Melting behaviour of isotactic polypropylene isothermally crystallized from the melt

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A detailed study using d.s.c. of the melting behaviour of isotactic polypropylene isothermally crystallized from the melt has been carried out. The origin of multiple fusion endotherms was sought. It is shown that at lower crystallization temperatures ($T_c \leqslant 400$ K), this phenomenon is dominated by crystal imperfections. On heating, the crystallized fraction undergoes reorganization or recrystallization resulting in a fraction consisting of crystals of greater degree of perfection, which melt at a higher temperature. As the crystallization temperature is increased, the crystallization proceeds more slowly accompanied by simultaneous annealing. Therefore, the extent of reorganization or recrystallization goes on decreasing with T_c. At higher crystallization temperatures ($T_c > 400$ K), the inbuilt defects in the molecular chain begin to dominate. At these temperatures, the multiple endotherms are caused by the presence of crystalline species having different degrees of crystal disorder and stereoblock character. It is further shown that the observed multiple values for the equilibrium melting temperature are also due to the presence of such crystalline species.

(Keywords: melting behaviour; isotactic polypropylene; differential scanning calorimetry; isothermal crystallization; annealing; stereo-irregularity)

INTRODUCTION

The melting behaviour of isotactic polypropylene crystallized in a number of different ways has been studied by several workers[1–5]. A common feature of all these investigations has been the observation of multiple fusion endotherms. The appearance of such multiple endotherms has been attributed to several factors such as two different crystal forms[1,2], discrete bunching of crystallites of varying degrees of perfection[3,4], difference in crystallite size[5], etc. None of these factors can fully explain the observed results. The origin of multiple fusion endotherms, therefore, still remains far from being completely understood. For a better understanding of this process, a systematic study of the isothermal crystallization of isotactic polypropylene is, therefore, in order. The present paper deals with the results of such a study. To elucidate further, the polypropylene sample was fractionated into three fractions having varying degrees of stereo-irregularity, i.e. the extent of head-to-head or tail-to-tail monomeric units in the polymer chain. Isothermal crystallization of these fractions was also investigated in detail.

A very important thermodynamic property of a crystalline polymer is its equilibrium melting temperature, T_m°. For isotactic polypropylene, several conflicting values of T_m° have been reported in the literature[5–7]. In the present work an attempt has been made to estimate the values of T_m° for the bulk and fractionated samples. This has helped in resolving the existing anomalies.

EXPERIMENTAL

In the present study a commercial grade sample of isotactic polypropylene (M6100) manufactured by Indian Petrochemicals Corporation Limited was used. Some of the bulk properties of this material are given in *Table 1*.

The solubility of isotactic polypropylene in different hydrocarbon solvents is a function of the chain stereo-irregularity[8]. It has been shown by Natta[8] that 100% stereoregular isotactic polypropylene is insoluble in n-octane; a sample having stereo-irregularity to the extent of 2.5 to 3.4% is insoluble in n-heptane; a sample having stereo-irregularity to the extent of 7.2 to 12.2% is soluble in n-heptane but is insoluble in n-hexane; and a sample having stereo-irregularity to an extent of 17.3 to 27.8% is soluble in n-hexane but is insoluble in n-pentane. This principle has been employed for fractionating the polypropylene sample used in this work. For this purpose, its solubilities in boiling n-octane, n-heptane, n-hexane and n-pentane were examined. The sample was found to be completely soluble in n-octane but partly soluble in n-heptane, n-hexane and n-pentane indicating that the initial sample contained three fractions of varying degrees of stereo-irregularity. These fractions were extracted by evaporating the corresponding solvent. Detailed characteristics of these fractions are given in *Table 2*.

A Perkin–Elmer DSC-1B differential scanning calorimeter (d.s.c.) was used for all isothermal crystallization and melting behaviour studies. Its temperature scale was calibrated against the melting temperatures of standard reference materials.

Isothermal crystallization was carried out in the sample can of the d.s.c. In every case 5–10 mg of the sample was first heated up to 460 K and kept at this temperature for about 30 min. This was done to erase any previous morphological history which the sample might be carrying. The sample was then cooled rapidly to the crystallization temperature and kept at this temperature for a time such that there was no further growth of crystallinity in the sample. This was ascertained from

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Table 1 Bulk properties of isotactic polypropylene sample

Property	Value
Density	0.902 g/cm^3
Weight-average molecular weight (M_w)	2.6×10^5
Molecular weight dispersion (M_w/M_n)	12.24
Melting temperature (granules)	436 K

Table 2 Characteristics of the fractions of isotactic polypropylene

Fraction	Relative proportion (%)	Insoluble in	Extent of stereo-irregularity (%)
I	32	n-heptane	2.5–3.4
II	66	n-hexane	7.2–12.2
III	2	n-pentane	17.3–27.8

dilatometric measurements. The sample was then cooled rapidly (32 K/min) to room temperature and the corresponding d.s.c. curve was recorded in every case. Absence of any crystallization peak in the d.s.c. traces during cooling further confirmed that the isothermal crystallization was complete and no fraction of the sample remained uncrystallized which was capable of crystallizing during cooling. However, in one case the sample was quenched directly from the melt phase by placing it in liquid nitrogen. For isothermal annealing, a crystallized sample was heated rapidly (32 K/min) in the sample can of the d.s.c. up to the annealing temperature. This was done to avoid any recrystallization during heating. Annealing was terminated after the desired time by cooling the sample rapidly to room temperature. No crystallization peak was observed during cooling.

The melting behaviour of the isothermally crystallized and annealed samples was studied in the Perkin–Elmer DSC-1B. The d.s.c. curves of the melting of these samples were recorded at a scan rate of 8 K/min or as otherwise mentioned. However, to investigate the effect of heating rate, the samples crystallized under identical conditions were heated at different rates.

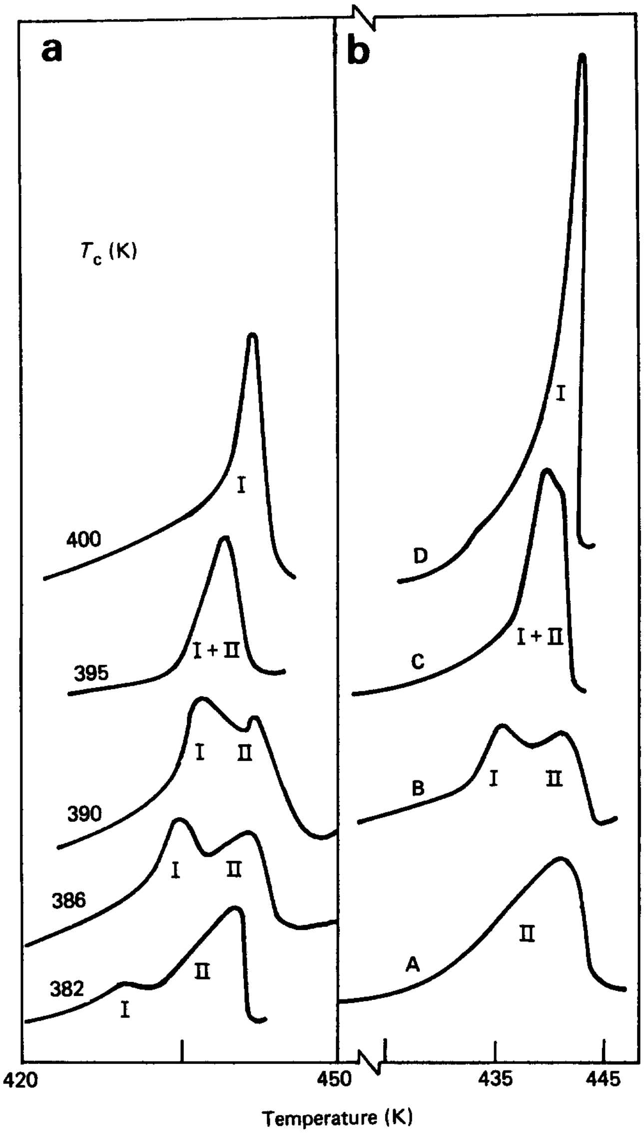

Figure 1 D.s.c. thermograms for melt crystallized isotactic polypropylene ($T_c \leqslant 400$ K): (a) Effect of crystallization temperature, T_c; the curves are for a heating rate 4 K/min. (b) Effect of heating rate on a sample crystallized at 386 K; curves A, B, C and D are for heating rates 2, 4, 8 and 16 K/min, respectively

RESULTS AND DISCUSSION

Some typical d.s.c. curves for the melting of isotactic polypropylene samples, completely crystallized at different temperatures, are shown in *Figures 1* and *2*. A general feature of these curves is the appearance of two fusion endotherms. The details of the melting behaviour are, however, found to depend on the crystallization temperature. On the basis of similarity in melting behaviour, the crystallized samples can be placed into two groups: (a) $T_c \leqslant 400$ K and (b) $T_c > 400$ K. The melting behaviour of samples characterizing each of these groups is therefore described and discussed separately.

Melting behaviour of samples crystallized at $T_c \leqslant 400$ *K*

The melting behaviour of samples crystallized at a temperature, T_c, such that $380\text{ K} \leqslant T_c \leqslant 400$ K, is typically represented by the d.s.c. curves shown in *Figure 1*. In each case the d.s.c. curve shows either two endotherms or is resolvable into two. Henceforth, the peak at the lower temperature is called peak I whilst the higher temperature is called peak II. It is observed that on heating a sample at a constant rate (4 K/min), the area under peak II decreases with increasing crystallization temperature (*Figure 1a*). For samples crystallized at a given temperature, the relative areas under peaks I and II depend strongly on the heating rate. This effect is illustrated by the results shown in *Figure 1b*. This Figure depicts some d.s.c. curves for the melting of samples crystallized at 386 K; the various curves are for different heating rates. It is observed that with increasing heating rate the area under peak I increases at the expense of the area under peak II and at high heating rates peak II more or less completely disappears (curve D in *Figure 1b*). This effect is better represented in *Figure 3* where the areas under the two peaks are plotted as a function of the heating rate. The sum of the two areas is found to be more or less independent of the heating rate. This observation shows that, on melting, the crystallinity of the sample is not affected by the heating rate. It is also clear from this Figure that at very slow or very fast heating rates only one melting peak is observed; at slow heating rates it is peak II and at fast heating rates it is peak I. The increase in area under peak I at the expense of area under peak II with increasing heating rate is indicative of some recrystallization or reorganization of the crystals

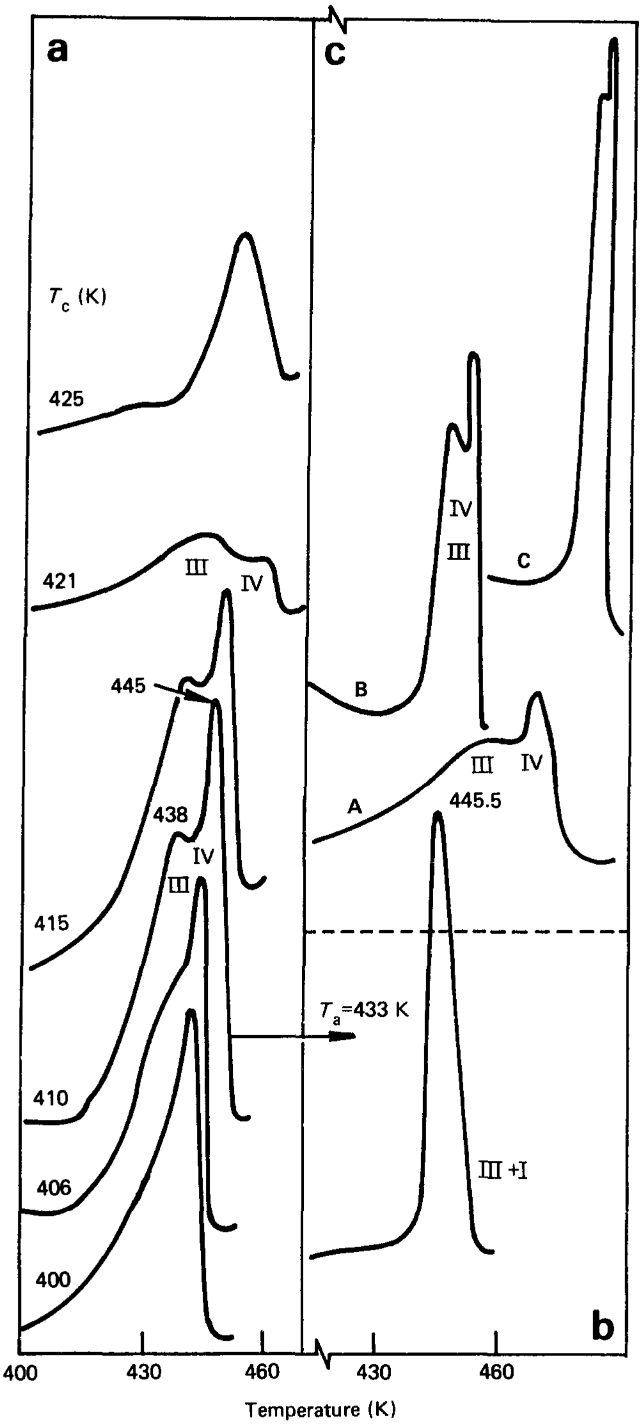

Figure 2 D.s.c. thermograms for melt crystallized isotactic polypropylene ($T_C > 400$ K): (a) Effect of crystallization temperature, T_C. (b) Effect of annealing; the sample crystallized at 410 K was annealed at 433 K for 60 min. (c) Effect of heating rate; curves A, B and C are for a sample crystallized at 410 K and for heating rates 4, 16 and 32 K/min, respectively

originally formed during isothermal crystallization. Peak I represents the melting of the crystals formed during isothermal crystallization. However, peak II is due to the melting of crystals of higher stability formed due to recrystallization or reorganization of crystals initially formed during isothermal crystallization.

The reorganization process involves (depending on the heating rate) crystal perfection or crystal thickening, or both. The former process takes place at low heating rates and it involves a solid–solid transition yielding crystals having a higher degree of perfection. These crystals melt at higher temperatures depending upon the degree of perfection achieved. If the heating rate is sufficiently slow, then this process can be followed by a thickening of the crystals so formed. On increasing the heating rate, less time is available for the crystal perfection to take place. In addition to reorganization some fraction of the original crystals formed can melt and recrystallize at higher temperatures leading to thicker and more perfect crystals and these would also melt at higher temperatures. As the heating rate is increased, less and less time is available for reorganization or recrystallization to take place and hence the fraction of the isothermally crystallized fraction undergoing this process decreases. This would lead to a decrease in area under peak II which is in agreement with our observation. Thus at a very high heating rate, no reorganization takes place and hence only one melting peak, namely peak I, is observed. On the other hand, if the heating rate is extremely low such that most of the isothermally crystallized fraction is reorganized or recrystallized, then also a single peak, peak II, is observed. The effect of heating rate on the peak temperatures of the two peaks is shown in *Figure 4*. It is observed that with increasing heating rate the peak II temperature decreases, whereas the peak I temperature increases. The decrease in the peak II temperature with increasing heating rate can be understood in terms of the lesser degree of perfection achieved. The increase in peak I temperature is a pure superheating effect.

The effect of crystallization temperature on the relative areas under peaks I and II for a given heating rate is

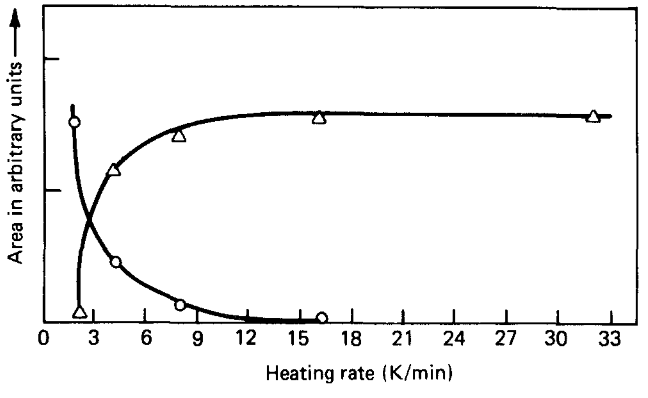

Figure 3 Dependence of area under the two peaks on heating rate: (△), peak I and (○), peak II

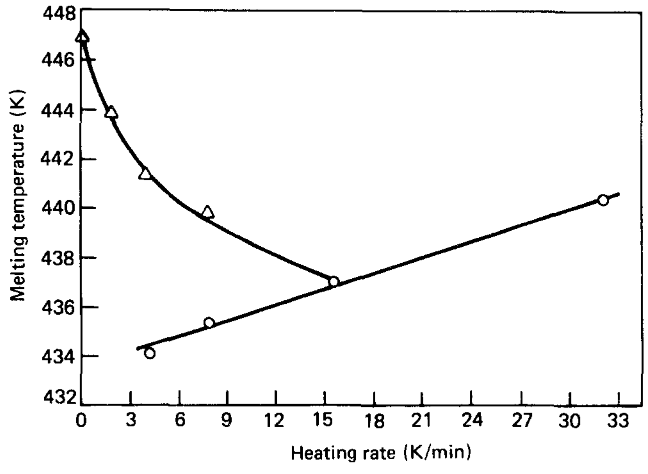

Figure 4 Effect of heating rate on the peak temperatures of peaks I and II: (○), peak I and (△), peak II

shown in *Figure 1a*. Here the different curves represent the melting behaviour of the samples crystallized at various temperatures but heated at a given rate (4 K/min). From these curves it is observed that with the increasing crystallization temperature, the area under the peak I increases while the area under the peak II decreases. At higher temperatures the crystallization proceeds at a slower rate resulting in more perfect crystals. Thus with increasing crystallization temperature, larger and larger fractions of the sample crystallize in the form of crystals having higher degrees of perfection and thus the fraction which would undergo reorganization on heating decreases. This would result in a decrease in the peak II area and a corresponding increase in the peak I area. On increasing T_c the peak temperature of peak I would also increase. Both these conclusions are in agreement with our observations. Further support to the above conclusion is provided by the fact that, at very low and very high crystallization temperatures, only one melting peak is observed. On quenching the polypropylene melt in liquid nitrogen and then heating the crystallized sample only one peak results, irrespective of the heating rate. Similarly to the peak II, defined earlier, the peak temperature of this peak is also found to decrease with the increasing heating rate (*Figure 5*). Thus in this case the crystallized fraction consists of defective crystals which undergo perfection during heating, the degree of perfection decreasing with increasing heating rate. For samples crystallized at 400 K, again a single melting peak is observed. In this case the peak temperature is found to increase with heating rate, similar to the peak I defined earlier. It shows that at 400 K the crystallization proceeds at a sufficiently slow rate for the extrinsic defects to be annealed out and better crystals to be formed. Thus 400 K represents a characteristic crystallization temperature beyond which the crystallized fraction does not exhibit any reorganization on heating.

Melting behaviour of samples crystallized at $T_c > 400$ *K*

The melting behaviour of samples crystallized at a temperature, T_c, such that $406\text{ K} \leqslant T_c \leqslant 425\text{ K}$, is typically represented by the d.s.c. curves shown in *Figure 2a*. Similarly to the samples crystallized at $T_c < 400$K, in these cases also the d.s.c. curve shows either two endothermic peaks or is resolvable into two. These peaks have been labelled as III and IV depending upon the peak temperatures. However, the relative peak areas under these peaks do not change appreciably with the heating rate. This is demonstrated in *Figure 2c*, where this Figure depicts the d.s.c. traces of a sample crystallized at 410 K and then heated at different rates. It suggests that peak IV is probably not due to the melting of a fraction formed as a result of reorganization or recrystallization of the initially crystallized fraction as in the previous case. Perhaps both these peaks correspond to the melting of two fractions formed during isothermal crystallization. The effect of heating rate on the two peak temperatures is shown in *Figure 6*. The behaviour of peak IV is characteristic of the normal superheating effect; however, it is less at lower heating rates. On the other hand, the behaviour of peak III is rather peculiar, where the peak temperature first decreases with increasing heating rate and then increases after a heating rate of about 16 K/min is reached. Even at higher rates, the superheating effect observed in this case is less than the corresponding effect for peak IV. At low heating rates the behaviour of peak III is similar to that of the peak II described earlier. Both these factors suggest that the crystals giving rise to peak III are initially defective and some kind of annealing takes place at lower heating rates. As the heating rate increases, the annealing effect decreases resulting in crystals having lower and lower melting temperatures and thus the peak temperature shows a decreasing trend. At faster heating rates (> 16 K/min), the superheating effect overtakes the annealing.

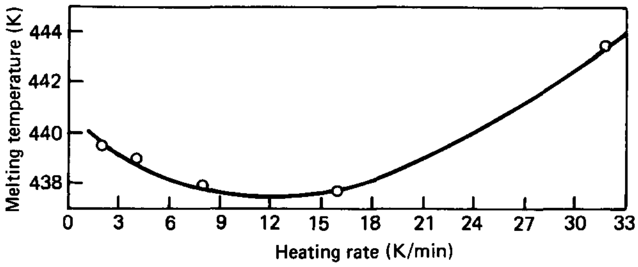

Figure 5 Effect of heating rate on the peak temperature of the sample quenched in liquid nitrogen

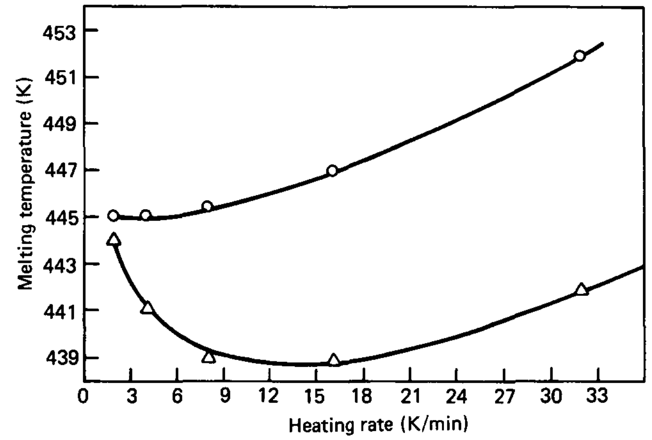

Figure 6 Effect of heating rate on the peak temperatures of peaks III and IV: (△), peak III and (○), peak IV

The effect of crystallization temperature on the formation of peaks III and IV is shown in *Figure 2a*. It is observed that up to about $T_c = 420$ K, the resolution between these peaks improves. A further increase in T_c results in a worsening of their resolution and at $T_c \geqslant 425$ K only one peak is observed. The question of the origin of these peaks (III and IV) is rather complex. This type of melting behaviour has been reported by various workers[5,7] and several explanations about the appearance of multiple melting peaks have been put forward. An explanation involving the presence of extended chain crystals does not seem to be satisfactory because the short crystallization half times involved (~20 min) are not sufficiently long to allow for the formation of extended chain crystals. Another possibility, involving two different crystal forms[1,2] such as α and γ, is also ruled out on the basis of WAXD studies which suggest only one crystal form, namely the α-form, to be predominantly formed. However, a small amount of γ-form crystals formed may act as surfaces for growth of α-crystal branches[1,3]. Such a secondary growth might result in smaller or imperfect crystals having a different melting temperature from that of the primary laths. From thermodynamic considerations, the probability for this kind of process taking place is expected to decrease with increasing crystallization temperature. Therefore, with increasing T_c, the area under peak III should decrease. The experimental evidence, however, does not favour such a conclusion. The other possible sources of multiple endotherms that could be considered are, (a) the melting of different crystalline planes, (b) crystallites of different sizes[5] and (c) two crystalline species having different crystal disorder[5] and stereo-block character[7]. From the melting studies of polyethylene single crystals it has been estimated that the difference in two melting peaks arising out of the melting of different crystalline planes is ~5 K. However, the observed difference between the two melting endotherms in polypropylene is about 7–10 K. Therefore, such a mechanism for double peak formation is not probable. Thus we are left only with options (b) and (c). Strictly speaking these two options are not different from each other but intimately interconnected.

To understand this problem further, annealing studies on isothermally crystallized samples have also been carried out at various temperatures higher than the corresponding T_c. A typical result of such a study is shown in *Figure 2b*. It represents a d.s.c. melting curve of a sample crystallized at 410 K and annealed at 433 K for 60 min. A comparison between the melting curves for annealed and unannealed samples shows that peak III is more susceptible to annealing effects than peak IV. In this particular case, as a consequence of annealing, the peak temperature of peak III changes from 438 K to 445.5 K but the peak temperature of peak IV remains practically unaltered and, in fact, on annealing the two peaks overlap with each other. In general it is observed that the peak temperature of peak III increases more rapidly with the annealing temperature and time than that of peak IV. This observation suggests that the crystalline material consists of two fractions having different degrees of defects. The fraction having a higher degree of defects melts at a lower temperature (peak III) and the fraction having a lesser degree of defects melts at a higher temperature (peak IV). Observation of a single melting peak at $T_c > 425$ K can also be understood in terms of this behaviour.

The results of isothermal crystallization of the polypropylene fractions I and II are also interesting in this context. These fractions represent isotactic polypropylene samples having different extents of stereo-irregularity. Both these fractions, when crystallized at $380 \leq T_c \leq 410$ K, always give rise to single melting endotherms (*Figure 7*). At any given crystallization temperature the fraction II melts at a temperature lower than the fraction I. This observation is in agreement with the fact that the fraction II has a larger extent of stereo-irregularity present in it as compared with fraction I. It further suggests that the fraction II crystals formed at any given T_c are either more defective or have smaller fold lengths and similarly, fraction I crystals are less defective and may have larger fold lengths. It is observed that on increasing the crystallization temperature, up to a certain extent the difference between the melting temperatures of the fractions I and II increases. Since there are very few annealing effects observed at temperatures lower than 415 K, the observed increase in melting temperature can be attributed to the increase in fold length of the respective crystals. As stated earlier, fraction II has larger number of defects in the form of stereo-irregularity per unit length, than fraction I. Now as the fold length increases, the number of such defects entering the crystal lattice is more in fraction II than in fraction I. Thus the negative effect of increasing number of defects in a crystal lattice is more in fraction II, consequently the melting temperature of this fraction does not increase as rapidly with T_c as that of fraction I. This concept is further supported by the WAXD results. *Figure 8* shows some X-ray diffractograms for the (110) reflection for unfractionated and fractionated samples crystallized at different temperatures. These were recorded at very slow scan rates (0.25°/min). In the unfractionated samples crystallized at $T_c > 400$ K, the appearance of a shoulder at a smaller diffraction angle is prominent. Whereas for fractionated samples (fraction II) no such shoulder was observed. At any T_c the value of the '*a*' parameter for the shoulder is higher than the main peak, suggesting inclusion of more defects in the crystal lattice. It is interesting to note that at any T_c the location of the shoulder is very close to that of

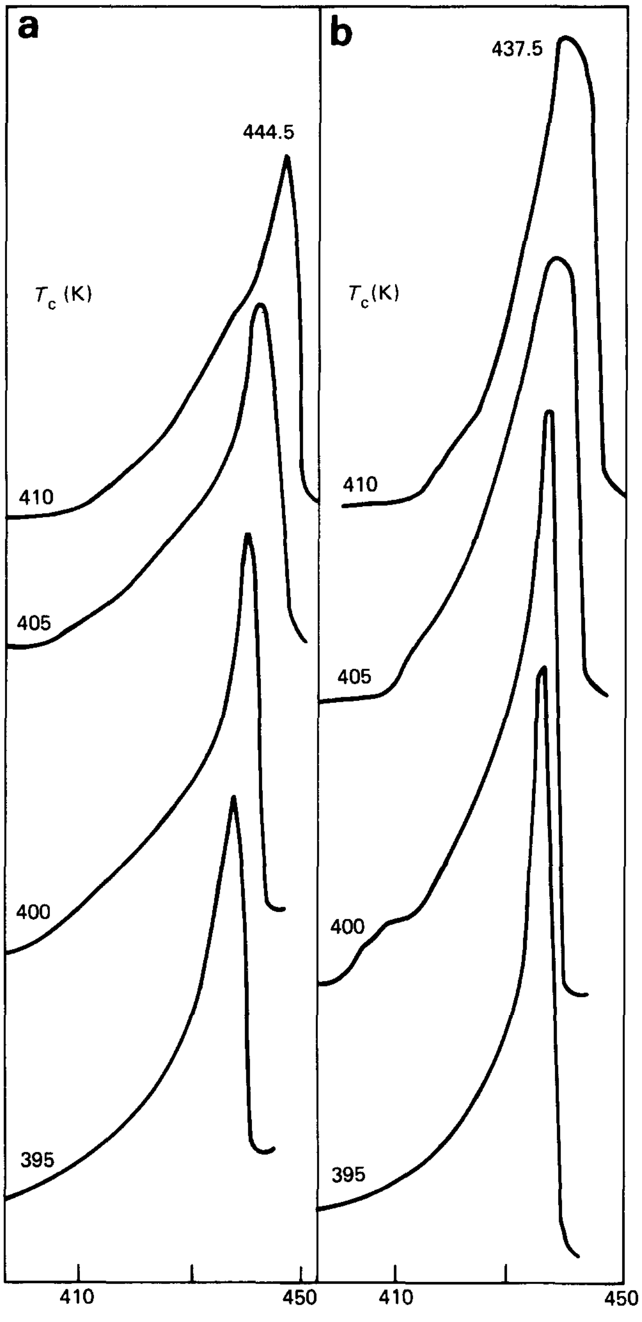

Figure 7 D.s.c. thermograms for fractions I and II crystallized at different temperatures: (a) fraction I and (b) fraction II

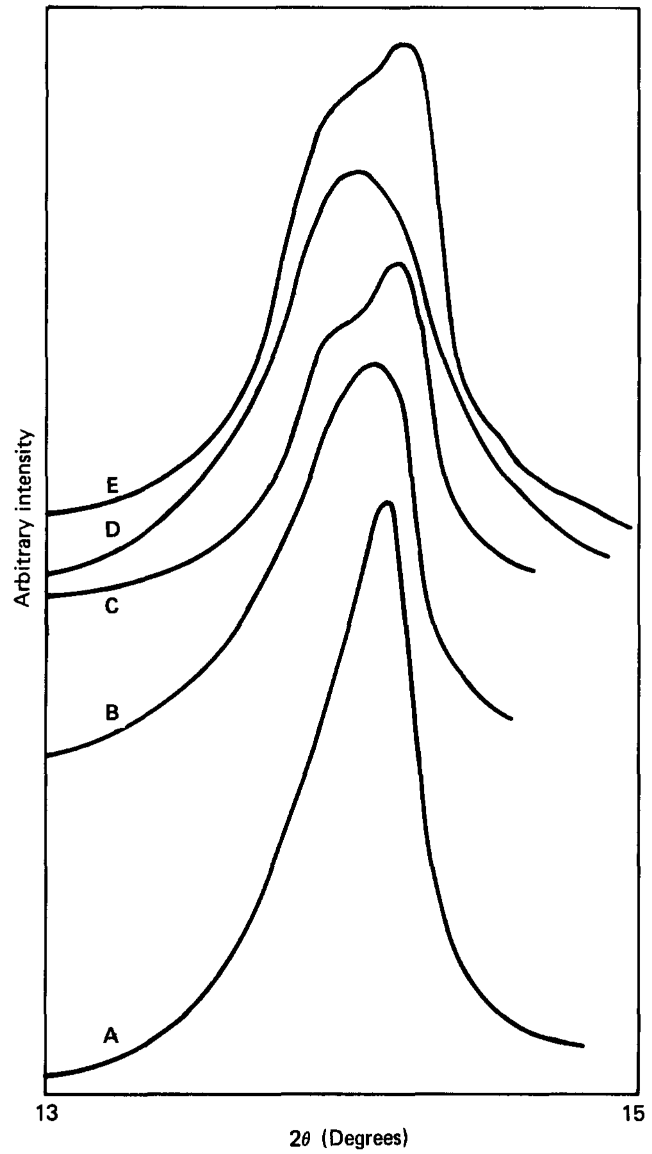

Figure 8 X-ray diffractograms for different fractionated and unfractionated isotactic polypropylene samples. Curves represent a plot of WAXD scattering intensity versus 2θ for the (110) reflection. The curves A, B and C are for unfractionated samples crystallized at 400, 406 and 410 K, respectively. The curve D is for a fractionated sample containing fraction II crystallized at 410 K. The curve E shows the effect of annealing for a sample crystallized at 410 K and annealed at 433 K for 60 min

the corresponding peak for fraction II. Furthermore, at $T_c = 410$ K, the melting temperatures of the fractions I and II are close to the peak temperatures of peaks IV and III, respectively.

The results of the annealing studies and the melting of fractions I and II suggest that perhaps the origin of the melting peaks III and IV lies in the presence of the two fractions (I and II) with varying extents of stereo-irregularity inside the fold period. Peak III is due to the melting of crystals belonging to fraction II and the peak IV is due to the melting of crystals formed out of the fraction I. Since in a given sample the relative proportion of these fractions is fixed and does not change with crystallization conditions or the heating rate, the relative areas under the peaks III and IV are also not affected significantly by these conditions. However, the resolution between these peaks is affected. It can, therefore, be concluded that at higher crystallization temperatures, $T_c > 400$ K, the appearance of multiple endotherms is due to crystalline species having different crystal disorder and stereo-block character.

Equilibrium melting temperature

Following the Hoffman and Weeks[10] or Klod and Bekkedahl[11] approach, the equilibrium melting temperature (T_m°) of a crystallizable long-chain molecule can be obtained by extrapolation of the experimental relation between the observed melting temperature, T_m, and the crystallization temperature, T_c, to the line representing $T_m = T_c$. A plot of the melting temperatures of the original isotactic polypropylene and the fractions I and II isothermally crystallized for sufficiently long times versus the crystallization temperature obtained from the present studies, is shown in *Figure 9*. In this plot, the points shown by filled circles belong to peak I for $T_c \leqslant 400$ K and to peak IV for $T_c > 400$ K. It can be seen that the points belonging to peak III and fraction II fall on one straight line while those corresponding to peak IV and fraction I fall on another straight line. This fact lends further support to our earlier conclusion about the origin of the peaks III and IV. It can, however, be observed that the melting temperatures corresponding to peak I ($T_c < 400$ K) also follow the upper straight line. This is perhaps due to the fact that at lower crystallization temperatures the intra-chain defects do not show up. The extrapolation of these two straight lines to $T_m = T_c$ leads to two values for the equilibrium melting temperature, namely 458 and 481 K. Let these be designated as T_{m1}° and T_{m2}°. These can be attributed to the two crystallizable species present in the isotactic polypropylene sample. Similar values have also been obtained by other workers[5-7]. The value obtained for T_{m1}° by most of the workers agrees with the present result. However, for T_{m2}° values ranging from 481 to 491 K have been reported. This could be attributed mainly to differences in various samples and partly to the uncertainty in extrapolation.

CONCLUSIONS

The present investigation provides a clearer picture of the multiple endotherms observed in the melting of isotactic polypropylene. At lower crystallization temperatures ($T_c \leqslant 400$ K), this phenomenon is dominated by the crystal

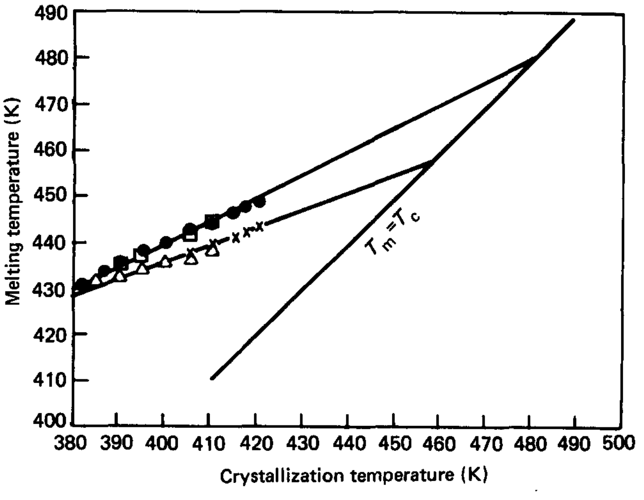

Figure 9 Variation of melting temperatures with the crystallization temperature, T_c: (●), peak I for $T_c \leqslant 400$ K and peak IV for $T_c > 400$ K; (×), peak III; (□), fraction I and (△), fraction II

imperfections. On heating, the crystallized fraction undergoes reorganization and recrystallization resulting in a fraction consisting of crystals of greater degree of perfection which melt at higher temperature. As the crystallization temperature is increased, the crystallization proceeds more slowly accompanied by a simultaneous annealing. Therefore, with increasing T_c the extent of reorganization or recrystallization decreases. The higher temperature peak (peak II) thus continues to diminish in size and ultimately at 400 K a single peak is observed. At these crystallization temperatures, perhaps the inbuilt defects in the molecular chain similar to the stereo-irregularity are not evident and at $T_c > 400$ K, these defects begin to play an important role. At these temperatures, the multiple endotherms are due to the presence of different crystalline species having different crystal disorder and stereo-block character.

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