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Dynamics of Polystyrene/Poly(vinyl methyl ether) Blends[†]

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ABSTRACT: Diffusion and viscosity measurements were performed on compatible binary mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME). Elastic recoil detection (ERD) studies show that the diffusion coefficient, D_G, of deuterated polystyrene (PS-*d*) chains into highly entangled mixtures of PS/PVME is well described by $D_G \sim M^{-2}$, where M is the molecular weight of the PS-*d* chains. Under conditions of $T - T_g = 100$ °C, where T_g is the glass transition temperature of the blend, the composition dependence of the friction factor of the PS-*d* chains exhibited a very large positive deviation from predictions made by the rule of additivity. The zero-shear-rate bulk viscosity, η, of the system exhibited a similar trend. Temperature-dependent measurements of the diffusivity of PS-*d* chains in a blend containing a weight fraction of $\varphi = 0.4$ of PVME and of the viscosity of the same blend revealed, within the limits of experimental error, that both log η and log (T/D_G) exhibited the same dependence on temperature.

Introduction

The theory of Doi and Edwards[1] has, for the most part, had great success at describing the dynamical properties of polymer melts. In this theory, the dynamics of the melt are assumed to be dominated by the one-dimensional motion of a single chain along an average trajectory, the primitive path, defined by a "tube". If it is assumed that if the environment into which this chain diffuses remains relatively immobile over a time scale τ_d, which characterizes the motion of the chain along the tube, and that the short-time dynamics are described by the Rouse model,[2] then the center of mass diffusion coefficient, D_G, of the chain is[1]

$$D_G = \frac{1}{3}\frac{Nb^2}{\pi^2\tau_d} \tag{1}$$

Here N is the number of monomers that compose the diffusing chain and b is a bond length. The relaxation time τ_d is given by

$$\tau_d = \frac{\zeta N^3 b^4}{\pi^2 k_B T a^2} \tag{2}$$

where k_B is the Boltzmann constant, T is the temperature, and ζ is the monomeric friction coefficient. The parameter a is a step length on the primitive path[1]

$$a^2 = \frac{4}{5}\frac{M_e}{M}Nb^2 \tag{3}$$

In this equation, M is the molecular weight of the diffusant and M_e is the entanglement molecular weight. It is clear from eq 1–3 that

$$D_G = D_0 M^{-2} \tag{4}$$

where D_0 is

$$D_0 = \frac{4}{15}\frac{M_0 M_e k_B T}{\zeta} \tag{5}$$

In this equation, M_0 is the molecular weight of a monomer on the diffusing chain. Experiments have shown that eq 4 adequately describes the molecular weight dependence of diffusion in highly entangled melts.[3–16]

The zero-shear-rate bulk viscosity of the melt is predicted[1] to be proportional to the relaxation time τ_d

$$\eta = \frac{\pi^2}{12}G_N{}^0\tau_d \tag{6}$$

where $G_N{}^0 = \rho RT/M_e$ is the plateau modulus of the melt,[17] R is the universal gas constant, and ρ is the density of the polymer.

The Doi–Edwards model suggests that in homopolymer melts, information about tracer diffusion may be estimated from bulk viscoelastic properties. This becomes clear by considering eqs 1 and 6 where it is shown that both η and D_G depend on τ_d. An obvious consequence of this is that log (T/D_G) should have a similar temperature dependence to log η. There is some experimental evidence that suggests that this is true for many homopolymers.[21–23] However, as shown by eqs 1 and 6, if the temperature dependence of τ_d, or ζ, is very small then the effect of the temperature dependence of $G_N{}^0$ becomes more important and log (T/D_G) and log η will have very different temperature dependencies. This is particularly true in the case of polybutadiene, as discussed in ref 8. A further consequence of this theory is that estimates of D_G may be made from knowledge of viscoelastic parameters of the melt. In particular, Graessley showed that[6]

$$D_0 = \frac{G_N{}^0}{135}M_e{}^2(\langle R^2\rangle/M)\frac{M_c}{\eta(M_c)} \tag{7}$$

where M_c is the critical molecular weight for viscous flow and $\langle R^2\rangle$ is the radius of gyration of a chain of molecular weight M. Estimates of D_G based on this prediction are in good agreement with the experimentally determined values.[1,6,8,9,14]

One noteworthy failure of the theory is its inability to predict the correct $N^{3.4}$ power law chain length dependence of viscosity. Modifications of the theory, such as the inclusion of tube-length fluctuations[18] and constraint release,[1,9,10,12,20,24–27] have made it possible to use this theory to predict other features of entangled homopolymer liquids.

Comparatively, far less is understood about diffusion and viscoelasticity in polymer blends. Much of the work on diffusion in blends has been devoted to understanding mutual diffusion. It is known that for miscible blends, which are characterized by a negative Flory–Huggins interaction parameter, χ, the mutual diffusion coefficient is enhanced over the case where $\chi = 0$.[11–13,28] A thermo-

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dynamic "slowing down" of mutual diffusion is observed in blends that are characterized by $\chi > 0$, yet still within the limit of single-phase stability.[29-33]

Very little work has been done to understand tracer diffusion in blends. Composto et al. have studied the tracer diffusion of deuterated polystyrene (PS-*d*) chains and of deuterated poly(xylenyl ether) (PXE-*d*) into miscible blends of PS and PXE.[11,12] They found that eq 4 gives a reliable description of tracer diffusion of the PS-*d* chains in these systems. The data on the PXE-*d* diffusion was limited. They further found that under conditions where data were compared at the same distance from the glass transition temperature of each blend, the friction coefficients of the PS-*d* and of the PXE-*d* chains exhibited huge positive deviations from predictions based on the rule of additivity.

The intent of this paper is to make some comparisons between diffusion and viscosity in a miscible polymer blend and to try to correlate the behavior with information concerning the thermodynamics of the system. We examined the temperature and molecular weight dependencies of the diffusion of PS-*d* chains into miscible binary mixtures of PS and PVME containing varying volume fractions, φ, of PVME using elastic recoil detection (ERD).[3-5] The temperature dependence of the diffusion in one blend containing 40% by weight of PVME was compared with that of the bulk viscosity of the same blend. We also compared the composition dependence of the friction factor of the PS-*d* chains in the blend with that of the viscosity of the blend under conditions of $T - T_g = 100$ °C. An attempt was made to correlate the behavior of the bulk viscosity with the φ dependence of the χ parameter.

Experimental Section

Since the ERD experimental technique has been described in detail elsewhere,[3-5] it will not be discussed here. The polymers used in this study were two polystyrenes, one of molecular weight 100 000 and the other of 200 000. A series of deuterated polystyrenes whose molecular weights varied from 87 000 to 520 000 were also used. The polystyrenes, which were purchased from Pressure Chemical, and the deuterated polystyrenes, purchased from Polymer Laboratories, were all characterized by molecular weight distributions of $M_w/M_n < 1.05$. The PVME used in this study had a molecular weight of 145 000 and a molecular weight distribution of $M_w/M_n < 1.3$. It was cationically polymerized by using BF_3–Et_2O and then fractionated. The procedure used to prepare samples for these ERD measurements is different from that described in previous publications.[3-5] The previous sample preparation procedure involved floating a thin deuterated polymer film from a bath of distilled water onto the surface of a polymer-coated wafer. Since this process allows water at the interface of the two films and since water is known to affect the phase equilibrium properties of PS/PVME blends, a different procedure had to be used.

A layer (~3 μm) of a PS/PVME blend was solution cast on a silicon substrate. A thin layer (~15 nm) of PS-*d* was spun onto a glass slide using a photoresist spinner. This layer was then floated off the substrate onto a bath of distilled water and then floated back onto the substrate. Water is now present at the interface of the glass substrate and the film. The film can therefore be easily removed. Following this, the coated wafer was placed on top of the outer surface of the PS-*d* film where both films, PS-*d* and PS/PVME, adhered. This process restricts water from the interface of the PS-*d* film and the PS/PVME blend. Samples of varying compositions and chain lengths were prepared. After the diffusion process was allowed to take place at elevated temperatures, ERD was used to determine the volume fraction versus depth profile of PS-*d* in the mixture.[3-5] The diffusion coefficient was then extracted from the profile by using the appropriate solution to the diffusion equation.[3-5] In situations in which the composition of PVME in the blend was high, and consequently the glass transition temperature of the blend was low, the ERD experiments were performed at liquid-nitrogen temperatures.

Measurements of the viscosity were made by using a Rheometrics RDS-2 in parallel-plate geometry.

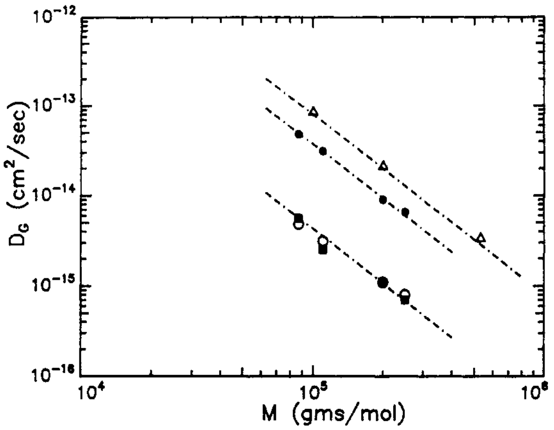

Figure 1. Molecular weight dependence of D_G. The filled circles represent the diffusivity in blends containing weight fractions of PVME of $\varphi = 0.4$ at 107 °C and the open circles data at 86 °C. The squares represent diffusion into PS/PVME blends of $\varphi = 0.12$ at 128 °C. The diffusivity of PS-*d* chains into blends of $\varphi = 0.8$ at 80 °C is represented by the triangles.

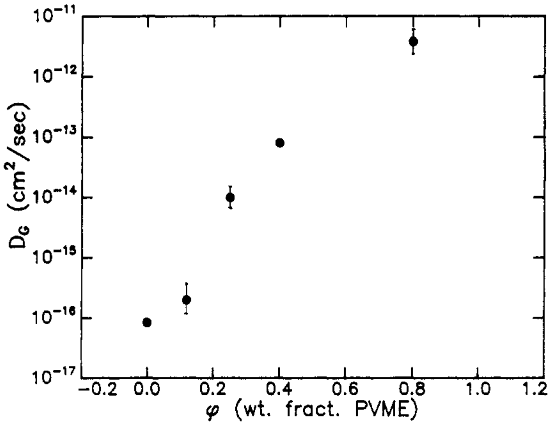

Figure 2. Compositional dependence of D_G at 120 °C is depicted here. The data at $\varphi = 0.12$, 0.4, and 0.8 were obtained by extrapolating temperature-dependent diffusion data obtained a few degrees (less than 18 °C) higher. The other points are actual data.

Results and Discussion

The data in Figure 1 show the diffusivity of PS-*d* chains of molecular weight M into blends of PS and PVME containing varying weight fractions, φ, of PVME. The circles depict the dependence of D_G on M for blends where the PVME weight fractions were $\varphi = 0.4$. The filled circles represent data at 107 °C and the open ones data at 86 °C. The squares depict the molecular weight dependence of D_G for blends of $\varphi = 0.12$ at a temperature of $T = 128$ °C. The diffusivity of PS-*d* chains in blends containing $\varphi = 0.8$ PVME at 80 °C is represented by the triangles. All sets of data show that D_G exhibits a M^{-2} dependence. As discussed earlier, this behavior is well documented in pure homopolymer melts.

It is apparent from the magnitudes of D_G in the figure that D_G exhibits a strong dependence on the weight fraction of PVME in the blends. This can be seen more clearly in Figure 2 where log D_G is plotted as a function of φ at a temperature of 120 °C. The diffusivities reported in this figure are of PS chains of $M = 100\ 000$. The log of the diffusivity varies approximately linearly with φ.

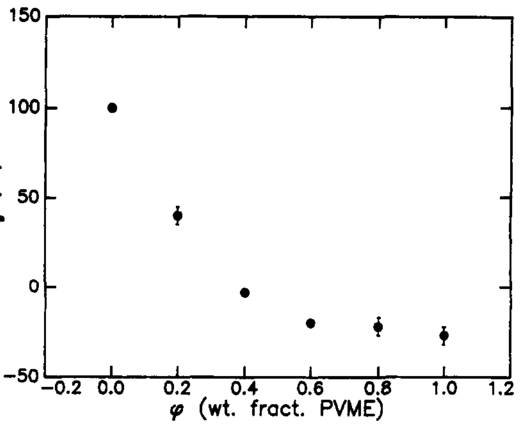

Figure 3. Compositional dependence of the glass transition temperatures of the PS/PVME blends. The data were obtained by using DSC.

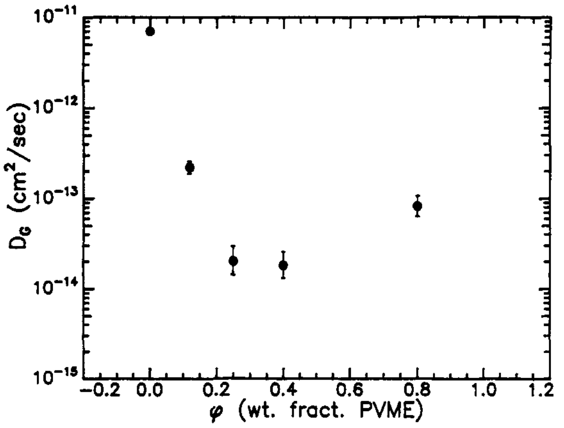

Figure 4. Dependence of D_G on φ at $T - T_g = 100$ °C. The error bars represent the uncertainty in T_g. The data at $\varphi = 0$, 0.4, and 0.8 are actual data obtained at $T = T_g + 100$ °C. The data point at $\varphi = 0.12$ was obtained by extrapolating temperature-dependent data from 15 °C below. The point at $\varphi = 0.25$ (at 130 °C) was obtained by interpolating data in the range of 105–145 °C.

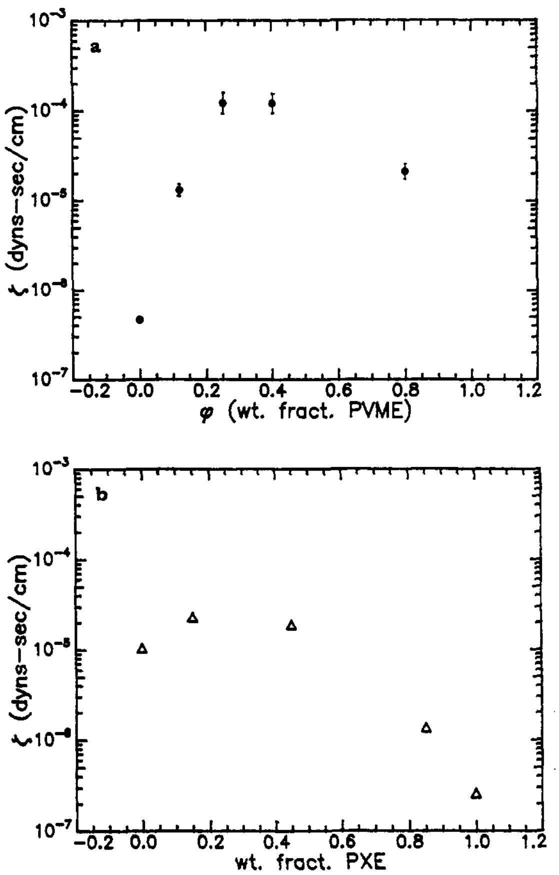

Figure 5. (a) Composition dependence of the friction coefficient of the PS-*d* chains in PS/PVME blends at $T - T_g = 100$ °C. (b) Composition dependence of the friction coefficient of the PS-*d* chains in PS/PXE blends at $T - T_g = 66$ °C. These data were taken from ref 12.

This plot, however, is misleading. The glass transition temperature, T_g, of the blend varies appreciably with φ, as shown in Figure 3. The T_g measurements were performed by using DSC. In these blends, T_g was defined as the onset of the transition (the values that we obtained are in excellent agreement with those published in ref 39). It is well-known that the mobilities, $1/\zeta$, of the chains increase rapidly with increasing temperature beyond T_g. Therefore a comparison at constant T cannot accurately represent the various correlations in the blend that affect the motion of the chains. A more rational comparison should be made at a constant distance above a given reference temperature, the glass transition temperature for each blend. This accounts for the compositional dependence of T_g. Only then can any rational statement be made about the mobilities of the chains.

The data in Figure 4 shows how log D_G varies with φ at 100 °C above the T_g of each blend. The diffusivity decreases over 2 orders of magnitude between $\varphi = 0$ and $\varphi \sim 0.4$, and for larger φ it increases slowly with increasing φ. This very large variation of D_G with φ at $T - T_g =$ constant was also observed in the PS/PXE system.[11,12]

The friction factor of PS in the blend can be determined from the data in Figure 4 using eq 5. The only parameter that is unknown in eq 5 is M_e, which is customarily determined from the plateau modulus of the melt. In the case of polymer blends, this is often not a trivial process since components in the blend may have very different relaxation times. For this reason, the plateau modulus is often not well-defined. An estimate of the M_e of the blend can be made from knowledge of an effective plateau modulus[12,38]

$$[G_N^0(\text{blend})]^{1/2} = \varphi[G_N^0(\text{PVME})]^{1/2} + (1 - \varphi)[G_N^0(\text{PS})]^{1/2} \quad (8)$$

The plateau moduli of the pure components, PS and PVME, were determined to be $G_N^0(\text{PS}) = 2.1 \times 10^6$ dyn/cm² and $G_N^0 = 2.6 \times 10^6$ dyn/cm², respectively. When the densities obtained from ref 39 are used together with the equation $M_e = \rho RT/G_N^0$, the entanglement molecular weight of each blend was determined. The friction factors obtained by the above procedure are plotted in Figure 5a. The data in this figure indicate that ζ increases rapidly with increasing φ until $\varphi \sim 0.4$; beyond this composition it decreases slowly. Figure 5b shows how the friction factor of PS-*d* chains in PS/PXE blends varies with the weight fraction of PXE in the blend. These data were extracted from ref 12. A comparison of the PS/PVME and PS/PXE data suggests that the flexibility of the chains in the mixtures cannot account for this huge variation of D_G with φ. The PXE chains are very stiff in comparison to the very flexible PVME chains. Furthermore, the T_g of PXE is ~220 °C higher than that of PVME. These findings concerning the behavior of D_G are corroborated by measurements of the orientation relaxation in uniaxially stretched PS/PVME and PS/PXE blends by Faivre et al.[34] and Lefebvre et al.,[35-37] respectively. They found that the PS chains acquired a much higher degree of orientation in both blends in comparison to pure PS. It is believed that the friction coefficient of PS in both blends is increased considerably because of the strong molecular

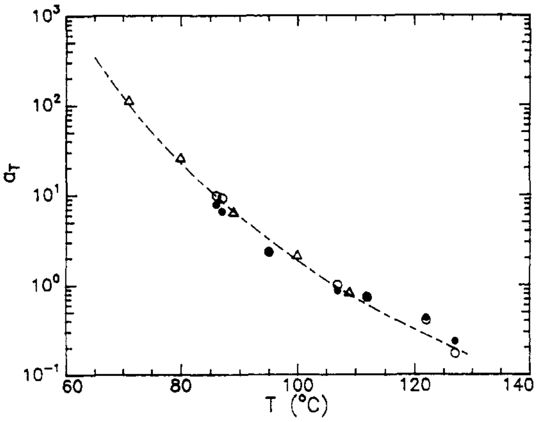

Figure 6. Temperature dependence on log $a_T = \eta(T)/\eta(T_0)$ (triangles) and of log $a_T = D_G(T_0)\,T/D_G(T)\,T_0$ (circles). The filled circles were obtained from the diffusion of PS-*d* chains of M = 87 and the open ones from chains of M = 100.

interactions between the components in the blends. These measurements were also performed at a constant distance above T_g. These measurements of Faivre et al.[34] only included weight fractions of PVME of $\varphi < 0.3$.

Since in homopolymer melts there is a great deal of evidence that suggests that information about a single chain property, namely, the tracer diffusion coefficient, may be obtained from a bulk property of the melt, the viscosity, a natural question arises. It concerns whether a related comparison can be made in mixtures. The monomeric friction factor in an A/B mixture is very complicated in comparison to that of pure homopolymer systems. In the homopolymer system, ζ is related to interactions between like species. In the blend it is related to interactions between like species, A–A (ζ_{AA}) and B–B (ζ_{BB}), and interactions between unlike A–B (ζ_{AB}) species. The manner in which the friction factors are related and their dependence on the interaction parameter, χ, as well as other microscopic thermodynamic parameters in the system are a matter of conjecture. However, it is worthwhile to make a number of *qualitative* comparisons between tracer diffusion and viscosity of this blend.

A comparison of the temperature dependence of the viscosity of a blend containing a weight fraction of $\varphi = 0.4$ of PVME with the diffusivity of PS-*d* chains into the same blend is shown in Figure 6. The triangles represent the temperature dependence of the log of the ratio of the η of the blend at temperature T to η at temperature T_0 = 380 K; $a_T = \eta(T)/\eta(T_0)$. The circles depict the temperature dependence of the log of $a_T = D_G(T_0)\,T/D_G(T)\,T_0$. The filled ones were obtained from the diffusion of PS-*d* chains of M = 87 000 and the open ones that of M = 100 000. Both the bulk viscosity and the tracer diffusion coefficient exhibit similar temperature dependencies. This result suggests that the matrix environment may control the temperature dependence of diffusion. The line drawn through the data was computed by using the Vogel–Fulcher equation[17]

$$\log a_T = A + B/(T - T_\infty) \qquad (9)$$

where B = 594 and T_∞ = 258 K. This temperature dependence differs from that of the pure components, shown in Figure 7. The data in Figure 7 represent the actual viscosity values plotted as a function of temperature. The constants B and T_∞ for PS are 637.5 and 323 K, respectively. No attempt was made to determine the Vogel parameters for the PVME.

Having established that log (T/D_G) and log η have similar temperature dependencies, it is worth investigating the dependence of the zero-shear-rate viscosity on the composition of the blend. The data on the viscosity we have are limited. The circles in Figure 8 show the dependence of η on the weight fraction of PVME in the blend at a temperature of T = 120 °C. This limited set of data exhibit a negative deviation from linearity. Ajji et al. measured the viscosity of PS/PVME blends at 160 °C. These data exhibited a nearly linear dependence on φ at a constant temperature.[40]

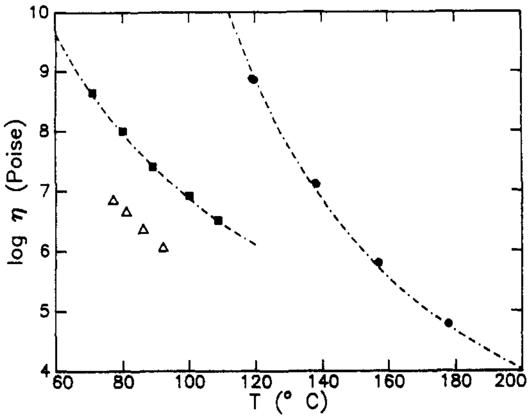

Figure 7. Temperature dependence of the viscosities of PS (circles), of PVME (triangles), and of a $\varphi = 0.4$ blend (squares).

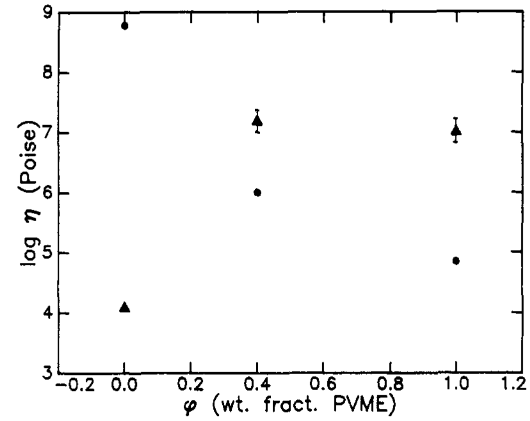

Figure 8. Viscosities of the PS/PVME blend at T = 120 °C (circles) and at $T - T_g$ = 100 °C (triangles).

It may be worth commenting on other PS/PVME data that have been published in the literature. Schneider and Wirbser[41] have compiled data from a variety of PS/PVME studies, including some of their own. The φ dependence of their viscosity data on the highly entangled PS/PVME blends is consistent with ours. Furthermore, their data on the glass transition temperatures for the entangled systems are in good agreement with our data and with other published data.[39] However, the temperature dependencies of the shift factors that they compiled from a variety of studies vary considerably. Our shift factors fall in the middle of the range they reported. There could be a variety of reasons for this huge variation in the temperature dependence of the shift factors. Most of the PVME samples studied were polydisperse, $M_w/M_n > 2$. The PVME that we used for this study had a $M_w/M_n <$ 1.3. The temperature range over which the shift factors were determined is not specified in many studies and in others it is too small to allow a meaningful comparison. Furthermore, Colby[50] has shown that time–temperature superposition evidently fails to work for polymer blends. The temperature dependence of some of the shift factors was obtained by this procedure. These are among a variety of possible reasons for the discrepancies in the various sets of data. To circumvent this problem, we have used the actual viscosities to determine temperature shifts instead of the shift factors. This is a far more reliable procedure.

It should be emphasized that measurements of the log of the viscosity in other homopolymer blends at constant T exhibit small deviations from linearity,[42-46] and in some cases linear dependencies,[47] on composition. There have been debates concerning whether the dependence should be linear or there should be deviations from the additivity rule.[47] This point, however, is irrelevant since a comparison at a constant temperature is inappropriate. As discussed earlier, a more rational comparison should be made at a constant distance above the glass transition temperature of each blend. The triangles in Figure 8 represent such a comparison. It is evident that like the diffusivity, the viscosity increases approximately 2 orders of magnitude between $\varphi = 0$ and $\varphi \approx 0.4$. The decrease is very slight for $\varphi > 0.4$. Recall that the same qualitative behavior was observed for the friction factor of the PS-*d* chains in the blend.

It follows from the data in Figure 8 that the friction factor associated with the viscosity of the blend behaves in this manner. This observation is by no means conclusive. To begin with, the relationship between the friction factors of homopolymers and of polymer mixtures is a matter of conjecture! The simplest approach to obtain a relationship could be to use the Doi–Edwards model, which predicts that the relaxation time $\tau_d = \varphi\tau_{\mathrm{PVME}}(\varphi) + (1-\varphi)\tau_{\mathrm{PS}}(\varphi)$, where τ_{PVME} and τ_{PS} are the relaxation times of the PVME and PS chains, respectively, in the blends. Recall that the relaxation times are proportional to the friction coefficients. The relaxation times could be determined if the diffusion coefficients of the PVME chains and of the PS chains in the blend were both known. The viscosity could then be calculated by using eq 4. In a later paper we will examine "tube renewal" effects in these blend systems.[48] This will allow us to extract the relaxation time of the PVME chains in the blend in an indirect manner. Reference 45 also suggests an alternative procedure.

A comment should be made concerning viscosity measurements of other homopolymer blend systems. Prest and Porter[49] have investigated the compositional dependence of the viscosity of PS/poly(phenylene oxide) (PPO) (*note that PPO is PXE mentioned above*) blends at constant free volume. Unfortunately, they could not perform measurements on blends that contained volume fractions of PPO (PXE) that were greater than 40%. These data, however, do exhibit some degree of curvature that suggests positive deviations from the additivity rule. As mentioned above, Composto et al. performed tracer diffusion measurements in this system and observed the same trends in D_{G} that we did in the PS/PVME system.[11,12] The other system that has been studied is the poly(methyl methacrylate) (PMMA)/poly(ethylene oxide) (PEO) system.[44,46] Like the PS/PXE system, measurements were only performed on blends that contained less than 40% PEO. Furthermore, two sets of measurements were performed by two independent groups and the data from both groups appear contradictory. PMMA/poly(vinylidene fluoride) (PVDF) is yet another blend system.[42,45,46] At constant temperature, the viscosity data exhibit slight deviations from linearity. One of the complications with this blend system is that PVDF does exhibit a tendency to crystallize at certain volume fractions in the blend. Therefore, this is not a good system in which to investigate these effects.

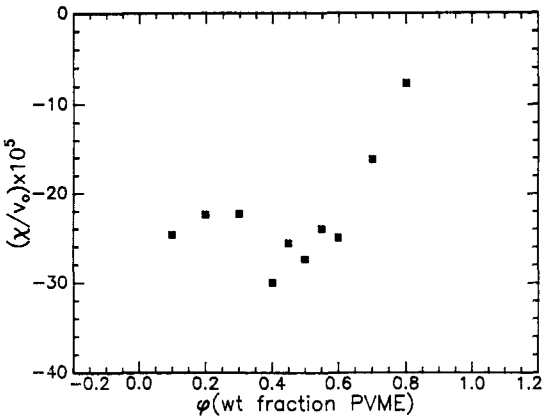

Figure 9. Plot of the compositional dependence of the interaction parameter, normalized by the specific volume, v_0 (cm^3/mol), of the blend, at $T - T_g = 100$ °C. These data were extracted from ref 53.

The log η of polymer blend systems that involve copolymers evidently do not exhibit large deviations from linearity. The log η of PMMA/poly(styrene–acrylonitrile) (SAN)[44,45] and the PAN/poly(styrene–maleic anhydride)[51,52] copolymer systems exhibit a nearly linear dependence on φ at a constant $T - T_g$ or at a constant free-volume state. It is obvious from this that copolymer mixtures exhibit very different viscoelastic behavior than do homopolymer mixtures. This is not surprising.

Having demonstrated the huge deviation of the viscosity from linearity and noting that the friction factors between the components of an A/B blend ($\zeta_{\mathrm{AA}}, \zeta_{\mathrm{BB}}, \zeta_{\mathrm{AB}}, \zeta_{\mathrm{BA}}$) should be influenced by the χ parameter, we feel it is worthwhile to investigate the compositional dependence of χ at a constant distance above the glass transition temperature. Such a comparison is shown in Figure 9.[53] The χ parameter exhibits negative deviations from the additivity rule. χ has its most negative value in the middle of the composition regime where the largest deviations of the viscosity and of the friction factors occur from linearity. When χ is most negative, it may be argued that a monomer of type A experiences a larger "frictional" resistance when traversing an environment of A/B molecules. While the results of the zero-shear-rate viscosity appear to be consistent with the variation with χ, a direct connection between a single chain property, such as D_{G}, is not clear-cut. The χ parameter should only directly affect the bulk mutual diffusion coefficient as opposed to D_{G}. The data suggest, nevertheless, that D_{G} may be affected indirectly through the friction factor.

Conclusion

We have demonstrated that the diffusion coefficient, D_{G}, of PS-*d* chains in binary mixtures of PS and PVME varies as M^{-2}. We have also shown that log (T/D_{G}), for chains diffusing in a blend containing 40% PVME, exhibits essentially the same temperature dependence as log η of the same blend. This temperature dependence differs from that of PS and of PVME. At a constant temperature, log D_{G} and log η exhibited an approximately linear dependence on φ. This finding concerning the viscosity is consistent with published data on this and other systems. However, since the mobilities of the chains increase rapidly beyond the highly composition-dependent T_g of each blend, comparisons were made at a constant distance above T_g. Under these conditions, the log of the friction factor extracted from D_{G} exhibited a huge positive deviation from linearity. Our limited data on the viscosity behaved similarly. This observation is by no means conclusive particularly because the relation between ζ and ζ_{vis} is a matter of conjecture at this point.

We investigated the compositional dependence of χ at $T - T_g = 100$ °C and found that χ had its most negative value in the middle of the composition regime where ζ and the viscosity deviated most from linearity. The PS/PVME data of Ajji et al. also exhibit the same trend when the T_g corrections are made. The behavior of a bulk property such as the viscosity is more readily rationalized in terms of χ. In the case of a single chain property such as D_G, the matter is less clear-cut. It appears, nevertheless, that D_G may be affected indirectly through the friction factor.

There is a variety of data on the viscosity of different homopolymer blend systems. Our limited data on the dependence of η on φ is not inconsistent with the findings in those systems. Interestingly, unlike homopolymer mixtures, the viscosity of mixtures that include copolymers exhibits only mild deviations from linearity under conditions of a constant distance above T_g or at a constant state of free volume. The information presented in this paper suggests a number of important problems that are yet unresolved.

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