Diffusion and Induced Crystallization in Polycarbonate

ROBERT A. WARE, STEVEN TIRTOWIDJOJO, and CLAUDE COHEN,
*School of Chemical Engineering, Cornell University, Ithaca, New York
14853*

Synopsis

The study of the effect of thickness on the mass uptake is shown to be quite helpful in the understanding of the complexities of polymer/organic penetrant sorption behavior. Isothermal diffusion results for methanol, acetone, and carbon tetrachloride in polycarbonate plates and films of various thicknesses ranging from 12 mils (0.030 cm) to $1/4$ in. (0.633 cm) are presented. The diffusion is purely Fickian only in the case of methanol, which is a poor solvent for polycarbonate and has a low level of saturation in it (0.06 g/g). Methanol does not lead to a detectable swelling or any appreciable crystallization of the polymer during the diffusion process. Acetone and carbon tetrachloride are much better solvents and lead to much higher saturation levels; they crystallize polycarbonate, and their mass uptake is anomalous. The diffusion of carbon tetrachloride exhibits initially a case II diffusion behavior followed for thicker plates by an intermediate behavior between case II and Fickian diffusion. The anomalous diffusion in the case of acetone appears to be associated primarily with surface effects.

INTRODUCTION

The diffusion of organic penetrants in amorphous glassy polymers has been the subject of much attention due to the "anomalous" or non-Fickian results that are often obtained. These anomalies are believed to be due to the relaxation motion of the polymer in response to swelling stresses that are created as penetrant enters the polymer network.[1,2] In some cases the diffusion process is accompanied by large-scale structural rearrangements in the polymer which can occur on the same time scale as that of penetrant diffusion and which leads to an induced crystallization of the original amorphous network. Polycarbonate and poly(ethylene terephthalate) are especially susceptible to solvent induced crystallization and have received the most attention.[3-5] As solvents permeate these polymers and allow easier movement of the polymer chains, there is less steric hindrance restricting the movement and reorientation of the polymer molecules to form the more thermodynamically favorable crystalline state.

We present here isothermal sorption data for methanol, acetone, and carbon tetrachloride in polycarbonate plates and films of various thickness. We show that the study of the effect of thickness $(2L)$ on the mass uptake (M_t) is quite useful in the understanding of the mass flux in these systems. A critical test for Fickian diffusion is that the sorption curves for all thicknesses plotted as M_t, the mass uptake in gram of solvent per gram of dry polymer at time t, vs. $\sqrt{t}/2L$, should follow a *single* curve which is linear at initial times.[6] Anomalous mass uptake behavior, when observed in the systems investigated here, appears to be caused primarily by surface effects (similar in some cases to the surface concentration relaxation phenomena observed in some non-crystallizable polymers[7])

rather than by the more complex anomalous behavior due to strain dependent diffusion coefficients.[2]

EXPERIMENTAL RESULTS

Extruded polycarbonate (PC) sheets and films (Tuffak) with nominal thicknesses ranging from 12 mils to $\frac{1}{4}$ in. were used in this study. The density of this material as quoted from the manufacturer's specifications[8] was 1.20 g/cm^3. The sheets were cut into small plates with an edge area of 10% or less of the total exposed surface area such that infinite slab geometry could be assumed. All plates were annealed at ~145°C for several days and then cooled slowly and weighed at room temperature before immersion into the diluent bath consisting of reagent grade methanol, acetone, or carbon tetrachloride. After immersion and at successive time intervals, samples were removed from the bath, quickly wiped, and weighed in stoppered containers. A different sample was used for each point on the weight gain plots in order to minimize errors due to penetrant evaporation. DSC measurements were done on a Perkin Elmer DSCl-B calorimeter; pure and saturated PC samples were used after having been dried in vacuum for two to three days.

Methanol/Polycarbonate

In the case of methanol, which is a relatively poor solvent to polycarbonate, the diffusion is entirely Fickian both at room temperature (22°C) and at 42°C as indicated by Figures 1 and 2. The straight line through the points on the $t^{1/2}$ scale and the fact that no thickness dependence on the rate of uptake was observed both for the M_t (g of solvent/g of polymer) and M'_t (g solvent/cm^2 exposed area) plots (not shown) indicate that the sorption is purely Fickian. The methanol/polycarbonate plate (0.169 cm) and film (0.041 cm) (Fig. 1) remained glassy and transparent during sorption at room temperature. The absence of
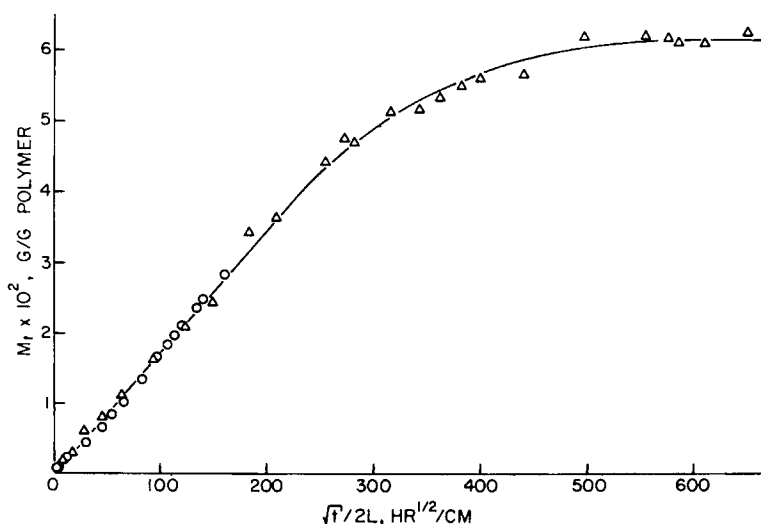

Fig. 1. Mass uptake per mass of dry polymer vs. $t^{1/2}/2L$ for methanol in PC at 22°C for plates of thicknesses $2L = 0.041$ cm (16 mil) (△) and $2L = 0.169$ cm ($\frac{1}{16}$ in.) (○).
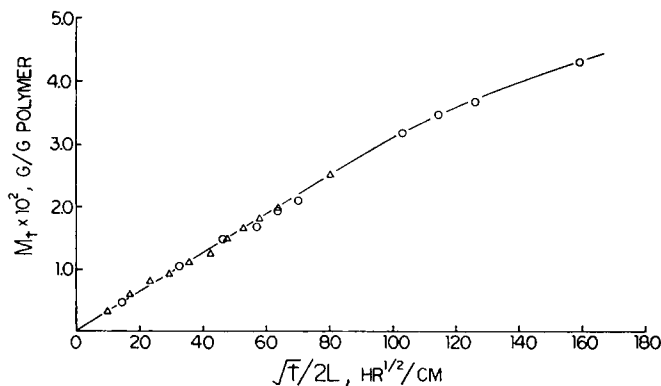
Fig. 2. Mass uptake per mass of dry polymer vs. $t^{1/2}/2L$ for methanol in PC at 42°C for plates of thicknesses $2L = 0.157$ cm ($\frac{1}{16}$ in.) (O) and $2L = 0.312$ cm ($\frac{1}{8}$ in.) ($\triangle$).

crystallization was confirmed by DSC measurements where only a T_g peak was observed at 425K. Minor crystallization did occur for the samples of thickness 2L equal to $\frac{1}{16}$ in. (0.157 cm) and $\frac{1}{8}$ in. (0.312 cm) at 42°C whose sorption curves are shown in Figure 2. These curves indicate Fickian diffusion, and it seems that most of the uptake takes place prior to the appearance of very faint opacity due to crystallinity.* The value of M_∞ at 42°C was determined to be 0.064 g/g. The value of the diffusion coefficient can be obtained in a straightforward manner[6] from the slope of the curves, and we find $D_{22°C} = 4.3 \times 10^{-10}$ cm^2/s and $D_{42°C} = 1.3 \times 10^{-9}$ cm^2/s. These values correspond to the diffusion of methanol in *amorphous* polycarbonate. Although the diffusion coefficient varies appreciably with temperature, the methanol solubility (M_∞) varies only from 0.062 to 0.064 g/g in the temperature range investigated.

Acetone/Polycarbonate

Data obtained at 25°C for acetone sorption into a polycarbonate film of thickness 2L equal to 0.030 cm (12 mils) and polycarbonate sheets of thickness 2L equal 0.162 cm ($\frac{1}{16}$ in.), 0.310 cm ($\frac{1}{8}$ in.), and 0.644 cm ($\frac{1}{4}$ in.) are presented in Figures 3 and 4. There are several unusual features about these sorption curves (Fig. 3): (1) The saturation levels M_∞ increases with decreasing thickness. (2) The thickness dependence is the reverse of what is usually observed in anomalous non-Fickian behavior where the data for thinner plates lie *below* those of thicker plates. (3) The sorption in the thin film goes through an overshoot before leveling off at its saturation level. (The sorption data for the thin film are based on the polymer weight obtained after drying the immersed samples. This was done to correct for a minor weight loss of polymer in the bath due to small crystallite grains breaking off the edge of the samples. This correction is negligible for the thicker plates.)

The value of $M_\infty = 0.265$ g acetone/g dry polycarbonate for the plate thickness 0.310 ($\frac{1}{8}$ in.) is in good agreement with that reported by Miller et al.[9] for the same thickness. Although these authors studied only one plate thickness and reported Fickian behavior, they obtained $M_\infty = 0.275$ g/g. The rapid initial rate of sorption observed here has been attributed by Wilkes and his co-workers[10] to

---

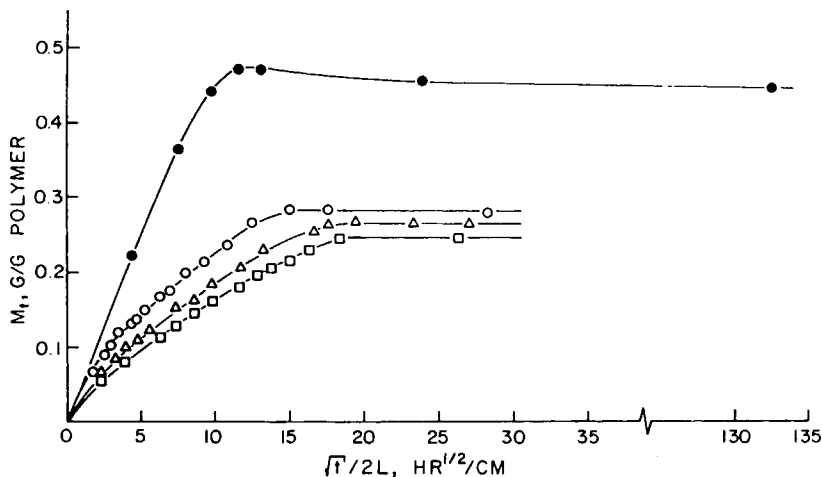* At 53°C, the degree of crystallization is much more pronounced.

Fig. 3. Mass uptake per mass of dry polymer vs. $t^{1/2}/2L$ for acetone in PC at 25°C for plates of thicknesses $2L = 0.030$ cm (12 mil) (●), $2L = 0.162$ cm (¹⁄₁₆ in.) (○), $2L = 0.310$ cm (¹⁄₈ in.) (△), and $2L = 0.644$ cm (¹⁄₄ in.) (□).

high cavitation or roughness induced at the polymer surface by the penetrating liquid which exposes, in effect, more surface area for transport. The high degree of surface cavitation observed via electron micrographs by these investigators appeared to be confined to approximately the first few mils (0.05 mm) of film thickness. It would thus be expected that the effect of the extra uptake at the surface due to cavitation plays a lesser role on M_∞ as the plate thickness increases, as observed in Figure 3. We also note that Turska and Benecki[5] quote a value of M_∞ equal to ~0.5 g/g at 25°C for a thickness of $2L = 0.01$ cm in agreement with our postulate. In Figure 5 we have plotted M_∞ vs. $2L$ to qualitatively indicate the trend of the variation of the equilibrium mass uptake. It is interesting that Kambour et al.[11] find the equilibrium sorption at ~23°C for a PC film (Lexan) of thickness $2L = 0.0025$ cm under *saturated acetone vapor* to be 0.297 cm³/cm³, which corresponds to 0.2 g/g assuming volume additivity. This value is likely to be the true equilibrium value of M_∞ without the extra sorption surface effects observed during liquid sorption experiments.† Figure 5 shows that M_∞ asymptotically tends to this value as the thickness of the plates is increased. DSC measurements on samples saturated in acetone exhibited a melting temperature peak at ~494K. The polycarbonate samples turned white and opaque almost immediately in the diffusion region where the polymer had sorbed the penetrant. The opacity of the immersed plates was much more pronounced in the case of acetone than in the case of methanol or carbon tetrachloride at room temperature; this is probably due to the surface cavitations and possibly to different super-structure forms in the acetone-induced crystallization[12] which strongly scatter visible light.

The sorption data for all the thicknesses investigated are plotted in Figure 4 in the form of M'_t (mass uptake in gram per exposed surface area in cm²) vs. the square root of time. The curves are all superimposable up to their respective saturation level, indicating that any strain dependence of the diffusion coeffi-

---

† A referee has kindly pointed out to us that scanning electron micrographs do indeed show much less cavitation (if any) for acetone vapor than for the liquid.
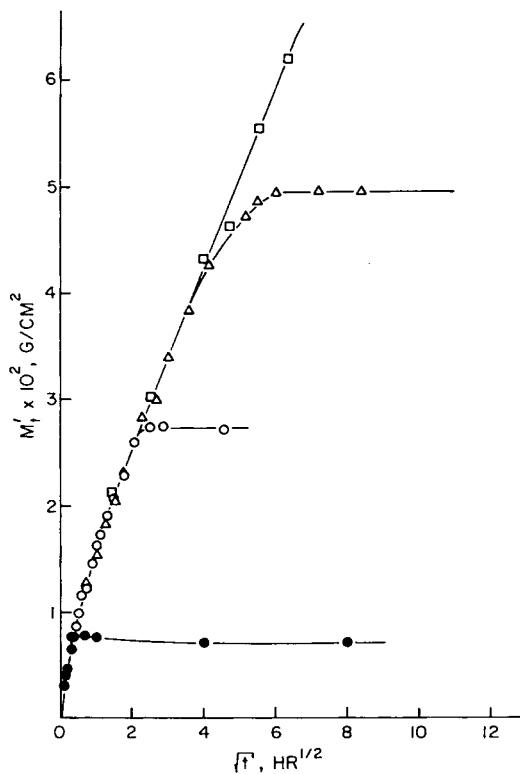
Fig. 4. Mass uptake per unit area vs. $t^{1/2}$ for acetone in PC at 25°C for plates of thicknesses $2L$ = 0.030 cm (12 mil) (●); $2L$ = 0.162 cm ($\frac{1}{16}$ in.) (O), $2L$ = 0.310 cm ($\frac{1}{8}$ in.) (△), and $2L$ = 0.644 cm ($\frac{1}{4}$ in.) (□).

cient,[1,2] if present, is not a contributing factor to the anomalies exhibited here. As has been noted by other investigators,[9,10] one could neglect the initial mass sorption data of the M_t plots in Figure 3 and draw straight lines fitting reasonably well the data after the initial transient effects (this is more obvious for the case of carbon tetrachloride reported in Fig. 6). In addition, the diffusion front of acetone in PC has been observed to proceed as $t^{1/2}$ after the initial period.[5,13] If a diffusion coefficient is extracted from the slope of the lines in Figure 3, it would lead to a thickness-dependent value. This is likely due to the surface cavitation effect on M_∞ previously discussed. The interpretation of the diffusion coefficients obtained by the procedure outlined above is further complicated by the fact that the calculated values represent average diffusion coefficients over amorphous and semicrystalline phases. If one assumes that crystallization occurs instantaneously behind the swelling front and applies Crank's[6] two-zone diffusion model, a calculation of the mass uptake curve will yield an averaged value between the diffusion coefficient in the amorphous glassy polymer phase and that in the partially crystallized swollen phase.

Carbon Tetrachloride/Polycarbonate

The mass uptake of CCl_4 in polycarbonate at 22°C was obtained for samples of two thicknesses, $2L$ = 0.03 cm and $2L$ = 0.173 cm. The sorption curves of sigmoidal shape shown in Figure 6 were obtained. The fact that the curves are
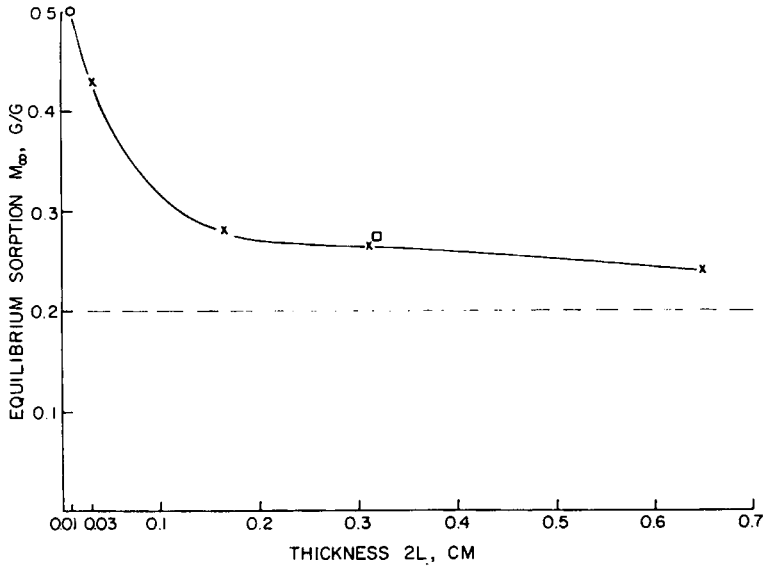
Fig. 5. Equilibrium sorption uptake of acetone in PC as a function of sheet thickness at room temperature: (X) this study; (O) from Ref. 5; (□) from Ref. 9. Dashed horizontal represents M_∞ of a 0.0025-cm PC Lexan film in saturated acetone vapor.[11]

nonsuperimposable for the two thicknesses investigated is a clear manifestation of non-Fickian behavior despite the good fit to straight lines observed beyond the initial transient effects. The superimposition of the data in the M_t' graph (Fig. 7) indicates that in this case, as in the case of acetone, the strain dependence of the diffusion coefficient was negligible. A fit of the data to the solution of the equation of Frisch et al.[14] who interpret anomalous behavior as due to a stress contribution to the mass flux was not very satisfactory[15] and will not be reported.

Miller et al.[9] have reported a square root of time-dependent mass uptake of carbon tetrachloride in PC; they have ignored, however, the initial sorption pe-
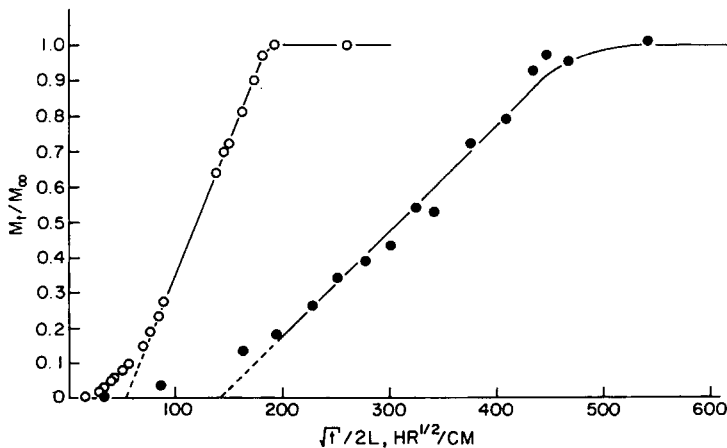

Fig. 6. Sorption curves for carbon tetrachloride in PC at 22°C for plates of thicknesses $2L = 0.030$ cm (12 mil) (●) and $2L = 0.173$ cm ($\frac{1}{16}$ in.) (O).
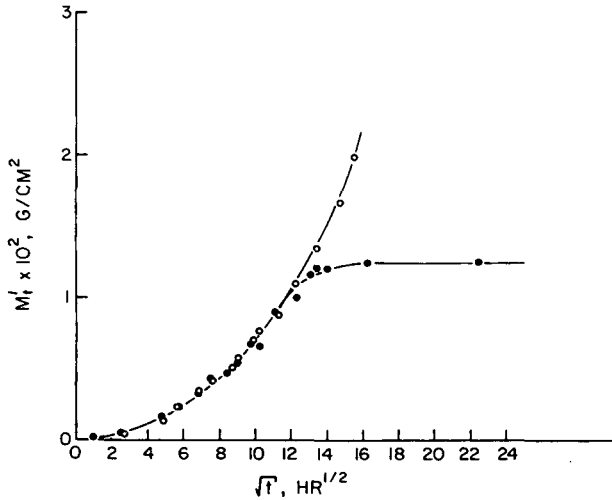
Fig. 7. Mass uptake per unit area vs. $t^{1/2}$ for carbon tetrachloride in PC at 22°C for plates of thicknesses $2L = 0.030$ cm (12 mil) (●) and $2L = 0.173$ cm ($^1/_{16}$ in.) (○).

riod.   In fact, it is very evident from the sorption data plotted vs. time (Figs. 8 and 9) that the initial sorption follows a typical case II diffusion, i.e., M_t and M_t' are proportional to t.   The slope of the M_t curves in Figure 8 are (within 10%) inversely proportional to the plate thickness.   This is consistent with the fact that the M_t' plots for all thicknesses follow the same curve (Fig. 9) with $M_t' = M_t \rho L$, where ρ is the polymer density.   Figure 10 shows the data plotted on log–log scales exhibiting the transition from the initial case II diffusion (slope 1.037) to more Fickian-type diffusion (slope 0.758) for the plate thickness $2L = 0.173$ cm; the diffusion in the thinnest plate ($2L = 0.030$ cm) remains case II practically up to saturation.
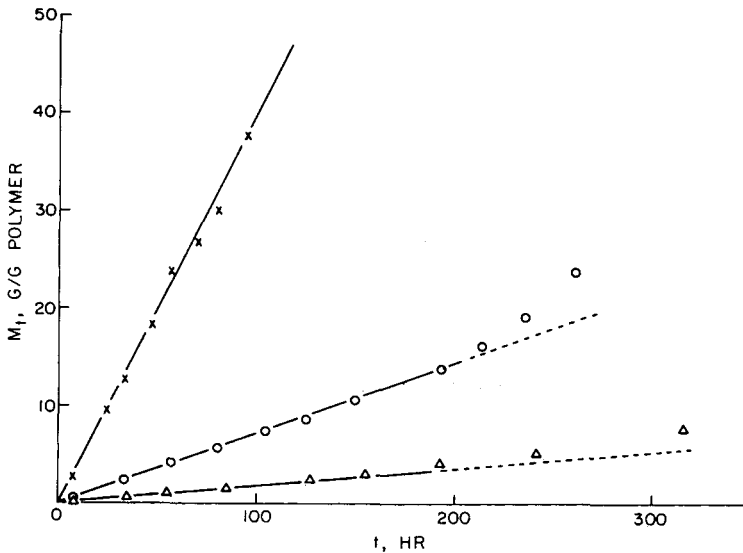

Fig. 8. Initial mass uptake per mass of dry polymer vs. t for carbon tetrachloride in PC at 22°C for plates of thicknesses $2L = 0.030$ cm (X), $2L = 0.173$ cm ($^1/_{16}$ in.) (○), and $2L = 0.633$ cm ($^1/_4$ in.) (△).
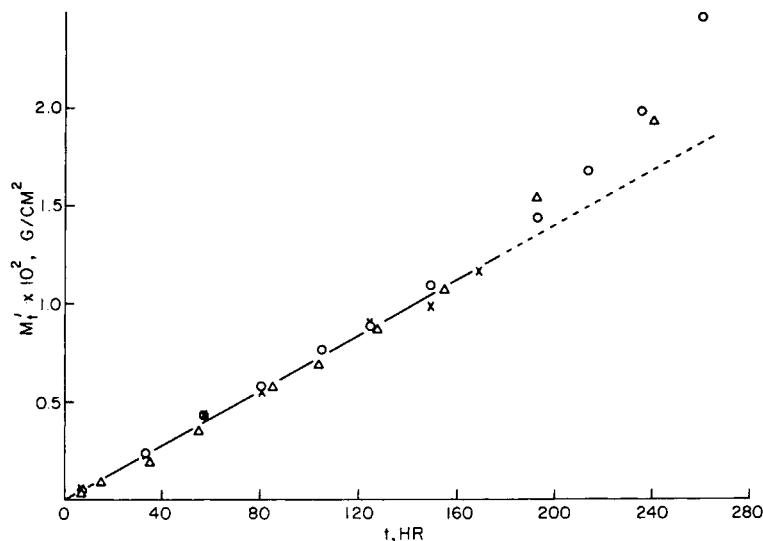
Fig. 9. Initial mass uptake of carbon tetrachloride per unit area of PC at 22°C for plates of thicknesses $2L = 0.030$ cm (X), $2L = 0.173$ cm (O), and $2L = 0.633$ cm (△).

An interpretation of the data could possibly be provided by a model similar to that of Long and Richman[7] based on surface relaxation, $C = C_0(1 - e^{-\beta t})$, where the surface of the plate is slowly reaching saturation C_0 as the molecules relax with a relaxation time β^{-1} to their new conformation. This implies a coupling between the conformation change at the surface and the diffusion phenomena which leads to the anomalous behavior observed. As the surface structure changes, the concentration at the surface will relax to its saturation level. In the case of CCl_4/polycarbonate considered here, the relaxation of the
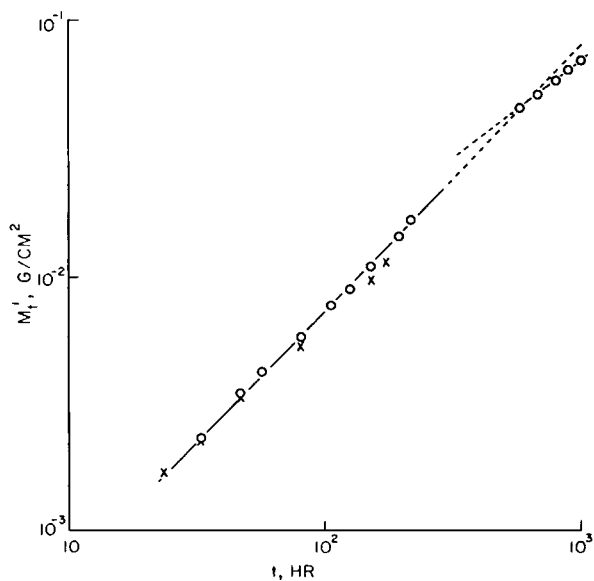

Fig. 10. Log–log plot of mass uptake vs. time of carbon tetrachloride in PC for plates of thicknesses $2L = 0.030$ cm (X) and $2L = 0.173$ cm (O).

surface concentration will be more complex and governed by the formation of a saturated semicrystalline phase, the kinetics of which would have to be taken into account. We shall not attempt such a modeling here; qualitatively, however, as in the case of the original surface concentration relaxation model, the thicker the plates, the more apparently Fickian the M_t-vs.-$\sqrt{t}/2L$ sorption curves would appear,[6] a trend indicated by the results of Figure 6. It should also be pointed out that values of the diffusion coefficient D obtained simply from the quasi-linear portion of the M_t-vs.-$t^{1/2}$ plots as is sometimes done are not meaningful. Values obtained in this manner differ by a factor of 10 for the results of the two plate thicknesses shown in Figure 6.

ANALYSIS AND DISCUSSION

The mass sorption curves for methanol, acetone, and carbon tetrachloride in thin polycarbonate film ($2L = 0.03$ cm) at ambient temperature are presented for comparison in Figure 11. The strikingly dissimilar saturation values for the three solvents in PC is a reflection of the differences in the degree of interaction between the polymer and each solvent. The polymer–solvent interaction parameter, χ, is often used to classify the quality of solvents for polymers. A value of χ below 0.5 implies that the liquid is a good solvent for the polymer. Values of χ for methanol, acetone, and carbon tetrachloride in PC have been estimated using the relation[16]

$$\chi = 0.35 + \frac{v_s}{RT} (\delta_s - \delta_p)^2 \tag{1}$$

where δ_s and δ_p are the solubility parameter values for the solvent and polymer, respectively, and v_s is the molar volume of the solvent. Data on the physical properties of polycarbonate and the three solvents investigated here are presented in Table I. The χ parameter for methanol at 25°C is calculated to be 2.06,
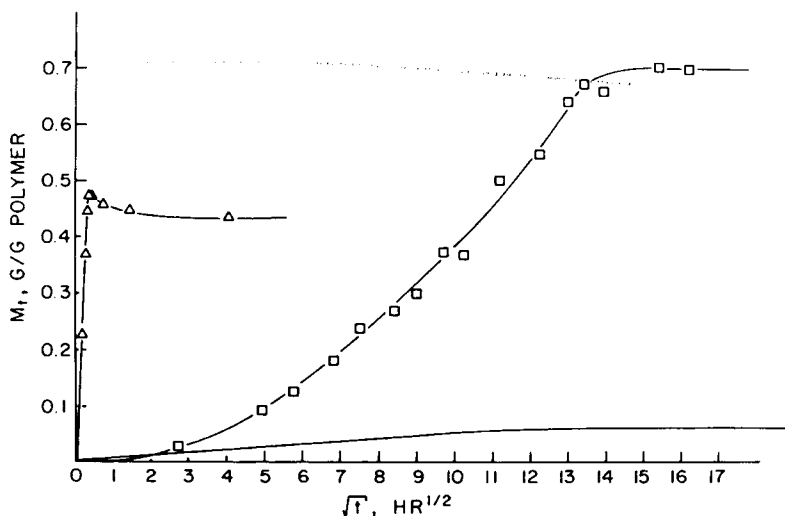

Fig. 11. Mass uptake per mass of dry polymer vs. $t^{1/2}$ for solvents at room temperature in PC film, $2L = 0.030$ cm (12 mil): methanol at 22°C (——), acetone at 25°C ($\triangle$), carbon tetrachloride at 22°C ($\square$).

TABLE I
Physical Data

	Reference
Polycarbonate	
$T_m^0 = 538K, 265°C$	17
$T_g^0 = 422K, 149°C$	8
$\Delta H_m = 26.8$ cal/g	23
$\delta = 9.5$ (cal/cm^3)$^{1/2}$	3
$\Delta\alpha = 3.8 \times 10^{-4}$ °C^{-1}	11
$\rho = 1.2$ g/cm^3	8
$\upsilon = 0.83$ cm^3/g	
Methanol	
$T_g^0 = 110K$	11
$\delta = 14.5$ (cal/cm^3)$^{1/2}$	4
$\alpha = 1.2 \times 10^{-3}$ °C^{-1}	11
$\rho = 0.79$ g/cm^3	
$\upsilon = 40.5$ cm^3/mol	
$M_\infty = 0.062$ g/g at 22°C	
Acetone	
$T_g^0 = T_m - 50 = 128K$	
$\delta = 9.75$ (cal/cm^3)$^{1/2}$	4
$\alpha = 1.2 \times 10^{-3}$ °C^{-1}	11
$\rho = 0.79$ g/cm^3	
$\upsilon = 73.2$ cm^3/mol	
$M_\infty = 0.24 - 0.40$ g/g at 25°C (thickness dependent)	
Carbon Tetrachloride	
$T_g^0 = T_m - 50 = 200K$	
$\delta = 8.65$ (cal/cm^3)$^{1/2}$	4
$\alpha = 1.2 \times 10^{-3}$ °C^{-1}	11
$\rho = 1.58$ g/cm^3	
$\upsilon = 97.1$ cm^3/mol	
$M_\infty = 0.69$ g/g at 22°C	

implying that methanol is a poor solvent for polycarbonate. This is consistent with the very low methanol content at saturation (0.062 g/g), indicating that little polymer swelling occurs. Hence, no interaction between polymer relaxation and penetrant diffusion is expected, and the Fickian mass uptake results shown in Figures 1 and 2 are an indication that none occurred prior to saturation. Similar calculations for acetone ($\chi = 0.36$) and carbon tetrachloride ($\chi = 0.47$) show that these liquids are much better solvents for PC than methanol, a fact verified by the much higher saturation values of 0.40 and 0.69 g/g for acetone and carbon tetrachloride, respectively.

The difficulty in crystallizing polycarbonate by thermal means despite its regular structure has been attributed by Conix and Jeurissen[17] to the small temperature range between the melting point T_m^0 (265°C) and the glass transition temperature T_g^0 (149°C) of the pure polymer. Supercooling the polymer well below T_m increases not only the thermodynamic driving force for crystallization but also the kinetic resistance to polymer segment mobility needed for reorientation from the amorphous to the crystalline state. The ability of certain polymers such as PC and PET to be crystallized in a solvent environment has been attributed to the ability of the solvent to plasticize the polymer and to depress T_g to a larger extent than T_m. The overall effect is to widen the temperature gap between T_m and T_g and thereby increase the temperature range of the

supercooled rubbery phase. As solvent volume fraction increases, the maximum crystallization growth rate increases, and the temperature at which it occurs is lowered. Makarewicz and Wilkes[18] have shown that a 50% increase in the gap between T_m and T_g for PET (corresponding to a solvent volume fraction of 0.2) can result in a tenfold increase in the polymer crystallization rate.

For the three solvents studied in this investigation, the T_m and T_g depressions based upon solvent content at saturation can be calculated. Significant solvent-induced crystallization of the PC as detected by DSC measurements is to be expected when the temperature of the sorption experiment is within the shifted T_m–T_g gap. The depression of the polymer melting point with the addition of solvent can be estimated from Flory's equation[19]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{RV_p}{\Delta H_m V_s}(\phi_s - \chi\phi_s^2) \qquad (2)$$

where T_m is the melting point at solvent volume fraction ϕ_s, T_m^0 is the melting point of the pure polymer (538K), V_s and V_p are the molar volumes of solvent and polymer, ΔH_m is the molar heat of fusion, and χ is the interaction parameter obtained from eq. (1). The dependence of T_g on solvent content may be assumed to be given by the Kelley–Bueche equation[20] based on free volume theory:

$$T_g = \frac{\Delta\alpha_p \, T_{g,p}^0 \, \phi_p + \alpha_s \, T_{g,s}^0 \, \phi_s}{\Delta\alpha_p \, \phi_p + \alpha_s \phi_s} \qquad (3)$$

where $T_{g,p}^0$ and $T_{g,s}^0$ are the glass transition temperatures of the pure polymer and solvent, respectively, ϕ_p and ϕ_s are the polymer and solvent volume fractions, $\Delta\alpha_p$ is the change in the polymer thermal expansion coefficient at T_g, and α_s is the solvent expansion coefficient. Data used for these temperature calculations are listed in Table I. Values of T_g^0 for acetone and CCl$_4$ were taken to be 50°C below their melting point (this is a rough estimate since no data could be found in the literature). The solvent expansion coefficient was taken as 1.2×10^{-3} °C^{-1} for all three liquids.[11]

The liquid volume fraction in the saturated polymer was obtained from the mass uptake results by assuming that the polymer and solvent volumes were additive. This leads to

$$M_\infty = \frac{\phi_s \rho_s}{\phi_p \rho_p} = \frac{\phi_s \rho_s}{(1 - \phi_s)\rho_p} \qquad (4)$$

where ρ_s and ρ_p are the pure solvent and polymer densities. The solvent volume fraction is then given by the relation

$$\phi_s = \frac{M_\infty}{\rho_s/\rho_p + M_\infty} \qquad (5)$$

The calculation for methanol sorption into PC at room temperature yields a depressed melting point of $T_m = 508K$ (235°C), versus $T_m^0 = 538K$ for the pure polymer, while the lowered glass transition is $T_g = 350K$ (77°C), versus $T_g^0 = 422K$. Hence, a sorption experiment at 25°C far below T_g is not expected to induce any significant polymer crystallization as has been observed. This situation is only slightly changed at the higher temperatures investigated here. The sorption of acetone into PC with $M_\infty = 0.24$ g/g results in a melting point depression to $T_m = 484K$ (211°C) and a lowering of the glass transition to $T_g =$

264K (-9°C); likewise, the sorption of carbon tetrachloride in PC results in T_m = 490K (217°C) and T_g = 284K (11°C). Hence, both acetone and carbon tetrachloride significantly reduce T_g of the polymer to below the experimental sorption temperature and approximately double the $T_m - T_g$ gap. These two solvents therefore create conditions that are favorable for spontaneous crystallization and do in fact induce partial crystallization of the polymer, as has been previously discussed.

The overshoot phenomenon previously reported in the literature[5,21] for the mass uptake of penetrants in PC under conditions favorable for solvent-induced crystallization has been observed in this study only for acetone sorption in the thin PC film ($2L$ = 0.03 cm) (see Figs. 3 and 11). This phenomenon has previously been interpreted as a sign that the polymer becomes saturated with solvent before the crystallization process is completed. As crystallization proceeds, solvent is rejected from the crystalline regions of the polymer, and hence the mass uptake decreases. An analysis of the competitive crystallization rate and solvent diffusion rate in the polymer based upon the modeling of Zachmann and Konrad[22] provides an interpretation for the acetone overshoot results observed here.

By analogy to the Thiele modulus employed to compare the ratio of diffusive to kinetic time scales in catalytic systems, Zachmann and Konrad define a ratio t_E/τ_2 as a measure of the characteristic time scale for solvent diffusion compared to the characteristic time for polymer crystallization. The crystallization half-time τ_2 for the polymer at the saturated solvent concentration is obtained from an Avrami-type crystallization rate expression, whereas t_E is the usual diffusive time scale, L^2/D, where L is the plate half thickness and D is the solvent diffusion coefficient. Zachmann and Konrad show that a value for t_E/τ_2 of order 100 separates the diffusion-controlled crystallization regime from the kinetic-controlled regime. For t_E/τ_2 ratios greater than 100, the crystallization rate is completely controlled by the rate of solvent diffusion into the polymer, and a front of crystallized material moves through the polymer immediately following the diffusion front. In this case, the penetrant is essentially diffusing into a structure similar to that present at saturation and no overshoot is seen. On the other hand, for t_E/τ_2 ratios much less than 100, the diffusion of solvent into the amorphous polymer is nearly complete before any significant crystallization occurs, and under these conditions the polymer crystallizes uniformly throughout to form the final equilibrium structure. In the latter case, overshoots in solvent mass uptake are to be expected since, as crystallization proceeds in the nearly saturated polymer, solvent would be expelled from the crystalline regions.

For acetone-induced crystallization of polycarbonate at 25°C free from solvent diffusion limitations, Turska and Benecki[5] reported τ_2 = 90 s. An approximate value for the diffusion coefficient of acetone in PC obtained in this study is 3 $\times$ 10^{-7} cm^2/s and is in agreement with that reported elsewhere.[5,9,13] For the various thicknesses of polycarbonate sheets investigated ($2L$ = 0.03, 0.162, 0.310, and 0.644 cm), we find that the ratio t_E/τ_2 is greater than 100 for all *except* the thinnest film (0.03 cm), for which t_E/τ_2 = 8. Hence, only in this thinnest film would crystallization be kinetic controlled and lead to an overshoot in the mass uptake, as is in fact observed (Fig. 3).

Since no overshoot is observed in the CCl$_4$/PC mass sorption results shown in Figure 6, it is presumed that the polymer is crystallized under diffusion-limited

conditions. By diffusion-limited we mean governed by the relaxation time t_E controlling the flux $\mathbf{j}$. In case II diffusion where $\mathbf{j} = -\mathbf{v}c$, t_E would be the ratio of the thickness L to the velocity v. This time scale can be obtained from Figures 8 or 9; however, as meaningful data on the rate of crystallization of PC by CCl_4 under diffusion free conditions are not available, a quantitative analysis of the ratio t_E/τ_2 as done for acetone is not possible.

CONCLUSIONS

Sorption experiments with plates of varied thickness can be used in a simple fashion to examine the mass flux behavior in glassy polymer systems.[2] The results on plates of polycarbonate presented here show that of the three solvents investigated, only methanol (with the lowest affinity to the polymer) gave purely Fickian results and was the least effective in inducing crystallization of the polymer. The diffusion coefficient of methanol in amorphous polycarbonate was easily extracted from the data to be $D_{22°C} = 4.3 \times 10^{-10}$ cm^2/s. Acetone and carbon tetrachloride led, each in its own way, to anomalous non-Fickian sorption. The thickness-dependent acetone sorption results can be understood in terms of the surface cavitation effect occurring in conjunction with solvent-induced polymer crystallization. The substantial variation of M_∞ with plate thickness and the simultaneous diffusion in amorphous and in partially crystalline polymer regions prohibits the calculation of meaningful diffusion coefficients simply from the slope of the linear parts of mass uptake plots. The observed overshoot in mass uptake of acetone prior to equilibration in the thinnest film (12 mils) can be satisfactorily explained in terms of the competitive penetrant diffusion and polymer crystallization rates. The sigmoidal sorption curves for carbon tetrachloride in polycarbonate possess an initial case II behavior which is followed for thicker plates by an intermediate behavior between case II and Fickian diffusion. The usual M_t vs. $\sqrt{t}/2L$ sorption curves may show, however, a misleading apparent Fickian diffusion after an initial surface equilibration period.[9] Finally, in all the sorption results we have obtained with polycarbonate, the M_t' curves of a given solvent (mass sorption per unit of exposed polymer area vs. $\sqrt{t}$) for different plate thicknesses superimpose on one another even when the diffusion is anomalous. The strain dependence of the diffusion coefficients which is important in some instances[2,6] is, therefore, negligible in the cases considered here.

References

1. H. L. Frisch, *Polym. Eng. Sci.*, **20**, 1 (1980).
2. R. A. Ware and C. Cohen, *J. Appl. Polym. Sci.*, **25**, 717 (1980).
3. P. J. Makarewicz and G. L. Wilkes, *J. Appl. Polym. Sci.*, **23**, 1619 (1979).
4. L. Rebenfeld, P. J. Makarewicz, H. D. Weigmann, and G. L. Wilkes, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C15**(2), 279 (1976).
5. E. Turska and W. Benecki, *J. Appl. Polym. Sci.*, **23**, 3489 (1979).
6. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1975.
7. F. A. Long and D. Richman, *J. Am. Chem. Soc.*, **82**, 513 (1960).
8. Tuffak Data, PL-1200b, Rohm and Haas Company, December 1976.
9. G. W. Miller, S. A. D. Visser, and A. S. Morecroft, *Polym. Eng. Sci.*, **11**, 73 (1971).
10. P. J. Makarewicz and G. L. Wilkes, *J. Polym. Sci., Phys. Ed.*, **16**, 1529 (1978).

11. R. P. Kambour, C. L. Gruner, and E. E. Ramagosa, *Macromolecules*, **7**, 248 (1974).

12. G. L. Wilkes, private communication.

13. G. L. Wilkes and J. Parlapiano, *Am. Chem. Soc. Div. Polym. Chem. Polym. Prep.*, **17**, 937 (1976).

14. H. L. Frisch, T. T. Wang, and T. K. Kwei, *J. Polym. Sci., Phys. Ed.*, **7**, 879 (1969); T. T. Wang, T. K. Kwei, and H. L. Frisch, *J. Polym. Sci., Phys. Ed.*, **7**, 2019 (1969).

15. R. A. Ware, unpublished results.

16. J. Biroš, L. Zeman, and D. Patterson, *Macromolecules*, **4**, 30 (1971).

17. A. Conix and L. Jeurissen, in *Plasticizers and Plasticization Processes*, *Adv. in Chem. Ser.*, **48**, 172 (1964).

18. P. J. Makarewicz and G. L. Wilkes, *J. Polym. Sci., Phys. Ed.*, **16**, 1559 (1978).

19. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1952, Chap. 13.

20. F. N. Kelley and F. J. Bueche, *J. Polym. Sci.*, **50**, 549 (1961).

21. R. P. Kambour, F. E. Karasz, and J. H. Daane, *J. Polym. Sci., Phys. Ed.*, **4**, 327 (1966).

22. H. G. Zachmann and G. Konrad, *Makromol. Chem.*, **118**, 189 (1968); see also Ref. 18.

23. E. Turska and H. Janeczek, *Polymer*, **20**, 855 (1979).