In Situ Small-Angle X-ray Scattering Experiment in Melt Spinning of High-Density Polyethylene

The effect of flow on the structure formation in polymeric melt under non-isothermal conditions has been attracting attention in both academic and industrial points of view. Fiber spinning is a process that primarily imposes extensional deformation on polymeric melt at the spinline during rapid cooling. In the industrial point of view, it is very important to elucidate the structure formation in the spinning process because the structure has a large effect on the properties of the obtained fibers. The structure formation in the spinning process is very complex because many phenomena (crystallization, phase separation, glass transition and so forth) occur in the process. An *in situ* experiment on the spinning process will provide fruitful information on the structure formation; however, the intensity of the X-ray beam of a conventional laboratory source is very weak for the experiment because the diameter of the spinning fiber is very thin; in the order of tens of microns. Therefore, synchrotron radiation is useful for a small sample such as a spinning fiber. An *in situ* X-ray scattering experiment on spinning process by synchrotron radiation [1] was carried out at HASYLAB, Hamburg, by Japanese and German researchers for the first time: although, this type of *in situ* experiment has not been carried out in Japan. We attempted an *in situ* small-angle X-ray scattering (SAXS) on the melt-spinning at SPring-8 and this may be the first trial of such an experiment in synchrotron facilities in Japan.

High density polyethylene (HDPE) was used as a sample in this experiment. The X-ray scattering experiments were carried out at beamline **BL40B2**. The custom-made spinning apparatus used in the *in situ* X-ray experiment is shown in Fig. 1. The apparatus has a vertical movement system that adjusts the position of the spinning fiber to the X-ray beam with an accuracy higher than 10 μm. Moreover, the distance from the nozzle to the incident X-ray beam can be changed along the spinline. A melt polymer was extruded from a small hole and drawn with take-up rollers. The energy of the incident X-ray was 8 keV (wavelength λ = 0.155 nm) and the scattered X-ray from the fiber was recorded on an imaging plate system.

Figure 2 shows the series of SAXS patterns obtained at different positions in the spinline. The distance L from the nozzle to the incident X-ray beam is depicted on the left top of each SAXS pattern. As L increased, the scattered intensity parallel to the fiber increased at first (L = 100 mm) and subsequently decreased (L = 300 mm). Moreover, the scattering angle dependence of the scattered intensity parallel to the fiber changed with L. We analyzed the scattered intensity as a function of the scattering vector q using a scattering theory [2] of a paracrystal model for oriented lamellar microdomains and obtained a model for the structure formed in the spinline. Highly oriented lamellar crystals were grown in the direction

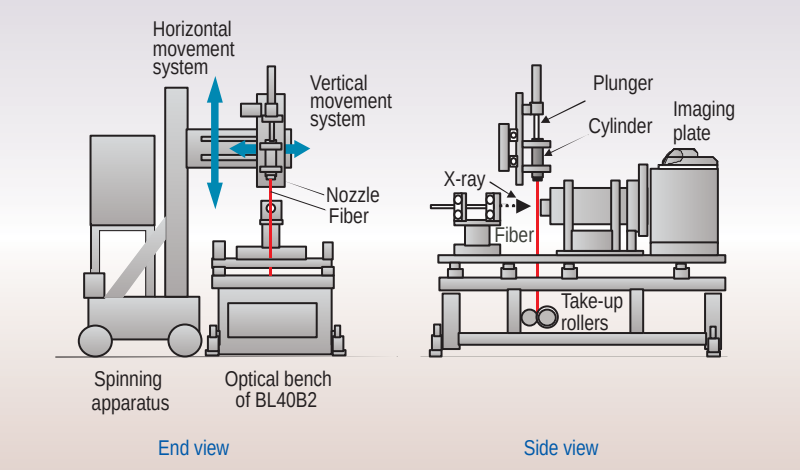

Fig. 1. Schematic representation of the spinning apparatus for *in situ* small-angle X-ray scattering in BL40B2.

for the structure formed in the spinline. Highly oriented lamellar crystals were grown in the direction parallel to the fiber. The average thickness of the lamellar crystals and the average frequency of density fluctuations concerning the lamellar crystals and amorphous regions are depicted in the figure. Moreover we should note the other feature of the scattering pattern indicated by an arrow "S." This is a "streak" pattern indicating the formation of a structure oriented parallel to the fiber. Voids or extended chain crystals can be attributed to the structure giving rise to the streak pattern; however, we cannot fix either of them from the SAXS results. It should be note that the intensity of the streak pattern became weak from L = 100 mm to 300 mm. This suggests that the structure giving rise to the steak pattern was smeared by the lamellar structure. We are going to elucidate the structure formation in the spinline by more detailed analysis of the scattered intensity and by electron microscopy of the fiber obtained in the *in situ* experiment in SPring-8.

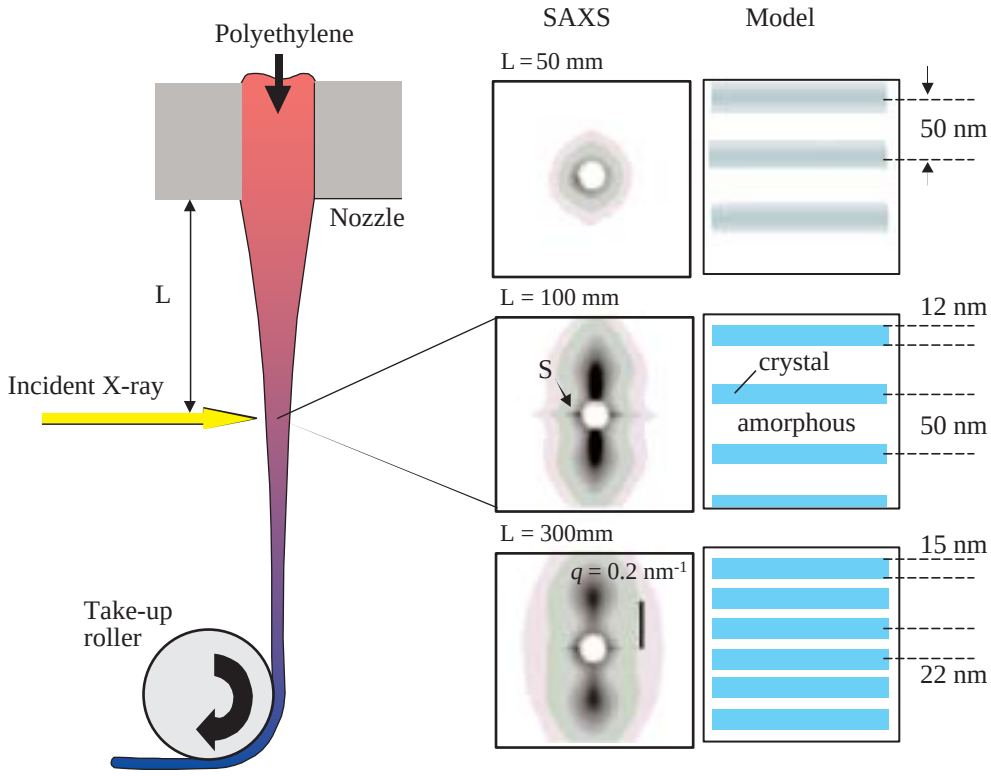

Fig. 2. *In situ* SAXS patterns obtained in the spinline. L is the distance from the nozzle to the incident X-ray beam. SAXS patterns inserted in this figure are taken at L = 50, 100 and 300 mm. A structure model derived from the analysis of the q dependence of scattered intensity parallel to the fiber is depicted on the right side of each SAXS pattern.

Hiroki Murase[a], Masaru Kotera[b] and Katsuhiko Nakamae[b]

(a) TOYOBO Research Center Co., Ltd.
(b) SPring-8 / JASRI

E-mail: hiroki_murase@kt.toyobo.co.jp

References

[1] Y. Hirahata *et al.*: Polymer **23** (1996) 5131.
[2] S. Sakurai *et al.*: J. Appl. Crystal. **24** (1991) 679.