Solvent-induced crystallization of isotactic polypropylene in cyclohexane at different temperatures

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The process of solvent-induced crystallization of smectic polypropylene in cyclohexane was investigated at three temperatures: 15, 25 and 35°C. At the lowest temperature the process of sorption is non-Fickian, going towards diffusion-controlled crystallization. At this temperature it is possible to distinguish two stages in the process of crystallization: in the first stage a fraction of the amorphous phase transforms into a more ordered phase, while in the second stage the crystallization of the smectic phase occurs. On increasing the temperature, the first stage becomes shorter, and at 35°C it is not possible to separate the two stages. The higher the temperature, the more effective is the transformation of the smectic into the monoclinic phase.

(Keywords: isotactic polypropylene; smectic form; solvent-induced crystallization)

INTRODUCTION

Isotactic polypropylene (iPP) can be easily quenched to a disordered state, generally called 'smectic polypropylene[1–4]. This form is stable at room temperature but transforms into the monoclinic α form by thermal[5–7] or solvent treatments[8,9]. Previous studies have shown that, when smectic iPP is kept in particular liquids, there is a complex structural rearrangement of the structure leading to the process of crystallization. It has been found that the higher the polymer–solvent interaction, the higher is the level of crystallinity induced. The most effective solvents in inducing crystallization were found to be cyclohexane, carbon tetrachloride and chloroform, whose solubility parameters are very close to the solubility parameters reported in the literature for iPP[10,11]. Crystallization induced by solvents is a very complex phenomenon, in which the type of solvent and the temperature play an important role[12]. We have already studied the influence of different solvents on the crystallization process and on the morphology of solvent crystallized samples[9,13]. In this paper we analyse the progress of crystallization in cyclohexane at three different temperatures. The aim is to investigate the effect of temperature on the kinetics of sorption and crystallization and on the structural changes induced by the solvent.

EXPERIMENTAL

Isotactic polypropylene (iPP) of $M_w = 307\,000$ and $M_n = 15\,600$ was a product of RAPRA (Great Britain). Smectic films (SM sample) were obtained by heating the iPP pellets to 200°C, pressing them into a film shape 0.02 cm thick and quickly cooling to −70°C in an acetone–dry ice bath. The density of the smectic film was 0.883 g cm^{-3} at 25°C, and for this sample we calculated a fraction of amorphous component $\alpha_a = 0.53$[14].

Different strips of the original film were immersed in cyclohexane at 15, 25 and 35°C for different lengths of time. Upon removal, the samples were blotted on filter paper and weighed in closed bottles. They were subsequently dried under vacuum at room temperature for many days.

Density measurements of the dried films were performed by floating the samples in a mixture of 1,2-dimethoxyethane and 2-ethoxyethanol.

Wide-angle X-ray scattering (WAXS) analysis on the dried films was carried out by a Philips PW 1050/71 powder diffractometer (Cu Kα Ni-filtered radiation) in the reflection mode, scanning the scattering 2ϑ angle continuously.

Vapour sorption was measured to determine the fraction of amorphous component in the different samples[14]. It was measured by a microgravimetric method using a quartz spring balance, having an extension of 18 mm mg^{-1}. The penetrant used was methylene chloride and the experiments were conducted at a temperature of 25°C. Sorption, i.e. equilibrium concentration of penetrant, was measured as a function of vapour activity $a = p/p_T$, where p is the pressure to which the sample was exposed and p_T the saturation pressure at the temperature of the experiment.

RESULTS AND DISCUSSION

In *Figure 1* the increase of concentration of sorbed cyclohexane, C_t (g/100 g dry polymer), is reported as a function of $t^{1/2}/d$, where t is the time and d the thickness (cm) of the film, for the temperatures of 15, 25 and 35°C. At 25 and 35°C, the increase of concentration is linear with square root of time, denoting Fickian diffusion, as often observed during solvent-induced crystallization[12]; at the lowest temperature, i.e. 15°C, the process becomes non-Fickian and a more than linear increase of concentration with square root of time appears. From the initial linear part of the curves at 25 and 35°C we derived the mean diffusion coefficient $\bar{D}$ (cm^2 s^{-1}); the values are

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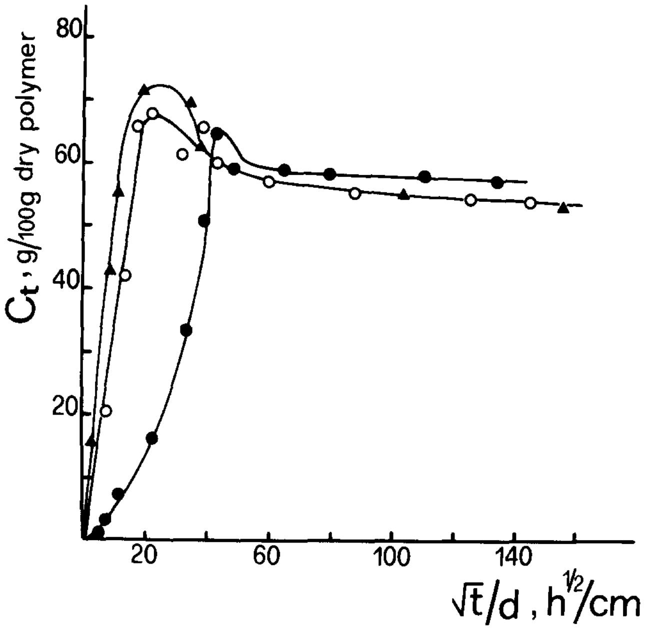

Figure 1 The increase of concentration of sorbed cyclohexane, C_t (g/100 g dry polymer), as a function of $t^{1/2}/d$ for temperatures of 15°C (●), 25°C (○) and 35°C (▲)

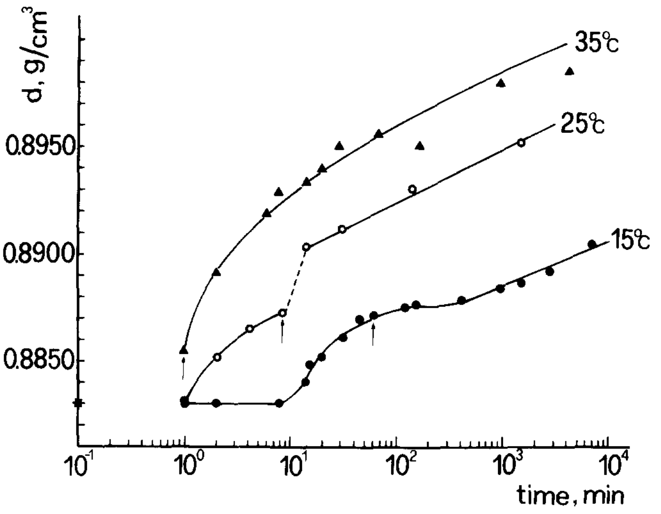

Figure 2 The density of films immersed in cyclohexane and dried as a function of the logarithm of immersion time for temperatures of 15°C (●), 25°C (○) and 35°C (▲)

respectively 1.4×10^{-7} and 2.9×10^{-7} cm^2 s^{-1}. These values give an activation energy for the diffusion process of about 4 kcal mol^{-1}. In all cases we observe a marked desorption during the measurement, indicative of crystallization. In fact, when crystallization starts, owing to the mobilizing presence of solvent molecules there is rejection of a fraction of solvent from the impermeable crystalline regions. The lower the temperature, the lesser is the desorption, going towards diffusion-controlled crystallization. As a matter of fact, when the crystallization is slower than diffusion it starts when the solvent has penetrated the whole polymer; then we observe the rejection of solvent due to crystallization.

The progress of crystallization was followed by measuring the increase of density of samples immersed in cyclohexane for different lengths of time. In *Figure 2* the density of the dried samples is reported as a function of logarithm of time of immersion in cyclohexane. The density of the starting smectic sample, reported with an asterisk, is 0.883 g cm^{-3}. At the lowest temperature, i.e. 15°C, we observe two stages in the increase of density, a first rapid increase after 8 min, followed by a plateau and then a linear increase with the logarithm of time. The first increase is complete after 1 h in the liquid, and then the second increase starts.

At 25°C only the sample immersed for 1 min has the same density as the starting SM sample, whereas after 2 min in the liquid the density has already increased. But at this temperature there is superposition of the two stages: we do not observe the first plateau but a sudden rise in density between 8 and 15 min of immersion in the liquid. Thereafter the increase of density is linear with logarithm of time. On increasing the temperature to 35°C, the first stage becomes even shorter and we observe the abrupt rise of density just after 1 min of immersion in the liquid, and the linear increase after 10 min.

In all cases, at the end of the process, the density has increased substantially with respect to the starting value of 0.883 g cm^{-3}. The final values after 48 h in the liquid are 0.8905, 0.8955 and 0.8990 g cm^{-3} respectively at 15, 25 and 35°C. Therefore the higher the temperature, the more effective is the transformation of the smectic into the monoclinic phase.

It is interesting to analyse the X-ray diffractograms of the samples corresponding to the different stages in the increase of density.

In *Figure 3* the wide-angle X-ray diffractograms of samples immersed in cyclohexane for different lengths of time at the three temperatures ((a) 15°C, (b) 25°C and (c) 35°C) are reported. Before 1 h at 15°C, 8 min at 25°C and 1 min at 35°C we do not observe any peak characteristic of the monoclinic form of iPP, but only a broadening of the smectic (1 1 0) reflection at $2\vartheta = 15°$. Therefore 1 h at 15°C, 8 min at 25°C and 1 min at 35°C are the times needed for the first appearance of the monoclinic phase. If we compare this result with the curve for increase of density reported in *Figure 2*, we observe that at these times (marked in the figure with an arrow) the value of density has already increased with respect to the starting SM sample. Therefore the density starts increasing well before the monoclinic reflections appear in the X-ray diffractograms. To follow the formation of the monoclinic phase, the reciprocal of the width at half-height (A) for the (1 1 0) strongest reflection ($2\vartheta \simeq 14°$) of polypropylene was chosen. The $1/A$ parameter is directly related only to the ordered phase and therefore gives different information with respect to the density. This parameter is reported in *Figure 4* as a function of logarithm of time for the three temperatures. At 15°C we observe the first increase of this parameter after 1 h of immersion in the liquid, whereas for shorter times even a decrease of $1/A$ is observable. This same behaviour shifted to shorter times is observable at 25°C, the increase of $1/A$ parameter being observable after 8 min of immersion in the liquid. At 35°C, we observe the $1/A$ increase just after 1 min of immersion in the liquid.

We have already shown that during crystallization in liquids there is a complex rearrangement of the structure, also involving a fraction of amorphous phase[13]. According to the present results of density and WAXS, we can suggest that the first stage in the increase of density corresponds to the transformation of a fraction of amorphous phase into more ordered phase (probably the smectic phase), and the second stage corresponds to

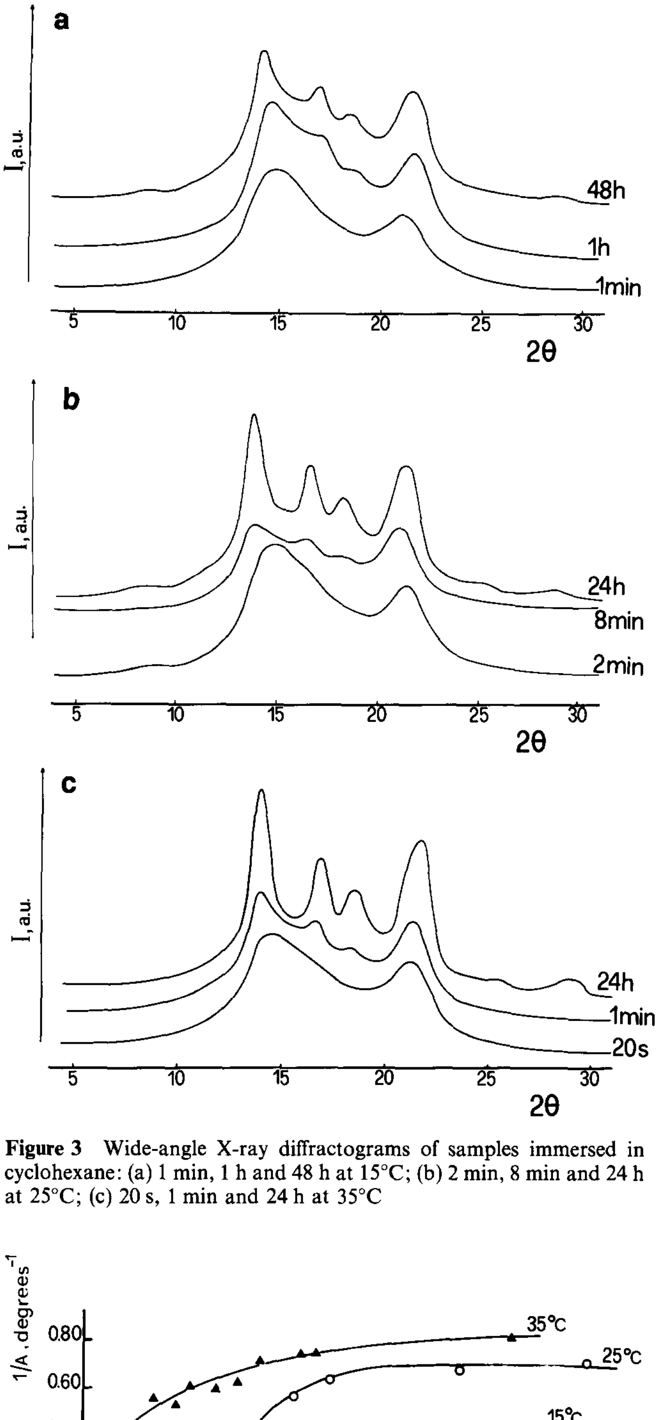

Figure 3 Wide-angle X-ray diffractograms of samples immersed in cyclohexane: (a) 1 min, 1 h and 48 h at 15°C; (b) 2 min, 8 min and 24 h at 25°C; (c) 20 s, 1 min and 24 h at 35°C

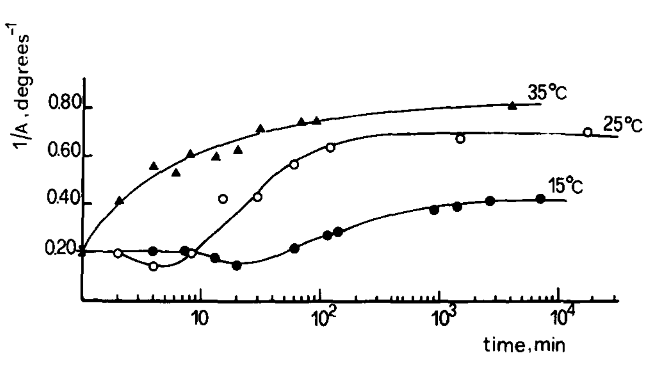

Figure 4 The reciprocal of the width at half-height (A) for the (1 1 0) strongest reflection ($2\vartheta = 14°$) of polypropylene as a function of the logarithm of immersion time for temperatures of 15°C (●), 25°C (○) and 35°C (▲)

crystallization of the smectic phase. As a matter of fact, the end of the first stage of density increase at 15 and 25°C coincides with the appearance in the WAXS of peaks characteristic of the monoclinic phase.

For the determination of the amorphous fraction during the process of crystallization, sorption of dichloromethane vapour was used. In fact, at low penetrant activity neither the crystalline nor the smectic phase sorb and diffuse the penetrant[14]. Sorption in the crystallized samples is therefore related only to the amorphous phase. We can therefore assume that the specific sorption is the same for all the samples and write:

$$C_{sp}(\mathrm{SM}) = C_{sp}(\mathrm{X}) = \frac{C_{eq}(\mathrm{SM})}{\alpha_a(\mathrm{SM})} = \frac{C_{eq}(\mathrm{X})}{\alpha_a(\mathrm{X})}$$

where (X) represents the crystallized sample. Therefore:

$$C_{eq}(\mathrm{SM})/C_{eq}(\mathrm{X}) = \alpha_a(SM)/\alpha_a(\mathrm{X})$$

and hence, from the ratio of sorption at each vapour activity, it is possible to derive the amorphous fraction of the crystallized samples, knowing $\alpha_a(\mathrm{SM})$ from a previous paper[14].

In *Figure 5* we report the equilibrium concentration of penetrant as a function of vapour activity $a = p/p_T$ for the starting SM sample and the samples immersed in cyclohexane for 1 and 24 h at 15°C, 8 min and 24 h at 25°C and 1 min at 35°C. We notice that the amorphous fraction decreases, as shown by the decrease of sorption, just after 1 h at 15°C, 8 min at 25°C and 1 min at 35°C and then remains constant and shows the same value even after the second stage of density increase is completed. This confirms that the first stage in the increase of density is due to a decrease of the amorphous fraction, whereas during the second stage there is no change in this parameter. The appearance of the monoclinic reflections at the beginning of the second stage indicates that the smectic phase starts crystallizing. It is worth noting that the amorphous fraction as derived by the sorption is the same for all the crystallized samples,

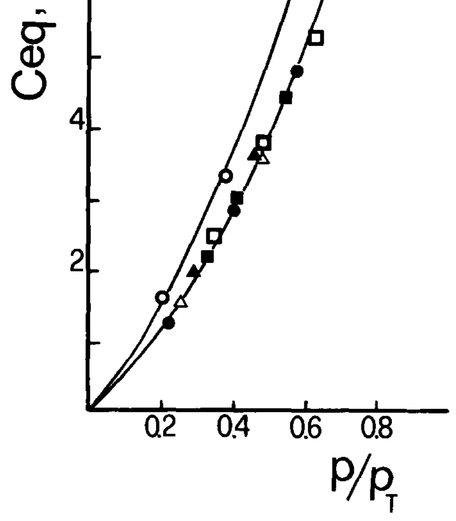

Figure 5 The equilibrium concentration of dichloromethane as a function of vapour activity $a = p/p_T$ for the starting SM sample (○) and for the samples immersed 1 h (●) and 24 h (△) at 15°C, 8 min (▲) and 24 h (□) at 25°C and 1 min at 35°C (■)

whereas the higher density and $1/A$ parameter on increasing the temperature of immersion indicate that the transformation of the smectic phase is more effective at higher temperatures.

CONCLUSIONS

The samples crystallized in cyclohexane at 15°C show two stages of increase of density: the first stage corresponds to the transformation of a fraction of amorphous phase into a more ordered phase, yet not the monoclinic phase. After this stage, the smectic phase crystallizes into the monoclinic form. On increasing the temperature the first stage becomes shorter and we observe a tendency to superposition of the two stages. At 35°C it is not possible to separate the two stages: in fact at this temperature the X-ray reflections of the monoclinic phase appear just after 1 min of immersion in the liquid.

REFERENCES

1 Natta, G., Peraldo, M. and Corradini, P. *Rend. Acc. Naz. Lincei* 1959, **26**, 14
2 Miller, R. L. *Polymer* 1960, **1**, 135
3 Wyckoff, H. W. *J. Polym. Sci.* 1962, **62**, 83
4 Bodor, G., Grell, M. and Kallo, A. *Faserforsch. Textil. Techn.* 1964, **15**, 527
5 Zannetti, R., Celotti, G., Fichera, A. and Francesconi, R. *Makromol. Chem.* 1969, **128**, 137
6 Hsu, C. C., Geil, P. H., Miyaji, H. and Asai, K. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2379
7 Grubb, D. T. and Yoon, D. Y. *Polym. Commun.* 1986, **27**, 84
8 Vittoria, V. *Polym. Commun.* 1985, **26**, 213
9 Vittoria, V. and Riva, F. *Macromolecules* 1986, **19**, 1975
10 Hayes, R. A. *J. Appl. Polym. Sci.* 1961, **5**, 318
11 Vocks, J. F. *J. Polym. Sci.* (*A-2*) 1964, 5319
12 Rebenfeld, L., Makarewicz, P. J., Weighmann, H. D. and Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem.* (*C*) 1976, **15** (2), 279
13 Vittoria, V., Olley, R. H. and Bassett, D. C. *Colloid Polym. Sci.* 1989, **267**, 661
14 Vittoria, V. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 452