Department of Chemical and Biomedical Engineering

Researci

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8:30 a.m. – 2:00 p.m. Friday, March 23

FAMU-FSU College of Engineering 2525 Pottsdamer St., Tallahassee, FL 32310



FAMU-FSU College of Engineering

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Schedule of Events

8:30am	Student Oral Presentations (Room B221)
10:00am	Keynote Presentation (Room B221)
11:10am	Poster Session 1 (1st-floor Connector)
12:10pm	Lunch (Room B221)
1:00pm	Poster Session 2 (1st-floor Connector)
2:00pm	Adjournment

Keynote Presentation

Emulsion and Foam Stability: One Drop and Bubble at a Time

Gerald G. Fuller, Ph.D. Department of Chemical Engineering, Stanford University

Abstract

The stability of emulsions and foams are affected by a number of physical processes. As thin liquid films surrounding bubbles and drops drain, film rupture can occur, leading to coalescence and to coarsening. A common approach to appreciating stability in these systems is to create a bulk emulsion or foam and to follow the rate of creaming (for an emulsion) or collapse and drainage (for a foam). In this lecture, an alternative approach is described whereby individual bubbles and drops are monitored as they approach a fluid/fluid interface until coalescence ensues. These measurements utilize a newly developed instrument, the Dynamic Fluid Film Interferometer (DFI) where draining film thicknesses can be measured in space and time as well as the pressure drop (Laplace pressure) across the interface. Application of the DFI to study two problems is presented: (1) coalescence of oil/water emulsions in the presence of asphaltenes and (2) antifoaming of lubricating oils.

Coalescence of oil/water emulsions in the presence of asphaltenes.

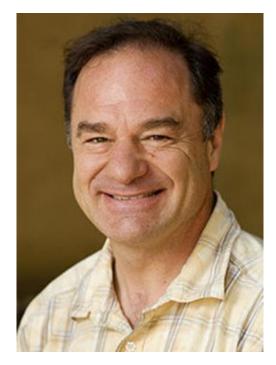
Asphaltenes are polyaromatic hydrocarbons defined by their solubility. For example, one classification as them soluble in toluene but insoluble in n-heptane. As heavy oils are increasingly being extracted, the asphaltenes are increasingly encountered in production. These complex molecules have surfactant-like qualities and readily attach to water/oil interfaces, making water removal difficult. This is a consequence of interfacial viscoelasticity that ensues upon asphaltene adsorption, which strengthens the skin on the surface of water droplets, which slows down and even arrests coalescence. Using the DFI in combination with methods to measure interfacial viscoelasticity, it is demonstrated that coalescence is strongly delayed when water drops are aged in the presence of asphaltenes. However, a second phenomenon occurs in the presence of asphaltenes, which was unexpected. A spontaneous emulsification occurs in in the presence of these compounds wherein micron-sized droplets of water coated with asphaltenes are produced. They reside in the oil phase in the vicinity of the interface and can act as de-emulsifiers and encourage the coalescence of large millimeter sized drops. Unfortunately, however, these small drops will generally exacerbate the removal of water from heavy oils.

Foaming in lubricant oils.

Foaming must be avoided in lubricating oils but this can be difficult since air entrainment is encouraged as mechanical, moving parts encounter air interfaces. For this reason, oils are usually formulated with the addition of antifoaming additives that accelerate bubble coalescence. In this example of the use of the DFI, the origin of foam stability in lubricate base oils is explored. In general, Marangoni stresses are the source of foam stability since these stresses can replenish draining liquid films existing between bubbles and extend their life time. Ordinarily, these stresses are a result of surfactants. However, in the case of non-aqueous lubricating oils, surfactants are never added and stable foams can be created, even in the case of isothermal systems (thermal gradients can also cause Marangoni stresses). Using the DFI we have established that soluto-capillary effects are the source of foam stability in lubricant oils. This occurs whenever the base oils are not purely a single components and is linked to differential evaporation of different components that might exist is oils. Since components with lower evaporation rates are generally more viscous and have higher surface tensions, Marangoni stresses will naturally appear and stabilize foams. This finding has important consequences on the design of lubricant oils.

Short Biography of Dr. Gerald G. Fuller

Dr. Fuller is the Fletcher Jones II Professor of Chemical Engineering at Stanford University. He received his B.S. in chemical engineering from the University of Calgary in 1975 and his PhD in chemical engineering from Caltech in 1980. Dr. Fuller is well known for his research on flow behaviors of complex soft materials, and their applications to human health, energy sciences, and environmental sciences. He is an elected member of National Academy of Engineering, a fellow of the American Physical Society, and a fellow of American Academy of Arts and Sciences.



List of Student Oral Presentations

- 1. "Luminescent Zero-Dimensional Organometal Halide Hybrids" by Chenkun Zhou
- 2. "Dielectric and Magnetic Properties of Nanoparticle Loaded Polystyrene as a Printable, Low-K Hybrid Material" by Faheem Muhammed
- 3. "Aggregation-induced Metabolic Reprogramming Achieved Through Size Dependent Release of Aldolase A" by Brent M. Bijonowski

Student Oral Presentation #1

Luminescent Zero-Dimensional Organometal Halide Hybrids

Chenkun Zhou¹, Haoran Lin¹, Yu Tian², Michael Worku², Chongin Pak², Michael Shatruk², Jennifer Neu², Tiglet Besara², Theo Siegrist¹, Yan Zhou², Peter Djurovich³, Mao-Hua Du⁴, Biwu Ma^{1,2}

¹FAMU-FSU College of Engineering, ²Florida State University, ³University of Southern California, ⁴Oak Ridge National Laboratory

Abstract

Organic-inorganic metal halide hybrids, consisting of a wide range of inorganic anions and organic cations, are an important class of hybrid crystalline materials with exceptional structure and property tunability. By choosing appropriate organic and inorganic components, the crystallographic structures can be finely controlled with the inorganic metal halide units forming three- (3D), two- (2D), one- (1D), and zerodimensional (0D) structures in the hybrids. The applications of these materials in optoelectronic devices have been extensively explored in recent years, including photovoltaic cells (PVs), light emitting diodes (LEDs), and lasers. The lowering of the structure dimensionality leads to the emerging of unique properties. For instance, unlike narrow emissions with small Stokes shift observed in typical 3D metal halide hybrids, strongly Stokes-shifted broadband photoluminescence has been realized in corrugated-2D, 1D, and 0D metal halide hybrids, as a result of exciton self-trapping or excited state structural reorganization. The versatility of this class of hybrid materials suggests there is a vast parameter space to explore novel structures to exhibit new and useful properties. In this talk, I will present our recent efforts in developing and studying new classes of 0D organometal halide hybrids. Due to the structural reorganization on the excited states, highly luminescent broadband emissions with large Stokes shift have been realized for these 0D organometal halide hybrids. Our work significantly advances the research in organic metal halide hybrids, and provides a platform for fundamental studies of structure-property relationship in bulk crystalline materials.

- 1. Zhou C, Lin H, Tian Y, Yuan Z, Clark R, Chen B, van de Burgt LJ, Wang JC, Zhou Y, Hanson K, Meisner QJ. Luminescent zero-dimensional organic metal halide hybrids with near-unity quantum efficiency. *Chem. Sci.* **2018**, 9: 586-593.
- Zhou C, Lin H, Shi H, Tian Y, Pak C, Shatruk M, Zhou Y, Djurovich P, Du MH, Ma B. A Zero-Dimensional Organic Seesaw-Shaped Tin Bromide with Highly Efficient Strongly Stokes-Shifted Deep-Red Emission. *Angew. Chem. Int. Ed.* 2018, 57: 1021-1024.
- Lin H, Zhou C, Tian Y, Siegrist T, Ma B. Low-Dimensional Organometal Halide Perovskites. ACS Energy Lett. 2018, 3: 54-62.

Dielectric and magnetic properties of nanoparticle loaded polystyrene as a printable, low-k hybrid material

Faheem Muhammed,¹ Subramanian Ramakrishnan¹, Parth Vakil², Geoffrey Strouse²

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Abstract

The development and miniaturization of electronics has increased the need for low-k dielectric materials for use in interconnect shielding. The primary goal of this work was to systematically modify the printed material to strike the balance between magnetic (permeability) and dielectric properties that provides maximal electronic shielding. The key in these applications is maximizing particle loadings in a polymer matrix while maintaining low dielectric constants and losses. Magnetic nanoparticles were dispersed in low-k thermoplastics and the dielectric properties were systematically studied as a function of particle type, concentration (0 to 13 volume percent), and surface coating. By varying the volume percentage of filler in the matrix, it is shown that one can increase the magnetic properties of the materials while minimizing unwanted contributions to the dielectric constant and dielectric loss. The well dispersed nanoparticle systems were successfully modeled through the Maxwell-Garnett (MG) theory thus giving one a predictive ability for the dielectric properties. High-precision (100 μ m resolution) additive manufacturing, combined with these materials, has demonstrated further reductions to the dielectric constant by controlled incorporation of air (k=1) in the system. The volume fraction of air present was tuned through topological optimization, computer aided structural design, and printing parameters. By treating the nanocomposite as a continuous matrix, and air as the filler, the MG theory was extended to the manufactured composites.

^{1.} Maex, K., et al., *Low dielectric constant materials for microelectronics*. Journal of Applied Physics, 2003. **93**(11): p. 8793-8841.

Aggregation-induced Metabolic Reprogramming Achieved Through Size Dependent Release of Aldolase A

Brent M. Bijonowski MSc¹, Susan Daraiseh PhD², Xuegang Yuan MSc¹, and Teng Ma PhD¹

¹Chemical and Biomedical Engineering; ²Biomedical Sciences, Florida State University, Tallahassee, FL 32310

Abstract

Cellular reprogramming arrising from self-assembled aggregation has been associated with limitations in oxygen diffusion; however, recent findings on non-hypoxic stabilization¹ and limited reduction in oxygen tension² have shown that this is not the case. hMSC Aggregation is characterized by a heterogeneous cellular organization resulting in chemical and biomechanical forces culminating in a shift in metabolism to increased glycolysis and decreased mitochondrial complex I activity. Research to-date has centered on molecular gradients with limited insight into the effects of biomechanical stress. We investigated aggregation of multiple sizes which resulted in size-dependent metabolic reconfiguration characterized by mitochondrial fission/fusion and release of aldolase A. Enhancement of PI3K phosphorylation in aggregated ASCs increases the aggregation-induced upregulation of glycolysis and downregulation of mitochondrial complex I in aggregates, whereas the impediment of PI3K phosphorylation in aggregate culture partially obstructs the cortical stress induced enhancement in glycolytic properties of aggregates. Our findings demonstrate that aggregation-induced mechanical reconfiguration plays a central role in driving metabolic reprogramming.

- 1. B. Follin, M. Juhl, S. Cohen, A. E. Perdersen, J. Kastrup and A. Ekbold, "Increased Paracrine Immunomodulatory Potential of Mesenchymal Stromal Cells in Three-Dimensional Culture," *Tissue Engineering Part B*, pp. 322-329, 2016.
- K. C. Murphy, B. P. Hung, S. Browne-Bourne, D. Zhou, J. Yeung, D. C. Genetos and J. K. Leach, "Measurement of oxygen tension within mesenchymal stem cell spheroids," *Royal Society*, vol. 14, no. 127, 2017.

List of Poster Presentations

Session 1

- 1. "In Vitro 3D Culture of Human Mesenchymal Stem Cell Enhances Cell Survival and Therapeutic Potential in Ischemic Stroke Treatment" by Xuegang Yuan
- 2. "Concentration Fluctuation during Nucleation in a Phase Separating Broad Ethylene Copolymer Leads to Partial Dissolution of Melt Memory" by Xuejian Chen
- 3. "Elastic instabilities in Taylor-Couette flow of a shear banding fluid" by Peter Rassolov
- 4. "A Study of the Structure and Dynamics near the Gel Boundary for Thermo-reversible Colloidal Gels" by Divya Bahadur
- 5. "Renewable 3D Printed Sensing Devices Using Cellulose Nanocrystals" by Bobby Haney
- 6. "Cell population balance of cardiovascular spheroids derived from human induced pluripotent stem cells" by Julie Bejoy
- 7. "Non-noble Co-Ni-Mo Electrocatalyst for Ethanol Electro-oxidation" by Wasu Chaitree
- 8. "Efficient Removal of Water and Organic Soluble NHC-Ru Catalyst via Either Host-Guest Interaction or Extraction" by Cheoljae Kim
- 9. "A New Temperature-Sensitive Sacrificial Layer for Functionalizing Live Cells with Microdevices" by Yu Miao
- 10. "Measuring Exchange Current Density in Solid Polystyrene Poly(ethylene oxide) Block Copolymer Electrolytes using Constant Potential Voltammetry" by Marc Berliner
- 11. "Transplantation of MPIO-Labeled hMSC Aggregates in a Rodent Model of Ischemic Stroke" by F. Andrew Bagdasarian
- 12. "Electrochemical activity of non-noble metal alloy Ni-Cu-Sn as catalyst towards oxidation of glycerol: A case for the Conceptual Glycerol/Ferric Redox Flow Battery" by James Akrasi
- 13. "Fabrication of lithium ion battery (LIB) electrodes via electroless encapsulation of C cloth with Sn, Sn-Cu alloy and the effect of annealing temperatures on electrode performance" by Venroy G. Watson
- 14. "Functionalization of Brain Region-specific Organoids with Isogenic Microglia-like Cells" by Liqing Song
- 15. "Assessment of Cellular Therapy in Acute Neurodegeneration at 21.1 T" by Shannon N. Helsper

Session 2

- 16. "The Influence of Liquid Conductivity on Electrical Breakdown and Hydrogen Peroxide Formation in Non-Thermal Plasma Generated in a Water Film Plasma Reactor" by Huihui Wang
- 17. "Synthesis and Adhesion Control of Glucose-based Bioadhesive via Strain-Promoted Azide-Alkyne Cycloaddition" by Irawan Pramudya
- 18. "Synergistic effects of heparin and hyaluronic acid on neural patterning of human induced pluripotent stem cells" by Julie Bejoy
- 19. "DTI-based Network Analysis of Female APP/PS1 Mouse Brains" by David Hike

- 20. "The Performance of 3D Printed Graphite Devices and their Dependence on Ink Rheological Properties" by Roneisha Blakeney
- 21. "Isolation and Characterization of Human Pluripotent Stem Cell-derived Exosomes" by Mark Marzano
- 22. "Assessment of Bound Sodium using Triple Quantum Selection vs. Inversion Recovery at 21.1 T" by Nastaren Abad
- 23. "Effect of Concentration on the Diffusion of salt in Block Copolymer Electrolyte" by Kyoungmin Kim
- 24. "Synthesis of Lightly-Crosslinked Zwitterionic Polymer-Based Bioinspired Adhesives for Intestinal Tissue Sealing" by Minkyu Kim
- 25. "Dynamics in Strongly Segregated Block Copolymers" by Gbenga Iyiola
- 26. "Flow of Wormlike Micellar Solutions Past a Sphere: Role of Micellar Relaxation Spectrum" by Shijian Wu
- 27. "Assembly of Human Stem Cell-Derived Vascular Spheroids and Cortical Spheroids to Model 3-D Brainlike Tissues" by Liqing Song
- 28. "Extensional Rheology as a mechanical tool for probing structural transitions in wormlike micellar systems" by Rose Omidvar
- 29. "Formation of Nitrogen Oxides by Nanosecond Pulsed Plasma Discharge along a Flowing Liquid Film" by Robert J. Wandell
- 30. "FTIR Spectroscopic Analysis of the Crystallization of Precision Halogen-substituted Polyethylenes" by Xiaoshi Zhang

In Vitro 3D Culture of Human Mesenchymal Stem Cell Enhances Cell Survival and Therapeutic Potential in Ischemic Stroke Treatment

Xuegang Yuan¹, Jens T. Rosenberg^{1,2}, Yijun Liu¹, Samuel C. Grant^{1,2}, and Teng Ma¹

¹Chemical and Biomedical Engineering, ²The National High Magnetic Field Laboratory, The Florida State University, Tallahassee FL

Abstract

Human mesenchymal stem cells (hMSCs) have been shown to enhance stroke lesion recovery through secretion of trophic factors that mediate inflammation and tissue repair. However, low cell survival and reduced secretory functions post-transplantation of culture-expanded hMSCs are the major barriers limiting the therapeutic efficacy of hMSCs in stroke treatment.^{1,2} In this study, we report the impact of in vitro threedimensional (3D) aggregation preconditioning of hMSCs for stroke treatment. 3D aggregation culture enhances hMSCs secretory profile, resistance to ischemic stress, in vivo survival at stroke lesion site, and stroke lesion recovery. Aggregate-derived hMSCs were labeled with micrometer-sized superparamagnetic iron oxide (MPIO) particle for in vivo magnetic resonance imaging (MRI) analysis, and then injected intraarterially in a rat stroke model with middle cerebral artery occlusion (MCAO). Compared to planer culture, aggregate-derived hMSCs are smaller in size with enhanced SDF-1a-induced migration.^{3,4} The secretory profile and immunomodulation of aggregate-derived hMSCs are also enhanced. PI3K/Akt signaling pathway was highly activated and contributes to the resistance of ischemia and oxidative stress in vitro, leading to higher post-transplanted cell survival rate at stroke lesion. MRI images of the stroke lesion showed increased ¹H and ²³Na signal as evidence of the influx of extracellular water and disruption of ionic homeostasis. Lesion volume analysis indicated enhanced recovery for 3D cultured hMSCs group. After one week of initial MRI, the decrease of MPIO contrast on T2* weighted images was calculated for cell clearance. Together, the results demonstrated that 3D aggregation of hMSCs is an effective strategy that enhances their therapeutic performance in stroke lesion recovery compared to standard planer culture.

- 1. Sart S., Tsai AC., Li Y., Ma T. Three-Dimensional Aggregates of Mesenchymal Stem Cells: Cellular Mechanisms, Biological Properties, and Applications. *Tissue Eng Part B Rev.* **2014**; 20(5): 365-380.
- 2. Rosenberg J., Yuan X., Grant S., Ma T. Tracking Mesenchymal Stem Cells Using Magnetic Resonance Imaging. *Brian Circulation*. 2016; 2(3): 108-113.
- 3. Tsai AC., Liu Y., Yuan X., Ma T. Compaction, Fusion, and Functional Activation of Three-Dimensional Human Mesenchymal Stem Cell Aggregate. *Tissue Eng Part A*. **2015**; 21(9-10): 1705-1719.
- Liu Y., Munoz N., Tsai AC., Logan TM., Ma T. Metabolic Reconfiguration Supports Reacquisition of Primitive Phenotype in Human Mesenchymal Stem Cell Aggregates. *Stem Cells*. 2016. 1549-4918.

Concentration Fluctuation during Nucleation in a Phase Separating Broad Ethylene Copolymer Leads to Partial Dissolution of Melt Memory

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³Chemical Engineering and Material Science, University of Minnesota, Twin Cities, MN, US

Abstract

Direct evidence of phase separation in the melt of an ethylene 1-hexene copolymer with a broad interchain distribution of comonomer is provided by SANS using samples with deuterium added via isotope exchange. SANS data display an upshift of scattering with decreasing melt temperature. The upper critical temperature for phase separation (T_{LLPS} , 150 °C) is found to be close to the melt temperature where an inversion of the crystallization rate was observed by DSC, thus providing strong evidence to the hypothesis of phase separation being the drive for dissolution of melt memory. The upshift of scattering is observed only below a critical scattering vector, consistent with the signature of nucleation during phase separation inside the metastable region. Approaching the melt by heating the crystals does not contribute to higher scattering compared to the scattering at melt temperatures approached by cooling from a high temperature melt, indicating that the metastable region covers a wide range of temperatures, thus preventing fast phase separation before crystallization during dynamic cooling. Time-resolved light scattering profiles and light transmittance followed by SALS in the protonated resin at 135 °C, below T_{LLPS} , reveal the nucleation and

growth stages of LLPS.[1] Dissolution of melt memory manifested as decrease of $T_{c,peak}$ in Figure 1 is found to occur mainly within the induction period and is associated with concentration fluctuations during nucleation. Bright-Field optical micrographs of the protonated resin collected at 135 °C after annealing for 24 hrs confirm the typical sea-island morphology associated with phase separation occurring via nucleation and growth. Light droplets, rich in highly-branched molecules, with an average diameter of 1.2 µm develop in this time frame and account for about 2.2% of the whole sample by mass.

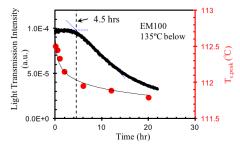


Figure 1. Light transmittance recorded as a function of annealing time in the melt of EM100 at 135 °C approached from below and compared with the melt time dependence of crystallization peak temperature ($T_{c,peak}$) recorded using DSC. The black dashed line marks the induction time that demarcates the nucleation and growth stages.

Balsara, N. P.; Lin, C.; Hammouda, B. Early Stages of Nucleation and Growth in a Polymer Blend. Phys. Rev. Lett. 1996, 77, 3847-3850.

Elastic instabilities in Taylor-Couette flow of a shear banding fluid

Peter Rassolov and Hadi Mohammadigoushki

Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee FL

Abstract

We report experiments on a shear banding wormlike micellar solution based on cetyltrimethylammonium bromide/sodium nitrate (CTAB/NaNO₃) in flow between two concentric cylinders (Taylor-Couette cell). A combination of flow visualization, particle tracking velocimetry and rheology allows us to access different planes of the Taylor-Couette cell. Beyond a critical shear rate we report formation of an elastic instability that is characterized by formation of bright waves in the axial direction of the Taylor-Couette cell. Additionally, measurements in the vorticity plane indicate that instability manifests itself in formation of an undulated interface between the high shear band and the low shear bands. Finally, bulk rheological measurements are compared with the local rheology measurements obtained with a locally resolved particle tracking velocimetry.

A Study of the Structure and Dynamics near the Gel Boundary for Thermo-reversible Colloidal Gels

Divya Bahadur, Subramanian Ramakrishnan

Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL

Abstract

Gels are formed when particles in solution aggregate to form a mechanically rigid system spanning network upon varying the concentration and/ or the strength of attraction between the particles. Subtle changes in these parameters can alter the formation times and the mechanical properties of the resultant gel by orders of magnitude. This sensitivity creates both a scientific challenge central to the field of soft matter but also an opportunity for designing suspensions tailored for specific applications. Such control is crucial to technologies in a diverse range of areas including ceramics, food processing, pharmaceuticals, etc. We examine the fluid to solid transition for a model system composed of nanometer scale octadecyl silica particles in decahydronaphthalene (82 nm and 110 nm, $\phi = 0.2$) that undergoes thermoreversible gelation. Taking advantage of newly developed x-ray scattering capabilities and the ability to tune precisely the strength of the particle attractions, we track the evolution in the microscopic organization and mobility of the particles and correlate them with the time-dependent macroscopic mechanical behavior of the suspensions. We find that the suspensions proceed through identical intermediate states of microscopic and macroscopic behavior even as the gel formation times vary by orders of magnitude upon changing the temperature (or, equivalently, strength of attraction) 0-2 K below the gel point. We propose a model of gel formation in the regime of weak attraction in which network formation is a hierarchical process whose initiation depends on the creation and stability of small clusters in which the particles arrange in locally favorable configurations. Finally, we introduce a scaling parameter that captures the similarity in the evolution of the gel as it forms at different strengths of attraction.

Renewable 3D Printed Sensing Devices Using Cellulose Nanocrystals

Bobby Haney, Dan Berrigan, Nick Glavin, Subramanian Ramakrishnan

Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL

Abstract

The alignment of nanostructures for nanomaterials remains a challenge for many different applications. It is important then to study methods to facilitate and characterize this alignment. We focused our efforts on the additive manufacturing of nanomaterials. In this work, suspensions of cellulose nanocrystals are optimized for 3D extrusion printing to induce crystal alignment along the printing direction.

Cellulose nanocrystals, thermoplastic polyurethane (TPU), and dimethyl sulfoxide (DMSO) are mixed together in a vial to form the ink suspension. Inks of 35, 55, and 80 vol% CNCs in dry composite were put into plastic syringe connected to a Nordson pump where a set pressure extrudes the syringe contents onto a surface. Each ink formulation was tested by extruding at different pressures with different sized nozzles to observe occasions of clogging, substrate surface spreading after extrusion, and drying effects after heating. The 35 vol% CNC ink allowed extrusion smooth connected lines using the smallest nozzle diameter. This is ideal because the smaller diameter permits higher shear of the ink for better alignment of cellulose nanocrystals. The 35 vol% CNC ink was therefore optimized through holding the CNC and TPU combined solids volume fraction constant at 20%. By maintaining the solids volume fraction, we are able to extrude CNC inks of varying cellulose concentrations using the 100 micron nozzle for the best 3D printing resolutions. We will move forward with mechanical testing of printed dogbone structures and finally adding other substances to make a sustainable conductive material.

Cell population balance of cardiovascular spheroids derived from human induced pluripotent stem cells

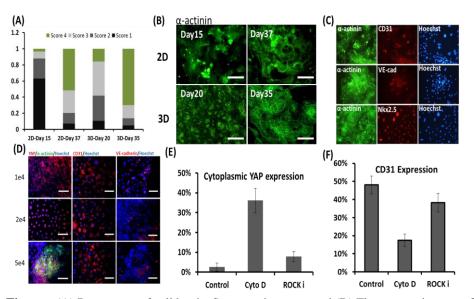
Julie Bejoy[#], Yuanwei Yan[#], Junfei Xia, Kyle Griffin, Jingjiao Guan, Yan Li*

Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Florida State University, Tallahassee, Florida, USA

Abstract

Stem cell-derived cardiomyocytes and vascular cells can be used for a variety of applications such as studying human heart development and modelling human disease in culture. In particular, protocols based on modulation of Wnt signaling were able to produce high quality of cardiomyocytes or vascular cells from human pluripotent stem cells (hPSCs). However, the mechanism behind the development of cardiovascular spheroids into either vascular or cardiac cells has not been well explored. Hippo/Yes-associated protein (YAP) signaling plays important roles in the regulation of heart size during organogenesis, but its impact on cardiovascular differentiation has been less evaluated. In this study, the impact of seeding density and the modulation of Hippo/YAP signaling on cardiovascular spheroids patterning was evaluated. The undifferentiated cells were seeded at different densities and Hippo/YAP signaling was modulated using ROCK inhibitor or Cytochalasin D (Cyto D). Compared to 2-D culture, 3-D cardiovascular spheroids exhibit higher levels of sarcomeric

striations and higher length-towidth ratios of α -actinin+ cells. The cells with higher seeding density exhibit a higher expression level of CD31 but lower level of VE-cadherin with less nuclear YAP expression. Cyto D treatment results in more cytoplasmic YAP and lower CD31 expression compared to ROCK inhibitor, indicating the roles of Hippo/YAP pathway in cardiovascular spheroid patterning. The gene expression of MMP-2/-3 and Notch-1 was further analyzed. The results should help our understanding of the underlying effects for the efficient patterning of cardiovascular spheroids after mesoderm formation from pluripotent stem cells.



Figures: (A) Percentage of cell by the Sacromeric scores and (B) Fluorescent images of cardiac marker α -actinin for 2D and 3D cultures. (C) Representative fluorescent images of cardiac markers: Nkx2.5 and α -actinin for 3D. (D) Fluorescent images of YAP, vascular markers CD31 and VE-cadherin for different seeding densities at day 22. The quantitative analysis of (E) cytoplasmic YAP and (F) CD31 expression.

Student Poster Presentation #7 (Session 1)

Non-noble Co-Ni-Mo Electrocatalyst for Ethanol Electro-oxidation

Wasu Chaitree and Egwu E. Kalu*

Department of Chemical & Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, Florida 32310, USA

Abstract

Ternary as-deposited Co-Ni-Mo electrocatalyst on carbon support was investigated for the ethanol oxidation. The electroless deposition method was used for the preparation and carbon substrate support (CCS) was made active for electroless deposition with Pd-ink. The effects of electroless deposition time, electro-oxidation temperature (30-60°C), and the effect of metallic species were investigated. SEM and XRD were used to study surface structure and composition. The electrocatalytic activity of the catalyst was measured and analyzed using cyclic voltammetric (CV) techniques. The result showed that CoNiMo/CCS was highly active in alkaline ethanol solution (0.5M NaOH+1 M EtOH) for ethanol oxidation. Tafel analysis showed the exchange current density for the catalyst prepared at 30 minutes deposition time ($1.3 \times 10^{-5} A/cm^2$) was an order of magnitude higher than that reported for Pt ($0.001 \times 10^{-5} A/cm^2$,[1]), and Pt/C ($0.033 \times 10^{-5} A/cm^2$,[1]). Additionally, the highest current density was observed at 60° C from CoNiMo prepared at 30 minutes deposition time. In addition, the comparison of the peak current density between tri-metallic (CoNiMo) and bi-metallic (CoMo) electrodes was investigated. The result shows that the peak current density from ternary Co-Ni-Mo was higher than that from the bimetallic Co-Mo electrocalalyst. Overall, this study provides a novel and effective non-noble electrocatalyst for ethanol electrooxidation.

Reference

1. Xu C, Shen PK, Ji X, Zeng R, Liu Y. 2005. Enhanced activity for ethanol electrooxidation on Pt–MgO/C catalysts. Electrochem Commun 7 (12):1305–1308.

Efficient Removal of Water and Organic Soluble NHC-Ru Catalyst via Either Host-Guest Interaction or Extraction

Cheoljae Kim and Hoyong Chung

Department of Chemical and Biomedical Engineering, Florida State University

Abstract

We have developed a highly-efficient recovery method for a transition metal catalyst in aqueous media via host-guest interactions using a newly-designed *N*-heterocyclic carbene (NHC) ligand. The new NHC ligand possesses an adamantyl (guest) tethered ethylene glycol unit for hydrophobic inclusion into the cavity of a β -cyclodextrin (β -CD) host compound. We applied this ligand to a ruthenium (Ru)-based olefin metathesis catalyst. The Ru catalyst demonstrated excellent performance in ring-closing metathesis (RCM), cross metathesis (CM), and ring-opening metathesis polymerization (ROMP) in aqueous media as well as in an organic solvent, CH₂Cl₂. After the reaction was complete, the lingering Ru residue was removed from aqueous solution with more than 99 % efficiency (as low as 53 ppm of Ru residue) by simple filtration utilizing a host-guest interaction between insoluble silica-grafted β -CD (host) and the adamantyl moiety (guest) on the catalyst. The adamantyl-containing Ru catalysts also demonstrated high recovery yield via phase selectivity when the reaction is run in organic solvent by partitioning the crude reaction mixture between layers of diethyl ether and water. In this way, after aqueous extraction of the catalyst, residual ruthenium levels were observed in the range of 6 ppm in the crude reaction product.

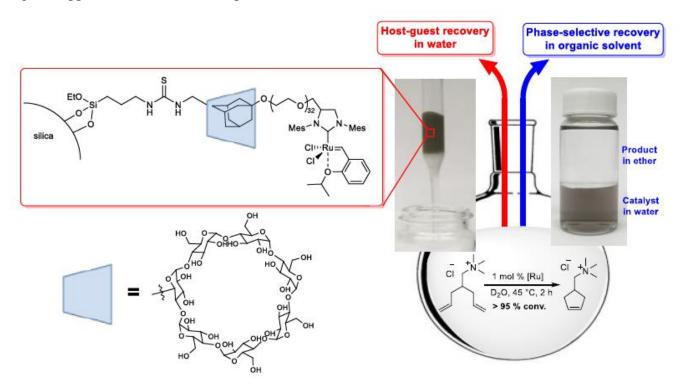


Figure 1. Illustration of removal of used catalyst via either host-guest interaction or aqueous extraction

A New Temperature-Sensitive Sacrificial Layer for Functionalizing Live Cells with Microdevices

Yu Miao^{1,*}, Wenhao Cheng^{1,*}, Xuegang Yuan¹, Tian Zhou², Teng Ma¹, Yi Ren², Jingjiao Guan¹

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Abstract

Adhering artificial micro/nanodevices to the surface of live cell can produce a cell/device hybrid system that possesses functionalities of both the cell and the devices, which has potential application in drug delivery, cell tracking and tissue engineering^{1,2}. Microcontact printing has been proven to be an efficient and low-cost manufacturing method for making such cell/device complexes^{3,4}. During the process, micro devices are printed on a sacrificial layer and then released later to form cell/device complexes. Our group has reported that poly(N-isopropylacrylamide) (PNIPAM) can be used as a temperature sensitive sacrificial layer, which enables immobilization of micro devices on substrate when temperature is higher than 32 °C. Microdevices

can be released when temperature drops below 32 °C. The present work has utilized gelatin as a new temperature-sensitive sacrificial layer, which enables immobilization of micro devices on substrate when temperature is around 8 °C and releasing of them when temperature goes to 37 °C. Immobilization of micro devices under low temperature can provide more ways to engineer the printed particle on the substrate.

Gelatin film Gelatin film Printed micro device Printed micro device Complex Released cell/device S7°C complex C co

Acknowledgmment

This work was supported by NSF Award #1547730.

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Measuring Exchange Current Density in Solid Polystyrene – Poly(ethylene oxide) Block Copolymer Electrolytes using Constant Potential Voltammetry

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Abstract

A novel method to determine exchange current density in solid polymer electrolytes was developed. Reaction kinetics of lithium electrodes were studied in solid polymer electrolytes consisting of lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) dissolved in polystyrene-b-poly(ethylene oxide) block copolymers. Symmetric Li cells were cycled with constant potential voltammetry at different temperatures to measure current. Butler-Volmer kinetics for semi-reversible reactions were applied to obtain exchange current density and the cathodic transfer coefficient. The electrochemical analysis for solid polymers is being verified using a rotating disk electrode setup with a liquid ferrocyanide/ferricyanide redox couple.

Transplantation of MPIO-Labeled hMSC Aggregates in a Rodent Model of Ischemic Stroke

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Abstract

High magnetic fields enable high resolution imaging and enhance the sensitivity for detection of cellular therapies in application to neurodegeneration caused by various ailments, such as ischemic stroke. A promising technique to alleviate and treat ischemic stroke is the cerebral injection of human mesenchymal stem cells (hMSC)¹. Here, large (~400 μ m) hMSC aggregates were labeled intracellularly with micron-sized particles of iron oxide (MPIO, Bangs Labs, IN) or superparamagnetic iron oxide nanoparticles (SPIO) with varying concentrations. These *in vitro* aggregates were scanned at 11.75 T to quantify contrast enhancement

relative to the transfection dose (Fig. 1). Bangs (0.89-µm average dia.) and SPIO (35-nm average diam.) concentrations were 1.8 µg/mL, 0.9 µg/mL, 0.45 µg/mL, and 0 µg/mL. hMSC were labeled for 12 hours, then aggregated for 2 days, with ~5000 hMSC/aggregate. SNR, CNR and Percent Contrast, relaxation and diffusional measurements were conducted for these in vitro samples over a range of acquisition parameters. In addition, using the lowest MPIO concentration, labeled hMSC aggregates were transplanted directly into the lateral ventricles or cortex of ischemic and naïve rats. Ex vivo brain images were acquired at 11.75 T to verify initial aggregate placement as well as potential dissociation and migration of individual hMSC following implantation. Initial results indicate potential cell

Fig. 1 SPIO (a) and MPIO (b) aggregates, in vitro, TE/TR =16.1/500

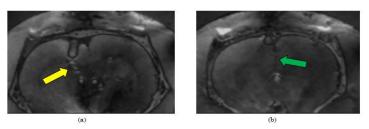


Fig. 2 Implantation site (a) and axial migration (b) of MPIO-labeled hMSC aggregates in a MCAO rat, day 3 post-transplantation (moving anterior to posterior, *ex vivo*, TE=7.6 ms, TR=500 ms).

migration over time following in vivo injection (Fig. 2).

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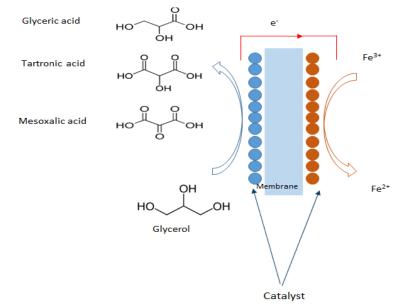
Electrochemical activity of non-noble metal alloy Ni-Cu-Sn as catalyst towards oxidation of glycerol: A case for the Conceptual Glycerol/Ferric Redox Flow Battery

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Abstract

Electro-catalytic oxidation of polyols is a very important path towards the production of high value chemicals. The electro-oxidation of glycerol using precious metals such as Au and Pt has been studied and known to be a source of several end products and has also been utilized in the concept of direct glycerol fuel cells to produce electrical energy additionally [1]. Herein an electro-catalyst comprising a non-noble metal alloy composition, namely nickel, copper and tin on carbon support have been fabricated using the electroless deposition method. The electrochemical activity of the prepared catalysts towards the glycerol oxidation reaction in acidic medium have then been evaluated using physical characterization, electrochemical and chromatographic methods. In the current study, the concept is applied to experimentally demonstrate the working principles of a glycerol-fed redox flow battery using an aqueous solution of a Fe^{2+}/Fe^{3+} couple as cathode [2]. Constant potential electrolysis coupled with high performance liquid chromatography were used to identify the various compounds generated as a result of the electro-catalytic conversion of glycerol.



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Fabrication of lithium ion battery (LIB) electrodes via electroless encapsulation of C cloth with Sn, Sn-Cu alloy and the effect of annealing temperatures on electrode performance

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Abstract

Over the last few decades a vast number of researchers have investigated various methods for the synthesis of tin alloy anode materials capable of repeated cycling, reduced tin pulverization, and capacity retention when used in lithium ion batteries (LIBs).¹⁻³ In this study, we report the use of woven carbon cloth as high surface area template for the deposition of Cu and subsequent encapsulation with Sn via facile electroless

coating method without the use of external power supply. The resulting material Sn-Cu@C-cloth was annealed at 200 °C and 400 °C and used as electrodes in LIB half-cells with Li metal as anode. Charge/discharge study at current density of 227 mAh/g indicated that Sn-Cu@C-cloth annealed at 200°C and 400 °C exhibited first cycle capacities of 745 mAh/g, and 1075 mAh/g, respectively, while the C-cloth substrate exhibited only 340 mAh/g. Preliminary results after fifty cycles indicated that the annealed Sn-Cu@C-cloth exhibited capacity retention of ~413 mAh/g. These indicate results that facile electroless encapsulation of carbon cloth as a cost-effective approach can potentially be used to fabricate Sn and CuSn alloys anode materials.

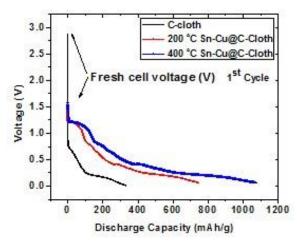


Figure 1. First cycle discharge capacity for half cells made from C-cloth, $200 \text{ }^{\circ}\text{C}$ Sn-Cu@C-cloth, and $400 \text{ }^{\circ}\text{C}$ Sn-Cu@C-cloth electrode materials.

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Functionalization of Brain Region-specific Organoids with Isogenic Microglia-like Cells

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Abstract

Brain organoids derived from human induced pluripotent stem cells (hiPSCs) are promising tools to study neurological disorders. However, most cortical organoids lack a microglia component, the resident immune cells in the brain. The objective of this study is to engineer brain-region-specific organoids from hiPSCs incorporated with isogenic microglia-like cells in order to enhance brain-like microenvironments. In this study, microglia-like cells were derived from hiPSCs using stage-wise growth factor induction into mesoderm. The derived microglia-like cells expressed several phenotypic markers, including CD11b, IBA-1, CX3CR1, and P2RY12, and phagocytosed micron-size super-paramagnetic iron oxide particles. Microglia-like cells were able to upregulate pro-inflammatory genes (TNF- α) and secrete anti-inflammatory cytokines (i.e., VEGF, TGF- β 1, and PGE2) when stimulated with amyloid β 42 oligomers, lipopolysaccharides, or dexamethasone. Dorsal cortical (higher expression of TBR1 and PAX6) and ventral (higher expression of Nkx2.1 and Prox-1) spheroids/organoids were derived from the same hiPSC line, which displayed action potentials and synaptic activities. Co-cultured the isogenic microglia-like cells with hiPSC-derived dorsal and ventral organoids

showed differential migration ability of microglia-like cells into different organoids. The immune responses of cocultured organoids to pro-inflammatory stimuli were investigated to model the functionality of brain region-specific neural cells and microglia-like cells. This study should advance our understanding of the effects of microglia on neural tissue function and establish a transformative approach to modulate cellular microenvironment during neurogenesis toward the goal of treating various neurological disorders [1].

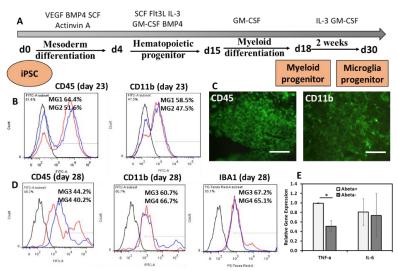


Figure 1. Derivation of microglia-like cells from hiPSCs

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Student Poster Presentation #15 (Session 1)

Assessment of Cellular Therapy in Acute Neurodegeneration at 21.1 T

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Abstract

Neurological damage resulting from stroke is a leading cause of serious long-term disability in the United States with more than 795,000 people suffering a stroke annually, of which approximately 17% result in death¹. It is evident that an effective therapy is needed to minimize short- and long-term damages, and human mesenchymal stem cells (hMSC) have been shown to exhibit therapeutic effects on tissue recovery following neurological damage². This study evaluates the potential for direct cerebral hMSC aggregate implantation as a cellular therapy targeting acute neurodegeneration using an ischemic stroke model.

in vivo Methods: Transient Middle Cerebral Artery Occlusion (MCAO) was instituted in Sprague Dawley rats

for 1.5 h immediately followed by intracerebral ventricular injection of twenty 400-□m dia. hMSC aggregates labeled with micron-sized particles of iron oxide (MPIO). These aggregates were targeted for injection into the contralateral ventricle of MCAO rats and compared to MPIO-labeled aggregates injected in naïve rats and untreated MCAO rats.

MRI/S methods: MRI/S was acquired *in vivo* on 1, 3 and 7d post-implantation utilizing the 21.1-T NHMFL magnet. High resolution fast spin echo (FSE), gradient-recalled echo (GRE) and sodium scans were acquired to assess localization of administered cells within the ventricular system, potential cellular migration and dissociation (Fig 1. a & d), as well as the ischemic lesion volume (Fig 1. b, c, e & f). Figure 1 demonstrates ischemic lesion recovery on 7 d as well as localization of aggregates within the right lateral ventricle with outward expansion of aggregates that is potentially indicative of cellular migration and dissociation.

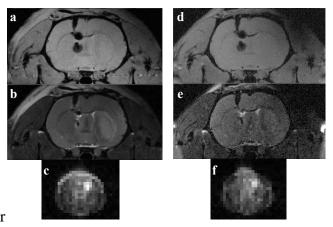


Figure 1 demonstrates *in vivo* MRI on days 3 (a, b, c) and 7 (b, d, f) post-implantation; (a, d) cellular localization in the left hemisphere with potential migration and dissociation (GRE; TE/TR=4/1000 ms, NEX=2, 50x50- μ m in-plane); (b, e) ischemic lesion in right hemisphere (FSE; TE/TR=25/6000 ms, NEX=2, 100x100- μ m in plane); and (c, f) sodium distribution (TE/TR = 0.7/60 ms, NEX=16, (1.6 mm)³).

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The Influence of Liquid Conductivity on Electrical Breakdown and Hydrogen Peroxide Formation in Non-Thermal Plasma Generated in a Water Film Plasma Reactor

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Abstract

Non-thermal plasma technology is under intensive investigation for the use in water treatment since the hydroxyl radical formed during the plasma discharge in contact with water is a strong oxidant and can degrade many organic pollutants¹. However, high liquid conductivity in some waste water can influence the electrical breakdown at a gas-liquid interface and thereby influence the formation of hydroxyl radicals causing reduced water treatment efficiency.

In the current study, we used a nanosecond pulsed power supply with a water film plasma reactor to investigate the influence of liquid conductivity on the electrical breakdown, H2O2 formation, and plasma properties, including the electron density, gas temperature, and electron temperature. The liquid conductivity of water was adjusted by adding potassium chloride. Both argon and helium were used as the carrier gas, and the sensitivity of both argon and helium discharges to the liquid conductivity were compared. The results show that the H2O2 production rate drops 5% and 10% for argon and helium discharges, respectively. The electron density slightly increases while the electron temperature decreases as the liquid conductivity was increased from 5μ S/cm to 40mS/cm. This result is correlated with the increase of current dissipation in the water as the liquid conductivity was increased. However, the reactor/power supply system has a high tolerance to liquid conductivity and can generate a strong discharge when the liquid conductivity is as high as 40 mS/cm. This result suggests that the system has potential for treating sea water. In comparison with our previous study², it is shown here that a nanosecond pulsed plasma discharge has a much better liquid conductivity tolerance than the microsecond pulsed discharge.

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Synthesis and Adhesion Control of Glucose-based Bioadhesive via Strain-Promoted Azide-Alkyne Cycloaddition

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Abstract

A glucose-based bioadhesive, poly(2-methacrylamido glucopyranose-co-N-methacryloyl-3,4-dihydroxyl-lphenylalanine-co-8-azidooctyl methacrylate) [poly(MG-co-MDOPA-co-AOM)], has been synthesized by thermally-initiated free radical polymerization. The new bioadhesive is composed of three modules: a hydrophilic glycopolymer segment, a mussels-inspired catechol segment, and a crosslinking azide segment. Poly(ethylene glycol) (PEG)-based crosslinker, (1R,8S,9s)-Bicyclo[6.1.0]non-4-yn-9-ylmethyl PEG (BCN-PEG) was synthesized separately. Bulk adhesion properties of the terpolymer were enhanced by covalent bond forming crosslinking via strain-promoted azide-alkyne cycloaddition (SPAAC). The occurrence of SPAAC was confirmed by ¹H NMR and FT-IR. After moistening the adhesive and a crosslinker, BCN-PEG with water, the adhesion properties were examined by a lap shear strength test on porcine skins. The control of adhesion was studied under various crosslinker concentrations, crosslinking durations, and crosslinker lengths. Even without crosslinking, the new terpolymer adhesive demonstrated 20-fold higher adhesion strength (115 kPa) compared to a commercial rubber cement (5.8 kPa). The most significant factor to control for adhesion was crosslinker length. BCN-PEG was tested with 134 and 43 repeating units of PEG. Crosslinking with the long crosslinker, BCN-PEG (PEG repeating units: 134), did not enhance adhesion strength meaningfully. However, crosslinking the short crosslinker BCN-PEG (repeating units: 43) showed significant improvement in work of adhesion (150% higher than uncrosslinked). The overall revealed features of strong adhesion on biological surfaces, structural similarity to natural carbohydrate, water compatibility, control lability of adhesion strength, and non-toxic adhesion enhancement principle via SPAAC crosslinking, suggest that the new glucose-based bioadhesive can be successfully used for biomedical applications.

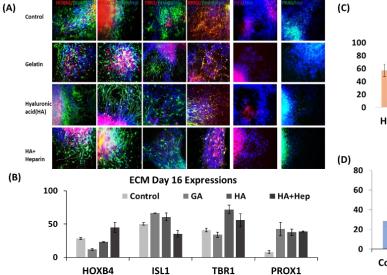
Synergistic effects of heparin and hyaluronic acid on neural patterning of human induced pluripotent stem cells

Julie Bejoy, Zhe Wang, Qing-Xiang Amy Sang, Yan Li*.

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Abstract

Lack of established animal models and inability to efficiently represent the human brain pathology lead to the development of human pluripotent stem cells (hPSCs) based brain tissue. Even though the development of brain organoids has enhanced our ability to understand the developing human brain and related disorders (e.g., Schizophrenia, microcephaly), the organoids still do not recapitulate the anatomical organization or connectivity patterns of human brain. Therefore, the optimization and evaluation of induction and signaling factors become important to develop next generation brain organoids. In this study, the impact of extracellular matrix (ECM) on the development of brain organoids from human stem cells was evaluated. Since Hyaluronic acid (HA) is a major brain ECM component that interacts with cells through several receptors, the neural protective and differentiating effects of HA were investigated. To mediate HA binding capacity, Heparin was added in addition to HA or grafted to HA to form hydrogels. The neural spheroids developed from hPSCs were treated with either HA or Heparin-HA complex (Hep-HA) and were analyzed for their impact on neural patterning. The results indicate that HA-Hep complex has a caudalizing effect on hPSC-derived neural spheroids. Cell signaling including Wnt and Hippo/Yes-associated protein (Yap) signaling was modulated (using Wnt inhibitor IWP4 or actin disruption agent Cytochalasin D respectively) to understand the underlying effect on the patterning by HA-Hep complex. Manipulation of Wnt or Hippo/Yap signaling was able to alter the impacts of ECMs on the neural patterning. The results from this study should enhance the understanding of influence of biomimetic ECM factors for brain organoid generation.



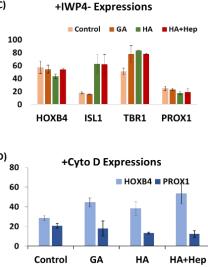


Figure: (A) Images of forebrain and hindbrain markers expressed by the neural cells treated with HA and Hep-HA complex. (B) Flow cytometry analysis of markers. various Impact of the (C) IWP4 (D) Cyto D treatment on the effect of patterning HA and Hep-HA complex analyzed using flow cytometry.

DTI-based Network Analysis of Female APP/PS1 Mouse Brains

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Abstract

Alzheimer's Disease (AD) is the most common form of dementia, characterized by memory loss and changes

in behavior. The most prevalent pre-clinical model is the APP/PS1 double transgenic mouse expressing human genes, amyloid precursor protein (APP) and presenilin-1 (PS1). Clinically, MRI is used to diagnosis AD by means of volumetrics, focusing mainly on hippocampal atrophy¹. During this study, diffusion tensor imaging (DTI) is applied at 11.75 T to the APP/PS1 model at multiple early time points with network theory analysis employed to examine structural connectivity alterations as a function of age compared to wild type controls. Seven network parameters were evaluated to determine local and global alterations: Clustering, Eccentricity, Betweenness Centrality, Closeness Centrality. Eigenvector Centrality, Harmonic Centrality, and Weighted Degree. Current data shows a drop in Fractional Anisotropy (FA) and a decrease in weighted degree in the hippocampus and piriform areas of the brain. Additionally, we detected a consistent significant increase in the Betweenness Centrality as a function of age in the piriform and parietal cortex.

This research could be utilized as a method of detecting AD and neurodegenerative diseases, allowing patients to receive treatment earlier and before symptoms present. Additionally, this work will help to expand the application of DTI and network theory to the identification and progression of other neurodegenerative diseases.

	Weighted Degree	Eccentricity	Centrality: Betweenness	Centrality: Closeness	Centrality: Eigenvector	Centrality: Harmonic	Clustering	
Piriform	×/√	×/√	×/√	√/×	×/√	√/×	×/√	
Parietal	×/×	×/×	√/×	√/×	×/×	√/×	√/×	
Temporal	×/√	√/×	×/×	√/×	√/×	√/×	×/√	Aoross Age
L. Hippo	×/√	×/×	×/√	×/×	×/×	×/×	×/√	69
R. Hippo	×/√	×/×	√/×	√/×	×/×	√/×	×/×	J
Piriform	×/√	√ √	×/×	√/×	×/√	√/×	×/√)
Parietal	×/×	√/×	×/×	√/×	√/×	√/×	×/×	Aoro
Temporal	×/√	√/×	×/×	√/×	×/×	√/×	√/√	Across Phenotype
L. Hippo	×/√	×/×	×/√	×/×	×/√	×/×	×/√	otype
R. Hippo	×/√	×/×	×/√	√/×	×/×	√/×	×/×	

Figure 1: Table showing significance of network parameter in the 5 areas of the brain studied. Red Regions show significance across age. Green Regions show significance across phenotype. Impacts of aging can be seen in closeness and harmonic centrality. Impacts of phenotype can be seen in older samples through weighted degree and clustering. In younger samples, impacts of phenotype can be seen in Eccentricity as well as closeness and harmonic centrality.

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The Performance of 3D Printed Graphite Devices and their Dependence on Ink Rheological Properties

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Abstract

The purpose of this study is to identify the relationship between the rheological percolation threshold (microscopic properties) and final device performance (macroscopic properties) of extrusion printed graphite devices. Theoretically, the rheological percolation threshold has been reached once the storage modulus and loss modulus are equal. At this critical concentration, the matrix viscosity increases abruptly due to the formation of an interconnected network of fillers¹. The current ink formulation for a thermal management device is composed of 9.30 wt% graphite nanoplatelets, 7.60 wt% milled carbon fiber, 7.10 wt% curing agent, and 75.9 wt% EPON 862². This formulation was determined through trial and error, combining random amounts of each filler until an ideal viscosity for printing was reached. This ink formulation will be systematically studied to determine the rheological percolation for the graphite dispersed in the epoxy has been found at 6.17 wt% (3.73 vol%). Once the rheological percolation threshold is determined for each filler, the device will be extrusion printed and the electrical and thermal conductivity will be measured, also at multiple weight percentages. Finally, the results from the rheology study will be combined with the final print properties to suggest an optimal ink formulation for maximum device performance.

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Isolation and Characterization of Human Pluripotent Stem Cellderived Exosomes

Mark Marzano, Julie Bejoy, Kyle Griffin, Yan Li

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Abstract

Multivesicular bodies (MVBs) are vesicle-containing endosomes that fuse with the plasma membrane of cells, releasing their contents to the extracellular environment. They contain a number of different vesicles including exosomes, which are produced intracellularly and in themselves contain a variety of different molecules, proteins, mRNA, miRNA, and other components. Exosomes have a major effect on normal and pathological processes in an organism. A major advantage that exosomes have for central nervous system (CNS) disorders is that they have the ability to cross the blood-brain barrier (BBB) quite easily. They can also be produced on a large scale for clinical purposes with more control. Human induced pluripotent stem (iPS) cells have some benefits when compared to other types of stem cells when it comes to exosome production. These types of cells allow for generation of different types of human neurons and glial cells as producers of exosomes. Another benefit is that iPS cells can be taken from a patient's own tissue, reducing the possibility of immune rejection. Isolating exosomes can be achieved by using cell culture supernatants. Cell culture media contains a few fragments and other types of vesicles produced from cells. The materials collected must be pure exosomes, and the main method for doing this is a series of centrifugation and ultracentrifugation steps. This process can be complicated and involves using different types of centrifuges that may not be available in most labs. Isolation can also be achieved at a brief, low-speed centrifugation by using Total Exosome Isolation reagent. This reagent can be added to cell culture media in order to concentrate the exosomes in the solution. The isolation process begins by harvesting cell culture media and centrifuging it at 2000x g for 30 min in order to remove cells and debris. A 0.2 micrometer filter will remove any particles over 200 nanometers. Exosomes from three different iPS cell cultures will be isolated: (i) undifferentiated group, (ii) mesoderm cell group, and (iii) neural cell group. The differences in the exosomes isolated from each group can be analyzed visually by electron microscopy, by flow cytometry, and by their ability to reduce apoptosis and oxidative stress. A large cooler can be used to keep the centrifuge at the desired temperature during isolation. Three samples can be attempted for each group for statistical significance. I plan to characterize the samples from the groups mentioned above after isolation in order to find similarities and differences in membrane proteins.

Assessment of Bound Sodium using Triple Quantum Selection vs. Inversion Recovery at 21.1 T

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Abstract

Triple Quantum (TQ) and Inversion Recovery (IR) techniques have been used to separate sodium (²³Na) MR signals between bound and bulk contributions based on differential relaxation rates and tissue properties [1-5]. Potentially, TQ and IR methods offer non-invasive techniques to detect intracellular sodium concentration changes dynamically. In pathologies, the classification and quantification of intra- versus extracellular sodium distributions may provide a direct probe of cellular function and viability related to ionic homeostasis and Na⁺-K⁺-ATPase transport. TQ experiments target the rotationally restricted bound fraction, whereas, IR techniques exploit T₁ relaxation differences of intra- versus extracellular ²³Na based on differential correlation times, often attributed to the intracellular compartment, as opposed to the more freely moving single quantum transition. To differing degrees, both approaches are impacted by reduced sensitivity, speed of acquisition, and exchange between and within compartments that could limit the actual localization of sodium signals. Performed at 21.1 T, this study compares the ²³Na TQ and IR techniques with regard to SNR, efficiency and specificity in both phantoms and *in vivo* preclinical models, which include ischemia and hydrocephalus, with a goal of identifying which approach provides the best discrimination of the bound sodium fraction or intracellular concentration.

Acknowledgements

This work was supported by the NIH (R01-NS072497 and RO1-NS102395) and User Collaborations Grant Program (to SCG) from the National High Magnetic Field Laboratory, which is funded by the NSF (DMR-1157490) and the State of Florida.

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Effect of Concentration on the Diffusion of salt in Block Copolymer Electrolyte

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Abstract

Solid polymer electrolytes (SPEs) are promising materials for energy storage systems providing improved safety due to their chemical and structural stability. They replace liquid electrolytes whose volatility and flammability cause battery failures to be violent. In addition, liquid electrolytes are not compatible with high energy electrodes like lithium metal. Technical limitations that delay the application of SPEs to batteries are the possibility of dendrite growth, when used with lithium metal, and low ionic conductivity.(1) Poly(styrene)-poly(ethylene oxide) block copolymers (SEO) have been investigated to suppress the dendrite growth by their high shear storage modulus.(2) Lithium bis-trifluoromethylsulfonimide (LiTFSI) was added to SEO to increase the electrical conductivity of SEO electrolytes.(3) An important parameter for ionic transport in this electrolyte is the salt diffusion coefficient, D, which depends on the microphase structure in the block copolymers.(4) In this study, the diffusion of LiTFSI in lamella structured SEO membranes was studied at 120 °C and different salt concentrations, reported as molar ratios of lithium ions to ethylene oxide repeat units and denoted r. Fourier Transform infrared – attenuated total reflectance spectroscopy (FTIR-ATR) was used to track the diffusion of salt from a high concentration polymer electrolyte membrane into a low concentration polymer electrolyte membrane. The low concentration membrane was in direct contact with the ATR crystal and the time-resolved absorbance near the membrane-crystal interface corresponds to the local salt concentration. Results are presented versus the average r of the two membranes ($r_{avg} = 0.025$ to 0.175 in this study). The apparent diffusion coefficients were $7.0 \pm 1.0 \times 10^{-8}$ cm²/s at different r_{avg} , but the results showed non-Fickian behavior. This behavior could be due to concentration-dependence of the diffusion coefficient observed in our previous work.(5)

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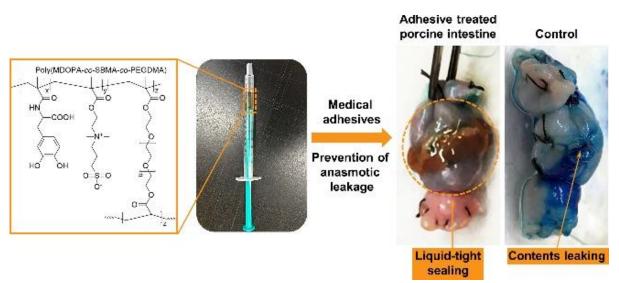
Synthesis of Lightly-Crosslinked Zwitterionic Polymer-Based Bioinspired Adhesives for Intestinal Tissue Sealing

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Abstract

In this work, new bioinspired medical adhesive is developed for preventing intestinal anastomotic leakage. The newly developed terpolymer possesses three different components: 1) A zwitterionic polymer, poly(sulfobetaine methacrylate) (polySBMA), for enhanced hydrophilicity and biocompatibility¹, 2) a Nmethacryloyl-3,4-dihydroxyl-L-phenylalanine (MDOPA) segment for improved bulk adhesion property of the polymer, and 3) poly(ethylene glycol) dimethacrylate (PEGDMA) as crosslinker for strengthening adhesion properties of the polymer by providing debonding resistance. The successful polymerization of poly(N-methacryloyl-3,4-dihydroxyl-L-phenylalanine-co-sulfobetaine methacrylate-co-poly(ethylene glycol) dimethacrylate) (poly(MDOPA-co-SBMA-co-PEGDMA)), synthesized by a convenient free-radical polymerization was clearly confirmed by ¹H NMR. In the lap shear strength tests utilizing porcine skin, the terpolymer adhesive demonstrated the optimal maximum adhesion strength and work of adhesion when the amounts of crosslinker PEGDMA reach to 1.5 - 2.5 mol %. Additionally, the adhesive was non-cytotoxic based on *in vitro* cytotoxicity cell experiments using human embryonic kidney (HEK293A) cells. Finally, the new poly(MDOPA-co-SBMA-co-PEGDMA) successfully prevented leakage from the sutured intestinal tissue in the ex vivo anastomosis experiments employing porcine intestine, representing that newly synthesized terpolymer adhesive is a promising biomedical adhesive which can provide a leak-proof barrier for application to intestinal anastomoses.



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Student Poster Presentation #25 (Session 2)

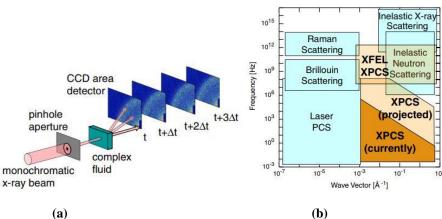
Dynamics in Strongly Segregated Block Copolymers

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Abstract

Block copolymers (BCPs) are promising materials for applications ranging from batteries to membrane separations. These materials could improve safety and energy efficiency of these applications if low transport can be overcome. BCPs are of interest primarily due to the microphase separated morphology that results from self-assembly. The distance over which the repeating nanostructure in BCPs is oriented is termed the grain size. While the nanostructured morphology is dictated by BCP composition, grain structure is determined by processing. A possible solution to improving transport in BCP membranes is to use the grain structure and grain dynamics to increase transport. X-ray photon correlation spectroscopy (XPCS) was used to examine grain dynamics. It can be used to measure dynamics in materials with electron density contrast, such as BCP melts. XPCS probes dynamics on similar time scales as visible light (10^{-4} to 10^{4} s). Advantages of XPCS over light scattering techniques are that it can be used with optically opaque samples and multiple scattering is not a concern. The most powerful aspect of XPCS is that it can access a broad range of length scales including atomic (light scattering is limited to structures larger than about 100 nm⁹). We will review how XPCS has been used to study materials on length scales similar to those found in BCPs.



(a)

Figure 1: (a) Schematic of a (small-angle) XPCS measurement. (b) Schematic representation of the approximate dynamic ranges of various spectroscopic techniques employing x-rays, neutrons, and visible light. The dark orange box refers to the region covered by XPCS today using area detectors. The light orange boxes show the additional regions that should be covered by XPCS beamlines that are either newly commissioned or currently under construction, including x-ray free electron lasers (XFELs) operating in the hard x-ray region [1]

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Flow of Wormlike Micellar Solutions Past a Sphere: Role of Micellar Relaxation Spectrum

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Abstract

Here we report the experiments on flow of cetylpyridinium chloride/sodium salicylate (CPCl/NaSal) wormlike micellar solutions past a falling sphere in a vertical column. Particle tracking velocimetry (PTV), particle image velocimetry (PIV), rheology and flow induced birefringence (FIB) are used to characterize the flow. Previous studies have shown that a falling sphere in wormlike micelles never reaches a constant terminal velocity beyond a critical extensional Deborah number, instead it settles with unsteady velocity.^[1-3] This behavior is attributed to the wormlike micellar chain scission in the wake of the sphere. Similar instabilities are also found in viscoelastic polymer solutions which chain break is not possible.^[4-6] The reasons of instabilities in polymer solutions are thought to be the results of the asymmetry of the polymer chain on flanks of the falling sphere or a single-mode relaxation spectrum of the polymer chains or the asymmetry in the polymer chain extensions on flanks of the falling sphere.. In this work, we examine the role of these micellar relaxation and gradients in extensions by considering two wormlike micelles that have different relaxation spectrum (comparing a single mode versus and a multi-mode Maxwell model) wormlike micellar solutions over a wide range of elasticity $(10^{-2} < De_E < 20)$ and inertia $(10^{-6} < Re < 10)$. Although we report unsteady motion for spheres that fall in wormlike micelles with a single-mode relaxation spectrum for $DeE \ge 2.6$, our results indicate that for equally or stronger extensional flows ($2.5 < De_E < 15$), the falling spheres in the wormlike micelles with a multi-mode Maxwell model never exhibit the unsteady motion. Thus, indicating the importance of the micellar relaxation spectrum on dynamics of the sphere sedimentation. We can always get unsteady motion in single-mode wormlike micelles when $De_E \ge 2.6$, but never get any unsteady motion for equally or stronger extensional flows $(2.5 < De_E < 15)$ in multi-mode wormlike micelles. In addition, for conditions that give rise to instability, flow induced birefringenceFIB indicates no sign of micellar extension gradients on sphere sideways. for unsteady motion cases. The results show that the micellar relaxation spectrum has a key role on dynamics of the sphere sedimentation.

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Assembly of Human Stem Cell-Derived Vascular Spheroids and Cortical Spheroids to Model 3-D Brain-like Tissues

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Abstract

Human cerebral spheroid models derived from induced pluripotent stem cells (iPSCs) provide novel tools for recapitulating the cytoarchitecture of human brain and for studying the biological mechanisms of neurological disorders. However, the heterotypic interactions of neurovascular units, composed of neurons, pericytes, astrocytes, and brain microvascular endothelial cells, in brain-like tissues are less investigated [1]. The objective of this study is to investigate the impacts of neurovascular interactions on the brain regional patterning and function. Hybrid neurovascular spheroids were constructed by fusion of human iPSC-derived cortical neural progenitor cell (NPC) spheroids, endothelial cell (EC) spheroids, and the supporting mesenchymal stem cells (MSCs). Single hybrid spheroids were constructed at different NPC: EC: MSC ratios of 4:2:0, 3:2:1 2:2:2, and 1:2:3 in low-attachment 96-well plates. The incorporation of MSCs upregulated the secretion levels of VEGF-A, PGE2, and TGF-B1. In addition, tri-culture spheroids promoted the expression of TBR1 (cortical layer VI) and Nkx2.1 (ventral cells), and matrix remodeling genes, MMP2 and MMP3, as well as Notch-1, indicating the crucial role of matrix remodeling and cell-cell communications on cortical spheroid patterning. Moreover, tri-culture system elevated blood-brain barrier gene expression (e.g., GLUT-1), CD31 expression, and tight junction protein ZO-1. Treatment of the CXCR4 antagonist, AMD3100, showed the immobilization of MSCs during spheroid fusion. This forebrain-like model has the potential applications in understanding cellular interplay of the neurovascular unit in the diseased human brain and screening the novel drugs before clinical trials.

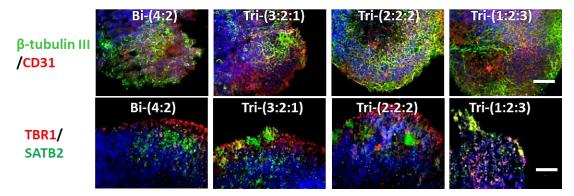


Figure 1. Representative immunohistochemistry staining of different hybrid cortical spheroids.

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Extensional Rheology as a Mechanical Tool for Probing Structural Transitions in Wormlike Micellar Systems

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Abstract

We used capillary break-up extensional rheometer (CaBER) to study two series of wormlike micelle solutions; sodium oleate/octyl trimethylammonium bromide (NaOA/OTAB) and Cetylpyridinium chloride/Sodium salicylate (CPyCL/NaSal). These systems show a peak in zero shear viscosity or shear relaxation time beyond a critical salt to surfactant ratio. Cryo-TEM images have indicated that system based on NaOA/OTAB experiences a transition from linear to shorter linear micelles beyond this maximum. However, linear wormlike micelles based on CPCI/NaSal become branched beyond the viscosity peak. In this study we investigated whether branched and shortening micellar systems can be distinguished via CaBER technique. Our results indicate that for most of extensional parameters, these systems behave similarly. However, some differences in filament life time has been detected in these two solutions.

Formation of Nitrogen Oxides by Nanosecond Pulsed Plasma Discharge along a Flowing Liquid Film

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Abstract

Nitrogen fixation of dry air with plasma discharges has been studied since the 1900's but has never gained commercial appeal due to the low every yield of the process as compared to other methods (Habor Bosch). Pulsed electrical discharge plasmas formed at the interface of a flowing gas-liquid film in small millimeter scale reactors [1] have been shown to be effective for chemical oxidation of organic compounds in the aqueous [2] and gas [3] phases due to the efficient production of hydroxyl radicals [4]. H₂O₂ formation from inert gas and liquid water with nanosecond discharges [5,6], in contrast to the earlier work with microsecond discharges [1-4], has been characterized with respect to the effect of electrical and plasma properties and can lead to more stable discharges that can operate over a wider range of conditions more efficiently [5,6]. In the present contribution, we report on the utilization of gas-liquid nanosecond pulsed discharges for the formation of nitrogen oxides, including NO and NO₂ in the gas phase and NO₂⁻ and NO₃⁻ in the liquid phase by adding N₂ to the influent gas. We will discuss the effect of varying inlet gas composition (e.g., N₂/O₂/argon), on the formation of these species as well as H₂O₂. Chemical analysis is performed using FTIR spectroscopy on the gas phase and ion chromatography in conjunction with UV-Vis spectroscopy on the liquid phase. Plasma properties including gas temperature and electron density as well the electrical characteristics (current and voltage) of the discharge will also be reported.

This work was supported by NSF (CBET: 1702166) and Florida State University.

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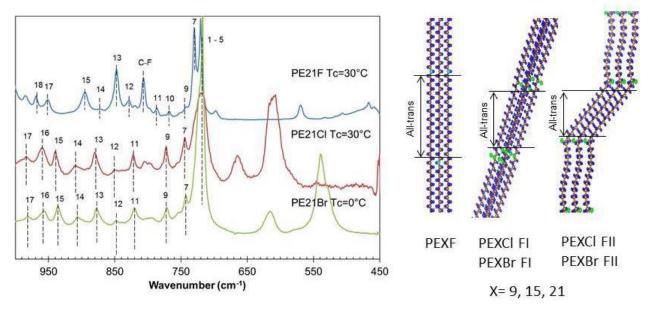
FTIR Spectroscopic Analysis of the Crystallization of Precision Halogen-substituted Polyethylenes

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Abstract

Polyethylenes with halogen substitution at a precise distance along the methylene backbone are unique models to study the effect of nano-structured chain-defects on folding and crystallization of polymers. Prior work has shown that a crystal structure transition occurs in precision chlorine and bromine substituted polyethylenes within one degree of undercooling. In the present work we have carried out a complete analysis of the FTIR progression rocking and stretching modes of series of isothermally crystallized samples using the simple oscillator model. The effect of halogen size to the periodic oscillation changes the effective number of oscillators between F and Cl or Br substituted systems. Quantitative analysis of the C-halogen stretching region and this analysis support the polymorphic transition and documents a C-C all-trans conformation of the methylenes between halogens. Upon crystallization from the melt below the transition temperature the chains pack in an all-trans planar conformation (Form I) with layered crystalline chlorines that present some longitudinal disorder. The crystals formed at higher temperatures pack in a non-planar herringbone-like structure (Form II) with a TGGT....TG'G'T backbone conformation around the substitution, while conserving the all-trans packing of the methylene sequence, as shown in the graphical abstract.



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