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A Novel Synthetic Approach to Stereo-Block Poly(lactic acid)

*Kazuki Fukushima, Yoshiharu Kimura**

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
E-mail: ykimura@kit.ac.jp

Summary: Stereoblock poly(lactic acid) (sb-PLA), consisting of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in a blocky sequence, can successfully be synthesized by solid-state polycondensation of a stereocomplexed mixture of PLLA and PDLA. First, the melt polycondensation of L- and D-lactic acids is conducted to obtain PLLA and PDLA with medium molecular weights. Then, both polymers are melt-blended to easily form the stereocomplex. The resulting stereocomplexed mixture (melt-blend) is subjected to solid-state polycondensation for chain extension. The molecular weight (M_w) of the resultant sb-PLA is strongly affected by the lactide/oligomer content in the melt-blend, which is determined by the melt-blending conditions, because it is directly correlated with the polymer crystallinity of the polycondensation products.

Keywords: block copolymers; melt-blend; solid-state polycondensation; stereo-block poly(lactic acid); stereocomplex

Introduction

The stereocomplex type poly(lactic acid) (sc-PLA), which is formed on mixing poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in a 1:1 ratio, has high potential for improving the heat resistivity of PLLA-based materials, because of its enhanced melting temperature (T_m) of 230 °C.[1] The ordinary melt-blending of PLLA and PDLA, however, produces their single polymer crystals preferentially,[2,3] and the formation of the sc-PLA materials is difficult, particularly with the high molecular weights of PLLA and PDLA.[4,5] One efficient method for obtaining sc-PLA is to use stereoblock poly(lactic acid) (sb-PLA), which consists of relatively short PLLA and PDLA segments in a blocky manner. Because of the neighboring effect of the PLLA and PDLA blocks, it readily forms a stereocomplex in a wide range of processing windows. sb-PLA was first synthesized by Ovitt and Coate[7,8] through stereo selective polymerization of racemic DL-lactide with a stereospecific catalyst.[9] However, the short L- and D-block sequences, as well as the racemic sequences arising in consequence of the rather low stereo selectivity of the catalyst, caused the melting temperature to descend to a level of 187 °C.[1] Therefore, an

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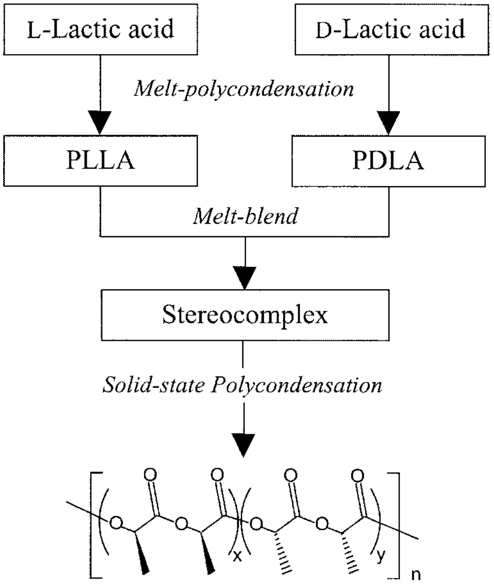
alternative effective method is needed for controlling the block length and crystallinity of sb-PLA.

Here, we report on a novel synthetic method for sb-PLA by application of the direct polycondensation of L- and D-lactic acids (Scheme I), involving both melt- and solid-state polycondensation. In the solid-state polycondensation, polymer crystallization accompanied by the stereocomplex formation is important to obtain a sb-PLA with a high molecular weight.[10, 11] The sb-PLA products synthesized in this way show a higher melting temperature in consequence of the controlled block lengths and the resulting higher molecular weight.



Stereoblock Poly(lactic acid)

Scheme 1. Synthesis of sb-PLA by melt/solid-state polycondensation.

Experimental

Materials. L-Lactic acid (99.3 %ee) was purchased from Wako Pure Chemical Industries, Ltd. (Tokyo), as a 90 wt% aqueous solution. D-Lactic acid (99.1 %ee) was supplied by Musashino Chemical Laboratory, Ltd (Tokyo), as a 90 wt% aqueous solution. Stannous dichloride dihydrate ($SnCl_2{\cdot}2H_2O$) and p-toluenesulfonic acid monohydrate (TSA) were purchased from Nacalai Tesque Co. (Kyoto). All these materials were used without further purification.

Measurements. 500 MHz ^{1}H- and 125 MHz ^{13}C- NMR spectra were measured on a Bruker ARX spectrometer in deuterated chloroform ($CDCl_3$) containing 10 vol% of 1,1,1,3,3,3,-hexafluoro-2-propanol (HFIP) with tetramethylsilane (TMS) as the internal reference.

The molecular weights (M_n and M_w) and the dispersity (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Shimadzu analyzer system consisting of a LC-10ADvp pump, a RID-10A refractive index detector, and a C-R7A Chromatopac data processor. A styrene-divinylbenzene copolymer gel column of Shodex HFIP-806 (8.0 mm I.D × 300 mm) was used, and HFIP containing 1 mol% sodium trifluoroacetate was used as the solvent at 40 °C. The molecular weight was calibrated according to poly(methyl methacrylate) (PMMA) standards.

The thermal properties of polymeric products were determined by differential scanning calorimetry (DSC) on a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 $ml \cdot min^{-1}$ and at a heating rate of 10 $°C \cdot min^{-1}$. The crystallinities of the single PLLA and sc-PLA were estimated from the melting endotherms, with reference to their theoretical heats of fusion: 93.0 Joule/g for PLLA and 142.0 Joule/g for sc-PLA.[14, 15]

Melt/solid-state polycondensation. Firstly, oligo(L-lactic acid) (OLLA) and oligo(D-lactic acid) (ODLA) were prepared by dehydration of 90 wt% aqueous solutions of L- and D-lactic acids, respectively.[10-12] The degree of polymerization (DP) of both oligomers obtained was about 8, corresponding to 570 Da in M_n. Secondly, each OLLA and ODLA was melt-polycondensed with 0.1 wt% of $SnCl_2 \cdot 2H_2O$ and TSA at 180 °C and 10 Torr for 3 h[11]. At the end of the reaction, PLLA and PDLA with medium molecular weights were obtained as a white solid.

The PLLA and PDLA thus prepared were pulverized, mixed in a flask at a 1:1 weight ratio, and thoroughly dried at room temperature for 2 h and at 110 °C for another 2 h in vacuum. The mixture was then heated to different temperatures, ranging from 170 to 250 °C under a nitrogen atmosphere, mechanically stirred for 10–20 min for blending, and then cooled. The melt-blending was also conducted by use of an ordinary single screw extruder (15 mmϕ) at different temperatures.

Each of the melt-blends obtained was again crushed into granules, and the resulting granules were placed into several test tubes. Then, each tube was heated according to different temperature programs at a reduced pressure of 0.5 Torr for 10–30 h. The temperature programs were selected so as for the polycondensates to keep their solid state; 1) by maintaining a constant temperature in a range from 140 to 200 °C and 2) by increasing the temperature stepwise from 140 to 190 °C at a rate of 10 °C per 5 h. The as-formed products were subjected to various analyses.

Results and Discussion

Synthesis of sb-PLA. Table 1 summarizes the typical results of the melt polycondensation of PLLA and PDLA, and the following solid-state co-polycondensation of sb-PLA conducted at different temperatures (with the constant temperature program).

Table 1. Typical results of stereo-block copolymerization.

Code	Processing Temperature. (°C)	Polymer Recovery (%)	M_w[a]	M_w/M_n[a]	T_g[b] (°C)	T_m[b] (°C)	X_c[b] (%)	ν
PLLA	180[c]	85	20,100	2.0	49	154	64	51[f]
PDLA	180[c]	92	22,200	2.0	50	154	62	28[f]
MB	200[d]	94	27,800	1.8	–	213	56	35[g]
SB1	140[e]	90	36,900	1.7	58	216	63	42[g]
SB2	160[e]	78	41,500	1.8	62	218	70	24[g]
SB3	180[e]	60	68,700	1.7	64	217	74	24[g]
SB4	200[e]	43	102,000	1.8	61	215	59	24[g]

[a] Determined by GPC relative to PMMA standards with HFIP as the eluent.
[b] Measured by DSC (heating rate; 10 °C/min).
[c] Melt-polycondensation temperature.
[d] Melt-blend temperature.
[e] Solid-state polycondensation temperature.
[f] Calculated based on optical purity.
[g] Determined by ^{13}C NMR. The theoretical value calculated from the Bernoullian statistics is 36.

The T_m values of the melt-polycondensate PLLA and PDLA are lower than generally reported (170–180 °C) because of their lower degree of polymerization. The M_w of the melt-blend (MB) becomes slightly higher than that of the starting PLLA or PDLA, probably because of the small change in hydrodynamic volume of the PLLA and PDLA mixture as compared with the single polymers. On the other hand, the dispersity (M_w/M_n) of the melt-blend became slightly lower than that of the starting PLLA or PDLA. It is therefore deduced that little polycondensation occurred in the polymers during the melt-blending. In the solid-state polycondensation of the melt-blend, the M_w of the products (SB1-4) increases with increasing reaction temperature, while their dispersity (M_w/M_n) is not as greatly changed, in spite of the heterogeneous reaction system. The polymer recovery, on the other hand, decreases with the reaction temperature, and at 200 °C (SB4) the final polymer yield is only 43 %. Figure 1 compares the time-courses of the M_w of the products in solid-state polycondensation with different temperature programs. When the reaction temperature is constant above 180 °C, the growth rate of M_w is relatively fast at the initial stage, exceeding 50,000 Da, although it levels off over 20 h. At 200 °C the M_w reaches 100,000 Da. With the stepwise temperature increase, in return, the M_w increase is quite limited (plotted with Δ in Figure 1) even though the temperature is raised up to 200 °C. This fact suggests that the reaction temperature should be higher than the T_m of the single polymers from the beginning of the solid-state polycondensation for significant increase of the M_w of sb-PLA.

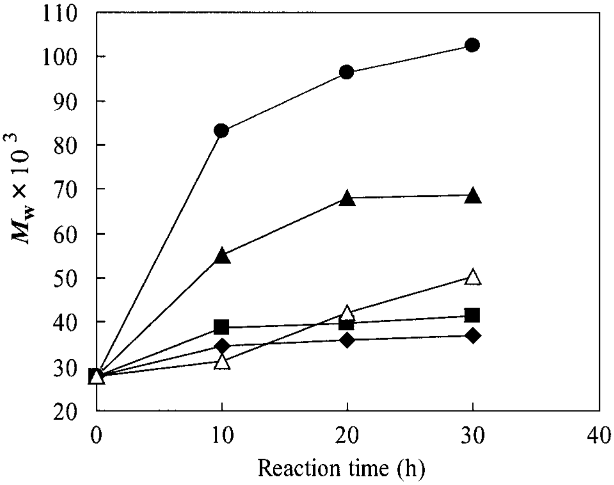


Figure 1. M_w changes in the solid-state polycondensation at 140 °C (◆), 160 °C (■), 180 °C (▲), and 200 °C (●), as compared with the case of the stepwise temperature increase from 140 to 190 °C at an increasing rate of 10 °C per 5 h (△).

Figure 2 shows the DSC curves of the final product (SB4) of the solid-state polycondensation and its precursor polymers (PLLA and MB). It is known that the former product has no single polymer crystals that have been retained in the melt-blend. The larger endothermic peaks shown for MB and SB4 are attributed to their larger heat of fusion

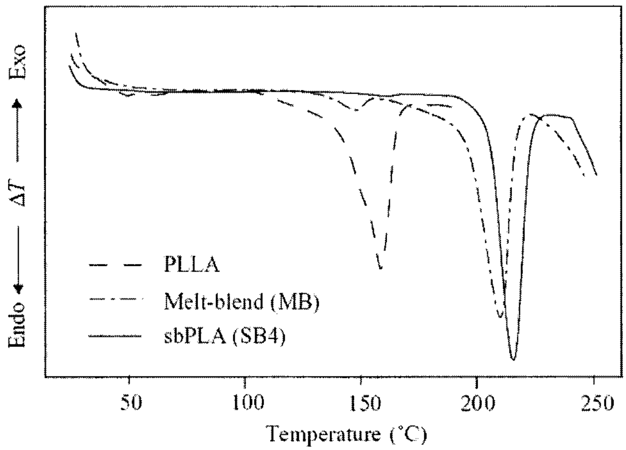


Figure 2. Comparison of DSC curves of the products at different reaction stages.

(142.0 Joule/g) than that of the PLLA single polymer (93.0 Joule/g). Figure 3 shows a typical ^{13}C-NMR spectrum of sb-PLA (SB4) in the carbonyl region and their peak assignments. The appearance of the *meso* (*m*)-rich sequences (peak **a**) and the absence of consecutive *r* sequences (e.g. *rr*, *rrr*, etc.) are indicative of the blocky nature, while the small peaks **a'** and **b** support the presence of the units connecting the enatiomeric block sequences. Based on this NMR analysis, the average block lengths (ν) can be calculated according to Bernoullian statistics, as shown in the last column of Table 1. The ν value of the melt-blend is almost identical with the arithmetic average of ν values of the original PLLA and PDLA and the theoretical value that is estimated by Bernoullian statistics, probably because little chain scrambling reaction may have occurred during the melt-blending. Furthermore, the ν value of the products of the solid-state polycondensation decreases with increasing reaction temperature, being inversely proportional to its M_w, X_c, and T_m. The longer reaction time and the higher reaction temperature likely cause an ester-interchange reaction with the shortening of the block length.

Mechanism of the solid-state polycondensation of sb-PLA. In general solid-state polycondensation, the dehydrative reaction is enhanced with an increase in the polymer crystallinity, because the polymer tails and catalysts are concentrated in the amorphous domain. When the solid-state polycondensation of the melt-blend of PLLA and PDLA is conducted at temperatures higher than the T_m of PLLA or PDLA, only the stereocomplex

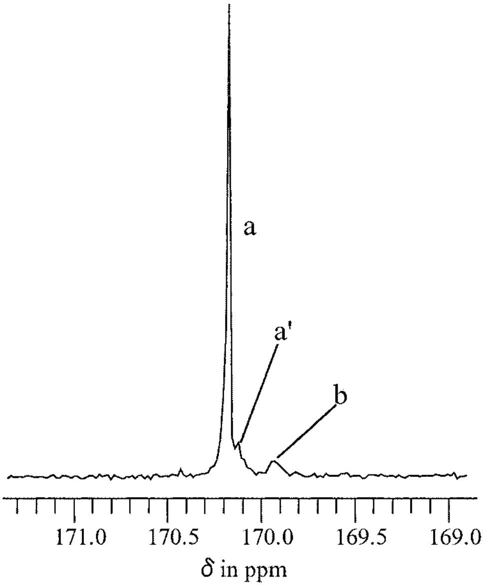


Figure 3. A typical ^{13}C NMR spectrum of the carbonyl region of sb-PLA (SB4) (125 MHz in $CDCl_3$ involving 10 % HFIP). C=O hexads: **a** (*mmmmm*, *rmmmm*, *mmmmr*) = 170.17; **a'** (*rmmmr*) = 170.11; **b** (*mmmrm, mrmmm, mmrmr, mmrmm, rmrmm, rmrmr, mrmrm*) = 169.92; (in ppm from TMS).

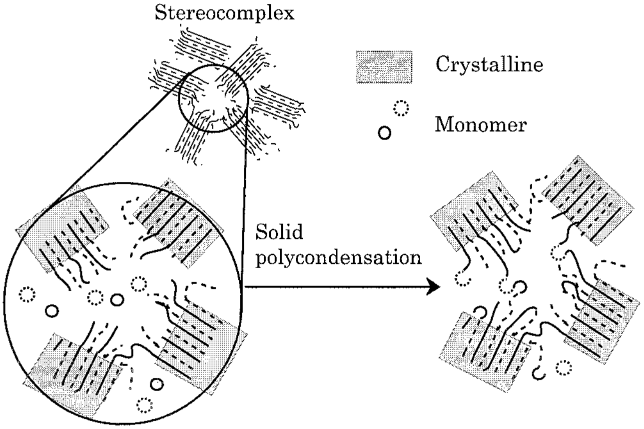


Figure 4. Schematic diagram for the solid-state structure of the solid-polycondensates.

crystals can grow without formation of the single-polymer crystals, allowing the molecular weight increase of sb-PLA. In this case, however, chain-elongation and transesterification among the hetero-sequences also happened to induce the unit-scrambling of the polymer chains to retard the polymer crystallizability. Also, D- and L-lactides are formed by the ring-chain equilibrium with the PLLA and PDLA macromolecular chains in the reaction system, and their re-polymerization, occurring randomly, produces random sequences (Figure 4). The randomized chains thus formed can never crystallize and are likely to stay in the amorphous domain, hindering propagation. They are, instead, involved in repeated transesterification until they are finally converted into lactides by depolymerization and removed from the reaction system by evaporation, with the increase in crystallinity. The decreased polymer recovery and increased crystallinity observed at the higher reaction temperatures (Table 1) can be explained by this mechanism. The exceptionally decreased crystallinity in SB4 prepared at 200 °C may be caused by the decreased size of the crystals, as revealed by the low-temperature shift of the melting endotherm, which is also apparent at high temperatures close to the T_m of the stereocomplex. In this context, the lactide/oligomer contents in the starting melt-blends should affect the racemization of polymer chains and the following transesterification in the solid polycondensate.

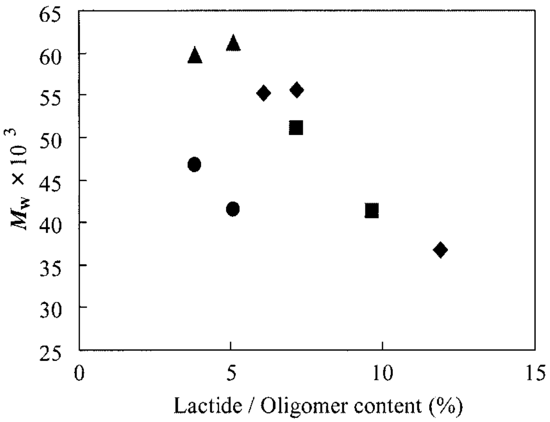


Figure 5. Correlation of the lactide/oligomer content in the melt-blend and the M_w of the solid-polycondensates prepared at different reaction temperatures for 30 h: 150 °C (■), 160 °C (●), 170 °C (◆), and 180 °C (▲).

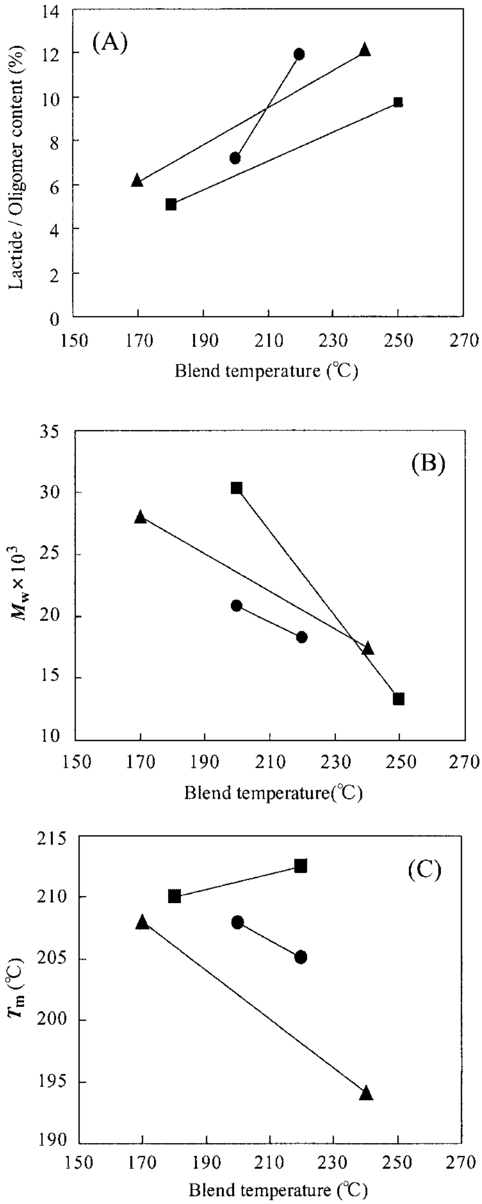


Figure 6. Effects of the blend temperature on (A) the lactide/oligomer content, (B) M_w, and (C) T_m of the melt-blend: for the blending times of 10 min (■) and 20 min (▲) and for melt blending with an extruder (●).

Effect of the melt-blending conditions. To ensure the above mechanism, the initial contents of lactides and oligomers in the melt-blends were determined by ^{1}H NMR spectroscopy,[13] and their effects on the following solid-state polycondensation were studied in detail. Figure 5 shows the correlation between the M_w of the sb-PLA formed by the solid-state polycondensation and the lactide/oligomer contents in the melt-blends. Although the data for the reaction temperature of 160 °C deviate somewhat from the others, there is a clear tendency for the molecular weight of the resultant sb-PLA to increase as the lactide/oligomer content in the melt-blend becomes lower. The initial lactide/oligomer content of MB (Table 1) was found to be 5.1 %. Therefore, the lactide/oligomer content should be greatly decreased to further increase the M_w of the sb-PLA.

Figure 6 shows the effects of the blending temperature on the lactide/oligomer content (A), M_w (B), and T_m (C) of the resultant melt-blends. It is known that the lactide/oligomer content becomes lower with decreases in blending temperature and time, regardless of the mixing tools (either extruding or batch stirring). The blending temperatures have a more striking effect on the M_w of the melt-blend, in particular dropping sharply above 210 °C, where thermal depolymerization of PLA is remarkable. The T_m of the melt-blends also shows a decreasing tendency with the blending temperature and time. Consequently, when melt blending is conducted at a high temperature for a long time, not only depolymerization, but also unit-scrambling, are induced to bring an increase of the lactide/oligomer content and a decrease of the T_m of the melt-blend. Therefore, the melt-blending of PLLA and PDLA should be done at temperatures as low as possible.

Conclusion

A high molecular weight sb-PLA was synthesized by solid-state polycondensation of the melt-blend of medium-molecular-weight PLLA and PDLA, which were both obtained by melt polycondensation of L- and D-lactic acids, respectively. The M_w of the sb-PLA increased with increasing reaction temperature and reaction time. The highest M_w of sb-PLA reached 100,000 Da, when solid-state polycondensation was conducted at 200 °C for 30 h. The M_w of sb-PLA was found to be influenced by the initial lactide/oligomer content in the melt-blend. These data revealed that, for obtaining a higher molecular weight of sb-PLA, the melt-blending temperature and time should be decreased so as to reduce the transesterification and depolymerization of the stereocomplexed mixture.

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