Dendritic Polymers Made from Vinyl Monomer

Cornell University chemists have discovered a technique for building dendritic polymers that could be used for making better adhesives, lubricants, and coatings for a variety of industrial uses. The technique, called "self-condensing vinyl polymerization," represents an approach to making materials with polymers that behave like dendrimers—polymers consisting of large, highly branched, globular molecules. Their work was published in the August 25 issue of *Science*.

The Cornell group, led by Jean M.J. Fréchet, professor of chemistry, made a hyperbranched polymer using a modified styrene monomer. Styrene is commonly used in Styrofoam and other materials.

The chemists "tricked" the molecule into reacting with itself for the growth of successive branches from the original stem. This was done by forming an ion on the modified part of the styrene monomer; this ion adds to another monomer forming the first branch. Successive additions multiply rapidly the number of branches and force the molecule to become globular.

"It's a globular molecule, not a strand, yet it is made from a vinyl monomer," Fréchet said. "To do this, we've effectively combined two methods of polymerization into one—vinyl polymerization with polycondensation. The polymerization proceeds by vinyl addition but with the 'looks' of a polycondensation, with bigger and bigger pieces coming together to form the treelike structure."

The advantage, from a molecular viewpoint, is that the molecules always have only one double bond like vinyl monomers, but they also have dozens or even hundreds of reactive groups. Normally, a polymer has only one reactive site, at its end. With hundreds of them, chemists can add a variety of properties.

Fréchet described the molecules as little globules with many reactive groups at their surface. If the surface is controlled, the globules are controlled; for example, they can be made red or sticky.

"The versatility of the approach stems from the fact that a variety of architectures may be obtained by using several monomers to produce unusual polymer architectures in one-pot reactions," Fréchet said. "For example, stars and dendritic hybrid structures can be obtained by sequential addition of appropriately selected monomers. Given the interesting properties of these hybrid structures, a fast synthetic process for their preparation would be very beneficial."

According to Fréchet, this "self-condensing polymerization" process may eventually become very cheap, making it useful for industry for coatings, lubricants, drug carriers, and other advanced or "smart" materials.

Pt/Li/Pt Edge Field Emitter Demonstrated

Scientists at the Naval Research Laboratory (NRL) have demonstrated proof-of-principle for a vertical thin film field emitter display (FED) cathode made of platinum and lithium. The development has applications toward low-cost, high-performance, energy-efficient flat-panel displays.

Using chemical-beam-deposition techniques, David S.Y. Hsu of the Chemistry Division and Henry Gray of the Electronics Science and Technology Division fabricated ungated vertical thin-film edge field emitters, consisting of vertical, free-standing platinum/lithium/platinum sandwich-layer and platinum film structures. This fabrication results in improved structural characteristics of deposited films. Extremely small-grain-sized films can be made to yield film edges of less than a 10-nm radius of curvature, which facilitates electric field enhancement. The fabrication process also allows the film edges to be oriented vertically to provide tighter angular dispersion in the resultant field-emitted electron beam, compared to previously reported horizontal thin-film-edge structures.

This fabrication technique also permits multilayer deposition of high quality metal-insulator-metal structures as well as the possibility of multimetal films for structural and emission current enhancements.

STM Images Reveal Flaw Formation in Films For Solar Panels and Large Flat-Panel Displays

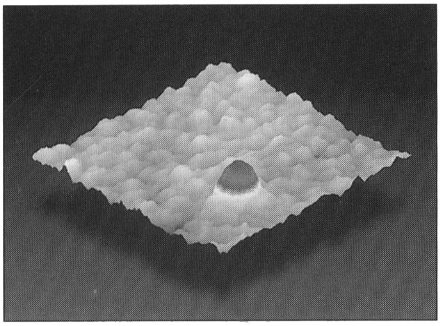
Researchers at JILA, a joint institute of the National Institute of Standards and Technology and the University of Colorado—Boulder, have made images of particles only a few nanometers wide that may be reducing the efficiency of certain light-sensitive films.

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

The team is studying the processes used to grow photovoltaic films over large surfaces. Such films are used in making solar energy panels and large flat-panel displays. The efficiency of the film in converting light into electrical current is best with homogenous, very thin films about 500 nm thick.

The researchers custom built a system for both growing thin films and examining them with an ultra-sensitive scanning tunneling microscope. They used the apparatus to grow amorphous (noncrystalline) films of silicon and hydrogen atoms with plasma-enhanced chemical vapor deposition (PECVD). Images of the film were then taken at various stages throughout the growth process. The images show particles 3 to 5 nanometers in size, which form in the vapor and bond to the film surface during growth. As a new layer of silicon and hydrogen atoms deposits on the surface, these clumps cause voids within the film.



A 3- to 5-nm-sized particle on the surface of a light-sensitive film.

"Many people have studied the production of larger particles during PECVD, but these particles are suspended in the plasma and do not reach the growing film. As far as we know, no one has...realize[d] that these can reach the growing film," said Alan Gallagher, principal investigator for the project. "If we can figure out how to keep these particles from forming or prevent them from reaching the film surface, we should be able to improve the film's ability to convert light into electrical current."

The JILA researchers also are developing a laser scattering system to detect the silicon/hydrogen clumps as they are forming in the plasma. Laser scattering detects larger particles but provides a method for real-time monitoring of particulate behavior in the plasma.

ATP Announces Selections for 1995

The Advanced Technology Program under the National Institute of Science and Technology named 17 selections for the General Competition for 1995 and eight selections for 1995 in the focus area of Materials Processing for Heavy Manufacturing.

Among the recipients in the General Competition are **Advanced Refractory Technologies, Inc.** (Buffalo, New York) for Diamondlike Nanocomposite Technology; **Ceramatec, Inc.** (Salt Lake City, Utah) for Development of a High-Pressure Oxygen Generator Using a Solid Electrolyte Oxygen Separation (SEOS) Technology; **FED Corporation** (Hopewell Junction, New York), **Analog Devices** (Greensboro, North Carolina), **BFGoodrich Avionics Systems** (Columbus, Ohio), **Cetek Technologies, Inc.** (Poughkeepsie, New York), **InfiMed, Inc.** (Liverpool, New York), and **Kaiser Electronics** (San Jose, California) for Technology Development for the Smart Display—A Versatile High-Performance Video Display Integrated with Electronics; **General Electric Company Corporate Research & Development** (Schenectady, New York) for Novel Synthetic Fused Quartz for Semiconductor Manufacturing; **General Electric Company Corporate Research & Development** (Schenectady, New York) and **EG&G Reticon** (Sunnyvale, California) for Low-Cost Amorphous Silicon Manufacturing Technology; **Optoelectronics Assembly Consortium** (Ann Arbor, Michigan), **Adept Technology, Inc.** (San Jose, California), **AT&T Bell Laboratories** (Princeton, New Jersey), **Boeing Company** (Kent, Washington), **Ford Motor Company** (Dearborn, Michigan), **Motorola, Inc. Phoenix Corporate Research Laboratories** (Tempe, Arizona), **New Jersey Institute of Technology Center for Manufacturing Systems** (Newark, New Jersey), and **National Center for Manufacturing Sciences** (Ann Arbor, Michigan) for Precision Optoelectronics Assembly Precision; **Teledyne Electronic Technologies** (Rancho Cordova, California) for Novel X-Ray Source for CT Scanners; **The Dow Chemical Company** (Midland, Michigan) and **IBM Microelectronics** (Hopewell Junction, New York) for Cost-Effective Planar Solid Oxide Fuel Cells for Power Generation; and **TROPEL Corporation** (Fairport, New York) for Noncontact Optical Metrology of Complex Surface Forms for Precision Industrial Manufacturing.

The recipients under Materials Processing for Heavy Manufacturing are **AlliedSignal, Inc.** (Torrance, California) for Aqueous Injection Molding for Low-Cost Fabrication of Silicon Nitride Components; **AlliedSignal, Inc.** (Morristown, New Jersey), **Stahl Specialty Co.** (Kingsville, Missouri), and **Top Die Casting Company, Inc.** (South Beloit, Illinois) for Low-Cost, Near-Net-Shape Aluminum Casting Processes for Automotive and Truck Components; **Caterpillar Inc.** (Peoria, Illinois), **A.O. Smith** (Milwaukee, Wisconsin), **The Lincoln Electric Co.** (Cleveland, Ohio), and **U.S. Steel** (Pittsburgh, Pennsylvania) for Fabrication of Advanced Structures Using Intelligent and Synergistic Materials Processing; **General Electric Company** (Schenectady, New York) for Intelligent Processing of Materials for Thermal Barrier Coatings; **Praxair Surface Technologies, Inc.** (Indianapolis, Indiana) for Ceramic Coating Technology for the Internal Surfaces of Tubular/Cylindrical Components; **Precision Castparts Corporation** (Portland, Oregon) for Development of Casting Technology to Produce Large Superalloy Castings for Industrial Applications; **Westinghouse Electric Corporation** (Orlando, Florida) and **PCC Airfoils, Inc.** (Beachwood, Ohio) for Cost-Effective Blade Manufacturing for Combustion Turbine Applications; and **Wyman-Gordon Company** (North Grafton, Massachusetts) for Cost-Effective, Near-Net-Shape, Superalloy Forgings for Power Generation Gas Turbines.

For more information about each project, contact Advanced Technology Program, National Institute of Standards and Technology, Administration Bldg. 101, Rm. A430, Quince Orchard & Clopper Roads, Gaithersburg, MD 20899-0001; or search for ATP news releases on the World Wide Web: http://www.nist.gov/.

SBIR Updates

Climax Research Services (Farmington Hills, Michigan) has received a Phase I award from the Department of Energy to develop a new high-chromium iron alloy tailored for pulp refiner plate applications in high-speed refining for the pulp and paper industry.

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

Tiltrotor Aircraft Conversion Hangs on Composite Rotor Blades

Edward C. Smith, assistant professor of aerospace engineering at Penn State, and Anna Howard, a graduate student in aerospace engineering, are working with NASA to develop analysis techniques to design composite rotor blades for commercial tiltrotor aircraft that will help reduce blade stresses, lower hub vibration, and improve reliability. Tiltrotor aircraft have oversized front-facing propellers when cruising from place to place, which tilt upward to become horizontally oriented, helicopterlike rotors for takeoff and landing.

The conversion from military version of the tiltrotor aircraft, the V22 Osprey, to passenger aircrafts involves much work. The Osprey is designed to be bulletproof, and the wings and rotors fold for storage on board a ship. Advanced composite materials make up most of the Osprey's fuselage and wings.

While the commercial version need not fold or be bulletproof, it will need to be quieter inside, for the comfort of passengers, and outside, to gain community acceptance. Like turboprops, the frame and skin of the fuselage will probably be aluminum, but the wings will remain composite. Composites and especially how they are arranged are the key to controlling vibration and providing added stability, according to Smith.

"Tiltrotors feature many safety improvements compared to conventional helicopters," said Smith. "The tiltrotor configuration, with one set of rotor blades on each wing tip, does not require a tail rotor, stabilizing the performance of rotorcraft for all weather, day and night operation."

The helicopter industry has also eliminated many of the hydraulic couplings for the rotors, substituting elastomeric bearings. These nonmoving, nonfluid substitutions for hydraulic couplings and ball bearings improve maintenance and reliability, and provide damping to control noise and vibration. The Penn State researchers believe that tailored composite materials used at the rotor hub and in the blade could replace damping mechanisms and improve acceptability of the tiltrotor.

Common composite materials are epoxy and graphite, glass, or Kevlar. These materials are produced in thin layers that are laminated to create the required flexibility and strength. Composites usually do not possess the same characteristics in all directions. They may be very flexible in one direction but rigid in the perpendicular direction.

"By carefully designing the orientations of the thin layers, the bending and twisting motions of the blade can be coupled together, thereby reducing vibration and improving stability of the rotor system," said Smith. "We can orient layers in virtually any direction, but, in reality, we only need subtle amounts of this coupling effect to introduce significant beneficial effects. Using this strategy, we can tailor the dynamics of the blades and still retain their desirable high strength and long life."

Tailoring the composite at the rotor hub adds stability and tailoring at the blades reduces vibration, according to the researchers.

"Coupled tailored materials have been used very successfully in forward, swept wing aircraft," said Smith. "There is no reason to believe that they will not work as well in tiltrotor craft wings and rotors."

Smith and Howard have designed analytical tools and completed a feasibility study of coupled tailored composites in tiltrotor craft rotors and blades. This includes comprehensive finite element models of rotor blades. The researchers are currently developing a refined structure for flexible beams for bearingless rotors.

Blue, Green, Orange Emitted by Polymer Electrochemical Cells

Researchers at UNIAX Corp. have developed a type of polymer-based light-emitter called a light-emitting electrochemical cell (LEC). They have built LECs, using different polymers, that emit blue, green, and orange light at low drive voltage and high photon/electron quantum efficiency.

While conjugated polymers, which are semiconducting and often luminescent, may be reversibly charged or doped, after doping they become highly conductive and their luminescence is quenched. Polymer chemist Qibing Pei and co-workers were able to exploit both the charge transfer doping and luminescent properties of conjugated polymers to make a light-emitting device. The active medium in an LEC contains a conjugated polymer with an added electrolyte. When a voltage is applied across two contact electrodes sandwiching the active medium, the conjugated polymer is p-doped at the anode side and n-doped at the cathode side. The added electrolyte provides the necessary ionic conductivity and dopants. Between the doped regimes, a p-n junction is formed *in situ*. Within this p-n junction, holes propagating from the anode toward the cathode radiatively recombine with electrons propagating from the cathode toward the anode. This p-n junction is dynamic and reversible.

An LEC, using aluminum, gold, or indium-tin oxide as the electrodes, turns on at around 3 V corresponding to the bandgap of the luminescent polymer, and emits bright light at less than 5 V. The devices fabricated show external photon/electron quantum efficiencies as high as 2%. This polymer light-emitter also shows long shelf life and working lifetimes.

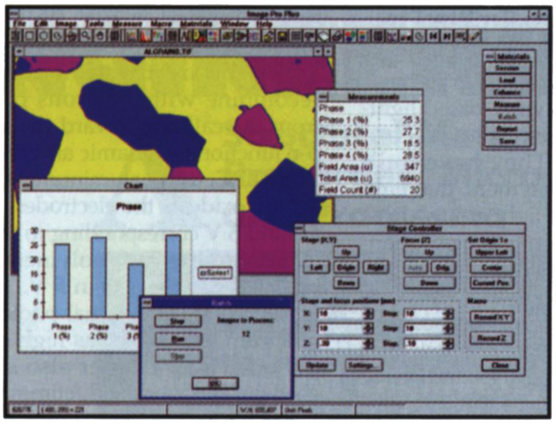
Pei presented this work at the 1995 Annual Meeting of the Optical Society of America in September. It is published in the August 25 issue of *Science*.

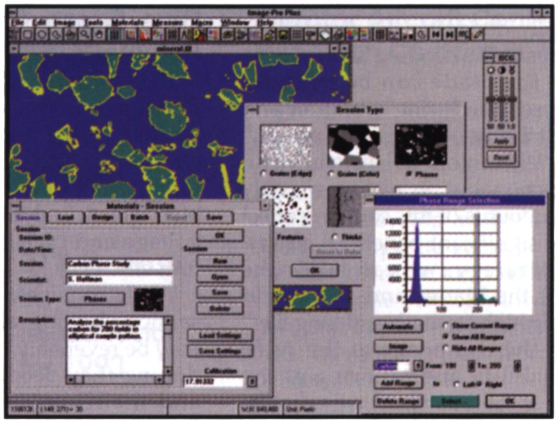
CWRU Researchers Develop Fire-Resistant Polymer for Improved Airplane Safety

In order to increase airplanes' resistance to catching fire during a crash, researchers at Case Western Reserve University (CWRU) have developed new polybenzoxazine plastics—a fire-resistant, synthetic polymer—to replace the

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

EXCELLENCE IN ANALYTICAL IMAGING SOFTWARE





Gearing Up for Image Analysis

Tired of spending a fortune on materials analysis systems? Well, cost-effective materials analysis is no longer a pipe dream! Whether you are involved in analyzing metals, ceramics, polymers, or other materials, Image-Pro Plus and Materials-Pro Analyzer will give you the test results you need quickly, accurately, and cost-effectively.

PUT THE POWER OF IMAGE-PRO PLUS AND MATERIALS-PRO ANALYZER TO WORK FOR YOU

Materials-Pro Analyzer, our "plug-in" module designed specifically for materials scientists, easily guides users through image acquisition using manual or automated stages. Sophisticated preprocessing routines and standard materials measurements allow you to determine grain size, gauge porosity and nodularity, and perform phase analysis. Complete and accurate statistical reporting is provided in a variety of industry standard data tables.

EASY TO USE AND EASY ON YOUR BUDGET

Materials-Pro Analyzer is Windows-based which means point-and-click simplicity. To make your job even easier, Materials-Pro Analyzer is written in standard material science terminology. It runs on standard PCs, and supports a wide variety of image hardware for easy system integration.

Image-Pro Plus and Materials-Pro Analyzer deliver all the power and functionality you need at a price you can afford.

BACKED BY A DECADE OF LEADERSHIP

Since 1985, Media Cybernetics has set the standard for image analysis software. Today, our Image-Pro Plus software enjoys the largest installed base in the industry. The Materials-Pro Analyzer module is a product of the same commitment to innovation and market responsiveness that has made us #1.

ACCEPT NO SUBSTITUTES

Use the #1 selling software from the leader in imaging technology. Supported by a worldwide network of dealers, we can answer your imaging questions and put together a system to match your application and your budget. Call today to find out how we can meet your image analysis needs.

1-800-992-4256

Image-Pro PLUS™

The Proven Solution

Visit MRS Exhibit Booth No. U200

MEDIA CYBERNETICS
The Imaging Experts

Site License and Maintenance Pricing Available.

8484 Georgia Avenue, Silver Spring, MD 20910 USA; 301-495-3305; FAX 301-495-5964

Images used with permission, *The Image Processing Handbook*, 2nd Ed., CRC Press

Circle No. 31 on Reader Service Card.

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

phenolic resins currently in use.

Inside the hull of an airplane is fiberglass insulation and a honeycomb panel surfaced with a decorative film. Hatsuo Ishida, a faculty member in the macromolecular science department in CWRU and principal investigator of this project, is researching the polymer to replace the resin used in the honeycomb panel.

Some of the polybenzoxazine plastics have an 85% char yield residue after burning, compared to 55% with the phenoloic resins commonly used in aircraft interiors. "Only about 15% of our polymer is lost to gas, and any gas from burning plastic is potentially dangerous," Ishida said. "The rate that the material will burn and the amount that burns are very important. Our plastic doesn't burn as much as other plastics."

Unlike phenolic resins, Ishida's polymer is better able to be tailored with properties such as nonflammability and processability. The polymers also display near-zero shrinkage when cured, a useful property for manufacturing. Materials shrink between three and 15% in going from a monomer to a polymer.

Piezoelectric Crystal Key to Electronically Controlled "Intelligent" Mechanical Seal

Research at the Georgia Institute of Technology has led to the development of an electronically controlled intelligent mechanical seal designed for turbopumps on liquid-fueled rocket engines.

At the heart of the intelligent seal is a piezoelectric crystal that deforms in proportion to the electrical voltage applied to it. Attached to one face of the seal, the crystal would adjust the spacing between critical moving parts in a rocket engine's turbopump. A closed loop control system would constantly monitor conditions within the seal and determine the voltage that should be applied to maintain proper clearances.

"The electronically controlled seal is similar in design to a conventional mechanical seal except that one of the faces is replaced with a deformable face assembly," said Richard Salant, professor of mechanical engineering at Georgia Tech. "That assembly consists of a thin carbon face bonded to a piezoelectric crystal. When a voltage is applied, the crystal deforms and causes the carbon face to similarly deform, thus changing the pressures and distance between the two faces. The greater the applied voltage, the larger the deformation. Therefore, by adjusting the voltage, you can control the separation between the two faces."

To determine how much voltage should be applied to the piezoelectric crystal, a closed loop control system constantly monitors conditions within the seal. The system is capable of utilizing either the

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

leakage rate or the face temperature as the feedback signal.

Salant said, "If operating conditions change such that face contact is imminent, the control system automatically increases the face separation. Similarly, if the control system senses that the leakage rate is excessive, the separation is reduced. The control system can respond to rapid changes in the operating conditions quickly and efficiently."

Slade Selected for F.M. Becket Memorial Award

Holly C. Slade of the University of Virginia has been selected for the F.M. Becket Memorial Award of The Electrochemical Society, Inc. The award encourages participation in the fields of electrochemical science and technology concerned with specialty materials and processes.

Slade will use the $2,500 award to support research in developing concise, analytical device models for amorphous silicon thin-film transistors that incorporate the effects of thermal and bias stress. This research is to be performed at Cambridge University in cooperation with Philips Research Laboratory, Redhill.

Currently pursuing her PhD degree at the University of Virginia, Slade has received her BSEE and MSEE under the Accelerated Bachelors/Masters Program and the Rodman Scholars Program from the University of Virginia in 1993.

Terwilliger Receives NSF Career Development Award

Chrysanthe D. Terwilliger, assistant professor of mechanical engineering at Worcester Polytechnic Institute (WPI), received an award from the National Science Foundation's Faculty Early Career Development (CAREER) Program. She is expected to receive $200,372 over four years that began June 1, 1995.

Terwilliger plans to use her funding for research on the synthesis and electrical characterization of ultrafine-grained ceramics. "Grain sizes in conventional materials are typically in the range of 1–100 microns," she said. "We will be attempting to synthesize dense ceramics with grain sizes on the order of 10 nanometers. We expect that these materials will have electrical properties which would be of use in chemical sensors."

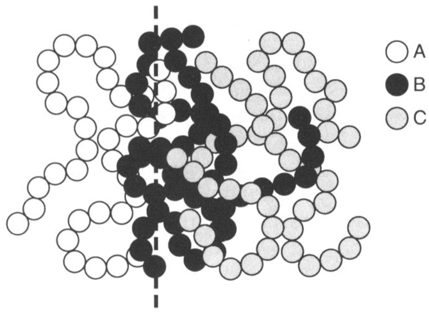
Terwilliger received a B.S. degree in mechanical engineering from WPI in 1988 and joined the faculty in 1993. She received her Ph.D. degree in materials science and engineering at MIT in 1993.

Interfacial Engineering Opens Route for Compatibilizing Polymer Blends

Researchers at the University of Pennsylvania developed a route for compatibilizing polymer blends. Russell Composto,

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press

a faculty member in Materials Science and Engineering, along with former postdoctoral student Alessandro Faldi and graduate student Jan Genzer, studied how the addition of polymer B to a two-phase A/C blend modifies the interfacial properties. For a system where B is miscible with C, but not with A, and the A-B interactions are less repulsive than the A-C ones, the B component was found to migrate to and accumulate at the A/B:C interface as shown in the figure. This internal segregation of B lowers interfacial tension, providing a stabilization of phase morphology, and broadens the interfacial width, providing better interpenetration of molecules across the interface. Both of these effects are expected to lead to an improvement in the mechanical properties of A/B:C blends, as was reported in the April 24 issue of *Physical Review Letters*.



Interface of a modified polymer blend.

Experimentally, the A/B:C interface is difficult to probe because it lies beneath the surface and is narrow, about 10 nm. Ion scattering techniques, although not commonly used on polymers, provide an excellent tool for seeing the interfacial region. In the A/B:C system, the interfacial segregation of B was measured by low-energy forward recoil spectrometry, a technique which uses incident helium ions to recoil hydrogen and deuterium nuclei from the near-surface region of the sample. These nuclei are then used to determine the depth profile across the A/B:C interface. The self-consistent field model of the A/B:C interface, also developed in Composto's group, was used to interpret the ion beam results. From the AB, AC, and B:C interaction parameters and the A, B, and C molecular weights, the interfacial properties including the interfacial excess of B, interfacial tension, and interfacial width can be determined. The interfacial segregation of B (and corresponding change in interfacial tension) was found to be dictated mainly by the difference between the A-B and A-C repulsive interactions, as predicted by E. Helfand of AT&T Bell Laboratories. As the molecular weight of B increases, the interfacial segregation of B also increases. This segregation broadens the interfacial region and provides better mechanical contact between the A and B:C phases. Based on these observations, the optimum compatibilizing effect is achieved when a small amount of high-molecular weight B is added to the A/C system. The potential for using homopolymers or random copolymers is particularly significant because both are easier and less expensive to prepare than block copolymer compatibilizers. Our studies show that the system properties can be finely controlled by a judicious choice of B, its molecular weight and concentration in the B:C mixture. ☐

https://doi.org/10.1557/S0883769400045498 Published online by Cambridge University Press