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The influence of stem conformation on the crystallization of isotactic polypropylene

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Abstract

The influence of stem conformation on the crystallization of *i*-PP is studied by growing α-form lamellae in melts of β-form lamellae at different temperatures. The melting of β-form lamellae and the crystallization of α-form lamellae is observed in situ at the interface of α- and β-form spherulites by AFM. The growth rate of α-form lamellae in the melt of β-form lamellae is much lower than that in the isotropic melt due to the stem conformation barrier, which originates from the difference in the α and β unit cell packing models.

Keywords: Polypropylene; AFM; Crystallization

1. Introduction

When polymer crystals are melted at a temperature just above the melting point, the partially ordered structures may still exist in the melt for a certain period of time, due to the low mobility and entanglement of polymer chains. Higher temperature is needed to destroy the partially ordered structures into the isotropic melt [1,2]. Usually, the existence of partially ordered structures in the melt can significantly promote the crystallization rate, similarly to crystallization from the preordered liquid crystal phase in liquid crystal polymers [3–5]. Isotactic polypropylene (*i*-PP) is an important semi-crystalline polymer. The crystallization and melting behaviors of *i*-PP have been well studied [6–10]. *i*-PP crystals are composed of helical chains, which can be either left- or right-handed. The different packing manner of *i*-PP chiral chains in the crystal lattice leads to the various forms of *i*-PP crystals: α-, β-, γ- and mesomorphic forms [11,12]. In the monoclinic unit cell of the α-form, layers of right-handed stems alternate with left-handed ones along the *b*-axis, while in the trigonal β-form, frustrated structures are formed and stem domains of one particular handedness are present. This crystal structure difference leads to an approximately 10 °C difference in the melting points of α- and β-form crystals, which can be easily discriminated by either differential scanning calorimetry or hot stage polarized optical microscopy [13,14]. Normally, the melting point of the β-form lamellae is near 152 °C, while the melting of α-form lamellae occurs above 164 °C. Moreover, the α-form lamellae can still grow in the temperature range from 152 to 164 °C. Suppose now that α-crystals grow from the melt of a newly melted adjacent β-crystal. The α-crystal requires an equal mixed of right- and left-handed helices, while the newly created melt of the β-crystal will have only one of these types [11,12,15]. Such a situation provides us an ideal case for studying the influence of stem conformation in the partially ordered melt of β-form crystals on the growth behaviors of α-form lamellae. In this work, the growth of α-form lamellae in the melts of the β-form *i*-PP crystals has been monitored in real time using a hot-stage atomic force microscopy (AFM) with high resolution at different temperatures. We provide direct experimental evidence to show that the helical stem conformation of *i*-PP chains may present in the melt of β-form *i*-PP crystals at a certain temperature range, which will influence the further growth of α-form lamellae.

2. Experimental section

2.1. Materials and sample preparation

i-PP with $\overline{M}_W = 4.12 \times 10^5$ and $\overline{M}_W/\overline{M}_N = 5.5$, as measured by gel permeation chromatography, was bought from Aldrich.

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It was dissolved in boiling *p*-xylene at 138 °C with a concentration of 10 mg mL^{-1}. Thin films with a thickness around 200 nm were prepared by spin-coating hot polymer solutions onto a freshly cleaved mica surface, which was preheated to 80 °C before spin coating, in order to evaporate the solvent quickly. The films were then dried in a vacuum oven at 50 °C for 24h to remove the residue solvent.

Atomic force microscopy (AFM) tapping-mode images were acquired using an AFM (NanoScope IIIA MultiMode™ Digital Instrument) equipped with a high temperature heating accessory. The experimental details of high temperature AFM can be found elsewhere [16,17]. Both height and phase images were recorded simultaneously, but only phase images are presented here. The set-point amplitude ratio ($r_{sp}=A_{sp}/A_0$, where A_{sp} is the set-point amplitude and is the amplitude of the free oscillation) was adjusted to be 0.7–0.9. Si tips (TESP, Digital Instruments) with a resonance frequency of approximately 300 kHz and a spring constant of about 40 N m^{-1} were used. Before AFM observation, the *i*-PP thin film was isothermally crystallized at 147 °C under N_2 protection after it was melted on the AFM hot stage at 200 °C for 5 min. The melting process of the newly formed lamellae was then observed by AFM in real time. For the growth of β-form lamellae, a selective β-nucleating agent was used to induce the growth of β-form spherulites.

3. Results and discussions

The α- and β-form *i*-PP lamellae can be easily distinguished by AFM phase imaging, since the lamellar shape, the branching and the growth behaviors in these two types of lamellae are significantly different, as shown in Fig. 1. The lath-like α-form and the extended sheet-like β-form lamellae are shown in Fig. 1(a) and (b). The unique cross-hatched α-form and densely parallel β-form lamellae are presented in Fig. 1(c) and (d). The average growth rates (averaged over several lamellae of both edge-on and flat-on orientations) of the α- and β-form lamellae have been determined by measuring the length of a specific lamella in consecutive time intervals using AFM at different crystallization temperatures [18]. We have shown that the cross-hatched and lath-like α-form lamellae had nearly the same growth rate at the same crystallization temperature. The average α-form lamellar growth rate is about 216 ± 10 nm min^{-1} at 157 °C when the thickness of *i*-PP films is 200 nm.

An interface of α- and β-form lamellae is selected for AFM observation, as shown in Fig. 2. The extended flat-on sheet-like lamellae with screw dislocations on the left and lath-like lamellae on the right part of Fig. 2(a) are attributed to β- and α-form lamellae respectively, and both kinds of lamellar structures were developed at 147 °C. At this temperature, the α-form lamellae can still grow. Some lath-like α-form lamellae are found overgrowing the surface of the β-form lamellae, as shown in Fig. 2(a). As the temperature was increased to 154 °C, the β-form lamellae are melted from the rim to the center, and the α-form lamellae can, on the other hand, grow as shown in Fig. 2(b). The spiral melting about the screw dislocation of the β-form lamellae suggests that the nucleus is more stable than the more distant lamellar parts. Most of the β-form lamellae melt as the temperature is increased from 154 to 156 °C, as shown in Fig. 2(b)–(d). A slightly increase of the temperature to 157 °C ensures the complete melting of β-form lamellae, as shown in Fig. 2(e). The sample is then held at this temperature and a continuous scan has been performed to record the growth process of α-form lamellae. Framed areas in Fig. 2(e) and (f) are selected as a reference to measure the length of lamellae 1 and 2. Fig. 2(f) shows the morphology after the sample has been held at 157 °C for 2 h. A comparison between Fig. 2(e) and (f), shows only slightly increase in lamellar length for both lamellae 1 and 2. The growth rate of the α-form lamellae at 157 °C from the melt of β-form lamellae is much slower than that grown in the isotropic melt, as summarized in Table 1. This suggests that

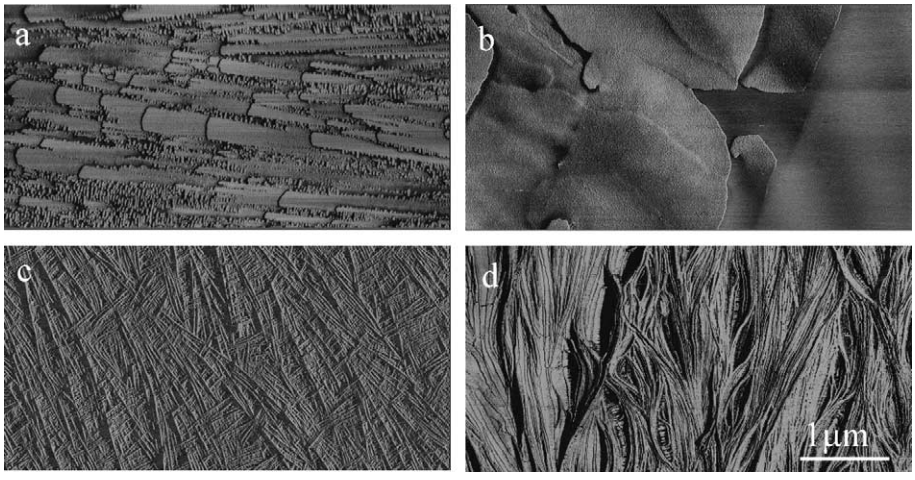

Fig. 1. Morphologies of *i*-PP lamellar crystals, (a) lath-like α-form lamellae; (b) extended sheet-like β-form lamellae; (c) cross-hatched α-form lamellae; (d) edge-on β-form lamellae.

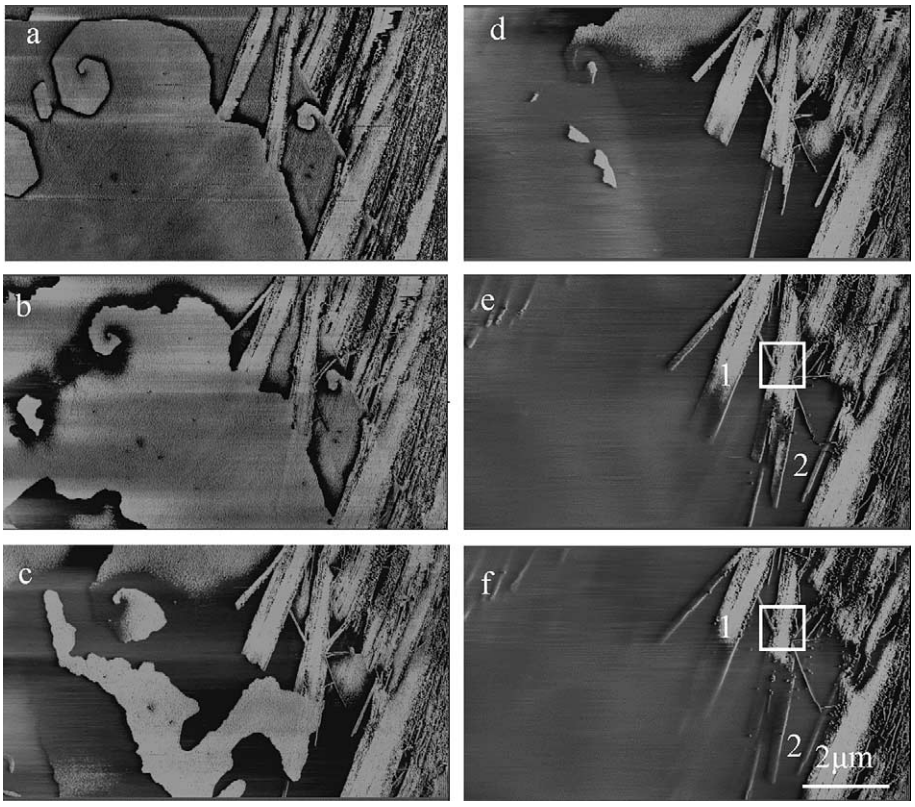

Fig. 2. The melting of β-form lamellae and the growth of α-form lath-like lamellae at an interface between the α- and β-form spherulites, (a) 147 °C; (b) 154 °C; (c) 155 °C; (d) 156 °C; (e) 157 °C. The time interval between two consecutive images is 30 min and (f) at 157 °C for 120 min.

the further crystallization of α-form lamellae in the melt of β-form lamellae is hindered under our experimental conditions.

To further investigate the influence of the stem conformation of the *i*-PP melt on the growth of α-form lamellae, the melt of β-form lamellae was heated to 159 and 161 °C and annealed there for 10 min, and then, the samples were crystallized at 157 °C. It was found that as the annealing temperature increases, the α-form lamellar growth rate increases significantly as summarized in Table 1. The average α-form lamellar growth rates are 1, 4 and 26 nm min^{-1} in the melts of the β-form lamellae annealed at 157, 159, and 161 °C, respectively. Moreover, if the annealing time is increased from 10 to 180 min at 161 °C, the growth rate of α-form lamellae slightly increases from 26 to 37 nm min^{-1}. For α-form lamellae growth in the isotropic melt (the isotropic melt is obtained by heating the samples up to 200 °C and annealing for 5 min), when the crystallization temperature is increased from 147 to 157 °C, the average growth rate (195 ± 10 nm min^{-1}) is similar to that crystallized in the melt quenched from 200 to 157 °C (216 ± 10 nm min^{-1}), as summarized in Table 1. Comparing the growth rate of α-form lamellae in the isotropic melt under the same thermal history, it can be seen that although the annealing temperature and time are prolonged, the average growth rate is still much lower than that in the isotropic melt.

Usually, the existence of partially ordered structures in the melt can significantly promote crystallization rates that are similar to crystallization from the preordered liquid crystal phase of liquid crystal polymers [3–5]. However, it is apparent that the growth of α-form lamellae in the melt of β-form lamellae becomes more difficult, even though the α-form lamellae already exist in the melt. It is known that the identical three-fold helical conformation is adopted in both the α- and β-form of *i*-PP, the chains pack in two different ways in their unit cells. The α-form has a monoclinic unit cell which contains four three-fold helical chains, having layers of right-

Table 1
The growth rates of α-form lamellae in the isotropic melt and the melts of β-form lamellae

Melts	The growth rate of α-form lamellar (nm min^{-1})
Isotropic melt,[a] crystallized at 157 °C	216 ± 10
Isotropic melt,[a] crystallized at 147 °C for 30 min, then crystallization at 157 °C	195 ± 10
The melts of β-form lamellae	
Crystallized at 157 °C	1 ± 0.3
Annealing at 159 °C for 10min, then crystallized at 157 °C	4 ± 0.5
Annealing at 161 °C for 10min, then crystallized at 157 °C	26 ± 3
Annealing at 161 °C for 180min, then crystallized at 157 °C	37 ± 3

[a] The isotropic melt is obtained by heating the samples up to 200 °C and annealing for 5 min.

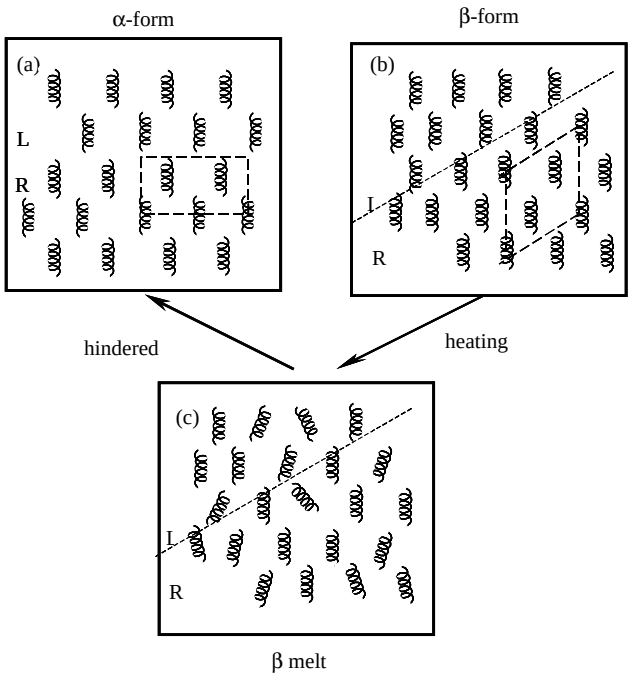

Fig. 3. Chain packing model of α- and β-phase, (a) monoclinic lattice of α-phase; (b) triagonal lattice of β-phase; (c) the collapsed β unit cell.

hand helices and left-hand helices alternated along the *b*-axis and only anti-chiral chains can be nearest neighbors. While the β-form has a triagonal unit cell with three isochiral helices, as schematically illustrated in Fig. 3(a) and (b). Recall that the melt of the newly melted β-form crystals should contain either all right-handed or all left-handed helices, while a growing α-form crystal demands a melt containing both handedness. In our study, when the sample was held at 157, 159, and 161 °C, just above the melting point of the β-form lamellae, the temperature is apparently not high enough to completely remix the locally ordered isochiral structure into a random chiral isotropic state. In this melt, the α-form growth front cannot be equally fed with chains of both chirality. With increasing annealing temperature and time, locally mixed chirality can develop through diffusion. The probability of anti-chiral stems migrating to the growth front, and consequently the average growth rate of α-form lamellae, is increased. These experiments clearly show that the residual helical stem conformations of *i*-PP chains remain in the melt of the β-form *i*-PP crystals over a certain temperature range, and thereby, negatively influence the further growth of α-form lamellae.

4. Conclusion

Utilizing a hot-stage AFM, the growth of α-form lamellae in the melt of β-form crystals was followed in situ at different temperatures. The melt of β-form lamellae still contain isochiral chains that cannot be directly incorporated into the α-form lamellae. Further growth of the α-form lamellae in this kind of melt is thus hindered. Remixing of chains of opposite chirality occurs slowly under the annealing conditions of this work, and, consequently, the growth rate of α-form crystals remains low.

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