Application of WAXD/SAXS Simultaneous Measurements to Study Aggregation Structure of Polyvinylfluoride in Ferroelectric Phase Transition Process

Polymeric materials consist of complicated aggregation state of chains. In semicrystalline polymers, for example, these chains gather together to form the crystalline region or a crystalline lamella. These lamellae are stacked together to construct a spherulite. It is essentially important to clarify the evolution process of this complicated hierarchical structure of polymers from the various viewpoints on angstrom-to-micrometer scale in order to design and control their physical and structural properties.

The time-resolved measurements of the wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) allow us to trace the hierarchical structural evolution process of polymers in the heating or cooling process, for example. There were many reports on the WAXD and/or SAXS experimental data [1,2]. The WAXD and SAXS measurements are usually performed separately for a sample by assuming the reproducibility of the experimental conditions. Strictly speaking, however, we have no guarantee for the reproducibility of the experimental conditions in the WAXD and SAXS measurements, since the polymeric material has a large hysteresis concerning the thermal or mechanical treatment. It is ideal to perform the simultaneous measurement of WAXD and SAXS for one sample under the completely same conditions.

A simultaneous 2D-WAXD/SAXS measurement system was installed for the public use at beamline **BL40B2**. We measured the temperature dependences of WAXD, SAXS and enthalpy change to investigate the crystal phase transition of poly(vinylidene fluoride) (PVDF) using this system combined with DSC equipment for the study of thermally-induced structural change in the heating or cooling process of polymers [3].

Figure 1 shows a photograph of the DSC/WAXD/SAXS measurement system built at BL40B2. The system is using a CMOS FP detector for WAXD, while a CCD detector coupled with X-ray imaging intensifier for SAXS, which can trace the change of the hierarchical structure of polymeric materials every few seconds. The data collection timing can be controlled by an external trigger which can synchronize the FD detector and II+CCD detector with the external instrument such as a DSC.

The uniaxially-oriented vinylidene fluoride-trifluoroethylene random copolymers are well known to show the ferroelectric phase transition between the polar form I crystal (I) and nonpolar crystalline phases (HT) in the heating and cooling processes. This allows us to speculate that PVDF form I may show a phase transition to the HT phase in much higher temperature region close to the melting point. However, the samples sometimes melted before the observation of the phase transition. We need to confirm the observation of form I -to- HT phase transition during the heating process at relatively fast rate to avoid the local sample melting. We were challenged to perform the simultaneous DSC/WAXD/SAXS measurement using the above-mentioned synchrotron system.

Figure 2 shows the 2-D WAXD and SAXS patterns measured for the uniaxially-oriented PVDF form I sample at 154.5°C and 164.6°C. The WAXD pattern at 154°C corresponds to that of pure form I crystal. The SAXS was the four-points scattering pattern, indicating a tilt of stacked lamellae about 50° from the

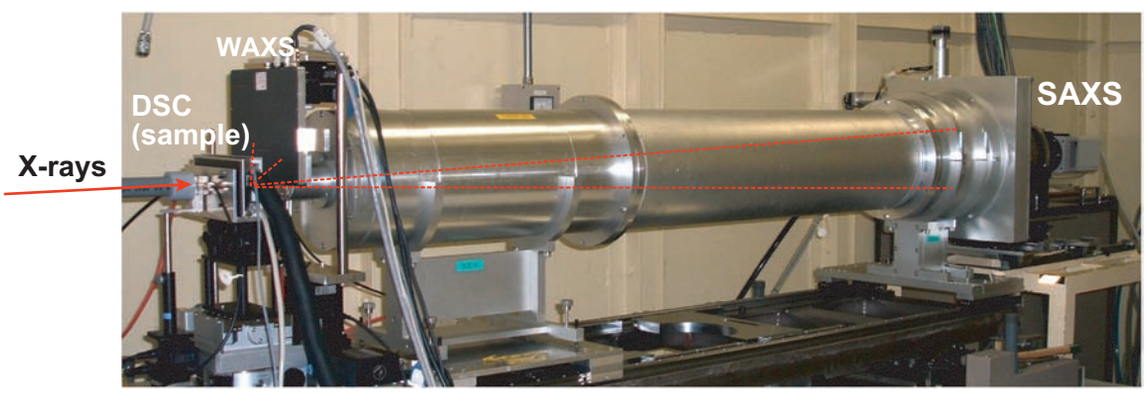

Fig. 1. Photograph of the DSC/WAXD/SAXS simultaneous measurement system built-up at beamline BL40B2.

draw axis. As the temperature increased, the intensity of form I reflections became weaker. In the WAXD pattern taken at 164.7°C, the new pattern was found to appear, which corresponded well to the X-ray diffraction pattern of HT phase. The SAXS pattern was found to change also drastically from the four-points scattering pattern to the meridional two-points scattering pattern. These changes in patterns suggested the tilting angle of lamellae became almost zero, and the long period increased remarkably from 10 nm to 53 nm.

Figure 3 shows the temperature dependences of X-ray reflection intensity estimated for form I and HT phase and that of the long period and lamellar tilting angle in comparison with the DSC thermogram. A shoulder detected in the lower temperature side of DSC peak corresponds to the phase transition from form I to HT phase.

In this way we succeeded in confirming the phase transition of PVDF form I occurring in the temperature region close to the melting point. The newly installed DSC/WAXD/SAXS measurement system has enabled us to detect these phase transition phenomena satisfactorily. As a result, we have been able to establish the important universal phenomenon common to many crystalline polymers: the morphological change of stacked lamellae occurs in strong association with the crystalline phase transition. The system will be improved regarding data collection and analysis.

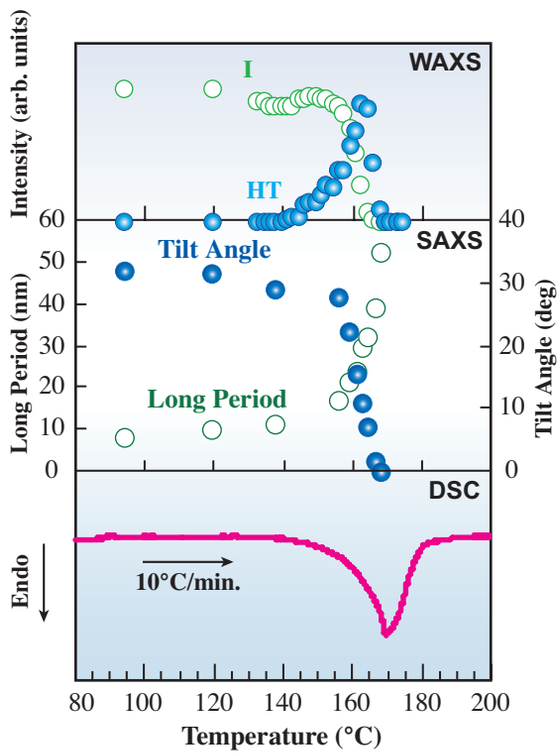

Fig. 3. Temperature dependences of long period and tilting angle of stacked lamellae, peak intensity of the (001)I and (002)HT reflections and DSC thermogram measured for the uniaxially-oriented PVDF form I in the heating process at 10.0 °C/min.

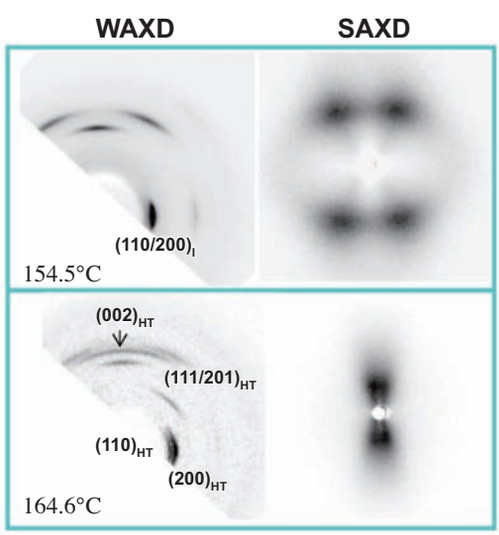

Fig. 2. WAXD and SAXS patterns measured simultaneously for oriented PVDF sample at 154.5 °C and 164.5 °C. The meridional direction is parallel to the oriented direction of sample.

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