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13. ABSTRACT (Maximum 200 words) The 1997 Asilomar Conference on Polymeric Materials focused on electroactive polymer systems. New directions were probed for use of such materials in power sources. The implications in biological integration of such systems were also explored. An attempt was made to understand and predict structure-property relationships by using hierarchical paradigms to describe these complex materials systems. Special emphasis were on the modeling of such polymers using advanced computer methods, and on the design and synthesis of new electroactive polymeric materials based on the predictions elucidated from these computational advances. As in previous years, this conference addressed the problems and opportunities that are arising with the emergence of a hierarchical approach to the design of new materials systems. Focus was on important questions such as the factors that gave rise to relatively discrete organizational levels of structure, the interactions between such levels and the synthesis of new "active" polymers with functional designs aimed at the efficient and selective transport of energy. The Twentieth Asilomar Conference focused particularly on new polymers with unusual properties, on polymers with switching characteristics, and on macromolecular neural networks for image processing.					
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PROCEEDINGS

*TWENTIETH ASILOMAR CONFERENCE
ON
POLYMERIC MATERIALS*

February 9-12, 1997

SPONSORED BY

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, North Carolina 27709

SUBMITTED BY

Eric Baer
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

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Program

Asilomar Conference



*Twentieth Asilomar Conference
on Polymeric Materials*

February 9-12, 1997

Pacific Grove, CA

***The Twentieth Asilomar Conference
on Polymeric Materials
February 9-12, 1997***

Invited Speakers

“New Microlayered Composite Systems”

**Professor Eric Baer
Case Western Reserve University
Cleveland, OH**

“Polymer Light Emitting Diodes”

**Dr. Nick Colaneri
UNIZX Corporation
Santa Barbara, CA**

***“Functionalization of Electroactive Conjugated Polymers for
Recognition of Biological Species”***

**Professor Francis Garnier
Laboratoire Materiaux Moleculaires
Thiais, FRANCE**

“Architectural Control of Graft Copolymer Morphology”

**Professor Samuel Gido
University of Massachusetts
Amherst, MA**

“Interdiffusion and Morphology Development in Polymer Microlayers”

**Professor Anne Hiltner
Case Western Reserve University
Cleveland, OH**

“Integration of Biocomposites with Synthetic Structures”

**Professor Tony Hodgson
Wollongong Hospital
New South Wales, AUSTRALIA**

“Negative Feedback Control Systems in Biology”

**Professor Michael LaBarbera
University of Chicago
Chicago, IL**

“Molecular Recognition Polymeric Membranes”

**Professor Charles Martin
Colorado State University
Fort Collins, CO**

“Polymers in 3D Optical Memories”

**Professor Peter Rentzepis
University of California at Irvine
Irvine, CA**

“Biosensors from Conducting Polymers”

**Dr. Lynne Samuelson
US Army Natick RD&E Center
Natick, MA**

“Conducting Polymers - Applications for the Electronics Industry”

**Dr. Jane Shaw
IBM Thomas J. Watson Research Center
Yorktown Heights, NY**

“High Performance Cyclic Olefin Polymers”

**Dr. Robert Shick
BFGoodrich Chemical Company
Brecksville, OH**

“Switchable Protein Assemblies”

**Professor David Tirrell
University of Massachusetts
Amherst, MA**

“Ion Conducting and Electro-Responsive Multiphase Polymers”

**Professor Gary Wnek
Virginia Commonwealth University
Richmond, VA**

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February 9-12, 1997

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Abstracts

Asilomar Conference



*Twentieth Asilomar Conference
on Polymeric Materials*

February 9-12, 1997

Pacific Grove, CA

NEW MICROLAYERED COMPOSITE SYSTEMS

by

Eric Baer

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Cleveland, Ohio 44106

ABSTRACT

Lessons from biology have revealed that natural materials systems have architectures that are specifically designed to accommodate a unique spectrum of required properties. These architectures always have many scale levels that are bound together by interfacial coupling or adhesion. Recently, new synthetic approaches have been used to develop macromolecular materials that "self-assemble" into nano-scale morphologies. This lecture addresses another approach - the "forced-assembly" of synthetic polymers at the nano-scale that in themselves are less complex and are currently available in commercial quantities.

Numerous examples illustrate how the coextrusion of film with three or more polymeric layers is used economically to achieve a desirable mix of end-use characteristics. More recently, layer-multiplying devices permit up to three polymers with dissimilar solid state structures and properties to be combined into unique microlayer and nanolayer laminates with thousands of layers. Studies of layered polymer composites with hundreds or thousands of alternating layers down to the nano-scale have revealed unique properties which are achievable when the layers are thin enough to produce synergistic combinations of key properties of the constituent components.

The applications of microlayer and nanolayer extrusion technology can be separated into two broad areas that are illustrated with specific examples. In the first area, new materials with very thin layers are created that exhibit improved and unique physical properties. The improved properties include mechanical, optical, barrier and electronic, and combinations of these properties. The second area emphasizes the usage of microlayer technology to generate large specific surface areas for fundamental studies of adhesion, diffusion and crystallization which can lead to the development of unique systems with gradient structures.

FUNCTIONALIZATION OF ELECTROACTIVE CONJUGATED POLYMERS FOR RECOGNITION OF BIOLOGICAL SPECIES

Francis Garnier

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Recognition of biological species, by the use of chemically designed architectures, is one of the most challenging field of research, both for the beauty of constructing biomimicking assemblies, and also for their large potential of applications, for instance as gene sensors. Various devices structures have been already proposed, in which reading of information generally involves an optical process, requiring a further time consuming chemical step. An electrical reading would be of interest, as it would allow a real time processing of data. With this aim, we have realized new functionalized macromolecular assemblies, which perform the following functions: i) *molecular wires*, owing to the presence of macromolecular chains of conjugated polypyrrole, which are known to possess high intrinsic electronic conduction, and ii) *chemical centers for biological recognition*, consisting of oligonucleotides grafted as pendent groups along the conducting macromolecular chains. These oligonucleotides, made from a known sequence of 14 bases, undergo highly specific hybridization, when in presence of a complementary nucleotide sequence in solution. The oligonucleotide hybridization, occurring on the pendent groups along the macromolecular polypyrrole chains, leads to a modification of the electrochemical response of this fonctionalized polypyrrole, which is explained in terms of a stiffening of the conjugated backbone environment. This modification of electrochemical signal corresponds thus to a molecular transduction of a biochemical information into an electrical signal.

It is experimentally confirmed that specific hybridization only occurs between the grafted oligonucleotide with its complementary oligonucleotide target, which is followed by a shift of some hundreds of millivolts in the oxidation potential of the polypyrrole backbone. This allows a potentiometric reading of the hybridization information. A potential window also exists in the voltammograms, in which hybridization is followed by a large variation of the electrical intensity, allowing an amperometric lecture of the recognition process. This amperometric response is directly related to the concentration of the complementary oligonucleotide target in solution, allowing an actual detection limit of about 10^{-11} moles. This sensitivity will be further improved by the use of a microelectrochemical transistor structure. High density $n \times n$ dot matrixes, each dot being coated with a different nucleotide sequence, showing fast and sensitive electrical reading, appear actually within reach.

**ARCHITECTURAL CONTROL OF GRAFT COPOLYMER
MORPHOLOGY
and LONG RANGE ORDER**

Samuel P. Gido

Polymer Science and Engineering Department
University of Massachusetts at Amherst

The effect of well defined graft copolymer architecture on the formation of self assembling morphologies with long range order has been systematically investigated. Four series of samples across a range of component volume fractions were characterized using TEM, and SAXS for different model architectures of polystyrene-polyisoprene single graft and double graft copolymers. The simplest architecture was an symmetric single graft, I_2S , or Y shaped molecule. This architecture, formed by grafting a poly(styrene) block onto the center of a poly(isoprene) backbone, is found to shift the volume fraction windows in which specific strongly microphase separated morphologies are observed to higher volume fractions of the PS graft material than in the corresponding linear diblock copolymers. The effects of asymmetric grafting of the single PS chain on the PI back bone was investigated in a series of I_aI_bS materials. Additionally the effect of multiple graft architecture was explored with S_2IS_2 (H-shaped) and (SI)I(SI) (π -shaped) materials, each of which has two trifunctional branch points per molecule. These results point toward the ability to control microstructure in microphase separated systems independently of component volume fractions by varying molecular architecture. Additionally, we have experimentally observed effects of molecular architecture on the ability of the materials to form microstructures with long range order.

Interdiffusion and Morphology Development in Polymer Microlayers

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Continuous multilayer extrusion is a method by which two or more dissimilar polymers are combined into laminates with hundreds or thousands of alternating layers. New classes of materials with unique mechanical, electrical or transport properties are possible with this process. Furthermore, the large interface to volume ratio creates opportunities for fundamental studies of interfacial phenomena such as adhesion, interfacial reactions, surface-nucleated crystallization, and diffusion. Because the coextrusion process requires stringent laminar flow conditions and short processing times, two miscible polymers can be brought into intimate contact with minimal mixing. Subsequently, gradient compositions can be produced by controlled interdiffusion.

Two studies illustrate this concept. (1) Models that combine Fick's law of diffusion with the observed crystallization kinetics describe concurrent crystallization and interdiffusion of two miscible glassy polymers, polycarbonate (PC) and a copolyester (KODAR), when they are annealed above their glass transition temperatures. Two conditions are analyzed: annealing at 200°C where interdiffusion is much faster than crystallization, and annealing at 195°C where the rates of crystallization and interdiffusion are comparable. (2) Interdiffusion of polyethylenes is examined by annealing an HDPE/LLDPE pair that co-crystallizes in isomorphic structures. Analysis of the DSC melting behavior, as the two melting endotherms shift into a single DSC peak, and the accompanying evolution of the gradient crystalline morphology reveal the dependence of the diffusion coefficient on molecular weight distribution.

Negative Feedback Control Systems in Biology

by

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Biological systems are the epitome of "smart" materials and structures, but their "intelligence" usually resides in negative feedback control systems rather than in raw computational prowess. Although biological systems represent a tempting model for materials scientists, they should be approached with due caution and humility - natural selection does not always choose the most obvious control variables, the function maintained may be only indirectly related to the mechanical properties of the materials, and the properties of the materials may be altered by subtle changes in organization or hierarchical structure. A potpourri of biological examples illustrate these points.

The circulatory systems of both vertebrates and a wide variety of invertebrates have architectures consistent with a simple cost-minimization model. In vertebrates, this architecture is achieved by local control of vessel diameter on both acute (smooth muscle tone) and chronic (vessel wall remodeling) time scales, but the control variable - local shear stress - is only indirectly related to the cost function. Invertebrates achieve the same end, but must be using some other, presently unknown, control variable. Natural selection is not unconstrained, but it is patently opportunistic.

On an evolutionary time scale, the long bones in vertebrates clearly maintain a constant safety factor by balancing body size against bone proportions and limb posture. On a shorter time scale (the lifetime of an individual), remodeling also maintains constant safety factors, but the obvious control variable, local strain, clearly can't explain all of the observations. Plants show a range of responses depending on the nature of the perturbation - simple shaking produces stiffer stems, loss of vertical orientation can induce wood that generates righting forces (by a clever manipulation of structure), but mechanical stimulation of leaves produces more compliant petioles (indirectly reducing the drag forces on the tree).

Spiders produce a silk drag line scaled to maintain constant safety factors for dynamic loads; the web of orb-weaving spiders closely approximates an ideal minimum weight/uniform stress structure. Under extreme loads, the silk strain crystallizes to increase its stiffness and strength, but returns to its original properties after unloading within a few minutes at ambient temperatures. A few other biological materials (e.g., slug mucus) are also known to reversibly alter their properties; natural selection has tuned properties to loading circumstances to maintain function. Echinoderms (starfish, sea urchins, etc.) can modulate the mechanical properties of their connective tissues on a time scale of seconds under direct nervous control. Control variables and the precise mechanism involved remain obscure, but the phenomenon is well documented and has permitted these animals to exploit a skeletal system unique among metazoans.

Molecular Recognition Polymeric Membranes

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Membrane-based chemical separations constitute an emerging research area and industrial technology.¹ The objective is to develop membranes that selectively transport a particular target molecule and reject (or transport at much lower rates) other molecules that might be present in the feed solution or gas. The simplest example is in industrial gas separations, for example, the separation of O₂ from air. While membrane-based gas separations are potentially less energy intense (green chemistry), polymeric materials with higher selectivities and higher permeant fluxes will be required before membrane-based processes make a major impact in this area. Opportunities also exist in pharmaceutical and petroleum separations, but, again, better materials will be required if membranes are to make inroads in these areas.

From a chemical view point, the key question to be addressed here is - how can molecular-recognition chemistry be incorporated into membranes. This talk will focus on this issue, and several different approaches for building molecular-recognition chemistry into membranes will be discussed.

The first borrows from Mother Nature, who has developed a number of exquisitely-selective molecular-recognition agents. The quintessential example is enzymes. However, enzymes accomplish two chemical events - selective chemical recognition of the substrate molecule followed by chemical transformation of this molecule. The later event is not desirable from a membrane-transport view point; in general, we do not want to chemically change the molecule we wish to separate from a mixture. A second problem concerns immobilization of the enzyme within a solid membrane such that the enzyme retains its activity. A new approach for enzyme immobilization in membranes that solves both of these problems will be presented. Applications to chiral separations will be described.

The second approach for building molecular recognition into membranes borrows from the well-known molecular imprinting concept.² This chemistry entails forming a highly cross-linked polymeric resin around the target molecule such that the resin contains chemical sites that selectively recognize the target molecule. We have used this approach to prepare ultrathin film composite membranes that selectively recognize and transport the bronchodilator theophylline.

- (1) Baker, R. W.; Cussler, E. L.; Eykamp, W.; Koros, W. J.; Riley, R. L.; Strathman, H. *Membrane separation systems recent developments and future directions*. Report to the US DOE Noyes Data Corp., Park Ridge, NJ, 1991.
- (2) Wulff, G. in *Polymeric Reagents and Catalysts*, W.T. Ford, Ed. ACS: Washington, DC, 1986; Vol. 308, pp 186-230.

Polymers in 3D Optical Memories

P.M. Rentzepis

(Abstract)

Photochromic materials have been used lately as switching media in various electronic devices. These materials are dispersed or copolymerized in various polymers and then molded into the form of disks or other shapes as needed for the particular device.

This talk will be focused on the utilization of photochromic materials in polymers for 3D optical memory devices. The excited states and metastable species involved in the photoreaction have been identified, and the spectra, formation and decay rates of all intermediate states involved in the photochemical reaction for the writing and reading processes have been studied by means of ultrafast spectroscopy.

These properties and the means for reading and writing information in 3D space will be discussed. An actual, working, prototype, 3D memory system based on these polymeric materials will be described and its components and function will be presented.

Biosensors from Conducting Polymers

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This research focuses on the coupling of biological receptors to conducting, electroactive polymers for biosensing applications. The rationale behind this coupling is to harvest the inherent molecular recognition capabilities of naturally occurring bioreceptors by incorporating them into a mechanically rugged, environmentally stable and yet electronically active matrix material. In this way the polymer is expected to provide ease of processability and ultimately, "intelligent" pathways for optimum signal transduction. In addition, these polymers may provide a unique mechanism to further "tune" the resulting properties of the system through manipulation of the redox potential of the polymer.

We have investigated several immobilization strategies to couple bioreceptors to conducting polymers which have proven to be facile, chemically mild, and versatile to a variety of systems. These techniques include Langmuir-Blodgett, electrochemical polymerization, enzymatic polymerization, and layer-by-layer electrostatic deposition. In the first case, streptavidin-biotin complexation was used to attach phycobiliproteins to a polythiophene-biotin modified surfactant monolayer. In the second case, glutaraldehyde coupling was used to bind various enzymes to electrochemically polymerized anisidine and phenylenediamine films. Enzymatic polymerization was used to simultaneously polymerize and trap enzymes into a polyphenol matrix. Lastly, layer-by-layer deposition was used where the bioreceptor served as the appropriate polycounterion to form alternating bioreceptor-polymer multilayer assemblies. Multiple enzyme layering was found to allow for sequential enzymatic reactions to be carried out in an "all in one" device.

The fabrication, characterization and resulting biosensing properties of each of these immobilization techniques will be discussed.

Abstract

Conducting Polymers: Applications for the Electronics Industry

J.M. Shaw

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The electronics industry has over the past thirty years been able to provide exponential increases in product performance as well as concomitant cost reductions at a level never before seen in this century. The rapid development and implementation of new materials has been a critical factor in this effort and will be key to new product development for the future. The research effort on intrinsically conducting polymers initiated in the '70s has led to new processible systems spanning a wide range of conductivities. This talk will provide an overview of conducting polymers and their applications 1) as charge dissipating coatings for the fabrication of high density semiconductor devices and the metrology of these devices, 2) as radiation sensitive polymers to pattern semiconductors, 3) as electrodes for electroplating of metals, for batteries, and for light emitting diodes, and 4) as materials to provide electromagnetic shielding for portable electronics. This talk will focus on polyaniline, a low cost, processible conducting polymer; the fundamental research which led to enhanced properties and conductivity; and its applications for the electronics industry.

High Performance Cyclic Olefin Polymers

R. Shick, BFGoodrich

BFGoodrich has been exploring cyclic olefin polymers for at least 20 years. Work in this area began when BFG was investigating alternate rubber systems and was doing work on the Ring-Opening-Metathesis Polymerization (ROMP) of norbornene. This system was eventually commercialized and is currently sold under the Tradename Norsorex™ by AtoChemie. BFG continued its interest in cyclic olefins and looked towards higher Tg materials. In the late 1980's BFG launched its Telene® Reaction Injection Molding (RIM) Business based on ROMP Dicyclopentadiene (DCPD). Today this business is growing rapidly and has license in Japan (Nippon Zeon) and a Joint Venture in Europe. At the same time BFG was doing work in RIM, we were also exploring the possibility of entering an optical polymers business based on hydrogenated ROMP cyclic olefins. Ultimately, BFG decided that a two step process, one for polymerization and another for hydrogenation, was not competitive. Nippon Zeon proceed with this approach and commercialized Zeonex® optical polymers based on ROMP/hydrogenated cyclic olefins. BFG markets and distributes this material in North America. This material is useful in creating very precise optical components due the materials inherently low birefringence and low moisture absorption. One application area which, while attractive, has alluded this material is injection molded ophthalmic lenses. While initial trials were very successful, aging trials exhibited an issue surrounding crack propagation. It is postulated that an unusual strain rate dependency, namely brittle failure at low strain rates and ductile failure at high strain rates may be intimately related.

Other companies have also been attracted to the cyclic olefin arena. Japan Synthetic Rubber also launched a ROMP/hydrogenated polymer, but thus far it has stayed in the experimental stages. Hoechst and Mitsui have combined forces and are launching Topas™, a family of norbornene(NB)/ethylene copolymers made possible by recent advances in metallocene catalyst systems. This is an attractive route since it uses an addition polymerization mechanism and forms a saturated backbone directly, avoiding the costly hydrogenation step. Unfortunately, the resulting polymers are extremely brittle for Tg's greater than 100°C. Both ROMP/hydrogenated and NB/ethylene copolymers have a practical limit in Tg of below 200°C.

BFG had a recent catalyst breakthrough which makes possible the direct homopolymerization of norbornene and copolymerization with substituted norbornenes to afford materials with extremely high Tg's (greater than 350°C), low moisture absorption, low dielectric constant, and excellent optical properties. BFG is actively pursuing the tailoring of these materials for electronic and optical applications. These applications will be generally described. In tailoring these addition cyclic olefins for various applications it is desirable to control the glass transition temperature and increase toughness. This has been accomplished but at the expense of the modulus. This trade-off will be explored and the author encourages speculation on ways this could be alleviated.

SWITCHABLE PROTEIN ASSEMBLIES

David A. Tirrell

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There is striking disparity in the levels of control of macromolecular architecture found in natural polymers (particularly proteins and nucleic acids) on one hand, and in synthetic polymers, on the other. The precisely controlled architectures of proteins, for example, are critical to the selective catalytic, transduction, and transport processes that sustain the complex chemical processes of cells and organisms. We have yet to achieve such functions in synthetic polymeric materials systems, owing in part to our inability to exercise sufficient control of molecular and supramolecular architecture. With these issues in mind, we have been exploring the synthesis and characterization of artificial proteins for use in materials applications. The design of such materials draws on ideas taken from polymer chemistry and physics and from structural biology, and exploits the sequence control and chain-length uniformity provided by genetic engineering. Motivating much of this work is the question: "What kinds of new materials properties can be achieved only in uniform chain populations and not in the statistical mixtures of chains prepared by conventional polymerization processes?" Five issues are under study: i). design and fabrication of polymeric crystals of controlled thickness and surface functionality, ii). incorporation of non-natural amino acids, iii). synthesis of monodisperse, polar, helical rods and the prospects for their assembly into larger-scale structures, iv). hybrid proteins combining natural and synthetic domains, and v). controlled gelation of rod-coil-rod proteins in response to physical and chemical signals. Particular attention will be given to the molecular switching properties of artificial protein assemblies.

Ion-Conducting and Electroresponsive Multiphase Polymers

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Polymeric electrolytes are attractive materials for use in batteries, fuel cells and electrochromic devices, where high ionic conductivity coupled with good mechanical properties and non-volatility are key attributes of these polymers. Work in our laboratory has focused on the synthesis and characterization of polymers having high Li^+ or H_3O^+ conductivities, and several synthetic approaches toward this end will be discussed. High proton conductivity is essential in hydrogen-based fuel cells, and we have discovered inexpensive block copolymer membranes which meet this need. Partial sulfonation of styrene-ethylene/butylene-styrene triblock polymer followed by solvent casting affords elastomeric hydrogels with conductivities of 0.07-0.09 S/cm when fully hydrated. Electron microscopy reveals that the sulfonated block copolymers consist of microdomains with thicknesses in the range of 200-300Å. Hydrogen fuel cells utilizing these membranes for operation at room temperature using air and without hydration of hydrogen gas have been demonstrated. These novel hydrogels have other interesting characteristics, such as the ability to deform in electric fields. Also, as numerous redox-active molecules may be ion-exchanged into the films, they are useful as coatings for chemically modified electrodes. Finally, we have explored the use of ionomers as hosts for ionic lumophores as tunable electroluminescent devices, and preliminary results will be presented.