# Temperature dependence of case II diffusion

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Rutherford backscattering spectrometry was used to measure the front velocity $V$ and the local volume fraction $\phi(x)$ *versus* depth $x$ of iodohexane in polystyrene as a function of temperature during case II diffusion. An effective viscosity $\eta_0$ of the pure polymer was found from the initial surface swelling kinetics, and the diffusion coefficient $D$ of iodohexane in the glass could be estimated from the iodohexane volume fraction profile $\phi(x)$. The case II front velocity is thermally activated, i.e. $V=V_0\exp(-\Delta H_V/k_BT)$, where $k_B$, $T$ and $V_0$ are the Boltzmann constant, absolute temperature and a constant, respectively. The activation enthalpy $\Delta H_V$ for the velocity is found to be $1.07\pm0.21$ eV. The viscosity and diffusion coefficients are also thermally activated, i.e. $\eta_0=\eta_\infty\exp(\Delta H_\eta/k_BT)$ and $D=D_0\exp(-\Delta H_D/k_BT)$, where $\eta_\infty$ and $D_0$ are constants. The activation enthalpies $\Delta H_\eta$ and $\Delta H_D$ are found to be 1.76 and 0.60 eV, respectively. These results strongly support recent models of the steady-state front motion in case II diffusion, which require that $V$ scales as $(D/\eta_0)^{1/2}$, with the consequence that $\Delta H_V=(\Delta H_D+\Delta H_\eta)/2$.

**(Keywords: Rutherford backscattering spectrometry; osmotic pressure; activation enthalpies; induction time)**

## INTRODUCTION

Case II diffusion of an organic penetrant in a polymer glass is characterized by the presence of a sharp front where the volume fraction $\phi$ of penetrant decreases abruptly with depth $x$, as illustrated in *Figure 1a*[1-3]. The gradient in $\phi$ behind the front is negligible whereas the concentration profile preceding the front, which is approximately $\phi=\phi_0\exp(-Vx/D)$, is consistent with Fickian diffusion (where $D$ is a diffusion coefficient characteristic of the glassy state) in front of a boundary moving with a constant velocity $V$ (ref. 4). As shown in *Figure 1*, some time must elapse before the $\phi(x,t)$ profile reaches its steady-state shape. The surface volume fraction $\phi_s$ does not reach its equilibrium value $\phi_e$ instantaneously, but does so rather over a period of time that can be as long as several weeks for low activities of the penetrant[3]. At short times the $\phi(x,t)$ profile appears qualitatively similar to that expected from Fickian diffusion with a surface concentration $\phi_s(t)$. Once $\phi_s$ reaches a critical value $\phi_c$, the front develops as shown in *Figure 1b*, the gradient $\partial\phi/\partial x$ becomes flat behind the front and $\phi$ there gradually approaches $\phi_e$.

While a number of models have been proposed to explain case II diffusion[5-7], the model of Thomas and Windle[1,8-11] appears to be the most successful of these. Their calculations based on the model suggest that the front velocity $V$ should scale temperature as $(D/\eta_0)^{1/2}$, where $\eta_0$ is the viscosity of the glass at zero penetrant concentration. In this paper we test this prediction by independently measuring $D$, $\eta_0$ and $V$ as a function of temperature.

### *The Thomas and Windle model of case II diffusion*

The work of Thomas and Windle[1,8-11] consolidated earlier work[6,7] in osmotic-pressure models of case II diffusion. They proposed a mathematical model for the case II mechanism and numerically solved the resulting non-linear equations. This model couples the viscoelastic response of the polymer chains to the osmotic pressure of the penetrant with Fickian diffusion. The viscoelastic response of the polymer, which is due to the relaxation of the polymer chains, describes the swelling that always occurs in case II polymer/penetrant systems. In the Thomas and Windle model, this viscoelastic response is represented by a simple linear viscous relationship[1]:

$$\partial\phi/\partial t=P/\eta \tag{1}$$

where $\phi$ is the penetrant volume fraction created by the osmotic pressure $P$ and $\eta$ is the viscosity of the polymer glass. The osmotic pressure is given by:

$$P=(k_BT/\Omega)\ln\Theta \tag{2}$$

with

$$\Theta=a_e/a$$

where $a_e$ is the activity of the penetrant at equilibrium, i.e. $P=0$, $a$ is the activity of the penetrant and $\Omega$ is the partial molecular volume of the penetrant. Thomas and Windle made the further simplifying assumption that the activity is proportional to the penetrant volume fraction, resulting in:

$$\Theta=\phi_e/\phi \tag{3}$$

where $\phi_e$ is the penetrant volume fraction at zero osmotic pressure. The viscosity was represented by:

$$\eta=\eta_0\exp(-m\phi) \tag{4}$$

where $m$ is a constant of the material.

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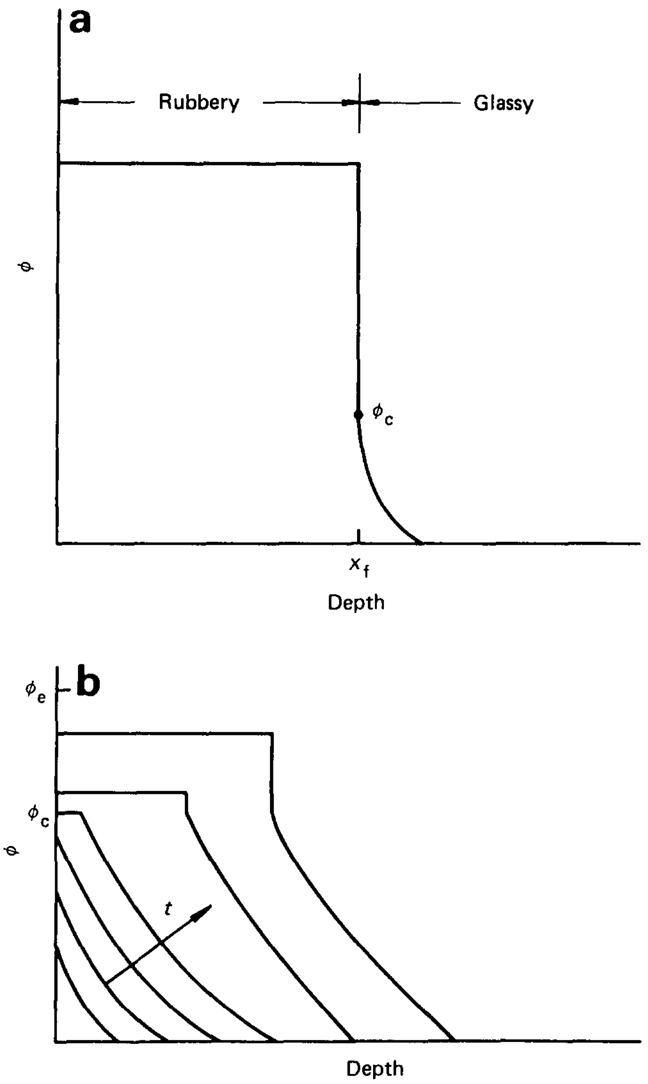

**Figure 1** (a) A schematic of the penetrant volume fraction $\phi$ *versus* depth below the surface for case II diffusion. The front position is $x$ and the penetrant volume fraction required for case II diffusion to begin is $\phi_c$. (b) A family of $\phi$ *versus* depth curves as exposure time advances. Case II diffusion begins when the penetrant volume fraction at the surface $\phi_s$ equals a critical value, $\phi_c$

Thomas and Windle wrote Fick's first law in terms of activity as[1]:

$$J = -D(\phi/a_e)\partial a_e/\partial x \tag{5a}$$

and Fick's second law as:

$$-\partial J/\partial x = \partial\phi/\partial t \tag{5b}$$

By coupling and solving equations (1) and (5) and selecting values for $m$, $\eta_0$ and $D$, they were able to generate diffusion profiles with sharp fronts and kinetics that agreed with gravimetric data.

### *The relationship between front velocity, diffusion coefficient and viscosity*

Thomas and Windle's numerical solutions to (1) and (5) suggest a relationship among the case II parameters[1], which can also be obtained by dimensional analysis, as shown in Appendix A. That relationship is:

$$V(T) = C\left(\frac{k_B T D(T)}{\Omega\eta_0(T)}\right)^{1/2} \tag{6}$$

where $C$ is a numerical constant dependent only on $m$. Hui *et al.*[12] subsequently obtained a solution to (1) and (5) that gives an asymptotic expression for the velocity of a propagating front with the same temperature dependence as equation (6). It has recently been demonstrated that modifications of (3) and (4) more accurately describe the kinetics of swelling at low penetrant activities[3]. In Appendix A it is shown that these modifications do not affect the temperature dependence of $V$.

Experiments have indicated that, in typical glassy polymer/penetrant systems, $V$ and $D$ are thermally activated with activation enthalpies of approximately 1 eV[13–16] and 0.6 eV[17], respectively. Therefore $V$ would typically vary by a factor of 8 and $D$ by a factor of 3 over a 15 K temperature interval near 300 K. Over the same temperature span $T^{1/2}$ varies by only 3%. Therefore the temperature dependence of $V$ can be approximated by:

$$V(T) \propto \left(\frac{D(T)}{\eta_0(T)}\right)^{1/2} \tag{7}$$

By measuring $V(T)$, $D(T)$ and $\eta_0(T)$ we can test the physical basis of the Thomas and Windle model and its modifications.

### *Experimental determination of V, D and $\eta_0$*

We will use Rutherford backscattering spectrometry (RBS) to measure penetrant volume fraction *versus* depth profiles like those shown schematically in *Figures 1a* and *1b*. By monitoring the front position after several different exposure times, the front velocity can be directly determined. The diffusion coefficient is assumed to be constant in the glass and can be obtained from the shape of the $\phi(x)$ profile ahead of the front. The form of this profile is approximately that predicted for Fickian diffusion ahead of a moving boundary (source) and is given by[2,4]:

$$\phi = \phi_c \exp(-Vx/D) \tag{8}$$

where $x$ is the distance ahead of the case II front and $\phi_c$ is the critical volume fraction of penetrant required for front formation. The value of $D$ can be obtained by fitting equation (8) to the $\phi(x)$ profile.

The viscosity of the glass $\eta_0$ is determined from the initial swelling kinetics at the surface. Using RBS the volume fraction $\phi_s$ at the surface is measured as a function of exposure time $t$. A numerical solution of equation (1) using a modified version of the Thomas and Windle model[3]:

$$t = (\eta_0/B')\int_{\phi_{fv}}^{\phi_s} [\exp(-m\phi)/\ln\Theta]\Theta^{-\alpha}\,d\phi \tag{9}$$

is used to fit the experimental $\phi_s(t)$ data. Here $B' = k_B T/\Omega$ and $\alpha = k_B T\alpha'/\Omega$, where $\alpha'$ is a parameter describing the osmotic pressure dependence of the viscosity; $\alpha'$ is assumed in what follows to scale as $1/T$ so that $\alpha$ is independent of $T$. The lower limit of the integral is the initial free volume fraction $\phi_{fv}$ that can be occupied by the penetrant molecules without polymer chain relaxation and is taken as 0.02[3,18].

The parameters $m$ and $\alpha$ primarily control the shape of a $\phi_s$ *versus* $\log t$ curve while changes in $\eta_0$ shift the curve parallel to the $\log t$ axis. Since the shape of the $\phi_s$ *versus* $\log t$ curve changes very little over the range of temperature covered by our experiments, $m$ and $\alpha$ are assumed to be independent of temperature. Therefore $\eta_0(T)$ can be determined by adjusting its value at each temperature to produce the best fit to the experimental $\phi_s(t)$ data.

## EXPERIMENTAL PROCEDURE

Rutherford backscattering spectrometry (RBS) has been established as a powerful technique for the analysis of diffusion profiles[3,19–21]. In this technique a beam of $He^{2+}$ ions is incident on the sample. By measuring the energy of the $He^{2+}$ ions backscattered from heavy nuclei in the penetrant molecules, a depth profile of the penetrant can be obtained[3,19–21]. This technique has been used to analyse the initial stages of case II diffusion of 1-iodohexane in polystyrene[2,3]. This penetrant/polymer system was selected because it exhibits case II diffusion and the concentration of the iodine 'tag' can be measured as a function of depth by RBS down to a depth of 4 $\mu$m below the surface. Details of the analysis of the RBS spectrum are given in previous papers[2,3].

### *Sample preparation*

The samples for the RBS experiments were prepared in the following way. Aluminium substrates were dip-coated in an 11% solution of polystyrene (PS) in toluene. The polystyrene had a molecular weight of 390 000 and a polydispersity index less than 1.10 as specified by the supplier, Pressure Chemical Co. The resulting films, which were approximately 4 $\mu$m thick, were then dried in air for 24 h. The samples were subsequently annealed at 125°C for 1 h and physically aged at 50°C for 24 h. Controlled physical ageing was found to be necessary so that reproducible diffusion profiles could be generated[22]. Ageing at 50°C was done to minimize the effects of further ageing at room temperature[23].

The iodohexane used as the penetrant was purchased as a copper-stabilized grade from Kodak. The PS samples were exposed to iodohexane vapour by placing them in an Erlenmeyer flask that contained a mixture of polystyrene and iodohexane in the bottom. Therefore $\phi_e$ was equal to that of the mixture. The temperature was controlled by placing the flask in a water bath, which had a temperature stability of $\pm 0.01$°C. After exposure to the iodohexane vapour for a certain time $t$, the samples were quickly immersed in liquid nitrogen, since the diffusion could be very rapid at room temperature. The samples were transferred to the liquid-nitrogen-cooled stage of the RBS apparatus under a dry nitrogen atmosphere in a glove bag to minimize water condensation on the sample surface. All RBS spectra were measured at a temperature below 100 K. Besides stopping further diffusion, the low temperature had the additional advantage of preventing mass loss and penetrant redistribution due to radiation damage in the polymer produced by the energetic $He^{2+}$ ions.

### *Experimental parameters*

At iodohexane activities greater than 0.45, the case II diffusion front was so sharp that it was impossible to measure the diffusion coefficient $D$. Therefore a value of $a_e = 0.37$ ($\phi_e = 0.16$) was chosen for the flasks because at this activity case II diffusion is established but the front velocity is slow enough that the diffusion coefficient in the glass can be obtained from the $\phi(x)$ profile ahead of the front[3]. Since case II front velocity was a strong function of activity near this value[3,24], considerable care was taken to maintain a constant activity. Approximately one week was allowed to elapse after a small amount of penetrant was added to the flask (such additions were necessary to maintain $\phi_e$ and the amounts required were determined by weighing the flask periodically), or after the temperature was changed. This waiting time ensured that equilibrium in the flask was established before a new sample was added. Samples were exposed to the iodohexane vapour for various times at temperatures of 25, 26.7, 30, 32.5, 35 and 40°C.

## RESULTS AND DISCUSSION

A family of $\phi$ *versus* depth profiles for the experiments performed at 30°C are shown in *Figure 2*. The maximum in $\phi$ in the swollen region is due to a small amount of out-diffusion of iodohexane during the quenching procedure. Similar profiles were obtained at all other temperatures if the exposure times were adjusted to smaller values at higher temperatures.

The front position, defined as the depth at which the slope of $\phi(x)$ is a maximum, is plotted as a function of time in *Figure 3* for the profiles in *Figure 2*. After an initial induction period, the case II front velocity $V$ was approximately constant, as shown in *Figure 3*; values of $V$ were obtained from the slope of this and similar plots. The diffusion coefficient $D$ of the glass was determined by applying equation (8) to the $\phi(x)$ profile ahead of the front; the diffusion coefficient $D_r$ of the swollen material behind the front is at least several orders of magnitude higher (a lower limit of $10^{-9}$ cm$^2$ s$^{-1}$ can be estimated) and is not important in determining the front velocity. The velocity used to extract $D$ from the fit was the one determined experimentally, e.g. from *Figure 3*. *Figure 4* shows a $\phi(x)$ depth profile and a typical fit.

Following the procedures outlined above, $\phi_s$, the penetrant volume fraction at the surface measured by

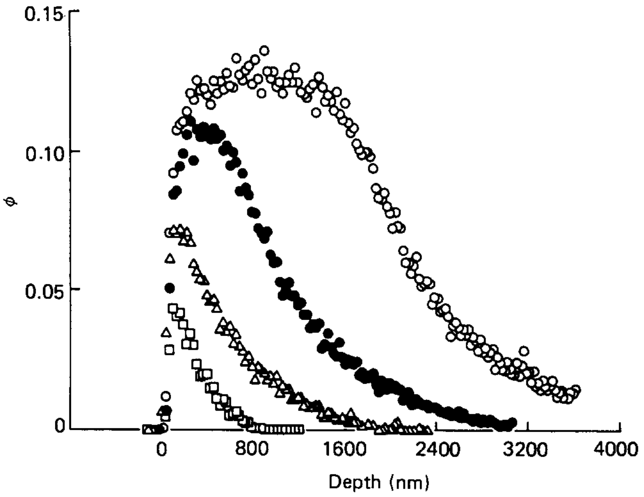

**Figure 2** A family of volume fraction *versus* depth curves of iodohexane in polystyrene at $a_e = 0.37$ ($\phi_e = 0.16$) and $T = 30$°C after exposure times $t = 3.3 \times 10^5$ (○), $1.6 \times 10^5$ (●), $6 \times 10^4$ (△) and $10^4$ s (□)

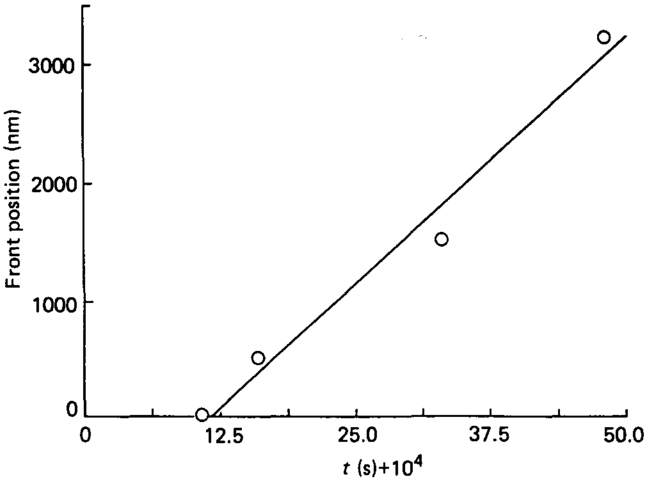

**Figure 3** The position of the front $x$ during case II diffusion of iodohexane in polystyrene *versus* exposure time for $a_e = 0.37$ and $T = 30°C$

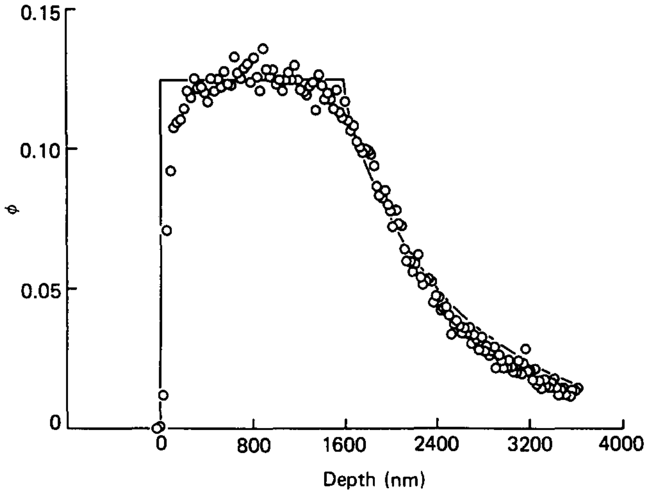

**Figure 4** A volume fraction *versus* depth profile of iodohexane in polystyrene at $a_e = 0.37$ and $T = 30°C$. The full curve is a solution to equation (8) with $V = 0.0085\,\mathrm{nm\,s^{-1}}$ and $D = 1.2 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$

RBS, was plotted as a function of time and compared to a numerical solution of equation (9). Values for $m = 25$ and $\alpha' = 1.31 \times 10^{-7}\,\mathrm{m^2\,N^{-1}}$ were selected as giving a theoretical curve with shape closest to that of the data. (This value of $\alpha'$ is close to that ($1.22 \times 10^{-7}\,\mathrm{m^2\,N^{-1}}$) obtained from creep experiments[3].) Since the value of $\eta_0$ does not affect the shape of the curve but only shifts it along the $\log t$ axis, $\eta_0$ was varied until the theoretical curve best overlaid the experimental data. The $\phi_s$ *versus* $\log t$ data for the iodohexane exposures at 25, 30 and 35°C are shown in *Figure 5*. Theoretical curves are also shown in this figure for the $\eta_0$ values that result in the best fits to the data. These values of $\eta_0$ are $\eta_0(25°C) = 2.5 \times 10^{15}$, $\eta_0(30°C) = 1.0 \times 10^{15}$ and $\eta_0(35°C) = 2.8 \times 10^{14}\,\mathrm{N\,s\,m^{-2}}$. Values of $\eta_0(T)$ were determined for all of the other temperatures using the same procedure.

The values of the logarithms of $V$, $D$ and $\eta_0$ obtained from the analysis of the RBS data are plotted *versus* $1/T$ in *Figures 6*, *7* and *8*, respectively*. The activation

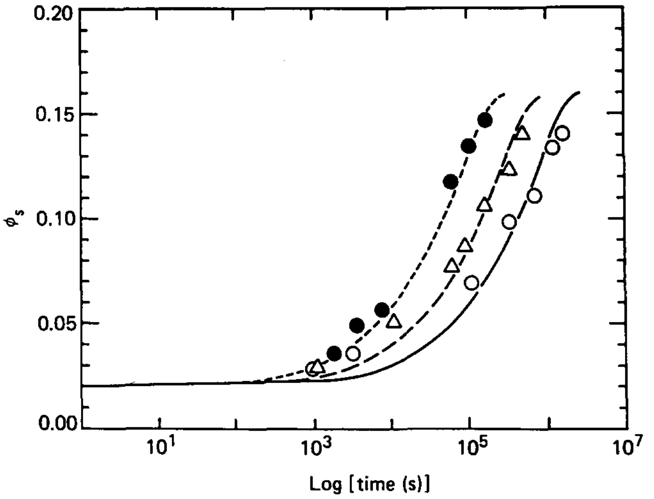

**Figure 5** Volume fraction of iodohexane at the surface of polystyrene *versus* log(exposure time) at $a_e = 0.37$ and $T = 25$ (○), 30 (△) and 35°C (●). The curves are obtained by numerically integrating equation (9) with $m = 25$, $\alpha' = 1.31 \times 10^{-7}\,\mathrm{m^2\,N^{-1}}$ and $\eta_0 = 2.5 \times 10^{15}$ (———), $1.0 \times 10^{15}$ (– – –) and $0.28 \times 10^{15}$ (·····) $\mathrm{N\,s\,m^{-2}}$

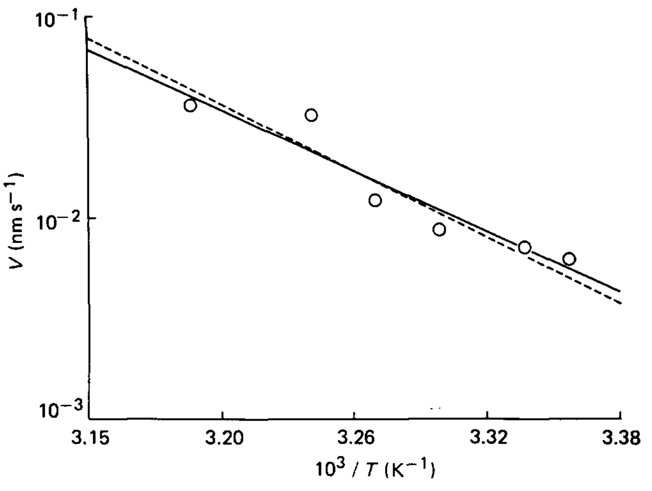

**Figure 6** The logarithm of the front velocity *versus* $1/T$ for polystyrene in iodohexane at $a_e = 0.37$. The full line is a linear least-squares fit to the data. The broken line corresponds to an activation enthalpy of 1.18 eV predicted by equation (11) using the experimentally determined activation enthalpies of $D$ and $\eta_0$

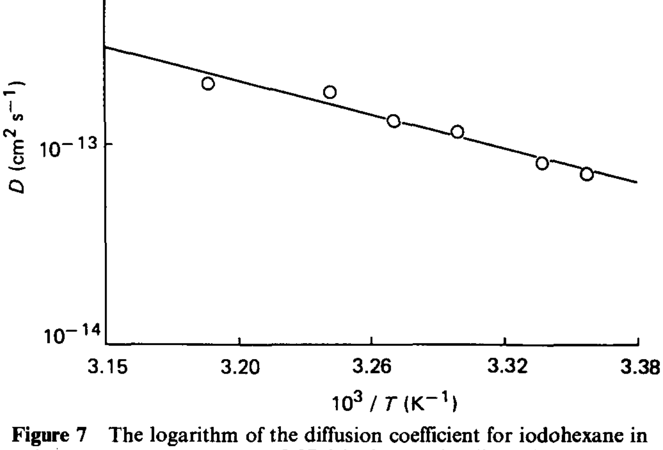

**Figure 7** The logarithm of the diffusion coefficient for iodohexane in polystyrene *versus* $1/T$ at $a_e = 0.37$. The full line is a linear least-squares fit to the data

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* At 40°C the $\eta_0$ point fell off the curve in *Figure 8*. It is believed that this occurred because $\phi_c$ changed abruptly at this temperature (see *Figure 9*). In Appendix A it is shown that one of the assumptions underlying the derivation of equation (11) is that $\phi_c$ is constant with temperature, hence the points at 40°C in *Figures 8* and *9* were not used to calculate the activation enthalpies of $\eta_0$ and $t_i$ respectively

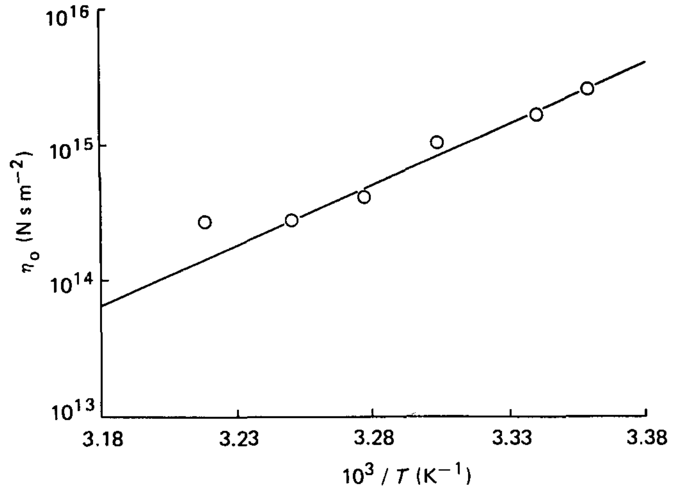

**Figure 8** The logarithm of the viscosity $\eta_0$ for iodohexane in polystyrene *versus* $1/T$ at $a_e = 0.37$. The full line is a linear least-squares fit to the data

enthalpies for the velocity, the diffusion coefficient and the viscosity were determined by fitting a line using least-squares linear regression to the data in *Figures 6, 7* and *8* respectively. The values were:

$$\Delta H_V = 1.07\,\text{eV}, \quad \sigma_V = \pm 0.21\,\text{eV}$$

$$\Delta H_D = 0.60\,\text{eV}, \quad \sigma_D = \pm 0.08\,\text{eV}$$

$$\Delta H_\eta = 1.76\,\text{eV}, \quad \sigma_\eta = \pm 0.31\,\text{eV}$$

where $\Delta H_V$, $\Delta H_D$ and $\Delta H_\eta$ are the activation enthalpies for front velocity, diffusion and viscosity respectively. The indicated error $\sigma$ is one standard deviation.

The Thomas and Windle model implies (equation (7)) that the front velocity $V(T)$ must scale as:

$$V(T) \propto \left(\frac{D(T)}{\eta_0(T)}\right)^{1/2} \tag{10}$$

where the proportionality constant is approximately independent of $T$ over the range of interest. Since all three quantities, $V(T)$, $D(T)$ and $\eta_0(T)$, are thermally activated, the activation enthalpies should be related by:

$$\Delta H_V = (\Delta H_D + \Delta H_\eta)/2 \tag{11}$$

The $\Delta H_V$ predicted from the average of $\Delta H_D$ and $\Delta H_\eta$ is 1.18 eV, which agrees with the experimental value of $\Delta H_V$ (1.07 eV) to within the error of the experiments.

The recent RBS experiments of Mills *et al.*[4] on the diffusion of 1,1,1-trichloroethane (TCE) in crosslinked Riston™ (major component poly(methyl methacrylate) (PMMA)) showed that the activation enthalpy of both the case II front velocity and the diffusion coefficient were the same, namely 1.19 eV. The $\Delta H_\eta$ was not measured. While equation (11) suggests that for Riston the activation enthalpy for $\eta_0$ should be approximately 1.19 eV, several caveats must be mentioned. The TCE used contained small amounts of small-molecule inhibitors, the removal of which decreased the $V$ by at least an order of magnitude[25]. The controlling diffusion for these experiments may not have been that of the TCE measured by RBS but that of the small-molecule inhibitors, which were invisible to RBS. Secondly, the glass transition temperature of the Riston lies in the range 55 to 60°C, suggesting that the PMMA composing the photoresist is plasticized, which almost certainly will affect the case II diffusion kinetics. (The glass transition temperature of pure PMMA is 100°C). For this reason we view the measurements of $D$ of TCE in this system with some suspicion. The present experiments involving a well characterized polymer, polystyrene, and a pure penetrant species, iodohexane, constitute a much better test of the Thomas and Windle model of case II diffusion.

## CONCLUSIONS

The case II front velocity $V$, diffusion coefficient $D$ and viscosity $\eta_0$ are thermally activated with activation enthalpies 1.07, 0.60 and 1.76 eV, respectively.

The front velocity $V(T)$ scales as:

$$V(T) \propto \left(\frac{D(T)}{\eta_0(T)}\right)^{1/2}$$

a form predicted by the Thomas and Windle model of case II diffusion.

## ACKNOWLEDGEMENTS

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## APPENDIX A

### *The derivation of the temperature dependence of the case II front velocity*

The governing equations for case II diffusion can be written in the form (from equations (1) and (5b) respectively):

$$\partial\phi/\partial t = Bf(m,\alpha,\phi,\phi_e) \tag{A1}$$

where $B = k_B T/\Omega\eta_0$, $f$ is a dimensionless function of its dimensionless arguments $m$, $\alpha$, $\phi$ and $\phi_e$ and:

$$\partial\phi/\partial t = \partial[D(\phi,T)\phi\,\partial \ln a_e/\partial x]/\partial x \tag{A2}$$

As in the Thomas and Windle model, we have assumed that the diffusivity is a function of $\phi$ and $T$ only. Consistent with the fact that the gradient of $\phi$ behind the front is negligible, the diffusivity $D_r$ behind the front must be much larger than $D$, the value in the glass ahead of the front; the diffusivity undergoes a rapid increase from $D$ to $D_r$ in a narrow region of depth at the front. Let $\phi^*$ be a characteristic concentration where the change in diffusivity is most rapid. We will assume that $\phi^*$ is independent of $T$. (In ref. 2, $\phi^*$ is taken to be $\phi_c$.) With these assumptions $D(\phi,T) = D(T)h(\phi/\phi^*)$, where $h$ is a dimensionless function of its dimensionless argument with the properties that:

$$h(\phi/\phi^*) \mapsto 1 \quad \text{for } \phi < \phi^*$$

$$h(\phi/\phi^*) \gg 1 \quad \text{for } \phi > \phi^*$$

For the Thomas and Windle model[1], $f$ in equation (A1) is:

$$f = \exp(m\phi)\ln \phi_e/\phi$$

whereas our modifications to this model resulted in[3]:

$$f = \exp(m\phi)\Theta^{\alpha}\ln \Theta$$

where $\Theta = \phi_e \exp(1-\phi_e)/\phi \exp(1-\phi)$. Thus the only dimensional quantities in all equations are $B$ and $D$, which have dimensions of $T^{-1}$ and $L^2T^{-1}$, respectively. From dimensional considerations the steady-state velocity must have the form:

$$V = (DB)^{1/2} g(m,\alpha,\phi_0,\phi_c) \qquad \text{(A3)}$$

where $\phi_0$ is the equilibrium volume fraction of the penetrant at the surface of the sample, and is assumed to be constant, and $g$ is an unknown dimensionless function of its dimensionless arguments, and is independent of $T$. The temperature dependence of $V$ is therefore given by $[D(T)B(T)]^{1/2}$ or:

$$V(T) \propto \left(\frac{k_B T D(T)}{\Omega \eta_0(T)}\right)^{1/2} \qquad \text{(A4)}$$

The original Thomas and Windle model is obtained when $\alpha$ in (A1) equals zero. Since the value of $\alpha$ does not affect the temperature dependence of $V$ in (A4), that dependence holds for all models that are of the form of (A1), i.e. for the modified Thomas and Windle model proposed in ref. 3 as well as for the original Thomas and Windle model.

## APPENDIX B

### *The induction time and the critical volume fraction for case II diffusion*

*Figure 2* shows that a critical $\phi_s$ must first be reached before case II diffusion can begin. Thus an induction time $t_i$ for case II diffusion exists[3]. This induction time can be estimated from a plot, e.g. *Figure 3*, of the front position *versus* time as the intercept of the $V$ = constant line on the time axis. By obtaining $\phi_s$ at the induction time, it is possible to estimate $\phi_c = \phi_s(t_i)$. At 30°C from *Figure 5*, $\phi_c = \phi_s(t_i = 10^5\ \text{s}) \approx 0.1$. This procedure was performed at all of the temperatures (see earlier footnote).

Integrating equation (9) to $\phi_s = \phi_c$ results in an expression for the induction time $t_i$ that should scale approximately with $\eta_0(T)$. Hence $t_i$ should be thermally activated with an activation enthalpy $\Delta H_{t_i}$ equal to that of $\eta_0(T)$. *Figure 9* is a plot of $t_i$ *versus* $1/T$. From the slope of the plot the activation enthalpy of the induction time is $2.13 \pm 0.19$ eV. This value was 0.37 eV greater than that of the viscosity but just within the experimental error of 0.37 eV. The value of the experimental error was determined by adding the squares of the errors in $\Delta H_{t_i}$ and $\Delta H_\eta$ and taking the square root. The values of $\phi_c$ are next to the data points for $t_i$ in *Figure 9*.

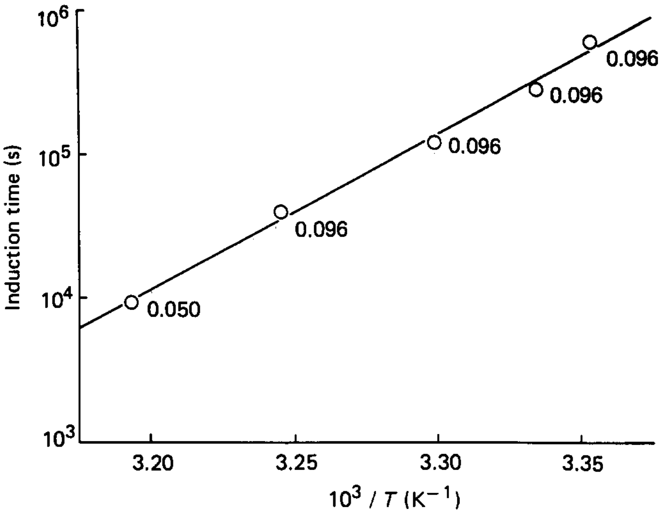

**Figure 9** The logarithm of the induction time for case II diffusion for iodohexane in polystyrene *versus* $1/T$ at $a_e = 0.37$. The full line is a linear least-squares fit to the data. The numbers next to each circle are values of $\phi_c$

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