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Direct Evidence of Polymer Nucleation during Induction Period----Degree of Supercooling Dependence

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Molecular mechanism of the induction period in nucleation is one of the most important unsolved problems in crystallization of materials. In the previous work, we obtained a direct evidence for the first time that nuclei are formed during the induction period is obtained by means of small angle X-ray scattering (SAXS). This confirmed that the nucleation process is the most essential one in the induction period of nucleation and denied another mechanism, such as the Spinodal decomposition, which has been proposed recently.

Purpose of this work is to confirm the above finding by observing the degree of supercooling dependence (ΔT) of the size of the nuclei, which are formed during the induction period. The size of the nucleus should increase in proportion to $1/\Delta T$, as the classical nucleation theory predicts. The size of the nuclei could be estimated by applying the "Gunier plot", because the isolated nuclei scatter within the melt.

Polyethylene (PE) was used as a model crystalline polymer. Nucleation agent (NA) was mixed with PE in order to increase the SAXS intensity Ix from the nuclei as large as 10^4 times than usual. Ix increased soon after quenching into crystallization temperature from the melt and saturated after some time (Fig.1).[1)]

Typical Guinier plot at a ΔT was shown in Fig. 1.[1)] The slope of the linear lines gives the radius of gyration Rg of the nuclei. The size of the nuclei was estimated from the Rg. Figure 1shows that the size of the nuclei does not change during the induction period and that the size was nearly similar to that of critical.

The size of the nuclei increased significantly with increase of $1/\Delta T$. This suggests that the nuclei are formed during the induction period. More detailed data is requested to confirm it definitely, which is the main purpose of the next experiment.

Reference

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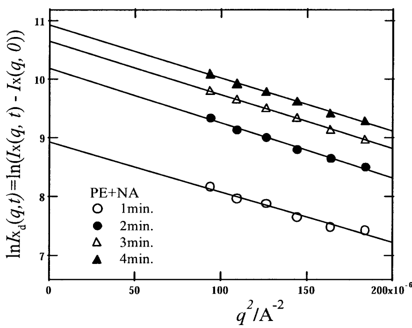

Figure 1 Typical Guinier plot at ΔT = 12.4K during the induction period.. The induction time is 3min. Inrease of Ix is the direct evidence of the nucleation during the induction period. The slope corresponds to Rg, i.e., the size of the nuclei. Therefore the size does not change during the induction period.

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DEVELOPMENT OF SMALL-ANGLE MICRO-DIFFRACTION TECHNIQUE USING HIGH FLUX BEAMLINE

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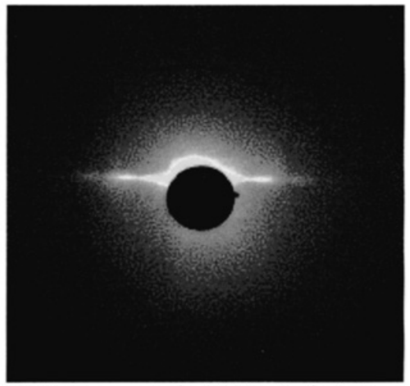
The High Flux beamline (BL40XU) in SPring-8 provides a photon flux of an order of 10^{15} in a focus of 0.25 mm horizontally, 0.04 mm vertically [1]. This high flux makes it possible to create an intense microbeam by pinhole optics. In calculation, even with a pinhole with a diameter of 5 µm, a flux of 2×10^{12} photons/sec can be obtained. We made a preliminary small-angle x-ray diffraction experiment using this beamline.

The peak x-ray energy was set to 12.4 keV (λ = 0.1 nm) by adjusting the undulator gap to 14.3 mm [2]. The front end slits were closed to 0.165 mm vertically, 0.50 mm horizontally to get an energy resolution of 2 % [1, 2]. A pinhole with a diameter of about 3 µm was set on remotely-controlled X, Z, tilt, and rotation stages. Slits were set at about 10 cm from the pinhole. These slits were used to cut the scatter from the edge of the pinhole. A specimen was placed just behind the slits. In order to remove the scatter effectively, it is ideal to place the slits as far from the pinhole as possible. However, since the x-ray beam diverges due to diffraction by the pinhole, it is necessary to place the specimen as close to the pinhole as possible. The distance of 10 cm between the pinhole and the slits was a compromise between these two conflicting conditions. The beam at the specimen was about 7 µm in diameter, as measured by using Beam Monitor 3.

A Be-windowed x-ray image intensifier (V5445P, Hamamatsu Photonics), lens-coupled to a cooled CCD camera (C4880-10-14A, Hamamatsu Photonics), was used as an x-ray detector. The path between the specimen and the detector, most of which was evacuated, was 1.5 m.

The figure below is a diffraction pattern from cuticle, the surface layer of a human hair, which is about 5 µm thick. The sharp inclined equatorial diffraction has peaks indexed approximately on the orders of a 22-nm repeat, as has been reported by Kreplak et al. (2001). This result demonstrates that the present system is useful in studying a few µm region using x-ray small-angle diffraction.



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