

A Novel Highly Efficient β -Nucleating Agent for Isotactic Polypropylene

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ABSTRACT: A novel highly efficient β -nucleating agent for isotactic polypropylene (iPP), hexahydrophthalic barium (HHPA-Ba), was found and its effects on the mechanical properties, the β -phase content, and crystallization behavior of iPP were investigated, respectively. The results show that the β -phase content of nucleated iPP (k_{β} value) can reach 80.2% with 0.4 wt % HHPA-Ba. The impact strength and crystallization peak temperature of nucleated iPP are greatly increased. Compared with pure iPP, the impact strength of nucleated iPP can increase 2.4

times. Meanwhile, the spherulite size of nucleated iPP is dramatically decreased than that of pure iPP. The Caze method was used to investigate the nonisothermal crystallization kinetics of nucleated iPP and the crystallization active energy was achieved by Kissinger method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 108–117, 2012

Key words: polypropylene; nucleating agent; crystallization behavior

INTRODUCTION

Recently, β -nucleated isotactic polypropylene (β -iPP) has received considerable interests due to its excellent thermal and mechanical performance.^{1–23} The toughness and heat distortion temperature of β -iPP are much higher than that of the α -iPP, which is very important from the viewpoint of industrial application. However, due to its lower stability in comparison with the α -modification the β -modification occurs sporadically and can only be formed under some critical conditions such as quenching the melt to a certain temperature range,^{4,5} directional crystallization in a thermal gradient field,^{6,7} shearing or elongation of the melt during crystallization,⁸ vibration-induced crystallization,^{9,10} or using β -nucleating agents.^{11–23}

Of these methods the addition of β -nucleating agents is the most effective to obtain a high level of the β -phase. Until now, only three classifications of compounds have been mainly used as β -nucleating agents: the first one is organic pigment,^{11–13} such as γ -quinacridone (Dye Permanent Red E3B), Indigosol

Gray/IBL, Indigosol Golden Yellow IGK, and Cibantine Blue 2B; the second one includes a minority of aromatic amide compounds,^{14–16} such as *N,N'*-dicyclohexylterephthalamide and *N,N'*-dicyclohexyl-2,6-naphthalene dicarboxamide (trade name NJStar NU-100); the third classification comprises certain Group IIA metal salts or their mixtures with some specific dicarboxylic acids.^{17–19} Of the third classification, all the β -nucleating agents which had been found were calcium carboxylate, such as calcium salt of pimelic acid and suberic acid and compounds of calcium stearate and pimelic acid. So far, there are no literatures about barium carboxylate acting as β -nucleating agents. Although American patent²⁴ has reported that metal salts of hexahydrophthalic acid can act as nucleating agents of polypropylene, it did not point out they can act as β -nucleating agents. It is well known that nucleating agents have two types of α - and β -nucleating agents. α -nucleating agents can improve the transparency and stiffness of iPP while β -nucleating agent can improve the toughness of iPP. Obviously, “nucleating and/or clarifying agents” in the patent means “ α -nucleating agents” because it only showed the effect of metal salts of hexahydrophthalic acid on the transparency (haze value) and stiffness (secant modulus) of polypropylene while not showed their effect on the toughness (impact strength or other parameters related to toughness). Meanwhile, the patent point out that barium salt of hexahydrophthalic acid is a highly ineffective nucleating agent. In our study, we found that barium salt of hexahydrophthalic acid (HHPA-Ba) was a highly efficient β -nucleating agent for iPP.

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In this article, the effects of the novel β -nucleating agent HHPA-Ba on the mechanical properties, the β -phase content, crystallization peak temperature (T_p), and the crystal morphology of iPP were investigated. In addition, the nonisothermal crystallization kinetics of both pure iPP and iPP/HHPA-Ba were investigated by using the Caze method.²⁵ The crystallization activation energy was evaluated by Kissinger's method.²⁶

EXPERIMENTAL

Materials

The isotactic polypropylene (iPP) (trade name T30S) used in this study was kindly provided by Jiujiang Petroleum Chemical (China), with a melt flow index (MFI) of 2.9 g/10 min (230°C/2.16 kg), $M_w = 24.4 \times 10^4$ g mol⁻¹, and $M_w/M_n = 4.05$. The β -nucleating agent is barium salt of hexahydrophthalic acid (HHPA-Ba), which is synthesized according to the patent.²⁴ The results of carbon and hydrogen elemental analyses, thermogravimetric analysis (TG), and infrared spectroscopy of HHPA-Ba indicate that its simple molecular structure corresponds to BaOOC₆H₁₀COO.H₂O. According to DSC and TG results under nitrogen atmosphere, HHPA-Ba loses its crystal water in the temperature range from 120 to 180°C and then the temperature corresponding to 1 wt % weight loss is $\sim 460^\circ\text{C}$. Therefore, BaOOC₆H₁₀COO play the role of nucleus and has excellent thermal stability at the processing condition.

Sample preparation

The β -nucleating agent HHPA-Ba, antioxidant (Irganox 1010 and 168, 0.1 wt % of iPP powders, respectively) and the iPP powders were dry-blended by high-speed mixer for 5 min. Then the mixture was extruded by a twin-screw extruder (SJSH-30, Nanjing Rubber and Plastics Machinery Plant, China) through a strand die and pelletized. The pellets were molded into standard test specimens by an injection-molding machine (CJ-80E, Guangdong Zhende Plastics Machinery Plant, China). The concentrations of the nucleating agent were 0.025, 0.05, 0.075, 0.1, 0.2, 0.4, and 0.8 wt % and the samples were denoted as PP0.25, PP0.5, PP0.75, PP1, PP2, PP4, and PP8, respectively. The pure iPP sample was designated as PP0, which was prepared by the same method for comparison.

Mechanical properties

The mechanical properties were measured according to ASTM test methods, such as D-638 for the tensile

strength and D-790 for the flexural modulus, using a universal testing machine (Shanghai D and G Measure Instrument, China). The Izod impact strength was tested on the basis of D-256, using an impact tester (Chengde Precision Tester, China). The reported values of the mechanical properties were averaged at five independent measurements.

Differential scanning calorimetry (DSC)

DSC (Diamond, Perkin-Elmer, USA) was carried out to measure the β -phase content, study the crystallization peak temperature, and analyze the nonisothermal crystallization kinetics. Temperature was calibrated before the measurements by using Indium as a standard medium.

β Fraction (β_c): β_c was estimated from DSC by the following expression²⁷:

$$\beta_c = (1 - \lambda)_\beta / [(1 - \lambda)_\beta + (1 - \lambda)_\alpha] \quad (1)$$

The degree of crystallinity ($1 - \lambda$) associated with each phase can be calculated from the ratio $\Delta H_a / \Delta H_u$, where ΔH_a and ΔH_u are the apparent and completely crystalline heats of fusion, respectively. The values of 177.0 and 168.5 J g⁻¹ were used for the ΔH_u for 100% crystalline α -iPP and 100% crystalline β -iPP, respectively.²⁸

The crystallization peak temperature (T_p) was determined from the crystallization curves. Measurements were performed with the samples of 3–5 mg at a standard heating and cooling rate of 10°C min⁻¹ under nitrogen starting from 50 to 200°C, and the samples were held at 200°C for 5 min to erase the thermal and mechanical history.

Nonisothermal crystallization experiments were carried out by cooling samples (PP0 and PP4) from 200 to 50°C by using different cooling rates. The exotherms were recorded at the cooling rates of 2.5, 5, 10, 20, and 40°C min⁻¹, respectively.

Polarized optical microscopy (POM)

The morphology studies of pure iPP and nucleated iPP were performed with the aid of an Olympus BX51 (Tokyo, Japan) polarized optical microscopy attached with a DP70 digital camera, and a THMS600 hot-stage (Linkam Scientific Instruments, UK). The extruded samples were placed between two microscopy slides, melted and pressed at 200°C for 5 min to erase any trace of crystal, and then rapidly cooled to a predetermined crystallization temperature. The samples were kept isothermal until the crystallization process was completed, and meanwhile, photographs were automatically taken.

Wide-angle X-ray scattering (WAXD)

Wide-angle X-ray scattering (WAXD) patterns were recorded in transmission with a Rigaku D/max-2550VB/PC apparatus (Japan). The wavelength used was Cu K α ($\lambda = 1.54 \text{ \AA}$) and spectra were recorded in the 2θ range of 5° – 35° (8° min^{-1}). The content of the β -crystal modification was determined according to standard procedures described in the literature,²⁹ employing the relation

$$k_\beta = \frac{H_\beta(300)}{H_\beta(300) + H_\alpha(110) + H_\alpha(040) + H_\alpha(130)} \quad (2)$$

where k_β denotes the relative content of β -phase (WAXD), $H_{\Omega(\text{hkl})}$ denotes the intensity of the respective (hkl) peak belonging to phase Ω (α or β ; always with respect to the amorphous halo).

Theory of nonisothermal crystallization

The Avrami equation^{30,31} is widely used to describe the polymer isothermal crystallization.

$$X_t = 1 - \exp(-Z(T)t^n) \quad (3)$$

where X_t is the relative crystallinity at time t , n is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, and $Z(T)$ is a constant containing the nucleation and growth parameters.

The Avrami equation has been extended by Ozawa³² to develop a simple method to study the nonisothermal experiment. The general form of Ozawa theory is written as follows:

$$X_v(T) = 1 - \exp(-K_T/\phi^m) \quad (4)$$

where K_T is the cooling crystallization function, ϕ is the cooling rate, and m is the Ozawa exponent that depends on the dimension of the crystal growth. But there is a main hypothesis in Ozawa method that n is independent of temperature and only a limited number of X_v data are available for the foregoing analysis, as the onset of crystallization varies considerably with the cooling rate.

Caze et al.²⁴ put forward a new method to modify Ozawa equation. They have assumed an exponential increase of K_T with T upon cooling. On the basis, the temperature at the peak and the two inflection points of the exotherm with skew Gaussian shape are linearly related to $\ln\phi$ to estimate the exponent n .

On the basis of the findings on the crystallization behavior of poly(ethylene terephthalate) and PP, Kim et al. proposed³³

$$\ln K_T = a(T - T_1) \quad (5)$$

where a and T_1 are empirical constants. If the extreme point of the pertinent $\partial X_v(T)/\partial T$ curve occurs at $T = T_q$ (crystallization peak temperature), i.e., $(\partial^2 X_v(T)/\partial T^2) T_q = 0$, we have:

$$K_T(T_q) = \phi^n \quad (6)$$

Combining eqs. (4)–(6) yields:

$$\ln[-\ln(1 - X_v(T))] = a(T - T_q) \quad (7)$$

Hence, a linear plot of $\ln[-\ln(1 - X_v(T))]$ against T would result in the constant a and the product $-aT_q$ from the gradient and intercept, respectively. At $T = T_q$ obtained from the foregoing algorithm, eqs. (6) and (7) lead to:

$$T_q = n \ln \phi / a + T_1 \quad (8)$$

As such, parameter n can be obtained from the linear plot of T_q against $\ln\phi/a$ in accordance with Eq. (8).

RESULTS AND DISCUSSION

Mechanical behavior

From the viewpoint of industrial application, it is necessary to investigate the effects of nucleating agent on mechanical properties. The effects of the novel nucleating agent HHPA-Ba on mechanical properties of iPP are shown in Figure 1.

The impact strength increase rapidly when HHPA-Ba is less than 0.4 wt %, and then keep constant with the further increase of HHPA-Ba. When the content of HHPA-Ba is 0.4 wt %, the impact strength of nucleated iPP was improved about 2.4 times compared with that of pure iPP, indicating that HHPA-Ba could significantly improve the toughness of iPP. From Figure 1(b,c), it can be seen that the tensile strength and flexural modulus of nucleated iPP slightly increase when the HHPA-Ba content is 0.025 wt % and then decreased rapidly with the increasing HHPA-Ba content. The tensile strength and flexural modulus of nucleated iPP reach a minimum when the HHPA-Ba content is 0.4 and 0.2 wt %, respectively, and then slightly increases with continuously higher agent content. The results show a reverse tendency with that of impact strength. Therefore, the 0.4 wt % seems to be a saturated concentration for HHPA-Ba.

Effect of the nucleating agent on the β -phase content of iPP

DSC and WAXD were usually used to characterize the β -phase content of iPP. However, the β -phase

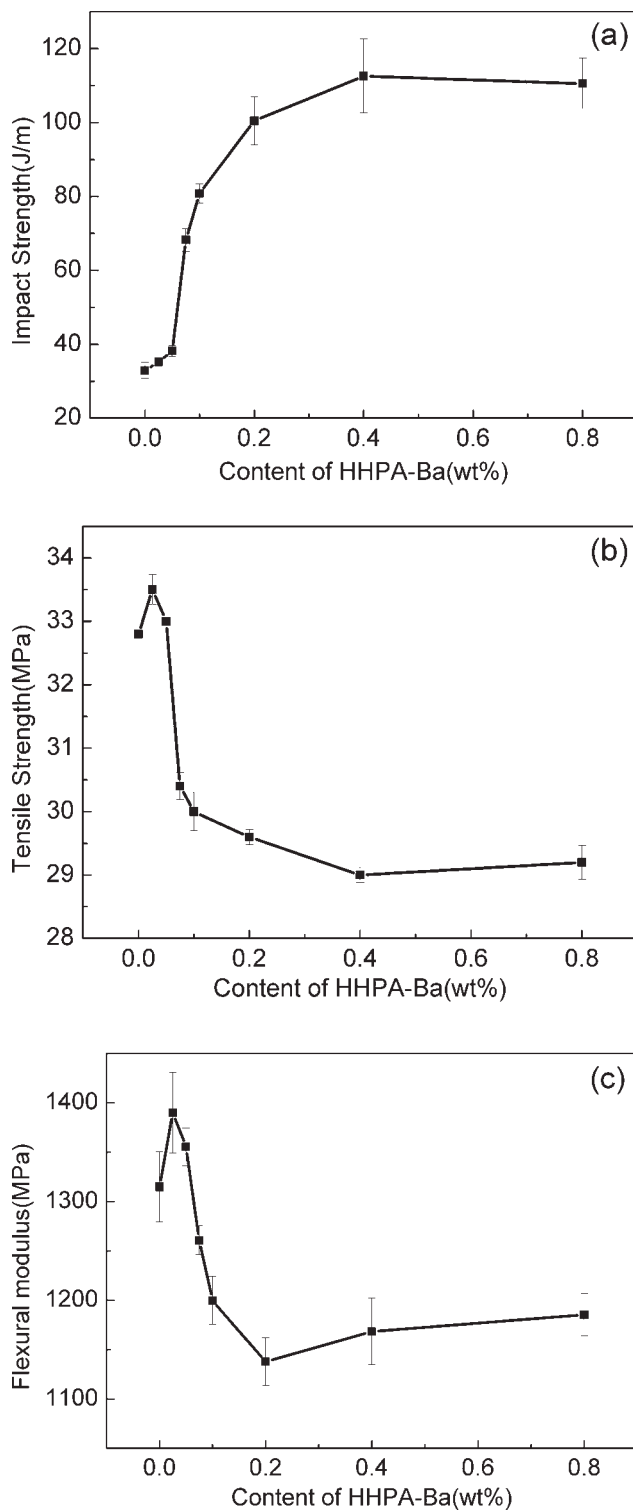


Figure 1 Mechanical properties of iPP as a function of HHPA-Ba content, (a) impact strength, (b) tensile strength, (c) flexural modulus.

content of iPP was not accurately calculated by DSC melting curves. One reason is that the exact determination of the β -phases is difficult by using DSC because the melting peaks of the α - and β -phases overlap each other. Another reason is the effect of

$\beta\alpha$ -recrystallization.^{34–36} β -iPP cooled below the critical temperature ($T_R^* = 100^\circ\text{C}$) reheated recrystallises into the α -phases through the partial melting of the β -phases ($\beta\alpha$ -recrystallization), which leads to an enhanced apparent α -content determined from the melting curves. Such recrystallization seriously complicates the proper determination of polymorphic composition. Therefore, the WAXD is more accurate than DSC to characterize the β -phase content of iPP. Therefore, for the quantification of the β -phase content in isothermally crystallized iPP samples, wide-angle X-ray diffraction (WAXD) was used. Figure 2 illustrates the WAXD patterns of PP0 and PP4 crystallized at 135°C under quiescent condition.

In this profile, (110) at $2\theta = 14.1^\circ$, (040) at 16.9° , (130) at 18.5° are the principal reflections of the α -phases of iPP, while (300) at about 16° is the principle reflection of the β -phases. They are considered as the marker peaks for α - and β -phases, respectively. It shows only α -phases exist in pure iPP. Comparing with that of pure iPP, an obvious difference can be seen in the pattern of iPP nucleated with 0.4 wt % HHPA-Ba. In this pattern, the (300) reflection of β -phases is clearly seen at 2θ about 16° , and its intensity is greater than that of α -phases. The k_β value of PP4 reaches 80.2%, which indicates that HHPA-Ba is an effective β -nucleating agent for iPP.

The effect of HHPA-Ba content on the k_β values is showed in Figure 3. The results show that the k_β value rapidly increases with the addition of HHPA-Ba, reaches 75.4% when HHPA-Ba percentage is 0.1 wt %, and then basically keep constant with a further increase of HHPA-Ba. The above results indicate that HHPA-Ba is an effective β -nucleating agent even at a low working concentration for iPP. However, HHPA-Ba is not a completely selective β -nucleating agent, as the related samples always contain

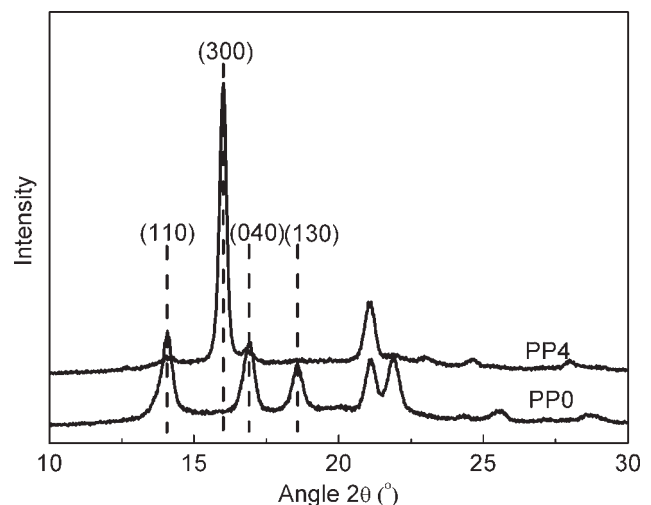


Figure 2 WAXD patterns of sample PP0 and PP4 crystallizing at 135°C under quiescent condition.

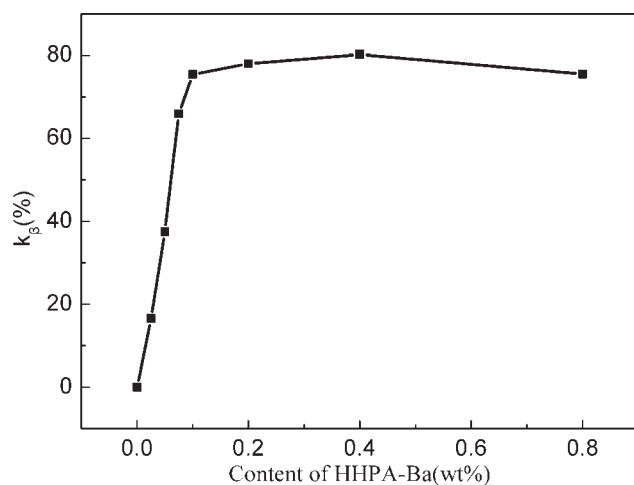


Figure 3 k_{β} value as a function of HHPA-Ba content.

both α - and β -modifications of iPP. The changing trend of k_{β} values is basically consistent with that of the impact strength for iPP/HHPA-Ba, which indicates that the improvement of impact strength of iPP is most likely from the increased content of β -phases. However, it is noted that the saturation concentration of HHPA-Ba from the results of mechanical properties and WAXD is different, which may result from the difference of crystallization condition of both measurement. Therefore, it is necessary to investigate the effect of crystallization condition on the β -phase content.

The effect of the cooling rate on the β -phase content of iPP

Most β -nucleating agents are sensitive to cooling rate.^{37,38} Therefore, DSC was applied to investigate the effect of cooling rate on the β -phase content. The melting curves of iPP nucleated with 0.4 wt % HHPA-Ba after crystallizing under different cooling rates are showed in Figure 4. The melting peak at low temperature is attributed to the β -phase and that at high temperature belongs to the α -phase. It can be seen that with the cooling rate decreased the melting peak temperature of α - and β -phase gradually increased. This phenomenon can be explained by the perfect degree of crystals. It is well known that the crystals are more perfect and the melting temperature is higher when iPP crystallizes in higher temperature. The slower the cooling rate, the longer will the crystallization time at high temperature area becomes, which resulted in increase of the perfect degree of crystals.

From the Figure 4 the β -phase content (β_c) was calculated by Eq. (1) and the result is listed in Figure 5. From Figure 5, it is found that the β -content gradually increased with the decrease of cooling rate. The β_c is 38% when the cooling rate is $100^{\circ}\text{C min}^{-1}$,

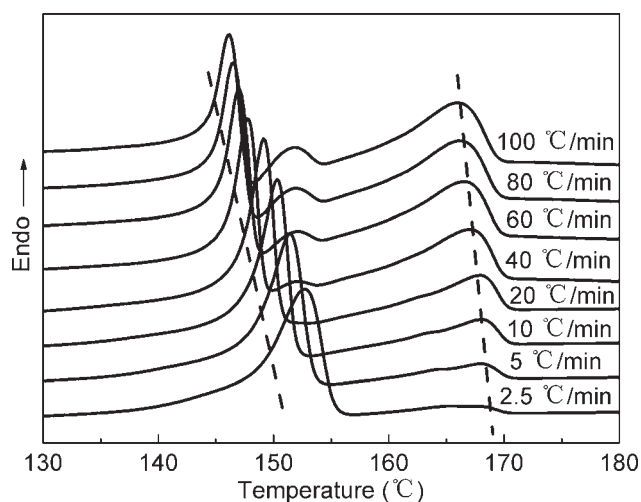


Figure 4 The melting curves of PP4 crystallizing at different cooling rates.

while it reaches 93.2% when the cooling rate is $2.5^{\circ}\text{C min}^{-1}$. The results showed that cooling rate greatly affect the β -phase content and lower cooling rate is favorable to the formation of β -phase for iPP nucleated with HHPA-Ba.

Crystallization behavior

To check the effect of the nucleating agent on crystallization behavior, the crystallization curves of iPP with different HHPA-Ba contents are plotted in Figure 6.

For the pure iPP (PP0), T_p is around 120°C . However, the incorporation of 0.2 wt % of the nucleating agent in the polymer produces a marked shift of the crystallization peak toward higher temperature ($T_p = 125^{\circ}\text{C}$). T_p of iPP shifts to higher temperature with the increasing of HHPA-Ba content. Figure 7 shows a plot of T_p as a function of HHPA-Ba content. It

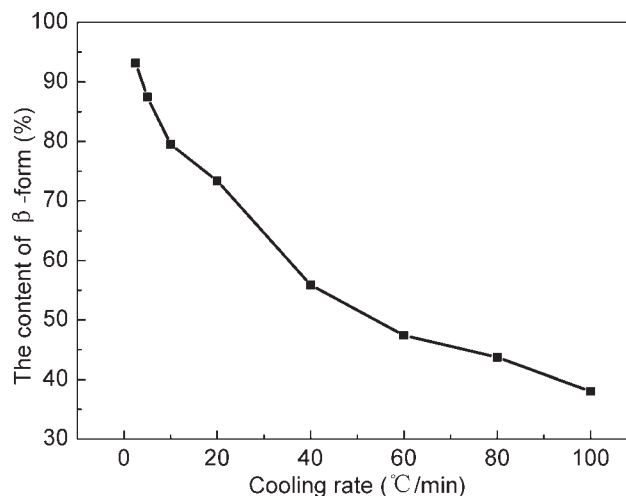


Figure 5 The β -phase content (β_c) as a function of cooling rates.

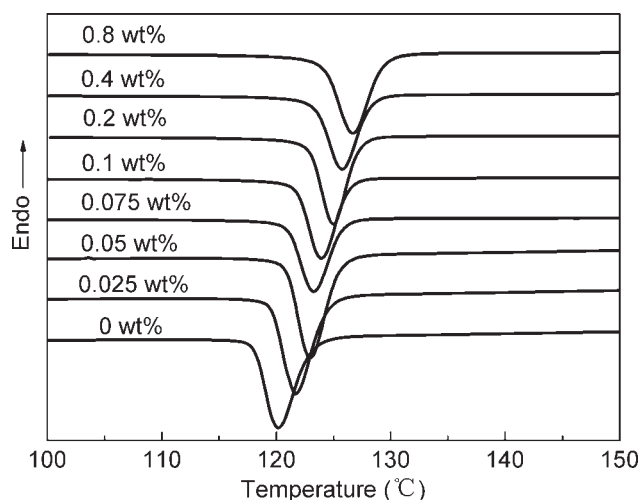


Figure 6 Crystallization curves of pure iPP and nucleated iPP.

can be seen that the increase of T_p is very strong when the content of HHPA-Ba is lower than 0.2 wt %, while that is weak when the content of HHPA-Ba is higher than 0.2 wt %. It indicates that more nucleating agent is less effective in increasing the crystallization peak temperature further.

β-nucleating agent affects not only the crystal form but also morphology of iPP. POM was applied to study the effect of HHPA-Ba on morphology of iPP. Polarized optical micrographs of pure iPP and nucleated iPP crystallized at 135°C are shown in Figure 8. The incorporation of HHPA-Ba induces the form of bright and colorized β-iPP which is like feather [Fig. 8(b,c)]. The spherulite diameter of pure iPP is more than 100 μm, and the incorporation of HHPA-Ba decreases the spherulite sizes. Because of the existence of a plenty of nucleus in the iPP/HHPA-Ba, the spherulites grow so fast that they overlap with each other. Therefore, the spherulite size of nucleated iPP is much smaller than that of virgin iPP. Furthermore, the spherulite size significantly decreases before the HHPA-Ba content reaches 0.2 wt % and then slightly decreases with the increasing HHPA-Ba content. This is in good agreement with the results of crystallization peak temperature.

Nonisothermal crystallization kinetics

Crystallization process of semicrystalline polymers can have a dramatic impact on the mechanical properties and hence is important in the final application. Practical processes usually proceed under nonisothermal crystallization conditions. To search for the optimum conditions in the industrial process and obtain products with better properties, it is necessary to have quantitative evaluations on the nonisothermal crystallization process. The 0.4 wt % content

of HHPA-Ba is chosen considering the fact that nucleated iPP shows better comprehensive mechanical properties at the content. The nonisothermal crystallization of iPP and nucleated iPP was carried out by DSC with cooling rates from 2.5 to 40°C min⁻¹. The thermograms of virgin iPP and nucleated iPP are plotted in Figure 9. It is evident that the crystallization temperature is affected by the cooling rate. The higher the cooling rate is, the lower the crystallization peak temperature becomes. Furthermore, it can be recognized that, at the same cooling rates, T_p of nucleated iPP is greatly increased compared with virgin iPP.

By means of integrating the partial areas under the DSC endotherm, the values of the crystalline weight fraction $X_w(T)$ can be obtained, as shown in Figure 10.

Crystallization half-time $t_{1/2}$ can be obtained from Figure 10 by equation $t = (T_0 - T)/\phi$ (where t is crystallization time, T_0 is the onset crystallization temperature, T is crystallization temperature at $X_w(T) = 50\%$ and ϕ is cooling rate). The results are listed in Table I. It can be seen that the addition of HHPA-Ba can obviously shorten $t_{1/2}$ of iPP, especially at lower cooling rate. When the cooling rate is 2.5°C min⁻¹, $t_{1/2}$ of PP4 is 93.6 s while that of PP0 is 150.5 s.

Now $X_w(T)$ can be converted into $X_v(T)$ by Eq. (9)³³:

$$X_v(T) = \frac{X_w(T) \frac{\rho_a}{\rho_c}}{1 - \left(1 - \frac{\rho_a}{\rho_c}\right) X_w(T)} \tag{9}$$

where ρ_a and ρ_c are the bulk densities of the polymer in the amorphous and pure α or β crystalline states, respectively. For iPP, the density of the amorphous phase is $\rho_a = 0.852$, and those of the pure α-

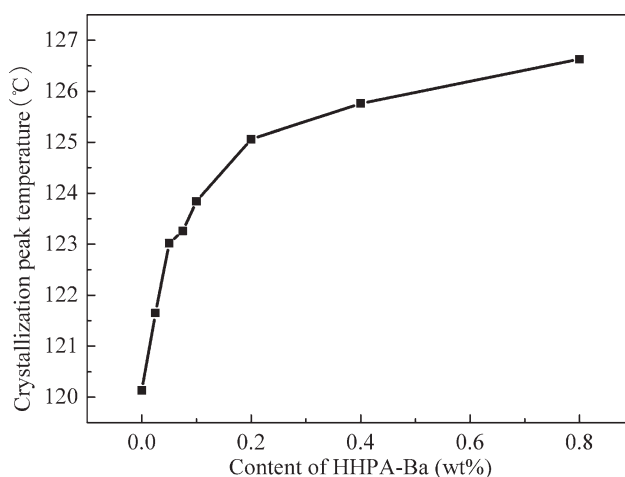


Figure 7 Dependence of the crystallization peak temperature on the content of HHPA-Ba.

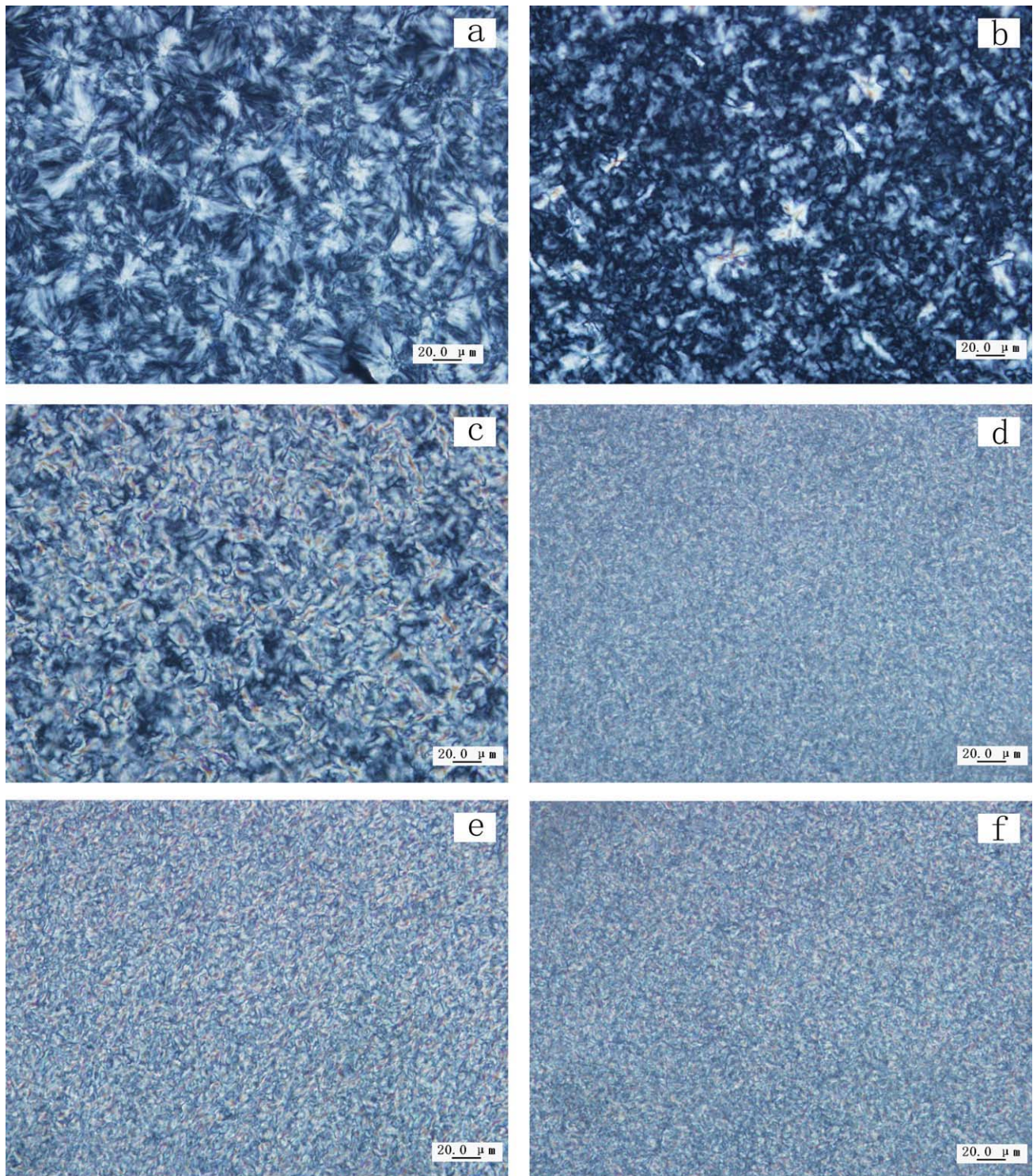


Figure 8 Polarized light microphotographs of morphology of (a) PP0, (b) PP0.25, (c) PP0.5, (d) PP1, (e) PP2, and (f) PP4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phase and pure β -phase are $\rho_{c\alpha} = 0.936^{39,40}$ and $\rho_{c\beta} = 0.922^{41,42}$ respectively. Accordingly, plots of $\ln[-\ln(1 - X_v(T))]$ versus T can be obtained (Fig. 11) and there is a good linear relationship in the initial crystallization stage. The values of a and $-aT_q$ can be determined from the slope and intercept of

each straight line, and the results are also listed in Table I.

Straight lines can be obtained from plots of T_q versus $\ln\phi/a$ under different cooling rates (Fig. 12), and Avrami exponents of iPP and nucleated iPP can be determined from the slope of each straight line. The

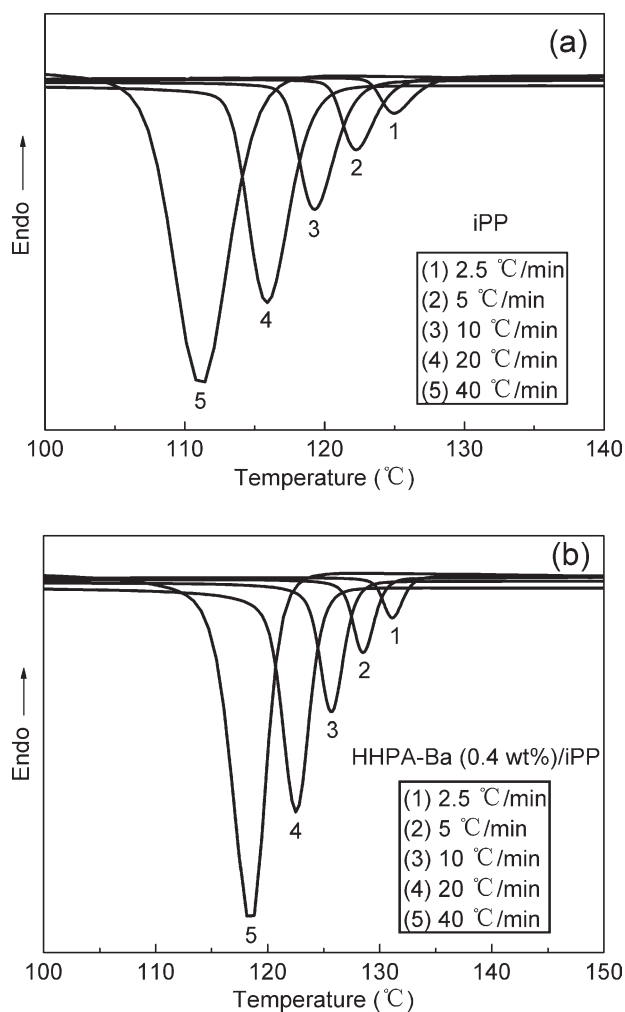


Figure 9 DSC cooling curves of (a) PP0 and (b) PP4.

results are also listed in Table I. It is known that Avrami exponent n strongly depends on both the mechanism of nucleation and morphology of crystal growth. The results show that the Avrami exponents of both pure iPP and nucleated iPP are close to 4. The Avrami exponent n of pure iPP indicates homogeneous nucleation and three-dimension spherical

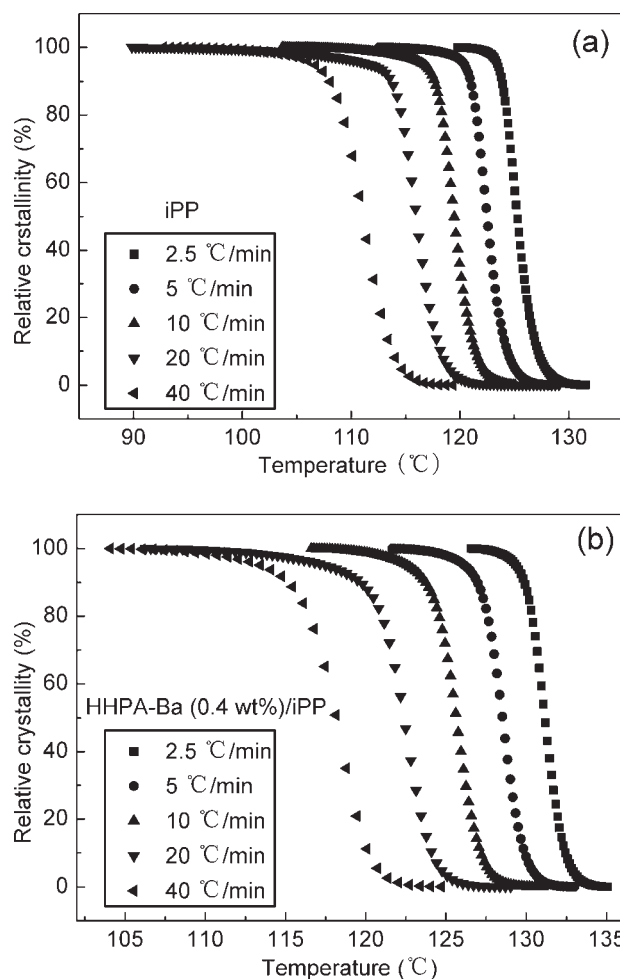


Figure 10 Relative crystallinity of (a) PP0 and (b) PP4 at different cooling rates.

growth, which had been confirmed by the POM micrographs [Fig. 8(a)]. For the nucleated iPP, heterogeneous nucleation has been confirmed by POM micrographs [Fig. 8(f)], which shows HHPA-Ba is an effective nucleating agent. Therefore, the Avrami exponent n for nucleated iPP could explain that the crystal growth occurs with heterogeneous nucleation

TABLE I
Nonisothermal Crystallization Kinetics Parameters of PP0 and PP4

Sample	Φ (°C min ⁻¹)	T_p^a (°C)	a	T_q^b (°C)	$t_{1/2}$ (s)	n
PP0	2.5	125.0	-1.09	125.0	150.5	3.93 ± 0.14
	5.0	122.3	-1.12	122.2	68.8	
	10	119.3	-1.07	119.2	33.8	
	20	115.9	-0.91	115.6	23.4	
	40	111.5	-0.85	110.8	11.4	
PP4	2.5	131.1	-1.68	131.0	93.6	4.33 ± 0.14
	5.0	128.5	-1.55	128.3	54.0	
	10	125.6	-1.37	125.4	32.4	
	20	122.5	-1.15	122.0	20.0	
	40	118.1	-1.05	117.8	9.8	

^a Determined from Fig. 9.

^b Calculated from Caze method.

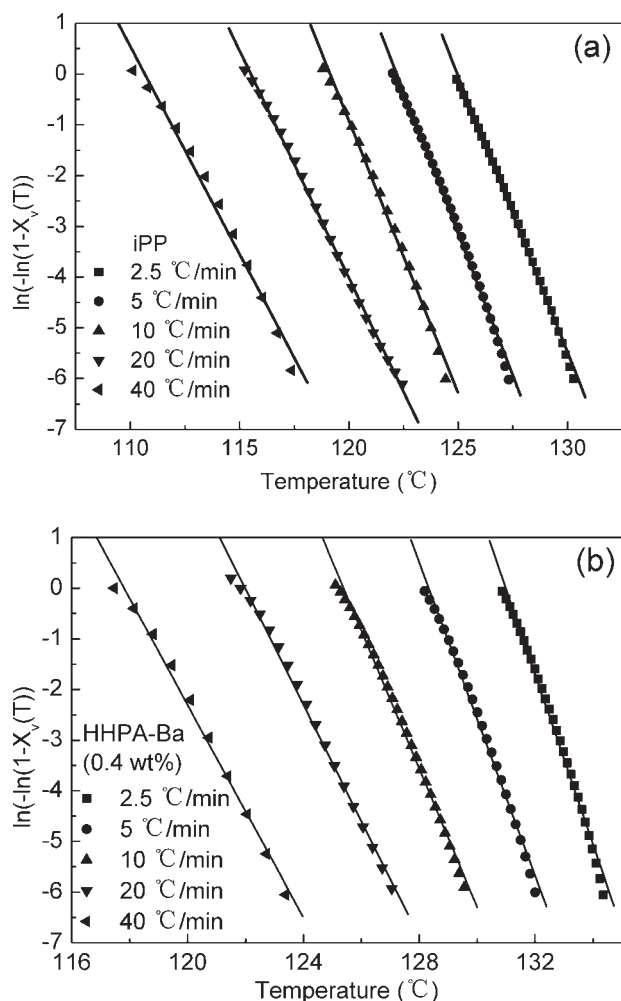


Figure 11 Plots of $\ln[-\ln(1 - X_v(T))]$ versus T for (a) PP0 and (b) PP4.

and multi-dimension growth. In the study of Fujimori et al.⁴³ and Wen Liang et al.,⁴⁴ the multi-dimension growth geometry was correlated with sheaf-like structures.

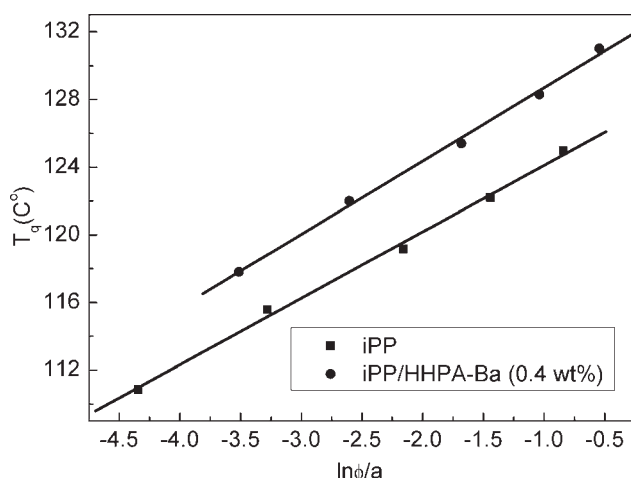


Figure 12 Plots of T_g versus $\ln\phi/a$ for PP0 and PP4.

Crystallization active energy

Considering the influence of the cooling rates on the nonisothermal crystallization process, Kissinger proposed that the activation energy could be determined by calculating the variation of the crystallization peak with the cooling rate.²⁵

$$d \ln(\phi/T_p^2)/d(1/T_p) = -\Delta E/R \quad (10)$$

where ϕ is the cooling rate, T_p is the crystallization peak temperature, and R is the gas constant. The crystallization activation energy (ΔE) is calculated from the slope of $\ln(\phi/T_p^2)$ versus $1/T_p$.

As shown in Figure 13, the ΔE of PP0 and PP4 during nonisothermal crystallization is determined to be 267.9 and 287.9 kJ mol⁻¹, respectively. In comparison, the ΔE of nucleated iPP is slightly higher than that of pure iPP. From the kinetics viewpoint, the activation energy could be correlated with the crystallization rate. Generally, high crystallization activation energy would hinder the crystallization and result in the decrease of crystallization rate. However, an opposite result is obtained in our study. The addition of HHPA-Ba increases the crystallization activation energy of iPP, but it increases the crystallization rate. The similar results were reported for other nucleating agents by several researchers.⁴⁵⁻⁴⁷ It has been considered that the effect of nucleating agent on polypropylene crystallization is twofold. On one hand, nucleating agents can serve as heterogeneous nucleating sites and favors crystallization growth of molecular in interface; on the other hand, nucleating agents may baffle the transfer of macromolecular segments from iPP melts to the crystal growth surface due to the weak interaction between nucleating agents and segments of iPP. The baffling effect may lead to the increase of ΔE . However, nucleation is the controlling step

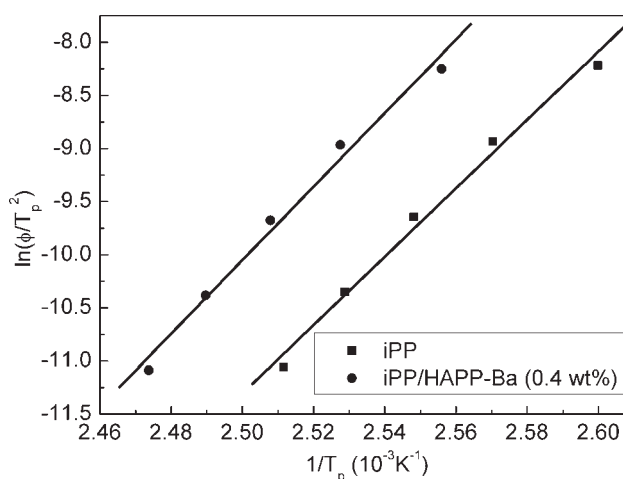


Figure 13 Kissinger plot for calculating the nonisothermal crystallization activation energies for PP0 and PP4.

during crystallization and the increasing of nucleation rate results in the increasing of the overall crystallization rate and crystallization temperature. The nucleating effect of HHPA-Ba can be found by POM (Fig. 8).

CONCLUSIONS

In this work, the effects of the novel highly efficient β -nucleating agent HHPA-Ba on the mechanical properties, the β -phase content, crystallization behavior, and nonisothermal crystallization kinetics of iPP were investigated. The main conclusions are summarized as follows:

1. With the increase of HHPA-Ba concentration, the impact strength of iPP nucleated with HHPA-Ba first increases and then decreases until constant. At the concentration 0.4 wt %, the impact strength of nucleated iPP increases about 2.4 times than that of pure iPP. Meanwhile, the tensile strength and flexural modulus decrease. The results show that HHPA-Ba could significantly improve the toughness of iPP.
2. The k_{β} values of iPP nucleated with HHPA-Ba first increased and then basically remained constant with the increasing of HHPA-Ba concentration. The k_{β} value of iPP nucleated with HHPA-Ba at the concentration of 0.4 wt % reaches 80.2%. The results show that HHPA-Ba is an effective β -nucleating agent for iPP.
3. The crystallization behavior studied by DSC and POM shows that the nucleating agent HHPA-Ba can greatly increase the crystallization peak temperature of iPP and sharply decreases spherulite sizes with the increasing HHPA-Ba content.
4. The Caze method was used to study the nonisothermal crystallization kinetics of virgin iPP and nucleated iPP. The result indicates that the type of nucleation and growth geometry of iPP is significantly changed in the presence of nucleating agent HHPA-Ba. The crystallization active energy is determined by Kissinger method and shows that the addition of HHPA-Ba slightly increases the crystallization activation energy of iPP.

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