

Molten Ring-Open Copolymerization of L-Lactide and Cyclic Trimethylene Carbonate

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ABSTRACT: The biodegradable poly(L-lactide-co-trimethylene carbonate) [poly(LLA-co-TMC)] was synthesized by molten ring-open copolymerization and the structure and properties of the copolymer were investigated by GPC, NMR, FTIR, DSC, and Instron testing. The copolymer with a higher LLA content had a higher initial molecular weight (M_n), but a lower final M_n . In contrast, the copolymer with a higher TMC content had a lower initial M_n , but its M_n increased with increasing reaction time and TMC content. The glass transition temperature (T_g), the melting temperature (T_m) and the crystallinity of the copolymer decreased with increasing TMC content. The elongation of the copolymer significantly increased with increasing TMC content while the toughness passed through a maximum. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1429–1434, 1998

Key words: molten ring-opening copolymerization; L-lactide; cyclic trimethylene carbonate

INTRODUCTION

The modification of the properties of the brittle biodegradable polyesters such as poly(hydroxyalkanonate), polylactide (PLA), and polyglycolide, has been intensively investigated.^{1–5} Usually a biodegradable or biocompatible rubber was introduced to toughen the brittle aliphatic polyester, so that the modified material remained biodegradable or biocompatible. The modifications could be achieved by both physical blending and chemical copolymerization. Owing to the high crystallinity of the aliphatic polyesters, few miscible blends with a biodegradable or biocompatible rubber have been reported. Poly(3-hydroxybutyrate)/poly(ethylene oxide) is one of them.⁶ In contrast, the modification via copolymerization provided a number of advantages because the archi-

ture of the biomaterial can be tailor made by random or sequence copolymerization (anionic or complex). Thus, a random, block or star copolymer can be synthesized. The copolymer properties such as glass transition temperature, melting temperature, crystallinity, toughness, and biodegradability can be easily controlled by varying the monomer composition in the feed, such as to meet different needs. Generally, the elongation and toughness of the brittle polyester can be significantly improved by incorporating rubber moieties in the copolymer.^{7–10}

The aliphatic polycarbonate, such as poly(trimethylene carbonate) (PTMC) rubber, can be hydrolyzed both *in vivo* and *in vitro*, and hence, possesses potential applications in biomedical and environmental areas.^{11–13} The introduction of carbonate linkages into a polyester constitutes an additional route for the improvement of the performance of polyesters. Because the carbonate linkage is more hydrophobic than the ester one, the copolymer is expected to be more stable to

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hydrolysis *in vitro* and, therefore, to have a much longer shelf life than PLA. However, because the hydrolysis of carbonate is faster *in vivo*,¹⁴ the copolymer can be used as a bioabsorbable material. Indeed, poly(glycolide-*co*-TMC) was used as a flexible, strong, and absorbable monofilament suture.⁴ Recently, Cai and Zhu¹⁵ reported the synthesis of an amorphous poly(*d,l*-lactide-*co*-trimethylene carbonate) and evaluated its biodegradability both *in vivo* and *in vitro*.

In this article, a semicrystalline biodegradable copolymer poly(L-lactide-*co*-trimethylene carbonate) [poly(LLA-*co*-TMC)] was prepared by the molten ring-open copolymerization. The effects of the trimethylene carbonate (TMC) content on the molecular weight, thermal, and mechanical properties of the copolymer were investigated.

EXPERIMENTAL SECTION

Materials

L-Lactide was purified by recrystallization from dry ethyl acetate and dried in a vacuum oven at room temperature for 24 h. The catalyst stannous octoate [Sn(oct)₂, Sigma, St. Louis, MO] was used as received. All other chemicals were purchased from Aldrich (Milwaukee, WI) and were purified by the standard methods.

Monomer Synthesis

The monomer 1,3-dioxan-2-one or cyclic trimethylene carbonate (TMC) was synthesized as follows¹⁶: 20 g (0.263 mol) 1,3-propanol, and 57.1 g (0.526 mol) ethyl chloroformate were dissolved in 300 mL tetrahydrofuran (THF) at 0°C. Subsequently, 56.2 g (0.552 mol) triethylamine (TEA) was added dropwise to the flask within 30 min, and the mixture was stirred for 2 additional h at 0°C. The precipitated TEA·HCl salt was removed by filtration and the excess THF distilled under reduced pressure. The residue was crystallized and recrystallized from the mixture of THF–ether two to six times, and the obtained white TMC crystal was dried under vacuum at room temperature before use. The structure and purity of TMC were confirmed by ¹H-NMR (2.10 ppm, m, 2H, CCH₂C; 4.44 ppm, t, 4H, CCH₂O).

Polymerization

The molten ring-open polymerization was carried out in a flask equipped with a magnetic stirrer

Table I Effect of Reaction Time on M_n and M_w/M_n of Poly(LLA-*co*-TMC)^a

Monomer Feed LLA/TMC (mol/mol)	Time h	Molecular Weight (M_n) g/mol	M_w/M_n
90/10	12	61,800	1.29
90/10	24	44,000	1.63
90/10	48	65,400	1.49
90/10	96	20,000	3.33
70/30	12	26,200	2.32
70/30	24	22,690	1.93
70/30	48	27,430	2.43
70/30	91	41,500	1.95

^a The molar ratio of monomer to catalyst is 500/1.

bar, using Sn(oct)₂, as catalyst. Selected amounts of monomers (total 3 g) and catalyst (for details see Tables I and II) were introduced into a flask inside a glove box filled with nitrogen and the reactants were degassed in vacuum. Then the flask was filled with nitrogen again, sealed, immersed into an oil bath at 110°C, and kept under magnetic stirring until the viscosity became very high. After 12–96 h of reaction, the polymer was removed from the flask by its dissolution in chloroform, purified by precipitation in hexane, washed with hexane two to three times and, finally, dried under reduced pressure.

Characterization

NMR Analysis

The ¹H-NMR analysis of the poly(LLA-*co*-TMC) samples was carried out with a GEMINI-300 NMR spectrometer using CDCl₃ as the solvent. The copolymer composition was calculated using the ¹H-NMR spectrum.

FTIR Analysis

The FTIR analysis was performed with a Perkin–Elmer 1760X FTIR instrument. The samples were dissolved in chloroform and cast onto NaCl plates. The scanning number was 32 and the resolution 2 cm⁻¹.

Molecular Weight Determination

The molecular weight data were obtained by gel permeation chromatography (GPC, Waters) at 30°C, using THF as eluent at a flow rate of 1 mL/

Table II Effect of Monomer Composition on the M_n and M_w/M_n ^a

LLA/TMC mol/mol (in the feed)	Time h	TMC Content mol % (calc.) (in copolymer)	TMC wt % Calc.	TMC Content wt % (found) (by ¹ H-NMR)	M_n g/mol	M_w/M_n
90/10	24	5.3	7.3	—	44,000	1.63
70/30	24	11.1	15.0	—	22,690	1.93
0/100	24	100	100	100	8,850	1.76 ^c
100/0	96	0	0	—	^b	—
90/10	96	5.3	7.3	7.8	20,000	3.33
80/20	95	11.1	15.0	14.2	37,840	1.54
70/30	91	17.7	23.3	23.7	41,500	1.95
70/30	94	17.7	23.3	18.1	9,740 ^d	1.85
60/40	96	25.0	32.1	—	48,000	1.86
50/50	95	33.3	41.5	—	21,000	1.78

^a The molar ratio of monomer to catalyst is 500/1.

^b PLLA is not soluble in THF.

^c The molar ratio of monomer to catalyst is about 100/1.

^d TMC was recrystallized twice, in all the other experiments the TMC was recrystallized six times.

min. Polystyrene standards were used to calibrate the molecular weight.

Thermal Analysis

The thermal behavior of the polymers was investigated using a DuPont 910 differential scanning calorimeter (DSC), under a nitrogen atmosphere. The samples were scanned from room temperature to 180°C, at a heating rate of 10°C/min, hold at 180°C for 1 min, and then quenched into liquid nitrogen. The samples were rescanned from -10 or -50 to 180°C (depending on the T_g of copolymer or homopolymer) at a heating rate of 10°C/min. The data were collected during the second scanning. The glass transition temperature (T_g) was taken as the midpoint of the heat capacity change; the cool crystallization temperature and the melting point were provided by the exo- and endo-thermal peaks, respectively.

Mechanical Properties Determination

Thin films of PLLA and copolymers were prepared by hot pressing at a temperature above their melting points and by cooling down quickly to about 5–10°C. The obtained films (0.10–0.15-mm thickness) were cut into dumbbell-shaped forms, as indicated by ASTM D.638-58T. The tensile testing was performed at room temperature, using an Instron Universal Testing Instrument (Model 1000), with an elongation rate of 10 mm/min. The yield and tensile strengths were calculated on the basis on the initial cross-section area of the speci-

men. The toughness (MJ/m^3), defined as the energy needed to break a sample of unit area and unit length, is given by the area under the stress-strain curve.

RESULTS AND DISCUSSION

The ring-open copolymerization of L-lactide and trimethylene carbonate was carried out in the molten state at 110°C for 0.5–4 days. The effect of the reaction time on the number-average molecular weight (M_n) of the copolymers obtained is presented in Table I. Three general trends can be noted: (a) the M_n of poly(LLA-co-7.3 wt % TMC) (high LLA content) is higher than that of poly(LLA-co-23 wt % TMC) (high TMC content) for the first 48 h; (b) the M_n of poly(LLA-co-7.3 wt % TMC) becomes, however, lower than that of poly(LLA-co-23 wt %) after 4 days of reaction; (c) the M_n does not change appreciably between 12 and 48 h of reaction. This happens because: (1) the reaction rate of LLA is faster than that of cyclic TMC; (2) the concentration of LLA is higher in LLA-7.3 wt % TMC than that in LLA-23 wt % TMC; and (3) the depolymerization reaction due to thermal degradation becomes significant only after a sufficient long time of heating at 110°C and the degradation affects more strongly the polymers with a higher content of LLA than those with a lower content. For these reasons, an optimum reaction time for a maximum M_n could be identified. The time is longer for higher TMC con-

tent; it is less than 12 h for the poly(LLA-co-7.3 wt % TMC) and greater than 48 h for the poly(LLA-co-23 wt % TMC). The degradation is associated with an increase in the ratio M_w/M_n ; hence, an increase in the broadness of the molecular weight distribution.

The effect of the monomer ratio on M_n of the copolymer is presented in Table II. The L-lactide content in the copolymer was calculated based on the $^1\text{H-NMR}$ spectra, and was found to be close to the monomer feed composition. Several factors affect, for a given catalyst concentration, the molecular weight of copolymer: (a) the purities of the reactants; and (b) the feed composition. The purity of TMC had a critical effect on the M_n of the copolymer. For instance, the TMC recrystallized twice from a THF-ether mixture possessed some impurities, detected by NMR, and a low molecular weight (less than 10^4) copolymer was obtained. In contrast, when the TMC was recrystallized six times, much less impurities were detected by NMR and a copolymer with a higher molecular weight (4×10^4) was obtained. This happens because impurities, such as traces of water and various functional groups, can initiate polymerization, and the larger the number of the initiation centers, the lower the M_n . For molar ratios LLA/TMC greater than 1.5 and a reaction time of 4 days, one can see that M_n increases with increasing TMC content. This happens because less depo-

lymerization takes place. However, for a molar ratio of 1 and a reaction time of 4 days, M_n is smaller than for a molar ratio of 1.5, because of the slower reaction rate of TMC. For a reaction time of 24 h (Table II), M_n increases with increasing LLA/TMC molar ratio, because the reaction of LLA is more rapid than that of TMC and less depolymerization occurs.

Figure 1 presents the $^1\text{H-NMR}$ spectrum of a copolymer containing about 80 mol % (77 wt %) L-lactide. It was reported that some carbon dioxide is eliminated during the cation ring-open polymerization of TMC and, hence, that some ether linkages are formed in the polycarbonate.¹⁸ However, no elimination of carbon dioxide was detected in our experiments, because no peak at 3.4 ppm, which can be assigned to $-\text{CH}_2-\text{O}-\text{CH}_2-$, is present.

Figure 2 depicts the FTIR spectra of pure PLLA (a), poly(L-lactide-co-41 wt % TMC) (b), and pure PTMC (c). The peaks at 1757 and 1185 cm^{-1} in (a) can be assigned to the $\text{C}=\text{O}$ stretching and the $-\text{C}-\text{C}-\text{O}$ asymmetric stretching frequencies of PLLA, respectively, and the peaks at 1745 and 1247 cm^{-1} in (c) to the $\text{C}=\text{O}$ stretching and $\text{O}-\text{C}-\text{O}$ asymmetric stretching frequencies of PTMC, respectively. The copolymer (b) has a $\text{C}=\text{O}$ stretching frequency at 1752 cm^{-1} , located between those of PLLA and PTMC, but retains the stretching frequencies at 1185 and 1248 cm^{-1} of the $\text{C}-\text{C}-\text{O}$ and $\text{O}-\text{C}-\text{O}$ asymmetric

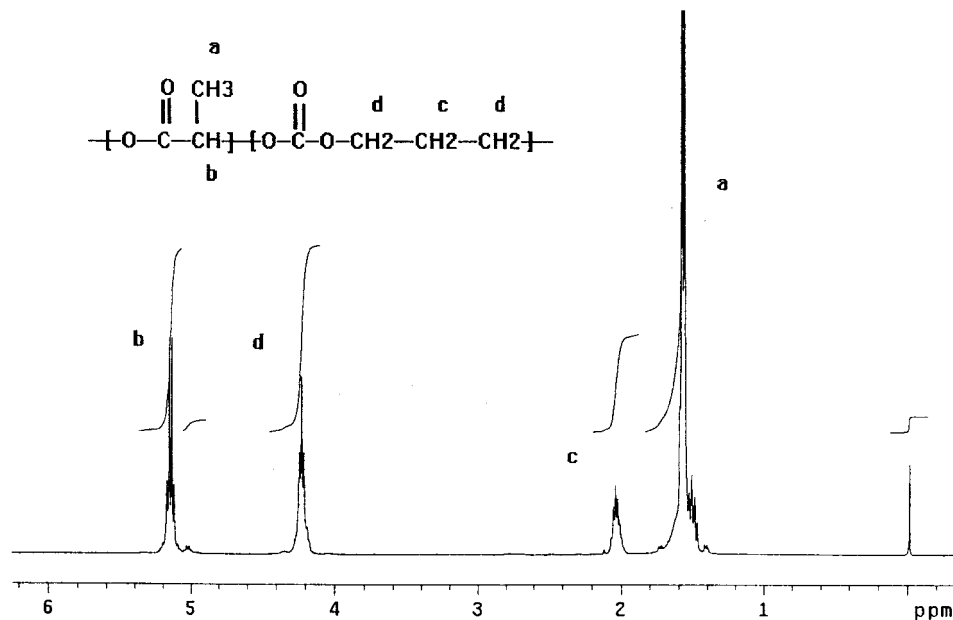


Figure 1 $^1\text{H-NMR}$ spectrum of poly(LLA-co-23 wt % TMC).

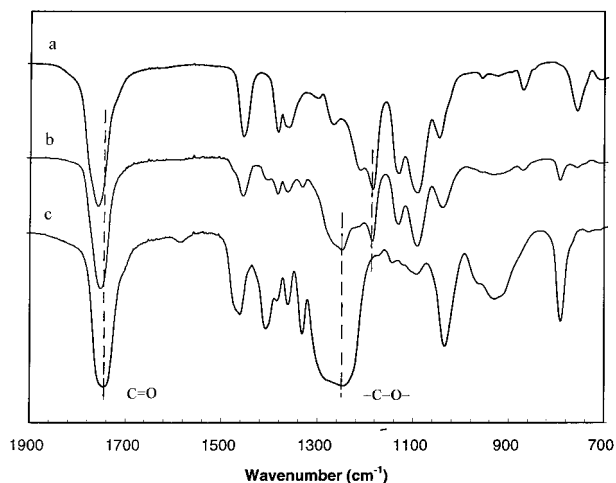


Figure 2 FTIR spectra of (a) PLLA, (b) poly(LLA-co-41.5 wt % TMC) and (c) PTMC.

stretchings of the ester and the carbonate moieties, respectively.

The DSC traces of copolymers are presented in Figure 3. The T_g and T_m of the copolymers decrease with increasing TMC content. For higher TMC contents, the heat of fusion of the PLLA crystals becomes smaller, indicating that the extent of crystallinity decreases.

The dependence of T_g on composition is in good agreement with the Fox equation:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where T_{g1} and T_{g2} , w_1 and w_2 are the T_g s and the weight fractions of the individual homopolymers, respectively. The results are plotted in Figure 3.

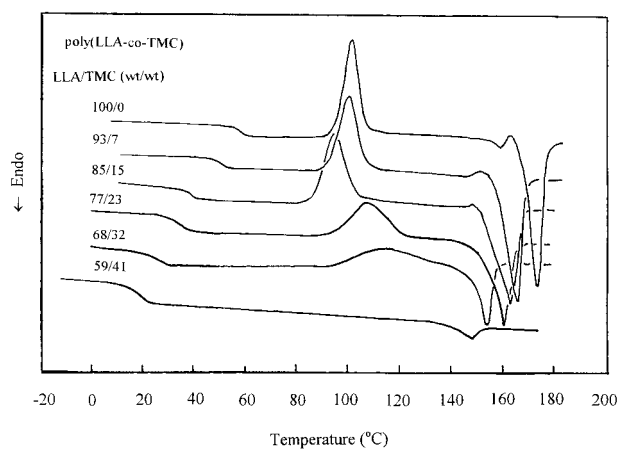


Figure 3 DSC traces of poly(LLA-co-TMC) with TMC content 0–41.5 wt %.

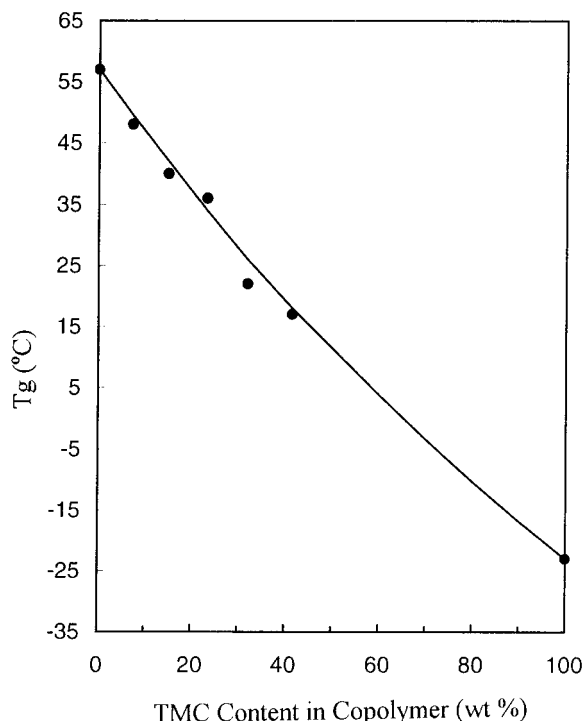


Figure 4 The dependence of T_g of the copolymer on the TMC content (●): experimental points; (—): Fox equation.

The mechanical properties of poly(LLA-co-TMC) are listed in Table III. For the pure PLLA, the elongation at break is very low, about 6%. With increasing TMC content in the copolymer, the elongation at break increases. At 15 wt % TMC, the elongation becomes about 15%, while when the TMC content increases to 32 wt %, the copolymer acquires a rubber behavior and the elongation increases significantly, up to 375%. This high elongation at break is associated with a T_g of 22°C, which is lower than the testing temperature (room temperature). The copolymer with 41.5 wt % TMC has a T_g of about 17°C, but being too soft no data could be collected regarding the mechanical properties, because no suitable film could be prepared. As expected, the yield and tensile strengths as well as the Young modulus decrease with increasing TMC content. The toughness increases with increasing TMC content as long as the latter is not too high. For too high values (greater than about 40 wt %), the material acquires a low toughness due to its low strength.

The copolymer properties can be adjusted by varying the monomer feed composition. The toughness of the copolymer can be tremendously increased by increasing the TMC content to 32 wt

Table III The Mechanical Properties of Poly(LLA-co-TMC)

TMC Content wt %	Yield Strength MPa	Tensile Strength MPa	Young Modulus MPa	Elongation %	Toughness MJ/m ³
0 (PLLA)	61	54	1400	6	2.5
15	62	55	1480	15	7
32	33	39	650	375	105

% (Table III). The T_g can be also controlled. For instance, the T_g of the copolymer with 23 wt % of TMC is about 36°C, which is close to the human body temperature. This copolymer possesses great toughness and good biodegradability *in vivo*, and can be used as a bioabsorbable material.

CONCLUSIONS

The molten ring open copolymerization of L-lactide (LLA) and trimethylene carbonate (TMC) was investigated and the structure and properties of poly(LLA-co-TMC) were studied by GPC, NMR, FTIR, DSC, and Instron testing. The reaction time and the monomer composition affect the molecular weight (M_n) of copolymers. When the reaction time is not too long, the M_n of the copolymer with a high LLA content is greater than that of the copolymer with a high TMC content. However, the M_n of copolymers increased with increasing PTMC content for long reaction times. The glass transition temperature (T_g), the melting temperature, and the crystallinity of the copolymers decrease with increasing TMC content due to the amorphous nature of PTMC.

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