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6. AUTHOR(S) Edwin L. Thomas

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Massachusetts Institute of Technology
77 Massachusetts Ave.
Cambridge MA 02139 8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Charles Lee
AFOSR/NC
110 Duncan Ave., Suite B115
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This project concerned the fundamental understanding of processing-structure and structure-property relations in block copolymer and liquid crystalline polymer systems. Key to our studies was the availability of model materials which afforded opportunities via new chemical compositions and physical properties. Transmission electron microscopy, low voltage high resolution scanning electron microscopy, light microscopy and atomic force microscopy as well as wide and small angle x-ray scattering were the principal characterization tools. We also employed a special roll cast process to form highly textured samples for investigation of their physical properties. Principal research accomplishments are grouped into 6 areas: influence of architecture on phase behavior; development of experimental techniques; microphase separation in block copolymers; large strain deformation of single crystal thermoplastic elastomers; morphology and dynamic interaction of defects in polymer liquid crystals; and technology transitions.

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Final Technical Report
F49620-94-1-0224
Influence of Composition, Chain Architecture and Processing
on Polymer Structure and Properties
April 1, 1994-March 31, 1997

Edwin L. Thomas
Department of Materials Science and Engineering
MIT
Cambridge MA 02139

Objectives:

This project concerned the fundamental understanding of processing-structure and structure-property relations in block copolymer and liquid crystalline polymer systems. Key to our studies was the availability of model materials which afforded opportunities via new chemical compositions and physical properties. Transmission electron microscopy, low voltage high resolution scanning electron microscopy, light microscopy and atomic force microscopy as well as wide and small angle x-ray scattering were the principal characterization tools. We also employed a special roll cast process to form highly textured samples for investigation of their physical properties. Principal research accomplishments are grouped into 6 areas:

- Influence of Architecture on Phase behavior
- Development of Experimental Techniques
- Microphase Separation in Block Copolymers
- Large Strain Deformation of Single Crystal Thermoplastic Elastomers
- Morphology and Dynamic Interaction of Defects in Polymer Liquid Crystals
- Technology Transitions

A total of 12 papers were published/submitted. Additionally, one U.S. patent was granted.

Accomplishments/New Findings:

Influence of Architecture on Phase Behavior

We investigated the effect of two unique chain architectures on the behavior of block copolymers: *cyclic* diblocks (1) and *miktoarm star* diblocks (2). We characterized microphase separated lamellar forming, cyclic polystyrene-polydimeylsiloxane (PS-PDMS)

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and polystyrene-poly 2-vinyl pyridine (PS-P2VP) diblock copolymers as well as their linear triblock precursors. In the triblock, the middle block may form both loop and bridge conformations whereas, in the cyclic diblock, both blocks must form loops. We found that the lamellar repeat spacing of the cyclic was always smaller than the linear triblock. This is caused by a fraction of the chain segments in the looped portions of the chains assuming trajectories which lie parallel to the A-B interfaces and do not contribute to increasing the repeat period.

In simple diblocks and triblocks, the microdomain morphology is dictated by the composition. In order to induce a new (*nonlamellar*) microdomain morphology at 50/50 composition, we designed architecturally complex multiblock copolymer molecules in conjunction with Prof. N. Hadjichristidis of the University of Athens, Greece. The copolymer molecules contain several blocks of different molecular weight, while remaining symmetric in overall composition. Five of the six samples were found to exhibit the lamellar morphology, but the sixth, a miktoarm inverse star with the highest molecular weight asymmetry between the outer and inner blocks of the arms exhibited a cubic tricontinuous structure. The transformation from the flat lamellar interface to the highly curved structure of a tricontinuous cubic microdomain morphology was proposed to result from the need to avoid overcrowding of looped-interior blocks and/or to avoid the extreme stretching of bridged-interior blocks in the star block copolymer. A tricontinuous microdomain structure lowers the entropic contribution of the interior blocks to the overall free energy because the peripheral junctions can move further apart on a curved interface and because the distances and directions between nearby regions of the interface are close enough and numerous so that the interior blocks can form some bridges. This work firmly establishes molecular architecture as an additional control parameter for block copolymer structure.

Development of Experimental Techniques:

Our group continues to develop state of the art microstructural characterization tools for polymeric materials. We published extensive reviews of both scanning electron microscopy (3) and transmission electron microscopy (4). Both SEM and TEM techniques have undergone recent developments which significantly extend their capabilities to morphological problems in polymer science and engineering. SEM of polymers has benefited enormously with the introduction of low voltage field emission electron sources, enabling uncoated or minimally coated insulating polymer specimens to be examined at a heretofore unsurpassed resolution. A number of structural features are present in polymers at the 5-10 nm length scale and can now be reliably imaged with low voltage high

resolution SEM. TEM of polymers is well established—however, high resolution lattice imaging TEM is quite difficult due to the radiation sensitivity of polymer crystals. Artifacts can occur due to both beam damage and inadequate understanding of the physics of the image formation process. Recent software allows microscopists to simulate images based on various candidate structural models for comparison to experimental data.

The discovery of complex microdomain structures such as the double diamond (Pn3m) and double gyroid (Ia3d) structures has driven the need for accurate mathematical models for their representation. In cooperation with mathematicians at Berkeley and the University of Bonn, Germany, we have developed level surface functions which model the families of the double diamond and double gyroid structure (5).

The domains of microphase separated block copolymers develop interfacial surfaces of approximately constant mean curvature in response to thermodynamic driving forces. Level surfaces are represented by certain real functions which satisfy the expression $F(x, y, z) = t$, where t is a constant. In general, these surfaces are non-self-intersecting and smooth, except at special values of the parameter t . We can construct periodic level surfaces according to the allowed reflections of a particular cubic space group; such triply periodic surfaces maintain the symmetries of the chosen space group and make attractive approximations to certain recently computed triply periodic surfaces of constant mean curvature. We pioneered the idea to model the structure of block copolymers by surfaces (the so-called Intermaterial Dividing Surface (IMDS)). We demonstrated the utility of level IMDS surfaces in simulating projections of tricontinuous microdomain morphologies for comparison with actual transmission electron micrographs for the determination of block copolymer microstructure. A software program, TEMsim (for Transmission Electron Microscopy simulation) was developed by our collaborators in the Mathematical Science Research Institute at Berkeley and is available (free) from <http://www.msri.org/Computing/jim/software/temsim/proj/>.

Microphase Separation in Block Copolymers

We are interested in the influence of a confining thin film on microdomain structure and on grain boundary defects. Monolayer thins of microdomains are easily produced by solvent casting onto substrates. Such 2-dimensionally ordered structures might be potential templates for lithography at a length scale below 100 nm, which is not easily accomplished even with electron beam techniques. We successfully formed two-dimensional periodic films and imaged both spherical and cylindrical forming microdomain samples and characterized the degree of microdomain order (6).

The second tricontinuous cubic microdomain structure in block copolymers, named the double gyroid (DG) in analogy to the previously discovered double diamond (DD) structure has a close resemblance in certain TEM images (in particular the [111] so-called "wagon wheel" image). We therefore decided to re-examine two star diblock copolymer specimens previously identified through SAXS and TEM as OBDD (DD). Employing an improved SAXS apparatus we found that the x-ray data in fact were better fit, for these samples, by the Ia3d space group of the DG structure rather than the Pn3m space group of the original DD structure (7). The revised structural assignment of the 6-arm and 18-arm starblocks remains tricontinuous, but the two interwoven minority component networks are 3-coordinated rather than 4-coordinated.

Large Strain Deformation of Single Crystal Thermoplastic Elastomers

By globally orienting the microdomains, a well-defined initial morphological state aids greatly in the interpretation and modeling of mechanical deformation and allows for exploitation of the inherent mechanical anisotropy of the cylindrical and lamellar structures. To better understand how the initial sample morphology influences the evolution of morphology at large strains, we prepared near-single-crystal styrene-diene triblock copolymer samples via our recently patented roll-casting process.

The evolution of the morphology of a well-defined single grain of stiff glassy cylinders in a rubbery matrix was observed as a function of deformation to determine the deformation mechanisms and how these depend on the orientation of the applied stress with respect to the microdomain structure (8). Static SAXS measurements of cylinder orientation demonstrated highly aligned cylinders ($<15^\circ$ misorientation) with the closest packed plane parallel to the film surface ($<12^\circ$ rotational misalignment.) The deformation perpendicular and parallel to the cylinder axis was followed via synchrotron SAXS with simultaneous measurement of load. Deformation was frozen in the TEM samples by high-energy electron irradiation, followed by OsO₄ staining.

Deformation perpendicular to the cylinder axis proceeds in two stages: low strain elastic deformation and high strain deformation, separated by a kinking instability. Initially the composite behaves as a constrained rubber in a state of plane strain. Lateral contraction occurs almost exclusively in the unconstrained direction giving rise to a Poisson ratio of 0.9 for the matrix. At a strain of approximately 130% a shear instability, occurring first in local regions of cylinder misalignment, causes a kinking of the cylinders on opposite sides of the kink in which the cylinders cooperatively turn towards the stretching direction (SD). Kinking relieves the plane strain constraint on the rubber allowing the lower energy process of shear rather than a higher energy bulk dilation process. At high strain the deformation

proceeds by continuous shear with an increase in spacing between cylinders along the SD as the matrix continues to contract laterally. TEM results provide direct evidence of a chevron texture of kinked cylinders when viewed at perpendicular incidence. At parallel incidence faults in the distorted hexagonal lattice are observed. The correlation lengths of the chevrons and faults are estimated to be 5 μm and 0.1 μm respectively. Both real and reciprocal space data are combined to construct a 3-D model of the deformed structure.

In addition to studying the deformation of neat triblocks, we examined the large strain behavior of a blend of mineral oil and a styrene-isoprene-styrene triblock (9). The blend formed polystyrene spheres arranged on a body-centered cubic lattice in a matrix composed of polyisoprene and mineral oil. The roll-cast sample exhibits approximately uniaxial symmetry around the rolling direction, which corresponds to the [111] crystallographic direction of the lattice. The glassy spheres act as physical crosslinks of known crosslinking functionality in the soft rubbery matrix. This oriented cubic material was also studied by a simultaneous tensile - SAXS experiment, where the sample was stretched up to 300% along the [111] direction. By monitoring the position of the (222) and (1 $\bar{1}$ 0) reflections, the deformation of the lattice is shown to be affine with the macroscopic deformation of the sample. The axial Poisson ratio was determined to be 0.45 to 0.47 over the entire range of deformation, and the glassy domains remained spherical throughout the deformation. Deformation of the microstructure is totally reversible upon unloading. A fault model is proposed to describe the microstructural changes induced by high-strain deformation.

Morphology and Dynamic Interaction of Defects in Polymer Liquid Crystals

The need to examine the production and interaction of defects under applied fields in LC polymers is apparent in order to help understand the processing-structure-property relationships in this important material class since LCP materials have high potential as high performance structural materials as well as electro-optical devices.

The nucleation and growth of a nematic phase from an isotropic matrix of a liquid crystal polyether, DHMS 7,9, was followed using polarized light video microscopy after cooling the sample below the isotropic to nematic transition. Nucleation was quickly followed by domain growth and then domain coalescence. Mechanisms were determined for creation of defects of strength $s = +1, -1, +1/2, -1/2$. At early times during the nucleation and growth process, anchoring conditions dominate the system. This leads to the creation of a single $s = +1$ defect within each domain. At late times, after many domains have coalesced, defects with $s < 0$ are seen in locations where impingement

occurred. These defects formed in DHMS-7,9 are a results of the competition between anchoring conditions and defect interaction events.

The effects of magnetic fields on defect texture were studied from both an experimental and theoretical point of view (10). Simulations of the director field distribution about Néel walls were developed by numerically solving Frank's equation of elasticity for the general case of arbitrary field angle and elastic anisotropy. A quantitative comparison between experiments and simulations was made in order to determine the elastic anisotropy. The results obtained with this mathematical method were in agreement with results obtained previously on the same polymer.

Technology Transitions:

Our patented roll-casting process developed under prior AFOSR support (91-0078) spawned a separate 2 year \$325,000 contract with Master Builders Inc. of Cleveland, Ohio for the development of anisotropic polymer solids. The aims of this contract were to extend the technology towards manufacture of highly mechanically anisotropic samples for use in expansion joints in concrete flooring. We built several new roll caster units incorporating larger and smaller rolls as well as temperature controlled rollers for rolling nonvolatile solvent samples (block copolymer-oil blends). Two publications sponsored by the Master Builders project which are strongly related to our AFOSR program are reported below:

Microstructural changes following thermal annealing or solvent annealing of roll-cast films with cylindrical and lamellar morphology were monitored using two-dimensional small angle X-ray scattering, transmission electron microscopy and thermomechanical analysis (11, 12). The microdomains in the unannealed films of cylindrical morphology were found to be assembled on a distorted hexagonal lattice, due to the roll-casting flow field. Thermal annealing significantly improved the alignment and packing of the cylinders, increased grain size, reduced the number of morphological defects and resulted in a 12% decrease in the area per junction. The microstructure of the unannealed films of lamellar morphology was observed to be composed of many small grains with low-angle helicoid surface twist boundaries. Annealing significantly reduced the number of grains and twist boundaries and resulted in a 7% decrease in the area per junction.

As processed films containing process-related residual stresses were also exposed to solvent vapors. Three solvents were used: toluene, which is a non preferential solvent for polystyrene and polybutadiene; methyl ethyl ketone, which is a preferential solvent for the polystyrene blocks; and hexane, which is a preferential solvent for the polybutadiene block. Solvent swelling significantly improved the symmetry of the hexagonal packing of

the cylindrical domains, which was initially distorted due to the roll-casting flow field. Solvent swelling was also found to improve the long range order in roll-cast film with lamellar morphology. Various phenomena were found to accompany the swelling and deswelling of films with both cylindrical and lamellar morphology with the three different solvents used. Especially intriguing results were observed for the case of swelling both morphologies in hexane. For films with a lamellar morphology, after 1 hour of swelling and 2 hours or subsequent deswelling the d-spacing decreased by 18%. For films with cylindrical morphology, a similar decrease of 9% was observed. The microstructural changes that accompanied the swelling of the structure were closely linked to the mobility of the glassy polystyrene blocks, the relaxation of process-related stress and the ability of the polybutadiene-polystyrene junctions at the interfaces to reposition and accommodate volume changes. Our results suggest that a thorough understanding of swelling and deswelling kinetics could be utilized to tailor a specific dimensional response of a block copolymer to solvent exposure.

Personnel Supported: (full or partial support)

Graduate students

C. Honeker
J. Chen
J. Gunther

Postdocs

Dr. R. Lescanec (now at Gillette)
Dr. L. Radzilowski
Dr. M. Wohlgemuth (von Humboldt Fellow from Univ. Bonn)

Undergraduates

C. Lambert (Mathematics, MIT, now PhD student at Univ. of Washington)

Degrees Granted

Dr. C. Honeker, PhD 6/97, Department of Materials Science and Engineering, "Large Strain Deformation Behavior of Oriented Triblock Copolymer Cylinders."

Dr. J. Gunther, PhD 6/97, Department of Materials Science and Engineering, "Defects in Liquid Crystal Polymers: Their Origins and Behavior in Magnetic and Flow Fields."

Dr. J. Chen, PhD 2/97, Department of Materials Science and Engineering, "Influence of A Liquid Crystalline Block on the Microstructure and Optical Properties of Block Copolymers."

Ms. E. Prasman, MS 2/97, Department of Materials Science and Engineering, "Morphology and Mechanical Behavior of Oriented Blends of Styrene-Isoprene-Styrene Triblock Copolymer Blends with Mineral Oil"

Collaborators

Y. Tselikas, Prof. N. Hadjichristidis (Univ. Athens)
Dr. L.J. Fetters (Exxon)
Prof. D.C. Martin (Univ. Michigan)
Dr. M. Capel (Brookhaven National Laboratory)
Dr. D.-K. Ding (International Center for Materials Research, Japan)

Patent Granted

Albalak, R. J. and Thomas, E. L., Method for Preparing Oriented Polymer Structures, US Air Force Invention No. 21,163, US Patent No. 5,622,668 (1997)

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2. *Macromolecules* 29, 3390-3396 (1996) (with Y. Tselikas, N. Hadjichristidis, R.L. Lescanec, C.C. Honeker and M. Wohlgemuth), "Architecturally Induced Tricontinuous Cubic Morphology in Compositionally Symmetric Miktoarm Star Block Copolymers."
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8. *Chemistry of Materials* 8, 1702-1714 (1996) (with C. Honeker), "Impact of Morphological Orientation in Determining Mechanical Properties in Block Copolymer Systems."

9. *J. Polymer Science (Physics)*, submitted December, 1996 (with E. Prasman), "High-Strain Tensile Deformation of a Sphere-Forming Triblock Copolymer/Mineral Oil Blend."
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11. *Polymer*, **38**, 3819-3825 (1997) (with R. Albalak and M. Capel), "Thermal Annealing of Roll-Cast Triblock Copolymer Films."
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