PROCEEDINGS

TWENTY-SECOND ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

February 14-17, 1999

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SUBMITTED BY

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13. ABSTRACT *(Maximum 200 words)*

At the 1999 Asilomar Conference on Polymeric Materials emphasis was on advanced polymers in nanostructural materials. The conference included such topics as fullerenes, nanotubes, dendrimers, nanofibers, and nanostructured organic/inorganic hybrid materials. Both synthetic polymeric materials and biological systems were considered. Special emphasis was on such issues as durability, property enhancement, compatibility, and on integration with inorganic, polymeric, and biological compounds. This year, the conference focused on the newly emerging nano materials systems. As in previous years, the conference addressed the problems and opportunities that are arising with the emergence of a hierarchical approach in the design of new materials systems. Such an approach may prove invaluable in the design of new polymers in nanostructured materials, their blends and composites, novel processing, and advanced materials systems in general. Focus was 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 polymers with functional designs aimed at interface/interphase control.

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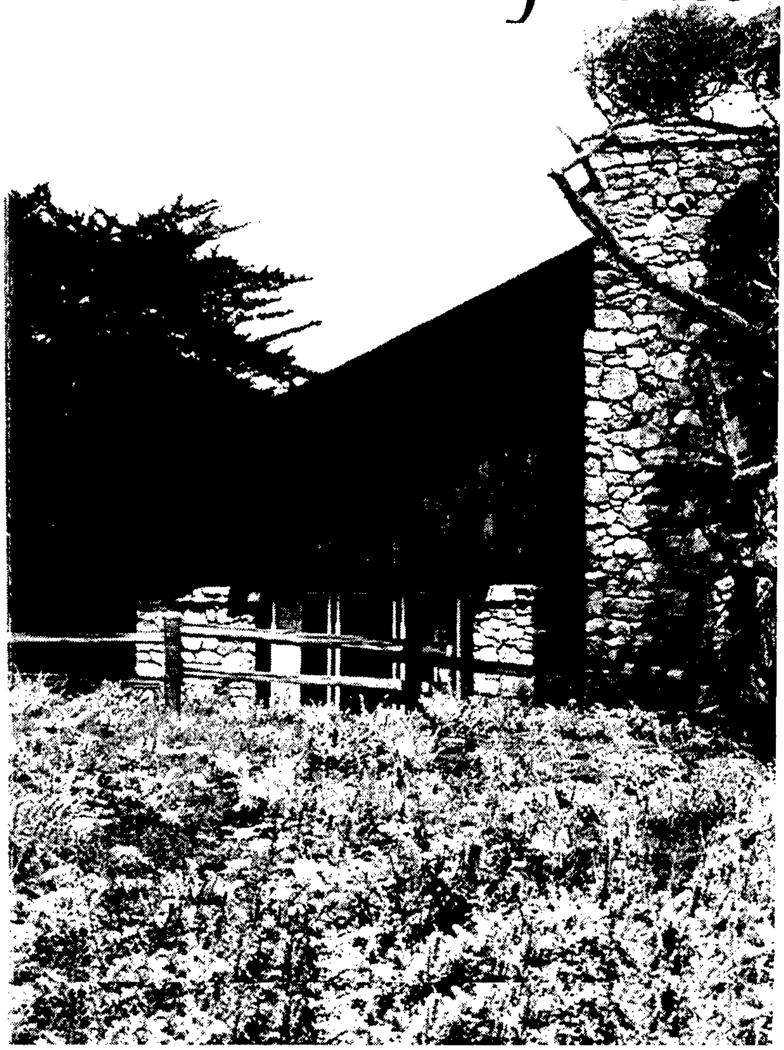
Asilomar Conference



Twenty-Second Asilomar Conference on Polymeric Materials

February 14-17, 1999

Pacific Grove, CA

Twenty-Second Asilomar Conference on Polymeric Materials
February 14-17, 1999

Invited Speakers

"Microlayer Structures with Anisotropic Conductivity"
Professor Eric Baer
Case Western Reserve University
Cleveland, OH

"Interfacing with Nature"
Professor Caroline Baillie
Imperial College
London, England

"Patterned Self-Assembled Polymeric Systems"
Professor Paula Hammond
Massachusetts Institute of Technology
Cambridge, MA

"Stress Management in Polymers: Insights from Atomic Force Microscopy"
Professor Paul Hansma
and
Professor Helen Hansma
University of California
Santa Barbara, CA

"Advanced 3-Dimensional Nanoscopic Materials for the Next Generation of Computers"
Dr. Craig Hawker
IBM Almaden Research Center
San Jose, CA

"Structure Property Relationships of Hyperbranched Polymers"
Professor Anne Hiltner
Case Western Reserve University
Cleveland, OH

"An Electronic Nose from Arrays of Polymer Composite Vapor Sensors"
Professor Nathan Lewis
California Institute of Technology
Pasadena, CA

"Mechanisms of Morphology Development and Control in Polymer-Polymer Blends"
Professor Chris Macosko
University of Minnesota
Minneapolis, MN

"Suprasupermolecular Chemistry: Chemistry within the Dendrimer"
Professor George Newkome
University of South Florida
Tampa, FL

"Elastomeric Nanocomposites"
Dr. Dennis Peiffer
Exxon Research and Engineering Company
Annadale, NJ

"Polymer Nanofibers"
Professor Darrell Reneker
University of Akron
Akron, OH

"Characterization of Nanostructures by Phase Separation and Crystallization"
Professor Richard Stein
University of Massachusetts
Amherst, MA

"Dendrimer-Based ALERT Ticket"
Dr. Ray Yin
US Army ERDEC
Aberdeen Proving Ground, MD

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February 14-17, 1999

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Abstracts

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22nd Asilomar Conference on Polymers
February 14-17, 1999

Microlayer Structures with Anisotropic Conductivity

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ABSTRACT

This lecture will focus on the processing of microlayered polymer composites with anisotropic electrical properties. Continuous layer-multiplying coextrusion offers a new approach for processing metal-filled polymers into conducting structures. In this process, filled and unfilled polymers are combined into unique structures with many alternating layers of two or more components. The total number of layers can range from tens to thousands. The ability of microlayering to "organize" anisotropic particles was used to obtain metal-filled polypropylene tape with highly anisotropic electrical properties. Orientation of metal flakes by microlayering increased the anisotropy in resistivity by two orders of magnitude over compression molding. Isolation of individual filled layers by alternating filled and unfilled layers resulted in materials with many independent conducting pathways. Filled layers with 10% (v/v) copper flakes or 15% (v/v) nickel flakes were conductive only if the filled layers were thick compared to the thickness of the flake particles. When the thickness of the filled layers approached the particle thickness, the conductive properties were lost. This behavior was understood by comparing the three-dimensional arrangement of flakes in thick conductive layers with the two-dimensional particle layout of thin non-conductive layers.

In preparation for additional studies with microlayered systems, the electrical and mechanical properties of a carbon filled elastomeric polyethylene copolymer were investigated. Carbon blacks and carbon fibers were blended into the matrix at various concentrations. The percolation thresholds of these composites ranged between 5% and 15% filler concentration and was dependent on the type of filler. With the carbon blacks, the electrical resistance is very reversible under cyclic deformation. However, in the case of carbon fibers, large variations in the resistance is observed that decreases under cyclic loading. Interpretations of these results involve the filler geometry and changes in filler-matrix interactions which occur upon stretching.

INTERFACING WITH NATURE

Caroline Baillie
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and Medicine

ABSTRACT
for
Asilomar Conference February 14-17, 1999

Biomimetics, bionics or simply learning from nature is an emerging approach to solving scientific or other issues by looking to nature to see what solutions might be inspired. An example of a well studied natural material is wood. It's structure and properties have been investigated for many years although rarely from a materials science perspective. This paper attempts to focus on a particular aspect of the natural polymer composite structure, that of the interface. In engineered fibre composites the interface is the most important feature as it is the medium by which the stress is transferred from the matrix to the fibres so that they may bear the load. Much research has been focussed on optimising the interfacial stress transfer, as it is always suggested that the interface needs to be weak for high toughness and strong for high strength of the composite. More recent studies have suggested that it may be moreadvantageous to create an interface which is not destructive in itsenergy absorbing capacity. This paper looks in a qualitative way, at the three different interfacial crack paths which may be likened to those occurring in engineered composites: interfacial, interlaminar, and intercellular (bundle/bundle interaction) and their proposed relation to energy absorption mechanisms. It also explores the influence of moisture on these fracture paths.

Hoof horn has also been identified as an extremely tough natural composite with a unique three dimensional structure composed of fibres embedded in a matrix. Fibrous composite materials are designed to optimise the properties of both components and there has been much effort in recent years to improve the three dimensional performance. For aerospace applications in particular delamination has been the subject of much research and alternative ways of Esewing together the laminates has been explored. Ancient weaving technology is often employed. Unlike other natural animal materials such as bone, keratin is a non-living tissue that cannot undergo remodelling and repair and as such it is of great importance as a subject of study for engineered composites which are also non-living. This paper explores the unique structure of hoof horn and considers possible implications of the structure on properties of this three dimensional composite.

Finally implications of this approach of studying natural materials will be considered in the light of results of the present Biomimetics focus group of Wissenshaftskolleg (Institute for Advanced Studies) Berlin 1998/1999.

PATTERNED SELF-ASSEMBLED POLYMERIC SYSTEMS

by

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ABSTRACT

Layer-by-layer assembly provides an excellent means to the supramolecular control of ultrathin film architectures, making it an inexpensive and economically viable approach to the design of polymeric thin films for electro-optical, sensor, membrane, and other applications. The basis of this process is the alternating adsorption of monolayers of oppositely charged polyions, enabling one to tailor properties within nanometer sized layers of a heterostructure. We have explored a means of confining the deposition of these layered structures to micron sized regions of the substrate surface using chemically patterned surfaces as templates. Self assembled monolayers (SAMs) functionalized with endgroups which promote and prevent adsorption are selectively attached to a metal or metal oxide surface. During the layer-by-layer process, specific regions promote adsorption while alternate sections of the surface prevent adsorption of the polyion film, resulting in patterned thin films with micron sized features. Initial work includes the establishment of adsorption conditions for the adsorption of strong polyelectrolytes that produce positive or reverse patterned images based on the ionic content and other processing conditions.

We have moved this concept toward the direction of weak, pH dependent polyelectrolyte systems which are more relevant to a number of electro-optical polymer and dye materials. In doing so, we have found that the selectivity of deposition is extremely sensitive not only to pH, but to the choice of polyamine or polyacid used in the layering process. Hydrogen bonding and hydrophobic interactions at the surface are important, and influence the relative amount of material deposited on the two surfaces. For example, the use of branched versus linear polyamines results in a marked difference in the preferred adsorption sites on the surface; these results are thought to be due, in part, to a difference in the ability of primary versus secondary amines to take place in hydrogen bonding, and in varying amounts of hydrophobicity along the polymer backbone.

Ultimately, the goal is to incorporate optically functional systems into these multilayer systems, and to form complex polymer microstructures unobtainable by conventional lithography. This has been demonstrated with the use of sulfonated electroluminescent dyes to form patterned organic luminescent thin films. Other systems, such as electrochromic viologens and polyviologens, are also under study. More complex patterned systems have been created by combining the knowledge of deposition conditions for various polyion pairs with our ability to vary process conditions from layer to layer. In this way, we have been able to adsorb new multilayers in the interstitial regions of an original patterned polyion film; this ability could lead to a number of interesting devices, including multiple color LED's and novel laterally patterned electroactive components. Finally, new approaches to the formation of a second set of patterns atop original patterns is currently being developed, and will be addressed.

STRESS MANAGEMENT IN POLYMERS: INSIGHTS FROM ATOMIC FORCE MICROSCOPY

by

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ABSTRACT

Atomic Force Microscopy of biopolymers is providing insights about a number of biological systems, including the abalone shell. The abalone shell must resist the stresses from predators such as otters armed with rocks if the abalone is to survive. The shell has, in fact, awesome mechanical properties. It is 97% calcium carbonate, but it is 3000 times more fracture resistant than a single crystal of calcium carbonate. The secret behind this fracture resistance is in the polymer adhesive that holds the shell together. The properties of this adhesive have been revealed in single-molecule pulling experiments with the Atomic Force Microscope. The secret is that the polymer molecules in the adhesive, including the recently sequenced protein Lustrin, are compacted into domains with bonds that require forces of order 100 to 500 picoNewtons to break open. These forces are lower than the force, 1 to 2 nanoNewtons, needed to break a strong bond such as the covalent bonds in the polymer backbone. As stress is applied, these polymers unfold rather than break, absorbing relatively large amounts of energy: of order 3000 times more energy than required to break a strong bond in a rigid single crystal.

Advanced 3-Dimensional Nanoscopic Materials for the Next Generation of Computers

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The continued prosperity of the global microelectronics industry (< $100 billion) is directly dependent on maintaining a continuing improvement in the control of structure on the nanometer scale. A key strategy in the future is to employ advanced concepts in chemistry to control structure and function on this size scale. We will demonstrate this concept by examining two critical cases, new polymers for lithography, and novel nanoporous materials for insulators.

In the development of advanced photoresists we have examined the effect of macromolecular architectures and structure on lithographic performance with special attention being paid to molecular weight and polydispersity control. The requirement of reactive and polar functional groups along the backbones of these polymeric photoresists precludes the use of anionic or cationic living polymerization procedures for their preparation. ëLivingí free radical procedures based on well defined alkoxyamine initiators were therefore developed for the synthesis of the desired block and graft copolymer structures. To permit large-scale synthesis of these materials, an improved synthesis of alkoxyamines was also developed based on the use of manganese based asymmetric epoxidation chemistry and Jacobsenís reagent.

In designing ultra-low K dielectric materials, accurate control of macromolecular architecture and structure has also been exploited in developing a novel 'reactive blending' approach to the templation of nanoscopic structure in thermosetting inorganic resins, such as silsesquioxanes. In this approach a mixture of the silsesquioxane organosilicate (SSQ) and a specifically engineered dendrimer are dissolved in a common solvent and simply spin-cast onto a silicon wafer. The thin film is then heated to ca. 200(C to vitrify and crosslink the blend of dendrimer and inorganic SSQ, thus locking in the templated nanostructure. Further heating to 400-450(C will decompose the organic dendrimer resulting in release of volatile fragments, which can then diffuse out of the matrix to give the desired nanoporous organosilicate. It is this nanoporous structure which leads to ultra-low dielectric constants of 2.0 or less.

Unlike linear polymers which cannot be used in this application, many of the unique features of dendrimers such as lack of chain entanglement, increased solubility, hindered diffusion in viscous media, and a large number of accessible chain ends can be exploited to enhance compatibility with the silicate network and control the decomposition profile. For example, the number and nature of the end groups, the length of the oligomeric arms and the overall molecular weight all play critical roles in determining the usefulness of these hybrid dendritic-linear templating agents.

Structure Property Relationships of Hyperbranched Polymers

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ABSTRACT

Structure-property relationships were studied in a series of hyperbranched polyesters based on dimethoxypropionic acid with ethoxylated pentaerythritol as the core. In thermograms, all the polyols exhibited a prominent glass transition and a small melting endotherm. By adapting a method used to calculate the glass transition temperature of dendritic polymers, it was possible to estimate the glass transition temperature of hyperbranched polymers. Because the glass transition occurred near ambient temperature, small changes in the glass transition temperature with generation number had a large effect on the mechanical properties. Polyols that were above the glass transition temperature were ductile. Polyols that were below the glass transition temperature were brittle. On the basis of X-ray diffraction measurements and atomic force microscopy, a hierarchical model of the polyol in the solid state is suggested. When deposited from dilute solution, the polyols form monolayer aggregates of spherical molecules. However, as a consequence of variations in arm length and degree of branching, the polyol molecules tend to be disk-shaped when molded into films and may stack into layered structures. Interactions between molecules are provided by hydrogen-bonding of terminal repeat units and possibly cocrystallization of linear segments. The observation of a yield stress indicates that the intermolecular associations provide a level of resistance to deformation. However, because the globular structure does not permit the usual processes of orientation and strain hardening, the neck gradually thins until it fractures at an engineering strain above 100%.

An Electronic Nose from Arrays of Polymer Composite Vapor Sensors

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ABSTRACT

We describe a method for generating a variety of chemically diverse, broadly responsive, low power vapor sensors. A key to our ability to fabricate chemically diverse sensing elements is the preparation of processable, air stable films of electrically conducting organic polymers. An array of such sensing elements produces a chemically reversible, diagnostic pattern of electrical resistance changes upon exposure to different odorants. Such conducting polymer elements are simply prepared and are readily modified chemically to respond to a broad range of analytes. In addition, these sensors yield a fairly rapid, low power, dc electrical signal in response to the vapor of interest, and their signals are readily integrated with software or hardware-based neural networks for purposes of analyte identification. Principle component analysis has demonstrated that such sensors can identify and quantify different airborne organic solvents, and can yield information on the components of gas mixtures.

MECHANISMS OF MORPHOLOGY DEVELOPMENT AND CONTROL IN POLYMER-POLYMER BLENDS

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Abstract

Polymer-polymer blends continue to be the most important method for achieving optimization of properties in plastics products. Over 30% of all plastics are blends. While miscible blends generally give average properties between the components, immiscible blends offer synergistic possibilities such as high modulus with high toughness; high flow with high impact strength or diffusion barriers with good mechanical properties and low cost. The key to performance of these immiscible blends is their morphology.

There are several important types of morphology which can lead to valuable property improvement:

emulsion - small polymer spheres well dispersed in a polymer matrix.
double emulsion - spheres inside spheres which are dispersed in another matrix.
microlayer - thin, parallel layers of one polymer in a matrix.
cocontinuous - two (or more) continuous, interpenetrating polymer phases.
ordered microphases - high block copolymer levels create nanometer-scale morphology

To be economical it is desirable to create these morphologies via melt mixing of powder or pellets in conventional compounding equipment. The melting stage during compounding is very important for morphology development. This presentation will demonstrate the role of melting or softening of each phase as well as their viscosity, elasticity and interfacial tension in morphology development. Interfacial modification with premade block copolymers or reactively formed copolymers can greatly alter morphology formation and stability. Experimental results will be presented which quantify the role of these additives.

SUPRASUPERMOLECULAR CHEMISTRY: CHEMISTRY WITHIN THE DENDRIMER

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Relationships between branched molecular architectures and supramolecular chemistry are examined and probed via design, development, and assembly of diverse utilitarian monomers. The topic of *supramolecular* chemistry has grown, since its inception by Lehn to encompass simple host-guest interactions as well as molecular events that extend to the evolution of life and the biosynthesis of contemporary biological systems; whereas the supermolecular aspects of this presentation arose with the advent of dendrimers and hyperbranched materials. These supermolecular species bridge the gap between traditional unnatural organic molecules (MW < 2,000 amu) and the "classical" polymers, generated from linear monomers. Thus, the melding of supramolecular chemistry *within* these supermolecules can then be envisioned as "suprasupermolecular" chemistry.

In order to assemble specifically designed supermolecules, one must create a series of well-defined polyfunctional monomers, each possessing a branching point as well as an appropriate center where the desired interaction will eventually occur. Such tailored assemblies can best be constructed by the use of appropriate *branched* building blocks rather than the standard, readily available, linear monomers. This concept is depicted in the Figure and will appear as a subtheme throughout the presentation.

Applications toward the assembly of materials with internal center(s) for molecular recognition, redox activities (catalysis), or metal connectivity using this branched monomer approach will be described.

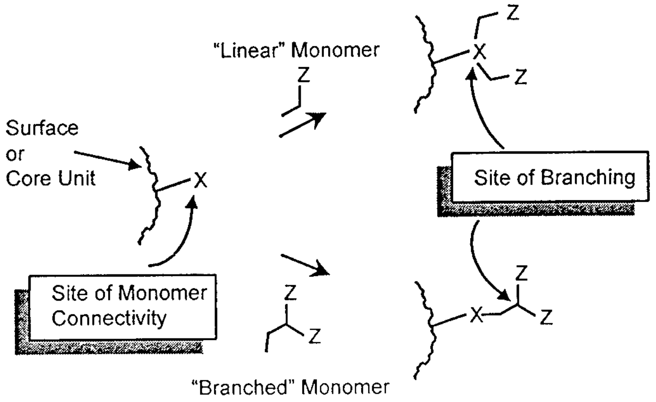

Figure. The two general methods for branched architecture construction.

ELASTOMERIC NANOCOMPOSITES

ASILOMAR CONFERENCE ON POLYMERIC MATERIALS

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Abstract

Nanocomposites, characterized by ultra-small particulate fillers embedded in a polymeric matrix, have aroused considerable scientific and technological interest. As the use of polymeric materials in highly demanding applications increases, this new class of composites provides a way for combining high strength, increased toughness, reduced permeability to liquids and gases, and enhanced transparency at low levels of filler content. Frequently used inorganic filler particulates, such as montmorillonite, are layered clay silicate minerals consisting of individual layers in the range of about 100 nm in length and 0.1 nm in thickness. If the original clay particles are successfully separated into their individual constituent layers, a large aspect is realized and optimum properties are developed.

In this presentation, the formation, structure and properties of several families of elastomeric nanocomposites are described. Initially, it was assumed that the structure of the intercalation agent would dictate whether intercalation or exfoliation prevailed. However, in a majority of materials a mixture of intercalation and exfoliation is observed. These elastomeric nanocomposites are best described as tactoidal in structure and possess properties that are superior to conventional composites. The reinforcement effect and the orientation of the silicate nanolayers improved the tensile properties and gas permeability significantly. Interestingly, at low filler concentrations, i.e. <10 wt %, tactoidal clay structures in an elastomeric matrix simultaneously improved the mechanical properties and gas impermeability, while little change is observed in the behavior of conventionally prepared composites at an equivalent filler content.

Polymer Nanofibers

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Polymer nanofibers have diameters from around 1 nanometer, which is near the diameter of a single polymer molecule, to around 1000 nanometers, which is a fraction of the diameter of a typical textile fiber. Single polymer molecules are found, using scanning probe microscopy, on a solid substrate, but the smallest nanofiber we have spun in air had a diameter of just under 3 nanometers, and contained about 40 polystyrene molecules in a typical cross section. Typical nanofibers produced by contemporary methods have diameters in the range from 100 to 500 nanometers. The nanofibers are arbitrarily long, and have a very high ratio of surface area to mass. The polymer molecules in nanofibers are often, but not always, extended along the axis of the fiber, as judged by birefringence or electron diffraction. Nanofibers are thin enough that they are transparent in ordinary transmission electron microscopes. Nanofibers have been made from a large number of different kinds of polymers, including: polymers used to make textile fibers; biopolymers such as DNA, proteins, silk and synthetic polypeptides; polymers that are precursors to carbon fibers or ceramic fibers; biocompatible polymers; electrically and ionically conducting polymers, and elastomeric polymers.

Electrospinning is a convenient way to create significant quantities of continuous nanofibers in the laboratory, although other methods involving fluid flow or phase separation are known. A high electric field at the surface of a polymer liquid produces forces that are opposed to surface tension. For many polymer solutions, in fields that are smaller than the electrical breakdown strength of air, the electrical forces are greater than the forces due to surface tension. Such a charged liquid surface is unstable, and charged jets of liquid are ejected to carry excess charge away. These jets often splay into smaller fibers under the influence of the radial component of the electrical forces. The small fibers dry, leaving nanofibers. The nanofibers are collected on a conducting sheet, a rotating drum, in liquids, or in other ways. The electrospinning process is inherently stable, and will run unattended for long times. In a vacuum, much higher electric fields can be sustained and the force on the surfaces become larger, so that polymer melts spin well in a vacuum.

Electrospinning combines electrodynamics, hydrodynamics, rheology, ionic conductivity, surface tension, elongational viscosity, aerodynamics, acceleration, and more, in complex ways that usually produce nanofibers. The drift velocities of the ions that are the important charge carriers is not as high as the rates at which the shape of the liquid surface changes, or as high as the velocity of the jet along its axis, so electric fields and ionic currents inside the fluid must be considered. The dynamic instabilities that create the jets from a liquid surface, or cause splaying, occur in a self-similar way over a range of scales.

Nanofibers are used in filters, protective clothing, and non-woven fabrics. They promise to be useful for applying pesticides to plants, creating lightweight structures such as light sails in space, for the creation of synthetic membranes with biological applications, as supports for enzymes or catalysts, in advanced composite materials, and in other ways.

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ABSTRACT

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CHARACTERIZATION OF NANOSTRUCTURES BY PHASE SEPARATION AND CRYSTALLIZATION

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Morphology at the nanoscale level may arise from a molten amorphous polymer by processes of amorphous/amorphous phase separation or by crystallization. These produce variations in density (or average refractive index) and/or anisotropy, arising from molecular or superstructure orientation. Density fluctuations on the sub-micrometer level may be detected by x-ray scattering techniques. These may be followed in real time during phase separation using intense x-ray sources provided by synchrotrons. Larger structures require the use of longer wavelength radiation employed in light scattering. Through use of polarization, fluctuations in density and orientation may be distinguished.

These techniques are illustrated in studying the crystallization of polyethylenes of varying degrees of branching and their blends. Through time dependent light scattering observations, the radial growth rate of spherulites may be followed, and along with x-ray measurements, the changes in degree of crystallinity may be measured . It is found that for many samples, crystallization continues after the spherulites become volume filling through secondary crystallization processes. In fact, with blends of linear and branched polyethylene at low supercooling, the linear component often completes its crystallization forming volume filling structures before appreciable amounts of the branched component crystallize. Thus, the linear component determines the size of the spherulite morphology and serves as a template governing the crystallization of the branched component.

The methods may be extended to the studies of oriented polymers where the growing structures are anisotropic, as "ellipsites", shish-kabobs, and fibrillar structures. The ability to conduct real time scattering studies permits the application of these techniques to processing studies. They may also be applied to the study of the melting of crystalline polymers in which case it is possible to distinguish whether the crystals form a miscible or phase separated melt.

These methods may also be applied to systems exhibiting amorphous/amorphous phase separation, occurring by nucleation-and-growth or spinodal processes and to systems where both such phase separation and crystallization processes occur together. The combination of light scattering with x-ray scattering permits their separation.

Dendrimer-Based ALERT® Ticket

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Early warning or detection of biological warfare agents is extremely important for protecting soldiers on a battlefield as well as civilians in urban areas. The current lateral-flow ALERT ticket offers many unique advantages (i.e. compact, easy to use, and, no power source requirement, etc.) over its bulky instrument counterparts. However, the current tickets lack high sensitivity and tend to give more false positive responses. In order to overcome these problems, we have synthesized a series of uniquely designed nanostructured polymeric materials. Among them, the rigid, spherical, tree-like dendrimers seem to be the best nanostructured polymers that are capable of orienting the antibody binding direction at nanoscopic size scale. As a result, the dendrimer-based ALERT® (Antibody Lateral-flow Economical Recognition) tickets can enhance the sensitivity by a factor of 5-10. In addition, after the introduction of "cheap" synthetic protein-like dendrimers, the ticket production cost has also been significantly reduced.