

# Structure Development 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 polymers” have attracted increasing attention as alternatives to petroleum-based polymers because of great concern about fossil fuel depletion and global warming [1]. 1,4:3,6-Dianhydrohexitols (DAHLs) are bio-based cyclic diols that have three stereoisomers differing in directions of two hydroxyl groups—isororbide, isomannide, and isoidide. Their characteristic cyclic structure and stereoisomerism give diverse and unique properties when they are introduced into the polymer backbone [2]. Bio-based polyesters composed of DAHLs and dicarboxylic acids show a wide variety of properties and biodegradability [3]. However, the crystallization of DAHL polyesters is still not well-understood, so that their possibility as crystalline plastics still remains unexplored. In our previous reports, the lamella structure of DAHL polyesters with C10–C12 dicarboxylic acid units was analyzed by synchrotron SAXS [4]. In this study, we investigate the development of crystal and lamella structures in the crystalline DAHL polyester composed of isomannide and C4 dicarboxylic acid units (M4; Fig. 1), which possesses crystal polymorphism ( $\alpha$ - and  $\beta$ -forms) [5], by synchrotron WAXD/SAXS simultaneous measurements.

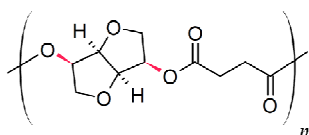


Fig. 1: Chemical structure of M4.

## 2 Experiment

Isomannide and succinyl chloride were polycondensed in bulk to M4 polyester with  $M_n = 10^4$  and  $M_w/M_n = 2.1$ .

WAXD/SAXS simultaneous measurements were performed at KEK PF BL-10C ( $\lambda = 0.14880$  nm) and BL-6A ( $\lambda = 0.15000$  nm). The handmade temperature-controlled stage was used for isothermal crystallization experiments. WAXD/SAXS analyses were done using the handmade software [6], which allowed 2D→1D conversion, background subtraction, and peak separation.

## 3 Results and Discussion

Fig. 2 shows time-resolved WAXD/SAXS curves of M4 during melt-crystallization at  $T_c = 140$  °C, before which its thermal history had been eliminated at 200 °C ( $> T_m$ ) for 1 min. In some WAXD curves (Fig. 2a), diffraction peaks derived from the  $\alpha$ - and  $\beta$ -forms ( $d =$

0.47 and 0.43 nm, respectively) are seen. It should be noted that at 140 °C the crystallization of the  $\alpha$ -form starts (emergence of the peak) and proceeds (increases in peak area) at an earlier time, as compared to that of the  $\beta$ -form. In the Lorentz-corrected SAXS curves (Fig. 2b), the scattering peak of crystalline lamella structure appears and its intensity increases with time. These results indicate that firstly the stacked lamella structure of the  $\alpha$ -crystal develops and subsequently that of the  $\beta$ -crystal independently forms. Namely, it is considered that the  $\alpha$ -crystals-rich domain and the  $\beta$ -crystals-rich one exist in the sample. WAXD/SAXS simultaneous measurements at different temperatures revealed different  $T_c$  dependence of crystallization behaviors for the  $\alpha$ - and  $\beta$ -forms.

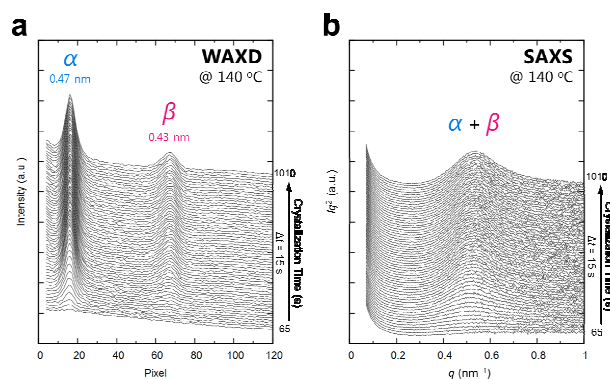


Fig. 2: Time-resolved WAXD/SAXS curves of M4 during melt-crystallization at 140 °C, before which thermal history had been erased at 200 °C for 1 min.

## Acknowledgement

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## References

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