



Flow induced crystallization in isotactic polypropylene during and after flow



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ABSTRACT

Using a unique slit flow device and in situ synchrotron X-ray methods, the entire evolution of flow induced crystallization in isotactic polypropylene (iPP) was studied from the start-up of flow up to completion of crystallization. Two WAXD detectors, including the ultrafast Pilatus and the two-dimensional Frelon, were combined to achieve a sufficient time resolution for a fairly short period (during and just after flow) and a sufficient spatial resolution for measuring the kinetics of different crystallites oriented in different directions. The complete evolution of these structures is obtained and this reveals several important issues on crystallization. Firstly, the appearance of crystallites can occur already within a short flow duration of maximum 0.25 s. The specific formation time strongly depends on the flow strength. The formation of crystallites just after flow can be distinguished from that occurring during flow, although both happen on the sub-second time scale. Next, we quantified the subsequent appearance of iPP daughter lamellae and determine the time dependent ratio between parent and daughter lamellae as a function of the flow strength. The average orientation of the initial shish is relatively high while the orientation of parent lamellae decreases with their lateral growth. Finally, at the experimental temperature of 145 °C and depending on the shear strength, iPP β -phase can be induced. The quantitative information provided by this data set is well suited for validation and extension of our models for flow induced crystallization of polymers. Such complete data sets, including the fully specified initial and boundary conditions are not available yet for the (nearly) processing conditions as we applied in this study.

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1. Introduction

For semi-crystalline polymers, the ultimate properties strongly depend on the features of crystalline structures formed during processing. This includes crystal modifications, degree of crystallinity, lamellar thickness, crystal orientation, etc. Therefore, it is crucial to understand how crystallization of various morphologies evolves during processing. The ultimate goal is to be able to predict the final crystallite structures and, from that, to predict the final properties.

According to classical crystallization theory, polymer crystallization is a two-step process: nucleation and crystal growth [1]. To start crystallization, stable nuclei are required. Spontaneous formation of stable nuclei follows the thermodynamic rule that the total Gibbs free energy change from melt to nuclei, $\Delta G = G_{\text{nuclei}} - G_{\text{melt}}$, has to be negative, which can be concretely expressed as $\Delta G = \Delta G_b + \Delta G_s$ with the bulk free energy change ΔG_b and surface free energy change ΔG_s . The nucleation process is determined by the competition between bulk and surface free energy changes, of which the former should overcome the latter to generate stable nuclei. This homogeneous nucleation rarely happens in reality, because contaminants (like catalyst residues) and dormant precursors provide extra surface which contribute to surface free energy term ΔG_s and consequently lower the nucleation barrier. More importantly, flow, as an unavoidable processing factor, affects nucleation in a different way. From a thermodynamic point of view, the application of flow raises the free energy, decreasing ΔG_b further and, therefore, promotes nucleation.

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Besides, flow induces anisotropy to the crystalline morphology and generates, for example, the typical shish-kebab structure [2] which consists of a fibrillar core oriented along the flow direction (shish) with transverse, periodically stacked lamellae (kebab). Flow can generate stable nuclei, able to initiate crystal growth, or “precursors” with some degree of order (positional or/and orientational; intra- or/and inter-molecule) that may nucleate for sufficient under-cooling or may relax in case of a relatively high temperature. Therefore, the first step is to understand what ordered structures are generated for what flow conditions.

Flow affects the crystallization by providing both extra nucleation sites and an orientation template, the former accelerates kinetics and the latter induces anisotropic lamellar growth. Li and co-workers [3,4] found that shear could induce conformational helices of isotactic polypropylene and consequently trigger the subsequent crystallization at high enough undercooling. The threadlike precursors of a “shear-induced structure” found by Kumaraswamy et al. [5], possess oriented molecular segments, detectable with birefringence, which cause the appearance of a skin layer in a slit flow. Shear-induced “bundles” that are densely packed and observable by small angle X-ray scattering (SAXS) can start crystallization in the vicinity of the melting temperature [6,7] and these crystalline seeds provide a perfectly matched crystal lattice for epitaxial growth. It is clear that the accelerated crystallization can even start during the period flow is imposed. Moreover, flow is able to induce crystal modification. For example, shear-induced iPP α -row nuclei (created by means of fiber-pulling) can initiate the growth of β -phase as well as the monoclinic α -phase [8].

The ideal experimental strategy should cover both the initial generation process of precursors/nuclei (from the start of flow), and the subsequent growth process (until completion of crystallization). However, precursors/nuclei can form quite rapidly [9] and to achieve in-situ tracking of their formation puts severe demands on the experimental methods used. Therefore, most of the previous studies focus on the crystallization after cessation of flow and infer the formation and properties of nuclei through the kinetics and morphology of the resulting crystallization. In this study, we investigated the rapid formation of structure (during and after flow) in detail using synchrotron radiation X-ray and detectors, with a high sample rate (30 frames/s). In a previous paper [10] we have given a detailed description of the experimental procedures and, the formation of flow induced structures reflected by the rheological response and SAXS signals for a commercial isotactic polypropylene (iPP). Indicated by the SAXS equatorial streaks it was demonstrated that, depending on the flow strength, densely packed structures, termed as shish, can be induced. For the same grade of iPP, wide angle X-ray diffraction (WAXD) was employed to gain detailed information on the evolution of the corresponding crystallites. For this purpose, two X-ray detectors (ultrafast Pilatus and 2D Frelon) were combined in order to get a high time-resolution and a clear picture of the various orientations, respectively. With this setup we could track the entire crystallization process. Moreover, birefringence is utilized to probe potential structures which are below the detection limit of X-ray.

The present work aims to clarify what objects are generated for various flow conditions and reveal in a quantitative sense the entire evolution of these objects, ultimately in order to bridge the gap between nuclei and the resulting crystalline structures.

Moreover, the same grade of iPP material has been worked on for years in our group (in experiments and simulations) and its physical properties and crystallization behavior under quiescent and mild flow conditions are well characterized [11–18]. However, the quantitative characterization of crystallization influenced by severe flow, close to processing conditions, is still needed. This is another important motivation for this study since it completes our

work on understanding strong flow induced crystallization behavior and, moreover, provides data for model validation and model extension/improvement (ongoing work).

2. Experimental section

2.1. Material

A commercial isotactic polypropylene (iPP, Borealis HD601CF, known as HD120MO before) is used in this work. Material properties are summarized in Table 1. Melting and crystallization temperatures are measured using differential scanning calorimetry (DSC) at a heating/cooling rate of 10 °C/min, sample weight: 3 ± 0.5 mg. Detailed information on other properties of this material can be found in the literature [11,16].

2.2. Flow device

The flow device used in this work is a slit flow operated on a multi-pass rheometer which has been described elsewhere [19]. The sample is confined between two servo hydraulically driven rectangular pistons in a slit with a cross-section, A , of $6 \text{ mm} \times 1.5 \text{ mm}$ (width, $W \times$ height, H). The two pistons move simultaneously in one direction to impose a shear field to the molten polymer. Two diamond windows are mounted in the middle of the flow cell allowing the passage of X-ray and laser light for in-situ characterization of structure evolution during and after flow.

The sample is first heated to 220 °C and kept at that temperature for 10 min in order to erase previous thermo- and mechanical history from sample preparation. Next, the relaxed melt is cooled to 145 °C. All shear and isothermal experiments were performed at this temperature. Flow strength can be varied by choosing different piston speed, V_{piston} . The piston speeds applied were 20, 40, 60, 80, 100, 120 and 140 mm/s and the corresponding apparent wall shear rates are 80, 160, 240, 320, 400, 480 and 560 s^{-1} , determined by $\dot{\gamma} = 6Q/WH^2$ with the volumetric flow rate $Q = V_{\text{piston}} \times A$ [20]. The flow time is fixed at 0.25 s for piston speeds ranging from 20 to 100 mm/s, and shortened to 0.23 and 0.20 s for 120 and 140 mm/s, respectively, due to limitation in the maximum piston displacement.

2.3. X-ray characterization

Small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) were used to characterize the entire crystallization process, including the short period of flow. All X-ray measurements were performed at the Dutch-Belgian (DUBBLE), beamline BM26B of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France [21,22]. The wavelength used was 1.033 Å.

SAXS measurements were carried out with a Pilatus 1M detector (981×1043 pixels of $172 \mu\text{m} \times 172 \mu\text{m}$) placed at a distance of 7.117 m. For the initial period of 1 s, which includes the period of flow, an acquisition rate of 30 frame/s was used. The SAXS results have been presented previously in detail [10] and will be discussed together with the WAXD results shown in this work.

Table 1
Properties of the iPP used in This Work.

Material	M_w (kg/mol)	M_w/M_n	T_m (°C)	T_c (°C)
iPP homopolymer	365	5.4	163	113

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