Synthesis and Chain Extension of Poly(L-lactic acid-*co*-succinic acid-*co*-1,4-butene diol)

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ABSTRACT: L-Lactic acid (LA) was copolymerized with succinic acid (SA) and 1,4-butenediol (1,4-BED) in bulk state with titanium(IV) butoxide as a catalyst to produce poly(LA-*co*-SA-*co*-1,4-BED) (PLASBED). Poly(L-lactic acid) (PLLA) homopolymer obtained from a direct condensation polymerization of LA had weight average molecular weight (M_w) less than 4.1×10^4 and was too brittle to prepare specimens for the tensile test. Addition of SA and 1,4-BED to LA produced PLASB with M_w as high as 1.4×10^5 and exhibited tensile properties comparable to a commercially available high-molecular-weight PLLA. Chain extension by intermolecular linking reaction through the unsaturated 1,4-BED units in PLASBED with benzoyl peroxide further increased the molecular weight and made PLASBED more ductile and flexible to show elongation at break as high as 450%. Biodegradability of PLASBED measured by the modified Sturm test was nearly independent of the 1,4-BED content. Gel formation during the chain extension did not exert any significant influence on the biodegradability either. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 95: 1116–1121, 2005

Key words: biodegradable; polyesters; copolymerization

INTRODUCTION

Collecting refuse in nondegradable plastic bags and burying them in soil makes the ground foundation of the burial sites unstable and gives rise to the water clogging phenomena, which causes rain water to overflow, leading to contamination of the surrounding river or soil.

Biodegradable plastic bags provide a clue to the solution for these problems. Replacing nondegradable packaging materials with biodegradable ones for single use receptacles, fishing tools, and leisure articles would reduce long-lasting refuse considerably to alleviate the burden of the burial soil or that of the incinerator.[1–4]

Poly(L-lactic acid) (PLLA) is synthesized from L-lactic acid (LA), which is renewable and sustainable. PLLA is degraded by hydrolytic cleavage of the ester bonds to give lactic acid and its low-molecular-weight oligomers, which can be metabolized by both soil and marine microorganisms.[5,6]

PLLA has been used for niche applications such as biomedical materials.[1,2,7] However Cargill Dow recently launched a project to develop PLLA and began to operate a PLLA production plant on a commercial scale[8] to produce PLLA as a general purpose plastic.[9,10]

Direct condensation polymerization of LA in bulk state yields only low-molecular-weight polymers due to low reaction equilibrium constant.[8,11] High-molecular-weight PLLA is produced either by direct condensation polymerization of LA in solution state or by ring-opening polymerization through the lactide intermediate. In the first route, solvent with a high boiling point is used to remove the dissociated water by means of an azeotropic distillation technique.[11] Disadvantages of this route are the relatively large reactor and purification facility for the used solvent.[8] The second route also requires multistep processes.

Recently, Mitsui Chemical succeeded in production of high-molecular-weight PLLA by solid state polycondensation of PLLA oligomer obtained from bulk state polycondensation of LA.[12]

Helminen et al.[13] introduced a triethoxysilane end group to DL-lactide oligomers and synthesized high-molecular-weight polymers based on lactic acid units through an intermolecular linking reaction.

In this study, LA was copolymerized with succinic acid (SA) and 1,4-butene diol (1,4-BED). Chain extension was carried out through the unsaturated 1,4-BED units with benzoyl peroxide (BPO) after the direct condensation copolymerization in bulk state.

Thermal and mechanical properties along with biodegradability of the copolymers were examined before and after the chain extension.

EXPERIMENTAL

Materials

BPO (Acros organics) was purified by precipitation from chloroform into methanol and recrystallized in methanol at 0°C. L-Lactic acid (Aldrich, Milwaukee, WI), 1,4-butenediol (Aldrich), succinic acid (Aldrich), and tetrabutyl titanate (TNBT, Aldrich) were used as received. Other chemicals were used as received without further purification.

Instrumentation

Molecular weight and its distribution were measured by using GPC (Waters model 410, Waters Instruments, Rochester, MN), tetrahydrofuran eluent, 1.0 mL/min, 40°C, column (porosity: 10 μm, Styragel® HR1, HR2, HR4), employing polystyrene (Showadenko SL-105, Japan) as a standard.

Copolymers were characterized by ^{1}H-NMR spectra recorded at room temperature on a FT-NMR spectrometer (Bruker AC-250, Bruker Instruments, Billerica, MA). The copolymer (10 mg) was dissolved in 0.5 mL of chloroform-d (20 wt/vol %) and was subjected to the ^{1}H-NMR measurements.

The thermal properties of the specimens were determined by DSC (Perkin–Elmer DSC 7, Norwalk, CT). Thermal history of the products was removed by scanning from 30 to 200°C with a heating rate of 20°C/min. After cooling down the sample at -200°C/min to 30°C, it was reheated at 20°C/min to 200°C and the second scan DSC thermograms were obtained.

Sheets for the specimens were made by hot pressing (Lab Press, CARVER) at 170°C for 1 min under 4.0 atm and quick immersion into ice water.

Mechanical properties of the films were determined with a universal test machine (Model No. 4200, Instron, Canton, MA) at a cross-head speed of 10 mm/min according to ASTM D 638 at 20°C $\pm$ 1°C in RH 65%.

SEM (S-4200, Hitach, Japan) was used to observe the fractured surface morphology. Specimens were fractured while immersed in liquid nitrogen.

Preparation of poly(L-latic acid-*co*-succinic acid-*co*-1,4-butene diol) (PLASBED)

L-Lactic acid (LA), 1,4-butene diol, and succinic acid were added to a three-neck reactor (500 mL) that was connected to a vacuum system via a liquid nitrogen trap. To remove water the reactor was immersed in an oil bath at 100°C under nitrogen atmosphere for 1 h and then the reactor was added with titanium(IV) butoxide (0.08 ml) and heated at 180°C under mechanical stirring (300 rpm) for 3 h. The pressure was reduced stepwise to reach 1 Torr and then the reaction was continued for another 40 h. Polymers obtained were repeatedly dissolved in chloroform and precipitated from *n*-hexane to remove unreacted monomers or byproduct oligomers followed by drying at 35°C in a vacuum oven to a constant weight.

Chain extension of PLASBED using benzoyl peroxide

The chain extension was carried out in bulk state under a hot press by pressing a PLASBED sheet containing BPO, which was prepared by a chloroform solution casting, under 200 atm at a predetermined temperature for 8 min. The gel content was determined as the portion, in wt %, of the nonextractable material divided by the total weight of the original sample after the Soxhlet extraction for 48 h with boiling chloroform.

Evaluation of biodegradability by the modified Sturm test

PLLA, PLLABED, or the chain-extended samples were suspended in a sheet form (200 μm) in the test medium. Biodegradation was monitored at 27°C for 28 days by the modified Sturm test using the experimental setup assembled according to ASTM D 5209–91.

RESULTS AND DISCUSSION

Synthesis of PLASBED

L-Lactic acid/succinic aid/1,4-butene diol were copolymerized using TNBT as a catalyst. ^{1}H-NMR spectra of the resulting copolymer (PLASBED) are compared with that of the PLLA homopolymer in Figure 1. The peaks at 5.0 $\sim$ 5.2 ppm and those at 1.5 ppm originate from the methine and methyl protons of PLLA, respectively.

The protons in the double bond of 1,4-BED units exhibit their peaks at 5.7 ppm. The peaks at 2.7 ppm are due to the protons of SA units. The intensity ratio of the peaks at 2.7 ppm to those at 5.7 ppm is approximately 2 : 1, indicating that the amount of SA units in PLASBED and that of 1,4-BED units are equivalent on molar basis.

Table I demonstrates the characteristics of PLASBED. Bulk condensation polymerization of L-lactic acid produced a PLLA homopolymer with weight average molecular weight (M_w) of 4.1 $\times$ 10^4. Addition of SA and 1.4-BED to LA (0.25 mol each per 100 mol of LA) increased M_w and polydispersity of PLASBED to 1.4 $\times$ 10^5 and 3.7, respectively. However further increase of SA and 1,4-BED concentration in the copolymerization reaction medium to 1.0 mol each per 100 mol of LA decreased the M_w of PLASBED to 7.6 $\times$ 10^4.
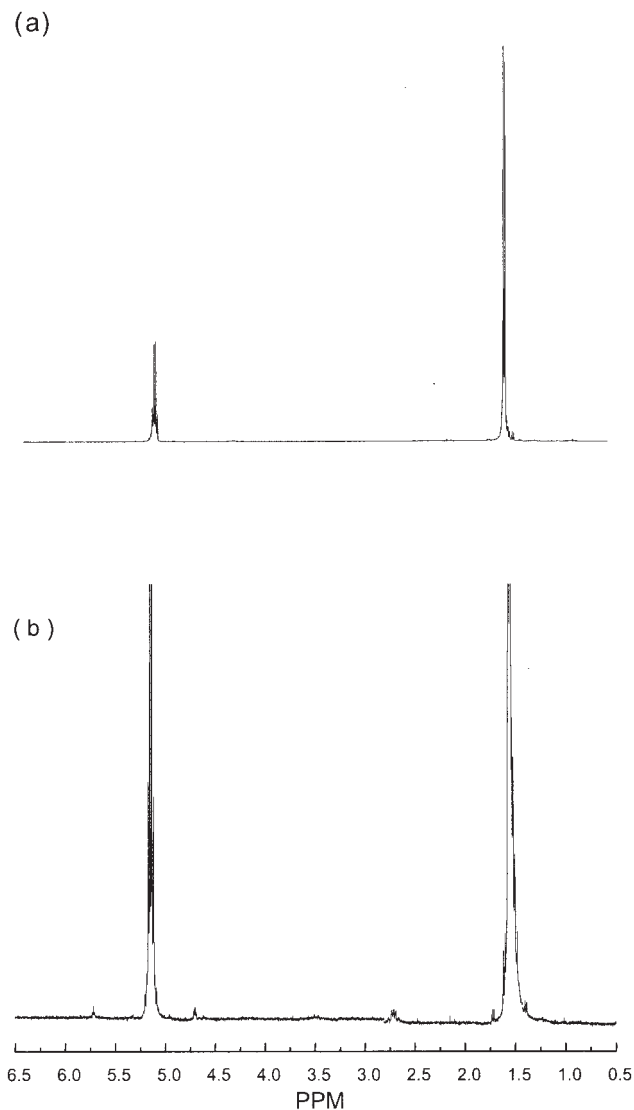
(a)

(b)

6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
                        PPM

Figure 1 ^{1}H-NMR spectra of PLLA homopolymer (a) and poly(L-lactic acid-*co*-succinic acid-*co*-1,4-butene diol) (PLASBED) (b).

The sample code in Table I, PLASBED 0.35, for example, indicates that PLASBED contains LA/SA/1,4-BED units at molar ratio of 100/0.35/0.35.

The as-produced PLASBED was completely soluble in chloroform, indicating that gel formation due to the intermolecular linking reaction of PLASBED through the unsaturated bonds of 1,4-BED units did not take place considerably during the copolymerization reaction.

Melting peak temperature (T_m), heat of fusion (ΔH_f), and glass transition temperature (T_g) of PLASBED were lower than those of the PLLA homopolymer.

Tensile properties of PLASBED are summarized in Table II. The PLLA homopolymer obtained from the bulk condensation polymerization was too brittle to prepare specimens for the tensile test. In contrast, PLASBED035 exhibited tensile properties comparable with those of a commercially produced high-molecular-weight PLLA purchased from Shimadzu Co. (Japan). PLASBED050 also showed an acceptable level of tensile properties, but PLASBED100 was too fragile to measure the tensile properties, as was the case of PLLA obtained from the direct bulk condensation polymerization.

Elongation at break of PLASBED depended strongly on the hot pressing temperature due probably to thermal deterioration.

Chain extension of PLASBED

PLASBED was chain extended by an intermolecular linking reaction through the unsaturated bonds of 1,4-BED units in PLASBED using BPO. The chain extension was realized under a hot press at 3 atm for 7.5 min.

Table III summarizes tensile properties of PLASBED after the chain extension. As was cited above, PLASBED100 was so brittle that measurement of its tensile properties was impossible. In sharp contrast, chain extension of PLASBED100 with 0.1 ~ 10 wt % of BPO improved the mechanical properties significantly, and the measurement of the tensile properties became feasible. Elongation at break reached almost 400% and the elongation modulus decreased to 80 MPa when the chain extension was carried out at 110°C with 1 wt % of

TABLE I
Characterization of Poly(L-lactic acid-*co*-succinic acid-*co*-1,4-butenediol) (PLASBED)

Sample code	Molar composition (Lactic acid/succinic acid/butene diol)		Thermal properties[a]			Molecular weight			Chloroform insoluble fraction (%)
	Feed	Copolymer product	T_m (°C)	ΔH (cal/g)	T_g (°C)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	
PLLA	100/0/0	100/0/0	152.4	34.1	62.9	2.3	4.1	1.8	0
PLASBED035	100/0.25/0.25	100/0.35/0.35	136.7	15.0	66.8	3.7	14	3.7	0
PLASBED060	100/0.50/0.50	100/0.60/0.60	131.5	21.6	56.4	3.9	13	3.4	0
PLASBED100	100/1.00/1.00	100/1.00/1.00	—	—	56.3	2.7	7.6	2.8	0

[a] Determined from the corresponding first scan DSC thermograms.

TABLE II
Tensile Properties of Poly(L-lactic acid-*co*-succinic acid-*co*-1,4-butenediol)(PLASBED)

Sample code	Hot pressing temperature[a] (°C)	E modulus (MPa)	Stress at maximum load (MPa)	Elongation at break (%)
PLLA[b]	150	n.d.	n.d.	n.d.
PLLA[c]	170	990 ± 170	50 ± 8.3	9.3 ± 1.6
	130	990 ± 86	32 ± 2.9	22 ± 11
PLASBED035	150	1200 ± 91	36 ± 3.8	9.1 ± 3.5
	170	1400 ± 15	35 ± 9.2	5.0 ± 0.9
	130	1100 ± 120	35 ± 6.0	6.7 ± 1.0
PLASBED050	150	1300 ± 140	36 ± 4.4	8.3 ± 4.7
	170	1400 ± 190	40 ± 6.0	5.6 ± 1.1
PLASBED100	150	n.d.	n.d.	n.d.

[a] Sample specimens were subjected to a hot press for 7.5 min.
[b] PLLA synthesized from direct bulk condensation of L-lactic acid ($M_n = 2.3 \times 10^4$ $M_w = 4.1 \times 10^4$).
[c] PLLA purchased from Shiamdzu Co. (Japan) ($M_n = 6.1 \times 10^4$ $M_w = 10.0 \times 10^4$).

BPO, indicating that the chain extension changed PLASBED to be more flexible and ductile.

Elongation at break increased and then decreased after a maximum as the chain extension temperature increased from 90 to 130°C.

The chloroform insoluble fraction of PLASBED100 became larger as the content of BPO and/or the chain extention temperature increased. It is worth noting that PLASBED after the chain extension at 110°C with 1 wt % of BPO was still completely soluble in chloroform despite the fact that the chain extension changed the tensile properties of PLASBED100 greatly.

Table IV demonstrates that the M_w of PLASBED100 increased from 7.6×10^4 to 2.3×10^5 and polydis-

TABLE III
Tensile Properties of PLASBED100[a] after chain extension with BPO

BPO content (wt %)	Chain extension temperature (°C)	E modulus (MPa)	Stress at maximum load (MPa)	Elongation at break (%)	Chloroform-insoluble fraction (%)
0.1	90	160 ± 25	9.4 ± 1.2	19 ± 6.2	0
	100	140 ± 25	11 ± 0.45	25 ± 4.7	0
	110	160 ± 11	11 ± 0.42	38 ± 8.1	0
	120	770 ± 44	19 ± 4.0	5.4 ± 1.6	0
	130	120 ± 10	2.1 ± 0.2	1.2 ± 0.54	0
0.5	90	110 ± 41	9.0 ± 1.7	16 ± 2.5	0
	100	120 ± 17	8.4 ± 1.1	17 ± 2.2	0
	110	150 ± 43	8.0 ± 0.74	87 ± 20	0
	120	740 ± 29	22 ± 3.8	5.6 ± 1.1	0
	130	650 ± 230	14 ± 6.7	4.3 ± 0.88	0
1.0	90	320 ± 31	8.8 ± 3.8	6.4 ± 1.4	0
	100	280 ± 33	11 ± 0.76	47 ± 13	0
	110	79 ± 18	11 ± 0.42	450 ± 180	0
	120	170 ± 30	5.4 ± 0.20	300 ± 50	20
	130	710 ± 71	25 ± 1.5	9.0 ± 2.5	30
5.0	90	120 ± 32	6.0 ± 1.1	57 ± 20	0
	100	210 ± 13	11 ± 0.20	31 ± 5.3	4
	110	17 ± 8.1	4.7 ± 0.55	420 ± 60	21
	120	75 ± 29	5.3 ± 1.8	240 ± 89	55
	130	420 ± 18	15 ± 2.3	36 ± 18	60
10	90	97 ± 14	7.2 ± 1.0	30 ± 9.3	8
	100	210 ± 24	8.9 ± 0.52	120 ± 13	20
	110	2.4 ± 1.1	4.4 ± 0.27	340 ± 32	59
	120	540 ± 100	17 ± 3.3	11 ± 5.4	78
	130	480 ± 34	14 ± 4.3	5.3 ± 9.5	100

[a] Copolymer composition (L-lactic acid: succinic acid: 1,4-butenediol : 100/1.0/1.0) on molar basis.

TABLE IV
Molecular Weight of the Chain-Extended PLASBED100

BPO content (wt %)	Chain extension temperature (°C)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_a	Glass transition temperature (°C)
0.0	—	2.7	7.6	2.8	56.3
	90	2.3	7.1	3.0	62.6
1.0	110	2.9	23	8.4	65.6
	130	1.9	8.6	4.6	66.8

persity was broadened from 2.8 to 8.4 due to the chain extension with 1 wt % of BPO at 110°C. The increase in M_w should contribute an important factor to the improvement of the tensile properties of PLASBED100.

Gelation of PLASBED100 took place as a result of the chain extension with 1 wt % of BPO at 130°C and 30 wt % of PLABSED100 became insoluble in chloroform.

It is curious to observe that the M_w of the chloroform-soluble fraction of PLASBED100 decreased from 2.3×10^5 to 8.6×10^4 as the chain extension temperature increased from 110 to 130°C. This can be rationalized as follows. As 1,4-BED units are incorporated randomly in PLASBED100, longer PLASBED100 molecules have a larger number of unsaturated bonds than shorter PLASBED100 molecules. Therefore it is more likely that longer PLASBED molecules bind to the gel fraction, leaving shorter PLASBED100 molecules behind to decrease the M_w of the chloroform-soluble fraction. Significant broadening of polydispersity after the chain extension supports this hypothesis. Thermal degradation at a higher temperature should be also responsible in part for the decreased M_w.

Degradation of PLASBED

Biodegradability of PLASBED was measured by using the modified Sturm test. It is generally accepted that polymer molecules with unsaturated bonds are biodegraded more slowly in comparison with those without unsaturated bonds. However, according to Figure 2, the biodegradability of PLASBED was nearly independent of the content of 1,4-BED in the range of 0 ~ 1.0 mol of 1,4-BED units/100 mol of LA units.

PLASBED100 subjected to chain extension at 110°C with 0 ~ 1.0 wt % of BPO was completely soluble in chloroform, but 21 and 59% of PLASBED100 became insoluble in chloroform when the BPO content was 5.0 and 10.0%, respectively (Table III). However Figure 3 reveals that biodegradability of PLASBED100 remained almost the same before and after the chain extension, indicating that gel formation did not retard biodegradation of PLASBED considerably.
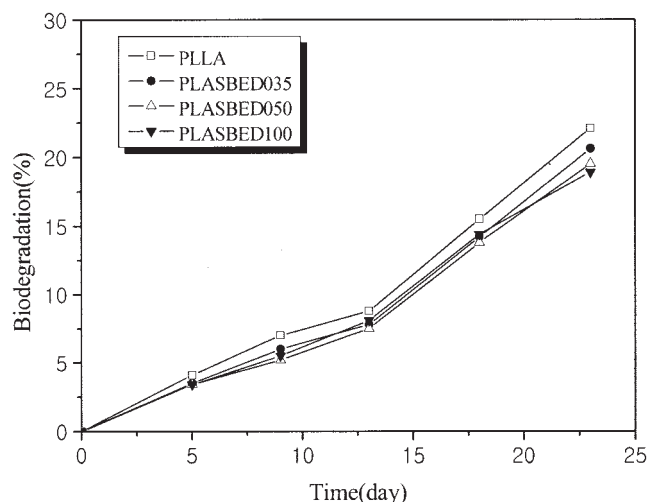
Figure 2 The modified Sturm test result for PLASBED as a function of 1,4-butene diol content.
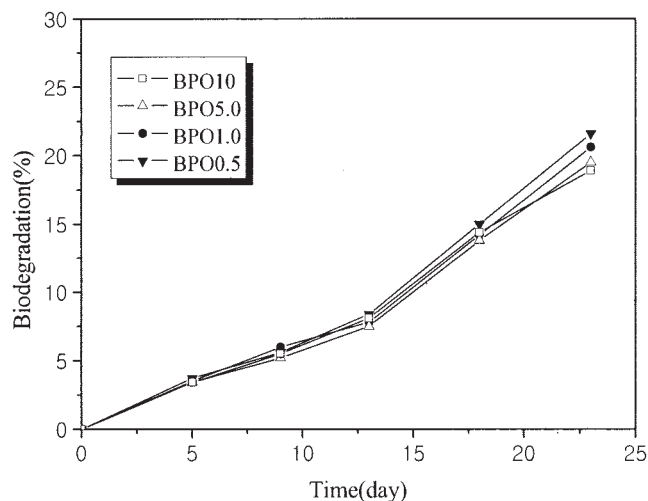

Figure 3 Biodegradation of PLASBED100 after the chain extension with different BPO concentration (wt %) under a hot press at 110°C measured by the modified Sturm test.

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