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Interdiffusion in blends of deuterated polystyrene and poly(α-methylstyrene)

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Abstract

The differing glass transitions between deuterated polystyrene and poly(α-methylstyrene) are shown to have a profound effect on their interdiffusion coefficient. We have measured the interdiffusion coefficient as a function of concentration and temperature for two blends. The results can be interpreted in terms of the 'fast' theory of interdiffusion with the temperature dependence obtained from a Williams–Landel–Ferry (WLF) treatment. The intradiffusion coefficients of the two polymers have also been deduced by this analysis. It is found that the deuterated polystyrene has a much more concentration-dependent intradiffusion coefficient than the poly(α-methylstyrene). Thermodynamic slowing down is also observed in one blend. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Interdiffusion, also known as mutual diffusion, is the process by which macroscopic composition gradients relax in polymer systems [1]. The means by which interfaces become homogeneous is controlled by interdiffusion. This is a collective process, in contrast to the single-chain motion of a polymer molecule in a matrix which is spatially homogeneous in composition. The latter is referred to as self-diffusion [1,2] when the matrix is composed of identical molecules to the test chain, and intradiffusion [1] when the matrix is different. In these cases the driving force for the motion is entropy and the mechanism for polymer motion is usually dominated by reptation.

Initial work on interdiffusion centred around two phenomena. Thermodynamic slowing down, in which the interdiffusion coefficient becomes zero as the critical point of demixing is approached from the one-phase region, was demonstrated for an isotopic polystyrene blend (d-PS/h-PS) [3,4]. Experiments also addressed the issue of whether the interdiffusion coefficient can be written in terms of the average of the components' intradiffusion coefficients. Two such averaging schemes have been proposed. In one there is assumed to be cancellation of material flux across a boundary; this leads to interdiffusion dominated by the slower-moving component (the slow theory [5,6]). In the other it is assumed that no osmotic pressure gradient is maintained; here the interdiffusion is dominated by the faster-moving component (the fast theory [7,8]). Despite contradictory results by different groups, it is now accepted that, in most cases involving high-molecular-weight polymers, the faster-moving component dominates the diffusion process [1,9–13].

When one component of the mixture is close to the glass transition, the rate of density relaxation in a near-glassy polymer may become important. It is also important to know whether density relaxations are rapid when a polymer intrudes into a glassy polymer. One study on a low-molecular-weight mixture of polystyrene and poly(methyl methacrylate) showed that around the glass transition the slow theory dominates, when density relaxations are slow, but that there is a thermal transition region above which the fast theory describes the interdiffusion coefficient [14,15]. In this case both components have similar glass transitions. We wish to consider a system in which one component is at or near its glass transition and so

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we have chosen a blend of deuterated polystyrene (d-PS) and poly(α-methylstyrene) (PαMS), which have glass transition temperatures (T_gs) of 373 K and ~453 K, respectively. With this partially miscible system we can measure the success of the fast theory in accounting for our data, consider the effect of the elevated glass transition of PαMS, and we can also search for thermodynamic slowing down.

2. Experimental

We measured interdiffusion coefficients at temperatures between 426 and 464 K for various mixtures, but concentrated on measurements at 453 K instead of constant $T - T_g$. Two blends were used: one symmetric, with a molecular weight (MW) of 49 000 and 50 000 (49k/50k) for the d-PS and PαMS, respectively; the other nearly symmetric with respective molecular weights of 27 000 and 21 400 (27k/21.4k). All polymers were purchased from Polymer Laboratories and have polydispersity indices less than 1.1. The glass transition temperatures of the PαMS samples were measured with a Perkin–Elmer DSC7 differential scanning calorimeter and found to be 456 and 446 K for the polymers with MW = 50 000 and 21 400, respectively. Gel permeation chromatography measurements and thermal gravimetric analysis confirmed that the PαMS did not degrade at these temperatures.

Samples were created by spin-casting a film (~0.5 μm thick) of a blend on to glass and another on to silicon. The sample spun on to glass was floated off on distilled water and picked up on the film cast on silicon, creating a bilayer. There was a small difference (~0.15) in the d-PS volume fraction between the two films. On annealing, the composition of the two layers is equalized by interdiffusion. We keep the difference in d-PS volume fraction between the two layers small because the interdiffusion coefficient has a strong composition dependence. By having the two layers at similar volume fractions, we limit the variation in the diffusion coefficient. Samples were annealed in a vacuum oven for different times and at different temperatures (considered accurate to ± 1 K). All samples were annealed in the miscible region of the phase diagram. The calculated phase diagram for the 49k/50k blend is shown in Fig. 1, along with the temperatures and volume fractions of the samples for both blends. If it was possible, up to three annealing times for one composition at the same temperature were used, to reduce the uncertainty in the measured diffusion coefficient.

The diffusion coefficients were measured by ^{3}He nuclear reaction analysis (NRA) at the Device Fabrication Facility at the University of Surrey, as previously described [16]. We therefore only summarize the essentials here. A 1.0 MeV ^{3}He$^+$ beam is incident, at an angle of 30°, to the sample. The helium ions react with deuterium present in the sample ejecting α-particles and protons, either of which can be detected. We choose to detect the protons. The energy of the protons is dependent on the energy of the reaction and increases with decreasing ^{3}He energy. Since the helium ions lose energy in passing through the sample (mainly through electronic collisions), the energy of ejected protons increases for reactions taking place deeper in the sample. The loss of ^{3}He energy with depth in polystyrene is tabulated [17] and so the depth at which the reaction takes place can be calculated. This enables a deuterium composition–depth profile to be established for a particular sample. The composition–depth profiles are convolved with the Gaussian resolution function of the experiment (about 40 nm at the sample surface in this configuration).

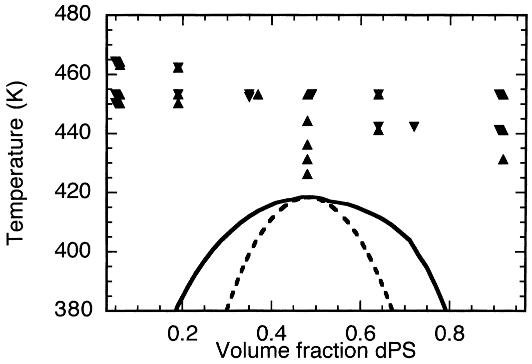

Fig. 1. Phase diagram for the 49k/50k blend, calculated using the value of χ given in Eq. (6). The spinodal is the dashed line and the binodal is the solid line. The phase diagram for the 27k/21.4k blend is not shown as the system is completely miscible, with a critical point well below the glass transition of polystyrene. The values of the temperature and composition at which interdiffusion measurements were taken are also shown for the 49k/50k blend (▲) and the 27k/21.4k blend (▼).

In each case the annealed samples were compared with unannealed samples. Examples are shown in Fig. 2. Some samples showed evidence of dewetting from the silicon substrate. This was easily visible with an optical microscope. Low-MW d-PS easily dewets from the unetched silicon substrate (the PαMS we use is stable on silicon) and so dewetting in d-PS-rich films is not a surprise. To prevent this from happening in the beam, the sample goniometer was cooled with liquid nitrogen during the experimental runs and in all experiments the layer richer in PαMS was in contact with the substrate.

3. Method of analysis and theory

Diffusion coefficients were obtained by fitting the data to solutions of the diffusion equation, which, if necessary, was solved numerically by means of finite difference methods [18]. In the first instance we assumed that the diffusion coefficient was independent of composition, but if this did not give a good fit to the data we assumed a composition dependence of the form

$$D = D_0 \exp(\alpha\phi) \quad (1)$$

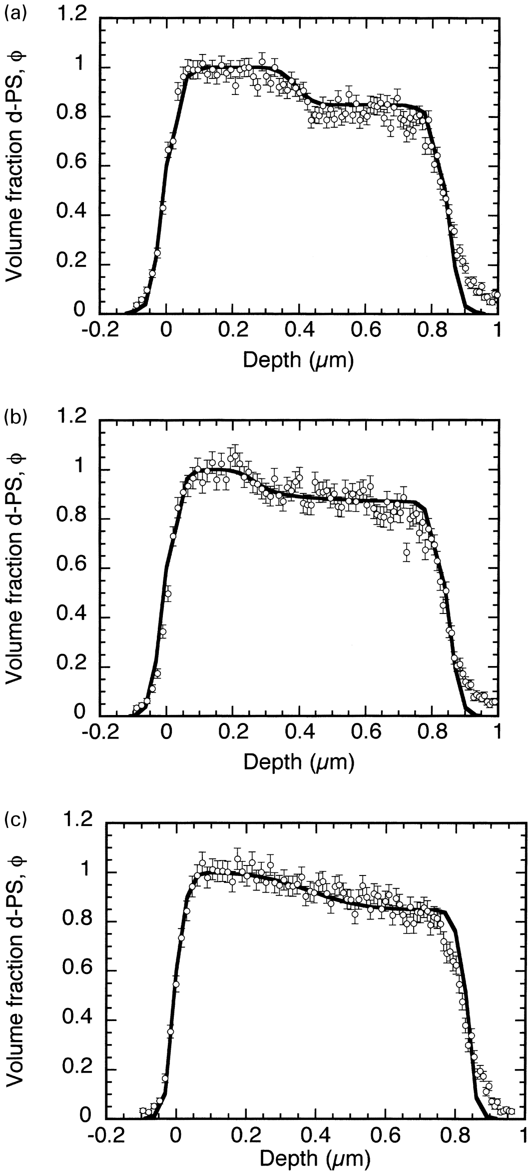

Fig. 2. Examples of bilayer data and best fits showing the 49k/50k blend with (initially) a 100% d-PS layer on one containing 85% d-PS. The data are for the unannealed sample (a), a sample annealed for 10 min at 441 K (b) and a sample annealed for 1 h at 431 K (c). The simulation in (b) reveals a composition-dependent diffusion coefficient which is $9.9 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}}$ at $\phi = 0.92$, whereas that in (c) reveals a composition-independent diffusion coefficient of $2.0 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}}$. Note the movement of the interface in (b).

where ϕ is the volume fraction of d-PS and α and D_0 are constants. This form has the advantage that if one makes the substitution $u = \exp(\alpha\phi)$, the diffusion equation becomes[3]

$$\frac{1}{D_0}\frac{\partial u}{\partial t} = u\frac{\partial^2 u}{\partial z^2}. \tag{2}$$

The method of finite differences can easily be applied to this equation, and the composition dependence enabled satisfactory fits to be obtained for all data that could not be fitted with a composition-independent diffusion coefficient. In this case, we took the diffusion coefficient as that calculated at the midpoint of the interface. The diffusion profiles were simulated by splitting a bilayer into small regions of thickness Δz and iterating in time in steps of Δt until the simulation matched the data. The resulting finite difference formula is

$$u_z^{t+\Delta t} = \frac{D_0 u_z^t \Delta t}{(\Delta z)^2}\left(u_{z+\Delta z}^t + u_{z-\Delta z}^t\right) + \left(1 - \frac{2D_0 u_z^t \Delta t}{(\Delta z)^2}\right)u_z^t \tag{3}$$

where u_z^t indicates the evaluation of u at time t and position z. Further details on the use of the exponential variation of diffusion coefficient with composition will be presented elsewhere [19].

The diffusion coefficients obtained for samples annealed at 453 K are shown in Fig. 3. To analyse these data, we consider the model proposed independently by Kramer and co-workers [7] and Sillescu [8]. This model suggests that the faster-moving component of the film is primarily responsible for the diffusion. It is given by the following equation

$$D_m = \left((1-\phi)N_\mathrm{A}D_\mathrm{A}^* + \phi N_\mathrm{B}D_\mathrm{B}^*\right)\left(\frac{1-\phi}{N_\mathrm{A}} + \frac{\phi}{N_\mathrm{B}} - 2\phi(1-\phi)\chi\right) \tag{4}$$

where D^* represents an intradiffusion coefficient, N is a polymerization index, χ is the Flory–Huggins interaction parameter and the subscripts A and B denote d-PS and PαMS, respectively. For the higher-molecular-weight system, we can simplify Eq. (4) by $N_\mathrm{A} = N_\mathrm{B} = 428$ (we have normalized the chain lengths slightly for our chosen lattice). We also tested the slow theory of interdiffusion on our data. The slow theory could not account for our results and so we do not consider it further.

The error on each reading is estimated to be 15%. This is the standard deviation of those data where more than one measurement was taken for a film at a constant temperature (we do not include data for films where the bottom layer is glassy PαMS, which show a time-dependent diffusion coefficient).

4. Results

4.1. The 49k/50k blend

The composition dependence of the interdiffusion coefficient is illustrated with the data of Fig. 3. The following observations demonstrate how one can start fitting to the diffusion coefficients. We observe, for the 49k/50k blend with the largest d-PS composition in Fig. 2(b), that the diffusion front has retreated from the middle of the bilayer towards the vacuum interface on annealing. This is evidence for a diffusion coefficient decreasing with increasing concentration. To achieve this, we see that here the d-PS

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[3] This equation has an analytical solution, obtained by the method of separation of variables, which, unfortunately, does not satisfy the boundary conditions that we must impose upon it.

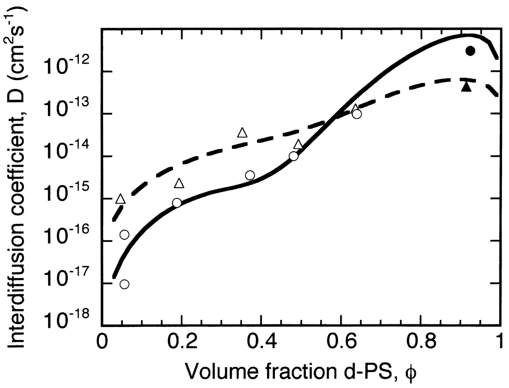

Fig. 3. Data and theoretical predictions obtained for samples at 453 K. The data are represented by ○ (49k/50k) and △ (27k/21.4k). Filled symbols represent a minimum value. The solid line is a fit to the 49k/50k data and the broken line one to the 27k/21.4k data. The volume fractions are the average of those of the two layers.

intradiffusion coefficient must be dominating the interdiffusion (since, as $\phi \rightarrow 1$, the only decreasing term in Eq. (4) is that of the d-PS intradiffusion). We observe, for this blend, that the diffusion coefficient drops from at least $3 \times 10^{-12}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 453 K to $1.8 \times 10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at 431 K. This implies that the dominant d-PS intradiffusion coefficient varies considerably with temperature. We write the intradiffusion coefficient of polymer i in the standard Williams–Landel–Ferry (WLF) form [20]

$$D_i^* = \frac{k_B T B_{0i}}{N_i^2} \exp\left(\frac{-b_i}{f_g + \alpha(T - T_g)}\right) \tag{5}$$

where the exponent is the WLF free volume term, and B_{0i} is a mobility constant which is dependent on the entanglement length of the polymer. f_g and α are universal constants, and we use values of 0.022 and 0.00048 K^{-1} respectively. k_B is Boltzmann's constant and T is the absolute temperature. The constant b_1, for d-PS, must be large to obtain such a large temperature variation, and the constant b_2 must be correspondingly small otherwise there would be negligible diffusion at small ϕ. With a small b_2, the ratio of B_{02}/B_{01} must be very small otherwise the PαMS intradiffusion coefficient would dominate the interdiffusion process over all volume fractions. With the remainder of the data we can optimize these parameters. We obtain a value of 5×10^{-14} for the ratio B_{02}/B_{01}, and 1.6 and 0.2 for b_1 and b_2, respectively. This theoretical prediction is included in Fig. 3. The rapid decline in diffusion coefficient for high ϕ is noticeable. We have shown experimental evidence for this rapid decline in diffusion coefficient in Fig. 2(b) for which we measured $D = 1.1 \times 10^7 \exp(-50\phi)\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, corroborating the large composition dependence at ϕ close to unity at 441 K. Interestingly, at 431 K, the composition dependence of the diffusion coefficient disappears at a volume fraction close to unity, in accordance with the theory, and indeed we find that we can use a Fickian diffusion coefficient to fit the data at this temperature [Fig. 2(c)]. Other annealing times for this blend at 431 and 441 K confirmed this behaviour.

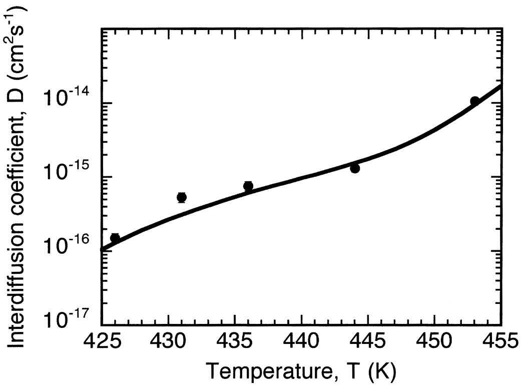

Fig. 4. Temperature dependence of the interdiffusion coefficient for the 49k/50k bilayers with $\phi = 0.48$. The solid line is the theoretical prediction.

4.2. Thermodynamic slowing down

A convincing test of our measured values of b_1, b_2 and B_{02}/B_{01} is obtained by considering the temperature variation of a film with a midpoint volume fraction, $\phi = 0.48$. The data and the theoretical prediction are included in Fig. 4. The value of χ obtained by Lin and Roe [21] predicts an upper critical solution temperature (UCST) of 430 K (this value is too large by a small amount since we observe diffusion at 426 K). We use the following value of χ:

$$\chi(\phi, T) = \frac{51}{T}\left(0.0626 - 0.0018\phi - 5.16 \times 10^{-5} T\right) \tag{6}$$

(we have merely reduced Lin and Roe's χ value by 4.5%) with a lattice parameter of 5.61 Å. This interaction parameter has a UCST of 418 K, so although we do not reach this temperature, we are beginning to see the effects of thermodynamic slowing down in the simulation. The data imply this too, but there are not enough points for there to be a definitive determination[4]. Attempts to observe the diffusion coefficient fall to zero would be difficult for this blend since the slow diffusion due to thermodynamic slowing down would be further compounded by the glass transition of the layer at the substrate being at 414 K. The changing slope in the data and prediction (see Fig. 4) shows the competition between the intradiffusion coefficients, and so enables us more accurately to determine our values of b_1 and b_2, and of the ratio B_{02}/B_{01}. Between 453 and 442 K there is a significant drop in the diffusion coefficient, but between 442 and 431 K the diffusion coefficient varies less before thermodynamic slowing down causes the interdiffusion coefficient to decrease further. The initial decrease, from 453 K, shows us that there is a large

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[4] Mean-field theory does not account for critical point fluctuations which have the effect of flattening the boundary between the one-phase and two-phase regions of the phase diagram [22]. The critical point will then appear at a temperature lower than that predicted by mean-field theory, and the value of χ used in these experiments may be slightly too low for this reason.

temperature dependence in the d-PS intradiffusion coefficient which is dominating in this temperature region. The plateau in the diffusion coefficient is where the PαMS intradiffusion coefficient begins to dominate and shows us that its temperature dependence is considerably less than that for d-PS.

4.3. The 27k/21.4k blend

To check these results, we have also a set of data at 453 K, shown in Fig. 3 for the low-MW blend. A fit to Eq. (4) is included, and here we have used values of 1.7 and 0.15 for b_1 and b_2 respectively, and a ratio B_{02}/B_{01} of 8×10^{-14}. The entanglement molecular weight of polystyrene is about 18 000, and that for PαMS is 13 500 [20], so we are confident that we are in the reptation regime, applying the correct theory and that Rouse dynamics do not apply. The good agreement between the parameters provides more evidence that the fast theory is applicable and applies to regions where free volume corrections are needed. The agreement between the two sets of data is worth commenting on as it is very surprising that, above $\phi \approx 0.6$, the higher-MW blend has the larger interdiffusion coefficient. As $\phi \longrightarrow 1$ we calculate that the intradiffusion coefficient for the 21.4k PαMS is slightly greater than that for the 50k PαMS ($1.7 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$ as opposed to $1.2 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$). While the reptation theory means that we would expect these values to differ by a factor of six, the simulation for the 49k/50k blend is varying rapidly with concentration in this region and small variations in the parameters obtained lead to large variations in the diffusion coefficients. We therefore attribute the discrepancy to the slight differences in b_1, b_2 and B_{02}/B_{01}, probably due to minor chemical differences between the two different PαMS samples which have significantly different T_gs (a difference of 10 K) for the two molecular weights.

4.4. Other observations

In the above we have analysed the data by using the usual Fox form for the glass transition [23]. A study of the glass transition of a blend of h-PS and PαMS has shown that the Couchman equation [24] better describes the volume fraction dependence of the blend [25]. Using the Couchman equation and values of the heat capacity increment, ΔC_p, of 0.29 and $0.22\,\mathrm{J\,g^{-1}\,K^{-1}}$ for PS and PαMS respectively, we need, for the 49k/50k blend, a value of 1×10^{-14} for B_{02}/B_{01} and $2 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$ for the PαMS intradiffusion as $\phi \longrightarrow 1$ at 453 K (b_1 and b_2 remain the same). For the lower-molecular-weight blend we do not need to change the parameters obtained when using the Couchman form for the glass transition temperature.

On the two occasions that we performed two runs at the same temperature for films in which the bottom layer was entirely PαMS, we observed the diffusion coefficient to fall off by at least an order of magnitude with increasing annealing time. For example, the 27k/21.4k blend was annealed at 464 K for 2 and 24 h, and the interdiffusion coefficient was measured at $\phi = 0.05$ as $1.2 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$ and $1.2 \times 10^{-14}\,\mathrm{cm^2\,s^{-1}}$, respectively. The 49k/50k blend also showed this behaviour when measured at 453 K for 24 h and 14 days. In this case, the interdiffusion coefficient dropped from (at $\phi = 0.06$) $1.4 \times 10^{-16}\,\mathrm{cm^2\,s^{-1}}$ to $9.6 \times 10^{-18}\,\mathrm{cm^2\,s^{-1}}$. (We also note that the interdiffusion coefficient measured for this blend at 464 K of $1.0 \times 10^{-15}\,\mathrm{cm^2\,s^{-1}}$ after 24 h falls to $6.2 \times 10^{-16}\,\mathrm{cm^2\,s^{-1}}$ after 70 h at 463 K.) Whilst the evidence is somewhat sketchy, we speculate that we are seeing the effect of density relaxations here. The situation is not unlike solvent (d-PS) diffusion into a glass (PαMS), and it is known that such density relaxations are not fast. However, such solvent diffusion is unlikely to decrease with time. Indeed, Case II diffusion, common in many solvent–polymer systems, has a solvent diffusion front moving into the matrix at a constant velocity. It has also been seen that the mode of diffusion changes around the glass transition [14,15]. This is a very interesting phenomenon, and it is hoped that further research will be conducted into this area of interdiffusion.

5. Discussion

5.1. Intradiffusion coefficients

In Fig. 5 we show the calculated intradiffusion coefficients at 436 and 453 K. From these intradiffusion coefficients we see that, at $\phi = 0.48$, D_B^* dominates at 436 K and the d-PS dominates at 453 K. This explains the *gradient* of the slope in Fig. 4 which is decreasing with decreasing temperature, rather than increasing as one might expect from thermodynamic slowing down, which only becomes significant at the lowest temperature measured (426 K). The dominance of PαMS intradiffusion over most of the composition range below 436 K is

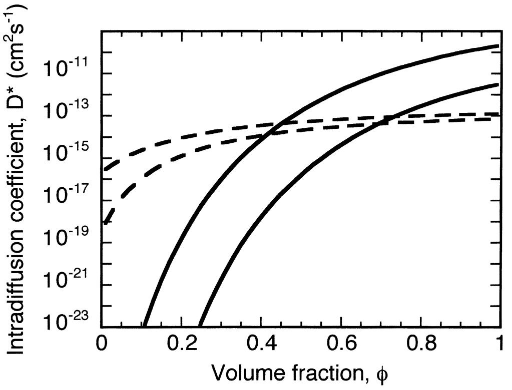

Fig. 5. Intradiffusion coefficients for the 49k/50k blend obtained from fits to the data calculated at 453 and 436 K. The solid lines are the d-PS intradiffusion coefficients and the broken line the PαMS intradiffusion coefficients. The coefficients at 453 K are the greater of each set.

somewhat unexpected. One would expect the PαMS to be unable to perform bond rotation to the same degree as the d-PS, and thus to be be less mobile.

We have seen that at high d-PS volume fractions there is a highly temperature-dependent interdiffusion coefficient which decreases with composition at 441 K [Fig. 2(b)]. This shows us that D_A^* is dominant over D_B^* at $\phi \approx 0.9$. We have also seen that at $\phi = 0.48$ D_A^* is no longer dominant over D_B^* as the temperature is lowered below 443 K. This follows from the size of the exponential term in Eq. (5); when $T - T_g$ is large, D_A^* dominates the interdiffusion process and when $T - T_g$ is small, D_B^* dominates. On this basis it follows also that D_B^* is the dominant diffusion coefficient at low volume fractions.

Are there other reasons why D_A^* should be lower than D_A^* at small ϕ? Although both blends studied are miscible at all concentrations over the temperatures studied, there is a repulsive thermodynamic interaction between the polymers; they have a positive interaction parameter. This means that d-PS chains will not be ideal in a PαMS matrix. Indeed, the characteristic length will be shorter than that of its unperturbed radius of gyration. It is not clear how much this will affect the intradiffusion coefficient. Similarly, conformational changes necessary for reptation to occur must also be inhibited. Bonds are not going to undergo facile rotation if such rotations bring them into contact with PαMS monomers. We must be specific here; we are not applying macroscopic thermodynamic considerations to the intradiffusion coefficient. These remain accounted for by the enthalpic term in the interdiffusion coefficient. We are considering local, microscopic motion and this must be contained within the intradiffusion coefficient. Interdiffusion and intradiffusion measurements on miscible blends are normally restricted to blends that have a very small interaction parameter (e.g. isotopic blends), or to truly miscible blends with a negative interaction parameter. In the former case the two components will have the same glass transition and the effect will not be observed; in the latter, the polymers mix for both thermodynamic and entropic reasons.

In a direct measurement of tracer diffusion[5] of d-PS into a blend of h-PS and PαMS, van der Grinten et al. [26] obtained a value for b of 1.1. This result is between our value of 1.6 and that of the self-diffusion of polystyrene (about 0.8) [20]. In other words, the increase in the d-PS tracer diffusion coefficient with temperature is much more dramatic when PαMS is present. We conclude that the free volume of d-PS contributes to its low intradiffusion coefficient in a PαMS-rich blend. There have been measurements in systems where the two components have different glass transitions. In the polystyrene/poly(xylenyl ether) system, Composto et al. [13] found that there was little difference in the value of b for the two components. In a blend of polystyrene and tetramethylbisphenol A polycarbonate (TMPC), the TMPC tracer diffusion coefficient, with a T_g even higher than that of PαMS, was found to have a greater temperature dependence than that of polystyrene [27].

5.2. Composition dependence of the monomeric friction coefficient

A possible weakness of the fast theory is in our assumption, which is widely made, of the additive nature of the individual intradiffusion coefficients in Eq. (4). We assume that B_{0i} is constant (Eq. (5)), but experiments have shown a composition dependence. In some blends it has been found that the monomeric friction coefficient was composition-dependent, even at constant fractional free volume (i.e., at constant $T - T_g$) [27,28]. These experiments were performed at 339 K (for a blend of polystyrene and poly(xylenyl ether)) [28] and 318 K (for a blend of polystyrene and TMPC) [27] above T_g. The mobility constant, B_{0i} in Eq. (5), is inversely proportional to the monomeric friction coefficient. The physical basis for the composition dependence was attributed to conformational changes as the polymer reptates in the mixture. In order to reptate, there must be co-operative rotational motion between adjacent bonds. Two bonds need to move together to prevent large motion at the end of the chain. However, the more space that a monomer occupies, the harder it is for it to reptate. This could well be significant in blends annealed close to the glass transition, where the d-PS monomer occupies more space than the PαMS monomer. It follows that there may be, for those blends with a small value of ϕ, a significant composition dependence in the monomeric friction coefficient. This phenomenon may also contribute to the surprising dominance of the PαMS intradiffusion coefficient at low volume fractions. One should not therefore assume that the large temperature dependence of the d-PS intradiffusion coefficient continues at lower volume fractions.

5.3. Constraint release

A further complication is added by the fact that we have ignored constraint release in our analysis [29–31]. The matrix is the same molecular weight as the diffusing molecule, and so can be expected to move the length of a tube in a time similar to that of the diffusing polymer. In this case the intradiffusion coefficient will be enhanced because some of the constraints provided by the original tube will have been removed (released). However, constraint release is usually negligible compared with reptation when the two polymers have similar molecular weights. We should only expect a constraint release effect at the extremities in volume fraction; for example, in a film rich in d-PS we

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[5] It is normally assumed that the tracer diffusion and intradiffusion coefficients are identical. This is not always the case [26] and we use the term tracer diffusion specifically to refer to measurements of the diffusion of a ‘trace’ component in a mixture.

should expect constraint release to affect the PαMS tracer diffusion coefficient because the matrix will be moving significantly faster than the trace polymer. We have no evidence for this situation since, at the maximum volume fractions attempted at 453 K, diffusion was too rapid to be measured (at lower temperatures the d-PS and PαMS intradiffusion coefficients are expected to be much closer in value and so constraint release is not expected to be a significant effect). In films rich in PαMS, on the other hand, the d-PS intradiffusion coefficient is negligible and so the effect of constraint release is also expected to be negligible.

6. Summary and conclusions

We have shown that interdiffusion in d-PS/PαMS bilayers can be interpreted in terms of the fast (Kramer–Sillescu) theory. The theory is valid over the entire composition range despite a variation in the diffusion coefficient of nearly six orders of magnitude over the measured range in the 49k/50k blend at 453 K. This concentration dependence of the interdiffusion coefficient probably originates in the concentration dependence of the intradiffusion coefficients and not thermodynamic slowing down. However, we observe the effect of thermodynamic slowing down on the interdiffusion coefficient as the temperature is lowered for the 49k/50k blend with $\phi = 0.48$.

Intradiffusion coefficients have been extracted from the data by assuming WLF behaviour. We see that the d-PS intradiffusion coefficient in PαMS has a greater temperature dependence than that of PαMS in d-PS. This large temperature dependence is due to the elevated glass transition temperature of PαMS. At low concentrations of d-PS, the PαMS intradiffusion coefficient is the dominant term in the interdiffusion coefficient.

We have also needed to include the Flory–Huggins interaction parameter in our analysis of the data to account for the effects of thermodynamic slowing down. A previously obtained χ value [21] is in good agreement with the value that we have used. Finally, we have mentioned tentative evidence that density relaxations may be important in diffusion of a viscoelastic polymer into a glassy polymer matrix.

To conclude, we note that interdiffusion in d-PS/PαMS blends is highly concentration-dependent but may be explained in terms of the 'fast' theory. To determine this interdiffusion coefficient, a simple WLF analysis of the individual intradiffusion coefficients and the known Flory–Huggins interaction parameter are sufficient. Our results can be analysed without resort to other factors such as concentration-dependent monomer friction coefficients [27,28] and the transition to the slow theory of diffusion in near-glassy systems [14,15].

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