Reptation in polymer blends

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Forward recoil spectrometry (FRES) was used to measure the tracer diffusion coefficients D_{PS}^* and D_{PXE}^* of deuterated polystyrene (d-PS) and deuterated poly(xylenyl ether) (d-PXE) chains in high molecular weight protonated blends of these polymers. The D^*s were shown to be independent of matrix molecular weights and to decrease as M^{-2}, where M is the tracer molecular weight, suggesting that the tracer diffusion of both species occurs by reptation. These D^*s were used to determine the monomeric friction coefficients $\zeta_{0,PS}$ and $\zeta_{0,PXE}$ of the individual PS and PXE macromolecules as a function of ϕ, the volume fraction of PS in the PS:PXE blend. Since $\zeta_{0,PS} \ll \zeta_{0,PXE}$ at each ϕ, the rate at which a PS molecule reptates is much greater than that of a PXE molecule, even though both chains are diffusing in identical surroundings. Part of this difference may be due to the difficulty of backbone bond rotation of the PXE molecule. However, even when measured at a constant temperature increment above the glass transition temperature, $\zeta_{0,PS}$ and $\zeta_{0,PXE}$ were observed to be markedly composition dependent. In addition the ratio $\zeta_{0,PS}/\zeta_{0,PXE}$ varied from a maximum of 4×10^{-2} near $\phi = 0.85$ to a minimum of 5×10^{-5} for $\phi = 0.0$. These results show that intramolecular barriers do not solely determine the ζ_0s of the components in this blend. Clearly, the interactions between the diffusing chains and the matrix chains also influence ζ_0.

(Keywords: polystyrene; poly(xylenyl ether); diffusion; monomeric friction coefficient; forward recoil spectrometry)

INTRODUCTION

The dynamics of melts of short polymer chains may be successfully modelled by considering each polymer chain to be a string of monomer 'beads' connected by entropic springs[1-5]. When each bead moves with a velocity v with respect to its surroundings it is assumed to experience a 'frictional' drag force, $\zeta_0 v$, where ζ_0 is called the monomeric friction coefficient. In this Rouse model the friction coefficient of the entire chain is simply given by the sum of the friction coefficients of its monomers, i.e.

$$\zeta = \zeta_0(M/M_0) \tag{1}$$

where M and M_0 are the molecular weights of the entire chain and a monomer, respectively. Each chain is assumed to undergo centre-of-mass motion in any direction subject only to the drag force on its monomers by their surroundings.

In entangled melts the viscoelasticity and diffusion become more complex due to the topological constraints exerted on long chains by their neighbours[6-8]. Here the most successful model[9] (reptation) considers the motion of a given chain to be confined to the axis of a tube (its primitive path) defined by the long chains surrounding it. The chain can execute a one-dimensional curvilinear diffusion along the contour of the tube but is prevented from moving normal to this contour by the constraining chains of the matrix. The curvilinear diffusion of the molecule within the tube is assumed to be described by the Rouse model, i.e. the curvilinear or tube diffusion

coefficient is given by

$$D_{tube} = \frac{k_B T M_0}{\zeta_0 M} \tag{2}$$

where k_B is Boltzmann's constant and T is absolute temperature. The centre-of-mass diffusion coefficient of the chains is then given by

$$D^* = D_R = D_0/M^2 \tag{3}$$

where D_0 the reptation constant is given by

$$D_0 = \tfrac{4}{15} k_B T M_0 M_e / \zeta_0 \tag{4}$$

where M_e is the entanglement molecular weight measured from the shear modulus or the rubbery plateau. The values of ζ_0 determined from measurements of D_0 are in good agreement with those determined from zero shear viscosity η_0 for single component melts[7,10].

When one attempts to extend the reptation model to compatible polymer blends (e.g. a binary blend of polymer A and polymer B) an important question arises. Can one use an average monomer friction coefficient to describe the viscoelasticity of the blend assuming that monomers from A chains and those from B chains experience, on the average, the same frictional resistance[11]? Until recently only indirect methods existed for inferring the answers, e.g. investigation of the orientation of different species in a deformed melt blend by infrared dichroism[12-14]. In this paper we use measurements of the tracer diffusion coefficients of the A and B chains (under conditions where reptation dominates diffusion) to determine the monomeric friction coefficients of each component of the blend as a function of blend compositon.

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The results show conclusively that the assumption of an average friction coefficient cannot be correct, as in some instances the monomeric friction coefficient of the A monomer is more than 10^4 times that of the B monomer. These results suggest that the monomeric friction coefficient is strongly influenced by a combination of inter- and intramolecular forces.

EXPERIMENTAL METHODS

Each sample consisted of a bilayer of a thin (≈ 20 nm) deuterated polystyrene (d-PS) or deuterated poly(xylenyl ether) (d-PXE) film on top of a thick ($\approx 2 \mu$m) film of a blend of protonated PS and PXE which served as the matrix into which the diffusion was carried out. The matrix film was prepared by pulling a 2 cm × 2 cm silicon wafer, at a constant rate, from a blend of PS:PXE dissolved in chloroform. The film of the deuterated tracer polymer was prepared from a chloroform solution of d-PS or d-PXE polymer by spin casting on a glass substrate. The deuterated film was floated off onto the surface of a water bath and then picked up with the thick matrix film.

The characteristics of the various polymers are given in *Tables 1* and *2*. The weight average molecular weights of the deuterated tracer polymers d-PS and d-PXE will be denoted by M_{PS} and M_{PXE} while those of the protonated chains will be denoted by P_{PS} and P_{PXE}, respectively. In previous studies, the entanglement molecular weight M_e of the PS:PXE blends was shown to be[15,16]

$$\frac{1}{M_e^{\frac{1}{2}}} = \frac{\phi}{M_{e,PS}^{\frac{1}{2}}} + \frac{1-\phi}{M_{e,PXE}^{\frac{1}{2}}} \qquad (5)$$

where $M_{e,PS} = 18\,000$ and $M_{e,PXE} = 3400$. The value for $M_{e,PXE}$ was extrapolated by a method described pre-

Table 1 Molecular weight characteristics of deuterated polymers

	M_w	M_w/M_n	Source
d-PS	55 000	1.06	Polymer Laboratories
d-PS	110 000	1.1	Polymer Laboratories
d-PS	255 000	1.1	Polymer Laboratories
d-PS	430 000	1.1	Polymer Laboratories
d-PS	520 000	1.1	Polymer Laboratories
d-PXE	19 000	1.9	General Electric
d-PXE	36 000	1.9	General Electric
d-PXE	48 000	2.4	General Electric
d-PXE	138 000	2.6	General Electric

M_w, M_n, weight average and number average molecular weight of deuterated diffusing species, respectively

Table 2 Molecular weight characteristics of protonated polymers

	P_w	P_w/P_n	Source
PS	390 000	1.06	Pressure Chemical
PS	900 000	1.1	Pressure Chemical
PS	2 000 000	1.2	Pressure Chemical
PS	20 000 000	1.3	Pressure Chemical
PXE	19 000	–	General Electric
PXE	35 000	2.3	General Electric
PXE	135 000	2.6	General Electric
PXE	$\approx 190\,000$	–	General Electric

P_w, P_n, weight average and number average molecular weight of protonated matrix species, respectively

viously[15]. The diffusion couples were heated to a temperature T under vacuum ($< 10^{-6}$ Torr*) for a given diffusion time t. After annealing, forward recoil spectrometry (FRES) was used to measure the volume fraction of the diffused d-PS and d-PXE chains as a function of depth. In this technique, a beam of doubly ionized helium ions with an energy $E_0 = 2.8$ MeV strikes the diffusion couple at a glancing angle. As a result of nuclear collisions, deuterium nuclei recoil from the surface of the film with an energy $E = \frac{2}{3}E_0$. However, deuterium nuclei originating from below the surface are detected at lower energies because the incident helium ion and recoiling deuterium nuclei lose energy via inelastic collisions with the electrons in the polymer. Since the yield of deuterium nuclei recoiling from the couple depends on the concentration of the deuterated species, the depth (x) *versus* volume fraction (ϕ) profile of the deuterium-labelled species is determined by the energy and number, respectively, of the deuterium nuclei which enter an energy sensitive detector. Details of this ion beam analysis technique have been published elsewhere[17-19].

Soon after the deuterated molecules begin diffusing into the matrix, the volume fraction ϕ of the diffusing species becomes dilute ($\phi < 0.07$) and, therefore, the volume fraction profile can be described by the tracer, or infinite dilution, diffusion coefficient D^*. The depth profile for monodisperse chains diffusing in a semi-infinite matrix is given by the solution of Fick's second law[20],

$$\phi(x) = \frac{1}{2}\left[\mathrm{erf}\left\{\frac{(h-x)}{w}\right\} + \mathrm{erf}\left\{\frac{(h+x)}{w}\right\} \right] \qquad (6)$$

where h, the initial thickness of the tracer film, is found by integrating the experimental depth profile and w is the characteristic diffusion distance, $2(D^*t)^{1/2}$. A theoretical volume fraction profile can be computed by convoluting $\phi(x)$ from equation (6) with the instrumental resolution function, a Gaussian with a full width at half maximum of 80 nm. The tracer diffusion coefficient D^* is varied until a good fit of the convoluted function to the experimental profile is achieved.

The tracer diffusion coefficient D^* of the polydisperse d-PXE chains was found by two methods. In the first method, the monodisperse solution, equation (6), was fitted to the peak ($x = 0$) of the volume fraction profile. Mills *et al.*[21] found that the tracer diffusion coefficient determined in this way yields the D^* corresponding to that of the weight average molecular weight of the polymer. In the other method, the monodisperse diffusion equation was modified by assuming that the d-PXE chains obeyed a Flory–Schultz distribution and diffused by reptation. As shown previously[15], both methods yield similar values for D^*.

RESULTS

Reptation in blends

To show that the reptation mechanism can be observed in blends, the tracer diffusion coefficients D^*_{PS} and D^*_{PXE} for d-PS and d-PXE chains of molecular weights M_{PS} and M_{PXE}, respectively, must satisfy two experimental criteria[9,22]. First, the measured D^*s should scale as M^{-2}:

$$D^*_{PS} = D_{R,PS} = D_{0,PS}M_{PS}^{-2} \qquad (7a)$$

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* 1 Torr $\approx$ 133 Pa

and

$$D^*_{PXE} = D_{R,PXE} = D_{0,PXE} M^{-2}_{PXE} \qquad (7b)$$

where the subscripts denote the diffusing species. Second, D^* should be independent of the molecular weights, P_{PS} and P_{PXE}, of the PS and PXE chains making up the matrix. This second condition is perhaps a more stringent test as D^*s which scale as approximately M^{-2} have been found when reptation clearly is not dominant[23-25]. Nevertheless, we demonstrate that it is possible to observe the $D^* \propto M^{-2}$ signature of reptation in PS:PXE blends at sufficiently high molecular weights of the matrix; previous experiments[15] also show that D^* is independent of matrix molecular weights at the P_{PS} and P_{PXE} of our present study.

As demonstrated in *Figure 1*, the tracer diffusion coefficient D^*_{PS} of d-PS chains of molecular weight M_{PS} was measured in blends of PS:PXE containing PS volume fractions of $\phi = 0.8$ and 0.6. To carry out diffusion, all samples were heated to 183°C; the weight average molecular weights of the matrix chains in the blends were 35000 and 390000 for PXE and PS, respectively. In both matrices, D^*_{PS} scaled as M^{-2} as predicted by reptation theory. Although both sets of D^*_{PS}s follow the same scaling law, the values of D^*_{PS} in the $\phi = 0.8$ matrix were shifted to much higher values, at a given M_{PS}, than the values of D^*_{PS} in the $\phi = 0.6$ matrix. Part of this shift can be attributed to the fact that the $\phi = 0.8$ matrix has a lower glass transition temperature ($T_g = 120°C$) than the $\phi = 0.6$ matrix ($T_g = 136°C$). Thus, suitable reference temperatures which account for the composition dependence of T_g must be chosen before any quantitative statements about polymer mobility in different PS:PXE blends can be made.
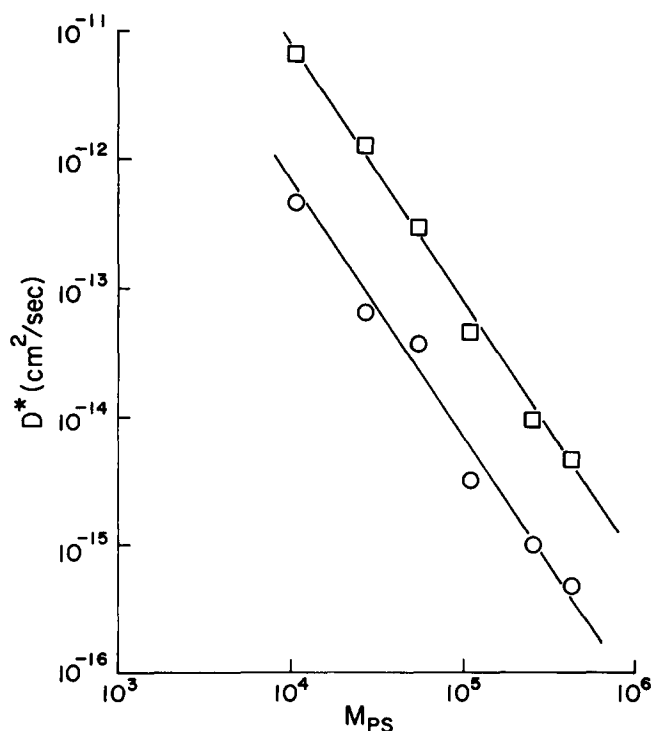

Figure 1 Tracer diffusion coefficient D^*_{PS} of d-PS chains *versus* molecular weight M_{PS} of d-PS chains at 183°C: □, ○, diffusion of d-PS chains in 0.8 and 0.6 volume fraction PS matrices, respectively; ——, predictions from the reptation model, equation (7a) where $D_{0,PS} = 9.2 \times 10^{-4}$ and 8.8×10^{-5} cm² s⁻¹ for the $\phi = 0.8$ and 0.6 matrix blends, respectively

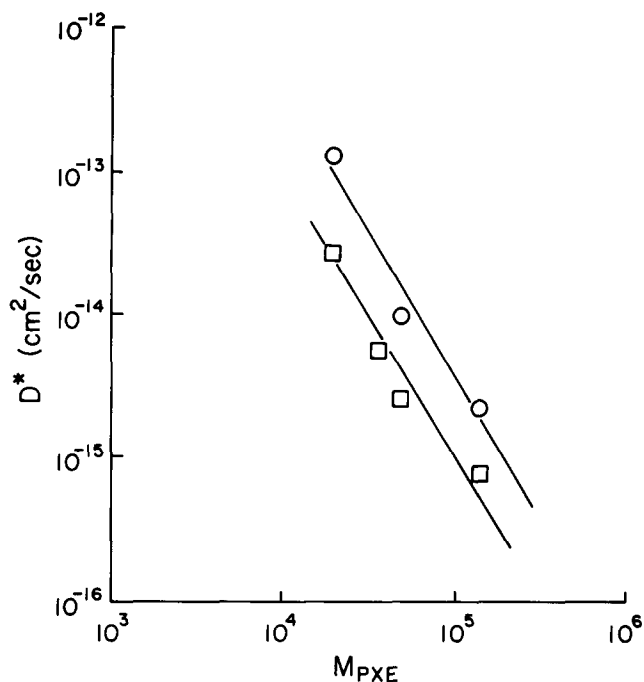**Figure 2** Tracer diffusion coefficient D^*_{PXE} of d-PXE chains *versus* molecular weight M_{PXE} of d-PXE chains: ○, □, diffusion of d-PXE chains in a pure PS matrix at 165°C and a pure PXE matrix at 295°C, respectively; ——, predictions from the reptation model, equation (7b), where $D_{0,PXE} = 3.9 \times 10^{-5}$ and 1.0×10^{-6} cm² s⁻¹ for the pure PS and PXE matrices, respectively

The solid lines in *Figure 1* show the D^*_{PS}s predicted by equation (7a), with $D_{0,PS}$ values of 9.2×10^{-4} and 8.8×10^{-5} cm² s⁻¹ for $\phi = 0.8$ (upper line) and 0.6, respectively. Both sets of experimental D^*_{PS}s agreed quite well with the M^{-2}_{PS} dependence predicted by the reptation theory. Since reptation dominates the D^*_{PS}s, the matrix molecular weights used in this study ($P_{PS} = 390000$, $P_{PXE} = 35000$) appear to be long enough to inhibit the constraint release of d-PS chains with molecular weights M_{PS} between 27000 and 430000. This observation is consistent with previous diffusion experiments[15] in which d-PS chains ($M_{PS} = 255000$) were diffused into a series of $\phi = 0.85$ matrices containing PS chains of various molecular weights P_{PS} and PXE chains with a molecular weight of 35000. For $P_{PS} \geqslant 390000$, D^*_{PS} was independent of P_{PS}. Since the two conditions for reptation are satisfied, we believe that the D^*s presented in *Figure 1* represent the first time the reptation mechanism has been shown to be the diffusion mechanism in a polymer blend.

The diffusion of d-PXE chains of weight average molecular weight M_{PXE} was studied in pure PS ($\phi = 1.0$) and pure PXE ($\phi = 0.0$) matrices. A plot of the tracer diffusion coefficient D^*_{PXE} *versus* M_{PXE} is shown in *Figure 2* for the two pure matrices, PS and PXE. The diffusion temperatures were 165 ($T - T_g = 60°C$) and 295°C ($T - T_g = 73°C$) for the PS and PXE matrices, respectively, and the matrix weight average molecular weights were 2000000 and 190000 for the matrix PS and matrix PXE chains. The D^*_{PXE}s measured in both the pure PS and the pure PXE matrices scaled approximately as M^{-2}_{PXE}, as predicted by reptation theory.

The theoretical predictions based on equation (7b) are shown as the lines in *Figure 2* where $D_{0,PXE} = 3.9 \times 10^{-5}$ and 1.0×10^{-5} cm² s⁻¹ for $\phi = 1.0$ and $\phi = 0.0$, respectively. The agreement between the experimental data and the

predicted values is reasonable. Previous diffusion experiments[15] in pure PXE matrices ($\phi = 0$) demonstrated that D^*_{PXE} ($M_{PXE} = 19\,000$ and $48\,000$) was independent of PXE matrix molecular weights for $P_{PXE} \geqslant 190\,000$. In the same study D^*_{PXE} ($19\,000 \leqslant M_{PXE} \leqslant 138\,000$) for d-PXE chains diffusing in pure PS was found to be independent of PS matrix molecular weight for $P_{PS} \geqslant 2\,000\,000$. Since the first condition ($D^*_{PXE} \propto M^{-2}_{PXE}$) for reptation is shown here (*Figure 2*) and the second (D^*_{PXE} independent of matrix molecular weight) was demonstrated in Reference 15, we assert that the D^*_{PXE}s measured in the pure PXE and pure PS matrices are dominated by the reptation mechanism.

Reptation constants and monomeric friction coefficients

While studying the reptation of d-PXE chains in the two different matrices (see *Figure 2*), the reptation constant $D_{0,PXE}$ in PS was found to be much greater than in PXE. Since $T - T_g$ was greater in the PXE matrix, it does not appear that this difference can be attributed to free volume effects, but rather it appears to indicate a fundamental difference between the monomeric friction coefficients measured in the two matrices. Before any quantitative comparisons between polymer mobilities can be made, however, the composition dependence of T_g should be taken into account by comparing the reptation constants, or monomeric friction coefficients, at a fixed temperature above the T_g of each blend.

As shown by the differential scanning calorimetry results in *Figure 3*, the glass transition temperature T_g of PS:PXE blends increased from 105 (pure PS) to 216°C (pure PXE) as the volume fraction ϕ of PS decreased from 1.0 to 0.0. The samples were heated at a rate of
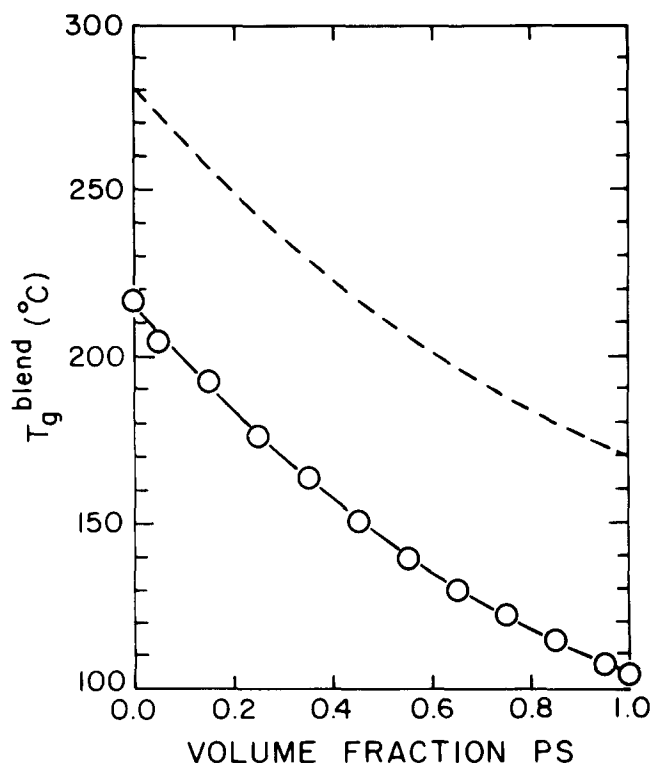

Figure 3 Glass transition temperature, T_g, of PS:PXE blends as a function of the volume fraction ϕ of PS. The weight average molecular weights of the PS and PXE were 390 000 and 35 000, respectively. ——, Polynomial fit to the data; ————, representing $T - T_g = 66°C$, shows the temperatures at which diffusion into the blend matrices was carried out

$10°C\,min^{-1}$. The solid line represents a polynomial fit to the data given by: $T_g(°C) = 216.5 - 173.8\phi + 75.1\phi^2 - 11.8\phi^3$. The PS and PXE polymers tested had weight average molecular weights of 390 000 and 35 000, respectively. Other groups have observed similar values of T_g for high molecular weight PS:PXE blends[11,26]. The dashed line represents a set of reference temperatures corresponding to $T = T_g + 66°C$.

The tracer diffusion coefficients D^*_{PS} and D^*_{PXE} for d-PS and d-PXE chains were measured in PS:PXE blends containing $\phi = 1.0$, 0.85, 0.55, 0.15 and 0.0 volume fraction PS. Since the matrix molecular weights were chosen to be large enough that the constraint release contribution to D^* was negligible, the tracer diffusion coefficients were dominated by the reptation mechanism, i.e. $D^* = D_R$. Thus the reptation constants $D_{0,PS}$ and $D_{0,PXE}$ were calculated by simply rearranging equations (7a) and (7b), respectively.

In *Figure 4a*, the reptation constants $D_{0,PS}$ and $D_{0,PXE}$ of PS and PXE chains are plotted as a function of the PS volume fraction ϕ in PS:PXE blends at $T - T_g = 66°C$. The solid lines are drawn only to serve as a guide to the eye. At constant ϕ, the magnitude of $D_{0,PS}$ was much greater than the magnitude of $D_{0,PXE}$, suggesting that PS was more mobile in the 'tube' determined by the chains in the matrix blend than PXE. As ϕ was varied, the reptation constants $D_{0,PS}$ and $D_{0,PXE}$ were found not only also to vary but also actually to diverge as ϕ was decreased. The reptation constant $D_{0,PS}$ of PS decreased at first as ϕ decreased, went through a minimum near $\phi = 0.85$ and then increased monotonically for $\phi \leqslant 0.6$. On the other hand, the reptation constant $D_{0,PXE}$ of PXE was initially fairly constant as ϕ decreased, began to decrease rapidly near $\phi = 0.75$, remained fairly constant between $0.2 \leqslant \phi \leqslant 0.5$ and then decreased slightly.

The large difference between the values of $D_{0,PS}$ and $D_{0,PXE}$ was illustrated by plotting the ratio $D_{0,PS}/D_{0,PXE}$ against the volume fraction ϕ of PS. Since this ratio was independent of reference temperature and matrix entanglement molecular weight, $D_{0,PS}/D_{0,PXE}$ provided an accurate meaure of the relative mobilities for PS and PXE in blends of PS:PXE. As shown in *Figure 5a*, $D_{0,PS}/D_{0,PXE}$ was not constant but varied quite strongly from a minimum of ≈ 20 near $\phi = 0.85$ to a maximum of $\approx 20\,000$ for $\phi = 0.0$. The magnitude and variation of $D_{0,PS}/D_{0,PXE}$ clearly show that, first, the mobility of a PS chain is greater than that of a PXE chain in the same blend and, second, the mobilities of PS and PXE do not have the same composition dependence.

The expression for the reptation constant D_0 (equation (4)) contains both the monomeric friction coefficient and the entanglement molecular weight M_e, the latter factor accounting for changes in the diameter of the Edwards tube. Since M_e changes with blend composition one should really compare the monomeric friction coefficients, which are calculated as

$$\zeta_{0,PS} = \tfrac{4}{15}k_B T M_0 M_e / D_{0,PS} \qquad (8a)$$

and

$$\zeta_{0,PXE} = \tfrac{4}{15}k_B T M_0 M_e / D_{0,PXE} \qquad (8b)$$

From equations (8a) and (8b), the monomeric friction coefficients $\zeta_{0,PS}$ and $\zeta_{0,PXE}$ of PS and PXE, respectively, were calculated from the reptation constants shown in *Figure 4a* and the entanglement molecular weights given
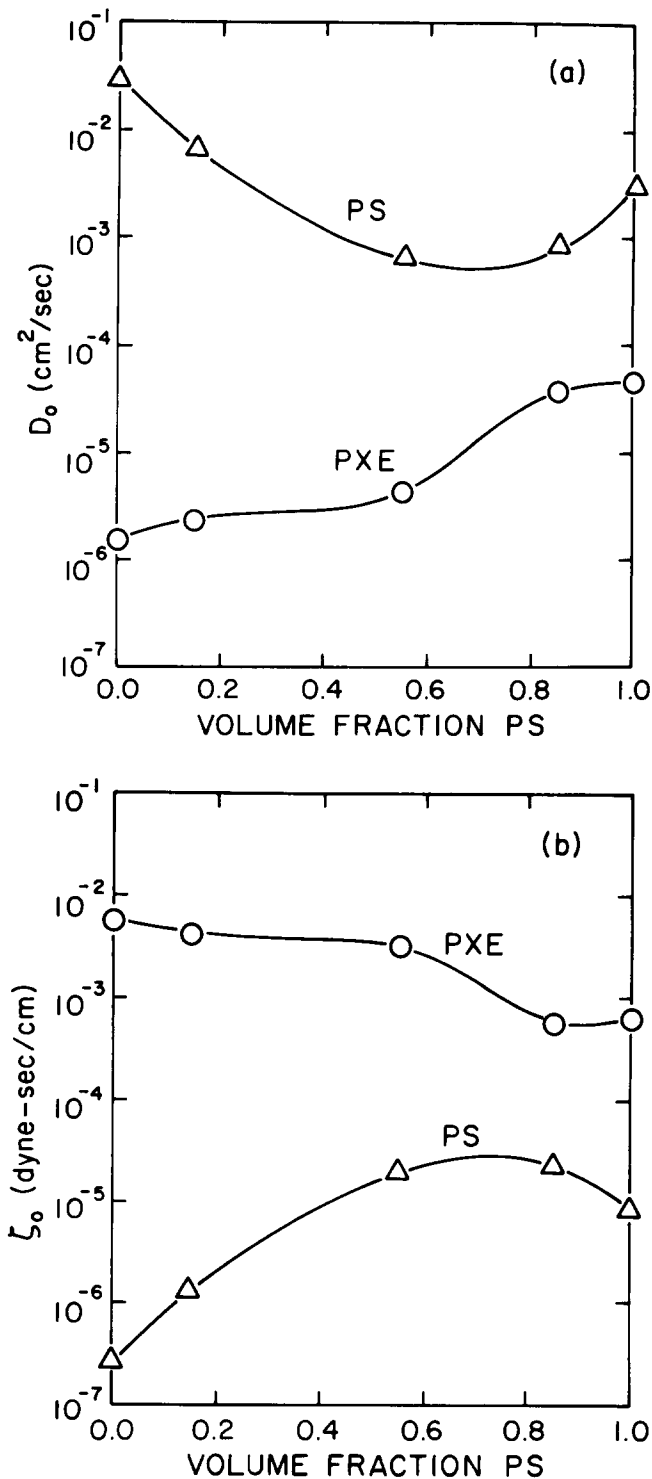
coefficient $\zeta_0(\phi)$ depended very strongly on composition, so the effect of composition on the reptation constant shown in *Figure 4a* is not simply an effect of the composition dependence on M_e but has its primary origins in the composition dependence of monomeric friction coefficients.

A popular class of models of polymeric melts invokes the importance of 'free volume' in determining rheological and viscoelastic properties. In reviewing the results in *Figure 4*, the question immediately arises whether the composition dependence observed is due to the fact that the constant $T - T_g = 66°C$ state is not a state of constant free volume. Since free volume at a fixed temperature above T_g increases with $\Delta\alpha$, the difference in expansion

Figure 4 (a) Reptation constants, $D_{0,PS}$ ($\triangle$) and $D_{0,PS}$ ($\bigcirc$) of PS and PXE *versus* volume fraction ϕ of PS in the PS:PXE matrix blend at $T - T_g = 66°C$. (b) Monomeric friction coefficients, $\zeta_{0,PS}$ ($\triangle$) and $\zeta_{0,PXE}$ ($\bigcirc$) of PS and PXE *versus* volume fraction ϕ of PS in the PS:PXE matrix blend at $T - T_g = 66°C$. All lines are drawn to serve as a guide to the eye

by equation (5). In *Figure 4b*, $\zeta_{0,PS}$ and $\zeta_{0,PXE}$ are plotted as a function of the volume fraction ϕ of PS in the PS:PXE blend at $T - T_g = 66°C$. As before, the solid lines are drawn as a guide to the eye. At all compositions, the monomeric friction coefficient for PS was less than that for PXE ($\zeta_{0,PS} < \zeta_{0,PXE}$), with the ratio $\zeta_{0,PS}/\zeta_{0,PXE}$ varying from a maximum of 4×10^{-2} near $\phi = 0.85$ to a minimum of 5×10^{-5} for $\phi = 0.0$, as shown in *Figure 5b*. As observed for $D_0(\phi)$ at $T - T_g = 66°C$, the monomeric friction
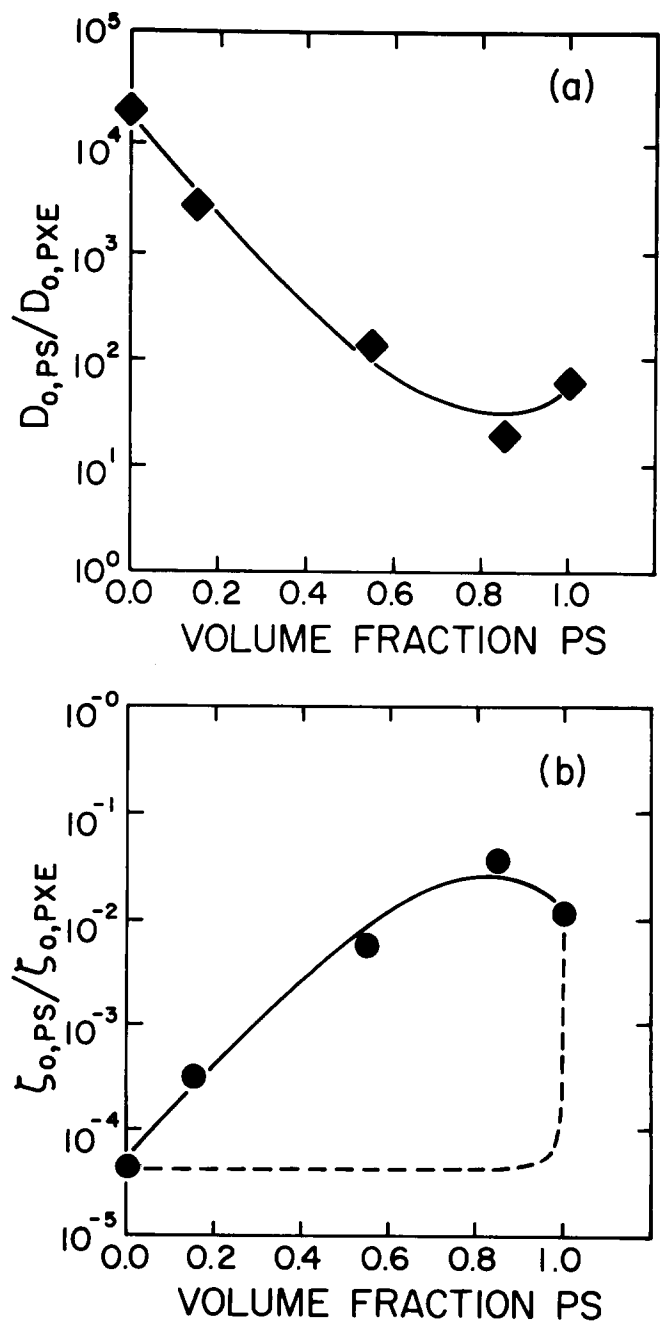

Figure 5 Ratio of (a) reptation constants $D_{0,PS}/D_{0,PXE}$ and (b) monomeric friction coefficients $\zeta_{0,PS}/\zeta_{0,PXE}$ of PS and PXE as a function of volume fraction ϕ of PS in the PS:PXE matrix blends measured at $T - T_g = 66°C$. ——, Guides to the eye; ----, prediction of the Brochard-Wyart model (equation (9))

coefficient between the melt and the glass, the melt properties in a polymer blend may change at constant $T-T_g$ simply because $\Delta\alpha$ is a function of composition. For the PS:PXE system, unfortunately, previous workers disagree not only on the magnitude of the composition dependence of $\Delta\alpha$ but also on its sign. Dynamic mechanical spectroscopy studies[11,27,*] indicate that one must go to a larger $T-T_g$ to achieve comparable properties in PXE-rich and PS-rich blends (implying $\Delta\alpha$ increases with ϕ), whereas direct measurements[26] of $\Delta\alpha$ in PS:PXE blends indicate that to achieve an iso free volume state one must go to a smaller $T-T_g$ in PXE rich blends than in PS rich ones ($\Delta\alpha$ decreases with ϕ). In the appendix we discuss this controversy further and correct *Figure 4b* to 'iso free volume' using each of these approaches. For now it suffices to point out that even if the free volume correction results in one of the monomeric friction coefficients becoming independent of composition, the other will still vary strongly with ϕ; the ratio of the friction coefficients shown in *Figure 5b* is independent of any correction for free volume since the correction changes each friction coefficient (PS and PXE) at the same composition by exactly the same factor. In the discussion which follows we emphasize the conclusion which can be drawn using only the free volume independent results of *Figure 5*.

DISCUSSION

One of our primary results is that the monomeric friction coefficients in the miscible PS:PXE blend are not equal: $\zeta_{0,PXE} > \zeta_{0,PS}$ over the whole composition range. This result is supported by the previous experiments of Monnerie and co-workers[12,13], who used infrared dichroism to monitor the orientation of both PS and PXE chains in melts of PS:PXE ($\phi \geqslant 0.65$). For $M_{w,PS} \approx 5M_{w,PXE}$, they found that the orientation of PXE decayed more slowly than the orientation of PS after the strain rate was suddenly set to zero (i.e. under stress relaxation). In similar experiments, Wang and Porter[14] also found that PXE chains lost their orientation more slowly than PS chains. Both sets of experiments are consistent with a smaller monomeric friction coefficient for PS than for PXE in the PS-rich blends and are thus in qualitative agreement with our measurements of the actual friction coefficients shown in *Figure 4b*.

What is even more surprising than the fact that the PXE monomeric friction coefficient is larger than the PS coefficient is the fact that the ratio of the two friction coefficients is so dependent on composition. One might hope that the simple model proposed recently by Brochard-Wyart[28], which allows the two friction coefficients to differ, would describe the composition dependence we observe. She relates the two measured monomeric friction coefficients to three microscopic friction coefficients, $\zeta_{PS,PS}$, $\zeta_{PS,PXE}$ and $\zeta_{PXE,PXE}$, which correspond to friction between PS and PS segments, PS and PXE segments and PXE and PXE segments, respectively, with the following equations:

$$\zeta_{0,PS} = \phi\zeta_{PS,PS} + (1-\phi)\zeta_{PS,PXE} \qquad (9a)$$

$$\zeta_{0,PXE} = \phi\zeta_{PS,PXE} + (1-\phi)\phi_{PXE,PXE} \qquad (9b)$$

We can thus write the following equation for the ratio $\zeta_{0,PS}/\zeta_{0,PXE}$:

$$\frac{\zeta_{0,PS}}{\zeta_{0,PXE}} = \frac{(\zeta_{PS,PS}/\zeta_{PS,PXE})\phi + (1-\phi)}{\phi + (\zeta_{PXE,PXE}/\zeta_{PS,PXE})(1-\phi)} \qquad (9c)$$

which depends only on the two ratios of microscopic friction coefficients, $\zeta_{PS,PS}/\zeta_{PS,PXE}$ and $\zeta_{PXE,PXE}/\zeta_{PS,PXE}$. If these two ratios, as might be hoped, are independent of PS volume fraction ϕ, then the ratios can be determined from any two points on *Figure 5b*, e.g. the ζ_0 ratios at $\phi = 0$ and $\phi = 1$, and equation (9c) should then be able to predict the ζ_0 ratios at all intermediate compositions. The dashed line in *Figure 5b* shows that the resulting fit to the data is poor; the simple three microscopic friction coefficient model cannot adequately describe our results on the PS:PXE system.

Part of this failure may be due to a naive picture of the character of the actual 'friction' involved in polymer melt diffusion. The concept of a monomeric friction coefficient originated in the attempt to describe the motion of a polymer molecule in a solvent. In that context it is known that the most important interactions are intermolecular, i.e. the hydrodynamic interactions between solvent molecules and polymer segments. The internal flexibility of the polymer molecule, which is governed by its intramolecular forces, can be shown to be irrelevant[29]. But diffusion in a melt, especially by reptation, is entirely different. The elementary steps in reptation can be envisaged as the propagation of 'stored length' or 'molecular kinks' along the length on the molecule within the 'tube'[9]; such propagation cannot occur, and the molecule cannot reptate, if it cannot change its conformation.

The influence of such internal barriers to bond rotation offers at least a partial rationalization for the fact that the friction coefficient of PXE is larger than that of PS. Based on conformation energy calculations[30], it is estimated that the barrier to rotation between the other stable conformations (involving $\pm 90°$ rotations) in PXE is rather large. If this barrier is larger than that for the $\pm 120°$ bond rotations in PS, as seems likely, that could account for part of the elevation of the monomeric friction coefficient of PXE with respect to that of PS in the same blend.

The influence of intramolecular barriers to rotation cannot be the whole story, however. If the intramolecular barriers were all that mattered, one could expect that the ratio of PS to PXE friction coefficients would be independent of matrix composition, which is clearly not the case. Moreover one would expect that the D*s of PS and PXE in a blend of fixed composition would be markedly different, with D* of PXE increasing much more rapidly with temperature than that of PS. Experiments made at $\phi = 0.55$, however, show that the D*s of the two different macromolecules have virtually identical temperature dependences[31].

An interesting possible resolution of these paradoxes is offered by the recent work of Helfand[32] on the dynamics of conformational transitions in melts. He points out that, if such conformational transitions were to take place by rotation about a single bond in the middle of a long macromolecule, then one of the macromolecular 'tails' attached to that bond would have to undergo a large swinging motion; clearly such motion is ruled out. He finds instead that such conformational transitions take

place by means of a concerted two-bond rotation, in which a second neighbour bond counter-rotates by the same angle as the first (rotating) bond. This concerted two-bond motion avoids any large rotation of the tails but introduces a small displacement of the tails relative to each other, which can be initially accommodated by small elastic strains of the molecule and its surroundings. Certainly, however, the larger the magnitude of the displacement of the tails the smaller the probability that this elementary two-bond motion will occur.

The relevance to the present discussion of polymer blends is that the longer the effective bond distance (the length of the stiff unit along the chain), the larger the displacement of the tails. In PS, where the bond distance is 1.54 Å*, we calculate that the displacement of the tails in the concerted two-bond motion is 2.52 Å. In PXE however, where the effective bond distance (the distance between oxygen atoms) is 5.52 Å, that displacement of the tails is increased to 6.76 Å, a factor of nearly three higher. Thus the concerted two-bond motion in PXE definitely perturbs its surroundings more than the same motion in PS. If those surroundings are PS rich (and thus relatively compliant), one can imagine that they can accommodate the increase in two-bond displacement on going from PS to PXE relatively easily. If those surroundings are PXE rich (and relatively non-compliant), however, they might have much more difficulty in accommodating the large PXE displacement. The PXE monomeric friction coefficient, which should reflect this difficulty, would become larger with respect to the PS monomeric friction coefficient as ϕ, the PS volume fraction in the blend, decreases. The behaviour of the friction coefficient ratio shown in *Figure 5b* is thus in qualitative agreement with this hypothesis.

Clearly, more experimental evidence is needed before we can draw firm conclusions about the interpretation of these monomeric friction coefficients and their concentration dependence. Since this is the first high molecular weight, miscible polymer blend in which the friction coefficients have been measured we need to extend these methods to other systems to discover whether the behaviour seen here is general or whether the PS:PXE blends are just a pathological case for some reason currently hidden from us. Comparison of these data with those from other techniques (e.g. dynamic mechanical spectroscopy, nuclear magnetic resonance) would be welcome. But, just as clearly, studies of the tracer diffusion coefficients in polymer blends offer a whole new experimental window, not only into the dynamics of individual polymer components in those blends but also into questions about the meaning of such apparently well established concepts as the monomeric friction coefficient itself.

CONCLUSIONS

(1) The reptation of d-PS and d-PXE chains in polymer blends has been observed. This is the first experimental observation of the reptation mechanism in miscible polymer blends.

(2) The monomeric friction coefficient of PS is much less than that of PXE in the same blend.

(3) At constant $T - T_g$ or constant fractional free volume, the monomeric friction coefficient of PS is

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* 1 Å $= 10^{-1}$ nm

observed to go through a maximum as the volume fraction ϕ of PS decreases, while the monomeric friction coefficient of PXE increases with decreasing ϕ.

(4) The observations that the ratio $\zeta_{0,PS}/\zeta_{0,PXE}$ varies quite strongly with ϕ suggests that both intra- and intermolecular forces influence the magnitude of the monomeric friction coefficient.

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APPENDIX: TEMPERATURES AT WHICH PS:PXE BLENDS HAVE THE SAME FRACTIONAL FREE VOLUME

In this appendix, we attempt to calculate the temperatures $T^\dagger$ at which PS:PXE blends have the same fractional free volume f and then use the Williams, Landel and Ferry equations to scale the reptation constants and monomeric friction coefficients of PS and PXE from $T - T_g = 66°C$ to a constant fractional free volume. The first approach is to compute the temperature $T^\dagger$ from measurements of volume *versus* temperature for the blends[26]. The fractional free volume of a melt is given by[33]

$$f = f_g + \Delta\alpha(T)(T - T_g) \tag{10}$$

where f_g is the fractional free volume at T_g. The average difference $\Delta\alpha(T)$ between the expansion coefficient of the melt $\alpha(T)$ and that of the glass α_g is given by

$$\Delta\alpha(T) = \frac{\int_{T_0}^{T_0} \alpha(T)\, dT}{T_0 - T_g} - \alpha_g \tag{11}$$

The $\alpha(T)$ is the temperature-dependent thermal expansion coefficient[26]

$$\alpha(°C^{-1}) = \tfrac{3}{2}dT^{\frac{1}{2}} \tag{12}$$

where T is absolute temperature (K) and d is a constant[26] (see *Table 3*) for each PS:PXE blend. In this paper we assume that $f_g = 0.028$[34] for all PS:PXE blends. Using $f = 0.045$ as a reference (PS at 171°C) and the data on d and α_g from Zoller and Hoehn[26], we compute the temperatures $T^\dagger$ at which the PS:PXE blends have the same fractional free volume by simply rearranging equation (10). *Table 3* shows the temperatures corresponding to $T - T_g = 66°C$ and as well as the $T^\dagger$ at which $f = 0.045$. These data appear to show that PXE-rich blends have more fractional free volume than the PS-rich blends at a constant $T - T_g = 66°C$; as a result, it is predicted that the iso free volume temperature $T^\dagger$ lies progressively further below the temperature at which $T - T_g = 66°C$ as the blends become more and more PXE rich, i.e. as ϕ goes from 1 to zero.

However, a second approach has been taken by Aurelio de Araujo and Stadler[27] (with similar results to one used previously by Prest and Porter[11]). They estimate the ratio $\Delta\alpha_{PXE}/\Delta\alpha_{PS}$ to be equal to the ratio $\Delta C_{p,PXE}/\Delta C_{p,PS}$, where the ΔC_ps are the jumps in the heat capacities of the pure PXE and PS at the respective glass transition temperatures. Aurelio de Araujo and Stadler conclude that the ratio equals 0.8 from a review of their own, and literature, data on ΔC_p. They use the value of $\Delta\alpha$ for PS given by Ferry[33] to obtain $f = 0.052$ for PS at 171°C and interpolate linearly between the values for PS and PXE to find the values of $\Delta\alpha$ for the blends. As shown in *Table 3*, the iso free volume temperatures $T^\dagger$ computed from these data lie progressively further above rather than below the temperature at which $T - T_g = 66°C$ as the blends become PXE rich, precisely the opposite to what is predicted by using the Zoller and Hoehn data.

By applying the WLF relationship[33] to the values of ζ_0 at $T - T_g = 66°C$, the reptation constants and monomeric friction coefficients at these two sets of very different iso free volume temperatures can be calculated[35]:

$$\frac{D_0(T^\dagger)}{T^\dagger} = \frac{D_0(T)}{T} a_T^{-1} \tag{13}$$

and[34]

$$\zeta_0(T^\dagger) = \zeta_0(T)a_T \tag{14}$$

where $\log(a_T) = -c_1^0(T - T^\dagger)/(c_2^0 + T - T^\dagger)$. The WLF constants are given by

$$c_2^0 = c_2^g + T - T_g \tag{15}$$

$$c_1^0 = c_1^g c_2^g/c_2^0 \tag{16}$$

$$c_2^g = f_g/\Delta\alpha(T_g) \tag{17}$$

and

$$c_1^g = B/2.303 f_g \tag{18}$$

where $B \approx 1$ and $\Delta\alpha(T_g)$ was taken as the value measured by Zoller and Hoehn[26,33].

The values of the monomeric friction coefficients, corrected using the two different sets of iso free volume temperatures, are very different, as can be seen in *Figure 6*. *Figure 6a* shows $\zeta_{0,PS}$ and $\zeta_{0,PXE}$ at the iso free volume temperatures computed using the experimental specific

Table 3 Temperature of PS:PXE blends at $T - T_g = 66°C$, $f = 0.045$ (directly determined from the data of Zoller and Hoehn[26]) and $f = 0.052$ (determined by the method of Aurelio de Araujo and Stadler[27])

Volume fraction of PS, ϕ	Expansion coefficient constant[26], $10^5 d$ (°C^{-1})	Expansion coefficient of glass[26], $10^4\alpha_g$ (°C^{-1})	Temperature $T = T_g + 66$ (°C)	Temperature at $f = 0.045$[26], $T^\dagger$ (°C)
1.00	1.78	2.86	171	171
0.85	1.84	2.85	181	175
0.55	1.95	2.41	206	185
0.15	2.10	2.11	258	226
0.00	2.16	2.09	282	248

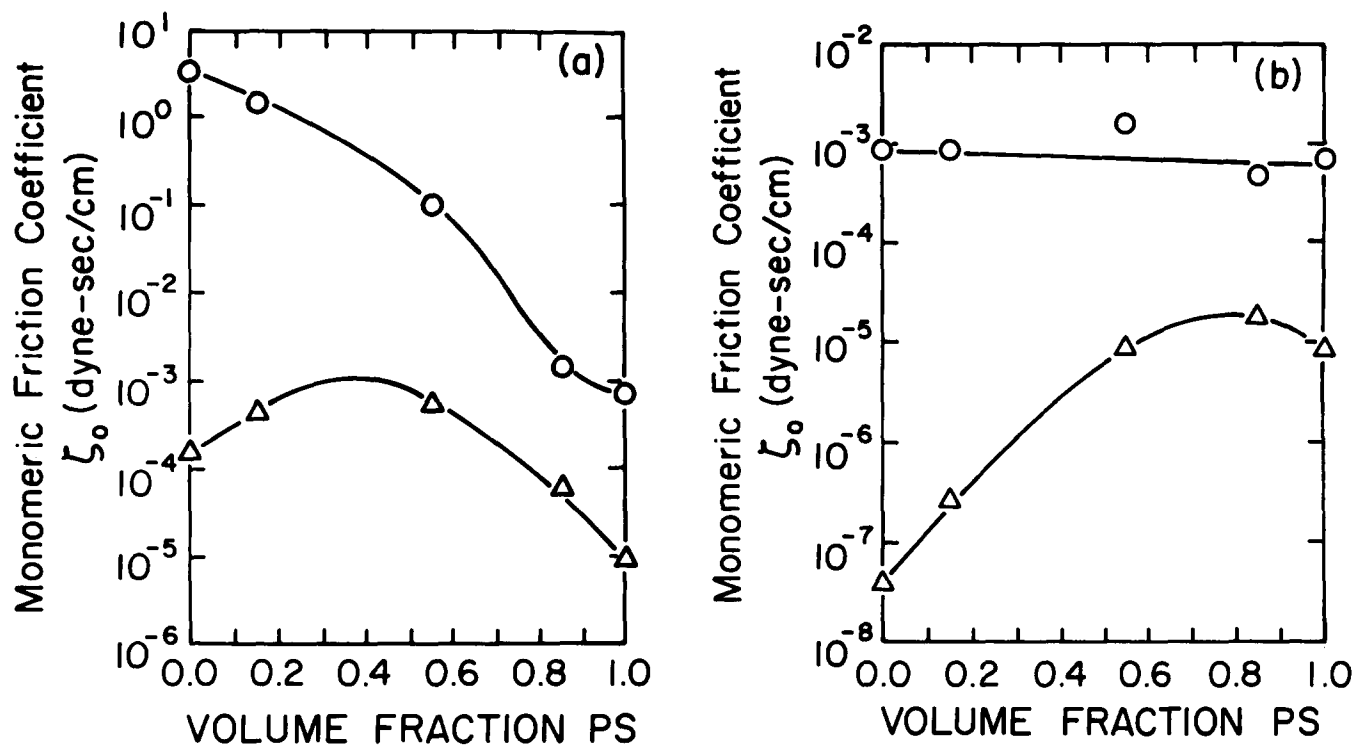|	Expansion coefficient difference[27], $10^4\Delta\alpha$ (°C^{-1})		Temperature at $f = 0.052$[27], $T^\dagger$ (°C)
1.00	3.70	171	171
0.85	3.59	181	183
0.55	3.37	206	212
0.15	3.07	258	271
0.00	2.96	282	298

Figure 6 Monomeric friction coefficients $\zeta_{0,PS}$ ($\triangle$) and $\zeta_{0,PXE}$ ($\bigcirc$) of PS and PXE, respectively, as a function of ϕ, the volume fraction of PS in the blend: (a) corrected to a constant fractional free volume $f=0.045$ using the volume *versus* temperature data of Zoller and Hoehn[26]; (b) corrected to a constant fractional free volume $f=0.052$ using the procedure of Aurelio de Araujo and Stadler[27]

volume *versus* temperature data of Zoller and Hoehn. *Figure 6b* shows the same quantities computed using the approach of Aurelio de Araujo and Stadler. In *Figure 6a*, the PXE friction coefficient increases by over three orders of magnitude from pure PS to pure PXE, while that of PS shows only a comparatively mild variation, increasing to a maximum at $\phi=0.55$ and then decreasing again. In *Figure 6b* the results are entirely the reverse. The

monomeric friction coefficient of PXE varies hardly at all with ϕ, while that for PS decreases strongly as ϕ is decreased past $\phi=0.55$. Given these two very different sets of 'iso free volume' friction coefficients, both produced by reasonable procedures, we have decided to rely in the text only on a ratio of friction coefficients which can be interpreted independently of any free volume correction.