Morphology of different types of isotactic polypropylene spherulites crystallized from melt

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The morphology of melt-grown spherulites of isotactic polypropylene (iPP) has been investigated by use of a polarizing microscope. The low molecular weight iPP, isothermally crystallized at 150–160°C, was found to form new types of spherulites. The spherulites termed types I and II by Keith *et al.*[2] exhibit a simple Maltese cross on a polarizing microscope with crossed polars. However, the new spherulites do not exhibit such a Maltese cross. These spherulites have been named 'pseudo-negative', 'pseudo-positive', 'neo-mixed' and 'flower-like' according to their morphologies, respectively. The structure of iPP spherulites crystallized isothermally at 155°C, does not belong to the α_1-form (C2/c) group but to the α_2-form ($P2_1/c$) group.

(Keywords: polypropylene; spherulites; crystallization; low molecular weight; morphology; polarizing microscope)

INTRODUCTION

Isotactic polypropylene (iPP) has polymorphs of the monoclinic (α)-, the hexagonal (β)-, the triclinic (γ)-crystal forms and the smectic-form[1,2]. The α-form is further classified into two limiting structures by order[3]; a disordered limiting structure (α_1) has a random distribution of up and down chains in each site of the unit cell of the space group C2/c. An ordered limiting structure (α_2) has well defined up and down helices in the $P2_1/c$. The α_1-form is the most widely occurring crystal structure. The α_2-form is derived from the α_1-form by annealing. Padden and Keith classified the spherulites of the iPP into the four distinct types according to morphologies[2]. Type I and II spherulites belong to the α-form and types III and IV, to the β-form. Norton and Keller investigated the morphology of the iPP spherulites, which crystallized in the temperature range 100–150°C, by using a polarizing microscope and a transmission electron microscope[4]. They found that each spherulite type is characterized by the arrangement of its constituent lamellae, i.e. the type I spherulite contains the predominant branching lamellae, so the value of birefringence is positive, while the type II spherulite is composed of the predominant radiating lamellae, so the value of birefringence is negative. On the other hand, Bassett and Olley found that the cross-hatching was present in spherulites grown at 160°C[5].

In this paper, the morphologies of the low molecular weight iPP spherulites, melt-crystallized at high temperature, will be discussed.

EXPERIMENTAL

Materials

The iPP of melt flow index (MFI) 120 g/10 min at 230°C from Tokuyama Soda Co. Ltd was used in this work.

Crystallization

The Kotaki Werks's apparatus consisted of a melt furnace, a crystallization silicone oil bath (controlled within ±0.5°C) and a polarizing microscope. The thin films of the iPP (about 50 μm) were fused between glass cover slips in the furnace at 230°C for 5 min and then rapidly transferred to the crystallization bath, maintained at a selected temperature in the range 150–155°C, until completely crystallized.

Spherulite morphology

The resulting films were examined with the polarizing microscope (Nikon Optiphot–Pol polarizing microscope) with a sensitive tinct plate or a $1/4\,\lambda$ plate.

The value of the birefringence was measured using a Berek compensator.

Spherulite structure

X-ray diffraction measurements were carried out by use of a Jeol JRX-12VB X-ray diffractometer (Ni-filtered Cu Kα, $\lambda = 1.54$ Å), equipped with a Rigaku-Denki microbeam X-ray camera ($\phi = 50\,\mu$m).

Order parameter

The ratio of the peak area $2\theta = 34.4 \sim 36.0°$ and $2\theta = 36.4 \sim 38.0°$ in X-ray diffraction patterns was used as an index of the degree of ordering[3]. Both melting point and heat of fusion were measured by use of the Mettler TA-3000 system, DSC-30.

RESULTS AND DISCUSSION

Spherulitic morphologies

Figure 1a illustrates the several types of the iPP spherulites crystallized isothermally at 155°C from the melt. The sign of the birefringence of these spherulites was determined by use of a sensitive tinct plate or with a $1/4\,\lambda$

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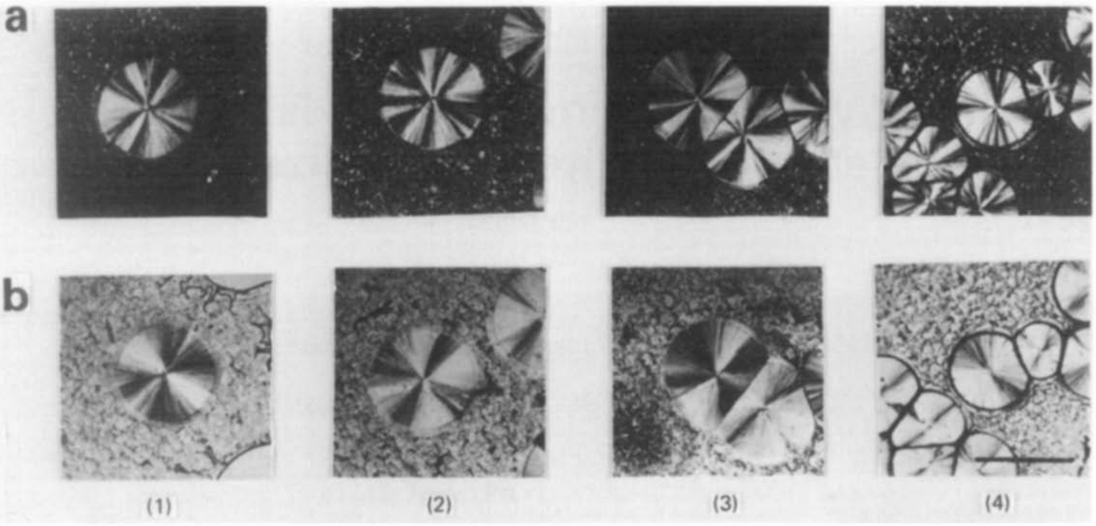

Figure 1 Spherulites of low molecular weight isotactic polypropylene (MFI 120 g/10 min), crystallized isothermally at 155°C from the melt. (a) Crossed polars, and (b) crossed polars with a $1/4\lambda$ plate. (1) Pseudo-negative, (2) neo-mixed, (3) pseudo-positive, (4) high temperature positive spherulites. Scale bar = $200\,\mu$m

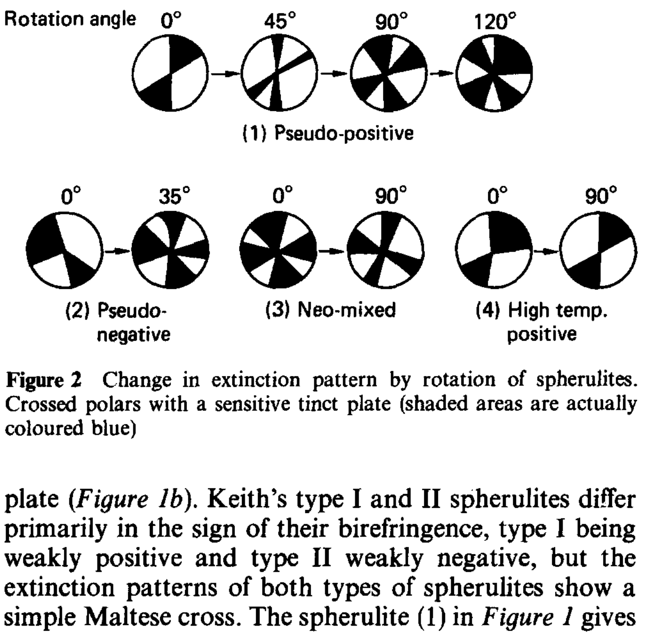

Figure 2 Change in extinction pattern by rotation of spherulites. Crossed polars with a sensitive tinct plate (shaded areas are actually coloured blue)

plate (*Figure 1b*). Keith's type I and II spherulites differ primarily in the sign of their birefringence, type I being weakly positive and type II weakly negative, but the extinction patterns of both types of spherulites show a simple Maltese cross. The spherulite (1) in *Figure 1* gives negative birefringence, and its extinction pattern between crossed polars exhibits several dark lines, which radiate from the centre of the spherulite, without showing a clear Maltese cross (*Figure 1a*). Therefore, spherulite (1) is distinguished from type II, and is defined as a 'pseudo-negative' spherulite. The birefringence value of this spherulite is estimated -0.005 to -0.008, but in some instances is -0.002 to -0.004 at the periphery of the spherulite. The spherulite (3) gives positive birefringence, and its extinction pattern is similar to the pseudo-negative one. Therefore, spherulite (3) is distinguished from type I, and is defined as a 'pseudo-positive' spherulite, the birefringence value of which is about 0.002. Spherulite (2) exhibits a dark, X-shaped pattern in crossed polars with a $1/4\lambda$ plate (*Figure 1b*), which is different from Keith's 'mixed' type, having random distributions of positively and negatively birefringent regions. Moreover, its extinction pattern is similar to the pseudo-negative and the pseudo-positive ones (*Figure 1a*). The sign of the birefringence of this spherulite cannot be determined, so spherulite (2) is defined as a 'neo-mixed' spherulite. Spherulite (4) gives positive birefringence, and its extinction pattern exhibits the same Maltese cross as Keith's type I. However, its structure (the detailed structure will be mentioned later) is distinguished from Keith's type I, and it is named as a 'high temperature positive' spherulite, the birefringence value of which is about 0.002 to 0.003.

Figure 2 shows the change of the birefringence of these spherulites observed by rotating the sample on the stage of the microscope under crossed polars with the sensitive tinct plate. While the overall appearance of the spherulites of types I and II does not change by rotation of the stage, i.e. with respect to the polarizer and analyser direction, the pseudo-negative and positive spherulites change to the similar pattern of the neo-mixed spherulite by rotation. Therefore, their structures seems to be very similar.

The extinction pattern of the high temperature positive spherulite does not change by rotation.

Other spherulites of the iPP, crystallized at 150°C from the melt, are shown in *Figure 3*. They are defined as 'flower-like' spherulites. In *Figure 3*, the Maltese cross of spherulite (3) takes the shape of ∞. The sign of the birefringence of the other flower-like spherulites shown in (1) and (2) changes from negative to positive towards the edge of the spherulite. The monoclinic spherulites of the iPP show a cross-hatched pattern, which is due to structures composed of mainly radiating lamellae and tangential branching lamellae, and the positive and negative spherulites should be distinguished by the presence and/or degree of cross-hatch[4].

Therefore, change of the birefringence of (1) and (2) in *Figure 3* reflects the increase of density of cross-hatching in the outer regions. Bassett gave the following two assumptions for the phenomena[6]: that there was crystallization on cooling within the framework of dominant radial lamellae formed at 150°C, and the alternative explanation that the increased cross-hatching is a consequence of changing molecular parameters (e.g. tacticity, molecular weight etc.). The behaviour of crystal growth was examined to elucidate the formation of the flower-like spherulite as shown in *Figure 4*.

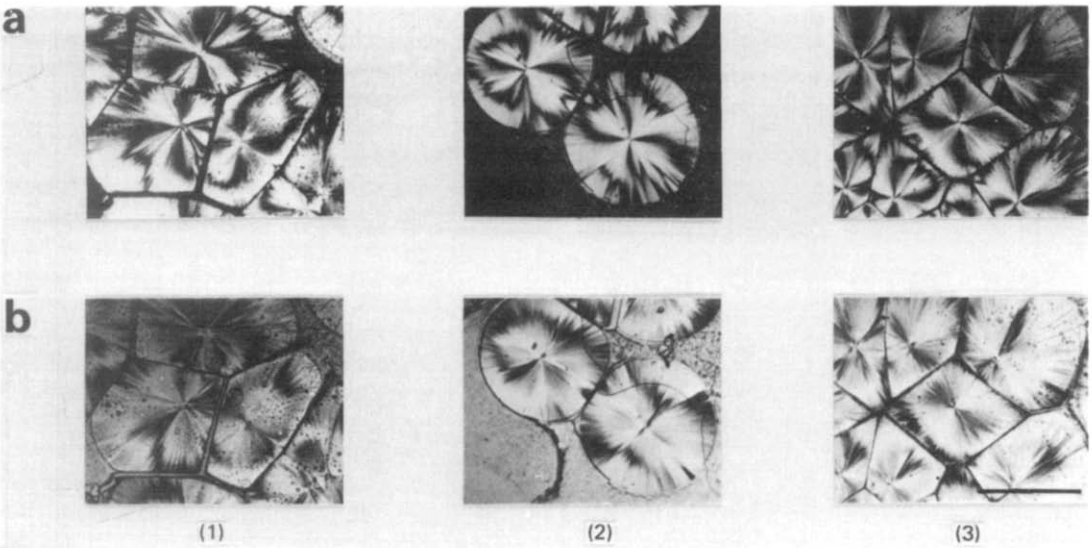

Figure 3 New spherulites of low molecular weight isotactic polypropylene, melt-crystallized at 150°C (flower-like). MFI 120 g/10 min. (a) Crossed polars, and (b) crossed polars with a 1/4 λ plate. Scale bar = 200 μm

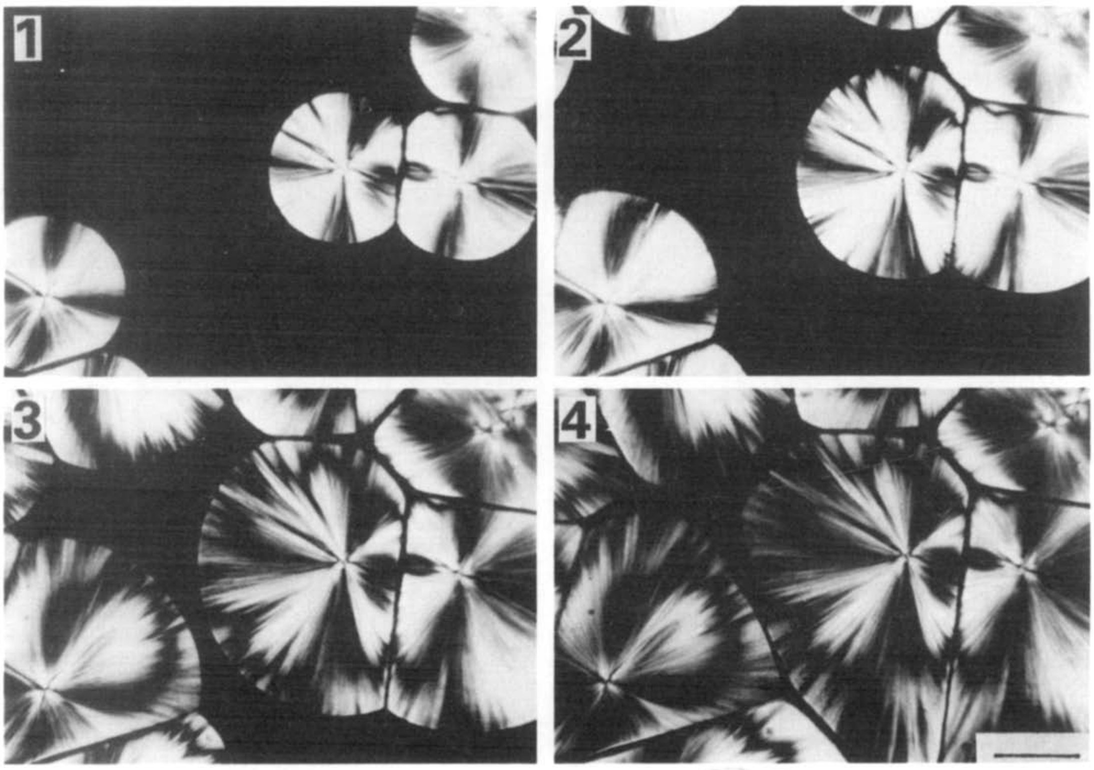

Figure 4 Crystal growth of low molecular weight isotactic polypropylene, melt crystallized at 150°C. MFI 120 g/10 min. (1) 21.2 h, (2) 31.8 h, (3) 46.0 h, (4) 70.0 h. Scale bar = 200 μm

A part of the Maltese cross type spherulites changes to the 'shape of ∞' or the neo-mixed type spherulite after 30 h. Moreover, after 40 h from onset of melt crystallization, the flower-like spherulites shown in (1) or (3) of *Figure 3* dominate in the specimen. The flower-like spherulites occur during spherulite growth, and they do not appear with the higher molecular weight iPP (e.g. MFI 0.1–20 g/10 min). The appearance of radial cracks in the outer (positive birefringent) regions of the flower-like spherulites would suggest the predominance of lower molecular weight PP in these regions. Therefore, the latter explanation should be plausible.

Spherulite structure

Figure 5 shows an X-ray diffraction pattern of the selected position of the iPP spherulite crystallized at 150–155°C. The pattern of the pseudo-negative spherulite is shown in (1) in *Figure 5*. Both (2) and (3) also show a similar pattern to (1). The pseudo-negative, neo-mixed and pseudo-positive spherulites have mixed orientation for the a*- and c-axes. The (0 4 0) reflection of the a*-axis oriented crystals and the (1 1 0) reflection of the c-axis oriented crystals do not exist on the same equator as shown in *Figure 5(1)*. *Figure 5(4)* shows the diffraction pattern of the high temperature positive spherulite. It has

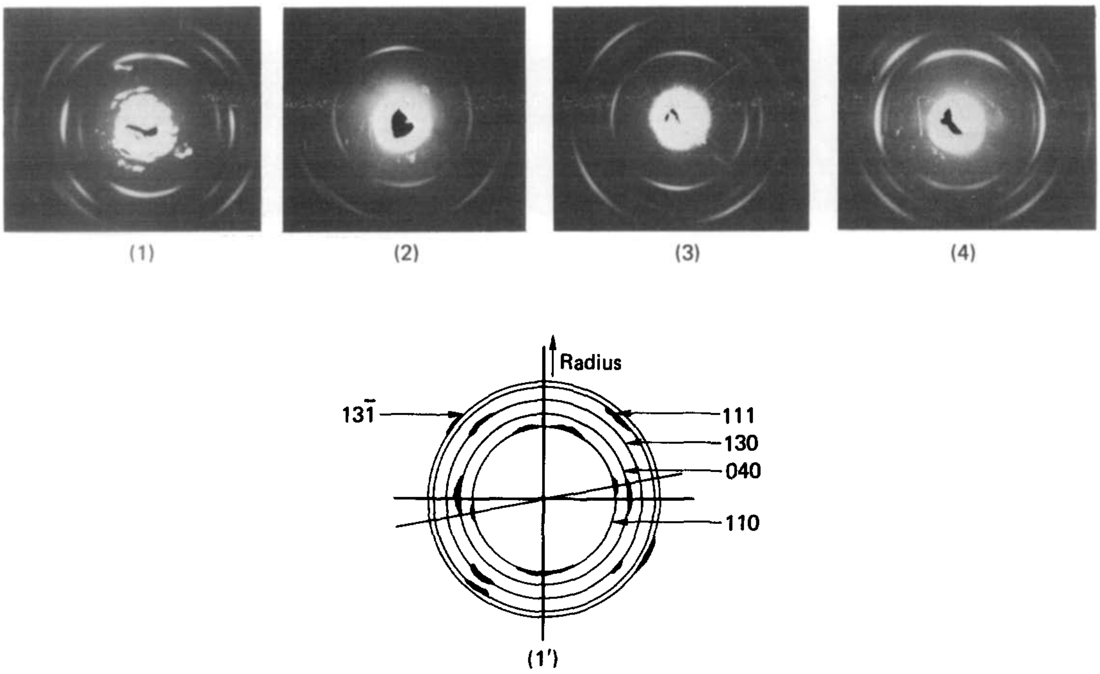

Figure 5 Microbeam X-ray diffraction patterns of different kinds of spherulites, grown at 155°C. (1) Pseudo-negative, (2) neo-mixed, (3) pseudo-positive, (4) high temperature positive spherulites. (1') Schematic drawing of (1)

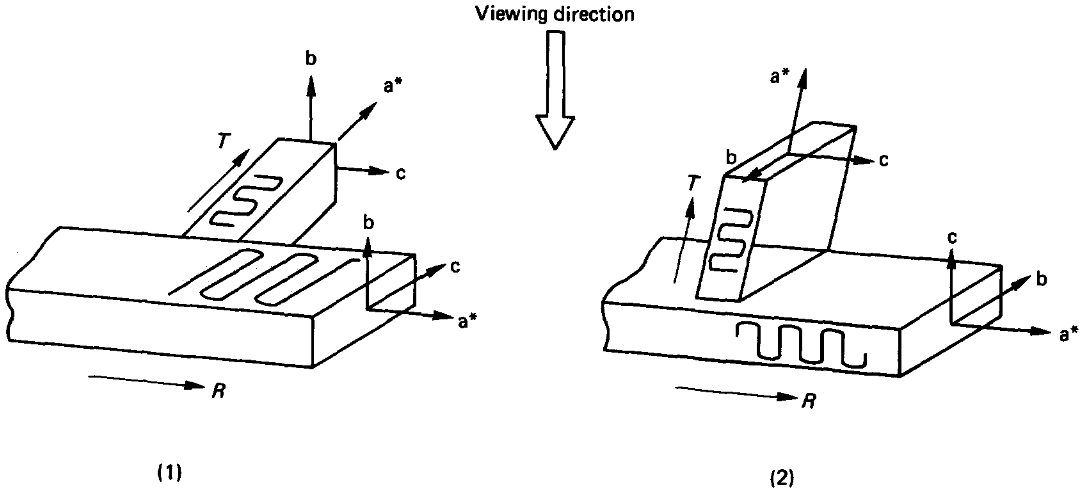

Figure 6 Schematic representation of spherulites structure. (1) Regular type, and (2) high temperature positive. R = spherulite radial direction, and T = tangential direction

the a*-axis in uni-orientation along the radius of the spherulite.

The lamellae in the spherulites are oriented either radially or approximately tangentially as illustrated in *Figure 6(1)*. The fraction of the radial lamellae is denoted by r and that of the tangential lamellae is denoted by t, the sum $(r + t)$ should be unity. The radial refractive index is approximately:

$$n_r - rn_{a*} + tn_c \qquad (1)$$

and the tangential one

$$n_t = tn_{a*} + rn_c \qquad (2)$$

so that the birefringence is

$$\Delta n = n_r - n_t = r(n_{a*} - n_c) + t(n_c - n_{a*}) \qquad (3)$$

where n_{a*}, n_b and n_c are the principal refractive indices of the α-form along the reciprocal axis a*, the b axis and the c axis, respectively. When the lamellae show only the radial a*-orientation, the fraction t is free. Then, such a spherulite must be positive birefringent.

$$\Delta n = n_{a*} - n_c < 0 \qquad (4)$$

Here

$$n_{a*} = 1.5067,$$
$$n_b = 1.5070,$$
$$n_c = 1.5419 \quad \text{(ref. 7)} \qquad (5)$$

The lamellae in the high temperature positive spherulites show only the radial a*-orientation (*Figure 5(4)*). However, it seems to be impossible that the birefringence of these spherulites is positive. Bassett[6] assumed that the radial lamellae have their c-axes effectively parallel to the viewing direction (*Figure 6(2)*). The c-axes in a few branching lamellae (cross-hatching lamellae) are near-

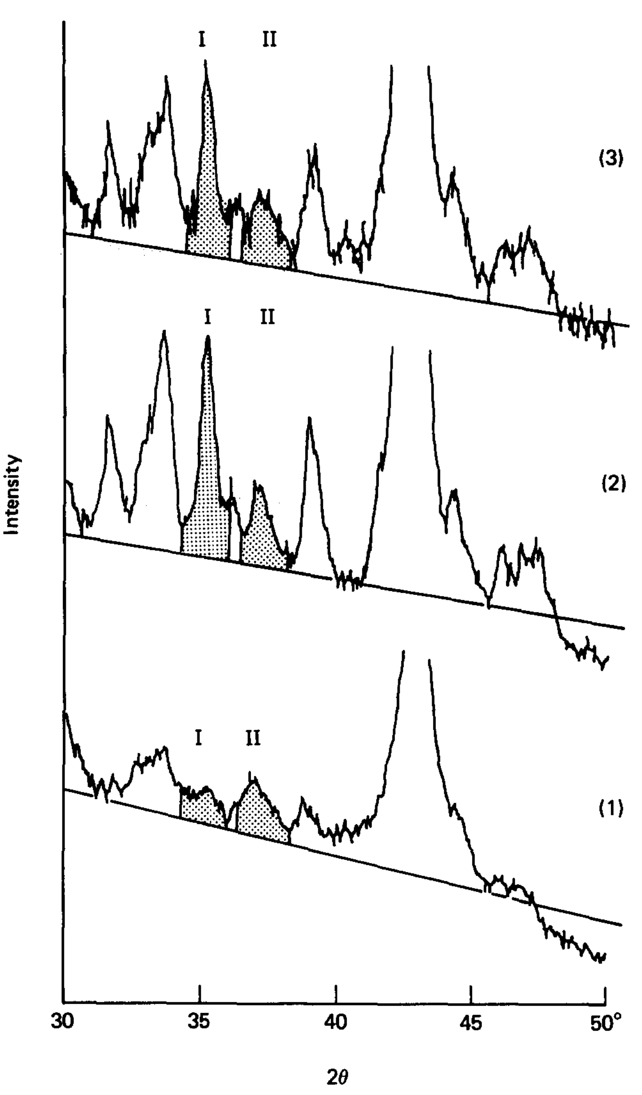

Figure 7 X-ray diffraction patterns of specimens. (1) Quenched from melt to room temperature (33°C). (2) Subsequently annealed of (1) at 160°C for 51 h. (3) Crystallized isothermally at 155°C for 70 h

Table 1 Dependence of order parameter (R) and thermal properties of iPP on thermal history

Thermal history	R	T_m (°C)	ΔH (J g^{-1})
Cooled from melt by constant rate ($-10\,\mathrm{K\,min^{-1}}$)	0.63	156.3	107
Quenched from melt	0.62	161.7	103
to 33°C	0.66	161.7	101
Annealed of above sample			
160°C for 51 h	2.02	168.8	123
155°C for 29 h	2.03	167.2	124
Isothermally crystallized			
155°C for 55 h	1.98	174.8	125
155°C for 70 h	1.95	171.9	121

PP: MFI 120 g/10 min at 230°C
D.s.c. scan: 10°C min^{-1}

radial in projection. Then,

$$n_r = rn_{a*} + tn_c \tag{6}$$

$$n_t = rn_b + tn_b = n_b \tag{7}$$

$$\Delta n = n_r - n_t = r(n_{a*} - n_b) + t(n_c - n_b) \tag{8}$$

Here,

$$(n_{a*} - n_b) \fallingdotseq 0, \qquad (n_c - n_b) > 0 \tag{9}$$

Therefore, even if the fraction of the branching lamellae exist, the birefringence exhibits a slightly positive value.

Order parameter

The X-ray diffraction patterns of the specimens with different thermal histories are shown in *Figure 7*. The order parameter R is shown in *Table 1*. Peak I, between $2\theta = 34.4°$ and 36.0°, has contributions from the reflections (1 7 1), (1 3 2) (with $h + k$ even) and (2 3 1), (0 5 2) (with $h + k$ odd), while peak II, between $2\theta = 36.4°$ and 38.0°, has contributions from the reflections (2 4 1) and (1 7 1). As for the α_1 form, only reflections with $(h + k)$ even are allowed[1]. However, as for the α_2-form, reflections with $(h + k)$ odd may also be

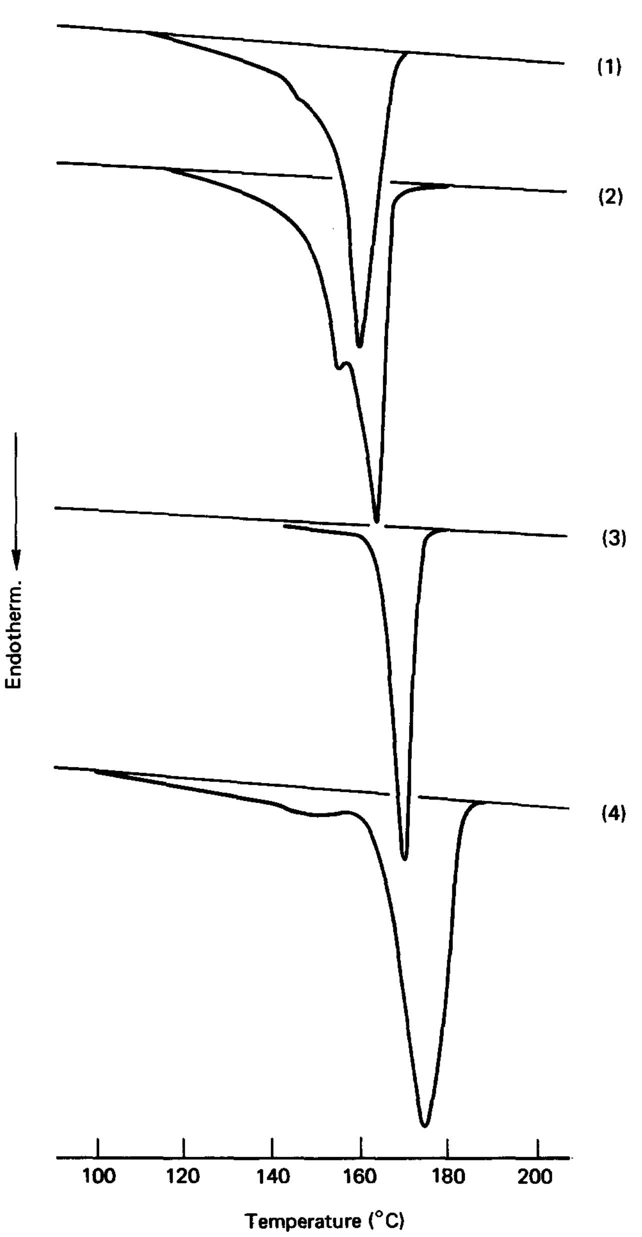

Figure 8 D.s.c. diagrams of specimens. Heating rate: 10 K min^{-1}. (1) Cooled from melt at constant rate ($-10\,\mathrm{K\,min^{-1}}$). (2) Quenched from melt to room temperature (33°C). (3) Subsequently annealed of (2) at 160°C for 51 h. (4) Crystallized isothermally at 155°C for 70 h

present, generally with lower intensity[8]. Corradini *et al.* observed that the order parameter R, the ratio of I to II, nearly reaches two for most ordered samples, which indicates the samples are closer to the limiting α_2-form. On the other hand, they observed that the most disordered samples show $R=0.5$, which suggests the closer limiting α_1-form. As the parameter R of the sample, melt-crystallized at 155°C, is about two, the sample should be mainly the α_2-form. The d.s.c. diagrams of the specimens with different thermal histories are shown in *Figure 8*. The melting point (T_m) and the melting heat (ΔH) of these samples are shown in *Table 1*. The samples, melt-crystallized at 155°C, have high T_m and ΔH, and they seem to be closer to the α_2-form.

CONCLUSIONS

(1) The spherulites of the low molecular weight iPP (i.e. MFI 120 g/10 min) melt-crystallized at above 150°C show a large variety of morphologies which do not belong to Keith's classification.

(2) When the crystallization takes place over 40 h at about 150°C, flower-like spherulites are formed from part of the Maltese cross spherulites. The inner regions of this spherulite show negative birefringence, whilst the outer regions show positive birefringence.

(3) The pseudo-positive, pseudo-negative, neo-mixed and high temperature positive spherulites are found in the iPP spherulites, melt-crystallized at about 155°C. The extinction patterns of these spherulites between crossed polars do not exhibit a simple Maltese cross.

(4) The spherulites termed types I and II by Keith *et al.* do not change in overall appearance by rotation of the specimen, when observed under cross polars with the sensitive tinct plate. However, both the pseudo-positive and pseudo-negative spherulites show a similar pattern to the neo-mixed spherulite on rotation. These patterns are due to structures composed of mainly radiating lamellae and tangential branching lamellae.

(5) The morphology of the high temperature positive spherulite is very similar to type I. However, the X-ray diffraction pattern of this spherulite shows a radiated uni-orientation.

(6) The spherulites, melt crystallized at high temperature (i.e. 155°C), are closer to the limiting α_2-structure.

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