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Diffusion in Dilute Polystyrene/Poly(phenylmethylsiloxane) Blends

Two polymer blends in the homogeneous region have been investigated by dynamic light scattering so far. These are the polymer mixtures polystyrene (PS)/poly(phenylmethylsiloxane) (PPMS)[1,2] and poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO).[3,4] Both the mutual diffusion coefficient (or interdiffusion) D and the static structure factor $S(0)$ have been measured at different volume fractions Φ in the range 0.1–0.9 and discussed in the framework of recent theoretical models.[5–9] The pertinent conclusions emerged from these studies may be summarized as follows: (1) Thermodynamic interactions play a significant role in accordance with all theoretical treatments. Unfavorable segment–segment interactions lead to a reduced interdiffusion, i.e., $D < D^\circ$, with D° being a weighted average of the tracer diffusivities of the mixture components.[6–9] (2) If the glass transition temperature, T_g, of the blend varies with composition, then a major dependence on concentration is introduced in addition to those predicted by the theories.[2] (3) For unentangled Rouse chains, i.e., $D_i \sim M_i^{-1}$ (i = A and B, the blend components), the average mobility D° is expected to be molecular weight (M) independent and verified experimentally.[4,11]

In a recent photon correlation study of very dilute homogeneous PS/PPMS blends ($\Phi_{PS} < 0.01$), the experimental D in the infinite dilution limit $\Phi_{PS} \rightarrow 0$ was reported to follow a molecular weight dependence close to $M^{-0.5}$ for M_w(PS) in the range 10 200–17 500 and constant M_w(PPMS) = 2600.[10] This trend was violated by the M_w(PS) = 2000 sample. In dilute polymer–polymer blends, T_g effects are unimportant and the knowledge of D is of considerable interest. There are, however, in our opinion several serious problems with the experimental conditions and analysis of those data. The used bulk PPMS sample was previously found to display significant dynamic light scattering arising from concentration fluctuations owing to the presence of oligomers.[12] This correlation function in the bulk PPMS will probably affect the experimental concentration correlation functions in the very dilute PS/PPMS blends as the associated scattering power is weak at low Φ_{PS}.[2] To extract the interdiffusion D, reported in ref 10, only a few initial points of normalized experimental correlation functions were used without regard to base line and amplitude. Moreover, in the analysis of D thus obtained, the importance of the static structure factor $S(0)$ (in the thermodynamic limit $q \rightarrow 0$, with q^{-1} being the probing wavelength) was entirely ignored although there was strong evidence of its influence (Figure 6 in ref 10). We have, therefore, undertaken the present investigation with the main objective to find the correct molecular weight dependence of D° by improving the data quality and pursuing a correct analysis of the experimental D.

Experimental Section. One PPMS sample (M_w = 2600, $M_w/M_n \sim 1.6$) from Petrarch systems (Lot 45106) and PS samples (M_w = 1700, 3800, 9000, and 16 700) with polydispersity index $M_w/M_n \sim 1.04$ were used. Dilute PS/PPMS mixtures at constant 0.5 wt % PS concentration were carefully prepared using the procedure described elsewhere.[13] The dust-free mixtures yielded only inherent light-scattering intensity whose isotropic component arises from concentration and density fluctuations.

The experimental time correlation function of the scattered light intensity in the VV geometry was measured with a 28 log spaced delay channel Malvern (K7027) single-clipped correlator. The light source was an argon ion laser (Spectra Physics 2020) operating at a single mode at 488 nm with a stabilized power of 100 mW. Measurements and analysis of the homodyne correlation function $G(q,t)$ were all as previously described.[2,4]

Results and Discussion. The net concentration correlation functions $C(q,t) = [G(q,t)/A - 1]^{1/2}$ using a fixed base line A were found to have an almost exponential shape,[14] so that a meaningful average relaxation time τ can

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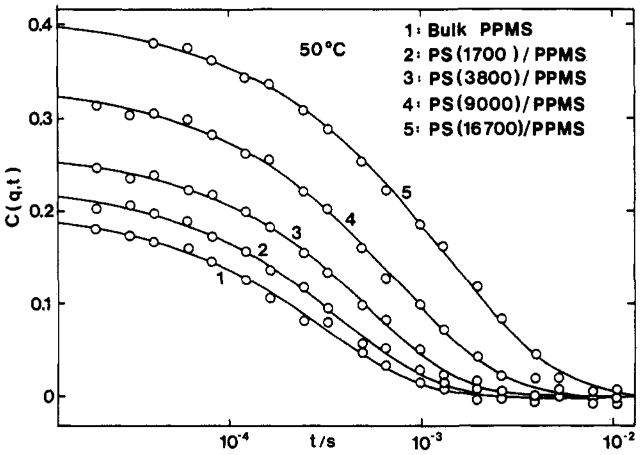

Figure 1. Net concentration correlation functions $C(q,t)$ for undiluted PPMS and four PS/PPMS blends with volume fraction $\Phi_{PS} = 5.1 \times 10^{-3}$ at 50 °C and $q = 2.78 \times 10^{-3}$ Å^{-1}. The solid curves represent KWW fits,[14] and the numbers in parentheses denote the weight average molecular weight of polystyrene.

be obtained. Figure 1 shows a semilog plot of the $C(q,t)$ for the blend PS/PPMS with different M_w(PS) and for the bulk PPMS at a scattering angle of 90° and at 50 °C. The solid lines on the plot are least-squares fits of the Kohlrausch–Williams–Watts (KWW) equation to the experimental $C(q,t)$.

Two pertinent aspects emerge from the data in Figure 1. (1) The bulk PPMS sample clearly displays a correlation function that was attributed to the concentration fluctuations.[12] At the temperatures considered here, the dynamics of the density fluctuations are too fast for the photon correlator.[15] (2) The short time intercept of the $C(q,t)$, which is a measure of the static structure factor $S(0)$, changes substantially with M_w(PS) at constant Φ and should therefore be taken into account for a correct interpretation of the interdiffusion results. Regrettably, the raw experimental $C(q,t)$ values were not shown in ref 10, so that a direct comparison is precluded. However, in view of the data in Figure 1, we cannot see any reason why only few initial points of $C(q,t)$ were used to extract the diffusion coefficient D in ref 10.

The mutual diffusion D in the present PS/PPMS mixtures for different M_w(PS) is calculated from the relation $D = 1/(\tau q^2)$.[1] Within the dynamic random-phase approximation, D in the regime $qR_0 \ll 1$ (R_0 being the radius of gyration) is given by the simple expression[6-9]

$$D = D°\Phi(1 - \Phi)/S(0) \qquad (1)$$

The static structure factor $S(0)$ can also be measured in the same light-scattering experiment.[2,16] At finite blend compositions the intermacromolecular forces reflected in the $S(0)$ affect seriously the interdiffusion.[3,17-19] For very dilute blends in the limit $\Phi_{PS} \rightarrow 0$, the interdifusion D in eq 1 approaches D_{PS}, the tracer diffusion coefficient of the minority chain (PS), as $S(0) \rightarrow N_{PS}\Phi_{PS}$ and $D° \rightarrow D_{PS}N_{PS}$. In fact, the concentration dependence of the measured Rayleigh ratio for the PS(9000)/PPMS mixture with Φ_{PS} varying from 5×10^{-3} to 6×10^{-2} was found to yield the M_W(PS) in the limit $\Phi_{PS} \rightarrow 0$. However, the second virial coefficient obtained from this concentration dependence is finite and amounts to -2×10^{-4} cm^{3}mol/g^2 at 50 °C. This finding indicates that phase separation will occur at higher M_w(PS), and hence D will be "slowing down".[3,17-19]

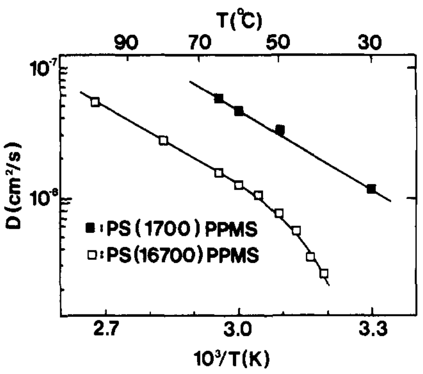

Figure 2. Measured interdiffusion D plotted as a function of temperature for two PS/PPMS blends with $\Phi_{PS} = 5.1 \times 10^{-3}$.

Table I
Mutual Diffusion Coefficients and Static Structure Factors for Dilute PS/PPMS Mixtures Containing a Volume Fraction $\Phi_{PS} = 5.1 \times 10^{-3}$ at 50 °C

sample	R_Φ,[a] 10^{-6} cm^{-1}	$S(0)$	D, 10^{-8} cm^2/s
PPMS	7.1 ± 0.5		
PS(1700)/PPMS	9.5 ± 0.2	0.15 ± 0.03	3.0 ± 0.1
PS(3800)/PPMS	10.9 ± 0.1	0.26 ± 0.04	2.3 ± 0.1
PS(9000)/PPMS	15.2 ± 0.1	0.52 ± 0.03	1.4 ± 0.1
PS(16700)/PPMS	22.1 ± 0.6	0.94 ± 0.06	0.76 ± 0.05

[a] $\lambda = 488$ nm.

Figure 2 shows a Arrhenius plot of the temperature dependence of D in PS(1700)/PPMS and PS(16700)/PPMS blends with the same Φ_{PS}. Clearly, deviations occur for the latter blend as the coexistence curve is approached, whereas at high temperatures both blends display experimentally the same activation energy. Similar behavior was reported for PEO/PPO blends at finite and extreme compositions.[19] It is important therefore, to consider $S(0)$ and proceed the analysis of the measured D through the purely dynamic transport coefficient $D°$. For the present mixture, the $S(0)$ can be obtained[16,19] from the measured Rayleigh ratio R_Φ of the blends only after the latter has been corrected[20] for the contribution of the "concentration fluctuations" in the bulk PPMS.

The values of R_Φ for the bulk PPMS component and the mixtures PS/PPMS are listed in Table I. For comparison, the R_Φ value (arising from density fluctuations) of the standard neat benzene amounts to 3.5×10^{-5} cm^{-1}.[21] The difference R_Φ(blend) − R_Φ(PPMS) is then used to compute $S(0)$ for the PS/PPMS blends, using the value 0.07 cm^3/g for the refractive index increment. On the other hand, the correction of the biased D due to the characteristic decay of bulk PPMS over a similar time range as the PS/PPMS blends at least for the two lower M_w(PS) values (curve 1 in Figure 1) would require a double-exponential representation of the experimental $C(q,t)$. However, the inclusion of the additional relaxation function will render the analysis of the $C(q,t)$ (Figure 1) ambiguous.

The measured composite variation of D with M_w(PS) at 50 °C and for $\Phi_{PS} = 5 \times 10^{-3}$ is depicted in Figure 3a. The upper part of Figure 3 shows the variation of $D°$ (eq 1) with M_w(PS) based on dynamic and static light-scattering measurements. The very weak residual dependence of M_w(PS), especially for M_w(PS) = 1700, is probably due to its weak excess intensity and the distortion of the $C(q,t)$ affecting the value of D. This insensitivity of $D°$ on M_w(PS) variation is in accordance with the theoretical prediction for unentangled "Rouse" *and not* "Zimm" chains[5-9] evaluated also for PEO/PPO,[4] poly(dimethylsiloxane)/poly(ethylmethylsiloxane)[11] at finite concentrations, and dilute PS/PPO[22] mixtures. The latter system is more suitable for verification of the theory since its monodisperse PPO component displays light-scattering intensity arising only from fast density fluctuations.[19] Rouse behavior for the dynamics of the bare PS chains should be

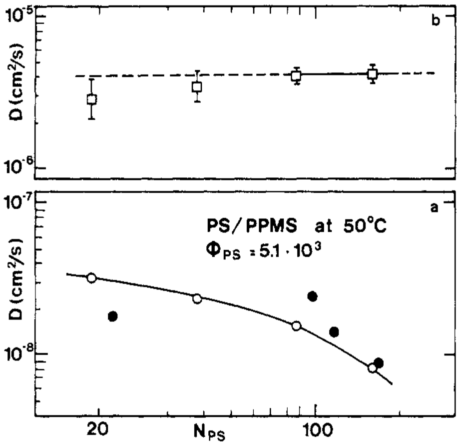

Figure 3. (a) Measured interdiffusion coefficient D in the polymer mixture PS/PPMS with $\Phi_{PS} = 5.1 \times 10^{-3}$ at 50 °C vs the degree of polymerization of PS. The solid symbols are for the interdiffusion data from ref 10. (b) This plot is constructed according to eq 1 and takes into account the thermodynamic interactions in the PS/PPMS blends; the transport coefficient $D°$ based on the data of (a) and the static structure factor listed in Table I. The lines are only to guide the eye.

expected from Kirkwood's diffusion equation;[23] the free-draining term dominates because of the short length of the PS chains and the high viscosity of the polymeric PPO solvent.

The molecular weight dependence in Figure 3a can therefore be accounted for mainly by the variation of $S(0)$ and D_{PS} with M_w(PS). Neglect of $S(0)$ and the type of analysis of $C(q,t)$ performed in ref 10 were probably the reasons for a misinterpretation of the composite interdiffusion coefficient. The latter is also shown (solid symbols) in Figure 3a for comparison. At 50 °C the reported phenomenological molecular weight dependence $D \sim M_w^{-0.34}$, considering only the three highest molecular weight data, contradicts the present discussion of the results for all samples in the framework of existing theories for interdiffusion in compatible blends. Besides, no single scaling law is applicable to the data in Figure 3a. The change of the slope at the highest M_w(PS) sample resembles the increase of $S(0)$ for this sample (Table I). Finally, the thermodynamic slowing down effect expected for unfavorable segment-segment interactions ($\chi_F > 0$) leads to the observed large reduction of the interdiffusion coefficient in Figure 2; i.e., $D \ll D°$.[17-19]

In summary, several aspects emerge from the present photon correlation study of the diffusional dynamics in dilute unentangled PS/PPMS mixtures with $\Phi_{PS} = 5.1 \times 10^{-3}$. A correct analysis of the interdiffusion data should always take into account the thermodynamic interactions between the blend components. For the mixtures with low M_w(PS), the data reduction is complicated by the presence of dynamic light scattering arising from concentration fluctuations in the bulk PPMS sample. As expected for $\chi_F > 0$, the transport coefficient $D°$ (eq 1) is larger than the interdiffusion D near the coexistence curve. There is a strong evidence for a molecular weight independent $D°$ suggesting Rouse behavior for the dynamics of the bare PS chains, in contradiction with the results of a recent study.[10]

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New Synthesis of Poly(phenylene sulfide)s through O_2 Oxidative Polymerization of Diphenyl Disulfide with VO Catalyst

Poly(*p*-phenylene sulfide) (PPS) is commercially produced from *p*-dichlorobenzene and sodium sulfide[1] at a rate of 10^4 tons/yr. Production rates continue to increase year by year. However, this polymerization proceeds at high pressure and temperature and is accompanied by a stoichiometric formation of salt as a byproduct.[2] The salt contamination degrades PPS properties such as electrical performance and moldability.

The ability to facile polymerization via selective oxidation utilizing the abundant and cheap oxidant oxygen often represents a desirable low-cost method for upgrading the value of a raw material. The most successful example is the oxidative polymerization of 2,6-dimethylphenol to yield poly(2,6-dimethyl-1,4-phenylene oxide) with a copper amine catalyst under an oxygen atmosphere at room temperature.[3] But if a similar method is applied to homologous thiophenol, only diphenyl disulfide is yielded due to the coupling of thiophenoxy radicals to each other.[4]

Studies in our laboratory on the preparation of PPS have revealed that thiophenol and diphenyl disulfide can be oxidatively polymerized to PPS via a cationic mechanism by electrical or chemical oxidations.[5,6] This communication describes a novel and convenient synthetic route to poly(phenylene sulfide)s (Scheme I). Diphenyl disulfide is polymerized to PPS with high purity in high yield, in the presence of a catalytic amount of vanadyl

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