



# ***UK Polymer Showcase***

**7<sup>th</sup>/8<sup>th</sup> September 2004  
Cedar Court Hotel (J39, M1)  
Wakefield WF4 3QZ**

## **Programme and Abstracts**



# UK POLYMER SHOWCASE

TUESDAY & WEDNESDAY  
7 & 8 September, 2004

THE CEDAR SUITE,  
THE CEDAR COURT HOTEL,  
DENBYDALE ROAD,  
WAKEFIELD,  
WF4 3QZ.

## PROGRAMME

### Tuesday, 7th September, 2004.

- 09.00 Registration
- 09.30 Professor Tom McLeish (Director, IRC in Polymer Science & Technology)  
*"Searching Through Polymer Dynamics with the Finest-toothed Comb"*
- 10.10 Dr. Martin Buzza (IRC Leeds)  
*"Rheology of Hyperbranched Polymers"*
- 10.30 Dr. Lian Hutchings (IRC Durham)  
*"HyperMacs and DendriMacs: The Next Generation of Well-defined, Branched Polymers"*
- 10.50 Coffee
- 11.10 Professor Ruth Duncan, (Centre for Polymer Therapeutics, Welsh School of Pharmacy, Cardiff University)  
*"Polymer Therapeutics: Biological Rationale for Design and Clinical Experience with the First Nanomedicines"*
- 11.50 Dr. Neil Cameron (Associate Director, IRC Durham)  
*"IRC Research at the Polymers-Bioscience Interface"*
- 12.10 Professor Sheila MacNeil, (Centre for Biomaterials and Tissue Engineering, University of Sheffield AND CellTran Ltd., Sheffield)  
*"Development of a Plasma Polymer Surface for Wound Healing"*
- 12.30 Lunch and Poster Session
- 14.00 **Directors' Introduction**  
Professor Tom McLeish, Director, IRC in Polymer Science & Technology  
*"15 Years of the IRC - and the rest...."*
- Professor Phil Coates, Associate Director, IRC Bradford  
*"Polymer Centre of Industrial Collaboration"*

- Richard Simpson, Faraday Plastics  
*"The Faraday Plastics and Polymers Partnership"*
- 14.30 Sebastian Conran, (Creative Director, Conran and Partners)  
*"Designer Plastics: The Guile, Art and Practicality of Successfully Designing with Polymers"*
- 15.10 Professor David Bott  
*"Department Stores, Chain Stores and Boutiques - The Future of the UK Chemical Industry"*
- 15.50 Tea
- 16.10 Dr. Wilhelm Huck, (Melville Laboratory, Department of Chemistry, University of Cambridge)  
*"Nanostructured Polymers in Optoelectronic Devices"*
- 19.00 Showcase Dinner in The Cedar Suite, Cedar Court Hotel

**Wednesday, 8th September, 2004.**

- 9.15 Registration for day 2 only delegates
- 9.30 Professor Tony Ryan, (Associate Director, IRC Sheffield)  
*"How does Flow Effect Crystallisation?"*
- 9.50 Professor Han Meijer, (Professor of Polymer Technology, Eindhoven University of Technology)  
*"Modelling and Validation of Viscoelastic Stress Induced Crystallization"*
- 10.30 Dr. Peter Hine (IRC, Leeds)  
*"Hot Compacted Polymer Composites: New Science and Technology"*
- 10.50 Coffee
- 11.10 Dr. Bill MacDonald, (DuPont Teijin Films)  
*"Flexible Electronics: Structural Materials Underpinning Functional Materials"*
- 11.50 Professor Richard Jones, (IRC Sheffield)  
*"Polymers at Interfaces: From Soft Nanotechnology to Plastic Electronics"*
- 12.10 Professor Phil Coates (Associate Director, IRC Bradford)  
*"The Dream Machine - Process and Product Measurements for Enhanced Process Understanding, Modelling and Control"*
- 12.30 Closing remarks/discussion/departure

**Please note: The exhibitions and poster displays will be continually on show during tea and coffee breaks.**

**ABSTRACTS**  
**OF**  
**LECTURES**

**UK POLYMER SHOWCASE**  
**7/8 SEPTEMBER 2004**  
**CEDAR COURT, WAKEFIELD**

**LIST OF ORAL PRESENTATIONS**

Professor Tom McLeish, Director IRC in Polymer Science & Technology	<b>Searching Through Polymer Dynamics with the Finest-toothed Comb....</b>
Dr. Martin Buzza IRC, Leeds	<b>Rheology of Hyperbranched Polymers</b>
Dr. Lian Hutchings IRC, Durham	<b>HyperMacs and DendriMacs. The next generation of well-defined, highly branched polymers.</b>
Professor Ruth Duncan Cardiff University	<b>Polymer Therapeutics: Biological Rationale for Design and Clinical Experience with the First Nanomedicines</b>
Dr. Neil Cameron IRC, Durham	<b>IRC Research at the Polymers-Bioscience Interface</b>
Professor Sheila MacNeil University of Sheffield	<b>Development of a Plasma Polymer Surface for Wound Healing</b>
<b><i>Directors' Introduction:</i></b> Professor Tom McLeish Professor Phil Coates Richard Simpson	<b>15 Years of the IRC - and the rest..... Polymer Centre of Industrial Collaboration The Faraday Plastics and Polymer Partnership</b>
Sebastian Conran Conran & Partners	<b>Designer Plastics: The Guile, Art and Practicality of Successfully Designing with Polymers.</b>
Professor David Bott	<b>Department Stores, Chain Stores and Boutiques - The Future of the UK Chemical Industry</b>
Dr. Wilhelm T. S. Huck University of Cambridge	<b>Nanostructured Polymers in Optoelectronic Devices</b>
Professor Tony Ryan Associate Director, IRC Sheffield	<b>How Does Flow Effect Polymer Crystallisation?</b>
Professor Han Meijer University of Eindhoven	<b>Modelling and Validation of Viscoelastic Stress Induced Crystallization</b>
Dr. Peter Hine IRC, Leeds	<b>Hot Compacted Polymer Composites: New Science and Technology</b>
Bill MacDonald, DuPont Teijin Films	<b>Flexible Electronics: Structural Materials Underpinning Functional Materials</b>
Professor Richard Jones University of Sheffield	<b>Polymers at Interfaces: From Plastic Electronics to Soft Nanotechnology</b>
Professor Phil Coates Associate Director, IRC Bradford	<b>The Dream Machine - Process and Product Measurements for Enhanced Process Understanding, Modeling and Control</b>

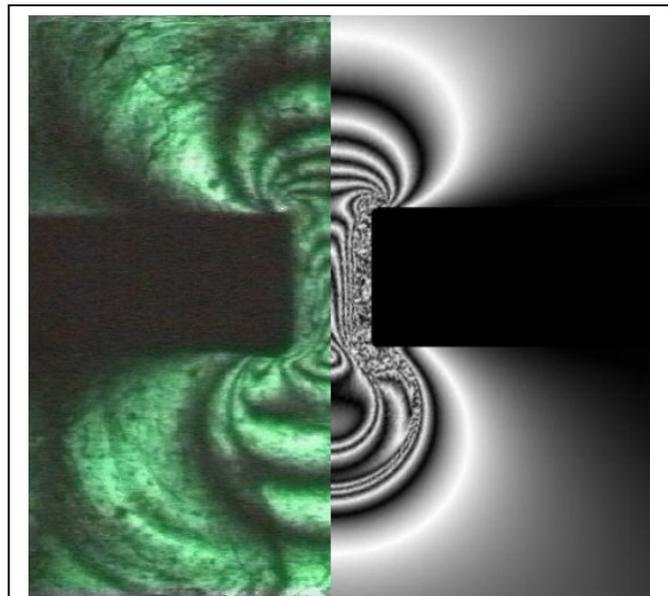
# Searching through polymer dynamics with the finest-toothed comb....

*Tom McLeish*  
*Director,*  
*IRC in Polymer Science & Technology*

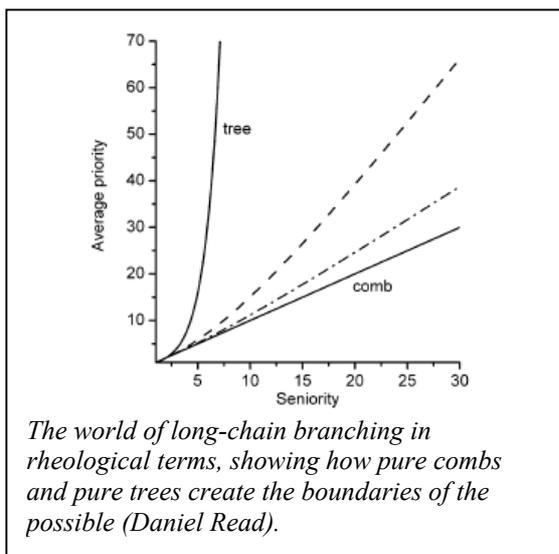
## ABSTRACT

From plastics processing to molecular biology, polymer chain architecture plays a vital role in design for purpose at the molecular level. Addressing the science of polymer architecture similarly requires the careful synthesis of model macromolecules in which not only molecular weight, but also architecture, is carefully controlled. Here we look, from several angles, at the remarkable properties of comb-like architectures as one model case of branched polymers.

Monodisperse combs of polybutadiene and their hydrogenated variants have been a vital test material in the cross-IRC collaboration in “Microscale Polymer Processing”. Recently extended by a 4-year grant from EPSRC, this large project followed several model classes of polymer melt from synthesis, through rheology to final process flows and products. Christine Fernyhough (Sheffield) manufactured sufficient comb material to process in neat form in the fully flow-visualised “Multipass Rheometer” in Malcolm Mackley’s laboratory (Cambridge), and to be measured in pure extensional flow by David Groves (Leeds). The rheological and flow-field results were compared with tube-model theories of how molecules control rheology by Nat Inkson (Leeds). Results show how using monodisperse materials in this way is akin to high-resolution microscopy: all the features are brought into sharper focus and can be treated in a more quantitative way.



*Pure comb melt stress-field in flow (left half) compared with predicted stresses from a molecular model (right) (Nat Inkson)*

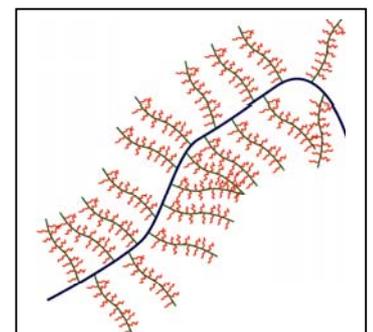


*The world of long-chain branching in rheological terms, showing how pure combs and pure trees create the boundaries of the possible (Daniel Read).*

The comb and the pure tree (dendrimer) together for the boundaries of the topological world in which all branched polymers exist. Industrial materials lie in the land between.

In a very different world, charged comb polymers in aqueous solution create important rheological properties in impact-resistant and lubricated areas of the body, such as load-bearing joints. Lubricating flow requires high “normal stresses” under shear – another property in which molecular combs in solution excel. Now entanglement physics is exchanged for electrostatics in solution, but the same underlying requirement is

present: tailor molecular stretch to the shear rates of the fluid!



*The naturally occurring comb polyelectrolyte system aggrecan, found as the viscoelastic matrix in cartilage composites*

# Rheology of Hyperbranched Polymers

*Martin Buzza*

*I.R.C. in Polymer Science & Technology, School of Physics & Astronomy,  
University of Leeds, Leeds LS2 9JT*

## **Abstract:**

Hyperbranched Polymers (HBPs) are randomly branched polymers formed by a one-pot synthesis of AB<sub>x</sub> type monomers ( $x \geq 2$ ), where A reacts exclusively with B. HBPs exhibit many of the intriguing rheological properties of regular dendrimers, e.g., the intrinsic viscosity varies non-monotonically with molecular weight, but they are much cheaper to synthesise compared to dendrimers. This makes HBPs ideal candidates for applications such as coating agents and rheology modifiers. In this study, we report melt rheology results for HBPs formed by the co-condensation of AB and AB<sub>2</sub>. Specifically two series of HBPs were prepared using AB<sub>2</sub> mole fractions of 10% and 1% respectively. This allowed us to systematically vary the branch length  $M_x$  from below to above the entanglement molecular weight  $M_e$ . Within each branch length class, we further varied the molecular weight by quenching at different reaction extents. For the 10% branch samples ( $M_x < M_e$ ), we were able to quantitatively model the low and intermediate frequency linear shear rheology data using a dynamic scaling theory based on the Rouse model. This indicates that entanglements are absent in these samples, remarkably, up to  $M_w = 250k$ . The 1% branched samples ( $M_x > M_e$ ) on the other hand showed clear evidence for entanglements for molecular weights as low as  $M_w = 32k$ . We modelled the rheology for the 1% branched series using the entangled star/linear blend theory of Milner & McLeish (*Macromolecules*, vol.31, p.9345, 1998) and preliminary results for the modelling are presented. Our study demonstrates conclusively that branch length is the crucial factor determining whether or not HBP melts are entangled.

# HyperMacs and DendriMacs. The next generation of well-defined, highly branched polymers.

*L. R. Hutchings and S. J. Roberts-Bleming*

*Interdisciplinary Research Centre in Polymer Science and  
Technology,*

*Department of Chemistry,*

*University of Durham,*

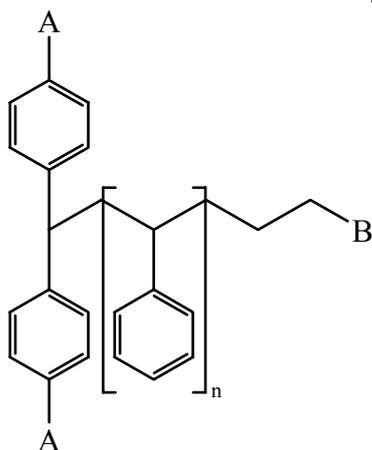
*DH1 3LE.*

*United Kingdom.*

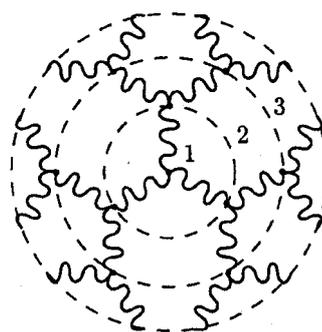
*E-Mail [l.r.hutchings@durham.ac.uk](mailto:l.r.hutchings@durham.ac.uk)*

## ABSTRACT

Research into the synthesis of branched polymers and the characterisation of their physical properties is extremely active. From dendrimers and hyperbranched polymers to stars, grafts, H-shaped polymers and pom-poms, this is an area that has been extensively researched. In a 'proof-of-concept' project novel branched polymers based on polystyrene will be synthesised by a combination of anionic polymerisation and condensation coupling. Macromonomers will be synthesised by anionic polymerisation using an initiator containing a protected functionality and terminated with a diphenylethylene derivative containing further protected functionalities. Following deprotection, the  $A_2B$  macromonomers (shown below Fig 1) can be coupled together by two methods. Firstly, a low-tech route in which the macromonomers are reacted together in a 'one pot' reaction to produce hyperbranched polymers (HyperMacs) and secondly, dendritic versions (DendriMacs) will be prepared using a convergent route (see below Fig 2). The beauty of this approach is that anionic polymerisation allows absolute control over the molecular weight of the macromonomer, which in turn means complete control over the molecular weight between branch points.



**Figure 1.**  $A_2B$  macromonomer



**Figure 2.** Three generation DendriMac

# IRC Research at the Polymers-Bioscience Interface

*Neil R. Cameron*

*IRC in Polymer Science and Technology, Department of Chemistry,  
University of Durham, South Road, Durham, DH1 3LE*

A rapidly expanding area of polymer science is at the interface with the life sciences, which encompasses cell culture, tissue engineering, controlled release and targeted delivery of bioactive molecules, biosensors, biocompatible surfaces and many other topics. A significant proportion of the Polymer IRC's research portfolio is focused at this interface. Hydrogel-based tissue engineering matrices are being prepared in Sheffield and their use as scaffolds for the regeneration of various tissue types is being explored. Related work in Durham involves the use of porous scaffolds for the regeneration of bladder tissue, as well as their use as matrices for the culture of cells in which matrix topology appears to influence cell growth and proliferation. Sugar-functionalised polymers (glycopolymers) are being prepared for targeted delivery applications, making use of the exquisite selectivity of membrane-bound glycoreceptors (lectins) for carbohydrates. Dendritic macromolecules are also being employed to yield multifunctional drug delivery vehicles. This lecture will highlight recent progress of the Polymer IRC in a few key areas of this exciting discipline.

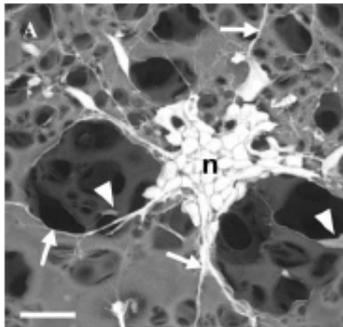


Figure: Neuronal bundle (n) growing on highly porous polymeric 3D cell culture matrix (scale bar = 50  $\mu\text{m}$ ).

# **Polymer Therapeutics: Biological Rationale for Design and Clinical Experience with the First Nanomedicines.**

***Ruth Duncan,  
Centre for Polymer Therapeutics,  
Welsh School of Pharmacy, Cardiff University, Cardiff CF10 3XF, UK***

The descriptor "polymer therapeutics" is an umbrella term that we coined to describe polymeric drugs, polymer-drug conjugates, polymer-protein conjugates, polymeric micelles to which drug is covalently bound, and multi-component polyplexes being developed as non-viral vectors. There is considerable hope that such bio-nanotechnologies, designed with an appreciation of the patho-physiology of normal and diseased tissue, using advanced polymer chemistry and precision engineering at a molecular level, will help realise the full therapeutic potential of the post-genomics era. From the industrial standpoint, these nanosized medicines are more like new chemical entities than conventional 'drug delivery systems or formulations' which simply entrap, solubilise or control drug release without resorting to chemical conjugation.

Conceptually, polymer therapeutics share many features with other macromolecular drugs (proteins, antibodies, oligonucleotides) and macromolecular prodrugs including immunoconjugates. A bonus, however, is the versatility of synthetic chemistry, which allows tailoring of molecular weight, addition of biomimetic features to the man-made construct with even the possibility to include bioresponsive elements. Over the last decade we have seen the transfer of several polymer-protein conjugates to market (including PEG-asparaginase, and PEG-GCSF) and > 11 polymer-anticancer drug conjugates into clinical development. Initially the anticancer drug conjugates incorporated well-known chemotherapeutic agents such as doxorubicin, paclitaxel and camptothecins. Clinically the most successful have been rationally designed in respect of their molecular weight, drug content and most importantly the polymer drug linker. Now that clinical proof of concept is established we are trying to develop more sophisticated second generation systems that will exploit either tumour, or tumour vasculature – specific targeting, improved delivery of novel natural product anticancer agents and also polymer-drug combinations.

Novel polymer architectures (eg dendrimers), biodegradable polymeric carriers incorporating the drug via pendant linkage or as a component of the polymer main-chain are also being explored. Whilst the first generation polymer-drug conjugates have used lysosomotropic delivery as the route of intracellular delivery, bioresponsive, endosomolytic polymers provide an opportunity for intracytoplasmic delivery of oligonucleotides and proteins (e.g. non-permanent toxins).

## **Reviews**

1. Duncan, R. The Dawning Era of Polymer Therapeutics. *Nature Reviews Drug Discovery* 2(5),347-360 (2003).
2. Duncan, R. Polymer-Drug Conjugates. In: *Handbook of Anticancer Drug Development*, D. Budman, H. Calvert, and E. Rowinsky (Eds.), Lippincott, Williams & Wilkins (2003) pp 239-260.
3. Duncan, R. (2004) *N*-(2-Hydroxypropyl)methacrylamide copolymer conjugates. In: *Polymeric Drug Delivery Systems* (Ed. Kwon, G.S.) Marcel Dekker, Inc., New York, in press.

## **Papers**

1. Malgesini, B., Verpilio, I., Duncan, R. and Ferruti, P. Poly(amido-amine)s carrying primary amino groups as side-substituents. *Macromolecular Rapid Communications* 23, 332-335 (2003).
2. Satchi-Fainao, R., Hailu, H., Davies, J.W., Summerford, C and Duncan, R. PDEPT: Polymer directed enzyme prodrug therapy: II. HPMA copolymer- $\beta$ -lactamase and HPMA copolymer-C-Dox as a model combination. *Bioconjugate Chemistry* 14, 797-804 (2003).
3. Tomlinson, R., Heller, J., Brocchini, S and Duncan, R. (2003) Polyacetal-doxorubicin conjugates designed for pH-dependent degradation. *Bioconjugate Chemistry* 14, 1098-1106.

4. Wan, K-W., Malgesini, B., Verpilio, I., Ferruti, P., Griffiths, P.C., Paul, A., Hann, A.C. and Duncan R. (2004) Poly(amidoamine) salt form affects pH-dependent membrane activity and polymer conformation in solution. *Biomacromolecules* 5, 1102-1109.
5. Shaunak, S., Thomas, S., Gianasi, E., Godwin, A., Jones, E. Duncan, R., Luthert, P., Patterson, S., Khaw, P. and Brocchini, S. (2004) Polyvalent dendrimer glucosamine conjugates prevent scar tissue formation. *Nature Biotechnol.* 22, 1-8.
6. Griffiths P.C. , Paul, A., Khayat, Z., Wan, K.-W., King S. M., Grillo, I., Schweins, R., Ferruti, P., Franchini, J. and Duncan R. (2004) Understanding the mechanism of action of poly(amidoamine)s as endosomolytic polymers; correlation of physicochemical and biological properties. *Biomacromolecules*, in press.

### **Short Biography**

Ruth Duncan is Professor of Cell Biology and Drug Delivery at the Welsh School of Pharmacy, School of Chemistry, Cardiff University, UK and Director of the Centre for Polymer Therapeutics. She completed her PhD studies in 1979 at Keele University and established there the CRC's Polymer-Controlled Drug Delivery Group. In 1992 she joined Farmitalia Carlo Erba (became Pharmacia now Pfizer) in Milan as Head of New Technologies. In 1994 she returned to the The School of Pharmacy, London, where she established the Centre for Polymer Therapeutics before relocating to Cardiff in 2000. She has contributed more than 200 scientific articles and patents, and has been a recipient of many awards including the Pfizer Research Award for Pharmaceutical Sciences, Young Investigator Award of the Controlled Release Society, Interdisciplinary Award of the Royal Society for Chemistry, the Millennium World Congress Pharmaceutical Scientist Award and the Berlin-Brandenburg Academy Monika Knutzner Award for Innovative Cancer Research. She is an elected member of the Academy of Sciences and Literature Mainz, and in 2004 is the Science Chair of the British Pharmaceutical Conference and the Chair of the European Science Foundation's Steering Committee : Forward Look on Nanomedicine.

# DEVELOPMENT OF A PLASMA POLYMER SURFACE FOR WOUND HEALING

MacNeil, S<sup>1,2</sup>, Moustafa, M<sup>1,2</sup>, Short, RD<sup>1,2</sup>, Haddow, DB<sup>1,2</sup>, Jarmalowicz, M<sup>2</sup>, Simpson, C<sup>1,2</sup>, Warner, R<sup>1</sup>, Glover, M<sup>1</sup>, Creagh, FM<sup>1</sup>, Heller, S<sup>1</sup>, Ralston, D<sup>1</sup>, Brotherston, M<sup>1</sup>  
<sup>1</sup>University of Sheffield Centre for Biomaterials and Tissue Engineering  
<sup>2</sup>CellTran Ltd, Portobello Centre, off Mappin Street, Sheffield, S1 4DT, UK

## Introduction

With an ageing population and an increasing incidence of diabetes in the western world many patients now live with non-healing ulcers. Clinical studies using tissue engineered products such as Dermagraft and Apligraf show that it is possible to improve the rate of healing in these chronic wounds but their management remains extremely challenging. There are biological (can these products be improved?) regulatory (should we use donor, xenobiotic or autologous material?) and economic (can therapies be made cost effective?) hurdles to be overcome.

## Aim

Against this background, our aim has been to develop a surface for the culture and transfer of autologous keratinocytes to assist in chronic wound healing seeking to deliver a system which will be simple to use for patients and clinicians, have little risk of disease transmission for the patient and significantly accelerate healing in particularly challenging wounds.

The approach we have adopted is of developing a plasma polymerised surface suitable for autologous keratinocyte attachment (1) and proliferation (2) from which cells can subsequently transfer to wound beds (3) - referred to as Myskin. The current paper describes preliminary clinical experiences of Myskin in patients with chronic wounds resistant to conventional therapy.

## Materials and Methods

Medical grade PVC carrier polymer (6cm discs) were coated with a plasma polymerised carboxylic acid containing surface as described previously (1-3).

Ethical Committee approval for the use of Myskin in patients with non-healing wounds (of at least four weeks duration) was obtained and informed consent was obtained from all patients. A split-thickness skin biopsy of 2 x 2 cm was taken from the skin of the thigh under local anaesthetic. This biopsy was then processed as described previously for keratinocyte culture and cells were expanded using conventional culture methodology, i.e. using Green's culture media with 10% bovine foetal calf serum expanding cells on murine J2 3T3 cells. The majority of cells were then stored in liquid nitrogen until required. When required keratinocytes were thawed 48 hours prior to application and seeded onto the Myskin dressing. Cells were delivered to patients, either in outpatient clinics (for the majority of patients) or on the ward for in-patients. Autologous keratinocytes on Myskin were applied once a week to the wounds and Myskin was replaced after four days with an appropriate dressing. Healed ulcers and wounds were followed up for a period of six months.

## Results and Discussion

Diabetic patients were aged 43-65 and we treated 9 ulcers and 6 patients which had been non-healing for one month to four years (median value 10 months). Complete healing was achieved in 6 out of 9 ulcers for these 6 patients, a reduction in ulcer size was achieved in one ulcer and no response was seen in one ulcer. Treatment was discontinued in one patient due to non-compliance after only 3 applications of Myskin. Wound healing took from 6-17 applications over 6-20 weeks. There were no recurrences in the healed ulcers after a follow up of 6 months (4). Figure 1 illustrates the appearance of one such ulcer which had been non-healing for two years and its appearance after 8 applications of Myskin.



Figure 1



Figure 2

Myskin was also used with good results in the treatment of an elderly patient with a non-healing pre-tibial wound as illustrated in Figure 2 and in the acute management of 2 patients with burns injuries where it was used to accelerate healing of donor sites. Clear evidence of transfer of autologous keratinocytes from the polymer dressing to the wound bed was evident in these patients. It was also used to reduce a foot ulcer in a patient with spina bifida. It is currently being used in the treatment of two patients with non-healing wounds due to the breakdown of earlier skin grafts required for burns injuries and in the treatment of extensive leg ulcers of 60 years duration in an elderly patient with encouraging results.

## **Conclusions**

Myskin offers a simple tissue engineering approach to the healing of a range of wounds suitable for in-patient and out-patient use and can achieve healing in wounds resistant to conventional therapy.

## **References**

1. France, RM et al (1998) J. Materials Chemistry 8, 37-42
2. Haddow, DB et al (1999) J Biomed Mater Res 47, 379-387
3. Haddow, DB et al (2003) J Biomed Mater Res 64A, 80-87
4. Moustafa M et al (2004) Diabetic Medicine, 21, 786-789

## **15 Years of the IRC - and the rest.....**

*Tom McLeish,  
Director,  
IRC in Polymer Science & Technology*

The IRC in Polymer Science and Technology began in 1989 as a consortium of research groups at the Universities of Leeds, Bradford and Durham. In September 2003 the Sheffield Polymer Centre joined with the IRC to form the current network of ~ 100 academics interested in polymers. It is a major UK, European and global focal point for multidisciplinary polymer science and its applications. A key objective of the IRC is to increase interactions between industry and the polymer scientists in the group. It does this through; membership of its Industrial Club, studentships, contract research and training courses. Many major companies in polymer related industries are already involved with the IRC, recognising the quality and breadth of the IRC's work and the benefits of dealing with an interdisciplinary unit.

# POLYMER CENTRE OF INDUSTRIAL COLLABORATION

**Director: Professor Phil Coates FREng:**  
**Commercial Manager: Dr. John McGrath, tel: 01274 233624**  
**Web sites: [www.polyeng.com](http://www.polyeng.com); [www.polymercic.com](http://www.polymercic.com)**

The Yorkshire Forward Polymer Centre of Industrial Collaboration operates within the world-class IRC polymer engineering laboratories at the University of Bradford. The Polymer CIC is a centre of research excellence for advanced materials processing, especially polymers, and computer modelling of processes and products, plus material and product characterisation and assists regional, national and international companies. One of the first group of 6 CICs covering various industry sectors, it offers short and long term R&D solutions and a gateway for companies of all sizes to access our extensive academic and industrial networks and research programmes. Companies in the following industry areas will benefit from our skills:

- *Raw materials* - polymers, compounds, additives;
- *Process* - trade processors and technology suppliers;
- *Applications* - processing polymers in-house to manufacture products for sale;
- *Associated areas* - supply chain i.e. those using polymers in their products.

*PolyLAB* is a dedicated area within our laboratories allowing companies to undertake small scale trials for process development, product evaluation and research testing - including scientific testing - with the support of hands-on technical expertise. Our activities are sponsored by a range of companies, including Moldflow, Kistler, David Standard, Smith & Nephew.

Our current programmes involve some 60 companies, with whom we aim to develop sustainable competitive advantage by:

- developing ideas;
- adding value to processes and products, and
- taking out cost by minimising waste or increasing efficiency.

We offer further assistance in the following ways:

- obtaining Knowledge Transfer Partnerships (we have several running at present) - in KTPs, companies can benefit from the expertise of high calibre graduates working within the company from 18 months up to 3 years to assist you realise a major project;
- networking events and seminars, including the Micromoulding Interest Group, the DTI In Process Measurements programme, and the EPSRC In Process Measurements Network all led by us (the latter also sponsoring the IRC Showcase meeting);
- helping companies to identify and access appropriate support.

We co-operate with several other groups and industry organisations around the UK, to ensure efficient response to industry.

## The Faraday Plastics and Polymers Partnership ([www.faraday-plastics.com](http://www.faraday-plastics.com))

Faraday Plastics has a mission of *enabling research to meet the critical technological challenges of the polymer sector*

Following an initial period when the Faraday focused on defining a set of 5 Flagship projects it has evolved in three main areas;

- Facilitating collaborative research
  - Over £3m of successful new projects in the last 12 months
- Technology Translation
  - 7 Technology Translators regularly interfacing with over 100 major industrial companies and the academic community
- Communication and dissemination
  - Regional meetings to promote the R&D ethos and Best Practice, Website dedicated to promoting the activities of the Partnership

In order to give a strategic focus and direction to these activities, Technology Road Mapping (TRM) has played a key role in identifying where the research needs lie and then influencing those preparing research submissions. To date the partnership has been involved in 3 major TRMs; Process Energy, Nano Composites and Tissue Engineering. Four major projects with a total value of ~£2m have been launched as a direct result of the Energy TRM. Further TRMs aligned with the technological and industrial foci of the partnership are planned and will be made available to the Faraday's community.

## **Designer Plastics: The Guile, Art and Practicality of Successfully Designing with Polymers**

### **PERSONAL PROFILE - SEBASTIAN CONRAN**

Born in 1956 Sebastian formatively spent most of his teenage holidays first working in Habitats then at the Conran Design studios. Then he trained in Industrial Design Engineering at Central School of Design gaining a reputation for simplicity and mechanical ingenuity. Later working with the Clash as designer of record sleeves, clothing and promotional material. In 1978 he joined Conran Associates as a junior designer and model-maker. Shortly later in 1979 he joined Wolff Olins - Britain's then leading corporate/brand identity consultancy taking creative responsibility for key accounts such as British Rail, Pilkington Glass and Shell Petroleum. In 1982 he joined Mothercare to take responsibility for the design and development of all childcare merchandise. Mothercare soon became an international benchmark brand in its product identity design.

In 1987 he started his own merchandise and brand development consultancy, Product Identity Design, working with a variety of international businesses (including ABN AMRO, A.T.Kearney, Bodum, Boots, Connolly, Ford, Gore-Tex, Hasbro, Marks & Spencer, NHS, Penguin, Philips, Rolls-Royce Aerospace, Science Museum, Tesco, Thermos, Virgin and WH Smith) on a wide range of projects. In 1999 he merged his design studio with his Conran Group's to form Conran & Partners, where Sebastian is now the Director responsible for all the Product and Graphics work.

Sebastian is au fait with a wide range of manufacturing techniques, his technical innovations and inventions have been involved in dozens of patents in a wide variety of fields and his work has been awarded numerous design, marketing and innovation awards. He is fully involved throughout the design process on all projects, leading the dedicated and professional team. There is a strongly structured approach to the creative, design and development process with an excellent track record for creating commercial success for its clients. Over years the studio has collectively been involved with the development of thousands of products in a wide variety of markets from initial ideas through to successful merchandise - from Concept to Customer!

He has taught design at the Royal College of Art and gives frequent lectures. He is a fellow of the RSA and Institute of Packaging, Trustee of the Design Museum and the Conran Foundation, ambassador to the children's charity ICAN, member of the Millennium Products selection panel and a frequently judges and sponsors many design awards. A founding contributor to Blueprint magazine he has written frequent articles and many books on design.

**Our ethos can be summed up by the dictum: 'Good design always adds value wherever it is applied'. And that value resides in the mind of the consumer and consists of the simple equation: Value = (Design + Quality + Brand) / Price**

## **"Department Stores, Chain Stores and Boutiques - The Future of the UK Chemical Industry"**

*Professor David Bott*

The chemical industry has undergone what seems to those within it to be tremendous changes over the last 10-15 years. Many propose that we are seeing the end of the UK chemical industry with many once large and powerful companies reduced in size and influence.

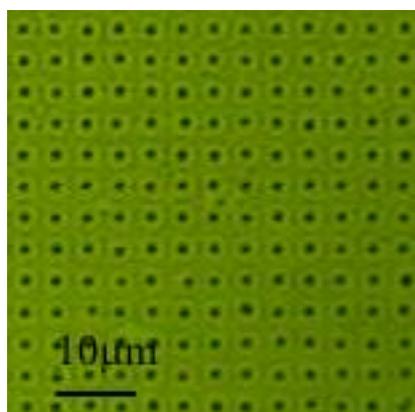
However, other industries have been through changes not dissimilar to these over the last 50 years and the history of the retail industry will be examined for parallels and lessons we can learn. It is likely that the UK chemical industry will not be better or worse, but merely different!!

# Nanostructured Polymers in Optoelectronic Devices

*Dr. Wilhelm T. S. Huck,  
Department of Chemistry,  
Melville Laboratory,  
University of Cambridge*

## A B S T R A C T

The potential uses of carbon in electronics have been studied for more than 50 years but, in the last decade, and particularly in the last five years, it has grown rapidly as the breadth of its potential applications has begun to be appreciated fully. Although these devices have considerable potential and are in some ways close to commercial applications, there are several shortcomings that need to be addressed before they can compete with Si-based device. Mobility is a key factor for many of the devices since it determines carrier transit times across bulk, surfaces and interfaces. Polymeric devices are commonly fabricated by spincoating the active components onto a surface. This fabrication technique leaves very little control over the order of the polymers at the molecular level. In fact, it ensures disorder. To significantly improve organic (opto)electronic devices and in particular polymeric devices, the degree of order in these devices needs to be improved dramatically. In this talk, a number of different strategies will be discussed, to order materials at the molecular, nanometer and micrometer level using combinations of self-assembly, polymer synthesis and soft-lithographic techniques such as phase-separation, embossing and contact printing. The effect of this order on the performance of LEDs, FETs, and photovoltaic devices will be illustrated.



**Figure:** *Fluorescence micrograph of phase-separated blend of semiconducting polyfluorenes on patterned ITO-PEDOT electrode. The resulting photonic structures leads to 100% improved LEDs due to efficient outcoupling of waveguided light*

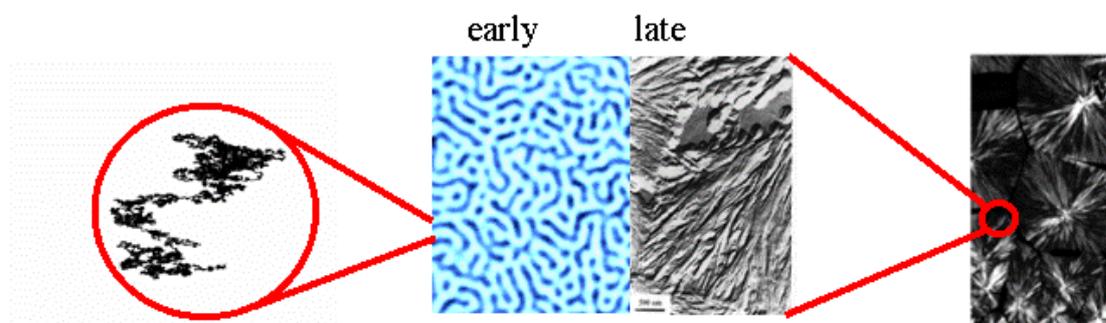
# How Does Flow Effect Polymer Crystallisation?

*Anthony J Ryan*

*The ICI Professor of Physical Chemistry and EPSRC Senior Media Fellow  
The Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK*

## *Abstract*

That polymer crystallisation is effected by flow is very well established by a wide range of experimental and theoretical studies. It is still, however, an open problem and there are many conflicting theories and experimental results. We have made some progress on the early stages of crystallisation in the quiescent state and are now asking questions about the interaction between flow and crystallisation and how to move from the molecular to the macroscopic size-scale.



We present our work on the effect of flow on crystallisation for a number of polymer types, flow geometries and measures of crystallinity. The materials studied are (1) linear homopolymers with both narrow and broad molecular weight distributions (2) specially synthesised comb polymers (3) blends of combs with narrow molecular weight distribution linear polymers (4) diblock and triblock copolymers.

We will clearly demonstrate that the low-strain rheology cannot be used to monitor the degree of crystallinity for a series of homopolymers and block copolymers. The behaviour of model homopolymer systems will be compared to the crystallisation kinetics of commercial polymers under both elongation, shear and quiescent conditions. Shear pulses cause massive nucleation and orientation in high molecular weight (and high MWD) commercial polymers. Extrusion and stretching show the development of a oriented structure as a precursor to crystallisation. Model linear polymers do not show these effects (at low M) but nucleation and orientation can be induced by doping with the appropriate combs. Simulations suggest that stretched strands deeply buried in comb polymers nucleate crystallisation. There are massive increases in crystallisation rate caused by shear but the crystallised material is not oriented! Can these strands remain stretched but be randomly reoriented? Or is it that length of the oriented strands decays to such an extent that they are overcome by a single nucleation event to make a spherulite?

# MODELLING AND VALIDATION OF VISCOELASTIC STRESS INDUCED CRYSTALLIZATION

*Gerrit W.M Peters and Han E.H. Meijer*

*Eindhoven University of Technology; Materials Technology ([www.mate.tue.nl](http://www.mate.tue.nl))*

The resulting properties of products made of semi-crystalline polymers strongly depend on both molecular properties and the processing conditions applied, i.e. the thermal-mechanical history experienced by the polymer in the process. Consequently, this thermal mechanical history (e.g. in injection moulding, film blowing or fiber spinning) has to be modeled in order to describe nucleation and crystallization kinetics and their dependence on flow-induced structure formation. The ultimate goal is to develop a modeling tool that is able to help to improve or optimize both: polymer synthesis and industrial processes.

Since many of the underlying relations are still not clear due to the complex mutual interaction of the parameters, optimization of properties in practice is still done by expensive and time consuming trial and error methods, which -at best- are based on cumulative experience. The need for a modeling tool became even more urgent since the development of metallocene-based catalysis yielding better-defined polymers with a controlled molecular weight distribution and stereo-regularity.

The lecture will focus on the development and experimental validation of a viscoelastic-stress-induced crystallization model, as developed over the years in our group, focusing on the injection molding process and coupling details of the polymers rheology with the resulting mechanical properties.

## REFERENCES

Papers:

H. Zuidema, G.W.M. Peters, H.E.H. Meijer, [\*Development and Validation of a Recoverable Strain Based Model for Flow-Induced Crystallization of Polymers\*](#), Macromol. Theory Simul., **10**(5), 447-460, (2001)

B.A.G. Schrauwen, L.E. Govaert, G.W.M. Peters, H.E.H. Meijer, [\*The influence of flow-induced crystallization on the impact toughness of high-density polyethylene\*](#), Macromol. Symp., **185**(1), 89-102, (2002)

G.W.M. Peters, F.H.M. Swartjes, H.E.H. Meijer, [\*A Recoverable Strain based Model for Flow-induced Crystallization\*](#), Macromol. Symp., **185**, 277-292, (2002)

Theses:

H. Zuidema, [\*Flow Induced Crystallization of Polymers\*](#), PhD. Thesis, 2000, TU/e Eindhoven, downloadable from: <http://www.mate.tue.nl/mate/publications/index.php/4>

F.H.M. Swartjes, [\*Stress Induced Crystallization in Elongational Flow\*](#), PhD. Thesis, 2001, TU/e Eindhoven, downloadable from: <http://www.mate.tue.nl/mate/publications/index.php/4>

B.A.G. Schrauwen, [\*Deformation and failure of semi-crystalline polymer systems\*](#), PhD. Thesis, 2003, TU/e Eindhoven, downloadable from: <http://www.mate.tue.nl/mate/publications/index.php/4>

J.A.W.van Dommelen, [\*Micromechanics of Particle-Modified Semicrystalline Polymers\*](#), PhD. Thesis, 2003, TU/e Eindhoven, downloadable from: <http://www.mate.tue.nl/mate/publications/index.php/4>

# Hot Compacted Polymer Composites: New Science and Technology

*Peter Hine*

*IRC in Polymer Science and Technology, University of Leeds, Leeds, LS2 9JT, UK*

A common approach to improving the properties of isotropic polymers is to mix the base polymer with a stiffer reinforcement, usually in the form of straight, chopped or woven glass fibres to form a polymer composite. While glass reinforced polymers are widely used, particularly in the automotive sector, they can still be relatively heavy, their impact and abrasion resistance are no match for metals (particularly at low temperatures), and glass fibres are usually a source of great irritation in the workplace. A second route to enhanced polymer properties is to produce preferred molecular orientation in the polymer by solid state drawing processes such as die drawing or hydrostatic extrusion. This results in a material with good specific properties and good impact performance, but it can be difficult to produce complicated shapes.

Our research over the last ten years has aimed at combining these two ideas to produce a new class of composite material by a process termed hot compaction. The aim was to exploit the outstanding mechanical properties of highly drawn fibres or tapes and use these as the reinforcing elements of an all polymer composite. In the hot compaction process, arrays of high drawn fibres or tapes are processed under suitable conditions of temperature and pressure such that a thin skin of each oriented element is melted. On cooling, this molten material freezes, or recrystallises, to bind the structure together and form the matrix of the composite. The resulting hot compacted sheet is therefore composed of a single identical, polymeric, material and by virtue of molecular continuity between the phases, has excellent fibre/matrix adhesion.

A substantial testing programme has shown that hot compacted sheets have properties that, in most cases, bridge between isotropic and glass filled polymers: that is apart from the impact strength which is much higher than most other materials, even at low temperatures. The most attractive material for a commercial application has been found to be hot compacted polypropylene tapes, due to the combination of good mechanical properties, outstanding impact performance, thermoformability and competitive cost. This material, tradename Curv<sup>TM</sup>, is now being commercially manufactured by BP AMOCO in Gronau, Germany ([www.curvonline.com](http://www.curvonline.com)). The applications under investigation for Curv<sup>TM</sup>, including sports armour, protective cases, safety shoes, automotive undershields and loudspeakers, make use of the attributes described above.

Research in recent years has focused on developing hot compacted sheets that can cope with even more demanding situations, such as temperatures greater than 100°C, high stresses over a long period and/or significant temperature changes, where polypropylene has problems. A key issue is to achieve these improvements without losing the crucial attributes of impact strength and thermoformability. The hot compaction technology has been found to be applicable to a wide range of oriented melt spinnable polymers, including polyesters (for example polyethylene terephthalate - PET), polyethylene, Nylon and polyoxymethylene (POM). A number of these polymers, particularly PET and POM, have been shown to have improved high temperature performance, improved creep and lower thermal expansion compared to polypropylene.

A second line of research for improved properties has been to explore reinforcing the oriented PP tapes with a nano-filler, for example carbon nano-tubes or clay particles. This research, while at an early stage, does suggest that the desired properties can be significantly improved with only small weight additions of the fillers, allowing the important properties of ductility and lightweight to be retained.

# **FLEXIBLE ELECTRONICS: STRUCTURAL MATERIALS UNDERPINNING FUNCTIONAL MATERIALS**

*Bill MacDonald,  
DuPont Teijin Films*

## **A B S T R A C T**

The concept of “plastic electronics” and of flexible displays in particular is increasingly gaining momentum and the current strong interest opens up new opportunities for combining the advantages of having a flexible substrate with roll to roll processing. However the flexible substrate will not necessarily be an off the shelf product - it will have to provide a combination of thermal performance, dimensional stability, printability to a range of solvents, solvent resistance coupled with commercial availability and be available in a form suitable for roll to roll processing. Surface quality and barrier properties may also be important. These substrates will be multilayer structures and can be considered as structural materials underpinning technologies based on functional materials. This contribution will describe new developments in polyester film substrates for this application area, will contrast polyesters with the different films that are potential substrates and will discuss early experience of using the films in displays, flexible circuitry and first generation active matrix backplanes.

# **POLYMERS AT INTERFACES: FROM SOFT NANOTECHNOLOGY TO PLASTIC ELECTRONICS**

*Richard A.L. Jones,  
Dept of Physics and Astronomy,  
University of Sheffield,  
Sheffield, UK.*

## **A B S T R A C T**

Polymers are often used in the form of thin films, and in this situation their properties are profoundly modified by the presence of interfaces. I will discuss the ways in which the composition of mixtures of polymers, the dynamics of polymers and the shapes that polymer molecules take up are all modified by surface effects. The interfacial physics of polymers involves fascinating fundamental physics, but it also has a profound bearing on potential new practical applications. These include the use of semiconducting polymers to make devices and the exploitation of the conformational response of polymer molecules to make functional nanoscale devices, like molecular motors.

## **The Dream Machine— Process and Product Measurements for Enhanced Process Understanding, Modeling and Control**

*Professor Phil Coates*

*Professor of Polymer Engineering, University of Bradford, UK and Associate Director, Interdisciplinary Research Centre in Polymer Science & Technology*

Can molecular and macroscopic measurements and computer modeling be combined in the Dream Machine? Such a processing machine would employ real-time material probes and process modeling to deliver controlled property products, to chosen specifications.

The use of process measurement techniques to characterize materials during processing is increasing, with the development of analytic techniques from retrospective, laboratory-based methods to near real-time process diagnostic and process control tools. Computer modeling is also growing in sophistication, and computational power is increasing dramatically.

There are three main drivers for measurements on polymer melts, to obtain data for:

- scientific understanding of particular features of the material, e.g. studies on how molecular topology influences bulk rheology in process-relevant flows, or spectroscopy used to assess molecular feature changes in a polymer during processing;
- modeling of real process flows, e.g. development of rheological models and constitutive equations for use in computer modeling of die flows, cavity filling, solid phase deformation and validation of process modelling;
- process trend monitoring, to evaluate if a manufacturing process is under control, with potential for closed loop control, by use of specific property or process variable measurements.

The range of measurement techniques which can be applied to polymers include: rheometric, optical, ultrasonic, spectroscopic (IR, UV, dielectric and nmr), aiming at measurement of flow properties, polymer structure, morphology and composition, additive concentration, dimensions, appearance, colour and consistency of production. Product characterisation is more established, and even wider-ranging.

Several techniques for in-process characterization of polymers and process analysis will be discussed, together with specific product assessments, with comparison with computer modeling of the process.

**ABSTRACTS**  
**OF**  
**POSTERS**

**UK POLYMER SHOWCASE**  
**7/8 SEPTEMBER 2004**  
**CEDAR COURT, WAKEFIELD**

**LIST OF POSTER PRESENTATIONS**

1. Ultrasonic Monitoring of Injection Moulding and Micromoulding  
Elaine Brown, IRC Bradford
2. Mesh Thermocouples for Temperature Measurement in Extrusion  
Dr. Adrian Kelly, IRC Bradford
3. Measurement and Prediction of Fibre Orientation Distribution within a Transverse Ribbed Specimen  
Dr. P. Caton-Rose, IRC Bradford
4. Water-Assisted Injection Moulding: Process Design and Characterisation  
Leigh Mulvaney-Johnson, IRC Bradford
5. Biaxially Oriented PP: Heat Transfer Aspect in the Double Bubble Process  
H. Benkreira and M. Talford, IRC Bradford
6. A Novel Extrusion Die: The Rotating Roller Die  
Prof. Hadj Benkreira, R. Patel, J. Paragreen and M. Fox, IRC Bradford
7. A Bench Top Polymer Mixer Reactor  
Prof. Hadj Benkreira, R. Patel and R. Butterfield, IRC Bradford
8. Small-scale Recirculation Flow Cells for Studies of Flowing Polymer Melts  
Dr. T. Gough, IRC Bradford
9. Micromoulding - Process Characterisation  
Ben R. Whiteside, IRC Bradford
10. Process Imaging Studies  
Rob Spares, IRC Bradford
11. The use of Nano Scale Particles to Enhance the Properties of Oriented Polypropylene  
Dr. Mark Bonner, IRC Leeds
12. Separator-free Rechargeable Lithium Ion Cells Produced by the Extrusion Lamination of Polymer Gel Electrolytes  
Professor I. M. Ward, IRC Leeds
13. Production and Properties of Highly Oriented Polymer Wires  
Jagan Mohanraj, IRC Leeds
14. Aggregation and gelation in randomly charged ionomer solutions  
Edoardo De Luca, IRC Leeds
15. Adsorption of DNA onto Oppositely Charged Spheres  
Alison Hodrien, IRC Leeds
16. Structure and Properties of Oriented Bioresorbable Fibres: Poly(Glycolic Acid)  
Horacio Montes de Oca and Mike Ries, IRC Leeds

17. Chain Transfer Agents for RAFT Polymerisations To Design Functionalised Polymers  
Mr. Pittaya Takolpuckdee, IRC Leeds
18. Synthesis and Characterization of Telechelic and Triblock Copolymers of ABA and ABC via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerisation  
Mr. Thomas Legge, IRC Leeds
19. Designing Polymer via Living Radical Polymerization for Industrial Applications  
Craig Mars, IRC Leeds
20. Synthesis of Controlled Polymer Architectures on a Cellulose Support via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization  
Mr. Debashish Roy, IRC Leeds
21. Thermoresponsive Micelles from Well Defined Block Copolymers Synthesized via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerisation  
Mr. Bo Liu, IRC Leeds
22. Novel Chain Transfer Agents for Reversible Addition Fragmentation Chain Transfer (RAFT) and Macromolecular Design by Interchange of Xanthate (MADIX) Polymerizations  
Mr. Murray Wood, IRC Leeds
23. Polymeric Architectures via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization  
Francois Vettier, IRC Leeds
24. Functional Materials Produced from Living Radical Polymerization  
Phuriphong Totsatitphisal, IRC Leeds
25. Structural Architecture of Branched Polymers and Modelling of Plastics Processing  
Dr. N. Inkson, IRC Leeds
26. Motion of Semi-Flexible Fibres under Shear  
Samantha Harris, Oliver Harlen, Tanniemola Liverpool, IRC Leeds
27. Competing Bubbles Growing in a Polymeric Foam  
Sally Everitt, Helen Wilson, Oliver Harlen, IRC Leeds
28. New Polymer Particles for Smart Release  
Dr. S. Rimmer, IRC Sheffield
29. High Throughput Analysis  
Dr. P. Fairclough, IRC Sheffield
30. Dynamic Nanoindentation as a Tool for Determining the Mechanical Properties of Thin Polymer Films  
Simon Hayes, IRC Sheffield
31. Micro Polymer Processing: Using Scattering Techniques to Investigate Polymer Processing  
Dr. E. Heeley, IRC Sheffield
32. Low Dimensional Polymer Electrolytes with High Ambient Lithium Conductivity  
Peter Wright, IRC Sheffield
33. Electrospinning for Tissue Engineering  
D. Norton, IRC Sheffield
34. Untangling the Mysteries of Comb Polymer Behaviour  
Dr. C. Fernyhough, IRC Sheffield

35. The Synthetic Muscle  
Paul Topham, IRC Sheffield
36. PEO-PBO-Diblock Copolymers Interdigitated Membrane Micro and Nano Vesicles  
Giuseppe Battaglia, IRC Sheffield
37. FaraPack Polymers Ltd.: Bespoke Short-term Polymer Synthesis, Feasibility and Testing Services  
Andrew Pryke, FaraPack
38. Transesterification of Poly(Ethylene Terephthalate) and Bisphenol-A-Polycarbonate.  
Michael Cannon, IRC Durham
39. Investigation of the structure and composition of a glass fibre size.  
Michael McGravey, IRC Durham
40. New Functional Materials via ROMP: An Approach to Electrostrictive Polymers  
Professor W. J. Feast, IRC Durham
41. Towards Antifreeze Glycoproteins: Solution Synthesis of Neoglycoconjugates  
Matt Gibson, IRC Durham
42. Synthesis of Novel Hydrophobic Acyclic Nitroxides: Study and Evaluation of Kinetic Rate Constants  
Olivier Lagrille, IRC Durham
43. Biomaterials for Soft Tissue Engineering  
Françoise Isaure, IRC Durham
44. Dendritic Functionalised Polymers  
A. Pillay Narrainen, IRC Durham
45. The Synthesis of Block Copolymers Through the Conversion of Living Anionic Polymerisation into Ring Opening Metathesis Polymerisation  
Tom C. Castle, Ezat Khoshravi and Lian R. Hutchings, IRC Durham
46. Analysis of PVDC Barrier Coatings on PET Film  
Richard Thompson, IRC Durham
47. Solvent Accelerated Polymer Diffusion in Thin Films  
Richard Thompson, IRC Durham
48. Diffusion of Polyethylene Oxide and Polymethylmethacrylate  
Kim Houghton, IRC Durham
49. Diffusion and Viscoelastic Measurements of Polystyrene Stars  
Stephen Collins, IRC Durham
50. Addition Polymerisation (AP) versus Ring Opening Metathesis Polymerisation (ROMP) for the Syntheses of a Series of Novel Polymers  
Alan Cooper, IRC Durham
51. Regeneration of Grubbs Catalyst in Ring Opening Metathesis Polymerisations  
Ezat Khosravi, IRC Durham
52. Polymeric Ionophoric Channels Based on 7-Oxanorbornenes  
Georgy Grancharov, IRC Durham
53. Development of Emulsion Templated Porous Materials for the Immobilisation of Biocatalysts  
Alex Duréault, IRC Durham

# ULTRASONIC MONITORING OF INJECTION MOULDING AND MICROMOULDING

EC Brown<sup>§</sup>, BR Whiteside<sup>§</sup>, Y Ono<sup>\*</sup>, C-K Jen<sup>\*</sup>, L Mulvaney-Johnson<sup>§</sup>,  
PD Coates<sup>§</sup>

<sup>§</sup>*IRC in Polymer Science & Technology, School of Engineering, Design & Technology,  
University of Bradford, Bradford, UK, BD7 1DP*

<sup>\*</sup>*Industrial Materials Institute, National Research Council Canada,  
Boucherville, Quebec, Canada, J4B 6Y4*

## ABSTRACT

In-process measurements using ultrasonic technology provide a powerful yet non-invasive insight into material conditions. High frequency sound waves (typically 5MHz to 15MHz) can be readily propagated through a metal extrusion die, barrel wall, nozzle or injection moulding tool, and into the polymer melt. Measurable ultrasonic variables include the transit time of the ultrasonic signal, sound velocity, attenuation and signal peak height. Changes in these parameters provide information on both material properties and process conditions such as pressure and temperature.

Using standard commercial sensors, solidification has been detected with the aid of both longitudinal and shear waves. In addition the transit time of longitudinal ultrasonic waves through HDPE has been measured during gas assisted injection moulding (GAIM), indicating the ability of this technology to assess part wall thickness in-situ before mould opening.

Recent developments in sensor technology have enabled the ultrasonic technique to be applied to micromoulding. Thick film piezoelectric ceramic transducers have been deposited on the barrel and on mould inserts used in micromoulding, by means of a sol-gel spray technique. The transducers can operate at high temperatures required on the barrel or an extrusion die (up to 500°C) and, since they are directly applied to the steel, issues of poor coupling do not arise.

Using the sol-gel transducers, measurements have successfully been made on:

- cavity filling, including flow front velocity
- detection of incomplete mould filling (short shots)
- solidification of the polymer in the mould
- changes in material properties, for example caused by material degradation.

The ultrasonic technique allows highly accurate, real time, non-invasive, in-process monitoring of injection moulding and micromoulding.

# **Mesh thermocouples for temperature measurement in extrusion**

*A L Kelly, E C Brown, P D Coates*

*IRC in Polymer Science & Technology, School of Engineering, Design & Technology,  
University of Bradford, BD7 1DP*

## **A B S T R A C T**

A range of measurement techniques have been used to investigate melt temperature fields in the die of a 63.5mm diameter single screw extruder. Melt temperature fields are complex and inherently difficult to measure, but can provide useful information about the melting performance of an extruder and stability of extrudate produced. Sensors used included flush-mounted and protruding thermocouples, thermocouple grids, ultrasound, and infrared. Melt flow was measured in a die adapter section of 38mm diameter for a range of screw geometries, polymers and extrusion conditions. A barrier flighted screw with Maddock mixer was compared to non-barrier flighted screws with gradually tapered and rapid transition regions.

Screw geometry was found to have significant effect on the melting capability and shape of the melt temperature profile produced. Complex 3D melt flows were detected. Lower temperature 'shoulder' regions were observed due to poor melting at higher screw speeds. The barrier flighted screw achieved most efficient melting and most even temperature profile across the melt. Fluctuations in melt temperature were observed over short periods of time, corresponding in some cases to the frequency of screw rotation or in extreme cases, at semi-random frequency due to poor melting and solid bed break-up.

# MEASUREMENT AND PREDICTION OF FIBRE ORIENTATION DISTRIBUTION WITHIN A TRANSVERSE RIBBED SPECIMEN

*P. Caton-Rose<sup>1</sup>, P. D. Coates<sup>1</sup>, B. Whiteside<sup>1</sup>*

*P. Hine and A. Duckett<sup>2</sup>*

*P. Jittman, C. Chapman and G. Smith<sup>3</sup>*

*<sup>1</sup>IRC in Polymer Engineering, University of Bradford*

*<sup>2</sup>IRC in Polymer Physics, University of Leeds*

*<sup>3</sup>University of Warwick*

## ABSTRACT

Short glass fibre reinforcement is well established as a means of significantly improving on mechanical performance without compromising processability, and many glass filled polymer grades and products are commercially available. Apart from the fibre and matrix properties, the mechanical properties of the final component are crucially dependent on the fibre orientation distribution (FOD) developed during the process, as well as other aspects such as the resulting fibre aspect ratio and the fibre/matrix interface.

In this poster we describe a comparison of the fibre orientation structures developed in a transverse ribbed plate during injection moulding, with those predicted using the Moldflow commercial software. Adjustments of the fibre interaction coefficient and Moldflow's thickness moment of interaction have been made to assess the relative effect of these parameters.

A novel comparison method has been developed using image analysis software employed during experimental FOD measurement to interpret the analysis data. Three locations, either side of the transverse rib and along the centreline, were selected to evaluate Moldflow predictions. All locations showed similar fibre orientation distributions as the measured part, although at higher degrees of orientation.

Recent work also displayed within this poster includes an evaluation of FOD predictions within a fully three-dimensional flow model. On completion of this work this information will be input into a knowledge-based system (KBE) for product design. Development of the KBE is currently underway at the University of Warwick.

# **Water Assisted Injection Moulding: Process design and characterisation.**

*L. Mulvaney-Johnson, T.D. Gough, A.J. Dawson, P. D. Coates.  
IRC in Polymer Science and Technology, University of Bradford.*

## **A B S T R A C T**

The Water Assisted Injection Moulding (WAIM) process has emerged as a viable technology to offer cycle time reductions and better internal surface finish over the more established Gas Assisted Injection Moulding (GAIM) technology. Automotive under-bonnet applications to carry engine fluids are frequently cited in PA6 and PA66 materials, typically fibre-filled. The internal surface finish of these products needs to be sufficiently smooth to prevent particulate break-off from the motion of the conveyed fluid and to minimise the hydraulic frictional losses.

Design guidelines for the tooling and processing information are necessary for industry to exploit this new technology in product applications. The development of the tooling and process have raised a number of key issues such as the placement of the water injection needle, the cavity formation around the needle, the location of the melt injection gate relative to the water outlet and provision for water extraction.

Initial process characterisation investigations have shown that residual wall thickness (RWT) tends to reduce with increasing water pressure during the primary water penetration phase; a similar trend is seen with the GAIM process. During the cooling phase holding pressure needs to be maintained, which has the effect of increasing the water volume as the melt contracts. The incompressibility of water results in a rapid fall in cavity pressure with what is likely to be a small percentage increase in water bubble volume.

Simulations of the water filling process are in their initial stages. The high heat transfer is well captured although the disparity between gas and water formed RWT is not so evident and more work in this area is therefore necessary. The phase of the water at the polymer interface is not known since polymer is at high temperature (typically up to 250C) and the water pressure at this interface is not yet known.

# **Biaxially Oriented PP: Heat Transfer Aspects in the Double Bubble Processes**

*H Benkreira and M C Talford,  
School of Engineering, Design and Technology,  
University of Bradford, BRADFORD*

## **A B S T R A C T**

The use of infra red energy in heating tubular plastic extrudates is considered, with particular reference to its application in the Double Bubble process for manufacturing Biaxially Oriented Polypropylene (BOPP) films. It is important that the temperature profile developed through the thickness of the extrudate is uniform at the point of deformation as otherwise the stress field during the deformation process can be significantly affected. This is demonstrated by curl and other defects in the finished film. However the heating operation accounts for a significant amount of the process operating cost and poor heater operation can result in a large amount of waste heat being generated. Experiments were conducted using both a purpose built rig and full-scale industrial bubble processes to determine the effects of heater temperature and air flow through the heater on the temperature profiles of tubular extrudates and air temperatures and heat transfer coefficients. Correlations were fit to the data to enable estimation of the air temperatures from knowledge of the process conditions and geometry. Heat transfer coefficients measured from the experiments were compared with theoretical predictions. The full range of data obtained was used to validate a mathematical model developed to describe the infra red heating process, based on heat conduction theory applied with suitable boundary conditions and solved using numerical techniques. The model predictions compare well with the operating data obtained, within the certainty of the process parameters used. The model was used in a parametric study based on a particular industrial process.

# **A Novel Extrusion Die: The Rotating Roller Die**

*H. Benkreira, R. Patel, J. Paragreen, M. Cox, M. Gale.  
School of Engineering, Design and Technology,  
University of Bradford.  
H.Benkreira@bradford.ac.uk*

## **A B S T R A C T**

The roller die is a novel die consisting of a pair of rollers separated by a gap from which the polymer can exit. The rollers can rotate either in the direction of flow to increase throughput or against the flow to increase die pressure. In the backward mode of operation, because of the counter flow action of the rollers, higher pressures can be generated in comparison to a stationary die. This presents the potential to be used in CO<sub>2</sub> foaming applications, where high die pressures are required for the CO<sub>2</sub> to dissolve in the melt, in order to obtain low density foams. Experiments have been carried out to quantify this back pressure effect and the reduction in foam density. A range of modeling techniques have been used alongside the experimental work, from 1D analytical models to viscoelastic 3D simulations.

The roller die also has the ability to control the shear and extensional rates through the die, which consequently effects die swell. Clearly this ability to easily control and vary extrudate thickness and texture could provide considerable cost saving to various industries, such as the synthetic wood industry. Analysis of the video footage of the roller die has allowed this effect to be quantified and backed with theory, allowing the swell to be predicted. The melts used for this study include LDPE, PS and PP. Experiments have been carried out using pure melts as well as foams blown small quantities of CO<sub>2</sub> to produce high density foam wood substitutes.

# **A Bench Top Polymer Mixer-Reactor**

*H Benkreira, M Gale, R Patel and R Butterfield  
School of Engineering ,Design and Technology, University of Bradford, BRADFORD, BD7 1DP,  
England*

## **A B S T R A C T**

In the processing industries, good mixing is the key to good production. With low viscosity fluids and dispersed solids this is easily achieved as turbulence and diffusion are effective drivers. When viscous and pasty materials (e.g. polymer melts and soft solids) are mixed with tiny amounts of non-dispersed solid agglomerates (e.g. pigments) this is not the case as the materials are so viscous. Currently the mechanism for dispersive mixing is not fully understood therefore development of new products relies a lot on experience and "know-how" when designing a mixer for such applications. The current laboratory size mixing equipment give poor dispersion and do not provide any confidence for scale up, therefore when developing new products this imposes on industry expensive trial and error formulation runs on different designs in pilot or full-scale production lines.

The scope of the present work includes a feasibility study of a newly developed prototype laboratory mixer to assess and determine its dispersive and distributive mixing characteristics. Analysis of the mixing characteristics has been carried out using polyethylene (Stamylan 2606 TX17) as the bulk polymer and a high melting point masterbatch as the tracer. Mixing has been carried out under various conditions of shear rate, shearing time and tracer concentration. Extrudate samples are collected, pressed and then viewed under a microscope. Images are taken at 2.5X magnification and the dispersion of the tracer is then analysed using software written in Optimas 6.0. Suitable software will be written to analyse the distribution of the tracer.

A computer model of the mixer will then be generated using Fluent's FIDAP CFD software, based up the Finite Element Method, which will be used to look at optimising the mixer and possible scale up of the mixer for larger applications.

This work is carried out using the experimental facilities funded by EPSRC grant GR/S14337/01. This gives the opportunities to interact with the Postdoctoral Research Assistant and the Research Student attached to this grant. The work is supervised by Professor H Benkreira, the Principal Investigator of this grant.

# **Small-scale recirculation flow cells for studies of flowing polymer melts**

*T Gough, R Spires, MT Martyn, J Bent\*, E. Heeley\* and P D Coates  
IRC in Polymer Engineering, University of Bradford, Bradford BD7 1DP, UK  
\*IRC in Polymer Science & Technology, University of Durham, Durham DH1 3LE, UK  
+Polymer Centre, University of Sheffield, Sheffield S3 7HF, UK*

Molecular properties of materials such as extent of branching, molecular weight and its distribution, and polydispersity are critical components in the understanding of polymer rheology and thus in processing behaviour. Commercial modelling software depends upon continuum mechanics approaches to polymer processing in the absence of any molecular scale information. The Microscale Polymer Processing MuPP project was set up between six UK universities and six European polymer producers in order to try to close this gap in understanding.

A key test for the project was attempting to understand and model the flow behaviour of small batch polymers within model complex process flows. To this end two recirculation flow cells with small volume charge (<200g) were designed, manufactured and commissioned in order to attempt measurements of velocity, stress and molecular configuration through contraction dies. Contraction flows have been studied for many years and present a 'simple' yet complex test of any numerical predictions of flow. The industrially relevant features of die swell, large entry pressure losses, non-linearity between pressure drop and flowrate and occurrence of instabilities above certain processing conditions can all be observed and measured using this simplified geometry and thus present an excellent test case for computational codes for non-Newtonian flows.

Full field stress and velocity measurements for a number of polymer melts through two abrupt contraction dies have been made utilising stress birefringence and particle tracking velocimetry techniques and show the effects of flowrate and geometry upon these variables. Complementary small angle neutron scattering (SANS) studies have allowed the first measurements of molecular radii of gyration within flowing melts allowing quantitative understanding of the effects of shear and extension upon molecular configuration. Small angle X-ray scattering (SAXS) studies, in a region of high shear, have allowed quantification of the effects of shear upon crystallisation.

These studies show the utility and versatility of these flow cells for studying a range of melt characteristics using only a handful of polymer pellets.

## **Micromoulding – Process Characterisation.**

**B.R. Whiteside, M.T. Martyn, P.D. Coates**

*IRC in Polymer Science & Technology, Dept of Mechanical & Medical Engineering  
University of Bradford, Bradford BD7 1DP, UK*

### **A B S T R A C T**

The micromoulding process, whilst fundamentally similar to that of conventional injection moulding, typically incorporates different processing techniques such as small scale plastication, low volume metering, high injection velocity and rapid cooling. This poster presents data which allows evaluation of the influence of these new technologies on process control and repeatability, and discusses the challenges involved in generating accurate process data as tooling technology advances realise cavities of decreasing size and increasing complexity.

A data acquisition suite capable of monitoring a number of process dynamics at high sampling rates has been installed onto a commercial micromoulding machine. Data were collected during the moulding of products having masses 0.3mg - 25mg over a range of process conditions. These data showed that injection and cavity pressure repeatability is inferior to many conventional injection moulding processes and highlighted the need for cavity pressure measurement for accurate process characterisation. Problems with sensor installation in such cavities are discussed and possible solutions are presented.

# Process Imaging Studies

*Spires R, Caton-Rose P, Coates PD*  
*IRC in Polymer Science & Technology, School of Engineering Design and Technology,*  
*University of Bradford, Bradford, UK BD7 1DP*

## A B S T R A C T

The ever increasing power of personal computers has largely been driven by the demands of the domestic consumer market. More recently the desire for multimedia products has led to significant developments of imaging equipment that is of high quality at a relatively low cost, along with suitable data transfer methods (e.g. USB and firewire) that are capable of transferring information to the pc at high speed. Traditionally scientific imaging studies have relied on CCD sensors that have lower noise on the recorded image than CMOS sensors. Image quality of the lower cost CMOS sensors is rapidly improving and their design often allows arbitrary regions of interest (ROI) to be imaged at frame rates that can be increased as the ROI reduces in size.

The work presented here gives an overview of the flexibility of these cameras and gives a flavour of the applications to which they can be applied. Specifically the applications are,

1. Detection of surface defects on extruded products produced using recycled PVC.
2. Digital particle image velocimetry (DPIV) investigation of velocity fields in a 4:1 abrupt contraction die.
3. Strain measurement of solid phase polymer samples deformed in an Instron tensile testing machine.

These case studies aptly demonstrate the capabilities of modern image sensors but are not shown as an exhaustive list. Low cost imaging may soon be as common as temperature and pressure for process monitoring as new applications emerge.

# **The use of Nano Scale particles to enhance the properties of oriented polypropylene.**

*M. Bonner, G. Bonzi, P.J. Hine & I.M. Ward  
IRC in Polymer Science & Technology, University of Leeds*

## **A B S T R A C T**

The use of nano scale particles to improve the mechanical properties of isotropic polymers has recently been extensively studied and reported, and it is well known that it is possible to significantly increase the isotropic modulus by use of just a few weight percent of the nano scale fillers. A wide range of nano-particles have been studied, including nano-clays and nano carbon fibres and tubes of a variety of structures, including vapour grown carbon fibres, and single and multi-wall carbon nano-tubes. The use of nano-clays has seen the greatest research interest, for while the properties enhancements are not quite as high as seen with the nano carbon fibres and tubes, the cost effectiveness of the clays make them very attractive. Industrial companies continue to launch new products and applications using components made from nanoclay filled polymers. GM recently announced the use of a nanoclay filled olefin material in a side panel of the Chevrolet Impala, and will this year sell around 500,000lbs of nanocomposite material.

The majority of this previous activity involves research into isotropic polymers. Our aim in this project has been to extend this research into oriented polymers (most notably polypropylene), with the goal of being able to use these oriented filled nanocomposite elements in the hot compaction process developed at the University of Leeds. A key issue is to obtain a significant increase in properties such as high temperature stiffness, strength and creep resistance, without sacrificing ductility and density. In addition small amounts of nano-clays are still considered to allow the material to be recycled, which can be an important consideration for the automotive industry.

2% to 10% by weight of nano scale clays has been blended with polypropylene using a twin screw extruder. Mechanical tests, together with scanning electron microscopy (SEM) and Wide Angle X-Ray Diffraction (WAXS) was then used to assess the properties and morphology of the blended materials. A particular target was to assess the degree of exfoliation that had occurred during blending. Exfoliation, or splitting up of the clay particles into nanometre thickness sheets, is crucial to obtain maximum reinforcing efficiency. The most promising grades were then drawn at an elevated temperature to produce oriented nanocomposite tapes. Morphological investigation, via SEM and WAXS, showed that solid phase drawing process produced preferred alignment in both the polymer matrix and the nanoclay particles, while mechanical measurements showed significant improvements in properties over the pure PP material.

# **Separator-Free Rechargeable Lithium Ion Cells produced by the Extrusion Lamination of Polymer Gel Electrolytes**

*I M Ward, H V St A Hubbard, S C Wellings and GP Thompson  
IRC in Polymer Science & Technology, School of Physics and Astronomy,  
University of Leeds, Leeds LS2 9JT, UK*

*J Kaschmitter and H P Wang, SpectraPower Inc., 230 S Vasco Road,  
Livermore, CA 94550, USA*

*and*

*E Cole and G Flickinger, British Technology Group, 10 Fleet Place,  
Limeburner Lane, London EC4M 7SB, UK*

## **ABSTRACT**

Polymer Gel Electrolytes (PGE) based on polyvinylidene fluoride (PVDF), lithium salts and appropriate solvent systems, developed at Leeds University, have been shown to form tough rigid films with conductivities approaching  $10^{-2}$  S/cm. A continuous process has now been developed for the construction of rechargeable lithium cells by extruding the PGE as a melt and directly laminating between the anode and cathode electrodes. On cooling, the solid PGE acts as electrolyte, separator and binds the cell laminate together from within requiring no external case. This process has been successfully applied for the fabrication of cells with electrodes developed by SpectraPower Inc. in a commercial process enabling cell laminates with PGE thickness of 50 microns or less and with energy densities of 150 Wh/kg. A prototype manufacturing facility has been set up to produce rechargeable cells of high specific capacity and high energy density. These developments will enable rechargeable lithium ion cells to be produced on a continuous and low cost process as flat sheets opening the way for novel battery geometries and applications.

# **Production and properties of highly oriented polymer wires**

**I. M. Ward<sup>a</sup>, J. Mohanraj<sup>b</sup>, B. Brew<sup>a</sup> & D. C. Barton<sup>b</sup>**

*(a) IRC Polymer Science & Tech., School of Physics & Astronomy, Univ. Leeds, UK*

*(b) Intelligent Systems, School of Mechanical Engineering, Univ. Leeds, UK*

## **A B S T R A C T**

Orientation of polymers in the solid-state has been used for a long time in enhancing the properties of the products. In this presentation, we describe the application of the Leeds die-drawing process to produce highly oriented polyacetal wires.

In the first part of this presentation, we compare the mechanical properties and structure of uniaxially oriented PolyOxyMethylene (POM) produced by two solid-state processes: hydrostatic extrusion and die-drawing. In the former process there is no net component of tensile stress whereas in the latter case the sample is subjected to net tensile stresses at the die-exit. The properties, structure and morphology of the oriented samples are compared and their differences are discussed.

In the second part of the presentation, we use finite element methods to analyze the strain rate distribution in a wire die-drawing process. The flow stress of an oriented polymer is highly sensitive to both the degree of plastic strain and the strain rate. In a wire die-drawing process using conical dies, the high strain rate, high strain and the tensile nature of the stress at the die-exit could cause internal damage to occur in the material, now oriented, during drawing and thus limit the draw speed. A method of designing profiled dies where the strain and strain-rate are controlled along the die-length is presented. The performance of the conical and profile die designs is compared using finite element simulations and experimentally under identical drawing conditions for the specific case of die-drawing of POM wire.

# Aggregation and gelation in randomly charged ionomer solutions

\*Edoardo De Luca<sup>1</sup>, Thomas A. Waigh<sup>1</sup>, Joon Seop Kim<sup>2</sup>

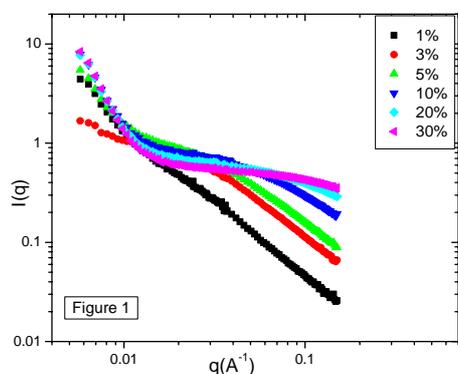
<sup>1</sup>*Polymers and complex fluids, School of Physics and Astronomy. University of Leeds. Leeds. UK.*

<sup>2</sup>*Department of polymer science & Engineering. Chosun University. Kwangju, Korea.*

## ABSTRACT

Ionomers are charged polymers with undissociated counterions. These counterions stay near to the polymer backbone forming dipole-dipole attractions between neighbouring chains<sup>1</sup> that can produce micelles or aggregates in low dielectric constant solvents or show polyelectrolyte behaviour in polar solvents. We are interested in understanding the aggregation behaviour of the dipolar groups in low dielectric constant solvents such as toluene.

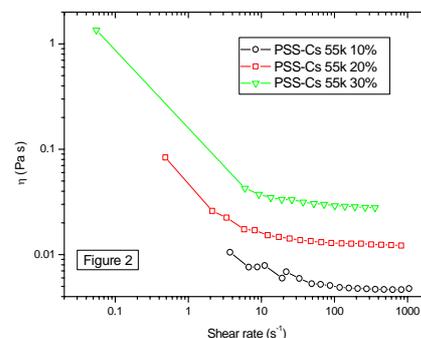
Polystyrene sulfonic acid of different molecular weight (50k, 100k, 200k) and 1% sulfonation were synthesised in the laboratory of Joon Seop Kim using the method of radical polymerisation and subsequently neutralised with caesium hydroxide.



SANS experiments on the samples have shown (figure 1) an excess scattering once the concentration is above the chain overlap concentration ( $c^*$ ) and the solution undergoes gelation. This upturn is generally known as Picot-Benoit<sup>2</sup> effect and it is interpreted by the concept of macromolecular association or frozen concentration fluctuations present in the sample as heterogeneities. We believe that in the ionomer samples the enhanced scattering is due to the dipole interaction of the charged groups that self assemble into micelles in the semi-dilute regime. The data can be fitted with the attractive potential function proposed by Medjahdi et al.<sup>3</sup> Their model can be applied only when anomalous scattering is observed

in the semi-dilute regime and this is in perfect agreement with our SANS data.

On the same samples shear viscosity experiments showed (figure 2) a Newtonian behaviour in the high stress regime and a quiescent region where the aggregates display stronger dipolar interactions. These physical cross-links can drive the system into a jammed situation where the system behaves like an elastic solid. Leibler et al.<sup>4</sup> presented a model for dynamics of entangled networks made up of linear chains with many temporary cross-links. At times shorter than the lifetime of a cross-link such networks behave as elastic rubbers (gels). On longer time scales the successive breaking of only a few cross-links allows the chain to diffuse along its confining tube. The motion of a chain is controlled by the concentration and lifetime of sticky points. We believe that these results can be interpreted in terms of stress-induced re-organisation of the dipolar interactions and can give new insight in understanding the behaviour of randomly charged ionomers.



## References

- 1 Young, A.M. et al. *Polymer*. **1998**, 39, 1525-1532.
- 2 Benoit, H. Picot, C. *Pure Appl. Chem.* **1966**,12, 545
- 3 Medjahdi, G. Sarazin, D. Francois, J. *Macromolecules*. **1991**, 28, 4138.
- 4 Leibler, L. Rubenstein, M. Colby, R.H. *Macromolecules*. **1991**, 24, 4701-4707.

# Adsorption of DNA onto oppositely charged spheres.

*Alison J. Hodrien, Alison M. Voice, Thomas A. Waigh.  
IRC in Polymer Science & Technology,  
University of Leeds*

## A B S T R A C T

The complexation behaviour of linear DNA (negatively charged) with sub-micron latex spheres, surface functionalised with amine groups (positively charged), is studied by dynamic light scattering (DLS), small-angle neutron scattering (SANS), small-angle x-ray scattering (SAXS), and micro rheology. The complexes are measured in solution as a function of component concentration ( $C_{DNA}$ ,  $C_{SPH}$ ) and added salt concentration ( $C_s$ ). In the absence of salt, measured radius increases with  $C_{DNA}$  ( $C_{SPH}$  held constant) up to a plateau value where charge of the complex is considered to be neutralised. The presence of salt causes a decrease in the measured complex radius (up to the point where components drop out of solution), which may be due either to increased flexibility of the chains allowing them to form a more compact layer on the sphere surface, or dissociation of the two components due to screened electrostatics. More detailed experiments to determine this are underway.

Motivation for this work stems from the growing body of theoretical and simulation literature on the subject, which currently lacks an equivalent body of experimental work for the purposes of comparison. Generally these works describe a range of structures (often in the form of complexation phase diagrams), from the chain tightly wrapping the sphere to the formation of large loops (or leaves) to give a rosette like complex. Parameters in the system under study have been limited to: sphere radius, chain length and salt concentration (affecting both electrostatic screening and chain flexibility), with the scope to vary pH (and therefore the charge on the two components) if required. Although much of the literature only examines systems containing one chain per sphere, we expect that general trends (e.g. layer thickness increasing as chain stiffness increases) will remain as predicted. As a secondary motivation, the phenomena of complexation between oppositely charged structures is already exploited by man and nature (e.g. industrially for colloidal stabilisation, and for DNA packaging within cells), and a better understanding of the physics behind the systems can only serve to provide further applications.

# Structure and properties of oriented bioresorbable fibres: poly(glycolic acid)

H. Montes de Oca, I. M. Ward<sup>(+)</sup>, M. E. Ries<sup>(+)</sup>, J. Rose<sup>(++)</sup>, D. Farrar<sup>(++)</sup>.

(+) Polymer IRC, Department of Physics and Astronomy, University of Leeds, UK.

(++) Smith and Nephew Group Research Centre, York Science Park, Heslington, York YO10 5DF, UK.

## ABSTRACT

Highly drawn hot compacted poly(glycolic acid) (PGA) fibres with adequate mechanical properties for biomedical applications are characterised by simultaneous SAXS/WAXS and <sup>1</sup>H NMR spectroscopy. <sup>1</sup>H NMR  $T_{1\rho}$  measurements suggest that two amorphous phases with different mobility and a crystalline highly rigid phase are encountered in the compacted fibres. The three phases have different relaxation times, each with some degree of anisotropy. The X-ray crystallite orientation averages  $P_2=0.99$  and  $P_4=0.96$  agree well with those estimated by <sup>1</sup>H NMR spectroscopy on the basis of the rigid lattice theory [1] and the published crystal structure [2] ( $P_2=0.96$  and  $P_4=0.94$ ), confirming highly oriented crystalline material.

Structure/property relationships of drawn fibres can be explained on the basis of the Takayanagi model [3]. Alternate amorphous and crystalline regions are developed after a drawing stage, giving rise to a two point SAXS pattern and sharp WAXS arcs characteristic of fully oriented crystalline regions. The lamella is considered aligned parallel with the draw direction and surrounded by a continuous amorphous phase. The modelling is carried out in a wide temperature range and requires an extensional modulus of around 60GPa for the crystalline region.

A relaxation stage after plastic deformation during processing makes the lamella tilt around 45° with respect to the draw direction, giving rise to a four point SAXS pattern. Nevertheless, the WAXS pattern shows sharp arcs, indicative of almost fully oriented crystalline regions. Hence, the elastic behaviour of this structure is governed by inter-lamellar shear, as in some high density polyethylene structures [4], but its modelling is complicated because the separation of the tensile and shear contributions to the deformation cannot be accurately carried out. It is observed that the lamellae align with the draw direction during degradation, changing its initial structure, giving rise to a two point SAXS pattern after 19 days of degradation. Rapid attack to the amorphous regions and partial re-crystallisation at early stages of degradation is observed. This is followed by hydrolysis of both, crystalline and amorphous regions at later stages where the lamellar rotation is more evident.

## References

- [1] McBrierty VJ, Ward IM. Brit J Appl Phys (J Phys D) 1968; 1: 2: 1529-42.
- [2] Chatani Y, Suehiro K, Okita Y, Tadokoro H, Chujo K. Die Makromolekulare Chemie 1968; 113: 215-29.
- [3] Takayanagi M, Imada K, Kajiyama T. J. Polym. Sci. C 1966; 15: 263.
- [4] Stachursky ZH, Ward IM. J Macromol Sci- Phys 1969; B3: 3: 445-94.

# Chain Transfer Agents for RAFT Polymerizations to Design Functionalized Polymers

*Pittaya Takolpuckdee and Sébastien Perrier*

*Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113*

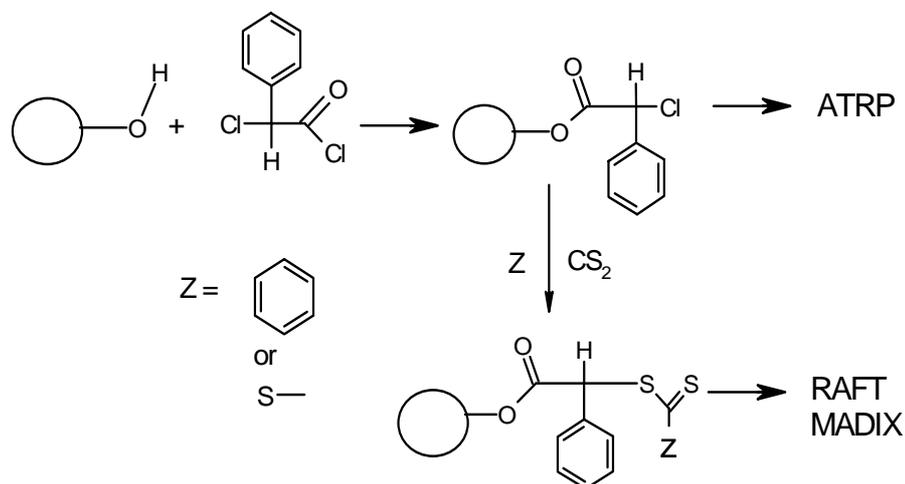
*343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

*Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds,*

*LS2 9JT*

## ABSTRACT

Reversible Addition Fragmentation Chain Transfer (RAFT) agents have been extensively used to prepare macromolecules derived from a wide range of vinyl monomers due to their capacity to create new polymeric architectures, e.g. linear, comb and star polymers, with low polydispersities. A key aspect for controlling RAFT polymerisation is in the design of chain transfer agent. A variety of novel chain transfer agents (CTAs) based on ester or amide groups have been prepared. Kinetics studies have been undertaken using a wide range of monomers. Homopolymers and block copolymers were synthesised including amphiphilic copolymers and block copolymers incorporating biodegradable blocks.



**Synthesis and Characterization of Telechelic and Triblock Copolymers of Type ABA  
and ABC via Reversible Addition Fragmentation Chain Transfer (RAFT)  
Polymerization**

*Thomas M Legge<sup>a,b</sup>, Andrew Slark<sup>c</sup> and Sébastien Perrier<sup>a,b</sup>*

<sup>a</sup> *Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113  
343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

<sup>b</sup> *Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds,  
LS2 9JT*

<sup>c</sup> *National Starch & Chemical Ltd. Wexham Road, Slough, Berkshire SL2 5DS*

The construction of polymeric materials atom by atom is attainable in a variety of different ways. Traditional routes to living and controlled polymers are limited by their low tolerance of monomer functionality and the extreme reaction conditions required. Reversible Addition Fragmentation Chain Transfer Polymerisation is a recently developed and powerful system which has been used to synthesize a variety of specialty polymers. The mechanism is free radical in nature and is of great interest to industry. In the present study triblock copolymers of type ABA have been synthesized using a novel Difunctional chain transfer agent (CTA). A blocks using styryl and methyl acrylate monomers and B blocks composed of methacrylate monomers were used. Polymerizations were carried out in bulk and in solution, with rates of polymerisation generally slower than traditional free radical. Macro RAFT agents from homopolymers with difunctionality were synthesized as an alternative route to ABA block copolymers. Homopolymers used included Poly(ethylene oxide) and Poly(propylene oxide). Polymers were fully characterized by NMR, FT-IR, GPC, TGA and DSC. Stereochemistry was found to be analogous to traditional free radical polymerizations. Control of chain length of blocks was achieved with molecular weights ranging from 8000-100000. Low molecular weight distributions were observed ranging from 1.1-1.4 and the living nature of the polymers was proved by GPC analysis. There are many potential uses for such triblock copolymers such as in adhesives, vibration dampeners and in high technology films. The great versatility of the current system has proved its suitability for manufacturing such materials.

# Designing Polymers via Living Radical Polymerization for Industrial Applications

*Craig Mars<sup>a,b</sup> and Sébastien Perrier<sup>a,b</sup>*

*<sup>a</sup> Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113 343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

*Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, LS2 9JT*

*<sup>b</sup> Designer Polymers Ltd, the University of Leeds, LS2 9JT*

## ABSTRACT

Reversible addition fragmentation chain transfer (RAFT) polymerisation and macromolecular design by interchange of xanthates (MADIX) offer a great flexibility for the synthesis of polymeric chains with predefined molecular weight and narrow molecular weight distribution. The wide range of monomers already successfully polymerised, the ease to scale-up the reaction and the high tolerance to functional groups of this relatively new process makes it the most suitable process for industrial use. This paper will discuss the versatility of RAFT/MADIX for large-scale processes and for specific application such as high-throughput polymerisations.



**Figure: Example of synthetic setup for high throughput polymerisation**

# **Synthesis of Controlled Polymer Architectures on a Cellulose Support via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization**

***Debashish Roy and Sébastien Perrier***

***Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113***

***343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk***

***Interdisciplinary Research Centre in Polymer Science and Technology, University of  
Leeds, LS2 9JT***

Cellulose is not only the most abundant organic raw material in nature but also it is inexpensive, biodegradable and a renewable resource. The physical and chemical properties of native cellulose can be altered by graft polymerisation and cellulose of improved properties with specific end use can be obtained. The grafting of styrene (St), N, N-dimethylacrylamide (DMA) and N-isopropylacrylamide (NIPAM) onto a cellulose support has been investigated by the use of living radical polymerisation techniques such as RAFT (reversible addition fragmentation chain transfer) polymerisation, in order to grow polymeric chains of predefined chain length and molecular weights. Cellulose support such as cotton fabrics were first modified by reacting the hydroxyl groups with 2-chloro-2-phenylacetyl chloride (CPAC) and further converted into cotton-dithioester chain transfer agent (cotton-s-methoxy-carbonylphenylmethyl dithiobenzoate, cotton-MCPDB) by Grignard reaction. The polymerisation of Styrene, DMA and NIPAM was mediated by this supported CTA, in dimethylformamide at 60 °C. The grafted cotton fabrics were analysed by gravimetry, FT-IR and DSC. The results obtained indicate that the copolymers had been successfully formed onto the cotton fabrics. The grafted polymers have also been cleaved from the cotton fabrics by acid hydrolysis for proton NMR and SEC (size exclusion chromatography) analysis.

# Thermoresponsive Micelles from Well Defined Block Copolymers Synthesized via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization.

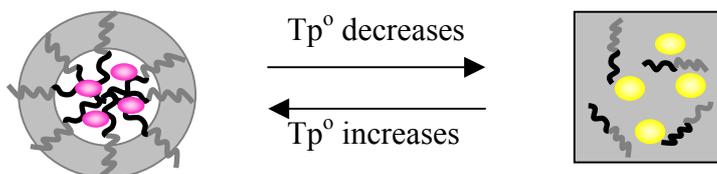
*Bo Liu and Sébastien Perrier*

*Department of Colour and Polymer Chemistry, The University of Leeds, LS2 9JT, tel: 0113 343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

*Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, LS2 9JT*

## ABSTRACT

The kinetics of N-isopropyl acrylamide (NIPAAm) polymerisation by RAFT have been studied. The resulting polymers were used as macro-chain transfer agent to synthesis ‘smart’ amphiphilic block copolymers with a switchable hydrophilic-hydrophobic block of poly(N-isopropyl acrylamide) (PNIPAAm) and an hydrophilic block (poly(N-dimethyl acrylamide), PDMA) or hydrophobic block (poly(methyl acrylate), PMA). All polymers were characterised by GPC,  $^1\text{H}$  NMR, differential scanning calorimetry (DSC). The reversible aggregates formed by the block copolymers of various compositions in aqueous solution have been characterised by  $^1\text{H}$  NMR, Dynamic Light Scattering (DLS) and tensiometry. In the case of PNIPAAm-*b*-PDM, aggregates are observed in aqueous solution by increasing the temperature to 40  $^{\circ}\text{C}$ , due to the collapse of the PNIPAAm structure, leading to a PNIPAAm hydrophobic block. Drug loading capacity has been illustrated with the use of the solvatochromic Reichardt’s dye and measured by UV/VIS.



**Novel Chain Transfer Agents for Reversible Addition Fragmentation Chain Transfer (RAFT) and Macromolecular Design by Interchange of Xanthate (MADIX) Polymerizations**

*Murray R Wood<sup>a,b</sup>, Dave Duncalf<sup>e</sup>, Steve Rannard<sup>f</sup> and Sébastien Perrier<sup>a,b</sup>*

<sup>a</sup> *Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113 343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

<sup>b</sup> *Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, LS2 9JT*

<sup>c</sup> *Unilever, Quarry Road East, Bebington, Wirral, CH63 3JW, UK.*

**A B S T R A C T**

Reversible addition fragmentation chain transfer (RAFT) polymerization and Molecular design by interchange of xanthates (MADIX) polymerization are the most recently developed method for controlled living radical polymerisations and are of particular interest for obtaining polymers with low polydispersities and well-defined architectures. RAFT and MADIX polymerisations work via degenerative chain transfer of di- or tri-thiocarbonate and xanthate (MADIX) chain transfer agents.

A new method has been conceived for the syntheses of chain transfer agents which makes use of the high selectivity and reactivity of 1, 1'-thiocarbonyl diimidazole, with primary, secondary and tertiary thiols (RAFT agents) and alcohols (MADIX agents).

Here will be presented the synthesis of chain transfer agents via the new method, and the corresponding kinetics studies with some common monomers; styrene, MA, MMA, and DMA.

# Polymeric Architectures via Reversible Addition Fragmentation Chain Transfer (RAFT) polymerization

*François Vettier and Sébastien Perrier*

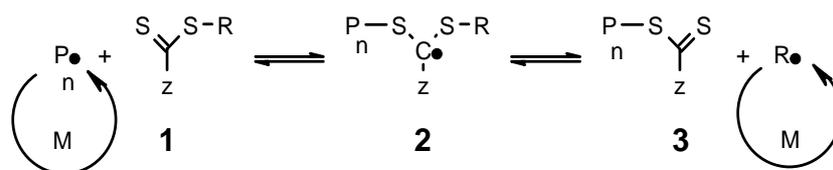
*Department of Colour and Polymer Chemistry, the University of Leeds, LS2*

*9JT, tel: 0113 343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

*Interdisciplinary Research Centre in Polymer Science and Technology,*

*University of Leeds, LS2 9JT*

Reversible addition fragmentation chain transfer (RAFT) polymerisation and macromolecular design by interchange of xanthates (MADIX) appear to be the most promising living radical polymerisation processes reported to date. The wide range of monomers already successfully polymerised, the ease to scale-up the reaction and the high tolerance to functional groups makes them the most suitable techniques for obtaining well-defined polymeric architectures. RAFT and MADIX are based on a similar process, the introduction of a small amount of dithioester of generic formula **1**, scheme 1 (chain transfer agent, CTA) in a classic free radical system (monomer + initiator). The transfer of the CTA between growing radical chains, present at very low concentration, and dormant polymer chains, present at higher concentration, will regulate the growth of the molecular weight, and limit the termination reactions (See Figure).



The careful choice of the R and Z group allows us to incorporate a wide range of functionalities in polymeric architectures. In this paper we will show the high versatility of RAFT polymerisation to design various polymeric architectures such as block copolymers, star (co)polymers, hyperbranched (co)polymers, etc. and specifically chain-end functionalised polymers.

# Functional Materials Produced from Living Radical Polymerization

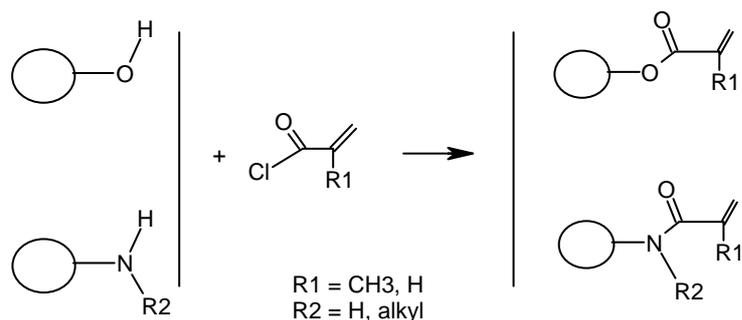
*Phuriphong Totsatitphisal and Sébastien Perrier*

*Department of Colour and Polymer Chemistry, the University of Leeds, LS2 9JT, tel: 0113*

*343 2932, fax: 0113 343 2947, s.perrier@leeds.ac.uk*

*Interdisciplinary Research Centre in Polymer Science and Technology, University of Leeds, LS2 9JT*

In the recent years, radical polymerisation has seen an increasing interest from industry and academia due to the rise of living radical polymerisation (LRP). LRP generates well-defined architectures, *e.g.* polymers with well-known degrees of polymerisation, molecular weight distributions, end functionalities, chain architectures and compositions. To date, the most important processes are nitroxide mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP) reversible addition fragmentation chain transfer (RAFT) polymerisation and macromolecular design by interchange of xanthate (MADIX). This paper will discuss the introduction of functionalities as pendant groups on polymeric chains. A simple and straightforward route is the transformation of hydroxyl bearing molecules or amine bearing molecules into acrylates / methacrylates (respectively) or acrylamides / methacrylamides (respectively), by esterification with acryloyl chloride or methacryloyl



chloride (See Figure) and their further polymerization by LRP techniques.

# STRUCTURAL ARCHITECTURE OF BRANCHED POLYMERS AND MODELLING OF PLASTICS PROCESSING

*Nathanael Inkson, Tom C.B. McLeish, Oliver Harlen, Tim Nicholson*

*Department of Applied Mathematics, The University of Leeds, UK  
phone: +44 (0)113 3432695 mobile: +44 (0)7791 549873, e-mail:  
njinkson@maths.leeds.ac.uk*

## ABSTRACT

The experimentally determined zero-shear viscosity of entangled branched polymers shows dramatic variation due to the topological arrangements of the branches in branched polymer melts. The position of the branch points, the length and number of the arms are essential to defining the rheological behaviour. Recent advances in the theory of molecular tube models have led to a much greater understanding in the linear rheology of linear, star, H-shaped, pom-pom and comb polymers. We make use of these molecular models to explore a theoretical parameter space to design polymer properties from topology alone. We explore how the zero shear viscosity varies for monodisperse comb polymers with varying arm lengths, backbone lengths and number of arms. We find that combs with the longest arms but the fewer numbers of branches give the highest predicted zero-shear viscosities, and that they obey exponential dependence on the length of the arms in the same way as star polymers. We find that the combs with long backbones and short arms lie very close to the 3.4 power law line obeyed by linear polymers. All other comb topologies are bounded by these extremes. Experimental data for the processing behaviour of tree-like branched polymers are presented for the first time as flow birefringence data obtained using a Multipass Rheometer with an 11/1 constriction entry and exit flow (Cambridge University). Matching of experimental processing data was obtained using the pom-pom constitutive model with the in-house Lagrangian finite element numerical simulation, flowSolve. The results show the direct coupling between molecular constitutive response and macroscopic processing behaviour, and differentiate flow effects that arise separately from orientation and stretch. We also accurately predict vortex growth in constriction flow geometries for the first time. This research was performed under the microscale polymer processing project ( $\mu$ PP), a consortium of academic and industrial partners.

# **Motion of Semi-Flexible Fibres under Shear**

*Samantha Harris, Oliver Harlen, Tanniemola Liverpool  
Department of Applied Mathematics, University of Leeds.*

## **A B S T R A C T**

High aspect ratio particles such as carbon and glass fibres are often added as fillers to polymers. Although these materials are stiff, their high aspect ratio makes them liable to bending during flow. Other examples of semi-flexible fibres include carbon nano-tubes, paper fibres and semi-flexible polymers such as the muscle protein actin. However, most theoretical studies assume that fibres are either rigid or completely flexible. In this project we are studying how fibres with a finite bending modulus deform in a shear flow.

The behaviour of a semi-flexible fibre in shear flow is modelled as a chain of shorter rods linked together. A bending torque is included at the joints between the rods to account for the flexibility. The simulation reproduces the C and S turns observed in experiments on semi-flexible fibres. The results for finite aspect ratio fibres predict changes to the period of rotation and drift between Jeffery orbits. The direction of drift for a flexible fibre depends on both the initial orientation and the fibre's flexibility.

We also present a linear analysis of how small distortions to a straight semi-flexible fibre grow when the flow places the fibre under compression. These results in agreement with our full simulations and the growth rates of the distortions to a straight allowing us to predict the most unstable mode at a particular flow rate.

# Competing Bubbles Growing in a Polymeric Foam

*Sally Everitt, Helen Wilson, Oliver Harlen  
School of Maths, University of Leeds*

## A B S T R A C T

Polymeric foams are foams consisting of either gas bubbles embedded in a polymeric solid, or a bi-continuous structure of air and solid polymer like a sponge. They are used in a vast range of applications from car steering wheels and shoe soles to furniture upholstery and cavity wall insulation.

In injection moulding, a polymeric liquid containing a foaming agent is injected at high pressure into a mould. As the pressure is reduced, bubbles nucleate and expand forming a foam. The properties of the final product are highly dependent on the size, distribution, and density of the bubbles.

We have investigated the late stages of this foam development, when bubbles have extended to the extent that they affect one another's growth. We first illustrate how a simple model, in which the gas diffuses instantly into the bubbles and the bubbles only interact through competition for the available gas, predicts the changes in the size distribution of bubbles over time.

Finally we demonstrate the direct influence polydisperse bubbles can have over one another by simulating the expansion of a two-dimensional hexagonal array of bubbles of two different sizes.

If the bubbles are well separated and only influence each other through competition for gas, the viscoelastic nature of the polymeric fluid widens the distribution of bubble sizes compared with a similar expansion in a purely Newtonian fluid. With closer bubbles, our hexagonal array is only a first study of the true effects and our choice of geometry is key. There are two bubble sizes with one occurring twice as often as the other. If the more common bubble is smaller than the other then the distribution is widened by viscoelasticity; otherwise the effect of the polymers is to narrow the bubble size distribution. The mechanism is the large polymer stresses which build up in the windows between bubbles: depending on the geometry these restrict the growth of one size of bubbles.

## New Polymers for Smart Delivery

Steve Rimmer,  
Department of Chemistry, University of Sheffield

Tel. 0114 2222 5965  
FAX 01977 618498  
S.Rimmer@sheffield.ac.uk

The poster will cover our recent work on the synthesis of stimuli responsive polymers, work that is directed in the long term in producing new materials for the delivery of therapeutics and other compounds with biological activity. Several systems will be described but the common themes will be that the stimuli responsive elements are based on repeat units of either poly(methyl vinyl ether), PMVE, or poly(N-isopropyl acrylamide), PNIPAM.

The first of these systems involves the use of our *ab initio* cationic polymerization techniques to produce oligomers of MVE with ester end groups. These end groups can then be used to prepare PMVE-*block*-polyester materials in which the polyester segment can be used to encapsulate a drug (5-FU in our current studies). These have been used either as micellar particles for delivery by thermally triggered flocculation; they are colloidally stable and mobile at room temperature but the particles flocculate as the temperature is raised to the physiological regime, which is above the LCST of PMVE. On the other hand we have films of these polymers that act as thermally responsive brushes. In this system we envisage that degradation and release will only occur once the PMVE is solvated; below the LCST. Another PMVE based material uses the *ab initio* technique to graft PMVE to polystyrene beads. The poster will also present briefly results from similar PNIPAM hydrogel brushes in which the arms are PNIPAM and the sublayer is a cross-linked hydrogel. These latter materials have been used as substrates for cell culture. Several other PNIPAM architectures are being studied including block and graft (brushes) copolymers. Recently we have used the RAFT technique to produce highly branched PNIPAM with imidazole end groups. These materials have been used to bind and extract a recombinant protein from the cell lysate from which it was prepared. In some cases this binding event triggers the transition through the LCST and we believe that this is one of the first instances of a biologically stimulated polymer system.

In conclusion we describe a large number of systems that are attracting interest from most areas of science and several commercial sectors, which will have many and wide ranging applications; including but not exclusively delivery. We always are open to new suggestions of collaborations in any area where these materials are of interest.

# High Throughput DTA Components for Cell Trays for Materials Science

*J.Patrick A. Fairclough, G. Royston. University of Sheffield, Sheffield, UK*

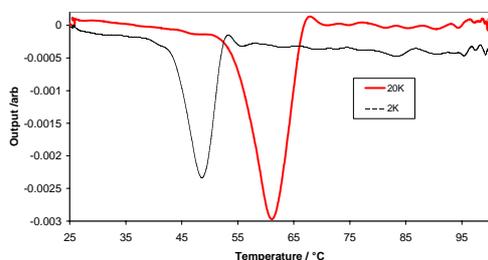
High Throughput Screening (HTS) is the process whereby a limited number of data parameters (often a simple yes/no) are determined for a large number of similar systems. Thus for instance it could be the gelation temperature for a series of different molecular weight and volume fraction surfactants. From this data general trends are identified, usually computationally using informatics. High Throughput Characterisation (HTC) extends this by determining a range of parameters via a suite of techniques over a range of variables.

HTC is in some ways a departure from traditional academic research methodologies. Traditionally a researcher would determine a wide range of parameters for a limited number of systems. From this thorough and often exhaustive characterisation, predictions are made for similar systems and thus the theory is tested. Industrial research has often followed a HTC approach where a number of options are tested, or screened, for a particular effect. This empirical approach has served industry well over the years. This proposal seeks to use the strengths of both systems.

High throughput materials science has developed in the wake of high throughput drug discovery. In drug discovery two factors have facilitated the process, the first is that most drugs are derivatives and as such HTS and in particular Cheminformatics can be used to great effect. The second important factor is that the testing medium, the cell tray, allow rapid parallel testing of the efficacy of a particular drug. This is not to say that drug discovery is in any way easy, it's just that the tools are available for early stage testing. In materials science the derivative approach has resulted in a number of promising materials for example in the fields of light emitting polymers. The second factor, the cell tray, is lacking in materials science.

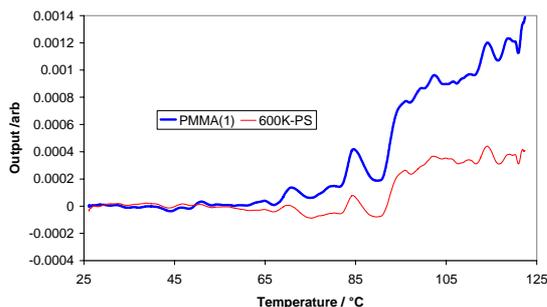
## Thermal Characterisation.

The simplest test required would be the determination of the glass transition temperature (T<sub>g</sub>) and melting point (T<sub>m</sub>). Conventionally this is performed by DSC or DTA (differential scanning calorimeter, differential thermal analysers). The DTA compares two thermocouple readings and as such is relatively simple to scale up to multiple samples. We have already achieved this for eight samples and have plans for the scale-up. In this case the sensing element is a thin film of aluminium that acts as a resistive temperature sensor.



**Figure 1** DTA traces for poly(oxyethylene) of two different molecular weights.

The resistive output from these elements, after suitable conditioning and interfacing electronics, is read into a PC and displayed as a function of temperature. As the sample and reference are heated relatively slowly (10C/min) they will maintain similar temperatures. As the sample undergoes a thermal transition, either T<sub>g</sub> or T<sub>m</sub>, the output will change. In the case of T<sub>g</sub> a characteristic “S” shaped curve, for T<sub>m</sub> a trough. Thus the transition temperature can be measured.



**Figure 2** DTA curves for polystyrene and polymethylmethacrylate.

The next step is to develop this into large arrays of devices and incorporate a heating mechanism so that we can produce a truly parallel DSC.

The ultimate goal is to produce an integrated disposable low cost device to provide materials science with the first cell tray. We are currently concentrating on the polymeric materials, mainly due to historical reasons, and with sufficient funding intend to roll this technology out over as many fields as possible.

Results will be presented for a range of test materials to show the efficacy of this method and its applicability to a wide range of materials.

# **DYNAMIC NANO-INDENTATION AS A TOOL FOR CHARACTERISING POLYMERIC MATERIALS AND THIN FILMS**

*A. A. Goruppa, S. A. Hayes and F. R. Jones  
Dept. Engineering Materials, Sheffield University, UK.*

## **A B S T R A C T**

Nano-indentation has opened up the possibility of investigating the mechanical properties of thin film materials. It is particularly suited to determination of the mechanical properties of ceramic, metallic and glassy coatings. However, the analysis of polymeric materials is generally more difficult, because of their viscoelastic behaviour. Dynamic nano-indentation offers the possibility of examining these properties in thin coatings. The technique is, however, unproven and validation by conventional thermal analysis techniques, such as dynamic mechanical and thermal analysis (DMTA) and differential scanning calorimetry (DSC) is required. This paper presents preliminary results from such a comparison.

The dynamic response of polymers depends on the loading frequency and the test temperature. Time-temperature superposition is a well-known technique for describing these properties. Therefore, precise control of the test temperature as well as the frequency is necessary. To achieve this, the authors collaborated with Hysitron to produce a thermal stage capable of cooling the sample to  $-15^{\circ}\text{C}$  and heating it to  $+125^{\circ}\text{C}$ . This stage was fitted in place of the standard sample stage on a DI Dimension 3100 AFM. The capabilities of the dynamic testing mode of the Hysitron system allow a wide range of testing temperatures at frequencies from 0.1 to 300 Hz. From these measurements, a mastercurve of property against reduced frequency (frequency adjusted to a single reference temperature) can be constructed, allowing the determination of the polymer properties under a wide variety of conditions. Such data has been used to provide a comparison with data obtained using conventional thermal analysis techniques. Examples will be given which show a favourable comparison, demonstrating that dynamic nano-indentation is a practical tool for the characterisation of thin polymeric films and coatings.

# Micro-scale Polymer Processing: using scattering techniques to investigate polymer processing.

E.L. Heeley<sup>a</sup>, C.M. Fernyhough<sup>a</sup>, T. Gough<sup>b</sup>, W. Bras<sup>c</sup>, A. J. Gleeson<sup>d</sup> & A. J. Ryan<sup>a</sup>.

<sup>a</sup>Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

<sup>b</sup>IRC in Polymer Science and Technology, School of Engineering, Design and Technology, University of Bradford, Bradford BD7 1DP, UK

<sup>c</sup>Dubble CRG, ESRF, B.P. 220, F-38043 Grenoble Cedex, France

<sup>d</sup>Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, UK

## A B S T R A C T

Following crystallization in semi-crystalline polymers such as polyethylene and polypropylene, can be achieved by using simultaneous Small- and Wide- Angle X-ray scattering (SAXS/WAXS) techniques. Here, SAXS probes the long-range order or macrostructure providing details of the lamellar spacing and WAXS gives information concerning the atomic ordering or microstructure of the system. Following the structure development (crystallization) in polymers is particularly important as this process leads to the stabilisation of the final product, influencing the aesthetic and mechanical properties of the material. Thus, to produce useful materials it is essential to understand and predict the crystallization process, which can be explored with a variety of scattering experiments. Several experiments, which allow us to follow the crystallization in polymers, have been performed using synchrotron radiation sources. Quiescent and shear-induced crystallization of samples have been studied using time resolved SAXS/WAXS on various beamlines at the Daresbury SRS and the ESRF. Here, we show how recent beamline developments with improved experimental techniques, can give an insight into mechanisms of early crystallization kinetics as well as the final crystalline morphology. For example, quiescent crystallization experiments have been performed using an *in-situ* DSC instrument on the Dubble-CRG station at the ESRF and 8.2 plus the new MPW station 6.2 at Daresbury SRS. This has allowed comparisons of SAXS/WAXS data to be made specifically, concerning new improvements made in detector technology, which have revealed information on the very early crystallization process. Shear-induced crystallization has also been investigated using SAXS/WAXS again on Dubble and station 16.1 at the Daresbury laboratory. An *in-situ* shearing device and an online extruder, has provided an insight into crystallization under the influence of flow. Finally, experiments involving simultaneous SAXS/WAXS and rheology have been performed on station ID2 at the ESRF. This unique set-up allows time resolved SAXS/WAXS data along with the rheological responses of the polymer to be obtained throughout the crystallization process.

All these techniques are currently being used to investigate the crystallization of commercial and novel polymer systems. The use of time resolved synchrotron radiation is an invaluable technique in probing such processes and this will enable us to expand our understanding of crystallization kinetics with relevance to industrial processing procedures. This is envisaged to give a better understanding of polymer processing towards improved materials for the future.

# Low-dimensional, solvent-free polymer electrolytes with high ambient lithium conductivity

J. Liu, Y Zheng, Y-P. Liao, G. Ungar and P. V. Wright

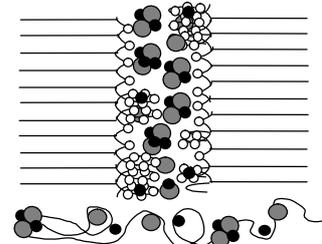
Dept. of Engineering Materials, University of Sheffield, Mappin St., Sheffield, S1 3JD UK

## Introduction

Recent work [1-3] has shown that mixtures of lithium salts in self-organised lamellae of amphiphilic polymers **I** (CmOn) with interphases of block copolymer **II** - $\{-(\text{CH}_2)_4\text{-O}\}_{-23}\text{-}(\text{CH}_2)_{12}\text{-O-}$ - give films having ambient conductivities  $\sigma \sim 10^{-3} \text{ S cm}^{-1}$  in impedance and extended DC polarisations between Li electrodes.

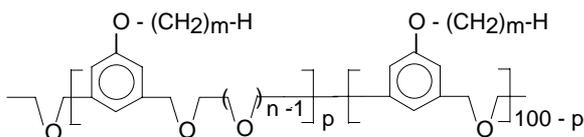
## Experimental

Two synthetic 'Williamson' procedures for **I** in which the halogen functions were *either* borne by the tetraethoxy monomer (Method X) *or* by the sidechain-bearing monomer (Method Y) have been compared.  $^1\text{H}$  NMR was performed using a Bruker AC250. GPC was carried out using a Hewlett-Packard 1090. DCS was performed on a Du Pont 910. FTIR was carried out using a Perkin-Elmer spectrum 2000. Simultaneous SAXS and WAXS measurements over ambient to 50°C were carried out using a MAR Research Image plate with 5 or 10 minute exposure times. Impedance measurements over the range 1-1MHz with an amplitude of 0.1V were carried out with Solartron 1287A ECI / 1250 FRA using ITO coated glass electrodes with a cellulose acetate or polyethylene spacer. Molecular dynamics modelling was performed with Cerius<sup>2</sup> molecular dynamics software.

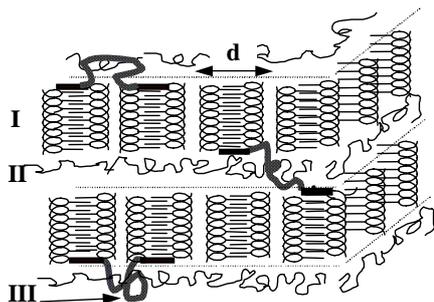


## Results and discussion

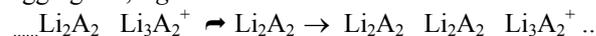
Extensive  $^1\text{H}$  NMR studies have shown that optimum conductivities are obtained when **I** is a copolymer of CmO5-CmO1 where p, the mol% of C16O5 units may be as low as 20%. The side groups lengths, m, are typically 16 or 18 but optimum sub-ambient conductivities have been observed with mixed side chain copolymers,  $m = 12 / 18(50\%/50\%)$



The amphiphilic monomers and product promote self-condensation of sidechain-bearing monomers in a heterogeneous reaction forming CmO1 units. However, Method X gave polyether and ester links whereas Method Y gave pure polyether as shown.



The stabilisation of the **I** / **II** interface ('wetting') is essential for ion transfer. Excellent reproducibility of conductivities have been obtained by incorporation of ABA block copolymer **III**  $\text{H}(\text{CH}_2)_{18} [(\text{CH}_2)_4\text{-O}]_{-50}\text{-}(\text{CH}_2)_{18}\text{H}$  in small proportion (~20% of **II**). SAXS and molecular dynamics modelling suggest that, in ionophobic CmO1 segments, salt exists mainly as quadrupoles, essentially *decoupled* from the polyether and in the copolymer separated ions occur in the (minor proportion) of helical CmO5 segments. We propose low activation energy conduction in an applied field could proceed by a  $\text{Li}^+$  hopping process between uncoupled aggregates, e.g.

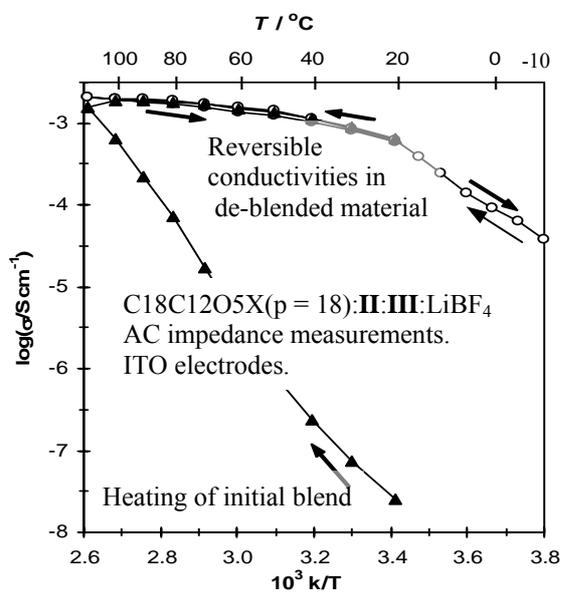


Similar conductivity plots are observed from either Method X or Method Y mixtures.

**Acknowledgments** We are grateful to EPSRC and the European Space Agency for supporting this work.

## References

- [1] F.Chia, Y.Zheng, J.Liu, N.Reeves, G.Ungar, P.V.Wright, *Electrochim. Acta*, 2003, **48**, 1939-1951.
- [2] Y. Zheng, J.Liu, Y-P. Liao, G.Ungar, P.V. Wright, *J. Chem. Soc. Dalton Trans.*, in press.
- [3] J.Liu, Y.Zheng, Y-P.Liao, G.Ungar, P.V.Wright, *J. Chem. Soc. Faraday Trans.*, in press.



# Electrospinning for Tissue Engineering

D. Norton<sup>1</sup>, A. Abbott<sup>1</sup>, T. Sun<sup>2</sup>, S. Mai<sup>1</sup>, J.W. Haycock<sup>2</sup>, S. MacNeil<sup>2,3</sup>, A.J. Ryan<sup>1</sup>

<sup>1</sup> *Department of Chemistry, University of Sheffield, SHEFFIELD, U.K*

<sup>2</sup> *Department of Engineering Materials, Sheffield University, Sir Robert Hadfield Building, Mappin Street, SHEFFIELD, U.K.*

<sup>3</sup> *Division of Clinical Sciences, Sheffield University, Northern General Hospital, SHEFFIELD, UK.*

## A B S T R A C T

Much research in tissue engineering focuses on synthesis of complex 3D polymer scaffolds containing functional biomolecules to which cells are introduced.

Minimal scaffolds without cell signalling or spatial information have been constructed by electrospinning. The electrospinning process parameters were varied to give a non-woven matrix with fibres of approximately 10  $\mu\text{m}$  diameter and interfibre spaces of 50-150  $\mu\text{m}$ , known to permit cellular entry.

It proved possible to produce a matrix of polystyrene (PS) fibres in which skin cells would proliferate. Furthermore, cells displayed native spatial 3D organisation when cultured at an air-liquid interface, even when all three cell types (fibroblasts, keratinocytes and endothelial cells) were introduced at random to the scaffold.

Initial studies used polystyrene (PS) as the matrix material whereas current efforts are concentrated upon poly(L-lactide) (PLLA) a biodegradable polymer which is a commonly used substrate for tissue engineering. Non-woven mats of PLLA have been produced with pore sizes and fibre diameters comparable to PS and their cell-culture and degradation will be reported.

# Untangling the Mysteries of Comb Polymer Behaviour

*C. M. Fernyhough and R.N. Young*  
*Department of Chemistry, University of Sheffield*

## A B S T R A C T

Industrially, the benefits of long-chain branching in polymer processing are well known. For example, low density polyethylene exhibits desirable properties such as strain hardening in extension and also shear-thinning. However, the effects due to molecular parameters such as branching density and the length of branches cannot be readily elucidated from examining industrial materials. Therefore, a systematic investigation has been conducted into the role of long-chain branching through the use of polymers produced using anionic polymerisation techniques. Using these techniques it is possible to produce near-monodisperse materials of a pre-determined molecular mass, and having the desired architecture. Initially, a series of model “comb” polyethylenes was synthesised via the hydrogenation of branched polybutadiene<sup>1,2</sup>. Two parameters were kept constant throughout the series: the backbone molecular mass and the average number of branches, the major variable being the mass of the branches. In addition, a series of polystyrene combs has been produced, the branch and backbone molecular mass remaining constant, with the average number of branches the major variable. The combs were examined using viscometry and light scattering and it was found that it was possible to relate the intrinsic viscosity and mean square average radius of gyration of the molecules to their overall structure by comparison with the analogous linear materials.

1. Fernyhough, C. M.; Young, R. N.; Poche, D.; Degroot, A. W.; Bosscher, F. *Macromolecules* **2001**, *34*, 7034-7041.
2. Daniels, D. R.; McLeish, T. C. B.; Crosby, B. J.; Young, R. N.; Fernyhough, C. M. *Macromolecules* **2001**, *34*, 7025-7033.

# The Synthetic Muscle

*Paul Topham<sup>1</sup>, Tony Ryan<sup>1</sup>, Jonathan Howse<sup>1</sup>, Colin Crook<sup>1</sup>, Richard A.L. Jones<sup>2</sup>  
Anthony Gleeson<sup>2</sup>, Wim Bras<sup>3</sup>*

1. Department of Chemistry, Sheffield University, Sheffield. S3 7HF
2. Department of Physics and Astronomy, Sheffield University, Sheffield. S3 7RH
3. SRS, Daresbury Laboratories, Daresbury

The phenomenology of shape-change polymer gels and brushes has been extensively studied theoretically and experimentally. Recently these stimuli responsive polymer gels have become of international interest as novel intelligent materials with sensor, processor and actuator functions. In these materials the swelling-deswelling behaviour is a change toward a stable equilibrium state following an external stimulus, an on-off oscillating state can be induced by oscillating the external conditions. Microscopic devices have been built and pH sensitive gels have been used to build “flow-sorter” valves for fluidic systems where the expansion and contraction of gels opened and closed 200  $\mu\text{m}$  channels.<sup>i</sup> We have prepared responsive gels based on polyelectrolytes (polymethacrylic acid) and a Landolt reaction that oscillates pH.<sup>ii</sup> A weak polyacid will, at low pH, be essentially charge-neutral, because the degree of dissociation of the carboxylic acid groups is relatively weak. In these circumstances water is a poor solvent for the polyacid and the gel collapses. However, as the pH is increased the acid groups dissociate and the polymer acquires a net charge; mutual repulsion between the charged chains causes them to stretch away from each other. Thus by oscillating the pH one can induce a macroscopic oscillation in the dimensions of a gel of a factor of 10 or more. Using triblock copolymers with hydrophobic end-blocks and polyelectrolyte mid-blocks we can make actuator systems that operate in one, two or three dimensions by use of lamellar, cylindrical and spherical gels, respectively.

In this particular experiment we have studied the volume change associated with a micro-phase separated gel of polymethylmethacrylate-block-polymethacrylic acid-block-polymethylmethacrylate situated in a pH oscillating chemical reaction. The volume fraction of the middle polyacid section will be such that the polymethylmethacrylate domains will exist as spheres in a cubic arrangement surrounded by a matrix of the polyacid. Changes in the pH cause the surrounding matrix to expand (base) and collapse (acid) thus altering the unit cell dimensions associated with the polymer domains. These oscillations have been monitored by SAXS to probe the molecular origin of the shape change. If the technology is to be scalable then the shape change should be affine, that is the macroscopic shape change should follow the separation of the nano-domains.

We present here data revealing the reversible change in unit cell dimensions of the microphase separated triblock polymer, as measured by SAXS, together with microscope images of the gel expanding and collapsing collected at the same time.

<sup>i</sup> Functional hydrogel structure for autonomous flow control inside microfluidic channels, Beebw DJ, Moore JS, Bauer JM, Yu Q, Liu RH, Devadoss C, Jo BH, Nature, **404**, (6778), 588, 2000.

<sup>ii</sup> Chemically induced oscillations in a pH-responsive hydrogel, Crook CJ, Smith A, Jones RAL, Ryan AJ, PHYSICAL CHEMISTRY CHEMICAL PHYSICS 4 (8): 1367-1369 2002

# PEO-PBO diblock copolymers interdigitated membrane micro and nano vesicles

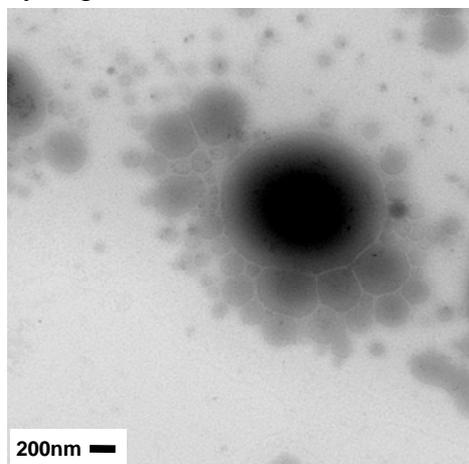
*Giuseppe Battaglia<sup>a</sup>, Raymond Olivier<sup>b</sup> and Anthony J. Ryan<sup>a</sup>*

<sup>a</sup>Department of Chemistry  
University of Sheffield, Dainton Building, Brook Hill,  
Sheffield, S3 7HF – United Kingdom

<sup>b</sup>ICI Strategic Technology Group,  
Wilton Center, Redcar TS10 4RF- United Kingdom  
g.battaglia@sheffield.ac.uk

## ABSTRACT

Phospholipids represent one of the primary components of nature; they are the building blocks of the cell membrane, organelles and vesicles. The latter are hollow spheres used as delivery system both inside and outside the cells. The amphiphilic ability of natural phospholipids to assemble into vesicles has recently been mimicked by wholly synthetic amphiphilic block copolymers. The synthetic nature of these copolymeric vesicles, named as Polymersomes [1,2], allow the application of a wide range of chemistry in order to design more stable and resistant vesicles with a flexible range of diameters and membrane thicknesses. In the present work, Polyethylene oxide-co-Polybutylene oxide (PEO-PBO) diblock copolymers, previously characterised in water and in bulk [3-6], have been selected in order to investigate their ability to self-assemble into polymeric vesicles. PEO-PBO vesicles have presented interdigitated membrane where thickness increases as the hydrophobic unit number increases, according to the segregation theory. Same behaviour was



observed in bulk state studies on PEO-PBO lamellar structures. This indicates that the hydrophobic membrane keeps the same morphology going from solid lamellar structures to vesicular aggregates. This geometry gives, moreover, the flexibility to design vesicles that have membrane thickness smaller than the same molecular weight phospholipid vesicles. Periodic analyses have also demonstrated that PEO-PBO vesicles are very stable over time. Thermal analysis has shown vesicle stability up to 70°C. PEO-PBO vesicles can therefore be a valid alternative to phospholipid vesicle technology.

# **FaraPack Polymers Ltd: Bespoke Short-term Polymer Synthesis, Feasibility and Testing Services.**

*Andy Pryke*  
*FaraPack Polymers Ltd.*

## **A B S T R A C T**

FaraPack Polymers Ltd. has been launched as a spin off from the polymer centre at the University of Sheffield, partly funded by Faraday Packaging, to fill the contract research and development gap between consultancy and postdoctoral/postgraduate projects. The projects we envisage being engaged in would typically be research feasibility studies perhaps ranging from a matter of days to a few months, where results obtained would either solve an in-house problem or prove the worth of funding a longer term more expensive research commitment again in-house or in an academic facility in the form of a postdoctoral fellow or a PhD student. Also we plan to offer a wide range of chemical and mechanical testing services tailored particularly to the polymer/packaging industry. These would mainly, we suspect, be supplemental to those techniques companies may already employ and be of use when additional or extraordinary information is required on a particular product.

In the six months or so the company has been in existence research has been carried out into high molecular weight well-defined diblock copolymers for use in printing, separation of granulated solid polymer blends by density, for recycling and polyacid-polymethacrylate diblocks for particle size research.

In the analysis and testing field, we have access within the chemistry department to rheology, elipsometry, X-ray scattering, chromatographic (HPLC GC GPC etc.), spectroscopic and elemental analysis techniques. Also in the university as a whole many more mechanical testing techniques are available including thermal analysis and microscopy.

# Transesterification of Poly(Ethylene Terephthalate) and Bisphenol-A-Polycarbonate.

Neil Cameron, Michael Cannon

[m.j.cannon@durham.ac.uk](mailto:m.j.cannon@durham.ac.uk)

*IRC in Polymer Science and Technology,  
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE*

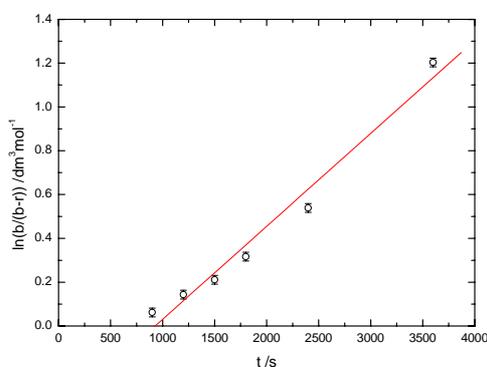
## Introduction

It has long been known that polyesters form random copolymers when heated with other polyesters or polycarbonates above their melting point.<sup>1-7</sup> Recent studies have obtained kinetic data on the rate of reaction of some of these mixtures. Work carried out on the mixture of poly(ethylene terephthalate) (PET) and bisphenol-A-polycarbonate (BPA) has produced conflicting results, with some studies concluding that it is a second order reversible process and others finding it to be more complicated and that there are unwanted side reactions.<sup>8,9</sup> This study seeks to address these discrepancies, obtaining kinetic data from <sup>1</sup>H and <sup>13</sup>C NMR, optical microscopy (OM), DSC and Thermal-Gravimetric Analysis (TGA) as well as Small Angle Neutron Scattering. It is found that the immiscibility of PET and BPA results in an induction time for reaction to occur but that after this time the reaction proceeds as a second order reversible process. Side reactions are evident from the production of gases and discoloration during heating. The reasons for these are not yet clear nor are the exact nature of the by-products but the latter are expected to include cyclic poly(ethylene glycol) and CO<sub>2</sub>.

## Kinetic Data

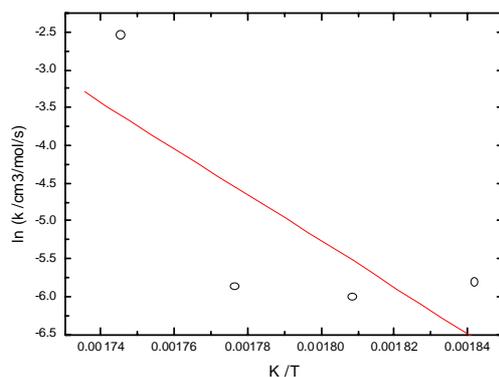
A 50/50 blend of BPA and PET was prepared by solution blending. Samples of this were heated under N<sub>2</sub> at 543, 553, 563 and 573K for times up to 1 hour. These samples were then dissolved in a mixture of deuterated dichloromethane (dDCM) and deuterated trifluoroacetic acid (dTFA) (4:1) and this was submitted for <sup>1</sup>H NMR analysis. Typically samples were of the order of 8mg and they were dissolved in 0.8ml of solvent. The spectra were analysed by integration of the peaks associated with the unreacted ethylene glycol (EG) and the unsymmetrical EG produced from the transesterification reaction. One peak has been attributed to the existence of EG between two BPA monomer units but this is very small in comparison to the other two and for the purposes of the kinetic calculation is ignored.

From the <sup>1</sup>H spectra it is possible to build up a kinetic model of how the reaction proceeds.



**Figure 1 Second order plot of <sup>1</sup>H data from PET/BPA samples reacted at 573K for times up to one hour with trendline of straight section.**

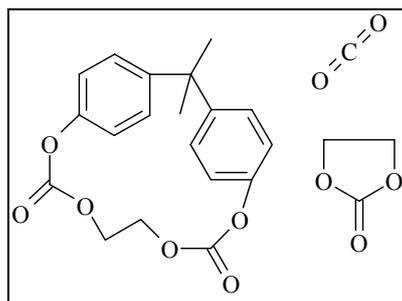
The reaction at all temperatures shows an induction time of some 15 minutes. After this time the reaction could be suggested to proceed in a linear fashion. The gradients are then taken and used in an Arrhenius plot. Using this, a value of 254kJ/mol is obtained for the activation energy (see figure 2). This is in agreement with some studies on poly(butyl terephthalate) with BPA but the majority of transesterification reactions have been found to have activation energies in the 130-50kJ/mol range. Further work to identify why there is an induction time is to be carried out starting with an analysis of end groups so that the reactants can be end-capped before reaction. This would reveal whether chain degradation is responsible for a rise in end groups leading to a greater rate of reaction or whether this is simply a diffusion limited process during the early stages.



**Figure 2 Arrhenius plot of data obtained from  $^1\text{H}$  NMR analysis of the reaction between PET/BPA between 543 and 573K.**

There are some problems with the  $^1\text{H}$  data from reactions at 543K, these data seem to give an anomalously large extent of reaction, possibly due to a combination of factors relating to the way in which the peaks in the NMR spectra overlap. It is hoped that further work by small angle neutron scattering (SANS) and  $^{13}\text{C}$  NMR will clarify this.

In the transesterification reactions reported in the literature of blends other than PET/BPA there are no side products such as the evolution of gas or yellowing reported. Such phenomena are observed for the reaction between PET and BPA and are ascribed to the evolution of  $\text{CO}_2$ , cyclic ethylene carbonate and other cyclic products containing repeat units.<sup>9</sup>



**Figure 3 Products found to evolve from PET/BPA at temperatures below 573K under  $\text{N}_2$ .**<sup>9</sup>

The logical conclusion is therefore that these products are released because the copolymer formed is less thermally stable than the two original polymers since these are not observed to be released to such a large extent at such low temperatures for the homopolymers. It is hoped that TG-MS work conducted soon will bear out these findings.

#### Conclusion

The reaction between PET and BPA is more complicated than a simple second order transesterification. Side reactions produce by-products and there is an induction period of some 15 minutes in the region studied during which the two immiscible polymers are made compatible with one another.

#### Acknowledgments

We should like to thank the EPSRC and Invista for financial support and practical assistance.



## References

- <sup>1</sup> Pilati F., Marianucci E., and Berti C., *J. Appl. Polym. Sci.*, 1985, 30.
- <sup>2</sup> Cruz C.A., Barlow J.W., and Paul D.R., *J. Appl. Polym. Sci.*, 1980, 25, 1549.
- <sup>3</sup> Nasser T.R., Paul D.R., and Barlow J.W., *J. Appl. Polym. Sci.*, 1979, 23, 85.
- <sup>4</sup> Murff S.R., Barlow J.W., and Paul D.R., *J. Appl. Polym. Sci.*, 1984, 29, 3288.
- <sup>5</sup> Linder H., Henrichs P.M., Hewitt J.M., and Massa D.J., *J. Chem. Phys.*, 1985, 82, 1585.
- <sup>6</sup> Chen X.Y. and Birley A.W., *Br. Polym. J.*, 1985, 17, 347.
- <sup>7</sup> Hanrahan B.D., Angeli S.R., and Runt J., *Polym. Bull.*, 1986, 15, 455.
- <sup>8</sup> Godard P., Dekoninck J.M., Devlesaver V., and Devaux J., *J. Polym. Sci.: Part A: Polym. Chem.*, 1986, 24, 3315.
- <sup>9</sup> G. Montaudo, C. Puglisi, and F. Samperi, *Polym. Degrad. Stabil.*, 1991, 31, 291.

# INVESTIGATION OF THE STRUCTURE AND COMPOSITION OF A GLASS FIBRE SIZE.

*Michael McGravey<sup>1</sup>, Neil Cameron<sup>1\*</sup>, Shayel Ahmed<sup>2\*</sup>*

<sup>1</sup>IRC in Polymer Science & Technology

Department of Chemistry

University of Durham, U.K.

DH1 3LE

[m.p.mcgravey@durham.ac.uk](mailto:m.p.mcgravey@durham.ac.uk)

<sup>2</sup>Vinamul Polymers

De Asslen Kuil 20, NL 6161 RD Geleen

The Netherlands

\*To whom correspondence should be addressed

## Abstract

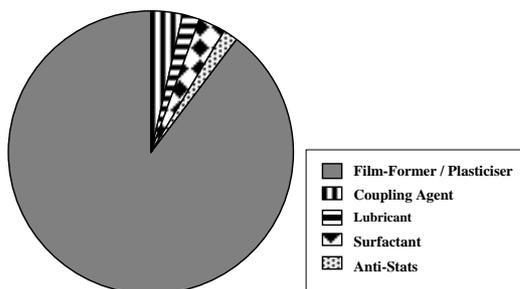
It has been highlighted that the nature of surface interactions between glass fibres, the film-former and other additives in the sizing formulation are key parameters in determining the fundamental properties of the final glass fibre product. The purpose of this work is to establish experimental techniques to investigate in detail the nature of these interactions and relate the roles of different components of the sizing formulation to final glass fibre properties. This research will hopefully lead to size formulations with increasingly more effective physical properties for use in the glass fibre industry.

## Introduction

Bare glass fibres do not stay bare for longer than a microsecond when exposed to the atmosphere. Water is absorbed into the glass, which causes the strength of the glass fibre to reduce by a factor of five and the drop in strength will continue if further exposed. To prevent this loss of strength, the glass fibres are coated with a protective layer commonly known as size. This is generally organic- or aqueous-based, preventing any atmospheric water from absorbing into the glass. As well as protecting the surface of the glass, the size also aids the handling of the product. For a size to be successful it must be able to undertake all of these tasks: [1]

- Convert a bundle of filaments into a strand.
- Allow this strand to be chopped cleanly.
- Give strand resistance to abrasion.
- Allow the strand to remain intact throughout all stages of the fibrising process.
- Keep the strand free from static electricity
- Allow the strands to fit together compactly but not permanently (taped).
- Allow the strand to be impregnated easily into another resin.
- Give the size a fast wet-out rate when no longer required.

To meet these requirements, a size, which consists of different components all combining to create a product with excellent and well suited application properties, is applied to the glass fibre.



**Figure 1.** Typical size formulation

This investigation aims to understand the chemistry occurring within the size, in particularly the effect of the migration of different species on the final physical properties of the glass fibre. Investigations into these species have been previously reported for different glass fibre sizes [2,3], however nothing specific to the present system has been studied.

In this research, a size with a film-former based on polyvinyl acetate (PVAc) is utilized. The PVAc emulsion is the predominant species in size formulations, however small amounts of other species (silicon-based coupling agents, lubricants and surfactants) are also present.

The results obtained using various methods of microscopy and different scattering techniques to probe the glass surface interactions are detailed below.

## Experimental

**Materials.** A size formulation based on a PVAc film-former was applied to a glass microscope slide. This was then allowed to dry under atmospheric conditions overnight.

**Analytical techniques.** *Environmental Scanning Electron Microscope (ESEM):* The ESEM images were produced using an FEI/Philips XL30 ESEM in low vacuum mode using a back-scattered electron (BSE) detector. This instrument provides clear images at a magnification of 12000x. The samples were mounted horizontally and vertically on the sample holder. The surface of the sample was investigated using the horizontal sample and the glass-size interface of the sample was investigated using the vertically mounted sample.

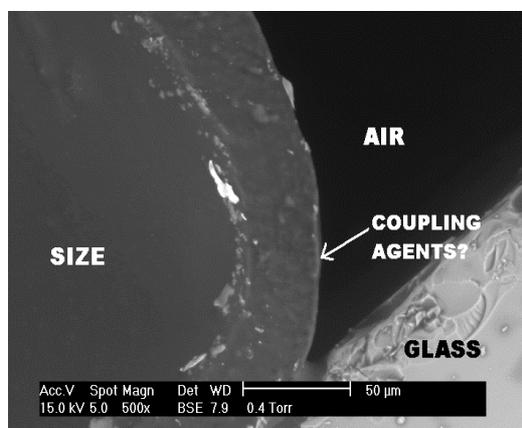
*Atomic Force Microscope (AFM):* AFM images were obtained using a Digital Instruments/Veeco Nanoscope IV multimode instrument. This technique also used a vertically mounted sample to investigate the interfacial region.

*Ion Beam Analysis (IBA):* IBA data was obtained using a NEC 5SDH Pelletron instrument and data manipulation was carried out using the Datafurnace software package. The sample was applied to a piece of silicon wafer (a thin glass slide) for this technique and a beam of  $^4\text{He}^+$  ions were used to obtain Rutherford Backscattering (RBS) data.

*ESEM Energy-Dispersive X-Ray Analysis (EDX):* EDX images and data were obtained using a FEI/Philips XL30 instrument with a Roentec Quantax EDX attachment. Sample preparation was similarly undertaken on a vertically-mounted sample plate to determine an elemental depth profile.

## Results and Discussion

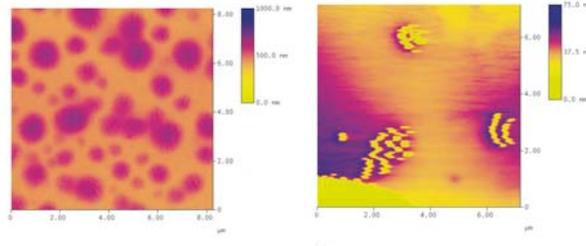
**ESEM.** Figure 2 shows an image of the glass-size interface. It is observed that a lighter distinct band is present, as well as the bulk of the PVAc film. The width of the light band is quite narrow (approximately 2.8  $\mu\text{m}$ ) when compared to the bulk film and the most likely explanation for its presence is the migration of coupling agents to the glass-size interface.



**Figure 2.** ESEM image of the peeled size on the glass

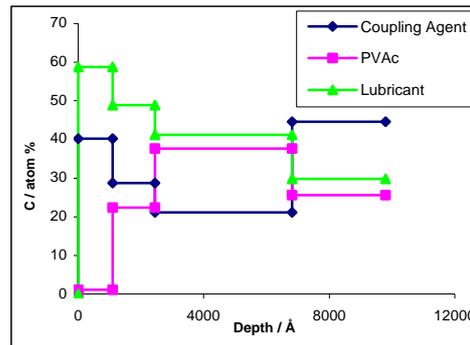
Coupling agents are added to improve the binding between the bulk film-former present in the size and the surface of the glass microscope slide [1]. Further investigation of this band is required to understand the specific nature of the migration of the coupling agents.

**AFM.** This technique was used to determine the surface topology of the size. Figure 3 shows an image of a sample of the film-former alone (left) compared to an image of the surface of the complete size (right). We can see that the film-formers surface has an uneven surface which arises from the PVAc particles whereas the size's surface is much smoother and the PVAc particles can no longer be distinguished. This probably arises due to the presence of lubricants at the top of the size creating another very thin band on top of the bulk PVAc film.



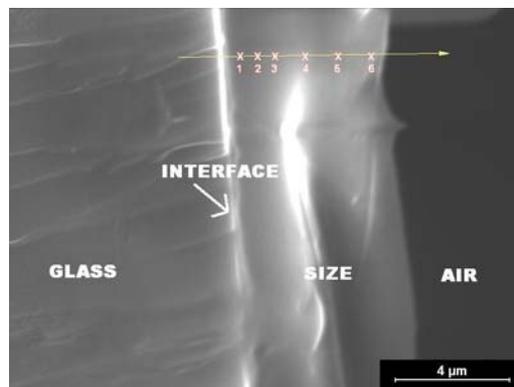
**Figure 3.** AFM image of the glass-size interface

**IBA.** This technique was used to determine a depth profile of the species present in the size.  $^4\text{He}^+$  ions are fired at the sample and collide with nuclei present in the size causing the ions to be scattered. The momentum of the scattered ions allows the structure of the sample to be determined. By changing the incidence angle of the ion beam a depth profile of the sample can be deduced. It was concluded from the data that the lubricant was mostly present at the surface of the size and the concentration of this decreases with distance into the sample. It was also found that the coupling agent is present throughout the size but its concentration increases nearer the silicon wafer interface, see figure 4.



**Figure 4.** Computer simulated depth profile of the size by IBA.

**EDX.** This technique was used to identify whether silicon-containing species were migrating to the glass-size interface. Figure 5 and Table 1 show that this is occurring because the majority of the silicon is found near the glass-size interface. This informs us that the coupling agents (as these are the only species containing silicon) are congregating here to facilitate coupling between the glass and the size.



**Figure 5.** EDX image of the glass-size interface.

Elemental composition measurements were taken at set points through the size as shown in figure 5 as crosses. The resulting elemental compositions are shown in table 1.

Cross	1	2	3	4	5	6
Dist / $\mu\text{m}$	0.5	1.0	1.5	2.5	3.5	4.5
% Carbon	53.5	56.6	57.0	56.6	57.7	53.5
% Oxygen	32.7	32.6	33.7	34.0	31.5	32.7
% Silicon	9.5	7.1	6.1	5.9	6.0	6.2

**Table 1.** Elemental depth profile of the sample at varying distances from the outer edge of the sample.

## **Conclusion**

Migration of silicon-based coupling agents was shown using ESEM and EDX techniques. Similarly migration of lubricants was shown using AFM and IBA techniques.

## **Acknowledgements**

I would like to acknowledge Dr R. Thompson & Mr S. Eggleston of Durham Universities Innovation Centre in Nanomaterials and Mr G. Staines of the Materials Analysis Unit at Newcastle University for providing assistance with the techniques used in this investigation.

## **References**

- [1] Lowenstein K.L., *The Manufacturing Technology of Continuous Glass Fibres (2<sup>nd</sup> Edn.)*, Elsevier, Amsterdam, **1983**
- [2] Mäder, E.; Moos, E.; Karger-Kocsis, J. *Compos. Part A* **2001**, *32*, 631
- [3] Gerard, J.F.; Mäder, E.; Zinck, P. *J. Mat. Sci.* **2001**, *36*, 5245

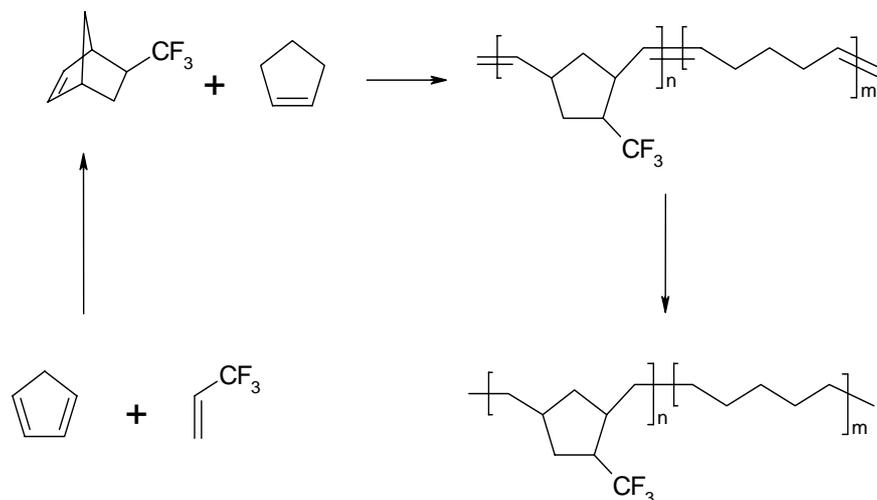
# New functional materials via ROMP: an approach to electrostrictive polymers.

*Jim Feast, Miquel Gimeno, Rachel Cochlin, Ezat Khosravi and Geoff Davies*

*Interdisciplinary Research Centre in Polymer Science and Technology, Durham University and Leeds University.*

## ABSTRACT

Many polar polymers fall into the category of expensive technologically useful speciality materials. For example, the co-polymers of vinylidene fluoride are important speciality elastomers, used as seals and gaskets in hydraulic systems, and the piezo and pyro electric properties of poled poly(vinylidene fluoride) homopolymer find use in devices such as hydrophones, piezoelectric loudspeakers and microphones and in pyroelectric sensors. One of the objectives of our work in this area is to establish routes to polar polymers displaying low glass transition temperatures, such materials might be additions to the range of elastomers and/or suitable for exploitation as electrostrictive materials. After initial attempts to use cyano and ester units as the polarity providers we turned our attention to fluorinated systems. The scheme below involves ring-opening metathesis polymerisation (ROMP) and copolymerisation of partially fluorinated bicyclo[2.2.1]hept-2-ene monomers, to give partially fluorinated poly(1,3-cyclopentylene vinylene)s, followed by hydrogenation of the double bonds to give saturated polar polymers.



Using this general scheme we have produced a range of new polar polymers with fluorine contents varying from 22% to 52% and glass transition temperatures varying between  $-22^{\circ}\text{C}$  and  $+125^{\circ}\text{C}$ . The evidence on which these assertions are based will be presented together with the implications of the work.

## Towards Antifreeze Glycoproteins: Solution Synthesis of Neoglycoconjugates:

*Matthew J. Gibson, Neil R. Cameron*

IRC in Polymer Science and Technology, University of Durham, Stockton Road, Durham, DH1 3LE, England  
Contact email: M.I.Gibson@durham.ac.uk

### Introduction

For cellular organisms to survive in subzero temperatures, mechanisms have evolved to prevent the process of freezing which is almost always fatal. Within polar latitudes water temperatures are nearly always below that of the freezing point of physiological solutions which in turn is below the freezing point of pure water at atmospheric pressure. Within cellular organisms the freezing point is in part reduced by the increased concentration of dissolved sugars and salts but the extent of this is limited by osmotic requirements.

Fish dwelling in polar oceans have developed (though not exclusively) an array of proteins which depress the freezing point of physiological solutions in a non-colligative manner. That is to say this depression, known as the thermal hysteresis, is not a thermodynamic effect, but rather a kinetic one. These proteins have been shown to depress the freezing point of a solution 300-500 times more than is predicted by colligative effects.

An interesting family of these proteins are known as 'antifreeze glycoproteins'. These display an Amino Acid repeat sequence of Thr-Al-Al. (Fig 1) The Threonine residue bears the disaccharide  $\beta$ -D-galactosyl-(1,3)- $\alpha$ -D-N-acetylgalactosamine, bound via the hydroxyl functionality.

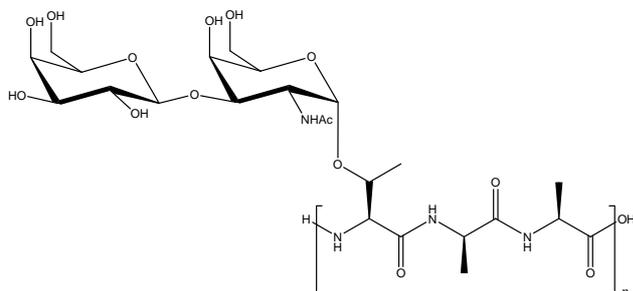


Figure 1. Structure of the repeat unit of an antifreeze glycoprotein.

The structural features important for this activity are not yet known. This research is towards producing mimics for elucidating this.

### Chain growth polymerisation of Amino Acid N-Carboxy Anhydrides NCA's

One of the most convenient methods of producing polypeptides is by the polymerisation of NCA's, formed by the action of phosgene (or suitable analogue) on amino acids.

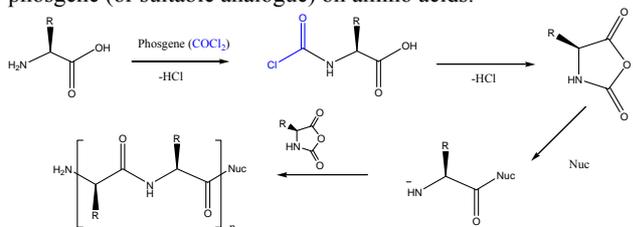


Figure 2. A general synthesis and polymerisation of NCA's

### Poly-threonine synthesis

O-Benzyl-L-threonine NCA (Fig 2) has been synthesised, then polymerised to a range of molecular weights equivalent to that of AFGPs (Fig 2). The benzyl protecting group can then be cleaved, to leave free hydroxyls, to be glycosylated as a mimic of AFGP.

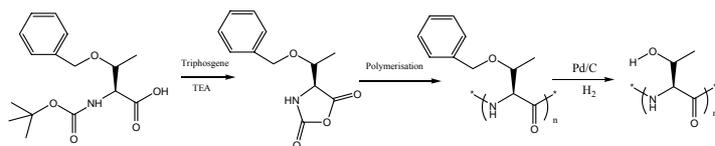


Figure 3. Synthesis of NCA followed by polymerisation

### Glycosylated Threonine NCA synthesis

Work is underway to develop a new method for the formation of 'glyco' NCA's. Glycosylation is achieved by  $\text{BF}_3$  mediated coupling with an acetylated sugar. No glycosylation occurs at the carboxylic acid by this method.

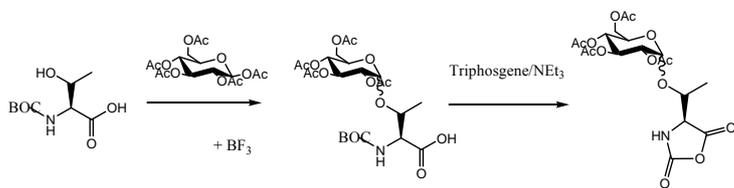


Figure 4. Synthetic route to 'glyco' NCA's

## Conclusions

This preliminary work has shown that there is potentially a solution phase route antifreeze glycoprotein mimics. The facile synthesis of O-Benzyl L-threonine NCA, offers an attractive route to glycoproteins, assuming the saccharide can be attached following polymerisation. An alternative method by which glycosylation monomer is used is currently being developed.

# Synthesis of Novel Hydrophobic Acyclic Nitroxides. Study and Evaluation of kinetic rate constants.

O. Lagrille<sup>†</sup>, N. R. Cameron<sup>†</sup> and P. A. Lovell<sup>‡</sup>.

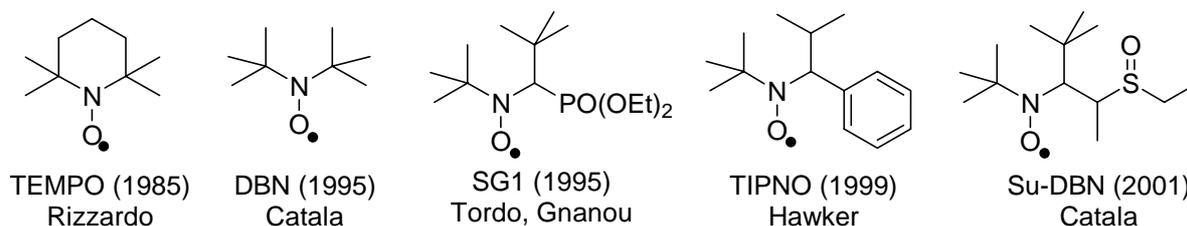
<sup>†</sup> IRC in Polymer Science and Technology, University of Durham, Dept. of Chemistry  
South Rd. Durham DH1 3LE U.K.

E-Mail: olivier.lagrille@durham.ac.uk, n.r.cameron@durham.ac.uk

<sup>‡</sup> Manchester Materials Science Center UMI ST, PO Box 88, Manchester M60 1QD  
E-Mail: pal@umist.ac.uk

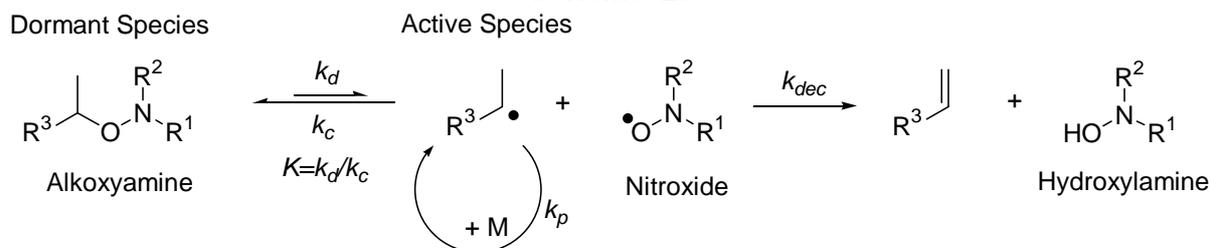
Since TEMPO<sup>(1)</sup> was shown to control the radical polymerisation of styrene, several new acyclic  $\alpha$ -H-bearing nitroxides and the corresponding alkoxyamines were developed by many authors (Scheme 1). Compared to TEMPO, these different nitroxides can control both the polymerisation of styrene and acrylates over a shorter timescale, giving predictable molar masses and narrow molar mass distributions.

**Scheme 1.**



The control of nitroxide-mediated radical polymerisation (NMP) using an alkoxyamine as initiator is due to the fast reversible formation of dormant species and active persistent radical species (nitroxides) illustrated by an equilibrium constant  $K = k_d/k_c$  (Scheme 2). The determination of some parameters such as  $K$  ( $k_d$  and  $k_c$ ) and also  $k_{dec}$  allows us to understand more the efficiency of alkoxyamines used in polymerisation.

**Scheme 2.**



Recently NMP has been used successfully in aqueous dispersed systems especially in miniemulsion with TEMPO and SG1 as nitroxides<sup>(2)</sup>. But these polymerisations were realised at temperatures larger than 100°C which require pressurised vessels. The present work deals with the synthesis of new hydrophobic acyclic nitroxides expected to be useful in radical miniemulsion polymerisation. We present the synthetic strategies employed to obtain these different nitroxides and the evaluation of kinetic rate constants in bulk polymerisation.

## References.

- (1) (a) Solomon, D. H.; Waverley, G.; Rizzardo E.; Hill, W.; Cacioli, P. *US Patent 4,581,429 1986*. (b) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987-2988.
- (2) (a) Pan, G.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *Macromolecules* **2001**, *34*, 481-488. (b) Keoshkerian, B.; MacLeod, P. J.; Georges, M. K. *Macromolecules* **2001**, *34*, 3594-3599. (c) Nicolas, J.; Charleux, B.; Guerret, O.; Magnat, S. *Macromolecules* **2004**, *37*, 4453-4463.

# **Biomaterials for Soft Tissue Engineering**

*Françoise Isaure<sup>a</sup>, Jenny Pettit<sup>b</sup>, Neil R. Cameron<sup>a</sup>, Jennifer Southgate<sup>b</sup>*

*a: University of Durham, Department of Chemistry, South Road, Durham, DH1 3LE, U.K.*

*b: Jack Birch Unit of Molecular Carcinogenesis, University of York, Department of Biology, York YO10 5YW, UK*

In the specific case of the urinary bladder, the cost of incontinence to the NHS has been estimated at £500 million per annum and there are around 2,800 potential patients per annum in the UK that would benefit from new strategies for chronic urinary incontinence and bladder reconstructive surgery. A number of approaches are being developed to find a practical and functional substitute for native bladder tissue. These include augmenting the urinary system with natural or synthetic biomaterials that will function as a scaffold for tissue regeneration and developing *in vitro* tissue-engineered constructs for transplantation.

We report here the preparation of non-porous films and porous membranes using the emulsion processing route and their biocompatibility in terms of supporting attachment and viability of normal human urothelial (NHU) cells and normal human bladder smooth muscle (SM) cells.

The films were prepared by casting a solution of commercial biocompatible poly(DL-lactide-*co*-glycolide) (75:25) (PLGA) and dichloromethane (DCM) on a microscope glass slide using the spin-coating method. The porous membranes were prepared using NaCl particles by the salt particle leaching technique. NaCl particles were added to the PLGA/DCM solution before casting and then dissolved in water to leave the porous structure. Different parameters, such as the concentration of PLGA, the spinning coat speed, the size and concentration of NaCl particles were studied to assess their influence on the morphology and biocompatibility of the films.

The attachment of the NHU and SM cells was assessed at 24h time period up to 7 days, by fixing films and visualising cell nuclei by staining with Hoechst 33258. The early results show that the cells attach and survive on the non-porous films after a long period of time such as at least a week. The biocompatibility of the porous films is currently under investigation.

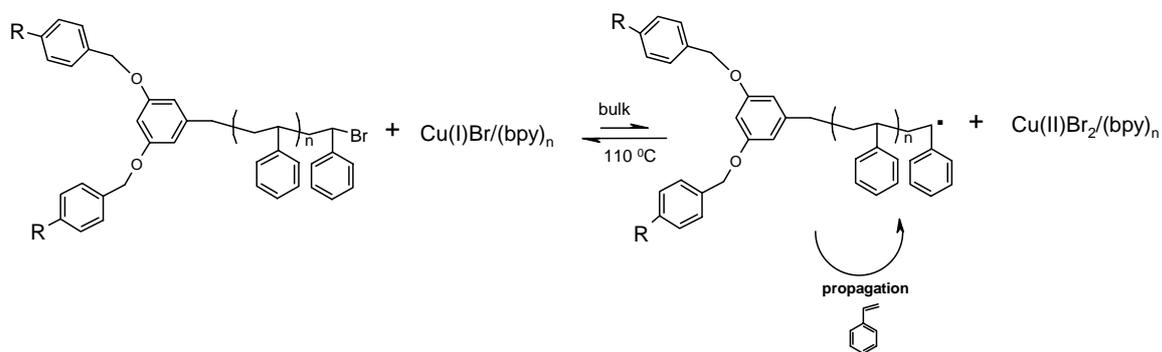
# DENDRITIC FUNCTIONALISED POLYMERS

A. Pillay Narrainen<sup>\*</sup>, L.R. Hutchings

*Department of Chemistry, University of Durham, UK*

## ABSTRACT

Fréchet-type poly(aryl ether) dendrons [1] with a focal bromine have been synthesised. These molecules can act as initiators for the metal-mediated living radical polymerisation (MMLRP) of styrene (scheme below). Controlled polymerisation was achieved with a system consisting of copper (I) bromide and bipyridine. Well-defined polystyrene with predicted molecular weights ( $M_n \sim 10\,000 \text{ g mol}^{-1}$ ) and fairly low polydispersity (1.2-1.3) have been obtained.  $^1\text{H NMR}$  shows the incorporation of the dendritic initiator in the isolated polymer. Migration of these polymers to interfaces offers the possibility of interface modification.



[1] Hawker, C.J.; Fréchet, J.M.J. *J. Am. Chem. Soc.* **1990**, *112*, 7638

\* E-mail: amilcar.pillay-narrainen@durham.ac.uk

# The Synthesis of Block Copolymers Through the Conversion of Living Anionic Polymerisation into Ring Opening Metathesis Polymerisation.

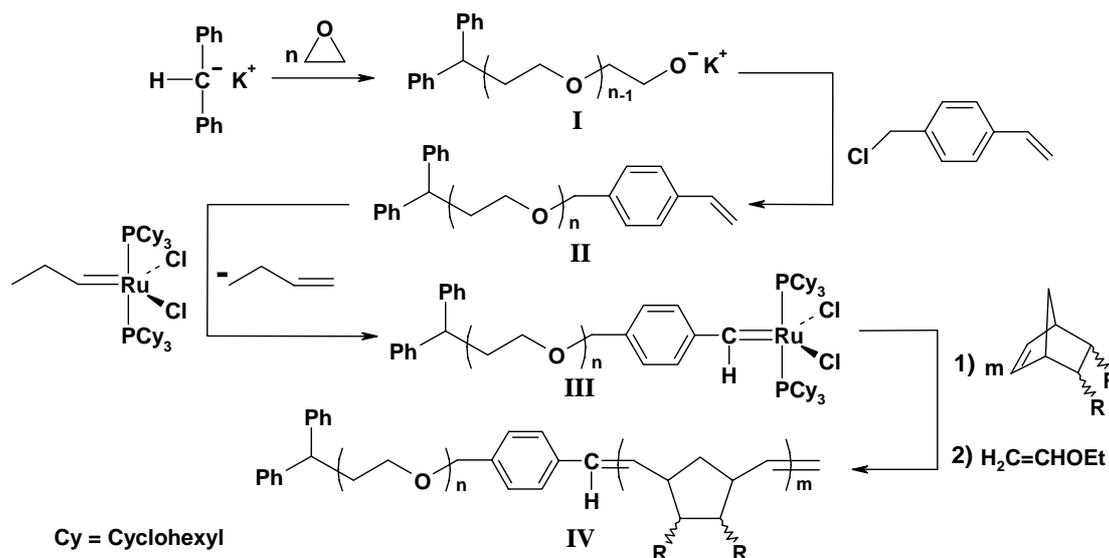
Tom C. Castle, Ezat Khosravi and Lian R. Hutchings.

IRC in Polymer Science and Technology, Department of Chemistry,  
University of Durham, South Road, Durham. DH1 3LE. United Kingdom.

E-mail: t.c.castle@durham.ac.uk

In the work reported here anionic polymerisation and ring opening metathesis polymerisation (ROMP) are combined to synthesise a range of block copolymers and determine their properties.

This process was first established by the conversion of the living anionic polymerisation of ethylene oxide into the living ROMP of norbornene derivatives. Living poly (ethylene oxide) (PEO) (**Scheme 1, I**) was functionalised using 4-vinylbenzyl chloride, in order to obtain macromonomers (macromolecular monomers) (**II**). The macromonomers were then converted by a metathesis reaction with a Grubbs ruthenium initiator into ruthenium macroinitiators (macromolecular initiators) (**III**). These macroinitiators initiate the ROMP of norbornene derivatives, hence synthesising block copolymers (**IV**).



Scheme 1 - The synthesis of a Poly (ethylene oxide-co-norbornene) copolymer.

In addition to block copolymers of PEO with polynorbornene (PNB), the successful extension of the work to block copolymers of PNB and alkyl lithium initiated polystyrene (PS) will be discussed.

# Analysis of PVDC Barrier Coatings on PET film

*R.L. Thompson<sup>1</sup> and M.R. Hodgson<sup>2</sup>*

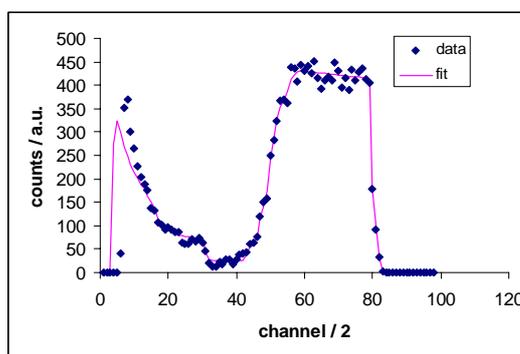
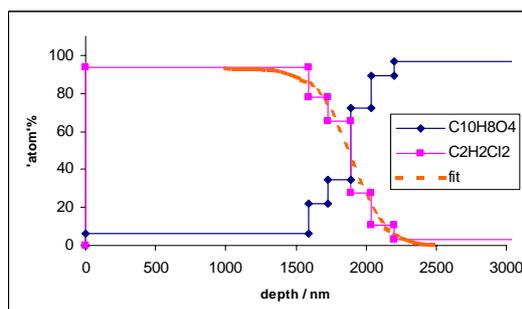
- 1** *Department of Chemistry, University of Durham, Durham, DH13LE*  
**2** *DuPont Teijin Films U.K. Ltd., PO Box 2002, Wilton Centre, Middlesbrough, TS90 8JF*

## ABSTRACT

The interface of multilayer films is crucial to the durability and performance of these materials in many of their applications. This is particularly pertinent for PVDC, which is used as a barrier coating on polymer films, since the integrity of the barrier layer is vital to its function.

Ion beam analysis has been used to investigate the nature of the interface between PET and PVDC-co-PMA, which has been overlaid from solution. Ion beam analysis is one of the only techniques that can be used to characterise a diffuse polymer-polymer interface over a range from a few tens of nanometers to several microns. Although halogenated polymers are susceptible to beam damage, we have found that this can be minimised by (i) cooling the sample and (ii) minimising the charge incident on any one point. Moreover, by measuring the rate of degradation of the sample in the beam, it is possible to resolve the true interfacial width from the raw data.

Figure 1. RBS data + simulation of best fit to obtain concentration gradient of PVDC.



used

Figure 2. Model used to generate fit to RBS data. The dashed curve is a fit to this model from which the interfacial width can be extracted.

Using this approach it is possible to characterise both film and interfacial thickness of multilayer films. The PVDC-co-PMA film on PET was found to be 1.8  $\mu\text{m}$  thick with an interfacial width of 0.22  $\mu\text{m}$ .

# Solvent Accelerated Polymer Diffusion in Thin Films

*R.L. Thompson and M.T. McDonald*

*Department of Chemistry, University of Durham, South Road, Durham, DH13LE*

## ABSTRACT

Whilst there have been many studies on the diffusion of solvents into solid polymers, and the diffusion of polymers in the melt, there is very little information on the related diffusion process of polymers when it is facilitated by the absorption of solvent vapour. This is a complex process involving the diffusion of polymers in highly concentrated solutions in the proximity of surfaces.

We have found that the interdiffusion of polystyrene increases with increasing cyclohexane solvent vapour pressure and temperature. Interdiffusion coefficients increase with decreasing molecular weight, but the behaviour is moderately well described by the  $M_w^{-2}$  power law that is expected from reptation theory.

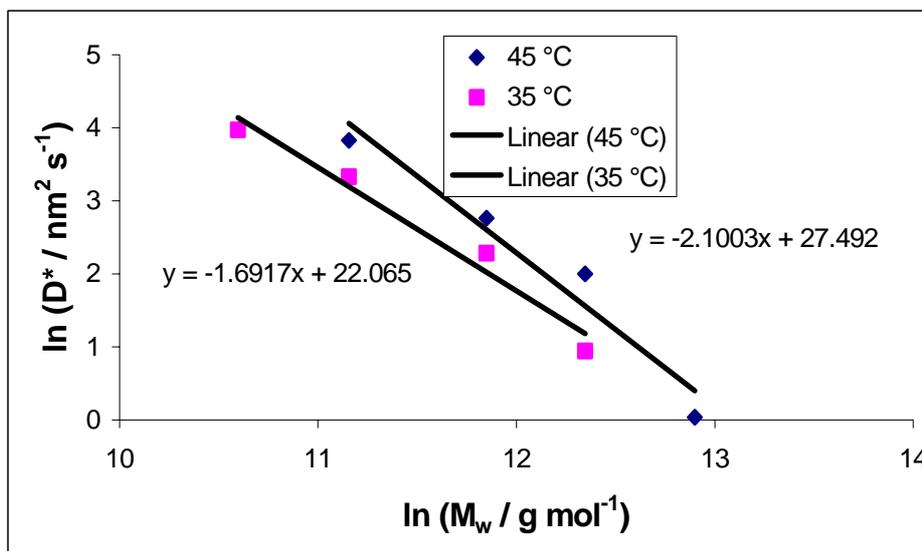


Figure 1.

**Molecular weight dependence of diffusion coefficient for solvent annealed films.**

Interestingly, we have also found that solvent mediated interdiffusion is slower in the case of extremely thin (<500 nm thick) films. This could be either because the motion of polymer chains in very thin solvent swollen films is suppressed, or because thicker films retain absorbed solvent for longer, leading to erroneous annealing times. These results are of importance for the wet processing of polymer films in multilayer devices such as OLEDs.

The authors are grateful for the support of this work via Nuffield Foundation undergraduate research bursary URB/01459/G.

# Diffusion of Polyethylene oxide and Polymethylmethacrylate

N. Clarke, K.A.Houghton, R.L.Thompson,

Department of Chemistry, University of Durham, Durham, UK

[K.A.Houghton@Durham.ac.uk](mailto:K.A.Houghton@Durham.ac.uk)

## Introduction

Polyethylene oxide (PEO) and polymethylmethacrylate (PMMA) are miscible at room temperature for PEO volume fractions up to circa 0.30, above which PEO phase separates to a separate semi-crystalline phase. In the present work the interaction parameters and diffusion of deuterated polyethylene oxide (d-PEO) and PMMA above the melting temperature of d-PEO but below the glass transition temperature of PMMA is observed using small angle neutron scattering (SANS) and elastic recoil detection analysis (ERD) respectively.

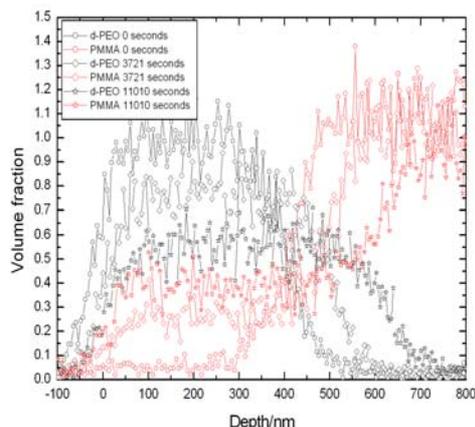
## ERD-Experimental

Each sample consisted of ~300nm deuterated polyethylene oxide (d-PEO) on top of a thick (~1 $\mu$ m) film of PMMA. The PMMA film was prepared by spin coating onto silicon wafer from toluene solution and then annealed at 413K to relax the PMMA. The upper d-PEO layer was spin coated from MEOH onto the relaxed PMMA layer. Various molecular weight combinations ranging from 17000gmol<sup>-1</sup> to 2016000 gmol<sup>-1</sup> were utilised. The bilayers were heated to a temperature T below the glass transition temperature of PMMA (405K) but above the melting temperature of d-PEO (337K) for a length of time t.

Elastic recoil detection analysis (ERD) measurements were carried out using the ion beam analysis system at Durham. The annealed polymer samples were bombarded by a beam of <sup>4</sup>He<sup>++</sup> ions with beam energy of 3.24 MeV and with a beam current of 10 nA. The beam was incident at an angle of 71° to the sample normal, after passing through a ~10 $\mu$ m Mylar film, light recoiled particles were detected at 150° to the incident beam (Cornell geometry) by an energy sensitive detector. A liquid nitrogen cooling system was used to reduce beam damage to the sample.

Data was converted to volume fraction profiles of deuterated and hydrogenous polymers as a function of depth from the surface by division by the equivalent ERD data for a fully mixed thick film of deuterated and hydrogenous polymer. A typical profile is shown in figure 1.

Volume fraction distribution profiles obtained for finite annealing times t could not be interpreted using the solution of Fick's second law of diffusion [1].



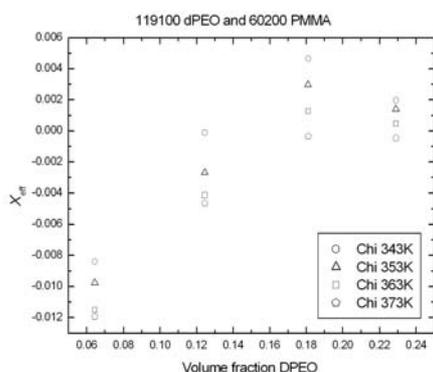
## ERD Results and Discussion

For temperatures below the glass transition of the PMMA (~380K) the diffusion of PMMA into the bulk of d-PEO is extremely rapid, reaching the surface in one 'step'. Subsequent swelling of PMMA into d-PEO occurs at a resolvable rate. Slight initial movement of d-PEO into the glassy PMMA bulk can be observed and measured. Therefore diffusion of a molten polymer into a glassy one was observed for high molecular weight polymers. A similar effect for PS/PPO interfaces with much lower molecular weights has been observed [2].

**Figure 1** Volume fraction profile of d-PEO (Mw = 121100 gmol<sup>-1</sup>) and PMMA (Mw = 96200 gmol<sup>-1</sup>) as a function of depth from the surface at various time t heated at 363K

## Small Angle Neutron Scattering-Experimental

Homogenous blends of d-PEO and PMMA with volume fraction of d-PEO in the blend mixtures of 0.05 <  $\phi_{d-PEO}$  < 0.4 were prepared by co-dissolving the two polymers in chloroform, pouring into a mould and allowing chloroform to evaporate. Each specimen so prepared was placed in a brass cell which could be placed in a temperature-controlled sample changer on the LOQ small angle neutron diffractometer at ISIS (Rutherford Appleton Laboratory, UK). Small angle neutron-scattering data were collected for each blend and the individual homopolymers at temperatures of 373K, 363K, 353K and 343K. All scattering patterns were isotropic indicating the absence of crystalline d-PEO. SANS data were analysed using the random phase approximation, allowing for the different segment volumes of PMMA and d-PEO, to find values for the effective interaction parameter  $\chi_{eff}$ .



## SANS Results and Discussion

The interaction parameter was small and negative for low volume fractions of d-PEO. Indicating that the two components formed a homogenous blend up to 0.4 volume fraction d-PEO. Allowing for the temperature dependence of  $\chi_{eff}$ , values found here agree with previous work done on this blend at temperatures above the Tg of PMMA [3].  $\chi_{eff}$  has a small negative temperature dependence, this may indicate that  $\chi_{eff}$  is not completely dominated by entropic contributions. For all combinations of PMMA and d-PEO the plot of  $\chi_{eff}$  as a function of temperature exhibited an increase from negative to positive with increasing d-PEO content and then a decrease in  $\chi_{eff}$  at higher volume fraction (0.2 <  $\phi_{d-PEO}$  < 0.4) as shown in figure 2. The interaction parameter shows no clear dependence on PMMA molecular weight.

**Figure 2.** Plot of  $\chi_{eff}$  as a function of volume fraction d-PEO (Mw = 121100) in PMMA (Mw = 60200) at different temperatures

## Conclusion

Deuterated polyethylene oxide above its melting temperature can diffuse into poly(methylmethacrylate) in its glassy state. Diffusion appears to slow down at a certain d-PEO composition. The interaction parameter between the two polymers allows them to form a homogeneous blend at low volume fractions of d-PEO but is highly composition dependent.

## References

- [1] J.Crank, 'The Mathematics of Diffusion', Oxford University Press, 1975
- [2] Lin, H.C; Tsai, I.F; Yang, A.C-M; Hsu, M.S; Ling, Y.C; *Macromolecules* **2003**, *36*, 2464
- [3] Hopkinson, I; Kiff, F.T; Richards, R. W; King, S. M; Farren, T; *Polymer* **1994**, *36*, 3523

## Diffusion and Viscoelastic Measurements of Polystyrene Stars.

*N. Clarke, F.R.Colley, S.A.Collins, L.R. Hutchings and R.L.Thompson  
Department of Chemistry, University of Durham, Durham, DH1 3LE, UK  
S.A.Collins@Durham.ac.uk*

### Introduction

The dynamics of linear molecules are well described by the tube model and the concept of reptation proposed by de Gennes [1] and Doi and Edwards [2].

In the case of non-linear architecture (e.g. star polymers) reptation is prevented by the branching. de Gennes [3] proposed that translational chain motion may occur via contour length fluctuations (i.e. arm retraction) followed by junction point or core ‘hopping’, where the free end of one or more of the star polymer’s arms moves back to the junction point before moving away again. As the retracted arm re-extends the junction may hop a short distance. Constraint release may also contribute, allowing the diffusion to proceed faster. The observed diffusion coefficient is given by:

$$D^* = D_0 + D_{CR} \quad (1)$$

where  $D_0$  and  $D_{CR}$  are the retractive and constraint release diffusion coefficients, respectively. Arm retraction is entropically unfavourable and the retraction time has an exponential dependence on the degree of polymerisation. It was proposed [4] that for stars

$$D_0 \sim (N/N_e)^{-\gamma} \exp([-27/56][N/N_e]) \quad (2)$$

where  $N$  and  $N_e$  are the degree of polymerisation of the star arms and the entanglement value, respectively.  $\gamma$  takes values of 29/14 if the core hops a distance of the order of  $a_0$  or 3/2 for a core hop greater than  $a_0$  (dynamic dilution [5]).

The zero shear viscosity is given by a similar exponential expression

$$\eta_0 \sim (N/N_e) \exp([-27/56][N/N_e]) \quad (3)$$

### Experimental

*Materials.* Both deuterated and hydrogenous 4-arm star polystyrenes were synthesized. Monodisperse PS arms were prepared by anionic polymerization methods. A coupling agent (1,6-bis(dichloromethylsilyl)hexane), was then used to create the star polymer. Both the arm and star  $M_w$  were determined by SEC.

*Ion Beam Analysis:* Bilayer samples were prepared on polished silicon wafers of <111> orientation. A thick lower layer of hPS was spin coated from toluene solution. The thin upper dPS layer was similarly spin coated onto a glass slide and floated onto the hPS layer. Samples were annealed at a specific temperature for a range of times.

NRA measurements performed using an ion beam accelerator system at Durham. A beam of  $^3\text{He}^+$  of various energies and were employed with varying geometries, depending on the sample.

The data collected was used to produce spectrum of volume fraction of dPS with depth from the sample surface using methods described elsewhere [6].

This volume fraction distribution may then be fitted with a Fickian diffusion profile. This profile has a characteristic interfacial width that broadens with diffusion and so the rate of diffusion may be then determined.

*Rheometry:* Storage and loss moduli were measured over the frequency range  $10^{-2} < \omega(\text{s}^{-1}) < 10^2$  for a range of temperatures (403 to 463K) using a parallel plate rheometer (plate size of 25mm diameter, gap of approximately 1 mm). All measurements were obtained with the

sample in a nitrogen atmosphere. The zero shear viscosity was then determined from the low frequency moduli.

## Results and Discussion

*Ion Beam:* Figure 1 shows  $D^*$  against matrix molecular weight for two dPS tracer stars (13k and 26k arm  $M_w$ ) for different annealing times. As expected the rate decreases with increasing matrix  $M_w$  and increases with temperature.

*Rheology:* The zero shear viscosities for each  $M_w$  star hPS is shown in figure 2 for the range of temperatures.

As expected  $\eta_0$  increases with  $M_w$  and decreases with increasing temperature. The data also shows reasonable agreement over this limited  $M_w$  range with the exponential form of  $\eta_0$  (eqn. (3)).

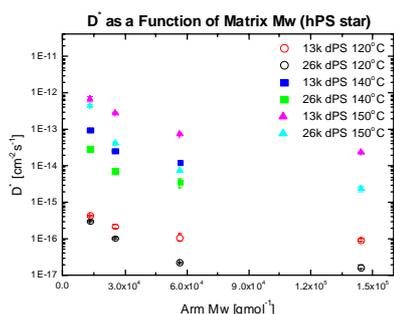


Figure 1

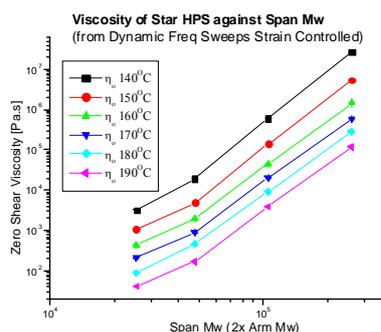


Figure 2

For self diffusion, the dependence of  $D_0$  and  $\eta_0$  on poorly known parameters can be removed as can the dominant exponential dependence on  $N$  using the product

$$D_0 \eta_0 \sim (N / N_e)^{-\chi} \quad (4)$$

where  $\chi$  takes the values of 0.5 for diluted tubes and 15/14 for undiluted tubes. Figure 3 shows  $D^* \eta_0$  as a function of  $M_w$ .

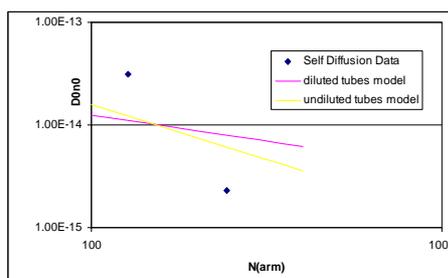


Figure 3.  $D^* \eta_0$  and  $D_0 \eta_0$  as a function of  $M_w$

This limited set of results does not seem to show particularly good agreement with the either of the diluted or undiluted models.

## Conclusion

The rheological data obtained for the star PS appear to agree with the theoretical model and previous experimental work although an extension to higher  $M_w$  is required to confirm the exponential increase in  $\eta_0$ .

Agreement appears to be poor between the product  $D^* \eta_0$  and the theoretical values for this preliminary data set, although of the two models, agreement is closer to the undiluted situation in agreement with [5]. In order to draw definite conclusions further self diffusion coefficients are required for an extended  $M_w$  range and for a larger range of annealing temperatures.

## References

- [1] P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, **1979**.
- [2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, Oxford, **1986**.
- [3] P. G. de Gennes, *J. Phys.*, **1975**, *36*, 1199.
- [4] A. L. Frischknecht and S. T. Milner, *Macromolecules*, **2000**, *33*, 9764.
- [5] R. C. Ball and T. C. B. McLeish, *Macromolecules*, **1989**, *22*, 1911.
- [6] C. R. Bartels, B. Crist, Jr, L. J. Fetters and W. W. Graessley, *Macromolecules*, **1986**, *19*, 785.

# Addition Polymerisation (AP) versus Ring Opening Metathesis Polymerisation (ROMP) for the Syntheses of a Series of Novel Polymers

Alan Cooper, Ezat Khosravi

IRC in Polymer Science and Technology, University of Durham  
South Road, Durham, DH1 3LE, UK  
Contact email: a.t.cooper@durham.ac.uk

## Introduction

Interest in poly(norbornene)s has increased dramatically over recent years because of their unique physical and optoelectronic properties, such as high glass transition temperature, optical transparency, and low birefringence. Norbornene is known to polymerise by several mechanisms (figure 1). Ring opening metathesis polymerisation (ROMP) yields poly(1,3-cyclopentylenevinylene), which retains one double bond in each polymeric repeat unit.<sup>(1)</sup> Cationic polymerisation generally produces moderate yields of poly(2,7-bicyclo[2.2.1]hept-2-ene) oligomer.<sup>(2)</sup> Vinyl addition polymerisation of the monomer produces poly(2,3-bicyclo[2.2.1]hept-2-ene), a saturated polymer.<sup>(2)</sup>

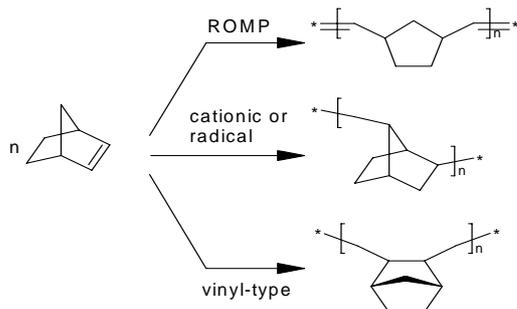


Figure 1. Schematic representation of the three different types of polymerisation for norbornene.<sup>(3)</sup>

The most established polymerisation of norbornene is ROMP. Academia has focused mainly on well-defined, single-component catalysts, which are usually metal-carbene complexes. The catalyst we utilise in our study is of this criterion and is a Grubbs ruthenium alkylidene complex.<sup>(4)</sup>

The interest in the addition polymerisation of functionalised norbornene derivatives has grown immensely in recent years due to the development of a family of late transition metal cationic catalysts which have been shown to have extremely high activity.<sup>(5)</sup> The Pd(II) based catalyst used in this study fits into this family of complexes.<sup>(5)</sup> The palladium and ruthenium catalysts used in this study are both ligated with tricyclohexylphosphine.

An issue relating to the polymerisation of functionalised norbornenes is that they are synthesised by the Diels-Alder reaction as mixtures of *endo* and *exo* isomers. Earlier work has shown that *endo*-functionalised norbornenes are polymerised more slowly than their corresponding *exo* isomers. The formation of chelates upon the coordination of the *endo*-functionalised norbornene has been shown to be responsible, in part, for the observed decrease in polymerisation rate.<sup>(3)</sup>

The functionalised norbornene monomers used in our study are of commercial interest because they are not synthesised by the usual Diels-Alder route. The procedure we used for the synthesis of *exo* norbornenol (>98:2 *exo/endo* selectivity) involves the reaction of acetic acid with excess norbornadiene at high temperature in the absence of a catalyst to give the *exo* monoacetate, followed by the usual saponification under alkaline conditions.<sup>(6)</sup> The corresponding *endo* norbornenol was produced via the oxidation of *exo* norbornenol, followed by reduction with L-Selectride at -78°C (>99:1 *endo/exo* selectivity).<sup>(7)</sup>

The monomers used in our study are hydroxy, ester or ether norbornene derivatives and are of particular interest because they are relatively easy to synthesise and introduce functionality at the polymer side chains (figure 2).

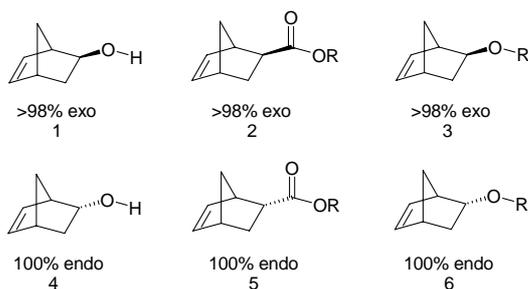


Figure 2. Monomers used in ROMP and addition polymerisation to introduce functionality at the polymer side chains. (R = Me, X)

These polymer side chains are important because they can hugely affect the properties of the resulting polymers and these could be used in optoelectronic applications. The effect of the *endo/exo*-2-substituent in norbornenes on the rate of polymerisation will be accessed using both ROMP and addition polymerisation catalysts with particular attention being given to the differing polymer properties obtained.

## Experimental

**Synthesis of *exo*-norbornenyl acetate.**<sup>(6)</sup> Norbornadiene (414 g, 4.5 mol) and glacial acetic acid (156 g, 2.6 mol) were charged to a 2 L stainless steel pressure vessel. The vessel was cooled, evacuated, sealed and heated to 190°C for 22 hrs. The reaction mixture was concentrated on a rotary evaporator to remove excess norbornadiene and acetic acid (the excess norbornadiene can be recovered, there should be little acetic acid remaining). The product *exo*-norbornyl acetate (350 g, 2.3 mol) was obtained by distillation (49°C, 6.5 mbar). GCMS and <sup>13</sup>C NMR analyses showed the product to have >98:2 *exo/endo* selectivity.

**Synthesis of *exo*-norbornenol.**<sup>(6)</sup> A round bottomed flask was charged with sodium hydroxide pellets (360 g, 9 mol), methanol (35 mL) and water (0.5 L). The solution was heated to 80°C under nitrogen with vigorous mechanical stirring and the *exo*-norbornyl acetate (350 g, 2.3 mol) was added dropwise. After the addition was complete, the mixture was allowed to cool with stirring overnight. The solid was

filtered and washed with water. It was dissolved in ether (1 L) and 10% aqueous HCl (175 mL). The ether layer was separated, washed with dilute sodium bicarbonate and brine. The ether solution was dried over MgSO<sub>4</sub>, filtered and concentrated at room temperature to give the product (219 g, 2 mol) as white crystals, mp 85-88°C, which was sufficiently pure for subsequent reactions. GCMS and <sup>13</sup>C NMR analyses showed the product to have >98:2 *exo:endo* selectivity.

**Synthesis of norbornenone.**<sup>(7)</sup> *Exo*-norbornenol (8.44 g, 76.6 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) was added via a cannula to a flame-dried flask containing CrO<sub>3</sub> (47.2 g, 472 mmol) and pyridine (76 mL, 945 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (600 mL). The reaction mixture was stirred for 48 hrs. The reaction mixture was filtered through a short plug of silica (eluted with CH<sub>2</sub>Cl<sub>2</sub>) and the organic layer was washed with 5% NaOH, 5% HCl, saturated NaCl, and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:hexanes = 1:4) to give the product (3.95 g, 36.5 mmol) as a white solid. Spectral data were identical to those in the literature.<sup>(8)</sup>

**Synthesis of endo-norbornenol.**<sup>(7)</sup> L-Selectride (1 M in THF, 40 mL, 40 mmol) was added to a flame-dried flask containing norbornenone (3.52 g, 32.6 mmol) in THF (35 mL) at -78°C. The reaction mixture was stirred at -78°C for 3 hrs and -20°C for 1 hr. After quenching with water (20 mL), the aqueous layer was extracted with diethyl ether (5 × 30 mL) and the combined organic layers were washed with water (100 mL), brine (100 mL), and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc:Hexanes = 3:7) to give the product (2.76 g, 25 mmol) as a colorless oil. Spectral data were identical to those reported in the literature.<sup>(9)</sup>

## References

- [1] Grubbs, R. H, *Handbook of Metathesis, Volume 3 – Applications in Polymer Synthesis*; Wilkinson, G; Stone, F; Abel, E; Eds., Pergamon Press: Oxford, UK. **1982**, 8, 499.
- [2] Gaylord, N. G; Deshpande, A. B; Mandal, B. M; Martan, M, *J. Macromol. Sci. Chem.* **1977**, *A11(5)*, 1053.
- [3] Hennis, A.D; Polley, J. D; Long, G. S; Sen, A; Yandulov, D; Lipian, J; Benedikt, G. M; Rhodes, L. F; Huffman, J, *Organometallics* **2001**, *20*, 2802.
- [4] Schwab, P; France, M. B; Ziller, J. W; Grubbs, R. H, *Angew. Chem. Int. Ed Engl.* **1995**, *34*, 2039.
- [5] Lipian, J; Minma, R. A; Fondran, J. C; Yandulov, D; Shick, R. A; Goodall, B. L; Rhodes, L. F, *Macromolecules* **2002**, *35*, 8969.
- [6] Feiring, A. E; Crawford, M. K; Farnham, W. B; French, R. H; Leffew, K. W; Petrov, V. A; Schadt, F. L; Wheland, R. C; Zumstag, F. C, *J. Fluorine Chem.* **2003**, *122*, 11-16.
- [7] Mayo, P; Orlova, G; Goddard, J. D; Tam, W, *J. Org. Chem.* **2001**, *66*, 5182.
- [8] Oppelzer, W; Chapuis, C; Dupuis, D; Guo, M, *Helv. Chim. Acta.* **1985**, *68*, 2100.
- [9] Fischer, W; Grob, C. A; Sprecher, G; Waldner, A, *Helv. Chim. Acta.* **1980**, *63*, 816.

## Acknowledgement

We would like to thank Promerus LLC for their funding and donation of palladium catalysts.

# Regeneration of Grubbs Catalyst in Ring Opening Metathesis Polymerisations

David M. Haigh, Ezat Khosravi, Alan M. Kenwright

Department of Chemistry  
University of Durham  
South Road, Durham, DH1 3LE, UK  
d.m.haigh@durham.ac.uk

## Introduction

The olefin metathesis reaction has become an invaluable synthetic tool for chemists. The ability to simultaneously cleave and reform carbon-carbon double bonds has led to its widespread use in the design of useful organic molecules<sup>1</sup> and polymers.<sup>2</sup> Olefin metathesis has achieved a leading role in synthetic methodology in the last decade mainly due to advances in the field of catalysis and organometallic chemistry, which have been heavily influenced by the work of Grubbs<sup>3-5</sup> and Schrock<sup>6</sup> in developing well-defined transition metal carbene complexes. ROMP reactions using well-defined initiators result in polymers with a narrow polydispersity index (PDI ~ 1.05-1.2). Generally, the initiator is totally consumed and the disappearance of the initiator alkylidene proton and the appearance of the propagating alkylidene protons can be seen in <sup>1</sup>H NMR spectra. In this paper we report the ROMP of 7-*t*-butoxynorbornadiene initiated by RuCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(=CHPh) [**1**], in which the initiator is first consumed and then regenerated at the expense of the living propagating species.

## Experimental

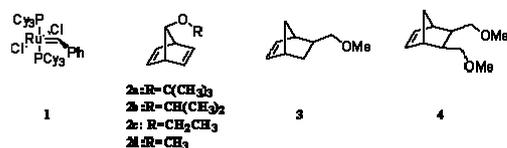
**Materials.** All reagents used were of standard reagent grade and purchased from Aldrich or Lancaster and used as supplied unless otherwise stated. CDCl<sub>3</sub> (Aldrich, 99.9%D, 0.03% v/v TMS) was dried over P<sub>2</sub>O<sub>5</sub> and distilled prior to use. Grubbs ruthenium initiator<sup>5</sup> [**1**], 7-*t*-butoxynorbornadiene<sup>7</sup> [**2a**], 7-methoxynorbornadiene<sup>8</sup> [**2d**], and *exo,exo*-5,6-bis(methoxymethyl)norbornene<sup>9</sup> [**4**] were synthesized according to literature procedures. 7-*iso*-propoxynorbornadiene<sup>8</sup> [**2b**], 7-ethoxynorbornadiene<sup>8</sup> [**2c**] and *exo*-5-methoxymethylnorbornene<sup>9</sup> [**3**] were synthesised by adaptations of procedures reported in the literature.

**General procedure for <sup>1</sup>H NMR scale ROMP reactions.** All ROMP reactions were prepared in a Braun glove box under a nitrogen atmosphere. **1** (10 mg) was dissolved in deuterated solvent (0.4 mL) and stirred for 5 minutes. The relevant monomer was dissolved in deuterated solvent (0.4 mL) and was injected into the initiator solution. The reaction mixture was stirred for 5 minutes and then transferred to an NMR tube fitted with a young's tap, which allows the vessel to be closed under a nitrogen atmosphere. The reactions were monitored by <sup>1</sup>H NMR spectroscopy every 15 minutes for the first 3 hours and then at appropriate periods until it was clear that no further reactions were taking place.

**Analytical techniques.** <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 400 or a Varian Inova 500 using deuterated solvent as lock. Chemical shifts are quoted in ppm, relative to tetramethylsilane (TMS), using TMS as the internal reference.

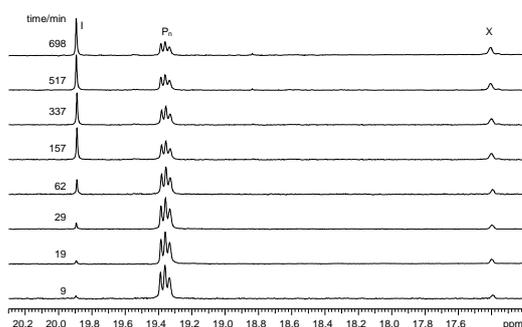
## Results and discussions

We recently made a remarkable observation when catalyst **1** was used to initiate the polymerisation of 7-*t*-butoxynorbornadiene **2a** (Figure 1) using a monomer: initiator ratio ([M]<sub>0</sub>/[I]<sub>0</sub>) of 50.<sup>10</sup>



**Figure 1.** Grubbs catalyst (**1**) and various strained cyclic olefins.

The reaction proceeds rapidly in  $\text{CDCl}_3$  with almost complete consumption of initiator to form propagating ruthenium alkylidene species which are then converted slowly, but not completely, back to initiator, implying a secondary metathesis reaction. The stack plot of the alkylidene proton region at intervals over a 12 hour period for this ROMP reaction, Figure 2, shows these extraordinary features, and it clearly exhibits the presence of three distinct signals. Resonances due to alkylidene protons of **1** appear at 19.9ppm, a propagating species ( $P_n$ ) has signals at 19.38, 19.36, 19.33ppm, and a species X appears at 17.44ppm. The three propagating signals ( $P_n$ ) are believed to arise due to the sensitivity of the chemical shift to the *cis/trans* isomerism of the adjacent double bond and to the *meso/racemic* isomerism of the adjacent dyad.<sup>11</sup>

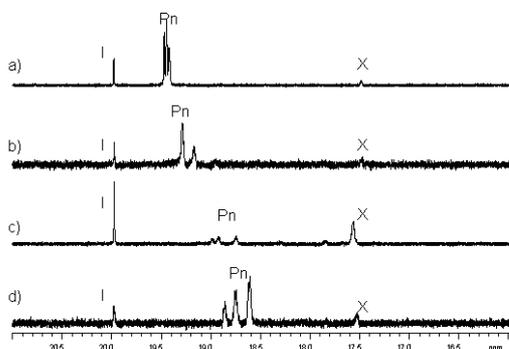


**Figure 2.**  $^1\text{H}$  NMR stack plot of the ROMP of **2a** initiated by **1** using  $[\text{M}]_0/[\text{I}]_0=50$  in  $\text{CDCl}_3$ .

The initiator is visibly regenerated at the expense of the propagating species as the reaction proceeds. This can only occur by a secondary metathesis reaction by either an intra- or intermolecular reaction at the living chain ends of the propagating species.

A small amount of another carbene species, labelled X, giving a broad signal at 17.44ppm, (Figure 2), is also formed which is extremely stable in solution. This observation of regeneration of the initiator during a ROMP reaction was the first of its kind and it has not been observed in any other systems. In particular, it has not been observed in the ROMP of 7-alkyl derivatives of norbornadiene.

To investigate how the steric bulk of the substituent in the 7-position of monomer effects the process of regeneration of the initiator, a series of new monomers, **2b-d** (Figure 1), containing alkoxy groups with decreasing steric hindrance have been prepared. The ROMP reactions of monomers **2a-d** initiated by **1** in  $\text{CDCl}_3$  were monitored by  $^1\text{H}$  NMR spectroscopy.



**Figure 3.** The alkylidene region (21-16ppm) of the  $^1\text{H}$  NMR spectra when monomers a) **2a**, b) **2b**, c) **2c** and d) **2d** are subjected to ROMP by **1** using a ratio of  $[\text{M}]_0/[\text{I}]_0=50$

The alkylidene region (21-16ppm) of these spectra are shown in figure 3 and they all exhibit a resonance for the residual initiator (I), the propagating species ( $P_n$ ) and the stable species X

at 19.98, 19.50-18.50, and ~17.5 ppm, respectively. Regeneration of the initiator is observed in all of these ROMP reactions, figure 4, and the extent of regeneration is found to increase as the steric bulk of the substituent in the 7-position increases.

These polymerisation reactions of monomers **2a-d** initiated by **1** also provide information on how the steric bulk of the substituent in the 7-position of the norbornadiene unit affects other aspects of the polymerisation process such as the rate of monomer consumption, figure 5, and the consumption of initiator at the start of the reaction, figure 6.

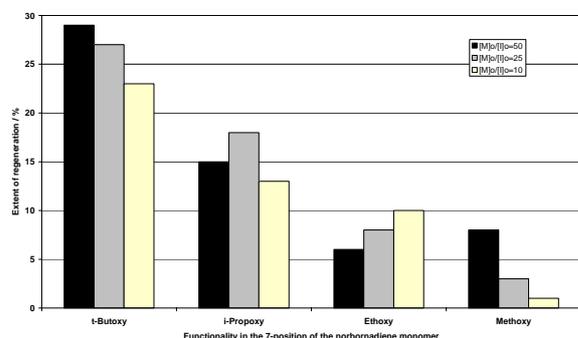


Figure 4. The effect of the steric bulk in the 7-position of the monomer and the  $[M]_0/[I]_0$  ratio on the extent of regeneration of **1**

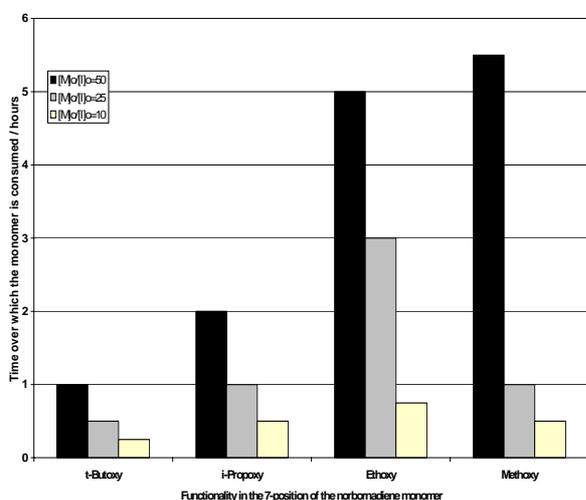


Figure 5. The effect of the steric bulk in the 7-position and the  $[M]_0/[I]_0$  ratio on the rate of consumption of monomer.

The effect of the magnitude of the  $[M]_0/[I]_0$  ratio on the regeneration of the initiator for the ROMP of monomers **2a-d** by **1** in  $CDCl_3$  has also been studied. Figures 4, 5 and 6 also show the results of the ROMP reactions performed on these monomers using  $[M]_0/[I]_0 = 50, 25$  and 10.

The general trend for the ROMP reactions described in figure 4, shows that as the  $[M]_0/[I]_0$  ratio is reduced the extent of regeneration of the initiator decreases, and figure 6 shows that when there is a lower concentration of monomer in the system, less of the initiator is consumed before propagation becomes the dominant process.

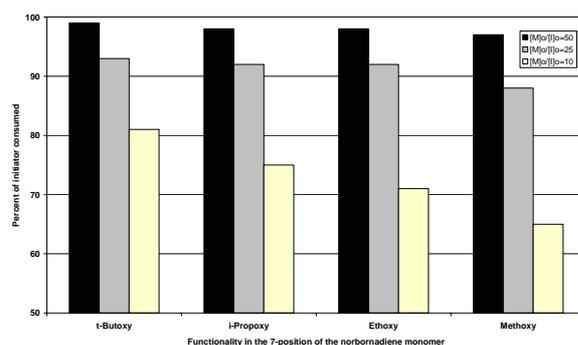


Figure 6. The effect of the steric bulk in the 7-position and the  $[M]_0/[I]_0$  ratio on the amount of initiator consumed at the start of the polymerisation.

We have already discussed in detail the observation of regeneration of the initiator at the expense of the propagating living chains when 7-substituted alkoxy norbornadiene monomers are subjected to ROMP initiated by **1**, and we now consider the appearance of species X in the alkylidene region of the  $^1\text{H}$  NMR's. The presence of species X during the ROMP of monomers **2a-d** is clearly shown in Figure 3. In all cases species X is stable and long-lived. When **2d** is subjected to ROMP using **1** with the ratio of  $[\text{M}]_0/[\text{I}]_0 = 50$ , species X is still visible in the  $^1\text{H}$  NMR spectra one month after the start of the polymerisation, and it is the only observable alkylidene species remaining in solution. When a second batch of **2d** (18 equivalents) is added to the solution, the monomer is consumed very slowly (20 days), but the appearance of the alkylidene region in  $^1\text{H}$  NMR remains unchanged i.e. only species X present. This observation implies that X is an active metathesis species, which is able to perform ROMP on strained cyclic olefins.

In order to establish whether the specific position of the alkoxy functionality within the monomer unit has any influence on the process of regeneration of the initiator, monomers with alkoxy groups in the 5 and/or 6 positions of norbornene have been prepared (3 and 4, Figure 1) and subjected to ROMP initiated by **1** in  $\text{CDCl}_3$ . The polymerisations were monitored by  $^1\text{H}$  NMR spectroscopy in the manner described previously. The resulting spectra indicate that there is no regeneration of the initiator and species X is not observed during either of these polymerisations. This suggests that the specific position of the alkoxy functionality plays a vital role in the regeneration of the initiator and on the formation of species X when alkoxy norbornadiene monomers are subjected to ROMP.

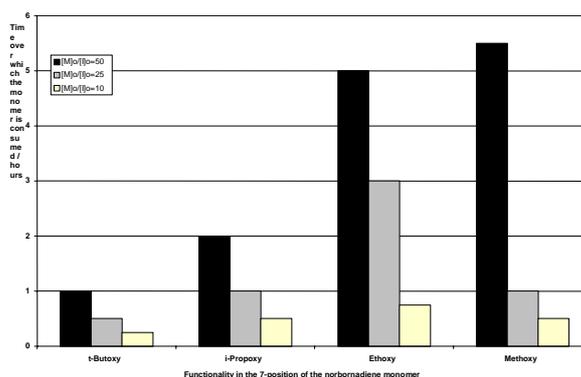
## Conclusions

The ROMP reactions of 7-alkoxy norbornadiene monomers (**2a-d**) using Grubbs well-defined ruthenium catalyst, showed that as the reactions proceeds the initiator is first consumed and then partially regenerated at the expense of the propagating species. A small amount of another carbene species X giving a broad signal at 17.44ppm, is also formed which is extremely stable in solution. Species X is found to be an active metathesis species and is able to perform ROMP on strained cyclic olefins. The extent of regeneration of the initiator is found to increase as the steric bulk of the substituent in the 7-position increases.

ROMP of monomers with alkoxy groups in the 5 and/or 6 positions of norbornene have been performed under similar conditions. These systems do not exhibit regeneration of the initiator and no species X is observed. This suggests that the alkoxy functionality plays a vital role in the regeneration of the initiator and it has a pronounced influence on the formation of species X.

## References

1. Furstner, A. *Alkene Metathesis in Organic Synthesis* Berlin:Springer, **1998**.
2. Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerisation* San Diego:Academic Press **1997**.
3. Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, 114, 3974.
4. Schwab, P.; France, M. B.; Ziller, J. W., Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2039.
5. Schwab, P. E.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, 118, 100.
6. Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, 112, 3875.
7. Story, P. R., *J. Org. Chem.*, **1961**, 26, 287
8. Lustgarten, R. K.; Richey, H. G. *J. Am. Chem. Soc.* **1974**, 96, 6393.
9. Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, 118, 784.
10. Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *Chem. Commun.* **1999**, 1209.
11. Ivin, K. J.; Kenwright, A. M.; Khosravi, E.; Hamilton, J. G. *Macromol. Chem. Phys.* **2001**, 202, 3624.



# Polymeric Ionophoric Channels Based on 7-Oxanorbornenes

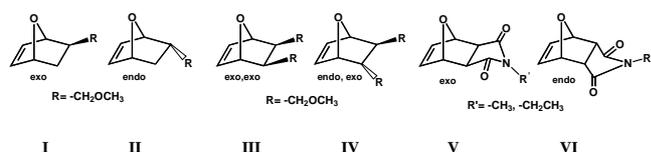
*Georgy Grancharov, Ezat Khosravi, Ritu Katak*

Department of Chemistry  
University of Durham  
South Road, Science Laboratories, Durham, DH1 3LE, UK  
georgy.grancharov@durham.ac.uk

The ionophoric properties of a range of compounds (e.g. crown ethers, antibiotics, etc) towards specific ions have been systematically analysed, determined and progressively applied [1,2] that is of great importance in drug-delivery studies, biological, medical and clinical analyses. First investigations about ion binding and complexing ability were performed using extraction studies, isolation of complexes, UV spectroscopy, potentiometric titrations [3,4].

In our studies artificial polymeric acyclic ionophores [5-7] based on 7-oxanorbornenes were synthesised by ring opening metathesis polymerisation (ROMP) and their ion binding properties were studied using electrochemical techniques e.g. potentiometry, voltammetry, scanning electrochemical microscopy (SECM), scanning Kelvin probe (SKP) microscopy.

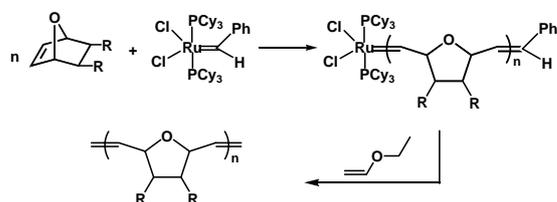
A series of 2,3-substituted-7-oxanorbornene monomers (**I-VI**, *Figure 1*) were readily synthesised by Diels-Alder reaction of furan with a number of dienophiles.



*Figure 1.*

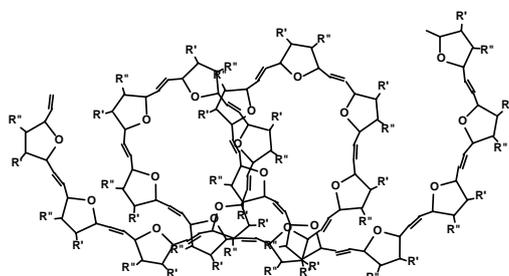
Bicyclic monomers such as 7-oxanorbornene and its derivatives are polymerised yielding unsaturated polymers. It has been demonstrated that well-defined initiators for ROMP allow the control of many aspects of the polymerization process, including cis/trans vinylene content and tacticity as well as important macromolecular parameters such as molecular weight and molecular weight distribution. Major advances achieved during recent years in the design of ROMP initiators which are tolerant towards polar functional groups (aldehydes, acids, alcohols) and aqueous environments has provided the polymer community with access to a wide range of novel functional materials, such as water-soluble polymers, polar polymers and biocompatible materials not previously available and has opened the possibility of using protic solvents and even water as the polymerization medium.

For our ROMP reactions we used the commercially available well-defined Grubbs ruthenium catalyst, phenylmethylene bis(tricyclohexylphosphine) ruthenium dichloride, which can be removed easily following polymerisation under simple conditions (*Figure 2*). A range of polymers of different chain length (molecular weight) were prepared to study the ion binding and ion selectivity properties.



*Figure 2.*

The preliminary molecular model studies of these polymers indicate their ability to form helical structures with all the THF oxygen facing into the interior of the helix (*Figure 3*):



**Helical structure of the polymers**

*Figure 3.*

This unique conformation allows these polymers in solution to act as useful acyclic ionophores. It was established that their binding possibilities depends on the configuration of the substituents of furan ring. These ionophores are similar to crown ethers i.e. they can bind through the oxygen lone pair. However, unlike the crowns, their cavities are not preformed and they can wrap around various cations depending on size and charge [5-7].

Thin membranes prepared from the different molecular weight polymers and self-assembled SH-terminated macromolecules on Au surface were used to investigate the ion binding possibility and ion dynamic behaviour of these polymeric materials. All analyses were performed by powerful tools for ionophoric determinations such as potentiometry and voltammetry combined with two relatively new techniques - SECM and SKP.

Polymers with different molecular weight were obtained by polymerisation of monomers **III** and **IV**.

First potentiometric measurements of the polymeric ionophores are based on detection of potential difference that can be described by the Nernst equation:

$$E = E_o + (2.303RT/nF) \cdot \log[c],$$

The electrode functions of polymers with different molecular weight (obtained on the base of **III** and **IV** monomer) were measured towards three cations with different ion size and charge- Na<sup>+</sup> (D=1.94Å), Ca<sup>2+</sup> (D=1.98Å) and methylene blue (MB<sup>+</sup>) large cation with Mw=373.9. The ion-binding properties of ROMP polymers towards MB<sup>+</sup> were determined also by measuring the aqueous MB solution's absorbance at λ=665nm before and after extraction with ROMP polymer solutions.

Results obtained for binding properties of the three polymers with different molecular weights for Na<sup>+</sup> cation are comparable with that measured for standard ionophores such as selective Na<sup>+</sup> ionophore III (Fluka) and 18-crown-6 ether. The potential responses of the polymers are situated between those obtained for standard ionophores. The results obtained for Ca<sup>2+</sup> are comparable with that obtained for the standard ionophores only for the polymers with lowest molecular weight. The UV-VIS analyses indicated that most of our polymers have ionophoric properties better than those of the crown ether towards MB<sup>+</sup> ions.

## References

- [1] C. J. Pedersen, *J. Am. Chem. Soc.*, **1967**, *89*, 7017.
- [2] C. J. Pedersen, H. K. Frensdorf, *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 16.
- [3] H. K. Frensdorf, *J. Am. Chem. Soc.*, **1971**, *93*, 600.
- [4] H. K. Frensdorf, *J. Am. Chem. Soc.*, **1971**, *93*, 4684.
- [5] D. J. Cram et al., *J. Am. Chem. Soc.*, **1977**, *99*, 2564.
- [6] S. Smith, W. J. Shultz, M. C. Etter, A. V. Pocius, *J. Am. Chem. Soc.*, **1980**, *102*, 7981.
- [7] R. H. Grubbs, B. Novak, *J. Am. Chem. Soc.*, **1988**, *110*, 960.

# Development of Emulsion Templated Porous Materials for the Immobilisation of Biocatalysts

*Alex Duréault, Neil R. Cameron*

*University of Durham, Department of Chemistry, South Road, Durham, DH1 3LE, UK*  
[alex.dureault@durham.ac.uk](mailto:alex.dureault@durham.ac.uk)

## Introduction

The application of enzymes in organic and polymer chemistry has become increasingly important in recent years<sup>1,2</sup>. Although the selectivity and specificity of enzyme mediated reactions has long been recognized, the development of new methodologies such as medium and protein engineering have led to an extended scope of application of biocatalysis in e.g. organic solvent environments<sup>3,4</sup>.

Inspired by nature enzyme cascade reactions have become a topic of investigation which holds great promise for the execution of complex synthetic pathways in one pot procedure<sup>5,6</sup>. One of the important challenges in this respect is to obtain control over positional assembly of the different catalytic species in order to create biocatalytic aggregates that are capable of performing multiple reaction steps in a predetermined order. For this purpose it is crucial to have access to carrier materials that contain recognition elements to which enzymes can specifically bind.

The European Research Training Network “Smart Assembly of Hybrid Biopolymers (SMASHYBIO)” is set up to develop new methodologies for the controlled aggregation of enzymes.

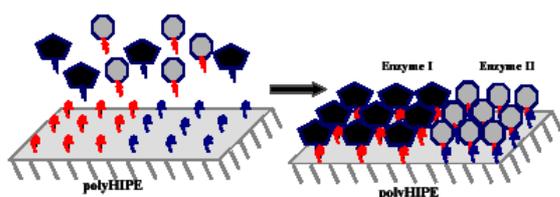


Figure 1. Schematic representation of the positional assembly process

Specifically, the aim of the presented work here is to prepare PolyHIPE<sup>7</sup> with functional handles for attachment of oligopeptides like elastin or leucine zipper fragments, both suitable for enzyme immobilisation.

PolyHIPEs are formed during polymerisation of the continuous phase of a high internal phase emulsion (HIPE). Such a material is defined as an emulsion in which the droplet phase takes up more than 74.05% of the emulsion volume, which represents the maximum volume that uniform spheres can occupy. One of the liquids is usually aqueous-based and the other is a water-insoluble organic liquid referred to as an oil. Both water-in-oil (w/o) and oil-in-water (o/w) types are possible. The droplet phase is usually termed ‘internal’ and the dispersion medium ‘the continuous phase’. In this case, the HIPE is formed by slow addition of the aqueous, droplet phase to a solution of surfactant in the monomeric, oil phase, under constant agitation. Polymerisation of the oil phase and subsequent removal of water leads to the highly porous structure.

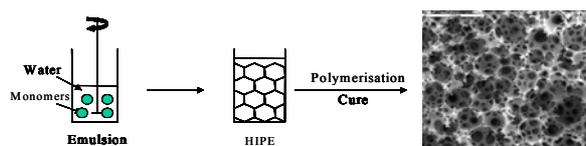
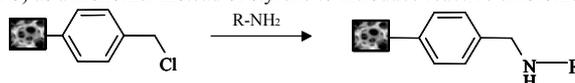


Figure 2. PolyHIPE synthesis and SEM

We used 4-vinylbenzylchloride (VBC) as a monomer instead of styrene to introduce reactive chloromethyl groups into such material.



Scheme 1. PolyHIPE functionalisation

Peptide solid phase synthesis was the first strategy for the attachment of protein fragment (elastin) on our carrier material.

The results obtained with the tris-amine PolyHIPE<sup>8</sup> for peptide solid phase synthesis are not as good as a current commercial resin [Wang : loading obtained in the same condition is around 0.9 mmol/g] but this can be explained by the fact that Wang resins are slightly cross-linked (around 1%) and are not monoliths like PolyHIPEs.

Different reactions have been made with different supports either as a powder or with the monolith as cubes [1 cm x 1 cm] in order to show the feasibility of performing reactions in a column. The results were better with the PolyHIPE as a powder compared to the cube [see table 2]; the diffusion is probably better in the powder.

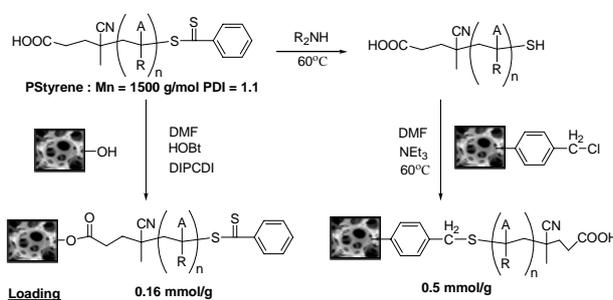
The successive addition of different amino acids enables us to graft the VPGVG sequence [elastin] onto the PolyHIPE support. (figure 3).



Figure 3. VPGVG grafted onto PolyHIPE

It has been shown previously that side chain polymers containing elastin-like pentapeptide repeats (ValProGlyValGly) maintain their thermoresponsive behaviour. We have assessed the self-assembly behavior of this VPGVG-PolyHIPE.

Another approach to graft a higher concentration of elastin like fragment was to use a VPGVG-monomer<sup>9</sup>. Indeed by controlling the free radical polymerisation of this monomer via the Reversible Addition Fragmentation Transfer (RAFT) process<sup>10</sup>, it should be possible to graft the VPGVG-polymer from or onto the PolyHIPE. The strategy “arm first” has been considered. It consists of the preparation of polymer via RAFT. The use of the functional polymer permits grafting onto PolyHIPE. Different reactions have been carried out as represented in scheme 2.



Scheme 2. Polymer grafting onto PolyHIPE

## Conclusions.

PolyHIPE is a versatile scaffold that can easily be adjusted for the incorporation of structural handles. The VPGVG sequence has been grafted *via* peptide solid phase synthesis and the self assembly behaviour of this material has been shown.

By using the controlled radical polymerisation (RAFT), the feasibility to graft polymer from or onto the support PolyHIPE has been shown.

## References.

- <sup>1</sup> Koeller, K. M.; Wong, C. H. *Nature* **2001**, 409, 232-240
- <sup>2</sup> Cheng, H. N.; Gross, R. A. *Biocatalysis in Polymer Science* **2003**, 840, 1-32
- <sup>3</sup> Klibanov, A. M. *Nature* **2001**, 409, 241-246
- <sup>4</sup> Arnold, F. H. *Nature* **2001**, 409, 253-257
- <sup>5</sup> Mayer, S. F.; Kroutil, W.; Faber, K. *Chem. Soc. Rev.* **2001**, 30, 332-339
- <sup>6</sup> Velot, C.; Teige, M.; Shatalin, K.; Skuta, G.; Sreer, P. A. *Protein Eng.* **1997**, 10, 14
- <sup>7</sup> The term PolyHIPE was first used by Unilever researchers; D. Barby and Z. Haq, U.S. Pat. 4522953, **1985**.
- <sup>8</sup> Krajnc, P.; Brown, J.; Cameron, N. R. *Org. Lett.* **2002**, 4 (15), 2497
- <sup>9</sup> Ayres, L.; Vos, M. R. J.; Adams, P. J. H.; Shklyarevskiy I. O., van Hest J. C. M. *Macromolecules* **2003**, 36 (16), 5967-5973.
- <sup>10</sup> Moad, G.; Chiefari, J.; Chong, Y.K.; Kristna, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo E.; Thang, S. H. *Polym. Int.* **2000**, 49, 993

# UK Polymer Showcase Partners



The IRC in Polymer Science and Technology began in 1989 as a consortium of research groups at the Universities of Leeds, Bradford and Durham. In September 2003 the Sheffield Polymer Centre joined with the IRC to form the current network of ~ 100 academics interested in polymers. It is a major UK, European and global focal point for multidisciplinary polymer science and its applications. A key objective of the IRC is to increase interactions between industry and the polymer scientists in the group. It does this through membership of its Industrial Club, studentships, contract research and training courses. Many major companies in polymer related industries are already involved with the IRC, recognising the quality and breadth of the IRC's work and the benefits of dealing with an interdisciplinary unit.

[www.polymerirc.org](http://www.polymerirc.org)



The Polymer Centre at the University of Sheffield brings together multi-disciplinary expertise embracing many topics at the forefront of polymer science and engineering. It consists of 41 academics and over 140 researchers working across seven different Departments. It offers expertise ranging from the synthesis and characterisation of new speciality polymers through to the application of polymer-based materials in advanced technologies - from batteries to visual displays, molecular machines to aircraft wings, and genetic engineering to tissue replacement.

[www.polymercentre.org.uk](http://www.polymercentre.org.uk)

***Access to expertise, at all IRC Centres, can be through a variety of formats: collaborative research, one-day courses, industrial seminars, taught and research degrees, analysis services, consultancy and joint ventures.***



The Faraday Packaging Partnership is a powerful R&D network, providing a unique resource to generate new thinking for the design, manufacture and supply of packaging for fast moving consumer goods. We support companies looking to enhance packaging in the food and drink, personal care, household, healthcare and pharmaceutical sectors to increase consumer value, through improved pack usability and functionality.

[www.faradaypackaging.com](http://www.faradaypackaging.com)



Faraday Plastics is the UK Government's prime R&D facilitator for the sector. The Faraday Partnerships aim to improve the competitiveness of industry by facilitating the interactions between the UK science and technology base and industry.

[www.faraday-plastics.com](http://www.faraday-plastics.com)



Polymer  
Centre of Industrial  
Collaboration



The Polymer CIC, in the IRC polymer engineering laboratories, is a centre of research excellence for advanced materials processing, especially polymers, and computer modelling of processes and products, plus material and product characterisation. It offers R&D solutions and a gateway for companies of all sizes. We also run the EPSRC Network for In Process Measurements – 12 Universities involved in sensors, process measurement and control, and ‘soft sensors’ combining modelling with measurement.

[www.polycic.com](http://www.polycic.com)

[www.polyeng.com](http://www.polyeng.com)

