Interdiffusion in the Partially Miscible Polymer Blend of Deuterated Polystyrene and Poly(styrene-*co*-bromostyrene)

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ABSTRACT: We have used elastic recoil detection (ERD) to measure the interdiffusion in the partially miscible polymer blend of deuterated polystyrene (DPS) and poly(styrene-*co*-bromostyrene) (PBr$_x$S). The fraction x of the comonomer and the molecular weights M_w were chosen such that the upper critical solution temperature (UCST) was well above the glass transition temperature. Annealing took place only in the two-phase region as was assured by interference contrast microscopy (ICT). One of the blend compositions on the binodal line could be extracted from the diffusion profiles at various annealing temperatures. The Flory-Huggins interaction parameter, calculated from the measured blend composition, is compared with SAXS measurements on similar blends of PS and PBr$_x$S.

Introduction

In recent times there has been much activity, experimental and theoretical, in the study of tracer diffusion, self-diffusion, and interdiffusion in compatible polymer blends.[1-12] Considerably less is known about interdiffusion in a partially miscible polymer blend. Rafailovich et al.[13] investigated interface formation in the partially miscible polymer blend of solution chlorinated polyethylene (SCPE) and poly(methyl methacrylate) (PMMA) with the method of Rutherford backscattering. They observed a slowing down of the averaged diffusion coefficient as the temperature was increased from the glass transition point beyond the lower critical solution temperature of the blend into the two-phase region. Green et al.[14] studied interdiffusion in a high molecular weight blend of deuterated polystyrene and polystyrene, which has an upper critical solution temperature (UCST).[15] They found a slowing down of the concentration-dependent interdiffusion coefficient as they lowered the temperature in the one-phase region toward the UCST of the blend.

In this paper we report on the observation of the interdiffusion in a blend with a miscibility gap in the partially miscible polymer blend of DPS and PBr$_x$S with the ERD method. Strobl et al.[16] have shown that the UCST of this blend can be controlled by the degree of bromination x in the copolymer. Elastic recoil detection (ERD) is a suitable method to profile the DPS concentration in the blend. Our results are compared with small-angle X-ray scattering data of polystyrene-poly(styrene-*co*-bromostyrene) blends in the one-phase region via the Flory-Huggins interaction parameter.

Experimental Section

The polystyrene and the deuterated polystyrene used in this work were purchased from Polymer Standards Service.[17] The bromination procedure of the polystyrene homopolymer (PS) is described elsewhere.[18] The degree of bromination x of the polystyrene and the molecular weights of both the polystyrene and the deuterated polystyrene were chosen for the blend to be in the two-phase region at ambient temperatures.[18] The data are listed in Table I. From the work of Strobl and co-workers,[16] the effective interaction parameter for PS-PBr$_x$S blends scales with the square of the degree of bromination times the interaction parameter between the polystyrene monomer and the comonomer. Therefore the critical temperature T_c is a function of Nx^2 only, where N is the degree of polymerizaton in a symmetrical blend. For a 50% PS-50% PBr$_x$S blend with $x = 0.205$ and $M_n = 43\,000$ g/mol for both PS and PBr$_x$S, they found phase separation at $T = 180$ °C.[19] The value of Nx^2 of the polymers in this work nearly equals the value above. By interference contrast microscopy (ICT) we found a 50% DPS-50% PBr$_x$S blend of the present polymers phase separated at $T = 178$ °C.

Table I
Characterization of the Polymers Used in This Work[a]

polymer	M_w, g/mol	U	x
DPS	129700	0.02	
PBr$_x$S	130000	0.03	0.119

[a] $U = M_w/M_n - 1$; x denotes the fraction of brominated styrene units.

To measure the interdiffusion profile in blends of DPS and PBr$_x$S, diffusion couples were made that consisted of a base film (≈1-2 μm) of PBr$_x$S and a top film (≈200-400 nm) of DPS. The base film was prepared by spreading a chloroform solution of PBr$_x$S on a polished silicon wafer. The top film was prepared by spreading a chloroform solution of DPS with an injection needle that was pressed horizontally on a glass slide. This film was floated off onto a surface of distilled water and then was picked up onto the base film on the silicon wafer. Uniformity of the top film was measured with interference methods. No surface roughness was detectable, but due to the preparation procedure there was a slight linear thickness variation that caused a somewhat wedge-shaped top film.

The DPS profile was measured by elastic recoil detection (ERD). In the ERD experiment a monoenergetic beam of ^{4}He$^+$ ions strikes the target at a glancing angle. Nuclei that are ejected out of the target are detected with an energy-dispersive Si detector at a given scattering angle. For ^{4}He$^+$ projectiles the energy transfer to the recoils is larger for deuterons than for protons. Nuclei recoiling from deeper layers in the target have a lower energy due to the energy loss of the incident and outgoing ions in the target. The energy scale can be converted into a depth scale and the counts in each channel of the recorded energy spectrum can be converted into a concentration scale for each isotope. For a ^{4}He$^+$ projectile energy of 2.9 MeV, a scattering angle of 30°, and a 10-μm-thick Mylar foil in front of the Si detector, which stopped the elastically scattered ^{4}He$^+$, the energies of recoiled protons from the surface and recoiled deuterons from deeper layers in the target overlapped in the energy spectra for a depth of ≥800 nm. This overlap determined the maximum depth for which the DPS was detectable. The depth resolution at the surface was 90 nm and below the DPS top layer greater then 100 nm as a consequence of the somewhat linear thickness variation of the top film. Details of the method are described elsewhere.[20]

It is also possible to measure the PBr$_x$S profile with the method of He Rutherford backscattering (RBS). In the RBS experiment the energies of the ^{4}He$^+$ projectiles, which are scattered to backward angles by heavier nuclei in the target, are measured. The energy of a projectile that is backscattered from a Br nucleus is larger than that of the one backscattered from a C nucleus. Projectiles scattered from deeper layers in the target have lower energies due to the energy loss in the target. Again the energy scale of the backscattered projectiles can be converted into a depth scale. In the RBS experiment the depth resolution should be better because there is no need of a stopper foil in front of the energy-dispersive detector. In the ERD experiment the depth

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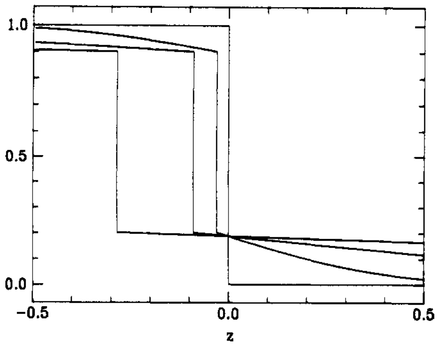

Figure 1. Computed results for $D_1 = D_2 = 10$, $\Phi_b^1 = 0.2$, and $\Phi_b^2 = 0.9$ at times $t = 0$, $t = 0.005$, $t = 0.05$, and $t = 0.5$ (arbitrary units).

resolution is mainly determined by energy straggling in the stopper foil.

Unfortunately PBr_xS is very sensitive to radiation damage. Evaporation of HBr changed the concentration profile of Br appreciably during data collection. This can be reduced by cooling the target with liquid nitrogen.[13] Measurements with a cooled sample holder are planned. Because of the low content of Br atoms in the diffusion couple, the measurement of the DPS profile with ERD is faster then the measurement of the PBr_xS profile with RBS. To evaluate the depth scale, we used the fitting functions for the energy loss of ions in matter listed by Ziegler.[21] This energy loss is not only a function of ion energy but also a function of the target composition. The low Br concentration does not affect the energy loss noticeably.

For each diffusion couple the initial DPS profile was measured. Then the couple was annealed in the scattering chamber ($p \leq 10^{-5}$ Torr) at temperatures greater than the glass transition temperature. After a given time the couple was quenched to ambient temperature and was shifted 3 mm upward with respect to the beam to avoid radiation effects on the diffusion profile. Then a new DPS profile was measured. In this way we gathered three profiles from each couple, one of the undiffused and two of the diffused couple after two different diffusion times.

Results and Discussion

It is instructive to discuss interdiffusion in a blend with a miscibility gap in terms of a steplike concentration dependence of the interdiffusion coefficient. We define a constant diffusion coefficient D_1 for $0 \leq \Phi \leq \Phi_b^1$, $D = 0$ for $\Phi_b^1 \leq \Phi \leq \Phi_b^2$, and a constant D_2 for $\Phi_b^2 \leq \Phi \leq 1$. Φ denotes the volume fraction of one component. Φ_b^1, Φ_b^2 denote the blend compositions on the binodal line. The initial conditions ($t = 0$) are $\Phi = 1$ for $z \leq 0$ and $\Phi = 0$ for $z \geq 0$. For $t \geq 0$ the diffusion equation must be solved seperately on both sides of the interface

$$\frac{\partial \Phi^i}{\partial t} = D_i \frac{\partial^2 \Phi^i}{\partial z^2} \tag{1}$$

with $i = 1$ for $z \geq R(t)$ and $i = 2$ for $z \leq R(t)$. $R(t)$ denotes the position of the interface at time $t \geq 0$. The solutions have to obey the following boundary conditions at the interface

$$\Phi^i|_R = \Phi_b^i \tag{2}$$

and because the diffusing substance must be conserved

$$\frac{dR}{dt}(\Phi_b^2 - \Phi_b^1) = D_1 \frac{\partial \Phi^1}{\partial z}\bigg|_R - D_2 \frac{\partial \Phi^2}{\partial z}\bigg|_R \tag{3}$$

This problem can be solved in a straightforward manner:[25]

$$\Phi^1(z,t) = \alpha \operatorname{erfc}\,(z/(4D_1t)^{1/2}) \qquad z \geq R(t) \tag{4}$$

$$\Phi^2(z,t) = 1 - \gamma \operatorname{erfc}\,(-z/(4D_2t)^{1/2}) \qquad z \leq R(t) \tag{5}$$

$$R(t) = \delta t^{1/2} \tag{6}$$

The three constants α, γ, and δ are determined by the three boundary conditions at the interface. The situation above should describe the experimental situation, as long as the volume fractions at the surfaces of the finite diffusion couple only differ slightly from 0 and 1. Figure 1 shows an example computed for $D_1 = D_2$, $\Phi_b^1 = 0.2$, and $\Phi_b^2 = 0.9$.

Figure 2 shows the measured profiles obtained from an unannealed couple and from the same couple after diffusion times of 2040 and 6060 s at a temperature of 179 °C. The profile of the unannealed couple shows the top film of DPS (Figure 2a). The front edge of the DPS profile has

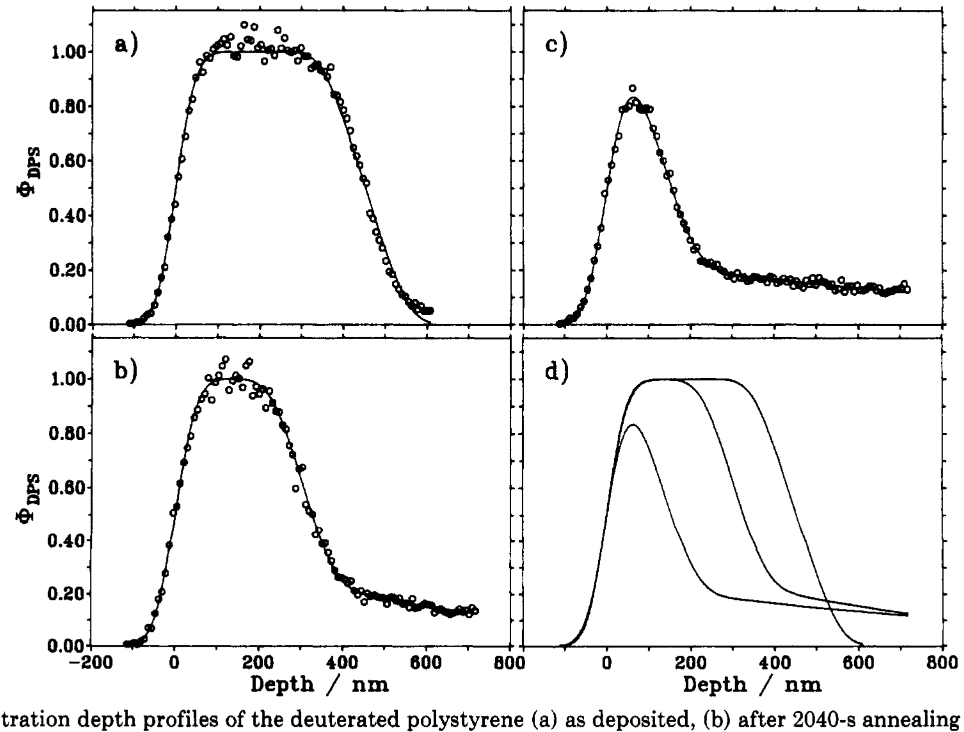

Figure 2. Concentration depth profiles of the deuterated polystyrene (a) as deposited, (b) after 2040-s annealing time, and (c) after 6060-s annealing time at a temperature of 179 °C. (d) Fitted concentration depth profiles from (a) – (c). There is no further broadening of the interface due to interdiffusion in the concentration regime Φ_b to 1.

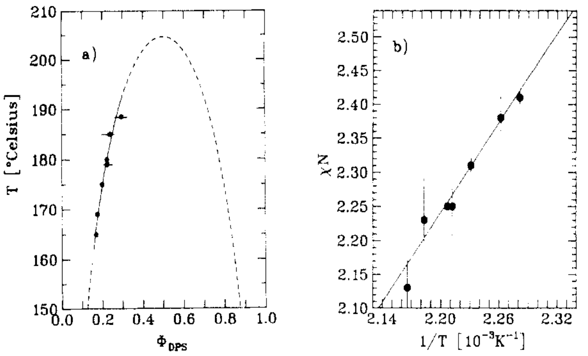

Figure 3. (a) Part of the binodal line calculated from $\chi = 1.84K/T - 0.0022$ in the concentration regime studied in this work and our data points. The broken line shows the extrapolation to the whole concentration regime. (b) $N\chi$ values calculated from eq 7. The error bars indicate the largest and lowest value if more than one Φ_b was measured at a fixed temperature. The points indicate the $N\chi$ calculated for the mean value of the measured Φ_b.

been fitted with a convolution of a homogeneous DPS concentration and a Gaussian with a fwhm of 90 nm. A larger broadening of the back edge is caused by the wedge-shaped DPS film as described previously; energy straggling would produce a much smaller effect at the back edge. After annealing some of the DPS had diffused into the PBr_xS but no diffusion of PBr_xS into the DPS could be measured within the accuracy of the method. For clarity Figure 2d (the fit used is explained later) shows that the slope of the back edge of the DPS phase remains constant while the interdiffusion is going on, indicating that the interface thickness must be significantly smaller than the depth resolution and that there is no further broadening due to diffusion. The interface was shifted toward the DPS rich side of the diffusion couple. Unfortunately the shift of the interface with increasing annealing time could not be measured quantitatively. The initial position of the interface is unknown because of the wedge-shaped top film and the target shifts after each profiling. We found the volume fraction Φ_b of the DPS at the interface to remain constant within the accuracy of the experimental method and to increase with increasing annealing temperature. All these are strong hints that we have measured the interdiffusion in a blend with a miscibility gap below the upper critical solution temperature (UCST).

To extract the volume fraction Φ_b from the DPS profile at the interface on the PBr_xS rich side, we used a theoretical shape with a constant volume fraction of 1 in front of the interface and an exponential decay behind it. This is motivated by two observations: First, the finite depth resolution does not allow a proper determination of the other blend composition (in front of the interface), which is close to 1, because the edges of the top layer are smoothed out. Second, the solution of the diffusion equation (eq 1) only applies to small diffusion times, as long as no diffusing substance reaches the surfaces of the finite diffusion couple. For larger times the reflecting boundaries will modify the solution. For simplicity we used an exponential decay. After convolution of this profile with the instrumental resolution, a Gaussian with a fwhm of 90 nm, and after an average was taken over a rectangular distribution of $R(t)$, it was fitted to the measured one. The averaging over $R(t)$ accounts for the wedge-shaped top film and the finite beam size, which defines the interval where the distribution is nonzero. The so found Φ_b is interpreted as one of two blend compositions on the binodal line. Results are shown in Figure 3a. The data show clearly the UCST behavior of the blend.

To quantify our data we recalculated the χ parameter in the Flory–Huggins theory. The χ parameter in a symmetrical blend and the blend composition on the binodal line Φ_b are connected via

$$N\chi(1 - 2\Phi_b) = \ln\left(\frac{1 - \Phi_b}{\Phi_b}\right) \qquad (7)$$

where N is the degree of polymerization. An approximate ratio r of the polymer molar volumes is obtained by using bulk (glassy) densities for polystyrene and partially brominated polystyrene with $x = 0.119$ and assuming volume additivity.[16] The molar volumes of DPS and PBr_xS are almost the same ($r = 0.973$, $x = 0.119$), so that we used the same N for both polymers. The χ values fit best to $\chi(T) = (1.84 \pm 0.17)K/T - (0.0022 \pm 0.0004)$; see Figure 3b.

We now compare our results to small-angle X-ray scattering data from Strobl and Urban.[22] In their experiment a 50% PS–50% PBr_xS blend was investigated in the one-phase region. The molecular weights of PS and PBr_xS were both 20 400 g/mol and the degree of bromination x was 0.31. They also found a linear dependence of χ with $1/T$. We rescaled their results to $x = 0.119$ with an equation cited by Koningsveld et al.[23] and originally derived by Simha and Branson:[24]

$$\chi = \chi_{DP}(1 - x) + \chi_{DBr}x - \chi_{PBr}x(1 - x) \qquad (8)$$

Equation 8 allows one to compute the effective interaction parameter in a blend of a homopolymer (DPS) and a copolymer (PBr_xS). The subscripts denote the interacting pairs of segments. χ_{DP} was recently measured by Bates and Wignall[15] and Green and Doyle.[14] χ_{PBr} was obtained from SAXS measurements of Strobl and Urban[22] by $\chi = x^2\chi_{PBr}$, to which eq 8 reduces for a PS–PBr_xS blend. No data are reported for χ_{DBr}, wich was set equal to χ_{PBr}. For a temperature of 181 °C, which lies in the range of the SAXS measurements and our measurements, eq 8 yields $\chi = 0.00148$, whereas our result is $\chi = 0.00185$. Koch and Strobl[26] investigated the concentration dependence of the χ parameter in a symmetric PS–PBr_xS blend with small-angle X-ray scattering. They found a slight variation of χ with a minimum value at $\Phi = 0.5$ and maximum values at $\Phi = 1$ and $\Phi = 0$. Sariban and Binder[27] presented Monte Carlo calculations on a finite lattice for $\chi(\Phi,T)$. These curves also show a minimum value at $\Phi = 0.5$. The above result is consistent with these observations because we have extracted the χ value at $\Phi \approx 0.2$.

Considering that the SAXS experiment works in Fourier space, that the ERD experiment works in direct space, and that the molecular weights, the degrees of bromination, and the concentration regime in both measurements were different, the resulting χ parameters are in good agreement. Therefore we conclude that we have interpreted the interdiffusion data in a reasonable manner within the framework of the Flory–Huggins theory.

Improvement of sample preparation and depth resolution should allow us to estimate simultaneously $\Phi_b{}^1$, $\Phi_b{}^2$, D_1, and D_2 in one experiment, as long as diffusion times are small enough. To describe the interdiffusion in a blend with a miscibility gap and the interface formation between the phases more properly (especially the width of the interface, which was assumed to be zero), one has to include gradient terms of Φ into the functional of the free energy of mixing. They prevent the diffusion coefficient from becoming negative under the spinodal line.

We conclude with a brief summary. We have measured the interdiffusion in the partially miscible polymer blend of DPS and PBr_xS with the ERD method. One of the blend compositions on the binodal line could be extracted from the diffusion profiles at various annealing temperatures. The other blend composition always was too close to unity to be measurable. The Flory–Huggins interaction parameter, calculated from the measured blend composition, is in good agreement with SAXS measurements on similar blends of PS and PBr_xS.

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An EPR Study of Copper(II) Complexes of Poly(L-ornithine) and Poly(L-2,4-diaminobutyric acid)

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ABSTRACT: The interactions of poly(L-ornithine) and poly(L-2,4-diaminobutyric acid) with copper(II) in aqueous solution have been investigated by using EPR and electronic spectroscopy and potentiometric titration as a function of pH between 2 and 13. As with the copper(II)–poly(L-lysine) system, many more complexes are found to be in pH-dependent equilibrium than previous reports for these systems have indicated. The complexes correspond to progressive replacement of the inner-sphere water molecules of the Cu(II) ion as the pH is raised, first by side-chain amines, then by deprotonated peptide nitrogens, and finally by hydroxide ligands. The length of the side chain strongly affects these equilibria. This is most noticeable in the unusual stability of the chelate of poly(L-2,4-diaminobutyric acid), where two amine and two deprotonated peptide ligands are bound to the copper even at pH values as low as 5. This provides evidence for a chelate effect indicating that adjacent Cu(II) ligands are nitrogen atoms from amine and peptide groups of the same amino acid residue, binding to form a six-membered ring. The similarity between the EPR parameters for the three systems indicates similar ligand environments in contrast to previous suggestions that deprotonated peptide nitrogens are adjacent ligands in the copper(II)–poly(ornithine) system.

Introduction

The interactions of copper(II) ions with polylysine, $(Lys)_n$, polyornithine, $(Orn)_n$, and poly(diaminobutyric acid), $(Dab)_n$, have been studied by a variety of techniques.[1-16] Although it is clear that the nature of the species present in solution depends strongly on pH, details of the structures of these species has remained elusive. We have previously reported the results of an investigation of the $Cu(Lys)_n$ system using EPR spectroscopy,[16] where we identified a series of pH-dependent equilibria that helped explain differences in interpretation of many previous experiments. We now report the extension of these studies to the polyornithine and polydiaminobutyric acid systems, whose side chains have one and two fewer CH_2 groups, respectively.

Experimental Details

Poly(L-lysine) hydrobromide of molecular mass 4000–15 000 and 70 000–150 000 was purchased from Sigma Chemical Co. Poly(L-ornithine) hydrobromide and poly(L-2,4-diaminobutyric acid) hydrobromide of molecular weight 40 000–75 000 and 8000–12 000, respectively, were prepared according to published methods.[17] The polymers were dissolved in deionized water. Copper(II) was added as a concentrated solution of the perchlorate salt (Aldrich Chemical Co., Inc.), and pH was adjusted by addition of small volumes of concentrated $HClO_4$ or NaOH solutions. Replacement of perchlorate by chloride had no effect on the results. Solutions were 0.005 M in amino acid residues for the EPR, absorption, and potentiometric work. In order to have a more rapid attainment of equilibrium and thus more reliable

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