

Note

CRYSTALLIZATION CHARACTERISTICS OF β -PHASE CRYSTALS IN COPOLYMERS OF POLYPROPYLENE WITH LOW ETHYLENE CONTENT

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Abstract Polypropylene copolymers (CPP) containing β -nucleating agent were investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and polarizing light microscopy (PLM). The results show that high content of β -phase crystals can also be formed for CPPs. Like PP homopolymers, the CPPs also have a most favorable temperature near 132°C for β -phase crystal growth. The crystallization rate of CPPs containing β -nucleating agent (β -CPP) is much greater than that of PP homopolymer containing β -nucleating agent (β -PP homopolymer). The observation of spherulite morphology of β -CPP and β -PP homopolymer shows that the spherulites of β -CPP are more imperfect than those of β -PP homopolymer.

Keywords Copolymer polypropylene, β -Nucleating agent, Differential scanning calorimetry, Wide angle X-ray diffraction, Spherulite

INTRODUCTION

Polypropylene copolymers (CPPs) with low ethylene content (< 10 wt%) have excellent low temperature impact resistance. Meanwhile, their comprehensive mechanical properties are kept at a high level^[1, 2]. Studies have proved that the good mechanical properties of polypropylene copolymers are attributed to their characteristic sequence structure and micro-phase structure^[3]. In previous work^[4, 5], it was indicated that CPP is not a simple ethylene-propylene copolymer, but a blend of a series of fractions. In these fractions, the composition and chain sequence structure change gradually from ethylene-propylene rubber (EPR) to PP matrix with very few ethylene segments in the PP chains. For different application purposes and requirements of properties, the chain structure of these fractions should be designed differently.

It is well known that the nucleating agents have been widely used for controlling the crystallization rate and the morphology of polypropylene homopolymers. Interesting results were obtained from our studies of the crystallization behavior of CPPs containing α -nucleating agent^[6-8]. After addition of the nucleating agent, the supercooling of CPP in non-isothermal crystallization reduced more comparing with that of the PP homopolymer. That is, the effect of nucleating agents on CPPs is more remarkable than that on PP homopolymers.

It is natural to ask whether the β -nucleating agent have the same influence on the formation of β -phase crystals in polypropylene copolymers. In this report, the crystallization behavior of CPPs in the presence of β -nucleating agent was investigated by differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), and polarizing light microscopy (PLM). The crystallization characteristics were discussed briefly.

EXPERIMENTAL

Materials

Two commercial CPPs used in this work were purchased from Olefin Chemical Industries Co. Ltd., Japan (CPPJ)

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and Belgium Neste Chemicals N. V. (CPPB), respectively. A PP homopolymer is also used here. The molecular characteristics are summarized in Table 1. In our previous work, it has been shown these CPPs are blends of four fractions: fraction A, the ethylene-propylene random copolymer, fraction B, the ethylene-propylene segmented copolymer, fraction C, the ethylene-propylene block copolymer and fraction D, the PP matrix with few ethylene units on the PP main chains. The content of different fractions for CPPs is shown in Table 2. The β -nucleating agent used is made by in house, and is a blend of pimelic acid and calcium hydroxide. Pellets of PP were premixed with nucleating agent and then blended in a sealed-mill at 180°C for 10 min.

Table 1. Molecular characterization of CPPB, CPPJ and PP homopolymer

Sample	$M_w (\times 10^{-5})$	W_E %	MFI (g/10 min)
CPPB	1.73	9.13	40
CPPJ	2.73	9.43	15
PP homopolymer	2.0	0	29

Table 2. The content of fractions in polypropylene copolymers

	Fraction A	Fraction B	Fraction C	Fraction D
CPPB	10.8	13.5	2.2	73.5
CPPJ	7.5	12.0	3.0	77.5

Differential Scanning Calorimetry (DSC) Study

All the samples were investigated by a Perkin-Elmer DSC-2C differential scanning calorimeter in an atmosphere of high purity nitrogen. The sample weight was 10 mg. In the isothermal crystallization, the samples were kept at 210°C for about 3 min to eliminate the thermal history, then quenched to the selected temperature between 120~144°C. After completion of isothermal crystallization, the samples were heated at a rate of 20 K/min. Thermal treatments of samples for non-isothermal crystallization were the same as those for isothermal crystallization, then the samples were cooled directly from 210°C to room temperature at a cooling rate of 20 K/min.

Wide Angle X-ray Diffraction (WAXD) Study

The samples of CPPs containing 0.5 wt% β -nucleating agent were studied by an MXP18AHF X-ray diffraction instrument produced by Mac Science Co Ltd. Samples were first pressed to a flake on a hot stage at 200°C, then cooled to room temperature naturally.

Polarizing Light Microscopy (PLM) Study

Samples containing 0.1 wt% nucleating agent for morphology observation were prepared by fusing a scrap of samples placed between 2 cover glasses. After melting at 230°C for 2 min, they were kept in a quasi-isothermal state at a selected temperature for 48 h.

RESULTS AND DISCUSSION

The DSC melting curves of CPPB and CPPJ containing β -nucleating agent (β -CPPB, β -CPPJ) after isothermal crystallization at different temperatures for sufficiently long time are shown in Fig. 1. There are 3 melting peaks in each curve. Similarly to the PP homopolymer^[9], the strongest one at 147~157°C should be attributed to the melting of β -phase crystals formed in the isothermal crystallization. The peak at 167°C is the melting peak (α -peak) of α -phase crystals formed in the isothermal crystallization. The last one at a temperature above 167°C represents the α -phase crystal recrystallized in the melting process, named as α' -peak. It is obvious that the melting peak of β -phase crystals in both Fig. 1(a) and Fig. 1(b) predominate over the α and α' -peaks, which means the relative content of β -phase crystal in copolymer polypropylene is much higher than that of the α -phase crystal. It can be concluded that β -phase crystals can also be formed for polypropylene copolymers in the presence of β -nucleating agent. Moreover, the content of β -phase crystal is considerably high.

This result has also been proved by the WAXD patterns, see Fig. 2. The previous work of Turner-Jones showed that^[10] a characteristic diffraction peak of β -phase crystal of polypropylene occurs at about 16° (2θ), which is due to the β (300) crystal plane. Peaks nearby are attributed to the diffraction of α (110), α (040) and α (130) crystal plane of α -phase crystals. It can be seen from Fig. 2 that the β (300) peak is the strongest in diffraction patterns of β -CPPJ and β -CPPB. In other words, the β -phase crystal content in β -CPPs is very high. In Fig. 2(a), the diffraction peaks of α -phase crystal in β -CPPJ is hardly resolvable. However, the α -peaks of β -CPPB are relatively strong. Because the EPR and EP block copolymer of CPP all have some effect on the crystallization of the PP matrix, the crystallization behavior of CPP is highly complex. Much more investigation should be undertaken.

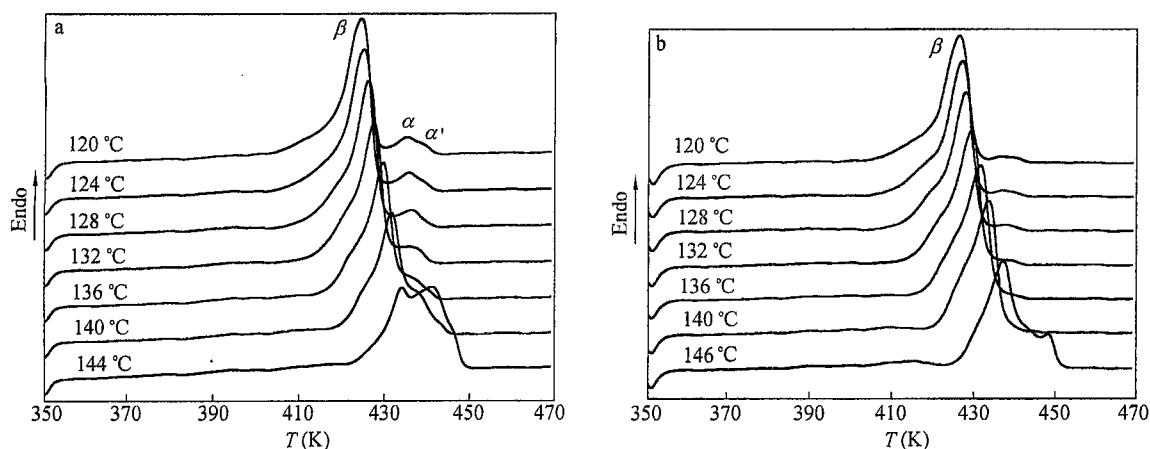


Fig. 1 The DSC melting curves for β -CPPJ and β -CPPB after isothermal crystallization at 134°C
a) β -CPPJ; b) β -CPPB

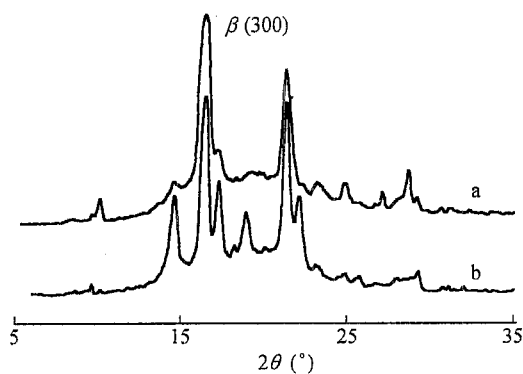


Fig. 2 The WAXD pattern for β -CPPJ and β -CPPB
a) β -CPPJ; b) β -CPPB

Studies of PP homopolymer containing β -nucleating agent indicated that^[11, 12] high content of β -phase crystal can only be obtained within a limited range of crystallization temperature and the optimum temperature for β -phase crystal growth is near 130°C . From the melting curves of β -CPPJ (Fig. 1a), it is apparent that the α -peak and α' -peak are smallest when samples are crystallized at 132°C . It means the content of β -phase crystal is the highest at this point. The same tendency can be seen in Fig. 1(b), though the α -peak and α' -peak are not so strong as in Fig. 1(a). So it can be concluded that an optimum temperature for β -phase crystal growth of polypropylene copolymers also exists. Similarly to PP homopolymer, the temperature is about 132°C too.

Figure 3 is the DSC curves of β -CPPB, β -CPPJ and β -PP homopolymer cooling from 210°C to room temperature in non-isothermal crystallization. Several characteristics can be obtained from Fig. 3. The first one is the initial crystallization temperature T_{onset} , where the DSC trace first departs from the baseline. The second one is the crystallization peak temperature T_c (the values are shown in Table 3). If the equilibrium melting temperature of samples are close, the higher T_{onset} and T_c mean a faster crystallization rate^[13]. As shown in Fig. 3, the T_{onset} and T_c changes following a sequence such as β -CPPJ > β -CPPB > β -PP homopolymer. It seems that the crystallization rates for the 3 samples have the following order β -CPPJ > β -CPPB > β -PP homopolymer. In the study of thermal behavior of PP/EPDM blends^[14], after the addition of a small amount of EPDM (<10 wt%), the crystallization rate of PP increased, which is attributed to the enhanced mobility of the PP segments thereby leading to a better alignment in the crystal lattice. In our previous work^[4, 5], it has been pointed out that the polypropylene copolymer is a blend of EPR, EP block copolymer and PP matrix, like PP/EPDM composite. Then it is understandable that the crystallization rate of copolymer polypropylene is faster than that of PP homopolymer. The isothermal crystallization DSC traces of β -CPPB, β -CPPJ and β -PP homopolymer are shown in Fig. 4. The half crystallization time $t_{1/2}$ is shown in Table 3. The value of $t_{1/2}$ of the 3 samples varies in the order β -CPPJ < β -CPPB < β -PP homopolymer. The crystallization rate should be contrary to such sequence. Both of the results obtained from isothermal and non-isothermal crystallization all show that the crystallization rate of β -phase crystal in CPPs is higher than that of the PP homopolymer.

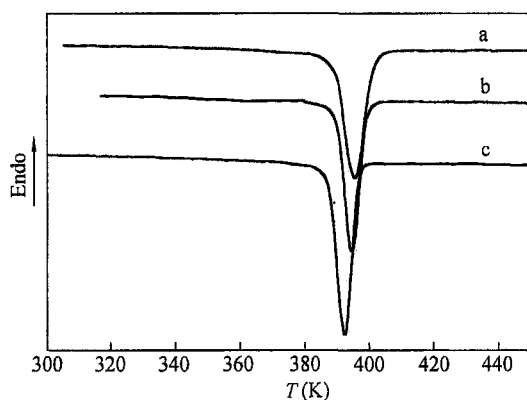


Fig. 3 The DSC curves of non-isothermal crystallization for β -CPPJ, β -CPPB and β -PP homopolymer (a) β -CPPJ, (b) β -CPPB and (c) β -PP homopolymers

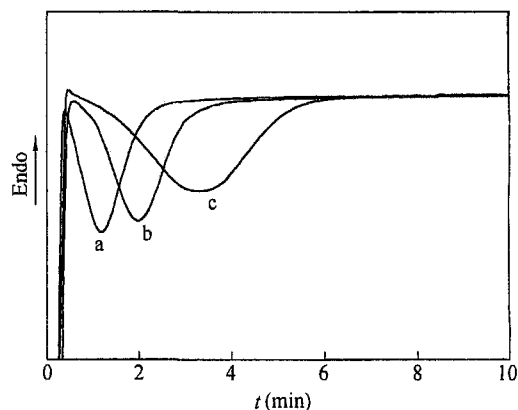


Fig. 4 The DSC curves of isothermal crystallization for β -CPPJ, β -CPPB and β -PP homopolymers, (a) β -CPPJ, (b) β -CPPB and (c) β -PP homopolymer at 134°C

Table 3. The characteristics of nonisothermal crystallization for β -CPPJ, β -CPPB and β -PP homopolymer

Sample	T_c (K)	ΔH_c (J/g)	$t_{1/2}$ (min)
β -CPPJ	396.6	84.01	1.0
β -CPPB	395.3	81.92	1.78
β -PP homopolymer	392.5	109.2	3.52

Note: The value of $t_{1/2}$ comes from the isothermal crystallization at 134°C.

The micrographs of β -CPPB, β -CPPJ and β -PP homopolymer are shown in Fig. 5. It can be seen that spherulites of the 3 β -samples are smaller than those of the original samples. It exhibits the effective nucleation of the β -nucleating agent. However, the crystals of β -CPPJ and β -CPPB are not as perfect as that of β -PP homopolymer. Non-crystalline component such as EPR in the polypropylene copolymer disperses inter- and intra- the spherulite of PP matrix, and it hinders the growth of the spherulite^[5]. Hence the crystals in the PP homopolymer are more perfect. On the other hand, the spherulite of β -CPPJ is less perfect than that of β -CPPB,

the same is observed for the original samples. As mentioned above, the crystallization of PP matrix in CPP is affected by many factors, and it is highly complicated. The differences of crystallization behavior of different CPPs and the differences between those of CPPs and PP homopolymer are all relating to the sequence structure to some extent. There is still much more work to be done to make clear the fundamentals of the crystallization behavior of polypropylene copolymers containing β -nucleating agent.

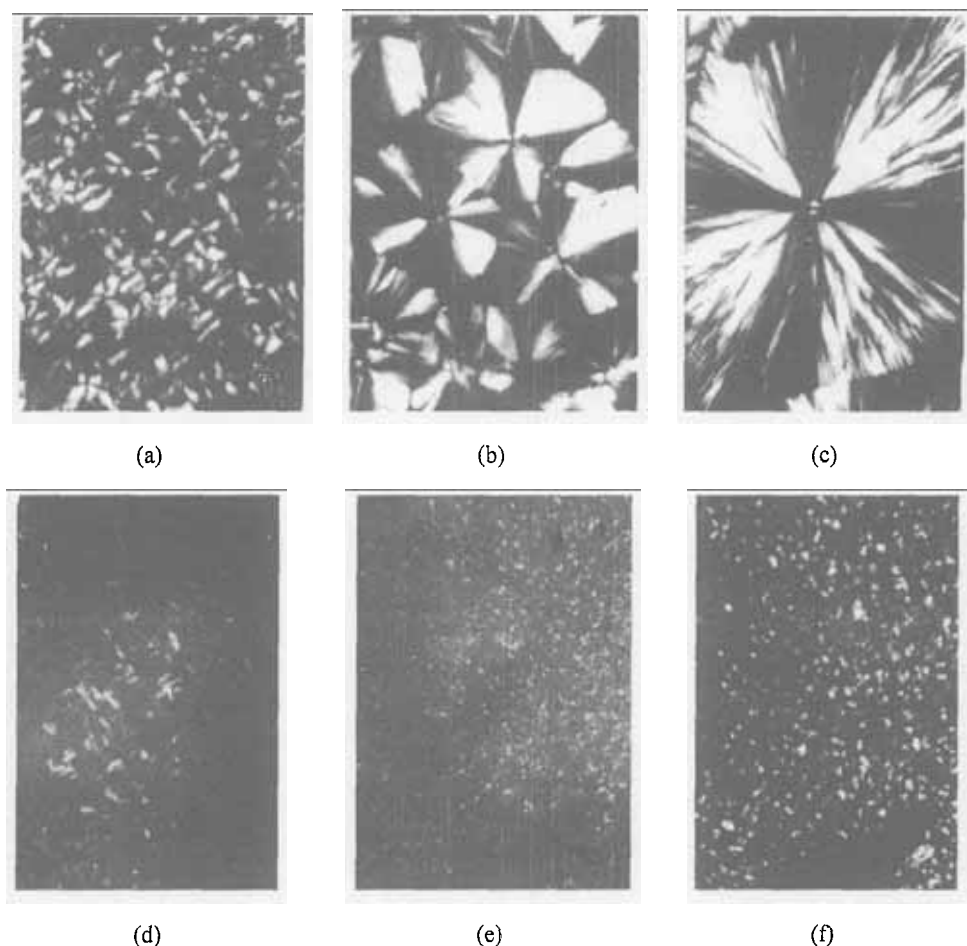


Fig. 5 The spherulite morphology of CPPJ, CPPB and PP homopolymer with and without nucleating agent (a) CPPJ, (b) CPPB, (c) PP homopolymer, (d) β -CPPJ, (e) β -CPPB and (f) β -PP homopolymer

CONCLUSIONS

Crystallization behavior of β -phase crystals of polypropylene copolymers is investigated. It is founded that high content of β -phase crystal can also be formed in CPPs. The optimum temperature for β -phase crystal growth of CPPs is near 132 °C too. Crystallization rate of β -CPPs is higher than that of β -PP homopolymer and the spherulites of CPPs are less perfect regardless of the presence of nucleating agent.

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