

“Green Materials: Design, Processes and Applications”

October 21, 2010
1:00 pm to 6:30 pm

Campus Center Atrium
New Jersey Institute of Technology
Newark, New Jersey

Organized by NJACS Polymer Topical Group

Sponsors:



GREEN MATERIALS: DESIGN, PROCESSES AND APPLICATIONS

October 21, 2010
1:00 PM to 6:30 PM (registration begins at 12 noon)
NJIT Campus Center Atrium; Summit St, Newark, NJ 07102

Organizers
BHANU P. S. CHAUHAN (*WILLIAM PATERSON UNIVERSITY*)
TOM PACANSKY (*APOLLO VENTURES, LLC*)

Sponsored by NJACS Polymer Topical Group

SCHEDULE

ENTRY	ACTIVITY	TIME
1	Welcome Remarks	1:00 PM
2	Richard A. Gross (Polytechnic Institute of NYU) Engineered Lipids Produced by Microbes and Their Use in Bio-Based Materials	1:10-1:50PM
3	Joseph V. Kurian (E. I. du Pont de Nemours and Company) “Renewably Sourced High Performance Sorona ® Polymer and Fibers”	1:50-2:30PM
4	Bhanu P. S. Chauhan (William Paterson University) “Green Catalytic Synthesis of New Functionalized Organosilicon Materials”	2:30-3:10 PM
	Coffee Break	3:10-3:50 PM
5	Ponisseril Somasundaran (Columbia University) “Greener Alternatives for Personal Care and Commodity Industries: Sugar Based Surfactants, Biopolymers and Their Synergistic Effects”	3:50-4:30 PM
6	James A. Moore (Rensselaer Polytechnic Institute) “Dead Leaves and Lawn Clippings: Waste or Opportunity?”	4:30-5:10 PM
	Poster Presentations	5:10-6:25 PM
	Concluding Remarks	6:25-6:30 PM

Richard A. Gross (Polytechnic Institute of NYU)

Engineered Lipids Produced by Microbes and Their Use in Bio-Based Materials

Abstract: ω -Hydroxyfatty acids are a new class of biobased monomers and chemical intermediates. They can be converted to surfactants, emulsifiers, cosmetic ingredients, fragrances, and more. However, previous to our work, ω -hydroxyfatty acids proved difficult and expensive to prepare by traditional organic synthesis, precluding their use in commodity materials. Here we report the identification and elimination of 16 genes from the diploid yeast *Candida tropicalis* genome, to engineer a strain capable of producing commercially viable yields of ω -hydroxyfatty acids. For example, after reintegration of a P450 and process optimization, volumetric yields higher than 150 g/L of 14-hydroxytetradecanoic acid was produced using methyl myristate as substrate. We also have shown that in this strain background, the extent to which fatty acids are oxidized by different P450s depends upon their chain length and unsaturation. A simple method was developed to prepare from *Candida tropicalis* fermentations 14-hydroxytetradecanoic acid methyl ester in high purity (>99.95%). This monomer was converted to poly(14-hydroxytetradecanoic acid) ($T_m = 96$ °C, $M_w = 160\,000$, $PDI = 2.3$) using $Ti(C_3H_7O)_4$ as catalyst (200 °C, 2 h under N_2 , 220 °C, 4 h under vacuum [<0.1 torr]). After compression molding, tensile tests showed that the polymer has a Young's modulus of 419?20 Mpa and elongation to break of 729?21%. Reactive blending of poly(ω -hydroxyfatty acids) with Natureworks PLA produced bioplastics with very good strength and ductility.



Sophorolipids consist of dimeric sophorose linked by a glycosidic bond to the penultimate hydroxyl group of an 18-carbon fatty acid. Our laboratory has produced these compounds by fermentation in up to 300 g/L volumetric yields. This paper will summarize how, by specific modification of sophorolipids, compounds were obtained that show promising activities as therapeutic agents (e.g. immunomodulators for treatment of septic shock and anti-cancer activity) and for use as antimicrobial agents. Modified forms of sophorolipids were identified that increase their activity against important human pathogens by 1000x relative to the natural structures. Furthermore, the structural complexity inherited from sophorolipids was translated into unique poly(sophorolipid) biomaterials. ROMP polymerization of natural diacetylated lactonic sophorolipids gave high molecular weight polymers with asymmetric bola-amphiphilic repeating units. Physical properties of these glycolipid-derived biomaterials will be described. References Dodds, D. R.; Gross, R. A., *Chemicals from biomass*. *Science*, 318 (5854), 1250-1251 (2007). Gross, R. A., Kalra, B; "Biodegradable Polymers for the Environment", *Science*, 297, 803-806 (2002). Yang et al. "Two-Step Biocatalytic Route to Biobased Functional Polyesters" *Biomacromolecules* 11(1), 259-68 (2010)

Speaker's Bio: Professor Richard A. Gross has a PhD (1986) in organic/polymer chemistry from Polytechnic University (Brooklyn, New York). He was a Postdoctoral Fellow at the University of Massachusetts (Amherst), followed by appointment as Assistant Professor, Associate Professor and full Professor at University of

Massachusetts (Lowell) from 1988-1998. Since 1998 he has occupied the Herman F. Mark Chair Professorship at Polytechnic University (New York). His research is focused on developing biocatalytic routes to monomers, macromers and polymers. He uses both cell free and whole-cell catalyst systems to investigate biocatalytic transformations such as lipase-catalyzed polyester synthesis, whole-cell routes to biosurfactants and fatty acid derived monomers, and protease-catalyzed transformations to polypeptides. He is also developing biomaterials with bioresorption rates controlled by embedded hydrolytic enzymes and glycolipid biosurfactants for agricultural and therapeutic applications. He has over 360 publications in peer reviewed journals cited about 6000 times, edited 5-books and has been granted or filed a total of 19 patents. He currently runs a group of 17 consisting of 5 postdoctoral and 12 Ph.D graduate students. Prof. Gross was the recipient of the 2003 Presidential Green Chemistry Award in the academic category. In 2007, he was inducted into the American Institute for Medical and Biological Engineering. In 2010 he was selected as the Turner Alfrey Visiting Professor. He recently founded SyntheZyme LLC to commercialize technologies developed in his laboratory.

His other Professional activities and honors include: Director of Polymer Research Institute (at POLY), 2003-2006; Director – NSF Center for Biocatalysis and Bioprocessing of Macromolecules (at POLY), 2000-present; NSF Presidential Young Investigator Award, 1990-1995; Presidential Award in Green Chemistry, 2003; Founder and Co-Editor of the Journal of Environmental Polymer Degradation, 1993-1998; Co-founder of the ACS journal Biomacromolecules, Co-Director of the NSF Biodegradable Polymer Research Center (at UMASS-Lowell), 1993-1998; Past President – U.S. Society on Biodegradable Polymers, 1999; Johnson and Johnson Focused Giving Award, 2000-2002; Editorial Board, Biomacromolecules (2000 to present); Editorial Board, J. Bioactive and Biocompatible Polymers (2001 to present); Editorial Board, Industrial Biotechnology (2005 to present); Editorial Board, Journal of Molecular Catalysis B: Enzymatic (2005 to present); Editorial Board Enzyme and Microbial Technology (EMT) (2005 to present); Engineering Conferences Foundation, Board of Directors (2002-2005); Director: Biomedical Engineering Masters Program (2001-2008, POLY & SUNY Downstate).

Joseph V. Kurian (E. I. du Pont de Nemours and Company)

Renewably Sourced High Performance Sorona® Polymer and Fibers

Abstract: There is a growing need to develop environmentally friendly materials that provide performance and functionality equivalent to or better than petroleum based materials. DuPont is committed to research and development that will increase the use of renewable materials in its offerings and reduce dependency on petroleum. There are many diverse applications for Renewably Sourced products ranging from fabrics to carpets, inks and coatings, to construction



materials and packaging. DuPont has recently commercialized an innovative family of polymers, Sorona®, based on the key ingredient 1,3-propanediol (PDO), derived from annually renewable agricultural feedstocks. Sorona® is a unique thermoplastic polymer that can be easily shaped into a variety of articles, including fibers, to offer a unique combination of properties, such as softness, comfort-stretch and recovery, easy care, dyeability and stain resistance. Sorona® imparts distinctive characteristics and design attributes to a vast array of fabrics and other specialty garments. Innovative Sorona® polymer and fiber technologies enable manufacturers of apparel, carpet, upholstery, specialty resins and packaging to use their existing assets to make new, higher-value products to meet customer needs. Sorona® polymer is commercially available for the textiles, carpets, engineering thermoplastics and packaging markets. This presentation will provide an overview of DuPont's efforts in renewably sourced materials (www.renewable.dupont.com), with special emphasis on the development and commercialization of Sorona® polymer (<http://www.sorona.dupont.com>). SmartStrand™ carpets made with DuPont™ Sorona® polymer offers a combination of permanent built-in stain protection, superior durability, amazing comfort and environmental benefits. Sorona® is one of the most revolutionary materials to hit the carpet industry in a long time. Mills and brand houses around the world are creating hundreds of fabrics using fibers manufactured with DuPont™ Sorona® polymer.

Speaker's Bio: Joe received a Ph.D. in Polymer Science from the University of Akron in Ohio, USA, working under the guidance of Professor Joseph P. Kennedy. He has a B.Sc. in Chemistry from Kerala University and a B.Tech in Polymer Science & Rubber Technology (1st Rank with distinction) from the University of Cochin, India. He joined DuPont, in 1990, as a Polymer Research Chemist in the Nylon business at Seaford, Delaware. At DuPont, he worked in a variety of roles including polymer and fiber research, new product development, process optimization, manufacturing and new business development. In 1995, he started research work in 3GT Sorona® project developing polymer grade 1,3-propanediol, polymerization technologies, various fiber technologies and applications know-how. He created and led the 3GT polymer team and then worked as the R&D Manager for the Sorona® and Cerenol® Polyol projects. He is an innovator with over 60 filed US patents (38 granted) and over 40 journal publications, including a book chapter on Sorona®. Joe has received several awards and recognition for his Sorona® polymer, process and renewably sourced materials work, including the Bolton-Carothers Innovative Science Award from DuPont in 2008 and the Corporate Sustainability Award in 2005. Joe has coordinated renewably sourced materials technologies (Sorona® EP, Biomax® PTT, Hytrel® RS, Zytel® RS, etc.) across various DuPont Business Units, including ABS, EP, P&IP, NOW and DPC. Joe and his research group played a vital role in the development and commercialization of Sorona® polymer and Cerenol® into various markets, including the filing of over 150 patents in polymer and application related technologies. DuPont has recently received several awards for the development of bio-PDO and Sorona® polymer including the Presidential Green Chemistry Award, Society of Plastics Engineers Environmental Division Award, IDEA 2007, "Most Visionary Innovation Award" by the China Central Television and the 2008 Frost & Sullivan Award. Joe's previous work experience includes GE Plastics (USA), Apollo Tires (India), and The

Rubber Research Institute of India. He is an active member of several professional and engineering societies and organized several symposiums in the area of renewably sourced materials. In 2007, he was nominated for the Design Magazine's "Engineer of the Year" Award. He is a passionate supporter of science activities for students, including the Science Olympiad, DuPont Challenge, and Science Fair. Joe and his family reside in Hockessin, Delaware.

Bhanu P. S. Chauhan (William Paterson University)

Green Catalytic Synthesis of New Functionalized Organosilicon Materials

Abstract: In industrial scale synthetic processes, the remediation of the catalyst and by-products waste is a very important issue for and particularly very critical, when the catalysts are very expensive and toxic. The solution to these issues via the development of the catalysts, which can be recycled and reused with similar efficiency can lead to green and inexpensive industrial process. We have been interested in producing catalytic routes to hybrid silicon based polymeric materials with highly precise tailoring of the pendant functional groups. The synthesis of hybrid polymers can be regarded as attractive avenue to develop new materials with wide-ranging desired property profiles. The choice of studying such systems is based on the utility of such polymers in applications ranging from coatings to highly sophisticated electronic materials.



In this context, we started investigating the possibility of using metal nanoparticles as catalysts for such transformations because of potential for attaining high selectivity and efficiency. During these investigations, we stumbled upon the nanoparticle based catalysts, which can take advantage of the small size and high surface area of nanoparticles to produce selective and "soluble" analogues of heterogeneous catalysts [1-4].

In this presentation, we will present and summarize our recent findings in this area of research in terms of producing silicon based hybrid polymers. In our system, organic functional groups are substituted on a main chain organic/organometallic/inorganic polymers in presence of Pd, Pt- nanoparticles (see the scheme bellow). We will describe utilization of this strategy to generate families of new inorganic/organic hybrid polymer systems derived from the polymeric templates such as polybutadienes and polyhydrosiloxane (PMHS). We will present the successful applications of the macromolecular catalytic routes involving (i) formation of carbon-heteroatom bonds (ii) formation of silicon-oxygen bonds and (iii) the investigations of regioselectivity of such transformations. In addition we will briefly discuss the physical and chemical properties of the new functional polymers.

Speaker's Bio: Professor Chauhan obtained his Ph. D. under the guidance of Professor Robert Corriu at Montpellier University, France and moved to the group of Professor Masato Tanaka at National Institute of Materials and Chemical Research in Japan as a NEDO research scientist. In 1997, he joined “center for main group chemistry” in the group of Professor Phil Boudjouk and worked there for almost three years. He was appointed assistant professor at Catholic University of America in August 2000 and moved to City University of New York-CSI in 2001. He joined William Paterson University (WPU) in 2007, and has been professor and chairperson of the chemistry department.

Professor Chauhan serves as editorial advisory board member of the “Applied Organometallic chemistry” (Wiley) and “Silicon” (Springer). He has served as co-director of NYSTAR funded research center “Center for Engineered Polymeric Materials” (CePM). He is also an advisory board member of ACS-New Jersey Polymer topical group. His research area is in the field of nanomaterials synthesis and their applications in national needs such as green catalysis, hybrid materials for new optical and data storage, and nanostructure based drug delivery vehicles. He has various patents and numerous peer reviewed publications and presentations in national and international meetings.

Ponisseril Somasundaran (Columbia University)

Greener Alternatives for Personal Care and Commodity Industries: Sugar Based Surfactants, Biopolymers and Their Synergistic Effects

Abstract: Surfactants and polymers are essential components of many products in personal care and commodity industries. The reagents used in these products are largely petroleum-based and are relatively toxic. Therefore, naturally derived (e.g. microbial or plant extracts) biosurfactants and biopolymers can be used as “greener” alternatives. These include sugar-based surfactants, hybrid polymers, and nanogels. They can be designed to form nanodomains that can be tuned to detect, extract, and deliver cosmetics/fragrances/drugs/toxins upon exposure to conditions at the application site. For e.g., Novel poly(acrylic acid) nanogels prepared by polymerization of acrylic acid in presence of N, N' – methylene bisacrylamide as the crosslinker showed extraction of 80% of amitriptyline, a pain killer compared to 18% for unmodified nanogels after modification with charged and hydrophobic groups. In another case, extraction of linalyl acetate (fragrance) into the nanogels was enhanced when they were hydrophobically modified with propyl and hexyl groups; the polyacrylamide-based 1% cross-linked poly(acrylic acid) nanogels could incorporate 38% of the linalyl acetate added to the system in 4 hours. Nanogels can be prepared also from materials such as starch, which is a plant product and is safer to use. These



nanogels are environmentally attractive and are ideal systems for release of cosmetic and pharmaceutical molecules at desired rates at desired sites.

There is a gamut of naturally derived reagents which can be used with conventional reagents to achieve desired performance utilizing the synergy between them. But the criteria to define the greenness of reagents are still debated. Thus, our objective is: (1) Development of a criteria-based matrix to evaluate “greenness;” (2) Performance evaluation of naturally-derived reagents, primarily biosurfactants and biopolymers; (3) Value proposition for usage of “greener” reagents and technologies for economic sustainability. The criteria in the matrix include LCA (Life cycle analysis) of reagents, biodegradability of reagents, processes involved in the production of raw materials, economic viability, etc. Finally, from a broader perspective considering their applications, the role of biosurfactants and biopolymers, and their synergistic effects with conventional reagents in consumer industries, skin care, oil-spill cleanup, pharmaceuticals, and mineral processing will be addressed.

Speaker's Bio: Professor Somasundaran received his M.S. and Ph.D. from the University of California at Berkeley and his Bachelor of Engineering from the Indian Institute of Science. He was the first Director of the Langmuir Center for Colloids & Interfaces and Chairman of the Henry Krumb School and Chair of Dept. of Chemical Engineering, Material Science & Mineral Engineering.

He was inducted in 1985 into the National Academy of Engineering, among the highest professional distinction that can be conferred to an engineer and later to the Chinese, India, Russian National Academies and Balkan Academy of Sciences/MT. He is the recipient of the Antoine M. Gaudin Award (1982), the Robert H. Richards Award (1987), the Arthur F. Taggart Award for best paper (1987) of AIME, "Most Distinguished Achievement in Engineering" award from AINA among others. In addition, he was awarded the "Ellis Island Medal of Honor" in 1990, the AIME Mineral Industry Education Award, 2006 and in 2009, elected to American Institute of Chemical Engineers (AIChE) Fellowship. In January 2010 he was awarded the Padma Shri, one of the highest civilian awards, by the Indian government.

He is the author/editor of fifteen books and of over 600 scientific publications and patents. He is the honorary editor-in-chief of the international journal "Colloids and Surfaces" and the editor of the "Encyclopedia of Surfactant and Colloid Science." He was the Chairman of the Board of the Engineering Foundation (1993-95) and currently on the board of the new United Engineering Foundation, Society of Cosmetic Scientists committee on scientific affairs, and Tulane University CE Advisory Board (see Who's Who in America and the World). He has served in Town Planning Board and the Board of Appeals.

James A. Moore (Rensselaer Polytechnic Institute)

Dead Leaves and Lawn Clippings: Waste or Opportunity?

Abstract: In July, 1969 we began preparing monomers from cellulose. Cellulose can be hydrolysed to glucose which can be oxidized to glucaric acid. Elimination of water and cyclization yields 2,5-furan dicarboxylic acid (2,5-FDA). Polymers were prepared by the standard methods of acid-catalyzed polyesterification and interfacial polycondensation of diacid chlorides. The polymers were characterized using Infrared, and NMR Spectroscopy. Molecular weights were assessed by viscosity and gpc. We have mostly used interfacial polycondensation of the acid chlorides as a route to polyesters and polyamides. Polymers with intrinsic viscosities in the range of 0.1 – 0.7 dl/g could be prepared.



Nonactin, a macrocyclic tetraester acts by binding potassium ions and disrupting synaptic signal transmission. A casual examination of this molecule led us to try to generate a helical polymeric analog. We tested the general idea by making reduced derivatives of 2,5-FDA. We also made polymers derived from the lactone and the analogous lactam from tetrahydro-2-hydroxymethyl-5 furoic acid and they exhibit varying degrees of ion binding ability.

The major hydrolytic degradation product of cellulose is levulinic acid that can be condensed with phenol to yield a bis-phenol called diphenolic acid which can be protected as a t-butyl ester. The ester allowed us to prepare a variety of homo- and copolycarbonates in which, after selective removal of the t-butyl group, the carboxyl group can be used as a site for further modification to generate novel materials.

Speaker's Bio: Education:

B. S., Chemistry, St John's University, Brooklyn, NY, 1961

Ph. D., Chemistry, Polytechnic Institute of Brooklyn, 1967

Career Highlights:

Prof. Moore was a National Institutes of Health Postdoctoral Fellow at the University of Mainz, West Germany in 1967 and in 1968 he was a Research Associate at the University of Michigan. In 1969 he joined the faculty of the Chemistry Department of Rensselaer Polytechnic Institute where he is currently Professor of Organic and Polymer Chemistry. He is a member of the American Chemical Society and was Associate Editor of *Macromolecules* from 1998 - 2010. He served as Chair of the Polymer Division of the American Chemical society in 2007. He is the author more than 250 publications, including 6 books and 13 patents. . In 1999 he was a co-recipient of the Presidential Green Chemistry Challenge Award for his work on generating polymers from waste cellulose.

Research Areas:

Professor Moore's research interests are concentrated in the general area of synthesis and chemical modification of polymeric materials. He is also active in several specific research areas such as the synthesis of radiation sensitive and thermally stable materials for use in the development of new composites and in microelectronic processing. He has developed new approaches to the synthesis of organic polymers as on-chip dielectrics by vapor phase deposition, and has also helped to develop a novel approach to the chromatographic purification of proteins.

Posters

1. Evaluation of Rheological Properties of Hybrid Organic-Inorganic Melting Gels

Mihaela Jitianu¹, Andrei Jitianu², Lisa Klein³

2. Studies of the Degradation of Poly(L-lactide), Poly(rac-lactide), Poly(ϵ -caprolactone), and Poly(ethylene terephthalate) in Marine Waters and Sediments

Patelunas, A. J.; Willig, K. N.; Rodriguez, C. N.; Bergman, R. P.; Mollah, A. K. M.; Aubrecht, K. B.

3. Printing Ink and Coating Compositions Containing Derivatives of Starch and Modified Starch

Nicole Harris, Irena Bienkowski, Jeannette Truncellito, Richard Durand, Sun Chemical, Carlstadt, NJ

4. RAFT Polymerization Applied to Luminescent Organoboron Monomers

Fei Cheng and Frieder Jaekle

5. MONOSILANES-TRIOCTYL AMINE STABILIZED SILVER NANO PARTICLES

Bhanu P. S. Chauhan*, Ramani Thekkathu, Gururajan Padmanaban and Hardika Shukla

6. A Comparative Study of Pt-Nanoparticle Catalyzed Hydrosilylation Reactions

Bhanu P. S. Chauhan*, Ramani Thekkathu and Ankita Shah

7. pH-DEPENDENT FUSION IN PHASE-SEPARATED LIPID MEMBRANES

Manali Bhagat and Stavroula Sofou

8. Isosorbide: A Renewable Material Building Block

Xianhong Feng, Jyoti Saini, Gabrielle Busto, Anthony J. East, Willis Hammond and Michael Jaffe

9. Superior Linear Calibration Curve Over a Wide Molecular Weight Separation Range by SEC Multipore Column Technology

Caitlyn Sun

Abstracts

1. Evaluation of Rheological Properties of Hybrid Organic-Inorganic Melting Gels

Mihaela Jitianu¹, Andrei Jitianu², Lisa Klein³

¹Department of Chemistry, William Paterson University, 300 Pompton Road Wayne, New Jersey 07470 ²Department of Chemistry, Lehman College, City University of New York, Davis Hall, 250 Bedford Park Boulevard West, Bronx, New York 10468 ³Department of Materials Science and Engineering, Rutgers University 607 Taylor Road, Piscataway, New Jersey 08854

The sol-gel method is an environmentally friendly method, because sol-gel processed materials are obtained at lower temperatures than these same materials would be by classical ceramic methods. For example, hybrid organic-inorganic materials such as organic modified silica glasses are possible using the sol-gel method.

The hybrid materials called “melting gels” prepared by the sol-gel method present an unusual behavior, which makes these gels suitable for applications such as protective coatings and seals. These are nanocomposite silica-based hybrid gels that are rigid at room temperature, but soften and flow repeatedly around 110°C. Once these gels have been consolidated at around 160°C, they no longer show the ability to soften. For their preparation, combinations of mono-substituted siloxanes and di-substituted siloxanes, such as methyl triethoxysilane (MTES) and dimethyl diethoxysilane (DMDES), were used. Their thermal stability and their glass transition temperature (T_g) were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The consolidation point was initially assessed empirically. These data were confirmed by rheological measurements by monitoring the changes in the elastic modulus (G') with temperature. In addition, the viscosities of these gels were measured as a function of temperature. The rheological studies support progressive cross-linking of the siloxane polymers around the consolidation temperature.

2. Studies of the Degradation of Poly(L-lactide), Poly(rac-lactide), Poly(ε-caprolactone), and Poly(ethylene terephthalate) in Marine Waters and Sediments

Patelunas, A. J.; Willig, K. N.; Rodriguez, C. N.; Bergman, R. P.; Mollah, A. K. M.; Aubrecht, K. B.

Sustainability Studies Program and Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400

Recent discoveries of the accumulation of plastic debris in the North Pacific and North Atlantic Subtropical Gyres have demonstrated the need to study the fate of synthetic polymers in the oceans. We have undertaken a study of the (bio)degradation of poly(ε-caprolactone), poly(rac-lactide), poly(L-lactide), and poly(ethylene terephthalate) in the sediments and waters of Old Fort Pond and Shinnecock Bay, near Southampton, NY. Samples removed from the field after 3 weeks, 10 weeks, and 14 weeks were analyzed by gravimetry, SEC, and 1H NMR spectroscopy. Significant mass loss (10-98%) was observed for all polymers except poly(ethylene terephthalate). Control experiments of degradation of polymers in sterilized seawater showed little (<2%) mass loss over the same time period. Bacteria were cultured from marine sediments collected where the polymer samples were put into the field. One isolated strain was found to form clear zones on agar plates containing emulsions of PCL, PLA, or PLLA. Efforts to genetically characterize this bacterium are underway.

3. Printing Ink and Coating Compositions Containing Derivatives of Starch and Modified Starch

Nicole Harris, Irena Bienkowski, Jeannette Truncellito, Richard Durand, Sun Chemical, Carlstadt, NJ

Increasing the biobased content of ink and coating formulations used to print on compostable substrates may improve the biodegradability, disintegration, and ecotoxicity of the printed article. Various printing ink and coating compositions were developed that contain low molecular weight starches or one or more chemically modified starch derivatives, a colorant, along with other additives, resins, and diluents. These inks or coatings can be formulated with high loadings of low molecular weight starches or chemically modified starch derivatives without a large increase in viscosity. Hydrolyzed starch and starch esters prepared there from resulted in materials with a wide range of compatibility in ink and coating formulations, including water-based, solvent-based, and solventless (reactive diluent). The ink formulations exhibited good stability over time and printed with good adhesion to paper, board, and plastic film. Surprisingly, readily water soluble starches were found to produce inks with good water resistance. In addition, the printed inks exhibited improved gloss and print density relative to a similar ink that did not contain starch.

4. RAFT Polymerization Applied to Luminescent Organoboron Monomers

Fei Cheng and Frieder Jaekle

Rutgers University-Newark, Department of Chemistry, 73 Warren Street, Newark, NJ 07102
During the past decade, organoboron polymers have attracted great attention because of their potential applications as electronic device materials, chemical sensors, polymeric catalysts and biomedical materials. Various synthetic methods, including transition metal catalyzed polymerization, conventional and controlled free radical polymerization, and post-polymerization modification, have been developed to synthesize organoboron polymers. Boron-modified initiators were also employed to prep. polymers with a boron functional end-group. Organoboron block copolymers are of particular interest, due to their self-assembled nanostructures and stimuli-responsive behavior in solution. Here, we report the synthesis of luminescent organoboron block copolymers with polystyrene as the second block through sequential RAFT polymerization. GPC and SLS characterization demonstrate good control, and narrowly dispersed block copolymers were obtained. Amphiphilic organoboron block copolymer with poly(ethylene oxide) (PEO) were synthesized as well by using trithiocarbonate-modified PEO as macro chain transfer agent. The polymers were characterized by multinuclear NMR, UV-Vis and fluorescence measurements. The self-assembly of the amphiphilic block copolymers was studied. Both block copolymers formed nano-sized fluorescent micellar structures in water.

5. MONOSILANES-TRIOCTYL AMINE STABILIZED SILVER NANO PARTICLES

Bhanu P. S. Chauhan*, Ramani Thekkathu, Gururajan Padmanaban and Hardika Shukla

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Silver nanoparticles are more attractive due to their remarkable size and shape dependent optical properties, highest efficiency of plasmon excitation and their role in surface-enhanced Raman spectroscopy (SERS) studies, catalysis, electronics, photonics, optoelectronics, sensing, and pharmaceuticals. Many successful methods have been reported to synthesize silver nanoparticles with different sizes and shapes in aqueous and organic media in which the chemical reduction of silver ions in solution phase is the most widely useful method. In this context, we had successfully demonstrated that polymeric hydrosiloxanes (PMHS) can act as excellent class of nanoreactors to reduce metals such as platinum, silver to generate stable and catalytically active nanoparticles.¹⁻³

In this work, we will present the reducing capacity of hydrophobic long- chain silanes in the reduction of silver complexes to produce corresponding silver nanoparticles. These silver nanoparticles are stable in presence of trialkylamines. A comparative study of the effect of chain length of silane and amine in the stabilization of silver nano-particles will be discussed. This system provides a simple, one step room temperature access to stable nanoparticles. We will also present the kinetic studies of the reduction process.

6. Study of Pt-Nanoparticle Catalyzed Hydrosilylation Reactions

Bhanu P. S. Chauhan*, Ramani Thekkathu and Ankita Shah

Engineered Nanomaterials Laboratory, Department of Chemistry

William Paterson University, 300 Pompton Road, Wayne, NJ 07470-2103

Since the discovery of metal catalyzed hydrosilylation, industrial applications of functional silanes, polysiloxanes and silicones have provided ample fuel for the continuation of the search for more efficient hydrosilylation catalysts.

1. As a result transition metals such as Pt, Rh, Ru, Cu, Co, Pd, and Ni have been found to be effective hydrosilylation catalysts.
2. In order to generate novel catalytic systems, we have been investigating hydrosilylation reactions by using poly-methylhydrosiloxane (PMHS) stabilized Pt-nanoclusters as catalysts and achieved high yields of β -hydrosilylated products.
3. In continuation of this work we synthesized different types of Pt-nanoparticles using octadecylsilane as a reducing agent and different stabilizing agents such as n-Trioctylamine, Triphenylphosphine, and Triphenylphosphine oxide. We then tested the reactivity of these nanoparticles as catalysts in hydrosilylation of styrene with Dimethyl octadecylsilane as a silylating agent and interestingly, we observed different products by changing the stabilizing agent (Scheme 1). We are further extending the scope of this reaction by using PMHS as a silylating agent and investigating the plausible mechanism for this reaction.

7. pH-DEPENDENT FUSION IN PHASE-SEPARATED LIPID MEMBRANES

Manali Bhagat and Stavroula Sofou

Department of Chemical and Biological Engineering, Polytechnic Institute of New York University, Brooklyn, NY-11201 (email: mbhaga01@students.poly.edu)

For the cytosolic delivery of therapeutic agents, fusion between a cellular membrane and a lipid-based drug delivery vehicle may improve therapeutic efficacy. In this work, the role of pH-dependent lipid heterogeneities on the fusogenicity of membranes was evaluated on model lipid bilayers in the form of unilamellar vesicles composed of lipid pairs at a fixed equimolar ratio of phosphatidylcholine (PC) and phosphatidic acid (PA) headgroups. The pH and the hydrophobic composition (lipid acyl tails) of membranes were systematically altered, and their effect on vesicle aggregation, membrane fusogenicity, content release and content mixing was evaluated. Lowering pH increases the extent of protonated PA headgroups forming phase-separated PA-rich heterogeneities and giving rise to molecular packing defects originating at the phase boundaries. The aggregates' size increases with lowering pH, and is independent of the membrane's hydrophobic composition. Contrary to aggregation, the initial rates of lipid mixing are proportional to pH, and also depend on membrane's hydrophobic composition. The apparent lipid-mixing rate constants are greater for membranes containing lipid pairs with mismatched acyl-tail lengths, followed by pairs with matching acyl tails in the gel state, and by pairs with matching tails where one lipid is close to its transition temperature. We propose a phenomenological model where the defective phase boundaries act as „sticking points' on the vesicle exterior via which vesicles aggregate upon contact followed by defect merging via intervesicle lipid mixing/exchange. Such heterogeneous bilayers in the form of drug encapsulating liposomes may potentially improve the therapeutic efficacy by fusing with endosomal membranes, therefore, increasing drug bioavailability. The work is supported by Susan Komen for the Cure, NYSTAR, and the Coulter Foundation.

8. Isosorbide: A Renewable Material Building Block

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Isosorbide (1) is a renewable organic building block readily available from starch by way of glucose and sorbitol. Because it is a diol, it provides an ideal monomer for modifying polyesters such as PET and PLLA. The hydroxyl groups in isosorbide have different stereochemistries, exo- and endo, and different reactivities, which make efficient incorporation into PET difficult. We have created a series of AB-monomers from isosorbide and its isomer, isoidide to make copolymerization easier. These AB monomers form unique homopolymers and can be incorporated as comonomers into PET, PLLA and other polyesters.

Isosorbide can be converted to a bisepoxide and crosslinked with standard curing agents to make a thermoset with properties similar to thermosets derived from bisphenol A (BPA). However,

the resulting thermoset is hygroscopic and loses its mechanical properties on exposure to moisture. We are investigating a number of approaches to reduce the hydrophilicity in order to develop a BPA epoxide replacement. If the isosorbide epoxide is converted to a polyol, it shows strong humectant properties with potential application in cosmetics and health care products.

Taking advantage of the different reactivities of the two hydroxyl groups in isosorbide, we have synthesized a series of asymmetric derivatives including plasticizer/stabilizers and sunscreens that cover the UVB and UVA regions of the solar spectrum.

Our efforts have demonstrated the versatility of isosorbide as a renewable Green Material.

Commercial Poster/Exhibit

9. Superior Linear Calibration Curve Over a Wide Molecular Weight Separation Range by SEC Multipore Column Technology

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Size exclusion chromatography (SEC) column technology is vital to the advancement of the chemical/biological industries. Multipore column technology is an advanced column technology, featuring monodisperse packing particles with a wide pore size distribution within each particle. It extends the molecular weight separation range and gives superior calibration curve linearity for reproducible molecular weight determination. This technology shows advantages over traditional coupling of columns or so-called mixed-bed columns, since it shows no inflection points in calibration curve and no corresponding distortion in the chromatogram. In this study, we complete an investigation on two commercially available multipore columns; one is a Tosoh TSKgel[®] SuperMultiporeHZ-M column and the other is Polymer Laboratories PolyPore column. The column characteristics including calibration curve linearity, slope, column efficiency and resolution were tested and compared.