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FINAL TECHNICAL REPORT

**ULTRASTRUCTURE PROCESSING OF MACROMOLECULAR
MATERIALS**

MIRP GRANT AFOSR 90-C-0019

10 February 1990 - 11 February 1993

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- I. **TITLE: Ultrastructure Processing of Macromolecular Materials**
- II. **PRINCIPAL INVESTIGATOR: Dr. Frank E. Karasz**
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- III. **GRANT NUMBER: AFOSR 90-C-0019**
February 10, 1990 - February 11, 1993
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VI. ABSTRACT

The report covers the operation of an AFOSR MIRP at the University of Massachusetts for the period 10 February 1990 to 11 February 1993.

The research has concurrently involved several areas of investigation in the physical chemistry of macromolecules. A major theme has been the study of the properties of **polymer blends**. Experimentally we have investigated the effects of microstructure on miscibility in a number of model systems by thermal, mechanical and varied novel spectroscopic techniques, and have also gained a wide understanding of the fundamental basis of the metastable miscibility found in an unexpectedly large number of high temperature systems, i.e. these typically involving polyimides or related materials with high Tg's. In complementary investigation we have performed **computer simulation** studies of the equilibrium behaviour of various blends and under several relevant constraints. Such calculations provide substantial insights into molecular behavior in binary systems at the segmental level. The work also investigated dynamic aspects, particularly phase separation at differing effective quench depths. Another line of investigation has concerned itself with **electro-optically active conjugated polymers**, principally poly(*p*-phenylene vinylene) and its derivatives, modifications and blends. Here the emphasis has been on gaining a detailed understanding of the structural properties and concurrently exploiting the several electro-optical effects for which these polymer systems are noted. These include non-linear optical phenomena and electroluminescence. Certain **solution**

properties of polymer systems have also been studied. In particular we have continued to use quasi-elastic light-scattering measurements to investigate **translational diffusion of solvated polymers** in porous media and other properties of polar and non-polar macromolecules. A synthetic effort in **side-chain liquid crystal polymers** has led to the systematic study of the thermal, mechanical, and dielectric properties of several representative series and, in some cases, of their mixtures. Other syntheses have aimed at providing **new polyimides**. A number of theoretical investigations related to the above projects have also been completed.

During the grant period some ninety-nine manuscripts were published or have been submitted as a result of AFOSR support, see Section VIII.

VII. DESCRIPTION OF RESEARCH UNDERTAKEN

The ninety-nine manuscripts published or submitted during the grant period and listed in Section VIII present full details of the research undertaken. Previous Annual Reports also describe results obtained. A further discussion of selected significant projects is presented below.

A. Miscibility in Model Copolymer Systems

Miscibility in blends of random copolymers of *o*-chlorostyrene and *p*-chlorostyrene [$P(oClSy-co-pClS_{1-y})$] with eight atactic polystyrene (aPS) fractions has been studied at temperatures ranging from 150°C to 300°C. From these data, the temperature dependence of the three segmental interaction parameters required to describe this system were obtained using this technique for the first time.

In addition, the miscibility and phase behavior in 50/50 wt % blends of chlorinated poly(vinyl chloride) (CPVC) and poly(acrylonitrile-co-butadiene) (AN-BT) copolymer have been investigated. It was found that the extent of miscibility of the CPVC/(AN-BT) system becomes larger with increasing chlorine content of CPVC, compared to that of the PVC/(AN-BT) system. The maximum miscibility region was found around 63 wt % Cl in the CPVC blend system. By assuming a random copolymer structure for both components and applying first-order mean field theory to the experimental results, the respective segmental interaction parameters, χ_{ij} 's were determined. The theoretical phase boundary is consistent with

experimental data. By studying the temperature effect on the phase behavior of this blend, lower critical solution temperature behavior was identified as evidenced by the contraction of the miscibility region at 170 °C.

This work was extended theoretically and experimentally to study sequence distribution effects (microstructure) in copolymer miscibility. Such effects can dominate the phenomenon under certain conditions.

Solid state NMR techniques were employed in novel fashion to study the micro-morphology of miscible blends. It is tacitly assumed, without direct evidence, that fulfillment of the "single Tg" criterion of miscibility implies complete inter-segmental mixing. Advanced NMR methodologies provide more definitive information about segmental distribution in such systems and in the case of the model PPO/PS system indicate that homogeneity at the segmental level is probably absent even in systems characterized by a substantially negative χ_{ij} .

B. Computer Simulations of Miscibility in Binary Systems

Interactions play a decisive role in polymer-polymer miscibility. However, direct elucidation of interactions from thermodynamic mixing properties is experimentally cumbersome because of high viscosity and glass transition temperature effects in polymer systems, and because there are theoretical problems attributable to the mean-field approximation. Therefore we are interested in Monte Carlo (MC) simulations which overcome some of these restrictions and are an alternative to the

experimental and purely theoretical approaches. Results of such simulations are available for only a few model systems. MC simulation provides insight into these systems in two ways. First, simulation is an independent method that is free of mean-field approximations, so it enables us to account both for connectivity of monomers within the chains and for concentration fluctuations due to nonrandom mixing. Second, this method is a useful supplement to the standard copolymer theory because it enables us to investigate χ_{blend} over the complete polymer composition range. This flexibility allows us to see whether χ_{blend} behaves according to the quadratic mixing rule over the total composition range $0 < x < 1$. In other words, we can determine whether the segmental interaction parameters χ_{ij} obtained from miscibility boundaries at two copolymer compositions accurately represent χ_{ij} over this range. During the grant period we have studied a range of binary systems by the MC technique in two and (mostly) three dimensions. The results have enabled us to cover a wide range of interaction energies and to "observe" mixing-demixing transitions in binary homopolymer and copolymer situations. The effect of chain flexibility and relative component concentrations on solvent and solute conformations (as well as on miscibility) have also been studied. In the later portion of the grant period we have extended these concepts to variable density situations (technically, grand or semi-grand canonical ensembles *vis-à-vis* the canonical ensembles of the initial work) especially appropriate for

homopolymer or miscible blend surfaces or immiscible blend interfaces. The results obtained are somewhat "ahead of experiment" and we are currently attempting to verify certain predictions regarding the surface effects.

Dynamic situations -- phase separations -- have also been explored. By changing the reduced segmental interaction energy from attractive to repulsive at time $t = 0$ we can simulate quenching experiments below the UCST -- and vary "quench depths" -- and thus observe the initial stages of phase decomposition. Good agreement with Cahn-Hilliard theory was obtained in regimes where direct experimental observation is difficult or impossible.

C. Polyarylene Vinylenes

Polyarylene vinylenes constitute the most chemically versatile π -conjugated macromolecule systems and have interest in their basic structure and properties as well as a wide variety of potential applications.

It has been known that doped (i.e. oxidized or reduced) members have high electrically conductivity, the exact nature of these complexes is one area of interest that has been investigated. The stage-1 phases of Cs-doped poly(*p*-phenylene vinylene) (PPV) have been investigated by *in situ* x-ray diffraction, using highly oriented vapor-doped samples. While the relative guest-host sizes are nearly equivalent, the resulting equatorial structures, as determined by structure-factor calculations, exhibit pronounced differences in the location and orientation of the polymer chains. PPV

samples are dominated by uniform chain-axis rotations within a base-centered orthorhombic lattice of the Cs^+ ions while polyacetylene undergoes displasive translations within a centered tetragonal lattice of the Rb^+ ions. Significant differences in the dopant-ion organization within the quasi-one-dimensional alkali-metal ion channels are also found. These temperature insensitive and polymer specific variations are indicative of local guest-host interactions which stabilize the respective structures. Further comparisons suggest that systematic intermediate-length-scale deviations from planarity by the polymer chains are probable. As a result, the electronic excitations may couple to polymeric torsional degrees of freedom.

In addition, solid-state ^2H quadrupole echo nuclear magnetic resonance (NMR) spectra and measurements of ^2H spin lattice relaxation times have been obtained (for example) for films of poly(*p*-phenylene vinylene) deuterated in the phenylene ring positions (PPV- d_4). NMR line shapes show that all the phenylene rings of PPV undergo 180° rotational jumps about the 1,4 ring axis ("ring flips") at 225°C . The temperature dependence of the ^2H line shapes show that the jump motion is thermally activated. The jump rate was also determined from the magnitude of the anisotropic T_2 relaxation associated with ^2H line shapes and from the curvature of inversion recovery intensity data. The experimental activation energy for jumps is comparable to the intramolecular potential barrier for rotation about phenylene vinylene bonds. ^2H NMR provides a method for

determining the phenylene vinylene rotational barrier in pristine PPV, and may potentially be used to study conjugation in conducting films.

Copolymers of various analogous structures incorporating hetero-atoms have been synthesized. Their characterization provided additional information regarding the effect of chemical and micro-structure on these π -conjugated systems.

D. Diffusion of Solvated Macromolecules in Constrained Media

The dynamics of a one-dimensional Brownian particle have been treated theoretically over a wide time scale in the presence of random reflecting barriers to complement our experimental studies. Green functions for particle motion with two kinds of barriers were formulated, one being diffusion with fixed random barriers and the other with stochastic random barriers. The stochastic barriers appear randomly on the time axis as well as with positional disorder and then, after a while, disappear. To treat these problems, we first developed a mean-field Green-function (MFG) theory. The effects of many barriers, regarded as a multiple perturbation to the free diffusion of the particle, were decomposed into many elements. Their average effects (the first cumulant of the random perturbation elements) were sequentially incorporated into the unperturbed Green function up to the number of the elements. The first-cumulant MFG was thus obtained and covers the whole range of the perturbation intensity of the mean element. Taking into account a higher-order correlation among

the perturbation elements yielded a higher-order cumulant MFG. By applying the first-cumulant and the second-cumulant MFG theories to the particle diffusion with fixed and with stochastic barriers, we calculated the mean-square displacement as a function of time. It was found that the first-cumulant MFG describes qualitatively the dynamic behavior of the particle on all the time scales, whereas the second-cumulant MFG gave a more accurate numerical coefficient in the estimation of the time-dependent mean-square displacement.

The complementary experimental program investigated the diffusion of macromolecules in a porous network of silica glass. The essential point is that a solvent iso-refractive with the silica (2-fluorotoluene) could be chosen which thus renders the motion of the solute (i.e. the polymer chains) visible. These measurements provided (often for the first time) data for comparison with theory and also revealed more subtle effects (e.g. with regard to concentration and bimodality) which have yet to be accounted for. We believe these measurements will have important applications in polymer separation science and technology.

E. Side-Chain Liquid Crystal Polymers

A series of side-chain liquid-crystalline copolymers, the poly[4-[1-(4-methoxy-4'-oxyazobenzene)-8-octyl]oxystyrene]-co-poly[4-[α -(4-methoxy-4'-oxyazobenzene)- ω -alkyl]oxystyrene]s, has been prepared in which the second spacer is varied in length from three methylene units up to twelve. The

properties of the copolymers are compared with those of the homopolymers, the poly[4-[α (4-methoxy-4'-oxyazobenzene)- ω -alkyl]oxystyrene]s. All the polymers exhibit smectic behavior with the exception of the propyl homopolymer, for which no mesophase is observed. The transition temperatures of the copolymers are similar to the mean values of the homopolymers. The largest deviations from this behavior were observed for copolymers containing either propyl or butyl spacers. In contrast the transitional entropies exhibited by the copolymers show significant negative deviations with the exception of dodecyl-octyl copolymer, for which a small positive deviation is observed. We interpret these differences in terms of steric factors. Electrically induced alignment of the LC polymer was also investigated.

F. Other Studies

The AFOSR grant provided opportunities for a considerable number of investigations in addition to the central themes outlined above (see Section VIII). Many of these concerned new materials (e.g. polyimides) or binary systems involving ultimately issues of heterogeneous non-polar or polar segment-segment interaction. Thus understanding the effect of microscopic interactions on macroscopic behavior may be considered the ultimate goal and achievement of the research.

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