

Effect of the block length and the molecular weight on the isothermal crystallization behavior of multi-stereoblock poly(lactic-acid)s



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ABSTRACT

Multi-stereoblock PLAs (multi-sb-PLA)s having the controlled block sequences between PLLA and PDLA were synthesized by the chain-extension of tri-stereoblock PLAs. These multi-sb-PLAs only crystallize into the stereocomplex without forming any traces of homo-chiral crystal. The effects of the block length and the total molecular weight on the isothermal crystallization behavior and the higher order structure of the multi-sb-PLAs were investigated. Observation of isothermal crystallization behavior revealed that the multi-sb-PLA with longer blocks and higher molecular weights started the crystallization at a lower temperature within a shorter period of time in a wider temperature range. The crystallization rate increases with increasing block length and the multi-sb-PLA with a longer blocks achieves higher degree of crystal. The multi-sb-PLA with a higher molecular weight forms more complete structure of the spherulite than that with a low molecular weight. Annealing of the amorphous multi-sb-PLA produced sc with two different lamellar thicknesses. One which melts at a higher temperature is a main sc phase with a lamellar thickness merely determined by the block length and the molecular weight regardless of the thermal history. The chains in the amorphous region only crystallized upon annealing and gradually grew with increasing annealing temperature giving some addition to the lamellar thickness of the samples detected by SAXS.

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1. Introduction

The stereocomplex crystal (sc), which forms in the equal blend of poly(*L*-lactic acid) (PLLA) and poly(*D*-lactic acid) (PDLA), has a high melting temperature as high as 230 °C, about 50 °C higher than that of PLLA or PDLA homo chiral crystal (hc) [1] and the rate of crystallization is quite high [2]. Because of these superior properties, poly(lactic acid) (PLA) which consists of sc as a crystalline phase is expected to be a high performance material. However, the simple melt blending of PLLA and PDLA having a higher molecular weight usually resulted in the PLA which consists of both hc and sc and the high thermal stability cannot be expected [2–5].

For improving the sc crystallization efficiency, so called stereoblock copolymers of PLLA and PDLA (sb-PLA) are utilized [6–9]. In the sb-PLA, both PLLA and PDLA sequences can be mixed in a molecular level to make the sc formation easier. The di- and tri-sb-

PLAs obtained in the multi-stage ring-opening polymerization (ROP) effectively produce sc showing the melting point much higher than that of PLLA with a similar molecular weight [10]. However the molecular weights of di- and tri-sb-PLAs are determined by the length of the blocks since the fractions of PLLA and PDLA are supposed to be equal for complete sc formation. The production and the properties of the multi-sb-PLAs have been reported by Masutani et al. [11,12] for the multi-sb-PLAs synthesized by the chain extension of tri-sb-PLAs prepared in the sequential ROP [11] and by dual terminal couplings of PLLA and PDLA prepolymers [12]. They showed an excellent thermal stability and thermo-mechanical properties of the multi-sb-PLAs because of the efficient formation of sc of fairly low molecular weight PLLA and PDLA chains retaining the high total molecular weight of the copolymers.

The present authors [13] have reported the basic thermal properties of multi-sb-PLAs with various block lengths and the molecular weights. They showed that T_g increases with the increase in the block length and decreases with the molecular weight of the

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multi-sb-PLA. T_m increases with the increase in the block length and the molecular weight of multi-sb-PLA. Further T_c in the heating process from the amorphous state decreases and that in the cooling process from the melt increases with the increase in the block length.

In this study, the effects of the block length and the molecular weight on the isothermal crystallization behavior and the resultant higher order structure of the same multi-sb-PLAs utilized in the previous study [13] were investigated.

2. Experimental

2.1. Materials and synthesis

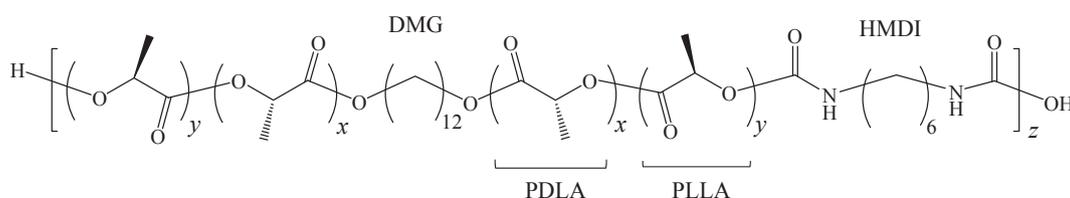
L- and *D*-lactides with an optical purity of 99% ee were supplied by Musashino Chemical Laboratory, Ltd. (Tokyo). The multi-sb-PLAs were synthesized according to the method reported by Masutani et al. [11]. The multi-sb-PLAs with molecular weight of approximately 60,000 (MSB-60) and 130,000 (MSB-130) were synthesized. The absolute value of the number average molecular weight M_n of the blocks and the multi-sb-PLAs were determined by ^1H NMR spectroscopy. From now on, the multi-sb-PLAs are termed by their block length and the molecular weight. For example, MSB-60-5k is a multi-sb-PLA with 5000 in block length and 60,000 in molecular weight. Further the series of multi-sb-PLAs with 60,000 and 130,000 in molecular weights are termed as MSB-60 and MSB-130, respectively. The multi-sb-PLA has a structure in which di-block copolymers consisting of short *L*- and *D*-blocks with the same length are connected with an initiator and a chain extender alternately at the ends of the same enantiometric blocks (Scheme 1). The molecular characteristics and the basic thermal property of multi-sb-PLAs are listed in Table 1. T_g s were determined in the 1st heating process of amorphous films and T_m s were determined in the 2nd heating process after cooling from molten state. Detailed ^1H NMR spectra of HO-PDLA-OH, tri-sb-PLA, and multi-sb-PLA, along with molecular characteristics and other thermal properties were reported in the previous paper [13].

The multi-sb-PLA synthesized was placed between two aluminum plates having a 100 μm thick metal spacer and subjected to compression molding using a Mini Test Press (MP-2FH: TOYOSEKI Co., Ltd., Japan). The sample was melted at 220 $^\circ\text{C}$, pressed at a pressure of 5 MPa for 40 s, and quenched in ice water to obtain an amorphous film. Then the amorphous films were annealed in an oven (Yamato DX31/41/61) at various temperatures ranging from 80 $^\circ\text{C}$ to 180 $^\circ\text{C}$ for 1 h.

2.2. Measurements and observation

2.2.1. Differential scanning calorimetry (DSC)

Thermal property was determined by using a differential scanning calorimetry, DSC3100SA, Material Analysis and Characterization (MAC Science CO, Ltd.) thermal analyzer under a nitrogen flow of 20 mL/min and at a heating rate of 10 $^\circ\text{C}/\text{min}$. A sample of approximately 2.0 mg was sealed in an aluminum pan and heated to 250 $^\circ\text{C}$. Alumina was used as a standard.



Scheme 1. Chemical structure of the multi-sb-PLA.

Table 1
Molecular characteristics and the thermal properties of MSB-60 and MSB-130 series.

Sample	Mn of D-block ^a	Mn of multi-sb-PLA ^a	T_g^b ($^\circ\text{C}$)	T_m^b ($^\circ\text{C}$)
MSB-60-2.5k	2500	58,900	195	479
MSB-60-5k	4900	61,000	189	389
MSB-60-10k	9800	59,500	237	455
MSB-60-20k	20,000	61,900	255	423
MSB-130-2.5k	2500	147,000	245	578
MSB-130-5k	5000	125,000	209	335
MSB-130-10k	9800	129,000	191	318
MSB-130-20k	20,000	136,000	232	377

^a Determined by ^1H NMR spectroscopy.

^b Determined by DSC.

2.2.2. Isothermal crystallization

Isothermal crystallization of the multi-sb-PLAs was observed with a polarizing optical microscope (ECLIPSE LV100POL, Nikon) equipped with a temperature controlled hot stage (Temperature controller TPC-100, ULVAC-RIKO). Multi-sb-PLA film was placed in the hot stage, heated to 220 $^\circ\text{C}$ and kept for 1 min to confirm the complete melting of the samples. Then the sample was quenched to the predetermined crystallization temperatures at a cooling rate of 200 $^\circ\text{C}/\text{min}$. Observation with a polarizing microscope was continued for 10 min and the images were recorded on a personal computer.

The progress of the crystallization was determined by tracing the optical density of the image. The image of the samples at a molten state was completely dark, since the polymer melt is optically isotropic. Once the spherulites were formed, the image turned to be bright. Optical density can be determined using the following equation:

$$\text{Optical density} = \log_{10}\{255/(255 - \text{mean gray value})\} \quad (1)$$

where, 255 is the maximum pixel value and the mean gray value is the average gray value within the selection. This is the sum of the gray values of all the pixels in the selection divided by the number of pixels.

2.3. Wide angle X-ray diffraction (WAXD)

WAXD patterns and their spectra were obtained with a wide angle X-ray diffraction (WAXD). WAXD patterns were obtained on a flat imaging plate using a nickel-filtered $\text{CuK}\alpha$ radiation of wavelength 0.1542 nm from a Rigaku RAD2C sealed beam X-ray generator operating at 40 kV and 20 mA.

2.4. Inverse fast fourier transformation (IFFT) of SAXS

SAXS profiles were obtained using an X-ray generator Rigaku USAXS-SB8/FR operating at 40 kV and 30 mA and PILATUS 100K as a detector. The wavelength of the X-ray used for the measurement was 0.154 nm and camera length was 852 mm.

The SAXS profiles obtained were subjected to the inverse fast

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