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Thomas R. Stengle*
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01003

Kenneth L. Williamson
Department of Chemistry
Mount Holyoke College
South Hadley, Massachusetts 01075

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Mutual Diffusion in a Compatible Binary Polymer Mixture. Variation with Composition

Recently, considerable theoretical interest has been focused on the dynamics of polymer mixtures.[1-5] For unentangled chains the mutual diffusion coefficient is given by

$$D(\phi) = 2D^0(\phi)|\chi_s(N_A,N_B,\phi) - \chi_F(T,\phi)|\phi(1-\phi) \quad (1)$$

where ϕ is the volume fraction of one component, χ_s and χ_F are the Flory–Huggins interaction parameters at the spinodal and in the homogeneous region, respectively, N_A and N_B are the polymerization indices, and D^0 is the average monomeric diffusivity, which depends on the microscopic Rouse mobilities of the two components and the blend composition. In all theoretical treatments so far, these microscopic Rouse mobilities are assumed to be independent of concentration. If the two materials, however, have quite different glass transition temperature (T_g), this assumption is obviously wrong.[6]

In two recent investigations of the mutual diffusion,[6,7] there were large differences between the mobilities of the pure components as reflectd in the large variation of the T_g with blend composition.[8,9] Since no microscopic theory exists for the average mobility $D^0(\phi)$, the interpretation of the experimental $D(\phi)$ needs careful consideration. In addition, the concentration dependence of the thermodynamic term ($\chi_s - \chi_F$) in eq 1 is important and was ignored in ref. 7. The reported enhancement of the mutual diffusion D in the middle ($\phi = 0.5$) of the composition range according to eq 1 can be true only if the product of D^0 and ($\chi_s - \chi_F$) is approximately independent of concentration. However, this was not the case in the mixture of ref 7. Enhanced mutual diffusivity due to segment interactions was recently reported for polystyrene/poly(phenylene oxide) using forward recoil spectrometry.[10] However, again, to partially compensate for the variation of T_g with blend composition, the $D(\phi)$ was checked at constant $T - T_g(\phi)$. This procedure was thoroughly examined in a light scattering study on a system of polystyrene/poly(phenylmethylsiloxane).[11]

The present polymer mixture polyethylene oxide (PEO) ($M_n = 600$)/poly(propylene oxide) (PPO) ($M_n = 1025$) with narrow molecular weight distributions in both cases supplied by Riedel de Haen was chosen mainly on account of the composition invariance of the average monomeric mobility D^0 as verified from viscosity measurements. The materials have polymerization indices lower than the entanglement value, and the mixture exhibits convenient upper critical solution temperature (UCST).[12] For these samples, the T_g has reached the asymptotic high molecular weight value[13] and both shear viscosity[13,14] and self-diffusion[14] scale with N and N^{-1}, respectively. Mutual diffusion coefficients were determined by measuring the correlation function of the light scattering intensity at a scattering angle of 90°. The light source was an argon ion laser (Spectra Physics 2020) operating at 488.0 nm with a power of 300 mW. Measurements of the mutual diffusion coefficient were performed in the binary mixture PEO/PPO at two temperatures, 361 and 376 K, and different blend compositions.

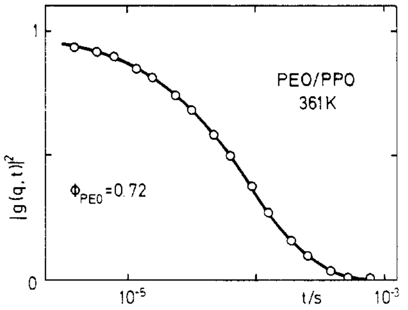

Figure 1. Measured normalized time correlation function of the scattered light intensity due to concentration fluctuations in the polymer mixture PEO/PPO at 361 K and PEO volume fraction $\phi = 0.72$. The solid curve represents a single-exponential fit.

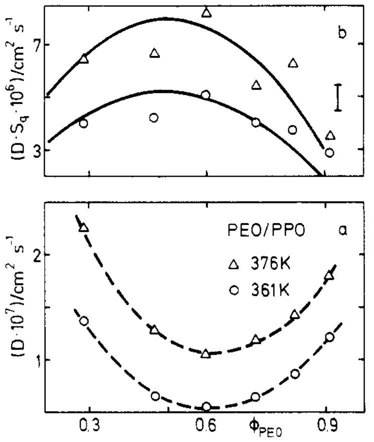

Figure 2. (a) Measured mutual diffusion coefficient D in the compatible mixture PEO/PPO at two temperatures vs. the volume fraction of PEO. The dashed lines are only to guide the eye. (b) This plot is constructed according to eq 1 and takes into account the thermodynamic interactions in the PEO/PPO mixture. This is accomplished by measuring the absolute light scattering intensity S_q due to the concentration fluctuations. The solid lines show the behavior of $D^0\phi(1-\phi)$, where the average monomeric diffusion D^0 amounts to 2.1×10^{-5} cm^2·s^{-1} at 361 K and 3.2×10^{-5} cm^2·s^{-1} at 376 K.

In a polymer blend, besides the scattering of the laser light by thermal density fluctuations, the major part of the total scattered intensity arises from concentration fluctuations, which can be analyzed by using photon correlation spectroscopy.[15] The corresponding time correlation functions were found to have an almost exponential shape with a relaxation rate $\Gamma = Dq^2$ where $1/q$ is the probing wavelength (~1000 Å). An example of the normalized correlation functions $|g(q,t)|^2$ for a volume fraction of PEO $\phi = 0.72$ at 361 K is given in Figure 1, from which Γ can be directly obtained. Alternatively, the static absolute scattered intensity S_q due to the concentration fluctuations is related to the thermodynamic term simply by $2S_q = 1/(\chi_s - \chi_F)$ in the limit $q \rightarrow 0$.[1,2] Thus, information about the thermodynamic driving force and the mutual diffusion coefficient in a compatible polymer blend can be obtained in a light scattering experiment.[11]

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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).

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

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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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