Microvoid formation process during the plastic deformation of β-form polypropylene

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The microvoid formation process that takes place during the plastic deformation of β-form polypropylene (PP) was investigated at different crystallization and drawing temperatures. It was found that the porosity increased with both a higher crystallization temperature and a lower drawing temperature. This fact could be understood in terms of the stability of the β crystals of the original film. The more stable β crystals that formed at a higher crystallization temperature had a lower molecular chain mobility and thus hindered the bulk contraction of the film, while at the same time the volume contraction caused by either a β–α or a β–smectic transformation inside the film enlarged the microvoids at the end, or between the microfibrils.

(Keywords: β-form polypropylene; microvoid; phase transformation)

INTRODUCTION

It is known that the β form of polypropylene (PP) can be obtained by melt crystallization of isotactic PP in the presence of a β nucleator. The metastable β-form crystals transform into α-form crystals during heating and deformation. Turner-Jones *et al.*[1] first reported that *c*-axis oriented β crystals cannot be obtained by drawing β-form PP because they convert to *c*-axis oriented α crystals during the deformation process. Fujiwara and coworkers[2–4] provided further evidence concerning this point by studying the deformation behaviour of the β-form PP produced by crystallizing the polymer melt in a temperature gradient. Moreover, the work of Shi *et al.* revealed that the β-form crystals transform into a smectic form at a drawing temperature below 80°C, but transform to the more stable α form at higher temperatures[5]. This phase transformation is a progressive process. The β crystals that are parallel to the tensile axis undergo the β–α or β–smectic transformation more easily than those at a tilt angle to the tensile axis.

On the other hand, all of the β-form PP specimens have been known to become opaque when they were stretched below 120–130°C[5], while the α-form specimens are partially opaque at lower drawing temperatures. This phenomenon was proved to be induced by microvoid formation, which is caused by a volume contraction during the β–α or β–smectic transformation. It was also reported[6] that similar microvoids are formed in various spinning and drawing processes of β-PP fibres and that the moisture absorption of the fibres is improved. Such microporous materials obtained by the plastic deformation of β-PP are therefore expected to be useful as membranes and other functional materials, and the mechanism of the microvoid formation and the bulk and surface properties of the drawn samples seems to be of great interest.

The purpose of this present study is to learn more about the changes in porosity, surface structure, and microporous morphology that occur during deformation of β-form PP films which were crystallized and drawn at different temperature, by which it is hoped the mechanism of microvoid formation may be clarified.

EXPERIMENTAL

Materials

Polypropylene pellets (melt index = 14), blended with 0.1 wt% of a newly developed β nucleator (NJSTAR) were supplied by the New Japan Chemical Co. Ltd (Kyoto)[7]. The pellets were placed between two aluminium plates and pressed at 200°C under a pressure of 2×10^7 Pa (200 kg cm^{-2}). The pressed sample (plus the aluminum plates) was then cooled in air, or quenched by a cold press that had been set at a predetermined crystallization temperature of 20, 50, 70 or 110°C, for 5, 10, 25 or 40 min, respectively. The β-PP films thus obtained had a thickness of 0.2 mm and a relative β-form content greater than 90%, as calculated by the *K* value.

Measurements

Scanning electron microscopy (SEM) studies were carried out by using a Jsm-25SII microscope or a Jsm 840 microscope. Wide-angle X-ray diffraction (WAXD) was measured on an X-ray diffractometer with a Rigaku 4036-A1 X-ray generator and a Rigaku PMG-A2 goniometer, while d.s.c. measurements were made on a Mac Science DSC 3100 thermal analyser.

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Porosity

Concerning the fact that liquid oil can penetrate the microvoids in the PP films, the porosity of the film is given as follows:

$$\varepsilon=\frac{W_s-W_d}{AL\rho}$$

where W_s and W_d are the weights of the film saturated with oil, and the dry film, respectively, and A, L, and ρ are the area and thickness of the film, and the density of the oil, respectively. The oil used in this work is salad oil ($\rho=0.925\ \mathrm{g\,cm^{-3}}$).

RESULTS AND DISCUSSION

Structure characterization of β-form PP

Since the β nucleator used in this experiment was so effective, β crystals could be generated even when the melting film was quenched at a temperature lower than 10°C. Therefore, PP films with different crystalline states were prepared by changing the crystallization temperature over the range from 10 to 110°C. The structure parameters of the β-form PP films obtained are summarized in *Table 1*. The K value (see table) is defined by the following equation:

$$K=\frac{H_{(300)}}{H_{(300)}+H_{(110)}+H_{(040)}+H_{(130)}}$$

This is usually used to describe the relative β-crystal content, where $H_{(hkl)}$ denotes the diffraction intensity of the (hkl) lattice plane of α and β crystals. As shown in *Table 1*, the K value of each β-form PP film reached as high as 90%, regardless of the crystallization temperature. This indicates that the relative β-form content was hardly affected by the crystallization temperature or cooling rate.

The degree of order of the molecular chain packing in the β-crystal lattice is represented by the S value, which is given by $H_{(301)}/(H_{(300)}+H_{(301)})$[8]. The (300) lattice plane is parallel to the molecular chain direction, and the (301) plane intersects the plane of the chain. Therefore, the ratio of their diffraction intensities represents the degree of order of the molecular chains packed in the direction perpendicular to the c-axis. *Table 1* gives closely similar S values for all of the specimen prepared at different temperatures, which suggests that the β crystals formed at lower temperatures have a similar order to those formed at higher temperatures, in terms of the crystal lattice.

Using Scherrer's equation, we calculated the crystallite dimensions in the directions perpendicular to the (300) and (301) planes, denoted by $t_{(300)}$ and $t_{(301)}$, respectively. The data in *Table 1* show no striking difference (within 8 Å) in the $t_{(300)}$ values among the films crystallized at different temperatures, but large differences in the $t_{(301)}$ values, which reached as high as 34 Å, with an increasing crystallization temperature from 10 to 110°C. This result can be explained as follows: when the film was crystallized at low temperatures, the molecular chain was 'frozen' quickly, and chains could only then array parallel within limited dimensions in the direction of the c-axis, although the molecular chains were able to fold well to grow lamellae and crystallites. In contrast, in the film crystallized at high temperatures, the crystallites grow so slowly that parallel chains could pack together over a longer distance, thus increasing the dimensions of the crystallites along the c-axis direction.

Table 1 Effect of crystallization temperature (T_{cr}) on the structure parameters of the β-PP films

T_{cr} (°C)	K^a	S^a	Crystal size (Å) $t_{(300)}$	$t_{(301)}$	Crystallinity (%) X_β	X_α	X_a
10	0.87	0.13	182	118	45	6.7	48
50	0.90	0.13	182	120	49	5.2	45
70	0.90	0.13	185	127	53	6.1	41
110	0.91	0.14	190	152	56	7.1	37

[a] See text for definition

The crystallinities of the α-form (X_α) and the β form (X_β) of PP can be expressed in terms of a 'conditional crystallinity'[8] as follows:

$$X_\alpha=\frac{A_{(110)}+A_{(040)}+A_{(130)}}{A_{(300)}+A_{(110)}+A_{(040)}+A_{(130)}+A_a}$$

and

$$X_\beta=\frac{A_{(300)}}{A_{(300)}+A_{(110)}+A_{(040)}+A_{(130)}+A_a}$$

where $A_{(hkl)}$ denotes the diffraction intensity of the (hkl) plane. From these equations, the amount of amorphous phase (X_a) is obtained by the expression $(1-X_\alpha-X_\beta)$. As shown in *Table 1*, the β crystallinity slightly increases with an increasing crystallization temperature, while the α crystallinity remains constant.

The sample prepared by arbitrary cooling in air was much different from the sample crystallized at 10°C because the cooling rate was very slow. We found that its structure parameters are almost identical with those of the film crystallized at 110°C. According to the former report, a decrease in the cooling rate has the same effect as an increase in the crystallization temperature[9]. Therefore, we can postulate that the β crystals of the air-cooled sample are as stable as those formed at high temperatures.

Porosity of uniaxially drawn films with free width

The porosities of the uniaxially drawn films were measured by swelling them with salad oil. It was found that the drawing temperature had an important effect on the porosity, especially for the samples crystallized at lower temperatures. *Table 2* demonstrates the relationship between the porosity and the drawing temperature for films prepared at various crystallization temperatures, and drawn uniaxially, with free width, in a ratio of 3.8. It is noted that the porosity decreases with increasing drawing temperature. At the same drawing temperature, it was found that the higher the crystallization temperature, then the higher was the porosity. There is a tendency for the drawing temperature at which the porosity becomes zero to be higher for the films crystallized at higher temperatures than for those crystallized at low temperatures. Although the film crystallized at 10°C became opaque after drawing, its porosity was zero even when the drawing temperature was lowered to 50°C. The film crystallized at 70°C did not become opaque when it was drawn at 130°C, and its porosity reached zero. The film crystallized at 110°C behaved in the same way at a drawing temperature of 150°C.

Scanning electron micrographs of the films drawn

Table 2 Porosity of the β-PP films drawn uniaxially with free width, at a drawing ratio of 3.8

T_{cr}[a] (°C)	T_{dr}[b] (°C)	Porosity (%)	Colour[c]	
			Drawn film	Oil-swollen film
10	50	0	O	O
	90	0	O	O
	110	0	T	T
70	50	13.7	O	T
	70	14.0	O	T
	90	2.95	O	O/T
	110	1.17	O	O
	130	0	T	T
110	50	39.2	O	T
	70	35.1	O	T
	90	27.4	O	T
	110	14.6	O	T
	130	1.5	O	O
	150	0	T	T

[a] Crystallization temperature
[b] Drawing temperature
[c] O, opaque; T, translucent

uniaxially, with free width, are shown in *Figure 1*. It can be seen that the surface of the film consists of bundles of microfibrils. Along the drawing direction in which the microfibrils align, large voids (size ~3 × 20 μm) are displayed. In the sample drawn at a higher ratio, the bundles of microfibrils are packed more closely, with the voids being thinner.

Porosity of uniaxially drawn films with constant width

In order to increase the porosity of the drawn films by hindering the microfibril packing, the β-PP films were drawn uniaxially with a constant width. *Table 3* shows the changes in porosity of the drawn films with different drawing temperatures for β-PP films crystallized at 10 and 110°C. Compared with the results obtained for the films drawn uniaxially with free width, the porosities of these films are much higher.

Figure 2 shows the variation of porosity with drawing ratio when the film crystallized at 110°C was drawn at 110°C. It is known that the porosity increased with increasing drawing ratio, but the increase levelled off

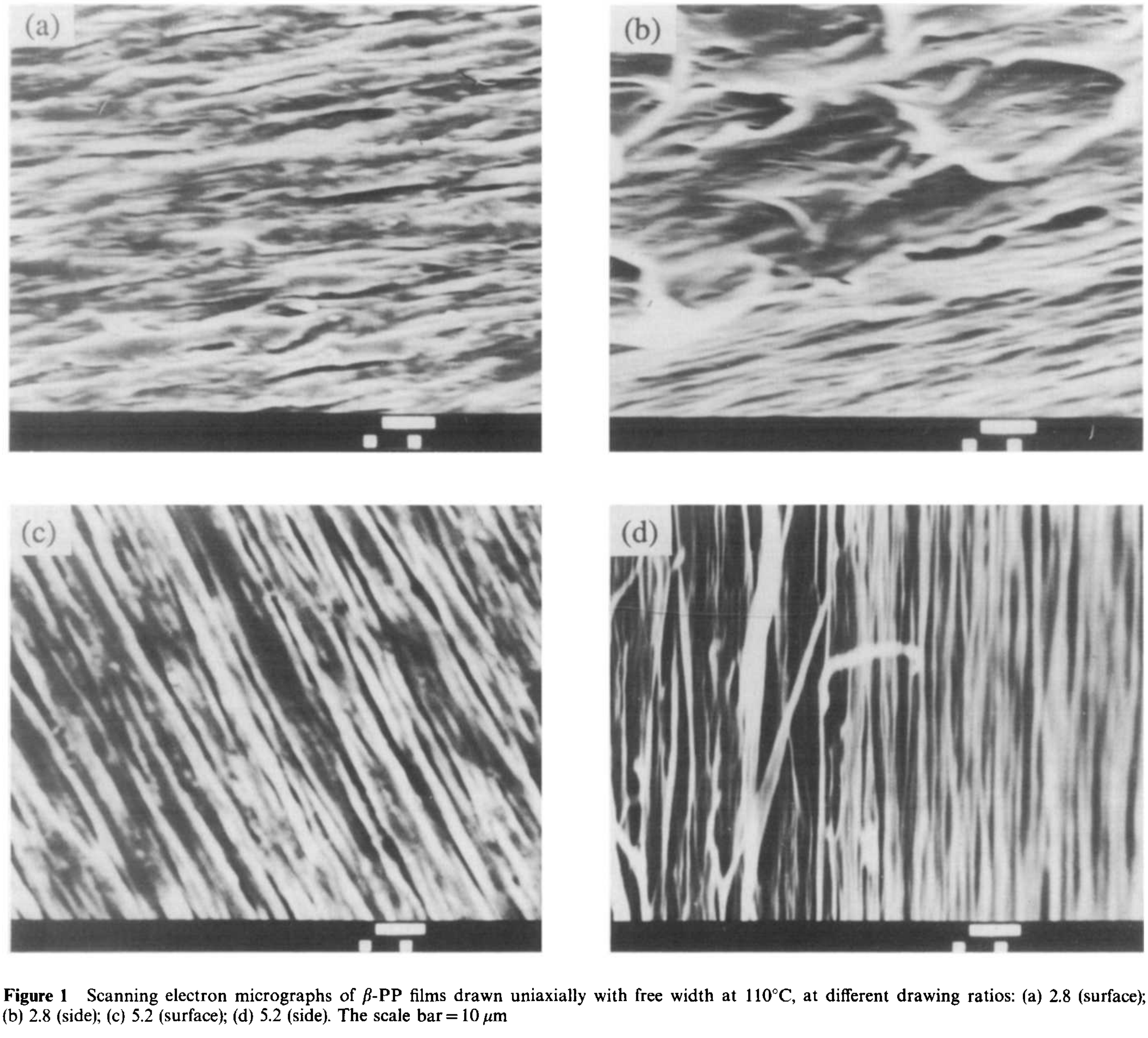

Figure 1 Scanning electron micrographs of β-PP films drawn uniaxially with free width at 110°C, at different drawing ratios: (a) 2.8 (surface); (b) 2.8 (side); (c) 5.2 (surface); (d) 5.2 (side). The scale bar = 10 μm

when the drawing ratio was larger than 2.5. This result indicated that most of the pores are formed in the early stages of deformation.

Scanning electron micrographs of the drawn film are compared in *Figure 3*. The film crystallized at 110°C and drawn at 130°C (*Figure 3b*) showed the existence of many microvoids between the microfibrils formed by the drawing process. The voids are ~0.1 μm in width and 1 μm in length and are distributed between the bundles of microfibrils along the stretching direction. It is also observed that the microfibrils crosslink with each other around the voids. The film crystallized at 10°C and drawn at 130°C has only a very few pores, these being distributed sporadically over the surface (as shown in *Figure 3a*). This structure is similar to that of a drawn film of α-PP. It is therefore deduced that in the later stages of deformation, where the porosity reached the highest value, the microfibrils are packed more densely in order to decrease the pore size and also compete with the formation of new pores.

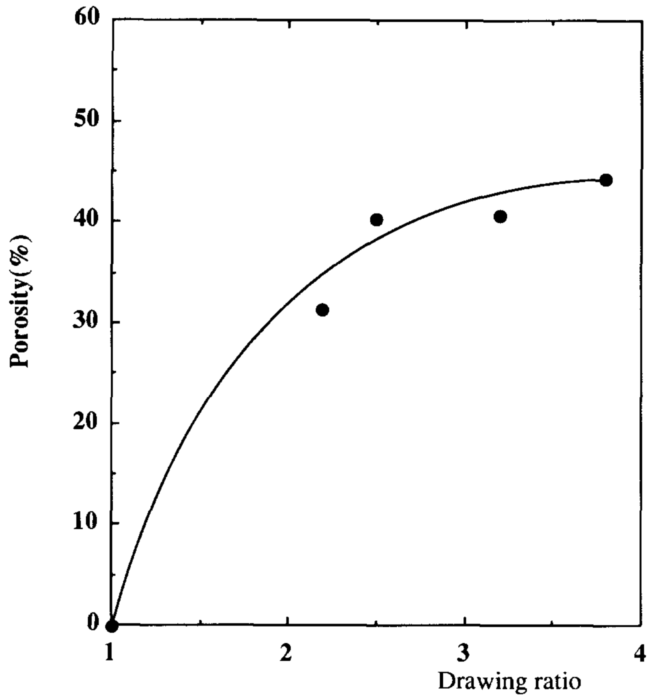

Figure 2 Variation of porosity with drawing ratio for the β-PP films (T_{cr} = 110°C) drawn uniaxially with constant width at 110°C

Porosity of biaxially drawn films

Biaxial drawing of the films crystallized at 10, 50, and 70°C was difficult because of the occurrence of necking, while that of the films crystallized at 110°C and cooled in air was successfully performed at relatively higher drawing temperatures. For this case, typical results for the films cooled in air are shown in *Table 4*. These data indicate that the porosity of the biaxially drawn films increases with an increasing drawing ratio. The film stretched at a drawing ratio of 1.7 × 1.9 has a very high porosity of 39%, which is close to the value obtained for hollow fibres of commercially available extra corporeal membrane oxygenator (ECMO)[10]. When the drawing ratio exceeded 1.7 × 1.9, the porosity showed no further increase.

The microvoid appearances of the biaxially drawn films are shown in *Figure 4*. It is confirmed that the quantity and dimensions of the microvoids increase with the drawing ratio. The specimen with a drawing ratio of 1.9 × 2.0 showed the most homogeneous pore distribution. In the specimen with a drawing ratio of 2.7 × 2.4, some pores became larger as a result of excessive stretching.

Microvoid formation process during drawing

The drawing of ordinary polyolefin specimens, such as α-form PP and polyethylene, usually involves a necking

Table 3 Effect of drawing temperature on the porosity of β-PP samples drawn uniaxially with constant width

T_{cr} (°C)[a]	Drawing ratio	T_{dr}[b] (°C)	Porosity (%)
10	2.5	90	22.3
		110	16.9
		130	2.16
		150	0
110	2.8	110	30.3
		130	30.8
		150	22.4

[a] Crystallization temperature
[b] Drawing temperature

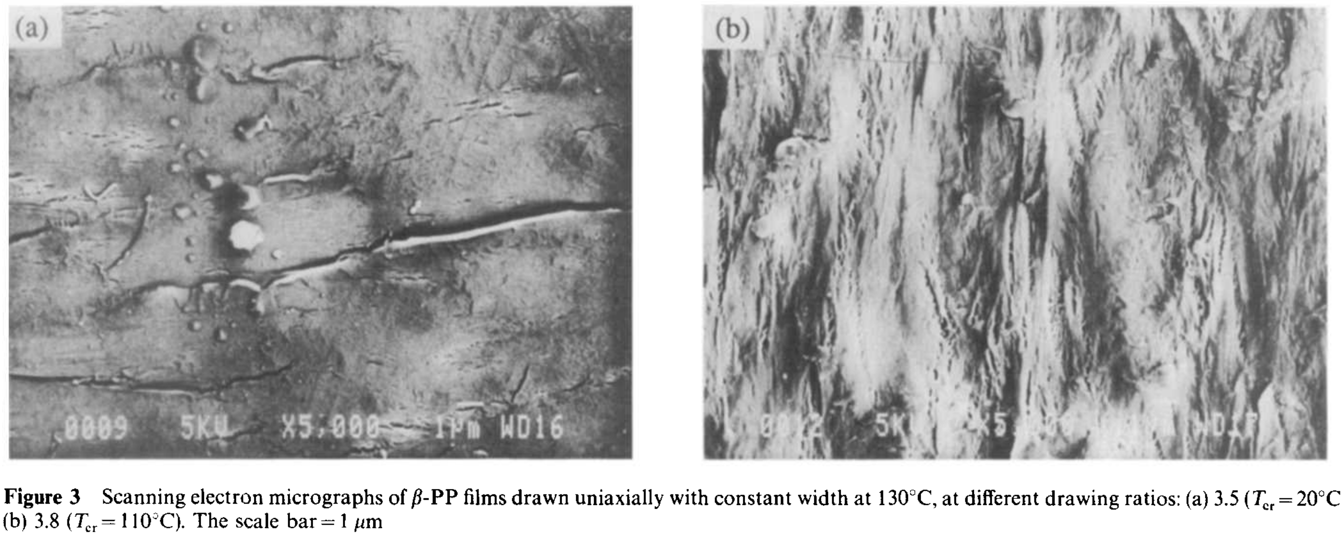

Figure 3 Scanning electron micrographs of β-PP films drawn uniaxially with constant width at 130°C, at different drawing ratios: (a) 3.5 (T_{cr} = 20°C); (b) 3.8 (T_{cr} = 110°C). The scale bar = 1 μm

process in which the stretched region must have a volume contraction corresponding to the increase in density resulting from crystallization and a denser packing of the microfibrils. We found that the β-PP films had a more homogeneous deformation, without any obvious necking formation during the drawing. As reported in the literature[5], the β crystals transform into α crystals when the β-PP specimen is drawn at temperatures higher than 80°C. Because the crystal density of the β form (0.921 g cm^{-3}) is lower than that of the α form (0.936 g cm^{-3}), phase transformation would accompany the volume contraction, a feature which has been considered to be the cause of microvoid formation[5]. However, the reason why the β-PP films crystallized and drawn at different temperatures, gave different porosities cannot be explained only by this β–α phase transformation. To discuss this question, the process of the β–α phase transformation was studied in detail.

Table 4 Effect of drawing ratio on the porosity of β-PP films[a] drawn biaxially at 125°C

Drawing ratio	Porosity (%)
1.1 × 1.4	16.1
1.3 × 1.5	23.6
1.7 × 1.9	39.3
2.0 × 2.1	38.1
2.8 × 2.6	39.0

[a] The original films were prepared by cooling in air

Figure 5 shows the typical changes in thickness and bulk volume of the film as a function of the drawing ratio for the β-PP films drawn uniaxially (with free width) at 110°C. It is known that the film crystallized at 110°C showed less decrease in thickness than the films crystallized at 10°C. The latter film displayed an obvious necking process when drawn at high temperatures, and

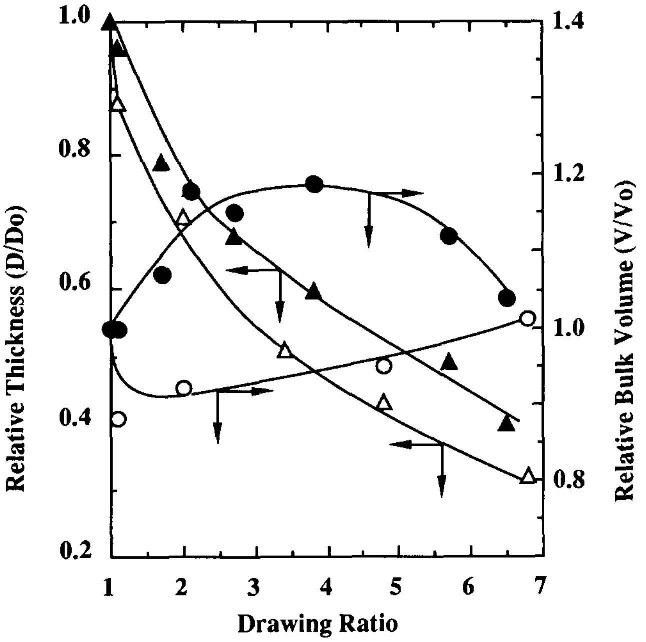

Figure 5 Variation of thickness and bulk volume of the β-PP films drawn uniaxially with free width at 110°C as a function of the drawing ratio. The original films were prepared at 10°C (△, ▲) and 110°C (○, ●)

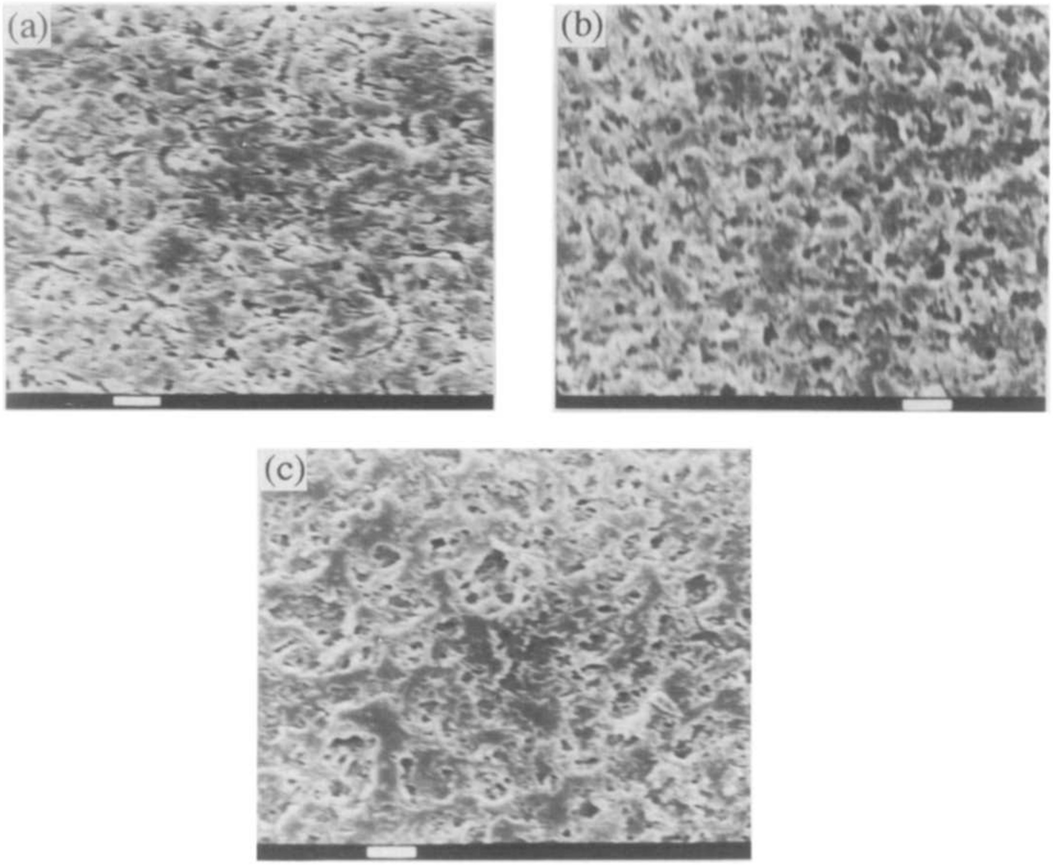

Figure 4 Scanning electron micrographs of β-PP films drawn biaxially at 125°C, at different drawing ratios: (a) 1.3 × 1.3; (b) 2.0 × 1.9; (c) 2.7 × 2.4. The scale bar = 10 μm

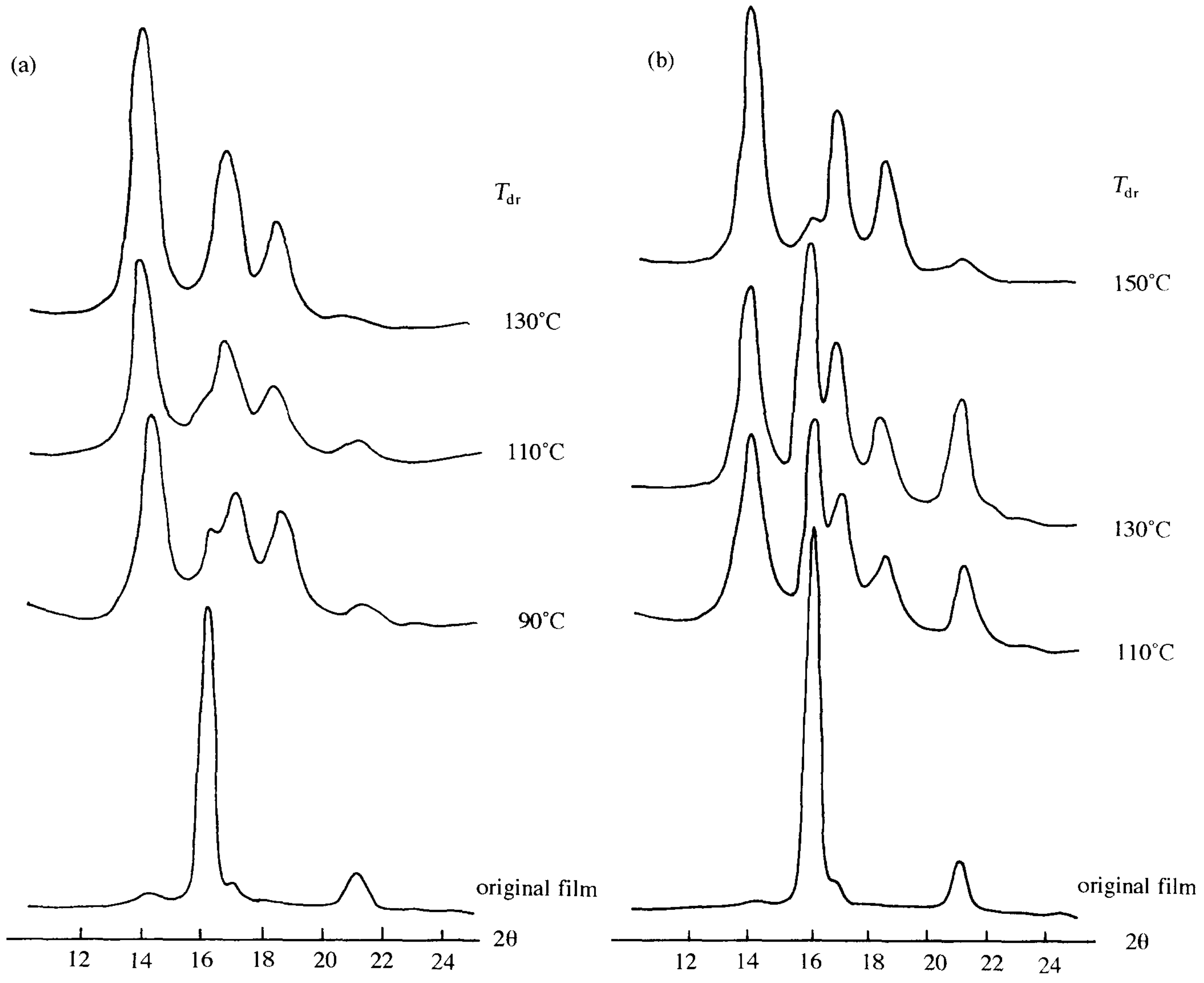

Figure 6 WAXD patterns of β-PP films drawn at different temperatures for films crystallized at (a) 10°C and (b) 110°C

its bulk volume decreased sharply at the beginning of drawing and gradually increased to the original value. In this case, few microvoids are formed. In contrast, in the film crystallized at 110°C, the bulk volume increased with an increasing drawing ratio, but decreased when the ratio exceeded 3.0. This sharp contrast in the polymer bulk volume shrinkage has a strong correlation with the large differences in porosity between the films crystallized at higher and lower temperatures, as observed in *Table 2*.

Figure 6 shows the wide-angle X-ray diffraction patterns of the films drawn uniaxially at various temperatures. Each of the films crystallized at 10°C (*Figure 6a*) exhibits much smaller diffraction peaks for the β crystal than those crystallized at 110°C (*Figure 6b*), when they were drawn at a defined temperature. The β–α transformation was almost complete when the former film was drawn unaxially in a 2.5 ratio at 130°C, while it was incomplete when the latter film was drawn at 150°C. These results strongly suggest that the β crystals that were formed at lower temperatures transformed into the α form much more quickly than those formed at higher temperatures.

Figure 7 shows the melting behaviour of β-PP films crystallized at different temperatures. As described previously[11], several melting peaks of the β crystal appeared during the d.s.c. heating cycle. For the specimen crystallized at 10°C, the melting peak was very small, although the β content, calculated from its K value, was almost 90%. It is therefore believed that the metastable β crystals which are formed in this specimen melt and recrystallize into more stable β and α crystals at relatively low temperatures. For the films crystallized at 110°C, the β crystals have higher melting points and cannot recrystallize into the α form below the melting point. In general, the lower the crystallization temperature, then the lower was the thermal stability of the β crystals.

Based on these findings, void formation should be related to the stability of the β crystals which is dependent on both temperature and deformation stress. As indicated by d.s.c. studies, the β–α transformation may occur by partial melting of the β crystals when the films crystallized at 10°C are drawn at high temperatures. Partial melting induces unfolding of the molecular chains, which are transformed into microfibrils of the α form under the stress applied by the drawing process. This type of β–α transformation, with a partial melting of the β crystals, cannot cause microvoid formation.

In the drawing of the films crystallized at 110°C, the β crystals with the higher stability are allowed to undergo a solid-state transformation into α crystals. The main

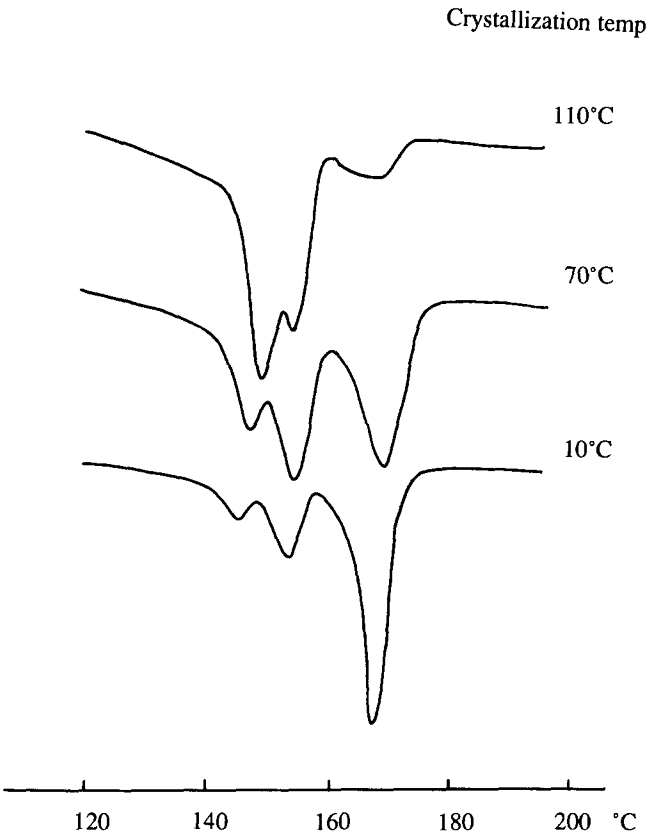

Figure 7 D.s.c. curves of the β-PP films crystallized at different temperatures

cause of this β–α transformation was deformation stress rather than heating. Because of the lower chain mobility of the stable β crystals in the larger crystallites, the bulk volume shrinkage is hindered, and many microvoids are formed between the microfibrils during drawing. When the drawing temperature reached 150°C, which is close to the melting point of the β crystals, many of the crystals are involved in the β–α transformation which occurs by a partial melting–recrystallization mechanism to give a material with a lower porosity.

These results can be summarized as follows. The β crystals formed at lower temperatures are unstable and have a smaller crystallite size. When this specimen is drawn, a β–α transformation easily takes place, and larger bulk shrinkage then occurred to give a lower porosity, with the phase transformation taking place via a partial melting–recrystallization process. In contrast, the β crystals formed at higher temperatures are stable enough and have a larger crystallize size. Since these stable crystals inhibit a bulk volume contraction of the film during deformation, the void formation is caused by a β–α transformation leading to high porosity. Therefore, the cause of microvoid formation in drawn β-PP can be ascribed to two factors: one is the volume contraction accompanied by the β–α phase transformation, while another is the hindered bulk volume shrinkage which takes place in the presence of stable β crystals. Currently, we are studying the detailed mechanism of microvoid formation and its relationship with the deformation and phase transformation of β crystals.

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