



Shear-induced pre-crystallization structures of long chain branched polypropylene under steady shear flow near the melting temperature

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ABSTRACT

Shear-induced crystallization of a long chain hyper-branched polypropylene (LCB-PP, denoted PP-3) was carried out at a relatively high temperature of 170 °C, close to its melting temperature of 158 °C. Small-angle X-ray scattering (SAXS) showed that the intensity ratio of the normal to the perpendicular to the shear (V/H) was always larger than 1 for PP-3, indicating that shish-like structures were predominately formed and further growth to kebab was suppressed in PP-3. The crystallization behavior of PP-3 can be explained by the nature of PP-3 that there were a large amount of crystallization nuclei due to their branching points, and the point-like precursors formed from these nuclei were arrayed linearly along the shear direction and transformed into thread-like precursors or premature shish; however, owing to the large amount of branching, further progress in crystallization was suppressed.

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1. Introduction

Shear-induced crystallization is a well-known phenomenon for polypropylene (PP) and widely studied in past several decades in terms of both industrial and fundamental points of view [1–6]. Shish-kebab structures [7], comprising the bundle of stretched chains parallel to the shear (shish) and the crystalline lamellae (kebab) nucleating onto the shish, are often formed in the shear-induced crystallization of PP. Since the kebabs grow epitaxially from the shish surface, the a-axis of their crystal is oriented normal to the shear direction. These kebabs are called primary kebabs. As crystallization goes on, the kebab orientation was gradually lost and sometimes spherulite formation overcomes the preceding shish-kebab structures. In injection molding, the finished products consist of three layers: skin, intermediate, and core layers. Since the intermediate layer is subjected to the largest shear, it contains shish-kebab structures [8–11]. Shish-kebab structures are considered as one of the molecular origins for high strength and high modulus. This is the reason why many studies have been performed in the last decades.

The formation of the shish-kebab structures has been investigated by many groups using time-resolved synchrotron X-ray. Somani et al [12–14], who investigated dynamics of the shear-induced crystallization of linear PPs, found that there is a critical shear rate for a given molecular weight (or a critical molecular weight at a given shear rate condition) to provide the oriented crystalline structures. Their shear rate range was 10–10² s⁻¹ and the shear-imposing time was relatively short (max. 5 s). Immediately upon the cessation of the shear, SAXS (small-angle X-ray scattering) indicated the appearance of large and highly oriented structures, while no crystal diffraction was observed in the corresponding WAXS (wide angle X-ray scattering). Later, Cavallo et al. [15] showed that this oriented structure is a shear-induced string-like nucleation precursor. Eventually, this oriented structure becomes shish structures during the crystallization. According to Kanaya et al. [16] the degree of crystallinity of the shish is much lower than generally believed. Another interesting point in the shear included crystallization of PP is that the β -form fraction was increased with increase of the shear rate [3,13].

Seki et al. [17] studied the role of long chains in shear-mediated crystallization by changing the long PP chain concentration (c) from 0 to twice of the concentration (c^*) at which the long chains overlap with each other. The number density and thickness of shish were affected by c and changed drastically at c near c^* . They presented

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a model as follows. The longer relaxation time of the entangled long chains can enhance the formation of point-like precursors such as local chain orientation, micro crystallite or tentative packing between PP helices. The point-like precursors behave like a physical-cross linking point and thus create dangling chains. The dangling chains are subject to further elongation due to the shear, which can cause to create new nucleation sites and formation of further point-like precursors along the elongated chains. This process propagates and eventually creates a string-like nucleation precursor. Kimata et al. [18] were appeared to obtain a different conclusion from Seki et al from small-angle neutron-scattering of a blend of long and short PP chains. Their data showed that long chains are not overrepresented in the shish relative to their concentration in the melt state. They speculate that the longest chains play a catalytic role, recruiting other chains adjacent to them into formation of the shish. If carefully examined the Seki's model, Kimata's results do not contradict Seki's model. This is because after the formation of linearly arrayed point-like precursors, the precursors may grow to thread-like nucleation precursor or shish by absorbing adjacent chains. In this growing and propagating process, the components with the higher mobility (i.e., the shorter chains) are more likely to be absorbed by the precursors than the longer chains. The important conclusion of these studies is that the presence of the minor components with a much larger relaxation time than the majority components drastically increases the crystallization rate and enhances the formation of the shish-kebab structures.

From the industrial points of view, the most feasible post-polymerization technique to add such longer relation components can be creating long chain branching (LCB) with electron beam radiation [19,20] or peroxide modification [21,22]. LCB-PPs generally have advantage over linear PPs because of high elongation viscosity (i.e., large melt strength [23]), so they are frequently used in several molding processes especially in extruded and foaming moldings. Generally speaking, the flow rates of these molding processes are relatively slower than injection molding and the residence time of melt polymer in the molding process is longer than that of injection molding. The molding temperatures in foaming or blow molding are sometimes set to be very low in order to accelerate the molding speed. For these reasons, to investigate shear-induced crystallization behavior of LCB-PP near the crystallization temperature is important from the industrial points; however there are a few studies reported so far.

Agarwal et al. [2] studied the shear-induced crystallization of LCB-PP produced by a diene monomer copolymerization technique using a metallocene catalyst (denoted hereinafter LCB-PP-diene). LCB-PP-diene exhibited improved properties for molding and had a significant population of highly branched-chains in the high molecular weight component of the molecular weight distribution. SAXS and WAXS showed that upon a step shear (rate = 60 s^{-1} , time = 0.25 s, at $T = 140 \text{ }^\circ\text{C}$ which is close to the crystallization temperature: T_c), the oriented crystal fraction was substantially higher in LCB-PP-diene than that in the linear PP. The shear-induced crystallization rate of LCB-PP-diene was analyzed by an Avrami model; the value of Avrami exponent ranged from 1.8 to 2.8 indicating a rod- or disk- like crystal growth geometry. In addition, the crystallization kinetics was enhanced by more than an order of magnitude when compared to linear iPP polymer under shear. These unique properties are strongly coupled to their broadened and complex relaxation behavior. However, LCB-PP-diene must constitute of comb type-based structures and thus the branched degree should be lower than commercially used hyper-branched LCB-PP. They observed the increase of triclinic γ from crystals with increase of

branching, suggesting that there is a relatively large amount of the regio-defect of the tacticity of PP.

In this work, we investigated the shear-induced crystallization of LCB-PP with hyper-branched structures, prepared with electron beam irradiated technique (hereinafter denoted LCB-PP-electron). We carried out the crystallization experiment at a relatively high temperature of $170 \text{ }^\circ\text{C}$, where we can expect the dominant presence or formation of the crystal precursors and the crystals with higher melting temperatures due to comprising extended chains. Here, T_m is defined as the peak maximum of the crystal melting determined with a heating experiment of DSC (differential scanning calorimeter). The LCB-PP crystallization behavior is discussed comparing with a linear PP that has a relatively broad molecular weight distribution as well as a conventional PP sample.

2. Experimental

2.1. Materials and molecular weight characterization

Table 1 summarizes the sample codes and their molecular and thermodynamic characteristics. Three types of PP were used. PP-1: a commercial grade homo linear PP polymerized with Ziegler-Natta catalyst, supplied from Japan Polypropylene Corporation (grade FY6), PP-2: a linear homo PP with a broad molecular weight distribution that was prepared by the two-step sequential polymerization technique with a Ziegler-Natta catalyst at a laboratory-scale plant of Japan Polychem Corporation, and PP-3: a long chain branched PP produced by Basell Polyolefins using electron beam irradiated technique, denoted by LCB-PP-electron, hereinafter [19,20,24]. All the samples had a similar melt flow rate around 2 and the degree of crystallinity was in the order of PP-2 > PP-1 > PP-3 and slightly different melting and crystallization temperatures, reflecting on their microstructures. For all of the samples used for X-ray, optical microscope and rheological measurements, we prepared circular plates with compression molding with a 1 mm thickness and pre-heated at $200 \text{ }^\circ\text{C}$ for 3 min followed by compression molding at $200 \text{ }^\circ\text{C}$ and 10 MPa for 3 min. DSC measurements were carried out with a Perkin Elmer DSC at a cooling or heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ to determine the crystallization (T_c) and melting (T_m) temperatures.

Size exclusion chromatography (SEC) was carried out to obtain the apparent molecular weight (M_{app}) for three samples with a Waters corporation ALC/GPC 150C, based on the standard polystyrene samples (Tosoh standard polystyrene F380, F288, F128, F80, F40, F20, F10, F4, F1, A5000, A2500 and A1000). The temperature of the column was controlled at $140 \text{ }^\circ\text{C}$ and *o*-dichlorobenzene (added 0.5 mg/ml of BHT as antioxidant) was used as the elute solution. The molecular weight distribution (MWD) defined by M_w/M_n was determined from the chromatogram. Only for PP-3, the weight average molecular weight (M_w) and the intrinsic viscosity ($[\eta]$) were determined with a multi-angle light scattering spectrometer (Wyatt Technology DAWN-E) and a viscometer combined with

Table 1
Sample codes and their characteristics.

Sample code	Type	MFR ^a	M_w^b	MWD ^b	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PP-1	Linear	2.4	3.8×10^5	4.7	161.3	91	118.5	−90
PP-2	Linear	1.8	4.4×10^5	10.7	164.9	104	125.3	−103
PP-3	LCB	2.5	3.4×10^5	6.3	158	79	129.4	−77

The melting (T_m) and crystallization (T_c) temperatures and their enthalpies were determined with DSC.

^a Melt Flow Rate measured at $230 \text{ }^\circ\text{C}$ and 2.16 Kgf (JIS K7210).

^b Determined by size exclusion chromatography.

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