

The 10th Annual

PolyMAC

Conference

Including the Research Groups of:

Alex Adronov
Michael Brook
Emily Cranston
Kari Dalnoki-Veress
Charles de Lannoy
Gillian Goward
Todd Hoare
Jose Moran-Mirabal

Robert Pelton
Kalai Saravanamuttu
Heather Sheardown
An-Chang Shi
Harald Stover
Michael Thompson
Li Xi
Shiping Zhu

December 12th, 2017
McMaster University, CIBC Hall



Schedule

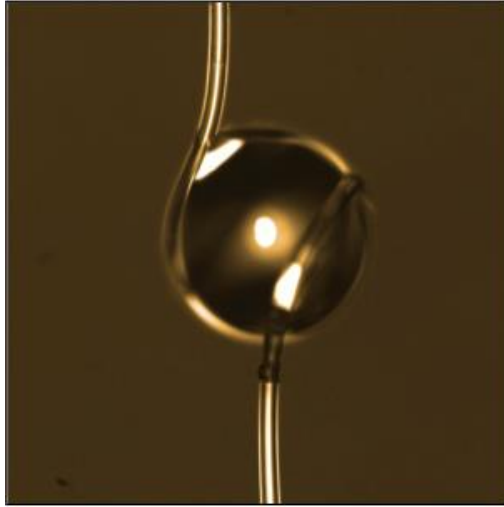
8:30 AM	<i>Registration & Breakfast</i>
9:00 AM	Invited Speaker: Kari Dalnoki-Veress
9:45 AM 10:00 AM	Darryl Fong Dongyang Li
10:15 AM	<i>Coffee Break</i>
10:30 AM 10:45 AM 11:00 AM 11:15 AM	Michael Majcher Robert Bui Carmen Lee Yin-Ning Zhou
11:30 AM	Poster Session
12:15AM	<i>Lunch</i>
1:15 PM	Invited Speaker: Dave Lawton
2:00 PM 2:15 PM	Gabrielle Foran Jeffrey Leung
2:30 PM	<i>Coffee Break</i>
2:45 PM 3:00 PM 3:15 PM 3:30 PM	Kushal Panchal Sijia Zheng Alex Hudson Dong Yang
3:45 PM	<i>Prizes & Closing Remarks</i>



Keynote Speaker

Kari Dalnoki-Veress

*Department of Physics & Astronomy, McMaster University, Hamilton, ON, Canada
PCT Lab, UMR CNRS 7083 Gulliver, ESPCI ParisTech, PSL Research University,
Paris, France*



The physics of soft materials is distinct from hard matter as the weaker intermolecular bonds can result in a large response to external stresses. In recent years, there has been a significant interest in understanding the interaction between a liquid's surface tension and a solid's elasticity: elastocapillarity. In particular, liquids can generate significant deformations of highly compliant materials. These elastocapillary interactions are highly relevant in a wide variety of systems including capillary origami, kirigami, and folding, soft tissues, wetting of fibers and hair, and micro-patterning of soft surfaces. In this talk I will summarize our recent work on the capillary interactions of liquid droplets with elastic surfaces.



Keynote Speaker

Dave Lawton

*Scale-up Engineering Group, Xerox Research Center of Canada, Mississauga, ON,
Canada*

David Lawton is a Senior Process Engineer and Client Relationship Manager at the Xerox Research Centre of Canada (XRCC) as well as a Subject Matter Expert working extensively on process design optimization for commercialization and manufacturing. He received both his B.Eng. and M.A.Sc degrees from McMaster University and joined XRCC in 2011. David's work focuses on process and scale-up engineering for both Xerox and client projects as well as the development of novel continuous processing methods. This talk will look at the type of projects that an engineer might work on in a materials research centre as well as how graduates can expect their knowledge to both transfer and broaden when working in industry.



Design and Fabrication of Nanostructured Hydrogel Delivery Vehicles from Biopolymer Nanoparticle Building Blocks

Michael J. Majcher and Todd Hoare

A dominant engineering constraint associated with the use of starch within the field of polymer chemistry is its inherent inhomogeneity of amorphous and crystalline domains which vary according to source and processing technique of native starch granules. Recently, researchers at EcoSynthetix in Burlington, ON have demonstrated the ability to create starch nanoparticles (SNPs) via reactive extrusion with solely amorphous domains and tunable size regimes (20-50 nm) on an industrial scale.¹ The resulting nanoparticles consist of a water-bound core and a hydrophilic exterior, rich in hydroxyl groups (-OH) available for subsequent modification.² Through the development of various research projects (two discussed here), our group has been able to exploit the advantageous characteristics of starch hydrogels for applications such the controlled delivery of diverse small molecules. More specifically, we have currently been working on loading 1) model fungicides (i.e. thiram) for delivery to Glycine max plants and 2) advanced peptide structures for targeted delivery to the central nervous system. For both projects, it is hypothesized that the combination of the nanodomain properties offered by the SNPs and the high surface area resulting from their subsequent degradation will be the driving force for the hydrogel's resulting mass transfer operations.

1. Wildi et al., Patent US 2011/0042851 A1

2. Ismail, H.; Irani, M.; Ahmad, Z. *Inter. J. Polym. Mat. & Polym. Biomater.*, 2012, 62, 411-420.

Dynamic Covalent Silicone Network Polymers: Imine-Based Elastomers

Robert Bui and Michael A. Brook

Most silicone elastomers are thermoset polymers that possess properties such as resistance to heat or electrical insulation. However, they cannot be repurposed or recycled. There is interest in making silicone polymers that crosslink with reversible bonds such as hydrogen bonding or metal-ligand interactions, which can respond to external stimuli such as heat, light, or addition of catalyst to promote reversible bond formation. This provides the ability to tune the properties of the elastomer after its formation or to repurpose it for other applications. We report a new class of polysiloxane-based stimulus-response material made by crosslinking aminopropyl-functionalized polydimethylsiloxane with aromatic aldehydes to create a silicone network crosslinked with Schiff-base bonds. The elastomers cure at room temperature, with high conversion functional group conversion, and the mechanical properties of the material are tuneable. The imine bonds remain dynamic and exhibit self-healing and adhesion through reactions with aldehydes, amines, or imines. The self-healing occurs through metathesis and transimination reactions which lead to no loss in crosslink density from healing; remarkably, the materials fail cohesively after healing. Adhesion studies found that the material selectively adheres to surfaces bearing amine groups through chemical bonding rather than physical adhesion. The dynamic imine materials are currently being examined for recycling and remoulding through manipulation of imine equilibria.



Capillary levelling of thin polymer steps on a liquid surface

Carmen Lee, Vincent Bertin, John Niven, Thomas Salez, Elie Raphael and Kari Dalnoki-Veress

Thin polymeric films have numerous technological applications and their stability has garnered intense interest. The stability and flow of the film is sensitive to the boundary conditions as the film thickness approaches the nanoscale. The flow associated with a thin polymer film on a solid substrate has been well studied, through the creation of a precise step in the topology of the film at the free air interface. As the system is heated to a liquid state, the step will be driven to flow and flatten to minimize excess surface energy. To probe a liquid-liquid boundary condition, an immiscible, less viscous polymer film is inserted between the stepped film and the solid substrate. Experimental results show that there is substantial deformation at the interface between the two polymers during the levelling process. The goal of this project is to examine the effect of a liquid-liquid boundary condition on the flow in thin films and verify our methodology as a robust tool for nanoscale rheology.

CO₂/N₂-Switchable Thermoresponse Ionic Liquid Copolymer

Yin-Ning Zhou^{ab}, Lei Lei^a, Zheng-Hong Luo^b, Shiping Zhu^a

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Thermoresponse random copolymers consisting of poly(N-isopropylacrylamide) (PNIPAM) and polymerized ionic liquid (IL) poly(1,1,3,3-tetramethylguanidine acrylate) (PTMGA) were synthesized via reversible addition-fragmentation chain transfer radical polymerization (RAFT). The phase transition behaviors of the copolymers in aqueous solution were studied through UV-vis transmission measurements. Their lower critical solution temperature (LCST) ranged from 30.5 to 73.2 °C, depending on the hydrophilic IL content. Additionally, the hydrophilicity of the copolymers could be regulated by gas treatments. Bubbling CO₂ led to lowering the transition temperature while bubbling N₂ resulted in its recovery. This CO₂/N₂ switchability became more profound with higher IL content. With the ability to undergo reversible protonation caused by the change of pH, the system showed good reversibility in LCST when bubbled with CO₂ and N₂. SO₂ could also be used to lower LCST. However, a basic compound (e.g., NaOH) was required for its recovery. The pH-dependent solution phase transition behavior provided great insight into the LCST regulation mechanism. The widest LCST shifting window (~ 12 °C) was found between pH 5.16 and 5.96, which could be fulfilled by the CO₂ regulation approach.¹

1. Y.-N. Zhou, L. Lei, Z.-H. Luo, S. Zhu, *Macromolecules* 2017.



Solid State ^{11}B NMR Study of Crosslinking in SiBA Polymers

Gabrielle Foran, Benjamin Macphail, Michael A. Brook, Gillian R. Goward

Silicone boronic acid (SiBA) polymers are ideal for use in contact lenses as silicone is highly biocompatible, flexible and breathable.¹ The inclusion of boronic acids further improves lens properties by offering pH-based tunability and in-situ drug delivery through saccharide binding.^{1,2} Although these materials are reliably synthesized and have well-characterized mechanical properties, boron coordination remains poorly understood.² To this end, ^{11}B NMR was used to identify 3- and 4-coordinate boron sites and the influence of factors including boron loading and polymer configuration on coordination. Quadrupolar ^{11}B nuclei interact asymmetrically with the electric field gradient giving rise to unique lineshapes that depend on nuclear environment symmetry.³ Lineshape fitting reveals significant structural information essential to the understanding of film formation.³ Coordination environments in SiBA polymers were compared with well-understood crystalline samples identifying 3- and 4-coordinate sites. Initial polymerization occurred through the formation of 3-coordinate sites. This was followed by crosslinking resulting in the formation of 4-coordinate sites. Identifying boron coordination number and the factors contributing to crosslinking is important as boron crosslinking affects polymer rigidity.

1. Kirchoff, S. et al. *Euro J. Pharmaceutics and Biopharmaceutics*, 2015, 95, 227-238
2. Zapeda-Velazquez, L. et al. *Poly. Chem.*, 2016, 7, 4458-4466
3. Autschbach, J. *Concepts in Magnetic Resonance Part A*, 2010, 36, 84-126

Polyethylene Glycol Methacrylate-Based Polymeric Micelles for Ocular Drug Delivery

Jeffrey Leung and Heather Sheardown

Ocular drug delivery to treat anterior segment diseases of the eye continues to be a very challenging task. Static barriers include tight junctions of the conjunctiva and dynamic barriers such as the high turnover rate of the tear film contribute to the impenetrable anterior surface.¹ As a result, conventional ophthalmic medication in the form of eye drops are quickly removed and only <5% of the administered dose is efficiently delivered to the anterior tissues. To improve drug delivery into the ocular tissues, polymeric micelles based on poly (D, L-lactide)-b-polyethylene glycol methacrylate (PLA- b-PEGMA) was used as a drug delivery vehicle to enhance drug solubility and to have a controlled drug release. Polyethylene glycol (PEG) has been previously shown to have mucopentrating properties through 2 mechanisms; 1. Low molecular weight (MW) PEG is unable to support adhesion 2. High PEG density sufficiently shields the hydrophobic core.² Based on this finding, atom transfer radical polymerization (ATRP) was used to synthesize a bottlebrush copolymer to improve hydrophilicity, neutrality, surface density and hydrophobic shielding.

1. Gaudana R. *American Association of Pharmaceutical Scientists*. 2010;12: 348-360.
2. Wang, Y. *Angewandte Chemie*. 2008; 47, 9726- 9729.



Mechanistic Understanding of Polymer-Plasticizer Systems Using Coarse-Grained Molecular Dynamics Simulation

Kushal Panchal and Li Xi

Plasticizers are a commonly used additive used in the polymer industry to make the plastic more pliable by simultaneously reducing the glass transition temperature and elastic modulus. As the plasticizer aids in polymer process-ability and making the it suitable for applications from industrial cables to sensitive medical equipment, the mechanism of plasticization is not fully understood. There are three basic theories used to explain plasticization: lubricity theory, gel theory, and free volume theory. The latter is a fundamental concept of polymer science that is used to calculate many polymer properties and is explore in further detailed. With molecular dynamics (MD) simulation, a coarse-grained (CG) model – simple bead-spring model that generalizes particles as a bead and connects them via a finite spring – is used to explore the impact of plasticizer size throughout the polymer system. The interaction characteristics of the plasticizer is explored by reducing a phthalate based plasticizer to a single bead. This gives better control on the variability of the mixture and pinpoint the significant contributions to plasticization. By understanding the mechanism of plasticization, it can then be used find an optimal plasticizer architecture to minimize the migration of the additive by increasing its compatibility.

3D printable, rapid cure silicone elastomers prepared using thiol-ene “click” chemistry

*Sijia Zheng, Yang Chen and Michael A. Brook**

Silicone elastomers are of commercial interest in a number of areas because of their ability to integrate both structure and function within manufactured silicone elastomers. To move beyond prototyping, new manufacturing methods and materials are required. 3D printing is advantageous over conventional technologies for the fabrication of sophisticated structures. To date, only simple extrusion-based printing methods have been used for the preparation of silicone structures. Methods to print objects with mixed moduli or other properties are not well developed. In our research, we are exploring the possibility of using photoinduced thiol-ene click chemistry as an efficient method to produce crosslinked networks. Photolysis avoids problems we have had with hydrosilylation thermal cure, slow moisture cure, and irreproducible Piers-Rubinsztajn cure in at 3D printer. Thiol-ene reactions are rapid and can be conducted in the presence of air and moisture to produce thioethers in near quantitative yield. Those features of thiol-ene cure allow for a relatively short printing period, high fidelity and friendly operating environment in 3D printing manufacturing. PDMS inks were formulated using a combination of chain-extender, cross-linker and base polymer. The ratio of chain-extender and catalyst was varied for certain inks to achieve a fast reaction and affect the hardness of the printed structures. Results show that this procedure allows for very fast cure times (<20 s) under UV radiation. The ability to print different types of multimodulus silicones will be presented.



Optochemical Organization: Transferring and Encoding Information in a Photopolymer

Alex Hudson, Matthew Ponte and Kalaichelvi Saravanamuttu

Optochemical organization exploits the modulation instability (MI) of broad beams in a photopolymerizing medium and their spontaneous division into massive populations ($>10,000 \text{ cm}^{-3}$) of self-trapped filaments. Because they originate from adventitious noise, filaments are typically positioned randomly in space. By contrast, when two (X, Z) or three (X, Y, Z) orthogonally propagating beams simultaneously undergo MI within the same photopolymer volume, the respective filament populations spontaneously intersect with their orthogonal counterparts and generate a 3D ordered lattice. We exploit these spontaneous interactions between orthogonally-propagating filaments to develop an all-optical information transfer and encoding technology. When Beam Z is patterned with dark (0) and bright (1) stripes, the orthogonal-propagating filaments of X self-organize into the corresponding random (0) and ordered (1) configurations. Information is thus transferred from Z to X. By introducing Beam Y—which, like Z, also bears a pattern of bright and dark stripes—it is possible to encode Beam X with more than one million unique patterns consisting of ordered and disordered sub-populations of filaments. Our findings open a new, all-optical route to the transfer and encoding of optical information, which may provide opportunities to compute with low-intensity, incoherent sources.

Towards Enhanced Paper Recycling with Degradable Microgel Wet-strength Adhesives

Dong Yang and Robert Pelton

Presented is a new approach to cellulose-based materials that are strong when wet, yet can be recycled after exposure to a weak reducing agent. Poly(N-isopropylacrylamide-co-acrylic acid) microgels were transformed into cellulose wet adhesives by incorporation of hydrazide or azetidinium groups that can form hydrazone or ester linkages to oxidized cellulose. Reductant-responsive wet adhesion was obtained by introducing cleavable disulfide linkages, either in the chains tethering adhesive groups, or by using disulfide crosslinks in the microgels. For adhesion measurements, wet cellulose membranes were laminated with microgel thin layers (15-45 mg/m²), and 90-degree peel test was used to determine the wet adhesion. Both types of disulfide derived adhesives gave maximum 70% reduction in wet adhesion after exposure to a reductant. This work demonstrates new routes to degradable cellulose wet adhesives, facilitating recycling of cellulose-based materials, including paper products.



Poster Presentations

Radially Distributed Waveguide Array (RDWA) for Light Guiding and Beam Manipulation

Kathryn Benincasa^a, Hao Lin^b, Cecile Fradin^b and Kalaichelvi Saravanamuttu^a

a Department of Chemistry & Chemical Biology, McMaster University

b Department of Physics & Astronomy, McMaster University

Natural compound eyes found in insects have many advantages such as fast movement detection, polarization sensitivity and a large field of view (FOV). The fabrication of artificial compound eyes for applications such as medical imaging, light collection and beam steering has become more popular. However, current methods of fabrication of artificial compound eyes is complicated and quite expensive. Using a method of fabrication developed by our group, we present an inexpensive and simple method to create structure inspired by compound eyes found in nature. The structure consists of multiple, radially arranged polymer light channels, otherwise known as waveguides, and is fabricated by launching an incandescent white light source into a photopolymer. This results in the self-trapping of light and the permanent formation of waveguides due to irreversible polymerisation reactions. The overall FOV for fabricated acrylate and epoxide bioinspired structures showed an increase in FOV of about 222% and 126% respectively, as compared to control samples without waveguides. Potential applications for these bioinspired structures include coatings for light collection energy devices (e.g. solar cells) and beam manipulation (e.g. output of LEDs).

Preparation of cell-loaded nanofibrous hydrogel via reactive electrospinning

Monika Budi Hartono, Fei Xu and Todd Hoare

Poly(ethylene glycol) (PEG) hydrogels have attracted significant interest for their hydrophilicity, cell compatibility and high water-content. In this project we are trying to mimic the extracellular matrix using poly(oligoethylene glycol methacrylate) (POEGMA) polymer that exhibits tuneable chemical and mechanical properties. POEGMA nanofibrous hydrogels were prepared via reactive electrospinning through crosslinking of functionalized hydrazide and aldehyde groups. It is a safe and efficient method to encapsulate cells in scaffold due to the versatility of electrospinning and in situ crosslinking without any post-treatment. In this report, cells were directly electrospun with POEGMA polymer to form a cell-scaffold. The cells were observed to be both on the surface and encapsulated within POEGMA nanofibers after electrospinning and cell proliferation was observed after culturing at 2 and 7 days. In order to increase biological functionality, POEGMA was functionalized with the ligand Arginylglycylaspartic acid for more effective cell adhesion and cell proliferation. Next, epithelial cells will be loaded on the surface of cell-scaffold. With this, we hope to be able to create a suitable synthetic scaffold including loaded cells to be used in tissue engineering as functional substitutes for damaged organs and tissues.



String method study of heterogeneous nucleation pathways

Sarah Dawson and An-Chang Shi

The self-assembly of block copolymers into ordered microphases typically proceeds through nucleation. The free-energy barrier and the nucleation pathway are altered in the presence of a nucleating agent. By exploiting this fact, recent theoretical work has shown that an appropriately designed substrate may be used to fabricate defect-free films of block copolymers in an ordered phase. In this work, we look at a method for quantifying the effect of heterogeneities on the nucleation pathway in a model system. We find the minimum free energy path between the initial, metastable state and the stable state using the string method. We investigate the change in height of the free-energy barrier when the interface is included. The results obtained are compared with those from classical nucleation theory.

Injectable Anisotropic Nanocomposite Hydrogels with Magnetically Aligned Cellulose Nanocrystals

Kevin De France, Emily Cranston and Todd Hoare

Injectable hydrogels, which combine many of the advantages of traditional hydrogels with a minimally invasive delivery, have attracted increased attention recently for tissue engineering applications. However, the inherent disorganized and isotropic network structure limits their clinical relevance, as many biological tissues display hierarchical structuring/anisotropy. Herein, we report a nanocomposite hydrogel composed of a chemically cross-linked poly(oligoethylene glycol methacrylate) (POEGMA) matrix and cellulose nanocrystals (CNCs) which undergo rapid orientation within the POEGMA network in situ when exposed to a magnetic field. Hydrogel anisotropy is demonstrated through small angle x-ray scattering and transmission electron microscopy, and is evidenced via changes in both hydrogel mechanical strength and swelling versus unaligned controls. Importantly, these anisotropic hydrogels are able to direct myoblast cell growth and differentiation, the first injectable hydrogels to do so, indicating that magnetic alignment of CNCs within hydrogels is a feasible platform for the development of functional anisotropic biomaterials for targeted tissue engineering applications.



Transfer of Structured Thin Films from PS to PDMS through solvent-assisted lift-off

Xiuping Ding, Yujie Zhu, Sokunhearath Saem, Jose M. Moran-Mirabal

The poor mechanical robustness of traditional rigid devices limited the applications that could conform to nonplanar surface and tolerate the deformation, which demands the device being both flexible and stretchable. The flexibility and stretchability will also essentially attribute to the low cost, scalable roll-to-roll processing. Here we create wrinkles by shrinking films sputtered on the pre-stretched shape memory polymer sheet¹⁻³ to gain stretchability and flexibility for intrinsically rigid materials. Then transferred the structured film directly onto the polydimethylsiloxane (PDMS) by creating bondings between PDMS and the films. By now, we have managed to transfer both metallic and nonmetallic materials, even the high Young's modulus materials like SiO₂ and Indium tin oxide (ITO) thin film, monolayer and multilayers (like ITO-Au-ITO multilayers), as well as very fine structure lower than 100 μm, from the rigid silicon substrate to PDMS with the stencil solvent-assisted method. The films obtained show good flexibility and stretchability, and it significantly help to keep all the fragile thin film completed during and after the transfer. This work is the key step to achieve the thin film flexible and stretchable device in one step.

1. Urdaneta, Mario G., Remi Delille, and Elisabeth Smela. *Adv. Mater.* 19 (18), 2629-2633, 2007.
2. Zhu Y. Moran-Mirabal J. *Adv. Electron. Mater.* 2 (3). 2016.
3. Yujie Zhu, Jose Moran-Mirabal. *Langmuir* 32(42), 11021-11028, 2016.

Synthetic Routes to Silicone-Modified Soybean Oil Copolymers

Cody Gale, Brandon Chin, Daniel Graiver, and Michael A. Brook

Continued concern over the impact of petrochemicals on the environment has led to a push to create materials using the principles of sustainability, while not compromising physiochemical properties of the products. Soybean oil is a high volume, commercial unsaturated triglyceride predominantly used for cooking applications although it has a long history in polymeric materials such as linoleum. We were curious to explore the possibility of increasing the value and utility of this green starting material by modifying it with silicone polymers. The double bonds present in soybean oil serve as the perfect platform for introducing synthetically useful siloxane functionality via thiol-ene click reactions, or through a peroxide catalyzed ene reaction. (3-Mercaptopropyl)trimethoxysilane and trimethoxyvinylsilane were grafted onto soybean oil using thermal thiol-ene, and peroxide-initiated ene reactions, respectively. The resulting alkoxy silane could then be used in two different reactions: The Piers-Rubinsztajn reaction (PR) and Room Temperature Vulcanization (RTV, moisture cure). The B(C₆F₅)₃-catalyzed PR reaction, using the modified soybean oil and hydride-containing polydimethylsiloxane (PDMS) led to foams, while RTV cure with silanol containing PDMS in the presence of tin gave elastomers. In both cases, it was possible to tune the properties of the products simply by controlling the length of crosslinker. A comparison between this process and the direct thiol-ene reaction of soybean oil with mercaptopropylsilicones will be made.



Mechanical Properties of All-Cellulose Nanocrystal Thin Films as a Function of Nanoparticle Orientation

Urooj Gill, Emily D. Cranston, Jose M. Moran-Mirabal

A fundamental understanding of the mechanical properties of cellulose nanocrystal (CNC)-based thin films is essential to expand their applications. Quantitative analysis of these properties lacks in the literature, where the few studies that have measured the elastic modulus reported significantly lower values than those predicted from the modulus of CNCs. In this work, we have used a shape-memory polymer-based structuring approach to form wrinkled CNC films and measure their elastic modulus. Films consisting solely of CNCs were fabricated with varying thicknesses and one of three types of CNC orientation: chiral-nematic, isotropic, or radial. This was achieved by drop casting the CNCs from aqueous suspensions, then drying through i) vacuum (chiral nematic), ii) heating (isotropic), or iii) spin-coating (radial). When visualized through polarized microscopy, films showed unique textures that changed with film thickness and drying procedure. These films were then structured through heat-induced shrinking of the substrate. Here, the wrinkle length and morphology of the structured thin films were easily tuned with changes in film thickness and drying conditions. Ongoing work aims to evaluate the films' moduli as a function of CNC orientation, where these structured all-CNC films may find applications in areas such as food packaging and paper-based electronics.

Microstructure of polyethylene and ultrasonic waves propagation

Felipe Gomes and Michael Thompson

Understanding the relationship between microstructure and plastic deformation of polyethylene is a key aspect for the production of reliable parts. Current characterization techniques either focus on very small areas of the sample or are destructive methods that cannot be used for in-line monitoring. Our research has demonstrated how ultrasonic testing, a non-destructive technique, can be used to characterize crystalline morphologies resulting from different processing history. Ultrasonic waves are influenced by residual stresses in the inter-crystalline region creating detectable spectral features after propagation. A non-linear parameter from the variation of harmonic peaks was used to differentiate bulk attributes of samples after flexural deformation below yielding. Modifications of microstructure due to annealing and oxy-thermal-degradation were observed and their effects to initial plastic deformation. This characterization tool will be applied for process monitoring and optimization, and for the design of parts to resist chemical penetration.



Electrically Conductive Membranes with Tunable Surface Properties

Mohamad Amin Halali, Charles François de Lannoy

Electrically conductive membranes (ECMs) have demonstrated to outperform conventional membranes in separation and inactivation of contaminants by engaging the microorganisms into redox reactions as well as limiting mineral scaling and biofouling. To scale up the ECMs, however, there is room to improve their performance by fabricating more stable, low-cost, controllable membranes in terms of porosity, electrical conductivity, and separation characteristics. In this work, we advanced the existing electrically conductive membranes surface by introducing different cross-linkers with different lengths. The conductive surface consists of –COOH functionalized carbon nanotubes bonded with PVA molecules. The dicarboxylic cross-linking agents with fixed lengths can further lodge themselves inside the conductive network to deliver a more controlled configuration in term of porosity and separation properties. The ECM surfaces were compared for their electrical conductivity, flux, pore size, and solute separation. Greater concentration of CNTs lead to greater surface conductivity, however both longer cross-linkers and higher cross-linking degree, also caused a greater surface conductivity of the nanocomposite. This is due to enabling greater dispersibility of the CNTs within the nanocomposite, leading to greater electrical percolation. Trans-membrane flux and solute separation were also related to the cross-linking degree and nanomaterial dispersion. It was demonstrated that flux increased with increasing cross-linking length. It was hypothesized that longer cross-linking chains may have formed a more porous, open structure within the nanocomposite.

Rapid Charge-Shifting, Cationic Polymers for Cell Encapsulation

Derrick E. Hastings, Samantha Ros, Nicholas A. D. Burke and Harald D. H. Stöver

The use of polyelectrolytes in biomaterials is becoming more prevalent because of the facile tunability of both the composition and properties in a broad range of applications such as temporary cell scaffold and prosthetics. Cell encapsulation via an alginate-polycation-alginate system has been investigated using poly-L-lysine to electrostatically complex with the carboxylate groups of an ionically crosslinked alginate bead.² However, these polymers evoke immune responses due to imperfect outer masking of dense patches of positive charge.³ The use of polymers composed of 1,3-bis(dimethylamino)propyl acrylate (BDMAPA) as a “charge-shifting” polycation allows for initial electrostatic complexation, followed by rapid decrease in overall net charge of the polymer coating in order to reduce the immune response evoked.⁵ We discuss the investigation of copolymers of BDMAPA and N-aminopropyl methacrylamide and their potential in cell encapsulation. Experimental results of copolymer optimization, alginate bead coating and cross-linking with poly(methylvinyl ether-alt-maleic anhydride) experiments will be presented

1. Gardner, C. M.; Potter M.A.; Stöver H.D.H. *J. Mater. Sci. Mater. Med.* 2012, 23, 181-193.
2. Orive, G.; Tam, S.; Pedraz, J.; Halle, J. *Biomaterials* 2006, 27, 3691-3700.
3. Ros, S.; Burke, N.A.D.; Stöver H.D.H. *Macromolecules* 2015, 48, 8958-8970.



Sequential Functionalization of a Natural Cross-linker Leads to Designer Silicone Networks

Scott E. Laengert, Alyssa F. Schneider, Eric Lovinger, Yang Chen and Michael A. Brook

Silicone polymers are used in a wide variety of practical applications including medical implants and electronic insulators. Silicones can be produced in various forms, such as gels, elastomers, hard plastics, and foams, but achieving precision control of network structures is challenging since functional groups introduced in industrial processing are often randomly distributed along the silicone backbone. We have developed a system for the construction of precise silicone networks using the natural product eugenol by taking advantage of its triple functionality in a selective and sequential manner.¹ The boron-catalyzed Piers-Rubinsztajn reaction, using H-terminated silicones to create Si-O-C bonds, reacts fastest with the phenol group and slower with the methoxy group.² By adding one equivalent of H-terminated silicone, the reaction at the phenol group takes place selectively and subsequent addition of a second portion leads to reaction of the methoxy group. Adding a platinum catalyst and a third equivalent of Si-H leads to a hydrosilylation reaction of the silicone with the allyl group and the creation of a Si-C bond.³ These two catalysts do not interfere with each other and the reactions can therefore be performed in any order in one reaction vessel, without the need for workup. A variety of H-terminated polysiloxanes can be easily used to form chain extended polymers in which the morphology of the material and its constituent parts can be manipulated at will.

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2. Grande, J.; Gonzaga, F.; Brook, M.A. *Dalton Transactions*, 2010, 39, 9369 – 9378.
3. Grande, J.; Urlich, T.; Dickie, T.; Brook, M.A. *Polymer Chemistry*, 2014, 5, 6728 – 6739.

Fabrication of Porous High-Surface Area Cellulose Nanocrystal Microparticles through a Sustainable Droplet Microfluidic Method

Daniel Levin, Emily Cranston, and Jose-Moran-Mirabal

Cellulose nanocrystals (CNC) are rod-like rigid nanoparticles derived from cellulose. Their high surface area, mechanical strength and non-cytotoxicity has elicited interest in this material for many applications. By introducing aldehyde and hydrazide groups to the surface of the crystals, chemical cross-linking can occur. Cross-linked networks of surface-modified CNCs can be fabricated, leading to larger, porous microparticles that retain the high surface area characteristics of CNCs, but are safer and easier to process. One obstacle lies in the half-ester sulfate groups on the surface of CNCs, which introduce negative charges and result in repulsive interactions that keep the CNCs colloidally stable in aqueous suspensions. To overcome this, our method makes use of water-in-oil droplet microfluidics to create uniform CNC droplets. Subsequent heating of the droplet allows the CNCs to be brought close enough to overcome electrostatic repulsion and crosslink as water evaporates. The resulting cross-linked particles show interesting properties, primarily their ability to swell in polar solvents, which vary as a function of the droplet's starting CNC concentration. These porous microparticles have potential applications as slow-release drug delivery agents.



Preparation of a Stable Cyclooctyne-Containing Polymer by Wittig Chemistry

Kelvin Li, Vladimir Kardelis and Alex Adronov

Creation of a large library of homologous conjugated polymers is difficult as it requires the preparation and polymerization of multiple monomers. Furthermore, preparing a library of homologous polymers with consistent degrees of polymerizations (DP) is even more challenging, as DPs can vary greatly between batches of different polymers. An alternative approach to creating a polymer library with different repeat units involves formation of a pre-polymer with a reactive repeat unit that can be quantitatively derivatized post-polymerization with a wide range of functional groups. Recently, we reported the preparation of a polyimine structure containing dibenzocyclooctynes within its repeat units, which was demonstrated to be easily and quantitatively derivatized under mild conditions with a variety of azides. However, the labile imine linkages are not stable under acidic conditions, and could not be utilized in biological applications as it decomposes in water. To circumvent this limitation, we utilized Wittig chemistry to form an analogous dibenzocyclooctyne bisaldehyde and a bis(triethyleneglycol)phenyldiphosphonium salt to yield a very stable DIBO-containing polymer, poly(phenyl-co-dibenzocyclooctyne). Using trialkylsilylides allowed for the preparation of a high molecular weight polymer ($M_n > 20$ kDa, $M_w > 38$ kDa). Upon exposure to an azide, the polymer undergoes quantitative strain-promoted alkyne-azide cycloaddition to yield the desired triazole. Various fluorescent polymers and cross-linked structures were efficiently prepared by functionalization of the polymer with the appropriate azide.

A Simple Hydrolytic Method to Prepare Silicone Material

Mengchen Liao, Yang Chen, and Michael A. Brook

Silicone elastomers and foams have been widely used for a large range of applications from automotive to cosmetic industries owing to their unique properties such as low electrical conductivity, biocompatibility, and gas permeability. Conventionally, hydrosilane-functional groups are widely used in the synthesis of silicon-based polymers and foams by the reaction of hydrosilanes with vinyl groups, normally catalyzed by Pt, Sn or other metals; if silanol groups are present they compete for the SiH groups and foams result. We report that $B(C_6F_5)_3$ catalyzes both the hydrolysis and condensation processes of silicones containing SiH groups to give linear silicone polymers and foams whose properties can be tailored simply by judicious choice of readily available, commercial hydrosilane starting materials. Model compound studies of pentamethyldisiloxane or bistrimethylsilyloxymethylsilane demonstrated that water is a reagent in the process, rather than an undesired contaminant that can quench the $B(C_6F_5)_3$ catalyst, as has been observed in some related reactions. Polymer studies using hydride-terminated PDMS with different molecular weights and tetramethyldisiloxane show chain extension after the addition of water and $B(C_6F_5)_3$ catalyst. The combination of hydroxyl-terminated PDMS mixed with hydride-terminated PDMS also leads to chain extension. The mechanical properties of silicone foams will be presented.



The Interactions of Optical Vortices with Photoresponsive Systems *Fariha Mahmood^a, Oscar A. Herrera Cortés^a, Alejandro V. Arzola^b, Karen Volke- Sepúlveda^b, and Kalaichelvi Saravanamuttu^a*

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Optical vortices are beams of light that exert a twisting force perpendicular to their direction of propagation. This force originates from the helical phase structure of the beam, which is characterized by an integer parameter, the topological charge. In addition to determining the magnitude of the twisting force, the topological charge also defines whether the force is exerted in a clockwise or counterclockwise direction.

We study the interactions of optical vortices with two photoresponsive materials. These materials increase refractive index upon irradiation due to two distinct reactions. In the first, the increase originates from the photoinitiated free radical polymerization of acrylate moieties in organosiloxane oligomers. In the second, there is a photo-oxidation of iodide into triiodide in the presence of $\text{Ru}(\text{bipy})_3\text{Cl}_2$. We have observed transformations of the initial ring-shaped beam into a number of intensity patterns, including filaments, concentric rings, and spirals. In both materials, we have captured responses that reflect the clockwise or counterclockwise twist of the input beam: rotating spirals in the organosiloxane, and filament rotation in the iodide-based system. Our experiments reveal that these responses are governed by a balance of optical and material parameters, allowing us to gain insight into their underlying mechanisms.

Rerouting Light Using Chemistry: Interactions of Self-Trapped Laser Beams

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Self-trapped beams are self-reinforcing waves that travel long distances (\gg Rayleigh length) without suffering significant changes to their profile. We find that self-trapped beams can be elicited through a variety of photochemical reactions from the (i) free-radical polymerization, (ii) $[\text{Ru}(\text{bpy})_3]^{2+}$ -mediated oxidation of iodide to the (iii) photo-reversible contraction of a spiropyran-functionalized hydrogel. Although originating from richly diverse molecular mechanisms, these systems all undergo a positive change in refractive index and in this way, satisfy the macroscopic prerequisite for self-trapping. These channels of higher refractive index are able to interact with one another, resulting in attraction, interweaving, and spiralling and ultimately can reroute optical beams depending on the material and initial optical profile. This study highlights the ability to generate these species in bulk polymer-based materials where the origin of refractive index changes are photochemical reactions, and looks at how modifications to the system and incident light affect the propagation of these self-trapped beams.



Degradable homogeneous microgels via self-assembly of reactive poly(N-isopropylacrylamide) oligomers

Eva Mueller and Todd Hoare

Conventional poly(N-isopropylacrylamide) (PNIPAM) microgels prepared via precipitation polymerization have been used in many applications. However, in the context of practical biomedical use *in vivo*, the lack of degradability of conventional PNIPAM microgels creates challenges in that conventional microgels cannot be cleared effectively from the body. In response, we have developed a self-assembly method in which well-defined hydrazide and aldehyde functionalized PNIPAM oligomers are used to form microgels linked by hydrolytically degradable hydrazone crosslinks. Interestingly, while conventional microgels have a dense core/diffuse shell structure due to the faster polymerization rate of the crosslinker used, a combination of surface force measurements, small angle neutron scattering, and ultrasmall angle neutron scattering confirmed that these self-assembled microgels have a homogeneously cross-linked internal structure. This somewhat surprising result is attributed to a combination of the dynamic nature of the hydrazone crosslinking chemistry and the assembly conditions used that promote polymer interdiffusion. Coupling the predictable diffusive and refractive properties enabled by the homogeneous internal structure with the degradability enabled by the assembly chemistry, we anticipate that these microgels offer opportunities to address challenges in drug delivery, biosensing, and optics.

Fabrication and Application of Cellulose-Based Aerogel Films

Tyler Or, Emily D. Cranston and Jose Moran-Mirabal

Aerogels are networks of physically or chemically linked polymers or nanomaterials that are cast at low concentrations, followed by a delicate solvent removal process that preserves the network's internal morphology. Desired for their high porosity and surface area, ultralow density, and superabsorbent properties, aerogels have attracted interest for applications in high-surface-area electrodes, catalysts, scaffolds, and filtering. However, an ongoing challenge is to produce patterned aerogel films with controlled thickness, shape, and internal morphology. Aerogel films retaining these properties after deposition are particularly promising. While the fabrication of traditional silica-based aerogel films has been extensively explored using methods such as dip coating, spin, spray, and surface tension coating with sol precursors, none of these provide precise control over both thickness and shape. In this work, a simple bench-top protocol for controlling the dimensions of organic aerogel films based on cellulose nanocrystals (CNCs) with or without poly(oligoethylene glycol methacrylate) (POEGMA) was developed based on a stencil lift-off approach. CNCs are rigid rod-shaped nanoparticles, extracted from natural cellulose, and in this case they have been chemically modified to crosslink between themselves or with the flexible POEGMA polymer. These aerogel films will be studied as 1) 3D scaffolds for fibroblasts, 2) gel polymer electrolytes in dye-sensitized solar cells (DSSCs), 3) organic templates to form mesoporous TiO₂ via atomic layer deposition, and 4) as a model system for the study of diffusion in crowded environments.



Enhanced Fields of View in Epoxide Waveguide Arrays doped with Au nanoparticles

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Polymer matrices doped with a dispersion of noble metal nanoparticles combine the strong plasmon resonance-based optical signatures of the latter with the flexibility and processibility of the former.¹ We have developed a nonlinear lithographic technique to generate large populations of epoxide waveguides containing a uniform dispersion of Au nanoparticles. The method is based on the self-trapping and spontaneous filamentation of a broad beam of white light propagating through a cationic polymerizable matrix doped with a gold salt, initiating the polymerization of epoxide moieties and simultaneously generating elemental Au nanoparticles.² Each white light filament inscribes a cylindrical waveguide, leading to an array of metallodielectric waveguides. Preliminary measurements indicate a significant, nearly 30 % increase in the field of view of the metallodielectric waveguide arrays relative to their all-dielectric counterparts.

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Rapidly Self-Assembled, Hydrophobically-Modified Poly(oligoethylene glycol methacrylate)-Based Nanogels for the Delivery of Poorly Water-Soluble Therapeutics

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Nanogels are advantageous drug carriers because their chemical and physical properties can be tuned to improve drug uptake, target specific tissues or cell types, control drug release and ultimately decrease the quantity of therapeutic required for effective intervention. However, many conventional nanogels do not easily degrade, a key barrier for use in biomedical applications. To address this concern, we have designed a rapid, thermally-driven self-assembly method to produce hydrogel-based nanoparticles composed of well-defined linear hydrazide and aldehyde-functionalized poly(oligoethylene glycol methacrylate) (POEGMA)-based precursor polymers that create stable nanogels cross-linked by covalent, hydrolytically degradable hydrazine bonds. This self-assembly method produces nanogels ~200 nm in size with low dispersity. Loading of olanzapine, an atypical antipsychotic drug used in the treatment of schizophrenia and bipolar disorder, occurs with encapsulation efficiencies up to 70%. These self-assembled nanogels are also able to mechanically deform, which can aid transport through tight junctions, such as the blood-brain barrier. The POEGMA-based system also enables long circulation times as the protein-repellent nature of the polymer helps to avoid biological clearance mechanisms. This facile self-assembly method demonstrates significant potential for efficient drug delivery to the brain.



Wood Pulp Plant Substrate to Save Phosphorus

Reem Zeitoun and Robert Pelton

Phosphorus has a great impact on the health and productivity of plants. It is an essential component of the organic compound adenosine triphosphate, which drives most of biochemical processes and of ribonucleic acid, which directs protein synthesis in plants. The total quantity of phosphorus is low in most native soils, and most of it exists in unavailable forms to the plants. There have been arguments about whether phosphorus is used up faster than economically extracted. The accessibility to available phosphorus rock reserves is declining, and mining costs are rising. The process of growing plants in a soilless media is called hydroponics. Hydroponics plant substrates such as perlite, rockwool, or gravel are used with plant nutrients to cultivate plants in greenhouses. These cultivation media are inert, chemically inactive, and not biodegradable. This work explores the usage of wood pulp as disposable plant substrate that is chemically active and has the capacity to store and release important plant nutrients such as phosphorus. Wood pulp chemical properties were controlled by oxidizing the fibers and adsorbing cationic polymers on them. Cellulosic wood fibers adsorption isotherms and nutrients storing/releasing were tested out under pH and competitive ions influence. Modified fibers were used as growing media for Arabidopsis seeds, showing a different growing behavior for the seeds.

Synthetic Polyampholytes as Macromolecular Cryoprotective Agents

Jing Zhao, Mitchell Johnson, Nicholas A.D. Burke and Harald D.H. Stöver

Cryoprotection is the process of long term storage of cells, tissues and organs, and cryoprotective agents are key to protect cells during the freeze-rewarm processes. However, current cryoprotective agents often involve DMSO and glycerol, which have some toxicity and require removal immediately after thawing. In order to develop new and safer cryoprotective agent, a series of polyampholytes were tested as cryoprotective agents for 3T3 fibroblast cells. Polyampholytes were prepared by dimethyl aminopropyl methacrylamide (DMAPMA), acrylic acid (AA) and N-tert-butylacrylamide (t-BuAAM) by free radical copolymerization. Cell viability was measured with a freeze-rewarm protocol, using 10% DMSO as control. The post-thaw cell viability was affected by the copolymer composition, molecular weight, polymer concentration and NaCl concentration. Polyampholyte with 30% DMAPMA and 70% AA gave best cell viability of 70%, without any additive, such as DMSO, anti-freeze protein, NaCl. The further introduction of t-BuAAM, a hydrophobic comonomer, increased the cell viability to 90%, which is as good as DMSO. In-situ cryo microscopy was used to show that the polyampholytes decrease ice crystal size and in addition phase separate from ice to provide an ice free local environment for cells that both protects cells from damage by intercellular ice crystals and inhibits recrystallization. The polyampholytes also help cells dehydrate and thereby reduces the likelihood of formation of damaging intracellular ice crystals.



Notes



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