

Transport Properties of Dichloromethane in Glassy Polymers. II. Amorphous Syndiotactic Polystyrene Films

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SYNOPSIS

Sorption and diffusion of dichloromethane vapor were measured in amorphous syndiotactic polystyrene films, obtained with different cooling conditions and after controlled aging times at different temperatures. The diffusional behavior, at the temperature of 25°C, was characterized by three stages, depending on penetrant activity. In the first stage, at low activity, the diffusion coefficient was independent of vapor concentration; the second stage was characterized by concentration-dependent diffusion, whereas in the third stage, at high activity, the strong interaction solvent-polymer increased the mobility, allowing the polymer crystallization. The different cooling conditions neither have an effect on the diffusional behavior nor on the sorption curve. The aging, both at room temperature and at 70°C, did not change the diffusion parameters, but led to the appearance of more and more anomalous sorption behavior. The sorption curve, as a function of vapor activity, did not show any difference for the fresh and the aged-at-room temperature samples, whereas the samples aged at 70°C presented a lower sorption at low activity. The presence of ordered domains, impermeable to the penetrant at low activity, was suggested on the basis of sorption results. The solvent-induced crystallization was investigated for all the samples. Crystallization was induced at an activity of 0.45 for the fresh and the aged-at-room temperature samples; at variance, the samples aged at 70°C crystallize at a slightly higher activity, reaching, nevertheless, a higher level of crystallinity. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Transport properties of gases and vapors have often been used to clarify the structural organization of polymers.¹⁻³ Diffusion can be related to the thermodynamic state of the permeable phase, and sorption to its fraction. The transport parameters can be easily correlated to the structural organization in the case of amorphous rubbery systems, for which 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 may involve time-dependent relaxation processes, determining an anomalous non-Fickian sorption

behavior.⁴⁻⁶ Furthermore, the mode of transport is strongly influenced by temperature and vapor activity, showing different features if a wide range of temperatures and activities are explored. According to Hopfenberg and Frish,⁷ a convenient way to visualize the different transport behaviors is a temperature-penetrant concentration diagram, in which various regions of diffusional transport are reported. In a previous article,⁸ we presented a study of the transport behavior of dichloromethane in atactic polystyrene (aPS). The analysis of transport properties in a series of films of aPS showed that the diffusional behavior can be characterized by three stages, depending on temperature and penetrant activity. In the first stage, at low activity, the diffusion coefficient is independent of vapor concentration, and diffusion occurs mainly in a frozen system. The second stage is characterized by diffusion parameters dependent on concentration, and the dependence was found to be of the exponential type, allowing the determination of a zero-concentration diffusion

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coefficient, D_0 , and a concentration coefficient, γ . In the third stage, at high penetrant activity, the strong interaction can induce structural transformations, such as crazing or partial dissolution. The different behavior is determined by the ratio of the characteristic time of diffusion and some characteristic time for molecular rearrangement (or 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 different stages of behavior. In the case of amorphous crystallizable polymers, the interaction with the vapor can induce a process of crystallization. The course of solvent-induced crystallization (SINC) depends on the relationship existing between the rate of diffusion of the solvent into the polymer and the rate of crystallization of the swollen polymer.⁹⁻¹² It is therefore important to study how the rate of diffusion depends on the initial structural organization of the polymer and how it influences the SINC.

Highly syndiotactic polystyrene (sPS) is an interesting system, due to its higher melting temperature and crystallization rate with respect to the isotactic isomer.¹³⁻¹⁴ A study of the transport properties of crystalline sPS samples showed that the amorphous phase behaves as the atactic polymer, and this allowed the determination of the amorphous fraction in different samples.¹⁵⁻¹⁸

In this article, we analyze the sorption and diffusion of dichloromethane vapor in amorphous samples of sPS. The aim is to identify also in sPS the different stages of behavior and to investigate the effect of different quenching temperatures and different aging conditions on the diffusional behavior of sPS. Furthermore, the process of solvent-induced crystallization is investigated, in order to recognize the effect of different structural organizations on the critical activity for crystallization to occur and on the attained level of crystallinity.

EXPERIMENTAL

Highly syndiotactic sPS powders were kindly supplied by Donegani (Novara, Italy).

Different amorphous films were prepared by heating sPS powders at 300°C, in a press, into a film shape of thickness 0.015–0.020 cm, and rapidly cooling to either –80°C, in a dry-ice acetone bath (Sample S–80), or 0°C, in a ice-water bath (sample S0). Both samples were analyzed as soon as prepared (samples FS–80 and FS0, respectively). Dif-

ferent films were stored for two months, either at room temperature (samples RS–80 and RS0), or at 70°C (samples 70S–80 and 70S0).

Transport properties, sorption, and diffusion were measured at 25°C by a microgravimetric method, using a quartz spring balance, which had an extension of 15 mm/mg. The penetrant was dichloromethane at different vapor activities. 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 is the saturation pressure at the temperature of the experiment.

The process of solvent-induced crystallization was followed on the samples exposed at different vapor activities and dried, by obtaining the infrared spectra, in which the crystallized samples present many bands that were not present in the amorphous sample.¹⁹⁻²⁰ Infrared spectra were detected at room temperature by using a Nicolet 5DXB FTIR Spectrophotometer, collecting for each sample 30 scans. The resolution was 4 cm⁻¹.

RESULTS AND DISCUSSION

Diffusion of Fresh Samples

In Figure 1, 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 concentration, and d (cm) is the thickness of the sample, at different activities, for the freshly prepared sample FS0.

All the curves, except at activity 0.4, 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 sorption curve at activity 0.4 shows a slower increase of concentration for short times, and values of c_t/c_{eq} linearly increasing with square root of time, after a point marked with an arrow in Figure 1. From this second part, a \bar{D} value for the corresponding activity was derived.

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 was necessary to find a correlation between \bar{D} and c_{eq} , allowing the

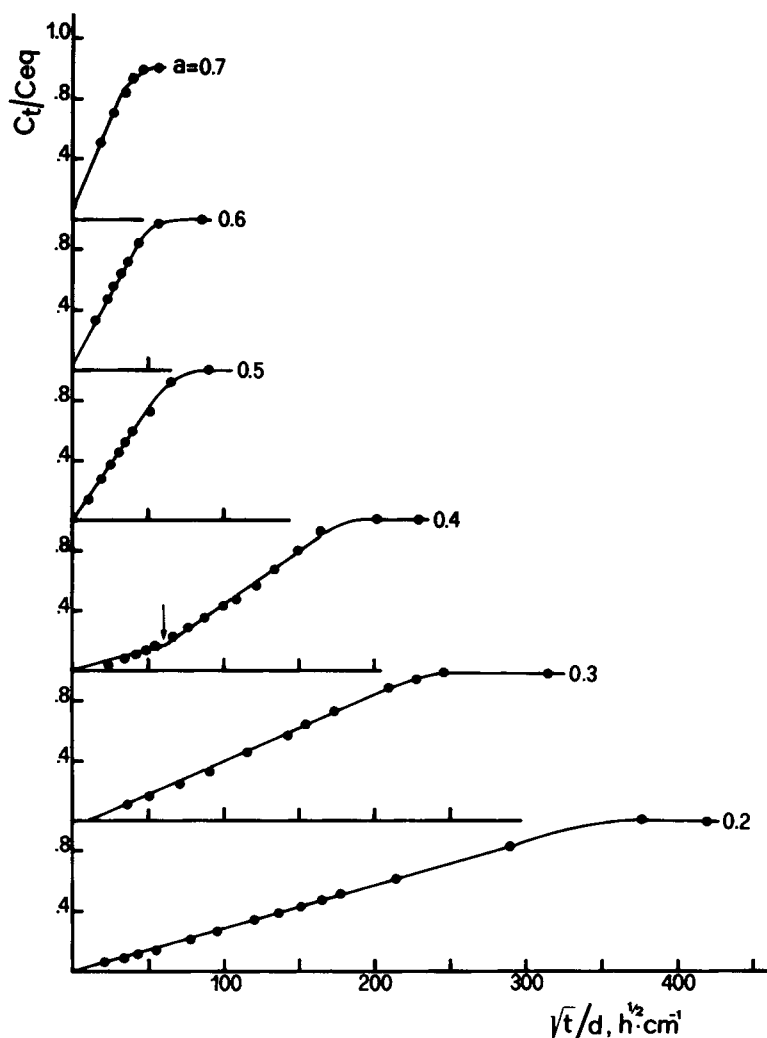


Figure 1 The reduced sorption curves, c_t/c_{eq} , as a function of \sqrt{t}/d ($h^{1/2} \text{ cm}^{-1}$) for sample FS0 at different activities.

extrapolation to $c_{eq} = 0$. Generally, the dependence of \bar{D} on c_{eq} is of the exponential form

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

in which γ is the concentration coefficient, related to the fractional free volume, and to the effectiveness with which the penetrant plasticizes the polymer.¹⁻³

Therefore, the logarithm of the \bar{D} values, calculated from eq. (1) and Figure 1, are reported in Figure 2(a) as a function of c_{eq} for samples FS0 and FS-80. The sorption curves of the last sample, not reported here, are Fickian at all the activities. The value of \bar{D} , derived from the anomalous curve of sample FS0 at activity 0.4, is marked with an arrow in Figure 2.

As in the case of aPS,⁸ in Figure 2 three stages of different behavior are clearly recognizable: At low

concentration, corresponding to low penetrant activity, diffusion values independent of concentration are observed; after a critical concentration, a linear dependence of \bar{D} on c_{eq} is manifested, whereas at still higher concentrations, we observe a curvature, after which diffusion becomes less concentration-dependent. In the fresh aPS samples, we were not able to detect the third stage, due to dissolution of the samples.⁸ In the present case of fresh sPS samples, the process of crystallization induced at high penetrant concentration prevented the sample dissolution. It was interesting to note that both samples, FS0 and FS-80, quenched at different temperatures, fit the same curve; the only difference was the appearance of anomalous behavior at activity 0.4, for Sample FS0.

From the first stage, it was possible to derive a diffusion parameter $D_{0,1}$, relative to the range of ac-

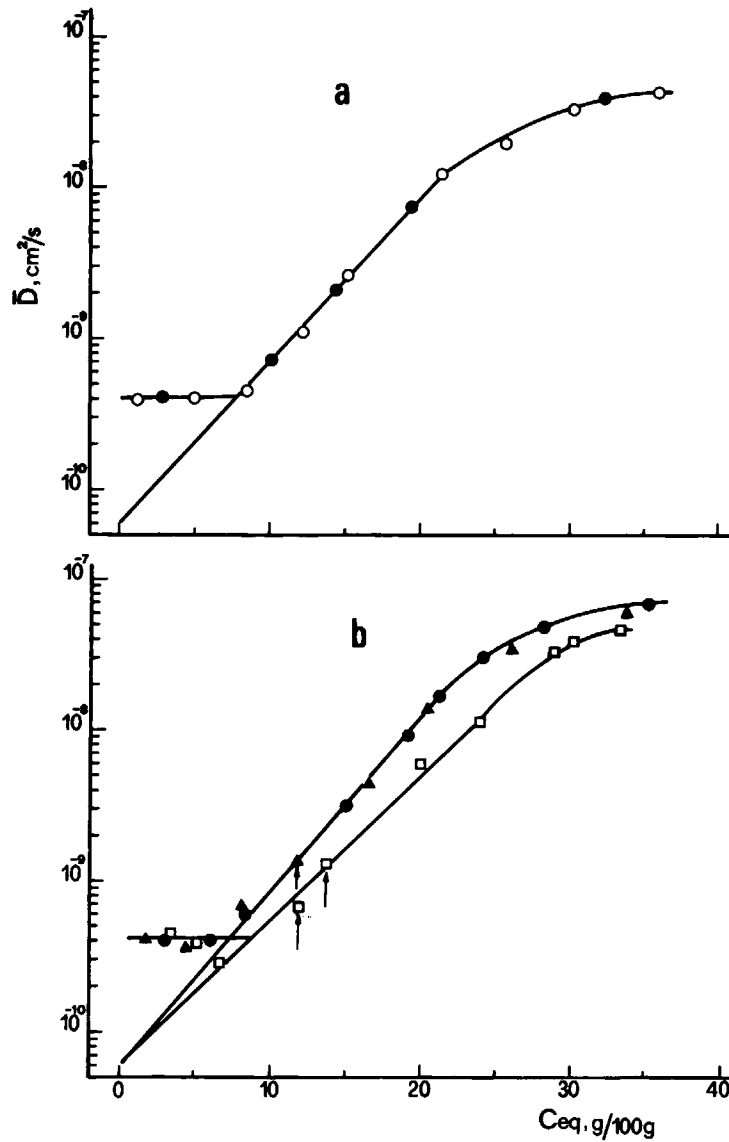


Figure 2 The logarithm of the mean diffusion coefficient \bar{D} , as a function of the vapor equilibrium concentration c_{eq} . (a) Sample FS0 (○) and sample FS-80 (●), (b) sample RS-80 (●), sample RS0 (▲), and sample 70S-80 (□).

Table I The Diffusion Parameters D_{01} (cm²/s), D_{02} (cm²/s) and γ for All the Analyzed Samples

Sample	$D_{01} \times 10^{10}$	$D_{02} \times 10^{11}$	γ
FS-80, FSO	4.5	5.5	25
RS-80, RSO	4.5	5.5	28
70S-80	4.5	5.5	23
aPS^a			
Fresh	4.6	12.2	23
Aged at Room T	4.7	5.2	28
Aged at 70°C	4.6	5.3	22

^a Data from Ref. 8.

tivity in which diffusion was 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. They are compared with the parameters derived for aPS in a previous article.⁸ Whereas the D_{01} parameters of aPS and sPS coincide, the D_{02} parameter of the former is higher, indicating a higher fraction of free volume in the fresh aPS samples.

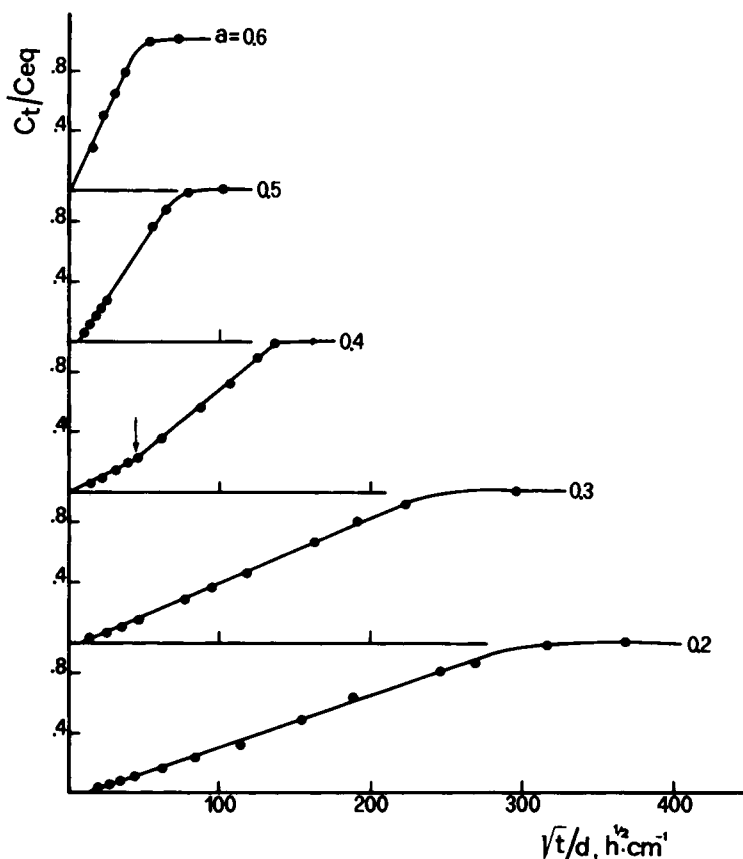


Figure 3 The reduced sorption curves, c_t/c_{eq} , as a function of \sqrt{t}/d ($h^{1/2} \text{ cm}^{-1}$) for sample RS-80 at different activities.

Diffusion of Aged Samples

In Figures 3 and 4, we report the reduced sorption curves for sample RS-80, aged for two months at room temperature, and sample 70S-80, aged for two months at 70°C. All the curves in Figure 3 show a Fickian behavior, except the curve at activity 0.4, which shows a slower increase of concentration for short times. A diffusion coefficient \bar{D} was derived from the second part of the sorption curve. In the case of sample 70S-80, anomalous curves appear at activity 0.35 and 0.40. Also in these cases, the diffusion coefficients were derived from the second part of the curve.

The logarithm of the diffusion values, derived from the Fickian curves, are reported in Figure 2 (b) as a function of concentration, also for RS0 samples; the values of \bar{D} , obtained from anomalous curves (sample RS-80 at activity 0.4 and sample 70S-80 at activities 0.35 and 0.4), are marked with an arrow in the figure. For the aged samples, we observed the three stages of behavior, as already observed for the fresh sPS samples and for the aged aPS samples of

a previous article.⁸ In the first stage, because of the low penetrant concentration, the polymer structure remains frozen and the relaxation times are very large as 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,⁷ this stage can be classified as Fickian diffusion below the glass transition temperature.

When the concentration of penetrant reaches a critical value, at a higher activity, the interaction between the penetrant and segments of the chain allows molecular rearrangements with a time scale comparable or less than diffusion, and we observe either anomalous curves, as at activities 0.4 for sample RS-80 and 0.35–0.4 for sample 70S-80, or Fickian curves, characterized by a concentration-dependent diffusion coefficient.

At still higher vapor activity, the high concentration of penetrant completely plasticizes the polymer, leading to high mobility of polymer chains. The interaction is so strong that structural transformations are possible, determining a transition in the

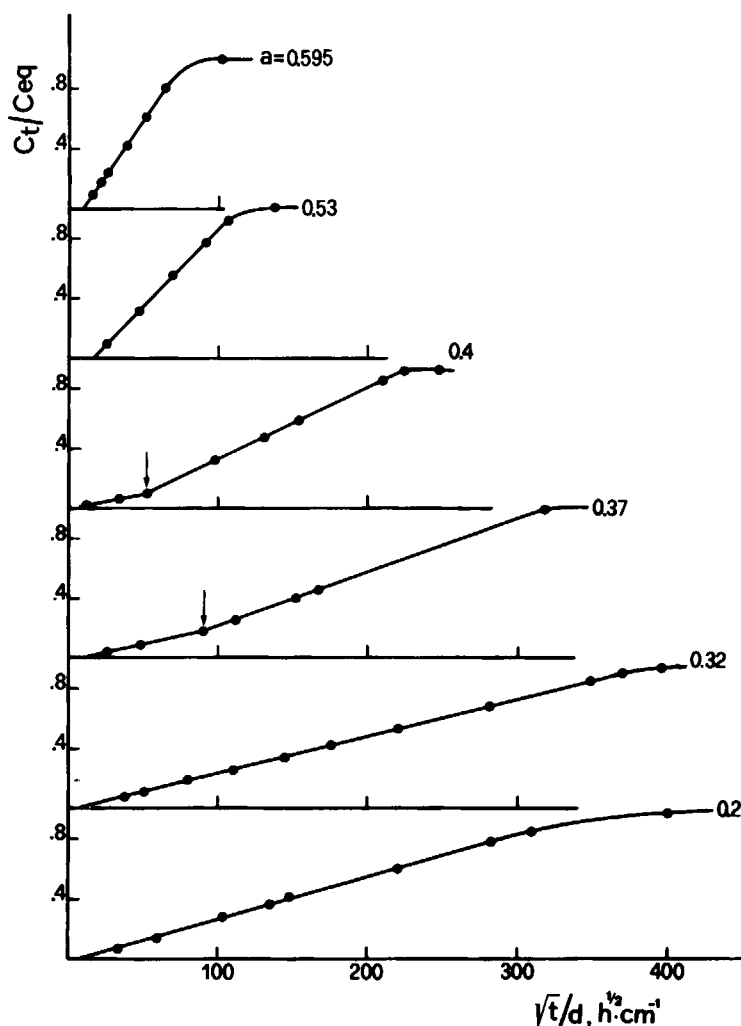


Figure 4 The reduced sorption curves, c_t/c_{eq} , as a function of \sqrt{t}/d ($h^{1/2} \text{ cm}^{-1}$) for sample 70S-80 at different activities.

diffusion-concentration curve. This transition is manifested by the curvature that occurs at a critical concentration. For amorphous crystallizable polymers, as sPS, the solvent-induced crystallization becomes possible in this range of vapor activity.

The D_{o1} and D_{o2} coefficients, derived from samples RS-80 and 70S-80 are reported in Table I, in which also the parameters, obtained for aPS in a previous article,⁸ are reported for comparison.

We can observe, from Table I, that the aging, either at room temperature or at 70°C, does not have an influence on the D_{o1} parameter. At low activity, the system is frozen and diffusion is independent of concentration; we observe the same D_{o1} as that observed for aPS. However, at variance with aPS, neither in the second stage do we observe different pa-

rameters for the fresh and aged samples; in fact, D_{o2} , both for the fresh and for the aged samples, is $5.5 \times 10^{-11} \text{ cm}^2/\text{s}$, and this value is similar to that of the aged aPS samples. Only the γ coefficients for the samples aged at room temperature show a difference. Aging produces a decrease of free volume and a related increase of relaxation times, and this is manifested in the appearance of anomalous sorption curves, and not in a difference of the thermodynamic D_o coefficient.

Samples S0 and S-80, quenched at different temperatures, behave in the same way, leading to the conclusion that there is no influence of the quenching temperature on the structural organization of the amorphous sample. The coincidence of D_o for aged atactic and syndiotactic PS confirms that the

amorphous phase behaves in a similar way and, therefore, the sorption is only related to the fraction of amorphous phase.¹⁵

Sorption

In Figure 5, 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 fresh FS-80 and FS0 samples, and the aged at room temperature RS-80 and RS0 samples, show the same equilibrium concentration of the sorbed vapor and the same dependence of sorption on vapor activity. A comparison with the sorption curve of aPS (also reported in Fig. 5), shows that atactic and syndiotactic samples fit the same curve up to activity 0.45, whereas at higher activities, the sorption of sPS is lower than

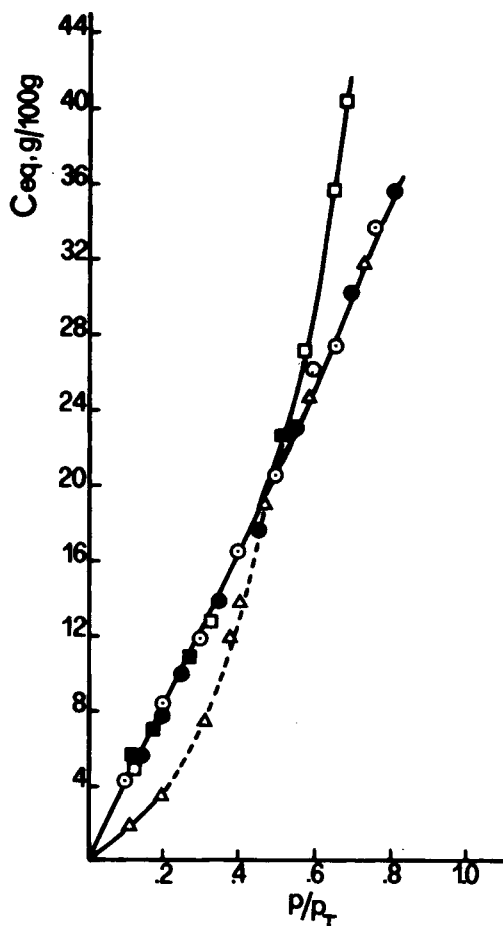


Figure 5 The equilibrium concentration of vapor as a function of activity $a = p/p_T$, for atactic polystyrene (\square), sample FS0 (\circ), sample RS0 (\bullet), sample RS-80 (\blacksquare), and sample 70S-80 (\triangle).

aPS, up to the highest investigated activity. This effect can be ascribed to the solvent-induced crystallization of sPS, that leads to a final sorption less than the amorphous sample, since the crystallized part is impermeable to the solvent. From the sorption curve, we can therefore infer that this process starts at activities higher than 0.45.

At variance with the samples aged at room temperature, the samples stored at 70°C show a lower sorption up to activity 0.25, an evident transition between activities 0.25 and 0.45, and the same sorption as the previous samples at activities higher than 0.45. In the case of aPS, for which we observed the same behavior, we suggested that ordered domains were present that were impermeable to the penetrant at low activity. The presence of ordered domains in aPS has been suggested in the past on the basis of electron diffraction and high resolution diffraction microscopy studies.²¹⁻²³

The ordered domains, 10 nm large, present in isotactic smectic polypropylene, were found to be impermeable to dichloromethane at low activity, becoming permeable at higher activities.²⁴⁻²⁵ In the case of sPS, we can assume that the annealing at 70°C favors the formation of ordered domains of such dimensions as to be impermeable to the vapor at low activity.

The transition in the sorption curve at activities higher than 0.25 can be a signal that the ordered domains become permeable to the vapor: this is confirmed by the observation that, after this transition, the equilibrium concentration of vapor equalizes that of the other samples.

Solvent Induced Crystallization

The crystallization of the amorphous samples, after sorption at different activities was investigated by infrared analysis.

When sPS crystallized by solvents, the chains in the crystalline phase assumed a helical conformation, including solvent molecules in the structure.²⁶ This structure was called δ form.²⁷ The infrared spectrum of the δ form shows many bands, not present in the amorphous sample, and therefore the appearance of these bands is indicative of the solvent-induced crystallization.¹⁹⁻²⁰

In Figure 6, the infrared spectra of the amorphous sample RS0 (a) and the same immersed in liquid dichloromethane at 25°C and dried (b) are shown. The bands characteristic of the helical structure appear at 499, 575, 935, 1170, and 1277 cm^{-1} , and they are marked with an arrow in Figure 6.

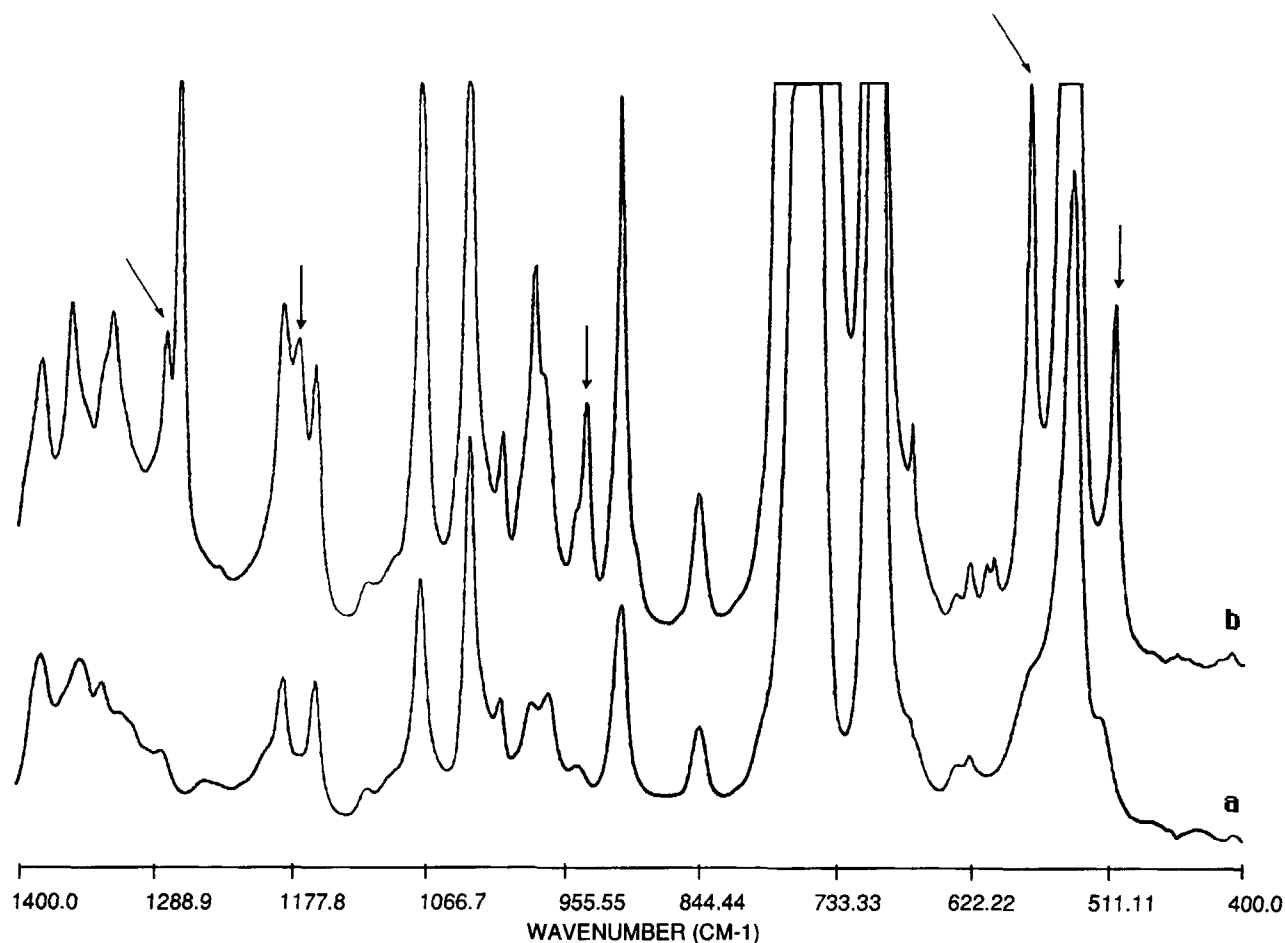


Figure 6 Infrared spectra of sample RS-80 (a) and the same after immersion in liquid dichloromethane (b).

The appearance and the growth of the helical structure in the vapor activity range was followed by measuring a structure-dependent parameter, H , which represented the ratio between the absorbance of a helical band and the absorbance of an internal reference band. In particular, we determined the parameters²⁸:

$$H_1 = \text{Absorbance } 575 \text{ cm}^{-1} / \text{Absorbance } 840 \text{ cm}^{-1}$$

$$H_2 = \text{Absorbance } 935 \text{ cm}^{-1} / \text{Absorbance } 906 \text{ cm}^{-1}$$

In Figure 7(a), the H_1 and H_2 parameters are reported, for the samples aged at room temperature, as a function of vapor activity to which they had been exposed; in Figure 7(b), the same parameters are reported for the samples aged at 70°C. We can observe a constant, practically zero value of H_1 and H_2 parameters up to a critical activity, a sharp increase, followed by an almost constant value, and a

further increase for the samples immersed in the liquid, at activity $a = 1$.

The samples aged at 70°C underwent the conformational transition at an activity slightly higher than the samples aged at room temperature (0.5 instead of 0.45), but they reached a higher value of the H parameters, particularly as relative to the 935 cm^{-1} band. Since we supposed the presence of ordered domains in the 70S samples, this result could mean that the crystallization was slightly delayed with respect to the samples aged at room temperature, but the crystallization process produced more perfect and larger structures. An X-ray analysis is in progress to confirm this suggestion.

CONCLUSIONS

The diffusional behavior of sPS, at 25°C, is characterized by three stages, depending on penetrant activity. In the first stage, at low activity, the dif-

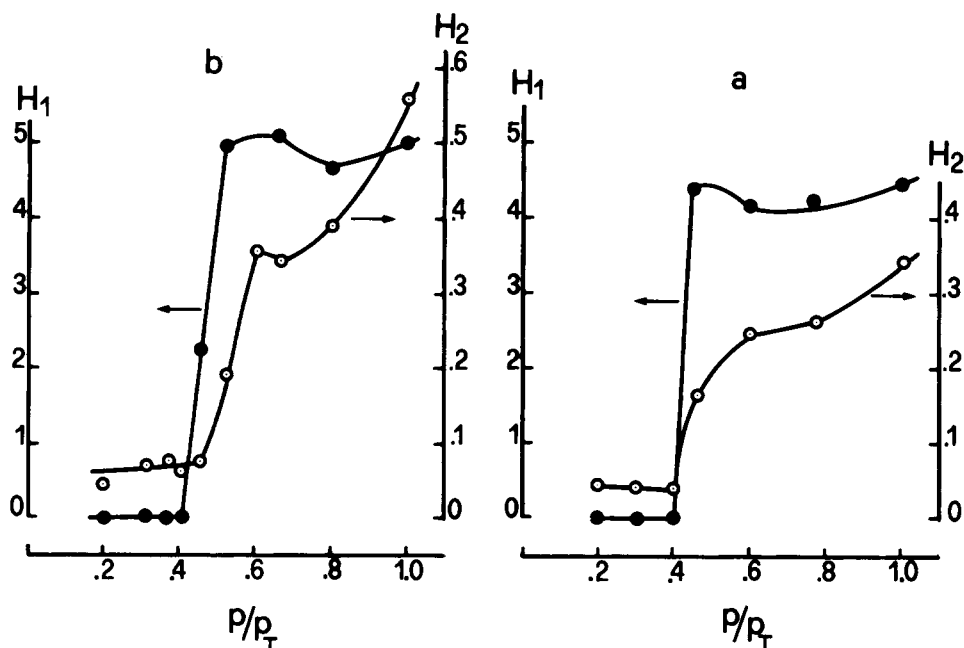


Figure 7 The infrared H_1 (●) and H_2 (○) parameters as a function of vapor activity. (a) samples RS-80 and RS0 (b) sample 70S-80.

fusion coefficient is independent of vapor concentration and diffusion occurs mainly in a frozen system. The second stage is characterized by diffusion parameters dependent on concentration, with a dependence of the exponential type, allowing the determination of a zero-concentration diffusion coefficient D_0 and a concentration coefficient γ . In the third stage, the strong interaction of solvent molecules induces the process of crystallization of the helical form of sPS.

At variance with aPS, for which the aging at room temperature produced a decrease of D_0 and an increase of γ coefficient in the second stage, in the case of sPS only, a higher tendency of anomalous sorption curves to appear is observed for the samples aged at room temperature. More and more anomalous curves are observed for the samples stored at 70°C. Nevertheless, the diffusion coefficients, derived from the second part of the anomalous curves, fit the same straight line as those derived from the Fickian curves.

The diffusion parameters for the aged sPS samples coincide with those for aPS, confirming that the amorphous phase behaves in a similar way in the isomers.

The aging at room temperature does not influence the sorption curve, as already observed for aPS. The sorption of sPS and aPS samples coincide up to the

activity, for which the SINC process is induced in sPS. At higher activities, a sorption lower than aPS indicates that the crystallizing part of sPS is impermeable to the solvent molecules.

At variance with the aging at room temperature, the curve of sorption as a function of vapor activity for sample 70S-80 shows a range in which the equilibrium concentration of vapor is lower than previously. We suggest that the aging at 70°C produces the formation of ordered domains of such dimensions as to be impermeable to the vapor at low activity. At a critical activity, the 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.

The process of solvent-induced crystallization is activated at activities higher than 0.45 for the fresh and the aged-at-room temperature samples; this is evident from the lower sorption in respect to the atactic polymer, and from the appearance of helical bands in the infrared spectra of the dried samples. A slightly higher activity, that is, 0.5, is needed for the crystallization to start in samples aged at 70°C. Nevertheless, the attained level of crystallinity is higher for the latter samples. This is evident from the higher values of relative intensity of the infrared helical bands.

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