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AUTHOR(S)
Frank E. Karasz

PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Massachusetts,
Materials Research Laboratory
Polymer Science & Engineering Dept
Amherst, MA 01003

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I. TITLE: Physical Properties of Polymers

(Ultrastructure Processing of Polymers)

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

III. GRANT NUMBER: AFOSR 80-0101

IV. DATES: 1 January 1980 - 30 September 1982

V. SENIOR RESEARCH PERSONNEL*:
Dr. C. Crosby
Dr. T. Ellis
Dr. X. Jin
Dr. Y. Maeda
Dr. M. Miller (MIRP)
Dr. G. ten Brinke
Dr. R. Vukovic

VI. JUNIOR RESEARCH PERSONNEL*:
V. Chacko
K. Djordjevic
S. Frederick (MIRP)
J. Schroeder
G. Tostiga (MIRP)
S. Zacharius

*Research Personnel supported through Faculty Associates after 1 October 1981 are indicated by MIRP.

VII. ABSTRACT OF ACCOMPLISHMENTS

This report covers the period January 1, 1980, to September 30, 1982. For the first twenty-one months the research undertaken was an extension of earlier AFOSR supported endeavors dealing mainly with the physical properties of polymer blends, the plasticization of epoxy and other network polymers by water and the characterization of stiff chain macromolecules by quasi-elastic light scattering. A number of other topics received attention, detailed below. On 1 October 1981 the objectives of AFOSR 80-0101 were expanded; it became a Multiple Investigator Research Project (MIRP) with a new focus for that of producing novel ultrastructural assemblies of macromolecules with electrical properties of interest. Two Faculty Associates, Professors R.W. Lenz and H.H. Winter, both of the Chemical Engineering Department here, were incorporated into the supported research program. However work on the previously identified areas in the physical properties of polymers, carried out by the P.I., was also continued, and is discussed below. The ultrastructural research program was therefore only at a relatively early stage at the conclusion of the time frame covered by this Report.

In the polymer blend research substantial progress was achieved in elucidating thermodynamic and structural factors underlying the phenomenon of miscibility in binary polymer systems. The effects of chemical structure, tacticity, molecular weight, temperature, and their components were investigated by a number of techniques including calorimetry, vapor absorption, inverse gas chromatography and by the establishment of binary or ternary phase diagrams for appropriate systems. These were typically poly(2,6-dimethyl phenylene oxide) (PPO) and a halogenated styrene polymer or copolymer. By the conclusion of the reporting period a fairly detailed understanding of these effects and some progress towards prediction of new effects, had been obtained.

The study of the plasticization of network polymers was prompted by an earlier study of the effect on water on epoxy resins. It was established that, contrary to some earlier suppositions, the relatively large depression in the glass transitions of epoxies by small amounts of absorbed water, could be accounted for by purely thermodynamic analysis and did not require, in particular, the concept of specific polymer-sorbate interactions. These ideas were extended, with some success, to other chemically cross-linked macromolecules.

The solution properties of the stiff chain macromolecule poly(p-phenylene benzbisthiazole) (PBT) were studied by depolarized forward scattering proton correlation spectroscopy (quasi-elastic light scattering). By this technique the persistence length and other important chain conformational parameters was obtained for the first time.

Other topics investigated include the properties of a novel composite in which ultra high molecular weight polyethylene is covalently bonded to filler particles, the conformational transitions in polypeptide systems and a number of theoretical problems.

As indicated above the MIRP project on ultrastructure was at a relatively early stage of development at the conclusion of this grant. Nevertheless progress had been on the synthesis of block copolymers with electrically active interior blocks and on the special processing achievable with extensional flow dies.

VIII. DESCRIPTION OF RESEARCH ACCOMPLISHED

The research completed during the grant period is divided into the following areas. In most cases, complete details are presented in the referenced publications or preprints (both available from the P.I.).

A. Polymer Blends

To understand the thermodynamic factors involving miscibility requires a knowledge of basic free energy of mixing data for the system. For some combinations of a halogenated polystyrene this was obtained from heat of solution measurements, (1). Other information was derived from dielectric relaxation data, (3,5) and from mechanical measurements, (2). The phase behavior of these polymers was extensively investigated (10,17,23,24,25,27,31,40,43). In general as the fraction of the halogenated styrene in the respective copolymers is increased, the LCST (lower critical solution temperature) decreases. In the case of copolymers of two dissimilar halogenated styrene units a "window of compatibility" appears (see, for example, ref. 25); a quantitative theory to account for this, which is in press (31), can be now used to calculate interaction parameters χ_{ij}, where i,j represent any monomer units within the system.

The significance of this development lies in the predictability of compatibility from the relatively easily determined χ_{ij}'s. This work has resulted in a number of reviews (2,4,9,12) and theoretical papers (13,18,28,36,40). Other systems have also been investigated, including the effect of tacticity in methacrylate polymers (32, and to be submitted). Crystallinity in these systems has been studied (39,44).

B. Plasticization of Network Polymers

The interaction of water was studied with respect to the effect of the diluent on the glass transition temperature, T_g. It is known that for example in epoxy resins relatively small amounts of water produce large depressions in T_g, (6,37). We were able to account for this effect purely in terms of thermodynamic factors ie. without the necessity of invoking "specific interactions". This treatment was extended to other network systems, (16) and theoretically (22). Quadrupole echo deuterium NMR studies (26) have recently confirmed that the water in epoxies is relatively mobile.

C. Quasi-elastic Light Scattering

Dynamic (quasi-elastic) light scattering can be used to characterize macromolecules in terms of size, conformation and, in favorable circumstances, size distribution. A specific form of this technique, forward depolarized scattering, yields rotational relaxation information directly, and is thus of use with respect to anisotropic conformations. In our work, forward depolarized light scattering was used to measure persistence lengths (a measure of chain stiffness) in poly(p-phenylene benzbisthiazole), (8). The properties of stiff chain polymers in more concentrated regimes was investigated in another study, (42).

D. Novel Composites

The interface between filler particles and a macromolecular matrix plays a key role in determining the mechanical properties of the composite. A novel composite was obtained in which the matrix (ultra high molecular weight polyethylene) was covalently bound to the surface of the filler particles ($CaCO_3$; Al_2O_3). The properties of this system were intensively examined, (14,15,29,33) in a morphological and mechanical property study.

E. Ultrastructure

a. Synthesis

The goal of this investigation has been to prepare block or graft copolymers which will form two distinct phases in the solid state, and in which one of the phases will be electrically conducting and the other not. To achieve this objective, the block or graft copolymers must be initially, at least, fusible or soluble so that well controlled and well characterized two-phase systems can be formed, and the phase structure must be maintained after doping one of the polymers to form the conducting phase.

One of the polymers for the conducting phase, which was selected for our initial study, was poly-2-vinylpyridine, PVP, which can be doped with either iodine or TCNB. This polymer can be obtained as a "living polymer" by anionic initiators, so AB block copolymers were prepared with both polystyrene, PS, and polybutadiene, PB, as the A blocks, which form the insulating phase and PVP as the B block for the conducting phase.

The diblock copolymers prepared could be solution cast into films that contained well developed two phase systems, which could be clearly seen by electron microscopy after selectively obtaining either the PB phase with osmium tetraoxide, OsO_4, or the PVP phase with iodine or methyl iodide. Considerable control including phase inversion can be achieved over the phase morphology by the manner in which the film is obtained, as well as by variation of polymer composition.

A second polymer under investigation, which has the potential of developing on doping conductivities as high as those of doped polyacetylenes, is polyphenylene vinylene, PPV. In all previous investigations described in the literature, this polymer has not been prepared in sufficiently high enough molecular weights from doped films for conductivity studies. However, we have investigated a new polymerization reaction by which we have been able to obtain strong films of the polymer by solution casting and reacting a precursor polymer. These films coula be doped with iodine to a metallic-like appearance; the conversion of the precursor film to the PPV film has been quantitatively achieved, and relatively high conductivities were obtained.

b. Extensional Flow Processing

A new technique has been developed for subjecting small polymeric samples to well defined extensional strains. The sample is introduced between two metal plates which are coated with a lubricant fluid. The sample is squeezed when the metal plates are driven together at a prescribed rate. The lubricant reduces the shear stresses in the sample to a level which is negligibly small. The instrument allows for measuring the squeezing force as well as the squeezing rate. Transient equibiaxial extensional viscosities as measured in this new device have been obtained. This is the first time that such an extensional viscosity has ever been measured for a molten polymer. The technique was developed further and is now capable of stretching at high temperatures and at prescribed rates. Preliminary descriptions of the studies described above are in press (34) and will be extensively discussed in papers to be submitted.

F. Other Investigations

Conformational transitions in stiff, hydrogen-bonded, helices in polypeptides were studied with respect to the effect of temperature, solvent composition and isotope substitution (H → D) (19,30, and to be submitted). A number of the related theoretical questions (38) were already referred to above.

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