Permeability of PEEK to Carbon Dioxide

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SYNOPSIS

Sorption and diffusion of carbon dioxide were measured in amorphous and crystalline poly(aryl-ether-ether-ketone) or PEEK, at different temperatures. The sorption follows Henry's law at all the investigated temperatures, and the reduction of sorption in the crystalline sample corresponds to the reduction of the amorphous phase as derived from X-rays. Due to a more tortuous path, the diffusion parameter in the crystalline sample is lower than in the amorphous one, whereas the activation energy of the diffusion process is similar for both the samples. The permeability to carbon dioxide was very low, comparable, or lower than other rigid polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The permeation of gases and vapours through polymeric films is a relevant topic in itself for technological applications of the material.[1,2] Moreover, the study of transport properties turned out to be a useful tool for obtaining information on the structural organization of the permeable phase.[3-5] In semicrystalline materials it has been generally found that the crystalline phase is impermeable to most gases and vapours, at least at low activity or low pressure of penetrant. In this case the permeable phase is the amorphous component, and therefore the obtained information mainly regards the microstructure of this component.[6-8]

Recently we found that semicrystalline samples of poly(aryl-ether-ether ketone) or PEEK, crystallized from the glassy state, contain a fraction of amorphous phase impermeable to the vapours of dichloromethane at low activity.[9] Already recognized by other authors[10] through thermal analysis, this fraction, named "rigid amorphous fraction," is present in poorly crystallized samples; and its presence and organization can affect the properties of the sample. We interpreted the impermeability of this fraction of the amorphous phase as due to the presence of "noncrystalline ordered zones," of such dimensions to be impermeable to the vapours of dichloromethane.

In this article we present the results of permeability of carbon dioxide in amorphous and crystalline samples of PEEK, with the aim to investigate the behaviour of the noncrystalline phase to the transport of a gas at different temperatures.

EXPERIMENTAL

Amorphous 25-μm thick films (sample A) were kindly supplied by ICI (Middlesbrough, Cleveland, U.K.). A crystalline film (sample B) was obtained by annealing sample A for 2 h at 260°C. In these conditions a fraction of the amorphous phase, not mobilized at the glass transition and impermeable to dichloromethane vapour, was formed.[9-10]

Differential scanning calorimetry (DSC) was carried out over the temperature range 0–450°C using a Mettler TA 3000 DSC purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 10 mg at a heating rate of 20°C min^{-1}.

Wide Angle X-ray diffractograms were obtained by using a PW 1050 Philips powder diffractometer (CuKα Ni filtered radiation). The scan rate was 2° φ min^{-1}. From the diffractogram the crystallinity was derived, as reported elsewhere.[11] Permeability measurements were conducted with a previously reported experimental approach.[12,13] It is based on the

detection of the gas pressure as function of time; the pressure decay gives the quantitative measurements of the gas transferred from the gas phase to the sample. Therefore it allows the determination of the equilibrium sorption, C_{eq}, at a given gas pressure, and of the diffusion coefficient D, from the initial stage of the sorption phenomenon.

RESULTS AND DISCUSSION

Transport Properties

In Figure 1 the equilibrium concentration of gas, C_{eq}, expressed in cm^3 (SPT) of carbon dioxide per cm^3 of bulk polymer, was reported for samples A and B as a function of the pressure P (atm) at 30 and 60°C. Although the two chosen temperatures were below the glass-transition temperature of the samples, we observed that the solubility was a linear function of the pressure, according to Henry's law:

$$C_{eq}(P) = S \times P$$

where S is the sorption coefficient. As expected, the sorption coefficient was lower for the crystalline sample B, and it decreased with the temperature for both samples. It is important to point out that the

pressure range studied is very restricted, limiting the possibility to see any "dual mode" curvature within this range.

In Figure 2 the diffusion coefficient, D (cm^2/s), derived from the early stage of increase of weight of the sample, is reported as a function of equilibrium concentration for samples A and B. The coefficient D can be dependent on the pressure and on the equilibrium concentration, C_{eq}; generally in systems following Henry's law, the coefficient D is independent of pressure, and, at any pressure, it can be assumed equal to D_0, the thermodynamic diffusion coefficient. As matter of fact, we observed a diffusion coefficient constant with the equilibrium concentration of sorbed gas, for the amorphous sample, as well as for the crystalline one. Its mean value therefore represents the thermodynamic diffusion coefficient D_0, at different temperatures. The diffusion coefficients for the two samples, the amorphous and the crystalline PEEK, are reported in Table I.

It appeared that at any temperature the diffusion coefficient for the amorphous sample was slightly higher than that of the crystalline one. This correlated with the tortuosity of the path for the diffusing penetrant molecules in the crystalline sample.[3-5] The impermeable crystals were obstacles, compelling the penetrant molecules through a longer path.
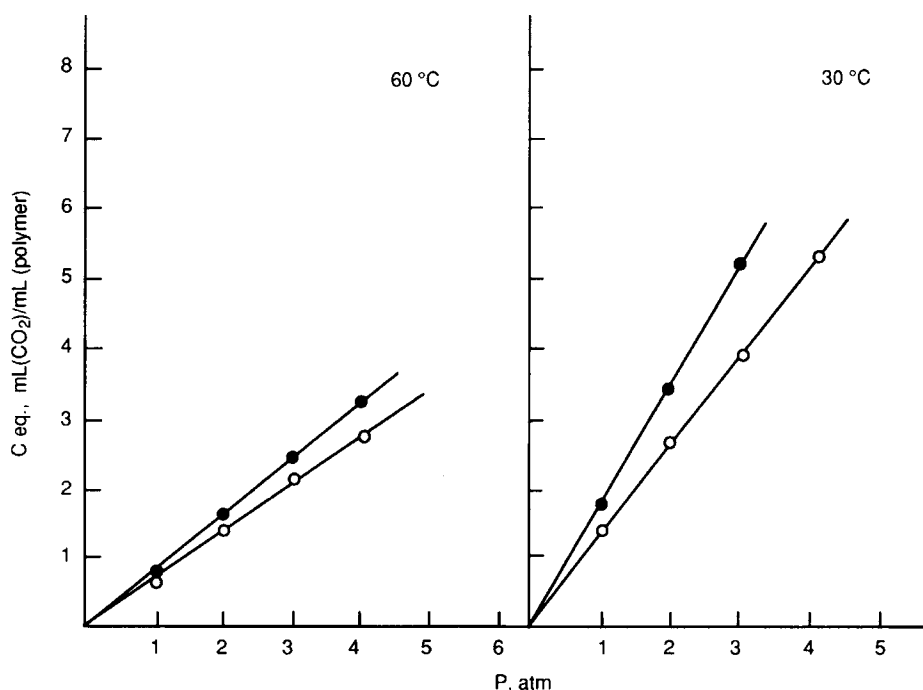

Figure 1   The equilibrium concentration of carbon dioxide, C_{eq} expressed as cm^3 gas (SPT)/cm^3 bulk polymer, is reported for and the amorphous sample A (●) and (○) the crystalline sample B as a function of the pressure at 30 and 60°C.
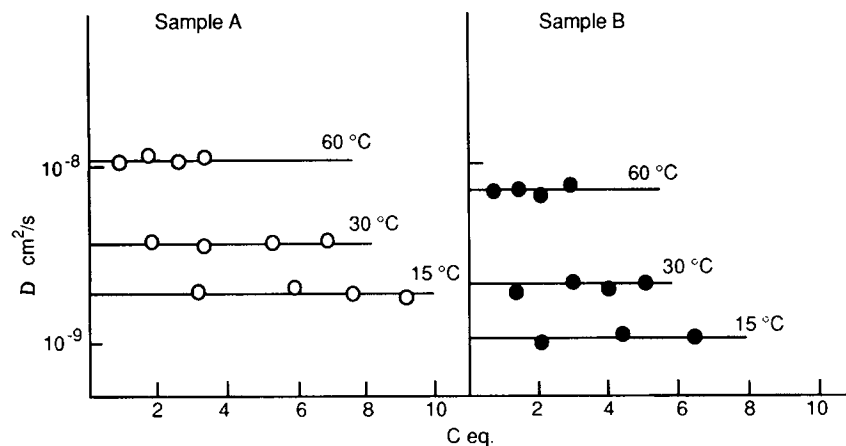
Figure 2 The diffusion coefficient, D cm^2/s, is reported as a function of the equilibrium concentration for (O) the amorphous sample A, and (●) the crystalline sample B, at 15, 30, and 60°C.

In Figure 3, D_0 values obtained for samples A and B, are reported as a function of $1/T$, giving two different straight lines with a similar slope. According to the Arrhenius law, the slope gives $E_a = 34.3$ kJ/mol as the activation energy for the diffusion process. This value is well in agreement with a Fickian activated process. It is very similar with the value of activation energy for the transport of carbon dioxide in polymethyl methacrylate at 25°C, which resulted in 33.1 kJ/mol.[14] From the value of sorption and diffusion at 30°C, it is possible to derive the permeability to carbon dioxide of PEEK amorphous and crystalline films. In fact the permeability is the product of sorption and diffusion:

$$P = S \times D$$

and it resulted in 6.1×10^{-9} and 2.4×10^{-9} cm^3 (STP)/cm $\times$ s $\times$ atm, respectively, for the amorphous and the crystalline sample. The permeability of PEEK to CO$_2$ was one order of magnitude lower than that of polyethyl methacrylate and biaxially oriented polystyrene.[14]

Permeability of Noncrystalline Phase

The crystallization of PEEK from the glassy state produced a fraction of the amorphous phase, which was not mobilized at the glass transition, and, for this reason, was named "rigid amorphous phase."[10] We called it "noncrystalline ordered phase," because this fraction, although not crystalline, is impermeable to CH$_2$Cl$_2$ at low activity; therefore the crystallinity, derived from sorption measurements, was higher than that derived from X-ray and DSC measurements.[9]

It was interesting to investigate whether this phase was impermeable to carbon dioxide as well. For this reason we determined the crystallinity of sample B with different methods, and compared the obtained values with the reduction of sorption of CO$_2$ at 30°C. In fact, assuming that the specific sorption of the amorphous phase is the same in all samples, the reduction of sorption in the crystalline sample B is due to the reduction of the amorphous fraction (x_a):

$$C_{eq}/x_a = C_{sp}.$$

From the sorption of the amorphous sample A, assumed as specific sorption, it was possible to derive x_a in the crystalline sample B, and compare this value with that obtained with different methods.

In Figure 4 the wide angle X-ray diffractogram and in Figure 5 the differential scanning calorimetric curve are reported for sample B. The crystallinity was derived from the diffactogram by comparing the area under the crystalline peaks, subtracting the
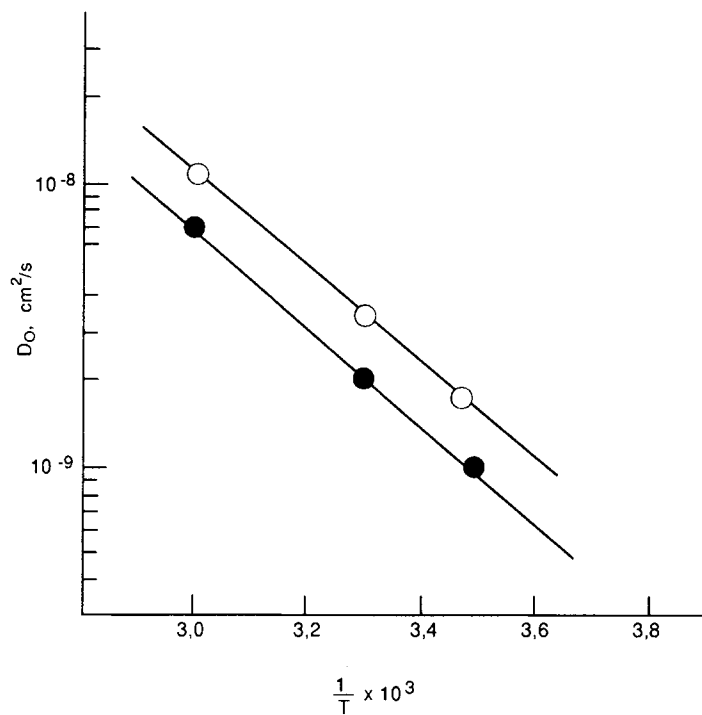
Table I Diffusion Coefficients, D_0 cm^2/s

Temperature (°C)	Sample A	Sample B
15	1.9×10^{-9}	1.1×10^{-9}
30	3.6×10^{-9}	2.0×10^{-9}
60	1.1×10^{-8}	7.1×10^{-9}

Figure 3   The thermodynamic diffusion coefficient D_0 cm^2/s is reported as a function of $1/T$ for (O) the amorphous sample A and (●) the crystalline sample B.
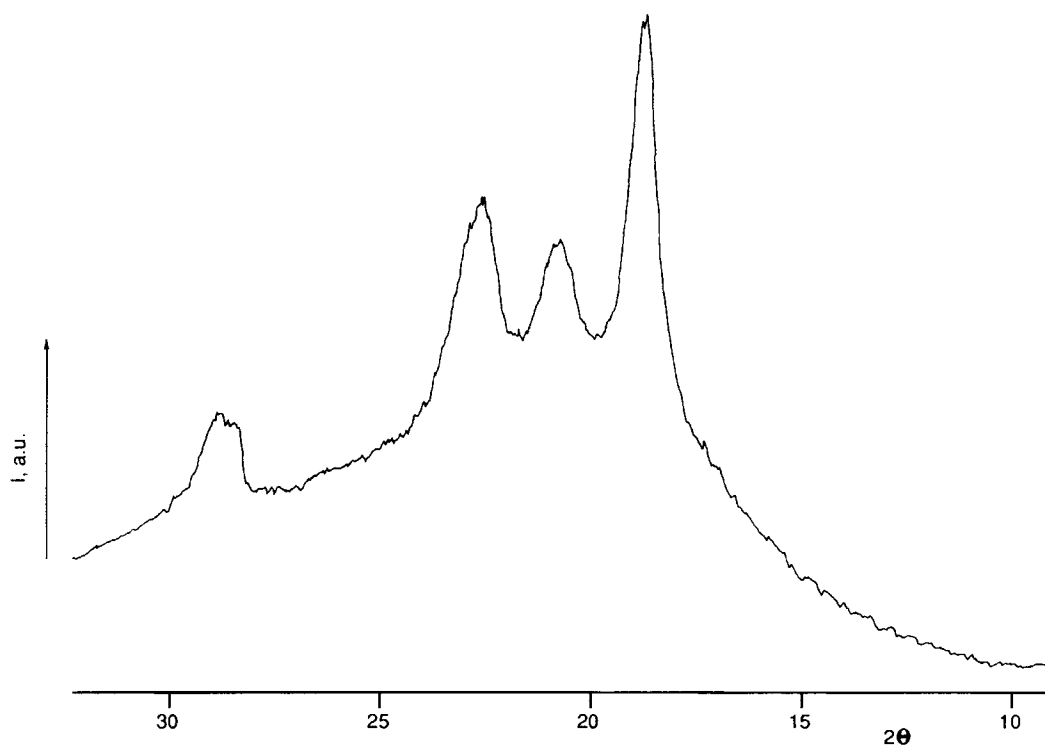

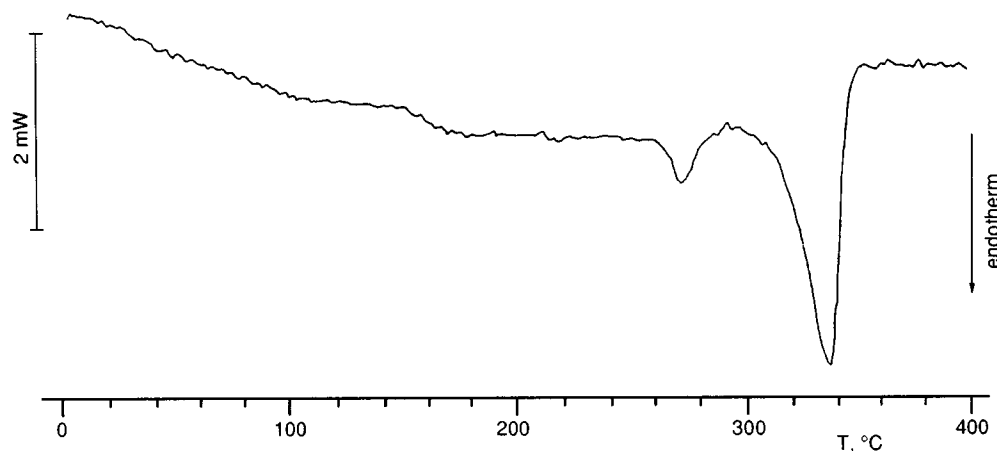**Figure 4**   The wide angle X-ray diffractogram of the crystalline sample B.

Figure 5   The DSC curve of the crystalline sample B.

amorphous area, and the total area[11]; from the DSC curve the crystallinity was obtained dividing the melting enthalpy by the value of the thermodynamic melting enthalpy, 130.0 J/g.

The values of crystallinity obtained with X-ray were 0.26, with DSC were 0.30, and with sorption were 0.25.

It is evident that the fraction of phase, permeable to carbon dioxide, was coincident with the amorphous fraction as derived from X-rays, and very near to the amorphous fraction, obtained from DSC.

For the crystalline sample B, the amorphous fraction, not mobilized at the glass transition, was about 0.5.[9] It is therefore evident that the rigid amorphous fraction is permeable to CO_2, and behaves, as far as the transport of this gas is concerned, as the mobile amorphous phase.

CONCLUSIONS

The study of sorption of CO_2 in crystalline and amorphous PEEK showed that the reduction of sorption in the crystalline sample corresponded to the reduction of the amorphous phase, as derived from X-ray measurements. This result indicates that the rigid amorphous fraction behaves, as far as the permeability is concerned, as the more mobile amorphous fraction. It is worth noting that there was very good agreement between the crystallinity derived either from X-rays and DSC, or from the sorption level.

The sorption of the gas follows Henry's law up to the highest investigated pressure, and the diffusion coefficient was found independent of concentration. Due to the tortuosity of the path, the diffusion coefficient was lower in the crystalline sample than in the amorphous one. The activation energy

for the diffusion was typical of an activated process and gave the same value for both the samples. The permeability of this polymer to carbon dioxide was very low, comparable to other rigid polymers.

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