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Synthesis and Characterization of Stereoblock Poly(lactic acid)s with Nonequivalent D/L Sequence Ratios

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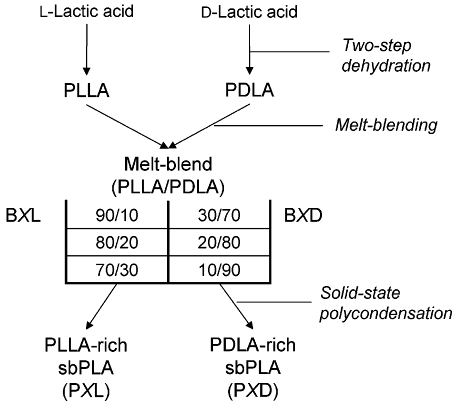
ABSTRACT: Stereoblock poly(lactic acid)s (sb-PLA) consisting of different ratios of D- and L-sequences were synthesized by a process involving solid-state polycondensation (SSP) of polymer blends of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) of medium molecular weight. Both PLLA and PDLA prepolymers were first prepared by direct melt-polycondensation of L- and D-lactic acids, respectively. These prepolymers were melt-blended in different ratios where their respective partial stereocomplexation could aid in the crystallization of the rich polymer. The melt-blends were then subjected to SSP at a temperature of 140−160 °C, which was lower than the melting temperature of the homochiral polymers. The resultant polymers consisted of longer block chains of the rich components and had molecular weights of higher than 100 kDa when either the PLLA or PDLA ratio in the feed was larger.

Introduction

Poly(L-lactic acid) (PLLA) has recently been drawing much attention as a bio-based polymer that can be derived from renewable natural resources. PLLA is a melt-processable, crystalline polymer, and its fibers and films show mechanical properties comparable to those of polystyrene and polypropylene.[1,2] The application of PLLA, however, has been rather limited until now because of its relatively poor injection moldability and low thermal stability as compared with the ordinary oil-based plastics commonly used. In fact, the highest service temperature of PLLA is lower than 120 °C for the highly crystallized products and even lower than 60 °C for the amorphous glassy products, although the melting temperature (T_m) of PLLA reaches 170−180 °C.[3] On the other hand, an equivalent mixture of PLLA and its enantiomer poly(D-lactic acid) (PDLA) is able to form a stereocomplex whose crystal structure is different from that of PLLA.[4] This stereocomplex-type poly(lactic acid) (sc-PLA) shows its T_m at 230 °C, which is 50 °C higher than that of PLLA or PDLA and thus should accordingly have higher mechanical properties than PLLA.[5] While PLLA has been utilized mainly for short-life purposes such as disposable dishes and agricultural mulching films in which the biodegradability is important,[6] sc-PLA can be used as high-performance materials with long lives such as structural materials and engineering plastics.[7] However, with high-molecular-weight polymers of PLLA and PDLA, the stereocomplex formation (stereocrystal formation) is frequently followed by the microphase separation of PLLA and PDLA and their simultaneous homochiral crystallization.[8] To improve the miscibility of PLLA and PDLA, several mixing processes and molding techniques have been investigated.[9,10] Use of block copolymers of PLLA and PDLA, i.e., stereoblock poly(lactic acid)s (sb-PLA), is also an efficient method for improving their miscibility due to the bonding of the D- and L-stereosequences which allows the stereocomplex formation much easier by the proximity effect.[11]

Scheme 1. Synthetic Procedure of Sb-PLA Comprising Nonequivalent D/L Sequence Ratios



It is known that sb-PLA can be prepared by the stereoselective ring-opening polymerization of *rac*-lactide using a chiral catalyst. This method may particularly be beneficial due to the efficient utilization of the inexpensive racemic monomer.[12−17] However, using direct polycondensation involving both melt-polycondensation (MPC) of lactic acid and solid-state post-polycondensation (SSP), we have recently demonstrated a completely different method in synthesizing sb-PLA. In this method, PLLA and PDLA having medium molecular weights were first prepared by MPC of L- and D-lactic acids, respectively, and both the resultant PLLA and PDLA were melt-blended to form the stereocomplex and subjected to SSP at temperatures higher than the T_m of PLLA or PDLA.[18,19] The polymer that was finally obtained was sb-PLA having a molecular weight of ca. 100 kDa. This increase of the molecular weight, however, was considerably less when compared to that observed in SSP of PLLA or PDLA single polymer system, which was even conducted at much lower temperature than the former. This fact may be because the elongated chains formed by the transesterification and the chain coupling among the heterochiral sequences increases the partial chain racemization and can hardly crystallize out of the amorphous domain in the solid state. Consequently, the presence of homopolymer domains is required for enhancing the crystallization of the elongated chains. For

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Table 1. Characteristics of PLLA and PDLA Prepared by MPC of OLLA and ODLA

code	recovery[a] (%)	M_n[b] (10^4)	M_w[b] (10^4)	M_w/M_n[b]	T_m[c] (°C)	ΔH_m[c] (%)	L/D[d] (%)
L1[e]	94	1.0	2.0	2.0	154	59	99.0/1.0
L2[f]	89	2.3	4.2	1.8	152	48	97.8/2.2
D1[e]	91	1.1	2.2	2.0	154	57	1.8/98.2
D2[f]	88	2.2	4.0	1.8	154	56	2.0/98.0

[a] Polymer recovery from the oligomer used (50 g). [b] Determined by GPC relative to PMMA standards with HFIP as eluent (40 °C). [c] Measured by DSC (heating rate: 20 °C/min). [d] Determined by the chiral-HPLC. [e] Obtained by MPC for 3 h. [f] Obtained by MPC for 5 h.

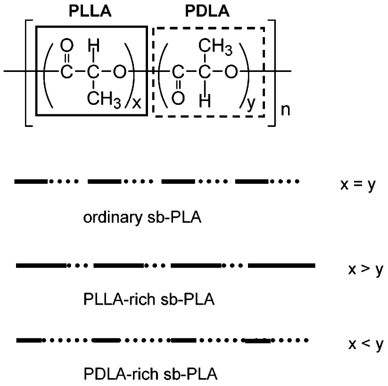

Figure 1. Various patterns of stereoblock poly(lactic acid)s.

synthesizing sb-PLA with higher molecular weight, therefore, the PLLA/PDLA mixed reactant subjected to SSP should comprise both the stereo- and homochiral crystals. On the basis of this concept, we tried to conduct SSP for the nonequivalent mixtures of PLLA and PDLA, as represented in Scheme 1.

Experimental Part

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 ($SnCl_2$) and *p*-toluenesulfonic acid monohydrate (TSA) were obtained from Nacalai Tesque Co. (Kyoto). 1,1,1,3,3,3-Hexafluoroisopropanol (HFIP) was received from Central Glass Co. Ltd. (Yamaguchi). All chemicals were used without further purification.

General Procedure of Melt-Polycondensation (MPC).[20−22] An aqueous solution of L- or D-lactic acid (235 g) was charged into a 500 mL three-necked separable flask equipped with a mechanical stirrer and a water-circulated Liebig condenser installed with a 100 mL receiver flask for collecting distilled water. The solution was heated up to 150 °C under mechanical stirring, and the water present in the system was removed with the inner pressure reduced slowly to 30 Torr over 2 h. After the inner pressure had reached 30 Torr, the heating and dehydration were continued for a further 6 h to obtain a transparent viscous melt of oligo(L-lactic acid) (OLLA) or oligo(D-lactic acid) (ODLA). The finally obtained OLLA or ODLA had an average degree of polymerization (DP) of 8 (168 g, recovery 71.5%).

Subsequently, each OLLA and ODLA (50 g) was mixed with the binary catalysts[21] $SnCl_2$ (0.05 g) and TSA (0.05 g) in a 200 mL three-necked separable flask equipped with a mechanical stirrer and a reflux condenser covered with a ribbon heater by which the lactide monomer formed was refluxed back into the flask effectively. Each mixture was then heated at 180 °C while being stirred under a reduced pressure of 10 Torr for 3−5 h to carry out MPC. The PLLA and PDLA obtained by this MPC had a medium molecular weight. The binary catalysts could effectively catalyze the MPC by preventing the discoloration of the polymer.[22] The colorless product finally obtained was then annealed for crystallization at 120 °C under a nitrogen atmosphere for 3 h, pulverized with an electric mill (Wonder Blender WB-1, Osaka Chemical), and dried in vacuo at room temperature for 2 h.

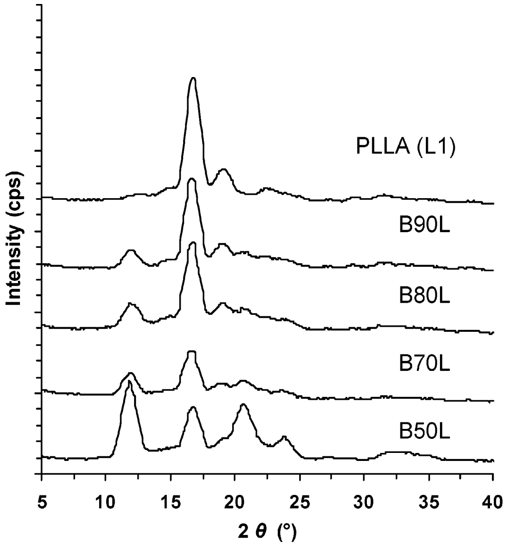

Figure 2. WAXD curves of the melt-blends B*X*L having different PLLA/PDLA ratios.

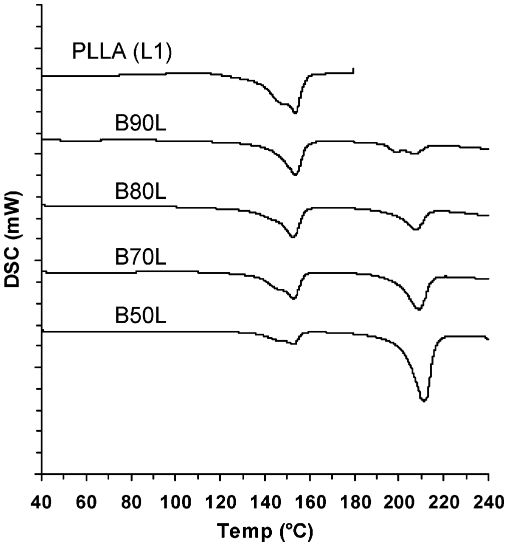

Figure 3. DSC thermograms of the melt-blends B*X*L having different PLLA/PDLA ratios (heating rate: 20 °C/min).

General Procedure of Solid-State Polycondensation (SSP). The PLLA and PDLA powders prepared above were mixed in a predetermined weight ratio, charged in a three-necked separable flask, and dried in vacuo at 110 °C for 2 h. Then the mixture was heated up to 175 °C while being mechanically stirred in a nitrogen atmosphere. The mixture was blended well after this had been continued for 10 min. The melt-blend obtained was cooled down to room temperature and then pulverized with an electric mill. A portion of the pulverized melt-blend (1.0 g) was subsequently charged into a test tube and subjected to SSP with the predetermined conditions. Two heating processes were employed; in process A the reaction temperature was kept at 140 °C for 30 h at 0.5 Torr, while in process B the temperature was raised at 10 °C increments from 140 to 160 °C every 10 h at 0.5 Torr. The produced polymer was analyzed without purification.

Measurements. 500 MHz ^1H NMR and 125 MHz ^{13}C NMR spectra were recorded on a Bruker ARX spectrometer in $CDCl_3$ containing 5 vol % 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). Gel permeation chromatography (GPC) was carried out using a Shodex HFIP-806 styrene−divinylbenzene copolymer gel column (8.0 mm diameter, 300 mm long) on a Shimadzu analyzer system consisting

Table 2. Preparation and Properties of Melt-blends of L1 and D1 at Different PLLA/PDLA Ratios

code	recovery (%)	M_n[a] (10^4)	M_w[a] (10^4)	M_w/M_n[a]	T_m^h [b,c] (°C)	T_m^s [b,c] (°C)	ΔH_m^h [b,d] (J/g)	ΔH_m^s [b,d] (J/g)	$\Delta H_m^h/\Delta H_m^s$
B90L	95	1.1	2.2	2.0	154	207	41	12	3.4
B80L	94	1.8	2.9	1.6	153	208	39	20	2.0
B70L	94	1.7	3.0	1.7	153	209	36	35	1.0
B50L	92	1.2	2.2	1.9	153	211	17	65	0.3

[a] Determined by GPC relative to PMMA standards with HFIP as the eluent (40 °C). [b] Measured by DSC (heating rate: 20 °C/min). [c] T_m^h and T_m^s are melting temperatures of the hc and sc crystals, respectively. [d] ΔH_m^h and ΔH_m^s represent the heat of fusion of the hc and sc crystals, respectively.

of a LC-10ADvp pump, a RID-10A refractive index detector, and a C-R7A Chromatopac data processor. HFIP containing 1 mM sodium trifluoroacetate was eluted at a flow rate of 0.6 mL/min at 40 °C. The molecular weight was calibrated with poly(methyl methacrylate) (PMMA) standards. Differential scanning calorimetry (DSC) was performed with a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 mL/min at a heating rate of 20 °C/min. Wide-angle X-ray diffraction (WAXD) was recorded on a Rigaku RINT-2100 FSL system using nickel-filtered Cu Kα radiation with a wavelength of 0.1542 nm in a 2θ range of 5−40° at a scan rate of 2°/min with a Rigaku RINT 2000 X-ray generator operated at 40 kV and 30 mA. The optical isomer ratios of the polymer products were determined by high-performance liquid chromatography using a chiral separation column (chiral-HPLC).[23] The analysis was conducted in 1.0 mM $CuSO_4$ aqueous solution at 40 °C on a Shimadzu HPLC system connected to a LC-10ADvp pump, a SPD-10Avp UV−vis detector (254 nm), and SUMICHIRAL OA-5000 silica gel column (4.6 mm diameter, 150 mm long). A sample polymer was hydrolyzed in a 1 N aqueous NaOH solution at room temperature. The resultant solution was then neutralized with 1 N aqueous H_2SO_4 solution and diluted with the eluent for injection.

Results and Discussion

PLLA and PDLA with Medium Molecular Weights. Table 1 summarizes the synthesis of the PLLA and PDLA prepolymers by the direct polycondensation involving the noncatalytic dehydration of L- and D-lactic acids to OLA and the following MPC of the OLA by the catalysis of the binary catalysts ($SnCl_2$/TSA). Prepolymers L1 and D1 were obtained after 3 h of MPC, while prepolymers L2 and D2 were obtained after 5 h of MPC. The molecular weights of L2 and D2 were higher than those of L1 and D1, although the polymer recoveries and optical purities were lower in L2 and D2 than in L1 and D1. These data are comparable with the previous findings on the MPC of L-lactic acid; a greater molecular weight can be attained with longer reaction time, higher temperature, and at a higher ratio of the catalysts, and the polymer recovery and optical purity become slightly lower with longer reaction time.[24] We could therefore control the molecular weight of the PLLA and PDLA prepolymers to the medium levels (20−40 kDa in M_w) by adjusting the reaction conditions. The melting temperature (T_m) of each of these prepolymers was considerably lower than that of the ordinary PLLA or PDLA because of their low DP. Since these prepolymers showed no glass transition behavior in their DSC, they ought to have been highly crystalline.

Melt-Blends of PLLA/PDLA. The PLLA and PDLA prepolymers having similar molecular weights were combined and melt-blended under mechanical stirring at around 170 °C with different blend ratios: PLLA/PDLA = 90/10, 80/20, 70/30, and 50/50. The blending temperature was set as low as possible because the lactate polymers involving the catalysts were likely to depolymerize into lactides above their T_m.[25] Table 2 summarizes the results of melt-blending at different PLLA/PDLA ratios. The melt-blends resulting from the combination of L1/D1 are denoted by the code numbers of B*XY*, where B refers to melt-blending sample, *X* shows the percent content (in wt %) of the *Y* component, and *Y* is L or D depending on whether PLLA or PDLA is the major component. It is known that the recovery of the melt-blend is very high at each PLLA/PDLA ratio because of the suppression of thermal decomposition of polymers as well as the suppression of the following sublimation of lactide during the melt-blending that was conducted under mild conditions.

Figure 2 shows the WAXD curves of the melt-blends obtained. The diffraction peaks observed at 12°, 21°, and 24° in 2θ are assigned to the stereocomplex (sc) crystals, while the peaks at 16.5° and 19° correspond to the homochiral (hc) crystals of PLLA and PDLA.[4,26,27] All the samples show both diffractions of hc and sc crystals; even B90L, having a low PDLA, contains sc crystals while B50L, having an equal amount of PLLA and PDLA, contains hc crystals, indicating that the mixing state of PLLA and PDLA was not complete. It is, however, revealed that the sc to hc crystal ratio increased as the PLLA/PDLA ratio approached 1:1.

Figure 3 shows the DSC curves of these melt-blends. Each curve shows two endothermic peaks around 160 and 210 °C, corresponding to the fusions of hc and sc crystals, respectively. The bimodal nature observed in some of the melting peaks can be attributed to the imperfect crystals that should be involved in the melting/recrystallization process in the heating scan. With the PLLA/PDLA ratio approaching 1:1, the endothermic peak due to hc crystals becomes smaller and that of sc crystals becomes larger. Table 2 summarizes the heat of fusion (ΔH_m) for both the hc and sc crystals of the samples as well as their T_m. The T_m of hc crystals is similar to each other in all the samples, whereas the T_m of sc crystals becomes lower with a decrease in PLLA/PDLA ratio. B90L involving rich PLLA shows the lowest T_m of sc crystals because the higher hc crystallinity interferes with the stereocomplexation of PDLA and PLLA. The relative ratio ($\Delta H_m^h/\Delta H_m^s$) of the heat of fusion of hc (ΔH_m^h) and sc (ΔH_m^s) crystals decreases with an increase in PDLA composition in relation to the crystal composition of the melt-blends.

Solid-State Polycondensation of the Melt-Blends. SSP of the melt-blends obtained above was conducted as previously reported.[22] Since the melt-blends exhibited no further crystallization behavior in their DSC, they ought to have sufficiently crystallized while cooled after the melt-blending. In addition, the binary catalysts ($SnCl_2$/TSA) used for the MPC were preserved in an active state in the melt-blends. Therefore, each of the melt-blends was directly subjected to SSP without annealing. This protocol is different from that used for the homopolymerization of PLLA.[22]

1. Effect of Reaction Process. SSP was conducted by using two heating processes: process A, employing a constant temperature of 140 °C, and process B, which employs a 10 °C incremental increase in temperature from 140 to 160 °C with an increase occurring 10 °C every 10 h. In both processes the starting temperature was set at 140 °C, which was slightly below the onset temperature of melting of the hc crystals involved in the melt-blends (Figure 3). Because in SSP the crystallinity and T_m of the reactant polymer become higher with the reaction time, the solid state can be maintained even with the gradual

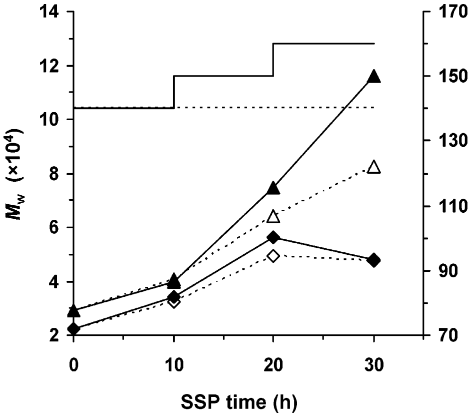

Figure 4. Time courses of molecular weights of $P80L_A$ (open triangles), $P80L_B$ (filled triangles), $P50L_A$ (open lozenges), and $P50L_B$ (filled lozenges) in the SSP of B80L and B50L. The upper dotted and solid lines without symbols indicate the temperature profiles of processes A and B, respectively.

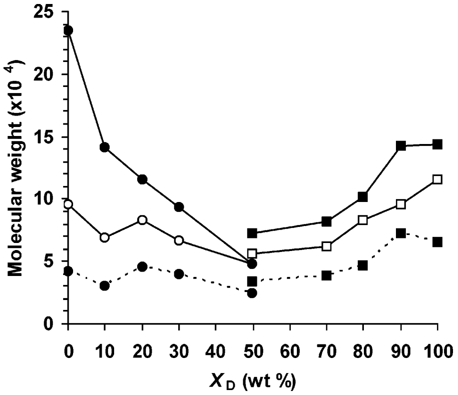

Figure 5. Effect of the PDLA composition (X_D) in the polymers on the molecular weights of the final SSP products prepared by process A (open symbols) and process B (filled symbols). The solid lines show the M_w changes, and the dotted lines represent the M_n changes. The PLLA-rich part ($0 \geq X_D \geq 50$) and PDLA-rich ($50 \geq X_D \geq 100$) systems were separately examined with different melt-blends.

increase in reaction temperature in Process B. Figure 4 shows typical changes in weight-average molecular weight (M_w) in the SSP as a function of reaction time for two Processes using B50L and B80L as the starting melt-blends. The upper lines without symbols show the temperature profiles of both processes. The polymers produced by the SSP are denoted as PXY_Z, where P refers to the SSP product, X shows the percent content (in wt %) of the Y component, and Y is L or D depending on which of PLLA or PDLA is the major component of the polymer, corresponding to the abbreviation BXY for the melt-blend. The subscript Z is shown by either A or B depending on the difference in the process, i.e., process A or B.

It is shown that the M_w of the SSP product becomes higher in process B than it does in process A, starting from the same melt-blends. With B80L, for example, the difference in M_w between $P80L_B$ and $P80L_A$ becomes higher with increases in reaction time and temperature. After 30 h of SSP the M_w reaches 130 kDa for $P80L_B$. On the other hand, the M_w difference between $P50L_B$ and $P50L_A$ is not so large even when the reaction time is increased. Their M_w reaches its maximum at 20 h and then decreases. This M_w decrease in the later stage of SSP was also observed in the former study.[18] It is therefore supported again that the SSP of B50L having PLLA/PDLA = 1/1 should be conducted at a high temperature of 200 °C to attain M_w higher than 100 kDa.[19] The time-dependent increases in M_w for both $P80L_A$ and $P80L_B$ suggest that the chain extension is effectively promoted with the rich ratio of PLLA or PDLA. In addition, process B is more effective than process A.

2. Effect of PLLA/PDLA Composition. Figure 5 shows the changes in the final M_w of the final SSP products obtained after the SSP for 30 h using both processes as a function of the PDLA content (X_D) in the initial melt-blends. It is clearly shown again that the M_w becomes higher in process B examined at every X_D than it does in process A. In both processes, the M_w becomes higher with X_D inclining to 0 or 100, i.e., having richer ratio of PLLA or PDLA. In the extreme cases where $X_D = 0$ and 100 for process B, the M_w of the produced PLLA and PDLA homoplymers reached 240 and 160 kDa, respectively. At $X_D =$ 10 and 90 and even at $X_D = 20$ and 80, the M_w surpasses 100 kDa, while that obtained at $30 \geq X_D \geq 70$ is much lower. In the previous SSP with a melt-blend consisting of PLLA and PDLA in a 1:1 ratio,[18] the M_w became higher only when the reaction temperature was as high as 200 °C. In the present SSP the M_w increases efficiently even at much lower reaction temperatures. Because the two sets of SSP at $0 \geq X_D \geq 50$ and $50 \geq X_D \geq 100$ were carried out by using different starting melt-blends of PLLA and PDLA, the M_w of $P50L_A$ and $P50L_B$ differ from those of $P50D_A$ and $P50D_B$. The slightly different optical purities of the PLLA and PDLA prepolymers prepared by MPC affect the crystallinity of the reactant polymers in SSP, resulting in the large difference in M_w of the final polymers $P100L_B$ (PLLA) and $P100D_B$ (PDLA). However, at the rich ratios of PLLA or PDLA similar M_w are recorded at the complementary compositions of the PLLA-rich (e.g., $X_D = 20$) and PDLA-rich (e.g., $X_D = 80$) systems. The effect of optical purity may be diminished significantly in this region because the total difference in L/D ratio between the two systems is compensated when the PLLA and PDLA prepolymers with slightly different optical purity are mixed.

As for the M_n of the SSP products, similar increasing tendencies are shown with X_D inclining to 0 and 100 (see the dotted lines for PXD_B and PXL_B). The slightly lower decreases observed at $X_D = 0$ and 10 for PXL_B may be related to the wide polydispersities ($M_w/M_n > 4.5$ as shown in Table 3) of the SSP products. The polymer chains around the hc domain may have enough mobility at the reaction temperature of SSP to be involved in the chain scrambling, while those around the sc domain are almost bound to escape from the chain scrambling. Therefore, the polydispersity of the SSP products became larger at $X_D < 10$ for PXL_B in the L-rich series (PXL_B) and at $X_D > 100$ for PXD_B in the D-rich series (PXD_B). As a consequence, the M_n increase in these X_D became limited.

Characterization of the sb-PLA. Table 3 summarizes the characteristics of the final SSP products obtained after 30 h with the SSP process B. There is a tendency that the final polymer recovery decreases with the PLLA content of the melt-blends inclining to 100. For example, the recovery of $P90L_B$ is 10 wt % lower than that of $P50L_B$. This decrease in polymer recovery is due to the sublimation of the lactide monomers that are likely formed by the ring−chain equilibrium. Since the thermally stable sc crystals decrease the mobility of the polymer chains in the vicinity, the lactide formation can be retarded in comparison with that of the PLLA or PDLA homopolymer-rich system. The recoveries higher than 70% are, however, much higher than those obtained in the previous SSP of the equivalent PLLA/PDLA system for which a high reaction temperature was used.[28]

Figure 6 shows the changes in the average number of lactate units (n) in the block sequences of the PLLA-rich melt-blends

Table 3. Characteristics of the Final SSP Products in the PLLA-Rich System (Process B, 30 h)

code	recovery (%)	$M_n{}^a$ (10^4)	$M_w{}^a$ (10^4)	$M_w/M_n{}^a$	$T_m{}^{h\,b,c}$ (°C)	$T_m{}^{s\,b,c}$ (°C)	$\Delta H_m{}^{h\,b,d}$ (J/g)	$\Delta H_m{}^{s\,b,d}$ (J/g)	$\Delta H_m{}^h/\Delta H_m{}^s$
P100L$_B$	69	4.2	23.5	5.6	176		87	0	
P90L$_B$	73	3.1	14.1	*4.6*	176	207	62	20	3.1
P80L$_B$	79	4.6	11.6	2.5	174	209	45	24	1.9
P70L$_B$	79	4.0	9.3	2.4	171	210	43	37	1.2
P50L$_B$	83	2.4	4.8	2.0	169	213	22	70	0.3

[a] Determined by GPC relative to PMMA standards with HFIP as the eluent (40 °C). [b] Measured by DSC (heating rate: 20 °C/min). [c] $T_m{}^h$ and $T_m{}^s$ are melting temperatures of the hc and sc crystals, respectively. [d] $\Delta H_m{}^h$ and $\Delta H_m{}^s$ represent the heat of fusion of the hc and sc crystals, respectively.

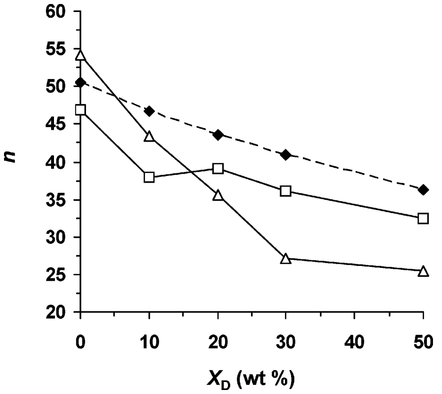

Figure 6. Changes in average number (n) of lactate units consisting of each block as a function of the PDLA composition (X_D) in the melt-blends BXL (open squares) and the final SSP products PXL as compared with the theoretical values calculated with the feed ratios and optical purities of the starting PLLA and PDLA prepolymers (filled lozenges).

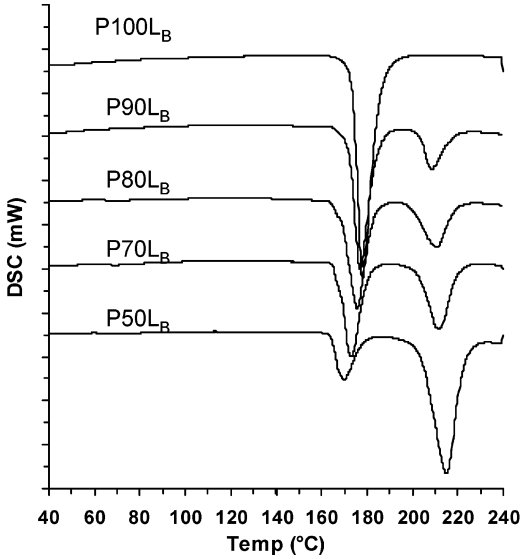

Figure 7. DSC thermograms of the final SSP products PXL$_B$ prepared by process B.

(BXL) and the corresponding SSP products (PXL) as a function of X_D. The value n was determined by referring to the integral ratios of the carbonyl signals based on the Bernoullian statistics.[12,18,29] The theoretical values can be derived from the average D (28) and L (51) sequences of the PDLA (D1) and PLLA (L1) prepolymers that are deduced from their optical purities.[30] It is known that the theoretical value decreases by increasing X_D because the n value of the PDLA (D1) prepolymer is lower than that of PLLA (L1) prepolymer. The experimental n values of the melt-blends are slightly lower than the theoretical values although their change concerning X_D is correspondent to that of the theoretical values. This difference of 10 or less in n value may be attributed to an experimental error or a slight chain scrambling between PLLA and PDLA during the melt-blending.

The n values of P100L$_B$ and P90L$_B$ become significantly higher than those of the corresponding B100L and B90L because of the elongation of the homosequences of PLLA and PDLA. On the other hand, the n values of P70L$_B$ and P50L$_B$ become much lower than those of the corresponding B70L and B50L. This decrease, indicating the shortening of the isotactic sequences, may be caused by the chain scrambling of the PLLA and PDLA blocks in SSP. Since the chain coupling and scrambling between PLLA and PDLA forms one racemic diad, the newly formed chain cannot crystallize and is likely involved in the further transesterification reactions to yield short homosequences of PLLA and PDLA. The alternative chain coupling and scrambling between the homopolymers can give longer homosequences that can crystallize out from the reaction system in an amorphous state. Around $X_D = 20$, both the reactions compete with each other, the n value of the P80L$_B$ is almost comparable to the theoretical value. The significantly broader polydispersity of P100L$_B$ and P90L$_B$ compared with P70L$_B$ and P50L$_B$ (Table 3) also supports the change in the reaction pattern in both extremes.

On the other hand, the n values of the D-rich sb-PLA (PXD) were significantly smaller than those of the L-rich sb-PLA (PXL) and showed a rather gentle decrease with X_D, i.e., $n = 23$ for P90D$_B$ and $n = 16$ for P50D$_B$. The theoretical n values at $X_D = 90$ and 50 were estimated as 25 and 24, respectively, based on the n values of 23 and 26 for the corresponding PLLA (L2) and PDLA (D2) prepolymers. The lower optical purities of L2 and D2 are responsible for the n values of BXD and PXD. These data reveal that the final SSP products are sb-PLA having different PLLA/PDLA block lengths and compositions that can be controlled by the feed ratios of the starting prepolymers, PLLA and PDLA having medium molecular weight.

Thermal Properties of sb-PLA. Figure 7 shows the DSC curves of the final SSP products PXL$_B$ having L-rich compositions. The endothermic peaks shown here are much deeper and sharper compared to those shown by the corresponding melt-blends in Figure 3. This result strongly suggests that the homochiral crystallization has been promoted during the SSP. The T_m and ΔH_m values corresponding to the hc and sc crystals are summarized in Table 3. The melting temperature of the hc crystals ($T_m{}^h$) increases with the PLLA content while that of the sc crystals ($T_m{}^s$) decreases with it. Because $T_m{}^h$ depends on molecular weight,[3] the larger value of $T_m{}^h$ supports the chain extension of the homopolymer sequences. It should be noted here that both the as-prepared P100L$_B$ and P90L$_B$, having the significantly wide polydispersities, show narrow melting endotherms at the ordinary T_m of hc crystals. This may be because the defects of the crystal lattice have been removed during the SSP in which polymer crystallization is promoted. Although the polymer chains with slightly lower molecular weights are involved in the crystals, they may be well situated in the crystal lattice by forming the complete helical conformation.

The opposite lower $T_m{}^s$ value indicates that the PLLA and PDLA chains involved in the sc crystals are shorter.[31] The heat of fusion of the hc ($\Delta H_m{}^h$) and sc ($\Delta H_m{}^s$) crystals changes with

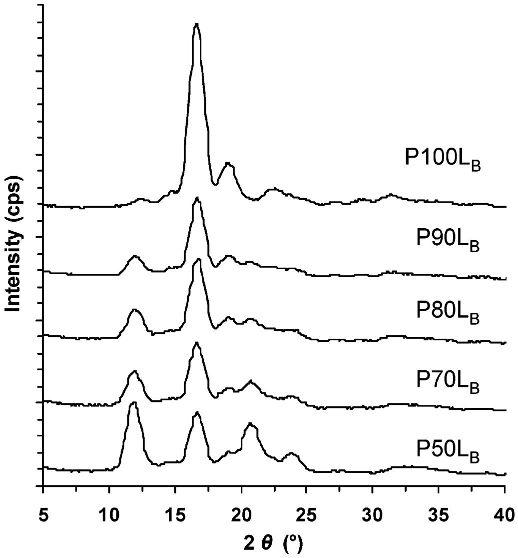

Figure 8. WAXD profiles of the final SSP products PXL$_B$ prepared by process B.

Table 4. L/D Unit Ratios of the Melt-Blends and the Final SSP Products

	enantiomer ratio (L/D in %)[a,b]				ΔL (%)[c]	
X_L	theor	BXL	PXL$_A$	PXL$_B$	PXL$_A$	PXL$_B$
100	99/1		98/2	99/1	1.1	0
90	89/11	89/11	88/12	89/11	0.8	0.5
80	80/20	80/20	80/20	80/20	0.1	0.4
70	70/30	70/30	69/31	69/31	0.8	1.1
50	50/50	53/47	51/49	50/50	1.8	3.0

[a] Determined directly from the peak ratios of L and D-lactic acids from the hydrolysis products of the sample polymers with chiral-HPLC. [b] Prepared from PLLA (L1:L/D = 99.0/1.0) and PDLA (D1:L/D = 1.8/98.2). [c] ΔL: percent difference in L-isomer contents between the melt-blends and the final SSP products.

the PLLA content, similar to T_m. Their ratios $\Delta H_m^h/\Delta H_m^s$ of P90L$_B$ and P80L$_B$ are slightly lower than those of the starting melt-blends (Table 2), whereas the same ratio of P70L$_B$ is even larger than that of the corresponding B70L. These ratios should not be correlated with the preferential crystallization of the hc crystals over sc crystals in SSP, considering the difference in specific heat of fusion between both crystal systems (142 J/g for sc[32] and 93 J/g for hc[33]); the hc crystallinity increases by increasing the L-abundance. Figure 8 shows the WAXD of PXL$_B$. Each of the curvatures is exactly the same as that shown by the corresponding melt-blends (Figure 2), except that the diffractions of the hc crystals are stronger in the SSP products.

It is therefore suggested that the crystal growth has occurred in the homopolymer domain as a result of increasing the molecular weight and that the sc crystal domain has been kept almost unchanged throughout SSP. Consequently, the thermal properties of the present sb-PLA are determined by the PLLA/PDLA composition, the DP of the homopolymer sequences, and the relevant hc to sc crystal composition.

Racemization. The enantiomeric ratios in the melt-blends and the final SSP products were determined by the chiral HPLC of their hydrolysis products to evaluate the degree of unit racemization during the reaction. The results are summarized in Table 4. The theoretical values are those calculated from the enantiomeric ratios of the starting PLLA and PDLA prepolymers.[34] The enantiomeric ratios determined for the melt-blends are comparable to the theoretical values, although in B50L the L-isomer ratio is only slightly higher. For the SSP products the ratios are also similar to the theoretical values. Percent differences in L-isomer contents between the melt-blends and the final SSP products (ΔL) are less than 3.0%. These small changes in the enantiomeric ratios suggest that little unit racemization has taken place during the melt-blending and SSP. Also, the differences in processes A and B are negligible in terms of effect.

Conclusion

sb-PLA having nonequivalent PLLA/PDLA compositions were successfully synthesized by SSP of the melt-blend of the PLLA and PDLA prepolymers with medium molecular weight that had been preformed by simple MPC. The SSP could be performed under mild reaction conditions with products high in yield. The molecular weight of the resultant sb-PLA became larger with the PLLA/PDLA ratio, inclining to 0 or 100 in which the block composition was PLLA- or PDLA-rich. The thermal properties of these sb-PLA were found to depend on the molecular weight and the composition of the block sequences. In the SSP the chain extension is mainly driven by the dehydrative coupling and the transesterification of the homopolymer chains, but not by those occurring between heterosequences. The homosequences elongated by the former reactions can crystallize out from the reaction system to allow concentration of the polymer tails and catalysts in the amorphous domain to lead further chain extension reactions. On the basis of this knowledge, we are now studying the SSP of the powder blend of PLLA and PDLA in which the hc domain can be preserved in high ratio and both the chain extension and the stereoblock formation are allowed even at the equivalent PLLA/PDLA ratio. By this way, it will be possible to prepare various sb-PLA products having higher molecular weight, different PLLA/PDLA compositions, and thermal properties by utilizing mild reaction conditions. We are also studying the properties of those PLA polymers that are different from conventional PLLA and the relevant derivatives comprising racemic sequences.

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(30) When the enantiomer contents in the starting PLLA and PDLA are denoted by L_{PLLA}, D_{PLLA}, L_{PDLA}, and D_{PDLA}, the possibilities of forming the meso (P_m) and racemic diads (P_r) in the simple melt-blend comprising x wt % of PLLA and y wt% of PDLA are given as follows: $P_m = (x[L_{PLLA}^2 + D_{PLLA}^2] + y[L_{PDLA}^2 + D_{PDLA}^2])/100^3$ $P_r = 2(xL_{PLLA}D_{PLLA} + yL_{PDLA}D_{PDLA})/100^3$. Note that $P_m + P_r = 1$, $P_m < 1$, $P_r < 1$, and $x + y = 100$. Thus, the average number of lactate units in each isotactic block (n) is derived as $n = 1/P_r = 1/(1 - P_m)$. For example, based on the enantiomer ratios of L1 (L/D = 99.0/1.0) and D1 (L/D = 1.8/98.2), P_m, P_r, and n for B90L ($x = 90$, $y = 10$) are $P_m(\text{B90L}) = (90 \times [99.0^2 + 1.0^2] + 10 \times [1.8^2 + 98.2^2])/100^3 = 0.979$, $P_r(\text{B90L}) = 2 \times (90 \times 99.0 \times 1.0 + 10 \times 1.8 \times 98.2)/100^3 = 0.021$, and $n = 1/0.021 = 47.6$. See ref 18.

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(34) If a melt-blend consists of x wt% of PLLA and y wt% of PDLA, the theoretical L-isomer (L_{th}) and D-isomer (D_{th}) contents are L_{th} (%) = $(xL_{PLLA} + yL_{PDLA})/100$ and D_{th} (%) = $(xD_{PLLA} + yD_{PDLA})/100$, where L_{PLLA}, D_{PLLA}, L_{PDLA}, and D_{PDLA} are defined as above. In the case of the B80L ($x = 80$, $y = 20$), $L_{th}(\text{B80L}) = (80 \times 99.0 + 20 \times 1.8)/100 = 79.6$ (%) and $D_{th}(\text{B80L}) = (80 \times 1.0 + 20 \times 98.2)/100 = 20.4$ (%).

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