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The variation of $D(\phi)$ with concentration, determined from the correlation functions such as that of Figure 1, is depicted in Figure 2a. A minimum at about $\phi = 0.6$ for PEO is apparent. According to eq 1 this rather strong reduction of the mutual mobility can be ascribed to the concentration dependence of the thermodynamic term $(\chi_s - \chi_F)$ as reflected in the scattering intensity S_q and the geometrical factor $\phi(1 - \phi)$; the average monomeric mobility D^0 in this mixture is assumed to be insensitive to its composition ϕ. The upper part of Figure 2 shows the variation of $D(\phi)S_q$ with concentration based on dynamic and static light scattering intensity measurements. The residual dependence on concentration is quantitatively due to the factor $\phi(1 - \phi)$ (compare with the solid line in Figure 2b).

The measured composite variation of $D(\phi)$ with composition in the mixture PEO/PPO is dominated by thermodynamic forces in contrast to the polystyrene/poly(phenylmethylsiloxane) system where the influence of the glass transition affecting D^0 (ϕ) is more important. For different relatively low polymerization indices the minimum[2] in χ_s is shifted toward the region rich in the shorter chain, i.e., PEO. It is therefore this that leads to the concentration dependence of $D(\phi)$ in Figure 2. After the composition dependence of the thermodynamic term is corrected for, a maximum near the middle of the mixture composition range appears, in agreement with the theoretical predictions comprised in eq 1 if D^0 is constant. Thus a correct analysis of the measured $D(\phi)$ should take into account both thermodynamic interactions and monomeric mobilities of the blend components.

Thermodynamic interactions and free volume effects determine the mutual diffusivity in miscible polymer blends according to recent theoretical treatments.[1–5] These parameters may strongly vary with mixture composition,[6] which in turn results in a distortion of the actually predicted concentration dependence for the mutual diffusion coefficient; any resemblance therefore to the theoretical behavior may be fortuitious.[7] At constant temperature, the mutual diffusion coefficient is reduced near the middle of the composition range but toward the region rich in the shorter PEO chain. Consideration of, however, the dominating thermodynamic interactions enhances the mutual diffusion coefficient in the middle of the composition range, in quantitative agreement with the theoretical prediction. Finally, the present work gives, to our knowledge, the first mutual diffusion coefficients for a polymer mixture with UCST and $\chi_F > 0$ where $D < D^0$ is expected (eq 1) and found experimentally (Figure 2a).

Acknowledgment. Useful ideas were contributed by Dr. M. G. Brereton of the University of Leeds and Prof. Dr. E. W. Fischer of the Max-Planck-Institut für Polymerforschung in Mainz.

Registry No. PEO, 25322-68-3; PPO, 25322-69-4.

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G. Fytas
Research Center of Crete and
Department of Chemistry
University of Crete
Iraklion, Crete, Greece

Received December 22, 1986

Effect of Homopolymer Molecular Weight on the Morphology of Block Copolymer/Homopolymer Blends

The mechanical properties of block copolymer systems can be tailored by the addition of homopolymers. Model systems based upon block copolymers and homopolymers with well-characterized architectures are useful in understanding the unusual properties of such blends. In this Communication, we present initial results from small-angle neutron scattering (SANS) studies of the morphology of triblock copolymer/homopolymer blends. In particular, the effect of homopolymer molecular weight on the microdomain structure of these blends is reported.

Transmission electron microscopy experiments indicate that the lamellar microphase geometry inherent to the triblock copolymer is retained in the blends. SANS data support this observation and are used to characterize the microdomain dimensions. For the homopolymer of lowest molecular weight, the block copolymer interdomain spacing is found to be reduced compared to that of the pure triblock copolymer. The domain spacing increases as the homopolymer chain length is increased, becoming extended when the degree of polymerization approaches that of the copolymer midblock. Macrophase separation of the homopolymer increases with homopolymer molecular weight and predominates when the homopolymer degree of polymerization exceeds that of the midblock sequence. These results are discussed in light of current thermodynamic theories addressing the microphase separation and microdomain structure in homopolymer/block copolymer blends.

A series of samples containing 20% by weight of hydrogenated butadiene (hPB) homopolymer in a matrix of styrene–hydrogenated butadiene–styrene (S–hB–S) triblock copolymer has been studied. Sample designations and characteristics are described in Table I. The polymers were prepared by anionic polymerization in benzene solvent using *n*-butyllithium as an initiator and dipiperidinylethane as a modifier to favor the 1,2-polybutadiene isomer. The butadiene homopolymer and copolymer sequences were hydrogenated with a homogeneous catalyst technique described by Falk.[1] Films were prepared by slow solvent casting from dichloromethane and annealed under vacuum for 2–4 h at 140 °C. Specimens for SANS analysis were prepared by stacking the films to a nominal thickness of 1 mm and were analyzed at the 30-m SANS facility of the National Center for Small-Angle Scattering Research at ORNL using a sample-to-detector

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Table I
Polymer Characterization

sample desig	GPC MW × 10^{-3}	polydispersity after hydrogenation	polydispersity before hydrogenation	% by wt PS	% 1,2-PB
H-CP	115	1.32	1.15	49	91
hPB-1	11	1.14	1.05		95
hPB-2	32	1.07	1.07		95
hPB-3	58	1.09	1.03		93
hPB-4	130 (122)[a]	1.13	1.03		98

[a] Before hydrogenation, membrane osmometry result.

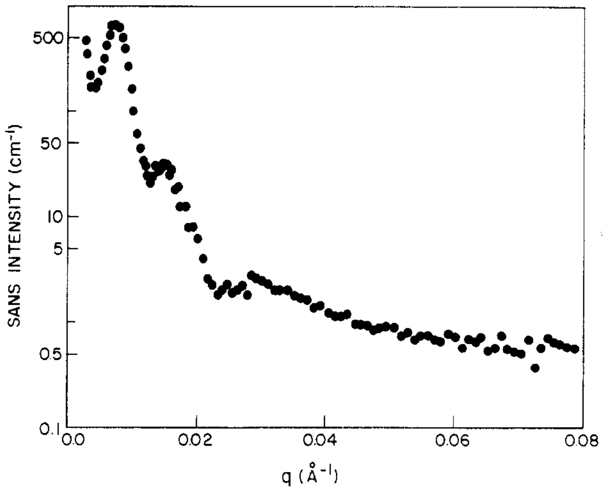

Figure 1. Uncorrected SANS data for a blend containing 20% by weight hPB-3 homopolymer in H-CP triblock copolymer.

distance of 19 m. Data were collected on a 2-D position-sensitive detector, calibrated against absolute intensity standards, radially averaged, and corrected for incoherent scattering. Details of the sample preparation, characterization, and data analysis are described elsewhere.[2,3]

SANS intensity data for the blends exhibit one to three maxima at positions characteristic of a lamellar microstructure. A typical SANS profile is shown in Figure 1. Transmission electron micrographs of unstained microtomed sections confirm the predominance of a lamellar geometry for all blends, although some hPB-rich macrophases are observed for blends containing higher molecular weight homopolymers.[3] The persistence of the lamellar microstructure is unexpected and may be due in part to the inability of these triblock systems to reach their predicted equilibrium morphology. However, we have found that our specimens consistently form lamellae when prepared in this manner, regardless of the rate of solvent evaporation and annealing conditions. Thus we feel that our results are indicative of a stable morphology.

A small amount of excess scattering at very low angles is attributed to the presence of the homopolymer macrophases and is modeled by the scattering from a Gaussian distribution of spherical particles.[3] The correction is small and has little effect on the correlation function analyses described below. The degree of macrophase separation can be characterized by calculating the integrated scattered intensity or invariant. If it is assumed that the macrophases are so large that they do not contribute to the small-angle scattering, the invariant Q may be approximated as

$$Q = \int_0^\infty I(\mathbf{q})\mathbf{q}^2\,d\mathbf{q} \approx (1 - f)\phi_{\mathrm{PS}}\phi_{\mathrm{hPB}}(\beta_{\mathrm{PS}} - \beta_{\mathrm{hPB}})^2$$

where $I(\mathbf{q})$ is the coherent scattered intensity as a function of the scattering vector $\mathbf{q}$. f is the volume fraction of macrophases. The volume fractions of the PS and hPB microphases are denoted ϕ_{PS} and ϕ_{hPB}, respectively, and their coherent scattering length densities are β_{PS} and β_{hPB}, respectively. From this expression, the invariant is directly proportional to the volume fraction of material contained in the microdomains of the blends. The SANS invariant is plotted as a function of homopolymer molecular weight, at fixed homopolymer content, in Figure 2. The decreasing trend in the invariant demonstrates qualitatively that the solubility of homopolymer within the block copolymer microdomains decreases rapidly as the homopolymer molecular weight increases. A more careful study by correlation function analysis indicates that essentially all of the lowest molecular weight homopolymer, hPB-1, is contained within the microdomains, while almost all of the homopolymer is excluded into macrophases when its molecular weight exceeds that of the copolymer midblock.[3]

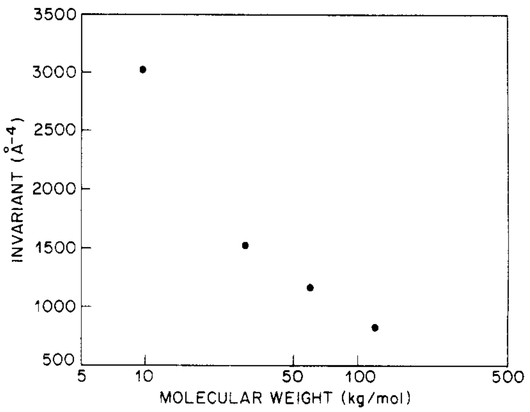

Figure 2. Effect of homopolymer molecular weight on the SANS invariant for blends containing 20% by weight homopolymer.

The structural parameters associated with the lamellar microdomains in the blends are obtained through analysis of one-dimensional correlation functions calculated by taking the appropriate Fourier transforms of the corrected data.[4] The long period or microdomain spacing is determined directly from the position of the first maximum of the correlation function.

Alternatively, the microdomain spacing is obtained by model calculations employing an ideal scattering density profile whose correlation function can be compared against the experimental correlation function. The model used in this work is based on the trapezoidal scattering density profile illustrated in Figure 3a. An interfacial region of 50 Å is assumed for all blends. The ideal correlation function and a Lorentzian damping function used to describe the decay in long-range correlations between microdomains are shown in Figure 3b. A representative comparison of the model and experimental correlation functions appears in Figure 3c.

The microdomain spacings estimated by the two methods are shown in Figure 4. For the blend with the highest molecular weight homopolymer, hPB-4, the microdomain spacing reverts to the value for the pure triblock copolymer, H-CP (denoted by the dotted line in Figure 4). This is consistent with the results of the invariant calculations and demonstrates that virtually all of the homopolymer is excluded from the microdomains in this blend. As the homopolymer molecular weight decreases to the value corresponding to that of the copolymer midblock (represented by the dashed vertical line), the homopolymer solubility becomes finite, and the microdomain spacing becomes larger, apparently expanding to accommodate the homopolymer within the midblock domain.

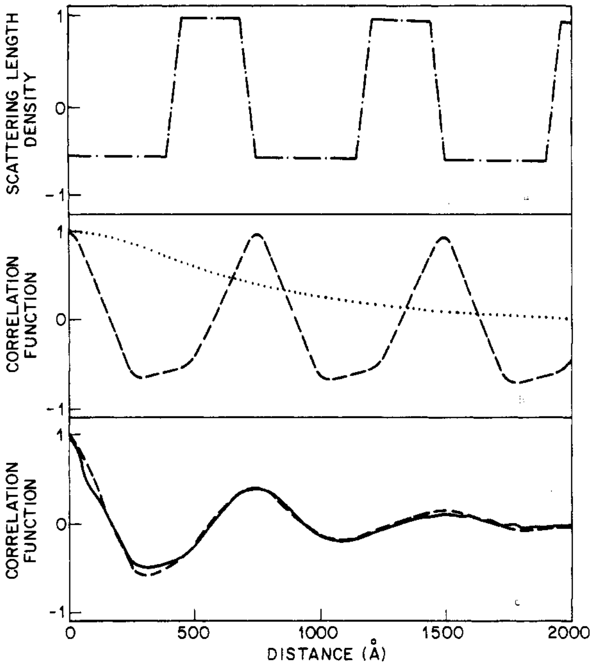

Figure 3. SANS model for correlation function analysis: (a) trapezoidal model for scattering density profile; (b) theoretical ideal correlation function (broken line) and Lorentzian damping function (dotted line); (c) comparison of experimental correlation function (solid line) with model calculation assuming a 650 Å half-width for the Lorentzian damping function (broken line).

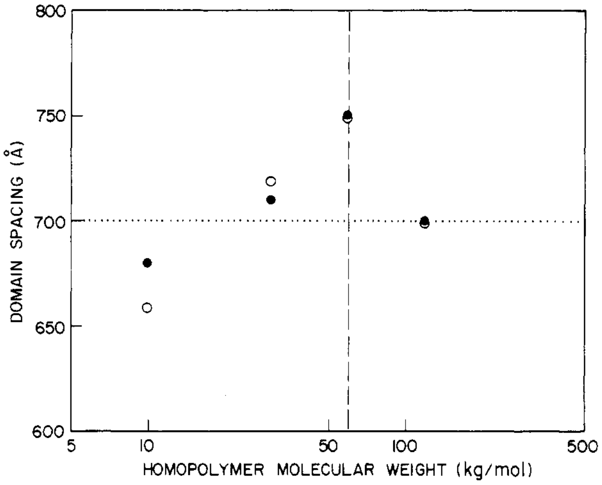

Figure 4. Long period as a function of homopolymer molecular weight. Open circles are values calculated from the position of the first maximum in the correlation function. Filled circles are data determined from the trapezoidal model comparison. The dotted line denotes the long period of the pure triblock copolymer; the dashed line indicates the equivalent molecular weight of the midblock segment.

A further decrease in homopolymer molecular weight below that of the midblock produces interesting results. Although the homopolymer solubility is increased, the characteristic size of the microdomains is seen to decrease. For the blend with the lowest molecular weight homopolymer, hPB-1, which has the highest homopolymer solubility, the domain spacing falls below that of the pure triblock copolymer. That is, the overall microdomain structure is contracted even though it accommodates essentially all of the homopolymer.

Although theories that specifically treat the case of microphase-separated homopolymer/triblock copolymer blends are not yet available, some qualitative explanation of the morphological behavior of these materials may be proposed from theories developed for diblock copolymers. In the theories of Helfand et al.,[5] the sequences in pure diblock copolymers assume extended configurations in order to fill space efficiently. SANS investigations[6,7] have provided experimental evidence for extended chain configurations in pure diblock copolymers, and initial SANS results suggest that the midblock sequence is also somewhat extended in the triblock copolymer, H-CP.[2]

The contraction observed in the lamellar spacing of the blend containing low molecular weight homopolymer (hPB-1) may be due to a relaxation of the constant density constraints on the midblock segments. The homopolymer chains are smaller and more mobile than the midblock segments and can distribute preferentially within the midblock domains to satisfy the constraints and allow the midblock segments to retract to a less constrained conformation.[8] In this fashion, the overall microdomain dimension may be reduced compared to that of the pure triblock copolymer.

Behavior similar to our experimental results is predicted by a theory that describes diblock copolymer/homopolymer blends in the homogeneous state.[9] For these systems, the spacings due to the correlation hole should vary with homopolymer molecular weight. In particular, a contraction at low molecular weight and an expansion at high molecular weight are predicted. It is not unreasonable to expect that similar behavior carries over into the microphase-separated state, since a discontinuity in the correlation length is not anticipated at the order–disorder transition.

A decrease in long period is also predicted for diblock copolymer systems to which a solvent good for both blocks has been added.[10,11] This effect is attributed to a decrease in the surface tension at the interface. In the case of homopolymer addition, however, the additive is expected to act more as a selective solvent and a diminution in surface tension may not be observed.

Microdomain expansion and the onset of macrophase separation, observed in this work for higher molecular weight homopolymers, are predicted for phase-separated diblock copolymer blended with homopolymer.[12,13] The homopolymer molecules become less mobile with molecular weight and can no longer distribute themselves preferentially within the microdomain as a result of their own size constraint. They cannot offset the extension of the copolymer sequences, and the increased volume fraction of the hPB segments causes the microdomain to swell. When the size of the homopolymer chain approaches or exceeds that of the midblock sequence, the entropic constraints involved in locating the homopolymer in the microdomain become restrictive, and macrophase separation of the homopolymer is favored. Under these conditions, the dimensions of the microdomains return to those of the pure block copolymer, consistent with our experimental results.

These qualitative considerations provide an initial explanation for the homopolymer molecular weight dependence of both the microdomain dimensions and the homopolymer solubility of the homopolymer/triblock copolymer blends we have examined. Experimental effort is currently focused on determining the individual domain dimensions, the actual spatial distribution of homopolymer within the microdomains, and the molecular configurations of the chains, in order to confirm these considerations.

We observe a strong dependence of the microdomain spacing and homopolymer solubility on the molecular weight of a hPB homopolymer diluent for blends based on a S–hB–S triblock copolymer. The microdomain structure contracts upon the addition of low molecular weight homopolymer and expands when longer homopolymer chains are added. These effects are qualitatively explained as the result of relaxing constant density and increased volume fraction constraints by the addition of small mobile homopolymer molecules.

Acknowledgment. We are grateful for the support received through grants from the Cottrell Research Program of the Research Corp. and the donors of the Petroleum Research Foundation, administered by the American Chemical Society. Also, the work at ORNL was sponsored in part by the National Science Foundation Grant No. DMR-7724459 through Interagency Agreement No. 40-636-77 with the U.S. Department of Energy under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. Lastly, much of this work was performed while X.Q., I.G., and J.T.K. were affiliated with Princeton University, Princeton, NJ.

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(14) AT&T Bell Laboratories.
(15) Technical University of Wroclaw.
(16) University of Connecticut.
(17) Oak Ridge National Laboratory.

X. Quan,[14] I. Gancarz,[15] J. T. Koberstein,*[16] and G. D. Wignall[17]

AT&T Bell Laboratories
Murray Hill, New Jersey 07974
Technical University of Wroclaw
Wroclaw, Poland
Institute of Materials Science
University of Connecticut
Storrs, Connecticut 06268
National Center for Small-Angle Scattering Research
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Received October 7, 1986

Local Intermolecular Structure in an Antiplasticized Glass by Solid-State NMR

An antiplasticized glass is a combination of a polymer with a low molecular weight diluent which results in a material with a higher modulus.[1,2] The increase in modulus is associated with a suppression of local chain motion,[3] and this suppression can sometimes be directly observed as the disappearance of a low-temperature mechanical loss peak[4,5] or as the slowing of a specific local reorientation in a solid-state NMR spectrum.[5,6]

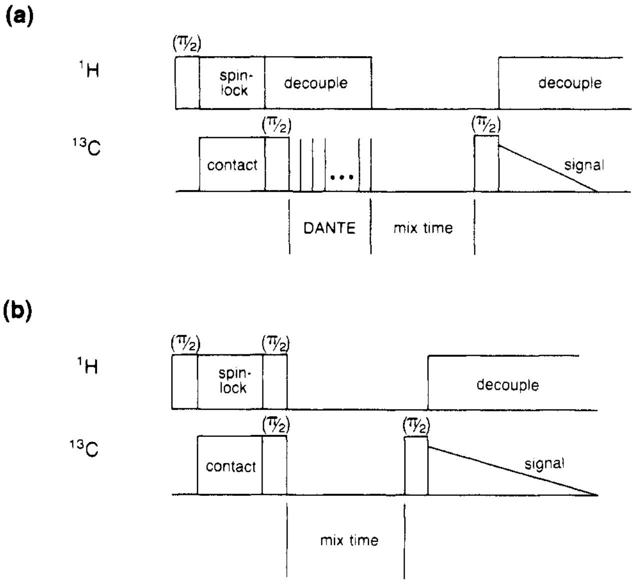

Figure 1. (a) Solid-state carbon-13 MASS pulse sequence for the measurement of spin diffusion. The pulse sequence begins with the normal cross polarization procedure. The first $\pi/2$ carbon pulse creates magnetization and the DANTE sequence selectively inverts the labeled magnetization. The mix time allows for spin diffusion between the inverted peak and the remaining resonances. The last $\pi/2$ carbon pulse just places magnetization in the xy plane for detection. (b) Solid-state carbon-13 MASS pulse sequence for the measurement of spin-lattice relaxation.[14]

Several mechanisms have been suggested for the increase in modulus and the associated suppression of sub-glass transition motion. A densification of the antiplasticized polymer is often noted[3,4] that is identified with a loss of free volume and thus a suppression of motion. At first glance, the addition of a low molecular weight diluent would be expected to increase free volume. Since just the opposite is observed for antiplasticizer, this type of diluent is supposed to go into the "holes" in the amorphous glass so as to alter the free volume distribution.[5]

To a certain extent, this explanation begs the question since it does not clearly identify the property that distinguishes a plasticizer from an antiplasticizer. Some investigators have proposed specific interactions between the polymer and the diluent as the key property of an antiplasticizer.[3,4,7] It is the purpose of this report to seek evidence for such a specific interaction by the presence of a preferred position of the antiplasticizer relative to the polymer repeat unit. The system to be examined is polycarbonate (BPA-PC) and di-*n*-butyl phthalate (DBP). The diluent, DBP, acts as an antiplasticizer at low concentrations and a plasticizer at high concentrations.[8]

The experimental approach for the determination of local structure will be carbon-13 spin diffusion between a labeled site on the DBP and various natural abundance sites in the BPA-PC repeat unit. Carbon-13 spin diffusion experiments have been developed[9,10] and have been used to demonstrate intimate mixing in blends.[11] However, no observation of spin diffusion has been made prior to this report which shows specificity at the level of chemical structure in an amorphous glass. Atomic site selectivity within a polymeric repeat unit has however been suggested as a desirable possibility in carbon-13 spin diffusion experiments.[11]

Carbon-13 labeled DBP enriched at one of the carbonyl sites was prepared from phthalic acid-α-^{13}C (99%) obtained from Merck, Inc. The phthalic acid was esterified with unlabeled 1-butanol. Diluent samples of 10 and 25 wt % were prepared by dissolving DBP and BPA-PC in

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