Deformation Behavior of Isotactic Polypropylene Spherulite during Hot Drawing Investigated by Simultaneous Microbeam SAXS-WAXS and POM Measurement

The clarification of the deformation mechanism of hierarchical structures of crystalline polymers during drawing, particularly the identification of the sequence of stress focusing in the polymer structure, is one of the most important issues in the polymer processing field, because it can greatly help in the design of materials with improved mechanical properties. However, the hierarchical structure of crystalline polymers generally has a spatial inhomogeneity and they are non-uniformly deformed under force fields such as drawing [1]. Furthermore, a plate-like crystalline structure, which is called the lamella structure, inside of a polymer spherulite sometimes has very complex morphologies such as twisting [2] and cross-hatched structures [3].

To obtain detailed information on the deformation behavior of the hierarchical structure in such complex polymer systems, a combinatorial approach of microbeam small- and wide-angle X-ray scattering (μSAXS-WAXS) simultaneous measurement is used, in which a unique method provides us the structural information in a wide-scale hierarchy at a local region. We applied μSAXS-WAXS to the observation of the deformation behavior of an isotactic polypropylene (iPP) spherulite during hot drawing [4].

iPP is one of the most intensively investigated crystalline polymers because of its wide applications to commodities such as automobile parts, packaging film, and plastic containers. Film products of iPP are usually processed through hot drawing. Moreover, iPP forms a cross-hatched structure in a spherulite, which is formed by an epitaxial growth of the lamella structure called the daughter lamella from a face of an already grown lamella called the parent lamella. In this study, we focused on the observation of the deformation behavior of cross-hatched structures in an iPP spherulite during hot drawing.

An iPP sample was prepared using polymerizing propene with a polymerization catalyst. A synthesized iPP sample with a melting temperature of 160°C was melted at 230°C and then isothermally crystallized at 130°C for several hours, and we finally obtained very large iPP spherulites of 300 μm diameter.

μSAXS-WAXS was performed at beamline **BL40XU**, which is a high-flux beamline equipped with a helical undulator upstream of the beamline. We generated a microbeam of about 5 μm diameter by merely inserting a micro-pinhole of 2 μm diameter combined with a large guard pinhole of 100 μm diameter with an interval of about 5 cm between them upstream of the sample position. As for the detector, we used a CCD detector coupled with an image intensifier for SAXS data acquisition and a flatpanel detector for WAXS data. The use of a two-dimensional detector for both SAXS and WAXS is essential for microbeam experiments because a crystal structure at a local area of spherulite has a high anisotropy. To track the deformation of a targeted spherulite during hot drawing, we designed a special uni-axial stretching machine that functions in sample position adjustment through microscopy observation, which is independent of the uni-axial stretching process itself.

In Fig. 1, sets of polarized optical microscopy (POM)-μSAXS-WAXS data simultaneously acquired before and after hot drawing are shown. We irradiated the red dot region of a microphotograph with an X-ray microbeam and obtained μSAXS-WAXS data. μSAXS data before drawing clearly showed a four-leaf clover pattern originating from a cross-hatched structure, while only two disordered spots were observed for the μSAXS data after drawing. There are large differences in μWAXS data between before and after drawing.

From μSAXS data during hot drawing, we calculated the positions of the peak and its FWHM for both the parent and daughter lamellae, and obtained

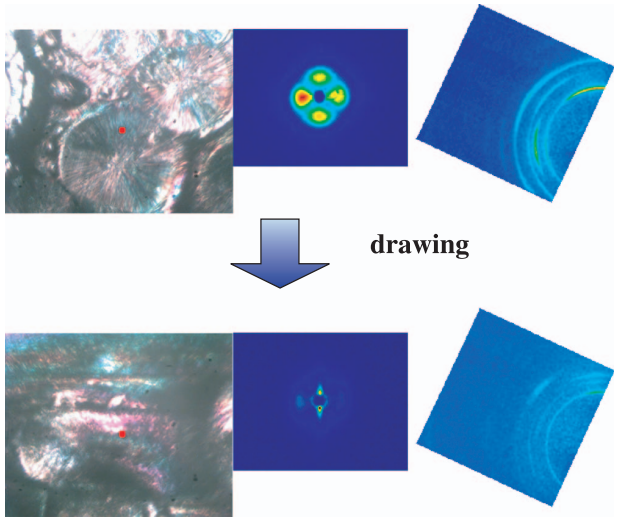

Fig. 1. POM, μSAXS and μWAXS patterns simultaneously acquired before and after hot drawing of polypropylene spherulite.

information on the relationship between the changes in the long period and the disordering of the lamellar long period. From μWAXS data, we calculated FWHM of WAXS peak and the azimuthal distribution of each diffraction peak, and estimated ordered crystal size and crystal orientation.

On the basis of these analyses, we clearly identified the sequence of stress focusing inside the cross-hatched structure during hot drawing and constructed its detailed deformation model as shown in Fig. 2. Initially, the long period simply increases, while no disordering of the stacking structure occurs, which indicates that the stretching of the amorphous region between lamellar crystals occurs before the disordering of the stacking structure (see Fig. 2(b)). Next, the disordering of the lamellar stacking structure and the decrease in the ordered crystal size of the parent lamella start, while no decrease in the crystal size of the daughter lamella occurs (Fig. 2(c) and 2(b')). Interestingly, the ordered crystal size of the daughter lamella is initially smaller than that of the parent lamella and is unchanged during the drawing until a drastic rearrangement starts. Finally, the rearrangement of crystal orientation drastically occurs through tilting, sliding and rotation processes (see Fig. 2(c) and 2(c')).

As shown above, μSAXS-WAXS is a very powerful probe for identifying the sequence of stress focusing during hot drawing and is greatly useful for various polymer systems with interesting morphologies such as the twisting structure and the interpenetrating spherulite structure.

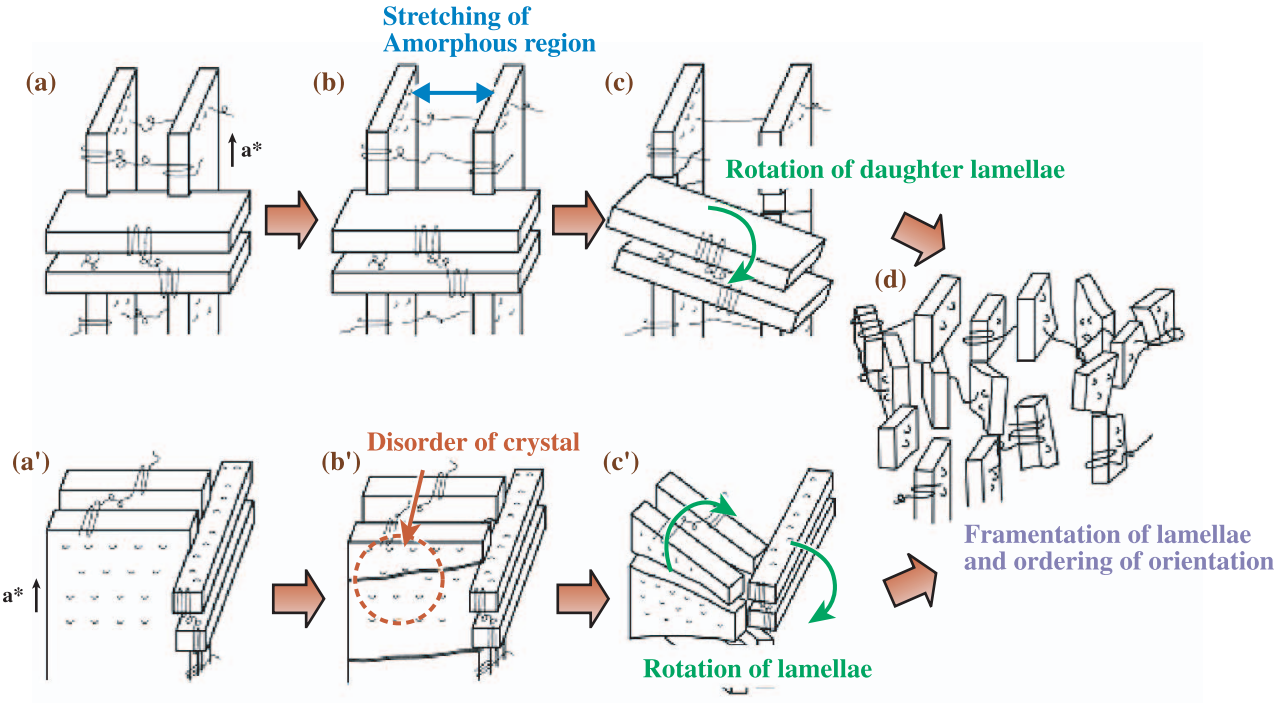

Fig. 2. Detailed deformation model of lamella structure constructed from μSAXS-WAXS results.

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