Comparison of premelting and recrystallization behaviour of β-phase isotactic polypropylene by heating and cooling at different rates

Yasuna Fujiwara, Tomoe Goto and Yasue Yamashita
Faculty of Science, Shizuoka University, Shizuoka 422, Japan

(Received 12 May 1986; revised 6 August 1986; accepted 14 August 1986)

Different heat treatments (heating and subsequent cooling with quick or slow rates but up to the same temperature in the melting range) were made on β-polypropylene (β-PP), and premelting and recrystallization behaviour were compared using d.s.c. and WAXS measurements. The results suggest that, under our experimental conditions, lamellar growth during heating and cooling takes place chiefly at the expense of, or under the existence of a melt neighbouring to the lamella, and that the growth in the solid state by molecular refolding plays a minor role. The influence of the recrystallized α-phase, yielded during heating, on the growth of β-form is also discussed.

(Keywords: β-polypropylene; premelting; recrystallization; d.s.c.; WAXS)

INTRODUCTION

Several theories have been proposed on the premelting of polymer lamellae, from the standpoints of boundary melting, selective melting from thinner lamellae, and melting from lamellae with exposed surfaces[1-6]. However, no conclusive theory has yet been established. Petermann has however observed the premelting and recrystallization behaviour in the lamellar texture directly by a TEM out-of-focus technique, and confirmed the location of a molten region in the texture and the growth of lamellae at the expense of the melt, or by solid-state molecular motion[7].

The melting, recrystallization or reorganization processes are naturally dependent on the heating and cooling procedures, and the resultant structure may be different depending on the procedure adopted. To elucidate these differences in texture, the β-form specimen of isotactic polypropylene (β-PP) was used. This form is as stable as the α-form, and the $\beta \leftrightarrow \alpha$ solid-state phase change does not take place. However, β-PP has the property that, after melting, it recrystallizes predominantly in the α-form by reason of its much higher rate of primary nucleation, except under large supercooling. This property results from its lower melting temperature as compared with the α-form. Therefore, when the $\beta \longrightarrow \alpha$ phase change is observed, the change is accompanied by melting of the β-form[8,9]. When β-PP is slowly heated, premelting proceeds near the melting temperature, and the molten region recrystallizes partly in the α-form and partly in the stabler β-form by the growth of remaining β-lamellae. The resultant β-PP structure, which was heated to a temperature (T_p) in its melting range and subsequently cooled, depends on the heating and cooling rate, and naturally the temperature T_p. Here the structure change at T_p and after each heating procedure was measured by WAXS and d.s.c. From these experimental results the premelting and recrystallization behaviour of β-PP was discussed.

EXPERIMENTAL

Material

The polymer used in this experiment was isotactic polypropylene (Chisso Co. Ltd, $M_v = 2.55 \times 10^5$, tacticity 97%, 0.23 mm thick sheet). This material was melt-crystallized by the temperature-gradient crystallization method, and a β-phase specimen plate was obtained, essentially composed of uniaxially oriented β-form lamellae[10]. By this method acorn-shaped small α-phase spherulites grow concurrently, scattering randomly in the β-form matrix (maximum size *ca.* 0.2 mm). The content depends on the crystallization conditions, specimen thickness, etc. The specimen used in this experiment contained $\sim 10\%$ of the α-phase. The crystallization temperature was estimated to be about 130°C.

D.s.c. measurement

D.s.c. measurements and specimen preparation for WAXS photographs were carried out using a Perkin–Elmer DSC-1B apparatus using a $1 \sim 4$ mg specimen. The heating procedures used were a combination of quick (hereafter abbreviated to 'q') or slow ('s') heating to T_p in the melting range, and subsequent q- or s-cooling. In the case of d.s.c. measurements $q = 20$°C/min and $s = 0.625$°C/min (the slowest scanning speed in our apparatus). q- or s-heating was initiated from 100°C, heated to T_p (equals 149°C, which is several degrees below the d.s.c. melting peak temperature, $T_m(\beta)$), and subsequently q- or s-cooled to 100°C. The resultant structure was measured by rescanning from this temperature with the constant heating rate of 20°C/min.

0032–3861/87/081253–04$03.00

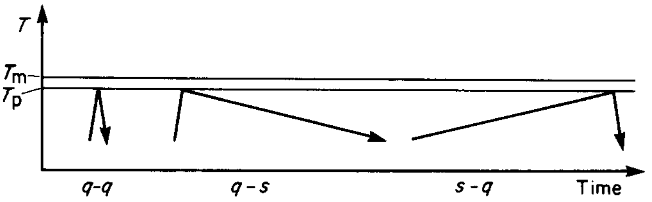

Figure 1 Illustration of heating procedures

X-ray diffraction

WAXS studies were carried out using Ni-filtered Cu-radiation from a Rigaku 4012 X-ray generator equipped with a Toshiba fine focus X-ray tube. PSPC* measurements were made using Rigaku PSPC system. The specimen was heated in a hot stage for WAXS purposes controlled by a temperature controller, both made in this laboratory. Heating procedures were fundamentally the same as for d.s.c. For the sake of X-ray counting at T_p, however, the specimen was held a minimum necessary time interval of 100s (occasionally 200s) at T_p. In the case of PSPC $q = 25 \pm 3$°C/min and $s = 0.50 \pm 0.03$°C/min for instrumental purposes. T_p was chosen to be several degrees below the melting temperature, where more than half of the β-lamellae premelt. *s*-Heating was started from 110°C and *s*-cooling was finished at this temperature, where the lower temperature range was quickly passed. The X-ray beam size used was 0.23 mm in diameter. The specimen plate was set perpendicular to the incident beam holding the lamellar axis vertical. PSPC was fixed on the equator. The recorded diffraction peak height and the background level at T_p were corrected by the temperature factor. WAXS photographs were taken at room temperature by an X-ray camera with a pinhole collimator 0.23 mm in diameter and with the camera distance 35 mm.

RESULTS AND DISCUSSION

In *Table 1* the relative estimation of β-phase and recrystallized α-phase quantities are shown, corresponding to before, at T_p, and after the heating procedures, obtained by PSPC measurements on the β-PP specimen. The β-phase quantity at each stage was estimated conventionally by the peak height ratio $(300)_\beta$ over its original peak height. The α-phase quantity as a result of recrystallization was likewise estimated by the peak height ratio $(110)_\alpha$ over its original $(300)_\beta$. Since the as-grown specimen includes small α-spherulites which range in comparative order of size up to the collimator diameter, and accordingly the intensity of the WAXS reflections from α-crystals in as-grown specimens differs from specimen to specimen, only the increment from the original α-peak height has any physical significance concerning the recrystallization process. Therefore, as for the α-quantity, the increment of α-peak height from the original is listed in *Table 1*. As a rough measure of the relative estimation of melt quantity, the elevation of background level resulting from melting is also shown in this Table, which was measured at $2\theta = 12°$ avoiding the crystalline reflections. The values given in *Table 1* do not represent mass fractions. In *Figure 2* d.s.c. rescan curves are shown and WAXS photographs for β-PP are shown in *Figure 3*, after heating procedures (including an untreated sample). From these experimental results the different types of behaviour caused by *q*- or *s*-heating and cooling will be discussed individually.

q–q procedure

Premelting goes on without sufficient time to reorganize to stabler lamellae and, accordingly, the melt quantity at T_p is large. By *q*-cooling the molten region

Table 1 Comparison of WAXS peak heights of β- and α-reflections, and background level elevation by melting

		Relative peak height (%)		
		q–q	*s–q*	*q–s*
$(300)_\beta$	Before heating	100	100	100
	At T_p	24	43	24
	After cooling	33	43	28
$(110)_\alpha$	Increment by heating to T_p	1	8	3
	Increment by cooling from T_p	10	3	12
	Total increment	11	11	15
	Background level elevation by melting at T_p ($2\theta = 12°$)	5	3	5

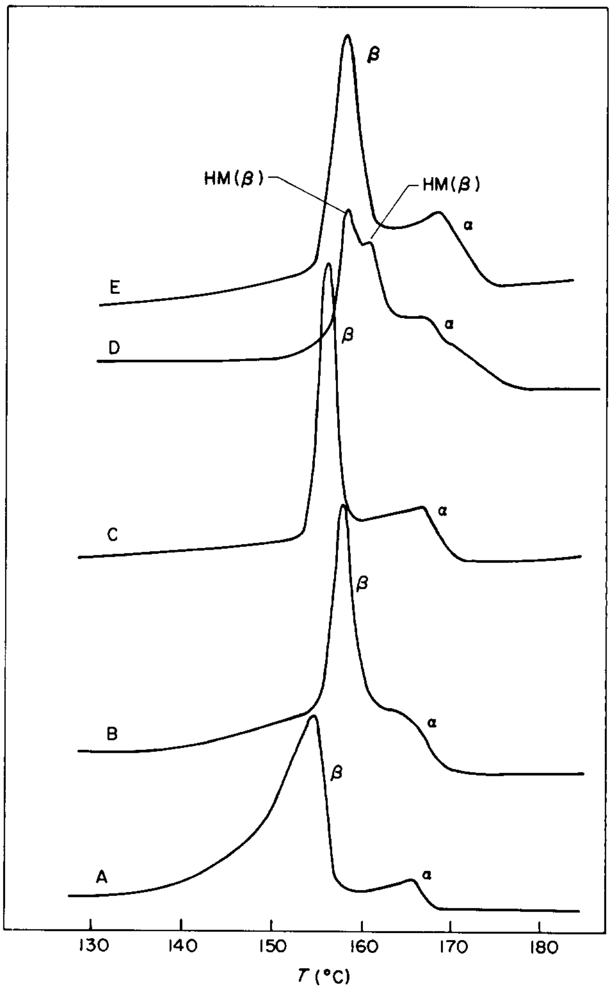

Figure 2 D.s.c. curves of β-PP (A) untreated, and after heating procedures: (B) *q–q*, (C) *s–q*, (D) *q–s*, and (E) *s–s*, $T_p = 149$°C

---

* PSPC: Position Sensitive Proportional Counter

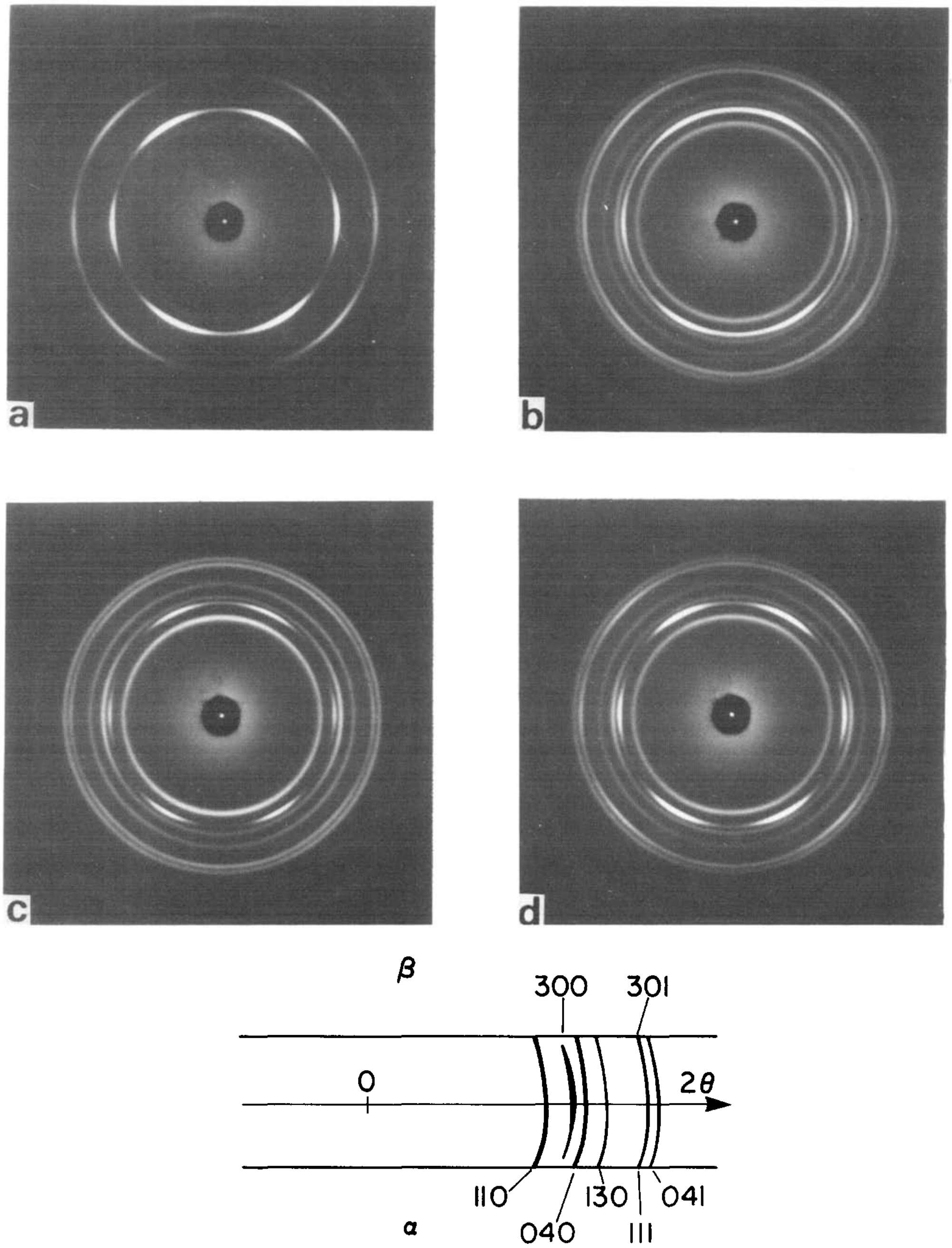

Figure 3 WAXS photographs of β-PP (a) untreated, and after heating procedures: (b) *q–q*, (c) *q–s*, and (d) *s–q*, $T_p = 149°C$, lamellar axis vertical

recrystallizes in the large part to the α-form. However, the amount of β-form also increases. The WAXS photograph for *q–q* in *Figure 3* shows the appearance of azimuthal broadening of the reflection arcs from β-crystals, compared with other heating procedures. Therefore, the real increase of the amount of the β-form during cooling may be still greater than estimated from PSPC peak heights, measured on the equatorial parts of the reflections. By inspecting the orientational disordering profile in this photograph, two considerations were made: (a) superposition of original, oriented reflection and uniform Debye–Scherrer ring, and (b) disordering of the preferred orientation. Point (a) may be interpreted as the primary nucleation and growth of the β-form in the molten region under larger supercooling. In fact when this material is fully melted and quenched, the β-form is observed as being mixed with the α-form. However, we could not find the same sort of β-pattern in *Figure 3* for *s–q*. If a recrystallization of this type takes place from the melt also in case of partial melting, it may be expected for *s–q* in WAXS, that a uniform ring with an intensity of about one half of *q–q* should appear proportionally to the melt quantity at T_p (see following section). It was also experimentally checked that, from the partially melted α-PP, that the β-form did not grow by *q*-cooling. These facts eliminate the possibility of the β-form proportion increasing by this mechanism. Point (b) may be interpreted as follows: the melt crystallizes as thinner β-lamellae on the lateral surfaces of the unmolten β-lamellae under large ΔT during *q*-cooling. Thereby orientational fluctuation of newly grown β-crystals with respect to the mother lamellae may result.

The d.s.c. melting temperature shifts *ca.* 3°C on the higher side, which indicates some reorganization of the lamellae remaining in the melt at T_p.

q–s procedure

The heating process is the same as for the *q–q* process. The increment of the β-form during *s*-cooling is smaller, whereas that for the α-form is larger compared with *q–q*. This is caused by the long stay at high temperature range. As the supercooling ΔT seen from $(T_m^0)_\alpha$ is somewhat larger than that seen from $(T_m^0)_\beta$ near T_p, then the α-form grows with a greater growth rate. A characteristic feature in the d.s.c. rescan is the appearance of a double peaked β-endotherm (see *Figure 2 q–s*). The lower and the higher temperature peaks will be known here as LM(β) and HM(β), respectively. The appearance of HM(β) was fairly sensitive to T_p, and it was observed that LM(β) diminishes whereas HM(β) increases by raising T_p by a few degrees. A still higher T_p brought about the appearance of the α-endotherm only indicating full melting of the β-lamellae. Another measurement was made starting the rescan from a higher temperature in the course of the *s*-cooling (145°C) instead of 100°C, and the result was that the height of LM(β) was almost unchanged whereas HM(β) became fainter. These supplementary experiments suggest that LM(β) corresponds to the melting of the remaining β-lamellae, whereas HM(β) corresponds to that of newly grown β-form. One more supplemental d.s.c. measurement was made using the *s–s* procedure to the same T_p as illustrated in *Figure 2*, in which we found the single peaked β-endotherm.

The nature of lamellar growth giving rise to HM(β) is not clear. If it takes place as lamellar thickening by sliding diffusion of molecular segments in the solid-state, such as refolding through interpenetration of molecules between adjacent lamellae, these d.s.c. results may not be explained[11]. Because the *s–s* procedure affords a longer time (about twice) to thicken, accordingly HM(β) must become larger after *s–s* than after *q–s*. Instead, if it is assumed that thickening can proceed at the expense of, or under the existence of a neighbouring melt, and further that thickening is hindered by the existence of the α-phase portion neighbouring to the β-lamella, which has been recrystallized in the premelted region during slow heating, then these d.s.c. results can be explained.

s–q procedure

Premelting goes on slowly but steadily until T_p is reached. The molten region can recrystallize successively again to the β-form and also to the α-form. Therefore at T_p the melt quantity is smaller, while the β- and α-quantities are larger than in case of *q*-heating. It can also be seen that, contrary to *q–s*, a single peaked β-endotherm is observed in the d.s.c. rescan in spite of being subjected to the same temperature–time integral effect as *q–s*. The difference may primarily be the result of successive recrystallization of pre-melted regions in the α-phase, before thickening of the β-lamellae proceeds under the existence of the melt.

Table 2 Melting temperatures of β-PP after heating procedures

Original T_m (°C)	T_p (°C)	T_m (°C)			
		q–q	*s–q*	*q–s*	*s–s*
154.5	149	157.5	155.7	158.0 161.0	157.8

Another characteristic feature is the lower rescan T_m compared with other heating procedures. In *Table 2* T_m values of β-PP are shown. We suppose that this may also be attributed to the influence of the α-texture on the lamellar reorganization. Looking back to the case of *q–q*, on the contrary, there is neither time for the reorganization of the β-lamellae nor time for the recrystallization of the melt to the α-texture. Therefore premelting proceeds, but any still remaining β-lamellae may reorganize easily even in a short time near T_p as they are surrounded by the melt. Accordingly the rescan T_m of *q–q* is rather higher than for *s–q*.

CONCLUSION

For the premelting and recrystallization of the β-lamellae of isotactic PP it was seen under our experimental conditions that:

(1) Lamellar growth during heating and cooling takes place chiefly at the expense of, or under the existence of, the melt neighbouring to the lamella. Lamellar growth in the solid-state looks to be playing a minor role.

(2) Suppressing effect on thickening of the β-lamellae is likely to be accompanied by a recrystallization of the melt to the α-phase during slow heating. The reason is not clear, but may be due primarily to successive recrystallization to α-crystals of premelted regions during the course of slow heating, thus consuming molten material, the existence of which is also necessary for any thickening of the β-lamellae.

REFERENCES

1 Fischer, E. W. *Kolloid Z. Z. Polym.* 1969, **231**, 458

2 Schulz, J. M., Fischer, E. W., Schaumburg, O. and Zachmann, H. A. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 239

3 Meyer, H. and Kilian, H. G. *Prog. Colloid Polym. Sci.* 1978, **64**, 166

4 Kilian, H. G. *Kolloid Z. Z. Polym.* 1969, **231**, 534

5 Hasse, J., Köhler, S. and Hosemann, R. *Z. Naturforsch.* 1978, **33a**, 1472

6 Hosemann, R. *Polymer* 1962, **3**, 349

7 Petermann, J., Miles, M. and Gleiter, H. *J. Macromol. Sci.* 1976, **B12**, 393

8 Turner Jones, A., Aizlewood, J. and Beckett, D. *Makromol. Chem.* 1964, **75**, 134

9 Samuels, R. J. and Yee, R. Y. *J. Polym. Sci., Polym. Phys. Edn.* 1972, **10**, 385

10 Fujiwara, Y. *Colloid Polym. Sci.* 1975, **253**, 273

11 Dreyfuss, P. and Keller, A. *J. Polym. Sci.* 1970, **B8**, 253