



Orientation of polymer chains in spherulites of poly(ethylene oxide)-urea inclusion compounds



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ABSTRACT

Orientation of polymer chains in the spherulites of polymer-small molecule inclusion compounds (IC) is an interesting issue. Two kinds of spherulite morphologies were observed in the metastable β phase of poly(ethylene oxide) (PEO)/urea IC under the same isothermal crystallization temperature. Via polarized micro-Fourier transform infrared spectroscopy and two-dimensional wide angle X-ray diffraction technique, we found that PEO chains in the two morphologies oriented differently: one along the radius and the other along the tangential direction of the spherulites. The β IC spherulites with polymer chains along the radial direction crystallized directly from melt. In contrast, the metastable spherulites with polymer chain oriented along the tangential direction among the preformed urea crystals. The phase transition from the metastable β spherulites to the stable α IC during heating was examined as well. For the both types of spherulites of the β IC, the conversion rate along polymer chain direction was lower than that perpendicular to the polymer chain. After phase transition, the orientations of PEO chains almost did not change. The two types of morphologies with different orientations of β IC crystals in the spherulites can be attributed to the competitive nucleation behavior of the β PEO-urea IC and pure urea crystals, which varies with the EO/urea molar ratio in the mixture melt. With the increasing EO/urea molar ratio, the fastest growth direction of β IC will change from the direction along the PEO chain to that normal to the PEO chain. Namely, the polymer/small molecule molar ratio has profound effect on the growth behavior of the β phase IC crystals.

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1. Introduction

Crystallization is a kind of molecular self-assembly process to form ordered solid states, among them spherulite is one of the most common crystalline morphologies. Spherulite usually consists of many densely packed crystal fibers radiating from the center, so the spherulite shows circular symmetry under optical microscope [1,2]. However, the crystal fibers in the spherulite still exhibit anisotropy, which is a fundamental feature of crystals. The molecular orientation in the spherulites is an interesting issue. It is generally accepted that the preferred growth direction of the crystal fibers is along the spherulite radius. For the spherulites of small molecules, both the long axes of the needle-like crystals and the long axes of the rod-like molecules are often in the radial direction [3–5]. In contrast, in the spherulites formed from flexible polymer chains,

the long axes of the lathlike crystals generally oriented along the radial direction, while the axis of polymer chains orients generally along the tangential direction due to chain folding [6–8]. Nevertheless, there exist some cases that polymer chains may change their axial directions in the spherulites. For example, in the cross-hatched lamellar crystals of the melt-grown isotactic polypropylene, the polymer chains could be along both the radial and tangential direction of the spherulites [9–12]. In banded polymer spherulites, the polymer lamellar crystals twist along the radial direction during growth, however, the chain axes are usually normal to the radial direction [2,13,14].

Some small molecules and polymer chains can form inclusion compound (IC), in which a certain component (the host) has in common the ability to incorporate the other (the guest) into the molecular cavities or interspace of the crystal lattices via generally *van der Waals* forces [15,16] or hydrogen bonding in some special cases [17,18]. Different from the simple mixture, inclusion compounds can form some new crystal structures and show different crystal properties and growth behaviors [19–24]. ICs may show

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spherulites under certain crystallization conditions [21,25,26]. The following questions arise naturally: What is the molecular orientation in the IC spherulites? Will the growth mechanism of the two-component crystal be different from that of the single component crystal? Few researchers have studied these questions so far. Damman et al. had studied the orientations and crystal structures of several IC systems formed from PEO and small aromatic molecules, and found that the PEO chain is not in the radius of spherulite in the most cases, while the polymer chain is along the drawing direction in stretched film of IC [26–30]. For example in the inclusion compound formed from resorcinol and PEO, the direction of PEO chain axis which is perpendicular to the benzene ring of the resorcinol molecule is along the tangent in the α form PEO-resorcinol IC spherulite, the 2–5 axis of resorcinol molecule as the a axis of crystal is along the radius of spherulite [26,27].

The inclusion compound formed from urea and poly(ethylene oxide) (PEO) has been intensively studied in the past decades [25,31–40]. PEO-urea ICs exhibit polymorphic crystal modifications, including the stable trigonal α modification [31] and the metastable tetragonal (usually for PEO with low molecular weight) [32] or orthorhombic β modification [33–35]. Here for simplicity, we name them the stable α phase and the metastable β phase, respectively. In the stable α phase, the channel structure formed by urea hosts is about 5.5–5.8 Å in diameter, which is suitable for the individual PEO chains with the 4_1 helical conformation (tgt)₄ to separately reside in the channels [31]. The detailed structure of the metastable β phase of PEO-urea IC is not clear yet [32,33,36].

Previous work in our group demonstrated that PEO chains oriented along the fastest growth direction of the edge-on α IC crystals [39]. However, the polymer chain orientations in the spherulites of the β PEO-urea ICs have not yet been reported up to our knowledge. In this work, we observed two kinds of spherulite morphologies in the β phase of the inclusion compound formed from PEO with an average molecular weight of 100 k and urea (PEO100k-urea IC). Via two-dimensional X-ray diffraction (2D-XRD) and polarized Fourier transform infrared spectroscopy (Polarized FT-IR), we verify the different PEO chain orientations in the two morphologies. Furthermore, the growth mechanism of the two different morphologies and their phase transformation to the α phase will be discussed.

2. Experimental

2.1. Sample preparation

Poly(ethylene oxide) (PEO) with viscosity-average molecular weight (M_v) of 100,000 g/mol and urea were purchased from Sigma-Aldrich and used without further purification. To produce the stable α IC crystals, a corresponding amount of urea was added to a concentrated water solution of PEO (10%, w/v). The molar ratio of the repeating units of PEO chain (EO) and urea was fixed at 4/7. The reason why we chose this molar ratio is that 4/7 is an appropriate molar ratio to study the different spherulite morphologies of the metastable β IC phase. If we further increase the ethylene oxide/urea molar ratio (e.g., 4/5), more complicated crystallization competition behavior will occur (e.g., the stable α IC phase will appear). If we further decrease the molar ratio (e.g., 4/9 or 4/11), urea will always crystallize first and only one type of β IC morphology can be observed. Complete dissolution of PEO and urea was accelerated by heating and stirring. PEO/urea IC crystals were prepared by freeze-drying after the solution had been frozen at -20 °C overnight according to reference [37]. The white solid of ICs after drying was ground to obtain powders.

The highly oriented fibers of the metastable β ICs with the molar ratio of 3/2 were prepared by electrospinning (Beijing

Yongkangleye SS-2505). The spinning solution of PEO and urea solved in methanol with the content of the two solutes about 22 wt % was introduced into a syringe equipped with a 0.6 mm diameter flat-end needle. A 13 kV positive electric voltage was applied on the needle tip and a 2 kV negative potential was imposed on the aluminum foil adhered on a high-speed rotating collector with the diameter of 10 cm and rotation rate of 6000 rpm. The distance between the needle and the collector was 10 cm and the solution flow rate was 0.02 ml/min. Highly oriented fiber film with the thickness of about 100 μ m could be obtained after continuously electrospinning for 1 h.

2.2. Characterization

In order to capture POM image and FT-IR spectra from the same sample, about 1.5 mg PEO100k-urea IC powders sandwiched between two CaF₂ windows with diameter of 15 mm and thickness of 1 mm were melted at 160 °C for 1 min, then quenched to a preset temperature on a hot-stage (Linkam LTS420) for isothermal crystallization. Polarized optical microscope (Olympus BX41P) equipped with a CCD camera (Moticam Pro 282A, Motic) was used to capture the spherulite morphology and crystallization behavior of IC crystals. To obtain the sign of birefringence, a first order tint plate (530 nm) was inserted between the sample and the analyzer.

Polarized Fourier transform infrared microscopy (Bruker Hyperion) was employed to record the IR spectra of a selected 100 \times 100 μ m² local area of different IC samples sandwiched between two CaF₂ windows. An infrared polarizer was inserted between the light source and sample. A total of 32 scans for signal averaging at a resolution of 4 cm⁻¹ from 4000 to 800 cm⁻¹ were needed for each sample spectrum.

Milligrams of samples from different spherulites can be carefully sliced under the objective lens of optical microscope. Spherulites with diameter of several millimeters make it possible to separate M1 and M2 fraction. Several fragments from the same type of spherulites can be collected for thermal analysis. Differential scanning calorimeter (Shimadzu DSC-60) was used in the thermal analysis of the ICs with a scanning rate of 10 °C/min under nitrogen atmosphere. An indium standard was used for calibration before measurement.

The samples for X-ray diffraction were prepared by sandwiched between two polyimide films with a spacer with thickness of about 200 μ m during the thermal treatment on the hot-stage, then the polyimide films were carefully removed to get the spherulite samples for the 2D-XRD measurement. Powder X-ray diffraction (PXRD) measurement was carried out at room temperature on a diffractometer (Bruker D8 Advance) with a speed of 4°/min using an increment of 0.02° from 5° to 50° under the Ni-filtered Cu K_{α} radiation (40 kV, 40 mA). Two-dimensional X-ray diffraction (2D-XRD) measurement was performed at room temperature on an X-ray scattering instrument (Xenocs Xeuss 2.0) with an area detector under Cu K_{α} radiation (50 kV, 0.6 mA). The beam size was about 1 mm and the exposure time was 300 s. The diameter of the metastable β IC spherulites we prepared was as large as several millimeters when crystallized at 80 °C, so the center of the spherulites could be easily marked and the radial direction could be clearly determined.

The surface morphologies of the highly oriented fibers of the β ICs prepared by electrospinning were studied by a scanning electron microscope (SEM) (TESCAN VEGA 3 SBH) with the acceleration voltage of 10 kV. The samples were sputtered with gold for 5 min prior to the measurement.

To determine the accurate EO/urea molar ratio in the different spherulites, the ¹H NMR spectra were recorded with a NMR spectrometer (JEOL, ECA-400M) using milligrams of spherulite

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