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Tracer diffusion of deuterated polystyrene into polystyrene–poly(α-methyl styrene) studied by nuclear reaction analysis

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The tracer diffusion of deuterated polystyrene (dPS) into natural polystyrene–poly(α-methyl styrene) (hPS–PαMS) blends has been studied as well as the diffusion of dPS–PαMS blends into hPS–PαMS blends. Nuclear reaction analysis (NRA) as a depth profiling technique is shown to be useful to study the different systems. The diffusion constants have been determined as a function of temperature and as a function of composition of the blend of the tracer and the matrix. Blends as a tracer show a strong enhancement in diffusion in comparison to the pure dPS tracer, indicating that the intradiffusion coefficient measured in a sample where there is no chemical gradient is much bigger than the tracer diffusion measured from a thin film of pure dPS. The glass transition temperature T_g has a considerable influence on the diffusion. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

NRA has become one of the commonly used tools to study polymer diffusion together with other techniques, such as forward recoil spectrometry[1–3], n.m.r. and, more recently, Rutherford backscattering (RBS) and neutron reflectometry. NRA was used initially to obtain a distribution profile of deuterium by energy analysing the α particles emitted by the d(^{3}He,p)^{4}He reaction[4] or by energy analysis of the protons emitted by the reaction[5]. It has subsequently been used to study polymer diffusion[6,7]. The relative ease with which direct depth profile spectra are obtained with NRA makes it an attractive technique to determine diffusion profiles and to deduce reliable diffusion constants.

Diffusion of polymers has been studied extensively in different polymer systems. Thermodynamic effects show up in the mutual diffusion close to the phase boundaries in a polymer blend. Thermodynamic slowing down decreases the diffusion coefficient of a polymer in a mixture when the system is taken from the miscible region closer to the two-phase region. Of the actual diffusion in the boundary region very little is known. The strong concentration dependence of the glass transition temperature in polymer blends reflects and is reflected in dramatic changes in local segment mobility with concentration, which in turn lead to strong and not wholly understood concentration dependences in all diffusion coefficients[8]. Recently the effect of the glass transition on mutual diffusion has been studied for symmetric PS–PαM blends[9].

The distinction is conventionally made in studies of diffusion between mutual diffusion (sometimes called interdiffusion), which involves thermodynamic effects such as slowing down close to a critical point, and thermodynamic enhancement in miscible polymers[2,10], and intradiffusion. Intradiffusion is a pure transport coefficient characterising the Brownian motion of a polymer chain in a chemically uniform environment, in contrast to interdiffusion, which characterises the relaxation of chemical composition gradients. A measurement of intradiffusion can be realised by an experiment in which a concentration gradient is set up between species A and a labelled analogue of species A, A*, in a uniform concentration of species B. However what has been more usually done is to measure a so-called 'tracer diffusion coefficient', in which a very thin layer of pure labelled A* is allowed to diffuse into a blend of A and B. Of course, in early times a chemical gradient is present so this measurement must involve the interdiffusion coefficient, but the assumption is made that after a long enough time and for a thin initial film the chemical gradient becomes negligible and that this tracer diffusion can be equated to the intradiffusion coefficient[2].

In this paper we test this assumption directly; we measure both a tracer diffusion coefficient of a thin, pure deuterated polystyrene layer (dPS) in a blend of polystyrene (PS) and poly(α-methyl styrene) (PαMS), and the true intradiffusion coefficient obtained by measuring the diffusion of a blend of dPS–PαMS into a matrix of PS–PαMS of the same PαMS composition. Anticipating our results, we find that in this system the assumption of equality between intra-diffusion coefficients and tracer diffusion coefficients proves to be substantially in error.

THEORETICAL BACKGROUND

Tracer diffusion describes the diffusion of molecules moving into a matrix of non-identical neighbours. In low

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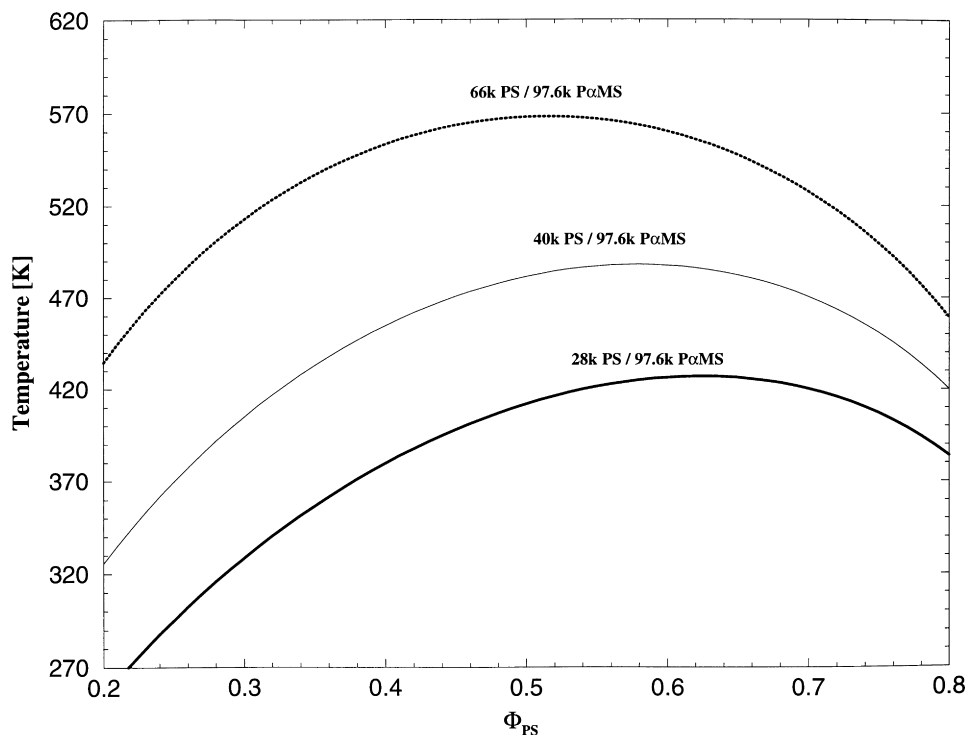
Figure 1 Phase diagrams for PS–PαMS of different molecular weights

molecular weight polymer systems the tracer diffusion can be described by the Rouse model, which is based on using monomer friction with the surrounding medium as the only intermolecular interaction. For the longer chains, which will be entangled to a certain degree, the reptation model[11,12] has proved to be a valid way of describing diffusion dynamics. These two models apply to binary polymer mixtures in the miscible phase.

The coexistence curve for PS–PαMS mixtures is found using the Flory–Huggins lattice model; the spinodal occurs at the volume fraction at which the chemical potential $\mu = (\partial G)/(\partial\phi)$ has a minimum

$$\frac{\partial^2 G}{\partial\phi^2} = 0 \qquad (1)$$

where G is the Flory–Huggins free energy of mixing:

$$G = \frac{\phi \log \phi}{N_1} + \frac{(1-\phi)\log(1-\phi)}{N_2} + \chi\phi(1-\phi) \qquad (2)$$

ϕ corresponds to the volume fraction of the polymer with chains of length N_1, $(1 - \phi)$ corresponds to the volume fraction of the polymer with chains of length N_2. The χ parameter has been determined by Lin and Roe[14] for dPS–PαMS:

$$\chi_{\phi,T} = 53.434 \times \frac{0.0608 + 0.0018\cdot(1-\phi) - 0.000056T}{T} \qquad (3)$$

In *Figure 1*, spinodal curves for PS–PαMS mixtures are shown for PαMS of molecular weight 97 600 and PS of molecular weight 28 000, 40 000 and 66 000. In the miscible region tracer diffusion can usually be well modelled by simple solutions to Fick's equation. The depth profile of chains diffusing into a matrix ($x \geq 0$) is given by[13]:

$$\phi(x) = \frac{1}{2}\left[\text{erf}\left(\frac{h-x}{w}\right) + \text{erf}\left(\frac{h+x}{w}\right)\right] \qquad (4)$$

where h is the initial thickness of the tracer layer and w is the diffusion distance after a time t:

$$w = 2\sqrt{D\cdot t}$$

As one approaches the spinodal curve, by varying the temperature or volume fraction, the diffusion will be altered. Thermodynamic slowing down will take place as the two-phase region is reached.

EXPERIMENT

A belt-driven van de Graaff accelerator provides ^{3}He ions of an energy up to 2 MeV. The ^{3}He ions react with ^{2}D to give ^{5}Li which decay to an α particle and a proton.

$$^3\text{He} + {}^2\text{D} \rightarrow {}^5\text{Li}^* \rightarrow \alpha + p + Q$$
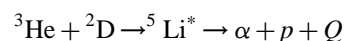
with an energy release (Q value) of 18.6 MeV. The experiments are carried out with a beam energy of 0.7 MeV. This enables the measurement of a depth profile of the deuterium over a range of 1 μm which is the total thickness of the bilayer. The proton energy spectrum is measured using an ORTEC 1500 μm, 100 mm^2 area surface barrier detector at 165° to the incident beam. The pulse height spectrum from this is recorded and translated to an energy spectrum. The energy calibration is performed using a triple-α calibration source (^{239}Pu, ^{241}Am, ^{244}Cm) placed near the detector. The proton energy is converted into the ^{3}He energy at interaction using reaction kinematics (conservation of energy and momentum). The range difference between the incident ^{3}He energy and the energy at interaction gives the inter-action depth. The proton energy spectrum from a sample is divided by the spectrum from a uniformly deuterated thick sample to yield the depth distribution of deuterons in the sample.

The sample is attached to a sample-holder in a vacuum chamber (pressure $\sim 10^{-6}$ Torr). The angle of the sample

surface to the incoming ^{3}He beam can be varied by a goniometer. This angle affects the resolution of the measurements. The resolution improves as the sample surface becomes more nearly parallel with the beam. At the same time, however, the depth which can be probed by the beam decreases. An angle of 15° for the sample surface relative to the beam direction is used. The sample-holder is attached to a cold finger which, when filled with liquid nitrogen, keeps the sample at a temperature low enough to ensure that the polymers will not be affected by the beam during the experiment.

In order to compare deuterium concentrations in different samples the yield has to be normalised to the number of ^{3}He ions hitting the sample. One way of doing this is to integrate all the charge accumulated on the sample. A disadvantage of this is that charge can build up on the sample depending on its conductivity; this will affect the actual integrated charge and thus the normalisation. This problem is avoided by using a monitor which integrates the beam current before it enters the vacuum chamber. This provides a measure of the beam intensity independent of the sample. One does have to make sure the beam profile is smaller than the sample area. The monitor we use consists of 10 gold wires of 0.06 mm diameter, intercepting ~6% of the beam. The effect this has on the resolution has been tested and shown to be negligible.

One of the advantages of NRA is the ease and speed with which samples can be measured. Samples can be changed using a loadlock attached to the vacuum chamber. The total process of changing a sample, i.e. getting the sample-holder with the old sample out of the vacuum, changing the sample, re-introducing it into the vacuum chamber and pumping down, takes no longer than 5 min. This, together with the fact that the average time needed to acquire good counting statistics (≈ 100 counts at half height of the leading edge) is of the order of 10 min, depending on the amount of deuterium in the sample, makes it possible to take four spectra an hour.

SAMPLES

The samples used in this experiment are bilayers consisting of a matrix blend of hPS–PαMS and a tracer: either a pure dPS tracer or a dPS–PαMS tracer blend. The polymers are dissolved in toluene after which the solution is spin cast on a Si wafer at a speed of 1900 rpm. for 30 s. The polymers to be used as tracer polymers are dissolved in toluene and spun cast on glass slides. The tracers are floated off on deionised water and picked up by the matrix. Samples are annealed in a vacuum oven.

Different sets of samples have been made. One set of samples consists of PαMS of molecular weight 21 400 and hPS of molecular weight 66 000, 28 000 and 10 000, with different volume fractions ϕ of hPS. The spinodal curve lies at low temperatures for these mixtures: critical temperatures are $T_c = 355$, 270 and 180 K, respectively. For these samples, diffusion takes place far in the miscible region.

Further samples that have been made consist of PαMS of molecular weight 97 000. dPS molecular weights of $M_w = 65\,700$, 40 700 and 28 400 have been used in the tracers. The corresponding molecular weights of hPS in the matrix were 73 500, 39 000 and 27 800. The spinodal curve for these mixtures lies at higher temperatures: the critical temperatures are now $T_c = 570$, 490 and 420 K, respectively. Changing the volume fraction of hPS, ϕ, in the matrix and varying the temperature moves the system from one side of the spinodal curve to the other.

The glass transition temperature, T_g, for dPS is 100°C and T_g for PαMS is 180°C.

EXPERIMENTAL RESULTS

For the first set, tracer diffusion coefficients are determined far in the miscible region. Bilayers of dPS tracers on top of hPS–PαMS blends at various volume fractions are annealed at 180°C. A typical diffusion spectrum is shown in *Figure 2* at two different volume fractions: $\phi = 0.4$ and 0.6. An
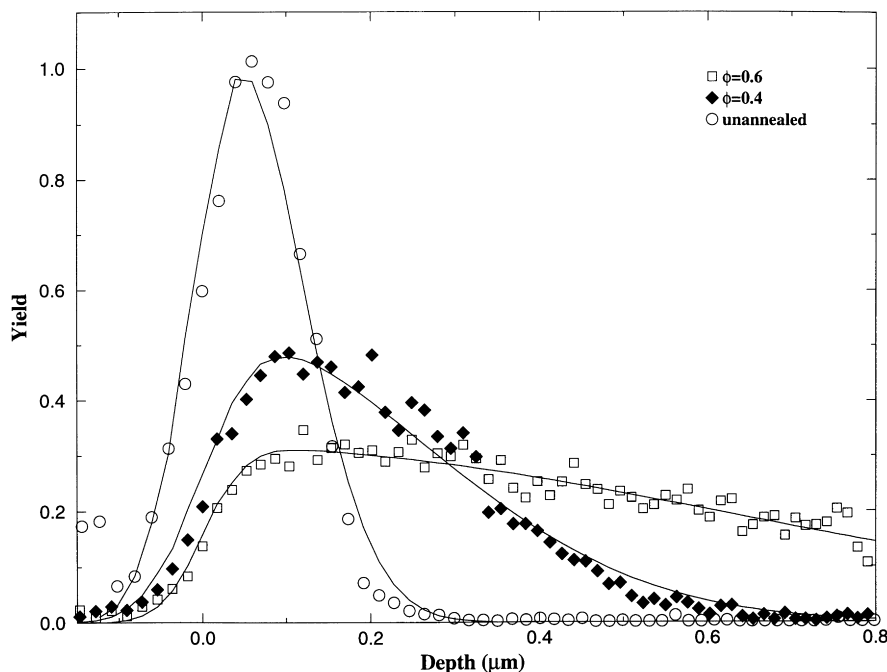
Figure 2 Diffusion profile of dPS ($M_w = 10\,000$) diffusing into an hPS–PαMS matrix at 180°C (hPS, $M_w = 10\,000$; PαMS, $M_w = 21\,400$). The volume fractions of hPS in the matrix are 0.4 and 0.6
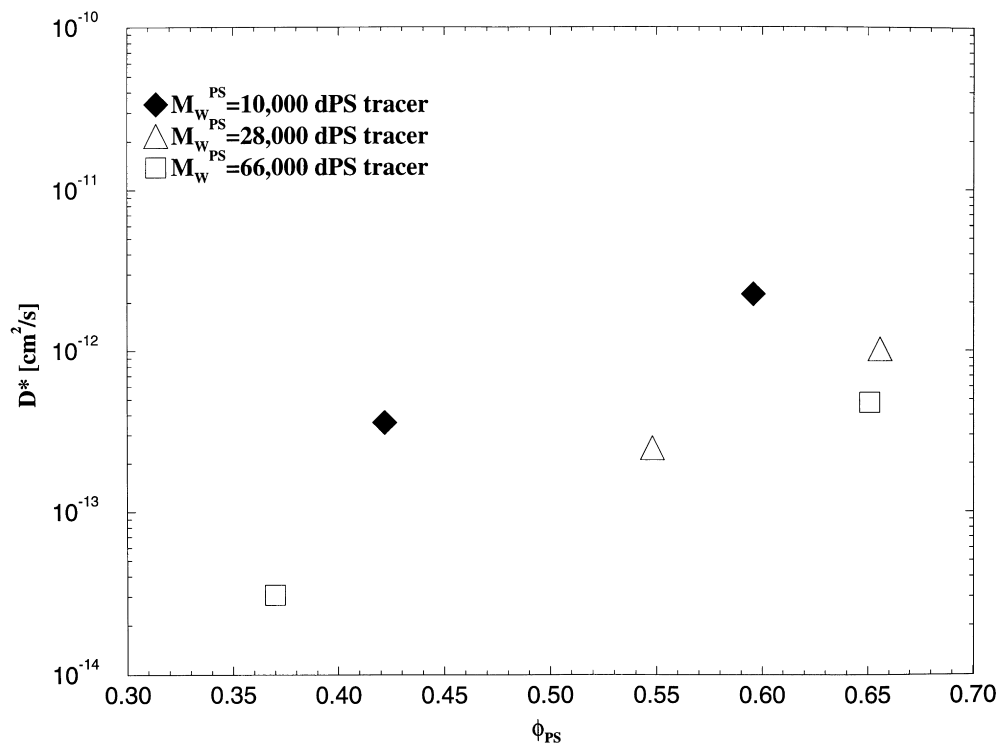
Figure 3 Diffusion coefficients in a PαMS/PS blend as a function of the volume fraction ϕ for different molecular weights of PS. $M_w^{\text{PαMS}} = 21\,400$
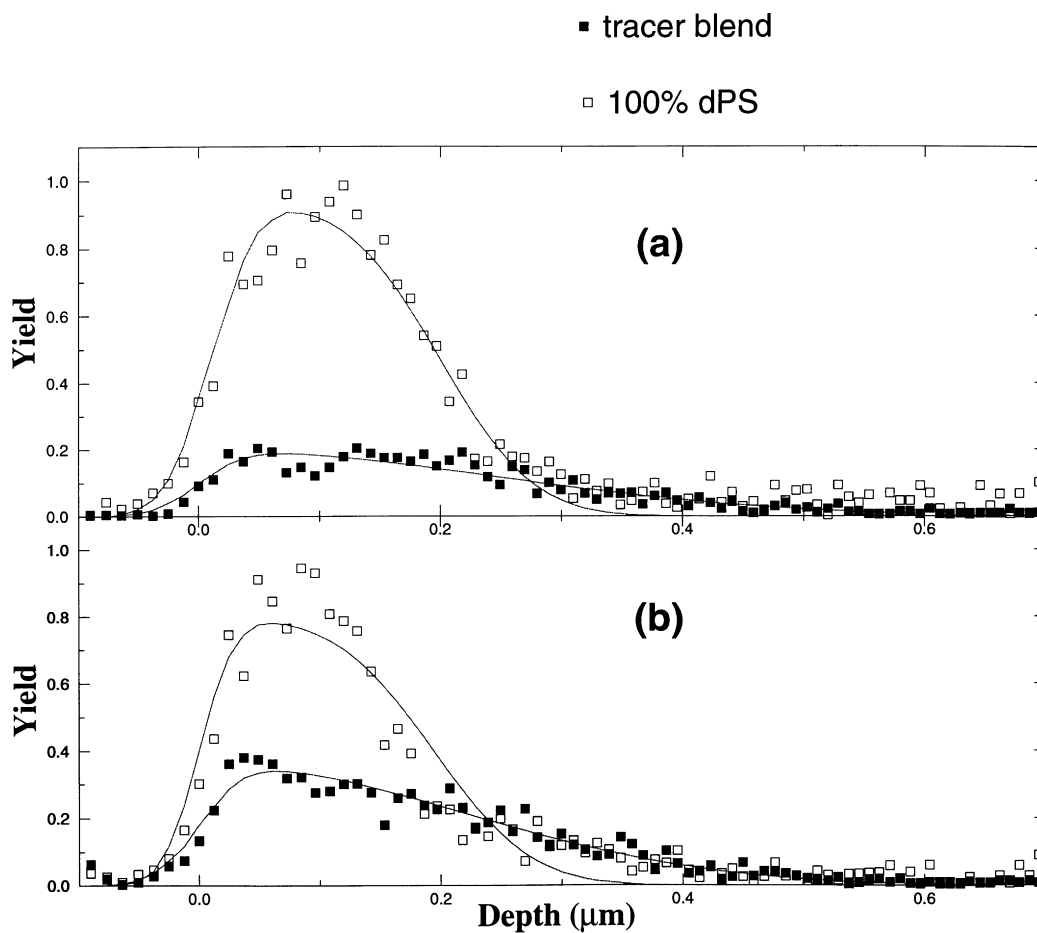

Figure 4 (a) Diffusion profile for a pure dPS tracer and a dPS–PαMS ($M_w^{\text{dPS}} = \mathbf{28\,400}$) **tracer blend into an hPS–PαMS** matrix (samples A1 and A2, respectively). (b) Diffusion profile for a pure dPS tracer and a dPS–PαMS ($M_w^{\text{dPS}} = \mathbf{40\,700}$) **tracer blend into an hPS–PαMS** matrix (samples B1 and B2, respectively). All the samples have been annealed at 169°C

Table 1 Sample details

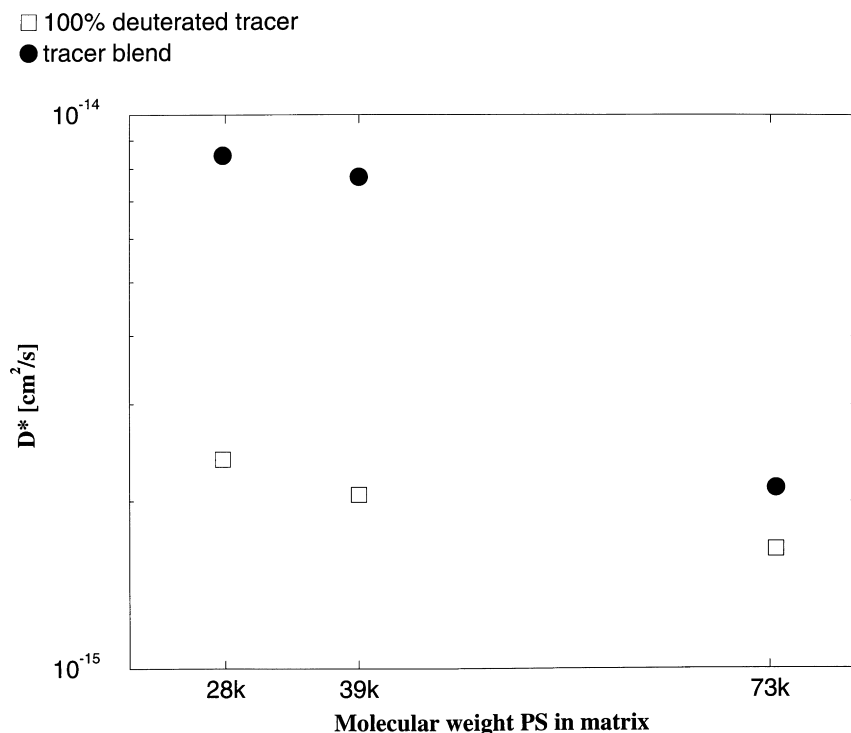| Sample	Matrix			Tracer		
	ϕ_{hPS}	M_w^{hPS}	$M_w^{P\alpha MS}$	ϕ_{dPS}	M_w^{dPS}	$M_w^{P\alpha MS}$
A1	0.36	27 800	97 600	1	28 400	—
A2	0.36	27 800	97 600	0.35	28 400	97 600
B1	0.36	39 000	97 600	1	40 700	—
B2	0.36	39 000	97 600	0.38	40 700	97 600

Figure 5 Tracer diffusion constants, D^*, as measured for three different molecular weights for the pure dPS tracer and the tracer blend. The dPS volume fraction in the tracer blends is 0.36 in each case, the molecular weights of dPS in the tracer are 28 400, 40 700 and 65 700. The molecular weights of hPS in the correspondonding matrix are 27 800, 39 000 and 73 500. $M_w^{P\alpha MS}$ in the matrix and tracer blend is 97 600. The hPS volume fraction in the matrix are 0.36 for all samples. The samples have been annealed at 169°C

unannealed sample is shown as well. The diffusion profiles follow a Fickian diffusion function, as expected in the miscible region. Spectra taken at different compositions all show Fickian diffusion. In *Figure 3* diffusion coefficients measured as a function of the volume fraction for polymers of different molecular weights are shown. As expected the diffusion coefficients are smaller as the molecular weight of the polymer increases. Furthermore, the diffusion coefficient increases with increasing hPS volume fraction. Now the glass transition temperature, T_g, of the blend can be described by the Fox equation assuming a linear dependence of $1/T_g$ on the volume fraction in the blend:

$$\frac{1}{T_g} = \frac{\phi}{T_{g1}} + \frac{1-\phi}{T_{g2}}$$

where T_{g1} corresponds to the glass transition temperature of the component of volume fraction ϕ, in our case PS, and T_{g2} corresponds to the component of volume fraction $1 - \phi$. Thus the diffusion coefficient increases as the difference between the annealing temperature ($T = 180$°C) and T_g increases.

In *Figure 4a* the diffusion profile for pure dPS tracer and a dPS–PαMS tracer blend into a matrix consisting of a hPS–PαMS blend is shown (samples A1 and A2,

respectively). The sample details are given in *Table 1*. In *Figure 4b* the diffusion profile is shown for a pure dPS tracer and a dPS–PαMS tracer blend into a matrix consisting of a hPS–PαMS blend (samples B1 and B2, respectively, from *Table 1*). The samples have been annealed simultaneously for 8 h at a temperature of 169°C. There is a striking difference between the diffusion of the pure dPS tracer and the diffusion of the tracer blends: the blends diffuse much faster into the matrix. The diffusion profiles have been fitted with a Fickian diffusion function. The profiles of the tracer blends follow Fickian diffusion, while the profiles for the pure dPS show a considerable deviation. The tracer diffusion constants, D^*, are plotted for three different molecular weights for the pure dPS tracer and the tracer blends in *Figure 5*.

The diffusion profiles have been taken at higher temperatures for matrix volume fractions ranging from $\phi = 0.2$ to 0.8. *Figure 6a,b* show the diffusion for $\phi = 0.2, 0.3$ and 0.8 for pure dPS tracer and a tracer blend, respectively. This time the volume fraction of the tracer blend did not correspond to the volume fraction of the matrix; the volume fraction of dPS was 0.4 in all cases. For these systems, samples with higher PS volume fractions have a higher diffusion coefficient. Also the tracer blends show
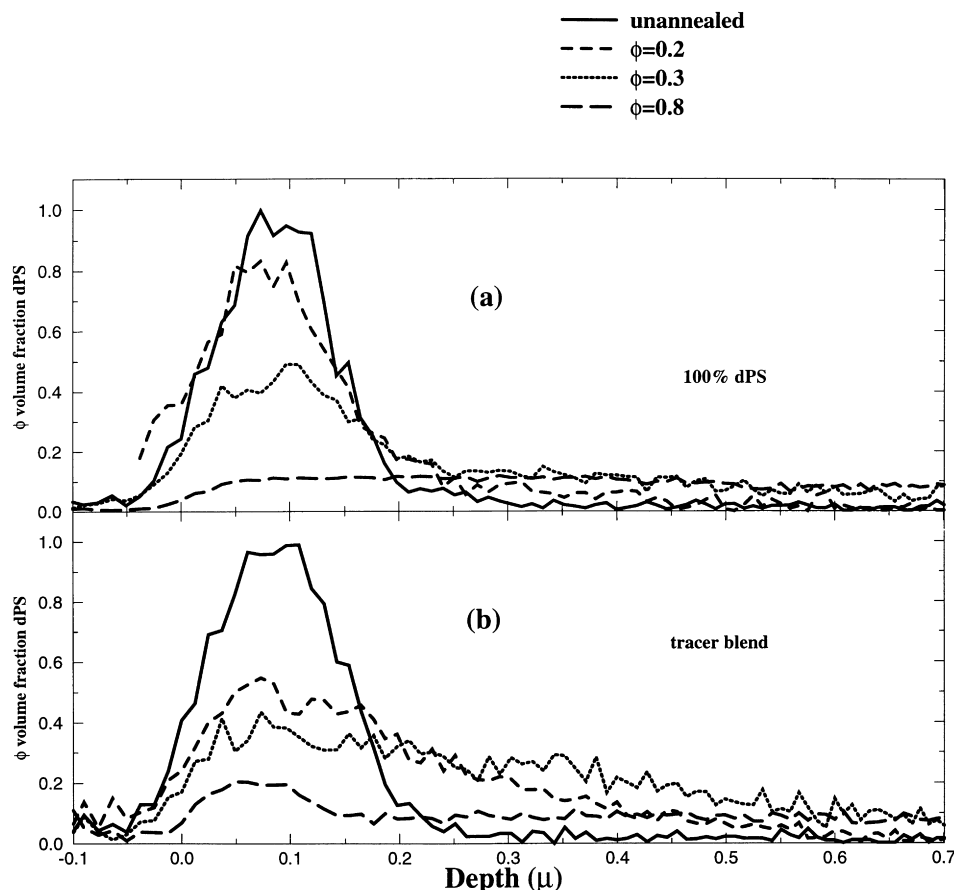
Figure 6 Diffusion profile for pure dPS tracer (a) and tracer blend (b) for hPS volume fractions in the matrix of $\phi = 0.2, 0.3$ and 0.8. The dPS volume fraction in the tracer blend is 0.4. The molecular weights of dPS and hPS are 40 700 and 39 000, respectively, the molecular weight of PαMS is 97 600. The samples were annealed at 190°C

considerably faster diffusion than the pure dPS tracer blends.

DISCUSSION

The tracer diffusion of PS into a PS–PαMS blend has been shown to depend on the difference between annealing temperature and T_g. Although increasing the volume fraction ϕ of PS in the blend takes the system closer to the two-phase region, a higher volume fraction also increases $T - T_g$. The greater diffusion coefficients at higher volume fraction can be attributed to the $T - T_g$ dependence: $\phi = \phi(T - T_g)$.

The diffusion constants for the blends of various composition in the range of $\phi = 0.2$–0.5 can be combined to give the diffusion constant as a function of $T - T_g$. The monomer mobility is proportional to the viscosity, η, which can be expressed as in the Vogel–Fulcher equation[15]:

$$\eta = A \exp\left[\frac{-B}{f_g + \Delta\alpha(T - T_g)}\right]$$

Using the values $\Delta\alpha = 4.8 \times 10^{-4}$ for the expansion coefficient of the free volume, $f_g = 0.025$ for the fractional free volume at $T = T_g$, and the expression for D^*/T[16], the tracer diffusion can be fitted to the monomer mobility.

$$\frac{D^*}{T} = A \exp\left[\frac{-B}{(T - T_\infty)}\right] \qquad (5)$$

where T_∞ is the Vogel temperature at which the free volume

vanishes:

$$f_g + \Delta\alpha(T - T_g) = \Delta\alpha(T - T_\infty)$$

In *Figure 7* D^*/T is shown as a function of $1000/(T - T_\infty)$. The fit of D^*/T to equation (5) gives values of $A = 1.1 \times 10^{-6}$ and $B = 1.092$. In pure PαMS B has been measured to be 1.6[9].

The intradiffusion coefficient as measured for tracer blends has been shown to be orders of magnitude faster than the tracer diffusion coefficient measured from a thin film of pure dPS. This is the case for the Fickian diffusion in the low molecular weight PαMS blends ($M_w^{P\alpha MS} = 21\,400$) as well as for the non-Fickian diffusion in the high molecular weight PαMS blends ($M_w^{P\alpha MS} = 97\,600$). This behaviour is observed for all the molecular weights of PS used and over the complete range of PS volume fraction in the tracer and blend.

Diffusion of a tracer blend rather than the diffusion of a pure dPS tracer alters the system in several ways. For one, there will be a mismatch in the T_g between the tracer and the matrix. However, polystyrene having the lower T_g in the PS–PαMS system, would lead to a lower diffusion coefficient for the tracer blends than for the pure dPS tracer. Obviously this cannot account for our observations. Another possible explanation for a difference in diffusion results from the interaction between tracer and matrix. The addition of matrix polymers to the tracer will change the interaction between the tracer and the matrix as a whole, making it more similar, and hence enhancing the diffusion for the tracer blends.
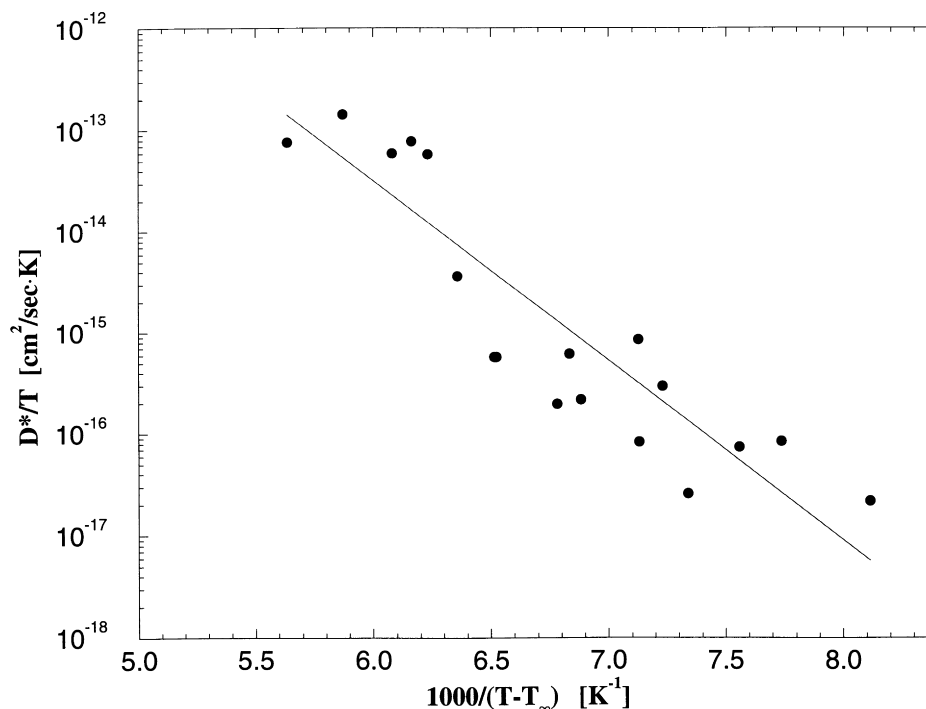
Figure 7 $D*/T$ as a function of $1/(T - T_\infty)$ for dPS/PαMS tracer blends ($M_\mathrm{w} = 40\,700$ and $97\,600$, respectively) into hPS/PαMS matrix blends ($M_\mathrm{w} = 39\,000$ and $97\,600$, respectively)

In conclusion one can say that one has to be very careful making the approximation that the tracer diffusion coefficient is the same as the intradiffusion coefficient. The two diffusion coefficients can be very different, though for the moment the reasons for this remain obscure.

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