

Higher-Order Structure of Bio-Based Polymers Derived from Isosorbide and Isomannide Revealed by Synchrotron Small-Angle X-ray Scattering

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1 Introduction

“Bio-based polymers” have attracted increasing attention as alternatives to petroleum-based polymers because of great concern about exhaustion of fossil fuels and global warming [1]. 1,4:3,6-Dianhydrohexitols (DAHLs) are bio-based sugar diols whose rigid cyclic structure is expected to give remarkable thermal and mechanical properties when introduced into the polymer backbone [2]. There are three stereoisomers differing in directions of two hydroxyl groups—isosorbide, isomannide, and isoidide (Fig. 1). Bio-based polyesters composed of DAHLs and dicarboxylic acids have been synthesized and their basic properties have been systematically investigated [3]. However, the crystallization of DAHL polyesters is still not well-understood. Previously, the higher-order structure of DAHL polyesters with C10 dicarboxylic acid units (DAHL-10) was analyzed by using synchrotron small-angle X-ray scattering (SR-SAXS) [4]. In this study, we investigate the higher-order structure of DAHL polyesters with C12 carboxylic acid units (DAHL-12) by SR-SAXS and compare with that of DAHL-10.

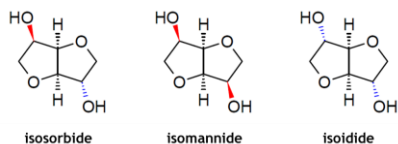


Fig. 1: Chemical structures of 1,4:3,6-dianhydrohexitols (DAHLs). The *endo* and *exo* C–O(H) bonds are shown in red and blue, respectively.

2 Experiment

Commercially-available DAHLs (isosorbide and isomannide) were polycondensed with dodecanedioyl dichloride. As a result, two types of DAHL polyesters were obtained with $M_n \approx 1.3 \times 10^4$ and $M_w/M_n \approx 1.9$ (Fig. 2). Polyesters containing isosorbide and isomannide units were named IS12 and IM12, respectively. Melt-crystallization treatments were done for sufficient time to complete the crystallization of as-polymerized samples.

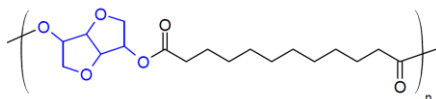


Fig. 2: Polyester composed of DAHL (shown in blue) and C12 dicarboxylic acid units.

SAXS measurements were performed at KEK PF BL-10C ($\lambda = 0.14880$ nm). SAXS analyses were done using the handmade software developed by Marubayashi [5].

3 Results and Discussion

Fig. 3a shows SAXS curves of DAHL-12 isothermally-crystallized at 30 °C. Scattering peaks can be seen for both IS12 and IM12, indicating the formation of the long period structure consisting of crystalline lamellae and amorphous layers. The long period L of IM12 (10.8 nm) is larger than that of IS12 (10.2 nm). Their correlation functions (Fig. 3b) indicate that the lamella thickness l_c of IM12 (3.6 nm) is larger than that of IS12 (2.8 nm), while there is almost no difference in the amorphous layer thickness l_a between IM12 (7.2 nm) and IS12 (7.4 nm). The same magnitude relationship is true for the parameters of the long period structure (L , l_c , l_a) of DAHL-10. These results should be linked with a longer fiber period of IM_n compared with IS_n ($n = 10$ or 12), i.e., a conformational difference in the crystallized state.

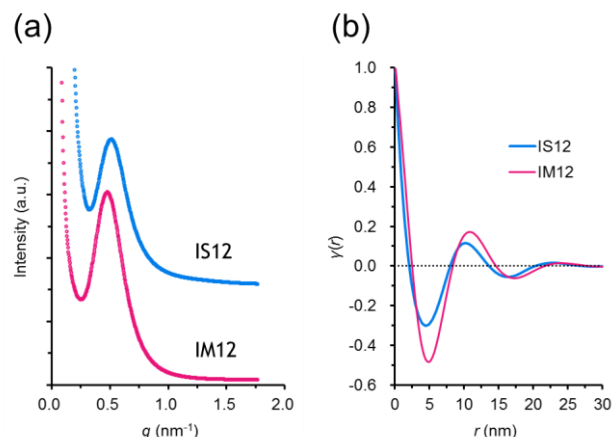


Fig. 3: (a) SAXS curves and (b) normalized one-dimensional correlation functions of DAHL-12 melt-crystallized at 30 °C for 15 h.

Acknowledgement

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References

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