

Effect of Isotacticity Distribution on the Crystallization and Melting Behavior of Polypropylene

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Received 15 July 2001; accepted 17 October 2001

ABSTRACT: The crystallization and melting behavior are closely related not only to the external conditions such as undercooling and cooling rate, but also to the chain structure characteristics such as isotacticity distribution. The isotacticity distribution of three commercial isotactic polypropylenes (iPP) used in this work was characterized using Temperature-Rising Elution Fractionation (TREF) combining with Size-Exclusion Chromatography (SEC). Their crystallization and melting behavior were observed by Differential Scanning Calorimetry (DSC) and Polarized Light Microscopy (PLM). The results indicated that for iPP with similar molecular weight and isotacticity, the difference in isotacticity distribution not only led to the variation in nucleation and growth rates of crystal, but also changed the perfection of crystals formed under the same condition, even causing the formation of different crystalline modification and the change in the equilibrium melting temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 333–341, 2002

Key words: polypropylene (PP); isotactic; crystallization; melt

INTRODUCTION

The crystallization and melting behavior of isotactic polypropylene (iPP) are closely related to its microstructure and the external conditions when these processes occur.^{1–5} The change of external conditions may result in the formation of crystal structure with different stabilities or the appearance of other crystalline modifications.^{3,6–10} For example, at high undercooling, the formation of the α modification was accompanied by the ap-

pearance of hexagonal crystalline form (β modification),^{11–13} the perfection of crystals formed in different conditions decreases with increasing undercooling, when the isothermal crystallization is carried out by quickly cooling to different temperature from the melt.^{5,14}

For stereoregular iPPs, the most important factor affecting crystallization and melting behavior may come from their structural difference. The effect of molecular weight,^{15–17} molecular weight distribution,¹⁸ and tacticity^{19–21} on the crystallization has been investigated by a number of authors. The results reported indicate that the linear growth rate of crystal markedly decreased with increasing molecular weight,¹⁶ but overall crystallization rate might rise because the increasing amount of intramolecular folded chain

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Contract grant sponsors: Special Funds for Major State Basic Research Projects; contract grant number: G1999064800.

Journal of Applied Polymer Science, Vol. 85, 333–341 (2002)
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nuclei could result in the higher nucleation density.¹⁷ For the samples with similar molecular weights and different tacticities, the linear crystal growth rate might increase by three orders of magnitude when the isotacticity of iPP rises from 0.787 to 0.988.²⁰

The multiple melting characteristics of iPP are usually observed (especially at a slower heating rate),^{3,5,21–28} and two explanations have been suggested. One is an irreversible melting process of metastable crystals that come from the existence of metastable crystal forms, thin lamellae, and defects in the crystals.^{21,22,26–28} Another is the preexistence of more than one crystal species in the polymer developed during crystallization.^{3,5,23–25} Furthermore, these two possibilities could be often cooperated with each other, which makes the melting behavior of iPP more complicated.²⁶ In fact, the correlation between the complicated melting characteristics and molecular structure of iPP has not been well established up to now.

Most commercial iPPs are the blends of some components with different molecular weight, molecular weight distribution, and tacticity.^{29–31} The isotactic elements distributed in various components are also possible to be different, which will cause the different crystallization and melting behavior of iPP. Temperature rising elution fractionation (TREF) technique allows one to definitely characterize the isotactic element distribution in the molecular chains with different chain lengths by combining Size Exclusion Chromatography (SEC) characterization.^{32,33} In this article, we take into account three commercial iPPs and attempt to elucidate the effect of microstructure features on the crystallization and melting behavior of these three iPPs.

EXPERIMENTAL

Materials

Isotactic polypropylene samples used in this investigation are three commercial film grade iPPs, which were generously provided by China Petroleum & Chemical Corporation. Their molecular characteristics are listed in Table I.

Fractionation and Molecular Weight Characterization

Three iPP samples were fractionated using the same temperature-rising elution procedure in our

Table I Molecular Characteristics of 3 iPPs

Sample*	M_n^a	M_w^b	M_w/M_n^b	Isotacticity ^c
iPP-68	68,000	380,000	5.6	95.2%
iPP-57	57,000	403,000	7.1	93.9%
iPP-56	56,000	330,000	5.9	93.3%

^a The last two letters in the sample name represents the magnitude of number-average molecular weight.

^b From SEC measurement results.

^c From ¹³C-NMR measurement results.

preparative TREF equipment. The entire fractionation process is described as follows: 1–2 wt % iPP sample was first dissolved in 1,2,4-trimethylbenzene at 140°C, and then introduced into the elution column of TREF under the N₂ pressure of 2 psi. The process to precipitate polypropylene onto the surface of the support was finished by cooling the polymer solution from 140°C to room temperature in 90 h. The elution step was carried out with trimethylbenzene at 110, 116, 118, 120, 125, and 140°C, respectively.

The molecular weight and molecular weight distribution for all the TREF fractions and original iPP samples were measured at 140°C by SEC (Waters 200). The solvent used was *o*-dichlorobenzene and solution concentration (w/v) was 0.1%. Four columns packed with silanized silica with pore sizes between 150–3500 Å were used, and the calibration was performed using polyolefin standard samples with broad molecular weight distribution.

Crystallization and Melting Behavior Characterization

All the crystallization and melting experiments of iPP samples were conducted on a differential scanning calorimetry (Netzsch DSC). The sample of 5–10 mg was first rapidly heated to 200°C and maintained at this temperature for 5 min to erase any previous morphological or heat history, and then quickly cooled to the desired crystallization temperature for isothermal crystallization. After completing of isothermal crystallization processes, the sample was heated immediately to 200°C at 20°C/min again. The corresponding crystallization and melting curves were recorded and normalized to the unit weight of the sample. The temperature calibration were conducted with the standard indium sample, whose melting point is 156.62°C at 10°C/min.

Polarized Light Microscopy (Leica-Wetzlar PLM) was used to observe the nucleation pro-

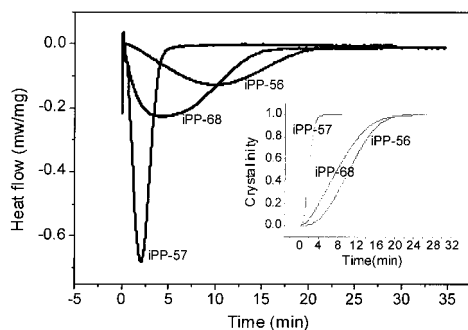


Figure 1 The DSC curves of isothermal crystallization at 125°C for three commercial iPP samples; inset gives the plot of crystallinity versus time corresponding to DSC curves.

cesses of three iPP samples under the same isothermal condition. The sample films were pressed between two microscopic slide to about 15 μm thickness (controlled by an aluminum film wedge) and annealed at 200°C for 20 min in a dry nitrogen atmosphere. Subsequently, the obtained samples were rapidly turned to a temperature-controlled hot stage to start the nucleation and crystallization of iPPs. The images were video-recorded via a charge-coupled devices (CCD) camera. To make the observations self-consistent, the viewing areas for the parallel and crosspolarizers are kept the same.

Wide-angle X-ray Diffraction (Rigaku, WAXD) was used to verify the crystalline modification of iPP that formed under isothermal conditions. After being held at 190°C for 30 min, the samples with the thickness of about 0.5 mm were quickly switched to a hot stage at 125°C and remained 120 min. All heat treatments were completed in N_2 atmosphere to avoid the degradation of iPP.

RESULTS AND DISCUSSION

The isothermal DSC curves of three iPP samples at 125°C are shown in Figure 1. The degree of crystallinity (crystalline weight fraction, X_w) changing with time for these three samples are also given in the inset of Figure 1, which were obtained by means of integrating the partial area under the thermograms, i.e.,

$$X_w = \int_0^t (dH/dt)dt / \int_0^\infty (dH/dt)dt \quad (1)$$

where the first integral is the heat generated at time t and the second one is the total heat when the crystallization is completed. It is seen from Figure 1 that the isothermal crystallization rates of iPP-57 is much faster than that of both iPP-56 and iPP-68, and the rate order for three iPP samples is

$$\nu_{\text{iPP-57}} > \nu_{\text{iPP-68}} > \nu_{\text{iPP-56}} \quad (2)$$

where ν represents the isothermal crystallization rate.

According to the results shown in Figure 1 and Table I, it is clear that the crystallization rate difference impossibly results from the disparity in the overall isotacticity of three iPP samples because the biggest isotacticity difference for these samples is not more than 1.3%. Furthermore, the order of crystallization rates is not in agreement with that of their isotacticities, i.e., the crystallization rate of the iPP-68 with isotacticity of 95.2% is markedly slower than that of the iPP-57 with 93.9% (see Table I). It implies that there may be other factors influencing the isothermal crystallization rates of three iPPs.

It is also interesting for explaining the above crystallization rate order of three iPPs from their molecular weights or molecular weight distributions. According to the results reported,^{17,34} both increasing molecular weight and broadening molecular weight distribution can accelerate the overall crystallization process. However, this explanation seems to be contradictory for the present situation. It is suitable for iPP-57 but not for iPP-68 and iPP-56, because the number-average molecular weight (M_n) of iPP-56 is the smallest and its molecular weight distribution (M_w/M_n) is also narrower than that of iPP-57. This seems to indicate that both M_n and M_w/M_n are not the main factors influencing the isothermal crystallization rate of iPP. So, what exactly is the main factor affecting iPP's isothermal crystallization process?

Actually, commercial iPPs are usually the mixture of many components with different molecular weight and molecular weight distribution. Further, the distribution of isotactic elements (or isotactic sequence distribution) in various components can be very different, which depends on the kind of catalyst used and the actual production condition.^{35,36} It has been recognized that the macroscopic properties of polymers cannot be uniquely determined by some average values.³³

For example, determining the molecular weight average of a polymer sample by light scattering or osmometry, or with amore crude estimation from melt flow index measurement is usually not sufficient to uniquely define the state of polymer material, because polymers with the same average molecular weights can possess other properties that differ markedly. Even the knowledge of the full molecular-weight distribution for iPP may not be sufficient for many practical applications, due to stereoirregularities. Therefore, the difference in the isothermal crystallization rates of the current three iPP samples is supposed to result from the microstructure disparity, i.e., the difference in microtacticity distribution, which implies that the isotactic elements or isotactic sequence length distributed in various components could be different.

TREF can provide one with more details about isotacticity distribution in polymer molecules with different chain lengths.^{32,33} In the fractionation using TREF, the process that precipitate semicrystalline polymer molecules to the surface of inert supports is a very important step. To avoid the secondary effects such as cocrystallization and molecular weight during precipitation, the cooling rate of polymer solution has to be carefully selected. Wild et al.³⁷ suggest an upper limit of 2°C/h for a variety of polyethylene types and 60 h to cool polymer solution from 140°C to room temperature for polypropylene. If these conditions can be met, the elution temperature of iPP samples is virtually molecular-weight independent, and mainly depends on their isotacticity disparity.

Figure 2(a) and (b) compare the M_n and relative weight content (weight percentage, wt %) of various temperature fractions for three iPP samples. These results were obtained under the condition of dilute solution (1–2 wt %) and the cooling time more than 60 h (90 h). Therefore, the results of TREF should mainly reflect the isotacticity distribution details of three iPP samples. It can be seen from Figure 2 that the elution temperature and M_n of the fraction with highest weight percentage are different for three iPP samples. As to iPP-68, M_n of the fraction (52.92 wt %) is about 61,000, and the elution temperature is at 125°C; these two values for iPP-57 and iPP-56 are about 158,000 and 116°C (57.61 wt %) as well as 35,000 and 110°C (48.2 wt %), respectively. The most fractions of iPP-68 were eluted at 125 and 110°C (the sum of two fractions is about 81 wt %) and M_n is in the range of 64,000–68,000, while the elu-

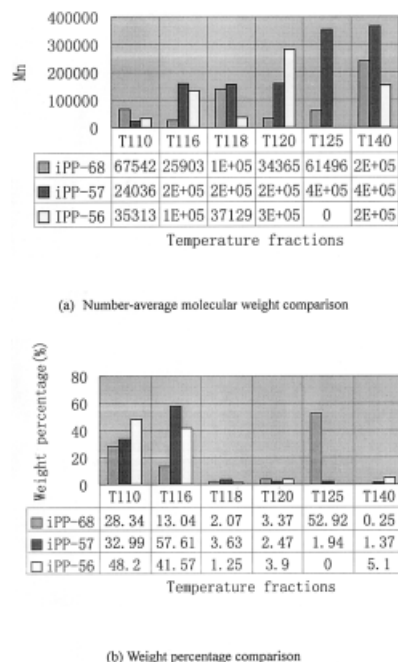


Figure 2 The number-average molecular weight (M_n) and weight percentage comparison of various fractions for 3 iPP samples.

tion temperatures (110 and 116°C) of the most fractions for iPP-57 and iPP-56 are lower than that of iPP-68, and molecular weight distribution is broader (from 24,000 to 158,000). These results indicate that for iPP-68 the most isotactic elements are distributed in the components with M_n of 64,000–68,000, and the isotactic sequence length could be larger than that of iPP-57 and iPP-56 eluted at 110 and 116°C. Obviously, the difference in isothermal crystallization rate for three iPP samples is closely related to their microstructure disparity.

The isothermal crystallization rate of iPP is mainly controlled by two processes: nucleation and growth.^{1,38} The rate of nucleation I^* , in terms of the classical theory developed by Gibbs, Kossel, and Volmer,^{38,39} can be written as

$$I^* = (NkT/h) \exp[-(\Delta G^* + \Delta G_\eta)/kT] \quad (3)$$

where N is related to the number of crystallizable elements, ΔG^* is the energy of formation of a nucleus of critical size, ΔG_η is the activation energy for chain transport, k is Boltzmann constant, T is temperature. Both ΔG^* and ΔG_η are constants as the crystallization temperature stays unchangeable. Therefore, I^* mainly depends on

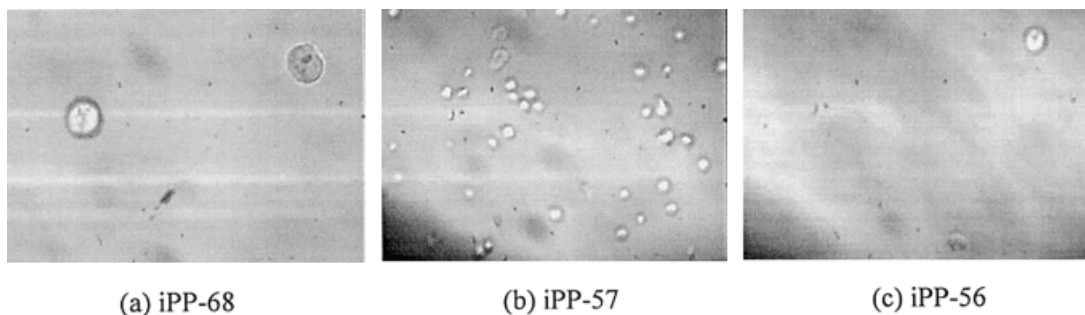


Figure 3 Comparison of nucleation rates for three iPPs crystallized at 125°C: (a) iPP-68, (b) iPP-57, and (c) iPP-56.

the number of crystallizable elements under the isothermal condition. From the TREF and GPC data, it can be seen that M_n of high-temperature fractions (including 125 and 140°C fractions) for iPP-57 is highest (354,000, 3.31 wt %), while M_n of the corresponding temperature fractions for iPP-56 and iPP-68 are 153,000 (only 140°C fraction, 5.1 wt %) and 62,000 (the average value of M_n for two fractions, 53.17 wt %). This allows one to suppose that for a single molecular chain of these high-temperature fractions the number of crystallizable elements (isotactic elements) of iPP-57 should be much higher than that of other two iPP samples, which leads to iPP-57 has the chain folded nucleation rate much higher than that of iPP-68 and iPP-56. Actually, the measurement results of polarized light microscopy (PLM) for the nucleus density of three iPPs also exhibit such a trend, which is given in Figure 3. However, it can be also observed from Figure 3 that although iPP-57 displayed the highest nucleation rate, the nucleation rates of iPP-68 and iPP-56 show no significant difference. It seems to indicate that neither a lesser component with high M_n and number of crystallizable elements (0.25 wt % for iPP-68) nor lower M_n corresponding to iPP-57 (153,000, 5.1 wt % for iPP-56) effectively accelerates the nucleation of iPP molecules under isothermal conditions.

On the other hand, the growth rate of crystals under isothermal conditions strongly depends on the molecular weight of iPP.¹⁶ More exactly speaking, the growth rate of iPP crystals should be closely related to the molecular size of the iPP molecule with crystallizable elements, which has a decisive effect on the reptation motion of a molecule during the isothermal crystal growth. It can be observed from Figure 2 that about 90 wt % of the isotactic elements are distributed in the frac-

tions of 61,000 (M_n) and 67,000 for iPP-68, in the fractions of 158,000 and 24,000 for iPP-57 and in the fractions of 133,000 and 35,000 for iPP-56. If the fastest crystallization rate of iPP-57 is attributed to its higher nucleation rate, the faster crystallization rate for iPP-68 could stem from the faster crystal growth rate corresponding to iPP-56. The relatively small molecular size makes iPP-68 molecules to possess higher reptation motion rate as the isothermal crystallization proceeds, which therefore makes iPP-68 to exhibit a faster overall crystallization rate than iPP-56 does.

The tacticity distribution of iPP not only affects its isothermal crystallization processes but also makes it to display specific melting behaviors. Figure 4 shows the melting curves for three iPP samples after isothermal crystallization at 125°C. All melting experiments were conducted at 20°C/min to minimize the recrystallization effect during heating.³ The melting peak temperatures (T_{mp}) and the melting heats (ΔH_m) for three iPPs

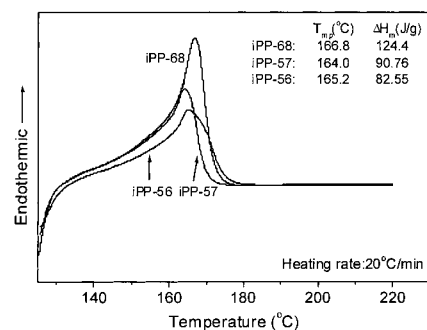


Figure 4 Comparison of melting curves for three iPPs subsequent to crystallization at 125°C, heating rate is 20°C/min; T_{mp} —melting peak temperature, ΔH_m —melting heat.

are given in Figure 4. It can be seen that T_{mp} and ΔH_m of iPP-68 are the highest: 166.8°C and 124.4 J/g, respectively. Furthermore, iPP-57 has the lowest T_{mp} and iPP-56 has the smallest ΔH_m .

The value of T_{mp} relates to the extent of crystal structure perfection while the magnitude of ΔH_m is directly associated with the degree of crystallinity of iPP. Under the same isothermal crystallization conditions, the variation in T_{mp} and ΔH_m should reflect the subtle difference of crystallization processes for three iPP samples, which is possible to mainly result from their microstructure disparity. Because 90% of isotactic elements for iPP-68 are distributed in the component with M_n of 60,000 or so, the higher crystal stability of iPP-68 (higher T_{mp}) can be attributed to the higher ability of reptation motion, which allows the molecular chains to rearrange themselves in time and to form the thicker lamellar crystal. In contrast, about 50% of isotactic elements for iPP-56 are located in the components with M_n of 133,00 or higher, increasing reptation retardation of molecular motion reduces the thickness of crystal lamellae and, therefore, the stability of crystal structure. For iPP-57, about 67% of isotactic elements are spread in the components with M_n of 156,000 or higher, which makes it to exhibit the lowest T_{mp} and lower ΔH_m .

Another interesting phenomenon can be observed from Figure 5, in which the shoulder of the melting peak for iPP-68 rises with increasing crystallization temperature while this phenomenon for iPP-57 [Fig. 5(b)] and iPP-56 [Fig. 5(c)] cannot be observed or distinguished. The melting temperature corresponding to the shoulder is displayed in Figure 5(a), and its value is in the vicinity of 156.2°C. Obviously, this result does not stem from the formation of instable crystal structure or recrystallization effect because herein all the experiments were performed under the same conditions and the heating rate used was 20°C/min. Furthermore, what is more important is the fact that the shoulder in the vicinity of 156.2°C for iPP-68 becomes more distinct with increasing temperature, which seems to imply the appearance of a small amount of different crystal modification (e.g., β modification) accompanying with the formation of α modification. The melting temperature of pure β modification for iPP was reported to be 156.8°C,⁴⁰ which just reconciles with the temperature of shoulder in iPP-68's melting curves.

The results of WAXD for three iPPs are displayed in Figure 6, and these results were ob-

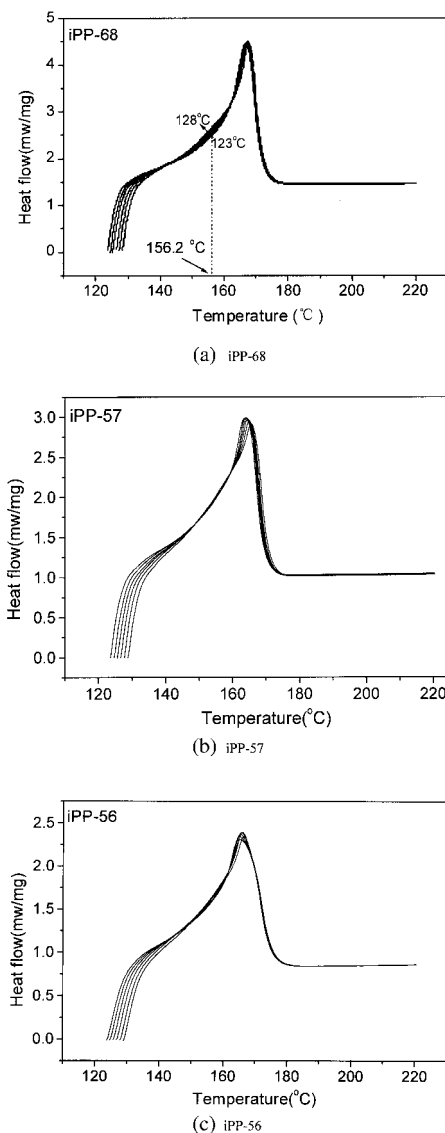


Figure 5 Melting curves of three iPP samples (123–128°C), heating rate is 20°C/min.

tained under the same experimental conditions: the samples first remained at 190°C for 30 min (N_2 atmosphere) and then quickly turned to a hot stage at 125°C for 120 min (N_2 atmosphere). The characteristic peak at 16° attributed to β modification (300) of iPP-68 can be clearly seen from Figure 6, while for iPP-57 this peak is nonexistent. Obviously, the WAXD results are in agreement with the DSC aforementioned observation. This indicates that the formation of β modification should also be dependent on the microstructure of iPP.

Besides adding the β nucleation agent, it has been extensively reviewed that the appearance of

β modification in iPP crystallization processes strongly depends on the applied external conditions.^{3,13} Usually, quenching or very slowly cooling ($<5^\circ\text{C}/\text{min}$) from the melt state will facilitate the formation of β modification for nonisothermal crystallizations. Under isothermal conditions, the temperature to facilitate the formation of β modification is in the range from 105 to 141°C .^{41,42} Beyond this range, the linear growth rate of β modification is slower than that of α modification, which is not in favor of the formation of β modification. The current crystallization temperatures (from 123 to 128°C) are in the above temperature range that facilitates the formation of β modification. Therefore, the disparity of melting behaviors for three iPPs seems to imply the correlation between the formation of β modification and microstructure distribution of isotacticity elements. From the data in Figure 2, it can be seen that the high-temperature fraction (125°C , 53 wt %) of iPP-68 is much larger than that of the other two iPP samples, which indicates that the isotactic sequence length average of iPP-68 is larger than that of iPP-57 and iPP-56, although M_n of the fraction at 125°C for iPP-68 is smaller than that of the fractions at 116°C for iPP-57 and iPP-56. This seems to prompt one that the formation of the β modification could be isotactic sequence length dependent, and furthermore, it is possible that the effect of the molecular weight is not neglected. In other words, the formation of β modification could be dependent on the microstructure of iPP, i.e., the isotactic sequence length of the component with certain molecular chain lengths. Such a microstructure prerequisite of iPP could

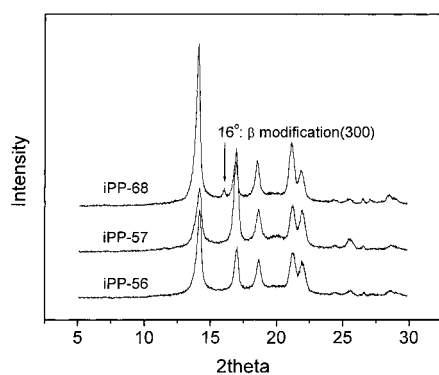


Figure 6 The WAXD evidence of β modification for iPP-68; the experiments were conducted under the same condition: after holding 190°C for 30 min, quickly turning the sample to a hot stage at 125°C (N_2) for 120 min.

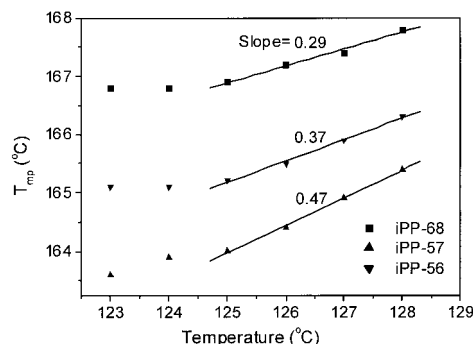


Figure 7 Melting peak temperature versus crystallization temperature for three iPP samples.

determine its preferential formation of β modification under isothermal conditions. However, this is not sufficient to establish the definite relationship between the microstructure of iPP and the formation of β modification only by means of the present three iPP experimental data. Some results of more detailed investigations about this aspect will be reported in future articles.

Figure 7 shows the change of T_{mp} of the three iPP samples with the crystallization temperature, T_c . The microstructure dependence of T_{mp} for the three iPPs can be clearly observed from the slopes of the three lines. It can be seen that the slopes of the three lines are 0.29, 0.37, and 0.47 for iPP-68, iPP-56, and iPP-57, respectively. Such a result is also in agreement with the isotactic element distribution in molecular chains with different lengths (see Fig. 2). Obviously, the different slope values will lead to the different equilibrium melting temperature (T_m°), which should be the reason why the difference in T_m° reported in the literature is from 456.2 to 483.2 K ,¹⁶ although these iPP samples presumably display the same average isotacticity. The effect of isotacticity distribution on the T_m° of iPPs will be further expanded in the subsequent works.

CONCLUSION

Isotactic polypropylene with similar molecular weight and isotacticity are possible to show different crystallization and melting behaviors due to their microstructure disparity. According to the results obtained in this work, the following conclusion can be drawn:

1. The components with high molecular weight and high content of isotactic elements can

significantly accelerate the nucleation of iPP, and therefore the overall crystallization rate distinctly rises; for those iPPs without a marked difference of nucleation rate, decreasing the molecular size containing crystallizable elements helps to accelerate the growth of the crystal and finally raises the overall crystallization rate.

2. When the molecular size containing crystallizable units is smaller, their crystals formed under the same isothermal condition displayed the higher melting peak temperature (T_{mp}), due to their faster reptation motion during the isothermal crystallization. Furthermore, the degree of crystallinity could be higher than that of iPP, whose molecular size containing crystallizable elements is larger.
- 3 With increasing molecular size containing crystallizable elements, the dependence of T_{mp} increases, which will result in the variation of equilibrium melting temperature (T_m°).
4. Under the same isothermal condition, decreasing molecular size containing crystallizable elements is possible to induce the formation of different crystalline modification, for example, β modification. However, the correlation between the formation of β modification and microstructure characteristics of molecular chains still needs to be further studied.

This research has been subsidized by the Special Funds for Major State Basic Research Projects (G1999064800) and Shanghai postdoctors.

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