Transport properties of dichloromethane in glassy polymers: 5. Poly(aryl ether ether ketone)

A. Michele and V. Vittoria*
Istituto di Richerche su Tecnologia dei Polimeri, CNR, Via Toiano 6, 80072 Arco Felice, Napoli, Italy
(Received 25 July 1991; revised 26 May 1992)

Sorption and diffusion of dichloromethane vapour were measured in poly(aryl ether ether ketone) films after different ageing times. In the fresh samples the diffusional behaviour is characterized by two stages: in the first stage the diffusion coefficient D is weakly dependent on concentration, and transport mainly occurs through a frozen system; whereas in the second stage a steep dependence of D on concentration was found. The aged samples also show an intermediate stage, characterized by an anomalous or non-Fickian sorption behaviour. Furthermore the diffusion coefficients of the aged samples are lower than those of the fresh samples, in agreement with a reduced fractional free volume.

Ageing at a temperature slightly lower than the glass transition temperature decreases the sorption at low activity, leading to the suggestion that ordered domains, impermeable to the vapour at low activity, are formed at this temperature. The process of solvent-induced crystallization on the amorphous samples was investigated, and it was found that crystallization is induced after activity 0.7. Both the fresh and the aged samples show the same behaviour, although the level of crystallinity attained was found to be higher for the latter samples.

(Keywords: transport properties; glassy polymer; poly(aryl ether ether ketone); dichloromethane; films; ageing)

INTRODUCTION

The study of transport properties of organic vapours in polymers is interesting from many points of view. First, many structural aspects of the polymer can be related to the sorption and diffusion of penetrants[1–3]; moreover, knowledge of the permeability of the material, and how it depends on the structural organization, is of fundamental importance in the application of polymers as barrier materials[4,5]. In glassy polymers the sorption of organic vapours and liquids may involve time-dependent relaxation processes, determining an anomalous, non-Fickian behaviour[6–9]. In this sense many experimental results of anomalous behaviour have been explained as a slow polymer rearrangement, or relaxation, following the first sorption. Besides molecular and structural parameters, the mode of transport is strongly influenced by temperature and vapour activity[6–8]. Therefore, the description of the transport behaviour for a given polymer–solvent system is meaningful only when the activity of the penetrant and temperature are clearly reported. In fact, for the same polymer–penetrant system it is possible to observe different behaviours, if a wide range of temperatures and activities are explored.

In the first paper of this series[10] we analysed the transport properties of dichloromethane in atactic polystyrene films, obtained with different cooling rates and aged in different conditions, and we found different stages of transport behaviour, depending on the vapour activity.

In the case of amorphous, crystallizable polymers, an additional effect can be studied. In fact, the interaction with particular solvents can lower the T_g of the polymer below the temperature of the experiment, increasing the chain mobility and allowing the crystallization process. The course of solvent-induced crystallization (SINC) depends on the relation existing between the rate of diffusion of the solvent into the polymer and the rate of crystallization of the swollen polymer[11–13]. 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.

Poly(aryl ether ether ketone) (PEEK) has received much attention as a high-performance engineering material. It can be obtained in the amorphous state, and undergoes a process of SINC in dichloromethane[14–17]. Physical ageing influences the mechanical properties of this polymer[18], and an influence on transport properties is to be expected. This, in turn, might influence the process of SINC.

In this paper we analyse the sorption and diffusion of dichloromethane vapour and liquid in amorphous PEEK. The purpose of this work is to study how ageing phenomena, at different temperatures, influence the transport properties and, as a consequence, the process of solvent-induced crystallization. Furthermore, the SINC process is not activated at low penetrant activity, and in this range the transport properties can be related

---

* To whom correspondence should be addressed

0032-3861/93/091898–06

to the structural organization of the amorphous polymer, aged in different conditions.

EXPERIMENTAL

Poly(aryl ether ether ketone) (PEEK) was kindly supplied by ICI (Middlesbrough, Cleveland, UK) in the form of amorphous, 0.0025 cm thick films (sample AA). Fresh amorphous films were obtained by melting sample AA in a hot press at 380–400°C into a film 0.003 cm thick, and rapidly quenching to −70°C in a dry ice–acetone bath (sample AF). This sample was analysed as soon as it was prepared. Sample AA was stored at 120°C, a temperature below the glass transition temperature of PEEK, for 1 month (sample A120). The transport properties of dichloromethane were measured at 25°C by a microgravimetric method using a quartz spring balance having an extension of 16 mm mg^{-1}. Sorption was measured as a function of vapour 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.

After sorption, the samples were dried under vacuum for many days, and the solvent-induced crystallization was investigated by infra-red analysis and wide-angle X-ray scattering.

Wide-angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer (Cu Kα Ni-filtered radiation). The scan rate was 2°θ min^{-1}.

Infra-red spectra were obtained at room temperature by using a Nicolet 5DXB *FT*i.r. spectrophotometer with a resolution of 4 cm^{-1} (30 scans collected).

RESULTS AND DISCUSSION

Diffusion of vapour in fresh samples

In *Figure 1* we report the reduced sorption curves, that is c_t/c_{eq} as a function of $t^{1/2}$, where c_t is the concentration of vapour at time t and c_{eq} is the equilibrium concentration, at different activities for the freshly prepared sample AF.

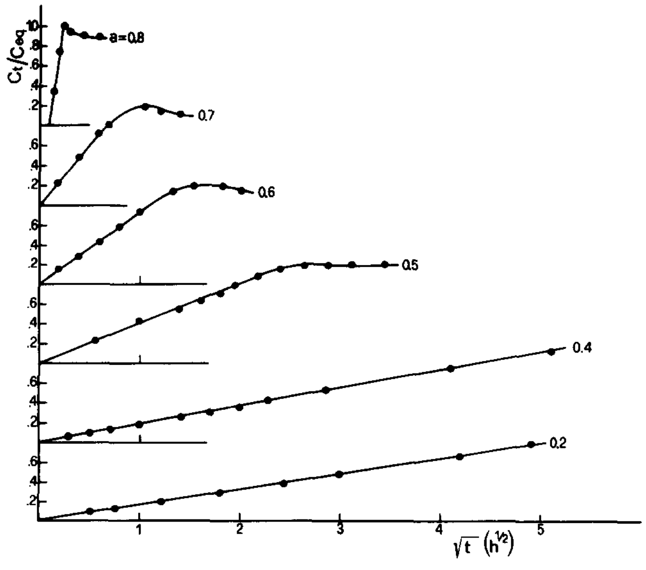

Figure 1 The reduced sorption curves, c_t/c_{eq}, as a function of $t^{1/2}$ (h$^{1/2}$), for the freshly prepared sample AF, at the indicated activities

All the curves show a linear increase of concentration with square root of time, a downward curvature and the equilibrium value of vapour concentration. This behaviour is typical of Fickian sorption curves; it is therefore possible, at each vapour activity, to derive[1] a mean diffusion coefficient, $\bar{D}$ (cm^2 s^{-1}), from the equation:

$$\frac{c_t}{c_{eq}} = \frac{4}{d}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{1}$$

where d is the thickness (cm) of the sample.

At penetrant activities higher than 0.6, after the attainment of the equilibrium concentration, a desorption of vapour is observed. This desorption can be associated with the process of solvent-induced crystallization. The amorphous PEEK is in fact prevented from crystallizing because it is in the glassy state; when, on increasing the vapour activity, the penetrant concentration is such as to lower the glass transition temperature below that of the experiment, crystallization can start, and we observe the rejection of a fraction of solvent, as already reported for other systems[11–13]. The crystals are in fact completely impermeable. The desorption becomes quicker and quicker on increasing the activity, and it depends on many factors: among these are the relative kinetics of crystallization with respect to the diffusion time, the critical concentration at which the crystallization starts and the thickness of the film. Also the level of crystallinity attained will depend on these factors[19].

The diffusion values $\bar{D}$, derived for each penetrant activity from equation (1), are mean values in the explored interval of concentration. To obtain the thermodynamic diffusion coefficient, 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 $\bar{D}$ on c_{eq} is of the exponential form:

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

in which γ is the concentration coefficient, related to the fractional free volume and to the effectiveness with which the penetrant plasticizes the polymer[2–5]. Therefore the logarithms of the $\bar{D}$ values, calculated from *Figure 1* and equation (1), are reported in *Figure 2* as a function of c_{eq}.

In the figure, two stages of behaviour are observed. At low penetrant concentration, corresponding to low activity, diffusion depends weakly on concentration; whereas after a critical activity, a steep dependence of diffusion on concentration is observed. The critical concentration, for observing the different behaviour, occurs at about 14% in the fresh sample. From the first zone it is possible to derive a zero-concentration diffusion parameter D_{01}, relative to the range of activity in which diffusion is weakly dependent on concentration; and from the second zone it is possible to extrapolate a D_{02} value, for this different zone of behaviour. The derived parameters are reported in *Table 1*, in which the γ coefficients obtained from equation (2) are also reported.

The possibility to observe a different diffusion behaviour, if a wide range of temperatures and activities are explored, has been discussed by Hopfenberg *et al.*[6]. In the first zone, owing to the low concentration of 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

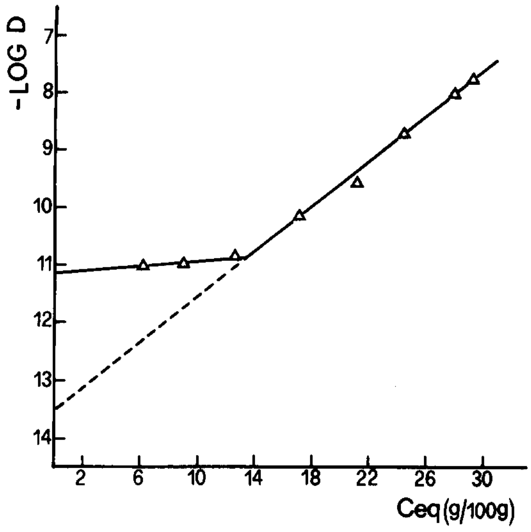

Figure 2 The negative logarithm of the mean diffusion coefficient, $-\log[D\ (\mathrm{cm}^2\ \mathrm{s}^{-1})]$, as a function of the equilibrium concentration, c_{eq} (g/100 g), for sample AF

Table 1 The zero-concentration diffusion coefficients, D_{01} ($\mathrm{cm}^2\ \mathrm{s}^{-1}$) and D_{02} ($\mathrm{cm}^2\ \mathrm{s}^{-1}$), and the concentration coefficients, γ_1 and γ_2, respectively, for the first and second zones of behaviour

Sample	$D_{01} \times 10^{12}$	γ_1	$D_{02} \times 10^{14}$	γ_2
AF	6.3	5.8	2.8	46
AA	2.6	13.5	1.8	47
*A*120	2.6	13.5	1.8	47

of chain segments. This region can be classified as a Fickian diffusion region below the glass transition temperature (stage I). When the concentration of penetrant reaches a critical value at a higher activity, the interaction between the penetrant and segments of chain allows molecular rearrangements, with a timescale less than that for diffusion, and we observe a diffusion coefficient much more dependent on concentration (stage II). We can expect that the solvent-induced crystallization will occur in the second zone.

In *Figures 3* and *4* the reduced sorption curves, c_t/c_{eq}, are reported as a function of square root of time respectively for sample AA, aged for many months at room temperature, and for sample A120, stored for 1 month at 120°C.

Sample AA shows Fickian sorption curves up to activity $a=0.6$; at this activity, a slow increase of concentration is observed for short times, whereas a steeper increase of sorption is observed after a critical value. An arrow in the figure indicates the point after which a second linear increase of sorption with $t^{1/2}$ is observed. At higher activities, again the sorption curves show an apparent Fickian behaviour, although in some cases the extrapolation of the linear part of the curve cannot be drawn through the origin. A curve passing through the origin would represent anomalous diffusion and not Fickian, as suggested.

Sample A120 shows the same behaviour, but the anomalous sorption curves appear at higher activities, $a=0.7$ and $a=0.75$, whereas again an apparent Fickian sorption curve is manifested at still higher values.

The logarithms of the diffusion values, derived from the Fickian curves, are reported in *Figure 5* as a function of concentration for samples AA and A120.

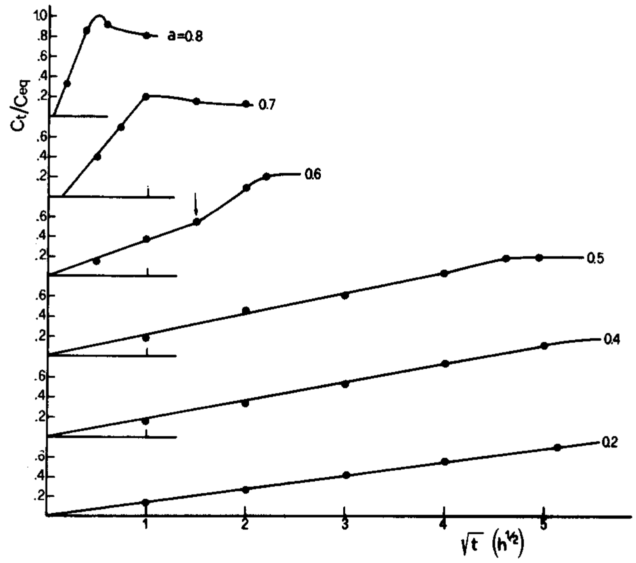

Figure 3 The reduced sorption curves, c_t/c_{eq}, as a function of $t^{1/2}$ ($\mathrm{h}^{1/2}$), for the aged sample AA, at the indicated activities

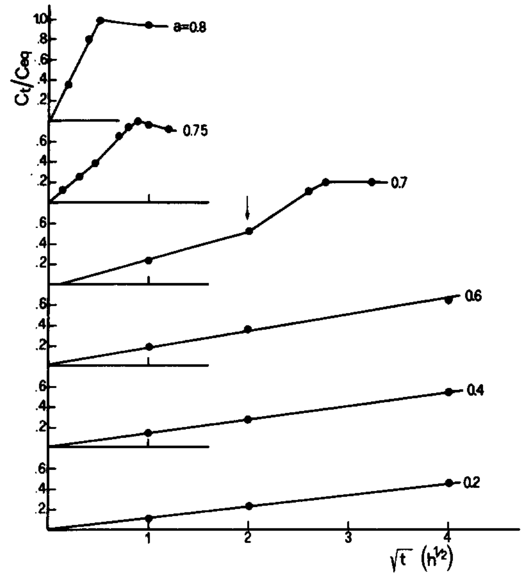

Figure 4 The reduced sorption curves, c_t/c_{eq}, as a function of $t^{1/2}$ ($\mathrm{h}^{1/2}$), for the aged sample A120, at the indicated activities

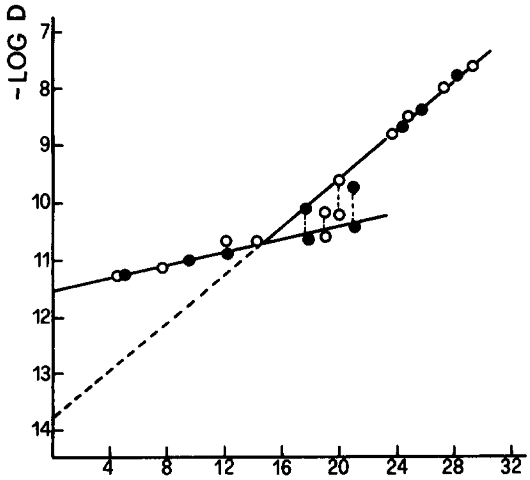

Figure 5 The negative logarithm of the mean diffusion coefficient, $-\log[D\ (\mathrm{cm}^2\ \mathrm{s}^{-1})]$, as a function of the equilibrium concentration, c_{eq} (g/100 g), for the aged samples AA (●) and A120 (○)

From the anomalous sorption curves, such as the kinked plots for $a=0.6$ in *Figure 3* and $a=0.7$ in *Figure 4*, it is meaningless to derive a value of the diffusion parameter $\bar{D}$. In fact, in the case of non-Fickian curves, geometric factors or relaxation effects, eventually operating during the diffusion process, prevent the utilization of transport models, which allow the determination of the diffusion parameters. Nevertheless, in a previous paper[10] we showed that, for atactic polystyrene, the diffusion parameters derived from the second linear part of the anomalous sorption curve fitted the same straight line as the parameters derived from the Fickian curves. In the present case of PEEK, two parameters were derived from the anomalous sorption curves, corresponding to the two stages, and these points are shown linked with broken lines in *Figure 5*. As is evident, the lower values fit the first straight line and the higher values fit the second straight line. This could be mere chance, but could also find an explanation in a future different model; therefore we prefer to report these points in *Figure 5*, although explaining that they are meaningless with the actual models.

For the aged samples three stages in the diffusion curve are observable. At low activity, and therefore low penetrant concentration, a linear dependence correlates diffusion and concentration, allowing the extrapolation to a zero-concentration diffusion coefficient D_{01}. At high activities (more than 0.7) a steeper dependence correlates diffusion and concentration, extrapolating to a lower zero-concentration diffusion coefficient D_{02}. At intermediate activities, between 0.6 and 0.7, an anomalous behaviour appears in the sorption curves, and the derived parameters are meaningless. Nevertheless we reported the values for the reasons explained above. In this range of activity, when the concentration of penetrant reaches a critical value, the interaction between the penetrant and longer and longer segments of chain allows molecular rearrangements, and we observe the anomalous behaviour.

The derived values of D_{01} and D_{02} are reported in *Table 1* and compared with the values of the fresh sample.

The ageing of the samples at room temperature and at 120°C has an influence on both D_{01} and D_{02}, although the influence on the second parameter is less. Ageing produces a decrease of free volume and related molecular mobility, and this is well reflected in a decreased diffusion coefficient and an increased concentration coefficient. Furthermore, the increase of the relaxation times leads to the appearance of anomalous sorption curves in a definite activity range.

Sorption behaviour

In *Figure 6* the equilibrium concentration of penetrant is reported as a function of dichloromethane activity $a=p/p_T$, for the fresh sample AF and the aged samples AA and A120. The sorption curves show different zones of behaviour: At low activity there is a linear dependence of sorption on activity, typical of ideal penetrant–polymer systems, following Henry's law. In this zone the diffusion is weakly dependent on concentration, as expected. After a critical activity, a more than linear dependence of c_{eq} on activity is observed, demonstrating an increased interaction, in agreement with the diffusion results. At still higher activities a maximum in the curve indicates that the samples, after the maximum, underwent the process of solvent-induced crystallization, showing a lower sorption than expected, since the crystallized fraction is impermeable.

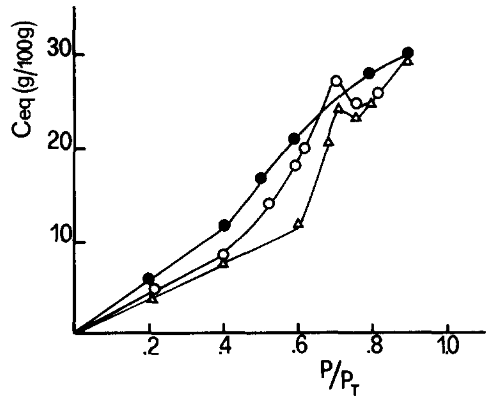

Figure 6 The equilibrium concentration of dichloromethane vapour as a function of the activity, $a=p/p_T$, for samples AF (●), AA (○) and A120 (△)

At low activity, where the behaviour is ideal, the level of sorption can be correlated with the free volume of the sample and the fraction of permeable phase. The diffusion values of the aged samples show that they have a lower free volume than the fresh sample; therefore the lower sorption can be explained. The comparison between the two aged samples, which have the same diffusion behaviour and the same values of D_{01} and D_{02}, needs a different explanation. In fact, the lower sorption of sample A120 with respect to sample AA cannot be explained by a lower free volume. We can hypothesize that annealing at a temperature slightly below T_g produces ordered zones in the sample, or increases the dimensions of ordered zones possibly present in the amorphous sample. When the ordered zones reach a critical dimension, they become impermeable to dichloromethane at low activity, producing a lower sorption than expected. At higher activities they can become permeable, and in fact we observe the same sorption as sample AA after activity $a=0.75$. The presence of local order in amorphous PEEK was observed when the polymer was melted below the equilibrium melting temperature[20], and also for other non-crystalline polymers, the presence of ordered zones was hypothesized[21]. The ordered domains can have such dimensions to be impermeable to the vapour at low activity, becoming permeable at a critical activity. This same suggestion was proposed for atactic polystyrene, showing the same behaviour after annealing at 70°C[10].

Solvent-induced crystallization

The crystallization of the amorphous samples after sorption at different activities was investigated by wide-angle X-ray scattering and infra-red analysis.

The X-ray diffractograms (WAXD) of crystalline PEEK have been well studied, and also the possibility to derive the crystallinity from WAXD has been reported[22].

In *Figure 7* the WAXD of the three samples, AF, AA and A120, immersed in liquid dichloromethane at 25°C and desorbed for many days under vacuum are reported, and compared with the WAXD of the amorphous PEEK. The liquid-induced crystallization is evident for all the samples, although, from the WAXD, a not well developed crystalline form can be inferred. In fact, among the strongest peaks of crystalline PEEK

($2\theta = 18.5°$, 20.6°, 22.5° and 28.5°), only that at 18.5° is very evident. The peak at 20.6° is either hardly evident (samples AF and A120) or absent (sample AA). The peak at 28.5° is very small and broad for all the crystallized samples, whereas that at 22.5° is completely absent. This result indicates that the crystalline form, obtained by SINC, is very disordered and/or of small dimensions. Previously other authors found that the ordered regions produced by SINC in liquid dichloromethane are different from those formed by thermal treatments[14,17].

The WAXD of samples exposed to dichloromethane in the vapour activity range and dried show that crystallization is induced at activity 0.7 for all the samples. Also for these samples the diffractograms show that only the peak at $2\theta = 18.5°$ is very intense, whereas the other peaks are very small or absent. From the WAXD the crystallinity was derived by comparing the crystalline area (subtracting the amorphous area) with the total area.

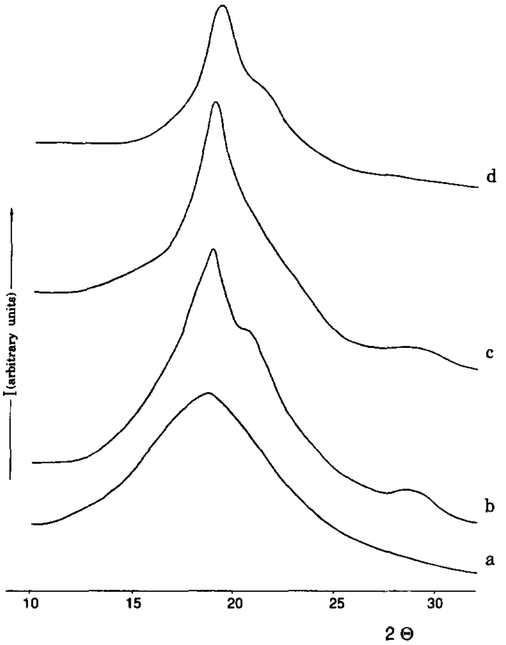

Figure 7 Wide-angle X-ray diffractograms of sample AA before sorption (a), and samples AF (b), AA (c) and A120 (d) after immersion in liquid dichloromethane and drying

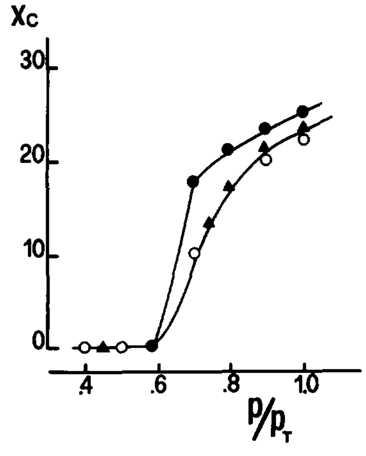

Figure 8 The crystallinity, x_c, derived from the diffractograms, as a function of the vapour activity to which the samples had been exposed, for samples AF (○), AA (●) and A120 (▲)

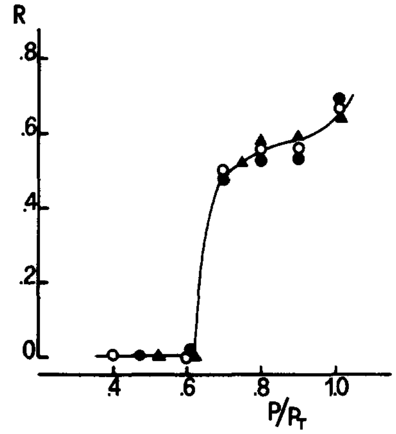

Figure 9 The ratio $R = A_{966}/A_{851}$ of the absorbance of the infra-red bands as a function of the vapour activity to which the sample had been exposed, for samples AF (○), AA (●) and A120 (▲)

The calculated crystallinity is reported in *Figure 8* as a function of the vapour activity to which the samples had been exposed. All the samples start crystallizing at activity $a = 0.7$; after a sharp increase, the value of crystallinity increases linearly up to the maximum value, which is slightly lower for the fresh sample AF.

Infra-red analysis has also been used to detect the onset of crystallization in amorphous PEEK. Comparing the infra-red spectra of amorphous and crystalline PEEK, it is evident that some bands become both sharper and more intense[23]. In particular, we used the absorbance of the band at 966 cm^{-1}, A_{966}, normalized by the absorbance of the band near 951 cm^{-1}, A_{951}. A correlation of the intensity of this band and the crystallinity measured by WAXD was reported[23].

In *Figure 9* we report the ratio $R = A_{966}/A_{951}$ as a function of the vapour activity to which the sample had been exposed, for all the samples. We observe a sharp increase of R at activity 0.7, a nearly constant value up to activity 0.9 and a further increase at activity $a = 1$. From the previously reported correlation between this ratio and the X-ray crystallinity[23], we derive for the samples crystallized in the liquid, at activity $a = 1$, a value of crystallinity of 25%, in good agreement with the value obtained by WAXD (see *Figure 7*).

CONCLUSIONS

The diffusion behaviour of dichloromethane in glassy amorphous PEEK of thickness 0.0025 cm shows different zones. At low penetrant activity we observe Fickian sorption curves, characterized by diffusion coefficients poorly dependent on concentration, that extrapolate to a zero-concentration diffusion coefficient D_{01}. At high penetrant activity the diffusion becomes strongly dependent on concentration, extrapolating to a much lower zero-concentration diffusion coefficient D_{02}.

Ageing produces a decrease of both D_{01} and D_{02}, in agreement with a decrease of free volume in the sample. Furthermore, for the aged samples we observe an intermediate zone of activity in which the interaction between the penetrant and segments of chain allows molecular rearrangements with a timescale comparable with diffusion, and we observe anomalous sorption curves.

Also, sorption is influenced by ageing, and we observe a lower sorption for the aged samples, explainable by a lower free volume, reflected also in a lower diffusion. However, the comparison between the two aged samples, one at room temperature and the other at 120°C, having the same diffusion parameters, suggests that ageing at a temperature slightly below T_g produces, in the amorphous sample, ordered zones impermeable to the vapour at low activity.

The process of solvent-induced crystallization is activated for all the samples at activity $a = 0.7$, although the fresh sample reaches a crystallinity lower than the aged samples. The X-ray analysis shows that the crystalline form obtained by SINC is very disordered and/or of small dimensions. A good agreement has been found between the values of crystallinity obtained by X-rays and infra-red measurements.

ACKNOWLEDGEMENT

This work was supported by Progetto Finalizzato 'Materiali Speciali per Tecnologie Avanzate'.

REFERENCES

1 Crank, J. and Park, G. S. 'Diffusion in Polymers', Academic Press, London, 1968

2 Rogers, C. E. 'Physics and Chemistry of the Organic Solid State', Interscience Publishers, New York, 1965

3 Peterlin, A. *J. Macromol. Sci.–Phys. (B)* 1975, **11**, 57

4 Hopfenberg, H. B. 'Permeability of Plastic Films and Coatings to Gases, Vapors and Liquids', Plenum Press, New York, 1974

5 Rogers, C. E. 'Polymer Permeability' (Ed. J. Comyn), Elsevier Applied Science, London, 1985, p. 11

6 Hopfenberg, H. B. and Stannet, V. 'The Physics of Glassy Polymers' (Ed. R. N. Howard), Applied Science, London, 1973, p. 504

7 Berens, A. R. and Hopfenberg, H. B. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1957

8 Alfrey, T. *Chem. Eng. News* 1965, **43**, 64

9 Hopfenberg, H. B. and Frish, H. L. *J. Polym. Sci. (B)* 1969, **7**, 405

10 Vittoria, V. and Ruvolo Filho, A. *J. Appl. Polym. Sci.* 1992, **44**, 2127

11 Zachmann, H. G. Z. *Z. Kolloid Polym.* 1963, **189**, 67

12 Rebenfeld, L., Makarewicz, P. S., Weighmann, H. D. and Wilkes, G. L. *J. Macromol. Sci.–Rev. Macromol. Chem. (C)* 1976, **15** (2), 279

13 Durning, C. J. and Russel, W. B. *Polymer* 1985, **26**, 119

14 Grayson, M. A. and Wolf, C. S. *J. Polym. Sci., Polym. Phys. Edn.* 1988, **26**, 2145

15 Stober, E. J. and Seferis, S. C. *Polym. Eng. Sci.* 1988, **28**, 634

16 Stober, E. J., Seferis, J. C. and Keenan, J. D. *Polymer* 1984, **25**, 1845

17 Mensitieri, G., Del Nobile, M. A., Apicella, A. and Nicolais, L. *J. Mater. Sci.* 1990, **25**, 2963

18 Kemmish, D. J. and Hay, J. N. *Polymer* 1985, **26**, 905

19 Vittoria, V. and Riva, F. *Macromolecules* 1986, **19**, 1975

20 Huiy Nguyen, X. and Ishida, H. *J. Polym. Sci. (B) Polym. Phys.* 1986, **24**, 1079

21 Keinath, S. E., Miller, R. L. and Rieke, J. K. 'Order in the Amorphous State of Polymers', Plenum Press, New York, 1987

22 Blundell, D. J. and Osborn, B. N. *Polymer* 1983, **24**, 953

23 Chalmers, J. M., Goskin, W. F. and Mackenzie, M. W. *Polym. Bull.* 1984, **11**, 433