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Tube Renewal Effects in Binary Polymer Mixtures

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ABSTRACT: The effects of tube renewal on the diffusion of deuterated polystyrene (d-PS) into binary mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME) were examined by using elastic recoil detection (ERD). The molecular weight and volume fraction, φ, of PVME were kept constant in each mixture while the molecular weight of PS was allowed to vary. The contribution of tube renewal to the diffusivity of the d-PS chains was smaller in these mixtures than observed for the diffusion of d-PS into PS hosts. A model based on the work of Klein and Graessley was developed to describe these observations. The relaxation times of the PVME chains in the mixtures were extracted from the data. This information, together with the relaxation times of the d-PS chains, was used to calculate the temperature dependence of the viscosity. The calculated values are in surprisingly good agreement with independent viscosity measurements.

Introduction

It is well documented that the diffusion of a single polymer chain of molecular weight M into a highly entangled melt is adequately described by[1-9]

$$D_R = D_0/M^2 \tag{1}$$

where[9]

$$D_0 = \frac{4}{15}\frac{M_0 M_e k_B T}{\zeta}$$

In this equation, M_e is the molecular weight between entanglements, ζ is the monomeric friction coefficient, k_B is the Boltzmann constant, T is the temperature, M_0 is the molecular weight of a monomer. Graessley[10] has shown that this equation can be rewritten in a form that allows one to compute D_R from knowledge of viscoelastic parameters

$$D_0 = \frac{G_N{}^\circ}{135} M_e{}^2 C \frac{M_c}{\eta_0(M_c)} \tag{2}$$

Here $C = \langle R^2\rangle/M$ is a constant and $\langle R^2\rangle$ is the radius of gyration of a chain of molecular weight M. $G_N{}^\circ$ is the plateau modulus of the polymer, M_c is the critical molecular weight, and $\eta_0(M_c)$ is the zero shear rate viscosity of the polymer when the molecular weight is $M = M_c$. Surprisingly, estimates of D_R that are made with eq 3 are in very good agreement with the measured values for many polymers.

Implicit in the derivation of eq 1 is that the motion of the diffusant occurs in a relatively immobile environment. If the topology of the "tube" into which the chain diffuses is altered on time scales comparable to τ, the relaxation time that characterizes the motion of the diffusant in the "tube", then eq 1 no longer provides an adequate description of the diffusion process. If reptation and tube renewal are independent, then the effects of tube renewal on the motion of the diffusant may be described by adding a second term to D_R (cf. eq 1).[11-15] This term has been proposed by Graessley to be[12]

$$D_G(M,P) = \alpha(z) D_0 \frac{M_e{}^2}{MP^3} \tag{3}$$

where z is a parameter that describes the "number of suitably situated constraints" per M_e. We have shown that a value of $\alpha(z) = 10.9$ ($z = 3.5$) yields an excellent description of the diffusion of deuterated polystyrene (d-PS) chains of molecular weight M into monodisperse PS hosts of molecular weight P.[17,18] Klein has suggested that the constraint release contribution is[11]

$$D_K(M,P) \sim \frac{M_e{}^{1/2}}{MP^{5/2}} \tag{4}$$

The differences in the power law dependences of P and M_e in eqs 3 and 4 arise from the fact that some of the constraints on the diffusant are interdependent.[11] A chain in the host environment can provide more than one constraint on the diffusant. The removal of such a chain will facilitate a larger center of mass motion of the diffusant than one that provides only one constraint. This reduces the effective relaxation time of the "tube" by a factor of $(M_e/P)^{1/2}$. Both predictions were compared with the diffusivity of d-PS chains into PS hosts and were found to give equally good descriptions of the data.[17,18] This arises primarily because the molecular weight regime over which the constraint release contribution becomes significant is relatively narrow.

In an earlier publication[19] we examined the diffusion of d-PS chains in PS/PVME blends. D was observed to vary as M^{-2}. The magnitude of the proportionality factor, $D_0 = D_0(\varphi)$, varied appreciably with φ, the volume fraction of PVME in the blend. A comparison of $D_0(\varphi)$ at a constant temperature above the glass transition temperature, T_g, of each blend ($T = T_g + 100$ °C) revealed that $D_0(\varphi{=}0.5)$ was approximately 2 orders of magnitude lower than $D_0(0)$ (diffusion into pure PS) and somewhat larger than $D_0(\varphi{=}0.8)$. Measurements of the diffusion of d-PS into pure PVME were not performed. The viscosity was also determined for pure PS, for pure PVME, and for a mixture containing 40% ($\varphi = 0.4$) PVME. At temperatures where $T = T_g + 100$ °C, the viscosity of the blend was over 2 orders of magnitude higher than that of PS and a factor of 3 larger than that of PVME. Under conditions of $T = T_g + 100$ °C, the friction factors of the d-PS chains in the blend were determined from the data using eq 1. The value of ζ at $\varphi \sim 0.5$ was over 2 orders of magnitude higher than it was near $\varphi = 0$. It was not possible to determine the friction factors or the relaxation times of the PVME chains in the blends since PVME could not be obtained in deuterated form.

In this paper we examine the diffusion of d-PS chains of molecular weight M into miscible binary systems of PS and PVME. The molecular weight of the PVME component was kept fixed and that of the PS component was allowed to vary. The relaxation times of the PVME chains in the blend were determined from these data using a model that describes tube renewal in blends. This information was used to calculate the viscosity of the PS/

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PVME blend systems. The calculations compared favorably with the measured values.

Experimental Section

The polystyrenes used in this study ranged in molecular weight from 50 to 900 kg/mol and were purchased from Pressure Chemical Co. A series of deuterated polystyrenes of molecular weights 530, 200, and 100 kg/mol were also used. These were purchased from Polymer Laboratories. The poly(vinyl methyl ether) used in this study was of molecular weight 145 kg/mol. The molecular weight distributions of both the undeuterated and deuterated polystyrenes were $M_w/M_n < 1.05$. The molecular weight distribution of the PVME was $M_w/M_n < 1.3$.

Bilayered samples were used in this study. Thin (~15 nm) layers of d-PS were placed in contact with thick films of blends of PS and PVME. The procedure used to prepare these samples was described in ref 19. The samples were annealed under high-vacuum conditions at various temperatures. Elastic recoil detection was then used to determine the volume fraction versus depth profile of the d-PS chains in the mixtures. The details of the measurements may be found in refs 20–22. The diffusion coefficients were extracted from the profile by fitting them with the appropriate solution to the diffusion equation.[20-22]

Results and Discussion

The data in Figure 1a represent the diffusivity of d-PS chains of molecular weight M (M = 100 (circles) and 200 kg/mol (squares)) into blends where the volume fraction of PVME was $\varphi = 0.1$. The molecular weight of the PVME in each blend was kept constant, $P_{\rm PVME}$ = 145 kg/mol, and that of the polystyrene, P, allowed to vary. The solid line represents the diffusivity of d-PS chains into PS hosts of molecular weight P. The dependence of D on P, for P less than approximately 10^5 g/mol, is due to constraint release effects.

Figure 1b shows the diffusivity of d-PS chains of M = 200 kg/mol (circles) and M = 520 kg/mol (squares) into PS/PVME blends containing 40% (φ = 0.4) PVME. Figure 1c shows similar plots for the same d-PS chains that diffused into blends containing 80% PVME. The solid line in each case represents the diffusivity of d-PS chains into pure PS hosts of molecular weight P. They were computed with the following equation:

$$\frac{D}{D_{\rm R}} = 1 + 10.9\frac{MM_{\rm e}^2}{P^3} \qquad (5)$$

This equation, derived by Graessley,[12] was shown to completely describe the diffusion of d-PS chains into PS hosts of molecular weight P.[17,18]

It is clear from the data in each figure that the contribution of constraint release to the diffusivity is reduced by the presence of the PVME chains. A composite plot of $D/D_{\rm R}$, the extent of reduction of the constraint release contribution, as a function of φ is shown in Figure 2. $D_{\rm R}$ is the diffusion coefficient of the d-PS chains in the plateau (reptation) regime of the plot, and D is the diffusion coefficient of the M-chain into the blend where the molecular weight of PS was P = 50 kg/mol. The triangles depict the decrease of the diffusion coefficient of the M = 520 kg/mol chain with φ, the squares represent that of the M = 200 kg/mol chains, and the circles that of the 100 kg/mol molecular weight chains.

Below, the effects of tube renewal on the motion of a single chain in a binary mixture is described. In general, the diffusion of a chain in an entangled melt may be described by[11-16]

$$D = D_{\rm R} + D_{\rm tube} \qquad (6)$$

where $D_{\rm tube}$ is the contribution due to constraint release or, equivalently, tube renewal. The derivation of the functional dependence of $D_{\rm tube}$ depends on knowledge of $\tau_{\rm tube}$, the longest relaxation time of the tube[11]

$$\tau_{\rm tube} = (M/M_{\rm e})^2 \tau_{\rm r}(P) \qquad (7)$$

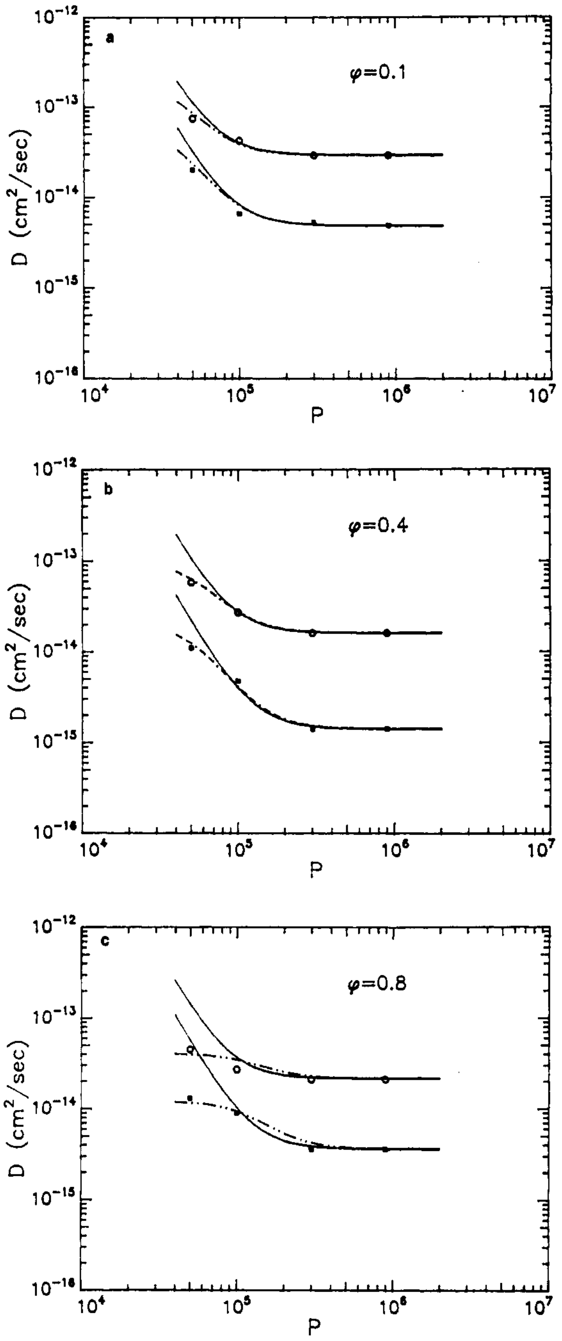

Figure 1. (a) Diffusion of d-PS chains of molecular weight M = 100 (circles) and 200 kg/mol (squares) into binary mixtures of PS and PVME containing 10 wt % PVME. The molecular weight of PS in the blend is P and that of the PVME is 145 kg/mol. The samples were allowed to diffuse at a temperature of 136 °C. The broken lines were computed with eq 5, and eq 16 was used to compute the solid lines. (b) Diffusion of d-PS of M = 200 (circles) and 520 kg/mol (squares) into blends containing 40% PVME. The solid and broken lines were computed with eqs 5 and 16, respectively. The diffusion process occurred at T = 128 °C. (c) Diffusion of d-PS of M = 200 (circles) and 520 kg/mol (squares) into blends containing 80% PVME. The solid and broken lines were computed with eqs 5 and 16, respectively. The diffusion process occurred at T = 80 °C.

Here, the "tube" is treated as a Rouse tube of $M/M_{\rm e}$ submolecules, and $\tau_{\rm r}$ is taken to be the relaxation time of a single host chain of molecular weight P. On the basis of Doi and Edwards[9]

$$\tau_{\rm r} = \frac{C}{3\pi^2}\frac{P^3}{D_0} \qquad (8)$$

Using the fact that

$$D_{\rm tube} \sim \langle R^2 \rangle / \tau_{\rm tube} \qquad (9)$$

together with eqs 6–9, we obtain an equation identical

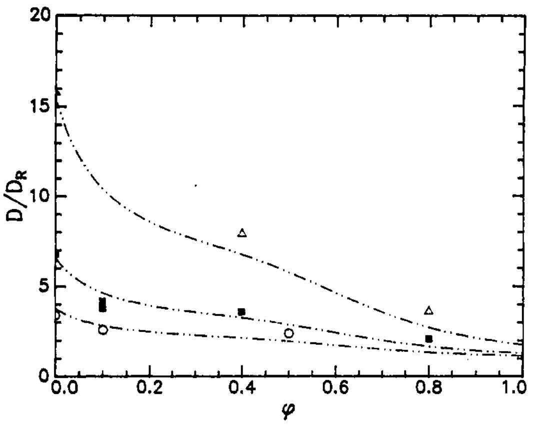

Figure 2. Extent to which the effects of constraint release in the blends is reduced as the weight fraction, φ, of PVME in the host is increased. The lines are not fits to the data. They were computed with eq 16. The triangles represent the diffusion of the M = 520 kg/mol chains into the hosts, the squares represent that of the M = 200 kg/mol chains, and the circles represent that of the M = 100 kg/mol chains.

with eq 5. This was shown by Klein earlier.[11] We can use a similar procedure to derive equations that describe the diffusion of a chain in a binary mixture.

To obtain an expression equivalent to eq 5 for the diffusion of a single chain of molecular weight M into a binary mixture of two monodisperse polymers, we first need to determine an effective tube relaxation time, $\tau_{\text{tube}}^{\text{eff}}(\varphi)$. We begin by relying on the concept that τ_r, the relaxation time of a chain diffusing by reptation alone in a monodisperse melt, can be defined in terms of the viscosity of the melt[9]

$$\eta_0 = \frac{\pi^2}{12} G_N^{\circ} \tau_r \qquad (10)$$

Note that this equation arises from

$$\eta_0 = \int_0^{\infty} G(t)\,dt \qquad (11)$$

Here, $G(t)$ is the stress relaxation modulus of the melt and is described by $G(t) = G_N^{\circ}F(t)$. $F(t)$ is the average fraction of the "tube" that the diffusing chain had not abandoned after time t. It has the following form:[9]

$$F(t) = \frac{8}{\pi^2}\sum_{p=0}^{\infty}\frac{1}{(2p+1)^2}\exp[-(2p+1)^2 t/\tau_r] \qquad (12)$$

In the case of a binary mixture of polymers, an effective relaxation time, analogous to τ_r, may be obtained. For chains diffusing by reptation in a binary mixture, the stress relaxation for the mixture may be written by using the additivity rule[9,23] (i.e., the motion of one chain is independent of the other)

$$G_{\text{blend}}(t) = G_N^{\circ}(\text{blend})[\varphi F_{\text{PVME}}(t) + (1-\varphi)F_{\text{PS}}(t)] \qquad (13)$$

Using eq 11 and comparing the result with eq 10, one obtains the result that the effective relaxation time for a "tube" segment is given by

$$\tau_r^{\text{eff}} = \varphi\tau_{\text{PVME}}(\varphi) + (1-\varphi)\tau_{\text{PS}}(\varphi) \qquad (14)$$

Note that $\tau_{\text{PS}}(\varphi)$ and $\tau_{\text{PVME}}(\varphi)$ are the relaxation times of the PS and PVME chains, respectively, in the blend, not of the pure components. The effective entanglement molecular weight of the blend, M_e^{eff}, is defined in terms of the plateau modulus of the blend[24,25]

$$G_N^{\circ}(\text{blend}) = [\varphi G_N^{\circ}(\text{PVME})^{1/2} + (1-\varphi)G_N^{\circ}(\text{PS})^{1/2}]^2 \qquad (15)$$

using the usual relation $M_e^{\text{eff}} = \rho RT/G_N^{\circ}(\text{blend})$.[26] Here, ρ is the density and R is the universal gas constant.

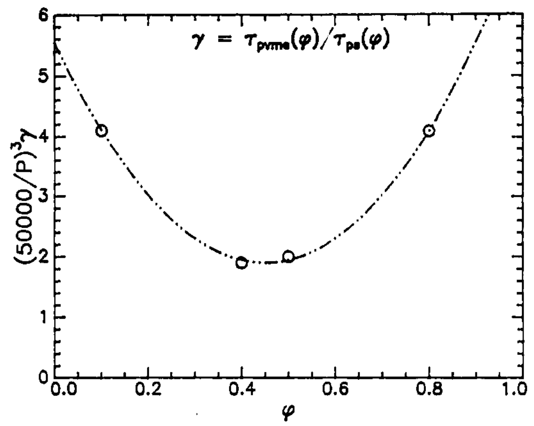

Figure 3. Dependence of $\gamma = \tau_{\text{PVME}}(\varphi)/\tau_{\text{PS}}(\varphi)$ on φ.

We are now able to derive an expression analogous to eq 5 for a single chain diffusing into a binary mixture. Equation 7 allows us to determine $\tau_{\text{tube}}^{\text{eff}}(\varphi)$ for the blend in terms of τ_r^{eff} and the M_e^{eff} of the blend. Equation 9 enables the determination of an effective "tube" diffusion coefficient for the blend, $D_{\text{tube}}^{\text{eff}}$. Using this information and the fact that the diffusion coefficient of a single chain into a binary mixture is $D = D_R(\varphi) + D_{\text{tube}}^{\text{eff}}(\varphi)$ (cf. eq 6), we obtain the following relation for D:

$$\frac{D}{D_R(\varphi)} = 1 + \frac{kMM_e^2(\text{PS})}{[\beta\varphi + (1-\varphi)]^4[\gamma\varphi + (1-\varphi)]P^3} \qquad (16)$$

In eq 16, β is the square root of the ratio of the entanglement molecular weight of PS to that of PVME ($\beta = M_e^{1/2}(\text{PS})/M_e^{1/2}(\text{PVME})$) and γ is the ratio of the relaxation time of the PVME chains to that of the PS chains in the blend ($\gamma = \tau_{\text{PVME}}(\varphi)/\tau_{\text{PS}}(\varphi)$). $D_R(\varphi)$ is the value of the diffusion coefficient in the plateau regions in Figures 1. Equation 16 looks similar to eq 5. Note that if the constant k is taken to be 10.9, eq 16 becomes eq 5 when $\varphi = 0$.

The broken lines drawn in Figure 1a–c were computed with eq 16. β was determined by noting that the M_e of PS is 18 kg/mol and that of PVME is 12 kg/mol. One fitting parameter, $\gamma = \tau_{\text{PVME}}(\varphi)/\tau_{\text{PS}}(\varphi)$, was varied to fit the data. The values of γ that were used for the fits are shown in Figure 3. γ exhibits a minimum in the middle of the concentration regime and necessarily has a P^{-3} dependence. Empirically, it may be described by

$$\gamma = \tau_{\text{PVME}}(\varphi)/\tau_{\text{PS}}(\varphi) = [19(\varphi - 0.45)^2 + 1.9](5 \times 10^4/P)^3 \qquad (17)$$

It is not clear why γ should have this form! The fact that it appears to be "well behaved" is interesting. Note that eq 17 is only valid in the regime $0.1 \le \varphi \le 0.8$. The lines drawn through the data in Figure 2 were computed with eq 16 and the values of γ extracted from fitting the data in Figure 1.

The above procedure, though it describes the data quite well, is a mean field approach and for this reason has limitations. In particular, we have defined an effective entanglement molecular weight for the blend as well as effective relaxation times for the "tube" in the mixture. The results of the analysis, nevertheless, are consistent.

A qualitative examination of the data reveals, for example, that the relaxation times of the PVME chains in the blend are larger than that of PS chains of molecular weight 50 kg/mol or less. The results of the analysis concur.

Table I
Comparison of the Experimental and Calculated Values of the Viscosity of a PS/PVME Blend Containing a Volume Fraction of PVME of $\varphi = 0.4$[a]

T, K	η^{measd}, P	D_R, cm^2/s	τ_{PS}, s	η^{calcd}, P
382	3.2×10^6	3.6×10^{-14}	4.2	5.6×10^6
373	8.4×10^6	1.5×10^{-14}	10.1	1.3×10^7
362	2.6×10^7	4.1×10^{-15}	37	4.9×10^7

[a] The molecular weight of PVME is 145 kg/mol and that of PS is 100 kg/mol.

A natural consequence of the foregoing analysis is that for pure reptation the viscosity of the blend is

$$\eta_0^{\text{blend}} = \frac{\pi^2}{12} G_N^\circ(\text{blend})[\varphi\tau_{\text{PVME}}(\varphi) + (1-\varphi)\tau_{\text{PS}}(\varphi)] \quad (18)$$

Note that if τ_{PS} and τ_{PVME} differed considerably a procedure described in ref 15 would have to be used. It is worthwhile to calculate the viscosity of the blend using eq 18 and compare it with actual measurements of the viscosity. The viscosities of PS/PVME blends of PVME of molecular weight 145 kg/mol and of PS of molecular weight 100 kg/mol are shown in Table I at three temperatures. The volume fraction of PVME in each blend was $\varphi = 0.4$. These data were taken from ref 19.

To calculate the viscosities of the blends, one must know the relaxation times of the chains. Equation 16 defines the relation between the relaxation times of the PS and PVME chains in the host environment. The relaxation times of the PS chains in the host environment can be obtained from the diffusion data in ref 19. The temperature dependence of the diffusion of d-PS chains into binary mixtures of PS and PVME where $D_R \sim M^{-2}$, independent of the molecular weight of the host environment, for blends containing a volume fraction of PVME of $\varphi = 0.4$ was shown to be well described by[19]

$$\log \frac{D_R(T_0)T}{D_R(T)T_0} = -4.87 + \frac{594}{T - 258} \quad (19)$$

The reference temperature was $T_0 = 380$ K. The values of D_R in the table were calculated from eq 19. With the result that $\tau_{PS} = CM/3\pi^2 D_R$ (cf. eqs 1 and 8), the relaxation times shown in Table I were computed. A value of $C = 4.5 \times 10^{-17}$ cm^2 was used.[17] It is clear from the data in the table that the agreement is surprisingly good. The viscosities could be calculated at other temperatures but it suffices only to calculate three of them in view of the fact that log η and log (T/D_R) were shown to exhibit the same temperature dependence.[19] It is straightforward to use the results in this paper to compute the friction factors of the d-PS chains in the blends (eq 8) and use the results to calculate the friction factors of the PVME chains (eq 17). This would enable one to calculate the viscosities for other PS/PVME blend systems.

Of course, a more complete study than discussed above would require measurement of the viscosity at other compositions to see whether the agreement remains as good. Certainly, complete agreement is by no means a verification of eq 18. It suggests, however, that this may be a viable empirical procedure, in the absence of a first-principles theory, that one may attempt to use to calculate viscosities in polymer blends. Any rigorous theory should address the friction coefficients in polymer blends at a fundamental level. It should not involve a mean field approach.

Conclusion

We have examined the effects of tube renewal on the diffusion of deuterated polystyrene chains in binary mixtures of polystyrene and poly(vinyl methyl ether). The data could be described by a model that was developed based on the work of Klein and Graessley. The results of the analysis of the data enabled the determination of the relaxation times of the PVME chains in the blend. This information, together with the relaxation times of the d-PS chains in the same blend system, was used to calculate the viscosities of a PS/PVME blend system as a function of temperature. The values calculated with this mean field approach are in surprisingly good agreement with independently measured values. This approach used to determine η is far from perfect. The ideal approach will require a non mean field theory to calculate η in polymer blends. Any such theory would first have to address the monomeric friction factor in blends at a fundamental level.

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