

## Synthesis and Properties of Triblock Copolymers from L-Lactide and Trimethylene Carbonate

Ji-Heung KIM,<sup>†</sup> Sun Young LEE, and Dong Jun CHUNG\*

Department of Chemical Engineering, \*Department of Polymer Science and Engineering,  
Polymer Technology Institute, Sungkyunkwan University,  
300 Chunchun, Jangan, Suwon, Kyunggi 440-746, Korea

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Modification of the properties of the brittle biodegradable polyesters such as polylactide (PLA), polyglycolide, and poly(hydroxy alcanoate) has been intensively investigated.<sup>1,2</sup> 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 because of its beneficial mechanical properties and adjustable hydrolyzability. Modification *via* copolymerization provides a number of advantages because the architecture and composition of the biomaterials can be tailored to control copolymer 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 a larger number of biomedical applications. Blocks with different physical properties, for example, one soft, amorphous and one hard, semicrystalline segment, can be utilized to modulate basic material behavior.<sup>3,4</sup> The mechanical properties of the polymer are enhanced by a microphase-separated morphology. The soft phase gives elasticity and degradation, whereas the rigid phase provides mechanical strength and also acts as a physical crosslinker. Poly(trimethylene carbonate) (PTMC), a simple aliphatic polycarbonate, with the reported glass transition temperature of  $-25^{\circ}\text{C}$ , is rubbery at room temperature and can be hydrolyzed both *in vivo* and *in vitro*, and hence, possesses potential applications in medical and environmental areas.<sup>5–7</sup> Indeed, poly(glycolide-co-TMC) was used as a flexible, strong, and absorbable monofilament suture.<sup>8</sup> Recently, Cai and Zhu reported the synthesis of an amorphous poly(D,L-lactide-co-TMC) and evaluated its biodegradation.<sup>9</sup> Also Ruckenstein and Yuan reported the synthesis and properties of semicrystalline biodegradable random copolymer, poly(LLA-co-TMC).<sup>10</sup>

In this article, we tried the synthesis of ABA-type triblock copolymer by sequential ring-opening polymerization of TMC and L-lactide in the presence of small amount of diol compound, and the primary characterizations by GPC, NMR, IR, and thermal analysis (DSC and TGA) are reported. The block copolymers possess a po-

tential uses in biomedical applications as a novel biodegradable thermoplastic elastomers.

### EXPERIMENTALS

#### Chemicals and Measurements

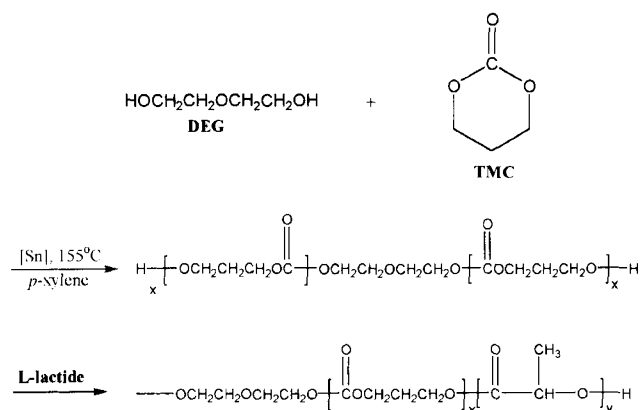
L-Lactide was purified by recrystallization from dry ethyl acetate and dried in vacuum at room temperature. Trimethylene carbonate (TMC) was purchased from Behringer Ingelheim and used as received. Diethylene glycol and stannous octoate was purchased from Aldrich Co. and used as received. *p*-Xylene was dried over calcium hydride ( $\text{CaH}_2$ ) for 24 h prior to distillation.

Infrared spectra were obtained on a Unicam 1000 FT-IR spectrometer.  $^1\text{H}$  NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer using  $\text{CDCl}_3$  as the solvent. Thermal analysis was carried out on a Perkin-Elmer DSC/TGA 7 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  $1\text{ mL min}^{-1}$ . Polystyrene standards were used to calibrate the molecular weight.

#### Synthesis of Triblock Copolymer, Poly(LLA-*b*-TMC-*b*-LLA)

A typical polymerization procedure is described as follows: All glassware was flame-dried prior to use. The desired amounts of TMC (3 g, 29.4 mmol), diethylene glycol (13  $\mu\text{L}$ , 0.5 mol% of TMC) and catalyst ( $\text{Sn}(\text{oct})_2$ , 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  $140^{\circ}\text{C}$  and a small amount 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.

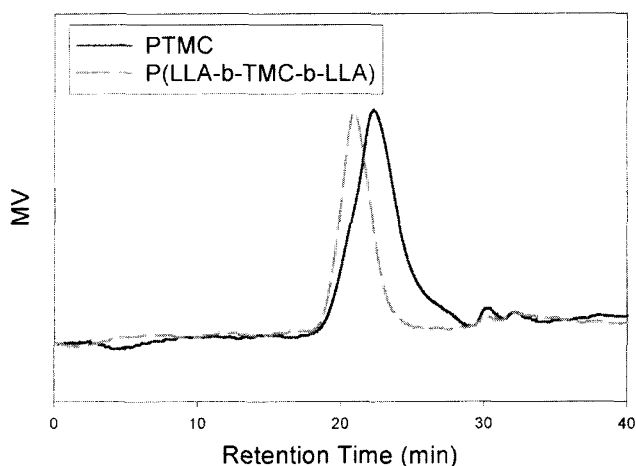
<sup>†</sup>To whom correspondence should be addressed.



**Table I.** Characteristics of Poly(LLA-*b*-TMC-*b*-LLA) tri-block copolymers

Polymer	DEG <sup>a</sup>	Yield <sup>b</sup>		$M_n$	$M_w$	$M_w/M_n$	TMC Content <sup>c</sup>
	mol% of TMC	%					
PMCLA 1	0.75	75	PTMC	6600	8700	1.33	43.3%
			Copolymer	10600	13000	1.22	
PMCLA 2	0.50	80	PTMC	8500	11700	1.38	48.6%
			Copolymer	22300	30000	1.35	

<sup>a</sup> Diethylene glycol, <sup>b</sup> copolymer yield, <sup>c</sup> TMC unit wt% in copolymer determined by <sup>1</sup>H NMR.

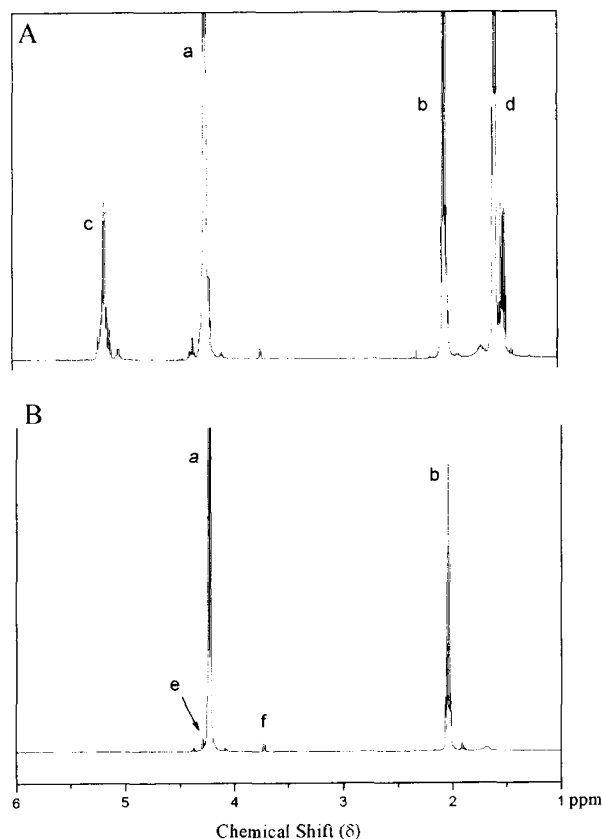
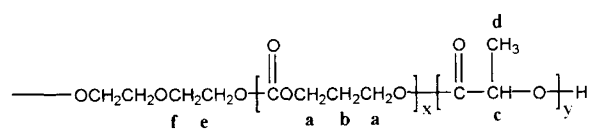


**Figure 1.** GPC spectra of PTMC prepolymer and P(LLA-*b*-TMC-*b*-LLA) triblock copolymer.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Triblock Copolymers.** Block copolymers were prepared by sequential ring-opening polymerization of TMC and L-LA in the presence of small amount of diethyleneglycol using stannous octoate and *p*-xylene as catalyst and solvent, respectively. The structure of the block copolymer was confirmed by <sup>1</sup>H NMR and IR spectroscopies as described below. The results of polymerization are shown in Table I. The block copolymers should possess an ABA-type triblock structure with different block lengths depending on concentrations of diol compound and monomer.

Molecular weights of poly(trimethylene carbonate) (PTMC) prepolymer and block copolymers were measured by gel permeation chromatography using PS standards.

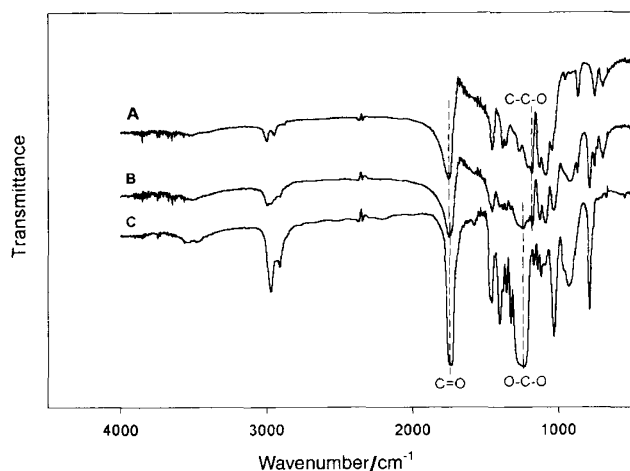


**Figure 2.** <sup>1</sup>H NMR spectra of (A) P(LLA-*b*-TMC-*b*-LLA), (B) PTMC prepolymer.

Figure 1 shows typical GPC chromatograms of PTMC prepolymer and a block copolymer. Because the molecular weight of prepolymer is relatively low, the molecular weight distribution seems rather broad. However, shift of distribution curve toward high molecular weight and unimodal distribution profiles of both prepolymer and block copolymer suggest good formation of block copolymer from this synthesis. The polydispersity of block copolymers was about 1.3, indicating relatively narrow distribution of the molecular weight.

A typical <sup>1</sup>H NMR of block copolymer 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) are shown at 2.06 and 4.24 ppm, respectively. Methylene protons assignable to the diethyleneglycol unit in the middle were observed at 3.73 and 4.29 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. The results are included in Table I. TMC content in the copolymers was 35–40 mol% (ca. 43–49 wt%), slightly higher compared to the feed composition (TMC 41.5 wt%).

Figure 3 depicts the FT-IR spectra of pure PLLA (A), block copolymer (B), and pure PTMC (C). Peaks at 1757



**Figure 3.** FT-IR spectra of (A) homo PLLA, (B) copolymer PMCLA 1, and (C) homo PTMC.

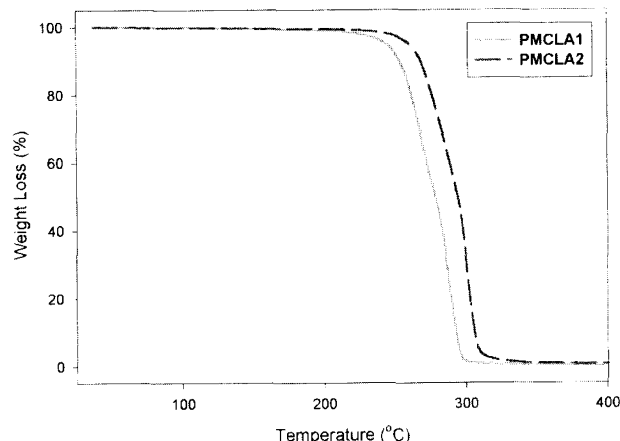
**Table II.** Thermal properties of Poly(LLA-*b*-TMC-*b*-LLA) triblock copolymers

Polymer	TGA	DSC (1st)		DSC (2nd)	
	$T_i$ /onset, °C	$T_m$ /peak, °C	$\Delta H_m$ /J g <sup>-1</sup>	$T_i$ /peak, °C	$\Delta H_c$ /J g <sup>-1</sup>
PMCLA 1	258	123	10.8 (19.0) <sup>a</sup>	98	-5.4
PMCLA 2	286	159	22.8 (44.3) <sup>a</sup>	88	-4.9

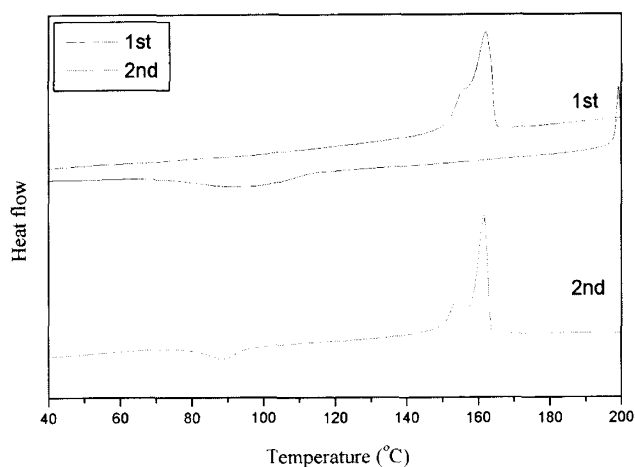
<sup>a</sup> Calculated value based on PLA block weight.

and 1185 cm<sup>-1</sup> in spectrum (A) can be assigned to the C=O stretching and the -C-C-O asymmetric stretching bands of PLLA, respectively, and the peaks at 1745 and 1247 cm<sup>-1</sup> in (C) to the C=O stretching and O-C-O asymmetric stretching bands of PTMC, respectively. Copolymer (B) has a C=O stretching band at 1752 cm<sup>-1</sup>, located between those of PLLA and PTMC, but retains stretching bands at 1185 and 1248 cm<sup>-1</sup> of the C-C-O and O-C-O asymmetric stretching of the ester and the carbonate groups, respectively.

**Thermal Properties.** The thermal characteristics of the block copolymers were analyzed by DSC and TGA, and the results are shown in Table II. The polymers were stable to about 250°C, with decomposition onset shifting toward higher temperature as molecular weight increased. Two step decomposition was discernible around the mid-point of the curves (Figure 4). DSC showed melting and crystallization behavior of the block copolymer. Typical thermograms (PMCLA 2) are shown in Figure 5. The first heating scan showed only PLA melting endotherm with the peak temperature of 162°C, and the following cooling scan showed a broad and weak crystallization exothermic transition at 110–80°C. The second heating scan of the same sample showed exothermic transition at 90°C corresponding to the cold crystallization, and melting transition again with peak temperature of 159°C with shoulder. The enthalpic value of the PLA melting peak was calculated to be 22.8 J g<sup>-1</sup>. At PLA content in the copolymer of 51.4 wt%, the enthalpy can be expressed as 44.3 J g<sup>-1</sup>-PLA. This high value means not only high crystallinity of the copolymer but the crystallization of PLA block is not hindered much by



**Figure 4.** TGA thermograms of block copolymers.



**Figure 5.** DSC thermograms of block copolymer, PMCLA 2 (upper curve: 1st heating and the following cooling scan, lower curve: 2nd heating scan, scanning rate: 10°C min<sup>-1</sup>).

the PTMC block. Also this result is obviously compared to the amorphous nature of random copolymer with similar composition.<sup>10</sup> Crystallinity was calculated as 47% based on the theoretical pure PLLA,<sup>11</sup> which is almost the same as that of normally prepared homo PLLA by solution polymerization.<sup>12</sup> This high crystallinity may result from phase segregated morphology of the prepared block copolymer which enhances the crystallization of PLA block by flexible and mobile PTMC segments with low glass transition temperature. For sample PMCLA 1, crystallinity of PLA block was relatively low, presumably due to the low molecular weight of copolymer.

To summarize, ABA-type triblock copolymers of L-lactide and trimethylene carbonate with given compositions were prepared by sequential polymerization and characterized. The polymers were highly crystalline with a fast crystallization rate. The high crystallinity of the block copolymer is in contrast to the amorphous nature of the corresponding random copolymer, suggesting phase-segregated morphology with crystalline PLLA and rubbery PTMC domains. This material provides a novel thermoplastic elastomer possessing desirable properties including biodegradability, biocompatibility and good mechanical properties. Detailed studies on

polymer synthesis with different molecular weight and compositions, morphology, thermal and mechanical properties, and degradation kinetics are currently in progress.

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