attraction plays the major role for the aggregation of solvophilic nanoparticles. On the other hand, the slow aggregation kinetics, hindered by the energy barrier associated with depletion interactions and low nanoparticle diffusivity, is responsible for the low degree of aggregation for solvophobic nanoparticles.

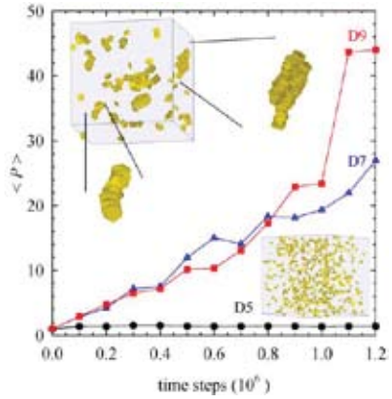

Figure 1. The variation of the mean aggregation number with the time steps for nanoplatelets D5, D7, and D9 in a polymer matrix L_s=12.

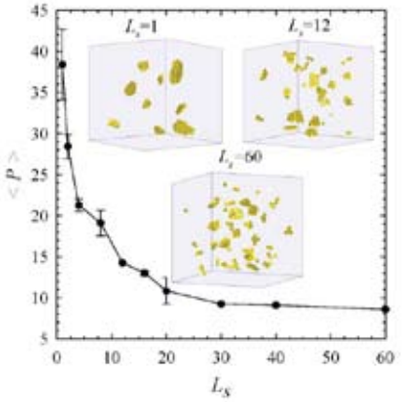

Figure 2. The variation of the mean aggregation number of organophobic nanocubes with the polymer length at the time steps 4×10^5. In the inset, aggregative snapshots for polymer lengths L_s=1, 12, and 60 are shown.

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Concentration of bio-ethanol through porous hydrophobic polymer membranes

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We proposed an evapomeation (EV) method as a membrane separation technique for organic liquid mixtures to keep the advantages of the pervaporation (PV) method and improved their disadvantages [1, 3]. We also proposed a temperature-difference controlled evapomeation (TDEV) method that can establish a temperature difference between the feed solution and the membrane surroundings [2, 3].

In this paper, in order to get high membrane performance in the concentration of aqueous ethanol solutions, porous poly(dimethyl siloxane) (PDMS) membranes were applied to the TDEV method. Permeation and separation characteristics for aqueous ethanol solutions through their porous PDMS membranes during TDEV under various conditions are discussed from the view point of membrane and permeants structure.

The characteristics of permeation and separation for aqueous solutions of low ethanol concentration through a porous PDMS membrane by TDEV are shown in Figure 1. Considerably high permselectivities for ethanol were observed from Figure 1. These results support that an application of porous PDMS membrane to the concentration in aqueous ethanol solutions is suitable.

In Figure 2, the permeation rate and ethanol concentration in the permeate for an aqueous solution of 10 wt% ethanol through a porous PDMS membrane by TDEV as a function of the temperature of the membrane surroundings are shown. With decreasing temperature of the membrane surroundings, the permeation rate decreased, but the permselectivity for ethanol increased remarkably. When the characteristics of permeation and separation for an aqueous solution of 10 wt% ethanol through porous PDMS membrane were compared with those through a dense PDMS membrane, the permselectivities for ethanol in their membranes were almost equal but the permeation rates for a porous PDMS membrane were higher by three orders of magnitude than those for a dense PDMS membrane. We will be able to discuss the mechanism of the permeation and separation in TDVE.

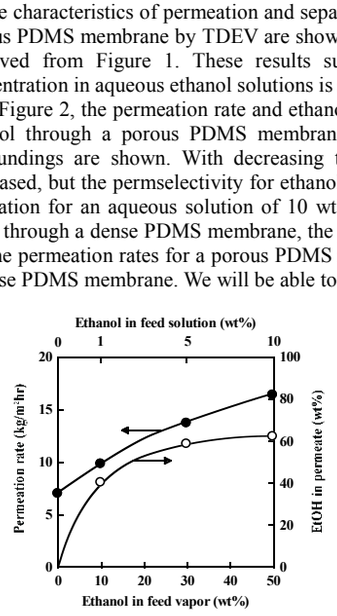

Figure 1. Effects of the feed vapor composition on the permeation rate and the ethanol concentration in the permeate through porous PDMS membrane by TDEV. Feed temperature: 40°C,temperature of membrane: 0°C.

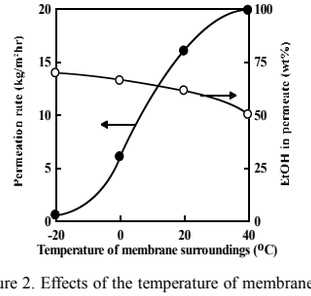

Figure 2. Effects of the temperature of membrane surroundings on the permeation rate and the ethanol concentration in the permeate through porous PDMS membrane by TDEV. Feed solution: aqueous solution of 10 wt% EtOH, feed temperature: 40 °C, reduced pressure: 5 Torr.

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Synthesis and Optical Properties of Dithienylethenes

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Organic photochromic molecules are compounds that reversibly switch colour with light, i.e., photoswitch, as shown in Figure 1. While there are a number of photochromic molecules that can switch in solution, there are fewer that can achieve the change in the solid-state. For this reason photochromic molecules based on dithienylethenes are of great interest because they can photoswitch in the crystal state with good switching speeds, fatigue-resistance and sensitivity. Upon UV light irradiation the "open form" of the dithienylethene undergoes a 6-π electrocyclic reaction forming a fused "closed form". The process can be reversed with visible light.

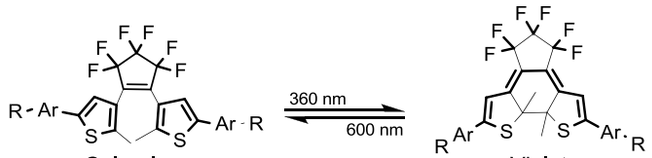

Figure. *Photoswitching of a dithienylethene photochromic molecule from an open form to a closed form.*

In this presentation, a facile synthetic methodology that enables access to a new library of dithienylethene-based photochromic molecules will be discussed. In addition, their solution and neat thin-film properties will be described.

Crosslink of graphene for energy applications

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Since its discovery in 2004, graphene has attracted enormous attention from both scientific and technological communities[1]. Developing three dimensional (3D) monolithic structures with this 2D building block is necessary for the practical application of graphene[2]. However, recent studies in the assembly of 3D graphene structure needs metal ion (or polymer) as a cross linker or takes a long time and require complex procedures.

In this study, we employed graphene oxide (GO) as a precursor to produce self-assembled 3D graphene monolith by a microwave hydrothermal approach (**Fig. 1**).UV-vis spectra and XPS demonstrated that graphene was formed by the microwave process. The interior cross linked microstructure of the self assembled graphene monolith (SGM) was revealed by scanning electron microscope (SEM), which shows that the monolithic structure is consist of porous intercalated graphene sheets that were stacking together. We attributed the crosslink of graphene to the $\pi \rightarrow \pi$ stacking force between the graphene sheets. The SGM was initially come out in the form of hydrogel with water content as high as 98.86% by weight. We find that this hydrogel is an ideal material for super capacitors. Galvanostatic charge-discharge measurement showed that the SGM can hold the specific capacitance of 334F/g at the current density of 50mA g^{-1}.This facile method to produce cross linked graphene has the advantage of easiness and scale up, which will facilitate the application of graphene in energy related areas.

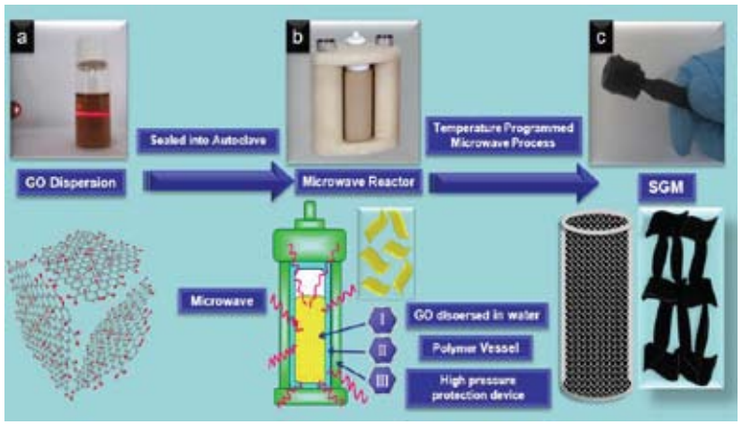

Fig 1. The proposed procedure of the self-assembly from GO to SGM. (a) GO was prepared and dispersed in water to form stable dispersion which demonstrated the typically colloid Tyndall phenomenon; (b) GO solution was then sealed into the microwave reactor to experience a temperature programmed microwave irradiation process; (c) A cylinder-like SGM was formed in the autoclave.

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Novel microcavitary hydrogel system for 3D culture and hepatogenic differentiation of murine induced pluripotent stem (iPS) cells

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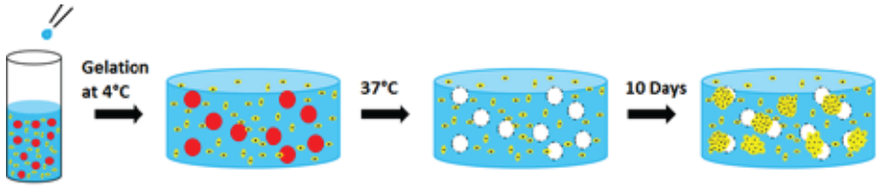
The discovery of induced pluripotent stem (iPS) cell technology has raised hopes in circumventing the current limitations in cell-based therapies where autologous stem cells could be generated from terminally differentiated somatic cells. Given the relatively short history on iPS cell research, most of the studies were scientific exploratory in nature and hence have minimal practical usage. In this study, we aimed to combine existing knowledge on iPS cell differentiation with three-dimensional (3D) scaffold platform so as to fabricate implantable constructs for liver regeneration. A microcavitary hydrogel (MCG) platform was employed for cell encapsulation since it has been shown that nutrients exchange could be further enhanced compared to simple non-MCG system. Moreover, our previous studies also provided evidence that MCG system facilitates aggregate formation[1,2] - in this case - colony or embryoid body (EB) formation. The MCG system employs gelatin microspheres as a temperature-sensitive porogen which dissolves only upon exposure to cell culture condition of 37°C to create micro-cavities within the alginate hydrogel. Since gelation of alginate hydrogel was carried out at 4°C, it ensures that no prior dissolution of microspheres would occur throughout the cell encapsulation process. The construction of cell-encapsulating MCG is demonstrated in Scheme 1. Murine iPS cells and embryonic stem cells (ESCs) were encapsulated respectively in alginate MCG system and after culturing for 10 days, colonies/ EBs were formed spontaneously. Differentiation conditions were then introduced to direct the cells toward endodermal lineage and subsequently hepatic lineage. Up-regulations of endoderm markers and hepatic markers were observed in both iPS cells and ESCs suggesting that iPS cells could differentiate as effectively as the ESCs in the 3D scaffolds. The results from this work provide foundation in understanding of iPS cell differentiation in 3D engineered environment and aid in future biomedical research of iPS technology.[3]

Scheme 1. Schematic illustration of the protocol for cell encapsulation. Pluripotent cells (murine iPS/ ESCs, in yellow) were encapsulated in alginate hydrogel (in blue) side by side mixed with gelatin microspheres based porogens (in red) on Day 0 and cultured in proliferation media for 10 days, during which the porogens were dissolved, the cavities were therefore created (in white) in gel phase (That is "MCG".), and the cell colonies were formed and gradually outgrew into the cavities. Subsequently, media was changed to RPMI 1640 medium supplemented with B27 and activin A for 4 days to induce endoderm formation. For hepatic lineage specification, media was changed to RPMI 1640 medium containing HGF until Day 20. Finally, hepatic maturation was carried out for 5 days before maintaining in hepatocyte culture medium till Day 30.[3]



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Redox-Cleavable Mikto-arm Star Polymers Synthesized by RAFT Polymerization

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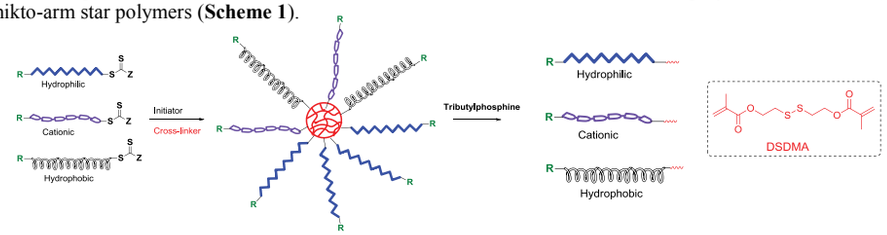
Introduction

RAFT polymerization is one of the widely used ways for polymer synthesis with complex architecture[1, 2]. Star polymers can be prepared by controlled polymerization techniques via three main methods: arm-first, core-first and grafting-to approaches[3]. The aim of this work was to prepare redox-cleavable mikto-arm star polymers by RAFT polymerization using arm-first approach.

Experiment

The approach comprises a homogenous RAFT polymerization process to prepare the arm polymers with different properties: hydrophilic [e.g., poly(oligo-(ethylene glycol methacrylate)$_{8\text{-}9}$)], cationic [e.g., poly(2-(dimethylamino)ethyl methacrylate)] and hydrophobic [e.g., poly(butyl methacrylate)]. A heterogeneous polymerization process was then involved to cross-link a mixture of the different arm polymers (macro-CTA) into mikto-arm star polymers (**Scheme 1**).



Scheme1: Synthetic approach used to prepare redox-cleavable mikto-arm star polymers by RAFT

Various parameters were studied to understand the formation of star polymers. These include the molar ratios of cross-linker; and the ratio of different arm polymers. When using a redox-cleavable cross-linker, such as disulfide-based dimethacrylate (DSDMA), the mikto-arm star polymers can be cleaved to linear polymers by adding tributylphosphine into star polymers solution. Gel permeation chromatography (GPC) traces show both formation and cleavage of star polymers (**Fig.1**).

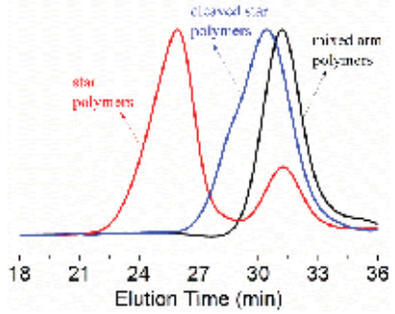


Figure 1: GPC traces showing the formation and cleavage of star polymers using DSDMA as cross-linker with [macro-CTA]: [mono]: [initiator]: [cross-linker] =1: 6: 0.3: 16.

Conclusion

Mikto-arm star polymers containing three different arm species were successfully synthesized by RAFT polymerization using arm-first approach. The redox-cleavable mikto-arm star polymers can be cleaved to linear polymers by tributylphosphine.

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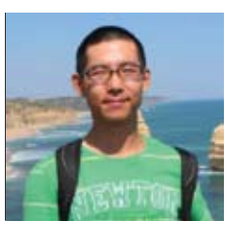

Preparation of Superabsorbent Polymers from Starches with Different Amylose/Amylopectin Ratios

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Abstract

Grafting polymerization onto starch backbones was performed to develop new types of biodegradable superabsorbent polymers (SAPs). Four corn starches with different amylose contents (4, 29, 50 and 80%) were used as model materials. Graft polymers were produced by grafting acrylamide onto cornstarch with ceric ammonium nitrate (CAN) as an initiator and N,N'-methylene-bisacrylamide (MBA) as crosslinker. Typically, 15 g corn starch was gelatinized in distilled water (80 mL) for 15 min at 100°C (for waxy and maize starches) or 121°C (for G50 and G80 starches); the gelatinized starch solution was transferred into a flask, equipped with a mechanical stirrer, condenser and nitrogen line, and 0.5 g CAN added at 60°C to react for 10 min under nitrogen atmosphere; a mixed solution of AM (15 g) and N-MBA (0.07 g) was added at 60°C to react for 120 min under nitrogen atmosphere; NaOH (6.84 g) in distilled water (125 mL) was added to the flask at 90°C for 120 min; the saponified product was washed with distilled water to a pH of 7 to remove ungrafted polymer, monomer and base, and then rewashed with ethanol. The macroscopic performance (water absorbency capacity, rheological properties) and microscopic characterization (by FTIR, NMR, TGA and acid hydrolysis) were implemented to explore the correlation between the amylose /amylopectin ratio of the parent starch and performance of starch-based SAPs. The most important structure parameters are the grafting ratio (GR) and average DP of the grafted PAM branch chain ($\bar{X}_n$). GR was obtained by TGA from the mass loss of starch backbone and PAM, verified by weight change during acid hydrolysis. $\bar{X}_n$ was obtained from NMR as (PAM ratio/M_{AM})/[(Starch ratio×Ratio of glucose units grafted)/$M_{glucose}$]. GR and efficiency increased with increasing amylose content, and these correlated with the water absorption ratio. $\bar{X}_n$ decreased with increasing amylopectin content[1]. This is most probably because the high molecular weight and branched structure of the amylopectin reduced the mobility of the polymer chains and increased viscosity. This means steric hindrance is stronger in the presence of highly branched amylopectin, which favoured short-long (rapid) termination compared to slower long-long termination[2] .The onset degradation temperature of the polyacrylamide grafted onto the starches increased by about 10°C, explained by strong bonding between the grafted polymer chains and the starch[3]. These grafting modifications on starch can also be made using a twin-roll mixer as a reactor[4], which establishes the basis for production in twin-screw extruder.

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Author Index

Notes:

ISSN: 0032-3896
EISSN: 1349-0540

Impact Factor: 1.258*
Ranking: 42/78 Polymer Science*

Official publication of The Society of Polymer Science, Japan (SPSJ)

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