

Jimmy W. Mays, Polymer Chemistry

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Research

My research interests include synthesis of linear and branched polymers and copolymers of controlled structure, especially via anionic polymerization; polymer molecular characterization via dilute solution techniques; polymers at interfaces; polymeric biomaterials; charged polymers; block copolymer morphology; and polymerization in room temperature ionic liquids.

Over the past several years, we have explored the synthesis and morphology of novel nanostructured graft copolymers, composed of poly(isoprene) (PI) backbones and polystyrene (PS) branches, having precisely tailored architectures. Examples of the types

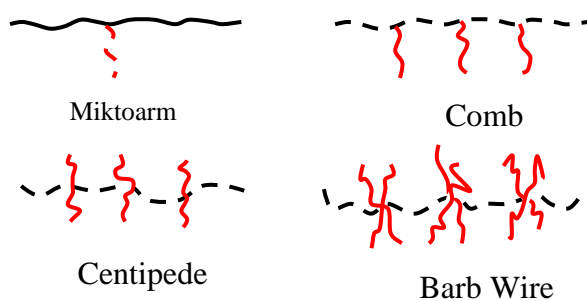


FIGURE 1 Graft copolymer architectures having regular branched architectures of controlled functionality.

of structures we have synthesized and studied are depicted in Figure 1.

Through these investigations on materials synthesized by highly specialized high vacuum anionic polymerization techniques, we have discovered how molecular architecture, composition, and blending can be used to systematically

manipulate the morphology and extent of long-range nanostructural order present in these materials.

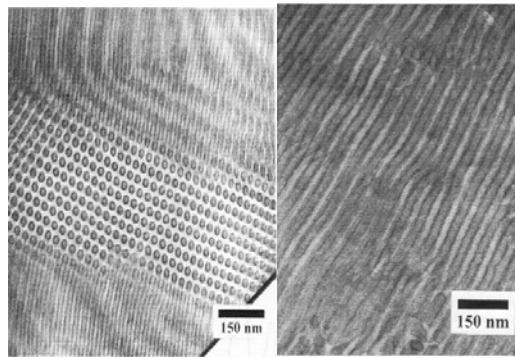
Recently, we have conducted studies on the tensile properties of some of these materials, most notably “centipede copolymers” consisting of a PI backbone with multiple regularly spaced branch points, each carrying two PS branches of identical chain length. It was found that centipede copolymers with 22 vol % PS and seven branch points are thermoplastic elastomers (TPEs) and show a surprisingly high strain at break of about 2100%, double that of commercial TPEs such as Kratons. *With increasing number of branches, strain at break and tensile strength increase, with strain at break being 2300% for a sample with 10 branch points.* These materials exhibit a wormlike microphase separated structure with much lower long-range order than TPEs such as Kraton. The combination of two branches at each branch point, combined with the large number of branch points per molecule, allows the elastic PI backbone to couple into a large number

of reinforcing PS domains, resulting in huge elasticity combined with a high tensile strength. The novel “barb wire” architecture (see Figure 1) where each branch point carries four branches could show an even further improvement in mechanical properties. We will utilize the requested SAXS equipment extensively in evaluating the dependence of block copolymer morphology on branched architecture and number of branch points in order to develop a new class of thermoplastic elastomers.

Another research area is synthesis and characterization of a new type of nanotube based on self-assembled block copolymers of polystyrene (PS) and poly(cyclohexadiene) (PCHD). PCHD is a structurally interesting polymer because it may be converted to poly(phenylene) (PP), a crystalline and chemically and thermally stable material, by aromatization. Furthermore, doping of PP will generate a conducting synthetic metal. We believe that using PCHD as a precursor to PP will avoid the major difficulty associated with synthesizing or processing high molecular weight poly(phenylene), which is an insoluble, intractable material. High molecular weight PCHD material will be processed into the appropriate form, then converted to PP.

We have synthesized poly(styrene-block-cyclohexadiene) and characterized the morphology of self-assembled, microphase-separated diblock copolymer of PS and

Figure 2: TEM Micrographs of PS/PCHD Diblocks. The light regions are PS and the dark regions are PCHD stained with osmium tetroxide. These specimens were prepared by solvent casting and annealing; shearing may be used to enhance long range order. (a) End on view of core-shell cylinders in band across the center of this image. (b) Side-on view of core-shell cylinders.



(a)

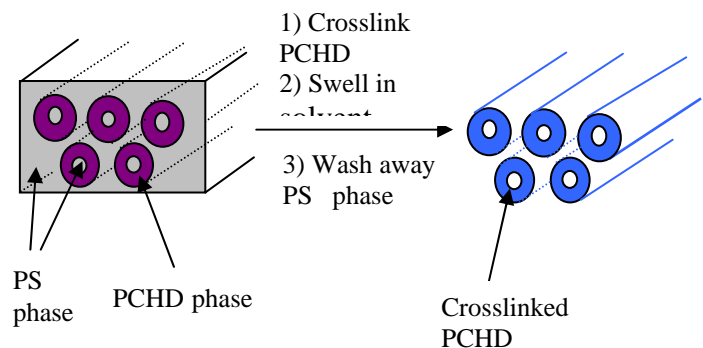
(b)

PCHD. An unusual core-shell cylinder-in-cylinder morphology not previously found in neat diblock copolymers was observed in three different specimens of different molecular

weights but all having similar composition (about 37% by volume PCHD). This structure consists of hexagonally packed cylinders of PCHD dispersed in a PS matrix; in the center of each PCHD cylinder there is a PS cylinder (Figure 2). The unusual morphology is attributed to conformational asymmetry present in this block copolymer (PCHD has a persistence length of about 7-8 nm).

This cylinder-in-cylinder structure is the precursor to the novel nanotubes; by removing the PS inside and outside the PCHD cylinders while stabilizing the PCHD phase, PCHD nanotubes may be produced. The diameter of the nanotubes is controlled by the molecular weight of the PCHD block.

Nanotubes are formed by casting films of the diblocks, as previously reported, annealing and or using shearing to orient



the dispersed cylinders, photocrosslinking of the PCHD phase, hydrolysis of the ester linkages under acidic conditions, and washing out of the PS material with solvents. These nanotubes will have hydroxyl groups on their surface due to cleavage of the ester linkages. *These groups may be used to attach things to the nanotubes or to promote interactions between the nanotubes and some matrix in which they are dispersed. We could chemically modify these surfaces to create a wide range of tunable surface chemistries.*

Brief Bio

Jimmy W. Mays, Distinguished Professor, received his B.S. degree in Polymer Science from the University of Southern Mississippi, and his Ph.D. degree in Polymer Science at the University of Akron. He then worked in industry for five years with Hercules, Inc., prior to joining the faculty in the Chemistry Department at the University of Alabama at Birmingham (UAB). Dr. Mays moved from UAB to a joint appointment at UT and Oak Ridge National Laboratory in January of 2002. He currently serves on the Editorial Advisory Boards of *Macromolecules* and the *Journal of Applied Polymer Science*. He is North American Regional Editor of *European Polymer Journal* and Associate Editor of the *International Journal of Polymer Analysis and Characterization*.

Representative Publications

"Utility of Interaction Chromatography for Probing Structural Purity of Model Branched Block Copolymers", S. Park, D. Cho, K. Im, T. Chang, D. Uhrig, and J. W. Mays, *Macromolecules*, 36, 5834 (2003).

"Synthesis and Evaluation of Biodegradable Multifunctional Polymer Networks", I. Chung, D. Xie, A. D. Puckett, and J. W. Mays, *Eur. Polym. J.*, 39, 1817-1822 (2003).

"Polymer Brushes by Living Anionic Surface Initiated Polymerization (LASIP) on Flat Silicon and Gold Surfaces: Homopolymers and Block Copolymers", R. Advincula, Q. Zhou, M. Park, S. Wang, J. Mays, G. Sakellariou, S. Pispas, and N. Hadjichristidis, *Langmuir*, 18, 8672-8684 (2002).

"Model Linear Block Co-, Ter- and Quaterpolymers of 1,3-Cyclohexadiene with Styrene, Isoprene and Butadiene", T. Tsoukatos, A. Avgeropoulos, N. Hadjichristidis, K. Hong, and J. W. Mays, *Macromolecules*, 35, 7928-35 (2002).

"Conventional Free Radical Polymerization in Room Temperature Ionic Liquids: A Green Approach to Commodity Polymers", K. Hong, H. Zhang, J. W. Mays, A. E. Visser, C. S. Brazel, J. D. Holbrey, W. M. Reichert, M. G. Benton, and R. D. Rogers, *Chem. Commun.*, 1368-1369 (2002).

"Synthesis of Combs, Centipedes, and Barbwires: Poly(isoprene-graft-styrene) Regular Multigraft Copolymers with Trifunctional, Tetrafunctional, and Hexafunctional Branch Points", D. Uhrig and J. W. Mays, *Macromolecules*, 35, 7182-7190 (2002).

"Synthesis of Block Copolymers of Styrene and Methyl Methacrylate by Conventional Radical Polymerization in Room Temperature Ionic Liquids", K. Hong, H. Zhang, and J. W. Mays, *Macromolecules*, 35, 5738- 41 (2002).

"The Preparation of Aggregation Stable Gold Nanoparticles using Star Block Copolymers", R. Advincula, M.K. Park, J. Youk; J. Locklin, J. Yang; J. Mays, *Langmuir* 18, 2455-58 (2002).

"Disjoining Pressures and Ordering in Thin Liquid Films Containing Charged Diblock Copolymers Adsorbed at the Interfaces", A. Saint-Jalmes, A. A. Sonin, M. Delsanti, P. Guenoun, J. Yang, J. W. Mays, and D. Langevin, *Langmuir*, 18, 2103-2110 (2002).

"A Study of Polyelectrolyte Brushes Formed from Adsorption of Amphiphilic Diblock Copolymers Using the Surface Forces Apparatus", M. Balestre, F. Li, P. Schorr, J. Yang, J. W. Mays, and M. Tirrell, *Macromolecules*, 35, 9480-9486 (2002).

"Synthesis and Characterization of Model Neutral/Ionic Block Copolymers of Various Architectures", J. Yang and J.W. Mays, *Macromolecules*, 35, 3433-38 (2002).

"Tetrafunctional Multigraft Copolymers as Novel Thermoplastic Elastomers", R. Weidisch, S. P. Gido, D. Uhrig, H. Iatrou, and J. Mays, *Macromolecules*, 34, 6333 (2001).