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Preparation and Chain-extension of P(LLA-*b*-TMC-*b*-LLA) Triblock Copolymers and Their Elastomeric Properties†

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Abstract: ABA triblock copolymers of L-lactide and trimethylene carbonate with several different compositions were prepared by sequential ring-opening polymerization in the presence of diethylene glycol. Also chain-extension reactions of the resulting copolymers were carried out using hexamethylene diisocyanate to produce relatively high molecular weight polymers, which could be cast into elastomeric tough films. The polymers with certain L-lactide contents were partially crystalline, exhibiting two-phase morphology. The polymer films showed reversible elastic behavior under tensile tension, providing a novel thermoplastic elastomer possessing desirable properties such as biodegradability and good mechanical properties.

Keywords : PLLA, PTMC, block copolymer, biodegradable, thermoplastic elastomer.

Introduction

Modification of the properties of the brittle biodegradable polyesters such as polylactide(PLA), polyglycolide, and poly(hydroxy alkanoate) has been intensively investigated.[1-3] Usually a biodegradable or biocompatible rubber is introduced to toughen the materials, so that the modified material remained biodegradable or biocompatible. PLA is one of the most intensively studied biodegradable synthetic polymers that have found significant applicability in the medical and pharmaceutical fields.[4] Interest in PLA as a commercial thermoplastic has been increasing, and large-scale production has recently been announced.[5] Though PLA is limited by its inherent brittleness, its properties can be significantly enhanced and broadened by modification via copolymerization, which provides a number of advantages because the architecture and composition of the biomaterials can be tailored to control the material properties (by anionic or coordinated polymerization). In particular, block copolymerization may offer a broader spectrum of mechanical and degradation properties in order to meet the demands of various applications. Blocks with different physical properties, for example, one soft(amorphous) and one hard(semicrystalline) segment, can be utilized to modulate basic material behavior.[6-10] For copolymers to be useful as thermoplastic elastomers, the controlled synthesis of ABA triblock copolymer is often required. The mechanical properties of the polymer are enhanced by a microphase-separated morphology in which the soft phase gives elasticity and degradation, whereas the rigid phase provides mechanical strength and also acts as a physical crosslinker. We were interested in using poly(trimethylene carbonate)(PTMC), a simple aliphatic polycarbonate, as soft, low T_g segment. PTMC with the reported glass transition temperature of -25 °C, is rubbery at room temperature and biodegradable both *in vivo* and *in vitro*, and hence, possesses potential applications in medical and environmental areas.[11-13] In our previous communication,[14] we discussed the synthesis of triblock copolymer of PLLA containing PTMC middle block with the basic molecular characteristics. Here we report, as an extension, the preparation and chain extension of several P(LLA-*b*-TMC-*b*-LLA) triblock copolymers with several different compositions. Also their thermal and tensile properties with film morphology as a potential thermoplastic elastomer will be discussed.

Experimental

Chemicals and Measurements. L-Lactide was purified by recrystallization twice from dry ethyl acetate and dried in vacuum at room temperature. Trimethylene carbonate(TMC) was purchased from Behringer Ingelheim and purified by sublimation. Diethylene glycol, hexamethylene diisocyanate (HMDI), stannous octoate was purchased from Aldrich Co.

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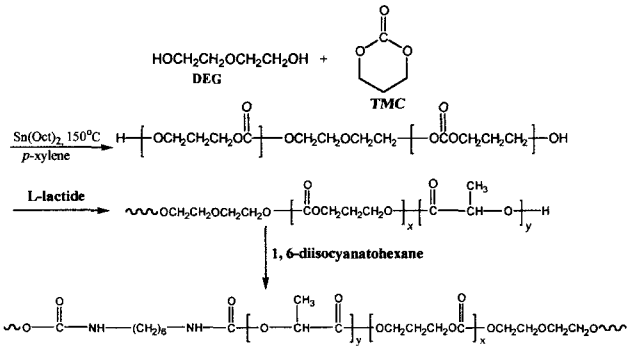
and used as received. *p*-Xylene was dried over calcium hydride(CaH_2) for 24 h prior to distillation.

Infrared spectra were obtained on a Unicam 1000 FT-IR spectrometer. ^{1}H NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer using $CDCl_3$ as the solvent. Thermal analysis was carried out on a Perkin Elmer DSC/TGA7 Series thermal analysis system. The molecular weight data were obtained by gel permeation chromatography (GPC, Waters) using chloroform as the eluent at a flow rate of 1 mL/min. Polystyrene standards were used to calibrate the molecular weight. Tensile test was carried out using Instron Model 5565, and the film morphology was observed by Optical Microscope (SAMWON Scientific Ind. Co. LTD) model CSB-HA3.

Synthesis and Chain-extension of Poly(LLA-*b*-TMC-*b*-LLA). i) A typical polymerization procedure was described previously; All glassware was flame-dried prior to use. The desired amounts of TMC(3 g, 29.4 mmol), diethylene glycol (13 μL, 0.5 mol% of TMC) and catalyst[$Sn(oct)_2$, 0.2 mol% of total monomer] were weighed into a 3-necked round flask under a nitrogen atmosphere inside a drybox. The flask was fitted with a magnetic stirrer and condenser. *p*-Xylene(15 mL) was transferred to a flask using a syringe. The homogeneous mixture was stirred for 24 h at 140 °C and a small amount aliquot was sampled for analysis. The second monomer, L-lactide(4.23 g, 29.4 mmol), was charged into the reaction flask and stirred for additional 24 h to obtain a viscous polymer solution. The polymer formed was isolated by precipitation into a large amount of methanol/hexane, purified by reprecipitation from chloroform solution, washed, and finally dried in vacuum to obtain white and bulky powder. ii) The block copolymer, above prepared, was dissolved in 30 mL of dry toluene and heated to about 130 °C to distilled off some part to remove moisture inside as an azeotropic mixture. Then, a predetermined amount of HMDI was added by injection with microsyringe, and the reaction mixture



was stirred for 4 h before precipitation into an excess amount of methanol. The resulting powder was filtered, washed, and dried in vacuum at 50 °C.

Results and Discussion

Synthesis and Chain-extension of Triblock Copolymers. Triblock copolymers were prepared by sequential ring-opening polymerization of TMC and L-LA in the presence of small amount of diethyleneglycol using stannous octoate as the catalyst. The molecular characteristics of the copolymers are shown in Table I. The molecular weight of the synthesized polymers were relatively low in the range of about M_n of 10,000 g/mol, and M_w of 15,000 g/mol, respectively, in a given reaction conditions. The basic structural characterization of copolymers by ^{1}H NMR, and IR have been carried out, though the results are already included in our previous report. Figure 1 shows typical GPC chromatograms of PTMC prepolymer, which was sampled during the polymerization reaction, and the corresponding block copolymer. A shift of distribution curve toward higher molecular weight and unimodal distribution profiles of both prepolymer and the final copolymer suggested good formation of block copolymer from this synthesis. The polydispersity of block

Table I. The Molecular Characteristics of the Triblock Copolymers

Copolymer	Yield(%)		M_n	M_w	M_w/M_n	TMC Content (mol%)
CP1	74	PTMC	6,400	9,300	1.45	
		Copolymer	10,700	13,900	1.30	52
CP2	76	PTMC	4,500	6,300	1.40	
		Copolymer	11,000	14,500	1.32	45.5
CP3	75	PTMC	6,600	8,700	1.32	
		Copolymer	14,200	21,000	1.48	43
CP4	82	PTMC	4,500	7,200	1.60	
		Copolymer	10,000	15,600	1.56	36
CP5	79	PTMC	5,100	8,500	1.67	
		Copolymer	10,100	14,300	1.41	26

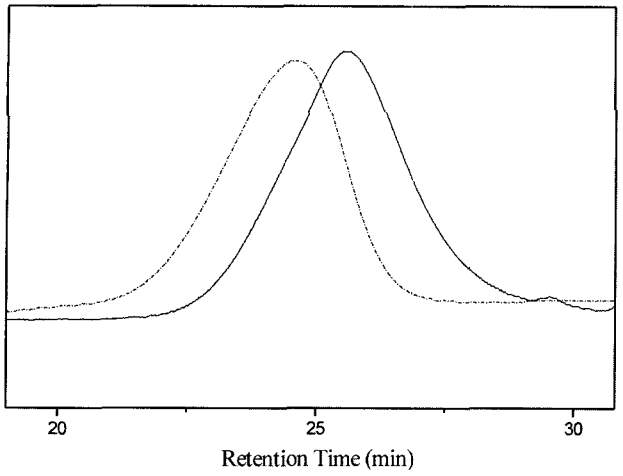


Figure 1. GPC chromatograms of PTMC prepolymer and the corresponding triblock copolymer.

copolymers was about 1.3~1.5, indicating relatively narrow distribution of the molecular weight.

To improve the molecular weight of the original triblock copolymer, a chain extension reaction was attempted. It is expected that the final copolymers possess hydroxyl group at both chain ends(see polymerization reaction scheme above), which are available for the chain extension process with appropriate reagents such as diisocyanate compound. In this case, the chain-extended polymers should have multiblock chain structure, at least in part.

Table II shows the results of chain extension for one copolymer CP1 using several different amount of diisocyanate compound (HMDI for this study). The chain-extended copolymer using HMDI with the [NCO]/[OH] ratio of 4 provided better result, giving 2.5~3 times of increase in the average molecular weight. From the GPC analysis for the triblock copolymer and its chain-extended samples, parallel shifts in distribution curve toward higher molecular weight were observed, though the molecular weight distribution became rather broader. When the amount of HMDI was increased more, a further increase in molecular weight of the resulting polymer, however, was not noticed. Also the formation of some amount of insoluble gel(3-4 wt%) was observed, which is probably caused by the crosslinking side reaction in urethane chemistry. All the other copolymers thus were chain-extended using the same molar amount of HMDI with the [NCO]/[OH] ratio of 4, as shown in Table III. All these polymers were used to cast film to study their morphology and basic tensile properties.

Table II. Results of Chain-extension Using Several Different Amount of Diisocyanate(HMDI) Compound (sample CP3)

Polymer	Yield(%)	M_n	M_w	M_w/M_n
CP3	75	14,200	21,000	1.48
CP-E1 [NCO]/[OH]* = 3	80	25,500	47,600	1.85
CP-E2 [NCO]/[OH] = 4	85	32,800	63,200	1.92
CP-E3 [NCO]/[OH] = 5	92	24,100	44,000	1.82

*[OH] was theoretically calculated from the M_n of copolymer.

A typical ^{1}H NMR spectrum of block copolymer after chain-extension is shown in Figure 2. The methine(**c**) and methyl protons(**d**) of the PLA block are shown at 5.17 and 1.5 ppm, and methylene protons(**a**, **b**) of PTMC are shown at 2.06 and 4.24 ppm, respectively. Also methylene protons, originated from HMDI moiety, were observed at 3.13 and 1.34 ppm to assure the incorporation of the unit in the copolymer structure. Monomer composition in the copolymer was determined from the integration ratio between proton signals **c** and **a**(as the results are included in Table I).

Figure 3 depicts the FT-IR spectra of triblock copolymer and the chain extended one. Copolymer (A) has a strong C=O stretching band at 1752 cm^{-1}, and at 1185 and 1248 cm^{-1} of the C-C-O and O-C-O asymmetric stretching of the

Table III. Results of Chain-extension Using HMDI with [NCO]/[OH] Ratio of 4

Polymer	Yield(%)	M_n	M_w	M_w/M_n
CP2	76	11,000	14,500	1.32
CP2-E	83	22,000	37,200	1.52
CP3	80	14,200	21,000	1.48
CP3-E	85	32,800	63,200	1.92
CP4	82	10,000	15,600	1.56
CP4-E	83	30,500	54,600	1.80
CP5	79	10,100	14,300	1.41
CP5-E	82	30,100	56,100	1.86

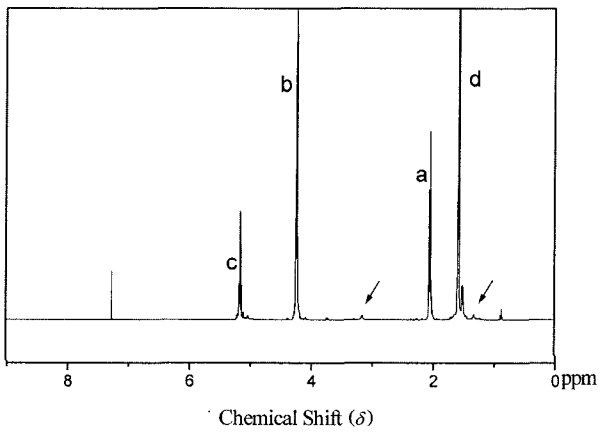


Figure 2. A typical ^{1}H NMR spectrum of a chain-extended triblock copolymer.

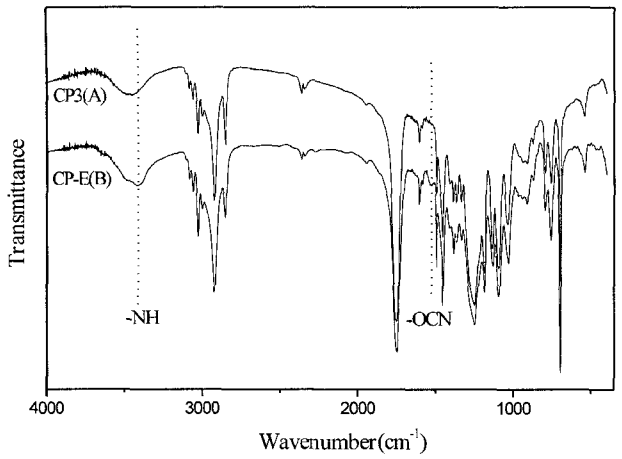


Figure 3. FT-IR spectra of triblock copolymer and the chain-extended one.

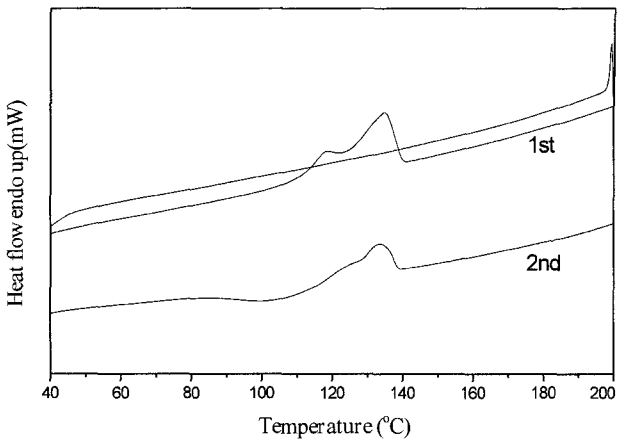


Figure 4. DSC thermograms of crystalline copolymer (CP4).

ester and the carbonate groups of the copolymer, respectively. From the chain-extended products, the characteristic absorption bands corresponding to NH stretching at 3420 cm^{-1}, and OCN at 1510 cm^{-1} of urethane group are observed, respectively, to confirm the structures.

Thermal Properties. From the TGA measurements, the copolymers were stable to about 250 °C, with the decomposition onset shifting toward higher temperature after chain-extension. The melting characteristics of the triblock copolymers and their chain-extended products, analyzed by DSC, are shown in Table IV. Also typical DSC thermograms of semi-crystalline copolymer (sample CP5) are shown in Figure 4. The first heating scan showed PLA melting endotherm with the peak temperature of 135 °C, and the following cooling scan showed a broad and weak crystallization exothermic transition at the temperature range of 80~110 °C. The second heating scan of the same sample showed a weak exothermic transition at 90~110 °C due to the cold crystallization, followed by melting transition again with peak temperature of 134 °C. The T_m and enthalpic value of the PLLA block in triblock copolymer was increasing as the LLA content are increased, as shown in Table IV. Below the LLA content of about 48 mol%, the material seems to remain amorphous in the given molecular weight range.[15] By the chain extension, both the T_m and enthalpic values are decreased to some extent, which are expected from the hindered crystallization of the resulting polymer with increased chain length and broadened molecular weight distribution. Even though the degree of crystallinity of each samples are different, the polymers consist of two separated phase, one with crystalline PLLA domain and the other PTMC-rich rubbery domain.

Table IV. The Thermal Characteristics of the Triblock Copolymers and Their Chain-extended Products (analyzed by DSC)

Polymer	DSC (1st)		DSC (2nd)			
	T_m (peak, °C)	ΔH_m (J/g)	T_m (peak, °C)	ΔH_m (J/g)	T_c (peak, °C)	ΔH_c (J/g)
CP2	120	7.5	-	-	-	-
CP2-E	101	3.7	-	-	-	-
CP3	127	16	131	3.5	98	-1.3
CP3-E	125	5.4	-	-	-	-
CP4	135	18.9	134	7.8	104	-3.6
CP4-E	127	14.1	-	-	-	-
CP5	138	26.2	131	26.4	95	-16
CP5-E	127	23.4	-	-	-	-

For sample CP2, the 2nd scan of quenched sample after first heating to 200 °C did not show the melting transition, presumably due to relatively lower content of PLLA block and the inherent slow crystallization rate. Also the 2nd scan of all the chain-extended samples did not show melting transition, suggesting amorphous nature of the quenched samples. Again, this will be caused by the sluggish crystallization of PLLA blocks with relatively low molecular weight and rather broad molecular weight distribution, together by a kind of phase mixing effect. For the one chain-extended sample, CP4-E, annealing experiment was carried out as time at the temperature of 80 °C to see the development of crystalline phase, and the resulting DSC thermograms are shown in Figure 5. As the annealing time was increased, the melting transition appeared at around 130 °C with a shoulder peak at lower temperature, indicating the development of crystallinity. The corresponding enthalpy increased up to 15 J/g in 1 h, but a further increase was negligible thereafter.

Morphology and Tensile Properties. The film morphology of different samples were observed by optical microscopy. The typical pictures are shown in Figure 6. The two phase morphology comprising crystalline PLLA domain, with increased domain size as the increasing LLA content, dispersed

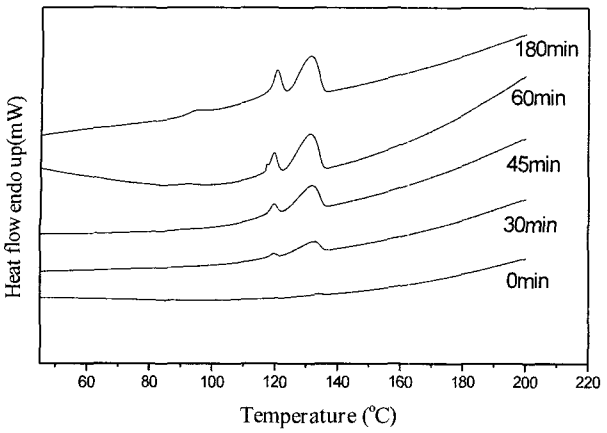


Figure 5. DSC thermograms with various annealing times for the sample CP3-E.

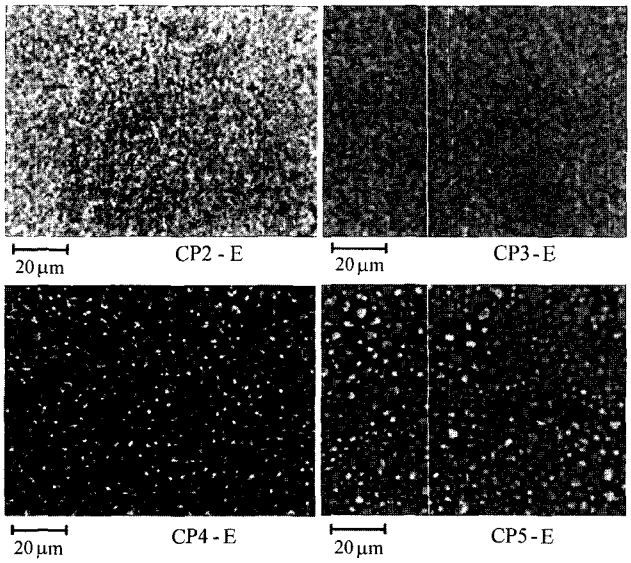


Figure 6. The film morphology of different samples by optical microscopy.

in an amorphous domain is discernible. The prepared ABA triblock copolymer and the chain-extended one, possessing one crystalline block and another low T_g rubbery component, formed two-phase morphology, inter-dispersed uniformly. So, these material can exhibit thermoplastic elastomer behavior similar to the other known conventional thermoplastic elastomers.

The tensile properties of the cast films (ca. 20~30 μm thick) from chain-extended polymers were measured by Instron, and the Stress-Strain curves are shown in Figure 7. The original translucent film was elongated to about 300~400% without failure, variable to some extent by the different sample thickness and pulling rate. The tensile strength of the sample showed increasing tendency linearly with the PLLA content, due to the enhanced crystallinity of samples.

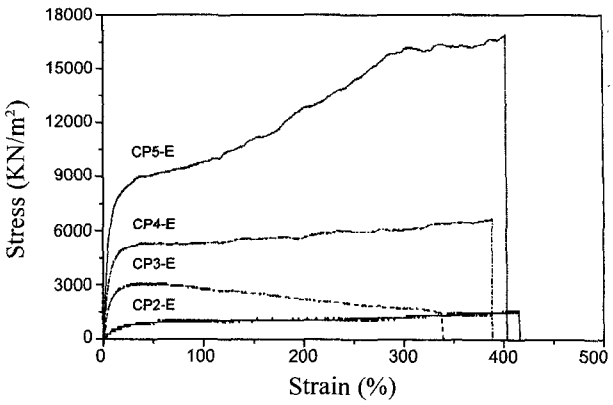


Figure 7. Stress-Strain curves of cast films measured by Instron.

The elongation at failure, however, did not show any tendency. While the film samples were pulled apart, the film became opaque gradually, presumable resulted from the compaction of crystalline phase accompanying by a possible stretch-induced crystallization. When the force to stretched film was released, the sample contracted and seemed to be recovered to nearly original state.

To summarize, ABA triblock copolymers of L-lactide and trimethylene carbonate with several different compositions were prepared and chain-extended to produce relatively high molecular weight polymers, which could be cast into elastomeric tough films. The polymers were partially crystalline and exhibited two-phase morphology. The polymer films showed reversible elastic behavior under tensile tension, which may provide a novel thermoplastic elastomer possessing desirable properties such as biodegradability and good mechanical properties. The synthesis of much higher molecular weight materials and the related degradation behavior is currently under investigation.

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References

(1) H. Brandl, R. A. Gross, R. W. Lenz, and R. C. Fuller, *Advances in Biochemical Engineering/Biotechnology*, T. K. Ghose and A. Fiechter, Eds., Springer, Berlin, 1990, Vol. 41, pp 77.
(2) S. Matsumura, K. Tsukada, and K. Toshima, *Macromolecules*, **39**, 3122 (1997).
(3) Y. K. Sung and S. W. Kim, *Korea Polym. J.*, **8(5)**, 199 (2000).
(4) E. S. Lipenski and R. G. Sinclair, *Chem. Eng. Prog.*, **82**, 26 (1986).
(5) A. Tullo, *Chemical and Engineering News*, **78(3)**, 13 (2000).
(6) K. Stridsberg and A.-C. Albertsson, *J. Polym. Sci., Polym. Chem.*, **38**, 1774 (2000).
(7) S. C. Schmidt and M. A. Hillmyer, *Macromolecules*, **32**, 4794 (1998).

(8) S. Zhang, Z. Hou, and K. E. Gonsalves, *J. Polym. Sci., Polym. Chem.*, **34**, 2737 (1996).
(9) L. Sipos, M. Zsuga, and G. Deak, *Macromol. Rapid Commun.*, **16**, 935 (1995).
(10) C. W. Lee, Y. G. Kang, and K. Jun, *Korea Polym. J.*, **9(2)**, 84 (2001).
(11) A.-C. Albertsson and M. Eklund, *J. Polym. Sci., Polym. Chem.*, **32**, 265 (1994).
(12) X. Chen, S. P. McCarthy, and R. A. Gross, *Macromolecules*, **30**, 3470 (1997).
(13) Y. Hori, Y. Gonda, Y. Takahashi, and T. Hagiwara, *Macromolecules*, **29**, 804 (1996).
(14) J.-H. Kim, S. Y. Lee, and D. J. Chung, *Polymer J.* **32(12)**, 1056 (2000).
(15) E. Ruckenstein and Y. Yuan, *J. Appl. Polym. Sci.*, **69**, 1429 (1998).