

# Chain Extension and Mechanical Properties of Unsaturated Aliphatic Copolyesters Based on Poly(L-lactic acid)

Eun-Soo Park,<sup>1</sup> Hae-Chul Cho,<sup>1</sup> Mal-Nam Kim,<sup>2</sup> Jin-San Yoon<sup>1</sup>

<sup>1</sup>Department of Polymer Science and Engineering, Inha University, 402-751 Incheon, South Korea

<sup>2</sup>Department of Biology, Sangmyung University, 110-743 Seoul, South Korea

Received 19 August 2002; accepted 6 February 2003

**ABSTRACT:** Chain extension of poly(L-lactic acid) (PLLA) with unsaturated groups (PLBM) was attempted using benzoyl peroxide (BPO) and the resulting variation in molecular weight and mechanical properties was explored. Bulk copolymerization of L-lactic acid (LA)/1,4-butanediol (BD)/maleic acid (MA) (100/1/1) isomerized some of the *cis*-structured maleate units into *trans*-structured fumarate units. The optically active LA promoted isomerization during the condensation polymerization. Chain extension of PLBM with BPO did not bring about a discernible increase in the molecular weight when the chain extension was carried out in various solvents with different radical abstraction abilities. In contrast, the hot pressing of PLBM containing BPO in-

creased the molecular weight and sometimes produced chloroform-insoluble gels depending on the BPO concentration and temperature. The chain extension at low temperatures increased the flexibility of PLBM considerably. However, PLBM lost the flexibility precipitously as the chain-extension temperature increased above 120°C. The biodegradation rate of PLBM was much slower than that of PLLA. The biodegradation rate was further lowered by the chain extension. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1802–1807, 2003

**Key words:** biodegradable; copolymerization; crosslinking; mechanical properties

## INTRODUCTION

Condensation polymerization of L-lactic acid (LA) in the bulk state produces poly(L-lactic acid) (PLLA) with a low molecular weight due to the equilibrium between PLLA and L-lactide as well as between PLLA and LA.<sup>1,2</sup> Solution polymerization of LA in organic solvents with a high boiling point<sup>3</sup> or ring-opening polymerization of L-lactide<sup>4–6</sup> has been used to produce high molecular weight PLLA. However, these techniques require multistep processes and increase the manufacturing cost considerably.

Recently, it was reported that ring-opening polymerization of L-lactide using a calcium-based catalyst proceeded very fast even at room temperature.<sup>7</sup> However, without a sophisticated facility, the molecular weight of PLLA by this technique remains in the range of several thousands. The molecular weight of aliphatic polyesters can also be increased by chain extension with chemicals such as diisocyanates, but this technique has been unsuccessful for PLLA chain extension.<sup>8–11</sup>

In this study, unsaturated PLLA was synthesized by the copolymerization of LA, 1,4-butanediol (BD), and

maleic acid (MA). Chain extension of the unsaturated PLLA (PLBM), that is, increase of the molecular weight of PLLA, was attempted through radical intermolecular linking reaction between the unsaturated bonds in PLBM using benzoyl peroxide (BPO). The elongation at break was increased astonishingly as a result of the extension in the bulk state under a hot press, indicating that low molecular weight PLLA molecules can be chain-extended during postprocessing procedures.

## EXPERIMENTAL

### Materials

BPO (Acros Organics, Morris Plains, NJ) was purified by precipitation from chloroform into methanol and recrystallized in methanol at 0°C. LA (85% aqueous solution), BD, MA, ethylene glycol dimethacrylate (DF), and triallyl cyanurate (TF) were all from Aldrich (Milwaukee, WI) and used as received.

### Characterizations

Molecular weight and its distribution was measured by gel permeation chromatography (GPC) [Waters 410, Waters, Milford, MA], an RI detector, THF eluent, 1.0 mL/min, 30°C, and a column (porosity: 10 μm, Stragel® HR 1, HR 2, HR 4, linear). Narrow molar mass polystyrene standards (Showadenko SL-105, Japan) were used for the universal calibration.

Correspondence to: J.-S. Yoon.

Contract grant sponsor: KOSEF; contract grant number: R01-1999-00288.

The thermal properties of the polymers were determined by DSC (Perkin–Elmer DSC 7, CT). The thermal history of the products was removed by scanning to 200°C at a heating rate of 20°C/min. After cooling the sample at 20°C/min to –100°C, it was reheated at 20°C/min to 200°C and DSC thermograms were obtained.

For nuclear magnetic resonance (NMR), the samples were dissolved in chloroform-*d* at room temperature and the sample concentration was about 1 wt/vol %. <sup>1</sup>H-NMR spectra were obtained using an NMR spectrometer working at 400 MHz (Varian Unity-Inova, Palo Alto, CA).

The mechanical properties of the polymers were measured using 1 × 4-cm dog-bone-type specimens. Tensile properties were characterized at a crosshead speed of 5 mm/min (Instron 4462, Hounsfield H25K-S, England). The gel content was determined as the portion, in weight percent, of the nonextractable material divided by the total weight of the original sample after Soxhlet extraction for 48 h with boiling chloroform.

### Polycondensation

An 85 wt % aqueous solution of LA, BD, and MA was 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 a nitrogen atmosphere for 1 h, then titanium(IV) butoxide was added to the reactor and heated at 180°C under mechanical stirring (300 rpm) for 3 h. The pressure was reduced stepwise to reach 2 torr, and then the reaction was continued for another 48 h. The 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

The chain extension of the copolymers was realized in solvents having different abilities of radical chain transfer. PLBM, 1.5 g, was dissolved in 100 mL of the purified solvent at ambient temperature, and then BPO and a multifunctional coagent (DF or TF) were added (5 wt % each). The reaction was advanced with gentle stirring at 60°C for 12 h. After completion of the reaction, the solution was slowly poured into *n*-hexane. The precipitate formed was washed with *n*-hexane twice and then dried in a vacuum oven at ambient temperature. The chain extension was carried out also in the bulk state under a hot press by pressing a PLBM sheet containing BPO, which was prepared by chloroform solution casting, under 200 atm at a predetermined temperature for 10 min. The product obtained

by the latter method was expected to have a higher molecular weight than that of the product made by the former method because of the absence of solvent radical chain-transfer reactions. The gel fraction was isolated by chloroform Soxhlet extraction for 48 h.

### Evaluation of biodegradability by the modified Sturm test

PLLA, PLBM, 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 D5209-91.<sup>13</sup>

## RESULTS AND DISCUSSION

Figure 1 shows <sup>1</sup>H-NMR spectra of the PLBM produced by copolymerization of an LA/BD/MA (100/1/1) mixture. Methyl protons and methine protons of the LA units exhibit their peaks at 1.7 and 4.55 ppm, respectively. The methine protons of MA appeared at 6.5 ppm, which shifted to 6.9 and 6.3 ppm when MA was copolymerized into PLBM as maleate and fumarate, respectively. The peaks at 1.65 and 4.1 ppm correspond to methylene protons of the BD units.

The composition of LA (*x*), BD (*y*), and MA (*z*) units in PLBM was determined from the well-resolved a, b, c, and f peaks in Figure 1 using the following equations:

$$x + y + z = 1 \quad (5a)$$

$$y = \frac{f}{4c} x \quad (5b)$$

$$z = \frac{a + b}{2c} x \quad (5c)$$

The content of the *cis*-structured maleate and the *trans*-structured fumarate units in PLBM was calculated from the a and b peaks, respectively.

The *trans/cis* ratio in an aliphatic polyester (PBSM) produced from BD/succinic acid (SA)/MA (50/45/5) was 0.34, and this ratio was nearly independent of the MA content in the copolymerization reaction medium.<sup>12</sup> In sharp contrast, the *trans/cis* ratio in PLBM produced from LA/BD/MA (100/1/1) was 0.86, indicating that the isomerization of MA units depend on the structural environment around the hydroxyl groups. This is not an unexpected result in that the isomerization from *cis* to *trans* could be promoted in the reaction between MA with the optically active LA. Dunjic et al.<sup>14</sup> also reported that the diol type, presence of aromatic acid, catalyst concentration, polymer-

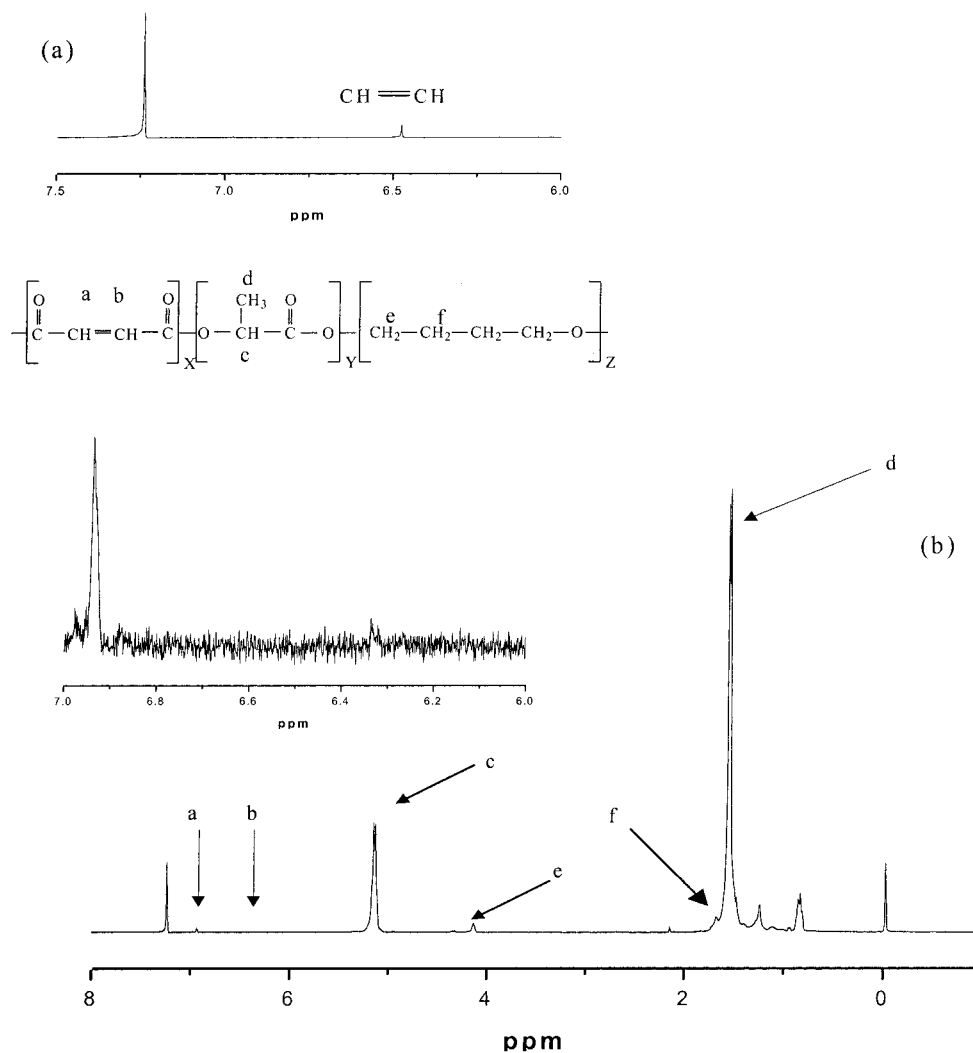


Figure 1 NMR spectrum of PLBM: (a) maleic acid; (b) PLBM.

ization temperature, and time affected the *cis/trans* isomerization.

When PLBM (0.1 g/mL in a chloroform solution) was reacted with BPO or with BPO/TF (each 5 wt % based on PLBM) at 60°C for 12 h, the *trans/cis* ratio was decreased from 0.86 to 0.56–0.59, while the ratio remained almost constant when PLBM was reacted with BPO/DF (Table I). GPC results on the molecular weight after the reaction are demonstrated in Table II.

The reaction with BPO or with BPO/TF brought about a slight increase in the molecular weight, but the molecular weight remained practically unchanged after the reaction with BPO/DF. The fact that the *trans/cis* ratio of PLBM did not change after the reaction with BPO/DF should be ascribed to the unsuccessful chain extension of PLBM with BPO/DF.

The chain extension with BPO in solvents such as benzene, 1,4-dioxane, and toluene, whose radical abstraction ability was lower than that of chloroform, did not discernibly increase the molecular weight of

PLBM either (Table III), and the gel content in PLBM from the reaction in the four solvents was nil. In marked contrast to PLBM, the molecular weight of PBSM increased two to three times depending on the

TABLE I  
Composition of the Unsaturated Aliphatic Polyesters Soluble in Chloroform

Sample code	BD	LA	MA		
			<i>cis</i>	<i>trans</i>	<i>trans/cis</i>
PLBM	0.027	1	0.035		0.86
			0.019	0.016	
PLBM-BPO	0.023	1	0.028		0.56
			0.018	0.010	
PLBM-BPO-DF	0.024	1	0.033		0.82
			0.018	0.015	
PLBM-BPO-TF	0.029	1	0.029		0.59
			0.018	0.011	

TABLE II  
Molecular Weight of the Aliphatic Polyesters Soluble in Chloroform Before and After Chain Extension

Sample code	Chain extension in chloroform solution			Insoluble <sup>b</sup> fraction
	$M_n \times 10^{-4}$ <sup>a</sup>	$M_w \times 10^{-4}$ <sup>a</sup>	PDI <sup>a</sup>	
PLBM	1.17	2.54	2.17	0%
PLBM-BPO	1.19	3.16	2.64	0%
PLBM-BPO-DF	1.19	2.72	2.27	0%
PLBM-BPO-DF	1.19	3.27	2.73	0%

<sup>a</sup> Determined by GPC.

<sup>b</sup> Determined after the Soxhlet extraction with boiling chloroform.

content of the unsaturated groups as a result of the chain extension with BPO in the chloroform solution.<sup>12</sup>

PLBM film was cast from a chloroform solution containing BPO and hot-pressed at various temperatures for 10 min. In the absence of BPO, the molecular weight remained practically unchanged after the hot pressing. However, the molecular weight increased and the molecular weight distribution broadened considerably as soon as 0.5 wt % of BPO was added. The amount of the gel fraction increased with an increase in the BPO content and/or with an increase in the reaction temperature.

The hot pressing of PBSM containing 2.3 mol % of MA units with 5 wt % of BPO at 150°C did not bring about any gelation, and the amount of the gel fraction in PBSM with 5.7 mol % of the unsaturated units barely reached 33.6% after chain extension.<sup>12</sup> In contrast, gelation began to take place in PLBM at 130°C with BPO as low as 0.5 wt %. At 150°C with 5 wt % of BPO, the gel fraction in PLBM amounted to 96%, indicating that the gelation in the bulk state took place more easily in PLBM than in PBSM.

A considerable increase of the molecular weight of PLBM, especially an increase of the weight-average molecular weight rather than that of the number-average one, was observed after chain extension when

TABLE III  
Molecular Weight of the Aliphatic Polyesters Soluble in Chloroform Before and After Chain Extension in Various Solvents

Solvent	Chain extension in various solvents			Insoluble <sup>b</sup> fraction
	$M_n \times 10^{-4}$ <sup>a</sup>	$M_w \times 10^{-4}$ <sup>a</sup>	PDI <sup>a</sup>	
PLBM	0.68	1.55	2.26	0%
Benzene	0.64	1.42	2.23	0%
1,4-Dioxane	0.66	1.59	2.40	0%
Chloroform	0.59	1.41	2.39	0%
Toluene	0.66	1.55	2.22	0%

<sup>a</sup> Determined by GPC.

<sup>b</sup> Determined after the Soxhlet extraction with boiling chloroform.

gelation did not occur.<sup>15</sup> However, when gelation took place, the molecular weight of the chloroform-soluble fraction of PLBM declined as the gel content increased. Jin et al.<sup>12</sup> also observed the molecular weight of the chloroform-soluble fraction of PBSM to decrease with an increase in the amount of the gel fraction. This can be ascribed to the fact that shorter polymer molecules would possess a smaller number of unsaturated units compared to longer ones, so that the shorter polymer molecules would have more chance to remain unanchored to the gel networks.<sup>11</sup>

The PLLA homopolymer having an  $M_w$  of  $1.06 \times 10^5$  exhibited its glass transition temperature ( $T_g$ ) at 64.5°C, while the  $T_g$  of PLBM with an  $M_w$  of  $2.5\text{--}3.0 \times 10^4$  appeared at 56.9°C. It was curious to observe that the  $T_g$  of the PLBM film made from the chloroform solution casting appeared at 30.3–32.4°C after hot pressing at 120°C for 10 min in the absence of BPO (PLBM120C0W). The experiments were repeated three times but gave similar results on the  $T_g$ . We do not have, at present, any clear explanation for the  $T_g$  shift to the lower temperature. Some chain branching could take place in PLBM during hot pressing even though an increase of  $M_w$  measured by GPC was not significant and the chain branching would decrease the  $T_g$ . The  $T_g$  of PLBM increased as the gel fraction increased due to the chain extension but did not exceed 45°C.

The effect of chain extension on the mechanical properties of PLBM is demonstrated in Table IV. The high molecular weight PLLA homopolymer was very brittle in that it showed a 1.7% elongation at break. As for PLBM, it was so mechanically fragile and brittle that its specimen for the tensile test could not even be prepared. However, the elongation at break of PLBM110C1W (PLBM film with 1 wt % BPO hot-pressed at 110°C for 10 min) was 45 times longer, and the maximum stress of PLBM110C1W was 11 times lower than were the respective properties of the high molecular weight PLLA homopolymer, indicating that the chain extension endowed PLBM with more ductile properties.

In comparing the experimental data of the tensile properties for PLBM120C1W, PLBM120C3W, and

**TABLE IV**  
**Molecular Weight of the Aliphatic Polyesters Soluble in Chloroform Before and After the Chain Extension Under a Hot Press**

Sample code	Chain extension under the hot press				
	$M_n$	$M_w$	PDI	Insoluble fraction (%)	$T_g$ (°C)
(1)					
PLBM	12,900	29,600	2.29	0	57
PLLA <sup>a</sup>	54,700	105,700	2.45	0	65
PLBM120C0W	13,400	27,600	2.06	0	32
PLBM120C0.5W	15,100	162,900	10.8	0	27
PLBM130C0.5W	14,100	150,200	10.7	4	27
PLBM140C0.5W	14,500	131,300	9.04	7	28
PLBM150C0.5W	14,600	126,000	8.62	7	29
PLBM160C0.5W	13,100	108,900	8.29	10	29
PLBM	11,700	25,400	2.17	0	57
PLBM100C1W	13,000	102,600	7.92	17	30
PLBM110C1W	9,400	36,500	3.88	22	29
PLBM120C1W	10,300	39,600	3.84	27	29
PLBM130C1W	11,200	43,000	3.83	29	30
PLBM140C1W	11,400	61,800	5.43	32	32
PLBM150C1W	11,200	59,400	5.30	34	32
PLBM160C1W	11,000	60,700	5.52	35	32
(2)					
PLBM	11,700	25,400	2.17	0	57
PLLA <sup>a</sup>	54,700	105,700	2.45	0	65
PLBM120C0W	13,100	26,900	2.05	0	30
PLBM120C5W	7,200	12,500	1.74	85	27
PLBM130C5W	7,400	13,800	1.87	86	30
PLBM140C5W	7,500	14,800	1.98	86	38
PLBM150C5W	6,000	13,000	2.18	84	38
PLBM160C5W	6,000	13,000	2.18	82	43
PLBM120C10W	7,000	12,600	1.79	95	28
PLBM130C10W	6,400	11,500	1.79	96	29
PLBM140C10W	6,100	11,400	1.87	97	34
PLBM150C10W	5,600	10,300	1.85	99	38
PLBM160C10W	5,700	10,500	1.83	99	45
(3)					
PLBM	11,700	25,400	2.17	0	57
PLLA <sup>a</sup>	54,700	105,700	2.45	0	65
PLBM120C0W	13,100	26,900	2.05	0	30
PLBM120C0.1W	12,400	38,800	3.13	0	28
PLBM120C0.5W <sup>b</sup>	12,900	64,900	5.03	0	27
PLBM120C1W	10,600	38,000	3.60	27	27
PLBM120C3W	6,600	16,100	2.45	85	28
PLBM150C1W	11,800	45,700	3.87	44	32
PLBM150C3W	7,400	14,200	1.91	84	33
PLBM150C5W	8,100	14,800	1.83	96	37
PLBM150C10W	5,600	10,300	1.85	99	38
PLBM150C15W	5,000	7,900	1.58	99	45

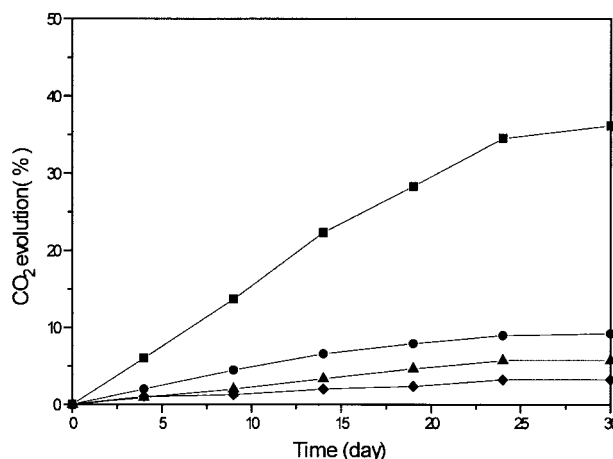
The acronym PLBM120C0.5W means that the chain-extension reaction was carried out at 120°C with 0.5 wt % of BPO for 10 min.

<sup>a</sup> PLLA (from Shimadzu Co.) annealed under a hot press at 120°C for 10 min.

<sup>b</sup> PLBM 120C05W in Table IV (1) and PLBM 120C0.5W in Table IV (3) were produced from PLBM having  $M_w$ 's of 29,600 and 25,400, respectively.

PLBM120C5W, it can be said that an excessive increase of the BPO content could be detrimental to the improvement of the tensile properties. The steep decrease of the elongation at break as the chain-extension temperature increased above 120°C, as could be perceived from the experimental data on the tensile properties of PLBM120C5W, PLBM130C5W, PLBM140C5W, PLBM150C5W, and PLBM160C5W (Table V), states clearly that the chain-extension temperature exerted the most crucially detrimental influence on the elongation at break. This conclusion can be confirmed by the fact that PLBM120C10W showed a higher elongation at break than that of PLBM150C5W even though the former had larger amount of the gel fraction than did the latter.

Figure 2 shows the modified Sturm test results for PLLA and PLBM. PLBM120C0W degraded much more slowly than did PLLA, even though the molecular weight of the former was much lower than that of the latter. The abrupt decrease in the biodegradation



**Figure 2** Modified Sturm test results for PLLA and PLBM: (■) PLLA (Shimadzu Co.); (●) PLBM120C0W; (▲) PLBM120C0.5W; (◆) PLBM120C5W.

rate was also observed when MA units were incorporated into PBS.<sup>12</sup> The chain extension further decreased the biodegradation rate of PLBM.

This work was supported by the Interdisciplinary Research Program of KOSEF (Grant No. R01-1999-00288). The authors thank Miss Ji Hye Shin for the modified Sturm test.

**TABLE V**

**Mechanical Properties of Unsaturated Aliphatic Polyesters After Chain Extension**

Sample code	Elongation at break (%)	Maximum stress (kg/mm <sup>2</sup> )	Gel content (%)
(1)			
PLLA <sup>a</sup>	2 ± 0.3	4.4 ± 1.3	0
PLBM100C1W	71 ± 16	0.3 ± 0.0	17
PLBM110C1W	77 ± 15	0.4 ± 0.1	22
PLBM120C1W	55 ± 8	0.6 ± 0.1	27
PLBM130C1W	25 ± 8	1.1 ± 0.4	29
PLBM120C3W	54 ± 12	0.5 ± 0.1	85
PLBM120C5W	53 ± 5	0.5 ± 0.1	85
PLBM130C5W	16 ± 6	0.7 ± 0.2	86
PLBM140C5W	10 ± 4	1.5 ± 0.4	86
PLBM150C5W	2 ± 0.6	1.0 ± 0.3	84
PLBM160C5W	2 ± 0.2	1.3 ± 0.3	83
(2)			
PLLA <sup>a</sup>	1.7 ± 0.3	4.4 ± 1.3	0
PLBM120C10W	17 ± 3.8	1.3 ± 0.4	95
PLBM140C10W	3.9 ± 1.2	1.7 ± 0.5	97
PLBM160C10W	0.7 ± 0.1	1.3 ± 0.3	96
PLBM150C3W	9.8 ± 2.1	0.9 ± 0.4	84
PLBM150C5W	1.1 ± 0.8	1.3 ± 0.3	96
PLBM150C15W	1.0 ± 0.8	1.2 ± 0.4	99

PLBM100C1W means that PLBM (BPO: 1 wt %) was chain-extended under a hot press at 100°C for 10 min.

<sup>a</sup> PLLA (from Shimadzu Co.) annealed under hot press at 120°C for 10 min.

## References

- Hiltunen, K.; Harkonen, M.; Seppala, J. V.; Vaananen, T. *Macromolecules* 1996, 29, 8677.
- Kim, S. H. Ph.D. Dissertation, Seoul National University, South Korea, 1992.
- Hiltunen, K.; Seppäiäö, J. V.; Härkäönen, M. *Macromolecules* 1997, 30, 373.
- Bailey, W.; Gapud, B. *Polym Prep* 1984, 25, 58.
- Deng, X.; Yuan, M.; Li, X.; Xiong, C. *Eur Polym J* 2000, 36, 1151.
- Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym Int* 1998, 46, 177.
- Zhong, Z.; Dijkstra, P. J.; Birg, C.; Westernhausen, M.; Feijen, J. *Macromolecules* 2001, 34, 3863.
- Lunt, J. *Polym Degrad Stab* 1998, 59, 145.
- Bogdanov, B.; Toncheva, V.; Schacht, E.; Finelli, L.; Sarti, B.; Scandola, M. *Polymer* 1999, 40, 3171.
- Hiltunen, K.; Seppäiäö, J. V.; Härkäönen, M. *J Appl Polym Sci* 1997, 64, 865.
- Yoon, J. S.; Jin, H. J.; Kim, D. S.; Cho, H. C.; Kim, M. N. *Polym Prepr* 2001, 42, 524.
- Jin, H. J.; Kim, D. S.; Lee, B. Y.; Kim, M. N.; Lee, I. M.; Lee, H. S.; Yoon, J. S. *J Polym Sci Part B Polym Phys* 2000, 38, 2240.
- Kim, M. N.; Kang, E. J. *Kor J Mycol* 1995, 23, 348.
- Dunjic, B.; Sepulchre, M. O.; Sepulchre, M.; Spassky, N.; Djonlagic, J. *Macromol Chem Phys* 1998, 199, 1051.
- Borda, J.; Bodnar, I.; Keki, S.; Sipos, L.; Zsuga, M. *J Polym Sci Part A Polym Chem* 2000, 38, 2925.