J Therm Anal Calorim (2009) 96:733–740
DOI 10.1007/s10973-009-0022-7

Thermal behavior of isotactic polypropylene in different content of β-nucleating agent

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Received: 9 October 2008 / Accepted: 26 January 2009

Abstract The effects of non-isothermal and isothermal crystallization on the formation of α- and β-phase in isotactic polypropylene (iPP) with different content of β-nucleating agent are investigated by differential scanning calorimetry (DSC). On non-isothermal crystallization, the content of β-phase and regularity of its crystals are depended on both cooling rate and the content of β-nucleating agent. The faster cooling rate is, the lower of melting peak temperature (T_{mp}) and crystallization peak temperature (T_{cp}) of α- and β-phase are. The enthalpy of fusion (ΔH) of β-phase increases with cooling rate in a certain range for the sample with 0.1 wt% β-nucleating agent (G_1) and decreases for that with 0.3 wt% β-nucleating agent (G_3). On isothermal crystallization, the enthalpy of fusion of β-phase in G_1 is higher than in G_3 which is related to the efficiency of nucleation in different concentration of nucleating center in two samples.

Keywords Isotactic polypropylene · β-Phase · β-Form · β-Nucleating agent · DSC · Recrystallization/reorganization

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Introduction

Under different conditions, isotactic polypropylene (iPP) can form different forms denoted as α-, β-, γ- and mesomorphic form [1]. Usually, iPP crystallizes into α-form, which is the best known and the most stable one. The γ-form in iPP forms in low molecular weight of iPP or under high pressure and the mesomorphic form forms by quenching. β-form is metastable in thermodynamics which is obtained under some special conditions such as high degree of super cooling [2], temperature gradient [3, 4], shear-induced crystallization [5, 6] or adding β-nucleating agent [7–12]. Adding β-nucleating agent is the most effective and accessible method to get a high level of β-PP [7–12]. There is a limited range of crystallization temperature to obtain a high level of β-phase. During the limited of the lower critical temperature ($T_{\alpha\beta} \approx$ 100–105 °C) and the upper critical temperature ($T_{\beta\alpha} = 140$ °C) the growth rate of β-form is faster than α-form and near 130 °C is the most favorable temperature to the growth of β-form [13–16]. Generally, wide X-ray diffractometer (WXRD), polarized light optical micrograph (PLOM), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) are used for the characterization of β-phase. The WXRD pattern shows the characteristics α-phase (110) (040) (130) (111) peak at 2θ of 14.2°, 17.0°,18.5°, 21.2°, respectively, and the main characteristic β-phase (300) peak at 2θ of 16.2° [8, 9, 17–19]. The content of β-phase (the k value) is calculated by the Turner–Jones equation with the integral intensity of the characteristics peaks [20]. PLOM micrographs show the growth process of the crystal and the size and the structure of the spherulite. It can be shown that β-nucleating agent can reduce the size of the crystals in iPP and increase the amount of nucleating center [8, 21]. SEM micrograph shows clearly the morphology or structure of the crystal which is related to

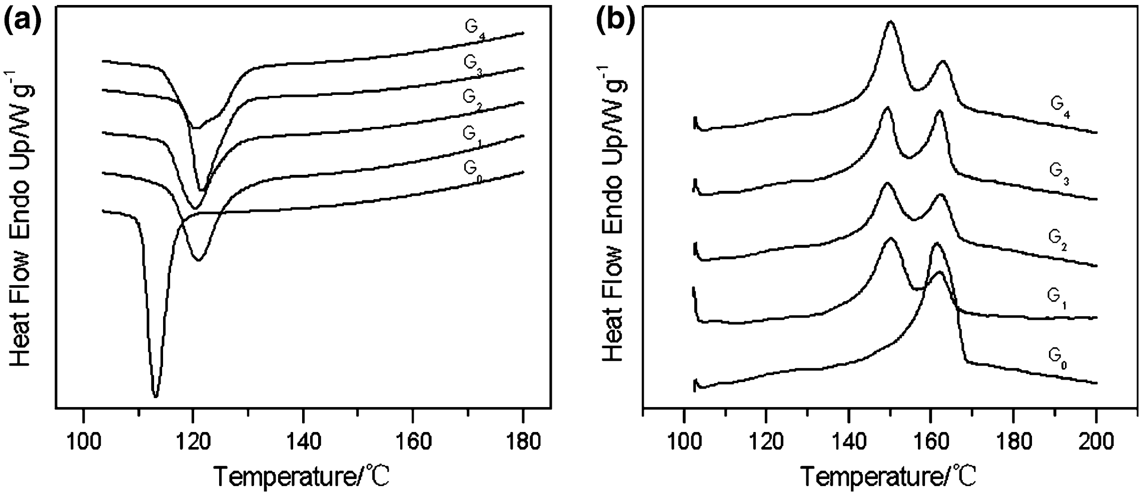

Fig. 1 Cooling and melting curves of the samples containing different content of β-nucleating agent: **a** cooling; **b** melting

the mechanical performance of iPP [9, 22–24]. It is found that two endothermic peaks of nucleated iPP are usually distributed on DSC melting curves. One is the $T_{\alpha mp}$ at higher temperature range (160–170 °C) and another one is the $T_{\beta mp}$ at lower temperature range (140–155 °C). Even three or four melting peak temperatures are observed on DSC melting curve and several explanations for the multiple-melting characteristics. The most common reason for the phenomenon is attributed to the recrystallization/reorganization processes of the chainfolded lamella which means that $\beta'\beta''$- or $\beta\alpha$-recrystallization is occurred [10, 11, 13, 14, 25–27]. Varga et al. [7, 13, 14] find that no $\beta\alpha$-recrystallization occurs during heating and only one melting peak of β-phase is appeared on DSC melting curve if the sample is not cooled down below the critical temperature ($T_R^* = 100$ °C) on crystallization.

It is reported that the crystallization process and the content of β-phase depends strongly on both the nucleating agent concentration, crystallization temperature and the kind of β-nucleating agent [7, 28]. In this paper, β-nucleating agent which is a compound of lanthanum and calcium stearate is chose for studying on the thermal behavior of iPP in detail with different content of β-nucleating agent. The effects of cooling rate, heating rate and isothermal crystallization temperature on melting or cooling peak temperature and enthalpy of fusion of neat and nucleated iPP are analyzed.

Experimental

Materials and samples preparation

iPP (T30S), produced by Maoming Petrochemical Co., China, was used with isotacticity index 95%, melt flow index (at 230 °C and 2.16 kg) 3.0 g/10 min and a mass-average molecular mass approx. 348000. β-nucleating agent was a compound of lanthanum and calcium stearate made by our lab [29, 30].

iPP was dissolved in hot xylene (138 °C) and slowly precipitated in acetone with continuous stirring in order to form small granular iPP. The precipitation was filtered and β-nucleating agent was uniformly dispersed in different amounts (0, 0.1, 0.2, 0.3, 0.4 wt% of the iPP). The samples were dried in the air and labelled as G_0, G_1, G_2, G_3 and G_4, respectively.

Differential scanning calorimetry analysis

Measurements were performed on a Perkin-Elmer Diamond DSC with a nitrogen purge at a flow rate of 20 mL s^{-1}. The instrument was calibrated for temperature and enthalpy by high purity indium (156.60 °C, 28.45 J g^{-1}) standard.

For Fig. 1, the samples were melted at a heating rate of 50 °C min^{-1} from 50 to 220 °C and hold at this temperature for 5 min in order to eliminate their thermal history, and then cooled to 100 °C at the rate of 10 °C min^{-1} and hold at 100 °C for 5 min. Subsequently, the samples were reheated at a heating rate of 10 °C min^{-1} from 100 to 220 °C.

The non-isothermal crystallization behaviors of G_1 and G_3 were studied by DSC at the cooling rates of 3, 5, 10, 20, 30, 40 and 50 °C min^{-1} and the heating rate was 10 °C min^{-1} from 100 to 220 °C. The melting behaviors of G_1 and G_3 were studied at the cooling rate of 40 °C min^{-1} from 220 to 100 °C and the heating rates were 5, 10, 20, 30, 40 and 50 °C min^{-1} from 100 to 220 °C, respectively.

The isothermal crystallization behaviors of G_1 and G_3 were also carried out by DSC at 100, 110, 120, 130, 135 and 140 °C, respectively. Firstly, G_1 and G_3 were melted at a heating rate of 50 °C min^{-1} from 50 to 220 °C and hold at this temperature for 5 min in order to eliminate their thermal history, then cooled to 140, 135, 130, 120, 110 or 100 °C at the rate of 50 °C min^{-1} and hold at these temperatures for 30 min, then cooled again to 100 °C at the rate of 10 °C min^{-1} and hold at 100 °C for 5 min. G_1 and G_3 were reheated at the heating rate of 10 °C min^{-1} from 100 to 220 °C.

α-Phase and β-phase melting peaks of some samples overlapped partially in the DSC curves. The specific enthalpy of fusion for α- and β-phase was determined according to the following calibration method. The total enthalpy of fusion, ΔH_T was integrated from 90 to 180 °C on the DSC thermogram. A vertical line was drawn through the minimum between the α- and β-phase melting peaks and the total enthalpy of fusion was divided into β-component, ΔH_β*, and α-component, ΔH_α*. Because the less perfect α-form melted before the minimum point during heating and gave rise to some contribution to the ΔH_β*, the true value of β-phase enthalpy of fusion, ΔH_β, has been approximated by a production of multiplying ΔH_β* with a calibration factor A according to Eq. 1–3 [31]:

$$\Delta H_\beta = A \times \Delta H_\beta^* \tag{1}$$

$$A = [1 - h_2/h_1]^{0.6} \tag{2}$$

$$\Delta H_\alpha = \Delta H_T - \Delta H_\beta \tag{3}$$

where h_1 and h_2 are the heights from the base line to the β-melting peak and the minimum point, respectively.

Results and discussion

Effect of the content of β-nucleating agent on thermal behavior of iPP

From Fig. 1, it can be seen that neat iPP and nucleated iPPs with different content of β-nucleating agent crystallize at different temperatures after melted, and then are re-melted in different melting peak temperatures and enthalpy of fusion. The datas of T_{cp}, $T_{\alpha mp}$, $T_{\beta mp}$, ΔH_T, ΔH_β and ΔH_α are listed in Table 1. It is shown that β-nucleating agent can increase 10 °C than neat iPP in T_{cp}. When the content of β-nucleating agent in nucleated iPPs is more than 0.3 wt%, the crystallization temperature become lower and broader than the other nucleated iPPs, in which the onset of the crystallization temperature is the same as the samples which contain 0.2 and 0.3 wt% of β-nucleating agent. The reason probably is that the excess β-nucleating agent causes to agglomerate and results in the loss of efficiency in increasing the T_{cp} [8, 12]. However, it is hard to understand that the agglomeration takes place by increasing the amount of β-nucleating agent. Some evidences from SEM micrographs should be provided in another paper for a new explanation about the number of nucleating center and intercrossing growth between the boundaries of β-spherulites.

Effect of cooling rate on non-isothermal crystallization behavior of iPP

The datas of T_{cp}, $T_{\beta mp}$ and $T_{\alpha mp}$ at different cooling rates for the samples of G_1 and G_3 are listed in Table 2. It is shown that the T_{cp}, $T_{\beta mp}$ and $T_{\alpha mp}$ increase with decreasing cooling rate. The shape and area of the endothermic peaks are different at different cooling rates presented in Figs. 2 and 3. Higher $T_{\beta mp}$ on DSC melting curve has been interpreted that the process on low cooling rate provides enough time to form perfect crystals for the molecular chain of iPP. With increasing the cooling rate (shorter crystallization time), it results in the lower $T_{\beta mp}$ and broader endothermic peak for decreasing the crystal order in the sample and even occurring $\beta'\beta''$-recrystallization/reorganization at fast cooling rate with double-melting peak area of β-PP appearing on DSC melting curves in G_3. This causes the discrepancy to the conclusion of only one melting peak of β-phase of Varga et al. $T_{\beta mp}$ is in a good correspondence with the T_{cp} which indicates that low cooling rate is benefit to the perfection of crystal which consists with the above conclusion.

The ΔH_T has the same tendency with cooling rate in G_1 and G_3. The low cooling rate (enough crystallization time) is benefit to increase the content of crystal. It is worth noting that ΔH_β in G_1 increases with increasing cooling rate, while ΔH_β in G_3 represents a reverse tendency below the cooling rate of 20 °C min^{-1} and the same tendency above the cooling rate of 20 °C min^{-1} Figs. 2b and 3b.

Table 1 Cooling, melting peak temperature and enthalpy of fusion of α- and β-phase in the samples

Samples	T_{cp} (°C)	$T_{\alpha mp}$ (°C)	$T_{\beta mp}$ (°C)	ΔH_T (J g^{-1})	ΔH_β (J g^{-1})	ΔH_α (J g^{-1})
G_0	113.08	161.19	–	79.13	–	79.13
G_1	120.87	164.21	149.98	84.0	46.59	37.41
G_2	120.34	162.19	149.28	85.79	36.86	48.93
G_3	121.64	161.18	149.24	101.08	44.44	56.64
G_4	120.52	163.04	150.12	110.67	57.54	52.75

Table 2 Cooling and melting peak temperatures of α- and β-phase in G_1 and G_3 with different cooling rates

Cooling rate (°C min^{-1})	G_1			G_3		
	T_{cp} (°C)	$T_{\beta mp}$ (°C)	$T_{\alpha mp}$ (°C)	T_{cp} (°C)	$T_{\beta mp}$ (°C)	$T_{\alpha mp}$ (°C)
3	125.88	151.96	165.70	126.53	150.90	163.47
5	123.84	150.97	165.03	124.59	150.24	162.81
10	120.87	149.98	164.21	121.64	149.24	161.18
20	117.65	149.32	163.88	118.09	148.41	161.31
30	115.36	148.98	164.56	117.10	147.92	160.83
40	115.42	148.65	164.05	117.72	147.91	160.99
50	115.27	148.66	163.10	117.40	147.92	160.83

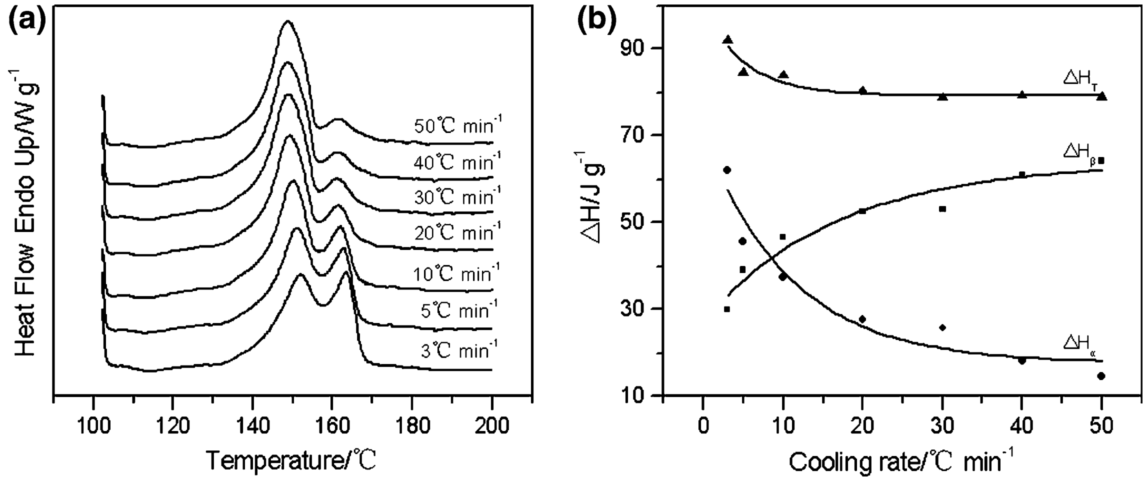

Fig. 2 Melting curves and enthalpy of fusion of G_1 at different cooling rates: **a** melting curves; **b** enthalpy of fusion

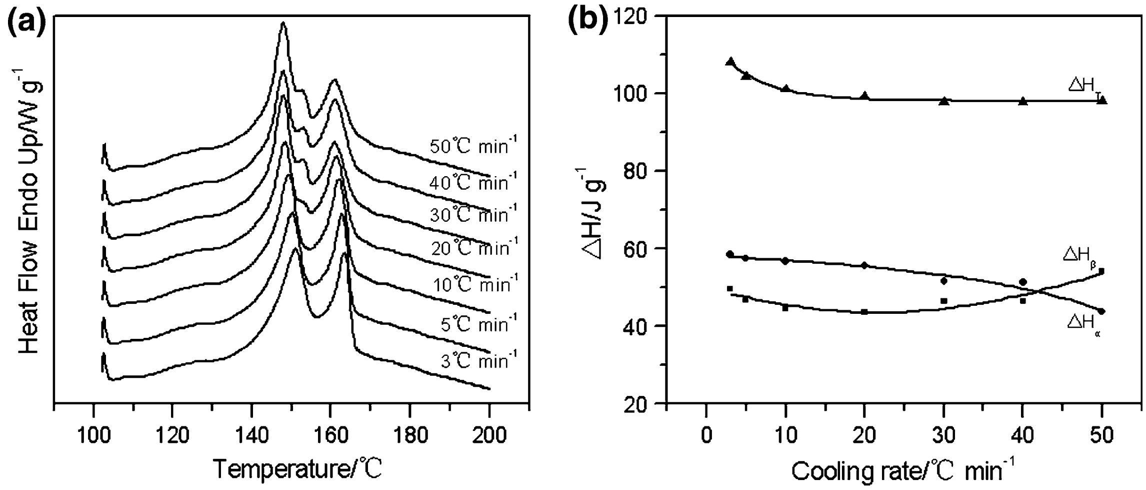

Fig. 3 Melting curves and enthalpy of fusion of G_3 at different cooling rates: **a** melting curves; **b** enthalpy of fusion

This phenomenon may be explained as the dependence of the content of β-phase on the cooling rate and the content of β-nucleating agent. In our opinion, the β-nucleating center in G_1 is dispersed sparsely to cover the whole sample in which the spacing between two nucleating centers is too far to grow into impinging other spherulites and forms some of α-spherulites between two β-spherulites at fast cooling rate. At low cooling rate, the far spacing results in the perfection structure and big size of β-spherulites which can impinge each other. Therefore the content of β-phase depends on not only the content of β-nucleating agent but also the cooling rate. The amount of nucleating

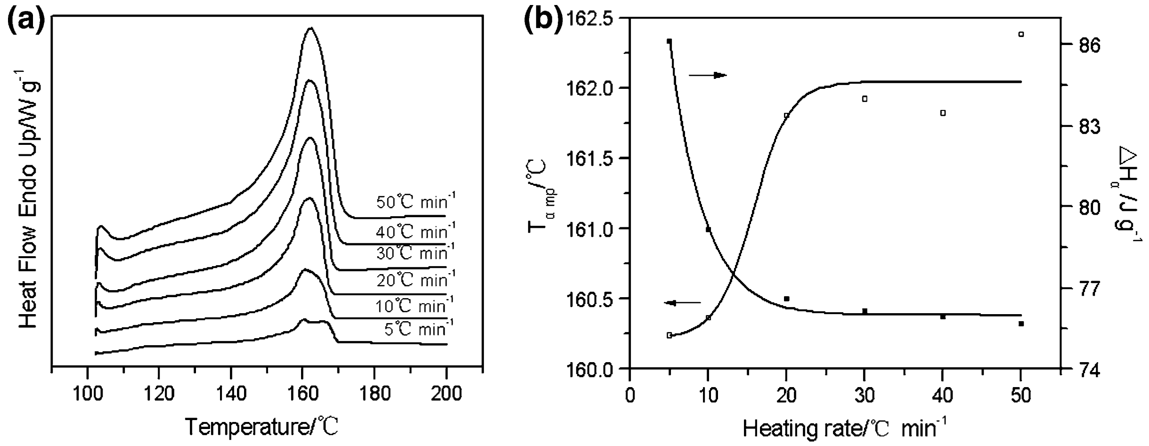

Fig. 4 **a** Melting curves of G_0 at different heating rates; **b** relationship between melting peak temperature of α-phase and enthalpy of fusion or heating rate

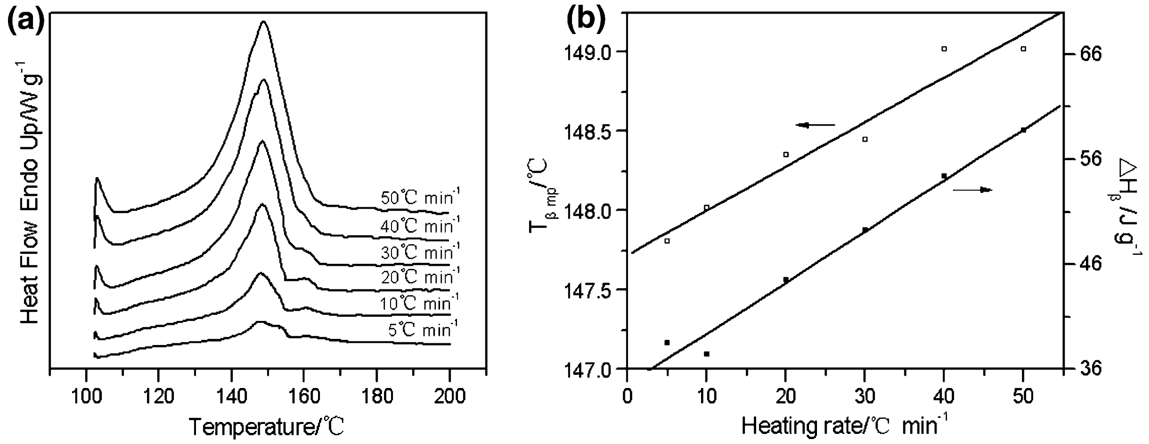

Fig. 5 **a** Melting curves of G_1 at different heating rates; **b** relationship between melting peak temperature of β-phase and enthalpy of fusion or heating rate

center in G_3 is large enough to disperse over the whole sample in the suitable place where the spherulites can grow up and impinge other spherulite whatever at fast cooling rate or low cooling rate. In the case, the action of β-nucleating agent is dominant.

Effect of heating rate on non-isothermal crystallization behavior of iPP

The melting behaviors of G_0, G_1 and G_3 at different heating rates from 5 to 50 °C min^{-1} are shown in Figs. 4, 5 and 6, respectively. At slow heating rate of 5 °C min^{-1}, double-melting peaks of α-phase in G_0 or β-phase in G_1 and G_3 are appeared on the melting curves. The interpretations of double-melting of α-PP are complicated and controversial [32–35]. With increasing the heating rate, the $T_{\alpha mp}$ (the second $T_{\alpha mp}$ is defaulted) increases presented in Fig. 4b, and then almost has a constant value, while the enthalpy of fusion has a reverse tendency. As can be seen from Figs. 5 and 6, the relationship between $T_{\beta mp}$ or enthalpy of fusion of β-phase and heating rate with different content of β-nucleating agent is different. A linear relationship between the $T_{\beta mp}$ or enthalpy of fusion of β-phase and heating rate is kept in G_1. However, the $T_{\beta mp}$ or enthalpy of fusion of β-phase shows a sigmoid relationship with heating rates in G_3. The second $T_{\alpha mp}$ or $T_{\beta mp}$ gradually reduces and then disappears above the heating rate of 20 °C min^{-1} seen in Figs. 4b, 5b and 6b which shows that fast heating rate inhibits the behavior of recrystallization/reorganization.

Effect of isothermal crystallization temperature on thermal behavior of iPP

The graphs of DSC in Figs. 7 and 8 are obtained for G_1 and G_3 crystallized at temperatures of 100, 110, 120, 130, 135, 140 °C, respectively. At the crystallization temperatures of 130 and 135 °C, nucleated iPP exhibit a higher perfection

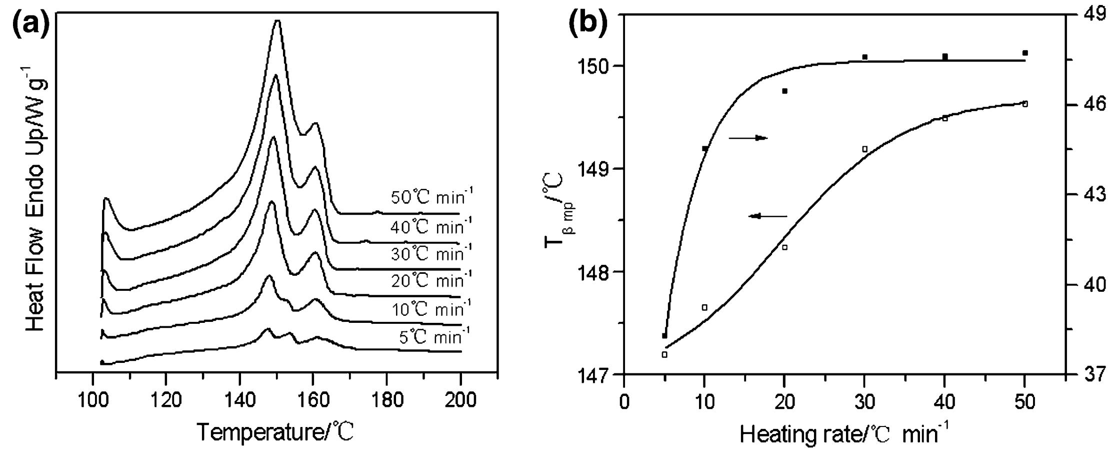

Fig. 6 **a** Melting curves of G_3 at different heating rates; **b** relationship between melting peak temperature of β-phase and enthalpy of fusion or heating rate

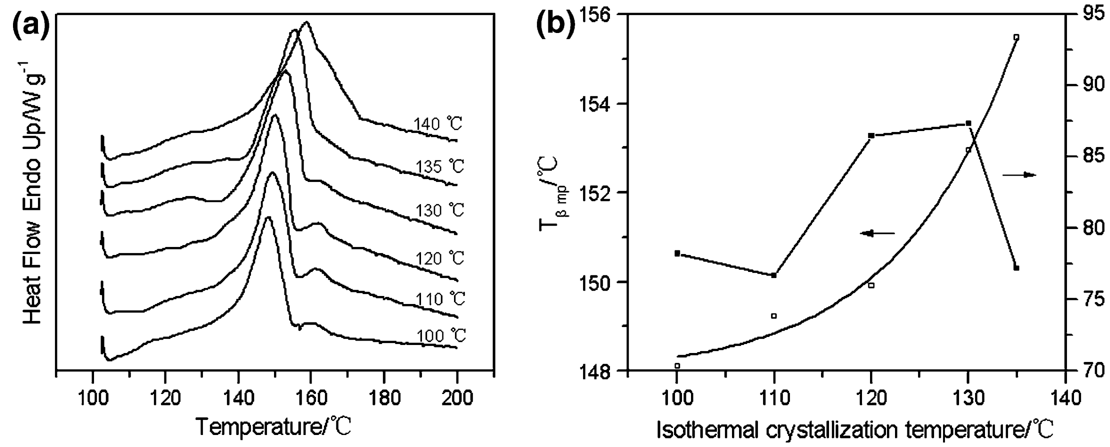

Fig. 7 **a** Melting curves of G_1 crystallized at different temperatures for 30 min; **b** relationship between isothermal crystallization temperature and melting peak temperature or enthalpy of fusion of β-phase

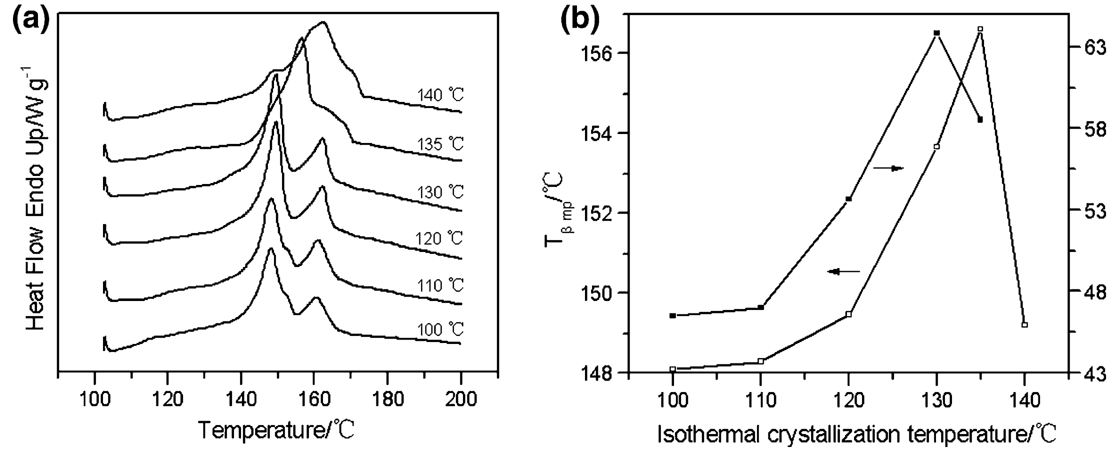

Fig. 8 **a** Melting curves of G_3 crystallized at different temperatures for 30 min; **b** relationship between isothermal crystallization temperature and melting peak temperature or enthalpy of fusion of β-phase

of β-form [28] and the content of β-phase which are shown by the increasing $T_{\beta mp}$ and ΔH_{β}. At the crystallization temperatures of 100, 110 and 120 °C, the lamella of β-form in nucleated iPP is lack of perfection and the content of β-phase is less than it at 130 and 135 °C. It is disadvantageous to the growth of β-form at crystallization temperature of 140 °C, at which almost all of the crystals are α-form. There are three melting peaks of α-phase which are named T_L, T_M and T_H, respectively, and observed by Zhang et al. [36]. It is shown that the crystallization temperature of nucleated iPP consists with the setting value (about 130 °C) which is the most beneficial to the perfection of the crystals. The shape and location of peaks for G_1 and G_3 crystallized at a certain temperature are almost same, but the content of β-phase in G_1 is more than it in G_3 and the content of α-phase in G_3 is more than it in G_1 shown in Figs. 7 and 8.

Conclusions

For the samples with different content of β-nucleating agent, the effects of cooling rate and crystallization temperature on the content of α- and β-phase and the structure of crystal are different. Proper content of β-nucleating agent (about 0.2–0.3 wt%) is effective to increase crystallization peak temperature. Under non-isothermal crystallization, the content and structure of the crystal are strongly affected by both cooling rate and the content of β-nucleating agent. The enthalpy of fusion of β-phase in G_1 and G_3 represent different tendencies when cooling rate is under 20 °C min^{-1}. The melting peak temperatures or enthalpy of fusion of β-phase with heating rate has different tendency with different content of β-nucleating agent. Under isothermal crystallization, the enthalpy of fusion of β-phase for G_1 is higher than G_3. Whatever on non-isothermal or isothermal crystallization, the α-phase in G_3 forms more easier than it in G_1. The fast cooling rate with high content of β-nucleating agent and slow heating rate can lead to occur the $\beta'\beta''$-recrystallization/reorganization.

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