Accelerating crystal−crystal transition in poly(1-butene) with two-step crystallization: An *in-situ* microscopic infrared imaging and microbeam X-ray diffraction study

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ABSTRACT

The crystal−crystal transition of isotactic polybutene-1 (iPB-1) from form II to I at room temperature is investigated with *in-situ* Fourier transform infrared spectroscopy (FTIR), Fourier transformation infrared microspectroscopic imaging (FTIRI) and synchrotron radiation scanning X-ray micro-diffraction (SR-μSXRD). The transition rate from form II to I shows a non-monotonic correlation with crystallization temperature on samples isothermally crystallized at different single temperatures. An abnormal spatial distribution of transition rate is observed in samples prepared with a two-step crystallization approach, in which samples crystallized at high temperature and then were quenched to low temperatures for further crystallization. A maximum transition rate occurs around the edge of large spherulites formed at high temperature, which cannot be interpreted by the effect of crystallization temperature alone. The accelerated transition rate in this region is attributed to internal stress, where an intermediate state, revealed with SR-μSXRD, may be the structural origin for the fast transition rate from form II to I.

1. Introduction

Solid−solid transition or crystal−crystal transition is widely observed in semicrystalline polymers, which affects not only industrial processing like post-stretch in fiber spinning and film stretching, but also the performance in their final application [1−9]. Unlike crystallization from homogeneous polymer melt, crystal−crystal transition generally takes place from a heterogeneous parent phase. In addition to the intrinsic coexistence of crystal and amorphous in semicrystalline polymer, heterogeneities in large scales are widely generated due to complex processing temperature and stress fields, which may result in heterogeneous distributions of subsequent crystal−crystal transition in space and time. These heterogeneities bring complication on interpreting spatial averaged experimental data and may be one of the reasons for controversial explanations.

iPB-1 is a good example for studying crystal−crystal transition [10−15]. A metastable form II of iPB-1 with tetragonal packing is generally obtained through crystallization from melt directly, which is assigned as a dynamic conformational disorder crystal by some groups [16−20]. Form II transforms into stable form I with hexagonal structure spontaneously soon after aging at room temperature [4,14,21]. The transformation is suggested to follow an approach that the (110) plane of form II becomes the same plane of form I, during which the helix displacement is minimized and the energetically unrealistic change of helix chirality is avoided [22−24]. As form I has a density of 4.74% higher than that of form II, the crystal−crystal transition may cause distortion and shrinkage of the molding product, which limits the application of iPB-1 in some aspects [23,25,26]. Thus understanding the crystal−crystal transition mechanism not only has its own scientific interest, but also is of importance for the industrial application of iPB-1, which may be beneficial on avoiding shrinkage-induced distortion with controlled spatial distribution of transition kinetics through designing processing and molecular parameters.

In addition to molecular nature [15,27−31] and conditions set for the crystal−crystal transition [32−38], the initial crystallization condition of form II is an important factor on controlling the transition kinetics, which still remains controversial. Azzurri et al. [29,39] reported that higher crystallization temperatures of form II led to a faster transition rate at temperature range from 80 °C to

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110 °C. It was explained that the fraction of tie chains that connect adjacent lamellar crystals dictated the difference of kinetics, where the tightening of tie molecules may induce internal stress acting on the lamellar crystals. On the other hand, crystallization through faster cooling was reported to lead to a higher fraction of tie chains, which was considered as rigid amorphous, though a lower degree of crystallinity was obtained [40]. Bearing the accelerating effect of external stress in mind [28,29,32], it seems natural that internal stress should promote form II to I transition, while initial crystallization temperature may not give a simply monotonic correlation as crystallization temperature affects not only the stability of lamellar crystal through lamellar thickness and lateral size but also the interaction between amorphous and crystal like internal stress [41–43].

In this work, the effect of crystallization temperature of form II on the crystal–crystal transition kinetics was studied with *in-situ* Fourier transformation infrared (FTIR) spectroscopy at room temperature, where the initial samples isothermally crystallized at different temperatures. Based on the result of isothermally crystallized samples, two-step crystallization experiment is designed to tune the structure of crystal, during which samples first crystallized at a high temperature (90 °C) and then were quenched to a second temperature for further crystallization. Fourier transformation infrared microspectroscopic imaging (FTIRI) and synchrotron radiation scanning X-ray micro-diffraction (SR-μSXRD) show that samples obtained through two-step crystallization have a fast transition zone at the interface between regions crystallized at high and low temperatures, where the accelerated transformation from form II to I is attributed to a transient state in this region. Current work also demonstrates that two-step crystallization is an effective approach to enhance the crystal–crystal transition from form II to I and may be beneficial to industrial production.

2. Experiment section

2.1. Materials

The isotactic polybutene-1 pellets (PB 0800M) used in this study was kindly supplied by Basell Company, with a melt flow index of 200 g/10 min (190 °C/2.16 kg, ISO 1133) and average M_n and M_w of about 25 and 77 kg/mol.

2.2. Sample preparations

Two different approaches to sample preparation are employed in this work. In order to establish the relation between crystallization temperature and transformation kinetics from form II to I at room temperature, samples crystallizing at single temperatures from −114 °C to 90 °C were prepared, which is named as one-step crystallization. In this approach, the iPB-1 films of 30–40 μm thickness placed on a copper ring with a diameter of about 3 mm were heated up to 170 °C and kept for 10 min in nitrogen atmosphere to erase thermal history. Then the samples were immediately put into cooling liquids with different temperatures for quenching. The quenched temperatures chosen here were −114, −70, 0, 25, 50, 70 and 90 °C. For the case of −114 and −70 °C, ethanol was used as cooling liquid, which were cooled by liquid nitrogen. For other temperatures, water is used as cooling liquid. After quenched to different required temperatures to isothermally crystallize, the samples were brought back to room temperature and immediately put onto FTIR sample stage to follow the transformation kinetics at room temperature.

The second approach is named as two-step crystallization. In this approach, after erasing thermal history as that in the first approach, samples crystallized at a high temperature (90 °C) first.

After the spherulites grew up to a size of about 150 μm, samples were quenched to different temperatures. For the convenience of comparison, the temperatures were set as same as those in the first approach, namely −114, −70, 0, 25, 50 and 70 °C, which were labeled as $S_{90-(-144)}$, $S_{90-(-70)}$, S_{90-0}, S_{90-25}, S_{90-50}, and S_{90-70} respectively for conciseness. After fully crystallized, the crystal–crystal transition behavior of these samples was measured with *in-situ* FTIRI and SR-μSXRD.

2.3. Measurements

In-situ FTIR spectroscopy was employed to follow the crystal–crystal transition from forms II to I. For samples prepared through one-step crystallization, a TENSOR 27 (Bruker) FTIR spectrometer was used. The measured spectrum wavenumber range was 3900–700 cm^{-1} with a resolution of 4 cm^{-1} and 128 scans were taken for averaging. The baseline of spectrum was carefully adjusted uniformly using OPUS 5.5 package. Height of peak was considered as integral intensities of the conformational bands in all of IR data in this study.

Samples prepared through two-step crystallization contain different domains with structures formed at two different temperatures. FTIRI and SR-μSXRD are effective tools to follow structural evolution over time with relatives high spatial resolution, which were employed to distinguish different transition kinetics at different domains of samples prepared through two-step crystallization. FTIRI measurement was performed on FTIR spectroscopy and micro-spectroscopic imaging endstation at National Synchrotron Radiation Laboratory. The endstation is equipped with a Bruker HYPERION 3000 microscope coupled with Bruker IFS 66v FTIR spectrometer. With a 64 × 64 elements Focal Plane Array (FPA) detector, 250 μm × 250 μm areas can be measured simultaneously. The collection and analysis methods are as same as those used in the first approach. SR-μSXRD measurements were carried out at BL15U beamline of Shanghai Synchrotron Radiation Facility (SSRF). Data from beam profile show that the area of the micro-spot is 3.9 μm × 3.9 μm. The X-ray wavelength was 0.124 nm and a Mar165 CCD detector (2048 × 2048 pixels of 80 μm) was employed to collect two dimensional (2D) diffraction patterns. Fit2D software from European Synchrotron Radiation Facility was used to analyze SR-μSXRD patterns [44].

An example for wide-angle X-ray data of partially transformed iPB-1 is shown in Fig. 1. It illustrates the circularly averaged linear intensity profiles from 2D WAXD pattern which is corrected for background scattering. To calculate the crystallinity index (CI) of form I and form II in a partially transformed iPB-1 sample, the peaks of form I, form II and amorphous are fitted using Origin software as shown in Fig. 1. The CI of two forms is calculated using the following equations proposed by Hsiao et al. [4]:

$$x_{I} = \frac{A_{I}}{A_{I} + A_{II} + A_{A}} \tag{1}$$

$$x_{II} = \frac{A_{II}}{A_{I} + A_{II} + A_{A}} \tag{2}$$

where A_I, A_{II}, A_A represent the integrated areas beneath peaks of the form I, the form II and amorphous, respectively.

3. Results

The effect of crystallization temperature on the transformation kinetics from forms II to I for samples prepared though one-step crystallization was studied first, which is also the basis for later