Fast Mutual Diffusion in Polymer Blends

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Mutual-diffusion and tracer-diffusion coefficients, D and D^*, are measured in the miscible polymer blend system polystyrene+poly(2,6-dimethyl-1,4-phenyleneoxide) by forward recoil spectrometry. We find D to be much larger than D^*, an increase that is predicted quantitatively by a theory which includes the entire chemical-potential driving force for interdiffusion.

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Mutual diffusion or interdiffusion in miscible polymer blends, aside from its practical importance in the control of phase separation and homogenization, is of great interest for testing the relations between the thermodynamics of such blends and their diffusion behavior. de Gennes[1] was first to point out that because the combinatorial entropy of mixing of polymers is so small, scaling as N^{-1} where N is the degree of polymerization, the mutual diffusion of chemically dissimilar polymers will be dominated by the excess enthalpy and entropy of segment-segment mixing. In the usual mean-field approximation, the excess Gibbs free energy of mixing per segment can be represented by a regular solution model,[2] so that

$$\Delta G_{\rm mix}^{\rm ex} = \chi \phi_A \phi_B k_{\rm B} T, \tag{1}$$

where $k_{\rm B}$, T, ϕ_A, and ϕ_B are Boltzmann's constant, absolute temperature, and volume fractions of the components A and B in the binary blend, respectively. The strength of the segment-segment interaction is represented by the Flory-Huggins interaction parameter χ. Within this approximation the mutual-diffusion coefficient D is given by[3]

$$D = [D_A^* N_A \phi_B + D_B^* N_B \phi_A]\{\phi_B/N_A + \phi_A/N_B - 2\phi_A\phi_B\chi\}, \tag{2}$$

where D^* and N are the tracer-diffusion coefficient and degree of polymerization of the polymer component represented by the subscript. The first two terms in the curly braces correspond to the combinatorial entropy of mixing and the last term is the excess thermodynamic term. For miscibility of high-N polymers, χ normally must be negative[4] and consequently the last term should significantly enhance diffusion over the case of chemically identical polymers where χ is 0. Such enhancement will be termed segment-interaction enhancement. Recent measurements[5] in polyvinylchloride:polycaprolactone (PVC:PCL) blends show a strong maximum in D at $\phi_{\rm PVC}=0.5$ in qualitative agreement with Eq. (2). Since the D^*'s of PVC and PCL were not measured, however, Eq. (2) could not be tested quantitatively.

In this Letter we present strong experimental evidence for segment-interaction–enhanced mutual diffusion in a miscible polymer blend. The polymers are deuterated polystyrene (d-PS) of weight-average molecular weight $M_w=255\,000$ ($N=2452$) and dispersity index 1.2, and poly(2,6-dimethyl-1,4-phenylene oxide), also named poly(xylenyl ether) (PXE), of $M_w=35\,000$ ($N=292$) and dispersity index 2.3. A base film ($\sim 2\ \mu$m thick) of PXE:d-PS is spin cast on a silicon-wafer substrate from a solution ($\phi_{\text{d-PS}}=\phi_1$) of the polymers in chloroform. A second film (~ 350 nm thick) is prepared from another solution of different composition ($\phi_{\text{d-PS}}=\phi_2$) by spin casting on a glass substrate. After drying, this film is floated off onto the surface of a water bath from where it is picked up on the coated Si wafer to produce a bilayer-film diffusion couple. The concentration versus depth profile of d-PS in the film is measured before and after diffusion in vacuum ($<10^{-6}$ Torr) at temperature T by forward recoil spectrometry (FRES). Details of this ion-beam analysis technique have been published elsewhere.[6-9]

Figure 1 shows the profile of volume fraction of d-PS versus depth x for a diffusion couple before and after diffusion for a time $t=1800$ sec at $T=206\,^\circ$C. The initial $\phi_{\text{d-PS}}$ of the bottom film is 0.60 while that of the top film is 0.51. The interface between the two films in the experimental $\phi(x)$ profile of the undiffused sample appears somewhat diffuse as a result of the limited instrumental resolution of the FRES technique. The solid line in Fig. 1(a) corresponds to a step

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function convoluted with the instrumental resolution function $r(x)$, a Gaussian with full width at half maximum of 80 nm. After diffusion however, the interface becomes significantly broadened as shown in Fig. 1(b). Since the composition of the couple varies by only 0.09, a single mutual-diffusion coefficient D should control the interdiffusion[10] and hence we expect a concentration profile given by[11]

$$\phi(x) = 0.5(\phi_2 - \phi_1)\{\mathrm{erf}[(h-x)/w] + \mathrm{erf}[(h+x)/w]\} + \phi_1, \tag{3}$$

where h is the thickness of the top film and $w = 2(Dt)^{0.5}$. The solid line in Fig. 1(b) represents the best fit of Eq. (3) to the data. This fit requires a D of 1.1×10^{-13} cm^2/sec which we take as the value at the interfacial composition. Values of the interdiffusion coefficient extracted in this way are plotted as functions of the composition of the interface in Fig. 2. To partially compensate for the decreasing glass-transition temperature T_g of the blend with increasing $\phi_{\text{d-PS}}$, T was adjusted so that $T - T_g$ was held constant at 66 °C.

To compare the D values with those predicted by Eq. (1) we measured the tracer-diffusion coefficients D^* of d-PS and d-PXE diffusing into blends of undeuterated PS:PXE. The d-PXE was synthesized at General Electric[12] and had a M_W of 46 000 and a dispersity index of 2.4. Bilayer films with a very thin pure deuterated polymer layer ($\sim$20 nm thick) on top of a thick film of the blend were diffused at $T - T_g = 66$ °C[13] and analyzed by means of FRES.[14,15] Since the deuterated polymers rapidly become dilute ($\phi < 0.05$) as diffusion proceeds, a true D^* is measured. The data on the polydisperse d-PXE were analyzed to yield the D^* of PXE of weight-average molecular weight M_W.[14] D^* for d-PS of different molecular weights M scaled as M^{-2} as predicted by the theory of reptation.[15-18]

The values of D^* so determined[19] for the PS and PXE components of the interdiffusion couples are also plotted in Fig. 2. The D^*'s depend differently on blend composition, with $D^*_{\text{d-PS}}$ surprisingly exhibiting a strong minimum with ϕ_{PS}, whereas $D^*_{\text{d-PXE}}$ increases monotonically as ϕ_{PS} approaches 1. D^* for the 35 000 PXE component is about a factor of 80 lower than D^* for the 255 000 d-PS component at the lower ϕ_{PS}'s. The most important result, however, is that the mutual diffusion coefficient D is almost an order of magnitude higher than either of the D^*'s of the components

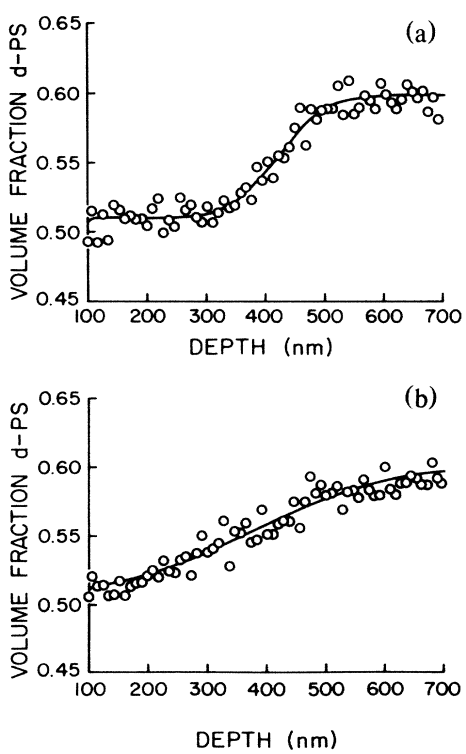

FIG. 1. Volume fraction of deuterated polystyrene in a d-PS:PXE thin-film diffusion couple: (a) as deposited, (b) after diffusion for 1800 sec at 206 °C.

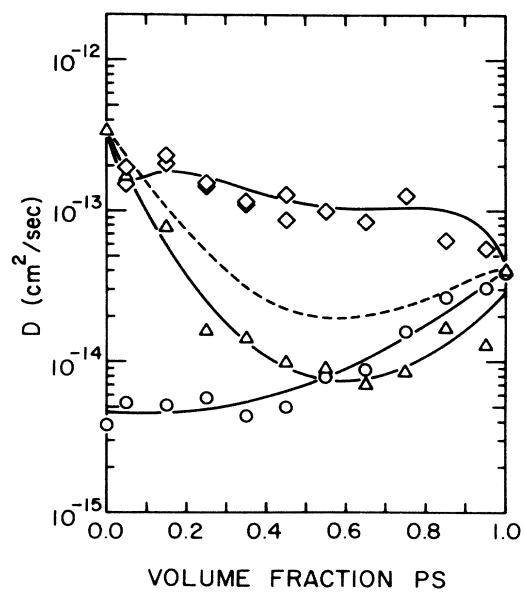

FIG. 2. Diffusion coefficients vs composition in the PS:PXE system. Circles and triangles, measured tracer-diffusion coefficients D^* of d-PXE ($M = 35\,000$) and d-PS ($M = 255\,000$) into blends of PS:PXE. Lozenges, measured interdiffusion coefficients in the d-PS:PXE diffusion couples. The lower solid lines represent smoothed values of $D^*_{\text{d-PXE}}$ and $D^*_{\text{d-PS}}$ used in the calculation. The upper solid line and dashed line represent the D predicted by Eq. (2) with, and without, segment-interaction enhancement, i.e., for $\chi = 0.145 - 78/T$ and $\chi = 0$.

of the blend, providing strong qualitative evidence for the existence of segment-interaction–enhanced mutual diffusion.

Quantitative confirmation of this conclusion can be obtained by computing the D expected if the mixing were ideal, i.e., $\chi=0$. This D is shown as the dashed line in Fig. 2. Clearly the mutual-diffusion kinetics are significantly increased by the negative χ parameter of this compatible blend. The experimental data are in good agreement with the D's (solid line) predicted from Eq. (2) using a value of $\chi=0.145-78/T$, corresponding to a range of values from 0.001 to −0.029 as T is decreased with $\phi_{\text{d-PS}}$ to maintain $T-T_g=66\,°\text{C}$. This $\chi(T)$ produces values that lie comfortably within the range of χ's determined for the d-PS:PXE system from small-angle neutron diffraction.[20]

In summary, we have observed unambiguous evidence of an increased mutual diffusion in a miscible polymer blend driven by the excess enthalpy and entropy of segment mixing, evidence that strongly supports the interpretation of the maximum in D in the PVC:PCL blends.[5] The observation has added significance in that it implies that previous observations of a strange molecular weight dependence of interdiffusion in the PVC:PCL blends ($D\sim M^{-1}$)[21] may be due to segment-interaction enhancement as first suggested by de Gennes.[1] Experiments to test the M_w dependence of D in the PS-PXE system should throw light on this point.

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[1]P. G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).

[2]P. J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, 1953), pp. 507–511.

[3]F. Brochard, J. Jouffrey, and P. Levinson, Macromolecules **16**, 1638 (1983). These authors arrive at a modified form of Eq. (2) in which the term in square brackets is replaced by $[\phi_B/D^*_A N_A+\phi_A/D^*_B N_B]^{-1}$, by assuming that an osmotic pressure gradient is built up so that no net mass flows occur as a result of diffusion. Equation (2) is derived by E. J. Kramer, P. F. Green, and C. J. Palmstrøm [Polymer **25**, 473 (1984)], and H. Sillescu [Makromol. Chem. Rapid Commun. **5**, 159 (1984)] by assuming no osmotic pressure gradient.

[4]Of course, χ could be positive but too small to cause phase separation for the molecular weights of the blend, but since χ is usually strongly temperature dependent such a delicate balance can only exist over a very narrow range of T. An exception is pairs of deuterated and hydrogenated polymers which apparently have extremely small positive χ's at all T. Nevertheless, at high enough molecular weight even these pairs undergo phase separation. See F. S. Bates, G. D. Wignall, and W. C. Koehler, Phys. Rev. Lett. **55**, 2425 (1985); F. S. Bates and G. D. Wignall, Macromolecules **19**, 934 (1986).

[5]R. A. L. Jones, J. Klein, and A. M. Donald, Nature (London) **321**, 161 (1986).

[6]B. L. Doyle and P. S. Peercy, Appl. Phys. Lett. **34**, 822 (1979).

[7]A. Turos and O. Meyer, Nucl. Instrum. Methods **149**, 92 (1984).

[8]P. J. Mills, P. F. Green, C. J. Palmstrøm, J. W. Mayer, and E. J. Kramer, Appl. Phys. Lett. **45**, 957 (1984).

[9]P. F. Green, P. J. Mills, C. J. Palmstrøm, J. W. Mayer, and E. J. Kramer, Phys. Rev. Lett. **53**, 2145 (1984).

[10]Strictly speaking, D is a function of composition both as a result of the explicit ϕ dependence in Eq. (2) and because the D^*'s vary with ϕ in this blend as a result of the decrease in glass-transition temperature with ϕ, from 216 °C at $\phi=0$ to 105 °C at $\phi=1$ as measured by differential scanning calorimetry at a rate of 10 °C per minute. Following the procedure of Ref. 5, we minimize this effect by making small the ϕ range of the couple. The D reported corresponds to the mean composition of the interface $(\phi_1+\phi_2)/2$.

[11]J. Crank, *The Mathematics of Diffusion* (Oxford Univ. Press, Oxford, 1975), 2nd ed., p. 15.

[12]D. M. White and S. A. Nye, Macromolecules **17**, 2643 (1984).

[13]Small deviations from this condition were corrected for by scaling D^*/T by a Williams-Landel-Ferry shift factor a_T, where $\ln(a_T)=c_1(T-T_g)/(c_2+T-T_g)$ and where $c_1=13.9$ and $c_2=51$. See N. Nemoto, I. N. Landry, and H. Yu, Polymer **25**, 141 (1984).

[14]P. J. Mills, P. F. Green, C. J. Palmstrøm, J. W. Mayer, and E. J. Kramer, Polym. Sci. Polym. Phys. Ed. **24**, 1 (1986).

[15]P. G. de Gennes, J. Chem. Phys. **55**, 4756 (1971).

[16]S. F. Edwards, in *Molecular Fluids,* edited by R. Balian and G. Weill (Gordon and Breach, London, 1976), p. 155.

[17]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979), p. 219.

[18]W. W. Graessley, Adv. Polym. Sci. **47**, 67 (1982).

[19]The D^* for the $M_w=255\,000$ d-PS was used directly; the D^* for the 35 000 PXE was found by scaling the D^* for the 46 000 d-PXE by the M^{-2} expected for reptation.

[20]A. Maconnachie, R. P. Kambour, D. M. White, S. Rostami, and D. J. Walsh, Macromolecules **17**, 2645 (1984), found the relation $\chi=0.121-77.9/T$ for dilute d-PXE in pure PS and $\chi=-0.033$ for dilute PS in PXE(glass), whereas R. P. Kambour, R. C. Bopp, A. Maconnachie, and W. J. MacKnight, Polymer **21**, 133 (1980), found $\chi\approx-0.04$ for d-PS in a glassy blend where $\phi_{\text{PS}}=0.09$. G. D. Wignall, H. R. Child, and F. Li-Aravena, Polymer **21**, 131 (1980), found $\chi\approx-0.006$ for dilute d-PS in PXE(glass), and A. Maconnachie, R. P. Kambour, and R. C. Bopp, Polymer **25**, 357 (1984), found $\chi=-0.020$ and −0.0029 for dilute d-PS in PXE(glass) ($\phi_{\text{PS}}=0$) and PS:PXE(glass) ($\phi_{\text{PS}}=0.5$), respectively. J. Jelenic, R. G.

Kirste, R. C. Oberthür, S. Schmitt-Strecker, and B. J. Schmitt, Macromol. Chem. **185**, 129 (1984), found $\chi = -0.0133$, -0.0079, -0.0034, and -0.0006 for dilute d-PS of molecular weights 25 000, 63 000, 188 000, and 465 000, respectively, in PXE(glass). For the glasses, the χ's presumably correspond to the equilibrium value just above the glass-transition temperature of the blend. We have used the coefficient of T^{-1} from the results of Maconnachie *et al.*, and have adjusted the second constant to produce the best fit.

[21]P. T. Gilmore, R. Falabella, and R. L. Lawrence, Macromolecules **13**, 880 (1980).