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# Effects of A Liquid-type Crystallization on Isothermal Crystallization Behaviors of Poly(L-Lactic Acid) as Analyzed by Simultaneous Small- and Wide-Angle X-Ray Scattering Measurements

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## 1 Introduction

Poly(L-lactic acid) (PLLA) is a biodegradable and biocompatible polymer which can be synthesized from renewable sources such as sugar, carbohydrate, etc. However, there existing some big problems of PLLA, which are low crystallization rate and low crystallinity. In order to overcome such drawbacks, nucleation agents have been incorporated into PLLA. In this study, we added a special liquid-type nucleation agent (organic acid monoglyceride; OMG) into PLLA in order to improve the crystallization abilities of PLLA. In this study, we conducted differential scanning calorimetric (DSC) measurements, polarizing optical microscopy (POM) observations, and simultaneous small- and wide-angle X-ray scattering (SWAXS) measurements to follow isothermal crystallization.

## 2 Experiment

There are two types of neat PLLA samples such as PLLA4032D (1.4 % D-content: D1.4) and PLLA2500HP (0.5 % D-content: D0.5) from Nature Works and PLLA with OMG (1% addition) such as D1.4/OMG and D0.5/OMG specimen. The non-isothermal crystallization took place in the heating process (with rates of 2.5, 5, 7.5 and 10˚C/min) of the specimen which was cooled down from the molten state, while the isothermal crystallization was induced by the T-jump from the molten state (at 200 ˚C) to a given crystallization temperatures (90, 110, 130˚C).

The SWAXS measurements were conducted at BL-10C of Photon Factory in High Energy Accelerator Research Organization (Tsukuba, Ibaraki, Japan). The beamline was composed of an approximate toroidal mirror, monochromator, four-quadrant slits, and a two-dimensional detector (PILATUS 300 K, DECTRIS Ltd., Baden, Switzerland), on which X-ray was focused. The sample-todetector distance was 2.0 m, and the wavelength of X-ray was 0.150 nm. Time-resolved SWAXS measurements wer performed upon temperature jump from 200ºC to 112.3ºC (cooling rate was approximately 90ºC/min). The time-resolved SAXS measurement was conducted with 30s step while the time-resolved WAXS was conducted with 5s step. The revolution of crystalline peak being ascribed to the long period of stacking of the crystalline lamellae, was analyzed as a function of time.

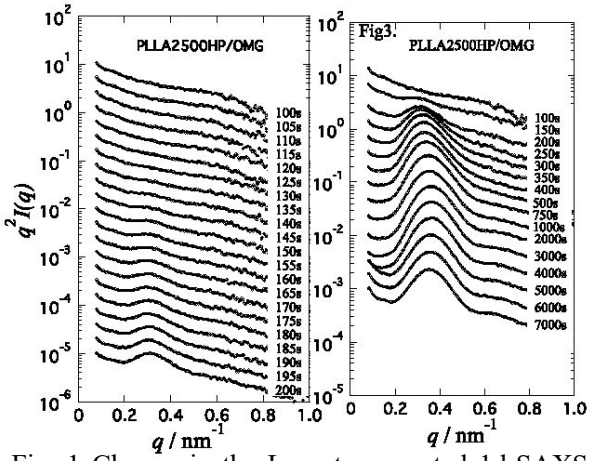


Fig. 1 Change in the Lorentz-corrected 1d-SAXS profiles (plots of $q^2I(q)$ vs. $q$, for the PLLA2500HP/OMG specimen.

## 3 Results and Discussion

Fig. 1 shows the typical changes in the Lorentz-corrected 1d-SAXS profiles (plots of $q^2I(q)$ vs. $q$, for the PLLA2500HP/OMG specimen. A broad peak finally appeared in the $q$-range of 0.3 ~ 0.36 nm$^{-1}$. This peak reflects the period of stacking of the lamellar crystals (so-called long period). Therefore, the onset time of the peak evolution can be a measure of the induction period of crystallization. In order to evaluate the onset time, computational peak decomposition was performed for the Lorentz-corrected SAXS profile. Thus obtained integrated peak intensity (peak area) was plotted as a function of the time elapsed, and by extrapolation of the dependencies, the onset time was finally evaluated. Based on thus evaluated onset time, it can be stated that the liquid OMG plays a role of crystallization agent.

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