

“Green Polymers: Materials, Processes and Products”

November 8, 2007
1:00 pm to 6:30 pm

Fiber Optics Materials Research Auditorium Rutgers
University
Busch Campus
Piscataway, NJ

Organized by NJACS Polymer Topical Group

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**Fiber Optics Materials Research Auditorium at Rutgers University,
Busch Campus, Piscataway, NJ**

Organized by NJACS Polymer Topical Group

- 1:00 PM Registration and poster setup
- 1:30 PM Welcome and opening remarks, Thomas J. Pacansky, Organizer and PTG Chair
- 1:35 PM Session I: Green Polymers: Materials and Processes, Ronald DeMartino, PTG Secretary and presiding
- 1:40 PM Green Chemistry and Entropic Control in Material Design, John C. Warner (Warner Babcock Institute for Green Chemistry)
- 2:10 PM Synthetic Absorbable Polymers - Molecular and Design Considerations for Implantable Medical Devices, Dennis Jamiolkowski (Ethicon, Inc. a Johnson & Johnson Co.)
- 2:40 PM The Preparation and Application of Highly Modified Starches, John S. Thomaides (ICI), L. Cimecioglu (ICI), K. Rodrigues (Alco), and M. Crossman (Alco)
- 3:10 PM Polyolefins – Their Role in Sustainable Development, D. N.Schulz , M. Arvedson, P. Bryant, M. Wu, D. J. Lohse, ExxonMobil Research and Engineering Co.
- 3:40 PM Break
- 3:55 PM Session II: Green Polymers: Product Application Approaches; Willis Hammond. PTG Treasurer and presiding
- 4:00 PM Polymers in High Performance Construction Materials, Charlene Wall (BASF)
- 4:30 PM Polymers for Printing Inks; A Green History, Richard Durand (Sun Chemical Co)
- 5:00 PM Green Polymers in Cosmetics, H. Karl Krummel (L'Oreal)
- 5:30 PM Concluding remarks, Thomas J. Pacansky
- 5:35 PM Poster session and mixer. Posters organized by Jin Zhang and Jingiang Li
- 6:30 PM Drawing for door prizes

Corporate Sponsors: ExxonMobil, Apollo Ventures

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Green Chemistry and Entropic Control in Materials Design

John C. Warner

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Abstract: The traditional construction of materials is usually driven by classical synthetic transformations involving the making and breaking of covalent bonds. These processes often require high energy input and highly reactive and hazardous materials. In natural systems, one typically encounters synthetic control schemes that are based on entropic forces rather than these human-designed enthalpic manipulations. In natural processes, phase changes and triggered mixing are often employed to direct systems towards or away from equilibrium conditions. The recognition of these "natural tendencies" allows one to design processes that have reduced toxicological and environmental impact. This presentation will describe results in non-covalent derivatization and bioinspired photopolymers that illustrate this shift towards entropic control.

John Warner received his BS in Chemistry from UMASS Boston, his MS and PhD from Princeton in Organic Chemistry. He worked at the Polaroid Corporation for nine years, and then went to UMASS Boston, where he has started the world's first Green Chemistry PhD program. He then moved to the University of Massachusetts Lowell where he directed a large research group working on a diverse set of projects involving green chemistry using principles of crystal engineering, molecular recognition and self assembly. His work combines aspects of community outreach, government policy and industrial collaboration. He has recently become President and Chief Technology Officer for The Warner-Babcock Institute for Green Chemistry. He is editor of *Green Chemistry Letters and Reviews*. He is associate editor of the journal *Organic Preparations and Procedures International* and on the editorial board of *Crystal Engineering* and *Crystal Growth and Design*. He recently received *The 2004 Presidential Award for Excellence in Science Mentoring* from President Bush, the *Outstanding Service to Nursing Award* from Sigma Theta Tau International Honor Society of Nursing and was *The 2006 Honorary Inductee into Alpha Lambda Delta the National Freshman Honor Society*. He was awarded the American Institute of Chemistry's Northeast Division's *Distinguished Chemist of the Year* for 2002. His recent patents in the fields of semiconductor design, biodegradable plastics, personal care products and polymeric photoresists are examples of how green chemistry principles can be immediately incorporated into commercially relevant applications. Warner is co-author of the book *Green Chemistry: Theory and Practice* and serves on the Board of Directors of the Green Chemistry Institute in Washington DC.

Synthetic Absorbable Polymers

Molecular and Design Considerations for Implantable Medical Devices

Dennis Jamiolkowski

Distinguished Research Fellow,
Ethicon, Inc., a Johnson & Johnson Company
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Abstract: Medical devices fabricated from synthetic absorbable polymers have enjoyed commercial success, are expected to provide an expanded role in implantable medical devices and controlled drug delivery, and will serve as a cornerstone technology for providing solutions for vital new areas of research such as tissue engineering. As such, they are of interest both for scientific, as well as commercial reasons.

From a medical device perspective, the materials to be discussed have been used to make a variety of commercially successful products. These include implantable surgical devices for wound closure applications such as sutures, and devices for orthopedic applications such as screws and plates. They have also been utilized for controlled drug delivery applications, especially in the form of microspheres. At present, the global market for medical devices based upon absorbable polyesters exceeds one billion dollars. Exciting new applications, including their use as scaffolds for tissue engineering, will further increase the commercial importance of these materials.

To understand how these materials achieve such widespread use across an array of disparate applications with varying constraints, an understanding of their structure-property performance profile is required. In turn, this understanding requires a discussion of not only the chemistry aspects of the systems, but their molecular morphology as well. Finally, mechanical design has been often used to circumvent physical property deficiencies. Toward this, some innovative design solutions will be presented.

Dennis D. Jamiolkowski: Shortly after receiving a B.S. in Honors Chemistry at Seton Hall University in 1974, Mr. Jamiolkowski joined the Exploratory Polymer Section of the Research Division of Ethicon, Inc., a Johnson & Johnson Company. Concurrently, he studied polymer chemistry at what is now known as Polytechnic University. The recipient of a Bell Laboratory Research Fellowship in 1973, he received J&J's Philip B. Hofmann Research Scientist Award for work conducted in the area of radiation-sterilizable absorbable polymers in 1983. He has been issued 81 U.S. patents and numerous foreign patents for his work. He has contributed over 40 articles, including chapters in seven books, to the open technical literature. Dennis has made eleven presentations at international and national technical meetings. He has been an invited speaker at a number of academic institutions including Cornell University, Rutgers University, Seton Hall University, University of Delaware, Georgian Court College, the State University of New York and Carnegie-Mellon University; he was an invited speaker at the 7th World Biomaterials Congress.

Dennis is a member of the Society for Biomaterials and is a former Chair of Johnson & Johnson's Council of Research Directors Polymer and Biomaterials Subcommittee. He is a Corporate Office of Science and Technology (COSAT) "Excellence in Science" Grant winner. In 2001 he received Johnson and Johnson's highest honor for research and development, the prestigious Johnson Medal. In 2003, he again received J&J's Philip B. Hofmann Research Scientist Award, this time for significant contributions in the area of new product/process development. As a member of R&D, Dennis has worked on a number of New Business Development initiatives approaching half a billion dollars in value. He is currently a Distinguished Research Fellow.

The Preparation and Application of Highly Modified Starches

John S. Thomaides¹, Levent Cimecioglu¹, Klin Rodrigues², and Martin Crossman²,¹ICI, Bridgewater Applied Research Group, 10 FINDERNE AVENUE, BRIDGEWATER, NEW JERSEY 08807 ²Alco Chemical, 909 Mueller Drive, Chattanooga, Tennessee 37406

Abstract: The preparation of modified polysaccharides with carboxylate and aldehyde functionality will be described. Such materials are useful in a variety of applications such as anti-scalants, dispersants, detergents, and fiberglass binders. They may also be used in oilfield applications.

John S. Thomaides is a Principal Business Scientist in the ICI Bridgewater Applied Research Group of ICI. During his nearly twenty years in industry, he has tackled many different technical assignments. His areas of expertise include organic and polymer synthesis, polysaccharide chemistry, and polymers for personal care. Currently, he is working on the modification of natural and synthetic polymers.

John did his undergraduate studies at Yale University where he received a B.S. in Chemistry. He continued his education at Columbia University where he received a Ph.D. in Organic Chemistry working with Professor Ronald Breslow. Following his stay at Columbia, he did post-doctoral research in Organometallic Chemistry at Princeton University with Professor Jeffrey Schwartz. John lives in central New Jersey with his wife and two daughters. His hobbies and interests outside of work include tennis, running, history, and trees. He also has a growing collection of exotic aquarium fish.

Polyolefins – Their Role in Sustainable Development

D. N. Schulz¹, M. Arvedson², P. Brant², D. Lohse¹, M. Wu¹
ExxonMobil Research and Engineering Co.¹
ExxonMobil Chemical Co.²

Abstract: Polyolefins (POs) are the most pervasive of all the thermoplastics. They are chemically inert, recyclable, energy recoverable and have a very wide range of applications. Although these materials are commodities, they continue to attract substantial research attention from both industry and academia. Polyolefins keep getting better because of advances in catalyst, process, products and applications. In particular metallocene and late transition metal catalysts have greatly enhanced the performance envelope of polyolefins. Polyolefins also have an important role in sustainability. This talk will examine various aspects of the life cycle of various polyolefins. For example, the environmental footprint of polyolefin manufacture will be compared with other common thermoplastics. We will also compare the life cycle of polyolefins in packaging vs. alternatives (e. g. paper, biodegradables). Polyolefins contributions to enhanced fuel economy and waste reduction in the automotive sector will be presented. Finally, the critical role of POs as enablers to energy production and conservation will be discussed.

Donald N. Schulz is currently Sr. Scientific Advisor at the Corporate Strategic Research Laboratories of ExxonMobil Research and Engineering Co. in Clinton, NJ. At Exxon he has held a variety of research and research management positions. He was the Section Head or Program Leader over 4 commercializations. Prior to joining Exxon, Don was a Group Leader at the Central Research Laboratories of the Firestone Tire and Rubber Co.

He received his Ph.D. from the University of Massachusetts in Amherst, Massachusetts in 1971 and was the CUMIRP Lecturer there in 1991. His research interests include polymer synthesis / modification, catalysis, functional polymers, and structure-property relationships. He is the coeditor of 5 books, author / coauthor of over 90 publications, inventor / coinventor of over 55 issued U. S. Patents. He has served on the Editorial Boards of *Rubber Reviews* (Chairman), *Rubber Chemistry and Technology*, *PMSE Preprints* (Editor), *Heteroatom Chemistry*, and *Isotopics* (Editor). In addition he has chaired two Gordon Research Conferences ("Ion-Containing Polymers" and "Elastomers, Networks and Gels"), as well as a number of symposia at ACS National meetings. Don is also a Past Chair, Vice Chair, Treasurer, and Program Chair of the PMSE Division of the ACS and Past Secretary General of ACS Macromolecular Secretariat.

Polymers in High Performance Construction Materials

Charlene Wall

Manager, Corporate Business Development, BASF Corporation

Abstract: BASF is committed to providing the best products, many of which are used in almost every component of a building. As a part of this strategy, BASF has developed and applied quantitative measurement tools to address the economic and environmental aspects of building sustainability, such as our eco-efficiency analysis.

BASF's eco-efficiency methodology was developed in 1996 and to date over 240 analyses have been completed. It evaluates the environmental and economic impacts of products and processes. Based upon the principles of ISO 14040, it contains additional enhancements that allow the results to be used as a concise decision-making tool.

Six environmental categories are evaluated:

- Raw materials consumption
- Energy consumption
- Land use
- Air, water and solid waste emissions
- Toxic potential of the substances employed and released
- Potential for misuse and risk potential.

Life-cycle data are compiled for each of these categories, a weighting scheme is used to aggregate the results, and they are normalized in order to generate the ecological fingerprint. The fingerprint depicts the relative impacts of the alternatives in each of the environmental categories.

Charlene Wall manages strategic business initiatives for BASF in North America, in markets including packaging and construction. She leads multi-functional teams to explore and foster business opportunities for sustainable and innovative technologies. She previously managed the North American Eco-efficiency Analysis program for the BASF Group, furthering BASF's position as a global leader by facilitating the integration of sustainable development into the North American businesses. In 2004, she played a key role in the launch of the American Institute of Chemical Engineer's Center for Sustainable Technology Practices, an industry consortium currently nearing the launch of a Sustainable Development Roadmap for technology development. Her 15 years of experience with BASF include roles in Product Development, Process Engineering, and Safety and Ecology.

Polymers for Printing Inks: A Green History

Richard Durand

Sun Chemical Corporation, Carlstadt, New Jersey

Abstract: Renewable resources as either directly used resinous materials for ink formulation or as building blocks for synthetic polymers have a long history in the ink industry. A survey of resins and polymers used in ink products will be presented. The driving forces between past and future usage of bio-based materials will be examined in relationship to the requirements of printing processes using the inks made from these materials and the final performance targets related to the end use of the printed products.

Rich Durand is currently Director /Analytical and Characterization Science (ACS) for Sun Chemical Corporation at their R&D Laboratory in Carlstadt, New Jersey. The ACS team provides various analytical support functions to the ink business units as well as polymer/material characterization and structure/property studies for new product development. During his tenure at Sun Chemical, he has held a variety of positions including Senior Scientist, Director/Newspaper R&D, Director/Knowledge Management. He has worked extensively in developing new products for a variety of applications as well as new characterization tools for the study of printing processes and inks. Prior to joining Sun Chemical Corporation, Rich was Assistant Professor of Chemistry at the University of Rhode Island where his research focus included electrocatalytic reduction of carbon dioxide and polyaniline conducting polymers.

He received a B.S. in Chemistry from Worcester Polytechnic Institute in 1979, and a Ph.D. in Chemistry from California Institute of Technology in 1983.

Green Polymers in Cosmetics.

Karl Krummel

L'Oreal

The talk will address the definition of Green Polymers, why Green Polymers are of interest to the cosmetic industry, and why they are of interest to L'Oreal in particular. It will further address the use of renewable raw materials from plants, the development of environmentally friendly processes and the manufacture of low eco-toxicity ingredients. Sustainable development is critical to all of our futures and is a challenge we all must face. We at L'Oreal are taking it a step further and are simultaneously addressing the impact of our activities on our common heritage by taking into account the protection of the health of present and future generations, the protection of the environment and biodiversity, and the concern for fair and responsible trade (i.e., avoiding "Bio-Piracy").

Karl, who is in charge of the Innovative Raw Materials Dept for L'OREAL R&D USA, will present L'OREAL vision and needs in this area.

Mr. Krummel received his BS in Chemical Engineering from Carnegie-Mellon University, Pittsburgh, Pennsylvania and his MBA from Xavier University, Cincinnati, Ohio.

He began his career with The Procter & Gamble Company developing household and personal care products. Over his 15 years with P&G, he worked on laundry detergents, bar soaps, shampoos, hair conditioners, permanent waves, and antiperspirants.

In 1992, Mr. Krummel joined ISP. He served as Senior Director, Hair Care Applications and Technical Services. In 1998, he moved to Guildford, Surrey County, UK to manage the 7 global labs of ISP as well as to head the hair care R&D effort.

In 2001, Mr. Krummel joined L'Oreal USA as Assistant Vice President, Corporate Research / Innovative Raw Materials. In this role, he and his department seek out new raw materials capable of delivering next generation product performance for introduction to the L'Oreal laboratories worldwide.

Mr. Krummel holds numerous patents, has served the **Society of Cosmetic Chemists** as Connecticut Chapter Chairman and as a member of the Committee of Scientific Affairs. Additionally, he received the designation of "New Product Development Professional" conferred by the **Product Development and Management Association**. He has served the **Cosmetics, Toiletries, and Fragrances Association** on the Scientific Advisory Council, the Nomenclature (INCI) Committee, and the Color Additive Committee, and was a speaker at the CTFA Annual Scientific Conference. He served as the first President of the **Association of Formulation Chemists** and is on the Advisory Board of **Cosmetics and Toiletries Magazine**. Karl is a member of the Board of Directors of **TRI Princeton**.

Mr. Krummel co-authored the chapter titled "Hair Conditioners" in The Chemistry and Manufacture of Cosmetics, Vol.II.

Karl and his wife, Beth, reside in Andover Township, New Jersey where she manages their Bed & Breakfast - **The Wooden Duck Inn**. Their three children are grown and are now living in Research Triangle, NC; Luanda, Angola; and Moscow, Russia.

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1. Electrospun Polyamide Nanofibers and Thin Films

Kris Behler, Mickael Havel, G. Korneva and Yury Gogotsi
Drexel University, A.J. Drexel Nanotechnology Institute
Department of Materials Science, 3141 Chestnut Street, Philadelphia, PA 19104

Polyamide-11 (PA-11) and polyamide-12 (PA-12) are high-performance polymers. PA-11 is produced from a green raw material: castor beans, making it very interesting with the rising cost of oil and other sources of polymers. They show remarkable stability in high temperature, high pressure environments and outstanding chemical resistance (e.g. strong acids, bases and most organic solvents). Thus, they are used as gas and petroleum pipelines and can be exposed to salt water.

While some polyamides have been successfully electrospun into fibers, PA-11 and PA-12 have remained a challenge. Using a mixture of formic acid and dichloromethane, PA-11 and PA-12 could be dissolved and subsequently electrospun into nanofibers of 100 nm and greater in diameter. Depending on the polymer concentration, ribbons and other structures were obtained in addition to the regular cylindrical fibers. The use of this new inexpensive solvent combination allows large volume manufacturing of polyamide nanofibers.

Electrospinning is a method of quick deposition of nanometer sized fibers that can be nonwoven or aligned fibers that can be upscaled to industrial quantities. The electrospinning process allows for thin films of fibers to be deposited. By control the deposition time and the polymer concentration the film thickness can be tailored and different electrical conductivities can be achieved. By using thermal means, the transparency of these films can be increased to >95% while still maintaining a conductive nature. Thin films (100nm to 1 μ m) can be used as a replacement for indium-tin-oxide (ITO) in such applications as solar cells and liquid crystal displays.

Multiwalled Carbon Nanotubes (MWCNTs), which possess high electrical conductivity, were self-assembled onto the PA-11 electrospun mats. The resulting composite showed a dense MWCNTs coverage even at low weight percents, yielding high electrical conductivity, up to 100 S/cm. MWCNT have been deposited on PA-11 and Polyacrylonitrile (PAN).

References:

Behler, K.; Havel, M.; Gogotsi, Y. *Polymer* **2007**, 48, 6617-6621
Nanotubes and Nanofibers. Ed. Y. Gogotsi; CRC: 2006

2. Adsorption of Various Carbonyl-Containing Polymers onto Silica

Mark E. Benn, Department of Chemistry and Geology, Fairleigh Dickinson University, Madison NJ;
Courtney Cunningham and Anita J. Brandolini, School of Theoretical and Applied Science, Ramapo College of New Jersey, Mahwah NJ

The effectiveness of paints and adhesives depends on the interaction between the polymer binder and the surface being coated. When polymers adsorb onto a substrate, some segments become bound to the surface, while other segments extend above it. We have been investigating the adsorption of various carbonyl-containing polymers onto silica (SiO₂). The primary focus has been on the polymethacrylates, but we have recently begun studying other polymers, such as aliphatic polyesters, cellulose esters, and poly(vinyl ketones). In the infrared (IR) spectra of these systems, the carbonyl absorbance is composed of two overlapping peaks, arising from the bound and unbound segments. Parameters extracted from analysis of these lineshapes can be interpreted in terms of the relative amounts of bound and unbound segments and the strength of the interaction between polymer and surface.

3. Naturally Derived Polymers for Conditioning Benefits in Hair and Skin Care

Andrew Douglass and Kraig Luczak

Rhodia, Inc. 8 Cedarbrook Drive, Cranbury, NJ 08512.
Rhodia, Inc. 350 George Patterson Blvd, PA 19007

Abstract: Guar gum is a natural, renewable polysaccharide extracted from guar beans. The polysaccharide polymer consists of galactose and mannose units and has a molecular weight in excess of 2 million Daltons. The natural polymer acts as a thickening agent and foam stabilizer and can be further functionalized via cationisation to provide multiple benefits. In a shampoo or body wash formulation the polymer is able to flocculate upon dilution delivering actives to the hair and skin as well as imparting a unique combination of sensorial and skin conditioning and protection benefits.

4. What Are the Sizes of Monomer Droplets in Miniemulsions?

Megan B. Casey, E. David Sudol, and M. S. El-Aasser

Emulsion Polymers Institute, Lehigh University, 111 Research Drive, Bethlehem, PA, USA

Miniemulsion technology offers the ability to produce latexes that cannot be prepared via conventional methods, such as those using highly water-insoluble monomers, or encapsulates of pigments, oils, and polymers. Fundamental understanding of miniemulsions has been hindered by the inability to measure and monitor their droplet size distribution (DSD), which is thought to lie in the range of 50 to 500 nm. The goals of this work are to characterize the DSD of miniemulsions, understand the mechanisms that determine it, and seek methods to control it.

Acoustic attenuation spectroscopy (AAS) was investigated to determine its feasibility for miniemulsion DSD characterization. Testing has shown promise, but dilution level, broadness of droplet size distribution, and surfactant concentration affect the results. In order to compare AAS with other sizing techniques, the DSD of a hexadecane miniemulsion was characterized by AAS as well as dynamic light scattering (DLS), capillary hydrodynamic fractionation (CHDF), and surfactant titration. There was fairly good agreement between these very different methods.

An indirect method of observing droplet size was explored. Styrene miniemulsions with various amounts of dissolved polystyrene were prepared and their DSDs characterized. After evaporation of the styrene, the DSD was then reanalyzed. Assuming that the composition of each droplet was initially the same, and that evaporation removed only styrene and left the polymer originally present in the droplet intact, the initial DSD could be inferred. However, the droplet size changed with the amount of dissolved polymer, indicating Ostwald ripening altered the initial composition of the droplets significantly.

In order to prevent droplets from degrading during analysis via conventional CHDF, the eluent must be saturated with monomer. A CHDF instrument was modified for use with styrene-saturated eluent to analyze styrene miniemulsions. The average droplet size was found to increase with time, but more slowly with higher costabilizer content, as expected. Similar results were obtained by AAS and surfactant titration.

The extent of Ostwald ripening in styrene miniemulsions was observed by centrifugation, imaging of the layers via optical microscopy, and determination of the droplet composition in each layer via GC. It was found that the costabilizer, hexadecane, becomes concentrated in the small droplets while it is diluted in large droplets, as expected, but to a surprisingly high extent. No monomer separation occurred after centrifugation of an octadecyl methacrylate miniemulsion, indicating little or no Ostwald ripening as expected due to the extremely low water solubility of this monomer.

5. Nanoscale Morphology of Well-Defined, Linear Poly(Ethylene-Acrylic Acid)

Ionomers: Effect of Neutralization

Christopher D. Chan¹, Travis W. Baughman², Kenneth B. Wagener³, Karen I. Winey⁴

¹Department of Chemical and Biomolecular Engineering, University of Pennsylvania, ²Macromolecular and Organic Chemistry, Technical University of Eindhoven, ³Department of Chemistry, University of Florida, ⁴Department of Material Science and Engineering, University of Pennsylvania

Commercial poly(ethylene-*co*-methacrylic acid) and its ionomers have been studied as branched, random copolymers that result from the free radical polymerization. We have synthesized and studied the nanoscale morphology of various linear poly(ethylene-*co*-acrylic acid) copolymers with precisely-distributed acid groups in an effort to explore the effect of chain architecture. The evenly-placed acid groups in linear P(E-AA) produced a unique peak in the X-ray data corresponding to a lamella structure with a spacing of 2.53nm. An all *trans*- conformation of 21 carbons in a linear polyethylene crystal is calculated to be 2.66nm. Here we study the effect of neutralizing the acid groups to different levels (25%, 50%, 75% and 100%) in linear P(E-AA) of 9.5%, acrylic acid with zinc acetate in solution. The zinc ion neutralizes the carboxylic acid groups as expected, however what is unexpected is that the ions also neutralize the acid groups within the crystal and thus enhance the acid-acid peak in the x-ray scattering. Aligning the polyethylene chains via drawing causes the acid-acid peak in both the unneutralized and the neutralized samples to orient perpendicular to the polyethylene backbone. The ionomer peak is unaffected by the drawing and we conclude that drawing the samples produces no effect on the ionic aggregates. Using scanning transmission electron microscopy (STEM), we observe the ionic aggregates decrease in diameter with increasing neutralization.

6. The Synthesis and Characterization of Elastin Based: Biodegradable Block Co-Polymers

Jennifer S. Haghpanah¹, Peter James Baker¹, Susheel K. Gunasekar¹,
Hanna Barra¹, Wendy Hom¹, Natalya Voloshchuk¹, Jin K. Montclare^{1,2},
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11203*¹²

Genetically engineered protein based polymers with controlled structures hold tremendous promise for the synthesis of novel biomaterials and drug delivery vehicles. By combining cartilage oligomeric matrix protein (COMP) and elastin (ELF) sequences, we generate di-block and tri-block co-polymers. It is of interest to characterize COMP and ELF individually, and as block polymers via biophysical methods to determine secondary structures and global macromolecular features. Microcalorimetry experiments indicate a high thermal stability of COMP. Binding studies with all-*trans* retinol suggest high binding affinity of COMP for this small molecule.

7. Polymer Single Crystal Mediated Gold Nanoparticle Assembly

Bing Li and Christopher Li*

A. J. Drexel Nanotechnology Institute and Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania 19104

2-Dimensional nanoparticle (NP) array has been extensively investigated and a number of techniques are available for fabricating this unique structure. One remaining technical challenge is controlling the inter-particle spacing, which could directly leads to numerous applications. We herein report a novel means to achieve tunable NP arrays by immobilizing AuNPs on polymer single crystal surface. The single crystals of thiol-terminated polyethylene oxide (PEO) were incubated in a monodisperse gold sol.

Strong Au-S chemical bonds were formed between the AuNPs and the PEO single crystal surfaces. The inter-particle spacing was controlled by the crystallization temperatures, thus the thickness of the PEO single crystals, the incubation time, and the annealing temperatures after incubation. Asymmetric binary AuNP complexes were fabricated by multiple depositions of AuNPs on the PEO single crystals. This research might lead to a novel method to fabricate NP arrays with controlled inter-particle distance from a few nanometers to ~100 nm distances.

8. “Sweet Polyesters”: Lipase-catalyzed synthesis of reduced sugars-based oligomers: exploring the reactivity of various reduced sugars

Jun Hu, Wei Gao, Ankur Kulshrestha and Richard A. Gross *

A series of 4-, 5- and 6-carbon reduced sugars were studied as monomers for immobilized *Candida antarctica* Lipase B (CALB) catalyzed polymerizations. Reactions were performed with a molar ratio of adipic acid to 1,8-octanediol to reduced sugars of 1.0:0.8:0.2. Molecular weight increase as a function of reaction time was measured. The following is the relative order of M_w as a function of polyol structure for 46 h polymerizations: D-mannitol (73.0 ± 0.4 K) > erythritol (38.1 ± 4.4 K), xylitol (42.3 ± 2.2 K), ribitol (38.4 ± 2.9 K) > D-glucitol (27.7 ± 2.0 K) > galactitol (11.0 ± 0.9 K).

Replicate experiments using a needle valve and a digital vacuum regulator showed that, reproducible results were obtained only with the digital vacuum regulator that more accurately controlled the reduced pressure in reaction vessels. From this limited set of polyols, no apparent correlation was found between polyol chain length and its polymerization by CALB catalysis. Plots of $\log[\eta]$ vs. $\log M_w$ were prepared from SEC-MALS-Viscosity analyses of poly(octamethylene adipate) and corresponding terpolymers with galactitol, D-glucitol and D-mannitol. Comparison of exponent a values from slopes of these plots showed copolymers from D-mannitol had the largest degree of branching and, therefore, greatest propensity for combined reactivity at both primary and secondary hydroxyl groups. Differences in alditol reactivity were analyzed with respect to their stereochemical configurations at polyol β -carbons, closest to terminal primary hydroxyl groups, and secondary hydroxyl groups, that upon reaction lead to branching.

9. Enzymatic Routes to Polycarbonates

Chen Liu, Zhaozhong Jiang, Wenchun Xie and Richard A. Gross*

NSF I/UCRC for Biocatalysis and Bioprocessing of Macromolecules, Polytechnic University, Six Metrotech Center, Brooklyn, NY 11201

High molecular weight ($M_w > 25\ 000$) poly(hexamethylene carbonate) (PHC) with polydispersity ($M_w/M_n \leq 2.2$) was successfully synthesized via copolymerization of diethyl carbonate with 1,6-hexanediol catalyzed by immobilized *Candida antarctica* Lipase B (CALB). Because diethyl carbonate is highly volatile, polymerizations were performed by a 1st stage oligomerization at low vacuum (600 mmHg pressure) followed by a 2nd stage polymerization under high vacuum (1-5 mmHg pressure). Enzymatic polycarbonate synthesis is preferably performed in solution (e.g. in diphenyl ether), although it also proceeds in solventless reactions albeit at reduced rates. Synthesized PHC contains hydroxyl and ethyl carbonate terminal groups. Influence of regulating the ratio of diethyl carbonate to 1,6-hexanediol in the monomer feed on polymer end-group structure was determined. Reaction conditions and monomer feed ratios resulting in PHC with exclusively hydroxyl or ethyl carbonate termini were established. The ability to synthesize PHC products with desired end-group structure is critical to their potential use as macromers in, for example, polyurethane synthesis. Mechanistic features of enzymatic polycarbonate synthesis were elucidated, which explain why high molecular weight PHC can be prepared at high (e.g. 4:1) diethyl carbonate to diol monomer feed ratios whereas conventional chemically-catalyzed step-polycondensation reactions of AA-BB type monomers require a 1:1 monomer feed ratio. That is, enzyme-catalyzed polycondensations between dialkyl carbonate and diol proceed via two pathways: (i) reaction between hydroxyl and carbonate end groups with elimination of alcohol, and (ii) transesterification between two carbonate end groups with elimination of dialkyl carbonate.

KEY WORDS: CALB, polycarbonates, condensation, end-group, mechanism.

10. Biosynthetic routes to omega-oxidized fatty acids and their conversion to polymers via lipase-catalyzed polymerizations

Wenhua Lu, Yixin Yang, Jiali Cai, Wenchun Xie, Minmin Cai and Richard A. Gross

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Abstract: Long-chain unsaturated α,ω -dicarboxylic acids are useful materials for macromer and polymer synthesis. However, they are currently unavailable by chemical synthesis since chemical oxidation cleaves double bonds resulting in by-products and *cis-trans* isomerization. In this work, biotransformations catalyzed by *Candida tropicalis* ATCC20962 were studied to prepare long-chain unsaturated diacids. For example, 1,18-*cis*-octadecenedioic and 1,22-*cis*-9-docosenedioic acids were successfully prepared from oleic and erucic acids, respectively. The concentration of 1, 18-*cis*-octadecenedioic acid and 1,22-*cis*-9-docosenedioic acid reached to 18 g/L and 14.2 g/L after 48 h and 72 h, respectively, in shaker-flask experiments. Higher productivity for 1, 18-*cis*-octadecenedioic acid was obtained by performing fed-batch cultures in a fermentor. After 60 h, 30 g/L of diacid was obtained with 0.5 g/h/L productivity. Structures of diacids were confirmed by GC-MS, IR and ¹H-NMR where it was shown that double bonds and substrate chain length remained intact during bioconversions to diacids. Using the purified unsaturated diacids as monomers, the direct lipase-catalyzed polycondensation of unactivated long-chain α, ω -dicarboxylic acid with 1,8-octanediol was studied in bulk as well as in diphenyl ether. Polyesters with high molecular weight (M_w 29,000-57,000) and low M_w/M_n (about 2.0) were obtained while the double bonds remained intact during polymerizations. The resulting unsaturated polyesters showed good thermal stability at high temperatures (by thermal gravimetric analysis) and low melting points ($T_m = 23\sim 40$ °C). The biotransformation of other fatty acids with different functional groups to omega-oxidized fatty acids and their corresponding polymerization to fatty-acid derived polymers are currently under study.

11. Rilsan® Polyamide 11: Powerful By Nature. Expanding BioPlastics into High Performance Applications

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Abstract: Polyamide-11 (PA11) is a high performance, lightweight bioplastic (plastic produced with 100% of the carbons coming from plant based renewable resources) with a unique combination of high performance properties. Compared to other high performance and engineering plastics, PA11 delivers an outstanding level of chemical, thermal and impact resistance over a wide range of flexibility. PA11 is widely used in applications where safety, durability and versatility are critical. Polyamide 11 is therefore frequently used as a cost effective replacement for metal or rubber in highly technical applications. PA11 is produced from renewable castor seeds and is commercialized by ARKEMA under the Rilsan® brand. The purpose of this poster is to present new data regarding the environmental benefits of PA11 as compared to other high performance polymers.

12. Photophysical characteristics and anion binding studies of triarylborane functionalized polystyrene.

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Abstract: The synthesis of luminescent organoborane functionalized polystyrene has been realized via facile tin-boron and copper-boron exchange reactions. The polymers are highly emissive both in solution and the solid state. The Lewis acidity and photophysical properties can be fine-tuned by attachment of different aryl groups to the boron centers. Distinct changes in the absorption and emission spectra are observed upon complexation, when cyanide and fluoride are added. Moreover the polymers show signal amplification indicating that polyolefins may be an interesting alternative to conjugated polymers for use as nucleophile sensors.

13. Modification of Polylactic Acid with Ionic Liquids

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In attempts to modify the degradation characteristics of polylactic acid (PLA) the addition of selected low MW ionic liquids, at concentration up to 5 wt%, was shown to result in enhanced degradation rates accompanied by plasticization and lubrication. Hydrolytic and thermal degradation were studied via mass changes, gel-permeation chromatography, SEM, pH changes and visual observations. Lubrication and plasticization were tested by measuring melt viscosity, friction coefficient, Tg and contact angle. The effects of the two different ionic liquids on properties and processability are explained in terms of their different chemical structures and interactions with the polymer.

14. BLOCK-ACRYLIC HOT MELT PRESSURE SENSITIVE ADHESIVES FOR GREEN MANUFACTURING OF MEDICAL TAPES

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Abstract: Styrenic block copolymers (SBCs) are the base polymers for the vast majority of hot melt pressure sensitive adhesives (PSAs). The phase separation of the high Tg styrene blocks upon cooling allows these materials to exhibit low melt viscosity yet high adhesive shear strength. Recently, new polymerization technologies have been developed to provide acrylics with the same type of blocky structure. The hard phase is ordinarily methyl methacrylate and the soft phase is composed of low Tg monomers with lower polarity, such as butyl acrylate. These new polymers combine the traditional property advantages of acrylics (such as UV and thermo-oxidative resistance, and high moisture vapor transmission rate (MVTR)) with the processing advantages of hot melts (low capital and energy costs, fast line speeds, and zero emissions). Utilizing this new block acrylic technology, adhesives have been developed for medical and industrial tapes. For medical tapes, formulas with exceptional softness and fast wet-out have been obtained, which provide excellent skin grab and long term wear with painless removal. For industrial tapes, block acrylic formulas exhibit improved heat resistance and thermo-oxidative stability vs. those based on SBCs.

15. Temperature experiments for improving accuracy in the calculation of the degree of crystallinity of polyamide-11

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The calculation of the degree of crystallinity of polymeric materials may be rendered difficult by the number of overlapping crystalline phases, amorphous halos, and smectic phases that contribute to the diffraction pattern. Rilsan® Polyamide-11, or polyundecanamide, produced by Arkema Inc., is a semi-crystalline eleven-carbon molecule belonging to the same family as Nylon® 6 or Nylon® 6,6. Rilsan®

PA-11 is a green polymer that presents the particularity of having a smectic phase along with four crystalline phases (1, 2). Hydrogen bonding between polymer chains leads to the formation of a smectic phase in the polymer, and this smectic phase gives a contribution to the signal in the same 2θ regions where we expect to observe the amorphous halo and some of the crystalline peaks. Additives in the polymer also give contributions in a narrow range of 2θ , which further complicates peak deconvolution work and the separation of amorphous and crystalline pattern contributions.

This poster will present how temperature experiments can help to better define the amorphous peak position at room temperature, how highly crystalline materials were used to further define a reliable peak deconvolution procedure following already published procedures (3, 4), how sample preparation can impact the measured crystallinity, and how degree of crystallinity calculated by DSC and XRD compare.

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16. Cutinase hydrolytic activity for polyethylene terephthalate

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Polyethylene terephthalate (PET) is the highest volume synthetic textile fiber. A disadvantage of polyester fibers is their low hydrophilicity. The surfaces are not easily wetted, which is necessary for applying finishing compounds and coloring agents. In addition, water is hindered from penetrating into pores of fabrics. Hence, methods for PET hydrolysis at surfaces would be useful for improving surface wet-ability, surface-cleaning and more. Cutinases were chosen as potential enzymes for catalysis of surface hydrolysis reactions since their natural function is catalysis of cutin, a structural polyester at plant surfaces. Herein, we report the activity of purified cutinases from *Humicola insolens* (HiC), *Pseudomonas mendocina* (PmC), and *Fusarium Solanii* (FsC) for hydrolysis of amorphous PET film in aqueous media using a pH-stat with NaOH as titrant. By this approach, the initial hydrolysis rate was monitored as μmole of added NaOH per hour and the effect of various reaction parameters such as reaction temperature, pH and enzyme concentration were determined. Then, using optimized temperature and pH conditions, PET films were incubated with cutinases for up to 4 days. The weight loss of incubated PET films was measured and the morphology of the films was studied using SEM. The maximum initial hydrolysis rate of $32 \mu\text{mole NaOH/h}$ was achieved using HiC at 75°C pH 8.5. This reaction condition resulted in a $98 \pm 0.5 \%$ PET weight loss after 4 days. PmC and FsC performed best at 50°C , resulting in an initial hydrolysis rate of $4 \mu\text{mole NaOH/h}$ and $6 \mu\text{mole NaOH/h}$, respectively, and PET weight loss after 4-day incubations of $5 \pm 1 \%$ and $6 \pm 4\%$, respectively. SEM analysis of PET films after 4-day incubations with PmC and FsC showed roughened surfaces with distinctly different morphologies. This study shows that cutinases have excellent potential to be used as an environmentally friendly mild method for surface roughening and further hydrolysis of PET materials. Enzyme-catalyzed hydrolysis of PET occurs by degradation from the surface, unlike chemical methods where hydrolysis occurs both at the surface and in the bulk.

17. Silicone Biotransformation

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ABSTRACT: Silicone-based macromers and polymers have great interests in numerous applications due to their versatile and unique properties. Generally, organosilicon based materials are synthesized by chemical methods under very harsh conditions that promote uncontrolled redistribution, side reactions, and decomposition of potentially functional groups and bonds (e.g., siloxane). In contrast, Biocatalysis or enzyme catalysis can proceed with high enantio- and regioselectivity under mild reaction conditions, circumvent protection-deprotection steps, and providing an attractive alternative to conventional chemical methods for the preparation of a wide range of small molecules, macromers, and polymers. Here, we describe the silicon biotransformation to form organosilicon carbohydrate macromers ("sweet silicones"), silicone polyamide and silicone polyesteramides.

Organosilicon-sugar conjugates "Sweet silicones" were prepared in a one step under mild reaction conditions (low temperature, solventless) via lipase-catalyzed esterification of organosilicon carboxylic diacids and the C1-O-alkylated α , β -ethyl glucoside. Specifically, acid-functionalized organosilicones reacted with the primary hydroxyl group at the C6 position of α , β -ethyl glucoside via regioselective esterification, and giving organosilicon carbohydrate macromers without protection-deprotection steps.

The synthesis of silicone polyamide and silicone polyesteramides was successfully performed in bulk at low temperature ($T = 70^{\circ}\text{C}$) via lipase-catalyzed polycondensation reactions using various feed mole ratios of diethyl adipate, 1,8 octanediol and α , β -(diaminopropyl)polydimethyl-siloxane (Si-NH₂). Silicone containing copolymers had M_n and PDI that ranged from 6-11 kDa and 1.2-2.2, respectively. The relative amount of amide and ester units along the polymer chains strongly affects the physical aspect of silicone containing polyesteramides. Consequently, the physical characteristics of materials changed from hard to sticky, with an intermediate composition range of displaying a waxy appearance.

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18. Polymer Nanofilms from Natural Product Feedstocks

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We have previously demonstrated the ability to synthesize uniform, conformal polymer films on a variety of substrates using a two-step deposition / polymerization process. This approach involves the physical vapor deposition of monomer onto a substrate, followed by exposure of the resulting monomer film to UV radiation to initiate polymerization. This process is capable of producing films of reproducible thickness from tens of nanometers to tens of microns. Additionally, since light is employed to initiate polymerization, standard photolithography techniques can be used to generate patterned films, thus allowing complete three-dimensional control over the final polymer film.

Most monomers studied to date exist in the liquid phase at room temperature, and therefore require that the substrate be cooled during the film formation process. By cooling the substrate to temperatures below 100K, it is possible to obtain monomer films that are completely amorphous. We have recently shown that, because the monomer molecules are frozen into this rather unusual physical state, it is possible to overcome steric limitations to polymerization that plague such species as 1,2-disubstituted ethylenes. Thus, it is possible to produce polymers with molecular weights between 10^5 and 10^6 with relatively short reaction times of minutes to hours.

The 1,2-disubstituted ethylene motif is found in a variety of natural product groups, including cinnamyl compounds, citronellyl compounds, and terpenes. It was found that a variety of cinnamyl compounds could be polymerized to high molecular weight. Attempts to polymerize

several terpenes did not produce any high molecular weight products, which was most likely the result of increased steric hindrance around the carbon-carbon double bond. Specific examples will be presented, along with a new kinetic model derived specifically to take into account the frozen amorphous state of the monomer molecules.

19. Miniemulsion Copolymerization of Polymerizable Fatty Acid-Derived Monomers

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Fatty acids have been used in alkyd-based paints for many years. They allow the alkyd resins to crosslink, creating a strong, durable film. With increasing environmental concerns, alkyd paints, which have high volatile organic compound (VOC) content, are being phased out in preference for low VOC latex paints. However, latex paints however still rely on VOC to plasticize the latex polymer during film formation. Still, regulations grow stricter, and eventually VOC content will not be tolerated. The solution is to impart crosslinking in latex films using fatty acid chains thus removing VOC and adding a renewable resource to an otherwise petroleum-based product.

To incorporate fatty acids into the latex we are functionalizing them with free radical polymerizable double bonds. Methacrylate double bonds were specifically chosen since they are very reactive and do not have an alpha hydrogen which could lead to crosslinking during polymerization. It is important that crosslinking only occurs during film formation so that a quantitative analysis can be done. The fatty acid chain must be unsaturated to crosslink it during film formation. C₁₈ fatty acid chains were chosen to test the amount of unsaturation needed, because they come in various degrees of unsaturation; one, two, and three double bond(s), which correspond to oleic, linoleic, and linolenic, respectively. Although starting with the fatty acid is a more direct approach, it was found that starting with the alcohol derivative of the fatty acid resulted in the formation of a purer product. Therefore oleyl alcohol and a mixture of linoleyl and oleyl alcohol were esterified with methacrylic anhydride to create oleyl methacrylate (OM) monomer and a mixture of linoleyl and oleyl methacrylate (LOM).

The OM and LOM were then copolymerized with 2-ethylhexyl methacrylate (EHMA) by miniemulsion copolymerization. EHMA was chosen since its polymer is film forming and uncrosslinked. Miniemulsion polymerization is used since the fatty acid-derived monomers (FAM) are very water insoluble and cannot migrate to the polymerization site in a conventional emulsion polymerization system. It was found that thermal initiation at 70 °C caused hydrogen abstraction in the unsaturated groups and crosslinking of the polymer during the polymerization. To overcome this problem the polymerization was carried out at room temperature using a redox initiation system. Future work will include measurement of the film properties such as crosslink density and tensile strength to determine the film's ability to crosslink and relating these findings back to FAM type and content.

20. Applications of Bio-Based 1,3-Propanediol:Cosmetics, Functional Fluids, Fibers, and Plastics

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DuPont Tate and Lyle's bio-based 1,3-propanediol product line provides high performance solutions for customers and markets while continuing to reduce our environmental footprint. Bio-based propanediol is available today and therefore a key contributor to DuPont's sustainability goals for 2015. The proprietary bio-based propanediol production process uses the non-depletable resource corn instead of petroleum-based feedstocks. An independent study has shown that the production of bio-based propanediol consumes about 40% less energy and has a 20% smaller global warming potential (GWP) than the production of its petroleum-based counterpart.

DuPont Tate & Lyle's Zemea™ propanediol, Susterra™ propanediol, DuPont™ Sorona® polymer and DuPont™ Cerenol™ polyols illustrate our development of products based on renewable feedstocks that give leading manufacturers the ability to replace petroleum-derived materials with high-

performance, sustainable solutions. Zemea™ propanediol replaces traditional glycols in cosmetics and personal care products, such as the deodorants of Terra Naturals. Reported benefits of Zemea™ propanediol in cosmetic and personal care applications include enhanced clarity, lack of irritation, and excellent sensory characteristics. Susterra™ propanediol offers a non-petroleum alternative for a wide range of industrial applications. Examples include Cryotech's BX36® runway deicing fluid, Kilfrost's DF Sustain™ Type I wing deicing fluid and Interstate Chemical's Bio-Green heat transfer fluid. DuPont™ Cerenol™ is a family of polyetherdiols that has proven its value-added properties in the personal care market, heat transfer fluids, thermoplastic elastomers including Spandex and Hytrel®, and automotive coatings. DuPont™ Sorona® polymer is optimized for fiber, spinning, and textile applications. Its beneficial properties like softness and resilience are derived from a unique, semi-crystalline molecular structure featuring a pronounced "kink" induced by the 1,3-propanediol fragment. Susterra™ propanediol is not only used in thermoplastic polyether, polyesters or polycarbonates, but can also be applied in thermoset materials, including unsaturated polyester resins (UPR's), crosslinked with vinylic systems. The preferred glycol for UPR's is 1,2-propanediol, due to its ability to induce isomerization in unsaturated diacid monomers. Susterra™ propanediol creates new opportunities in thermoset applications like composites and coatings with improvements in production and end-use properties as well as with the addition of bio-based content to the polymer.

21. Novel Amphiphilic Scorpion-like and Star-like Macromolecules as Drug Carriers

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Novel amphiphilic star-like macromolecules (ASM) and amphiphilic scorpion-like macromolecules (AScM) with double-chained and single-chained tails were synthesized and characterized. All macromolecules are composed of mucic acid-based hydrophobic "heads" and poly(ethylene glycol)-based hydrophilic "tails". Two different ASMs (M12P5 and M12P2x2) and two different AScMs (NC12P5 and NC12P2x2) were investigated to explore how branched PEG chains influence particle size, water-solubility, drug loading capacity, drug release rate and micelle stability. A hydrophobic, anti-inflammatory drug (indomethacin) was used to evaluate the encapsulation ability and release rate from the macromolecules. The double-chained macromolecules reduced the micellar sizes (10 nm for AScM, 22 nm for ASM) compared to single-chained macromolecules (18 nm for AScM, 48 nm for ASM). Through oil/water emulsion methods, drug-loading efficiency of ASM reached nearly 50%, higher than the self-assembled micelle AScMs, which display a drug-loading efficiency 30%. Indomethacin-loaded ASM released 52% of free drug within 50 hours, compared with 78% for AScM. Dynamic light scattering experiments showed that ASM minimized protein interactions. Double-chained macromolecules perform as well or better than single-chained ones as drug delivery systems.

22. Preparation of Polymer/Semiconductor and Polymer/Metal Nanocomposites from Ionomer

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ABSTRACT: Preparation of polymer/semiconductor nanocomposites from poly(methyl methacrylate) (PMMA) ionomer was compared with that from PMMA. It was found that ionically bound cadmium cations (Cd²⁺) to PMMA ionomer were localized upon hydrogen sulfide (H₂S) treatment, and small cadmium sulfide (CdS) nanoparticles were made within the ionic domains of the ionomeric PMMA. Because of their small size, these CdS nanoparticles were not discernible by wide angle X-ray diffraction (WAXD); but, physically dispersed Cd²⁺ into PMMA produced, upon H₂S treatment, much larger CdS nanoclusters in the PMMA matrix, which were greater than 2 nm as measured by WAXD. It was further observed that, upon thermal treatment at an elevated temperature, CdS nanoparticles prepared from PMMA

ionomer aggregated further and that glass transition temperature (T_g) of PMMA/CdS nanocomposites was slightly increased during nanoparticle aggregation.

The possibility of reduction of Cd^{2+} to cadmium atom (Cd^0) upon ultraviolet (UV) light irradiation of a highly porous Cd^{2+} -containing PMMA ionomer powder to generate polymer/metal nanocomposites was investigated as well. It was detected by WAXD that the size of the locally ordered Cd^{2+} ionic aggregates in the PMMA ionomer progressively diminished upon UV light exposure, indicating the occurrence of metallization from Cd^{2+} to Cd^0 . However, the cadmium metal nanoparticles developed by the UV light treatment were not discerned by WAXD presumably due to the difficulty of their aggregation within Cd^{2+} ionic domains. The chemical localization method and the UV light metallization process, respectively, developed on Cd^{2+} -containing PMMA ionomer to prepare PMMA/CdS and PMMA/Cd nanocomposites may be extended to other ionomers and metallic elements to fabricate various polymer/semiconductor and polymer/metal nanocomposites.

KEYWORDS: nanocomposite, ionomer, localization, reduction, nanoparticle, nanocluster, aggregation, metallization.

23. ACS Green Chemistry Institute: Recent Activities Relevant to Green Polymers

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The mission of the American Chemical Society Green Chemistry Institute (ACS GCI) is to advance the implementation of green chemistry and engineering principles into all aspects of the chemical enterprise. ACS GCI seeks to be the premier change agent that has the knowledge, expertise, and capabilities to catalyze the movement of the chemical enterprise toward sustainability through the application of green chemistry principles. ACS GCI seeks to achieve this vision through work in several strategic areas: research, education, industrial implementation, communication, and policy advocacy. The poster will highlight recent activities in these areas and provide examples that are especially relevant to green polymers.

Research

- Grant programs
- Databases

Education

- Annual Summer School and Student Workshops
- New books
- Training for professionals in industry and academia

Industrial Implementation

- ACS GCI Pharmaceutical Roundtable with 8 member companies and expanding
- 9 Green Chemistry Business Case Studies developed for use in MBA programs
- Reports on Quantifying the Benefits and Enhanced Security

Communication

- National and International conferences, including the Annual Green Chemistry & Engineering Conference
- Annual Awards Programs: Kenneth G. Hancock Memorial Award, Joseph Breen Memorial Student Fellowship, Presidential Green Chemistry Challenge Awards, and ACS Award for Affordable Green Chemistry

Policy Advocacy

- Barriers to green chemistry implementation
- Green Chemistry Research and Development Act under consideration by US Congress

More information on these topics and more can be found at www.acs.org/greenchemistry.

24. Green Nanoparticles

Janos Borbely[#] and John F. Hartmann*

ElizaNor Polymer, LLC* (Princeton Junction, NJ) in collaboration with BBS Nanotechnology, Ltd.# (Debrecen, Hungary) has created an array of polymer-based nanoparticles for application in a variety of commercial arenas.

Pharmaceutical Delivery Systems

1. *Cancer-targeting nanoparticle*: In collaboration with Prof. Tamara Minko of Rutgers School of Pharmacy, a fluorescein-labelled nanoparticle with a receptor ligand and composed of two natural biopolymers and stabilized by ionic bonds was readily taken up cancer cells *in vitro*. Particles lacking the ligand were not taken up or to a very limited extent. Early studies in intact mice, failed to show toxicity. These early stage-studies will be continued by assessing the uptake of particles carrying chemotherapeutic payloads.

2. *Gene Delivery*: Early *in vitro* studies have demonstrated that nanoparticles labeled with two fluorescent dyes and composed of the same biopolymers mentioned above, delivered and released a payload of nucleic acid upon entering the cell.

Environmental

1. *VOC Reduction*: Synthetic nanoparticles as a replacement for resins in paint, coatings and ink will allow a significant reduction in VOCs in these products. Those properties which are dependent upon the linear resins, e.g. viscosity, hardness and adhesiveness are quantitatively retained or improved by the nanoparticle preparations.

2. *Removal of heavy metal contaminants from drinking and waste water*: A nanoparticle composed of natural and biodegradable poly gamma glutamic acid, binds metal ions such as lead. Following removal with an ultrafilter and separation of the metal from the polymer by simple pH adjustment, the particle can be reused. Once exhausted the metal-denuded particle can be composted in an environmentally compatible manner. Quantitative studies have demonstrated that the particle has two-three times the metal binding capacity beyond ion exchange resins, e.g. Dowex and Varion KCO.

Cosmetics and Cosmeceuticals

Skin care Products: We have created sub-micron particles composed of hyaluronic acid (HA), the size and charge of which can be controlled. Because of its dramatically lower viscosity, compared to linear HA, it offers a significant potential advantage beyond currently marketed injectable dermal fillers.

Dentistry

1. *Composite Fillings*: By replacing in part the organic phase of composite filling of a widely-used product with our nanoparticle preparation of biocompatible acrylics resulted in a doubling of hardness and a 50% reduction in shrinkage.

25. Organic-Inorganic Silica based Melting Gels

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[#] Energy Storage Group

An important requirement in the electronic industry, in an effort to develop low energy consuming electronics, is to provide protective - hermetic materials. These protective materials should have the ability to prevent the contamination of the critical components of the electronic devices from the invasion of the contaminants such as water and gasses from the external environment.

A family of hybrid organically-modified silica “melting gels” prepared by the sol-gel method is one of the answers to this challenge. The hybrid protective materials have two means to prevent the penetration of the contaminants. The organic groups bonded to the inorganic network increase the hydrophobicity of the surface and the organic groups block the porosity and reduce the surface area.

These gels were prepared over a wide range of compositions using Methyltriethoxysilane (MTEOS) and Dimethyldiethoxysilane (DMDES). The melting gels were prepared in solutions by hydrolysis-polycondensation reactions, followed by concentration and gelation. The interesting property of melting gels is that the dried, rigid gels are able to soften and flow at temperatures in the range 100-120°C and then to be consolidated at temperatures between 135° and 160°C, after which the gel no longer softens.

This poster will present, the preparation procedure of the melting gels, and the thermal behavior of the gels at the consolidation point. Thermal behavior was investigated using thermal gravimetric analysis (TGA) coupled with infrared spectrometry (FT-IR) for gas evolution analysis and differential scanning calorimetry (DSC). The DSC analysis showed an endothermic effect at the consolidation temperature which varies as a function of proportion

between organic mono-substituted and di-substituted alkoxides (MTES/DMDES). A direct correlation between the melting gel composition and glass transition point (T_g) was found. The temperature of glass transition decreased with increasing of the di-substituted alkoxide concentration. The T_g decreased from -0.3°C at the 25 mol% DMDES to -56.7°C at 50% mol% DMDES.

These gels have been used to obtain coatings about $\sim 1\text{mm}$ thickness on different supports including mica and polycarbonate. The surfaces of the films were investigated using ATR-FT-IR, micro-Raman spectroscopy, and Atomic Force Microscopy. The coatings have no visible cracks. Results of micro-Raman spectroscopy show that methyl groups are concentrated at the surface of the films, increasing the hydrophobicity. The hydrophobicity was estimated by contact angle measurements. All gels displayed a contact angle greater than 90° .

26. From oligo(p-phenylene vinylene)s to n type polyazines

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Polyazines (PAZs), within the general family of Schiff-base polymers, feature $\text{N}=\text{CH}$ linkages that are isoelectronic with $\text{HC}=\text{CH}$ groups. In addition to their known characteristics, e.g., thermal stability, strength, high modulus, some Schiff-base polymers more recently have been receiving attention due to their semi-conducting and non-linear optical properties, making them potential candidates for a variety of applications, e.g. in optical fibers. In this work, an efficient polycondensation of α,ω -diformyl functional oligo(p-phenylene vinylene) (OPV) with hydrazine afforded soluble and processable conjugated polymers. The polymers feature extended delocalized conjugated electron systems with integrated azine linkages. The products were analyzed in regard to microstructure, chain length, and electro-optical properties. Size exclusion chromatography yielded molecular weights M_n up to $\sim 8,700\text{-}10,500\text{ g/mol}$, relative to polystyrene. The optical properties showed absorption maxima from ~ 455 to $\sim 487\text{ nm}$ (CHCl_3 solutions), red shifted by 31-60 nm relative to the monomer aromats, indicating conjugation through the azine linkages. The emission maxima are observed from $\sim 515\text{ nm}$ to $\sim 560\text{ nm}$ (CHCl_3 solutions). Differential pulse voltammetry diagram shows that the products represent a rare example of n-doped conjugated organic polymers. However, no conductivity could be observed.

27. Making Oligo-peptide Synthesis Look Easy: Papain-catalyzed Oligo(γ -ethyl-L-glutamate)

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Poly(α -amino acid) synthesis by ring-opening polymerization of α -amino acid N-carboxylic anhydrides (NCAs) provides high molecular weight polypeptides [1,2]. However, NCA synthesis requires the use of highly toxic phosgene or its equivalent. Reaction conditions require strict removal of water and high monomer purity. NCA ring-opening does not provide control of amino acid sequence along chains. An alternative route to poly(amino acids) is by thermal or acid-catalyzed polymerizations. For example, thermal condensation polymerization of aspartic acid followed by alkaline hydrolysis gives poly(aspartic acid) [3]. However, harsh polymerization conditions required results in aspartic acid racemization and formation of α - and β -linked repeat units.

By using protease-catalysis to synthesis oligopeptides, one can avoid racemization, decrease requirements for protection-deprotection steps, utilize readily renewable and potentially inexpensive amino acid monomers, and use mild non-hazardous operating conditions[7,8]. Furthermore, we envision that some extent of sequence control will be achieved by ‘tuning’ catalyst selectivity.

This poster describes papain-catalyzed oligomerizations of diethyl glutamate. The effects of pH, medium ionicity, buffer strength and reaction time on the oligomerizations and products formed are described.