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Structure Transition of Bio-Based Polyester Derived from Isomannide and Succinic Acid Revealed by Synchrotron WAXD/SAXS Simultaneous Measurements

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1 Introduction

"Bio-based plastics" have attracted increasing attention as alternatives to petroleum-based plastics because of great concern about fossil fuel depletion and global warming [1]. Isohexides are bio-based cyclic diols that have three stereoisomers differing in directions of two hydroxyl groups—isosorbide, isomannide, and isoidide. Bio-based polyesters composed of isohexides and diacids show a wide variety of properties and biodegradability, depending on the diol stereoisomerism and the alkylene chain length [2,3]. However, the crystallization of isohexide polyesters is still not well-understood, so that their possibility as crystalline plastics still remains unexplored. We have investigated the development of crystal and lamella structures in the polyester composed of isomannide and C4 diacid units (M4), which possesses crystal polymorphism (α- and β-forms), by synchrotron WAXD/SAXS simultaneous measurements [4]. In this study, we examine the structure transition of M4 α-form during a heating process by synchrotron WAXD/SAXS simultaneous measurements.

2 Experiment

Isomannide and succinyl chloride were polycondensed in bulk to M4 polyester with $M_n = 10^4$ and $M_w/M_n = 2.1$. M4/chloroform solution was cast to obtain a crystallized sample with only the α-form crystals.

WAXD/SAXS simultaneous measurements were performed at KEK PF BL-6A (λ = 0.1500 nm) and BL-10C (λ = 0.1488 nm) using an FP84HT TA Microscopy Cell (METTLER) for heating from 30 to 210 °C at 10 °C/min. Sample was packed in a washer, whose temperature was measured by a resistance temperature detector. WAXD/SAXS analyses were done using the handmade software [5].

3 Results and Discussion

Fig. 1 depicts changes of WAXD curves of M4 during a heating process at 10 °C/min. Fig. 2 shows changes of total crystallinity (X_c, black), the strongest-peak area of the α-form (A_α, blue), and that of the β-form (A_β, red) of M4 during a heating process at 10 °C/min. X_c (α- and β-forms) and A_α drastically decrease at temperatures ≥ 160 °C. Simultaneously, the peak of β-form appears, though its area (A_β) is very small. Here, A_α is comparable to A_β, if X_c (α) is similar to X_c (β). These results indicate that the transition mechanism from α- to β-forms is the melt-recrystallization, not the solid-solid transition.

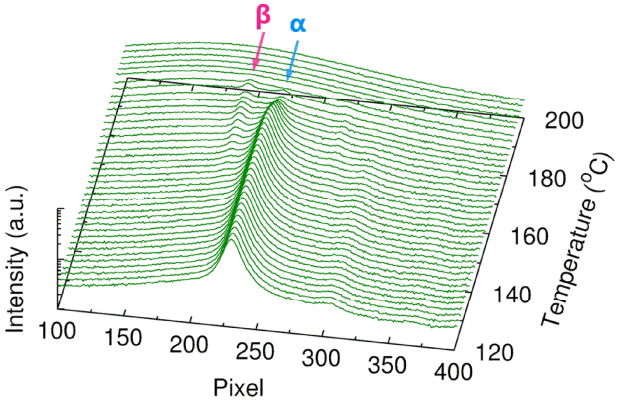

Fig. 1: Changes of WAXD curves of M4 during a heating process at 10 °C/min. M4 initially has only the α-form.

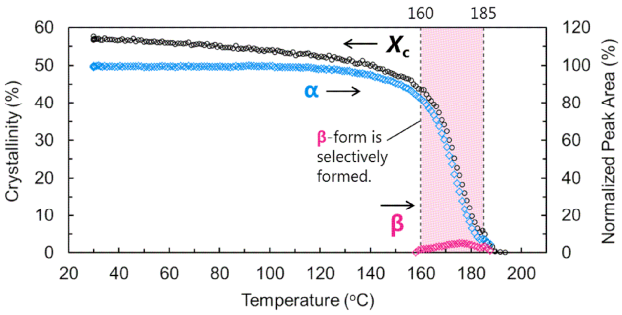

Fig. 2: Changes of total crystallinity (X_c, black), the strongest-peak area of α-form (A_α, blue), and that of β-form (A_β, red) of M4 during a heating process at 10 °C/min. Temperature range of 160–185 °C is colored with red, at which the β-form is selectively formed.

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References

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