

Transport Properties of Dichloromethane in Glassy Polymers. I. Atactic Polystyrene Films

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SYNOPSIS

Sorption and diffusion of dichloromethane vapor were measured in atactic polystyrene films, obtained with different cooling conditions and after controlled aging times at different temperatures. The diffusional behavior is characterized by three zones, depending on temperature and penetrant activity. In Zone I, at low activity, the diffusion coefficient is independent of vapor concentration; Zone II is characterized by concentration-dependent diffusion, whereas in Zone III structural transformations are possible. The study of diffusion at three temperatures allowed building of a temperature-penetrant concentration diagram, which is very useful to visualize the different zones of behavior. The aging at room temperature has no effect on the curve of sorption as a function of vapor activity, whereas it determines two effects on the diffusion: a decrease of the zero concentration diffusion coefficient and a more and more anomalous behavior with the aging time. The aging at 70°C produces the same effects on the diffusion behavior as the aging at room temperature; in addition, a decrease sorption is observed at low penetrant activity. The possible presence of ordered domains, impermeable to the vapor, in the samples stored at 70°C, was suggested on the basis of sorption results.

INTRODUCTION

The sorption and diffusion of gases and organic vapors in polymers is a relevant topic both for theoretical and for technological interest. Careful analysis of transport properties can help clarify many structural aspects of the polymer¹⁻³; on the other hand, knowledge of permeability is essential in the application of polymers as barrier materials.^{4,5}

Structural organization and morphology markedly affect the properties of semicrystalline polymers; in the case of amorphous glassy polymers, the processing conditions have a strong influence in determining the physical properties of the material.⁶ When amorphous polymers are cooled from the molten state, through the glass transition temperature, to the glassy state, free volume is frozen into

the glassy matrix; the more severe the quenching conditions, the greater the free volume content and, therefore, the molecular mobility. On the other hand, slow cooling conditions will produce less free volume and, as a consequence, a reduced molecular mobility. Furthermore, after cooling through the glass transition temperature, the polymer is not in equilibrium and will undergo a process of physical aging, manifested in a decrease of volume with time.⁷ Physical aging is important in a narrow temperature range, generally between the so called T_β and T_g . However, in the case of atactic polystyrene, it has been found that isothermal volume contraction persists even if the aging temperature is below T_β .⁸

The free volume and the related molecular mobility are very important factors in determining the physical properties of the glassy polymers; in particular, they significantly influence the transport properties of the material.^{2-5,9}

In amorphous rubbery systems, the relaxation times are generally shorter than the diffusion times and sorption curves following a Fickian behavior are observed. In glassy polymers, the sorption of organic vapors and liquids may involve time-dependent re-

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laxation processes, determining an anomalous, non-Fickian sorption behavior. In this sense, many experimental results of anomalous behavior have been explained as a slow polymer rearrangement or as relaxation following a first stage of Fickian diffusion-controlled sorption. As example, gravimetric studies of the sorption of organic vapors by atactic polystyrene (aPS) powders have demonstrated that the penetrant vapor can be used as a molecular probe, monitoring glassy-state relaxations, occurring in the absence of the penetrant.¹⁰

Besides molecular and structural parameters, as molecular weight, thermal history, and orientation, the mode of transport is strongly influenced by temperature and vapor activity. Therefore, the description of transport behavior for a given polymer-solvent system is meaningful only when the activity of the penetrant and temperature are clearly reported. Therefore, for the same polymer-penetrant system, it is possible to observe different behavior if a wide range of temperature and activities are explored.

A convenient way to visualize the different transport behaviors is a temperature-penetrant concentration diagram, in which various regions of diffusional transport are reported.^{11,12} In this diagram, it is possible to recognize the behavior of the polymer-penetrant system with different experimental conditions, i.e., temperature and activity. It has been shown that the polymer solvent system can exhibit some of the following phenomena: (a) concentration-independent Fickian diffusion; (b) concentration-dependent Fickian diffusion; (c) anomalous sorption; (d) case II transport; (e) solvent crazing; and (f) swelling fracture.

The different behavior is determined by the ratio of the characteristic time of diffusion and some characteristic time for molecular rearrangement and the relaxation process in the polymer-solvent system. Therefore, the "structure" of the polymer sample, in terms of free volume and related molecular mobility, ought to have a strong influence on the quantitative values of such diagrams.

So far, some studies have been published on the transport properties of dichloromethane in aPS,¹³⁻¹⁶ giving a poor general agreement both on the type of transport and on the value of the transport coefficients. Differences in the sample preparation and/or in the elapsed aging time of the examined samples can significantly change the structural characteristic of the polymer in the glassy state and, therefore, the transport behavior.

In this paper, we analyze aPS films, obtained with different cooling conditions and different aging times. The transport properties of dichloromethane

vapor were measured in a wide range of activity and at different temperatures. The purpose of this work is manifold, aiming particularly to

- (a) investigate the effect of different cooling conditions on the transport properties;
- (b) investigate the effect of aging at different temperatures; and
- (c) establish the temperature-penetrant concentration diagram for the aPS-CH₂Cl₂ system.

EXPERIMENTAL

Atactic polystyrene (aPS) powders of $M_n = 74,300$ and $M_w = 291,000$ were kindly supplied by RAPRA (UK). Different films were prepared by heating the powders above T_g , at 140°C, in a press, into a film shape of thickness 0.01–0.02 cm and cooling with different rates; sample A was cooled to room temperature in 5 min; sample B was cooled in 2 h.

Sample A was analyzed soon after the cooling process (sample A0), after 1 month (sample A1); after 6 months (sample A6); and after 1 year (sample A12) of storage at room temperature. A different film A was stored at 70°C for 2 months (Sample 70A2) and 1 year (Sample 70A12). Sample B was analyzed after 1 month (sample B1) and 2 months (sample B2) of storage at room temperature.

Transport properties, sorption, and diffusion were measured by a microgravimetric method, using a quartz spring balance, having an extension of 16 mm/mg. The penetrant was CH₂Cl₂ and the experiments were conducted at temperatures of 25, 40, and 60°C. Sorption was measured as a function of vapor activity $a = p/p_T$, where p is the actual pressure to which the sample was exposed, and p_T , the saturation pressure at the temperature of the experiment.

Wide-angle X-ray diffractograms (WAXD) were obtained by using a PW1050 Philips powder diffractometer (CuK α -Ni-filtered radiation). The scan rate was 1° ϑ /min.

RESULTS AND DISCUSSION

Wide-angle X-ray Scattering

Figure 1 shows the WAXD obtained for sample A0, freshly cooled (a); sample A12 stored at room temperature for 1 year (b); and sample 70A12 stored at 70°C for 1 year (c). The WAXD of aPS has been

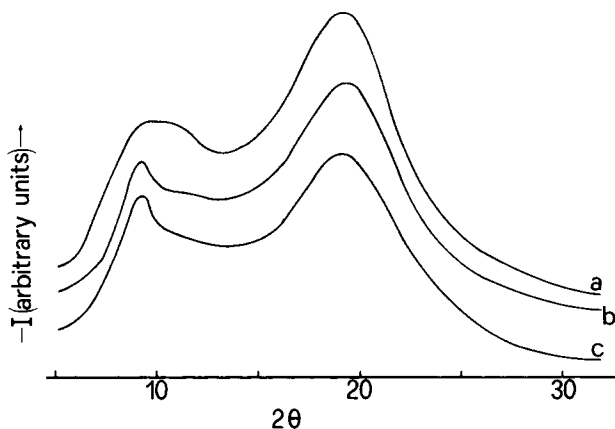


Figure 1 Wide-angle X-ray diffractograms (WAXD) of sample A0 (a), A12 (b), and 70A12 (c).

carefully analyzed in the past,^{17,18} leading to the conclusion that the peak at higher angle is due to intrachain correlation between phenyl groups, whereas the peak at lower angle is due to correlations between chains. In a more recent analysis,¹⁹ the effect on the lower angle peak of correlations between phenyl groups that are attached to different, but

neighboring, chains has been considered, leading to an interesting superchain model, in which the phenyl groups segregate on a molecular scale to form stacks.

Observing the pattern, the angle of maximum intensity can be related to average molecular distances; the half-width measures the spread about these average distances, and the height of the peak measures to a first approximation the amount of material present at the average distance.

In the case of our samples, the higher angle peak, corresponding to intrachain phenyl distance, does not change with aging, whereas the lower angle peak shifts to still lower angles, and a narrowing is observed around the maximum intensity angle. Therefore, the aging both at room temperature and at 70°C has influence on the structural organization of the glass.

Diffusion of Rapidly Cooled Samples Aged at Room Temperature

In Figure 2 we report the reduced sorption curves, that is, c_t/c_{eq} as a function of \sqrt{t}/d , where c_t is the concentration of vapor at time t ; c_{eq} , the equilibrium

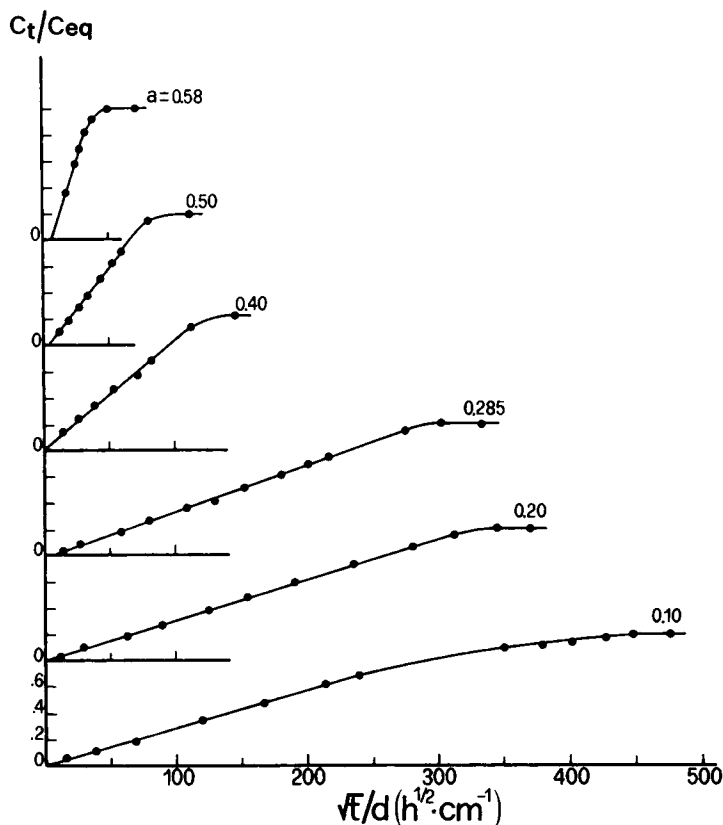


Figure 2 The reduced sorption curves, c_t/c_{eq} , as a function of \sqrt{t}/d ($h^{1/2} \text{ cm}^{-1}$) for sample A0 at different activities.

concentration; and d , the thickness (cm) of the sample, at different activities, for the freshly prepared sample A0.

All the curves show a linear increase of concentration with square root of time, a downward curvature, and the equilibrium value of vapor concentration. This behavior is typical of Fickian sorption curves; it is therefore possible, at each vapor activity, to derive a mean diffusion coefficient (1) from the equation

$$c_t/c_{eq} = 4/d\sqrt{Dt/\pi} \quad (1)$$

The derived \bar{D} values are mean values in the explored interval of concentration. To obtain the thermodynamic diffusion coefficient D_0 , related to the free volume of the sample, it is necessary to find a correlation between \bar{D} and c_{eq} , allowing the extrapolation to $c_{eq} = 0$. Generally, the dependence of D on c_{eq} is of the exponential form

$$\bar{D} = D_0 \exp(\gamma c) \quad (2)$$

in which γ is the concentration coefficient, related to the fractional free volume and to the effectiveness with which the penetrant plasticizes the polymer.^{2,3}

Therefore, the logarithm of the \bar{D} values, calculated from eq. (1) and Figure 2, are reported in Figure 3(a) as a function of c_{eq} for sample A0 and sample A1, aged 1 month at room temperature. The reduced sorption curves of this sample, not reported here, also show a regular Fickian behavior.

In Figure 3, two zones of different behavior are clearly recognizable: At low concentration, corresponding to low penetrant activity, diffusion values independent of concentration are observed, whereas at higher activities, a linear dependence of D on c_{eq} is manifested. From the first zone, it is possible to derive a diffusion parameter D_{01} , relative to the range of activity in which diffusion is independent of concentration; from the straight line representing the dependence of \bar{D} on c_{eq} , we can extrapolate to zero-penetrant concentration a parameter D_{02} , relative to the range of activity in which diffusion exponentially depends on the concentration. The derived parameters are reported in Table I, in which also the γ coefficient, obtained from eq. (2), is reported.

Figure 4 shows the reduced sorption curves for sample A12 aged 1 year at room temperature. Sample A2, not reported here, shows a Fickian behavior at all the activities.

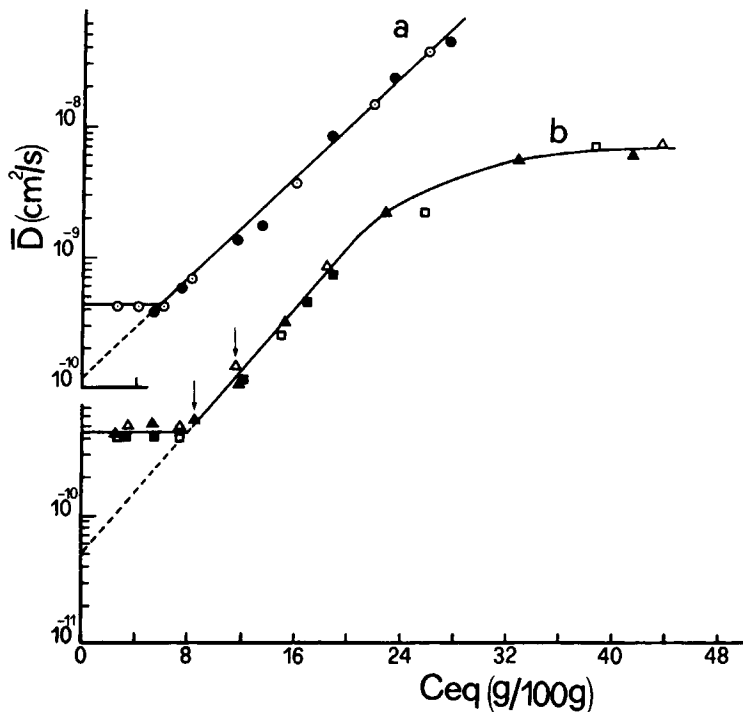


Figure 3 The logarithm of the mean diffusion coefficients D , as a function of the vapor equilibrium concentration c_{eq} : (a) sample A0 (○); sample A1 (●); (b) sample A2 (■); sample A6 (▲); sample A12 (△); sample B1 and B2 (□).

Table I Zero Concentration Diffusion Coefficients, D_{01} and D_{02} (cm^2/s), and Concentration Coefficient γ , for All the Samples

Sample	T ($^{\circ}\text{C}$)	$D_{01} \times 10^{10}$	$D_{02} \times 10^{11}$	γ
A0, A1	25	4.6	12.2	23
A2, A6, S12	25	4.7	5.2	28
B1, B2	25	4.7	5.2	28
70A2, 70A12	25	4.6	5.3	22
A2	40	11.1	24.2	26
A2	60	28.1	85.1	27

Sample A12 shows a Fickian behavior at all the activities, except at $a = 0.3$, where a slower increase of concentration is observed for short times; the same behavior is manifested by sample A6, not reported here, at activity $a = 0.2$. An arrow indicates the point after which a second linear increase of sorption with \sqrt{t} is observed. From this second part, a \bar{D} value for the correspondent activity was derived. The logarithm of the diffusion values, derived from the Fickian curves, are reported in Figure 3 (b) as a function of concentration; the two values of \bar{D} , obtained from the anomalous curves (sample A6 at activity 0.2 and sample A12 at activity 0.3), are marked with an arrow in the figure.

For the aged samples, we observe three different zones:

- a diffusion independent of concentration, at low activity;
- a concentration-dependent diffusion at intermediate activities; and
- a curvature, after which diffusion becomes less concentration-dependent, at high activities.

The freshly prepared sample could not be tested at high activities, due to partial dissolution; therefore we do not observe the curvature in Figure 3 (a).

The D_{01} and D_{02} coefficients, derived from the first and second zones, are reported in Table I. The D_{02} parameter of the aged samples, $5.2 \times 10^{-11} \text{ cm}^2/\text{s}$, is well in agreement with previous values for the same system.^{14,15} In the first zone, because of the low concentration of the penetrant, the polymer structure remains frozen and the relaxation times are very large compared with the diffusion time: Probably, diffusion of the penetrant occurs through voids that are dynamically formed by oscillation of chain segments. According to Hopfenberg and Frish,¹² this region can be classified as a Fickian diffusion region below the glass-transition temperature (Zone I).

When the concentration of penetrant reaches a critical value (c_f), at a higher activity, the interaction between the penetrant and segments of chain

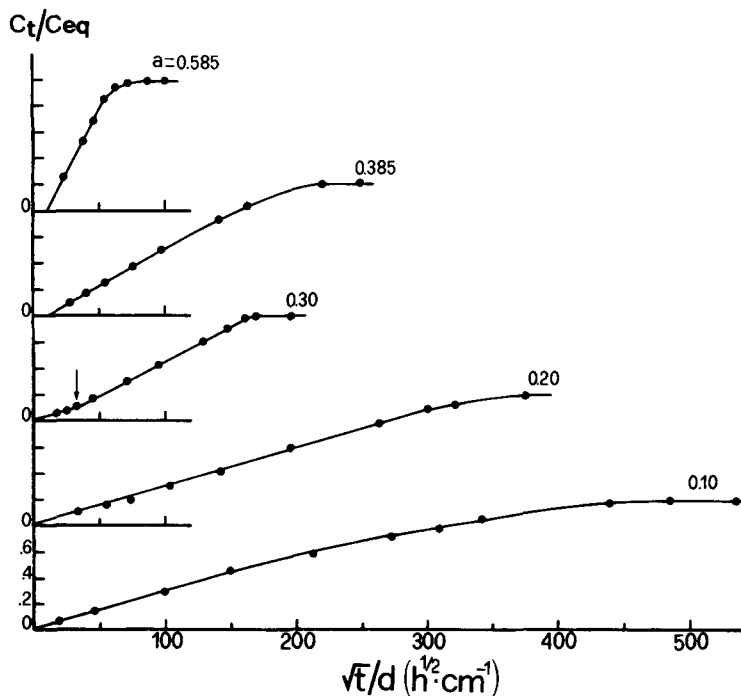


Figure 4 The reduced sorption curves for sample A12, at different activities.

allows molecular rearrangements, with a time scale comparable or less than diffusion, and we observe either anomalous curves, as at activities 0.2 and 0.3, respectively, for sample A6 and A12, or Fickian curves, characterized by a concentration-dependent diffusion coefficient (Zone II).

At still higher vapor activity (Zone III), the high concentration of penetrant completely plasticizes the polymer, leading to high mobility of polymer chains. The interaction is so strong that structural transformations, as clustering of solvent molecules, crazing, and partial dissolution are possible, determining a transition in the diffusion-concentration curve. This transition is manifested by the curvature, which occurs at a critical concentration (c_{II}). The critical vapor concentrations, for a different zone of behavior to occur, are reported in Table II for sample A2.

The aging of the sample at room temperature has little influence on the diffusion parameters in the first zone, at low activity, in which diffusion is independent of concentration; in fact, we observe very similar values of D_{01} , both for the fresh and the aged samples (Table I); only the critical concentration for the transition to the second zone is slightly higher in the aged samples (8% vs. 6.5%). In Zone I, the system is frozen and therefore the relaxation times are, in any case, much slower than diffusion.

The influence of the aging time is observable in the second zone, where the extrapolation to zero concentration gives a lower D_0 for the aged samples and a higher γ coefficient. In this zone, the interaction with the penetrant at higher activity makes longer and longer chain segments more mobile and involved in the diffusion process, leading to a concentration-dependent diffusion coefficient.

Aging produces a decrease of free volume and related molecular mobility, and this is well reflected in a decreased diffusion coefficient and increased concentration coefficient. Furthermore, the increase of relaxation times leads to the appearance of anomalous sorption curves, as observed for the well-aged A6 and A12 samples.

Table II Critical Concentrations (c_I and c_{II}), after Which a Different Diffusion Behavior Is Observed, for Sample A2 at Different Temperatures

T (°C)	c_I	c_{II}
25	8%	24%
40	6%	16%
60	4%	10%

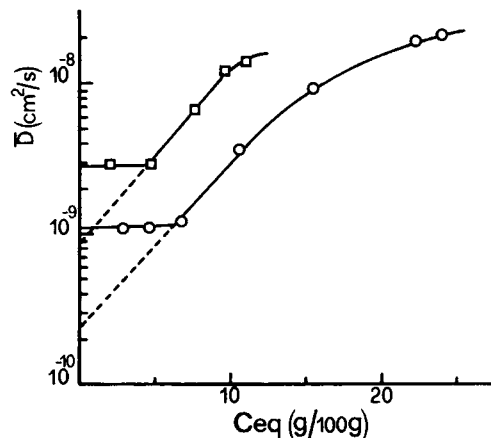


Figure 5 The logarithm of the diffusion coefficients as a function of the vapor equilibrium concentration, for sample A2 at 40°C (○) and 60°C (□).

Diffusion of Sample A2 at Different Temperatures

The sample aged 2 months at room temperature was also analyzed at 40 and 60°C. The sorption curves at these temperatures, not reported here, were Fickian, and the logarithm of the \bar{D} values, derived at different activities, is reported in Figure 5 as a function of concentration.

Also, at 40 and 60°C, we observe the three zones, in which the behavior is different. In Table I, the extrapolated D_{01} , D_{02} , and the concentration coefficients are reported for the different temperatures, whereas in Table II, the critical concentrations for the appearance of a different behavior are reported.

The activation energies for diffusion in Zones I and II can be calculated (2), according to the relation

$$D = D_a \exp(-E/RT) \quad (3)$$

where D_a is the preexponential factor, and E , the activation energy. In Figure 6, the zero concentration diffusion coefficients D_{01} and D_{02} are reported as a function of $1/T$. In the explored temperature range, we observe a good linear correlation, giving $E_I = 9.8$ kcal/mol for diffusion in Zone I and $E_{II} = 16.2$ kcal/mol for diffusion in Zone II. Both values of activation energies are compatible with Fickian diffusion processes, the lower value of E_I being in agreement with a less activated diffusion in a frozen system.

If we report the critical concentration of penetrant necessary to induce the passage in a different zone of behavior at the three different temperatures, we are able to build the temperature-penetrant concentration diagram, reported in Figure 7, in which the different zones are well recognizable.

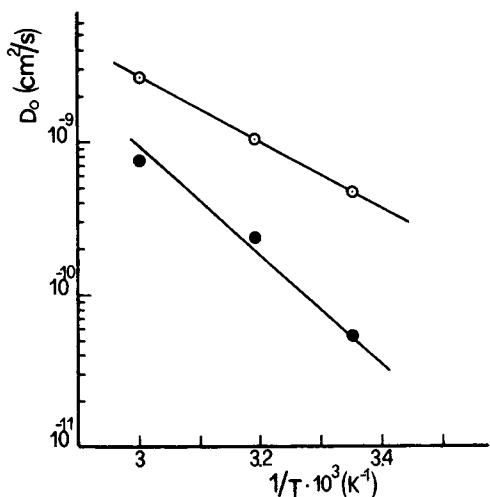


Figure 6 The logarithm of the zero-concentration diffusion coefficient, D_0 (cm^2/s), as a function of the inverse of the temperature $1/T$ (K^{-1}), in Zone I (\circ) and Zone II (\bullet).

Zone I is characterized by a diffusion coefficient independent of concentration, in which there is small interaction between solvent and polymer, whereas in Zone II, a stronger interaction induces a plasticization, which is reflected in a concentration-dependent diffusion and a higher activation energy.

The anomalous sorption curves can appear in Zone II, when relaxation times become comparable with diffusion times, and this, in turn, depends also on the thickness of the sample. Using samples with the same thickness, as we did, the anomalous behavior is manifested for aged samples, at higher activities for longer aging times. In Zone III, the interaction is very strong, producing in the freshly prepared sample partial dissolution.

Diffusion of Slowly Cooled Samples

The slowly cooled B samples were analyzed at 25°C . In Figure 8, the reduced sorption curves for sample B2, slowly cooled from the melt and aged at room temperature for 2 months, are reported as a function of \sqrt{t}/d . All the curves show a Fickian behavior, as does sample B1, not reported here. The logarithm of the derived \bar{D} values are reported as a function of concentration in Figure 3 (b), for samples B1 and B2. Also, for the slow-cooled samples, we observe the three zones, and the experimental values of the diffusion coefficients fit the same curve as that of the rapidly cooled samples A, and therefore they extrapolate to the same D_0 , as reported in Table I. The comparison between sample A1 and B1, aged 1

month at room temperature, shows that the slowly cooled sample has a lower free volume, as expected, and therefore shows a lower D_{O_2} and a higher γ coefficient. These values are equal to the values of the rapidly cooled samples A, aged 6 months and 1 year at room temperature. This is in agreement with the lower free volume of the starting sample B.

Diffusion of Rapidly Cooled Samples Aged at 70°C

The effect of aging was investigated at a temperature intermediate between T_β and T_g of aPS, that is, at 70°C . At this temperature, the aging is accelerated and, also, sub- T_g annealing phenomena can occur.

Figure 9 shows the reduced sorption curves of samples 70A2 and 70A12, aged 2 months and 1 year, respectively, at 70°C . Sample 70A2 shows a Fickian behavior up to activity $a = 0.4$. At this activity, a slower stage appears in the sorption curve for short times. The non-Fickian behavior disappears at activity $a = 0.6$. Sample 70A12, whose sorption curves are reported in the same figure, shows a similar behavior, that is, the appearance of anomalous behavior at activity $a = 0.4$. But, in this case, the slower stage, coincident with that of 70A2 sample, extends for a longer time, before the starting of the second stage, and this second straight line is almost parallel to the previous one. For sample 70A12, the non-Fickian behavior extends up to activity 0.6, where still a slower stage is present. The diffusion coefficients, obtained through eq. (2), from the Fickian

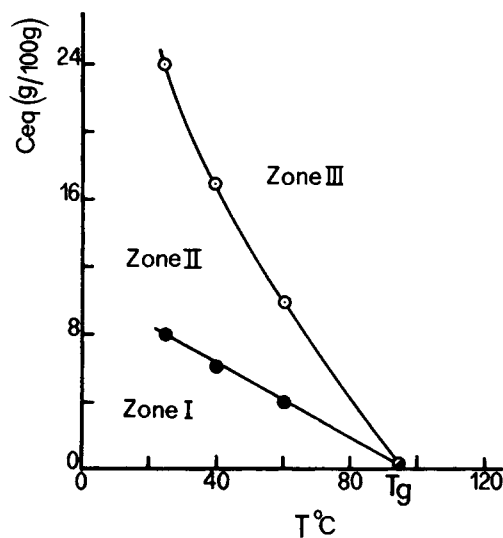


Figure 7 The critical concentration, after which a different diffusion behavior is observed, as a function of the temperature T ($^\circ\text{C}$).

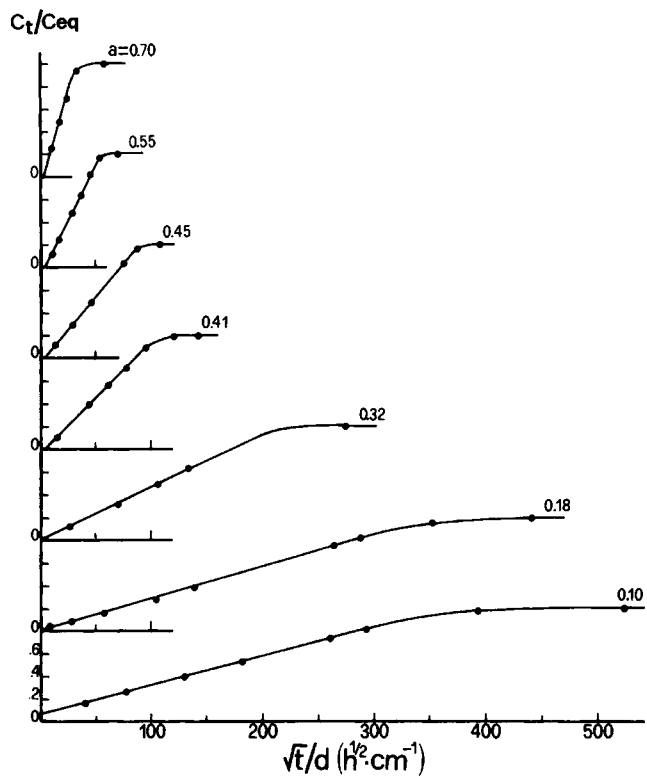


Figure 8 The reduced sorption curves for sample B2 at different activities.

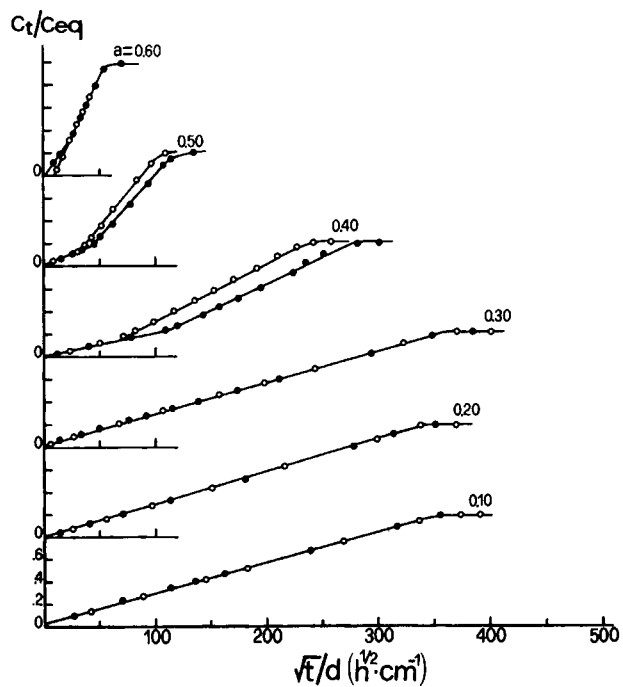


Figure 9 The reduced sorption curves for sample 70A2 (○) and 70A12 (●) at different activities.

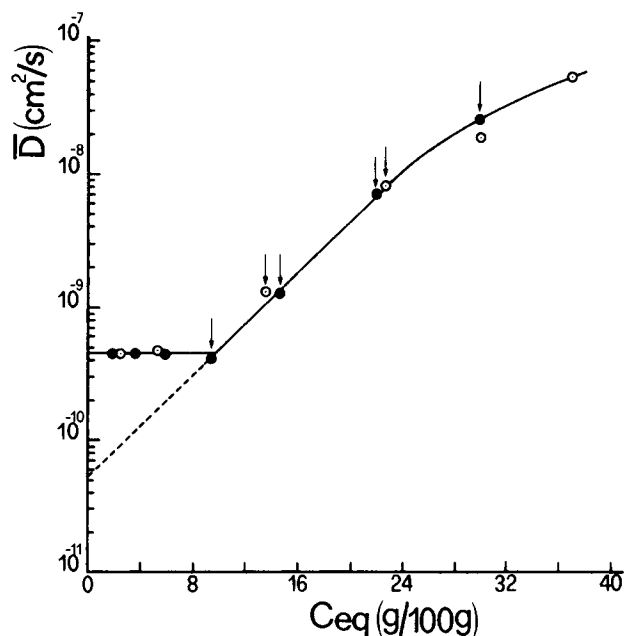


Figure 10 The logarithm of the diffusion coefficients D , as a function of vapor equilibrium concentration, for sample 70A2 (○) and 70A12 (●).

curves and from the second stage of the anomalous curves are reported in Figure 10.

We observe the three zones of different behavior, and, although all the values in the second zone are derived from anomalous curves, they agree well with the previous values obtained for samples showing Fickian behavior. In fact, the straight line extrapolates to the same D_{02} of the samples aged at room temperature (Table I).

Therefore, the aging has two effects on the diffusion behavior: A first effect is manifested in a few months and consists in a decrease of D_{02} and an increase of the γ coefficient with aging time; afterward, the value of D_{02} does not change more, but a more and more pronounced anomalous behavior appears in the sorption curves. This second effect is well evident when comparing the sorption curves of samples 70A2 and 70A12, for which a longer slow stage appears at all the activities.

Sorption

In Figure 11 the equilibrium concentration of dichloromethane vapor is reported as a function of vapor activity for all the analyzed samples. In the limit of the experimental error, the slowly cooled samples and the rapidly cooled samples, stored at room temperature for different times, show the same equilibrium concentration of sorbed vapor and the same dependence of sorption on vapor activity.

The three zones of diffusion behavior can be recognized in the sorption curve. As matter of fact, up to penetrant concentration of 7–8%, the increase of sorption is linear with activity, following Henry's law. This behavior is typical of an ideal system, in which there is no strong interaction between polymer and solvent. After this concentration, a positive deviation can be observed, with a behavior following the Flory–Huggins description.⁵ At activities higher than 0.6, a steeper and steeper curvature shows that important structural transformations are operative with these penetrant concentrations. Moreover, the freshly prepared samples partially dissolve during the experiment at high activity.

At variance with the behavior of all the samples aged at room temperature, the samples stored at

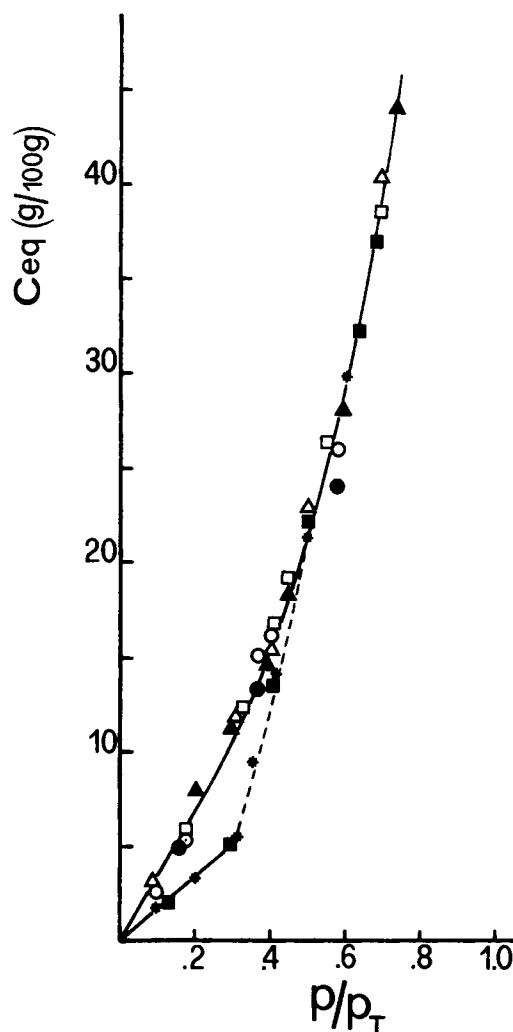


Figure 11 The equilibrium concentration of vapor as a function of activity $a = p/p_T$, for sample A0 (○), A2 (●), A6 (△), A12 (▲), B2 (□), 70A2 (■), and 70A12 (*).

70°C show a lower sorption, up to an activity of 0.35, an evident transition between activities 0.35 and 0.45, and the same sorption as the previous samples at activities higher than 0.45.

The reduction of free volume, due to the aging at 70°C, could be responsible for the lower sorption, although the behavior of samples A6 and A12 does not show any tendency toward a decrease of sorption with aging time. Furthermore, the transition in the sorption curve, after which the sorption values of the 70A2 and 70A12 samples coincide with those of the other samples, could not be easily explained. A different hypothesis that could be suggested is related to the possibility that in the amorphous samples domains of local order can exist and that these ordered regions are impermeable to the vapor at low activity. We can hypothesize that annealing for a long time at a temperature of 70°C favors the formation of these ordered domains in the amorphous sample and that there is a critical dimension beyond which they become impermeable at low vapor activity.

The presence of ordered regions, ranging in size between 1.5 and 4.5 nm, was suggested in aPS on the basis of electron diffraction and high-resolution diffraction microscopy studies.²⁰ So far, many experimental results have been explained, invoking the presence of local order in amorphous systems^{21,22}; therefore, it would not be unexpected if ordered domains were formed in aPS after long annealing at 70°C and that they were impermeable to dichloromethane vapor at low activity, due to increased dimensions.

The ordered domains, 10 nm large, present in isotactic smectic polypropylene,^{23,24} were found to be impermeable to dichloromethane at low activity, becoming permeable at higher activities.²⁵ Also, in the case of aPS, after activity $a = 0.35$, a transition in the sorption curve can be a signal that the ordered domains become permeable to the vapor and that the equilibrium concentration of vapor equalizes that of the other samples.

Figure 12 shows the equilibrium concentration of dichloromethane as a function of activity at the three different temperatures: 25, 40, and 60°C for sample A2 (a) and sample 70A2 (b). The sorption of sample A2 is independent of temperature at each activity, showing that the enthalpy of solution is zero for the system aPS—CH₂Cl₂. At variance, sample 70A2 shows, at low vapor activity, a higher and higher sorption, increasing the temperature, with, at 60°C, the curve of sample 70A2 coincident with that of sample A2. Also, this result could be explained by

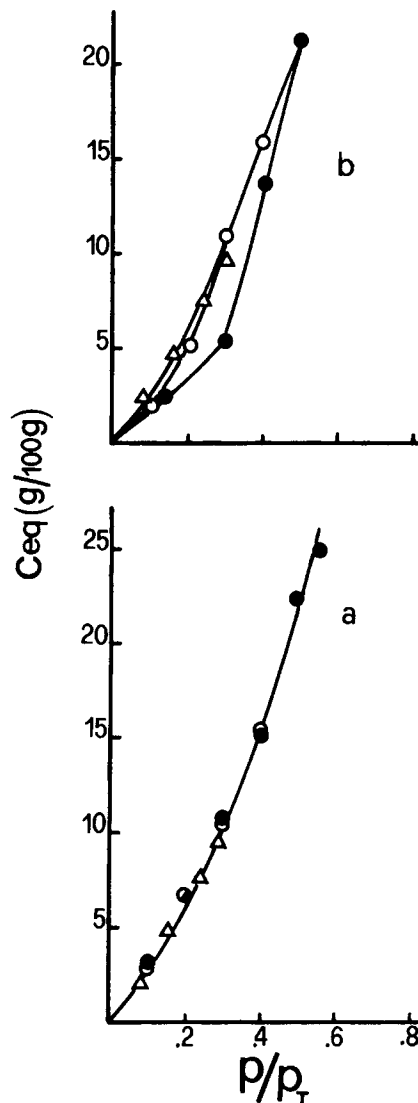


Figure 12 The equilibrium concentration of vapor as a function of activity: (a) sample A2 at 25°C (●), 40°C (○), and 60°C (△); (b) sample 70A2 at 25°C (●), 40°C (○), and 60°C (△).

the presence of ordered domains, which become permeable at lower and lower activity, increasing the temperature. The curve at 40°C shows the transition at activity $a = 0.2$; this could mean that, at this temperature, only at activities lower than 0.2 are the ordered domains impermeable to the vapor. At 60°C, they are permeable already at the lowest investigated activity. Again, the same behavior was shown by smectic polypropylene, in which the ordered domains become permeable after $a = 0.2$ at 40°C.²⁶

The possibility of the presence of ordered domains is not in disagreement with X-ray results. The aging

produces an evident narrowing of the peak at lower angle, due to interaction between the chains; this sharpening can be observed both in samples A12 and 70A12. Probably, the ordered regions must reach a critical dimension in order to become impermeable. However, the presence of domains, still permeable, in which the chains are not fully random, could produce the anomalous non-Fickian behavior; in this sense, it is interesting to note that the anomalous behavior appears at activities increasing with the aging time and at all the activities in Zone II for samples 70A2 and 70A12.

CONCLUSIONS

The analysis of transport properties of dichloromethane in a series of films of aPS has shown that the diffusional behavior can be characterized by three zones, depending on temperature and penetrant activity. In Zone I, at low activity, the diffusion coefficient is independent of vapor concentration, and diffusion occurs mainly in a frozen system. Zone II is characterized by diffusion parameters dependent on concentration, and the dependence was found of the exponential type, allowing the determination of a zero-concentration diffusion coefficient D_0 and a concentration coefficient γ . In Zone III, the strong interaction can induce structural transformations, as clustering of solvent molecules, crazing, or partial dissolution. The determination of the critical penetrant concentrations, needed for the passage in a different zone of behavior, at three different temperatures, allowed building of the temperature-penetrant concentration diagram, which is very useful to visualize the different zones of behavior.

The aging at room temperature determined two effects on the diffusion behavior. The first effect was a different dependence of diffusion on concentration, in the second zone, determining the extrapolation of a lower D_{02} and a higher γ coefficient for the well-aged samples. The lower zero-concentration diffusion parameter was found for the sample aged 2 months at room temperature; longer aging times did not change this parameter, but determined a second effect, i.e., a change in the appearance of the sorption curves was observed. As matter of fact, after 6 months of aging, anomalous non-Fickian sorption curves appear, and this behavior appears evident at increasing activity for increasing aging times.

The curve of sorption as a function of vapor activity is not influenced by the aging at room tem-

perature. The storage at 70°C produces the same effects on the diffusion behavior as does the aging at room temperature, but they are anticipated; in fact, the anomalous behavior already appears in the sample aged 2 months, whereas 6 months are needed at room temperature. At variance with the aging at room temperature, the curve of sorption as a function of vapor activity shows a range in which the equilibrium concentration of vapor is lower than previously. The invariance of sorption for the samples aged at room temperature, and principally the transition in the sorption curve, leads to the suggestion that the aging at 70°C produces the formation of ordered domains, impermeable to the vapor at low activity. At a critical activity, a transition in the sorption curve indicates that these domains are becoming permeable to the vapor. In fact, after this transition, the sorption follows the same curve as do the other samples. This is a possible explanation for the reduced sorption of these samples, and it requires further investigation to confirm or disprove this suggestion.

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