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ORIGINAL ARTICLE

Synthesis and properties of stereo di- and tri-block polylactides of different block compositions by terminal Diels-Alder coupling of poly-L-lactide and poly-D-lactide prepolymers

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Mono-anthracene-terminated poly-L-lactide (A-PLLA) and mono-maleimide-terminated poly-D-lactide (M-PDLA) were prepared by ordinary lactide polymerization with initiators containing the corresponding functional groups. The resulting A-PLLA was allowed to dimerize by the reaction of its terminal hydroxyl with hexamethylene diisocyanate (HMDI) to obtain bis-anthracene-terminated PLLA (A-PLLA-A). The terminal Diels-Alder coupling between A-PLLA and M-PDLA and between A-PLLA-A and M-PDLA spontaneously gave stereo di- (d-sb-PLA) and tri-block (t-sb-PLA) copolymers, respectively, whose block sequences could be readily controlled by changing the molecular weight of the A-PLLA and M-PDLA prepolymers. The resultant d-sb-PLA and t-sb-PLA samples were found to have excellent thermal and thermo-mechanical properties due to the easy formation of stereocomplex crystals of PLLA and PDLA. These synthetic methods, which were based on polymer coupling, can be a facile route to the fabrication of stereo block polylactides possessing excellent properties.

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INTRODUCTION

Much recent attention has been paid to both biobased polymers that can be synthesized from naturally occurring substances and platform chemicals derived from biomass by combining the biological and chemical conversion processes. Until now, several aliphatic polyesters, such as poly(lactide)s (PLA), poly(butylene succinate) (PBS), and poly(3-hydroxyalkanoate)s (PHA), have been accepted by industries as the first manufacturing products.[1] Bio-originated polyamides, polycarbonates, and acrylic polymers are now under development as next generation polymers. Among these biobased polymers, only PLAs are now manufactured on a large scale and used as plastic materials for general purposes. Two enantiomeric isomers, poly-L-lactide (PLLA) and poly-D-lactide (PDLA), are present in PLAs depending on the chirality of the lactic acid component, and PLLA, consisting of naturally abundant L-lactic acid, is generally utilized because of its balanced properties and cost.[2–4] In practical applications, however, the thermal and mechanical properties of PLLA are significantly poorer than those of the conventional oil-based polymers, which limits its utility.[5] Therefore, much effort has been made to improve the resistance of PLLA to heat. However, it is known that the combination of enantiomeric PLLA and PDLA generates stereocomplex (sc) crystals that exhibit a melting temperature (T_m) of 230 °C, i.e., 50 °C higher than that of PLLA.[6–10] The stereocomplex-type PLA (sc-PLA) can achieve high performance materials with a degree of heat resistance that has never been accomplished with PLLA alone. However, the simple mixing of PLLA and PDLA polymers with high molecular weight likely results in the formation of both homo-chiral (hc) and sc crystals to retard the heat resistibility of the processed materials.[7,8] Therefore, we have pursued the development of stereoblock-type polylactides (sb-PLA) consisting of PLLA and PDLA sequences because even with PLLA-rich compositions, sb-PLAs can easily form sc crystals with little hc crystallization and exhibit excellent properties.[11–19] This improved sc crystallization can be attributed to molecular mixing within the enantiomeric blocks. We have recently disclosed a novel method for the synthesis of stereo di-block PLAs (d-sb-PLA) by the terminal Diels-Alder coupling of PLLA and PDLA prepolymers with anthracene and maleimide terminal moieties.[19] In this approach, for example, mono-anthranyl PLLA (A-PLLA) and mono-maleimid-N-yl PDLA (M-PDLA) prepolymers are first prepared by the ordinary ring-opening polymerization (ROP) of L- and D-lactides, respectively. These mono-functional prepolymers are mixed and then undergo the Diels-Alder coupling to finally obtain a d-sb-PLA with a high molecular weight (Scheme 1). This method is characterized by

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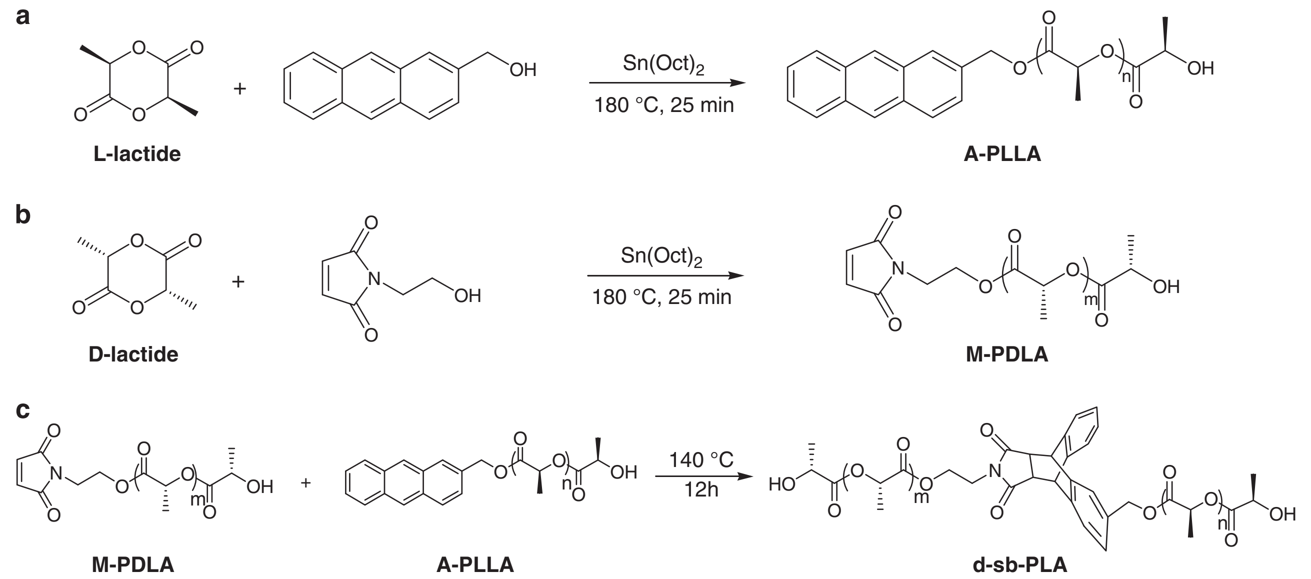
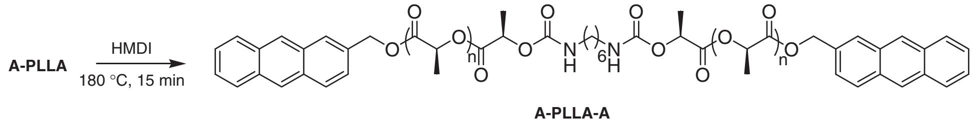


Scheme 1 The synthesis of A-PLLA and M-PDLA and the following Diels-Alder coupling to obtain the d-sb-PLAs.



Scheme 2 The synthesis of A-PLLA-A by the dimerization of A-PLLA.

well-controlled block lengths and compositions that can be determined by the molecular weights of the prepolymers as well as by the excellent stereo-complexibility of the resultant d-sb-PLAs. In this study, we prepare various d-sb-PLAs with different PLLA and PDLA block lengths and compositions by utilizing this terminal coupling method. We also synthesize stereo tri-block PLAs (t-sb-PLA) by expanding this method to other prepolymer combinations in which M-PDLAs are reacted with bis-anthranyl PLLAs (A-PLLA-A) prepared by the reaction of the hydroxyl terminal of A-PLLAs (the alternative terminal group) with 1,6-hexamethylene diisocyanate (HMDI) for dimerization (Scheme 2). Then, the Diels-Alder reactions of the di-functional A-PLLA-A and the mono-functional M-PDLA prepolymers are conducted to obtain t-sb-PLAs (PDLA-PLLA-PDLA) with different block sequences and lengths (Scheme 3). With these d- and t-sb-PLA samples, we clarify the relationship between the thermal properties and the block structures.

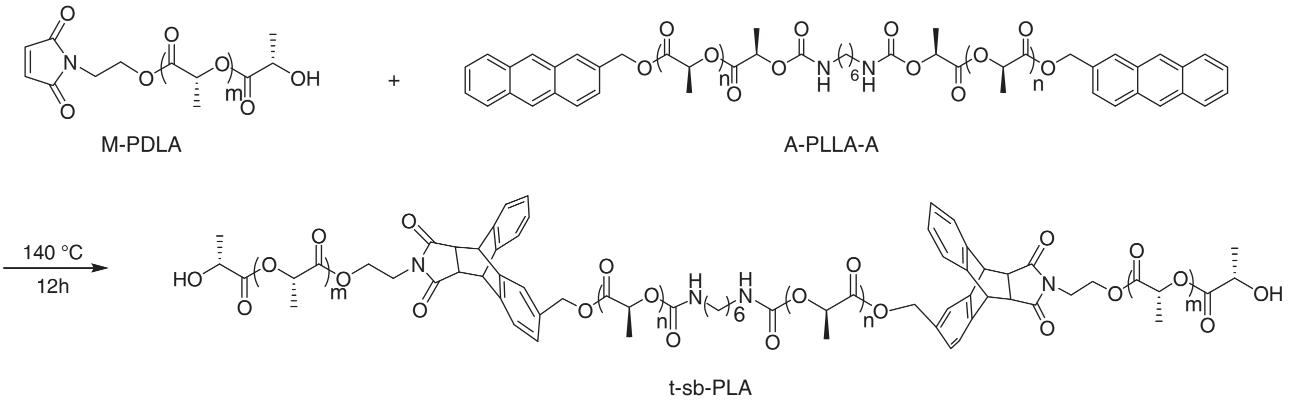
MATERIALS AND METHODS

Materials

The L- and D-lactides were supplied by Musashino Chemical Research Laboratory, Ltd. (Tokyo, Japan). Their optical purity was over 99.9% ee. 2-(Hydroxymethyl)anthracene (AN, 98%) and HMDI were supplied by Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). N-(2-Hydroxyethyl)maleimide (MA, 99%) and tin octoate ($Sn(Oct)_2$, 95%) were purchased from Strem Chemicals (Newburyport, MA) and Sigma-Aldrich (St Louis, MO), respectively, via Sasaki Chemical Co., Ltd. (Kyoto, Japan). The $Sn(Oct)_2$ was purified by distillation before use and dissolved in distilled toluene at a concentration of 0.20 g/ml under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2, 99.5%) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 98%) were purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan) and Central Glass Co., Ltd. (Hofu, Yamaguchi, Japan), respectively. These reagents and solvents were used without purification, unless specifically noted.

Measurements

The number- (M_n(gpc)) and weight-average (M_w(gpc)) molecular weights were determined by gel permeation chromatography (GPC) recorded on a system comprised of a Shimadzu (Kyoto) LC-20AD HPLC pump and a Shimadzu RID-10 A differential refractive index detector. Two Tosoh (Tokyo, Japan) TSK gel Super HZM-N columns (3.0 μm 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 × 3.5 cm) were installed in the system, and chloroform was used as the eluent. The measurement was carried out at 30 °C at a flow rate of 0.25 ml min^{-1}. Polystyrene (PS) standards were used to calibrate the molecular weights, which ranged from 1 090 000 to 500 Da. The ^{1}H NMR (600 MHz) spectra 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. Differential scanning calorimetry (DSC) was conducted on a Shimadzu DSC-50 thermal analyzer under a nitrogen flow of 20 ml min^{-1} and at a heating rate of 10 °C min^{-1}. A sample of approximately 3.0 mg was heated to 240 °C in the first scan, quenched in liquid nitrogen, and heated again from 30 °C to 250 °C in the second heating scan. Wide-angle X-ray scattering (WAXS) patterns were recorded on a Rigaku 2100 FSL X-ray diffraction system with a Rigaku RINT 2000 X-ray generator operated at 40 kV and 50 mA, using nickel-filtered Cu-Kα radiation ($\lambda = 0.1542$ nm) in a 2θ angle range from 5° to 40° at a scan rate of 2° min^{-1}. Dynamic mechanical analysis (DMA) was measured on a Rheogel-E4000 (UBM Co., Ltd., Japan) working in the tension mode at a constant frequency of 10 Hz. The measurements were carried out in a temperature range from 30 to 240 °C at a heating rate of 3 °C min^{-1}.



Scheme 3 The Diels-Alder couplings of M-PDLA and A-PLLA-A to obtain the tri-sb-PLAs.

Syntheses of A-PLLA and M-PDLA

The procedures used here have been reported previously. To synthesize the A-PLLA, both the L-lactide (3.0 g, 20.8 mmol) and AN (41.7 mg, 0.20 mmol) were charged in a 50-ml, two-necked flask equipped with a mechanical stirrer. The flask was evacuated to 10 Pa at room temperature for 1 h and then purged with nitrogen. The evacuation/nitrogen purge was repeated six times to thoroughly dry the reactants. Subsequently, a portion of the catalyst solution (including 0.083 mmol of $Sn(Oct)_2$, i.e., 0.4 mol% of L-lactide) was added to it with a syringe. The flask was desiccated at high vacuum for 1 h at room temperature to remove the toluene and then was filled with nitrogen. Next, the flask was heated at 180 °C for 25 min while stirring for polymerization. The polymeric product was dissolved in CH_2Cl_2 and poured into excess methanol. The precipitate was filtered, washed with methanol several times, and dried in vacuum to obtain the A-PLLA with an M_n of 15 kDa.

To synthesize the M-PDLA, both D-lactide (3.0 g, 20.8 mmol) and MA (28.2 mg, 0.2 mmol) were charged in a 50-ml, two-necked flask equipped with a mechanical stirrer and thoroughly dried under vacuum. Subsequently, a portion of the catalyst solution (including 0.083 mmol of $Sn(Oct)_2$, i.e., 0.4 mol% of D-lactide) was added to the flask. Then, the polymerization and product isolation were conducted as described above to yield the M-PDLA with an M_n of 15 kDa.

Several A-PLLA and M-PDLA samples were synthesized with different molecular weights. In this work, the prepolymers are named A-PLLA(x) and M-PDLA(y), respectively, by putting their M_n numbers, in kDa, in the parentheses.

A-PLLA(15): ^1H NMR (600 MHz, in $CDCl_3$): δ 1.56–1.6 (d, CH_3 of the lactate unit), 4.3–4.4 (q, CH-OH of the terminal lactate), 5.1–5.2 (q, CH of the lactate unit), 5.38 (AB q, CH_2- of the AN unit), and 7.41 (dd), 7.5–7.6 (m), 7.97 (s), 8.03 (d), 8.45 (s) for the aromatic protons of the AN unit. The M_n (nmr) was determined by the integral ratios of the signals at δ 4.3–4.4 and δ 5.1–5.2 p.p.m.

M-PDLA(15): ^1H NMR (600 MHz, in $CDCl_3$): δ 1.56–1.6 (d, CH_3 of the lactate unit), 4.3–4.4 (q, *C*H-OH of the terminal lactate), 5.1–5.2 (q, *C*H of the lactate unit), and 3.7–3.9 (m, N-CH_2-C of the MA unit), 4.2–4.4 (m, C-CH_2-O of the MA unit), and 6.75 (s, -CH = CH- of the MA unit). The M_n (nmr) was determined by the integral ratios of the signals at δ 5.1–5.2 and δ 4.3–4.4 p.p.m. Because the latter signal was duplicated with the C-CH_2-O signal of the MA unit, its integral ratio was evaluated in reference to that of the N-CH_2-C signal of the MA unit.

Synthesis of A-PLLA-A

For example, the A-PLLA(7.5) was first prepared by the ROP of L-lactide (3.0 g, 20.8 mmol) by using AN (83.3 mg, 0.40 mmol) and $Sn(Oct)_2$ (0.4 mol% of L-LA) as the initiator and catalyst, respectively, as described in the above synthesis of A-PLLA. In the final step of this polymerization, exactly half an equivalent molar amount of HMDI (34 mg, 0.20 mmol) relative to AN was added to the system and reacted with the polymerization product for 15 min while stirring under identical conditions. The obtained reaction product was finally dissolved in CH_2Cl_2 and then re-precipitated with excess methanol. The precipitates were filtered, washed with methanol several times, and dried under vacuum at 80 °C for 6 h.

Several A-PLLA-A samples with different molecular weights were synthesized from the corresponding A-PLLA prepolymers. These A-PLLA-A prepolymers are also named A-PLLA-A(2x), in which 2x denotes the M_n values, which are nearly twice that (x) of the A-PLLA prepolymers.

A-PLLA-A(15): ^1H NMR (600 MHz, in $CDCl_3$, Figure 1): δ 1.3–1.4 (s, C-CH_2-C of the HMDI unit), 1.56–1.6 (d, CH_3 of the lactate unit), 3.1–3.2 (q, N-CH_2-C of the HMDI unit), 4.9–5.0 (q, C-CH-OC(O)NH- of the linking lactate), 5.1–5.2 (q, CH of the lactate unit), 5.38 (AB q, CH_2- of the AN unit), and 7.41 (dd), 7.5–7.6 (m), 7.97 (s), 8.03 (d), 8.45 (s) for the aromatic protons of the AN unit.

Synthesis of d-sb-PLA by Diels-Alder Coupling of A-PLLA and M-PDLA

The reaction process has been reported previously.[19] In summary, predetermined amounts of A-PLLA (15) (1.0 g) and M-PDLA(15) (1.0 g) were dissolved in a mixture of CH_2Cl_2 and HFIP (5 ml, CH_2Cl_2/ HFIP = 4/1 v/v%) and reprecipitated into excess methanol. The precipitated polymer mixture was dried under vacuum at room temperature for 3 h. A portion of the polymer mixture was charged in a glass reactor and heated at 140 °C under a nitrogen atmosphere for 12 h. While heating, the polymer mixture softened in the early stage and solidified quickly after the Diels-Alder reaction process. The resulting polymer was reprecipitated by using a solvent system of CH_2Cl_2/ HFIP mixture (solvent) and methanol (precipitant) and dried under vacuum at 80 °C for 8 h. The polymer samples resulting from the combinations of A-PLLA (x) and M-PDLA(y) are named d-sb-PLA (x-y).

d-sb-PLA (15–15): ^1H NMR (600 MHz, $CDCl_3$): 1.56–1.6 (d, CH_3 for PLA), 4.9–5.0 (s, C-CH-O at the terminal of PLA), 5.1–5.2 (q, CH for PLA), 4.78 (d), and 7.1–7.4 (m) (for the anthracene unit), 3.3–3.4 (m), and 3.6–3.8 (m) (for the maleimide unit), 3.1–3.3 (m), and 3.4–3.6 (m) (for the connections of the Diels-Alder adduct).

Synthesis of t-sb-PLA by Diels-Alder Coupling of A-PLLA-A and M-PDLA

A typical example follows. Predetermined amounts of A-PLLA-A(15) (1.0 g) and M-PDLA(7.5) (1.0 g) were dissolved in a mixture of CH_2Cl_2 and HFIP (5 ml, CH_2Cl_2/ HFIP = 4/1 v/v%) at room temperature. The solution was then poured into excess methanol to precipitate the polymer mixture of A-PLLA-A(15) and M-PDLA(7.5). The precipitates were dried under vacuum at 80 °C for 8 h and then pulverized. The subsequent Diels-Alder reaction and product isolation were conducted as described in the above synthesis of d-sb-PLA. The

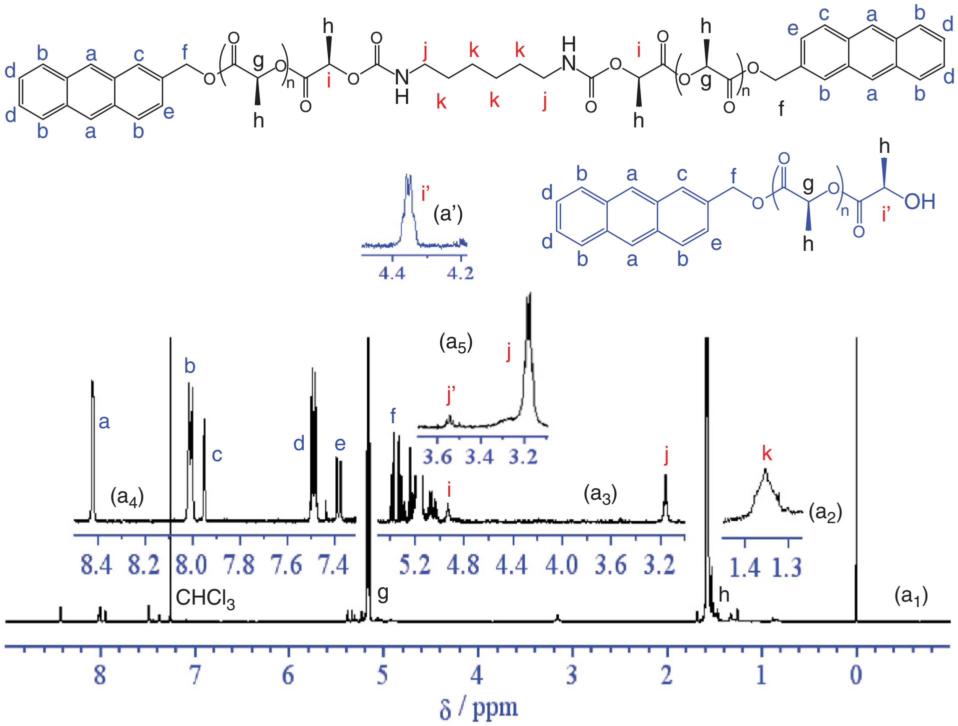


Figure 1 The ^{1}H NMR spectra of A-PLLA-A(15): (a_1) a full spectrum, (a_2-a_5) the expanded spectra for the weak signals, and (a′) an expanded spectrum of the A-PLLA(7.5) for comparison.

resulting polymer samples were prepared from the combinations of A-PLLA-A(2x) and M-PDLA(y) and were named t-sb-PLA(y-2x-y).

t-sb-PLA(7.5-15-7.5): ^{1}H NMR (600 MHz, $CDCl_3$, Figure 2): 1.56–1.6 (d, CH_3 for PLA), 4.9–5.0 (s, C-CH-O at the terminal of PLA), 5.1–5.2 (q, CH for PLA), 4.78 (d), and 7.1–7.4 (m) (for the anthracene unit), 3.3–3.4 (m), and 3.6–3.8 (m) (for the maleimide unit), and 1.3–1.4 (s, C-CH_2-C for HMDI unit), 3.1–3.2 (q, N-CH_2-C for HMDI unit), 3.1–3.3 (m), and 3.4–3.6 (m) (for the connections of the Diels-Alder adduct).

Preparation of Hot-pressed Films

Each polymer sample was placed between two aluminum plates with a spacer size of 40 × 40 × 0.1 mm^3 and subjected to hot-pressing using an Mini Test Press Model MP-2FH (TOYOSEKI Co., Ltd., Japan) apparatus. The sample was melted at 240 °C, pressed at a pressure of 5 MPa for 3 min, and quenched in ice-water to obtain an amorphous film. The sample was then annealed at 140 °C for 3 h.

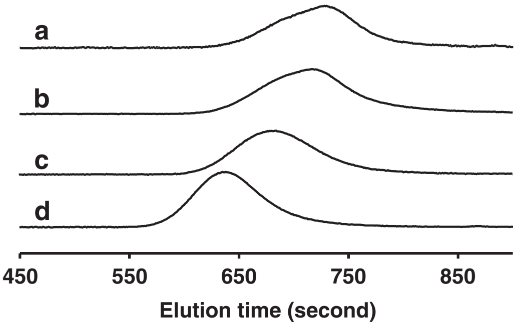


Figure 2 The GPC curves of (**a**) A-PLLA(7.5), (**b**) M-PDLA(7.5), (**c**) A-PLLA-A(15), and (**d**) t-sb-PLA(7.5-15-7.5).

RESULTS AND DISCUSSION

Synthesis of d-sb-PLAs having different PLLA/PDLA block ratios

As reported previously,[19] the mono-anthracene-terminated A-PLLA(x) and mono-maleimide-terminated M-PDLA(y) were prepared by the ordinary tin-catalyzed ROP of L- and D-lactides in the presence of AN and MA as the initiators, respectively (Schemes 1a and 1b). Table 1 summarizes the results of the preparations of A-PLLA(x) and M-PDLA(y) with different chain lengths. The monomer conversion was very high for each synthesis run, and the M_n(nmr) values of the A-PLLA(x) and M-PDLA(y) prepolymers nearly corresponded to the M_n(th) values estimated from the monomer-to-initiator ratios in the feed and monomer conversions. In comparison to the M_n(nmr) values, the significantly larger M_n(gpc) values may be attributed to the fact that the PLA polymers with molecular weights of the present range (10^3–10^4 kDa) likely show larger hydrodynamic volumes than the standard polymers in chloroform. However, the increasing tendencies of M_n(nmr) and M_n(gpc) were consistent with each other, supporting the correlation of the molecular weights. These data, together with the structural data shown in the Experimental section, support the formations of A-PLLA(x) and M-PDLA(y). Here, six samples were prepared for each series of A-PLLA(x) and M-PDLA(y).

By combining the A-PLLA(x) and M-PDLA(y) samples, for which the M_n of the former (x) was larger than that of the latter (y), the Diels-Alder coupling reactions were conducted at 140 °C (Scheme 3) to synthesize six d-sb-PLA(x-y) samples in the form of PLLA-b-PDLA whose PLLA block was equal to or longer than the PDLA block (x⩾y) at different block ratios (Scheme 1c). The structural characterization of the resultant d-sb-PLAs is described in the Experimental section. Table 2 summarizes the results of the coupling

Table 1 The Synthesis of A-PLLA(x) and M-PDLA(y)

Prepolymer	$[M]_0/[I]_0$	*Conversion (%)*	*Mn(th) (10^{-3})*	*Mn^a(nmr) (10^{-3})*	*Mn^b(gpc) (10^{-3})*	*Mw^b(gpc) (10^{-3})*	*Mw/Mn^b*
A-PLLA (15)	103.8	97.3	14.9	15.1	22.1	28.7	1.3
A-PLLA (21)	146.1	98.4	21.0	21.3	34.1	47.7	1.4
A-PLLA (24)	167.6	97.8	24.1	25.2	42.7	59.8	1.4
A-PLLA (50)	347.5	95.2	50.0	50.2	71.5	107.2	1.5
A-PLLA (70)	486.9	95.2	70.1	71.9	117.0	187.2	1.6
A-PLLA (80)	544.5	95.6	78.4	77.8	120.0	180.0	1.5
M-PDLA (6)	41.8	96.7	6.0	6.6	11.0	15.4	1.4
M-PDLA (9)	62.5	97.6	9.0	8.6	15.4	21.6	1.4
M-PDLA (15)	104.5	95.5	15.0	16.0	23.0	34.5	1.5
M-PDLA (20)	138.9	96.1	20.2	21.2	34.1	47.7	1.4
M-PDLA (30)	208.4	96.1	30.0	26.2	51.3	71.8	1.4
M-PDLA (50)	347.7	95.8	50.1	52.4	73.2	110.0	1.5

[a] Determined by ^{1}H NMR.
[b] Determined by GPC relative to polystyrene standards with $CHCl_3$ as the eluent.

Table 2 The results of Diels-Alder Reaction of A-PLLA(x) and M-PDLA(y) to obtain d-sb-PLA(x-y)

d-sb-PLA x-y	*Combination*	*PDLA (%)*	*Mn(th) (10^{-3})*	*Mn^a(gpc) (10^{-3})*	*Mw^a(gpc) (10^{-3})*	*Mw/Mn^a*	*T_m^{b} (°C)*	*X_c^{c} (%)*
15-15	A-PLLA (15)/ M-PDLA (15)	50	30.1	46.3	81.8	1.8	235.5	34.9
21-9	A-PLLA (21)/ M-PDLA (9)	30	30.0	43.2	84.2	1.9	229.6	30.4
24-6	A-PLLA (24)/ M-PDLA (6)	20	29.9	43.4	95.2	2.2	219.3	24.7
50-50	A-PLLA (50)/ M-PDLA (50)	50	98.6	91.0	220.0	2.4	215.4	33.9
70-30	A-PLLA (70)/ M-PDLA (30)	30	100.1	105.2	188.2	1.8	205.2	24.2
80-20	A-PLLA (80)/ M-PDLA (20)	20	100.0	113.5	188.7	1.7	206.2	17.6

[a] Determined by GPC relative to polystyrene standards with $CHCl_3$ as the eluent.
[b] Determined by DSC (the 2nd scan).
[c] Calculated on the basis of the specific heat of fusions of sc crystals (142 J/g).

reactions. Here, the total M_n(th) values of the d-sb-PLAs were 30 and 100 kDa in the series with x-y indices of 24-6, 21-9, and 15-15 and those with x-y of 80-20, 70-30 and 50-50, respectively. The former series exhibited somewhat larger M_n(gpc) values than the M_n(th) values estimated from the total M_n(th) values of the two prepolymers, whereas the latter series, with higher molecular weights, had M_n(gpc) values almost equal to the M_n(th) values, supporting the almost quantitative Diels-Alder coupling between the anthracene and maleimide terminals.[19]

Synthesis of A-PLLA-A

Because each of the anthracene-terminated A-PLLA samples possesses a hydroxyl group in the opposite polymer tail, it can be used for the post-polymerization reaction with HMDI. Hence, as soon as the first ROP of L-lactide was concluded, we added HMDI (a half molar amount of the initiator AN) to the as-formed A-PLLA without isolation for its dimerization (one-pot reaction). Because the $Sn(Oct)_2$ used for the ROP was able to sufficiently catalyze the urethane formation between the isocyanate and hydroxyl groups, the dimeric product A-PLLA-A(2x) was obtained in a high conversion rate in a short reaction time of 15 min. Figure 1 shows a typical ^{1}H-NMR spectrum of the as-prepared A-PLLA-A(15) sample, in which several characteristic signals are enlarged in spectra a_3-a_5 and compared with the signal (a′) in the spectrum of the A-PLLA(7.5) prepolymer. The signal assignments are designated by the alphabetical symbols and summarized in the Experimental section. In summary, A-PLLA(7.5) exhibits a hydroxymethine signal due to the terminal lactate unit at δ 4.3–4.4 p.p.m. (signal *i*′ in the expanded spectrum a′ for A-PLLA(7.5)). This signal is completely absent in A-PLLA-A(15) and is replaced by the carbamoyloxymethine signal shown at δ 4.9–5.0 p.p.m. (signal *i* in spectrum a_3), which can be attributed to the linking of the lactate unit with the urethane group. Additionally, A-PLLA-A(15) exhibits HMDI-originated alkylene-methylene signals at δ 1.3–1.4 p.p.m. (signal *k* in spectrum a_2) and N-methylene signals at δ 3.1–3.2 p.p.m. (signal *j* in spectrum a_3), whereas the N-methylene signal of HMDI are shown at δ 3.5–3.6 p.p.m. as a very weak signal (signal *j'* in the expanded spectrum a_5), which nearly disappeared following purification. The conversion of this coupling reaction was determined from the integral ratios of the N-methylene signals, which were identified to be as high as 97%. However, the signals from the anthracene moieties (expanded spectrum a_4) were unchanged both before and following the coupling. The spectroscopic data strongly support the dimeric structures of A-PLLA-A(15), in which two A-PLLA(7.5) chains are connected through two urethane linkages. The M_n(nmr) values of the coupling products were estimated from the integral ratios of the methine signals of the linking units C-C*H*-OC(O)NH- (δ 4.9–5.0 p.p.m.) and the main chain units C-C*H*-OC(O) (δ 5.1–5.2 p.p.m.) by considering the dimeric structure.

Table 3 summarizes the examined isocyanate coupling reactions. It should be noted that the data for A-PLLA(x) are recorded for the intermediate prepolymers isolated after the ROP, which was separately performed for characterization. In the coupling reaction, the conversion exceeded 96%, as described above. The non-quantitative conversion may be due to the evaporation of a small amount of HMDI while in the reaction vessel. Figure 2 compares the typical GPC curves of (a) A-PLLA(7.5) and (c) its coupling product A-PLLA-A(15). It is

Table 3 The synthesis of A-PLLA-A(2x) by dimerization of A-PLLA(x)

Prepolymer	*$[M]_0/[I]_0$*	*Conversion (%)*	*Coupling products*	*HMDI conversion (%)*	*Mn(th) (10^{-3})*	*Mn[a](nmr) (10^{-3})*	*Mn[b](gpc) (10^{-3})*	*Mw[b](gpc) (10^{-3})*	*Mw/Mn[b]*
A-PLLA (7.5)	52.1	95.6			7.5	7.6	13.6	25.1	1.9
			A-PLLA-A (15)	97.5	14.6		23.4	41.6	1.8
A-PLLA (10.5)	72.9	95.1			10.5	10.8	16.5	27.2	1.7
			A-PLLA-A (21)	98.3	20.6		35.0	63.0	1.8
A-PLLA (12)	83.2	95.2			12.0	12.7	19.5	29.4	1.5
			A-PLLA-A (24)	97.5	23.4		40.0	72.0	1.8
A-PLLA (25)	173.0	94.5			24.9	22.0	37.4	68.4	1.8
			A-PLLA-A (50)	97.0	48.3		62.3	116.0	1.9
A-PLLA (35)	243.0	94.0			35.0	31.1	60.9	108.0	1.8
			A-PLLA-A (70)	97.0	67.9		113.0	200.0	1.8
A-PLLA (40)	278.0	94.9			40.0	37.0	68.2	123.0	1.8
			A-PLLA-A (80)	98.0	78.4		121.0	206.0	1.6

[a]Determined by ^{1}H NMR.
[b]Determined by GPC relative to polystyrene standards with $CHCl_3$ as the eluent.

evident that the latter curve has shifted to a higher molecular weight region without the development of a shoulder peak around the region where the former curve is shown. As summarized in Table 3, the M_n(gpc) value of each A-PLLA-A(2x) was approximately twice that of the corresponding A-PLLA(x) in spite of the slightly wider polydispersity shown. These results strongly support the fact that the coupling products were the dimers of A-PLLA(x) and that their M_n(th) values were equal to 2x. Because the M_n(nmr) values of A-PLLA-A(2x) estimated above were almost comparable to the M_n(th) values, the latter values (15, 21, 24, 50, 70 and 80 kDa) are used as the 2x for naming the six A-PLLA-A samples.

Synthesis of t-sb-PLAs by the reaction of A-PLLA-A and M-PDLA

The Diels-Alder coupling of A-PLLA-A(2x) and M-PDLA(y) was conducted at 140 °C (Scheme 3) to synthesize the t-sb-PLAs. For this purpose, six prepolymers of M-PDLA(y) (y = 3.0, 4.5, 7.5, 10, 15, and 25) were newly prepared (see Supplementary Table S1 in the supporting data) and combined with the A-PLLA-A(2x) prepolymers (2x = 15, 21, 24, 50, 70, and 80) to prepare t-sb-PLA(y-2x-y) (y-2x-y: 3-24-3, 4.5-21-4.5, 7.5-15-7.5, 10-80-10, 15-70-15, 25-50-25). A typical GPC curve of t-sb-PLA(7.5-15-7.5), as synthesized from A-PLLA-A(15) and M-PDLA(7.5), is presented in Figure 2, in which a significant molecular weight increase is shown with the uni-modal nature preserved. Figure 3 shows the ^{1}H-NMR spectrum of this product. The expanded region (spectrum b_2) exhibits new signals at δ 3.1–3.3 (signal *d*) and 3.4–3.6 p.p.m. (signal *c*), which can be assigned to the Diels-Alder adducts, together with the faint aromatic and olefinic proton signals from the anthracene (δ 7.4–8.5 p.p.m.) and maleimide moieties (δ 6.75 p.p.m.), as compared with those shown in Figure 1 (a4) and Figure 3 (b'), respectively. The data supported the quantitative formation of the Diels-Alder adducts between either the terminal groups of A-PLLA-A(15) and M-PDLA(7.5) or the triblock structure of the t-sb-PLAs(7.5-15-7.5).

Table 4 summarizes the synthesis of the six t-sb-PLAs whose PLLA/PDLA chirality ratios are 1/1 in 7.5-15-7.5 and 25-50-25 but PLLA-rich in the other products. Their M_n(gpc) and M_w(gpc) values were higher than those of the corresponding prepolymers, but the polydispersities were almost comparable with those of the A-PLLA-A(2x) prepolymers. The M_n(gpc) values of the lower molecular weight series (7.5-15-7.5, 4.5-21-4.5, and 3-24-3) were also somewhat larger than the M_n(th) values estimated from the total M_n(th) values of the three prepolymers. In the high molecular weight series (25-50-25, 15-70-15, and 10-80-10), the M_n(gpc) values were almost equal to the total M_n(th) values of the prepolymers. These GPC features are similar to those of the d-sb-PLAs shown above.

Thermal properties of d- and t-sb-PLAs

Figures 4 and 5 show the DSC curves of the obtained d- and t-sb-PLA samples in the second heating scan, respectively. Each sample showed both an exothermic peak at approximately 100 °C and an endothermic peak above 200 °C, which are attributed to the cold crystallization and the subsequent melting of the sc crystals, respectively. No melting behavior of hc crystals was noted, even in the samples having PLLA-rich compositions. This behavior is similar to that shown by the sb-PLA samples prepared by other methods;[19] however, the samples were different from the polymer blends of PLLA and PDLA homopolymers for which sc crystallization is likely accompanied by homo-chiral crystallization, particularly those of polymers with high M_n. Because the retro Diels-Alder reaction between anthracene and maleimide has been known to take place above 250 °C,[20] the present adducts are expected to be thermally stable up to the T_m of the sc crystals.

Figures 6a and b show the changes in melting temperature (T_{ms}) and heat of fusion (ΔH_{ms}), respectively, of the sc crystals, as determined by DSC, plotted as a function of the PDLA content for the various series of d- and t-sb-PLA samples. For both samples, the T_{ms} and ΔH_{ms} become higher as the PLLA/PDLA block ratios approach 1:1 due to the associated increased sc-crystallinity (Tables 2 and 4). Additionally, the effect of the molecular weight distribution is expected to be minimal because the M_w/M_n values of the samples were not significantly different from each other. In the d-sb-PLAs, the T_{ms} values were significantly higher in the lower M_n series (30 kDa) than in the higher M_n series (100 kDa); however, in the t-sb-PLAs, the values became slightly higher in the higher M_n series (100 kDa). When the d-sb-PLAs and t-sb-PLAs are compared, the T_{ms} values of the former samples were higher than those of the latter samples in the low M_n series (30 kDa), whereas the opposite relation was exhibited in the high M_n series (100 kDa). Furthermore, the ΔH_{ms} values were higher in the low M_n series than in the high M_n series with PLLA-rich compositions of both the d-sb-PLAs and t-sb-PLAs, whereas the values became nearly identical at the equivalent composition of PLLA/PDLA = 1/1. There was also a tendency for the t-sb-PLA samples to show increased crystallinity (or ΔH_{ms}) versus the d-sb-PLAs with equal PLLA/PDLA compositions within the same M_n series. These contrasting results may be explained by the different

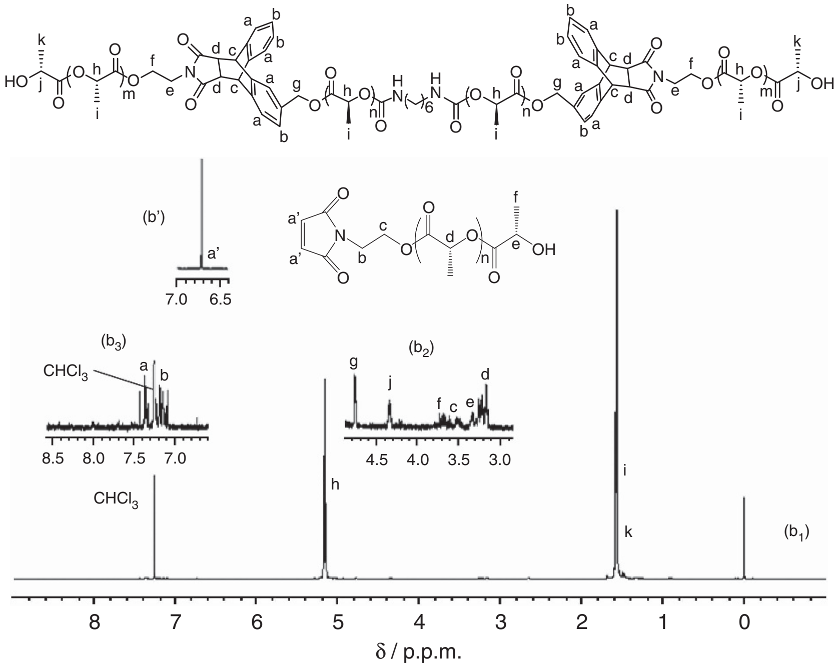


Figure 3 The ^{1}H NMR spectra of the as-prepared t-sb-PLA(7.5-15-7.5): (b_1) the full spectrum, (b_2-b_3) the expanded spectra for the weak signals, and (b') an expanded spectrum of the M-PDLA(7.5) for comparison.

Table 4 The results of Diels-Alder reaction of A-PLLA-A(2x) and M-PDLA(y) to obtain t-sb-PLA(y-2x-y)

t-sb-PLA y-2x-y	*Combination*	*PDLA (%)*	*Mn(th) (10^{-3})*	*Mn^a(gpc) (10^{-3})*	*Mw^a(gpc) (10^{-3})*	*Mw/Mn^a*	*T_m^b (°C)*	*X_c^c (%)*
7.5-15-7.5	A-PLLA-A (15)/ M-PDLA (7.5)	50	29.4	45.3	77.0	1.7	212.0	39.9
4.5-21-4.5	A-PLLA-A (21)/ M-PDLA (4.5)	30	29.6	43.5	82.7	1.9	204.7	31.6
3-24-3	A-PLLA-A (24)/ M-PDLA (3)	20	29.6	44.4	93.2	2.1	203.4	23.7
25-50-25	A-PLLA-A (50)/ M-PDLA (25)	50	98.3	92.9	190.0	2.0	220.1	41.1
15-70-15	A-PLLA-A (70)/ M-PDLA (15)	30	97.9	114.0	205.0	1.8	215.0	28.2
10-80-10	A-PLLA-A (80)/ M-PDLA (10)	20	98.4	109.0	207.0	1.9	211.3	18.5

[a] Determined by GPC relative to polystyrene standards with $CHCl_3$ as the eluent.
[b] Determined by DSC (the 2nd scan).
[c] Calculated on the basis of the specific heat of fusions of sc crystals (142 J/g).

sc-crystallizability of d-sb-PLAs and t-sb-PLAs consisting of different block lengths of PLLA and PDLA. In the lower M_n series (30 kDa), the t-sb-PLAs ought to have relatively shorter PDLA blocks than the d-sb-PLAs, which cannot form stable sc-crystallites, exhibiting lower T_{ms} values compared to those of d-sb-PLAs. However, the tri-block system is able to attain larger ΔH_{ms} values and higher crystallinities than the di-block system because the tri-block system ideally possesses stronger intermolecular interactions. Similarly, within the high M_n series (100 kDa), each of the enantiomeric blocks should have higher exclusion volumes and are likely separated from each other to make their sc crystallization more difficult. This effect was readily observed in the d-sb-PLAs of higher Mn (100 kDa), which show the lowest T_{ms} and ΔH_{ms} values. In contrast, ΔH_{ms} or crystallinity became the highest in the t-sb-PLA having an M_n of 100 kDa and an equivalent composition of PLLA/PDLA = 1/1, for which the block lengths were sufficiently high to effectively form the stable crystals. The T_{ms} and ΔH_{ms} may therefore be related to the ease with which the sc crystallites grow and the content of sc crystals formed, respectively. In accounting for crystallinity, the latter is expected to be greater in the t-sb-PLAs, and the T_{ms}, related to either the crystal size or the lamella thickness, is expected to be larger in the d-sb-PLAs.

It has been reported that sc-crystals with the parallel arrangement of PLLA and PDLA chains are more stable than those with anti-parallel arrangements.[21] The large difference in T_{ms} between the t-sb-PLA and d-sb-PLAs may be related to the different arrangements of the enantiomeric blocks, although the present data are not sufficient to draw a conclusion. However, the glass transition temperature (T_g) values are nearly equivalent for the d-sb-PLA and t-sb-PLA samples with similar amorphous domains.

Thermomechanical properties of polymer films of d- and t-sb-PLAs

The above d- and t-sb-PLA samples of high M_n series were fabricated into polymer films by ordinary hot-pressing at 240 °C and subsequent annealing at 140 °C for crystallization. The resulting polymer films were nearly transparent following annealing. Figure 7 shows the typical WAXS patterns of the representative films of the d- and t-sb-PLAs with PLLA/PDLA = 50/50 before and after annealing. It is evident that the melt-quenched films were amorphous, whereas the annealed films became highly crystalline, forming only sc crystals. The DSC analysis of these films (see Supplementary Table S2 in the Supplementary data) also supported the complete sc crystallinity of the annealed d- and t-sb-PLA films, except for the film of t-sb-PLA (15-70-15), which exhibited a small amount of hc crystals (4.5%) in conjunction with sc crystals. The small amount of hc crystals may have been produced during the long annealing process carried out at 140 °C. In contrast, the d-sb-PLA (70-30) with a PLLA/PDLA composition identical to that of the t-sb-PLA (15-70-15) showed a lack of hc crystallization following annealing. Therefore, we believe the two PDLA side blocks of t-sb-PLA (15-70-15) are too short to completely suppress the hc crystallization of the long PLLA center block. The sc crystallinities of the t-sb-PLA (25-50-25) and d-sb-PLA (50-50) were determined to be 49.3 and 36.6%, respectively, whereas those of the t-sb-PLA (15-70-15) and d-sb-PLA (70-30) were 33.2 and 30.2%, respectively. The t-sb-PLA system appears to exhibit a slightly higher crystallinity than the d-sb-PLA system, likely because of the stronger intermolecular interactions of the former. Because the annealed films retained transparency, the sc crystals involved are likely small in size. Figure 8 shows the rheological properties of the d- and t-sb-PLA films compared with those of a PLLA film ($M_n = 100$ kDa, control). It can be observed that the drop in G' was suppressed up to 200 °C in both the d- and t-sb-PLA films. In particular, the t-sb-PLA(25-50-25) film, showing the highest T_{ms} and ΔH_{ms}, exhibited the highest thermal resistivity in terms of the modulus drop throughout the whole temperature range (Figure 8a). Even around the α

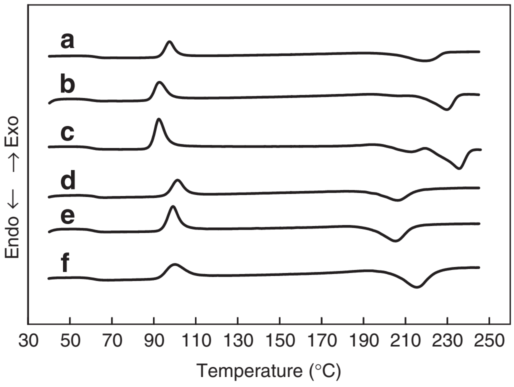


Figure 4 The DSC curves of d-sb-PLAs(x-y), x-y: (**a**) 24-6, (**b**) 21-9, (**c**) 15-15, (**d**) 80-20, (**e**) 70-30, and (**f**) 50-50 (in the second heating scan).

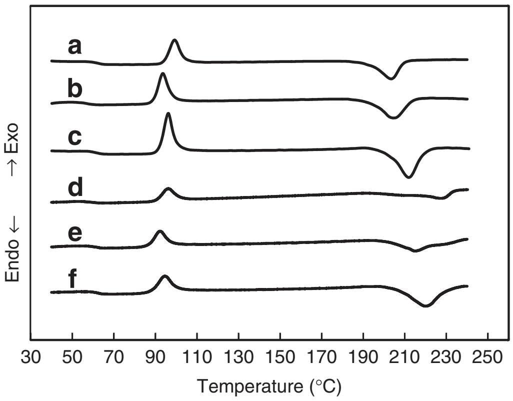


Figure 5 The DSC curves of t-sb-PLA(y-2x-y), y-2x-y: (**a**) 3-24-3, (**b**) 4.5-21-4.5, (**c**) 7.5-15-7.5, (**d**) 10-80-10, (**e**) 15-70-15, and (**f**) 25-50-25 (in the second heating scan).

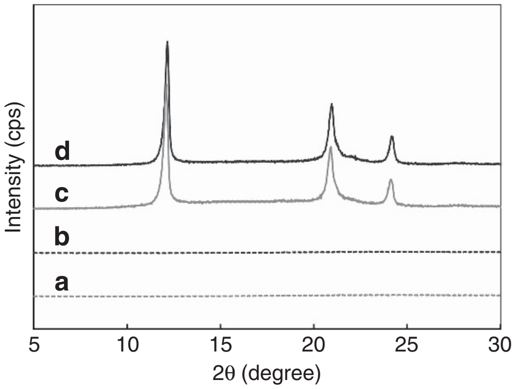


Figure 7 The WAXS patterns of the (**a**) melt-quenched and (**c**) annealed films of d-sb-PLA: 50-50 and the (**b**) melt-quenched and (**d**) annealed films of t-sb-PLA: 25-50-25. Due to the normalization of the intensities, the diffraction curves of (**a**) and (**b**) were flattened.

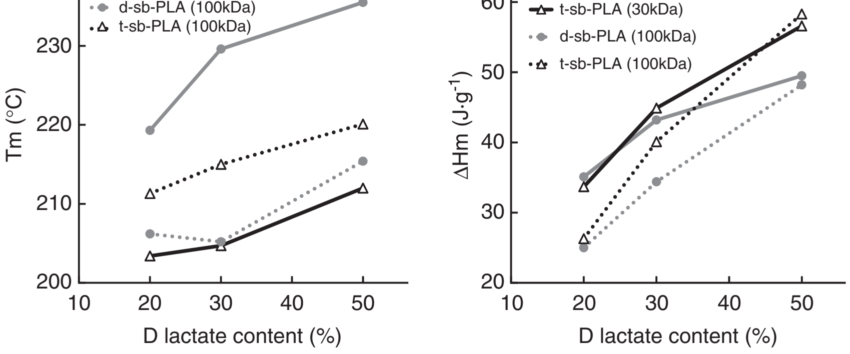


Figure 6 The changes in T_{ms} (**a**) and ΔH_{ms} (**b**) plotted as a function of PDLA content for the d- and t-sb-PLA samples of the two series of $M_n = 30$ and 100 kDa.

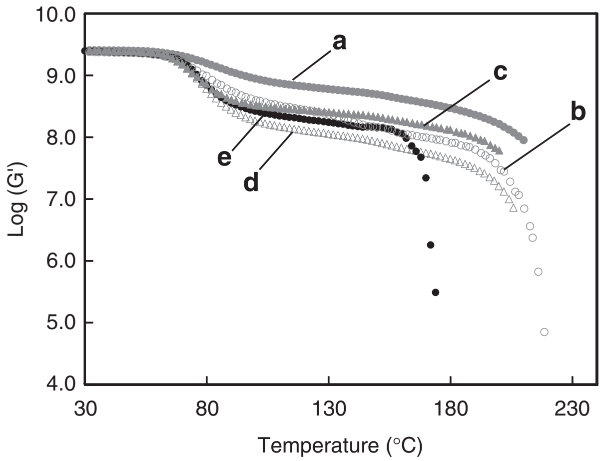


Figure 8 The thermomechanical properties of the melt-quenched and annealed films of t-sb-PLA(y-2x-y), y-2x-y= (**a**) 25-50-25 and (**b**) 15-70-15, and d-sb-PLA(x-y), x-y= (**c**) 50-50 and (**d**) 70-30, as compared with those of (**e**) a PLLA film (control).

relaxation temperature (or T_g), the change in G' was minimized. The t-sb-PLA films showed lower G' changes than the d-sb-PLA films with identical compositions. This behavior also can be attributed to the favored intermolecular interactions within the tri-block system. Therefore, t-sb-PLAs can provide thermo-resistant plastic materials for a variety of applications.

CONCLUSIONS

The d- and t-sb-PLA copolymers with different PLLA and PDLA block lengths and compositions were successfully prepared by utilizing the terminal Diels-Alder coupling method. The prepolymers of A-PLLA and M-PDLA were first prepared by the ROP of L- and D-lactides, respectively, and the di-anthracene-terminated A-PLLA-A was successfully synthesized by the reaction of A-PLLA and HMDI. Then, combinations of A-PLLA/M-PDLA and A-PLLA-A/M-PDLA gave d-sb-PLAs and t-sb-PLAs by spontaneous Diels-Alder coupling. Their block lengths and sequences were determined by the molecular weights of the prepolymers, as first synthesized. The resultant d-sb-PLA(x-y) and t-sb-PLA(y-2x-y) were found to have different thermal properties. The d-sb-PLA(15-15), which consisted of an equivalent length of the two enantiomeric blocks, showed the highest T_{ms} in the copolymers. The t-sb-PLAs were readily fabricated into transparent polymer films by hot-pressing. These films were found to have excellent thermal stability and mechanical properties because of the high sc crystallinity. This synthetic method, based on terminal couplings, can afford a convenient route to the fabrication of stereo block copolymers of PLLA and PDLA showing different thermal and mechanical properties.

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