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# Temperature dependence of the mutual diffusion coefficient of deuterated polystyrene and poly(methyl methacrylate)

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Nuclear reaction analysis is used to study the mutual diffusion of low molecular weight deuterated polystyrene and poly(methyl methacrylate). The diffusion process is found to follow the ''slow'' theory predictions at low annealing temperatures and the ''fast'' theory predictions at higher temperatures. The change from one theory to the other occurs over a temperature range which depends on the polymer molecular weights. Within this range the mutual diffusion coefficient is described by the equations developed by Shearmur *et al.* [Macromolecules **29**, 7269 (1996)]. [S1063-651X(97)50204-2]

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Polymer interdiffusion is an important aspect of polymer molecular welding technology in areas involving adhesion, joining and fusion mechanisms, and various polymer processing operations where melt flows contact to form weldlines [1]. Unlike tracer or self-diffusion, the thermodynamic interactions between the polymers during the interdiffusion process play a key role; they govern both the rate at which the macroscopic composition gradients relax and the interfacial width between the two constituents.

Based on the Flory-Huggins liquid lattice model, the mutual diffusion coefficient $D_M$ can be written as [2]

$$D_M = D_0\left[\frac{1-\phi}{N_1} + \frac{\phi}{N_2} - 2\chi\phi(1-\phi)\right], \tag{1}$$

with $\phi$ the volume fraction of component 1, $N_{1,2}$ the degrees of polymerization of components 1 and 2, and $\chi$ the Flory-Huggins interaction parameter. For a system in which the tracer diffusion coefficients ($D^*$) of both components are equal, and for $N_1 = N_2$, $D_0$ is either the reptation constant [3] [$D_0 = (4N_e k_B T)/(15\zeta) = D^*_{1,2}$] with $N_e$ the polymer entanglement length and $\zeta$ the friction coefficient or, for low molecular weight polymers, $D_0 = k_B T/\zeta$ (the Rouse constant). In most real cases the component tracer diffusion coefficients differ due to different frictional properties and/or different chain lengths of the constituents. $D_0$ is then assumed to be some weighted average of the intrinsic mobilities of the individual components of the system. However, for polymer systems, as indeed for other materials, there is no thermodynamic justification for the existence of such a relationship, and any expression must consequently contain certain assumptions. These considerations have led to the Hartley-Crank [4] and Darken [5] equations, describing $D_M$ for binary liquid and metal systems respectively. For polymers various approaches have led to two distinct equations.

Assuming polymer incompressibility and hence equal and opposite polymer fluxes, a dynamic random-phase approximation [6,7] predicts $D_0$ to be the geometric mean of the tracer diffusion coefficients:

$$D_0 = \left[\frac{1-\phi}{D_1^* N_1} + \frac{\phi}{D_2^* N_2}\right]^{-1}. \tag{2}$$

Over a large concentration range the mutual diffusion coefficient is then expected to be dominated by the slower diffusing specie: the ''slow'' theory.

In contrast other treatments [8,9], which assume that local density inhomogeneities can exist but are rapidly relaxed, we predict $D_0$ to be the arithmetic mean of the tracer diffusion coefficients:

$$D_0 = D_1^* N_1(1-\phi) + D_2^* N_2 \phi. \tag{3}$$

Here $D_M$ is dominated by the faster diffusing specie: the ''fast'' theory. This is in fact equivalent to the Hartley-Crank and Darken equations.

Little evidence exists to support the slow theory [10], but in the past decade a substantial amount of experimental evidence has been acquired backing the fast theory [11]. Recently, however, highly asymmetric diffusion profiles which cannot be described by either the fast or slow theories have been obtained [12–14]. In Ref. [14], numerical solutions to Fick's diffusion equation

$$\frac{\partial\phi}{\partial t} = \frac{\partial}{\partial x}\left(D(\phi)\frac{\partial\phi}{\partial x}\right), \tag{4}$$

accurately following the diffusion profiles recorded for the interdiffusion of low molecular weight deuterated polystyrene and poly(methyl methacrylate), were obtained. A mutual diffusion coefficient described by

$$D_M = D_A \quad \text{for} \quad \phi_{d\text{-PS}} < \phi_c, \tag{5a}$$

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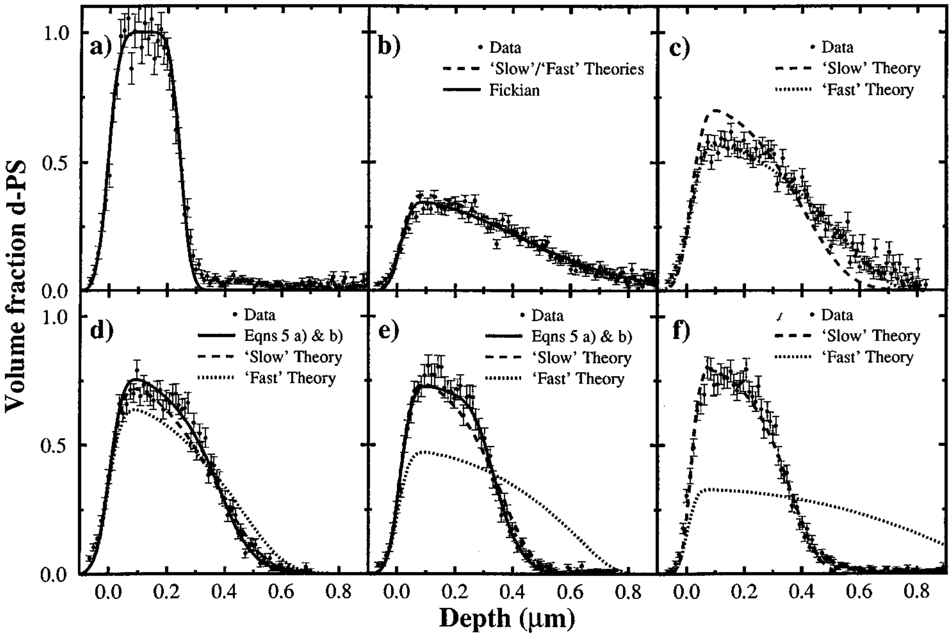

FIG. 1. Depth profiles obtained by nuclear reaction analysis for samples annealed at various temperatures. (a) Unannealed. (b) 5 min at 134 °C, shown with the best Fickian fit. (c) 40 min at 118 °C. (d) 6 h at 105 °C, shown with the numerical solution to Fick's equation using Eqs. (5a) and (5b). (d) 34 h at 96 °C, shown with the numerical solution to Fick's equation using Eqs. (5a) and (5b). (e) 49 days at 85 °C. All figures show numerical solutions to Fick's equation from the ''slow'' and the ''fast'' theories.

$$D_M = D_A + D_B(\exp[A(\phi - \phi_c)] - 1) \quad \text{for} \quad \phi_{d\text{-PS}} > \phi_c, \tag{5b}$$

with $\phi = \phi_{d\text{-PS}}$ was needed to fit the data. $D_B$ and $A$ appeared to depend on physical properties of the two components and $D_A$ followed the slow theory. The parameter $\phi_c$ was seen to vary linearly with temperature, and by extrapolation appeared to fall from 1 to 0 over a temperature range which depended on the polymer molecular weights. The results indicated that below 85 °C ($ie \approx T_g + 10$ °C, where $\phi_c \to 1$) the diffusion coefficient would be described by the slow theory. At temperatures where $\phi_c \to 0$, the fast theory was expected to describe $D_M$. However, these predictions were not tested in Ref. [14], and form the basis for this paper.

In the present study deuterated polystyrene ($d$-PS) ($M_w = 4550$, $M_w/M_n = 1.04$, $T_g = 73$ °C) and poly(methyl methacrylate) ($M_w = 2900$, $M_w/M_n = 1.07$, and $T_g = 71$ °C), purchased from Polymer Laboratories Ltd., were used to create bilayers $\approx 1$ $\mu$m thick on a silicon wafer substrate following the method described in Ref. [14]. After drying, the samples were annealed in a vacuum oven ($\approx 10^{-1}$ Torr) at eight temperatures between 85 and 150 °C. A minimum of six samples were annealed at each temperature for varying lengths of time in order to increase the accuracy of the results. Depth profiles of the $d$-PS were obtained by nuclear reaction analysis at the Van de Graaff accelerator facility of the University of Surrey, according to the method previously described [15]. Numerical solutions to Eq. (4) were derived by the method of finite differences [16]. To match the diffusion profiles accurately, the numerical solutions and Fickian fits were convoluted with a Gaussian function ($\sigma = 250$ nm) to take account of the instrumental resolution. Although the figures show at most one depth profile from samples annealed at any given temperature, the numerical solutions presented in the figures correspond to those showing the best correlation with the data obtained from the complete set of samples annealed at that temperature.

Figure 1(a) shows a depth profile obtained from an unannealed sample. The steplike distribution of the $d$-PS indicates the existence of a sharp boundary between the pure $d$-PS and PMMA layers and proves that negligible diffusion takes place during the sample preparation. This profile corresponds to the initial profile of all the samples. Altering these values by as little as 20% no longer results in accurate correlation over the complete set of samples.

The depth profiles obtained from samples annealed at 134 °C [Fig. 1(b)] show simple Fickian diffusion profiles. They were fitted by the equation

$$\phi(x) = \frac{1}{2}(\phi_1 - \phi_2)\left[\operatorname{erf}\left(\frac{h-x}{w}\right) + \operatorname{erf}\left(\frac{h+x}{w}\right)\right], \tag{6}$$

where $h$ is the thickness of the original $d$-PS film, using a constant diffusion coefficient $D = D_M = 1.2 \times 10^{-12}$ $\text{cm}^2\,\text{s}^{-1}$. This result suggests, as do those in Ref. [14], that the tracer diffusion coefficients of both components are independent of concentration. This is thought to be true for blends in which $T_g = T_g(\phi)$ [6,8], as is the case in the system investigated here. In the absence of evidence to the contrary, we have therefore assumed that the tracer diffusion coefficients are $\phi$ independent. At 134 °C, $D^*_{d\text{-PS}} = D^*_{\text{PMMA}} = D^*$, and the slow and fast theories predict the same results. Numerical solutions to Fick's equation were calculated with both theories (using $\chi = 0.0202 + 3.06/T$ [17]) and are also shown in Fig. 1(b). They are almost identical to the Fickian fit due to the low value of $\chi$.

At annealing temperatures of 105 and 96 °C, numerical solutions to Eq. (4) using the diffusion coefficient of Eqs.

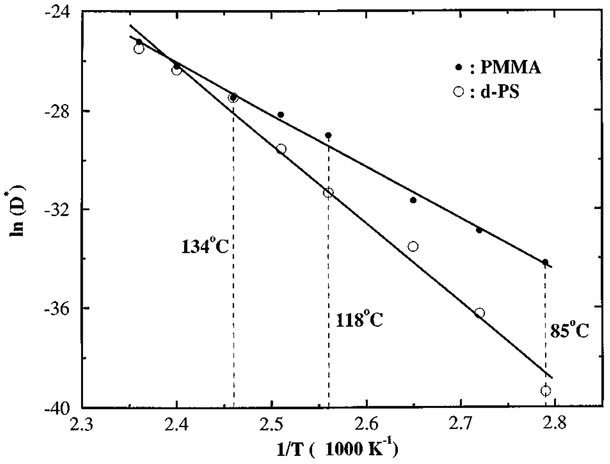

FIG. 2. Arrhenius plot of the *d*-PS and PMMA tracer diffusion coefficients with the best straight-line regression fits to the data.

(5a) and (5b) are seen to follow the data accurately [Figs. 1(d) and 1(e)] using $\phi$=0.61 and 0.32, respectively. This indicates agreement with the results of Ref. [14] with the transition from $\phi$=1 to 0 occurring over a smaller temperature range due to the lower molecular weight of the PMMA used in this study. Numerical solutions using the slow and fast theories are shown in both figures, and are seen to be inadequate for describing the data.

Figure 1(f) shows the depth profile of a sample annealed at 85 °C for 49 days. As suggested by the results of Ref. [14], the slow theory provides an accurate prediction of the mutual diffusion coefficient, with numerical solutions showing excellent agreement with profiles acquired at all annealing times between one day and 80 days. This data represents only the second study providing experimental support for the slow theory. The first was obtained by dynamic light scattering in a blend of unentangled PPO and PEO [10].

On the other hand, the samples annealed at 118 °C, where $\phi_c$ of Eqs. (5a) and (5b) is 0, show excellent agreement with numerical solutions obtained with the fast theory [Fig. 1(c)].

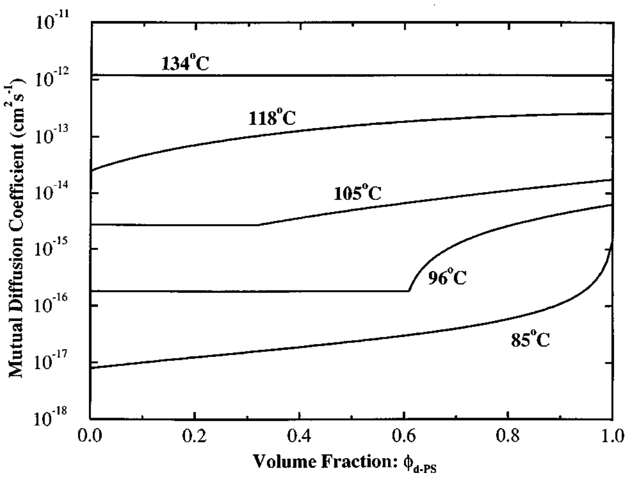

FIG. 3. Summary of the concentration dependence of mutual diffusion coefficients which produce numerical solutions to Fick's equation that follow the data accurately at various annealing temperatures.

TABLE I. Tracer diffusion coefficients used to obtain numerical solutions.

| $T$ (°C) | $D^*_{d\text{-PS}}$ (cm$^2$ s$^{-1}$) | $D^*_{\text{PMMA}}$ (cm$^2$ s$^{-1}$) |
|---|---|---|
| 85 | $7.9\times10^{-18}$ | $1.4\times10^{-15}$ |
| 96 | $1.8\times10^{-16}$ | $5.2\times10^{-15}$ |
| 105 | $2.7\times10^{-15}$ | $1.8\times10^{-14}$ |
| 118 | $2.5\times10^{-14}$ | $2.6\times10^{-13}$ |
| 126 | $1.5\times10^{-13}$ | $6.0\times10^{-13}$ |
| 134 | $1.2\times10^{-12}$ | $1.2\times10^{-12}$ |
| 144 | $3.6\times10^{-12}$ | $4.2\times10^{-12}$ |
| 150 | $8.4\times10^{-12}$ | $1.1\times10^{-11}$ |

The tracer diffusion coefficients used to obtain numerical solutions at all temperatures are listed in Table I.

Therefore, studying one system at two temperatures, we have observed diffusion profiles which are predicted by either the slow or fast theory. The two theories appear to represent limiting cases, each dominating over a certain range of temperatures: the slow theory at low temperatures and the fast theory at higher temperatures. Between these two limits, $D_M$ is described by Eqs. (5a) and (5b), with $\phi_c$ varying linearly between 1 and 0 with increasing temperature. These results are in qualitative agreement with a recent theory of Akcasu, Nägele, and Klein [18] based on the discussion of the two relaxation modes measured in dynamic light-scattering experiments, as well as with a free volume interpretation. At low temperatures, close to the $T_g$ of the polymers, only small amounts of free volume are present in the system, which is therefore incompressible. This is the assumption made by Brochard, Jouffrey, and Levinson [6] in their derivation of the slow theory. At high temperatures, free volume or vacancies appear, enabling the small localized density inhomogeneities assumed by Kramer, Green, and Palmstrøm [8] in the derivation of the fast theory. These results are in contradiction to another recent theory by Brereton [19]. He writes down and solves the differential equations of motion of all monomers in a polymer system, concluding that the fast theory should dominate at low temperatures and the slow theory at high temperatures.

The results presented in this study also explain why so little experimental evidence exists supporting the slow theory. Most polymer interdiffusion studies have looked at high molecular weight polymers (≈100 000 g mol$^{-1}$) in which diffusion at observable rates will only occur far above $T_g$ where, according to this study, the fast theory will dominate. To observe diffusion where the slow theory dominates therefore requires both long annealing times (up to 80 days for this study) and low molecular weight polymers possessing high tracer diffusion coefficients. Indeed, both sets of data supporting the slow theory have been acquired from unentangled polymers.

At annealing temperatures greater than 118 °C, the diffusion profiles were found to compare equally well with numerical solutions obtained from both the slow and fast theories. This is because of the near equality of the *d*-PS and PMMA tracer diffusion coefficients in that temperature range, shown by the Arrhenius plot in Fig. 2. As discussed above for the samples annealed at 134 °C, the slow and fast theories are then very similar. A summary of the concentration dependence of the mutual diffusion coefficients, found to produce numerical solutions accurately following the data recorded after annealing samples at the various temperatures, is shown in Fig. 3. The slow and fast theory concentration dependencies are clearly visible, separated by the thermal transition region described by Eqs. (5a) and (5b). The simple Fickian diffusion coefficient obtained when $D^*_{d\text{-PS}} = D^*_{\text{PMMA}}$ is also shown. Future work should include a quantitative comparison of these results to the theory of Ref. [18], as well as attempts to observe both slow and fast theories in other systems.

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