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Interdiffusion of deuterated and protonated poly(methyl methacrylate)

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Nuclear Reaction Analysis is used to study the interdiffusion of deuterated and protonated poly(methyl methacrylate). The diffusion process is found to follow the fast theory predictions and self diffusion is seen to be governed by pure reptation with no evidence of constraint release. The diffusion coefficients scale with temperature according to the Williams-Landel-Ferry equation and are in good agreement with values calculated from viscoelastic parameters using the reptation theory; they are however, about fifty times smaller than other recently published values for similar molecular weights. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymer diffusion was studied extensively for many years by various techniques in order to both understand the theoretical aspects governing the process and to provide quantitative data for practical use[1]. Theoretical aspects include both the methods of polymer molecular motion (Rouse[2], reptation[3] and constraint release[4]) and those of bulk polymer transport. The latter has centered around 'thermodynamic slowing down' in the vicinity of the spinodal[5] and more recently on the relative merits of the fast[6,7] and slow[8,9] theories. These studies have mostly been limited to polystryene (PS), polyethylene (PE), poly(ethylene oxide) (PEO) and poly(vinyl chloride) (PVC), there being little knowledge of diffusion coefficients for other polymers. However, a number of other polymers, such as poly(methyl methacrylate) (PMMA), are widely used commercially and a detailed knowledge of their strength at interfaces is critical for their use in various welding applications such as adhesion and fusion processes. This strength depends on diffusion mechanisms and coefficients.

Jud *et al.*[10] were among the first to look at PMMA blends, calculating diffusion coefficients at temperatures just above the glass transition temperature (T_g) of their polymers, in the range $T_g < T < T_g + 15$ K. Their calculations were based on measurements of the fracture toughness at the interface of welded samples, but their model linking these measurements to diffusion coefficients contained as yet unverified assumptions about the diffusion mechanisms involved in the welding process. For this work they used a commercial PMMA with a large molecular weight distribution ($M_w/M_n = 2$) and unknown tacticity. Since then three other studies of the interdiffusion of PMMA into PMMA were reported. In a study which concentrated on determining diffusion coefficients of polymers in matrices of phase separated diblock copolymers of PS and PMMA, Green *et al.*[11] obtained some data on the tracer diffusion of deuterated poly(methyl methacrylate) (d-PMMA) in PMMA. More recently Van Alsten and Lustig[12] used attenuated total reflectance (ATR) spectroscopy to measure the diffusion coefficients at various temperatures. Liu *et al.*[13] used X-ray reflectometry to measure the displacement of gold markers at the bilayer interface, from which they calculated tracer diffusion coefficients according to the fast theory. This though, requires assumptions about the behaviour of the gold layer during the diffusion process and therefore casts doubt on the numerical values they obtain. Because of the assumptions required in the models outlined above a more direct measurement of the diffusion profiles is required in order to obtain accurate diffusion coefficients.

In this study we investigate the mutual diffusion of d-PMMA of various molecular weights into PMMA, at various temperatures above T_g. The data is acquired by nuclear reaction analysis (NRA), a technique used for many years in the surface analysis of materials[14,15] but only recently applied to polymers[16,17]. The resolution (≈ 250 Å) and the depth of profiling ($\approx 1\ \mu$m) under normal operating conditions, enable the determination of diffusion coefficients in the range of 10^{-13} to $10^{-18}\ \mathrm{cm^2\,s^{-1}}$; ideal for polymers in the proximity of their T_gs.

EXPERIMENTAL

The polymers used are described in *Table 1*. All polymers were supplied by Polymer Laboratories Ltd. and are monodisperse. Their tacticity is approximately 50% syndiotactic, 45% isotactic and 5% atactic. The glass transition temperatures are measured by DSC using a Perkin–Elmer DSC7 with a heating rate of 10°C min^{-1}. The samples are made by spin coating a PMMA film ($\approx 0.8\ \mu$m) from a toluene solution (≈ 100 gl^{-1}) onto a silicon wafer substrate. For this work all samples were made using the same matrix PMMA, of molecular weight 100 250. A d-PMMA film ($\approx 0.2\ \mu$m) is then spin coated onto a glass microscope slide. After waiting several hours for the remaining toluene to evaporate, the film is floated off onto

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Table 1 Polymers use in this work

Polymer type	Molecular Weight ($gmol^{-1}$)	M_w/M_n	Degree of polymerisation: N	T_g (°C)
d-PMMA	23200	1.09	215	119.4
d-PMMA	82500	1.04	754	119.7
d-PMMA	127000	1.04	1176	117.3
PMMA	100250	1.05	1033	121.7

distilled water and picked up by the PMMA coated silicon wafer. The bilayer is then dried for 24 h before annealing. Samples are annealed at 149, 162, 171 and 181°C. For each d-PMMA molecular weight and at each temperature, six samples are made and annealed for different lengths of time in order to increase the accuracy of the measured diffusion coefficients.

NRA is performed at the University of Surrey using a 0.7 MeV $^3He^+$ ion beam from a Van de Graaff accelerator. This energy corresponds to the maximum in the cross-section of the reaction;

$$d + {}^3\mathrm{He} \rightarrow {}^5\mathrm{Li}* \rightarrow \alpha + p \qquad (1)$$

and is also optimum for energy resolution. The protons are detected at an angle of 156° to the beam by an energy sensitive silicon surface barrier detector (thickness 1500 μm). Knowing the density of the sample material, the proton energy spectrum yields the deuterium depth profile. Normalisation to a profile obtained from a uniformly deuterated sample gives the deuterium concentration profile of the labelled polymer. The sample is oriented at an angle of 30° to the beam to allow both good resolution and reasonable depth penetration. Under these operating conditions a depth of $\approx$ 1 μm can be profiled with a depth independent resolution of $\approx$ 250 Å. Because of the high sensitivity of PMMA to radiation, care is taken to minimise sample damage. The beam current is maintained at a low level ($\approx$10 nA) and the sample is back-cooled with liquid nitrogen by using a hollow sample holder. The sample orientation also has the effect of spreading the beam spot over an area twice as large as the beam cross-section. Spectra are acquired in $\approx$ 20 min. Examination of the sample after bombardment shows only a faint yellowing which suggests that damage is negligible.

Previous ion beam analysis of PMMA using NRA at forward detection angles has been unsuccessful[18] largely caused by the technique's sensitive geometry. NRA, with the detector placed at a large back angle, is relatively insensitive to small azimuthal angular changes[19]. The size of the beam spot can therefore be much larger than for forward angle detection (typically 5 × 10 mm^2 compared to 1 × 10 mm^2 for forward angle detection) leading to much lower beam current densities on the sample. In addition the acceptance angle of the detector can be large, providing faster acquisition times without significant loss of depth resolution. These two major advantages of backward angle detection over forward angle detection NRA, combined with the sample cooling, allow clean spectra to be obtained from PMMA samples before excessive beam damage occurs.

THEORY

Diffusion in polymers can be described by Fick's second law[20], which in one dimension is;

$$\frac{\delta\phi}{\delta t} = \frac{\delta}{\delta x}\left(D\frac{\delta\phi}{\delta x}\right) \qquad (2)$$

where ϕ is concentration, t is time and D is the diffusion coefficient. In the case of a constant diffusion coefficient, the solution to this equation is given by;

$$\phi = \frac{1}{2}(\phi_2 - \phi_1)\left[erf\left(h + \frac{x}{w}\right) + erf\left(h - \frac{x}{w}\right)\right] + \phi_1 \qquad (3)$$

where ϕ_1 and ϕ_2 are the concentrations of the traced polymer in the bottom and top layers of the sample respectively; h is the initial thickness of the top layer and w is the characteristic depth of diffusion, defined as $w = (4Dt)^{1/2}$. In most cases however, the diffusion coefficient is not constant but heavily concentration dependent and equation (2) cannot be solved analytically. Instead, either numerical solutions must be found or equation (3) is used in the method of finite differences; applying it to samples in which $\phi_2 - \phi_1$ is very small ($\approx$ 0.1) and assuming that within that range D does remain constant.

Both the fast and slow theories describe mutual diffusion coefficients in polymers. They are both derived from a Flory–Huggins lattice[21] containing vacancies, using Onsager formalism. The slow theory assumes that the fluxes of the two polymers are equal and opposite which leads to a stationary interface. In contrast, the fast theory, assumes a zero osmotic pressure across the interface, which leads to an interfacial movement towards the faster diffusing component as the interdiffusion progresses. For long chains ($N > N_c$ the entanglement length) of chemically identical polymers, the fast theory equation derived by Kramer *et al.*[6] assuming reptation dynamics, is;

$$D_F = N_e B_0 k_B T\left(1 - \frac{\phi}{N_A} + \frac{\phi}{N_B}\right)^2 \qquad (4)$$

where B_0 is a constant related to the polymer segment mobilities, N_A and N_B are degrees of polymerisation of the deuterated and hydrogenated polymers respectively, and $\phi = \phi_A$. Using this equation assumes that the Flory–Huggins interaction parameter (χ) is zero, meaning that the labelling with deuterium is innocuous. This is not always the

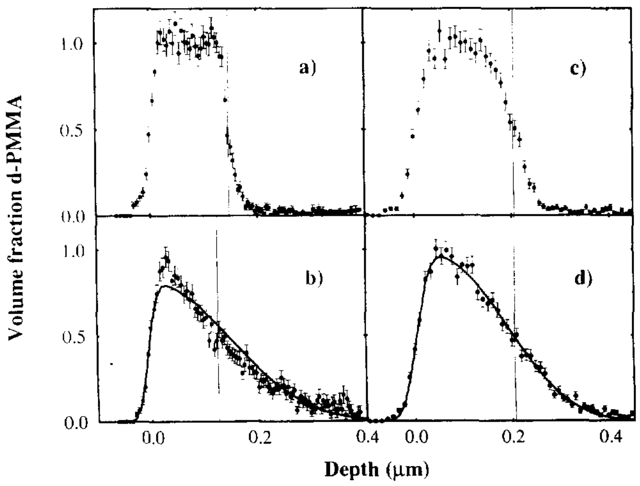

Figure 1 Diffusion profiles; (a) and (b) obtained from 23 200 $gmol^{-1}$ d-PMMA samples annealed at 149°C for 0 and 4 days, respectively and showing a slight movement of the interface indicating fast mode diffusion; (c) and (d) obtained from 127 000 $gmol^{-1}$ d-PMMA annealed at 162°C for 0 and 3 days, respectively and showing no interfacial movement caused by the similarity in degrees of polymerisation. The diffused profiles (b) and (d) are shown along with the best Fickian fits to the data. The fit is inadequate for the system containing polymers of widely varying degrees of polymerisation, (b) but is seen to be very good for the system containing polymers with chains of similar length, (d)

case, as shown by Green and Doyle[5], but here we initially assume that it is.

RESULTS AND DISCUSSION

Typical profiles are shown in *Figure 1a–d*. *Figure 1a* and *b* are obtained respectively from an unannealed sample of 23 200 gmol^{-1} d – PMMA on 100 250 gmol^{-1} PMMA and from one annealed for 4 days at 149°C. In both cases the vertical line indicates the approximate position of the interface (the half height of the trailing edge), which is seen to move towards the lower molecular weight and more mobile d-PMMA by approximately 20 nm. This is a very small movement which would be greatly enhanced by the study of samples made from polymers with a larger disparity in molecular weights. This observation is consistent with the fast-theory only and we shall therefore use equation (4) to obtain numerical solutions to Fick's equation for comparison with the data. *Figure 1c* and *d* show profiles obtained respectively from an unannealed sample of 127 000 gmol^{-1} d-PMMA on 100 250 gmol^{-1} PMMA and from one annealed for 3 days at 162°C. Again the vertical lines indicate the position of the interface which here is seen to remain stationary. This is because both the deuterated and hydrogenated polymers have very similar degrees of polymerisation and the diffusion coefficient is therefore expected to be independent of concentration (as long as $\chi = 0$). Equation (3) can then be used (with $\phi_2 = 1$ and $\phi_1 = 0$) to fit the profiles obtained from these samples. A time sequence of such profiles is shown in *Figure 2*, along with the best fit to each profile using equation (3) convoluted with a Gaussian (FWHM = 600 Å) to take account of the system resolution. These results are summarised in *Figure 3*, where the best straight line fit to the data at each temperature yields the self diffusion coefficient (D_S) shown in *Table 2*.

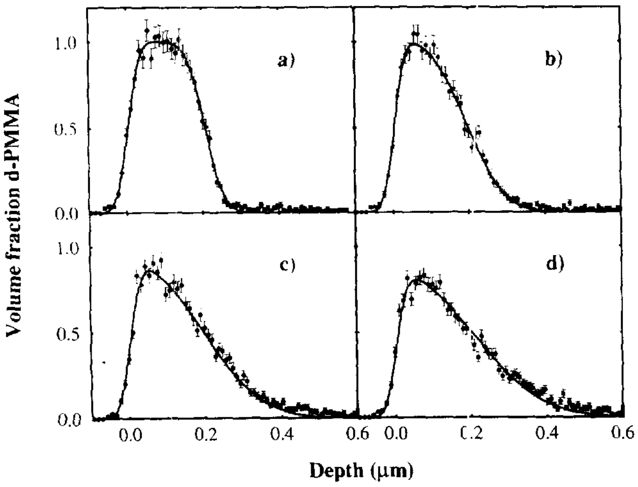

Figure 2 Profiles obtained from 127 000 gmol^{-1} d-PMMA annealed at 162°C for (a) unannealed, (b) 2 days, (c) 5 days and (d) 9 days. The solid lines show the best fit to the data using equation (2) in a simple Fickian model

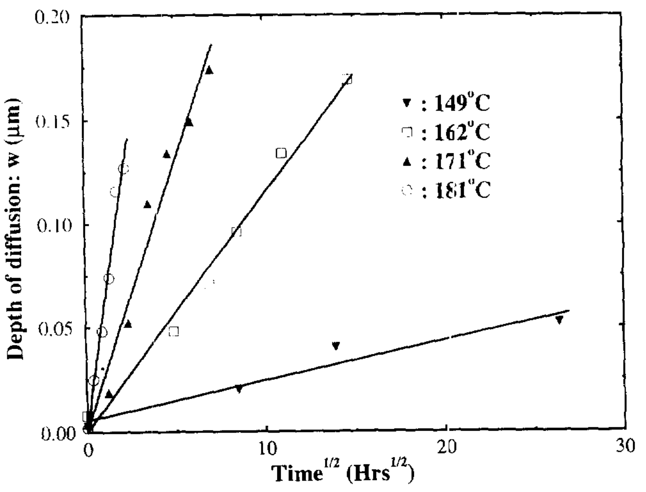

Figure 3 Depths of diffusion obtained from the 127 000 gmol^{-1} d-PMMA samples at the various temperatures plotted versus $t^{1/2}$. The solid lines are the best straight line fits to the data. The slope of each line, $(4Dt)^{1/2}$, yields the PMMA self diffusion coefficient

Figure 4 shows profiles obtained from the 23 200 gmol^{-1} d-PMMA samples annealed for various lengths of time at 171°C, together with the numerical solutions to equation (2) obtained using equation (4) with the method of finite differences[20]. Comparison of the data to the numerical solutions shows excellent agreement which is also observed at all other temperatures and with the other molecular weights. Our assumption of $\chi = 0$ is therefore valid at least to a first approximation. In reality χ is probably a very small positive value having little effect on the diffusion. Numerical solutions suggest that $\chi \leq 10^{-3}$ which is in reasonable agreement with published values of χ for slightly higher molecular weight blends of syndiotactic d-PMMA and PMMA[22]. *Figure 5* shows a summary of the diffusion coefficients used to obtain the numerical solutions. For clarity's sake only the sets for 149°C and 181°C are shown, but those at 162°C show the same characteristics. The tracer

Table 2 Diffusion coefficients of 127 000 gmol^{-1} d-PMMA in 100 250 gmol^{-1} PMMA

Temperature (°C)	D_s (cm^{2}s^{-1})	Temperature (°C)	D_s (cm^{2}s^{-1})
149	3.0×10^{-18}	171	4.6×10^{-16}
162	9.1×10^{-17}	181	2.4×10^{-15}

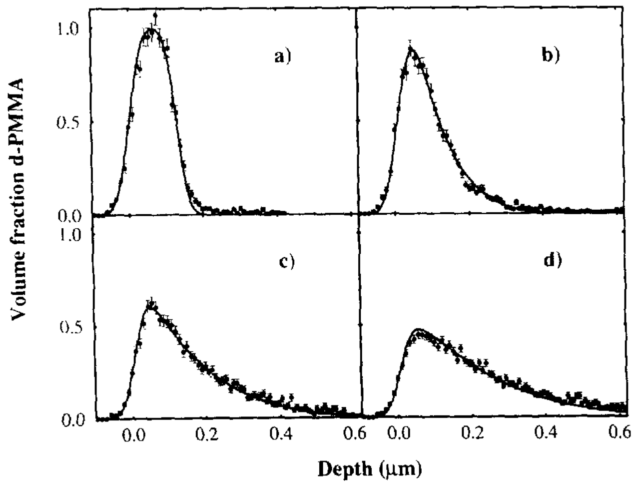

Figure 4 Comparison of the numerical solutions to Fick's equation with the diffusion profiles obtained from 23 200 gmol^{-1} d-PMMA samples annealed at 171°C for (a) unannealed, (b) 40 min, (c) 150 min and (d) 240 min. The number of loops performed in the program calculating the numerical solutions is directly proportional to the annealing time of the samples: 1 loop = 3.75 s → 150 min = 2400 loops

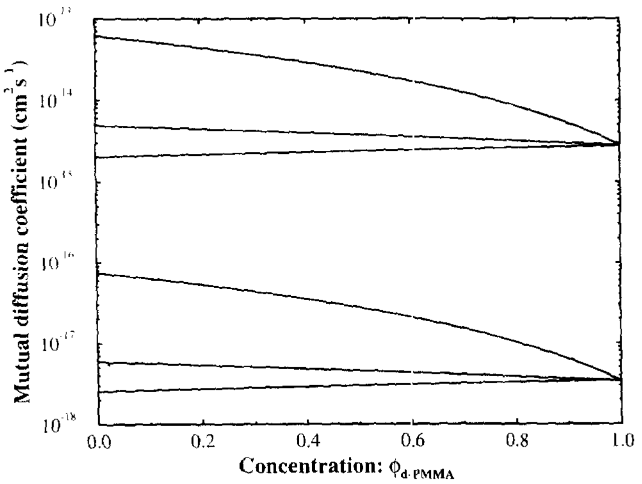

Figure 5 Summary of the diffusion coefficients found to accurately simulate the data at 149°C and 181°C. In each set the lower line represents the 127 000 $g mol^{-1}$ d-PMMA, the middle line represents the 82 500 $g mol^{-1}$ d-PMMA and the upper line represents the 23 200 $g mol^{-1}$

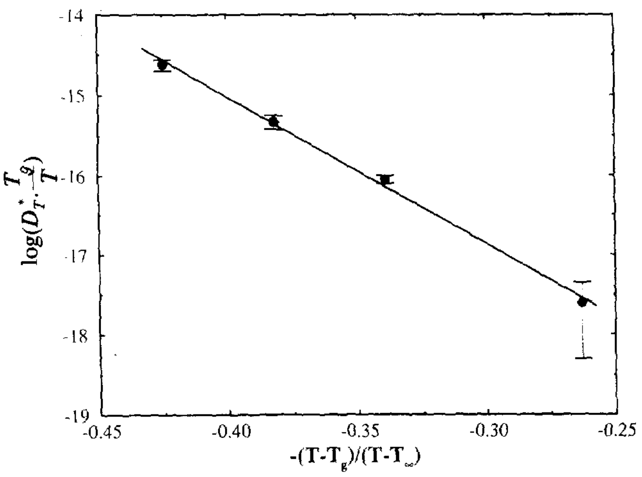

Figure 6 Plot of $\log(\frac{D_T^* \cdot T_g}{T})$ against $-(T - T_g)/(T - T_\infty)$ where D_T* is D_S the self – diffusion coefficient taken from *Table 2*. The straight line fit indicates compliance to the WLF equation

diffusion coefficient of the PMMA (ie D_{Mutual} as $\phi \rightarrow 1$) is seen to be independent of the molecular weight of the d-PMMA. A consequence of this when using equation (4) to obtain numerical solutions, is that the d-PMMA tracer diffusion coefficients (ie D_{Mutual} as $\phi \rightarrow 0$) scale as M_{d-PMMA}^{-2}. These observations suggest that the diffusion observed here is in a pure reptation regime, with no evidence of constraint release, for d-PMMA molecular weights up to and including self diffusion. We therefore write $D_S = D_0 M_{d-PMMA}^{-2}$, where D_0 is the reptation constant.

It should be noted that numerical solutions showing good agreement with the data can also be obtained whilst using the slow theory. For the 82 500 and 127 000 d-PMMA molecular weights, the fast and slow theories are almost identical because of the near equality of the PMMA and d-PMMA tracer diffusion coefficients. However, for the 23 200 molecular weight d-PMMA, good slow theory agreement with the data is obtained only if the tracer diffusion coefficients are altered. Although in this case, the tracer diffusion coefficients are no longer found to agree with either the Rouse, reptation or constraint release theories, indicating again that the diffusion is governed by the fast theory. Agreement between the slow theory predictions and the data is only possible because of the very small interfacial movement. A greater molecular weight disparity between the PMMA and the d-PMMA should show profiles unobtainable from the slow theory.

Figure 5 also shows that the tracer diffusion coefficients are strongly temperature dependent and so we write the Williams-Landel-Ferry equation for well entangled polymers[23]:

$$\log\left(\frac{D_T^* T_0}{D_{T_0}^* T}\right) = \frac{-c_1^0 (T - T_0)}{T - T_\infty} \qquad (5)$$

where c_1^0 is a constant dependent on the polymeric monomer friction coefficient, $D_{T_0}^*$ is the tracer diffusion coefficient at a reference temperature T_0 and T_∞ is the Vogel temperature taken to be 308 K for PMMA[23]. *Figure 6* shows a plot of $\log\left(\frac{D_T^* T_0}{T}\right)$ against $-(T - T_0)/(T - T_\infty)$ where D_T^* is D_S the self-diffusion coefficient from *Table 2* and T_0 is taken to be T_g = 119°C. The slope of the best straight line fit has a value of $c_1^0 = 18.4$; somewhat less than the value of 34 tabulated by Ferry[23]. An Arrhenius approach to the temperature dependence of the diffusion coefficient also gives a straight line, with an activation energy of 371 $kJ mol^{-1}$. This is similar to the 400 $kJ mol^{-1}$ reported by McCrum *et al.*[24], the 320 $kJ mol^{-1}$ by Green *et al.*[25] and the 274 $kJ mol^{-1}$ by Jud *et al.*[10] but substantially larger than the 109 $kJ mol^{-1}$ found by Van Alsten and Lustig[12].

Jud *et al.*[10] estimated the self diffusion of PMMA of molecular weight 1.2×10^5 g at $T = T_g + 15$ K, to be 10^{-17} $cm^2 s^{-1}$. Using equation (5) to scale our values down to $T - T_g = 15$ K, we obtain 2.5×10^{-20} $cm^2 s^{-1}$ (i.e. a factor of 400 times smaller). However, their estimate is based on a model linking the fracture toughness in the interface of a welded sample to the self diffusion coefficient, but the interpretation of crack-healing and the accuracy of this model are debatable because of possible influences of surface effects and segmental movement[26]. In addition they were using a commercial PMMA with a high polydispersity ($M_w/M_n = 2$) which could also account for their excessively high value.

Comparing the self diffusion coefficients of Van Alsten and Lustig[12] and the tracer diffusion coefficients of Liu *et al.*[13], our values are found to be approximately 20 and 70 times lower respectively, for polymers of similar molecular weights at the same $T - T_g$. Van Alsten and Lustig performed infrared ATR spectroscopy on a slightly asymmetric polymer pair (146 000 $g mol^{-1}$ d-PMMA and 88 000 $g mol^{-1}$ PMMA) but assumed, in their fits, that the diffusion coefficient was concentration independent. However, equation (4) predicts a variation of D_F by a factor of 2 between $\phi = 0$ and $\phi = 1$ for these molecular weights. The difference could therefore be reduced to a factor of 10 depending on their exact sample and experimental arrangements which are not explicitly stated. Liu *et al.* performed X-ray reflectivity to determine the movement of gold markers at the polymer interface, from which they calculated the tracer diffusion coefficients of the polymers according to the fast theory[6]. However, whereas the surface layer of gold does appear to remain fixed at the surface[27], the movement and the effect of the interfacial gold layer are not fully understood. The fast theory assumes that the interfacial gold layer will remain at the interface and therefore move with the swelling of the slower component[6,13], but Shull and Kellock[28] have shown that the gold particles will tend to diffuse into the two polymers either side of the interface at rates inversely proportional to the polymer viscosities. This casts doubt on Liu *et al.*'s interpretation of their measurement. Also Kunz and Stamm[29] observed the $t^{1/4}$ dependence of the interfacial broadening between d-PMMA and PMMA by neutron reflectivity, long after the expected $t^{1/2}$ dependence predicted by the results of Liu *et al.* when interpreted in the reptation theory. The lower diffusion coefficients reported here are consistent with Kunz and Stamm's result.

Our data is also consistent with the results of Green *et al.*[11]; at 185°C their data indicates that $D^*_{\text{d-PMMA}} = 10^{-14}\,\text{cm}^2\,\text{s}^{-1}$ for $M_w = 10^5\,\text{gmol}^{-1}$. Using the WLF equation to scale the values obtained in this study to 185°C for the same molecular weight polymer, yields a tracer diffusion coeffient of $4.5 \times 10^{-15}\,\text{cm}^2\,\text{s}^{-1}$; only a factor of 2 difference and hence in very good agreement.

In a pure reptation regime, as appears to be the case here, the tracer diffusion coefficient can be related to measured viscoelastic parameters[30,31]:

$$D^*_{\text{rep}} = \left(\frac{4}{15}\right)\left(\frac{M_o M_e k_B T}{\zeta_o}\right)\frac{1}{M^2} \tag{6}$$

where M_o, M_e and M are the monomer, entanglement and polymer molecular weights, k_B is the Boltzmann constant the ζ_o is the monomeric friction coefficient at temperature T. Using $M_e = 4800\,\text{gmol}^{-1}$ [23] and interpolating between the shear compliance points measured by Plazek *et al.*[32] to obtain the monomer friction coefficient of atactic PMMA at $T - T_g = 43$ K we obtain $D = 1.9 \times 10^{-16}\,\text{cm}^2\,\text{s}^{-1}$. Very good agreement is obtained between this value and the value measured in this work at 162°C (ie $T - T_g = 43$ K): $9.1 \times 10^{-17}\,\text{cm}^2\,\text{s}^{-1}$, where again, the results differ only by a factor of 2. Similar accord between the viscoelastic data and theory of equation (6) and experimental diffusion coefficients, was already found and reported by a number of groups in polystyrene and polyethylene systems (see Ref. [1] for a comprehensive review of the subject), as well as in PMMA[25].

SUMMARY

The interdiffusion of deuterated and protonated PMMA was studied using Nuclear Reaction Analysis. Diffusion profiles were compared to numerical solutions to Fick's equation using fast theory predictions and were seen to be in excellent agreement. The Flory-Huggins interaction parameter (χ) was estimated to be lower than 10^{-3}. Although the diffusion coefficients determined in this work showed discrepancies with most previously published values, they provide good agreement with the reptation theory predictions based on viscoelastic data. They were also seen to scale with temperature according to Williams-Landel-Ferry equation.

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