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Emerging Polymer Technologies Summit

ABSTRACT BOOK

PLENARY SESSION 1

Hydrogels with Dynamic Phototunable Properties and their Application in Regenerative Biology

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Hydrogels possess a number of material properties that render them useful as synthetic extracellular matrices for 3D cell culture or cell delivery systems for regenerative medicine; these properties include cytocompatibility, ease of functionalization, and physical properties similar to many soft tissues. Many synthetic hydrogel systems are highly tunable, both in terms of their mechanical and biochemical properties, and when combined with advanced processing methods, experimenters can create hydrogels with gradients, patterned ligands or other hierarchical structures found in native tissues. While the ability to control and manipulate hydrogel properties across many size scales has been powerful, the native extracellular matrix (ECM) is a dynamic environment, particularly during development, wound healing, and disease, and biological and mechanical signals can change dramatically with time. The ability to dynamically tune hydrogel properties can be lost in many synthetic ECM mimics, especially if they are crosslinked and functionalized by irreversible covalent bonds. In an effort to capture the variable nature of native cellular microenvironments, we have synthesized hydrogels containing allyl sulfide functionalities1 that are capable of rapid photoinduced network reorganization. Poly(ethylene glycol) (PEG) based hydrogels are formed through a bioorthogonal click reaction and macromolecular precursors that incorporate allyl sulfides within the network crosslinks. In the presence of a photoinitiator, the crosslinks undergo a light-mediated addition fragmentation chain-transfer (AFCT) reaction, which can be conducted in cell-laden hydrogels. This talk will provide examples where the AFCT reaction is leveraged to erode, stiffen/soften, or induce transient plasticity for biomaterials applications. For example, when an excess of monofunctional thiols are added to the system, AFCT reorganization favors the production of uncrosslinked allyl sulfide functionalities, decreasing crosslink density and eventually resulting in complete degradation of the hydrogel. This degradable formulation is useful for rapidly eroding cell-laden gels to generate topographical features or selectively capture cells for analysis or expansion. We have further used this photodegradation strategies to direct the growth and differentiation of intestinal organoids, with applications for screening of drug delivery systems. Conversely, photoinitiation in the presence of a multifunctional thiol allows radical-mediated reorganization into a more highly crosslinked state. These thiol-ene reactions can be used in conjunction to reversibly and repeatedly soften or stiffen hydrogel substrates, and this talk will highlight their application for studying mechanotransduction of human mesenchymal stem cells (MSCs) and improving in vitro expansion conditions to promote the MSC reparative phenotype. Finally, the reversibility of the AFCT reaction allows for spatiotemporal control over the hydrogels viscoelastic properties, with the hydrogel reverting to an elastic state upon removal of the light source. As cells are known to respond to time-dependent substrate mechanics, this has allowed us to investigate the effects of viscoelastic mechanotransduction with controlled doses of adaptability. Additionally, precise sub-cellular illumination allows user-directed detachment of cellular adhesion sites and measuring the effect of viscoelasticity on focal adhesion tension.

References

1. Brown, Tobin E., Marozas, Ian A., and Anseth, Kristi S. “Amplified photodegradation of cell-laden hydrogels via an additionfragmentation chain transfer reaction,” Advanced Materials, 2017, 29, 1605001.

Organic Nanoparticles for Sensing, Imaging and Therapy

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There is an increasing trend of using organic nanoparticles and especially light-harvesting conjugated polymer nanoparticles as active materials for sensing, imaging and therapy applications. The recent results show that conjugated polymer nanoparticles could be fabricated to have tunable sizes and emission, with over 10-fold brightness as compared to inorganic quantum dots with a similar dimension. In addition, their large absorption cross-sections have also enabled them to be used as photoacoustic contrast agents and for photothermal and photo dynamic therapy. In this talk, I will discuss different strategies to form water-dispersible conjugated polymer nanoparticles and their applications as signal reporters or signal amplifiers for chemical and biological sensing/imaging and therapy.[1] In addition, I will also briefly introduce our recent progress in organic nanoparticles with aggregation-induced emission features as replacement for quantum dots in various applications.[2,3]

References

1. Kai Li and Bin Liu*. Polymer-encapsulated Organic Nanoparticles for Fluorescence and Photoacoustic Imaging. *Chem. Soc. Rev*. 2014, 43, 6570–6597.
2. Dan Ding Kai Li, Bin Liu* and Benzhong Tang*, Bioprobes Based on AIE Fluorogens, *Acc. Chem. Res*., 2013, 46, 2441–2453.
3. Guangxue Feng, Ryan Kwok, Benzhong Tang* and Bin Liu*. Functionality and Versatility of Aggregation-Induced Emission (AIE) Luminogens, Appl. Phys. Rev. 2017, 4, 021307.

PLENARY SESSION 2

Polymeric Nanocapsules: From Encapsulation to Selective Release

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Control over the nanoscopic scale opens nearly endless opportunities for many scientific areas. In particular polymeric nanoparticles offer the versatility to cover a wide range of mesoscopic properties for sophisticated applications. However, making smart nanoparticles is inevitably linked to a deep understanding of the overall physico-chemical principle of their formation. By means of the miniemulsion process, we design custom-made nanoparticles and nanocapsules for nearly any purpose ranging from self healing (of steel) to biomedical applications. This is facilitated by the enormous versatility of the miniemulsion process that has been developed and conceptually understood by our group. Moreover, the accumulation of understanding the formation process has led to successful and precise control of important nanoparticle parameters such as size, shape, morphology, surface functionalization and modification, degradation, release kinetics. This degree of control is unique and allows us to tune specific properties tailored to particular applications; the successful up-scaling of process is of technical relevance. Furthermore, the encapsulation and release of a great variety of payloads, ranging from hydrophobic to hydrophilic substances has been successfully achieved in a highly controlled manner and with an unmatched high encapsulation efficiency. Additionally, it will be shown how the interaction of the nanoparticles and nanocapsules with synthetic and biological matter is influenced by the characteristics of the nanoparticles and nanocapsules.

In the talk, we will show how to control protein adsorption onto nanocapsules. How the nanoparticles interact with the medium surrounding them is especially important in the biomedical area. We are one of a few research groups worldwide that are capable of performing multi-angle DLS on concentrated human blood serum as a routine measurement to monitor aggregation events between nanocapsules and human blood serum. Mass spectrometry is used for the identification of the adsorbed proteins and for the first time for the determination of the adsorption kinetics. Using ITC we are first able to monitor binding kinetics between nanocapsules with whole serum as well as with specific proteins.

We also present new strategies where traditional methodologies employed for corrosion protection are married with the concept of self-healing. Efficient anticorrosion properties can be achieved by the encapsulation of corrosion inhibitors and/or of monomers and catalysts for self-healing reactions. The design of nanocontainers for anticorrosion comprises a shell that is responsive to stimuli induced by corrosion and a core containing the healing substance. We present the requirements for their design, their synthesis, and their applications in coatings for metal substrates. The important factors to be taken into account and the future directions are also discussed.

RAFT: Past, Present and Future Challenges

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The advent of reversible-deactivation radical polymerizations (RDRPs) such as Reversible Addition-Fragmentation Chain Transfer (RAFT) [1,2] polymerization developed at CSIRO has proven to be the method of choices for making better polymers. The process is simply conducted by the addition of an organic thiocarbonylthio compound (RAFT agent) to an otherwise conventional radical polymerization. With appropriate selection of the RAFT agent and reaction conditions, the process is applicable to majority of monomers subject to radical polymerization. It can be used to synthesise well-defined homo, gradient, diblock, triblock and star polymers as well as more complex architectures such as microgels and polymer brushes.[3-6] RAFT-derived polymers have been used in a multitude of applications including polymer therapeutics, drug delivery, biosensors, plastic solar cells, microelectronics, desalination membranes, cosmetics, lubricants, surfactants, paints, inks and adhesives, etc. Since 1998, more than 600 US patent applications have been filed by in excess of 60 companies and the rate of patenting continues to increase. To this date, eight companies have RAFT-based products in the market place and 6 others will release products in the next 12-18 months.

In this talk, history of the discovery of RAFT process, its recent developments and applications, and future challenges will be presented.

References

1. T. P. Le, G. Moad, E. Rizzardo and S. H. Thang, PCT/US97/12540, WO98/01478 (*Chem. Abstr*. (1998) 128: 115390).
2. J. Chiefari, Y.K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. Le, R. T.A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, **1998**, *31*, 5559-5562.
3. G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem*. **2005**, *58*, 379-410.
4. G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem*. **2006**, *59*, 669-692.
5. G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem*. **2009**, *62*, 1402-1472.
6. G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem*. **2012**, *65*, 985-1076.

CONCURRENT SESSION 1: Polymers for medical and biological applications

Combating Multi-Drug Resistance Bacteria with Polymer Solutions, Coatings and Hydrogels

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In the recent year, the appearance of multiple resistances of the antimicrobial agent toward the different types of pathogenic bacteria is the most prominent threat to the global public health. The invention of antibiotic to the medical field has great impact on human mortality and morbidity. However, the multi drug resistance (MDR) effect of the pathogenic bacterial towards commonly used antibiotics has impeded the treatment of bacterial infections.

In the recent few decades, the Antimicrobial polymers (AMPos) have been widely used as a promising antimicrobial alternative to combat the infectious disease caused by MDR bacterial. Hence, unlike traditional antibiotics, AMPos interact with the bacterial membrane through non-specific electrostatic interaction. This electrostatic mode of interaction offers the AMPos to progressively interact with the bacterial with a less likely hood of bacterial resistance. We have developed numerous cationic polymer solutions that are bactericidal in vivo with a murine wound model.

We have also developed a series of antibacterial hydrogel based on AMPos that is intrinsically antibacterial and non-leachable. For example, in a wound infection mice model to compare the efficacy of our hydrogel with commercial antimicrobial wound dressings (Allevyn Ag and Algisite Ag, Smith & Nephew), NTUWound1 hydrogel performed better by killing 4.3 log order (>99.99%) of Methicillin-resistant *Staphylococcus aureus* (*MRSA USA300*) and 4.1 log order (>99.99%) of *Pseudomonas aeruginosa 01* (*PA01*) in a 0 h infection model, and 3.8 log order (>99.9%) of *MRSA USA300* and 3.2 log order (>99.9%) of *PA01* in a 24 h infection model. The in vivo bacterial killings were much higher than the commercial antimicrobial wound dressings. Our NTUWound1 hydrogel is also non-inflammatory and non-pyrogenic, as it significantly reduces the number of inflammatory cells in infected mice skin to a non-infected wounded level.

Advanced Polymers for New and Improved Medical Devices

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The effective control of biointerfacial interactions provides the key to a broad range of new and improved biomedical devices used *in vitro* and *in vivo*, such as cell culture tools, biosensors and implantable medical devices. In the context of medical devices, the development of coatings that result in reduced infection rates is of particular interest in the context of the growing use of such devices and the rapid rise of antimicrobial resistance. At this point in time, promising strategies to reduce the formation of biofilms and related infections are focused on the combination of multiple layers of defence that do not carry the risk of raising resistance [1].

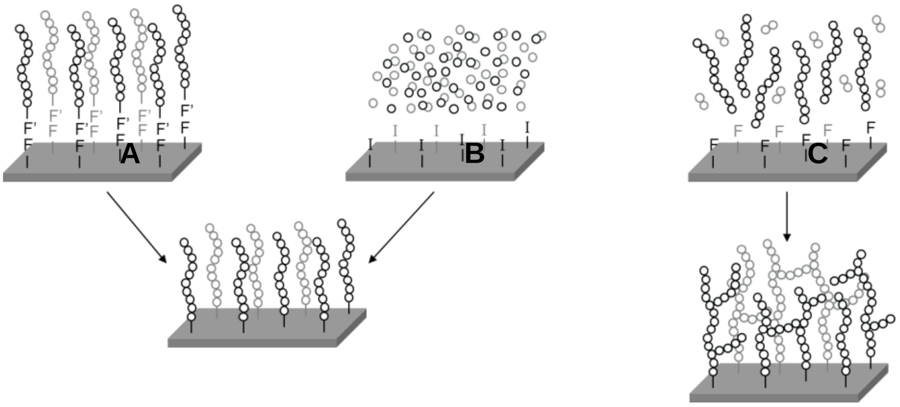

Figure 1. Different surface modification approaches based on “grafting to” (A), “grafting from” (B) and crosslinking methods (C) provide different advantages [1].

Here we have combined coatings that reduce non-specific biointerfacial interactions with the release or display of antimicrobial agents. However, other layers of defence can be used, such as certain types of topography [2]. We have used high-density graft polymer coatings as well as crosslinked coatings (Figure 1) to achieve highly effective reduction of protein fouling, cell and tissue adhesion as well as biofilm formation *in vitro* and *in vivo* [3]. These coatings have been combined with a range of antimicrobial agents that are either released, such as silver ions or agents that are covalently immobilised, such as the antimicrobial peptide melimine [4] or the bacterial quorum sensing inhibitor dihydropyrrol-2-one [5]. Our results demonstrate that the combination of multiple layers of defence leads to statistically significant improvements in regard to biofilm formation for a range of relevant microbes. It is expected that these robust, one-step combination coatings will find applications in a range of medical devices.

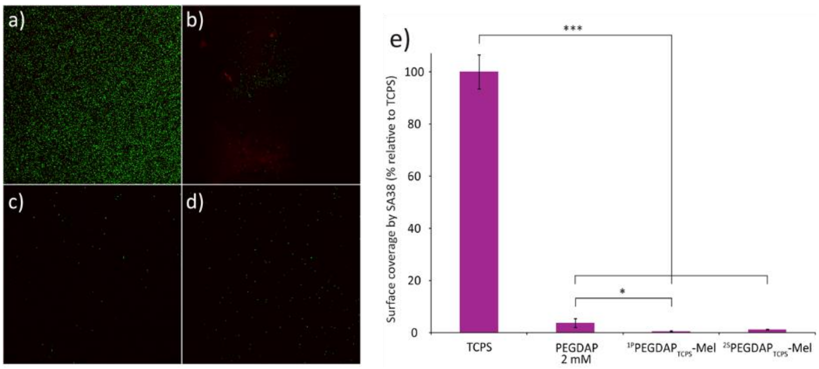

Figure 2. Live/dead stained confocal images (a-d) and surface coverage (e) of S. aureus on crosslinked poly(ethylene glycol)-based coatings and coatings displaying the antimicrobial peptide melamine in comparison to TCPS control [4].

References

1. Salwiczek M, Qu Y, Gardiner J, Strugnell RA, Lithgow T, McLean KM, Thissen H, Emerging rules for effective antimicrobial coatings, *Trends in Biotechnology* **2014**, 32, 82-90.
2. Koegler P, Clayton A, Thissen H, Santos GN, Kingshott P, The influence of nanostructured materials on biointerfacial interactions, *Advanced Drug Delivery Reviews* **2012**, 64, 1820–1839.
3. Thissen H, Gengenbach T, du Toit R, Sweeney D, Kingshott P, Griesser HJ, Meagher L, Clinical observations of biofouling on PEO coated silicone hydrogel contact lenses, *Biomaterials* **2010**, 31, 5510-5519.
4. Ozcelik B, Chen R, Glattauer V, Kumar N, Willcox MDP, Thissen H, Crosslinked platform coatings incorporating bioactive signals for the control of biointerfacial interactions, *Macromolecular Bioscience* **2017**, 17, 1600315.
5. Ozcelik B., Ho K.K.K., Glattauer V., Willcox M., Kumar N., Thissen H., Poly(ethylene glycol)-based coatings combining low-biofouling and quorum sensing inhibiting properties to reduce bacterial colonisation, *ACS Biomaterials Science & Engineering* **2017**, 3, 78-87.

Smart Soft Matter Enabled Nanomedicines

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Synthetic functional materials designed specifically to respond to biological cues are the subject of intense research interest due to their possible application in nanomedicine drug delivery. These “smart” materials offer not only new avenues for overcoming some of the current limitations in drug delivery via nanomedicines but also opens pathways to new treatment strategies. In this Invited Talk I will highlight current research in the following two areas:

1. Improved Subcellular Targeting: Novel polymers which respond to biochemical differences between the extra-and intracellular environments are useful for preparing particles which can chaperone a therapeutic agent in the systemic extracellular environment, and release said agent only when the particle is internalized by a target cell and in a specific sub cellular location. For example, the specific subcellular targeting of internalized receptor signaling complexes may offer new hope for the treatment of a range of chronic disorders (Figure 1).

2. Designed Biomimetic Antibacterial Polymers: Translating the functional motifs of antibacterial lipopeptides to synthetic polymers opens new approaches for addressing increasing global concerns of drug resistant bacteria. We have developed new synthetic antibacterial peptide analogues that exhibit broad spectrum antibacterial activity using the latest polymer synthesis techniques.

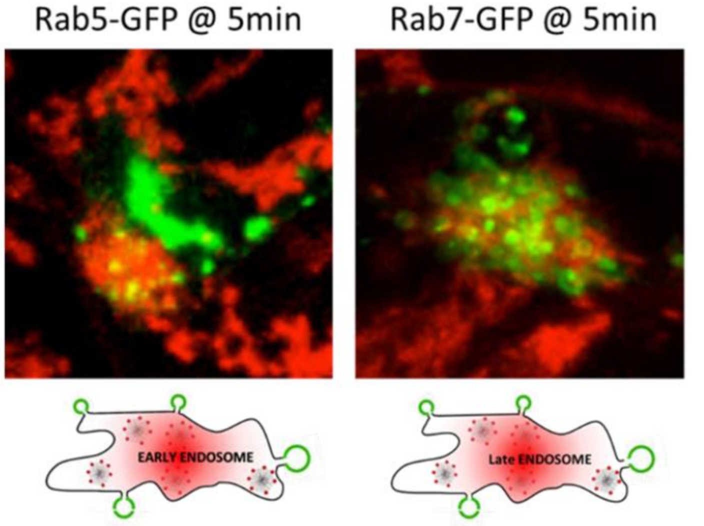

Figure 1: Subcellular localisation of designed “smart” soft matter nanoparticles in HEK cells

References

1. JF Quinn, MR Whittaker, TP Davis (2017) Glutathione responsive polymers and their application in drug delivery systems. Polymer Chemistry Advance Article DOI: 10.1039/C6PY01365A
2. F Ercole, MR Whittaker, JF Quinn, TP Davis (2015) Cholesterol Modified Self-Assemblies and Their Application to Nanomedicine. Biomacromolecules 16 (7), 1886-1914.
3. JF Quinn, MR Whittaker, TP Davis (2015) Delivering nitric oxide with nanoparticles. Journal of Controlled Release 205, 190-205.NP Truong, MR Whittaker, CW Mak, TP Davis (2015) The importance of nanoparticle shape in cancer drug delivery. Expert opinion on drug delivery 12 (1), 129-14
4. C Boyer, PB Zetterlund, MR Whittaker (2014) Synthesis of complex macromolecules using iterative copper (0)-mediated radical polymerization. Journal of Polymer Science Part A: Polymer Chemistry 52 (15), 2083-2098.

RAFT: A Platform Technology – Antibody-Polymer-Drug Conjugates for Biomedical Applications

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We have developed a platform drug-delivery technology based on the versatility of the Reversible Addition-Fragmentation chain Transfer (RAFT) process to help deliver polymer-based materials for biomedical applications. The approach is based on developing RAFT technology to address key clinical and technical challenges for the use of polymeric materials in therapeutic delivery systems. We report therapeutic antibody-polymer conjugates and antibody-polymer-drug conjugates, where the polymer acts as a carrier for both a small molecule cytotoxic drug as well as a therapeutic protein, such as an antibody. In order to understand the influence of polymer structure, composition and size on biological performance, we report the results of two, first in class, ADME studies. These studies assess the pharmacokinetics of a range of homo-polymer and co-polymer antibody-fragment conjugates, in animal models (seven RAFT polymers and one control). The first study used a set of polymers alone, and the second study contained a set of antibody fragment-polymer conjugates. The clearance rate of the polymers from plasma in the polymer alone study showed unexpected differences that could not be simply assigned to molecular weight, between the different polymers in the study. All of the antibody fragment-polymer conjugates investigated had increased elimination phase half-lives over the PEG control, and although differences were observed within the circulating half-life between the conjugates (arising from the different polymer compositions), the excretion volume is fairly consistent. This result confirms that this range of RAFT polymers are a suitable platform for delivery of proteins and targeted delivery of small molecule drugs. We have conjugated an ADME optimised, complex, high molecular weight, terpolymer containing a number of cytotoxic drugs, attached *via* cleavable linkers, to antibody fragments and the results of a drug-loaded polymer-antibody fragment conjugate (***Figure 1***) *in vivo* efficacy study will be reported.

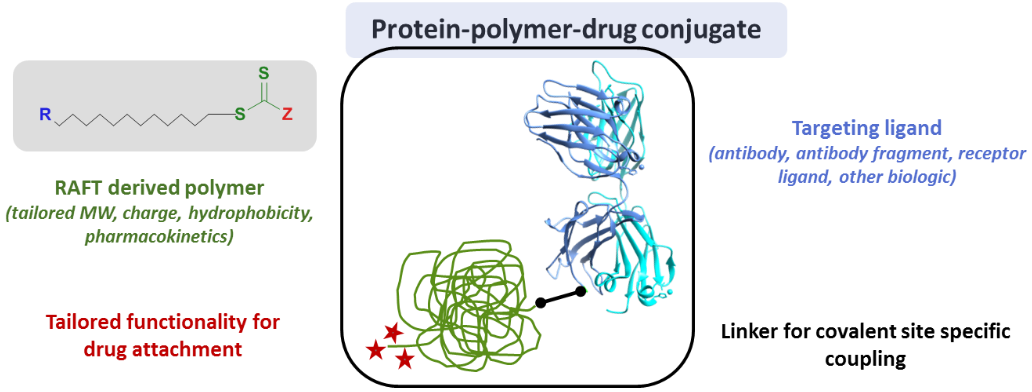

Figure 1: Protein-polymer-drug conjugates for targeted delivery of cytotoxic drugs.

All-atom Simulations of Polymeric Superstructures in Aqueous Solution

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The self-assembly of complex polymeric nanostructures is governed by specific molecular interactions that are often difficult to study experimentally at the atomic level. Molecular simulation techniques have been shown to aid in the understanding of structure and dynamic behaviour of polymer surfaces and nanomaterials.[1,2] Here, we have applied all-atom molecular dynamics simulations to gain insight into the mechanism of formation of polymeric superstructures for use as drug delivery capsules and other applications.[3,4] Recent experimental work has demonstrated that polyphenols coordinated to metal ions are able to form metal-organic complexes that in turn can form larger superstructures when mixed with diverse material templates (**Fig.1**).[5] Interestingly, while polyphenols are known to strongly bind to a wide variety of surfaces, in the absence of metal ions no superstructures are formed. To gain a better understanding of the role of various system parameters on the superstructure formation we model the adsorption of metal-polyphenol complexes and free polyphenol clusters on hydrophobic surfaces using all-atom molecular dynamics in aqueous solution. We examine adsorption mechanisms and configurations, specific and non-specific interactions between the polyphenol complex and polymeric substrate as well as the hydration mechanism while varying the ionic strength of the solution. The results of this work provide insight into the molecular mechanism of superstructure formation as well as enable a rational choice of the synthesis parameters to achieve desired system properties.

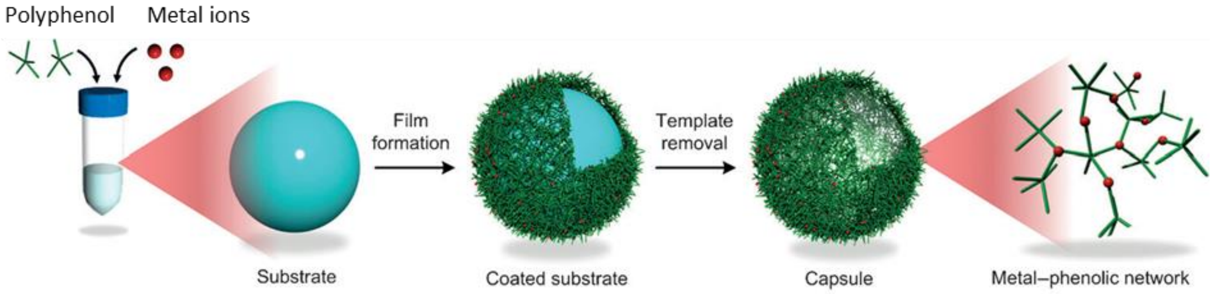

Figure 1. Assembly of polyphenol and metal ions to form a metal-phenolic network film on a particulate template, followed by the subsequent formation of a metal-phenolic network capsule. Adapted from reference 3.

References

1. D. Henry, G. Yiapanis, E. Evans, I. Yarovsky, *J. Phys. Chem. B* **2005**, *109*, 17224-17231.
2. C. Charchar, A. Christofferson, N. Todorova, I. Yarovsky, *Small* **2016**, *12*, 2395-2418.
3. J. Guo, B. Tardy, A. Christofferson, Y. Dai, J. Richardson, W. Zhu, M. Hu, Y. Ju, J. Cui, R. Dagastine, I. Yarovsky, F. Caruso, *Nat. Nanotechnol.* **2016**, *11*, 1105-1111.
4. J. Guo, J. Richardson, Q. Besford, A. Christofferson, Y. Dai, C. Ong, B. Tardy, K. Liang, G. Choi, J. Cui, P. Yoo, I. Yarovsky, F. Caruso, *Langmuir* **2017**, *33*, 10616-10622.
5. J. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J. Richardson, Y. Yan, K. Peter, D. von Elverfeldt, C. Hagemeyer, F. Caruso, *Angew. Chem. Int. Ed.* **2014**, *53*, 5546-5551.

CONCURRENT SESSION 2: Polymers for the environment and sustainability

Desigining Polymer Systems for the Environment and Sustainability

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With seabirds trapped in multipack drink rings, and mid-ocean islands of indestructible rubbish, the idea that plastics could play a big part in a sustainable future world might seem far-fetched. However, new smart plastics may yet rescue the reputation of this all-consuming 20th century material. Research into novel polymer blends and inorganic/organic hybrid materials could reduce the need for air conditioning in cars and buildings, and open alternative solutions for energy harvesting. We will present recent efforts in our group to design plastics of desired functions targeted for a greener world. One line of our enquiry is to explore the potential of plastics that can offer the same flexibility, softness and light weight as usual ‘plastics’ but that can control the flow of light and heat. We demonstrate, for instance, that simple hybrid materials based on poly(vinylalcohol) and titanium oxide hydrates allow to produce mirrors that reflect heat while being fully transparent in the visible wave length rgime. Organic semiconductor:insulator blends using, e.g., the commodity polymer high-density polyethylene as the insulator, open new opportunities for the more robust fabrciation of organic solar cells. Similar aspects in the organic transistor field will also be addressed.

Organic Solar Cells and Solar Paint: From Benchtop to Rooftop and Beyond

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Organic photovoltaics (OPV) are poised to play a major role in the global energy portfolio driven by their capability to be printed at high speeds across large areas using roll-to-roll (R2R) processing techniques; creating the tantalising vision of coating every roof and other suitable building surface with photovoltaic materials at extremely low cost. Indeed, recent full economic modelling of the balance of materials (BOM) and balance of system (BOS) costs, have highlighted the long-term commercial viability of OPV-based technology in today's energy marketplace.

However, the chlorinated solvents that are used in current OPV technology are under continual regulatory pressure due to their hazardous and toxic nature. Indeed, increasingly harsh technical requirements for using these solvents means that their implementation in high speed printing lines will be highly problematic if not economically impractical. In addition, tailoring device morphology across large areas is fraught with difficulty due to the challenge of controlling phase segregation of polymer mixtures using conventional printing. Water-based polymer nanoparticle dispersions (solar paint) offer the prospect of simultaneously controlling the nanoscale architecture of the active layer whilst eliminating the need for hazardous organic solvents during device fabrication. However, the behaviour of these nanoparticulate devices is complex and thus understanding their structure-function relationships requires characterisation techniques that can probe chemical structure on the nanoscale. In this paper we review our progress in understanding the structure-function relationships of organic electronic nanoparticulate thin films. In particular, I will discuss how scanning transmission X-ray microscopy is an invaluable tool for characterising these materials.

Finally, I will explore the future prospects and economics for large scale manufacture of solar cells based on printing. I will discuss our recent achievements in the development of a fully operating R2R printing line and installation of a 100 square metre printed solar cell testing facility at the University of Newcastle, Australia.

Ion Percolation Behavior of Poly(Ethylene Oxide)/Polyacrylate-Based Composite Polymer Electrolytes

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The classic composite polymer electrolytes (CPEs) with lithium (Li) salt and nanofiller dissolved in poly(ethylene oxide) (PEO), display low conductivity σ ~10^{-5} S cm^{-1} which prohibit them from practical applications for rechargeable batteries. Blending of PEO (semicrystalline polymer) with polyacrylates (amorphous polymer) [*e.g.* poly(methyl methacrylate) (PMMA) [glass transition temperature (T_g) = 105 °C], copolymer of polyacrylate (PAc) (T_g = 30 °C), poly(methyl acrylate) (PMA) (T_g = 13 °C)] results in miscible blends in molten state for all compositions. We focus on matrix-droplet microstructure of the blends with content of PEO in excess. Blends with addition of Li salt at relatively high mass fraction of salt (~$W_S > 0.10$) are still miscible in molten state. Upon cooling from the melt, crystallization of PEO takes place and hence phase separation of PEO crystalline phase and amorphous phase of multi-components (PEO, polyacrylate and salt) can be noticed. In these systems, there are PEO spherulites surrounded by amorphous phase of miscible PEO, polyacrylate and salt. The percolation path lies in the amorphous phase of the blends. In amorphous phase, PEO, PMMA, PAc and PMA possess oxygen in their respective chemical structures, which may be able to interact with the Li salt added. The conductivity of PEO-salt mixtures is slightly higher than that of the miscible systems of PEO/PMMA/salt or PEO/PAc/Li but lower than PEO/PMA/Li. This may be due to reduced segmental motion cause by the increased T_g of the blends in amorphous phase and hence a decrease in motion of ions in the amorphous phase of PEO. For PEO/PMA/Li when PEO in excess, the T_g of the blends is still far below room temperature, hence the motion of ion at room temperature is not much affected. We observe also the percolation path lies in the amorphous PEO-rich phase of the blends. Hence, higher conductivity is noted for this system.

Addition of low mass fraction of nanofiller ($W_F < 0.05$) induces phase separation of miscible blends (in the melt) at $W_S = 0.12$. Again, we focus on the matrix-droplet microstructure of the CPEs. With judicious selection of materials at optimum compositions of blends and appreciable concentration of salt and nanofiller, preferential solubility of salt is at PEO phase for the percolation pathway and nanofiller is located at the interface of the parent polymers at high salt concentration. This is because the added nanofiller does not like polyacrylate phase and it loses in competing with Li salt to interact with PEO phase. For selected CPEs, enhancement of conductivity is noted as compared to PEO-salt mixtures. This may be due to the addition of nanofiller may counterbalance the negative effect of stiffer segmental motion of polymer chains (mainly PEO) when polymers interact with salt. If the polymer chains do not interact well with nanofiller, a very loose interfacial region around the nanofiller may exist. This region of lower polymer density and sufficiently high salt concentration may facilitate ion motion in interfacial region, which may lead to enhanced ionic conductivity.

Commercial Development of Polymerised Ionic Liquid Block Copolymers as Solid Polymer Electrolytes

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Recent reports of lithium batteries exploding and catching fire has increased the focus on developing safer, high-performing batteries for consumer electronics applications. Solid polymer electrolytes (SPE) offer a safer alternative to the flammable liquid electrolytes currently found in lithium batteries, since SPEs are non-flammable solids with high thermal, chemical and electrochemical stability.1-5 However, practical SPEs as thin films in batteries are yet to be commercially available due to reduced conductance, insufficient mechanical strength and scale-up difficulties.1, 2

We have undertaken a development and commercialization program for a new class ofsolid polymer electrolytes known as polymerised ionic liquid block copolymers (PILBlocs). These PIL Blocs are diblock copolymers, where one block imparts mechanical strength and the second block contains pendant ionic groups (resembling ionic liquids) to promote conductivity (Figure 1).6-8These PIL Blocs polymers have been shown to exhibit microdomains with various morphologies, where the polymer's morphology is important for conductivity performance.7, 8
For any successful commercial development program, an efficient, large scale synthesis of these new materials needs to be developed and demonstrated. The controlled free radical polymerisation technique, Reversible Addition-Fragmentation Chain-Transfer (RAFT)9 is well-suited for synthesising these PIL Blocs, since RAFT is already commercially demonstrated and affords polymers with predetermined molecular weights and narrow distributions.10, 11RAFT is also compatible with conventional polymerisation reactors and various polymerization conditions.10, 11
This talk will focus on the preparation of PIL Blocs using RAFT and the adaptation of synthetic methods to establish a robust protocol for accessing kilogram quantities for commercial evaluation in devices.

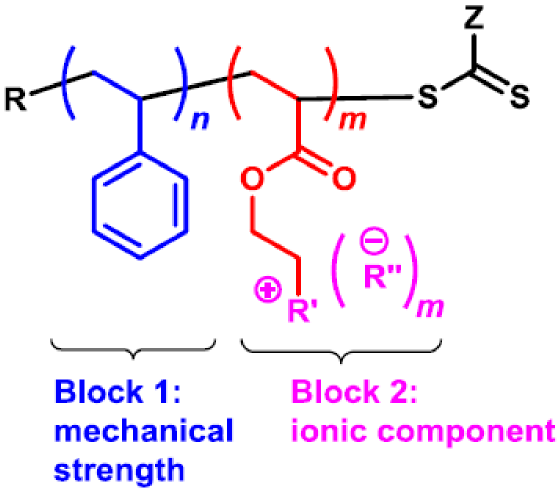

Figure 1: PILBloc structure

References

1. Yue, L., Ma, J., Zhang, J., Zhao, J., Dong, S., Liu, Z., Cui, G. and Chen, L., All solid-state polymer electrolytes for high-performance lithium ion batteries, *Energy Storage Materials*, **2016**, *5*, 139-164.
2. Muldoon, J., Bucur, C. B., Boaretto, N., Gregory, T. and di Noto, V., Polymers: Opening Doors to Future Batteries, *Polym. Rev.*, **2015**, *55*, 208-246.
3. Agrawal, R. C. and Pandey, G. P., Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview, *J. Phys. D: Appl. Phys.*, **2008**, *41*, 223001.
4. MacFarlane, D. R., Sun, J., Meakin, P., Fasoulopoulos, P., Hey, J. and Forsyth, M., Structure-property relationships in plasticized solid polymer electrolytes, *Electrochim. Acta*, **1995**, *40*, 2131-2136.
5. Bouchet, R., Maria, S., Meziane, R., Aboulaich, A., Lienafa, L., Bonnet, J.-P., Phan, T. N. T., Bertin, D., Gigmes, D., Devaux, D., Denoyel, R. and Armand, M., Single-ion BAB triblock copolymers as highly efficient electrolytes for lithium-metal batteries, *Nat. Mater.*, **2013**, *12*, 452-457.
6. Ye, Y., Choi, J.-H., Winey, K. I. and Elabd, Y. A., Polymerized Ionic Liquid Block and Random Copolymers: Effect of Weak Microphase Separation on Ion Transport, *Macromolecules*, **2012**, *45*, 7027-7035.
7. Choi, J.-H., Ye, Y., Elabd, Y. A. and Winey, K. I., Network Structure and Strong Microphase Separation for High Ion Conductivity in Polymerized Ionic Liquid Block Copolymers, *Macromolecules*, **2013**, *46*, 5290-5300.
8. Meek, K. M. and Elabd, Y. A., Polymerized ionic liquid block copolymers for electrochemical energy, *J. Mater. Chem. A*, **2015**, *3*, 24187-24194.
9. Chiefari, J., Chong, Y. K., Ercole, F., Krstina, J., Jeffery, J., Le, T. P. T., Mayadunne, R. T. A., Meijs, G. F., Moad, C. L., Moad, G., Rizzardo, E. and Thang, S. H., Living Free-Radical Polymerization by Reversible Addition−Fragmentation Chain Transfer: The RAFT Process, *Macromolecules*, **1998**, *31*, 5559-5562.
10. Moad, G., Rizzardo, E. and Thang, S. H., Toward Living Radical Polymerization, *Acc. Chem. Res.*, **2008**, *41*, 1133-1142.
11. Moad, G., Rizzardo, E. and Thang, S. H., Living Radical Polymerization by the RAFT Process – A Third Update, *Aust. J. Chem.*, **2012**, *65*, 985-1076.

Gel-Polymer Electrolytes for Electrochemical Sensing Applications.

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Amperometric gas sensors have been extensively used over the past several decades for the measurement of target gases including oxygen, carbon dioxide and hydrogen sulphide. Many commercial sensors comprise of three electrodes (working, counter and reference) connected by an electrolyte and covered by a gas-permeable membrane. In recent years, room temperature ionic liquids (RTILs) have been investigated as a replacement solvent in sensors1 due to their favourable properties including wide electrochemical windows, intrinsic conductivity, high chemical and physical stability and the ability to dissolve a wide range of analyte gases. In particular, the non-volatile nature of RTILs eliminates the need for a membrane, and they have been suggested as electrolytes in “membrane-free” gas sensors. However, one of the issues with RTILs is their inherent tendency to flow, which does not make for a very robust sensor for portable applications, due to electrolyte spillage.

To overcome this, in our recent work, we have mixed a RTIL with poly(methyl methacrylate) (PMMA) to produce a gel polymer electrolyte (GPE) that does not flow.2 The GPE was then tested for its viability in gas sensing applications, using oxygen (O2) as a model gas. A linear O2 reduction current vs. concentration over the range 10–100 vol% O2 was found using cyclic voltammetry (CV). Identical CVs on the electrode at different geometries (e.g. upright, sideways, upside down) were observed, whereas CVs in the neat RTIL were significantly altered.2 We also employed the same GPE with a Pt microarray thin-film electrode (MATFE) as a robust sensor for long-term continuous monitoring of oxygen.3 The microarray TFE has advantages of high current density and low ohmic drop contributions, in addition to less build-up of electrochemical products over time. This resulted in a considerable improvement in the long-term performance of our GPE/MATFE system.3 Further, a more stable and reproducible results were demonstrated in the GPE compared to the neat RTIL, especially at very low O2 concentrations (e.g. 0.1%).3 The ease of mass production and low cost of the electrode array, along with the minimal amounts of RTIL/PMMA required, make this a viable sensing device for oxygen detection on a bulk scale in a wide range of environmental conditions.

We had also observed that the GPE was less affected by moisture compared to the neat RTIL.2 Hence, by using a more hydrophobic RTIL/polymer mixture, we developed a new electrochemical method to directly detect and quantify the explosive compound 2,4,6-trinitrotoluene (TNT) in aqueous solutions (see Figure 1).4 The RTIL acted to preconcentrate TNT into the GPE and provided ionic conductivity. The polymer provided both sufficient viscosity to ensure mechanical stability of the GPE and strong hydrophobicity to minimize leaching of the RTIL. Using square wave voltammetry, linear plots of peak current vs cumulative concentration of TNT were obtained, giving an averaged limit of detection of 0.37 μg/mL in the aqueous phase concentration. Additionally, the voltammetry of the first reduction peak of TNT in [P14,6,6,6][NTf2] was unaffected by the presence of oxygen in contrast to that observed in an imidazolium-based RTIL providing excellent selectivity over oxygen in real environments. The sensor device was able to quickly and easily quantify TNT concentrations at typical ground water contamination levels. The low-cost and portability of the sensor device, along with the minimal amounts of GPE materials required, make this a viable platform for the onsite monitoring of explosives, which is currently a significant operational challenge.

These polymer/RTIL based materials can readily be extended to the sensing of other chemicals and gases; and we are presently pursuing the further development of new ionically-conducting polymer-based materials for specialized environmental sensing applications.

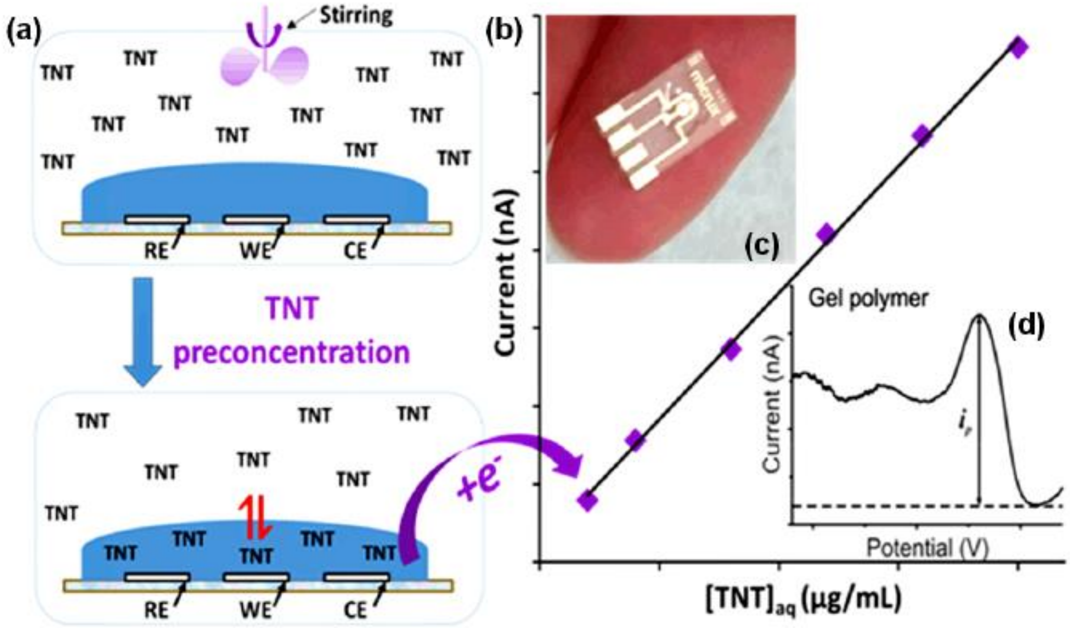

Figure 1 (a) Direct detection of 2,4,6-trinitrotoluene (TNT) in the aqueous phase, **(c)** using an ionic liquid gel-polymer electrolyte film deposited onto a miniaturized, disposable integrated electrode. **(b)** The TNT electroreduction current obeys a linear trend with varying concentrations of TNT, giving an average limit of detection of 0.37 μg/mL of TNT in the aqueous phase. **(d)** A typical square-wave voltammogram of pre-concentrated TNT obtained after 15 mins of soaking in contaminated water, showing a clear reduction peak above background.

References

1. Silvester, D. S., Recent advances in the use of ionic liquids for electrochemical sensing. *Analyst*, **2011**, 136, 4871.
2. Lee, J., Du Plessis, G., Arrigan, D.W.M. and Silvester D.S., Towards improving the robustness of electrochemical gas sensors: impact of PMMA addition on the sensing of oxygen in an ionic liquid. *Analytical Methods*, **2015**, 7, 7327.
3. Lee, J. and Silvester, D.S., Low-cost microarray thin-film electrodes with ionic liquid gel-polymer electrolytes for miniaturised oxygen sensing, *Analyst*, **2016**, 141, 3705.
4. Yu, H.A., Lee, J., Lewis, S.W. and Silvester, D.S., Detection of 2,4,6-trinitrotoluene using a miniaturized, disposable electrochemical sensor with an ionic liquid gel-polymer electrolyte film, *Analytical Chemistry*, **2017**, 89, 4729.

CONCURRENT SESSION 3: Polymers for medical, biological and personal care applications

New Strategies in the Development of Polymer-Based Nanoformulations for Therapeutics Delivery

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Controlled radical polymerization has allowed the synthesis of a wide range of polymers with well-defined architectures. The reversible addition fragmentation chain transfer process has been particularly useful in the development of polymers for biomedical applications due to the ease of the polymerization in aqueous conditions, easy purification, the easy the removal of the RAFT agent if needed to minimize any toxicities associated with the RAFT agent. As carbohydrates play important role in the biosystems, our laboratory has particularly being interested in the design and synthesis of glycopolymers with advanced structures for therapeutics delivery. Considering their biomedical uses, the approach, compositions, molecular weights, molecular weight distributions and architectures are considered carefully for such applications. As such, we have developed a number of unique strategies and carbohydrate based polymeric materials for the delivery of nucleic acids, radiosensitizers and also for cryopreservation. This talk will provide an overview of the different types of polymers and nanoformulations we have developed for those applications.

References

1. Diaz-Dussan D, Nakagawa Y, Peng YY, Ebara M, Kumar P, Narain R. Effective and Specific Gene Silencing of Epidermal Growth Factor Receptors Mediated by Conjugated Oxaborole and Galactose-Based Polymers ACS Macro Letters 2017 6, 768-774
2. Jiang K, Wang Y, Thakur G, Kotsuchibashi Y, Naicker S, Narain R, Rapid and Highly Sensitive Detection of Dopamine Using Conjugated Oxaborole-Based Polymer and Glycopolymer Systems ACS Applied Materials & Interfaces 2017, 9, 15225-15231
3. Wang Y, Li L, Kotsuchibashi Y, Vshyvenko S, Liu Y, Hall D, Zeng H. Self-Healing and Injectable Shear Thinning Hydrogels Based on Dynamic Oxaborole-Diol Covalent Cross-Linking ACS Biomaterials Science & Engineering 2016, 20, 2315-2323

4. Quan S, Kumar P, Narain R. Cationic Galactose-Conjugated Copolymers for Epidermal Growth Factor (EGFR) Knockdown in Cervical Adenocarcinoma ACS Biomaterials Science & Engineering 2016, 2, 853-859
5. Quan S, Wang Y, Zhou A, Kumar P, Narain R. Galactose-based thermosensitive nanogels for targeted drug delivery of iodoazomycin arabinofuranoside (IAZA) for theranostic management of hypoxic hepatocellular carcinoma Biomacromolecules 2015, 16, 1978-1986
6. Sunasee R, Adokoh CK, Darkwa J, Narain R. Therapeutic potential of carbohydrate-based polymeric and nanoparticle systems Expert Opinion on Drug Delivery 2014, 11, 867-884
7. Ahmed M, Narain R. Progress of RAFT based polymers in gene delivery Progress in Polymer Science 2013, 38, 767-790

Utilising Molecular Imaging to Understand Polymer Behaviour In Vivo

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Polymer and nanoparticle-based devices have evolved to significantly enhance therapeutic efficacy.1 However, in order to be truly effective, these polymeric devices must maintain their physical and chemical integrity under physiological conditions – this can only be achieved by developing a strong understanding of the fundamental properties of the nanomaterial -delivery system, in addition to identifying and successfully *delivering* new therapies. Central to the development of these future therapeutic platforms, is the field of theranostics. This is the premise that future medical devices need to be capable of delivering a therapeutic dose to the correct site within the body, but must also possess mechanisms for online diagnosis, monitoring of disease progression and visualisation of drug delivery, release and efficacy of treatment.2 Such materials require significant advancements in chemistry, materials science and engineering such that the nanomedicine is complementary with the biological milieu.

While there are countless examples of polymer or nanoparticle systems that show efficacy in animal models, the ability to rationally-optimise the materials is hindered by the inability to directly assess the behaviour of the materials *in vivo*. For example, improvements in administration for most biologically-targeted polymeric nanomaterial systems are achieved by monitoring efficacy in animals rather than monitoring the fundamental behaviour of the nanomaterial itself (e.g. measuring efficacy, rather than quantifying how a change in material properties results in a biological response).3 In this presentation, we describe recent efforts to develop self-reporting nanomedicines for a truly closed-loop approach to medicine, where nanomaterial behaviour is monitored in real-time using molecular imaging as a function of therapy.

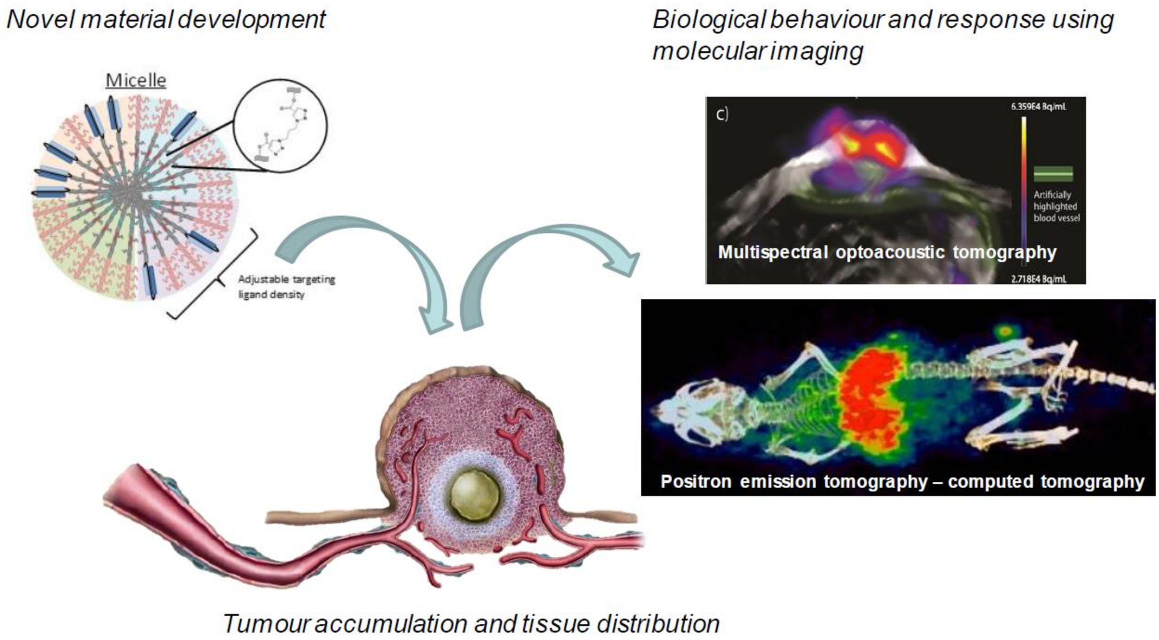

Figure 1. Schematic representation of novel targeted nanomaterials where the targeting ligand density is modulated to investigate the effect on biodistribution and tumour targeting in vivo using various molecular imaging techniques.

References

1. D Bobo, KJ Robinson, J Islam, KJ Thurecht and SR Corrie. Nanoparticle-based medicines: A review of FDA-approved materials and clinical trials to date. Pharmaceutical Research, 2016, 33(10). 2373-2387.
2. NRB Boase, I Blakey and KJ Thurecht. Molecular imaging with polymers. Polymer Chemistry, 2012, 3(6), 1384-1389.
3. AK Pearce, JD Simpson, NL Fletcher, ZH Houston, AV Fuchs, PFJ Russell, AK Whittaker and KJ Thurecht. Biomaterials. 2017, 141, 330-339.

iBodies: Modular Synthetic Antibody Mimetics Based on Hydrophilic Polymers Decorated with Functional Moieties as Tools for Molecular Recognition and Imaging

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Monoclonal antibodies are widely used tools for research, diagnostics and anticancer therapy. However, their use is compromised by high production cost, limited stability, and complicated chemical modification. Recently, we reported the design and development of synthetic polymer conjugates capable of replacing antibodies in number of *in vitro* applications used in biochemistry such as ELISA, flow cytometry, immunocytochemistry, and immunoprecipitation, and also useful for specific imaging of tumors. The conjugates, named "iBodies", consist of a hydrophilic copolymer decorated with low-molecular-weight compounds that function as targeting ligands, affinity anchors (typically biotin), and imaging probes (fluorophores or radiolabels)1,2.

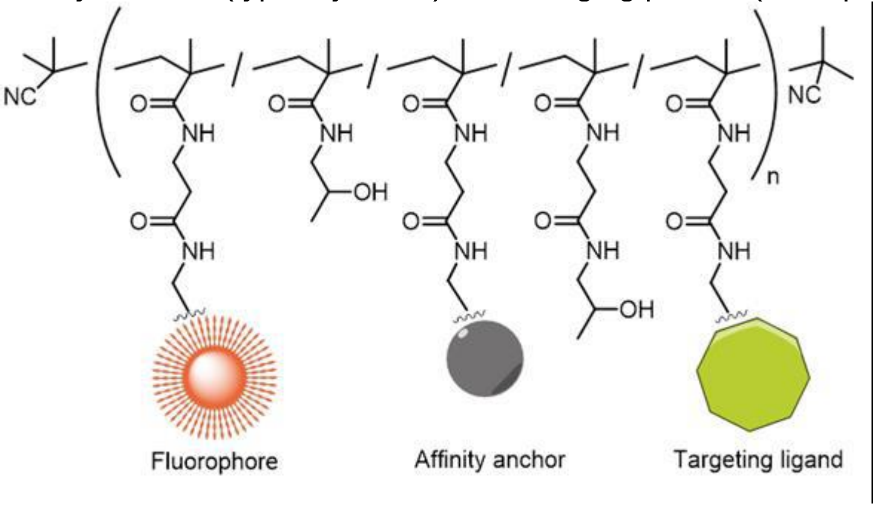

Figure 1: Schematic structure of iBody

We chose and synthetized water-soluble and biocompatible *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymers since they have been used for the development of drug delivery carriers, imaging agents and polymer drugs 3. Chosen carrier, the HPMA based copolymer, is a multivalent synthetic macromolecule with a number of reactive groups which enable covalent attachment of various ligands. These polymers were synthetized by controlled polymerization technique RAFT in the presence of trithiocarbonate chain transfer agent in organic solvents. Molecular weights of prepared copolymers were in range of 30 000 to 70 000 g/mol with polydispersities bellow 1,2. Content of comonomers units with reactive thiazolidine-2-

thione groups were between 8 - 20 mol%. These reactive groups allow covalent attachment of different ligands bearing primary amino group at common conditions and at room temperature.

We prepared specific conjugates targeting several important proteins, such as prostate specific membrane antigen, fibroblast activating protein, carbonic anhydrase IX and number of other medicinally relevant enzymes. We used these iBodies for enzyme inhibition, protein isolation, immobilization, quantitation, and live cell imaging. Specific iBodies could also be prepared for a non-enzyme proteins for which a suitable ligand is known, such as opioid receptors or proteins containing a polyhistidine tag (His-tag).

Our data indicate this highly modular and versatile polymer system can be used to produce inexpensive and stable antibody substitutes directed toward virtually any protein of interest with a known ligand, and in the future could be used also for specific anticancer drug delivery.

This work was financially supported by grant of Czech Science Foundation (grant No.16-02938S).

References

1. Šácha P. Knedlík, T., Schimer, J., Tykvart, J., Parolek, J., Navrátil, V., Dvořáková, P., Sedlák, F., Ulbrich, K., Strohalm, J., Majer, P., Šubr, V., Konvalinka, J. iBodies: Modular Synthetic Antibody Mimetics Based on Hydrophilic Polymers Decorated with Functional Moieties. *Angew Chem Int Ed*, **2016**, 55 (7), 2356-2360.
2. Dvořáková P., Bušek P., Knedlík T., Schimer J., Etrych T., Kostka L., Stollinová Šromová L., Šubr V., Šácha P., Šedo A., Konvalinka J. Inhibitor-Decorated Polymer Conjugates Targeting Fibroblast Activation Protein, *J Med Chem,* **2017***,* submitted
3. Ulbrich K., Holá K., Šubr V., Bakandritsos A.,Tuček J., Zbořil R. Targeted Drug Delivery with Polymers and Magnetic Nanoparticles: Covalent and Noncovalent Approaches, Release Control, and Clinical Studies. *Chem Rev*, **2016**, 116 (9), 5338-5431

Ultilization Natural Rubber as a Promising Material for Medical Applications

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In our research, we consider that new rubber consumption including natural rubber (NR) is increasing worldwide. Therefore, it is intended to increase in the production of natural rubber and development of high performance materials from NR instead of synthetic rubber. For instance, the production of car tires from NR is one of the innovative stratergy for the green technology. However, the technical problem in the NR to substitute a synthetic rubber at the present is known to be very difficult. For instance, there is a problem with the manufacturing process to purify natural rubber, because the cost to purify is so high and it has many difficulties to be grown into a widespread technology in a developing country such as Vietnam. Therefore, the key concept of our work will be focused on how to ultilize natural rubber as a promising materials for low carbon emission system. New technology implementation is highly demanded to promote the development of high performance materials based on NR for and low-carbon emission industry.

Keywords: natural rubber, purification, low carbon emision, high performance materials

Chicken Feather Keratin Hair Conditioner

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The goal of this study was to produce an extracted form of keratin and to characterise several aspects of its behaviour that may have implications for its general use as a biomaterial. Hence, a purified chicken feather keratin extracted using sodium sulphide as a reducing agent, fabricated into hair conditioner, was used in hair treatments to determine its interactions with the cell tissues.

Keratin powder was added to commercial conditioner at 2.5 and 5.0 %, thoroughly mixed manually and left overnight before applying onto natural untreated human hair samples, for 5 min, followed by rinsing the hairs with tap water. Commercial hair conditioner containing no added keratin was used as control. The impact of the experimental and commercial keratin-enriched conditioners on the structure of natural untreated hair was investigated by using an FEI Quanta 200 scanning electron microscope with a 20kV acceleration voltage under high vacuum. Tensile properties of treated and untreated hair were evaluated via tensile mechanical analysis (stress–strain analysis). Prior to testing, the diameters of the hair were measured using a Dino-Lite digital microscope. Specimen preparation for a single fibre tensile testing was carried out according to ASTM D3822 47, using a paper template to mount the fibre and grip it to the tensile clamps. Tensile testing was performed using a TA Instruments DMA Q800 (at 30 °C; ramped force from 0.2 to 18 N at 0.01 N min−1) equipment to measure stress–strain properties of the hairs.

The SEM images demonstrating the morphology of the natural human hair, treated with experimental keratin-enriched (0.5 %) and commercial keratin conditioners are shown in Figure 1. The keratin-treated hair images showed some keratin residues. Figure 1(a) presents the untreated hair whereas Figure 1(b) treated with our experimental control conditioner containing no keratin. Compared with untreated hair, the scales of the hair treated with conditioner looked smoother. Figure 1(c) hair treated with experimental conditioner containing 2.5 %keratin. Keratin particles were observed on it and no obvious differences were noticeable compared with the hair treated with the control conditioner. In Figure 1(d) hair showed scales with improved sealing when experimental conditioner containing 5.0 % keratin was applied. Figure 1(e) hair treated with commercial keratin conditioner (with an unknown amount of keratin) showed sealed scales similar to hair treated with experimental conditioner with 2.5 % keratin. The higher resolution images show the sealing of the scales more clearly.

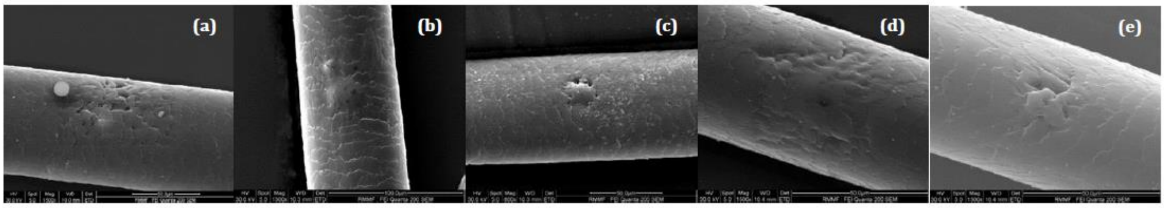


Figure 1: Natural human hair at 800X to 1500X magnifications: (a) Untreated, (b) Treated with experimental keratin-free conditioner (c) Treated with experimental conditioner with 2.5 % keratin, (d) Treated with experimental conditioner with 5.0 % keratin, (e) Treated with commercial keratin conditioner

The effect of keratin in the experimental (control, 2.5 and 5.0 %) and commercial keratin conditioners, on the stress–strain properties of natural hair was evaluated with a DMA Q800 system as shown in Figure 2. Table 1shows the average values of the Elastic modulus (*E*), yield stress, breaking stress, strain at break, diameter values associated with 20 similar natural hair, untreated and treated with experimental conditioners containing 2.5-5.0 % keratin, determined with90 % confidence. The toughest hair belonged to the specimen treated with 5 % keratin concentration as its*E*, which was the initial slope of the stress–strain curve at 0.25 % strain (as per the ASTM E 111-97 standard 56), was0.5 GPa. The softest hair was the untreated natural hair with *E*of 0.36 GPa. Even though it was the strongest of all with 6.7 MPa yield stress. As the area below the stress–strain curve associated with the natural hair treated with experimental conditioner containing 5 % keratin (stress of 19 MPa and the corresponding strain value of 55 %),was considerably larger than other samples, it was concluded that this hair specimen was significantly tougher than all, which confirms the visual difference in hair structure in Figure 1(d). Conversely, the natural hair treated with commercial keratin conditioner was the most brittle specimen (stress of 8MPa and the corresponding strain value of 12 %).

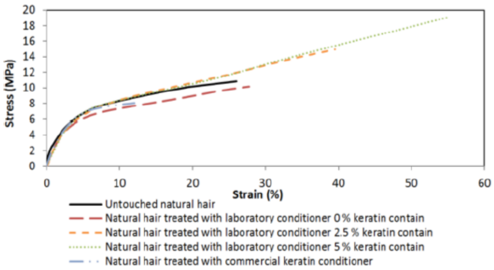
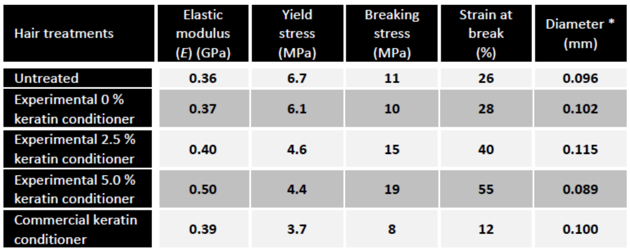


Figure 2: Tensile stress–strain curve of human hair

Table 1: Mechanical properties of keratin-treated and untreated human hair



Hair treatments	Elastic modulus (*E*) (GPa)	Yield stress (MPa)	Breaking stress (MPa)	Strain at break (%)	Diameter * (mm)
Untreated	0.36	6.7	11	26	0.096
Experimental 0 % keratin conditioner	0.37	6.1	10	28	0.102
Experimental 2.5 % keratin conditioner	0.40	4.6	15	40	0.115
Experimental 5.0 % keratin conditioner	0.50	4.4	19	55	0.089
Commercial keratin conditioner	0.39	3.7	8	12	0.100

* The mean diameter value of five-point measurements of 20 hairs.

This study confirmed that chicken feather keratin demonstrates excellent compatibility in biological protein-based materials such as hair conditioner, thus the waste feathers can be used as a suitable source of keratin, rather than disposing of in landfill.

Isolation of Polymers from Marine Wastes and Development of Pharmaceutical Formulations

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The polymers such as gelatin & chitosan were isolated from marine wastes and the isolated polymers were subjected to preformulation studies viz solubility, ashvalue, bulkdensity, viscocity,PHdetermination,Degree of Deacetylation,etc., The drug-polymer compatibility was analyzed and the results reveals that there was no interference in the functional group of the isolated polymers.By using isolated and marketed polymers ,the sustained release (SR) tablets were formulated.The formulated tablets were subjected to preliminary characterization such as hardness, friability ,dissolution and disintegration . The above said parameters of SR tablet prepared with polymers from marine waste were exactly same as the tablets prepared with synthetic polymers. The hardness test & friability test indicates good mechanical strength & resistance. and dissolution study revealed that the tablet with natural gelatine and chitosan have almost same dissolution properties as that of the tablets with prepared synthetic polymers. Present study demonstrated the utilization of marine waste in preparation of chitosan and gelatin by using simple technology. It can be concluded from the study that marine wastes can be utilized to develop inexpensive, biodegradable, echofriendly and pharmaceutically useful polymers.

Reference

1. Kurita K Chitin and chitosan: functional biopolymers from marine crustaceans.Mar Biotechnol (NY). 2006 May-Jun;8(3):203-26
2. Sorota Rawdkuen,Natthawut Thitipramote,Optimisation of extraction conditions and characteristics of skin gelatin from Nile tilapia (*Oreochromis niloticus*). Int J Food Sci Technol 2010; 45: 1807–1813.
3. Rosemary Anima Fori, Isolation andcharacterization of collagens from the skin, scale and bone ofdeep - sea redfish (*Sebastes mentella*). Food Chem 2008; 108:616

CONCURRENT SESSION 4: Polymers for the environment and sustainability

Helen Millicer
Vinyl Australia (Australia)

Churchill Fellowship 2018 - Project Summary

The Winston Churchill Memorial Trust was established in 1965 to honour the memory of Sir Winston Churchill. Each year the Trust selects Fellows to travel to gain new knowledge and insights that can be practically applied to positively impact our Australian communities and society.

Project aim: To increase recycling and reprocessing of plastics in Australia

One of our best opportunities to create a more sustainable and productive future is to shift to a circular economy. However, we have major gaps in our recycling systems, and a largely linear economy relying on virgin materials. Our plastics consumption is large, around 3,000,000 tonnes per year (enough to fill 40% of the MCG each year) and for a decade our plastics recycling rate has been low, ~ 12-14% (329,000 tonnes). This study tour will focus on plastic with a view to applying the learnings for a circular, sustainable economy.

While we use so much plastic, our risks in Australia are:

1. We rely upon export of plastic 'waste' to Asia for over 50% of our recycling. The quantity of plastics reprocessed for manufacturing in Australia has fallen in real terms over the last decade as governments and companies have focused on easy export to Asia
2. In mid-2017 China announced it will restrict imports of poor quality unsorted plastics, potentially closing the door to many Australian sorting facilities, and sending even more plastic to landfill
3. Our recycling focus is largely packaging. We have no strategies and programs addressing durable plastics in Australia; virtually all our durable plastics end up in landfill or the environment
4. Our strategies, contracts, pricing, systems and programs have prioritised efficiency and volume for collections for export over quality and value for end products
5. Waste companies are increasing pressure on governments to build plants that burn plastics in waste to energy facilities, for poor environmental outcomes compared to reprocessing and renewables
6. Too few private collectors and governments know of and engage with local manufacturers in Australia who could use recycled plastics in product
7. Our manufacturers, jobs and industries are at a disadvantage over international competitors as they are struggling to obtain reliable plastic recyclate, and have a higher environmental footprint.

What we need to do and what I intend to investigate to bring back to Australia for the 21st century:

8. Strategies, targets and programs that are designed for a robust, productive and sustainable circular economy, one that is focussed on end markets and value,

not only volume collections, that lifts our recycling rates, puts materials back into product in Australia and reduces our environmental impact.

This project will involve engagement with world leaders who have plans for the 21st century delivering recycling and reprocessing/manufacturing results for a sustainable and circular economy.

Priority destinations are:
Government agencies, manufacturers, think-tanks and peak industry bodies in UK, Belgium, Germany and Malaysia where they are undertaking circular economy strategies and programs.
In particular the European Commission, Ellen MacArthur Foundation, WRAP UK, World Resources Institute, Vinyl Plus, Plastics Europe, European Plastics Recyclers, Hamburg Chamber of Commerce, Cradle to Cradle EPEA, Waste Management Assoc of Malaysia and Malaysian Plastics Manufacturers Assoc.

Priority areas for investigation useful to Australia:
Laws, strategies, regulations, market mechanisms and incentives, partnerships, stewardship models, separation systems, design and end product manufacturing.

When: It is proposed this scholarship travel will be undertaken in April-May 2018.

Helen Millicer, GAICD, hmillicer@optusnet.com.au, 0413 875 872, LinkedIn profile
Honoured to be: Principal One Planet Consulting; Manager Recycling Strategies, Vinyl Council of Australia; Panel member, New Energy Jobs Fund; Board Director, Loddon Mallee Waste & Resource Recovery Group; President, Alternative Technology Assoc; Advisor, UN Global Cities Program; Columnist, Business Environment Network.

Growing Cotton With Less Water Using an Environmentally Responsive Polymer

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Pre-formed plastic mulch films are widely used in agriculture to enhance crop production and increase yields by conserving soil moisture. Typically, these films are produced from non-degradable materials such as poly(ethylene) which are removed and disposed of after each growing season, raising concern about environmental pollution and soil contamination. We aim to circumvent these environmental issues by using water-borne, degradable polymers that can be sprayed directly onto the soil surface to form a barrier that reduces soil-water evaporation and eliminates soil contamination issues.1,2

In this paper, we discuss aspects of material design, synthesis and surface characterization of environmentally responsive poly(dimethylsiloxane)-poly(ethylene glycol), PDMS-PEG, poly(urethane) systems. These polymers have been designed to reversibly change their surface properties from hydrophobic to hydrophilic depending on the polarity of the contacting medium. We are exploiting these properties to both capture and preserve water in soil (for example from rainfall/irrigating events), consequently increasing the amount of water available to plants and improving crop water use efficiency. Preliminary findings from our glasshouse experiment demonstrate that use of this polymer has the potential to reduce the amount of water needed to grow cotton.

References

1. Adhikari, R.; Bristow, K. L.; Casey, P. S.; Freischmidt, G.; Hornbuckle, J. W.; Adhikari, B. Preformed and sprayable polymeric mulch film to improve agricultural water use efficiency, *Agricultural Water Management* 169, 1 2016
2. Johnston, P., Freischmidt, G., Easton, C. D., Greaves, M., Casey, P. S., Bristow, K. L., Gunatillake, P. A., Adhikari, R. (2016), Hydrophobic-hydrophilic surface switching properties of nonchain extended poly(urethane)s for use in agriculture to minimize soil water evaporation and permit water infiltration. *Journal of Applied Polymer Science*, 44756. doi: 10.1002/app.44756

Surface Decontaminant Based on the Polyvinyl Alcohol-Borate Hydrogel and Magnetic Adsorbent for the Volume Reduction of Radioactive Waste After Use

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Radioactive materials have been extensively used in various industrial and research fields, particularly for nuclear research and industry. During their utilization, various surfaces, such as concrete, steel, and paint, in most nuclear facilities become necessarily contaminated with radioactive materials. Thus, surface decontamination is a very important technology for radioactive material utilization and even for decommissioning nuclear facilities because surface contamination can be transferred to workers by contact, and it may become airborne if not treated.1Meanwhile, the nuclear accident at the Fukushima Daiichi nuclear power station in 2011 unfortunately released large amounts of radioactive cesium into the environment, which also affected various urban structures, such as roofs, building exterior surfaces, and roads in a wide area.

In this study, a magnet-sensitive and strippable polymeric coating that consists of a magnetic adsorbent with 137Cs adsorption properties using a polyvinyl alcohol(PVA)-borate complex based hydrogel with highly elastic properties was developed for surface decontamination. Magnetic adsorbents, magnetic nanoparticles coated with Prussian blue, were synthesized by following the procedure previously reported by our group.2The boronate grafted alginate was prepared by grafting 3-aminophenylboronic acid onto alginate using 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride coupling agent. Fig 1(a) shows the synthetic route of boronate grafted alginate. The strippable hydrogel was formed by complex between boronate grafted alginate and polyvinyl alcohol on the basis of reversible boate-diol ester bond interactions (fig 1(b)).

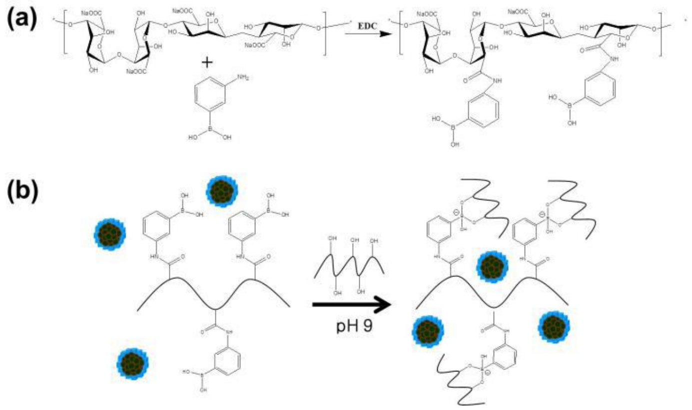

Figure. 1.(a) The synthetic route of boronate grafted alginate, (b) Formation of hydrogel containing magnetic adsorbent for surface decontamination

The aqueous polymeric solution of borate-conjugated alginate(Alg)and PVA containing magnetic adsorbent could be easily applied to 137Cs-contaminated surfaces via the spray or brush method. The mixture solution on the surface subsequently formsan adsorbent/PVA/Alg-borate hydrogel film that is strippable from the surface. This hydrogel based polymeric coating displayed a good removal efficiency of 83% for 137Cs-contaminated surfaces (painted surface) due to the presence of the Cs adsorbent, which had a large distribution coefficient for Cs (3.34×104mL/g).2The generated volume of the radioactive wastes after surface decontamination was simply reduced due to the magnetic separation of the adsorbent from the used polymeric coating. Furthermore, this new ecofriendly volume reduction method for radioactive waste demonstrated the reusability of borate compound conjugated Alg and PVA for further surface decontamination because almost all of the 137Cs (99.838%) captured in the used polymeric coating was removed by magnetic separation of the adsorbent. Therefore, the adsorbent/hydrogel-based polymeric coating system has excellent potential as a new cost-effective surface decontaminant.

References

1. M. Manolopoulou, E. Vagena, S. Stoulos, A. Ioannidou, C. Papastefanou, Radioiodine and radiocesium in Thessaloniki, Northern Greece due to the Fukushima nuclear accident, *J. Environ. Radioact*., **2011**, 102, 796-797**.**
2. H.-M. Yang, S.-C. Jang, S. B. Hong, K.-W. Lee, C. Roh, Y. S. Huh and B.-K. Seo, Prussian blue-functionalized magnetic nanoclusters for the removal of radioactive Cesium from water, *J. Alloy. Compd*., **2016**, 657, 387-393.

Defect-free PIM-1 Hollow Fiber Membranes

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Microporous polymers are one of the newest classes of materials investigated for membrane applications. Polymers of intrinsic microporosity (PIMs) have rigid backbones that lead to high permeabilities and good selectivities along with solution processability, particularly for gas separation applications. Current research on PIMs has been exclusively performed on flat sheet membranes to understand fundamental membrane properties. To bridge the gap between the development of new high performance polymers and industrially attractive technologies, more efficient membrane units such as hollow fibers are needed. To date, only dilute PIM-1 containing blends have been fabricated into these large surface area to volume ratio, highly scalable membrane modules, partly due to somewhat unfavorable polymer solubility properties. This work is the first to demonstrate the fabrication of defect-free, integrally skinned, asymmetric PIM-1 hollow fiber membranes utilizing an immiscible liquid protective layer. Spinning techniques capable of addressing specific challenges presented by PIM-1 solutions are discussed. The work here describes the process of developing spin dopes, fabricating hollow fibers, and testing the resulting membrane modules. Ideal selectivity between various gas pairs was used to assess the quality of the membranes. The observed selectivities are in good agreement with previously reported PIM-1 flat sheet membrane analogs, and in fact slightly higher. The methods discussed could be expanded to fabricating hollow fiber membranes from other novel microporous polymers and PIMs.

Preparation and Characterization of Zno/PES Hybrid Film Photocatalyst for the Degradation of Methyl Orange Aqueous Phase

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Zinc oxide (ZnO) nanoparticles were immobilized into polyethersulfone (PES) matrix to prepare hybrid film photocatalyst. The photocatalytic performance of the photocatalyst with respect to methyl orange (MO) degradation was clearly improved through the addition of the nanoparticles. The films were prepared by dispersing different amounts of hydrophilic ZnO (5–19 wt.%) into the polymer solution containing PES and N-methyl-2-pyrrolidone (NMP) in the appropriate portions. SEM-EDX and AFM were used to investigate the dispersion and surface properties of the ZnO within the polymer matrix. While XRD and XPS were employed to study the chemical state and crystallinity of the prepared films, respectively. The photocatalytic performance were observed to increase with the amount of added ZnO. Particularly, the PES/ZnO film photocatalyst with 17 wt.% of ZnO displayed the highest degradation efficiency with almost 100% of MO removal under the original conditions. Additionally, the reusability study revealed that the best film photocatalyst demonstrated a comparable degradation performance for 5 cycles without the requirement of post-treatment while the efficiency was retained.

References

1. S. Mozia, D. Darowna, R. Wróbel, A.W. Morawski, A study on the stability of polyethersulfone ultrafiltration membranes in a photocatalytic membrane reactor, J. Memb. Sci., 2015, 495, 176–186.
2. K. Fischer, M. Kühnert, R. Gläser, A. Schulze, Photocatalytic degradation and toxicity evaluation of diclofenac by nanotubular titanium dioxide–PES membrane in a static and continuous setup, RSC Adv., 2015, 5, 16340–16348.
3. Z. Adlan, M. Hir, P. Moradihamedani, A.H. Abdullah, M.A. Mohamed, Immobilization of TiO2 into polyethersulfone matrix as hybrid film photocatalyst for effective degradation of methyl orange dye, Mater. Sci. Semicond. Process., 2017, 57, 157–165.
4. H. Rajabi, N. Ghaemi, S.S. Madaeni, P. Daraei, B. Astinchap, S. Zinadini, S. Hossein, Nano-ZnO embedded mixed matrix polyethersulfone (PES) membrane : Influence of nanofiller shape on characterization and fouling resistance, Appl. Surf. Sci., 2015, 349, 66–77.
5. K. De Sitter, C. Dotremont, I. Genne, L. Stoops, The use of nanoparticles as alternative pore former for the production of more sustainable polyethersulfone ultrafiltration membranes, J. Memb. Sci., 2014, 471, 168–178.

Functional Starch Based Hydrogels: Sustainable Material Solutions for Wastewater Industries

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Hydrogels are a novel class of functional biopolymers with a unique set of properties such as high water content, flexibility and biocompatibility. Their dynamic response to external stimuli differentiates them from other polymeric materials and their tailorablity makes them excellent candidates for the design of smart devices, applicable in a variety of technological fields(1). In order to produce hydrogels, both natural and synthetic hydrophilic polymers can be chemically cross-linked in a reactive environment. Recently, natural biopolymers such as polysaccharides have gained great attention as a sustainable source of materials to produce smart hydrogels. Starch in particular has shown great application potential as an economical feedstock in this area. In addition to being chemically modifiable, starch is abundant, renewable and biodegradable (2). Starch hydrogels have recently been identified as having potential to be successfully employed in a variety of unconventional applications, with one such application being the removal of industrial pollutants and reactive ions from wastewater. Although various wastewater treatment methods and resource recovery systems such as coagulation, precipitation, adsorption and advanced oxidation processes are available (3), the majority of them are not sustainable solutions nor economically viable. Among these methods, adsorption using modified starches has become the procedure of choice for resource recovery from industrial effluents (4). The existing starch based hydrogels are currently only found in the laboratory and have limited functionality as nutrient recovery systems, specifically in complex solutions such as municipal or agricultural wastewater (5). Therefore, the development of affordable and smart resource recovery systems based on starch hydrogels is a propitious approach for reducing the environmental impact of industrial pollution (6). Our aim is to develop a novel processing method, based on reactive extrusion, for industrial scale production of starch based smart hydrogels for recycling of nutrient from synthetic solutions, as well as for the treatment of actual industrial wastewater.

References

1. Samal SK, Dash M, Dubruel P, Van Vlierberghe S. Smart polymer hydrogels: properties, synthesis and applications. **2014,** 237-70.
2. Shrestha AK, Halley PJ. Chapter 5 - Starch Modification to Develop Novel Starch-Biopolymer Blends: State of Art and Perspectives A2 - Avérous, Peter J. HalleyLuc. In: *Starch Polymers. Amsterdam: Elsevier*; **2014**, p. 105-43.
3. Ahmed M, Hasan CK, Rahman H, Ali Hossain M, Uddin SA. Prospects of using wastewater as a resource-nutrient recovery and energy generation. *American Journal of Environmental Sciences*, **2015**,11, (2), 99-114.

4. Crini G. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, **2005**, 30, (1), 38-70.
5. Xiao C. Current advances of chemical and physical starch-based hydrogels. *Starch - Stärke,* **2013**, 65, (1-2), 82-8.
6. Dragan ES. Design and applications of interpenetrating polymer network hydrogels. A review. *Chemical Engineering Journal*, **2014,** 243, 572-90.

Utilization of Fish Waste as Starting Material for Protein Based Thermoplastics

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Recent developments of biodegradable polymers have greatly been driven by a desire to replace synthetic plastics. However, commercialization of protein based thermoplastics is considered slow than other biobased polymers such as thermoplastic starch and polylactic acid (PLA). Among protein based plastics, utilization of fish protein has not been explored to any great extent. [1] Using fish waste as a starting material for thermoplastics may solve disposal of waste problem. Interestingly, it could potentially replace plastic product in agriculture industry that is used as one-off application such as mulch film. The objective of this study was to characterize the performance of fish waste to assess its potential as thermoplastics material. Fish waste containing fish head, bones and fins was collected from local fish product processing plant before further cooking, pressing, drying and milling into fish powder at 600 μm. The fish powder was analysed using Kjeldahl method to determine the protein content. Transformation of fish protein into thermoplastics involves addition of additives such as water, a protein denaturant (urea), a reducing agent (sodium sulfite, SS), a surfactant (sodium dodecylsulfate, SDS) and plasticizer (glycerol) using twin screw extruder. The extrudate produced was further granulated and compression moulded. Differential Scanning calorimeter (DSC) was carried out to measure the glass transition temperature at different glycerol loading (0-35pph). The morphology of the samples was observed using Scanning Electron Microscopy (SEM) while the mechanical properties was measured through Instron Tensile Machine. The results revealed that protein content in fish waste was 46%. Addition of 10pph of urea, 3pph of SS and SDS, 20pph of water and glycerol (0-35pph) were successfully produced a smooth surface extrudate during extrusion and a consolidated dumbbell sample after compression moulding. In the absence of glycerol (0pph), the sample was rigid, brittle and was difficult to compression moulded. Addition of 20pph glycerol increased the processability of the fish protein and homogenous polymer were produced. At 35pph glycerol, a wet mix was observed during mixing (before extrusion) that produced soft consolidated extrudate. Thermal analysis showed that the addition of glycerol gave plasticization effect by lowering the Tg from 42.1 °C to 33.1°C. Further heating to 200 oC showed a decreased in denaturation temperature from 200 °C to 130 °C. This indicated that the addition of plasticizer influence the Tg by increasing the free volume which allows the polymer molecules to move past each other, making it more flexible. The thermal denaturation of the sample with addition of glycerol (20pph and 35pph samples) exhibited two peaks corresponding to the endothermic transitions of low molecular weight 7S globulin and high molecular weight 11S globulin in the fish protein.[2] Figure 1 showed the SEM morphology of fish waste powder and fish waste thermoplastic. It was observed that the morphology of fish waste powder was a mixture

of a large and small particles. Protein agglomeration was also observed. Addition of additives and further processing change the protein agglomeration behaviour to a ductile properties. It would appear that the protein was able to elongate independently. Mechanical properties showed that without plasticizer, a rigid and brittle sample was produced compared to plasticized sample. However, overall, the mechanical properties obtained was unsatisfactory. It was found that the interaction of protein in fish waste was poor and optimization on formulation is needed to produce satisfactory mechanical properties. Indeed, the protein based thermoplastic from fish waste was able to generate consolidated thermoplastics properties and could be developed into excellent biodegradable polymer.

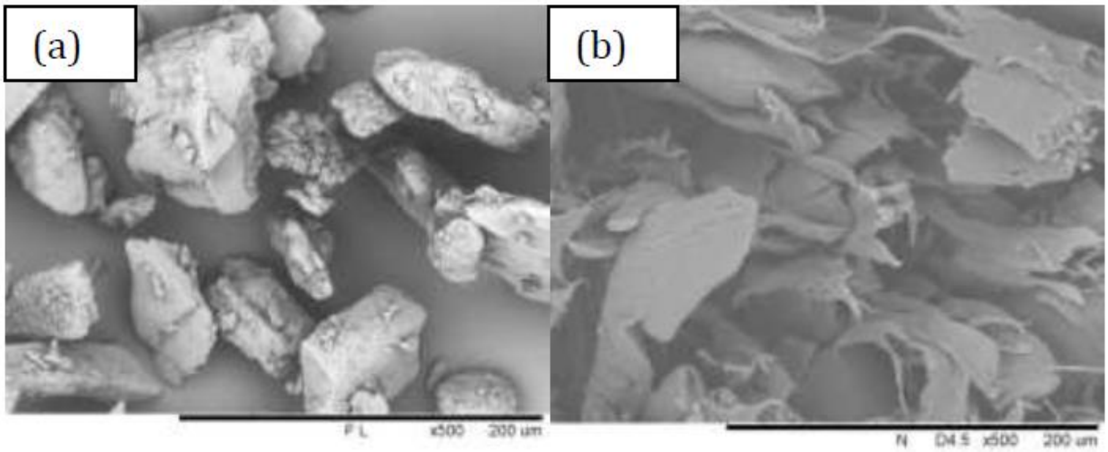

Figure 1: SEM morphology of fish waste powder (a) and fish waste protein thermoplastic (b)

References

1. Svenson, J., A.S. Walallavita, and C.J.R. Verbeek, *Evaluation of fishmeal as starting material for producing biodegradable protein-based thermoplastic polymers.* Waste and Biomass Valorization, 2013. 4(1): p. 147-159.
2. Mo, X. and X. Sun, *Plasticization of soy protein polymer by polyol-based plasticizers.* Journal of the American Oil Chemists' Society, 2002. 79(2): p. 197-202.

CONCURRENT SESSION 5: Polymer 3D printing and processing

Designing Composite Materials for Extreme Loads and Resilient Infrastructure

A/Prof Tuan Ngo

Director of the Advanced Protective Technologies for Engineering Structures (APTES) Group and Research Director of the ARC Training Centre for Advanced Manufacturing of Prefabricated Housing, Department of Infrastructure Engineering
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The construction industry has faced severe challenges over the past two decades. Spiralling costs of building materials and construction have made housing less affordable. Innovative designs, lightweight and high performance composite materials, and new construction techniques are urgently needed for producing sustainable, reusable, smart and cost-effective structures. In addition to that, the frequency and intensity of disasters have been steadily increasing in the last decades and will continue to do so. Many critical infrastructure as well buildings are particularly vulnerable, evidenced in the prevalence of floods, cyclones, and bush fires in recent years, exacerbated by populations heavily concentrated in cities and regional centres. A/Prof. Tuan Ngo's presentation will highlight the key challenges in designing composite structures for these extreme events and new innovations in high performance composite materials, building systems, and construction techniques for resilient and sustainable infrastructure.

His presentation will cover the emerging technologies in new materials and systems for prefabricated modular construction including:

- Composite lightweight materials and building systems
- Additive manufacturing (3D printing) for construction
-

He will demonstrate through case studies the benefits of adopting these technologies such as:

- Construction up to 60% faster than traditional methods
- Reduce total costs by up to 50%
- Achieve 100% re-use of componentry
- Recycle 80% of site waste
- Reduce transport, labour, and site preliminaries by 70%

A Dual Cure Approach to Overcoming Material Property Issues in Polymer 3D Printing

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Additive manufacturing (AM), commonly known as 3D Printing, encompasses a wide range of processes and materials and is becoming an increasingly popular method of fabricating low-cost parts. Applications range from simple prototyping through to advanced aerospace components and medical implants. Key advantages include reduced waste, the ability to make geometries that cannot be made by any other method, and the low setup cost compared to casting or moulding, making AM ideal for short-run production or customised products as well as on-demand manufacturing for spare parts to reduce cost while improving response time.

The properties of AM produced polymers are usually inferior to those produced by traditional fabrication methods such as injection moulding and extrusion, limiting use of the small range of commercially available polymers to low-precision product prototyping and novelty applications. This is due to the very slow deposition, heating, cooling and curing processes and, most importantly, the layered structures that are inherent in AM techniques which lead to anisotropy in polymer parts produced in this way.

One method to overcome this issue may be to use a combination of monomers to initially crosslink the shape of the part within the AM process, and then use a separate polymerisation to crosslink across the interfaces and bind the layers together more effectively, reducing anisotropy. In this study a dual-curing system of UV-initiated dimethacrylate and thermally-initiated epoxy polymers was investigated. The sequence of curing steps was found to be important, with fast UV curing followed by a thermal post-cure found to create a more complex 3-phase structure, which can be seen by dynamic mechanical analysis (DMA). The transparency of the samples indicates that these domains are on a very fine scale (<100nm) and may be due to the formation of interpenetrating networks where the two polymers remain intermingled, but phase separated into domains as small as 10nm.

Fabrication and Characterisation of thermoplastic materials: 3D printing versus injection moulding

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Abstract: 3D printing, as an additive manufacturing (AM) technology, has been developed as a revolutionary manufacturing process. It may be potential to replace conventional manufacturing processes. 3D printing process – Fused Deposition Modelling/Fused Filament Fabrication (FDM/FFF) has been developed to rapidly print thermoplastic products while the traditional manufacturing process – injection moulding has been well used for fabricating thermoplastic products with a long history.

In this study, a comparison study is experimentally and numerically conducted to investigate the fabrication of two commonly-used 3D printing thermoplastic materials – Acrylonitrile Butadiene Styrene (ABS) and Polylactic Acid (PLA) using both 3D printing and injection moulding. The samples' material properties and mechanical behaviours are characterised via uniaxial tension and three point bending tests according to ASTM standard. Mechanical properties of final-product materials are found influenced by manufacturing processes and controlled by main factors that affect that processes. To optimise the 3D printing process using available 3D printers at lab, correlations between main control parameters and material properties of ABS and PLA are extracted based on the experimental results obtained considering the mould injection as a benchmarking process. Finite element analysis –based numerical modelling and simulation are developed and applied for conducting a parametric study to guide the adjustment of main control parameters of layer-by-layer 3D printing process as a material design tool.

Keywords: 3D printing, injection moulding, material properties, thermoplastics, finite element analysis

Alginate-Sulfate Nanocellulose Bioinks for Cartilage Bioprinting Application

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INTRODUCTION: The lack of available materials for bioprinting applications is currently what is holding this promising technology back. A good bioink should not only be biologically active but also have the proper rheological properties. A combination of materials is often superior over single materials and necessary to fulfil both the biological and rheological requirements. Here we present a combination of the biologically active biopolymer alginate sulfate, which was shown to be chondrogenic and induce cell proliferation and spreading [1], and the viscosity modifying agent nanocellulose (NC).

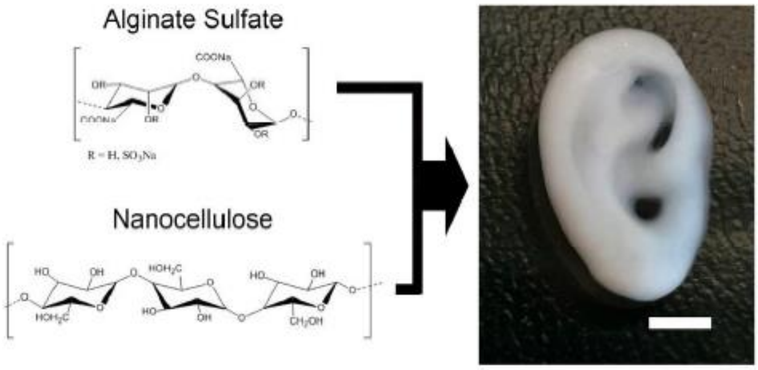

Figure 1: Chemical structure of alginate sulfate and nanocellulose. A combination of the two materials allows the creation of a bioink which can be used for the 3D bioprinting of complex structures, here a miniature ear. Scale bar is 5 mm.

METHODS: Rheological measurements were performed to assess the flow behaviour and gelation properties of alginate sulfate when mixed with NC. Bovine chondrocytes were encapsulated in alginate and alginate sulfate with or without NC and the viability and cell morphology was investigated at day 1, 14 and 28. Cells were also printed using the alginate sulfate-NC bioink with different needle diameters and shapes and cell viability and morphology were evaluated. COMSOL simulations were performed to see if differences between the printed and the encapsulated cells arise from differences in maximum and average shear stresses occurring in the different printing geometries.

RESULTS: Rheological measurements revealed that, despite the lower viscosity of alginate sulfate solutions compared to unmodified alginate, the flow properties of the final bioink with NC were only slightly influenced. Mechanical properties of alginate sulfate-NC were equal to alginate NC after increasing the alginate sulfate concentration in the bioink. Cells showed a round morphology at every time point in the alginate and alginate-NC gels, whereas in the alginate sulfate and alginate sulfate-NC samples the cells started spreading after 14 days in culture. Only when the printing geometry was optimized was the ability of cells in alginate sulphate to spread and proliferate maintained. Simulations revealed differences in the average and maximum shear stress between conical and straight needles of different diameters which might explain the differences in the cells ability to spread or not in the printed samples.

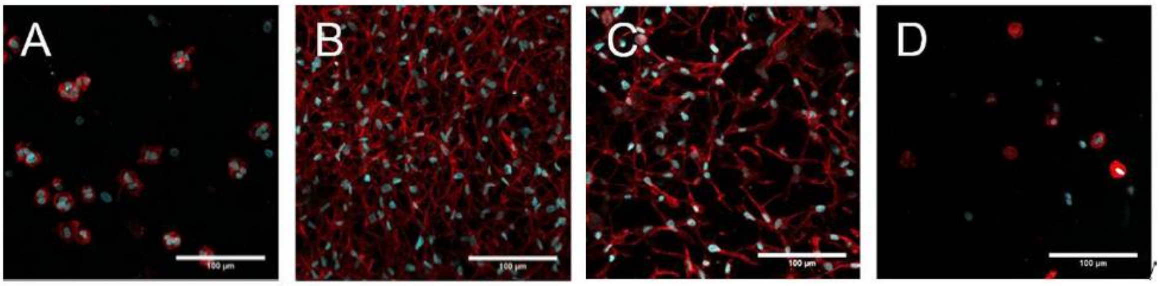

Figure 2: Chondrocyte morphology at day 28 encapsulated in alginate-NC (A) or alginate sulfate-NC (B) or printed with alginate sulfate-NC with a straight 413 µm (C) or 159 µm (D) needle. Scale Bar is 100 µm.

DISCUSSION & CONCLUSIONS: Alginate sulfate maintained its mitogenic properties and effects on cell spreading in the presence of NC. The NC addition made alginate sulfate a printable material, but restrictions remain in regards to usable inner needle diameters and shapes for cells to survive and show the spreading behaviour.

ACKNOWLEDGEMENTS: This work was supported by ETH Research Grant ETH-23 14-1, FIFA/F-MARC and EU program Eureka and Vinnova.

References

1. Mhanna, R, Kashyap, A, Palazzolo, G, Vallmajo-Martin, Q, Becher, J, Moeller, S, Schnabelrauch, M and Zenobi-Wong, M. Chondrocyte Culture in Three Dimensional Alginate Sulfate Hydrogels Promotes Proliferation While Maintaining Expression of Chondrogenic Markers, *Tissue engineering. Part A,* **2014**, 20, 1454-1464

Development of Electrically Conductive Polymeric Filaments for Additive Manufacturing

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Carbon monoxide reduced graphene (CO-rG) was compounded with polyamide-6 (PA6) by melt-mixing to investigate the suitability of CO-rG as novel filler for enhanced mechanical properties in PA6-based composites. CO-rG was first exfoliated via probe ultrasonication in p-xylene prior to melt-mixing. Nanocomposites of differing compositions were then prepared and characterised for their elastic modulus, tensile yield strength and strain at break. Interactions between CO-rG and PA6 were characterised via Fourier-transform infrared spectroscopy (FTIR) and observed via scanning electron microscopy (SEM). Significantly enhanced mechanical properties were achieved even at low CO-rG content. FTIR spectroscopy confirmed the existence of hydrogen bonding between CO-rG and PA6. SEM imaging indicated uniform dispersion of CO-rG in PA6.

CONCURRENT SESSION 6: Advanced materials

Extremely High Current Density in Organic Polymer Light-Emitting Devices

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The demonstration of the first laser in 1960 led to a revolution in everyday life. Today, lasers are ubiquitous and can be found in CD/DVD players, printers, supermarket scanners, and medical equipment. The development of new types of lasers with expanded applications remains a major research activity worldwide. One class of lasing materials currently attracting considerable attention is organic semiconductor polymers. They combine the simple manufacturing of plastics with favorable optoelectronic properties such as high photoluminescence quantum yield, strong absorption/gain, and broad spectra. Therefore, there is great interest in developing an electrically-pumped organic semiconductor laser (OSL), as it would provide a new class of lasers. Although full-color monitors of organic light-emitting diodes (OLEDs) are already available in the market, electrical pumping remains a very challenging problem for conventional OLEDs. Particularly, for electrical excitation of OSLs, extremely high current density more than 1 kA/cm^2 is required [1,2]. However, the maximum current density of OLEDs are typically limited to 1-10 A/cm^2 due to the effect of exciton quenching and photon loss processes [1,2] and, consequently, electrical excitation of OSLs has not been realized. Very recently, to address this limitation, we focus on organic electrochemical light-emitting cells [3]. These light-emitting devices have p-i-n homojunction with highly conductive active area owing to electro-chemical carrier doping, which is irrealizable for OLEDs. As the results, we demonstrated the effective light emission with extremely high current density more than 1 kA/cm^2, which is the first important milestone for future electrically-pumped OSLs [4-6].

References

1. Samuel, I. D. W., Namdas, E. B. and Turnbull, G. A. How to recognize lasing, *Nat. Photon.*, **2009**, 3, 546.
2. Takenobu, T. et al., High Current Density in Light-Emitting Transistors of Organic Single Crystals, *Phys. Rev. Lett.*, **2008**, 100, 066601.
3. Sakanoue, T. and Takenobu, T. et al., Optically pumped amplified spontaneous emission in an ionic liquid-based polymer light-emitting electrochemical cell, *Appl. Phys. Lett.*, **2012**, 100, 263301.
4. Sakanoue, T. and Takenobu, T. et al., High Current Injection into Dynamic p–n Homojunction in Polymer Light-Emitting Electrochemical Cells, *Adv. Mater.*, **2017**, 29, 1606392.
5. Pu, J. and Takenobu, T. et al., A Versatile and Simple Approach to Generate Light Emission in Semiconductors Mediated by Electric Double Layers, *Adv. Mater.*, **2017**, 29, 1606918.
6. Sakanoue, T. and Takenobu, T. et al., An Ionic Liquid That Dissolves Semiconducting Polymers: A Promising Electrolyte for Bright, Efficient, and Stable Light-Emitting Electrochemical Cells, *Chem. Mater.,* **2017***,* 29, 6122–6129.

Functional Polymer Composites for Nanoscale Information Optics

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Photonics has transformed massively our everyday life and global economy for a sustainable future. Nanophotonics, which studies optical science and technology at a nanoscale, has enabled the development of nano-scale optical and photonic devices that provide a green-technology platform. Polymers doped with nano-particles can result in a new range of functions that can be induced, switched and modified by nanoscale optical probes. In this talk, I will show that functional polymer composites can provide a new horizon for the development of ultrahigh-capacity optical storage devices, nano-engineered biomimetic photonics, and wide-angle-optical display.

Study of the RAFT Homopolymerization and Copolymerization of *N*-[3-(Dimethylamino)Propyl]-Methacrylamide Hydrochloride and Evaluation of the Cytotoxicity of the Resulting Homo- and Copolymers

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The reversible addition-fragmentation chain transfer (RAFT) polymerization of *N*-[3-(dimethylamino)propyl]methacrylamide hydrochloride (DMAPMA.HCl) was studied. A detailed investigation of the effect of RAFT polymerization conditions was carried out. The polymerization was conducted in a solvent mixture of water (acidic pH) and 2-propanol in the ratio of 2:1 using 4-cyanopentanoic acid dithiobenzoate (CTP) as the chain transfer agent (CTA), and 4,4'-azobis(4-cyanovaleric acid) (ACVA) as the initiator which was found to be the optimal condition to access well-defined homopolymers. The synthesis in acidic media and purification with precipitation in acetone allowed the good retention of dithioester chain end groups. The p(DMAPMA.HCl)-based macroCTA was prepared and successfully used in the diblock copolymerization of 2-lactobionamidoethyl methacrylamide (LAEMA), 2-Aminoethyl methacrylamide hydrochloride (AEMA), *N*-(3-aminopropyl) morpholine methacrylamide (MPMA), and 2-methacryloyloxyethyl phosphorylcholine (MPC). Statistical DMAPMA.HCl-based copolymers of those monomers were also synthesized. Finally, the *in vitro* cytotoxicity of the resulting homo and copolymers of DMAPMA.HCl was investigated by the MTT assay in Hela cells.

References

1. Vasilieva, YA, Thomas, DB, Scales, CW, and McCormick, CL. Direct Controlled Polymerization of a Cationic Methacrylamido Monomer in Aqueous Media via the RAFT Process*, Macromolecules*, **2004**, 37 (8), 2728-2737.
2. Cunningham, MF. Controlled/living radical polymerization in aqueous dispersed systems, *Progress in Polymer Science*, **2008**, 33 (4), 365-398.
3. Deng, Z, Ahmed, M, and Narain, R. Novel well-defined glycopolymers synthesized via the reversible addition fragmentation chain transfer process in aqueous media, *Journal of Polymer Science Part A: Polymer Chemistry*, **2009**, 47 (2), 614-627.
4. Fischer, D, Li, Y, Ahlemeyer, B, Krieglstein, J, and Kissel, T. In vitro cytotoxicity testing of polycations: influence of polymer structure on cell viability and hemolysis, *Biomaterials*, **2003**, 24 (7), 1121-1131.
5. Ahmed, M, and Narain, R. The effect of polymer architecture, composition, and molecular weight on the properties of glycopolymer-based non-viral gene delivery systems, *Biomaterials*, **2011**, 32 (22), 5279-5290.

Energy Harvesting Technologies Enabling Battery-less Internet of Things by selectively developed polymer

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Internet of things (IoT) represents one of the biggest technology trends, which transform every physical object to an information source; revolutionizing the way we interact with our surroundings. It aims to provide ubiquitous connectivity between trillions of multi-role devices, such as sensors and actuators, everywhere at any time. To reach the full potential of autonomous and ubiquitous connectivity of IoT, the IoT devices must be tiny while including sensing, processing and wireless communications capabilities. Such requirements impose several strict limitations on the energy storage and power management of IoT devices; that is cable-power and battery replacement are not viable options. This research aims at providing a comprehensive study on energy harvesting techniques as alternative and promising solutions to power IoT devices. We present the main design challenges of IoT devices in terms of energy and power and provide design considerations for a successful implementations of battery-free IoT devices. The main focus of this work is on vibration energy harvesting techniques using piezoelectric Polyvinylidene fluoride (PVDF) for several IoT applications, and briefly present a newly developed piezoelectric materials in form of film, powder and fibre with enhanced electrical properties.

References

1. R. V. Prasad, S. Devasenapathy, V. S. Rao, and J. Vazifehdan, “Reincarnation in the ambiance: Devices and networks with energy harvesting,”IEEE Communications Surveys & Tutorials, **2014**, 16, 1,195–213.
2. T. Torfs, T. Sterken, S. Brebels, J. Santana, R. van den Hoven, V. Spiering, N. Bertsch, D. Trapani, and D. Zonta, “Low power wireless sensor network for building monitoring,” IEEE Sensors Journal, **2013**, 13, 3, 909–915.
3. M. M. Abolhasani, K. Shirvanimoghaddam, and M. Naebe, “PVDF/graphene composite nanofibers with enhanced piezoelectric performance for development of robust nanogenerators,” Composites Science and Technology, **2016**, 138, 49-56

Osteoblasts Behaviour and hBM-MSC Osteogenic Differentiation towards Surface Engineered PLA Microspheres

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The study was focused on osteoblasts response towards surface engineered PLA microspheres using NaOH hydrolysis. In this study, surface engineered PLA microspheres were evaluated in terms of wall thickness and porosity prior to *in vitro* studies. NaOH hydrolysis at different concentrations (0.1 M, 0.3 M and 0.5 M) were conducted to introduce hydrophilicity on the PLA. Morphology changes showed that the highest concentration of NaOH (0.5 M) has the highest hydrolysis effect as the highest wall thickness were observed with 3.52 μm (Figure 1). Furthermore, the surface engineered PLA microspheres also aided the attachment of osteoblast cells as seen in Figure 2. An enhanced cells migration was observed for all surface engineered PLA microspheres during migration assay as compared to control. Overall, 100 % cells closure was obtained after two days of cells migration assay conducted. The increment in hydrophilicity of the surface modified PLA microspheres provides favorable surface for cellular attachment of osteoblast, which reflected by the positive DAPI stain of the cell nucleus. Surface engineered PLA microspheres enhanced the capability of the PLA in facilitating the differentiation process of MSCs into osteogenic lineage since positive stain only being observed in modified PLA. These results indicate that the surface engineered PLA microspheres were non-toxic for biological environments and improved hydrophilicity make it a potential candidate as drug delivery vehicle as the cells can adhere, attached and proliferated inside it.

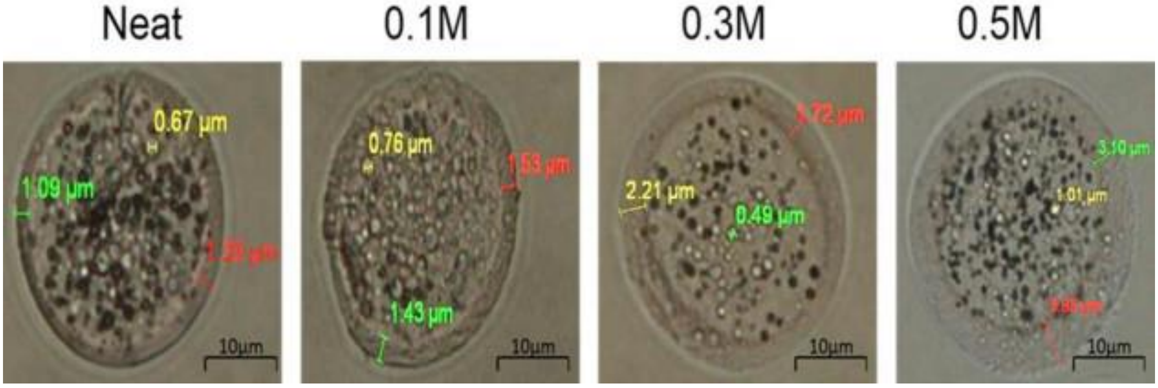

Figure 1: Cross section of neat and surface engineered PLA microspheres at different NaOH concentration (0 – 0.5 M) (Mag: 40x)

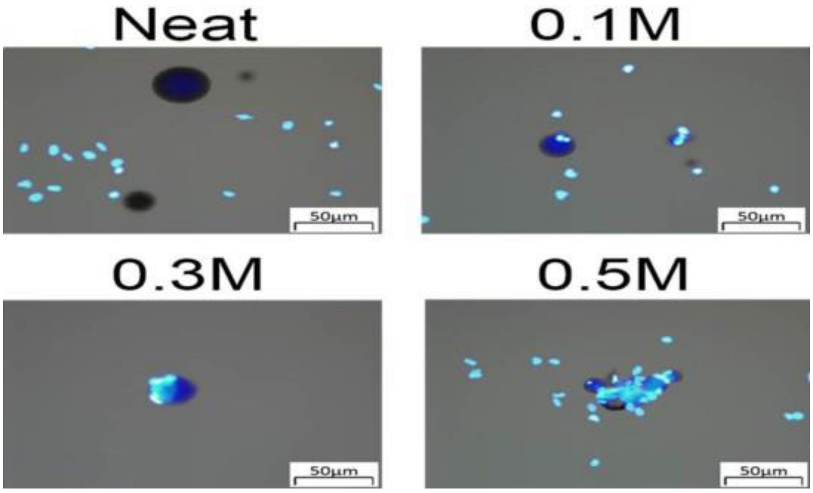

Figure 2: Osteoblast cells attachment assay on surface engineered PLA microspheres at different NaOH concentration (0 – 0.5 M)

References

1. Shenguo, W., Wenjin, C. and Jainzhong, B. Bulk and surface modifications of polylactide. *Anal Bioanal Chem*. **2005**, 381, 547-556.
2. Bosco, R., van den Beucken, J., Leeuwenburgh, S. and Jensen, J. Surface Engineering for Bone Implants: A Trend from Passisve to Active Surfaces. *Coating.* **2012**, 2, 95-119.
3. Migliaresi, C. and Motta, A. *Scaffolds for Tissue Engineering: Biological Design, Materials and Fabrication*, **2014** ISBN 9814463205.
4. Rudolph, A., Teske, M., Illner, S., Kiefel, V., Sternberg, K., Grabow, N. et al. Surface Modification of Biodegradable Polymers towards Better Biocompatibility and Lower Thrombogenicity. *Plos ONE*. **2015**, 10(12) 1-17.
5. Javaid, M. A. and Kaartinen, M. T. Mesenchymal Stem Cell-based Bone Tissue Engineering. *International Dental Journal of Student's Research*. 1(3) (2013) 24–35.

CONCURRENT SESSION 7: Academia-Industry collaboration

Polymers to Products –Translating Polymer Science to Industry

Dr. John Tsanaktsidis,
CSIRO (Australia)

Industry-University Partnerships: Arranged Marriage or Perfect Match?

Prof.Michelle Gee

RMIT University (Australia)

Driving collaboration is a mantra commonly seen in business mission statements. The strategy underlying this ethos is that collaboration with universities and research institutes provides access to world class technologies. Alignment of these technologies with the needs of industry gives a business the competitive edge. In spite of this, industry-university partnerships are not common and often fail to deliver.

The release of the Australian Government's National Innovation and Science Agenda and research impact as a measure of success are parts of clear push for universities to work more closely with industry to foster an innovation-based economy. But isn't this just an arranged partnership and a recipe for failure? Don't we all want to find our perfect match?

In 2015, after a long career as a research and teaching academic, I was recruited from academia to join Boeing. As a tech head, I was drawn by what might be on the other side. In my role at Boeing, I have helped drive business development by growing partnerships with universities and arranging perfect R&D matches. In what was a steep learning curve and a thrilling ride, I was able to marry my two worlds. Now, in 2017 I am returning to academia to bring what I have learnt from business development through industry R&D to the university sector. In my talk, I want to share with you some of the lessons I've learned along the way, seeing what research means from both sides, so that you might find your perfect R&D match in this age of innovation.

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

Dr Predrag Micic

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Plastics pipes are arteries of our civilization. Polyethylene (PE) pipeline business is constantly experiencing change. Over the past 50 years the R&D activities of both universities and polyethylene technology companies has resulted in several new generations of PE for pipe. PE100 pipe grade is the newest generation enabling manufacture and installation of cost efficient and safe and long lasting pipe networks.

This work describes collaboration between Qenos and the research partner Univation on a new resin for high performance polyethylene pipe. In broad terms, Universities, the Science Industry research and industrial organisations have different views on what constitutes success. Universities focus on the quality of research with the highest ranking being given to research that transforms its immediate discipline through excellent publications.

The research focused Science Industry organisation seeks to turn an idea into a product and can view success in measures such as inventions and patents, companies started, initial product made and licenses sold.

An industrial organisation wants to take products to market and views success in terms of volume sold with a keen eye on cost, quality and time to market. Collaboration is always the best way forward, however different priorities may lead to division in paths taken by different organisations and limit opportunity for creating value.

Qenos and its research partner Univation demonstrated that collaboration and process of combining fundamental research with applied research and application knowledge generated a solution that met all the requirements of the PE100 specification. The recognition of mutual dependency led to the drafting of a commercialisation agreement and a much closer association on the development of the product. The two organisations teamed up as true research and commercialisation partners.

Manufacturing Futures Research Institute – New Manufacturing Processes for Next Generation Polymer Materials

Bronwyn Fox

Manufacturing Futures Research Institute
Swinburne University of Technology – Hawthorn, Melbourne - Australia

Manufacturing Futures Research Institute at Swinburne brings together a multi-disciplinary team to create a research Centre of Excellence in Australia around Industry 4.0. The team includes manufacturing technologists, materials scientists, industrial and architectural designers, digital, data and visualisation specialists with business and marketing experts. Manufacturing Futures aims to work together with industry partners to solve key challenges through integration of innovative design platforms, advanced manufacturing technologies, materials and information systems. Manufacturing Futures will distinguish itself from more conventional advanced manufacturing research initiatives by focusing on globally relevant projects identified by key industry partners to deliver real-world outcomes.

Swinburne is currently developing Australia's first Industry 4.0 test lab that will be an open access facility for the automation of high volume carbon fibre composite production. The carbon fibre composite manufacturing is predicted as the viable niche for global industry, but positioning industries to participate in this growth market will require the development of flexible, automated composite production processes. The major challenge for the industry is to increase production rates through automation thereby also reducing cost, enabling high volume manufacture and broadening the applications for carbon fibre composites.

The other major focus for the Institute is on 'Industrialisation of graphene products manufacturing'. Commercialisation of graphene products requires material produced at scale with replicable quality that meets their specific application needs. The ultimate challenge arises from the batch-to-batch variation in the graphite precursor materials, multiplicity of manufacturing processes impact of this variability on the properties and performance. Swinburne is currently establishing the world's first Graphene Certification Facility to deliver certified graphene products. This facility will explore the unique capabilities of graphene in a wide spectrum of applications.

Polymerization-Induced Self-Assembly (PISA) Based on Conventional (Non-Living) Radical Polymerization

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Polymer nanoparticles find a wide variety of applications in areas as diverse as material science, health care products and nanomedicine. The traditional focus has been on spherical particles, simply because this geometry is by far the most accessible from a synthesis perspective. Recent progress in the area of radical polymerization in dispersed systems via the so called polymerization-induced self-assembly (PISA)1,2approach has opened the door to facile and large scale preparation of nano-objects with more complex non-spherical shapes such as worms, rods, and vesicles. These novel nano-structures typically exhibit very different properties from their spherical analogues. Hollow polymeric nanoparticles, including vesicles, represent another interesting category of nano-objects with wide applications in *e.g.*nanomedicine

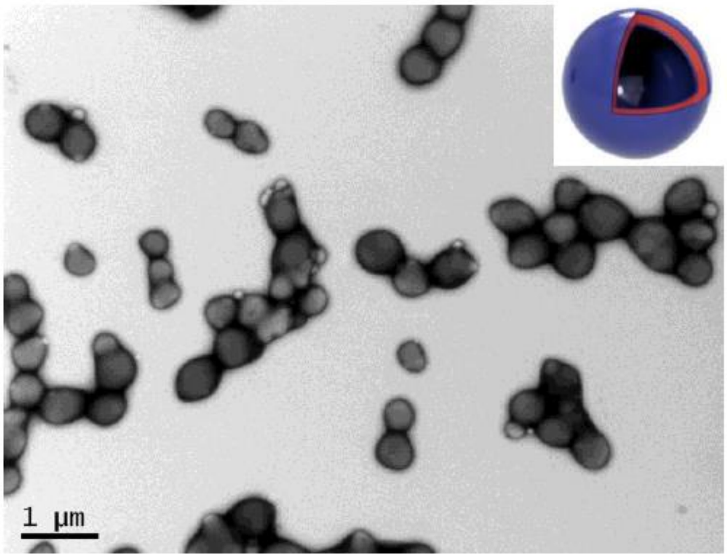

Fig. 1. Vesicles obtained by polymerization-induced self-assembly (PISA) based on a conventional (non-living) radical polymerization system.

The PISA technique to date depends on controlled/living radical polymerization (CLRP) approaches,1most notably reversible addition-fragmentation chain transfer (RAFT) polymerization.2A solvophilic block is chain extended with a monomer that yields a solvophobic block, resulting in generation of an amphiphilic diblock copolymer that subsequently self-assembles into polymer particles of a wide variety of morphologies depending on a number of experimental factors, most notably the relative block lengths. This presentation will be concerned with a novel approach towards PISA, whereby diblock copolymers are generated in situ without exploitation of CLRP techniques, but via conventional "non-living" radical polymerization.3This approach may havethe potential to significantly expand the scope of PISA for synthesis of polymeric (nano)particles of a wide range of morphologies.

References

1. Zetterlund, P.B.; Thickett, S.C.; Perrier, S.; Bourgeat-Lami, E.; Lansalot, M. Controlled/Living Radical Polymerization in Dispersed Systems: An Update, *Chem. Rev.*, **2015**, 115, 9745-9800.
2. Canning, S.L.; Smith, G.N.; Armes, S.P. A Critical Appraisal of RAFT-Mediated Polymerization-Induced Self Assembly, *Macromolecules*, **2016**, 49, 1985-2001.
3. Zhou, D.; Kuchel, R.P.; Zetterlund, *P.B. Manuscript in preparation*.

From Stimuli-Responsive Polymersomes to Aggregation-Induced-Emission Polymersomes

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Synthetic amphiphilic polymers have been developed since last decades for the purpose of forming self-assembled polymer vesicles (polymersomes) which mimick lipid vesicles (liposomes). Polymersomes are much more stable, more robust and less permeable than liposomes due to the high molecular weight of polymers. Another interesting feature of polymersomes is that their properties can be finely adjusted by chemical design of the amphiphilic building blocks. These nanostructures are currently studied as a means of drug delivery and biomedical imaging for their ability to entrap hydrophobic molecules in the membrane and encapsulate hydrophilic ones in the inner aqueous compartment. Our group has focussed, since several years, on the tailor-design of smart polymersomes with biocompatible and biodegradable building blocks, stimuli-responsive release functions and/or aggregation-induced-emission properties.1-7 In this talk, I will first present an example of photo-responsive polymersomes based on liquid crystal polymers,4,5 to show an innovative nano-actuator design by combining the properties of two kinds of soft materials, polymers and liquid crystals. Then a reduction-sensitive liquid crystal polymersome, which can release encapsulated molecules under the action of intracellular reduction agent (glutathione), will be discribed.6 Polymersomes made from new biodegradable and biocompatible building blocks based on polyaminoacids will also be discussed.7 At the end, I will present our recent efforts at the development of aggregation-induced-emission polymersomes by combining polymer nanostructures with AIE luminogens (AIEgens) in order to provide innovative approaches to cell/tissue imaging and *in vivo* study of drug bio-distribution.

References

1. Jia, L. and Li, M.-H. Liquid crystalline polymer vesicles: thermotropic phases in lyotropic structures, *Liquid Crystals,* **2013**, 1, 1–17.
2. Zou, T., Dembele, F., Beugnet, A., Sengmanivong, L., Trepout, S., Marco, S., de Marco, A. and Li, M.-H. Nanobody-functionalized PEG-*b*-PCL polymersomes and their targeting study, *J. Biotech.* **2015**, 214, 147-155.

3. Ferji, K., Nouvel, C., Babin, J., Li, M.-H., Gaillard, C., Nicol, E., Chassenieux, C. and Six, J.-L. Polymersomes from amphiphilic glycopolymers containing polymeric liquid crystal grafts, *ACS Macro Lett.* **2015**, 4, 1119-1122.
4. Mabrouk, E., Cuvelier, D., Brochard-Wyart, F., Nassoy, P. and Li, M.-H. Bursting of sensitive polymersomes induced by curling, *Proc. Natl. Acad. Sci. U. S. A.*, **2009**, 106, 7294-7298.
5. del Barrio, J., Oriol, L., Sánchez, C., Serrano, J.-L., Di-Cicco, A., Keller, P. and Li M.-H. Self-Assembly of Linear-Dendritic Diblock Copolymers: from Nanofibers to Polymersomes, *J. Am. Chem. Soc.*, **2010**, 132, 3762-3769.
6. Jia, L., Cui, D., Bignon, J., Di-Cicco, A., Wdzieczak-Bakala, J., Liu, J. and Li, M.-H. Reduction-Responsive Cholesterol-Based Block Copolymer Vesicles for Drug Delivery, *Biomacromolecules* **2014**, 15, 2206–2217.
7. Deng, Y., Zou, T., Tao, X., Semetey, V., Trepout, S., Marco, S., Ling, J. and Li, M.-H. Polysarcosine-*block*-Poly(ε-Caprolactone) by Ring-Opening Polymerization of Sarcosine N-Thiocarboxyanhydride: Synthesis and Thermo-responsive Self-Assembly. *Biomacromolecules* **2015**, 6, 3265–3274.

Macromolecular Precision Engineering with Light

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Installing chemical functionality at precise locations within complex macromolecules as well as onto three dimensional constructs prepared by 3D laser lithograpy in the mildest possible fashion (visible light) and without any catalyst becomes possible with efficient light driven, quantitative ligation protocols.[1-7] Advanced light-induced processes enable the parallel encoding of multiple molecules onto predefined locations on 3D microstructures in one step[8] as well as the wavelength dependent addressing of specific parts of a macromolecule for its highly orthogonal functionalization (λ-orthogonal photochemistry).[9] The lecture will highlight how macromolecular ligations can be directed in their selectivity by the application of light (light induced reaction manifolds),[10] how light can be used as an orthogonal trigger in macromolecular chain folding,[11] how the high efficiency of light driven chemistry can be exploited for the synthesis of sequence defined macromolecules[12] or explore how diffraction unlimited laser lithography becomes possible based on depletable photochemistry concepts.[13] The lecture will also highlight examples of wavelength dependent reactivity mapping of radical photoinitiation and ligation systems.[14,15]

References

1. (a) Delaittre, G.; Goldmann, A. S.; Mueller, J. O.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 11388–11403: (b) Barner-Kowollik, C.; Bastmeyer, M.; Blasco, E.; Delaittre, G.; Mueller, P.; Richter, B.; Wegener, M. Angew. Chem. Int. Ed. 2017, doi.10.1002.anie.201704695.
2. (a) Mueller, J. O.; Schmidt, F. G.; Blinco, J. P.; Barner-Kowollik, C. Angew. Chem. Int. Ed., 2015, 54, 10284–10288; (b) Lederhose, P.; Wuest, K. N. R.; Barner-Kowollik, C.; Blinco, J. P. Chem. Commun. 2016, 52, 5928-5931.
3. Altintas, O.; Glassner, M.; Rodriguez-Emmenegger, C.; Welle, A.; Trouillet, V.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 5777–5783.
4. Pauloehrl, T.; Welle, A.; Bruns, M.; Linkert, K.; Börner, H. G.; Bastmeyer, M.; Delaittre, G.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2013, 52, 9714–9718.
5. Frick, E.; Anastasaki, A.; Haddleton, D. M.; Barner-Kowollik, C. J. Am. Chem. Soc. 2015, 137, 6889–6896.
6. Pauloehrl, T.; Delaittre, G.; Winkler V.; Welle, A.; Bruns, M.; Börner, H. G.; Greiner, A. M.; Bastmeyer, M.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2012, 51, 1071–1074.
7. Claus, T. K.; Telitel, S.; Welle, A.; Bastmeyer, M.; Vogt, A. P.; Delaittre, G.; Barner-Kowollik, C. Chem. Commun. 2017, 53, 1599-1602.

8. Claus, T. K.; Richter, B.; Hahn, V.; Welle, A.; Kayser, S.; Wegener, M.; Bastmeyer, M.; Delaittre, G.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2016, 55, 3817-3822.
9. Hiltebrandt, K.; Pauloehrl, T.; Blinco, J. P.; Linkert, K.; Börner, H. G.; Barner-Kowollik, C. Angew. Chem. Int. Ed. 2015, 54, 2838–2843.
10. Hiltebrandt, K., Elies, K.; d'Hooge, D.; Blinco, J.; Barner-Kowollik, C. J. Am Chem. Soc. 2016, 138, 1142−1145.
11. Greb, L.; Mutlu, H.; Barner-Kowollik, C.; Lehn, J. M. J. Am. Chem. Soc. 2016, 138, 1142−1145.
12. (a) Zydziak, N.; Feist, F.; Huber, B.; Mueller, J. O.; Barner Kowollik, C. Chem. Comm. 2015, 51, 1799-1802; (b) Zydziak, N.; Konrad, W.; Feist, F.; Barner-Kowollik, C. 2016, Nat. Comm. 7, 13672.
13. Mueller, P.; Zieger, M. M.; Richter, B.; Quick, A. S.; Fischer, J.; Mueller, J. B.; Zhou, L.; Nienhaus, U.; Bastmeyer, M.; Barner-Kowollik, C.; Wegener, M. ACS Nano 2017, 1, 6396-6403.
14. Fast, D. E.; Lauer, A.; Menzel, J. P.; Kelterer, A.-M.; Gescheidt, G.; Barner-Kowollik, C. Macromolecules 2017, 50, 1815-1823. 15. Tuten, B.; Menzel, J. P.; Pahnke, K.; Blinco, J. P.; Barner-Kowollik, C. Chem. Commun. 2017, 53, 4501-4504.

Structure-Property Relationships in Tactic Acrylate Ester Polymers

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Directly calculating the bulk properties of polymers presents a significant computational challenge. Polymers are generally amorphous, and thus able to adopt a wide range of configurations. Despite this complexity however, the fundamental chemical information contained within a polymer is generally quite small, as the polymer is made up of a small number of repeating units. The bulk properties of polymers can therefore be seen as being effectively encoded within a relatively small number of parameters. These may include structural features of the polymer chains, internal chain flexibility and non-bonding interactions between chain segments. Understanding how each of these factors influences the bulk properties of the polymer can lead to the ability to create polymers tailored to specific applications.

In this presentation, structure-property relationships for a range of20acrylate ester polymers is discussed. A particular focus of this work is in determining how the tacticity of the polymer chains can be included in the descriptive model. Although other machine learning methods, such as neural networks have been applied to this problem, they do not provide insight into the factors that influence polymer properties.1In order to elucidate the correlation of the structural features of the polymer models with their corresponding bulk properties, datasets of 100 randomly generated structures were created for each polymer and tacticity. Each structure contained 8 oligomers, with each oligomer made up of 8 monomers. An example structure for poly(methyl methacrylate) is shown in (Fig.1). These structures were optimised using tight-binding electronic density functional theory.2To capture some of the internal dynamics of the polymers, molecular dynamics simulations were also used to model the motions of single oligomers of 10 repeat units. These simulations were repeated at different temperatures to estimate structural time correlation properties within the polymer chain.

Using these datasets a range of descriptors were then calculated to characterize each polymer and tacticity combination. Focus was given to descriptors that are able to distinguish between both the chemical composition and stereochemistry of the polymer chains. To determine the relevance of these descriptors, a correlation model predicting the glass transition temperature was created based on available experimental data. The glass transition temperature is a good test for the applicability of structure-property relationship models, as this temperature has been shown to vary substantially with tacticity. From the correlation model some of the most important descriptors relate to the torsional configuration of the polymer chains, such as the relative orientation and motion of the polymer side groups. The relative energies of different configurations is also shown to be an important factor.

The utility of the correlation model was then tested based on comparisons to the results of all atom molecular dynamics simulations on 3 acrylate ester polymers. These simulations involve models including 40 polymer chains each containing 40 monomers, and comprise in excess of 20,000 atoms. An example of the backbone structure of such a model is also shown in (Fig.1). In these simulations the glass transition temperature is estimated through simulated annealing of the polymer melt to determine the temperature at which the rate of thermal expansion changes. These simulations show that the structure-property relationship method is better able to predict the experimental glass transition temperature, demonstrating the efficacy of this approach.

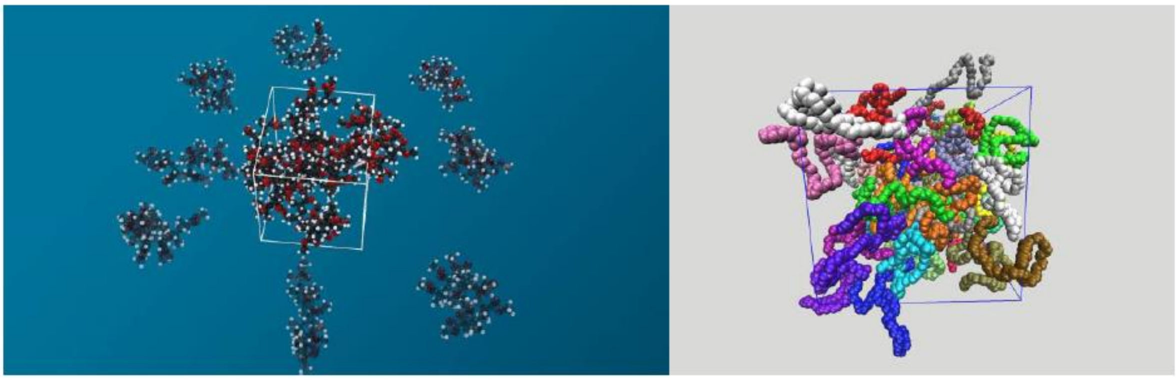

Figure 1. Example molecular models for poly(methyl methacrylate) for both structure-property datasets (left) and molecular dynamics simulations showing only backboneatoms (right).

References

1. Duce, C, Micheli, A, Starita, A, Tiné, M and Solaro , R. Prediction of the glass transition temperature of (meth)acrylic polymers containing phenyl groups by recursive neural network, *Polymer*, **2007**, 48, 7121.
2. Gaus, M, Cui, Q and Elstnew, M. DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB), *Journal of chemical theory and computation*, **2011**, 7, 931-948.

Photoinaddimer of Photopolymerization: a New Role of *N*-Vinylcarbazole

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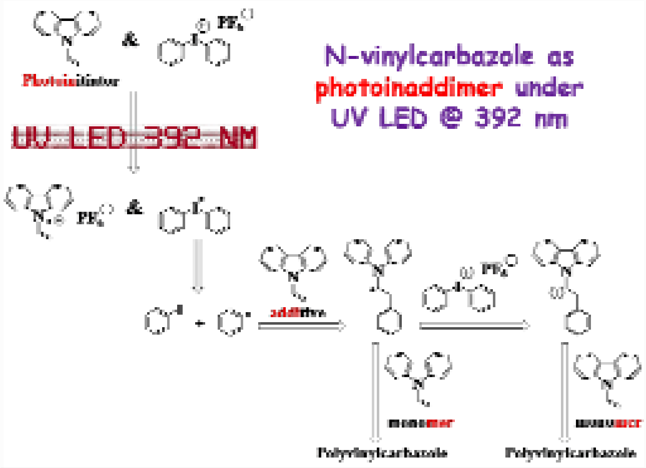
Ultraviolet (UV) light-emitting diode (LED) technology has gained growing interests and acceptance in the photopolymerization field in recent years.[1] Compared to the traditional mercury-based lamps which have been widely utilized in UV curing markets, UV-LED lamps offer many advantages including faster on/off switching, lower energy consumption and operating costs, longer lifetime, lower heat generation (no IR light), improved robustness, and compact design, to name but a few.[1] One of the most significant demands to carry out UV-LED-induced photopolymerization is the use of suitable photoinitiators optimized for the emission wavelengths of UV LEDs (e.g. 385 nm or 395 nm).[2, 3] However, there are fewer choices of photoinitiators for this application in markets and it is still a challenge to design and develop novel photoinitiating systems (PISs) whilst taking costs of the end-user into account.[1] Even though increasing number of newly synthesized photoinitiators have been reported to exhibit excellent photoinitiation ability under various LED irradiations and demonstrated considerable academic value,[4] the preparation of these novel photoinitiators normally require complicated chemical synthesis steps. And the exploitation of existing and commercial chemical compounds for the application as photoinitiators with UV LED irradiation remains an alternative approach.

N-vinylcarbazole (NVK) is a monomer normally used for the synthesis of polyvinylcarbazole (PVK) which finds applications in optoelectronic or photorefractive systems.[5] Interestingly, it has been reported that NVK or PVK can act as photosensitizers for iodonium salts (Iod) to initiate cationic photopolymerization under the irradiation of the mercury arc lamp with 313 nm emission band.[6] However, to the best of our knowledge, no study has been reported on the use of NVK/Iod photoinitiating system (PIS) for various types of photopolymerization reactions upon exposure to UV LEDs with the emission wavelength longer than 380 nm.

In the presentation, *N*-vinylcarbazole (NVK) can act simultaneously as a photoinitiator, an additive and a monomer (photoinaddimer) of photopolymerization upon exposure to the household UV LED bulb (emission wavelength centered at 392 nm). Even though the light absorption spectrum of NVK exhibits weak overlapping with the emission spectrum of the UV LED (392 nm), the active species (i.e. radicals and cations) can be generated from the interaction between NVK and diphenyliodonium hexafluorophosphate (Iod) under irradiation of this LED device, which is investigated by steady state photolysis and electron spin resonance spin-trapping methods. Interestingly, the generated radicals and cations from the NVK/Iod system demonstrate high efficiency to initiate the free radical photopolymerization of (meth)acrylates and the cationic photopolymerization of epoxide and divinyl ether under the UV LED (392 nm) irradiation, and the one-step simultaneous catonic/radical photopolymerization of expoxide/acrylate blend can lead to the formation of tack free polyacrylate/polyetherbased interpenetrated polymer network (IPN) film within 10 minutes even when the polymerization process is exposed to the atmosphere highlighting the high efficiency of the system to reduce the oxygen inhibition effect. More interestingly, NVK/Iod system can also initiate the photopolymerization of NVK under the UV LED (392 nm) irradiation to produce polyvinylcarbazole, and NVK acts as both a photoinitiator and a monomer in the system.



References

1. Cordon C, Miller C. UV-LED: Presented by RadTech-The Association for UV & EB Technology: RadTech International; 2013.
2. Zhang J, Zivic N, Dumur F, Xiao P, Graff B, Fouassier JP, Gigmes D, Lalevée J. UV-violet-blue LED induced polymerizations: Specific photoinitiating systems at 365, 385, 395 and 405 nm. Polymer. **2014**, 55, 6641-8.
3. Zhang J, Sallenave X, Bui T-T, Dumur F, Xiao P, Graff B, Gigmes D, Fouassier JP, Lalevée J. LED-Induced Polymerization (385, 405, and 455 nm) Using Star-Shaped Tris(4-(thiophen-2-yl)phenyl)amine Derivatives as Light-Harvesting Photoinitiators. Macromol Chem Phys. **2015**, 216, 218-27.
4. Xiao P, Zhang J, Dumur F, Tehfe MA, Morlet-Savary F, Graff B, Gigmes D, Fouassier JP, Lalevée J. Visible light sensitive photoinitiating systems: Recent progress in cationic and radical photopolymerization reactions under soft conditions. Prog Polym Sci. **2015**, 41, 32-66.
5. Pina J, Seixas de Melo J, Burrows HD, Monkman AP, Navaratnam S. On the triplet state of poly(N-vinylcarbazole). Chem Phys Lett. **2004**, 400, 441-5.
6. Hua Y, Crivello JV. Development of Polymeric Photosensitizers for Photoinitiated Cationic Polymerization. Macromolecules. **2001**, 34, 2488-94.

Stimuli Responsive Hybrid Materials System based on Controlled Interaction of Polymers and Organic Molecules

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In organic conjugated material system, a rational chemical structure design is inevitable to obtain requested properties in functional applications. Beyond molecular design to regulate intrinsic properties of molecules, design strategies to control interactions and assemblies of organic conjugated materials enables unique optical properties for various applications. In this presentation, interesting polymer and molecular systems which exhibit unique optical property based on controlled interaction between molecules as well as surrounding environment will be introduced to realize stimuli responsive hybrid materials system for sensor and optical applications. First, through insightful design consideration for both intrachain and interchain properties, the optical properties of three different conjugated polymers are sophisticatedly tailored to exhibit identical color in solution manifesting the same intramolecular optical properties by conjugated backbone design. In contrast, the series of conjugated polymers show distinct color gradation in the aggregated state due to the controlled intermolecular packing tendency through side chain design. Utilizing conjugated polymers as security inks, latent optical information encoding is demonstrated that reveals and conceals hidden information upon aggregation/deaggregation of conjugated polymers. Also, a highly selective alcohol and water sensor is devised based on the controlled interaction differences between fluorescent organic molecules and environment including ceramic substrates and analyte solvents. The sensor array can discriminate physicochemically similar liquids such as ethanol, methanol, ethylene glycol, and water. The molecular design principles discussed in this presentation will depict an insightful picture on how optical properties of conjugated organic molecules and polymers can be designed for various applications.

References

1. Chung, K. Design of Organic Materials with Unique Supramolecular Assembly for Optical, Electronic, and Biomedical Applications, *Ph.D. dissertation, University of Michigan, Ann Arbor, US*, **2016**
2. Chung, K., McAllister, A., Bilby, D., Kim, B.-G., Kwon, M. S., Kioupakis, E., Kim, J. Designing interchain and intrachain properties of conjugated polymers for latent optical information encoding, *Chem. Sci.*, **2015**, 6, 6980–6985
3. Chung, K. Yang, D. S., Jung, J., Seo, D., Kwon, M. S., Kim, J., A Novel Mechanism for Chemical Sensing Based on Solvent−Fluorophore−Substrate Interaction: Highly Selective Alcohol and Water Sensor with Large Fluorescence Signal Contrast, *ACS Appl. Mater. Interfaces* **2016**, 8, 28124−28129

CONCURRENT SESSION 9: Translational Research

Polymer Banknotes in Australia – the Past, Present and Future

Greg Dicinoski

Reserve Bank of Australia, Note Issue, Craigieburn, Victoria, Australia, 3064

This presentation will detail the developmental history of the Australian polymer banknote, from the rationale for the change from paper to polymer, the CSIRO development project for the polymer bank note and the transfer of the technology to the Reserve Bank of Australia(RBA). A synopsis of the process required to translate the technology developed by the CSIRO into a production-ready process for the large-scale manufacture of polymer banknotes, a process we refer to as the "banknotisation" of the technology, will be discussed including the challenges faced. We will cover the manufacture of the polymer film along with the printing technology used on banknotes. An important part of this process is the RBA ensuring that the polymer banknotes are fit-for-purpose in circulation, which needs to take into consideration the changing landscape for banknotes. In particular, automated validation, processing and handling of banknotes is far more significant today than when polymer banknotes were first introduced and the RBA needs to ensure that, in addition to providing easily recognised security features for the public, the banknotes also meet the requirements of industry stakeholders.

The polymer material used in Australian banknotes for the past 25-plus years is now not only a security feature in itself, but also a platform technology for the incorporation of sophisticated security features. This presentation will also detail the history and operation of security features used on Australian banknotes dating back to 1988, including the new banknote series that was launched commencing on 1 September 2016. The discussion around security features will highlight the new technology involved in the application of these to the polymer platform. This presentation will conclude with a discussion around future research directions investigating novel security features for later generations of Australian banknotes. As there are many areas in which research is being undertaken, a number of key areas will be highlighted and these include UV lithography, metamaterials and flexible electronics. Some specific examples will be provided in the discussion to highlight these important areas.

Sustained-Release Hydrogel Implants for Glaucoma Therapy

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Glaucoma, a progressive optic neuropathy, is a leading cause of blindness worldwide. The most common treatment involves daily instillation of eye drops designed to reduce intraocular pressure (IOP). However, less than 10 % of the instilled drug reaches aqueous humour and patient compliance to daily administration of drops is poor.1,2 In order to overcome these limitations, recent efforts have been directed to development of new ocular drug delivery systems, such as ocular implants.1,3

Here we present the synthesis, characterisation and application in vivo of biodegradable poly(ethylene glycol)-based hydrogels covalently conjugated to latanoprost free acid (LtpFA), a prostaglandin analogue. LtpFA-hydrogel rod-shaped implants were fabricated in situ by copper-catalysed azide-alkyne cycloaddition (CuAAC) polymerisation between a poly(ethylene glycol) (PEG) 4arm azide cross-linker and a dialkyne monomer bearing a pendant LtpFA drug. Controlled and tuneable release of the prostaglandin analogue is achieved by means of hydrolysis of a degradable link between the drug and the backbone of the hydrogel polymer under physiological conditions.

In vivo studies were conducted in glaucomatous dogs. First, a pharmacokinetic study was performed, identifying intracameral administration as the preferential loci of administration for LtpFA implants. Next, a dose escalation study demonstrated that a daily dose of 220 ng LtpFA achieves a 40 % reduction in mean diurnal intraocular pressure (IOP). Finally, an efficacy study involving LtpFA-releasing implants with various biodegradation chemistries was carried out. Three implants (PA5004, PA5108 and PA5024) were found to lower both IOP similarly to conventional topical Xalatan® treatment (refer Figure 1) and reduced the diurnal IOP fluctuations typically observed with Xalatan® eyedrops. PA5004, PA5108 and PA5024 showed biodegradation rates of 9 weeks, 18 weeks and > 26 weeks, respectively. All implants were well tolerated with no clinical signs of intraocular inflammation.

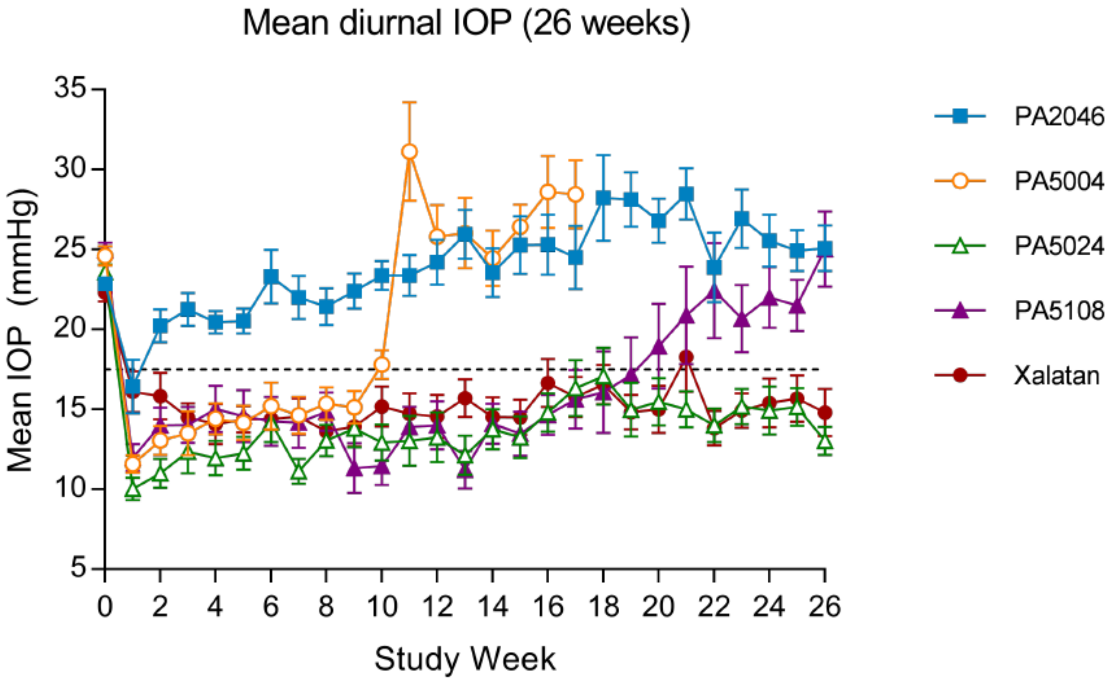


Figure 1. Mean diurnal intraocular pressure (IOP) ± standard error of mean versus time in glaucomatous dogs.

References

1. I. Januleviciene, L. Siaudvytyte, R. Barsauskaite, Ophthalmic Drug Delivery in Glaucoma - A Review, Pharmaceutics, 2012, 4, 243-251.
2. H.H. Chan, T.T. Wong, E. Lamoureux, S. Perera, A Survey on the Preference of Sustained Glaucoma Drug Delivery Systems by Singaporean Chinese Patients: A Comparison Between Subconjunctival, Intracameral, and Punctal Plug Routes, J. Glaucoma, 2015, 24 (7), 485-492.
3. D. Ghate, H.F. Edelhauser, Barriers to Glaucoma Drug Delivery, J. Glaucoma, 2008, 17 (2), 147-156.

StarpharmaDendrimers: Commercial Application

Dr.Filippa Shub

Starpharma(Australia)

Starpharma is an ASX listed biotechnology company with a unique proprietary polymer platform. It has a proven track record of commercialisation and has dendrimer products in various stages of development from preclinical to on market. The company manages risk with diversification across two portfolios, the more mature VivaGel® Portfolio of products, and the early stage DEP® clinical development programs. Starpharma's core programs are focused on the development of high value innovative therapies for diseases with high unmet need, including Oncology (Phase I), Women's Health (Post Phase III and Registered) and Ophthalmology (Pre-clinical). Starpharma has recently divested its Agrochemicals business to Agrium for $35M, demonstrating successful value add in the industrial dendrimers business.

Creating a Carbon Fibre Industry for Australia

Prof. Russell Varley
Carbon Nexus, Deakin University

Carbon Nexus located at Deakin University's Waurn Ponds Campus, is the only open access carbon fibre research facility in the world. It houses an industrial pilot and research scale carbon fibre processing line, a white fibre wet spinning line and extensive composite manufacturing facilities. We conduct research across the entire carbon fibre value chain, from precursor development, synthesis of low cost carbon fibre, to next generation polymer matrices. This talk will briefly introduce the research activities at Carbon Nexus focussing on our research into carbon fibre synthesis and the race towards low cost carbon fibre.

POLYKETONE: High Performance Thermoplastic Polymer

Jun-Hyoung Park

President, Hyosung Corporation, Chemical Performance Group

POLYKETONE Polymers are a new class of revolutionary engineering thermoplastics which is changing people’s perceptions about the future for such materials.

These tough, semi-crystalline polymers were originally made possible as the result of an important catalyst discovery at the Shell Research Laboratories in Amsterdam, whose commercialization could not be continued after 1999.

In 2004, HYOSUNG started the research of new technology to produce this unique polymer at commercial level and succeeded in 2013.

POLYKETONE Polymers have the perfectly alternating structure made of carbon monoxides and alpha olefins such as ethylene. POLYKETONE offers a unique balance of processing and performance properties which, in combination, can satisfy a very broad range of applications. This potential stimulates innovative thinking in product designers, expanding their horizons in an unprecedented way.

By challenging conventional thinking about the use of engineering thermoplastics, POLYKETONE Polymers are capable of turning the unexpected into reality.

The commercialization of aliphatic polyketones, as POLYKETONE Polymers, has been widely acknowledged in the polymer industry as one of the most significant developments since the introduction of polyamides and polycarbonate.

Previously, the global market for engineering thermoplastics consisted of the so-called "Big Five": polyamides, polyesters, polyacetals, polycarbonates and modified polyphenylene oxide. The introduction of POLYKETONE Polymers means that the "Big Five" is set to become the "Big Six”. Because of their enormous potential for new applications, POLYKETONE Polymers are expanding the global market for engineering thermoplastics into new areas.

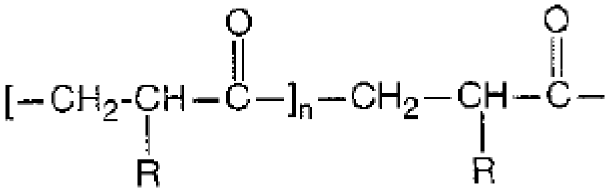
Now, the pilot production facility is operating at capacity of 1,000MT/Year in Yong-yeon, Ulsan, South Korea. The first factory at commercial level of production 50,000MT/Year is currently in operation from July of 2015 at the same site in Korea.

POLYKETONE Polymers are characterized by a carbon-carbon backbone consisting of carbon monoxide and alpha-olefins. Their perfectly alternating structure gives rise to a unique combination of performance properties:

- Short molding cycles and good mold definition
- Low warpage and no need for conditioning
- Superior resilience and snappability
- Very good impact performance over a broad temperature range

- High chemical resistance and barrier performance
- Very good hydrolytic stability
- Good friction and wear characteristics.

These polymers are suitable for injection molding, extrusion, rotational molding and blow molding as well as the production of coatings, films and fibers. In most cases, POLYKETONE Polymers can be processed using standard equipment.



$$[-CH_2-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-]_n-CH_2-\underset{R}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-$$

Where R may represent for example either H or CH_3

<u>Figure. The chemical structure of Polyketone</u>

POLYKETONE Polymer chains are flexible and possess the molecular symmetry and cohesive energy, derived from the perfectly alternating polyketone groups, necessary to produce a tough, high-melting-point, semi-crystalline thermoplastic suitable for a broad range of applications.

In the polymerization process, a second olefinic monomer such as propylene may be randomly substituted with ethylene to produce a terpolymer. The controlled addition of termonomers facilitates the related properties.

The broad chemical resistance exhibited by POLYKETONE Polymers is strongly influenced by their di-polar and semi-crystalline morphology.

POLYKETONE Polymers are widely used in hydrocarbon barrier applications. This is a consequence of their di-polar nature which confers resistance to attack and permeation by aliphatic and aromatic hydrocarbons.

In addition, the symmetry and chain flexibility of POLYKETONE Polymers promote crystallization, which, in turn, promotes resistance to swelling and dissolution in all but the strongest polar environments.

In aqueous environments, POLYKETONE Polymers absorb a limited amount of water which results in mild plasticization, yet their carbon-carbon backbone ensures that they also exhibit good hydrolytic stability.

<u>Consider the Potential of Polymer that</u>

- Combines resistance to many fuels and aggressive chemicals with good barrier properties
- Is stiff, strong and wear resistant, but at the same time demonstrates resilience and snap-ability

- Easily fills complex molds, yet shows little warpage or distortion
- Retains its properties not only in sub-zero temperatures but also in "hot under the hood" type applications

Only one class of thermoplastic offers such a unique combination of performance and processing properties: POLYKETONE Polymers.

-END-

Should I Patent?

Richard Grant

Chemical and Life Sciences Team, Spruson & Ferguson Pty Ltd.

E-mail: richard.grant@spruson.com

This presentation will present various considerations relevant to the decision as to whether to patent an invention. These can be considered under three broad headings:

1) Does the invention represent patentable subject matter? Contentious subject matter areas in this regard include isolated nucleotide sequences, computer related inventions and business methods. Additionally, it is necessary to consider novelty and inventiveness of the invention. These considerations may differ in different patent jurisdictions.

2) Is the ownership of the invention clear? Typically an inventor will *prima facie*own the invention, but an organisation may obtain rights to the invention, commonly by way of an assignment or byway ofa contract of employment (which may be implied or explicit). Difficulties can arise in respect of students at universities and contractors.

3) Is it financially beneficial to patent the invention? Aspects to be considered in this regard are the expected route for monetisation of the invention, the expected revenue from the invention the product lifetime of the invention (including development and commercialisation lead times) and strategic matters. Once again, these considerations may differ in different patent jurisdictions.

Options will be discussed to address situations in which one or more of these considerations present problems.

CONCURRENT SESSION 10: Polymer Fundamentals

Remote Control Polymerization Catalysts

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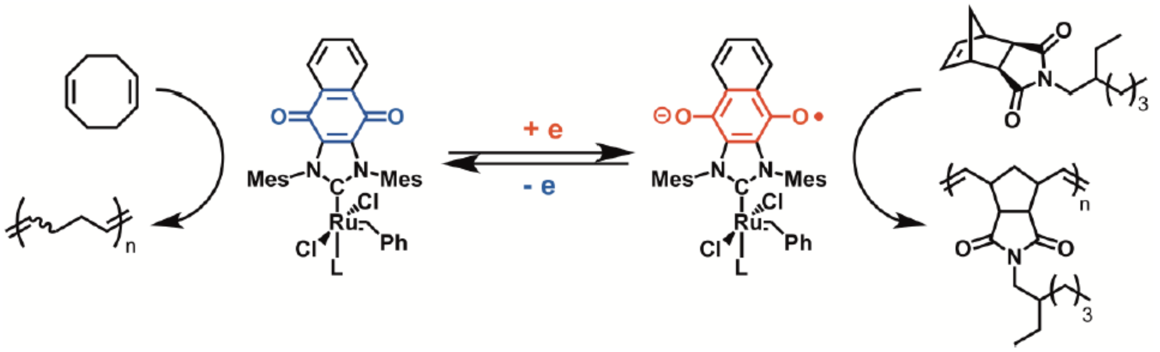
This presentation will describe our recent results on using various types of stimuli, including light and redox chemistry, to control polymerization reactions. Our efforts were rooted in the design and deployment of photo-or redox-switchable N-heterocyclic carbenes (NHCs). Depending on their oxidation state or structure, the NHCs were found to display different spectroscopic signatures as well as chemical reactivities. Such features enabled the “on demand” ring-opening polymerizations (ROPs) of various monomers, which facilitated fine control over the sizes and properties of the resultant polymers. The NHCs were also successfully ligated to a variety of transition metals, including Ru, and used to catalyzering-opening metathesis polymerizations (ROMPs). In some cases, the intrinsic monomer selectivities of certain polymerization catalysts were found to be dependent on the state of the NHC ligand(see Figure below)which enabled access to unique types of copolymers. A series of computational studies revealed how steric and electronic effects separately influence the transition states adopted by each form of the catalyst and provided activation energies that were in good agreement with the relative reaction rate constants that were measured by experiment. The presentation will conclude with some perspectives on using various stimuli to remotely control synthetic macromolecular chemistry.



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References

1. Teator, A. J., Lastovickova, D. N. and Bielawski, C. W. *Chem. Rev.*, **2016**, 116, 1969-1992.
2. Teator, A. J. and Bielawski, C. W. *J. Polym Sci. Part A: Polym. Chem.*, **2017**, in press (DOI: 10.1002/pola.28665).
3. Lastovickova, D. N., Shao, H., Lu, G., Liu, P. and Bielawski, C. W. *Chem. Eur. J.*, **2017**, 23, 5994-6000.
4. Teator, A. J., Shao, H., Lu, G., Liu, P. and Bielawski, C. W. *Organometallics*, **2017**, 36, 490-497.

Cyclodextrin-Mediated RAFT Aqueous Dispersion Polymerization

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Recently, polymerization-induced self-assembly (PISA) has been developed to access block copolymer (BCP)self-assemblies directly in much higher concentrations compared to traditional post-polymerization self-assembly techniques.1-6For aqueous dispersion polymerization, it requires water-soluble monomers that form water-insoluble polymers. Therefore, the technique is not suitable for water-immiscible monomers. We aim to achieve an aqueous dispersion PISA process of water-immiscible monomers using host-guest chemistry. One-step polymerization-induced self-assembly (PISA) by dispersion polymerization of hydrophobic monomers directly in water was studied, based on cyclodextrin(CD)-mediated host-guest complexation. The polymerization is realized by reversible addition-fragmentation chain transfer (RAFT) polymerization of CD/styrene complexes in water with an end-functionalized polyethylene glycol (PEG) as a macro-chain transfer agent(macro-CTA). Through the polymerization, CDs dissociate from polystyrene (PS) blocks because of the hydrophobic interactions between neighboring phenyl moieties. Accordingly, the resulted amphiphilic PEG-*b*-PS diblock copolymers could self-assemble in situ into nanoparticles with various morphologies. By targeting different copolymer compositions, various spheres, worms, nanoplates, ribbons, and nanotubes were obtained controllably. This technique can be easily extended to n-butyl acrylate and potentially to many other hydrophobic monomers. We believe that the CD-mediated aqueous dispersion polymerization of water-immiscible monomers could be a powerful technique for the construction of nanomaterials with different morphology.

References

1. Charleux, B.; Delaittre, G.; Rieger, J.; D'Agosto, F., *Macromolecules* **2012,** *45*, 6753-6765.
2. Sun, J.-T.; Hong, C.-Y.; Pan, C.-Y., *Soft Matter* **2012,** *8*, 7753-7767.
3. Karagoz, B.; Esser, L.; Duong, H. T.; Basuki, J. S.; Boyer, C.; Davis, T. P., *Polymer Chemistry* **2014,** *5*, 350-355.
4. Warren, N. J.; Armes, S. P., *J. Am. Chem. Soc.* **2014,** *136*, 10174-10185.
5. Derry, M. J.; Fielding, L. A.; Armes, S. P., *Prog. Polym. Sci.* **2016,** *52*, 1-18.
6. Huo, M.; Ye, Q.; Che, H.;Wang, X.; Wei, Y.; Yuan, J., *Macromolecules*, **2017**, *50*, 1126-1133.

Controlled Radical Polymerization in Photo-curing toward Unique Graded Nanostructures

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UV-curing process based on photo-induced radical polymerization has been widely utilized for inks, paints, adhesives, and photo-resist materials. Especially, facile tuning of UV intensity, wavelength, irradiation area etc, has enabled their industrial applications, however the precise control of photo-polymerization is not trivial due to their too rapid reaction time (within seconds). Delicate balance of reaction kinetics, deformation (shrinkage), and phase-separation associated to polymer network formation needs to be considered.

Controlled (or living) radical polymerization techniques such as ATRP have greatly impacted the advancement of polymer synthesis in the last 20 years, allowing well-defined polymers with precise molecular weight distribution and segment blocks. Recently, further temporal (on/off) control of polymerization via external stimuli such as photo-excitation has proposed and gained increased attention.[1-3] Here we focus on organo-catalyzed iodine-transfer controlled radical polymerization, which allows reversible photo-activation of polymeric dormant without metal catalysts. In this study, we synthesized polymeric dormant with C-I endgroup and utilized to the UV-curing process to challenge the precise control of photo-polymerization and phase-segregation simultaneously.

Organo-catalyzed iodine-transfer radical polymerization was performed on methyl methacrylate, glycidyl methacrylate (GMA) and other co-monomers, and termination with acrylate monomers to yield the corresponding polymeric dormants with terminal C-I endgroup. Chain extension reactions via thermal and photo-activation proceeded successfully to yield the corresponding block copolymers, which was verified by DOSY-NMR and SEC profiles. The utilization of polymeric dormant to the photo-controlled polymerization of mono-/di-functional acrylates yielded bicontinuous nanodomains with unique graded size distribution. Detailed morphological studies were investigated by AFM and 3D TEM tomography. The evolved nanostructures will be discussed correlated with the photo-curing conditions.

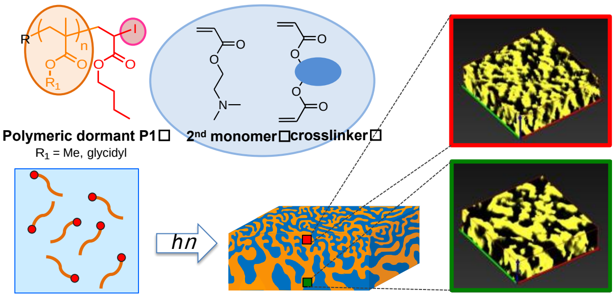

Figure. Controlled Photo-curing from polymeric dormant and nanodomain formation

Acknowledgements

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References

1. C. J. Hawker, et al., J. Am. Chem. Soc., 2014, 136, 16096. [2] A. Goto, et al., J. Am. Chem. Soc., 2013, 135, 11131. [3] G. M. Miyake, et al., Science, 2016, 352, 1082.

Polyethylene Furanoate by Ring-opening Polymerization

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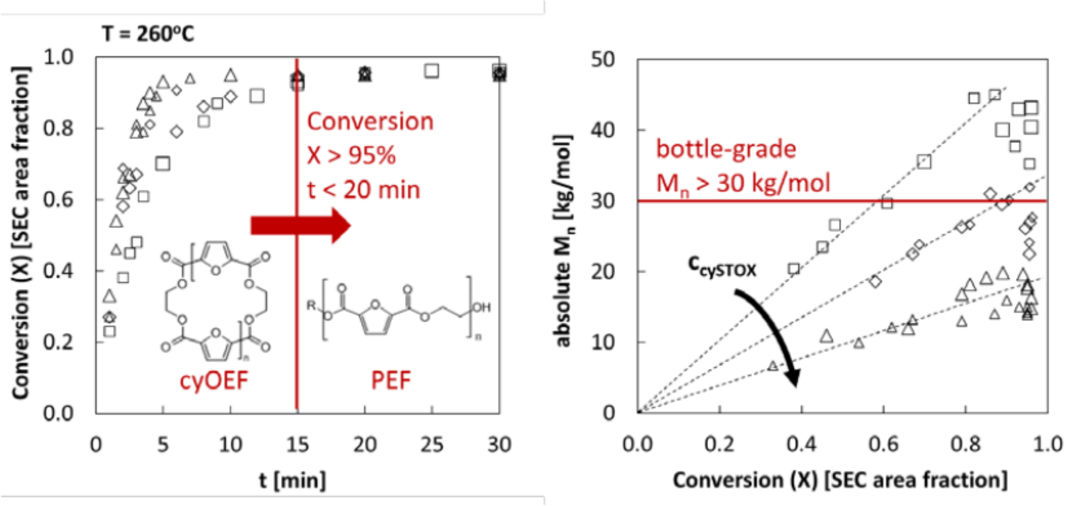
Furanic polyesters like polyethylene furanoate (PEF) have been ranked among the top potential chemicals by the US-DOE and may replace one of the world's dominant fossil-based plastics, polyethylene terephthalate (PET). Recent efforts both in research and industrial production were invariably based on polycondensation (PC-SSP), which is burdened with the necessary removal of condensation byproducts to reach high conversions and molecular weights, and thus typically requires reaction times in the order of days [1]. Cyclic monomers do not have endgroups and thus render byproduct removal unnecessary, which enables ROP as a living chain-growth mechanism to deliver high conversion to PEF within an hour [2,3].

Cyclic PEF monomers (cyOEF) can be derived from 100% renewables-based building blocks furandicarboxylic acid and ethylene glycol via different synthesis routes, which all exploit the favorable shift of the ring-chain-equilibrium to cyclics in dilution [4]. Synthesis pathways such as depolymerization and evaporative cyclization of short PEF oligomers in aromatic solvents have yielded >95% cyOEF, with a ring-size distribution from dimer to heptamer. Maximization of material turnover as well as minimization of waste is possible by full recycling of unconverted linears and solvents. Purification of cyOEF from residual linears via adsorption to yield >99% cycles was found essential for ROP to deliver 1) sufficiently high molecular weights, 2) reproducible reaction control and 3) colorless products.

PEF applicable to typical commercial applications of PET can then be produced from high purity cyOEF. cyOEF were subjected to catalytic ROP to form PEF in yields of >95% and bottle-grade molecular weights (Mw~60'000 g/mol) [5]. The reaction is usually complete after less than 1 h, which, even combined with cyOEF synthesis time of several hours, outperforms commonly applied solid-state polycondensation substantially. The cyclic oligomers exhibit a distribution of ring sizes, where the individual species show melting temperatures ranging from 270 to 370oC and different reactivity. Successful conversion of each observed cyclic species was achieved well below their melting points using 250-280oC with tin-based catalysts such as FDA-approved tin-octoate. Lower temperatures are actually beneficial and allow for higher achievable molecular weights, due to the more limited impact of degrading side-reactions.

The scale-up to larger (kilogram) volumes and processing is currently ongoing, to prove the industrial feasibility of the process and to produce enough material for quality assessment.



References

1. Gomes, M., Gandini, A., Silvestre, A.J.D. and Reis, B., Synthesis and characterization of poly(2,5-furan dicarboxylate)s based on a variety of diols, *J. Polym. Sci. A: Polym. Chem.*, **2011**, 49, 3759-3768.
2. Pfister, D., Storti, G., Tancini, F., Costa, L.I. and Morbidelli, M., Synthesis and Ring-Opening Polymerization of Cyclic Butylene 2,5-Furandicarboxylate, *Macromol. Chem. Phys.*, **2015**, 216, 2141-2146.
3. Costa, L.I., Morbidelli, M., Nising, P. et al., WO2014139602(3) A1, **2013.**
4. Burch, R.R., Lustig, S.R. and Spinu, M., Synthesis of cyclic oligoesters and their rapid polymerization to high molecular weight, *Macromolecules*, **2000**, 33, 5053-5064.
5. Rosenboom, J.G., De Roo, J., Storti, G. and Morbidelli, M., Diffusion (DOSY) 1H NMR as an Alternative Method for Molecular Weight Determination of Poly(ethylene furanoate) (PEF) Polyesters, *Macromol. Chem. Phys.*, **2017**, 218, 160043.

Ziegler Natta Catalyst Activity Improvement in Ethylene Polymerization

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Polyethylene is normally the largest annual worldwide consumption of polyolefins. Accordingly, much attention has been paid on the improvement of Ziegler-Natta catalyst because of its significant effect on the property and microstructure of the polymer. Many types of Ziegler-Natta catalyst based on titanium or vanadium compounds are generally employed in the industrial polymerization. A few reports indicated that the addition of some modifiers, such as ZnCl2, AlCl3, LiCl, MnCl2, and NaCl, into the catalyst system would lead to the increase in the catalyst activity and chemical composition distribution. In our work, the Lewis acids, AlCl3 and BCl3, were particularly selected but not simply mixed in the catalyst system. They were in fact generated in situ from the added organoaluminium halide and BCl3/SiO2, respectively, after the addition of TiCl4. By this technic, the catalyst activity was dramatically increased and higher chemical composition distribution of ethylene α-olefin copolymer was resulted comparing to the normal addition of AlCl3 into the catalyst system. Moreover, not only common co-monomers at higher percentages, but also long-chain α-olefins can be incorporated into the polymer which has never been reported before. In this presentation, the new catalyst preparation method as well as the effect of an in situ-generated Lewis acid on the catalyst behavior and performance will be discussed.

References

1. Sutheerawat Samingprai, Onteera Yenjitrattanawalee, Chaya Chandavasu, High activity olefin polymerization catalyst compromising boron-containing silica support and the preparation thereof, US9096696.
2. Patcharaporn Kaivalchatchawal, Sutheerawat Samingprai, Takeshi Shiono, Piyasan Praserthdam, Bunjerd Jongsomjit, Effect of Ga- and BCl3-modified silica-supported [t-BuNSiMe2(2,7-t-Bu2Flu)]TiMe2/MAO catalyst on ethylene/1-hexene copolymerization, *European Polymer Journal*, **2012**, 48, 1304-1312.
3. Samanukul, N., Tantayanon, S., Samingprai, and Chuencheep, W. “Comonomer Incorporation of Ethylene Polymerization for HDPE Using the Different Preparation Technique of Ziegler-Natta Catalyst”, Pure and Applied Chemistry International Conference 2016 (PACCON 2016), February 9-11, 2016, Bangkok, Thailand.

Tailored Modification of Thioacrylates in a Versatile, Sequence-Defined Procedure for Macromolecular Precision and Multi-Functionalisation

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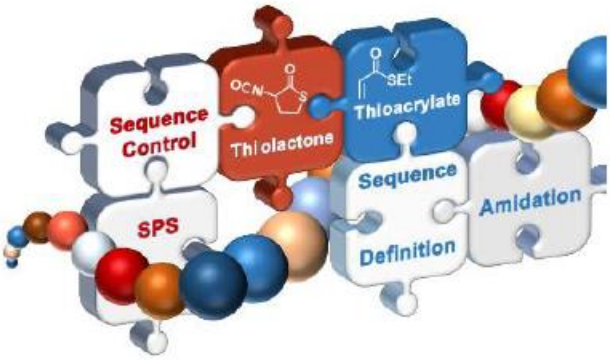

Figure 1: Graphic to illustrate the combination of thiolactone and thioacrylate chemistries in sequence-defined synthesis.

The field of polymer chemistry has grown exponentially in recent decades, yielding macromolecules with unprecedented physical properties and design for far-reaching applications. However, when it comes to complete structural control over the precise, monomeric sequence order, Nature is way ahead.1,2This emerging field of sequence-defined chemistry has led to an evolution in synthetic macromolecules which take inspiration from Nature, resulting in tailor-made, complex architectures, with precise control over the monomeric sequence, which aim to achieve the precise, structural control currently observed in bio-polymers such as DNA.3

This collaborative effort, presented here, exhibits recent significant progress made in the field of sequence-defined chemistry. At Ghent University, we have married together expertise in thiolactone chemistry and iterative techniques to develop new protocols that push the boundaries of precision synthesis and control over macromolecular architectures.3-4 Whilst at Queen Mary University of London, extensive work into the synthesis thioacrylates have proved to be fruitful, resulting in a new class of functional monomers which have been successfully polymerised by RAFT.5

We herein present our latest work, demonstrating a new and versatile, synthetic approach which incorporates thioacrylates together with a thiolactone-based, iterative protocol.6 Through a thiophenol catalysed amidation reaction, we are able to selectively insert functional side groups (primary amines) to the growing oligomer, thus resulting in a multi-functionalised, sequence-defined, monodisperse macromolecule (Figure 2). Careful design of this four-step protocol is such that, within each step, protecting groups are not required, greatly simplifying the synthesis. We aim to demonstrate through this presentation how this emerging area of precision synthesis can now play a crucial role in polymer science and how this can directly influence future advanced polymer applications, such as information storage or biomedical application.

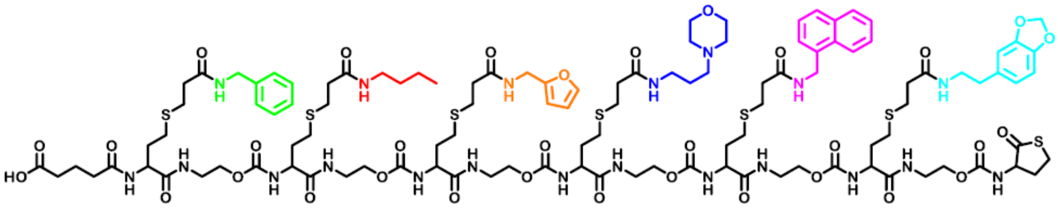

Figure 2: Multi-functional oligomer synthesised by herein reported protocol with thiophenol catalysed side-group insertion.6

References

1. Badi, N. and Lutz, J-F. Sequence control in polymer synthesis, *Chemical Society Reviews*, **2009**, 38, 3383-3390.
2. Espeel, P and Du Prez, F.E. “Click” -Inspired Chemistry in Macromolecular Science: Matching Recent Progress and User Expectations, *Macromolecules*, **2015**, 48, 2-14.
3. Martens, S. Van den Begin, J. Madder, A. Du Prez, F.E. and Espeel, P. Automated Synthesis of Monodisperse Oligomers, Featuring Sequence Control and Tailored Funcationalization, *Journal of the American Chemical Society*, **2016**, 138, 14182-14185.
4. Espeel, P. Carrette, L.L.G. Bury, K. Capenberghs, S. Martins, J.C. Du Prez, F.E. and Madder, A. Multifunctionalized sequence-defined oligomers from a single building block, *Angewandte Chemie International Edition*, **2013**, 52, 13261-13264.
5. Aksakal, S. and Becer, C.R. Poly(thioacrylate)s: Expanding the monomer toolbox of functional polymers, *Polymer Chemistry*, **2016**, 7, 7011-7018.
6. Holloway, J.O. Aksakal, S. Du Prez, F.E. and Becer, C.R. Tailored modification of thioacrylates in a versatile, sequence-defined procedure, *Submitted*.

Preparation of Polymeric Nanoparticles and the development of the topical formulation in the treatment of skin infection

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Now a days the plant derived polymers have evoked tremendous interest due to their diverse pharmaceutical applications such as diluents, binders, disintegrates in the preparation of the tablets, thickeners in oral liquids and they are also used in cosmetics. These polymers are biocompatible, cheap and easily available . Acne is caused by the bacteria *Propionibacterium acnes* live on the skin produces infection. Clindamycin is an antibiotic. It is used to treat infections associated with anaerobic bacteria i.e. acne. The nanoparticles sizes ranging from 500 to 1000nm The biopolymer (Pectin) is extracted from the fruit wastes (Orange and lemon peels) and all the physiochemical evaluations such as organoleptic properties, solubility, pH ,loss on drying, bulk density, flow properties and particle size analysis were done. The isolated pectin posses same property like the marketed sample. Using the pectin the nanoparticles were prepared by controlled gellification method. While preparing these nanoparticle, the drug clindamycin is being incorporated. The drug loaded nanoparticle is subjected to the preliminary evaluation tests such as surface morphology, Zeta potential, particle size analysis, X-ray diffraction studies, drug lading efficiency ,drug release kinetics and stability studies were performed. The prepared nanoparticle was used for the preparation of the topical gel and the in-vitro evaluation studies such as Viscosity ,spread ability studies, swelling index etc. were performed. Finally the microbiological studies were performed in order to asses its anti bacterial activity. Comparing the effect with the markedly available gel, the formulation prepared with the natural polymer as a gel containing the drug loaded polymeric nanoparticles posses more activity than the conventional gel formulation. So it has been concluded that by using the natural biopolymer obtained from the fruit waste, the cost of the formulation is drastically reduced and more over the formulation prepared using the biopolymer extracted from the fruit wastes posses good anti bacterial activity and passes all the in vitro tests.

References

1. Suchada Piriyaprasartha b,Pornsak Sriamornsak,Flocculating and suspending properties of commercial citrus pectin and pectin extracted from pomelo (Citrus maxima) peel ,Carbohydrate Polymer 83 **2011** 561-568
2. Ogaji,Ikoni J. ,Audu Peter,Jennifer D. Advances in Natural Polymers as Pharmaceutical Excipients Pharmaceutica Analytica Acta,3,**2012** ,1-16

3. Castro GA, Ferreira LA,Novel vesicular and particulate drug delivery systems for topical treatment of acne, Expert Opin Drug Deli,.5(6),**2008**, 665-79**.**
4. Amber Vyas, Avinesh Kumar Sonker, and Bina Gidwani Carrier-Based Drug Delivery System for Treatment of Acne Scientific World Journal. **2014**, 276260

CONCURRENT SESSION 11: Fibres, textiles and advanced materials

Nanocelluloses: From Wood to Advanced Materials

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Forest industries are traditionally related to wood products for housing, furnishing or pulp and papers manufacturing, etc. Since the discovery of nanocellulose substrates this picture is being moving toward the development of more advanced materials for more sophisticated applications. Nanocelluloses, including nanofibrillated and nanocrystalline cellulose, are the fundamental constitutive polymeric motifs of macroscopic cellulosic-based fibers. They are the frontrunner for the emergence of the nanotechnology application in the forest sector as they have garnered in the materials community a tremendous level of attention that does not appear to be waning. These biopolymeric assemblies warrant such attention not only because of their inherent renewability, sustainability and abundance but also for their unsurpassed quintessential physical and chemical properties. They have been the subject of a wide array of research efforts as nanomaterial precursors due to their low cost, availability, renewability, light-weight, nanoscale dimension, and unique morphology. Functional advanced materials based on these building blocks, such as foams, hydrogels, films, nanopapers, and scaffolds for medical applications or as fillers for composite materials are emerging. This presentation will summarize on nanocellulose features and properties and provide some key examples for their use as building blocks for advanced nanomaterials.

Textile Innovation and Materials and Design

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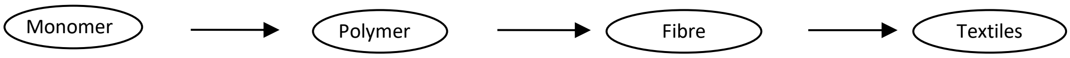
The word “Textile” was originally used to define a woven fabric and it refers to any material made of interlacing fibres or yarns. Each textile is made of fibres and each individual fibre is made of millions of individual long molecular chains of discrete chemical structure (named polymers) which determine the fibre properties. It is important to understand the polymer structure of fibre and, ultimately, how polymer properties influence textile applications. Textile materials are used in everyday life, in the form of sportswear, dresses, protective wear (bullet proof, chemical and heat resistance suits, space suits for instance), accessories, furniture, medical applications (artificial vessels, bandages, disposable sheets and sutures) and transportation materials (flooring, belts and brake linings). Smart fabrics offer a combination of electronic functionality and textile characteristics, necessitating the integration of new materials/polymer and technology into the fabric/fibre to make them smart.



Depending on the applications, the characteristics of synthetic textiles can be controlled chemically by modifying the polymer involved in their synthesis. Incorporating nano molecules and nanotechnology into existing monomers/polymers can give textiles unique properties, such as a material with anti-odour and antibacterial properties, or a fabric that carries a favourite fragrance. These classes of textiles are named ‘technical textiles’, where function is the primary criterion. These materials are most commonly used in agriculture, building, road construction, household applications and medical textiles.

Another class of textiles has the capacity to sense and respond to environmental conditions or chemical, electrical and magnetic stimuli. Named smart textiles, they offer far more than traditional fabrics, including the capacity to communicate, transform, conduct energy and even grow. Interactive or electronic textiles and wearable electronics offer a combination of electronic functionality and textile characteristics. They are composed of conductive polymer/metal yarn or printing conductive ink. Other forms of smart textiles may include a fabric that changes colour in response to heat, a smart shirt able to monitor the wearer’s vital signals, a musical jacket and an adapting temperature jacket.

Recent research has identified a simple approach to creating bended artificial muscle fibre or nanofibre that becomes super-coiled when twisted, with the ability to expand and contract in response to the prevailing conditions. This has many potential applications, including the detection of volatile compounds in the environment or use as a scaffold to support neuron growth or repairs to spinal cord damage.

Important points and properties must be considered before developing new textiles. What special property should the textile possess (eg. performance or protection? Bullet proof or water proof?) Is the new material durable, comfortable and safe to be in contact with the skin? Can the produced textile be easily cleaned and stored?

Finally, the design process for new textile types must take a cross-disciplinary approach, combining science, art, logical reasoning and creative practice.

References

1. Sinclair, R. Textiles and fashion: Materials, Design and technology, Dec **2014**, Edited by Sinclair R., Woodhead Publishing (WP), Cambridge, UK
2. Gate C. Jasbir K. The Textile Book, May **2002**, Berg Publishers, UK
3. Textile technology and Design: from Interior Space to other Space, Jan **2016**, Edited by Schneiderman D. and Winton Alexa G., Bloomsbury Publishing, UK
4. Koncar V. Introduction to smart textiles and their applications, *Smart Textiles and their Applications,* 2016, WP, 1-8.
5. Qin Y. An overview of medical textile products, Medical textile Materials, **2016**, WP, UK, 13-22
6. Gidi A. Lanata A, Valenza G. Scilingo Enzo P. Baragli P, validation of smart textile electrodes for electrocardiogram monitoring in free moving horses, *Journal of Veterinary Behavior: Clinical application and research*, **2017**, 17, 19-23
7. Attia Nour F. Mousa M. Synthesis of smart coating for furniture textile and their flammability and hydrophobic properties, *Progress in Organic Coatings*, **2017**, 110, 204-209.
8. Shishoo R. Introduction to textiles in sport, *Textiles for Sportswear*, **2015**, Edited by Shishoo R., WP, UK, 3-16
9. Yun Young J. Hong Won G. Kim Do Y. Kim Hae J. Jun Y. Lee H. E-textile gas sensors composed of molybdenum disulfide and reduced grapheme oxide for high response and reliability, *Sensors and Actuators B: Chemical*, **2017**, 248, 829-835.
10. Bergmann, J.H.M. McGregor A.H. Body-worn sensor design: what do patients and clinician's want? *Annals of Biomedical Engineering*, 39 (9) (2011), pp. 2299–231
11. Carpi F. Rossi D. De. Electroactive polymer-based devices for e-textiles in biomedicine. *IEEE Transactions of Information Technology in Biomedicine*, 9 (3) (2005), pp. 295–31
12. Montgomery, B. The benefit of textile design research to the textile designer. Duck: *Journal for Research in Textiles and Textile Design,* **2010**, 1.

Spider Silk: From Genome to Super Fibre

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Spider dragline silks are as extensible as rubber, stronger than steel and tougher than Kevlar® depending on species.1 Developing dragline silk–like materials is thus of immense interest, with a plenitude of applications earmarked.2 We know much about the diversity of dragline silk properties across species1-3 but the genetic and biochemical origins of its property diversity are not well known. This knowledge gap hampers attempts to create artificial silks.2 Our cross-disciplinary project provides for a broader understanding of the interactions between genetics, protein expression, protein nanostructures, and fiber mechanics. Significantly, our project forms the framework for the development of synthetic silk-like materials.

References

1. RV Lewis Spider silk: ancient Ideas for new biomaterials. *Chem. Rev*. **2006** 106, 3762-74.
2. F Vollrath, D Porter, C Holland The science of silks. *MRS Bulletin* **2013** 38, 73-80.
3. Blamires SJ, Blackledge TA, Tso IM Physicochemical property variation in spider silk: ecology, evolution, and synthetic production. *Ann Rev Entomol* **2017** 62, 443-460.

A Combined Coagulation-Catalytic Modification Approach to Increase Radial Degree of Stabilisation of Polyacrylonitrile Fibre

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Higher mechanical properties of carbon fibres are achievable by improving radial structural homogeneity of stabilised fibres. Since carbon fibres are produced in two thermal reaction steps, heterogeneous radial conversions in stabilisation and carbonisation steps decreases mechanical properties of fibres [1]. In this study, a combined coagulation-catalyst diffusion approach is applied to enhance radial diffusion of ammonium iron (II) sulphate as the catalyst of stabilisation to increase radial homogeneity of stabilised and mechanical properties of carbonised fibres. Figure 1 shows IR maps of unreacted cyanide groups in stabilised control and chemically treated precursor fibres. AS it is presented in graphs, the maximum unreacted cyanide bonds ratio are 1.264 and 1.119 for control and chemically treated fibres. The reduction approve the catalytic effect of ammonium iron (II) sulphate on conjugation of cyanide bonds.

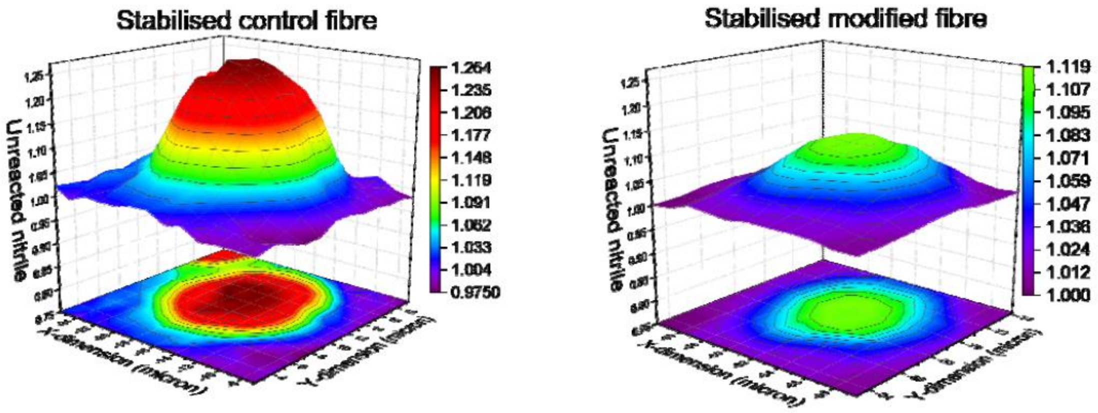

Figure 1: Radial conversion of unreacted nitrile groups

Then by chemical treatment of precursor fibres, the same degree of conversion is achievable at lower stabilisation temperature or less reaction time. Since stabilisation step is the slowest and the most energy consuming part of the manufacturing process, reducing reaction time or temperature saves a notable amount of energy and cost and reduce the final price of carbon fibres.

References

1. Khayyam, H., Naebe, M., Bab-Hadiashar, A., Jamshidi, F., Li, Q., Atkiss, S. and Buckmaster, D., "Stochastic optimization models for energy management in carbonization process of carbon fiber production," *Applied Energy,* **2015**, 158, 13-18
2. Badii, K., Church, J. S., Golkarnarenji, G., Naebe, M., and Khayyam, H., Chemical structure based prediction of PAN and oxidized PAN fiber density through a non-linear mathematical model, *Polyemr Degradation and Stability,* **2016**, 131, 53-61

CONCURRENT SESSION 13: Polymers for medical and biological applications

Polymer Scaffolds for 3D Cell Culture, Tissue Engineering and Regenerative Medicine

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The presentation will discuss some of our work on the development of highly porous polymeric materials as scaffolds for 3D cell culture, tissue engineering and regenerative medicine. The materials are produced by a technique known as emulsion templating, which generates porous polymers (polyHIPEs) with a very well-defined and fully interconnected network of pores in the size range 20-100 microns. Features such as the pore size, degree of interconnection, porosity, mechanical properties and surface chemistry can be varied to produce materials tailored for different applications. Polystyrene-based versions of these materials are produced commercially as scaffolds for 3D cell culture in vitro (tradename Alvetex®).

The main focus of the presentation will concern recent work on the development of degradable materials intended for tissue engineering and regenerative medicine applications. These are produced by light-actived thiol-ene network formation, which, due to the speed of cure, can be adapted to 3D printing (stereolithography) platforms. Recent results from current projects focussed on a range of tissue engineering/regenerative medicine applications, including human pluripotent stem cells, human neural precursor cells, hematopoietic stem cells, osteoblastic cells and endometrial cells, will be presented.

Figure 1 – Left: SEM image of a cross-section of polyHIPE scaffold for tissue engineering; middle: scaffolds labeled with fluorescein *O*-acrylate (FA) illuminated under UV light (from left 0, 1 and 2 mol% FA); right: histology image (H & E staining) of human neural precursor cells grown on a polyHIPE scaffold for 14 days.

References

1. Johnson, D.W., Langford, C.R., Didsbury, M.P., Lipp, B., Przyborski, S.A., Cameron, N.R. “Fully Biodegradable and Biocompatible Emulsion Templated Polymer Scaffolds by Thiol-Acrylate Polymerization of Polycaprolactone Macromonomers”, *Polym. Chem.* **6**,7256 – 7263 **(**2015).
2. Chen, C., Eissa, A.M., Schiller, T.L., Cameron, N.R. “Emulsion-templated Porous Polymers Prepared by Thiol-ene and Thiol-yne Photopolymerisation using Multifunctional Acrylate and Non-acrylate Monomers”, *Polymer*, 2017. DOI: 10.1016/j.polymer.2017.04.021
3. Lee, A, Langford, C.R., Rodriguez-Lorenzo, L.M., Thissen, H., Cameron, N.R. “Bioceramic Nanocomposite Thiol-Acrylate PolyHIPE Scaffolds for Enhanced Osteoblastic Cell Culture in 3D”, *Biomater. Sci.*, 2017, DOI: 10.1039/C7BM00292K.

3D Cell culture systems for materials testing and evaluation

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The conventional approach to cell culture uses 2D surfaces to attach and grow cells on tissue culture polystyrene (TCPS). These systems are used to examine the fundamental biological pathways of disease, evaluate the cytotoxicity of biomaterials, explore biochemical pathways and model wound healing (to name just a few). While these systems are central to much of our current research paradigm, it is well established that they fail to reproduce many of the cell-cell signalling and external cues experienced by cells in tissue.[1] Research over the last 5-10 years has shown that cell behaviour in 2D varies significantly from that in 3D, with variations in a range of properties including cell shape, gene profile and migration behaviour.[2, 3]

Our goal is to develop and validate the materials, sensors and construction principles required for *reproducible, scalable and monitored* 3D in vitro models. Using skin as our exemplar, this talk will focus on the challenge faced by our team in creating model 3D skin systems suitable for evaluating a range of materials and biological interactions including optimisation of tissue scaffold materials, testing of wound dressings and evaluations of treatments for infection. Three toolboxes that are required for the model development will be explored 1) selection of materials, cells and devices; 2) reporting and sensing methods; and 3) validation and verification of the model systems.

References

1. N. Alépée, Altex (2014).
2. M. R. Carvalho, D. Lima, R. L. Reis, V. M. Correlo and J. M. Oliveira, Trends Biotechnol 33 (11), 667-678 (2015).
3. D. W. Hutmacher, B. M. Holzapfel, E. M. De-Juan-Pardo, B. A. Pereira, S. J. Ellem, D. Loessner and G. P. Risbridger, Current Opinion in Biotechnology 35, 127-132 (2015).
4. K. Wrzesinski, M. C. Magnone, L. V. Hansen, M. E. Kruse, T. Bergauer, M. Bobadilla, M. Gubler, J. Mizrahi, K. L. Zhang, C. M. Andreasen, K. E. Joensen, S. M. Andersen, J. B. Olesen, O. B. S. de Muckadell and S. J. Fey, Toxicol Res-Uk 2 (3), 163-172 (2013).

Photocurable Gelatin Hydrogels for Cell Encapsulation

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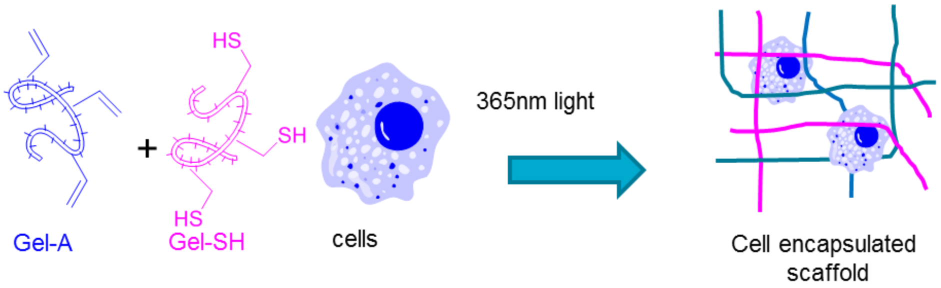
Introduction Tissue engineering requires the implantation of cells along with a supportive scaffold. As such, degradable support scaffolds that are amenable to minimally invasive implantation are attractive. With this in mind, we have explored the use of phototriggered thiol-ene reactions as a method to produce injectable and photocurable cell supportive scaffolds that can be cured in the presence of cells.



Methods Vinyl functionalised gelatines were produced from gelatine and vinyl anhydrides (eg: acrylate and pentanoic anhydride).[1] Light triggered thiol-ene reactions were used to crosslink the vinyl functionalised gelatines with multifunctional thiols included thiolated gelatine. The rheological properties of the precursor formulations as well as the final gels and their cure profiles were measured using photorheology. The effect of solids content, ratio of components and light intensity were investigated. The water content, optical transparency and mechanical properties and microscopic morphologies of the gels were also measured. The ability of bovine corneal endothelial cells (bCECs) and fibroblast cells (L929) to grow on the gels was investigated. Finally *in situ* curing of the gel in the presence of cell was also explored.

Results Thiol-ene crosslinked gelatines were able to be cured within 2min of exposure to 365nm light resulting in optically transparent gels with water contents about 80-85%. The resulting soft gels possessed high viability of both L929 and bCECs (>80%). The mechanical properties of the gels could be tuned by altering the feed ratio of the components and the light intensity used during the cure.

Conclusions Phototriggered thiol-ene reactions are rapid and facile methods of crosslinking gelatines. They resulted in transparent gels with mechanical properties suitable for soft tissue replacements. Moreover, they could be cured in the presence of cell and maintain high viability. The resulting materials are promising candidates for corneal tissue engineering substrates.

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References

1. Li, Lingli, et al., ‘Tissue engineering materials‘, CN104548196A.

Cell-Responsive Hydrogels for Enhanced Tissue Regeneration

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Extracellular matrix (ECM) molecules have the ability to interact specifically with each other to form three-dimensional networks that create supportive microenvironments for cells that are dynamically modulated (degraded and rebuilt) by the same cells during tissue genesis and remodelling. Current hydrogel systems are unable to recapitulate such matrix remodelling characteristics. In this work, we have designed and validated hydrogels capable of retaining specific cell secreted proteins from encapsulated cells during tissue genesis. We have achieved this by creating a polyethylene glycol (PEG)-based hydrogel system of tuneable mechanics that incorporates protein binding peptides (PBPs) that encode specific recruitment of cell-secreted proteins. Our PBPs were firstly synthesized, characterised and their binding affinity to the specific ECM proteins validated using quartz crystal microbalance with dissipation (QCM-D). A norbonene functionalized 8 arm PEG was also synthesized and during crosslinking with 4 arm thiol-functionalised PEGs, the ECM-specific thiol-modified PBPs were incorporated. Immunofluorescence staining was used to investigate the binding of exogenously added proteins throughout the functionalized PEG gels. The ability of these gels to recruit secreted protein from encapsulated mesenchymal stem cells (MSCs) was then investigated. Our results confirm that the gels can be tailored to for a wide range of mechanical properties by varying UV exposure time, monomer and cross-linker concentrations. Furthermore, 2D and 3D assessments of PBPs when presented pendant to PEG chains, in the presence or absence of MSCs, confirmed the ability of these peptides to bind specific ECM proteins with high affinity.

Tailoring Polymer Brush Composition and Function for Directing Stem Cell Behaviors and Tissue Patterning

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Surfaces modified with polymer brushes have a promising future in biointerface design. Coating for implant and scaffolds for tissue engineering have been fabricated using these modified surfaces, exploiting their multivalent nature to present specific biological cues known to enhance cellular adhesion, proliferation and direct cellular differentiation towards specific lineages.[1, 2]

Stem cells play a key role in the development of an organism and, later in life,the maintenance and regeneration of tissues. *In vivo*, stem cell behavior depends on the properties of complex niches that provide an intricate array of biochemical and biophysical signals. Over time, adult stem cells suffer dysfunction in self-renewal and lineage potential. The main hypothesis behind this change of behaviour is the modification of both the local and the systemic factors present in the niches.[3]Gaining further insights into the complex regulation of adult stem cell maintenance is key to understanding the processes of generalized tissue degeneration associated with ageing. Hence, to mimic the complexities of stem cell-niche interactions and facilitate a more rapid transition towards clinical and pharmaceutical applications, polymer brush interfaces would allow the ability to manipulate stem cells *in vitro* by using polymer brush itself or bioactive properties of additionally attached biological cues.[1, 4]

Polymer brushes can be generated *via* controlled surface initiated polymerization, in which an initiator molecule is coupled to the surface where polymer propagates from the initiator molecule, allowing a closer control of the architectural features of the resulting brush. Here, we describe a high throughput method to synthesize surfaces modified by polymer brushes using surface-initiated RAFT polymerization. Through automation, we are able to synthesize arrays of polymer brush surfaces with varying degrees of polymer chain length and functionalities. The high multivalency of these polymer brush surfaces, allows the facile attachment of bioactive materials to influence cellular behaviour and screen a wide variety of factors that could potentially determine stem cell fate in ageing.

References

1. Tsai, HA, Shen, CN, and Chang YC. Use of Surface Properties to Control the Growth and Differentiation of Mouse Fetal Liver Stem/Progenitor Cell Colonies, *Biomacromolecules*, **2012,** 13(11), 3483-3493.
2. Kim, W, and Jung, J. Polymer brush: a promising grafting approach to scaffolds for tissue engineering, *BMB Reports*, **2016**, 49(12), 655-661.

3. Conboy, IM, and Rando, TA. Aging, Stem Cells and Tissue Regeneration: Lessons from Muscle. *Cell Cycle*, **2005**, 4(3), 407-410.
4. Psarra, E, Foster, E, König, U, You, J, Ueda, Y, Eichhorn, KJ, Müller, M, Stamm, M, Revzin, A, and Uhlmann, P. Growth Factor-Bearing Polymer Brushes - Versatile Bioactive Substrates Influencing Cell Response*, Biomacromolecules*, **2015**, 16(11), 3530-3542.

Elucidating Design Criteria for Biocompatibility Through Molecular Dynamics Simulation of Protein Adsorption on Functionalised Surfaces

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Controlling the interaction of biological molecules with surfaces and nanoparticles (NPs) is critical for the development of new nano- and biotechnologies. Interactions between NPs and proteins in particular, can determine the fate of NPs *in vivo*. Poly-(ethylene glycol) (PEG) functionalised NPs have shown both decreased protein adsorption and cellular uptake, with PEG considered the gold standard for the development of biocompatible surfaces. PEG is non-biodegradable and with the risk of accumulation in the body it is desirable to identify biologically compatible alternatives for NP surface functionalisation. Design of biocompatible surfaces requires a detailed understanding of the molecular scale mechanisms of protein adsorption at these interfaces. It is understood that protein/surface interactions are influenced by both surface chemistry and morphology. In addition, the composition of the protein surface is known to influence adsorption behaviour. This molecular dynamics study investigates the interaction of two proteins: ubiquitin and DaaE adhesin, with four different ligand functionalised surfaces of varying hydrophobicity. The relationship between ligand dynamics, surface hydrophilicity and the stability of adsorbed proteins at these surfaces is examined. Furthermore, the study is used to test and extend a previously reported design hypothesis for a low biofouling surface based on maximising interfacial hydration while increasing ligand entropy to create multiple free energy barriers working against protein adsorption (Penna M, Yarovsky I *et al*., Fara. Disc., 2016)

References

Penna, M., et al. (2016). "Surface heterogeneity: a friend or foe of protein adsorption - insights from theoretical simulations." Faraday Discuss **191**: 435-464.

CONCURRENT SESSION 14: Advanced materials

Enhanced Mechanical Performance Induced by Dynamic Crosslinks

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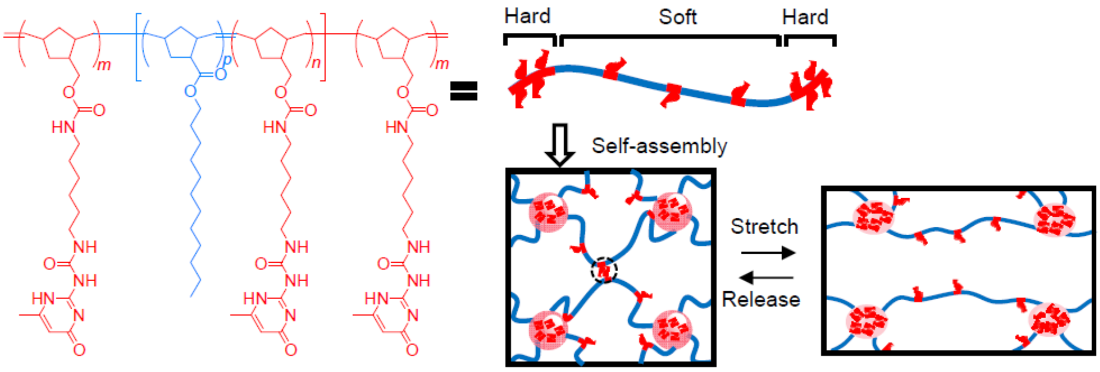
Inspired by the structure of mussel byssus cuticles, a microphase-separated structure with different physical crosslink densities is introduced to elastomers by a carefully designed comonomer sequence distribution of hydrogen bonding units in ABA-type triblock copolymers.1 The A and B blocks are a homopolymer of norbornene functionalized with 2-ureido-4[1H]-pyrimidone [PUN] and a random copolymer of UN and flexible monomer of dodecanyl noeboenene [P(DN-*r*-UN)], respectively. Owing to the quadruple hydrogen bonding between ureidopyrimidone, the A block forms hard domain with dense and robust crosslinks that prevents macroscopic deformation, while the B block forms a softer matrix with sparse and dynamic crosslinks. Under external load, the dynamic crosslinks work as sacrificial bonds to dissipate energy by fracturing themselves, which helps to enhance modulus and tensile strength as well as extensibility of the block copolymers. As a result, they exhibit good toughness (≈62 MJ m−3), which is much higher than those of random copolymers of P(DN-*r*-UN), and homo-blockpolymers of PUN-*b*-PDN-*b*-PUN.

They also exhibits self-healing ability, and most notably, excellent self-recoverability. When PUN-*b*-P(DN-*r*-UN)-*b*-PUN was first loaded to 350% strain and then unloaded, a large hysteresis was observed in the stress strain curve, indicating that many dynamic crosslinks were broken to dissipate energy during loading. When the cyclic tests were repeated soon after the first cycle, the hysteresis area decreased significantly. However, when the cyclic test was repeated after leaving the sample at room temperature for 12 h, the loading curve recovered almost the same level as in the first loading. Even when the polymer was first loaded to 17 MPa stress and 650% strain, which corresponds to the hysteresis > 27 MJ m−3, the loading curve recovered again after a delay of 24 h. To the best of our knowledge, no examples of tough polymers possessing self-recoverability exceeding 10 MJ m-3 have been reported despite recent important progress in the fabrication of tough materials. So, the combination of toughness, self-healing, and self-recovery expands the range of applications of these advanced dynamic materials.



References

1. Shoma Yoshida, Hirotaka Ejima, and Naoko Yoshie. Tough Elastomers with Superior Self-recoverability Induced by Bioinspired Multiphase Design, *Adv. Funct. Mater.*, **2017**, in press (DOI: 10.1002/adfm.201701670).

Engineering Nanocomposite Membranes for Critical Environmental Challenges

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Growing environmental applications in water and gas separation pose new and interesting demands on both material and process design. At the UNESCO Centre for Membrane Science and Technology, our research spans new membrane materials for both water treatment and gas separation. For water and wastewater treatment, some of the major challenges are for separation and treatment of recalcitrant streams such as hypersaline feeds and micropollutants. For gas separation, CO_2 capture as well as hydrogen separation are of particular interest.

We have focused on the effects of blending of 1D, 2D and 3D (framework) materials to enhance membrane performance. Our group has also focused on the synthesis of polymer nanocomposite membranes for gas separation via layer-by-layer coating and in-situ crystallization on porous polymer membrane surfaces. Addition of pre-synthesized ZIF-8, functionalized UiO66, hallyosite nanotubes and graphene oxide into PEO-PA block copolymers can produce thin, nanocomposite membranes with significantly improved CO_2 separation performance. This strategy has also been applied to enhance performance of dense film coatings of membrane distillation/pervaporation membranes for the treatment of hypersaline effluents.

Alternatively thin film ZIF-8 layer can be synthesized as a coherent ultrathin layer onto the polymer membrane surfaces using a facile, rapid, one-pot approach. These pure ZIF membranes were showed unusual flexibility as well as one of the highest H_2 permeances for molecular sieving ZIF-8 membranes. This and other strategies to functionalize surfaces to more effectively grow MOFs on polymer substrates can be potentially exploited to produce high surface area devices for separation and sensing. We are now exploring the potential coupling of MOF-enzyme complexes with membrane separation.

Synthesis of Semiconducting Elastomers Having “Soft” Polythiophene Segments

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π-Conjugated polymers have received much attention as building materials for wearable electronics. Since wearable devices are put on mobile parts, such as human skin and organ, the devices should be durable toward not only flexural strain but also stretching strain.1,2 However, π-conjugated polymers are generally brittle and weak for stretching strain because of their high crystallinity. To address this issue, we have proposed three concepts of “softening” polymer designs based on typical *p*-type semiconducting polythiophene materials as follows: (a) Introduction of flexible trisiloxane pendant chains onto a polythiophene backbone, (b) introduction of an elastomeric segment within the main chain of a polythiophene, forming an ABA triblock copolymer where A and B are head-to-tail regioregular poly(3-hexylthiophene) (P3HT) and polyisobutylene (PIB) segments, respectively, and (c) introduction of a regio-isomeric polythiophene with twisted head-to-head/tail-to-tail regioregularity (HHTT-P3HT) within the main chain of a polythiophene, forming a “regioblock” copolythiophene.

According to the concept (a), the thiophene monomer having trisiloxane units could be polymerized by Kumada Catalyst-Transfer Polymerization (KCTP) to afford well-defined poly(1,1,1,3,3,5,5-heptametyl-5-(6’-(thien-3’’-yl)hexyl)trisiloxane-2”,5”-diyl) (P3SiHT) with low dispersity, which was viscous material with fluidity.3 To the best of our knowledge, it is the first time to obtain a “liquid” polythiophene at room temperature. In addition, we are successful in synthesizing novel all-conjugated hard-soft-hard ABA triblock copolymer, where A and B were P3HT and P3SiHT, respectively, based on KCTP method and sequential monomer addition technique. The formation of phase separated P3HT and P3SiHT domains in the triblock copolymer (P3HT-*b*-P3SiHT-*b*-P3HT) was supported by differential scanning calorimetry (DSC) and grazing-incidence small-angle X-ray scattering (GISAXS). Finally, P3HT-*b*-P3SiHT-*b*-P3HT showed a valanced properties of a high organic thin-film transistor (OTFT) hole mobility (1.06 x 10-2 cm2/V/s) and low tensile modulus (8.35 MPa) at the 5% strain (c.f., ~10-2 cm2/V/s and ~ 1 GPa/5% strain for P3HT).

By the concept (b), the middle segment has been changed from the above P3SiHT to PIB, which possesses an excellent elastomeric property. A thermoplastic elastomer of ABA triblock copolymer, P3HT-*b*-PIB-*b*-P3HT, could be synthesized by the combination of KCTP and living cationic polymerization systems. The synthetic strategy includes three steps: (i) ω-chain-end-functionalization of P3HT with an alkyne moiety, (ii) α,ω-chain-end-functionalization of PIB with azide moieties, and (iii) click reaction between them in the presence of a cupper catalyst. The P3HT-*b*-PIB-*b*-P3HT thin film showed a hierarchical morphology of vertical microphase separation between

P3HT and PIB domains in which typical crystalline packed structures of P3HT was observed with the “edge-on” orientation in the phase-separated P3HT domains by GISAXS and atomic force microscopy (AFM). P3HT-*b*-PIB-*b*-P3HT showed an acceptable OTFT hole mobility (3.00 x 10-3 cm2/V/s) and very low tensile modulus (1.14 MPa) at the 10% strain. Interestingly, a very high elasticity (340%) at break was recorded (see Figure below). This success can be explained by the existence of periodic phase separation between P3HT and PIB domains which might play an important role of less trade-off relationship between charge mobility and elasticity.

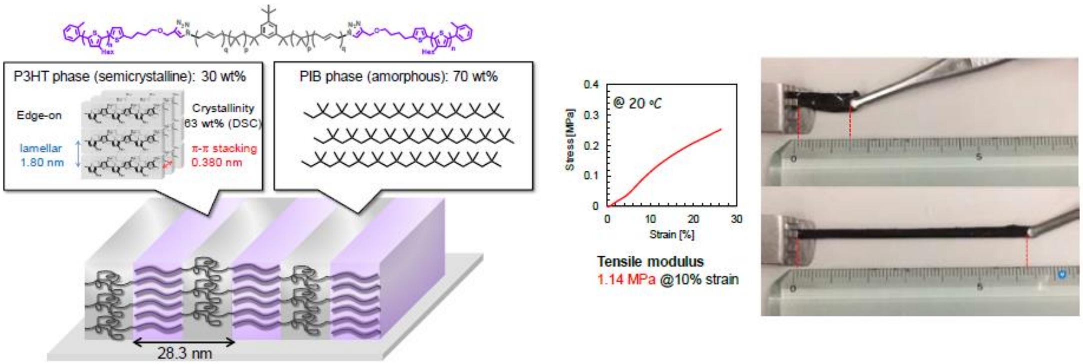

Figure 1. Concept (b). Hierarchical structure of P3HT-*b*-PIB-*b*-P3HT (left) and its mechanical properties (right).

Finally based on the concept (c), HHTT-P3HT having a controlled molecular weight and low dispersity was synthesized by the Negishi Catalyst-Transfer Polycondensation (NCTP) system using *t*Bu2Zn·2LiCl. Furthermore, “regioblock” copolythiophenes consisting of HHTT-P3HT and P3HT segments could be synthesized by NCTP, in which the monomer addition sequence, that is, HHTT-P3HT block (1st) and HT-P3HT block (2nd), could be firstly adopted. The decent yield (54-65%) of regioblock copolythiophene is an advantageous point for the NCTP system, presumably derived from the carefully optimized conditions forming the quasi-living polymer of HHTT-P3HT with a stable chain end, -CNi(dcpe)Br (dcpe = 1,2-bis(dicyclohexylphosphino)ethane), suited for the smooth crossover reaction and polymerization to the 2nd monomer for HT-P3HT. The obtained regioblock copolythiophene showed a phase separation between the crystalline HT-P3HT domains and exclusive amorphous domains, as characterized by GISAXS and AFM. Although the OTFT mobility and mechanical properties are under investigation, the “softening” effect by introducing regio-isomeric segments into a polythiophene was proved by the decreasing melting and crystallization temperatures depending on the composition of HHTT-P3HT segments in the regioblock copolythiophenes.

References

1. Bao, Z. and Chen, X. Flexible and Stretchable Devices, *Adv. Mater.*, **2016**, 28, 4177-4179.
2. Xu, J. et al. Highly Stretchable Polymer Semiconductor Films Through the Nanoconfinement Effect, *Science*, **2017**, 355, 59-64.

3. Miyane, S., Mori, H., Higahsihara, T. Synthesis and Characterization of All-Conjugated Hard-Soft-Hard ABA Triblock Copolythiophenes, *Microsyst. Technol.*, **2016**, 22, 3-10.

An advanced epoxy-based nanocomposite as an adhesive material

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Adhesive bonding has become popular in recent years due to the capability of joining metals, ceramics, polymers, composites etc. This technology is using extensively in many applications such as automotive, aerospace, and electronic engineering due to its low specific weight, low cost, good damping properties, and uniform strength throughout the joint [1]. Epoxy resins are the widely used structural adhesives for joining different components in aerospace and advanced automotive applications due to their excellent adhesion property and corrosion resistance [2]. However, the joint strength of the epoxy adhesive joints is low when contrasted with the mechanical joints. The inadequate strength of the epoxy and poor resistance to crack initiation and propagation are the reasons for the lower joint strength.

Carbon nanomaterials such as Carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) attract a great deal of interest due to their exceptional mechanical, electrical and thermal properties. High stiffness and strength of the carbon nanomaterials makes exceptional reinforcement for developing structural and functional polymer composite materials [3]. Recently, two-dimensional (2D) nanostructures such as GNPs have emerged as favorable fillers for polymer matrices. GNPs are promising reinforcement for polymer composites because of their high aspect ratio, unique planar structure, and low manufacturing cost. This study is focused on development of epoxy adhesive material with enhanced mechanical properties and bonding behavior as joints by incorporating GNPs. Material properties including tensile strength, Young's modulus of pure epoxy and nano-filler reinforced composites are investigated under static loading conditions. Single lap shear strength of pure epoxy and nano-filler reinforced epoxy adhesive joints are examined. The effect of the weight ratios of the GNPS ranging from 0.2, 0.5 and 1 wt.% …..on the material properties are studied. It is found that the tensile strength and Young's modulus of the composite are significantly increased with the addition of nano-filler. To determine the joint performance of the new nanocomposite as an adhesive material, single lap shear tests were conducted using aluminum sheets as substrates. It was observed that the lap shear strength of the adhesive bonded joints increased with the nano-filler content. The study also indicated that increasing the amount of the GNPS beyond a certain weight fraction reduced the shear strength of the joint.

References

1. Banea M, da Silva LF. Adhesively bonded joints in composite materials: an overview. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications. 2009;223(1):1-18.
2. Burkholder GL, Kwon YW, Pollak RD. Effect of carbon nanotube reinforcement on fracture strength of composite adhesive joints. Journal of materials science. 2011;46(10):3370-7.

3. Ma P-C, Siddiqui NA, Marom G, Kim J-K. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. Composites Part A: Applied Science and Manufacturing. 2010;41(10):1345-67.
4. Coleman JN, Khan U, Blau WJ, Gun'ko YK. Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites. Carbon. 2006;44(9):1624-52.
5. Bhattacharya M. Polymer nanocomposites—a comparison between carbon nanotubes, graphene, and clay as nanofillers. Materials. 2016;9(4):262.

High Adhesion and Thermal Performance of Waterborne Polyacrylate Laminating Adhesives Chemically Reinforced With Modified Porous Clay

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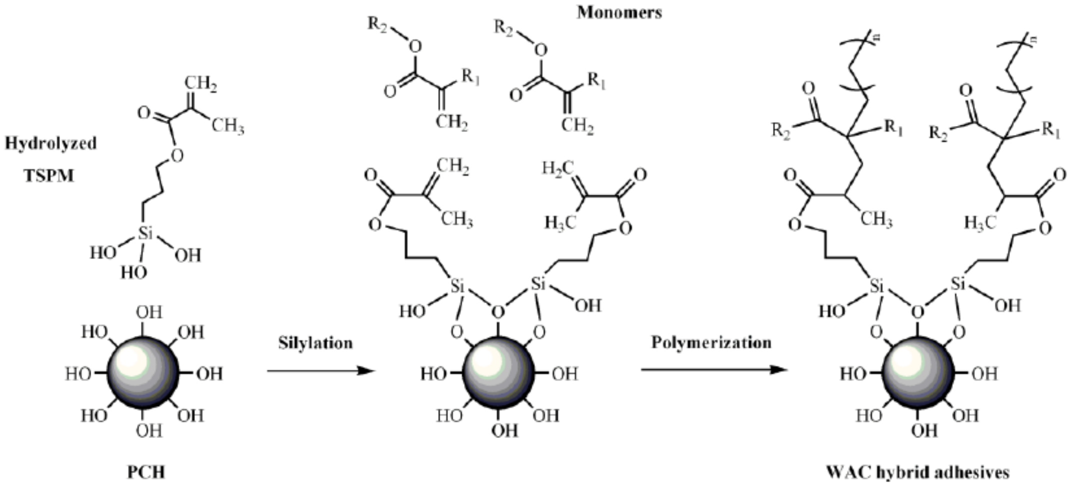
Due to a serious debonding problem and poor thermal properties, a novel water borne polyacrylate (WAC) laminating adhesive based on an organic/inorganic hybrid structure has been developed. A reinforcing material, 3-(trimethoxysilyl)propylmethacrylate (TSPM)-functionalized porous clay heterostructure named as MPCH, was formulated to promote a chemical bonding within the copolymers (2-ethylhexyl acrylate, ethylene glycol methyl ether acrylate, 2-(hydroxyethyl) methacrylate, styrene and acrylic acid) matrix during the batch wise emulsion polymerization process. Fourier-self deconvolution was used to examine internal strength of WAC hybrid laminating adhesive with varying MPCH loading levels. The FE-SEM micrograph revealed the presence of well-dispersed MPCH distributed throughout the polyacrylate matrix. The WAC hybrid laminating adhesive offered excellent thermal properties (low glass transition temperature and high degradation temperature).The optimal adhesive performance, in terms of 180°peel strength of untreated polypropylene/paper laminated joints, of 140.2 N/m was accomplished using 1.5 wt.% of MPCH. Consequently, the WAC hybrid laminating adhesive with free volatile organic compound (VOC) emission has been evaluated for the manufacturing flexible packaging.

References

1. Romo-Uribe, Ángel, Arcos-Casarrubias, JoséAntonio, Hernandez-Vargas, M.Lizbeth, Reyes-Mayer, Adriana, Aguilar-Franco, Manuel and Bagdhachi, Jamil. Acrylate hybrid nanocomposite coatings based on SiO2 nanoparticles by *in-situ* batch emulsion polymerization, *Progress in Organic Coatings*, **2016**, 97, 288-300.
2. Bonnefond, Audrey, Mičušík, Matej, Paulis, María, Leiza, JoséRamonGarmendia, Teixeira, RobertoF.A. and Bon, StefanA.F. Morphology and properties of waterborne adhesives made from hybrid polyacrylic/montmorillonite clay colloidal dispersions showing improved tack and shear resistance, *Colloid and Polymer Science*, **2013**, 291, 167-180.
3. Kango, Sarita, Kalia, Susheel, Celli, Annamaria, Njuguna, James, Habibi, Youssef and Kumar, RajeshKishore. Surface modification of inorganic

nanoparticles for development of organic-inorganic nanocomposites - A review, *Progress in Polymer Science*, **2013**, 38, 1232-1261.



CONCURRENT SESSION 15: Polymers for medical and biological applications

Polymer-diamond composites for medical implants

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Polycaprolactone (PCL) is a readily utilised polymer for additive manufacturing. As biomedicine and 3D printing intersect, PCL is becoming more popular for biomedical applications as it is a FDA approved implantable material with slow *in vivo* chemical breakdown. Diamond on the other hand is an inert biomaterial with extensive properties as a biomaterial. Here we show that we can incorporate fluorescent nanodiamonds into the PCL scaffold to image beneath the skin of a deceased porcine pinna. Further, we show that by adding the nanodiamonds to the polymer we can improve its hydrophobicity producing a superior cell-interfacing material than PCL alone.

Carbohydrate-based Macromolecular Self-assemblies and their Biological Functions

Prof. Guosong Chen
Fudan University (China)

Antiviral macromolecular prodrug carriers

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Worldwide, approximately 71 million people are chronically infected with Hep C (HVC) and 37 million people are infected with HIV.1 Currently there is no vaccine available for both these viral infections and antiviral drugs are administered as the antiviral therapy. Despite the approval of several different inhibitors, therapy is often hampered by rapid elimination of the drugs from the body, high cytotoxicity, and poor uptake by infected cells. In addition, poor adherence of these inhibitors, often as a result of the burden of frequent administration and toxic side effects, can in the case of HIV lead to resistant strains.

This talk will present over 3 years of work performed at CSIRO and in collaboration with the Burnett Institute, Aarhus University Hospital and Aarhus University on antiviral macromolecular prodrugs (MP). Our initial studies looked at the synthesis of a novel library of MPs with a broad-spectrum antiviral agent, ribavirin (RBV) through automated robotic high-throughput synthesis. A library of copolymers via RAFT polymerisation of acrylic acid (AA), methacrylic acid (MAA)2 and 2-hydroxypropyl methacrylamide (HPMA)3 with RBV (meth)acrylate, with differing molar mass and RBV content, were made. A molar mass ‘sweet spot’ was observed in the library of the polyanionic MPs that also revealed a concerted activity of the carrier polymer and the prodrug in inhibition of NO production in macrophages (a marker for HVC induced inflammation). Further efforts focussed on the development of PHPMA copolymers with RBV-methacrylate that showed dual activity in both HIV-antiretroviral and hepatitis models to address co-infection of HIV & HVC.3 The high-throughput synthetic approach also addressed MP copolymer systems of azidothymidine (AZT) methacrylate and HPMA & MAA, that significantly extended duration of activity of the MP as compared to AZT in an HIV-BaL/TZM-bl cell system.4

This work then lead to the design of polymers comprised of lower pKa sulfonate side chains as well as pendent self-immolative linkers that permit glutathione–mediated release of lamivudine (3TC), a reverse transcriptase inhibitor.5 We demonstrate that the polymers can act as (i) an entry inhibitor, (ii) a kinase-independent reverse transcriptase inhibitor mediated by the anionic character of the polymers, as well as (iii) a kinase-dependent reverse transcriptase inhibitor mediated by the release of 3TC.

This work culminated in the design of a combination therapy MP, which have the capability to release two reverse transcriptase inhibitors zidovudine (AZT) and lamivudine (3TC) (Figure 1) from the MP via self-immolative linkers that permit glutathione–mediated release of the inhibitors.6 Controlled release of the prodrugs provided high potency against HIV replication and under certain formulations demonstrate synergistic antiviral effects. The devised polymers are envisioned to provide a longer circulation time and could provide an outcome for patients who are infected with an AZT or a 3TC resistant HIV strain as well as providing a safer and effective antiviral therapy without the need for frequent administration.

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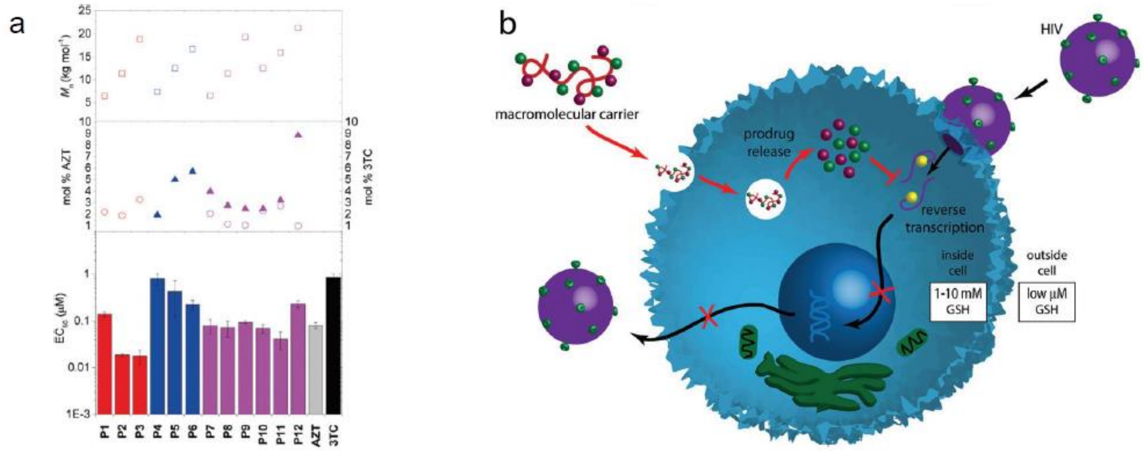

Figure 1: a) Molar mass, AZT and 3TC composition and anti-HIV potency (total prodrug EC50) of the polymers synthesised in this study. Polymers are colour coded according to monomer composition, red: AZT SIL and HPMA (P1-P3); blue: 3TC SIL (P4-P6); magenta: (P7-P12). The open circles indicate AZT SIL contents and closed triangles indicate 3TC SIL contents. The total polymer EC50 values were determined from 3 or 4 independent HIV infectivity assays. b) Illustration showing prodrug release from macromolecular carrier mediated by glutathione (GSH) inside the host cell leading to the inhibition of viral reverse transcription, ultimately causing inhibition of the HIV replication process.

References

1. http://www.who.int/mediacentre/factsheets/fs164/en/ and http://www.who.int/hiv/en/
2. A. A. A. Smith, B. M. Wohl, M. B. L. Kryger, N. Hedemann, C. Guerrero-Sanchez, A. Postma, A. N. Zelikin. Macromolecular Prodrugs of Ribavirin: Concerted Efforts of the Carrier and the Drug, Adv. Healthcare Mater. 2014, 3, 1404.
3. A. A. A. Smith, K. Zuwala, M. B. L. Kryger, B. M. Wohl, C. Guerrero-Sanchez, M. Tolstrup, A. Postma, A. N. Zelikin. Macromolecular prodrugs of ribavirin: towards a treatment for co-infection with HIV and HCV, Chem. Sci. 2015, 6, 264.
4. K. Zuwala, A. A. A. Smith, A. Postma, C. Guerrero-Sanchez, P. Ruiz-Sanchis, J. Melchjorsen, M. Tolstrup, A. N. Zelikin. Polymers Fight HIV: Potent (Pro)Drugs Identified Through Parallel Automated Synthesis, Adv. Healthcare Mater., 2015, 4, 46.

5. M. Danial, A. H. F. Andersen, K. Zuwala, S. Cosson, C. F. Riber, A. A. A. Smith, M. Tolstrup, G. Moad, A. N. Zelikin, A. Postma. Triple Activity of Lamivudine Releasing Sulfonated Polymers against HIV-1, Mol. Pharmaceutics, 2016, 13, 2397.
6. M. Danial, S. Telwatte, D. Tyssen, S. Cosson, G. Tachedjian, G. Moad, A. Postma. Combination anti-HIV therapy via tandem release of prodrugs from macromolecular carriers, Polym. Chem., 2016, 7, 7477.

Ultilization Natural Rubber as a Promising Material for Medical Applications

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In our research, we consider that new rubber consumption including natural rubber (NR) is increasing worldwide. Therefore, it is intended to increase in the production of natural rubber and development of high performance materials from NR instead of synthetic rubber. For instance, the production of car tires from NR is one of the innovative stratergy for the green technology. However, the technical problem in the NR to substitute a synthetic rubber at the present is known to be very difficult. For instance, there is a problem with the manufacturing process to purify natural rubber, because the cost to purify is so high and it has many difficulties to be grown into a widespread technology in a developing country such as Vietnam. Therefore, the key concept of our work will be focused on how to ultilize natural rubber as a promising materials for low carbon emission system. New technology implementation is highly demanded to promote the development of high performance materials based on NR for and low-carbon emission industry.

Keywords: natural rubber, purification, low carbon emision, high performance materials

HPMA-based polymer drug carriers: simplified method of the effective polymer system synthesis

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The copolymers based on *N*-(2-hydroxypropyl)methacrylamide (HPMA) have been and are extensively studied as the polymer carriers of various drugs, especially anticancer agents for several decades.1 The HPMA copolymer conjugate with anticancer drug doxorubicin bound via pH-sensitive hydrazone bond is highly efficient in the tumor treatment and its activity was tested on human patients.2 Due to the novel polymerization techniques, e.g. Reversible addition-fragmentation chain transfer (RAFT) polymerization, well-defined polymers with narrow dispersity (Đ below 1.1) of molecular weight can be obtained. In addition, the development of a simple and effective synthetic method, using an environmentally friendly, reproducible approach as well as an economical process is in great demand in pharmaceutical industry. The scale-up production of HPMA copolymers with low dispersity requires highly reproducible, precise and inexpensive synthesis method. Here, we describe novel synthesis of well-defined linear and star HPMA copolymers in high yields optimized for subsequent scale-up production with minimized consumption of organic solvents and other chemicals. We developed a new procedure for selective deprotection of the tert-butoxycarbonyl (Boc) group for amine and hydrazide groups on HPMA copolymers prepared by controlled radical RAFT copolymerization. Moreover, we have optimized the procedure with the aim to remove the trithiocarbonyl (TTC) polymer end groups during the deprotection of Boc group. We studied the kinetic and efficacy of the deprotection reaction as well as the dependence of deprotection reaction on the structure of polymers (e.g. linear vs. star-like). The synthetic procedure was optimized for conducting in boiling water and compared to previously published methods it requires less reaction steps and purification procedures. Therefore, we believe that the present study enables synthesis of polymer-based drug carriers more efficiently compared to previous methods used up to now and can be widely spread in the synthesis of polymeric drug delivery systems intended for *in vivo* use. Short time and no need for additional purification step after deprotection reaction are two of the highly-valued benefits of this method. We were able to reduce the number of synthetic and purification steps and also significantly reduce the consumption of organic solvents with this new procedure. Also possibility of one pot deprotection and simultaneously TTC polymer end-groups removal predetermine this method for future scale-up optimization and wider use.

References:

1. Kopeček, J. and P. Kopečková. HPMA copolymers: origins, early developments, present, and future. *Adv. Drug Delivery Rev*., 2010. **62**(2): p. 122-149.
2. H. Dozono, S. Yanazume, H. Nakamura, T. Etrych, P. Chytil, K. Ulbrich, J. Fang, T Arimura, T. D, H. Kobayashi, M. Ikoma and H. Maeda, HPMA copolymer-conjugated pirarubicin in multimodal treatment of a patient with stage IV prostate cancer and extensive lung and bone metastases, Targeted Oncology 11 (2016) 101-106

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Photo-Cross-Linkable and Thermo-Sensitive Poloxamer-Based Hydrogel for the Development of Injectable Protein Depot and Sustained Release System

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Thermo-sensitive polymers have attracted increasing interest over the two past decades, particularly in the fields of drug delivery and tissue engineering.1 Due to their inherent thermo-reversible nature, Poloxamers (PEO-PPO-PEO triblock copolymers) have a great potential to serve as an injectable drug depot, particularly, since they have been used widely for clinical use.2 Typically, below room temperature an aqueous poloxamer solution is liquid allowing minimally invasive injection into the desired tissue site, which then instantaneously forms a hydrogel *in situ* at body temperature encapsulating the drug.

However, the resulting hydrogels are typically unstable due to dilution, and thus unsuitable for prolonged release of drugs.3 Here we conducted systematic study of covalently stabilised poloxamer-based hydrogels for the development of sustained release drug delivery system.

Stabilization of poloxamer was achieved by terminal acrylation of the block copolymers, followed by their photomediated cross-linking at their self-assembled hydrogel state. Structure-property-relationships of the gelation are investigated using different poloxamer types (HLBs, e.g. F-127, F-108, F-87, P-105, and P123) and concentration. Small angle X-ray scattering (SAXS) was used to investigate the self-assembled structure of the poloxamer before and after the photo-mediated cross-linking at different temperature. Release kinetic of protein and hydrophobic small molecules from the depot was correlated with the poloxamer type and its cross-linking degree. Facile fabrication of poloxamer-based hydrogels exhibiting higher stability in aqueous environment was demonstrated, which has potential for prolonged delivery of drugs from an injectable depot. The understanding about the poloxamer self-assembled structure and degree of cross-linking provide versatility to tailor different drugs and dosage form.

References:

1. Kamaly, N.; Yameen, B.; Wu, J.; Farokhzad, O. C. *Chemical Reviews*, **2016**, *116*, 2602-2663.
2. Lee, H. Park, T. G. *Journal of Biomedical Materials Research Part A* **2009**, *88*, 797-806.
3. Di Biase, M. de Leonardis, P. Castelletto, V. Hamley, I. W. Derby, B. Tirelli, N. *Soft Matter* **2011**, *7*, 4928-4937.

CONCURRENT SESSION 16: Advanced Materials

Improving Geotextile Properties of Sodium Smectite-polymer Intercalated Nanocomposites.

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Geosynthetic fabrics, incorporating smectite clays are used as liners to contain leachates from landfills and mining ponds. The barrier properties of these liners are significantly improved by incorporating cyclic carbonates into the clay interlayers, enabling the formation of stable intercalated complexes with hydrated Na-smectite, which maintains swollen states. Nanocomposites of sodium smectite with polyether- and polystyrene-containing pendant cyclic carbonates offer a novel approach to improving hydraulic barrier properties of Na-smectite liners to saline leachates. The cyclic carbonate polyethers were prepared by cationic ring opening polymerization of a cyclic carbonate-containing epoxide, whilst polystyrene polymers having pendant cyclic carbonate groups were obtained from radical photopolymerization of styrene. This study showed that Na-smectite nanocomposites of these polymers were able to be formed via clay *in-situ* polymerization and solution intercalation methods. X-ray diffraction (XRD) and FTIR analysis confirmed that the polyether can be intercalated within the layers of smectite via *in-situ* as well as solution intercalation of the pre-formed polymer.

Directing Surface Segregation in Thin Polymeric Films for Lithographic Applications

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Extreme ultraviolet lithography (EUVL) is the most promising next-generation lithography candidate for device manufacturing at the sub-20nm half-pitch node [1]. However, in order for EUV to enter production, several challenges remain to be addressed. For example, out-of-band (OOB) photons emitted by the EUV source along with the desired EUV wavelengths can significantly deteriorate lithographic patterning performance. Conventional EUV photoresists have evolved from materials designed for lithography at 193 nm and 248 nm, whilst the wavelength of out-of-band radiation is generally from 150~400 nm. Hence if OOB light generated from plasma source reaches the wafer plane, and the resist is sensitive to that light, then contrast and LER will be reduced, resulting in degraded imaging performance [2, 3].

Recently, several studies have addressed these problems by developing an OOB protection layer or topcoat (OBPL) [1, 4]. However, the application of a separate OOB protection layer has certain restrictions, for example the topcoat must not mix with the resist, and it must be removable during the development process. Furthermore, the extra processing step for coating of the separate OBPL on the photoresist is not desirable. Therefore, we have developed an embedded topcoat with the ability to absorb out-of-band radiation for EUV lithography photoresists. One of the main characteristics of the topcoat polymer is that it possesses low surface energy. In order to promote the formation of a top-layer via phase separation from the photoresist, the polymer bears surface-active moieties such as fluorinated groups. The introduction of such species as single moieties or as polymeric segments has been investigated in this study. In addition, another important characteristic of the embedded polymer is that it has absorbance across the range of OOB wavelengths. In order to absorb such wavelength photons, the polymeric top-coat includes deep ultraviolet (DUV) absorbers such as benzene, anthracene or naphthalene groups. In addition, the embedded topcoat polymer has a solubility switching unit. In order to ensure that the topcoat can dissolve in the alkaline solution during the development step, the polymer contains solubilizer units, which can improve the solubility and the compatibility of the topcoat polymer in alkaline solution after irradiation.

In this study we describe the design of a surface-active polymer,5 which is able to undergo phase segregation from a photoresist matrix to form a topcoat. The variety of surface agents (fluorinated, hydrocarbon, etc.) and quantity required to provide the most effective phase separation from the photoresist has been investigated. The phase segregation has been confirmed through TOF-SIMS, XPS and AM-FM viscoelastic characterization. Besides, the absorbance of DUV radiation of embedded topcoat was characterized by ellipsometry. Finally, the lithographic performance resist containing the embedded topcoat was evaluated using EBL exposure.

References

1. Fujitani, N., Topcoat solution for outgassing and out-of-band light in extreme-UV lithography. SPIE Newsroom, 2013.
2. Inukai, K., Sharma S., Nakagawa, H., Shimizu, M., Kimura, T., Effects of Out of Band Radiation on EUV Resist Performance. Proc. Of SPIE, 2012. 8322.
3. Roberts, J.M., Bristow, R.L., Younkin, T.R., Fedynyshyn, T.H., Astolfi, D.K., Cabral, A., Sensitivity of EUV resists to out-of-band radiation. Proc. of SPIE, 2009. 7273: 72731W-1.
4. Sakamoto, R., Onishi, R., Fujitani N., Ho, B.C. New Approach for Reducing the Out of Band effect and Outgassing by Applying To Coat Materials. ECS Trans., 2013. 52(1): 259-265.
5. Du, K., Siauw, M., Valade, D., Jasieniak, M., Voelcker, N., Trefonas, P., Thackeray, J., Blakey, I., Whittaker, A.K., 297. Embedded top-coat for reducing the effect out of band radiation in EUV lithography, Proc. of SPIE, 2017, 101460D.

Advanced Functional Polymeric Semiconductor Based Thin Film Transistor Devices for Wide Range of Applications

A/Prof. Prashant Sonar
Queensland University of Technology (Australia)

Macromolecular Materials for Sensing

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Conjugated polymers are of great interest due to their wide applicability in the next generation of optoelectronic devices, such as LEDs and sensors. In this seminar, the preparation, photophysical characterization and sensing of a series of highly luminescent poly(fluorene-alt-phenylene)s (PFP) were studied. These PFP polymers varied the phenylene linkage in the 1,4 (PFP-p), 1,3 (PFP-m) and 1,2 (PFP-o) positions. The photoluminescence of these polymers ranged from ultraviolet to blue in colour in both solution and film states by simply varying the linkage of the phenylene moiety. Stern-Volmer quenching studies revealed that these poly(fluorene-alt-phenylene) polymers are highly sensitive towards nitroaromatic materials, particularly in comparison to the reference poly(9,9-di-n-hexylflourene) (PDHF) in solution. The solid-state fluorescence quenching of the PFP-p and PFP-m films using various analytes was analysed and related to the reference PDHF. The differences observed are attributed to both thermodynamic and diffusion kinetic factors.

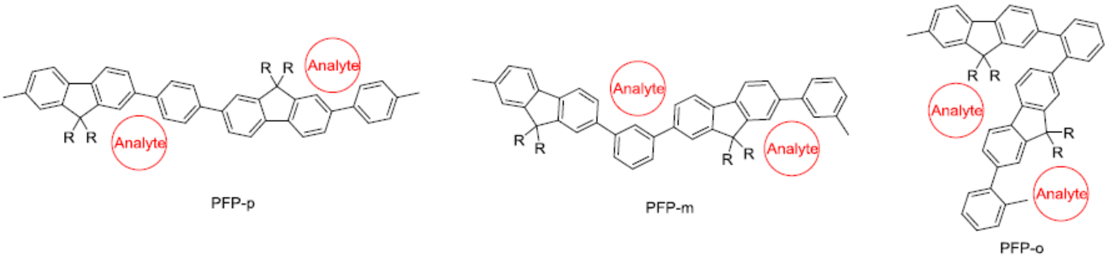

Figure 1: Two-dimensional view of PFP mimics using two repeat units with potential voids where analytes (scaled to a nitroaromatic) could occupy.

Porous PDMS/Carbon Nanofiber Composites for Stretchable Strain Sensors

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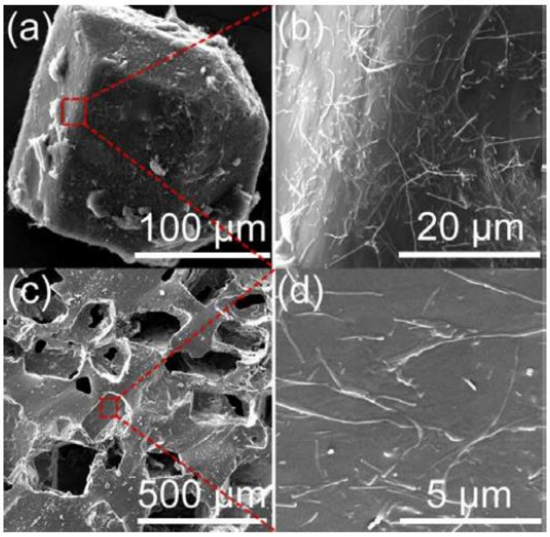
Pressure/strain sensors with flexible, stretchable, and wearable features have recently attracted tremendous attention and shown great potential applications in human-friendly interactive devices, electronic skin, human health monitoring, and sport performance monitoring.1 Flexible and stretchable sensors capable of high strain are one of the key components of wearable electronics since the movement of human joints can generate strains as high as 55% unpon stretching and contracting.2 However, conventional metallic strain gauges can only detect up to ~ 5% strain with low sensitivity (gauge factor is typically 2). Recently, nano-structured materials made of metal nanoparticles, nanowires, carbon nanotubes, graphene have received strong interest as the conductive building blocks for innovative strain sensors with high sensitivity and high stretchability.3 To achieve high electrical conductivity and stretchability, conductive nanomaterials are usually incorporated into elastic polymers. However, poor dispersion of nanomaterials in polymers and the relatively low electric conductivity largely limits their applications.4 By proper structural design, three dimensional (3D) conductive networks can be introduced into polymers to obtain sufficiently high electrical conductivity and stretchability needed for wearable sensors.3, 5

In this study, we report a new and facile method to fabricate stretchable porous conductive polydimethylsiloxane/carbon nanofiber composites (denoted by p-PDMS/CNFs) for the application as strain/pressure sensors. Sugar particles coated with CNFs (**Figs. 1a-b**) are used as pore-creating agent. After curing PDMS and removing sugar particles, porous PDMS composites with CNFs are prepared (**Figs. 1c-d**). The CNFs originally on the surfaces of sugar particles are embedded in PDMS pore walls, forming 3D conductive networks, resulting in high electrical conductivity (0.033 S/m). The CNFs are supported by the polymer, leading to excellent durability. The resulting 3D porous structure exhibits much improved stretchability compared with their solid counterparts. Under quasi-static loading, the electrical resistance increases with tensile strain and decreases under compression (**Figs. 2a-b**). **Figs. 2c-d** show the resistance changes over six cycles with varying levels of peak strain ranging from 10% to 50%. The ΔR/R0 increases upon stretching and gradually decreases during unloading. A complete opposite trend is observed under compression. Moreover, the sensors can nearly recover its resistance after unloading. The stretching deformation widens the inter-CNFs distance, thus increasing the tunneling resistance and contact resistance. In contrast, under compressive strain, the opposite occurs: electrical resistance decreases with compressive strain. The high sensitivity and reliable sensing performance endow these highly stretchable nanocomposites with a great potential as flexible sensors for wearable electronics.



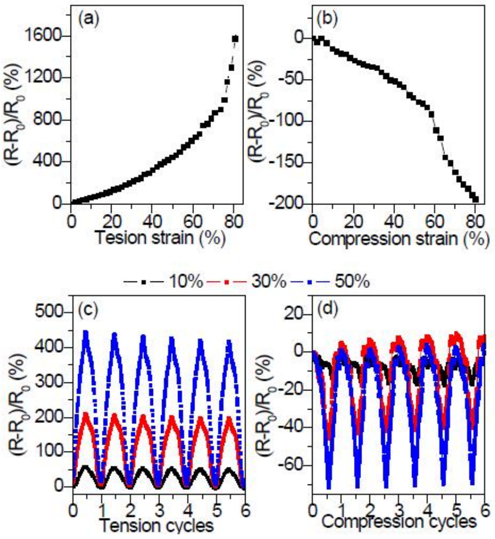


Fig. 1. SEM images of (a) and (b) a sugar particle coated with CNFs; (c) and (d) porous p-PDMS-CNFs.

Fig. 2. Piezoresistivity of p-PDMS/CNFs: normalized resistance change under (a) static and (c) cyclic tension; normalized resistance change under (b) static and (d) cyclic compression.

References

1. Y. Pang; H. Tian; L. Tao; Y. Li; X. Wang; N. Deng; Y. Yang; T.-L. Ren, *ACS Applied Materials & Interfaces*, **2016**, 8(40), 26458–26462.
2. Yan, C. Y.; Wang, J. X.; Kang, W. B.; Cui, M. Q.; Wang, X.; Foo, C. Y.; Chee, K. J.; Lee, P. S. *Advanced Materials* **2014,** *26* (13), 2022-2027.
3. Wu, S.; Ladani, R. B.; Zhang, J.; Ghorbani, K.; Zhang, X.; Mouritz, A. P.; Kinloch, A. J.; Wang, C. H. *ACS Applied Materials & Interfaces* **2016,** *8* (37), 24853-24861.
4. Li, Y. Q.; Samad, Y. A.; Polychronopoulou, K.; Alhassan, S. M.; Liao, K.. *Scientific Reports* **2014,** *4*, 6.
5. Samad, Y. A.; Li, Y.; Schiffer, A.; Alhassan, S. M.; Liao, K. *Small* **2015,** *11* (20), 2380-2385.

Poly(*N*-Isopropylacrylamide) Capped Plasmonic Nanoparticles as Resonance Intensity-Based Temperature Sensors With Linear Correlation

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Thermosensitive polymer capped plasmonic nanoparticles are novel thermal nanofluids with potential sensing applications. Previous research efforts have been focused only on monitoring plasmonic resonance peak shifts as temperature varied; however, to date, no linear relationship between the resonance peak shift and temperature has been established. Here, we systematically investigate how plasmonic resonance peak intensity responds to solution temperature using poly(Nisopropylacrylamide)-capped gold nanorods (AuNRs) and nanobipyramids (AuNBPs) under aggregation free conditions and our results clearly reveal the linear correlation between longitudinal resonance peak intensity and solution temperature for both AuNRs and AuNBPs. AuNBPs have sharper ends than AuNRs, resulting in greater thermo-sensitivity due to the presence of stronger 'hot spots'. Further analytical and numerical studies demonstrate chemical interface damping effects by surfacecapping ligand configurational changes and these theoretical results agree well with our experimental observations. In addition, our damping based sensing is reversible with excellent durability, indicating the possibility of potential real-world temperature sensing applications.

References

1. Liu, Y.; Dai, X.; Mallawaarachchi, S.; Hapuarachchi, H.; Shi, Q.; Dong, D.; Thang, S.; Premaratne, M. and Cheng, W. Poly(*N*-isopropylacrylamide) capped plasmonic nanoparticles as resonance intensity-based temperature sensors with linear correlation, *Journal of Materials Chemistry C*, **2017**, DOI: 10.1039/c7tc04051b

CONCURRENT SESSION 17: Responsive Polymers

The Thiol-Thioester Exchange in Network and Linear Polymers

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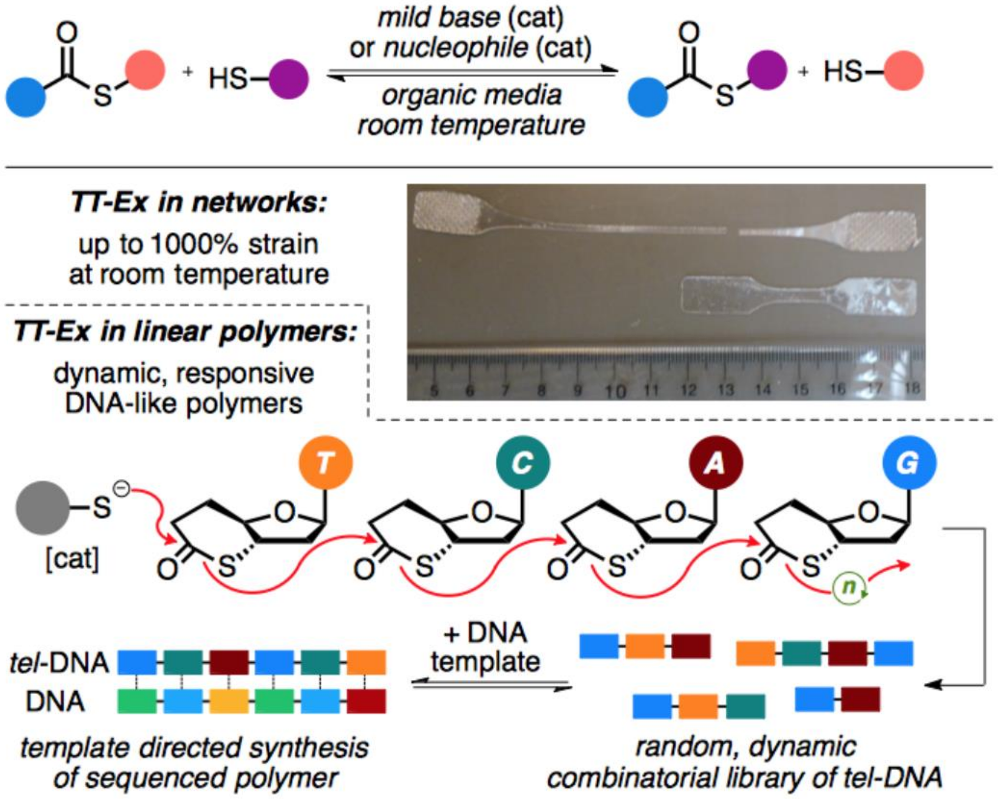
Dynamic bonds are covalent linkages which, if given specific stimuli, can form an equilibrium between exchanging reactants and their products. Recent work by our lab has developed dynamic functional groups which can be seemlessly incorporated into network or linear polymers and harnesses the supurb reactivity and chemoselectivity of thiyl radicals and thiolate anions. These dynamic functionalities act as crosslinks in network polymers or in the backbone of linear polymers and are easily adapted to various stimuli including light, heat, or chemical. Here we show recent developments towards the formation of dynamic liquid crystalline networks and thioester-based networks both responsive towards light in order to develop shape shifting and remoldable photopolymers. Additionally, we demonstrate a sequence shifting, dynamic thioester-linked DNA-like polymer by implementing a covalently exchangeable thioester backbone. We believe that the broad implementation of this chemistry demonstrates the breadth of this approach towards the formation of smart, responsive polymers.



Stimuli-responsive Polymers in Membranes and Solutions

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Stimuli-responsive polymers are a promising class of materials for switchable devices. In this presentation the use of stimuli-responssive polymers as pore forming block in isoporous membranes will be discussed, where the effective pore size can be tuned by pH value and temperature.[1] Furthermore results on (meth)acrylic homo- and copolymers will be presented which display a more complex stimuli-responsive behaviour. Aqueous solutions of narrowly distributed poly[2-(*N*-morpholino)ethyl methacrylate] (PMEMA) will be discussed. The polymer shows a peculiar three-step aggregation behavior upon heating; an effect which has hitherto barely been reported for other polymers. The phenomenon is discussed in terms of mesoglobule formation (1st step) as well as by an unusual distinct disruption of hydrophobic hydration (2nd step) and hydrogen bonding to the hydrophilic aggregate surface (3rd step), which leads to precipitation. Furthermore, the influence of different anions (salting-out (kosmotropic) and salting-in (chaotropic) along the Hofmeister series) on the solubility properties is presented.[2] Also the solution and bulk structures of block copolymers of PMEMA with polystyrene will be discussed. [3]

Finally poly[*N*-acryloylpiperidine-*random*-*N*-acryloylpyrrolidine] (poly[APi-*r*-APy]) as a novel thermoresponsive copolymer will be introduced. One of its attractive features is that the lower critical solution temperature (LCST) in aqueous solution can be easily adjusted between almost 0°C to approx. 50°C. A second ‘good’ solvent influences the thermoresponsiveness of the system as will be shown on solvent mixtures of water with different alcohols. The chemical structure of the alcohols was systematically varied, leading to either upwards or downwards shifts of the cloud point. The results are discussed in terms of polymer–additive as well as additive–water interactions and help to gain a more detailed understanding of water interactions with amphiphilic additives and, hence, of cononsolvency phenomena.[4]

References:

1. J. I. Clodt, V. Filiz, S. Rangou, K. Buhr, C. Abetz, D. Höche, J. Hahn, A. Jung, V. Abetz, *Adv. Funct. Mater.* **2013**, *23*, 731-738.
2. S. Eggers, B. Fischer, V. Abetz, *Macromol. Chem. Phys.* **2016**, *217*, 735-747.
3. S. Eggers, F. Lauterbach, V. Abetz, *Polymer* **2016**, *107*, 357-367.
4. N. Lucht, S. Eggers, V. Abetz, *Polym. Chem.* **2017**,DOI: 10.1039/C6PY01751G

Specific Ion Effects on Thermoresponsive Polymer Brushes

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Specific ion effectsplay an important role in determining theconformationofbrushes of thethermoresponsive polymerpoly(N isopropylacrylamide) (PNIPAM).[1] Increasing concentrations of the kosmotropic acetate anion lower the lower critical solution temperature (LSCT), while chaotropic thiocyanate anions increase the LCST.Neutron reflectivity, ellipsometry, quartz crystal mircobalanceand atomic force microscopy measurements demonstrate these effects impact the physicochemical properties of the brush beyond a simple modulation of the temperature response to higher/lower temperatures.[2]Polymer density profiles normal to the interface produced from neutron reflectivity data demonstratedirect evidence of a vertical phase separation within the brush at temperatures around the LCST. Furthermore, the presence of thiocyanate ions broadened the LCST transition which is attributed to an electrosteric stabilisation mechanism.Atomic force microscopy measurements indicatethe acetate ions render the brush more resistant to compression by a colloidal probe.

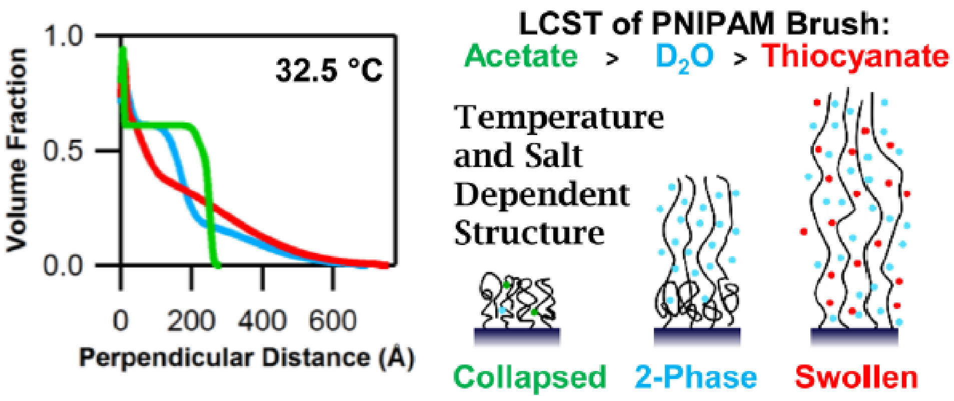

Figure 1: Poly(N isopropylacrylamide)brush volume fraction profilesderived from neutron reflectivity data in the absence and presence of added salt, andschematic representations of the possible brush morphologies.[2]

Here we also discuss specific ion effects on the conformation of brushes of poly(2-2-(methoxyethoxy)ethyl methacrylate)(PMEO2MA)and copolymers with poly(oligo(ethylene glycol) methacrylate)(POEGMA). These brushes show a much broader temperature response than PNIPAM and a greater influence of anion identity.[3]The brush volume fraction profiles derived from neutron reflectivity data show no evidence of internal phase separation, rather a smooth transition from an extended conformation (low temperature) to a block-like structure (high temperature) is observed. The presenceof acetate or thiocyanate ionshad a similar effect on the LCST of a PMEO2MA brush as for a PNIPAM brush, however the magnitudeof the shift in LCST is much greater for the PMEO2MA brush.Finally, we demonstrate the stability and bulk behaviour of suspensions of brush-modified colloidal silica particles can be finely controlled by temperature and anion identity.

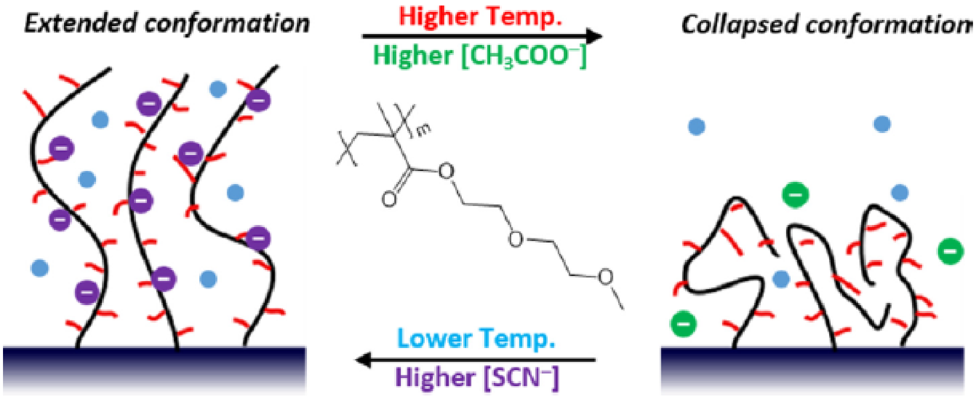

Figure 2: Conformations of a PMEO2MA brush in the presence of added electrolyte at low and high temperature.[3]

References

1. Ben A. Humphreys, Joshua D. Willott, Tim J. Murdoch, Grant B. Webber, Erica J. Wanless. Specific ion modulated thermoresponse of poly(N-isopropylacrylamide) brushes, *Physical Chemistry Chemical Physics*, **2016**, 18, 6037-6046.
2. Tim J. Murdoch, Ben A. Humphreys, Joshua D. Willott, Kasimir P. Gregory, Stuart W. Prescott, Andrew Nelson, Erica J. Wanless, Grant B. Webber. Specific Anion Effects on the Internal Structure of a Poly(N-isopropylacrylamide) Brush, *Macromolecules*, **2016**, 49, 6050-6060.
3. Timothy J. Murdoch, Ben A. Humphreys, Joshua D. Willott, Stuart W. Prescott, Andrew Nelson, Grant B. Webber, Erica J. Wanless. Enhanced specific ion effects in ethylene glycol-based thermoresponsive polymer brushes, *Journal of Colloid and Interface Science*, **2017**, 490, 869-878.

Modular Synthesis of Photodegradable Hydrogels Responsive to Long Wavelength Ultraviolet and Blue Light

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Polymeric hydrogels have been utilized for encapsulation of bioactive components to both prevent degradation and allow controlled release until a stimulus triggers a change in the hydrogel network structure. Among the various triggers possible for hydrogel degradation, light stimulation is highly attractive because it can be achieved remotely with excellent spatial and temporal precision.1,2 Current photodegradablehydrogel platform mostly utilizes the photo-cleavage of ortho-nitrobenzyl or coumarin derivatives that absorb light in the 320-410 nm region, restricting the degradation triggered by UV light.3In addition, the syntheses of such photo-labile compounds follow multi-step procedures with generally low total yield. In this work, we present a facile approach to the synthesis of a library of photolabile linkers responsive to a broad spectrum of cytocompatible wavelength (365-530 nm)of light. The utility of these linkers in the preparation of photodegradable hydrogels for selective encapsulation and release of living cellsis demonstrated.

References

1. Kloxin, A. M.; Kasko, A. M.; Salinas, C. N.; Anseth, K. S. Photodegradable Hydrogels for Dynamic Tuning of Physical and Chemical Properties. *Science* **2009**, 324, 59.
2. Truong, V. X.; Tsang, K. M.; Simon, G. P.; Boyd, R. L.; Evans, R. A.; Thissen, H.; Forsythe, J. S., Photodegradable Gelatin-Based Hydrogels Prepared by Bioorthogonal Click Chemistry for Cell Encapsulation and Release. *Biomacromolecules* **2015**, 16, 2246.
3. Zhu, C.; Ninh, C.; Bettinger, C. J., Photoreconfigurable Polymers for Biomedical Applications: Chemistry and Macromolecular Engineering. *Biomacromolecules* **2014**, 15, 3474.

CONCURRENT SESSION 18: Metal Organic Frameworks

Recent Adventures with Porous Materials: Triggered Release and Anti-aging Membranes

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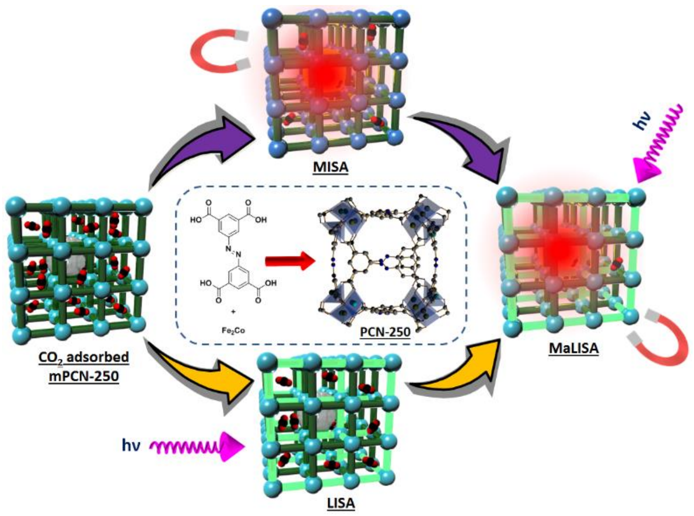

Abstract: Metal Organic Frameworks (MOFs) show unprecedented capacity to store small molecules, however, the proposed methods to release these molecules are not yet feasible at a meaningful scale, largely due to the strong binding of stored molecules and the thermally insulating nature of the adsorbent. For example, carbon capture (and release and subsequent storage) from coal-fired power plants has been estimated to require between 25 and 40% of the energy output of the power plant though a more recent estimate was even higher. Whilst desorption from insulators such as zeolites has been overcome by the passing of hot gas through the bed, this is at an efficiency cost, and lowers the versatility of use. This problem is even more acute given the potential platform applications of MOFs where large flows of hot gas are often not at all possible. This presentation will describe the incorporation of metal nanoparticles within MOFs and the use of magnetic induction heating to release a series of stored molecules with unprecedented efficiency, known as magnetic induction swing adsorption (MISA). Magnetic induction is the most energy efficient means of heating, hence its widespread usage in domestic cooking. Its use within Metal Organic Frameworks, where we have been able to show they act as ‘nanoheaters’, overcomes the inherently thermally insulating nature and we have been able to release 100% of stored molecules. Further research has shown combination with light responsive moieties further increases the energy efficiency (MaLISA), and recently ther energy efficiency record was broken with these materials.

Aging in super-glassy polymers such as poly(trimethylsilylpropyne) (PTMSP) prohibits it from being used in polymer membranes for separating gas mixtures. While these polymers are initially very porous and large amounts of gas can selectively pass through them, they quickly pack into a denser phase becoming much less porous and permeable. This age-old problem has been solved by the use of an ultraporous

additive that allows PTMSP to maintain its low-density, porous initial state by absorbing a portion of the polymer chains within its pores, and holding them in position. This is the first time that this aging process has been stopped in PTMSP without diminishing its properties when prepared as a gas separation membrane. In fact, the membrane properties are enhanced with an additive, and over approximately one year of long-term measurements show that the performance is maintained.

The addition of a very specific porous microparticle forms an interwoven nanocomposite with PTMSP, freezing the structure and hence stopping the aging process, but doing so whilst increasing the permeability and maintaining the selectivity. Porous Aromatic Frameworks (PAFs) are carbon-based structures formed by the self-condensation of tetrahedral monomer nodes to establish an ultraporous array. The regular nanopores of around 1.2 nm diameter are attractive for the intercalation of polymer side-chain components when incorporated within the PTMSP matrix, thereby freezing the as-cast lower-density polymer structure in place and stopping the aging process. This mechanism is distinct from the enhanced permeability effect of non-porous nanoparticle and porous nanoparticle additions to PTMSP that prop open the polymer chains at the nanoparticle/polymer boundary but do not prevent aging.

Polymer Chemistry in Coordination Nanochannels

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Metal-Organic Frameworks (MOFs) prepared by self-assembly of metal ions and organic ligands have attracted much attention because of their wide applications in gas storage, molecular recognition, and catalysis.1The characteristic features of MOFs are highly regular channel structures, controllable channel sizesapproximating molecular dimensions, and designable surface functionality. Use oftheir regulated and tunable nanochannels for a field of polymerization can allow multi-level controls of the resulting polymerstructures(Figure 1).2In addition, construction of nanocomposites between MOFs and polymers will provide unprecedented material platforms to accomplish many nanoscale functions (Figure 1).3

Controlled radical polymerization of vinyl monomers can be attained in MOF nanochannels, showing many remarkable effects of pore size, shape, and functionality on the structures and alignment of the resulting polymers.4 For example, stereo- and regioregularity of polymers could be systematically controlled depending on the pore structure.4b-e Controlled uniaxial alignment of vinyl polymer chains was achieved by host-guest cross-polymerization.4f Use of MOFs as removable templates was a promising method for the preparation of morphological polymer particles as well as the mixing of immiscible polymer pairs at the molecular level.4g,h Recently, we have also developed radical polymerization using porous organic cages with dynamic and responsive packing structure, showing enzyme-mimetic behaviors that cannot be attained in conventional rigid hosts.4i

A variety of polymerization reactions can be also promoted in functionalized MOFs.5 For example, MOFs with specific basic sites accelerated stereo- and monomer-selective polymerization of substituted acetylenes.5a Oxidative polymerizations of pyrrole within 2D and 3D MOFs containing redox-active sites gave polypyrroles whose orientations were directly related to the original host templates.5b,c Controlled polymerization of unprotected saccharide monomers could be performed in MOFs, producing linear and porous polysahharides from 1D and 3D channels, respectively.5d,e In addition, inorganic polymers, including silica and poly(ferrocenylsilane), were succesfully prepared with regulated structures from MOF nanochannels.5f,g

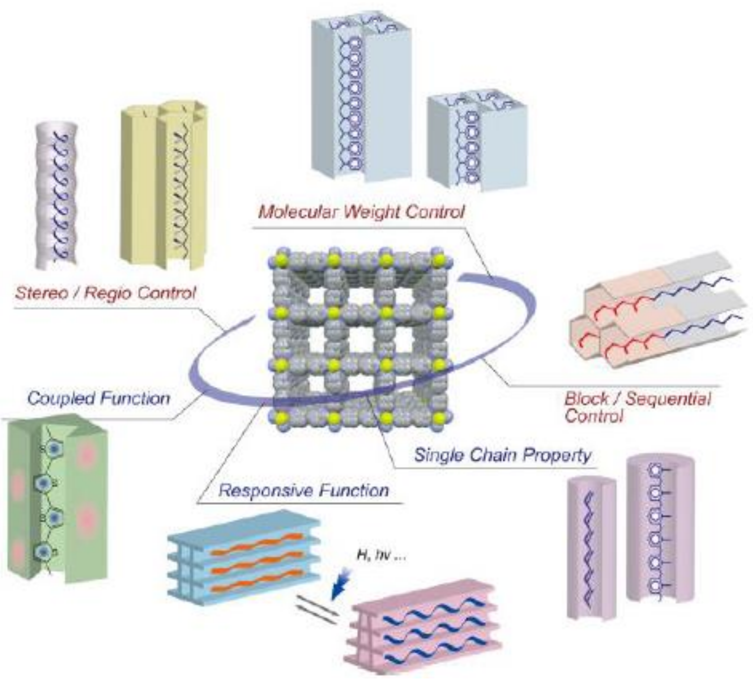

Figure 1. MOFs can allow precision controls of polymerizations as well as preparation of new composites with remarkable properties.

Polymers confined in nanochannels of MOFs have distinctly different properties to those in the bulk state because of the formation of specific polymer assemblies and conformations.6 For example, incorporation of poly(ethylene glycol) (PEG) into MOFs enabled observation of thermal transitions of only a few chain assemblies.6a,b Confinement of conducting polymers, such as poly(vinyl carbazole), polythiophene, polysilane, in one-dimensional channels of MOFs led to increase in their conductivity because of the specific conformational changes.6c-e Nanostructuration of the polymer chains in MOFs was a very useful way for gas adsorption and sensing systems.6f Fluorescent oligomers accommodated in a flexible MOF showed conformational variations concurrently with the host structural change during gas adsorption, which is a key for fluorescent detection of gases.6g,h We also developed new autonomous chemical motors by integrating MOFs and self-assembling peptides.6i-k

References

1. (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Kitagawa, S.; Kitaura, R.; Noro, S.-i. *Angew. Chem. Int. Ed*. **2004,** *43,* 2334. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.
2. (a) Uemura, T.; Horike, S.; Kitagawa, S. *Chem. Asian J*. **2006**, *1*, 36. (b) Uemura, T.; Yanai, N.; Kitagawa, S. *Chem. Soc. Rev*. **2009**, *38*, 1228.
3. Kitao, T.; Zhang, Y.; Kitagawa, S.; Wang, B.; Uemura, T. *Chem. Soc. Rev.* **2017**, *46,* 3108.
4. (a) Uemura, T. *et al., Chem. Commun*. **2005**, 5968. (b) Uemura, T.; Hiramatsu, D. Kubota, Y.; Takata, M.; Kitagawa, S. *Angew. Chem. Int. Ed*. **2007**, *46*, 4987. (c) Uemura, T.; Ono, Y.; Kitagawa, K.; Kitagawa, S. *Macromolecules* **2008**, *41*, 87. (d) Uemura, T.; Ono, Y.; Hijikata, Y.; Kitagawa, S. *J. Am. Chem. Soc*. **2010**, *132*, 4917. (e) Uemura, T.; Nakanishi, R.; Mochizuki, S.; Murata, Y.; Kitagawa, S. *Chem. Commun*. **2015**, *51*, 9892. (f) Distefano, G. *et al., Nature Chem*. **2013**, *5*, 335. (g) Uemura, T.; Kaseda, T.; Kitagawa, S. *Chem. Mater*. **2013**, *25*, 3772. (h) Uemura, T. *et al., Nature Commun*. **2015**, *6,* 743. (i) Uemura, T.; Nakanishi,

R.; Mochizuki, S.; Kitagawa, S.; Mizuno, M. *Angew. Chem. Int. Ed*. **2016**, *55,* 6443.

5. (a) Uemura, T.; Kitaura, R.; Ohta, Y.; Nagaoka, M.; Kitagawa, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 4112. (b) Yanai, N. *et al., Angew. Chem. Int. Ed*. **2008**, *47*, 9883. (c) Uemura, T.; Kadowaki, Y.; Yanai, N.; Kitagawa, S. *Chem. Mater*. **2009**, *21*, 4096. (d) Kobayashi, Y.; Horie, Y.; Honjo, K.; Uemura, T.; Kitagawa, S. *Chem. Commun.* **2016**, *52*, 5156. (e) Kobayashi, Y.; Honjo, K.; Kitagawa, S.; Uemura, T. *ACS. Appl. Mater. Interface* **2017**, *9*, 11373. (f) Uemura, T.; Hiramatsu, D.; Yoshida, K.; Isoda, S.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 9216. (g) Kobayashi, Y.; Honjo, K.; Kitagawa, S.; Gwyther, J.; Manners, I.; Uemura, T. *Chem. Commun.* **2017**, *in press*.
6. (a) Uemura, T. *et al., Nature Commun*. **2010**, *1*, 83. (b) Yanai, N.; Uemura, T.; Kitagawa, S. *Chem. Mater*. **2012**, *24*, 4744. (c) Uemura, T. *et al., J. Am. Chem. Soc*. **2012**, *134*, 4501. (d) MacLean, M. W. A. *et al., Angew. Chem. Int. Ed*. **2016**, *55*, 708. (e) Kitao, T. *et al., J. Am. Chem. Soc*. **2015**, *137*, 5231. (f) Le Ouay, B.; Boudot, M.; Kitao, T.; Yanagida, T.; Kitagawa, S.; Uemura, T. *J. Am. Chem. Soc.* **2016**, *138*, 10088. (g) Yanai, N. *et al., Nature Mater*. **2011**, *10*, 787. (h) Le Ouay, B.; Kitagawa, S.; Uemura, T. *J. Am. Chem. Soc.* **2017**, *in press*. (i) Ikezoe, Y.; Washino, G.; Uemura, T.; Kitagawa, S.; Matsui, H. *Nature Mater*. **2012**, *11*, 1081. (j) Ikezoe, Y. *et al., Adv. Mater.* **2015**, *27*, 288. (k) Ikezoe, Y. *et al., Nano Lett.* **2015**, *15*, 4019.

The Effect of The Aliphatic Carboxylate Linkers on the Electronic Structures, Chemical Bonding and Optical Properties of the Uranium-Based Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are drawing increased interest for their high stability and porosity leading to their potential applications in separation, catalysis, and photoelectric processes. Recent studies have identified the role of aminated linkers in band-gap reduction of different MOFs. Uranyl-containing MOFs are of particular interest due to their photo-luminescent properties and their photocatalytic activity. We recently studied the electronic structures of a series of uranyl based MOFs that contain aliphatic dicarboxylate linkers of different lengths. Recently a much-debated issue in this research area is how to control the electronic properties of MOFs in order to exploit a particular characteristic of them. Two factors, namely the length and type of the linkers and the type of metal centers, are considered to be the most influential. In this computational study, we explored the role of the length of the linkers on the electronic properties of these MOFs. We provide a detail analysis of chemical bonding, charge distribution, geometric and electronic structural properties, and optical properties for the first time. Our analyses show that the uranyl metallic subunit in all MOFs has ionic bonding characteristics. The organic carboxylate linkers, on the other hand, show predominantly covalent bonding characteristics. Simulated optical properties, such as refractive index, absorption coefficient, optical conductivity, reflectivity, and electron energy-loss spectrum are obtained from the calculated frequency dependent dielectric constants. These properties indicate some promising application of these MOFs as photo-catalyst. In particular, substantial absorption in the energy range of the visible part of electromagnetic spectrum shown by these MOFs can be explored further for application in solar energy sector. Our results also indicate to a possible way to tune the band gap through, e.g., doping, and hence pave the path to a potential application of these MOFs as photo-catalysts.

Polymerization of Metal-Organic Nanocages into High Dimensional Architectures

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The assembly of nanometric-units, such as nanoparticles and nanocubes, generates various nano polymers with unique properties. In comparison with nanoparticles, nanocages have two different types of surfaces, both of which can enhance the surface area, and thus enhance the targeted properties, such as sensing and catalysis, while the polymerization of nanocages has been rarely investigated, probably due to the difficulty on forming and controlling the interactions between the neighbourhood nanocages. As one kind of nanocage, metal-organic nanocage (MONC) has been found wide applications in molecule delivery, catalysis, and nano capsulation. Different from metal or protein nanocages, MONCs have definite and rigid monomeric structures as well as potential open metal sites and coordinative active functional groups, which are possibility to interact with each other to assemble MONC into polymers. Herein, we exhibit the selective coordination-driven polymerization of MONC into 2D and 3D hybrid polymers based on a MONC unit, $[\mathrm{Cu24(L)24(H2O)16(DMA)8}]\cdot\mathrm{15MeOH}\cdot\mathrm{42DMA}$ (1, H2L = 5- hydroxy-1,3-benzenedicarboxylic acid), via the kinetics and thermodynamics control. Transformation from 2D to 3D MONC polymer has been achieved as well. Compared with MONC, the 2D and 3D polymers exhibit significant improvements on stability, surface area and gas-adsorption properties.

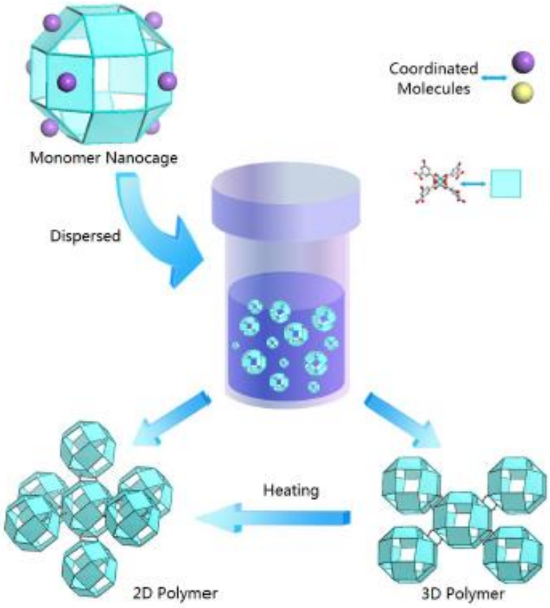

Figure 1. Polymerization of MONC into 2D and 3D polymers.

References

1. Macdonald, J. E., Sadan, M. B.; Houben, L., Popov, I. and Banin, U. Nat. Mater., 2010, 9, 810.
2. Li, J.-R. and Zhou, H.-C. Nat. Chem., 2010, 2, 893.
3. Gao, W.-Y., Chen, Y., Niu, Y., Williams, K., Cash, L., Perez, P. J., Wojtas, L., Cai, J., Chen, Y.-S. and Ma, S. Angew Chem. Int. Ed., 2014, 53, 2615.
4. Liu, T. F., Chen, Y. P., Yakovenko, A. A. and Zhou, H. C. J. Am. Chem. Soc., 2012, 134, 17358.
5. Niu, Z., Fang, S., Liu, X., Ma, S., Ma, J.-G. and Cheng, P. J. Am. Chem. Soc., 2015, 137, 14873.

POSTER PRESENTATIONS

P01

A Bovine Serum Albumin-Based Dynamic-Curing Tissue Glue with High Biocompatibility for Multipurpose Internal Medical Applications

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The existing tissue adhesives today have various weak points in biological compatibility, which make them not ideal for internal medical conditions. Herein, a mussel-inspired multifunctional Bovine serum albumin (BSA)-Citrate acid (CA)-Dopamine tissue glue (BCD) was newly developed aiming at multi-internal biomedical applications. BSA was taken as the backbone to ensure the tissue adhesive's high biocompatibility while CA was introduced as a dual-functional intermediate to protect amino-groups in BSA and to increase reactive sites for catechol group engraftment concurrently. An enhancing adhesion could be formed between adherent tissues developing from chelate to covalent interactions spontaneously by addition of Fe3+ and NaOH one-off. The developed BCD tissue glue possesses more than 10-fold stronger adhesive strength over the commercially available fibrin glue in wet environment, and it also has proper gelation kinetics, gentle swelling behavior, controllable in vivo and in vitro degradation rate, and good in vitro cyto-compatibility. The desirable results obtained from animal models in evaluation of the seroma prevention and instant hemostatic abilities verified BCD's great potential as a multifunctional tissue adhesive. And its excellent in vivo biocompatibility further confirmed its superiority to be used in internal medical conditions.

References

1. Bouten, P.J.M., Zonjee, M., Bender, J., Yauw, S.T.K., van Goor, H., van Hest, J.C.M., Hoogenboom, R., The chemistry of tissue adhesive materials, *Prog Polym Sci,* **2014**, 39, 1375-1405.

P02

An investigation into the development of polymer grafting on a 3D printed titanium alloy for implant applications

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Despite the success of total hip replacements, problems such as aseptic loosening, implant fracture,and stress shielding remain a serious concern[1]. Commonly used hip implant materials possesshigher stiffness compared to native femoral bone. 3D printed titanium alloy, on the other hand, has an interconnected pore structure. This exhibits the potential to assist bone ingrowth [2]and to reduce the stiffness discrepancy between the implant and bone, eliminating stress shielding effects [3].

However, the surface roughness is high for 3D printed materials,affecting bio-interfaces. In this study, polymer grafting onto titanium alloy surfaces was undertaken to minimize the effect of surface roughness and to improvesurface properties. The morphology and surface structures of polymer grafted titanium alloys were evaluated and compared with the untreated polished and unpolished surfaces in terms of wettability, morphology and elemental distribution. The polymer grafted surface was found to exhibit better wettability and lower surface roughness compared to untreated 3D printed titanium alloy surfaces. A uniform continuous layer of polymer was confirmed on titanium alloy substrate by compositional analysis. The polymer grafted surface provided aphospholipid-like layer on surfaces that mimic the natural articular cartilage.

References

1. Fousová, M., et al., *Promising characteristics of gradient porosity Ti-6Al-4V alloy prepared by SLM process.* Journal of the Mechanical Behavior of Biomedical Materials, 2017. **69**: p. 368-376.
2. Tan, X., et al., *Metallic powder-bed based 3D printing of cellular scaffolds for orthopaedic implants: A state-of-the-art review on manufacturing, topological design, mechanical properties and biocompatibility.* Materials Science and Engineering: C, 2017.
3. Ghosh, S. and S. Abanteriba, *Status of surface modification techniques for artificial hip implants.* Science and Technology of Advanced Materials, 2016. **17**(1): p. 715-735.

P03

Synthesis of macro-porous materials via controlled aggregation of colloidal polymer particles

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Porous materials are widely used for many different applications, ranging from catalysis to chromatography to thermal and sound insulation. In particular, macro-porous polymers exhibit unique behaviors in chromatographic applications thanks to the large set of macro-pores, which allow internal convective flow, quickly carrying large molecules (such as biomolecules) to interact with the pore surface. These materials, also called perfusive materials, allow to establish good separation performance at high flows, due to their flow-independent behavior.

Different manufacturing methods can be applied to produce macroscopic porous polymer particles. Most of them involve a poor solvent of the polymer (the so-called porogen) as pore generating component, which needs to be fully extracted after the synthesis. An alternative is to use controlled aggregation of colloidal polymer nanoparticles and take advantage of the structure and morphology of the formed clusters. Thanks to their fractal nature, such clusters have pore sizes ranging from few nanometers to microns, thus suitable to fulfill the perfusive behavior requirements. A method based on this concept is explored in this contribution. Named “Reactive Gelation” [1], it is composed of three major steps: starting from an aqueous dispersion of colloidal polymer nano-particles (so-called latex) swollen by a mixture containing monomer and initiator, micron-size clusters are formed by controlled aggregation of the primary particles and finally hardened by post-polymerization through heating. This last process “freezes” the aggregate structure, ensuring the mechanical stability required to withstand high flowrates and pressure drops.

Aiming at developing an easily scalable process for the production of optimized and versatile perfusive materials for chromatographic applications, in this contribution novel manufacturing methods are presented involving different aggregation regimes. In particular, the first approach is shear-induced aggregation performed by passing the latexes through a Z-shaped microchannel at high flow-rate. An example of cluster obtained this way is shown in Figure 1, left. On the other hand, segmented stagnant aggregation is applied in the second approach taking advantage of an initial water-in-oil emulsion, finally reversed to produce suitable polymer aggregates. The different aggregation mechanisms result in clusters with different porous structure. The cluster morphology as well as the pore size distribution of the different materials have been systematically investigated and their respective chromatographic performance assessed by standard pulse experiments (Figure 1, right).

A major drawback associated with this type of materials is their low surface area, typically in the order of tens of square meters per gram. Different strategies of surface functionalization can be used to contrast this limitation. Among them, the use of polymer brushes grown from the pore surface by controlled free-radical polymerization will be discussed. More specifically, when made of temperature-responsive polymers, these brushes can be elongated from or collapsed on the pore surface depending upon the operating temperature [2]. This way, temperature instead of eluent composition can be effectively used to tune adsorptivity of the target species, a quite novel and convenient alternative to the conventional gradient chromatography. Pulse chromatography applications of this type of materials will be finally shown.

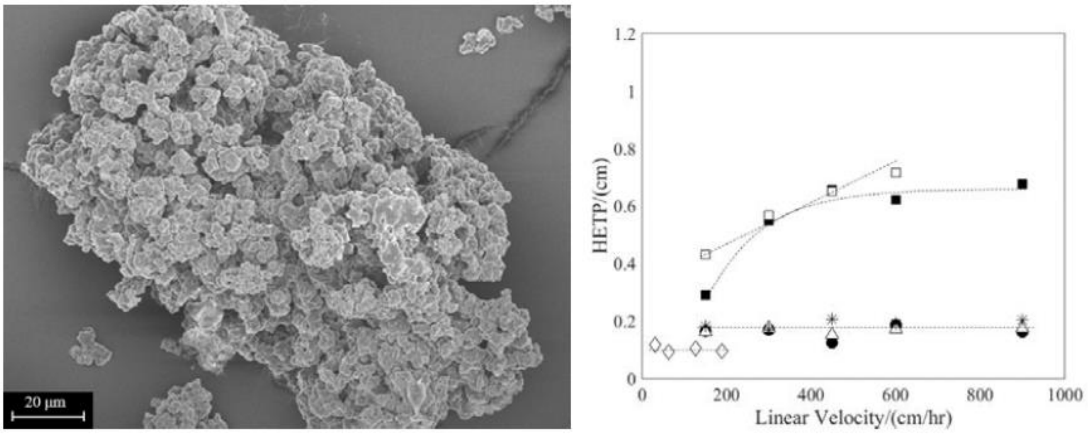

Figure 1: left: SEM picture of a cluster produced using the microchannel (left); right: column efficiency (HETP, Height Equivalent to a Theoretical Plate) vs. velocity with dextran 15 KDa as tracer and different packings (Eshmuno CPX (empty squares), POROS 50 HS (filled squares), CIM® r-Protein A DISK (empty diamonds), our own materials (filled dots, empty triangles and asterisks).

References

1. Marti, N., Quattrini, F., Butté, A. and Morbidelli, M., Production of Polymeric Materials with Controlled Pore Structure: the “Reactive Gelation” Process, *Macromol. Mater. Eng.*, **2005**, 290, 221-229.
2. Lamprou, A., Gavriilidou, A.F.M, Storti, G., Soos, M., Morbidelli, M., Application of polymeric macroporous supports for temperature-responsive chromatography of pharmaceuticals, *J. Chromat. A*, **2015**, 1407, 90-99.

P04

Improved Dielectric and Ferroelectric Properties in Cobalt Ferrite Doped PVDF Multiferroic Polymer Composites

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We report the effect of cobalt ferrite (CoFe2O4) nanoparticles on dielectric and ferroelectric properties of poly(vinylidene fluoride)(PVDF). Large enhancements in dielectric constant and remanent polarization upon addition of 5 wt.% CoFe2O4nanoparticles to PVDF have been observed. Nearly 17% increase of dielectric constant and 31% increase in remanent polarization was observed in PVDF-CoFe2O4nanocomposite films as compared to pristine PVDF films prepared under identical conditions. These enhancements were accompanied by a decrease in crystallinity and an increase in electroactive β-phase content as evidenced by X-ray diffraction and fourier transform infrared spectroscopy, respectively. A 5% increase in the amount of β-phase content is also observed in nanocomposite films. These enhancements in dielectric constant and remanent polarization are attributed to the influence of CoFe2O4nanoparticles on nucleation, morphology,dipole aligning and dipole pinning behaviour of PVDF1.

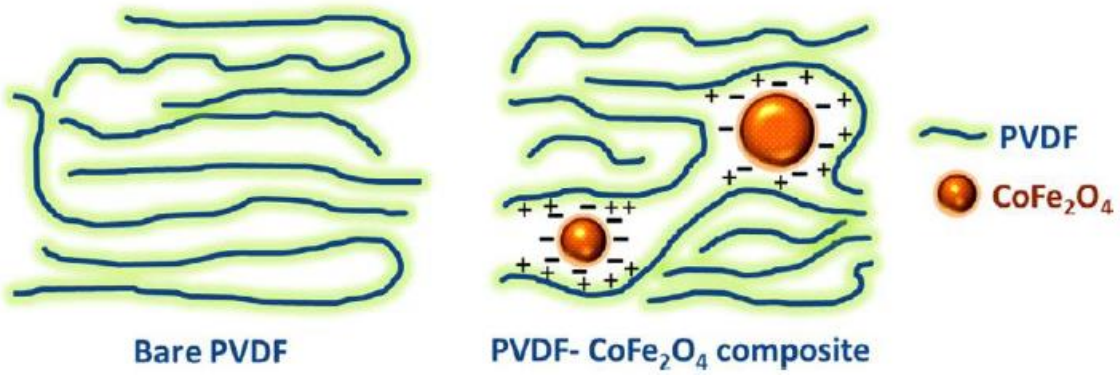

Figure 1. Schematic depicts influence of nanoparticles on the alignment of polymer chains in nanocomposite, electrostatic interaction between CoFe2O4 fillers and PVDF. Incorporation of nanoparticles disrupts the ordered alignment of polymer chains while simultaneously enhancing electroactive β-phase content in polymer nanocomposite.

References

1. G Suresh, S Jatav, M S Ramachandra Rao and Dillip K Satapathy. Enhancement of dielectric and ferroelectric properties in cobalt ferrite doped poly(vinylidene fluoride) multiferroic composites, *Materials Research Express*, **2017**, 4, 075301.

P05

Biomaterial Applications of Avian-Keratin Refinement

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Annually, landfills worldwide receive millions of tons of poultry feathers that take decades to biodegrade and cause a variety of environmental issues. They can carry diseases that endanger human health as well as that of flora and fauna. A portion of these waste feathers is incinerated, producing CO_2 and harmful SO_2 emissions. However, these feathers contain over 90 % keratin protein, which can be used for many applications such as cosmetics, healing products, and tissue engineering. The aim is to reduce the disposal of and better utilise feather waste, which the poultry industry currently pays for. Using chicken feathers as a sustainable source of keratin instead of materials like wool would reduce emissions (since poultry farming is less carbon-intensive than sheep farming) and utilise a major waste stream of the poultry industry (rather than wool, which has many other applications). The extraction process we have developed is greener than current technologies and will reduce the production time and cost, while increasing the yield.

P06

Developing Bio-Functional Nanomaterials through Protein-Polymer Conjugates

Kristofer Cupic

University of Melbourne (Australia)

P07

Lignin Chemical Depolymerization Using Redistribution Mechanism in Green Solvents and Repolymerization of Depolymerized Products

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Lignin is one of the most abundant renewable bio material that has the potential to yield valuable low molecular weight aromatic compounds when selectively depolymerize. In biosphere 3 x 1011 tons of lignins are exist with 2 x 1010 tons generated annually (1). Lignin is a three dimensional hetero polymer built up of hydroxylated and methoxylated phenyl propane units (C9). The α,β- unsaturated C6C3 precursors of the lignin are coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol (2).

Lignin has a similar aryl ether structure to poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in its network (Fig.1). PPO is widely used as a high-performance engineering plastic because it has excellent physical properties. We have previously demonstrated that PPO successfully depolymerized in water and ionic liquid (3). The aim of the research is to use water and ionic liquid as green solvents for the depolymerization of lignin using redistribution mechanism. It has been demonstrated that lignins can be extensively depolymerized under oxidative conditions using Cu(II) complexes and a monomeric *para*-blocked phenol (4-*tert*-butyl-2,6-dimethylphenol [TBDMP]) in water and ionic liquid [C2mim][ABS] (4, 5). Novel lignin based thermoplastic copolyester was successfully synthesised by the esterification of oligomeric lignin with sebacoyl chloride in the presence of Triethylamine (TEA) as a base (4).

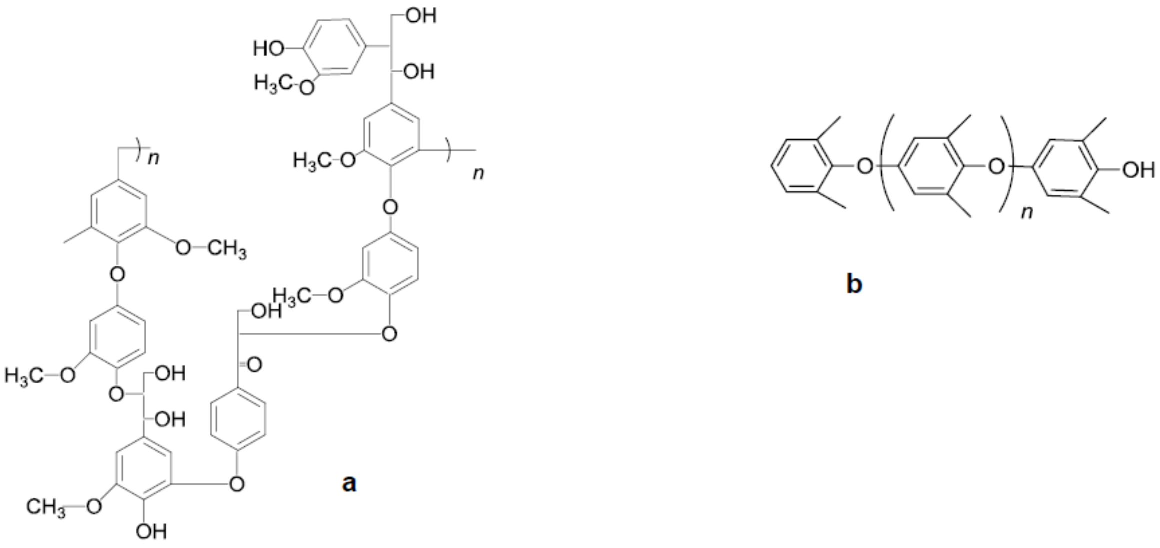

Figure 1. “Representative” lignin structure **(a)** and PPO **(b)**

References

1. J. F. Stanzione, J. M. Sadler, J. J. L. Scala and R. P. Wool, Lignin model compounds as bio-based reactive diluents for liquid molding resins, *ChemSusChem,* **2012**, 5, 1291 – 1297

2. E. Alder, *Wood science and technology,* **1977**, 11, 169
3. Nanayakkara S, Patti, A.F., Saito, K., *Australian Journal of Chemistry*, **2013**, 66, 60-66
4. Nanayakkara S, Patti, A.F., Saito, K., Chemical depolymerisation of lignin using redistribution mechanism with phenols and repolymerization of depolymerized products, *Green Chemistry*, **2014**, 16, 1897-1903
5. Nanayakkara S, Patti, A.F., Saito, K., Lignin Depolymerisation with Phenol via Redistribution Mechanism in Ionic Liquids, *ACS Sustainable Chem. Eng.*, **2014,** *2*, pp 2159–2164

P08

“DESIGN, SYNTHESIS AND CHARACTERIZATION OF NEW LIGANDS FOR THE FORMATION OF MOFs”

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Metal-Organic Frameworks, MOFs are a class of crystalline materials formed by the union of coordinated metal atoms to organic ligands to generate structures in one, two or three dimensions. These materials have generated great interest in recent years due to their multiple applications in various areas including: gas adsorption, colorimetric sensors, controlled release of drugs, catalysis, etc.

The study of these structures and the almost unlimited combinations between metals (coordination) and ligands (geometry) is our main interest, since in this way the area surfaces of the new synthesized MOFs will be determined only by the characteristics of their basic building units.

We synthesize C3 symmetric ligands containing chromophore fragments, according to the following reaction scheme (Figure 1 and Figure 2):

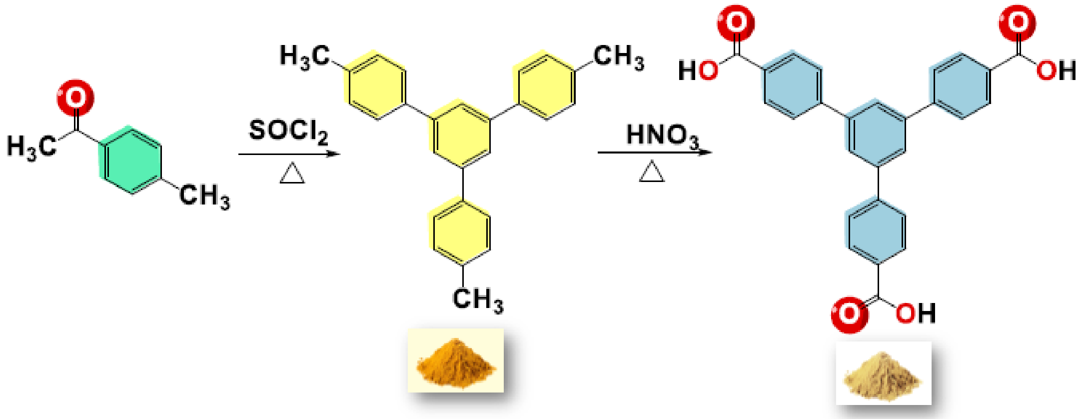

Figure 1. Synthesis of ligands type H3BTB, first part.

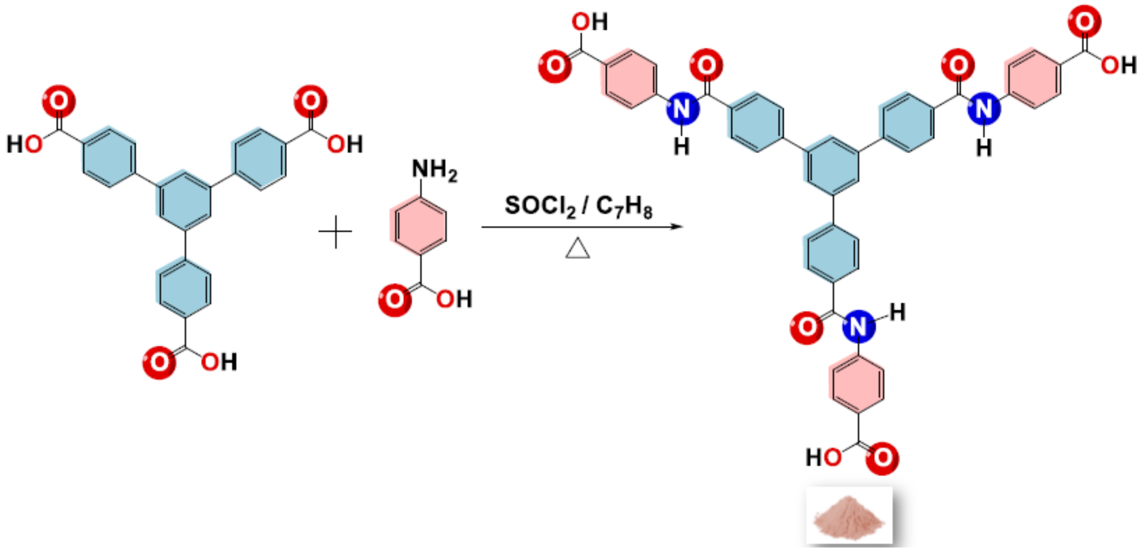

Figure 2. Expansion of the H3BTB ligand by the incorporation of a chromophoric fragment from to give H3BTB-tris-amide ligand, second part.

This new ligand is being reacted with some metals from period 6 to form the corresponding MOF.

Finally, we conclude that we have synthesized the ligands of the first part with yields higher than 83%, which were character ized by their physical and spectroscopic constants using the IR-FT technique, 1H and 13C NMR.

Additionally, the synthesis of a new ligand in moderate yields was obtained, proposed for the formation of a new MOF. The obtaining of this new MOF is determinant for the development of our project due to the expected in its final structure, the increase of its cavities with respect to the ligand synthesized in the first part.

References

1. Kitagawa S., Kitaura R., Noro S., Functional porous coordination polymers, *Angew. Chem. Int.,* **2004,** 43, 2334–2375
2. Beltran H. I., Serna S. L., Nuñez M. L., Flores J., Simeón R. L., An alkaline one-pot metathesis reaction to give a [Cu3(BTC)2] MOF at r.t., with free Cu coordination sites and enhanced hydrogen uptake properties, *RSC Adv.,* **2013,** 3, 10962-10972.

P09

Photopolymerization of Triazolinediones: Regulating Thermal Reactivity by Different Colours of Light

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The precise control of chemical reactivity by external stimuli, specifically temperature and light, is of critical importance for the design of adaptive and 'on demand' programmable materials.1Light in particular serves as a highly fascinating and well-defined switch that allows for high levels of spatial and temporal resolution enabling site-selective processes (e.g. surface patterning, 3D scaffold design and 3D laser lithography).2In addition, light-induced protocols offer the potential to establish sequential photochemical reactions in a so-called λ-orthogonal manner, simply by activating different chromophores each at their distinct wavelength.3While the development of such wavelength-orthogonal systems has received some attention, the exploitation of light to serve as a gate to switch between thermally and chemically activated reaction channels is almost non-explored and constitutes a key next frontier within the realm of reaction control. Yet, no reaction manifolds are currently available in which the thermal reactivity of molecules can be completely switched off upon a photonic stimulus.

Herein, we pioneer exactly such a concept, based upon the reversible photopolymerization of triazolinediones (TADs) –highly enabling synthetic tools in polymer science4,5–upon visible light irradiation.6In the context of trapping experiments we demonstrate that this polymerization leads to the quantitative photodeactivation of TADs, thereby providing a selective on-and off-switch of their unique thermal reactivity. Following the in-depth study of the photopolymerization, we next combined the visible light-induced transformation of TADs with the well-established UV-induced photo-enol ligation chemistry of *o*-methylbenzophenones to provide a novel independent λ-orthogonal system. The careful selection of a thermal TAD-based click reaction finally let us to pioneer an unprecedented reaction manifold in which light is used as a gate to selectively switch between a thermally and photochemically activated reaction channel, thus establishing an on demand switchable reaction output.

Theregulation of TADs' thermal reactivity by different colours of light not only opens their exploitation in small molecule ligations but also in the design of novel photoresists potentially enabling sub-diffraction coding.

References

1. Tasdelen, M.A.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.*, **2016**, 52, 19.
2. Barner-Kowollik, C., Bastmeyer, M., Blasco, E., Mueller, P., Delaittre, G., Richter, B., Wegener, M. *Angew. Chem., Int. Ed.*, **2017**, 10.1002/anie.201704695.
3. Hiltebrandt, K.; Pauloehrl, T.; Blinco, J.P.; Linkert, K., Börner, H.G., Barner-Kowollik, C. *Angew. Chem., Int. Ed.*, **2015**, 54, 2838.
4. Billiet, S.; De Bruycker, K.; Driessen, F., Goossens, H., Van Speybroeck, V., Winne, J.M., Du Prez, F.E. *Nat. Chem.*, **2014**, 6, 815.
5. De Bruycker, K.; Billier, S.; Houck, H.A., Chattopadhyay, S., Winne, J.M., Du Prez, F.E. *Chem. Rev.*, **2016**, 116, 3919.
6. Pirkle, W.H.; Stickler, J.C.. *J. Am. Chem. Soc.*, **1970**, 92, 7497.

P10

Beach plastic and associated microbes – what is the relationship?

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Plastic pollution is recognized as one of the major threats to aquatic environment. Most of the focus has been on large plastic, but recently it has been recognized that smaller plastics (microplastics) present even bigger threat to aquatic biota. Recent survey of plastic around beaches in Australia conducted by CSIRO showed correlation between large cities and plastic number found on beaches nearby. Plastic found in the aquatic environment represents a perfect substrate for growth of microorganisms, forming biofilm on such substrate. This is a potential threat to aquatic ecosystems, because of the ability of plastic to move between different water bodies, transporting microorganisms to large distances, often to areas where they would be normally found. This is particularly true for toxic or pathogenic microorganisms. Research on plastic-associated microbes so far showed that such microbes show temporal and regional preference, as well as a preference for a particular plastic type. We focused our survey of plastic-associated microbes on citizen science approach, by collecting at least 10 plastic fragments from beaches around Australia and conducing molecular analysis on microbes form these plastic fragments. We have used Illlumina next generation sequencing platform to determine microbes associated with each plastic fragment, and FTIR to determine what plastic polymer each fragment represented. Dominant microbial communities belonged to Alpha- and Gammaproteobacteria.

Even though there was no clear association between microbe groups and plastic type, there was a partial grouping of microbes by location. In samples from Lord Howe Island we were able to determine origin of plastic found on the beach actually coming from nearby wastewater treatment plant, by the presence of genera usually associated with such environment. Relationship of microbes and plastic is a complex one, and needs to be investigated even further in future research.

P11

A Novel Strategy for Precision Network Formation Based on *Para*-Fluoro Thiol Ligation

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In this work, we introduce the para-Fluoro-Thiol reaction (PFTR) chemistry as a new strategy for network synthesis.1 Due to their light weight and their attitude to be recovered and re-used, polymer networks are an important class of material network which find application in several field such as energy, wastewater treatment and biomedical drug carriers.

Aside the composition, structural imperfections and the degree of cross-linking strongly influence the performance of the material itself.2 As a consequence, the achievement of ´ideal network´ has recently received significant attention from material scientists.3 Here, we show how, by designing a novel fluorinated linker, one could tune and introduce selectivity to the reaction during network formation. To assist the elucidation of the PFTR mechanism a model reaction with a monothiol is presented. The versatility of the entire concept is further demonstrated by employing several bifunctional thiols.

In addition, an in-depth analytical characterization of the networks is provided. Especially, X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS), are suggested as analytical tools for the quantification and confirmation of network formation.

References

1. F. Cavalli, H. Mutlu, S. O. Steinmueller and L. Barner, *Polym. Chem.*, 2017, **8**, 3778-3782.
2. H. Zhou, J. Woo, A. M. Cok, M. Wang, B. D. Olsen and J. A. Johnson, *PNAS*, 2012, **109**, 19119-19124.
3. G. Hild, *Prog. Polym. Sci.*, 1998, **23**, 1019-1149.

P12

Lignin Chemical Depolymerisation Using Ionic Liquids and Microwave

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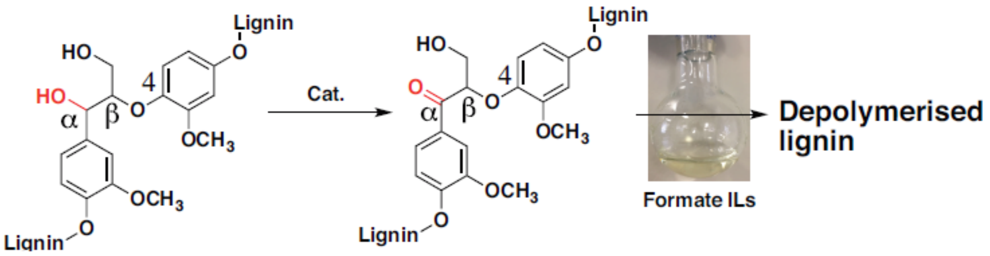
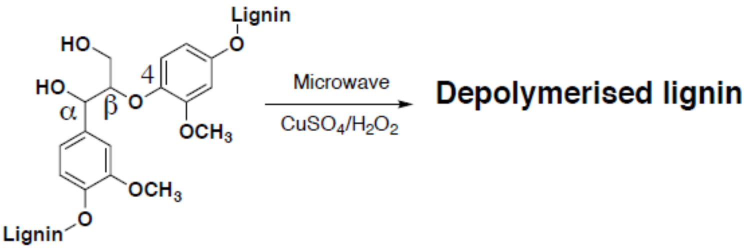
Lignin has been widely studied as a sustainable source of renewable materials, particularly aromatic feedstock chemicals, which are in great and increasing need in the world. Lignin oxidation and depolymerisation presents a promising approach to produce functionalized phenolic products. In this work, two novel pathways of oxidative degradation of lignin have been investigated. The first strategy is that oxidize lignin with copper acetate, which was then depolymerised by a formate ionic liquid resulting in ethyl acetate soluble and also water-soluble depolymerised lignin products. The β-O-4 bonds in lignin were oxidized and then depolymerised by arecyclable ionic liquid, 2-hydroxy ethylammonium formate, at the temperature of 110°C for 24 hours. 2-Hydroxy ethylammonium formate, which could dissolve lignin acting as a solvent, was found to also catalyse the depolymerisation of the oxidised lignin. The second strategy is using copper sulphate as a catalyst to proceed the oxidative depolymerisation with the assistant of microwave. Lignin was successfully depolymerised in these two methods and depolymerised products were also characterised.



Scheme 1: Proposed mechanism of β-O-4 bonds oxidation and depolymerisation



Scheme 2: Lignin depolymerisation with assistant of microwave

References

1. Dai, J., Patti, F. A., Longe, L., Garnier, G., and Saito, K. Oxidized lignin depolymerisation using formate ionic liquid as catalyst and solvent, *ChemCatChem*, **2017**, 9, 2684-2690.

P13

Theoretical Framework to Design Efficient Acceptors for Organic Solar Cells: Molecular Modelling at DFT Level of Study

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In an effort to design high-performance small molecule electron acceptor materials for use in heterojunction solar cells, the present study describes the use of computational chemistry to design and examine the potential of small molecule acceptors. Herein, we have designed four acceptor molecules with different structure and systematically determined the electronic and optical properties of these systems. All acceptor molecules were tested against two donors viz. poly(3-hexylthiophene-2,5-diyl) (P3HT) and poly(dithieno[3,2-b:2,3-d]pyrrole thiophene) (PDTPr-T) with high activity observed against PDTPr-T. These newly designed compounds displayed high open circuit voltage (eVoC) values compared to phenyl-C61-butyric acid methyl ester (PCBM), whereas the electron injection driving force (ΔGinject.) values were found to be comparatively lower. In the case of PDTPr-T donor, all acceptor molecules showed balanced properties, while for P3HT donor, all designed acceptors show low ΔGinjec. to overcome exciton binding energy.

Quantum chemical modelling of acceptors at molecular level may lead to an efficient organic solar cells (OSCs): The potential of non-fullerene acceptor materials for bulk-heterojunction in OSCs

P14

Photo-Healable Crosslinked Epoxy Polymers Using Photoreversible Crosslinker

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Intrinsically self-healing polymers (SHPs) have the ability to heal damage by the use of an appropriate stimulus1,2. This healing can restore the mechanical properties of a damaged polymer allowing for return to service without the need for replacement of the polymer. When used as a coating, a SHP can ensure the continued protection of the underlying structure after damage, withminimal downtime of the component and no replacing of the coating is necessary. This project involves the synthesis of numerous crosslinked epoxy polymers that are capable of healing surface scratches by irradiation with UV-light. The structure of the synthesised polymers and the desired self-healing ability wasconfirmed by IR & UV-Vis spectroscopyand characterisedby DSC, DMA and TGA.

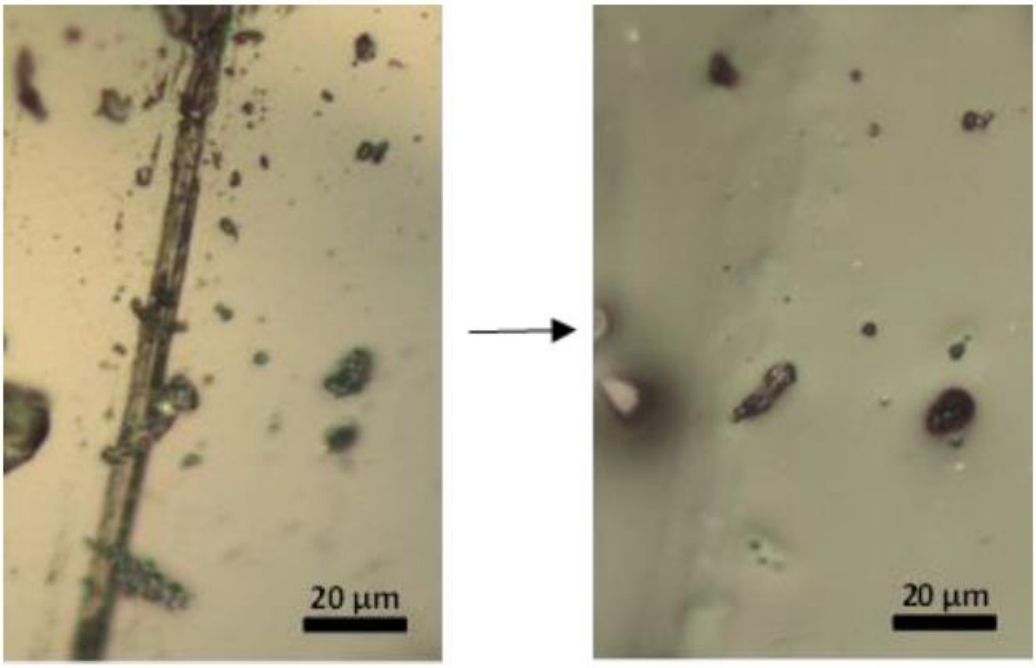

Figure 1. Optical Microscopy images of the self-healing of the created light-healable coating. The incident scratch on the surface of the polymer (left) is seen to heal (right) after the light treatment.

References

1. G. L. Fiore, S. J. Rowan and C. Weder. Optically healable polymers. Chemical Society Reviews, 2013, 42, 7278-7288.

2. D. Habault, H. Zhang and Y. Zhao. Light-triggered self-healing and shape-memory polymers. Chemical Society Reviews, 2013, 42, 7244-7256.

P15

The Glycolysis of PET Copolymers for Chemically Recycling Process of PET Derivatives

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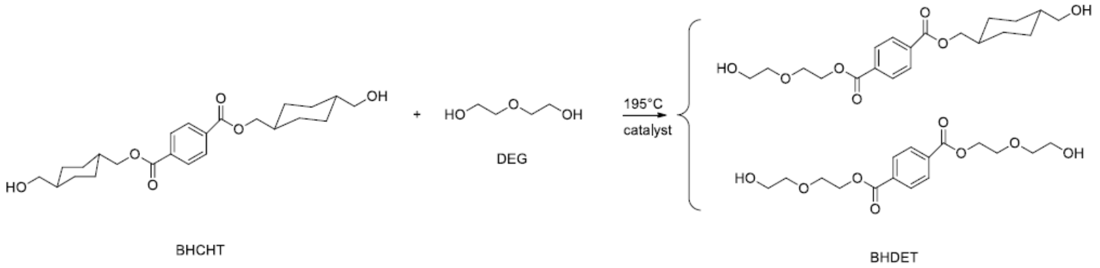
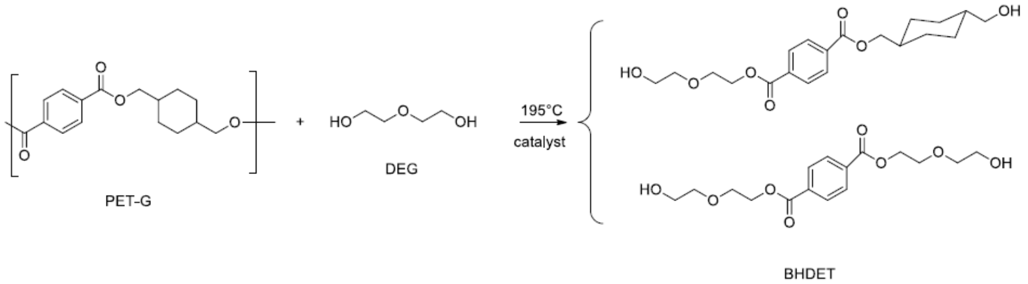
PET-G (poly ethylene terephthalate glycol modified) is a transparentamorphous copolyester, in which CHDM was added to replace ethylene glycol moiety to the polymer backbone. In many recent years, it has become one of the most preferably-using polymers in the industry and technology because of its better excellent secondary porosity, optical and thermoforming properties and several advantages in impact and chemical resistance than that of conventional PET (poly ethyleneterephthalate). However, this wide application gave a numerous environmental challenges to scientists such as the less degradation of PET-G in the nature, poor reactivity in glycolysis process for secondary recycling uses. In this study, we investigate the glycolysis process of PET-G including effective catalyst systems which has not been fully studied comparing to conventional PET of whichhuge investigation have been performed. The investigation of glycolysis process for PET-G, a favorable chemical recycling method of PET-G, has been performed by surveying the how fast the trans-esterification of bis (4-hydroxymethyl)cyclohexylmethyl terephthalate (BHCHT)as a model compound of PET-G went on when each catalyst system was applied to the reaction. Beside, each catalyst system was also used for the real PET-G glycolysis in order to verify their actual effect in specific conditions. As the model compound of PET-G, BHCHT was prepared for examining the rate of trans-esterification of each catalytic systems by the reaction of BHET (bis(2-hydroxyethyl) terephthalate) and CHDM (cyclohexyldimethanol),and its structure and reaction products were determined by 1H-NMR analysis. The glycolysis on BHCHT were carried on with combination of catalysts of zinc acetate, DABCO (1,4-diazabicyclo[2.2.2]octane), and sodium ethoxide. The large retardation of glycolysis rate of PET-G relative to PET was observed through study of model reactions for BHCHT and BHET(as a model compound of conventional PET)with DEG. In addition, the catalytic efficiency was obtained by monitoring the reaction rate of the model trans-esterification and the real copolymer glycolysis. As the result, in trans-esterification process, the mixture of Zinc acetate and DABCO showed the largely increased catalytic effect showing 4 times enhanced glycolysis rate. The developed catalytic systems were applied for real glycolysis of PET-G, and obtained enhanced result where the glycolysis rate of PET-G showed twice faster than the rate from zinc acetate.



Model trans-esterification BHCHT



PET-G glycolysis

P16

The Modification of Protein Fibre for Photo Stability

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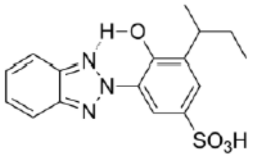
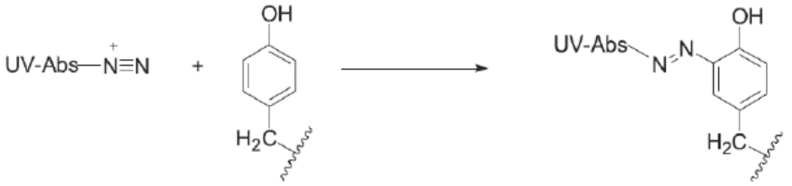
UV radiation (280–380 nm) in the presence of atmospheric oxygen results in rapid photoyellowing of protein fibres, such as wool and silk, that is accelerated in the presence of water, by peroxide bleaching and bleaching/FWA treatment. Photo degradation of protein fibre acts with photochemical and photophysical routes. UV-absorbing chromophores in the form of the aromatic amino acid residues absorb in the UV region between 250 and 320nm, such as (1) Tryptophan (2) Tyrosine (Tyr) (3) Phenyl alanine (Phe). Tyrosine (Tyr) is the most abundant aromatic residue in both silk (5.4 mol%) and wool (3.9 mol%). A sulphonated hydroxyphenyl benzotriazole UV absorber was developed and commercialized in the 1990s named UV FAST W. It can be applied to wool and silk to decrease yellowing and improve the light colour fastness. However, the wet fastness of this UV absorber is not good enough.



In our research, a hydroxyphenyl benzotriazole UV absorber containing an aromatic primary amine group was designed and synthesized, and this UV absorber was grafted to the tyrosine residues on silk fibroin using diazonium coupling chemistry.



The electrophilic aromatic substitution reaction formed a covalent bond between the tyrosine residues on silk (wool) and the hydroxyphenyl benzotriazole UV absorber containing an aromatic primary amine group, which is highly durable for wet process relative to UV FAST W. The results showed that modification with higher amounts of UV absorber on silk or wool led to a very small color change and less decrease in strength during extension than untreated silk or wool fabric after UV irradiation, even though alkali processing and coupling modification cause a decrease in tensile strength of silk (wool). These results indicated that the modification of protein fibers with the diazonium salt of UV absorber containing an aromatic amine group improved the photo stability by releasing the absorbed energy. Acknowledgement This work was supported by National Natural Science Foundation of China (No. 51673176), Zhejiang Provincial Natural Science Foundation of China (LY16B060006).

P17

Synthesis of Ultra-High Molecular Weight ABA Triblock Copolymers using RAFT Polymerisation, End Group Modification, and Chain Coupling

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Ultra-high molecular weight (UHMW) polymers (*M*n> 500 kDa) are widely used in numerous industrial applications, including but not limited to waste water treatment, mining and minerals processing, oil recovery, and hydraulic fracturing.1The synthesis of well-controlled UHMW polymers using reversible deactivation radical polymerisation techniques remains a challenge and has only been the centre of attention in a few isolated studies.1,2Although UHMW was achieved in these studies, the complexity in architecture has primarily been linear homopolymers and AB diblock copolymers. To date, only one recent study has reported the synthesis of UHMW ABA triblock copolymers.3However, the molecular weight (*M*n) of the polymers was only up to approximately 500 kDa. The ability to investigate and develop novel UHMW polymers with higher molecular weight and advanced architectures could give rise to a whole new class of materials with unique properties that have the potential to be further implemented in current industrial applications. We hereby report a new pathway to synthesise UHMW ABA triblock copolymers using a combination of reversible addition-fragmentation chain transfer (RAFT) polymerisation, end group modification, and chain coupling (Figure 1).

S S RAFT Polymerisations Aminolysis and Chain Coupling Mn < 173 kDa Đ < 1.20 Mn > 500 kDa Đ < 1.50 Mn > 1,000 kDa Đ < 1.70

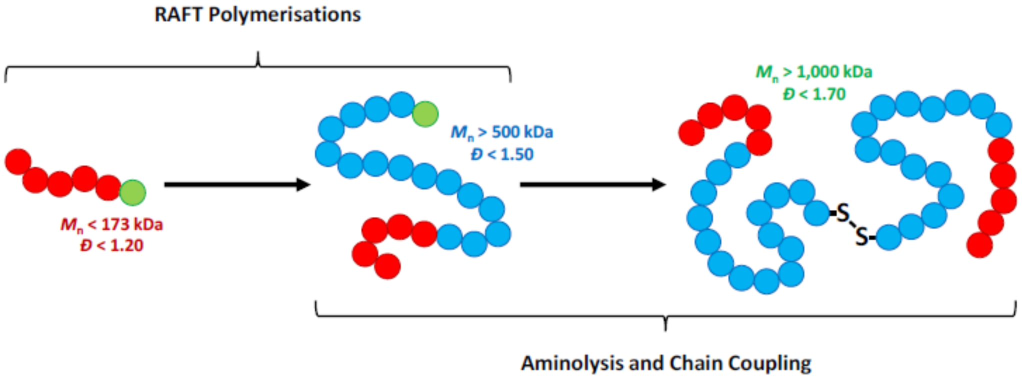

Figure 1. Overall schematic for the synthesis of the UHMW ABA triblock copolymers.

A simple two-stage aqueous RAFT-mediated gel polymerisation technique was initially used to synthesise high molecular weight AB diblock copolymers with low dispersities

(*Đ*< 1.50). The use of said gel polymerisation method in combination with a redox initiation system allowed for the rapid chain propagation of water-soluble monomers under low reaction temperatures(below ambient). These polymers were subsequently used in the final aqueous aminolysis stage where the thiocarbonylthio terminal was converted to thiol functionality, which spontaneously couple under oxidative condition to form disulfide bridges between the AB diblock copolymers to produce the final UHMW ABA triblock copolymers.

References

1. Read, Emmanuelle, Guinaudeau, Aymeric, Wilson, D. James, Cadix, Arnaud, Violleau, Frédéric, and Destarac, Mathias. Low temperature RAFT/MADIX gel polymerisation: access to controlled ultra-high molar mass polyacrylamides, *Polymer Chemistry*, **2014**, 5, 2202-2207.
2. Carmean, R. Nicholas, Becker, Troy E, Sims, Michael B, and Sumerlin, Brent S. Ultra-High Molecular Weights via Aqueous Reversible-Deactivation Radical Polymerization, *Chem*, **2017**, 2, 93-101.
3. Despax, Laurie, Fitremann, Juliette, Destarac, Mathias, and Harrisson, Simon. Low concentration thermoresponsive hydrogels from readily accessible triblock copolymers, *Polymer Chemistry*, **2016**, 7, 3375-3377.

P18

A Study of The Reactivity of Monomers For Co-Polymerization of Polyphenylene Sulfide

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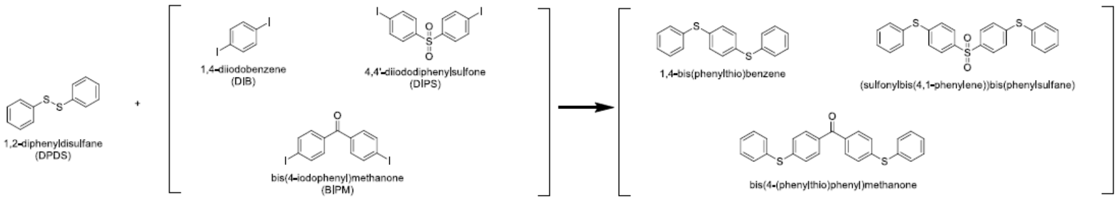
In the recent developing trends of automotive and electronics, there is a strong demand for functional polymers which have high thermal property, chemically resistance, dielectric feature and flame retardation, so as to surpass the properties of conventional plastic products. Polyphenylene sulfide(PPS), which have especially superior thermal property and chemically-resistance, meets those requirements to be used as engineering plastics. The new polymerization process of polyphenylene sulfide(PPS) through direct-melt reaction process of sulfur and *p*-diiodobenzene (p-DIB) has been developed. The introduction of various kinds of co-monomers into the polyphenylene sulfide(PPS) to increase mechanical properties are also attracting many researcher's interests. In this study, in order to investigate the reactivity and stability of diiodo-monomer with sulfur, diphenylene disulfide(DPDS) was used as a reactant for sulphur in PPS polymerization, which is enable to make an observation of the intermediate product, for model reaction, because the polyphenylene sulifde(PPS) resin from p-DIB and sulfur is insoluble into organic solvents after formation of long chain polymeric species. For PPS copolymerization, the reactivity of diiodo compounds that have various kinds of functional group were investigated. Among the diiodo compounds, 4,4'-diiododiphenyl sulfone(DIPS) and bis(4-iodophenyl)methanone(BIPM) were investigated. We analysed the reactivity and stability of carbonyl and sulfonyl group with certain reaction ratios by 1H NMR monitoring method. 1H-NMR spectra were collected according to the reaction time, in which formation of intermediate products and transformation of product were analysed. From the reactions between diphenylene disulfide(DPDS) and bis(4-iodophenyl)methanone(BIPM), it was found that even with an excess amount of sulfur radical, subsidiary or substitution reaction did not happen, and we determined the structure of the products made from diphenylene disulfide(DPDS) and bis(4-iodophenyl)methanone(BIPM). Also, it was found that when DPDS, DIB, and BIPM reacted competitively as in a co-polymerization process, bis(4-iodophenyl)methanone(BIPM) reacted slower than *p*-diiodobenzene (p- DIB), and the relative reactivity of BIPM to p-DIB was determined. The reaction between diphenylene disulfide(DPDS) and 4,4- diodophenylsulfone(DIPS) series were carried out. It was found that the substitution reaction from 4,4-diodophenylsulfone(DIPS) to 1,4-bis(phenylthio)benzene occurred partially during the reactions indicating sulfonyl group is not stable to excess thinly radical. The relative reactivity ratio of DIPS with p-DIB also determined through in various reaction ratios.


1,2-diphenyldisulfane
(DPDS)
+
1,4-diiodobenzene
(DIB)
4,4'-diiododiphenylsulfone
(DIPS)
bis(4-iodophenyl)methanone
(BIPM)
1,4-bis(phenylthio)benzene
(sulfonylbis(4,1-phenylene))bis(phenylsulfane)
bis(4-(phenylthio)phenyl)methanone

<scheme of model reaction of diiodo monomers with DPDS>

P19

Light-Driven Artificial Muscles with Liquid Crystal Elastomers

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Scientists have been interested in biomimetic research that mimics organic species to a micro-robotic device with novel functionalities and accessibility. However, the implementation of the electric-driven microrobots using the complex electronic circuits, power sources is challenging in microscale. For the medical application, the electric-driven devices hardly work inside the human body because the electric current with a few milliamperes traveling through the human heart for a split second can cause the life-threatening irregular heart rhythms.

Another approach is desired for robotic actuators. In recent years, Liquid Crystal Elastomer (LCE) has been investigated as an actuating material, and in particular, its shape can be under the control of different external stimuli, e.g., heat, light or electric field [1]. Especially, light-driven LCE actuators have been the most attracting approach because the deformation of LCEs could be designed by various optical properties such as wavelength, intensity, polarization with high spatial and temporal resolution. Therefore, many applications such as tunable photonic systems have been proposed [2].

Liquid crystals (LCs) are those materials having properties between conventional liquid and solid crystal. For example, LCs may behave like the fluid, but those molecules have been oriented in a crystalline way. Such oriented crystalline order of the molecules with a unique molecular orientation/phase shows the optical property like the birefringence [2, 3]. For example, LC molecules in the nematic phase have no positional order but have self-organized in a long-range direction where the long axes stay parallel to each other. This direction has a particular refractive index, while the other two axes are equivalent and show the ordinary refractive index. Uniaxial alignment and easy reorientation properties make nematic LC be used widely in displays industry. LCE, regarded as a polymer with the property of elasticity like ‘rubber,' is composed of microscopically polymeric chains, entangle to a network by crosslinkers that dominate macroscopic properties like deformation [3]. For example, the change of molecular orientation in LCE actuator results in different strains within one monolithic layer: an expansion on one surface and contraction on the other [4]. As a consequence, pronounced light induced bending deformation occurs. The molecular alignments in LCEs play a major role in bending deformation.

The paper has successfully demonstrated experimentally the LCE stripe, regarded as an artificial muscles, can be deformed by the exposure of the visible light within a few decades of milliseconds. The LCE fabrication process is similar to that of LC cells, but the LCs was transformed from the liquid state to a polymer as illustrated in Fig. 1. First, two cleaned glass slides were coated with Poly (vinyl Alcohol) (PVA) and the homeotropic alignment layer. The spin parameter was 4000 rpm lasting for the 60s, and the constant acceleration was 4000 rpm/min. The two samples with PVA and a homeotropic layer were placed on the heat plate in 1000C for 10 minutes and 1800C for 30 minutes, respectively. The glass slides with PVA coating needs to be rubbed by the rubbing machine. For LC cell fabrication, two cleaned glass were glued with the 20 μm spacers. The mixtures consisting of LC monomer, phenyl Ester, Crosslinker, Initiator, dye, and aniline was prepared by magnetically stirring the LC mixture at 70 °C (100 r.p.m.) for 1 hour. The mixture was filled into the glass cell under the constant temperature at 800C and cooled down to the room temperature for the splayed nematic alignment.

Finally, the Light Emitting Diode (LED) UV light was used to polymerize the LC cells for 2 minutes. Finally, LCE strips were cut from the sample film [5]. The performance of deformation was analyzed a stripe of LCE with 1mm in width under the illustration of the external source with the power density 500 mW/cm2 as shown in Fig.2. The backside of the LCE stripe (the righthand side in Fig. 2) resulted in the expansion because the alignment of the LCs is perpendicular to the surface of the glass slide. The other side of the LCE stripe with the alignments along the surface of glass slides was reacted with the contraction. The whole process of the bending deformation takes a prompt response around 70 ms. The LCE stripe was reversible at the closed stage. Therefore, such light-driven soft material can be treated as an artificial muscle. More complicated movements of the smart artificial muscle can be optimized by the designed pattern of the alignment of LC monomers in LCEs. Therefore, robotics employing smart materials such as LCEs has seen tremendous progress during the past decade. Moreover, the actuation process can affect the absorption of light that fuels the photomechanical motion, which in return provides feedback and modulates the initial actuation. For example, a roll of the LCE stripes expects such feedback-type actuators to become pertinent in intelligent micro-robotic systems, therefore bringing innovative alternatives for soft-robotic technologies. The results are under examination.

In conclusion, we have demonstrated a light-powered LCE stripe, capable of mimicking the behavior of contraction and expansion of the muscle. More sophisticated designs of a light-driven microrobot like walker, swimmer or flyer are under investigation. Such miniature system demonstrates an automatic, optically driven device, which may provide a pathway towards autonomous, intelligent micro-robotics.

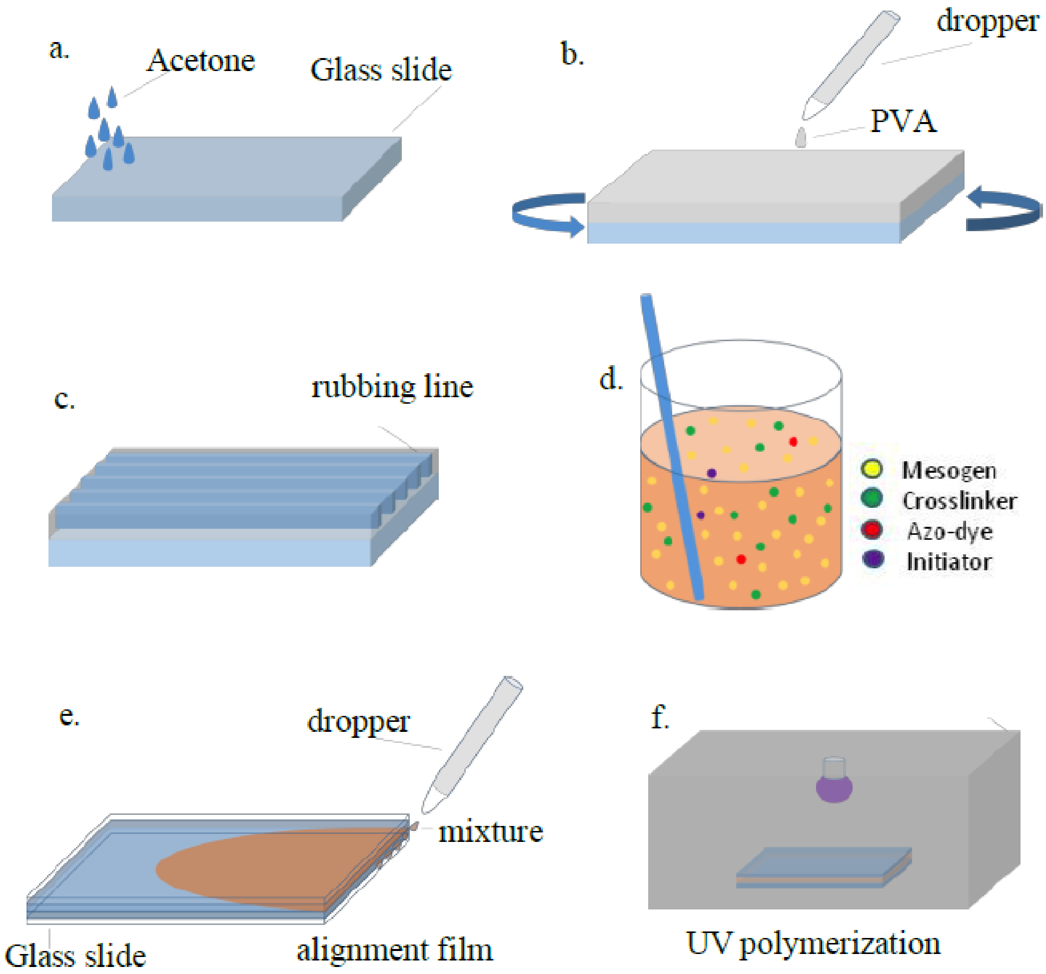

Figure 1: The fabrication processes of the LCEs film. (a) The cleaning of glass slides (b) One of the glass slides were coated with PVA with (c) and rubbed with an alignment. The other glass slide was coated with homeotropic alignment layer. The empty cell were made of the two glass slides with PVA and homeotropic alignment layer on each side with 20µm spacers. (d) The mixture was (e) dropped into the LC cell and (f) was polymerized by UV light.

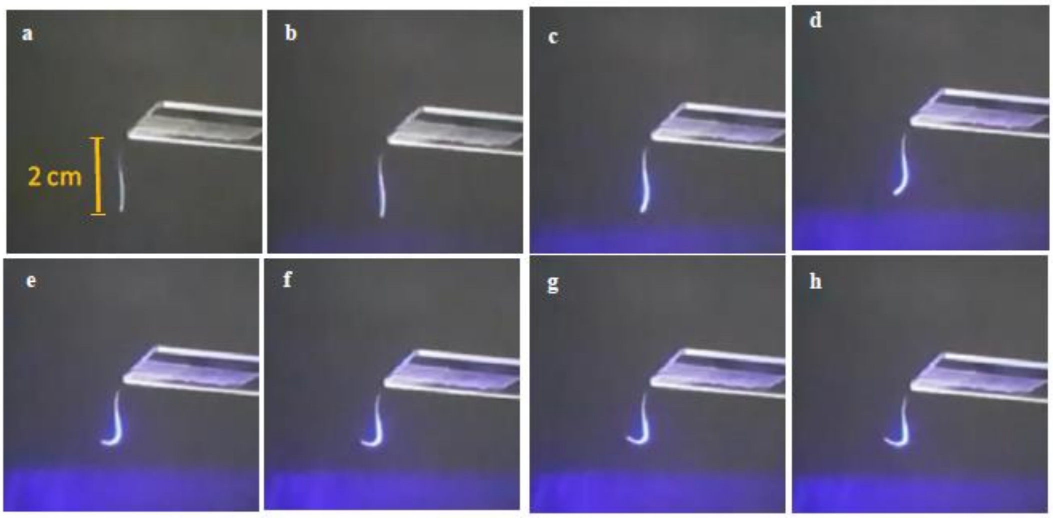

Figure 2: The bending deformation of LCE stripe under the illumination of UV light. (a) The length of the LCE stripe is around 2 cm and one side of the LCE stripe is fixed. The UV light illuminated on the sample and the bending LCE stripes were recorded after (b) 10 ms (c) 20 ms (d) 30 ms (e) 40 ms (f) 50 ms (g) 60 ms and (h) 70 ms ms.

Reference

1. H. Zeng, “High-resolution 3D direct laser writing for liquid-crystalline elastomer microstructures”, Adv. Matt. **26,** 2319-2322 (2014).
2. M. Warner, E. M. Terentjev, “Liquid Crystal Elastomers” (2005)
3. Broer, Crawford “Cross-linked Liquid Crystaline System”
4. H. Zeng, “Thesis-Light Driven Microscopic Robot”, (2014)
5. U. S. Patent, “Liquid Crystal Elastomers” , US 6,312,770 B1 (2001)

P20

Topochemical Photo-Reversible Polymerization of Coumarin Derivatives

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Topochemical polymerization can be used to synthesis complex materials in stereo regular manner. Such reaction considered green as it occurs in solid state without usingany solvent or catalyst. It is known that coumarin can undergo2π+2π reversible cycloaddition reaction under UV light. The monomers were designed to havecoumarin units which canwork as atopochemical polymerizationsites.The crystal structure of the produced monomers were characterized by SC-XRD and Powder-XRD. XRD data showed that the stacking of the coumarin ringisplayinganimportant role in directing the photo active olefin to be parallel to each other(Figure 1).The monomers were polymerized under irradiation at 365 nm UV light via 2π+2π cycloaddition reaction(Figure 2). The obtained polymers was able to photo-depolymerized underirradiation at 254 nm UV light and gave monomers. .The polymers and depolymerized monomers were characterized by NMR, IR, DSC and GPC.

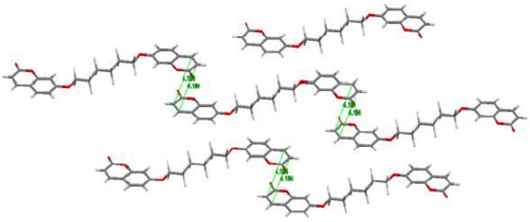
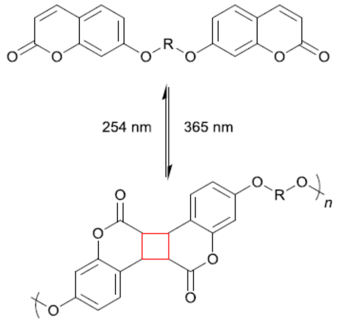


Figure 1 Crystal structure of bis hexyl coumarin monomer (**2**).



R= $(CH_2)_4$ =1, $(CH_2)_6$- =2
and $(CH_2)_8$-=3

Figure 2 Reversible polymerization of the synthesised monomer.

P21

A Crosslinkable Polymer as Binder for Si Electrode in Lithium-Ion Batteries

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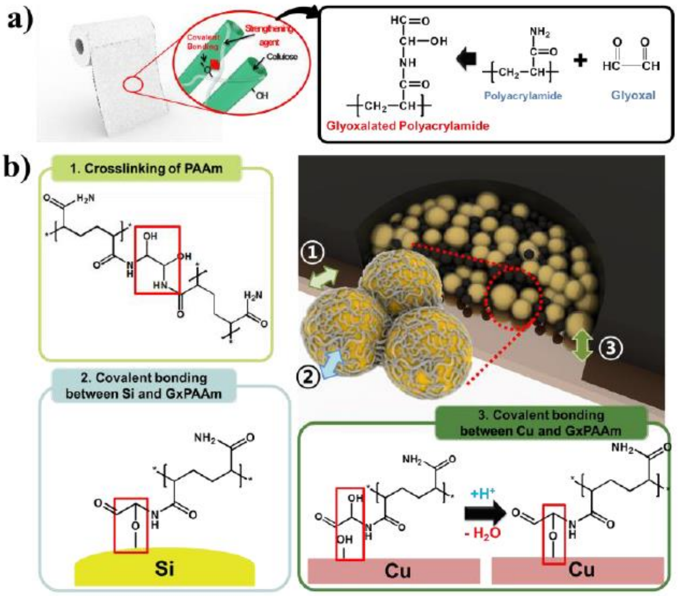
Si as an anode material for lithium ion batteries (LIBs) has proven its exceptionally high theo-retical specific capacity (~ 4,200 mAh/g), which surpasses conventional graphite. (~ 372 mAh/g) However, Si-based anodes suffer from poor cycling stability due to their large volumetric changes during repeated Li insertion. Recently, new approaches related to engineering an efficient binder for Si electrode have been proposed, and proved that binder is the key component for improved properties and performances. We herein demonstrate highly cross-linked polymeric binder (glyoxalated polyacrylamide) with an enhanced mechanical property by applying wet-strengthening chemistry used in paper industry. Mechanical and electrochemical properties of GxPAAm were varied by adjusting side chain of GxPAAm. At certain pH value, the electrode with Si and GxPAAm showed excellent cycle stability, indicating that the properties of the polymeric binder are highly relevant for the cycling stability.



References

1. Jung-Keun Yoo, Jaebeom Jeon, Kisuk Kang,* and Yeon Sik Jung,* Glyoxalated Polyacrylamide as a Covalently Attachable and Rapidly Cross-linkable Binder for Si Electrode in Lithium Ion Batteries, *Electronic Materials Letters*, **2017,** 13, 136-141.

P23

Oral Protein Delivery of RAFT – Insulin Bioconjugates

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Subcutaneous injection is the main therapy of pharmaceuticals protein[1]. However, the main limitation is that it has a low patients' compliance and is also associated with many side-effects. Insulin is one of the protein superfamily and is a major treatment for Type 1 and some of the Type 2 diabetes patients. The most common therapy of insulin is twice a day injection. This type of treatment is painful and as a result encourage noncompliance by patients. Accordingly, oral insulin delivery would be a more preferred and convenient choice. As it follows the normal physiological pathway, delivered via the hepatic portal circulation[2]. Polymer - insulin conjugation is a promising way in improving insulin oral delivery efficiency. The bioconjugation can improve biopharmaceutical properties through the size enlargement, surface masking, charge modification and epitope shielding[3]. We have successfully synthesized a bioconjugation via in-situ preparation of polymer-insulin conjugates through reversible additionfragmentation chain transfer polymerization (RAFT). It has advantages in convenient purification and controlling site and the number of polymer chain conjugated to insulin.

References

1. Cleland, J. Protein delivery from biodegradable microspheres. In *Protein Delivery,* 2002, 1-43, Springer US.
2. Ramesan R, Sharma C. Challenges and advances in nanoparticle-based oral insulin delivery[J], Expert review of medical devices, 2009, 6, 665-676.
3. Caliceti P, Veronese F M. Pharmacokinetic and biodistribution properties of poly (ethylene glycol)–protein conjugates[J], Advanced drug delivery reviews, 2003, 55, 1261-1277.

P24

Radical Addition towards Electrophilic and Nucleophilic RAFT agents

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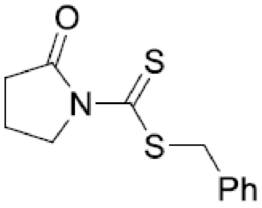
Reversible addition-fragmentation chain transfer (RAFT) polymerization is a convenient and versatile polymerization tool. It has the ability to effect a high level of control to a wide range of monomers thus achieving polymers with well-defined properties such as molecular weights, compositions, shapes and architectures.1 Dithiobenzoates, trithiocarbonates, dithiocarbamates and xanthates are the four main classes of RAFT agents. A variety of RAFT agents have been widely reported. The effectiveness of the RAFT agent depends strongly on the properties of the free radical leaving group R, and its ability to be a good homolytic leaving group and the resulting radical to be able to efficiently re-initiate polymerization.2 To the best of our knowledge, the effect of the electrophilic and nucleophilic nature of the C=S bond of the RAFT agents towards radical addition has not been previously reported. Using RAFT agents such as benzyl 2-pyrrolidone-1-carbodithioate (**1**) and benzyl *N*-phathaloyl-1-carbodithioate (**2**) (Figure 1) we observed a cross-over activity simply due to the nature of the electrophilicity and nucleophilicity of the C=S bond of the RAFT agent towards radical addition of alkyl acrylates and styrene. Investigations into the molecular orbital calculations of the philicity of the RAFT agents are currently underway.



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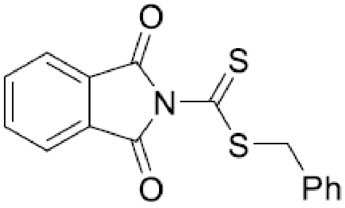

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Figure 1: RAFT agents

References

1. Moad, G.; Rizzardo, E.; Thang, S. H. Living Radical Polymerization- A Second Update, *Australian Journal of Chemistry,* 2009, 62, 1402-1472.
2. Moad, G.; Rizzardo, E.; Thang, S. H. Living Radical Polymerization- A Third Update, *Australian Journal of Chemistry,* **2012**, 65, 985-1076.

P25

BiobasedPolystyrene-Like Polymer From Lignin Oligomers and SyringicAcid Derivatives

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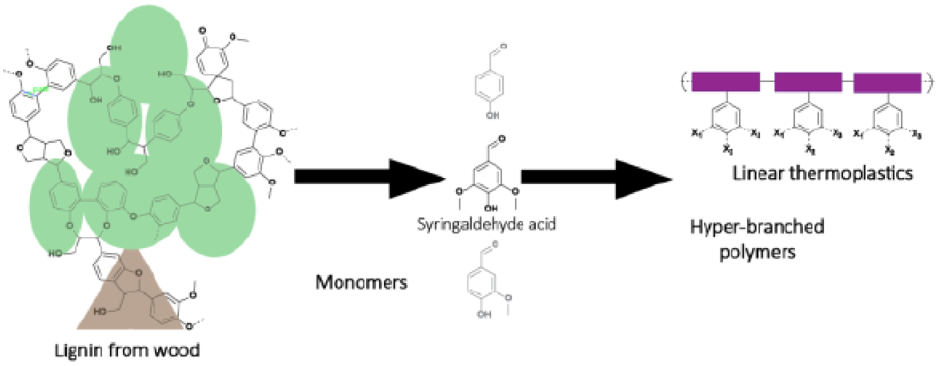
Lignin is the second most abundant renewable biopolymer which combined with cellulose represent over 70% of the worldwide biomass. It is also thefirst source of renewable aromatic compounds. Value added products from lignin are still very limited. Here, we aim at breaking down lignin into a series of small aromatic compounds, including variations of syringaldehyde, vanillin and 4-hydroxybenzaldehyde. These three aromatics compounds are themost promising biobased building-block value addedchemicals or polymers. In this work, syringic acid and its derivatives are studied for the synthesis of newhigh value addedbiobased thermoplastic polymers. The use of new type of chemistry that have never beenreported for lignin repolymerisationsuch as ADMET or thiol-ene chemistry.Different strategies were considered for monomer synthesis, including functionalizationthrough the phenol or carboxylic acid group.Few variations of polystyrene-like polymerfrom syringic acid presented most promising results, with molecular weight of up to million and compelling thermomechanical properties. This presentation will summarizes the success and learning of this research platform.



P26

Responsive Nanoparticles for Probing Cellular Behaviour

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P27

Well-Defined Water Based Acrylic Dispersions for VOC-Compliant Performance Coatings

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Abstract:

In this project, we prepared a novel self-stabilised poly(methyl methacrylate)-*co*-poly(butyl methacrylate) block copolymer emulsion for volatile organic compound (VOC) compliant coatings. A polymerisable macro-surfactant was synthesised by reversible addition-fragmentation chain transfer polymerisation (RAFT) as the emulsifier and the macro-RAFT agent for the chain extension reaction. Proton nuclear magnetic resonance (1H NMR) and gel permeation chromatography (GPC) proved that the conversion of the polymerisation reaction and the molecular weight distribution of the achieved copolymer were good. The particle size distribution and the amount of coagulum of the resulting emulsion were investigated by dynamic light scattering (DLS) and electron microscopy (EM). Atomic force microscopy (AFM) was used to evaluate the surface morphology of the latex film. The results show that the emulsion prepared by this method is well-defined, stable and it can form latex film with good quality.

References

1. (a) Ma, S. H.; Thang, S. H.; Rizzardo, E.; Moad, G. Aqueous dispersions containing cyclopolymer dispersants. US5571850 A, **1996**; (b) Thang, S. H.; Rizzardo, E.; Moad, G. Cyclopolymerization monomers and polymers. US5830966 A, **1998**.
2. Such, C. H.; Rizzardo, E.; Serelis, A. K.; Hawkett, B. S.; Gilbert, R. G.; Ferguson, C. J.; Hughes, R. J. Aqueous dispersions of polymer particles. US7745553 B2, **2010**.

P28

Polymeric Ionic Liquids for the Integration of Electrochemical and QCM Sensors

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In quest of accuracy and reliability for chemical sensors comparable to that of biosensors, the hyphenation of two highly successful probes in the sensing arena i.e., electrochemical (E) and QCM sensors, so as to obtain orthogonal signals has been utilized in this work and this setup is further enhanced by the application of polymeric ionic liquid materials. The prerequisites for this design include efficient immobilization of sensing materials, no interference and coupling between adjacent sensors, non-interfering instrumental setups, and correct interpretation of combined data. These prerequisites has been accomplished in the course of this work firstly by fabrication and testing of innovative inverted mesa EQCM structures and finalizing the mesa and electrode geometries. Then the actual methodologies of data extraction were established by combining nano-gravimetry to amperometric, voltammetric, and impedance analysis in various real life conditions. Various electrochemical control functions and the extension to impedance spectroscopy has extended the breadth of analysis for the accurate sensing systems for broad range of analytes including those that are not redox active. The final protocol was benchmarked against individual electrochemical and QCM sensing as well as GC-MS to assess the real benefits and the probability to succeed in the future product development. All the analysis results indicated that the polymeric materials such as poly-ionic liquids are hugely significant for such integration of multi transduction formats.

P29

Simple, Straightforward and Efficient Synthesis of Polyhydroquinolines Under Mild Reaction Conditions

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Organic synthesis involving green techniques is the main objective in present scenario therefore emphasis is being laid on the adoption of cleaner, safer and environmental benign reaction conditions avoiding the use of organic, volatile, harmful solvents for carrying out various chemical transformations in organic synthesis. Further heterocycles containing nitrogen have significance and gaining prominent position due to the fact that many of these carry out some physiological functions in living cells as well as used in industrial and pharmaceutical fields.

Among the various heterocycles, polyhydroqinolines posses interesting biochemical activities and are widely used as precursor for various natural products. So herein, we describe an environmental friendly, efficient, simple and straightforward pathway for the synthesis of polyhydroquinolines. The multiple component reaction involves condensation of ethylacetoacetate, dimedone, ammonium acetate and differently substituted arylaldehydes in specific ratio at room temperature. In view of this, great interest has been carried out on various chemical transformations under heterogenous conditions to have noteworthy recyclability. In this products are formed in single step with simple work up procedure. Among the reported methods, this proves to be a new innovative one step strategy which affords the desired products in much higher yields using zinc acetate as a catalyst. This procedure finds its applicablity as in it catalyst could be easily recovered via simple filtration technique, being simple in operation, high yield of products and avoiding toxic solvents making this method more convenient than previous ones.

P30

Novel Blood Compatible Ionically-Crosslinked Polyurethane Elastomers Modified with Sulfated Alginate

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In this study, we synthesized a novel anticoagulant polyurethane (PU) elastomer from polycaprolactone (PCL) diol, hexamethylene diisocyanate (HDI) and N-methyldiethanolamine (MDEA) and hydrophobized sulfated alginate. The chemical structure of both modified alginate and alginate-based PUs were confirmed using different spectroscopies of FTIR, NMR, EDX and elemental analysis. This polymer showed appropriate and tunable mechanical properties (ultimate tensile strength: 7 MPa and elongation at break up to 1000%) idealized it for tissue engineering of different tissues. These perfect mechanicalproperties are due to a chemical network of covalent interactions with a dual ionic network made by interactions between cationic urethane prepolymer (tertiary ammonium groups of acidified PUs) and anionic groups of alginate (i.e. carboxylate and sulfate groups). The synthesized bioelastomers showed a higher duration of anticoagulant activity compared to other samples (PCL, neat PU, and ePTFE prosthesis), up to 240 minutes, due to the presence of sulfated alginate interfering in blood clotting process. The polymer also shows lower platelet adhesion in compared to other samples. The toxicity of the polymers was tested by MTS assay. The obtained results proved that the synthesized bioelastomers can be biocompatible and non-toxic, with a defined structure, mechanical properties and anticoagulant activity. These features make this polymeras a suitable candidate to be used for different tissues or medical devices in the future.

Keywords: polyurethane elastomers, sulfated alginate, anticoagulant property.

References

1. Daemi, H, Rajabi, S, Sardon, H, Barikani, M, Khademhosseini, A and Baharvand, H. A robust super-tough biodegradable elastomer engineered by supramolecular ionic interactions, *Biomaterials*, **2016**, 84, 54-63.
2. Arlov, Ø, Lillelund, F, Sundan, A, Espevik, T and Skjåk-Bræk, G. Heparin-Like Properties of Sulfated Alginates with Defined Sequences and Sulfation Degrees, *Biomacromolecules,* **2014**, 15, 2744−2750.

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Extraction of Marine Mollusc polymer and Development of Nanoparticulate Formulation of Ofloxacin

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The main objective of the present research work is to prepare the nanoparticles for the sustained delivery of Ofloxacin which possess less biological half–life. Studies have been carried out on the preparation of nanoparticles with ink of Cuttle fish (*Sepia*) belonging to the marine mollusc *Sepia officinalis*. The selected nanoparticle formulations i.e. OF6 were subjected to *In-Vivo* pharmacokinetic parameters viz. elimination rate constant, absorbtion rate constant, AUC, C max, T max and biological half life. *In-Vivo* drug analysis generally showed good release profile in a sustained manner as detailed below. The OF6 formulation with the particle size 1000 nm showed 87.00% release at the 24th hour. The physico-chemical characteristics of the polymer, *Sepia* (Cuttle fish ink) used in the preparation of nanoparticles of Ofloxacin showed that it is non-toxic and biocompatible. In the kinetic release studies, on changing the drug–polymer ratios, a significant change could be noticed in the release profile of the drugs experimented. The zeta potential values for all the selected formulations were positive. The results further showed that there was a good entrapment and more than 60% of the drugs was found to be entrapped in the above said drug formulation. The stability parameters studied as per the ICH guidelines. The IR studies of physical mixture showed that there was no interaction between the drug and polymer. The formulation OF6 were therefore considered as good oral-controlled release formulation of Ofloxacin.

References:

1. Charles D. Derby Escape by Inking and Secreting: Marine Molluscs Avoid Predators Through a Rich Array of Chemicals and Mechanisms Biol. Bull. 213: 274 –289. (December 2007)
2. Lamprecht.A, Biodegradable monodispersed nanoparticles prepared by pressure homogenization emulsification, Int.J.Pharm. 184(1999) 97-105.
3. Kayserl. O, The impact of Nanobiotechnology on the development of new drug delivery systems, Current pharmaceutical biotechnology 6,2005,3-5.