



# Thermal properties of the multi-stereo block poly(lactic acid)s with various block lengths



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## ABSTRACT

Multi-sb-PLAs with molecular weights of approximately 60,000 (MSB-60) and 130,000 (MSB-130) with various block lengths were synthesized. These have a structure in which di-block copolymers consisting of *L*- and *D*-blocks with the same length are connected with 1,12-dodecanediol (DMG), an initiator and hexamethylene diisocyanate (HMDI), a chain extender alternately. DSC analyses revealed that  $T_g$  increases with the increase in the block length and the multi-sb-PLA with a lower molecular weight has higher  $T_g$  at a constant block length. These are attributable to the higher concentration of DMG and HMDI in the multi-sb-PLA.  $T_m$  increases with the increase in the block length and the molecular weight of multi-sb-PLA and those of MSB-60 and MSB-130 get close to a constant value at higher block length. The variation of  $T_m$  seems to be attributable to change in the lateral dimension of lamella rather than that of the thickness.  $T_c$  in the heating process from the amorphous solid decreases and that in the cooling process from the melt increases with the increase in the block length, indicating that the multi-sb-PLA with a long block has a wider temperature range of the crystallization.

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## 1. Introduction

Poly(lactide) (PLA) is one of the bio-based polymers synthesized from renewable resources and has been expected to be replaced to the conventional fossil resource-based materials. Lactic acids, the monomer of PLA, have *L*- and *D*-isomers. The two isomers of lactic acid can produce three distinct materials: poly(*L*-lactic acid) (PLLA) and poly(*D*-lactic acid) (PDLA) are semicrystalline materials with a regular chain structure and have a melting temperature around 180 °C [1–3]. The racemic mixture of *L*- and *D*-lactic acids produces an amorphous poly(*D,L*-lactic acid) (PDLLA) with an atactic chain structure [4].

It has been known that the blending of two isomeric PLAs, poly(*L*-lactide) (PLLA) and poly(*D*-lactide) (PDLA), leads to the stereocomplex (sc) formation [5] with its melting temperature around 235 °C. However sc-PLA obtained by the simple blending of PLLA and PDLA does not always show sufficient sc formation because of the co-crystallization of individual component (hc)

along with the sc crystallization [6–8]. Because of the co-formation of hc and sc, the products such as fibers, films and injection molded parts prepared from such simple blends do not show a good thermal resistance for the high-temperature applications.

On the other hand, it is known that the poly(lactide)s consisting of the blocky stereosequences of *L*- and *D*-lactides, so called stereoblock poly(lactide)s (sb-PLA), tend to exclusively form sc [9–12]. The sb-PLAs can be obtained in three different ways. One of them is the stereo-selective synthesis by utilizing an aluminum catalyst with enantiomeric Schiff base ligands reported by Spassky et al. [13]. Since this report, various researchers reported the stereo-selective polymerization to obtain sb-PLAs. However the melting point of these sb-PLA were rather low almost equivalent to that of highly optically pure PLLA.

Di- and tri-sb-PLAs can be obtained by two-stage ring opening polymerization (ROP) of *L*- or *D*-lactide [14–16]. Initiation of the first polymerization of *L*- or *D*-lactide using mono- and di-alcohol as initiators gives a mono- and di-hydroxy terminated poly(lactide)s, respectively, and these poly(lactide)s can be further used as mono- and di-functional macro-initiators for the subsequent polymerization of the enantiometric lactide. The sb-PLAs obtained in these multi-stage ROP show the melting point much higher than that of

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PLLA with a similar molecular weight. The production of the multi-sb-PLAs utilizing the tri-sb-PLAs prepared in this sequential ROP has been reported by Masutani et al. [10]. The tri-sb-PLAs were further subjected to the chain-extending reaction to multi-sb-PLAs using di-isocyanate as a chain-extender.

Multi-sb-PLAs consisting of relatively short enantiomeric segments were prepared by the solid-state polymerization (SSP) of the mixture of PLLA and PDLA with medium molecular weight as prepolymers. PLLA and PDLA effectively crystallize into sc and the sc mixture was subjected to SSP to obtain the multi-sb-PLA with a molecular weight as high as  $1 \times 10^5$  [11].

In this study, the multi-sb-PLAs with various block lengths were synthesized according to the method reported by Masutani et al. [17]. Oligo-*D*-lactic acids with various molecular weights were synthesized by the 1st ROP of *D*-lactide. Then tri-sb-PLAs were synthesized by the 2nd ROP of *L*-lactide using oligo-*D*-lactic acids as a macro-initiator. Further the chain extension reaction was performed for these tri-sb-PLAs to obtain multi-sb-PLAs. This method is characterized by the well controlled block length and composition of the resultant multi-sb-PLAs because they ought to be determined by the molecular weights of the starting PDLA and PLLA prepolymers. Although the total molecular weight of di- and tri-sb-PLAs are directly related to the block length, that of the multi-sb-PLA can be designed independently of the block length. So the effects of the block lengths and the total molecular weight of the multi-sb-PLA on the thermal property and the crystallization behavior can be examined separately.

## 2. Experimental

### 2.1. Materials

*L*- and *D*-lactides with optical purities of 99% ee were supplied by Musashino Chemical Laboratory, Ltd. (Tokyo). As a catalyst, tin octate ( $\text{Sn}(\text{Oct})_2$ , 95%) was purchased from Strem Chemicals (Newburyport, MA) and Sigma-Aldrich (St Louis, MO) via Sasaki Chemical Co. Ltd. (Kyoto, Japan) and purified by distillation before use and dissolved in distilled toluene at a concentration of 0.20 g/ml under a nitrogen atmosphere. As an initiator, 1,12-Dodecanediol (dodecamethylene glycol: DMG, 97%) was purchased from Nacalai Tesque Co. Ltd. (Kyoto). Hexamethylene diisocyanate (HMDI) were supplied by Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). HMDI was purified by distillation before use. Solvents, dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99.5%) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 98%) were purchased from Kanto Chemical Co. Ltd. (Tokyo) and Central Glass Co. Ltd. (Hofu, Yamaguchi, Japan), respectively. DMG and solvents were used without purification unless specifically noted.

### 2.2. Synthesis of multi-sb-PLAs

#### 2.2.1. Synthesis of di-hydroxy terminated poly(*D*-lactide)s

Multi-sb-PLAs were synthesized following the method reported by Masutani et al. [10]. Scheme 1(a) shows the synthesis of di-hydroxy terminated poly(*D*-lactide)s (HO-PDLA-OH)s by 1st step ROP of *D*-lactide. HO-PDLA-OHs were synthesized by ring opening polymerization of *D*-lactide using DMG as an initiator. In order to synthesize HO-PDLA-OH with theoretical molecular weights ( $M_{n(\text{th})}$ ) of 2,500, 5,000, 10,000, and 20,000 g/mol, the pre-determined amounts of *D*-lactide and DMG were introduced into a 50 ml round-bottomed flask with a stirrer. The flask was sealed under vacuum (10 Pa) and dried under room temperature for 6 h after degassing. Nitrogen gas was circulated in the flask to prevent air from entering the flask. The mixture of *D*-lactide and DMG was kept stirred during the drying process. Then  $4 \times 10^{-4}$  mol of  $\text{Sn}(\text{Oct})_2$  equivalent to *D*-lactide was introduced and the

polymerization was allowed to proceed at 180 °C for 25 min. HO-PDLA-OHs obtained were dried at 120 °C under vacuum (10 Pa) for 12 h after synthesis in order to remove the residual monomer.

#### 2.2.2. Synthesis of tri-sb-PLAs and multi-sb-PLAs

The synthesis of tri-sb-PLAs was conducted by the ring opening polymerization (ROP) of *L*-lactide using HO-PDLA-OH as a macro-initiator as shown in Scheme 1(b). *L*-lactide was introduced into a 50 ml round-bottomed flask containing HO-PDLA-OH. The flask was sealed under vacuum (10 Pa) at 80 °C and dried under room temperature for 7 h. A predetermined amount of catalyst solution  $4 \times 10^{-4}$  mol of  $\text{Sn}(\text{Oct})_2$  was added to the reaction system. The mixture of HO-PDLA-OH and *L*-lactide was then heated at 190 °C with stirring for 20 min to obtain tri-sb-PLA (PLLA-PDLA-PLLA).

Scheme 1(c) shows the synthesis of multi-sb-PLAs by the chain-extension of tri-sb-PLA comprising the equimolar PLLA and PDLA lactate units. A chain extender, HMDI was introduced to tri-sb-PLAs and the chain extending reaction was continued to proceed at 190 °C for 15 min. At the end of the reaction, the multi-sb-PLA obtained was cooled, dissolved in the mixture of  $\text{CH}_2\text{Cl}_2$  and HFIP ( $\text{CH}_2\text{Cl}_2/\text{HFIP} = 8/2$ ), and reprecipitated into an excess of methanol. The precipitates were filtered, washed with methanol several times, and dried in vacuum at 80 °C for 6 h and the multi-sb-PLAs with molecular weight of 60,000 (MSB-60) and 130,000 (MSB-130) have been successfully synthesized. Each multi-sb-PLA has various block length ranging approximately from 2500 to 20,000. From now on, HO-PDLA-OH and tri-sb-PLAs are termed by their block length for example PDLA-2.5k and tri-sb-PLA-2.5k, respectively and 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.

#### 2.2.3. Determination of molecular weights

The number average molecular weight determined by  $^1\text{H}$  NMR (600 MHz) spectra, ( $M_{n(\text{nmr})}$ ), were recorded on a Bruker (Karlsruhe, Germany) AV600 spectrometer for samples dissolved in deuterated chloroform using 0.03 vol% tetramethylsilane (TMS) as the internal standard. The number- and weight-average molecular weights of tri-sb-PLAs and multi-sb-PLAs, ( $M_{n(\text{GPC})}$ ) and ( $M_{w(\text{GPC})}$ ), respectively, were determined by gel permeation chromatography (GPC), recorded on a system comprised of a Shimadzu (Kyoto) LC-20AD HPLC pump and a Shimadzu RID-10A differential refractive index detector. Two Tosoh (Tokyo, Japan) TSK gel Super HZM-N columns (3.0  $\mu\text{m}$  in bead size, molecular weight exclusion range of 700,000–500 Da) with a Tosoh TSK Super HZ-L guard column (4.6 mm ID  $\times$  3.5 cm) were installed in the system, and chloroform was used as the eluent. The measurement was carried out with a precipitation sample of approximately 2.0 mg dissolved in 0.4 ml chloroform at 40 °C at a flow rate of 0.25 ml  $\text{min}^{-1}$ . Polystyrene (PS) standards were used to calibrate the molecular weight ranging from 1,090,000–500 Da.

### 2.3. Infrared spectroscopy

FT-IR spectra of the multi-sb-PLA films in an amorphous state were recorded on Spectrum One Spectrometer (Perkin Elmer, USA) from 4000  $\text{cm}^{-1}$  to 500  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  in wave number at room temperature.

### 2.4. Thermal properties

Thermal property of the multi-sb-PLAs was determined by using a differential scanning calorimetry, DSC3100SA, Material Analysis

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