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EFFECT OF STRUCTURE ON PHYSICAL PROPERTIES OF POLYMERS

Air Force Office of
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Frank E. Karasz

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The overall objective of this research program has been to investigate the physical nature of macromolecular systems as a function of the chemical and stereochemical structure of the macromolecule. A potential improvement in important facets of polymer properties was an underlying premise in the design and execution of the research. The work performed included investigations of the behavior of polymers in solution, as well as in the solid state and was accompanied by a program of theoretical studies to complement the experimental

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work. One focus of the research was the area of polymer-polymer interactions in binary blends, in which factors influencing compatibility, i.e., mutual solubility, were systematically investigated by a number of thermodynamic techniques. Heats of polymer mixing were obtained for selected systems and shown to be useful in predicting phase behavior otherwise obscured by non-equilibrium effects. The latter were also investigated theoretically in studies of the effect of domain size and composition on glass transition temperatures and allied phenomena. Another area of research concerned the physical properties of model epoxy network systems, and in particular, the effect of water on these properties. A characteristic of cross-linked polymers is their ready plasticization by relatively small amounts of low molecular weight materials and the basis of this observation has been explained on a thermodynamic basis. Solution properties of polymers were studied by means of quasi-elastic light scattering. The effect of an ionic structural component on macromolecular conformation was examined in some detail in model copolymers of acrylic acid and ethyl acrylate. This technique was also employed in studies of solubilized stiff chain polymers of high persistence length, while a complementary theoretical investigation dealt with this problem in more general terms as part of an investigation of rigid and near-rigid rod conformations using the so-called n-broken rod approximation. Mechanical properties of polymers were studied in a newly developed apparatus which measured the resonant vibrational frequencies of rigid beams in an extremely precise manner. From this it was possible to determine elongational and shear moduli on the same sample (as a function of temperature and, in principle, pressure, etc.) and hence Poisson's ratio for the polymer, a parameter important in composite theory and practise. Finally, mention is made of a number of miscellaneous investigations and advances, including the development of a precision high pressure differential thermal analysis aparatus capable of measurements up to 7000 kbars. These and other studies are described in the body of this report.

FINAL REPORT

EFFECT ON STRUCTURE ON PHYSICAL PROPERTIES OF POLYMERS

Grant AFOSR 76-2983

1 January 1976 - 31 December 1979

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CONTENTS

I. TITLE: Effect of Structure on Physical Properties of Polymers.

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VII. ABSTRACT OF ACCOMPLISHMENTS.

The overall objective of this research program has been to investigate the physical nature of macromolecular systems as a function of the chemical and stereochemical structure of the macromolecule. A potential improvement in important facets of polymer properties was an underlying premise in the design and execution of the research. The work performed included investigations of the behavior of polymers in solution, as well as in the solid state and was accompanied by a program of theoretical studies to complement the experimental work. One focus of the research was the area of polymer-polymer interactions in binary blends, in which factors influencing compatibility, i.e., mutual solubility, were systematically investigated by a number of thermodynamic techniques. Heats of polymer mixing were obtained for selected systems and shown to be useful in predicting phase behavior otherwise obscured by non-equilibrium effects. The latter were also investigated theoretically in studies of the effect of domain size and composition on glass transition temperatures and allied phenomena. Another area of research concerned the physical properties of model epoxy network systems, and in particular, the effect of water on these properties. A characteristic of cross-linked polymers is their ready plasticization by relatively small amounts of low molecular weight materials and the basis of this observation has been explained on a thermodynamic basis. Solution properties of polymers were studied by means of quasi-elastic light scattering. The effect of an ionic structural component on macromolecular conformation was examined in some detail in model copolymers of acrylic acid and ethyl acrylate. This technique was also employed in studies of solubilized stiff chain polymers of high persistence length, while a complementary theoretical investigation dealt with this problem in more general terms as part of an investigationof rigid and near-rigid rod conformations using the so-called n-broken rod approximation.

Mechanical properties of polymers were studied in a newly developed apparatus which measured the resonant vibrational frequencies of rigid beams in an extremely precise manner. From this it was possible to determine elongational and shear moduli on the same sample (as a function of temperature and, in principle, pressure, etc.) and hence Poisson's ratio for the polymer, a parameter important in composite theory and practise.

Finally, mention is made of a number of miscellaneous investigations and advances, including the development of a precision high pressure differential thermal analysis apparatus capable of measurements up to 7000 kbars. These and other studies are described in the body of this report.

VIII. DESCRIPTION OF RESEARCH ACCOMPLISHED.

The research completed during the grant period may be divided into the following areas:

A. Polymer Blends.

A successful and versatile method for improving polymer properties in general and for obtaining materials with a given sub-set of desired properties in particular is by blending two or more homopolymers. However, most binary systems of macromolecules are incompatible by any one or more of the several available criteria for miscibility, and a fundamental objective of this work has thus been to understand the principles of compatibilization and the properties of compatible polymer pairs. A research strategy has been to study a known system and to perturb it by chemical modifications, by temperature, by pressure (in current experiments), and by the addition of third components, to thereby drive the system to the compatibility-incompatibility transition. This is usually achieved readily for, as has been implied above, compatibility in polymers is a tenuous condition, a fact originating in the absence of a large entropic term in the mixing free energy, ΔG_m, for macromolecules. Additional problems in studying compatibility in polymers may include the difficulty of attaining equilibrium, the complications introduced by crystallization, and the fact that compatibility itself may be judged by several criteria (1,2). It is only in recent times that it has been established, for a few systems, that compatibility does indeed correspond to the formation of segmental level solutions, in parallel with low molecular weight systems.

We have been interested, for the last several years, in systems based on poly (2,6-dimethyl phenylene oxide) (PPO) with polystyrene (PS). We have shown that the PPO-PS mixture is compatible over the entire composition range and over an unusually wide temperature range. Compatibility is reduced as the PS chain is partially halogenated, i.e., as copolymers of styrene with, for example 2-chlorostyrene (OCS), are used instead of homopolymeric PS in the blends, (3,4). Reduced compatibility is manifested by the appearance of a high temperature two phase regime in the phase diagram, with a lower critical solution temperature (LCST). The LCST decreases as the molar fraction of OCS in the copolymer increases. Eventually, equilibrium can no longer be attained as the LCST approaches the glass transition (Tg) and the system is said to be "incompatible" (although, in fact, small portions of the phase diagram corresponding to a single phase regime will still prevail.) The quantitative aspects of this phenomenon in terms of partially fluorinated, chlorinated and brominated polystyrenes have been developed, (5,6). Isomeric effects have been studied by comparing, for example, the 2-chloro with the 4-chlorostyrene copolymer, (7). Fairly subtle effects (pointing to the great sensitivity of the compatibility phenomenon) have been observed, also, in studying copolymers of 2-chloro and 4-chlorostyrene polymers with PPO, in which a "compatibility window" is seen for certain copolymer compositions.

These studies have been complemented by studies of the thermodynamic parameters associated with the mixing process. Because of the afore-mentioned absence of a mixing entropy term, ΔG_m is determined largely by the corresponding enthalpy, ΔH_m. The latter quantity is not readily measured for polymers, but we have succeeded in doing so using an indirect cycle in which heats of solution of components and blends are determined, (8). One of the more surprising results of these studies has been that evidence was obtained for the existence of low temperature two phase regimes implying upper critical solution temperatures (UCST's) in certain cases. UCST's are normally obscured by the non-equilibrium region below T_g, (9-12).

Other physical properties of compatible and near-compatible systems have also been studied. These include the large deformation mechanical behavior of PPO-PS (13, 14) and of PPO with PS-POCS copolymers (15), and a number of investigations of the dielectric behavior of these and related systems variations. The loss spectra of PS/POCS for example has been studied in some detail as a function of molecular weight (17), and the opportunity was taken to compare the behavior in this case of physical blends and random copolymers of the same overall composition,(16-19). Thermally stimulated discharge (TSD) in polymer electrets involving these materials have also been investigated, (20). A beginning has been made with the study of polymer-polymer interactions in ternary systems in which the third component is a mutual solvent, (21).

B. Interaction of Water with Epoxy Polymers.

The interaction of water and epoxies represents a wider problem in which the effect of non-solubilizing small molecules on given polymers is investigated. The water-epoxy problem is of special significance because of the wide adoption of epoxy resins as matrix materials in high performance composites. Epoxy based materials can be complicated in terms of chemical structure and morphology and investigations using several parallel techniques are desirable. We have chosen to utilize equilibrium sorbtion and diffusion, calorimetry, I.R. spectroscopy, and nuclear magnetic resonance in studies of model epoxy water systems.

It has been shown that sorbed water plasticizes epoxy resins with a resultant depression in T_g. The solubility and kinetics diffusion of water in a model system were investigated (22). The nature of the sorbed water in such systems can often be understood in terms of "freezable" and "non-freezable" components by studying the behavior of the water-polymer system around 0°C, (23,24). Wide line NMR has also provided considerable evidence concerning bound small molecules. In a later publication we examined the high temperature absorbtion behavior of water in a model epoxy-diamine system. It was noted that as cross-link density increased the heat capacity discontinuity (ΔC_p) at T_g (per unit mass) decreased substantially, while T_g itself increased. Both these related phenomena can be explained in terms of conventional polymeric concepts, e.g. T_g increases because of a decrease in free volume, while ΔC_p decreased as the size of a polymeric "bead" (the effective unit involved in librational motion at T_g) is enlarged by crosslinking. However, it was also shown in a complementary theoretical study of the T_g of mixtures (see below) that, for small amounts of absorbed solvent, the depression in T_g is proportional to $1/\Delta C_p$. Thus the rather remarkable effect of a few percent of absorbed moisture on the properties of highly crosslinked epoxy resins is explained, (25). Extension of these concepts to other systems has been initiated.

C. Quasi-Elastic Light Scattering.

The development of optical heterodyne techniques for spectral line-width studies of light scattered from polymer solutions in the past decade has yielded an important new tool for the characterization of the size and conformation of macromolecular chains in dilute solution. Experimental techniques of considerable sophistication involving photon-counting and subsequent quasi-real time Fourier transformations and/or autocorrelation function computation have been developed which permit the rapid and precise measurement of translational diffusion constants for such macromolecules under a variety of conditions,(26).

Thus we have explored in considerable detail the conformational properties of a polyelectrolyte, a random copolymer of ethyl acrylate and acrylic acid. (This copolymer is also soluble in unionized form in several organic solvents). The effect of pH and ionic strength on D_T has been explored both as a function of M.W. and solute concentration. Second virial coefficients characterizing the thermodynamic behavior of this system are known from earlier studies but the present measurements have yielded new and valuable information on hydrodynamic solute-solute and solute-solvent interactions. In chemically similar systems the existence of a coil-coil conformational transition has been postulated for some time on the basis of several solution thermodynamic measurements; our D_T results appear to lend some support to this claim,(27).

More recently, we have been using a rather more difficult experimental variation in this technique in which the depolarized forward scattered component of the incident light is studied. This measurement provides rotational relaxation times and rotational diffusion constants for anisometric macromolecules. Investigations of polymers of the poly(benzthiazole)(PBT) type in chlorosulfonic acid have provided firm evidence for the rigidity of this molecule with measured persistence lengths of the order of 400 A, (28).

D. Vibrations in Thick Beams.

Resonant frequency and amplitude decay measurements of polymeric samples in the form of thin beams--reeds--have long been used as a comparatively simple method of characterizing the dynamical mechanical characteristics of such materials. The quantities obtained from such studies are principally $E'(\omega)$ and $E''(\omega)$, the frequency dependent elongational storage and loss moduli respectively. The complete determination of the elastic properties of an isotropic material requires measurement of a second quantity, e.g. the shear modulus G, or Poisson's ratio ν. Tha analysis of flexural vibrations in a thick beam though experimentally and mathematically more complex offored the possibility of a complete determination of the corresponding elastic properties in a single set of measurements, since vibrations in such beams involve shear as well as longitudinal deformation. We have earlier developed an experimental technique to utilize this concept by measuring with high precision resonant flexural frequencies of sample beams up to the tenth or higher mode to obtain shear and longitudinal moduli. We have now also found that longitudinal vibrations can be used to calculate these parameters. The experimental techniques are somewhat more involved but the theoretical analysis is simplified. The procedure yields the longitudinal modulus and Poissons ratio directly. For example, in a frequency independent regime (small tan δ) the following equation may be used:

$$\frac{f_n}{n} = \left(\frac{E}{\rho}\right)^{\frac{1}{2}} \frac{1}{2L} - n^2\left[\left(\frac{E}{\rho}\right)^{\frac{1}{2}} \frac{1}{2L} \left(\frac{\pi\nu R}{2L}\right)^2\right] \qquad (1)$$

in which f_n is the resonant frequency of the n^{th} longitudinal mode in a cylindrical rod of length L, radius R and density ρ. For polymers where frequency dispersion is generally non-negligible, a technique has been developed in which deviations from linearity of f_n/n vs. n^2 [eqn. (1)] can be used to calculate $E''(\omega) = E'(\omega) \tan \delta$.

We have applied this technique first to a silicate glass (30), then to poly (butylene terephthalate) (31), with satisfactory results.

Some advantages of this technique are that ν can be obtained directly on a single sample under controlled conditions under conditions of essentially infinitesimal strain. Poisson's ratio, although important in composite theory, is not readily available for most polymers and the fine structure in this parameter, e.g., as a function of temperature, has seldom been determined.

E. Theoretical Studies

Several theoretical contributions were published during the grant period. In one (32), the basis and implications of the separation of the fusion entropy, ΔS_f, into configurational (ΔS_c), and volume change (ΔS_v) contributions were examined. Contrary to generally accepted beliefs, this separation is not possible on thermodynamic grounds. Thus, calculations which determine ΔS_c a priori, for example, from chain statistical considerations, while of interest in themselves cannot use agreement with the value obtained from ΔS_f as support. These ideas were illustrated with a number of numerical examples.

The glass transition was the focus of several contributions. One of the phenomenological problems associated with this transition is the effect of domain size upon T_g and, indeed, upon the transitional manifestation in general. There are two principal sources of changes in T_g; the effect of surface energy, and the role of the interface in the mixing of the domains with the matrix material. We have examined these relationships (33) and shown that the effects, though small, are within experimental error in domains of a few hundred angstroms extent. In a later paper we extended these ideas to polymer transitions in general (34), and to other materials (35) and parameters (36).

The composition dependence in glass transitions was also studied,(37), from a classical thermodynamic point of view. An expression was obtained for T_g in terms of the T_g's and the ΔC_p's (at T_g) of the components. It was shown that this could be reduced to one or more of the empirical relations which have been used to calculate T_g in mixtures. Another problem associated with glass transitions occures in the determination of T_g of highly crystalline polymers. This problem was reviewed, and using our earlier heat capacity data for ultra-high molecular weight polyethylene, it was shown that a value of around 145°K was consistent with all existing data. The implications of comparing branched and linear polymers was discussed.

Finally, a comprehensive theory of the hydrodynamic properties of polymers in stiff chain conformations was developed, (39). The model adopted was the so-called n-broken rod in which the chain is viewed as n+1 rigid segments connected by n "universal joints." As n increases the properties approach those of the classical flexible chain.

F. Other Work

Brief mention may be made of one acquisition of high pressure (~7kbars) DTA equipment with considerable sensitivity, (40). This has enabled us to examine effects of pressure on melting and, perhaps more importantly, glass transitions in polymers. We have been able, for example, to examine experimentally, for the first time, the effect of pressure on ΔC_p in polystyrene. Several other studies have been completed, (41). A review of the effect of stereoregularity on bulk properties of polymers (42), and of the solid state behavior of polymer blends (43), were published.

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