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Transport properties of the mesomorphic form of poly(ethylene terephthalate)

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The mesomorphic form of poly(ethylene terephthalate), present in samples drawn at 60°C at a draw ratio of 4, was studied by analysing the transport properties of dichloromethane vapours. The reduced sorption with respect to the amorphous sample indicates that the mesophase is impermeable to the vapours at low activity, and this allows the determination of the fraction of mesophase in the drawn samples. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); transport properties; mesomorphic form)

Introduction

Poly(ethylene terephthalate) (PET) is the most commercially important polyester, and many authors have investigated the correlations between the structural organization and the properties of this polymer. Beside the crystalline and amorphous phases, a mesomorphic form of PET has often been recognized and described[1-7]. It can be obtained by drawing amorphous samples at temperatures below glass transition, and shows a well defined X-ray diffraction pattern[6,7]. It is transformed into the crystalline phase at temperatures higher than 80°C[8].

The transport properties, sorption and diffusion, are very useful in investigating the amorphous component of a polymer, even when a mesophase is present[9-13]. In many cases, the mesophase has proved impermeable to vapours at low activity, behaving like the crystalline phase. This study is therefore important from the technological point of view, since the possibility of improving the impermeability of PET films is required for many applications.

The aim of this paper is to investigate the sorption and diffusion of dichloromethane in the mesomorphic form of PET, obtained by drawing, and compare them to the transport properties of a completely amorphous PET sample, thus obtaining information on the permeability of the mesophase.

Experimental

PET pellets with an intrinsic viscosity of 0.84 dl g^{-1} were kindly supplied by Montefibre S.p.A. Amorphous films (sample A) were obtained by moulding, at 290°C, the pellets into a 0.1 mm thick film and quenching at 0°C in an ice–water bath. The films were drawn in an Instron Mod. 4301 up to a draw ratio of 4 at 60°C (sample B). These conditions have been used by other authors to obtain the mesomorphic form of PET.

The transport properties were measured according to a previously described[14] microgravimetric method, using a quartz spring balance with an extension of 20 mm mg^{-1}. The penetrant used was dichloromethane and the temperature was 25°C. Sorption was measured as a function of the vapour 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.

Wide angle X-ray diffraction (WAXD) patterns were obtained using a Seifert Debyeflex 1001 diffractometer with photographic recording in a cylindrical camera of 114.6 mm radius; Cu Kα-Ni filtered radiation was used.

Results and discussion

Figure 1 shows the photographic records of samples A (a) and B (b). Sample A shows the characteristic halo of unoriented amorphous PET samples, centred at 19.5° of 2ϑ. In sample B the halo is mainly concentrated on the equator, due to the orientation process. At our drawing temperature of 60°C stress-induced crystallization does not occur, due to the limited mobility below the glass transition temperature. In fact, only very weak crystalline reflections concentrated on the equator can be observed, indicating incipient crystallization. The X-ray pattern appears more characteristic of the anisotropic non-crystalline phase, already described as mesophase[6,7]. The presence of a meridional reflection at 43° of 2ϑ confirms the presence of the mesophase. We can, therefore, conclude that drawing at 60°C oriented the sample without allowing stress-induced crystallization but producing a fraction of mesophase.

The transport properties, sorption and diffusion, of dichloromethane in sample B were investigated and compared with those of sample A. In the transport of vapours in glassy polymers, diffusion and molecular relaxation phenomena can be coupled phenomena, taking place in a similar time scale and demonstrating a non-Fickian behaviour[15].The transport of dichloromethane in PET shows Fickian characteristics for sample A, tested a few days after preparation; for sample B non-Fickian anomalies are evident, particularly at low activities. Nonetheless, at intermediate activities, it was possible to derive a reliable diffusion coefficient. Generally diffusion shows an exponential dependence on concentration; it is therefore possible to extrapolate to

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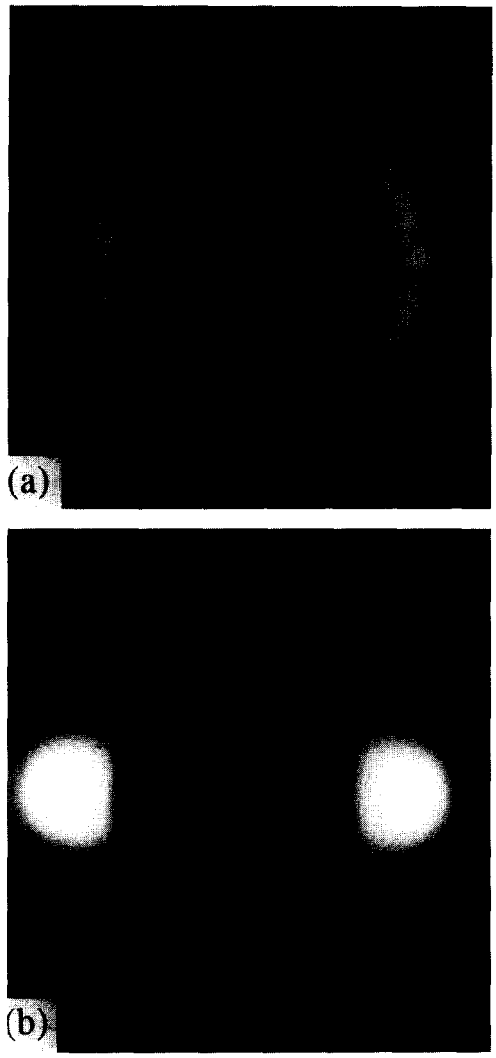

Figure 1 Photographic record of the WAXD of samples A (a) and B (b)

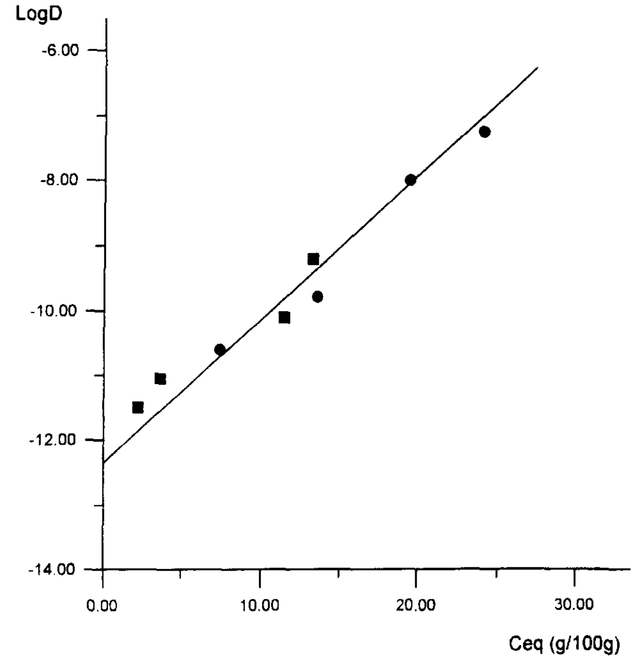

Figure 2 Logarithm of the diffusion coefficient, D ($cm^2 s^{-1}$), as a function of equilibrium concentration, c_{eq} (wt%), for samples A (●) and B (■)

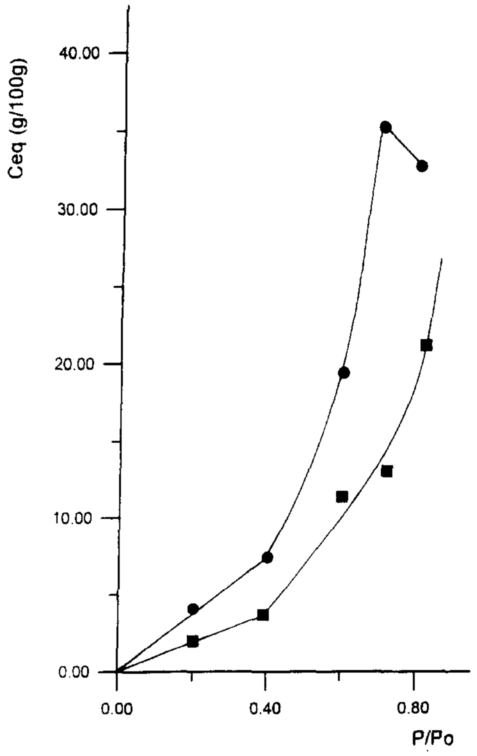

Figure 3 Equilibrium concentration c_{eq} (wt%) as a function of vapour activity, p/p_0, for samples A (●) and B (■)

zero penetrant concentration, obtaining the thermodynamic diffusion parameter D_0 which is related to the fractional free volume and thermodynamic state of the permeable phase.

In *Figure 2* the logarithm of the diffusion coefficient, D ($cm^2 s^{-1}$), is reported as a function of concentration for the two samples. The experimental points for the drawn sample B fit the same straight line as the amorphous sample A, and the extrapolated values of D_0, at zero concentration of penetrant, are coincident at $4.5 \times 10^{-13} cm^2 s^{-1}$. This result allows us to suggest that the amorphous phase is the only permeable phase. For sample B, in fact, the question whether the mesophase component contributes to penetrant diffusion can be answered by the results shown in *Figure 2*. The coincidence of D_0 for the two samples leads to the conclusion that the mesophase does not contribute to diffusion, and that the amorphous component in both samples behaves in a similar way. Neither the orientation nor the different tortuosity of the penetrant path influence the value of the zero concentration diffusion coefficient D_0.

It is worth noting that the orientation does not substantially change the value of D_0 as, instead, happens in semicrystalline polymers. In that case, a dramatic decrease of the D_0 coefficient, associated with the orientation of the samples, was found[15–17]. On the contrary, we found that the orientation in an amorphous polymer, as atactic polystyrene, does not decrease the diffusion coefficient[18]. In the present case, the presence of a mesophase does not reduce the diffusion parameter of the amorphous component.

In *Figure 3* the equilibrium concentration of vapour, c_{eq} (wt%) is plotted as a function of vapour activity at

25°C. Sample B shows sorption lower than that of the amorphous sample A at all the activities. If we assume that the mesophase neither allows diffusion nor sorbs the penetrant, the reduction of sorption can be related to the reduction of the amorphous phase due to the presence of the mesophase. The reduction of sorption can be associated neither to the crystallinity, which is very small, nor to the orientation of the chains in the sample; if that were the case, we would have observed a much lower diffusion coefficient. In the case of oriented semicrystalline polymers, the reduction of the diffusion coefficient is many orders of magnitude larger than the reduction of sorption.

It is possible to derive the fraction of mesophase from the reduction of sorption. If the specific sorption of the amorphous sample is the same in the two samples at low vapour activity, the equilibrium sorption of the drawn sample is reduced by the amorphous fraction, according to the equation:

$$c_{\mathrm{eq}} = c_{\mathrm{sp}} X_{\mathrm{a}} = c_{\mathrm{sp}}(1 - X_{\mathrm{m}}) \qquad (1)$$

where c_{sp} is the equilibrium concentration of the amorphous sample, X_{a} and X_{m} are the fractions of amorphous phase and mesophase, respectively. The fraction of mesophase, derived from the sorption at low activity from equation (1), is 0.55. This value is well in agreement with the fraction of mesophase derived for samples drawn at a similar draw ratio at 50°C[8].

We can conclude, therefore, that the mesophase, present in samples of PET drawn at temperatures below glass transition, is impermeable to the vapours of dichloromethane. Furthermore, the reduction of sorption, with respect to the completely amorphous sample allows the determination of the fraction of mesophase.

Work is in progress to investigate mesophases obtained at different drawing temperatures and draw ratios, and also the behaviour of the mesophase in samples in which the crystalline phase is also present.

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References

1 Bonart, R. *Kolloid-Z.* 1966, **213**, 1

2 Prevorsek, D. C. *J. Polym. Sci. (C)* 1971, **32**, 343

3 Lindner, W. L. *Polymer* 1973, **14**, 9

4 Napolitano, M. J. and Moet, A. J. *J. Appl. Polym. Sci.* 1987, **34**

5 Fakirov, S. and Evstatiev, M. *Polymer* 1990, **31**, 431

6 Auriemma, F., Corradini, P., De Rosa, C., Guerra, G., Petraccone, V., Bianchi, R. and Di Dino, G. *Macromolecules* 1992, **25**, 2490

7 Nicholson, T. M., Davies, G. R. and Ward, I. M. *Polymer* 1994, **35**, 4259

8 Sun, T., Zhang, A., Li, F. M. and Porter, R. S. *Polymer* 1988, **29**, 2115

9 Vittoria, V. *J. Polym. Sci. Polym. Phys. Ed.* 1986, **24**, 451

10 Vittoria, V., Ruvolo, A. and de Candia, F. *J. Macromol. Sci. Phys.* 1990, **B29**, 411

11 Michele, A. and Vittoria, V. *Polym. Commun.* 1991, **32**, 232

12 de Candia, F., Ruvolo, A. and Vittoria, V. *J. Macromol. Sci. Phys. Ed.* 1992, **B31**, 133

13 de Candia, F., Guadagno, L. and Vittoria, V. *J. Macromol. Sci. Phys. Ed.* 1995, **B34**, 279

14 Araimo, L., de Candia, F., Vittoria, V. and Peterlin, A. *J. Polym. Sci. Phys. Ed.* 1978, **16**, 2087

15 Hopfenbergh, H. B. and Stannett, V. in 'The Physics of Glassy Polymers' (Ed. R. N. Howard), Applied Science Publications, London, 1973

16 de Candia, F., Russo, R., Vittoria, V. and Peterlin, A. *J. Polym. Sci. Phys. Ed.* 1982, **20**, 269

17 Vittoria, V., de Candia, F., Capodanno, V. and Vittoria, V. *J. Macromol. Sci. Phys.* 1986, **B25**, 365

18 Vittoria, V. and Ruvolo Filho, A. *J. Appl. Polym. Sci.* 1993, **49**, 257