

## Nearly pure $\alpha 2$ form crystals obtained by melt crystallization of high tacticity isotactic polypropylene

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The effect of tacticity on the formation of the most ordered form of  $\alpha 2$  modification of crystals of isotactic polypropylene (iPP) during melt crystallization at atmospheric pressure has been investigated. It was found that melt crystallization of iPP with 99.5% isotacticity at 150°C resulted in nearly 100% pure  $\alpha 2$  form crystals, i.e. fraction of  $\alpha 2$  ( $f(\alpha 2)$ ) = 1. At temperatures higher than 150°C,  $f(\alpha 2)$  was found to decrease from unity. The present study on the two different molecular weight samples showed that molecular weight does not influence the  $\alpha 2$  formation. The results are explained on the basis of the effect of chain mobility and thermal expansion on the regularity of interchain packing. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords:  $\alpha 2$  form of crystals of iPP; melt crystallization; isotacticity)

### Introduction

It was reported earlier that annealing of isotactic polypropylene (iPP) at higher temperatures results in structural transformation from the  $\alpha 1$  form to the  $\alpha 2$  form<sup>1</sup>. They correspond to C2/c and P21/c crystallographic symmetries, respectively<sup>1-3</sup>, which are related to the order of up-and-down positioning of the chains. Tacticity of the iPP in our previous study<sup>1</sup> was not high enough—approximately 93%. X-ray diffraction studies showed that the fraction of  $\alpha 2$  ( $f(\alpha 2)$ ) increases with increasing annealing temperature ( $T_a$ ) and reaches a maximum value of ca. 0.8 at  $T_a = 150^\circ\text{C}$  in the case of unoriented samples and at  $T_a = 170^\circ\text{C}$  in the case of oriented ones<sup>1</sup>. So far, 100% pure  $\alpha 2$  ( $f(\alpha 2) = 1$ ) form crystals have not been obtained, therefore, it has been difficult to determine the correct crystal structure of the  $\alpha 2$  form. Studies on iPP with various isotacticities have shown that unit cell parameters, crystallinity, crystallite size and lamellar crystal size are found to be dependent on isotacticity<sup>4-6</sup>.

In the present study, the formation of the  $\alpha 2$  form was studied for iPP samples with very high isotacticity (99.5%) during crystallization from the melt at different crystallization temperatures ( $T_c$ ). It was expected that iPP with very high tacticity will facilitate the formation of more ordered  $\alpha 2$ , which will enable the final correct crystal structure of the  $\alpha 2$  form to be determined. Two different molecular weight samples were studied.

### Experimental

**Materials.** High tacticity iPP samples with 99.5% in pentad [mmmm] were supplied by Japan Polyolefines Co. Ltd. Samples with two molecular weights were studied. A higher molecular weight sample with  $M_w = 196 \times 10^3$  and  $M_w/M_n = 5.6$  and a lower molecular weight sample with  $M_w = 86.4 \times 10^3$  and  $M_w/M_n = 5.6$  were used for the study.

**Crystallization of samples.** Samples were filled in a capillary tube and the tube was vacuum sealed. The sample was then melted and immersed in a silicone oil bath maintained at the desired  $T_c$ . Crystallization was carried out for time periods varying from 1 day to several days, depending on the  $T_c$ . Upon completion of crystallization, samples were quenched in frozen acetone.

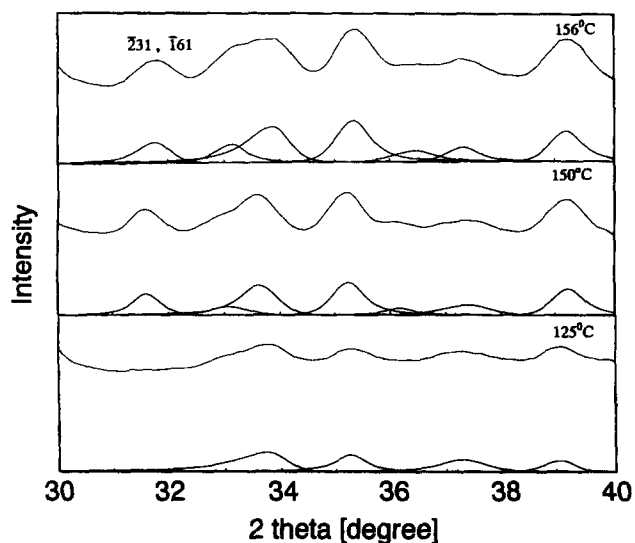
**X-ray diffraction studies and estimation of  $\alpha 2$  fraction.** Wide angle X-ray diffractions of the samples were studied using Rigaku's Rint X-ray diffractometer. The X-ray beam used was  $\text{CuK}_\alpha$  radiation from a rotating anode generator. The beam was monochromatized using a graphite crystal. The sample was rotated during the exposure. Wide angle X-ray diffraction patterns were recorded using an imaging plate with a high resolution of 25  $\mu\text{m}$ . The digitized image was obtained from the imaging plate using an imaging plate reader, Rigaku R-Axix DS3, and analysed using a computer. Reliable integrated intensity ( $I$ ) of each Debye-Scherrer ring was obtained by using software developed by us. Details of this method will be discussed in a separate publication. The  $I-2\theta$  curve was comparable to the one obtained by the conventional counter methods and the noise was low enough (Figure 1). The peaks were resolved using a curve resolution program and amorphous contribution was removed as described earlier<sup>7</sup>.

As described in the earlier papers<sup>1,8-10</sup>, the two modifications  $\alpha 1$  and  $\alpha 2$  have similar X-ray patterns for the reflections  $hkl$  with  $h+k = \text{even}$ , whereas the reflections  $hkl$  with  $h+k = \text{odd}$ , for example  $\bar{2}31$  and  $\bar{1}61$ , are systematically absent in the  $\alpha 1$  form owing to the extinction rule. Therefore, the  $f(\alpha 2)$  can be estimated from the following expression, which is a simplified method from the procedure used in Hikosaka and Seto<sup>1</sup>.

$$f(\alpha 2) = CI_{\alpha(o)} \quad \text{where } C = I_{c(e)}/I_{\alpha(e)} \quad (1)$$

where  $C$  is a scaling factor defined by the above secondary relation,  $I_{\alpha(o)}$  and  $I_{c(o)}$  are observed and calculated intensities of a reflection with  $h+k = \text{odd}$ , respectively, and  $I_{\alpha(e)}$  and

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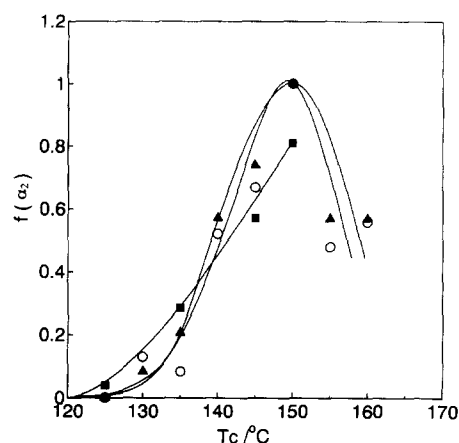
**Figure 1** Typical resolved  $2\theta$ - $I$  curves of lower molecular weight iPP ( $M_w = 86.4 \times 10^3$  and  $M_w/M_n = 5.6$ ) crystallized at 125, 150 and 156°C, respectively. The upper and lower curves indicate the original one and peak-separated

$I_{c(e)}$  are observed and calculated intensities of a reflection with  $h + k = \text{even}$ , respectively. In this study  $I_c$  was taken as the calculated intensity for the  $\alpha 2$  form model given in Hikosaka and Seto<sup>1</sup>. Here it is assumed that the  $I_c$  in Hikosaka and Seto<sup>1</sup> were nearly correct. It is obvious that this assumption is not definite so far, because 100% pure  $\alpha 2$  material has not been obtained yet. Therefore, the  $I_c$  is tentative but enough to estimate approximate  $f(\alpha 2)$ . The correct  $f(\alpha 2)$  will be obtainable in the near future using the iteration method after obtaining nearly 100% pure  $\alpha 2$  material.

Reflections  $hkl$ s with  $h + k = \text{odd}$  and  $h + k = \text{even}$  used in this study were  $\bar{2}31$  and  $\bar{1}61$  and 110, respectively. The observed intensities were corrected as was done in the previous work using the same temperature factor  $B = 8^1$ .

### Results

Figure 1 shows typical resolved  $2\theta$ - $I$  curves in the range of  $2\theta = 30^\circ$  to  $40^\circ$  for low molecular weight iPP crystallized at temperatures of 125, 150 and 156°C. It can be noticed that the intensity of reflection  $\bar{2}31$  and  $\bar{1}61$  at  $2\theta = 31.8$  is absent for the sample crystallized at 125°C and is very strong at 150°C. At  $T_c = 156^\circ\text{C}$  the intensity of reflection  $\bar{2}31$  and  $\bar{1}61$  is weaker than that at 150°C. Figure 2 shows the estimated  $f(\alpha 2)$  for both high molecular weight and lower molecular weight samples as a function of  $T_c$ . Data for the lower isotacticity (93%) iPP taken from the previous work<sup>1</sup> are also shown for comparison. Here, the relation that  $m$  in Hikosaka and Seto<sup>1</sup> equals the square of  $f(\alpha 2)$  was used. The  $f(\alpha 2)$  increases with  $T_c$  and attains a value of unity at a temperature of 150°C and shows a decreasing tendency. A comparison with the previous data for the lower tacticity iPP showed that in the present case there is a significant increase in the  $f(\alpha 2)$  value, reaching a value of unity. Therefore, the effect of tacticity in the formation of a more ordered state is evident here. The higher tacticity iPP can arrange themselves into an ordered up-and-down position more perfectly than the lower tacticity iPP. Another observation is that there is no difference between the two molecular weight samples with regard to the relation between degree of ordering and  $T_c$ . Both show the same tendency. The start of



**Figure 2** Fraction of  $\alpha 2$  ( $f(\alpha 2)$ ) as a function of crystallization temperature  $T_c$ .  $\circ$ , lower molecular weight iPP;  $\blacktriangle$ , higher molecular weight iPP;  $\blacksquare$ , referential data for the conventional low tacticity iPP taken from Hikosaka and Seto<sup>1</sup> observed on oriented samples

the appearance of the peak at  $\bar{2}31$  and  $\bar{1}61$  is also at the same  $T_c$ .

### Discussion

It is shown for the first time that nearly pure  $\alpha 2$  form crystals ( $f(\alpha 2) = 1$ ) were obtained when iPP with very high tacticity (99.5%) was crystallized from the melt at atmospheric pressure. The very high tacticity of the present iPP may have facilitated the formation of a more ordered  $\alpha 2$  form. It was reported earlier<sup>4-6</sup> that lower tacticity iPP includes more point defects in the lamellae than iPP with higher tacticity, as a result of which the interchain distance, i.e. the size of the unit cell also increases. As the interchain distance increases, the difference in interchain packing energy levels with respect to the formation of  $\alpha 1$  and  $\alpha 2$  will become smaller, which will result in the formation of both  $\alpha 1$  and  $\alpha 2$ . On the other hand, iPP with high tacticity tends to exclude defects<sup>11</sup>, resulting in a smaller interchain distance and the much lower energy level  $\alpha 2$  packing may become favourable. At lower temperatures, the mobility is relatively low and the crystal growth rate is fast. As a result of this, the chance of replacement from  $\alpha 1$  into  $\alpha 2$  packing during growth is low. With an increase in  $T_c$  up to 150°C, the increasing mobility seems to favour  $\alpha 2$  crystal formation. This is the reason why  $f(\alpha 2)$  increased with increase in  $T_c$ .

It is interesting to note that the  $f(\alpha 2)$  decreases above a  $T_c$  of 150°C. At  $T_c$  higher than 150°C, although the mobility is high and growth rate is low, there may be significant thermal expansion, which results in comparable energy levels for  $\alpha 1$  and  $\alpha 2$ . This will result in a decrease in the  $\alpha 2$  fraction. At higher temperatures, increased mobility will result in an increase in lamellar thickness through sliding diffusion<sup>12,13</sup>. Some studies on the crystallized materials showed<sup>14</sup> that the melting temperature increased with  $T_c$  above 150°C. This indicates that the lamellar thickening continues to increase, while the ordering phenomena becomes slower.

The present results on the two molecular weight samples showed that the effect of molecular weight on the  $\alpha 2$  formation is not detectable. In the present case, both samples showed the same tendency. This may probably be due to the fact that the local mobility rather than the chain length is the major factor influencing the crystallization in the ordered or disordered form. This point cannot be

discussed with certainty at the moment as the molecular weight distribution in the samples is rather high.

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