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Synthesis and Physical Properties of Poly(L-lactic acid)-Poly(dimethyl siloxane) Multiblock Copolymers Prepared by Direct Polycondensation

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ABSTRACT: Multiblock copolymers consisting of poly(L-lactic acid) and poly(dimethyl siloxane) were prepared by the polycondensation of oligo(L-lactic acid) (OLLA) with dihydroxyl-terminated oligo(dimethyl siloxane) and dicarboxyl-terminated oligo(dimethyl siloxane). Copolymers with number-average molecular weights of 18,000−33,000 Da and various content ratios of oligo(dimethyl siloxane) (ODMS) unit were obtained by changing the feed ratio of these oligomers. A film prepared from the copolymer with an ODMS content ratio of 0.37 exhibited two independent peaks at −107°C and 37°C in the mechanical loss tangent for temperature dependence, suggesting the formation of microphase separation between the OLLA and ODMS segments. The film had a tensile strength of 3.2 MPa and a high elongation of 132%. The film also exhibited a high strain recovery even after repeated straining. The incorporation of dimethyl siloxane units as multiblock segments was confirmed to improve the flexibility of poly(L-lactic acid). © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40211.

KEYWORDS: poly(L-lactic acid); poly(dimethyl siloxane); block copolymer; mechanical property; elasticity

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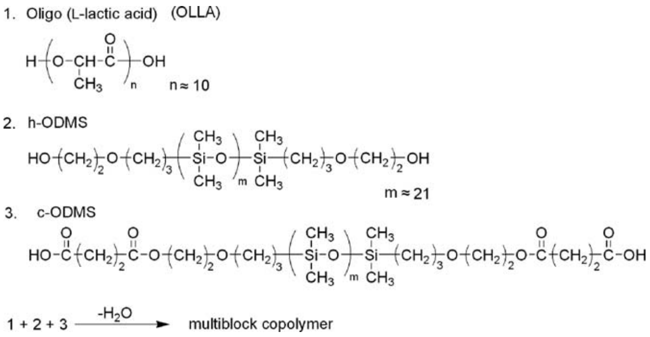
INTRODUCTION

Aliphatic polyesters have been energetically investigated in recent years because of their excellent biodegradability and biocompatibility. Among them, poly(L-lactic acid) (PLLA) has been widely applied as an environmentally friendly material and it has also been used in medical applications including surgical sutures, drug carriers, and tissue-engineering materials.[1–8] However, PLLA still has ample space for improvement in its mechanical and thermal properties in order to further expand its applications. For example, the improvement of the fairly low impact strength and elongation at break inherent in PLLA will lead to the creation of new rubbery materials and orthopedic applications.[9,10] Incorporating soft segments into the main chain of PLLA has been attempted to improve its flexibility and reduce its brittleness. The synthesis of PLLA block copolymers containing poly(ethylene glycol) (PEG) as a soft segment has been fairly well studied.[11–17] Zhu et al. have reported the characterization of poly(lactide)-PEG triblock copolymers prepared by using lactide and PEG with hydroxyl end-groups.[11] The tensile elongation of the copolymers increases with the content ratio of PEG in the copolymer. The copolymer with a PEG content of 58 mol % exhibited a high elongation of over 500%. Yamaoka et al. have reported the physical properties of multiblock copolymers consisting of PLLA and poly(oxypropylene-*co*-oxyethylene) in detail.[12] The tensile strength and modulus of the copolymers decrease as the content ratio of the poly(oxypropylene-*co*-oxyethylene) unit increases, and one such copolymer exhibited a fairly high elongation of 1460%. The synthesis and characterization of PLLA-poly(ε-caprolactone) block copolymers have also been investigated.[18] These block copolymers have tensile strengths of 10−20 MPa and high elongations of ca. 600%. Among them, the multiblock-type copolymer with a content ratio of PLLA to poly(ε-caprolactone) of 1.5 exhibited a strain recovery of more than 95% at 100% strain, whereas the triblock copolymer and random copolymer exhibited very low strain recoveries.

Poly(dimethyl siloxane) (PDMS) is another suitable soft segment for incorporation into PLLA to improve its properties. This is because PDMS has not only a fairly low glass-transition temperature (T_g) but also high biocompatibility. Moreover, in contrast to hydrophilic PEG segments, the hydrophobicity inherent in PDMS might enable the PLLA copolymer to be utilized in new applications. There are some studies on the PLLA block copolymer containing PDMS segments.[13,19–23] Kricheldorf et al. have reported the synthesis and characterization of A-B-A type triblock copolymers with various kinds of soft segments, and they examined one such copolymer with PDMS as the B block.[13] Their report focuses on blocks of poly(L-lactide) and



Scheme 1. Synthesis of PLLA-PDMS multiblock copolymer.

poly(D-lactide) and the accompanying differences in crystallinity of the resulting block copolymer. PLLA triblock copolymers with PDMS segments have been also studied by Hazer et al.[20] The triblock copolymer, which is prepared by using PDMS with two amino end groups, exhibited somewhat higher elongation than neat PLLA, but the maximum elongation remained at 17%. Bachari et al. prepared multiblock-type copolymers consisting of PLLA and PDMS segments by the condensation of α,ω-diallyl PLLA and α,ω-disily PDMS.[24] They discuss the influence of the length of the PDMS segment on the thermal property of the copolymers, and they did not discuss the mechanical properties. The properties, especially the mechanical properties of multiblock copolymers consisting of PLLA and PDMS are of interest to those interested in their applications; however, very few studies have investigated or reported on this information. We have attempted to prepare multiblock copolymers consisting of PLLA and PDMS by the condensation of oligo(L-lactic acid) (OLLA) with dihydroxyl-terminated oligo(dimethyl siloxane) (h-ODMS) and dicarboxyl-terminated oligo(dimethyl siloxane) (c-ODMS) in order to characterize them. In this report, the physical properties, especially the mechanical properties, are discussed.

EXPERIMENTAL

Materials

L-Lactic acid (92% aqueous solution), diphenyl ether, and succinic anhydride were purchased from Wako Chemicals (Osaka, Japan) and used as received. Sn(II) 2-ethylhexanoate was also purchased from Wako Chemicals and purified according to the literature.[25]

α,ω-bis(3-(2-Hydroxyethoxy)propyl)-oligo(dimethyl siloxane), which was used as h-ODMS in this work, was supplied by Shin-Etsu Chemical (Tokyo, Japan). The average degree of polymerization of h-ODMS was confirmed to be ca. 21 by the quantitative measurement of hydroxyl groups. Other reagents were used as received.

Oligomers

L-Lactic acid (50 g) was dehydrated at 150°C under atmospheric pressure for 1 h, and then under 50 mmHg of pressure for 3 h. A high viscous liquid of OLLA was obtained. The average degree of polymerization of OLLA was calculated to be ca. 10 from the integral ratio of the methine signal at 4.4 ppm (CH of the hydroxyl terminal of the 2-hydro-propionate unit) to that at 5.2 ppm (CH for the L-lactic acid) in a ^{1}H-NMR spectrum.[12]

Dicarboxyl-terminated oligo(dimethyl siloxane) was prepared by the addition of succinic anhydride to h-ODMS. h-ODMS (10 g) and 0.58 g of triethyl amine were dissolved in 150 mL of benzene, and then 5.7 g of succinic anhydride was added to the solution. After refluxing the solution for 5 h, the benzene and triethyl amine were removed with an evaporator. The residue was purified by extraction with *n*-hexane and methanol. The chemical structures of oligomers used in this work are presented in Scheme 1.

Copolymerization

OLLA, h-ODMS, c-ODMS, and diphenyl ether as solvent were added by weight into a flask equipped with a reflux condenser. The total amount of oligomers was adjusted to 10 g, and the same molar amounts of h-ODMS and c-ODMS were always used. After the addition of 10 mg of Sn(II) 2-ethylhexanoate, the mixture was stirred on a magnetic stirrer at 150°C under 30 mmHg pressure for 2 h, and further at 160°C under 20 mmHg pressure for 15 h. The coolant water that passed through the reflux condenser was thermo-controlled to allow for the vaporization of eliminated water and the reflux of diphenyl ether at the same time. After removing the diphenyl ether under reduced pressure, the product was dissolved in chloroform and poured into an excess of methanol. The precipitate was dissolved again in chloroform and poured into *n*-hexane. The precipitate polymer was dried at room temperature in vacuo. A PLLA homopolymer, which was used for the control for physical property investigations, was prepared from OLLA by a similar procedure to the one described above.

Film Preparation

Block copolymers were hot-pressed at their respective melting temperatures and immediately quenched in order to prepare film samples with thickness of ca. 0.15 mm. The heat-treatment of the film samples was carried out at 100°C for 1 h under an inert atmosphere.

Measurements

^{1}H-NMR spectra were recorded with a Bruker spectrometer DRX500 by using 5% solutions in $CDCl_3$. Chemical shifts (δ) were given in ppm using the signal for residual undeuterated solvent as an internal reference. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography. The analyzer was made up of a Hitachi L-7110 pump and L-7490 RI detector. A Shodex K-806L gel column was used with chloroform as the eluent at 35°C. Polystyrene standards were used for calibration. Elemental analysis was performed on a Yanaco CHN corder MT-5. The wide-angle X-ray diffraction patterns of the film samples were recorded with an X-ray diffractometer (Rint2000; Rigaku) using Ni-filtered Cu Kα radiation. The melting temperatures (T_m) of the copolymers were measured with a Thermoflex DSC 8230 (Rigaku) under nitrogen at a heating rate of 10°C/min. The enthalpy of fusion (ΔH_f) was calculated from the area of the melting peak on a thermogram by calibrating with 2-naphthol.

The dynamic storage modulus (E') and the mechanical loss tangent (tan δ) were measured on a 20 mm length, 4 mm width, and ca. 0.15 mm thick film at a heating rate of 2°C/min using a

Table I. Multiblock Copolymerization of OLLA with ODMS

Sample name of product	OLLA:h-ODMS: c-ODMS in feed (molar ratio)	Yield (%)	M_n	M_w/M_n	DMS/LA in product[a]		ODMS/OLLA in product[b] (molar ratio)
					NMR	Elem.	
PLLA	1:0:0	76	42,300	2.27	0	0	0
BCP(0.05)	64:1:1	38	30,100	1.88	0.10	0.11	0.046
BCP(0.1)	32:1:1	64	32,800	1.70	0.23	0.21	0.11
BCP(0.2)	16:1:1	61	28,200	1.79	0.44	0.45	0.29
BCP(0.4)	8:1:1	44	17,900	1.73	0.78	0.78	0.37
BCP(0.9)	4:1:1	13	20,400	1.44	1.92	2.08	0.91
BCP(3.4)	1:1:1	28	23,100	1.62	7.14	6.75	3.4

[a] Molar ratio of dimethyl siloxane to lactic acid monomer unit calculated by NMR spectrum and elemental analysis.
[b] Calculated from the value of (DMS/LA).

dynamic viscoelastic analyzer (Rheo-Station DVE-V4; UBM, Muko, Japan). The test was strain-controlled at an amplitude of 4 μm and at a frequency of 110 Hz. Tensile tests were measured on 40 mm length, 4 mm width, and ca. 0.15 mm thick film segments at a crosshead speed of 40 mm/min and at room temperature using a Tensilon Universal Tester RTC-1350A (A&D, Tokyo, Japan). The tensile strength and Young's modulus were evaluated from stress–strain curves and the data are presented as averages from the measurement of >20 samples. Cyclic tensile testing was performed by repeatedly stretching each film to 1.5 times of its original length.

RESULT AND DISCUSSION

Block Copolymerization

Multiblock copolymers with various compositions were prepared by changing the feed ratio of ODMS to OLLA in polycondensation. Table I shows the results of the multiblock copolymerization. The block copolymer with M_n of 30,100 Da was obtained with a 38% yield when OLLA, h-ODMS, and c-ODMS were fed with a molar ratio of 64:1:1. The PLLA homopolymer, which was prepared by the polycondensation of OLLA alone under the same conditions, had M_n of 42,300 Da. The block copolymerization with ODMS caused some decrease in the molecular weight of the resultant copolymers, and afforded the copolymers with M_n values of about 18,000−33,000 Da. The block copolymer prepared with a feed ratio of 1:1:1 was a highly viscous liquid, and all other block copolymers prepared with different feed ratios were solid at room temperature.

^{1}H-NMR spectra of the block copolymers are shown in Figure 1. In addition to the signals assigned to the methyl proton (δ = 1.6 ppm) and the methine proton (δ = 5.2 ppm) in the lactyl unit, the signal at δ = 0.1 ppm assigned to the methyl protons of the dimethyl siloxane unit was observed in the spectra, indicating that the ODMS segments were incorporated into the main chain.[13] Molar compositions of the block copolymer were determined by the integral ratio of these proton signals and also by elemental analysis (Table I). The content of the dimethyl siloxane unit in the copolymers increased linearly as the feed ratio of h-ODMS and c-ODMS to OLLA increased in the copolymerization. Assuming that none of the fed OLLA was subjected to any depolymerization during block copolymerization, the molar ratio of ODMS to the OLLA unit in the copolymer was 0.046 with a feed ratio of OLLA:h-ODMS:c-ODMS = 64:1:1, and it was 0.11 with a feed ratio of OLLA:h-ODMS:c-ODMS = 32:1:1. When the feed ratio was OLLA:h-ODMS:c-ODMS = 4:1:1, the molar ratio of ODMS to the OLLA unit of the product was 0.91. Copolymer samples are hereafter designated as BCP(x), where x is the composition ratio.

Mechanical and Thermal Properties

Polymer films were prepared from BCP(0.05), BCP(0.1), BCP(0.2), and BCP(0.4), while neither BCP(0.9) nor BCP(3.4) exhibited film-formability. Figure 2 shows the temperature dependences of the E' and the tan δ of nonheat-treated BCP(0.1), BCP(0.4), and PLLA films. The E' of PLLA was 3.3 GPa at −130°C and this was maintained up to ca. 50°C, and then it decreased rapidly beyond 55°C. The peak of tan δ was observed at 74°C, which is attributable to the main glass transition, i.e., the micro-Brownian motions of skeletal chains in the

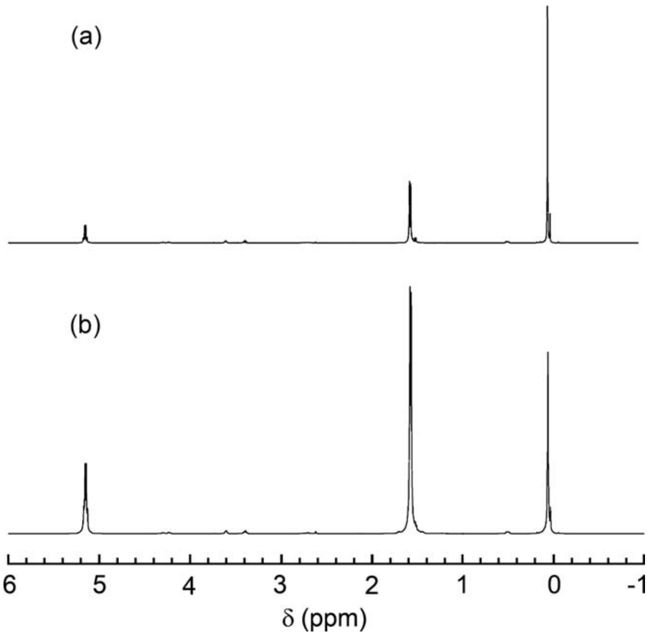


Figure 1. ^{1}H-NMR spectra of multiblock copolymers:(a),BCP(0.4); (b),BCP(0.1).

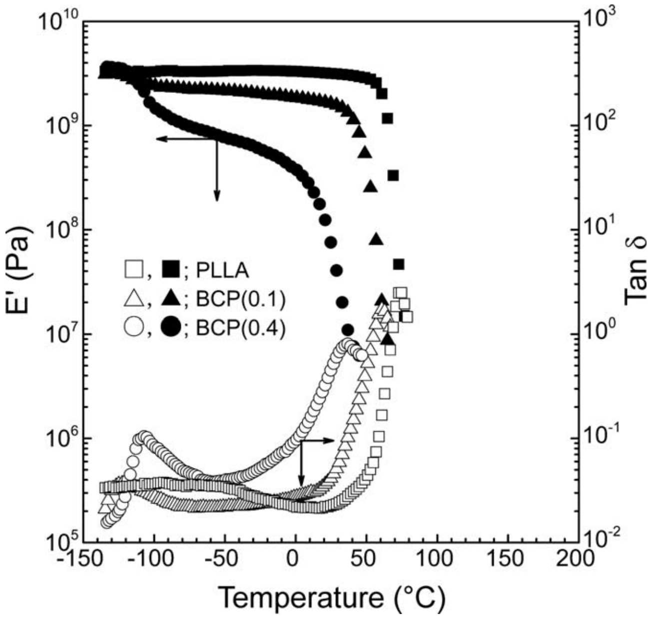


Figure 2. Temperature dependences of E' and tan δ of nonheat-treated films.

amorphous region. The E' of BCP(0.1) exhibited a gradual decrease up to 35°C and then an abrupt decrease. The peak tan δ of BCP(0.1) was observed at 61°C, which is a lower temperature compared with PLLA. In the BCP(0.4) film, a distinct tan δ peak appeared at −107°C in addition to the peak at 37°C due to the dispersion of skeletal chains of OLLA segments. The E' of BCP(0.4) dropped largely in the two temperature regions corresponding to these peaks. The glass-transition temperature of ordinary neat poly(dimethyl siloxane) is known to be −127°C.[26] Accordingly, the peak observed at −107°C in BCP(0.4) was ascribed to the dispersion of the main chain in the ODMS sequence. The finding that the dispersions of OLLA sequences and ODMS sequences were observed at each individual temperature indicated the formation of microphase separation of these segments.[27,28]

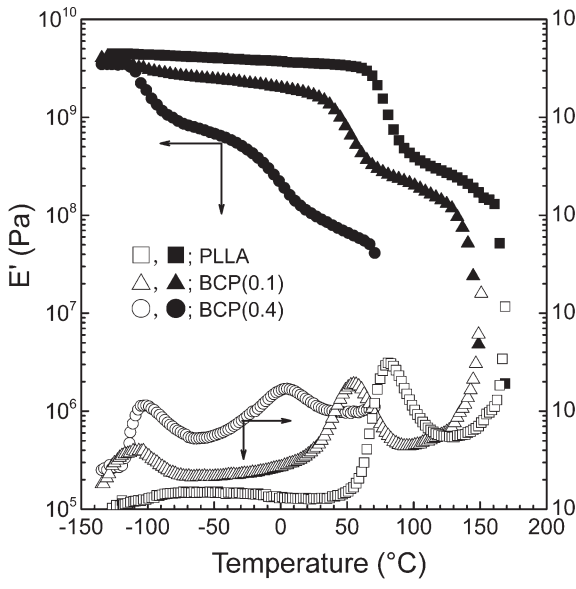


Figure 3. Temperature dependences of E' and tan δ of heat-treated films.

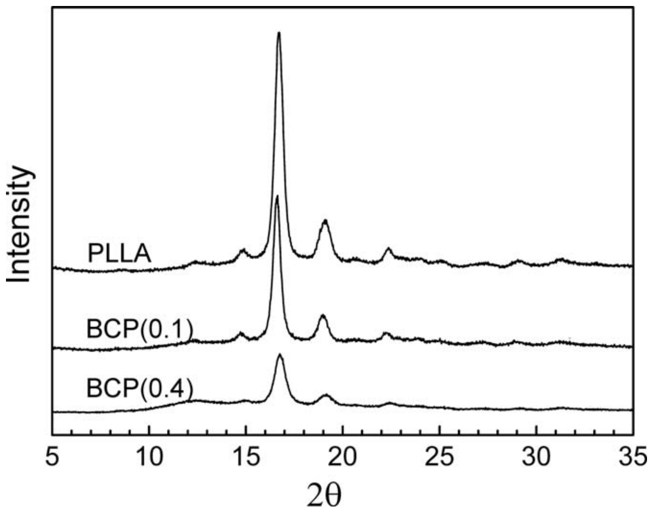


Figure 4. X-ray diffraction profiles of heat-treated films.

Figure 3 shows the temperature dependences of E' and tan δ of the films heat-treated at 100°C. Every film exhibited a flat region of the E' values above their respective main T_g, which was attributed to the crystallization of OLLA sequences due to heat treatment. The lowering of the peak value of tan δ in every film compared with the corresponding nonheat-treated film also indicated the reduction in the amorphous region. The glass-transition of the PLLA film shifted to the higher temperature of 81°C, and the film began to flow at ca. 160°C. BCP(0.1) exhibited a T_g of 55°C and a liquid flow above 130°C, whereas BCP(0.4) exhibited a T_g of 3°C and a liquid flow above 70°C. The glass-transition of PLLA shifted to a higher temperature due to heat-treatment, while the glass-transitions of BCP(0.1) and BCP(0.4) shifted to lower temperatures. This is presumably due to the rearrangement of amorphous regions caused by the progression of the crystallization in the OLLA sequences.

X-ray diffraction profiles of the heat-treated films are shown in Figure 4. The distinct diffraction peaks of the PLLA film appeared at 2θ = 14.8°, 16.7°, 19.1°, and 22.3°, which were assigned to reflections of the 010/104, 200/110, 203/014, and 210 planes of the PLLA crystals, respectively.[29–33] The diffraction peaks of both BCP(0.1) and BCP(0.4) films agreed well with those of the PLLA film. However, the peak intensities of the

Table II. Thermal Properties of Multiblock Copolymers

Sample	T_m (°C)	ΔH_f (J/g)
PLLA	155	39.3
BCP(0.05)	153	33.2
BCP(0.1)	152	31.8
BCP(0.2)	128	20.1
BCP(0.4)	124	18.4
BCP(0.9)	88	2.5

Table III. Tensile Mechanical Properties of Multiblock Copolymer Films[a]

	Tensile strength		Young's modulus		Elongation at break	
Sample	(MPa)	*SD*	(GPa)	*SD*	(%)	*SD*
PLLA[b]	56.2	3.3	4.3	0.6	4.8	0.8
heat-treated[c]	59.3	4.8	4.7	0.6	4.1	1.8
BCP(0.1)[b]	20.5	2.7	3.1	0.2	5.8	1.0
heat-treated[c]	24.4	1.4	3.5	0.2	5.0	0.5
BCP(0.4)[b]	3.2	0.1	0.15	0.02	132.0	30.7
heat-treated[c]	4.0	0.4	0.20	0.01	29.5	4.7

[a] Measured at room temperature.
[b] Nonheat-treated film.
[c] Heat-treated film at 100°C.

BCP(0.1) film were lower than those of the PLLA film, and the intensities of the BCP(0.4) film were even lower. It was confirmed that OLLA segments formed crystals even in these block copolymers and the amounts of the crystals decreased as the content ratio of the ODMS unit increased.

The T_m and ΔH_f of the heat-treated films are listed in Table II. The PLLA film exhibited a T_m of 155°C and ΔH_f of 39.3 J/g. The degree of crystallinity of this film was estimated to be ca. 42% based on the fact that the theoretical ΔH_f of PLLA crystal is 93.6 J/g.[34] In the cases of BCP(0.05) and BCP(0.1), where the content ratios of the ODMS unit were not much higher, the T_ms and ΔH_fs values were not very different from those of neat PLLA. Whereas, BCP(0.2) and BCP(0.4) exhibited fairly lower T_ms and smaller ΔH_fs values compared with neat PLLA.

Results of the tensile test on the copolymer films are listed in Table III. The nonheat-treated PLLA film had a tensile strength of 56 MPa and a Young's modulus of 4.3 GPa. The tensile strength of the BCP(0.4) film dropped to about 1/20th of that of PLLA. Incorporating ODMS segments resulted in large reduction in tensile strength. As for the elongation at break, BCP(0.4) exhibited a high elongation of 132% although there was nearly no observed difference between PLLA and BCP(0.1). Even the heat-treated BCP(0.4) film showed an elongation of 29%, where the progression of crystallization by heat-treatment resulted in decreasing the elongation. The elongations of di- and triblock copolymers containing dimethyl siloxane segments has been reported to remain at low values of less than 20%.[20] It was found that the multiblock type copolymer consisting of lactyl and dimethyl siloxane segments improved the flexibility and brittleness. Figure 5 shows stress−strain curves when the nonheat-treated BCP(0.4) film is repeatedly stretched to 1.5 times of its original length. A permanent deformation of ca. 5% arose after first stretching and subsequent loosening, and it reduced gradually per further stretch. The BCP(0.4) film exhibited elastomeric behavior. The ODMS segments probably extended without dislocating the anchor nodes of PLLA crystals which acted as physical cross-linkages.

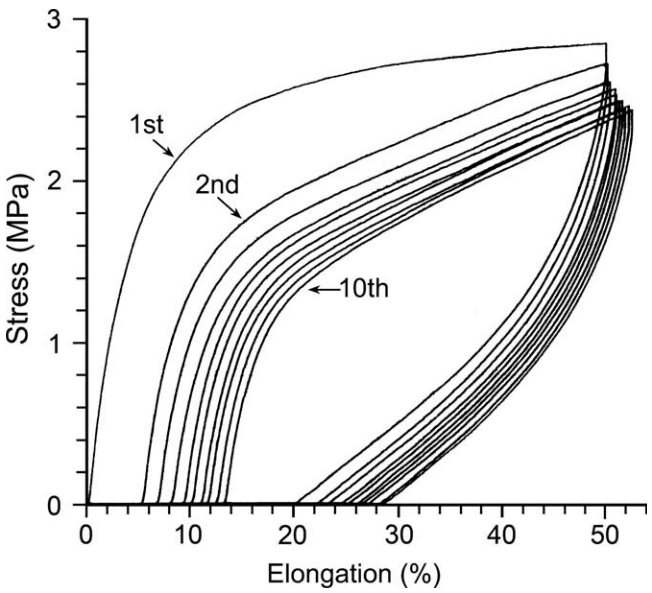


Figure 5. Stress−strain curves of nonheat-treated BCP (0.4) film stretched repeatedly to 1.5 times of its original length.

CONCLUSIONS

PLLA-PDMS multiblock copolymers were prepared by the polycondensation of OLLA with dihydroxyl-terminated ODMS and dicarboxyl-terminated ODMS. Molecular weights of the block copolymer were 18,000−33,000 Da, and the content ratio of dimethyl siloxane segments increased as the ratio of ODMS in the copolymerization feed increased. The OLLA and ODMS segments in the copolymer are thought to form a microphase separation because the dispersions of their segments were observed at each individual temperature with dynamic mechanical spectroscopy. The film prepared from the copolymer with an ODMS mol ratio of 0.37 exhibited a tensile strength of 3.2 MPa and a high elongation of 132%. The film also showed a high strain recovery in repeated stretching. The multiblock copolymerization of OLLA with ODMS was confirmed to improve the mechanical properties of PLLA and provide a material with new characteristics.

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