

Comparative Investigation on Crystallization Conditions Dependence of Polymorphs Composition for β -Nucleated Propylene/Ethylene Copolymer and Propylene Homopolymer

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ABSTRACT: The crystallization conditions dependence of polymorphs composition in β nucleated propylene/ethylene copolymers (PPR) and propylene homopolymers (PPH) were comparatively investigated via wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) measurements. It is interesting to note that the amount of β form as a function of crystallization conditions presents an opposite trend for the β nucleated PPR and the β nucleated PPH under the conditions we investigated. For the β nucleated copolymers, the content of β form shows also an opposite tendency with that of γ form with the change of crystallization conditions. The formation of γ form is preferred under lower cooling rates or higher isothermal crystallization temperatures, whereas

the amount of β form increased with increasing the cooling rates or decreasing the isothermal temperatures. This opposite tendency could be interpreted in terms of the competition between the β nucleation ability of β nucleating agent and the γ nucleation action of the comonomer defects. The existing comonomer defects that favor the formation of γ form may suppress the nucleation ability of β nucleating agent. A higher proportion of β form in PPR containing a β nucleating agent could be achieved under faster cooling rates or lower crystallization temperatures. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3247–3254, 2010

Key words: propylene/ethylene copolymer; crystallization; polymorphism

INTRODUCTION

Isotactic polypropylene (iPP) has developed into one of the most useful plastics materials with a large family of homopolymerized polypropylene (PPH), random-copolymerized polypropylene (PPR), and block-copolymerized polypropylene (PPB, i.e. polypropylene in-reactor alloys). It is widely used in many applications, owing to a combination of outstanding properties and low cost. A primary limitation of PPH is its unsatisfactory impact strength, especially at low temperatures. Copolymerization of propylene with other olefins is a useful method to overcome this shortcoming and its copolymers have been presenting diverse promising properties.^{1–3} Random copolymer of propylene with low content

ethylene is one of the successful examples. A small amount of randomly inserted ethylene could be regarded as chemical defects along the iPP chains, which induces a better transparency and higher impact strength compared with PPH.^{3–7} As a semi-crystalline polymeric material, these improved final properties of PPR are strongly depended upon its crystallization characteristics, which is closely related to the process conditions and intrinsic macromolecular structures.^{4,5}

As widely acknowledged, iPP is a typical polymorphic material with several crystalline forms, such as α , β , and γ form, as well as a intermediate order mesomorphic phase.^{8–13} The mesomorphic phase between crystalline and amorphous phases is usually obtained on rapid cooling from the melt and may be considered as a frozen intermediate ordering state during crystallization, which is caused by a quenching solidification process, which hinders molecular motions necessary for crystallization.^{11–13} The most common crystalline form is α form, while the occurrence of β or γ crystalline form is observed only under special conditions. A higher proportion of the β form can be achieved only by melt crystallization with the aid of certain heterogeneous nucleating agents,^{14–16} by directional crystallization

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in certain temperature gradients,¹⁷ or from melts subject to shear.¹⁸ Among these means, the addition of so-called β nucleating agents is the most effective and practical method.^{15,16,19} Crystallization of iPP in γ form is strongly dependent upon the crystallization pressures and macromolecular structure. The occurrence of γ form has been reported in various iPP samples crystallized from melt under elevated pressures,^{20,21} or in PPH with low molecular weights,²² with the presence of chain defects or chemical heterogeneity caused by atacticity,^{23,24} and especially in PPR with small amount of ethylene.^{25–29}

Compared with PPH, the disturbance of regularity of polymer chain by the inclusion of the comonomer defects in PPR highly enhances the tendency to γ -crystallization. Since Turner-Jones et al.²⁵ firstly revealed the effect of ethylene comonomeric units on the γ form development, the competition between α and γ forms in PPR have been intensively studied by many workers,^{26,27} it is found that the amount of γ form is proportional to the ethylene content and lower cooling rates are also in favor of the formation of γ form. Foresta et al.²⁸ and Shi et al.²⁹ also confirmed the early findings proposed by Turner-Jones et al. and found that some traditional α nucleating agents could enhance the γ form formation.

From a practical point of view, the β form is the most attractive one because of its improved impact-resistance.^{10,16} A particular growth feature of β form is the transformation from metastable β form into α form.^{10,15,30} Many studies dealt with the kinetic characteristics of growths of iPP contained a certain content of β form and these comprehensive investigations revealed that the formation of β form had an upper and lower (threshold) temperature, $T(\beta\alpha) \sim 140^\circ\text{C}$ and $T(\alpha\beta) \sim 100^\circ\text{C}$, respectively.^{10,30} Zhang et al.³¹ and Varga et al.³² found that a disturbance of regularity of iPP chain results in a reduced tendency to β crystallization and the temperature range to form β form is narrower for PPR than PPH. This might be ascribed to the fact that the growth rate of α form is always higher than that of β form during the kinetic measurements of isothermal growth in PPR.^{16,33} In addition, a thermodynamically controlled transition from β to α crystallization may also appear during the crystallization. Varga³² found that this phenomenon might be lowered by increasing the density of the β -nuclei in the resin, e.g. by increasing the concentration of the nucleating agent. More recently, Na et al.³⁴ found that the introduction of a β nucleating agent based on N,N' -dicyclohexylterephthalamide could induce the formation of both the β form and γ form in PPR at low cooling rates, and they ascribed this to the nucleating duality of used nucleating agent. Busse et al.³⁵ found that the polymorphs of PPR may be tuned by changing the polymer composition, adding the nucleating

agent and choosing an appropriate crystallization temperature regime under isothermal condition. Although more and more attention have been paid to the β nucleated PPR, the interrelation of various crystalline forms and the dependence of special crystalline forms on crystallization condition, as well as the methodology for controlling the composition of polymorphs in PPR, are yet to be studied in greater detail.

With the progress in research of β -nucleating agents, more and more effective β -nucleating agents have been developed and successfully applied. Up to now, four classes of commercial available β -nucleating agents are widely used: a minority of aromatic ring compounds such as γ -quinacridone (Dye Permanent Red E3B),^{14,36} two-component mixtures based on pimelic acid and calcium stearate,^{31,37} calcium salts of some dicarboxylic acids such as suberate and calcium pimelate,^{38–40} and substituted aromatic bisamides including N,N' -dicyclohexylterephthalamide and N,N' -dicyclohexyl-2,6-naphthalene dicarboxamide.^{41–46} We early found that a rare earth β nucleating agent could effectively induce the formation of β form in PPH,^{19,47} Therefore, in this work, we used this β nucleating agent to study the effects of crystallization conditions on the polymorphism and crystallization behavior of β nucleated propylene/ethylene copolymer and propylene homopolymer under isothermal and nonisothermal conditions. These results would be helpful for developing the technique of controllably tailoring the proportions of modifications composition of polypropylene as well as the final properties.

EXPERIMENTAL

Materials and samples preparation

A propylene/ethylene random copolymer (PPR), C4220, produced by Yanshan Petrochemical Co. (Beijing, China) was used: it has a melt flow rate (MFR) of 0.3 g/10 min (230°C, 2.160 kg) and the ethylene content is about 5 mol %. The Ziegler-Natta propylene homopolymer (PPH) used was F401, which has a MFR of 2.5 g/10 min and isotactic index of 96.5%. The β nucleating agent, WBG, was a heteronuclear dimetal complex of lanthanum and calcium. It was kindly provided by Guangdong Winner Functional Materials Co., (Foshan City, China). Introduction of the β nucleating agent into the polymer was performed by melt blending using a PLE-651 Brabender Mixer (Brabender, Germany) at 180°C. The nucleated PPR and PPH containing both 0.08 wt % of WBG denoted as PPR-008 and PPH-008, respectively, for convenience. The obtained mixtures were subsequently molded into 0.4-mm thick sheets at 190°C in a press under a pressure of 15 MPa for 5 min

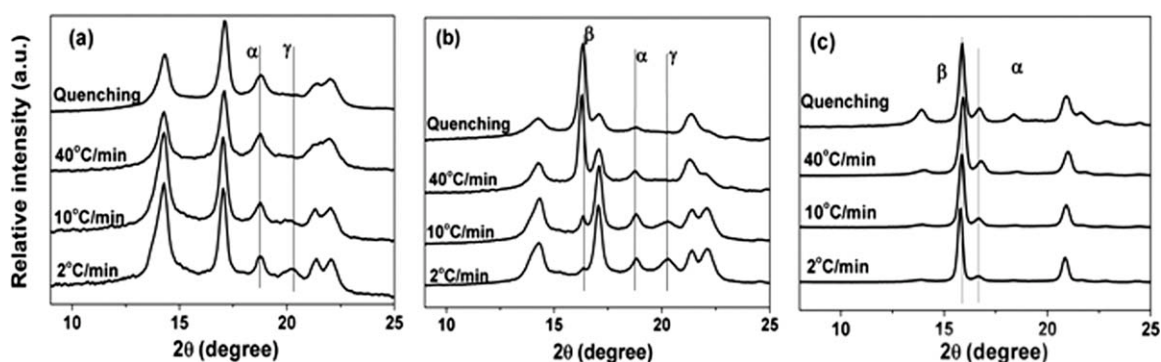


Figure 1 X-ray diffraction patterns of samples crystallized at various cooling rates for (a) neat PPR, (b) PPR-008, and (c) PPH-008.

and then quenched to room temperature. We estimated that the cooling rate of samples subjected to during thus quenching treatment is approximately 90–110°C/min. To investigate the crystallization behaviors of samples under nonisothermal conditions, the sheets with thickness of 0.4 mm were also prepared by first melting at 200°C for 5 min and then cooling to 40°C at different cooling rates ranging from 2 to 40°C/min controlled by a hot stage (THMS600 Linkam, England). The temperature of hot stage can be kept constant within 0.1°C and nitrogen gas was purged through the hot stage during measurements. Crystallization from the melt of PPR-008 samples were also performed under isothermal conditions ranging from 110 to 128°C controlled by the same hot stage.

Measurement

Wide angle X-ray diffraction (WAXD) measurements were performed using a PANalytical X'pert diffractometer (PANalytical, Netherlands) in a reflection mode using Ni-filtered CuK α radiation under 40 kV and 40 mA. Radial scans of intensity versus diffraction angle 2θ were recorded in the region of 5°–25°. The method proposed by Obadal et al.²⁰ was used to determine the fraction of each crystalline from WAXD data for all the samples in this study. The spherulitic morphologies of PPR-008 crystallized under cooling rates of 2 and 40°C/min were respectively observed using an Olympus BX-51 polarized light microscope (PLM) (Olympus, Japan) with the Linkam-THM600 hot stage. The samples for PLM observation were prepared by melting and squeezing to films. These films were kept in hot stage between two microscope slides and each sample was heated to 200°C and kept at this temperature for 5 min to erase its thermal history before subsequently cooled to room temperature at different cooling rates. DSC measurements were performed using a DSC822e Thermal Analysis System (Mettler-Toledo Instruments, Switzerland) in nitrogen atmosphere.

Samples crystallized under different cooling rates were firstly heated to 200°C at a rate of 10°C/min and maintained there for 5 min, then cooled to 40°C at 10°C/min to record the melting and crystallization process.

RESULTS AND DISCUSSION

Polymorphism under nonisothermal conditions

WAXD patterns of neat PPR, PPR-008, and PPH-008 nonisothermally crystallized at various cooling rates, as well as the relative proportions of different polymorphs as functions of the cooling rates are shown in Figures 1 and 2, respectively. For the neat PPR [Figs. 1(a) and 2(a)], there is no β form present under all cooling rates used in this work. As demonstrated by many previous workers, the amount of γ form largely decreased and α form increased in neat PPR with the increase of the cooling rate,^{26,27} and our work accords with this very well. In the case of PPR-008 [Figs. 1(b) and 2(b)], the occurrence of β form is observed and its proportion is increased with the increased cooling rate. The relative proportion of the β form in the crystalline part, which was determined by WAXD data using the method proposed by Obadal et al.,²⁰ is only 7% for the sample crystallized at a cooling rate of 2°C/min, while this value is up to 53 and 69% for the 40°C/min crystallized sample and the quenching sample, respectively (the cooling rate for quenching was simply treated as 100°C/min). These results are also confirmed in the morphological features. Figure 3(a,b) show the PLM photographs of PPR-008 crystallized at 2°C/min and 40°C/min, respectively. For the PPR-008 crystallized at 2°C/min, the ultimate crystallized spherulitic structure is large and perfect, with an obvious Maltese cross and a radius about 50–100 μm which indicates the dominant structure is α form. However, for the PPR-008 crystallized at 40°C/min, as shown in Figure 3(b), the spherulites size became much smaller and a large amount of β -spherulites with

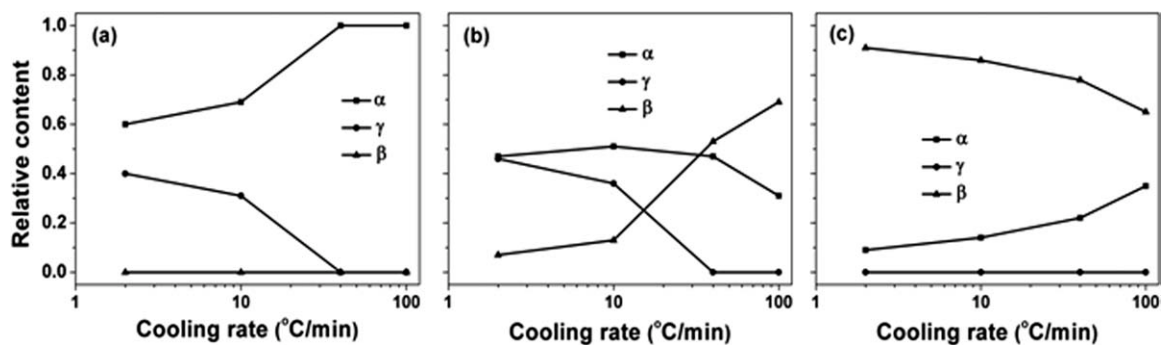


Figure 2 Relative proportions of various polymorphs as function of the cooling rates for (a) neat PPR, (b) PPR-008, and (c) PPH-008.

higher birefringence can be observed in the final morphology.

Analogously to neat PPR, the γ form in PPR-008 is only obtained under low cooling rates and its content largely decreased at high cooling rates. It is observed the occurrence of β form shows the absolutely opposite tendency as γ form in PPR-008 under nonisothermal conditions we used. For control, the polymorphism behavior of β nucleated PPH was also investigated. In the β nucleated PPH sample PPH-008 [Figs. 1(c) and 2(c)], it can be seen that no any γ form occurrence and the proportion of β form slightly decreases with the increasing of the cooling rate. It is interesting to note that the amount of β form as a function of the cooling rate in β nucleated Ziegler-Natta PPH follows a trend opposite to that in β nucleated PPR.

Recently, Krache et al.⁴⁰ found that the amount of β form as a function of the cooling rate in β nucleating agent containing metallocenic PPH similarly followed a trend opposite to that in the Ziegler-Natta PPH. They ascribed these behaviors to the different type and distribution of the insertion defects along the polymer chains. The distribution of the defects influences the average length of the crystallizable sequences and then influences the crystallization

behavior of PPH. In the case of metallocenic PPH, the distribution of the defects is random and even a very small amount of defects could reduce the length of the regular isotactic sequence leading to the formation the γ crystalline form.^{26–28} On the contrary, the majority of defects may be segregated in a small fraction of poorly crystallizable area and much longer regular isotactic sequence could be produced for Ziegler-Natta PPH, inducing the crystallization of the α form even with a relatively high concentration of defects.⁴⁸

Similarly to metallocenic PPH, the comonomer defects which randomly distributed along the chains in PPR (the insertion defect is stereodeflect or regio-defect in metallocenic PPH while that is comonomer defect in PPR) maybe lead to a shorter of the regular isotactic sequence and γ form is therefore easier to obtain. The majority of defects may be segregated in a small fraction of poorly crystallizable area and much longer regular isotactic sequence could be produced for Ziegler-Natta PPH. The opposite trend of the amount of β form as a function of the cooling rate for PPR-008 and PPH-008 may be ascribed to the inclusion of randomly distributed ethylene monomer defects along the polymer chains in PPR. In sample PPR-008, the opposite tendency for γ and

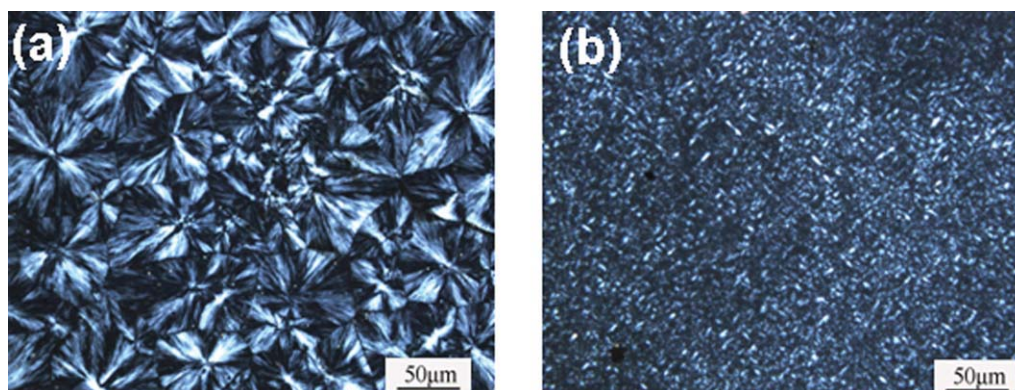


Figure 3 PLM photographs of PPR-008 nonisothermally crystallized at 2°C/min (a) and 40°C/min (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

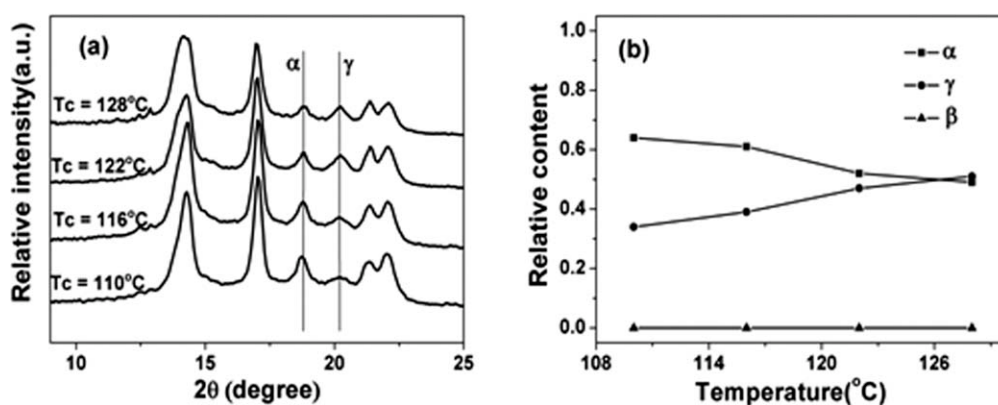


Figure 4 X-ray diffraction patterns (a) and relative proportions of various polymorphs (b) as function of the isothermal temperatures for neat PPR sample.

β form content may be attributed to the competition between the nucleation effect of β nucleating agent inducing the formation of the β form and the γ nucleation ability of the comonomer defects in PPR, the existing comonomer defects largely suppressed the effect of the β nucleating agent at low cooling rates.

Polymorphism under isothermal conditions

The polymorphs of PPR with and without β nucleating agent were also investigated under isothermal crystallization conditions. A number of previous reports^{26,27} suggested that a mixture of α and γ forms frequently existed in the neat PPR under isothermal conditions and increasing the crystallization temperature favors the formation of γ form. As shown in Figure 4(a), no features associated with β form on the WAXD patterns of neat PPR, but two peaks stand for α form at $2\Theta = 18.5^\circ$ and that at $2\Theta = 20.1^\circ$ accounting the γ form, are observed under all the crystallization temperatures studied. It means that a mixture of α and γ forms existed in the neat copolymer. The detailed composition of the crystal-

line forms determined from Figure 4(a) are shown in Figure 4(b). The relative content of γ form is only 34% at the temperature of 110°C , while this value increased to 51% at the temperature of 128°C . The γ form is preferred with a higher crystallization temperature and this result shows a good correspondence with the early findings.^{26,27} On the WAXD patterns of PPR-008 samples [Fig. 5(a)], the (300) diffraction peak of β form located at $2\Theta = 16.0^\circ$ appeared and its intensity is more pronounced for the sample isothermally crystallized at lower temperature. The relative proportions of various polymorphs as function of the crystallization temperatures are shown in Figure 5(b). It can be concluded that the γ form in PPR-008 is increased with increasing the crystallization temperature, which is similar to the neat PPR samples, while the amount of the β form presents a trend just opposite to that for the γ form. The lower the crystallization temperature, the higher amount of β form could be obtained.

It is well known that for β nucleated Ziegler-Natta PPH, larger amounts of β form were easy to obtain when crystallized at relatively higher crystallization

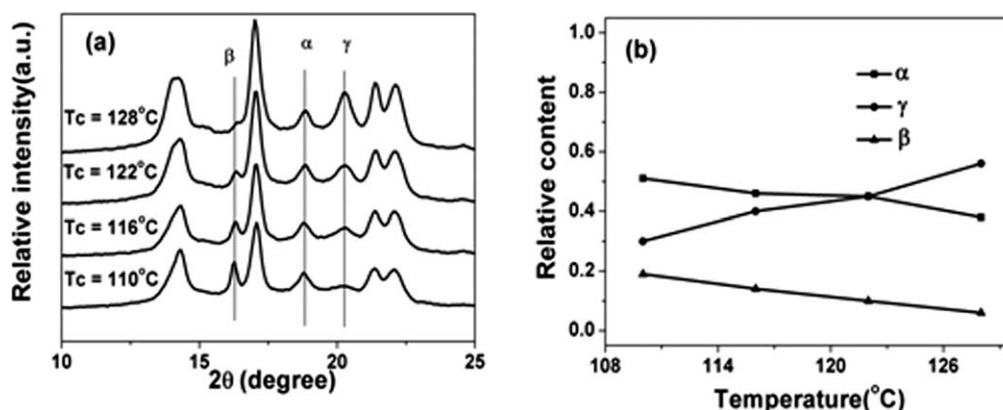


Figure 5 X-ray diffraction patterns (a) and relative proportions of various polymorphs (b) as function of the isothermal temperatures for the PPR-008 sample.

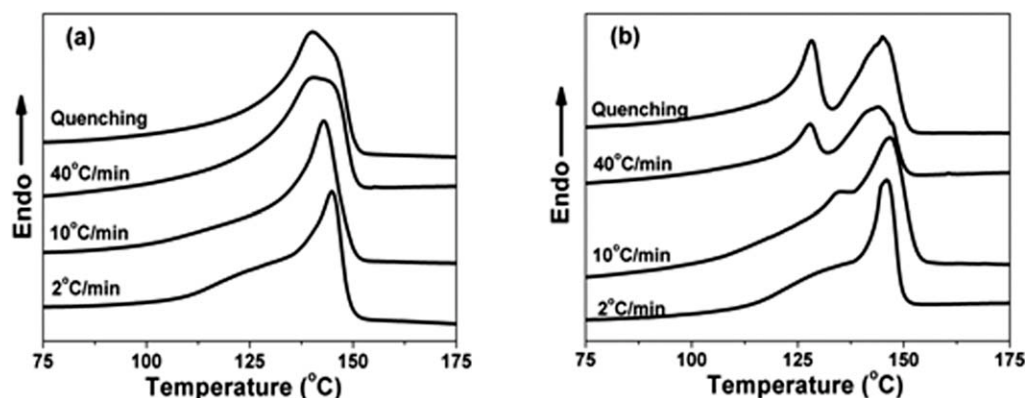


Figure 6 DSC melting traces of PPR (a) and PPR-008 (b) crystallized under various cooling conditions.

temperatures and the proportion of the β form in this system is increased with the crystallization temperature.⁴⁰ In vivid contrast, as shown from Figure 5(b), the content of the β form in PPR-008 is about 20% at a crystallization temperature of 110°C, while this value decreased to only 6% when crystallized under 128°C. These results reveal that the β nucleating agent induced more β form and the nucleating agent is more effective in inducing the formation of β form under relatively low temperatures. Because the chain regularity of PPR has been disturbed by the introduction of the comonomer units and the PPR usually crystallizes at lower temperature at which the PPH crystallizes too fast to accurately record, it is difficult to compare the isothermal crystallization behavior of PPR and PPH in the same range of crystallization temperature. However, in the temperature range we investigated here, the opposite crystallization temperature dependence of the proportion of β form for β nucleated PPH and PPR is unquestionable.

The crystallization process of PP can be divided into two steps: nucleation and growth. In principle, the overall crystallization rate is nucleation-controlled at high temperatures and growth controlled at low temperatures.^{49,50} In other words, within certain temperature range, the effect of the present nucleating is more obvious under higher crystallization temperatures where the self nucleation of PP is difficult and the nucleating agents could offer large amounts of heterogeneous nuclei. In β nucleated PPR system, the comonomer defects which favors the formation of γ form largely suppressed the nucleation ability of β nucleating agent that induces the formation of the β form. At a high crystallization temperature or low cooling rate, ethylene comonomer units in PPR acting as configurational chain defects could easily favor the growth of the γ form, and this effect predominates over the efficiency of the β nucleating agent. Therefore, it is observed that the present β nucleating agent could only induce rel-

atively higher amount of β form under a lower crystallization temperature or a faster cooling rate where the γ nucleation ability of the comonomer is weak.

Melting and crystallization behavior

The polymorphic behavior of PPR and PPR-008 samples prepared at various cooling rates were also investigated with DSC measurements. The DSC traces of first heating scan for samples cut from these 0.4-mm thick sheets, which were also used for WAXD measures as mentioned in Section 3.1, were recorded and shown in Figure 6. In the case of pure PPR [Fig. 6(a)], there is only a single melting peak at peak temperature of 141–145°C, which may be contributed to the melting of α form, for all samples crystallized at different cooling rates. The melting curves shift to a higher temperature with decreasing cooling rate, which may attribute to the annealing effect during the crystallization. However, for the β -nucleated specimens [Fig. 6(b)], these traces exhibit multiple endotherms which may be assigned to the existence of α and β crystalline forms.^{31,32} The endotherm at lower peak temperature of located at 128–134°C could be associated with the melting of the β form while another endotherm located at 144–146°C is characteristic for the melting of the α form. The calorimetric curves usually cannot give exact quantitative information on the polymorphic composition unless the possible β - α transformation may be eliminated during the melting process.^{10,30,31} In this work, to ensure the completion of the nonisothermal crystallization, all the β nucleated PPR samples were cooled to temperatures far below than the $T(\alpha\beta)$, which is approximately 100°C for PPH. As a result, the β - α transformation is obviously occurred during the melting process of β nucleated PPR samples. However, the relative proportion of α or β crystalline form could be approximately estimated from the relative intensities of the two different endotherms on the corresponding melting curves. It can be seen that

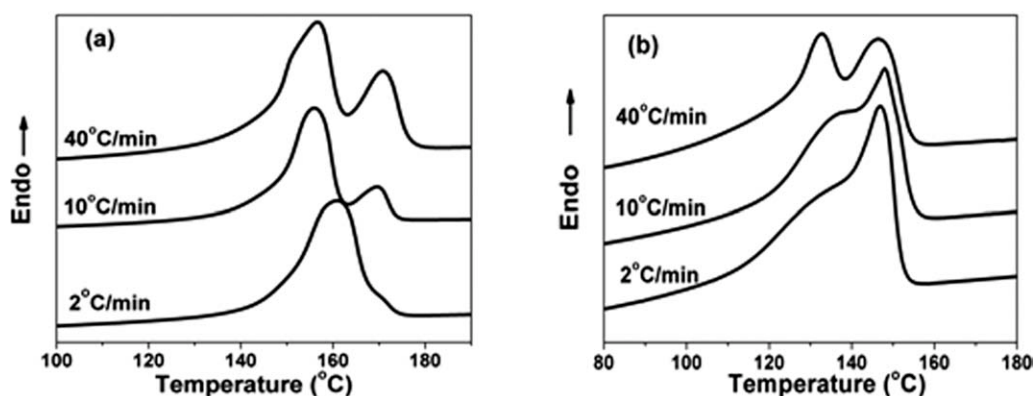


Figure 7 DSC second melting traces of PPH-008 (a) and PPR-008 (b) crystallized at various cooling rates.

on DSC traces of the quenching sample or 40°C/min crystallized sample, the peak associated with β form are in evidence, while only quite a small peak appearing at lower temperatures for the sample crystallized at 2°C/min. These results suggested that the β form is easier to obtain in PPR-008 under higher cooling rates and the relative amount of β crystalline form decreased with the lowering of cooling rates.

In addition to the first melting traces, the second melting traces of samples were also recorded by DSC to further confirm the cooling rates dependence of composition of various crystalline forms. After first heating to 200°C and keeping at there for 5 min to eliminate processing history, each sample were cooled 40°C at cooling rate of 40, 10, and 2°C/min, and subsequently heated again to 200°C at an identical rate of 10°C/min. The DSC second melting traces of PPH-008 and PPR-008 are shown in Figure 7. From Figure 7(a), it can be found that the relative proportion of the peak for β form is increased with decreasing the cooling rates. Almost only melting peak for β form may be observed on the melting traces of PPH-008 crystallized at cooling rate of 2°C/min. In contrast, as shown in Figure 7(b), the relative proportion of the peak for β form is decreased with decreasing the cooling rates. Both the DSC and WAXD measurements give the same conclusion on the proportion of each crystalline form as functions of crystallization conditions: the β form is easier to obtain under higher cooling rates for β nucleated PPR.

To investigate the effect of β nucleating agent on the crystallization process of PPR and PPH, nonisothermal experiments were performed and the corresponding DSC curves are shown in Figure 8. After eliminating the thermal history, each sample was cooled from 200 to 40°C at 10°C/min to determine the temperature at which the maximum rate of crystallization occurs. It can be seen that the crystallization peak temperature is 127°C for PPH-008, which is higher 10°C than that of neat PPH. For PPR-008,

this temperature is only enhanced by 4°C compared with the neat PPR. The weaker nucleation effect of β nucleating agent in PPR-008 could also be revealed in the final crystalline structures. Under the identical cooling condition (e.g. at 10°C/min), the addition of 0.08 wt % nucleating agent could only induce the formation of 13% of the β form in PPR-008, whereas the same amount of nucleating agent could lead to the crystallization of 86% of the β form in PPH-008. It could be explained that the nucleation effect of β nucleating agent in PPR is largely depressed by the comonomer defects which could induce the formation of the γ form.

CONCLUSIONS

The polymorphism and crystallization behavior of a propylene/ethylene copolymer (PPR) crystallized in the presence of a β nucleating agent was studied under nonisothermal or isothermal conditions. It is evident that the polymorphism behavior of the copolymer is strongly dependent on the addition of the

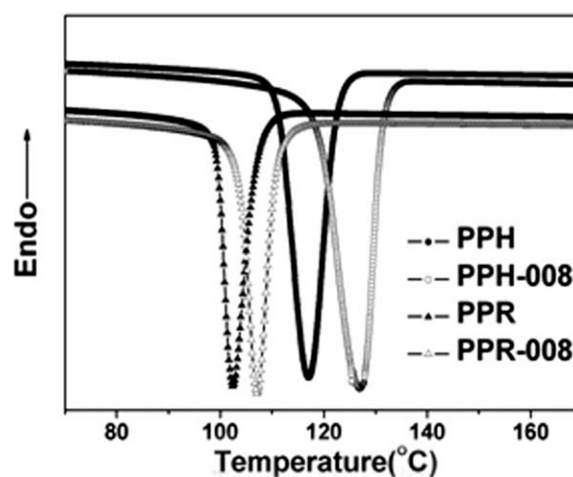


Figure 8 DSC crystallization curves for the indicated samples.

nucleating agent and the crystallization conditions. For the PPR, the β form can be additionally introduced with the addition of β nucleating agent and three-phase crystalline systems could be obtained. Higher amount of β form is preferred under a faster cooling rate or a higher isothermal crystallization temperature for the conditions investigated in this work. The change of the amount of β form shows an absolutely opposite tendency as γ form in β nucleated PPR were observed both under nonisothermal and isothermal conditions. It is interesting to find that the amount of β form as a function of the cooling rate or isothermal crystallization temperature in β nucleated PPR follows a trend opposite to that in β nucleated Ziegler-Natta PPH. These behaviors could be explained by the competition between the nucleation of β nucleating agent inducing the formation of the β form and the γ nucleation ability of the comonomer defects.

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