

**ABSTRACTS
OF
POSTERS**



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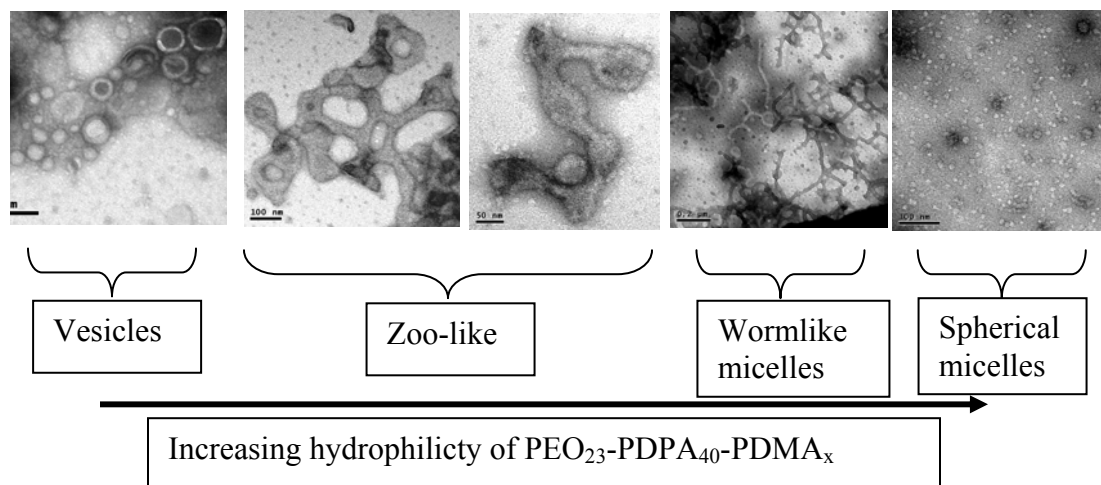
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Amphiphilic and responsive ABC block copolymers and their dilute solution behaviour, from vesicles to micelles

*Adam J Blanz, Stephen P Armes, Anthony J Ryan**
University of Sheffield, Department of Chemistry

An array of responsive amphiphilic ABC block copolymers (where A and C are hydrophilic and B is 'pH-switchable' between hydrophilic at low pH and hydrophobic in neutral conditions, $pK_a \approx 6.4$) have been synthesised with low polydispersity via Atom Transfer Radical Polymerisation. These polymers contain varying molecular weights of each block, where A = polyethylene oxide (PEO), B = poly(2-(diisopropylamino)ethyl methacrylate) and C = poly(2-(dimethylamino)ethyl methacrylate). A set of block copolymers have been synthesised with the basic structure PEO₂₃-PDPA₄₀-PDMA_x (where x ranges from 5-108) and were characterised in dilute solution at pH 7 using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS). It was discovered that as the hydrophilicity was increased with increasing 'x' length, there was a transition from vesicles, then through to a zoo-like morphology with high genus, wormlike micelles and finally spherical micelles. The electrophoretic mobility measurements of the surface charge of the self-assembled particles suggests that the higher volume PDMA block is on the outer layer of all the block copolymer aggregates. Different block-volumes using the same constituent polymer blocks have been synthesised to see if the biocompatible PEO can be the selectively tuned to the outer face. Vesicular aggregates are observed using dilute solutions of PEO₁₁₃-PDPA₇₅-PDMA₁₄, but electrophoretic measurements now suggest a charge neutral particle – indicative of PEO on the outer face. These vesicles may be of use for drug and gene delivery, as the cationic nature of PDMA makes it a suitable candidate for DNA binding and the biocompatibility of PEO enables these particles to take on a 'stealth' nature.



Biomimetic polymer vesicles for efficient cytosolic delivery

Marzia Massignani¹, Irene Canton¹, Hannah Lomas¹, Adam Blaznas²,
Steve Armes², and Giuseppe Battaglia¹

¹Biomaterials and Tissue Engineering Group, Department of Engineering Materials,
University of Sheffield

²Department of Chemistry, University of Sheffield

A B S T R A C T

We present a novel intracellular delivery vector based on the ability of a synthetic amphiphilic block copolymer to mimic biological phospholipids by forming membrane-enclosed structures, specifically nanometer-sized vesicles. We report the use of a pH-sensitive diblock copolymer that forms vesicles at neutral pH, and dissolves completely as unimers at endocytic pH. This transition drives a sudden increase in osmotic pressure when contained within a semi-permeable phospholipid membrane causing its lysis. When polymer vesicles are internalized within cells, this sudden increase in osmotic pressure enables escape from the endocytic pathway into the cell cytosol.



Computational Biophysics at Leeds: Dynamics of Biological Polymers

Presented by Josh Berryman on behalf of

Sarah Harris, Students & Postdocs

University of Leeds

A B S T R A C T

The three most important classes of biological molecules are the nucleic acids, lipids and proteins. All of these exist in the body as long polymer chains with complex yet also highly ordered dynamic and structural properties. Our group studies these systems (particularly proteins and nucleic acids) by classical and quantum numerical simulation. When the shapes and movements of these systems are understood, their mechanisms of action as molecular machinery can be replicated and controlled.



COUPLED 3D STRESS, VELOCITY AND TEMPERATURE FIELD MEASUREMENTS FOR FLOWING LINEAR AND BRANCHED POLYMER MELTS

T Gough, R Spares, AL Kelly and PD Coates

IRC in Polymer Engineering, University of Bradford, Bradford BD7 1DP, UK

Abstract

Abrupt contraction geometries are rarely intentionally used in industrial processing of polymer melts since they pose the potential of polymer stagnation, degradation as well as the effects of processing inhomogeneities. However, such geometries provide challenging complex flows for testing of, in general two-dimensional, numerical simulations, the testing of rheological parameters and validation of modelling of the flow response of melts with tailored architecture. Consequently, abrupt contraction flows of polymer melts have long been studied in order to provide experimental test cases for the development of numerical codes and constitutive equations. Though it is widely recognized that these flows are three dimensional in nature very little experimental data has been produced to quantify the flow in the third dimension. Stress, velocity and temperature field measurements are presented for contraction flows of well characterised linear and branched materials through abrupt contraction and x-slot flow cells. The techniques utilised include stress birefringence, particle tracking velocimetry and thermocouple meshes. In addition to the more typical measurements in the streamwise/normal (x-y) plane data in the streamwise/cross-stream (x-z) plane have also been obtained providing the first detailed measurements of the three dimensional nature of these flows.



Controlled formation of vesicular gels using amphiphilic block copolymers

Tom Smart, Giuseppe Battaglia and Tony Ryan

Biomaterials and Tissue Engineering Group, Department of Engineering Materials, Kroto
Research Institute, University of Sheffield, S3 7HQ.

Email: t.smart@shef.ac.uk

Amphiphilic block copolymers self-assemble into various structures in water, due to the different interactions of the respective hydrophilic and hydrophobic domains. At low concentrations they form dispersed isotropic structures of short-range order, one of which is vesicles. Poly(ethylene oxide) has been used to induce aggregation of poly(ethylene oxide)-co-poly(butylene oxide) (EB) copolymer vesicles to form a network of interconnected vesicles. The kinetics of formation of this network and the final structure have been monitored by confocal microscopy, dynamic light scattering, small angle x-ray scattering and transmission electron microscopy. It has been found that the rate and extent of aggregation can be controlled. We hope to explore the use of interconnected vesicle networks as a stealth delivery system on a macromolecular scale for use in the body. Amongst other things we wish to investigate the vesicle network as a carrier for stem cells.



DEGRADATION OF COMMODITY POLYMERS

G.J.HUNT, N.R.CAMERON

*IRC in Polymer Science and Technology, Department of Chemistry,
University of Durham,
Durham, DH1 3LE, United Kingdom
Email: g.j.hunt@durham.ac.uk*

Polymers are produced on an enormous scale globally and find use in a wide range of applications depending upon their structure and production cost. A study in 2000 commissioned by the Association of Plastics Manufactures in Europe (AMPE) found that 42% of all plastic produced is used for packaging. Factor this into other short term applications that plastics are used in and this leads to a considerable amount of plastic waste, which at present is not dealt with adequately. The majority of plastic waste is either incinerated - generating toxic substances - or placed in landfill sites where it can take many decades to decompose. It is estimated that 22% of all landfill sites are occupied by waste plastics. Methods to degrade commodity polymers selectively are scarce at best; a thorough understanding of how different polymers degrade is required along with the capital investment before sustainable progress can be made in this area. Current research in the area of polymer degradation is highlighted.



DEVELOPMENT OF SELF-HEALING SYSTEMS BASED ON ROMP-CROSSLINKING

Mariusz Majchrzak¹, Ezat Khosravi¹, Peter Hine²

¹*IRC in Polymer Science and Technology, University of Durham,*

²*IRC in Polymer Science and Technology, School of Physics and Astronomy, Leeds University*

Biological systems in which damage triggers an automatic healing response have attracted the attention of many researchers lately. It resulted in development of polymer composite materials which are able to heal/repair themselves when micro-cracks have been formed [1, 2].

In general, healing in polymeric resins can be defined as a means of halting crack growth and restoring some degree of the virgin material's fracture toughness *via* the healing process.

The main aim of our research is to develop self-healing polymer systems that will be expected to mimic many of the features of a biological system. The self-healing system proposed here is based on incorporating microencapsulated mixtures of mono- and di-functional norbornene monomers (healing agent) and Grubbs' ruthenium initiators (catalyst) within the epoxy resin (polymer matrix).

In this poster we focus on our initial studies on developing self-healing system based on ROMP of mixtures of the above mentioned norbornene derivatives compounds. The self-healing process in our system is based on polymerisation and in-situ crosslinking using Grubbs' ruthenium catalysts - 1st and 2nd generations.

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Directed Phase Separation of Polymer Blends on Filled Patterned Polymer Brushes

Claire Wilshaw, Anthony J. Ryan

Department of Chemistry, University of Sheffield, Brookhill, Sheffield, S3 7HF

A filled patterned polymer brush (or binary patterned brush) can be defined as a substrate covered by adjacent regions of two different polymer brushes. Various methods have been used to produce these materials, but until last year, these were all based on the use of photolithography, and were specific to particular polymers. We aim to use a soft lithography based approach to produce filled patterned polymer brushes on silicon substrates. Recently, Huck et al¹ published a soft lithography based approach to the production of a variety of filled patterned brushes on gold substrates. However, the use of silicon as a substrate and trichlorosilane based ATRP initiators present additional challenges. The likely synthetic route can be split into five steps:

1. Clean silicon wafer and microcontact print the trichlorosilane ATRP initiator.
2. 'Grow' poly(methyl methacrylate) brush by ATRP.
3. Dehalogenate the active chain ends.
4. Coat the remaining bare regions of the substrate with ATRP initiator.
5. 'Grow' polystyrene brush by ATRP.

We present our current progress towards this goal. Brushes will be characterised using a variety of methods including ellipsometry, AFM, SEM and XPS.

Most polymer blends are only miscible under certain conditions, and undergo phase separation when they are quenched into the two-phase region of their phase diagram.

The behaviour of a blend depends on its composition, temperature, and how long the mixture is given to self organise. Quenching into the two phase region causes spinodal decomposition: spontaneous phase separation into a co-continuous structure, with a preferred length scale dominating. A chemically patterned substrate can influence the phase separation of thin films of polymer blends². We aim to investigate the effect of a binary patterned polymer brush on a thin film of a polymer blend. This could lead to applications in the manufacture of complex microstructured materials by self assembly. However, phase separation on binary patterned brush substrates is likely to be complex – the brush layer can interact with the polymer blend, leading to interesting new morphologies.

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The effect of solvents in Poly- dioctyl-fluorene-co-bithiophene (F8T2) / Poly-methyl-methacrylate (PMMA) interfaces

Ana B.Rodríguez-Rodríguez^{1*}, Anthony M. Higgins², Henning Sirringhaus³, Samson Chang²,
Shalom Goffri³, Chuan Liu³, Rob Dalglish⁴,
Fabrice C. Simon⁵, J. Martin¹, Mark Geoghegan¹

¹ University of Sheffield. Department of Physics and Astronomy. Sheffield S3 7RH, UK

² Multidisciplinary Nanotechnology Centre, School of Engineering, Swansea University, Swansea SA2 8PP, UK

³ Cavendish Laboratory. University of Cambridge. Cambridge CB3 0HE, UK

⁴ Isis. Rutherford-Appleton Laboratory. Chilton. Didcot OX11 0QX, UK

⁵ LLB. EA-Saclay, 91191 Gif-sur-Yvette Cedex, FRANCE

*a.rodriquez@sheffield.ac.uk

Using conjugated polymers as the active materials in electronic and optoelectronic devices opens up the possibility of fabricating all-polymer devices using solution processing technologies. The fabrication of good quality organic field-effect transistors (OFETs) is crucial to a number of polymer-based devices, such as active matrix displays and integrated circuits for product identification tags. In this study we investigate the structure of poly- dioctyl-fluorene-co-bithiophene (F8T2) / poly-methyl-methacrylate (PMMA) bilayers and the relation between interface roughness and device performance. This is carried by the use of surface and interfacial analysis techniques such as neutron reflectivity (NR) and Scanning Force Microscopy (SFM). Samples had deuterated PMMA spin coated from toluene as the gate dielectric, five different molecular weights were employed for the study. The semiconducting polymer was F8T2, spun from solution. For the F8T2 solution, several ratios of mixed toluene and cyclohexane were used as the solvent.

It was observed the proper mixture of solvents for F8T2 spin-casted on a PMMA layer will lead to the production of good bilayers whose interfacial roughness are determined by the solvent mixture. Along to these samples, OFETs, with the same film characteristics, were made. They proved to be independent on the interfacial roughness when the gate dielectric was spun on top of the semiconducting polymer but not in the inverse configuration.



The Effect of Weave Style on the Mechanical Properties of Single Polymer Composites.

*P.J.Hine, Y.Bozec and I.M.Ward
IRC in Polymer Science and Technology
School of Physics and Astronomy, University of Leeds, Leeds, UK*

ABSTRACT

Single, or self reinforced, polymer composites are an emerging and important new class of composite materials. What makes them unique is that both the reinforcing elements and the matrix phase are polymers, and in most cases the same polymer: this contrasts with traditional composite materials where the reinforcing element is usually a glass or carbon fibre. The reinforcing polymer fibres or tapes are produced by a solid state drawing process which gives very high preferred molecular orientation, resulting in high specific stiffness and strength. The resulting composites, made from these highly oriented polymer fibres or tapes, display a unique combination of lightweight, good mechanical properties and exceptional impact performance and can be much more easily recycled compared to carbon or glass filled polymer composites. These materials can be considered as forming a bridge between isotropic polymers and traditional fibre reinforced composites, having the density, thermoformability and recyclability of pure polymers with mechanical properties that are competitive with, for instance, chopped glass reinforced polymer composites.

A key issue is what structure to use for the reinforcing element component. The most convenient arrangement is to weave the oriented polymer fibres or tapes into a cloth: multiple layers of cloth can then be 'hot compacted' to form the final composite material. Woven layers have been found to be the most suitable form for a continuous process: the current commercialised material (Curv™) utilises a double belt press fed by a number of rolls of woven oriented polypropylene tapes. Commercial products have begun to appear using these materials, including a Nike Shinguard (BPS Contour) and a range of suitcases by Samsonite (X-Lite).

In this poster we will describe an investigation into the effect of the woven architecture (the weave style) on the mechanical properties of the hot compacted sheet. It will be shown that, due to the woven nature of the material, both the in-plane modulus and thermal expansion are a combination of the longitudinal and transverse properties of the oriented elements, as well as any effects of crimp due to the weave style. In addition, the woven architecture imparts an elastic constraint to the material, by virtue of the elastic anisotropy of the component fibres and tapes. In this work we have developed a simple model to aid understanding of the effects of mechanical and thermal anisotropy, and we will compare its predictions with experimental measurements for both woven polyethylene fibres and woven polypropylene tapes. Finally, the weave style affects the aesthetic of the final product and examples will be shown to illustrate this aspect.



Elastic Fibres Based on Polyolefin Elastomers

Guido Bramante, Federica Albiero, Mikhail Gelfer, Hongyu Chen, Benjamin Poon, Fabio D'Ottaviano, Deborah Chiu, Jose M. Rego, Bernard Dems.

*The Dow Chemical Company
Specialty Plastics and Elastomers Research
2301 Brazosport Blvd.
Freeport, Texas 77541
United States of America*

ABSTRACT

The discovery of INSITE™ Catalyst technology in the mid 1980's enabled The Dow Chemical Company to offer new elastic fibre capabilities. DOW XLA™ Elastic fibre is the first crosslinked polyolefin fibre offered in the textile market. Developed and commercialized by The Dow Chemical Company, DOW XLA™ Elastic fibre brings to the apparel market unique value propositions such as chlorine resistance, UV resistance, process chemicals resistance, unique comfort fit and durability. The elastomeric behaviour of this unique product is associated with a molecular network of polymer chains with two types of junctions: fringed micelle crystallites and covalent crosslinks. While the level of crystallinity affects tensile and recovery behaviour at ambient temperature, the covalent crosslink network plays a fundamental role in maintaining the integrity of the polymer network at elevated temperature. Because of this unique structure DOW XLA™ Elastic fibre offers excellent thermal resistance properties, and low temperatures for heat-setting. In this work, the technical features of DOW XLA™ Elastic fibre are explained and value propositions exhibited.

DOW XLA™ Elastic fibre has been adopted by top brands all over the globe confirming the great interest of the textile industry of Dow's innovative fibre. Since 2004, DOW XLA™ Elastic fibre is used in most of the textile applications like denim, ready to wear clothing, work wear, swimwear, active wear, and intimates.

DOW XLA Elastic Fibre™ is a trademark of the Dow Chemical Company



Engineering Polymer Informatics

Nico Adams, Jen Ryder, Nicholas England, David Jessop, Peter Murray-Rust

Unilever Centre for Molecular Science Informatics, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW

A B S T R A C T

Polymers are ubiquitous in modern life and are present in almost every item of daily use. Despite their large and growing market, polymer data, which can be used for the development of new formulations and polymeric products is hard to come by, as it is usually available only in proprietary databases or accessible in an unstructured and badly curated form, which is hard for computers to extract and process. This presents a serious obstacle to the rapid computer-aided design of new products.

The poster describes the development of an information model for polymers. It summarizes the development of Polymer Markup Language (PML), which allows a granular description of polymer structure in a semantically rigorous and parsable way. Furthermore, it is designed to hold other types of polymer relevant information, such as group contributions, reaction information and property data. The language lives in an ecosystem of other markup languages, which can all be used to describe polymer(-related) properties.

Furthermore, the poster discusses the development of a polymer ontology. Ontologies are data models representing a domain, in our case polymers, and are used to reason over objects in the domain and the relationships between them. Ontologies are valuable for structured comparative searching of knowledge, document classification, knowledge sharing between information systems and the development of machine generated hypotheses.



FIBRIL-TYPE STRUCTURES FROM TETRAPEPTIDE-POLYMER CONJUGATES

N. Tzokova, C. Fernyhough*, P. Topham*, S. Martin*, A.J. Ryan* D. Adams**, and M. Butler***

**University of Sheffield, Sheffield, S3 7HF*

***Unilever Corporate Research, Colworth Park, Sharnbrook, Bedfordshire, MK44 1LQ*

ABSTRACT

The self-assembled structures in dilute aqueous solution of conjugates consisting of PEG and hydrophobic short homopeptide were investigated by means of transmission electron microscopy (TEM), atomic force microscopy (AFM), rheology, small-angle X-ray scattering (SAXS) and circular dichroism spectroscopy (CD). The samples were prepared by molecularly dissolving the conjugate in good solvent for both parts and followed by slow addition of water solution to promote self-assembly. Further for some of the samples the solvent was removed via dialysis against pure water. TEM, AFM, and SAXS show presence of fibrils type structures, which morphology and dimensions depend strongly of the common solvent used for molecular dissolving as well as if the sample has been dialysed. CD indicates that the secondary structure of the peptide in the solution is a beta-sheet type. The rheology (frequency sweep, RT) results shows for all samples at the plateau region (low frequencies) that the values for G' is bigger than G'' . G' was an order of magnitude higher for sample prior to dialysis compare corresponding dialysed one. Interesting was that the viscosity dips at intermediate shear rates.



Flow visualisation of the micromoulding process.

*BEN WHITESIDE
POLYMER IRC
UNIVERSITY OF BRADFORD*

A B S T R A C T

Flow phenomena during the filling of a micro-injection moulding (micromoulding) cavity have been observed using a custom optical train. The total time taken for material to enter the cavity, cool and freeze is typically of the order of ten milliseconds, therefore the system is required to obtain images at frame rates in excess of 3000 frames per second. A range of data can be acquired including flow front profile and position, birefringence data and shrinkage measurement using Newton's rings. This data provides a valuable insight into material behaviour during the process for a range of thermoplastics, biomaterials and nano-filled composites.



Functional Nanomaterials *via* Living/Controlled Self-Assembly of Organometallic Block Copolymers

Xiao-Song Wang
Department of Colour and Polymer Chemistry
University of Leeds

A B S T R A C T

Living/controlled aggregation of organometallic block copolymers in solution will be presented. As a result, the cylindrical micelles of organometallic block copolymers can be controlled in terms of their length, chemical composition and architecture. In addition, the organometallic nature of the polymers has endowed the micelles with a range of interesting property for functional nanomaterials.



Gene Delivery using pH-Sensitive Polymer Vesicles

Hannah Lomas^{1*}, Irene Canton¹, Marzia Massignani¹, Sheila MacNeil¹, Adam Blanazs², Jianzhong Du², Steven P. Armes², Andrew L. Lewis³ and Giuseppe Battaglia¹

¹*Biomaterials and Tissue Engineering Group, Department of Engineering Materials, The Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield, S3 7HQ, UK.*

²*Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK.*

³*Biocompatibles UK Ltd., Chapman House, Farnham Business Park, Weydon Lane, Farnham, Surrey GU9 8QL, UK.*

*E-mail: h.lomas@sheffield.ac.uk

We present a novel gene delivery vector based on the ability of a synthetic amphiphilic block copolymer to mimic biological phospholipids by forming membrane-enclosed structures, specifically nanometer-sized vesicles. The block copolymer comprises a biocompatible, hydrophilic polymer, PMPC [poly(2-methacryloxyethyl phosphorylcholine)], and a pH-sensitive polymer, PDPA [poly(2-(diisopropylamino)-ethyl methacrylate)], which can bind nucleic acids. The block copolymer self-assembles into vesicles at neutral pH, and dissolves completely as unimers at endocytic pH. GFP-encoding plasmid DNA has been successfully encapsulated inside the polymer vesicles, and delivered intracellularly. We report that DNA-loaded vesicles are able to transfect both human primary cells (human dermal fibroblasts) and an animal cell line (Chinese hamster ovary cells) through the pH- triggered collapse of the vesicle.



HIGH STRENGTH POLYMERS - COMBINING FIBRE REINFORCEMENT AND SOLID PHASE MOLECULAR ORIENTATION - EXPERIMENTAL INVESTIGATION'

*Omar Alkoles, Fin Caton-Rose, Pete Hine, I M Ward, P D Coates
Polymer IRC,
University of Bradford*

ABSTRACT

Short glass fibre reinforcement is well established as a means of significantly improving 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 a fibre reinforced 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. Whilst this statement is true for melt processing, it is possible to further improve composite mechanical properties by orientation of the polymer chains within the matrix material.

Such orientation can be produced during solid phase processes such as roller or die drawing. Within these posters we describe an initial investigation of the combining effects of short glass fibre reinforcement of polypropylene and solid phase polymer matrix alignment through die drawing on final fibre orientation, fibre degradation, mechanical properties and finite element analysis of the process.



HIGH STRENGTH POLYMERS - COMBINING FIBRE REINFORCEMENT AND SOLID PHASE MOLECULAR ORIENTATION - FINITE ELEMENT ANALYSIS

*Fin Caton-Rose, Omar Alkoles, Pete Hine, I M Ward, P D Coates
Polymer IRC,
University of Bradford*

Abstract

Short glass fibre reinforcement is well established as a means of significantly improving 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 a fibre reinforced 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. Whilst this statement is true for melt processing, it is possible to further improve composite mechanical properties by orientation of the polymer chains within the matrix material.

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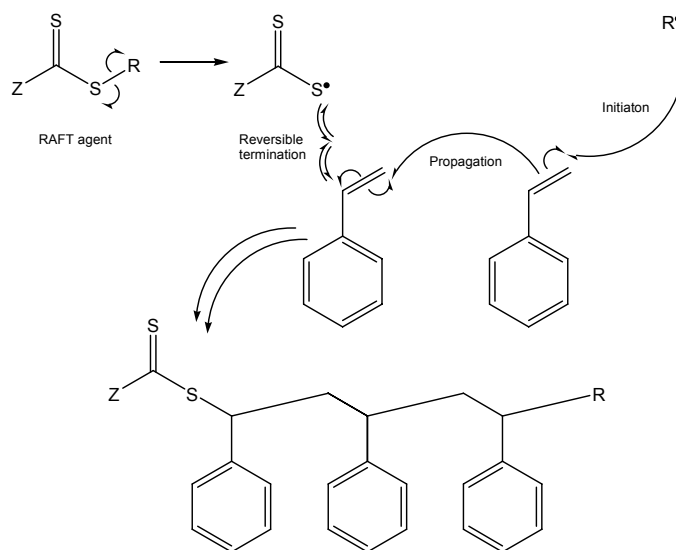
Imparting End-functionality to a Polymer in a One-step Synthesis via RAFT Polymerisation with the use of a Functionalised RAFT Agent

Will Bergius
Polymer IRC, Durham University

ABSTRACT

Radical addition-fragmentation transfer (RAFT) polymerisation is an extremely versatile controlled radical polymerisation (CRP) technique. The main advantages of RAFT over other CRP techniques such as ATRP and even NMP is that a far wider range of monomers can be polymerised, more functionalities are tolerated, as well as a broad range of solvents including water, a wide range of temperatures are appropriate (20-150°C), and it is suitable for use in several different types of process (bulk, suspension, emulsion etc).

Our work is focussed on the polymerisation of a monomer containing a functional group that would make it incompatible with most other controlled methods of polymerisation. We aim to design several functionalised RAFT chain transfer agents in order to make various end-functionalised polymers with low polydispersities.

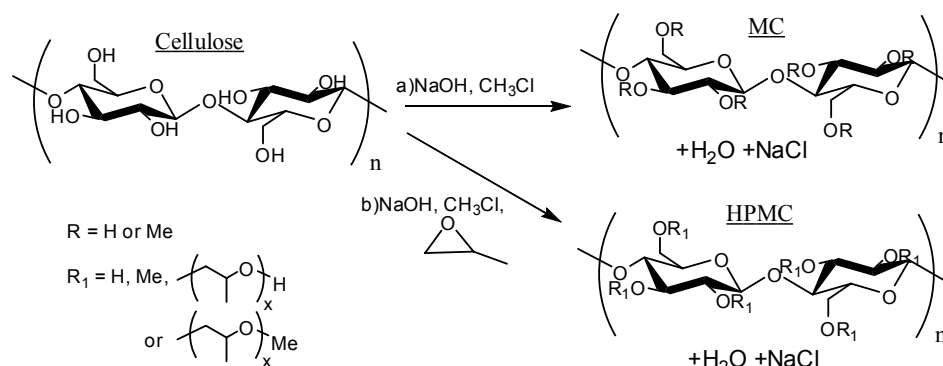


The above diagram shows the net result (not an accurate mechanism!) of polymerising styrene with a generic RAFT chain transfer agent, showing how the R group from the RAFT agent becomes the end group of the resulting polymer. It is this R group that can be tailored (within certain limitations) to impart the specific end-functionality desired in the resulting polymer.

Light Scattering Analysis of Aqueous Cellulose Ether Systems.

Oscar Kelly; Yu Hao; Dr. Patrick J. Fairclough; Prof. Anthony J. Ryan; @ The University Of Sheffield Polymer Centre.

Cellulose ethers have been utilised in a wide range of industrial applications for many years. Predominately, uses have focused around the methyl and hydroxypropylmethyl cellulose varieties. They are traditionally prepared using heterogeneous aqueous slurry reaction mixture in a bulk reactor;



Scheme 1:- traditional reaction pathways for the synthesis of methyl cellulose and hydroxypropylmethyl cellulose compounds.

The industrial applicability of these polymeric materials stems from their aqueous properties. In aqueous solution they demonstrate very high water retention capabilities, a property which is utilised in building materials such as cement and mortar. They also demonstrate a solution-gel transition upon heating. This process is coupled to a cloud point and is completely thermo-reversible, though with significant hysteresis. The gelation properties have been investigated for use within pharmaceutical industries as possible drug delivery matrices.

The mechanism of gelation is still poorly understood. Some previous work has suggested that the process is driven by spinodal decomposition; the coupling of cloud point to the transition is also corroborative to this idea. Microscopy images of the systems suggest that at the transition temperature the system undergoes the beginnings of spinodal separation. This work is focussed on utilising small angle light scattering techniques to determine the length scale of the spinodal separation. The long term aim of the small angle light scattering experiments is to construct phase diagrams for aqueous cellulose ether systems to help optimise their property-performance capabilities.

The techniques of dynamic and static light scattering have also been employed to investigate how the relative size of molecules changes as a function of temperature. With the hypothesis that, if the transition is phase separation driven then there should be a collapse in molecular size at the transition temperature for solutions well below the critical overlap concentration, c^* . As a result of the polymer-solvent interaction changing from an attractive to a repulsive interaction and the polymer collapsing on itself.

Mechanism of phase separation in thin polymer film in controlled solvent atmosphere

Parvaneh Mokarian, Sasha Y. Heriot, Jonathan R. Howse, Mark Geoghegan and Richard A.L.Jones

*Polymer physics group
Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH*

P.Mokarian@shef.ac.uk

ABSTRACT

Immiscible polymers, particularly thin polymer films are widely used and have potential for many practical applications for example polymer based field-effect transistors, LEDs and photovoltaic devices. Their phase behaviour, morphology and thermodynamic properties have been object of intensive studies during the past few decades. The efficiency of opto-electronic devices is highly related to film morphology, it is therefore very important to have a deep understanding of the film formation process. Knowing which, we could tailor the structure providing good device efficiency. In spite of much work and many models for spin coating process, there is not a universal theory to explain the mechanism of polymer film formation and predict the phase behaviour precisely. One possible reason could be that so far many of the studies have been restricted to analysis of the structure of the final film. The process being non equilibrium, it is not very accurate to deduce complex details from the end point alone. On the other hand, due to fast solvent evaporation, it is very difficult to study the process during film formation. In our study we have developed a technique based on small angle light scattering and light reflectivity that make it possible to study the process of phase separation in spin cast films *in situ* during formation. We shall present data obtained from the machine during the formation of PS/PMMA films under controlled solvent atmosphere and discuss the effect of solvent vapour concentration on phase separation of PS/PMMA thin films. The data obtained from the experiment will be compared with a model demonstrating a better understanding of film evolution.



Nanofunctionalization of Hydrogels using amphiphilic copolymers.

Miriam V. Flores-Merino¹, Anthony J. Ryan², Gwen Reilly¹, and Giuseppe Battaglia¹.

1. Biomaterials and Tissue Engineering Group, Department of Engineering Materials, The Kroto Institute, University of Sheffield, Sheffield, UK.

2. Department of Chemistry, University of Sheffield, Sheffield, UK

ABSTRACT

We have developed chemical hydrogels containing nanoparticles made of amphiphilic (hydrophilic/ hydrophobic) copolymers. These self-assemble into spherical micelles, cylindrical micelles, and vesicles according to the hydrophile/hydrophobe ratio. The main objective of the work is to studying how these nanoparticles improve the characteristics of the hydrogels to make them suitable for biomedical applications such as tissue engineering, cell, growth factor or drug delivery systems for anticancer therapies.



Neck-in Prediction in Film Casting using the Pom-Pom constitutive equations

Suneel Kunamaneni
MuPP/KTN Fellow

ABSTRACT

One of the main application of LDPE resins are in cast films. In this process a melt curtain is extruded through a narrow die slot, across an air gap or a liquid bath, and then onto a pair of (or just a single) take-up or chill rolls (see figure). Efforts to increase production speed or reduce film thickness by going to higher draw ratio (take-up speed/extrudate speed) are hampered by edge neck-in and bead formation, as well as other process instabilities (draw resonance, edge weave). These instabilities give rise to spontaneous thickness and width oscillations.

A good predictive model requires a constitutive relation that adequately describes the rheological response of the melt at the shear and extension rates of the process. In this study we predict and compare neck-in for two different LDPE grades using the engineering analysis of Doi combined with the Pom-Pom constitutive model. The Doi analysis is based on the Deborah-Erwin model which assumes uniaxial extension at the edge and planar extension in the centre part of the film.



A Novel Laboratory Distributive and Dispersive Mixer & Applications.

*Professor H.Benkreira, Dr R.Patel, Mr R.Butterfield
IRC in Polymer Science and Technology
School of Engineering, Design and Technology
University of Bradford, Bradford. UK*

ABSTRACT

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, sponsored by EPSRC grant GR/S14337/01 includes a feasibility study of a newly developed prototype laboratory mixer to assess and determine its dispersive and distributive mixing characteristics. The work is based on an invention by the applicants to reproduce the dispersive-distributive mixing achieved in large co-rotating twin screw extruders but in a very small device holding typically 10 to 100g of material. The principle of operation is based on combining two opposing flows: a single screw extruder circulation flow with a twin screw extruder mixing flow. The mixing is carried out as a batch but on its completion, the single screw extruder flow is reversed and becomes co-current with the twin extruder flow to enable the discharging of the batch through a die. This invention provides a new opportunity to develop new products quickly, safely and cheaply. It has also other spin-offs particularly as a research tool for studying mixing and developing new, more efficient, mixing flows. The poster will describe experiments carried out to demonstrate the feasibility of this mini mixer to reproduce large scale mixing.



Numerical Simulations of Suspensions of Elastic Particles in Polymer Melts

*Dr Ahamadi Malidi & Dr Oliver Harlen
School of Mathematics & Polymer IRC, University of Leeds*

ABSTRACT

Elastic particles are often added to polymer melts as impact modifiers. Unlike rigid fillers, elastic particles can deform during flow and so modify the rheology of the polymer melt. To study the rheology of such multiphase systems we perform direct simulations of the motion of the elastic particles in a viscoelastic matrix under simple shear or extensional flow.

In order to make the computations tractable we solve the flow in a unit cell containing a small number of particles with doubly periodic boundary conditions on a self-replicating lattice to replicate a suspension on an infinite domain. In shear flow our method is equivalent to the Lees-Edwards boundary condition, while in extension we use the Kraynik-Reinelt cell structure that provides a self-replicating lattice. This allows simulations to be carried out to large strains. The continuous phase is modelled using the tube based constitutive models developed at the Leeds Polymer IRC, such as the pom-pom model for branched polymer melts or the Roliepoly model for linear polymers.

In shear flow, isotropic filler particles deform into ellipses. However, unlike rigid elliptical particles which rotate during shear flow, elastic particles perform a “tank-treading” motion in which the surface of the particle rotates, but bounding shape remains fixed. The shear viscosity is found to be lower than for a polymer filled with rigid particles, however, there is now a phase lag due to the particle elasticity. We will also show comparisons for extensional flows where the filled particles become stretched in the direction of extension.



A Parameter-Free Prediction of Non-Linear Polymer Rheology from Molecular structure

M. Kapnistos¹, C. Das¹, D. J. Read², T. C. B. McLeish¹

¹Polymer IRC, Department of Physics & Astronomy, University of Leeds

²Department of Applied Mathematics, University of Leeds

Abstract

In recent years the association between molecular structure and linear rheology has been established and well-understood through the tube concept and its extensions (e.g. McLeish, Adv. Phys. 2002). However, for industrial branched polymeric material at processing conditions, the nonlinear properties are more important. A large number of phenomenological models have been developed to describe the nonlinear response of polymers. But none of these models take in account of the underlying molecular structure, leading to a fitting procedure with arbitrary fit parameters rather than a parameter free prediction scheme.

In our approach, we use a numerical scheme (Das et al, J. Rheol. 2006) to calculate the relaxation of branched polymers from an ensemble of molecular structure in the linear regime. We then, separate the contribution to the stress decay to a large number of pom-pom modes (McLeish et al, J. Rheol. 1998) with the stretch time and the priority variables corresponding to the actual ensemble of molecules involved (Inkson et al, J. Rheol. 1999). These multimode pom-poms allow us to predict the nonlinear properties without any fitting parameter.



Peptide-functional poly(*N*-isopropylacrylamide)s

J.W. Lapworth¹, A.M. Miles¹, S. Rimmer¹ & P.V. Hatton²

¹*Polymer Centre, Department of Chemistry, University of Sheffield, UK*

²*Department of Adult Dental Care, School of Dentistry, University of Sheffield, UK*

Poly(*N*-isopropylacrylamide) (PNIPAM) is a prototypical thermoresponsive polymer which has shown great promise as the active component in smart materials for a wide range of applications¹⁻³. The polymer is unusual because it is soluble in water only *below* a lower critical solution temperature (LCST): At this temperature a rapid and reversible transition occurs which is manifested as either reversed solubility, for isolated polymer chains, or swelling-deswelling behaviour in crosslinked networks. The ability to functionalise such polymers with well defined peptide sequences is desirable both in terms of their chemical functionality and their specific interactions with biological systems at the molecular level.

In this work, the aim is to prepare well defined peptide sequences using solid phase peptide synthesis (SPPS) and incorporate them into PNIPAM polymers. Highly-branched polymers were afforded by polymerization of *N*-isopropylacrylamide in the presence of a styrene-functional RAFT agent². The polymer end groups were modified by reaction with 4,4'-azobis(4-cyanopentanoic acid) to give acid functionality. Following activation using NHS/DCC the polymer was reacted with the free amine from a synthetic tripeptide sequence to afford peptide-ended highly-branched polymer. The reversed-solubility of the branched materials was maintained, albeit with a shift in the LCST.

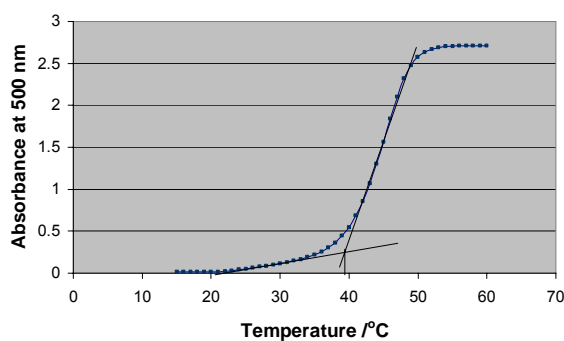


Figure 1: Lower critical solution temperature of highly branched poly(*N*-isopropylacrylamide) with acid end groups.

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pH Responsive Block Copolymer Vesicles

C. J. Fairgrieve, J. P. A. Fairclough, A. J. Ryan,
Department of Chemistry, University of Sheffield, Sheffield, S3
7HF, UK.*

This study focuses on the dilute solution behaviour of pH responsive block copolymers of dimethylsiloxane and acrylic acid. The acrylic acid block has been hydrolysed from t-butyl acrylate and the polymer contains a residual element of the t-butyl acrylate.

Amphiphilic block copolymers in dilute solution form aggregates, commonly vesicles and micelles depending on the relative volume of the hydrophilic and hydrophobic blocks.

Analysis has been carried out by light microscopy and dynamic light scattering to observe the various aggregate structures formed in dilute aqueous solution. Further studies of the systems are currently being carried out by Transmission Electron Microscopy and Small Angle X-Ray Scattering.

The presence of varying levels of hydrophobic t-butyl acrylate groups within the hydrophilic acrylic acid block, results in a change in the transition pH of the polymers. This alters the responsive behaviour of the polymers.

The intention of this work is to study the various structures formed by PDMS-PAA block copolymers and the mechanism(s) involved in transitions between the structures. This can then be used to improve the understanding of the release of an encapsulated substance.



PMMA Clay Nanocomposites

Judith Elder, Nigel Clarke and Lian Hutchings

Polymer IRC, University of Durham, Durham, DH1 3LE, UK

E-mail: judith.elder@durham.ac.uk

ABSTRACT

Polymer clay nanocomposites (PCN) consisting of a poly(methyl methacrylate) (PMMA) matrix and the organically modified clay, Cloisite 15a were studied. The PCN were synthesised in-situ using a suspension polymerization method in the presence of a chain transfer agent. The PCN have been characterised using gel permeation chromatography (GPC), x-ray diffraction and oscillatory shear rheology. By varying the amount of clay present in the PCN it was hoped that a better understanding of the effect of the clay on the polymer matrix would be obtained. Also an insight into the effect of the clay on the molecular weight of the polymer matrix could be obtained.

The x-ray diffraction indicates that a high degree of intercalation of the clay within the PMMA matrix has been achieved. An increase of 5.3Å in the d001 spacing is seen which confirms the presence of PMMA within the gallery of the clay. The molecular weight of the polymer matrix was determined via GPC. An initial increase in molecular weight was seen with increasing clay content however this effect plateaus off and a constant molecular weight is seen. The largest increase in molecular weight was of 830% which is a significant increase. However further experimentation leads to the conclusion that the change in molecular weight is due to a reaction between the CTA and the clay rather than a reaction between the clay and the propagating PMMA chains.

From oscillatory shear rheology the TTS principle was used to produce master curves of the PCN. A large shift in the reptation relaxation time is seen compared to pure PMMA matrix. It is believed that any effect of the clay on the rheological properties will become hidden due to the large change in the molecular weight. It can also be noted that samples of the same molecular weight but with varying clay content produce similar G' and G'' data.



Poly(ethylene-alt-maleic anhydride) as a route to highly reactive surfaces

David W Johnson, Neil R Cameron

*Polymer IRC, Chemistry Dept., University Science Labs, University of Durham, South Road,
Durham, DH1 3LE*

d.w.johnson@dur.ac.uk

A B S T R A C T

Poly(ethylene-alt-maleic anhydride) belongs to a family of alpha-olefin-maleic anhydride copolymers. These copolymers are characteristic in their structural uniformity, predictable composition and post polymerisation reactivity through the anhydride co-monomer. Traditionally, these polymers find applications as emulsion stabilizers, surfactants and viscosity modifiers. However, it is only relatively recently that the potential for chemical modification was realised.

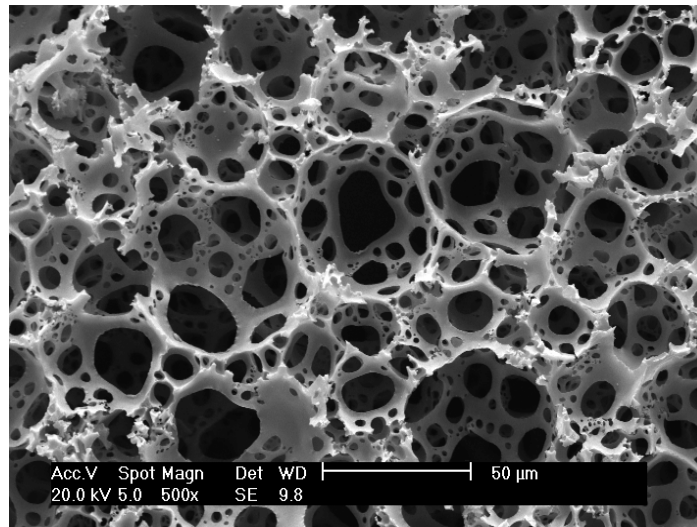
The chemistry and physical properties have been thoroughly examined; through this it became apparent that the polymer would be best utilised in the production of functional surfaces. To this end silicon surfaces, modified with amine bearing silanes, were coated with polymer to provide covalently bound anhydride groups. These groups were then further reacted with appropriate nucleophiles to introduce desirable chemistry to the surface.



PolyHIPEs for Three-Dimensional Cell Culture

Caroline Zeyfert, Neil R Cameron, Stefan A Przyborski

*Polymer IRC, Chemistry Dept. University Science Labs,
University of Durham,
South Road, Durham, DH1 3LE*



SEM Photograph of a typical PolyHIPE

Polymerised -high-internal-phase-emulsions (PolyHIPEs) have been extensively studied and characterised. This process of forming an emulsion and then curing it creates a highly porous material with suggested uses including ion-exchange resins and catalyst supports as well as for cell culture. Varying the parameters of the parent emulsion can control features of the resulting material, such as void diameters and interconnects.

Previous work has been done on tailoring the morphology of styrene-divinylbenzene PolyHIPEs to produce suitable non-biodegradable scaffolds for cell culture. This project focuses on modifying the surface of the PolyHIPE by different means such as chemical and plasmachemical, in order to produce functional materials on which to routinely grow cells *in-vitro*.

The advantage of this material over similar three-dimensional systems is that the underlying structure is similar to that of tissue-culture polystyrene (TCPS), so should not adversely affect cell growth.



Polypropylene-Carbon Nanofibre Composites Manufactured by Hot Compaction

R J Foster, P J Hine and I M Ward

IRC in Polymer Science and Technology, Polymers and Complex Fluids Group, School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT

Nanoscale fillers offer the potential for significant enhancement of a range of polymer properties, as they are available in a wide variety of shapes and mechanical properties. Filler types range from single walled carbon nanotubes, (large aspect ratios, >1000 and moduli approaching 1TPa), to more readily available clays and mineral fillers. The objective of this project has been to study the effects of adding commercially available Carbon Nanofibres (CNF) to the properties of Polypropylene (PP).

Hot Compaction, a process developed at the University of Leeds, utilises high modulus, highly oriented elements to form thick section, homogeneous sheets without the need to introduce a second phase of different chemical composition. These ‘single polymer’ composites are produced by selective surface melting on the surface of the oriented elements; on cooling, this molten material re-crystallises to form a matrix phase and bind the oriented elements together. Blending of PP-CNF has been achieved using a twin screw extruder, with processing conditions optimised for maximum tensile mechanical properties, specifically Young’s modulus. The nanocomposite has been drawn into oriented tapes and subsequently taken through the hot compaction process, again optimising to achieve maximum Young’s modulus. The portfolio of mechanical properties of the isotropic and hot compacted nanocomposite composites will be reported. In addition, differential scanning calorimetry (DSC), dynamic light scattering (DLS) and scanning electron microscopy (SEM) has been used to investigate the structure-property relationship of the PP-CNF material.

Previous work on hot compaction [1-3] has shown that a crucial property of the hot compacted material is the delamination force required to peel apart the woven layers in the composite structure. Recent work has shown that the incorporation of CNF to the hot compacted PP sheet significantly improves this force required to delaminate the layers. Both pure and composite interleaved films have also been introduced, and the effect that these films have upon the peel strength will also be reported.

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Responsive weak polyelectrolytes: from brushes to single chains□□

M. P. Weir, A. J. Parnell, S. Y. Heriot and R. A. L. Jones□□
Department of Physics and Astronomy, University of Sheffield

Polyelectrolytes are polymer molecules with a fraction of charged monomers along the chain. In strong polyelectrolytes the charges are fixed and hence the fraction of charged monomers is constant. In a weak (or annealed) polyelectrolyte the charges are not fixed but instead the degree of charging is dictated by an equilibrium between association/dissociation of salt moieties along the chain. The responsive nature of polyelectrolytes can be explored by tethering them at one end to a surface, e.g. silicon, at sufficient grafting density to form brushes. Polyelectrolyte brushes demonstrate rich responsive behaviour due to the competition between conformational stretching, osmotic pressure and the electrostatic interactions originating from the charges on the chains. Weak polyelectrolyte brushes are of particular interest because of the added complexity introduced by the variability of the charge fraction.

The responsive nature of weak polyelectrolyte brushes was studied using atomic force microscopy (AFM), ellipsometry, neutron reflectivity, and single molecule force spectroscopy (SMFS). Poly(diethyl-aminoethyl methacrylate) (PDEAEMA) weak polybase brushes grafted from Si surfaces via atom transfer radical polymerization (ATRP) were shown to swell in acidic conditions (pH <4) but to remain in a collapsed conformation in neutral or basic conditions. Neutron reflectivity, AFM and ellipsometry data in D₂O all confirmed that similar poly(2-dimethyl-aminoethyl methacrylate) (PDMAEMA) brushes were also swollen by an applied electric field.

SMFS was used to study conformational changes at the molecular level in poly(methacrylic acid) (PMAA) weak polyacid brushes. PMAA brushes grafted from the underside of an AFM cantilever using ATRP were interacted with a bare Si surface and were shown to adopt more extended conformations in basic conditions (pH >10). The ultimate refinement of this SMFS experiment is a measurement of the single molecule motor cycle, a single polymer molecule cycling its conformation from collapsed to stretched in response to an external trigger. In the proposed scheme, PDMAEMA chains will be grafted to the tip of an AFM cantilever at low grafting densities. SMFS will be used to study the chain conformation as a function of pH. In-situ cyclic variation of the pH of the sub-phase by an oscillating chemical reaction could lead to the force measurement of an autonomous molecular motor cycle.



RHEOLOGY OF 4-ARM POLYSTYRENE STAR-SHAPED POLYMERS

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

ABSTRACT

A series of monodisperse 4-arm polystyrene star-shaped polymers with varying molecular weight have been synthesized using anionic polymerization techniques. The series covers the range from unentangled ($N/N_e < 1$) to highly entangled ($N/N_e \sim 20$).

The rheological behaviour of these polymers has been studied using an AR2000 rheometer (TA instruments) with 25mm diameter parallel plates. Data was obtained in the linear viscoelastic regime, over a range of temperatures (140-200°C), using small strains. Time temperature superposition was then employed to shift the individual data sets for each of the molecular weights to produce a master curve at a reference temperature of 160°C.

The data was fitted with the Milner-McLeish theoretical model for stress relaxation in star polymers [1] using standard parameters for PS (plateau modulus ($G_0 = 2.2 \times 10^5$ Pa), entanglement molecular weight ($m_e \sim 15000$ g mol⁻¹), segment length ($b \sim 0.7$ nm), Rouse relaxation for an entanglement segment ($\tau_e \sim 1.5 \times 10^{-3}$ s)).

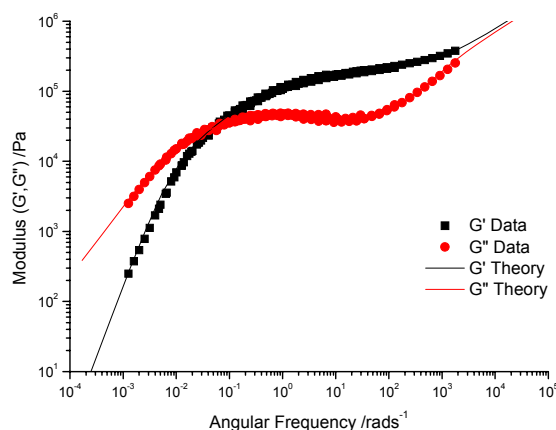


Figure 2: Comparison of data and theory for PS star with 140k arm molecular weight.

Reasonable agreement was found between experiment and theory using a single value of m_e , however it was found that it was possible to obtain very good agreement if the value of m_e was increased slightly with increasing arm molecular weight (c.f. Figure 1).

[1] Milner S. T., McLeish T. C. B., *Macromolecules*, **1997**, *30*, 2159.



Rheo-optical study of polystyrene matrix filled with highly cross-linked polystyrene beads.

M. Tassieri¹, J. Embery¹, T. Lord², C. Tufano³, P. Hine¹

¹School of Physics & Astronomy, University of Leeds, LS2 9JT, UK.

²Dept. of Chemical Engineering, University of Cambridge, CB2 3RA, UK.

³Dept. of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600MB Eindhoven, Netherlands.

ABSTRACT

A comprehensive rheo-optical study has been carried out on a polydisperse commercial polystyrene, filled with highly cross-linked PS-beads (normally used for gel permeation chromatography, GPC). The beads have an average diameter of 10 μm . Blends with a mass/volume fraction of 1%, 5% and 10% have been investigated. The matrix and the beads have approximately the same refractive indices due to the fact that they are both PS. This limits the turbidity allowing the use of rheo-optical techniques to study the blends properties.

In order to understand the effect of filler concentration on the rheological behaviour of the composite blends, results obtained by performing (1) linear and (2) non-linear shear rheology, (3) extensional rheology, (4) die swell, (5) Multi-pass rheometer (MPR) tests, (6) Linkam shear cell tests (CSS 450, Linkam Scientific Instruments) and (7) scanning electron microscopy (SEM) image analysis were compared.

The main results are summarised as follows: (I) the viscosity increases linearly with filler concentration, (II) the PS's viscosity overshoot in the transient measurements is reduced by the presence of the filler, (III) an increase in viscosity at low strains, followed by debonding around the PS beads at larger strain units and higher strain rates, (IV) die swelling decreases linearly with filler concentration ($\sim 6\%$ per mass fraction), (V) MPR results show an increase in flow birefringence with increase in fraction of beads, coupled with an increase in pressure drop. Cavitation is also observed when the flow has ceased, (VI) real-time cavitations, chaining and banding of the particles are observed in shear flow, (VII) SEM image analysis confirm *debonding* and *cavitation*. This phenomenon occurs for all three blended systems investigated under all flow conditions applied.



Self assembly of a polybutadiene-poly(methacrylic acid) copolymer in water: Effect of pH on morphology and kinetics

*Christine Fernyhough**, *Giuseppe Battaglia[†]* and *Anthony Ryan**

**Department of Chemistry, University of Sheffield*

[†]Department of Engineering Materials, University of Sheffield

ABSTRACT

Polybutadiene-poly(methacrylic acid) belongs to a class of materials known as amphiphilic block copolymers. The polybutadiene is very hydrophobic but it is covalently bonded to poly(methacrylic acid) which is hydrophilic in character. The copolymer can be directly dissolved in water where it forms different structures depending on the pH. Increasing the pH increases the degree of ionisation of the PMAA and thus the degree of repulsion between neighbouring chains. As a result, very large vesicles become smaller vesicles and then worm-like micelles and finally micelles are formed as the solution becomes more basic. Transmission Electron Microscopy, Dynamic Light Scattering and zeta-potential measurements have been used to examine the transitions between the different species and it has been possible to elucidate the mechanisms by which the transitions occur. The kinetics of the transformations have also been studied with the vesicle to cylinder to micelle transition being found to be much quicker than the reverse process.



A Simulation Study of Gas Transport Processes In PET

Simon N. Butler, & David B. Adolf
Polymer IRC, University of Leeds

ABSTRACT

The diffusion of small penetrants through polymer matrices is an area of great interest in a number of areas, notably in medicine and in the packaging industry. Detailed knowledge of how the structure and behaviour of a polymer affects gas transport properties may inform the optimisation of their molecular design. However, although there is significant interest in this area, the simulation of gas transport processes presents a number of challenges.

Firstly, and most significantly, the most interesting and useful regime in which to apply this work is the glassy state. At temperatures below the glass transition, diffusion is a slow process beyond the practical reach of current computational methods. This limits any investigation to the melt state where the timescales associated with gas transport processes (usually on the order of ~ 100 ps for polymeric fluids) are accessible. However, this necessarily means that results obtained in this regime must be extrapolated to be of practical interest.

Also, although direct molecular dynamics of diffusion processes is relatively straightforward, the sorption processes are more difficult. The diffusion of penetrant molecules requires only a bulk polymer phase to be simulated. By contrast, in order to observe both sorption modes, a dual phase gas-melt system is required. However, NpT-MD simulations of such systems suffer rapid disappearance of the gas phase thus removing any sorption processes. Despite these problems, simulation is able to investigate these processes at the atomistic level. Direct access to information about the dynamics of polymers during diffusion processes provides a further reason for persistence in the area of simulation.

We present details of an investigation into simulation methods of examining gas transport and sorption processes in poly(ethylene terephthalate). A novel method developed by Kikuchi and co-workers to enable NpT-MD simulations of gas-polymer systems has been evaluated and compared to available experimental data and existing simulation approaches. The effect of gas sorption and motion on the local dynamics of the melt is also examined.



STABILITY OF EXTRUDATES EXITING FROM THE ROTATING ROLLER DIE

*Andrew Preece
Polymer IRC
University of Bradford*

Abstract:

In the classical extrusion of polymer melts, the die inherently has stationary walls and through these, stresses are developed near them which contribute to melt instabilities. The question arises then, how would these instabilities be affected if the walls were moving? The rotating roller die is a new device in which the walls are moving. It consists of a pair of rollers, which can rotate backwards (counter to the extrusion flow) or forward (for increased throughput). The rotating roller die was originally developed at Bradford University for the production of low-density polymer foams (20kg/m³ or less). The die works on the principle that by rotating the flow counter to the extruder flow, high pressures can be generated without the need of narrowing the die gap. Such an arrangement allows the injection of CO₂ directly into a polymer melt at high pressures. This produces the required solubility hence the low foam densities. In this new research application, we investigate the effect of wall movement, i.e. roller rotation on melt stability and compare the results when the rollers are stationary. The aim of the work is both academic in that it helps explain further the flow origin of melt instabilities but also practical - to develop higher throughput and more stable die operation that currently observed with classical dies.



Synthesis and Characterisation of Flame Retardant Polymers Based on Polyacrylonitrile

A.Cook, J.R.Ebdon, R.England and B.J.Hunt

*The Polymer Centre, Department of Chemistry, University of Sheffield,
Dainton Building, Brook Hill, Sheffield S3 7HF, UK*

A B S T R A C T

Polymers find application in many areas and are now an essential part of everyday life. Despite their many desirable properties they are mostly organic in nature and therefore prone to burning. In many applications an important requirement is that they should be non-flammable. Traditionally they have been rendered flame retardant by the use of additives such as antimony, aluminium and bromine-containing compounds. Large amounts of these additives (up to 40%) are needed to have a significant flame-retarding effect and consequently have an adverse effect on the mechanical properties. There is also concern for the environmental impact of some of these materials.

Our approach has been to incorporate flame retardant monomers into the polymer chain. Much smaller quantities are needed (<5%) and therefore have a minimal effect on mechanical and other properties.

This poster reports on investigations into the copolymerisation of monomers containing phosphorus and nitrogen with acrylonitrile. These comonomers have a beneficial effect on reducing the flammability of polyacrylonitrile. Further studies have looked at the effect of incorporating nanoclays and carbon nanotubes into the polymers in order to further enhance their flame resistance.

The materials have been fully characterised by NMR spectroscopy, size exclusion chromatography, thermogravimetric analysis and scanning and transmission electron microscopies. Their flammability properties were determined by 'limiting oxygen index' measurements.



Temperature dependant phagocytosis of highly branched poly(N-isopropyl acrylamide-co-1,2 propandiol-3-methacrylate)s prepared by RAFT polymerization

S. Hopkins^{1,2}, S. Rimmer¹ and S. MacNeil²

¹ *The Polymer and Biomaterials Chemistry Laboratory, Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK*

² *Tissue Engineering Group, Kroto Research Institute, North Campus, University of Sheffield, Broad Lane, Sheffield, S3 7HQ, UK*

A B S T R A C T

Stimuli responsive polymers have been synthesised and the formulation tuned in order to form sub-micron particles when the temperature is above the lower critical solution temperature (LCST)^[1]. The highly branched NIPAM polymers are not stabilised by a surfactant system, all stabilisation is due to the highly branched poly(NIPAM) architecture of the globules above the LCST.

Fluorescently labelled highly branched poly(N-isopropyl acrylamide-co-1,2 propandiol-3-methacrylate)s^[2] were prepared using reversible addition-fragmentation chain transfer (RAFT) polymerisation. By designing the feed composition it was possible to synthesise polymers with an LCST of between 35 and 37 °C. Therefore, at the usual cell culture temperatures, the polymers are above the LCST and form stable aggregates. Fluorescently labelling with AMMA ensures that the polymers fluoresce in the blue region and can be visualised in fibroblast cells in culture. The phagocytosis was temperature dependant and does not occur below the LCST when the polymers are in the open chain, fully solvated and non aggregated state.

References:

- [1] S. Carter, S. Rimmer, A. Sturdy, M. Webb, *Macromolecular Bioscience*, **2005**, 5, 373-378.
- [2] S. Hopkins, S. Carter, L. Swanson, S. MacNeil, S. Rimmer, *Journal of Materials Chemistry*, **2007**, DOI: 10.1039/b708415c



Templated Formation of Giant Unilamellar Polymer Vesicles with Narrow Size Distributions.

Jonathan R. Howse¹, Richard A.L. Jones², Giuseppe Battaglia³, Robert E. Ducker⁴, Graham J. Leggett⁴, Anthony J. Ryan⁴.

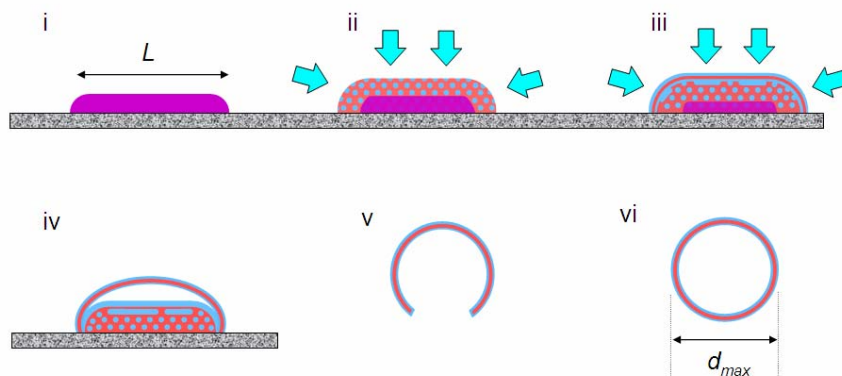
1. Department of Chemical and Process Engineering, University of Sheffield, Sheffield S1 7JD, UK

2. Department of Physics and Astronomy, University of Sheffield, Sheffield. S3 7RH.

3. Department of Engineering Materials, University of Sheffield, Sheffield S3 7HQ, UK

4. Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

Unilamellar polymer vesicles form when a block copolymer self-assembles into a single bilayer structure, with a hydrophobic core and hydrophilic surfaces, and the resulting membrane folds over and rearranges by connecting its edges to enclose a space. The physics of self-assembly specifies the membrane thickness of the resulting vesicle, but, both for polymer vesicles and the familiar phospholipid vesicles (liposomes), no mechanism strongly selects for the overall size, so the size distribution of vesicles tends to be very polydisperse. We describe a new method for the fast and spontaneous formation of micron-sized unilamellar polymer vesicles with a narrow overall size distribution. We demonstrate that we are able to create vesicles with a size predefined by the underlying pattern of the surface from which it was formed. This combines ‘top-down’ control of micron sized features (vesicle diameter) by lithography with ‘bottom-up’ control on nanometer sized features (membrane thickness) by molecular self-assembly.



Thermoreversible Gelation of cellulose ethers in an Aqueous System

Hao Yu, Oscar Kelly, Patrick. Fairclough and Anthony J. Ryan
Department of Chemistry, University of Sheffield, S3 7HF, UK

A B S T R A C T

Cellulose ethers (CE's) are water soluble polymers derived from cellulose, which play an important role in industry applications, such as food, pharmaceuticals, construction products, cosmetics, and so on. Two basic types of commercial cellulose ethers products, Methyl cellulose (MC) and Hydroxypropyl methylcellulose (HPMC) exhibit unusual property of forming thermoreversible gels in aqueous solution. They can form a gel on heating and return to liquid state on cooling. These physical gels are completely reversible without making or breaking any covalent bonds. Unfortunately, limited knowledge of the molecular structure, gel properties and performance prevent the improvement of industry applications. This project focus on understanding the gel mechanism, gel structure, gel mechanical properties and the effect of additives; we are also concerned the relationships between them.

The gel mechanism of aqueous solution of CE's system has been the subject of major discussions for many years. This system can be described as a composite of water and polymer, and the gel morphology is related to how that gel structure evolved. In theory, the gel formation process can be interpreted in terms of the phase separation by two mechanisms: the nucleation growth and the spinodal decomposition. The gel growth mechanism can be observed by optical microscopy at supramolecular distance scale ($>2000\text{nm}$), the effect of factors on the gel growth mechanism have been discussed, including temperature rate, concentration of polymer and additives. The scattering and diffraction methods have been used to study the structural information at macromolecular distance scale ($10\sim 2000\text{nm}$), such as light scattering (SLS and DLS) and small angle X-ray/light scattering (SAXS/SALS). My colleague Oscar Kelly discusses the scattering results in his poster.

According to the rheology data, we know that this gel is temperature dependent, it is thermoreversible and an obviously hysteresis exists during a thermal cycle. Cellulose ethers are also time dependent gels in aqueous solution. The Winton and Chambon [1] method has been used to detect the gel point, where $\tan\delta$ is independent of experimental frequency.

Reference:

[1] .Winter, H.H. and F. Chambon, *Analysis of linear viscoelasticity of a crosslinking polymer at the gel point*. Journal of Rheology (New York, NY, United States), 1986. **30**(2): p. 367-82.



Universal parameters for control of molecular orientation in polymer processing

Oleksandr O. Mykhaylyk¹, Pierre Chambon¹, Richard S. Graham², J. Patrick A. Fairclough¹, Peter D. Olmsted² & Anthony J Ryan¹

¹ *Department of Chemistry, University of Sheffield, Brookhill, Sheffield S3 7HF, UK.*

² *School of Physics & Astronomy, University of Leeds, Leeds LS2 9JT, UK.*

The world consumption of polymers (10^8 tonnes per annum) amounts to 1.5 kg per person per month. The majority of this material is semicrystalline and inevitably these crystals are oriented by flow during processing. Optimising properties, to either minimise use or maximise benefits, needs an understanding of how relaxation of flow-induced orientation competes with crystallisation. The conventional wisdom is that the longest chains in an ensemble form the "shish" upon which the bulk of the material crystallises as "kebabs". Critical examination finds that the longest chains play a catalytic role recruiting other chains into the formation of shish. A universal parameter for the formation of shish-kebab structures, the specific work of flow, and a simple method by which it may be measured for any given ensemble of polymers are provided in this presentation. The magnitude of the specific work required to create oriented structure (shish-kebab structure) depends on both the chemical structure of the polymer and its molecular weight distribution as these both affect the longest relaxation time and has profound implications for the design and operation of polymer processing equipment.

