Macromol. Symp. ***147****, 155–165 (1999)*

HETEROGENEITY OF CRYSTALLINE STRUCTURE OF INJECTION-MOULDED AND DRAWN ISOTACTIC POLYPROPYLENE STUDIED BY DSC

J. Kratochvíl, J. Kotek, A. Sikora, M. Raab*

Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

SUMMARY: Differential scanning calorimetry (DSC) was used to characterize crystalline structure of injection-moulded specimens of isotactic polypropylene and corresponding materials prepared by solid-state drawing at various temperatures. It was shown that the DSC can assess the differences between individual specimens and structural gradients and heterogeneities within one typical test piece. In particular, relative proportions of the crystalline α and β modifications in different locations of an injection-moulded specimen and structural transformation in the neck shoulder could be established. Variations of the crystalline structure along the edge of drawn specimens were interpreted as a record of temperature and stress fluctuations in the propagating neck shoulder.

INTRODUCTION

Semicrystalline polymers such as isotactic polypropylene are heterogeneous by definition as they consist of crystalline regions (lamellae) embedded in an amorphous matrix. The interphase between the crystalline and amorphous portions of the material is sometimes considered a third structural component. Individual crystalline regions are not uniform. They show statistical variation in size, perfection, orientation and in the way of forming more complex structural systems, spherulites. In the case of isotactic polypropylene, the ability to crystallize in three different modifications, α (monoclinic), β (hexagonal) and γ (triclinic) is another source of morphological heterogeneity. In most cases, only α and β modifications are of practical importance. Besides, real semicrystalline polymer materials inevitably contain randomly distributed impurities, inclusions, defects and flaws of different nature and origin. Finally, in structural parts or test pieces for mechanical measurement (both pressed and injection-moulded), macroscopic inhomogeneity can be observed, e.g., gradients in morphological parameters, variation in molecular orientation and core-shell effects. The assessment of heterogeneities and irregularities at various structural levels is important for structural understanding of macroscopic mechanical behaviour. In particular, the interrelations between flaws of various nature and ultimate mechanical behaviour have been well

CCC 1022-1360/99/$ 17.50+.50/0

recognized. It is also well known that the course of the solid-state drawing is affected not only by the time and temperature conditions but also by the initial morphology. Recently a structural model of the crystalline β modification has been suggested based on a notion of extended-chain crystallites interconnected by continuous chains in the amorphous matrix1). This model is able to explain the enhanced toughness, better drawability and higher orientation achieved by solid-state drawing of the crystalline β modification as compared with the modification α.

During solid-state drawing, the original lamellar or spherulitic morphology of semicrystalline polymers is transformed into fibrillar texture. This transformation is concentrated in a shoulder of propagating "telescopic" neck. While the structures before and after the transition have been described in full detail and their models generally accepted, the exact mechanism of structural changes in the neck shoulder is still an object of some controversy2,3). The classic (Peterlin) model4) assumes that the transformation from lamellae to microfibrils merely requires a chain tilt and slip in a limited region of "micronecks". An alternative concept5) suggests that the transformation from a lamella to a fibril depends solely on phase transition. The stored mechanical energy is assumed to cause local "melting" of the crystalline regions. In the subsequent step, the action of the mechanical stress field causes chain extension and crystallization. It is assumed that the resulting morphology contains *shish-kebabs* similar to those produced by crystallization from polymer solution in a flow field. It is important to note that this theory5) concerns a solid-state phase transition. Even if the temperature in the "living" neck shoulder might markedly increase due to the dissipation of mechanical energy by plastic deformation, it does not necessarily exceed the melting temperature of the semicrystalline polymer.

Interrelations between structural defects and heterogeneities of the original spherulitic material, the drawing process and heterogeneity of the resulting drawn polymer are another riddle. If a propagating neck approaches a heterogeneity larger than a certain critical size, it stops and breaks in its shoulder. The origin of the failure is then located at a distance from the fracture zone unlike that of the brittle fracture where the fracture locus is always found on the fracture surface. On the other hand, it has been shown experimentally that during the neck propagation, not only individual molecules but also larger objects, inclusions or even macroscopic fibres can be processed by the moving neck shoulder and become oriented along the drawing direction6). However, even in this case the intrinsic heterogeneities affect the drawing process. They cause temperature and stress fluctuations in localized regions of the neck. These processes, in turn, are imprinted as irregularities or heterogeneities in the structure of the oriented material. Thus, differences in drawability (natural draw ratio) in neighbouring locations of the original material cause mutual longitudinal slips between adjacent fibrils and lead to fibrillation$^{7)}$. At the same time, temperature fluctuations in the propagating neck cause differences in crystalline structure along a particular fibril.

Heterogeneities in crystalline structures of both spherulitic and fibrilar samples can be assessed by various structure-sensitive methods. In particular, light and electron microscopies offer a direct insight into the form and arrangement of individual structural elements and, in combination with image analysis, they can characterize their statistical parameters. Details of the crystalline structure itself can be obtained by X-ray diffraction (both WAXS and SAXS). Differential scanning calorimetry (DSC) might seem to be less suitable for the study of microstructural heterogeneities as it yields average characteristics of macroscopic samples. Nevertheless, a careful sampling together with the high precision of contemporary differential scanning calorimeters can give not only general average characteristics of the crystalline structure but also detect small amounts of minor components or impurities. In particular, multiple endotherm peaks of isotactic polypropylene were ascribed to crystallites of different order$^{8)}$.

The application of DSC to characterize heterogeneities and gradients in the crystalline structure of both injection-moulded and solid-state drawn specimens of isotactic polypropylene was the aim of the present work.

EXPERIMENTAL

Materials

The material used in this study was isotactic polypropylene (homopolymer) Mosten 58.412 supplied by Chemopetrol Litvínov, Czech Republic. The manufacturer characterizes the material by the melt flow index of 3 g/10 min (21.2 N, 230 °C), weight-average molecular weight M_W of about 170 000, polydispersity index $M_w/M_n = 9$ and index of isotacticity 98 %.

From pellets of this polymer standard, dumbbell specimens (ASTM D638, Type I) were injection-moulded on a Battenfeld BA 750/200 injection-moulding machine at the Polymer Institute, Brno, Czech Republic. The injection-moulding conditions are summarized in Table I.

Table I: Processing conditions of injection-moulded specimens

Heating zone temperatures	210 - 220 - 230 °C
Die temperature	240 °C
Mould temperature	60 °C
Screw compression ratio	2.3
Screw back pressure	0.5 MPa
Injection pressure	62.7 MPa
Holding pressure	62.7 MPa
Holding pressure time	30 s
Freezing time	15 s
Cycle time	60 s

Oriented samples of this material were prepared by solid-state drawing at various temperatures. The preparation details were as follows.

Drawing

The injection-moulded specimens were drawn in a temperature cabinet of an Instron 6025 tester at cross-head speed of 20 mm/min at various temperatures in the range 23-140 °C. The test pieces were conditioned for 30 min before drawing, then drawn at a particular temperature, after drawing kept for 30 min under constant deformation at the respective test temperature and finally cooled down to laboratory temperature during 30 min under the same deformation. The achieved natural draw ratio was in the range of 5.0-5.5, slightly depending on the draw temperature. Upon drawing, the original specimen cross-section of 10 × 4 mm decreased to approx. 4.5 × 1.5 mm. To distinguish between the effects of drawing and annealing during this process, control specimens were inserted into the temperature cabinet and exposed to the same thermal history as the drawn specimens, except for drawing.

Differential Scanning Calorimetry

A Perkin-Elmer DSC 2 differential scanning calorimeter was employed for the DSC measurements. Samples of about 5 mg taken from selected locations of the specimen were closed in aluminium sample pans and scanned in the temperature range 300-480 K at the heating rate 10 K/min. During the DCS scan, the system was flushed with dry nitrogen. The temperature scale was calibrated with cyclohexane and indium, the power output was calibrated with Al_2O_3. Melting temperature T_m was taken at a maximum of the melting endotherm. Crystallinities were calculated from the values of measured heats of fusion wherein the value 137.9 J/g for 100 % crystalline isotactic polypropylene was used9).

Sampling for DSC

Figure 1 shows a sketch of an injection-moulded dumbbell test specimen with selected sampling locations. The individual samples were carefully cut out from the core and edge parts by means of a fine saw and a fine file to match into the sample pans. During this operation, extreme care was taken to avoid heating or stressing the samples.

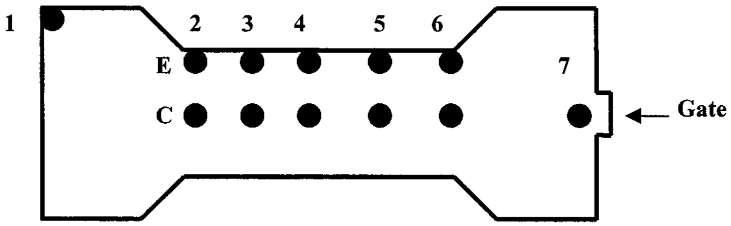

Fig. 1: Schematic sketch of a dumbbell specimen of injection-moulded isotactic polypropylene with depicted sampling locations. E = edge, C = core.

In sampling the drawn specimens, average samples of about 2 × 1.5 × 1 mm were cut out by means of a scalpel from the central (longitudinally) region of the drawn material wherein the core as well as edge parts were included. Control undrawn samples were cut from the injection-moulded specimens subjected to the same thermal treatment as the drawn specimens. Attempts were also made to cut the samples specifically from the core and edge parts of the drawn specimens. However, this sampling procedure did not prove to be satisfactorily reproducible. Therefore, another procedure was applied in later stages of the study. Herein, a specimen drawn at 100 °C was deep-cooled by dipping in liquid nitrogen to make it brittle. By means of a steel wedge, the oriented material was longitudinally split into three approximately equal parts - one core and two edge parts. Individual samples for DSC measurements were then cut by means of a scalpel from the core and edge parts of the split oriented material. This sampling was repeated for several cross-sections of the drawn specimen.

RESULTS AND DISCUSSION

Undrawn Injection-Moulded Specimens

Thermograms of the samples taken from an original injection-moulded specimen are shown in Figures 2 and 3. Quantitative evaluations of the DSC thermograms of these samples are summarized in Table II.

Table II: Crystallinities and melting temperatures of samples taken from original injection-moulded specimens[a]

Sample[b]	1	2		3		4		5		6		7
	E	C	E	C	E	C	E	C	E	C	E	C
Crystallinity, %	50.5	51.4	50.2	51.5	50.0	50.0	51.9	50.5	50.6	50.0	49.1	50.0
T_m, K (main)	442.1	443.8	441.5	441.8	442.1	443.1	442.8	442.8	442.9	442.9	441.5	443.9
T_m, K (shoulder)	-	-	-	-	-	-	-	420.0	-	419.5	-	419.4

[a] see Fig. 1; [b] C = core, E = edge

Samples taken from the specimen portions distant from the injection-moulding gate (Nos. 1-4) exhibit simple DSC thermograms with one broad endotherm with maximum at about 442 K (Fig. 2). Crystallinities of these samples ranged between 50.0 and 52.0 %. No apparent trend was ascertained either in melting temperature or in crystallinity with respect to the longitudinal and/or core-edge position of these samples in the original specimen. Splitting of the main endotherm in samples 4C and 4E (Fig. 2) might be attributed to local heterogeneities in lamellar thickness.

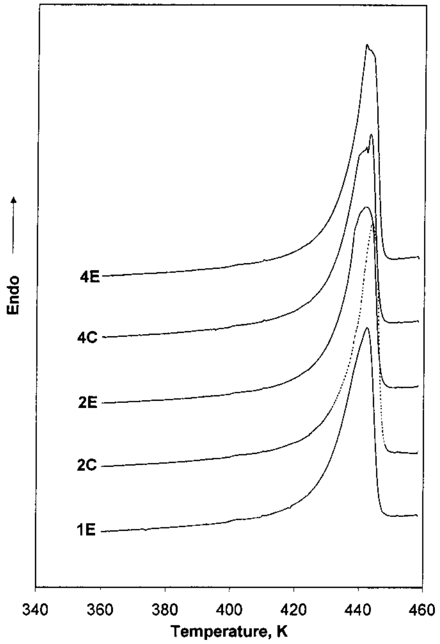

Fig. 2: DSC thermograms of average samples of injection-moulded undrawn isotactic polypropylene taken from the region distant from the injection gate. (For denotation of thermograms, see Fig. 1.)

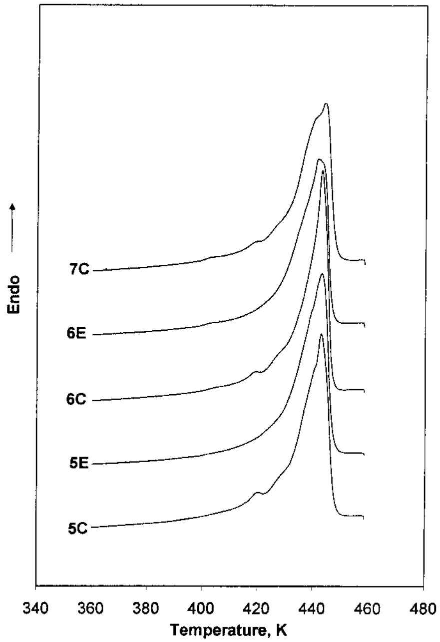

Fig. 3: DSC thermograms of average samples of injection-moulded undrawn isotactic polypropylene taken from the region adjacent to the injection gate. (For denotation of thermograms, see Fig. 1.)

Thermograms of samples taken from the core region adjacent to the moulding gate (Fig. 3, Nos. 5-7) showed crystallinities and melting temperatures of the main endotherm within the same range as samples 1-4. However, the DSC thermograms of samples 5-7 revealed a melting behaviour that varied with the core-edge position. Thermograms of the edge samples (Fig. 3, 5E, 6E) were quite similar to those of samples 1-4 (Fig. 2). However, an additional endotherm at about 420 K was found in samples of the core region adjacent to the gate of the injection-moulded test specimens (Fig. 3, thermograms 5C, 6C, 7C). This small but reproducible shoulder peak could reflect the presence of the crystalline β modification of isotactic polypropylene in this specimen region which was previously observed by WAXS2).

In the next step of the study, the undrawn injection-moulded specimens were exposed to the same thermal history as the drawn specimens (see below) within the temperature range 23-140 °C. The results of crystallinities and melting temperatures of the average samples taken from the injection-moulded specimens are summarized in the upper part of Table III. Thermograms of the undrawn samples annealed at 23 and 100 °C are shown in Figure 4 (23 U and 100 U). The thermograms feature single melting endotherms with the maximum at 440-442 K. No relation between the maximum of the endotherm and annealing temperature was found. A slight shoulder hump at 436 K was found on the thermogram of the undrawn sample annealed at 100 °C. The degree of crystallinity of the original undrawn specimen (53.1 %) did not change upon annealing within the temperature range 60-120 °C. A certain increase (up to 54.3 %) was found for the highest applied annealing temperature of 140 °C only.

Table III: Crystallinities and melting temperatures of average samples of undrawn and drawn specimens of isotactic polypropylene

	T_{ann} (°C)	23	60	80	100	120	140
Undrawn	Cryst. (%)	53.1	53.2	53.1	52.5	51.2	54.3
	T_m, K	441.8	442.5	442.2	(436), 442.5	440.2	441.5
Drawn	Cryst. (%)	61.5	62.6	62.2	61.7	62.2	67.0
	T_m (K)	(434.6)	(434)	(435.6)	(436)	(436)	(440.8)
		(438.4)	(440)	439.5	(441)	(441.5)	443.8
		443.2	443.5	443.2	443.2	444.2	-

Drawn Specimens

Crystallinities and melting temperatures of average samples taken from the specimens drawn at various temperatures in the range of 23-140 °C are summarized in the lower part of Table III. Endotherms of the samples drawn at 23 and 100 °C are shown in Figure 4 (thermograms 23 D and 100 D). Quantitative evaluation of the thermograms revealed a significant increase (8 - 13 %, in absolute values) in crystallinities of the drawn specimens as compared with the corresponding undrawn specimens subjected to the same thermal treatment (Table III). The highest crystallinity of 67 % was found for the sample drawn at 140 °C where, obviously, the synergistic effect of drawing and annealing took place.

Drawing of isotactic polypropylene at various temperatures was associated with the appearance of a marked heterogeneity in the lamellar thickness (melting temperature) distribution which was demonstrated by the occurrence of several peaks or distinct shoulder humps in DSC thermogram (see Fig. 4, thermograms 23 D and 100 D). Generally, the increase in crystallinity on drawing was mainly associated with the increase in the endotherm at 443-444 K. In most drawn samples, a side peak at about 436 K was detected. It is apparent that during drawing, a preferential formation of lamellae of a certain thickness and additional crystallization of thicker, more perfect lamellae take place.

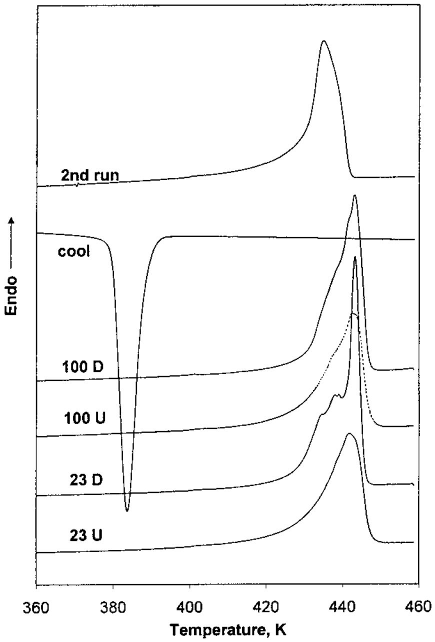

Fig. 4: DSC thermograms of average samples of isotactic polypropylene. 1st run: 23 U, 100 U, undrawn specimens annealed at 23 and 100 °C; 23 D, 100 D, specimens drawn at 23 and 100 °C. Cooling run: -10 K/min after 1st run to 480 K. 2nd run: +10 K/min after cooling to 300 K.

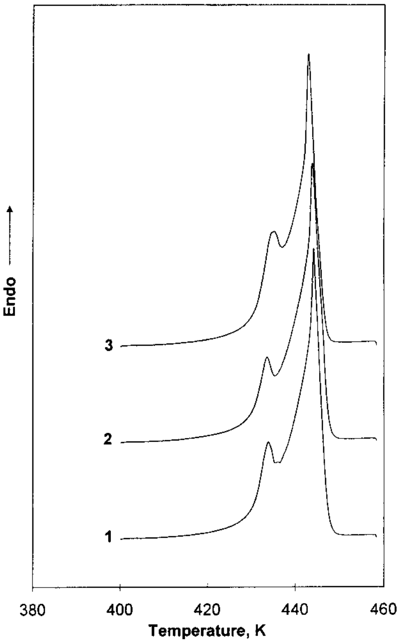

Fig. 5: DSC thermograms of three samples taken from adjacent core locations of the isotactic polypropylene specimen drawn at 100 °C.

Figure 4 also presents the thermograms of the cooling and re-heating runs of a sample of isotactic polypropylene after its melting during the first DSC scan to 480 K. In the cooling run at the cooling rate -10 K/min, the sample showed a single sharp crystallization exotherm with a minimum at 383.5 K. The thermogram of the subsequent re-heating DSC scan shows one smooth endotherm demonstrating that all lamellae preferentially formed during the drawing process, disappeared during melting and crystallinity (about 53 %), and returned to the value of the original injection-moulded specimen. However, maximum of the melting endotherm in the second run is markedly shifted to a lower temperature (about 435 K), which implies that the lamellae formed from the melt state during cooling are significantly less perfect (thinner) than those formed in the specimen during injection moulding.

DSC analyses of the samples taken from different locations of drawn specimens suggested some differences between the core and edge parts. However, reproducibility of these analyses was poor. Therefore, we adopted a new sampling procedure (see Experimental) which provided an improved reproducibility. This reproducibility is well demonstrated in Fig. 5 where thermograms of the samples taken from adjacent core locations of the specimen drawn at 100 °C are shown. The increase in crystallinity of drawn samples was accompanied by heightening and narrowing of the main sharp endotherm at 443-444 K and by the occurrence of an additional shoulder peak at about 435 K. From the qualitative as well as quantitative points of view, the thermograms are virtually identical. This implies that a reasonable degree of homogeneity in crystalline structure exists in the core part of a drawn specimen of isotactic polypropylene.

The situation is somewhat different for the samples taken from adjacent edge locations of the specimen drawn at 100 °C (Fig. 6). Here, the lower melting shoulder endotherm at 435 K corresponds to the same peak in the core samples. The main peak at 443 K is obviously less profound as compared with the core samples. Moreover, another higher-temperature shoulder endotherm at about 446 K occurred in some edge samples. The occurrence and shape of this small peak, however, varied along the drawn specimen. Taking into consideration the good reproducibility of the improved sampling procedure and DSC analysis discussed above (Fig. 5), this peak can be attributed to local heterogeneities in the lamellar thickness and perfection in the edge part of the drawn specimen.

Hence, the multiple peak endotherms of drawn samples suggest the presence of three types of crystallites differing in crystal perfection. The least perfect crystallites melting at 435 K might grow in the neck shoulder from ordered nuclei latently present in the injection-moulded material.

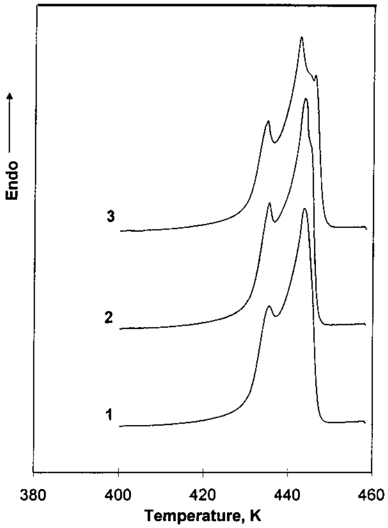

Fig. 6: DSC thermograms of three samples taken from adjacent edge locations of the isotactic polypropylene specimen drawn at 100 °C.

The main peak at 443 K corresponds to the original crystallites but with improved crystalline order which is particularly manifested by heightening and narrowing of the main peak in the core part of the drawn specimen. Finally, the observed heterogeneities in the crystalline structure of the highest perfection (highest melting temperature) along the edge stripe of the drawn specimen can be interpreted as a record of oscillations of temperature and stress during neck propagation3). Thus, the results seem to support the concept of partial melting and recrystallization in the propagating neck shoulder4).

CONCLUSIONS

The results presented in this work have shown that a standard DSC analysis is sensitive enough to reveal details of crystalline structure of injection-moulded and drawn specimens of isotactic polypropylene. In particular, the increase in crystallinity upon drawing and the effect of drawing temperature could be assessed. The degree of crystallinity evaluated by the DSC method is in good agreement with data obtained by wide-angle X-ray diffraction.

Several types of heterogeneities can be detected:

(1) Differences between various injection-moulded test specimens as represented by corresponding samples.

(2) Differences between crystalline structure within individual injection-moulded test specimens including core-shell effects and the presence of crystalline β modification.

(3) Heterogeneities along the edge of drawn material. These can be interpreted as a record of temperature and stress fluctuations during structural transformations in the propagating neck shoulder.

Acknowledgement

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Projects Nos. A4050904 and A4050605). Financial support from the Grant Agency of the Czech Republic (Projects Nos. 106/98/0718 and 106/99/P011) is also gratefully acknowledged.

References

1. Raab M., Kotek J., Baldrian J., Grellmann W.: J. Appl. Polym. Sci. **69**, 2255 (1998)
2. Liu Y., Truss R. W.: J. Polym. Sci., Part B: Polym. Phys. **32,** 2037 (1994)
3. Raab M., Sova M.: Collect. Czech. Chem. Commun. **60**, 2006 (1995)
4. Peterlin A.: J. Mater. Sci. **6,** 490 (1971)
5. Juska T., Harrison I.R.: Polym. Eng. Sci. **22,** 766 (1982)
6. Sova M., Raab M., Sližová M.: J. Mater. Sci. 28, 6516 (1993)
7. Peterlin A.: Int. J. Fracture **11**, 761 (1975)
8. Guerra G. et. al.: J. Polym. Sci., Part B: Polym. Phys. **22,** 1029 (1984)
9. Alonso M., Gonzales A., de Saja J.A.: Plast. Rubber Compos. Process. Appl. **24**, 131 (1995)