High pressure d.t.a. study on the melting and crystallization of isotactic polypropylene

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The melting and crystallization behaviour of isotactic polypropylene (iPP) in the α (*monoclinic*) *and* γ (triclinic) crystalline modifications has been studied by differential thermal analysis (d.t.a.) under high pressure. The d.t.a. melting thermograms of the sample prepared by slow cooling from the melt at atmospheric pressure (α form) and high pressure (γ form) show single endothermic peaks up to about 4600 bar in isobaric measurements. Two isolated melting point curves, corresponding to the melting of the α and γ modifications, were obtained and the melting points were fitted to a quadratic equation as a function of the pressure (bar). The slope of the curve at atmospheric pressure has been determined accurately for each crystalline form. Two curves were observed for the pressure dependence of the crystallization peak temperature in the d.t.a. curve. The origin of the separated crystallization curves is discussed in relation to the degradation of the iPP melt-crystallized under high pressure.

INTRODUCTION

Isotactic polypropylene (iPP) crystallizes in normal monoclinic α form when cooled slowly from the melt at atmospheric pressure. Under high pressure conditions, it crystallizes in the γ form (triclinic unit cell) by slow cooling from the melt. Dilatometry has been a usual method in the study of the melting and crystallization behaviour of iPP under high pressure. Baer and Kardos[1] measured the volume change of iPP up to 2 kbar and reported the value of 68K/kbar for the slope of the curve of the melting temperature T_m as a function of pressure in the low pressure range. Recently, Leute *et al.*[2] reported 38K/kbar as the slope dT_m/dP up to 1 kbar for fractionated iPP samples.

The melting temperature of polymer crystals depends on the crystalline form. In iPP, the melting temperature of the α modification is about 12°C higher than that of the γ modification at atmospheric pressure. Therefore, the pressure dependence of the melting temperature of iPP should be determined for each crystalline form. Micro-differential thermal analysis (d.t.a.) is a useful method for the study of melting and crystallization of crystalline polymers under hydrostatic high pressure[3-6]. Phase diagrams have been determined accurately for some polymer crystals.

In this paper, the melting and crystallization behaviour of the α and γ form crystals in iPP by means of d.t.a. under hydrostatic high pressure is presented. The pressure dependence of the melting and crystallization temperatures was determined accurately for both crystalline forms.

EXPERIMENTAL

Commercial grade iPP pellets (Mitsubishi MA6 M_w = 420 000) supplied by Mitsubishi Yuka Co. was used as the original material. The high pressure d.t.a. apparatus described elsewhere was used in this study[7]. A sheathed alumel–chromel thermocouple (Philips Co., 1 mm outside diameter) was used as the open type. A sample of about 4 mg weight was put on the hot junction of thermocouple and covered by epoxy resin to prevent contamination by the pressure transmitting fluid. Silicone oil of 10 cs in viscosity was used as the pressure transmitting fluid. Pressure was measured by a manganin manometer calibrated against the melting of mercury under high pressure[8]. The high pressure d.t.a. cell was heated by the sheathed heaters surrounding the outside of the cell. The heating rate was 5°C $\min^{-1}$ and the cooling rate was 6°C $\min^{-1}$ for all the d.t.a. runs.

The α form crystal was prepared by slow cooling from the melt at atmospheric pressure of the sample put on the thermocouple junction. The γ form crystal was prepared by melt-crystallization of the same sample by the same cooling rate as the d.t.a. at 2450 bar, because it is an appropriate pressure for crystallization of the γ form crystal as described in the Results and Discussion section. As the sample for the X-ray diffractometer scans, iPP plate (12 × 7 mm) was covered by epoxy resin and melt-crystallized under high pressure. The temperature of the plate sample during crystallization was monitored by an adjacent thermocouple junction. The heating and cooling rate was the same as that for the d.t.a. run. The viscosity-average molecular weight $\bar{M}_\eta$ of the iPP samples with different thermal history was determined from the data of intrinsic viscosity measured in decalin solution at 135°C. In the calculation of $\bar{M}_\eta$, Kinsinger's relation[9]

$$[\eta] = 1.1 \times 10^{-4} \times \bar{M}_\eta^{\,0.8}$$

was used. Where $[\eta]$ is the intrinsic viscosity.

RESULTS AND DISCUSSION

Appropriate pressure for the γ form crystallization

Formation of the γ form in iPP under high pressure has been reported originally by Kardos *et al.*[10] by the dilatometric method. According to them, the d.t.a. melting curve at atmospheric pressure for the sample

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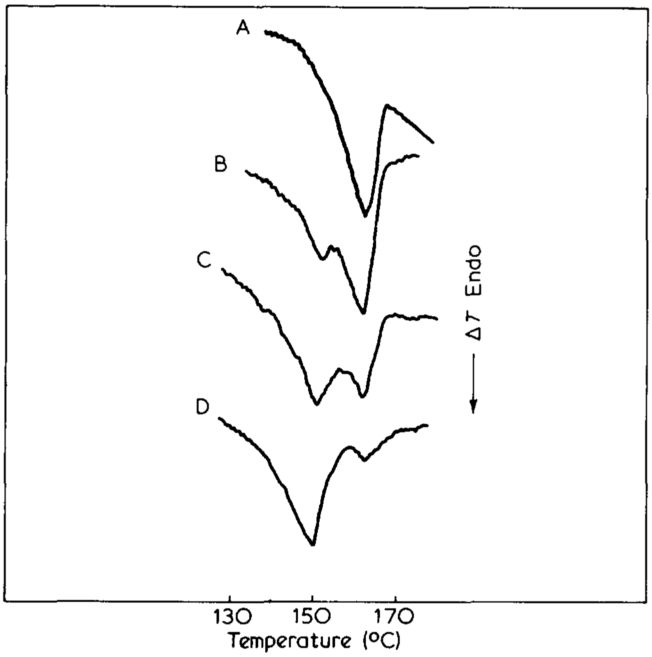

Figure 1 D.t.a. curves for melting at 1 atm on iPP crystallized under various pressures: A, 1; B, 447; C, 944; D, 2728 bar

melt-crystallized at 3000 atm shows a shoulder of the α form melting at the high temperature side of the melting peak of the γ form crystal. At the crystallization pressure of 5000 atm, the d.t.a. melting thermogram shows a single peak at a scan speed of 40°C min^{-1}. The γ form prepared in this way is metastable and conversion to the α form occurs during heating at a scan speed of 5°C/min[11]. In order to investigate the effect of pressure on the melting behaviour of the γ form crystal, it should be stable and a solid–solid phase transition should not occur during heating in the d.t.a. scan. The most appropriate pressure for the formation of the stable γ form is determined first of all. *Figure 1* shows the d.t.a. thermograms at 1 atm on the sample crystallized under high pressure by slow cooling (cooling rate 6°C min^{-1}). The low temperature endothermic peak due to melting of the γ form increases in intensity with increasing crystallization pressure. In the d.t.a. curve at 2728 bar, the temperature of main peak is at 150°C and a small peak is observed at about 164°C. The high temperature peak is considered to be the melting peak of α form transformed during heating partially from the γ form.

The quantity of the stable γ form produced is enough to allow its study. Most of the γ form obtained by slow cooling under high pressure is stable as reported by Morrow[12] and melts in the γ form without conversion to the α form.

To determine the appropriate pressure for crystallization of the γ form, the X-ray diffraction scan was performed at 1 atm on the plate-like sample melt-crystallized at various pressures. *Figure 2* shows the X-ray diffractometer scans around 20° at 2θ angle. The peak at 16.68° is due to the (130) reflection of the α form and the peak at 20.18° is due to the (130) reflection of the γ form. The relative percentage content of the γ form crystal in the sample was determined by assuming that the summation of the area under the peaks of the (130) reflection for both crystalline forms in the spectra, was held constant for all the spectra. *Figure 3* shows the percentage content of the γ form crystal as a function of the crystallization pressure P_c. The data for the γ form content obtained by the same method on the d.t.a. thermograms are also plotted in the figure. The γ form content increases with P_c and is saturated at about 2000 bar. Consequently, it is necessary to employ crystallization above 2000 bar to make the sample of high γ form content. However, high pressure and high temperature crystallization induces conditions suitable for degradation of iPP chain, especially above 300°C[13]. Therefore, in this study, crystallization was performed at 2450 bar to make the sample of less degradable stable γ form crystal.

Melting behaviour of the α and γ forms under high pressure

The d.t.a. thermograms for melting of the α form are shown in *Figure 4*. They exhibit a single endothermic peak for the whole pressure range. Additional peaks, as

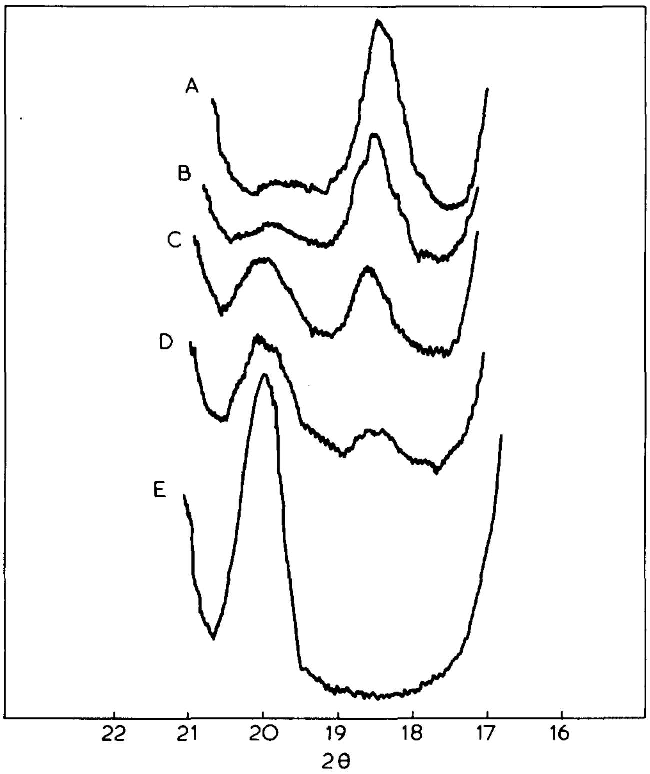

Figure 2 The X-ray diffraction scan for iPP crystallized at various pressures: A, 1; B, 232; C, 515; D, 899; E, 2397 bar

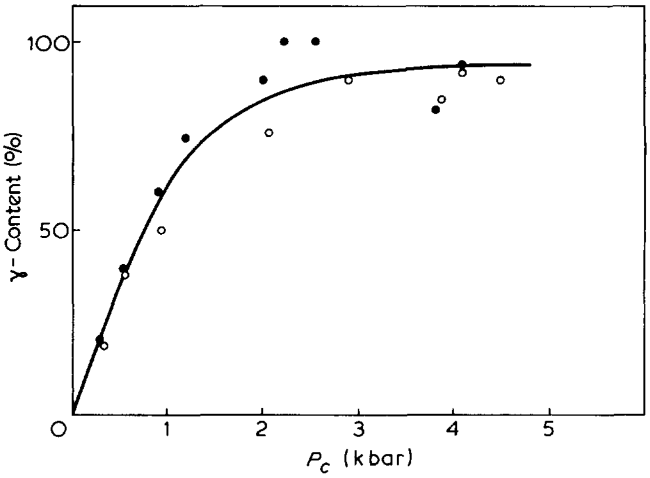

Figure 3 Change of the γ form content with crystallization pressure P_c. ●, X-ray; ○, d.t.a.

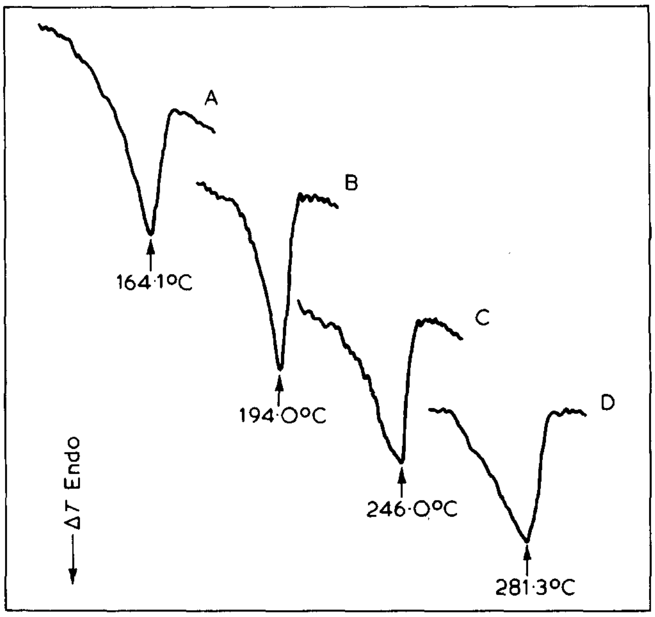

Figure 4 D.t.a. melting curves for the α form under high pressure: A, 1; B, 823; C, 2748; D, 4602 bar

observed in the d.t.a. melting curve of polyethylene or polyvinylidene fluoride, do not appear. In these polymers, the d.t.a. thermograms for melting under high pressure exhibit one or two additional peaks near the main melting peak of the original crystal. One of these new peaks was assigned to the solid–solid phase transition. A high pressure phase or solid–solid phase transition does not seem to exist under high pressure in iPP.

Figure 5 shows the d.t.a. thermograms of the γ form melting under various pressures. At high pressures, they exhibit a single endothermic peak of γ form melting as observed in the case of the α form melting under high pressure, so that the γ form is considered to melt in its crystalline form without conversion. At 1 atm, the partial conversion of the metastable γ form to the α form occurs, as already stated. The d.t.a. thermograms for crystallization during cooling from the melt at various pressures show a single sharp exothermic peak for all the pressure ranges studied. The sample of iPP crystallized by slow cooling under high pressure contains the α and γ form crystals in different ratios depending on the crystallization pressure as already shown in *Figure 1*. Comparison of these experimental facts led to the idea that crystallization to the α and γ form crystals can occur at the same temperature and at a given pressure.

Pressure dependence of T_m *and* T_c *in iPP*

The experimental data for T_m (the peak temperature in the d.t.a. curve) of the α and γ form crystals are plotted against pressure in *Figure 6*. The data fit the following quadratic equations

$$T_m = 164.1 + 0.0366\,P - 2.548\times10^{-6}\,P^2 \;\ldots\; \alpha\,\text{form}$$

$$T_m = 150.6 + 0.0395\,P - 2.980\times10^{-6}\,P^2 \;\ldots\; \gamma\,\text{form}$$

$$(P \text{ in bar, } T_m \text{ in } {}^\circ\text{C})$$

with standard deviations of 0.74°C and 1.02°C for the α and γ forms, respectively. From the above equation, the pressure dependence of the melting temperature at 1 atm $(\mathrm{d}T_m/\mathrm{d}P)_{P=1}$ is easily obtained, i.e., 0.0366°C/bar for the α form and 0.0395°C/bar for the γ form crystal. The mean value for both crystalline forms is 0.0381°C/bar and corresponds to the value reported by Leute *et al.*[2] for iPP without separating the two crystalline forms.

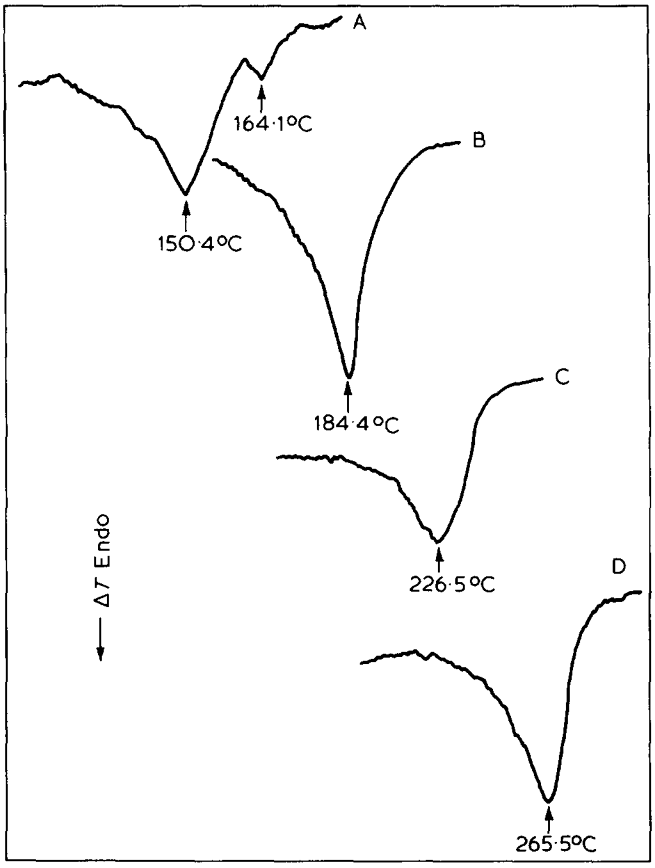

Figure 5 D.t.a. melting curves for the γ form under high pressure: A, 1; B, 936; C, 2474; D, 4381 bar

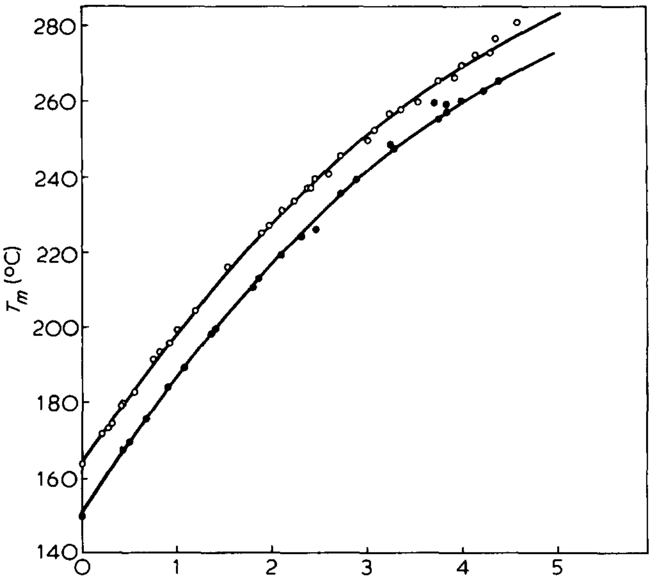

Figure 6 Pressure dependence of melting temperature of the α and γ forms. ○, α form; ●, γ form

The experimental data for T_c (the peak temperature in the d.t.a. crystallization curve) as a function of pressure are plotted in *Figure 7*. The T_c on the new sample and the

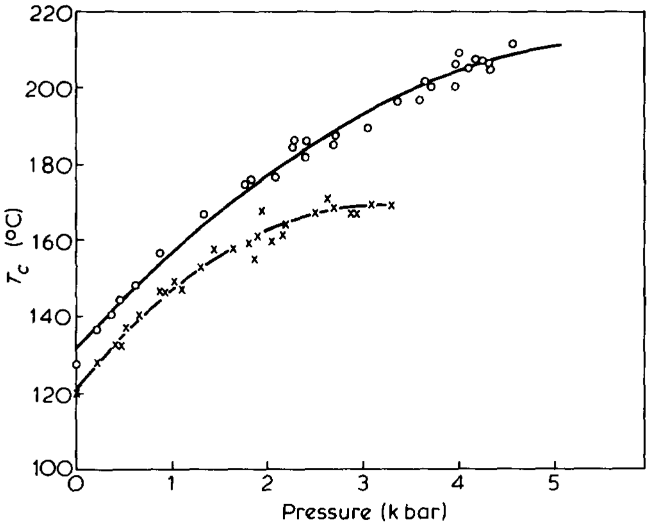

Figure 7 Pressure dependence of the crystallization temperature of iPP: X, the sample before melt-crystallization above 3400 bar; O, the sample after melt-crystallization above 3400 bar

melt-crystallized sample under high pressure below 3400 bar is plotted on the lower curve but once melt and crystallization was performed above 3400 bar, crystallization of the sample occurs at a higher temperature than crystallization of the original sample does. In these circumstances, the crystallization peak temperature in the d.t.a. curve under high pressure goes up and is plotted on the upper curve. The data fit the following quadratic equations

$$T_{c1} = 120.68 + 0.0307\,P - 4.935 \times 10^{-6}\,P^2$$

$$T_{c2} = 131.15 + 0.0276\,P - 2.312 \times 10^{-6}\,P^2$$

$$(P \text{ in bar, } T_{c1} \text{ and } T_{c2} \text{ in °C})$$

where T_{c1} and T_{c2} are the lower and higher crystallization temperatures at pressure P, respectively.

In order to investigate the origin of the occurrence of the two separate crystallization point curves, the average molecular weights of the sample melt-crystallized above 3400 bar and below 3400 bar were compared. The average molecular weight of the original material was 420 000. If it is crystallized from the melt at 2750 bar, the degradation is not severe and the molecular weight falls to 380 000. But the original sample is crystallized from the melt at 3900 bar, $\bar{M}_\eta$ is only 147 000. Conclusively, it seems to us that the melt and the crystallization of iPP above 3400 bar produces drastic degradation and the effect appears only in the crystallization point curve. The degradation is not effective on the melting temperature at 1 atm and under high pressure.

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