

UK POLYMER SHOWCASE SEPTEMBER 2006

ABSTRACTS

OF

POSTERS

LIST OF POSTER PRESENTATIONS

1. Deformation behaviour of Polyoxymethylene at elevated temperatures
J. Mohanraj, D. C. Barton, C. G'Sell and I. M. Ward, University of Leeds
2. Biomaterials for soft tissue engineering: Design of Polyester-based non-porous films and 3D porous scaffolds
G. Rohman, J. Petit, N. R. Cameron and J. Southgate, University of Durham
3. Development of nanoparticles for cell protection
S. Hopkins, S. Rimmer and S. MacNeil, University of Sheffield
4. Synthesis of well-defined glycopolymers
Carl Barker, University of Durham
5. Synthesize and characterisation of block copolymers of polyoxyethylene and polylactide with different architectures
S. Mai, A. Abbot, D. Norton, R. McKean and A. J. Ryan, University of Sheffield
6. Iridescent block copolymer coatings – Adhesion and fabrication
N. Tzokova, P. Fairclough, and C. Fernyhough, University of Sheffield
7. Simulations of particle suspensions in viscoelastic fluids
A. Malidi and O. G. Harlen, University of Leeds
8. The application of pair distance distribution functions to structural analysis of core-shell particles
O. O. Mykhaylyk, A. J. Ryan, N. Tzokova and N. Williams, University of Sheffield
9. Electrospinning of Poly(methyl methacrylate)-*block*-poly(2-(diethylamino)ethyl methacrylate)-*block*-poly(methyl methacrylate) (PMMA-*b*-PDEA-*b*-PMMA) and Poly(methyl methacrylate)-*block*-poly(methacrylic acid)-*block*-poly(methyl methacrylate) (PMMA-*b*-PMMA) Triblock Copolymers
J. Swann, J. R. Howse, P. D. Topham and A. J. Ryan, University of Sheffield
10. Biomimetic polymeric vesicles for gene delivery: first steps towards engineering a synthetic virum
H. Lomas, I. Canton, S. MacNeil, J. Du, S. P. Armes, A. J. Ryan, A. L. Lewis and G. Battaglia, University of Sheffield
11. Spontaneous Formation of Monodisperse Polymer Vesicles
J. R. Howse, R. A. L. Jones, A. J. Ryan, University of Sheffield
12. Tuning the Surface Properties of Cellulose using RAFT Graft Polymerisation
D. Roy, J. T. Guthrie and S. Perrier, University of Leeds

13. HyperMacs – Synthesis and Rheology
J. M. Dodds, L. R. Hutchings, N. Clarke and E. De Luca, University of Durham
14. Time-resolved fluorescence anisotropy measurements in the study of thermoresponsive polymers
R. Rutkaite, S. Rimmer, I. Soutar and L. Swanson, University of Sheffield
15. Use of TIPNO-based Alkoxyamines in nitroxide-mediated miniemulsion polymerisation
R. J. Blanchard, N. R. Cameron, O. Lagrille and P. A. Lovell, Universities of Durham and Manchester
16. Volatile organic gas sensors based on optical changes induced in porphyrins by exposure to a range of analytes
A. Dunbar, T. H. Richardson, A. J. McNaughton, W. Barford, J. Hutchinson and C. A. Hunter, University of Sheffield
17. The synthesis and characterisation of amphiphilic ABC triblock copolymers and self-assembly in aqueous conditions – the formation of responsive asymmetric polymersomes
A. J. Blanz, G. Battaglia, S. P. Armes and A. J. Ryan, University of Sheffield
18. Synthesis of well-defined polymers as part of the “Microscale polymer processing 2” project
P. Chambon, C. M. Fernyhough and A. J. Ryan, University of Sheffield
19. Redox Enzymes in Tethered Lipid Membranes
L. J. C. Jeuken, R. J. Bushby, S. D. Connell, S. D. Evans, A. Erbe and P. J. F. Henderson, University of Leeds
20. The Synthetic Muscle
P. D. Topham, J. R. Howse, C. J. Crook, S. P. Armes, R. A. L. Jones and A. J. Ryan, University of Sheffield
21. Systematic studies of the effect of peptide length on β -sheet tape self assembly
R. P. W. Davies, University of Leeds
22. Gas and vapour sensing characteristics of Langmuir-Schaeffer thiol encapsulated gold nanoparticle thin films
M. D. Hanwell, S. Y. Heriot, T. H. Richardson and N. Cowlam, University of Sheffield
23. The preparation of well-defined poly(diethylamino ethyl methacrylate) brushes by ATRP
K. Xu and A. J. Ryan, University of Sheffield
24. MUPP2 by Royal Demand
J. Embery, University of Leeds

25. A tearing energy study of oriented and relaxed polystyrene in the glassy state
J. Embery, R. S. Graham, R. A. Duckett, D. Groves, M. Collis, M. R. Mackley
and T. C. B. McLeish, Universities of Leeds and Cambridge
26. Probing the stress hardening phenomenon by combined SANS, birefringence and
extensional Rheology
J. Embery, R. S. Graham, L. R. Hutchings, Universities of Leeds and Durham
27. Non-linear shear flow behaviour of monodisperse polyisoprene melts
D. Auhl, J. Ramirez, A. E. Likhtman, T. C. B. McLeish, P. Chambon and C.
Fernyhough, Universities of Leeds and Sheffield
28. Dendritic fluorocarbon end-functionalized polymers as additives to modify
polymer properties at surfaces and interfaces
L. R. Hutchings, A. P. Narrainen, I. A. Ansari, N. Clark and R. L. Thompson,
University of Durham
29. Electrochemical screening of self-assembling β -sheet peptide interactions with
lipid monolayers
E. Protopapa, A. Aggeli, A. Nelson, University of Leeds
30. Solution behaviour of pH-responsive amphiphilic block copolymers
C. M. Fernyhough and A. J. Ryan, University of Sheffield
31. A novel laboratory distributive and dispersive mixer and applications
H. Benkreira, R. Patel and R. Butterfield, University of Bradford
32. Dynamic wetting in coating flows
H. Benkreira, R. Patel, I. Khan and S. Buscaino, University of Bradford
33. A novel rotating roll die and applications
H. Benkreira, R. Patel, J. Preece, University of Bradford
34. Cold extrusion of fibre and granular waste into acoustic materials
H. Benkreira, K. Horoshenkov, R. Patel and A. Khan, University of Bradford
35. Some optical properties of fluorescently modified amyloid fibrils
K. Channon, C. Silver and C. MacPhee, Universities of Cambridge and Montreal
36. On the dynamics of semiflexible polymer solutions in the tightly entangled regime
M. Tassierie, L. Barbu-Tudoran, J. Trinick, R. M. L. Evans and T. A. Waigh,
University of Leeds
37. Smart Polymer Detection Systems
B. Ryan, University of Sheffield
38. Novel highly branched polymers synthesised via RAFT polymerisation and their
characterisations
P. Mounteney, S. Perrier, D. Duncalf and S. Rannard, University of Leeds and
Unilever Research

39. Z-supported RAFT graft polymerisation: Towards the synthesis of true living polymers
Youliang Zhao and Sebastien Perrier, University of Leeds

40. 3D simulation of water and gas assisted injection moulding
L. Mulvaney-Johnson, E. C. Brown, P. D. Coates, A. J. Dawson, J. Sienz, J. F. T. Pittman, A. Polynkin, J. Butler, B. Brookshaw and K. Crow, Universities of Bradford and Swansea and Cinpres Gas Injection

41. Multiblock Copolymers via RAFT Polymerisation
H. Gemici, T. M. Legge and S. Perrier, University of Leeds

42. In-process measurements for polymer processing
J. Sweeney, P. Caton-Rose, R. Spares and P. D. Coates, University of Bradford

43. A unified model of necking and shearbanding in amorphous and semicrystalline polymers
J. Sweeney, P. Caton-Rose, R. Spares and P. D. Coates, University of Bradford

44. Mechanical property predictions in fibre reinforced polyamide injection moulded parts using measured and predicted fibre orientation within ABAQUS
P. Caton-Rose, P. Hine, A. Duckett, B. Whiteside and P. D. Coates, Universities of Bradford and Leeds

45. Modelling and characterisation of polymer/clay nanocomposites in the processing regime
P. E. Spencer, J. Sweeney, W. Al-Shabib and P. D. Coates, University of Bradford

46. Rechargeable lithium ion cells produced by the extrusion lamination of polymer gel electrolytes
I. M. Ward, H. V. St. A. Hubbard, G. Thompson, J. Kaschmitter, H. P. Wang, E. Cole and G. Flickenger, University of Leeds, SpectraPower Inc., and British Technology Group

47. Understanding the links between molecular aspects and stress-strain behaviour in polystyrene
P. J. Hine, R. A. Duckett and D. J. Read, University of Leeds

48. Controlled synthesis of isoprene via RAFT polymerisation
V. Jitchum and S. Perrier, University of Leeds

49. Light responsive polymers by reversible addition fragmentation chain transfer (RAFT) polymerisation
W. Sriprom, M. Neel, B. M. Heron, C. D. Gabbutt, S. Perrier, University of Leeds
50. WVTR by external ion beam analysis
A. S. Clough, S. A. Collins, F. E. Gauntlett, M. R. Hodgson, C. Jeynes, M. S. Rihawy, A. M. Todd and R. L. Thompson, Universities of Durham, and Surrey, and DuPont Teijin Films Wilton
51. PMMA nanocomposites: Synthesis, processing and Physical Characterisation
J. Elder, N. Clarke and L. R. Hutchings, University of Durham
52. Dendritically Functionalised Polymers as Surface Modifying Additives
I. A. Ansari, N. Clarke, L. R. Hutchings, A. P. Narrainen and R. L. Thompson, University of Durham
53. Physical Chemistry of Cell-Mineral Interactions
Rasika Fernando, University of Sheffield
54. The effect of high shear mixing on the mechanical properties of Carbon nanofibres reinforced Polypropylene
R. J. Foster, P. J. Hine, M. Tassieri and I. M. Ward, University of Leeds.

Deformation behaviour of Polyoxymethylene at elevated temperatures

J. Mohanraj¹, D. C. Barton¹, C. G'Sell² & I. M. Ward³

¹*School of Mechanical Engineering, University of Leeds, Leeds, United Kingdom*

²*Ecole des Mines de Nancy, Nancy, France*

³*School of Physics and Astronomy, University of Leeds, Leeds, United Kingdom*

ABSTRACT

Substantial improvement in the properties as a result of molecular orientation has initiated the development of several thermoforming processes to orient semi-crystalline and amorphous polymers. Though these processes have attracted substantial scientific and practical interests, scaling up these processes to a normal industrial environment requires detailed investigations of the various process parameters. More recently computer simulations have been widely used to predict the response of polymer in solid phase thermoforming processes and also to optimise the thermoforming conditions. However for polymers, successful quantitative predictions are more difficult due to the sensitivity of the material to temperature, strain, strain-rate and hydrostatic pressure. Most constitutive models available for polymers are based on tensile tests with isochoric assumptions. It has also been assumed that the yield behaviour is independent of the hydrostatic component of stress. The aim of this work is to check the validity of these assumptions by investigating the material behaviour accurately under various loading conditions.

In this presentation, the deformation behaviour of polyoxymethylene has been studied in uniaxial tension, simple shear and plane strain compression at 160 °C (a typical solid phase processing temperature) for strain rates from 10^{-4} s^{-1} to 1 s^{-1} . In uniaxial tension the stress-strain behaviour was determined by a novel video-controlled testing system. The measurements showed that there was a very significant evolution of volumetric strain, indicating that damage mechanisms are playing a key role in the plastic deformation behaviour. All tests showed similar deformation stages with a short region of visco-elastic behaviour followed by a rounded yield point. The von Mises equivalent yield stress for these tests showed a linear relationship with logarithmic strain rate. After yielding, all stress-strain curves showed a long plastic deformation regime, which in shear occurred at constant stress. In plane strain compression there was also only a very small increase in stress, in contrast to uniaxial tension where very significant strain hardening was observed at high strains, which is attributed to the onset of structural changes. Post mortem characterisation of the damage in the samples have been performed by a novel X-ray densitometry technique and by scanning electron microscopy.

Biomaterials for Soft Tissue Engineering: Design of Polyester-based Non-Porous Films and 3D Porous Scaffolds

G. ROHMAN^a, J. PETTIT^b, N. R. CAMERON^a, J. SOUTHGATE^b

^a University of Durham, Department of Chemistry, South Road, Durham, DH1 3LE

^b University of York, Department of Biology, Jack Birch Unit of Molecular Carcinogenesis, YO10 5YW

A B S T R A C T

A number of bladder conditions such as severe dysfunction, trauma and cancer can affect the capacity and compliance of the bladder, compromising its purpose and resulting in renal damage and chronic debilitating urinary incontinence^{1,2}. Tissue engineering applications are consequently being utilised in an attempt to reconstruct and surgically repair the bladder.

The choice of scaffold is crucial in tissue engineering as it must encourage cells to interact with each other and with the scaffold material to produce tissues of the desired characteristics³. This study was designed to investigate the ability of human urothelial (NHU) and smooth muscle (USM) cells to adhere and proliferate on polyester scaffolds. In a preliminary study, poly(D,L-lactide-*co*-glycolide) (PLGA) and poly(ϵ -caprolactone) (PCL)-based two dimensional films were prepared using the spin-coating method. The concentration of polyester in the spin-coated solution was varied leading to different film thicknesses. 3D porous PLGA or PCL scaffolds were also prepared using an emulsion processing route.

Both types of cells were seeded onto the films and cell attachment and proliferation were analysed up to 7 days. In order to explain the variation in cell growth with film characteristics, some film properties such as surface morphology, degradation behaviour and mechanical properties have been extensively studied. The first results have demonstrated that NHU and USM cells were compatible with PLGA and PCL films. However, cells appeared to grow better on the PLGA films and on thicker films, regardless of the polyester nature. Only the mechanical properties were affected by the variation of film thicknesses, with a decrease of both loss and storage moduli when increasing the film thickness. PLGA film moduli were also found to be lower than those of the PCL films. As a matter of fact, films with the lowest moduli seem to provide the most favourable substrate for bladder cell growth as they match better the mechanical properties of the intended site of implantation.

Early results of USM cells seeded on porous scaffolds are promising. Actually, cells were present on the surface and within the scaffold structure after 7 days of incubation. USM cells were also found to be evenly distributed throughout the scaffold.

¹ Thapa, A.; Miller, D. C.; Webster, T. J.; Haberstroh, K. M. *Biomaterials* **2003**, *24*, 2915-2926.

² Pattison, M. A.; Wurster, S.; Webster, T. J.; Haberstroh, K. M. *Biomaterials* **2005**, *26*, 2491-2500.

³ Sachlos, E.; Czernuszka, J. T. *Europ. Cells Mater.* **2003**, *5*, 29-40.

DEVELOPMENT OF NANOPARTICLES FOR CELL PROTECTION

S. Hopkins¹, 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
Chp04sah@sheffield.ac.uk

ABSTRACT

Tissue engineered constructs are susceptible to acute oxidative stress until the blood supply has been achieved. The blood supply is necessary for cells to receive nutrients and to cope with metabolic waste. While tissue engineered cells or tissue are within the laboratory there is the opportunity to introduce protective agents such as antioxidants and anti-inflammatory drugs.

Fluorescently labelled highly branched poly(N-isopropyl acrylamide)-co-glycerol monomethacrylate¹ have been prepared using reversible addition-fragmentation chain transfer (RAFT) polymerisation. These random highly branched polymers are thermally responsive and therefore we can take advantage of the fact that the polymers form stable particles above the LCST thus enabling them to encapsulate/release protective agents into cells. By fluorescently labelling the polymer it is possible to visualise the polymer when internalised by cells.

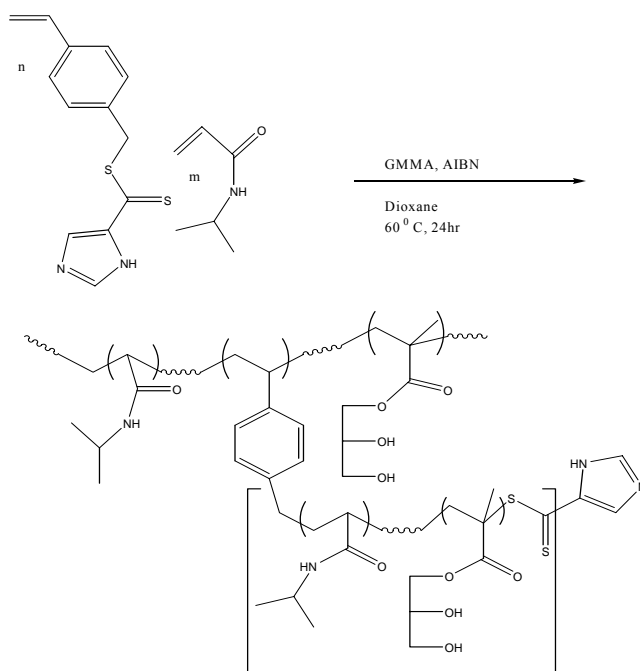


Figure 1. Synthesis of random highly branched polymers¹

- 1) S. Carter, S. Rimmer, A. Sturdy, M. Webb, *Macromolecular Bioscience*, **2005**, *5*, 373-378.

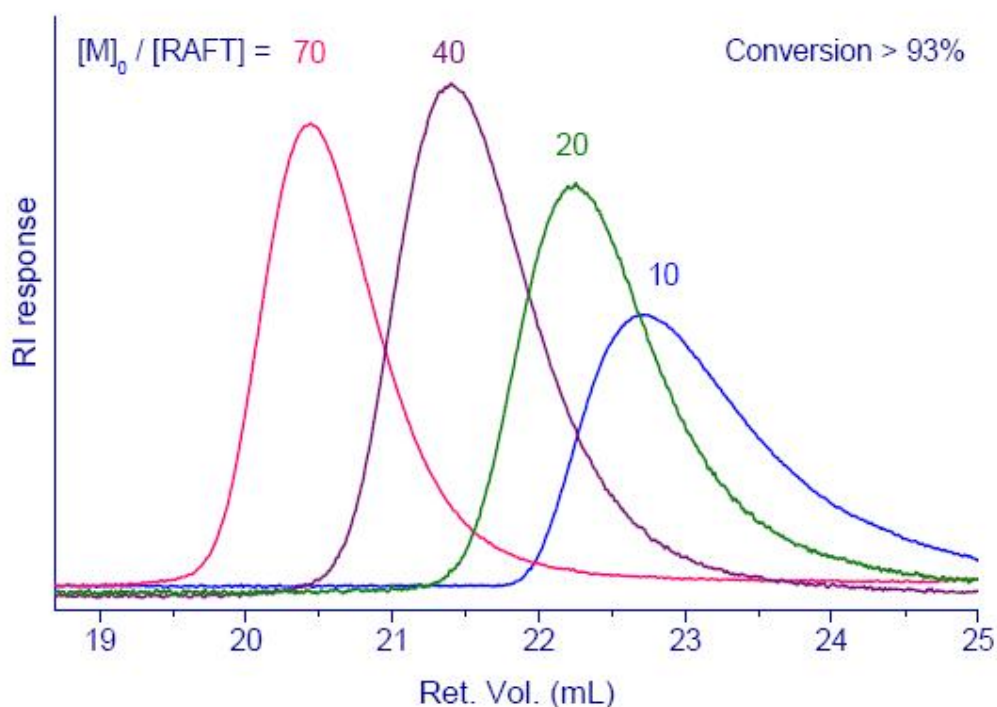
SYNTHESIS OF WELL-DEFINED GLYCOPOLYMERS

Carl Barker,
University of Durham, South Road, Durham, DH1 3LE
c.a.barker@durham.ac.uk

ABSTRACT

Reversible addition-fragmentation chain transfer (RAFT) polymerization has been utilised in the successful synthesis of a range of well-defined glyco-oligomers and homopolymers for a variety of applications.

The influence of several parameters on the kinetics of the RAFT homopolymerization of a vinyl-substituted unprotected glycoside monomer in aqueous media were investigated, and the results of this study were then utilised to adjust the polymerization conditions for the synthesis of well-defined glyco-oligomers with degree of polymerisation in the range 10-70. The oligomers obtained all had a polydispersity index of 1.06-1.12 and were synthesised in relatively high yield.



Size exclusion chromatography traces of the obtained oligomers for various target degrees of polymerisation (Conditions: eluant DMF, 0.1% w/v LiBr, 0.05% w/v BHT, 1 mL/min, 60°C, normalised areas).

Unprotected vinyl glyco-monomers were synthesised by a lipase-catalysed, regioselective acylation of a substituted glycopyranoside in anhydrous conditions. An initial kinetic investigation of the effect of various parameters on this reaction has also begun.

Synthesize and Characterisation of Block Copolymers of Polyoxyethylene and Polylactide with different architectures

Shaomin Mai, Annie Abbot, David Norton, Robert McKean and Tony Ryan
**Department of Chemistry, University of Sheffield, Brookhill, Sheffield. S3 7HF.
UK**

A B S T R A C T

The diblock, triblock and multiblock copolymers of polyoxyethylene (PEO) and Polylactide (PLA), of which the PEO blocks have molecular weight of about 2000 Da, were synthesized. The diblock and triblock copolymers were synthesized by polymerizing L-lactide (PLLA) or D,L-lactide (PDLLA) monomer onto a performed monohydroxy or dihydroxy-ended poly(ethylene oxide). Stannous octoate was used as the catalyst due to its high efficiency. The multiblock copolymers were synthesized by transesterification.

Their bulk microstructures and physical properties were characterized by SAXS/WAXS, DSC, advanced contact angle measurement and XPS. Some samples were electrospun into fibers and characterized by SEM.

The WAXS results showed, that for triblock copolymers, the crystallizability of PEO blocks was very much decreased due to its covalently binding to PLA blocks at both ends. In diblock and multiblock copolymers with the PEO content high enough, diffraction peaks from crystalline PEO were detected. These were confirmed by the DSC results where a melting peak assigned to PEO was detected from these samples. The PLLA blocks are crystalline in the block copolymers and SAXS results confirmed lamellar crystalline structures. Both DSC and contact angle measurement indicated that most of the end blocks of the transesterified sample are PEO blocks.

IRIDESCENT BLOCK COPOLYMER COATINGS – ADHESION AND FABRICATION

*Nadejda Tzokova, J. Patrick A. Fairclough, Christine M. Fernyhough
Department of Chemistry*

University of Sheffield

A B S T R A C T

High molecular weight almost symmetrical styrene-b-isoprene diblock copolymers were used as materials for producing iridescent coatings. Two ways of promoting adhesion of the coating to the substrate, corona treated biaxially oriented PP, were proposed – compatibility and chemical adhesion. The chemical bonding between the coating and the substrate was found to be the most suitable option. The isoprene block was selectively functionalised by introducing a small amount of hydroxyl groups which allowed attachment of the coating to the substrate by simultaneous ‘self-priming’ and cross-linking using isocyanates. The coating was applied by drawing bar as a concentrated, already structured, block copolymer solution. SAXS, UV-VIS and digital photography shows that the drying process initially removes sufficient solvent for chain stretching to take place and the domain spacing initially increases giving a red shift in the coating colour. Further drying removes the remaining solvent, the system contracts, the domain spacing decreases and a blue shift change in the colour is observed.

Simulations of particle suspensions in viscoelastic fluids

*Ahamadi Malidi, Oliver Harlen
School of Mathematics, University of Leeds*

A B S T R A C T

In many polymer processing applications filler particles such as glass beads are added to the polymer matrix. To study the rheology of such multiphase systems we perform direct simulations of the motion of the suspended particles when subjected to an external linear flow, such as 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.

We show that in shear flow changes in the rheology due to the addition of filler particles in polymer melts (described by the pom-pom or RoliePoly constitutive laws) can be accounted for by a simple shifting of the strain-rate and shear stress. However, this does not hold for dilute polymer solutions modelled using dumbbell constitutive laws, such as the Oldroyd B and FENE models. We will also compare our simulation results with rheological measurements on suspensions of glass spheres in polystyrene melts. Finally we will show results for planar extensional flow.

The application of pair distance distribution functions to structural analysis of core-shell particles

Oleksandr O. Mykhaylyk¹, Anthony J. Ryan¹, Nadezhda Tzokova¹ and Neal Williams²
¹Department of Chemistry, University of Sheffield, Sheffield, South Yorkshire, S3 7HF, United Kingdom

²ICI Paints, Wexham Road, Slough, Berkshire, SL2 5DS, United Kingdom

A structure of core-shell latex particles of polymethylmethacrylate (the core) and polyurethane (the shell) of various sizes (in a range of 25 – 90 nm) have been investigated by methods of small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM). A set of SAXS patterns has been obtained for each sample using contrast variation method. An evolution of distance distribution functions, extracted from SAXS using regularization method, for the latexes dissolved in various sucrose solutions has been used to obtain structural parameters of the particles such as core size, shell thickness, density of the polymers. It has been demonstrated that distance distribution function obtained for latex particles in sucrose solutions, in a range of electron densities matching the electron densities of the polymers composing the core-shell particles (especially within an average electron density of the particles, Figures 1 and 2) is sensitive to deviations in both geometrical parameters of the particles and electron density of the polymers. In this particular work this effect has been used to measure the electron density deviations within the particle's core and the particle's shell (Figure 2). The effect of phase separation, which could take place in the PU, on the distance distribution function is estimated using Monte-Carlo simulations where the phase-separated PU shell is represented by spherical caps surrounded by the rest of the shell simulating the location of hard and soft PU segments respectively.

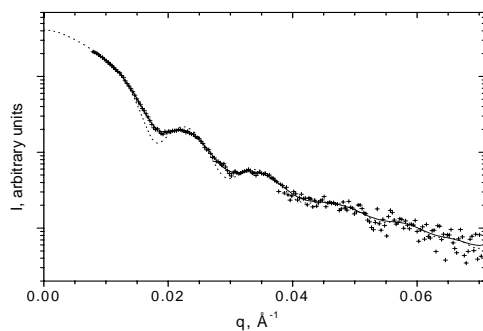


Figure 1. A representative SAXS pattern (recorded at SRS Daresbury Lab, station 16.1, camera length 6m) obtained from core-shell polymethylmethacrylate- polyurethane particles dissolved (volume fraction about 2%) in a water sucrose solution with density 1.12 g/cm³ (crosses) and smeared and desmeared fitting profile (solid and dotted line respectively) to this data.

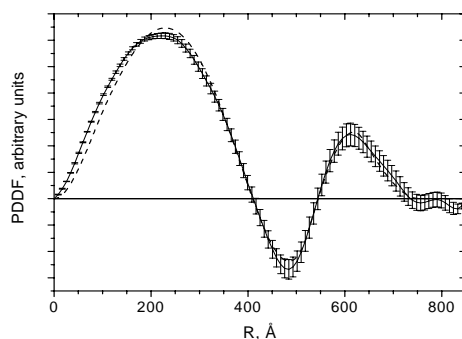


Figure 2. A distance distribution function obtained from SAXS patterns represented in Figure 1 (solid line with error bars, GNOM package developed by D. Svergun has been used). Analytical expression of core-shell particles' distance distribution function developed in this work to fit the data led to the following parameters in this particular case: core radius 263 Å, thickness of the shell 114 Å, electron density of the solvent 0.369 electrons/Å³, average electron density of the core 0.379 electrons/Å³, average electron density of the shell 0.363 electrons/Å³ and integral width of Gaussian distribution of electron density in both the core and the shell 0.015 electrons/Å³ and 0.005 electrons/Å³ respectively. The dashed line represents results of the fitting. The straight line shows zero value of the distance distribution functions.

The morphology of dried films formed was found to be an ordered array of PMMA spherical domains (defined by the original particles core) embedded in PU matrix originating from the shell of the particles. The correlation distances between neighbouring PMMA domains in the dried films measured from SAXS patterns have values similar to those which would be predicted using the geometrical parameters of the latex particles and close packing during film formation.

Electrospinning of Poly(methyl methacrylate) - *block* - poly(2-(diethylamino)ethyl methacrylate)-*block*-poly(methyl methacrylate) (PMMA-*b*-PDEA-*b*-PMMA) and Poly(methyl methacrylate) -*block* - poly(methacrylic acid)-*block*-poly(methyl methacrylate) (PMMA-*b*-PMAA-*b*-PMMA) Triblock Copolymers

Joshua Swann, J. R. Howse, P. D. Topham and A. J. Ryan
Department of Chemistry,
University of Sheffield, Sheffield S3 7HF, UK

A self-assembled triblock copolymer gel based on (PMMA-*b*-PMAA-*b*-PMMA) was previously demonstrated to show affine changes in volume when placed in a pH oscillating chemical reaction[1]. The response of the gel was measured both microscopically and macroscopically using SAXS and optical microscopy respectively. The specific power the gel can develop when placed in the oscillating chemical reaction was estimated to be 20 mW kg⁻¹.

The specific power the gel can produce is ultimately limited by diffusion as it is the response of the polymer chain to its surrounding chemical environment and mass transport which controls the collapse transition. Processing responsive material with smaller dimensions provides a route to reducing diffusion times and ultimately increasing the specific power of the material.

Electrospinning is a technique used to generate ultrathin fine fibres. Ultrathin fibres of the polyacid will have very large surface areas compared to gel pieces and consequently have smaller diffusion times. A reduction in the gel dimensions by a factor of 100 is expected to increase the response rate of the polymer by a factor of 10⁴, making the specific power comparable to striated muscle.

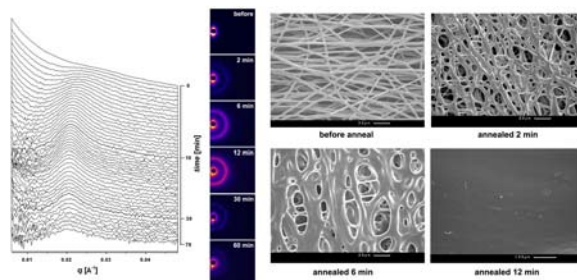


Figure 1. SAXS data and SEM micrograph images of the THF annealing process of electrospun fibres processed from a PMMA-*b*-PDEA-*b*-PMMA/THF solution (35 wt%)[2].

Electrospun fibres of PMMA-*b*-PDEA-*b*-PMMA, an analogous pH responsive polybase material have been produced. The effect of solvent annealing on self assembly is shown in figure 1.

Electrospun fibres of both pH responsive polyacid and polybase material will be studied to compare the rate of expansion of fibrous networks of different fibre thicknesses and to a macroscopic gel piece.

1. Jonathan R. Howse, et al., *Reciprocating Power Generation in a Chemically Driven Synthetic Muscle*. Nano Letters, 2005. **6**(1): p. 73-77.
2. Topham, P.D., *Study of pH-Responsive Polymer Systems for use in Molecular Machines*, in *Chemistry*. 2006, University of Sheffield: Sheffield.

Biomimetic polymeric vesicles for gene delivery: first steps towards engineering a synthetic virus

Hannah Lomas¹, Irene Canton¹, Sheila Mac Neil^{1,2}, Jianzhong Du³, Steven P. Armes³, Anthony J. Ryan³, Andrew L. Lewis⁴, and Giuseppe Battaglia¹

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

²Division of Clinical Sciences, Northern General Hospital, University of Sheffield, Sheffield, United Kingdom

³Department of Chemistry, University of Sheffield, Dainton Building, Sheffield S3 7HF, United Kingdom

⁴Biocompatibles UK Ltd., Chapman House, Farnham Business Park, Weydon Lane, Farnham, Surrey GU9 8QL, UK

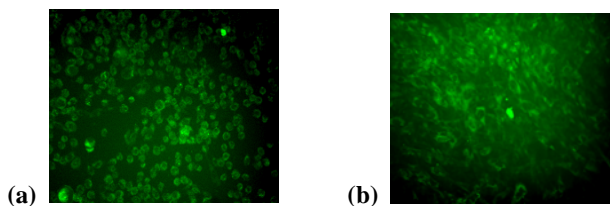
Introduction

Gene therapy is defined as the introduction of genes into an individual's cells and tissues to treat a disease. The successful delivery of genes into the nucleus of target cells is essential for gene therapy to be effective.¹ Viruses are currently the most efficient gene delivery vectors, but the gene expression from viral vectors is not long term², and they have been found to interact with the human immune system.³ There has therefore been much recent interest in the design of nonviral gene delivery systems. Nonviral gene delivery vectors should contain a cationic component (lipid or polymer)¹ to bind nucleic acids, which are highly charged species. They also need to be designed so that they survive the extracellular environment and protect the nucleic acid, since charged species such as plasma proteins⁴ can compete with the cationic species for the binding of nucleic acids. This may result in the nucleic acid being displaced from the gene delivery vector, leading to a very short circulation time in the bloodstream.⁵

The aim of the present contribution is to design an efficient nonviral gene delivery vehicle that combines a nucleic acid binding polymer with a hydrophilic polymer. Herein an amphiphilic block copolymer consisting of a nucleic acid-binding, pH-sensitive polyelectrolyte poly(2-(diisopropylamino)ethyl methacrylate) (PDPA) and biocompatible, hydrophilic poly(2-methacryloxyethyl phosphorylcholine) (PMPC), has been investigated as a potential gene delivery vector. This block copolymer has been shown to form vesicles in aqueous solution that are colloidally stable at physiological pH.⁶ The vesicles are pH-sensitive and dissociate below the PDPA pK_a of approximately 6.3.⁶ Below its pK_a, PDPA is protonated, soluble in water and weakly cationic. Above the pK_a, deprotonation of the PDPA tertiary amine groups occurs, triggering the self-assembly of the block copolymer into vesicles under aqueous conditions. The block copolymer mimics the amphiphilic nature of natural phospholipid membranes⁷, with its dual hydrophilic-hydrophobic character, and like phospholipids, it can self-assemble into vesicles.⁸

Results

PMPC-PDPA vesicles are able to encapsulate plasmid DNA molecules encoding green fluorescent protein (GFP), as proven by UV spectrophotometry. Chinese ovarian hamster (CHO) and human primary cells (human dermal fibroblasts [HDF]) were treated with PMPC-PDPA vesicles encapsulating GFP reporter constructs. Fluorescent micrographs of the living CHO (a) and HDF (b) cells were taken after two days incubation with the GFP-plasmid loaded vesicles and show expression of the GFP reporter construct in the cell cytosol. These initial results suggest that these copolymer vesicles could be used as effective nanosized gene delivery vehicles.



References

- 1) Khalil, I. A., Kogure, K., Akita, H. and Harashima, H. Uptake pathways and subsequent intracellular trafficking in nonviral gene delivery. *Pharmacol. Rev.* **58**, 32-45 (2006).
- 2) Thomas, C. E., Ehrhardt, A. and Kay, M. A. Progress and problems with the use of viral vectors for gene therapy. *Nature Rev. Genet.* **4**, 346-358 (2003).
- 3) Hollon, T. Researchers and regulators reflect on first gene therapy death. *Nature Med.* **6**, 6 (2000).
- 4) Hashida, M. et al. Pharmacokinetics and targeted delivery of proteins and genes. *J. Control. Release* **41**, 91-97 (1996).
- 5) Poulton, C. W., Seymour, L. W. Key issues in non-viral gene delivery. *Advanced Drug Delivery Rev.* **46**, 187-203 (2001).
- 6) Du, J., Tang, Y., Lewis, A. L. and Armes, S. P. pH Sensitive Vesicles Based on a Biocompatible Zwitterionic Diblock Copolymer. *J. Am. Chem. Soc.* **127**, 17982-17983 (2005).
- 7) Battaglia, G. and Ryan, A. J. Bilayers and Interdigitation in Block Copolymer Vesicles. *J. Am. Chem. Soc.* **127**, 8757-8764 (2005).
- 8) Discher, D. E. and Eisenberg, A. Polymer vesicles. *Science* **297**, 967-73 (2002).

Spontaneous Formation of Monodisperse Polymer Vesicles.

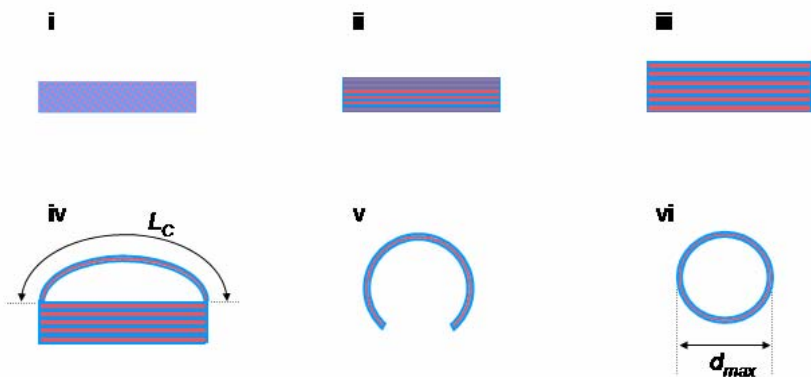
Jonathan R. Howse¹, Richard A. L. Jones¹, Tony Ryan².

¹ *Dept. of Physics and Astronomy, Sheffield University, Sheffield S3 7RH*

² *Dept. of Chemistry, Sheffield University, Sheffield S3 7HF*

ABSTRACT:

The spontaneous formation of micron sized monodisperse, single walled polymer vesicles is described. The formation of a polymeric vesicle is controlled by the diffusion of water into self-assembled micron sized dewetted domains of block copolymer on a modified silicon substrate. The size of the resulting vesicle is shown to be restricted by the size of the bulk polymer microdomain. A thiol treated gold surface was patterned using 244 nm laser lithography to create a patterned hydrophilic, fluorophilic, surface upon which poly(ethylene oxide)-co-poly(butylene oxide) spontaneously dewets. The hydration, and subsequent vesicle formation, of a Rhodamine labeled poly(ethylene oxide)-co-poly(butylene oxide) copolymer on substrates that generate two different dewetted lengths has been monitored by Confocal Laser Scanning Microscopy. The diameter of the vesicles produced has been analyzed and is compared to that dictated by the underlying pattern. We have shown that for a single polymer we are able to spontaneously create unilamellar monodisperse vesicles of a defined size. For a single patterned substrate further control may be obtained depending upon the exterior surface contour length of the polymer exposed to the aqueous environment.



Tuning the Surface Properties of Cellulose using RAFT Graft Polymerisation

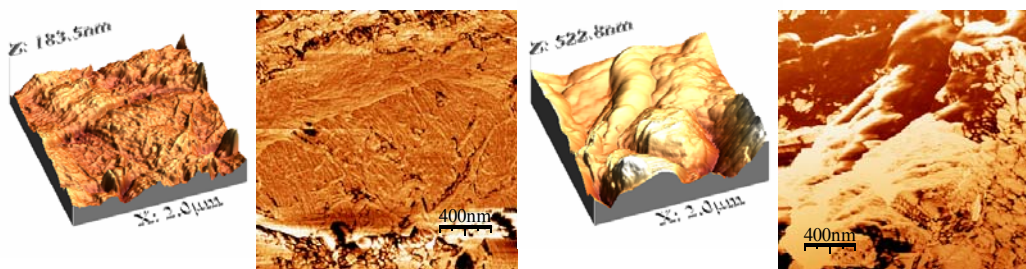
D. ROY *, J. T. GUTHRIE and S. PERRIER

Department of Colour and Polymer Chemistry, The University of Leeds, Leeds, LS2 9JT, UNITED KINGDOM

E-mail: ccdrde@leeds.ac.uk Web page: www.leedspolymers.leeds.ac.uk

Recently, the living radical polymerisation techniques have gained importance to achieve well defined and living polymer grafts from the different solid surfaces such as poly(propylene) lanterns, carbon nanotubes, silica, and gold nano particles. The surface modification of the cellulose fibres through graft polymerization is also of great interest to the researcher due to their wide range of potential applications.

To achieve well controlled graft polymeric chains from cellulosic surfaces, the reversible addition fragmentation chain transfer (RAFT) process is used. The chemical modification of the hydroxyl groups of cellulose through an esterification process followed by a Grignard reaction is the key mechanism to the formation of a cellulose-based RAFT agent. This RAFT agent is then used to mediate the graft polymerisation of 2-(dimethylamino)ethylmethacrylate from cellulose filter paper. After quaternisation, this cellulose substrate can be used as antibacterial biodegradable surface in medical industry. Due to the presence of active living end group, the graft block copolymerisation is also possible. Poly(styrene) is successfully copolymerised from the PDMAEMA-grafted cellulose fibres which alters the wetting behaviour of cellulose surface. This graft block copolymer has also potential applications in many fields.



Virgin cellulose

Cellulose graft copolymer

References:

1. Roy, D. *Aust. J. Chem.* **2006**, *59*, 229.
2. Roy, D.; Guthrie, J.T.; Perrier, S. *Macromolecules* **2005**, *38*, 10363.

HyperMacs – Synthesis and Rheology.

*Jonathan M. Dodds, Lian R. Hutchings, Nigel Clarke, Edoardo De Luca
IRC in Polymer Science and Technology, Department of Chemistry, Durham
University, Durham DH1 3LE, UK*

ABSTRACT.

HyperMacs are long-chain (hyper)branched polymers formed by the polycondensation of an AB₂ macromonomers. We describe the effect of stirring, reaction solvent, concentration, base and gas flow in the Williamson ether synthesis of polystyrene HyperMacs using macromonomers prepared using anionic polymerization. It is demonstrated that efficient mechanical stirring increases the extent to which the reaction proceeds. N-Methyl-2-pyrrolidone (NMP) was found to be a worse and N,N-Dimethylacetamide (DMAc) as good a solvent for the synthesis of HyperMacs in N,N-Dimethylformamide (DMF). Macromonomer solution concentration (%w/v) was shown to be optimal between 30-50 %. Increased gas flow across the reaction solution for the removal of volatile impurities from did not increase the extent of HyperMac coupling. Caesium carbonate increased reaction rate of the polycondensation reaction, but did not extend the final end point of the reaction.

Melt rheology showed fractionated polystyrene HyperMacs to be thermorheological simple, obeying William-Landel-Ferry (WLF) behaviour. Zero shear viscosities of the material were shown to increase with molecular weight and the melts display shear thinning behaviour. HyperMacs showed little evidence for relaxation by reptation and agreed well with the Cayley tree model for hierarchical relaxation in tube models of branched polymers, implying HyperMacs exhibit architectures similar to long chain branched polymers obtained commercially from metallocene catalysts.

Time-resolved fluorescence anisotropy measurements in the study of thermoresponsive polymers

Ramune Rutkaite, Stephen Rimmer, Ian Soutar, Linda Swanson

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

Email: r.rutkaite@sheffield.ac.uk

A B S T R A C T

Thermoresponsive water-soluble polymers constitute an important class of ‘smart’ materials, which will respond, in a dramatic fashion, to changes in, for example, the temperature, salinity or pH of their environment. We present recent data highlighting the power of time-resolved fluorescence anisotropy measurements (TRAMS) in the study of the thermoresponsive behaviour of poly(N-isopropylacrylamide), PNIPAM and NIPAM-based systems. PNIPAM exhibits thermo-reversible phase separation behaviour in aqueous solution and undergoes a conformational change at 32°C from an expanded chain to a compact globular structure. This occurs at the lower critical solution temperature (LCST). Manipulation of the conformational switch of PNIPAM results through changing the hydrophilic to hydrophobic balance within the polymer via simple copolymerisation. However, although a degree of control over the LCST is possible through such a strategy, copolymerization serves to reduce the magnitude of the transition. Synthesis of graft copolymers based on NIPAM is offered as a solution to this problem: fine tuning of the thermal response through control of the entropic term governing the thermodynamics of the process can be achieved as revealed by TRAMS. Independent fluorescence labelling of both the backbone and the grafts allows the contribution of the chain dynamics from each of these sites to the thermal response to be monitored. Understanding the roles of the hydrophobic:hydrophilic ratio and the number of chain ends within the polymer is crucial to exercising a degree of control over the conformational transition without any reduction in magnitude.

USE OF TIPNO-BASED ALKOXYAMINES IN NITROXIDE-MEDIATED MINIEMULSION POLYMERISATION

ROBERT J. BLANCHARD^b, NEIL R. CAMERON^{a*}, OLIVIER LAGRILLE^a
and PETER A. LOVELL^{b*}

^aIRC in Polymer Science and Technology, University of Durham, Department of
Chemistry, South Road, DH1 3LE, United Kingdom, ^bMaterials Science Centre,
School of Materials, The University of Manchester, Grosvenor Street, Manchester,
M1 7HS, United Kingdom

* email: n.r.cameron@durham.ac.uk web: www.dur.ac.uk/chemistry
pete.lovell@manchester.ac.uk www.materials.manchester.ac.uk

ABSTRACT

Nitroxide-mediated polymerisation (NMP) has become well-established for achieving controlled radical polymerisation following pioneering work with 2,2,6,6-tetra-methyl-piperidine-*N*-oxyl (TEMPO) [1-3]. Several new acyclic α -H-bearing nitroxides and the corresponding alkoxyamines have been developed by many authors and NMP has been carried out successfully in aqueous dispersed systems, especially in miniemulsion, using *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (SG1) and 2,2,5-tri-methyl-4-phenyl-3-azahexane-3-nitroxide (TIPNO) or their derivatives as nitroxides [e.g., 4-8].

The present work concerns design and synthesis of hydrophobic acyclic nitroxides for effecting miniemulsion polymerisation below 100 °C. The TIPNO skeleton was chosen because it is more amenable to the introduction of bulky, hydrophobic species. The aim was to prepare a family of nitroxides and alkoxyamines with controlled structural variations and to investigate effects of nitroxide and alkoxyamine structure on bulk and miniemulsion polymerisation of styrene and *n*-butyl acrylate. This paper will describe some of the new hydrophobic nitroxides [9] and will report results from initial studies of the use of TIPNO-derived alkoxyamines in bulk and miniemulsion polymerisation of styrene at 125 °C and 90 °C.

1. D.H. Solomon, E. Rizzardo, P. Cacioli, U.S. Patent 4,581,429, 1985
2. D.H. Solomon, *J. Polym. Sci., Polym. Chem.*, 2005, 43, 5748-5764.
3. M.K. Georges, R.P.N. Veregin, P.M. Kazmaier, G.K. Hamer, *Macromolecules*, 1993, 26, 2987-2988
4. C. Farcet, M. Lansalot, B. Charleux, R. Pirri, J.P. Vairon, *Macromolecules*, 2000, 33, 8559-8570
5. B. Keoshkerian, A.R. Szkurhan, M.K. Georges, *Macromolecules*, 2001, 34, 6531-6532
6. M. Lansalot, C. Farcet, B. Charleux, J.P. Vairon, R. Pirri, P. Tordo, in *Controlled / Living Radical Polymerization*, K. Matyjaszewski (Ed.), *ACS, Symp. Ser.*, 2000, 768, Chapter 10
7. C. Farcet, B. Charleux, R. Pirri, *Macromolecules*, 2001, 34, 3823-3826
8. J. Nicolas, B. Charleux, O. Guerret and S. Magnet, *Macromolecules*, 2004, 37, 4453-4463
9. O. Lagrille, N.R. Cameron, P.A. Lovell, R. Blanchard, A.E. Goeta and R. Koch, *J. Polym. Sci., Polym. Chem.*, 2006, 44, 1926-1940

Volatile organic gas sensors based on optical changes induced in porphyrins by exposure to a range of analytes

Alan Dunbar^a, Tim H. Richardson^a, Alex J. McNaughton^a, William Barford^a, Jordan Hutchinson^b and Chris A. Hunter^b

^a Department of Physics & Astronomy, University of Sheffield, Hicks Building, Hounsfield Road, Sheffield S3 7RH, UK (a.dunbar@shef.ac.uk)

ABSTRACT

The suitability of seven different porphyrin compounds for use as gas sensors for various different organic analytes has been investigated. The porphyrin compounds examined were the Zn, Sn, Mg, Au, Co, Mn and free base derivatives of 5,10,15,20-tetrakis[3,4-bis(2-ethylhexyloxy)phenyl]-21*H*,23*H*-porphyrine. These molecules are highly stable and exhibit colourful characteristic absorption spectra in the visible range, see Figure 1(a). Exposure to various analytes induces changes in the optical spectra owing to charge transfer between the the analyte and the delocalized π -electron system within the highly conjugated molecule¹.

Solid state Langmuir-Blodgett (LB) films of the porphyrins have been prepared on glass substrates and exposed to those analytes that exhibited a response in the solution experiments. The dynamics of the changes in the absorption spectra of the solid state LB films have been investigated. The results show that some of the porphyrins / analyte pairs are stable, have fast responses and good recovery and therefore are suitable for use in solid state gas sensors, see Figure 1.

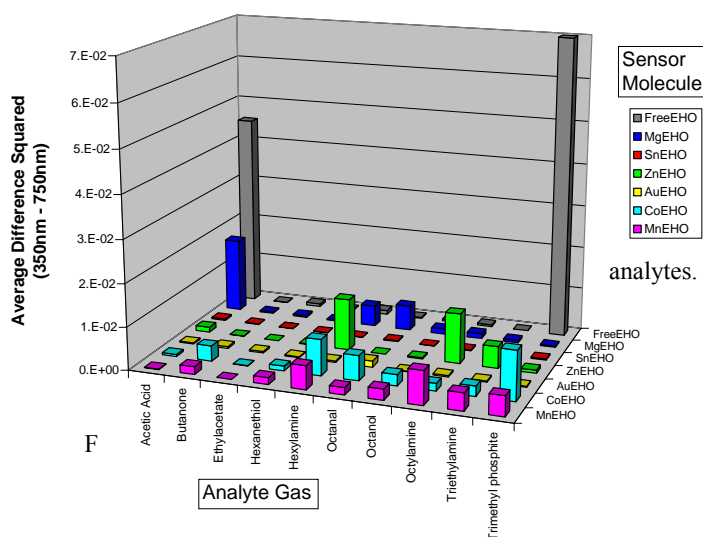


Figure 1

The response strength of the seven different porphyrins upon exposure to various volatile organic analytes.

At present we are looking for a flat, transparent and hydrophobic polymer substrate which will improve the spreading of the sensor films to replace the HMDS treated glass substrates used at present.

¹ DunbarA, Richardson TH, McNaughton AJ, Barford W, Hutchinson J and Hunter CA. *Colloids and Surfaces A: Physiochem. Eng. Aspects* vol.284-285, 2006; p339-344.

**THE SYNTHESIS AND CHARACTERISATION OF
AMPHIPHILIC ABC TRIBLOCK COPOLYMERS AND SELF-
ASSEMBLY IN AQUEOUS CONDITIONS – THE FORMATION
OF RESPONSIVE ASYMMETRIC POLYMERSOMES.**

Adam J. Blanz, Giuseppe Battaglia, Steve P. Armes, Tony J. Ryan

A B S T R A C T

The synthesis of amphiphilic ABC membrane-forming triblock copolymers of varying block type and length has been undertaken and the self-assembly of them in aqueous solution analysed. Using hydrophilic polymers as the 'A' and 'C' blocks which phase separate and a hydrophobic 'B' block, should lead to the formation of asymmetric vesicular membranes. For example, block 'A' could form the inner membrane and the block 'C' the outer membrane. However, varying morphologies are witnessed using Transmission Electron Microscopy (TEM), including spherical micelles, cylindrical micelles and vesicles depending on relative hydrophobic volume fraction of the copolymer. Evidence of curvature setting, hence vesicle diameter, has been witnessed using thermo-responsive poly(ethylene oxide)-*block*-poly(hydroxypropyl methacrylate)-*block*-poly(glycerol methacrylate) (PEO-PHPMA-PGMA) triblock copolymers. By varying the relative lengths of the hydrophilic PEO and PGMA blocks and keeping the hydrophobic volume approximately constant, the diameter of the vesicle can be modified. Also, as the hydrophobic HPMA block is thermo-responsive (LCST = 5°C) these polymersomes dissolve at low temperatures.

Synthesis of Well-Defined Polymers as part of the “Microscale Polymer Processing 2” Project

Pierre Chambon, Christine M. Fernyhough, Antony J. Ryan

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

ABSTRACT

The μPP^2 project⁽¹⁾ aims to understand and predict the behavior of complex polymeric materials (*e.g.* mass-produced polyethylene containing a mixture of low and high molecular weight, linear and chain-branched macromolecules) in order for industry to create specific products in terms of properties, cost and environmental protection.

This purpose involves a multi-disciplinary approach that gathers scientists from various disciplines. Thus physicists, chemists, engineers, mathematicians and computer scientists work together to solve this problem.

Physicists create mathematical models to describe how materials will flow taking into consideration the different parameters of each polymer (*i.e.* molecular weight and architecture of the chains). Therefore very well defined polymers, in terms of molecular weight distribution and architecture, are needed to test and confirm these theoretical models. This is the role of chemists.

By using techniques such as anionic polymerization we can synthesize polymers whose parameters are known with great accuracy. Hence polymers varying by their chemical nature, molecular weight and architecture have been synthesized regarding the needs of the project:

- A series of linear polyisoprenes have been prepared via anionic polymerization and the rheology examined both for pure compounds and for bimodal blends.
- Linear and comb-like Polybutadienes have been synthesized via anionic polymerization and hydrogenated in homogeneous conditions so as to obtain Low Density Polyethylene models. These samples have been made for crystallography studies where we are looking for the formation of “shish-kebab” structures. In industrial materials, these structures are believed to be due to the presence of a few slow relaxation-time chains (*i.e.* long chains and/or long-chain branching materials) in a low molecular weight matrix.
- Lightly branched hydrogenous polystyrene comb has been made as a precursor to deuterated homologues (*i.e.* fully deuterated comb, deuterated backbone/hydrogenous branches, hydrogenous backbone/deuterated branches). A contrast between the backbone and the branches is expected by studying these “labeled” materials by neutron scattering.

The different steps of the preparation of these materials will be described: synthetic strategy, purification and characterization.

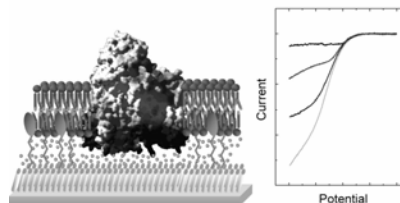
(1) Website: <http://www.mupp2.co.uk/>

Redox Enzymes in Tethered Lipid Membranes

Lars J.C. Jeuken, Richard J. Bushby, Simon D. Connell, Stephen D. Evans, Andreas Erbe, Peter J.F. Henderson

School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, United Kingdom; e-mail: L.J.C.Jeuken@leeds.ac.uk

An electrode surface is presented that enables the characterization of redox-active membrane enzymes in a native-like environment. An ubiquinol oxidase from *Escherichia coli*, cytochrome bo₃ (*cbo*₃), has been co-immobilized into tethered bilayer lipid membranes (tBLMs). The tBLM is formed on gold surfaces functionalized with cholesterol tethers which insert into the lower leaflet of the membrane. The planar membrane architecture is formed by self-assembly of protein-reconstituted proteoliposomes or total inner-membrane extracts from *E. coli*. The surface structure is characterized by spectroscopy and microscopy. The functionality of *cbo*₃ is investigated electrochemically and is confirmed by the catalytic reduction of oxygen. Interfacial electron transfer to *cbo*₃ is mediated by the membrane-localized ubiquinol, the physiological electron donor of *cbo*₃.



For purified and membrane reconstituted *cbo*₃, the enzyme coverages on the surface could be established with AFM (2-8.5 fmol·cm⁻²). The coverage estimated using the enzyme's electrochemical activity was the same, indicating that most - if not all - *cbo*₃ on the surface is catalytically active and thus retains its integrity during immobilization. Using total-inner membrane extracts of *E. coli* higher *cbo*₃ activities could be obtained corresponding to coverages of ~30 fmol·cm⁻². The apparent K_m for oxygen of $0.5 \pm 0.3 \mu\text{M}$ is one of order of magnitude lower than that reported previously.

The Synthetic Muscle

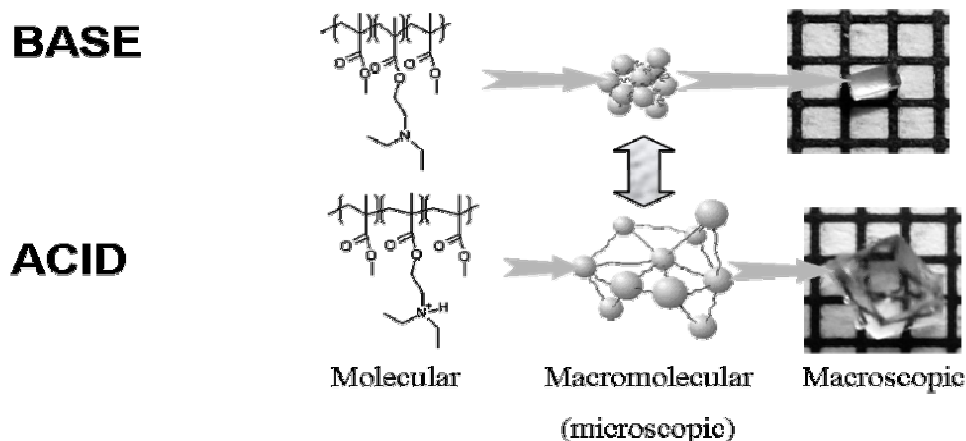
Paul D. Topham, Jonathan R. Howse, Colin J. Crook, Steven P. Armes, Richard A. L. Jones, Anthony J. Ryan.
University of Sheffield, Sheffield, UK
p.topham@shef.ac.uk

ABSTRACT

The specific aim of this project is to make systems with pH responsive polymers that have potential applications as molecular muscles, motors, pumps and valves. Such motors could be useful in biomimetic systems being used as macromolecular machines to simulate biological processes. To achieve this, the main objective of the research was to synthesise ‘smart’ polymers, which selectively exhibit a pH induced volume transition (i.e. do work at the molecular level). On development of such systems, it is possible to combine them with a pH oscillating reaction to yield a periodic change in volume. This fluctuation in size will exert an external force, which can be effectively channelled to power a molecular motor.

Two main targets are identified in achieving this; the synthesis of a polyacid system and a polybase system. The different polymer behaviour will oppose one another at each pH extreme. Also, by producing copolymeric material of the polymers (by introducing hydrophobic segments) the molecular activity can be monitored by SAXS as the responsive materials “pulsate”. Alongside this, polyelectrolyte brushes are to be synthesised because the ultimate in miniaturisation of polymeric material is the single chain. This will allow one to monitor the effect that the external environment has on individual polymer chains that make up a responsive polymer layer. Also, this material can be used to create surfaces whose permeability changes as a function of pH for use in molecular pumps and valves.

Here we report an example of such a molecular machine, the “bipolymeric” strip, whereby a polyacid and polybase are adhered lengthways to each other, analogous to a bimetallic strip. When exposed to the a pH-oscillatory system, the device operates in much the same way as its metallic counterpart (with the state of the strip depending on pH as opposed to temperature). At low pH a contraction in the polyacid (and expansion in the polybase) bends the strip in the direction of the polyacid. At neutral pH the opposite occurs; i.e. the strip bends towards the contracted polybase. The triblock copolymer hydrogels used contain a weak polyelectrolyte midblock (poly(methacrylic acid) [PMAA] or, as shown in the figure, poly(2-(diethylamino)ethyl methacrylate) [PDEA]), “capped” with poly(methyl methacrylate) chain ends) which expand and contract in three dimensions when held in a cyclic pH-oscillating reaction.



SYSTEMATIC STUDIES OF THE EFFECT OF PEPTIDE LENGTH ON B-SHEET TAPE SELF ASSEMBLY

*R. P. W. Davies
SOMS Department of Chemistry
University of Leeds
Woodhouse Lane
Leeds LS2 9JT*

Chm0rpd@leeds.ac.uk

ABSTRACT

Phil Davies is currently studying for his PhD at the department of chemistry and the SOMS centre at the university of Leeds, under the supervision of Dr Amalia Aggeli. He has received his BSc and MRes in chemistry at the same institution.

In the SOMS centre the biological β -sheet motif has been previously exploited to design simple de novo peptides that adopt β -strand conformation. These peptides self-assemble in one dimension in a hierarchical manner to form a variety of well defined twisted elongated nano structures such as β -sheet tapes (single molecule in thickness), ribbons (a pair of stacked tapes back to back), fibrils (a bundle of stacked ribbons) and fibres (a pair of fibrils interacting edge-to-edge). The overall aim of the research of the peptide group in the SOMS centre is to understand the fundamental factors that govern peptide self-assembly and to apply this knowledge to the design of useful peptidic materials with a combination of properties appropriate for applications in nanotechnology, chemical and pharmaceutical industries

My specific research project aims to demonstrate quantitatively how specific peptide molecular parameters affect the energetics of peptide self-assembly and morphology of the aggregates in the dilute regime. As well as their material properties in the semi dilute regime

We gratefully acknowledge the financial contribution of the SOMS centre, DOW chemicals and the Royal Society (Amalia Aggeli is a Royal Society research fellow)

Gas and Vapour Sensing Characteristics of Langmuir-Schaeffer

Thiol Encapsulated Gold Nanoparticle Thin Films

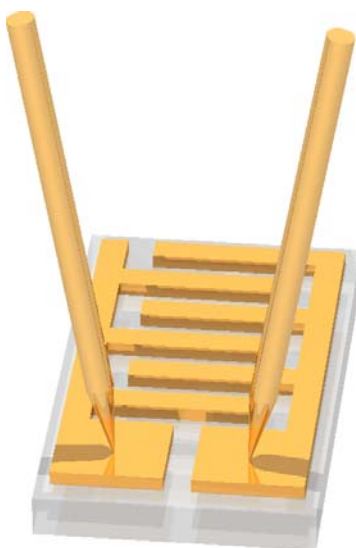
Marcus D. Hanwell, Sasha Y. Heriot, Tim H. Richardson and N. Cowlam
Department of Physics & Astronomy, University of Sheffield, Hicks
Building,
Hounsfield Road, Sheffield, S3 7RH (UK).

Email: m.hanwell@sheffield.ac.uk

A B S T R A C T

Thiol encapsulated gold nanoparticles can be used as sensitive probes of gas or vapour concentrations. The conductivity of a thin film of two or more layers of such nanoparticle arrays can be measured using interdigitated gold electrodes. The conductivity arises as a result of quantum tunneling between the conductive gold nanoparticle cores and the insulating thiol/air medium between them. It is thus very sensitive to small changes in the inter-nanoparticle separation and/or the permittivity of the medium between the gold cores.

The conductivity of various films deposited under differing deposition conditions has been examined for several different encapsulating thiols. A number of organic vapours and gases have been used to test the response of the films as well as their recovery after exposure and their longer term degradation after subsequent exposures of the films. The efficiency of the gas sensing characteristics of the thin film devices was also correlated with deposition conditions in order to optimize device production. In particular NO₂ gas was examined, along with some organic vapours. Detector efficiency and recovery was also examined at elevated temperatures.



The Preparation of Well-Defined Poly(Diethylamino Ethyl Methacrylate) Brushes by ATRP

*Keqin Xu and Tony Ryan
Department of Chemistry, University of Sheffield,
Sheffield S3 7TY*

A B S T R A C T

The pH stimuli responsive polymer brushes and gels have become of interest as novel intelligent materials with sensor, processor and actuator functions. We prepared 2-Bromoisobutyrate-functionalized colloidal initiators and used them in atom transfer radical polymerisation for the preparation of poly (diethylamino ethyl methacrylate) (PDEA) brushes on submicrometer-sized silica particles. These organic-inorganic hybrid particles have been characterized by elemental microanalyses, FT-IR spectroscopy, dynamic light scattering, and scanning electron microscopy. The densities of polymer brushes ranged 0.01-1.0 chain/nm².

MuPP2 by Royal Demand

*John Embery
IRC in Polymer Science & Technology,
University of Leeds*

A B S T R A C T

A photographic resume of four days in July, when the Microscale Polymer Processing team exhibit "Puzzling Plastics" was presented at the Royal Society. The "Extruder Simulator" proved to be a hit with its colourful visuals and interactive design. The team were on hand ten hours per day to provide practical explanations of molecular extension, polymer processing and analysis and the application in everyday life. Four thousand visitors attended, many of the public being students with an enthusiasm for science.

A TEARING ENERGY STUDY OF ORIENTED AND RELAXED POLYSTYRENE IN THE GLASSY STATE

*J. Embery¹, R. S. Graham¹, R. A. Duckett¹, D. Groves¹, M. Collis², M. R. Mackley²
and T. C. B. McLeish¹*

*¹ IRC in Polymer Science & Technology, University of Leeds
² Department of Chemical Engineering, University of Cambridge*

A B S T R A C T

Tear strengths have been measured of polystyrenes to determine effects of molecular weight/distribution and molecular orientation. Samples were produced by drawing at temperatures of 113°C or 148°C and orientation monitored via birefringence. The fracture energy, G_{3C} was measured at 20°C by tearing was found to be highly anisotropic.

Probing the stress hardening phenomenon by combined SANS, birefringence and extensional Rheology

*J. Embery, R. S. Graham, L.R.Hutchings
IRC in Polymer Science & Technology, University of Leeds
and
IRC in Polymer Science & Technology, University of Durham*

A B S T R A C T

A novel extensional rheometer fitting, the SER (Sentmanat Elongational Rheometer) has been utilised to produce polystyrene tapes under specific strain, extension rate and relaxation regimes. The purpose of this was to investigate the orientation on the short and long length-scale imposed by the variation in condition. Modelling has been used to . Neutron scattering carried out at a later point and the comparison with model prediction will complete the investigation

NON-LINEAR SHEAR FLOW BEHAVIOUR OF MONODISPERSE POLYISOPRENE MELTS

*D. Auhl¹, J. Ramirez¹, A. E. Likhtman¹, T. C. B. McLeish¹, P. Chambon²,
C. Fernyhough²*

*¹Interdisciplinary Research Center (IRC) in Polymer Science and
Technology*

and ²University of Leeds, LS2 9JT Leeds, United Kingdom (GB)

E-mail: phyda@phys-irc.leeds.ac.uk

A B S T R A C T

Non-linear rheological properties of polymer melts at large strains are of high interest for the processing performance of thermoplastics and its prediction using constitutive equations. In the literature not much data have been published about the non-linear shear flow behaviour in the case of monodisperse polymer melts.

Experimental and theoretical work on the non-linear shear flow behaviour of linear monodisperse polyisoprene melts is presented. The molecular weights of the samples studied differ in about two orders of magnitude resulting in a large range for the number of entanglements. Non-linear viscoelastic properties in shear have been determined at different temperatures from constant strain-rate tests, followed by reverse flow and relaxation tests. The results on the non-linear viscoelastic behaviour are compared to the predictions of molecular models such as a tube CCR model, which are capable of describing non-linear shear flow of entangled polymers. Model parameters have been determined from the linear viscoelastic behaviour using master curves of dynamic-mechanical data. Characteristic features of the flow curves, e. g. the shear stress overshoot, are discussed as a function of average molecular weight, temperature, and strain rate, respectively.

DENDRITIC FLUOROCARBON END-FUNCTIONALIZED POLYMERS AS ADDITIVES TO MODIFY POLYMER PROPERTIES AT SURFACES AND INTERFACES

L. R. Hutchings, *Amilcar Pillay Narrainen*, Imtiyaz A. Ansari, Nigel Clarke and Richard L. Thompson.

IRC in Polymer Science and Technology,
Department of Chemistry, University of Durham, Durham DH1 4LE, UK
amilcar.pillay-narrainen@durham.ac.uk

ABSTRACT

In this work we describe the synthesis and use of fluorinated polymer additives (example shown in Figure 1) which can be added to a bulk polymer to achieve low surface energies. Fréchet-type poly(arylether) dendrons with two, three and four peripheral C_8F_{17} groups were prepared. The core functionality of the dendrons was chosen so as to provide suitable initiation in the copper mediated living radical polymerisation of styrene and MMA. The control of the polymerisations will be discussed.

These fluorocarbon end-functionalised polymers were blended with unfunctionalised hydrogenous polymer and spin-coated into thin films. The surface adsorption behaviour as investigated by ion beam analysis (deuterated additives) revealed strong adsorption at the film surfaces. Contact angle measurements also showed significant changes in surface properties. The dependence of the adsorption of the additives and contact angles will be discussed in terms of the number of fluorocarbon groups and the molecular weight of the functionalised polymer. The effect of annealing the films is also investigated.

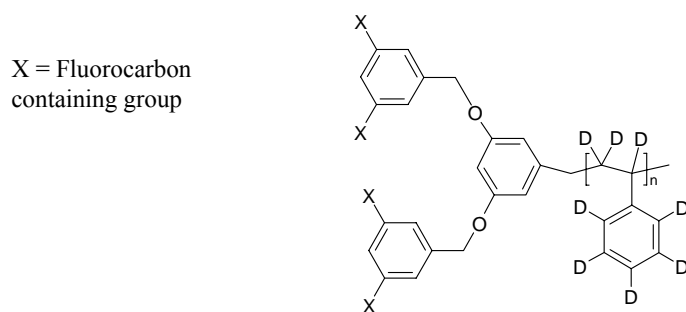


Figure 1. Typical dendritic functionalized deuterated polystyrene prepared

Electrochemical screening of self-assembling β -sheet peptide interactions with lipid monolayers

E. Protopapa, A. Aggeli, A. Nelson

Centre for Self-Organising Molecular Systems, School of Chemistry, University of Leeds, LS2 9JT, UK

A B S T R A C T

The aim of this project is to investigate and compare the interactions of Alzheimer's A β peptide and of a series of designed self-assembling β -sheet forming peptides with a model monolayer phospholipid dioleoyl phosphatidylcholine (DOPC) using electrochemistry in neutral solution conditions (pH~7.6) in presence of 100 mM KCl with 10 mM phosphate buffer.

Self-assembling peptides can be designed to interact in one-dimension in solution above a critical concentration to form well defined nm-long nanostructures, such as tapes, ribbons, fibrils and fibres. Amphiphilic self-assembling tapes can interact with the water-lipid interface and also penetrate the lipid bilayer and form transmembrane β -barrel pores with ion channelling activity. These well-defined peptide aggregates are good model systems that can advance our understanding of biological protein-like self-assembly, peptide aggregation in pathological situations (e.g. amyloid diseases), protein-lipid interactions, structure and function of β -barrel integral membrane proteins, and the role of lipid membranes in formation and stabilisation of pathological amyloid structures. In addition peptides can be designed to self-assemble in physiological solution conditions to form three-dimensional solid-like gel networks that are currently investigated as matrices for tissue engineering and for personal care products. It is imperative to establish the potential of such peptides to interact and self-assemble in lipid membranes in order to avoid designing peptidic materials with potential toxic/harmful effects in the body.

This project illustrates the advantages of using an electrochemical membrane-mimetic system to further the understanding of phospholipid-peptide interactions. This assignment is a continuation of a three year EPSRC funded programme of research co-ordinated by Dr Laurence Andrew Nelson, with the participation of Dr Amalia Aggeli in the SOMS centre at the University of Leeds.

Solution Behaviour of pH-Responsive Amphiphilic Block Copolymers

Christine M. Fernyhough and Anthony J. Ryan,

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

The solution behaviour of two block copolymers of similar mass and composition was compared. A polybutadiene-poly(acrylic acid) (PB-PAA) with a calculated volume fraction of poly(acrylic acid) of 0.30 was found to predominantly form vesicles at pH7 (Figure 1) using Transmission Electron Microscopy (TEM) analysis. The vesicles appeared to be stable over a wide pH range i.e. vesicles are formed at pHs greater than 5.

Poly(butadiene)-poly(*meth*acrylic acid) (PB-PMAA) also formed vesicles but in this instance a significant proportion of species were wormlike micelles at neutral pH (Figure 2). On increasing the pH, micelles formed (Figures 3 & 4) reflecting the increase in repulsive forces between the acid chains. The PB-PMAA was calculated to have an acid volume fraction of 0.32 which may be sufficient to increase the stability of worm-like micelles compared to the PB-PAA system¹ and provide a pathway to the formation of micelles.

Preliminary results comparing the two polymers will be presented, including TEM, Dynamic Light Scattering (DLS) and zeta potential measurements. Results for the electroformation of micron-size vesicles will also be shown; these reflect the findings for nano-vesicles. The factors affecting the delicate balance between the observed structures such as volume fraction of the acid block, hydrophilic-hydrophobic effects and the pka of the acids will be discussed.

Figure 1: TEM of PB-PAA at pH 7

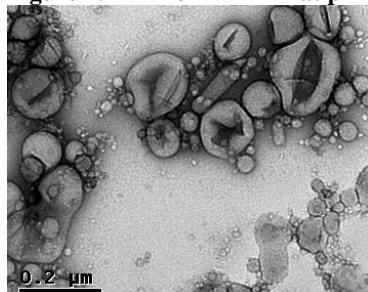


Figure 3 TEM of PB-PMAA on raising the pH from 7 to 10.5

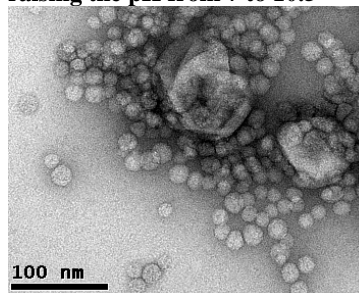


Figure 2 TEM of PB-PMAA at pH7

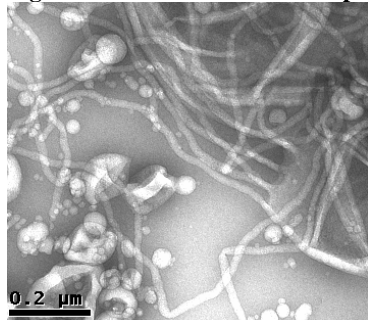
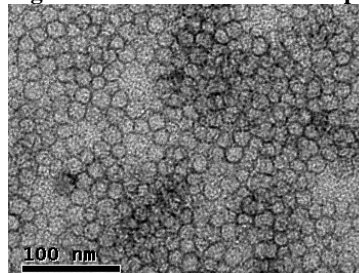


Figure 4 TEM of PB-PMAA at pH12



1. Geng, Y.; Ahmed, F.; Bhasin, N.; Discher, D. E. *Journal of Physical Chemistry B* **2005**, 109, (9), 3772-3779.

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 minimixer to reproduce large scale mixing.

Dynamic Wetting in Coating Flows.

*Professor H.Benkreira, Dr R.Patel, Mr I.Khan and Miss S. Buscaino
IRC in Polymer Science and Technology
School of Engineering, Design and Technology
University of Bradford, Bradford. UK*

ABSTRACT

Air entrainment, in all its forms, afflicts most industrial coating operations. It will always occur under certain critical conditions, usually low speeds particularly when the coating fluid is viscous. To overcome this limitation, industry retorts to experimenting with various substrates, playing on roughness, surface energies and other properties to improve productivity.

Most academic studies on air entrainment have been made in dip coating, where the geometry is simple and the experiments easy to perform. All experiments have however been made at atmospheric pressure. In this work we examine the effect of low vacuum on dynamic wetting to assess the role of air on its entrainment. Data on air entrainment velocities and dynamic contact angles will be presented and compared with data collected at atmospheric pressures.

A Novel Rotating Roll Die & Applications

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

ABSTRACT

The rotating roller die is an exciting new development in polymer extrusion and was the result of an EPSRC sponsored project (GR/M87085). The novel feature of the die is that unlike traditional extrusion dies it is not */stationary/* but consists of a pair of rotating rollers which can oppose or drag the extrusion flow. In the counter-flow mode, very large pressure can be developed in the die without having to reduce the gap. High-pressure (>100bars) extrusion without sheet thickness reduction opens up new opportunities for developing new green processing routes. One example is in the production of low-density thick plastic foams. Rather than using the environmentally damaging HCFC (named by the 1987 Montreal Protocol for banning from 2020), supercritical CO₂ instead can be used as the foam-blowing agent. Also, supercritical CO₂ is known as a plasticiser even in very small proportion (1%) and its addition to polymers enables their processing at lower temperatures. This is useful particularly with recycled plastics, which have a tendency to degrade at normal extrusion temperature. Any reduction in processing temperature in this application will enhance processing and encourage recycling, i.e. green processing.

Now extrusion is not limited to plastics but is used hot or cold to process soft solids like food, slurries, industrial and pharmaceutical pastes, as well as metals and ceramics. This new rotating roller die has now enhanced extrusion and can enable it to operate as “*a structuro/*” or a reactor at controlled high pressures as well as temperatures where liquid can be injected to a viscous mass and catalysts added directly or coated onto the screw. There lies an opportunity to develop new technologies/products with green & sustainability in mind.

The poster will describe research work carried out with this die.

Cold Extrusion of Fibre and Granular Waste into Acoustic Materials

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

ABSTRACT

The purpose of the research is to* *structure waste granular materials* *from plastic and rubber waste (cut and shredded textile wastes, granular rubber waste from tyres and trimmings from car industry and post-consumer carpet waste in particular) and blend them with additives and a liquid binder to produce new materials that could be used to shield us against noise, vibration and electromagnetic waves. The potential market for acoustic materials is huge. Applications include motorway and railway noise barriers, acoustic underlay and panels, sound proofed drainage in homes and building and electromagnetic proofing of public places (suppression of mobile phone communication for example). This market is rapidly increasing due to the increasing public expectation for quieter environment and the progressive legislation to control noise. This route of meeting society demands using waste from industrial and post-consumer sources also conforms to the needs of developing sustainable technologies and materials.

The novelty of the work resides in the approach to processing the material. Rather than using batch methods, here we apply polymer processing knowledge, extrusion and coating in particular to process these structures continuously, cleanly and safely.

The poster will present initial experimental work carried out with carpet waste material directly extruded with binders to produce a range of porous structure. The design and operation parameters of the extruder will be presented together with the properties evaluation methods of the structure of the samples. A theoretical insight will also be given to underpin this initial study.

Some Optical Properties of Fluorescently Modified Amyloid Fibrils

Kevin Channon^{*†}, *Dr Carlos Silva*[‡] & *Dr Cait MacPhee*[†]

[†]*Biological & Soft Systems, Cavendish Laboratory, University of Cambridge, Cambridge, UK, CB3 0HE*

[‡]*Département de Physique, Université de Montréal, Montréal, Québec, Canada*

ABSTRACT

Amyloid plaques, as found in the organs of individuals suffering from a number of degenerative diseases, are found mainly to constitute fibrous protein aggregates². These aggregates may be made *in vitro* from almost any protein, or poly-peptide – not limited to the disease-causing ones³. The structure formed is very stable and resistant to relatively harsh conditions.

In this study we aim to investigate the following key points: -

- ⇒ What is the plasticity of the amyloid structure to chemical modification with small molecules?
- ⇒ What are the effects of incorporating small molecules into the fibrils? Both on the fibril structure and the label molecule.
- ⇒ What effects are induced in the label molecules upon fibrilisation?
- ⇒ Can we make macromolecular equivalents of di-block co-polymers that display features such as exciton migration and trapping or semi-conducting effects?

Numerous spectroscopic techniques are employed, including steady-state and time-resolve fluorescence methods and circular dichroism, FTIR and raman spectroscopy. A number of microscopic techniques are also used, such as AFM, SNOM and confocal microscopy.

This work shows that additional groups, with interesting properties, can be successfully incorporated into the amyloid structure. As such, the amyloid fibril structure could be used as an 'all-purpose' molecular scaffold for the assembly of a multitude of molecules that would otherwise not assemble in any useful manner. We also use this principle to demonstrate a rudimentary macromolecular light-harvesting amyloid fibril structure.

² Dobson, *Protein misfolding, evolution and disease*, TiBS (1999), **24**, 329 – 332.

³ Fändrich *et al*, *Amyloid fibrils from muscle myoglobin*, Nature (2001), **410**, 165 – 166.

On the dynamics of semiflexible polymer solutions in the tightly entangled regime.

Authors:

<i>Mr. Manlio Tassieri</i>	<i>phymt@phys-irc.leeds.ac.uk</i>
<i>Dr. Lucian Barbu-Tudoran</i>	<i>lbarbu@hasdeu.ubbcluj.ro</i>
<i>Prof. John Trinick</i>	<i>j.trinick@leeds.ac.uk</i>
<i>Dr. Richard M. L. Evans</i>	<i>phyre@phys-irc.leeds.ac.uk</i>
<i>Dr. Tom A. Waigh</i>	<i>t.a.waigh@leeds.ac.uk</i>

ABSTRACT

We present experimental evidence that the effective medium approximation (EMA) developed by D.C. Morse (*Phys. Rev. E. 2001*) provides not only the correct scaling for the average tube diameter D_e ($D_e \sim \rho^{-1/2}$, where ρ is the contour length per unit volume), but also a good quantitative estimation of the macroscopic plateau modulus G ($G \sim \rho^{4/3} L_p^{-1/3}$, where L_p is the persistence length) of semiflexible polymer solutions in the tightly entangled concentration regime.

Previous theoretical studies have described the dynamics and viscoelasticity of very highly entangled solutions of semiflexible polymers in terms of the following scaling laws: $D_e \sim \rho^{-3/5} L_p^{-1/5}$ and $G \sim \rho^{7/5} L_p^{-1/5}$. Similar results have been obtained by Morse by considering a self-consistent binary collision approximation (BCA).

In this work both the EMA and BCA scaling predictions has been tested in the study of F-actin solutions by using a novel experimental approach, which combines passive particle tracking microrheology and dynamic light scattering. These techniques allow, respectively, independent measurements of G (T.G. Mason and D.A. Weitz, *Phys. Rev. Lett. 1995*) and L_p (K. Kroy and E. Frey, *Phys. Rev. E. 1997*). Combining these two parameters we discriminate between the two approximations, in contrast with the majority of previous experimental studies, which are mainly focused on the concentration functionality of G .

Smart Polymer Detection Systems

Ben Ryan
University of Sheffield

A B S T R A C T

This project is concerned with the investigation of chemistries that may lead to intelligent devices which could be incorporated into packaging as sensors.

Smart polymers are materials that respond in a clear and abrupt manner to an external stimulus. The smart response of polymethacrylic acid (PMAA) is initiated by changing the pH of the solution which results in a change in conformation of the polymer. Photophysical techniques are being used to detect this response which could lead to a visual sensor device based on PMAA. Recent results indicate that a smart response is induced in PMAA on exposure to carbon dioxide (which forms carbonic acid in aqueous solution).

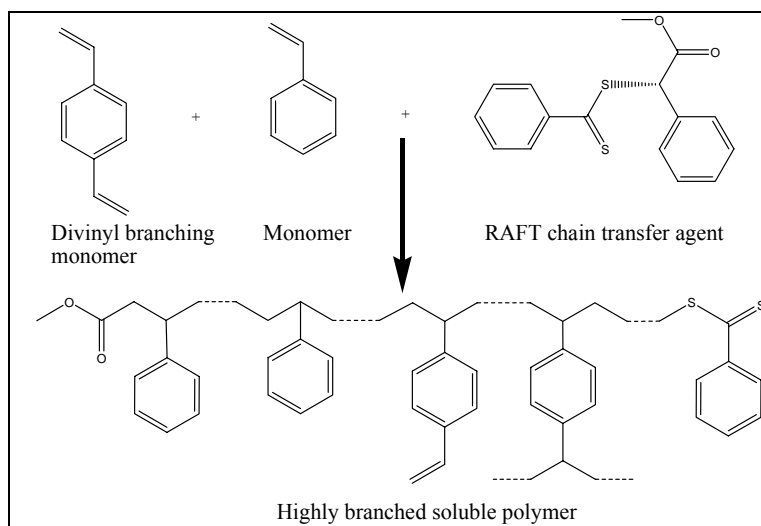
Since carbon dioxide is one of the volatiles released when fresh produce ripens it is hoped that a PMAA based gel when incorporated into food packaging will act as a ripeness sensor.

NOVEL HIGHLY BRANCHED POLYMERS SYNTHESISED VIA RAFT POLYMERISATION AND THEIR CHARACTERISATIONS

Philip Mounteney (a), Sebastien Perrier(a), Dave Duncalf(b) and Steve Rannard(b)*
(a)Department of Colour and Polymer Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
ccd9pem@gmail.com*, <http://www.leedspolymers.leeds.ac.uk/>
(b)Unilever Research & Development, Port Sunlight Laboratories, Quarry Road East, Bebington, Wirral, L63 3JW, UK

ABSTRACT

A one-pot RAFT polymerisation was used to synthesise novel well-defined dendritic polymers, via copolymerisation of styryl or methacrylate monomers with a divinyl branching agent (Scheme 1).¹ The use of a living radical system ensured good control over the architecture of these highly branched polymers, and opens the way to new structures (e.g. multi-arm star polymers with dendritic cores) via a one-step synthesis. Variation in concentration of branching agents allowed the synthesis of highly branched polymers of different molecular weights and polydispersities, and was also found to affect the rate of branching. This communication will present our latest findings on the synthetic parameters to consider in order to permit facile syntheses of these novel dendritic polymers, with tailored physical properties.



Scheme 1. Synthesis of highly branched soluble polymers via a RAFT methodology

- (1) Liu, B. L.; Kazlauciusas, A.; Guthrie, J. T.; Perrier, S. *Macromolecules* **2005**, *38*, 2131-2136.

Z-SUPPORTED RAFT GRAFT POLYMERIZATION: TOWARDS THE SYNTHESIS OF TRUE LIVING POLYMERS

Youliang Zhao, Sébastien Perrier

*Department of Colour and Polymer Chemistry, University of Leeds, LS2 9JT, UK
ccdyzh@leeds.ac.uk*

ABSTRACT

The surface modification of inorganic particles and synthetic resins has attracted increasing interest due to their unique properties and potential applications. In recent years, living radical polymerization has been widely used to grow polymer chains on the surface of solid supports such as functionalized silica, silicon wafer, CdS, gold, carbon nanotube, Merrifield resin, and cellulose. Among them, reversible addition-fragmentation chain transfer (RAFT) polymerization is among the most versatile and promising approaches to date due to its compatibility with a wide range of monomers and reaction conditions. In general, RAFT graft polymerization based on solid supports can be performed using both the R-group approach where the chain transfer agent (CTA) is attached to the backbone via the leaving and reinitiating R group and the Z-group approach where the CTA is attached to the backbone via the stabilizing Z group. However, reports on Z-supported RAFT polymerization of vinyl monomers from a solid support are scarce. In this study, RAFT polymerization of methyl acrylate (MA), butyl acrylate (BA), methyl methacrylate (MMA) and styrene (St) mediated by silica-supported 3-(methoxycarbonyl-phenyl-methylsulfanylthio carbonylsulfanyl)propionic acid (Si-MPPA) was investigated. For RAFT polymerization of MA conducted in toluene at 60 °C, effects of monomer concentration, AIBN content, monomer-to-Si-CTA ratio, free CTA content, and reaction time on polymerization were studied in detail. The pseudo-first-order polymerization kinetics was maintained until high conversion up to 80%, while polymerization behaviors in solution and on the surface of solid support were different, evident from the distinct evolution of molecular weight of free and grafted polymers with monomer conversion. The introduction of a free CTA such as MPPA and 2-(2-cyanopropyl) dithiobenzoate (CPDB) in solution during polymerization could significantly improve the control on molecular weight and polydispersity of grafted polymers, and the polymerization in the presence of CPDB was more controlled than that using MPPA. The resultant homopolymer grafted silica was utilized as a macro-CTA to mediate chain extension polymerization, and a series of diblock copolymer grafted silica hybrids were prepared. Aminolysis of the polymers allowed the recovery of the polymeric chains showing 100% chain extension, as illustrated by the complete shift of GPC traces and low polydispersity ($M_w/M_n < 1.2$). This efficient chain extension polymerization confirmed the original macro CTAs had “true” living homopolymer chains covalently attached to the surface.

3D simulation of Water and Gas Assisted Injection Moulding

*L. Mulvaney-Johnson , E. C. Brown, P. D. Coates, A. J. Dawson (a),
J. Sienz, J. F. T. Pittman, A. Polynkin (b)
J. Butler, B. Brookshaw, K. Crow (c)*

(a) IRC in Polymer Science and Engineering, University of Bradford, UK

*(b) Centre for Polymer Processing Simulation and Design, University of
Swansea, UK*

(c) Cinpres Gas Injection, Middlewich, Cheshire, UK

ABSTRACT

A modelling formulation is being developed to accurately capture the physical behaviour of the cavity filling and cooling phases of the Water Assisted Injection Moulding (WAIM) and Gas Assisted Injection Moulding (GAIM) processes. Validation of the moulding simulation is carried out using an instrumented mould that attempts to provide temperature and pressure data from selected points. In addition, ultrasound is adopted to “see” the bubble front progression and residual wall thickness, therefore attempting to monitor the progression of the bubble through the polymer melt between sensors and obtain in-process wall thickness measurements respectively.

Multiblock Copolymers via RAFT Polymerization

Hesna Gemici*, Thomas Martyn Legge, Sebastien Perrier
Department of Colour and Polymer Chemistry, University of Leeds,
Woodhouse Lane, Leeds, LS2 9JT
efy0hg@leeds.ac.uk, www.leedspolymers.leeds.ac.uk

ABSTRACT

Reversible addition-fragmentation chain transfer (RAFT) polymerization is a versatile process, compatible with a wide range of monomers, solvents and reaction conditions, and which produces polymers of controlled molecular weights, narrow polydispersities and with high chain-end functionality retention.^(1,2,3) In this work, the thiocarbonyl thio chain-end functionalities of telechelic polymers produced by RAFT were reduced into thiols, and further reacted to form disulfide bridges, and produce high molecular weight multiblock (co)polymers. The reactions is fully reversible, and allows to reversibly produce high molecular weight polymers from telechelic, near monodispersed building blocks. This is the first example of the use of RAFT polymerisation, coupled with thiol chemistry, to synthesise such materials. This procedure proves much easier than the previously published route via ATRP.⁽⁴⁾

References

1. Chiefari J., Chong Y. K., Ercole F., Krstina J., Jeffery J., Le T. P. T., Mayadunne R. T. A., Meijs G. F., Moad C. L., Moad G., Rizzardo E., Thang S. H. *Macromolecules*, **1998**, 31, 5559.
2. Moad G., Rizzardo E., Thang S. H., *Aust. J. Chem.*, **2005**, 58, 379.
3. Perrier S., Takolpuckdee P., *J. Polym Sci. Part A: Polym Chem.*, **2005**, 43, 5347.
4. Tsarevsky, N.V., Matyjaszewski, K., *Macromolecules*, **2002**, 35, 9009

In-Process Measurements for Polymer Processing

*J Sweeney, P Caton-Rose, R Spares and P D Coates
IRC in Polymer Engineering, University of Bradford, Bradford, UK*

ABSTRACT

A two year D.T.I. funded project to investigate and promote the use of in-process measurements for polymer processing is described. The project, run in collaboration with over 40 companies, aims to enhance the competitiveness of UK industry by improving product quality, repeatability and control. Accurate measurements made under actual process histories (stress, strain, velocity and temperature fields) can provide useful information regarding process variation, melt consistency, product morphology and molecular architecture. Measurement techniques under investigation here include spectroscopy, ultrasound, rheology, imaging, thermal fields and energy consumption. A range of extrusion and moulding processes are included, with particular emphasis on challenging high strain rate processes and materials such as nanocomposites, recycled polymers and bio-polymers.

A Unified Model of Necking and Shearbanding in Amorphous and Semicrystalline Polymers.

*J Sweeney, P Caton-Rose, R Spares and P D Coates
IRC in Polymer Engineering, University of Bradford, Bradford, UK*

ABSTRACT

In tensile stretching, many polymers undergo strain localisation. The geometrical form of the localisation can take the form of either a shear band or an approximately symmetric neck. We present a constitutive model of the early stages of deformation that predicts which form the localisation takes. The model consists of an Eyring process acting with a Gaussian network, implemented numerically. A Levy-Mises flow rule associated with the Eyring process has a tendency to produce shear bands. A relatively stiff Gaussian network is used in a model of polycarbonate that ensures that most of the strain is taken up by the Eyring process, resulting in shearbanding. By contrast, a relatively soft Gaussian network is used in a model of polyethylene, which takes up the greater part of the strain, resulting in a neck. The predictions are compared with experiments. For polyethylene, a two Eyring process model is introduced for better accuracy.

Mechanical Property Predictions in Fibre Reinforced Polyamide Injection Moulded Parts Using Measured and Predicted Fibre Orientation Within ABAQUS

P. Caton-Rose (a), P. Hine, A Duckett (b), B Whiteside and P. D. Coates (a)
(a) IRC in Polymer Engineering, University of Bradford, Bradford, UK,
(b) Department of Physics, University of Leeds, Leeds, UK.

ABSTRACT

In this poster we discuss the use of ABAQUS finite element software for the prediction of short fibre reinforced polyamide injection moulded parts subjected to bending loads. The analysis uses a shell mesh with composite material data provided by two distinct routes. Firstly, using fibre orientation predictions from a Moldflow MPI 5.0 midplane analysis and a proprietary translator provided by ABAQUS Ltd. The second route uses measured fibre orientation data from the University of Leeds image analysis system and translated into composite material data using the Tandon-Weng model. Using these two routes it is possible to assess the errors incurred during Moldflow analysis stages in terms of both predicted fibre orientation errors and the final mechanical properties of the composite material. The initial investigation compares tensile and three-point bend response of two strips either side of a transverse rib on a flat plate in addition to the evaluation the deformation of commercial automotive pedal.

Modelling and characterisation of polymer/clay nanocomposites in the processing regime.

*P E Spencer, J H Sweeney, W Al-Shabib and P D Coates
IRC in Polymer Engineering, University of Bradford, Bradford, UK*

ABSTRACT

Dramatic improvements in mechanical performance have been observed in polymer/clay nanocomposites, in which silicate platelets of nanoscale thickness are dispersed within a polymer matrix. The benefits over conventional composites derive primarily from the exceptionally large particle surface area achievable with the addition of only a small amount of particles (less than 5% by weight). In order to deal with the multiscale nature of the problem, a parameter-passing approach has been adopted, in which appropriate parameters determined from smaller-scale simulations act as the basis for larger-scale models. On the atomistic level, the properties of the clay platelets and the interface region are determined from molecular statics calculations using environmentally-dependant interatomic potentials. On the micron lengthscale, the nanocomposite is modelled using a statistical “Representative Volume Element” approach, in which a statistical ensemble of cells are generated according to given distributions in platelet shape, position and orientation (extracted from a large number of TEM micrographs). The effective mechanical properties of the composite system are determined using Finite Element Analysis for large strains, and passed up the lengthscale to be incorporated in models to predict processing behavior and final part properties. In relating the details at the molecular level with the material at the macroscopic level, it becomes possible to design materials to suit our needs. This EPSRC funded work forms part of a multidisciplinary collaborative project involving Bradford, Oxford and Queen's University Belfast.

Rechargeable Lithium Ion Cells Produced by the Extrusion Lamination of Polymer Gel Electrolytes

*I. M. Ward, H. V. StA. Hubbard, G. Thompson, IRC in Polymer Science & Technology, University of Leeds
J. Kaschmitter, H. P. Wang, SpectraPower Inc,
E. Cole and G. Flickenger, British Technology Group*

A B S T R A C T

Polymer Gel Electrolytes (PGE) based on polyvinylidene fluoride (PVDF) lithium salts and appropriate solvents 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.

Understanding the links between molecular aspects and stress-strain behaviour in polystyrene

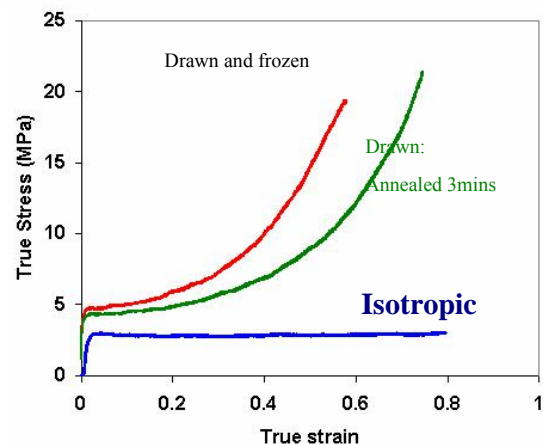
P.J.Hine*, R.A.Duckett* and D.J.Read#

- - School of Physics and Astronomy, University of Leeds, Leeds, LS2 9JT, UK
- # - School of Applied Mathematics, University of Leeds, Leeds, LS2 9JT, UK

This study is part of the second UK government sponsored Microscale Polymer Processing project (MUPP2 - www.mupp2.com). The broad goal of this project is to understand how molecular variables affect polymer processing and ultimately solid state mechanical properties. In the section of the work reported here, the aim is to establish links between molecular features and the glassy stress-strain behaviour. In the initial programme of study, we have worked with a commercially available polystyrene, BASF 158k, which has a molecular weight of 274,000g/mol and a polydispersity of 2.74. The aim has been to establish how molecular orientation at different length scales affects the stress-strain behaviour. This has been achieved by looking at the effect of the combination of a predetermined level of orientation, followed by an annealing stage, on the true stress/true strain curve.

The experiments have been designed around a knowledge of the various relaxation times involved with the polymer, calculated from the molecular based theories developed in the first MUPP project at Leeds [1]. Strips of polystyrene (14mm wide and 0.25mm thick), were extruded using a microspinner. Shrinkage measurements at 120°C showed around 5% shrinkage in these extruded strips, so they were annealed at 140°C for 1 hour, after which the shrinkage was measured to be zero. The samples were next drawn in a temperature controlled oven at 115°C to a draw ratio of 4:1. The samples were then either frozen immediately, or annealed at this temperature for times between 3 minutes (corresponding to the Rouse time of a single entanglement segment) and 24 hours (corresponding to the mean reptation time). The aim of the annealing process was to relax a set amount of the molecular orientation put in during the drawing process. After this the birefringence and shrinkage of the samples was measured, and the stress-strain behaviour was then measured at a lower temperature of 105°C.

The results obtained show that with annealing, the birefringence drops much more rapidly with annealing time than the shrinkage. This can be linked to the relaxation processes at short times relaxing short range order much more quickly than longer range (network) order. This behaviour is also reflected in the measured stress-strain curves. A sample annealed for three minutes at 115°C (and tested at 105°C) shows a significant lag in the onset of strain hardening, but the strain hardening region superimposes very well if the annealed sample is shifted along the strain axis by a set amount.



1. Collis et al, Constriction flows of monodisperse linear entangled polymers: Multiscale modeling and flow visualization, Journal of Rheology -- March/April 2005 -- Volume 49, Issue 2, pp. 501-522

CONTROLLED SYNTHESIS OF ISOPRENE VIA RAFT POLYMERIZATION

V JITCHUM, S PERRIER

Department of Colour and Polymer Chemistry, University of Leeds, LS2 9JT, UK
ccdvy@leeds.ac.uk, www.leedspolymers.leeds.ac.uk

ABSTRACT

We report the use of chain transfer agents to mediate the RAFT polymerization of isoprene. Homopolymers and block copolymers with controlled molecular weight and polydispersities as low as 1.2 were obtained. The polymerization conditions were optimized by variation of monomer / chain transfer agent ratios, initiator amount, and temperature. The effect of RAFT polymerization on the final composition of the polymer (1,2; 1,4 and 3,4 addition on the monomer) was also investigated.

LIGHT RESPONSIVE POLYMERS BY REVERSIBLE ADDITION FRAGMENTATION CHAIN TRANSFER (RAFT) POLYMERISATION

W SRIPROM, M NEEL, B M HERON, C D GABBUTT, S PERRIER
Department of Colour and Polymer Chemistry, University of Leeds, LS2 9JT, UK
ccdws@leeds.ac.uk, www.leedspolymers.leeds.ac.uk

A B S T R A C T

Photochromic copolymers of styrene and acrylate derivatives with the photochromic monomer 9-acryloyloxy-[3, 3-bis-(4-methoxyphenyl)]-3*H*-naphtho[2, 1-*b*]pyran were synthesized by reversible addition fragmentation chain transfer polymerization. The use of a living radical polymerization system allowed the control of the polymer content in photochromes. The photochromic properties of the synthesized copolymers were assessed in solution and in films. The fade rate of the block copolymer solutions was found to be faster than that of the films. However, well-controlled photochromic block copolymers were also synthesized via RAFT, and their self-assembly in the bulk was found to enhance the fade rate of the film.

WVTR by External Ion Beam Analysis

*A.S. Clough¹, S.A. Collins², F. E. Gauntlett¹, M. R. Hodgson³,
C. Jeynes⁴, M. S. Rihawy^{1,5}, A. M. Todd² and R. L. Thompson²*

1. Dept. Physics, University of Surrey

2. Dept. Chemistry, University of Durham

3. DuPont Teijin Films Ltd., Wilton

4. Ion Beam Centre, Advanced Technology Institute, University of Surrey

*5. Permanent Address: Atomic Energy Commission, P.O. Box 6091, Damascus,
Syria*

ABSTRACT

A new approach for water vapour transmission rate (WVTR) measurement is demonstrated that uses an external ion beam. “Sandwich” specimens were prepared comprising two films of the barrier material (PET) surrounding a thin film of hydrophilic poly(ethylene-oxide), “PEO”. Deuterated water (D₂O) permeating PET barrier films was trapped by the PEO, and quantified using ³He⁺⁺ nuclear reaction analysis and proton detection. WVTR was determined from the rate of D₂O accumulation in the PEO layer. This approach may be applied both to poor barrier films with WVTRs of $> 200 \text{ g m}^{-2} \text{ day}^{-1}$, and may extend to films whose barrier properties exceed levels that can be characterised with conventional techniques. Variation in the proton energy distribution provides a means of measuring D₂O migration within test samples. Strategies for improving the sensitivity and accuracy of this method for WVTR characterisation are discussed.

PMMA Nanocomposites: Synthesis, Processing and Physical Characterisation

*J. Elder, N. Clarke and L. R. Hutchings
IRC in Polymer Science & Technology,
University of Durham*

Abstract

Poly(methyl methacrylate) clay composites have been synthesised using a suspension polymerization technique containing 4% of organically modified clay. Modulated differential scanning calorimetry (MDSC) and thermal gravimetric analysis (TGA) were used to characterise the thermal stability of the polymer clay nanocomposites (PCN). X-ray diffraction was used to determine the extent of exfoliation and oscillatory shear rheology was used to detect any changes in the modulus and relaxation time.

X-ray diffraction of the PCN showed that the clay has become intercalated into the PMMA matrix. On heat pressing the gallery spacing was found to increase either due to a melt intercalation process or by the reordering of the PMMA chains. The presence of the clay particles produced a slight increase in the T_g and degradation temperature.

DENDRITICALLY FUNCTIONALISED POLYMERS AS SURFACE MODIFYING ADDITIVES

*I. A. Ansari, N. Clarke, L. R. Hutchings, A. P. Narrainen and R. L. Thompson
IRC in Polymer Science & Technology,
University of Durham*

We have synthesized a series of linear deuterio-polystyrene (dPS) chains from fluorocarbon (FC) functionalised dendritic initiators (Fig. 1). This approach enables us to add relatively large quantities of surface-active fluorocarbon groups onto the end of a polymer that is compatible with a bulk polymer. We are investigating the effect on self-segregation of polymers carrying multiple end-functionality by various techniques.

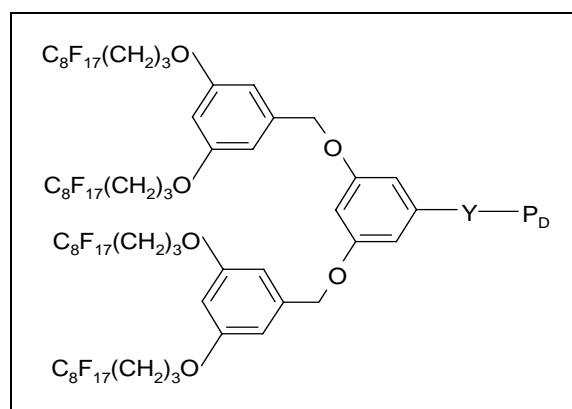


Fig. 1: Sketch of 4xFC dendron functionalised polymer chain with P_D as a linear dPS chain

We have studied the adsorption, diffusion and aggregation properties of these materials in blended films with unfunctionalised polystyrene. Nuclear reaction analysis (NRA) showed that the functionalised polymers spontaneously segregate to the film surface within a few seconds of the spin-coating process. This indicates that these materials have an appreciable surface – activity, even in solutions. Surface excess concentrations measured approach closely the value expected for saturated monolayer from which the homopolymer is largely excluded.

Contact angle measurements using both dodecane and water indicates a substantial (~50%) reduction in surface energy as saturation of the surface is approached.

Small Angle Neutron Scattering (SANS) experiments helped in understanding the aggregation of these materials in bulk while Neutron Reflectivity (NR) showed the possibility of multilayer absorption. The results obtained by SANS compliment our findings by NRA that these materials adsorb extremely strongly to film surfaces. The evidence from NR data for a possible multilayer absorption was confirmed by Transmission Electron Microscopy (TEM).

Physical Chemistry of Cell-Mineral Interactions

Rasika Fernando
Department of Chemistry
University of Sheffield

A B S T R A C T

The overall aim of the research is to understand the interactions between the various components of soil and groundwater which lead to microbial activity. Thus it may be possible to predict and manage such activity within contaminated soils and ultimately, reduce and convert pollutants *in situ* to less harmful forms using natural biodegradation processes. The essential scope of these studies is to qualitatively and quantitatively characterise the contribution of changes in polymer conformation and surface binding to cell-mineral interaction potentials as a controlling factor in cell adhesion for attached growth using simple intensity and lifetime measurements and time-resolved anisotropy measurements

The effect of high shear mixing on the mechanical properties of Carbon nanofibre reinforced Polypropylene

R J Foster, P J Hine, M Tassieri 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*

A B S T R A C T

Recent research at Leeds has involved the incorporation of carbon nanofibres (CNF) into hot compacted polypropylene. Tensile testing has shown an increase in the mechanical properties of the resultant hot compacted composite sheet, which are in reasonable agreement with modelling [1]. However, this initial study did not take into account the effect of the high shear experienced by the CNF within the twin screw extruder during blending.

This current study has built upon the work by Hine et al [1], in measuring the aspect ratio of the CNF at various stages of blending (after a single mix, after 4 mixes and after 7 mixes), and comparing the predicted Young's modulus of isotropic composite material, determined from each measured aspect ratio, to the measured Young's modulus of isotropic compression moulded sheets made at each stage of blending. We show that using a simple modelling technique (Cox-Krenchel) [2], the predicted modulus is in good agreement to that determined by static tensile testing.

Dynamic light scattering (DLS) was used to determine the length of the CNF at each stage, utilising a technique developed by Badaire et al [3] to fit the DLS autocorrelation function. Scanning electron Microscopy (SEM) image analysis was used to determine the diameter of the CNF.