In the investigations of polymer blends we have continued efforts in the areas of microstructural effects on miscibility in copolymers, of segmental interactions (hydrogen bonding) in high temperature blends and in solid state NMR studies of blend structure. In our studies of electrically and non-linearly active conjugated polymers we have emphasized structural studies of poly-π-phenylene vinylene and derivatives, blends, and analogues. We have also completed ultrastructural processing investigations on these materials as well as collaborative studies of the effect of processing on the optical properties.

The computer simulation studies of binary polymer systems in the grant period have been extended to cover copolymer blends, mixtures containing semi-flexible chains, and dynamic aspects of phase decomposition. The use of quasi-elastic light scattering has been extended to investigate the effect of molecular architecture on diffusion in porous media. Other studies in the grant period covered liquid crystalline polymer behavior, dielectric properties of composites and the properties of solvated polyions.
ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS

MIRP GRANT AFOSR 89-0069
10 October 1988 - 9 February 1990

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003

Approved for public release; distribution unlimited.
TECHNICAL REPORT

ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR MATERIALS

MIRP GRANT AFOSR 89-0069

10 October 1988 - 9 February 1990

Frank E. Karasz
Department of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01003
ACKNOWLEDGEMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Senior Program Manager, Directorate of Chemical Sciences, and to other members of the Directorate, for their unfailing cooperation, help and courtesy extended to him during the period of this grant.
CONTENTS

I. TITLE
II. PRINCIPAL INVESTIGATOR
III. GRANT NUMBERS/DATES
IV. SENIOR RESEARCH PERSONNEL
V. JUNIOR RESEARCH PERSONNEL
VI. ABSTRACT OF ACCOMPLISHMENTS
VII. DESCRIPTION OF RESEARCH UNDERTAKEN
VIII. PUBLICATIONS
I. TITLE: Ultrastructure Processing of Macromolecular Materials

II. PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz  
Polymer Science & Engineering  
University of Massachusetts  
Amherst, Massachusetts 01003

III. GRANT NUMBER: AFOSR 89-0069 (October 10, 1988 - February 9, 1990)

IV. FACULTY ASSOCIATES: Professor W. J. MacKnight (PSE)  
Professor Paul Lahti (Chemistry)

SENIOR RESEARCH PERSONNEL: Dr. J. Obrzut  
Dr. T. Bleha  
Dr. W. Liang  
Dr. S. O'Donohue  
Dr. P. Musto  
Dr. L. Wu  
Dr. A. Sikora  
Dr. D. Rice  
Dr. R. McCoy  
Dr. J. Simon  
Dr. Z. Chai

V. JUNIOR RESEARCH PERSONNEL: R. Gregorius  
W. Nachlis  
M. Masse  
Y. Guo  
F. Denton
VI. ABSTRACT

This report is for the period 10 October 1988 to 9 February 1990 and covers the operation of an AFOSR MIRP at the University of Massachusetts. During this period the research program contained components dealing with polymer blends, electro- and optically-active polymers, computer simulation of blend phenomena, dynamic light scattering measuring diffusion in porous media, and aspects of ultrastructural processing. The MIRP program constitutes the core research complementing an AFOSR/DARPA URI contract which was initiated here on 1 January 1987.

In the investigations of polymer blends we have continued efforts in the areas of microstructural effects on miscibility in copolymers, of segmental interactions (hydrogen bonding) in high temperature blends and in solid state NMR studies of blend structure. In our studies of electrically and non-linearly active conjugated polymers we have emphasized structural studies of poly-p-phenylene vinylene and derivatives, blends, and analogues. We have also completed ultrastructural processing investigations on these materials as well as collaborative studies of the effect of processing on the optical properties.

The computer simulation studies of binary polymer systems in the grant period have been extended to cover copolymer blends, mixtures containing semi-flexible chains, and dynamic aspects of phase decomposition. The use of quasi-elastic light scattering has been extended to investigate the effect of molecular architecture on diffusion in porous media. Other studies in the grant period
covered liquid crystalline polymer behavior, dielectric properties of composites and the properties of solvated polyions.

Some fifty-nine papers were published or are in press as a result of AFOSR support in the grant period.

VII. DESCRIPTION OF RESEARCH UNDERTAKEN

Some fifty-nine (59) manuscripts were published or are in press in the grant period. A selection of results is presented below.

A. Miscibility in Random and Block Copolymers

Blends of PPO and polystyrene (PS) are known to be miscible over the whole range of compositions and accessible temperatures. Miscibility has sometimes been attributed to the formation of specific interactions between PS and PPO which lead to favorable heats of mixing. The segmental interaction parameter for blends of PPO and PS, $\chi_{\text{PPO},\text{PS}}$, has been estimated to be about -0.1.

A different phase behavior will be expected as the styrene units in the chain are systematically substituted by a second component. In this contribution, two limiting cases with respect to the distribution of the components in the copolymer have been studied: 1) PPO has been blended with random copolymers of styrene (S) and methyl methacrylate (MMA) [P(S-r-MMA)]; and 2) PPO has been blended with block copolymers containing these components, [P(S-b-MMA)].

A great deal of interest has been shown in miscibility of mixtures of block copolymers and the corresponding homopolymers. It has been shown that the
miscibility is sensitive to the molecular weight ratio of the homopolymer and the corresponding block of the copolymer, i.e., miscibility is directed by an entropic effect. When the ratio exceeds unity, the entropy change becomes highly unfavorable for mixing. However, when PPO is blended with diblock copolymers of styrene and methyl methacrylate the phase behavior is also governed by the interaction parameters $\chi_{\text{PPO/PS}}$ and $\chi_{\text{PPO/MMA}}$. Because of the comparatively large negative value of $\chi_{\text{PPO/PS}}$ it might be expected that the unfavorable entropic effect can be compensated for and to a certain extent, miscibility between PPO and the styrene block may occur essentially as in the case of the corresponding homopolymers. This was indeed shown to be the case very recently for PPO with PS-containing blocks but a solubility limit was also shown to occur if the molecular weights became too disparate. In the present study blends of PPO and the block copolymers of styrene and MMA behave essentially as the corresponding homopolymers in terms of miscibility.

B. Computer Simulations

Numerical simulation of binary mixtures of homopolymers in either two or three dimensions have yielded considerable microscopic information on equilibrium lattice conformations and have permitted examination of the deviations from the mean-field treatment usually applied to such polymer blends. Such computer simulations can readily be performed for a range of interaction energies and have demonstrated effects of mixing, segregation, hole formation, etc. as a function of this parameter.
Mixtures of random or near-random copolymers which have received substantial experimental investigation in our laboratory offer an opportunity of examining the effect of additional degrees of freedom in composition and in microstructure and show effects which are peculiar to such systems. For example, it is known that if the intramolecular repulsive interactions between unlike moieties in a statistical copolymer are sufficiently large relative to the intermolecular interactions in the system, a miscible domain may appear for a range of copolymer compositions, even if all the segmental interactions in the system are repulsive.

In this simulation interactions in copolymer-homopolymer \((A_xB_{1-x}/A_yB_{1-y})\) mixtures containing equal amounts of the two respective components were studied as a function of the copolymer compositions \(x\) and \(|x-y|\) respectively, and of segmental interaction energies using simulations of chains on a planar square lattice. The effective interaction parameter \(\chi_{\text{blend}}\) for regimes corresponding to miscibility was less strongly dependent on \(x\) (or \(|x-y|\) ) than predicted by the mean-field square power rule, and the number of heterocontacts varied widely from that calculated by random mixing. In the immiscibility regime the effective \(\chi_{\text{blend}}\) becomes asymptotic as a result of phase separation.

It has been commonly concluded that mean-field theory works reasonable well in dense polymer systems since to a good approximation the segment density can be considered uniform. Here we find that high density is a necessary but not always a sufficient condition. In systems with large concentration fluctuations,
such as immiscible polymer mixtures, the simple mean-field treatment with random mixing obviously becomes inapplicable.

C. Diffusion in Constrained Media

The study of polymer transport in porous media has theoretical importance as well as relevance to many phenomena of technological and scientific interest. Experiments such as transport across track-etched membranes transient diffusion into porous glass and broadening of chromatographic peaks have been directed towards relating macroscopic diffusion to the microscopic parameters characterizing the polymer and the porous medium. The major disadvantage of these phenomenological techniques is that knowledge of the boundary layer resistance to transport and the equilibrium partitioning coefficient of the polymer between the unbounded solution and the pore space are necessary for the interpretation of the data. Attempts to explore directly the movement of molecules within the porous medium have employed the experimental techniques of forced Rayleigh scattering, pulsed field-gradient spin-echo NMR and quasi-elastic light-scattering. Recently, we have reported the direct measurement of the diffusion of linear flexible polystyrene in porous glasses by quasi-elastic light scattering (QELS). This technique has the advantage of probing directly the diffusion in pores inside a single fragment of porous material, under thermodynamic equilibrium conditions. These measurements showed that the reduced diffusion in the controlled pore glasses relative to the unbounded solution can be understood in terms of structural effects and hydrodynamic interactions,
wh i are separable phenomena. We have now completed the direct measurement by dynamic light scattering, of the macroscopic diffusion coefficient $D_0$ (at low $q$) of linear, 4-arm star and 8-arm star polyisoprene in silica controlled pore glass, for values of the confinement parameter $\lambda_H = R_H/R_p < 0.1$, where $R_H$ is the hydrodynamic radius of the polymer and $R_p$ is the radius of the pores in the glass. The reduced diffusion in the pores is found to depend on the molecular architecture of the polymer. For a given $\lambda_H$, the branched polymers diffuse more slowly than 4-arm stars of the same hydrodynamic radius. The results were compared to hydrodynamic theories for hard spheres in isolated cylindrical pores. Our results indicate that the hydrodynamic radius of a polymer derived from its diffusion coefficient in dilute unbounded solution does not uniquely describe the hydrodynamic effects of a constraining wall on its diffusion behavior. Our data suggest that the presence of two length scales in the porous material could play an important role in the diffusion of strongly confined chains, in accordance with the theoretical model of Muthukumar and Baumgartner.

D. Biaxial Orientation of PPV

In previous work we have shown that the electrically conducting polymer, poly(p-phenylene vinylene) (PPV) can be prepared in the form of highly uniaxially oriented continuous film by simultaneous heating and stretching of the processible poly(sulfonium salt) precursor. Moreover it was shown that upon chemical doping with strong electron acceptors, these films exhibit high anisotropic electrical conductivity. Conductivity in the direction of orientation may exceed that in the
transverse direction by up to a factor of eighty.

We have developed two processes by which the poly(sulfonium salt) PPV precursor can be oriented biaxially. The first is a two-stage sequential stretching operation which is a modification of the uniaxial stretching process. This process allows non-equibiaxial stretching over a wide range of deformation ratios. The second process is a film blowing technique which involves an equibiaxial planar extension. The resulting films were examined using X-ray diffraction prior to chemical doping with SbF$_5$ vapor. Biaxial orientation was shown to exert considerable influence over the attainable electrical conductivity and mechanical properties.

E. Poly(2,5 Dimethoxy Phenylene Vinylene)

A coordinated study on electrochemical, magnetic, optical and transport properties of poly(dimethoxy phenylene vinylene), PDMPV, using \textit{in situ} electrochemical doping techniques was completed. Properties were correlated through a common axis of applied voltage. Electrochemical doping shows ca. 100\% coulombic efficiency up to an applied potential of 3.8 V vs. lithium in propylene carbonate electrolyte. Conductivity increases in a reversible manner to a maximum of 250 $\Omega^{-1}$cm$^{-1}$ and an applied potential of 3.9V. Potentials in excess of 3.9V cause an irreversible decrease in conductivity. Spin and charge show a 1:1 relation only to very low doping levels. Two paramagnetic species are produced on doping. A maximum spin concentration is observed at ca. 3.7 V. The UV-Vis-NIR spectra of doped PDMPV show at least five absorption bands, at 4.8, 3.7, 2.5, 1.7,
and 0.6 eV. The first three bands decrease with doping and the latter two increase. When analyzed by the polaron/bipolaron model, the optical data imply significant symmetry breaking. Contributions to the optical activity from polarons and bipolarons are determined from the EPR results and are found to be different for both peaks, implying greater symmetry breaking effects for polarons. An electrochemical analysis of EPR results suggested that polaron interaction energies are ca. 0.45 eV greater than those for bipolarons.
VIII. PUBLICATIONS


5. Colloid & Polymer Science 267, 552-555 (1989) (with G. Banhegyi and F.P. LaMantia) "Comment on the "Dielectric Properties of LDPE/Ny6 Blends".


33. Biennial Polymer Symposium, "Thermal and Phase Behavior in Miscible Polybenzimidazole/Polyetherimide Blends" (in press)


37. Die Makromolekulare Chemie, "Fourier Transform Infrared Spectroscopy of the Polymorphic Forms of Syndiotactic Polystyrene" (in press)

38. Chemistry of Materials, "Highly Ordered Fibers from the Discotic Phase of Copper (II) Pentacosadiynoate: A Route to Oriented Poly(diacetylene)" (in press)


40. Macromolecules, "Characterization of Chain Orientation in Drawn Poly(p-phenylene vinylene) by 2H Quadrupole Echo NMR Spectroscopy" (in press)

41. Liquid Crystals, "Dielectric Relaxation Spectroscopy and Molecular Dynamics of a Liquid-Crystalline Copolymer having Longitudinally and Laterally attached Mesogenic Groups as Side Chains" (in press)


43. Polymer-Plastic Technology & Engineering, "Applied Dielectric Spectroscopy of Polymeric Composites" (in press)
44. Polymer Commun., "Blending Effects in the Polymorphism of Syndiotactic Polystyrene Crystallized from the Quenched Amorphous Phase" (in press)

45. Liquid Crystals, "Side-Chain Liquid Crystalline Copolymers Containing Charge Transfer Groups" (in press)


52. Journal of Polymer Science, Part B, "2H NMR Characterization of Phenylene Ring Flip Motion in Annealed Poly(p-phenylene vinylene) PPV Films" (in press)

53. Polymer, "Investigation of H₂SO₄ Doped, Ring Deuterated Poly(p-Phenylene Vinylene) Using Solid State 2H Quadrupole Echo NMR Spectroscopy" (in press)


55. Die Makromolekulare Chemis, "Transitional Properties of Liquid Crystalline Side-Chain Polymers Derived from Poly(hydroxystyrene)" (in press)

56. Polymer, "Molecular Orientation of Highly Drawn Poly(p-2-methoxyphenylene vinylene)" (in press)


59. Polymer, "Preparation of Poly(p-Phenylene Vinylene) Deuterium Labeled in the Vinylene Positions" (in press)