

# Highly Crystalline Poly(lactic acid)(PLA) Alloys Containing Stereocomplexes

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## ABSTRACT

Stereoblock poly(lactic acid) (sb-PLA) composed of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in a block sequence is expected to be a bio-based material with high thermal stability. This work reports the synthesis of sb-PLA with high molecular weight and high degree of complex formation by catalytic polycondensation using a combination of enantiometric PLA oligomers with different oligomer lengths. The thermal and structural changes in these materials upon reaction were investigated by DSC, GPC, and  $^{13}\text{C}$  NMR spectroscopy. It was revealed that the PLA oligomers synthesized with a widely used tin catalyst causes a side reaction to form dimeric lactide so that the molecular weight did not increase efficiently during the polycondensation. By contrast, the PLA oligomers synthesized with a methanesulfonic acid catalyst studied for the first time in the present study suppresses side reactions, thereby forming sb-PLA with higher molecular weight at a higher yield. Furthermore, it was also shown that the molecular weight of the starting PLA oligomers significantly affects the final molecular weight and sc crystallinity of sb-PLA.

**Keywords:** poly(lactic acid), stereocomplex, stereoblock copolymer, catalyst, molecular weight

## 1 INTRODUCTION

Poly(lactic acid) (PLA) is a bio-based polymer with good biodegradability and biocompatibility, which is producible from renewable resources such as sugarcane and corn starch. Because of its environmental adaptability, PLA is a fascinating material of importance to the increasing concern about the development of a sustainable society. Industrial applications of PLA, however, has been limited due to its insufficient heat resistance, since the thermal properties such as heat deflection temperature were

Oligomer	Molecular weight <sup>a</sup> $M_n$	Molecular weight <sup>a</sup> $M_w$	Thermal properties <sup>b</sup> $T_g$ (°C)	$T_m$ (°C)	Catalyst
PLLA-H-SO	$4.0 \times 10^4$	$9.4 \times 10^4$	59	167	$\text{CH}_3\text{SO}_3\text{H}$
PDLA-H-SO	$3.5 \times 10^4$	$7.4 \times 10^4$	59	162	$\text{CH}_3\text{SO}_3\text{H}$
PDLA-L-SO	$1.3 \times 10^4$	$2.7 \times 10^4$	53	158	$\text{CH}_3\text{SO}_3\text{H}$
PLLA-H-Sn	$4.3 \times 10^4$	$9.0 \times 10^4$	53	163	$\text{SnCl}_2(\text{II})$
PDLA-H-Sn	$2.8 \times 10^4$	$5.8 \times 10^4$	51	155	$\text{SnCl}_2(\text{II})$
PDLA-L-Sn	$1.8 \times 10^4$	$3.4 \times 10^4$	49	158	$\text{SnCl}_2(\text{II})$

mainly controlled by its glass transition temperature ( $T_g$ ) of ca. 60 °C [1], which is low.

Recently, stereoblock poly(lactic acid) (sb-PLA) composed of PLLA and PDLA in a block sequence has been reported. This method allows PLA to form stereocomplex (sc) crystals between L- and D-lactyl segments. For example, Kimura and his coworkers have developed a synthetic procedure of multi-block sb-PLA by solid state polycondensation (SSP), producing sb-PLA with high molecular weight and high degree of sc formation.[2,3] In their method, they used PLLA and PDLA with low molecular weight ( $M_w = 18,000\sim46,000$  g/mol) synthesized from L- and D-lactic acids in the presence of stannous dichloride dihydrate ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and *p*-toluenesulfonic acid monohydrate (TSA) as catalyst. And then, complexation between PLLA and PDLA was carried out, followed by SSP to obtain sb-PLA. However, they did not study effects of the molecular weight of the PLA starting oligomeric materials and the catalyst used for their synthesis on the final product of sb-PLA.

In our present study we focused on the production of sb-PLA with high molecular weight and high degree of sc crystallinity by SSP, changing the reaction conditions from the previous studies [2,3] and on the investigation of effects of the molecular weight of the enantiometric PLAs used for polycondensation and the catalysts used for their synthesis. The resultant sb-PLA was analyzed by gel permeation chromatography (GPC), x-ray diffraction (XRD), differential scanning calorimetry (DSC), and  $^{13}\text{C}$  NMR spectroscopy.

## 2 EXPERIMENTAL

### 2.1 Materials

First, PLLA and PDLA with various weight average molecular weight ( $M_w$ ) were synthesized using lactic acid monomer in the presence of 1,000 ppm of either methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) or tin chloride (II) ( $\text{SnCl}_2$ ) as catalyst by direct polycondensation reaction. In this report, these PLA starting materials used for SSP are denoted as “oligomer” for convenience, in which the

Table 1: Characteristics of PLLA and PDLA oligomers.

a : The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were measured by GPC using chloroform as eluent at a flow rate of 10 ml/min at 40 °C.

b : Glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) were determined by DSC. The samples were heated at the rate of 10 °C/min in the  $\text{N}_2$  atmosphere.

PLA with  $M_w$  higher and lower than 50,000 g/mol are distinguished by H and L, respectively. Furthermore, the PLA synthesized with methanesulfonic acid and tin chloride (II) are denoted by -SO and -Sn, respectively. Table 1 summarizes characteristics of the oligomers used in this study.

## 2.2 Preparation of Melt-blended PLA (mb-PLA) and Stereoblock PLA (sb-PLA)

A stoichiometric amount of dried enantiometric PLA oligomers was melt-blended at 190 °C for 2 min with a twin blade mixer and the resultant powdery materials were denoted as mb-PLA. Then they were heated step-wise under 35~48 Pa for SSP; (150 °C, 10 h) → (170 °C, 12 h) → (190 °C, various times). The resultant materials were washed by 5 wt% acetone solution of hydrochloric acid to deactivate the catalyst remained in the samples, furthermore followed by a careful wash by methanol several times. The so-obtained products were denoted as sb-PLA.

## 2.3 Analysis

Glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and crystallinity ( $X_c$ ) of PLA samples were estimated by DSC at a heating rate of 10 °C/min. Crystallinity of homo-chiral (hc) and stereocomplex (sc) crystals were calculated using the theoretical heat of fusion (93.1 J/g and 142 J/g for 100 % hc and sc, respectively).[4,5] X-ray diffraction measurements (XRD) were performed with a Cu( $K_{\alpha}$ ) radiation in the 2θ range between 2 and 40° at a scan speed of 2 °/min at room temperature. The number-average and weight-average molecular weights ( $M_n$  and  $M_w$ , respectively) were estimated by GPC. Average block length ( $v_{av}$ ) of sb-PLA was estimated by 100MHz  $^{13}\text{C}$  NMR spectrometer.

## 3 RESULTS and DISCUSSION

### 3.1 Characteristics of mb-PLA

Table 2 shows combinations of oligomers used for preparation of mb-PLA and their characteristics obtained by the DSC and GPC measurements. The mb-PLA prepared from a combination of PLA oligomers with higher

Table 2: Characteristics of mb-PLA investigated by DSC and GPC.

mb-PLA	Combination of oligomers	Molecular weight			Thermal properties			Crystallinity	
		$M_{w\ av}$ (g/mol)	$M_n$ (g/mol)	$M_w$ (g/mol)	$T_g$ (°C)	$T_m$ (hc) (°C)	$T_m$ (sc) (°C)	$X_c$ (hc) (%)	$X_c$ (sc) (%)
mb-HH-SO	PLLA-H-SO/PDLA-H-SO	$8.4 \times 10^4$	$3.5 \times 10^4$	$6.6 \times 10^4$	57	164	216	1.8	36.0
mb-HL-SO	PLLA-H-SO/PDLA-L-SO	$6.1 \times 10^4$	$1.8 \times 10^4$	$5.0 \times 10^4$	56	161	218	1.9	47.2
mb-HL-SnSO	PLLA-H-SO/PDLA-L-Sn	$6.4 \times 10^4$	$8.8 \times 10^3$	$2.8 \times 10^4$	39	157	219	1.5	47.3
mb-HH-Sn	PLLA-H-Sn/PDLA-H-Sn	$7.6 \times 10^4$	$2.7 \times 10^4$	$5.2 \times 10^4$	43	158	215	0.2	42.6

molecular weight ( $M_w > 50,000$  g/mol) and lower molecular weight ( $M_w < 50,000$  g/mol) is denoted as HL and that of both PLLA and PDLA with  $M_w$  over 50,000 is denoted as HH in this report. In the table, the  $M_n$  and  $M_w$  of the mb-PLA after melt blending are given, in addition to a mean value of  $M_w$  ( $M_{w\ av}$ ) for PLLA and PDLA oligomers before the melt blending.

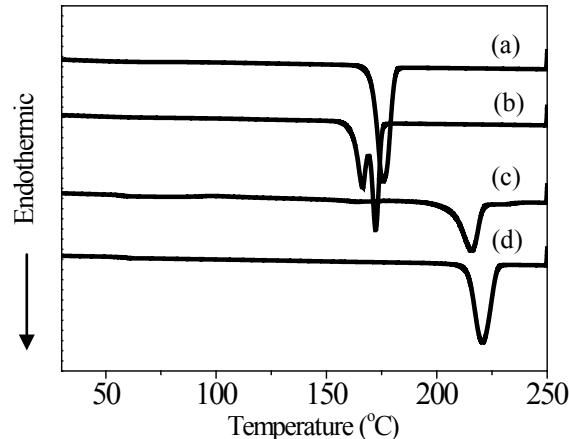


Figure 1: Thermal behavior of (mb and sb)-HH-SO measured by DSC. [(a): PLLA-H-SO; (b): PDLA-H-SO; (c): mb-HH-SO; (d): sb-HH-SO (total polymerization time = 243 h)]

In Figure 1 and Table 2 showing the DSC results, all mb-PLA samples indicated a trace of the  $T_m$  peak originated from hc crystals,  $T_m$  (hc), at ca. 160 °C, which corresponded to 0.2 % ~ 1.9 % of crystallinity. However, a melting peak of sc crystals,  $T_m$  (sc), appeared at ca. 215 °C, which is about 55 °C higher than the former  $T_m$  (hc), and indicated mb-PLA samples formed high crystallinity of sc at 36~47 %. In this regard, mb-HH-SO prepared from the combination of oligomers with higher  $M_w$  showed the lower sc crystallinity among the samples, whereas mb-HL-SnSO prepared from the combination of lower  $M_w$  achieved higher sc crystallinity. This fact indicates that the shorter the oligomer length used for melt-blending is, the easier to form sc crystals.

Furthermore, in this study it was demonstrated that the stereocomplexation easily proceeded under a melt-blending conducted at low rotation speed (3 rpm) for short blending time (2 min) at 190 °C in a mixer, which indicates that neither rigorous mixing nor long mixing time is necessary to form sc. However, although the conditions as mild as possible were employed in the present study, all  $M_w$  of the resultant mb-PLAs significantly decreased upon melt-

blending compared to the averaged  $M_w$  of original PLLA and PDLA oligomers ( $M_{w\text{ av}}$ ). A possible cause of the decrease in  $M_w$  might be both hydrolysis of the ester linkage in the PLA main chain and dissociation of lactide molecules during the melt-blending at high temperature. Especially, the results shown in Table 2 indicated that mb-PLA prepared from PLA oligomers synthesized with Sn catalyst tended to show a larger decrease in  $M_w$  compared to that prepared with SO catalyst. For example, the  $M_w$  of mb-HH-SO, mb-HL-SO, mb-HL-SnSO, and mb-HH-Sn decreased upon melt blending by 21 %, 18 %, 56 %, and 32 %, respectively, compared to the  $M_{w\text{ av}}$ . Thus, the decrease in molecular weight is accelerated, even when one of the PLA oligomers is synthesized with the Sn catalyst so that the PLA oligomers both synthesized with the SO catalyst are preferred for the preparation of mb-PLA.

### 3.2. Thermal Properties of sb-PLA

Next, SSP of the mb-PLA was carried out by step-wise heating under 35~48 Pa, (150 °C, 10 h) → (170 °C, 12 h) → (190 °C, various times), to produce sb-PLA, in which the reaction was conducted under  $T_m$  (sc) preserving the stereocomplex crystals already formed during the preparation of mb-PLA.

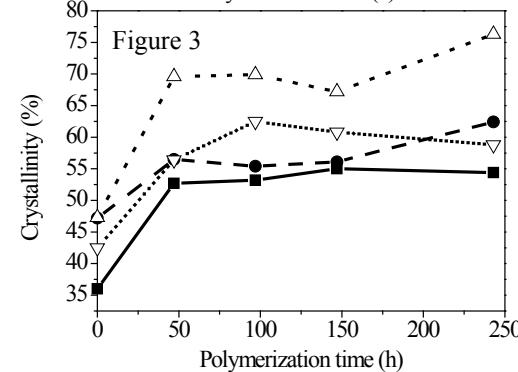
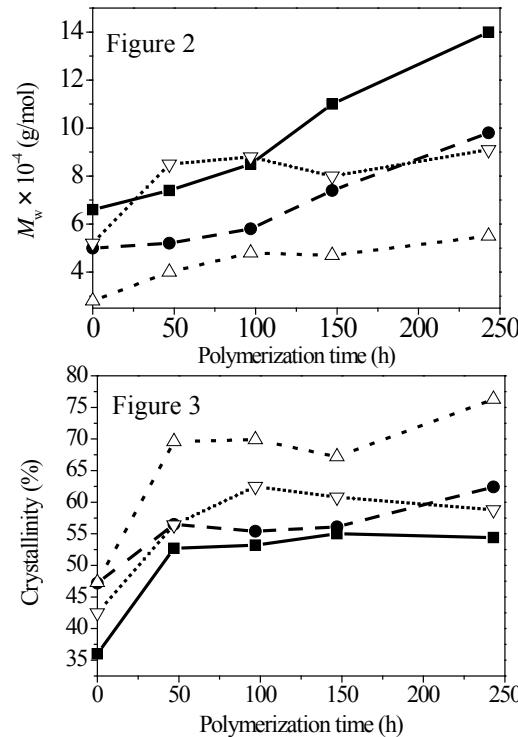
In the DSC measurement of sb-PLA sample (total time of the heat treatment = 243 h) in Figure 1, the  $T_m$  peak of hc crystals disappeared completely, and only the melting peak of sc crystals appeared at 221 °C, which was 5 °C higher than  $T_m$ (sc) of mb-PLA. Moreover, the  $T_m$  peak of sc crystals became larger upon SSP compared to that of mb-PLA. The XRD pattern of the pristine PLLA oligomer also showed a sharp and strong peak appeared at  $2\theta = 17^\circ$  in addition to smaller peaks at  $2\theta = 15, 19$ , and  $22.5^\circ$ , all of which correspond to the hc crystals. On the other hand, for sb- and mb-PLA, only diffraction peaks corresponding to the sc crystals were observed at  $2\theta = 12, 21$ , and  $24^\circ$ .[2]

The molecular weight,  $T_g$  and  $T_m$  of the sb-PLA are summarized with its  $X_c$  value in Table 3. Interestingly,  $T_g$  of the sb-HL-SnSO and sb-HH-Sn containing Sn decreased significantly to ca. 40 °C upon SSP, whereas that of sb-HH-

SO and sb-HL-SO containing only SO remained at as high as 57-59 °C.

### 3.3. Molecular Structure of sb-PLA

Figure 2 shows the relationship between polymerization time and a change in weight average molecular weight of sb-PLA. It is demonstrated that the  $M_w$  of each sample increased with the polymerization time. Here, in Figure 2 sb-HH-SO and sb-HL-SO containing SO (without Sn) shown by the closed symbols efficiently increased the  $M_w$  and achieved higher molecular weight ( $M_w = 140,000$  and 98,000 g/mol, respectively). By contrast, sb-HL-SnSO and sb-HH-Sn containing traditional Sn shown by the open symbols increased the  $M_w$  very slowly. Especially, a change after 47 h of the polymerization time showed imperceptible gradations. The difference caused by catalysts used for the PLA oligomers shall be discussed later again.



Figures 2 and 3: Weight-average molecular weight and sc-crystallinity of sb-PLA versus polymerization time. [■: sb-HH-SO; ●: sb-HL-SO; △: sb-HL-SnSO; ▽: sb-HH-Sn]

Figure 3 illustrates a change in sc crystallinity with an increase in the SSP time. It was demonstrated that the sc crystallinity increased as the polymerization time, which was prominent at the initial stage of polymerization. Amazingly, all samples achieved more than 54 % of sc crystallinity without containing any hc crystals. Here, there was a clear tendency that the lower the  $M_w$  of sb-PLA is, the higher the sc crystallinity. Furthermore, it is noteworthy that sb-HL-SO with  $M_w = 98,000$  g/mol and sb-

Table 3: Thermal properties of sb-PLA (total polymerization time = 243 h) measured by DSC and GPC.

HH-SO with 140,000 g/mol achieved 62 % and 54 % of  $X_c$ (sc), respectively. This difference was caused by exchanging PDLA-H to PDLA-L during a preparation of mb-PLA. Since PDLA-L with  $M_w < 50,000$  has lower viscosity and higher mobility than PDLA-H, it can probably easily align along a template of the other enantiomeric oligomer with  $M_w > 50,000$ , i.e., PLLA-H in this case, via intermolecular interactions.

Furthermore, it is reported that depolymerization to generate dimeric lactide is accompanied by the transesterification as a side reaction during SSP [2], which causes a suppression of the increase in  $M_w$  and a significant decrease in the yield. So, a change of the yield upon SSP in this study is given in Figure 4. Surprisingly, sb-HH-SO and sb-HL-SO containing only SO catalyst maintained a yield of 97.1 ~ 98.6% even after 243 h of polycondensation, whereas sb-HL-SnSO and sb-HH-Sn containing Sn catalyst dramatically decreased their yield to 68.1 ~ 71.5%. This clearly suggests that the SO catalyst inhibits the undesirable side reaction and efficiently increases the molecular weight during SSP. On the other hand, the residual Sn catalyst induces the side reaction from the initial stage of SSP, thereby resulting in the inefficient increase in the molecular weight. Thus, it was demonstrated that the SO catalyst used in a synthesis of sb-PLA for the first time is a more effective catalyst than the conventional the Sn catalyst, which clearly indicates an importance of the catalyst choice.

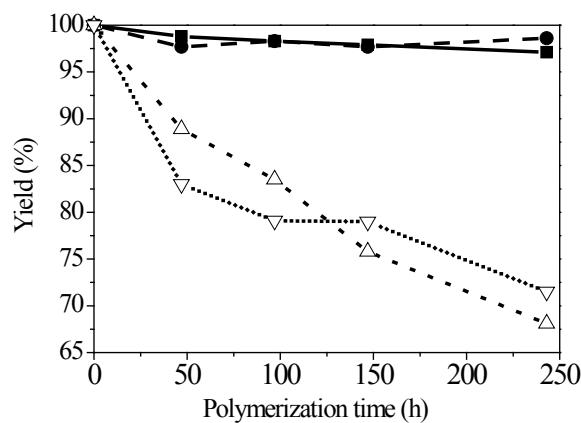


Figure 4: Yield of sb-PLA versus polymerization time [The symbols are the same as those in Figures 2 and 3].

As a next step, the average block length ( $v_{av}$ ) of sb-PLA was estimated by  $^{13}\text{C}$  NMR spectrum and Bernoullian statistics.[2] As discussed previously from the results of yield that in sb-PLA containing the Sn catalyst more significant side reaction occurs upon SSP compared to in sb-PLA containing only the SO catalyst, the phenomenon is reflected as a more significant reduction of the  $v_{av}$  value in the former sb-PLA compared to the latter system.

In the study of Kimura et al., it was also observed that the block length of sb-PLA synthesized in the presence of both  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and TSA catalysts is diminished

dramatically after SSP compared to starting mb-PLA and that the yield was dropped to 43~63 % [3]. Their results strongly support our previous observations that the side reaction is promoted by a residual of the Sn catalyst, resulting in the suppression of enhancement of molecular weight and the significant decrease in yield during the SSP. On the other hand, the SO catalyst hardly promotes the side reaction so that the reduction of the  $v_{av}$  for sb-PLA is much smaller, thereby the yield of sb-PLA is very high and its structure is more ordered.

Moreover, these different effects of the catalyst result in the  $T_g$  descent, which was only observed in sb-PLA containing the Sn catalyst, as shown in Table 3. It was speculated that the dimeric lactide produced by the side reaction might be work as a plasticizer and/or that higher number of the junction between PLLA and PDLA blocks would facilitate molecular mobility of the sb-PLA.

#### 4. CONCLUSIONS

The molecular weight of PLA enantiomeric oligomers used for the SSP affects the sc crystallinity and final molecular weight of sb-PLA, with a shorter oligomer length giving rise to a higher sc crystallinity. Furthermore, the catalyst used for the PLA oligomers in the SSP affects the final structure and yield of sb-PLA. The SO catalyst studied in the present work for the first time is capable of inhibiting the side reaction that generates dimeric lactide and to increase the molecular weight more efficiently during the SSP so that the original block length of L- or D-lactyl is maintained. By contrast, the Sn catalyst commonly used for the PLA synthesis induces a significant side reaction, which reduces the  $T_g$  by ca. 15 °C and decreases the yield of sb-PLA. Thus, the selection of catalyst used for a synthesis of PLA oligomers and the initial molecular weight of the oligomers significantly affects the final molecular weight, sc crystallinity and yield of sb-PLA.

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