



In-situ investigation on the structural evolution of mesomorphic isotactic polypropylene in a continuous heating process



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ABSTRACT

The microstructural changes of mesomorphic iPP from mesophase to α transition at a molecular level in a continuous heating process have been studied by in-situ Fourier-transform infrared (FT-IR) spectroscopy, in-situ X-ray scattering using synchrotron radiation, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Microstructural change corresponding to helical conformation variation in the temperature range between 20 and 60 °C was detected by IR spectroscopy, which may originate from the glass transition of rigid amorphous fraction (RAF). The helical sequence with 12 monomer units is found to exist in RAF. The contents of helical sequences with different number of monomers exhibit different variation trends in the course of meso- α transition and the following process of partial melting and perfection of α crystal. A plausible mechanism was proposed that RAF experiences glass transition firstly at low temperature, and then serve as α nuclei to trigger the meso- α transition at higher temperature. This work provides a new insight into the mechanism of microstructural evolution of the meso- α transformation of iPP.

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1. Introduction

Isotactic polypropylene (iPP) continues to attract both scientific and industrial attention since its successful synthesis by using Ziegler-Natta catalyst more than 60 years ago [1]. iPP is a semicrystalline polymer with a typical polymorphic behavior. iPP may crystallize in α , β , γ crystal and mesophase depending on the crystallization conditions [1–6]. Since Natta [7] reported mesophase of iPP in 1959, mesophase has received extensive attention [8–13]. Generally, the mesophase of iPP can be formed by annealing the completely amorphous phase or by quenching the quiescent melt at a cooling rate of more than 100 K/s but lower than 1000 K/s or by cold drawing crystallized iPP samples [14,15]. Similar to crystalline phase, the molecular segments of mesophase preserve the 3_1 helical conformation, but lose three dimensional long-range order [16,17]. Recently the local packing structure of the

mesophase of iPP was reported to be very similar to that of the β phase of iPP [18]. Mesophase obtained by annealing amorphous iPP or directly quenching the iPP melt exhibits nodular morphology [19], and the nodule size is of about 5–20 nm depending on the formation condition [15].

Mesophase has the degree of ordering that are intermediate between the crystalline phase and the amorphous phase [1]. Under appropriate cooling conditions, mesophase can be formed in most of semicrystalline polymers, such as polyethylene [14], isotactic and syndiotactic polypropylene [20], isotactic poly(1-butene) [14], poly(ethylene terephthalate) (PET) [21], poly(lactic acid) [22,23] etc. Mesophase is unstable and will transform to thermodynamically stable crystalline structure upon elevating temperature [24]. The formation and transformation process of mesophase are of great significance for understanding the crystallization of polymer [5]. Therefore, as an important phase of polypropylene, transformation of mesophase of iPP during the heating process has been widely investigated by small angle X-ray scattering and wide angle X-ray diffraction (SAXS/WAXD) [5,25–27], atomic force microscope (AFM) [14,28,29], Fourier transform infrared (FTIR) spectroscopy

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[30,31], fast scanning chip calorimetry (FSC) [32] and other techniques [33].

In-situ FTIR spectroscopy is widely used for studying subtle conformational adjustments of polymer chains and order–disorder phase transition [34–36]. The infrared spectrum of iPP has rich regular helical conformation bands, and the assignment of each helical band is clear [30,35,37–42]. This allows us to study the microstructural evolution of quenched iPP during heating at a molecular level. Zhao [31] reported that the short helical sequences extended into long helical ones before 120 °C and the long-chain helices experienced melt-recrystallization after 120 °C during a stepwise heating of quenched iPP by using FTIR spectroscopy. Wang [30] compared the structural transformation of solution electrospun iPP mesophase with that of melt-quenched iPP during the stepwise annealing process, and found that the fraction of the amorphous phase showed no change prior to initial crystal melting neither in electrospun fiber nor in the melt-quenched film.

In the heating process of quenched iPP, a small endothermic peak centered at 40–60 °C can be observed in the conventional DSC heating curve while there is no obvious change from X-ray diffraction results [33]. The relaxation of rigid amorphous fraction (RAF) located at the boundary between the mesophase and the bulk amorphous phase [43], a glass transition-like behavior [33], the chain reorganization of the interfacial region of the mesophase [30] and the melting of mesophase [26,27,44] were suggested to be responsible for this small endothermic peak in DSC curve. However, the nature of this small endothermic peak is still not clear. Based on the different understanding on this endothermic peak, different mechanisms have been proposed to elucidate the mesophase- α crystal transition. Liquid-solid phase transition was proposed by some researchers who ascribed the endothermic peak to the melting of mesophase [5,26,27]. Wang [5] proposed that the endothermic peak corresponds to the partial melting process of the mesophase leaving the laterally ordered molecular chains to be the initial crystalline nuclei followed by formation of α crystal through secondary nucleation or conventional crystal-growth process. Jin [27] and Ferrero [26] put forward a mechanism in which the mesophase underwent melting and a subsequent recrystallization into monoclinic α crystal. However, others proposed the mesophase- α crystal transition occurred via a solid-solid transition process without the melting of mesophase. Namely, the small endothermic peak in the DSC heating curve had nothing to do with melting of mesophase. Androsch et al. [29] suggested complete melting of mesophase did not occur based on the fact that the nodules size of the initial mesophase domains did not change. Marega [25] suggested the mesomorphic- α transition is associated with molecular chain rearrangement without melt-recrystallization. Wang [30] speculated the small endothermic peak is related to the chain reorganization occurred at the interfacial region of the mesophase, then new α -form nuclei formed at the interface of mesomorphic domains, followed by a progressive transformation of mesophase to α crystal. Therefore, the structural change of the small endothermic peak in DSC curve is very important to understand the subsequent meso- α transition.

To understand the meso- α transition process, condensed structural feature of mesomorphic iPP need to be considered. In the three phase model of semicrystalline polymers, i. e. crystalline (C), mobile amorphous (MAF) and intermediate phase, the intermediate phase is coupled at the interface between crystalline and mobile amorphous phase, namely RAF [44,45]. The RAF has been found in most semicrystalline polymers [16,46–49]. The confinement of molecular chains at the interface reduces the local mobility of segments and leads to an improved glass transition temperature (T_g) of the RAF which was even higher than the melting temperature of these semicrystalline polymer, such as poly (phenylene

oxide) [50]. The RAF of iPP devitrified between 325 K and 370 K and was about 50 °C higher than that of MAF derived from DSC results [16]. The ‘small endothermic peak’ in low temperature range prior to the mesophase-crystal transition in the DSC heating process was found not only in iPP, but also in other polymers such as poly (oxymethylene) (POM), PET and poly (butylene terephthalate) (PBT) [44,51–53]. Although interpretation of this peak was controversial for iPP, it has been verified that the ‘small endothermic peak’ before the cold crystallization in POM and PET is related to the devitrifying (relaxation) of RAF [44,51,52]. Considering that one of the structural features of iPP crystallized in mesomorphic phase is that a large amount of RAF (about 40%) coexist with relatively little MAF [44,45]. Therefore, the RAF may be helpful to understand the meso- α transition and will be taken into consideration in our work.

Moreover, in the initial stages of crystallization mechanism proposed by Strobl [54], the mesophase may act as ‘precursor’, then produced a granular crystalline layer via structure transition and finally transformed into lamellar crystallites. This mechanism has been accepted by other researchers [55,56]. However, there is still no consensus about the mechanism of meso- α transition, so it is critical to have the structural evolution details for understanding the transition process from mesophase to α crystal.

The high sensitivity of IR spectroscopy to the conformational change of iPP and advancement of precisely temperature controlling technique enable us to investigate the microstructural transformation of mesophase in the heating process of mesomorphic iPP at a molecular level. However, previous reports concentrated on the meso- α transition in a stepwise heating process. Detailed study on mesophase- α crystal transition in a continuous heating process by in-situ FTIR spectroscopy is still lacking and the microstructural change for the small endothermic peak in the conventional DSC heating curve was neglected in the previous IR spectral study of mesomorphic iPP, which is directly linked to the mechanism of meso- α transition. In this paper, the microstructural changes of mesomorphic iPP in the continuous heating process have been investigated by the combination of in-situ FTIR and WAXD/SAXS technique. Especially, the structural change of mesomorphic iPP before 60 °C was focused. And a plausible transition mechanism of mesomorphic iPP based on considering the important role of RAF was proposed.

2. Experimental section

2.1. Sample preparation

iPP is a commercial product of SINOPEC Beijing Yanshan Company (MFR = 3.6 g/10 min at 230 °C/2.16 Kg). To obtain the mesophase of iPP, an iPP film with thickness of about 80 μ m was heated to 210 °C and held for 5 min, then was quickly immersed into ice water mixture. The quenched films were stored in the refrigerator with the temperature of -18 °C.

To help understanding the transformation process of mesophase to α crystal, iPP with different microstructures were obtained by annealing the quenched iPP film at different temperatures. The quenched iPP films were heated from room temperature to different annealing temperatures (20, 40, 50, 60, 80 and 140 °C) at 3 °C/min and held for 3 min, then quickly immersed into ice water.

2.2. In-situ WAXD/SAXS measurement

In situ WAXD/SAXS measurements equipped with Linkam LTS350 hot stage were carried out at the beamline 1W2A-SAXS of the Beijing Synchrotron Radiation Facility (BSRF) [57]. The wavelength of the radiation source was 1.54 Å. The distance from sample

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