

# Biodegradable Lactone Copolymers. I. Characterization and Mechanical Behavior of $\epsilon$ -Caprolactone and Lactide Copolymers

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## SYNOPSIS

Copolymers of  $\epsilon$ -caprolactone and L-lactide ( $\epsilon$ -CL/L-LA) and  $\epsilon$ -caprolactone and DL-lactide ( $\epsilon$ -CL/DL-LA) were synthesized with compositions 80/20, 60/40, and 40/60 (wt % in feed). The polymerization temperature was 140°C and Sn(II)octoate was used as a catalyst. The effect of the comonomer ratio on the thermal and mechanical properties of the copolymers was investigated by size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) spectrometry, and tensile testing. The copolymers differed widely in their physical characteristics, ranging from weak elastomers to tougher thermoplastics according to the ratio of  $\epsilon$ -CL and LA in the copolymerization. Poly(L-lactide) (PLLA), poly(DL-lactide) (PDLLA), and poly( $\epsilon$ -caprolactone) (PCL) homopolymers were studied as references. The tensile modulus and tensile strength were much higher for PLLA, PDLLA, and PCL homopolymers than for the copolymers. The maximum strain was very low for PLLA and PDLLA, whereas the copolymers and PCL exhibited large elongation. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

In the family of polyesters, PCL occupies a unique position: It is at the same time biodegradable and miscible with a variety of polymers and it crystallizes very readily. A lack of toxicity and great permeability have already found wide use for PCL in medical applications, in which environment it has a useful life-span approaching 1 yr. PLA has been widely used in medical applications due to the biocompatibility, good mechanical properties, and relatively fast biodegradability. PLA is found in two forms: crystalline PLLA and amorphous PDLLA.<sup>1-3</sup>

Much current research on biomaterials is focused on copolymers of different types. Copolymer systems exhibit a broad range of properties depending on the type and proportions of their constituent monomers. The diverse possibilities challenge the researcher to optimize properties and produce biomaterials tailor-made for specific applications. With their unique

chemical and physical properties, block copolymers, containing sequences of different monomers, are of increasing significance for both theoretical and practical purposes.

Over the past years, the hydrolyzable and biocompatible copolymers of  $\epsilon$ -CL and LA have been of great interest for medical applications. Small amounts of elastic copolymers may be of interest for nonmedical applications as well, e.g., as impact modifiers in brittle polyesters.  $\epsilon$ -CL appears to be a suitable comonomer for the preparation of a diversified family of copolymers with mechanical properties ranging from elastomeric to rigid. The good elongation characteristics of elastomeric copolymers make them suitable for applications where elasticity and degradability are required in the same product. The way chosen to produce these polymers is almost exclusively ring-opening polymerization.<sup>4-6</sup>

The synthesis of  $\epsilon$ -CL/LA copolymers and other lactone polymers has been widely studied in recent years. Most studies have focused on the polymerization parameters and on different catalysts and much less on the mechanical properties of the product.<sup>3,4,7-9</sup> The changes occurring in the mechanical

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**Table I Copolymer Compositions (<sup>13</sup>C-NMR), Molecular Weights, and Appearance of P(CL/LA) Copolymers**

Sample	Composition in Copolymer (Wt%)	Composition in Copolymer (mol %)	As-polymerized		<i>D</i>	Appearance
			$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)		
P(CL80/L-LA20)	75/25	79/21	177,000	358,000	2.1	Plasticlike, waxy, elastic
P(CL80/DL-LA20)	73/27	77/23	114,000	264,000	2.3	Plasticlike, waxy, elastic
P(CL60/L-LA40)	49/51	55/45	131,000	274,000	2.1	Gummy, weak
P(CL60/DL-LA40)	49/51	55/45	128,000	263,000	2.1	Gummy, weak
P(CL60/DL-LA40) <sup>i</sup> <sup>a</sup>	55/45	61/39	115,000	206,000	1.8	Gummy, weak
P(CL40/L-LA60)	33/67	39/61	137,000	309,000	2.2	Tough, elastic plastic
P(CL40/DL-LA60)	29/71	34/66	94,000	197,000	2.1	Gummy, weak

<sup>a</sup> Polymerized with initiator.

properties during hydrolysis are of current interest for medical applications as well as other for general applications. In our present series of studies (Parts I–III, printed here successively), we have been concerned with larger than test-tube scale polymerizations of  $\epsilon$ -CL/LA copolymers and their hydrolytic degradation and mechanical properties.

In Part I, we report on the synthesis of  $\epsilon$ -CL/L-LA and  $\epsilon$ -CL/DL-LA copolymers in compositions of 80/20, 60/40, and 40/60 (wt % in feed) using stannous octoate as a catalyst. The results of *in vitro* studies on the changes in molecular weight, crystallinity, and especially, the mechanical properties during hydrolysis will be reported in Parts II and III, which follow.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactone (Fluka) was dried over molecular sieves. L- and DL-lactide (Purac) were recrystallized

from dried toluene and dried for 24 h at 40°C under reduced pressure before polymerizations. Stannous octoate (Sigma) and glycerol (Rhône-Poulenc) were used as received. Poly(L-lactide) and poly(DL-lactide) were obtained from Neste Chemicals and poly( $\epsilon$ -caprolactone) (TONE P767E) was from Union Carbide Co.

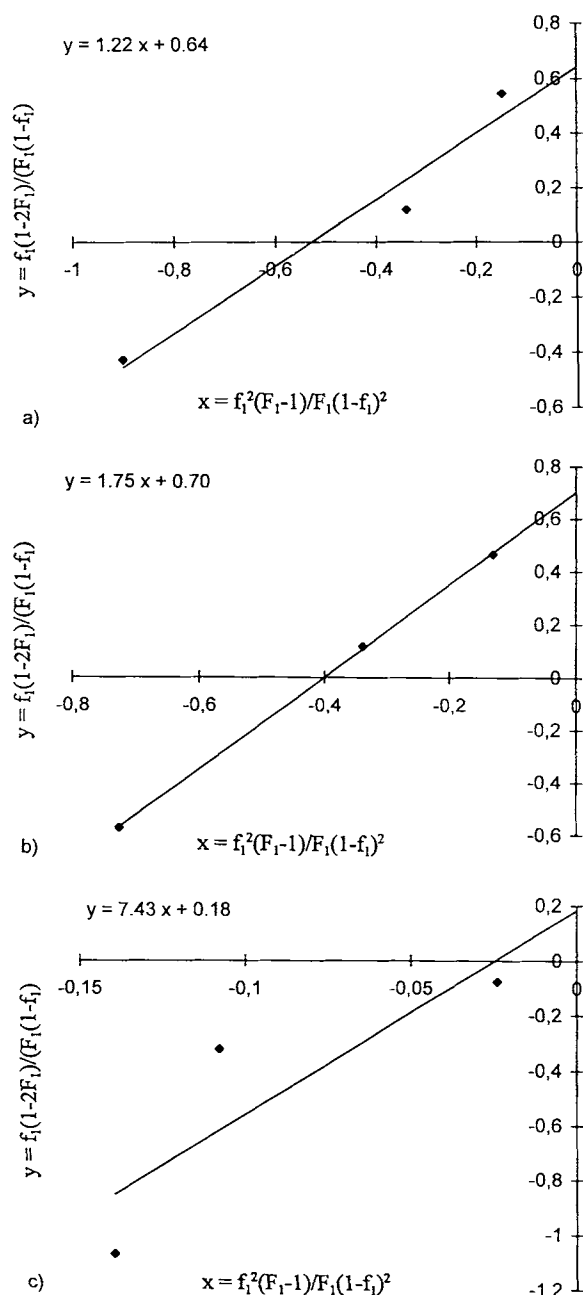
### Polymerization Procedure

The polymerizations were carried out in bulk under a nitrogen atmosphere with Sn(II) octoate as the catalyst. The amount of the catalyst was  $1.2 \times 10^{-3}$  mol/mol monomer. The polymerization glass flask with a stirrer was immersed in an oil bath at 140°C for 3 h. One copolymer in this study was polymerized using glycerol as the initiator ( $5.7 \times 10^{-4}$  mol/mol monomer). The as-polymerized copolymers were kept in a vacuum chamber at 40°C for 5 days to evaporate monomer residues. The copolymers were stored in dry conditions.

**Table II Amount of Random Structure for the Caproyl and Lactidyl Units, Amount of Transesterification, and Sequence Lengths of P(CL/LA) Copolymers**

Sample	Amount of Random Structure for Caproyl Units (%)	Amount of Random Structure for Lactidyl Units (%)	Transesterification (%)	Sequence Length of $\delta$ -CL
P(CL80/L-LA20)	3.1	30.1	3.3	6.8
P(CL80/DL-LA20)	2.9	33.9	4.9	7.3
P(CL60/L-LA40)	8.4	20.2	3.0	4.0
P(CL60/DL-LA40)	6.8	15.2	2.9	4.0
P(CL60/DL-LA40) <sup>i</sup> <sup>a</sup>	9.0	27.0	6.6	3.6
P(CL40/L-LA60)	21.6	11.6	2.1	2.4
P(CL40/DL-LA60)	18.1	13.5	2.1	2.4

<sup>a</sup> Polymerized with initiator.



**Figure 1** Plots of the Fineman–Ross equation for the determination of apparent reactivity ratios of (a) L-LA and  $\epsilon$ -CL at high conversion, (b) DL-LA and  $\epsilon$ -CL at high conversion, and (c) L-LA and  $\epsilon$ -CL at lower conversion. In the equations,  $f_1$  is the mol fraction of lactide in feed and  $F_1$  is the mol fraction of lactidyl units in copolymer.

### Molding

The samples for shore and tensile testing were prepared by compression molding (Fontijne TP 400) at different temperatures depending on the sample [P(CL80/L-LA20), P(CL80/DL-LA20), P(CL60/

L-LA40), P(CL40/L-LA60): 160°C; P(CL60/DL-LA40): 140°C; P(CL60/DL-LA40)i: 130°C; P(CL40/DL-LA60): 120°C]. Test specimens were punched out from molded plates with an Elastocon EP 02 puncher. Homopolymer samples for tensile testing were injection-molded (Engel ES200/40; PLLA, PDLLA: 200°C and PCL: 120°C).

### Molecular Weight Determination

Molecular weights were determined by room-temperature SEC (Water System Interface Module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp, and four linear PL gel columns:  $10^4$ ,  $10^5$ ,  $10^3$ , and  $100 \text{ \AA}$  connected in series). Tetrahydrofuran was used as the solvent and eluent for copolymers and PCL and chloroform for PLLA and PDLLA. The samples were filtered through a  $0.5 \mu\text{m}$  Millex SR filter. The injected volume was  $200 \mu\text{L}$  and the flow rate  $1 \text{ mL/min}$ . Monodisperse polystyrene standards were used for primary calibration, which means that the Mark–Houwink constants were not used.

### Thermal Analysis

Glass transition and melting temperatures were measured by DSC (PL). Nitrogen was used as a sweeping gas. Samples (5–10 mg) were heated twice (at a rate of  $10^\circ\text{C/min}$ ) to ensure that their thermal histories were similar. The temperature range was between  $-100^\circ\text{C}$  and  $+200^\circ\text{C}$  depending on the samples.

### NMR Measurements

The structures of copolymers were determined with a Varian Unity 400 NMR spectrometer working at  $100.577 \text{ MHz}$  for  $^{13}\text{C}$  and at  $399.96 \text{ MHz}$  for  $^1\text{H}$ . Sample concentrations, in 5 mm tubes, were 10% by weight in chloroform- $d_1$  for  $^{13}\text{C}$ -NMR and 1% by weight for  $^1\text{H}$ -NMR. Measurement temperatures were  $45^\circ\text{C}$  for  $^{13}\text{C}$ -NMR and  $18^\circ\text{C}$  for  $^1\text{H}$ -NMR. The internal standard was tetramethylsilane, and chemical shifts were expressed in ppm. For the purification of samples, copolymers were dissolved in dichloromethane and precipitated in ethanol.

### Shore

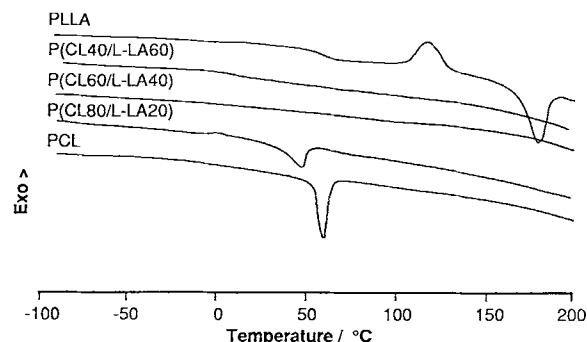
The shore hardness was measured with an Atsfaar shore durometer according to the standard ISO 868-1978(E).

### Tensile Testing

The tensile tests of the compression-molded copolymers (4 × 10 × 80 mm) and injection-molded homopolymers (4 × 10 × 110 mm) were done on an Instron 4204 tensile testing machine equipped with a computer adapting the standard ISO/R 527-1966(E). The mechanical properties of the homopolymers and copolymers were measured using a tensile tester at a crosshead speed of 5 mm/min. The mechanical values for the homopolymers and copolymers were measured for five parallel dry specimens and five parallel air-conditioned specimens (air-conditioned specimens were allowed to rest for 72 h at 23°C and 50% relative humidity).

## RESULTS AND DISCUSSION

The copolymers of  $\epsilon$ -CL and LA were polymerized in bulk at 140°C using stannous octoate as the catalyst. Copolymers, monomer compositions in feed, copolymer compositions determined by <sup>13</sup>C-NMR, molecular weights, molecular weight distributions, and physical appearance are presented in Table I. These copolymers differed greatly in appearance, from plasticlike to gummy according to the monomer composition. The conversions of the polymerizations were about 92–99%, with the residual monomer mainly  $\epsilon$ -CL. These conversion measurements were based on monomer evaporation from the polymerized samples in a vacuum chamber at 40°C.



**Figure 2** Typical DSC thermograms of P(CL/L-LA) copolymers and PCL and PLLA homopolymers.

### Structure of the Copolymers

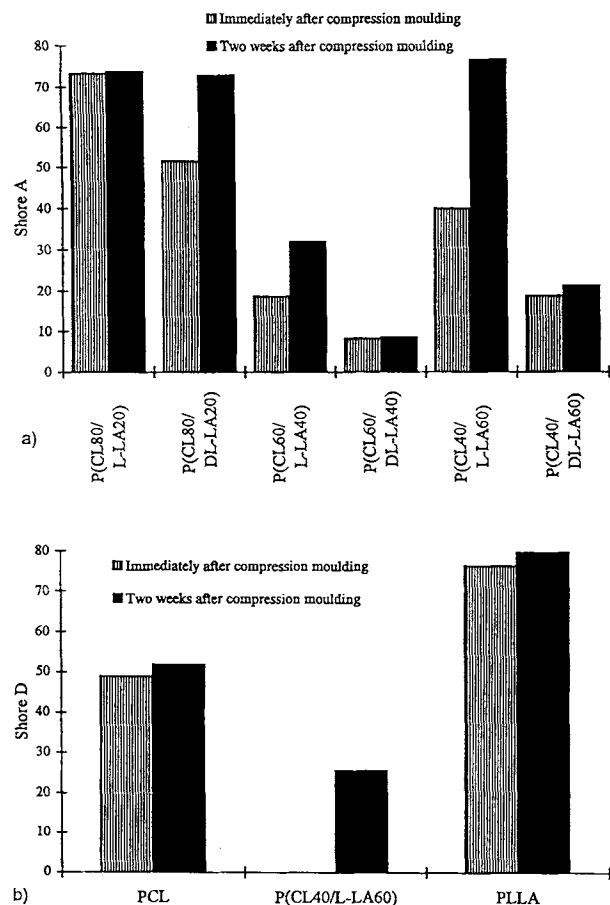
Copolymers of  $\epsilon$ -CL with DL-LA reportedly have a more blocky structure than those containing L-LA, and they are less sensitive to transesterification reactions.<sup>9</sup> This effect was not observed in our copolymer compositions. Our copolymers were block copolymers with minor amounts of random structure. The amount of random structure in copolymer was calculated from 68.0 to 69.6 ppm for the lactidyl units and from 24 to 26 ppm for the caproyl units (Table II). The amount of random structure for the caproyl units increased with decreasing amount of  $\epsilon$ -CL in the copolymer. Correspondingly, the amount of random structure for lactidyl units increased with a decreasing amount of LA.

The blocky structures may be randomized by transesterification reactions.<sup>9,10</sup> Small peaks due to transesterification were seen in <sup>13</sup>C-NMR spectra,

**Table III** Heats of Fusion and Glass Transition and Melting Temperatures of P(CL/LA) Copolymers and PLLA, PDLLA, and PCL Homopolymers

Sample	$T_g$ (°C)	$T_m$ (°C)	$\Delta H$ (J/g)
Copolymers			
P(CL80/L-LA20)	-53.8	42.4	8.8
P(CL80/DL-LA20)	-50.9	36.5	4.6
P(CL60/L-LA40)	-25.0	—	—
P(CL60/DL-LA40)	-30.0	—	—
P(CL60/DL-LA40) <sup>a</sup>	-28.0	—	—
P(CL40/L-LA60)	~ -3.8	—	—
P(CL40/DL-LA60)	~ -1.0	MHM	—
Homopolymers			
PLLA	55.5	174.8	52.2
PDLLA	49.1	—	—
PCL	—	59.7	27.7

<sup>a</sup> Polymerized with initiator.



**Figure 3** Shore hardness: (a) shore A values for the copolymers; (b) shore D values for P(CL40/L-LA60) copolymer and PCL and PLLA homopolymers.

e.g., at 65.1 and 68.5 ppm or at 170.8 and 172.5 ppm. The amount of transesterification was calculated from the region 63.5 to 69.5 ppm. The results showed minor transesterification for all of the copolymers (Table II).

The sequence lengths of  $\epsilon$ -CL were determined from the  $\gamma$ -methylene region (chemical shifts from 24 to 25 ppm) in the  $^{13}\text{C}$ -NMR spectra assuming that transesterification does not take place. The experimental average lengths of caproyl units ( $l_{\text{CL}}^e$ ) were calculated by eq. (1)<sup>10</sup>:

$$l_{\text{CL}}^e = \frac{\{LL\text{Cap}LL\} + \{\text{CapCap}LL\} + \{LL\text{Cap}Cap\} + \{\text{CapCap}Cap\}}{\{LL\text{Cap}LL\} + 1/2(\{\text{CapCap}LL\} + \{LL\text{Cap}Cap\})} \quad (1)$$

where *LL* is the lactidyl unit and *Cap* is caproyl unit. In our polymerization conditions, the sequence lengths of caproyl units varied from 2.4 to 7.3 de-

pending on the copolymer composition (Table II). The longest sequence lengths of caproyl units were obtained for P(CL80/LA20) copolymers. The average monomer sequence lengths determined by  $^{13}\text{C}$ -NMR are greatly influenced by the polymerization conditions.<sup>10,11</sup> As reported in previous work,<sup>12</sup> for the copolymerization of LA with  $\epsilon$ -CL in the presence of tin octoate, longer sequences (5–6 units) can be obtained only at moderate temperatures (< 70°C). However, the ratio of the monomers in the feed evidently affects the sequence lengths.

Copolymers with blocky structures are produced by monomers differing in reactivity. The reactivity ratios of  $\epsilon$ -CL and LA monomers can be determined by the Fineman–Ross method,<sup>12,13</sup> in which the reactivity ratio of LA ( $r_1$ ) and reactivity ratio of  $\epsilon$ -CL ( $r_2$ ) are calculated according to the equations presented in Figure 1. The values of  $r_1$  and  $r_2$  are determined from the slope and intercept of the line, respectively. The Fineman–Ross method is accurate for low conversions<sup>13,14</sup> and with several different monomer compositions. Figure 1(a) and (b) show plots giving the values  $r_1 = 1.22$  and  $r_2 = 0.64$  in the high-conversion copolymerization of  $\epsilon$ -CL with L-LA and  $r_1 = 1.75$  and  $r_2 = 0.70$  in the high-conversion copolymerization of  $\epsilon$ -CL with DL-LA. The reactivity ratios were also determined for lower-conversion copolymerizations of  $\epsilon$ -CL with L-LA, where conversions, determined by  $^1\text{H}$ -NMR, were 25–50% depending on the copolymer composition. Figure 1(c) shows a plot with a poorer correlation factor, giving the values  $r_1 = 7.43$  and  $r_2 = 0.18$ . There is a clear difference in the reactivity ratios depending on the conversion. It can be concluded from the reactivity ratios in lower-conversion copolymerizations that the product is then almost exclusively a PLA homopolymer. In any case, LA is more reactive than is  $\epsilon$ -CL. For experimental reasons, it is difficult to achieve a low conversion and at the same time have an amount of polymer that can be treated or purified by precipitation.

As reported in many earlier publications,<sup>11,12,15,16</sup> the polymerization rate of LA is higher than that of  $\epsilon$ -CL. The decrease in the blockiness of the copolymers at higher temperatures may be due not only to the increased transesterification reactions but also to the difference in reactivity of L-LA and  $\epsilon$ -CL at higher temperatures.

### Thermal Properties of the Copolymers

The heat of fusion, the glass transition, and the melting temperatures of P(CL/LA) copolymers and PCL, PDLA, and PLLA homopolymers are col-

**Table IV** Molecular Weights of P(CL/LA) Copolymers and PLLA, PDLLA, and PCL Homopolymers After Processing

Sample	After Processing		<i>D</i>
	$\bar{M}_n$ (g/mol)	$\bar{M}_w$ (g/mol)	
Copolymers			
P(CL80/L-LA20)	105,000	219,000	2.1
P(CL80/DL-LA20)	107,000	231,000	2.2
P(CL60/L-LA40)	103,000	215,000	2.1
P(CL60/DL-LA40)	75,000	176,000	2.3
P(CL60/DL-LA40) <sup>a</sup>	52,000	97,000	1.9
P(CL40/L-LA60)	74,000	145,000	2.0
P(CL40/DL-LA60)	92,000	182,000	2.0
Homopolymers			
PLLA	50,000	114,000	2.3
PDLLA	48,000	90,000	1.9
PCL	60,000	100,000	1.7

<sup>a</sup> Polymerized with initiator.

lected in Table III. Typical DCS thermograms are presented in Figure 2. The copolymers that consisted of 80 wt %  $\epsilon$ -CL in the feed were capable of crystallizing and showed low glass transition temperatures. The copolymers ranging in composition from 40 to 60 wt %  $\epsilon$ -CL in the feed were amorphous. Glass transition temperature decreased with increase of  $\epsilon$ -CL content in the copolymer. According to other studies,<sup>17</sup> this is due to the increase in mobility of the five methylene groups which act as soft segments in the copolymer chain. The DSC results of some other research groups<sup>11,16</sup> for these copolymers are about the same.

According to Vanhoorne et al.,<sup>9</sup> the glass transition ( $T_g$ ) and the melting ( $T_m$ ) temperatures of copolymers depend on the comonomer distribution. For instance, a block copolymer usually exhibits two  $T_g$ 's, in contrast to a random copolymer which exhibits only one. This effect was not apparent in our copolymers. As seen in Figure 2, for some of our copolymers, even one glass transition temperature was hard to see exactly by our DSC method.

The crystallinity of P(CL40/L-LA60) was seen as a small melting endotherm (at about 130°C) in the DSC thermogram during the first heating of the sample. The actual melting point (145°C,  $\Delta H = 13.2$  J/g) of the copolymer in the second heating was seen only when the melting and cooling rates of the sample were extremely slow (2°C/min), indicating that the crystallinity of the copolymer was low.

### Mechanical Properties of Copolymers

The copolymers and homopolymers were processed for the mechanical tests and further hydrolysis tests reported in Parts II and III of this study. Since polymers degrade during processing, molecular weights were measured after this step (Table IV). The PLLA, PDLLA, and PCL homopolymers were used in the mechanical tests as references. Since the mechanical properties of polymers can be further improved by optimizing the processing parameters, the data on mechanical strength reported here should be considered indicative of but not necessarily the best possible values.

The P(CL80/DL-LA20), P(CL60/L-LA40), and P(CL40/L-LA60) copolymers showed progressive hardening with time at room temperature, indicating a tendency for post-crystallization of homopolymeric sequences. Some other publications<sup>11,16</sup> have also reported on the postcrystallization effect. This effect can be seen in the shore measurements [Fig. 3(a)]: Shore A values were 40% larger for the P(CL80/DL-LA20), 71% larger for P(CL60/L-LA40), and 90% larger for P(CL40/L-LA60) when measured 2 weeks after processing. Shore values for the other copolymers and the homopolymers did not change with time.

The different  $\epsilon$ -CL and LA compositions of the copolymers had a clear effect on the tensile properties, as can be seen in Table V. The copolymers differed widely in their physical characteristics,

Table V Tensile Properties of P(CL/LA) Copolymers and PLLA, PDLLA, and PCL Homopolymers

Sample	Tensile Modulus (MPa)	Maximum Stress (kPa)	Yield Stress (kPa)	Maximum Strain (%)	Elongation at Yield (%)
Copolymers					
P(CL80/L-LA20)					
Dry	52 ± 6	1900 ± 360	1800 ± 300	30 ± 17	7 ± 1
Air-conditioned	55 ± 2	2000 ± 280	1800 ± 380	79 ± 10	6 ± 3
P(CL80/DL-LA20)					
Dry	30 ± 3	1600 ± 280	1200 ± 210	> 100	9 ± 4
Air-conditioned	34 ± 2	1400 ± 340	1300 ± 220	> 100	10 ± 5
P(CL60/L-LA40)					
Dry	2.8 ± 1	80 ± 14	16 ± 10	98 ± 28	1.2 ± 0.2
Air-conditioned	1.8 ± 0.2	120 ± 60	35 ± 2	84 ± 30	2.6 ± 1.8
P(CL60/DL-LA40)					
Dry	2.1 ± 0.8	23 ± 0	9 <sup>a</sup>	> 100	0.24 ± 0.19
Air-conditioned	6.4 ± 2.9	13 ± 0	6 <sup>a</sup>	> 100	0.10 ± 0.05
P(CL60/DL-LA40) <sup>i</sup> <sup>b</sup>					
Dry	1.9 ± 1.1	45 ± 10	12 ± 10	> 100	0.9 ± 0.7
Air-conditioned	2.7 ± 1.2	16 ± 10	8 <sup>a</sup>	> 100	0.14 ± 0.13
P(CL40/L-LA60)					
Dry	30 ± 7	3000 ± 560	2500 ± 530	87 ± 28	32 ± 12
Air-conditioned	34 ± 5	3330 ± 180	3300 ± 180	> 100	35 ± 5
P(CL40/DL-LA60)					
Dry	2.8 ± 3.7	80 ± 10	10 ± 0	> 100	0.7 ± 0.5
Air-conditioned	3.0 ± 1.9	70 ± 10	10 ± 0	> 100	0.6 ± 0.3
Homopolymers					
PLLA					
Dry	1720 ± 50	46,500 ± 1300	— <sup>c</sup>	2.9 ± 0.2	—
Air-conditioned	1620 ± 70	44,500 ± 3600	— <sup>c</sup>	3.0 ± 0.4	—
PDLLA					
Dry	1930 ± 80	34,500 ± 1400	— <sup>c</sup>	2.0 ± 0.0	—
Air-conditioned	1540 ± 70	33,000 ± 1800	— <sup>c</sup>	2.5 ± 0.1	—
PCL					
Dry	250 ± 10	15,000 ± 260	15,000 ± 260	> 100	20 ± 1
Air-conditioned	260 ± 3	15,500 ± 140	16,000 ± 180	> 100	20 ± 2

<sup>a</sup> Yield stress at offset of 1% of elongation.

<sup>b</sup> Polymerized with initiator.

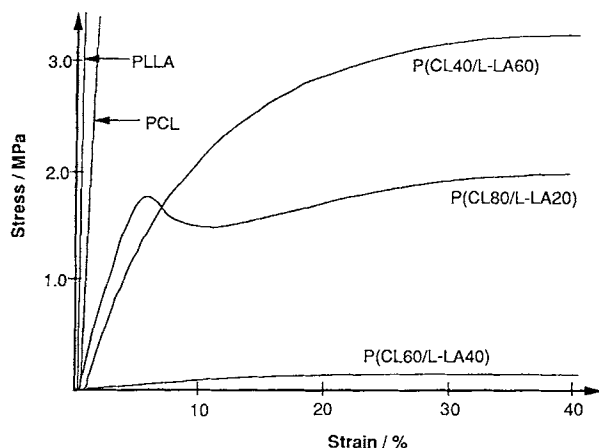
<sup>c</sup> No yield point.

ranging from weak elastomers to tougher thermoplastics.

PLLA and PDLLA were hard and brittle; PCL was tough. Higher average sequence lengths and higher crystallinity result in higher tensile modulus and tensile strength, and, as expected, tensile modulus and tensile strength were much higher for PLLA, PDLLA, and PCL homopolymers than for the copolymers. The maximum strain was very low for PLLA and PDLLA, whereas it was > 100% for nearly all the copolymers and for PCL. The tensile strength was greater for copolymers containing L-LA than for those containing DL-LA. This is due

to the crystallinity of L-LA sequences compared to the amorphousness of DL-LA sequences. Amorphous P(CL60/L-LA40), P(CL60/DL-LA40), and P(CL40/DL-LA60) copolymers were weak but they exhibited significant elongation. The values for dry and air-conditioned samples differed slightly. The humidity of the air plasticized the materials somewhat.

The shapes of the stress-strain curves of the homopolymers and copolymers were quite different, as seen in Figure 4. The curves are for air-conditioned samples. P(CL80/L-LA20) exhibited yield deformation and ductile failure, P(CL60/L-LA40)



**Figure 4** Stress-strain diagrams of P(CL80/L-LA20), P(CL60/L-LA40), and P(CL40/L-LA60) copolymers and PCL and PLLA homopolymers.

exhibited rubberlike behavior, and P(CL40/L-LA60) was tough and rubberlike.

## CONCLUSIONS

Variation of the composition offers a valuable method of tailoring the mechanical properties, biocompatibility, and biodegradability of P(CL/LA) copolymers. Understanding of the mechanical behavior is essential to the development of new applications.

In this study, the copolymers of  $\epsilon$ -CL/L-LA and  $\epsilon$ -CL/DL-LA were synthesized with compositions 80/20, 60/40, and 40/60 (wt % in feed). The products were block copolymers with some random structure. The amount of transesterification was minor. Depending on the copolymer composition, the sequence lengths of caproyl units varied from 2.4 to 7.3, with the longest sequences obtained for P(CL80/LA20) copolymers. The copolymers P(CL80/L-LA20) and P(CL80/DL-LA20) were capable of crystallizing, whereas P(CL60/L-LA40), P(CL60/DL-LA40), P(CL40/L-LA60), and P(CL40/DL-LA60) showed only a glass transition temperature and were amorphous. Glass transition temperature decreased with increase of the  $\epsilon$ -CL content in the copolymer. The P(CL80/DL-LA20), P(CL60/L-LA40), and P(CL40/L-LA60) copolymers showed progressive hardening with time at room temperature, indicating a tendency for post-crystallization of homopolymeric sequences in these copolymers. The tensile modulus and tensile strength were much higher for PLLA, PDLA, and

PCL homopolymers than for the copolymers. The maximum strain was very low for PLLA and PDLA, whereas it was  $> 100\%$  for PCL and for nearly all the copolymers.

*In vitro* studies on the hydrolytic degradation of  $\epsilon$ -CL/LA copolymers and PLLA, PDLA, and PCL homopolymers and the effect of hydrolysis on the thermal and mechanical properties are reported in Parts II and III of this series.

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