Transport Properties of Dichloromethane in Glassy Polymers. VI. Poly(ethylene terephthalate)

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SYNOPSIS

Sorption and diffusion of dichloromethane vapor in amorphous poly(ethylene tere-phthalate) (PET) were investigated, with the aim of studying how aging phenomena, at different temperatures, influence the transport properties. It has been found that aging produces the appearance of non-Fickian behavior in the sorption curves as well as the reduction of the diffusion coefficients. Furthermore, aging at 60°C reduces the sorption of vapor at low activity, and this led to the hypothesis of the presence of ordered domains in the aged samples. In this case, the process of solvent-induced crystallization is favored, and it appears at lower activity. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The sorption and diffusion of gases and organic vapors in polymers is important for theoretical as well as for technological reasons. Careful analysis of transport properties can help clarify many structural aspects of the polymer[1-3]; on the other hand, knowledge of permeability is essential in the application of polymers as barrier materials.[4,5] Previous studies from this laboratory have shown the influence that cooling conditions and aging temperatures and times have on the sorption and diffusion of dichloromethane vapor in glassy polymers, as atactic and syndiotactic polystyrene[6-9] and poly(aryl ether ether ketone).[10] For all the samples, we found that the diffusional behavior was characterized by three stages, depending on vapor activity, at constant temperature. In the first stage, at low activity, a diffusion coefficient independent of concentration was found; the second stage, occurring above a critical activity, was characterized by concentration-dependent diffusion, whereas in the third stage, at high activ-ity, the strong solvent–polymer interactions induce structural transformations, as solvent-induced crystallization for amorphous crystallizable poly-mers. The influence of cooling conditions and aging time on the transport parameters and on the appearance of anomalous non-Fickian behavior was analyzed, and it was shown that the aging at room temperature reduces the diffusion coefficient, without influencing the sorption properties. At variance, the aging at temperatures slightly below the glass transition temperature reduces the sorption at low activity; this led us to hypothesize the presence of domains impermeable to the vapors at low activity, which segregate during the sub-T_g aging.

Poly(ethylene terephthalate) (PET) is one of the most commercially important polyesters, and in many applications, the knowledge of its permeability is of fundamental importance. We therefore extended our investigation of transport properties, as a function of aging conditions, to this polymer, and in this article, we present the results of such studies. We analyzed the sorption and diffusion of dichloromethane vapor in amorphous PET, with the aim of studying how aging phenomena, at different temperatures, influence the transport properties. Furthermore, it is known that amorphous PET under-

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goes a process of solvent-induced crystallization (SINC) in dichloromethane,[11-13] and in this article, we analyze also the influence of the aging on the SINC process.

EXPERIMENTAL

Pellets of PET of intrinsic viscosity 0.84 dL/g were kindly supplied by Montefibre (Italy). Amorphous films were prepared by heating PET pellets at 280°C in a press into a film shape of thickness 0.005 mm and rapidly cooling to 0°C in an ice-water bath. A sample was analyzed as soon as prepared (sample AF), whereas different films were stored either 1 year at room temperature (sample ART) or 1 month at 60°C (sample A60).

Wide-angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer (CuKα–Ni-filtered radiation). The scan rate was 2° θ/min.

Differential scanning calorimetry (DSC) was carried out over the temperature range −80 to 300°C, using a Mettler TA3000 DSC instrument purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 10 mg at a heating rate of 10°C/min.

Infrared spectra were obtained at room temperature by using a Nicolet 5DXB FTIR spectrophotometer with a resolution of 4 cm^{-1} (30 scans collected). Transport properties, sorption and diffusion, were measured by a microgravimetric method, using a quartz spring balance, having an extension of 18 mm/mg. The penetrant was CH_2Cl_2 and the experiments were conducted at 25°C. Sorption was measured as a function of vapor activity $a = p/p_0$, where p is the actual pressure to which the sample was exposed, and p_0, the saturation pressure at the temperature of the experiment.

RESULTS AND DISCUSSION

Structure of the Samples

Figure 1 shows the wide-angle X-ray diffractograms of sample AF, analyzed as soon as prepared, sample ART, aged at room temperature, and sample A60, aged at 60°C. The broad peak centered at 19.5° of 2θ corresponds to the diffraction of amorphous PET. It is evident that neither the intensity nor the diffraction angle change with the aging. Of course,
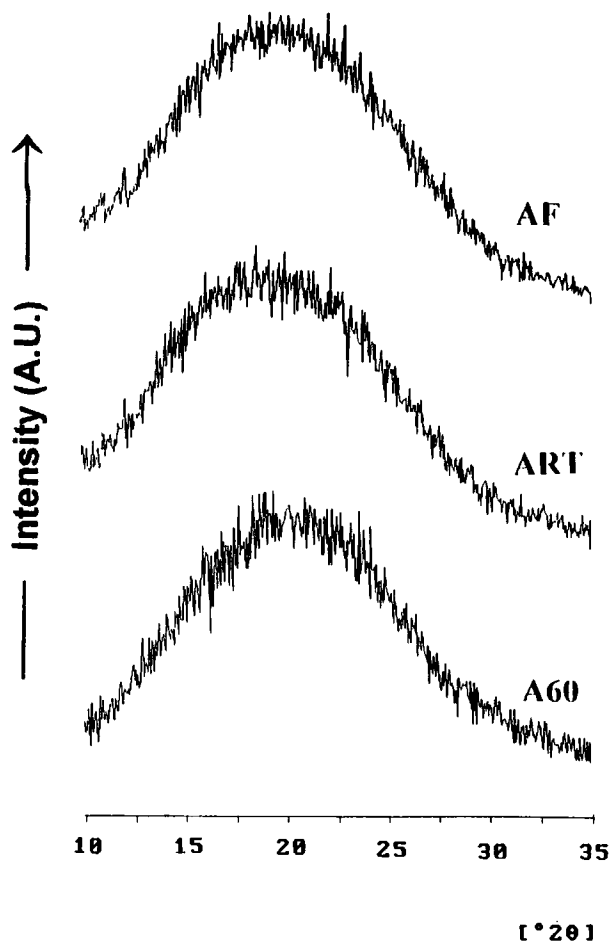
Figure 1 Wide-angle X-ray diffractogram of samples AF, ART, and A60.

crystallization due to the aging is excluded. The same result was obtained with FTIR. Infrared spectra of the three samples, not reported here, were analyzed in the range where a crystalline band of PET, at 973 cm^{-1}, appears. No evidence of a relevant change of this band was obtained.

DSC curves of the three samples are reported in Figure 2. All the amorphous samples crystallize during the scanning; the sample aged at room temperature shows a slightly lower crystallization temperature in respect to the others, whereas no change was observed in the crystallization enthalpy. Instead, in the range of the glass transition temperature, some differences are evidenced. In fact, the aged samples show an endotherm at the T_g, being more evident for the sample aged at 60°C. The appearance of an endotherm at T_g has been generally correlated with kinetics factors[14]; it is interesting that, in our case, it appears and becomes more evident with the aging.
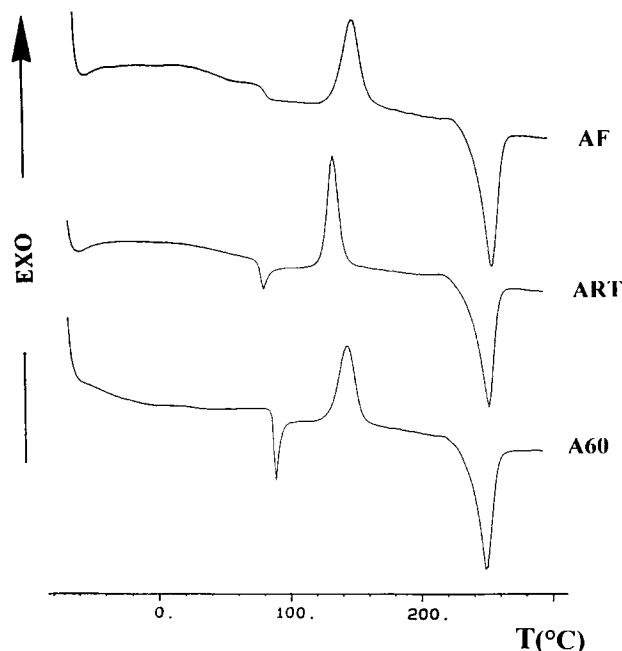
Figure 2   Differential scanning calorimetry curves of samples AF, ART, and A60.

Diffusion of Dichloromethane Vapor

In Figure 3, we report the reduced sorption curves, i.e., c_t/c_{eq}, as a function of $\sqrt{t}$, where c_t is the concentration of vapor at time t, and c_{eq}, the equilibrium concentration, at different activities, for the fresh sample AF. All the curves show a linear increase of concentration with the 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 from the initial part of the curve to derive the diffusion coefficient, D, from the equation

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

The derived 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 D and c_{eq}, allowing the extrapolation to $c_{eq} = 0$. Generally, the dependence of D on c_{eq} is of the exponential form:

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

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

Therefore, the logarithm of the D values, calculated from eq. (1) and Figure 3, are reported in Figure 4 as a function of c_{eq}.

In Figures 5 and 6, the sorption curves c_t/c_{eq} are reported as a function of the square root of time, respectively, for samples ART and A60. Sample ART shows Fickian sorption curves, except at low activity, where a steeper increase of sorption is observed for short times. A more pronounced non-Fickian behavior is shown at low activity by sample A60. The sorption anomalies extend up to activity 0.5, where a Fickian behavior characterizes the sorption. The logarithm of the diffusion values, derived both from the Fickian curves, and from the linear part of the anomalous one, are reported in Figure 4 as a function of the equilibrium concentration. For all the samples, we observe two zones:

1. A diffusion independent of concentration, at low activity;
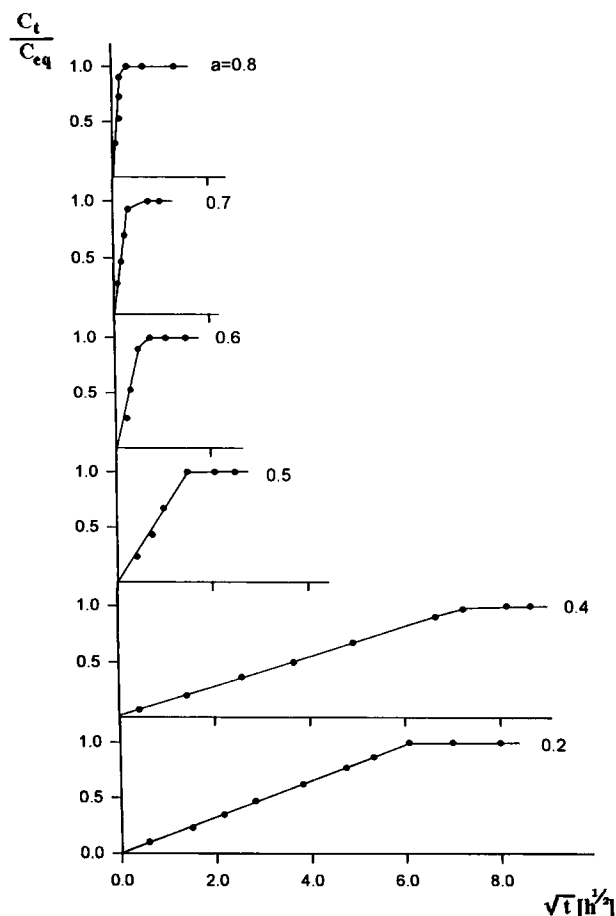
Figure 3   The reduced sorption curves, c_t/c_{eq}, as a function of $\sqrt{t}$ for sample AF at different activities.
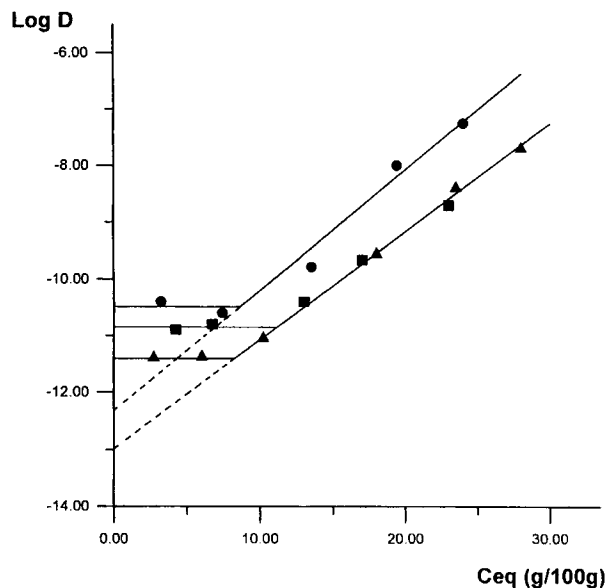
Figure 4 The logarithm of the D parameters as a function of c_{eq} for the samples (●) AF, (■) ART, and (▲) A60.

### 2. A concentration-dependent diffusion at intermediate activities.

From the two zones, it is possible to derive two zero-concentration diffusion coefficients, D_{01} and D_{02}, for the three samples. Their values are reported in Table I. 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 to the diffusion times: Probably, diffusion of the permeant occurs through voids that are dynamically formed by oscillation of chain segments. According to Hopfenbergh and Frish,[15] this region can be classified as a Fickian diffusion region below the glass transition temperature. The diffusion parameter is therefore representative of the fractional free volume frozen in the sample below the T_g. The three samples show a decreasing D_{01} with the aging time. This indicates that the aging produces a decrease of free volume, as expected. It is worth noting that, in the case of PET, the diffusion coefficient is sensitive to this reduction, in contrast with polystyrene, for which an invariance of the D_{01} parameter was observed with the aging time.[6]

When the concentration reaches a critical value, at a higher activity, the interaction between the penetrant and the segments of the chain allows molecular rearrangements, with a time scale comparable or less than diffusion, and we observe either anomalous curves or Fickian curves characterized by a concentration-dependent diffusion coefficient.

The critical value of concentration is about 10% for all the samples; this value corresponds to the concentration of solvent necessary to lower the glass transition temperature of the sample to the temperature of the experiment. The influence of the aging time is observable also in this zone. In fact, the extrapolation to zero concentration gives a lower D_0 for the aged samples. 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 the free volume and related molecular mobility, and this is well reflected in a decreased diffusion coefficient. It is worth noting that, in the second zone, the two aged samples fit the same straight line.
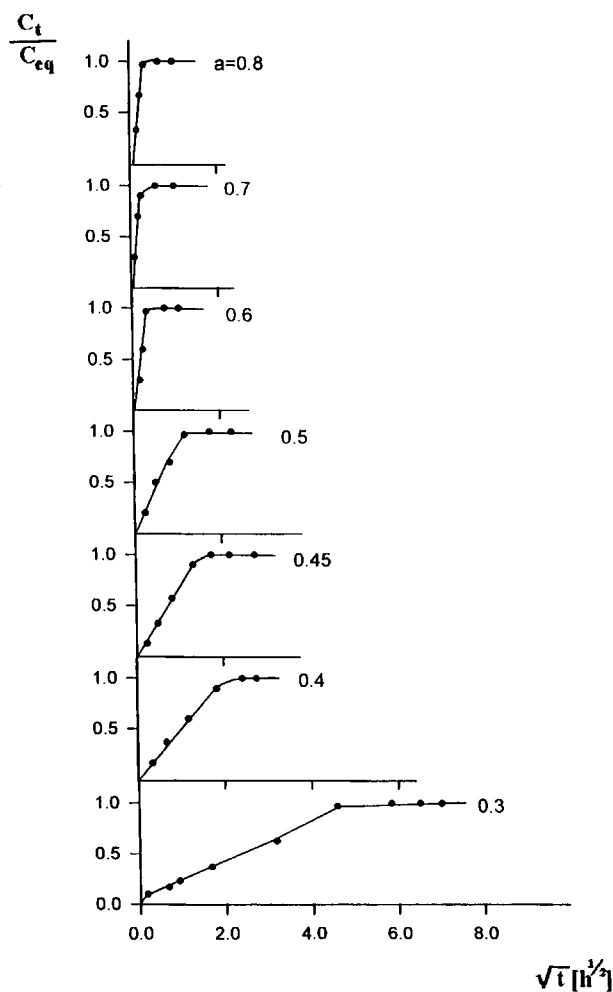
Figure 5 The reduced sorption curves, c_t/c_{eq} as a function of $\sqrt{t}$ for sample ART at different activities.
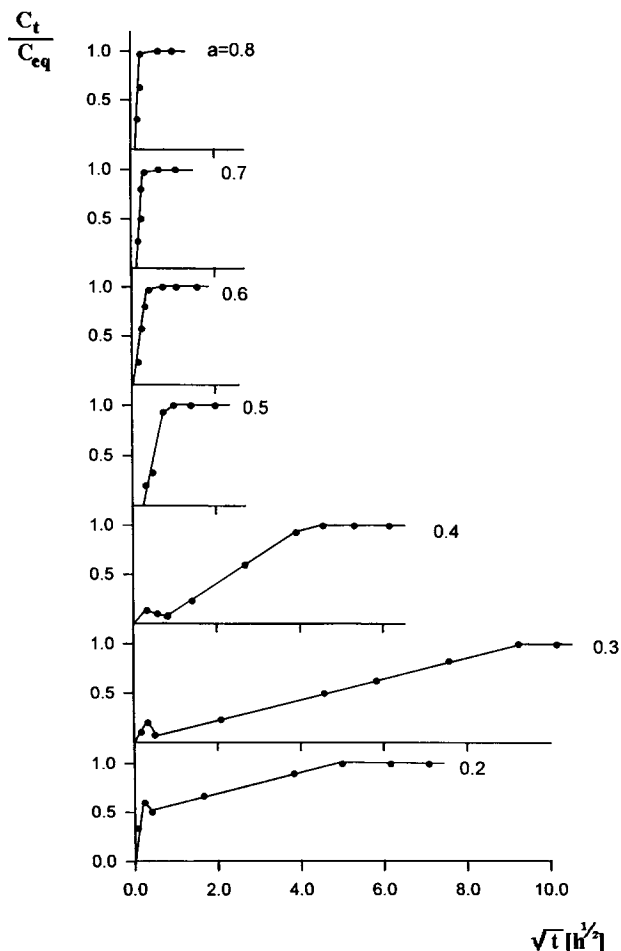
Figure 6 The reduced sorption curves, c_t/c_{eq}, as a function of $\sqrt{t}$ for sample A60 at different activities.

At still higher vapor activity, the high concentration of penetrant completely platicizes the polymer, leading to high mobility of the polymer chains and allowing a process of solvent-induced crystallization (SINC). In this zone, diffusion coefficients are not reliable. In fact, the solvent molecules, expulsed from the crystallites, can interfere with the diffusional flux. The influence of the aging on the SINC process will be discussed in the following.

Sorption

In Figure 7, the equilibrium concentration of the penetrant is reported as a function of activity, $a = p/p_0$, for the fresh sample AF and for the aged samples ART and A60. The three zones of diffusional behavior can be recognized in the sorption curve: At low activity, a linear increase of sorption is observed

Table I   Diffusion Coefficients D (cm²/s), Equilibrium Concentration at Activity $a = 0.2$, and Concentration Coefficient γ for the Three Samples

Sample	$D_{01} \cdot 10^{11}$	$D_{02} \cdot 10^{13}$	c_{eq} ($a = 0.2$)	γ
AF	3.16	4.64	5	25
ART	1.41	1.05	5	16
A60	0.398	1.05	1.6	16

for the three samples. This behavior, following the Henry's law, is typical of an ideal system, in which there is no strong interaction between polymer and solvent. At intermediate activities, a positive deviation can be observed, with a behavior following the Flory-Huggins description. This description is, in fact, relative to interacting polymer-solvent systems. At high activities, a decrease of sorption with increasing activity is observed. This behavior is typical
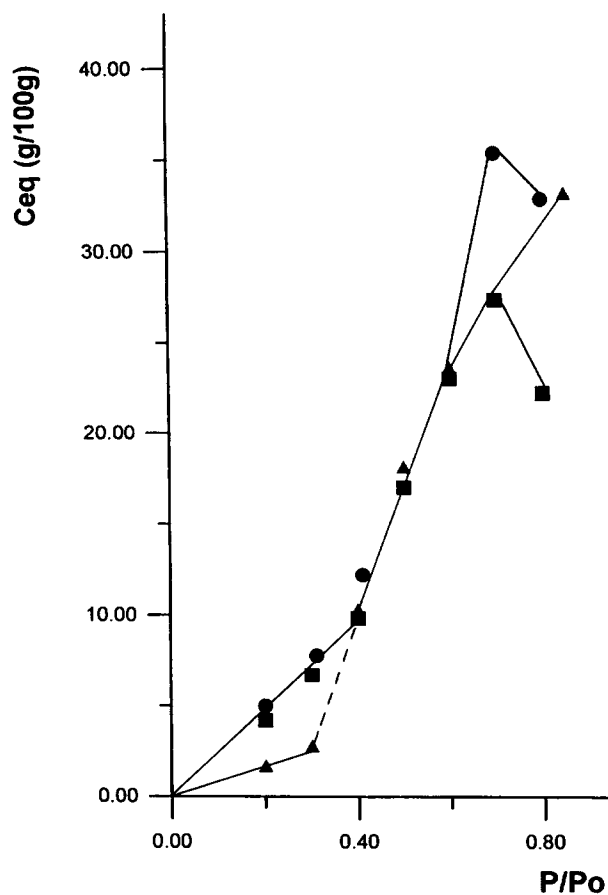

Figure 7 The equilibrium concentration of dichloromethane, c_{eq} (g/100 g), as a function of vapor activity $a = p/p_0$, for the samples (●) AF, (■) ART, and (▲) A60.

of the SINC process. As matter of fact, when the crystallization occurs in a shorter time scale in respect to the diffusion, the solvent is expulsed from the crystallites before the diffusion process is complete and a lower final concentration of vapor is to be expected.

At low activity, where the behavior is ideal, the level of sorption can be correlated to the free volume of the sample and to the fraction of the permeable phase. The free volume of the aged samples is lower than that of the fresh sample, but this decrease cannot explain the reduced sorption of sample A60 at low activity. In fact, the fresh and the aged at room-temperature samples show the same sorption. In analogy with the other investigated systems, we can hypothesize that, also in PET, annealing at a temperature below T_g produces ordered zones or increases the dimensions of ordered zones already present in the fresh sample. When the ordered zones reach a critical dimension, they become impermeable to dichloromethane at low activity. At high activity, they become permeable, and we observe a transition in the curve and the same sorption as of the other samples after an activity of 0.4.

Solvent-induced Crystallization

The crystallization of the amorphous samples after sorption at different activities was investigated by infrared analysis. The intensity of the band appearing at 973 cm^{-1} is, in fact, correlated with the presence of the *trans* conformation of the — O — C — C — O — group. The intensity of this conformational band was followed for the samples taken at different activities of dichloromethane vapor and dried for many hours under vacuum. A correction was performed, dividing the measured value by the intensity of the band at 1578 cm^{-1}, which is not sensitive to the different conformations.[16] In Figure 8, we report the ratio $R = A_{973}/A_{1578}$ as a function of the vapor activity to which the sample had been exposed for all the samples. For the aged samples, we observe a constant value of R up to an activity of 0.4, a sharp increase between activities of 0.4 and 0.5, and a linear increase at higher activities. At variance, the fresh sample shows the increase of the R parameter between activities of 0.5 and 0.6. Therefore, the solvent-induced crystallization is delayed in the sample as soon as it is prepared, although it reaches the same R parameter as the aged samples at high activity.
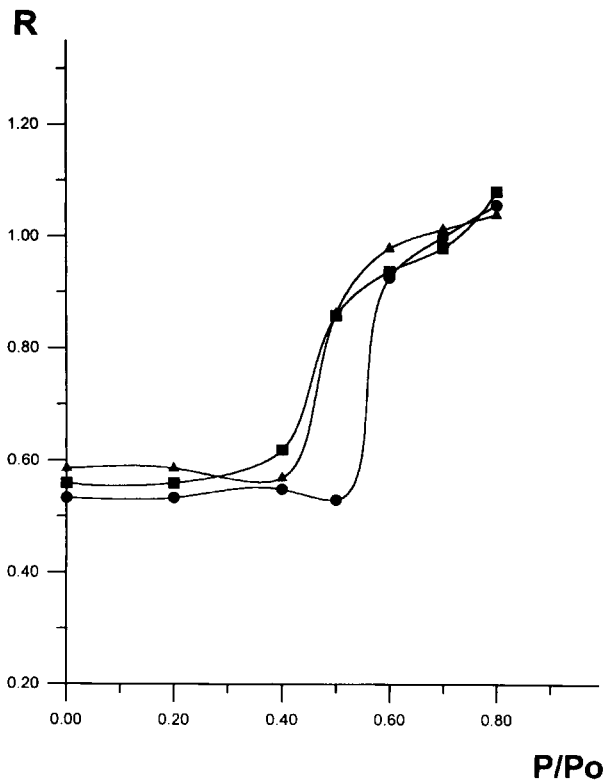
Figure 8 The infrared R parameter as a function of vapor activity for samples (●) AF, (■) ART, and (▲) A60.

CONCLUSIONS

The diffusional behavior of dichloromethane in glassy amorphous PET shows characteristics similar to those of the other investigated glassy polymers. At low penetrant activity, the diffusion coefficients are poorly dependent on concentration and a D_{01} parameter was obtained for this first zone. At higher activities, the diffusion becomes strongly dependent on concentration, extrapolating to a lower zero-concentration diffusion coefficient D_{02}. Aging produces a decrease of both the D_{01} and D_{02} parameters. Furthermore, aging at 60°C reduces the sorption of vapor at low activity. This result led us to hypothesize the presence of ordered domains, impermeable to the vapor. At higher activities, they become permeable, and, in fact, the sorption follows the same curve as that of the others.

The process of solvent-induced crystallization is activated after an activity of 0.4 for the aged samples. In the fresh sample, this process is delayed. In this case, a more ordered structural organization in the aged samples can favor the process of solvent-induced crystallization.

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