Program

Asilomar Conference

Twenty-Fourth Asilomar Conference on Polymeric Materials

February 4-7, 2001

Pacific, Grove, CA

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
February 12, 2001

3. REPORT TYPE AND DATES COVERED
7/1/2000 - 6/30/2001 - FINAL

4. TITLE AND SUBTITLE
Twenty-Fourth Asilomar Conference on Polymeric Materials

5. FUNDING NUMBERS
DAAD19-00-1-0457

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

RECEIVED
FEB 13 2001
By

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO
41483.1-CH-CF

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The 2001 Asilomar Conference on Polymeric Materials emphasized nanostructured polymeric systems. The conference included such topics as multifunctional dendrimers, nanoscale processing and fabrication, periodically modulated nanocomposites, nanoparticles and nanotubes in composites, and multifunctional supramolecular polymers. Application of these polymeric systems in permselectivity, photonic integrated circuits, optical switches, and as unique materials for nanoelectronics were discussed. Special emphasis was on the integration at the nanoscale of macromolecular, inorganic and biological materials. This year, in particular, the conference focused on the newly emerging nanostructured polymeric systems. Focus was also on important questions such as the factors that give rise to relatively discrete organizational levels of structure, the interactions between such levels and the synthesis of new linear and hyperbranched polymers with functional designs aimed at interface/interphase control. As in previous years, this conference addressed the problems and opportunities that are arising with the emergence of an hierarchical approach to the design of new materials systems.

14. SUBJECT TERMS
Nanostructured polymeric systems, multifunctional dendrimers nanoscale processing, nanoparticles and nanotubes, nanoelectronics, synthetic routes, macromolecular designs

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18

PROCEEDINGS

TWENTY-FOURTH ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

February 4-7, 2001

SPONSORED BY

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Research Triangle Park, North Carolina 27709

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February 4-7, 2001

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New Nanolayered Polymer Composites by Continuous Coextrusion

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

Nanolayer coextrusion technology makes possible continuous melt processing of films and sheets that can readily comprise thousands of layers containing two or more alternating polymers. Layer thicknesses have readily been made in the range of several microns down to ten nonometers by varying the number of layers and the layer composition.

Nanolayered films are of interest because of the potential for developing materials systems with novel mechanical, transport, electrical and optical properties. Since the radius of gyration of macromolecules can readily exceed the nanolayer thickness, the surrounding layers can be used to impart dimensional constraint at the molecular level. Examples will be given of polyethylene and polypropylene nanolayers undergoing constraint crystallization between surrounding thicker and stiffer amorphous layers. We have found new hierarchical morphologies which have promise as highly efficient reinforcing structures. Solid state orientation studies are currently being conducted to further achieve nanolayer thickness reduction. Ultimately, nanolayer break-up may provide molecular reinforcement between two dissimilar polymers (molecular blending).

Recently, we have invented nanolayered nonlinear dielectric optical structures that have a substantial modulation in the nonlinear dielectric constant across the sample. When the period of the modulation is on the order of the wavelength of light, these materials systems act as 1-D photonic crystals. Nanolayered materials, which have an intensity dependent transmission and reflection, can act as nonlinear mirrors, optical limiters; and, possibly function in optical switching and other opto-electronic devices. These new nanolayered materials were made by combining recent developments in nonlinear dyes with continuous nanolayer coextrusion technology.

Finally, new layered architectures leading to "block" and "gradient" structures will be revealed. As a result, the creation of new nanolayerd structures with carefully designed property spectra are entering a new stage of scientific exploration.

Twenty-Fourth Asilomar Conference on Polymers

Barry J. Bauer
NIST
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ABSTRACT

In recent years, the synthesis and structure of dendrimers have been extensively studied. Solution properties of dendrimers have been characterized at NIST, showing that high generation dendrimers are spherical with the tendency to order. They have interior structures that can incorporate a variety of molecules. Polyamidoamine (PAMAM) dendrimers have the ability to act as templates for the formation of metallic and inorganic nanoclusters such as gold or cadmium sulfide. Dendrimers can also be uniformly dispersed in a solid, polymeric matrix by the use of sequential polymerizations, such as by dissolving dendrimers in 2-hydroxyethyl methacrylate and polymerizing the solvent, or by reacting the terminal amino groups of dendrimers with end functionalized poly(ethylene glycol). Nanoclusters can be uniformly dispersed in these polymeric composites either by reacting dendrimers that contain nanoclusters, or by forming them inside composite structure. The structure of the dendrimer / nanocluster / polymer matrix has been extensively characterized by small angle neutron and x-ray scattering and by transmission electron microscopy. These new organic-inorganic hybrid materials may be important for a combination of optical, electronic, magnetic, or catalytic properties of the nanoclusters with the mechanical properties of the polymer network.

Structural Studies during Processing of High-Strength Fibers

by
Benjamin Chu
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The structure and morphology of spun polymer fibers are highly dependent on the spinning conditions used during processing. The crystallinity and the orientation of the polymer chains developed between the spinneret and the take-up device usually form the base for the mechanical performance of the fiber. There has been significant interest in fibers with high modulus and high tensile strength. Polybenzoxazole (PBO), which has a rigid-rod molecular structure, is one of the high performance fibers of great interest.

The general method for the manufacture of PBO fiber starts with a dry-jet wet-spinning process from a polymer solution. Often the solvent used for processing PBO is polyphosphoric acid (PPA). With a PBO molecular weight of _10,000 and a concentration of around 13-15% in PPA (often called "dope"), the solution extruded from the spinneret can develop lyotropic liquid crystalline characteristics. Fibers drawn from such a solution can achieve a high degree of orientation. The fiber structure in the liquid crystalline state is fixed by coagulation with water. Post processing, such as heat-set under tension, can further enhance the fiber strength. Thus, it is very interesting to study the changes of structure and morphology *in situ* during the spinning and the coagulation processes.

Wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS) are routine methods for investigating the structure and the morphology of oriented polymers. However, the scattered intensity from polymer fibers is often weak, seriously limiting the applicability of these methods to monitor the fiber processes in real time. For PBO, the case may even be more severe because the PBO draw ratio can be as high as 40, resulting in the formation of very thin (~50 μm) monofilament fibers, containing most of the PPA in a composition that is a very strong X-ray absorber. Fortunately, with brilliant synchrotron X-rays, high quality SAXS/WAXD patterns from either monofilament or small bundles of the fiber can be obtained using a relatively short data collection time period. Thus, synchrotron X-ray scattering and diffraction techniques have become extremely important probes to perform on-line characterizations of structural and morphological changes during fiber processing.

In this lecture, SAXS/WAXD results during the solution spinning of PBO fibers at the X27C Advanced Polymers Beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) will be discussed, in terms of different stages of processing from (1) before coagulation, (2) after coagulation, (3) as-spun fiber, to (4) heat-treated fiber. Quantitative results of the structural and morphological changes in the fibers under different spinning conditions will be presented, mainly by using a unique image analysis method.

Kinetics and Mechanisms of Morphological Changes in Block Copolymers in Solution

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ABSTRACT

The self-assembly of block copolymers, especially in solution and on surfaces, has been the subject of intense research. In this group, we have shown that highly asymmetric amphiphilic block copolymers (consisting of short soluble and long insoluble blocks) can yield, in aqueous solution, crew-cut aggregates of a very wide range of morphologies and sizes, including spheres, rods, bicontinuous structures (both rod-like and tubular), lamellae, vesicles, a well as a range of compound structures, which are described briefly. Both thermodynamic and kinetic aspects are involved in the formation of the aggregates; their relative importance varies depending on the detailed conditions. From the thermodynamic point of view, the three parameters which are morphogenically most relevant are core chain stretching, corona chain interactions and interfacial energy. Anything that can influence one or more of these parameters is a morphogenic factor. These include, among others, block length ratios, water content, presence and type of microions, nature of solvent and temperature. Partial morphological 3 component phase diagrams are presented which explore the effect of several variables; also, it is shown that several of the observed structures, including the vesicles, have been quenched from an equilibrium state. The kinetics and mechanisms of two transitions are discussed in detail, i.e. the sphere to rod and the rod to vesicle transitions, as well as the reverse processes. Finally, it is shown that many of the structures seen in these block copolymer systems bear a strong resemblance to intracellular morphologies.

Mechanical assembly of oligomers and polymers on elastomer surfaces[1]

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It is well known that the surface properties of materials, such as wetting and lubrication, can be successfully tailored by terminally attaching various organic modifiers. Typically, self-assembled monolayers (SAM) are utilized to prepare chemically and structurally well-defined surfaces. Because SAMs are formed through self-assembly the packing density of the SAM is set by the interplay between the chemical and structural nature of the SAM molecules and the means of their attachment to the substrate. In some situations, the fixed packing density of the SAMs limits the stability of the monolayer and its resistance to surface reconstruction.

We have recently developed a novel method of independently controlling the grafting density of end-anchored molecules on substrates.[2] The technique is based on combining: 1) the grafting reaction between chlorosilane moieties and surface hydroxyl functionalities, and 2) mechanical manipulation of the surface grafting points. An elastomeric network film is stretched (by Δx) and treated with UV/ozone to produce the surface hydroxyl groups. Chlorosilanes are deposited from vapor and form a SAM. The strain is subsequently released from the substrate, which returns to its original size, causing the grafted molecules to form a densely organized "mechanically assembled monoloayer" (MAM). As a proof of concept we created MAMs from semifluorinated molecules (SF-MAMs). Our experiments reveal that the SF-MAM surfaces are super-hydrophobic; the water contact angle increases with increasing Δx and culminates at a value of 135° for $\Delta x \approx 80\%$. These SF-MAMs are highly resistant to surface reconstruction - while SF-SAMs on non-stretched surfaces reconstructed only after several hours, the surfaces of SF-MAMs immersed in water for 7 days (followed by a subsequent storage under ambient laboratory conditions for 6 months) stayed virtually unmodified.

Recently we have extended the MAM technology to produce polymer brushes with variable grafting densities using MAPA (="mechanically assisted polymer assembly").[3] MAPA is based on: 1) chemically attaching polymerization initiators to the surface of an elastomeric network that has been previously stretched by a certain length, Δx, and 2) growing end-anchored macromolecules using surface initiated ("grafting from") atom transfer living radical polymerization. After the polymerization, the strain is removed from the substrate and the grafted macromolecules stretch away form the substrate forming a dense polymer brush. We demonstrate the feasibility of MAPA by preparing high-density polymer brushes of poly(acryl amide), PAAm. We show that, as expected, the grafting density of the PAAm brushes can be increased by increasing Δx.

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[1] Supported through the NSF CAREER award and NCSU's College of Engineering start-up funds.

[2] J. Genzer and K. Efimenko, *Science* **290**, 2130 (2000).

[3] T. Wu, K. Efimenko and J. Genzer, *Communication to the Editor of Macromolecules*, in press.

Synthetic Strategies toward Novel Metallodendrimers and Biodendrimers

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Dendrimers are globular monodisperse polymers composed of repeating branching units emitting from a central core. These macromolecules are synthesized using either a divergent (from core to surface) or a convergent (from surface to core) approach. Since the reports by Tomalia and Newkome, this research area has undergone tremendous growth in the last decade. Compared to linear polymers, dendrimers have small polydispersity indexes (PDI) with well-defined interior and exterior regions, possess high surface area to volume ratios, and exhibit numerous end groups for functionalization. Our laboratory is synthesizing and characterizing novel metallodendrimers and biodendrimers.

Metallodendrimers are of wide-spread interest for potential uses as light harvesting collectors, high density information banks, multi-wavelength sensitizers, and molecular electronic sensors. We are using an automated, solid-phase, and efficient approach to synthesize well-defined ruthenium dendrimers, based on advances made in automated DNA synthesis. We have prepared a ruthenium complex as well as an organic branching linker that both possess: 1) a primary hydroxyl protected with the acid labile dimethoxy trityl group, and 2) a secondary hydroxyl derivatized with a cyanoethyl diisopropylphosphoramidite group. These monomers are amenable for use in an automated DNA synthesizer for constructing ruthenium dendrons and dendrimers.

Biodendrimers are a new class of dendritic macromolecules composed entirely of building blocks known to be biocompatible or degradable *in vivo* to natural metabolites. These new biopolymers are of potential interest for a variety of applications ranging from drug delivery to tissue engineering. We will report the divergent synthesis and characterization of a first, second, and third generation dendrimer composed of glycerol and lactic acid. These poly(glycerol-lactic acid) dendrimers (**PGLLA**) possess a number of favorable properties for medical applications.

Tuning Polymer Topology by Transition Metal Catalysis

Zhibin Guan
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Abstract

This presentation will discuss our recent efforts on the control of polymer topology using late transition metal catalysts, with the goal of creating polymers with new topologies from simple existing monomers. In the first strategy, hyperbranched polymers were synthesized by controlling the competition between propagation and chain transfer for free radical polymerization of divinyl monomers using a special chain transfer catalyst (SCT).[1] Controlled by the SCT catalyst, the free radical polymerization of divinyl monomers gives soluble hyperbranched polymers instead of insoluble networks. The intrinsic viscosity of the hyperbranched polymers is much lower than that of their linear analogs and shows no dependence on molecular weight. The low solution viscosity and the high functionalities of these hyperbranched polymers make them promising materials for practical applications such as surface coating and photo-polymerization. In the second strategy, polyethylene topology was successfully controlled by regulating the competition between propagation and "chain walking" for ethylene polymerization using the Brookhart's palladium-α-diimine catalyst.[2] We demonstrated that polyethylenes with a full spectrum of topologies could be obtained by simply changing ethylene polymerization pressure. Although the total branching density and the distribution of short chain branches are relatively constant, the branching topology changes dramatically with polymerization pressure, varying from linear with many short branches at higher ethylene pressures to a densely branched, arborescent globular structure at very low ethylene pressures. Polymers synthesized at the lowest ethylene pressure exhibited dilute solution parameters similar to those observed for dendrimers or many-armed stars, and segment density approaching that of a hard sphere. Our ability to produce polymers with continuous topologies without changing the chemical structure provides a unique opportunity for fundamental investigation of the topological effects on polymer physical properties.

References:
1. Zhibin Guan *US Patent 5767211.*
2. Zhibin Guan, P. Cotts, E. McCord, S. McLain *Science* **1999**, *283*, 2059.

Structure-Property Relationships in New Olefin Copolymers

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The homogeneous comonomer distribution and relative narrow molecular weight distribution of metallocene ethylene copolymers make them excellent models for studying structure-property relationships of ethylene copolymers and miscibility behavior of ethylene copolymer blends.

The copolymers offer a broad range of solid state structures and properties from highly crystalline thermoplastics to amorphous rubbers and glasses. Copolymers of ethylene with styrene (ESIs) are compared with the more extensively studied homogeneous ethylene-octene copolymers. Combined observations from a variety of experimental techniques reveal that the crystalline phase depends on the amount of comonomer but is not strongly affected by whether the comonomer is styrene or octene. This is consistent with exclusion of both comonomers from the crystal. However, large differences in the amorphous phase arise from the higher glass transition of ESIs. These features have important implications for the deformation behavior.

Binary blends of ESIs are miscible if the difference in styrene content is less than about 9 wt%. In a very small range of compositional differences, estimated from 9-10 wt% styrene, partial miscibility is clearly evident. Despite the chemical similarity of the blend components, the phase diagram of partially miscible blends can be obtained with AFM. Analysis of the phase behavior requires consideration of the molecular weight distribution even though the polydispersity of ESIs is relatively small. One consequence of the molecular weight distribution is the dependence of phase composition on initial blend composition. This is because lower molecular weight fractions are more soluble in the other blend component than higher molecular weight fractions. The interaction parameter obtained by considering molecular weight distribution is independent of molecular weight and is proportional to the square of the styrene content difference.

Polarizable Electret Polymer Films Fabricated Nanolayer-by-Nanolayer

Presenter: Geoffrey A. Lindsay, US Navy, China Lake, CA

Co-Authors: M. Joseph Roberts, Andrew P. Chafin, Richard A. Hollins, Peter Zarras,
John D. Stenger-Smith, Larry Merwin, US Navy, China Lake, CA
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ABSTRACT

Progress will be reviewed on ambient-temperature processing of thin-films of novel chromophoric polymers that are of interest primarily because of their second-order nonlinear optical properties useful in high bandwidth optical modulators. These films may also have useful piezoelectric and pyroelectric properties. Several thin-film processing techniques were investigated, including the Langmuir-Blodgett method, the alternating polyelectrolyte deposition method, and variations of these. Novel chromophoric polymers were prepared with structural motifs purposefully designed to impart polar order in the film during layer-by-layer processing. Understanding thestructure-processing-properties relationships has been a major part of this study, and there is yet much to be learned. Retaining polar order in the multilayer films as hundreds of monolayers are deposited, minimizing the optical scattering, and achieving long-term thermal stability above 85 *C are major goals.

Nano-analytic Techniques for Determination of Micromechanical Effects in Heterogeneous Polymers

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Structure or morphology and mechanical properties of polymeric materials are linked by the micromechanical processes of deformation and fracture, i.e. by micromechanics. Improved knowledge of the micromechanical processes provides a very direct way of improving the mechanical properties of polymers. The term „micromechanics“ covers all processes on mesoscopic, microscopic, and nanometer scales that occur inside a material in response to an external mechanical loading. On the one hand these processes strongly depend on the diverse molecular structures and the morphology of the polymeric materials. On the other hand they are influenced by loading conditions such as temperature, loading velocity or stress state. Therefore, the micromechanical mechanisms show a very broad variety.

To study directly micromechanical processes three main electron microscopic (EM) techniques exist: The first is the investigation of fracture surfaces in the SEM or in the ESEM. The second is the deformation of bulk material, followed by investigating the changes at the surfaces by SEM or ESEM. Changes inside the bulk material are studied by preparing ultrathin sections by using an ultramicrotome and investigating by TEM. The third is the deformation of thin films or semithin sections in a tensile device and investigation of the deformed sample directly by SEM, ESEM, TEM, HVEM or SFM. Since these techniques also allow to study morphological details, they enable us to investigate structure-property-corelations in a very direct way. When going from the first technique to the second and third techniques more details of micromechanical processes are revealed and investigated in their dependence on real morphology. The second and third techniques enable investigation of morphology and of deformation processes with high resolution. Some of the tensile devices enable one to perform deformation tests at lower or higher temperatures (from
-180^0C up to $+200^0$C).

Using the different techniques several polymers have been studied:

- Blends of HDPE and VLDPE: Particles of highly branched VLDPE (very low density PE) in a matrix of HDPE (high density PE) initiate a pronounced plastic deformation of the adjacent matrix strands. Because of the total absence of radiation damage in the SFM (atomic force microscope) a real *in situ* study of deformation processes of the crystalline lamellae and the interlamellar amorphous regions is possible.

- Starblock copolymers of PS/PB with lamellar structure: Thin PS layers with thicknesses smaller than a critical thickness are deformed without any crazes in a homogeneous manner up to several 100%. This effect of „thin layer yielding“ can be used as a new toughening mechanism.

Soft Material Science of Self-Assembling Fuids

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When most people think of the "materials" in materials science they think of solid objects that can be held in your hand. Fluids can also be tailored, high technology materials – however they run through your fingers! In this presentation we discuss some high technology applications of fluids that are a result of self-assembly. The first section covers problems involving the interactions between surfactant structures and soluble polymers. The second involves self-assembly in the formation of organic nanoparticles.

I. Polymer-Surfactant Systems

The first problem involves the control of surfactant self-assembly to tune rheology. In several applications it is desirable to have a fluid with tunable rheology that resists irreversible shear degradation. Examples of these applications include oil field drilling fluids, lubricants for machine tools, and agricultural spraying. If high molecular weight polymers are used to control rheology, shear degradation occurs and fluid viscosity drops over time. However, if rheology is controlled by weak, reversible (hydrophobic) interactions these associations can break in strong shear fields and reform under lower shear. This leads to stable and tunable fluid rheology. Neutron scattering under shear is used to clarify the structure of the association fluid in the case of hydrophobically modified polymers interacting with rod-like surfactant micelles.

The second problem involves the miscibilization of polymers in concentrated surfactant phases. Polymers do not mix with surfactant lamellar or hexagonal phases because the polymer suffers too great a loss of configurational entropy. By balancing the entropy loss with the gain of hydrophobic interaction energy it is possible to miscibilize the system. Using neutron scattering we show the effect on the surfactant membrane stiffness of the interacting hydrophobically modified polymer.

The third problem involves templating polymerizations with surfactant mesophases. For several oil/water/surfactant systems "cubic phases" can be obtained which are periodic, oil and water bi-continuous structures. We have successfully polymerized monomers in the aqueous phase to produce regular micro-porous gels with periodicity of 5 to 800 nm. These materials offer interesting opportunities for new classes of separation media, filtration media, and enzyme encapsulation supports.

Finally, block copolymer assembly can be used to protect organic nanoparticles to allow formation of pharmaceutical formulations. It is difficult to form organic nanoparticles by precipitation or crystallization at high concentrations because the high supersaturation levels produce growth too rapid to be controlled at the nanometer scale. The incorporation of block copolymers that co-precipitate with the drug offer a means of controlling particle aggregation if the kinetics of polymer micellization can be matched to the kinetics of nucleation and growth. Also, the mixing must be sufficiently rapid to have micromixing faster than the kinetics of nucleation and growth so that uniform particle size can be achieved. Impingement mixing at high energy levels is used to produce rapid micromixing.

BIOMIMETICS:
NANOMATERIAL DESIGN AND ASSEMBLY VIA BIOLOGY

Mehmet Sarikaya,*
with Francois Baneyx,+ Malcolm Snead,# & Stanley Brown§
*Materials Science & Eng., & +Chemical Eng., University of Washington, Seattle, WA, USA; #
Craniofacial Molecular Biology, University of Southern California, Los Angeles, CA, USA; &
§Molecular Biology, University of Copenhagen, Denmark

Structural and compositional control of inorganic materials at the molecular-scale is a key in the synthesis of novel functional material systems. Biological hard tissues are models for engineering materials as biocomposites have excellent combination of physical properties due to their highly controlled chemistry, structures, dimensions and morphologies. In addition to an inorganic phase, a common denominator in all hard tissues (bacterial particles, ordered films, spicules, spines, shells, bones and dental tissues, A-D) is the presence of polymeric biomacromolecules (proteins and polysaccharides) that may be enzymes, nucleators, habit modifiers, and scaffolds, and control intricate nano-and micro-structures of biocomposites from the molecular to the macro-levels through biochemical interactions.

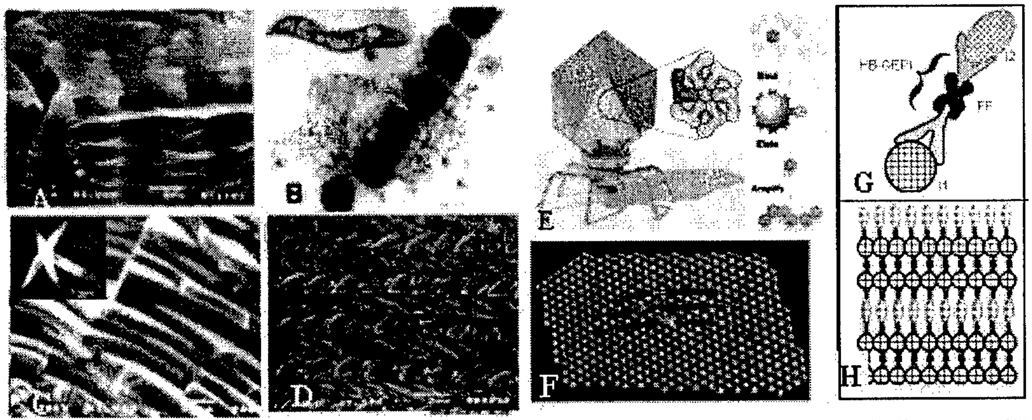

Figure: Biological functional hybrid nanostructures: (A) Growth edge of abalone shell, nacre (*Haliotis rufescens*); (B) Magnetite (Fe_3O_4) nanoparticles in magnetotactic bacteria (*Aquaspirillum magnetotacticum*); (C) Layered, non-crystalline siliceous spicule of a sponge spicule (*Rosella*), a waveguide (D) Intricate cross-hatched rods, bundles of ultrafine hydroxyapatite crystallites, in the enamel (mouse tooth). (E) Principle of phage display for selecting genetically-engineered proteins for inorganics (GEPI); (F) Conformation of GEPI on a gold lattice. (G) and (H) Principles of heterobifunctional GEPI and its use in 3D assembly of nanoparticles.

For developing truly biomimetic material systems for practical engineering applications, we must address three issues. The first is a fundamental understanding of the processes in which proteins control formation and 2- and 3-D organization of inorganic phases. As we will demonstrate, proteins' role in various biosynthesis stages involves collection and transport of inorganic ions, co-assembly into arrays of nuclei, and regulated growth into size and morphology leading to a hybrid multifunctional system (A-D). The second issue concerns with engineering proteins with affinity to inorganic surfaces. Although proteins can be isolated from hard tissues using biochemical approaches, a more practical strategy is to use genetic engineering techniques. Combinatorial biological techniques, phage display (E) and cell-surface display, allow isolation of polypeptides with specific recognition elements for inorganic surfaces (F), including those not realized by natural proteins, in the absence of *apriori* prediction of necessary structures. Finally, in the third area, we will discuss the use of GEPI in materials nanoassembly (G & H). Genetically-engineered proteins have potential significant implications in tailoring surfaces, formation and assembly of ordered and complex structures of metals, functional ceramics, polymers, semiconductors, ferroelectrics, and magnetics in applications of nanotechnology, smart materials, bioimplants, drug delivery, tissue engineering, and molecular electronics.

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Twenty-Fourth Asilomar Conference
on Polymeric Materials
February 4-7, 2001

"Bibenzoate Polyesters – Materials of Intermediate Structure"

David A. Schiraldi
KoSa

Abstract

Polyesters based on the rigid rod monomer, 4,4🕯-bibenzoic acid are known to form structures ranging from those of typical semicrystalline thermoplastics, to those of liquid crystals. Copolyesters containing 4,4🕯-bibenzoic and terephthalic acids and ethylene glycol, exhibit a range of orientation-dependent behaviors, depending on specific composition and orientation conditions. These behaviors, and their effects upon fibers and barrier film properties, will be discussed.

Invited talk to be presented at the Twenty-Fourth Asilomar Conference on Polymeric Materials, Pacific Grove, California, 4-7 February 2001.

NANOPARTICLE AND NANOTUBE FILLED COMPOSITES

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It is now possible to create a variety of nanostructured composite materials with novel properties using polymer, ceramic, and carbon nanoscale building blocks [1]. The properties of these nanocomposites are dramatically different from the corresponding matrix material and they can be engineered by means of careful control of filler dispersion. For example, ceramic/polymer nanocomposites can exhibit superior scratch resistance, increased values of modulus combined with increased strain to failure, enhanced dimensional stability, and novel interactions with biological cells [2-4]. On the other hand, carbon-nanotube/ceramic nanocomposites can exhibit significantly increased fracture toughness while maintaining high hardness values [5]. Also, carbon-nanotube/polymer nanocomposites can have an increased modulus, with a larger increase in compression than in tension, and an eight order of magnitude increase in electrical conductivity at low filler volume fractions. An overview of some recent results on nanostructured composites will be presented along with a discussion of some future opportunities and challenges in this exciting new area.

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Polymeric Nano-materials – Ionomers and Nanotube Composites

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Polymers with nano-scale structures include ionomers, nanocomposites, and block copolymers. During this presentation I will focus on our application of new experimental tools to the study of ionomer morphology and our application of polymer processing methods to the production of nanotube-polymer composites.

Ionomers are critical materials in coatings, adhesives, packaging and fuel cells and are currently being explored for additional applications involving permselectivity. Ionomers owe their valuable properties to the acidic monomeric units that are neutralized with cations and subsequently assemble into nano-scale aggregates. The structure of these ionic aggregates has long been the subject of SAXS studies. In contrast, we are applying scanning transmission electron microscopy (STEM) and more recently analytical transmission electron microscopy (ATEM) methods to determine ionomer morphology. Results will be presented for various materials including semi-crystalline polyethylene-based ionomers and amorphous polystyrene-based ionomers. The former show primarily spherical aggregates, while the latter exhibit vesicular aggregates.

Individual carbon nanotubes have demonstrated far superior mechanical, thermal and electrical properties relative to carbon fibers. Thus, an obvious direction is to produce nanotube-polymer composites in an attempt to harness these extraordinary properties. I will describe our early successes in producing polymer composites with single-wall carbon nanotubes and their subsequently enhanced mechanical and electrical properties. By using polymer melt processing methods we obtained outstanding nanotube alignment, as measured by Raman spectroscopy. Work continues as we extend the range of matrix polymers to include thermosets.

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