Thermochimica Acta, 117 (1987) 97–103
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MELTING BEHAVIOUR OF ORIENTED ISOTACTIC POLYPROPYLENE

Y.S. YADAV * and P.C. JAIN

Department of Physics and Astrophysics, University of Delhi, Delhi 110 007 (India)

(Received 1 January 1987)

ABSTRACT

A detailed study of the melting behaviour of oriented isotactic polypropylene has been carried out using differential scanning calorimetry. The orientation in isotactic polypropylene was produced by extruding it in solid phase. At extrusion ratio (ER) greater than four, two melting peaks were observed. With increasing ER, the lower temperature peak was found to shift to higher temperatures. The corresponding shift in the higher temperature peak was much less. It is shown that these peaks originate in the melting of crystalline species having different degrees of crystal disorder and stereo-block character.

INTRODUCTION

In recent years much attention has been paid to the structure and properties of ultrahigh-modulus materials prepared by drawing or extrusion of thermoplastics [1–8]. The present work deals with the extrusion of isotactic polypropylene in solid phase. The extrudate exhibits interesting melting behaviour; for extrusion ratio (ER) 4 to 12, double melting peaks are observed.

EXPERIMENTAL

The isotactic polypropylene sample used in this investigation was similar to that used earlier [9]. Some of the bulk properties of the sample used are given in Table 1.

The solid state extrusion was carried out in a piston-cylinder assembly using a tapered die. Details of the set-up and the die used are described elsewhere [10]. The effect of various processing conditions on the quality of the extrudate has been studied earlier [11]. In the present investigation, solid

---

* Presently at the Department of Physics, Government College, Narnaul, India.

TABLE 1

Bulk properties of an 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

state extrusion was carried out at 418 K by applying a pressure of 1.2 kbar. The maximum extrusion ratio obtained was 18. The extrudate consisted of highly transparent strands of material. Samples of varying extrusion ratio were obtained by cutting thin slices of the extrudate normal to the flow direction at different distances from the starting end. The melting behaviour was investigated by using a Perkin-Elmer differential scanning calorimeter model DSC-1B. The temperature scale of the instrument was calibrated using standard reference materials. The primary reference material used was Indium ($T_m = 429$ K and $H_f = 6.8$ cal g^{-1}). For melting behaviour study 2–10 mg of sample weight was used. In general a heating rate of 8 K min^{-1} was employed.

The WAXD studies were carried out using a Philips PW 1130/00 X-ray diffractometer which provided nickel filtered Cu K_α radiations from a high intensity tube. The radiation detector used was a scintillation counter.

RESULTS AND DISCUSSION

Some typical DSC curves for the melting of oriented isotactic polypropylene samples of varying extrusion ratio are shown in Fig. 1. An unoriented sample exhibits a broad melting peak. The sharpness of the melting peak increases with increasing extrusion ratio. At extrusion ratio, ER > 4, two melting peaks are observed; one occurring at a lower temperature (peak I) and another at a higher temperature (peak II). The dependence of the melting temperature corresponding to these peaks on the extrusion ratio is shown in Fig. 2. The melting temperature corresponding to peak I is found to increase with the extrusion ratio. However, the changes in the melting temperature corresponding to peak II are small. At extrusion ratio 15, the change in peak I temperature overtakes that in peak II and the two peaks overlap giving rise to a single peak. With increasing extrusion ratio, the area under the peak I increases while that under peak II remains unaltered.

Occurrence of multiple melting peaks is a common phenomenon with most polymers. To explain this phenomenon, several explanations such as secondary crystallization, difference in degree of crystalline perfection, dif-

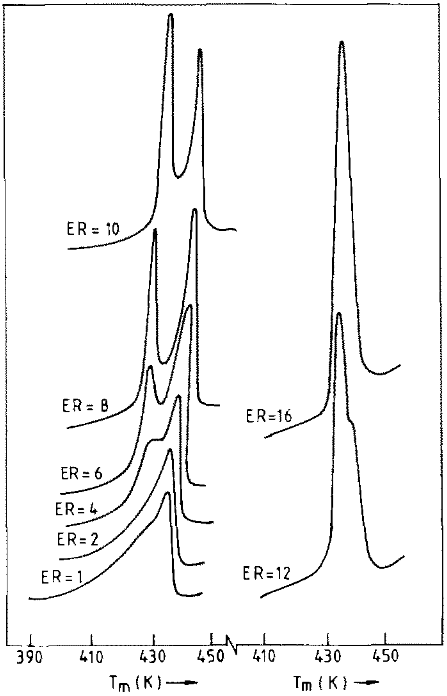

Fig. 1. DSC curves for the melting of oriented isotactic polypropylene samples of varying extrusion ratio.

ferent lattice structures, partial melting followed by recrystallization, different extent of stereo-irregularity, etc., have been advanced [9,12,13]. In the case of isothermally crystallized isotactic polypropylene, it has been shown [9] that for samples crystallized at $T_c < 400$ K double melting peak formation is caused by melting followed by recrystallization/reorganization, while

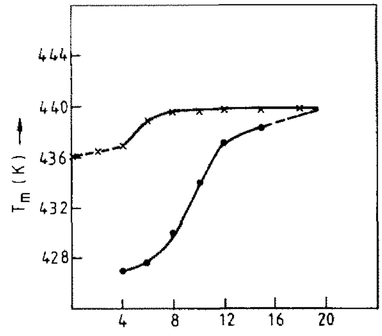

Fig. 2. Dependence of melting temperature on the extrusion ratio: (●) peak I, (×) peak II. The dashed portions represent cases where a single melting peak has been observed.

for samples crystallized at $T_c > 400$ K the appearance of two melting peaks is caused by the existence of crystalline species having different degrees of crystal disorder and stereo-block character.

In our study, the possibility of different lattice structures contributing to multiple melting phenomena has been ruled out on the basis of WAXD studies carried out on extruded samples. These studies have revealed that the lattice structure of the oriented isotactic polypropylene samples does not depend on the extrusion ratio.

To study the contribution of recrystallization and/or reorganization during heating, the extruded samples having extrusion ratio 8 were heated at different rates. The corresponding DSC melting curves are shown in Fig. 3. It can be observed that with increasing heating rate, the melting temperatures of both the peaks increase. Even at high heating rates (~ 64 K min^{-1}), evidence for two melting peaks is observed. Peak I shows a higher degree of superheating compared with peak II. This is shown by the fact that with increasing heating rate, the two peaks come closer. The areas under the two peaks, however, are found to be more or less independent of the heating rate. From these observations it can be inferred that there is no recrystalliza-

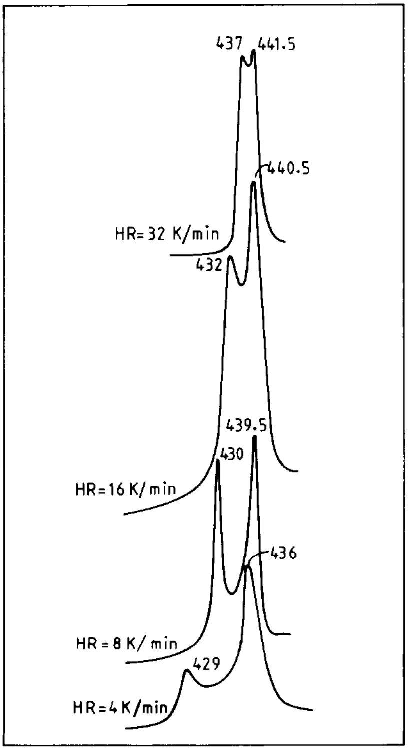

Fig. 3. Effect of heating rate on the melting behaviour of an extruded sample (ER = 8).

tion and/or reorganization during heating. There are two crystalline fractions originally present in the extruded samples. The fraction melting under peak I has a larger degree of crystal disorder than the fraction melting under peak II. This situation is similar to that observed for isotactic polypropylene samples isothermally crystallized at $T_c > 400$ K [9].

The two fractions giving rise to two melting peaks could arise from crystallites of different sizes and/or different extent of stereo-irregularity. To investigate this, annealing studies of samples of different extrusion ratios were undertaken. A typical result of such studies is shown in Fig. 4. This Figure depicts the DSC melting curves of extruded sample having ER = 10 annealed at 425 K for different times. It is seen that with increasing annealing time the shift in the melting temperature corresponding to peak I is much more than that for peak II. At annealing times $\geqslant$ 60 min, the two peaks completely overlap each other giving rise to a single peak. At higher annealing temperatures this process is completed faster. From these studies it can be concluded that peak I is due to the melting of crystallites with more defects and peak II is due to the melting of crystallites with fewer defects. As reported earlier [9], the isotactic polypropylene sample used in the present investigation contains about 32% of a fraction with about 2–3% stereo-irregularity and 66% of a fraction with about 7–12% stereo-irregularity. It is the melting behaviour of the oriented forms of these two fractions which is reflected in the form of peaks I and II; peak I corresponds to the

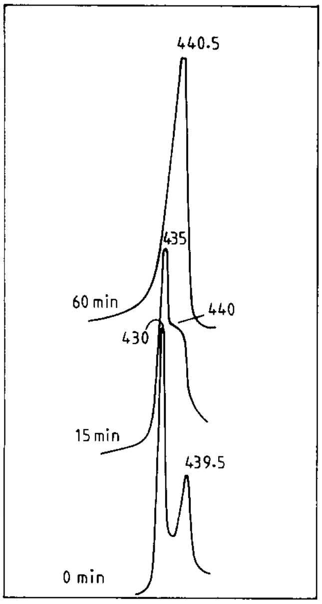

Fig. 4. Annealing effect; DSC melting curves of extruded samples (ER = 10) annealed at 425 K for different times.

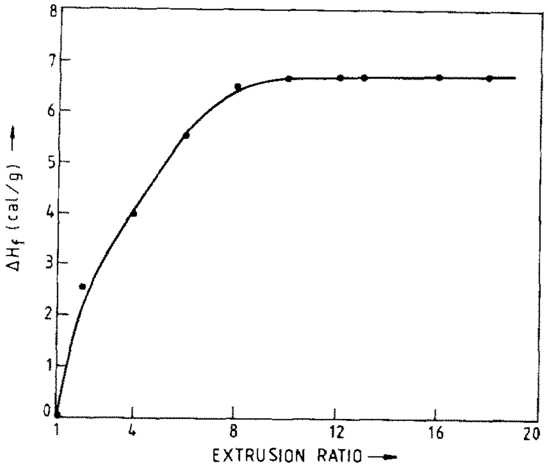

Fig. 5. The dependence of the observed heat of fusion of the oriented isotactic polypropylene on the extrusion ratio.

melting of the oriented form of the second fraction and peak II to that of the first fraction.

The dependence of the heat of fusion of the oriented isotactic polypropylene on the extrusion ratio is shown in Fig. 5. This Figure depicts the dependence of the increase in the heat of fusion due to orientation on the extrusion ratio. The observed change in the heat of fusion increases with the extrusion ratio up to ER = 8 and then tends to become constant. Similar behaviour has also been reported for polyethylene [7]. The increase in the heat of fusion with increasing extrusion ratio can be attributed to the orientation of the amorphous phase. The maximum increase in the heat of fusion is 6.5 cal g^{-1} which is the same as observed for polyethylene [7].

ACKNOWLEDGEMENTS

The authors acknowledge with thanks the assistance from U.N.D.P. Financial support from the University Grants Commission, Government of India is gratefully acknowledged.

REFERENCES

1 P. Predecki and W.O. Statton, J. Polym. Sci., Part B 10 (1972) 87.
2 William G. Perkins and R.S. Porter, J. Mater. Sci., 12 (1977) 2355.
3 G. Capaccio and I.M. Ward, Polym. Eng. Sci., 15 (1975) 219.
4 R.J. Samuels, Structured Polymer Properties, Wiley, New York, 1974.
5 A. Cifferri and I.M. Ward (Eds.), Ultra-high Modulus Polymers, Applied Science, London, 1979.

6 I. M. Ward (Ed.), Structure and Properties of Oriented Polymers, Applied Science, London, 1975.
7 K. Dhawan, D.R. Chaubey, Y.S. Yadav, P.C. Jain and V.S. Nanda, Polym. J., 12 (1980) 411.
8 W.P. Leung and C.L. Choy, J. Polym. Sci., Polym. Phys. Ed., 21 (1983) 725.
9 Y.S. Yadav and P.C. Jain, Polymer, 27 (1986) 721.
10 K. Dhawan, V.S. Nanda and P.C. Jain, Indian J. Technol., 19(4) (1981) 149.
11 A.K. Jain, Ph.D. Thesis, University of Delhi, 1981, unpublished.
12 M. Tadoki and T. Kawagauchi, J. Polym. Sci., Polym. Phys. Ed., 15 (1977) 1067.
13 H.J. Oswald, E.A. Turi, H.J. Harget and Y.P. Khanna, J. Macromol. Sci., Phys., 13 (1977) 231.