Macromolecules 1993, 26, 5310–5315

Interdiffusion in a Homogeneous Polymer Blend Far above Its Glass Transition Temperature

G. Meier,[*,†] G. Fytas,[‡] B. Momper,[†] and G. Fleischer[§]

Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500 Mainz, Germany, Foundation for Research and Technology, Hellas, P.O. Box 1527, 711 10 Heraklion, Crete, Greece, and Fachbereich für Physik der Universität Leipzig, Linnéstrasse 5, O-7010 Leipzig, Germany

Received March 23, 1993; Revised Manuscript Received June 28, 1993[●]

ABSTRACT: We report measurements of the mutual diffusion coefficient D of the compatible polymer mixture poly(dimethylsiloxane)/poly(ethylmethylsiloxane), PDMS/PEMS, with degrees of polymerization $N_A = 80$ and $N_B = 90$, respectively, at various compositions and temperatures. We have employed photon correlation spectroscopy PCS to obtain both D and the static structure factor $S(q=0)$. Additionally, we have measured the self-diffusion coefficient D_s by pulsed-field gradient NMR. The friction coefficients derived from the latter experiments have been compared with those from measurements of the dynamic shear modulus. For this model system far above the glass transition and macrophase separation we found a consistency between the dynamic quantities D_s, the viscosity, and the kinetic factor D^0 relevant for polymer interdiffusion. The resulting composition dependence for D^0 is given by the reciprocal friction coefficient ζ_0^{-1} extracted from the mechanical measurement, a result only in harmony with the so-called "fast mode" approach and a more recent random phase approximation.[23]

Introduction

Mutual diffusivity in binary A/B polymer mixtures is controlled by the thermodynamic interactions between the chemically dissimilar polymer components (A, B) and their mobilities.[1] Whereas the former domination is experimentally documented,[2–5] the functional form of the kinetic factor D^0 is still controversial. On the theoretical side, two different equations[6–12] known as the "fast" and "slow" modes, have been proposed to describe the composition dependence of D^0 in terms of the tracer diffusivities D_i^0 (i = A, B) of the pure constituent components. Besides the neglect of velocity cross correlations[13,14] that lead to these two analytical forms, the strong assumption of composition, ϕ, independent D_i^0's requires negligible glass transition, T_g, effects. In real polymer mixtures, however, the fact that $T_g(\phi)$ is usually composition dependent renders the comparison to the theoretical predictions for $D^0(\phi)$ ambiguous.

Experimental investigations of D at constant ϕ have revealed the rather striking insensitivity of D^0 to the degree of polymerization N_i for unentangled Rouse chains, i.e. $D_i^0 \propto N_i^{-1}$ [14,15] and favored either[4,5,16,17] the fast or[2,18,19] the slow mode theory. Variation of ϕ usually complicates the data analysis due to $T_g(\phi)$ effects, that are not encountered in the theoretical treatments. In fact, a mean field consideration[20] of the forces ultimately responsible for T_g effects has recently suggested that slow or fast type behavior is related to the nearness of T_g to the experimental temperature T. This tendency has also been shown in recent computer simulation results.[21] Therefore, comparison between theoretical predictions and experimental evidence is meaningful if the latter can meet the assumptions of the theory.

In the present study, we report on the mutual diffusivity of poly(dimethylsiloxane)/poly(methylethylsiloxane) (PDMS/PEMS) with $N_A = 80$ and $N_B = 90$ at different ϕ and T's. We employed photon correlation spectroscopy (PCS) in the polarized mode to obtain D and static structure factor $S(0)$ (in the $q \to 0$ limit) of the concentration fluctuation ϕ_q (q is the scattering wave vector). The present system was carefully chosen on account of (a) its virtually ϕ independent T_g (≈145 K) which is much lower than the experimental T (>260 K), (b) its low critical temperature T_c (~120 K) and hence diminution of the thermodynamic forces (~1/$S(0)$), and (c) its components which possess different self-diffusivities whose relative magnitudes, more importantly, vary with T, i.e. $D_A^0(T) \geq D_B^0(T)$. In addition to the PCS data, we have performed dynamic shear mechanical measurements of the average friction $\zeta(\phi)$ and pulsed-field gradient NMR measurements of the self-diffusivities. The main objective of this report is to study the dependence of D on ϕ and D_i^0's and compare it with the prediction of the existing theoretical treatments of interdiffusion in compatible undiluted polymer blends.

Theoretical Background

In a compatible incompressible polymer blend, the thermal concentration fluctuations $\phi_q = \phi_q(A) = -\phi_q(B)$ determine the dynamic structure factor[9–11]

$$S(q,t) = \langle \phi_q(t)\phi_{-q}(0)\rangle = S(q)\exp(-Dq^2t) \qquad (1)$$

where $S(q) = \langle|\phi_q(0)|^2\rangle$ is the static structure factor with $\langle|\phi_q(0)|^2\rangle$ being the Fourier transform of the mean square concentration fluctuations. In the mean field theory,[22] $S(q)$ is related to the scattering power S_i^0 of the noninteracting coils and the segment interaction parameters χ_F by

$$1/S(q,T) = 1/(v_A S_A^0) + 1/(v_B S_B^0) - 2\chi_F(T)/v_0 \qquad (2)$$

where v_i is the segmental volume of component i and v_0 is the volume of the reference unit cell. For $q\xi_i \ll 1$, with ξ_i being the correlation length of ϕ_q, the q independent structure factor $S(0)$ is written in the form

$$1/S(0,T) = 2(\chi_s - \chi_F) = (v_A\phi_A N_A)^{-1} + (v_B\phi_B N_B)^{-1} - 2\chi_F(T) \qquad (3)$$

where χ_s denotes the interaction parameter $\chi_F(T_c)$ at the spinodal.

[†] Max-Planck-Institut für Polymerforschung.

[‡] Foundation for Research and Technology.

[§] Fachbereich für Physik der Universität Leipzig.

[●] Abstract published in *Advance ACS Abstracts*, September 1, 1993.

0024-9297/93/2226-5310$04.00/0

The mutual diffusion D in the exponential equation (1) is written as the product of a kinetic factor (D^0), a thermodynamic factor ($S(0,T)^{-1}$), and a geometrical factor.[1,6-8,10,11]

$$D = \phi_A\phi_B D^0/S(0) \tag{4}$$

The transport coefficient D^0 is expressed in terms of the bare self-diffusion coefficients D_i^0's, but the analytical form is in dispute between the theoretical approaches. Under conditions of microscopic incompressibility, the mean field expression for D^0 reads[8,10,11]

$$1/D^0 = \phi_B/(D_A{}^0N_A) + \phi_A/(D_B{}^0N_B) \tag{5}$$

whereas other treatments[6,7] allowing different diffuse segment fluxes lead to a Hartley–Crank type of equation:

$$D^0 = \phi_B D_A{}^0 N_A + \phi_A D_B{}^0 N_B \tag{6}$$

However, there are arguments[12] and computer simulations[13,21] that suggest the approximate nature of these two simple relations. Moreover for a real mixture, $D_A{}^0$ and $D_B{}^0$ relate to the actual blend composition ϕ and not to the limiting values of the pure states.

In the Onsager formulation of the current densities linked to the gradients of the chemical potentials there are four phenomenological Onsager coefficients λ_{AA}, λ_{BB}, λ_{AB}, and λ_{BA}. Keeping the nondiagonal terms $\lambda_{AB} = \lambda_{BA}$ for a vanishing number of vacancies, one obtains[13,21]

$$D^0 = (\lambda_{AA}\lambda_{BB} - \lambda_{AB}{}^2)/(\lambda_{AA} + 2\lambda_{AB} + \lambda_{BB}) \tag{7}$$

To derive the previous simple relations, it was assumed that $\lambda_{AB} = 0$ and $D_A{}^0 = \lambda_{AA}(1 - \phi_A)/N_A$, $D_B{}^0 = \lambda_{BB}(1 - \phi_B)/N_B$.

The relation of the diffusivities $D_A{}^0$ and $D_B{}^0$ to the pure melt self-diffusion coefficients is a difficult task requiring a molecular theory of $1/D^0$, the relevant microscopic friction coefficient. In a recent random phase approximation (RPA) approach for an incompressible ternary system with the third component treated as vacancies the derived expression for D^0 incorporates both the slow (eq 5) and fast (eq 6) mode equations. For unentangled chains[23]

$$D^0 = \left[\frac{D_A{}^0N_A}{\phi_A} + \frac{D_B{}^0N_B}{\phi_B} - \frac{(D_A{}^0N_A - D_B{}^0N_B)^2}{\phi_A D_A{}^0N_A + \phi_B D_B{}^0N_B + \phi_C D_C{}^0N_C}\right]\phi_A\phi_B \tag{8}$$

with ϕ_c, $D_c{}^0$, and N_c being the volume fraction, the self-diffusion, and degree of polymerization of the c component (vacancies). Equations 5 and 6 can be recovered by eq 8 when $\phi_c D_c{}^0 N_c$ approaches zero or infinity, respectively. Thus, far away from T_g the third term in eq 8 can be neglected, recovering the fast mode equation (6).

Alternatively, it was recently shown[20] that a relation between D and D_i^0's can be derived using a "mean field approach of T_g". It reads

$$(D^0)^{-1} = (1 - U)(D_s{}^0)^{-1} + U(D_f{}^0)^{-1} \tag{9}$$

where $D_s{}^0$ and $D_f{}^0$ denote the D^0 of the slow (eq 5) and fast (eq 6) modes and D_i^0's are now pure melt self-diffusivities. The parameter $U(T)$ is a measure of the closeness of T to T_g. Far above T_g ($T \gg T_g$), $U = 0$ and D is predicted to follow $D_s{}^0$, i.e. a linear dependence on composition of the friction $\zeta = kT/D_s{}^0$. At the other extreme near T_g, D should follow $D_f{}^0$ and show a linear ϕ dependence of the mobility.

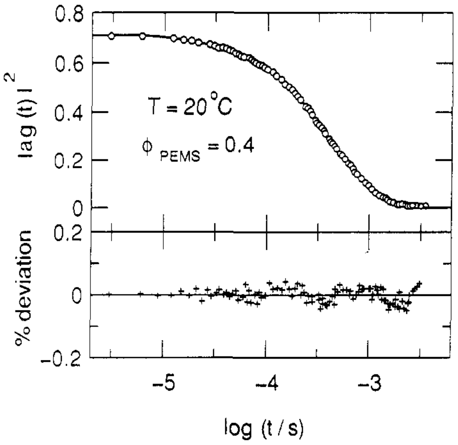

Figure 1. Unnormalized intensity correlation function $|\alpha g(q,t)|^2$ for a homogeneous blend PDMS (80)/PEMS (90) with volume fraction $\phi_B = 0.4$ at $q = 2.6 \times 10^{-3}$ Å^{-1}. The solid line indicates a single exponential fit with residuals shown in the lower part of the figure.

Experimental Section

Materials. The polymers PDMS and PEMS were synthesized by anionic ring polymerization of methylcyclotrisiloxane and triethyltrimethylcyclotrisiloxane, respectively, and characterized as described elsewhere.[24] The degree of polymerization N amounts to 80 and 90, respectively, for PDMS and PEMS, with T_g(PDMS) = 148 K and T_g(PEMS) = 141 K. Blends of different composition ϕ were prepared by direct filtration through a 0.22-μm Millipore filter into a dust-free round light scattering call of $^1/_2$-in. outer diameter.

Photon Correlation Spectroscopy (PCS). The polarized intensity correlation function $G(q,t)$ was measured at different scattering angles θ (40–130°) and temperatures T (−10 ° to +100 °C) using a 128-channel full correlator (Brookhaven BI 2030). The light source was an argon ion laser (Spectra Physics 2020) operating at λ = 488 nm with a power of 150 mW. The desired normalized electric field correlation function $g(q,t) = S(q,t)/S(q)$ (eq 1) is given, under homodyne conditions, by

$$G(q,t) = \langle I(q)\rangle^2(1 + f^*|\alpha g(q,t)|^2) \tag{10}$$

with $\langle I(q)\rangle$ being the mean light scattering intensity at wavevector $q = (4\pi n/\lambda)\sin\theta/2$ (n is the refractive index of the medium), f^* an instrumental factor, and α the fraction of the total intensity $I(q)$ arising from concentration fluctuations with correlation times slower than about 10^{-6} s. Figure 1 shows a typical semilog plot of the unmormalized function $|\alpha g(q,t)|^2$ of a homogeneous PDMS/PEMS blend with ϕ = 0.4 at 20 °C. The adequate single exponential fit according to eq 1 is demonstrated by the residual plot of Figure 1. The intercept at short times $\alpha^2 \cong 0.72$ suggests that about 85% of the light scattering intensity arises from ϕ_q.

Pulsed-Field Gradient NMR. Pulsed-field gradient NMR (PFG-NMR) measures the self-diffusion coefficient D_s of particles bearing ^{1}H nuclei if the field gradient is applied as a pulse during the spin echo experiment. The resulting attenuation ψ of the echo is given by[25]

$$\psi = \exp(-\gamma^2\delta^2g^2\Delta D_s) \tag{11}$$

with γ being the gyromagnetic ratio, δ and g the width and the height of the field gradient pulses, and Δ its separation in time. In the case of having more than one species, like here, one measures the tracer diffusion coefficient and ψ is modified according to

$$\psi = \sum p_i \exp(-\gamma^2\delta^2g^2\Delta D_i) \tag{12}$$

with p_i being proportional to the number of protons causing the attenuation of the echo. For the present mixture resolution of ψ into two exponents would probably require deuteration of one of the polymer components. In our case, however, all attenuation curves were found to be single exponential with respect to δ^2 within experimental error, which means $D_A \approx D_B \approx D_s = kT/\langle\zeta\rangle N$.

Table I. Interdiffusion Coefficient D and Kinetic Factor D^0 (eq 4) in a PDMS (80)/PEMS (90) Blend (D's in cm²/s)

	263 K		293 K		373 K	
ϕ_{PMES}	10^9D	10^6D^0	10^8D	10^6D^0	10^7D	10^5D^0
0				5.4[a]		
0.06	20.0		4.2	3.8		
0.10	13.6	1.81	3.9	3.6	2.0	1.48
0.2	12.1	1.74	3.1	3.3	1.8	1.28
0.4	18.2	1.35	2.2	2.62	1.0	1.17
0.5	7.3	1.26	1.9	2.48	1.0	1.15
0.6	6.5	1.1	1.8	2.33	0.97	1.06
0.8	6.8	0.79	1.8	1.84	0.96	0.81
0.9	6.2		1.7	1.55	1.4	0.94
0.95	5.9		1.6	1.35		
1.0				2.7[a]		

[a] From self-diffusion data $D^0 = D_sN$.

Dynamic Shear Mechanical Measurements. The real and imaginary parts of the shear moduli were measured with a Rheometrics RMS-800 spectrometer. The imaginary part $G''(\omega)$ is related to the shear viscosity η_s via

$$\eta_s = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \qquad (13)$$

For every mixture at the given temperature over the range $10^{-1} < \omega/\mathrm{rad\ s^{-1}} < 10^2$ the common plateau at low shear rates was reached which allows a reliable determination of η_s.

Results

The fit of a single exponential decay function for $g(q,t)$ to the experimental $G(q,t)$ in eq 10

$$[G(q,t)/|\langle I(q)\rangle|^2 - 1)]/f^* = \alpha \exp(-\Gamma(q)t) \qquad (14)$$

leads to the interdiffusion coefficient $D = \Gamma/q^2$ and the fraction α. The static structure factor $S(q)$ can be obtained from the Rayleigh ratio $R_\phi(q)$ due to the concentration fluctuations by

$$S(q) = R_\phi(q)\lambda^4\rho/[4\pi^2n^2(\partial n/\partial\phi)^2] \qquad (15)$$

where ρ is the number density and $\partial n/\partial\phi$, the refractive index, amounts to the difference of the refractive indices of the two components since n of the blend depends linearly on ϕ. For PDMS, $n_A = (1.515\text{–}3.8) \times 10^{-4}T$ and for PEMS $n_B = (1.526\text{–}3.3) \times 10^{-4}T$ (T in K). The Rayleigh ratio $R_\phi(q)$ can be obtained either from $\langle I(q)\rangle$ after subtraction of the contribution of the density fluctuations in pure melts and/or from $I_\phi(q) = \alpha\langle I(q)\rangle$ as described elsewhere.[14,26] For the present low molecular weight blend very far from T_c, $S(q)$ is predicted[11,22] and found insensitive to q variations. Hence, for light scattering q's, $S(q) = S(0)$, the thermodynamic limit.

The "kinetic factor", D^0 can be computed from eq 4 since in all theoretical treatments the thermodynamic factor is the same (eq 3). The experimental values of D and the computed values of D^0 are listed in Table I. Figure 2 shows the variation of D, $S(0)$, and D^0 of the PDMS/PEMS blend at 20 °C. The static structure factor is dominated by the entropic contribution $(2\chi_s)^{-1}$ (eq 3), shown as a solid line in Figure 2. Using $v_A = 76$ cm³/mol, $v_B = 90$ cm³/mol, and $v_0 = (v_Av_B)^{1/2}$, we compute from the experimental value $S(0) = 32$ at $\phi = 0.5$ and $\chi_s = 0.024$ the interactions parameter $\chi_F = 8 \times 10^{-3}$ at 20 °C. This is in agreement with the reported χ_F value in a higher molecular weight and hence a less compatible PDMS/PEMS blend.[26]

The composition dependence of D is similar to that of the kinetic factor D^0. For $\chi_F = 0$ and a symmetric blend ($v_AN_A = v_BN_B$), the ϕ dependence of $\phi_A\phi_B/S(0)$ in eq 4 is exactly canceled, i.e. $D = D^0/N$. For the present system, it is possible to vary the ratio $D_A{}^0/D_B{}^0$ with T despite the fact that $T \gg T_{g,A} \cong T_{g,B}$. This is feasible, because the pure components possess different activation parameters $B = c_1c_2$ in the WLF temperature equation[27] deduced from the viscosity measurements.

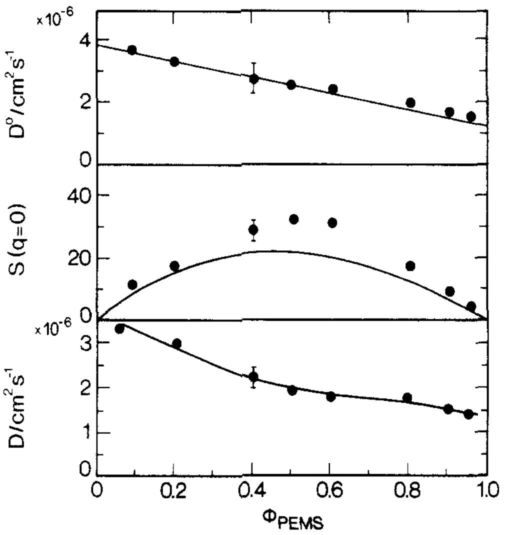

Figure 2. Interdiffusion (D), static structure factor ($S(0)$), and kinetic factor D^0 as a function of ϕ_{PEMS} in the PDMS (80)/PEMS (90) blend at 20 °C. The solid line denotes the entropic contribution $(2\chi_s)^{-1}$ to $S(0)$ (eq 3).

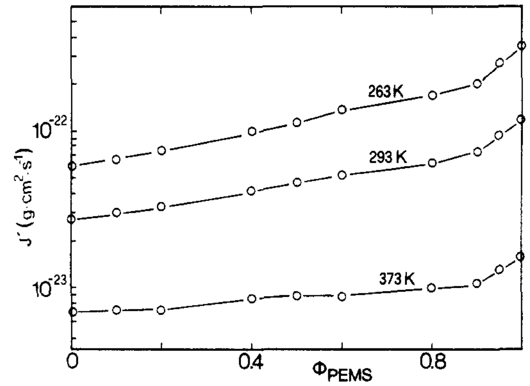

Figure 3. Semilog plot of the friction $\zeta' = \zeta b^2$ (eq 16) in the PDMS/PEMS blend at three temperatures.

From the shear mechanical data, we have calculated the local friction coefficient $\zeta' \equiv \zeta_0b^2$ assuming Rouse dynamic[28]

$$\zeta' = \eta 36M_0{}^2/\rho N_AM \qquad (16)$$

where $M_0 = \phi_AM_A + \phi_BM_B$ and $\rho = \phi A\rho_A + \phi_B\rho_B$, respectively, are the molecular weight of the repeating unit and the density of the blend. The variation of log ζ' with blend composition is clearly nonlinear,[29] as visualized in Figure 3. The friction ζ' is larger in bulk PEMS, and moreover the ratio $\zeta'(\mathrm{PEMS})/\zeta'(\mathrm{PDMS})$ increases with decreasing T. In fact, the activation energy E_A obtained from the Arrhenius fit of the experimental η_s is an increasing function of the ϕ_{PEMS} composition in the blend. Over the temperature range −20 to +100 °C, far above T_g, the Arrhenius E_A can be represented by E_A (kJ/mol) = $15.9 + 6.91\phi_{\mathrm{PEMS}}$.

The length b of the statistical segment, necessary to compute the local friction $\zeta = \zeta'/b^2$, should depend on ϕ, since the pure components have different values ($b_A = 5.8$ Å, $b_B = 6.4$ Å).[26] We can estimate $b(\phi)$, however, independently by assuming the same ζ for interdiffusion (kT/D^0) and η (as discussed in the next section).

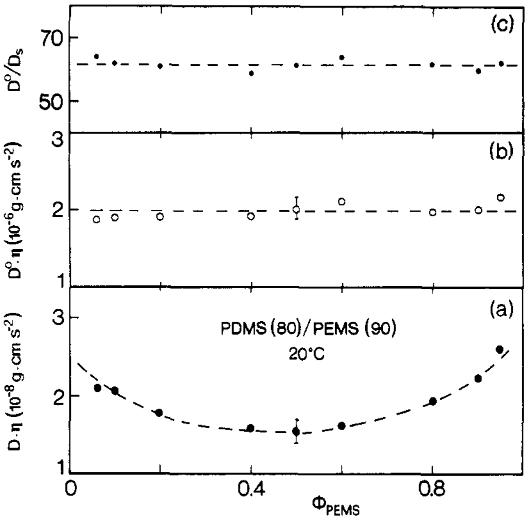

Figure 4. The variation of $D\eta$ (a), $D^0\eta$ (b), and D^0/D_s (c) with composition in the PDMS/PEMS blend at 20 °C. D is the interdiffusion, D^0 is the kinetic factor (eq 4), D_s is the average self-diffusion coefficient, and η, is the experimental shear viscosity.

Discussion

A. Comparison with Shear Viscosity. Mass transport is directly connected with the viscosity of the medium, and a typical example is the well-known Stokes–Einstein equation for Brownian diffusion. It is likely that a relation $D \sim 1/\eta$ should also hold for interdiffusion if the thermodynamic factor equally affects both D and η, and moreover T_g effects do not play any role.[30]

The product of the experimental quantities $D\eta$ at 20 °C is plotted at different compositions in Figure 4a. The displayed behavior reveals two interesting features for the interdiffusion dynamics in compatible blends well above T_c (~120 K). Due to still unfavorable ($\chi_F > 0$) thermodynamic interactions (Figure 2b), D is slowing down in the middle of the ϕ range where η appears to be less sensitive (see Figure 4b) to the compositions fluctuations. However, the product $D\eta$ exceeds the value of about 2×10^{-8} g cm s^{-2} at the edge of the ϕ range where the influence of χ_F is very small ($\chi_s \gg \chi_F$). $D\eta$ is larger for blends rich in rigid PEMS chains since b(PEMS) > b(PDMS) and hence enhanced η at high $\phi_{\rm PEMS}$ values (eq 16, Figure 3).

The purely kinetic factor D^0 should scale with η^{-1} over the whole ϕ range. There is, however, a hint of small deviations at high $\phi_{\rm PEMS}$, which again reflect differences in the chain stiffness of PDMS and PEMS chains. Alternatively, the ratio between D^0 and the average self-diffusivity D_s obtained from PFG-NMR is virtually ϕ independent (Figure 4c). For Rouse dynamics, obeyed by the present blend[15] and freely rotated chain, D^0/D_s should amount to about 85 (the average degree of polymerization). For a real chain, however, the ratio is reduced at most by the ratio of the number of statistical segments N_s over N. In the present case this ratio is estimated to be 1.5. The observed value is by 25% lower, and at present we can speculate on the origin of this additional disparity. It could arise from faster D_s values due to the different averaging behavior in the NMR experiment[31] and uncertainties in the absolute Rayleigh ratio $R_\phi(q)$ (eq 15) affecting directly the calculation of D^0 (eq 4).

The local mobility kTb^2/ζ' can be obtained from the viscosity data (eq 16) and the segment length b, which is computed at 20 °C by identifying $D^0 = kT/\zeta_0$. b increases systematically from 5.1 to 6 with $\phi_{\rm PEMS}$ of the rigid PEMS chain. We have then used these values to compute kTb^2/ζ' at 263 and 373 K from the data of Figure 3. The results are plotted versus $\phi_{\rm PEMS}$ in Figure 5 along with D^0. At 263 and 373 K, the mobility kT/ζ_0 is respectively lower and higher than D^0. The two quantities can be forced into agreement if b is decreasing with T. This is an expected conformational behavior and the temperature coefficient $db/dT \simeq 1.4 \times 10^{-3}$ Å/K is a typical value. For bulk PDMS, this coefficient is reported[32] to be 4×10^{-3} Å/K based on a rotational isomeric state model calculation. Based on the data of Figures 4 and 5 a consistent agreement between D_s, η, and D^0 has been established over the whole ϕ range using physically meaningful values of b. Hence, the composition dependence of D^0 is that of $1/\zeta_0$. This is not an unexpected result since D and hence D^0 are referred to the thermodynamic limit $\xi q \ll 1$.

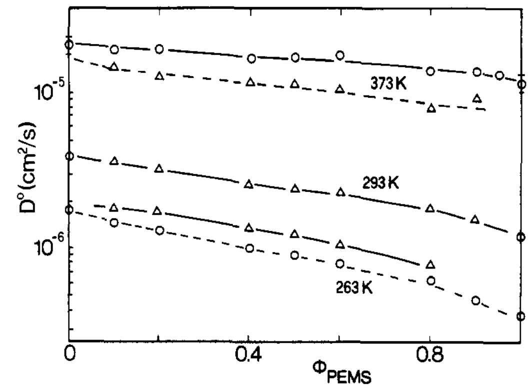

Figure 5. Composition dependence of the kinetic factor $D^0(\Delta)$ and the mobility $kT/\zeta_0(0)$ from the viscosity data at three different T's. At 293 K, the equivalence of D^0 and kT/ζ_0 was taken for granted to compute the segment length b (eq 16).

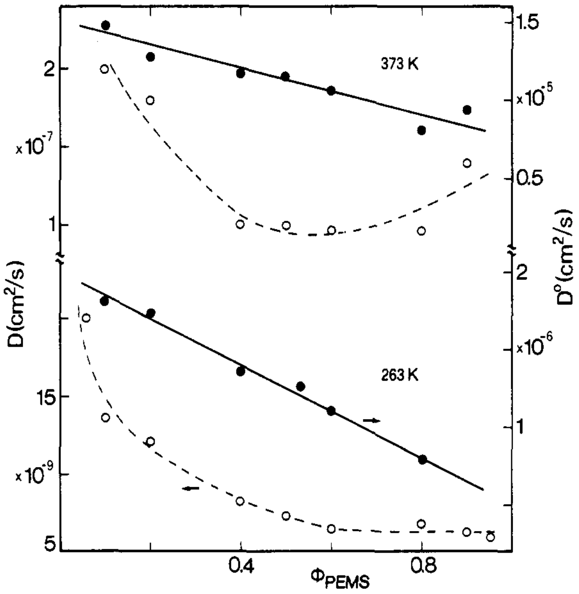

Figure 6. Interdiffusion D and kinetic factor D^0 versus composition $\phi_{\rm PEMS}$ at two temperatures. The dashed lines are to guide the eye whereas the solid lines denote linear fits, according to eq 6.

B. Composition Dependence. The variation of the interdiffusion coefficient with ϕ at 263 and 373 K is shown in Figure 6. At the highest T and near the middle of the composition range $D(\phi)$ exhibits a minimum which becomes less pronounced with decreasing T (see also Figure 2). At 263 K, no extremum is present and $D(\phi)$ is a decreasing function of $\phi_{\rm PEMS}$. The different behavior of $D(\phi)$ at high and low T is respectively a manifestation of the thermodynamic and mobility effects. For a symmetric

($N_A = N_B = N$) blend, eq 4 takes the simple form

$$D(\phi) = \frac{D^0(\phi)}{N}(1 - 2\chi N\phi_A\phi_B) \qquad (17)$$

which for $\chi > 0$ predicts smaller interdiffusivity than self-diffusivity (D^0/N) with a minimum near $\phi = 0.5$. At 373 K the self-mobilities $w_i^0 = kT/\zeta_i$ approach each other ($w_A/w_B \cong 1.7$, Figure 5) and hence $D^0(\phi)$ becomes a weak function of ϕ. The thermodynamic slowing down of D is therefore measurable in blends with similar self-mobilities.[5] At 373 K and $\phi = 0.5$, χ_F is estimated to be 6.5×10^{-3}, which is positive and smaller than that at 293 K. Alternatively, at 263 K $w_A/w_B \cong 5$ and the reduced mobility at high ϕ_{PEMS} determines the composition dependence of D. In fact $D^0(\phi)$ computed from eq 4 becomes stronger composition dependent (Figures 2 and 6) with decreasing T. Thus, eqs 4 and 17 can account for the measured composition dependence of D in PDMS/PEMS blends if $D^0(\phi)$ is a decreasing function of ϕ_{PEMS}.

As mentioned in the Introduction, the presence blend is a model system since the experimental T_i's are far above T_c and T_g of the mixture with $T_{g,A} \cong T_{g,B}$. Therefore, the random-phase approximation and its strong assumption concerning the ϕ independence of the self-diffusivities in the blend is best fulfilled. Hence the ϕ dependence of the disputed (eqs 5–7) kinetic factor can be compared with the experimental $D^0(\phi)$, shown in Figures 2 and 6. At all three T's eq 6 provides a better fit to the experimental D^0 than eq 5. However, the ratio D_f^0/D_s^0 between the predicted values of the fast and the slow mode equations for composition independent self-mobilities at $\phi = 0.5$ is $(\lambda + 1)^2/4\lambda$ where $\lambda = w(\text{PDMS})/w(\text{PEMS})$. At 373 K, D_f^0 and D_s^0 differ by about 7% whereas at 263 K this disparity increases to about 75%. Consequently, we discuss $D^0(\phi)$ at this lowest T for which the theoretical predictions deviate much more than the experimental uncertainty in D^0.

The fit of eq 6 to the experimental $D^0(\phi)$ of Figure 6 yields $w(\text{PDMS}) = 2 \times 10^{-6}$ cm^2/s and slope $(\lambda - 1)/\lambda = 0.75 \pm 0.03$ at 263 K with a correlation coefficient of 0.996. The last compares favorably with the value of 0.79 obtained from the viscosity data of the bulk blend components. In contrast, the fit of eq 5 to the same $D^0(\phi)$ data has a correlation coefficient of 0.96 and yields slope $(\lambda - 1) = 2.6$ which is more than 30% less than the expected value. On the premise that D_A^0 and D_B^0 are ϕ independent, the data of Figures 2 and 6 rather favor the linear composition dependence predicted by the fast mode theory.

The segmental mobilities or the self-diffusivities D_i^0 are not necessarily intrinsic properties of the pure melts. D_i^0 should rather be taken as the tracer diffusion coefficients at the given blend composition.[12] In fact, the PFG-NMR experiment can be reasonably described by single exponential decay over the whole composition range despite the fact that the self-diffusion coefficients of the pure components are different by a factor of 2.3 at 20 °C. If this disparity and the contribution of each component to the spin echo were ϕ independent, then the decay curves would experimentally deviate from the single exponential form at least at $\phi = 0.5$. However, such deviation was not observed and thus a single average self-diffusion coefficient was extracted (Figure 4). Nevertheless, the composition dependence of this D_s coefficient is still closer to the straight line, given by eq 6. Assuming a similar linear ϕ dependence for the D_i^0's, the linear dependence of the D^0 according to eq 6 is still preserved.

The actual value of the simplified formulas, eqs 5 and 6 lies in the connection of the interdiffusion in the blend with the self-diffusion coefficient of its homopolymer constituents. These simple expressions represent approximately the real situation and can be derived from more general expressions under certain assumptions for the relevant microscopic friction coefficient.[12] Neglect of cross correlations in the velocities of segments of different polymers leads to the fast mode equation. This should be a reasonable approximation far away from T_g, and it is supported by the present results. On the contrary in this limit eq 9 would predict slow mode behavior ($U \rightarrow 0$).

C. Current Situation. There is theoretical and experimental agreement as far as the thermodynamic factor $S(0)$ and the N dependence of D^0 for unentangled blends are concerned. In all theoretical expressions, the diffusivities of the pure melts appear as product $D_i^0N_i$ so that Rouse behavior has been established for unentangled blends. Thus the separation of the thermodynamic and kinetic effects on D is generally accepted mainly because the experimental slowing down of the interdiffusion can be accounted for by eq 4. Inconsistent conclusions, however, are drawn for the validity of the approximate formulas (eqs 5 and 6) so far. This is probably due to the fulfillment of the assumptions that led to eqs 5 and 6 and the adoption[12] of the reptation result, i.e. $D_i^0 \sim N_i^{-2}$.

On the experimental side the molecular weight dependence of D^0 at constant ϕ for entangled blends, where one[14] or both[4,18] components exceed the critical degree of polymerization N^* at which entanglements become effective, was compared with the predictions of eqs 5 and 6. For quenched PS/PVME blends,[18] time resolved light scattering led to $D^0(N)$ data following either eq 6 or eq 5 at low and high N_{PS}, respectively. We should mention that the data analysis in ref 18 was based on the reptation result and the overall N dependence was represented by eq 8 (modified for entangled blends). In the interdiffusion study of entangled PS/PXE blend[4] by means of forward recoil spectrometry (requiring also a built-in concentration gradient), the conclusive support of the fast mode equation (6) has been questioned in the more recent ref 18 (Figure 14). For the PEO/PPO blends far above T_g the $D^0(N_{PEO})$ results, obtained from PCS at thermal equilibrium, have also favored the fast mode theory. However, both equations can describe the data in refs 14 and 18 when instead of the reptation result one would include the matrix effect,[12] i.e. $D_i \cong (N_C/N_A + N_C/N_B)/N_i$.

The composition dependence of $D^0(\phi)$ when $T_g(\phi)$ effects are virtually absent has been investigated for PEO/PPO[6] and the present system. For the former blend, the deviation of $D^0(\phi)$ near the middle of the composition range from both eqs 5 and 6 has been described to the failure of the mean field theory due to the proximity to T_c. Thus only the present system appears to best meet the theoretical assumptions with regard to $D_i^0(\phi)$.

Finally, on the theoretical side, eqs 8 and 9 which relate D to the self-diffusion coefficients D_i^0 of the pure melts can predict eqs 5 and 6 as limiting cases, however, with contradicting conditions. The observed linear ϕ dependence of the mobility factor D^0 in the low molecular weight PDMS/PEMS blends far above T_g is in favor of eq 8 which is also in accord with the overall N dependence of D^0 in PS/PVME mixtures.[18]

References and Notes

(1) Binder, K.; Sillescu, H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H., et al., Eds.; Wiley: New York, 1989; Supplement Volume, p 297.

(2) Brereton, M. G.; Fischer, E. W.; Fytas, G.; Murschall, U. *J. Chem. Phys.* **1987**, *86*, 5174.

(3) Green, P. F.; Doyle, B. L. *Macromolecules* **1987**, *20*, 2471.

(4) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* 1988, *21*, 2580.
(5) Kanetakis, J.; Fytas, G. *Macromolecules* 1989, *22*, 3452.
(6) Kramer, E. J.; Green, P.; Palmstrom, C. *Polymer* 1984, *25*, 473.
(7) Sillescu, H. *Makromol. Chem., Rapid Commun.* 1984, *5*, 519; 1987, *8*, 393.
(8) Akcasu, A. Z.; Benmouna, M.; Benoit, H. *Polymer* 1986, *27*, 1935.
(9) de Gennes, P. G. *J. Chem. Phys.* 1980, *72*, 4756.
(10) Brochard, F.; de Gennes, P. G. *Physica A* 1983, *118A*, 289.
(11) Binder, K. *J. Chem. Phys.* 1983, *79*, 6387.
(12) Hess, W.; Akcasu, A. Z. *J. Phys. Fr.* 1988, *49*, 1261.
(13) Kehr, K. W.; Binder, K.; Reulein, S. M. *Phys. Rev.* 1989, *B39*, 4891.
(14) Kanetakis, J.; Fytas, G. *J. Chem. Phys.* 1987, *87*, 5048.
(15) Momper, B.; Meier, G.; Fischer, E. W. *J. Non-Cryst. Solids* 1991, *131/133*, 624.
(16) Wang, C. H.; Zhang, X. Q.; Fytas, G.; Kanetakis, I. *J. Chem. Phys.* 1989, *91*, 3160.
(17) Jordan, E. A.; Ball, R. C.; Donald, A. M.; Fetters, L. J.; Jones, R. A. L.; Klein, J. *Macromolecules* 1988, *21*, 235.
(18) Feng, Y.; Han, C. C.; Takenaka, M.; Hashimoto, T. *Polymer* 1992, *33*, 2719.
(19) Garbella, R. W.; Wendorff, J. H. *Makromol. Chem., Macromol. Symp.* 1988, *18*, 53.
(20) Brereton, M. G. *Prog. Colloid Polym. Sci.* 1993, *91*, 8.
(21) Binder, K.; Sariban, A.; Deutsch, H. P. *J. Non-Cryst. Solids* 1991, *131/133*, 635.
(22) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(23) Akcasu, A. Z.; Naegele, G.; Klein, R. *Macromolecules* 1991, *24*, 4408.
(24) Momper, B. Ph.D. Thesis, University of Mainz, 1989.
(25) Kärger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* 1988, *12*, 1.
(26) Meier, G.; Momper, B.; Fischer, E. W. *J. Chem. Phys.* 1992, *97*, 5884.
(27) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980; Chapter 10.
(28) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, UK, 1986.
(29) Wu, S. *Polymer* 1987, *28*, 1144; *J. Polym. Sci., Polym. Phys. Ed.* 1987, *25*, 557.
(30) Rössler, E. *Phys. Rev. Lett.* 1990, *65*, 1595.
(31) Fleischer, G.; Geschke, D.; Kärger, J.; Heink, W. *J. Magn. Reson.* 1985, *65*, 429.
(32) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience Publishers: New York, 1969.