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# Matrix Effects on Diffusion in Polymer Blends

**Russell J. Composto* and Edward J. Kramer**

*Department of Materials Science and Engineering and the Materials Science Center, Bard Hall, Cornell University, Ithaca, New York 14853*

**Dwain M. White**

*General Electric Corporate Research and Development, Schenectady, New York 12301*

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ABSTRACT: 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 into protonated blends of these polymers. The volume fraction $\phi$ and molecular weight $P_{PS}$ of the protonated PS component of the blend were varied but the weight-average molecular weight of the PXE was held constant at 35 000. Both $D^*_{PS}$ and $D^*_{PXE}$ were independent of $P_{PS}$ for values larger than the characteristic molecular weight $P^{\dagger}_{PS}$. In this regime reptation is the dominant diffusion mechanism. For $P_{PS} < P^{\dagger}_{PS}$ the constraint release mechanism becomes dominant with $D^*$'s increasing with decreasing $P_{PS}$. In a pure PS matrix ($\phi = 1.0$), $D^*_{PXE}$ increases roughly as $P_{PS}^{-3}$ for $P_{PS} < P^{\dagger}_{PS}$; as $\phi$ decreases from 1.0 to 0.15 however, the dependence of the $D^*$'s on $P_{PS}$ becomes weaker, reflecting the fact that the increasing fraction of slower PXE matrix chains serves as progressively longer lived constraints. Nevertheless the self-diffusion of d-PXE into PXE (where both the diffusant and matrix have the same molecular weight) is dominated by constraint release, unlike the case of d-PS into PS. The Graessley model of constraint release can provide a good fit to the experimental data but only if $z$, the number of suitably situated constraints, is allowed to change from one blend to another.

## Introduction

Diffusion of polymer molecules that are nearly chemically identical (e.g., deuterated polystyrene in polystyrene) has been studied extensively over the past several years.[1-7] However, relatively few experiments have explored polymer diffusion in chemically dissimilar polymer blends.[8-11,34-36] Polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide), or poly(xylenyl ether) (PXE), provide an ideal system for study because PS:PXE blends are miscible over the entire range of composition and molecular weight.[12-14] Tracer diffusion coefficients, $D^*$, are found by diffusing trace quantities of deuterated polystyrene (d-PS) or deuterated poly(xylenyl ether) (d-PXE), respectively, into blends of protonated PS and PXE chains. Because the effects of isotopic labeling are negligible, the tracer diffusion coefficient of a deuterated molecule is equivalent to the $D^*$ of a protonated molecule of the same molecular weight: $D^*_{d\text{-}PS} = D^*_{PS}$ and $D^*_{d\text{-}PXE} = D^*_{PXE}$.[15] Measurements of $D^*$ as a function of diffusant molecular weight $M_{PS}$ or $M_{PXE}$, matrix molecular weight $P_{PS}$ or $P_{PXE}$, and matrix composition, expressed here as the volume fraction $\phi$ of PS, can increase our understanding of the diffusion mechanisms which occur in such blends and provide new tests of the reptation and constraint release theories.

The reptation theory proposed by de Gennes[16] describes the dynamics of a long polymer chain diffusing in a cross-linked gel or an entangled polymer melt.[17-19] The diffusing chain moves by crawling (reptating) along a virtual tube which is defined by the topological constraints provided by the neighboring chains.[20] Because these neighboring chains are themselves diffusing, the tube is not fixed and renews its configuration over a period of time called the tube relaxation time, $\tau_{tube}$. If the tube relaxation time $\tau_{tube}$ is much longer than the reptation time $\tau_R$ required for the diffusing chain to crawl out of the tube, the constraints remain essentially fixed and the translational motion of the diffusing chain is dominated by the reptation mechanism. However, if the chains surrounding the diffusing chain are sufficiently short, the tube can reorganize on a time scale less than the reptation time, i.e., $\tau_{tube} < \tau_R$. This reorganization allows the diffusing chain to diffuse by a mechanism called constraint release or tube renewal.

Although many self-diffusion experiments exist,[1-7] theories based on the constraint release mechanism[17,21,22] have not been rigorously tested for a polymer blend system because such a test requires knowledge of the tracer diffusion coefficients of both components of the blend. In this paper, we measure the tracer diffusion coefficients, $D^*_{PS}$ and $D^*_{PXE}$, of PS or PXE in PS:PXE blends ranging from pure PS to pure PXE, and compare the measured $D^*$'s with those predicted by the reptation and generalized constraint release model.

## Theory

**Reptation.** The reptation diffusion coefficient $D_{R,A}$ of A can be expressed as

$$D_{R,A} = D_{0,A} M_A^{-2} \tag{1}$$

where $D_{0,A}$, which we call the reptation constant of polymer A, is given by

$$D_{0,A} = \left(\frac{4}{15}\right)\left(\frac{M_0 M_e k_B T}{\zeta_{0,A}}\right) \tag{2}$$

In eq 2 the parameters correspond to $\zeta_{0,A}$, the monomeric friction coefficient; $k_B$, the Boltzmann constant; $T$, the absolute temperature; and $M_0$, the monomer molecule weight of A. If the matrix is a blend, the entanglement molecular weight $M_e$ containing a volume fraction $\phi$ of A chains and $(1 - \phi)$ of B chains is

$$\frac{1}{M_e^{1/2}} = \frac{\phi}{M_{e,A}^{1/2}} + \frac{1-\phi}{M_{e,B}^{1/2}} \tag{3}$$

where $M_{e,A}$ and $M_{e,B}$ are the entanglement molecular

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* Current address: Department of Materials Science and Engineering and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104.

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weights of the pure components. A derivation of eq 3 is given in the Appendix. An identical form for $M_e$ was derived from a different model by Tsenoglou.[25] Our measurements[34,37] and subsequent ones by Green et al.[36] show that the reptation diffusion coefficient $D_{R,A}$ for an A chain diffusing in a highly entangled A:B blend scales as $M_A^{-2}$. In addition, we have also observed the second signature of reptation, namely, that $D_{R,A}$ was independent of the molecular weight of the matrix chains in a highly entangled system.

**Constraint Release.** A long chain of polymer A crawling in a virtual tube will diffuse slowly by reptation if the topological constraints remain fixed for much longer than the reptation time of A; however, because the neighboring chains are also diffusing, the tube itself can diffuse.[17-19] In a blend, two types of constraints, A and B, prevent the diffusing chain from moving in a direction perpendicular to the tube. Assuming that the matrix chains are reptating, the reptation times of each species and therefore the tube relaxation time $\tau_{tube}$ will depend on the molecular weights $P_A$ and $P_B$ and the reptation constants $D_{0,A}$ and $D_{0,B}$ of the matrix A and B chains, respectively.

If the reptation and constraint release mechanisms are independent, the tracer diffusion coefficient of A can be written as the sum of the reptation and constraint release diffusion coefficients[7,17]

$$D_A = D_{R,A} + D_{CR,A} \tag{4}$$

Graessley has developed a very useful model to describe constraint release in a matrix of monodisperse, chemically identical chains. Our goal is to generalize Graessley's model in order to describe constraint release in a matrix of two chemically different polymer molecules.[37] A similar procedure was used by Green in ref 35. Because the PXE component is polydisperse, the effects of matrix polydispersity on constraint release will also be considered.

In a monodisperse one-component matrix of long A chains, any given A chain is reptating randomly within a tube while simultaneously creating new portions of the tube. This process is described mathematically by a function $F_A(t)$, which is the fraction of the original tube not yet disengaged by a reptating polymer chain after time $t$; i.e.

$$F_A(t) = \sum_i w_i \exp\left\{\frac{-t}{(\tau_{R,A})_i}\right\} \tag{5}$$

where $w_i$ is the weight fraction of an A chain of degree of polymerization $i$.[17] For a monodisperse matrix, eq 5 simplifies to $F_A = \exp(-t/\tau_{R,A})$. The reptation time for monodisperse A chains is

$$\tau_{R,A} = \frac{K_A}{3\pi^2}\frac{M_A^3}{D_{0,A}} \tag{6}$$

where $K_A$ is the ratio $\langle R_A^2\rangle/M_A$ and $\langle R_A^2\rangle$ is the mean square end-to-end distance of the A molecule. In a polydisperse matrix, one might envision that extreme molecular weight chains in the distribution could diffuse by mechanisms other than reptation; e.g., the longer A chains themselves might diffuse by a constraint release mechanism or the shorter A chains might diffuse by a Rouse mechanism. In this paper, these alternative diffusion mechanisms will be ignored; clearly, more theoretical work is needed to achieve a fully self-consistent model for constraint release in polydisperse matrices. Because the probability of any constraint being due to an A chain is equal to the volume fraction $\phi$ of A chains, the generalized expression for $F(t)$ in a two-component matrix of A and B chains is

$$F(t) = \phi F_A(t) + (1-\phi)F_B(t) \tag{7}$$

where the A or B polymers can be either monodisperse or polydisperse.

The fraction $F_A(t)$ of the initial path still occupied by the diffusing A chain defines yet another parameter: the waiting time $\tau_w$. In Graessley's model the cross section of the tube is defined at each step along the tube by $z$ matrix molecules, or "suitably situated constraints". For a matrix of A chains, the time necessary for the release of a constraint, defined as the waiting time $\tau_w$, is given by

$$\tau_w = \int_0^\infty dt\, [F_A(t)]^z \tag{8}$$

As the number of suitably situated constraints $z$ increases, the probability that the tube undergoes a constraint release step must increase and therefore, from eq 8, the waiting time must decrease. Alternatively, because only one of the $z$ constraints needs to diffuse away, the waiting time must decrease with increasing $z$. Following Graessley,[17] the general expression for the constraint release diffusion coefficient of an A chain diffusing in a homogeneous matrix is given by

$$D_{CR,A} = \frac{1}{12}\frac{a^2}{N\tau_w} = \frac{4}{75}\frac{K_A M_e^2}{M_A \tau_w} \tag{9}$$

where the waiting time $\tau_w$ depends on the matrix components, dispersity, and reptation times. For the case of a monodisperse one-component matrix the waiting time is simply

$$\tau_w = (\pi^2/12)^z \tau_R \tag{10}$$

From eqs 6, 9, and 10 the constraint release diffusion coefficient for an A chain of molecular weight $M_A$ diffusing in a matrix of A chains of molecular weight $P_A$ is

$$D_{CR,A} = \alpha_{CR}\frac{D_{0,A}M_e^2}{M_A P_A^3} \tag{11}$$

where $\alpha_{CR} = (48/25)z(12/\pi^2)^{z-1}$. Green et al.[7] have demonstrated that the constraint release of d-PS chains into PS is successfully described by eq 11. For A chains diffusing in a monodisperse B matrix we have

$$D_{CR,A} = \alpha_{CR}\frac{K_A}{K_B}\frac{D_{0,B}M_e^2}{M_B P_B^3} \tag{12}$$

This expression explicitly shows that a complete description of constraint release in polymer blends requires knowledge of the reptation constants of *both* components.

In an earlier publication[34] we determined the concentration dependence of the reptation constants of PS and PXE, $D_{0,PS}$ and $D_{0,PXE}$, in a PS:PXE blend containing a volume fraction $\phi$ of PS. At constant $\phi$, the magnitude of $D_{0,PS}$ was much greater than that of $D_{0,PXE}$, suggesting that PS was much more mobile in the "tube" determined by the chains in the matrix blend than was PXE. As $\phi$ decreased, $D_{0,PS}$ decreased at first, went through a minimum near $\phi = 0.85$, and then increased. On the other hand, $D_{0,PXE}$ was initially constant as $\phi$ decreased, began to decrease rapidly near $\phi = 0.75$, remained fairly constant in the range $0.2 < \phi < 0.5$, and then decreased slightly. In a diffusion study of PS and poly(vinyl methyl ether) (PVME), the reptation constant of PS was found to exhibit a minimum.[36] However, the $\phi$ dependence of PVME was not determined. Furnished with $D_{0,PS}(\phi)$ and $D_{0,PXE}(\phi)$, we can fully describe the tube mobility and therefore can test Graessley's generalized constraint release model using our data on PS:PXE blends.

## Experimental Methods

**Sample Preparation.** 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 (~2 μm) film of a blend of protonated PS and PXE which served as a matrix into which diffusion was carried out. Because of favorable specific interactions (negative interaction parameter), the PS:PXE blends are miscible at all compositions, molecular weights, and relevant temperatures.[38] The matrix film was prepared by pulling a 2 cm × 2 cm silicon wafer at a constant rate from a PS:PXE blend dissolved in chloroform. The weight-average molecular weights of the PS and PXE polymers in the matrix film will be denoted as $P_{PS}$ and $P_{PXE}$, respectively, and ranged from 55 000 to 20 000 000 for PS and 19 000 to ~190 000 for PXE. The polydispersity indices ($M_w/M_n$) for the relatively monodisperse PS samples were ≤1.1 except for the 20 000 000 PS sample, which had a dispersity index of 1.3. The dispersity index for the polydisperse PXE samples ranged from 1.9 to 2.6 as $P_{PXE}$ increased from 19 000 to 190 000. The polydispersity index of the 190 000 PXE was not measured. A 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 weight-average molecular weights of the d-PS and d-PXE polymers will be denoted as $M_{PS}$ and $M_{PXE}$, respectively, and ranged from 55 000 to 915 000 for d-PS and 19 000 to 138 000 for d-PXE. The dispersity indices for the d-PS samples were ≤1.1, while the dispersity index for the d-PXE ranged from 1.9 to 2.6. The deuterated film was floated off onto the surface of a water bath and then picked up with the thick matrix film.

**Sample Characterization.** The glass transition temperature $T_g$ of the PS:PXE blends varied from 105 °C for pure PS to 216 °C for pure PXE. The composition dependence of $T_g$ as measured by differential scanning calorimetry (DSC) is given by $T_g$ (°C) = $215.4 - 173.8\phi + 75.1\phi^2 - 11.8\phi^3$, where $\phi$ is the volume fraction of PS.[34] Typical DSC samples had masses of approximately 7 mg, and the weight-average molecular weights of the PS and PXE were 390 000 and 35 000, respectively. The samples were heated at a rate of 10 °C/min. The DSC technique was also used to find the glass transition temperatures of PXE as a function of its number-average molecular weight $M_{n,PXE}$ with the result $T_g$ (°C) = $224 - 1.2 \times 10^5/M_{n,PXE}$.

**FRES Measurement and Analysis.** The diffusion couples were heated to a temperature $T$ under vacuum ($<10^6$ Torr) for a given diffusion time $t$. To ensure that the time to reach the final temperature $T$ was a small fraction of this diffusion time, no samples were diffused for less than 5 min. The maximum diffusion time used in these studies was 48 h with a temperature variation during this time of ±0.7 °C. The volume fraction profiles of d-PS and d-PXE after diffusion into the blend matrix films were determined by forward recoil spectrometry (FRES). 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 with an energy $E = (2/3)E_0$. 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. Because the yield of the recoiling nuclei depends on the concentration of the deuterated species, the depth ($x$) versus volume fraction ($\varphi$) profile of the deuterium-labeled 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.[7,27,28] Plots a and b of Figure 1 show the experimental volume fraction profiles for d-PS of weight-average molecular weight $M_{PS}$ = 255 000 and d-PXE of $M_{PXE}$ = 48 000, respectively, diffusing into PS:PXE matrices containing 0.55 volume fraction PS at 206 °C.

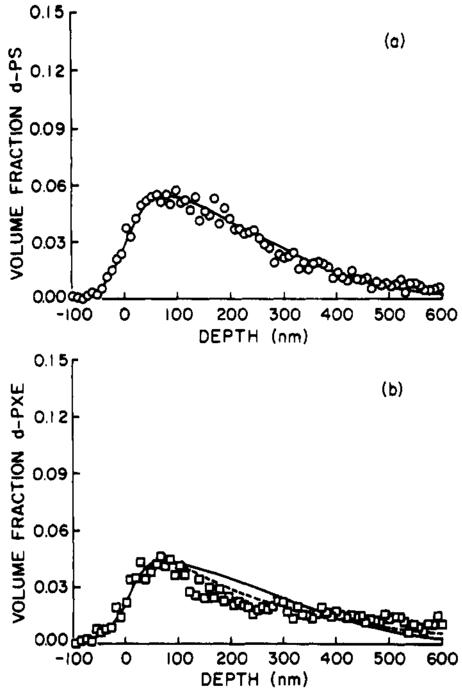

**Figure 1.** Volume fraction of deuterated polystyrene (a) and deuterated poly(xylenyl ether) (b) versus depth in a PS:PXE diffusion couple. The diffusion temperature is 206 °C and the volume fraction of PS in the matrix blend is 0.55 with a weight-average molecular weight of 50 000 for PS and 35 000 for PXE. The molecular weights of the d-PS and d-PXE are 255 000 and 48 000, respectively. The solid lines are the monodisperse fits to the data: (a) $D^*_{PS} = 1.8 \times 10^{-14}$ cm²/s and (b) $D^*_{PXE} = 4.2 \times 10^{-15}$ cm²/s. The dashed line in (b) is the polydisperse fit using the same $D^*_{PXE}$.

Soon after the deuterated molecules begin diffusing into the matrix, the volume fraction $\varphi$ of the deuterium-labeled species becomes dilute ($\varphi < 0.07$) and therefore the volume fraction profile can be described by the tracer, or infinite dilution, diffusion coefficient. The depth profile for monodisperse chains diffusing in a semiinfinite matrix is given by the solution to Fick's second law[29]

$$\phi(x) = \frac{1}{2}\left[\operatorname{erf}\left(\frac{h-x}{w}\right) + \operatorname{erf}\left(\frac{h+x}{w}\right)\right] \qquad (13)$$

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 $\varphi(x)$ from eq 13 with the instrumental resolution function, a Gaussian with a full width at half-maximum of 80 nm. The tracer diffusion coefficient is varied until a good fit of the convoluted function to the experimental profile is achieved. The solid line in Figure 1a represents the best fit to the data using $D^*_{PS} = 1.8 \times 10^{-14}$ cm²/s.

The tracer diffusion coefficient of the polydisperse d-PXE chains was found by two methods. First, the monodisperse solution, eq 13, was fit to the peak of the volume fraction profile. Mills et al.[30] found that the tracer diffusion coefficient determined in this way yields the $D^*$ corresponding to the weight-average molecular weight. In the second method, the monodisperse solution, eq 13, was modified by assuming that the polydispersity of the d-PXE chains obeyed a Flory–Schultz[31] distribution and that all chains diffused by reptation. This polydisperse theoretical profile was then fit to the entire concentration profile. As shown in Figure 1b, the best fits of the monodisperse (solid line) and polydisperse (dashed line) solutions to the data yield the same value of the tracer diffusion coefficient, i.e., $D^*_{PXE} = 4.2 \times 10^{-15}$ cm²/s.

## Results

The tracer diffusion coefficients $D^*$ of d-PS and d-PXE chains were measured in PS:PXE blends containing PS volume fractions $\phi$ = 1.0, 0.85, 0.55, 0.15, and 0.00. Because the glass transition temperature $T_g$ increased with decreasing $\phi$, $D^*$'s were measured at a temperature 66 °C above the $T_g$ of each blend. For the pure PXE matrices,

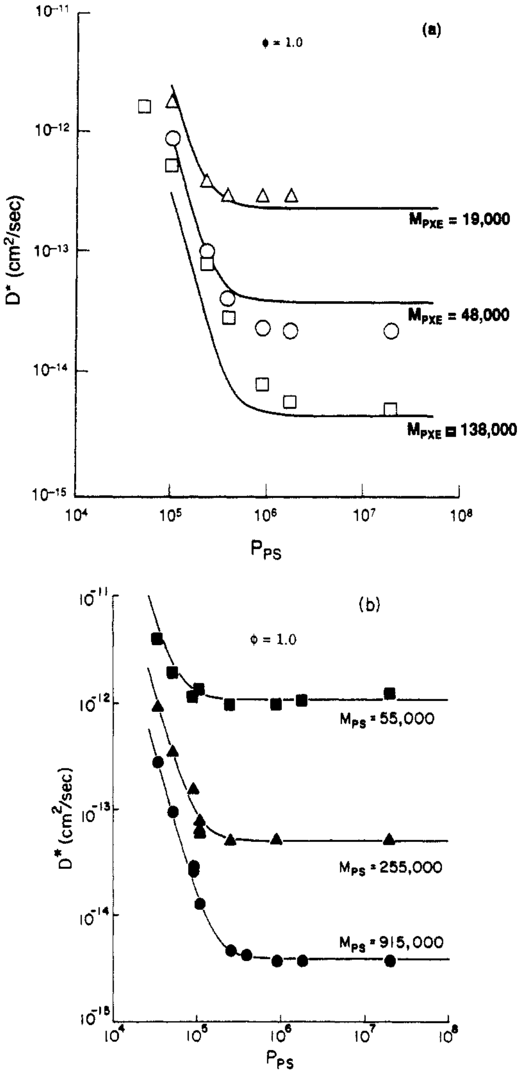

**Figure 2.** (a) Tracer diffusion coefficient $D^*_{PXE}$ of poly(xylenyl ether) versus the matrix molecular weight $P_{PS}$ of polystyrene at 171 °C. The weight-average molecular weights of the diffusing d-PXE chains are 19 000 (open triangles), 48 000 (open circles), and 138 000 (open squares). The solid lines show the $D^*_{PXE}$'s predicted by eq 14 where $D_{0,PXE} = 8.8 \times 10^{-5}$ cm²/s and $M_e$ = 18 000. For all three fits, $z = 6.6$. (b) Tracer diffusion coefficients $D^*_{PS}$ of polystyrene versus the matrix molecular weight $P_{PS}$ of polystyrene at 171 °C (from Green et al.[7]). The molecular weight of the diffusing d-PS chains are 55 000 (solid squares), 255 000 (solid triangles), and 915 000 (solid circles). The solid lines show the $D^*_{PS}$'s predicted by eqs 1, 4, and 11 where $D_{0,PS} = 3.3 \times 10^{-3}$ cm²/s and $M_e$ = 18 000. The value of $z$ is 3.5 for all molecular weights.

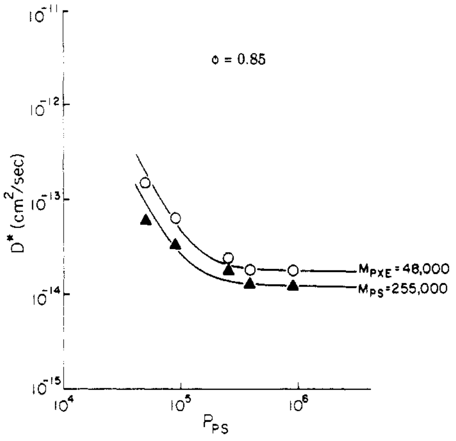

**Figure 3.** Tracer diffusion coefficients $D^*_{PS}$ and $D^*_{PXE}$ of 255 000 d-PS chains (solid triangles) and 48 000 d-PXE chains (open circles) versus matrix molecular weight $P_{PS}$ of PS chains in a blend which contains 0.85 volume fraction PS. The weight-average molecular weight $P_{PXE}$ of the matrix PXE chains is 35 000 and the temperature is 181 °C, 66 °C above $T_g$. The solid lines show the $D^*$'s predicted by eqs 4, 7, 13, and 21 where $D_{0,PS} = 8.5 \times 10^{-4}$ cm²/s, $D_{0,PXE} = 4.0 \times 10^{-5}$ cm²/s, and $M_e$ = 12 600. The values of $z$ are 10 and 3.5 for d-PS and d-PXE, respectively.

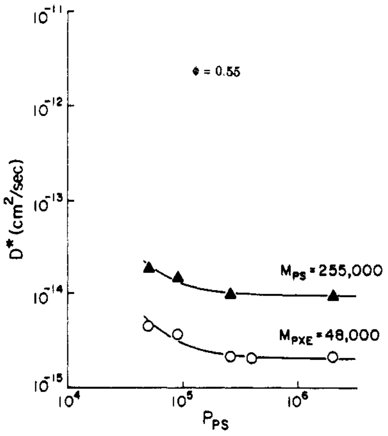

**Figure 4.** Tracer diffusion coefficients $D^*_{PS}$ and $D^*_{PXE}$ of 255 000 d-PS chains (solid triangles) and 48 000 d-PXE chains (open circles) versus matrix molecular weight $P_{PS}$ of PS chains in a blend which contains 0.55 volume fraction PS. The weight-average molecular weight $P_{PXE}$ of the matrix PXE chains is 35 000 and the diffusion temperature is 206 °C, 66 °C above $T_g$. The solid lines show the $D^*$'s predicted by eqs 4, 7, 13, and 21 where $D_{0,PS} = 6.5 \times 10^{-4}$ cm²/s, $D_{0,PXE} = 4.5 \times 10^{-6}$ cm²/s, and $M_e$ = 7200. The values of $z$ are 9 and 2.2 for d-PS and d-PXE, respectively.

$D^*$'s were calculated by scaling to $(T - T_g)$ = 66 °C using WLF scaling.[34]

Diffusion in a pure PS matrix ($\phi$ = 1.0) exhibited a strong dependence on the matrix molecular weight. As demonstrated in Figure 2a, the tracer diffusion coefficient $D^*_{PXE}$ of d-PXE chains increased rapidly as the matrix molecular weight $P_{PS}$ was decreased. At high $P_{PS}$, $D^*_{PXE}$ decreased as approximately $M_{PXE}^{-2}$ and was independent of $P_{PS}$, as predicted by reptation theory. As $P_{PS}$ decreased below a characteristic molecular weight $P^\dagger_{PS}$, $D^*_{PXE}$ increased rapidly, implying that constraint release contributed to the tracer diffusion coefficient. The characteristic molecular weights $P^\dagger_{PS}$ measured from Figure 2a were ~160 000, ~420 000, and ~790 000 for $M_{PXE}$ = 19 000, 48 000, and 138 000, respectively.

In contrast, Green et al.[7] found that the characteristic molecular weights for d-PS chains diffusing in a PS matrix were much less than the $P^\dagger_{PS}$'s of the d-PXE/PS system for similar molecular weights of d-PS and d-PXE. These results are shown in Figure 2b. For example, the characteristic molecular weight for d-PS chains of molecular weight 255 000 is about 100 000.

As $\phi$ was decreased from 1.0 to 0.15, the tracer diffusion coefficients became less dependent on the molecular weight $P_{PS}$ of the PS chains in the matrix. In the three matrices ($\phi$ = 0.85, 0.55, and 0.15) studied, $P_{PS}$ was varied while the weight-average molecular weight $P_{PXE}$ of the matrix PXE was held constant at 35 000. Furthermore, the diffusing species in all three blends had the same weight-average molecular weights, 255 000 for d-PS and 48 000 for d-PXE. As shown in Figure 3, the tracer diffusion coefficients, $D^*_{PS}$ and $D^*_{PXE}$, increased as $P_{PS}$ was decreased in a $\phi$ = 0.85 blend. However, this increase was much weaker than that observed for the diffusion of d-PS or d-PXE into matrix films of pure PS (see Figure 2). A transition was observed at $P^\dagger_{PS}$ ~ 320 000 for d-PS and ~240 000 for d-PXE. Figure 4 shows that the tracer diffusion coefficients, $D^*_{PS}$ and $D^*_{PXE}$, varied slowly as $P_{PS}$ was decreased in a $\phi$ = 0.55 matrix blend. In this blend the large volume

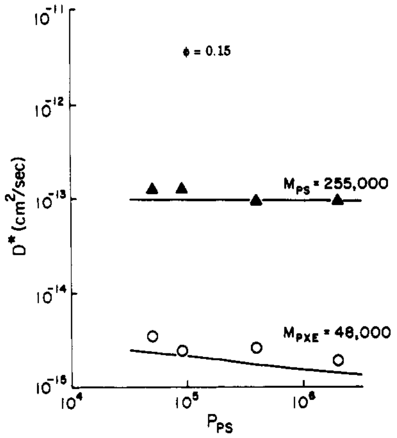

**Figure 5.** Tracer diffusion coefficients $D^*_{PS}$ and $D^*_{PXE}$ of 255 000 d-PS chains (solid triangles) and 48 000 d-PXE chains (open circles) versus matrix molecular weight $P_{PS}$ of PS chains in a blend which contains 0.15 volume fraction PS. The weight-average molecular weight $P_{PXE}$ of the matrix PXE chains is 35 000 and the temperature is 158 °C, 66 °C above $T_g$. The solid lines show the $D^*$'s predicted by eqs 4, 7, 13, and 21 where $D_{0,PS} = 6.4 \times 10^{-3}$ cm$^2$/s, $D_{0,PXE} = 2.3 \times 10^{-6}$ cm$^2$/s, and $M_e = 4100$. The value of $z$ is 3.5 for both d-PS and d-PXE.

fraction of long-lived PXE constraints effectively quenched most of the constraint release contribution to the $D^*$'s as demonstrated by the weak transition between constraint release and reptation at roughly $P^\dagger_{PS} \sim 250\,000$ for both d-PS and d-PXE.

As demonstrated in Figure 5, when the volume fraction of PS in the matrix was decreased to 0.15, both tracer diffusion coefficients, $D^*_{PS}$ and $D^*_{PXE}$, where found to be insensitive to changes in $P_{PS}$ as observed previously in the $\phi = 0.55$ matrix. The magnitude and slope of the $D^*_{PXE}$ data were quite similar in both blends, while only the magnitude of the $D^*_{PS}$ data increased upon decreasing $\phi$ to 0.15. The transition from constraint release to reptation was extremely diffuse in this system. The tracer diffusion coefficient of d-PXE was also measured in a matrix with weight-average molecular weights of 1 800 000 and 135 000 for PS and PXE, respectively. The $D^*_{PXE}$ measured was 1.8 times smaller than the $D^*_{PXE}$ measured in a matrix with weight-average molecular weights of 1 800 000 and 35 000 for PS and PXE, respectively, suggesting that diffusion of the PXE chains in the lower $P_{PXE}$ matrix contributed a small constraint release component to the $D^*_{PXE}$ data shown in Figure 5.

The diffusion of d-PS and d-PXE behaved quite differently when each was diffused in pure PXE matrices ($\phi = 0.0$) of weight-average molecular weight $P_{PXE}$. To partially compensate for the molecular weight dependence of the $T_g$ of PXE, the tracer diffusion coefficients were measured at $(T - T_g) = 66$ °C for each PXE matrix. As shown in Figure 6a the tracer diffusion coefficient $D^*_{PS}$ of the d-PS chains of molecular weight 255 000 was independent of $P_{PXE}$, suggesting that reptation dominates $D^*_{PS}$.

As shown in Figure 6b, in contrast to the diffusion of d-PS chains, the tracer diffusion coefficient $D^*_{PXE}$ of d-PXE chains increased quite strongly as $P_{PXE}$ decreased. At low $P_{PXE}$, the tracer diffusion coefficient scaled as approximately $P_{PXE}^{-3}$, a result consistent with the theory of constraint release. Here, $P^\dagger_{PS}$ increased from $\sim$63 000 for $M_{PXE}$ = 19 000 to $\sim$150 000 for $M_{PS}$ = 48 000. Thus even for $M_{PXE} \gg M_{e,PXE}$ the *self-diffusion* ($M_{PXE} = P_{PXE}$) of PXE chains was in a regime dominated by the *constraint release mechanism*. This result contrasts with the pure PS case, where reptation dominates self-diffusion (see Figure 2b).

## Discussion

The tracer diffusion coefficient for a d-PS test chain surrounded by other PS chains has been successfully described by combining the reptation mechanism, which depends on the mobility of the d-PS chain, and the constraint release mechanism, which depends on the mobility of the matrix chains. In the case of d-PS/PS, the same reptation constant $D_{0,PS}$ determines the reptation time $\tau_{R,PS}$ of the diffusing chain and the waiting time $\tau_{w,PS}$ of the tube. Rather than using fast-moving d-PS chains, consider diffusing slowly moving d-PXE chains into the PS matrix. Combining eqs 4 and 12, the tracer diffusion coefficient is

$$D^*_{PXE} = \frac{D_{0,PXE}}{M_{PXE}^2} + \alpha_{CR}\frac{K_{PXE}}{K_{PS}}\frac{D_{0,PS}M_e^2}{M_{PXE}P_{PS}^3} \qquad (14)$$

Thus for a slowly diffusing test chain of d-PXE surrounded by rapidly moving matrix chains ($D_{0,PS} > D_{0,PXE}$), $D_{CR,PXE}$ can be much greater than $D_{R,PXE}$ even when $M_{PXE} = P_{PS}$. This prediction will be supported by our experiments. The characteristic matrix molecular weight of the matrix PS chains at which $D_{CR,PXE} = D_{R,PXE}$ is given by

$$P^\dagger_{PS} = \left[\alpha_{CR}\frac{K_{PXE}}{K_{PS}}M_e^2M_{PXE}\right]^{1/3}\left[\frac{D_{0,PS}}{D_{0,PXE}}\right]^{1/3} \qquad (15)$$

The predicted values of $D^*$ based on eq 14 are shown as the solid lines in Figure 2a. The reptation constants are determined from the $D^*$'s measured into the highest $P_{PS}$ matrices and result in $D_{0,PS} = 3.3 \times 10^{-3}$ cm$^2$/s and $D_{0,PXE} = 8.8 \times 10^{-5}$ cm$^2$/s. The entanglement molecular weight is 18 000 and a value of $z = 6.6$ is chosen. Although our experimental values of $P^\dagger_{PS}$ increase with $M_{PXE}$, as predicted qualitatively by eq 15, only the $P^\dagger_{PS}$ values for $M_{PXE}$ = 19 000 and 48 000 are in quantitative agreement. Both the theoretical and experimental $D^*_{PXE}$'s scale as approximately $P_{PS}^{-3}$ at low $P_{PS}$, which suggests that constraint release dominates diffusion in this regime. As clearly demonstrated by the $M_{PXE}$ = 138 000 data, constraint release dominates $D^*_{PXE}$ over a very wide range of matrix molecular weights $P_{PS}$ (from $\sim M_{e,PS}$ to 1 000 000). Thus, the d-PXE/PS system is an excellent choice for future constraint release studies.

It is informative to compare these results with those for d-PS diffusing in PS at $(T - T_g) = 66$ °C.[7] Comparing the $D^*_{PS}$'s in Figure 2b with the $D^*_{PXE}$'s in Figure 2a of the same molecular weights, one observes that $P^\dagger_{PS}$ for the d-PXE chains is shifted to much higher values of $P_{PS}$. From eq 15, the characteristic molecular weight for d-PXE diffusing in PS can be expressed as $P^\dagger_{d\text{-}PXE/PS} = P^\dagger_{d\text{-}PS/PS}[D_{0,PS}/D_{0,PXE}]^{1/3}$, where $P^\dagger_{d\text{-}PS/PS}$ corresponds to the diffusion of d-PS in PS.[32] Inasmuch as $D_{0,PS}/D_{0,PXE}$ = 38 at 171 °C, the observation that $P^\dagger_{d\text{-}PXE/PS}$ is greater than $P^\dagger_{d\text{-}PS/PS}$ is in qualitative agreement with the previous expression. As predicted by eq 14, the reptation diffusion coefficient should dominate the self-diffusion of PS ($M_{PS} = P_{PS}$) for $M_{PS} \gg M_{e,PS}$. This prediction is confirmed by the PS tracer diffusion coefficients shown in Figure 2b. It is interesting to note that the tracer diffusion coefficients $D^*_{PXE}$ for d-PXE diffusing in PS are dominated by constraint release when the molecular weights of the d-PXE and PS chains are equal, $M_{PXE} = P_{PS}$. As noted previously, it is the large value of $D_{0,PS}/D_{0,PXE}$ which is responsible for the dominance of the constraint release term.

In the examples cited above, the deuterated chain is diffusing in a monodisperse matrix of PS. However, if the matrix consists of monodisperse PS and polydisperse PXE

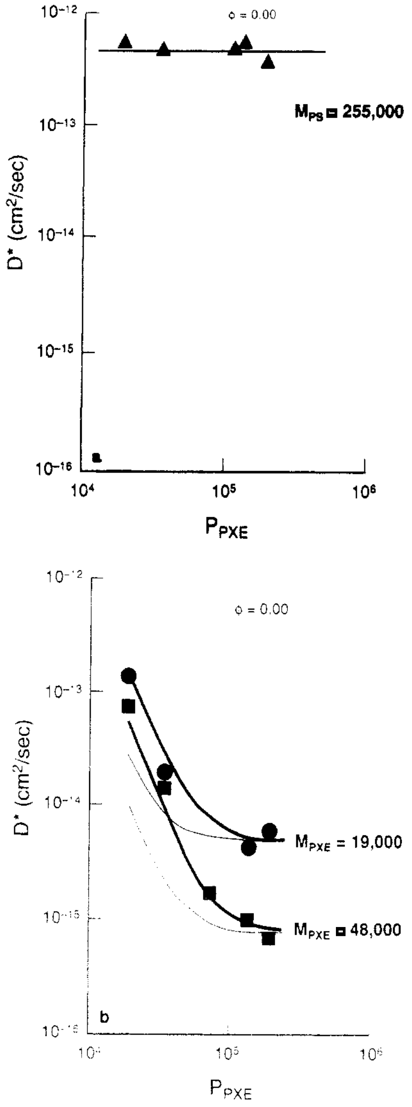

**Figure 6.** (a) Tracer diffusion coefficient $D^*_{PS}$ of polystyrene versus the matrix molecular weight $P_{PXE}$ of poly(xylenyl ether) at $(T - T_g) = 66$ °C. The weight-average molecular weight of the diffusing d-PS is 255 000 (solid triangles). The solid line shows the $D^*_{PS}$'s predicted by eqs 4, 7, 13, and 21 where $D_{0,PS} = 2.9 \times 10^{-2}$ cm²/s and $M_e = 3400$. The value of $z$ is 3.5 (b) Tracer diffusion coefficient $D^*_{PXE}$ of poly(xylenyl ether) versus the matrix molecular weight $P_{PXE}$ of PXE at $(T - T_g) = 66$ °C. The weight-average molecular weights of the diffusing d-PXE chains are 19 000 (solid circles) and 48 000 (solid squares). The thick lines show the calculated $D^*_{PXE}$'s including matrix polydispersity where $D_{0,PXE} = 1.8 \times 10^{-6}$ cm²/s, $M_e = 3400$, and $z \sim 11$. The thin lines are the monodisperse predictions based on eq 11 where $z \sim 11$.

chains, the waiting time must be expressed in a more general form:

$$\tau_w = \int_0^\infty dt\, [\phi e^{-t/\tau_{R,PS}} + (1-\phi)\sum_i w_i e^{-t/(\tau_{R,PXE})_i}]^z \qquad (16)$$

where $\phi$ is the volume fraction of PS chains in the matrix. The reptation times in eq 16 are found by measuring $D_R$, substituting $D_R$ in eq 1 to find $D_0$, and then substituting $D_0$ into eq 6 to find $\tau_R$. To ensure that $D^* = D_R$, $D^*$ is measured in a regime where $D^*$ is independent of $P_{PS}$ and $P_{PXE}$. In the PS/PVME study, the reptation constant of PVME was unknown and therefore taken as a fitting parameter. A universal value of $z \sim 3.5$ for polystyrene[7] and polybutadiene[23] has been proposed and seems reasonable on physical grounds. However, because a universal value of $z$ is unable to predict our experimental data, we will use $z$ as a simple fitting parameter.

Based on eqs 4, 9, and 16 the theoretical predictions for $D^*_{PXE}$ and $D^*_{PS}$ in a $\phi = 0.85$ matrix blend are shown as the solid lines in Figure 3. Values of $z = 3.5$ and 10 are used for the d-PXE and d-PS predictions, respectively. The large number of suitably situated constraints surrounding the d-PS chains effectively enhances the contribution of $D^*_{CR}$ to $D^*_{PS}$. At low $P_{PS}$, the $D^*$'s increase much more slowly than the $P_{PS}^{-3}$ dependence which was observed in pure PS matrices (see Figure 2). Considering that the virtual tube now consists of only 0.85 volume fraction of PS chains interspersed with slower moving PXE ones, $D_{CR}$ should depend more weakly on $P_{PS}$ than in the pure PS matrix and therefore one expects a decrease in the slope at low $P_{PS}$. Because $D_{R,PS}$ and $D_{R,PXE}$ are almost equal (see Figure 2), the $P^\dagger_{PS}$'s of both the d-PS and d-PXE chains, respectively, are expected, and observed, to be roughly the same. Comparison of Figures 2a and 3 shows that $P^\dagger_{PS}$ for the 48 000 molecular weight d-PXE shifts from ~420 000 to ~240 000 as $\phi$ decreases from 1.0 to 0.85. Because the ratio $D_{0,PS}/D_{0,PXE}$ also decreases from 38 to 21, the diffusing d-PXE chains become more mobile relative to the matrix PS chains, and therefore the matrix constraints appear fixed for a longer time in the $\phi = 0.85$ blend.[34]

The theoretical predictions for $D^*_{PXE}$ and $D^*_{PS}$ in a 0.55 volume fraction PS matrix are shown as the solid lines in Figure 4. Values of $z = 2.2$ and 9.0 are used for the d-PXE and d-PS predictions, respectively. The small value of $z$ for d-PXE acts to decrease the constraint release contribution to $D^*_{PXE}$, while the large value of $z$ for d-PS enhances the constraint release contribution. Since the theoretical and experimental values of $D^*$ both increase only slightly with decreasing $P_{PS}$, constraint release is much weaker in this matrix than in the previous matrix of $\phi = 0.85$ (see Figure 3). The knee of the log $D^*$ vs log $P_{PS}$ plot has shifted to much lower matrix molecular weights $P^\dagger_{PS}$ when compared with the pure PS matrix (see Figures 2). This shift in $P^\dagger_{PS}$ can be attributed to the decrease in $M_e$ and a simultaneous increase in the volume fraction of the slowly diffusing PXE species.

Similarly, the theoretical predictions for $D^*_{PXE}$ and $D^*_{PS}$ in a 0.15 volume fraction PS matrix are shown as the solid lines in Figure 5. Values of $z = 3.5$ are used for both the d-PXE and d-PS predictions; however, the predicted $D^*$'s in this blend are relatively insensitive to the value of $z$ chosen. The reptation constant $D_{0,PXE}$ was calculated from the $D^*_{PXE}$ measured in a matrix blend with weight-average molecular weights of 1 800 000 and 135 000 for PS and PXE, respectively. The higher molecular weight PXE was necessary to completely quench any constraint release contribution to $D^*$. Similar to the $\phi = 0.55$ matrix, the weak increase of $D^*_{PS}$ and $D^*_{PXE}$ with decreasing $\phi$ prevents any comparison between the experimental and theoretical slopes from being made. Qualitatively, a gradual increase in $D^*_{PXE}$ is observed both experimentally and theoretically. However, no such increase in $D^*$ is predicted for the d-PS chains because of the vast difference in mobilities between the rapidly diffusing d-PS and the slowly diffusing PXE chains.

The waiting time of a pure polydisperse PXE matrix, $\phi = 0$, can be calculated from eq 16. Using eqs 4, 9, and 16, the theoretical $D^*_{PS}$ in a pure PXE matrix is calculated and shown as the solid line in Figure 6a. The value of $z$ is 3.5; as in the $\phi = 0.15$ matrix, $D^*$ is not sensitive to changes in $z$. Because the d-PS chains are far more mobile than the matrix PXE chains ($D_{0,PS} \gg D_{0,PXE}$), constraint release is neither predicted nor observed.

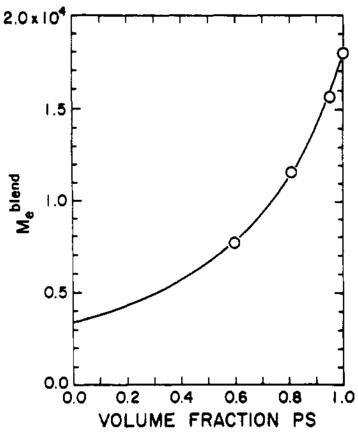

**Figure 7.** Entanglement molecular weight $M_e$ of a polystyrene: poly(xylenyl ether) blend versus the volume fraction $\phi$ of PS. The solid line represents the $M_e$ predicted by eq A8 with $M_{e,\mathrm{PXE}}$ adjusted to produce the best fit to the experimental data. Values of $M_{e,\mathrm{PS}}$ = 18 000 and $M_{e,\mathrm{PXE}}$ = 3400 were used.

The theoretical predictions for $D^*_{\mathrm{PXE}}$ in a pure PXE matrix are represented by the various lines in Figure 6b. Using a Flory–Schultz distribution for $w_i$ in eq 16 and $z \sim 11$ to calculate $D^*_{\mathrm{CR}}$, the theoretical prediction (thick solid line) is in good agreement with the experimental data. To demonstrate the effect of polydispersity on $D^*_{\mathrm{CR}}$, $D_{\mathrm{CR,PXE}}$ was determined by using the weight-average molecular weight of the matrix in eq 11, $P_{\mathrm{PXE}} = P_{\mathrm{w,PXE}}$. Using $z = 11$, this approach leads to the $D^*_{\mathrm{PXE}}$'s given by the solid lines. Upon comparison of the polydisperse and monodisperse calculations, the constraint release contribution to $D^*$ is clearly increased when one includes polydispersity effects, a trend in agreement with our experimental results. By increasing the value of $z$ (or $\alpha_{\mathrm{CR}}$) in eq 11 until the monodisperse theory and $D^*_{\mathrm{PXE}}$ data coincide, an unphysically large number of suitability situated constraints, 18, is required. As mentioned previously, the reptation and constraint release theories predict that reptation should dominate self-diffusion for $M \gg M_e$. Thus a large $z$ forces the self-diffusion coefficient predicted by these theories into the constraint release regime. Smith and co-workers[1] observed a similar constraint release contribution in the poly(propylene oxide) (PPO) system.

The simple constraint release picture is incapable of describing the complexities of matrix-dependent diffusion in polymer blends. The experimental tracer diffusion coefficients can only be predicted if one assumes an unphysically large number of suitably situated constraints. Constraint release also fails to predict the rheological behavior of monodisperse binary mixtures.[39] However, recent molecular theories[40,41] accurately predict the linear viscoelastic properties of commercial and model polydisperse entangled polymer melts.[42] Moreover, the double-reptation model of des Cloizeaux provides an improved expression for the relaxation function $F(t)$, which leads to the elusive 3.4 scaling of viscosity. In the double-reptation framework, our PS:PXE system of chemically dissimilar chains contains three types of pairwise entanglements which define the fraction of original entanglements left at time $t$. The PS:PS and PXE:PXE entanglements are simply described by the monodisperse and polydisperse relaxation function, respectively. The PS:PXE entanglements, to a first approximation, can be treated by replacing a sluggish PXE chain with an "equivalent" PS chain (i.e., one with the same reptation time). To test these ideas, tracer diffusion measurements in a mixture of two chain lengths, both above $M_e$, are in progress.

## Conclusions

1. The reptation constants for PS are much greater than those of PXE for all blend compositions.
2. As the volume fraction of the PS component in the matrix blend decreases from $\phi$ = 1.0 to $\phi$ = 0.15, the constraint release mechanism becomes weaker for both d-PS and d-PXE diffusion.
3. Self-diffusion ($M_{\mathrm{PXE}} = P_{\mathrm{PXE}}$) of polydisperse PXE chains, however, is dominated by the constraint release mechanism.
4. The Graessley model of constraint release provides a good fit to the experimental data but requires a $z$, the number of suitably situated constraints, which varies from one blend to another.

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## Appendix: Entanglement Molecular Weight of a Polymer Blend

Graessley and Edwards[33] have proposed a universal law relating the plateau modulus $G^\circ_{\mathrm{N}}$ to measurable properties: the number of chains per unit volume $\nu$, the chain length $L^\dagger$, and the Kuhn step length $\Lambda$. Assuming that only large-scale changes in chain conformation contribute to $G^\circ_{\mathrm{N}}$, the plateau modulus can be expressed as

$$G^\circ_{\mathrm{N}} = K_1(\nu L^\dagger)^2 \Lambda k_{\mathrm{B}} T \tag{A1}$$

where $\nu L^\dagger$ is the total length of polymer per unit volume, $k_{\mathrm{B}}$ is the Boltzmann constant, $T$ is the absolute temperature and $K_1$ is an (almost) universal dimensionless constant which is approximately equal to 0.01. The plateau moduli of the two pure components, polymers A and B, are

$$G^\circ_{\mathrm{N,A}} = K_1(\nu L^\dagger)_{\mathrm{A}}{}^2 \Lambda_{\mathrm{A}} k_{\mathrm{B}} T \tag{A2}$$

and

$$G^\circ_{\mathrm{N,B}} = K_1(\nu L^\dagger)_{\mathrm{B}}{}^2 \Lambda_{\mathrm{B}} k_{\mathrm{B}} T \tag{A3}$$

For a blend consisting of a volume fraction $\phi$ of component A, the total length of polymer per unit volume is

$$(\nu L^\dagger)_{\mathrm{blend}} = \phi(\nu L^\dagger)_{\mathrm{A}} + (1-\phi)(\nu L^\dagger)_{\mathrm{B}} \tag{A4}$$

From eqs A1–A4, the plateau modulus of a blend is given as

$$G^\circ_{\mathrm{N}} = \Lambda_{\mathrm{blend}}[\phi(G^\circ_{\mathrm{N,A}}/\Lambda_{\mathrm{A}})^{1/2} + (1-\phi)(G^\circ_{\mathrm{N,B}}/\Lambda_{\mathrm{B}})^{1/2}]^2 \tag{A5}$$

In general, the Kuhn step lengths of the A and B polymers are different. However, for PS and PXE, we have $\Lambda_{\mathrm{PS}} \approx$ 1.58 nm and $\Lambda_{\mathrm{PXE}} \approx$ 1.54 nm, and therefore the Kuhn step length of the blend and the pure components can be considered to be equal. So eq A5 reduces to

$$G^\circ_N = [\phi(G^\circ_{N,A})^{1/2} + (1-\phi)(G^\circ_{N,B})^{1/2}]^2 \qquad (A6)$$

An identical form for $G^\circ_N$ was derived from a different model by Tsenoglou.[25] The entanglement molecular weight $M_e$ is related to the plateau modulus $G^\circ_N$ by the expression

$$M_e = (\rho T N_A k_B)/G^\circ_N \qquad (A7)$$

where $\rho$ is the polymer density and $N_A$ is Avogadro's number. Substituting this expression for the plateau modulus of the pure components into eq A6 yields an equation for the entanglement molecular weight of the blend

$$M_e^{-1} = [\phi(M_{e,A})^{-1/2} + (1-\phi)(M_{e,B})^{-1/2}]^2 \qquad (A8)$$

As shown in Figure 7, the entanglement molecular weights from the experiments of Prest and Porter[13] are plotted as a function of the volume fraction of PS in the PS:PXE blend. The solid line is the fit of eq A8 to the data where $M_{e,PXE} = 3400$ and $M_{e,PS} = 18\,000$. The agreement to these data is quite good as also pointed out by Tsenoglou. We therefore use eq A8 with these values of the $M_e$'s of the pure component to obtain $M_e$ for the PS:PXE blends of arbitrary composition.

## List of Symbols

| | |
|---|---|
| $\tau_{tube}$ | tube relaxation time |
| $\tau_{R,A}$ | reptation time of an A chain |
| $\tau_w$ | mean waiting time |
| $M_{w,A} = M_A$ | weight-average molecular weight of the diffusing A chains |
| $M_e$ | entanglement molecular weight of the matrix |
| $\langle R_A^2 \rangle$ | mean square end-to-end distance of an A chain |
| $K_A$ | constant for A species, i.e., $\langle R_A^2 \rangle = K_A M_A$ |
| $D_{R0,A}$ | Rouse diffusion coefficient of A chains |
| $\zeta_{0,A}$ | monomeric friction coefficient of A chains |
| $D_{0,A}$ | reptation constant of A chains |
| $D_{R,A}$ | reptation diffusion coefficient of A chains |
| $F_A(t)$ | fraction of original tube not yet disengaged by a reptating A chain after time $t$ |
| $D_{CR,A}$ | constraint release diffusion coefficient of A chains |
| $P_{w,A} = P_A$ | weight-average molecular weight of A chains in the matrix |
| $P^\dagger$ | weight-average molecular weight of matrix chains at which $D_R = D_{CR}$ |
| $z$ | number of suitably situated constraints in Graessley model of constraint release |
| $\alpha_{CR}$ | constraint release constant |
| $D^*_A$ | tracer diffusion coefficient of A chains |
| $w_i$ | weight fraction of chains with molecular weight $M_i$ |
| $h$ | tracer film thickness |
| $w$ | characteristic diffusion distance, $2(D^*t)^{1/2}$ |
| $T_g$ | glass transition temperature |
| $\phi$ | volume fraction of A chains in matrix blend |
| $1-\phi$ | volume fraction of B chains in matrix blend |
| $\varphi$ | volume fraction of diffusing d-A chains |
| $T$ | absolute temperature, K |
| $k_B$ | Boltzmann constant |
| $G^\circ_N$ | plateau modulus |
| $K_1$ | dimensionless constant, $\approx 0.01$ |
| $\nu$ | number of chains per unit volume |
| $L^\dagger$ | chain length |
| $\Lambda$ | Kuhn step length |

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**Registry No.** PS (homopolymer), 9003-53-6; PXE (homopolymer), 39342-71-7.