Discontinuous Reorientation of Crystal Lattice and Its Relation to Higher-order Structure Changes in Drawing Process of Polyethylene Fibers

Crystalline polymers, in general, show a complicated aggregated structure composed of stacked lamellae in a hierarchical structure system. It is important to know how such complicated structure changes their features in the deformation process for a deeper understanding of the mechanical properties of polymer materials. So far, the most polymer structural studies for deformation had been about materials with a random distribution of crystalline lamellae [1], and the results, therefore, had not enabled us to reach a conclusive explanation about the mechanical deformation mechanism. It is a good idea to employ a polymer sample with preferentially-oriented lamellar structure to trace the behavior of each lamella in the deformation process. One typical polymer giving such preferential orientation is a polyethylene (PE) sample produced by spinning the melt during the natural cooling process. This sample possesses a relatively high degree of the crystallographic *a*-axial orientation along the fiber axis. We carried out *in situ* and simultaneous measurements of wide-angle (WAXD) and small-angle X-ray scatterings (SAXS) and Raman scattering at beamline **BL40B2**. Consequently, we discovered discontinuous *a*-to-*c*-axial reorientational behaviors of the orthorhombic crystal lattice and its relation to the higher-order structural changes in the cold drawing process of preferentially-oriented PE fibers.

Figure 1 shows time-resolved WAXD and SAXS patterns during the deformation of an *a*-axially-oriented low-density PE (LDPE) sample. The intensity distributions of WAXD are also shown for 110 and 200 reflections as a function of azimuthal angle. As seen in the figure, the *a*-axis oriented along the fiber direction (90°) before stretching. But when a sample was stretched slightly, the intensity distribution was swapped in the direction perpendicular to the fiber axis (0°). During stretching, X-ray intensities were observed around only 0° and 90° direction areas and no intermediate state was observed. This is the first experimental evidence of a discontinuous transition between the two types of crystal lattice with mutually perpendicular orientation structure (refer to Fig. 2). It should be noted that such a discontinuous

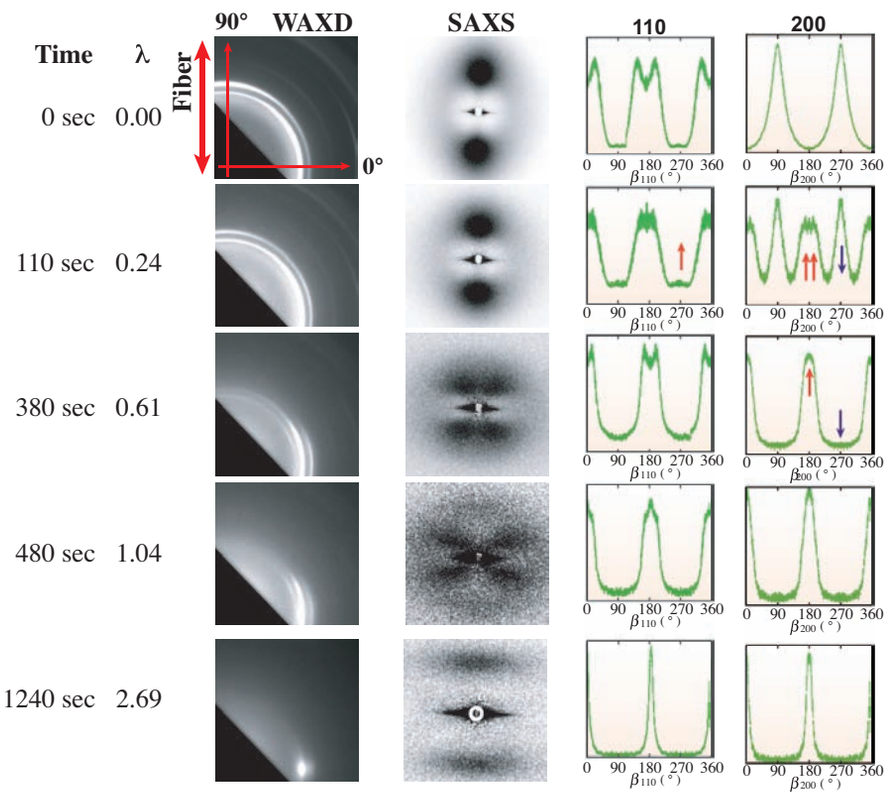

Fig. 1. WAXD and SAXS patterns change of the *a*-axially-oriented low-density polyethylene fiber during the mechanical deformation process under tension. The intensity changes of 200 and 110 X-ray reflections are also indicated with respect to the azimuthal angle β, where β = 0° and 180° correspond to the fiber direction.

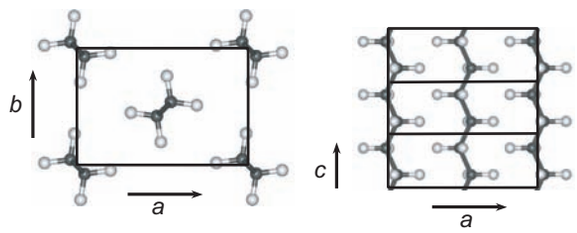

Fig. 2. Crystal structure of orthorhombic polyethylene.

reorientation of the crystal lattice occurs before the start of a remarkable deformation of lamellar stacking structure as seen in the observed SAXS patterns.

In the middle stage of sample stretching, the SAXS pattern changed from a 2-point meridional pattern to a 4-point scattering pattern, indicating the slippage of the neighboring lamellae by shearing stress. This slippage angle was increased up to 60° (see Fig. 3). In the mean time, the long period of the lamellar sequence increased continuously from 160 Å to 360 Å.

In the final stage of stretching, a necked zone appeared in the fiber sample, and then the additional outer 4-point pattern was observed in SAXS pattern.

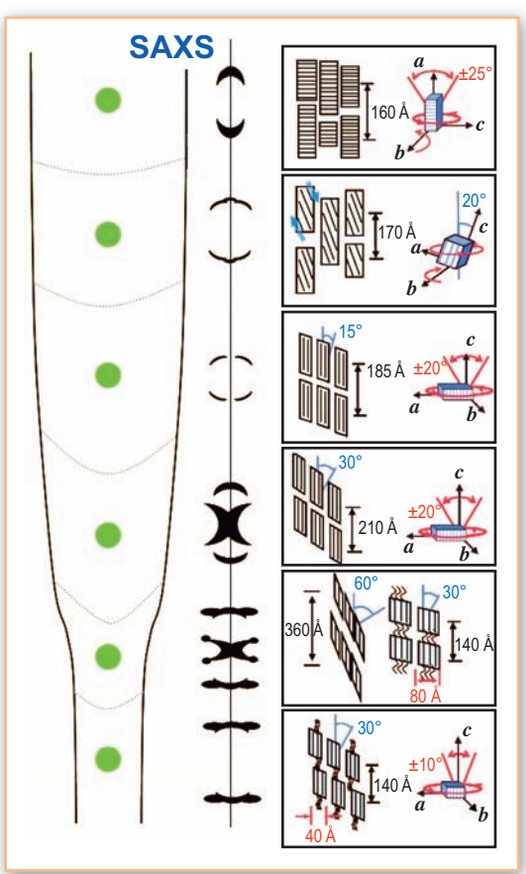

Fig. 3. Schematic illustration of the reorientation of crystal lattice and the stacked lamellar structure change in the cold drawing process of the *a*-axially-oriented low density polyethylene fiber. The SAXS pattern change is also given for reference.

These outer peaks correspond to a lamellar long period of 140 Å, which has no longer systematic relationship with the long period found at the middle stage. We, therefore, interpret these observations as an indication that the already-existing lamellar structure is melted, followed by recrystallization as a new fibrillar structure under the tensile force.

Figure 3 shows a schematic illustration determined from this experiment for the structural changes in the crystal lattice and stacked lamellar structure at various positions in the necked sample. In the proposed structural model, the *discontinuous and almost perpendicular* reorientation from the *a*-axis to the *c*-axis is shown at an early stage of stretching where the magnitude of lamellar deformation is quite slight. One of the promising scenarios to explain this deformation mechanism is that a kinked structure in the extended zigzag chains might be formed through the trans-to-gauche exchange motion under shearing stress as illustrated in Fig. 4. The scenario we suggested shall have an outcome in which this kinked part grows gradually to form the crystal lattice domain with a *c*-axial orientation along the stretching direction with an increase of strain.

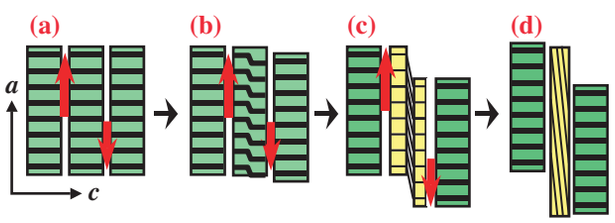

Fig. 4. Schematic illustration of the transformation from the *a*-axially-oriented structure to the *c*-axially-oriented structure in the tensile deformation process, which is assumed to be caused by a generation of kinked structures within the lamella by the action of shearing stress.

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References

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