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An unusual promotion of γ-crystals in metallocene-made isotactic polypropylene from orientational relaxation and favorable temperature window induced by shear

Yan Wang [a, b], Jian Zhao [a], Minjie Qu [a], Jing Guo [a], Shu-Gui Yang [b], Jun Lei [b], Jia-Zhuang Xu [b, *], Yan-Hui Chen [c], Zhong-Ming Li [b, **], Benjamin S. Hsiao [d]

[a] School of Textile and Material Engineering, Dalian Polytechnic University, Dalian 116034, China
[b] College of Polymer Science and Engineering and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China
[c] Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an 710072, China
[d] Department of Chemistry, Stony Brook University, Stony Brook, NY 11794-3400, USA

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ABSTRACT

Combined effects of shear flow and non-isothermal processing, which were akin to the practical industrial processing, on the crystallization of metallocene-made isotactic polypropylene (m-*i*PP) were investigated by *in-situ* synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) techniques. The simultaneous appearance of α- and γ-crystals was observed in quiescent samples, while shear flow led to the occurrence of α-crystals prior to γ-crystals at the initial stage of crystallization. Although the local alignment of chain segments promoted by shear flow facilitated the α-crystals, the relaxation of oriented chains was experimentally confirmed to boost the formation of γ-crystals. Interestingly, the resultant γ-crystal content was higher in the sheared samples than the quiescent counterparts at a given cooling rate and further increased with the decrease of cooling rates. Such a discrepancy was not only related to shear-induced orientation and relaxation, but also was accredited to the advanced crystallization temperature window, which was favorable for the γ-crystal growth. It was quite different from the isothermal crystallization situation, where the formation of γ-crystals was depressed in presence of shear flow. The dynamic competition between α-crystal and γ-crystal formation under the effects of shear during the non-isothermal crystallization was discussed. Our work is of valuable reference to tailor the crystalline structure of m-*i*PP during practical processing and hence to acquire the desired performance of products.

1. Introduction

Isotactic polypropylene (*i*PP), one of the most appealing members in polyolefin family, possesses versatile and well-balanced performance intimately associated with its unique polymorphisms. The *i*PP mainly has three crystalline modifications (α, β, and γ-crystals), which share the same helical conformation, i.e., a three-fold helix with a 6.5 Å chain axis repeat distance, but have different packing mode [1–4]. Prominent strength of the typical α-crystals and excellent toughness of the β-crystals have been well documented in the open literature [5–8]. However, the property of γ-crystals is rarely reported, although the unparallel chain arrangement might endow it with superior elastic modulus and yield strength [9]. Such a predicament is essentially stuck by poor understanding of the formation and manipulation of γ-crystals, which is worth the efforts to uncover the structure-property relationship of γ-crystals and to fully exploit the application range of *i*PP.

Up to now, it has attained a broad consensus that the formation of γ-crystals requires harsh conditions in terms of molecular configuration and crystallization environment, such as special chain structures, elevated crystallization temperatures, and/or pressure [10–18]. For instance, the molecular chain with short regular isotactic sequences is inclined to generate γ-crystals [10–12]. A higher amount of γ-crystal usually develops at high

* Corresponding author.
** Corresponding author.
E-mail addresses: jzxu@scu.edu.cn (J.-Z. Xu), zmli@scu.edu.cn (Z.-M. Li).

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crystallization temperatures depending on the molecular weight and defect contents [14,15]. The α-crystals and γ-crystals coexist at low pressures, while γ-crystals become dominant at high pressures (e.g., 2000 bar) [19]. However, these cognitions are established based on the results from quiescent conditions.

Given the indispensable flow fields in practical processing, the role of shear flow in the formation of γ-crystals has received continuous attention. It is demonstrated that during the isothermal crystallization, the application of shear flow significantly influenced the formation and morphology of γ-crystals [17,20–22]. The γ-crystals accompanied with the other two crystalline components (α- and β-form) are induced by shear, although the faster dissolution of the β- and γ-forms may occur subsequently due to their initial instability [20]. The oriented γ-crystals were incorporated and branched on parent α-lamellae as well as directly to the shish backbone [22]. Under a strong shear field, the emergence of γ-crystals was delayed and the γ-crystal content was suppressed, attributing to the fact that the oriented chains had little chance to form γ-crystals [21]. In the presence of pressure, the formation of γ-form showed facilitation (<3.7 s^{-1}), suppression (3.7–9.1 s^{-1}), and inexistence (>9.1 s^{-1}) with the shear rate [17]. When the exploration is broadened to the practical polymer processing, the influence of shear flow on the γ-crystals has not been reconciled. Kalay et al. found that the fraction of γ-crystals was increased in the injection-molded ZN-*i*PP, attributing to the pronounced molecular orientation [23]. Our previous study imposed an intense shear flow to the m-*i*PP melt during the injection molding and found that the γ-crystal content varied dramatically (f_γ = 0.57–0.74) at different inner distance from the skin of the molded samples [24]. In these cases, crystallization of *i*PP proceeds under non-isothermal conditions, since thermoplastic semi-crystalline polymers are often cooled from the molten state in the actual processing. Therefore, it is imperative to gain the insights into the effects of shear flow on the γ-crystal formation during the non-isothermal crystallization.

In this study, polymorphic behavior of metallocene-made isotactic polypropylene (m-*i*PP) was investigated under the combination of shear flow with non-isothermal processing, which stimulated the thermomechanical history of real polymer processing. *In-situ* synchrotron wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were used to monitor the structure evolution at different cooling rates. It was found that the α-crystals appeared prior to γ-crystals in clear contrast to the simultaneous appearance of these two crystals in quiescent samples. Of interest, the final content of γ-crystals was increased in the sheared samples irrespective of cooling rates. It was quite different from the observation under isothermal crystallization situations, where the γ-crystal formation was restrained by the shear flow. Such a discrepancy was explained from the aspect of nucleation, chain relaxation and lamellae growth. These intriguing results unclosed here was helpful to tune the structure and content of γ-crystals in the *i*PP products.

2. Experimental section

2.1. Material

Commercially available *i*PP, polymerized by metallecene catalyst, was supplied by the Basel Co., Netherlands. The detailed information of the raw material, such as molecular weight, polydispersity, nominal melting temperature, and content of triad stereo-sequences, were summarized in Table 1.

2.2. Experimental procedures

A modified shearing stage (Linkam CSS-450) was used to accurately control the thermomechanical history. The ring specimen (outer diameter = 20 mm, inner diameter = 10 mm, and thickness = 0.5 mm) was stamped from the compression-molded sheet and was sandwiched between two X-ray windows (diamond and Kapton film) in the Linkam shear stage. The gap between the two windows was adjusted to fit the sample thickness. The thermomechanical profile is shown in Fig. 1: (a) Heat the specimen from room temperature to 200 °C at a rate of 30 °C/min; (b) Hold at 200 °C for 5 min to eliminate any thermal history; (c) Cool down to 145 °C at a rate of 30 °C/min; (d) Maintain 3 min for equilibrium and then impose the shear (500% shear strain for 30 s) upon the melt; (e) Cool from 145 °C to 65 °C at a preset rate of 10, 5, and 1 °C/min. The selection principle of shear intensity hereby was introduced in the Supporting Information (SI) [25–28]. The data collection was initiated right after the shear was imposed. The sheared samples were designed to as S10, S5, and S1, where the behind number corresponds to the cooling rate. For comparison, the quiescent samples were short for Q10, Q5, and Q1.

Table 1
Information of metallocene-made isotactic polypropylene.

Commercial NO.	M_w(g/mol)	M_w/M_n	T_m(°C)	[*mr*]%	[*rr*]%	[*mm*]%
562N	407,000	2.25	145	3.09	0.386	96.05

2.3. In-situ wide-angle X-ray diffraction and small-angle X-ray diffraction measurements

In-situ 2D-WAXD and 2D-SAXS measurements were carried out at the Advanced Polymer Beamline (X27C) in the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL, USA). A 2D MAR CCD X-ray detector (MAR, USA) was employed for the detection of 2D-WAXD images, with an image resolution of 1024 × 1024 pixels (pixel size = 158 μm). The sample-to-detector distance was 107 mm for WAXD measurements (calibrated by an aluminum oxide standard) and 1789.7 mm for SAXS measurements (calibrated by a silver behenate standard). The acquisition interval for each scattering pattern was 30 s. All X-ray images (SAXS and WAXD) were corrected via background scattering, air scattering, and beam fluctuations. 2D WAXD patterns were integrated over the polar angle to convert to 1D scattering profile, according to the function of $|q| = 4\pi \sin\theta/\lambda$, with q being the absolute value of the scattering vector, λ being the wavelength

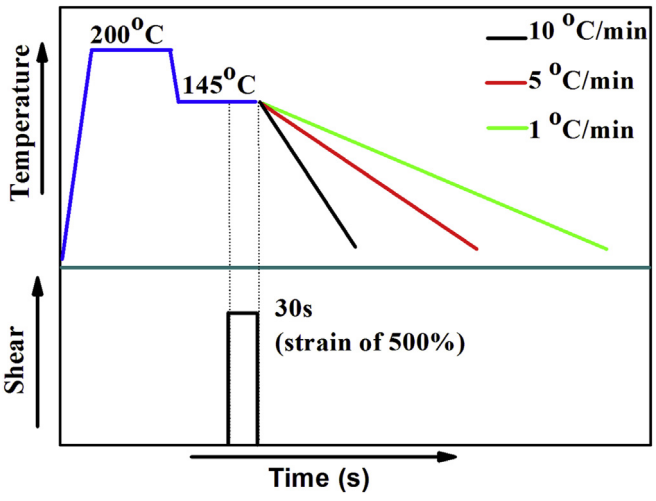

Fig. 1. Schematics of the thermomechanical history protocol of the sheared m-*i*PP.