UK Polymer Showcase

6th/7th September 2005

Cedar Court Hotel
(J39, M1)
Wakefield WF4 3QZ

Programme
and
Abstracts

UK POLYMER SHOWCASE

TUESDAY & WEDNESDAY
6 & 7 September, 2005

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

P R O G R A M M E

Tuesday 6th September 2005.

09.00	Registration
10.00	"Introduction" Professor Tom McLeish, Director, Polymer IRC
10.20	Dr. Nigel Clarke, University of Durham *"Self Assembly of Polymer Composites"*
10.40	Dr. Amalia Aggeli, University of Leeds *"Protein-like Self-assembly as the route towards smart polymers for nanotechnology"*
11.00	Dr. Andy Wilson, University of Leeds *"Hydrogen Bonding Building Blocks for Non-covalent Synthesis"*
11.20	**COFFEE**
11.50	Prof. Rudy Koopmans, Dow Benelux NV *"RD Challenges for the 21st Century: Sustainable Materials"*
12.20	Dr. Andrew Cooper, University of Liverpool *""*
12.50	**DISCUSSION**
13.00	**LUNCH and POSTER SESSION**
14.30	Dr. Alan Smith, DTI, UK MNT Network *"The Role of the UK MNT Network"*
15.00	Professor Dame Julia Higgins FRS, Imperial College, London *"Integrating the Four Ps"*
15.30	Dr. Jim Darwent, Unilever Central Research *"Current and Future Applications of Polymers in Home and Personal Care Products"*
16.00	**TEA**
16.30	Dr. Harald Egner, Fraunhofer TEG, Germany *"Fraunhofer - Innovative Routes to Polymer Processing"*
17.00	Prof. Markus Antonietti, University of Pottsdam *"Functional Block Polymers for the Control of Nanostructure Materials*
18.30 for 19.00	**SHOWCASE DINNER** **Cedar Suite, Cedar Court Hotel**

Wednesday, 7th September 2005.

09.30	Dr. Motohiro Seki, Mitsubishi Chemical Group, Japan *"Study on Shear-mediated Crystallization of iPP"*
10.00	Dr. Tim Gough, University of Bradford *"In-process Measurements for Monitoring of Polymer Melt Flows"*
10.20	Prof. Tony Ryan, University of Sheffield *"Electrospinning of Micro- and Nano-fibres for Tissue Engineering"*
10.50	**COFFEE**
11.20	Prof. Steve Armes, University of Sheffield *"Controlled-structure Biocompatible Block Copolymers"*
11.40	Dr. Ben Punchard, Faraday Packaging Partnership *"Plastic in Packaging: All Wrapped Up?"*
12.10	Prof. Michael Turner, University of Manchester *"Organic Materials for Electronics Consortium (OMEC)"*
12.40	Closing remarks/Discussion

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

ABSTRACTS

OF

LECTURES

UK POLYMER SHOWCASE
6/7 SEPTEMBER 2005
CEDAR COURT, WAKEFIELD

LIST OF ORAL PRESENTATIONS

Professor Tom McLeish, Director, Polymer IRC	Welcome and Introduction
Dr. Nigel Clarke, University of Durham	"Self-assembly of Polymer Composites"
Dr. Amalia Aggeli, University of Leeds	"Protein-like Self-assembly as the Route Towards Smart Polymers for Nanotechnology"
Dr. Andy Wilson, University of Leeds	"Hydrogen Bonding Building Blocks for Non-covalent Synthesis"
Professor Rudy Koopmans, Dow Benelux NV, Netherlands	"RD Challenges for the 21st Century: Sustainable Materials"
Professor Andrew Cooper University of Liverpool	"Polymer Synthesis using Supercritical Fluid Solvents: How Green is Now?"
Dr. Alan Smith, DTI	"The Role of the UK MNT Network"
Professor Dame Julia Higgins, FRS Imperial College, London	"Integrating the Four Ps"
Dr. Jim Darwent, Unilever Central Research	"Current and Future Applications of Polymers in Home and Personal Care Products"
Dr. Harald Egner, Fraunhofer TEG	"Fraunhofer - innovative routes to polymer processing"
Professor Markus Antonietti University of Potsdam	"Functional Block Polymers for the Control of Nanostructure Materials"
Dr. Motohiro Seki, Mitsubishi Chemical Group	"Study on Shear-mediated Crystallization of iPP"
Dr. Tim Gough, University of Bradford	"In-process Measurements for Monitoring of Polymer Melt Flows"
Professor Tony Ryan, University of Sheffield	"Electrospinning of Micro and Nano-fibres for Tissue Engineering"
Professor Steve Armes, University of Sheffield	"Controlled-structure Biocompatible Block Copolymers"
Dr. Ben Punchard, Faraday Packaging Partnership	"Plastic in Packaging: All Wrapped UP?"
Professor Michael Turner University of Manchester	"Organic Materials for Electronics Consortium (OMEC)"

Self Assembled Polymer Composites

Nigel Clarke, Ian Henderson and Gavin Buxton
Department of Chemistry, University of Durham, Durham, DH1 3LE

A B S T R A C T

Exploiting nature's ability to turn raw ingredients into remarkable materials has long been a goal of fundamental and applied science. One active area of research involves polymer mixtures that phase separate to form elegant structures with microscopic dimensions. The resultant materials, which often have properties substantially greater than the sum of the parts, have found applications as adhesives, coatings and even lightweight aircraft components. A drawback of phase separation in polymer blends is that a lack of control over the final structure limits our ability to tune the properties. This impedes the development of blends for more exotic applications, such as electronics and photonics. To overcome this limitation, we have recently proposed a method in which nano or micron sized polymer particles are dissolved in a liquid bath of a chemically different polymer. If the temperature is altered before complete dissolution, the two types of polymer may no longer want to mix. The laws of nature then ensure that, with the need to phase separate, unusual and perhaps even technologically useful materials emerge. To illustrate this concept, we show how ring-shaped doughnuts can be coaxed into briefly forming from circular particles; the shell of the doughnut is the same polymer as the original particle, but the hole is filled with the bath polymer. We also consider the consequences of different starting structures. The method opens a new avenue for fabricating tailored structures, whose range and dimensions are constrained only by the variety of sizes and shapes of the original particles.

PROTEIN-LIKE SELF-ASSEMBLY AS A ROUTE TOWARDS SMART POLYMERS FOR NANOTECHNOLOGY

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A B S T R A C T

Exploiting the intrinsic self-assembling property of peptides we have recently shown that it is possible to form a hierarchy of new and well-defined polymeric materials. In particular oligomeric peptides can be designed to adopt a β-strand conformation and to self-assemble in one dimension, in appropriate solution conditions, to form elongated one-molecule thick polymeric β-sheet tapes, ribbons (a pair of stacked tapes), fibrils (a twisted stack of ribbons) and fibres (entwined fibrils). Self-assembly is understood theoretically and is driven by numerous intermolecular peptide backbone hydrogen bonds as well as side-chain interactions. These polymers at concentrations above *ca.*0.1mM can form nematic fluids, and nematic or isotropic organogels and hydrogels.

By appropriate peptide design there is the opportunities to create tailor-made polymers with specific unique combination of desirable surface, responsive, mechanical and functional properties appropriate for usage of these materials in a wide range of applications eg as scaffolds for tissue engineering, controlled drug delivery systems, and personal care products.

References

1) Designed self-assembled β-sheet peptide fibrils as templates for silica nanotubes, Meegan, J, Aggeli, A, Boden, N, Brydson, R, Brown, A, Carrick, L, Brough, A, Hussain, A, Ansell, R, *Advanced Functional Materials,* **14**, 31-37, 2004

2) Fluorescence studies and tryptophan-tryptophan energy migration in pH-triggered self-assembled β-sheet ribbons, Kayser, V, Turton, D, Aggeli, A, Beevers, A, Reid, G, and Beddard, G, *J. Am. Chem. Soc.,* **126**, 336-343, 2004

3) EFTEM investigation of silica nanotubes produced using designed self assembling β-sheet peptide fibrils as templates, Meegan JE, Aggeli A, Boden N, Brydson R, Brown AP, Carrick L, Ansell RJ *Inst Phys Conf Ser* **179**, 475-478, 2004

4) The internal dynamic modes of charged self-assembled peptide fibrils Carrick L, Tassieri M, Waigh TA, Aggeli A, Boden N, Bell C, Fisher J, Ingham E, Evans RML *Langmuir* **21**, 3733-3737, 2005

5) Adsorption and self-assembly of peptides on mica substrates, C. Whitehouse, J. Fang, A. Aggeli, M. Bell, R. Brydson, C. W.G. Fishwick, J. Henderson, C. M. Knobler, R. W. Owens, N. H. Thomson, D. A. Smith & N. Boden, *Angewandte Chemie Int. Ed.,* **44**, 1965-1968, 2005.

6) Interaction of self-assembling *β*-sheet peptides with phospholipid monolayers, E. Protopapa, A. Aggeli, A. Nelson, N.Boden, L.C.Salay & P.F.Knowles, *Medical Engineering & Physic*s, in press.

Hydrogen Bonding Building Blocks for Non-Covalent Synthesis

Dr Andy J Wilson

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A B S T R A C T

Non-covalent synthesis is highly topical because dynamic architectures can be obtained *via* hierarchical expression of molecular properties, and this may find use in a plethora of materials settings.[1] Hydrogen bonds are attractive for assembly because of the strong, selective and directional interaction conferred by specific arrangements of hydrogen bond accepting and donating groups. Several groups have pursued the synthesis of hydrogen-bonding building blocks and studied their various modes of assembly in solution and the solid state.[2,3] However, it is recognized that alternatives capable of strong and selective hetero and homodimerisation are necessary. Furthermore rendering such assemblies kinetically inert so that the benefits of the assembly process are enjoyed across a range of environmental stresses is an unsolved problem.[4] In this presentation we shall discuss (i) self-assembly and polymerization of benzenetricarboxamides and (ii) synthesis and molecular recognition properties of uriedoimidazoles and amidoisocytosines.

1. Brunsveld, L., Folmer, B. J. B., Meijer, E. W. Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071-4097.
2. S. C. Zimmerman, P. S. Corbin, *Struct. Bonding*. **2000**, *96*, 63-94.
3. R. P. Sijbesma, E. W. Meijer, *Chem. Commun.* **2003**, 5-16.
4. A. J. Wilson, M. Masuda, R.P. Sijbesma, E. W. Meijer: *Angew. Chem. Int. Ed.*, **2005**, *44*, 2275-2270.

R&D Challenges for the 21st Century – Sustainable Materials

Prof. R. J. Koopmans – Core R&D
Dow Benelux BV – P.O. Box 48 – 4530 AA Terneuzen – The Netherlands

A B S T R A C T

Most commonly known plastics have been discovered or invented in the first half of the 20th century and researched, developed and engineered for the last 50 years into indispensable materials for a functioning society. With few exceptions most plastics have become commodity materials for markets that require cost competitiveness, consistent quality, and flawless performance. However, the societal outlook on future material needs indicates a trend towards a novel class of polymeric materials that is both sustainable and functional. This awareness is founded on the observations of an over-reliance on non-sustainable petroleum feedstock; a lack of versatility for the current synthetic polymeric materials having singular molecular properties; the advance in biotechnology as an enabling strategy towards green chemistry.

This challenges the R&D community in academia and industry to reinvent the way polymeric materials are conceived and to revisit the chemistry and physics of naturally occurring materials. Particularly the latter, reflecting upon polysaccharides, polypeptides and polynucleotides, offers a new field of research and development with unprecedented opportunities for innovative materials development going beyond the performance and application range of current synthetic polymers. Some approaches as to how this can be addressed will be presented.

Polymer Synthesis using Supercritical Fluid Solvents: How Green is Now?

Professor Andrew I. Cooper,
Department of Chemistry & Centre for High Throughput Materials Discovery,
University of Liverpool, Liverpool L69 7ZD, UK

Supercritical carbon dioxide has attracted much interest recently as an alternative solvent for the synthesis and processing of polymers. It is unclear, however, that many of the approaches touted in the literature are likely to have real commercial application; nor, indeed, that they are really more sustainable when all environmental considerations are taken into account. In this lecture we will discuss some of our recent research where we have attempted to tackle issues such as reaction pressure, surfactant cost, and surfactant degradability in order to develop processes that may have real practical application.

References:

(1) B. Tan and A. I. Cooper, *J. Am. Chem. Soc.*, **2005** *127*, 8938.
(2) B. Tan, H. M. Woods, P. Licence, S. M. Howdle and A. I. Cooper, *Macromolecules*, **2005** *38*, 1691.
(3) C. L. Bray, B. Tan, C. D. Wood and A. I. Cooper, *J. Mater. Chem.*, **2005**, *15*, 456.
(4) R. Butler, I. Hopkinson, and A. I. Cooper, *J. Am. Chem. Soc.*, **2003**, *125*, 14473.
(5) C. D. Wood and A. I. Cooper, *Macromolecules*, **2003** *36*, 7534.
(6) A. K. Hebb, K. Senoo, R. Bhat and A. I. Cooper, *Chem. Mater.* **2003** *15*, 2061.
(7) C. D. Wood, K. Senoo, C. Martin, J. Cuellar and A. I. Cooper, *Macromolecules*, **2002** *35*, 6453.
(8) R. Butler, C. M. Davies and A. I. Cooper, *Adv. Mater.*, **2001** *13*, 1459.

THE ROLE OF THE UK MNT NETWORK

Dr. Alan Smith
Department of Trade and Industry

A B S T R A C T

The DTI has established the MNT Network to help coordinate the fragmented activities in nanotechnology throughout the UK, with a view to maximising the benefits that this emerging technology will have on the country's economy.

Most of the early applications for nanotechnology, which will be illustrated, are in the materials arena, so the Network is keen to ensure that the UK is ready to exploit the potential markets, and develop new ones, as quickly as possible. With this in mind, a number of activities are already underway and these will be described.

The Government is also supporting better awareness of how nanotechnology is likely to change people's lives, and is also keeping an eye on the potential risk issues that are being associated with nanoparticles.

Integrating the four Ps

Better, faster, more efficient production of new polymeric materials by exploitation of the feedback loop through polymer synthesis through polymerisation processes to property characterisation.

E.Alpay, S.Gretton-Watson, J.S.Higgins, J. H. G. Steinke
Imperial College London

A B S T R A C T

The quality of polymeric materials depends crucially on the complex interaction of the synthesis route with the reaction engineering of their production and subsequent processing. Molecular weight, molecular weight distribution, copolymer statistics, branch distribution, are among key factors determining end properties so that as well as new synthetic routes and new reactor design, detailed modelling becomes vital in controlling and optimising properties of innovative polymeric materials. The P4 project was formed to leverage the expertise available in the different facets of polymer science at Imperial College in the Departments of Chemical Engineering and Chemistry, resulting in a team that could collectively address the synthesis of materials with novel properties and their optimal production in bulk quantities. With a focus on hyper-branched polymers we have developed models for the molecular weight averages and the degree of branching and produced materials for trials in the area of rheology modifiers, coatings, dental applications, biodegradation and gene delivery.

Future Direction for Polymers in Home and Personal Care Products

Dr Jim Darwent

Vice President Corporate Research,
Unilever Colworth,
Sharnbrook, Bedford
MK44 1LQ

Home and personal care products are part of our everyday life. They are so familiar that we take them for granted and are generally unaware of the technology that is used in simple products such as shampoos and detergents. Polymers are one of the key ingredients in these products and give a wide range of benefits. Indeed polymers have been the major source of innovation in home and personal care products in the past twenty years. In the future new understanding and new types of polymeric materials will continue to provide an important stimulus for improved products.

The first use of polymers in laundry products was as anti-redeposition agents to give improved cleaning in dirty water. This application was followed by a growth of innovation in phosphate free detergents which depend on polymers to prevent calcium ions precipitating the surface active detergents. More recently polymers have been used to deliver clothes care benefits through colour protection, fibre lubrication and perfume delivery.

In shampoos and conditioners, polymers provide the active mechanism to deliver softness, hair care and styling benefits. This depends on “smart chemistry” to give targeted deposition in products that are primarily designed to be very effective at removing materials from the surface of hair.

Polymers are also important in controlling the structure of products, for example the stability and dissolution properties of granules in washing powder and the thickness and flow of skin creams and shampoos. An interesting new application is the use of polymers to swell rapidly and disintegrate washing tablets in seconds when they are added to water.

Looking to the future there are very major challenges for the home and personal care industry where new polymer technologies will make a difference. The search for biodegradable polymers remains a significant challenge. New block co-polymers and low cost peptides offer great promise for delivering caring benefits to skin, hair and clothes bringing a little more comfort to everyday life.

"Fraunhofer - Innovative Routes to Polymer Processing"

Dr. Harald Egner,
Fraunhofer TEG, Germany

A B S T R A C T

The Fraunhofer-Gesellschaft is one of Europe's leading organisations for technical and organisational innovations. The presentation will give you an overview over all fields of the engineering sciences covered by Fraunhofer as well as its structure of roughly 80 research units, including 58 Fraunhofer Institutes, at over 40 different locations throughout Germany and some 12,500 staff. A special focus will be on materials and particularly on polymer technologies.

A special contribution will be made by the Fraunhofer Institute for chemical technology (Fraunhofer ICT), a unique research and development facility carrying out research on energetic materials, energetic systems, polymer engineering, applied electrochemistry and environmental engineering.
An insight will be provided into latest activities in polymer-processing with a focus on the development and processing of fibre reinforced thermoplastics and duroplastic materials, integrative injection-moulding, extrusion and compounding processes, microwave and plasma applications in polymer processing and polymer after-treatment, foam processing technology for particle foam and extrusion foaming and on tooling technology for injection and compression moulding.

The presentation will show how unique combinations of process technologies, like the application of microwave technology in polymer processing, the integration of high pressure technology into the compounding/extrusion processing or the integration of tailored fibre placement into the processing of long fibre reinforced thermoplastics will result in new processing routes for polymers and how customers can profit from these developments, e.g. in automotive industry, compounding or injection moulding.
Some examples of projects demonstrate the opportunities how to co-operate successfully with Fraunhofer.

Functional block polymers for the control of the nanostructure of materials

Markus Antonietti , Helmut Cölfen, Bernd Smarsly

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Amphiphilic block copolymers (ABC´s) can have very special functions: their structure can be controlled such that interfaces between materials with very different chemical character, polarity, or cohesion energy can be addressed in a much broader range than currently possible with low molecular weight surfactants[i] .

That way, nanoparticles and other nanoobjects can be stabilized, whereas selectivity of adsorption and geometrical features of the polymer also give control over the mutual alignment of the nanosized building blocks. This is the potential base for encoded self assembly due to programmed forces, i.e. spontaneous self-organization of the single colloidal entities into ordered superstructures.

This contribution will highlight two different examples for the generation of mesostructured materials which both make use of special amphiphilic polymers but in different modes of operation:

Nanocasting and porous materials by block copolymer templates: The lyotropic phases of water soluble ABC´s can be used via "nanocasting" to generate mesoporous materials with high stability and order. Here, the continuous phase around the polymer assembly is carefully solidified, and removal of the template results in a hollow negative replicate of the original structure, revealing also structural detail with nanometer precision. I will especially focus on crystalline materials with advanced applications

Double hydrophilic block copolymers in crystallization control: Double hydrophilic block copolymers are a newly designed group of polymers which step specifically into crystallization processes and allow generation of new crystalline nanostructures, some of them reminding the structures found in biomineralization. The action of these polymer is unexpectedly manifold and occurs on different levels: simple sequestering of ions, enhanced specific nucleation, stabilization of specific surfaces, but also colloidal stabilization and mutual arrangement of nanoscopic building blocks.

[1] S. Förster, M. Antonietti, Adv.Mater **1998,** *10,* 195

Study on Shear-Mediated Crystallization of iPP

Motohiro Seki and Takao Usami
Polymer Design Laboratory, Mitsubishi Chemical Group Science and Technology Research Center, Inc. No1, Toho, Yokkaichi, Mie 510-0885 Japan

Molecular and structural variables that dominate the crystallization kinetics and the crystalline morphology of isotactic Polypropylene(iPP), which affects the mechanical properties have been studied. In this study, the role of long chains in shear-mediated crystallization was investigated by *in-situ* rheo-optical measurements and *ex-situ* microscopic observations. In order to elucidate the effects of long chains, we prepared the model mixture samples in which fractionated iPP (L-PP) with high molecular weight (MW) and narrow molecular weight distribution was blended with a metallocene iPP (Base-PP) with lower molecular weight and narrow molecular weight distribution. The concentration of L-PP (c) was varied ranging from 0 to twice the concentration (c^*) at which L-PP coils overlap. The crystallization of all blends after cessation of transient shearing was accelerated, while the quiescent crystallization kinetics were not affected by the addition of L-PP. A distinctive change in the development of birefringence after shearing was observed when the wall shear stress (σ_w) exceeded a critical value (σ^*). Below σ^*, irrespective of c, the birefringence after transient shearing increased gradually, reaching a small value at the end of crystallization. Above σ^*, a brief interval of shear induced highly oriented growth, manifested in the birefringence after cessation of flow growing strongly and reaching a large value as crystallization proceeded. Further, the rate of growth of the birefringence exhibited a strong, non-linear c dependence. The morphology of the skin layer which affects the mechanical properties showed a shish-kebab type structure observed by TEM for samples subjected to stresses above σ^*. The number density and thickness of shish were affected by c and changed drastically at c near the overlap concentration of the long chains. This indicates that the role of long chains in shear-induced oriented crystallization is cooperative (rather than a single chain effect), enhanced by long chain-long chain overlap.

In-process measurements for monitoring of polymer melt flows

T Gough

IRC in Polymer Engineering, School of Engineering, Design and Technology, University of Bradford, Bradford BD7 1DP, UK

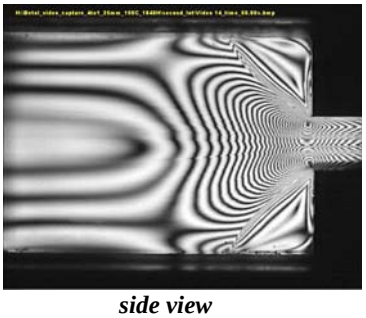
Abstract

Quantitative simulation of polymer melt flows for the purposes of prediction of industrial processes relies upon the production of reliable experimental data to verify models and to set the limits of applicability of numerical codes. In order to provide rigorous testing of these codes high quality experimental data are essential.

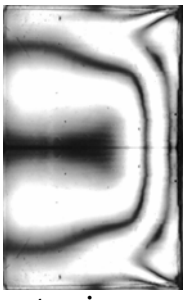
Abrupt contraction geometries have been studied for the purpose of non-Newtonian flow code validation and continue to provide a demanding test of polymer melt flow simulations. Despite the apparently simple geometry a number of physical challenges must be met by non-Newtonian flow models including those provided by sharp corners and combined shear and extensional flows.

These flows have been probed using a variety of experimental techniques of which several examples will be shown. These include stress birefringence, particle tracking velocimetry and neutron scattering. As a consequence of these measurements quantification of full field stress differences, velocities and molecular configuration are possible. In general these flows have only been experimentally studied in two dimensions (denoted as the streamwise and normal dimensions) and the corresponding modelling has been constrained to the assumption of planar flow. Clearly, for industrial processes this assumption is rarely the case and thus the generality of such models is open to question.

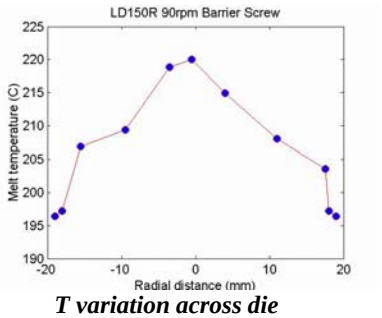
A key development in the modelling of polymer melt flows will be the adaptation of the extended pom-pom model to three-dimensional flows (a key goal of the recently EPSRC funded Microscale Polymer Processing 2 grant). In order for the simulations to be validated, a range of experiments is necessary to probe both the streamwise-normal and the streamwise-cross stream planes. By suitable modification of a flow cell mounted on a 38mm single screw extruder we have studied the development of stress and velocity fields in both planes following extruder start-up for a series of nine flowrates. A seemingly inherent overshoot in wall pressure is observed for all flowrates studied and it is postulated that this is due to a combination of compressibility and temperature fields.



side view



top view



T variation across die

It is widely known that temperature has a significant effect on polymer rheology and thus on melt flow parameters. Temperature field measurement is difficult to achieve in melt flows owing to lack of prior knowledge of emissivities (necessary for IR measurements) and due to the high pressure fields typically developed in extrusion and injection moulding. In order to measure such quantities we have implemented, during extrusion, thermocouple meshes and temperature-sensitive fluorescent dyes coupled to spectrometers. Though still in the developmental stages these measurements show clearly that we ignore such effects at our peril. Temperature variations of 30^{o}C, with their associated effects on rheology, are typical in extrusion dies.

ELECTROSPINNING OF MICRO- AND NANO-FIBRES FOR TISSUE ENGINEERING

Tony Ryan
University of Sheffield

ABSTRACT

Much research in tissue engineering focuses on synthesis of complex 3D polymer scaffolds containing functional biomolecules to which cells are introduced. Typical scaffolds are macroscopically porous with struts or fibres ~10 microns thick at a packing fraction of ~0.1 and these dimensions appear to be conserved across a wide range of scaffold processing techniques. Electrospinning is ideally placed to deliver such a morphology. First, we will review the technique of electrospinning, the underlying physics and the state-of-the-art-technology. Then we will pose the question "will any material work as a scaffold if it has the right morphology?". A minimal scaffold, without cell signalling or spatial information, has been made by electrospinning and used as a scaffold to study the growth of skin fibroblasts, keratinocytes and endothelial cells, as single and co-cultured populations (± growth-factor containing serum proteins). In the absence of serum, keratinocytes, fibroblasts and endothelial cells did not grow when cultured alone. However, when fibroblasts were co-cultured with keratinocytes and endothelial cells, expansion of all three occurred, even in the absence of serum. Furthermore, cells displayed native spatial 3D organisation when cultured at an air-liquid interface, even when all three cell types were introduced at random to the scaffold, whereas a submerged scaffold enable only random proliferation. Not only does co-culture with fibroblasts enable other cells to proliferate without serum, but also self organisation occurs according to the native epidermal/dermal structure given the symmetry breaking field of an air/water interface. Finally, we will look to the future of electrospun scaffolds in other areas of tissue engineering such as bladder, tendon and bone.

Synthesis and Characterization of Biocompatible Block Copolymers

Prof. Steve P. Armes,
Department of Chemistry, University of Sheffield.

We describe the synthesis via Atom Transfer Radical Polymerisation (ATRP) of a wide range of well-defined stimulus-responsive block copolymers based on 2-(methacryloyloxy)ethyl phosphorylcholine [MPC], a commercially available monomer that confers clinically proven biocompatibility. For example, AB diblock copolymers comprising MPC and 2-(diisopropylamino) ethyl methacrylate [DPA] form highly hydrophobic nano-sized micelles under physiological conditions. These MPC-DPA diblock copolymer micelles can be loaded with up to 5 w/w % of anti-cancer drugs such as taxol or tamoxifen, which can be released when the local (intra-cellular) pH falls to 5.5 due to the pH-sensitive nature of the DPA block. Moreover, the use of functional ATRP initiators allows folic acid groups to be placed on the end of the MPC blocks, which enables cell targeting strategies based on the folate receptor mechanism to be explored. Replacing the DPA block with 2-(dimethylamino)ethyl methacrylate [DMA] allows efficient condensation of DNA: the precise morphology of the copolymer:DNA complex depends markedly on the block composition. If MPC comprises the central 'B' block of an ABA triblock copolymer, either pH-responsive (A = DPA) or thermo-responsive (A = *N*-isopropylacrylamide) gelators can be obtained. Soft, free-standing gels can be obtained that are sufficiently biocompatible to enable V79 hamster lung cells to be cultured.

References

1. E. J. Lobb, I. Ma, N. C. Billingham, S. P. Armes and A. L. Lewis, *J. Am. Chem. Soc*., 123, 7913 (2001).

2. I. Ma, E. J. Lobb, N. C. Billingham, S. P. Armes, A. L. Lewis, A. W. Lloyd, J. P. Salvage *Macromolecules*, 35, 9306 (2002).

3. Y. Ma, Y. Tang, N. C. Billingham, S. P. Armes, A. L. Lewis, A. W. Lloyd, J. P. Salvage, *Macromolecules*, 36, 3475 (2003).

4. Y. Ma, Y. Tang, N. C. Billingham, S. P. Armes and A. L. Lewis, *Biomacromolecules*, 4, 864 (2003).

5. J. Lam, Y. Ma, S. P. Armes, A. L. Lewis and S. Stolnik, *J. Controlled Release*, 100, 293 (2004).

6. Y. Li, R. Narain, Y. Ma, A. L. Lewis and S. P. Armes, *Chem. Comm*., 2746 (2004).

7. C. Li, Y. Tang, S. P. Armes, C. J. Morris, S. F. Rose, A. W. Lloyd, and A. L. Lewis, *Biomacromolecules,* 6, 994 (2005).

8. M. Licciardi, Y. Tang, N. C. Billingham, S. P. Armes and A. L. Lewis, *Biomacromolecules*, 6, 1085 (2005).

Plastic in Packaging, All Wrapped Up?

Dr. Ben Punchard
Technical & Social Trends Researcher
Editor: ALERT
Faraday Packaging Partnership

A B S T R A C T

In the UK this year snack bars alone will count for over 1 billion units of flexible plastic packaging. Plastic in packaging is **HUGE**. With yogurt pots, salad bags, tubs, plastic bottles, etc. it seems that plastic has packaging all wrapped up. So where's the room for innovation? Can we make a better yogurt pot? If we ask the consumer the answer is a very quick *yes!* The main importance of packaging is moving ever further away from storage and protection towards lifestyle delivery and that's where the new world of soft nanotechnology and functional materials can breathe new life into old packaging, adding interest, excitement, convenience, branding, etc… This talk will discuss this move from functional to funky and highlight some of the emerging research that could lead the way.

The UK Organic Materials for Electronics Consortium

Professor M.L. Turner
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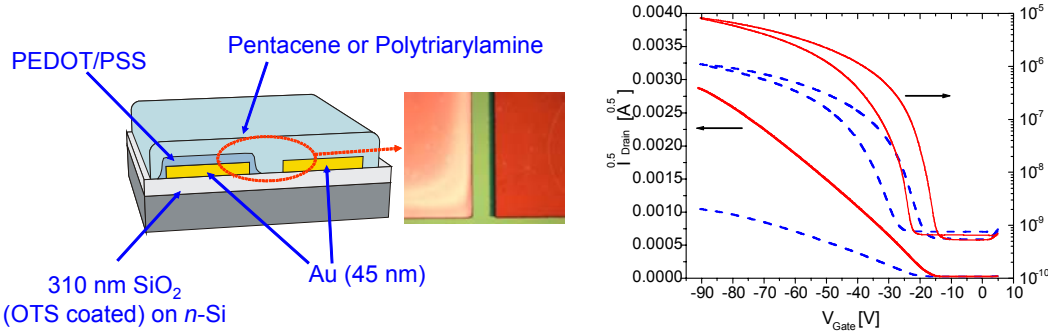
A B S T R A C T

Recent work from the Organic Materials for Electronics Consortium of the Engineering and Physical Sciences Research Council, UK will be presented. The interdisciplinary consortium consists of research groups from the School of Chemistry, University of Manchester, the Department of Physics and Astronomy and the Department of Chemistry at the University of Sheffield, Department of Physics and Astronomy at the University of Cardiff and Merck KGaA, Manchester.



Recent work discussed will look at the contacts, dielectrics and semiconductors employed in the fabrication of organic field effect transistors (OFET device structure shown above with example of the IV characteristics). Specific items of interest include:

(i) The synthesis, characterisation of new organic semiconductors
(ii) The use of anodised gate insulators in OFETs
(iii) The use of phase image electrochemical force microscopy in organic electronics.

ABSTRACTS

OF

POSTERS

UK POLYMER SHOWCASE
6/7 SEPTEMBER 2005
CEDAR COURT, WAKEFIELD

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18. Ocular and Dermal Hydration: The Release of Natural Moisturising Agents from Hydrogels
    R. Bahia and B. Tighe, Aston University

19. Radical Ring-Opening Polymerisation Behaviour of Vinyl Cyclopropane
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20. Selective Adsorption of Mixed Organo Silanes with Differing Reactive Groups on E-glass Surfaces
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24. Structure-Property Relationships in Co^2 Assisted Processed Polymers
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25. The Study of Thin Film Formation of Semiconducting Polymer Blends During Spin Coating by means of In-situ Light Scattering
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26. Synthesis and Physico-Chemical Studies of Designed Self-Assembling Peptides
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27. Synthesis of Dendritic Fluorocarbon End-functionalized Polymers
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30. The Synthetic Muscle
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    Helen Middleton, University of Warwick

A Coarse-Graining Approach to the Simulation of Macromolecular Liquid Crystals

Mark R. Wilson & Zak E. Hughes

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Macromolecular systems pose a real challenge to modellers. Large numbers of atoms make macromolecules difficult to study atomistically, particularly when the molecules themselves form mesophases, which order over large length-scales. These problems are compounded by the relatively long time-scales associated with molecular motion in macromolecules and the (even) longer time-scales associated with changes in molecular order. New and accurate approaches to coarse-graining are clearly required to enable researchers to simulate the phase behaviour of macromolecular liquid crystals.

We have recently made progress in this area by building and running simulations of coarse-grained models of liquid crystal macromolecules: polymers and dendrimers. In this paper we present some initial results for coarse-grained models of a side-chain liquid crystal polymer [1] and a carbosilane dendrimer fuctionalised with branches that are terminated by mesogenic groups [2]. In both systems liquid crystal phases are observed.

[1] Molecular dynamics simulations of side chain liquid crystal polymer molecules in isotropic and liquid crystalline melts. L. M. Stimson and M. R. Wilson, *J. Chem. Phys,* 2005 (in press).

[2] Coarse-grained simulation studies of a liquid crystal dendrimer: towards computational predictions of nanoscale structure through microphase separation. Z. E. Hughes, M. R. Wilson and L. M. Stimson, *Soft Matter*, 2005 (in press).

Applications of Parallel-Tempering
Methods to the Simulation of Molecular Systems

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Complex molecular simulations can often be problematic as the system easily gets stuck in energy wells, which are separated from other minima by high-energy barriers. This means that the sampling is poor and thus physical quantities cannot be calculated accurately. Things are particularly difficult for macromolecules and poor conformational relaxation provides the main difficulty to successful simulation of many such systems at a molecular level. Extended ensemble methods are an attempt to improve this situation. These methods involve running a number of non-interacting replicas of the same system each at a different temperature or with a softened potential. After a certain amount of time an attempt is made to swap a pair of these systems, with the swap being accepted or rejected based on a Monte Carlo acceptance criterion.

We have applied temperature parallel-tempering and potential softening using the Tsallis potential [1] to two different systems; a united atom alkane chain and a liquid crystal dendrimer [2]. The results of the simulations compare the effectiveness of temperature parallel-tempering and potential softening; and show how the new methods can lead to a fundamental improvement in the simulation of macromolecular systems.

[1] Replica-Exchange Method Using the Generalized Effective Potential. Soonmin Jang, Seokmin Shin and Youngshang Pak, 2003, *Phys. Rev. Lett.*, 91(5), 058305.

[2] A Liquid-Crystalline Silsesquioxane Dendrimer Exhibiting Chiral Nematic & Columnar Mesophases. Isabel M. Saez, John W. Gooby and Robert M. Richardson, 2001. *Chem. Eur. J*, 7(13), 2758.

Comb Polymers: From Industry to Biology

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A series of monodisperse polystyrene combs was synthesized via anionic polymerisation techniques. Conditions were established whereby a long linear polystyrene backbone (PS) was chloromethylated using zinc (II) chloride, side-reactions such as Friedel-Crafts alkylation being suppressed. An excess of diphenylethylene-capped polystyryllithium (PSLi) was then reacted with the functionalized backbone to yield materials having long chain branching. A series of materials were produced where the branch molecular mass remained near-constant throughout the series, the average number of branches being the major variable. The series of polymers was synthesised in order to examine the effects of long-chain branching on the processing behaviour of polymers as part of the EPSRC-funded and industrially-sponsored Microscale Polymer Processing Project (MuPP).

The polystyrene combs were later reacted with sulfuric acid to yield water-soluble poly(styrenesulfonic acid) combs and then neutralized using either sodium or caesium hydroxide. The extent of sulfonation was determined via titration and Nuclear Magnetic Resonance Spectroscopy. Aqueous Size Exclusion Chromatography confirmed that the structure of the polymers were largely unaffected by either cross-linking or fragmentation during sulfonation. The resultant polyelectrolyte combs are similar in structure to naturally occurring proteoglycans and they could potentially be used in cartilage replacement. The synthetic combs have been examined, and compared to aggrecans, using a variety of scattering techniques by Aris Papagiannopoulos and Tom Waigh in the Department of Physics in Leeds; their work will be displayed separately.

Design and Preparation of New Carbazole Based Conjugated Polymers.

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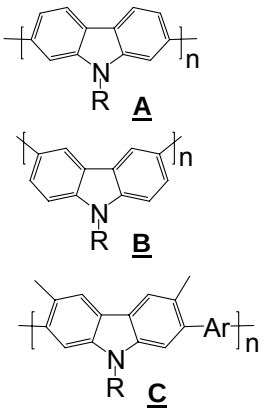
Research in the area of conjugated polymers has attracted significant interest recently in view of their exciting prospects for application in a range of electronic devices. An important area, which has seen major advances, is concerned with development of materials for opto-electronic uses and the past decade has seen the development of a range of conjugated polymers with great promise for application in polymer based light emitting diodes [1] (PLED's) and solar cells [2].
Poly(*p*-phenylene) (PPP's) and polyfluorene derivatives have been studied extensively as good candidates for use as blue emitting polymers as well as energy transfer donors for lower band gap fluorophores, however, there are still improvements to be made in terms of the stability of these materials and their operating lifetimes in devices before they could be used effectively.

Scheme 1



Recently, we have developed new preparation routes to two families of carbazole main chain conjugated polymers in which the carbazole repeat units are linked either through the 2,7-positions, poly(9-alkylcarbazole-2,7-diyl)s [3] (structure **A**, scheme 1) or the 3,6-positions, poly(9-alkylcarbazole-3,6-diyl)s [4] (structure **B**, scheme 1).
While electronic delocalisation along polymer chains is limited to about two carbazole rings in the case of poly(9-alkylcarbazole-3,6-diyl)s **B**, regardless of the nature of alkyl group substituents, it is further extended in the case of poly(9-alkylcarbazole-2,7-diyl)s **A**. We have also undertaken fluorescence studies on the resulting polymers. These studies reveal greater quantum efficiencies for poly(9-alkylcarbazole-2,7-diyl)s **A**, (fluorescence quantum yield $\phi_{fl} = 0.80 \pm 0.08$ in CH_2Cl_2 relative to quinine sulphate) in comparison with their poly(9-alkylcarbazole-3,6-diyl)s **B** analogues (fluorescence quantum yield $\phi_{fl} = 0.065 \pm 0.006$ in CH_2Cl_2 relative to quinine sulphate).
Electrochemical investigations on poly(9-alkylcarbazole-2,7-diyl)s have revealed that these materials are unstable under electrolytic conditions. This could be attributed to the formation of new species as a result of creation of new linkages between the 3,6-positions of adjacent polymer chains within the films.
In this work, we will present our results on the preparation, characterisation and investigation of the photophysical and electroluminescent properties of 2,7-linked 9-alkyl-carbazole polymers and copolymers (structures **C**, scheme 1) where the 3,6-positions have been substituted with methyl groups in order to prevent cross-linking side reactions.

Acknowledgements
We wish to thank EPSRC for financial support of this work.

References

[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund and W. R. Salaneck, *Nature,* (1999), **397**, 121.
[2] C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.,* (2001), **11**, 15.
[3] A. Iraqi and I. Wataru, *Chem. Mater.,* (2004), **16**, 442.
[4] A. Iraqi and I. Wataru, *J. Polym. Sci. Part A: Polym. Chem.,* (2004), **42**, 6041.

Development of biocompatible formulations for the airway delivery of immunoglobulins

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Poly(lactide-co-glycolide) (PLGA) microspheres can be used to encapsulate protein drugs to afford stability, modify release and the aerodynamic properties required for inhalation delivery. The microspheres can be fabricated from a w/o/w double emulsion, where the protein, protected in its own aqueous phase is dispersed in an organic phase containing the PLGA that is in turn dispersed in an outer aqueous phase. Microparticles can then be produced by solvent evaporation, or as in this work, by spray drying. Typically poly(vinyl alcohol) (PVA) has been used as an emulsifier (1). However, when spray drying, the PVA is retained in the final product. Therefore, an alternative emulsifier was sought as large quantities of PVA may not be suitable for lung delivery. Dipalmitoylphosphatidylchloline (DPPC), a component of human lung surfactant, was selected as an alternative emulsifier for investigation. Lactose, another GRAS excipient, has also been included in the external phase.

Spray dried microspheres loaded with the model antibody, human IgG, were produced using double-emulsion formulations. Batches were produced with various quantities of PVA (0-200 mg), with and without 24 mg DPPC. The PVA was divided equally by mass between the internal and external aqueous phases. The DPPC was dissolved in the organic phase with 200 mg PLGA, as previously described (2). The external aqueous phase contained 500 mg of lactose to aid emulsion stability and good spray drying properties in the absence of large quantities of PVA. Samples of the powder products were assessed for protein loading and burst release, by a modified Bradford assay, geometric diameter by laser diffraction, morphology by scanning electron microscopy, antibody integrity by gel electrophoresis and ELISA, and PVA content by an iodine-based assay. A lead formulation was selected, and its spray drying parameters were optimised by means of a 2^4 factorial experiment.

Without DPPC, 100 mg of PVA was an optimum amount for protein loading. Below this, the encapsulation efficiency decreased probably due to a destabilisation of the double-emulsion. Addition of DPPC at all PVA concentrations improved the encapsulation efficiency, and a good loading (77% encapsulation efficiency) maintained, even in the absence of PVA. Reduction of PVA content reduced the burst release, from 65% release in one hour to <5%, possibly because PVA may disrupt the polymer matrix, such that much of the encapsulated protein is released when the PVA quickly dissolves. It is also thought that DPPC increases surface hydrophobicity, thus further delaying release. There was little effect on particle size; all formulations produced microparticles with a modal diameter of 3 μm, ideal for pulmonary delivery. SEM images indicate that the non-PVA, DPPC-containing particles may have different surface properties compared to PVA-containing particles. Also, these particles appeared relatively non-aggregated, and thus are potentially free-flowing and non-cohesive. This may be due to a hydrophobic surface afforded by the DPPC that would be advantageous for dry powder inhalation, or suspension in propellants. The formulation without PVA was selected for optimisation. It was found that increasing inlet temperature and atomisation flow rate, and decreasing pump speed and aspiration rate, improved yields, without appearing to adversely affect antibody loading, or structural integrity. Alteration of these parameters also appeared to have an effect on particle diameter. This could potentially allow particles to be engineered to a specific size for targeting specific areas of the respiratory tract.

1. Ogawa Y et al (1988) Chem. & Pharm. Bull.36: 1095-1103
2. Evora C et al (1998) J Cont. Rel. 51: 143-152

Development of Nanoparticles for Cell Protection

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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. Synthesis of biodegradable polymers and the uptake of polystyrene beads within fibroblast cells has been the starting point for this research.

Effect of branch-on-branch architecture in stress relaxation of metallocene catalyzed branched polyethylene

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The reaction pathways for metallocene catalyzed branched polyethylene have been studied in details in the literature. A single parameter, branching probability, determines the number and mass fraction of polymers, which have branch-on-branch architecture. Stress relaxation for a branch-on-branch polymer can be modelled as a multi-dimensional Kramers problem. We introduce approximations to cast this as an effective one-dimensional problem, which can be handled efficiently in a computer program. Our calculations are in quantitative agreement with a series of metallocene catalyzed polyethylene resins. In addition to this calculation, in our computation we can exclude branch-on-branch architectures. For moderate values of branching probability, the numbers of branch-on-branch polymers are a small fraction of the total number of polymers. But, we find that such exclusion lowers the zero-shear-rate viscosity by an amount, which is a steep function of the branching probability. For branching-probabilities such that less than 1% of the molecules by number have branch-on-branch architectures, excluding branch-on-branch molecules can lead to a lower viscosity by two orders of magnitude.

Electrospinning for Tissue Engineering

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ABSTRACT

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

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

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

Initial studies used PS as the matrix material whereas current efforts are concentrated upon biodegradable/ biocompatible materials. Scaffolds of many different materials have been successfully made and cells have been grown upon them.

Electrospinning of Ultrafine Fibres of pH Responsive Block Copolymer

L. Wang, P. Topham, C. J. Crook, J. R. Howse, D. Norton, R. J. McKean, A. J. Ryan
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Electrospinning is a straightforward method to produce ultra-thin fibers (tens of manometers to several microns) from polymer solutions. It could take advantage of the high surface to volume ratio to make very efficient sensors and nanotechnology devices.

The ability of individual polymer molecules to react to changes in temperature or chemical environment with drastic changes in size and conformation has been appreciated for many years. Recently, the triblock copolymers, poly(methyl methacrylate)-poly(methacrylic acid)-poly(methyl methacrylate) (PMMA-PMAA-PMMA) and PMMA- poly((diethylamino)ethyl methacrylate) (PDEMA)-PMMA, comprising of polyacid and polybase mid-blocks respectively, have been synthesized and found that these polyelectrolyte materials display their predicted response to changes in pH. The fibers of the triblock copolymers, PMMA-PMAA-PMMA PMMA-PDEMA-PMMA were produce by the electrospinning. The influence of the composition of a multicomponent solvent, tetrahydrafuran (THF) and dimethylformamide (DMF), on the surface morphology and diameter distribution of the block copolymer fibers was investigated. The results showed that the average diameter of the fibers using the multicomponent solvents were thinner than when using either of the two components and the diameter distribution of the fibers became narrower.

Enhancement of Cell Adhesion in Acrylic Hydrogels: Amine Functionalisation

Paul Wyman[†], *Claire Johnson*[‡], *Sheila McNeil*[‡] *and Stephen Rimmer*[†]
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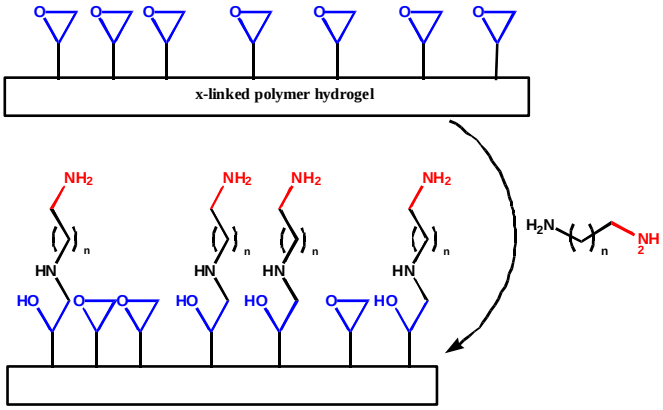
A range of acrylic hydrogels based on glycerol monomethacrylate co-polymerised with lauryl methacrylate and ethyleneglycol-dimethacrylate have been synthesised and assayed for cell adhesion (Bovine Keratocytes). These hydrogels are shown to have poor cell adhesion characteristics for a wide range of equilibrium water contents and monomer compositions. A small subset of these polymers with fixed equilibrium water content, but varying degrees of cross-linking and hydrophobe have been selected and modified to allow further functionalisation. The addition of a polymerisable epoxides into these co-polymers has enabled reactions with alkyl amines and other functionalities. We present preliminary results demonstrating that a range of di-amines can be coupled to the hydrogel surfaces which, in certain cases, results in a marked improvement in both cell adhesion and proliferation relative to the non-functional systems.



Functionalisation of an acrylic hydrogel by ring-opening of co-polymerised epoxides with alkyl-diamines

FaraPack Polymers – The Spin-Out Success Story

FaraPack Polymers Limited was launched in July 2004, as a joint venture between The Polymer Centre at the University of Sheffield and the Faraday Packaging Partnership. FaraPack Polymers is a spin-out company from the University of Sheffield and is owned by Sheffield University Enterprise Limited (SUEL). FaraPack Polymers offers a unique, rapid service combining packaging expertise and "know-how" to solve technical problems and develop innovative materials for the packaging industry. The core areas of expertise are based on delivering improved packaging through: materials developments and applications; bespoke synthesis of new polymeric materials; problem solving and innovation; and testing and analysis.

FaraPack was specifically set up to bridge the gap in the market for short-term research projects in the packaging industry: Universities offer long-term research projects through PhD students and post-doctorial researchers, and short-term research, typically up to a few days, through academic consultancy. Industry on the other hand often requires shore-term research of a few weeks to a few months. FaraPack Polymers Limited forms the bridge between University capabilities and Industry requirements. The company is based within the University and cannot only draw on its own dedicated team of experts, but also on expertise and resources supplied by the Polymer Centre. It is an excellent tool for technology and knowledge transfer between the University and Industry.

Fluoro Polyurethane Foams for Use in an Artificial Cornea

Joyleen Collier, S. Rimmer* and S. MacNeil.

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

The cornea is the dome-shaped window that covers the front of the eye; its two major functions are protection of the eye contents and to serve as the principal optical element of the eye. The latter requires the criteria of transparency. Any one of the three corneal cell types, the epithelium, keratocytes or endothelium may cause corneal opacity by their dysfunction. Irreversible loss of vision may occur and maybe corrected by performance of a Keratoplasty; surgical replacement of damaged sections of cornea with healthy donor corneal tissue. The objective is to create artificial polymeric implants as substitutes for donor corneas, that may be colonised by a patients own cells.

A construct consisting of a synthetic transparent hydrogel domain and a porous skirt is to be utilized. The porous skirt will consist of polyurethane foam, allowing infiltration of cells into the implant. This research endeavours to develop this porous skirt without the use of traditional Silicone surfactants adopted in conventional polyurethane foam synthesis. Current development is in the synthesis of fluorinated acetonide monomers for inclusion into the polyol pre-polymer of the polyurethane foam, to aid in the stabilization of bubble formation in the foaming process. Various fluorinated esters and ketones were reacted with Glycidyl Methacrylate in the presence of tetrabutylammonium bromide for acetonide formation. The use of monomer starve fed emulsion polymerization and ozonolysis is being used in synthesis of the pre-polymer.

Hypermacs and Dendrimacs – well defined highly branched polymers

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Abstract

Synthesis of model polymers with predictable molecular weights, low molecular weight distributions and well defined architecture have proved helpful in the understanding of the correlation between the molecular structure and the physical properties of the polymeric materials. Synthesis of such materials, however, is often demanding and time consuming and can result to relatively modest polymer yields. Nevertheless, the notable contributions that have been made by model polymers in the field of polymer science make the synthetic efforts worthwhile.

A strategy for synthesis of two classes of polymers, HyperMacs and DendriMacs, with highly branched architectures is described based on well defined 1,4-polybutadiene macromonomers. The materials are essentially long-chain branched analogues of classical hyperbranched polymers and dendrimers. We will attempt to use a two step synthetic strategy to make these kinds of polymers. The first step involves synthesis of well-defined AB_2 macromonomers by anionic polymerisation using an alkyllithium initiator that contains protected alcohol functionality and an end capping diphenylethylene derivative containing two protected phenols. The second step involves polycondensation reaction of the macromonomers into highly branched architectures either via a one-pot polycondensation reaction to give imperfectly, long-chain (hyper)branched architectures, HyperMacs, or via a step wise convergent coupling method to make well defined dendritically branched polymers, DendriMacs. Since the synthesised polymers have well-defined and closely controlled parameters between branch points they can be used as models in understanding the influence that branching has on rheology and process properties of the polymer.

We present here preliminary results on the synthesis of polybutadiene macromonomers with particular emphasis on controlling the polydispersity and the macrostructure.

The influence of Heat Treatment on the surface composition of Poly(3,4-ethylene dioxythiophene)-Poly(styrene sulftonate) Blends .

Anna Rodriguez, University of Sheffield

Poly(3,4 ethylene dioxythiophene) (PEDOT) in the form of a polymeric complex with poly(4-styrene sulfonate) (PSS) has emerged as one of the most used conducting polymers. Here we presente a work of this complex crosslinked with glycerol. The crosslinked process facilitates device fabrication by allowing for example, the spin-coating of active layers without destroying the underlying PEDOT/PSS layer. Previous studies using neutron reflectometry in deuterated PSS demonstrate that PSS segregation to the surface can be controlled by heat treatment (Paul C. Jukes 2004). In the current study solutions of dPSS/hPSS/PEDOT in pure water were prepared with different concentrations (6:0:1, 4:6:1, 9:6:1, 14:6:1, and,19:6:1 by weight). Glycerol was added as the cross-linking agent at 5% by weight. Such solutions were spin-casted onto 5 cm silicon wafers, after which, they were placed in the oven in order to induce crosslinking at 180°C for 30 minutes. . Further heat treatment was applied to study the temperature dependence of segregation. Neutron reflectivity measurements were performed in the prepared samples. Our first experiments reveal that there is a slight excess of glycerol, which segregates to the surface of the film.

References:

P.C. Jukes, S.J. Martin, A.M. Higgins, M. Geoghegan, R.A.L. Jones, S. Langridge, A. Wehrum, S. Kirchmeyer, *Adv. Mater*. **2004**,16,9.

MICELLE FORMING HYDROGELS FOR TOPICAL DELIVERY OF IBUPROFEN AND SODIUM IBUPROFEN

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Thermo-responsive hydrogels based on the amphiphilic triblock copolymer [poly ethylene glycol]-[polypropylene oxide]-[polyethylene glycol] (Pluronics F68) are used to prepare a drug delivery system for the anti-inflammatory drugs ibuprofen and sodium ibuprofen. In aqueous solution, the surfactant copolymers form micelles on the size of 10-100nm. The hydrophobic PPO forms the inner core of the micelle and the hydrophilic PEG forms the outer corona. The most common form of ibuprofen is extremely hydrophobic and insoluble in water; however, it is shown that it can be dissolved in the hydrophobic core of the micelle to form "nano-packets" of drug up to ~2.5 % . In contrast, the polar form of ibuprofen, sodium ibuprofen, is shown to be readily soluble in the hydrophilic matrix material surrounding the micelle.

These co-polymer solutions undergo a sharp transition from a flowing, viscous liquid to a self-supporting clear and transparent gel on heating. This transition is a classical sol-gel transition. The transition temperature decreases with copolymer content. Importantly, the transition can be made to occur at the physiologically important temperature of 37^{o}C by suitable adjustment of composition.

The gelation temperature is affected by incorporation of the drugs. Dissolution of non-polar ibuprofen into the hydrophobic micelle core is shown to decrease the gelation temperature. In contrast, incorporation of polar sodium ibuprofen into the hydrophilic matrix is shown to increase the gelation temperature.

Nanostructure and crystallisation behaviour in PA6 - Montmorillonite nanocomposites produced by melt compounding: The influence of matrix viscosity and clay modification.

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Abstract

Four commercial grades of PA6 with differing viscosities (i.e. molecular weight) were mixed with 5%w/w Cloisite 93A organoclay by twin-screw extrusion to produce nanocomposites. Identical processing conditions were used in order to assess the influence of matrix molecular weight on the resultant nanostructure and crystallisation behaviour. Wide angle X-ray diffraction (WAXD) and Transmission electron microscopy (TEM) were used to investigate the nanostructures produced and differential scanning calorimetery (DSC) was used to investigate melting and crystallisation behaviour. WAXD studies indicated that more highly exfoliated structures were produced when matrix molecular weight was high and improved clay dispersion was confirmed by TEM. Additionally the injection moulded samples used for XRD analysis indicated a γ dominated crystal structure as would be expected after rapid cooling. The diffractograms indicate an increase in crystal perfection for the samples containing clays. DSC analysis revealed the clay acted as a nucleating agent and that this effect was greater with the lower molecular weight matrices. Additionally, interesting melting behaviour was observed on samples that had been subject to slow (i.e. DSC) cooling. For the unmodified polymers the lower viscosity materials exhibited a α crystal structure while the higher molecular weight materials exhibited a mixed α and γ crystal structure. Addition of clay resulted in more γ crystallisation occurring as molecular weight increased except in the case of the highest molecular weight material were a mixed α and γ crystal structure was observed. A higher level of crystallinity was observed in lower molecular weight samples.

NANOSTRUCTURED POROUS MATERIALS BASED ON DESIGNED SELF-ASSEMBLING PEPTIDES

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Peptides are versatile molecules, thus the mechanical, structural, surface, bioactive and responsive properties of the material can be precisely controlled by rational peptide design, to suit specific applications.

Peptides are biopolymers and can be produced in a sustainable manner, cheaply and in bulk by genetic engineering using e.g. non-food crops. This is an attractive alternative to polymer companies, which seek new ways of making multifunctional polymeric materials, not based on oil.

In recent years, enormous research effort has been put into understanding and controlling the properties of self-assembling peptide hydrogels and organogels and also to develop their applications both in Leeds and worldwide.

In collaboration with DOW we are using the self-assembling peptide organogel or hydrogel state as a route to forming highly versatile and multi functional porous materials and in particular aerogels or foams. Aerogels are materials with extremely low densities ($\geq$ 95% v/v air), with large open pores and a high inner surface area.

Current methods for production of polymer based aerogels and foams are: supercritical fluid processing (SCF), particulate leaching, sol-gel processing and phase separation. In this project SCF processing and phase separation have been used due to the compatibility of the peptide gels with these processes.

Aerogels and foams can find applications in medicine as solid substrates for cell and tissue growth, in separation of gaseous substances (e.g. nicotine filter), chiral foams for the separation of chiral substances, in personnel care products, foams with protein like enzymatic activity for catalysis and as insulators.

We gratefully acknowledge the financial contribution of DOW chemicals and of the Royal Society (A.A. is a Royal Society research fellow).

Ocular and Dermal Hydration: The Release of Natural Moisturising Agents from Hydrogels

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Purpose:
To investigate the release of natural moisturising factors from monophasic and biphasic hydrogels which have the potential to counteract unacceptable symptoms of dryness associated with the eye or skin.

Method:
Monophasic hydrogels were loaded with 2-pyrrolidone-5-carboxylic acid (PCA) and biphasic gels were loaded with either PCA or Vitamin E. The active agents were released into either an aqueous substrate or a lipoidal substrate. The actives were extracted from the substrates and UV spectroscopy was used to calculate the concentration of the actives released.

Results:
Release of a component from a polymer matrix into another phase is governed by its size, charge, structural affinity and octanol water-partition coefficient. This study illustrates that it is possible to release hydrophilic/ hydrophobic actives from a biphasic hydrogel through an aqueous/ lipoidal route respectively with release profiles adjusted to give the required delivery characteristics. Vitamin E can be released from biphasic hydrogels into the lipid layer of the eye to replace lipid solid antioxidants adsorbed into the lens.

Conclusions:
The aqueous environment dominates the eye and the lipoidal environment dominates the skin. Breakdown in these environments and control mechanisms results in dry skin or dry eye symptomology. Early stages of dry eye in particular contact lens induced can be resolved by the delivery of selected natural moisturising factors. The use of a contact lens as a delivery matrix offers great potential in this respect provided that subtleties of the release mechanisms are properly understood.

Radical ring-opening polymerisation behaviour of vinyl cyclopropane

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Abstract

Radical ring-opening polymerisation of 1,1-bis (ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) as well as copolymerisations with methylmethacrylate (MMA), butyl methacrylate (BMA) and lauryl methacrylate (LMA) were carried out in the presence of 2,2-azobis (*iso*butyronitrile) (AIBN) or benzoyl peroxide (BPO) with in the temperature range 60^{o}C to 80^{o}C both in solution (dry chlorobenzene as a solvent) and the bulk. In both cases, the yields and molecular weights of the copolymers were lower that those of the homopolymers. Structural analysis of the polymers suggested that radical ring-opening polymerisation proceeded through 1,5-ring-opening followed by intramolecular cyclisation. Radical emulsion polymerisations of ECVCP were also examined in the presence of potassium peroxide (KPS) as an initiator. ECVCP underwent soap-in emulsion and soap-free emulsion polymerisations satisfactory to afford the ring-opened polymer in good yields.

Selective adsorption of mixed organo silanes with differing reactive groups on E-glass surfaces

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Organo silanes, used as adhesion promoters or coupling agents, have a polymer-compatible organic group and three hydrolysable alkoxy functional groups. γ-Aminopropyltriethoxysilane (APS) and γ-glycidoxypropyltrimethoxysilane (GPS) are typical examples which provide a substrate, such as a glass surface with compatibility and potential coupling to the resin. APS has been chosen because of its wide ranging applications as well as the presence of a nitrogen atom which enables a detailed surface analysis. GPS has received less attention because of the lack of a diagnostic element. In order to determine the extent of the interaction of GPS with glass surfaces, it is necessary to differentiate between the silicon from the silane deposit and that from the glass substrate.

In this work, model E-glass fibres were prepared by washing unsized E-glass fibres with nitric acid. In order to silanize the model E-glass fibres, the silane solutions were prepared at a concentration of 0.1%, 0.5% and 1.0% by weight respectively. The model E-glass fibres (after nitric acid treatment) were immersed in the solutions of APS, GPS and APS/GPS (1:1) for 15 minutes at room temperature. Then they were washed with fresh deionised water for three times and dried in a vacuum oven.

The high resolution XPS was carried out using the SCIENTA ESCA 300 spectrometer of the National Centre for Surface Spectroscopy (NCESS), Daresbury, UK. Photoelectrons were excited by the monochromatic Al Kα X-ray source (hγ = 1486.7 eV). For each sample the XPS spectra were recorded at 45° take-off-angle. O1s (533.0 eV) was employed as a reference for the calculation of the binding energy. The FWHM of Si2p peaks was fixed relatively to the Si2p 3/2 peak from the substrate respectively, which was 1.5 eV ± 0.1 eV.

The XPS results have shown that the nitric acid treatment removed the metal ions components such as Al and Ca from the E-glass surfaces (at least to a depth corresponding to the take-off-angle of 45°) and produced a model silica-rich surface composed of mainly Si-O and Si-OH. When APS and GPS deposit onto a model E-glass surface, the Si 2p3/2 and Si 2p1/2 peaks can be fitted with the components from the silane at the binding energies of 102.4 eV and 103.1 eV and the components from the substrate at the binding energies of 103.5 eV and 104.2 eV. So it is possible to differentiate the Si contribution from the silane (SiO_3C) and from the substrate (SiO_4), and also possible to determine the extent of GPS adsorption onto model E-glass surfaces. In the case of APS/GPS mixed silane coated model E-glass surfaces, the adsorption isotherms for APS and GPS have been obtained by comparing the N 1s peak intensity with the relative intensities of the components in the Si 2p3/2 and Si 2p1/2 peaks for SiO_4 and SiO_3C.

The authors would like to thank Owens-Corning for the financial support and the glass fibres. The authors acknowledge EPSRC for the funding access to NCESS facility at Daresbury Laboratory.

This work is more fully described in the poster presented at this meeting.

Self-assembly of Polymeric "Wavelength Selective" Materials.

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A B S T R A C T

Wavelength selective materials are multilayer stacks which act as a diffraction grating and have the ability to reflect light of a specific wavelength.
The self-assembly of block co-polymers into layers is a novel method of forming a multi-stack material.

Block co-polymers and homopolymers were prepared by living anionic polymerisation (LAP) to ensure well-defined polymers with low levels of compositional heterogeneity.

A melt-cast mixture of a block co-polymer and the homopolymers of its two components was prepared and using the SAXS technique, an X-ray scattering pattern from the sample was recorded over 18 hours. Mathematical manipulation of the data indicated that peaks occurred in the pattern θ, 2θ, 3θ, 4θ etc., indicating self-assembly of the 1-D "lamellar" structure.

Structural and Mechanical Characterization of Oriented Polyoxymethylene Produced by Tensile and Compressive Deformation Processes

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Structural defects, such as micro-voids, present in a polymer can act as potential failure sites when the polymer is deformed. Such premature fracture limits the potential of the polymer in commercial applications like solid-state wire drawing processes, where high drawing speed and enhanced mechanical properties are of prime importance.

In this work the focus will be on polyoxymethylene (POM). Past research on POM subjected to tensile deformation has shown that this polymer is very susceptible to structural defects such as micro-voids. In this work we compare the mechanical properties and structure of uniaxially oriented polyoxymethylene (POM) produced by two solid-state processes: hydrostatic extrusion and die-drawing. In the former process there is no net component of tensile stress whereas in the latter case the sample is subjected to net tensile stresses at the die exit. The tensile nature of the stress in die-drawing causes void formation in the oriented sample whereas, in the case of hydrostatic extrusion, voids are suppressed due to the compressive stress fields.

The changes in the structure and void formation have been monitored by undertaking SAXS studies using synchrotron radiation source at Daresbury laboratories. There is a clear evidence for major difference between the samples produced by hydrostatic and die-drawing. The tensile modulus, strength, density, thermal and structural properties of the oriented samples are also compared and their differences are discussed.

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

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Abstract

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

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

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

References

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

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STRUCTURE-PROPERTY RELATIONSHIPS IN CO_2 ASSISTED PROCESSED POLYMERS

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Liquid and supercritical CO_2 has been shown to strongly plasticize thermoplastics during melt processing, enabling a significant reduction in viscosity and/or processing at a lower than normal temperature. Independent studies at Rapra Technology and Brunel University have demonstrated that under well-defined processing conditions, these effects can be applied to the production of extruded and injection molded products in a compact or unfoamed state. There is considerable commercial opportunity for exploiting this development in the polymer processing industry, leading to potential savings in energy costs, increased productivity and technical advances with certain material types and formulations.

However, a full understanding of the interactions between CO_2 and polymer melts and the influence of this processing aid on the structure and properties of processed polymer has not been realized. In particular, questions remain as to how rapidly the gas diffuses from solidified polymer, what influence it has on polymer microstructure, whether or not it remains in solution or does it generate micro-voids and what are the consequences of any structural changes on mechanical properties in the short and longer term.

Successful commercialization of the technology will require a full understanding of these effects in order to provide confidence and understanding about the products obtained with properties at least as good as conventional processing technologies, but with the added process enhancement mentioned above.

The purpose of this project, therefore, is to explore these questions at a fundamental level using a systematic approach to processing, structure and property characterization, with selected polymers of commercial relevance differing in chemical composition, microstructure and formulation.

The study of thin film formation of semiconducting polymer blends during spin coating by means of in-situ light scattering

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Thin films of blends of incompatible semiconducting polymers shows promised potential in opto-electronic devices such as LEDs and photovoltaics. These films are usually formed by spin-coating. Due to the intrinsic immiscibility of most macromolecule blends, polymer mixtures typically demix during the rapid removal of the solvent in casting process and leave a complex phase separated structure. The performance of the device is highly related to morphology of the thin film structure, since charge and energy transfer happen at interface throughout the film. Therefore it is crucial to have a deep understanding of phase separation behaviour in polymer blends. Achieving this point makes it possible to control the structure of the polymer film and consequently gives the opportunity of designing the desired structures that yield the required device performance.

Most previous studies that have been made of phase separation in spin-coated film have been restricted to an analysis of the structure of the final film. As this is a non-equilibrium process, it is obviously difficult to deduce the details of the phase transformation process from the end point alone.
In the present work we demonstrate how the time resolved small angle light scattering and light reflectivity technique can be used to study the development of the phase separation and evolution of film thickness as a function of time during the spin coating process.
The polymers used were different composition of PS/PB blend in toluene solvent. A light scattering apparatus with integrated spin-coater measures specular reflectivity which is used to monitor changes in the film thickness and off specular scattering is used to observe the onset of the phase separation. The reflectivity shows a series of peaks and troughs that correspond to constructive and destructive interference of the reflected lights as the film thickness decreases. Different sets of similar fringes could possibly imply the formation of layers parallel to the substrate. To get more clear idea about the film formation phenomenon we are working on a model which shows a good compatibility with the data obtained from the experiments.

Synthesis and Physico-Chemical Studies of Designed Self-Assembling Peptides

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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 nanostructures 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, such as charged amino acid side chains, hydrophobicity and peptide length, affect the energetics of peptide self-assembly, stability 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).

Synthesis of Dendritic Fluorocarbon End-functionalized Polymers

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Fréchet-type poly(arylether) dendrons with peripheral fluorocarbon groups and a core benzyl bromide group have been prepared. The latter were successfully employed in the copper mediated living radical polymerisation of styrene-d_8 giving polymers of predicted molecular weights and narrow polydispersities (figure 1). Contact angle measurements were used to investigate the adsorption of these materials to the air-polymer surface in blended films with unfunctionalised hydrogenous polystyrene. It is seen that the longer fluorocarbon groups have a significant effect on contact angles. Early results also show dependence on number of fluorocarbon groups and molecular weight of functionalised polymer. The effect of annealing the films is also discussed.

X = Fluorocarbon group

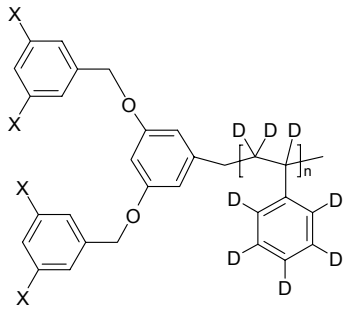

Figure 1. Typical dendritic functionalized deuterated polystyrene prepared

Synthesis of Glycoprotein Mimics

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Introduction

Natural polypeptides (proteins) are essential to life[1]. They provide mechanical support (collagen), catalysis (enzymes), transport (O_2 by haemoglobin) and recognition (antibodies) functions to name a few. It is possible to synthesise replicas[2] of these using either solid phase techniques, or bioengineering. The production of synthetic variants of these compounds draws attention in the fields of drug delivery, tissue engineering and nanotechnology. Carbohydrate bearing proteins ('glycoproteins') are known to have molecular and even ice crystal face recognition abilities. This work is towards creating controlled glycoprotein mimics

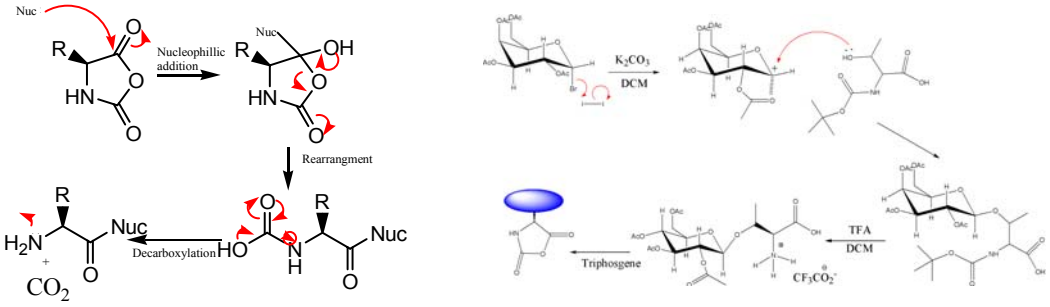

Figure 1.(left) Polymerisation mechanism of NCA monomers. R= Bzl-O-CH(CH3. (right) . *Glycosylation procedure using acetobromo α-D glucose*

Controlled polymerisation of NCAs

Poly(amino acids) can be conveniently prepared by the ring opening polymerisation[3](Fig.1a) of NCAs, in a chain growth mechanism. The most common initiators are primary amines which have a high nucleophilicty:basicity ratio. Polymers formed by this method tend to be poorly defined (PD>1.4) with multimodal molecular weight distributions and not reach 100% conversion. Following the pioneering work of Hadjichristidis et al[4] we have found that extensive purification[5]of the NCAs combined with dry solvents and vacuum techniques allow controlled polymerisation. We have exemplified this through the polymerisation of O-benzyl L-threonine NCA which has not been previously reported[7]. 1st order polymerisation kinetics are observed indicating a single polymerisation mechanism, using solution state IR spectroscopy to monitor monomer consumption.

N-BOC protected L-threonine has been glycosylated with acetobromo α-D galactose and acetobromo α-D glucose using I_2 as the Lewis acid promoter[6] (Fig. 1b). Glycosylation occurred exclusively at the hydroxyl position with β selectivity. The N-BOC protecting group can be cleaved using TFA without affecting the glycosidic linkage.

Conclusions

Controlled polymerisation of O-benzyl L-threonine is possible when high purity monomers are used in conjunction with vacuum line techniques. A new, facile route to sugar bearing NCAs using Boc chemistry has also been described, which will allow novel carbohydrate functionalised peptidic materials to be synthesised.

References

1. Stryer L, Biochemistry, 4th Ed, Freeman, New York, 1996
2. Sherrington D, J.Polym.Sci.Pt.A, 2001, 39, 2364-2377
3. Kricheldorf HR, Amino acid N Carboxy Anhydrides and related Heterocycles. Springer-Verlag, 1987
4. Aliferis T, Iatrou H, Hadkichristidis N, Biomacromolecules, 2004, 5, 1653-1656
5. Poche D, Moore M, Bowles J, Syn Comm, 1999, 29, 843-854
6. Kartha et al J.Chem.Soc., Perkin Trans. 1, 2001, 770-772
7. No reports of this have been found on the chemical abstracts service

Synthesis of gold nanoparticles functionalised with biologically active polymers for potential biomedical applications

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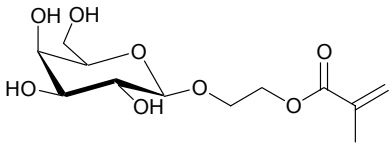

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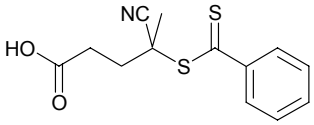

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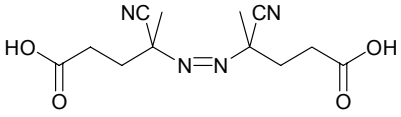

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Gold nanoparticles featuring biologically active carbohydrates have been shown to have potential applications as tools in biological studies[1,2] and anti-tumour agents.[3,4] Glycopolymers, synthetic polymers featuring pendant carbohydrate moieties, have also been shown to display stronger lectin binding compared to single carbohydrates. Reversible addition-fragmentation chain transfer (RAFT) polymerisation has been demonstrated as a useful technique for the controlled synthesis of glycopolymers,[5-7] and RAFT polymers have been used in the synthesis of gold nanoparticles.[8-10] We have applied RAFT to the aqueous polymerisation of 2-(β-D-galactosyloxy)ethyl methacrylate (GalEMA, **1**), the polymers of which have been previously investigated with respect to biological activity.[11] The monomer was synthesised by the glycosylation of 2-hydroxyethyl methacrylate with β-D-galactose pentaacetate using $BF_3.Et_2O$ as the promoter, β-stereoselectivity is ensured by neighbouring group participation. The monomer is yielded by removal of the acetyl protective groups with NaOMe/MeOH. Polymerisations were performed at 70°C under aqueous conditions using (4-cyanopentanoic acid)-4-dithiobenzoate (CPADB, **2**) as the chain transfer agent and 4,4'-azobis(4-cyanopentanoic acid) (ACPA, **3**) as the initiator; kinetic experiments have been completed and the polymers characterised by SEC, IR, and ^1H and ^{13}C NMR. Gold nanoparticles have been synthesised by the *in situ* reduction of the dithioester terminus of the polymer in the presence of $HAuCl_4$, resulting in particles with a gold core and a glycopolymer corona; the particles have been analysed by SEC, TEM, dynamic light scattering and ^1H NMR. The biological activity of the particles has been demonstrated by the agglomeration of agarose beads functionalised by peanut agglutinin, a lectin that has been shown to bind with poly(GalEMA).[11]

(1) de la Fuente, J. M.; Barrientos, A. G.; Rojas, T. C.; Rojo, J.; Cañada, J.; Fernández, A.; Penadés, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 2257-2261.
(2) Barrientos, A. G.; de la Fuente, J. M.; Rojas, T. C.; Fernández, A.; Penadés, S. *Chem. Eur. J.* **2003**, *9*, 1909-1921.
(3) Rojo, J.; Diaz, V.; de la Fuente, J. M.; Segura, I.; Barrientos, A. G.; Riese, H. H.; Bernade, A.; Penadés, S. *Chembiochem* **2004**, *5*, 291-297.
(4) Svarovsky, S. A.; Szekely, Z.; Barchi, J. J. *Tetrahedron: Asymmetry* **2005**, *16*, 587-598.
(5) Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. *Polymer* **2003**, *44*, 6761-6765.
(6) Albertin, L.; Kohlert, C.; Stenzel, M.; Foster, L. J. R.; Davis, T. P. *Biomacromolecules* **2004**, *5*, 255-260.
(7) Albertin, L.; Stenzel, M.; Barner-Kowollik, C.; Foster, L. J. R.; Davis, T. P. *Macromolecules* **2004**, *37*, 7530-7537.
(8) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; McCormick, C. L. *J. Am. Chem. Soc.* **2002**, *124*, 11562-11563.
(9) Shan, J.; Nuopponen, M.; Jiang, H.; Kauppinen, E.; Tenhu, H. *Macromolecules* **2003**, *36*, 4526-4533.
(10) Shan, J.; Nuopponen, M.; Jiang, H.; Viitala, T.; Kauppinen, E.; Kontturi, K.; Tenhu, H. *Macromolecules* **2005**, *38*, 2918-2926.
(11) Ambrosi, M.; Cameron, N. R.; Davis, B. G.; Stolnik, S. *Org. Biomol. Chem.* **2005**, *3*, 1476-1480.

The Synthetic Muscle

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The aim of this project is to create systems with pH responsive polymers that can be combined to produce a working synthetic muscle. Such systems are based upon 'smart' polymers that selectively exhibit a pH induced volume transition i.e. do work at the molecular level. On development of such 'motors', it is possible to combine them with a pH oscillating reaction to yield a periodic change in volume. This fluctuation in size exerts an external force which can be controlled and channelled into powering a muscle.
Experimental studies include:

- X-ray Scattering techniques to follow the length scale changes at the molecular level.
- Optical Microscopy to monitor the macroscopic length scale changes.
- Force measurement apparatus designed to follow the amount of work done by the gel during an oscillation.

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Viscoplastic Behaviour of Ultra-High Molecular Weight Polyethylene

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At the University of Bradford we have been working on the experimental characterisation of the mechanical properties of UHMWPE. Combining Eyring processes and molecular network models, we have successfully devised a large deformation theory that is implemented numerically. When this model is incorporated into a Finite Element Analysis (FEA) we shall gain the ability to predict the behaviour of medical implant components.

A thorough understanding of the mechanical behaviour of UHMWPE is required so that its fracture behaviour can be accurately modelled. The viscoelastic behaviour of the material has been explored by uniaxial compression testing over a range of strain rates using an Instron testing machine. There are a number of factors that need to be accounted for in order to avoid misleading experimental results. These are: errors in the strain measurement arising from machine deflection; non-uniaxiality of the specimen strain field arising from friction at the bearing surfaces; and temperature changes from adiabatic heating.

Machine deflection was monitored by the use of an extensometer to measure the specimen compression directly.

To explore frictional effects, tests were carried out to observe how coating the bearing surfaces with Vaseline would affect the results. Also, the effect of aspect ratio was examined by comparing specimens of length 5mm, 10mm and 15mm.

Temperatures were measured during testing via the use of embedded thermocouples as specimens were compressed to 40% strain. Temperature rises of up to 12°C were recorded.

In the main testing programme, 10mm diameter cylindrical specimens of length 10mm were compressed to 40% strain at different rates. The specimens were analysed at 10%, 20%, 30% and 35% by examining the behaviour of stress as a function of the logarithm of strain rate, as would be appropriate for the identification of Eyring processes.

The results showed that the Eyring Model gave an effective representation of stress over wide ranging strain rates. The use of a two process model was a simplification, and resulted in an over-abrupt transition in the gradients of the stress-strain curves; a spectrum of processes would be more realistic, but at a greater computational cost.

Non-uniaxial data is required to fully define these models, and this is now being explored experimentally. Work is also in progress on the implementation of this model into finite element code.

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Water soluble active ester co-polymers synthesised by TMMLRP for bioconjugation.

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Transition metal mediated living radical polymerisation (TMMLRP) can be used to obtain polymers with good molecular weight control and narrow molecular weight distributions. Unfortunately methacrylamides are difficult to successfully polymerise with good control via this method. A way around this is to synthesise N-hyroxysuccinimide containing polymers and then conjugate the polymer with a primary amine containing molecule. N-Hydroxysuccinimide functionalised polymers have been previously used for the successful conjugation of amino functionalised species to polymers[1-2] in order to obtain poly (methacrylamide) species which constitute a group of biocompatible[3-4], water-soluble[5] and low toxicity polymers that are of much interest for medicinal[6-8], industrial and agricultural applications. Poly(ethylene glycol) is desirable as a co-monomer as it will afford good solubility for the polymer making any further reactions more versatile, whereas in the case of poly (N-hydroxysuccinimide methacrylate) the polymers are insoluble in most organic solvents making them difficult to react and rendering them unsuitable for most biological applications.

This work concerns the synthesis, via TMMLRP, of a series of copolymers of poly (ethylene glycol) and N-Hydroxysuccinimide, with varying percentage incorporations of the co-monomers. These are desirable as water-soluble precursors to methacrylamide-based antibiotic-polymer conjugates. The advantages of being able to synthesis polymer-drug conjugates by TMMLRP are that the narrow molecular weight distribution allows targeting of the polymer size to penetrate certain regions within cells or organisms. It also allows functionalisation of the chain end groups so, for example, they could be targeted to have an affinity for a particular bacteria cell surface.[9]

REFERENCES

1. Godwin, A.; Hartenstein, M.; Mueller, A.H.E. and Brocchini, S. *Angew. Chem. Int. Ed*. 2001. 40. 3. 594- 597.
2. Monge, S. and Haddleton, D.M. Eur. Polym. J. 2004. 40. 37-45.
3. Singhal, J.P. and Ray, A.R. *Biomaterials*. 2002. 23. 1139-1145.
4. Rihova, B. *Adv. Drug Delivery Reviews*. 1996. 21. 157-176.
5. Duncan, R. and Kopecek, *J. Adv. Polym. Sci*. 1984. 57. 51-101.
6. Mayhood, T.; Kaushik, N.; Pandey, P.K.; Kashanchi, F.; Deng, L.W. and Pandey, V.N. *Biochemistry*. 2000. 39. 11532-11539.
7. Pillai, O. and Panchagnula, R. *Curr. Opin. Chem. Biol*. 2001. 5. 447-451.
8. Haddleton, D.M.; Crossman, M.C.; Dana, B.H.; Duncalf, D.J.; Heming, A.M.; Kukulj, D. and Shooter, A.J. *Macromolecules*. 1999. 32. 2110-2119
9. Duncan, R. *Nature Reviews*. 2003. 2. 347-360.