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Higher-Order Structure Analysis of Bio-Based Polyesters Derived from 1,4:3,6-Dianhydrohexitols by Using Synchrotron Small-Angle X-ray Scattering

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1 Introduction

"Bio-based polymers" have attracted much 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 (DAH) are sugar diols with characteristic heterocyclic structure [2], whose rigid cyclic structure is expected to give remarkable thermal and mechanical properties as building blocks for bio-based polymers. As shown in Fig. 1, there are three isomers differing in directions of two hydroxyl groups—isosorbide, isomannide, and isoidide. Bio-based polyesters composed of DAH and dicarboxylic acids were synthesized and their basic properties containing biodegradability were systematically investigated [3]. However, crystallization of DAH polyesters is not well-understood. In this study, we investigated the higher-order structure of DAH polyesters by using synchrotron small-angle X-ray scattering (SR-SAXS).

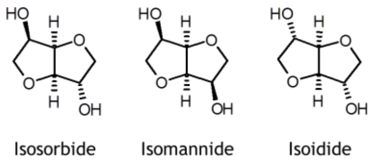

Fig. 1: Chemical structures of 1,4:3,6-dianhydrohexitols.

2 Experiment

Isosorbide and isomannide were used as diols. Adipoyl chloride and sebacoyl chloride were used as dicarboxylic chlorides. Four types of DAH polyesters (an example in Fig. 2) were synthesized by polycondensation of DAH and dicarboxylic chlorides ($M_n \approx 1.0 \times 10^4$, $M_w/M_n \approx 1.5$). Polyesters composed of isosorbide with adipic acid (C6) and sebacic acid (C10) were named IS6 and IS10, respectively. In a similar manner, those composed of isomannide with adipic acid and sebacic acid were referred to as IM6 and IM10, respectively. Melt-crystallization treatments for sufficient time to complete crystallization were done for as-polymerized IS10.

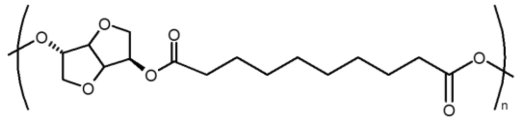

Fig. 2: Chemical structure of bio-based polyester composed of isosorbide and sebacic acid (IS10).

SAXS measurements were performed at KEK PF BL-10C. A series of X-ray structure analyses were done using the handmade software developed by Marubayashi [4].

3 Results and Discussion

Fig. 3a shows SAXS curves of the as-polymerized DAH polyesters. Semicrystalline DAH polyesters (IS10 and IM10) showed typical scattering peaks derived from the stacked lamellar structure. Long periods of IS10 and IM10 were calculated to be 10.7 and 12.2 nm, respectively. On the other hand, no scattering peaks were observed in amorphous DAH polyesters (IS6 and IM6).

Fig. 3b shows SAXS curves of the melt-crystallized IS10 samples. Long periods were ca. 11 nm, which is comparable to that of as-polymerized IS10 (10.7 nm). The crystallization temperature (T_c) dependence of long periods was not so large. In regard to this point, a further investigation would be required.

The next goal is determining lamellar and amorphous layer thicknesses of IS10 and IM10. Also, T_c dependence of long periods for IM10 should be clarified and compared with the results of IS10.

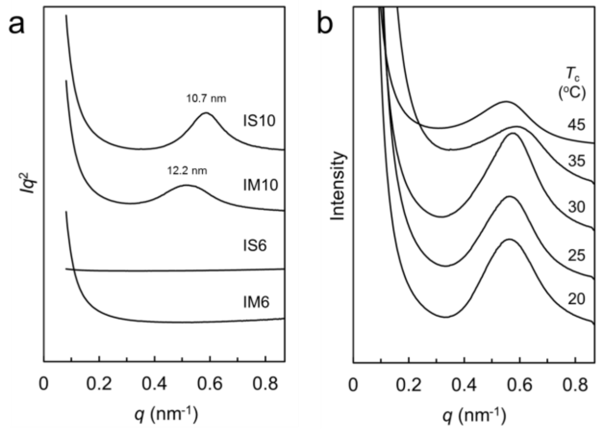

Fig. 3: (a) SAXS curves of as-polymerized DAH polyesters. (b) SAXS curves of melt-crystallized IS10.

Acknowledgement

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References

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