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Synthesis and Characterization of Poly(L-lactide)−Poly(ϵ-caprolactone) Multiblock Copolymers

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ABSTRACT: New poly(L-lactide) (PLLA)−poly(ϵ-caprolactone) (PCL) multiblock copolymers were prepared by using the coupling reaction between the bischloroformates of carboxylated PLLA with PCL-diol in the presence of pyridine. All the copolymers were characterized by ^{1}H NMR and GPC and investigated further by using DSC, TGA, SAXD, WAXD, polarizing microscope, and Instron testing. The molecular weights of PLLA−PCL multiblock copolymers produced lay in the range 40 000−50 000. The multiblock copolymers produced exhibited only one melting peak, corresponding to the PLLA phase, even at a relatively high PCL content, whereas the PLLA−PCL−PLLA triblock copolymers had two melting peaks. The tensile moduli and strengths of the triblock copolymer were very high. On the other hand, the multiblock copolymers were flexible and elastic with relatively good mechanical properties. These copolymers behaved like thermoplastic elastomer due to the presence of physical cross-linking and strain recoveries of more than 95% at 100% strain. Degradation of the copolymers was investigated in PBS for up to 150 days. The random copolymer was found to be rapidly degraded, while the triblock and multiblock polymers were slowly degraded. The molecular weight of the multiblock copolymers decreased with time, but there were no significant changes in their chemical compositions. From ^{1}H NMR studies, chain scission occurred in the PLLA blocks.

Introduction

Aliphatic polyesters such as polyglycolide (PGA), polylactide (PLA), poly(ϵ-caprolactone) (PCL) and their copolymers have received great interest in medical applications, such as drug delivery systems, sutures, artificial skins, orthopedics, and scaffold for tissue engineering, because of their excellent biodegradabilities and biocompatibilities.[1−8] PLLA is one of the most intensively studied polymers in orthopedic applications because of its good mechanical properties.[9−13] However, copolymers of PCL may expand its applications because with this material it becomes possible to fabricate a varied family of bioabsorbable materials with soft, elastic compositions. Moreover, the elongation characteristics of elastomeric copolymers make them suitable for applications where elasticity and degradability are required in the same product.[14−16]

The syntheses of ϵ-CL/LA copolymers and other lactone polymers have been widely studied in recent years.[17−19] Most studies have focused on random, diblock, and triblock copolymers.[20−22] To expand the properties of ϵ-CL/LA copolymers, we synthesized new PLLA−PCL multiblock copolymers. PLLA−PCL multiblock copolymers were prepared by using coupling reactions between two short blocks in the absence of chain extending compounds.

The chemical structures, thermal properties, crystallization characteristics, mechanical properties, and strain recoveries of multiblock copolymer were characterized using ^{1}H NMR, DSC, wide-angle X-ray diffraction (WAXD), small-angle X-ray diffraction (SAXD), and Instron testing. Our research was mainly concerned with the synthesis, physical properties, strain recovery properties, and degradation characteristics of the copolymers. We found that multiblock copolymers with various improved properties, including processability, biodegradability, and strain recovery, can be obtained.

Experimental Section

Materials. Poly(ϵ-caprolactone)diols (Polysciences, Sigma-Aldrich) with of M_n 530, 1250, and 2000 were purified by precipitation from chloroform into diethyl ether and used after drying at 30 °C under vacuum. L-Lactide was purchased from Purac and recrystallized from dried ethyl acetate in a dry nitrogen atmosphere and then thoroughly dried for 24 h in a vacuum at 30 °C before use. The stannous octoate (Sn-oct) from Sigma was distilled under reduced pressure at 175 °C before use. 1,6-Hexanediol, 1,4-dioxane, methylene chloride, and pyridine were distilled over calcium hydride.

Synthesis of PLLA Homopolymer. L-Lactide (1 mol), stannous octoate [5 mmol, monomer/catalyst ratio (M/C) = 200], and 1,6-hexanediol (25 mmol) were weighed into a round-bottomed flask equipped with a mechanical stirrer. The flask was purged with dry nitrogen and immersed in an oil bath at 130 °C for 5 h. The product was dissolved in chloroform and microfiltered through a 0.45 μm pore membrane filter. The polymer was precipitated by pouring the polymer solution into an excess of methanol, filtered, and dried under vacuum.

Synthesis of Dicarboxylated PLLA. PLLA (30 g, 5 mmol), succinic anhydride (10 mmol), DMAP (10 mmol), and triethylamine (10 mmol) were dissolved in 1,4-dioxane (200 mL) and left overnight at room temperature. The filtered solution was precipitated by adding ether, and the polymer precipitate was dried under vacuum for 3 days at room temperature. From ^{1}H NMR analysis, it was found that the ring of the succinic anhydride had been opened by a hydroxyl group. Thus, a terminal carboxyl group was introduced into the PLLA.

Synthesis of COCl-Terminated PLLA (PLLA-diCOCl). Dicarboxylated PLLA (10 g, 1.7 mmol) was dissolved in purified methylene chloride and thionyl chloride (0.4 g, 3.4 mmol), and two drops of dimethylformamide (DMF) were

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Table 1. Molecular Weight Characterization of Polymers

code	polymer	M_n	M_w[b]	M_w/M_n[b]	ratio[c]
PCL0.5	PCL	540[a]/690[b]	1010	1.46	1.28
PCL2	PCL	1970[a]/2460[b]	3370	1.37	1.25
PCL3	PCL	3180[a]/4070[b]	6186	1.52	1.29
PL3	PLLA	3410[a]/4430[b]	5670	1.28	1.30
PL6	PLLA	5950[a]/7700[b]	10550	1.37	1.29
PL7	PLLA	7400[a]/8890[b]	12800	1.44	1.20
PL9	PLLA	9300[a]/11200[b]	14450	1.29	1.21
PL3PCL2	multiblock	29600[b]	54500	1.84	
PL6PCL2	multiblock	38600[b]	122500	3.17	
PL7PCL2	multiblock	36300[b]	66700	1.84	
PL9PCL2	multiblock	46500[b]	96700	2.08	
PL6PCL0.5	multiblock	16400[b]	36000	2.20	
PL6PCL3	multiblock	34700[b]	85000	2.45	
PL/PCL/PL	triblock	50600[b]	94300	1.86	
PLCL5/5	random	30000[b]	49800	1.66	

[a] Calculated from ^{1}H NMR spectra. [b] Estimated by GPC (PS calibrated GPC measurements overestimate the actual molecular weights of aliphatic polyesters by 50–100% (depending on their structures and molecular weights)).[23] [c] Calculated from the M_n(GPC) relative to M_n(NMR).

added to the solution. The reaction was carried out at 60 °C for over about 3 h, and the reaction solution was then distilled under vacuum to remove the solvent and unreacted thionyl chloride. From ^{1}H NMR analysis, it was found that the acyl halide (COCl) group had been introduced at the end of PLLA. The product was used immediately for the coupling reaction.

Synthesis of PLLA–PCL Multiblock Copolymers. The PLLA-diCOCl and PCL-diol (HO-PCL-OH) were put in a flask under a nitrogen atmosphere. The molar feed ratio of PLLA-diCOCl and PCL-diol was 1:1. An ice bath was used to maintain the reaction at a sufficiently low temperature, and then purified pyridine was added dropwise. The reaction system was maintained at room temperature, and the reaction was carried out for 24 h. The reacted solution was precipitated using methanol, and the PLLA–PCL multiblock copolymer so obtained was dried under vacuum at ambient temperature for at least 12 h.

Synthesis of PLLA–PCL–PLLA Triblock Copolymers. ϵ-Caprolactone (100 mmol), stannous octoate [0.02 mmol, monomer/catalyst ratio (M/C) = 5000], and 1,6-hexanediol [0.5 mmol, monomer/initiator ratio (M/I) = 200] were weighed into a three-necked round-bottomed flask equipped with a mechanical stirrer. The flask was purged with dry nitrogen and immersed in an oil bath at 110 °C for 40 h. L-Lactide (100 mmol) and stannous octoate [0.02 mmol, monomer/catalyst ratio (M/C) = 5000] were then weighed into the flask, which was purged with dry nitrogen, and immersed in an oil bath at 120 °C for 150 h. The product so obtained was dissolved in chloroform, microfiltered through a 0.45 μm pore membrane filter, precipitated by pouring into an excess of methanol, filtered, and dried under vacuum.

Synthesis of PLLA–PCL Random Copolymers (PLCL). ϵ-Caprolactone (100 mmol), L-lactide (100 mmol), stannous octoate (1 mmol), and 1,6-hexanediol (0.5 mmol) were weighed into a glass ampule equipped with a magnetic stirring bar. The ampule was sealed under vacuum after purging three times with nitrogen at 90 °C and heated to 150 °C in an oil bath for 24 h with stirring. After reaction, the ampule was broken; the polymer was then dissolved in chloroform and microfiltered through a 0.45 μm pore membrane filter. It was precipitated by pouring the polymer solution into an excess of methanol, filtered, and dried under vacuum.

Molding. The samples used for tensile and recovery testing were prepared by compression molding (Carver Laboratory Press) at different temperatures, depending on the sample [PL3PCL2, PL6PCL2, PL7PCL2, PL6PCL0.5, PL6PCL3: 155 °C; PL9PCL2, PL/PCL/PL: 170 °C; PLCL5/5: 60 °C] (see Table 1 for sample code). Test specimens were punched out from molded plates using a dog-bone puncher.

Measurement. ^{1}H NMR spectra were recorded in $CDCl_3$ at room temperature using Varian UNITY Unity-300 (300 MHz) and Unity-600 (600 MHz) units. The molecular weight and distribution of the polymers were measured by GPC (Waters HPLC system—410 differential refractometer, three PLGel columns (HR2, HR4, and HR5E), 515 pump). Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 0.5 mL/min. Calibration was performed using polystyrene standards to determine absolute weight-average and number-average molecular weights (M_w and M_n). Differential scanning calorimetry (DSC) thermograms were obtained using a TA Instrument, Inc., TA5000/DSC2950 at a heating rate of 10 °C/min. Values of glass transition temperatures (T_g) were taken from the midpoints of the transition zones. Wide-angle X-ray diffractometric analyses were carried out using a diffractometer equipped with a Cu KR (λ = 0.154 nm) source, using a Rigaku International Corp. model D/MAX 2500. Small-angle X-ray diffraction measurements (SAXD) carried using a synchrotron radiation X-ray beam, beamline 4C1 at Pohang Light Source (Korea). The storage ring was operated at an energy level of 2 GeV. SAXS employs point-focusing optics with a silicon double-crystal monochromator and a bent cylindrical mirror. The incident beam intensity, with a wavelength of 0.149 nm, was monitored using an ionization chamber to correct minor decreases in the primary beam intensity during measurements. For optical microscopy measurements, a polarizing optical microscope, Leitz Ortholex II, equipped with a heating device was used. The sample was placed on a glass plate, heated to its melting temperature (T_m), and then cooled at 10 °C/min to 120 °C. Mechanical properties and the elasticity of the copolymers were determined by Instron testing (Instron Corp., model 5567). The degradation morphology of polymers was analyzed with a scanning electron microscope (SEM, Hitachi, Tokyo, Japan). Samples were cut using a razor blade and then mounted on aluminum pins using double-sided adhesive tape. Prior to microscopical examination, the samples were sputter-coated with gold layer using a sputter-coater (Eiko IB3, Tokyo, Japan), and the microscope was operated at 15 kV to image samples.

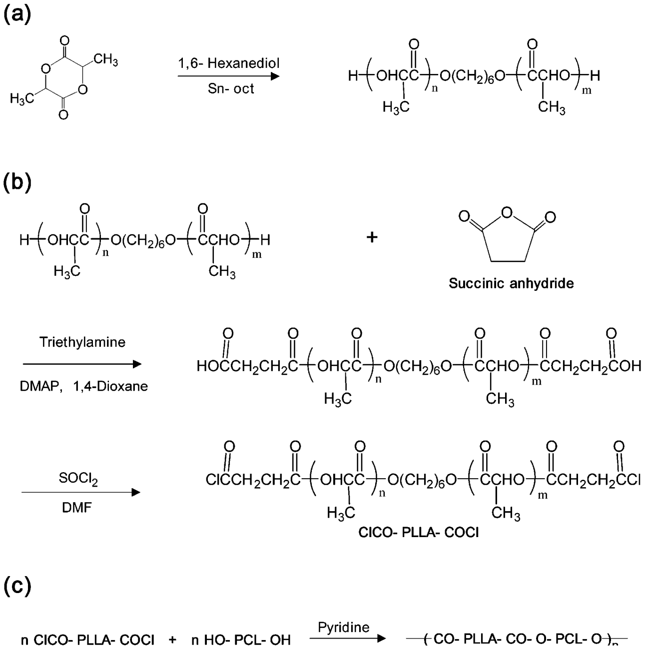
Biodegradation Test. The molded samples were cut into a rectangular shape with dimensions of 10 × 10 × 0.2 mm^3 for in vitro degradation studies. The cut specimens were placed in closed bottles containing 50 mL of phosphate buffer solution (PBS, pH 7.4) at 37 °C for 150 days. After 20, 40, 60, 80, 100, 120, and 150 days, the films were washed with distilled water and dried in a vacuum. The molecular weights of the polymers were measured by GPC. The degradation rates were estimated by the mass loss (%) and molecular weight reduction (%) calculated with the equation shown in the caption of Figures 9 and 10. The aspect of the films was observed by scanning electron microscope (SEM).

Results and Discussion

Synthesis. PLLA–PCL multiblock copolymers were synthesized by coupling PLLA and PCL segments. PLLA-diCOOH was prepared by reacting PLLA with succinic anhydride (Scheme 1b). DMAP and TEA were used as catalysts and 1,4-dioxane as solvent. Figure 1c shows the ^{1}H NMR spectrum of PLLA with a COOH end group. The terminal methine proton (Figure 1b, a′) disappeared after the reaction with succinic anhydride. The methylene proton formed by the reaction with succinic anhydride was located at δ 2.62 (Figure 1c, d). The ratio of the protons from the 1,6-hexanediol unit (Figure 1c, b) to the protons from the succinic anhydride unit (Figure 1c, d) was about 2.

PLLA-diCOOH was reacted with thionyl chloride to convert the carboxyl group into an acyl halide group. This reaction was carried out for 3 h at 60 °C in methylene chloride. Figure 1d shows the ^{1}H NMR spectrum of PLLA with a COCl end group. The two terminal methylene protons (Figure 1c, d) were at δ 3.25 (Figure 1d, e) and δ 2.72 (Figure 1d, d), respectively, due to the different electronegativities of COOH and

Scheme 1. Synthetic Pathway for PLLA−PCL Multiblock Copolymer



COCl. PLLA-diCOCl reacts easily with moisture during storage. Thus, it was used for the next step immediately after it was prepared.

The PLLA−PCL multiblock copolymer was synthesized by coupling PLLA-diCOCl with PCL-diol (Scheme 1c), using pyridine as a catalyst. It removed the HCl produced during the reaction and thus promoted the forward reaction. Furthermore, since the addition of pyridine caused an exothermic reaction, it was added gradually in small amounts at 0 °C. Figure 2 shows the ^{1}H NMR spectrum of the PLLA−PCL multiblock copolymer. The two separated methylene protons (Figure 1d, d and e) at the terminus of PLLA-diCOCl had become a single proton peak at δ 2.65 (Figure 2, h). Figure 3 shows the GPC chromatogram of the multiblock copolymer. This single peak indicated the absence of unreacted PLLA or PCL. From these analyses, we confirmed the completeness of PLLA−PCL multiblock copolymer reaction. By changing the molecular weight of each component, PLLA−PCL multiblock copolymers of various molecular weights were prepared. Triblock and random copolymers were also synthesized for comparative purposes.

PLLA−PCL−PLLA triblock copolymer was prepared by two-step polymerization.[22] Initially, PCL-diol was prepared by the ring-opening polymerization of ϵ-caprolactone in melt form at 110 °C for 40 h in the presence of stannous octoate as catalyst (monomer/catalyst molar ratio M/C = 5000) and 1,6-hexanediol as an initiator (M/I = 200). In the second step, PCL-diol prepolymer, which has terminal hydroxyl groups, was used to initiate the ring-opening copolymerization of L-lactide at 120 °C for 150 h. A random copolymer of ϵ-caprolactone and L-lactide was synthesized by the ring-opening polymerization of ϵ-caprolactone and L-lactide with 1,6-hexandiol in the presence of Sn-oct.

The DSC thermograms of the copolymers produced are present in Figure 4 and Table 2. PCL0.5 was an amorphous compound, whereas PCL2 and PCL3 were semicrystalline exhibiting melting temperatures (T_m) of 45 and 48 °C, respectively. PL6 was semicrystalline with a T_m of 169 °C and a T_g and a T_c of 45 and 85 °C, respectively. Triblock copolymer showed a double melting peak, reflecting the presence of two crystalline domains. The two endotherms of the triblock copolymer at T_{m1} = 54 °C and T_{m2} = 165 °C were assigned to PCL and PLLA domains (Figure 4). Multiblock copolymers showed only one melting peak, at ca. 150 °C, which corresponds to the melting of PLLA blocks, by X-ray diffraction data (Figure 5). Moreover, the melting temperatures of multiblock copolymers were lower than those of polylactide homopolymer. These trends were assigned to block interferences leading to lower crystallinity (Table 2). For the random copolymer, no melting peak was observed due to the shorter monomer sequence length.

Table 2. Thermal Properties and Crystallinity Data for the Polymers

code	T_g (°C)	T_c (°C)	T_m (°C)	crystallinity (%)
PCL0.5				
PCL2		21.4	45.0	76.7
PCL3		23.7	48.0	75.9
PL3	42.7	98.5	145.0	40.9
PL6	49.6	108.0	152.0	40.0
PL7	48.1	105.3	154.8	45.1
PL9	63.5	113.0	180.5	52.3
PL3PCL2	6.2	81.7	123.2	17.5
PL6PCL2	21.6	76.2	151.1	40
PL7PCL2	25.1	77.8	153.6	35.5
PL9PCL2	32.3	80.6	160.3	40.3
PL6PCL0.5	44	92	154	45
PL6PCL3	10.6	65.9	144.2	26.6
PL/PCL/PL		13/80	54/165	64
PLCL5/5	−8.5			

Morphology. Figure 5 presents the X-ray diffraction spectra of the copolymers vs that of the starting homopolymers. PL6 showed two main peaks at 2θ = 16.7° and 19.1°, whereas PCL2 showed an intense peak at 2θ = 21.4° and two smaller peaks at 22.0° and 23.7°. It should be noted that the crystallization rate of PCL is much faster than that of PLLA at room temperature. However, the multiblock copolymer showed different crystallization behavior as compared with that of triblock copolymer. For multiblock copolymer two intense peaks were observed at 16.7° and 19.1° irrespective of the PCL block length. These peaks corresponded to the diffraction of PLLA crystals. This meant that PLLA could crystallize from its melt independent of the PCL block length. However, the lack of diffraction peaks typical of crystalline PCL in the spectra of the multiblock copolymers showed that PCL blocks do not to crystallize. As the triblock copolymer produced the diffraction patterns of PCL and of PLLA, PLLA blocks in the multiblock copolymers seem to prevent the crystallization of PCL, which had a shorter chain length than the triblock copolymer.

SAXD was used to determine the specific equilibrium morphologies of the synthesized samples. Because of microphase separation in the block copolymer, SAXD analysis showed a single reflection. The absence of higher orders of reflections was a consequence of a wider spread in lamella thickness and the absence of regularly stacked lamella. The lamella thickness of multiblock copolymer was smaller than that of triblock copolymer (Figure 6). This might be attributed to crystalline packing. Multiblock copolymer formed a spherical or hexagonally packed cylinder, whereas triblock copolymer packed as a lamellar structure. This difference may be due to block lengths.

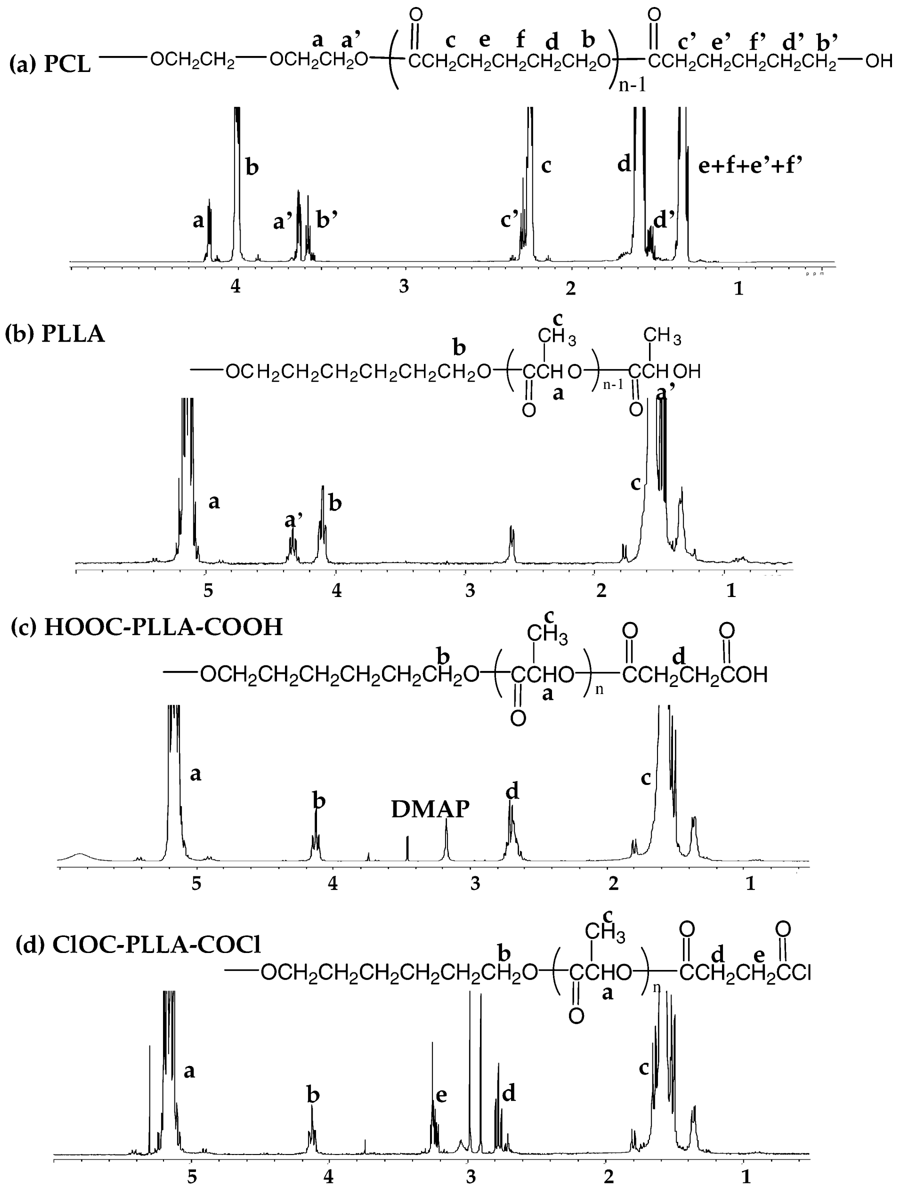


Figure 1. ^{1}H NMR spectra of (a) PCL, (b) PLLA, (c) HOOC−PLLA−COOH, and (d) ClOC−PLLA−COCl.

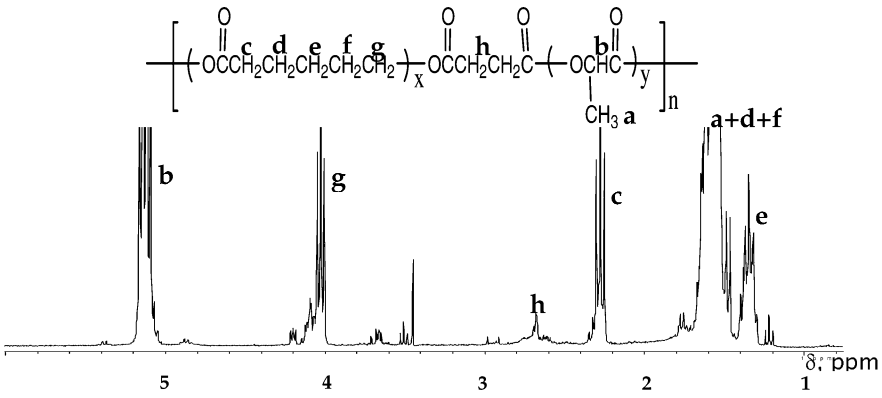


Figure 2. ^{1}H NMR spectrum of PLLA−PCL multiblock copolymer.

The crystalline morphologies of the multiblock and triblock copolymers were presented in Figure 7. All polymers showed a spherulitic morphology, irrespective of the PCL block length. Crystals were formed in film after about 1−5 min melting and crystallization lasted for 60 min. The crystallization of PL/PCL/PL is faster than that of multiblock copolymers. For triblock copolymer, the PLLA block length was very much larger than in multiblock copolymers; thus, the PLLA blocks could crystallize independent of PCL block length.

Tensile Properties. Mechanical testing was carried out for multiblock, triblock, and random copolymers.

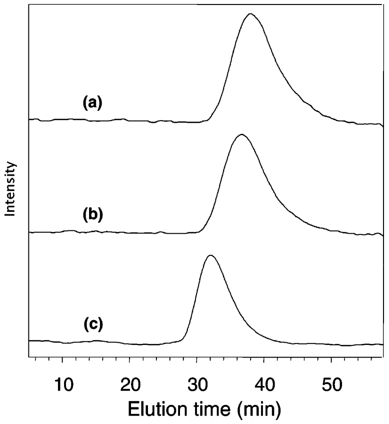


Figure 3. GPC curves of (a) PCL, (b) PLLA, and (c) PLLA−PCL multiblock copolymer.

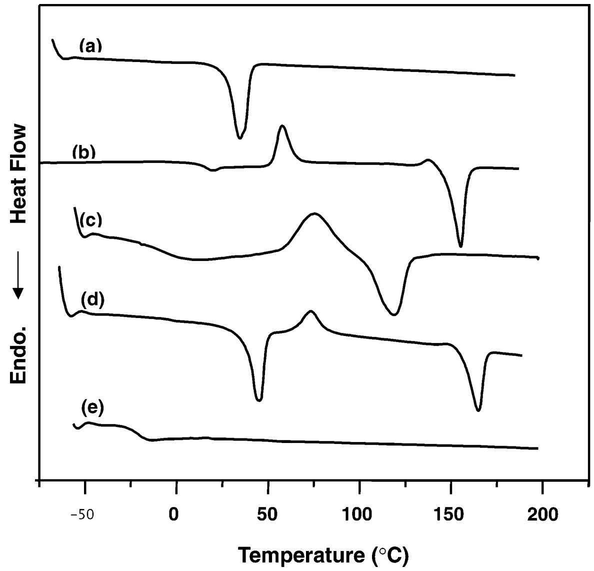


Figure 4. DSC thermograms of (a) PCL, (b) PLLA, (c) PLLA−PCL multiblock copolymer, (d) PLLA−PCL−PLLA triblock copolymer, and (e) PLCL5/5 random copolymer.

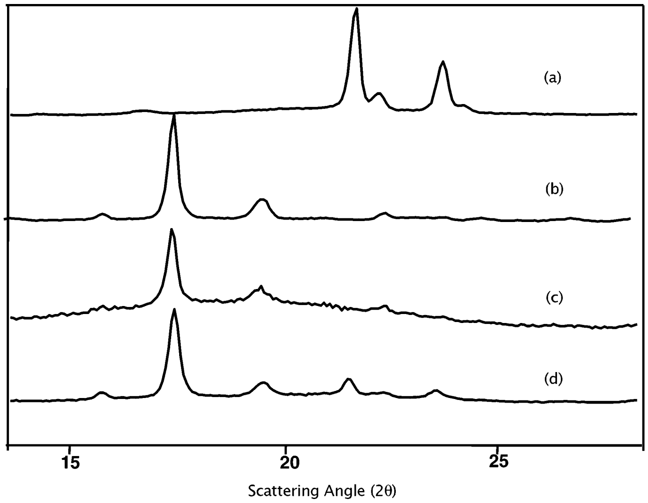


Figure 5. WAXD patterns of (a) PCL, (b) PLLA, (c) PLLA−PCL multiblock copolymer, and (d) PLLA−PCL−PLLA triblock copolymer.

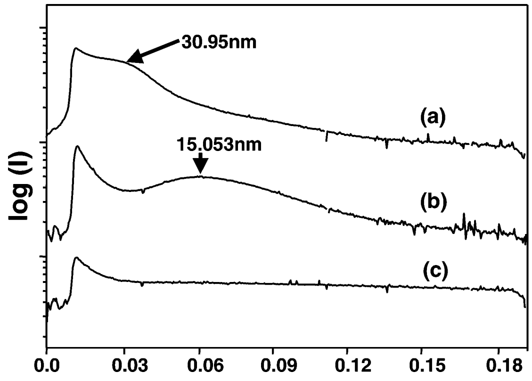


Figure 6. SAXS profile for (a) PLLA−PCL−PLLA triblock copolymer, (b) PLLA−PCL multiblock copolymer, and (c) PLCL5/5 random copolymer.

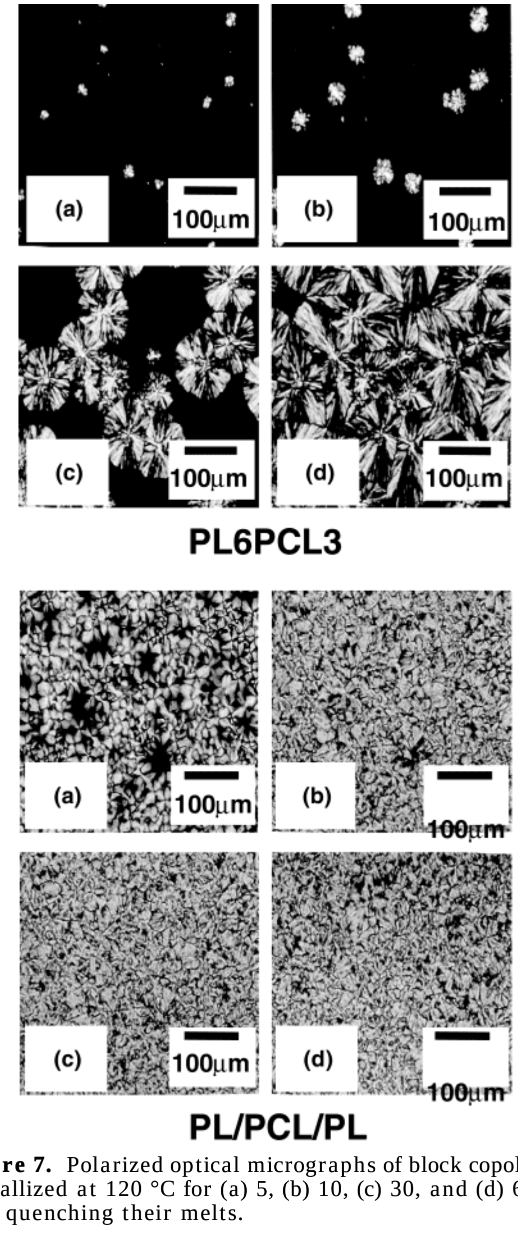


Figure 7. Polarized optical micrographs of block copolymers crystallized at 120 °C for (a) 5, (b) 10, (c) 30, and (d) 60 min after quenching their melts.

Table 3 summarized the tensile properties of the representative films, and as expected, the tensile strengths and tensile moduli of PL/PCL/PL were much higher than those of multiblock copolymers. PLCL5/5 had lowest tensile strength and tensile modulus because of its amorphous nature. For the homologue of the multiblock copolymers, higher average block lengths and higher crystallinities result in higher tensile strengths and tensile moduli. The tensile properties of the multiblock copolymers characterized them as tra-

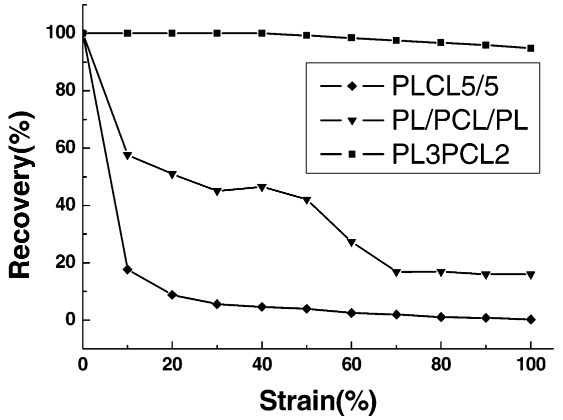


Figure 8. Elastic properties of PL3PCL2, PL/PCL/PL, and PLCL5/5.

Table 3. Tensile Properties of the Copolymers

code	tensil strenth (MPa)	modulus (MPa)	elongation at break (%)
PL3PCL2	6.93	9.0	645
PL7PCL2	12.6	104	560
PL9PCL2	18.35	165	512
PL6PCL2	10.83	39.3	618
PL6PCL3	16.48	21.4	738
PL/PCL/PL	20.02	220.8	654
PLCL5/5	0.001	0.6	468

ditional thermoplastic elastomers, consisting of crystalline hard domains of PLLA and amorphous soft domains of PCL. In this system, the crystalline PLLA domains are expected to serve as physical cross-linking points, which are the main contributors to mechanical strength and elasticity because they hold the soft domains together in a network structure.

A significant effect on recovery from strain was observed as shown in Figure 8. Multiblock copolymers showed recoveries higher than 95% at 100% strain, whereas the recoveries of triblock and random copolymers were very low, usually below 50% at 100% strain. An amorphous PCL may be able to extend further without dislocating the anchor nodes of the PLLA-segment crystals, which act as physical cross-links in the formation of the PCL-segment network. On the other hand, the higher level of crystallizability of the longer PCL chains may impose restrictions on the relaxation of the extended chains. Therefore, recovery of multiblock copolymers was higher than that of triblock copolymers.

Degradation. The hydrolytic degradation of the copolymers was investigated in terms of its relationship to different block lengths. Crystallinity, block length, and polymer structures are possible factors contributing to accelerated degradation. Molecular weight information (M_w, M_n, and polydispersity (M_w/M_n)) was obtained by GPC. To better illustration of molecular level changes during hydrolysis, the data are plotted in Figures 9 and 10, which show changes in M_n and mass loss for multiblock, triblock, and random copolymers during a degradation period of 150 days. It is evident that the degradation of the random copolymer is much faster than those of the triblock or multiblock polymers. The differences between the random polymer and the others also confirmed that degradation occurs easier in amorphous regions than in crystalline regions.

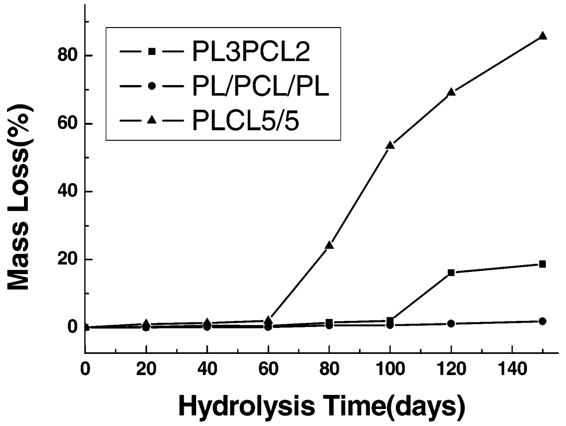


Figure 9. Mass loss of PL3PCL2, PL/PCL/PL, and PLCL5/5 by degradation. Mass loss (%) = 100 × $(W_0 - W_t)/W_0$, where W_0 = initial weight and W_t = weight after degradation.

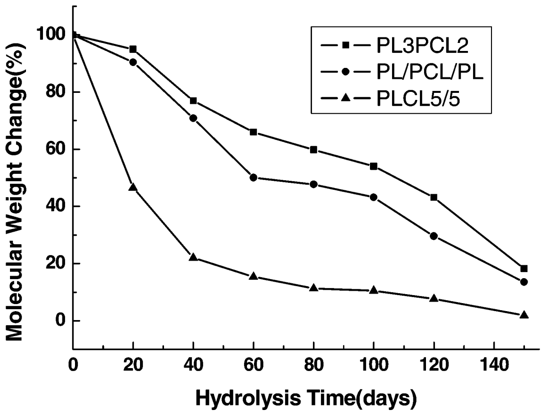


Figure 10. Molecular weight changes ofPL3PCL2, PL/PCL/PL, and PLCL5/5 as determined by GPC. Molecular weight change (%) = 100 × $(M_0 - M_t)/M_0$, where M_0 = initial molecular weight and M_t = molecular weight after degradation.

The molecular weights of the multiblock copolymers decreased with time, but there were no significant changes in the copolymer composition (PLLA portion were slightly reduced) because the multibolock copolymer films retained their initial shapes and mass for up to 100 days.

The morphology of copolymers during degradation is shown in Figure 11. After 60 days of incubation the surface of copolymers appeared smooth without pores and cracks. After 100 days of incubation the multiblock copolymers showed a rough and porous surface, indicative of the ongoing erosion. A different picture was obtained for the triblock copolymers with some cracks and pores for 100 days. After 150 days of incubation the surface pores and cracks were seen growing into the film, and the surface showed channel-like structure. As the chain session occurred in PLLA block, the amorphous PCL blocks of the multiblock copolymers which had short block length hydrolyzed easily than triblock copolymers. Therefore, the small particles were broken from the film and removed while triblock copolymers had long block length and did not hydrolyze. Therefore, tirblock copolymers retained their shapes and mass. Figure 12 showed a representative DSC thermogram overlay of the copolymers. The corresponding changes in morphology appeared to be consistent with expectations. As degradation proceeds, the endotherm of PCL blocks of multiblock copolymer was greater within crystalline phase, whereas that of PLLA blocks were smaller. This reason was that the PLLA blocks broke down and the disturbance to the PCL blocks were

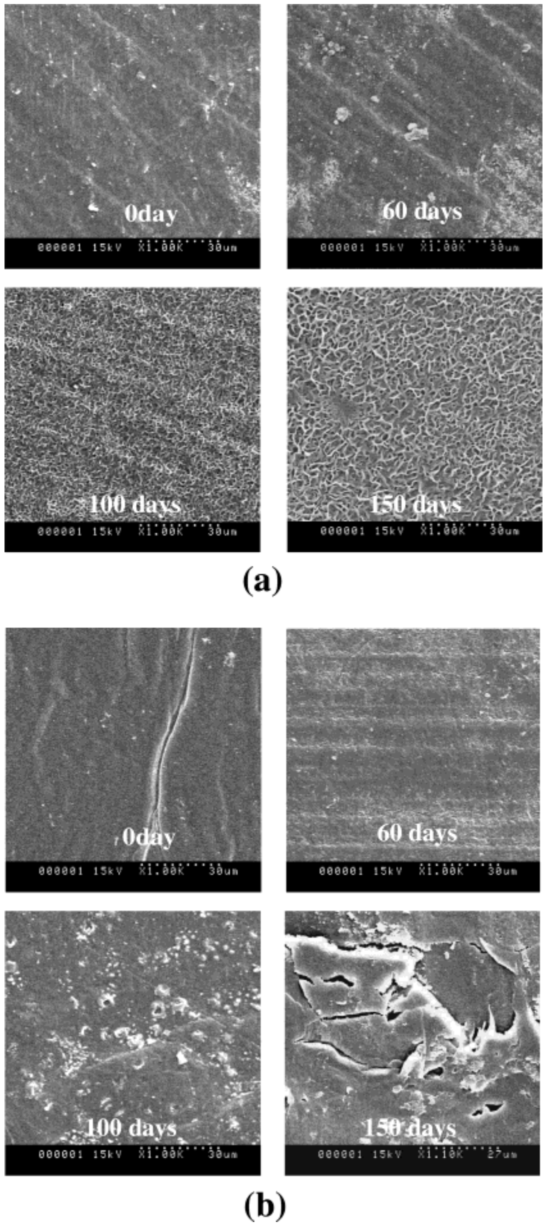


Figure 11. SEM photographs of the surface of (a) PLLA−PCL multiblock copolymer and (b) PLLA−PCL−PLLA triblock copolymer during biodegradation test.

decreased. PCL blocks, therefore, could be crystallized. Triblock copolymer was not exhibited significant changes.

For the multiblock copolymers, chain scission might occur in the PLLA blocks or in the PCL blocks. The slight decreases observed in the PLLA portion of the copolymer composition implied that the chain scission occurred fast in the PLLA blocks. The NMR spectra in Figure 13 support this result. During the first 80 days, no significant changes in the spectra were observed. Beyond 100 days a new signal appeared at 4.3 ppm, which was attributed to a methine (CH) proton in PLLA chain ends, and the integration ratio of this signal increased with degradation time. This new signal implies that chain scission occurred in the PLLA blocks.

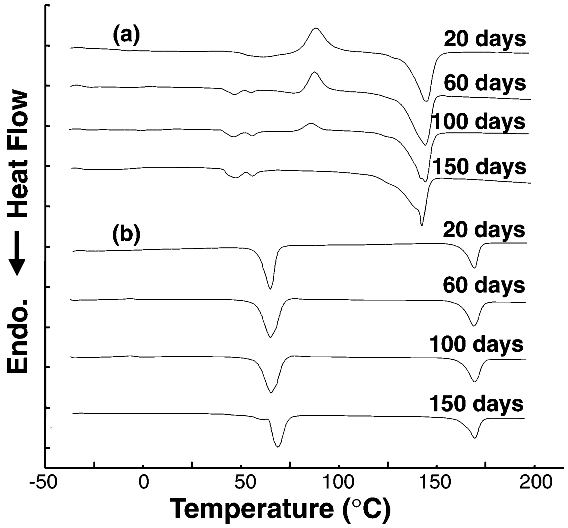


Figure 12. DSC thermogram overlay of (a) multiblock and (b) triblock copolymers during degradation.

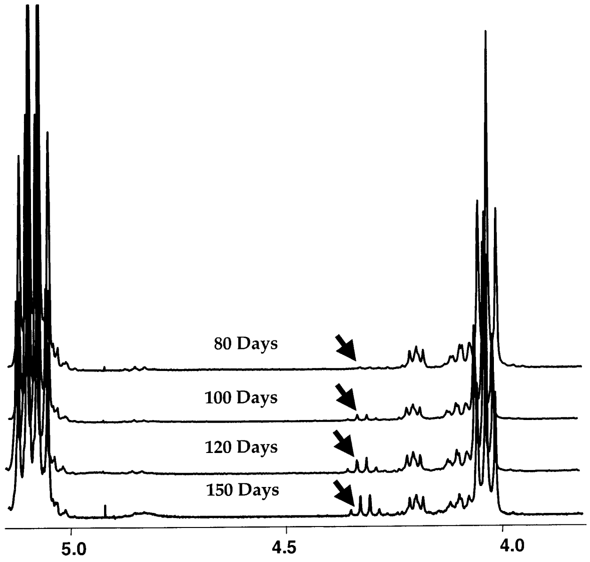


Figure 13. ^{1}H NMR spectrum of multiblock copolymer.

Conclusions

New PLLA−PCL multiblock copolymers were synthesized by using a coupling reaction between the bischloroformates of dicarboxylated PLLA and PCL-diol in the presence of pyridine. Copolymers produced were characterized by NMR, GPC, SAXD, and WAXD. PLLA−PCL multiblock copolymers exhibited only one melting peak, which corresponded to the PLLA phase, whereas PLLA−PCL−PLLA triblock copolymer had two melting peaks. These materials were found to have good mechanical properties and to behave like thermoplastic elastomer. These copolymers were found to have strain recoveries higher than 95% at 100% strain. Degradation of these copolymers was investigated in PBS for 150 days. The random copolymer was rapidly degraded, while the triblock and multiblock polymers were more stable. The molecular weights of the multiblock copolymers decreased with time, but no significant changes in their chemical compositions were observed. From ^{1}H NMR studies, chain scission occurred in the PLLA blocks. These biodegradable and elastic copolymers may be of importance in biomedical applications, where the matching of the compliances of materials and living tissues is of most importance.

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