Effect of pressure on the melting and crystallization behaviour of isotactic polybutene-1

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The formation, melting and phase transition of isotactic polybutene-1 under high hydrostatic pressures were studied by high-pressure d.t.a. and X-ray diffraction up to 5 kbar. The d.t.a. thermogram of melting of form I shows a single endothermic peak up to 5 kbar. Form II crystallized directly from the melt at atmospheric pressure is metastable and it transforms to form I by the application of pressure. Above 900 bar, it transforms to form I completely and the endothermic peak of melting of form II is not observed. On crystallization from the melt under high pressure, the percentage content of form I′ increases with crystallization pressure and at 1.6 kbar only form I′ is crystallized. Above 2 kbar form II′, which shows the same X-ray diffraction pattern as form II, is crystallized from the melt. The percentage content of form II′ increases with pressure above 2 kbar, and that of form I′ decreases up to 5 kbar. Upon heating under high pressure above 2 kbar, a solid–solid transition from form II′ to form I′ is observed in d.t.a. traces and the transition is confirmed by high-pressure X-ray diffraction. The melting temperature is expressed in the form of a quadratic equation as a function of pressure for four different forms in IPB-1.

Keywords Pressure; melting behaviour; crystallization behaviour; isotactic polybutene-1

INTRODUCTION

Isotactic polybutene-1 (IPB-1) shows complicated crystallization and crystal–crystal transition behaviour in different polymorphs at atmospheric pressure, especially in solution-grown crystals[1–3].

On crystallization from the melt at atmospheric pressure, IPB-1 crystallizes in metastable form II (tetragonal) and gradually transforms to stable form I (rhombohedral) on standing at room temperature and atmospheric pressure. Form III, which is also stable at room temperature, is produced by crystallization in a dilute solution of a certain solvent.

The application of pressure makes the phenomena more complicated. The transformation of form II to form I is known to be accelerated by the application of pressure of only a few hundred bars[4]. The melt crystallization of IPB-1 under high pressure produces stable form I′ which shows the same X-ray diffraction pattern as form I but has a much lower melting temperature (96° vs. 130°C) at atmospheric pressure.

The pressure dependence of melting temperature (T_m) has been studied for many crystalline polymers in recent years[5]. In IPB-1, the volume change of form I at elevated pressure was measured with a dilatometer by Armeniades and Baer[6]. They reported the pressure dependence of T_m and thermodynamic values of form I. Their work is considered to be the only one on IPB-1 concerned with high pressure, except for the early work by Natta *et al.*[4]

In this paper, the change with pressure of the d.t.a. thermograms of melting for four crystalline forms of IPB-1 including a new form crystallized under high pressure is reported. Crystallization in different polymorphs under high pressure is investigated by d.t.a. and X-ray diffraction. The pressure change of T_m for four crystalline forms is determined in the form of a quadratic equation and the coefficients are determined from the experimental data. The solid–solid phase transition from high-pressure-crystallized form II′ to form I′ at high-pressure is also investigated.

EXPERIMENTAL

The sample studied was pellets of high molecular weight IPB-1 polymerized by Scientific Polymer Products Inc., and the molecular weight determined by viscosity measurements in decalin at 115°C was 945 000.

The high-pressure d.t.a. apparatus used in this study was reported elsewhere[7]. A sample of about 8 mg was put on the hot junction of a thermocouple and covered by epoxy resin. The d.t.a. measurement for form II sample at elevated pressure was performed on the sample at the thermocouple junction just after cooling to room temperature from the melting point at atmospheric pressure. The d.t.a. measurement for form I was performed on a sample transformed from form II by ageing for 5 days at room temperature and 1 atm. The high-pressure d.t.a. measurement for form I was performed for a sample transformed from form II by the application of pressure above 1 kbar. The d.t.a. thermogram of melting of form I′ under high pressure was obtained on a sample crystallized during cooling from the melt under high pressure. The heating rate of the d.t.a. experiment was 5°C min^{-1} and the cooling rate around crystallization temperature was about 6°C min^{-1}. The cooling rate in the initial stages (high temperature) was high but it changed to low at low temperature.

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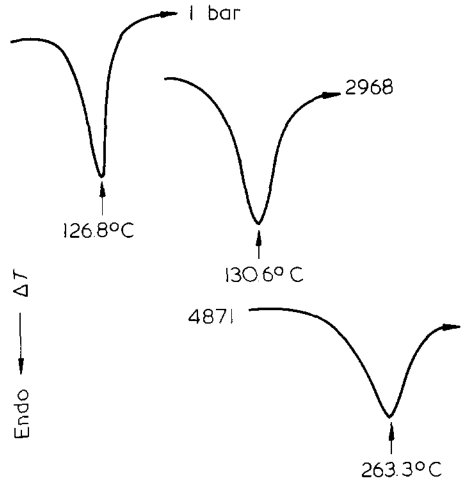

Figure 1 D.t.a. traces of melting of form I under various pressures

A high-pressure and high-temperature X-ray camera was used to take the powder pattern on cyclindrical film to clarify the nature of the phase transition that appeared as an endothermic peak (shoulder) in the d.t.a. traces under high pressure for the sample crystallized under high pressure.

A position-sensitive proportional counter (PSPC) system coupled with a high-pressure X-ray diffraction cell[8] was used (by courtesy of Professor Takemura of Kyushu University) to observe the melting and crystallization process under high pressure.

RESULTS AND DISCUSSION

Melting of form I and form II under high pressure

The experimental melting temperature of form I at 1 atm is between 120° and 130°C, depending on crystallite size[9]. The d.t.a. thermogram of melting of form I shows a single endothermic peak (peak temperature at 126.8°C) at 1 atm in our experiment as shown in *Figure 1*. The peak moves to higher temperature with increasing pressure and the peak becomes broad, but multiple peaks were not observed up to 5 kbar. No indications of the solid–solid phase transition from form I to the other crystalline modifications under high pressure as observed in the d.t.a. traces in polyethylene[10–12] and poly(vinylidene fluoride)[13] were observed.

Figure 2 shows the effect of pressure on the nature of the d.t.a. traces of melting of form II. Form II is metastable and transformed to form I at atmospheric pressure and room temperature with the transition half-time ranging from 250 min to 1600 min. It is also transformed to form I by the application of pressure. In the d.t.a. trace of melting of form II in the isobaric measurement at 366 bar, a small endothermic peak is observed on the high-temperature side of the melting peak of form II. The peak is attributed to the melting of form I transformed from form II by the application of pressure. The relative intensities of the high-temperature melting peak increase with applied pressure and the low-temperature peak intensity decreases with pressure up to 900 bar. At 966 bar, no peak of melting of form II is observed in the thermogram as shown in the lowest curve in *Figure 2*: form II crystallized from the melt at atmospheric pressure is considered to be transformed to form I completely above 900 bar.

Crystallization of IPB-1 under high pressure

According to Armeniades and Baer[6], crystallization of IPB-1 from the melt under high pressure up to 1 kbar produces form II which is transformed to form I spontaneously by a pressure effect, and above 1 kbar forms I and I′ crystallize directly from the melt. The typical d.t.a. traces of melting at atmospheric pressure on IPB-1 crystallized at various pressures up to 1.8 kbar are shown in *Figure 3*. The d.t.a. trace of the sample crystallized at 1 atm shows a single endothermic peak due to the melting of form II but the d.t.a. traces of the sample crystallized under high pressure up to 1.5 kbar show two peaks. The peak position of the high-temperature endotherm corresponds to the melting point of form I and the peak position of the low-temperature peak corresponds to the melting point of form I′. Form I thus existing is considered to have been transformed from form II crystallized initially under pressure as stated in ref. 6. The intensity of the melting peak of form I′ increases with crystallization pressure but that of form I decreases up to 1.6 kbar. If crystallization is performed above 1.6 kbar, only the endothermic peak of melting of form I′ is observed, i.e. only crystallization to stable form I′ seems to occur above 1.6 kbar.

The d.t.a. traces of the sample crystallized above 2 kbar show two endothermic peaks again. *Figure 4* shows the typical d.t.a. thermograms of melting at 1 atm of a sample crystallized above 2 kbar. At 2.27 kbar, a small peak is observed on the high-temperature side of the melting peak of form I′ in the d.t.a. trace. The peak temperature is very close to the melting point of form II. The intensity of the high-temperature peak increases with pressure and that of

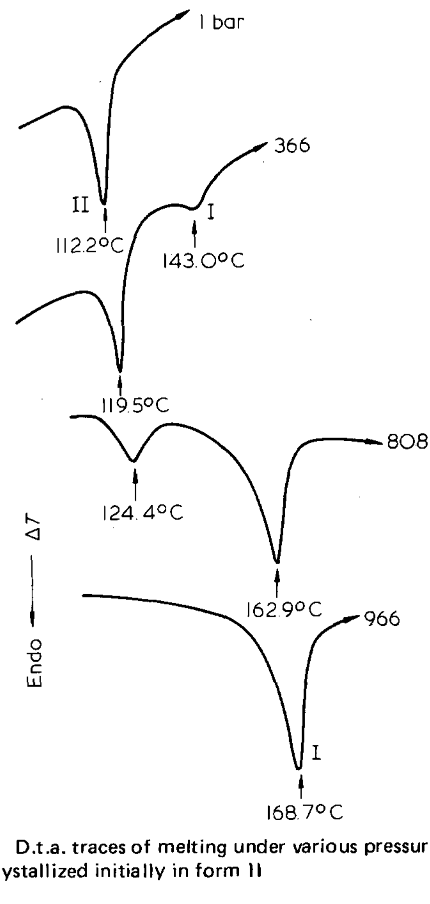

Figure 2 D.t.a. traces of melting under various pressures on a sample crystallized initially in form II

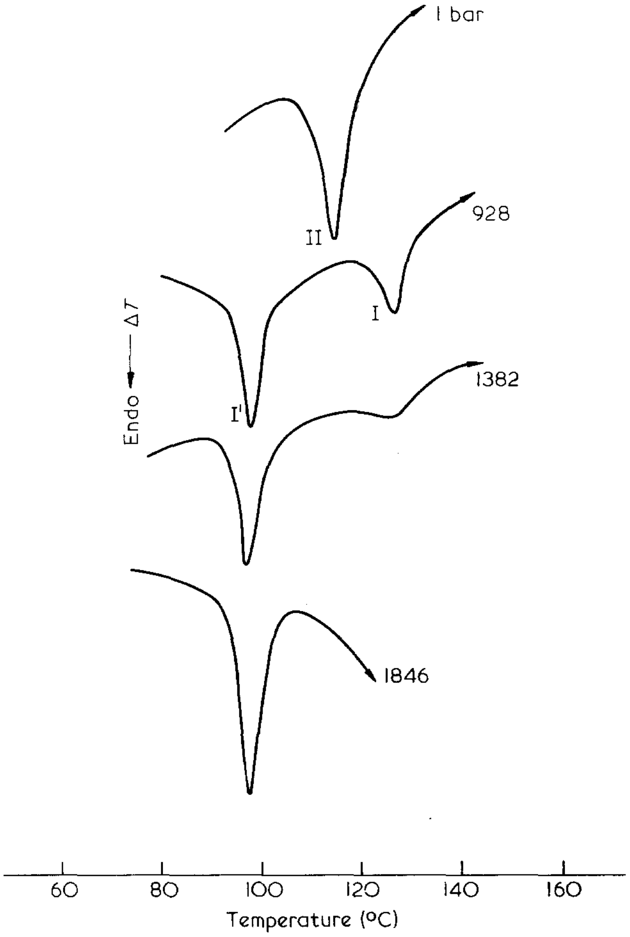

Figure 3 D.t.a. traces of melting at atmospheric pressure on a sample crystallized under pressure

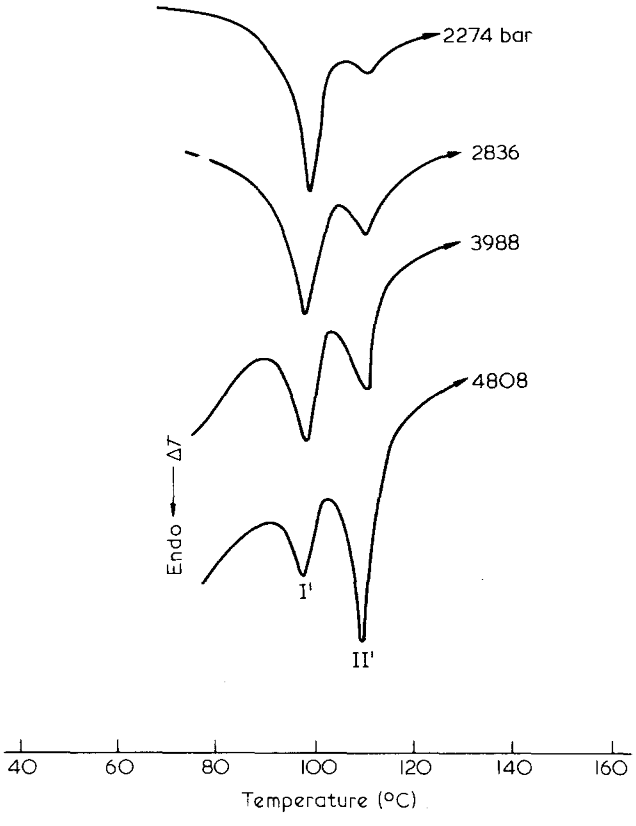

Figure 4 D.t.a. traces of melting at atmospheric pressure on a sample crystallized under high pressure up to 5 kbar

form I' decreases, in contrast to the pressure change of the intensity below 1.6 kbar that is shown in *Figure 3*.

The percentage content of form I' was determined by comparison of peak areas for each form in the d.t.a. trace of melting. *Figure 5* shows the change of form I' content with crystallization pressure. The percentage content of form I' increases drastically with crystallization pressure up to 1.5 kbar. Between 1.5 and 2 kbar, only form I' is crystallized from the melt. Above 2 kbar, the relative intensity of form I' decreases with crystallization pressure. To characterize the crystalline form of the high-pressure-crystallized sample which shows the high-temperature melting peak in *Figure 4*, X-ray diffractometer scans were performed. *Figure 6* shows the X-ray diffractometer scan on a sample crystallized at various pressures. In *Figure 6c*, we can observe mixed diffraction lines from forms I' and II for the sample crystallized at 4.8 kbar. The d.t.a. and X-ray diffraction experiments show conclusively that high-pressure crystallization of IPB-1 from the melt above 2

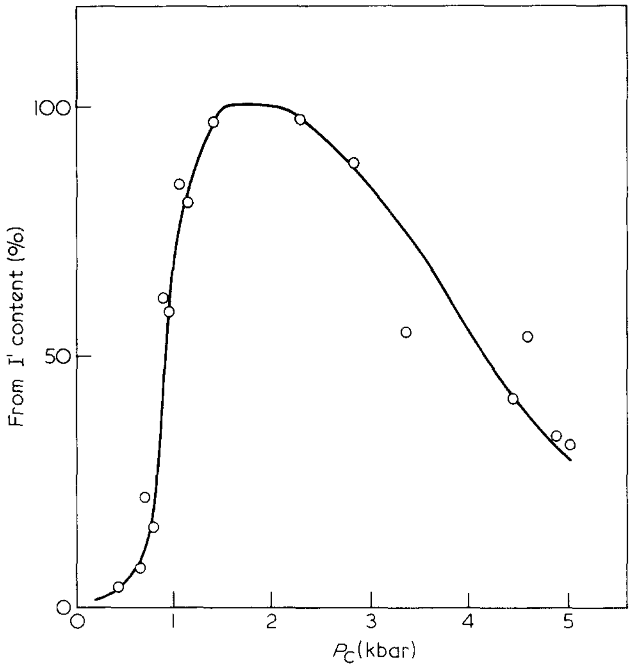

Figure 5 Form I' content as a function of crystallization pressure

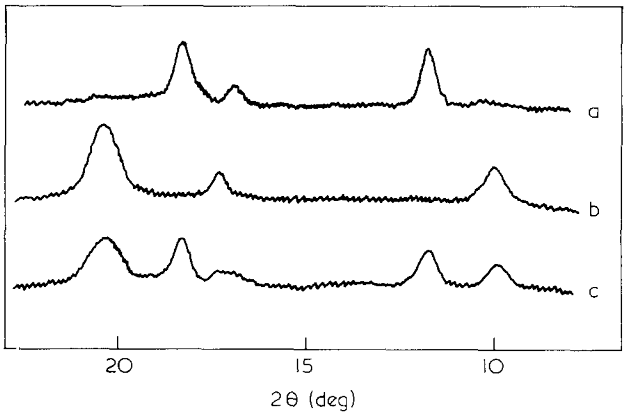

Figure 6 Comparison of the X-ray diffractometer scans on three samples: (a) form II crystallized at 1 atm from the melt; (b) form I' crystallized under a pressure of 2 kbar; (c) sample crystallized at 4.8 kbar

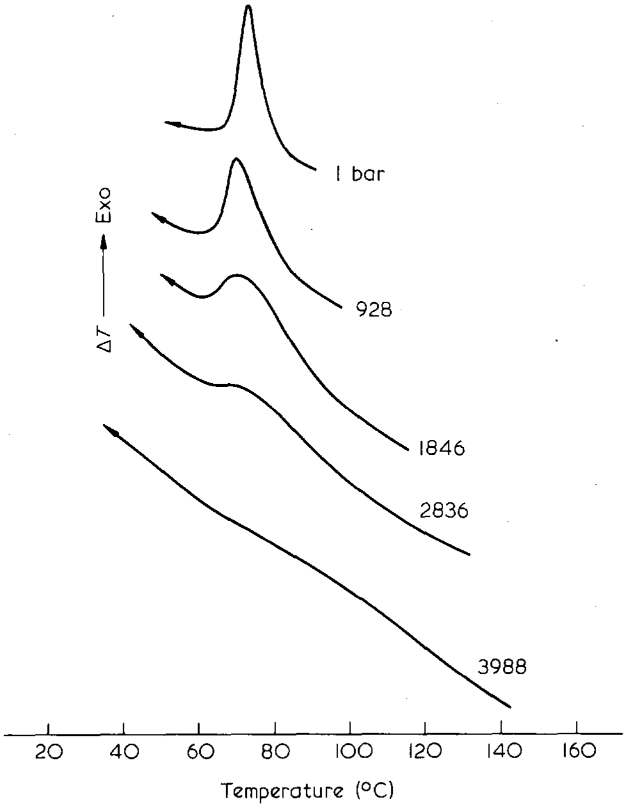

Figure 7 D.t.a. traces of crystallization of IPB-1 under high pressure

kbar produces forms I′ and II directly. The high-pressure-crystallized form II is called form II′ hereafter, because the melting temperature of this form is lower than that of form II crystallized at 1 atm and the pressure dependence of T_m is completely different. Form II′ increases with crystallization pressure above 2 kbar, in contrast to the decrease in content of form I′. The form II′ content also depends on the cooling rate under the crystallization pressure. The data in *Figures 4* and *5* are obtained using a cooling rate of ~6°C min^{-1}. By slow cooling, the percentage content of form I′ increases and that of II′ decreases. The percentage contents are reversed by high-speed cooling. Form II′ is metastable and it transforms to form I′ on standing at room temperature and atmospheric pressure. The transformation was confirmed by d.t.a. and X-ray diffractometer scans. Under high pressure, form II′ is more stable than form II crystallized normally but still transforms to form I′.

The d.t.a. traces of crystallization of IPB-1 at elevated pressure are shown in *Figure 7*. In the other polyolefins, for example polyethylene[11] and isotactic polypropylene[14], the exothermic peak of crystallization is observed in the d.t.a. trace under high pressure up to 5 kbar, and the peak shifts to higher temperature with pressure. In IPB-1, however, the exothermic peak of crystallization becomes broad and the peak height decreases with pressure as was the case of polychlorotrifluoroethylene[7]. Above 3 kbar, it is impossible to distinguish the peak from the baseline of the d.t.a. curve. The peak temperature is almost constant with pressure change.

In order to investigate the crystallization and melting behaviour of IPB-1 under high pressure, a PSPC system in connection with a high-pressure X-ray cell with Be metal window was used. The utility of the system for high-pressure work has been reported in detail already[8,13]. *Figure 8* shows the series of X-ray diffraction patterns for different temperatures at 1.47 kbar as a typical example. The sample melt-crystallized at 1 atm shows a (200) diffraction peak of form II at 11.8° in 2θ at room

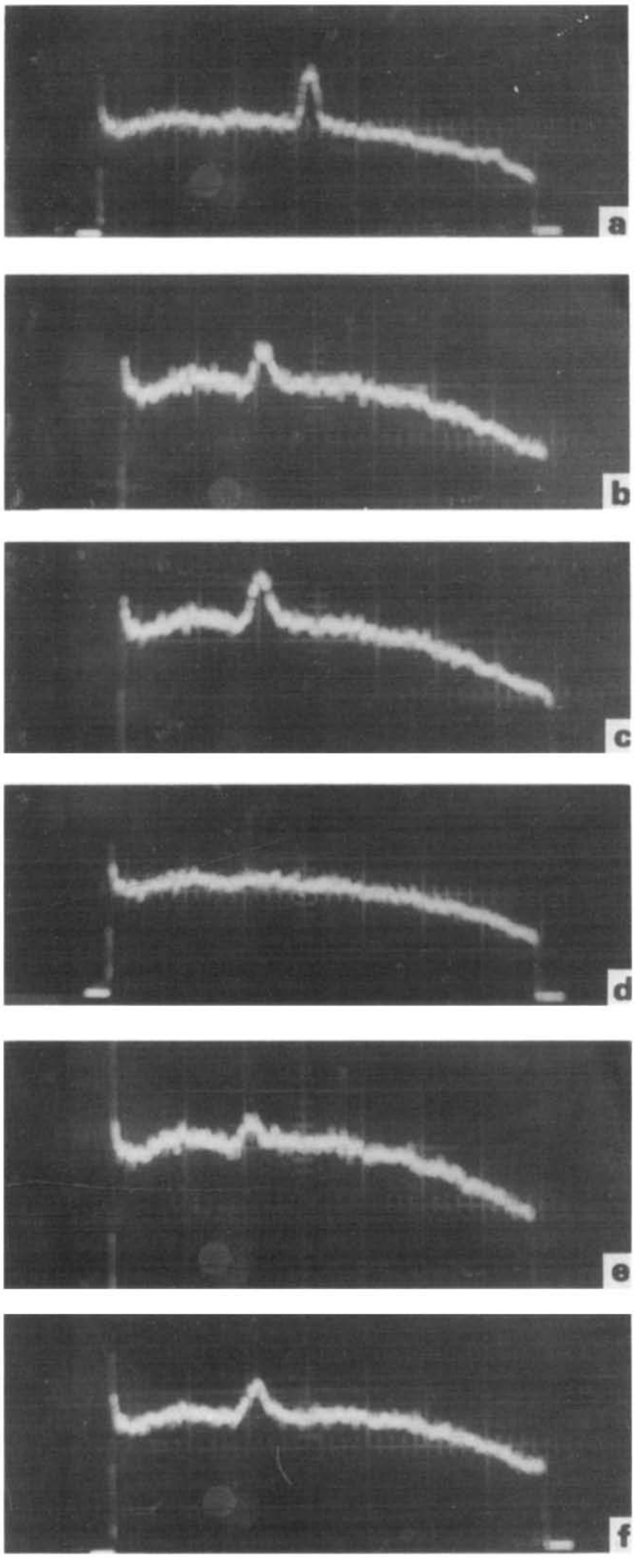

Figure 8 The X-ray diffraction patterns observed by PSPC system during heating and cooling: (a) 25°C, 1 atm; (b) 25°C, 1.47 kbar; (c) 155°C, 1.47 kbar; (d) 191°C, 1.47 kbar; (e) 104°C, 1.47 kbar; (f) 50°C, 1.47 kbar

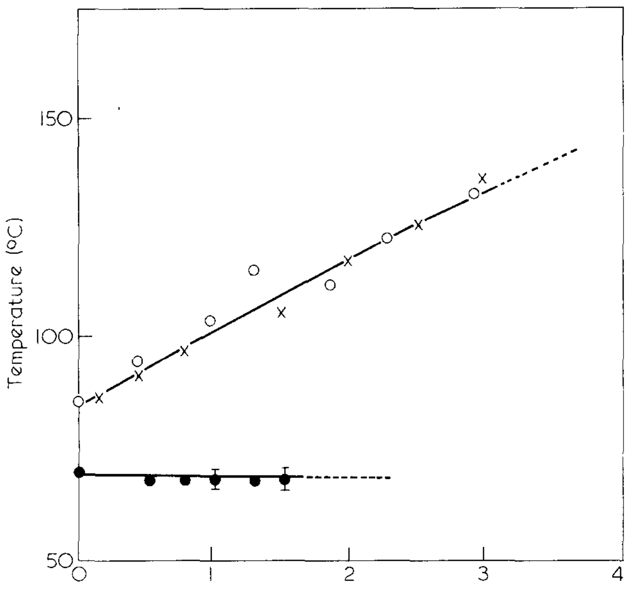

Figure 9 Crystallization temperature as a function of pressure: ○, starting point of crystallization by X-ray diffraction; X, starting point of crystallization by d.t.a.; ●, peak temperature of d.t.a. thermogram

temperature and atmospheric pressure (a). By the application of pressure of 1.47 kbar, the diffraction peak of form II disappears and only the diffraction peak of form I is observed at 10.0°. During heating at 1.47 kbar, the sample keeps the same crystalline form (c). At 191°C, it melts completely and no diffraction peaks were observed (d). On cooling, the (110) diffraction line of form I′ begins to appear at 104°C, where crystallization starts (e) and the intensity of the diffraction peak increases gradually with decreasing temperature (f). The starting points of crystallization thus determined by X-ray diffraction are plotted against pressure in *Figure 9*. The starting points were also determined in the d.t.a. thermogram as the intersection point at the extension of the baseline and the extension of the high-temperature side of the curve of the thermogram of crystallization, and are plotted in *Figure 9*. The starting point of crystallization increases with pressure. The peak temperature in the d.t.a. thermogram of crystallization is also plotted as a function of pressure in the Figure. The peak temperature does not seem to change with increasing pressure up to 1.5 kbar. The temperature difference between the starting point and the peak increases with pressure. This indicates that the crystallization rate decreases with pressure in IPB-1.

Melting of high-pressure-crystallized IPB-1 under pressure

As already stated, high-pressure crystallization of IPB-1 from the melt above 2 kbar produces forms I′ and II′. The d.t.a. thermograms of melting of high-pressure-crystallized forms I′ and II′ were investigated under high pressure up to 5 kbar. As shown in *Figure 10*, the intensity of the melting peak of form II′ decreases with increasing pressure in the experiment performed without releasing the pressure to 1 atm. In contrast, the intensity of the melting peak of form I′ increases with increasing pressure. This fact indicates that the solid–solid transition from form II′ to form I′ is accelerated by the elevation of pressure in the d.t.a. experiment. The decrease of crystallinity of the sample by the application of pressure is not considered because, if it occurs, the intensity of both melting peaks (II′ and I′) should decrease together. A small endothermic peak of melting appears in the d.t.a. curve at 1.5 kbar for high-pressure-crystallized form II′, so that a small amount of form II′ can exist without transformation to the other form up to 2 kbar, where the small peak still remains.

If the d.t.a. measurement is performed at elevated pressure after reducing the pressure to 1 atm from the crystallization pressure, the thermogram shows different features from the d.t.a. curve obtained in the experiment under high pressure changed directly with the crystallization pressure without reducing the pressure to 1 atm. *Figure 11* shows an example of the d.t.a. curve of IPB-1 obtained at 4.8 kbar after reducing the pressure to 1 atm from the crystallization pressure of 4.8 kbar. The melting endotherm of forms I and I′ is observed. Form I in this stage is considered to be transformed from form II′ during the application of pressure, because form II′ exists at 1 atm (the top trace in *Figure 10*).

The d.t.a. trace of melting of IPB-1 under a pressure converted directly from the crystallization pressure changes with pressure above 2 kbar. *Figure 12* shows the effect of pressure on the d.t.a. traces of melting of the high-pressure-crystallized sample. At ~2 kbar a single peak of melting of form I′ is observed, but at 2.9 kbar a small shoulder appears on the low-temperature side of the melting peak of form I′. The temperature difference between the peak of melting of form I′ and the shoulder as indicated by the arrows increases gradually with pressure. The temperature of the shoulder is plotted against pressure in *Figure 13*. In order to clarify the origin of the

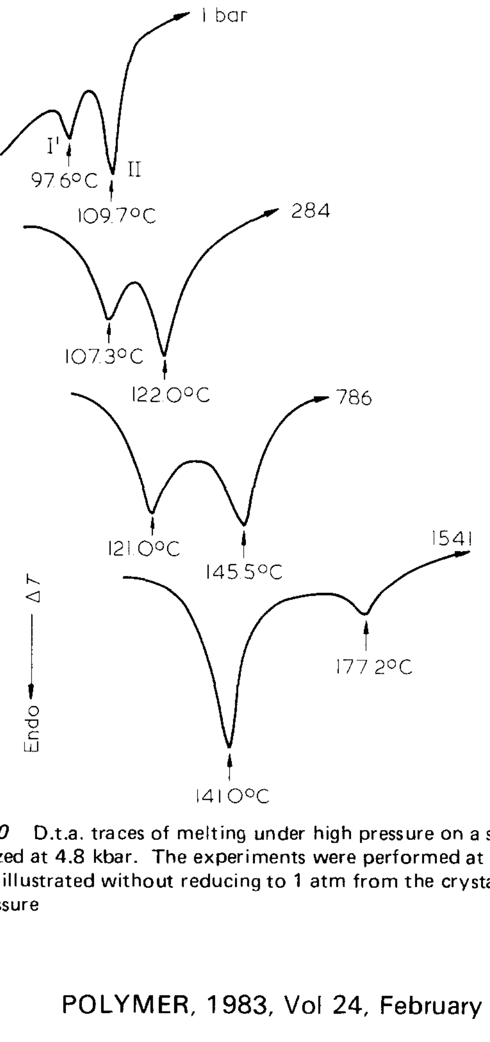

Figure 10 D.t.a. traces of melting under high pressure on a sample crystallized at 4.8 kbar. The experiments were performed at the pressure illustrated without reducing to 1 atm from the crystallization pressure

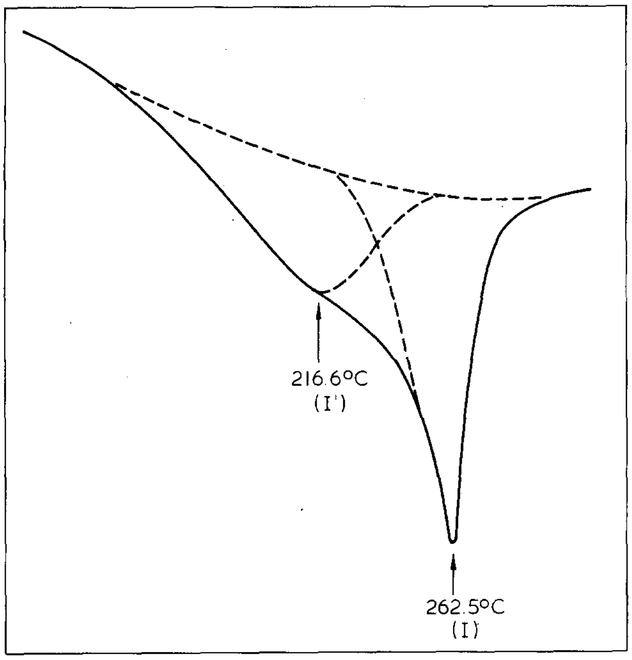

Figure 11 D.t.a. trace of melting under 4.8 kbar after reducing the pressure to 1 atm from the crystallization pressure

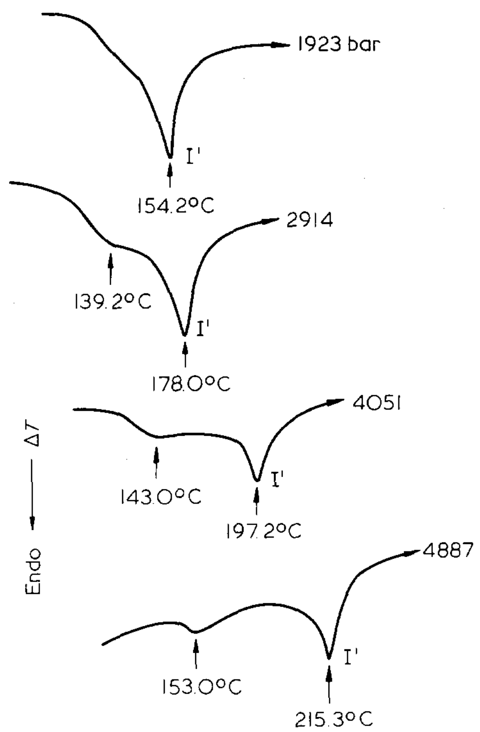

Figure 12 D.t.a. traces of melting under high pressure from 2 to 5 kbar for a sample crystallized under a pressure of 4.8 kbar

endothermic peak (shoulder), a high-pressure X-ray camera was used. The X-ray diffraction photographs taken on cylindrical film at 1 atm and 10°C and at 3 kbar and 155°C on a sample crystallized at 4.8 kbar are shown in *Figures 14a* and *b*. The diffraction lines from forms I′ and II′ at atmospheric pressure for the sample crystallized at 4.8 kbar can be clearly observed. When the sample is heated to 155°C at 3 kbar, only the diffraction pattern of form I′ is observed (b). In the d.t.a. trace of melting in *Figure 12*, no endothermic peak appears at the melting temperature of form I, so that the shoulder in the d.t.a. trace is attributed to the solid–solid phase transition from form II′ to form I′. The X-ray diffraction pattern at atmospheric pressure and room temperature taken after the second experiment shows the same pattern as *Figure 14b*, and therefore the transition is believed to be an irreversible process. Here, the idea that the shoulder is due to the melting of form II′ may be ruled out because the melting temperature of form II′ is very high (about 200°C at 2 kbar) as shown later in *Figure 15*.

Pressure dependence of melting temperature in each form

In IPB-1, the pressure dependence of the melting temperature has only been reported for form I[6]. We can now determine the pressure dependence of the melting temperature for four polymorphs by using the data in d.t.a. experiments under high pressure described in the earlier section. The peak temperature in the d.t.a. thermogram is plotted as a function of pressure in *Figure*

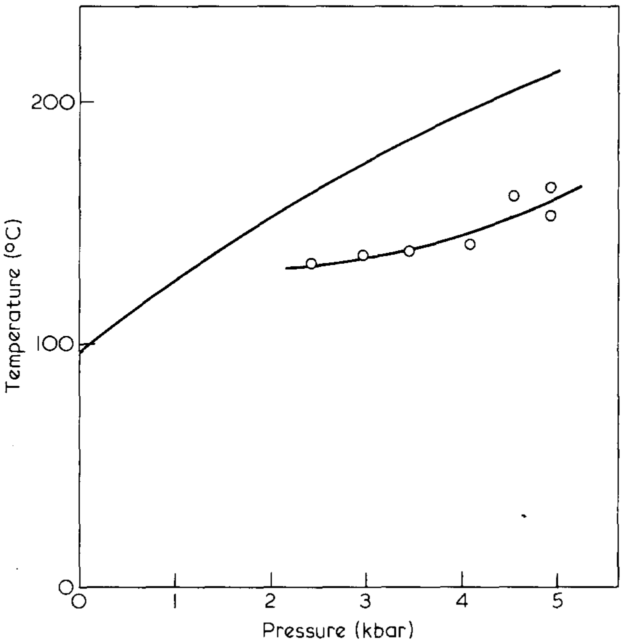

Figure 13 Temperature of shoulder vs. pressure. The full curve is the melting curve of form I′

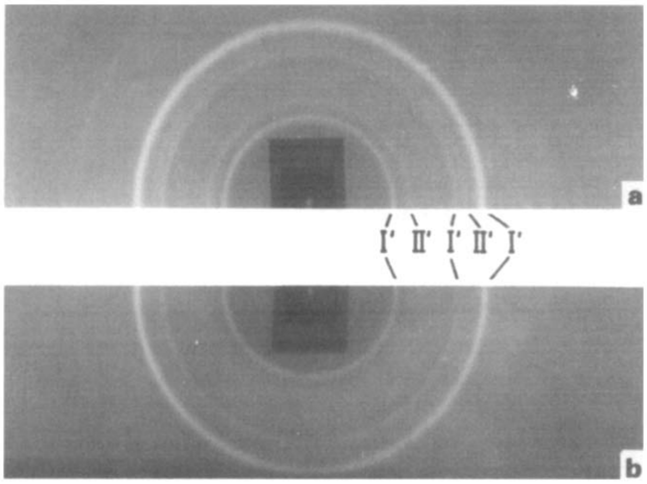

Figure 14 The X-ray diffraction pattern of a sample crystallized at 4.8 kbar: (a) 10°C, 1 atm; (b) 155°C, 3 kbar

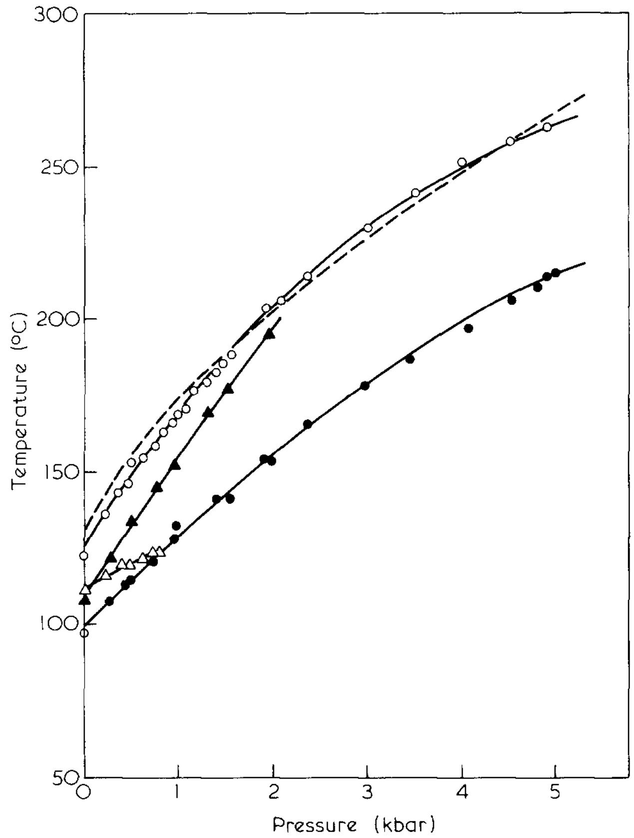

Figure 15 Melting curve for forms I, I′, II and II′: ○, form I; ●, form I′; △, form II; ▲, form II′; — — — —, by Armeniades and Baer

Table 1

	A (°C)	B ($\times 10^{-2}$) (°C bar^{-1})	C ($\times 10^{-6}$) (°C bar^{-2})	$(dT_m/dP)_{1\,atm}$ (°C bar^{-1})
I	127.7	4.55	3.65	45.5
II	112.1	2.38	1.06	23.8
I′	99.2	3.18	1.72	31.8
II′	109.8	4.73	1.53	48.7
I				52.3[a]

[a] Armeniades and Baer

15 for four polymorphs. In comparison with the result of Armeniades and Baer[6], T_m of form I below 1.5 kbar by d.t.a. is slightly low and between 1.5 and 4.5 kbar the value is higher than their value. The slope of the melting curve (dT_m/dP) for form I′ is smaller than for form I up to 3.5 kbar. The data for all the polymorphs were fitted to the conventional quadratic equation,

$$T_m = A + BP + CP^2$$

and the coefficients A, B and C were determined by the least-squares method. *Table 1* lists the values of A, B and C thus determined. The values of $(dT_m/dP)_{1\,atm}$ are also listed. The value of $(dT_m/dP)_{1\,atm}$ for form I in this study is 45.5°C kbar^{-1} and is smaller than the value reported by Armeniades and Baer. The value for form I′ is 31.8°C kbar^{-1}, which is much smaller than the value for form I. The difference between the two forms may be due to a difference between the fold planes of their crystalline lamellae as suggested by Armeniades and Baer. The difference in T_m at 1 atm (about 30°C) for the two polymorphs cannot be explained in terms of crystallite size and perfection alone. Haase *et al.*[9] obtained a straight line for T_m vs. the reciprocal mean crystallite size and reported the melting temperature for an infinite crystal of IPB-1 (form I) as 138.6°C. If we use 96°C as T_m and 155 Å as long period of form I′, and 130°C as T_m and 300 Å as long period for form I (the data from Armeniades and Baer), we can obtain the ratio of surface free energy of folded lamellae from the well known Thomson–Gibbs equation by assuming equal Δh_f (enthalpy of fusion) for both forms. The surface free energy for form I′ thus obtained is about 2.5 times greater than that of form I. A relatively large number of sharp folds are assumed to exist on the surface of form I crystallite compared with form I′. The application of pressure may be sensitive to molecular motion in sharp folds compared with disordered loops, and the difference in the amount of sharp folding is considered to reflect the difference in pressure dependence of T_m for forms I and I′. Holland and Miller[1] used 'twinned hexagonal' to name form I crystal and 'untwinned hexagonal' for form I′ crystal from observation of the electron diffraction patterns of solution-grown crystals. However, it is impossible to explain the difference in T_m at 1 atm and in pressure dependence of T_m by this model alone.

The slope of dT_m/dP for high-pressure-crystallized form II′ is the highest for all the polymorphs in IPB-1 and at 1 atm it is almost twice that of form II crystallized at atmospheric pressure. Such a large difference of the value $(dT_m/dP)_{1\,atm}$ suggests a difference in the inside of the crystallites. Form II′ crystallized under high pressure may have many more defects in the crystallite.

CONCLUSIONS

The results presented in this paper are summarized as follows. The d.t.a. traces of melting of form I show a single endothermic peak under high hydrostatic pressures up to 5 kbar. Form II crystallized at 1 atm or under high pressure below 1 kbar transforms to form I by the application of pressure up to 900 bar. Above 900 bar, it transforms completely to form I. Under high pressure below 1.5 kbar, IPB-1 crystallizes in forms I′ and II directly from the melt, and form II transforms rapidly to form I. Between 1.6 and 2 kbar, only form I′ is crystallized from the melt. Above 2 kbar, form I′ and form II′, which shows the same X-ray diffraction pattern as form II, are crystallized from the melt and the percentage content of form II′ increases with crystallization pressure up to 5 kbar.

The solid–solid phase transition from form II′ to form I′ is observed in the heating process under high pressure changed directly from the crystallization pressure. Form II′ is metastable at atmospheric pressure and transforms to form I′ on standing at room temperature.

The pressure dependences of T_m for four crystalline forms were determined by the pressure change of the peak temperature of d.t.a. curves of melting. The melting temperature was represented as a function of pressure in the form of a quadratic equation. The value of $(dT_m/dP)_{1\,atm}$ is largest for form II′.

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