# Emerging Polymer Technologies Summit 2016

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# Book of Abstracts

14 – 16 December, Melbourne, AUSTRALIA

# Abstracts of the
# PLENARY LECTURES

# Living Radical and Living Cationic Polymerizations: Emerging Technology for Precision Functional Polymers

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This lecture will discuss the development of two precision (living) polymerizations (Fig. 1), not simply to look back the past but to look forward to the future of polymer chemistry: The first Lewis acid-catalyzed living cationic polymerization in 1984; the first metal-catalyzed living radical polymerization in 1995. Their discovery has triggered a vivid revitalization of the fields, extensive efforts for precision polymer synthesis (Fig. 2), and a worldwide development of precision polymer materials therefrom (Fig. 3). A current focus of interest for the future is directed to the precision sequence control on macromolecules of carbon backbones (Fig. 4): Why has nature adopted mostly heteroatom-backboned macromolecules for biopolymers?

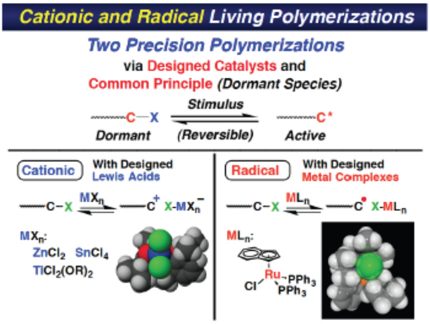


**Fig. 1.** Two living polymerizations.

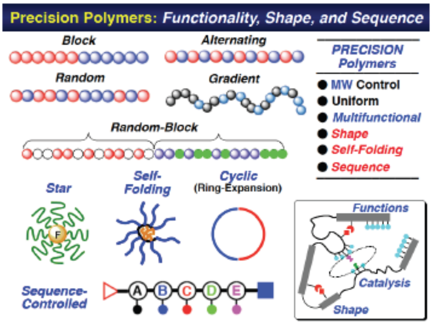
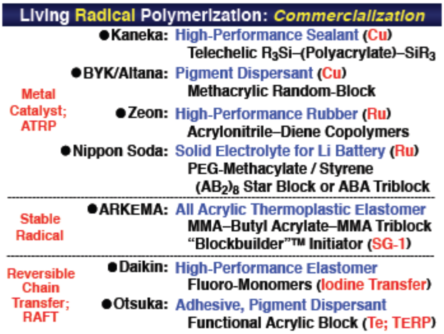


**Fig. 2.** Precision functional polymers.


**Living Radical Polymerization: Commercialization**

Metal Catalyst; ATRP

- **Kaneka:** High-Performance Sealant (Cu)
  Telechelic $R_3Si$–(Polyacrylate)–$SiR_3$
- **BYK/Altana:** Pigment Dispersant (Cu)
  Methacrylic Random-Block
- **Zeon:** High-Performance Rubber (Ru)
  Acrylonitrile–Diene Copolymers
- **Nippon Soda:** Solid Electrolyte for Li Battery (Ru)
  PEG-Methacylate / Styrene
  $(AB_2)_8$ Star Block or ABA Triblock

Stable Radical

- **ARKEMA:** All Acrylic Thermoplastic Elastomer
  MMA–Butyl Acrylate–MMA Triblock
  "Blockbuilder"™ Initiator (SG-1)

Reversible Chain Transfer; RAFT

- **Daikin:** High-Performance Elastomer
  Fluoro-Monomers (Iodine Transfer)
- **Otsuka:** Adhesive, Pigment Dispersant
  Functional Acrylic Block (Te; TERP)

**Fig. 3.** Commercialization efforts.

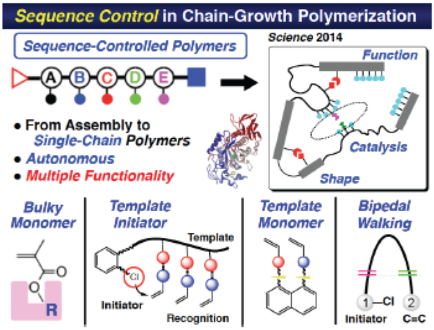


**Fig. 4**. Sequence-controlled polymers

# Albumin-Micelles via a one-pot Technology Platform for the Delivery of Drugs

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Abraxane©, in an injectable formulation of paclitaxel where the drug is bound to albumin as a delivery vehicle (nab technology). This is one of the few nano-formulations that have made it on the market today. The secret of this technology developed by Desai and co-workers lies within the simplicity of the approach while being highly effective during treatment of cancer. The nab technology produces particles has however disadvantages as it is not suitable for hydrophilic drugs and does not allow particle size modifications. We have adopted a new strategy by employing polymer-albumin conjugates. The attached polymer determines the interaction with the drug allowing fine-tuning the system for any drug delivery problem. This technique was tested on hydrophobic drugs, metal-based drugs and nucleic acid drugs [1]. In this presentation, we will discuss conjugation strategies between polymer and albumin and the self-assembly process into nanoparticles. These nanoparticles are loaded with various drugs and tested using various cancer cell lines.

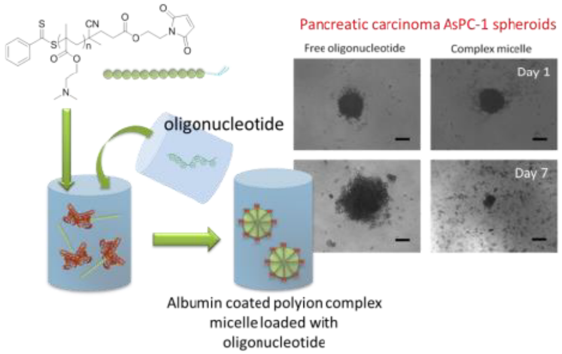

**Fig. 1**. Synthesis of albumin-based drug carrier

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# Oversight of the Printed Organic Solar Cell Project in Victoria, Australia

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In this presentation I shall summarise the progress made in the Victorian Organic Solar Cell Consortium towards the development of modules of fully printed solar cells. The programme involved assembling a team of chemists, physicists and engineers to work collaboratively at the interface of their disciplines to realize a common goal. The team started with computational design of light harvesting and electron transporting materials, and systematically examined their physical and optoelectronic properties. Those materials that met the selection criteria were taken further in evaluation of laboratory bulk heterojunction, dye sensitised solar cells and perovskite solar cells. Selection of the most promising devices allowed translation to evaluation in fully printed modules. Device efficiencies and module lifetimes were measured under ambient operating conditions.

# Arranging polymer materials for enhanced performance 3D printing, spinning, knitting and braiding

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For decades we have built mountains of knowledge allowing us to synthesise polymer materials with predesigned function from the molecular level. This has allowed us to create polymers that conduct electricity, can act as artificial muscles, are capable of drug release and even tuned to interact with specific living cells.

However, during those same decades it seems fundamental breakthroughs in research laboratories and the building of manufacturing industries were on diverging pathways. Somehow, the link between advances in science and engineering and fabrication were lost creating a void in our ability to realise practically useful structures and devices.

Well that has all changed!

The advent of additive fabrication enables diverse materials to be integrated to deliver useful systems. The impact of this dramatic change on our ability to create wearable and implantable technologies based on polymers will be illustrated.

3D printed implants for tissue regeneration based on a combination of polymer components and living cells will be presented.

Fundamental advances in science and engineering have re-engaged with our ability to make stuff.

The ability to create is back in the hands of the creative!

# Building the polymeric platform technologies

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Conventional polymers are normally produced in a linear form. With the development of controlled chain polymerization methods, synthesis of polymers with different architectures becomes possible. New architectures can be made as block, star, multi-star, branched, tree-like, brush polymer or thin film forms. When different architectures made from biomacromolecules, these new materials can deliver new properties. There is a clear link between the macromolecular architecture made under a specific method and the function of the final products that material can provide in applications.

This presentation will introduce our recently developed platform technologies based mordent polymer chemistry. The examples will be photo-induced controlled polymerization using RAFT agent, Continuous Assembly of Polymer (CAP) technology, which creates macromolecular architectures in 3D forms. The 3rd example is peptide-based star polymer and their anti-bacterial activities. Specific examples will be presented for these platform technologies and Figure 1 illustrates one example indicating RAFT polymerization without using initiator under visible light at room temperature.

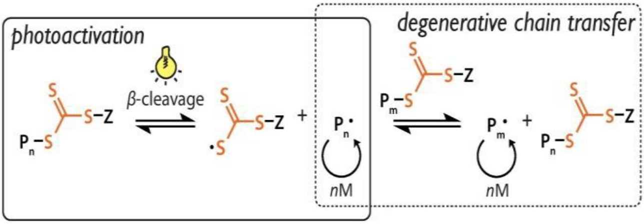

*Figure 1. Blue LED induced controlled polymerization without initiator and catalyst.*

## Breaking Moore's Law

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The semi-conductor and storage industries are governed by Moore's Law, an extrapolative observation made by Gordon Moore where the areal density of elements on a chip increases by a factor of two every year. Both industries, using primarily "top-down" photolithographic processes, face the inevitable limitation of optical resolution in dictating the minimum feature size achievable. While the wavelength of the radiation can be reduced, the sensitivity of the photoresists and the high vacuum conditions required, as the wavelength decreases out of the visible wavelength range, place severe restriction on the minimum size scale and, hence, maximum areal density achievable. Block copolymer thin films, having arrays of ultra-small domain size and pitch, can significantly increase the areal density of elements and can be used as templates or scaffolds for high-resolution nanofabrication. Yet, even this molecular, "bottom-up" approach, the most promising strategy to date, has its limitations. Achieving a sub-10 nm pitch has been a challenge using the self-assembly of block copolymers, due to the phase mixing of the copolymer domains as the copolymer transitions from the ordered into a disordered state. One strategy to overcome this limitation is to use *entropy*, as opposed to enthalpy, to one's benefit and vary the chain architecture, reducing possible molecular configurations. Using star block copolymers the multi-arm star architecture is shown enhance the ordering in block copolymers, enabling the generation of nanostructures on size scales smaller than currently possible. Multi-arm star block copolymers require a lower segregation strength to maintain an ordered state when compared to diblock copolymers, providing ordered nanostructures with periods well below 10 nm. An alternate strategy is to use *enthalpy* and increase the segmental interaction parameter. Here a simple diblock can be hydrolyzed in the solid *state* to massively increase segmental interactions. This chemical conversion structurally transforms a phase-mixed block copolymer into a highly ordered array of domains 3 nm in size, the smallest ever achieved. This morphogenesis can be used to generate materials that are easily processible and enable the generation of structures of even smaller limits, breaking, in fact exceeding Moore's Law for the areal density of elements.

## Industry-driven polymer research in a Cooperative Research Centre

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The Cooperative Research Centre for Polymers (CRCP) has been funded since 1992 by the Australian Government's Cooperative Research Centre Programme. It has establishedindustry-lead and outcome-focused partnerships between industry and research organisations toconduct high quality research and solve industry problems. During that time, 24 companies, 14 universities, 3 Government research organisations (CSIRO, ANSTO and DSTO),and 7 end users have been participants in the CRC. Its activities have included more than 43 projects of at least 3-years duration,and their commercial outcomes have included 45 patent applications, 18 licence agreements and 3 spin-off companies.

The presentation will explain the unique role of CRCs in the Australian innovation system, and the practices that have evolved in the CRCPfor identifying high impact projects through discussions with companies, assembling high performing teams to conduct the research,and ensuring that the prospects of successful commercial outcomes are maximized.

TheCRCPmethodology willbe exemplified by drawing on illustrative case studieswhich show how these practices have been applied,and the resulting polymer science and technologies that have been developed.The CRCP's researchhas developed products for a wide range of applications. The common challenge has been tailoring the architecture and compositions of polymers to provide the novel properties required by companies. Earlier phases of the CRCP focused on modifying the properties of commodity polymers to meet the needs of the plastics industry. The activities evolved to developing functional polymers tailored to meet the needs of companies operating in many sector of the economy including: health, mining, agricultureandenergy,as well as manufacturing. During its current period of funding the CRCPis seeking to establish Australian manufacturing as a leading provider and exporter of products that meet emerging global needs in three areas -health therapies and delivery, water and food security, and low-cost solar energy -using enabling and sustainable advanced polymer technology.

# Commercialisation of public research innovation projects that use Controlled Radical Polymerization (CRP): Networks, Intellectual Property and Business Models

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Technological innovation is defined as inventing a product and taking it to market. While having a “great idea” is essential and important, alone it is not sufficient to result in commercialisation. Innovation is a social process that depends upon the building of relationships resulting from substantial search endeavours, but which is also highly dependent on the ability to exploit knowledge and agreement around the business model among the innovation partners.

However, there are inherent tensions and difficulties in the innovation process which relate to issues of networks, intellectual property (IP) and also business models can constrain the process of innovation, particularly when the commercialisation is of public research. For example, a major impediment is that commercialisation of public research requires the coming together of two very different communities of practice – public research organisations and private firms – each with their own values, measures of worth, language, hierarchy and business models. The ability of public research organisations (PROs) to understand the commercial imperatives of private firms is also key, as is the firm’s ability (or inability) to gain full advantage of IP. Using the latest advances in statistical models for multilevel social networks, and in-depth interview data, the presentation will detail the important substructures of collaboration networks with respect to the innovation process. This presentation examines innovation projects at multiple sites around the world that involve the use of Controlled Radical Polymerisation (CRP, i.e., techniques for reversible deactivation radical polymerization like RAFT, ATRP and NMP). Networks, both personal and organisational, between research institutes who specialise in CRP and firms who wish to apply CRP to innovate will be discussed with respect to commercialisation success. Particular focus will be given to the various networks of collaboration, advice and trust amongst PROs worldwide. It is noted that PROs have significantly different business models when engaging with firms which may have important implications for commercialisation outcomes. Lastly, the exploitation of IP is a particularly important issue to firms that is perhaps not as well understood by PROs as it should be, which may significantly hinder the commercialisation of innovation projects that use CRP, and thus the global uptake of products, processes and services that utilise CRP.

# Multiscale Simulations for Soft Matter: From Molecular Details to Technically Relevant Properties

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The relation between atomistic structure, architecture, molecular weight and material properties is of basic concern of modern soft matter science. A typical additional focus is the relation between structure and function in nanoscopic molecular assemblies. Here computer simulations on different levels of resolution play an increasingly important role. This is achieved by two different approaches, namely by sequential multiscale descriptions or adaptive schemes, which allow for a free exchange of particles (atoms, molecules) between the different levels of resolution.
A typical application for adaptive schemes is the solvation of smart polymers in mixed (good) solvents, called co(non)solvency, while structure formation of polymeric materials, e.g. for organic electronics, has been studied by a sequential scheme.

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# Designing polymers for cell culture and safer implantable devices

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Materials scientists are starting to tackle the key issue of the size of materials space– the number of materials such as polymers that could be made using accessible starting materials and known reactions. Clearly, there are almost an infinite number of such materials. Although materials high throughput synthesis and testing facilities like the RAMP centre at CSIRO[1] will make a strong impact, these methods alone will not find all useful polymers and other materials in a vast sea of possibilities.

Computational methods simulate, model, and predict polymer properties orders of magnitude faster than any automated experiments[2]. Coupled with recent developments in in silico deep learning and Darwinian evolution, a paradigm-shift in materials discovery emerges[3]. We will describe these new computational developments and provide two case studies showing how they accelerate the discovery of polymers for stem cell culture, and polymers for implants that resist bacterial biofilm formation[4-6].

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# Cascade synthesis of nanoparticle-polymer composites

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Organo-transformations executed through cascade synthesis imitate Nature by combining multiple reactants and / or catalysts in a single “pot” with multiple sequential or tandem reaction steps generating a complex target molecule. While the application of cascade concepts has received significant interest in natural products chemistry, notably fewer reports have been made applying this methodology for the production of polymeric nanomaterials. The multi-step, cascade synthesis of self-supporting, hierarchically structured nanoparticle hydrogel composites will be discussed. Composites are prepared in two ways. The first approach employs non-covalent, lamellar lyotropic mesophases composed of amphiphiles (lipids and co-surfactant) that support the reactive constituents, a mixture of hydroxyl- and acrylate- end-derivatized triblock copolymers and a suitable metal ion. The reaction sequence begins with the auto-reduction of the metal ions by the triblock copolymer which leads to both the production of nanoparticles and a transition metal redox cycle which serves to catalyse the acrylate end-derviatized polymer to yield a network polymer. The second system uses a ionic liquid amphiphilic monomer, with a mixture of a PEG and PEG-diacrylate. Optical spectroscopy and TEM monitored the reduction of metal ions and evolution into nanoparticles. ATR/FT-IR spectroscopy and thermal analysis confirms acrylate crosslinking to yield the polymer network. X-ray scattering (SAXS and WAXS) monitored the evolution of structure and revealed the presence of confined semi-crystalline PEO/PEG. The resultant hydrogels can be reversibly swollen without loss of the well-entrained nanoparticles with full recovery of composite structure. Optical spectroscopy probes solvent-state modulation of the surface plasmon resonance, demonstrating solvent-mediated modulation of the internal NP packing arrangement.

# RAFT (co)polymerization of the conjugated diene monomers

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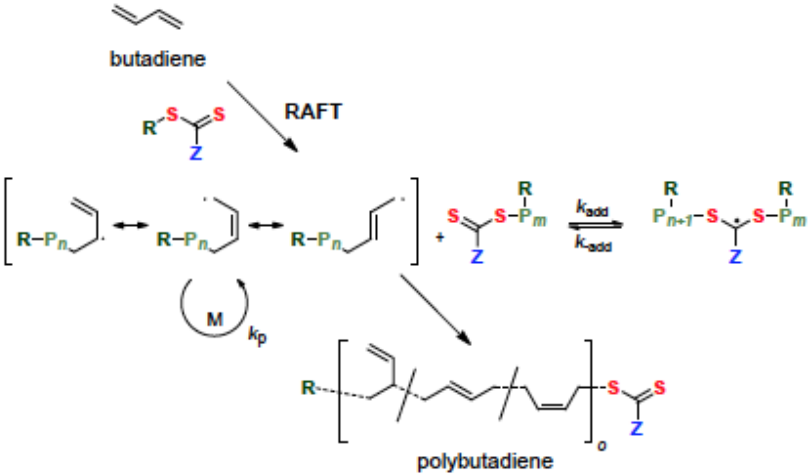
This paper will discuss reversible addition–fragmentation chain transfer (RAFT) (co)polymerization of industrially significant conjugated diene monomers, specifically butadiene, isoprene and chloroprene with a focus on polymerizations performed in heterogeneous media. The goal common to most recent work in this area has been to define the polymerization conditions necessary to minimize crosslink formation, thereby providing a low-dispersity polymer with defined architecture and composition while, at the same time, achieving an acceptable (i.e. maximizing) monomer conversion and polymerization rate. Several strategies will be considered.



## References

G. Moad. RAFT (co)polymerization of the conjugated diene monomers: butadiene, isoprene and chloroprene. *Polym. Int.* **2016,** *Ahead of Print*, doi: 10.1002/pi.5173.

# Abstracts of the
# CONCURENT SESSIONS

# Concurent session 1 - Polymer synthesis

## Organocatalyzed Living Radical Polymerization: Synthetic Technique and Application to Materials

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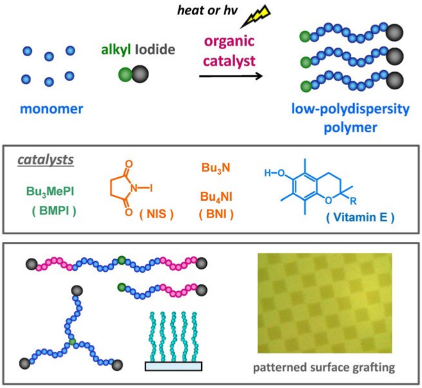
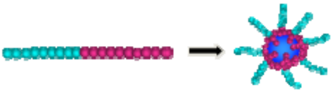
Living radical polymerization has attracted growing attention as a useful and powerful technique for preparing architecturally controlled polymers. We have developed living radical polymerization via organic catalysis.[1] This system is the first living radical polymerization for the use of non-metal catalysts. The catalysts are commercially available inexpensive organic molecules. The polymerizations are easy to operate, amenable to a variety of monomers and polymer structures, controlled by both thermal heating and photo irradiation, and hence useful for a variety of polymer material designs. This polymerization is now commercially used to produce block copolymers for pigment dispersion in industry. The reaction mechanism, macromolecular design, and applications to materials will be presented.





## References

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## Amphiphilic RAFT Polymers as Biofilm-Busting Antimicrobials

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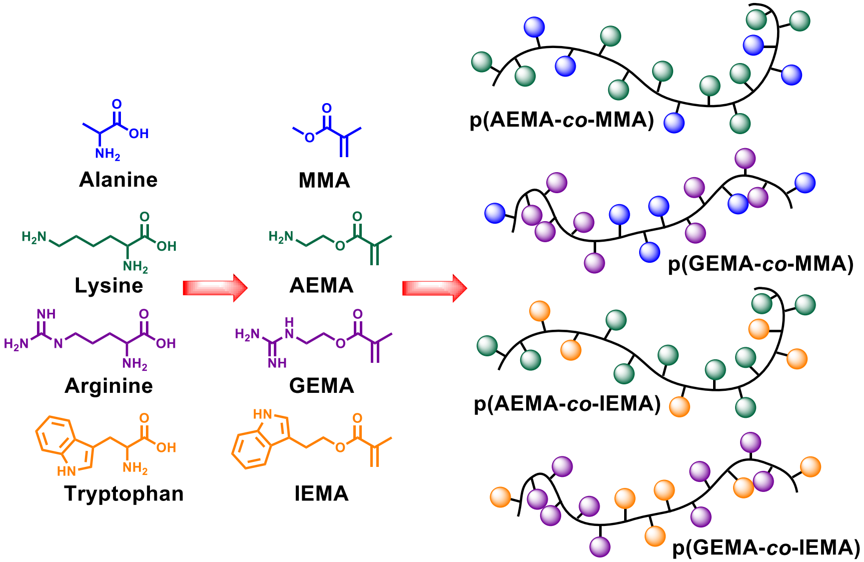
Naturally occurring antimicrobial peptides (AMPs) have been honed by evolution over millions of years to give highly safe and efficacious antimicrobials. Their movement from the bench to clinic is yet to be realised, however, due to the limitations of these peptides as drugs.

Our work focusses on finding ways to capture the essential features of these peptides using polymers. These polymers are not only able to incorporate the global structural features of these peptides in a polymethacrylate construct (e.g. high cationic charge and low molecular weight), but also mimic specific amino acids that are key to peptide activity (e.g. lysine, arginine, tryptophan).

Extensive structure-activity studies have been performed to identify optimised polymer candidates that show potent activity against bacteria (eg. MIC = 10 µg/ml for *S. epidermidis*), fungal strains (eg. MIC = 2 µg/ml for *C. albicans*) and low toxicity towards human blood cells. These patented polymers have also highly effective agents against single and mixed biofilms of *S. aureus* and *C. albicans*. A single optimized candidate, PG4, for instance, was able to eradicate 94% of *S. aureus* and 80.3% of *C. albicans* cells at a concentration of 128µg/ml, well outperforming gold standard antibiotics tested at 10 times this concentration. This unique biofilm-busting activity identifies our cationic polymethacrylates as important leads for the development of a new generation of antimicrobial agents to tackle microbial resistance.



# Scaling up hemicelluloses production: a source of xylan-based building-blocks for functional biomaterials

Julien Rosselgong Saint-Amans[1], Maud Chemin[1,2], Frédérique Ham-Pichavant[1,2], Maud Coloignier[3], Guillaume Chollet[3], Denilson da Silva Perez[4], Gilles Labat[4], Henri Cramail[*,1,2], Stéphane Grelier[*,1,2] Sébastien Lecommandoux[*,1,2]

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Knowing that the fossil fuel available on earth will be spent in the foreseeable future and that oil prices will raise sharply, the development of new chemicals from renewable resources is nowadays a strategic research area. Within the last two decades, there has been a growing interest in lignocellulosic biomass, which is a sustainable resource to produce fuels, chemicals, and materials[1]. Contrarily to cellulose that is the most industrialized polysaccharide, woody hemicelluloses are less valued. The most abundant hemicellulosic polymers are xylans – essentially linear heteropolysaccharides (Fig. 1) - accounting for 25-35% of the dry biomass of woody tissues. Extensive literature data report on the isolation, characterization, derivatization and applications of xylans[1-5]. Moreover the chemical modification and the degradation of hemicelluloses into oligosaccharides are still a challenging task and would open the route to biomacromolecular engineering.

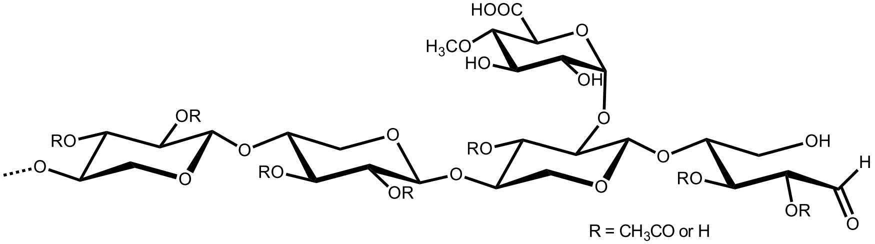

**Fig. 1: Chemical structural formula for O-acetyl-(4-O-methylglucurono)xylan**

This work aims at studying chemical modification through periodate oxidation[6] and acidic hydrolysis[7] of xylan from beechwood. More precisely, the periodate oxidation of xylan at a rate of 0.2 NaIO4/xylose leads to 5-6 oxidized units per chain, bringing new aldehyde functions in a controlled manner. Sulfuric acidic hydrolysis leads to well-defined oligomers with an average of six xylose units per chain and with an aldehyde group at the reductive end[8,9]. Reductive amination was used on the aldehyde functions of xylan derivatives to functionalize them, either with a double bond or with an azide function. Click chemistry will then open the route to macromolecular engineering and thus new opportunities to valorize this high potential bio-resource as functional materials. A scale up of the hydrophilic block will allow a potential large library of amphiphilic block copolymers to be made with different types of applications.

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# Utilising reversible deactivation radical polymerization for the rational design of structured polymeric interfaces

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On many substrates, polymer surface coatings used to control wettability or chemical functionality are unstable or meta-stable. Under appropriate conditions, the polymeric film will break apart via a process known as dewetting. Polymers such as polystyrene (typically prepared via anionic polymerization) have previously been used to study this phenomenon, specifically the influence of molecular weight and melt viscosity.

We have taken advantage of the phenomenon of polymer thin film dewetting and, combined with reversible addition fragmentation chain transfer (RAFT) polymerization, used these methodologies to design specific patterned polymeric interfaces. These surfaces possess both chemical and topographical contrast, and have been used in specific applications such as atmospheric water harvesting and spatial control of biomolecules.[1-3] The control over molecular weight, dispersity and hence melt viscosity via RAFT is crucial for rational surface design. The simplicity of both polymer synthesis and surface preparation holds promise for future materials science applications where such structured surfaces are desired.

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# Synthesis and Evaluation of Star-Like Polyacrylamides for Enhanced Oil Recovery (EOR)

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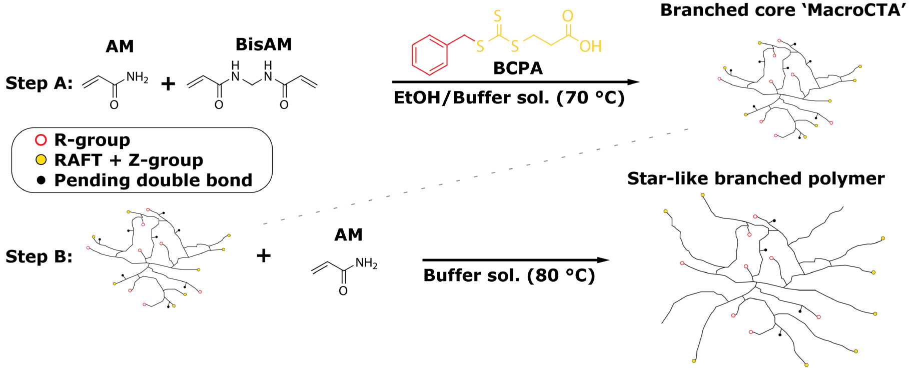
Star-like branched polyacrylamides (SB-PAMs) were synthesised by RAFT copolymerization of acrylamide (AM) and a bifunctional monomer (BisAM), followed by chain extension. The amount of BisAM and the addition of AM during chain extension have been systematically varied. The obtained macroCTAs had MWs in the range of 2.2 - 7.8 x $10^3$ g/mol and polydispersity indices between 1.2 and 15.1. Variations in the AM addition during chain extension revealed the presence of progressing longer arms upon higher AM additions. Rheological measurements showed unique properties for the SB-PAMs, as those are more robust under shear and more tolerant to salt than their linear analogues. EOR performance was evaluated by simulating oil recovery performance in a 2-dimensional flow cell. The latter experiments displayed that SB-PAMs perform approximately 3 times more efficient than their linear analogues in recovering residual oil out of dead ends. High salt concentrations did not degrade the solution viscosity of the SB-PAM, contrary to commercial hydrolysed. Thus, SB-PAMs are more resilient under harsh reservoir conditions, making them attractive for application in EOR.



Acknowledgement: This research forms part of the research programme of the Dutch Polymer Institute (DPI), project #778

# Concurent session 2 - Polymers for medical and biological applications

## Amphiphilic Core-Shell Nanoparticles as Emerging Nanomaterials for Biological Applications

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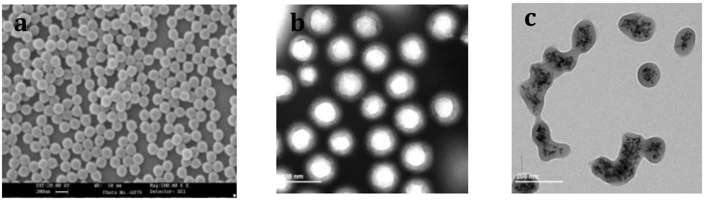
Nanoparticles are increasingly employed in medicine and biology as sensors, image contrast agents and drug delivery vehicles. Processes at the interface between nanoparticles and the biological environment determine the performance, behaviour, fate and potential toxicity of the particles. Understanding and controlling particle surface chemistry and interfacial processes are therefore critically important. In this presentation, three types of nanoparticles including nanocarriers for gene delivery; magnetic-responsive nanocomposite particles for MRI diagnosis; and polymer-based fluorescent nanoparticles for cell imaging will be highlighted. Our results demonstrate that these novel types of nanoparticles are promising theranostics agents for future nanomedicine.

a) Highly uniform polymer particles; b) Amphiphilic particles with well- defined core-shell nanostructure; c) Amphiphilic composite particles containing magnetic nanoparticles in the cores.



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# Thermogelling Polymers – An Emerging Biomaterial for Biomedical Applications

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Rapidly aging societies, demands for improved organ functions and repair of damaged tissues has led to the use of synthetic materials in different parts of the human body. Traditional covalent chemistry has served us well in terms of the design of materials. The future of soft biomaterials demands ease of synthesis, multi-functionality and efficacy. Supramolecular hydrogels are part of the next-generation of materials to enter the biomedical arena. These materials are three-dimensional entities built from crosslinking agents, which bond non-covalently (via hydrogen bonds, π–π stacking and van der Waals interactions) to produce fibers and crosslinking among fibers.

Thermogelling polymers are a unique class of materials that have the ability to undergo a sol-to-gel transition when the temperature of the solution is raised. [1-6] This change is reversible and has been the subject of intense research in the last decade. These materials have been used for drug delivery, gene delivery and tissue engineering. New design strategies for thermogelling polymers have emerged in recent years. The properties of these materials are vastly different from their covalent counterparts and the exciting developments are summarized in this talk. I will also provide updates on new fluorescent, photo-responsive as well as new in vivo results on cancer drug delivery using these thermogels.

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# Biopolymer microhydrogels as injectable vaccine delivery systems showing persistently high antibody levels

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Polymeric materials are playing an increasing role in the effective delivery of therapeutic agents including advances in immunological functions associated with vaccination. Additionally, devices such as osmotic pumps and implants are being developed to overcome the multiple dosing frequently required to establish and maintain protective immune responses. Here, non-compliance represents a significant constraint to effective health care in many populations, while in animal welfare it represents a significant economic burden to communities. We have shown previously that (i) biopolymer derived nano- and microparticles control vaccine trafficking and cell uptake thereby modulating ensuing immune responses, and (ii) a degradable biopolymer vaccine depot induces high levels of antibody persistently to 1 year in mice, advancing delivery device technologies towards single injection polymer based options.

Here, we now show that biopolymer microhydrogels can be synthesized to contain protein antibodies during crosslinking that are capable of being delivered to intercellular pathways and that this immunoactivity can be further enhanced by their linking co-stimulatory moieties to the gel network. The protein antigen forms an equilibrium with the aqueous system associated with each microhydrogel which is maintained by forming a stable water-in-oil emulsion with a hydrophobic adjuvant oil. In this study, we investigate the microstructure and stability of this polymer hydrogel-in-oil emulsion through microscopy and rheology and illustrate the persistent high levels of immunological response of this single injection emulsion vaccine compared injected conventional analogues in large animals over 6 months.

# Enabling Non-viral Technologies for Genome Editing

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Non-viral gene delivery systems promise to be the long-term future for delivering gene therapies in vivo in a safe and controllable manner. However, non-viral vectors commonly sacrifice gene delivery efficiency for reduced toxicity, struggling to deliver the genetic payload to particular cell lines. Additionally, recent development in genetic and epigenetic engineering is largely reliant on the use of large plasmids such as those encoding for CRISPRs or TALEs, where packaging and delivery efficiency decreases further. Therefore, clinical implementation of these technologies is inhibited, as safe and effective delivery of all therapeutic components to the nuclei of the target tissue remains a challenge. Here we will describe the design and synthesis of a novel dendronized polymer, and the translation and optimisation of the developed agent to an in vivo model. We will demonstrate how the agent can deliver multiple and large DNA plasmids more efficiently in vitro than the current gold standard, Lipofectamine 2000. Next we will discuss the effect of fluorination on enhancing transfection efficiency and serum resistance. Finally, we will demonstrate the upregulation of a tumour suppressor gene by delivery of CRISPR and TALEs, yielding a functional outcome in both in vitro and in vivo settings. These experiments will provide critical insights into how our polymer formulation represents a new class of highly efficient agents as we move towards the development of non-viral gene therapeutics.

# Photo-modulated Ocular Drug Delivery of Biomacromolecular Therapeutics

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Age-related macular degeneration (AMD) is the leading cause of blindness in Australia today.1 The only way to save vision requires ongoing invasive monthly injections of biomacromolecular anti-angiogenics to the eye.2 A drug delivery reservoir which enables sustained 'on-demand' release of therapeutics would be beneficial, since it will significantly reduce the number of injections into the back of the eye.3 Here we report the fabrication of a photo-responsive drug delivery system based on a thermo-responsive polymer containing light sensitive nanoparticles and therapeutic payloads(Fig. 1). Released biomacromolecules exhibited above 85% retention of their biological activity. The formulation did not show *in vitro* toxicity to ocular cells, and can be injected subconjunctivally through a 30-gauge needle. Due to its minimum toxicity, tuneable drug release rates and high versatility, this photo-modulated drug delivery system has a potential to improve the treatment of ocular diseases.

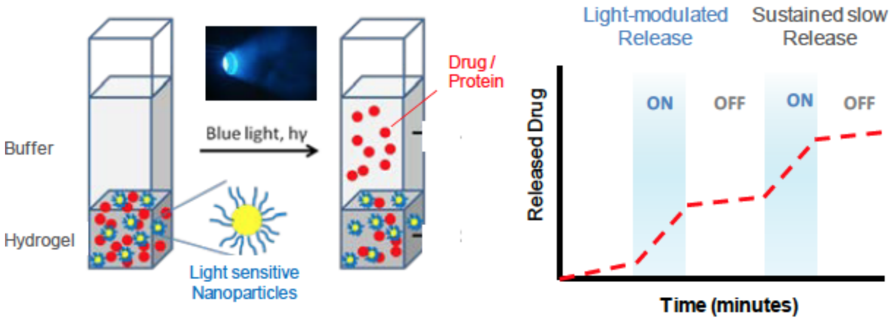

**Figure 1**. Schematic representation of photo-modulated drug/protein release from the hydrogen, and the release profile of the drug into the buffer in the absence (OFF) and presence of light (ON).

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# Concurent session 3 - Electro materials

## Synergisms Between Molecular Design and Materials Processing for Flexible Devices

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Printed, flexible electronics are potentiallow cost alternatives for devices in a range of industries including health care, security, and energy. Deviceperformance depends critically on semiconducting polymer structure; but importantly, electronic characteristics are closely tied to process parameters which govern alignment at the nano-through macro-scales. Significant structure-process-property relationships facilitatingenhancement of long-range order will be described. For instance, poly-(3-hexylthiophene) (P3HT)exhibitsalyotropic liquid crystalline phase duringsolvent-evaporation induced self-assembly. Further, aggregation and orientation of the polymer in solution can be facilitated by a number of techniques that take advantage of kinetic and thermodynamic factors. From the perspective of molecular design,incorporation of branched side chainswiththe branching position beingremote from the polymer backbone merges the advantages of improved solubility with effective π–π intermolecular interactions normally associated with linear chains on conjugated polymers. Such effects can significantly impact the device performance of a wide range of conjugated polymers, particularly donor-acceptor systems. Theinsightsobtained through studiesaimed at linking molecular design to materials processing may allow for simple, controllable, and cost-effective methodologies for achieving high performance in plastic electronic and photovoltaic devices.

# Electrospinning of piezoelectric nanofibre webs

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Electrospinning offers a simple but efficient approach to directly produce piezoelectric nanofibres. The high electric field intensity and intensive fibre stretching during electrospinning contribute to high *β* crystal phase content and oriented electric dipoles within electrospun nanofibres. These allow randomly orientated nanofibre webs to have strong mechanical-to-electric conversion ability[1]. Nanofibre webs with an interconnected fibre structure show not only improved energy conversion efficiency but also increased mechanical strength and structure integrity[3]. Piezoelectric nanofibres can even convert acoustic waves and noise into electricity with a large power output (**Fig. 1**)[4]. Needleless electrospinning is efficient to produce piezoelectric nanofibres on a large scale with enhanced energy conversion behaviors[4]. This talk gives the background and state-of-the-art of the piezoelectric nanofibre research undertaken mainly in the Institute for Frontier Materials, Deakin University.

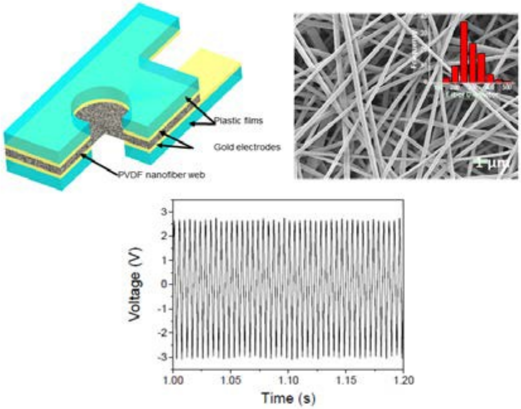

**Figure 1**. Nanofibre device for conversion of acoustic waves into electricity (left up), morphology of the nanofibres under SEM and histogram of the fibre diameter distribution (right up), and voltage output of the device under sound.

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# Compartmentalised Polymer Architectures as Templates for Uniform Hybrid Nanomaterials

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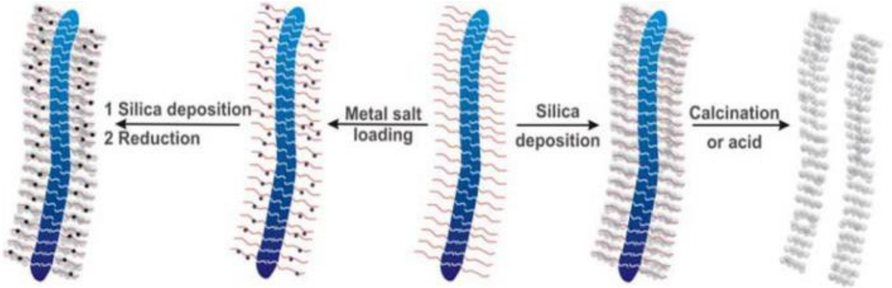
Hybrid nanomaterials, such as nanowires and nanotubes, have attracted immense interest as building blocks, interconnects and functional units in the fabrication of electronic, optoelectronic and electrochemical nanoscale devices. The template-directed production of hybrid nanomaterials is becoming increasingly straightforward using polymer architectures with distinctly separated reaction domains.
This talk will highlight the use of tailor-made polymer architectures and their use in the fabrication of anisotropic hybrid nanomaterials.



**Scheme 1**. Cylindrical polymer templates can be used to produce hybrid nanotubes.

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# Designing Organic and Aqueous Processable/Compatible Conjugated Polymers for Charge Storage

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Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly stable electroactive polymer used in a variety of applications ranging from electrochromics, to charge storage, to biomedical materials. In order to obtain a polymer that can be solution processed, but retains the desirable properties of PEDOT, specifically its high capacitance, we have designed and prepared a series of soluble polymers by copolymerizing EDOT with solubilizing 3,4-propylenedioxythiophene derivatives in varying ratios via direct arylation polymerization. Using the optimized structures/ratios obtained, we functionalized the polymers with ester side chains to allow chemical defunctionalization of the polymers through hydrolysis to yield conjugated polyelectrolytes that are readily soluble in water. Post processing functionalization of the polymer film using dilute acid creates a solvent resistant film that is compatible with both organic and aqueous electrolyte solutions for redox switching. Devices of these polymers demonstrate exceptionally rapid switching (up to 10 V/s) compared to similar polymers using typical aliphatic side chains in both organic (LiBTI/PC) and aqueous (LiBTI or NaCl/Water) electrolyte solutions.

# Concurent session 4 - Polymers for medical and biomedical applications

## Biochemically Active Nanostructures Incorporating Macromolecular Gasotransmitter Donors

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Cell signaling processes are important in a range of physiological events ranging from vasodilation to cell proliferation.[1] As such, materials that can mediate such signaling processes may be extremely useful. This presentation will describe our recent work on the synthesis of novel macromolecules capable of influencing cell signaling processes. Specifically, macromolecules for delivering hydrogen sulphide (H2S) and nitric oxide (two of the so-called gasotransmitters) will be discussed. Moreover, the ability of the donors to release H2S over physiologically relevant concentrations and timescales will be demonstrated by examining the stimulation of ERK and PKC signaling in HEK293 cells. H2S release from the macromolecular donor over time scales consistent with the signaling observations was also interrogated using an H2S-selective fluorescent probe in live cells. Our results demonstrate that the use of macromolecular H2S donors enables the stimulation of spatiotemporally confined cell signaling events.

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# Biodegradable Nanogel Star Polymers: A Platform for Programmable Macromolecular Self-Assembly and Cargo Delivery

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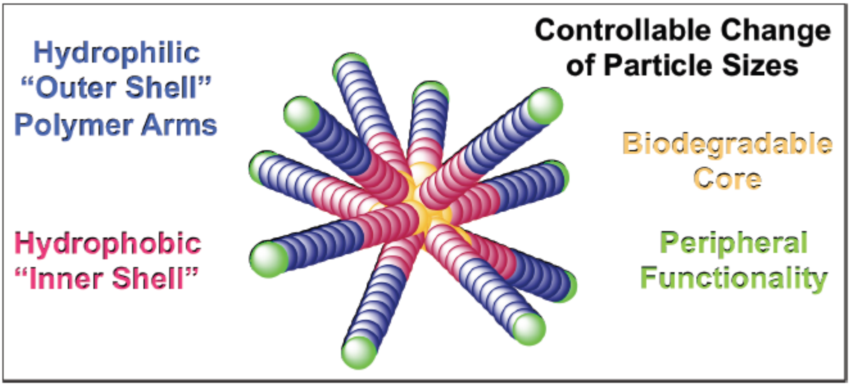
This presentation will provide the insight onto the formation of biodegradable gel-core star polymers. The combination of molecular simulation results with experimental data supports "stepwise" mechanism of star polymer formation utilizing "arm first" approach. Solvent dependent behavior of star polymer's gel-core has been investigated utilizing molecular simulation and 1 H NMR diffusion studies.[1] The obtained results provide insight on the ability of star polymers to spontaneously encapsulate hydrophobic cargo and their potential application as drug delivery vehicles.[2,3]



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## Nano-Crystalline Glycosaminoglycan Delivery Vectors

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We have recently developed a novel hybrid nano-crystalline vector for the delivery of glycosaminoglycans (GAG). There has been growing interests in the therapeutic use of GAG recently due to the demonstrated ability of members of the GAG family to mediate bone[1] and cartilage repair[2] and other such similar regenerative medicine applications. However, clinical use of GAG has been limited due to the poor *in vivo* stability, rapid clearance and wide spread off-target effects characteristic of compounds in the GAG family. Encapsulation of GAG compounds in a delivery vector can potentially eliminate much of the clinical limitations in the therapeutic use of GAG in the clinic. Formulating encapsulation strategies for GAG compounds is particularly challenging due to their high molecular weight and particular biochemistry which precludes the use of complexation vectors in the condensation of GAG for encapsulation. As such, traditional core-shell and nanoprecipitation methods for drug loading have poor success when used with GAG, with the need for alternative approaches towards formulating delivery vectors for GAG. To address the need for a GAG delivery vector, we have developed a novel hybrid core-shell type nanoparticles with the core consisting solely of GAG in a nano-crystalline form, and the shell consisting of polymer composites assembled in-situ via polycondensation of siloxanes. Encapsulation of nano-crystalline GAG is enabled by a unique surface antagonist approach to control the size and dispersity of the GAG core. The nanoparticles thus created have loading capacity routinely greater than 90%, with tuneable release from 4 hours to 40 days of the encapsulated GAG. In addition, the particles are monodispersed and have controllable particle size varying from 30-1000 nm.

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## Investigation of Formulation Composition on the Gelling Properties of Drug-Loaded Poloxamer Gels

Manisha Sharma[1,*], Kaushik Chandramouli[1], Prabhat Bhusal[1], Zimei Wu[1], Jolyene Alphonso[1], Joyce Chow[1], Divya Patel[1], Riddhi Ramakrishna[1], Seung Jae Yeo[1], Andrew Hill[2], Jacob Munro[3], Simon Young[3], Darren Svirskis[1]

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Poloxamer based in-situ gelling systems are widely explored for controlled drug delivery because of their biocompatible nature and tunable sol-to-gel transition temperatures [1]. Such systems are attractive as they can be injected through a syringe at ambient temperatures and will gel in the body forming a high viscosity and sustained release depot. However the gelling temperature along with mechanical, rheological and release behavior from poloxamers are affected by the additives and compositions of the formulations. The current study focusses on the effect of lidocaine and poloxamer composition on the gelling properties. Various poloxamer formulations were prepared containing Poloxamer 407 (P407) and Poloxamer 188 (P188) in varying concentrations with and without lidocaine. The developed formulations were characterized for phase transition temperature (by tube inversion method), intermolecular interactions (by FTIR), mechanical property (by texture analyzer) and in vitro drug release. The sol-to-gel transition temperatures of the formulations were in the range of 27.3±1.3°C to 38.0±1.7°C. Formulations with sol-to-gel transition between 28°C and 33°C was selected and characterized. Altering the weight ratios of P407 and P188 affected the sol-gel transition temperature, mechanical properties and in vitro drug release behavior. Addition of lidocaine affected the gelation temperature of the formulations (Table 1).

**Table 1**: Effect of lidocaine on the gelation.

| Formulations | Gelation temperature (°C) mean± SD (n=3) | |
|---|---|---|
| | Without Lidocaine | With Lidocaine |
| F2 | 41.0± 0.0 | 33.7± 0.5 |
| F4 | 38.0± 0.0 | 33.0± 0.0 |
| F7 | 42.0± 0.0 | 29.9± 1.2 |

**Table 2**: Peak position of characteristic temperature of selected formulations bands observed in FTIR spectra.

| Functional group | Peak position (Wavenumber $cm^{-1}$) | | |
|---|---|---|---|
| | Lidocaine | Poloxamer (P407/ P188) | Formulation (F4) |
| O-H | - | 3491/ 3492 | 3496 |
| C=O | 1662 | - | 1666 |
| N-H | 3244 | - | 3246 |

Evidence of intermolecular interactions between lidocaine and the poloxamers were observed by FTIR analysis following Gaussian-Lorentzian curve fitting [2]. Shifts in characteristic infrared band wavenumber of lidocaine carbonyl and amine groups suggested hydrogen bonding between lidocaine and poloxamers (Table 2). An increase in P407 concentration resulted in an increase in gel strength. The most promising formulation (F4) formed stronger gels and showed a sustained release of lignocaine over 48 h. Sol-to-gel transition of the poloxamers based in-situ gelling system is affected by the type and compositions of the polaxamer used. Lidocaine showed intermolecular interaction with the poloxamers decreasing the gelation temperature of the system. Increase in both poloxamers concentration resulted in a stronger gel which were able to provide sustained release for longer duration.

Acknowledgements: Faculty Research Development Fund (FRDF), University of Auckland, New Zealand.

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# 3D Printed Poly Lactic Acid Ballistic Contraceptive Device for Wildlife Administration

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Compared to traditional methods of contraception in wildlife, ballistic drug delivery can offer target specificity, flexible formulations and a wide range of dosages for various size animals. In this study, fused deposition modeling (FDM) based 3D printing technology is utilized to develop custom made poly lactic acid (PLA) ballistic devices containing progesterone. The device was designed using computer-aided design software (AutoCAD 2016, USA). The 0.177 caliber 900FPS air-rifle bullets were printed using an UP Mini 3D Printer (3D Printing Systems, NZ) with 1.75 mm PLA filaments (UP PLA-C-13-01, 3D Printing Systems, NZ) in both horizontal and vertical orientations. Mechanical properties of the darts were tested using a TA.TX plus texture analyzer (Stable Micro Systems, UK). Progesterone as loaded into PLA (5% w/w) by hot melt extrusion (Noztek Pro, Noztek,UK). Drug contining darts were placed in a 100ml of release media containing 62.5% ethanol and 37.5% double distilled water maitained at 37°C in a shaking water bath (New Brunswick Scientific, USA). Samples (2ml) were collected at predetermined time points up to 28h and equal amount of fresh media was added in the release system to maintain the total volume. The concentration of progesterone in the release media was determined by UV spectrophotometry (Ultrospec 7000, GE Lifesciences, UK). The compression force required to break the horizontally printed darts was significantly greater than the force required for the vertically printed darts. The release data (Figure 1) shows a controlled release with an absence of a burst release and about 0.98 mg progesterone released by 24h.

# Concurent session 5 - Successful translation and industry collaboration

## Engaging with Industry - Overcoming the Language Barrier

Chris Such
The innovation center, Dulux, Australia

Various publications have highlighted the low position of Australia amongst OECD countries with respect to industry/research sector engagement. The Federal Government is examining various ways in which research engagement can be increased. The objective of an 'ideas boom' is easy to say but more difficult to achieve.

Australian industry will select research partners who have capabilities to deliver what they want. Being in business is about making choices and getting research outcomes efficiently. Very often, success as an industrially engaged researcher is dependent on your ability to relate to a practical problem and identify what technology changes are required to solve it. The discussion to date has not really given sufficient consideration to the building of long-term research relationships that evolve joint solutions.

The speaker has 30 plus years of experience in the coatings industry has included over 20 years in exploratory research and research management roles and the remainder in techno/commercial roles servicing large industrial customers. Following the separation of Dulux from ICI in 1998 and Orica in 2010 he has had the responsibility of establishing a new strategic research portfolio with Australian research groups including universities and CSIRO.

This talk will examine some of the ways for improving engagement and overcoming any language barriers for good industry/research sector collaboration.

# Why Doesn't Excellent and Well Directed Research Always Yield a Product in the Market Place?

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The ultimate success for a researcher working with an industry partner is that that research should result in a product in the market place that is turning a good profit for the industry partner, making life more comfortable and sustainable for the population at large and returning good royalties to the research provider that he or she works for. That is the ultimate success. This talk will examine some of the reasons why good and inventive science does not always reach this ultimate research objective.

The speaker has 25 years of experience working as a contract and collaborative research provider to industry, initially as Technical Manager and then Technical Director of a company providing contract research services to the worldwide agrochemical industry and presently as Director of KCPC. KCPC has a research income of more than $2M per year, much of which is derived from direct industry funding.

KCPC has been working with RAFT in disperse phase systems in the context of industrial research since about 2000, has worked continuously with 2 of its industry partners for more than 17 years and another for more than 14 years.

This talk will examine some of the reasons why good science generates good outcomes in collaborations with good industry partners but still does not result in products in the market place. Some of the reasons are:

Reactor requirements too sophisticated for available plant, outcomes no longer in line with company objectives, changes in company management structure, product unnecessarily complex, improvements in product performance insufficient to warrant new product launch, raw materials required not consistent with long term contracts, etc.

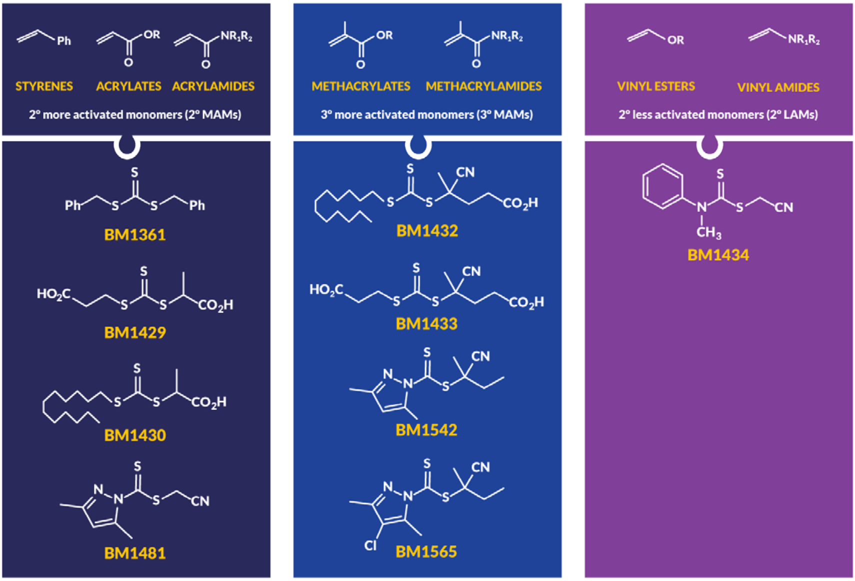
## Commercial RAFT agents at Boron Molecular

Justine Walter and Ken Sullivan
Boron Molecular, Postal PO Box 756, Noble Park, Victoria 3174, Australia,

RAFT (Reversible Addition Fragmentation chain Transfer) polymerization is a Reversible Deactivation Radical Polymerization (RDRP) process which, with appropriate attention to reagents and reaction conditions, can result in the synthesis of well-defined, end- functionalized, polymers with precisely controlled structure, molecular weight, architecture, and polydispersity. RAFT technology has revolutionized polymer synthesis and spawned a new generation of polymeric materials, with many new applications in a wide range of fields including engineering materials, electronics, healthcare and biotechnology expected.

Since the discovery of RAFT in the late 1990's, a number of different RAFT Agents have been developed to address the needs of different monomer classes. However, the single biggest deterrent to the use of this technology has been the ability to manufacture at commercial scale. A selection of versatile, low odour, low cost RAFT agents were targeted for commercial manufacture by Boron Molecular and are now available in gram to metric tonne quantities. The manufacture of RAFT agents at commercial scale has enabled the uptake of RAFT technology into new markets and Boron Molecular currently has a number of their RAFT agents in development with large multinational companies.

RAFT Agent Monomer Selection Guide



# From test tube to supermarket shelf: Translational polymer research

P. J. Halley

School of Chemical Engineering, University of Queensland, Australia

This talk will outline case studies of translating polymer research, from biodegradable food packaging, ovitraps for dengue fever control, modified yowie capsules, and degradable polymer agricultural films. More specifically the talk will focus on best practices (and practices you can learn from) in the fundamental research, applied research and scale-up and translation process. Some conclusions on selective hiring, project team management and translation champions will be made.

# Concurent session 6 - Polymer self-assembly

## Polymer-based Soft Plasmene Nanosheets, Nanoribbons and Origami

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My nanobionics research lab concentrate on the design of soft/hard nanohybrids based on metallic nanoparticles capped by soft ligands including DNA, polymer and alkyl molecules. We have successfully applied such soft particles to four major directions: (1) assembling soft plasmonic nanoparticle superlattice sheets (soft plasmene sheets)[1-5]; (2) fabricating electronic skins (e-skins) for wearable sensors[6-8]; (3) fabricating soft energy devices[9]; (4) DNA aptamer-targeted and light-controlled drug delivery[10].

In this talk, I will focus on the discussion of the first project for producing soft, elastic, two-dimensional plasmonic nanoparticle superlattice sheets (soft plasmene sheets) by self-assembly of polystyrene-capped metal nanoparticles. The soft nanosheets could be folded into 1D nanoribbons and 3D origami, and they can serve as a new-class SERS substrate which is soft, elastic and surface-attachable. This enabled the direct chemical identification on topologically complex surfaces such as banknotes and coins, and application as new-generation of anti-counterfeit security labels.

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# H2S Gasotransmitter-Responsive Polymer Vesicles

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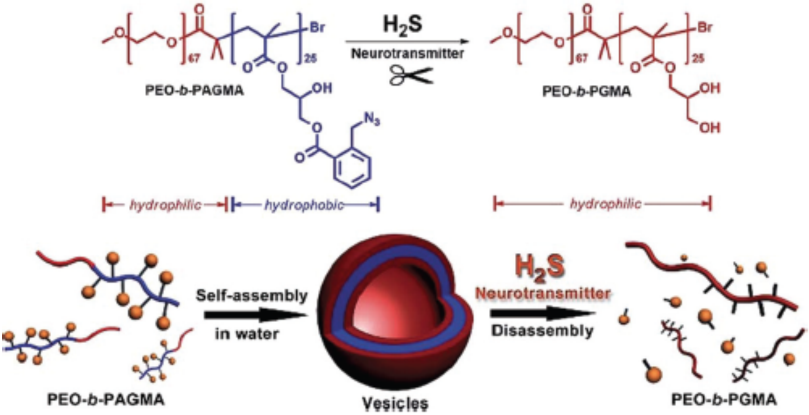
Building biomimetic polymer vesicles that can sense a biological signaling molecule is a tremendous challenge in the cross-frontier of chemistry and biology. We have developed a new kind of o-azidomethylbenzoate (AzMB)-containing block copolymers that can respond to an endogenous signaling molecule, hydrogen sulfide (H2S). Such a gasotransmitter is able to trigger cascade chemical reactions to sever the AzMB side functionalities, which alters the polymer amphiphilicity and leads to a controllable disassembly of the self assembly vesicle structure. Moreover, if we introduce cystathionine **γ**-lyase (CSE), a specific enzyme converting cysteine into H2S, onto the vesicular membrane, the polymersomes can extend their responsive scope from H2S to specific amino acid bioactivator. We envisage that this polymer model would open up a new avenue to constructing biosignal-triggered nanocapsules for intracellular applications.



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# Photo-chemical reaction and polymerisation of DNA-base containing bolaamphiphiles

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In this work, we used some of the topochemical principles[1,2] to create light responsive materials by designing and synthesising self- assembling structures. The incorporation of photodimerising units such as thymine is expected to enhance photo-chemical reaction and polymerisation throughout the self-assemblies. Photo-responsive self- assemblies based on bio-inspired bolaamphiphiles with oligo (ethylene oxide) hydrophilic outer segments and a hydrophobic inner segment with thymine were synthesised. These self-assembling structures were designed so they meet the criteria governing the photroreactivity of molecules.[2] The morphology and the molecular weight of the self-assemblies after the UV irradiation were investigated by NMR, GPC, DLS and TEM.

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# Synthesis and Self-Assembly of Discrete Dimethylsiloxane-Lactic Acid Diblock Co-Oligomers: New Materials for Nanolithography

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Diblock copolymers are perfect candidates to generate well-ordered systems with sub-100 nm feature sizes. Because of the broad application scope, studies on the self-assembly of these materials and the resulting microphase separated systems is conducted by many research groups. Reducing the feature size and number of defects is one of the focus points of this research. However, the possible consequences of chain length dispersity is often neglected. Although some studies showed that composition inhomogeneity is acceptable in the intermediate dispersity regime ($Đ$ = 1.05–2.00),[1] truly monodisperse systems ($Đ$ = 1) have only been studied computationally. To bridge this dispersity gap, and evaluate the limits of precision polymer synthesis and phase separation of a perfectly defined polymeric system, we developed a scalable synthesis route for discrete length (i.e. monodisperse) diblock 'co-oligomers' based on dimethylsiloxane and lactic acid monomers.[2,3] Using an iterative approach and orthogonal protective group chemistry, we were able to obtain multigram quantities of monodisperse oligodi-methylsiloxane, and both atactic and isotactic oligolactic acid blocks. A unique library of fully monodisperse diblock co-oligomers with varying length and composition (DP = 25-100) was finally obtained by careful ligation of these blocks. Detailed studies of the phase separation gave unprecedented insights in the phase separation of these low MW block co-oligomers.

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# Water soluble fullerenes by solvent exchange and polymer self-assembly methods

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Abstract: Buckminsterfullerene (C60), metallofullerene and related carbon materials have drawn significant attention since their discovery and have numerous applications such as solar cells[1], bio- medicine[2] and drug delivery[3]. However, one of the main challenges of C60 or metallofullerene for use in the biological sciences is their negligible solubility in aqueous solutions. In this research, two different strategies have been explored to make water soluble C60. The first strategy is the solvent exchange technique, which is a method of transferring C60 from an organic solvent into water under stirring or sonication. The use of tetrahydrofuran as a solvent to produce dispersed fullerenes that are water soluble is widely reported and extensively utilised[4]. We have developed a related method based on the use of N, N-dimethylformamide (DMF). Our results have shown that the solvent exchange technique using THF results in partial oxidation and degradation of C60, in contrast, the DMF evaporative method results in greater oxidation and degradation of C60 but significantly enhanced colloidal stability in buffer. The second method is to self-assemble C60 with amphiphilic polymer forming hybrid nanoparticles. Amphiphilic block copolymers poly(2-(diethylamino)ethyl methacrylate)- b-poly(ethylene glycol) methyl ether methacrylate (PDEAEMA-b-PEGMA) were synthesized via Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization. PDEAEMA polymers are attractive for its pH responsiveness with pKa ~ 7 which is in the range of variation of pH values between healthy and cancerous tissues. Our research has potential to generate responsive fullerene materials with application in biomedicine.

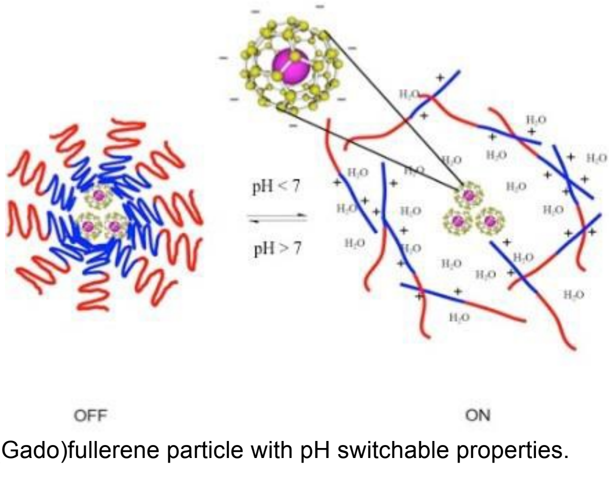

**Figure.** Polymer/(Gado)fullerene particle with pH switchable properties.

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# Exploring the interplay of phase segregation and hydrogen bonding in folded polymers

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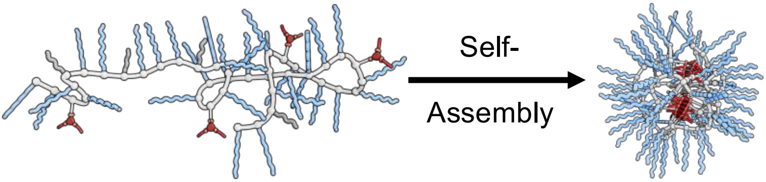
The controlled folding of individual polymer chains into single-chain polymeric nanoparticle (SCPN) has received considerable attention over the last couple of years. By combining the fields of small molecule self- assembly and polymer chemistry, unique macromolecular architectures are obtained. Not only are such systems interesting from a fundamental point of view, because of their resemblance to protein, their unique ability to create nanoparticles with well-organized structured domains makes it a modular platform for applications like catalysis, sensing and drug delivery.[1]

Since structure and function are closely related, we aim to acquire more in- depth insight in the folding behavior, structure and the dynamics of such polymeric systems. Hereto, we studied water-soluble polymers grafted with structuring supramolecular motives, as well as aliphatic units using the combination of spectroscopic and scattering techniques.[2,3]



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# Concurent session 7 - Industry collaboration

## Advanced automatic sorting and recycling of packaging polymers based on intelligent labels

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A new way of rapidly sorting packaging into high purity streams (> 99%) has been developed based on intelligent labels with invisible markers that can be detected and sorted using existing high-speed optical sorting systems used in MRFs with minor modifications.
The principles have been proven[1,2] using a range of commercially available UV responsive fluorescent markers with high emission yields. Full-scale commercial optical sorting trials utilized PP, HDPE and PET as reference materials. The trials were conducted at the MRF facilities of Tomra in Germany. A purpose built UV-LED array increased detection sensitivity. Marker concentrations down to 2,000ppm could be reliably detected under commercial sorting conditions of 3m/s and 1.9 tonne per hour. Packages labeled with the invisible markers were positively sorted from mixed packaging waste with a yield of 74% and a purity of 93% in a single pass. A double pass would achieve a calculated purity of 99.5%, which exceeds the EU standards for food-grade HDPE recycling.

Unlike existing NIR sorting systems, this technology uses commercial labeling and decoration methods to sort targeted streams potentially including food-contact plastics, bioplastics, chemical packaging, automotive plastics, black plastics and different grades of one plastic. This technique has the potential to create new recycling loops for food grade PP, milk bottle sorting and PET products.

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# Accelerating collaborative innovation

James Wiltshire

Australia & New Zealand Dow Chemical

**Abstract:**

The importance of collaborative partnerships to drive new solutions and product developments is very well recognised in the industry. However, the reality of how we go about this and the level of success that is achieved are often not as ideal as we would like. This presentation aims to provide some insights from the perspective of a large global corporation on the challenges we face around external collaboration, both with customers and external research agencies, and how we can overcome these obstacles.

## Perspectives on commercialisation from Carbon Nexus

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**Abstract:**

Carbon Nexus is a unique carbon fibre composites research centre and at the same time, a production facility for customized carbon fibre materials.

Working on a wide range of contract research projects and commercialisation activities with industry partners in diverse market segments, we have experienced a range of translation models and outcomes.

This presentation will describe several examples of fruitful collaborative research and development projects with some of our key partners, including Futuris and Quickstep. We will explore the funding models utilised, the project management processes followed, and our practices to maintain these successful collaborative relationships.

# Concurent session 8 - Smart materials

## Light responsive click-based hydrogels for cell culture applications

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Hydrogels provide favorable 2- and 3-D microenvironments for the maintenance and expansion of cells. It is advantageous to change the properties of the hydrogel during cell culture to match the dynamic nature of biological processes. This can be achieved using light degradable hydrogels, which allow both the physical and chemical cell-signaling properties to be altered with precise spatiotemporal control.

This presentation will outline a range of light responsive hydrogels which were synthesized using radical polymerization or bioorthogonal click crosslinking chemistry. In particular, we have focused our work on the development of gelatin-based light responsive hydrogels platforms, which allow cell adhesion and differentiation without additional biofunctionalisation. Examples will be shown showing the versatility of these biomaterials such as the alignment of cardiomyocytes for more synchronous beating[1], 3D culture of fibroblasts [2] and for mesenchymal stem cell differentiation.

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# Preparation, Properties, and Application of Meldrum's Acid Derivatives Based Thermosetting Resins

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Thermosetting resins exhibit their basic properties majorly depending on their chemical structures and the characteristics of curing reactions. This issue usually defines the type of thermosetting resins, such as epoxies, phenolics, bismaleimides, cyanate esters, and vinyl esters which have been widely used in various applications. This work demonstrates a new class of thermosetting resins with Meldrum's acid (MA) derivatives as monomers. The curing reaction of the MA derivatives includes generation of ketene groups from MA thermolysis reaction and addition reaction between ketene groups. As the MA thermolysis reaction would evolve acetone and $CO_2$ molecules which might result in air-trapped micro-cavities in the resulting thermosetting resins. The prepared MA-based resins have high fractions of free volume and inherent low-k values (about 2.0-2.5) at 1 MHz. The feature of *in situ* formation of micro cavities is also attractive for preparation of polymeric membranes for gas separation. MA-modified polyimide membranes exhibiting high hydrogen selectivity have been demonstrated.

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# Transparent Stretchable Electronics – Towards Wearable Gas and UV Sensors

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Electronics and sensors pervade all aspects of life, needing solutions to make them less obtrusive, which is where fully transparent electronics come into play. Our research focus has been to realize stretchable electronic devices with highly functional characteristics while being optically transparent.

All electronic devices rely on oxide materials – these are in the form of ultra-thin coatings, often prepared at high temperatures. Integration of multifunctional oxide thin layers in stretchable polymer devices would create enhanced functionality and performance. This integration has been limited by the brittle nature of oxides and high temperature processing requirements.

Our research has addressed this key bottleneck with a ubiquitous transfer process. This process utilised the naturally weak adhesion of platinum to silicon, and this allows us to create electronics on a rigid substrate such as silicon and then peel off the layers to transfer onto a stretchable polymer substrate. This process also results in a unique 'micro-tectonic' surface, creating opportunities to explore new stretchable device applications. This process has been successfully demonstrated using transparent indium tin oxide, zinc oxide, and titanium dioxide thin films (all deposited at high temperatures) with stretchability of up to 15%, which is exceptionally high for a brittle oxide.

With this process, we have demonstrated room temperature gas and UV sensors (among other applications), which retain their functionality when stretched. The ability to combine any functional oxide with biocompatible substrate material creates the potential for consumer electronics applications in wearable electronics.

# Super-stretchy gels through macrocrosslinking

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For many applications the mechanical performance of gels is critical, but gels are notoriously weak and prone to fracture. The reason for this is not known exactly, but may relate to the great inhomogeneity of cross-link lengths and the lack of stress relieving mechanisms in a standard gel. In recent years a range methods have been employed to increase the toughness and elasticity of hydrogels. These include homogenous cross- linkers, clay nanocomposites, reversible folding, slip-ring systems, and double networks.

We have produced a series of gels (85% water) that show extraordinary toughness and are the most stretchy gels produced anywhere to date. They can be reversibly stretched almost 180 x before breaking, with a breaking strain of 10 Mpa which is approaching standard (non gel) polymers such as PMMA. They can be compressed by 98% to 16 MPa without damage and suffer indignities like being hit with a hammer and dropped from very large heights with no blemishes. They are produced with standard monomers but using small amounts of a new macro-crosslinker. We postulate that the network design allows for the synthesis of very long chains between crosslinks.

**Fig 1.** 1 cm gel being stretched by hand 100 x

# Hydrolysable Copolymers for Antifouling Paints

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This work focuses on the synthesis and assessment of the antifouling (AF) performance of silyl ester methacrylic copolymer-based coatings. These hydrolysable copolymers were synthesized via the reversible additionfragmentation chain transfer (RAFT) polymerization [1, 2] and were selected as binders for developing copper-free chemically active AF coatings. Results from erosion tests under dynamic conditions demonstrated the control of the polishing process of AF coatings. Bioassays demonstrated that the silyl ester methacrylic binders themselves displayed low AF activity against marine foulings whilst copolymer-based coatings containing Sea-Nine, zinc pyrithione as co-biocides were promising candidates inhibiting the settlement of marine macroorganisms [3].

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# Concurent session 9 - Enabling technologies

## The use of continuous flow processing for the synthesis of speciality polymers

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Continuous flow processing is becoming an increasingly disruptive technology within several sectors of the chemical manufacturing industry, due to new innovative flow reactor designs on one side, and the need for highly efficient chemical production on the other. These new continuous flow reactors consist of either tubular or plate-type modules in which the chemical reactions take place under well-defined flow conditions. Flow reactors offer many advantages over conventional batch reactors, including enhanced process control, higher yields & purities, shorter reaction times, better scalability, smaller physical footprint and superior inherent safety. Over the past years, CSIRO has invested heavily in the use of continuous flow technology for use in polymerizations, developing a series of intensified continuous processes for polymer manufacture via radical, anionic and cationic polymerizations, in either solution phase or emulsions. In particular the use of continuous flow reactors for RAFT (Reversible Addition Fragmentation chain Transfer) polymerizations1,2 and subsequent on-processing3 of the resulting polymers has been studied by our group. RAFT allows for the synthesis of polymers with narrow molecular weight distributions and well-defined end groups, as well as complex architectures, such as blocks, stars and others. In January 2016 the Centre for Industrial Flow Chemistry at CSIRO was established as a technology platform providing access to our cutting-edge research into industrial continuous flow processing for Australian and international chemical manufacturers. The center's facilities operate stateof-the-art flow chemistry reactor technology for development and optimization of chemical processes from discovery to pilot plant scale, including a wide range of polymerizations.

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## CSIRO’s rapid automated materials & processing centre

Shaun C. Howard

Rapid Automated Materials & Processing (RAMP) Centre CSIRO Manufacturing

The demands for materials and processing solutions by the manufacturing, defence, health and technology industries require acceleration in the time taken to conduct research and development. The Rapid Automated Materials & Processing centre is a national scientific resource where robotics, informatics and technical expertise are available to SMEs, start-ups, academic researchers and large organisations alike, to help solve processing and formulation challenges, to discover advanced materials, and to allow the optimisation of new products. The improved research productivity gains from using high-throughput and automated experimentations mean that the scientific solutions discovered can reach the marketplace in a timely, sustainable, resource and cost-efficient manner.

An overview of the centre’s capabilities will be shown, along with case studies relevant to the polymer community.

## Introduction to the ARC Future Fibres Hub

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The Future Fibres Industrial Transformation Research Hub is an Australian Research Council (ARC) supported initiative which strives to accelerate the transformation of the Australia manufacturing industry by developing novel fibre technologies to facilitate more sustainable, advanced manufacturing of fibre materials and products that will impact on significant global issues, including reducing our environmental footprint and improving public health and wellbeing. Led by Deakin University, the Hub brings together five industrial partners: HeiQ Australia, Carbon Revolution, Quickstep Automotive, Ear Science Institute Australia and Draggin Jeans. They are joined by experts from CSIRO and international higher education institutions to conduct cutting edge research and development into new synthetic and natural fibre technologies.

The Hub Research Program contains three streams:

- Nanofibres: development of the emerging industry to create polymeric nanofibres, including high-throughput production and applications.
- Advanced carbon fibres: development of next generation carbon fibres and resin systems for advanced composites.
- High value-added applications for fibres: development of fibre-based biomaterials, and abrasion resistant protective apparel.

This presentation will introduce the newly established ARC Future Fibres Hub and give an overview of the Research Program.

## Electrostatic formation of polymer latex stabilised liquid marbles

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Recently we have shown that an electrostatic route for the preparation of liquid marbles,[1] can occur more easily for smaller drops and larger particles than traditionally thought.[2] Thus it is apparent that the 'rules' for electrostatic formation of liquid marbles are quite different to those for conventional direct-contact formation by rolling liquid droplets on a powder bed.[3]

Here we present results from our electrostatic formation method as applied to polymer latex stabilised liquid marbles.[2] Observations on the influence of drop and particle size on this process will be discussed by bringing an earthed water drop of volume 3 – 7 µL into proximity with a bed of highly-charged polystyrene particles of diameter 22 – 153 µm. Under certain applied potentials the particles jump to and coat the drop, producing a particle-liquid aggregate that dropped to the bed surface in the form of either a stable liquid marble or a particle-stabilised sessile drop. Comparison is made with polypyrrole-coated polystyrene latex stabilised liquid marbles formed via the same route.

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## Polysulfide Polymers for Economical Mercury Capture

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Mercury pollution plagues many environmental and industrial sectors. For example, this toxic metal is encountered in gold mining, oil and gas processing, and coal combustion. From gold mining alone, more than 15 million people are exposed to mercury around the world, leading to irreversible neurological damage and embryotoxic effects. In all of these
sectors, a simple and economical technology is needed to remove mercury from air, water and soil. This presentation will describe a polymer that meets this need. Specifically, our lab has developed a polysulfide polymer made entirely from industrial by-products and renewable sources that is highly effective at capturing both inorganic and metallic mercury from complex mixtures. The polymer is prepared in a single step by the direct reaction of sulfur (a by-product of the petroleum industry) with various plant oils (all renewable building blocks). The resulting polymer not only binds to mercury, but also changes colour upon capturing the metal. In this way, it is also a sensor. Field trials are underway with several industrial partners and environmental agencies to facilitate the transition of this laboratory discovery to a commercially available mercury absorbent. More generally, this project represents a larger effort of our laboratory to convert waste materials and renewables into useful polymers. In this specific instance, we aim to help combat the global mercury crisis and protect the environment and human health.

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# Concurent session 11 - Polymer synthesis

## Polymer Mixtures with Gradient Morphology Designed by Photopolymerization

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Gradient structures are ubiquitous in *Nature* because the involving kinetic processes are not uniform and often take place over a very long time. The idea of fabricating polymers with gradient structures actually started from the *"gradient polymer composites project"* initiated by M. Shen and M. Bever back in the beginning of 1970s.1) To design polymers with physical properties continuously varying along a specific direction (*uniaxial*), diffusion of the guest monomer into a host polymer was promoted and followed by polymerization to produce a concentration gradient of the guest polymer in the mixture.

Here, we will demonstrate a more general way of designing polymers with gradient morphology by combining phase separation induced by photo-polymerization and the computer-assisted irradiation (CAI) method.2)

The following experiments will be described and discussed together with the formation kinetics of:

1. Continuous morphology along the thickness direction (Z-axis) of the sample.3)
2. Unidirectional graded bi-continuous structures exclusively in the XY plane.4)

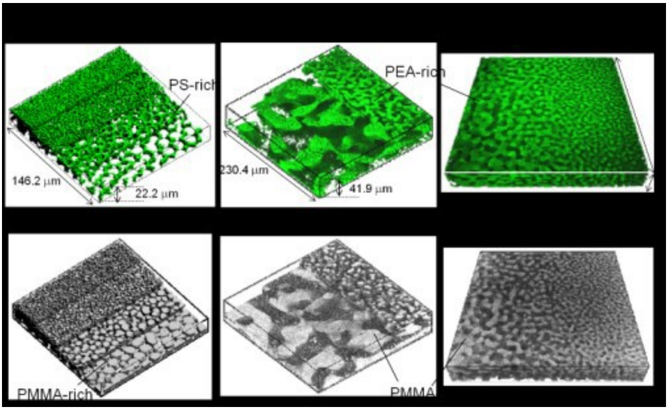

***Fig 1.*** *Spatially graded morphology of PS/PMMA (left) and PEA/MMA (center & right) semi-IPN obtained by photo-*

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## Structural Modifications of Polymers by Pulsed Electrical Discharges in

## Liquids

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Pulsed electrical discharges generated at atmospheric pressure in liquids have become one of the most interesting techniques for the functionalization of polymers [1-2]. The generation of plasmas in liquids with short high voltage pulses for material modification is very new, but the approach offers the potential to be highly flexible with regard to their range of applications. When water is subjected to a high electric field, a high amount of excited species, such as hydrogen, oxygen, nitrogen, and hydroxyl radicals are produced, which may efficiently interact with molecules and bulk-materials, inducing structural modifications [3-5]. Furthermore, plasma in liquids methods are offering a number of additional capabilities. Liquid plasma-assisted functionalisation is faster than solution chemistry and a one-step approach [1]. The material surface tailoring with different functionalities is also possible, due to a wide range of functional groups that can be generated in liquid plasma by using anionic or cationic solutions. Different processes in plasmas that are generated in liquids and reactions set in motion accordingly are determined by the way the electrical energy that is provided is dissipated in different mechanisms [3].

Our experiments have shown that structural modifications of polymers obtained when using 10 ns voltage pulses differ significantly from treatments with plasmas in liquids that have been generated when applying longer pulses (50 µs) [2, 4]. The surface hydrophobicity of the polyimide films increased with treatment time, while the relative permittivity decreased after the water plasma treatment [4-5]. Nanosecond high voltage pulses have induced an increase of the unsaturated bondings on the polyimide surface, while the segregation of polarizable groups at the film surface was responsible for the increased surface hydrophobicity when discharges were generated with microsecond high voltage pulses. The surface of polyimides that were treated by nanosecond pulse discharges in distilled water have shown a topographical rearrangement of the polymeric chains . The degree of intermolecular order increased after the plasma exposure, the distance between the polymer chains is increased or decreased, depending on the plasma parameters and materials used in the discharge. The results have shown that electrical discharges in liquids may be used for a controlled and efficient structural modification of polymers.

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# Selective photocatalysis: A new tool for polymer chemist

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**KEYWORDS:** Chlorophyll, controlled/“living” radical polymerization, photochemistry, photoinduced electron transfer (PET), reversible addition-fragmentation chain transfer (RAFT), and photoredox catalyst

The emergence of efficient photoredox catalysts using transition metals, such as iridium and ruthenium, have recently emerged as efficient catalysts to perform organic reactions under visible light. Such catalysts have allowed to carry complex organic reaction without the formation of side products. In this presentation, we expend their uses for the synthesis of complex macromolecules and the modification of macromolecules under visible light. According to the nature of photoredox catalysts, different polymerizations can be achieved using different wavelengths. In this presentation, we demonstrated that a large range of photoredox catalysts can activate a photoinduced electron transfer (PET) process, which initiates a reversible addition fragmentation chain transfer polymerization (RAFT) under blue LED and red LED lights ($\lambda_{max}$ = 435 and 625 nm). This process controls a large range of non- and functional monomers, including pentafluorophenyl acrylate, hydroethyl methacrylate, glycidyl methacrylate, *N,N*-dimethylaminoethyl methacrylate, etc. with an excellent control of the molecular weights and polydispersities. The end group fidelity was demonstrated by NMR, UV-vis spectroscopy, and by successful chain extensions to prepare diblock opolymers.

# Efficient and High MW PE Production Using Highly Active Multi-nuclear Group-IV Metal Catalysts

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Polyethylene (PE) is one of the largest synthetic resins in the world, widely used in our daily lives and industries. It is also one of the practical biocompatible materials. In industry, Group-IV metals play an important role in the production of practical catalysts for ethylene polymerization. To produce high MW PE in a more efficient way, we designed multi-nuclear catalysts1 using specially designed tetradentate ligands via (1) one-step self-assembly strategy,2 (2) two-step programmed self-assembly strategy,3 and (3) one-step mixed ligands self-assembly strategy.3 Accordingly, we have synthesized a new family of multi-nuclear group-IV metal catalysts with bis-phenoxy-imine ligands bearing different bridging spacers.

Compared to corresponding mono-nuclear single-site catalysts, all the new catalysts demonstrated the advantages: (1) increase catalytic activity and stability, (2) produce higher MW polymers, and (3) suppress reactor fouling with optimized bridging spacer.

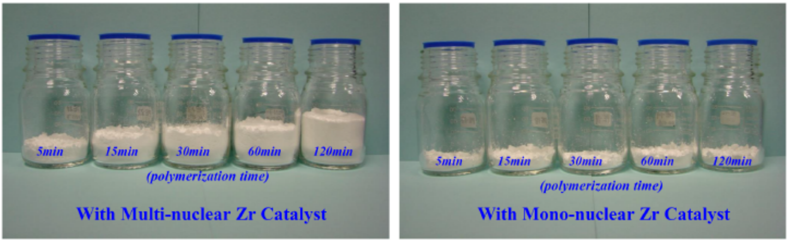

Fig .1 PE produced with multi-nuclear and mono-nuclear Zr Catalysts.

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# Synthesis of perfluorocarbon-containing alternating copolymers

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Here, perfluorocarbon-containing alternating copolymers were obtained by utilizing of the reductive quenching cycle of photo-catalyst Ru(bpy)3Cl2 under irradiation of visible light. The difunctional monomer 1,8- diiodoperfluorooctane (signified as A), was added onto unconjugated diene monomer (signified as B) alternatively and efficiently at room temperature (25 $^{O}$C). From the viewpoint of macroscopic level, the two difunctional monomers were “stringed” up alternatively and linear perfluorocarbon- containing alternating copolymers $(AB)_n$ was obtained correspondingly. This novel polymerization method may open up a new era not only for the radical polymerization of unconjugated dienes but also for the construction of high-molecular perfluorocarbon-containing alternating copolymers.

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# Concurent session 12 - Composites and other smart materials

## Cellulose nanofibres from spinifex arid grasses: "Greener, Longer and Tougher", thanks to 20 million years of resilient adaptation

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We recently discovered1-3 that a unique, very high grade of cellulose nanofibre can be readily and cost-effectively produced from endemic Australian spinifex grasses from the Triodia genus. These fascinating extremophile grasses, with over 20 million years of evolution, have presented us with a most unique source for nanocellulose. Our fibrillation process involves a mild pulping procedure followed by either a low mechanical energy treatment or a mild sulfuric acid hydrolysis. We have demonstrated that a high content of residucal hemicellulose and lignin in bleached and unbleached pulp results in superior cell wall deconstruction, and consequently, the production of longer and more flexible nanofibres. When benchmarked against the other leading academic and commercially available materials, spinifex nanofibres have the highest aspect ratio compared against nanofibres obtained through the mechanical or chemical treatments of the other sources of cellulose. This novelty means that our method of fibrillation, and more importantly, this source of cellulose (Triodia includes 69 species) have the potential to directly address the current technological bottlenecks that have so far limited the widespread translation of nanocellulose technology into more applications. This presentation will give an overview of our team's research and technology development activities related to spinifex nanofibre production, with potential applications including ultrathin condoms and gloves, polymer composites, ultra-tough paper products and low cost, renewable carbon fibres. It will also introduce a landmark umbrella agreement and commercial partnership between The University of Queensland (UQ) and The Indjalandji-Dhidhanu traditional owner group, which has provided a framework accommodating shared future commercial benefits and Indigenous economic development from the generated project IP.

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# Nanogold and Nanosilver Polymer Composites and Their Potential Applications

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Nanogold and nanosilver polymer composites of polyurethane and nylon plastics and polyurethane latex suspensions have been synthesized,and their structural, optical and antimicrobialpropertiescharacterised. Here, the gold and silver nanoparticles are formedwithin the polymer matrix and are chemically bound to the nitrogen groups of the polyurethane and nylonrespectively, forming robust compositesthat can be drawn into fine fibres or moulded and shaped by conventional thermoplastic processes. The size and shape of the metal nanoparticles and hence the colour of the composite materialscan be controlled by the matrix and the metal ion concentration. The nanogoldcompositesare pink to purple in colour, and the nanosilvercompositesare yellow to brown, due to the surface plasmon resonance absorption of light by the gold and silver nanoparticles respectively. The colour changes with increasing nanometal content (Figure 1). Thesecomposite polymers exhibit interesting optical propertiesand effective antimicrobial activity against *Staphylococcus aureus*and *Escherichia coli*bacteria. In addition, the nanosilver and nanogold polyurethane paints displaymarine antifouling properties. Potential applications includefood packaging, surface coatings, healthcare, textiles, water purification and water and air filters,where robustness and antimicrobial effectiveness are required.

# Additive free polypropylene based thermoplastic vulcanizates by electron induced reactive processing

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Reactive processing involves three sub-processes like diffusion and mixing, heat transport and chemical reaction. It is increasingly used for reactive blending, functionalization, long chain branching, grafting and dynamical vulcanization in order to prepare customer tailored polymer materials. Nevertheless, the use of temperature sensitive initiators leads to a strong coupling of all sub-processes. Consequently, it remains difficult to control reactive extrusion. Some basic limitations are slow molecular diffusion on a microscopic scale in viscous liquids, changed viscosity due to chemical reaction as well as influence of shear stresses and rates of deformation on chemical reaction due to use of one processing volume for mixing and chemical reaction. Finally, all these difficulties lead to undesired side reactions and side products. In order to overcome these drawbacks and to design a sustainable reactive process, no temperature sensitive chemical initiators have to be used. With respect to technology readiness level, electron induced reactive processing (EIReP) was developed. This paper reports on its test [1-4] and guidelines for preparing additive free Thermoplastic Vulcanizates (TPVs) [5] by EIReP. Finally, toughened polypropylene was prepared with improved mechanical performance [6].

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# Effect of silica-gel materials on the flame retardancy and thermal properties of EP/APP composites

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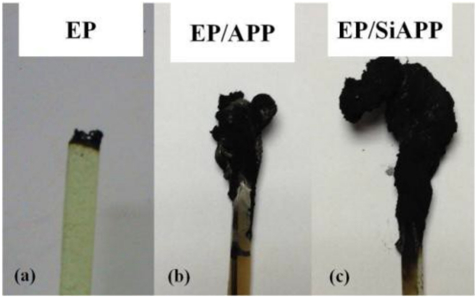

Figure. 1. Photos of residues after LOI test: (a) EP, (b) EP/APP, and (c) EP/SiAPP.

Ammonium polyphosphate (APP), a widely used intumescent flame retardant, have been microencapsulated by silica-gel with the aim of enhancing the flame retardancy and thermal stability between EP matrix and APP. The structure of silica-gel microencapsulated ammonium polyphosphate (SiAPP) was characterized by Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). The flame retadancy and thermal stability were investigated by limiting oxygen index (LOI) test (the residue char was shown in Figure 1), UL-94 test, Cone calorimeter and TGA. The results indicated that silica-gel could dramatically increase the LOI value and thermal stability, and decrease the heat realse rate and total heat realse of the EP/SiAPP composite [1]. Moreover, the EP/SiAPP composite revealed excellent smoke suppression performance during combustion and an intumescent char layer is formed to protect the inner polymer matrix.

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## Photochromic Properties of Spiropyrans in Polymer Matrices

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Spiropyrans (SP) are of particular interest in materials because of their photochromic properties and were first reported by Fischer and Hirshberg in 19521.When exposed to UV light, cleavage of the carbon-oxygen bonding on SP molecules occurs, producing the conjugated coloured merocyanine (MC) form2. When the MC is heated or illuminated by visible light it then reverts to the SP structure. The MC molecules can potentially form H or J aggregates and it is known that J-aggregates can delay the conversion back to SP3. Since the polarities of the MC and SP forms are different, the photo switching process can be affected by various polymer enviroments4 (e.g. amorphous, semicrystalline) and in co-polymers where the SP is bound covalently as a side group. In the present paper we report the effect of various polymer media on the photochromism of a SP with potential applications as chemical UVdosimeters or packaging of UV sensitive food. The polymers used were polymethylmethacrylate (PMMA), amorphus polycarbonate (APC), polystyrene (PS) and polyvinylidene fluoride (PVDF). Copolymers of SP with poly(methyl methacrylate-co-methacrylic acid) and poly(ethylene-coacrylic acid) were also investigated.

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# In situ fiber-reinforced composite films of poly(lactic acid)/low density polyethylene blends: Effects of compositions on morphology, transport, and mechanical properties

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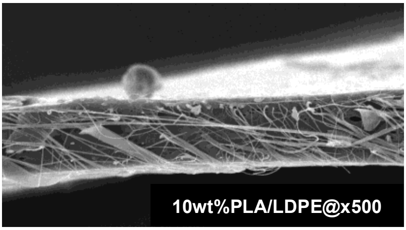
This study aimed to investigate the effects of blend compositions on packaging-related properties of blown films of poly(lactic acid) (PLA) and low density polyethylene (LDPE). Blend films with PLA contents of 5-20 wt% and films of 10wt%PLA/LDPE with PE- *co*-MA compatibilizer concentrations of 0.5-1.5 phr were produced and compared. SEM micrographs of cryofractured, cross-sections of the blend films revealed that PLA microdomains dispersed throughout the film in forms of long fiber (L/D>100) and ribbon. Number of fibers and ribbons increased with an increase of PLA content. Compatibilizer used did not affect the structure of the PLA dispersed phase. The fiber alignment was mainly in machine direction (MD) resulting in anisotropic tensile properties. Modulus and tensile strength improved significantly in MD but not in transverse direction (TD). In contrast, elongation at break increased in TD not MD as PLA content increased. OTR of the blend decreased while WVTR increased with the amount of PLA used. Again compatibilizer showed minimal effect on the transport properties. In short, flow behavior and ratio of the two polymer components played a key role on morphology and hence mechanical and transport properties. To the best of the authors' knowledge, this study is the first ever to report in situ fiber-reinforced composite of PLA/LDPE blend system.



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# Concurent session 13 - Smart materials

## Polymeric Draw Media for Forward Osmosis Desalination

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Forward osmosis (FO) represents a newer form of membrane technology suitable for desalination and water purification. Compared to conventional processes such as reverse osmosis, FO is lower energy and lower fouling, operating on differences in osmotic pressures between the feed and draw solutions. This imbalance causes the water to move through the membrane, to be reclaimed on the other side. There are a range of strategies involving draw solutes but our groups work has involved the use of stimuli- responsive hydrogels to both induce the water flow and then to reclaim the resultant fresh water[1]. A simple way is to grind the hydrogel into particles.

In this talk, a number of strategies we have developed to enhance the hydrogel behavior will be shown. These include the incorporation of temperature-responsive repeat units into the matrix, which change hydrogel polarity on raising temperature in order to make the hydrogels hydrophobic and release water (alternative energies such as solar, or waste energy can be used). We have used additives of carbon particles or graphene oxide to improve properties, the latter leading to improved flux and swelling ratio). Such black particles also enhance the absorption of light. The use of magnetic particles in the hydrogels allowed drying by magnetic field- induced heating. The configuration of the hydrogel into an interpenetrating form (in a foam) also led to much higher flux materials, almost an order of magnitude greater than powder alone. Along similar lines, recent work has used coated polymer fibres, where water flux and dewatering flux were also roughly twice that of the hydrogel particles.

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## Polymer Brushes Grafted Conjugated Polymers as Dynamic Biointerfaces

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Grafting of polymeric side chains onto conjugated polymer backbones provide a versatile route towards designer conjugated polymers with added functionality, tunability in their optoelectronic properties, processability and responsiveness to stimuli. In our previous work with charged brushes, we have demonstrated a potential-dependent switch[1,2]. In this presentation we will discuss polymeric brushes grafted from conductive polymer films which display dynamic surface switching dependent on either pH [3], or salt, temperature [4] and electrode potential. Such surfaces present novel and exiting biointerfaces with multiple control parameters, with a range of additional possible applications, such as in micro- and nanofluidics and chromatography separation.

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## Green polymers from dynamic polymers to lignin based polymers

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Dynamic polymers (reversible polymers) represent a relatively new class of materials that possess bonds capable of reversibly connecting and disconnecting monomers in response to stimuli such as heat or light. These reversible bonds can be used to construct a recyclable polymer via material polymerization and depolymerization, on demand.[1] Thymine, one of the nucleic acid bases of DNA, has the propensity to reversibly photo-dimerize in the solid-state. Our research exploits this reversible dimerization to develop novel reversible polymers using di-thymine monomers.[2] The design and synthesis of various di-thymine monomers, determination of monomer crystal structures, and characterization of the photoproducts using NMR, UV- vis, GPC, and other polymer characterization techniques will be discussed in the presentation.

Catalytic "chemical" depolymerization of lignin will also be discussed.[3] A new lignin chemical depolymerization was developed using redistribution mechanism with phenols and copper catalysts under mild condition in water. The advantage of the technology is not just producing oligomers as a source of aromatics but also producing monomers for thermoprocessable lignin based polymers.

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# Lobster-inspired Hybrid Actuator

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Polymers are recently used to construct a novel class of soft robots made from soft material. Such "soft" design enables lighter structure, continuum motion, lower fabrication cost, and easier customization, making soft robot a potential solution to safety issues in physical human-robot interactions, i.e. medical robot, service robots, wearable devices. One major challenge in soft robotics is in fundamental research on the explicit modeling of the highly non-linear motions generated by polymers with soft nature.

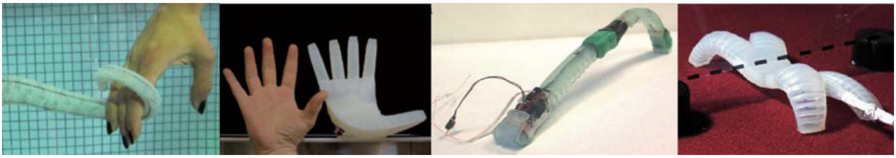

*Fig. 1 Examples of soft robot designs made from polymers, from left to right, including octopus- inspired grasping[1], under-actuated dexterous hand[2], caterpillar-inspired locomotion[3], and multi- gait quadruped[4].*

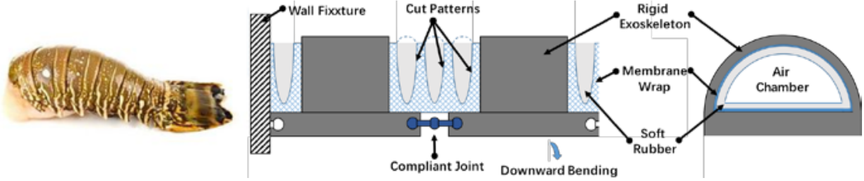

*Fig. 2 Design inspiration from lobster abdomen & tail, and illustration of the proposed hybrid actuator, combining a soft rubber with an empty chamber, wrapped by a thin layer of non- extendable membrane with cut patterns, enclosed by a rigid skeleton.*

This paper presents a novel bio-inspired hybrid actuator in Fig. 2 with the following design features, opening doors for novel soft robots that can be analytically modelled using traditional kinematic and control theory:
The design concept is derived from the biomechanical structure of lobster abdomen combining rigid, soft and membrane material, which is first of its kind in literature;
A piece of soft rubber, made by polymers such as silicone, with an empty chamber is actuated by pneumatic power source for deformable actuation, mimicking the large lump of muscles in the lobster abdomen, making the actuator light in weight, high in power-to-weight ratio, and easy in customization;
A rigid exoskeleton is designed to enclose the soft rubber with stiff links and compliant joints for mechanically explicit spatial motions, mimicking the exoskeletons of the lobster tail, making it possible to explicitly characterize the actuated motion using classical kinematic theory of a robotic revolute joint;

Programmable motions are further implemented by attaching a thin and non-extendable layer of membrane with specific cut patterns, wrapped around the soft rubber, over the compliant joint between the stiff links, enabling programmable deformations of the soft rubber for desirable actuation.

Inspired by lobster tails, the proposed hybrid robotic actuator harnesses the non-linear deformations in the soft rubber by the serial jointed rigid exoskeletons, where programmable motion is achieved through the cut patterns on the membrane layer, generating desirable actuations that can be explicitly described using classical theories in mechanism kinematics. A testing platform is currently under development to further characterize the mechanical performance of this hybrid actuator. Development of the proposed hybrid actuator can be further implemented in assistive and rehabilitation robots augmenting individuals with functional grasp pathologies, aiming at improving their quality of life.

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# Strain sensors based on graphene aerogel composites

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Stretchable strain sensors have recently been extensively investigated to meet the rising demand of wearable electronics. Nanomaterials, such as metal nanoparticles, nanowires, carbon nanotubes, and particularly, graphene nanosheets have been demonstrated as promising building blocks for innovative strain sensors due to their superior mechanical and electrical properties [1]. However, development of strain sensors with both high sensitivity and high stretchability is still a grand challenge.

Here we present the fabrication of highly sensitive stretchable strain sensors based on the composite of three-dimensional graphene (graphene aerogel, GA) and polydimethylsiloxane (PDMS). The composites exhibit high sensitivity with a gauge factor up to ~ 39.3 (**Figure 1a**). The sensors exhibit excellent durability and stability, with the electrical response remaining nearly unchanged after nearly 10,000 cycles (**Figure 1b**). More importantly, the sensor sensitivity can be adjusted by simply changing the concentration of the starting graphene oxide suspension and/or the freeze drying temperatures, which alters the pore size and pore wall thickness of the GA. The results demonstrate that the higher the graphene oxide concentration, the lower the sensitivity. Additionally, sensors consist of GA fabricated at -80 $^{o}$C exhibit highest sensitivity within -195 $^{o}$C and -20 $^{o}$C freezing temperature range. The variation of the sensitivity is found to correlate with changes in the pore structure (**Figure 1a**), which makes it possible to customer design sensors with specific piezoresistive behavior.

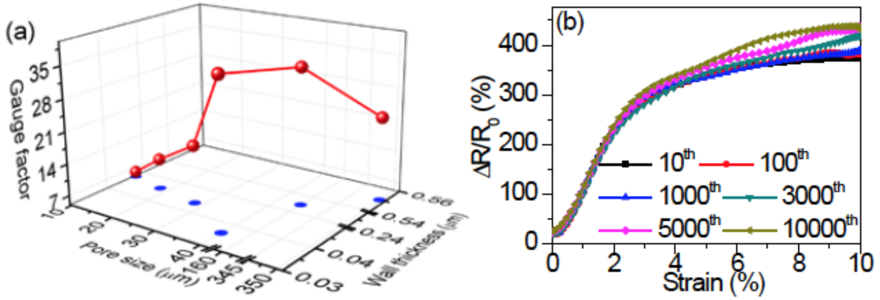

**Figure** 1. (a) Gauge factor (monotonic tension) of GA/PDMS composite sensors versus pore size and pore wall thickness of GA; (b) ΔR/R0 versus ε curves for multiple-cycle tests up to 10000 cycles.

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# Enhancing the properties and expanding applicability of poly(propylene carbonate)

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Poly(propylene carbonate) (PPC) is a thermoplastic aliphatic polyester prepared via the co-polymerisation of carbon dioxide (CO2) and propylene oxide[1]. In addition to providing a value-added use for CO2, PPC's additional benefits include biodegradability[2], renewability of monomers, cost effectiveness, transparency and exceptional barrier and elastic/ductile properties. Despite its great potential, its applicability is significantly limited due to its poor mechanical strength and low glass transition temperature Tg of ~40°C[3], often leading to cold flow under ambient conditions. Therefore, improving the strength, rigidity and structural integrity of PPC is necessary in order to expand its application and market areas.

Co-polymers of poly(propylene carbonate) and poly(caprolactone triol) (PCLT) were synthesised via a simple yet effective one-pot, two-step method, without the need for catalyst or solvent. Through the introduction of a minimal amount of PCLT, the thermal stability, strength, stiffness and damping ability of PPC was enhanced, while also restricting creep and flow. Additionally, PCLT-PPC co-polymers were flexible and easily moulded into shapes while maintaining their form and structural integrity.

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# Concurent session 13 - Surfaces

## Prebiotic Polymers for Coatings in Biomedical and Material Sciences

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Prebiotic chemistry is the study of the chemistry required for the origin of life to have arisen.[1] We report the first application of prebiotic chemistry and specifically prebiotic polymers to materials science.

Polymers of HCN have been proposed as one class of polymers of possible prebiotic relevance.[2] We have drawn upon the work investigating HCN polymers in the prebiotic field and applied it as a solution to material science challenges Here we have used aminomalononitrile (**1**)[3], as a convenient precursor to HCN polymers, which spontaneously polymerizes to give a brown complex nitrogenous polymer (**Fig. 1**). We found that the aqueous polymerization, can be used to coat a wide range of organic and inorganic substrates.[4] We will present details of coating methodology and the interaction of the coating with biology. This discovery opens the door to the re-examination of 60 years of experimental prebiotic chemical research from the point of view of its application to polymer, material and life sciences.

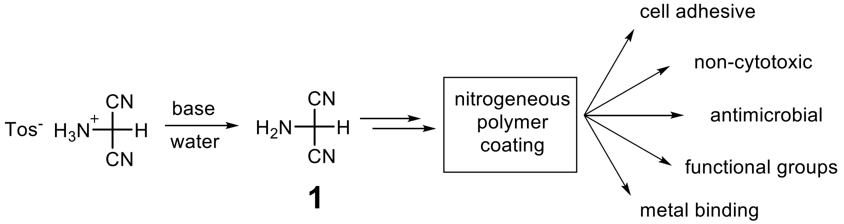

**Figure 1**. Polymerization of aminomalononitrile **1** to produce a highly nitrogenous polymer coating with a variety of applications.

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# Antimicrobial coatings for reverse osmosis membranes

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One of the major issues affecting membrane based desalination and water treatment is biofouling. Our research has focused on the development of anti-biofouling polymeric coatings for polyamide (PA) thin film composite (TFC) reverse osmosis (RO) membranes used to desalt water. Various techniques for modifying these surfaces including, surface initiated activators regeneration by electron transfer (ARGET) atom transfer radical polymerisation (ATRP)[1-3] and interfacial co-polymerisation will be discussed relative to industry needs and upscaling potential. The talk will focus on the polymerisation of the antimicrobial agents, sulfobetaine methacrylate (SBMA),[1] [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MTAC) [2,3] and eugenyl methacrylate (EgMA). [4] Modified membranes were tested for their ability to permeate water and reject salt in comparison to unmodified membranes. Studies were also undertaken to determine the chlorine tolerance of the modified membranes, and with regards to their anti- biofouling properties. A brief overview of attempts to license the interfacial co-polymerisation method are highlighted.

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## Colloidal crystal based micro- and nanostructures as biomaterial surfaces

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The control of interfacial interactions at biomaterial surfaces is the key to a broad range of biomedical applications including stem cell growth, prevention of biofilm formation and control of other adverse responses such as inflammation and thrombosis. The specific surface properties of biomaterials such as micro- and nanotopography and specific chemistry can profoundly influence how cells and bacteria attach and grow on surfaces of biomedical importance. Recently, we have established a group of elaborate surfaces that display ordered topographies with tuneable chemistry based on self-assembled binary colloidal crystals (BCCs). They are introduced as surfaces for applications including cell culture, patterns to manipulate bacterial-surface interactions and as templates to generate chemical patterns using thin film processes such as plasma polymerisation, sputter coating and glancing angle deposition (GLAD). The BCCs are fabricated using evaporation induced colloidal self-assembly (EICSA) using combinations of micron and nanometer sized spherical particles. We show that such surfaces have potential to control not only attachment but also the behaviour (including differentiation) of stem cells, osteoblasts, and fibroblasts. We also demonstrate that the colloidal crystals patterns can be selectively functionalised with hydrophilic polymer brushes to control attachment of medically relevant bacteria such as *Pseudomonas aeruginosa.* In summary, self-assembled colloidal crystal based surface modification have the potential to be used in a range of biomaterials applications due to the ease of fabrication and complexity of surfaces that are possible to generate, enabling a capability to answer important biological questions that so far limit clinical usage of new polymer based surfaces.

# Controlling the Uniformity of Plasma Polymerised Acrylic Acid Films with Reactor Geometry

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Plasma polymerization modifies surfaces via the deposition of a thin film containing specific functional groups. The organic monomer is introduced into the chamber as a vapour, fragmented via radio frequency and deposited onto all surfaces in contact with the plasma1 . Acrylic acid is a commonly used monomer for plasma polymerisation and produces a negatively charged carboxylic acid terminated surface. Plasma polymerised acrylic acid (ppAAc) surfaces have been used for a number of applications such as adhesion or cell promoting interfaces2 . Plasma polymerization was carried out in a custom-built stainless steel Tshaped reactor. The aluminium disk electrode was located in three different positions (end, front and top), to investigate its influence on ppAAc film uniformity. ppAAc films were deposited at 30W, 1.5 sccm for 20 min. The surface chemistry was analysed with X-ray photoelectron spectroscopy while the film thickness was determined using spectroscopic ellipsometry. With the electrode at the front, the ppAAc film thicknesses decreased while the carboxylic acid group concentrations increased as the distance from the electrode increased due to decreased fragmentation further from the electrode. For the electrode at the front, two sample zones were observed with once again thicker films with lower carboxylic acid concentrations for the films closest to the electrode. For the electrode at the top, the film thicknesses and surface chemistry were more uniform than for either of the other configurations as all of the samples were the same distance from the electrode. These results have shown that reactor geometry is important for producing uniform ppAAc films.

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# Fundamental Understanding on Scratch Behaviour of Polymeric Films and Laminates

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Polymeric films are extensively used in a wide range of applications thanks to their recyclability, low cost, and good physical and mechanical properties. However, these properties are significantly affected by several tribological damages such as scratch. In this study, we investigate the scratch behavior of polymeric films and laminates using an ASTM/ISO scratch testing methodology and finite element methods (FEM) simulation. The effects of molecular orientation and architecture through the incorporation of ethylene comonomer, on the scratch resistance of polypropylene-based films were determined. Results show that tensile properties of the films increase with higher film orientation and lower ethylene comonomer in PP, which leads to a better scratch resistance. The FEM modeling results suggest that the improvement of scratch resistance is associated with the shift of stress concentration from the film-substrate interface toward the film surface. Also, the parametric study conducted using FEM analysis indicates that the scratch resistance of PP films is insensitive to their Young's modulus. Instead, yield stress and strain hardening slope are the main constitutive parameters responsible for the observed improvement in scratch performances. Moreover, the scratch behavior of polypropylene-polyamide laminates was studied. Preliminary results demonstrate that PP/PA laminates have better scratch performances than PA/PP laminates. This is attributed to the low coefficient of friction of PA surfaces and the functionally graded structure of PP/PA system on the aluminum substrate. More experimental tests and FEM simulations will be consistently performed to generate more data and support our results before presenting them at the upcoming EPTS summit. It is believed that this study opens up new avenues for the design of polymeric laminates and thin films with better scratch performances.

# Abstracts of the
# POSTER PREZENTATIONS

# Development of pharmaceutical grade carrageenan from local Indonesian *Euchema* cottonii

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*Euchema cottonii* as a good source of kappa carrageenan, can be abundantly cultivated in Indonesian coastal areas. The optimum results for producing semi refined carrageenan (SRC) polymer depending upon the sample history and extraction process parameters [1,2,3]. The effects of these parameters on carrageenan quality such as rendemen (yield value), gel viscosity, gel strength, sulphite residue content, Loss on Drying (LoD), and other parameters according to The United States Pharmacopoiea (USP) and Handbook of Pharmaceutical Excipients had been studied. The results showed that alkaline treatment (type and concentration) strongly influenced the yield value, gel viscosity and gel strength. The value of LoD was independent of alkaline treatment but more to be strongly influenced by method of extraction. *Euchema cottonii* from spot area of sample gave the heavy metal free of carrageenan, as one of pharmaceutical excipient parameter. The Total plate count (ALT), *E. Coli* and Salmonella numbers were depended upon extraction process and production technology. By optimisation process including different extraction process and production apparatus, the pharmaceutical grade carrageenan from local Indonesian *Euchema cottonii* had been thoroughly studied. The kappa karagenan in samples were confirmed by Infra Red Spectrofotometry.

Keywords : Carrageenan, *Euchema cottonii*, Pharmaceutical grade

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# Incorporation of RAFT Synthesised Hyperbranched Polymers into Solid Networks by Photoinitiated Thiol-ene Reactions.

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There is a need for control over the structure of polymer networks for specific end applications in areas such as biomaterials, 3D printing and coatings. [1,2] Currently, polymer networks produced are largely restricted to the commercial availability of monomers. Additionally the desired purity of these monomers is often lacking. This is a shortcoming that drastically limits the structural composition of networks formed and in turn restricts the physical properties. With control of polymer network structures through tailored synthetic design of the monomers, designer networks can be produced with desired physical properties. Our aim is to create designer photo curable hyperbranched based resins for 3D printing application, and ultimately use a printing rig fitted with a monochromatic light source to cure complex structures layer by layer.

Hyperbranched polymers (HPs) can be synthesised by RAFT polymerisation of hydroxy-functional acrylates using a RAFT agent bearing a polymerizable group, affording a HP with pendant hydroxyl groups. The hydroxyl groups in the synthesised HPs can then be functionalised to vinyl groups (Fig.1).

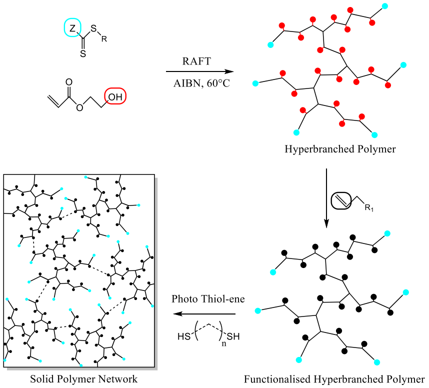

**Figure 1**. Scheme showing the step by step synthesis of functionalised RAFT synthesised hyperbranched polymers being incorporated into solid networks by thiol-

ene reaction with dithiol molecules.

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# Polymer based hybrid materials for improved hydrocarbon sensor response

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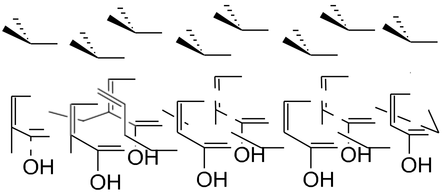
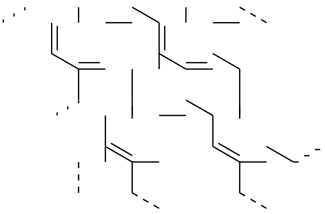
Infrared sensors based on attenuated total reflectance (ATR) spectroscopy have attracted significant interest for the environmental analysis of hydrocarbons in water.[1] The material that is coated onto the surface of the ATR crystal/waveguide material is critical for the analytical performance of the ATR waveguide. The coating generally comprises of a glassy low Tg polymer which is able to partition the species of interest into the evanescent field and exclude other substances that would lead to interfering effects. In an effort to improve the analytical properties (i.e., sensitivity and selectivity) of our chemical sensors we have investigated new hybrid materials such as polymer-calixarene composites. Calixarenes are container shaped molecules which are known to interact and bind with a variety of small molecules via host-guest interactions[2]. In addition, we have also investigated composites incorporating hypercrosslinked aromatic resins, which are known to have high surface areas, are highly dispersible and can increase the permeability of separation membranes[3]. In this paper, we present the sorption and sensing properties of various polymer-composites.



p-tert-butyl calix[8] arene



hypercrosslinked aromatic resin

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# Non-biofouling Properties of Graft-Type Gel with Concentrated Polymer Brush Structure

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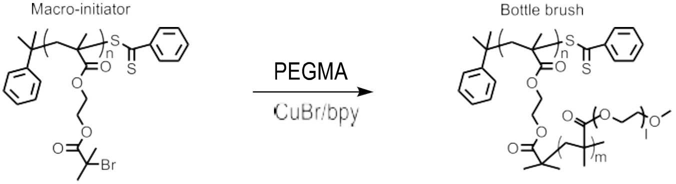
Recently, we have successfully prepared well-defined, concentrated polymer brushes (CPBs) by living radical polymerization and demonstrated non-biofouling properties of the CPBs [1-3]. In this study, in order to develop simple and versatile coatings with such non-biofouling properties, we have newly designed and synthesized a graft-type gel by cross-linking between graft-chain ends of bottle brushes. Bottle brushes were prepared by atom transfer radical polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) using poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) as a macro-initiator (Scheme 1). Coating films of the bottle brushes and a cross-linker were prepared on silicon wafers by spin-coating.

Subsequently, the films were cross-linked by heating at 120 °C for 2 hours. We examined protein adsorption, cell adhesion, and bacteria adhesion on the films. By optimizing the bottle brush structure (e.g., graft chain length), the coatings showed excellent non-biofouling properties similar t typical CPBs. The details will be discussed.

**Scheme 1.** Preparation of the bottle brush.



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# Study on Production of Banana Fiber-Reinforced Composites

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This study attempted to extract fibers from banana plant, observe the structure of the obtained fibers (figure 1) and utilize in the production of banana fiber-reinforced composites. Acrylonitrile Butadiene Styrene (ABS) was used as the matrix. ABS sheets prepared from its pellets by using hot- pressing method was used to produce unidirectional (UD) banana fiber- reinforced composite. It was found that the optimum condition for the composite processing was at 170 °C, 100kg/cm$^2$ in 20 min with 30 wt% of banana fiber. The three dimensional structure of the obtained fibers observed by Xray-CT was used to explain the relation between the processing conditions and the mechanical properties of the composites.

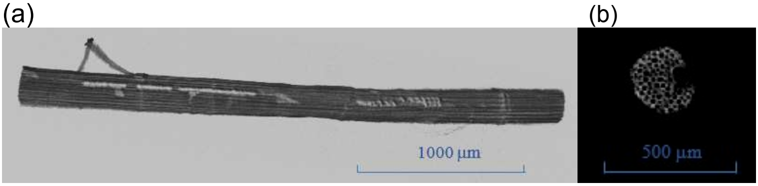

Figure 1: Structure of banana fibers observed by Xray-CT
(a) along the length; (b) cross-section of the fiber

It was worth noting that the tensile strength of composite was *c.a.* 2.5 times comparing to that of ABS sample, 1.8 times comparing to that of nypa palm fiber-reinforced ABS composite.

In addition, styrene polymerization was applied to increase the interfacial strength between fibers and matrix. Various polymerization conditions such as amount of initiator, reaction time, reaction temperature were respectively observed.

# Hierarchical Composites with High Volume Fractions of Carbon Nanotubes

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Carbon nanotubes (CNTs) were grown onto quartz and alumina fabric via catalytic chemical vapour deposition. The fabric was used to prepare novel hierarchically structured composites with high volume fractions of CNTs. The wettability and bonding of the CNT-coated fabric was improved by functionalisation using oxygen plasma, prior to epoxy resin infusion. The plasma treated, CNT-coated quartz/epoxy composites showed an 80% increase in the in-plane shear strength over quartz/epoxy composites, while the CNT-alumina/epoxy composites showed greater than 300% increase in the in-plane shear strength.

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# Visibility of polymers in medical imaging techniques

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Polymers have been a long interest in the medical field for their biodegradability, their ease to handle, their cost and their versatility. They have been used as excipients for drug delivery as well as material for devices[1,2].

In addition, the trend going towards customized medicine[3], polymers are of very high research interest in health science.

The main focus of research in polymers for medical devices application is often the biodegradability rate and the mechanical properties, meanwhile the radio-opacity is an other issue that we will try to address in this study.
Considering the different imaging techniques used in the medical field, we decided to study the visibility of different ingredients depending on the preferred imaging technique used for implantation of medical devices.
Our goal in this study is to implement an easy and low cost manufacturing technique that will provide visibility for medical devices under the most common medical imaging techniques.

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# Effect of Coagulation Bath Composition on Oxygen Enrichment of Cellulose Acetate Membrane

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Oxygen enrichment system has long been recognized in many industrial processes where its products contained more than 21% oxygen ($O_2$). This system is crucial especially for the air-fuel ratio combustion industries since the used of oxygen-enriched air can help to increase the energy efficiency of the combustion process. Membrane separation technologies have been proved to be among the top separation technologies in industries. Research had been done continuously in order to improve the membranes efficiency. The objective of this research were to examine the effect of using various composition of water–N-methyl-2-pyrrolidone (NMP) mixture in coagulation bath on cellulose acetate (CA) membrane morphologies and gas separation performance. NMP was added between 0 to 50 vol% into the water coagulation bath. The polymer dope solution was prepared by dissolving 23 wt% CA polymer resin in NMP. Dry/wet phase inversion technique had been employed to fabricate the flat sheet asymmetric CA membrane with a fixed solvent evaporation time of 15s. The membrane separation performances were measured using soap bubble meter with pure $O_2$ and nitrogen ($N_2$) gases. Prior to gas permeation testing, the prepared membrane was silicone coated to seal any surface defects. The structure of the membrane had been examined using Variable Pressure Scanning Electron Microscopy (VPSEM). By increasing the NMP concentration, the finger-like structures were reduced and sponge-like structure starting to form better. The optimum concentration was at 10 vol% of NMP in water coagulation bath with the highest selectivity value of 10.69 and $O_2$ permeability of approximately 1.00 GPU. Hence, in this study; manipulation of coagulation bath composition had significant improvement on the CA membrane gas performance in term of selectivity with only slight reduction of permeability.

Acknowledgement: We gratefully acknowledge the financial support from Universiti Teknologi Malaysia and Ministry of Higher Education Malaysia (Grant no: 4L116 and 4F652).

# Effect of IONPs as Nano-fillers on PSf Haemodialysis Membrane Structure and Separation Characteristics

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Membrane is the heart of haemodialysis treatment in removing excess metabolic waste such as urea. Although polyvinylpyrrolidone (PVP) has been working well as pore former agent when blended with polysulfone (PSf), this haemodialysis membrane suffers low-flux problem, which affects the end-stage renal failure (ESRF) patients. To overcome this limitation, iron oxide nanoparticles (IONPs) were added to PSf membrane matrix as nano- fillers to modify the membrane structure in favour of endowing better separation characteristics. To reduce the aggregation effect of IONPs in the dope solution, citric acid was added. The membrane morphology and separation performance were investigated for the neat membrane and membrane incorporated with 0.2 wt% of IONPs. The membranes were characterised in terms of morphology, pure water flux (PWF) and protein rejection using bovine serum albumin (BSA). The decrease in contact angle value from $66.62^{o}$ to $46.23^{o}$ for PSf/IONPs membrane indicated the increase in surface hydrophilicity, which provides the positive influences on the PWF and BSA rejection of the membrane. The PWF increased from 23.73 $Lm^{-2}h^{-1}$ to 36.28 $Lm^{-2}h^{-1}$ as IONPs were added due to oxygen content of IONPs and the large surface area offered, which had improved the affinity of membrane towards water molecules. IONPs that were homogenously embedded in the inner skin layer as revealed by microscopic images also helped in facilitating water molecules. The same trend was observed for protein rejection, in which the PSf/IONPs membrane rejected 95.6% of BSA compared to 91% protein rejection obtained from the neat membrane. The incorporation of IONPs enhanced the separation characteristics of PSf membrane for haemodialysis application.

**Acknowledgement:** We gratefully acknowledge the financial support from Universiti Teknologi Malaysia and Ministry of Higher Education Malaysia (Grant no: 01G46 and 4J206).

# Functional Alkynyl-terminated Star-Shaped Carbonates Synthesized with $CO_2$ as Feedstock

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Multi-branching carbonates[1] with functional terminals can serve as core to synthesize useful dendritic[2] and polymeric materials.[3] The design of new synthetic route to such carbonates in an environmentally benign way is the key to synthesize more functional materials, especially biocompatible materials. Here we report that new star-shaped alkynyl-terminated carbonates (Fig.1) can be synthesized in good isolated yields under very mild conditions (1 atm $CO_2$ and RT) promoted by a cheap base ($K_2CO_3$) and tetrabutylammonium bromide (TBAB).[4] The six terminal alkynyls carried by the star-shaped molecules provides a key access to more complex and functionalized polymeric materials.

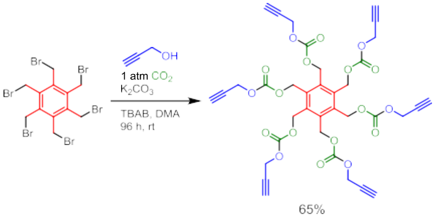

Fig .1 Synthesis and structure of hexa-carbonate-acetylene compound.

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# Natural fiber composite flame retarded by zinc borate or hybrid of zinc borate and alumina tri-hydrate: Flammability, thermal and mechanical properties

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Alumina trihydrate (ATH) and zinc borate (ZB) as flame retardant agents are capable of improving flame resistivity of fiber reinforced composites. The current work investigates the effect of ATH and ZB particles on flammability, thermal, mechanical performances and surface morphology of empty fruit bunch (EFB) fiber polymer material, based on vertical Bunsen burner, bomb calorimetry, thermogravimetric (TGA), tension, flexure, impact and scanning electron microscope (SEM) test results. The formulations with concentration of 5%, 10% and 15% ZB and 15% ATH/ZB coupled by weight percentage were compared with the control composite (EFB/epoxy). The best flammability and thermal results were observed with 15·wt% ZB loading amongst all tested flame retardant (FR) containing formulations. Zero drip flame time, lowest total flame time and lowest mass loss were recorded for this composite from vertical Bunsen burner experiment. The gross heat (GH) of combustion for this sample was attained to reduce by 11.72% relative to the control from bomb calorimetry study. As obtained in TGA results, mass residue and thermal degradation temperature of 15·wt% ZB loaded composite increased by 124.7% and 4.88% compared to the control. It was observed that the control showed greatest tensile strength and elongation at break except for 5·wt% ZB containing composite, which showed 1.57% higher than the elongation at break of control. For flexural properties, strength and strain dropped with the incorporation of FRs. Composites with 15·wt% ZB and 10% ZB loading improved the impact strength compared to the control while the rest of formulations experienced a drop.

# Magnetite-functionalized graphene/poly (styrene- butadiene-styrene) nanocomposites: Thermal and mechanical properties

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Advanced polymer composites containing hybrid filler are gaining increasing attention due to their multifunctional applications. In this work, poly (styrene-butadiene-styrene) (SBS) composites containing magnetite- functionalized graphene were prepared by a dissolution-dispersion- precipitation solution method. This method was chosen due to its simplicity and cost effectiveness in producing polymer composites with multifunctional properties. The compatibility between polymer, filler and solvent used were enhanced through p-p interaction between their respective aromatic systems of p-electrons. Evidently through SEM and XRD, amounts of magnetite-graphene were well distributed over SBS which indicates good polymer-filler interaction. Improvements in SBS properties with respect to magnetite-graphene loading in terms of thermal stability, tensile mechanical, dynamic mechanical and creep-recovery properties were demonstrated. Magnetite-graphene at 5 wt·% improved the yield strength and Young's modulus of SBS by 66% and 146%, respectively. Similarly, observed increase in storage modulus and loss modulus of the composites show reinforcement effect of the filler even at low concentration. The reinforcement effect had a more pronounced effect on the polybutadiene phase in SBS. The creep and recovery at different temperature conditions were modelled using Burger's model and Weibull distribution function. As expected, creep strain increased with temperature but reduced with filler concentration.

# Synthesis of Hydrophobic Natural Fiber and Yarn using Rod-like Silica and Chitosan as Surface Modifier

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Hydrophobic textile is a type of smart fabrics. Some of it are commonly coated with small particles and finally treated by water repellent agent in terms of acquiring its hydrophobic property. This research describes how hydrophobic textile could be formed from its initial form of fabrics which are fibers and yarns. Fibers synthesis process was commenced through wet spinning of viscose rayon mixed with silica which has been formerly produced using sol-gel method. These nano-size particles were also attached on yarns from Ramie plant. Subsequently, fibers and yarns were dip-coated with chitosan solution and been dried out. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) mapping results showed that rod-like silica were well dispersed on the fibre and yarn surfaces, performing roughness and creating hydrophobic effect with chitosan on its outer layer. Several characterization methods correlated to water absorption of the fibers were conducted. Fibers swelling percentage decreased from 50.2% to 17.13%, while moisture regain (MR) number also decreased from 14.28 to 10.72. In addition, water contact angle of Ramie yarns exceeds 135 degrees and remained even after 30 minutes of water droplet.

# Formulation of Chloramphenicol Opthtalmic Hydrogel using Hydroxy Propyl Methyl Cellulose (HPMC)

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Faculty of Pharmacy Universitas Padjadjaran Indonesia
Email : insan.sunan.kurniawansyah@unpad.ac.id

## ABSTRACT

Formulation of ophthalmic preparation is an important factor in the ophthalmic drug delivery system. An example is hydrogel which increases retention time of drug on the eye compared to conventional preparations. A research conducted on formulation and evaluation of Chloramphenicol ophthalmic hydrogel with various concentration of Hydroxypropyl methylcellulose (HPMC), F1 (0,2 % HPMC), F2 (0,3 % HPMC), F3 (0,4 % HPMC) and F4 (0,5 % HPMC), intended to create ophthalmic hydrogel safe for use. Evaluations tests comprised organoleptic, pH, viscosity and rate. Observations were done on sterility, potency and in vitro drug release. Results indicated concentration of basis had similar effect on evaluations but not in viscosity and release rate. It was obtained that F4 (0,5 % HPMC) has least Chloramphenicol diffused at 5 minutes 11,01 % and 71,13 % after 8 hours. The in vitro drug release from the hydrogel, significantly influenced by HPMC concentration which enhanced the bioavailability through longer pre-corneal residence time and ability to sustain the release of the drug.

Keywords: Bioavaibility, Chloramphenicol, Opthalmic Hydrogel, HPMC.

# Banana Starch Nanocrystals/ Poly(butylene succinate) Bio- nanocomposite Films: Influences of Chemical Modification with Long-Chain Fatty Acid on Physical and Mechanical Properties

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In this research, bio-nanocomposites were prepared by using poly (butylene succinate) (PBS) as a matrix and starch nanocrystals (SNC) as a reinforcing filler at various SNC content. SNC was synthesized from banana starch by hydrolysis with sulphuric acid solution. The obtained starch granules after hydrolysis were characterized by laser particle size analyser, XRD, and TEM. It was found that banana SNC exhibited approximately 30-70 nm of particle size and 47.13% of crystallinity. After that, the banana SNC was modified by esterification reaction with lauroyl chloride in an alkali reaction medium for improving the interfacial adhesion between the matrix and the reinforcing filler. Subsequently, PBS and banana SNC were mixed and transferred into films by using a twin screw extruder and a chill-roll casting film extrusion, respectively. Effects of unmodified and modified banana SNC content on properties of PBS bio-nanocomposite films were investigated in terms of wettability, water absorption, water vapour transmission rate, thermal properties, and tensile properties. Preliminary results revealed that the addition of modified banana SNC into PBS brought about the increment of the tensile strength and the percentage elongation at break. The highest tensile strength of PBS nanocomposite films was observed at 1 wt% of modified banana SNC. The tensile strength was increased upto 3.8% compared with the neat PBS. This is due to the hydrophobicity of modified banana SNC after modification with lauroyl chloride, leading to greater compatibility with PBS matrix.

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# Lamellar and micellar phases of pluronic F127: Insights from computer simulations

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**Motivation:** Poloxamers, also known as Pluronics (PL), are linear triblock copolymers. Flanked by hydrophilic blocks of poly(ethylene oxide), the center of the copolymer is made up of hydrophobic poly(propylene oxide). PL have been proposed as biomaterials for the design of drug delivery systems. Aditionally, alteration of physicochemical properties of lipid bilayers by PL unimers could lead to enhance the passive transport of some drugs. In a previous work, we determined through simulations the stability of the interaction of PL F127 unimers with lipid bilayers[1]. In particular we found that u-shape (**U**) and straight (**S**) unimers were stable within the bilayer. The goal of this study is to evaluate the stability of lamellar and micellar phases of the copolymers, considering the unimer internal structure (U or S).

**Methods:** Molecular Dynamics (MD) simulations were carried out using a Coarse Grain (CG) F127 and water model. We investigate two kind of structures:

-Lamellar phases: we compared the stability of monolayers (**S**) and bilayers (U) formed by this copolymers.

-Micellar phases: we investigated the internal micelle structure of pre- and self-assembled micelle.

**Results and conclusions**: Through this work we were able to shed light to the molecular structre of the lamelar and micellar phases of PL F127 and caputre important features that will improve our understaning of this polymers as a drug delivery sistems. Evenmore, the size of micellar structure found here were in good agreement with dynamic light scattering measurements.

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# Equilibrium Moisture Content of a Crosslinked Epoxy Network via Molecular Dynamics Simulations

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This study presents molecular dynamics (MD) simulation methods for determining the solubility limit of water in a crosslinked epoxy network. Procedures are first presented for dynamically crosslinking an epoxy network consisting of diglycidyl ether bisphenol a (DGEBA) and isophorone diamine (IPD). Water molecules are then introduced into the crosslinked DGEBA- IPD structure. The excess chemical potential for the absorbed water was determined through combining thermodynamic integration and Widom's test particle insertion methods. The limiting moisture uptake of the epoxy structure was determined through comparing the reduced chemical potential of the water held within the epoxy to that of pure water. The DGEBA-IPD epoxy system was found to have a moisture solubility of 3.50–3.75 wt.% when immersed in water at 300 K.

## Isolation and modification of durian seed (*Duriozibethinus* Murr) Starchby acid hydrolysis

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Durian (*Durio zibethinus* Murr) seeds has been found as fruit refuses. Durian has large size which has high content of starch. The purpose of this research was to isolate the starch from durian seeds, and modified it through acid hydrolysis. The isolation of native starch was conducted by using conventional methods, while the modification was by acid hydrolysis using hydrochloric acid (HCl) 2N. Starch quality testing were include microscopic, solubility, acidity, loss on drying, ash content, and microbial limit. Physicochemical properties characterization were include flowability, density, bulk gelatinization temperature and viscosity, amylose content, and degree of whiteness. The results showed that isolation process gave a yield value of 17.68% starch. Starch quality investigation showed that the starch met the Indonesian Pharmacopoeia standards. Brabender viscoamylograph testing showed an increase in viscosity, showing that acid modified durian seed starch had a higher viscosity level compared to native one. Modification of starch also improved its flowability.

Key words: durian, starch, acid modification

# Effect of colour, gloss, and surface texture perception on scratch and mar visibility resistance in polymers

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Scratch and mar damages can critically impact the aesthetics of polymeric surfaces. Their quantification poses considerable challenges, especially for subtle mar damage. Here, we report a new standardized approach that utilizes a modified ASTM/ISO scratch test standard and a psychophysical tool to quantify scratch and mar visibility. The new methodology was then used to study the influence of fatty amide slip agent, colour, gloss, and texture perception on scratch and mar visibility resistance. The slip agent modifiers improved both scratch and mar visibility resistance. The studied colours, gloss levels, and surface texture have limited influence on scratch visibility onset. However, faint mar damage is more sensitive to surface perceptual properties. Green, glossy, and smooth surfaces tend to have less mar visibility resistance. It has been found that overall visibility throughout the entire damage path is a better indicator for ranking mar damage. Results show that contrast slope variation parameter can consistently quantify mar visibility and simulate human perception. To have a better insight on mar behaviour, an experimental and finite element method (FEM) parametric analysis will be performed and results will be presented at the EPTS summit. This analysis will provide a useful tool to determine the effect of the polymer constitutive of physical properties on mar resistance. This unique approach paves the way for a straightforward universal standard that can be utilized to reliably quantify scratch and mar visibility in polymers, thereby opening up a new avenue for the design of polymeric materials with better scratch and mar visibility resistance.

# Study of solvent type effect on preparation of ethyl cellulose microparticles by solvent evaporation method double emulsion system (W/O/W) using focused beam reflectance measurement (FBRM)

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The purpose of this study was to investigate effect of solvent type on solidification rate of ethyl cellulose (EC) microparticles and particle size/distribution of the emulsion droplets/hardened microparticles during solvent evaporation process using focused beam reflectance measurement (FBRM). EC microparticles were prepared by a W/O/W-solvent evaporation method using various solvents, including dichloromethane, dichloromethane:methanol (1:1), ethyl acetate and chloroform. The particle size/distribution of the emulsion droplets/hardened microparticles was monitored by FBRM. The morphology of EC microparticles was characterized by scanning electron microscopy (SEM). The transformation of the emulsion droplets into solid microparticles for all solvents occured within the first 10-90 min. The square weighted mean chord length of EC microparticles which were prepared using chloroform was smallest, but the chord counts was no the highest. The chord length distribution (CLD) measured by FBRM showed that a larger particle size mean gave longer CLD and a lower peak of particle number. SEM data revealed that the morphology of microparticles was influenced by type of solvent. FBRM can be employed for online monitoring of the shift in the microparticle CLD and detect transformation of the emulsion droplets into solid microparticles during the solvent evaporation process. The microparticle CLD and transformation process was strongly influenced by solvent type.

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## Self-healing polymers using photo-responsive dynamic reactions

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Different acrylate polymers were synthesized, which consisted of n-butyl methacrylate (BMA), methylacrylate(MA), hexyl methacrylate(HMA) or ethyl acrylate(EA) and photo-responsive unit, 7-hydroxymethacrloyloxy coumarin dimer, as a crosslinker. The produced polymers can be decrosslinked/crosslinked due to the reversibility of the coumarin unit when irrradiated with 254 nm and 365 nm UV light, respectively. Scratches on the surface of the crosslinked polymers can be healed such that they disappear under microscope, through the photo chemical opening and closing of the crosslinking unit, as charactrerized by IR and UV. In addition, the capabilties of these dynamic polymers to self-heal was measured through their tendency to restore mechanical properties after deformation and failure.

# Synthetic Challenges on the Road to High Performance Conjugated Polymers for Organic Photovoltaics

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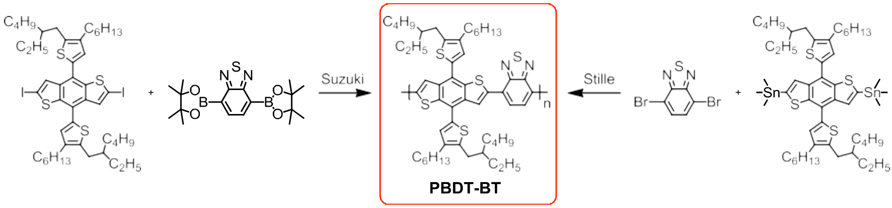
Conjugated polymers have been widely used in bulk heterojunction organic solar cells most often as the electron donor component of the device. There is a large variety of structures based around the electron rich-electron poor push-pull design and a number of reviews have been written on the subject.[1] While there are some basic design rules, the chances of designing a new polymer with high device performance remain low. The problem lies with the fact that appropriate molecular structure design is only one piece of the puzzle for achieving high device performance. Other factors include synthetic methodology, molecular weight of the polymer, solution processability and bulk semiconducting properties of the material.

In this report, we will share our experience of designing and making conjugated polymers with the aim of developing a high performance material for fully printed large area solar cells. Examples will be presented to show the influence of the synthesis method and variation in polymer molecular weight.[2] We will also discuss further strategies for the controlled synthesis of polymers, such as AB-monomer polycondensation.



OPV with up to 9.5% efficiency

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# Gas Separation Properties of Carbon Tubular Membrane derived from Matrimid

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An emerging technology in membrane gas separation is facilitated by the demand in membranes with desirable mechanical properties and, most importantly, improved separation performances. Due to some advantages over traditional methods such as pressure swing adsorption, cryogenic distillation and amine absorption, the membrane separation technology is rapidly developing[1]. Carbon membranes were identified as promising candidates for gas separation application[2]. The utilization of tubular support for carbon membrane preparation is beneficial for gas separation by providing high membrane area per unit volume. Moreover, it is mechanically stronger than conventional flat substrate. In this study, tubular carbon membrane derived from Matrimid was fabricated via the dip-coating method. Three different carbonization temperatures (600°C, 750°C and 850°C) were used in order to produce a high performance carbon membrane. The physicochemical properties of the carbon membrane are highly dependent on the final carbonization temperature. By increasing the carbonization temperature, it will result in higher micropores and increased gas pair selectivity. On the other hand, low carbonization temperatures will constrict pore formation and result in lower gas separation properties. The carbon membrane carbonized at 850°C showed the highest gas separation properties for $CO_2/CH_4$ selectivity of 87.30 with $CO_2$ permeance of 287.36 GPU. The resultant membrane is compared with the literatures, highlighting the potential of carbon tubular membrane for future membrane development.

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# Effects of incorporating ferrihydrite nanoparticles on physicochemical properties of polysulfone membranes to be used for water/wastewater treatment

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This study aimed to investigate the effects of ferrihydrite (Fh) nanoparticle loading on the physicochemical properties of flat sheet polysulfone (PSf) membranes fabricated via phase inversion method. The morphologies and physicochemical properties of prepared Fh and PSf/Fh mixed matrix membranes (MMMs) were characterized using TEM, XRD, FTIR, SEM, AFM, pure water flux analysis, contact angle measurement and membrane porosity analysis. TEM analysis showed that Fh nanoparticles possessed irregular structure with diameter less than 10 nm while XRD analysis indicated that the synthesized Fh showed two broad peaks, which then can be referred as 2-line Fh. FTIR study indicated that new O-H band was formed when Fh was added into membrane matrix. SEM analysis showed the formation of a typical asymmetric membrane structure with elongated fingerlike and looser porous layer. From the study, it has been found out that increasing the loading of Fh significantly enhanced membrane pure water flux from

230.2 L/m$^2$h (M-Fh 0%) to 726.6 L/m$^2$h (M-Fh 15.3%), attributed by the improved membranes structures, membrane wettability, surface roughness and overall porosity. The findings suggested that the PSf membrane made of highest Fh loading (M-Fh 15.3%) was the best performing membrane, owing to its improved physicochemical properties and enabling its better use for water/wastewater treatment.

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# Altering the emission and absorption properties of conjugated polymers using convective self-assembly

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Convective self-assembly (CSA) generally produces highly ordered structures of various nanoparticles[1,2]. Here, we show that, by controlling the deposition speed, substrate temperature and polymer concentration, CSA method leads to thin films comprised of molecules possessing highly oriented chain conformation over large surface area. For example, performing CSA on short chains of conjugated oligothiophenes ($TH_{13}$) leads to highly ordered structures (Figure 1 left). Their optoelectronic properties are visibly changed in comparison to as spin cast samples of same material that adopts rather disordered microstructure (depicted in Figure 1 right). Moreover, significantly different morphologies (porous-like or nanoparticle- like) with altered absorption and emission properties can also be obtained when performing CSA on conjugated polyfluorene (PFO). The advantage of CSA method relies on its high reproducibility and applicability over large surface areas (i.e. several squared centimeters) on any type of compatible (flexible) substrate.

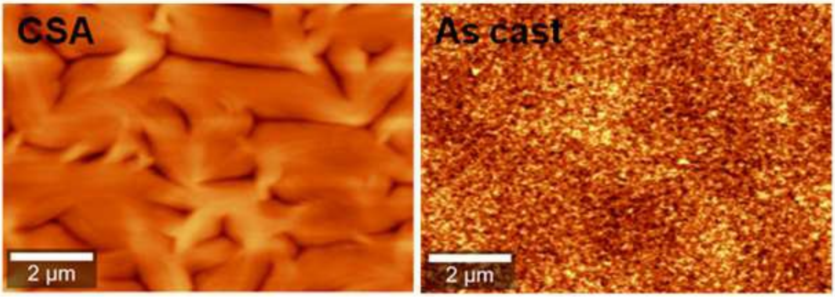

Figure 1. AFM images comparing a CSA ordered $TH_{13}$ film (left) with an as spin cast film (right).

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# Optical, Mechanical, and Morphological Properties of Poly(lactic acid)/Poly(butylene adipate-co-terephthalate) Blend Films: Effect of Temperatures and Chill Roll's Velocities

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In this work, poly(lactic acid) (PLA)/poly(butylene adipate-co-terephthalate) (PBAT) at 80/20 wt% composition was focused to produce peelable lidding films. Optical properties (haze), apparently, can cause by internal (bulk) and external (surface) light scattering. Bulk haze comes from difference in phases or density (inhomogeneities) inside the films, while surface haze can come from crystallinity induced haze and/or extrusion haze. Reducing light scattering could be achieved by selecting the proper processing conditions. Thus, in this study, the effects of processing conditions consisted of temperature profiles along cast extruder (as die temperatures of 165 and 200 °C) and chill roll's velocities (CV) (1, 3, 5, and 6 m/min) on optical and mechanical properties which were related to film morphologies were investigated. Haze of prepared films could be reduced at high temperature due to decreasing of melt elasticity. However, CV affected optical and mechanical properties differently at each temperature. The films produced at low temperature had an orientation effect from CV than high temperature. That is, haze could be reduced by increasing CV from 1 m/min to 5 m/min due to decreasing size of elongated PBAT minor phases. At low CV of 1 m/min, total haze was 8.0 %, whereas at high CV of 5 m/min showed optimized haze that decreased to 4.4%. Moreover, films prepared at high CV provided high orientation than films produced at low CV resulting in high degree of crystallinity. As a result, tensile strength of films could be increased with increasing CV.

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# Synthesis, structure-property relationships of polyphosphoramides with high char residues

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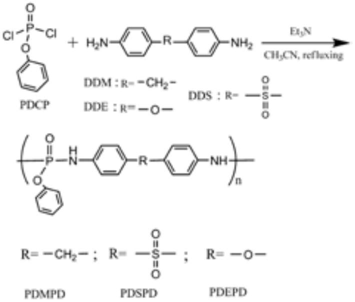
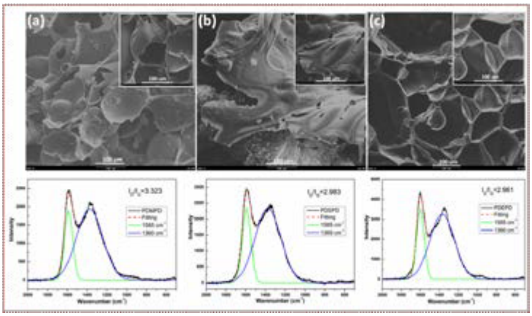
A series of polyphosphoramides with high char residue were successfully synthesized using solution polycondensation and well characterized. The thermal properties, flammability were investigated by Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and microscale combustion calorimeter (MCC). The evolved gases during decomposition were also analyzed using Fourier transform infrared coupled with the thermogravimetric analyzer (TG-IR) technique. The char residues of the polyphosphoramides were investigated by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and Raman spectroscopy. The results showed that polyphosphoramides with sufficient molecular weights could be obtained, having high glass transition temperatures ($T_g$s), high thermal stabilities as well as lower flammability depending on the diamines incorporated. The char residues showed much difference among each other. Interestingly, one sample containing ether group in the backbone exhibited honeycomb-like char morphology, associated with high graphitization degree.





# Polypyrrole coated Fe3O4 nanoparticles for light-triggered release of glutamate

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Polypyrrole, a biocompatible material [1], has emerged as an interesting material for biomedical applications from neural implants[2] to photothermal cancer treatment[3]. Here, we make use of its optical absorbance in the visible and near-infrared[4] to synthesise a polypyrrole-coated magnetite nanoparticle that can be used for the targeted release of glutamate, a key neural transmitter[5]. We show the effect of reaction pH during the ammonia persulfate oxidative polymerisation and the resulting effect on the optical and electrical properties of the doped polymer. Magnetite nanoparticles were then coated with glutamate-doped polypyrrole, producing a structure that can be magnetically driven. We show the resulting glutamate release profile under progressive light illumination at various wavelengths.

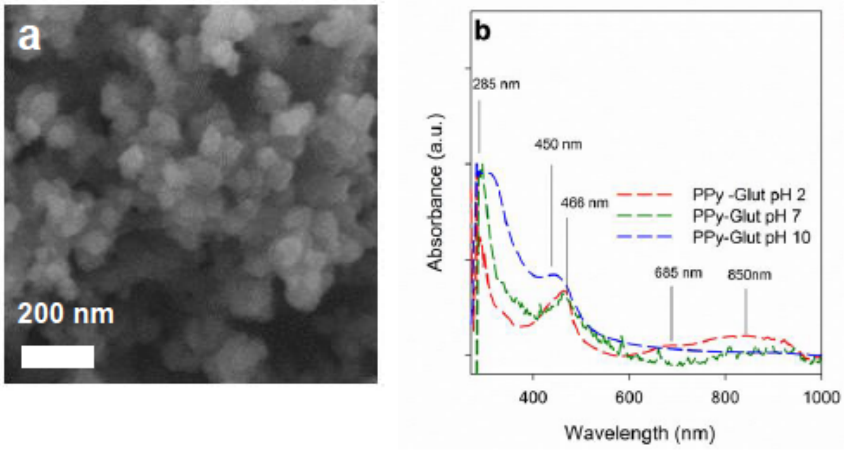

**Fig. 1** a) SEM, and b) optical absorbance spectra of glutamic acid – doped polypyrrole.

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L. K. Bak, A. Schousboe, H. S. Waagepetersen,

# Development of patch using chitosan as polymer matrix

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Patch is a transdermal dosage form that has increasing number of applications for its simplicity with controlled release profile of drug. The ability to provide controlled release manner of drug is developed by the use of polymer as the matrix. In this research, patch of ketoprofen were formulated using various concentrations of chitosan as matrix. Preparation of the transdermal patches was conducted by using solvent evaporation method. Characterization of patch were included physical characteristic, homogeneity, drug assay, drug permeation and stability study. Permeation test were performed in vitro by using Franz diffusion cells with shed snake's skin of Phyton reticulatus as diffusion membrane for 24 hours. The result showed that Chitosan is a potential polymer to be used as matrix for patches since it was stable and gave peel off ability. Permeability test showed that a decrease in permeation of ketoprofen was in line with the increase of chitosan as matrix. Formula containing chitosan 1% and tween 80 0,3% as permeation enhancer gave the highest permeation number as much as 99,15%.

Keywords: Chitosan, Transdermal patch, Ketoprofen

## Protein Transport Studies of Human Epidermal Growth Factor (hEGF) Recombinant of *E. coli* on Extracellular Secretory of Signal Peptide of Outer Membrane Protein A (OmpA)

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Extracellular expression system of *Escherichia coli* has more advantage than intracellular expression system because it can avoid misfolding of the target protein, obtain a high biological activity, and simplify the purification process without cell disruption. Human Epidermal Growth Factor (hEGF) is
6.2 kDa polypeptide consist of a short strand of 53 amino acid residues with three disulfide bridges needed for cells proliferation, differentiation and migration to be used for therapeutic and cosmetics. Extracellular expression of recombinant hEGF was performed using the signal peptide ompA (*outer membrane protein A)* through SecB-dependent pathways to direct the target protein to the periplasm. The purposes of this study were to analyze the transport patterns of hEGF recombinant secretory, and to determine the optimal concentration of harvested hEGF. The methods included transformation of *E. coli* BL21 (DE3) as host cell using plasmid pD881-ompA with electroporatic method; expression of hEGF using L- ramnose as an inducer; characterization of the expressed hEGF using SDS-PAGE, and determination of the recombinant hEGF concentration using ELISA. The results showed extracellular expression of recombinant hEGF indicated by the presence of band on SDS-PAGE gel approximately at 6.2 kDa with the increase of band thickness on periplasm lane and medium lane during 8 hours of induction phase. The transfer pattern of hEGF was occurred from soluble fraction (cytoplasm) to the periplasm then to the medium during 20 hours of induction phase. It was indicated by SDS- PAGE gel that showed the decrease of 6,2 kDa band thickness on periplasm lane and the increase of 6,2 kDa band thickness on medium lane. The recombinant hEGF concentration harvested from the medium was 71.25 μg/mL. Either periplasm extraction or isolation of hEGF from the culture medium can potentially be developed for a scaled-up production.

**Keywords:** Recombinant hEGF, extracellular secretory of *E. coli* BL21, SDS-PAGE, ELISA.

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# Pervaporation separation of water –organic azeotropic mixtures using Poly vinyl alcohol nanocomposite membrane

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The field of pervaporation technology is presently in a state of rapid growth and innovation. Many different membranes have been developed during the past half century and new pervaporation processes are constantly emerging from academic, industrial, and governmental laboratories. The development of new membrane material with higher selectivity and permeation flux are the main aspects of pervaporation process. The main objective of the present work is to study the effect of nanofillers such as bentonite nanoclay, MWCNNT, graphene oxide on the pervaporation separation of organic – water azeotropic mixtures. Water is a universal solvent and forms azeotrops with large number of organic solvents. In this work, novel Poly(vinyl alcohol) based nanocomposite membranes are developed and employed for the separation of water from organic – water azeotropic mixtures. XRD and TEM analysis showed the well exfoliated and distributed nanofiller structure in the crosslinked PVA matrix. The interaction of PVA with nanofillers and hydrophilic character of the membranes were characterized by FT-IR spectra and contact angle analysis, respectively. Effect of nanoclay, carbon nanotube, graphene oxide loading on the pervaporation performance of Poly(vinyl alcohol) nanocomposite membranes is studied. At lower filler loading, the separation efficiency of Poly(vinyl alcohol) membranes increased and able to separate 95% water from the azeotropic mixtures.

# Characterization and properties of nanosilica/epoxy-titane nanocomposite with titanate coupling agent

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Silica-epoxy nanocomposites have become very common among nanocomposites. Charactersitics of the composites depend on the nanosilica and curing agent. In this paper, we present some research results on manufacturing nanocomposites using epoxy, nanosilica and tetrabutyltitanate hardener. Before compounding, the surface of nanosilica was modified by titanate coupling agent (TC-2) to improve compatibility with epoxy resin and hardener. The grafting efficiency of agent to $SiO_2$ - nanoparticles at different reaction conditions which was determined by thermal gravimetric analysis (TG) achieved 13.18%. FT-IR spectra, EDS, and TEM confirmed that TC-2 was succsessfully grafted onto $SiO_2$ through Ti-O-Si chemical bonding. Modified nanosilica dispersed well into the system of epoxy resin and hardener. The mechanical properties, thermal resistant behavior and microstructure of nanocomposite, were determined by tensile, impact test, TG analysis and scanning electron microscopy. These results showed that the heat resistant character of the modified nanosilica/epoxy-titanate system increased from 283 to 389 $^oC$, mechanical properties increased by 10 to 15% compared to unmodified nanosilica. The optimal content of modified nanosilica is 3%.

# Miscibility Study of Polyimide and Highly Permeable Polymers

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Polyimide possesses high thermal resistance, chemical resistance, mechanical properties and good processibility. These superior properties have made it as a potential material for various applications in both research development and industrial applications. On the other hand, polymers of intrinsic microporosity, specifically PIM-1 have gained much attention recently due to their large surface rea, highly rigid and contorted ladder-type structure that yield a large fractional free volume. In this study, we have discovered a new miscible polymer blend systems, namely polyimide Matrimid and carboxylated PIM-1 (cPIM-1). This blend system is miscible at a molecular level over the whole composition range as confirmed by polarized microscopy, atomic force microscopy, differential scanning calorimetry, Fourier transform infrared spectroscopy and X-ray diffraction. A good agreement between experimental and predicted gas permeability and selectivity is obtained. The incorporating of cPIM-1 in Matrimid has significantly improves the plasticization pressure for all membranes.

# Effects of Local Osmotic Pressure on Phase Separation in Polymer Blends Driven by Polymerization.

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Phase separation of a mixture of poly (ethyl acrylate) (PEA) and methyl methacrylate (MMA) was induced by UV light irradiation by using Computer-Assisted Irradiation method (CAI method).[1]

In photo-polymerization, the yield of polymer increases with the light intensity. Therefore, a difference in the local free energy exists between the high light intensity and low light intensity areas, resulting in a local osmotic pressure, by which the graded morphologies emerge.

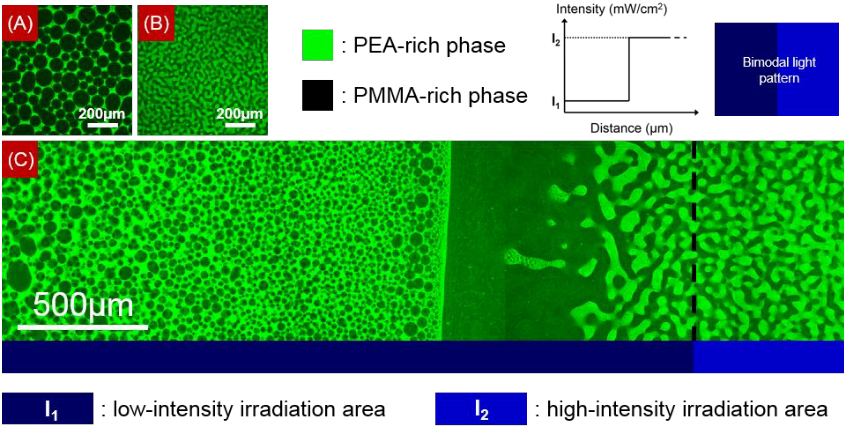

Figure.1 CLSM image of the stationary morphology obtained by irradiation with uniform and bimodal light patterns for a PEA/MMA=(13/87) at 25 °C, (A) uniform light pattern with I=0.01mW/cm$^2$, (B) uniform light pattern with I=0.4mW/cm$^2$, (C) bimodal light pattern with I1=0.01mW/cm$^2$, I2=0.4mW/cm$^2$.

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# Polymeric micelles with pH-sensitive NIR fluorescence imaging and controlled drug delivery functions

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Self-assembled pH-responsive NIR emission micelles[1] entrapped with doxorubicin (DOX) within the cores by the electrostatic interactions for fluorescence imaging and chemotherapy applications was developed. The block copolymer, poly(methacrylic acid)-*block*-poly[(poly(ethylene glycol) methyl ether methacrylate)-*co*-boron dipyrromethene derivatives] (**PMAA- *b*-P(PEGMA-*co*-BODIPY)**), was synthesized *via* reversible addition- fragmentation chain transfer (RAFT) polymerization, and the molecular weight distribution of this copolymer was narrow ($M_w/M_n$ = 1.31). The NIR fluorescence enhancement induced by the phenol/phenolate interconversion equilibrium works as a switch in response to the intracellular pH fluctuations.[2] DOX-loaded **PMAA-*b*-P(PEGMA-*co*- BODIPY)** micelles can detect the physiological pH fluctuations with a p*K*a near physiological conditions (~7.52), and showed pH-responsive collapse and an obvious acid promoted anticancer drug release behavior (over 58.8- 62.8% in 10 h). Real-time imaging of intracellular pH variations was performed and a significant chemotherapy effect was demonstrated against HeLa cells.

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# Enhancing the Photoluminescence Emission of Conjugated Polyfluorene by Light Processing

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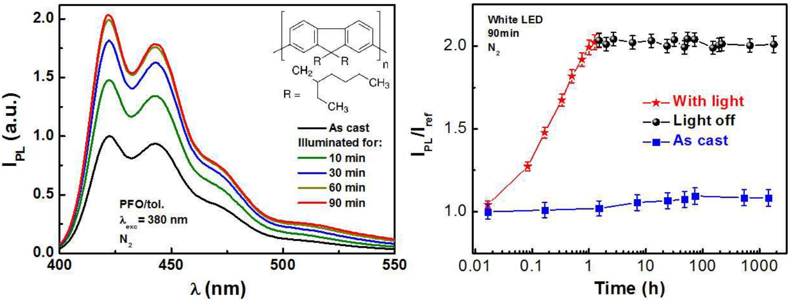
We show here that treatment of thin films of conjugated polyfluorene by illumination with white light leads to an increase of the intensity of their photoluminescence by roughly 100% (Figure 1 left). The corresponding enhancement of absorbance was much less pronounced. We tentatively explain this significant enhancement of the photoluminescence by a possible change in polymer chain conformation induced by photoexcitations even below the glass transition temperature. Interestingly, the photoluminescence remains at the enhanced level for more than 1700 hours after the exposure of films to white light (Figure 1 right), likely due to the fact that below the glass transition temperature no restoring force could return the conjugated chains into their initial conformational state.

Figure 1. (left) Normalized emission spectra recorded for a thin film of polyfluorene before and and after illumination. (right) Evolution of the 422 nm emission peak intensity during the treatment of polyfluorene film with light (stars) and after subsequently stopping the treatment (spheres).



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## A 3D Printed Veterinary Drug Delivery Device: *In Vitro* Characterisation

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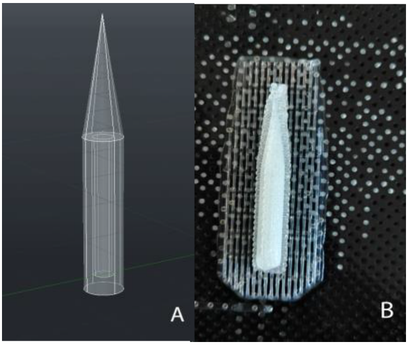
Remote drug delivery to wildlife has considerable advantages including target animal specificity and ease of administration. 3D printing is an emerging polymer technology to manufacture a drug delivery device with customized dosage, high accuracy and flexible release profiles. This study aims to fabricate progesterone-loaded darts printed using poly (ϵ- caprolactone) (PCL) or poly lactic acid (PLA) biodegradable polymers.

Progesterone was loaded into PLA/PCL (5,10 and 15% w/w) by hot melt extrusion (Noztek Pro, Noztek,UK). The devices were designed for 0.177 caliber 900FPS air-rifle (Fig.1A) and printed by a fused deposition modelling 3D printer (UP Mini 3D Printer, 3D Printing Systems, NZ) with drug-loaded filament (Fig.1B). In vitro drug release studies were performed in 62.5% ethanol and 37.5% double distilled water maintained at 37°C in a shaking water bath (New Brunswick Scientific, USA). Samples were collected at predetermined times and concentrations were determined by UV spectrophotometry. 3D printed devices were further characterised using scanning electron microscope (SEM), differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR).

**Conclusion:** The release data showed a desirable slow drug release profile. Release profiles of different polymer compositions were compared to identify the most suitable combination. SEM morphological data allowed the visualisation of matrix porosity. DSC and FTIR studies were used to study drug-polymer interactions during the extrusion process.

Figure 1. Dart designed(A) and printed(B)



## Renewable Resources for Binder Synthesis in Coating Applications

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**Keywords:** Renewable resources, Coatings, CNSL, Binders

**Abstract:** With continuous depletion of petrochemical feedstock and their rising prices, the chemical industry is now looking for alternative renewable and sustainable materials. Till date number of researchers have reported various possible chemistries to produce high performance functional materials from renewable resources. These materials have been proved to be suitable replacements for their petroleum counterparts in resin synthesis, adhesives, paints, coatings, composites, constructions, pharmaceuticals, and food applications etc.

In view of this, we have explored few of renewable resources including vegetable oils and fatty acids, Tartaric acid, Citric acid, Cashew Nut Shell liquid (CNSL) etc for their various modifications and suitable applications in coatings. This paper focuses on development of polyols, polyamines, epoxies and hybrid materials based on CNSL which can be used as coating components.[1-6] The research work being presented in this paper also discusses waterborne coatings derived from the natural resources.[7]

The paper also explains modification of vegetable oils, fatty acids as well as hydroxy acids for various curing chemistries for development of solvent borne and waterborne coatings. Non-isocyanate polyurethanes derived from vegetable oils and fatty acids and their applications would also be discussed.[8]

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# Modification of conductive polymers nanostructures via nanocrystalline cellulose

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Conductive polymers polypyrrole (PPY) and polyaniline (PANI) were prepared by in- situ polymerization of monomers templated by nanocrystalline cellulose (NCC).The net polymers (PPY and PANI) showing obvious alteration with presence of NCC during polymerization. The morphological alterations were observed via field-emission scanning electron microscopy (FESEM) and the elements of surface was detected by Energy Dispersive X-ray Spectroscopy (EDX).

# Adsorption of Polyvinylpyrrolidone over the Silica Surface: As Affected by Pretreatment of Adsorbent and Molar Mass of Polymer Adsorbate

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The adsorption of polyvinylpyrrolidone over the surface of silica has been investigated. The impact of molar mass of the polymer, pH, and pretreatment temperature of silica particles have been evaluated by means of FTIR spectroscopy and electrophoretic measurements. The silica particles used have narrow particle size distribution. The zeta potential of the aqueous silica suspension was decreased with the increase in pH. The amount of polymer adsorbed was increased with the increase in pretreatment temperature, time, concentration, pH, zeta potential, and molar mass of the polymer. The addition of polymer to the system increased the zeta potential due to adsorption of polymer on the surface of the particles. However, the impact increased with the increase in molecular mass of the polymer. The IR spectra obtained before and after adsorption of polymer concluded that, mostly, hydrogen bonding is responsible for the adsorption phenomena; however, hydrophobic interactions also play a significant role. The mechanism has been investigated and established through FTIR spectroscopy.

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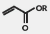
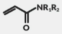
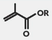
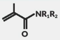
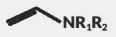
## RAFT AGENTS **SELECTION TABLE**

| | SOLUBILITY (Log P*) |  STYRENES |  ACRYLATES |  ACRYLAMIDES |  METHACRYLATES |  METHACRYLAMIDES |  VINYL ESTERS |  VINYL AMIDES |
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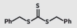
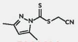
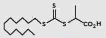
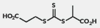
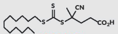
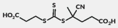
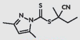
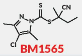
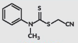
|  **BM1361** | 🟠 5.68 | 🟣 | 🟣 | 🟣 | 🟡 | 🟡 | 🟡 | 🟡 |
|  **BM1481** | 🟠 2.56 | 🔵 | 🔵 | 🔵 | 🟡 | 🟡 | 🟣 | 🟣 |
|  **BM1430** | 🟠 6.56 | 🔵 | 🔵 | 🔵 | 🟡 | 🟡 | 🟡 | 🟡 |
|  **BM1429** | 🩵 1.54 | 🔵 | 🔵 | 🔵 | 🟡 | 🟡 | 🟡 | 🟡 |
|  **BM1432** | 🟠 6.93 | 🔵 | 🔵 | 🔵 | 🔵 | 🔵 | 🟡 | 🟡 |
|  **BM1433** | 🩵 1.90 | 🔵 | 🔵 | 🔵 | 🔵 | 🔵 | 🟡 | 🟡 |
|  **BM1542** | 🟠 3.93 | 🔵 | 🔵 | 🔵 | 🟢 | 🟢 | 🟣 | 🟣 |
|  **BM1565** | 🟠 4.49 | 🔵 | 🔵 | 🔵 | 🟣 | 🟣 | 🟣 | 🟣 |
|  **BM1434** | 🟠 3.47 | 🟡 | 🟡 | 🟡 | 🟡 | 🟡 | 🔵 | 🔵 |

🟠 solvent soluble *values obtained from ChemDraw
🩵 water and solvent soluble (amphiphilic)
🔵 Excellent control of MW; narrow PDI (< 1.1)
🟢 Good control of MW; broad PDI (>1.3)
🟣 Excellent control of MW; moderate PDI (1.1–1.3)
🟡 Not suitable

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John Landells has over 12 years' experience in the patent attorney profession. He has extensive experience in the fields of plastics and polymer chemistry and synthetic organic chemistry. He works with various companies and universities in Australia and overseas in the drafting, filing, prosecution and provision of strategic advice for Australian, New Zealand and overseas applications.

John is a registered patent attorney and legal practitioner in Australia and New Zealand. He is a Partner in the Melbourne Chemistry team.

Andrew Gregory is an Associate in the Sydney Chemistry team and is an experienced chemist with over 10 years' laboratory experience leading scientific projects. He has extensive knowledge in organic and inorganic chemistry, with a particular focus in the field of polymers.

As a registered Australian and New Zealand patent attorney, Andrew provides advice to both domestic and international clients.

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Meet DCC's representatives, Grace Chan and Dario Buso, at the EPTS 2016.

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