

STRUCTURAL TRANSITION OF POLY[*(R)*-3-HYDROXYBUTYRATE] SINGLE CRYSTALS ON HEATING AS REVEALED BY SAXS AND WAXD

Poly[*(R)*-3-hydroxybutyrate] (P(3HB)) is a biodegradable thermoplastic material, produced from renewable carbon sources by bacteria as intercellular carbon and energy reserves. P(3HB) has thus attracted much attention as a material to solve problems concerning energy resources and disposal of solid waste. Enzymatic degradation of P(3HB) material by extracellular P(3HB) depolymerase occurs first at amorphous regions and subsequently at the crystalline regions. Accordingly, the crystalline regions in the material play an important role in the regulation of the biodegradability as well as the physical properties. For wide applications of P(3HB) the physical properties of the material should be improved more.

Annealing is a treatment method to improve the physical properties as a result of the change in morphology of crystalline regions and removing a residual stress, etc., by heating. Polymer crystals, which are lamellar crystals with folded chains, can reorganize into more stable state, thickened crystals, by heating below their equilibrium melting temperature. The evidences provided from the annealing experiments of polymer crystals have contributed to the development the high-performance polymer materials, although the molecular mechanism of the crystal thickening during annealing has been still an object of argument. In P(3HB), there is a few works on the annealing behavior and the thickening mechanism at a molecular level is still unclear. Here, the real-time annealing experiments of P(3HB) crystal by synchrotron radiation small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) are reported [1,2].

The number-average molecular weight and polydispersity of P(3HB) used here are 15,000 and 1.6. Single crystals of P(3HB) were grown isothermally in its dilute solution at desired crystallization temperatures (T_c). The sedimented single crystal mats were obtained by a filtration after the suspension was cooled down to room temperature, and then dried under vacuum. The single crystal mats were set in the sample holder, and heated from room temperature to around 180 °C at a heating rate of 10 °C / min. Real-time SAXS and WAXD measurements were carried out at BL45XU beamline. Thermal properties of the single crystal mats were evaluated by differential scanning calorimetry (DSC).

Figure 1(a) shows two-dimensional (2D) SAXS patterns of the sedimented mats of P(3HB) single crystals grown at 60 °C. These images were taken at elevated temperatures. The meridian corresponds to the lamellar stacking direction in the sedimented mats. On the meridian, scattering peak from the stacking period of original crystals is clearly recognized as indicated with the yellow arrowheads. The lamellar thickness was estimated as 4.0 nm. The original peak shifted little on heating up to 120 °C. A new scattering peak at a lower angle was observed at an annealing temperature (T_a), as indicated with the red arrowheads in Fig. 1(a). Figure 1(b) shows the corresponding circular-averaged 1D profiles. It was found that the crystals exhibit discontinuous increase in thickness during the transition, and the population of reorganized crystals increases while that of original ones decrease with temperature. The similar behavior was also observed in the single crystals grown at other crystallization temperatures. The onset of the transition was found to depend on the crystallization temperature. Namely, the transition occurs at higher temperatures with the increase of the original lamellar thickness.

The changes in lamellar thickness against T_a for

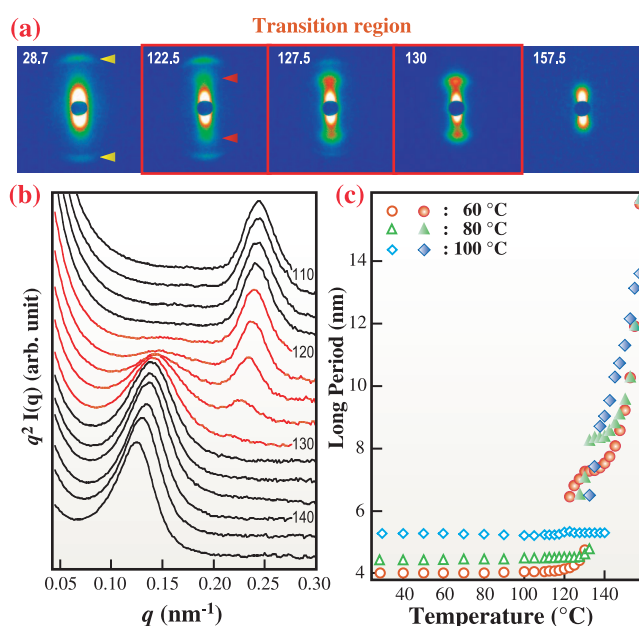


Fig. 1. 2D SAXS patterns (a) and integrated 1D profiles (b) of P(3HB) single crystals grown at 60 °C. In (b), the red lines correspond to the profiles in the transition region. (c) Long period plotted against annealing temperature. Open and filled symbols represent long periods of original and reorganized crystals, respectively.

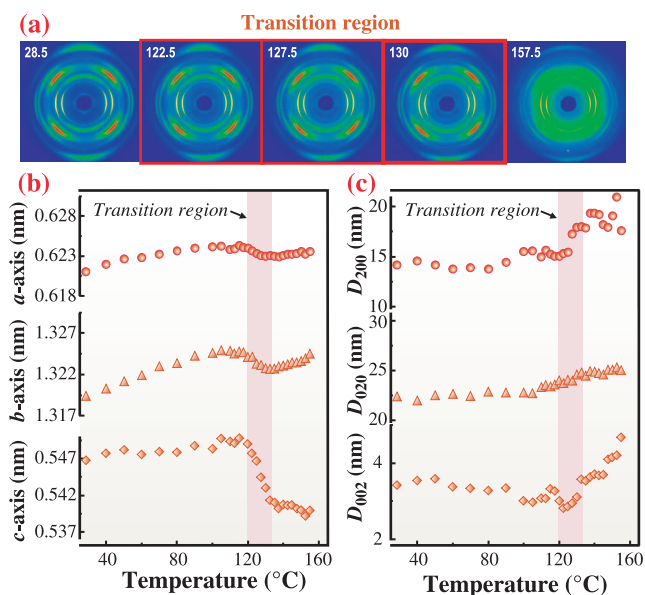


Fig. 2. (a) 2D WAXD patterns of P(3HB) single crystals grown at 60 °C. (b) Lattice dimension plotted against annealing temperature for $T_c = 60$ °C. (c) Crystallite size plotted against annealing temperature for $T_c = 60$ °C.

the single crystals grown at 60, 80, and 100 °C are shown in Fig. 1(c). This figure clearly demonstrates a discontinuous lamellar thickening and the coexistence of the two populations with different lamellar thicknesses. After the discontinuous increase, the remaining peak shifted to lower angles, and finally diminished due to complete melting.

The representative 2D WAXD patterns are shown in Fig. 2(a). Well-resolved fiber diffraction patterns of P(3HB) crystal were obtained. From the 2D WAXD patterns, temperature dependence of lattice dimensions (*a*-, *b*-, and *c*-axes), apparent crystallite size (D_{200} , D_{020} and D_{002}), which were estimated from the peak positions and widths, are shown in Fig. 2(b) and 2(c). The crystal lattice, i.e., intermolecular distance, expanded gradually with temperature, and the lattice dimensions turn to contract at the onset of lamellar thickening. This fact means that the chains registered in the original crystal are released and then rearranged. The D_{002} , which corresponds to crystalline core thickness, also started to increase in response to lamellar thickening, indicating that the discontinuous increase is accompanied by not only the formation of amorphous layer between crystals but also the real thickening of crystal

As shown in Fig. 3, the crystallinity first decreased and then recovered during the thickening process. On the other hand, the lamellar thickening was accompanied by endo- and exothermic signals in DSC. Therefore, the discontinuous lamellar thickening of P(3HB) single crystal is caused by

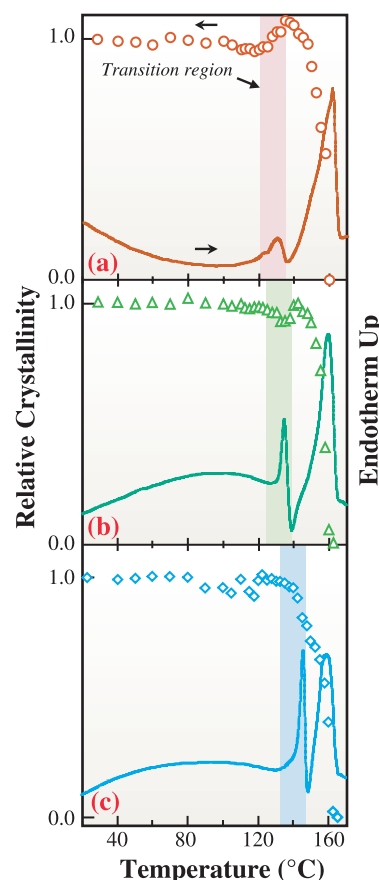


Fig. 3. Crystallinity plotted against annealing temperature and DSC curve; (a) $T_c = 60$ °C, (b) 80 °C, and (c) 100 °C.

melting and recrystallization. The degree of recovery in crystallinity fell with increasing in the original lamellar. This is because the crystallization rate becomes slower with increasing in the temperature region where the transition occurs. We have considered that the discontinuous lamellar thickening is cooperative process with the adjacent crystals along the stacking direction. The chains released from the lattice mutually diffuse, leading to a thicker crystal, into the space in which the adjacent crystal existed [2].

Mashiro Fujita^{a,*}, Tadahisa Iwata^b and Kazuki Ito^c

^a Bioengineering Laboratory, RIKEN Wako Institute

^b Graduate School of Agricultural and Life Sciences, The University of Tokyo

^c SPring-8 / RIKEN

*E-mail: mfujita@riken.jp

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