

Polymer Communication

Study on the formation of β -crystal during the crystallization process of polypropylene reactor granule

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Abstract

A notable amount of PP β -crystal (30%, by X-ray diffraction pattern) has been found in the PP samples as polymerized at normal static isothermal crystallization conditions without using any extra nucleating agents. Existence of catalyst residues in the sample is decisive, which slows down the crystallization rate facilitating the formation of β -form spherulites. Comparatively, high molecular weight PP favors the formation of β -form spherulites, deducting from no β -crystal detected in the degraded samples. Finally, high isotacticity is also required for obtaining qualitative β -form spherulites, demonstrated by increased β -crystal content after removal of weak crystalline fraction of the sample.

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1. Introduction

Isotactic polypropylene (iPP) is known for its three common crystal forms [1]. Recently, β -iPP has attracted many interests as it possesses some advantageous mechanical properties such as the high toughness, drawability and thermal deformation temperature as compared with α -iPP due to the β – α transition. As the β -iPP is in a metastable phase, it can be rarely obtained in a significant amount in commercial iPP products, unless crystallization conditions facilitating to the β -phase growth are taken [2–6].

There are several approaches for obtaining β -iPP in substantial amount, for instance, utilization of β -nucleating agent [3–13], copolymerization with other monomer [14,15], crystallization induced by shear [16–19], and crystallization under force field or magnetic field [20,21]. Comparatively, β -

nucleating agent has been used and studied more widely and extensively.

Recently, significant amount (ca. 30%) of β -crystal in the iPP products as obtained from the reactor has been found during the isothermal crystallization process in our laboratory without using any β -nucleating agents. This article attempts to identify the characteristics of the samples to explore the mechanism of β -crystal formation during the isothermal crystallization process. The efforts are focused on the aspects possibly affecting crystallization process including catalyst residues remained in the sample, molecular weight and heterogeneity in stereoregularity of the original polypropylene.

2. Experimental part

2.1. Materials

MgCl₂ supported Ziegler–Natta catalyst was kindly provided by Dingjide Co. Ltd with diisobutyl phthalate as internal electron donor. Polypropylene was synthesized in a 2 l stainless steel autoclave for 2 h with AlEt₃ as co-catalyst and

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dicyclohexane dimethoxymethyl silane as external electron donor. The two samples as polymerized are named PP0 and PP1.

2.2. Sample preparation

2.2.1. Deashed sample

PP1 (1.5 g) was dissolved in 200 ml xylene containing 0.2 g antioxidant (1010). The sample was collected after filtering, precipitating in large amount of ethanol, washing with ethanol for several times and drying under vacuum. The sample was named PP2.

2.2.2. Degraded sample

PP1 (45 g) was mixed with accurately weighted dicumyl peroxide (DCP) in a Hakke batch mixer at 200 °C for 5 min. By controlling the DCP amount used, degraded samples of different molecular weights were prepared and named PP3 and PP4.

2.2.3. Fractionated sample

PP0 weighted accurately was immersed in xylene containing antioxidant (1010) at 112 °C for 4 h. After vacuum drying, insoluble fraction (89%) was collected and named PP5.

2.3. DSC analysis

The crystallization measurements were carried out using a Perkin–Elmer Diamond differential scanning calorimeter under nitrogen. Sample (10 mg) was heated from 50 °C to 200 °C at a scanning rate of 10 °C/min, kept for 1 min and then cooled from 200 °C to 50 °C at a cooling rate of 10 °C/min. Isothermal crystallization was performed by cooling the sample from 200 °C to 130 °C at a rate of 70 °C/min and then keeping at that temperature for 30 min.

2.4. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction experiments were conducted on a PW1700 X-ray diffractometer. Graphite monochromatic Cu K α radiation was employed as a radiation source. Thermal treatments of the samples were exactly the same as that in DSC measurements. The relative content of the β -crystal in the sample was measured in terms of K_{β} value, calculated by using Turner–Jones equation [22].

2.5. Molecular weight measurements

The molecular weight and the molecular weight distribution of the samples were determined at 150 °C by a PL-GPC 220 high-temperature chromatograph equipped with three PL-gel 10 μ m Mixed-BLS type columns and 1,2,4-trichlorobenzene (TCB) was employed as solvent at a flow rate of 1.0 ml/min. Calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

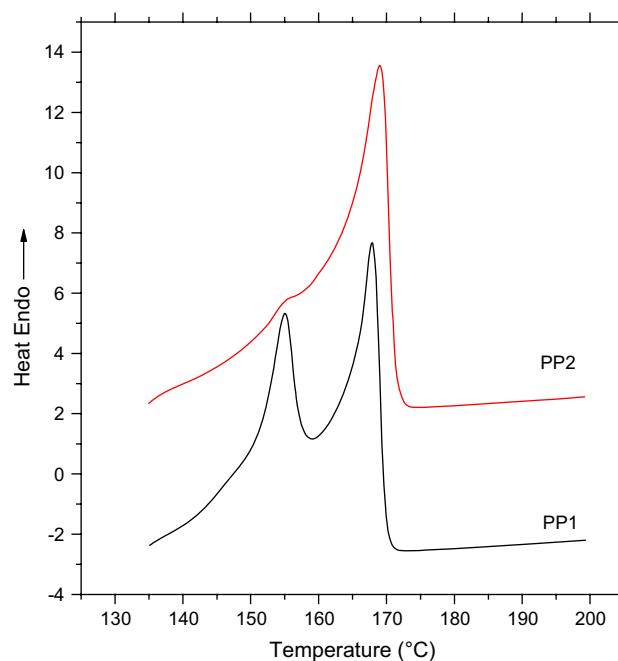


Fig. 1. DSC analysis of PP samples, PP1: as polymerized; PP2: deashed.

3. Results and discussion

3.1. Formation of β -crystal induced by catalyst residue (CR)

In Fig. 1, the sample PP1 as polymerized shows clearly β -crystal melting peaks at 154 °C. The XRD patterns of PP1 (Fig. 2) show a characteristic β (300) peak at 2θ of 15.8° and peaks of α (110), α (040) and α (130) corresponding to

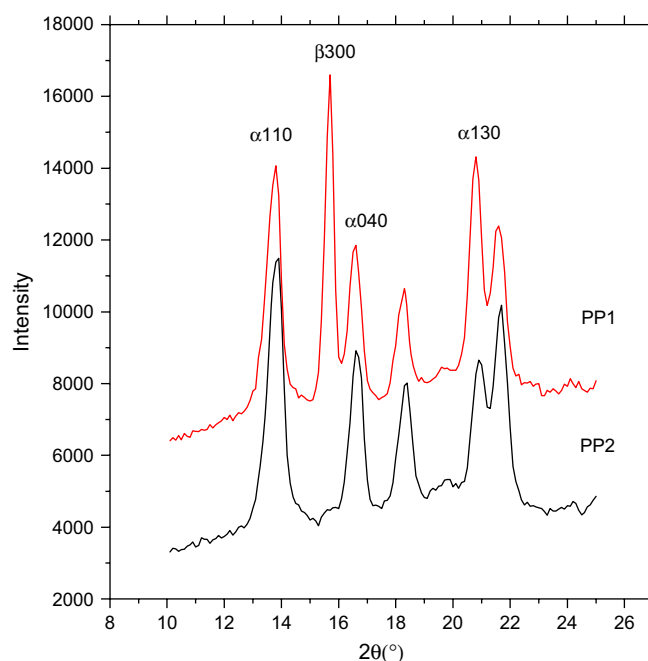


Fig. 2. XRD patterns of PP samples, PP1: as polymerized; PP2: deashed.

Table 1
The molecular parameters and β -crystal content (K_β) of PP samples

Sample	CR content (wt%)	\bar{M}_w (10^{-4})	II ^a (%)	K_β (%)
PP0	0.0025	81	>99	22.2
PP1	0.0026	110	>99	30.3

^a Isotacticity index (II) is measured by the weight percent of heptane insoluble fraction.

2θ of 13.8° , 16.6° and 20.8° . In contrast, characteristic peak of β -crystal of deashed sample (PP2) disappears as shown in Figs. 1 and 2. This implies that catalyst residue in the sample is decisive for the formation of β -crystal.

The CR content, calculated by means of reciprocal of the catalytic activity, and relative content of β -crystal (K_β) are tabulated in Table 1. It is amazing to see that a tiny amount of catalyst residue can induce the samples to form β -crystal in substantial amount, differentiating from the nucleating agent induced system where quantitative amount of nucleating agent has to be used for obtaining β -crystal effectively [23]. As reported by Lozano et al., finely dispersed inorganic filler can effectively induce the formation of β -crystal [24], the dispersion of catalyst residual in the PP sample is far more fine than that of any filler filled systems, owing to the nature of polymerization process [25,26].

Fig. 3 shows the difference in crystallization rate of the samples before (PP1) and after (PP2) deashing process, where much faster crystallization rate of PP2 is evidenced, indicating crystallization rate is slowed down by even tiny amount of catalyst residual in the sample PP1. As the polymer chain grows on the surface of the catalyst subparticle during polymerization [27], many of the polypropylene chains have been anchored on the surface of catalyst particle to form a star-like

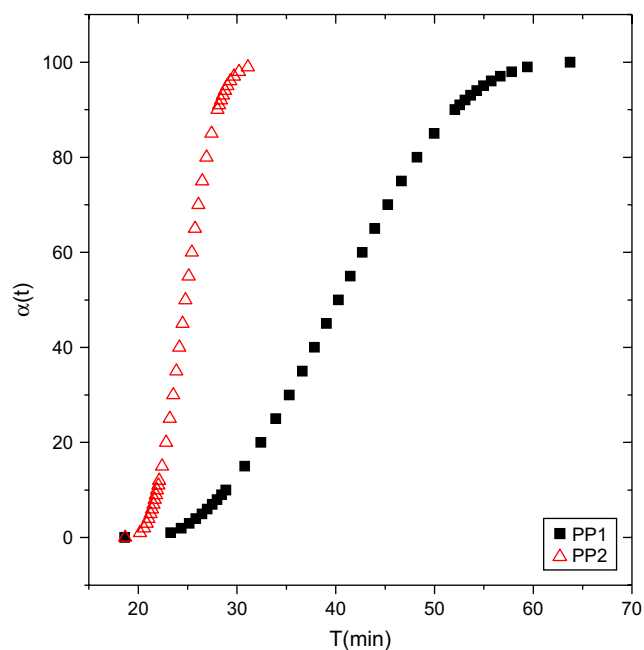


Fig. 3. Development of relative degree of crystallinity ($\alpha(t)$) with time for isothermal crystallization of PP1 and PP2.

Table 2
Molecular weight and β -crystal contents (K_β) of PP samples before (PP1) and after degradation process (PP3, PP4)

Sample	\bar{M}_w (10^{-4})	Polydispersity	$T_{m\alpha}$ ($^\circ\text{C}$)	$T_{m\beta}$ ($^\circ\text{C}$)	K_β (%)
PP1	110	5.5	168.4	154.5	30.3
PP3	12.7	2.5	163.1	—	0
PP4	9.7	2.2	161.2	—	0

structure with the catalyst particle as the junction, the movement of polymer chains tends to be restrained to some extent and crystallization rate slows down as a consequence. It has been known that the too fast crystallization rate is unfavorable for the growth of β -iPP spherulite [11], probably implying that the formation of monoclinic spherulite (α -form) is much faster than that of hexagonal one (β -form).

3.2. Effects of the molecular weight on β -crystal formation

Table 2 shows that β -crystal cannot be detected by both DSC and X-ray diffraction examinations in low molecular weight samples obtained from the degradation of PP1. Since the longer polymer chains are more sensitive to the radical degradation, the evidence of decreased molecular weight and narrowed molecular weight distribution suggests that relatively high molecular weight fraction in the sample should be essential for the formation of β -crystal.

3.3. Effects of weak crystallized fraction on β -crystal formation

To further examine the effects of the intermolecular heterogeneity in stereoregularity of sample on the formation of β -crystal, the weak crystallized fraction has been removed by extraction with xylene at 112°C as compared with the original sample (PP0). From Table 3, xylene-insoluble fraction (PP5) shows relatively higher β -crystal content (K_β). Results of DSC analysis from Fig. 4 indicate the stronger β -crystal melting peak of PP5, accompanied by about 1°C increased $T_{m\alpha}$ and $T_{m\beta}$ in comparison to that of PP0. Accordingly, the weak crystallized fraction is unfavorable for crystallization of both α -crystal and β -crystal, while from the data in Table 3, crystallization of β -crystal seems to be more sensitive to the weak crystallized fraction than that of α -crystal, implying that the high isotacticity is required for the formation of β -crystal, in other words, the formation of β -crystal is more strict and difficult than that of α -crystal.

Table 3
 β -crystal contents (K_β) of original PP sample (PP0) and its xylene-insoluble fraction (PP5)

Sample	$T_{m\alpha}$ ($^\circ\text{C}$)	$T_{m\beta}$ ($^\circ\text{C}$)	[mmmm] (%)	K_β (%)
PP0	166.9	154.3	97.8	22.2
PP5	167.7	155.2	100	26.5

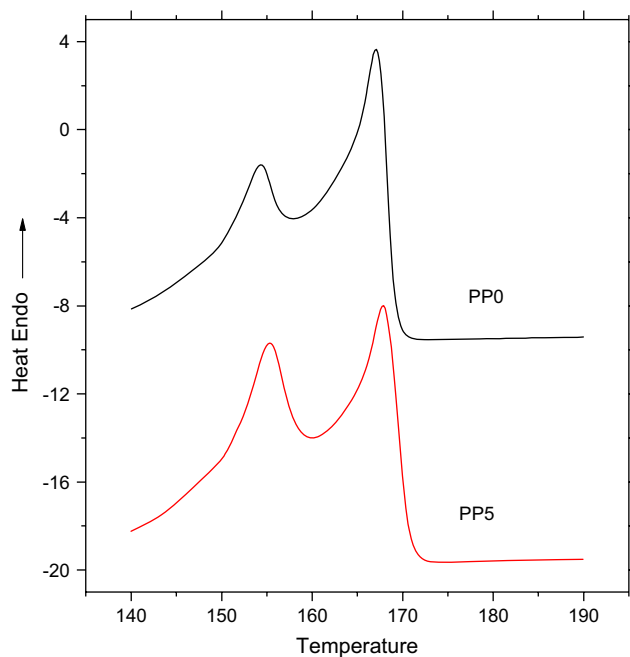


Fig. 4. Melting of original PP sample (PP0) and its xylene-insoluble fraction (PP5).

4. Conclusion

The aspects affecting the formation of PP β -crystal in the PP sample as polymerized are investigated. While the catalyst residual in the sample is demonstrated to be dominant factor, molecular weight and isotacticity of the sample are also demonstrated to be the important factors for the formation of β -crystal.

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