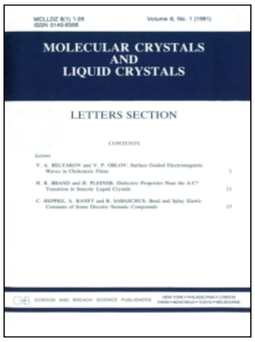

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Synthesis and characterization of biodegradable triblock copolymers from L, D-lactides and poly(ethylene carbonate)

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ABSTRACT
To develop carbon dioxide (CO_2)-reducible polymeric materials, block copolymers (PLA-PEC-PLA) of CO_2-reducible polymers, poly(lactide) (PLA) and poly(ethylene carbonate) (PEC) were synthesized by the ring-opening polymerization of lactide in the presence of PEC diol using stannous octoate. Differential scanning calorimetry and contact angle measurements showed that the incorporation of the PEC block decrease the crystallinity of PLA and increases the hydrophilicity and flexibility due to its compatibility. The enzymatic degradation in Tris-HCl buffer containing proteinase K showed that the degradation rate of L-PLA-PEC-L-PLA was faster than that of L-PLA due to the decreased crystallization and increased hydrophilicity after copolymerization as well as degradation of PEC.

KEYWORDS
carbon dioxide; poly(lactide); poly(ethylene carbonate); biodegradation

Introduction

Sustainable and eco-friendly polymers, natural polymers, bio-based polymers, and degradable polyesters are of growing interest because of the environmental concerns associated with waste plastics and emissions of carbon dioxide from the preparation of petroleum-based polymers. Polymers have found a variety of applications in all facets of life and industry. However, most synthetic polymers are manufactured from petroleum-derived sources. These materials are not readily biodegradable because of their resistance to microbial degradation, and they have accumulated in the environment [1,2]. Synthetic plastics are the cause of various environmental problems resulting from the disposal of petroleum-based polymers, which are very stable in the environment. These facts have stimulated interest in biodegradable polymers [2]. Biodegradable polymers, such as poly(lactide) (PLA), and their copolymers have received significant attention because the raw material, lactic acid (LA), can be efficiently produced by the fermentation of renewable resources [3]. PLA has been widely used in a variety of biomedical applications, drug delivery devices, scaffolds for tissue engineering and other related applications [3–5].

Since people started to unearth fossil fuel, the rate of carbon dioxide (CO_2) emissions has rapidly increased, leading to global warming [6]. Therefore, recent trends in commercial

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goods require the reduction of CO_2 emissions during processing. Additionally, the method of CO_2 consumption is important. Poly(ethylene carbonate) (PEC) can be produced by the reaction of CO_2 and ethylene oxide under a catalyst [6–8]. Additionally, PEC is one of a few polymers that undergoes rapid in vivo degradation via surface erosion [7,8].

In this study, we report aliphatic biodegradable triblock copolymers, PLA-PEC-PLAs, in which one block is PEC and both end blocks are poly(L-lactide) (L-PLA) or poly(D-lactide) (D-PLA). We investigated the physical properties of the block copolymers and the enzymatic degradation of L-PLA and its copolymers.

Experimental

L-Lactide and D-lactide were purchased from Purac (Netherlands) and were recrystallized from anhydrous ethyl acetate. Hydroxyl-terminated PEC (M_n: 1684 g/mol, SK energy, Korea) was vacuum-dried at 80°C for 24 hr prior to use. Stannous octoate and proteinase K (41 U/mg) were purchased from Sigma and were used without further purification. All other reagents were analytical grade.

PLA-PEC-PLA triblock copolymers were synthesized by ring-opening polymerization. PEC and LA were introduced into a dried polymerization tube. High-viscosity stannous octoate was diluted with *n*-hexane and added into the reactor. The mixture was kept under vacuum at 70°C for 24 hr to remove the organic volatiles. Then, the reactor was purged with nitrogen several times and sealed under vacuum. The polymerization was allowed to proceed at 150°C for 90 min with stirring. After 3 hr, the obtained product was purified by dissolution/precipitation using chloroform as a solvent and methanol as a non-solvent.

The molecular weights were determined by gel permeation chromatography (GPC) using a Waters Model 1515 pump and a Model 2424 refractive index detector with three Waters Styragel columns (HR1, HR2, HR5E). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. The chemical compositions of the triblock copolymers were measured by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR, JEOL JNM ECP-400, 400 MHz) with *d*-chloroform as the solvent. The thermal properties of the samples were obtained by differential scanning calorimetry (DSC, METTLER TOLEDO, DSC1) with a 10°C/min heating rate.

Water contact angles were measured using drop shape analysis (DSA, Krüss, DSA 100) at room temperature with a 500 μL syringe, a 0.5 mm diameter and 38 mm length needle and 3 μL of water. For the degradation study, thin films were prepared by spin-coating at 2000 rpm onto a slide glass. Each specimen was placed in 10 mL of 0.5 M Tris-HCl buffer solution ($pH = 8.6$) containing 0.5 mg of proteinase K at 37.5°C. After the desired time, specimens were removed and washed with distilled water five times and then dried at room temperature for 24 hr. The surface morphologies of the PLA-PEC-PLAs and L-PLA films were measured by atomic force microscopy (AFM, Seiko Instruments Inc., SPA 400).

Results and discussion

The copolymerization of L-lactide, D-lactide and PEC with different compositions was performed, and the resulting properties are summarized in Table 1. The block ratio of lactide and PEC varied from 2 to 13. Fig. 1 shows the ^{1}H-NMR spectrum of L-PLA-PEC-PLA8. The ^{1}H-NMR peaks, marked with letters from *a* to *d* for PLA-PEC-PLA, were appointed to the corresponding hydrogen atoms of the copolymer. Peaks *a*, at 5.17 ppm, and *b*, at 1.60 ppm, from PLA were assigned to C-H and C-H_3, respectively. The peak at 4.40 ppm was assigned to the CH_2-CH_2 of PEC. The GPC traces of all copolymers showed a unimodal peak without

Table 1. Physicochemical properties of the polymers synthesized in this study.

Sample	Block ratio* (PLA/PEC)	T_g(°C) 2nd	T_m (°C)	ΔH (J/g)	M_n*	M_n	PDI
L-PLA		52.94	165.14	63.93		13,615	1.25
PEC		− 13.37				1,684	1.09
L-PLA-PEC-PLA2	1.65	28.94	110.69	8.21	4,463	4,785	1.13
L-PLA-PEC-PLA4	4.59	43.76	144.44	32.33	9,414	8,820	1.39
L-PLA-PEC-PLA8	8.40	49.44	148.78	36.02	15,830	13,290	1.49
L-PLA-PEC-PLA12	11.64	51.77	150.60	37.40	21,286	12,914	1.50
L-PLA-PEC-PLA13	12.40	53.44	160.85	44.84	22,566	21,508	1.34
D-PLA-PEC-PLA2	2.43	37.10	132.12	26.88	5,776	6,091	1.24
D-PLA-PEC-PLA4	4.14	44.59	141.64	32.61	8,656	7,325	1.35
D-PLA-PEC-PLA8	7.83	49.21	146.65	33.12	14,870	12,231	1.49
D-PLA-PEC-PLA12	11.05	50.11	150.42	37.02	20,292	13,713	1.53
D-PLA-PEC-PLA13	9.03	44.13	154.28	37.44	16,891	15,410	1.34
Blend**		47.46	205.30	53.98	15,350	12,761	

* The block ratio and number averaged molecular weight (Mn∗) of the PLA-PEC-PLAs were calculated from the ^{1}H-NMR data.
**L-PLA-PEC-PLA8/D-PLA-PEC-PLA8 blend (50/50 by wt %).

a peak at PEC itself (Fig. 2). These results indicate that the copolymerization was successfully completed.

The thermal properties of PLA-PEC-PLA were obtained from DSC measurements. As shown in Fig. 3, all DSC peaks of the copolymers show a single glass transition temperature (T_g) between both of the homopolymer T_gs, which indicates that both blocks in the copolymers are compatible. The T_g and melting temperature (T_m) of the copolymers increased with increasing PLA block (see Table 1). The peaks of the second heating run did not show any T_m traces, regardless of the copolymer composition, even though the T_m peak of L-PLA in the second scan was observed, which suggests that the crystallization of the L-PLA blocks in the

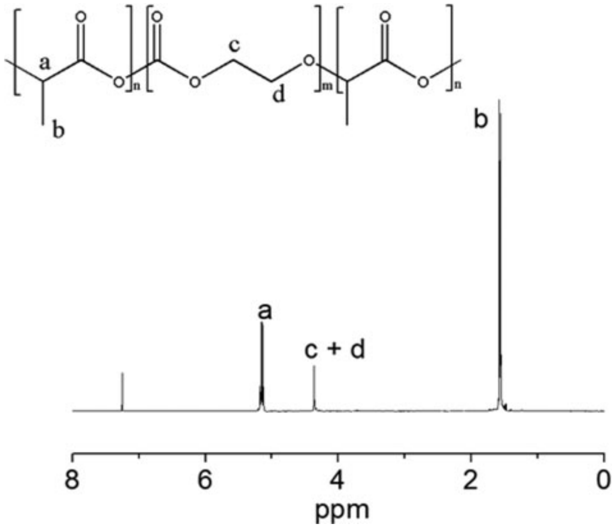

Figure 1. ^{1}H-NMR spectrum of L-PLA-PEC-PLA8.

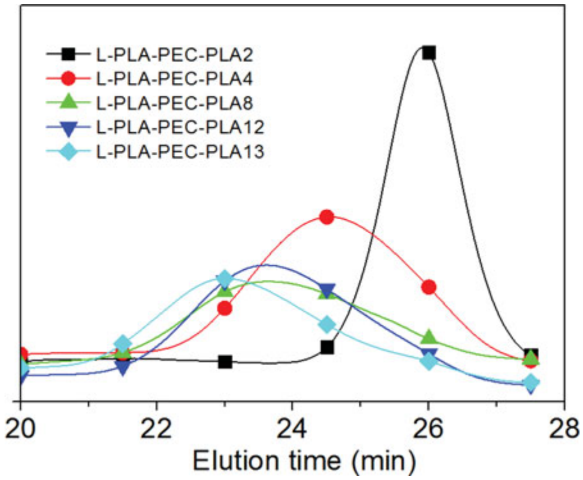

Figure 2. GPC traces of L-PLA-PEC-PLAs.

copolymers was interrupted by the strong interaction between the two blocks. Fig. 4 shows the water-contact angle images of PEC, L-PLA and the copolymers with different compositions. The contact angles of the samples increased with PLA content in the copolymers. PEC is more hydrophilic than PLA because the PEC unit has more oxygen atoms than the PLA unit (see Fig. 1 copolymer structure). According to the contact angle data, the difference in the surface energies of both components is low, whereas the interaction between them is strong. Therefore, surface segregation of PLA was not observed.

The surface morphologies of the PLA-PEC-PLA and L-PLA films before and after enzymatic degradation were observed by AFM, as shown in Fig. 5. After 30 min and 2 hr degradation, pits were observed on the surface of L-PLA-PEC-PLA8 whereas only a few tiny pits appeared on the D-PLA-PEC-PLA8 film. Because D-PLA is inactive to the enzyme proteinase K, the morphological change of D-PLA-PEC-PLA8 after enzymatic degradation is due to the degradation of PEC. The degradation rate of L-PLA-PEC-PLA8 was faster than that of L-PLA due to the increased hydrophilicity, low crystallinity, and degradability of PEC. In the case of the blend films, the pit size of L-PLA-PEC-PLA8 was larger than that of the L-PLA-PEC-PLA8/ D-PLA-PEC-PLA8 blend due to the stability of the stereocomplex between D-PLA and L-PLA.

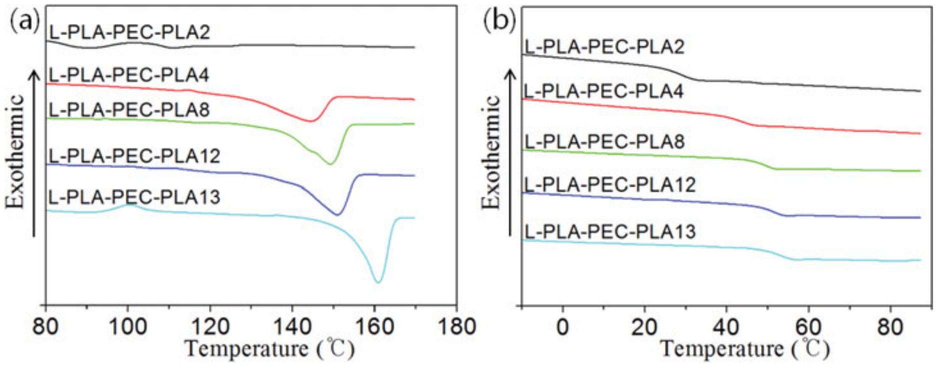

Figure 3. DSC thermograms of L-PLA-PEC-PLAs. The first heating run (a) and second heating run (b).

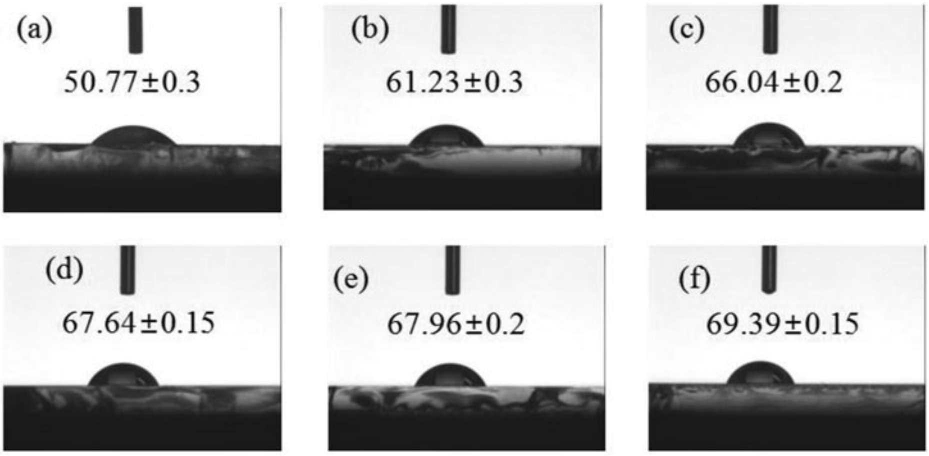

Figure 4. Optical images of the static contact angle of PEC, L-PLA and copolymers: (a) PEC, (b) L-PLA-PEC-PLA2, (c) L-PLA-PEC-PLA4, (d) L-PLA-PEC-PLA8, (e) L-PLA-PEC-PLA12, (f) L-PLA.

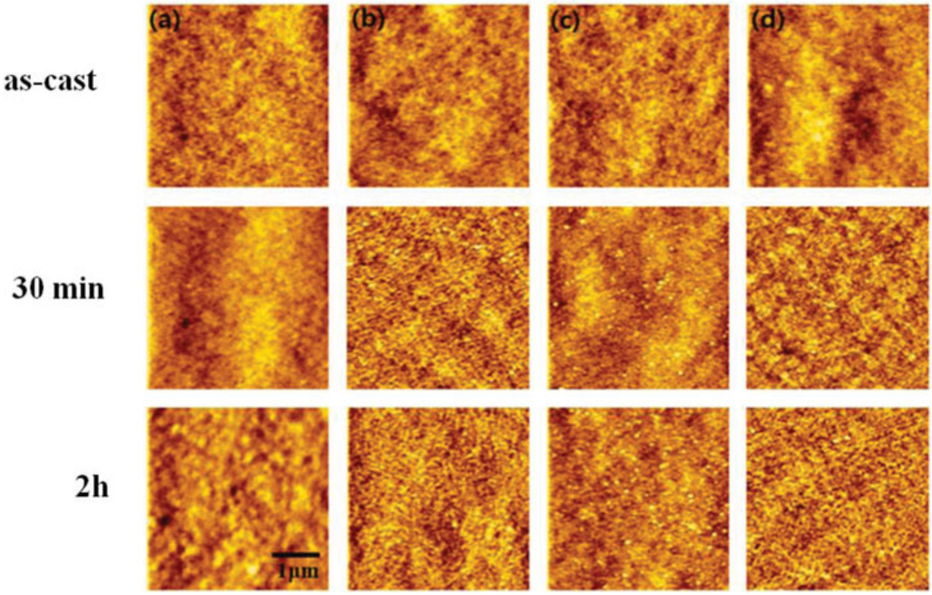

Figure 5. Surface topographic images of PLA-PEC-PLA films: (a) L-PLA, (b) L-PLA-PEC-PLA8, (c) D-PLA-PEC-PLA8, (d) L-PLA-PEC-PLA8/D-PLA-PEC-PLA8 blends (5/5).

Conclusion

Although the development of eco-friendly PLA is in its early stages compared with that of conventional polymers, the potential applications of PLA as a biodegradable and environmental-friendly polymer are promising. Similarly, PEC synthesized by CO_2 is biodegradable. Therefore, both polymers can reduce CO_2 emissions. To minimize CO_2 emissions from polymeric materials, a series of biodegradable triblock copolymers of PLA-PEC-PLA was synthesized from L-lactide, D-lactide and PEC. The chain length and molecular weight of the copolymers can be controlled by changing the feed ratio of lactide/PEC. All copolymers showed a single T_g due to the compatibility. The L-PLA-PEC-PLA was more hydrophilic than L-PLA according to the contact angle measurement. According to the degradation behavior of the copolymers and homopolymer in the presence of proteinase K, L-PLA-PEC-PLA underwent faster degradation than L-PLA. Therefore, the degradation rate and flexibility could be controlled by copolymerization.

Acknowledgments

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