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The effect of molecular size on non-Fickian sorption in glassy polymers

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Rutherford backscattering spectrometry has been used to determine the concentration against depth profiles of n-iodoalkanes diffusing into a polymer glass photoresist. All the iodoalkanes smaller than iodohexane show strongly non-Fickian, or Case II, diffusion. After an induction time a sharp front forms, with almost no concentration gradient behind the front. Ahead of the front the concentration decreases exponentially with depth, a form predicted for Fickian diffusion ahead of a moving boundary. Values of the diffusion coefficient D extracted from this Fickian precursor decrease strongly with n, the number of carbon atoms in the iodoalkane. A similar decrease is observed for the front velocity, the magnitude of which is in qualitative agreement with that predicted by the Thomas and Windle model of Case II diffusion. For the larger values of n, D decreases as n^{-2}, prompting speculation that these longer chains diffuse into the glass by a reptation-like mechanism.

1. Introduction

Ever since it was observed [1] that the kinetics of sorption of penetrants in glassy polymers frequently failed to follow the $t^{1/2}$ kinetics anticipated from Fick's second law, the reasons for this behaviour have been sought. A large number of theoretical explanations have been proposed [2–18] but the experimental evidence for, or against, these has been limited. For instance, the usual gravimetric methods give little information on the concentration profile of the penetrant, and while crude profiles can be obtained by optical [19, 20] or radiotracer [21] methods, their depth resolution is such that the fine details of the diffusion profile are lost. Recently we have demonstrated that Rutherford backscattering spectrometry (RBS) can be used to reveal such details with a depth resolution of better than 30 nm and a sensitivity of less than 50 p.p.m. [22]. In this paper we report the effects of molecular size of the penetrant on the non-Fickian diffusion.

2. Experimental procedure

2.1. Sample preparation

The polymer investigated was a commercial dry film photoresist, Riston$^{\text{TM}}$, manufactured by DuPont. The 60 μm thick resist was crosslinked with UV irradiation. The resist has a glass transition temperature T_g just below 60° C and its nominal chemical composition as determined by RBS is close to that of polymethylmethacrylate (PMMA). The resist was bonded to a thin copper foil which, in turn, was attached to a 1 mm thick aluminium sheet with epoxy adhesive. Such a procedure was necessary to prevent the sample from curling when exposed to the penetrant and to provide an electrically conducting backing to minimize charging of the polymer layer in the ion beam during analysis.

The penetrants investigated were the series of n-iodoalkanes, from iodomethane to iodohexane. The samples were immersed in penetrant liquid at 25° C. After various exposure times the samples were taken from the bath and excess liquid was quickly removed from their surfaces by a stream of nitrogen gas before they were plunged into a bath of liquid nitrogen. This procedure is reasonably effective in "freezing in" the concentration profile of penetrant that exists in the polymer just before removal, but some loss of the smaller penetrants from the sample surface is inevitable. The samples were kept in the liquid nitrogen until they could be transferred, within a dry nitrogen filled glove bag, to the RBS analysis stage. The stage itself was cooled with liquid nitrogen to maintain the concentration profile during analysis and to prevent motion of molecular fragments produced by radiation damage.

2.2. Rutherford backscattering spectrometry

Only a brief description of RBS is given here since details are available elsewhere [22, 24]. A monoenergetic beam of $^4\text{H}^{++}$ ions is incident on the sample and the energy distribution of the ions backscattered by nuclei in the sample is measured. The atomic composition of the sample can be determined because ions scattered from heavier nuclei retain a higher fraction of their original energy. The composition can be calculated from the Rutherford scattering cross-sections of the elements, which for backscattering are given by

$$\sigma = \left(\frac{e^2 zZ}{4E_0}\right)^2 \left[\sin^{-4}\left(\frac{\theta}{2}\right) - 2\left(\frac{m}{M}\right)^2 + \ldots\right] \quad (1)$$

where z and m and Z and M are the charge and mass of the ion and target nucleus, respectively, e is the electronic charge, E_0 is the energy of the incident beam and θ is the scattering angle. For the He^{++} ion beam

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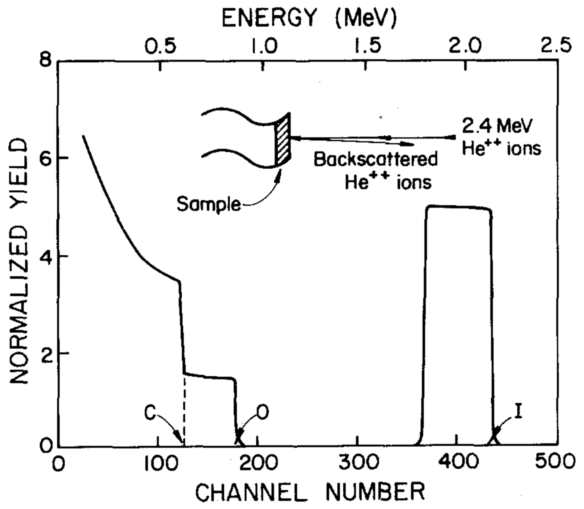

Figure 1 Simulated Rutherford backscattering spectrum from a Riston sample, the outer 1 μm of which has been swollen with a uniform concentration of iodomethane of 0.15 molecules per monomer of PMMA. The energies at which He^{++} ions are backscattered by carbon, oxygen and iodine at the surface are marked.

of energy 2.4 MeV used here, iodine can be detected in quantities greater than 200 p.p.m. even for relatively small ion fluences (5 μC).

Ions scattered from nuclei below the surface emerge with lower energies than those scattered from nuclei at the surface, due to the fact that the ions lose energy to inelastic electron collisions on the way into, and out of, the sample. The RBS spectrum, consisting of the number of backscattered ions against energy, can thus be converted into a composition against depth profile. Typically the concentration of an iodoalkane diffusing into a polymer can be followed with a depth resolution of $\sim$ 300 nm over a depth of $\sim$ 3 μm using the scattering from the iodine nuclei [22, 24]. The RBS spectrum expected for an outer 1 μm layer of Riston, uniformly swollen to a concentration of 0.15 iodomethane molecules per monomer of PMMA, is shown in Fig. 1. The energies of ions backscattered from carbon, oxygen and iodine nuclei at the surface of the resist are marked.

3. Results and discussion

Fig. 2 shows the experimental RBS spectra obtained from Riston exposed to iodomethane for 4, 8 and 16 sec. During the surface drying some of the iodomethane diffuses out of the sample, resulting in a gradual increase in yield below the energy $\sim$ 2.1 MeV that corresponds to iodine at the surface (cf. the abrupt increase in the yield of the simulated spectrum in Fig. 1). It is clear, however, that the iodomethane diffusion in the resist is non-Fickian, Case II diffusion [23]. A swollen layer of relatively uniform iodomethane concentration forms and advances into the polymer at a constant velocity. The glass transition temperature of the polymer in this layer is depressed to below room temperature so that the layer is rubbery. Ahead of the swollen layer, or front, the concentration decays exponentially in the glass, as predicted for Fickian diffusion ahead of a moving boundary [10–13, 22]. A schematic drawing of the concentration profile, showing the Fickian precursor, is displayed in Fig. 3.

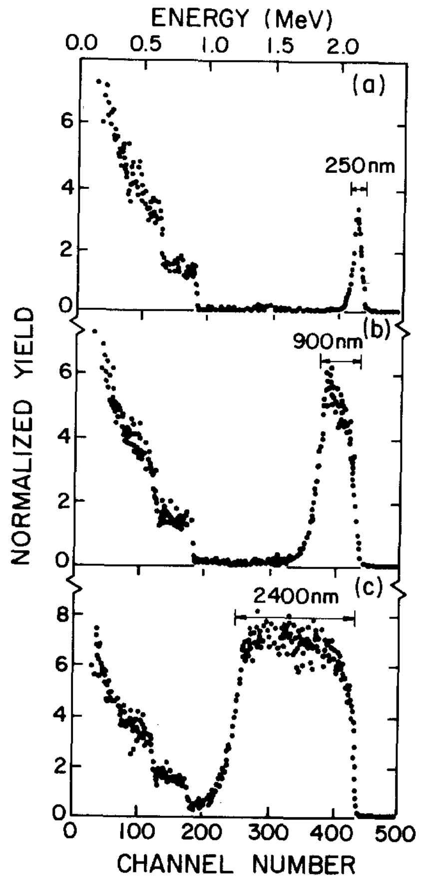

Figure 2 Rutherford backscattering spectra from Riston exposed to iodomethane for (a) 4, (b) 8 and (c) 16 sec at 25° C.

A similar series of RBS spectra from Riston exposed to iodoethane for 10, 20, 40, and 80 sec is shown in Fig. 4. Iodoethane also exhibits Case II diffusion but the rate is much slower than that of iodomethane. The velocity v of the front decreases substantially. There is also little outdiffusion of iodoethane from the rubbery layer during drying. One can observe that an induction time is necessary for the iodoethane concentration in the swollen layer to reach its equilibrium concentration. For example the iodoethane concentration rises from 0.09 molecules per monomer after 10 sec to its equilibrium value of 0.15 molecules per monomer only after 40 sec.

This trend towards decreased front velocities and longer induction times continues as one selects progressively larger penetrant molecules. RBS spectra showing the diffusion of n-iodopentane in the resist are displayed in Fig. 5 and represent an interesting extreme. The diffusion appears Fickian after an exposure of 3600 sec and the surface concentration of penetrant has almost reached its equilibrium value. However after 6000 sec a swollen layer of constant composition develops. Case II diffusion only becomes well established after 8640 sec. It appears that a critical penetrant concentration at the surface is necessary for the front to form. Presumably this is the concentration necessary to plasticize the polymer sufficiently so that its T_g is below the ambient temperature.

Fig. 5 shows the RBS spectra for the complete series of iodoalkanes when the thickness of the swollen layer is approximately 1 μm. For n-iodohexane a true Case II diffusion profile has not developed even after

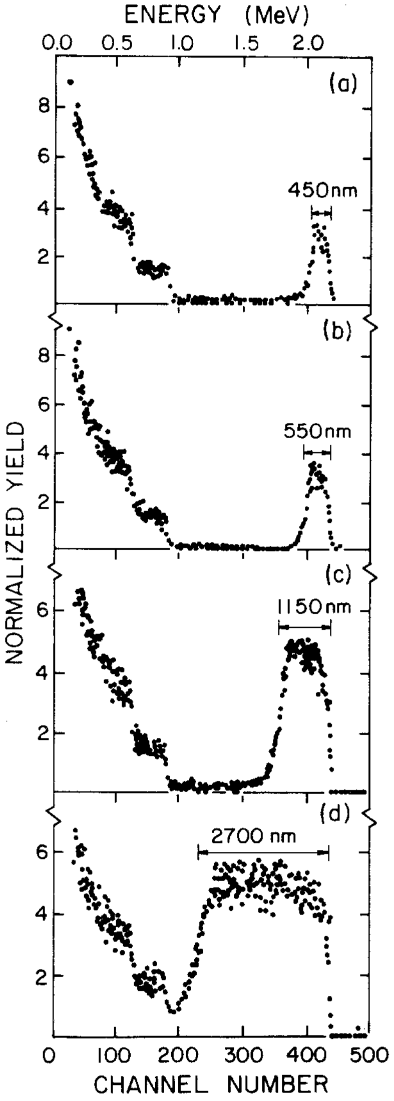

Figure 3 Rutherford backscattering spectra from Riston exposed to iodoethane for (a) 10, (b) 20, (c) 40 and (d) 80 sec at 25° C.

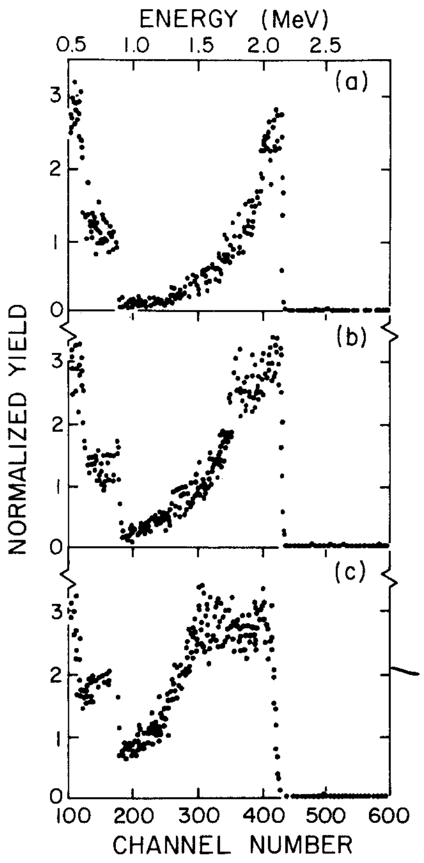

Figure 4 Rutherford backscattering spectra from Riston exposed to n-iodopentane for (a) 3600, (b) 6000 and (c) 8640 sec at 25° C.

7200 sec. Converting the energy scale of the RBS spectrum into a depth scale for backscattering from iodine as illustrated in Fig. 2, we can estimate the steady-state front velocity v from spectra taken after several exposure times. Fig. 6a shows these velocities as a function of the molecular volume v_m of the iodoalkane penetrant. The front velocity decreases approximately exponentially as the molecular volume of the penetrant increases, but somewhat more slowly for the larger iodoalkanes than for the smaller ones.

We have demonstrated previously [22] that the steady-state concentration profile can be modelled by Fickian diffusion ahead of a moving boundary [10–13] so that

$$\phi(x) = \phi_0 \exp(-vx/D) \tag{2}$$

where ϕ is concentration, D is a Fickian diffusion coefficient of the penetrant in the glass ahead of the front, x is distance ahead, and v the velocity, of the boundary. The concentration ϕ_0 is that necessary to plasticize the resist so that its glass transition temperature T_g is reduced to the ambient temperature. At the front ϕ increases abruptly to a concentration ϕ_∞ in equilibrium with the liquid. The kinetics of this increase are controlled by the mechanical response of the polymer to the osmotic swelling pressure [20]. Since the diffusion coefficient increases markedly in the rubbery swollen layer the concentration gradient behind the front is negligible. This profile is shown schematically in Fig. 7a.

As demonstrated previously, one can extract the value of D by fitting the experimental steady-state concentration profiles using Equation 2. However, for the present experiments many of the spectra were obtained before a steady state was truly achieved. One can still analyse these spectra using an approximate solution to the corresponding heat flow problem* which is given by

$$\phi(\mathbf{x}, \mathbf{t}) = 0.5\phi_0 \left[\exp(-\mathbf{x})\,\mathrm{erfc}\left(\frac{\mathbf{x}-\mathbf{t}}{2\mathbf{t}^{1/2}}\right) + \mathrm{erfc}\left(\frac{\mathbf{x}+\mathbf{t}}{2\mathbf{t}^{1/2}}\right)\right] \tag{3}$$

where $\mathbf{x}$ and $\mathbf{t}$ are normalized distance ahead of the front and normalized time given by

$$\mathbf{x} = vx/D \tag{4}$$

and

$$\mathbf{t} = v^2 t/D \tag{5}$$

The normalized time $\mathbf{t}$ is also numerically equal to the normalized distance behind the front after time t. By adding a region of constant composition ϕ_∞ of this

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*We assume that the concentration ϕ_0 is established at the surface at $t = 0$ and thereafter the front moves inward with a constant velocity v. The corresponding heat flow problem is solved by Carslaw and Jaeger [25].

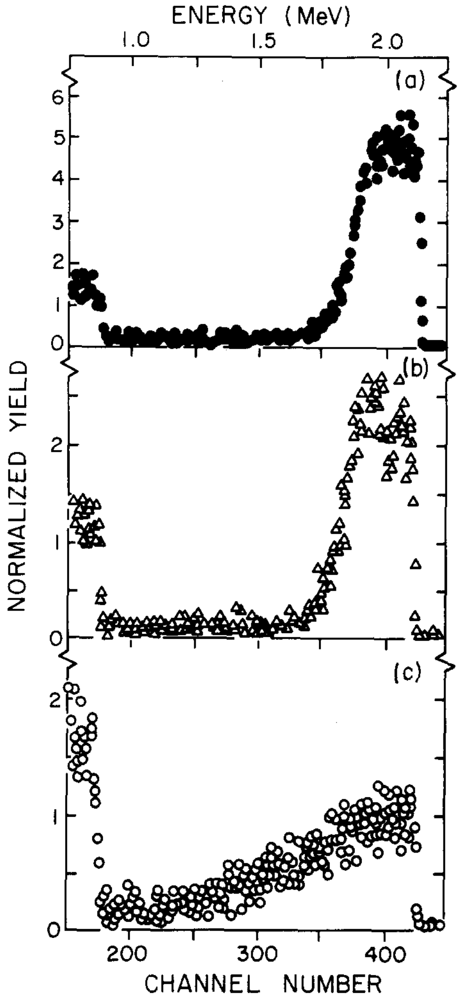

Figure 5 Rutherford backscattering spectra from Riston exposed to (a) n-iodopropane for 240 sec, (b) n-iodobutane for 600 sec, (c) n-iodohexane for 7200 sec. Compare with iodomethane after 8 sec (Fig. 2b), iodoethane after 40 sec (Fig. 3c) and iodopentane after 3600 sec (Fig. 4a).

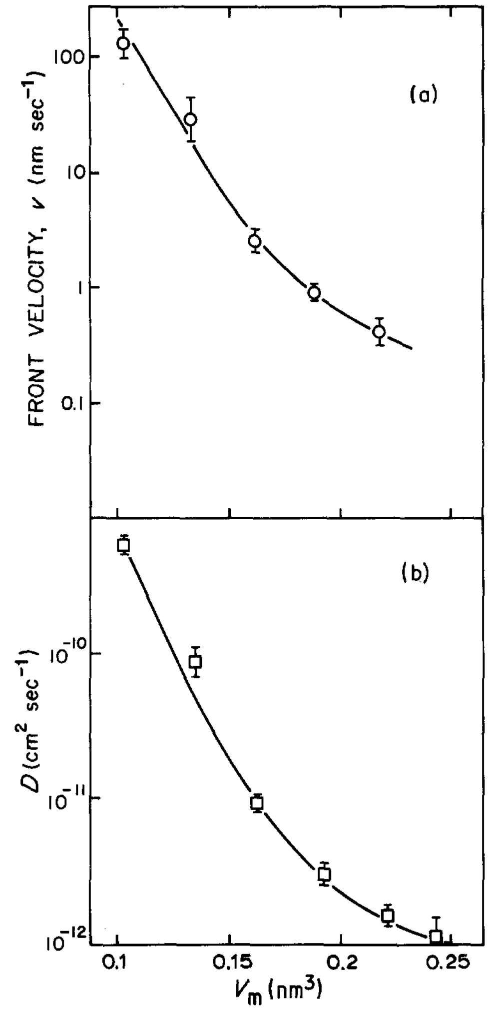

Figure 6 (a) Front velocity against molecular volume V_m of the iodoalkane molecule. (b) Diffusion coefficient of iodoalkane molecule in Riston against its molecular volume.

depth to the profiles predicted by Equation 3, one obtains the profiles shown in Fig. 7b.

Even though the observation of an induction time means that the assumption of a constant front velocity is not strictly valid, the calculated concentration profiles are very similar to those observed. At small t the profile is well described by $\phi_0 \operatorname{erfc}[x/2(Dt)^{1/2}]$, whereas at long times the solution converges asymptotically to the steady state solution of Equation 2. Experimental examples of the short-time and long-time extremes are shown in Figs 8a and b, respectively. In each case the solid line is a simulated spectrum obtained using the concentration profile predicted by Equation 3. The front velocity v is measured experimentally and ϕ_0, ϕ_∞ and D are adjusted to give the best fit to the data.

By using a similar procedure, D for all the iodoalkanes in the resist could be determined. The values of D obtained are shown in Fig. 6b. The value of D decreases markedly with molecular size in a manner that parallels the decrease in front velocity v. The values of ϕ_∞ and ϕ_0 used to achieve the fits are displayed in Table I. The osmotic swelling pressure P_0 at the front can be determined approximately from these data using the relation [18]†

$$P_0 = \left(\frac{k_B T}{V_m}\right)\ln\left(\frac{\phi_\infty}{\phi_0}\right) \qquad (6)$$

where k_B is the Boltzmann constant and V_m is the partial molecular volume of the penetrant. The values so determined are also displayed in Table I. Values are not computed for iodomethane due to the uncertainties introduced by the outdiffusion. The observed increase in ϕ_0 with molecular volume is consistent with our assignment of ϕ_0 as the concentration corresponding to plasticization of the resist to ambient temperature, and the fact that the plasticizing ability of small molecules decreases with size.

TABLE I Properties of penetrants and the polymer resist

Penetrant	Volume fraction		Osmotic pressure	Viscosity
	ϕ_∞	ϕ_0	P_0 (MPa)	η_0 (10^{10} poise)*
iodoethane	0.53	0.25	23.2	0.9
n-iodopropane	0.59	0.33	14.8	7.5
n-iodobutane	0.54	0.40	6.6	5.3
n-iodopentane	0.57	0.51	2.5	4.5

*1 poise = 10^{-1} N sec m^{-2}.

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†This form assumes that Henry's law is valid, i.e. that the activity of the penetrant is proportional to ϕ up to ϕ_∞ and that the partial molecular volume of the penetrant is equal to its molecular volume V_m.

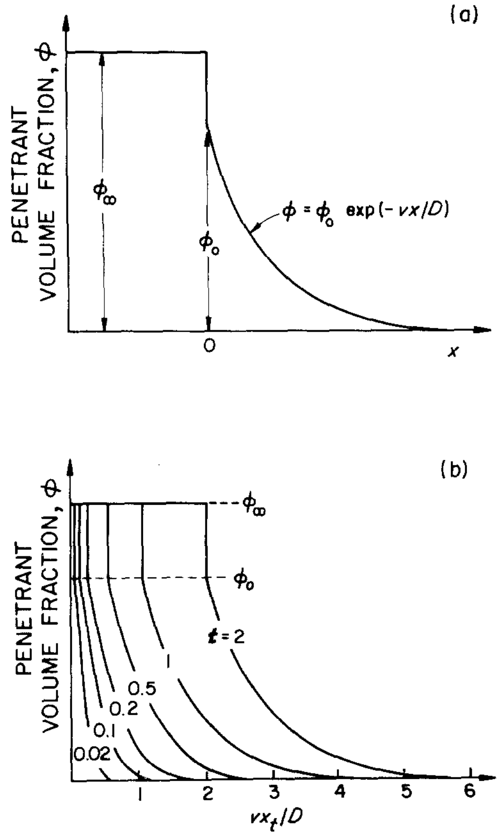

Figure 7 (a) Schematic drawing of the steady state concentration profile (Fickian precursor) ahead of the front. (b) The development of the steady state profile calculated using Equation 4. The coordinate x_t is the total distance from the sample surface. The normalized time *t* is equal to v^2t/d; for **t** > 2 the profile approximates the steady state profile.

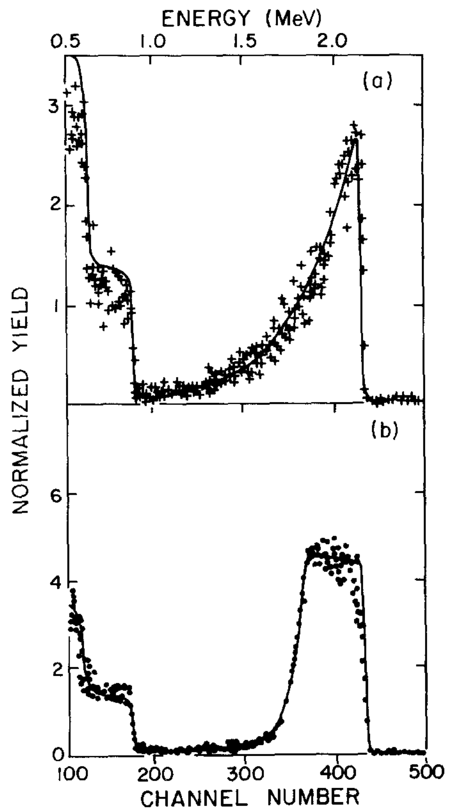

Figure 8 RBS spectrum of Riston exposed to (a) iodopentane for 3600 sec, (b) iodoethane for 40 sec. The solid lines show the simulated RBS spectra using the predicted concentration profiles from Equation 4 and the ϕ_x, ϕ_0, and D values in Table I.

We have previously shown that the Thomas and Windle model [18] of Case II diffusion leads to an approximate relationship between the front velocity, the osmotic swelling pressure and the viscosity η_0 of the polymer at the front that is given by

$$v = (DP_0/\eta_0\phi_0)^{1/2} \tag{7}$$

To test the applicability of Equation 7 we have used it to derive values of η_0 from the measured D, P_0 and ϕ_0 and these are displayed in the last column of Table I. While the value of η_0 for iodoethane is low, the values for the other penetrants are very similar and of a reasonable magnitude for the viscosity of a polymer near the glass transition. One possible reason for the low value of the viscosity for iodoethane penetration is the assumption in the Thomas and Windle model of linear viscoelastic response to the swelling pressure. At the larger values of P_0 one must expect a more rapid than linear increase in swelling rate with P_0 and thus a lower value of apparent polymer viscosity. The 23 MPa value of swelling pressure at the front for iodoethane should be large enough to cause plastic yielding of the polymer glass at temperatures not too far below T_g.

The observed dependence of D on molecular size is interesting. From free-volume theory one might expect that the diffusion coefficient of a molecule of volume V_m in the glass should vary as

$$D = D_0 \exp(-\alpha V_m) \tag{8}$$

where α and D_0 are constants at constant temperature. This form follows both from assuming that a hole of volume V_m next to the molecule is necessary for an elementary jump to occur, and from the expectation that the activation energy for the molecule to jump into such an existing hole is proportional to its volume. However, as can be seen from Fig. 6b the straight-line relationship predicted by Equation 8 does not obtain. The longer iodoalkanes diffuse much faster than would be predicted on the basis of the shorter ones.

The reason for the failure of these simple volume concepts is probably the tacit assumption that the molecule is spherical and can diffuse with equal probability in all directions. In actuality the n-iodoalkanes are linear molecules; in the restricted surroundings of the glass such a molecule should be able to diffuse along its own contour much more readily than normal to its contour. In the context of quasilattice models of a polymer glass the presence of a single lattice vacancy adjacent to the end of the molecule will allow the molecule to diffuse along its length by one lattice step. In contrast a molecule of length n lattice cells requires n vacancies to diffuse normal to its contour. Just as polymer molecules in an entangled melt diffuse by reptation, one might expect that linear molecules diffusing in a polymer glass would have to execute a similar motion. Since reptation gives a diffusion coefficient that decreases as the square of the length of the diffusing molecule, one may speculate that $D \propto n^{-2}$, in the limit of large n, where n is the number of carbon atoms in the iodoalkane. The experimental values of D exhibit this trend, as is demonstrated in Fig. 9, in

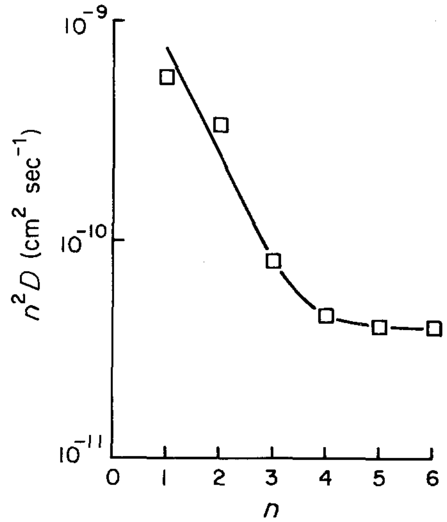

Figure 9 Diffusion coefficient of iodoalkane (number of carbons n) times n^2 against n showing that this product approaches a constant for the longer iodoalkanes.

which the product Dn^2 tends towards a constant value at the larger values of n.

4. Conclusions

All the n-iodoalkanes, from iodomethane to iodopentane, exhibit Case II diffusion in Riston photoresist. All show sharp diffusion fronts, with little or no concentration gradient behind the front and a Fickian precursor concentration profile in the glass ahead of the front. The front velocity and the diffusion coefficient in the glass decrease strongly with molecular length. The magnitudes of the front velocity are in qualitative agreement with those predicted by the coupled diffusion–mechanical relaxation model of Thomas and Windle. The values of the diffusion coefficient decrease less rapidly for the larger iodoalkanes than would be predicted by molecular volume arguments, and it is speculated these can diffuse faster by a reptation-like mechanism.

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