Diffusion in blends of poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile)

Eugene Kim*
Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853, USA

and Edward J. Kramer†
Department of Materials Science and Engineering and the Materials Science Center, Cornell University, Ithaca, NY 14853, USA

and Wan C. Wu and Paul D. Garrett
The Chemical Group of Monsanto Company, 730 Worcester Street, Springfield, MA 01151, USA
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Forward recoil spectrometry was used to obtain the tracer (D^*) and mutual ($\tilde{D}$) diffusion coefficients in a miscible polymer blend of poly(methyl methacrylate) (PMMA, $T_g = 136°C$) and poly(styrene-*co*-acrylonitrile) with ~23 wt% acrylonitrile content (SAN, $T_g = 112°C$). For blends with SAN weight fraction w of 0.2 and 0.5, the temperature dependence of D^* for both species was nearly identical. Tracer diffusion coefficients D^*_{PMMA} and D^*_{SAN} were determined for matrices consisting of 176 000 molecular weight SAN ($w = 0.5$) and various molecular weights of PMMA ranging from 27 000 to 840 000. The results were consistent with those expected from the mechanisms of reptation and constraint release. Analysis of the tracer diffusion coefficients D^* showed that SAN has a monomer friction coefficient, $\zeta_{0,PMMA}$, about five times smaller than that of PMMA ($\zeta_{0,PMMA}$) in a matrix of pure PMMA, but the difference decreased monotonically as w increased, so that the ζ_0 values were nearly equal when $w = 1$. Corresponding to this relative change in ζ_0, the glass transition process is broad for PMMA-rich blends and narrow for SAN-rich ones, raising the possibility that the difference in ζ_0 in the PMMA-rich blends is due to the existence of two local glass transitions, one for each species in the blend. For blends at the composition of $w = 0.5$, the $\tilde{D}$ was measured as a function of PMMA molecular weight. The data followed closely the predictions of the fast theory, the result expected if $\tilde{D}$ is ultimately controlled by the diffusion of the faster moving species. From the measurements of $\tilde{D}$ and D^* at 187°C, the composition dependence of the Flory interaction parameter was also obtained, which showed good agreement with the recent small angle neutron scattering results by Hahn *et al.*

(Keywords: tracer diffusion coefficient; mutual diffusion coefficient; fast theory)

INTRODUCTION

Poly(methyl methacrylate) (PMMA) and the random copolymer (SAN) of styrene (S) and acrylonitrile (AN) form a miscible blend over the entire composition range within certain limits of AN content (9–33 wt%)[1,2]. The interesting feature of this blend is that even though no exothermic binary interaction exists between either PMMA and AN or PMMA and S units, the strong intramolecular repulsive interaction between S and AN units causes the blend to have a negative enthalpy of mixing[3,4]. The thermodynamic interaction in the blend has been investigated using small angle neutron scattering (SANS)[5–7], and the phase separation phenomena have been studied above the lower critical solution temperature (*LCST*)[8,9]. The kinetics of the development of adhesion at the interface between the two polymers has also been investigated using ellipsometric[10,11] and fracture strength measurements[1,12,13]. However, there are still some fundamental questions which are not fully answered because direct diffusion measurements are not yet available, and we are going to address those questions.

Diffusion experiments have been shown to provide valuable information about both dynamic[14–17] and thermodynamic[18–20] aspects of miscible polymer blends. We used forward recoil spectrometry (FRES) for the depth profiling of deuterium and hydrogen atoms to obtain both tracer and mutual diffusion coefficients. Some established theories of diffusion in polymer blends, necessary for the present investigation, are briefly reviewed. The experimental procedure is described, and

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[*] Present address: Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA
[†] To whom correspondence should be addressed

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the results on tracer and mutual diffusion are discussed followed by a summary.

Tracer diffusion

Measurement of tracer diffusion allows one to directly probe mobility of the diffusing species under the influence of surrounding molecules. This can be done by monitoring the concentration gradient of the probe molecules after diffusion for overall concentrations which are dilute enough that the corresponding diffusion coefficient is independent of the amount of the probe molecules present in the matrix (the mutual diffusion situation, where the bulk convective flow of the materials takes place, will be discussed later). For a tracer chain constrained by a highly entangled matrix of other polymer chains[16,17,21], the reptation model predicts that the tracer diffusion coefficient $D^*_{\mathrm{rep},i}$ will be independent of the molecular weight of the matrix chains and will decrease as M_i^{-2}, where M_i is the molecular weight of the tracer chain, namely:

$$D^*_{\mathrm{rep},i}=\frac{D_{0,i}}{M_i^2} \tag{1}$$

$$D_{0,i}=\frac{4}{15}\,\frac{M_{0,i}M_{\mathrm{e,blend}}k_{\mathrm{B}}T}{\zeta_{0,i}} \tag{2}$$

where $M_{0,i}$ and $\zeta_{0,i}$ are the molecular weight of the monomer unit* and monomer friction coefficient of component i, respectively, $M_{\mathrm{e,blend}}$ is the entanglement molecular weight M_{e} of the blend as a whole, and $k_{\mathrm{B}}T$ has its usual meaning. In this model, the tracer molecule is imagined to undergo a curvilinear motion along a tube-like path, the lateral dimensions of which are determined by the constraints offered by the matrix chains (entanglement). The mobility of the monomer segment is characterized phenomenologically by a monomer friction coefficient, ζ_0. The characteristic relaxation time for a given polymer i, called reptation time $\tau_{\mathrm{R},i}$, was derived as[22]:

$$\tau_{\mathrm{R},i}=\frac{\langle R_i^2\rangle M_i^2}{3\pi^2 D_{0,i}} \tag{3}$$

where $\langle R_i^2\rangle$ is the mean square end-to-end distance.

On the other hand, when the tracer chain is in an entangled, but not sufficiently slowly relaxing environment, an additional contribution is considered which is called constraint release[22]. The overall diffusion coefficient becomes the sum of the contributions of reptation and constraint release:

$$D_i^*=D^*_{\mathrm{rep},i}+D^*_{\mathrm{CR},i} \tag{4}$$

We adopt the formulation of Composto *et al.*[15] for $D^*_{\mathrm{CR},i}$ in miscible polymer blends which was developed based on the original idea of Graessley[22]. He introduced one extra parameter, z, which represents the number of suitably situated constraints (reflecting the strength of the contribution of the mechanism). The constraint release diffusion coefficient was written as:

$$D^*_{\mathrm{CR},i}=\frac{4\langle R_i^2\rangle M^2_{\mathrm{e,blend}}}{75M_i^2\tau_{\mathrm{w}}} \tag{5}$$

where τ_{w}, called waiting time, was given by:

$$\tau_{\mathrm{w}}\cong\int_0^\infty \mathrm{d}t\left[\phi_1\exp\left(\frac{-t}{\tau_{\mathrm{R},1}}\right)+\phi_2\exp\left(\frac{-t}{\tau_{\mathrm{R},2}}\right)\right]^z \tag{6}$$

In the blend of polystyrene (PS) and poly(xylenyl ether)[15], the molecular weight dependence experiments showed that z was different for each component chain and also was a strong function of composition (ranging from 2.2 to 19.0), while for the homopolymers PS[23] and polybutadiene[24], a value of ~3.5 was found.

Mutual diffusion

For mutual diffusion, the mobilities of both species 1 and 2 in a binary blend are important and the full free energy of mixing (not just the combinatorial entropy which was the only driving force for tracer diffusion, but also enthalpic and non-combinatorial entropic contributions) drives the interpenetration process. It has been experimentally shown that the mutual diffusion rate was enhanced[20,25] or inhibited[18], depending on the thermodynamic contributions other than the combinatorial entropy. The second derivative of the free energy of mixing with respect to the composition gives the extra thermodynamic driving force for diffusion:

$$\frac{\mathrm{d}^2\left(\dfrac{\Delta g_{\mathrm{mix}}}{RT}\right)}{\mathrm{d}\phi_1^2}=2(\chi_{\mathrm{s}}-\chi) \tag{7}$$

where χ is the Flory interaction parameter and χ_{s} is its value at the spinoidal given by:

$$\chi_{\mathrm{s}}=\frac{1}{2}\left(\frac{1}{\phi_1N_1}+\frac{1}{\phi_2N_2}\right) \tag{8}$$

In the above equation, N_i is the degree of polymerization which is obtained from the molar volume of polymer i divided by the lattice reference volume, v_0. The mutual diffusion coefficient was written as:

$$\tilde{D}=\frac{\mathrm{d}^2\left(\dfrac{\Delta g_{\mathrm{mix}}}{RT}\right)}{\mathrm{d}\phi_1^2}\phi_1\phi_2D_{\mathrm{T}} \tag{9}$$

The relationship between the above mobility factor, D_{T}, and the tracer diffusion coefficients of component molecules has been proposed[26-30]. Based on instantaneous relaxation of the osmotic pressure, Kramer *et al.*[26] and Sillescu[27] arrived at the result (called the 'fast theory') that the mutual diffusion is essentially governed by the fastest moving species. In the fast theory, convective bulk flow compensates for the mismatch in fluxes of the two species. The intrinsic transport coefficient D_{T} was given as follows:

$$D_{\mathrm{T}}=\phi_2D_1^*N_1+\phi_1D_2^*N_2 \tag{10a}$$

On the other hand, Brochard *et al.*[28,29] proposed a

To maintain a consistency in the use of degree of polymerization throughout this paper, the size of the monomer unit was defined to be the same as that of a lattice site. For the copolymer SAN, it was already defined as an average quantity and the difference in the size of structural monomer units was small (78.9 cm^3 mol^{-1} for SAN and 84.0 cm^3 mol^{-1} for PMMA). The lattice reference volume, v_0, was chosen as the geometric mean of the volume of the constituent structural monomer units (81.4 cm^3 mol^{-1}) and then the molecular weight of the monomer unit, $M_{0,i}$, was calculated by multiplying v_0 by the density of polymer i (1.08 g mol^{-1} for SAN, 1.14 g mol^{-1} for d-SAN and 1.28 g mol^{-1} for d-PMMA) different expression (called the 'slow theory') based on a build up of the osmotic pressure during the diffusion process so that the fluxes in both directions should cancel. They claimed that:

$$\frac{1}{D_T} = \frac{\phi_2}{D_1^* N_1} + \frac{\phi_1}{D_2^* N_2} \tag{10b}$$

While the slow theory also contains certain comprehensive features, recent experiments on the molecular weight dependence of $\tilde{D}$[14,25] and on the displacement of markers at the interface in a diffusion couple[31–33] strongly support the fast theory. However, recent experiments which apparently agree with the slow theory can also be found. Yukioka *et al.*[10,11] have measured the kinetics of the broadening of the interface between SAN and PMMA using ellipsometry, from which they extracted a mutual diffusion coefficient $\tilde{D}$. They claimed that the molecular weight dependence of $\tilde{D}$ could be explained by the slow theory. We will make a precise comparison of the two theories for SAN/PMMA blends when the mobility factor D_T is varied by changing the degree of polymerization of a component chain. This procedure is possible due to the fact that all the parameters in D_T, including both tracer diffusion coefficients, can be measured independently.

EXPERIMENTAL

The molecular weights of various polymers of protonated and deuterated (d-)SAN and PMMA which have polydispersity indices of ~2 and close to 1, respectively, are listed in *Tables 1* and *2*. Azeotropic AN content (~23 wt%) SAN was used throughout the studies except for the study on the effect of AN content level on tracer diffusion where protonated SAN with 27.2 wt% AN was also used. In d-PMMA every hydrogen was replaced by deuterium whereas in d-SAN only hydrogens in the styrene units were replaced by deuterium. Protonated SANs were commercial samples from Monsanto Chemical Co. and d-SAN was synthesized by polymerizing a mixture of acrylonitrile and perdeuterated styrene monomers using t-butyl peroctoate as a free radical initiator and terpinolene as a chain transfer agent. The details of the synthesis are discussed elsewhere[34]. The *LCST*[5] for the blend of PMMA and SAN with 25 wt% AN content and the ceiling temperature of PMMA[35] were known to be ~250°C and 220°C, respectively, and our experimental temperatures did not exceed 220°C.

Details of the sample preparation, the FRES measurements and their analysis to obtain diffusion coefficients have been presented elsewhere[15,16,25,36] and will only be briefly described here. For tracer diffusion measurements, the bottom matrix layer of the (protonated) blend (~1 μm thick) was first prepared by spin casting a solution of the polymers in methyl isobutyl ketone onto a Si wafer. A thin (<20 nm) layer of the deuterium labelled tracer polymer was spun cast onto a glass slide and floated off onto the surface of a deionized water bath. From there it was picked up on the thick matrix film.

Table 1 Weight-average molecular weight and polydispersity indices of protonated and deuterated poly(methyl methacrylate) (PMMA and d-PMMA, respectively)

	M_w	M_w/M_n	Source
PMMA	27000	1.11	Polymer Laboratories
	64000	1.09	Polymer Laboratories
	107000	1.1	Polymer Laboratories
	136000	1.1	Kodak
	185000	1.1	Polymer Laboratories
	334000	1.30	Kodak
	840000	1.53	Kodak
d-PMMA	39000	1.1	Polymer Laboratories
	57500	1.06	Polymer Laboratories
	83000	1.05	Polymer Laboratories
	165000	1.19	Kodak
	317000	1.05	Polymer Laboratories
	546000	<1.5	Kodak

Table 2 Weight-average molecular weight, polydispersity indices and acrylonitrile content of protonated and deuterated poly(styrene-*co*-acrylonitrile) (SAN and d-SAN, respectively)

	M_w	M_w/M_n	AN (wt%)	Source
SAN	176000	2.36	22.9	Monsanto
d-SAN	114000	1.96	22.6	Monsanto
d-SAN	179000	2.20	22.4	Monsanto
SAN27	242000	2.98	27.2	Monsanto

The thickness of the tracer layer was made to be thin enough so that the tracer polymers became rapidly diluted to a small concentration. When the thickness of the top layer of d-SAN was <~20 nm, which led to a concentration profile in which the concentration of the deuterated species is always <10% after diffusion, the diffusion coefficient obtained did not change by decreasing the thickness further. When d-PMMA was put on the surface, however, surface segregation of d-PMMA happened after diffusion due to its lower surface energy[37]. In this case, we obtained D^* in two ways: (1) the part of the FRES spectrum at the surface which was different from the Fickian profile was ignored and only the profile well below the surface was analysed to determine D^*; or (2) a tri-layer film was prepared in which the tracer layer was sandwiched by two matrix layers so that d-PMMA was not in initial contact with the surface and so diffusion could take place in both directions. Both methods resulted in values of D^* which were indistinguishable.

For measuring the mutual diffusion coefficient, we used d-PMMA which has a narrower molecular weight distribution and has more deuterium content than d-SAN as the labelled component, so that a more accurate $\tilde{D}$ determination was possible. The difference in concentration between the two layers was made to be small (10%) in order to minimize the influence of the composition dependence of $\tilde{D}$ on the analysis: a top layer ~300 nm thick with a weight fraction of SAN of $w+0.05$ (or $w-0.05$) was put on a bottom layer with a concentration of $w-0.05$ (or $w+0.05$). During the data collection, the sample was placed on the copper block which was cooled by circulating liquid nitrogen and a low beam current was used (<10 nA) to minimize the ion beam damage of PMMA. The data were checked after different $^4He^{2+}$ ion fluences to see whether the shape

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* The slow theory was later modified so that equation (10b) holds when the diffusion distance is larger than a length $\sqrt{D_1^* \tau_{R,2}}$, which is the depth scale of swelling of slow chain 2 by fast moving chain 1 (ref. 29). Our diffusion distance was made to be ~150 nm, and it was sufficiently larger than the above swelling depth which was calculated to be <40 nm in the molecular weight range studied

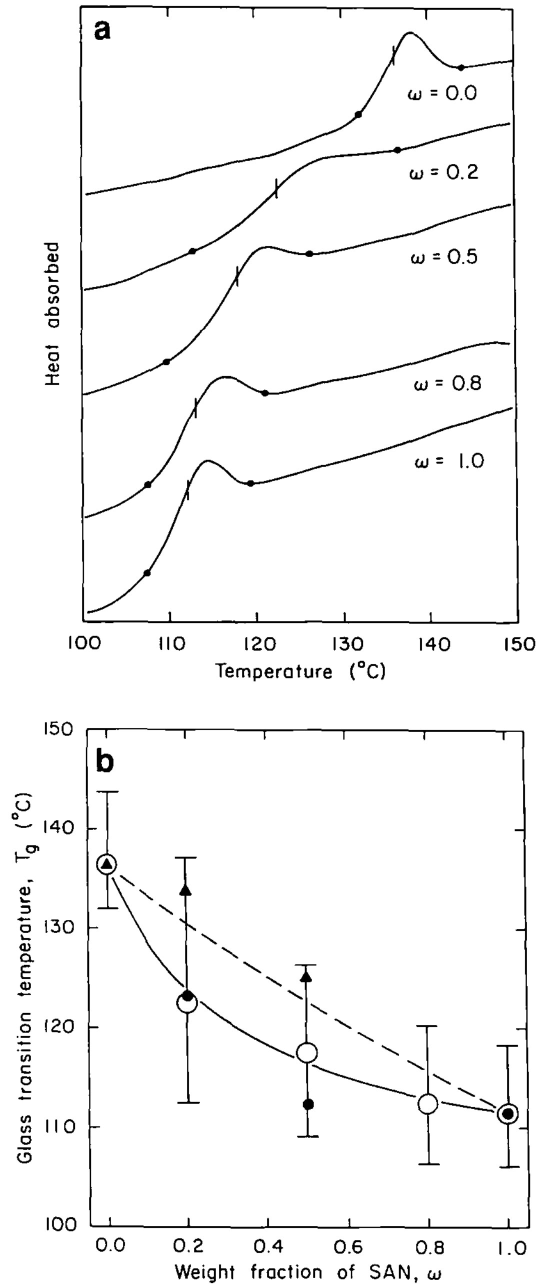

Figure 1 (a) Shape of the glass transition at various compositions measured by d.s.c. at a heating rate of 10°C min^{-1}. The inflection points as well as the starting and ending points of the transitions are also marked. (b) Glass transition temperature T_g (d.s.c.) *versus* weight fraction w of 176000 molecular weight SAN mixed with 334000 molecular weight PMMA. Glass transition temperature (inflection point, ○) and its breadth (starting and ending point of the transition) were determined from (a). The solid and the broken lines represents the predictions of the Gordon-Taylor equation with $K = 0.25$ and of the Fox equation, respectively. The local glass transition temperatures T_g' of SAN (●) and PMMA (▲) obtained by assuming that T_g' for each component is the temperature at which the monomer friction coefficient equals 1000 and 83 dyn s cm^{-1}, respectively, are also shown

of the peak remained the same; within experimental errors no effect of ion fluence was observed.

The glass transition process was investigated using d.s.c. (DSC 910, Du Pont Instruments). The samples with $w = 0$, 0.2, 0.5, 0.8 and 1 made of 176000 molecular weight SAN and 334000 molecular weight PMMA were annealed at 140°C under vacuum for 3 days and then cooled to room temperature. The d.s.c. scan was made as the samples were heated at a rate of 10°C min^{-1}. The resulting d.s.c. data at the various compositions are shown in *Figure 1a*. The glass transition temperature (T_g (d.s.c)) was determined by the inflection point and the breadths were obtained by the onset and termination of the transition (*Figure 1b*). The difference in T_g (d.s.c.) between the two pure components was observed to be 24°C, which was comparable to but larger than the values obtained by Suess *et al.*[2] (~15°C) and by Naito *et al.*[38] (19°C). As noted by Suess *et al.*[2], the glass transition became extraordinarily broad as the blend becomes PMMA rich ($w = 0.2$). Our composition dependence data were not in agreement with the Fox equation [equation (11)] unlike the observations of Suess *et al.*[2], but the Gordon-Taylor equation with $K \cong 0.25$ [equation (12)] gave a better fit, which is again in disagreement with the observation by Naito *et al.*[38] who found that $K \cong 1$ explained their data well*. The equations are:

$$\frac{1}{T_g} = \frac{w}{T_{g,\mathrm{SAN}}} + \frac{1-w}{T_{g,\mathrm{PMMA}}} \tag{11}$$

$$T_g = \frac{wT_{g,\mathrm{SAN}} + [K(1-w)T_{g,\mathrm{PMMA}}]}{w + K(1-w)} \tag{12}$$

Finally we used the entanglement molecular weights of the blends measured by Wu[39] from the plateau modulus data, which showed a weak composition dependence (varied from 8800 for pure PMMA to 11500 for $w \cong 0.8$).

RESULTS AND DISCUSSION

Molecular weight dependence of tracer diffusion

The tracer diffusion coefficients of d-SAN ($M_{\mathrm{d\text{-}SAN}} = 179000$) and d-PMMA (various molecular weights $M_{\mathrm{d\text{-}PMMA}}$) were measured as a function of the molecular weight of PMMA (P_{PMMA}) in a blend ($w = 0.5$) with SAN of fixed molecular weight ($P_{\mathrm{SAN}} = 176000$) at a temperature of 181°C. These data are plotted in *Figure 2*. The values of D^* remained unchanged for high enough P_{PMMA} and began to increase at smaller P_{PMMA}, which could be explained by the onset of a contribution of the constraint release mechanism at these P_{PMMA} values. The tracer diffusion coefficients of d-PMMA for the high P_{PMMA} ($= 334000$) blend where the values of $D^*_{\mathrm{d\text{-}PMMA}}$ were independent of matrix molecular weight are plotted as a function of $M_{\mathrm{d\text{-}PMMA}}$ in *Figure 3*. A linear least square fit to the data gave a slope of -2.17 which was in good agreement with reptation prediction of -2. In *Figure 2* the tracer diffusion coefficients are compared to predictions based on equation (4). When a value of 3.5 for the number of suitably situated constraints, z, was used, the contribution of constraint release was too small to fit the data at low P_{PMMA}. In order to fit the data, $z \cong 5.5$ has to be used for both $D^*_{\mathrm{d\text{-}PMMA}}$ and $D^*_{\mathrm{d\text{-}SAN}}$, which indicates that both chains are influenced to a similar extent by the constraint release mechanism. Han and Kim[40] also investigated the zero shear rate viscosity in SAN/PMMA blends at various compositons. They used equation (6) for the waiting time and a value of z in the

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* Naito *et al.* claimed that the value of K could be given as a ratio of the thermal expansion coefficient of the free volume of the component species, and the value of 0.25 is unrealistically small in this respect

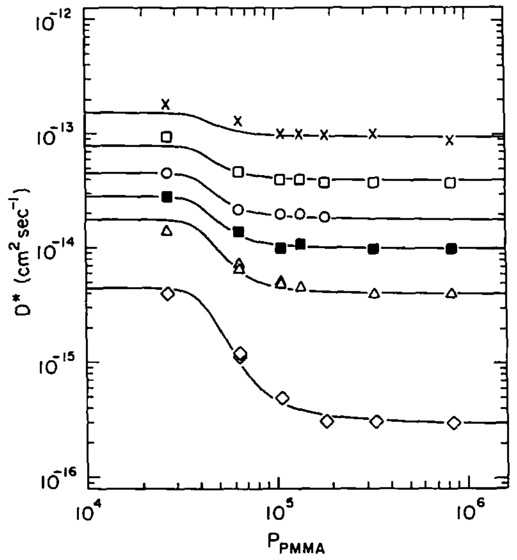

Figure 2 Tracer diffusion coefficients, D^*_{SAN} and D^*_{PMMA}, of d-SAN and d-PMMA were measured at 182°C as a function of the molecular weight of PMMA in the matrix, P_{PMMA}, in a blend of $w=0.5$ made with SAN of fixed $P_{SAN}=176000$. Tracer molecules used were d-SAN of 179000 (■), and various molecular weight of d-PMMA, $M_{d\text{-}PMMA}$: 39000 (×), 57500 (□), 83000 (○), 165000 (△), and 546000 (◇). Solid lines were the predictions obtained using equation (4). The number of suitably situated constraints, z, used was 5.5, to take the constraint release contribution into account

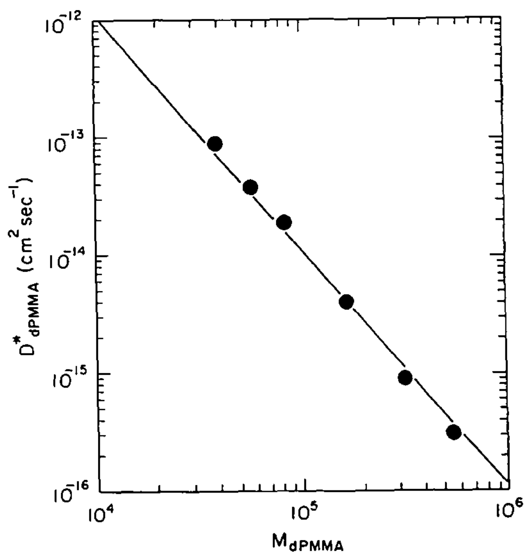

Figure 3 Tracer diffusion coefficient D^*_{PMMA} of d-PMMA chains *versus* molecular weight $M_{d\text{-}PMMA}$ of d-PMMA chains in the matrices with a weight fraction w of SAN of 0.5 at 182°C (●). The matrix molecular weight of SAN and PMMA, P_{SAN} and P_{PMMA}, were 176000 and 334000, respectively. The solid line has a slope of -2

range of ~3–6 to produce a prediction which fit their data reasonably. Our results at $w=0.5$, while more sensitive to z, are in agreement with their results.

Temperature dependence of tracer diffusion

The temperature dependence of tracer diffusion coefficients is shown in *Figures 4a* and *b* for $w=0.2$ and 0.5, respectively. The values of D^* were shifted to those of a tracer chain with the molecular weight of 100000* using equation (1) to make possible a comparison at the same molecular weight. Dynamic processes in amorphous materials have been well described by the Vogel-Fulcher equation which can be derived from the free volume model[41]. The main source of the temperature dependence is that of ζ_0 which is given by the Vogel-Fulcher equation as[42]:

$$-\log\frac{D^*}{T}\propto\ln\zeta_0=A+\frac{B}{T-T_\infty}\tag{13}$$

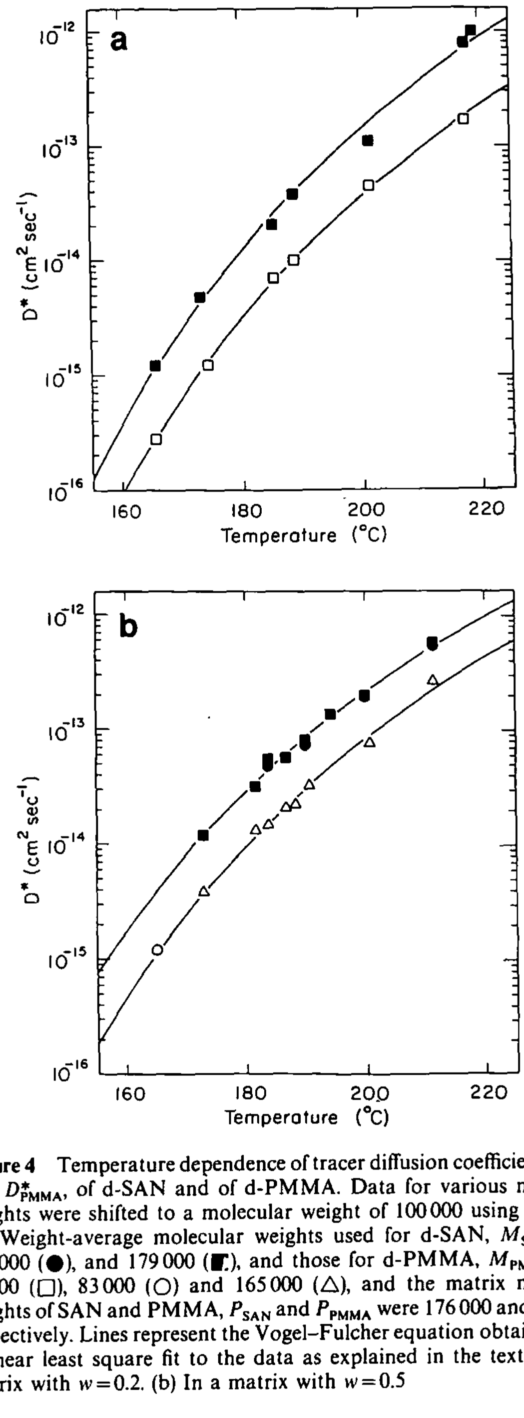

Figure 4 Temperature dependence of tracer diffusion coefficients, D^*_{SAN} and D^*_{PMMA}, of d-SAN and of d-PMMA. Data for various molecular weights were shifted to a molecular weight of 100000 using equation (1). Weight-average molecular weights used for d-SAN, M_{SAN}, were 114000 (●), and 179000 (■), and those for d-PMMA, M_{PMMA}, were 57500 (□), 83000 (○) and 165000 (△), and the matrix molecular weights of SAN and PMMA, P_{SAN} and P_{PMMA} were 176000 and 334000, respectively. Lines represent the Vogel-Fulcher equation obtained from a linear least square fit to the data as explained in the text. (a) In a matrix with $w=0.2$. (b) In a matrix with $w=0.5$

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*The data in *Figure 4b* show that the d-SAN with two different molecular weights (114000 and 179000) could be scaled by M^{-2} to nearly the same values, suggesting that reptation mechanism also holds for d-SAN where T_∞ is the Vogel temperature at which the (extrapolated) free volume vanishes. We used the values of T_∞ obtained by Wu[39] which were 58.3°C below T_g at all compositions. As seen in *Figure 4*, the D^* of the two chains varied with temperature in a similar fashion (i.e. nearly the same values of T_∞ and B apply to both), which also implies that the time-temperature superposition principle should hold. However, the component chains did not have the same monomer friction coefficient with that for PMMA being almost five times that for SAN resulting in a $D_{0,\mathrm{SAN}} \cong 5D_{0,\mathrm{PMMA}}$ for $w = 0.2$. The glass transition is a kinetic process with a corresponding correlation time τ_{T_g} which takes place at a temperature significantly above T_∞. The τ_{T_g} is a function of the heating rate, and at a given finite value of heating rate, it would be proportional to ζ_0. Following the pioneering work of Chung *et al.*[43] who showed that the different species in a miscible polymer blend had different local T_gs, we defined local T_gs for PS and tetramethylbisphenol-A polycarbonate (TMPC) in the miscible blend of the two from our measurements of ζ_0 derived from tracer diffusion coefficients of the two species[17]. The local T_g was defined for each species in the blend to be the temperature at which ζ_0 becomes the value for the pure component at the T_g measured by d.s.c. The phenomenological value of ζ_0 at T_g(d.s.c.) could be estimated from the extrapolation of the self diffusion coefficient (D^* of the deuterated species into the same species which is not deuterated). Using this value of ζ_0, T_gs of each species at various compositions could be obtained. Interesting consequences were that the local T_gs for each species were different at various compositions, which was also in accord with the broadening of the glass transition shown by d.s.c., and that the component with the higher T_g as a pure component showed a higher local T_g, and as a consequence a larger ζ_0, in the blend. The temperature-dependent self diffusion coefficients of SAN[34] and PMMA[*] were used to obtain ζ_0s at T_g(d.s.c.). These turned out to be 1000 dyn s cm^{-1} for SAN and 83 dyn s cm^{-1} for PMMA[†]. The local T_gs for SAN and PMMA in the blends were obtained by finding the temperatures at which ζ_0s for each species becomes the corresponding value for the pure component (i.e. 1000 dyn s cm^{-1} for SAN and 83 dyn s cm^{-1} for PMMA). We obtained new T_g' and T_∞' $(= T_g' - 58.3)$[39] and the corresponding Vogel-Fulcher plots for ζ_0 are shown in *Figures 5a* (at $w = 0.2$) and *b* (at $w = 0.5$). In both cases, the magnitude of each ζ_0 at the same $1/(T - T_\infty')$ became comparable, but some difference in the slope was created by the separate choice of T_∞' for each component. In *Figure 1b* the new T_g's are shown. In spite of the possible error in extrapolation procedure, they are seen to be well within the broad transition observed experimentally. In addition, the value for d-PMMA was significantly higher than that for d-SAN. The difference still remains if the same value of ζ_0 at T_g (any value between the above two ζ_0 values) is used for both species to find the T_gs. This result was again in agreement with the previous hypothesis[17] that PMMA which has a higher T_g as a pure component has a higher local T_g than SAN in blend. This larger local T_g may account for some of the difference in ζ_0 between the two components in the blend. However, the differences in these local T_gs are small compared to the breadth of transition, especially in the blend with $w = 0.2$.

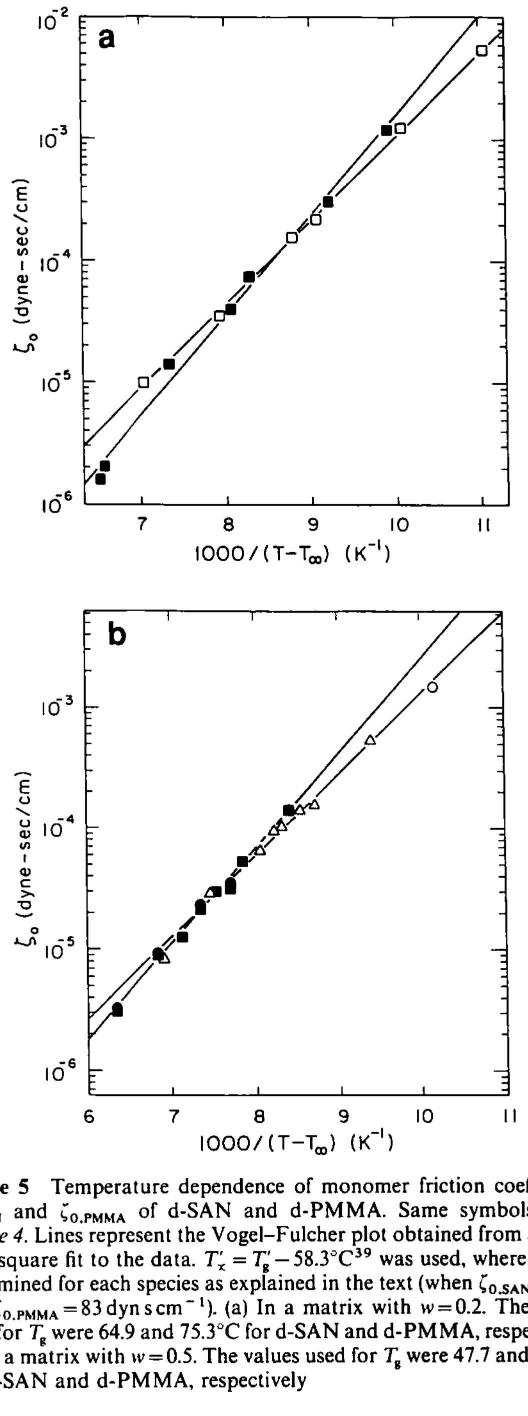

Figure 5 Temperature dependence of monomer friction coefficients $\zeta_{0,\mathrm{SAN}}$ and $\zeta_{0,\mathrm{PMMA}}$ of d-SAN and d-PMMA. Same symbols as in *Figure 4*. Lines represent the Vogel–Fulcher plot obtained from a linear least square fit to the data. $T_\infty' = T_g' - 58.3$°C[39] was used, where T_g' was determined for each species as explained in the text (when $\zeta_{0,\mathrm{SAN}} = 1000$ and $\zeta_{0,\mathrm{PMMA}} = 83$ dyn s cm^{-1}). (a) In a matrix with $w = 0.2$. The values used for T_g were 64.9 and 75.3°C for d-SAN and d-PMMA, respectively. (b) In a matrix with $w = 0.5$. The values used for T_g were 47.7 and 66.7°C for d-SAN and d-PMMA, respectively

Composition dependence of tracer diffusion

We investigated the influence of changing composition on tracer diffusion, and thus ζ_0. The D^*s were measured at 187°C in matrices composed of SAN of molecular weight of 176 000 and PMMA of molecular weight of

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[*] We used the value of $B(=1118)$ and $T_\infty - T_g(=80°\mathrm{C})$ in the Vogel-Fulcher equation obtained by Green *et al.*[44] and the value of $\zeta_{0,\mathrm{PMMA}}$ at 187°C (3.0×10^{-4} dyn s cm^{-1}) which was calculated from self diffusion data of PMMA was extrapolated to T_g

[†] These values were larger than the one in the PS/TMPC blend where nearly the same value ($\sim$23 dyn s cm^{-1}) for both d-PS and d-TMPC were found. Considering the facts that the extrapolation is done in log scale (log 23 ~ 1.4, log 83 ~ 1.9 and log 1000 = 3) and the small error in the slope could be easily magnified down at T_g

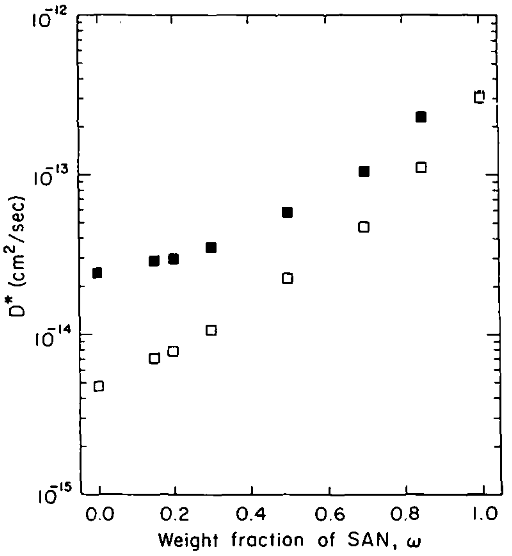

Figure 6 Tracer diffusion coefficients of d-SAN and d-PMMA, D^*_{SAN} (■) and D^*_{PMMA} (□), measured as a function of weight fraction w of SAN in the matrix at 187°C using d-SAN (179000) and d-PMMA (58000), respectively, and shifted to a molecular weight of 100000 using equation (1)

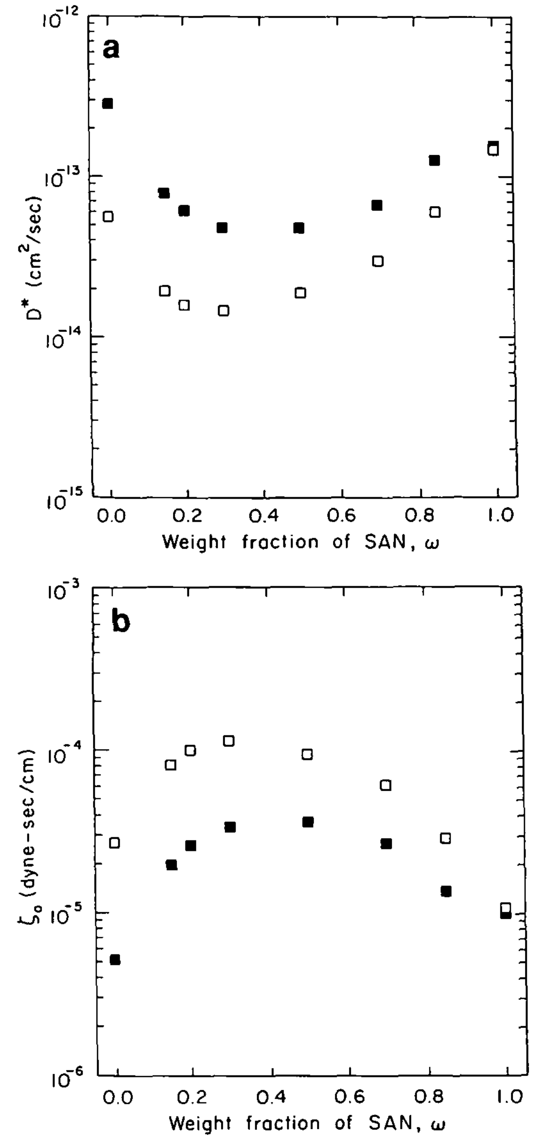

Figure 7 (a) Tracer diffusion coefficients of d-SAN and d-PMMA, D^*_{SAN} (■) and D^*_{PMMA} (□), measured as a function of weight fraction w of SAN in the matrix, were shifted to the temperature $T = T_g$(d.s.c.) + 69°C using the Gordon-Taylor equation with $K = 0.25$ for the intermediate compositions. (b) Monomer friction coefficients of d-SAN and d-PMMA, $\zeta_{0,\text{SAN}}$ (■) and $\zeta_{0,\text{PMMA}}$ (□), respectively, as a function of weight fraction w of SAN and at the same temperature as (a)

840000 using the tracer molecules of d-SAN of molecular weight of 179000 and d-PMMA of molecular weight of 58000. The D^*s were scaled, using equation (1), to the same molecular weight (100000) to account for the difference in molecular weights between the two tracers. The results are shown in *Figure 6*. It was observed that D^*s of both species increased as w was increased, which was mainly due to the decrease in T_g. The self diffusion coefficient of SAN ($D^*_{\text{d-SAN}}$ into SAN) was 70 times larger than that of PMMA ($D^*_{\text{d-PMMA}}$ into PMMA) at the same temperature. These results were in agreement with the results found by Fowler *et al.*[1] that the rate of adhesion development was slower for PMMA-PMMA joints than for SAN-SAN joints. These data at 187°C were then scaled, using the Williams-Landel-Ferry relation, to a temperature 69°C above T_g(d.s.c.) of each blend to account for the difference in T_g. We used the Gordon-Taylor equation with $K = 0.25$ to find the T_gs at the intermediate compositions. The resulting D^*s are shown in *Figure 7a*. Monomer friction coefficients for both species, $\zeta_{0,\text{SAN}}$ and $\zeta_{0,\text{PMMA}}$, were calculated using equations (1) and (2) (*Figure 7b*). There is a maximum in ζ_0 (and a minimum in D^*) as a function of w, which is mainly due to the shape of T_g(d.s.c.) as a function of composition (*Figure 1b*)*. The ratio of the monomer friction coefficients was plotted (*Figure 8*) which is now nearly independent of the choice of the reference temperature. It is interesting to note that there was almost no difference between $\zeta_{0,\text{SAN}}$ and $\zeta_{0,\text{PMMA}}$ in a pure SAN matrix whereas the difference emerges and became larger as w approaches 0. The increasing difference between the ζ_0s seems to correlate with the broadening of the glass transition (*Figures 1a* and *b*) as w becomes small, a broadening which we hypothesize is due mainly to the existence of locally different T_gs for the PMMA and SAN in these blends. The higher local T_g of the PMMA with respect to SAN in these low w blends may account for some of the difference between $\zeta_{0,\text{PMMA}}$ and $\zeta_{0,\text{SAN}}$ which develops as $w \rightarrow 0$.

Another interesting observation was on the tracer diffusion coefficients of d-SAN and d-PMMA into SAN with increased AN content (SAN27: 27.2 wt%, *Table 2*) which decreases the miscibility[1,2,7] in comparison to the SAN used thus far (22.9 wt% AN content). It was found for the d-SAN tracer that there was no difference in D^*[34], which again demonstrates that the thermodynamic interaction is not directly linked to the chain mobility factor. However, for the d-PMMA tracer the diffusion into SAN27 was about five times slower ($D_0 = 0.00083\,\text{cm}^2\,\text{g}^2\,\text{s}^{-1}$ at 187°C) than into SAN with 22.9 wt% AN content ($D_0 = 0.0044\,\text{cm}^2\,\text{g}^2\,\text{s}^{-1}$). As will be seen later, the composition dependence of χ also does not show a simple correlation between the thermodynamic interaction and the dynamic friction factor.

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* If the Fox equation [equation (11)] or the Gordon-Taylor equation with $K = 1$ [equation (12)] is used for interpolating T_g between $w = 0$ and 1, this behaviour is reduced

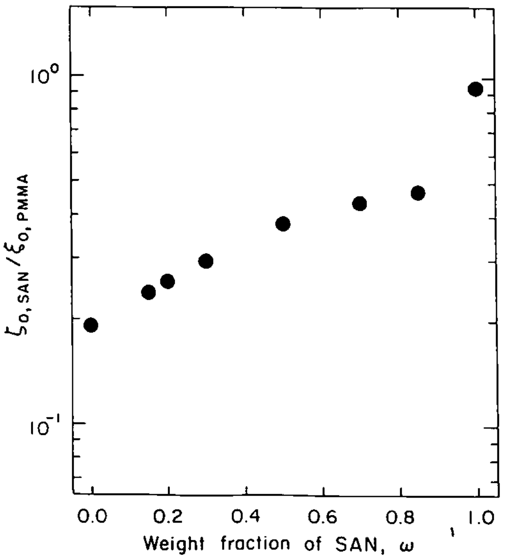

Figure 8 Ratio of monomer friction coefficients of d-SAN to d-PMMA, $\zeta_{0,SAN}/\zeta_{0,PMMA}$ (●), *versus* the weight fraction w of SAN in the matrix shifted to the temperature $T = T_g$(d.s.c.)+69°C

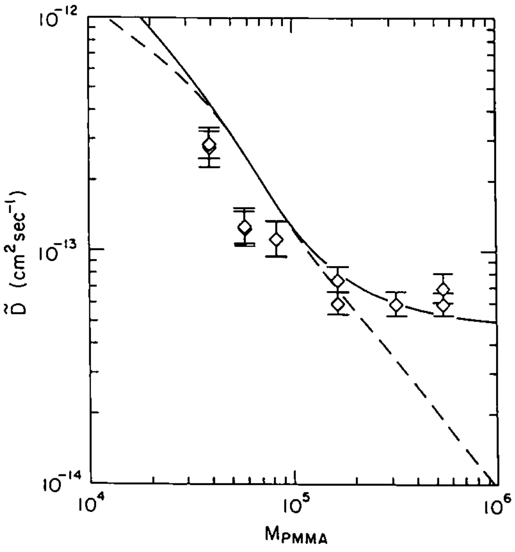

Figure 9 Mutual diffusion coefficients, $\tilde{D}$, as a function of molecular weight of d-PMMA at 181°C for the weight fraction w of SAN of 0.5. The solid and broken lines represent the fast and slow theory predictions using $\chi = 0.01$, respectively

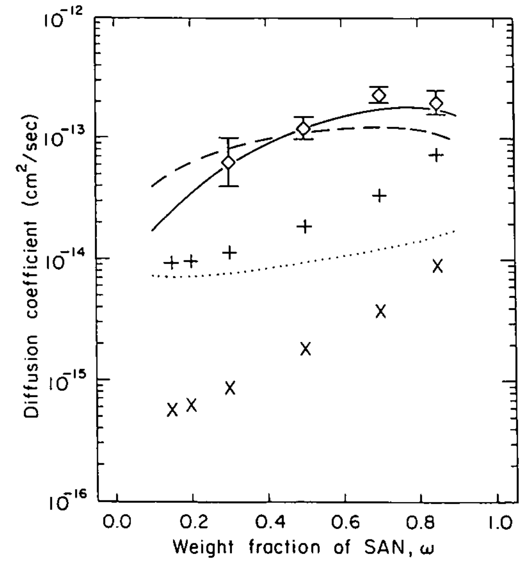

Figure 10 Mutual and tracer diffusion coefficients in the blends of SAN (176 000) and PMMA (317 000) as a function of composition at 187°C. The tracer diffusion coefficients of d-SAN and d-PMMA, D^*_{SAN} (+) and D^*_{PMMA} (×), were scaled to the molecular weights of 176 000 and 317 000 using equation (1) and the mutual diffusion coefficients $\tilde{D}$ (◇) in the d-PMMA/SAN diffusion couples of the same molecular weights were drawn and compared with the $\tilde{D}$ prediction using $\chi = 0$ (···), using the composition independent $\chi = 0.0108$ (- - -) and using $\chi = -0.0008 - 0.0209w$ (——) which is extracted from small angle neutron scattering experiments by Hahn *et al.*[5]

Molecular weight dependence of mutual diffusion

The mutual diffusion coefficient, $\tilde{D}$, was also measured as a function of molecular weight of d-PMMA at the same temperature as above (181°C) for the composition of $w = 0.5$ using SAN of $P_{SAN} = 176\,000$ (*Figure 9*). The data for $\tilde{D}$ and D^* were used to check the validity of the 'fast' and 'slow' theory [equations (10a) and (10b)] predictions for the mobility factor D_T. As shown in *Figure 9* the prediction of fast theory using a χ of -0.01 is in good agreement with the data whereas the prediction of the slow theory shows a substantial deviation: as the molecular weight of d-PMMA was increased the $\tilde{D}$ decreased much less than predicted by the slow theory. These results are thus in direct conflict with the conclusions of Yukioka *et al.*[10,11] on the same system. The results of Yukioka *et al.* are however not as straightforward to interpret as they claim. First, they put two pure layers of SAN and PMMA in contact and measured the broadening of the interface. However, $\tilde{D}$ is a function of composition (as shown below) and describing the interface broadening in this case in terms of a composition independent diffusion coefficient is an unwarranted approximation. Second, they used the following equation derived from the slow theory, which can only be true assuming that tracer diffusion takes place via reptation mechanism ($D^* \propto M^{-2}$) and two component chains possess the same D_0 in equation (1) (i.e. $D_{0,PMMA} = D_{0,SAN}$):

$$\tilde{D} \propto \frac{1}{\phi_2 N_1 + \phi_1 N_2} \tag{14}$$

However, it was shown not only that D_0s are not the same (they are different by about a factor of 3 at $w = 0.5$), but also that the constraint release mechanism makes a significant contribution to D^* for blends made from lower molecular weight of PMMA (*Figure 2*) since their molecular weights ranged 10 000 to 821 000. Their SAN molecular weight 160 000 was comparable to ours (176 000). Without information about the mobility factor of each individual chain, i.e. the D_0 and the M dependence of the D^*s, the prediction of the fast and slow theories can be misleading.

Composition dependence of mutual diffusion

The mutual and tracer diffusion coefficients at 187°C are plotted as a function of composition in *Figure 10* after shifting the D^*s using equation (1)* to those at the

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* Due to the high molecular weight of PMMA (317 000) the constraint release contribution using $z = 5.5$ was calculated to be negligibly small over the composition range studied here ($0 \leqslant w \leqslant 0.85$)

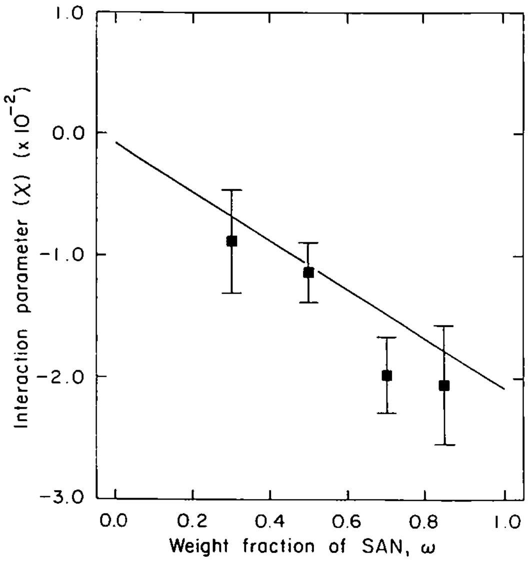

Figure 11 Interaction parameter χ (■) at 187°C as a function of the weight fraction w of SAN in the matrix compared with the small angle neutron scattering results of Hahn *et al.*[5] (——)

molecular weights used for mutual diffusion experiments (d-PMMA of molecular weight of 317000 and SAN of molecular weight of 176000). In accord with the finding of Fowler *et al.*[1] that the development of adhesion by interdiffusion was more rapid for a SAN/PMMA couple than for either SAN/SAN or PMMA/PMMA ones, we find that $\tilde{D}$ is clearly larger than would be predicted for athermal mixing. The increase in $\tilde{D}$ is due to the favourable (negative) excess free energy of mixing. We calculated χ as a function of composition using equations (9) and (10a) (*Figure 11*). The relatively large error bar in χ is due to the relative large error of the $\tilde{D}$ measurement* shown in *Figure 10*. Hahn *et al.*[5] measured χ as a function of composition for d-PMMA mixed with SAN of 19wt% AN at 140 and 200°C by small angle neutron scattering. We interpolated their data† assuming the temperature dependence of χ to be $A+B/T$ with A and B being constant. The $\chi(w)$ ($=-0.0008-0.0209w$) at 187°C thus obtained was plotted in the *Figure 11* as the solid line, which is in reasonable agreement with our measured values of χ. The predicted mutual diffusion coefficients using the above χ (the solid line in *Figure 11*) and the experimental D^*s for both species were drawn in *Figure 10* as a solid line. The $\tilde{D}$ was also drawn using a constant χ ($=0.0108$ which is the value at $w=0.5$ from Hahn *et al.*[5]) in *Figure 10* as a broken line. Only a small difference is seen, but imposing the composition dependence of χ found by SANS improved the fit.

CONCLUSIONS

In the miscible polymer blends of SAN and PMMA, we have demonstrated how diffusion information can be utilized to investigate thermodynamic as well as dynamic aspects of mixing.

Tracer diffusion

- Using sufficiently high molecular weight matrices at $w=0.5$, D^* of deuterated chains of both species scaled nearly as M^{-2} as the reptation model predicts.
- As the molecular weight of PMMA in the matrices with a fixed molecular weight of SAN (at $w=0.5$) decreased, the constraint release mechanism made an increasing contribution to D^* The data could be fit with a z, the number of suitably situated constraints, of 5.5
- For matrices with SAN weight fraction $w=0.2$ and 0.5, the temperature dependence of D^* for both species was nearly identical. Analysis based on the assumption that each species retains its own T_g in a blend and that this T_g corresponds to the temperature where ζ_0 equals that for pure component at its T_g(d.s.c.), shows that the new (local) T_gs of both species are well within the breadth of glass transition measured by d.s.c., with a higher value for the species which has a higher T_g as a pure component (i.e. PMMA) as observed in other systems[17].
- The monomer friction coefficients of the two species ($\zeta_{0,\mathrm{SAN}}$ and $\zeta_{0,\mathrm{PMMA}}$) were nearly the same in pure SAN and the ratio of $\zeta_{0,\mathrm{SAN}}/\zeta_{0,\mathrm{PMMA}}$ decreases monotonically as the PMMA content in the blend increases. In pure PMMA, $\zeta_{0,\mathrm{PMMA}}$ was larger than $\zeta_{0,\mathrm{SAN}}$ by a factor of 5. This behaviour is qualitatively in accord with the broadening of T_g(d.s.c.) in the PMMA-rich blends: the more the local T_gs of the components in the blend differ (thus broadening of the transition), the more different the individual diffusion coefficient (and monomer friction coefficients) are at some temperature above T_g.

Mutual diffusion

- For a blend with $w=0.5$ made with SAN of $M=176000$, $\tilde{D}$ was measured as a function of the molecular weight of d-PMMA at 181°C. The mutual diffusion coefficient follows closely the predictions of the fast theory with a Flory parameter -0.01, the result expected if it is controlled by the diffusion of the faster moving species.
- The composition dependence of mutual diffusion and the Flory interaction parameter χ was investigated at 187°C. The latter showed good agreement with the recent small angle neutron scattering results of Hahn *et al.*[5]

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* At higher temperatures close to the spinodal temperature, $\tilde{D}$ was too large to be measured accurately, and on the other hand at lower temperatures, small uncertainties in $\tilde{D}$ were magnified in χ and gave rise to a larger error, preventing us from accurately measuring the temperature dependence of χ with the present technique

† The SAN used in our diffusion measurements had a ~4wt% higher AN content than theirs. While the interaction parameters as a function of AN content are still not accurately available, our interaction parameter χ would be expected to be smaller than that of Hahn *et al.*[5] as Fowler *et al.*[1] and Yukioka *et al.*[11] observed that the diffusion rate was the greatest near 15wt% AN and decreases as the AN content departs away from this value until miscibility eventually vanishes at ~9 and 33%

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