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A morphological study of a highly structurally regular isotactic poly(propylene) fraction

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Abstract

Studies of the thermal properties and lamellar morphology of a highly structurally regular fraction of a Ziegler–Natta type isotactic poly(propylene) have been carried out. This fraction has an isotacticity content of *mmmm* = 0.995 and a molar fraction of defects of 0.001. It is thus, among the most structurally regular isotactic poly(propylene) samples whose properties are reported. Differential scanning calorimetry as well as electron and optical microscopy were used to characterize the specimens.

The fraction was crystallized from the melt over a very wide range of crystallization temperatures (135°C ≤ T_c ≤ 167°C). Monoclinic, α type crystals were formed over the whole crystallization range. The formation of cross-hatching, or lamellae branching, was also observed over the complete interval of crystallization temperatures. The formation of the tangential 'daughter' lamellae at temperatures greater than 160°C can be attributed to the high structural regularity of the fraction studied. Relatively low crystallization temperatures (130°C to 150°C) show extended regions of woven lamellae having similar thicknesses with occasional groups of parallel long radiating lamellae. A morphology of rather thick long radiating lamellae and thin, transverse lamellae is formed at temperatures ≥ 160°C. The angle between the daughter and mother lamellae of approximately 100° is in agreement with crystallographic predictions.

The two endotherms that are observed by differential scanning calorimetry can be identified with the melting of the two distinct lamellae populations. It is consistent with the optical microscopy observations where a change in the sign of the birefringence is observed on the melting of the daughter lamellae. When formed at relatively high temperatures (T_c > 160°C) the mother lamellae subsequently melt at temperatures > 180°C.

Keywords: Ziegler-Natta; Isotactic poly(propylene); Lamellar morphology

1. Introduction

The lamellar and crystallographic habits of the monoclinic (α) phase of polypropylene are unique among flexible chain molecules. At the level of the electron microscope, a three dimensional array of nearly orthogonal ''cross-hatched'' lamellae is usually found [1–3]. Based on models [1,4,5] the details of the molecular arrangement of the branching has been explained in terms of a homoepitaxial crystallization of daughter lamellae on the lateral 010 face of the parent ones [6]. It has been established that the fusion of isotactic poly(propylene), prepared either by Ziegler–Natta or metallocene type catalysts, gives two melting endotherms. The interpretation of the two endotherms has been a matter of controversial debate in the literature [7–12]

The main purpose of this work is to develop an understanding of the origin of the double peaks and to ascertain their relation, if any, to the unique branched lamellar morphology. To accomplish this we have carried out a detailed transmission electron microscopy (TEM) study of an isotactic poly(propylene) fraction that was crystallized from the melt at different temperatures, including very high ones, that are not usually studied. In addition to the DSC studies of this fraction, the melting characteristic of the spherulites that develop were also investigated by optical microscopy.

Virtually all studies of this type have been carried out with unfractioned, commercial isotactic poly(propylenes) prepared with conventional Ziegler–Natta type catalysts. Such polymers are not suitable for basic studies of either

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thermodynamic properties or morphology in terms of chain structure. The reason is the broad distribution of the molecular length and inter-chain defect composition that is characteristic of these poly(propylenes) [13,14]. A detailed fractionation of this type of polypropylene has indicated that a strong correlation exists between the variables related to molecular structure [14,15]. The longer molecules were found to contain fewer chain defects and the shorter ones have the greatest number. This distribution of molecular weight and chain defects make it very important that fractions, or samples having narrow molecular weight and composition distributions, be used in studies of properties and morphology. For this reason a fraction of very high stereoregularity, among the most structurally regular isotactic poly(propylene) samples that have been studied was selected for this work. In addition, in order to accomplish a more comprehensive analysis of the properties, and to develop a broader base to interpret the lamellar morphology, the isothermal crystallizations were extended to very high temperatures.

2. Experimental part

The poly(propylene) fraction used in this work is fraction E-18 of the solvent–nonsolvent fractionation carried out by Paukkeri et al. (See Table 2 of Ref. [14]). It is clear from this table that as the fractionation proceeds with increasing amounts of solvent, the molecular weights of the fractions increase. Paralleling this increase, the isotacticity content measured as a fraction of pentads by NMR (*mmmm*) also increases. The poly(propylene) fraction of interest, E-18, is among the most stereoregular ones. It is characterized by $Mw = 490\,000$ *g/mol*, $Mw/Mn = 2.8$ and $mmmm = 0.995$. From the analysis of the stereoirregular-type of pentads in the ^{13}CNMR spectrum (see Table 3 of Ref. [14]) only one stereo-type CH_3 inversion is found to be present in this fraction. The ratio of the *mmmr* (or *mmrr*) to the *mrrm* pentads is 2 to 1, thus confirming the presence of only this type of defect. Uncorrected inversions (*mmrm/rmrr*), consecutive stereo irregular-type placements, or syndiotactic blocks were not found in this fraction. Based on the *mmmr* pentads, the molar fraction of defects is calculated as 0.001 [16]. This fraction is among the most structurally regular isotactic poly(propylene) samples whose morphology and properties have been studied heretofore.

The molar fraction of stereo defects of a poly(propylene) chain should not be taken as one minus the molar fraction of isotactic pentads as has been done in other work [17]. For example, if this procedure was carried out with fraction E-18, which has only one type of well defined defect, the total molar fraction of defects (per monomeric unit) would have been overestimated five fold. The consequences of this overestimation can be quite serious, as for example, in the analysis of the melting point depression of the pure polymer by the presence of chain defects, and in the analysis of crystallization kinetics by means of nucleation theories [17]. The arbitrarily chosen isotacticity, is a useful qualitative parameter for the comparison of a given stereoirregular polymer relative to others. However, it cannot be used in any quantitative analysis of the influence of chain defects.

Small amounts of this fraction were placed in thin wall glass tubes with 5 mm internal diameter and were then sealed under vacuum. The tubes were immersed in an oil bath, preset at 220°C, for 15 min and rapidly transferred to other thermostated baths that were preset to the desired crystallization temperature. TEM analysis of the fraction E-18 were carried out after crystallization at the following temperatures and times: 136°C(100 min), 150°C (5900 min), 160°C (9840 min), 165°C (19740 min) and 167°C (32880 min). These experiments thus encompass a very wide range in crystallization temperatures. These include crystallization temperatures of 160°C and higher, temperatures that are not usually reported in morphology and property studies. Self-seeding techniques were not used, even for crystallization at the highest temperatures. After the required crystallization time elapsed the tubes were taken from the oil baths and rapidly submerged in ice water before opening. The samples were collected at room temperature.

Melting points were recorded by differential scanning calorimetry at 10°/min, using either a Perkin-Elmer DSC-2B or a DSC-7, both calibrated for temperature with indium. The degrees of crystallinity were calculated using the heat of fusion of a perfectly crystalline poly(propylene) as 2100 cal/mol [18,19].

Thin sections of the samples were prepared for optical microscopy. Sections, 3 μm thick, were cut at − 30°C on glass knives in a Reichert–Jung Ultracut E ultramicrotome equipped with FC-4D cryostage. Sections were analyzed using a Leitz polarizing light microscope and a first order red (λ) plate for determination of the sign of birefringence of spherulites [20]. During the microscopic observation, sections were heated in a Mettler FP52 hot stage operated at heating rates of 0.2°/min and 1°/min. In an additional experiment a thin film of this fraction was mounted between two cover slips in a Linkam hot stage model TP-93 fitted in an Olympus BH-2 microscope. The sample was melted at 200°C for 2 min and cooled at 40°/min to 160°C. The film was allowed to crystallize at this temperature for approximately 1000 min. The spherulites were further melted without previous cooling.

Samples to be analyzed by TEM were stained with ruthenium tetroxide vapors for 7 h and sectioned at ambient temperature using the ultramicrotome and diamond knife with a water floatation bath [21]. The sections were analyzed in a Philips EM-300 transmission electron microscope at 100 kV accelerating voltage.

WAXS diffractograms were obtained in a slit-collimated Siemens D-500 diffractometer operating in a 2θ range between 4° and 40°. Filtered Cu K_α radiation was used as source.

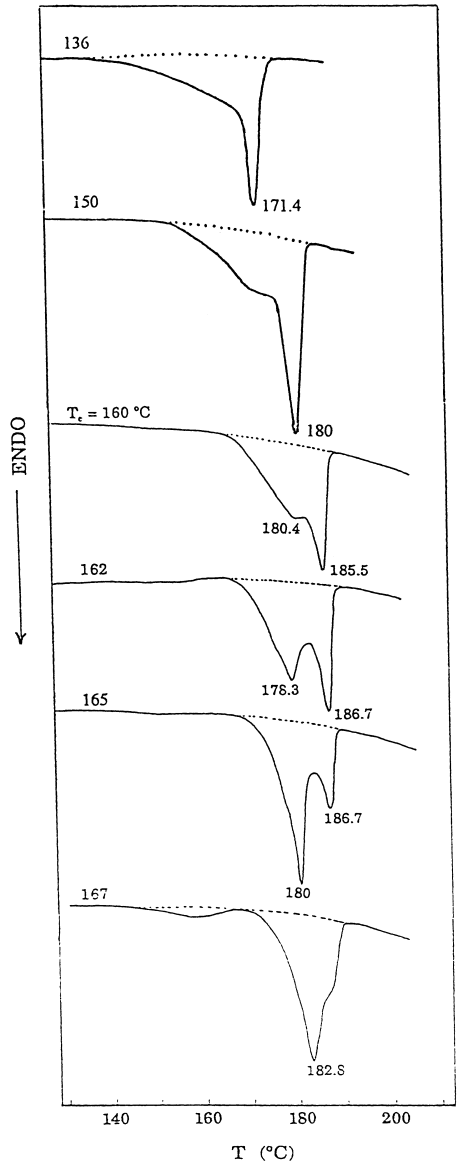


Fig. 1. DSC melting curves of an isotactic poly(propylene) fraction of high structural regularity crystallized at the indicated temperatures.

3. Results and discussion

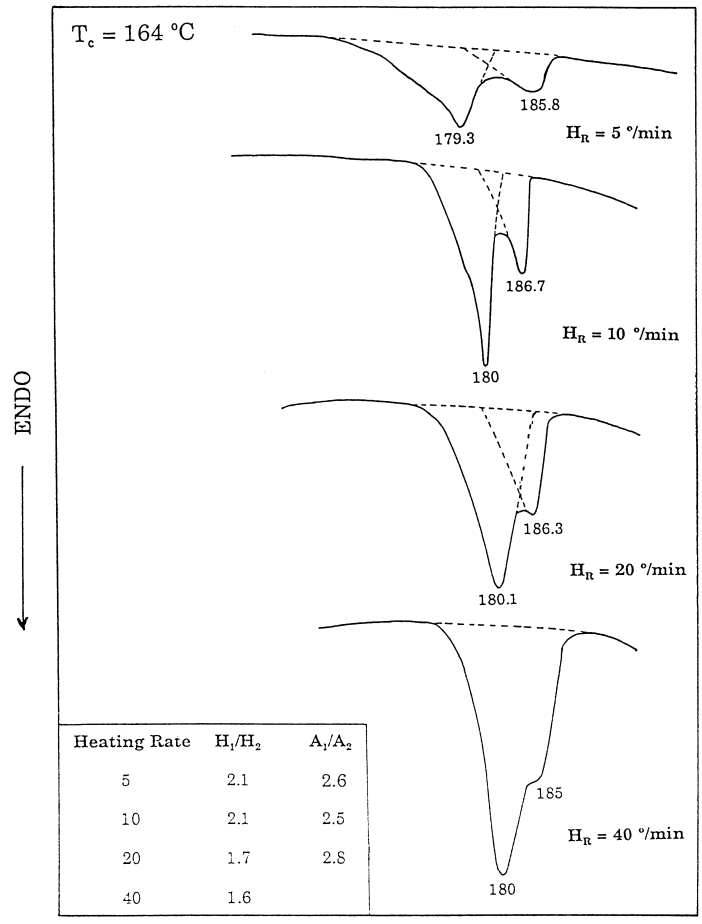
The high structural regularity of the poly(propylene) fraction studied here allows it to be crystallized isothermally over a very wide temperature range, without the need of self-seeding techniques. This fraction was also free of nucleating agents. The DSC thermograms of the fusion process of the crystals obtained isothermally between 136°C and 167°C are shown in Fig. 1.

In spite of the high regularity (high isotacticity) of this fraction, two melting points are obtained at most of the isothermal crystallization temperatures. In the crystallization temperature interval between 136°C and 143°C a broad shoulder in the low temperature region is observed that is followed by a sharp melting peak. The shoulder develops into a well defined peak with increasing crystallization temperatures. The intensities of both melting peaks increase with crystallization temperature up to 162°C. A qualitative analysis of the two endothermic peaks indicates that the intensity of the low melting peak increases with T_c and is lower than that of the high temperature peak up to a T_c of ≈162°C. The melting behavior of the crystals formed at higher temperatures ($T_c > 162°C$) is different. The relative intensity of the two melting peaks is reversed with increasing T_c. The high melting temperature peak does not appear to increase with increasing T_c while the low temperature peak clearly increases.

We are interested in understanding the basis for the two melting endotherms that are observed. One possible reason is the formation of different crystalline polymorphs that have different melting temperatures. Isotactic poly(propylene) is known to form different crystalline structures, depending on the crystallization conditions [22]. Wide angle X-ray diffractograms were obtained after crystallization at 136°C, 160°C and 165°C. In all these cases only the α monoclinic form was obtained with this fraction. Thus, polymorphism can not be the cause of the two melting peaks in this situation.

The two melting endotherms which are observed have also been attributed to a melting-recrystallization process during heating subsequent to crystallization [8,9,23]. In this case, the high melting peak would correspond to the fusion of crystals that have recrystallized during the melting process and are thus not related to the structure and morphology of the original sample. A detailed DSC study of this problem led Petraccone et al. [23] to conclude that at relatively low crystallization temperatures, at which thin, more imperfect crystals are formed, the double peak-shape endotherms are the result of partial melting followed by recrystallization during heating. The sample studied by these authors, an unfractionated poly(propylene), did not show multiple endotherms after crystallization at temperatures above ≈ 150°C. However, the structurally regular isotactic poly(propylene) fraction of the present study gives two endotherms after crystallization at temperatures both above and below 150°C.

In order to ascertain whether melting-recrystallization was the cause of the two endothermic peaks in the sample studied here, fusion experiments at varying heating rates were carried out subsequent to crystallization at a relatively low temperature, 133°C, and a higher one, 164°C. If the high temperature endotherm is consequence of melting and recrystallization during heating, more rapid heating should diminish, or eliminate, the area corresponding to this peak. Fig. 2 shows thermograms for the fraction crystallized at 164°C at heating rates varying between 5 and 40 K/min. The ratio of the relative heights of both peaks is given in the figure, and is constant with heating rate. The small variations that are observed are within the experimental error of the measurement. Attempts were also made to manually deconvolute the areas of both peaks by linearly extrapolating the overlapping trailing edges of the peaks to the common



Heating Rate	H_1/H_2	A_1/A_2
5	2.1	2.6
10	2.1	2.5
20	1.7	2.8
40	1.6	

Fig. 2. DSC melting curves at different heating rates of the IPP fraction crystallized at 164°C. The heating rates are indicated. H_1/H_2 and A_1/A_2 are the ratios between the peak height or areas of the two endotherms.

base line. The ratio of the calculated areas, also listed in Fig. 2, is approximately constant with heating rate. We therefore conclude that the two endotherms observed at 164°C are not a consequence of partial melting-recrystallization.

The results of similar experiments carried out after crystallization at 133°C are shown in Fig. 3. In this case, the ratio of the relative heights of both peaks, H_1/H_2, increases with increasing heating rate. A conventional interpretation of these results, in line with other works [23–25], would be that the high melting temperature peak (~169°C) represents the melting of crystals formed by recrystallization (or partial recrystallization) during heating of those that were initially formed at 133°C. The lower temperature peak near 160°C may arise from partial melting of the sample, while the peak at ~169°C would represent the melting of the recrystallized material. The presence of only a shoulder at temperatures ~160°C for the lowest heating rates used in Fig. 3 would indicate a very rapid melting-recrystallization under these conditions.

It is thus concluded that although melting-recrystallization appears to occur during the fusion of the crystals formed at relatively low crystallization temperatures, the two melting endotherms observed after crystallization at temperatures above 150°C are not a consequence of recrystallization during the melting process. When different heating rates were used to melt the isothermally formed crystals from Ziegler–Natta commercial, unfractionated type poly(propylenes) crystallized at 145°C, the area, and relative intensity of each peak did not change with heating rate [11].

There is also the distinct possibility that the two endotherms could be associated with the melting of the two populations of lamellar structures that are found in isotactic poly(propylene). To investigate this possibility it is necessary to examine the details of the lamellar morphology and its variation with crystallization temperature. Studies by Bassett and Olley [2,26] and by Keller and Norton [3], using unfractionated Ziegler–Natta type isotactic poly(propylenes), pointed out that two lamellar populations, associated with the dominant and daughter lamellae, have been observed for the unfractionated polymer at crystallization temperatures <160°C [2,3]. These investigators concluded that the population of lamellar branching decreases with increasing crystallization temperature and was nonexistent after crystallization at 160°C [2,5][1].

[1] Bassett and Olley considered the possibility that the daughter lamellae, if formed at 160°C, may have been destroyed during the staining process [2].

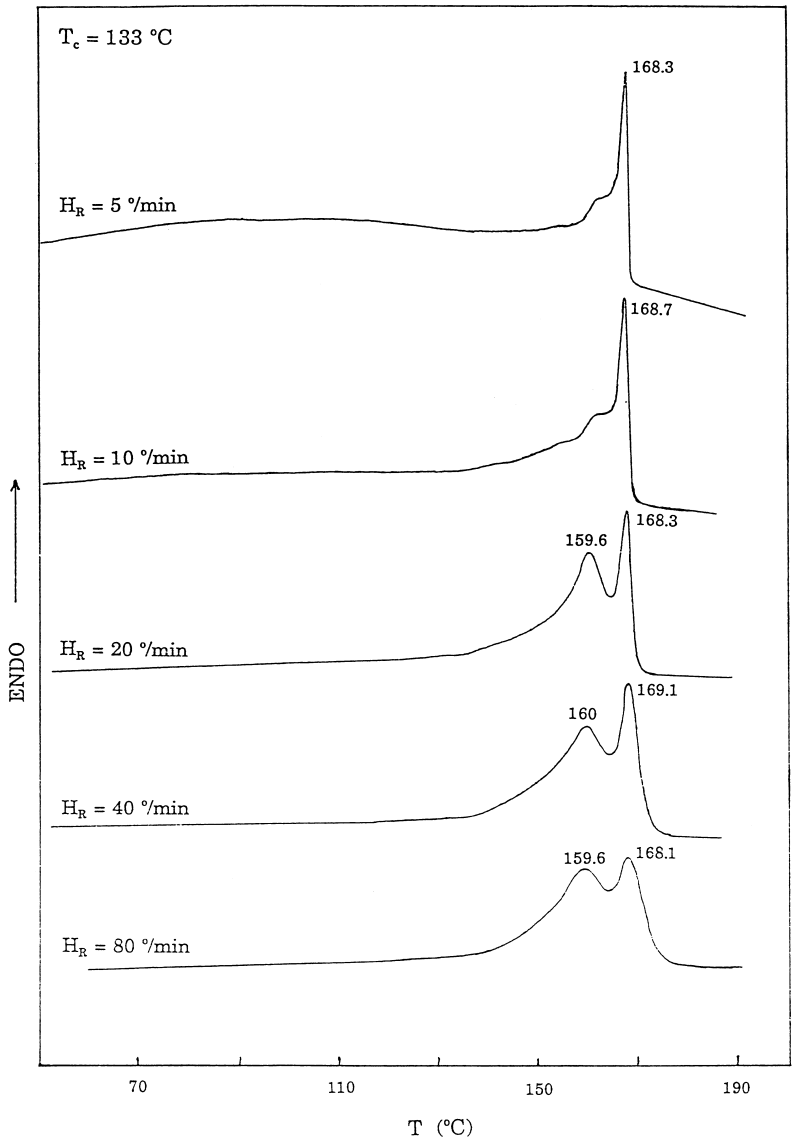


Fig. 3. DSC melting curves at different heating rates of the same IPP fraction crystallized at 133°C. The heating rates are indicated. (The endotherms are facing up in this figure.)

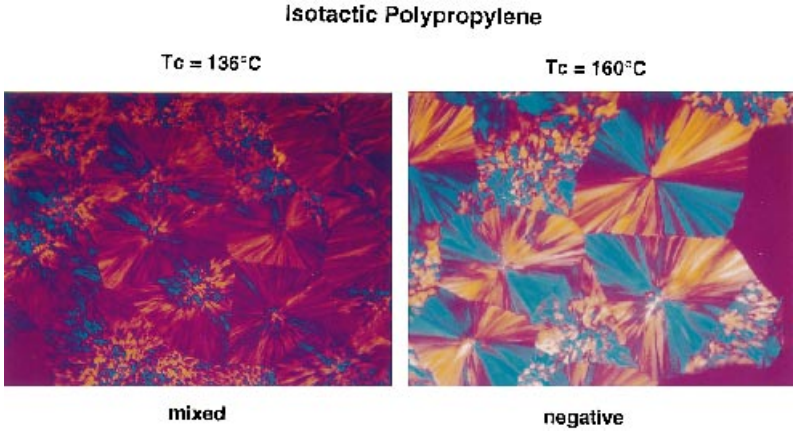


Fig. 4. Optical micrographs of thin sections of the IPP fraction crystallized at the indicated temperatures. The sign of the birefringence was obtained using a first order λ plate and cross polarized light microscopy.

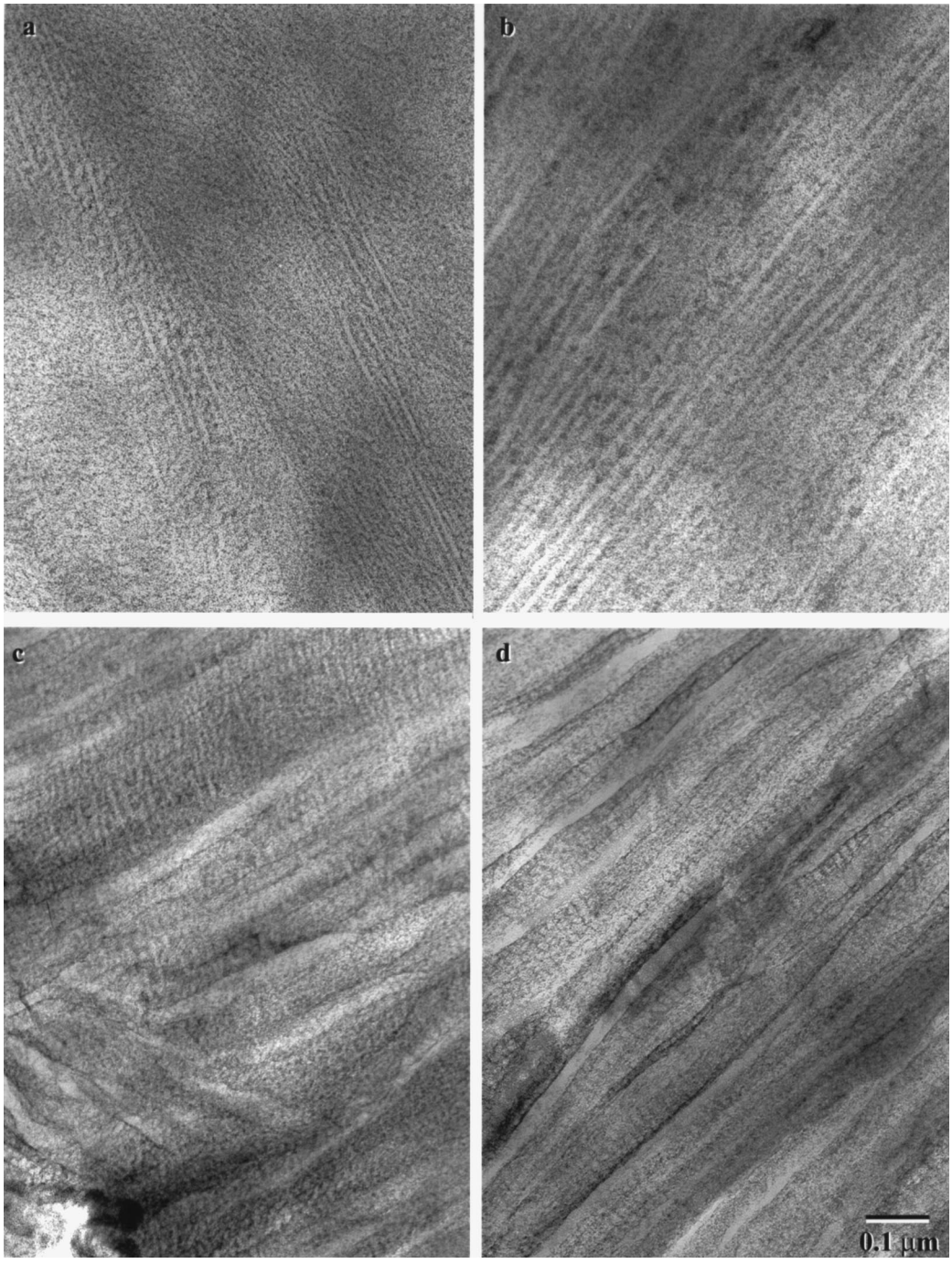


Fig. 5. Representative transmission electron micrographs of the variation of the lamellar morphology of the IPP fraction crystallized at different temperatures. (a) $T_c = 136°C$, (b) $T_c = 160°C$, (c) $T_c = 165°C$, (d) $T_c = 167°C$. The radial direction follows the long straight lamellae in all the micrographs (see text).

Similar conclusions were drawn from the results of other transmission microscopy studies in unfractionated materials [3,5,27]. Therefore, in order to explore the possibility that the origin of the two endotherms reside in the unique lamellar morphology it is necessary to ascertain whether two lamellar populations are actually formed at the higher crystallization temperatures. If this turns out to be so, then the question as to whether the two lamellar populations observed at all crystallization temperatures can be associated with the two melting endotherms needs to be addressed. Therefore, the lamellar characteristics as a function of crystallization temperature are revisited in this work using a highly isotactic sample. Transmission electron and optical microscopy studies of the spherulites formed at crystallization temperatures above 160°C, as well as at lower temperatures, were carried out.

Thin ($\approx$10 μm) sections of the polymer crystallized at different temperatures were observed by polarized light optical microscopy with a first order red plate (λ plate).

Some examples of these are given in Fig. 4. Rather large, well developed spherulites are observed at all crystallization temperatures, with diameters ranging from 140 μm at 136°C to 230 μm at the highest crystallization temperatures. Specimens crystallized at temperatures below 145°C give spherulites that are weakly negative birefringent although some weak mixed character is present near the center of some spherulites. Spherulites formed between 150°C and 167°C have a negative birefringence. This alteration in birefringence with crystallization temperature follows the morphological changes previously observed in unfractionated isotactic poly(propylenes) crystallized below 160°C [2,3,20,26,28]. Weakly positive spherulites were obtained at temperatures below 134°C in the unfractionated polymer but the morphology of the fraction at temperatures below 136°C was not studied[2]. The change from mixed or weakly negative spherulites to predominantly negative spherulites with increasing crystallization temperature is in agreement with a decrease in cross-hatching. However, it is uncertain from just the optical micrographs if tangential lamellae, or cross-hatching, vanishes at the highest crystallization temperatures or a greater population of dominant lamellae overtakes the possible influence of the tangential lamellae on the total sign of the birefringence.

To determine whether daughter lamellae are formed at crystallization temperatures ≥160°C, transmission electron micrographs were obtained over the complete range of crystallization temperatures studied. Representative micrographs are given in Fig. 5. Fig. 5(a) shows that for the sample crystallized at the relatively low temperature of 136°C, the spherulites present regions of profuse cross-hatching (upper left of the micrograph), similar to that shown for the unfractionated polymer [3]. There are also other regions in the micrograph of long parallel radiating lamellae where the branching is less well defined and appears to be formed of short, thin daughter lamellae (lower right of the micrograph). Very straight radial lamellae with only small amounts of tangential cross-hatching were found by Norton and Keller in an unfractionated polypropylene crystallized at 136°C [3]. At lower temperatures dense cross-hatching was observed by these and other investigators [3,27]. The lamellar morphology found in the spherulites formed at 150°C is quite different from that reported from electron microscopy for unfractionated poly(propylene) crystallized at similar temperatures [3,26] or for fractions having larger amounts of structural irregularities [30]. Groups of very long parallel radiating lamellae are found interconnected by very thin short branches. Few isolated regions show thick branched lamellae.

Representative micrographs of the fraction crystallized at 160°C, 165°C and 167°C are given in Fig. 5(b), (c) and (d). It is evident from these micrographs that at these high crystallization temperatures (≥160°C) the long, radiating, dominant lamellae are well formed. We can also deduce that the internal perfection which is manifested as graininess within the lamellae, is quite good since they are almost free of stain. The presence of a large concentration of short tangential lamellae that grow at regular distances and are tangential to the dominant lamellae is also clear, particularly at the highest T_c. The angle between the tangential lamellae and the radial long lamellae of Fig. 5 is approximately 100°. The possibility can be raised that the large number of thin, cross-hatched lamellae, observed after crystallization temperatures ≥160°C, are formed on quenching. However, as is shown in Fig.1, no quenching peaks are observed in the thermograms. In addition, the spherulites grown in thin films at temperatures ≥160°C display negative birefringence at their early stages of development. Gradually, however, with time a mixed birefringence develops, thus, giving a clear indication that lamellar branching occurs at the isothermal crystallization temperatures [31].

The formation and growth of the branched, tangential lamellae, that are illustrated in Fig. 5, are in agreement with the epitaxial crystallization explanation given by Lotz and Wittman [6]. The branched lamellae grow tangentially from the dominant lamellae at an angle very close to 100° as predicted. At this angle there are favorable interactions between the methyl side group of helices that have the same hand [6]. A recent study of the unit cell dimensions of the monoclinic phase formed at high temperatures also indicates that epitaxial crystallization is crystallographically feasible at these temperatures. The differences in dimension between the a and c axis at low and high crystallization temperatures are small, varying only from 2.3% to 3.5% [32].

Contrary to previous conclusions [2,3], it is clear from Fig. 5 that profuse lamellar branching is found after crystallization at high as well as at low crystallization temperatures. The formation of daughter lamellae of the type shown in Fig. 5(b), (c) and (d) at crystallization temperatures greater than, or equal to 160°C, could be a consequence of the high structural regularity of the fraction studied in this work. Thus, daughter lamellae were not observed in unfractionated isotactic poly(propylenes) crystallized at these temperatures [2,5].

The variation in the dominant-daughter lamellae pattern with changing crystallization temperature is not unique to the highly regularly structured fraction studied here. Metallocene type isotactic poly(propylenes), that have highly regular structures, have also been studied and give a very similar pattern [33].

[2] The comparison of morphological features obtained in the highly structurally regular fraction and the unfractionated polymers should properly be based on undercoolings rather than actual temperatures. The undercoolings should be obtained from the equilibrium melting temperature of the respective polymers and not from the directly observed values. The equilibrium melting temperatures can be calculated from theory [29]. A conventional Ziegler type isotactic poly(propylene) contains approximately 1 mol% of defects. Thus, the calculated equilibrium melting temperature of the fraction differs only by 2° from that of the conventional polymer. Hence the morphology of the fraction crystallized at temperatures > 162°C is studied at smaller undercoolings than those previously reported [2,3].

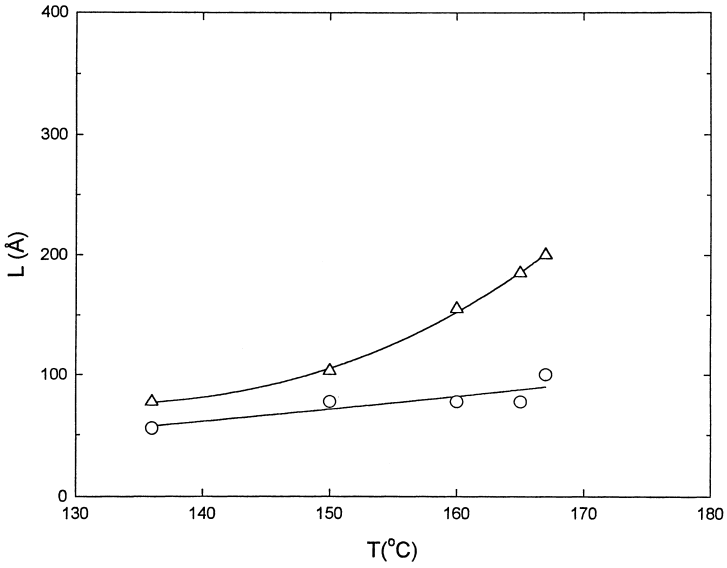


Fig. 6. Variation with crystallization temperature of the average thickness of mother (△) and daughter (○) lamellae in the middle and peripheral regions of the spherulites.

The difference in thicknesses between the dominant, radiating lamellae and the tangential daughter lamellae is also evident in the micrographs of Fig. 5. The character of the branching at the lowest crystallization temperatures is different from that at the higher ones. At low crystallization temperatures, there is essentially no difference in the thickness of the dominant and branched lamellae. They show some similarity to the original quadrite-type cross-hatch morphology described by Khoury [1]. At the higher crystallization temperatures long, parallel and well-formed dominant lamellae develop along with extensive thin, tangential lamellae.

The lamellar thicknesses of both, radial and transversal lamellae were measured in several regions, mainly at half distance from the center and outer parts of the spherulites. The averaged values are plotted as a function of the crystallization temperature in Fig. 6. The variation in the thickness of the dominant lamellae (±40 Å) is larger than that of the tangential ones (±15 Å) at any given temperature. In the crystallization temperature interval between 130°C and 150°C, where small regions of thin long parallel lamellae are seen along with extensive cross-hatched areas, the dominant and branched lamellae have about the same thickness (60–75 Å). For crystallization above 150°C, the differences in thickness between the dominant and tangential lamellae begin to increase. This difference becomes enhanced when crystallization is carried out at temperatures above 160°C. For example, after crystallization at 167°C the thickness of the tangential lamellae still remains about 75 Å while the dominant lamellae average ≈200 Å thick. The lamellar thickness of the center of the spherulites also increases progressively with crystallization temperature. They change from about 100 Å at 136°C to close to 350 Å at 167°C.

Differences in thicknesses between the dominant (radial) and transversal lamellae have been recently reported by White and Bassett [34] for an unfractionated isotactic poly(propylene). Although the nominal values of the thicknesses reported in the work of White and Bassett are larger than those reported here, the variation of the thickness of both lamellae types follows a similar pattern with temperature than that shown in Fig. 6 for the highly structurally regular fraction. Only crystallization temperatures up to 141°C were studied in Bassett's work, thus the observed difference in thicknesses was small, between 10 Å and 20 Å, in agreement with the data of Fig. 6.

The electron microscopic studies have clearly established the presence of (cross-hatched) dominant and daughter lamellae, after crystallization at temperatures up to and including 167°C. It is an open question as to the lamellar morphology that develops after isothermal crystallization above this temperature. An inordinate amount of time would be required to complete the crystallization under these conditions. It is then appropriate to examine the relationship, if any, between this unique morphological feature of isotactic poly(propylene) and the fusion process. To investigate if the origin of the two endothermic peaks lies in the two populations of lamellar thicknesses, we have studied, by means of polarized light microscopy, the changes in the birefringence of the spherulites as they were heated at a constant rate. We take advantage of the characteristically different birefringences that are associated with the radial and transversal lamellae. Two examples of this type of measurement are given in Figs. 7 and 8.

A set of optical micrographs of the thin sliced sample and the accompanying DSC thermogram are shown in Fig. 7 for a specimen crystallized at 136°C. Crystallization at this temperature produces mixed type spherulites, with a tendency towards a negative character when observed at

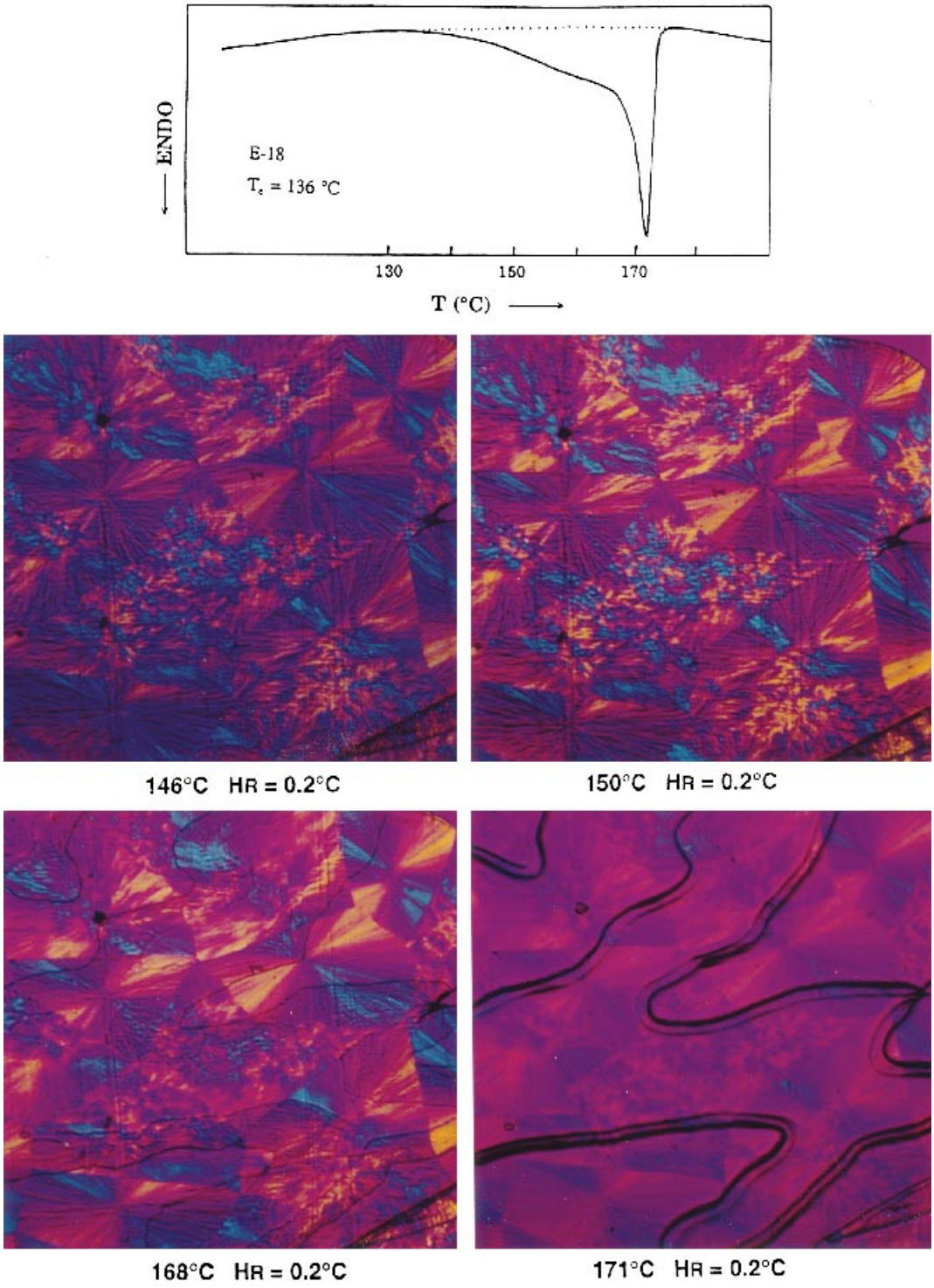


Fig. 7. DSC melting curve of the fraction crystallized at T_c = 136°C and optical micrographs at different stages during melting. A layer of molten material is seen at 168°C. Spherulitic birefringence is seen up to 171°C. 10 μm sections of the previously crystallized sample were used for optical microscopy.

room temperature. During heating at a constant heating rate, the spherulitic pattern remains unchanged from room temperature up to about 150°C. At 150°C, the temperature that corresponds to the beginning of the low temperature shoulder of the endotherm, there is a sudden change in the global brightness of the spherulitic pattern. The spherulites still maintain a blend of negative and positive weak birefringence. However, the negative character becomes much better defined. Brighter, well defined, preferentially negative spherulites are also found at temperatures of 168°C which is close to the maximum in the high temperature endotherm. The spherulitic pattern vanishes at

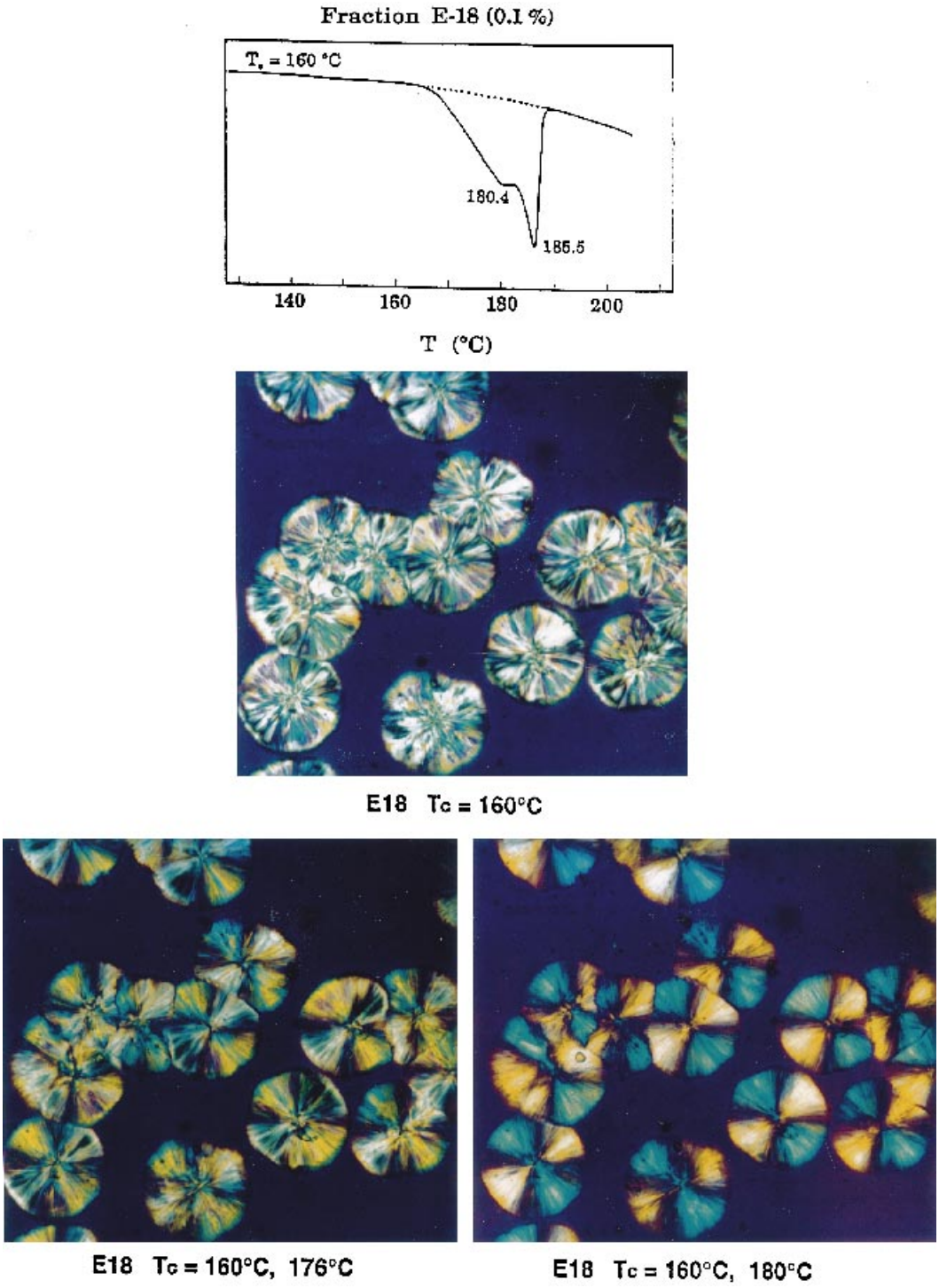


Fig. 8. DSC endotherm of the fraction crystallized at 160°C and optical micrographs of the same fraction crystallized at 160°C in a hot stage and melted without previous cooling below 160°C. The micrographs show the initial mixed birefringence at the crystallization temperature and the change in the sign of the birefringence at temperatures corresponding to the low temperature DSC endotherm. This change is in agreement with the preferential melting of tangential, daughter lamellae.

≈171°C–172°C in total agreement with the melting peak. In the temperature region between 150°C and 165°C the radiating lines of the spherulites (associated with radiating lamella bundles) become more diffuse, which is indicative of the homogeneous melting of thin imperfect crystals. In fact, a thin molten layer is already apparent on the surface of the section at 168°C which wets the slide and overslip, decreases scattering and thus leads to a better light transmission. The change to spherulites having increasingly more negative birefringence on heating is indicative of a fusion

process in which the transverse, daughter, lamellae melt first and the dominant do so at a higher temperature. Thus, although the thermograms shown in Fig. 3, for the sample crystallized at a similar temperature, are consistent with a partial melting/recrystallization phenomenon during fusion, the ''two-stage'' type of melting observed by optical microscopy will also be manifested as two DSC peaks. Each of the peaks would be associated with the melting of either the mother or daughter lamellae respectively. The relative intensity of each peak could be related to the relative rate of melting of both types of lamellae. We should recognize that in the study of the melting behavior of isotactic polypropylenes we are not considering the simple classical crystallite lamellar morphology. The unique morphology involved brings up additional considerations. Optical microscopy clearly shows an initial melting of daughter lamellae even after crystallization at relatively low temperatures as shown in Fig. 7. However, some reorganization of these thin crystallites during fusion is also feasible, and the double endotherms could be a consequence of both processes.

Fig. 8 illustrates the results of a similar experiment for the fraction crystallized at 160°C (for ≈1000 min) in the hot stage. The DSC thermogram gives two well defined peaks located at ≈180.4°C and at 185.5°C. The micrograph on the left shows the spherulites grown at 160°C in the hot stage mounted in the microscope. The spherulites display a mixed-type birefringence indicating that both radial and tangential lamellae form the main spherulitic texture. The spherulites were then heated, without previous cooling, and the changes in birefringence recorded and compared with the thermogram. At temperatures ≈170°C the spherulitic texture begins to show changes, in that the radial lamellar structure appears better defined. This observation is consistent with the thermogram. The middle micrograph in Fig. 8 shows the spherulites at 176°C. It is clear that part of the lamellar structure located in the inside of the spherulites has melted, and the radiating morphology becomes more pronounced. At 180°C, a temperature that corresponds to the peak of the low temperature endotherm, the birefringence of the spherulites has definitely changed from mixed to preferentially negative as shown in the micrograph in the far right. This drastic change in the birefringence must be a consequence of the complete melting of tangential lamellae and would correspond to the low temperature endotherm. As the dominant lamellae for this highly regularly-structured, high molecular weight fraction, crystallized at relatively high temperatures, are preferentially oriented in the radial direction (see Fig. 5), the selective melting of the tangential lamellae leaves spherulites with strongly negative birefringence. Increasing temperature the transmitted light intensity decreases. The spherulitic pattern and negative character are preserved almost up to complete melting. The complete melting of the spherulites takes place at about 185°C in complete agreement with the high temperature peak in the thermogram.

The changes in spherulitic structure and birefringence with temperature can be identified with the melting of the two different types of lamellae over the complete range of crystallization temperatures. This finding can be in turn correlated with the two endothermic melting peaks that are observed. At a temperature corresponding to the low temperature endotherm the spherulites become negatively birefringent, and the radiating structure of lamellar bundles become much sharper. This is consistent with the preferential melting of the thinner, tangential daughter lamellae. The higher temperature endotherm can then be associated with the melting of the thicker, well-developed, dominant, radiating lamellae. We have noted that the spherulitic structures are still maintained to very high melting temperatures (183°C–184°C). As the integrity of the spherulite is conserved until the last stage of melting, we conclude, consistent with the above, that the dominant lamellae melt last and are represented by the high temperature endotherm.

As the birefingence studies have demonstrated that the low temperature endotherm corresponds to melting of daughter lamellae and the highest to dominant lamellae, it would be desirable to obtain the fractional content of both type of lamellae from the heat of fusion after deconvolution of DSC peaks. While at crystallization of 136°C, 150°C and 162°C there seem to be a good correlation between the amount of cross-hatching observed in the micrographs and the relative areas of the two peaks, at crystallization of 165°C and 167°C the area in the electron micrographs occupied by the transversal lamellae does not seem to be significantly larger than that of the dominant lamellae. Thus, the determination of the concentration of each type of lamellae directly from the heat of fusion corresponding to each endotherm would not be quantitative. The difficulty in the deconvolution of the DSC peaks of thermograms such as the lowest in Fig. 1 is also a problem in any quantitative analysis.

The observation of a melting endotherm at 186.7°C (see Fig. 1) for the isotactic poly(propylene) fraction studied, which only contains 0.1% of chain structural irregularities and lamellae thicknesses that are less than ≈350 Å, raises the question as to the equilibrium melting temperature, T_m^0, for this polymer. The proper value of T_m^0 has been a controversial matter for many years. Estimates range from 185°C to 210°C [7,23,24,35]. In recent work T_m^0 was estimated to be 186°C for the pure isotactic polymer [36,37]. This value for T_m^0 was based on a study of an unfractionated Ziegler–Natta type poly(propylene) that had an isotactic pentad fraction of only 0.907 and approximately 1% of structural irregularities. Conventional extrapolation methods were used to obtain this estimate of T_m^0 for the polymer that was not completely isotactic. Pertinent to this general problem, and unique to isotactic poly(propylene), is the possible influence that the daughter lamellae might have on the melting of the dominant lamellae. This possibility will be examined in detail in a forthcoming publication [38].

4. Conclusions

The morphological study carried out on a well characterized, isotactic poly(propylene) fraction clearly reveals extensive cross-hatching not only for the samples crystallized at the lowest temperatures, but also in those crystallized at $T_c > 160$°C (corresponding to smaller undercoolings than those previously studied for unfractionated samples). Moreover, the character of the cross-hatching displayed at relatively low crystallizations (130°C–150°C) is quite different than that shown at the highest temperatures. The former follows some of the cross-hatching usually found in the literature with highly woven lamellae of about the same thickness, with occasional groups of long, parallel, radiating lamellae. However, the cross-hatching shown after high temperature crystallization is made of radiating, dominant lamellae that are rather thick, long and well-formed and very thin, daughter lamellae. The transmission electron micrographs indicate a nearly constant angle between daughter and mother lamellae in accord with the molecular and crystallographic predictions [6].

The two melting endotherms observed by differential scanning calorimetry can be correlated with the fusion of these two populations of crystals and is consistent with the observations found by optical microscopy, i.e., a change of birefringence at the melting of the daughter lamellae and disappearance of dominant lamellae at $T > 180$°C.

The thin daughter lamellae shows a small variation in thickness with increasing crystallization temperature (75–100 Å) while the variation of the dominant lamellae is much greater (100–350 Å). Melting temperatures as high as 186.7°C have been directly observed in spite of the relatively thin lamellae observed in these samples.

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