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Direct crystal growth of isotactic polybutene-1 trigonal phase in the melt: *In-situ* observation

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Abstract

The morphology and crystal growth kinetics of isotactic polybutene-1 trigonal phase in molten thin films have been studied with transmission electron microscopy, electron diffraction and optical microscopy. The growth rate of trigonal crystals was determined by *in-situ* optical microscopy. It is one-hundredth that of the isotactic polybutene (it-PB1) tetragonal crystals. The growth rate of trigonal crystals, as well as that of tetragonal crystals, shows the supercooling dependence derived from the nucleation theory. Trigonal crystals grown at 75 and 90.1 °C possessed well-facetted morphology, which suggests the existence of flat growth faces required for nucleation theory between 75 and 90.1 °C. This is consistent with the observed temperature dependence of trigonal crystal growth rate in accordance with the nucleation theory.

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1. Introduction

Isotactic polybutene-1 (it-PB1) is a semicrystalline polyolefin, which exhibits outstanding mechanical properties and pronounced polymorphs that depend on its crystallization conditions. Three different polymorphs, designated trigonal, tetragonal and orthorhombic phases, have been reported in the literature [1–13]. Crystallization in the bulk under atmospheric pressure yields the tetragonal phase with $\frac{11}{3}$ helical chains [1–3]. The tetragonal phase is unstable. When stored at room temperature, the tetragonal phase undergoes a solid–solid transformation into the trigonal phase with $\frac{3}{1}$ helical chains. The orthorhombic phase has $\frac{4}{1}$ helices and is obtained from solution [6–8]. Solution crystallization also yields the trigonal phase.

Despite its excellent mechanical properties, the applications of it-PB1 have been limited considerably by the spontaneous tetragonal–trigonal solid-state transformation. The transformation corresponds to a densification and shrinkage of crystals and brings about severe deformation of molded objects. Therefore, bypassing this unstable tetragonal crystallization is of great significance from a practical standpoint.

Numerous attempts have been made to form the trigonal phase in the melt. The earliest challengers were Powers et al. [14], who used trigonal crystals obtained by solid-state transformation from the tetragonal phase as nuclei and attempted to observe the growth of trigonal crystals in the melt. This was, unfortunately, not successful, and they hypothesized that the growth rate of trigonal crystals is "exceedingly" slower than that of tetragonal crystals.

In the 1990s, Kopp et al. [15] reported a breakthrough in forming the trigonal phase. They successfully crystallized the trigonal phase in the melt via epitaxy on aromatic acids or salts, and demonstrated that the trigonal phase can grow in the melt even under atmospheric pressure if appropriate substrates are provided. At an elevated temperature of 110 °C, Zhang et al. [16] found that trigonal crystals can be obtained from the molten ultrathin films under atmospheric pressure.

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We presented another solution to this issue in our previous works [17,18]. Using solution-grown trigonal crystals as nuclei, we demonstrated that the trigonal phase could grow in the melt via self-seeding at an atmospheric pressure. The self-seeding crystallization does not require the aid of epitaxy and can be applied to crystallization at lower temperatures, which can be an advantage from the standpoint of bulk melt molding. In this paper we report the growth kinetics and morphology of lateral growth shape of melt-crystallized it-PB1 formed by self-seeding.

2. Experimental procedure

The it-PB1 used in this study was purchased from Scientific Polymer Products ($M_w = 185{,}000$; the melt index is 20 g/10 min). Thin it-PB1 films were prepared by casting a 0.1 wt% *p*-xylene solution onto carbon-coated mica kept at 60 °C on a hot plate. The films were dried in air, an appropriate film thickness of ca. 80 nm being judged by a gold interference color.

Crystallization was carried out on a hot stage (Mettler FP82). The it-PB1 films were heated at 128–135 °C for 2 min and cooled to a crystallization temperature between 65 and 90.1 °C at a rate of 15 K min^{-1}. *In-situ* observations of the crystallization process were performed using an optical microscope (OM; Nikon OPTIPHOT2); the growth rate was determined from the time dependence of the radius or the major axis of crystals observed by an OM.

Transmission electron microscopy (TEM; JEOL JEM-1200EXII) was used to identify crystal structures. Samples were examined immediately after crystallization and quenching. The it-PB1–carbon films were floated on a water surface, picked up on electron microscope grids and used as samples.

3. Results and discussion

Fig. 1 shows an OM image of an it-PB1 thin film that was heated at 132 °C for 2 min and then isothermally crystallized at 75 °C. Planar flat-on crystals with somewhat hexagonal morphology are observed. These crystals are encapsulated within a much larger spherulite of the tetragonal phase, which has already been reported to grow from the melt in the literature [1–3].

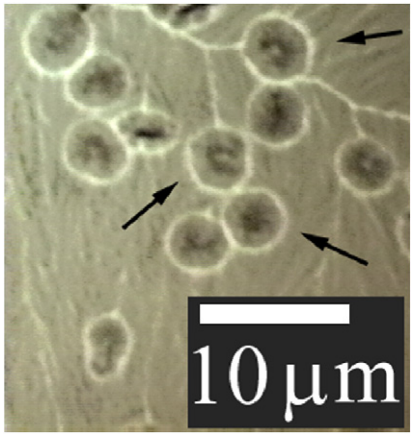

Fig. 1. Optical micrograph of it-PB1 trigonal crystals grown at 75 °C. The trigonal crystals are surrounded by a tetragonal spherulite. The crystals indicated by the arrows show somewhat hexagonal morphology.

When the above-crystallized sample was heated again, the flat-on crystals retained their shape up to 124 °C; the surrounding tetragonal spherulites melted below 110 °C, which is consistent with the melting temperature of the tetragonal crystals we reported in our previous work [19]. The morphology and melting behavior indicate that the flat-on crystals are in a different phase from the surrounding tetragonal crystals.

We confirmed by TEM that the crystals are in the trigonal form. Fig. 2 shows a transmission electron micrograph of an it-PB1 film that was heat-treated at 132 °C for 2 min and then isothermally crystallized at 75 °C, and its corresponding electron diffraction pattern. A somewhat hexagonal-shaped crystal similar to those observed in the OM image can be seen. The electron diffraction pattern shows a net pattern with hexagonal symmetry, and all the Bragg reflections could be indexed with the trigonal form of it-PB1. The electron micrograph and diffraction pattern demonstrate that the crystal grown from the melt is a single crystal in the trigonal form. OM and TEM observations indicate that the flat-on crystals are characterized as trigonal crystals grown in the melt.

As mentioned above, trigonal crystals are known to be obtained in solutions. The it-PB1 films used in this study

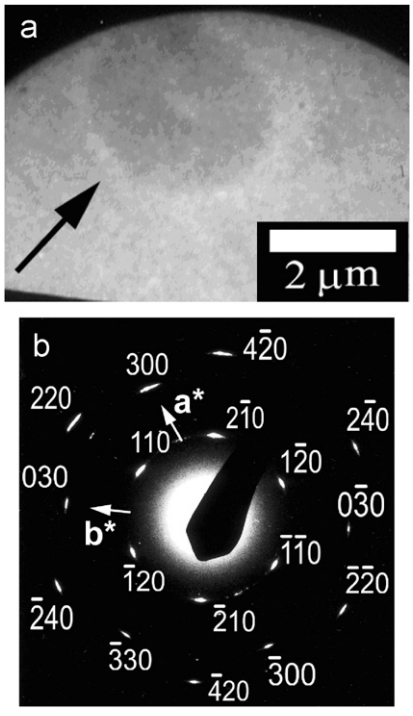

Fig. 2. (a) Electron micrograph and (b) its corresponding selected area electron diffraction pattern of an it-PB1 single flat-on crystal in the trigonal form grown at 75 °C. An it-PB1 crystal is indicated by an arrow. The arc in the upper part of (a) is an area-selecting aperture.