

Structural Dynamics of Substituted Poly(lactic acid) with *sec*-Butyl Side Chains Revealed by Synchrotron SAXS/WAXD Simultaneous Measurements

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1 Introduction

Recently, the side-chain-substituted poly(lactic acid)s (SPLAs) have attracted much attention to overcome weakness of poly(L-lactic acid) (PLLA), one of the representative bio-based plastics [1,2]. Poly[(2*S*,3*S*)-2-hydroxy-3-methylpentanoic acid] [P(L-2H3MP)] is one of the crystalline SPLAs [2]. We found that P(L-2H3MP) showed a complicated multiple melting behavior by thermal analysis. However, its mechanism is still unclear.

In this study, we investigated the dynamics of higher-order and crystal structures of P(L-2H3MP) during a heating process by using time-resolved synchrotron SAXS/WAXD simultaneous measurements.

2 Experiment

P(L-2H3MP) with $M_n = 70$ kg/mol was synthesized by ring-opening polymerization of cyclic dimers of the L- α -hydroxy acid derived from L-isoleucine [1–3]. The melt-crystallized sample was prepared by thermal annealing (210 °C, 1 min \rightarrow 165 °C, 3 h \rightarrow LN₂ quench).

SAXS/WAXD simultaneous measurements were performed at KEK PF BL-6A and 10C ($\lambda = 0.1500$ and 0.1488 nm, respectively) using an FP84HT TA Microscopy Cell (METTLER) for heating from 30 to 210 °C at 20 °C/min, during which the data acquisition and interval times were set to 2.5 and 0.5 seconds, respectively. The temperature of samples packed in a washer was measured by a resistance temperature detector. SAXS/WAXD analyses were done using the handmade software [4].

3 Results and Discussion

Fig. 1 shows the changes of Lorentz-corrected SAXS profiles during the heating process for P(L-2H3MP) which had been isothermally-crystallized at 165 °C. In SAXS profiles below 150 °C (blue), peaks at lower and higher q would be ascribed to the alternating structure composed of thicker lamellar crystals and amorphous layers, and that of thinner lamellae and amorphous layers, respectively. The high- q peak shifted to lower q with increasing temperature, and when temperature reached 150 °C, this peak was no longer observed. In SAXS profiles above 150 °C (red), only the low- q peak was seen until melting. In the differential scanning calorimetry (DSC) curve, three endothermic peaks were observed: the annealing peak temperature (T_a) < T_{m1} < T_{m2} . The T_a peak was seen just above 165 °C, indicating that the high- q SAXS peak was responsible for the annealing peak. The WAXD data showed no changes in the crystal structure during the heating process. Therefore, the annealing peak on the DSC curve should be explained by the melting of thin (and

probably disordered) lamellar crystals. However, the origin of T_{m1} and T_{m2} (distribution in lamella thickness and/or melt-recrystallization-remelt) is still an open question.

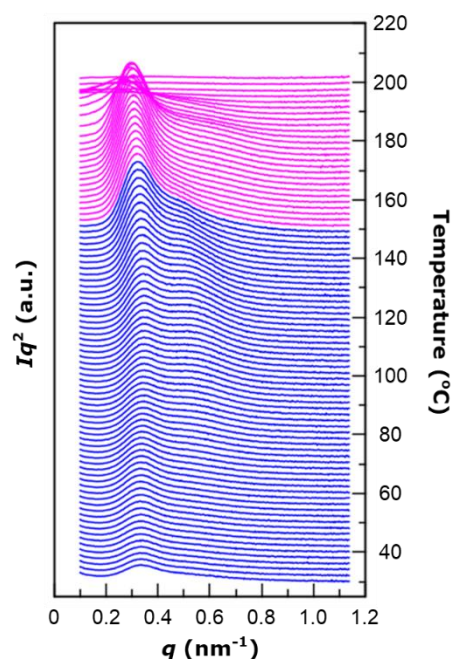


Fig. 1: Changes of Lorentz-corrected SAXS profiles during the heating process at 20 °C/min for P(L-2H3MP) which had been isothermally-crystallized at 165 °C. SAXS profiles below/above 150 °C are shown in blue/red.

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