Diffusion of deuterated toluene in polystyrene

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The diffusion of deuterated toluene (d-toluene) from the vapour into glassy polystyrene has been studied using forward recoil spectrometry (FRES) over a range of temperatures (20–35°C) and d-toluene activities (0.10 to 0.35). At the highest d-toluene activity a Case II diffusion front is observed to form and propagate at a constant velocity into the polymer. The velocity is thermally activated with an activation enthalpy, ΔH_V, of 1.49 eV. The diffusion coefficient, D, of d-toluene into the glass can be extracted from the measured concentration profile ahead of the front and was also found to be thermally activated with an activation enthalpy, ΔH_D, of 1.12 eV. Because the Thomas and Windle model of Case II diffusion predicts that $\Delta H_V = (\Delta H_D + \Delta H_\eta)/2$, where ΔH_η is the activation enthalpy for viscous creep of glassy polystyrene, previously determined to be 1.76 eV, we can compare the predictions of this model with experiment. The good agreement observed gives further evidence that the basic premise of the Thomas and Windle model of Case II diffusion is correct. Measurements of D at low d-toluene activities as well as the exchange diffusion coefficient were made and yield values that are in reasonable agreement with those extracted from the concentration profile ahead of the Case II front. These results show that D is approximately independent of d-toluene volume fraction below the critical volume fraction, ϕ_c, for Case II front formation.

(Keywords: diffusion; d-toluene; forward recoil spectrometry; FRES)

INTRODUCTION

For organic solvents which swell glassy polymers significantly, an extreme situation, known as Case II diffusion[1], can occur. In Case II diffusion the solvent volume fraction at the surface, ϕ_s, increases until a critical concentration, ϕ_c, is reached at the surface at which time the Case II front forms and moves into the polymer at a constant velocity[2–5]. The first attempts at models of Case II diffusion used variable material properties[6–8], or two stage diffusion[9–11], but were not able to explain the constant velocity of the Case II front. Crank's[7] introduction of the swelling stress of the solvent to the diffusion equations gave the first in a series of quantitative models[12–18] which led to the Thomas and Windle[19–23] (TW) model of Case II diffusion. For a summary of the development of models of Case II diffusion see Lasky[24].

Measurement of the diffusion coefficient of an organic solvent in a polymer glass is complicated by the slow mechanical response of the polymer chains to the osmotic stress produced by the solvent. The coupling of the mechanical response of a polymer glass and diffusion of the solvent means that Fick's second law of diffusion must be modified to describe adequately the solvent penetration[12–13]. Once the Case II front has formed, the concentration of diffusant in the front stays relatively constant, so the Case II front acts as a moving boundary of nearly constant concentration. For a reference frame moving with the Case II front, the conditions ahead of the front approach steady state[25].

For flat samples where the diffusion distance is small compared to the size of the sample, the diffusion equation can be solved in one dimension. For steady state diffusion described by a diffusion coefficient, D, ahead of a boundary moving with a constant velocity, V, Fick's second law can be written:

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial \phi}{\partial x} + V\phi\right) = 0 \tag{1}$$

where ϕ is the volume fraction solvent, t is time, and x is the distance ahead of the boundary. Thus for a Case II diffusion front, the solution for the Fickian precursor ahead of the front when D is not a function of solvent concentration is[26]:

$$\phi = \phi_c \exp(-Vx/D) \tag{2}$$

Mills *et al.*[27] used Rutherford backscattering spectrometry (RBS) to measure concentration profiles of solvents which contained heavy atoms such as iodine or chlorine. The concentration profile at successive exposure times can be used to find V, and equation (2) can be fitted to the Fickian precursor to get a value of D. RBS works best for a thin layer containing a heavy element on top of a substrate made up of light elements, and so is ideal for the initial diffusion of solvents containing a heavy atom into polymers of carbon and hydrogen. For hydrocarbon solvents such as toluene, with no heavy elements to act as a tag, backscattering from the solvent can not be distinguished from that of the polymer matrix.

The problem of providing a tag for hydrocarbon solvents can be solved by replacing the hydrogen atoms with deuterium. Deuterated toluene (d-toluene) was used in this study as the tagged solvent, and protonated toluene (h-toluene) was used to give an initial concentration to some samples. Using a deuterated analogue of a solvent gives a chemically similar molecule to the

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protonated solvent. While there exist small thermodynamic differences between deuterated and protonated organic molecules[28], these differences only have significant effects on diffusion for high molecular weights[29]. The solvent volume fraction *versus* depth for the d-toluene diffusion into protonated polystyrene (h-PS) is found by using forward recoil spectrometry (FRES) to measure the atomic fraction of deuterium *versus* depth in the PS sample[30,31]. The volume fraction of d-toluene is calculated from the atomic fraction of deuterium using the densities of pure toluene and PS assuming that the molecular volumes are additive in solution. Fitting equation (2) to the ϕ *versus* depth profiles from FRES gives values of D at several temperatures from which the activation enthalpy for diffusion, ΔH_D, can be calculated. The value of ΔH_D is compared to predictions made using the TW model.

EXPERIMENTAL

Sample preparation and d-toluene exposure

Forward scattering measurements are extremely sensitive to the scattering angle, so a great deal of care must be taken to produce flat samples and to maintain a constant angle between the incoming beam and the detector. The polymer used in this study was monodisperse polystyrene with a molecular weight of 390000 purchased from Pressure Chemical Company. Films about 20 μm thick were prepared by dipping a glass slide in a 12% solution of the polystyrene in toluene. The films were dried, sliced, and floated off in water onto aluminum substrates. The aluminum substrates were diamond polished to provide a flat surface, then etched with a 20% sodium hydroxide solution to improve the polymer adhesion.

After the PS film was floated onto the substrate, being careful not to trap any air bubbles underneath, the film was bonded to the aluminum surface by suspending the film over toluene liquid for about 100 s. As the PS film absorbed toluene it would swell and wet the surface of the aluminum. The films were then dried for 4 h, vacuum annealed at 125°C for 1 h, and aged at 50°C for 1 day. FRES measurements of films cast from d-toluene and annealed as above showed that the residual solvent concentration was below the sensitivity of the FRES instrument, less than 0.01 atomic fraction deuterium.

The samples were exposed to d-toluene vapours in a flask above a solution of the d-toluene and polystyrene. The concentration of d-toluene in the solution determines the activity of the vapour in the flask. The samples were first brought to the same temperature as the vapour, then suspended vertically in the flask, well away from the flask walls. Calculations[32] show that the reduction in the activity of toluene at the surface of the sample due either to vapour transport effects or to depletion of toluene from the vapour will be negligible for the experimental conditions used in this study. The temperature of the flask was controlled to ± 0.1°C by a water bath. In order to be able to study diffusion without simultaneous changes in overall polymer swelling or solvent concentration, some of the samples were allowed to absorb an initial concentration of protonated solvent by exposing them in a flask of low activity h-toluene for times ranging from 1 to 7 days, then rapidly transferring the samples to a flask containing d-toluene vapour. The samples with an initial volume fraction h-toluene were then exposed and analysed in the same manner as pure PS samples.

After the samples were removed from the d-toluene flask they were immediately immersed in liquid nitrogen to freeze the concentration profile in place. The dewar of liquid nitrogen was kept within 10 cm of the sample to allow a transfer time of under 1 s to be achieved. All subsequent handling of the samples until they entered the FRES vacuum chamber was done under the liquid nitrogen, or in a glove bag filled with dry nitrogen, to prevent water vapour from collecting on the surface of the cold sample during the rapid transfer from the liquid nitrogen to the vacuum chamber load lock. The sample stage in the FRES vacuum chamber was also cooled with liquid nitrogen to minimize the effect of radiation damage caused by the ion beam on the measured concentration profile.

Determination of the concentration profile using FRES

The atomic fraction of deuterium in the sample is found by directing a 3 MeV beam of doubly charged helium nuclei at the sample, then measuring the energy and yield of the hydrogen and deuterium nuclei which recoil from the sample. The helium beam and the recoiling nuclei will lose energy due to inelastic collisions with the electrons in the polymer, so the energy of the detected nuclei gives a measure of the depth in the polymer from which the nuclei recoiled. The number of deuterium nuclei detected is compared to the spectrum from a standard sample to find the concentration of deuterium in the sample under investigation. *Figure 1* shows the typical geometry for FRES.

The volume fraction *versus* depth of d-toluene in PS can be measured using FRES to a depth of 0.75 μm (see *Figure 2*). For depths greater than 0.75 μm the energy of the recoiling deuterons overlaps that of the protons recoiling from the surface. While it is possible to deconvolute the signal into hydrogen and deuterium components, for low levels of d-toluene the signal from the deuterium is lost in the noise of the hydrogen peak. The hydrogen and deuterium nuclei recoiling from the sample are separated from forward scattered helium nuclei by a 10.6 μm thick mylar foil in front of the detector. Electronic interactions with the atoms in the mylar foil cause additional uncertainty in the measurement of the energy of the nuclei which pass through the

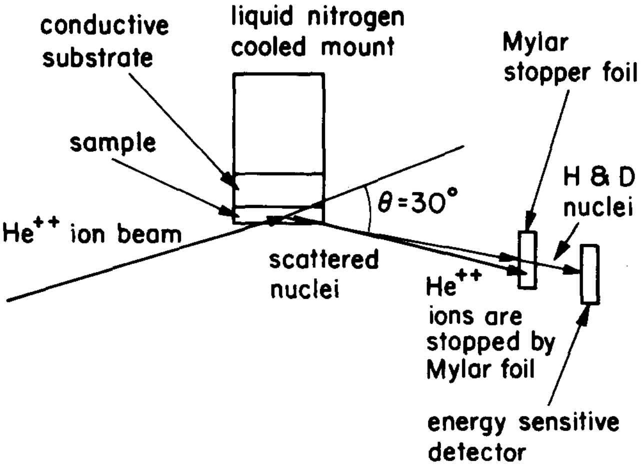

Figure 1 Schematic diagram showing the geometry of the ion beam and sample for a typical FRES analysis

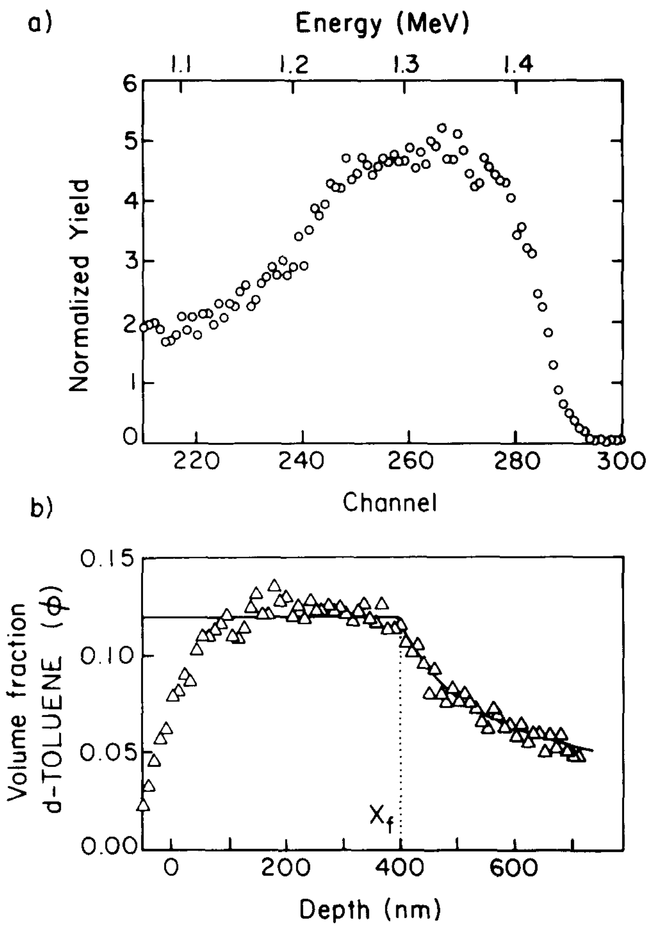

Figure 2 (a) FRES spectrum of PS sample exposed to 0.35 activity d-toluene for 1920 s at 30°C. (b) Volume fraction *versus* depth profile calculated from the data in (a). The solid line was obtained from a simulation fit to the spectrum in (a)

foil, while the helium nuclei are stopped within the foil. The uncertainty in the detected energy of a deuterium ion is 45 KeV which gives an uncertainty in the depth scale of 80 nm. The uncertainty of the measurement of the energy leads to the rounding of the FRES spectrum shown in *Figure 2a*. The analysis of the FRES spectrum accounts for the effect of the resolution of the detector by fitting the experimental data to a simulated spectrum calculated from a numerical model of the concentration profile in the sample[33]. The simulated spectrum is convoluted with a Gaussian function to match the effect of the detector resolution.

RESULTS

Case II diffusion of d-toluene into pure PS

From a FRES spectrum, such as that shown in *Figure 2a*, the depth of the Case II front, x_f, is found by fitting a simulated spectrum to the data. The d-toluene concentration profile in *Figure 2b* shows the constant concentration front, and *Figure 3* shows the linear relationship of the Case II front depth with time, which are characteristic of Case II diffusion[1]. So from the data in *Figures 2* and *3* we can conclude that d-toluene diffuses into PS by Case II diffusion.

The Case II front velocity is the slope of a Case II front penetration depth *versus* exposure time plot such as *Figure 3*, and the induction time for Case II diffusion to begin, t_i, is the intercept on the abscissa. *Table 1* lists V and t_i for Case II diffusion at several temperatures, for PS samples exposed to vapour over a 0.15 equilibrium volume fraction, ϕ_{eq} (0.35 activity) mixture of d-toluene in PS.

Figure 4 shows a plot of the logarithm of V *versus* $1/T$; the error bars are 95% confidence limits. The activation enthalpy for V, ΔH_V, is calculated from the slope of *Figure 4* and found to be 1.49 eV with a standard deviation of 0.06 eV. Once V is known, D is calculated by fitting equation (2) to the data points ahead of the Case II front. *Figure 5* shows the average values of D *versus* $1/T$; the error bars are 95% confidence limits for the data. The slope of the plot can be used to calculate the activation enthalpy for D, ΔH_D, which is found to be 1.12 eV with a standard deviation of 0.03 eV.

The simulations and fits are calculated using a multivariable search algorithm developed by Doolittle[34]. The unknowns from equation (2) to be found by the fit are D and ϕ_c. *Figure 6a* shows the sensitivity of the data to D. Five simulations using different values of D have been overlaid on the experimental spectrum. In *Figure 6b* the chi squared error function, χ^2, for the simulation is plotted *versus* D. The search algorithm finds the optimum value of D by fitting a parabola through χ^2 and using the predicted minimum value for the next iteration.

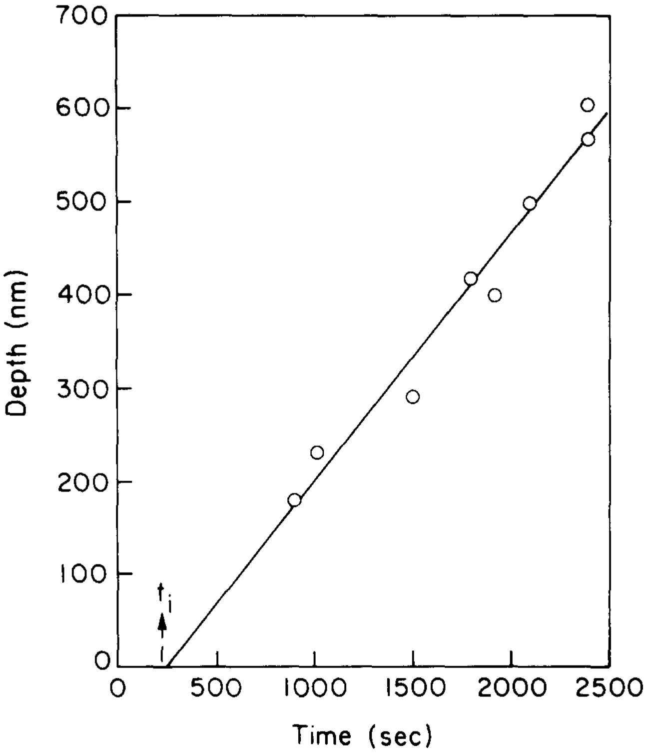

Figure 3 Case II front depth *versus* exposure time for 0.35 activity d-toluene at 30°C. The solid line is a linear least squares fit to the data

Table 1 Case II front velocity and induction time *versus* temperature

T (°C)	V (nm s^{-1})	t_i (s)
20	0.04	911
25	0.12	326
30	0.27	296
35	0.72	27

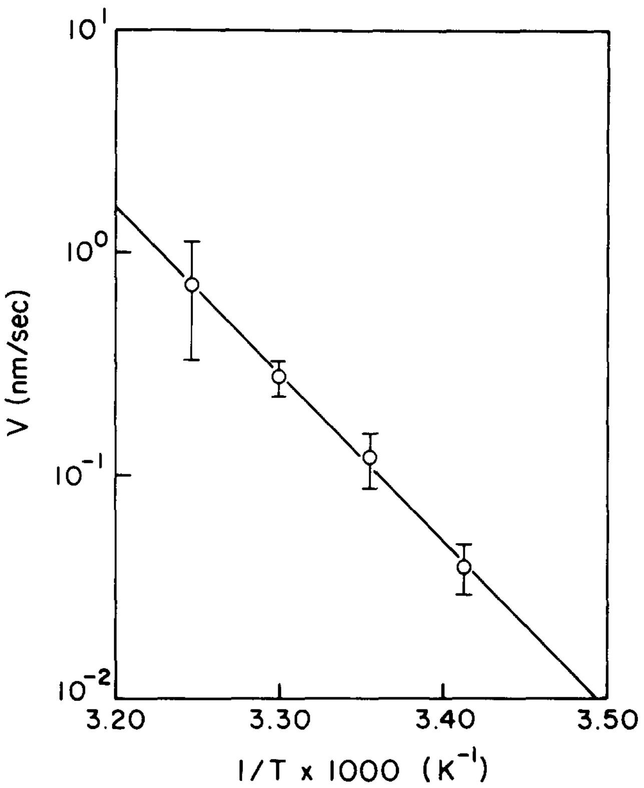

Figure 4 The logarithm of V for d-toluene in PS *versus* $1/T$ at 0.35 activity. The solid line is a linear least squares fit to the data

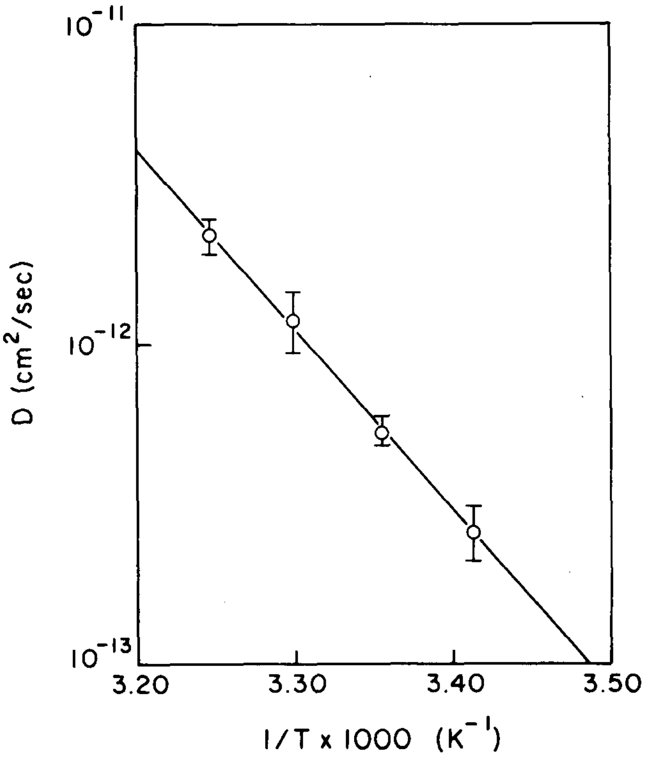

Figure 5 The logarithm of D for d-toluene in PS *versus* $1/T$ at 0.35 activity. The solid line is a linear least squares fit to the data

Fickian diffusion of d-toluene into PS and the effect of an initial volume fraction of h-toluene

In the previous section results are shown which clearly indicate that the diffusion of d-toluene in PS for $\phi_{eq} = 0.15$ (0.35 vapour activity) occurs by Case II diffusion. The linear kinetics and constant front concentration which are characteristic of Case II diffusion are shown in *Figures 2b* and *3*.

Equation (2) fits well to the steady state diffusion profile ahead of the front with a constant value of D; however, a moderate variation in D with d-toluene volume fraction can not be ruled out due to the noise and limited depth resolution of the FRES spectra. In order to test the assumption of a D independent of ϕ, PS samples with no initial concentration of h-toluene were exposed to d-toluene vapour with ϕ_{eq} less than ϕ_c. For absorption of d-toluene with equilibrium volume fractions below the critical volume fraction for Case II diffusion, the d-toluene concentration will be changing with depth and time. The classical solution for Fick's second law applies if ϕ_s and D are constant:

$$\phi = \phi_s erfc[x/2(Dt)^{1/2}] \qquad (3)$$

Because the actual concentration at the surface increases as the polymer swells, and D may change with ϕ, equation (3) is only approximate. Lasky[35] compared fits using equation (3) to a finite difference calculation of the volume fraction *versus* depth profile of iodohexane in PS using a variable ϕ_s, and found that both calculations gave very similar values of D. *Table 2* shows the result of fitting equation (3) to FRES spectra for PS exposed for successive times at 25°C to d-toluene vapour

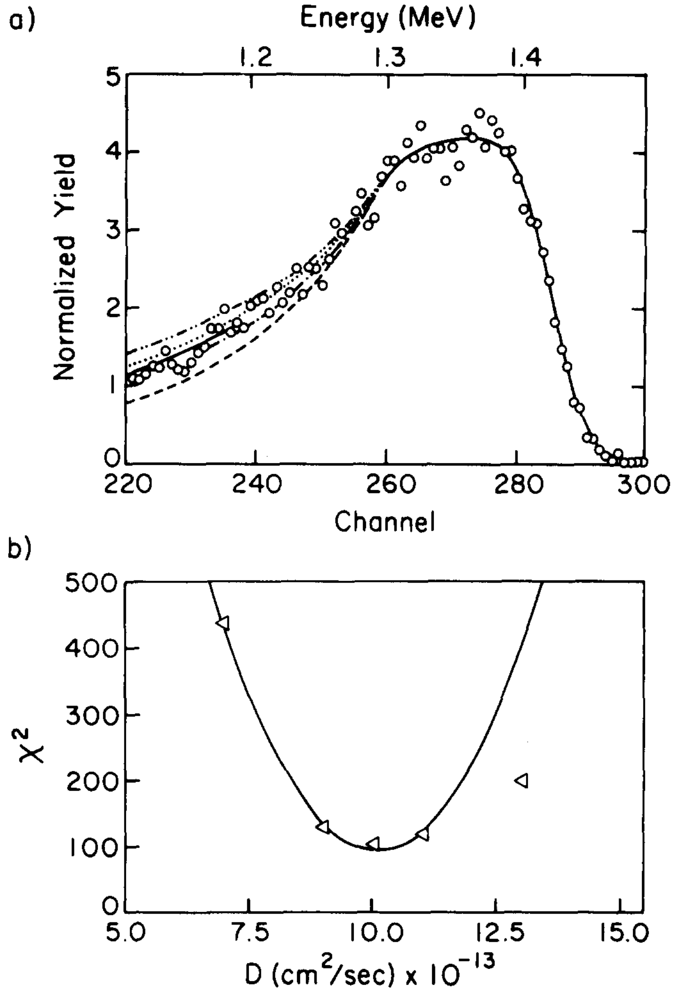

Figure 6 (a) FRES spectrum of PS sample exposed to 0.35 activity d-toluene for 1500 s at 30°C, with simulations for several values of D. (b) χ^2 error function for simulations to the data in (a). The solid line is a quadratic least squares fit to the first four points

Table 2 D and ϕ_s *versus* exposure time for $\phi_{eq} = 0.09$ d-toluene

Time (s)	D (cm^2 s^{-1})	ϕ_s
14940	2.0×10^{-13}	0.068
8400	4.5×10^{-13}	0.042
7220	4.0×10^{-13}	0.053
3720	5.0×10^{-13}	0.042
3600	4.5×10^{-13}	0.041
3600	4.5×10^{-13}	0.041
1800	4.0×10^{-13}	0.041
900	4.0×10^{-13}	0.032

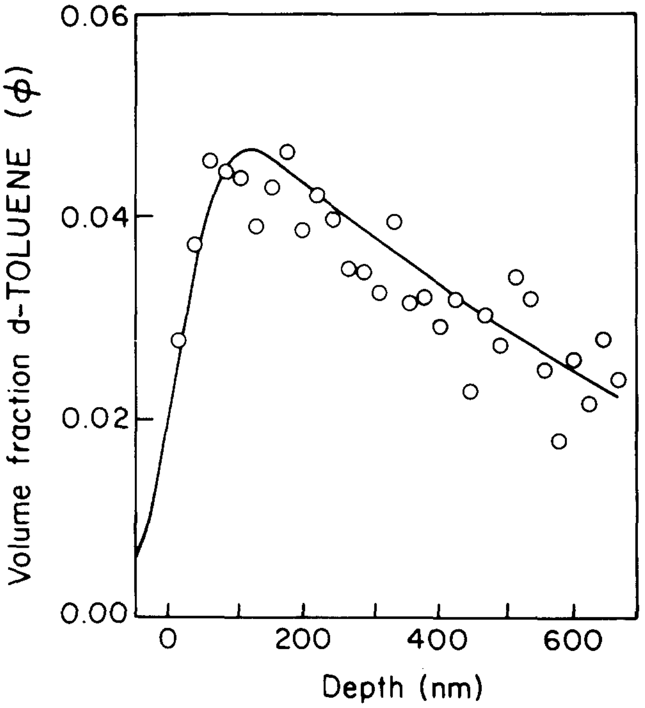

Figure 7 Volume fraction *versus* depth profile of a PS sample exposed to $\phi_{eq} = 0.09$ (0.22 vapour activity) d-toluene for 3600 s at 25°C. The solid line is calculated from a simulation of the FRES spectrum

with an equilibrium volume fraction of 0.09 (0.22 vapour activity).

For the longest exposure time in *Table 2*, 14940 s, the concentration profile does not decrease significantly over the depth of the FRES measurement, so the fit to find D is not very accurate. *Figure 7* shows ϕ *versus* depth for one of the PS samples used to calculate D in *Table 2*, where the solid line is a simulation using equation (3) for ϕ *versus* depth. In *Table 2* the average value of D is 4×10^{-13} cm^2 s^{-1} and the standard deviation, σ, is 0.9×10^{-13} cm^2 s^{-1}, or 22%. The approximate value for D is very close to the value given in *Table 3* for diffusion ahead of the Case II front. As expected, ϕ_s in *Table 2* increases with time as a result of the slow swelling of the polymer glass driven by the solvent osmotic pressure[25].

Repeating the above study with a 0.07 equilibrium volume fraction (0.18 vapour activity) d-toluene gives a very similar result: the average D is 5×10^{-13} cm^2 s^{-1}, and the standard deviation is 1×10^{-13} cm^2 s^{-1}, or 20%. The accuracy of the data is not sufficient to see a change in D with such a small difference in the volume fraction of the solvent.

Values of D for several equilibrium volume fractions, ϕ_{eq}, of d-toluene are shown in *Table 3*. In this table, the only measurement of D found by fitting the concentration profile ahead of the Case II diffusion front is the value at $\phi_{eq} = 0.15$, all the others use equation (3) to find the values of D. For the transient diffusion when $\phi < \phi_c$, the different values of D in *Table 3* are all within 1 standard deviation of the average value of 6×10^{-13} cm^2 s^{-1}, so that these differences are not significant.

All of the values in *Table 3* were measured from concentration profiles that start from an initial volume fraction, ϕ_i, of zero. The form of equations (2) and (3) is such that the volume fraction is low over the majority of the profile, so it is not surprising that D measured from these profiles is independent of ϕ_{eq}, because for the majority of the depth range, ϕ is nearly the same. A more sensitive test to determine whether D changes with ϕ is to start with a uniform initial concentration of protonated solvent and watch it exchange with deuterated solvent vapour. Starting with such an initial concentration of solvent also allows measurements of D to be made without interference from possible effects due to swelling of the polymer by the solvent.

To perform such an experiment the PS sample was exposed to h-toluene vapour for several days to allow it to come to a uniform initial volume fraction. The sample was then switched to a flask containing d-toluene vapour to introduce tagged molecules at the surface and the diffusion of the tagged molecules into the polymer was tracked using FRES. The diffusion of tagged molecules without changes in the total solvent volume fraction (h-toluene + d-toluene) gives the exchange diffusion coefficient, D^+.

For the interdiffusion of two components with similar values of D^+ and a low concentration of tagged molecules, the diffusion coefficient describing tagged molecules is known as the self diffusion coefficient. In a polymer/solvent system, the polymer molecules swell, but only the solvent molecules have any significant motion due to diffusion, while the concentration of tagged molecules is larger than for tracer experiments, so D^+ is called the exchange diffusion coefficient instead of the self diffusion coefficient. D^+ can be measured by exposing the samples first to h-toluene, then to d-toluene vapour with the same equilibrium volume fraction.

For an initial volume fraction, ϕ_i, of 0.07 h-toluene and ϕ_{eq} of 0.07 (0.18 vapour activity) d-toluene diffusing into PS at 25°C, the average D^+ is 7×10^{-13} cm^2 s^{-1}. D^+ is found by fitting the FRES spectrum to the concentration profile expected from Fickian diffusion (equation 3). Since the polymer is already swollen with h-toluene, the total concentration of h-toluene and d-toluene at the surface should be constant, so equation (3) is an exact solution to Fick's second law. The values of D^+ shown in *Table 4* are similar to the values of D shown in *Table 3*. *Table 4* shows values of D^+ for two different values of ϕ which are within 1 standard deviation, so the values are not significantly different. *Table 5* shows D for samples with an initial volume fraction of h-toluene exposed to a higher concentration

Table 3 *D versus* equilibrium volume fraction d-toluene

ϕ_{eq}	D (cm^2 s^{-1})	σ (10^{-13} cm^2 s^{-1})
0.04	9×10^{-13}	3
0.07	5×10^{-13}	1
0.09	4×10^{-13}	1
0.15	5×10^{-13}	1

Table 4 D^+ *versus* equilibrium volume fraction d-toluene at 25°C

$\phi_{eq} = \phi_i$	D^+ (cm^2 s^{-1})	σ (cm^2 s^{-1})
0.04	6×10^{-13}	1.1×10^{-13}
0.07	7×10^{-13}	0.3×10^{-13}

Table 5 *D versus* initial and equilibrium volume fraction d-toluene at 25°C

		D (cm^2 s^{-1})	
↓ ϕ_{eq}	$\phi_i \rightarrow$ 0.04	0.07	0.09
0.07	9×10^{-13}		
0.15	6×10^{-13}	12×10^{-13}	37×10^{-13}

of d-toluene. The analysis of the samples where ϕ_{eq} is greater than ϕ_i is complicated by several processes which occur simultaneously: exchange of h-toluene and d-toluene, additional absorption of d-toluene, and swelling of the polymer. In *Table 5*, for ϕ_{eq} of 0.15, there is a significant increase in D for ϕ_i greater than 0.04.

DISCUSSION

For a given vapour activity there is a limited temperature range over which the Case II front velocity of toluene can be accurately measured by the techniques described above. For temperatures below 20°C the volume fraction in the Fickian precursor decreases slowly with depth, so it becomes very difficult to distinguish the position of the Case II front. For temperatures above 35°C, the variation in the data becomes large, possibly due to the increased vapour pressure of toluene causing significant losses while transferring the sample into and out of the flask. In spite of the limitations of the experimental technique the temperature range was sufficient to calculate activation enthalpies for D and V.

The Thomas and Windle model of Case II diffusion can be used to derive an equation for V[35]:

$$V = \sqrt{(CTD(T)/\eta_0(T))} \qquad (4)$$

where C is a constant, T is the absolute temperature, and η_0 is the viscosity of the pure polymer glass. The temperature dependence of equation (4) can be used to derive a relationship between ΔH_D and ΔH_V[35]:

$$\Delta H_V = (\Delta H_D + \Delta H_\eta)/2 \qquad (5)$$

where ΔH_η is the activation enthalpy for the polymer viscosity and is given by Lasky *et al.*[35] for PS as 1.76 eV with a standard deviation of 0.31 eV. Substituting the measured value of ΔH_D for d-toluene in PS, and the value of ΔH_η into equation (5) gives a predicted value for ΔH_V of 1.44 eV which is within 1 standard deviation of the measured value of 1.49 eV $\pm$ 0.06 eV. The activation enthalpy given by Lasky *et al.* for the flexible molecule iodohexane diffusing in PS is 0.60 eV, considerably smaller than ΔH_D for the rigid d-toluene molecule, 1.12 eV. Nevertheless the activation enthalpies for the Case II front velocity differ as predicted by equation (5), i.e. $\Delta H_V = 1.07 \pm 0.21$ eV for iodohexane in PS and $\Delta H_V = 1.49 \pm 0.06$ eV for d-toluene in PS. These results show convincingly the basic ideas of the Thomas and Windle model of Case II diffusion are correct.

The activation enthalpy, ΔH_D, (1.12 eV) for d-toluene diffusion in glassy polystyrene is surprisingly close to ΔH_m the activation enthalpy for rotational motion of d-toluene in PS. This quantity has been measured by Rössler[36] using nuclear magnetic resonance (n.m.r.) to be 1.0 eV at his lowest d-toluene volume fraction (0.19) in PS. The similarity of the two values might prompt speculation that the necessity for the reorientation of the toluene molecule as it diffuses is an important factor in the resistance to its diffusive motion. However, extrapolation of the average toluene rotational times determined by n.m.r. to our conditions yields values of $< 10^{-10}$ s. Thus the average toluene molecule makes many rotations ($> 10^6$) in the average time it takes the molecule to translate by diffusion only 1 Å! With these orders of magnitude it is difficult to believe that the rotation of the toluene molecule can be the rate controlling step in its translational diffusion. The close agreement of the activation enthalpy for rotational and translational diffusion must be coincidence.

CONCLUSIONS

Forward recoil spectrometry has been shown to be a very useful depth profiling method for studying Case II diffusion. It will allow any organic solvent which can be isotopically labelled by substituting deuterium for hydrogen to be profiled and thus greatly extends the range of penetrants that can be investigated by ion beam analysis beyond those (with heavy atom tags) previously accessible using Rutherford backscattering spectrometry.

Deuterated toluene at an activity of 0.35 diffuses into glassy polystyrene by Case II diffusion over a range of temperatures of 20–35°C. Both the front velocity and the diffusion coefficient of d-toluene obtained by fitting the concentration profile ahead of the front are thermally activated, but with different activation enthalpies, 1.49 eV *versus* 1.12 eV. This difference strongly supports the basic premise of the Thomas and Windle model of Case II diffusion, which proposes that the front velocity is controlled by both the diffusion ahead of the front and the swelling rate of the glass, the latter dependent on the mechanical relaxation of the polymer chains in response to the osmotic stress of the solvent.

Measurements of D at low d-toluene activities and measurements of the exchange diffusion coefficient D^+ are approximately independent of the activity of d-toluene and the concentration of h-toluene in the polystyrene. These agree well with those values extracted from the concentration profile ahead of the Case II front at higher d-toluene activities.

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