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Novel morphology of isotactic polypropylene crystal generated by a rapid temperature jump method

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Abstract

Novel morphology of isotactic polypropylene (iPP) crystal, which is quite different from that of usual spherulite, has been observed by scanning electron microscope (SEM). The crystals show 'bamboo leaf-like (BL)' shape with α-monoclinic high crystallinity. The BL crystals are formed by neither melt nor glass crystallization, but by a complicated annealing process that goes through mesomorphic phase of iPP. Substrates are not essential for the formation of BL crystals, since the BL crystals are formed both on glass surface and free surface as well as in bulk. Along with the annealing process, a possible explanation for the mechanism of the formation of the BL crystal is proposed.

Keywords: Mesomorphic phase; Isotactic polypropylene; Rapid temperature jump

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1. Introduction

When polymers in bulk are crystallized quiescently by thermal processing, crystal aggregates of spherical silhouette are usually formed, which are well known as 'spherulite'. So it is rare case that the crystallite which having special morphology other than spherulite, especially of large size, is produced. Two types of forming mechanism for the spherulite have been presented [1]; (a) radial growth of needle crystals in all directions from a central nucleus, and (b) successive branching from both ends of an originally unidirectional single crystal. The former type is popularly observed in inorganic and low molecular weight organic substances. The later is popular in polymer that essentially forms lamellar crystal. If the branching of the lamella, which is considered to occur by impurities, defects, thermal agitation, etc., is effectively inhibited, the unidirectional growth of a single crystal is probably kept up.

Hikosaka et al. [2,3] have succeeded in producing large (~30 μm) polymer crystals of leaf- or cigar-like shape by applying high pressure (0.4–0.5 GPa) to a molten polyethylene (PE) of low degree of supercooling (ΔT). They concluded that such large crystals of PE are formed through lamellar thickening due to the continuous chain sliding from folded chain crystal (FCC) to extended chain crystal (ECC) [4,5]. They also commented that such a sliding motion is assisted by the mobile hexagonal phase [6] that was formed under high pressure. In some cases, end products by way of high-pressure process show the six-fold symmetry as a legacy of the hexagonal-to-orthorhombic transition [7].

In this paper, we report on the formation of another large crystals of isotactic polypropylene (iPP) having novel morphology. It is similar to a lath-like α-monoclinic crystal [8], but the branching is effectively inhibited. We address it here as 'bamboo leaf-like (BL) crystal'. The BL crystals of iPP are rather readily formed under atmospheric pressure only by thermal processing. The processing is rather complicated in comparison with normal melt or glass crystallization. Physical implication of the role of each step of the processing will be discussed.

2. Experimental section

2.1. Sample

The sample used in the experiments was isotactic polypropylene (iPP) with molecular weight of $M_w = 208,000$ and the molecular weight distribution of $M_w/M_n = 5.47$. This iPP was synthesized using Zieglar–Natta catalysts. The melting temperature (T_m) of this sample

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was 164 °C determined at a heating rate of 4 °C/min using a differential scanning calorimeter, Perkin–Elmer DSC7.

2.2. Thermal processing

(i) First, a molten iPP sample is quenched rapidly to a low temperature T_1 (≈ 0 °C) so as to yield mesomorphic phase. For the formation of mesomorphic iPP, especially high cooling rate (ca. 80 °C/s) is required [9,10]. (ii) Second, mesomorphic iPP is reheated to a certain narrow temperature range T_2 (ca. 150–160 °C). A period of time Δt_2 ($= 10$ s–60 min) is kept at T_2. (iii) Third, the sample is requenched to a crystallization temperature T_x ($= 120$ °C–T_2). A period of time Δt_x is kept at T_x, and then quenched to room temperature. The third step could be replaced by a relatively slow cooling, or T_x could be equalized with T_2 when T_2 is not so high. Since present thermal processing is an empirical one to form the BL crystal, physical implication to do so will be discussed after experimental results. In what follows, this type of crystallization is addressed simply as 'meso crystallization'.

2.3. Apparatus for thermal processing

The *meso* crystallization described above was conducted using a laboratory made temperature jump apparatus. The temperature jump of this apparatus is driven simply by rapidly exchanging of large heat capacitor blocks to which a sample of very small heat capacity contacts. Thus, the typical initial cooling rate of this apparatus attains ca. 300 °C/s when monitored by thermocouple of thin filament buried in a sample (0.15 mm thickness) sandwiched by two cover glasses (0.15 mm thickness). This rate has enough allowance for the condition for the formation of mesomorphic phase of iPP (80 °C/s). The advantage of this apparatus is that it is so arranged to enable in situ optical measurements. The apparatus can handle cover glass sandwiched sample and also one side uncovered sample. The former case suits for observations of inside bulk using transmission microscope and the later case suits for observations of free surface using reflection microscope. The flaw in the later case is that the exact temperature cannot be monitored since the free surface faces to the atmosphere. The real temperature of the free surface is perhaps few degrees lower than the indicated one. Commercialized apparatus that is assembled on the basis of our prototype is now available from Japan Hightech and Linkam as LK-300.

2.4. Microscope observations and X-ray scattering

Scanning electron microscope (SEM), optical microscope (OM), and confocal laser scanning microscope (CLSM) observations were carried out using a JEOL JSM-5510, a Nikon Optiphot 2-Pol, and a Lasertec 1LM21, respectively. Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were carried out using a Rigaku RINT 2200 and the beam line BL-10C in Photon Factory at National Laboratory for High Energy Physics, Tsukuba Japan, respectively.

3. Results and discussion

3.1. SEM image of typical BL crystal

Figs. 1 and 2 show the SEM images of the typical BL crystals obtained by *meso* crystallization and the ordinary spherulites obtained by melt crystallization, respectively. Both specimens were annealed one side uncovered and no chemical etching was conducted after the annealing process. Therefore, it can be said that the morphological appearances in these figures were self-organized on the free surface without substrate. Other annealing conditions are seen in the figure captions. It is clearly seen that in Fig. 1 the BL crystals of 10–25 μm in length are selectively generated in the whole field, whereas in Fig. 2 the familiar spherulites of 15–20 μm in diameter are selectively generated. Thus, the morphologies of these two types show drastic contrast. It should be noted that the BL crystal has morphology of unidirectional growth with a size comparable to or greater than that of the normal spherulite's, therefore, it can be said that the branching of lamella was effectively inhibited. Getting off the track a little, similar scenery of Fig. 1 is often seen on the ground of a bamboo grove. That is the reason we addressed the present crystal of iPP as 'bamboo leaf-like (BL) crystal'.

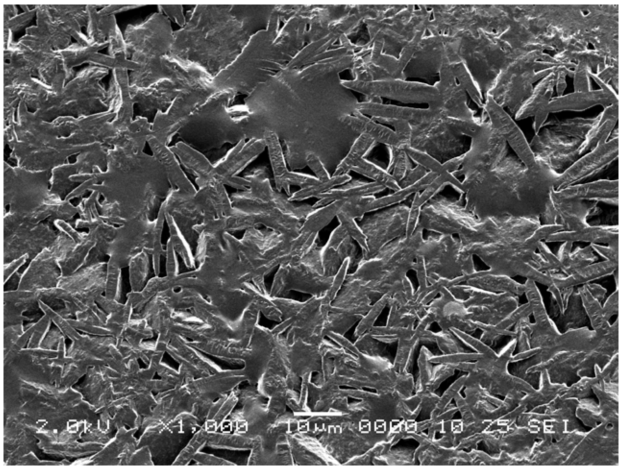

Fig. 1. Scanning electron microscope (SEM) image of the typical 'bamboo leaf-like (BL) crystal' of isotactic polypropylene (iPP), when crystallized by the rapid temperature jump method (*meso* crystallization). Upper side surface was uncovered during crystallization ($T_2 = 162$ °C, $\Delta t_2 = 10$ min, $T_x = 130$ °C and $\Delta t_x = 2$ min).

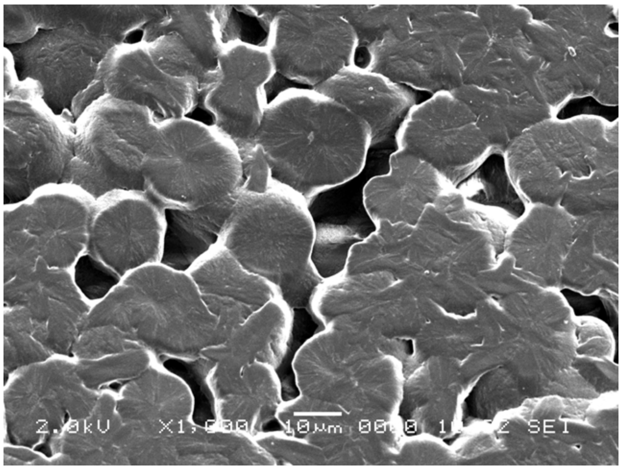

Fig. 2. Scanning electron microscope (SEM) image of the ordinary spherulites of isotactic polypropylene (iPP), crystallized directly from molten state (melt crystallization). Upper side surface was uncovered during crystallization ($T_x = 130$ °C and $\Delta t_x = 5$ min).

3.2. Effect of substrate

Fig. 3(a) shows a surface image of a sample obtained by *meso* crystallization. In this case, it should be noted that the cover glass was removed after crystallization. As is naturally expected that the observed surface is almost flat since this is roughly a replica of the glass surface, but the outlines of the BL crystals can barely be observed. Thus, the BL crystals can be formed on glass surface as well as on free surface (see, Fig. 1). Fig. 3(b) shows a surface image of a sample obtained by usual melt crystallization. In this case also the cover glass was removed after crystallization. Merely outlines of the spherulites are seen. Consequently, the presence of a glass substrate probably neither assist nor hider the formation of the BL crystals. Fig. 3(c) shows an in situ observation of inside bulk during *meso* crystallization. Small growing BL crystals are definitely seen in this figure although the observation by a transmission microscope cannot follow up to the termination of crystallization because the overlapping of crystals makes the image obscure.

3.3. Mechanism of formation of BL crystal

In general, the crystallization of polymer from glassy state by heating is likely to yield smaller size spherulite than the crystallization directly from the molten state by cooling [11], but usually their morphology does not differ so much. The present *meso* crystallization that includes multiple rapid temperature jumps cannot be categorized simply as the glass or melt crystallizations in a narrow sense. The point is that the crystallization proceeds by way of the mesomorphic phase. In what follows we consider the role of the mesomorphic phase in the present crystallization mechanism.

The structure of the mesomorphic phase [12] of iPP is a long-standing dispute. The local structure of the mesomorphic phase of iPP observed by wide-angle X-ray diffraction (WAXD) shows a little bit higher order [12,13] than that of an amorphous of atactic polypropylene (aPP), but is far from claiming it as a proper crystal; meanwhile, a long period is observed by small-angle X-ray scattering (SAXS) [14,15]. Therefore, it can be said that the mesomorphic phase of iPP is meta-stable and has some intermediate structure between crystal and amorphous. This uncertain mode of expressions is shared as a common understanding; however, there are different ideas in matters of detail. Since early period, on one hand, there have been opinions that it has a structure of a highly distorted α-monoclinic crystal phase [16,17]. On the other hand, the mesomorphic phase of iPP has been considered to have a hexagonal crystallographic symmetry [18,19]. Provided that the structure of the mesomorphic phase of iPP is hexagonal-like, it has a good chance for the chain mobility as was mentioned in introduction [2,6]. Miyamoto et al. [15] showed that the structure of the mesomorphic phase of iPP observed by WAXD and SAXS is highly transformable within the framework of the mesomorphic phase depending

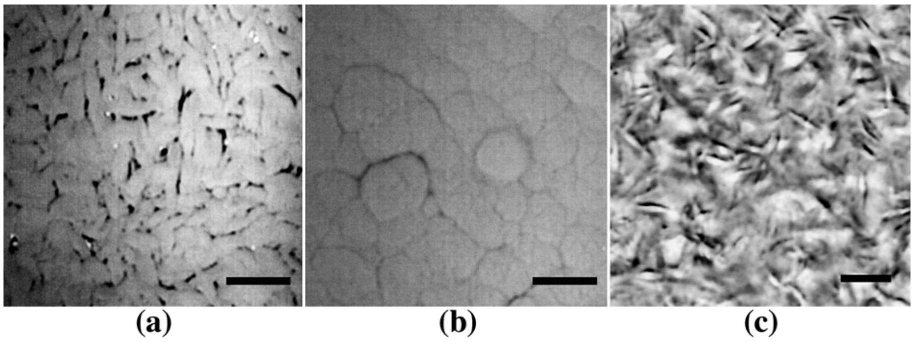

Fig. 3. (a) Confocal laser scanning microscope (CLSM) image of cover glass removed surface of isotactic polypropylene (iPP) after *meso* crystallization. Both sides of surface were covered by the glasses during crystallization ($T_2 = 156$ °C, $\Delta t_2 = 30$ s, $T_x = 125$ °C, $\Delta t_x = 2$ min, scale bar = 10 μm). (b) CLSM image of cover glass removed surface of iPP after usual melt crystallization. Again, both sides of surface were covered by the glasses during crystallization ($T_x = 125$ °C and $\Delta t_x = 5$ min). (c) In situ optical microscope (OM) image of isotactic polypropylene (iPP) of inside bulk during *meso* crystallization with both side covered by glass ($T_2 = 156$ °C, $\Delta t_2 = 30$ s, $T_x = 130$ °C, $t_x = 30$ s, scale bar = 10 μm).

on the temperature even sufficiently below ($-35- +25$ °C) the transition temperature of mesomorphic to α-monoclinic crystal phase, $T_{m\alpha} = 40$ [20,21]–80 °C [22,23]. Thus the degree of orderliness of the mesomorphic phase of iPP has a wide distribution depending on the thermal history, and this may be one of the reasons for the controversy on its structure. Setting aside the question of its structure, it can be said practically the mesomorphic phase of iPP has a mobile nature.

The mesomorphic phase of iPP has a bilateral character. In addition to the mobile nature above mentioned, the mesomorphic phase of iPP has retardancy for crystallization. According to a recent investigation by Okui et al. [24] iPP shows the highest crystal growth rate (≈ 80 μm/s) at around 80 °C when crystallized from melt. With this crystal growth rate, whole sample area is covered by spherulites within a second or so. In contrast to the fact, any observable spherulites of micrometer size are hardly generated even after a hundred seconds when crystallized from mesomorphic phase at 80 °C. Therefore, the mesomorphic phase of iPP itself is less ready for crystallization as compared to a supercooled melt at the same temperature. It is attributable to the high meta-stability of mesomorpic phase. However, if crystallization can be triggered by some means with small numbers of nucleus, the crystals are expected to grow neatly assisted by the mobile nature. The empirical reheating process to T_2 probably functions as this role. In other words, during a period Δt_2 kept at T_2, the sample is subjected to nucleation and selection of BL crystals. Such a reheated mesomorphic phase easily decays into normal 'supercooled' molten state by excessive heating and elapsing of time. Anyhow the complete melting of mesomorphic phase, in other words a reset of thermal history up to then, leads to the recovery of ordinary behavior of the crystallization of iPP from the molten state. In this sense, such a reheated mesomorphic phase may be called a hypothetical 'superheated' mesomorphic phase. The assumed superheating of the mesomorphic phase of iPP is still more unacknowledged notion yet. At least OM observation cannot distinguish a difference between a superheated mesomorphic state ($T_2 = 155$ °C, $t_2 = 5$ min) and a supercooled molten state (5 min after quenching from melt to 155 °C), namely both of them are just transparent, however, the final morphology of the BL crystal that was produced by way of this hypothetical state is decisively different from the usual melt crystallized spherulite. The requenching process to a crystallization temperature T_x accelerates crystal growth rate and probably helps the characteristics of reheated mesomorphic phase to last longer.

Another role of the reheated mesomorphic phase for the formation of BL crystal is a deterrent effect against the branching of lamella. Bassett et al. [8] crystallized iPP at a temperature of low degree of supercooling ($T = 160$ °C). They obtained fairly oriented crystals, i.e. sheaf-like or lath-like crystals, but the branching was not fully inhibited. The above discussed retardancy effect of mesomorphic phase for crystallization perhaps inhibits additional branching nucleation to the unidirectionally growing lamella.

The effect that affects on the recrystallization behavior of polymer of once heated just below and above the melting temperature is usually called 'self-nucleation' [25] and 'melt memory effect' [26], respectively. In a broad sense, the *meso* crystallization may be categorized into these effects, however, neither the self-nucleation [26–28] nor the melt memory effect [29] have so far produced the BL crystals.

3.4. Supporting experiments by X-ray scattering

Although, current communication is intended to report the finding of a novel morphology of iPP crystal, some supporting experiments by X-ray scattering is shown before closing. The BL crystals grew until the good part of matrix was run out (Fig. 1). The usual spherulites of iPP also grow until they impinge each other (Fig. 2), but the spherulites always include some portion of noncrystalline region within each domain of spherulite. According to WAXD (Fig. 4), an iPP sample by *meso* crystallization ($T_2 = 160$ °C, $\Delta t_2 = 30$ s, $T_x = 150$ °C, $\Delta t_x = 6$ h) showed higher crystallinity and sharper α-monoclinic diffraction than that of melt crystallization ($T_x = 150$ °C, $\Delta t_x = 6$ h). By a polarizing microscope observation, the BL crystals were colored in a monochrome within each domain of the BL crystal. These facts suggest that the BL crystals are single crystal. Also according to SAXS (Fig. 5), scattering intensity of the long period of lamella begins to decrease and a lower angle upturn begins to increase after a long annealing ($\Delta t_2 > 40$ min) at $T_2 = 155$ °C. This observation suggests an extension process of the folded chain. These collateral evidences show that the BL crystal has a good chance to be an ECC single crystal. Further research on the more specific condition for the formation of larger BL crystal, detailed morphology and

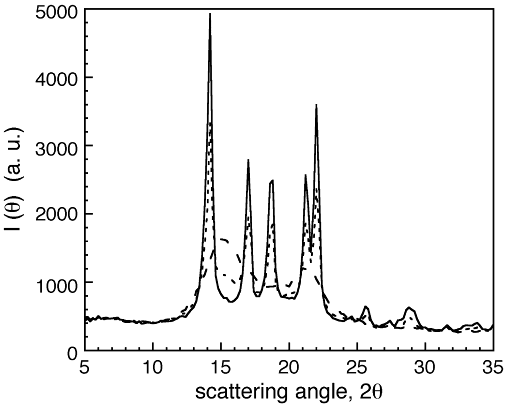

Fig. 4. Wide-angle X-ray diffraction (WAXD) of isotactic polypropylene samples. Solid line: an iPP sample obtained by *meso* crystallization ($T_2 = 160$ °C, $\Delta t_2 = 30$ s, $T_x = 150$ °C, $\Delta t_x = 6$ h). Dotted line: an iPP sample obtained by melt crystallization ($T_x = 150$ °C, $\Delta t_x = 6$ h). Broken line: a mosomorphic iPP.

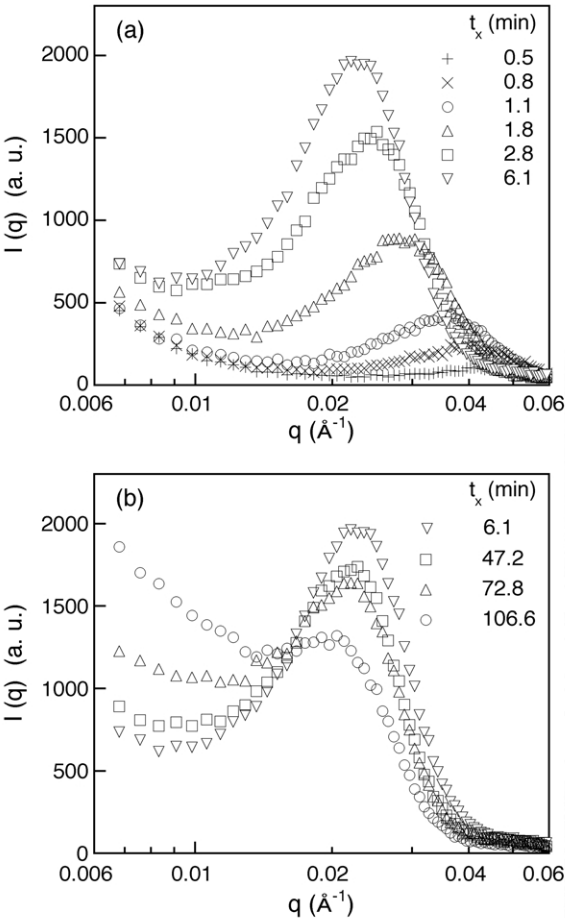

Fig. 5. Time evolution of small-angle X-ray scattering (SAXS) from a *meso* crystallizing isotactic polypropylene sample ($T_2 = T_x = 155$ °C). (a): $t_x = 0.5–6.1$ min. (b): $t_x = 6.1–106.6$ min.

kinetics of the growth is now undertaken and the results will be reported subsequently.

Acknowledgements

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