# New Core-sheath Structure of Poly[(*R*)-3-hydroxybutyrate] Fibers Revealed by Micro-beam X-ray Diffraction

Plastic products have gained universal use not only in food, clothing and shelter, but also in the transportation, construction, medical and leisure industries. There is a growing demand for bio-based and biodegradable polymers as a solution to problems concerning energy resources, the global environment and solid waste management. Research on bio-based and biodegradable plastics and polymers has been carried out worldwide with the aim of achieving a balance between human activities and the natural environment.

A wide variety of bacteria synthesize an optically active polymer of (*R*)-3-hydroxybutyric acid and accumulate it as intracellular carbon and energy storage material. Poly[(*R*)-3-hydroxybutyrate] (P(3HB)) isolated from bacteria is extensively studied as biodegradable and biocompatible thermoplastic with a melting temperature of ~180ºC (Fig. 1). P(3HB) was discovered by Maurice Lemoignei of Institute Pasteur, France, in the 1920s, and until now many researchers have been investigating its physical properties, crystal structure, and biosynthesis and biodegradation mechanisms among others. P(3HB) was initially produced by Imperial Chemical Industries by using an industrial-scale fermentation process in the 1980s. In 1995, the process and related patents were bought by Monsanto and subsequently acquired by Metabolix. Recently, Lenz and Marchessault have reported a historical review of the chemical, biochemical and microbial highlights of P(3HB) covering a discovery time span of 75 years [1].

Recently, we have succeeded in processing P(3HB) fibers with a high tensile strength and acceptable mechanical properties by a method combining cold-drawing and two-step-drawing procedures [2,3]. We present, herein, highly ordered structures in monofilaments revealed by micro-beam X-ray diffractions using synchrotron radiation.

Until now, three research groups have succeeded in obtaining melt-spun fibers with tensile strengths of 190 ~ 420 MPa from P(3HB) (weight-average-molecular-weight ($M_w$) of 0.3 ~ 0.8 × $10^6$ ) produced by wild-type bacteria. However, the strength of such fibers is not sufficient for industrial and medical applications as fishing line and suture among others. Furthermore, it is well known that the mechanical properties of P(3HB) fibers and films markedly deteriorate by a process of secondary crystallization.

We have developed several new drawing techniques for obtaining strong P(3HB) fibers. Amorphous fibers were obtained by quenching melt-spun fibers of ultra-high-molecular-weight P(3HB) (UHMW-P(3HB)) with $M_w$ = 5.3 × $10^6$ in ice water. The cold-drawing of amorphous fibers of UHMW-P(3HB) was achieved easily and reproducibly at a temperature below but near the glass transition temperature of 4ºC in ice water with two sets of rolls. The cold-drawn amorphous fibers were kept at room temperature for several minutes to generate the crystal nucleus, and then two-step drawing was applied using a stretching machine at room temperature to further increase the degree of chain orientation. The cold-drawn fibers were easily drawn at a very low stress by more than 1000%, but elastic recovery occurred on release from the stretching machine. Accordingly, annealing procedure is required to fix the extended polymer chains. Figure 2 shows the two-step drawn fibers processed from UHMW-P(3HB).

The tensile strength of two-step-drawn and annealed fibers linearly increased with the ratio of two-step drawing. When the total drawn ratio reached 60 times (cold-drawn for 6 times and two-step-drawn for 10 times), the tensile strength increased to 1320 MPa. This value is higher than those of poly(ethylene), poly(propylene), poly(ethylene

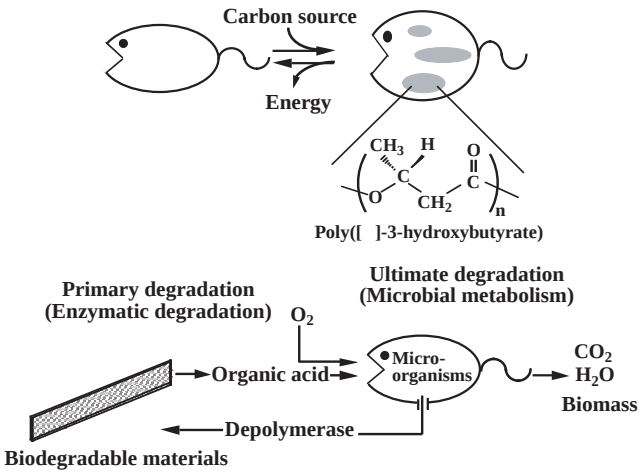


Fig. 1. Biosynthesis and biodegradation processes of P(3HB) and its copolymers.

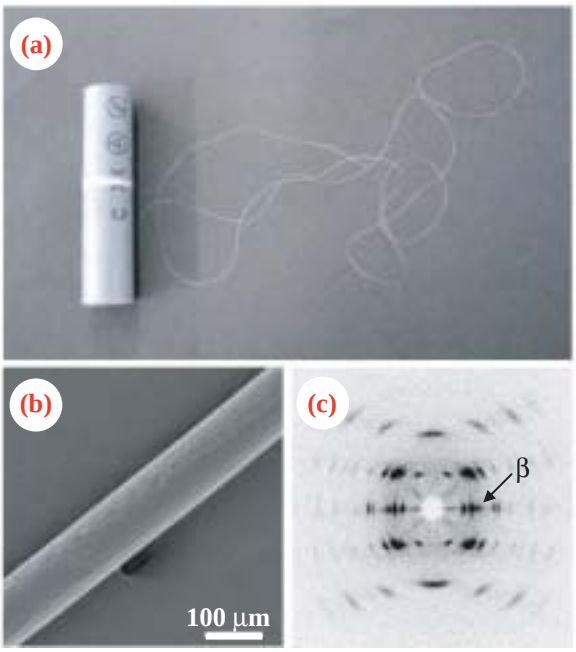


Fig. 2. **(a)** UHMW-P(3HB) fiber processed by cold-drawing (6 times) in ice water and two-step-drawing (10 times) at room temperature, and subsequently annealed at 50°C. **(b)** Scanning electron micrograph and **(c)** X-ray fiber pattern of UHMW-P(3HB) fiber.

terephtalate), and poly(vinyl alcohol) of industrial grade, and poly(glycolic acid) used as suture. Thus, it was revealed that the P(3HB) homopolymer becomes a much attractive material from the viewpoint of mechanical properties.

An X-ray fiber pattern for a bundle of ten pieces of P(3HB) fibers obtained using the laboratory X-ray source (beam size: 300 μm) is shown in Fig. 2(c). This pattern includes reflections from both the $\alpha$-form ($2_1$ helix conformation) [4] and $\beta$-form (planar zigzag conformation) [5] of P(3HB) simultaneously. It is well known that P(3HB) crystallizes as an orthorhombic crystal system with a space group of $P2_12_12_1$ ($\alpha$-form), and that $\beta$-form is introduced from the orientation of free chains in amorphous regions between $\alpha$-form lamellar crystals. Thus, the generation of $\beta$-form seems to introduce the increase in tensile strength.

To reveal the detailed fiber structure and the distribution of the two types of molecular conformation in mono-filaments, the micro-beam X-ray diffraction was performed using synchrotron radiation at beamline **BL47XU**. The beam size was focused onto 0.5 μm spot with a Fresnel zone plate and a mono-filament was linearly scanned perpendicular to the fiber axis in 2 μm steps [2,3].

Figure 3 shows micro-beam X-ray diffraction patterns of a two-step-drawn P(3HB) mono-filament obtained from three marked points in the microscope image. In the micro-beam X-ray fiber pattern of No. 1 (edge part), all the reflections were indexed by only the $\alpha$-form crystal system with a $2_1$ helix conformation. However, in the patterns of No. 2 and 3 (center part), the other reflection indexed by the $\beta$-form (planar zigzag conformation) was observed, together with $\alpha$-form crystal system with $2_1$ helix conformation.

These results indicate that a strong two-step-drawn UHMW-P(3HB) fiber has a core-sheath structure with only a $2_1$ helix conformation ($\alpha$-form) in the sheath region and with both a planar zigzag conformation ($\beta$-form) and a $2_1$ helix conformation ($\alpha$-form) in the core region.

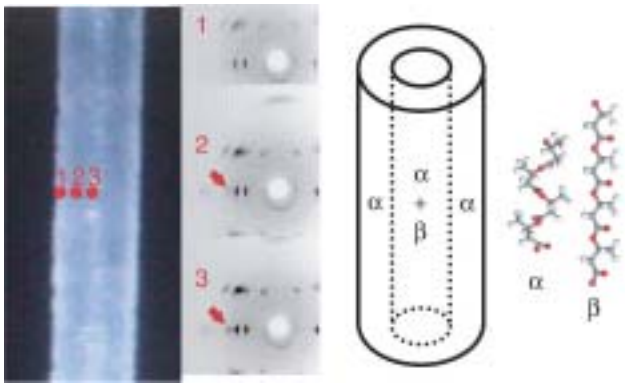


Fig. 3. Micro-beam X-ray fiber pattern of cold-drawn and two-step-drawn UHMW-P(3HB) mono-filament recorded from three marked points in microscope image, and a schematic display of core-sheath structure with two kinds of molecular structures revealed by micro-beam X-ray diffractions. The arrows indicate the reflection derived from the $\beta$-form.

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