

Diffusion and Some Structural Effects of Two Chlorinated Hydrocarbon Solvents in Bisphenol A Polycarbonate

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Synopsis

$\text{CH}_2\text{ClCH}_2\text{Cl}$ and CHCl_3 , in which bisphenol A polycarbonate is normally readily soluble, were sorbed into the polymer from the liquid phase at 24–25°C. Sorption behavior was studied over a range of solvent activities (ambient concentrations), and the effects of repeated sorptions were observed. Penetration was strongly dependent on solvent concentration and on the previous history of the polymer. Time dependence was also observed, evidently associated with the rate of relaxation processes in the polymer surface since the effects increased logarithmically with solvent activity. Analysis of sorption curves, supplemented by DSC and density determinations, showed that the sorbed solvents caused a structural rearrangement (ordering) of the polymer when present above the critical content of 0.3 w/w. The rearrangement was not identical with that caused by heating the polymer, as evidenced by differences in subsequent solvent sorption behavior.

INTRODUCTION

Owing to its high T_g (140–150°C for commercial polymers),^{1–3} bisphenol A polycarbonate is amorphous when cooled rapidly from the melt as in molding. Subsequent heating above the T_g can cause crystallization up to a maximum of about 30% crystalline material content.^{4–8} The long induction period (about a week) and high temperatures required (190–205°C) reflect the difficulty of crystallization, attributable to chain stiffness, relatively long chain repeat distance, and large mass of the repeat unit of this polymer.^{8–11} Secondary crystalline formations, including fibrils, lamellae, and spherulites, have been observed in heat-crystallized polycarbonate films.^{12–14} Such crystalline forms also appear in the presence of good solvents^{15–17} and swelling agents.^{11,18,19} Crystallization by either heat or solvents has been said to conform to a relationship of the Avrami type, but

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the values of the constants and power indices, and their suggested interpretation in terms of physical phenomena, are different for the two cases.^{5,11,18}

More recently, evidence has been forthcoming from electron microscopy, DTA, calorimetric, and mechanical studies^{3,20-23} that short-range, sub-crystalline order may be produced in bisphenol A polycarbonate by heating below the T_g and that it may also arise in the presence of solvents.²¹

The presence of molecular order or its development with ingress of penetrants would be expected to influence diffusion in polycarbonate, especially where the penetrants are good solvents for the polymer and hence presumably the most likely to promote or facilitate structural changes. Solvent penetration and interactions with the polymer are of considerable practical interest in solvent bonding of polycarbonate components.

In the present study, 1,2-dichloroethane and chloroform were sorbed into polycarbonate at 25°C. Both these compounds are good solvents for the polymer; the first is often used for solvent bonding. Sorption was from a liquid mixture of solvent with *n*-heptane, an inert diluent used to vary the solvent activity, chosen *inter alia* for its lack of affinity for polycarbonate and miscibility with the "active" solvents. There is good evidence that in systems of this general type, the diluent does not interfere with the sorption of the "active" solvent.^{24,25} According to Miller et al.,¹⁹ a diluent (isopropanol) was not sorbed by polycarbonate from mixtures with liquids which are not good solvents for polycarbonate but can enter and swell the polymer (toluene, benzene, and carbon tetrachloride). The "inertness" of the diluent must depend on the relative rates of sorption and diffusive mixing in the liquid state; if it is not sufficiently maintained in a particular system (e.g., as the polymer expands with ingress of the "active" penetrant), the significance and extent of the resulting complication in the interpretation of experimental data may be difficult to assess. Pointer experiments at the start of the present study indicated that, as in the systems referred to above, there was no undue interference by the diluent: only small amounts (a few per cent) of *n*-heptane were found, by direct determination, to have entered the polymer from mixtures which contained the highest proportions of the "active" solvent and thus gave rise to the highest equilibrium contents of the latter in the polymer (>50% by weight, see e.g., Fig. 13).

EXPERIMENTAL

Experimental Specimens and Reagents

The sorption experiments were carried out on rectangular specimens (50.8 mm × 25.4 mm × approximately 0.0152 mm, i.e., 2 in. × 1 in. × 0.006 in.) of film compression molded from Makrolon 3100 L (Bayer Chemicals). The molecular weight of this polymer was 36,000, calculated from the limiting viscosity number determined in 1% THF solution by a procedure based on that of Shulz and Horbach.^{26,27} It was not significantly re-

duced by compression molding into film. The films exhibited no optical effects under a polarizing microscope and gave diffuse x-ray diffraction spectra typical of amorphous polymers.

The 1,2-dichloroethane and chloroform were, respectively, of special purity and analar grades (BDH), and analar *n*-heptane (BDH) was used.

Sorption by Standard (Untreated) Film Specimens

With the specimen dimensions used, the "edge area" was less than 1% of the total face area, hence diffusion was sensibly one-dimensional. The specimens were immersed, with agitation, in mixtures of the "active" penetrants with *n*-heptane and the solvent take-up was followed by weighing at suitable intervals until equilibrium was attained. The weight loss on desorption (in air) was also followed by weighing. In sorption experiments, the volume of the mixtures was such that the maximum amount of the "active" penetrant sorbed by the film specimen was a negligible fraction of the amount present in the mixture.

Most experiments were carried out in duplicate. In these, the agreement between the individual determinations of a pair was very good for 1,2-dichloroethane and somewhat less close but still good for chloroform.

Concentrations of the chloroform-*n*-heptane mixtures ranged from 60 mole-% down to 20 mole-%, and those of the 1,2-dichloroethane mixtures from 50 mole-% down to 13 mole-%. Above the upper concentration limits, the film surface was visibly attacked. In most experiments two complete sorption/desorption cycles were carried out and in some, also a third sorption.

Sorption by Heat-Treated Films

It was of interest to compare sorption by polymer previously structurally modified by heating with that by polymer which had undergone a structural rearrangement under the influence of solvent in a first sorption/desorption cycle (vide infra).

A polymer film, from which sorption specimens were subsequently cut, was heated at 190°C on a flat, adhesive support under nitrogen for a total of 18 days. According to literature data,^{2,4,5} these conditions should promote maximum rates and highest degrees of crystallization. Progressive opacification was observed after the first six days. 1,2-Dichloroethane, 40 mole-% and 54.5 mole-% chloroform in *n*-heptane were sorbed into specimens cut out of the heat-treated film. The experiments were then repeated with ordinary film specimens which had already undergone one sorption/desorption cycle with the solvents at these particular concentrations.

Ancillary Experiments

DSC curves were obtained with the Perkin Elmer DSC IB apparatus, and the crystalline peak areas were used to calculate the crystalline material content of film specimens after heat treatment or solvent treatment.

Densities and density changes of the same specimens were determined in a density gradient column set up according to the method of BS 3715:1964 with aqueous CaNO_3 solutions of densities 1.679 and 1.275.

RESULTS AND DISCUSSION

Sorption by Untreated Films

Normalized curves representative of a typical repeated sorption experiment are shown in Figure 1, where M_t and M_E are respectively solvent contents at a given time t and at equilibrium.

Clearly the first sorption curve is different from subsequent sorption curves while desorption curves are all of the same type. This was found typical of all the repeated sorption experiments.

In the first sorption, as in most practical treatments (e.g., solvent bonding of moldings or exposure to solvent vapor to improve mechanical properties²⁸), the polymer encounters the solvent for the first time. The results of the first sorption are, therefore, of the greatest practical significance.

The rate of first sorption, up to almost the maximum solvent content, was regularly dependent on solvent activity (ambient concentration), as shown by the curves of Figures 2 and 3. Similar, if less strongly pronounced dependence was observed also in second and subsequent cycle sorptions.

Some of the first-sorption curves for 1,2-dichloroethane had multiple peaks in the maximum region. That this effect was not spurious was il-

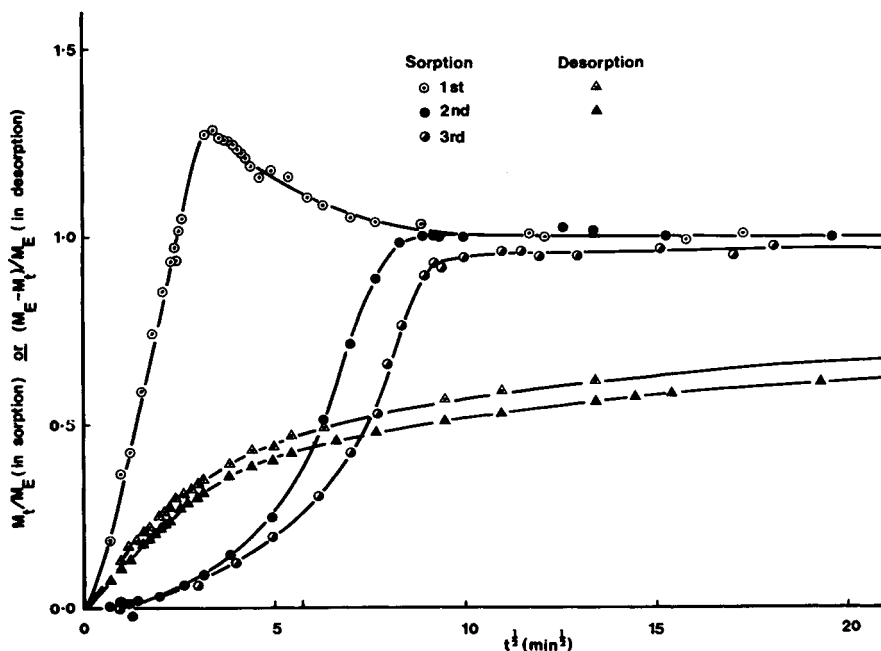


Fig. 1. Repeated sorption of 50 mole-% CHCl_3 .

illustrated by the reproducibility in this area of curves obtained in duplicate experiments. A slight tendency toward resolution of the maximum peaks was observed also with chloroform.

The principal features of the sorption curves at varying solvent activities, and the main inferences they support, are as follows:

a. The difference in form between the first-sorption curves and all subsequent sorption curves for ambient solvent concentrations greater than 20 mole-% for $\text{CH}_2\text{ClCH}_2\text{Cl}$ and 25 mole-% for CHCl_3 shows that at these concentrations the mode of sorption depends on the previous history of the polymer and that the latter is structurally modified in the course of first encounter with the solvent.

b. Except at the lowest concentrations (see Figs. 2 and 3), the first-sorption curves go through a maximum before equilibrating at a lower solvent content level. This parallels the findings of Kambour²⁹ and Mercier, Groeninckx, and Lesne³⁰ in experiments on sorption of acetone and dichloromethane vapors. These authors were among the first to interpret the maxima as indicative of a structural rearrangement involving partial exclusion of the penetrant. The fact that our second and subsequent sorption curves no longer exhibit the maxima provides further supporting evidence for this.

c. The "tail" in the initial portion of the first-sorption curves for both solvents diminishes and finally disappears with increasing ambient solvent concentration. The slopes of the tail portions are lower than those of the main rectilinear portions of the same curves. When the latter portions are extrapolated to intersect the $t^{1/2}$ axis and the squares of the intercepts (i.e., the t -values, here styled "induction periods") are plotted on the log scale against solvent activity, the plots are linear over several decades for both solvents (see Fig. 4). This type of relationship has been found to be characteristic of stress relaxation processes in rubbery polymers.³¹ Such interpretation of the plot of Figure 4 accords with the suggestion that in some polymer-penetrant systems sorption is initially retarded by the finite time necessary for the relaxation of the molecular chains in the polymer surface.^{32,33}

d. Except for the lowest solvent activities (at which the first sorption curves have no maxima), the main portion of the curves is essentially rectilinear almost up to the maximum solvent content. This indicates that, once the surface relaxation has taken place, the take-up of solvent in the conditions of first sorption is essentially by Fickian diffusion (albeit concentration dependent; cf. increasing slopes of the straight portion of the curves in Figs. 2 and 3). A mean penetration coefficient (\bar{P}) calculated from the slope of the straight part of the normalized curve will therefore be equivalent to the mean diffusion coefficient for that part of the process, uncorrected for the effects of mass transfer.

At the higher ambient solvent concentrations used, where initial sorption is not time dependent (no tails on the curves in Figs. 2 and 3), \bar{P} will be identical with \bar{D} calculated from the well-known relationships³⁴⁻³⁶ involving either the half-time sorption value or the slope of the rectilinear part of the

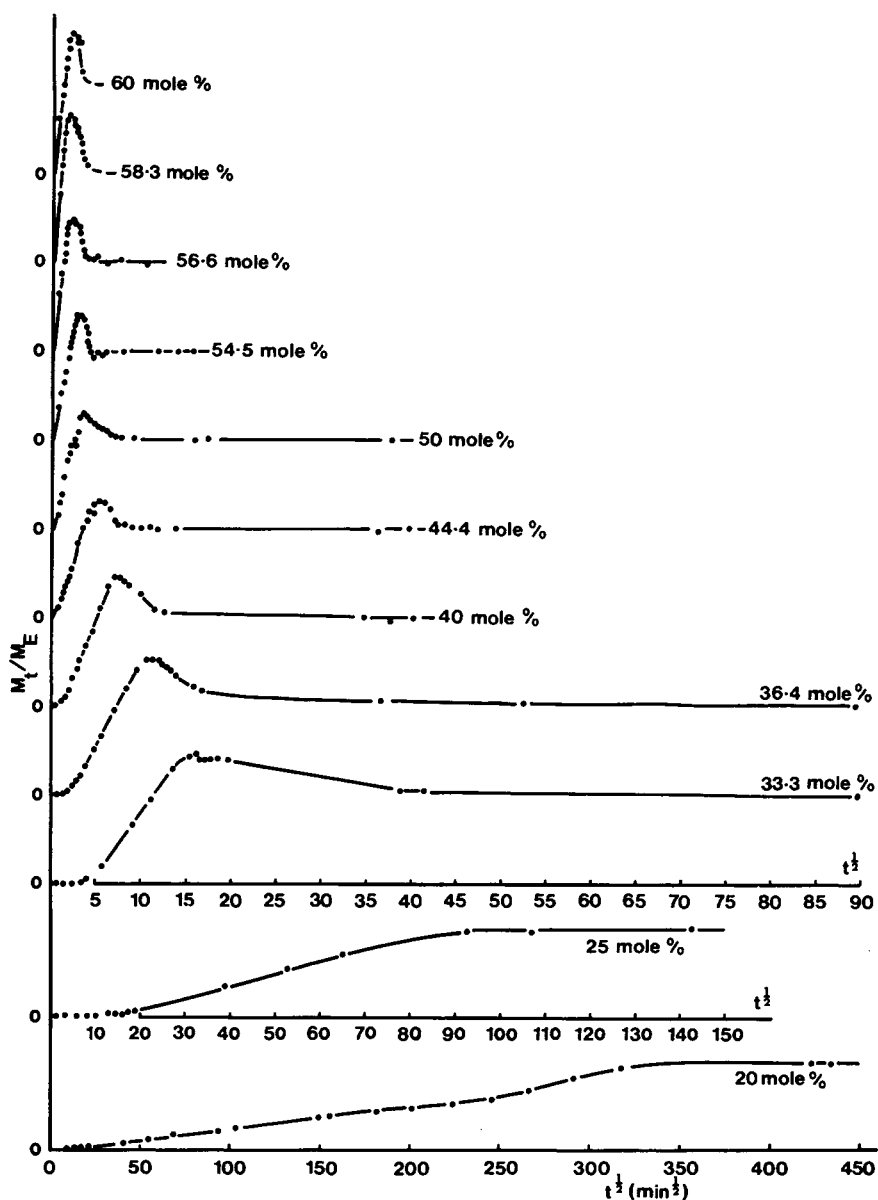


Fig. 2. First sorption curves for CHCl_3 (at the ambient concentrations shown).

normalized sorption curve. The identity should extend to conditions, e.g., in solvent bonding of moulded polycarbonate parts, where concentrated solvents are used (i.e., the solvent activity is even higher than the highest in our experiments). In fact, \bar{D} values determined at 25°C by a different method for the two solvents undiluted were $5.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$

for 1,2-dichloroethane and $6.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for chloroform.^{37,38} These figures agree well with \bar{P} values for our highest solvent activities, where the curves of Figures 5 and 6 begin to flatten out, suggesting that further increase in solvent activity may not cause \bar{P} to increase much more.

For the lower solvent activities, where time effects appear, \bar{P} will represent the mean diffusion coefficient for the main part of the sorption process

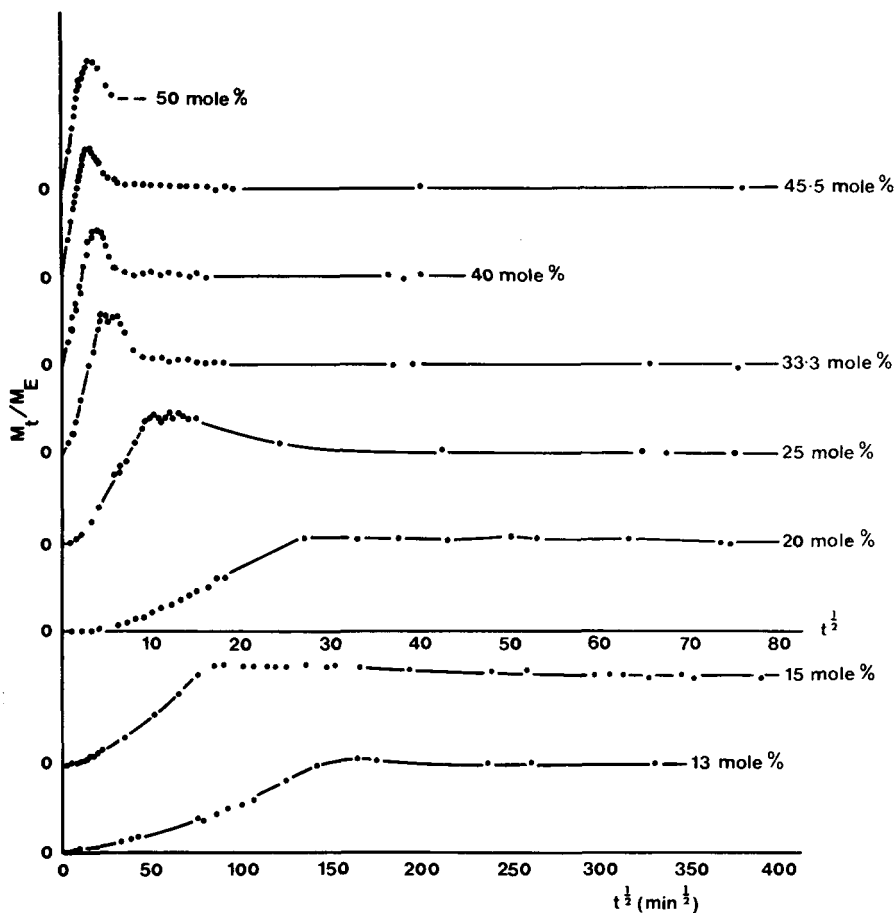


Fig. 3. First sorption curves for $\text{CH}_2\text{ClCH}_2\text{Cl}$ (at the ambient concentrations shown).

after the initial surface relaxation has taken place. It could be argued that M_{max} and not M_E is the proper equilibrium value for the conditions of first sorption. However, \bar{P} values calculated from slopes of M_t/M_{max} versus $t^{1/2}$ plots differ only by a factor of about 2 from those presented here.

The \bar{P} values plotted in Figures 5 and 6 were calculated from the relationship

$$\bar{P} = (\pi/16)(Kl)^2 \quad (1)$$

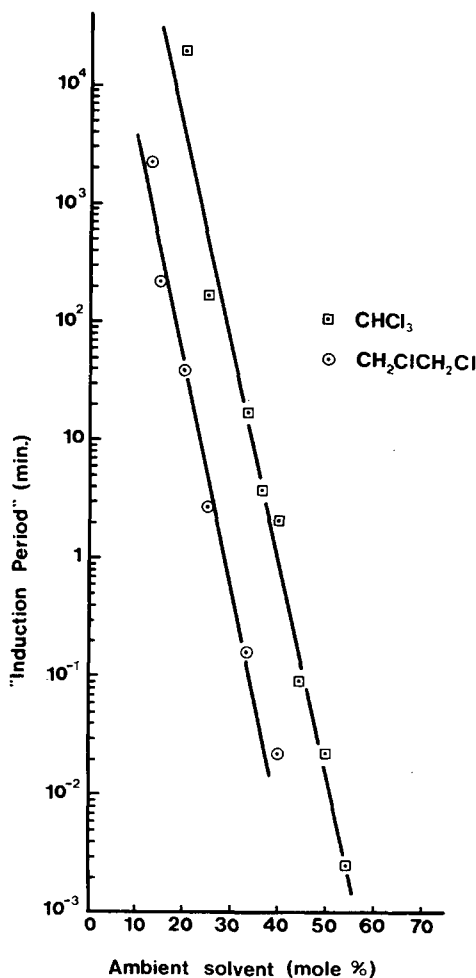


Fig. 4. "Induction period" vs. ambient solvent concentration.

where K is the slope of the rectilinear portion of the normalized sorption graph, equal to $(M_i/M_E)/t^{1/2}$, and l is the film thickness (cm). This is an alternative form of the equation^{35, 39}

$$\bar{D} = (\pi/16)R^2 \quad (2)$$

which is applicable in conditions of concentration-dependent diffusion.³⁵ In eq. (2), $R = (M_i/M_E)/t^{1/2}$.

The graph of Figure 5 is linear over much of the concentration range indicating a relationship for $D(c)$ of the type $D(c) = D_0 e^{Kc}$. For diffusion at zero solvent concentration, extrapolation of the curves of Figure 5 gives $\bar{P}_0 = 1.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ for chloroform and $\bar{P}_0 = 2.0 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for 1,2-dichloroethane. The figure for chloroform is in reasonable agreement with one published by Sobiczewski and Wajnryb⁴⁰ on the basis of a few ex-

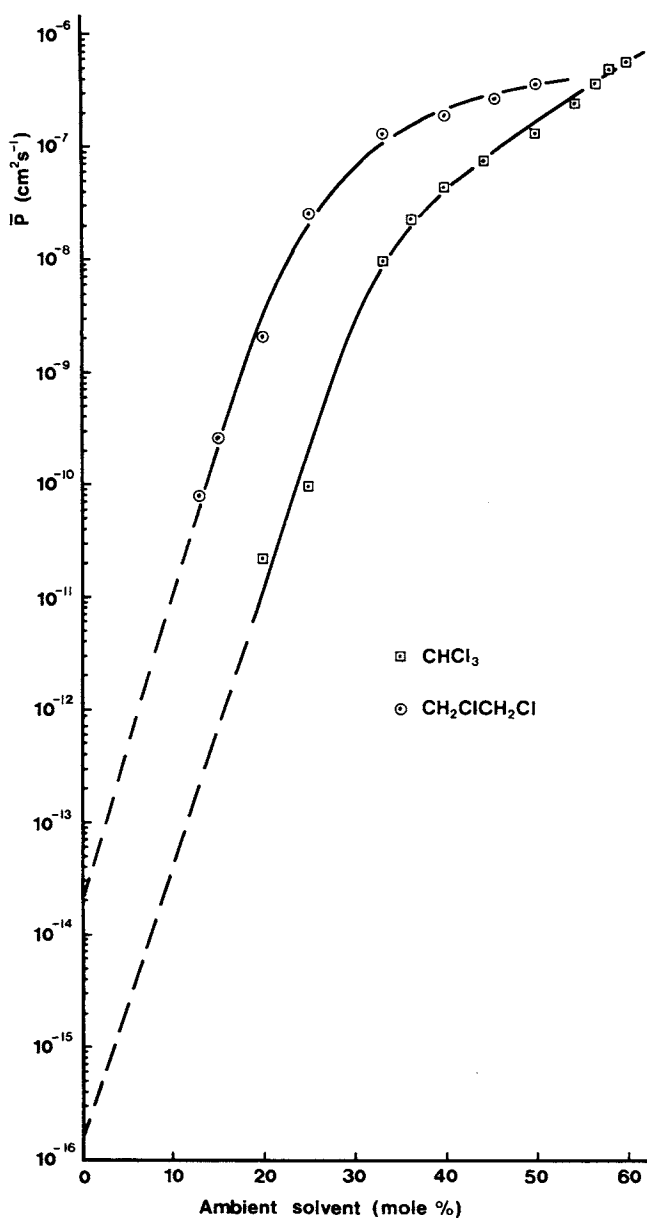


Fig. 5. Mean penetration coefficient \bar{P} vs. ambient solvent concentration.

periments on sorption of chloroform vapor at low partial pressure. No relevant figures appear to have been published for 1,2-dichloroethane.

The curves of Figure 5 may be regarded as consisting of two lines of different slope corresponding respectively to diffusion below and above the effective T_g of the system at the temperature of the experiments and inter-

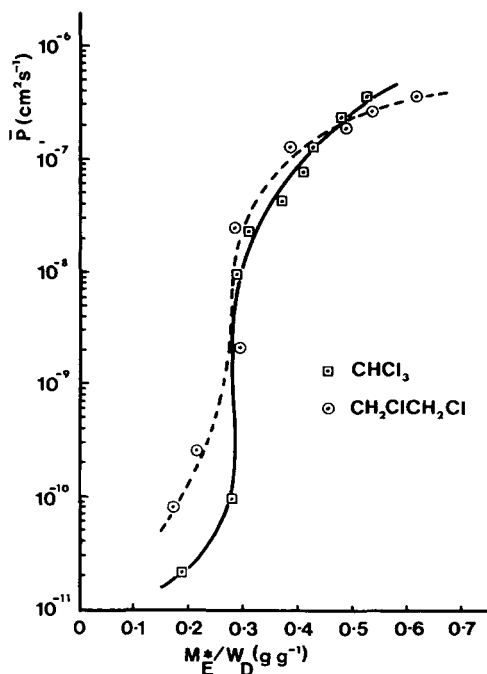


Fig. 6. Mean penetration coefficient \bar{P} vs. solvent content at equilibrium (compensated for relative effect of structural rearrangement).

secting at the point where the ambient solvent concentration gives the sorbed solvent concentration in the polymer at equilibrium appropriate to the effective T_g . It can be seen that the point of intersection is approximately at 30 mole-% solvent, which agrees well with a similar conclusion from the joint consideration of Figure 6 and 13.

e. The distorted sigmoid shape of first-sorption curves for the lowest solvent activities, and of all second- and third-sorption curves, is characteristic of non-Fickian "anomalous" behavior,³⁶ as is the shape of the corresponding desorption curves and the fact that they cross the sorption curves before equilibrium. These features, often associated with glassy polymers,³⁶ suggest that in first sorptions at the lowest ambient solvent concentrations, the polymer-penetrant system never reached its effective T_g . This is further confirmed by the plots of Figures 6 and 13 in which the steps in the curves correspond to the solvent content (approximately 0.3) at effective T_g . The shape of the curve in Figure 6 is as predicted by Frisch et al. for D versus penetrant concentration in a glassy polymer, on the basis of sorption of solvents by lightly crosslinked epoxy resins.⁴¹

In the second and subsequent sorptions where the polymer has already undergone a structural rearrangement involving at least some crystallization (vide infra), its diffusional behavior may be likened to that of a partly crosslinked, but essentially glassy system. This is consistent with the shape of the sorption and desorption curves.

f. The "tails" are the most prominent feature of the second and subsequent sorption curves. Their length increases and the slope decreases somewhat in consecutive sorptions. In some solvent-polymer systems, such behavior has been ascribed to "orientation anomalies"³⁶ in diffusion resulting from preferential orientation of polymer molecules in the surface. Such orientation can indeed arise in a sorption/desorption cycle.³³ The repeated sorption/desorption curves are also of the general type expected for a sheet with a surface skin,³⁵ and an oriented surface layer could behave as a skin. Microscopic examination in polarized light of films used in sorption experiments showed that the surface became structured and anisotropic.³⁷

Sorption by Heat-Modified Films

The results of sorption experiments on heat-modified films are shown in Figures 7 and 8. In these plots, the ordinates are solvent contents per unit dry polymer weight (not M_i/M_E values) because this illustrates better the difference in the final solvent contents. Although the heat-treated film had been visibly modified (made opaque) by the treatment and had developed crystallinity (vide infra), its first sorption pattern is generally similar to that of the standard untreated films and different from that of solvent-modified film (second-cycle sorption). This suggests that the structural modifications brought about by heating and solvent action may be different or that the distribution of the rearranged material in the heat-modified film may be different. The "tails" on the sorption curves for the heat-treated films are comparatively short, and the slope of the rectilinear portion is low in comparison with that of the relevant first-sorption curves for untreated films. These features suggest that, unlike solvent treatment, the heat treatment did not produce an oriented or crystalline "skin" but that the ordering was much more evenly distributed throughout the body,

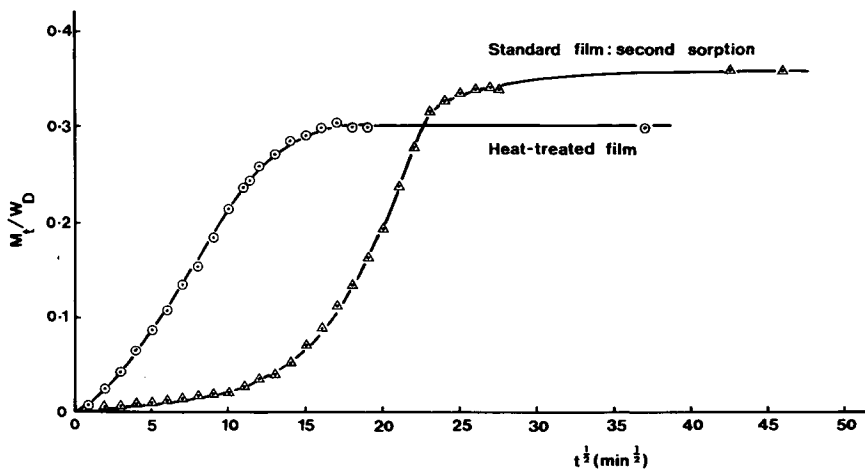


Fig. 7. Sorption of 40 mole-% $\text{CH}_2\text{ClCH}_2\text{Cl}$.

reducing the overall rate of solvent penetration but not modifying its general pattern.

Structural Changes Caused by Heating and/or Solvent Sorption

In the first-sorption experiments at the highest solvent activities, the differences between the maximum solvent content (M_{\max}) and the final equilibrium content (M_E) are large, amounting, on a volume basis, to nearly one quarter of the original "dry" volume of the film specimen (V_f). This is reasonable, indirect evidence that most, if not all, of the rearrangement takes place after M_{\max} has been reached or at least approached in these experiments.

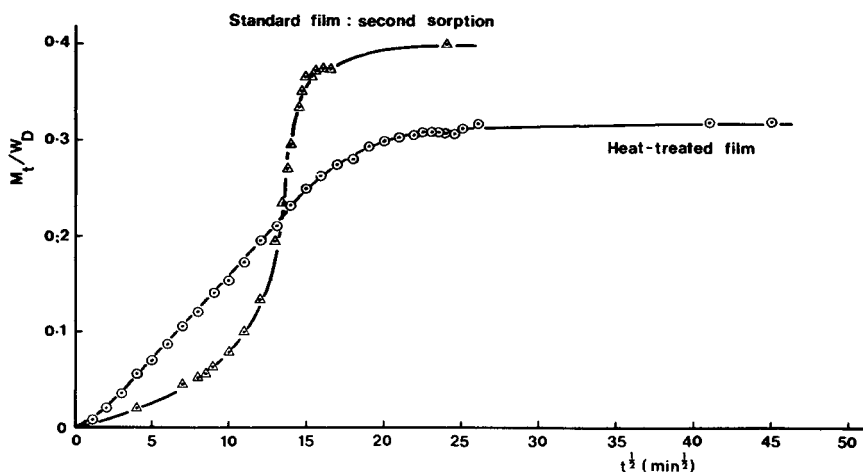


Fig. 8. Sorption of 54.4 mole-% CHCl_3 .

The evidence also indicates that the film thickness used was not excessive in the sense that very little, if any, rearrangement can be taking place in the "outer layers" before the whole of the film is penetrated by the solvent. The particular film specimen thickness used was chosen because it is comparable with the thickness of the polymer layer initially penetrated by solvent in the production of solvent-promoted joints in polycarbonate.^{37, 42} The volume fraction just mentioned, i.e.,

$$\gamma = \frac{M_{\max} - M_E}{\rho_s V_f} \quad (3)$$

where ρ_s is the density of the solvent (in bulk), cannot be directly equated to the volume of polymer actually rearranged. However, it does provide a relative index of the extent of rearrangement and the numerical values could actually be comparable, bearing in mind that the greatest rearrangements reported to have been achieved by heating were about 30%.⁴⁻⁸ Further

evidence for the applicability of the index is provided by a plot (Fig. 9) of γ against M_{\max} for both solvents.

An index based entirely on the weight of penetrant expelled in the sorption of acetone into polycarbonate, viz., $\chi_w = (W_{\max} - W_{\infty})/W_{\max}$ has been used previously by Kambour et al.²⁹ However, we believe that γ of eq. (3) is less critically dependent on the assumption that the distribution of penetrant in the polymer is completely uniform and that it is also less sensitive to experimental error in the actual determination.³⁷

At final equilibrium the remaining solvent will reside in that part of the polymer which is accessible to it. This may be expressed, on a relative basis, by applying a correction based on the appropriate value of γ to the actual equilibrium solvent content figures of individual experiments:

$$M^*_E/W_D = (M_E/W_D)/(1 - \gamma). \quad (4)$$

Equilibrium content values corrected in this way have been plotted as abscissae in Figure 6. A plot of γ against the maximum solvent content per unit polymer weight (Fig. 9) shows that, considering the two solvents together, no structural rearrangement takes place below the solvent content of about 0.2; regression analysis gives a straight line through all the points, with a correlation coefficient of 0.939.

That the rearrangement involves some crystallization and some non-crystalline ordering is indicated by the data listed in Table I. In com-

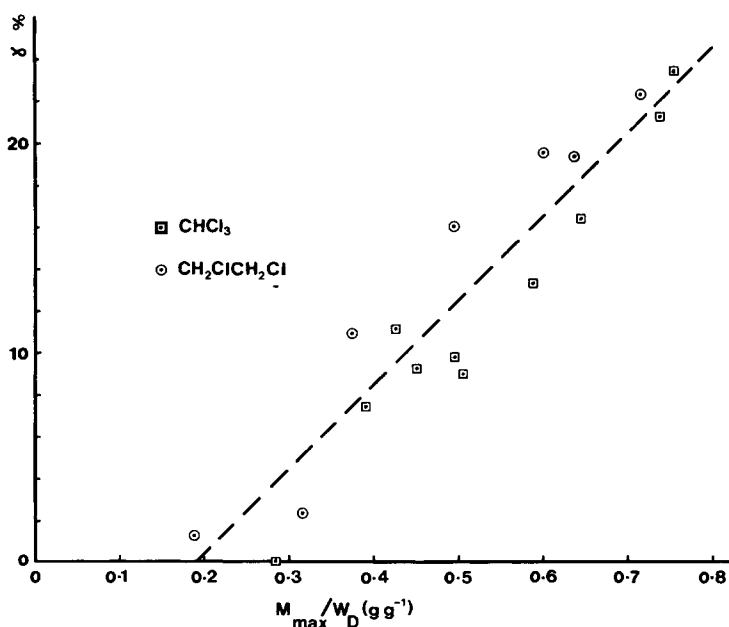


Fig. 9. Structural rearrangement index γ vs. maximum solvent content per unit "dry" weight of polymer.

puting the "percentage crystallinities" from DSC peak areas, the figure of 7600 cal (equivalent to 30 cal/g) was taken, after Kambour et al.,²⁹ as the molar heat of fusion of the ideal polycarbonate crystal. This is also fairly close to the value obtained recently by Mercier and Legras⁴³ (26.2 cal/g).

It is clear from an inspection of the curves of Figure 2 and 3, as well as from general consideration of the sorption results, that the width of the base of the maximum peak on the sorption curve must be directly related to the total time for expulsion of excess solvent (i.e., completion of the rearrangement) and that the *rate* of solvent expulsion (presumably directly

TABLE I
Summary of Data on Structural Rearrangement

Code	Film specimens Description	Degree of crystallinity, %		Structural rearrangement from sorption data γ , %
		By DSC $\sigma = \frac{100 \times \Delta H_s^a}{\Delta H_c}$	From density $\sigma' = (\rho_s - \rho_a)/\Delta\rho^b$	
Q	Amorphous film (quenched from the melt in liquid N ₂)	0.0	0.0	—
1	Film as molded	0.0	0.8	—
2	Heat-treated film	8.6	8.7	—
	Films after sorption at:			
3	13 mole-% CH ₂ ClCH ₂ Cl	0.0	Voids developed in these films. Density below lower limit of column (1.1699)	1.2
4	20 mole-% CHCl ₃	0.0		0.0
5	33 mole-% CH ₂ ClCH ₂ Cl	9.5		15.9
6	40 mole-% CHCl ₃	9.7		14.9
7	45.5 mole-% CH ₂ ClCH ₂ Cl	16.9		19.2
8	58.3 mole-% CHCl ₃	11.9		23.3
9	Heat-treated film after sorption of 40 mole-% CH ₂ ClCH ₂ Cl	15.2		0.8
10	Film after second-cycle sorption of 40 mole-% CH ₂ ClCH ₂ Cl	14.0		19.4 ^c

^a Where ΔH_s = heat of fusion of specimen in cal/g (from peak area); ΔH_c = 30 cal/g.

^b Where ρ_s = measured density of specimen; ρ_a = density of amorphous specimen (= 1.1965 g/ml); $\Delta\rho$ = 0.1535 = difference between ρ of fully crystalline material (= 1.35 g/ml, after Bonart⁹) and ρ_a .

^c Original change after first sorption; no further change in second sorption.

associated with the rate of rearrangement) will be reflected in the right-hand side slope ("negative" slope) of the peak. In Figure 10, the "negative" slopes of the maximum peaks are plotted against the ambient solvent concentration, and in Figure 11 the approximate "total time of rearrangement" values (Δt_c) are similarly plotted; Δt_c was calculated as schematically shown in Figure 12.

Deriving Δt_c in the way shown makes allowance for the possibility that the rearrangement may start sometime before the maximum sorption point,

suggested by deviation of the plot from a straight line before the maximum value is reached. Similarly, the point of intersection of the extrapolated "equilibrium" portion of the curve and the "negative" slope of the maximum peak is a reasonable indication of the time when equilibrium is first reached. The curves of Figure 10 and 11 demonstrated the functional relationship between solvent activity on one hand and Δt_c and the "negative" slope of the maximum peak on the other. Moreover, the remarkable similarity in the shape of the curves for one and the same solvent in the two figures, and in the mutual relationship of the curves for different solvents from figure to figure, support the view that Δt_c and the "negative"

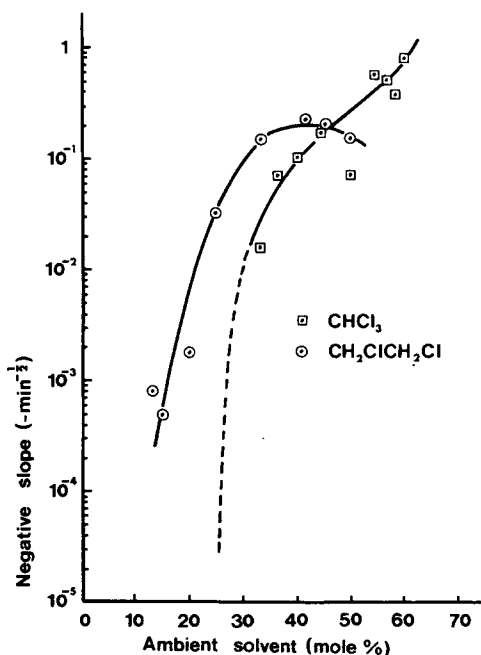


Fig. 10. Rate of structural rearrangement ("negative" slope of maximum peak) vs. ambient solvent concentration.

slope of the maximum peak respectively do indeed represent fairly closely total time for solvent expulsion (or rearrangement) and the rate at which this proceeds. The present data do not explain adequately why the shapes of the curves for chloroform are different from those of the corresponding 1,2-dichloroethane curves. The fact that the curves cross over at about 45-50 mole-% ambient solvent concentration shows that above this concentration the total time for the structural rearrangement is shorter and the rate of the main part of the rearrangement is faster with chloroform than it is with 1,2-dichloroethane. This accords well with observations of the development of spherulites in bisphenol A polycarbonate treated with the two solvents⁴² and also fits in with the crossover of the penetration

coefficient curves in Figure 6. Finally, it may be mentioned that the maximum sorption isotherms at 25°C (maximum solvent sorbed per unit polymer dry weight versus ambient solvent concentration) for the two solvents into polycarbonate contain inflections at points corresponding to about 45 mole-% solvent concentration.³⁷ (See Fig. B.) Considered together, these data suggest that the principal factors instrumental in the relationships indicated by Figures 10 and 11 are the chemical structure of the two solvents and their interaction with the polymer in the solvent-swollen state.

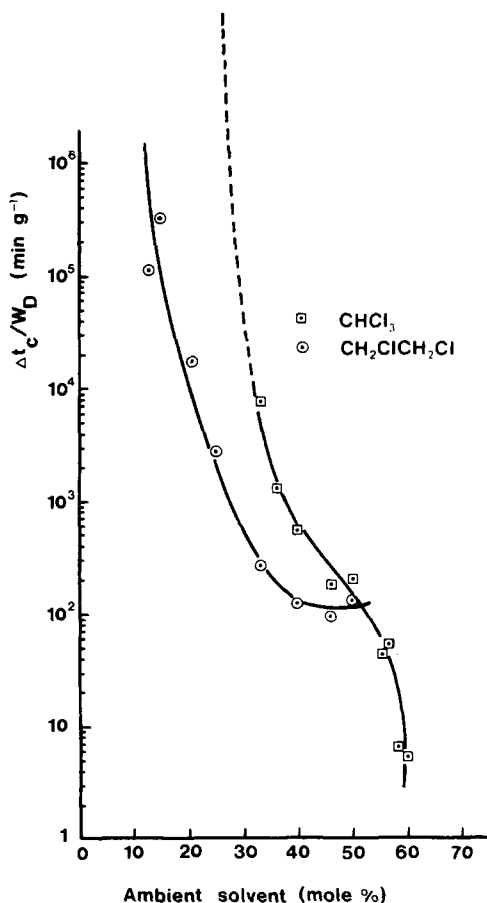


Fig. 11. Duration of structural rearrangement per unit "dry" polymer weight vs. ambient solvent concentration.

Opacification of the film specimens was noticed in the course of sorption at all but the lowest solvent concentrations. A similar phenomenon during sorption of certain solvent vapors was attributed by Mercier et al.³⁰ to the development of crystallinity. This is the logical explanation in relation also to our specimens, particularly as those subjected to the intermediate

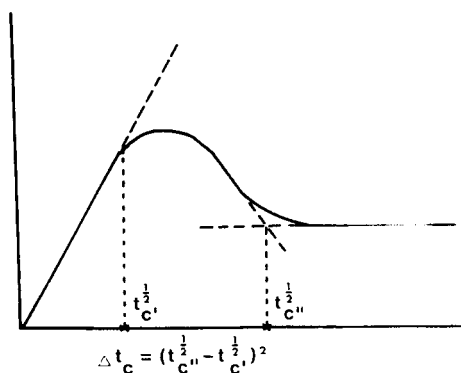


Fig. 12. Derivation of Δt_c from sorption graph: schematic representation.

and high solvent activities were found to have undergone rearrangement including crystallization (as evidenced by peaks on the DSC curves and the maxima on the sorption curves). However, the opacity in our specimens must also be due in part to the formation of microvoids or crazes as evidenced by the fact that despite the rearrangement, which would be expected to increase the density, the densities of the opacified samples were

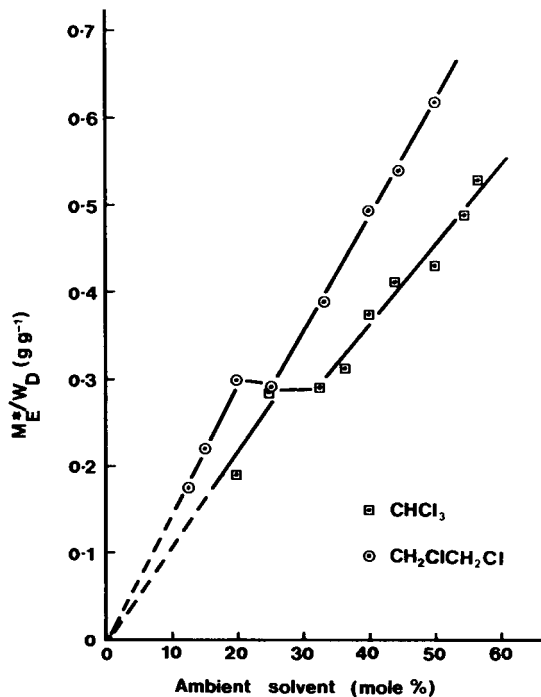


Fig. 13. Equilibrium sorption isotherms (compensated for relative effect of structural rearrangement) for CH_2ClCH_2Cl and $CHCl_3$ at $25^\circ C$.

found to be lower than those of the amorphous polymer (specimens 3–10 in Table I). Crazing of bisphenol A polycarbonate as a result of sorption of penetrants (which were not, however, good solvents for the polymer) has been reported recently by Miller et al.¹⁹

According to Hopfenberg and Frisch,⁴⁴ different types of diffusion behavior previously believed to be governed by the nature of the components of a polymer–penetrant system may in fact depend only upon the temperature and penetrant activity. The systems discussed here support this prediction in that at one and the same temperature and depending on the penetrant activity (ambient concentration), both the solvents studied exhibited Fickian diffusion (concentration dependent), crazing effects, and, at the lowest concentration used, “anomalous” diffusion behavior.

CONCLUSIONS

In glassy bisphenol A polycarbonate, the diffusion of 1,2-dichloroethane and chloroform (both good solvents for the polymer) at 24–25°C is strongly dependent on concentration in two senses: (i) The rate of diffusion increases steeply with ambient solvent concentration. (ii) The pattern of diffusion changes from essentially Fickian (concentration dependent) at high ambient solvent concentrations to non-Fickian “anomalous” at low concentrations.

This transition coincides with the attainment of the critical solvent content (approximately 0.3 w/w in the polymer). At this solvent concentration, the systems studied reached their effective T_g at the temperature of the experiments.

Absorption of solvents to or above the critical content causes structural rearrangement of the polymer making diffusion dependent in this sense on the history of the sample. The pattern of diffusion changes markedly after the originally glassy polymer has been morphologically modified by absorption of solvent or by heating.

Solvent-actuated structural rearrangement proceeds at an appreciable rate above the critical solvent content. It is generally similar to, but not identical with, rearrangement caused by heating, since the two affect further diffusion differently.

Diffusion of the two solvents was also found to be time dependent, since at the lower solvent activities it was appreciably slowed down initially by relaxation processes in the surface of the polymer. The effect is particularly strongly manifested in polymer which has been pretreated with a solvent (i.e., on the second and subsequent solvent sorptions by the same specimen). The magnitude of the effect increases with the severity of previous solvent treatment or the number of such treatments. Pretreatment by heating can also affect the initial rate of diffusion.

Analysis of the sorption data, in conjunction with the results of DSC and density determinations, suggests that structural rearrangement in-

volves crystallization and also ordering of a less well-defined kind. In this respect, the action of the two solvents is similar to that of acetone vapor described previously by Kambour.²⁹

We are grateful to Mr. F. Burford of Kingston Polytechnic for assistance with the DSC work.

This work was supported by the Ministry of Defence Procurement Executive.

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Received December 15, 1972

Revised August 29, 1973