Investigation of the ageing of isotactic polypropylene via transport properties

V. Vittoria
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia del CNR, Via Toiano 6, 80072 Arco Felice, Naples, Italy
(Received 21 October 1987; revised 20 November 1987; accepted 24 November 1987)

Transport properties of a crystalline and a smectic film of isotactic polypropylene were investigated as a function of ageing time at room temperature. The results of density measurements, infra-red analysis and transport parameters support two different mechanisms of ageing. The first, very rapid, consists of a decrease of the amorphous fraction. The second, which is superimposed on the first, consists of a progressive reduction of mobility of the amorphous component. This second effect can be completely erased by a thermal treatment of the samples.

(Keywords: isotactic polypropylene; smectic form; crystalline form; physical ageing; thermoreversibility of ageing)

INTRODUCTION

The phenomenon of physical ageing is very interesting from both a theoretical and a practical point of view[1,2]. The changes that can occur in a material with ageing can affect its application, performance and lifetime; therefore a study of this effect is very important.

Isotactic polypropylene (iPP), crystallized or quenched rapidly from the melt, undergoes a strong enhancement of mechanical properties and an increase of density during ageing at room temperature[3-11]. This effect has principally been studied on the smectic form of iPP[3-6], obtained by quenching the polymer melt at low temperatures, but ageing of the monoclinic form is also reported[7-9]. All the interpretations of this effect point out that the processes due to the ageing phenomenon occur in the amorphous and intercrystalline regions. As a matter of fact during ageing of iPP all the authors noticed the absence of changes in the X-ray diffraction pattern, infra-red spectrum and electron diffraction pattern. However, the real nature of this phenomenon is still in debate.

The transport properties can be used as a molecular probe sensitive to structural changes in the amorphous component[12,13]. The crystalline component is assumed to be completely impermeable, and the transport parameters can be related to the thermodynamic properties of the amorphous component and to the morphology of the system.

We have already reported a study of the dependence of transport parameters on ageing time for a film of iPP quenched at 100°C, and therefore free of smectic form[14]. The interpretation of transport properties supports two different mechanisms of ageing. The first, very rapid, gives rise to a decrease of amorphous fraction corresponding to most of the increase of density. The second effect, which is superimposed on the first, consists of a decrease of the mobility of the amorphous chains. The reduction of mobility of the amorphous phase corresponding to a decrease of free volume is in agreement with other results and with the theory and results of Struik[1,7].

In this work we have analyzed the behaviour of a smectic film, rapidly quenched from the melt to very low temperature, and of two thinner films of iPP, one of which was slowly crystallized from the melt and the other rapidly quenched to very low temperature. We therefore have the possibility of comparing the effect of ageing in a monoclinic and a smectic sample. Furthermore the reduction of thickness involves more rapid diffusion measurements and allows a more careful examination for short ageing times.

EXPERIMENTAL

Isotactic polypropylene of $M_w = 307\,000$ and $M_n = 15\,600$ supplied by RAPRA (UK) was used. The crystalline films were obtained by heating the iPP pellets at 200°C, pressing them into film shape with a thickness of 0.005 cm, and quickly cooling them to 110°C and then slowly to room temperature (sample C). The smectic films were obtained by quenching the melt into an acetone–dry ice bath at −70°C. The thickness of the films was 0.005 cm (sample B) and 0.02 cm (sample S). A few minutes after preparation, the thin films were brought to room temperature and tested as soon as possible (samples B0 and C0). For these samples the ageing time was just the time necessary for the measurement. A different series of samples were stored at room temperature, in the dark, for 2 days (B2 and C2), 30 days (B30 and C30) and 365 days (B365 and C365), before the measurements were performed. Sample S was tested soon (S0), after 30 days (S30), 60 days (S60)and 480 days (S480). This sample has a thickness similar to that of the crystalline sample used in the previous work[14].

The transport properties, sorption and diffusion were measured by a microgravimetric method, using a quartz spring balance having an extension of 20 mm mg^{-1}. The penetrant was CH_2Cl_2 and the temperature of the experiment was 25°C. Sorption was measured as a function of vapour activity $a = p/p_T$ where p is the actual vapour pressure to which the sample was exposed and p_T the saturation vapour pressure at 25°C.

For samples B and C the successive sorption method was used; starting from the lowest vapour pressure the

0032-3861/88/061118-06$03.00
© 1988 Butterworth & Co. (Publishers) Ltd.

activity was increased up to the highest, waiting for each measurement for the establishment of the equilibrium sorption. For the thicker sample S a new sample was prepared for each measurement and the integral sorption method was used. The instrumentation and the methods used for the measurement of transport properties have been extensively described in a previous paper[15].

Density measurements were made by floating the samples in a mixture of 1,2-dimethoxyethane and 2-ethoxyethanol and weighing the liquid mixture with a picnometer.

Infra-red spectra were obtained with a Nicolet 5DXB Fourier transform spectrophotometer with a resolution of 4 cm^{-1} (20 scans average).

RESULTS

Smectic sample of thickness 0.02 cm

In *Figure 1* the increase of density as a function of ageing time is reported for sample S. This is a smectic sample and the results show that the density increases fast in the first hours whereas a levelling off for longer ageing times is observable. A slow increase of density is observable for very long ageing times (1 and 2 years).

In the same figure we report the ratio $R = A_{998}/A_{973}$ of the absorbances of the infra-red bands at 998 and 973 cm^{-1}. The 998 cm^{-1} band of the infra-red spectrum of iPP is a regularity band generally used for estimating the helical content and therefore the crystallinity in a sample. On the other hand, the 973 cm^{-1} band is quite insensitive to the helical content and therefore it is used as an internal reference for measuring the fraction of helical segments[16-18]. Although in the 998 cm^{-1} band there is also a contribution from the amorphous regions[16], the increase of R can be qualitatively associated with further crystallization. In fact, during crystallization, there is helix growth and the ratio (R) of absorbances of the two bands, A_{998}/A_{973}, consequently increases. From *Figure 1* we can observe that, in the same interval of time in which there is an increase of density, R also increases, levelling off after a few hours. This result is in agreement with a decrease of amorphous fraction and a corresponding increase in the smectic content; in fact the infra-red spectrum of iPP in the smectic phase is identical to that of crystalline iPP[19].

Therefore the increase of density and the increase of molecules in the helical conformation, shown by the increase of the ratio R, lead us to conclude that in the first few hours there is a decrease of amorphous fraction in the sample. This first, rapid transformation after the quenching of the sample from the melt corresponds to the first mechanism we have hypothesized in the crystalline sample of the same thickness[14], although in the smectic sample the transformation seems more rapid. As a matter of fact, it is complete within a few hours.

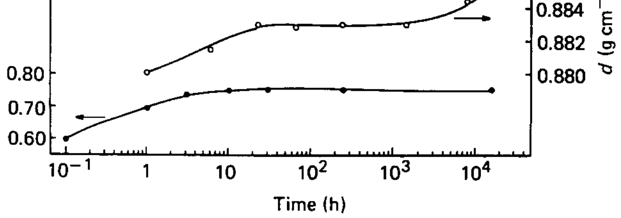

Figure 1 The density d of sample S and the ratio R between the absorbances of the infra-red bands at 998 and 973 cm^{-1} as functions of the ageing time

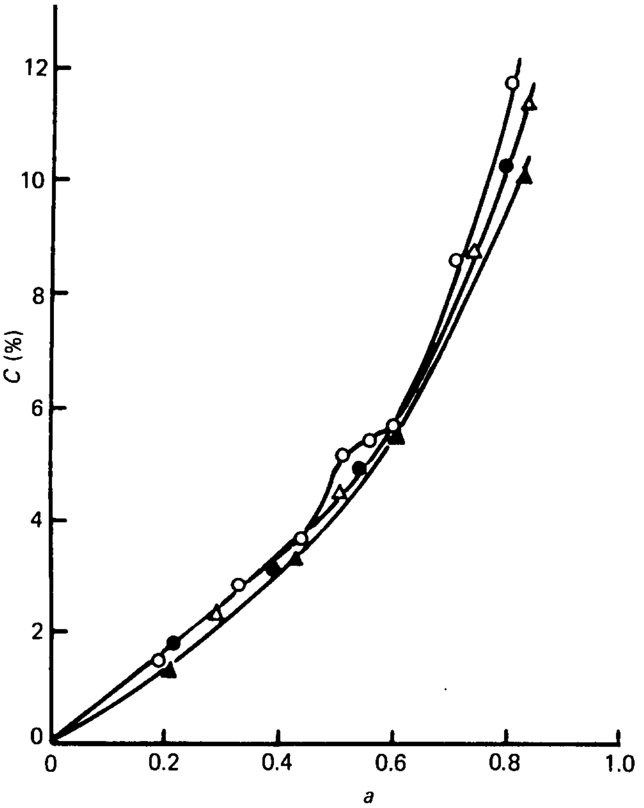

Figure 2 The equilibrium bulk concentration of CH_2Cl_2 as a function of vapour activity $a = p/p_T$ for samples S0 (○), S20 (●), S60 (△) and S480 (▲)

The absence of changes in the infra-red spectrum for longer ageing times is in agreement with previous results[3,4], indicating that the observed further changes occur only in the amorphous regions. They can be better followed by the study of transport properties.

In *Figure 2* we report the equilibrium bulk concentration C_{eq} of penetrant CH_2Cl_2 sorbed by the sample, in weight per cent, as a function of vapour activity, expressed as $a = p/p_T$, for sample S0 measured shortly after preparation and for samples S20, S60 and S480. The equilibrium bulk concentration of penetrant sorbed depends on the fraction of sorbing phase and on its fractional free volume[12]. The difference between the S0 and S20 sample is meaningful when the measurement time is small compared with the time in which the variation of density is observable. The longest sorption experiment, that is at the lowest vapour pressure, takes 5–6 h to reach equilibrium and this time is comparable with the time necessary to obtain the maximum of density; therefore we do not expect to see a difference in the sorption curve. As a matter of fact the two curves are only different at high penetrant activity, when the time of measurement is much shorter. A remarkable difference between the S0 and S20 curves is the appearance in S0 of a sharp transition at activity $a = 0.4$ to 0.5. We have suggested that in this range of activity the smectic phase starts sorbing the penetrant[20]. In the aged sample this is a gradual process appearing after activity 0.4; on the contrary, in the fresh sample the transition is easily observable. When the vapour penetrates into the smectic phase we observe the phenomenon of solvent-induced crystallization of this phase, due to the mobilizing solvent molecules[21]. The appearance of a sharp transition in the fresh sample could be due to a difference of crystallization kinetics between this sample and the aged samples.

The sample aged 60 days has the same sorption curve as S20, whereas the sorption points for S480 go on a lower curve. If there is no change in the fraction of amorphous phase, as evident from *Figure 1*, the reduction of equilibrium sorption can be ascribed to a reduction of fractional free volume (FFV). The influence of FFV is more pronounced on diffusion than on sorption[12]; the results of diffusion are therefore more important to clarify this aspect.

If we report at each vapour activity the reduced sorption, i.e. C_t/C_{eq}, as a function of square root of time, from the initial linear part of the curve, provided it shows a Fickian behaviour we can derive the mean diffusion coefficient[13] from the equation:

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

where C_t is the concentration at time t and C_{eq} the equilibrium concentration; d is the thickness of the sample. The dependence of diffusion on concentration was found to be in accordance with the relation:

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

where D_0 is the thermodynamic diffusion coefficient and γ the concentration coefficient. Also the γ coefficient is related to the fractional free volume and hence to the mobility of the sorbing phase. It increases when the FFV decreases.

In *Figure 3* the mean diffusion coefficient $\bar{D}$ is reported as a function of concentration for the samples S0, S20, S60 and S480. The transition we observed in *Figure 2* in the sorption curve is even more evident in the diffusion data of sample S0. At a concentration of 5 %, corresponding to penetrant activity 0.5, there is a clear change in the dependence of diffusion on concentration; this corresponds to the concentration at which the smectic phase becomes permeable, and in the sample freshly prepared the transition is very sharp. The experimental points for samples S20 and S60 fit the same straight line, whereas the sample S480 shows a lower D_0 and a higher γ coefficient. This result, relating to a smectic sample, is similar to that obtained for a crystalline sample[14]; there is a decrease of D_0 and an increase of γ on going from the sample as obtained to the aged samples. But, at variance with the crystalline sample, the smectic sample shows an interval of time in which the transport parameters do not change. In particular, samples S20 and S60 have the same diffusion and concentration coefficients. The difference is observable for sample S480 aged for more than 1 year. Although the influence of ageing time on the transport parameters is less on the smectic sample than on the crystalline one, the mechanism of ageing seems the same in the two samples. First there is a decrease of amorphous fraction, a process that is quite rapid; superimposed on this we observe a decrease of mobility of the amorphous chains. Since the time to reach equilibrium concentration at low penetrant activity for this sample is very long, we reduced the thickness of the sample to investigate short ageing times.

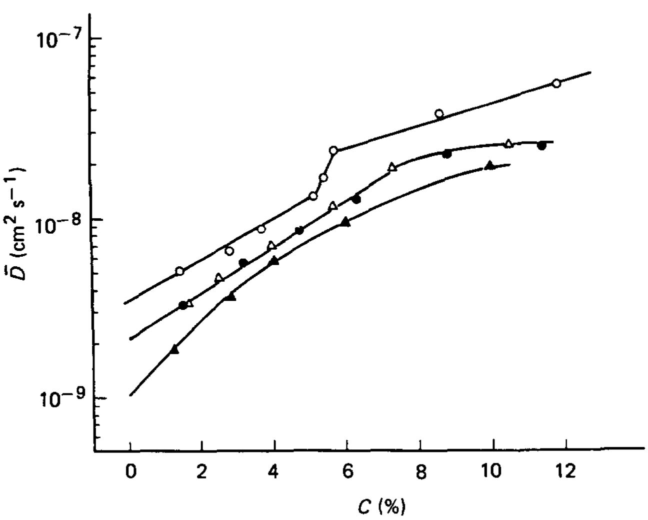

Figure 3 The diffusion coefficient $\bar{D}$ as a function of equilibrium concentration for samples S0 (○), S20 (●), S60 (△) and S480 (▲)

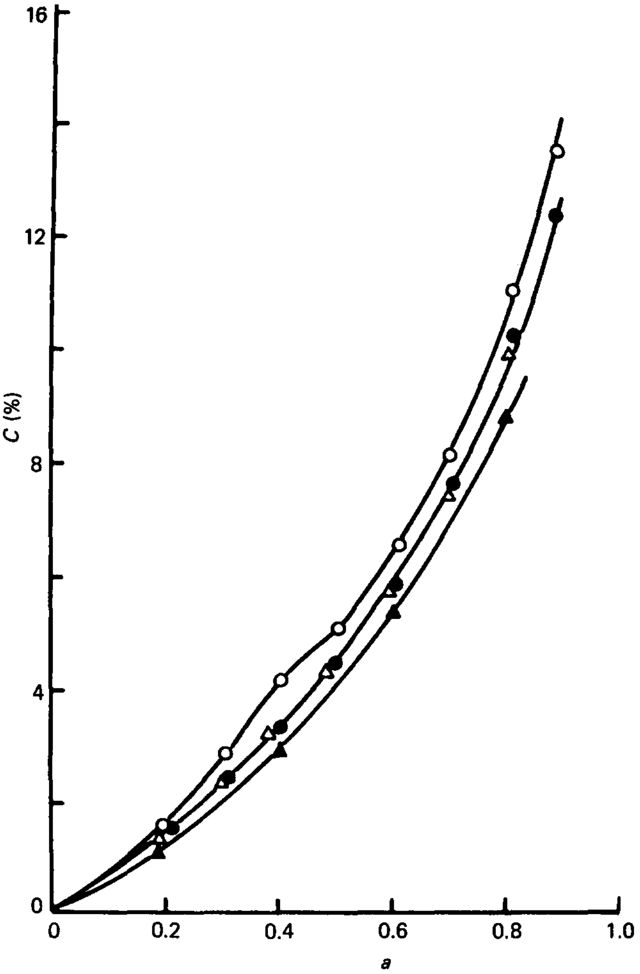

Figure 4 The equilibrium bulk concentration of CH_2Cl_2 as a function of vapour activity $a=p/p_T$ for samples B0 (○), B2 (●), B30 (△) and B365 (▲)

Smectic sample of thickness 0.005 cm

In *Figure 4* we report the equilibrium bulk concentration as a function of activity of penetrant sorbed by sample B, which is a smectic sample with a thickness 0.005 cm. This thickness is one-quarter of the previous value. Also in this case we observe the transition in the activity range 0.4–0.5, when the smectic phase becomes permeable. With this thickness we are able to see the difference in sorption between the sample measured soon (B0) and the sample with 2 days of ageing (B2). The experimental points for the sample aged for 30 days (B30) go on the same curve as sample B2, whereas a lower curve is fitted by sample B365 aged for 1 year.

The equilibrium concentration at each vapour activity can be related to the fraction of amorphous component and to its thermodynamic state. The density of the sample as prepared (B0) was measured as soon as possible and gave a value of 0.8815 g cm^{-3}. If we derive the mass fraction of smectic component from the equation:

$$\alpha_{sm} = \frac{d_{sm}}{d} \frac{d - d_a}{d_{sm} - d_a} \tag{3}$$

where α_{sm} is the mass fraction of smectic phase, d the density of the sample, d_{sm} and d_a the ideal smectic and ideal amorphous densities (0.916 g cm^{-3} and 0.856 g cm^{-3} respectively)[20], we obtain a value $\alpha_{sm} = 44.2\%$ and therefore $\alpha_a = 55.8\%$ in the fresh sample.

The density of the sample aged 2 days is 0.8855 g cm^{-3}, from which we obtain a fraction $\alpha_{sm} = 50.9\%$ and $\alpha_a = 49.1\%$. The ratio of the amorphous fractions in samples B0 and B2 is:

$$\alpha_a(\mathrm{B0})/\alpha_a(\mathrm{B2}) = 1.14 \tag{4}$$

This ratio corresponds exactly to the ratio of the equilibrium sorption at each vapour activity, that is:

$$C_{eq}(\mathrm{B0})/C_{eq}(\mathrm{B2}) = 1.14 \tag{5}$$

Therefore we can affirm that the first decrease of equilibrium sorption is due to the decrease of amorphous fraction. The fact that the equilibrium concentration points for sample B30, aged 30 days, are the same as for sample B2 confirms that, after the first few hours, there is no change in the amorphous fraction of the sample, but only a slow reduction of fractional free volume. As a matter of fact the sample B365, aged for 1 year, has a lower sorption, although its density has not changed much with respect to the B2 and B20 samples.

In *Figure 5* the mean diffusion coefficient $\bar{D}$ is shown as a function of concentration for the samples B0, B2, B30 and B365. As in the case of the S sample, the B0 sample shows the transition at penetrant concentration 4–5% and a higher diffusion coefficient extrapolated at zero penetrant concentration. The B2 and B30 samples fit the same straight line, whereas the well aged sample B365 shows a much lower D_0 and higher γ, which means a reduced fractional free volume. Furthermore, curvature in the logarithmic plot of diffusion *versus* concentration appears for the sample B365 aged for 1 year, indicating that the slope γ is varying with concentration. This behaviour has also been found for samples S480 (*Figure 3*) and C365 (*Figure 7*). It is associated with the appearance of non-Fickian anomalies in the sorption curves. The principal factors contributing to non-Fickian behaviour are probably structural relaxation processes and the concurrent immobilization of penetrant. An analysis of clustering in the aged samples will be performed in order to study the onset of this behaviour.

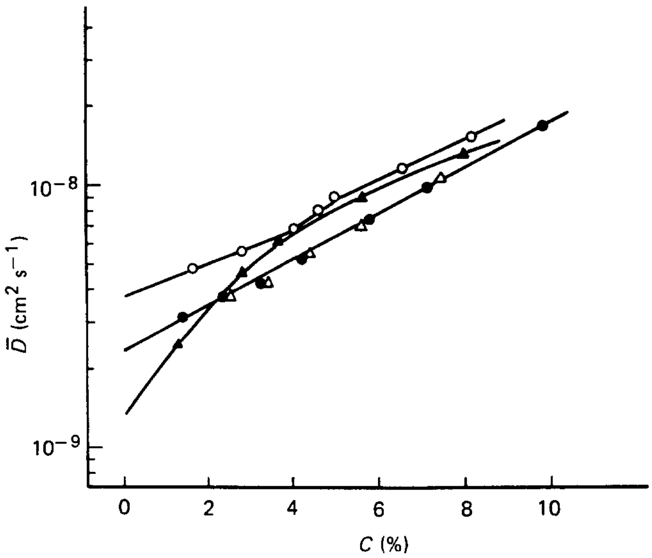

Figure 5 The diffusion coefficient $\bar{D}$ as a function of equilibrium concentration for samples B0 (○), B2 (●), B30 (△) and B365 (▲)

Crystalline sample of thickness 0.005 cm

The samples investigated so far have been obtained by rapid quenching; the crystalline sample of the previous paper was obtained by quenching the pressed melt at 100°C, and the samples of this paper (S and B) were obtained by quenching the melt at −70°C. To eliminate the possibility that some ageing phenomena were due to relaxation of residual stress following the quenching of the samples, we have also studied the transport properties of a crystalline sample not quenched but slowly crystallized at 110°C (sample C). The thickness of this sample is 0.005 cm in order to have, also in this case, the possibility to investigate short ageing times.

In *Figure 6* we report the equilibrium bulk concentration of penetrant sorbed by the samples C0, C2, C30 and C365 as a function of activity $a = p/p_T$. As in the previous cases, we have a decrease of sorption in the first 2 days of ageing, whereas the sample C30 aged for 30 days shows the same sorption as sample C2.

As we have done for the smectic sample, we can derive the amorphous fraction from the density of the sample. Sample C0 has a density 0.8998 g cm^{-3}, to which corresponds an amorphous fraction $\alpha_a = 49.2\%$; sample C2 has a density 0.9040 g cm^{-3} and a corresponding $\alpha_a = 37.7\%$. The ratio of $\alpha_a(\mathrm{C0})/\alpha_a(\mathrm{C2})$ is 1.14 and it corresponds exactly to the ratio of equilibrium sorption at each vapour activity for samples C0 and C2. The density of the sample C30, that is, 0.9050 g cm^{-3}, gives an amorphous fraction of 37.5%. This value is such as to justify the same sorption values.

As for the sample C365, aged for 1 year, the reduced sorption shown by the figure is indicative of a change of thermodynamic state of the amorphous component with long ageing times. Since the sorption is proportional to the fractional free volume of the polymer, a reduced value of this quantity and hence a reduced mobility in the amorphous component is consistent with this result.

Since the molecular mobility affects the diffusion coefficients much more, the results of diffusion measurements are even more important to clarify this aspect. We report these results in *Figure 7*. It is worth noting that all the samples fit different straight lines with different D_0 and γ. The variation of D_0 and γ for sample C30 with respect to sample C2 occurs in spite of the constant value of equilibrium sorption. Since the equilibrium sorption depends principally on the

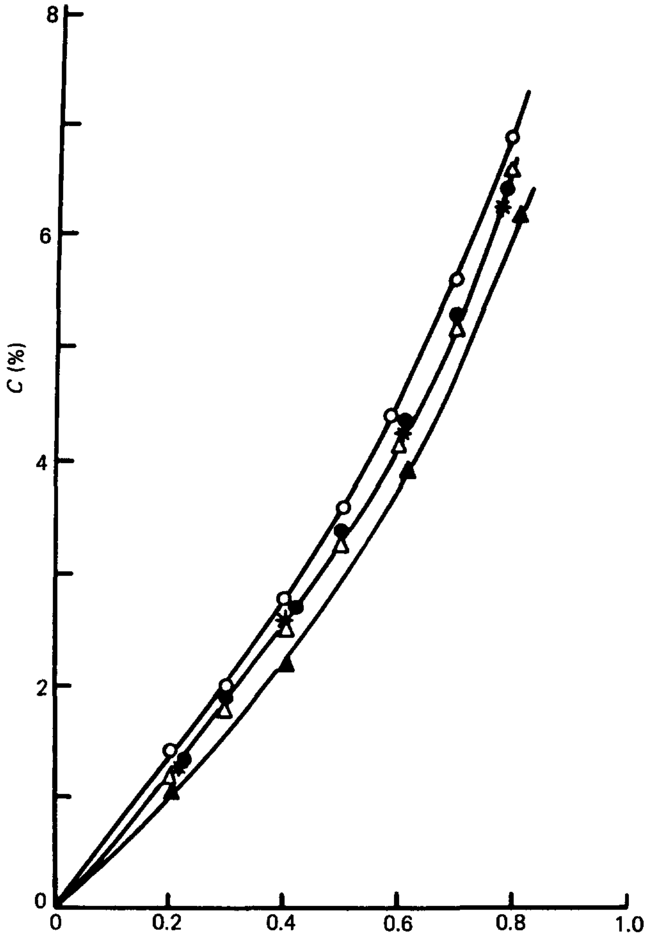

Figure 6 The equilibrium bulk concentration of CH_2Cl_2 as a function of vapour activity $a = p/p_T$ for samples C0 (○), C2 (●), C30 (△), C365 (▲) and C365 heated 1 h at 80°C (*)

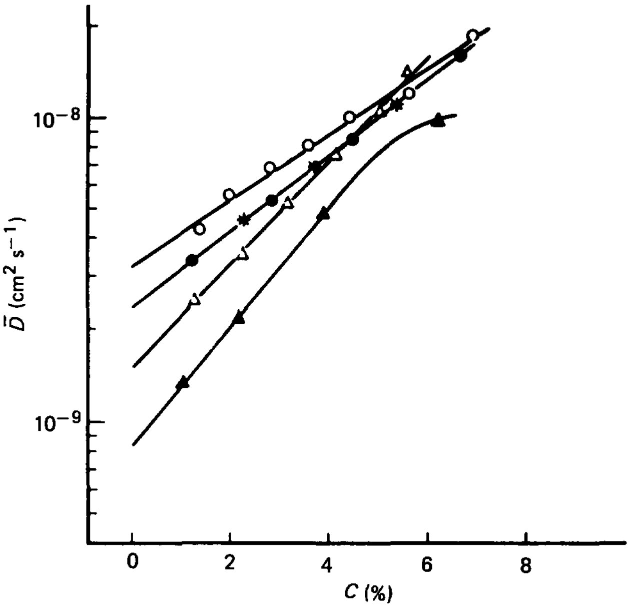

Figure 7 The diffusion coefficient $\bar{D}$ as a function of equilibrium concentration for samples C0 (○), C2 (●), C30 (△), C365 (▲) and C365 heated 1 h at 80°C (*)

amorphous fraction while D_0 and γ depend more on molecular mobility, these results again agree with the hypothesis that in the first few hours there is a decrease of amorphous fraction in the sample, whereas in subsequent storage at room temperature a progressive reduction of molecular mobility occurs.

The results of transport properties of this sample, slowly crystallized, are very similar to the results of a quenched sample[14]; both agree with the results and theory of Struik[1]. Although the theory of this author principally considers amorphous solids at temperatures below the glass transition, he extended this theory to semicrystalline polymers also at temperatures above T_g. In these materials there are regions in which the amorphous phase is undisturbed as well as regions in which the presence of the crystals disturbs the amorphous phase, reducing its mobility. The main consequence of this immobilization is that the glass transition will be extended towards the high-temperature side; therefore, even above T_g of the bulk amorphous materials, some parts of the amorphous phase are rubbery, other parts are glassy and still other parts will just be passing their glass transition. Therefore, for such materials, ageing will persist even at temperatures above T_g. In the case of iPP, the value generally reported in the literature for T_g is about 0°C, but recently much evidence for a broadening of the T_g interval[22] or of a double T_g has been reported[23]. The results of Struik, who studied creep properties as well as volume relaxation measurements as a function of ageing time, agree with the model of an extended glass transition for iPP. For simplicity, this author assumes that there are only two clearly distinct T_g values, a lower T_g^L and an upper T_g^U, and he finds ageing behaviour that agrees perfectly with the theoretical one. T_g^L is found between -20 and 0°C and T_g^U lies above 80°C. At 25°C we are therefore under the upper T_g and isotactic polypropylene undergoes physical ageing.

The basic property that changes during physical ageing is the segmental mobility and therefore the relaxation times that are directly related to the mobility. Our results on diffusion are in agreement with a reduction of fractional free volume and therefore of mobility with ageing time. In our case there is a first process, lasting a few hours, in which we observe a decrease of the amorphous fraction; subsequently we observe a progressive reduction of mobility of the amorphous phase.

Thermoreversibility of ageing

According to the theory of Struik, ageing is thermoreversible: when the aged material is heated to above T_g, it 'forgets' its history, any previous ageing it may have undergone below T_g having been erased.

In the case of amorphous polymers, to establish whether a certain ageing effect is due to physical ageing, it suffices to check whether the original properties of the material can be restored by heating it to just above T_g. We have performed this test with the sample C aged for 365 days. The sample has been heated for 1 h at 80°C, which is indicated as the upper T_g^U for iPP[7]. After cooling at 25°C the sample has again been submitted to a cycle of sorption. In *Figure 6* the equilibrium bulk concentrations as a function of vapour activity for this sample are reported with asterisks. The sorption has the same value at each vapour activity as the samples aged for 2 days and 30 days. As for the diffusion values of this heated sample, the experimental points fit the same straight line as the C2 sample. This means that the sample has completely recovered the transport parameters it had before the start of ageing.

This result is very important because it confirms that ageing of sample C is real physical ageing as reported by Struik. The result that the transport parameters of the heated sample do not recover the first curve (corresponding to sample C0) is also very important, because this confirms that the first change in the sorption is really due to a decrease of amorphous fraction, not recoverable, whereas the decrease of transport parameters after this first stage can be recovered by thermal treatment.

CONCLUSIONS

We have measured the transport parameters of CH_2Cl_2 in crystalline and smectic films of isotactic polypropylene as a function of ageing time. The structurally different smectic and crystalline samples behave, in terms of ageing, in qualitatively the same way. The transport properties can, in fact, be explained by two different mechanisms of ageing. The first is a decrease of amorphous fraction corresponding to the majority of the increase of density. The second effect, which is superimposed on the first, is very similar to the physical ageing of amorphous materials under T_g and semicrystalline polymers above T_g described by Struik. It consists of a progressive reduction of fractional free volume and therefore of mobility of the amorphous component, as evidenced by the reduction of the diffusion coefficient and the increase of the concentration coefficient γ. These effects of ageing can be completely erased by heating the samples above the upper T_g.

REFERENCES

1 Struik, L. C. E. 'Physical Aging in Amorphous Polymers and Other Materials', Elsevier, Amsterdam, 1978
2 Dunn, C. M. R. and Turner, J. *Polymer* 1974, **15**, 451
3 Schael, G. W. *J. Appl. Polym. Sci.* 1966, **10**, 901
4 Gezovich, D. M. and Geil, P. H. *Polym. Eng. Sci.* 1968, **8**, 202
5 Kapour, S. and Rogers, C. E. *J. Polym. Sci., Polym. Phys. Edn.* 1972, **10**, 2107
6 Baum, J. J. and Schultz, J. M. *J. Appl. Polym. Sci.* 1981, **26**, 1579
7 Struik, L. C. E. TNO Delft Publication No. P5, 1986
8 Chai, C. K. and McCrum, N. G. *Polymer* 1980, **21**, 706
9 Buckley, C. P. and Habibullah, M. J. *Appl. Polym. Sci.* 1981, **26**, 2613
10 Hutchinson, J. M. and McCrum, N. G. *Nature, Phys.* 1974, **252**, 295
11 Struik, L. C. E. *Plast. Rubber Process. Appl.* 1982, **2**, 41
12 Peterlin, A. *J. Macromol. Sci.-Phys.* 1975, **11**, 57
13 Crank, J. 'The Mathematics of Diffusion', Oxford University Press, London, 1975
14 Vittoria, V. *Polym. Commun.* 1987, **28**, 199
15 Araimo, L., de Candia, F., Vittoria, V. and Peterlin, A. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2087
16 Zerbi, G., Gussoni, M. and Ciampelli, F. *Spectrochim. Acta* 1967, **23**, 301
17 Kissin, Yu. V. and Rishina, L. A. *Eur. Polym. J.* 1976, **12**, 757
18 Glotin, M., Rahalkar, R. R., Hendra, P. J., Cudby, M. E. and Willis, H. A. *Polymer* 1981, **22**, 731
19 Miller, R. L. *Polymer* 1959, **1**, 135
20 Vittoria, V. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 451
21 Vittoria, V. *Polym. Commun.* 1985, **26**, 213
22 Wunderlich, B. and Grebowicz, J. *Adv. Polym. Sci.* 1984, **60**/**61**, 1
23 Boyer, R. F. *J. Macromol. Sci.-Phys.* 1973, **B8**(3-4), 503