



A new model for mesomorphic-monoclinic phase transition of isotactic polypropylene



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ARTICLE INFO

Article history:

Received 21 September 2016

Received in revised form

17 November 2016

Accepted 26 November 2016

Available online 27 November 2016

Keywords:

Conformational reorganization

Phase transition

X-ray scattering

ABSTRACT

In this study, Fourier transform infrared spectroscopy, synchrotron small-angle and wide-angle X-ray scattering were employed to reveal the underlying mechanism leading to conformational reorganization during mesomorphic-monoclinic phase transition. Results indicated that conformational reorganization occurred from 50 to 130 °C, evidenced by conformational infrared bands at 800 and 841 cm⁻¹. The conformation reorganization led to an immediate increase in the density fluctuation but not induced phase transition immediately. Only when the long period started to increase quickly from 80 °C, can phase transition occur. This indicated that intrachain conformational ordering occurred prior to crystalline ordering. Moreover, temperature dependence of long period changed before and after phase transition, implying that chain sliding was the main driven force for the phase transition rather than rewinding and translation of single stems. With the new information obtained, a two-step model for phase transition was proposed. Within a single-chain bundle, two adjacent helices with opposite handedness can interlock into double helices with higher density, and urge each other extending to entire stem during moving along opposite directions with the help of chain slipping, resulting in ordered arrangement of helical stems. Afterwards, single-chain clusters coalesce, leading to interchain crystalline ordering. The new model is helpful to understand the phenomena related to mesomorphic iPP.

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1. Introduction

As an intermediate state between amorphous and crystalline isotactic polypropylene (iPP), mesomorphic iPP has been paid attention constantly since the 1950s [1]. However, its structure and related phenomena have not been elucidated completely. The researches on mesomorphic iPP concentrate mainly on three aspects. The first one is its formation condition. It is well known that mesomorphic iPP can be obtained simply by quenching iPP melt to ice water. However, to determine accurately the cooling rate and temperature required for the formation of mesomorphic iPP was extremely difficult a few decades ago, since then it was still a huge challenge technically to observe structural change in such high cooling rate [2,3]. Until recently, accurate conditions were identified with scanning nanocalorimetry: the cooling rate should be

larger than 90 °C/s and the temperature should be below 40 °C [4]. Note that the cooling rate for the formation of mesomorphic iPP could be reduced significantly through addition of comonomers revealed by recent investigations [5–9]. The second one is its structural assignment. Unlike other phases of iPP, no consensus has been reached on its structure due to lacking of enough structural information. Some researchers regarded mesomorphic iPP as smectic phase [1,9,10]. Other researchers attributed it to crystal with defects: paracrystalline [10] or conformationally disordered crystals [11]. However, in either model, it is well-accepted that parallel aligned helices of different handedness are arranged randomly in the lateral direction, being terminated by helix reversals or other conformational defects [12]. Recently, new information on the structure of mesomorphic iPP was obtained with solid-state NMR spectroscopy and spin-dynamics simulations: individual iPP chains adopt adjacent reentry sequences with an average folding number $\langle n \rangle = 3-4$, and it had higher mobility than that in monoclinic crystal [13,14]. We also investigated mesomorphic iPP with polarized optical microscope, synchrotron small-

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angle (SAXS) and wide-angle X-ray (WAXD) scattering in recent years [15,16]. Results indicated that except crystal residuals, some metastable helical aggregates with higher melting temperature existed in the mesomorphic iPP melt, which accelerated spherulitic growth and formed a transition layer between amorphous and lamella layers, different from normal melt crystallization, indicating structural complexity of mesomorphic iPP.

The third one is the mechanism of mesomorphic-monoclinic crystal phase transition. As mentioned above, the helices with different handedness are arranged randomly in the lateral direction, hence the conformation needs to be reorganized before phase transition. In principle, FTIR is the most powerful tool to extract the information on conformational reorganization. However, the employment of FTIR in the study was scarce because the highly similarity of FTIR spectra of mesomorphic and monoclinic crystal [17]. Additionally, conformation reorganization is achieved by rearrangement of entire stems, which length is around 10 nm [18]. In such scale, SAXS is the best tool to monitor its structural change, however, the useful information obtained by SAXS was limited also due to the similarity [18,19]. The most used tools for the study of phase transition were WAXD, atomic force microscopy (AFM) and various scanning calorimetries [19–28]. With AFM results, Androsch proposed a model for the phase transition [23]. It was assumed that to meet the requirement for handedness, a helical stem could change freely from right-handed to left-handed or from left-handed to right-handed or move to a new position, without affecting other stems. This model is questionable. As found by solid-state NMR [13,14], every stem is a sequence in an adjacent reentry cluster, thus it cannot move freely. When the helical stem translates or its handedness reverses, it is hard to imagine that no influence is stressed on other stems in a same cluster. Thus the phase transition from mesomorphic to monoclinic iPP crystal was investigated again systematically with FTIR, synchrotron SAXS and WAXD.

2. Experimental section

2.1. Materials

The iPP sample used in this study has a weight-average molecular weight of 720 kg/mol and a polydispersity of 4.8, which was kindly supplied by SABIC-Europe. A mesomorphic iPP film with a thickness of 100 μm was obtained by quenching the molten film to ice-water after erasure of thermal history at 220 $^{\circ}\text{C}$ for 5 min. After preparation, the mesomorphic iPP film was preserved at 0 $^{\circ}\text{C}$ to prevent phase transition before measurements.

2.2. Fourier transform infrared spectroscopy

The conformational change during mesomorphic–monoclinic phase transition was studied using Tensor 27 FTIR spectrometer (Bruker) equipped with a home-made hot stage. After a mesomorphic film was sandwiched by two ZnSe windows in the hot stage, it was heated at a rate of 2 $^{\circ}\text{C}/\text{min}$ during FTIR measurements from 30 to 180 $^{\circ}\text{C}$. For comparison, change in conformational bands of crystalline iPP was also monitored during heating with the same rate. The crystallized iPP was obtained by isothermal crystallization at 135 $^{\circ}\text{C}$ after erasure of thermal history at 220 $^{\circ}\text{C}$ for 5 min. The spectrum was collected every 1 min at a 4 cm^{-1} resolution by averaging 64 scans. The wavenumber range was from 4000 to 600 cm^{-1} . Peak area was taken as the integral intensity of a conformational band in this study.

2.3. Synchrotron wide-angle and small-angle X-ray scattering

Mesomorphic–monoclinic phase transition during heating of

mesomorphic iPP was also monitored with synchrotron SAXS and WAXD at the beamline BL16B of Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-ray beam was fixed at 0.124 nm. The sample-to-detector distance was set to 185.25 and 2500 mm for WAXD and SAXS measurements, respectively. The same hot stage used in FTIR measurements was also used in the synchrotron X-ray scattering measurements. Instead of ZeSn infrared windows, a sample was sandwiched between Kapton films before heating with a rate of 2 $^{\circ}\text{C}/\text{min}$. Because the beamline BL16B cannot collect two dimensional (2D) WAXD and SAXS patterns simultaneously, two same experiments were performed to collect 2D WAXD and SAXS patterns by a Mar165 CCD detector, respectively. The exposure time is 30 s both for WAXD and SAXS patterns, which was collected every 2.5 min 2D WAXD and SAXS patterns were analyzed with Fit2D software from European Synchrotron Radiation Facility.

3. Results

3.1. Synchrotron wide-angle X-ray diffraction

To monitor structural change during heating of mesomorphic iPP, synchrotron WAXD was employed firstly. Fig. 1 shows 1D WAXD intensity profiles at various temperatures. Below 80 $^{\circ}\text{C}$, X-ray intensity profile remains unchanged basically during increasing temperature (see Fig. 1a). From 80 to 130 $^{\circ}\text{C}$, the mesomorphic iPP peaks at 14.1 and 21 $^{\circ}$ are replaced gradually by diffraction peaks of monoclinic crystal (110), (040), (130), (111) and (–131) (see Fig. 1b), indicating mesomorphic-monoclinic phase transition. 80 $^{\circ}\text{C}$ can be regarded as the onset temperature, since it is the lowest temperature to observe diffraction peaks, for example the (130) peak at 18.6 $^{\circ}$ (see insert in Fig. 1a). Further increasing temperature from 130 $^{\circ}\text{C}$ does not affect X-ray intensity profile evidently until melting at 160 $^{\circ}\text{C}$ (see Fig. 1c).

To clarify the relationship between crystalline, mesomorphic and amorphous iPP during phase transition, their fractions in the sample at various temperatures were determined using multi-peak fitting. As shown in Fig. 2a, crystalline, mesomorphic and amorphous peaks can be fitted perfectly. The fitted result was plotted in Fig. 2b. From Fig. 2b, it can be seen that phase transition starts from 80 $^{\circ}\text{C}$ and completes at 135 $^{\circ}\text{C}$, and the transition rate is greater in the temperature range from 90 to 120 $^{\circ}\text{C}$. Additionally, amorphous fraction remains unchanged before 135 $^{\circ}\text{C}$, indicating that phase transition occurs in solid state as pointed out by other researchers [7,11,28].

3.2. Fourier transform infrared spectroscopy

FTIR was employed to study the conformational reorganization during phase transition. To check if characteristic bands for conformational reorganization exist or not, FTIR difference spectra were employed and compared with those of crystalline iPP. The crystallized iPP was obtained by isothermal crystallization at 135 $^{\circ}\text{C}$ after erasure of thermal history at 220 $^{\circ}\text{C}$ for 5 min. The FTIR difference spectra were obtained by subtracting the first FTIR spectrum at room temperature from every spectrum to detect tiny change in conformational bands in the early stage of phase transition. After careful comparison, two characteristic bands were identified, which intensities had different temperature dependences from those of crystalline iPP. The first conformational band locates at 808 cm^{-1} . Fig. 3a–b shows changes in the absorbance band at 808 cm^{-1} during heating of mesomorphic and crystalline iPP, respectively. For crystalline iPP, the peak area decreases throughout the heating, indicating relaxation of long helices. However, during heating of mesomorphic iPP, it seems that the

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