# Synthesis and Characterization of a Biodegradable Thermoplastic Poly(ester−urethane) Elastomer

**Janne Kylmä and Jukka V. Seppälä***

*Helsinki University of Technology, Department of Chemical Technology, Kemistintie 1, FIN-02150 Espoo, Finland*

*Received October 22, 1996; Revised Manuscript Received March 10, 1997*[⊗]

ABSTRACT: Thermoplastic poly(ester−urethanes) were polymerized in a two-step process: a condensation copolymerization of lactic acid (LA) and ϵ-caprolactone (CL), using stannous octoate as catalyst, followed by an increase in the molecular weight through urethane linking. The use of 1,4-butanediol results in oligomer molecules with hydroxyl functionality at both ends. The effect of comonomer ratio on the thermal and mechanical properties of the poly(ester−urethane) was investigated. SEC, FTIR, and $^{13}$C NMR were used to confirm the formation and structure of the polymer; a random sequence distribution of the comonomer units was concluded along the polymeric chains. All poly(ester−urethanes) were amorphous, with $T_g$ varying from 53 to −45 °C. Poly(ester−urethanes) with a small amount of CL units were rigid, having a tensile modulus of 1700−2100 MPa, maximum stress of 36−47 MPa, and maximum strain of 4−7%. CL-rich poly(ester−urethanes) were highly elastomeric with maximum stress of 9 MPa and with maximum strain over 1000%. Hydrolytic degradation was studied in phosphate buffer solution (pH 7.4) at 37 °C.

## Introduction

Biodegradable materials are of current interest both for environmental reasons and in biomedical applications. In optimizing the key properties required of these biopolymers, i.e. thermal and tensile properties and rate of biodegradation, the best way to proceed is to copolymerize two different monomers. In our laboratory we have been investigating lactide and lactones.[1−3] Lactide, the cyclic dimer of lactic acid, is a well-known monomer used extensively for the synthesis of bioabsorbable polymers for biomedical applications. With respect to lactones, attention has been drawn to ϵ-caprolactone, which is readily available from petrochemical sources and easily converted into high molecular weight chains by organometallic catalysts. Poly(ϵ-caprolactone), which readily crystallizes, is known for its unique set of properties, including biocompatibility, biodegradability, and miscibility with a variety of polymers.

Ring-opening copolymerization of lactides, ϵ-caprolactone, and other comonomers has been studied by several researchers. Properties of these copolymers range widely, from those of flexible elastomers to those of stiff plastics. In the achievement of elastic properties, interest has focused on block copolymers of L-lactide with ϵ-caprolactone,[1,4] 1,5-dioxepan-2-one,[5] isobutylene,[6] and β-methyl-δ-valerolactone[7] and also on polyurethane networks[8−10] and cross-linked poly(ester−urethane).[11]

In previous papers,[12−14] we have reported the synthesis of thermoplastic poly(ester−urethanes) by a two-step process: a condensation polymerization of lactic acid to hydroxyl-terminated telechelic prepolymer, followed by an increase in molecular weight with 1,6-hexamethylene diisocyanate. Recently, we improved the heat resistance of lactic acid-based poly(ester−urethane) through the incorporation of rigid groups in the polymer chain.[15] We showed that this method is a highly efficient one for converting lactic acid to high molecular weight polymer, and it offers considerable scope for structural modification.

The aim of the research described was to synthesize a novel series of thermoplastic poly(ester−urethane) elastomers based on L-lactic acid and ϵ-caprolactone. This article will discuss the effect of monomer composition on the thermal and mechanical properties, and the hydrolytic degradability of poly(L-lactic acid-*co*-ϵ-caprolactone-urethanes).

## Experimental Section

**Prepolymer Synthesis.** The prepolymers for urethane synthesis were condensation polymerized in a rotation evaporator. L-Lactic acid (85−90% L-lactic acid in water, 99% optically pure; Fluka) and DL-lactic acid (~90% lactic acid in water, containing 50% L-lactic acid and 50% D-lactic acid; Fluka) were purified by distillation under vacuum. Typically, 450 g of purified L-lactic acid (70 mol %) and, as a comonomer, 244 g of ϵ-caprolactone (used as received, Fluka) (30 mol %) were added to a 2000-mL evaporating flask. 1,4-Butanediol (12.9 g, 2 mol %, used as received, Fluka) was added to produce hydroxyl-terminated oligomers. The catalyst was 0.35 g of Sn(II) octoate (0.05 wt %, Sigma). The flask was purged with nitrogen and placed in an oil bath. The rotation speed was approximately 100 rpm. In most cases the reaction mixture was polymerized at 210 °C, with a continuous nitrogen stream fed under the surface of the melt, at a reduced pressure of 50 mbar.

**Polyurethane Synthesis.** The poly(ester−urethane) was prepared in a melt using 1,6-hexamethylene diisocyanate (Fluka) as a chain extender. The polymers were synthesized in a 300-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer incorporating a nitrogen inlet valve. Typically, 40 g of poly(L-lactic acid-*co*-ϵ-caprolactone) prepolymer was introduced to the flask and melted in an oil bath at 150 °C, after which the flask was purged with nitrogen at room temperature to remove residual air. Then 2.4 g of 1,6-hexamethylene diisocyanate was added to the stirred liquid oligomer, and the temperature was then raised to the polymerization temperature of 180 °C. The polymerization was followed by taking samples every 10 min and analyzing the samples by SEC and FTIR. All products were used without further purification.

**Measurements.** The molecular weights were determined by size exclusion chromatography, SEC (Waters System Interface module, Waters 510 HPLC Pump, Waters 410 Differential Refractometer, Waters 700 Satellite Wisp), using monodisperse polystyrene standards for calibration. Measurements were made at room temperature with four linear PL

---

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

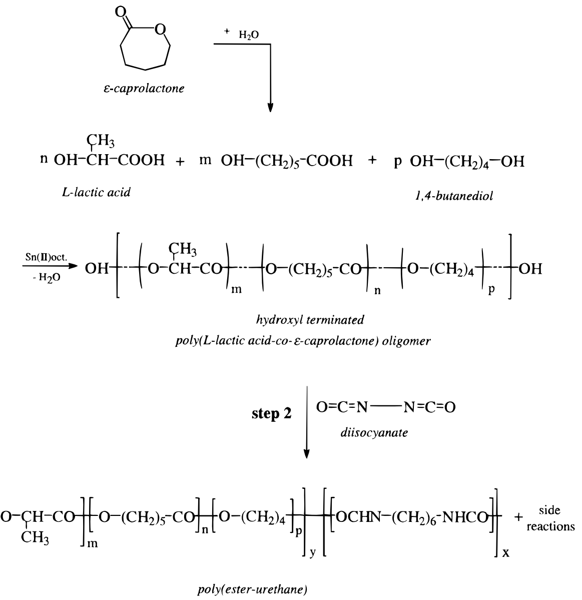

**Figure 1.** Polymerization scheme for poly(L-lactic acid-*co*-ε-caprolactone−urethane).

gel columns ($10^4$, $10^5$, $10^3$, and 100 Å). Chloroform was used as solvent with a flow rate of 1 mL/min.

The thermal properties were determined with a Polymer Laboratories differential scanning calorimeter between −100 and 180 °C with a heating and cooling rate of 10 °C/min. Glass transition temperatures were recorded during the second heating scan to ensure identical thermal histories.

Proton-decoupled $^{13}$C NMR spectra with NOE were obtained with a Varian Unity 400 spectrometer working at 100.557 MHz. Sample concentrations in 5-mm tubes were 10% by weight in $CDCl_3$ with TMS as the internal reference.

FTIR spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer, using film samples cast on a potassium bromide plate from 1 wt % chloroform solutions.

The degree of cross-linking (i.e., gel content) of the polymerized poly(ester−urethane) was measured by extracting the soluble phase in boiling acetone (56 °C) for 20 h. The gel content was determined as the weight of the inextractable material divided by the total weight of the original sample.

Tensile tests of the compression-molded polymers (2 mm × 10 mm × 50 mm) were performed on an Instron 4204 tensile testing machine equipped with a computer, adopting the standard ISO/R 527-1966(E). The mechanical properties of the homopolymer and copolymers were measured using a tensile tester at a crosshead speed of 5 mm/min for PEU, P(LA97/CL3)U, P(LA96/CL4)U, and P(LA94/CL6)U and 50 mm/min for other poly(ester−urethanes). The mechanical values for the polymers were measured for five parallel air-conditioned specimens, which had been left for 72 h at 23 °C and 50% relative humidity.

**Hydrolysis Tests.** The poly(ester−urethane) test specimens for hydrolysis were punched out from compression molded (Fontijne TP 400) plates with an Elastocon EP 02 puncher. Test specimens of 10 mm × 10 mm × 3 mm were immersed in 30 mL of phosphate buffer solution of pH 7.4 in test tubes and shaken in the gently mixed water baths at 37 °C. The buffer solution was changed each week. At given time intervals specimens were removed from test tubes, flushed with distilled water, and weighed. The test specimens were dried under vacuum at room temperature until they reached a constant weight, from which mass loss and molecular weight were determined. Water absorption was calculated as the difference between the weight of the wet polymer after hydrolysis and the weight of dried polymer, divided by the weight of the dried polymer. Mass losses were calculated for each sample by comparing the dry weight remaining at a specific time and the initial weight.

## Results and Discussion

The thermoplastic poly(ester−urethanes), PEUs, were polymerized in a two-step process for lactic acid polymerization illustrated in Figure 1: in the first step the L-lactic acid (LA) and ε-caprolactone (CL) were condensation copolymerized to low molecular weight prepolymer, and in the second step the molecular weight was raised by using diisocyanate as chain extender. The use of 2 mol % 1,4-butanediol results in prepolymer molecules with hydroxyl functionality at both ends. The polycondensation of cyclic ε-caprolactone proceeds through a linear 6-hydroxycaproic acid produced by hydrolysis of CL.[16]

Table 1 sets out the conditions and results of the prepolymer synthesis: monomer compositions in feed, time and temperature of the polymerization, molecular weights, molecular weight distributions, and DSC measurements of the copolymers. The copolymers of lactic acid and ε-caprolactone were low molecular weight hydroxyl-terminated oligomers, whose physical appearance varied greatly with monomer composition from solid to waxy. Like the corresponding poly(ester−urethanes), the oligomers were amorphous. Only the CL-rich oligomer (LA25/CL75) exhibited slight crystal-

**Table 1. Results of the Synthesis of Prepolymer from Lactic Acid and ε-Caprolactone**

| | monomer composition in feed[a] (mole fraction) | | polymerization conditions[b] | | GPC | | | DSC | | acid number |
|---|---|---|---|---|---|---|---|---|---|---|
| prepolymer | L-LA | ε-CL | time (h) | temp (°C) | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | MWD | $T_g$ (°C) | $T_m$ (°C) | |
| (LA97/CL03) | 0.97 | 0.03 | 16 | 210 | 7300 | 11 400 | 1.56 | 33 | | 2 |
| (LA96/CL04) | 0.96 | 0.04 | 24 | 210 | 7200 | 11 200 | 1.55 | 28 | | 2 |
| (LA95/CL05) | 0.95 | 0.05 | 25 | 210 | 8000 | 11 800 | 1.47 | 28 | | 4 |
| (LA94/CL06) | 0.94 | 0.06 | 24 | 210 | 7200 | 11 400 | 1.58 | 26 | | 1 |
| (LA90/CL10) | 0.90 | 0.10 | 24 | 210 | 7100 | 11 200 | 1.59 | 17 | | 4 |
| (LA88/CL12) | 0.88 | 0.12 | 16 | 200 | 5900 | 9 700 | 1.63 | 13 | | 5 |
| (LA85/CL15) | 0.85 | 0.15 | 25 | 210 | 8400 | 12 700 | 1.52 | 10 | | 5 |
| (LA82/CL18) | 0.82 | 0.18 | 24 | 210 | 7700 | 12 400 | 1.61 | 4 | | 3 |
| (LA76/CL24) | 0.76 | 0.24 | 22 | 210 | 6200 | 11 700 | 1.88 | −3 | | 3 |
| (LA70/CL30) | 0.70 | 0.30 | 24 | 210 | 6300 | 12 800 | 2.01 | −12 | | 3 |
| (LA65/CL35) | 0.65 | 0.35 | 16 | 200 | 4900 | 9 700 | 1.63 | −20 | | 6 |
| (LA53/CL47) | 0.53 | 0.47 | 16 | 200 | 6700 | 11 800 | 1.80 | −37 | | 3 |
| (LA50/CL50) | 0.50 | 0.50 | 24 | 210 | 5600 | 14 300 | 2.54 | −35 | | 2 |
| (LA45/CL55) | 0.45 | 0.55 | 24 | 210 | 5100 | 15 000 | 2.93 | −41 | | 3 |
| (LA30/CL70) | 0.30 | 0.70 | 24 | 210 | 8200 | 17 700 | 2.15 | −50 | | 2 |
| (LA25/CL75) | 0.25 | 0.75 | 16 | 200 | 5900 | 12 800 | 2.17 | −55 | 27 | 6 |
| (LA35DL35/CL30) | (0.70)[c] | 0.30 | 24 | 210 | 7100 | 12 200 | 1.72 | −14 | | 3 |
| (DL70/CL30) | (0.70)[d] | 0.30 | 24 | 210 | 5400 | 12 700 | 2.33 | −14 | | 3 |

[a] 2 mol % 1,4-butanediol. [b] 0.05 wt % Sn(II) octoate. [c] 35 mol % L-lactic acid, 35 mol % DL-lactic acid. [d] 70 mol % DL-lactic acid.

**Table 2. Effect of the Amount of Diisocyanate in the Synthesis of Polyurethane from Hydroxyl-Terminated Poly(L-lactic acid-*co*-ϵ-caprolactone) Prepolymer of LA/CL Composition 70/30 mol %**

| | | | GPC | | | DSC | |
|---|---|---|---|---|---|---|---|
| sample | amount of diisocyanate (mL) | solubility in $CHCl_3$ | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | MWD | $T_g$ (°C) | gel content (wt %) |
| 1 | 2.1 | soluble | 66 000 | 149 000 | 2.25 | −1 | 0 |
| 2 | 2.3 | soluble | 95 000 | 323 000 | 3.40 | −2 | 0 |
| 3 | 2.5 | insoluble | | | | −1 | 62 |
| 4 | 2.7 | insoluble | | | | −1 | 73 |
| 5 | 2.9 | insoluble | | | | −1 | 75 |

**Table 3. Results of the Urethane Synthesis and Mechanical Properties of Poly(L-lactic acid-*co*-ϵ-caprolactone−urethanes)**

| | composition | GPC | | | DSC | mechanical properties | | |
|---|---|---|---|---|---|---|---|---|
| urethane | (LA/CL) (mol %) | $\bar{M}_n$ (g/mol) | $\bar{M}_w$ (g/mol) | MWD | $T_g$ (°C) | tensile modulus (MPa) | maximum stress (MPa) | maximum strain (%) |
| PEU[a] | (100/0) | 41 000 | 187 000 | 4.60 | 53 | 1900 ± 60 | 47 ± 2 | 3.7 ± 0.3 |
| P(LA97/CL03)U | (97/3) | 69 200 | 307 000 | 4.45 | 45 | 2100 ± 50 | 43 ± 1 | 4.7 ± 1.7 |
| P(LA96/CL04)U | (96/4) | 76 000 | 449 000 | 5.92 | 40 | 1700 ± 130 | 36 ± 1 | 6.9 ± 4.6 |
| P(LA94/CL06)U | (94/6) | 60 100 | 270 000 | 4.49 | 35 | 1300 ± 130 | 23 ± 3 | 420 ± 20 |
| P(LA88/CL12)U | (88/12) | 77 000 | 257 000 | 3.33 | 28 | 80 ± 20 | 8.6 ± 0.4 | 440 ± 40 |
| P(LA82/CL18)U | (82/18) | 59 500 | 240 000 | 4.03 | 12 | nd[b] | nd | nd |
| P(LA76/CL24)U | (76/24) | 73 800 | 387 000 | 5.24 | 9 | 1.7 ± 0.6 | 0.4 ± 0.1 | >1000 |
| P(LA70/CL30)U | (70/30) | 65 400 | 117 000 | 1.80 | −3 | 1.4 ± 0.1 | 1.5 ± 0.2 | >1000 |
| P(LA65/CL35)U | (65/35) | 96 900 | 508 000 | 5.24 | −5 | 1.5 ± 0.2 | 1.6 ± 0.1 | 900 ± 50 |
| P(LA53/CL47)U | (53/47) | 91 000 | 228 000 | 2.50 | −24 | 1.6 ± 0.3 | 0.2 ± 0.1 | 730 ± 70 |
| P(LA50/CL50)U | (50/50) | 70 700 | 314 000 | 4.45 | −26 | 1.5 ± 0.3 | 1.6 ± 0.3 | >1000 |
| P(LA45/CL55)U | (45/55) | 74 500 | 292 000 | 3.92 | −30 | nd | nd | nd |
| P(LA30/CL70)U | (30/70) | 60 200 | 268 000 | 4.45 | −45 | 1.7 ± 0.1 | 1.8 ± 0.1 | 590 ± 50 |
| P(LA25/CL75)U | (25/75) | 82 900 | 415 000 | 5.01 | nd | 5.3 ± 1.4 | 0.09 ± 0.01 | >1000 |
| P(LA35DL35/CL30)U | (70/30) | 65 100 | 230 000 | 3.53 | −3 | 1.1 ± 0.1 | 1.3 ± 0.3 | >1000 |
| P(DL70/CL30)U | (70/30) | 53 500 | 202 000 | 3.78 | −4 | 1.4 ± 0.3 | 1.5 ± 0.3 | 940 ± 170 |

[a] From previous studies.[15] [b] nd, not detected.

lization, but it still produced amorphous polyurethane. To investigate the effect of configurational structure, prepolymers were prepared from DL-lactic acid (DL) in the same way and with the same CL content as (LA70/CL30). Neither the polymerization of the prepolymers nor polyurethane synthesis was configuration dependent: molecular weights as well as thermal properties were comparable. The effect of different configurational structures on the structure of the oligomers and mechanical properties is discussed below.

High molecular weight thermoplastic polymers, poly(L-lactic acid-*co*-ϵ-caprolactone−urethanes), P(LA/CL)U, were synthesized by reacting hydroxyl-terminated (LA/CL) prepolymers and aliphatic 1,6-hexamethylene diisocyanate. Table 2 shows the relationship between the amount of diisocyanate and the molecular weight and gel content of P(LA70/CL30)U. Increasing the diisocyanate content led to the formation of a network structure because of the reaction of excess isocyanate with moisture, urethane, and urea groups, to give urea, allophanate, and biuret, respectively. The results of the urethane synthesis are summarized in Table 3. The physical appearance of thermoplastic poly(ester−urethane) depends on the monomer composition. Polymers with high lactic acid content were rigid, urethane plastics, while CL-rich polymers were elastomeric due to the flexible nature of the caprolactone repeat unit.

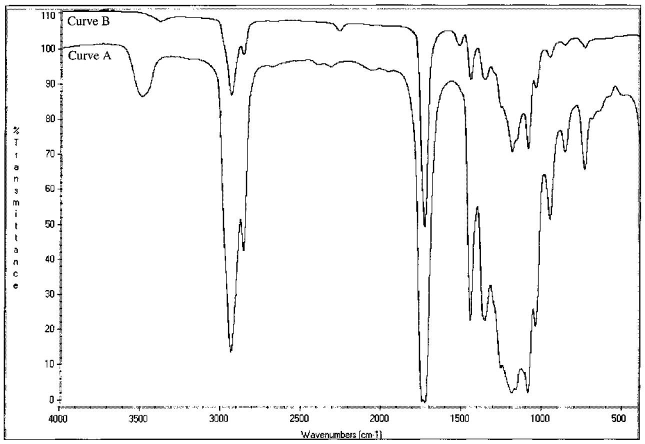

**Figure 2.** FTIR spectrum of poly(L-lactic acid-*co*-ϵ-caprolactone) prepolymer (curve A) and corresponding urethane (curve B).

Figure 2 shows a representative FTIR spectrum of poly(L-lactic acid-*co*-ϵ-caprolactone) prepolymer (curve A) and the corresponding poly(ester−urethane) sample (curve B). This polymerization method results in hydroxy−telechelic polyesters, as confirmed by the strong hydroxyl absorption band at 3500 $cm^{-1}$. In addition, an absorption band at 1750 $cm^{-1}$ confirms the formation of O−C=O ester bonds. The urethane linkage is characterized by the NH absorption region. The major NH absorption occurs at 3330 $cm^{-1}$ and is attributed to hydrogen-bonded NH groups. In addition, the amide absorption at 1530 $cm^{-1}$ is characteristic of urethane functionality. The absorption peak at 2270 $cm^{-1}$, which is attributed to isosyanate groups, was used to follow the progression of the linking reaction.

**Structure of the Oligomers.** A representative $^{13}C$ NMR spectrum of the (L-lactic acid-*co*-ϵ-caprolactone) oligomer is shown in Figure 3. The composition of the copolymers was determined by $^{13}C$ NMR analysis from the carbonyl signals. The results showed the copolymer composition to be in satisfactory agreement with the comonomer feed ratio (Table 4): copolymer compositions were within 0.4−8.8% of the initial feed ratios.

The sequence analysis of LA/CL oligomers was carried out by $^{13}C$ NMR spectroscopy according to the method proposed by Kricheldorf and *co*-workers.[17,18] Carbonyl signals (between 169 and 174 ppm) were used in the calculation of the average block lengths $\bar{L}$ because of

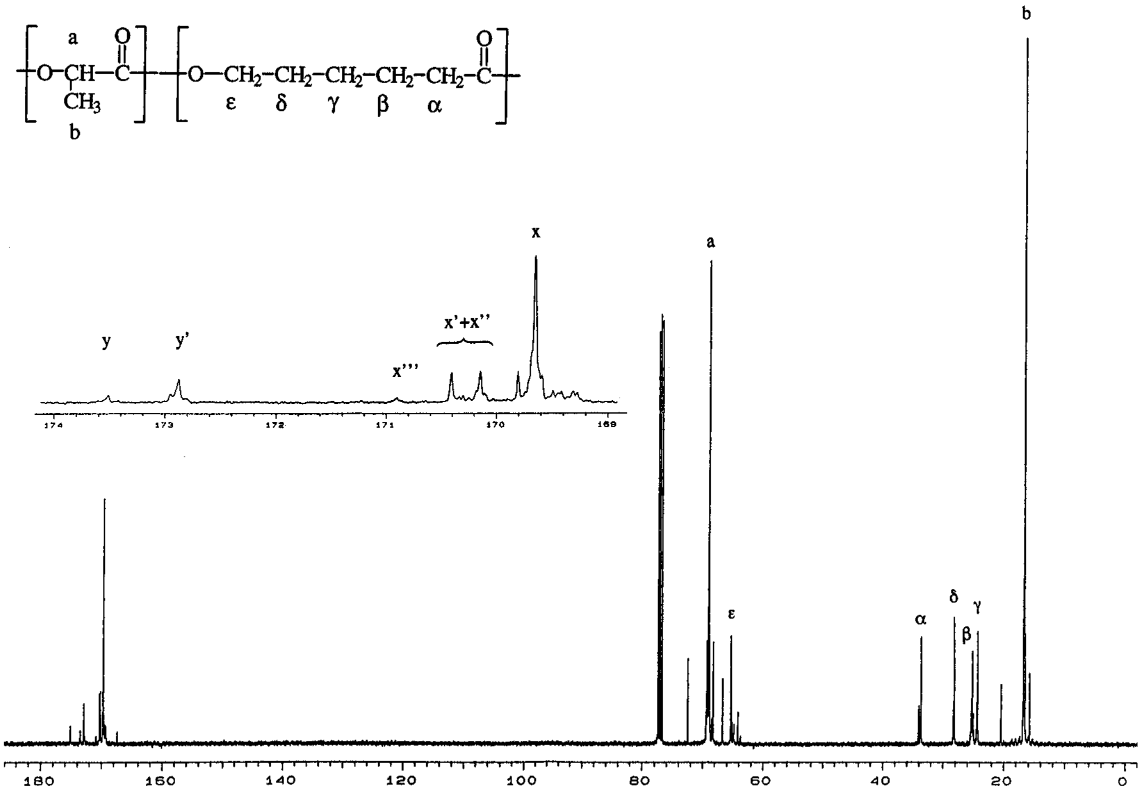

**Figure 3.** $^{13}$C NMR spectrum of the (L-lactic acid-*co*-ε-caprolactone) oligomer in CDCl$_3$.

**Table 4. $^{13}$C NMR Integration Results for Poly(lactic acid-*co*-ε-caprolactone) Prepolymers**

| | monomer composition in feed | | | $^{13}$C NMR composition in copolymer | | average sequence lengths | | |
|---|---|---|---|---|---|---|---|---|
| prepolymer | L-LA | DL-LA | ε-CL | LA | CL | $\bar{L}_{lac}$ | $\bar{L}_{cap}$ | other lactic isomers (mol %) |
| (LA97/CL03) | 0.97 | | 0.03 | 0.971 | 0.029 | 21.8 | 1.2 | 22 |
| (LA96/CL04) | 0.96 | | 0.04 | 0.947 | 0.053 | 12.1 | 1.2 | 22 |
| (LA95/CL05) | 0.95 | | 0.05 | 0.939 | 0.061 | 9.0 | 1.2 | 23 |
| (LA94/CL06) | 0.94 | | 0.06 | 0.930 | 0.070 | 10.5 | 1.2 | 23 |
| (LA90/CL10) | 0.90 | | 0.10 | 0.882 | 0.118 | 7.1 | 1.2 | 21 |
| (LA88/CL12) | 0.88 | | 0.12 | 0.868 | 0.132 | 8.8 | 1.3 | 14 |
| (LA85/CL15) | 0.85 | | 0.15 | 0.822 | 0.178 | 5.6 | 1.3 | 21 |
| (LA82/CL18) | 0.82 | | 0.18 | 0.807 | 0.193 | 4.8 | 1.4 | 22 |
| (LA76/CL24) | 0.76 | | 0.24 | 0.743 | 0.257 | 4.0 | 1.5 | 13 |
| (LA70/CL30) | 0.70 | | 0.30 | 0.685 | 0.315 | 3.3 | 1.5 | 14 |
| (LA65/CL35) | 0.65 | | 0.35 | 0.637 | 0.363 | 2.6 | 2.0 | 2 |
| (LA53/CL47) | 0.53 | | 0.47 | 0.457 | 0.543 | 2.3 | 2.1 | [a] |
| (LA50/CL50) | 0.50 | | 0.50 | 0.479 | 0.521 | 2.0 | 2.1 | 7 |
| (LA45/CL55) | 0.45 | | 0.55 | 0.434 | 0.566 | 1.8 | 2.3 | 9 |
| (LA30/CL70) | 0.30 | | 0.70 | 0.270 | 0.730 | 1.4 | 3.4 | [a] |
| (LA25/CL75) | 0.25 | | 0.75 | 0.209 | 0.791 | 1.5 | 5.3 | [a] |
| (LA70/CL30) | 0.70 | | 0.30 | 0.685 | 0.315 | 3.3 | 1.5 | 14 |
| (LA35DL35/CL30) | 0.35 | 0.35 | 0.30 | 0.691 | 0.309 | 3.4 | 1.6 | 32 |
| (DL70/CL30) | | 0.70 | 0.30 | 0.694 | 0.306 | 3.4 | 1.5 | 36 |

[a] Unable to measure (<2 mol %).

their high sensitivity to the chemical environment. The average lengths of the caprolactone blocks ($\bar{L}_{cap}$) were calculated from the dyad peaks of the CO signals according to eq 1.

$$\bar{L}_{cap} = \frac{I_{CC}}{I_{CL}} + 1 \tag{1}$$

$I_{CC}$ is the intensity of a peak representing the C−C dyad (*y* in Figure 3), and $I_{CL}$ is the intensity of a peak representing the C−L dyad (C = caprolactone, L = lactidyl units; *y*′ in Figure 3). The average lengths of the lactyl blocks ($\bar{L}_{lac}$) were calculated from the triad peaks of the CO signals according to eq 2.

$$\bar{L}_{lac} = \frac{I_{LLL} + (I_{LLC} + I_{CLL})/2}{I_{CLC} + (I_{LLC} + I_{CLL})/2} + 1 \tag{2}$$

$I_{LLL}$ is the intensity of a peak representing the L−L−L sequence (*x* in Figure 3), $I_{LLC}$ and $I_{CLL}$ are the intensities of peaks representing the triads of two lactyl and one caprolactone unit (*x*′ or *x*″), and $I_{CLC}$ is the intensity of a peak representing the C−L−C triad (*x*‴).

Table 4 summarizes the sequence analysis data. The results showed the copolymers to have a short average block length, which means that they are statistical. As expected, at a LA/CL monomer composition of 50/50 mol % the average block lengths were more or less the same.

The presence of different configurational structures, i.e., D-lactic acid units in the polymer chains, can be seen

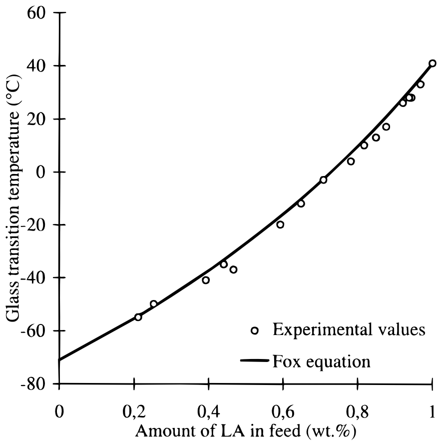

**Figure 4.** Glass transition temperature of (L-lactic acid-*co*-$\epsilon$-caprolactone) oligomers and Fox equation plotted against the amount of L-lactic acid.

in the enlargement of the spectrum in Figure 3. Every polymer exhibits four peaks in the carbonyl area (169.2−196.5 ppm). The peaks were shown in a previous publication[12] to be due to different optical isomers in the polymer chain, and this was confirmed here by preparing polymers (LA35/DL35/CL30) and (DL70/CL30) from D,L-lactic acid in the same way as polymer (LA70/CL30). Amounts of the different optical isomers were calculated from the peak integrals in the carbonyl area. The amounts were fairly large in all polymers and might explain why they were amorphous. This behavior is in agreement with the results of previous studies on lactic acid-based poly(ester−urethane). As seen in Table 4, when the content of CL in the copolymer was increased above 30 mol % in the copolymer, the amounts of different optical isomers were less than 10 mol %.

**Thermal Properties.** The glass transition temperatures of the (LA/CL) oligomers and the poly(ester−urethanes) were determined by DSC measurements. As expected, $\epsilon$-caprolactone units increased the chain flexibility and mobility and caused a considerable decrease in the glass transition temperature. In Figure 4, the experimental values of oligomers are shown against the Fox equation[19] (eq 3), which predicts the glass transition temperature, $T_{gco}$, of random copolymers.

$$\frac{1}{T_{gco}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (3)$$

were $w_1$ and $w_2$ are the weight fractions of the two monomers whose homopolymers have the glass transition temperatures $T_{g1}$ and $T_{g2}$. The $T_{g1}$ (hydroxyl-terminated LA prepolymer;[12] $\bar{M}_n = 7900$ g/mol) is set to 41 °C, and $T_{g2}$ (poly($\epsilon$-caprolactone);[20] $\bar{M}_n = 4000$ g/mol) to −71 °C. The experimental values are a little lower but still in very good agreement with the Fox equation: $T_g$ decreases in the same manner with an increase in $\epsilon$-caprolactone content in the copolymer.

Thermal properties of the poly(L-lactic acid-*co*-$\epsilon$-caprolactone−urethanes) correlate with the properties of the prepolymer: an increase of molecular weight and the formation of hydrogen bonds increase the $T_g$ of the poly(ester−urethane) by about 9−12 °C compared with that of the parent polyester prepolymer.

**Tensile Properties.** Results of the tensile testing are summarized in Table 3. The shapes of the stress−strain curves of the poly(ester−urethanes) were quite different, as seen in Figure 5. The numbers shown at the end of the curves indicate the LA/CL molar composition of the polymer. Poly(ester−urethane) containing only lactic acid is hard and brittle, having a high tensile modulus of 2.0 GPa, a tensile strength of 47 MPa, and a maximum strain of 3.5%. The mechanical properties of poly(L-lactic acid-*co*-$\epsilon$-caprolactone−urethane) were found to depend heavily on the composition of the prepolymer and to be greatly affected by the introduction even of a small amount of CL units.

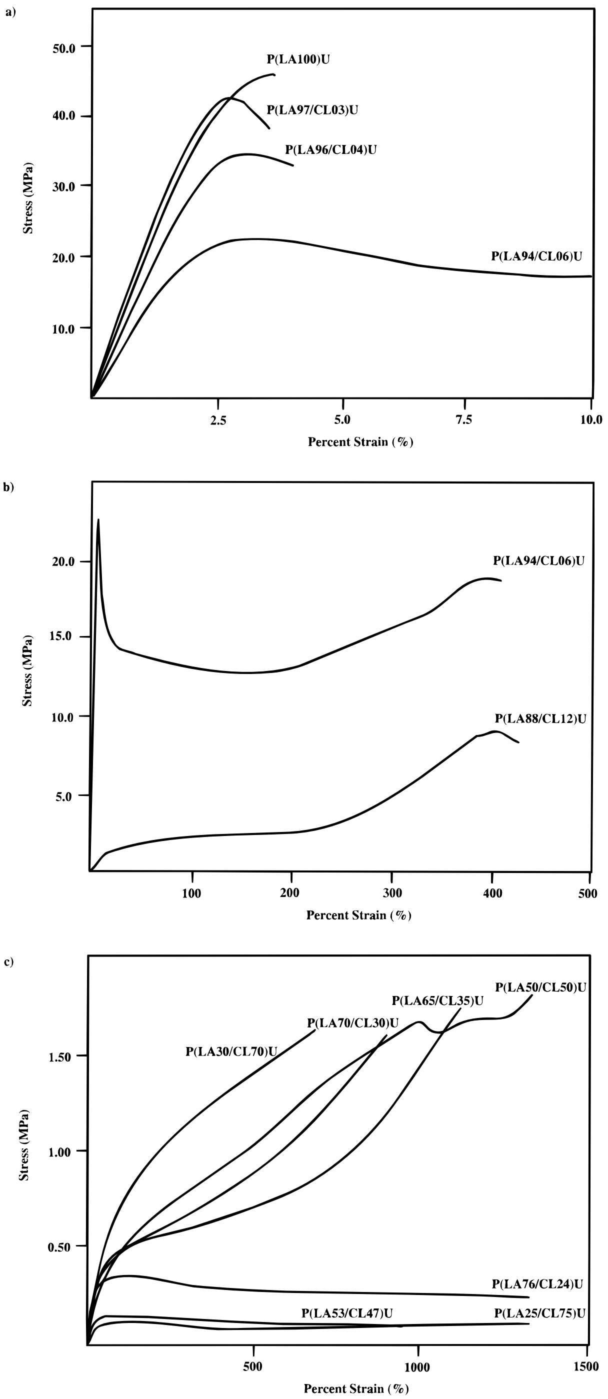

**Figure 5.** Stress−strain curves of poly(L-lactic acid-*co*-$\epsilon$-caprolactone−urethanes) with LA compositions of (a) 100−94 mol %, (b) 94−88 mol %, and (c) 76−25 mol %.

As seen from Figure 5a, the maximum strain increased with $\epsilon$-caprolactone content in P(LA97/CL3)U and P(LA96/CL4)U, while tensile stress decreased slightly. P(LA94/CL6)U exhibited yield deformation and ductile failure, and the maximum strain was >400%. All polymers with less than 10 mol % CL in the prepolymer exhibited plastic properties, whereas

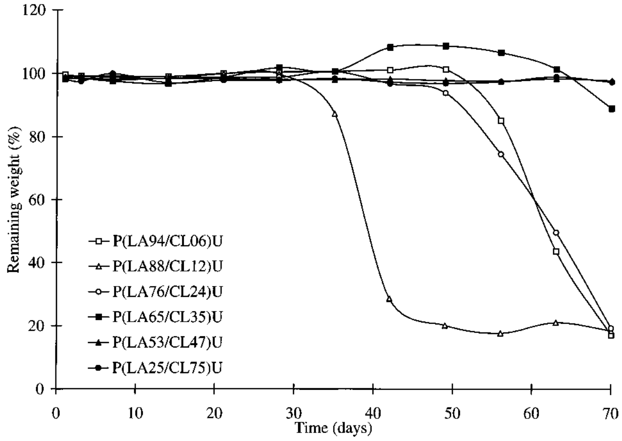

**Figure 6.** Mass loss of poly(L-lactic acid-*co*-ϵ-caprolactone−urethanes) during a degradation time.

other polymers exhibited typical rubber properties and managed to recover completely from more than 1000% extension. Tensile modulus and maximum stress were considerably lower in P(LA94/CL06)U and P(LA88/CL12)U (Figure 5b). P(LA94/CL06)U exhibited the characteristic yield point typical of plastic, whereas P(LA88/CL12)U showed transitions typical of elastic properties. P(LA/CL)Us with higher ϵ-caprolactone content had lower tensile strengths, but they exhibited significant elongation, as seen in Figure 5c. The poly(ester−urethane) with the highest CL content, P(LA25/CL75)U, was very soft and had the lowest tensile stress values. A test on poly(ester−urethanes) of L- or DL-lactic acid/ϵ-caprolactone composition 70/30 mol % showed that the different configurational structures had no effect on mechanical properties.

The tensile properties of the PEUs were found to be a direct function of the glass transition temperature, which is related to the composition of the polyester prepolymer. As long as the temperature is below the $T_g$ of the polymer, polymer chains in the amorphous regions will be fairly immobile and able to contribute to the strength of the material. When the amount of ϵ-caprolactone in the prepolymer increases over 12 mol %, the glass transition temperatures of the urethanes are below room temperature and PEUs exhibit a dramatic decrease in modulus and maximum stress.

**Hydrolysis.** Hydrolytic degradation of poly(L-lactic acid-*co*-ϵ-caprolactone−urethanes) was investigated by monitoring the changes in the pH of the phosphate buffer solution and in the water absorption, weight, and molecular weight of polymer disks during immersion in phosphate buffer solution of pH 7.4 at 37 °C. During the first few days of hydrolysis, water absorption of the poly(ester−urethanes) varied from 2 to 7 wt %. After a constant increase in water content, polymers with higher ϵ-caprolactone contents attained their water absorption equilibrium with a water content of 60−70% in about 4 weeks. P(LA88/CL12)U displayed the most significant water uptake after 30 days, whereas P(LA94/CL06)U and P(LA76/CL24)U increased their water content over 100% at the end of the hydrolysis period. Water absorption of the present poly(ester−urethanes) was considerably larger than that for copolymers of L-lactide and ϵ-caprolactone that we prepared earlier[2] by ring-opening polymerization.

The water absorption and mass loss profiles (Figure 6) were essentially identical. P(LA88/CL12)U exhibited after 30 days, and P(LA94/CL06)U and P(LA76/CL24)U after 50 days, a mass loss of more than 80% of initial mass. Higher CL content in PEU exhibited less than 10% weight loss, and CL-rich poly(ester−urethanes) showed less than 3% weight loss during a predetermined degradation time. The rate of hydrolysis was clearly faster for poly(ester−urethanes) where the amount of LA relative to CL was larger. Changes in the pH, which describe the production of carboxylic acids formed by hydrolysis, were observed at exactly the same time as the mass losses.

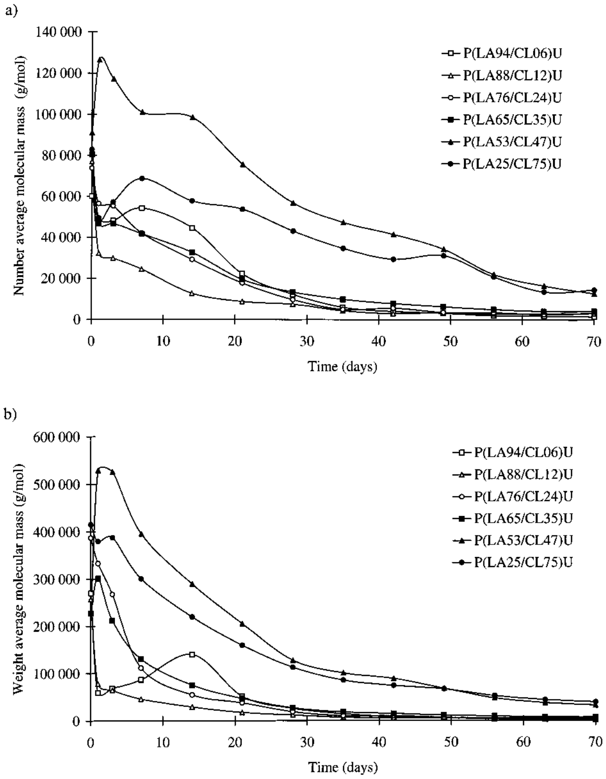

**Figure 7.** Loss of (a) number average and (b) weight average molecular weights during hydrolysis at 37 °C. Table 1. Results of the synthesis of prepolymer from lactic acid and ϵ-caprolactone.

Mass loss was not simultaneous with loss of molecular weight (Figure 7) but lagged behind, indicating bulk erosion of the polymer sample by random chain scission. A characteristic for a bulk degradation is that the weight of the sample remains constant for a relatively long period and that weight loss only starts when the molecular weight of the polymer chains has decreased sufficiently.[21] The molecular weights of the polymers decreased continuously after they were exposed to the phosphate buffer solution. During the first few days, the molecular weight of polymers with relatively flexible chains, especially P(LA53/CL47)U, increased slightly evidently due to the reaction of unreacted isocyanate groups with water, forming urea groups. This reaction could have had an effect on the hydrolytic degradation rate of the CL-rich polymers. The molecular weight of P(LA53/CL47)U and P(LA25/CL75)U did not decrease sufficiently that mass loss could occur within the set degradation time. The number average molecular weight of these polymers had reached a level of only 13 000−14 000 g/mol when the other PEUs were at a level of 2000−4000 g/mol and already showed a weight loss.

## Conclusions

Biodegradable, thermoplastic poly(ester−urethanes) were synthesized in a two-step process: a condensation polymerization of lactic acid and $\epsilon$-caprolactone to hydroxyl-terminated telechelic prepolymer, followed by an increase in molecular weight through reaction with diisocyanate. As shown by NMR studies the prepolymer composition corresponded to the comonomer feed ratio and the prepolymers had a random structure. All poly(ester–urethanes) were amorphous, and the glass transition temperature decreased with an increase in the $\epsilon$-caprolactone content.

The poly(L-lactic acid-*co*-$\epsilon$-caprolactone-urethanes) varied from rigid plastic to soft elastomers and varied widely in their mechanical properties with monomer composition. Small amounts of $\epsilon$-caprolactone increased the maximum strain, and at higher CL content the poly(ester–urethanes) exhibited significant elongation. Tensile modulus and maximum stress decreased in proportion to the $\epsilon$-caprolactone content. In degradation experiments, poly(ester–urethanes) with high L-lactic acid content underwent weight loss at an earlier stage than polymers with low LA content.

**Acknowledgment.** Lic. Tech. Kari Hiltunen is gratefully thanked for his help with the NMR measurements, and Charlotta Tuovinen is gratefully thanked for assistance with the hydrolysis tests.

## References and Notes

(1) Hiljanen-Vainio, M.; Karjalainen, T.; Seppälä, J. *J. Appl. Polym. Sci.* **1996**, *59*, 1281.
(2) Malin, M.; Hiljanen-Vainio, M.; Karjalainen, T.; Seppälä, J. *J. Appl. Polym. Sci.* **1996**, *59*, 1289.
(3) Karjalainen, T.; Hiljanen-Vainio, M.; Malin, M.; Seppälä, J. *J. Appl. Polym. Sci.* **1996**, *59*, 1299.
(4) Grijpma, D. W.; Zondervan, G. J.; Pennings, A. J. *Polym. Bull.* **1991**, *25*, 327.
(5) Löfgren, A.; Renstad, R.; Albertsson, A.-C. *J. Appl. Polym. Sci.* **1995**, *55*, 1589.
(6) Sipos, L.; Zsuga, M.; Deák, G. *Macromol. Rapid Commun.* **1995**, *16*, 935.
(7) Nakayama, A.; Kawasaki, N.; Arvanitoyannis, I.; Iyoda, J.; Yamamoto, N. *Polymer* **1995**, *36*, 1295.
(8) Storey, R. F.; Wiggins, J. S.; Pucket, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2345.
(9) Storey, R. F.; Herring, K. R.; Hoffman, D. C. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1759.
(10) Bruin, P.; Veenstra, G. J.; Nijenhuis, A. J.; Pennings, A. J. *Macromol. Chem., Rapid Commun.* **1988**, *9*, 589.
(11) Pitt, C. G.; Gu, Z.-W.; Ingram, P.; Hendren, F. W. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 955.
(12) Hiltunen, K.; Härkönen, M.; Seppälä, J. V.; Väänänen, T. *Macromolecules* **1997**, *29*, 8677.
(13) Hiltunen, K.; Härkönen, M.; Seppälä, J. V. *J. Appl. Polym. Sci.* **1997**, *63*, 1091.
(14) Seppälä, J. V.; Selin, J.-F.; Su, T. Fin. Pat. 92592, App. 16.10.1992, Acc. 12.12.1994.
(15) Kylmä, J.; Härkönen, M.; Seppälä, J. V. *J. Appl. Polym. Sci.* **1997**, *63*, 1865.
(16) Fukuzaki, H.; Yoshida, M.; Asano, M.; Kumakura, M.; Mashimo, T.; Yuasa, H.; Imai, K.; Yamanaka, H. *Polymer* **1990**, *31*, 2006.
(17) Kricheldorf, H. R.; Mang, T.; Jonte, J. M. *Macromolecules* **1984**, *17*, 2173.
(18) Kricheldorf H. R.; Kreiser, I. *J. Macromol. Sci.–Chem.* **1987**, *A24*, 1345.
(19) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
(20) Nabeth, B.; Corniglion, I.; Pascault, J. P. *J. Polym. Sci., Polym. Phys.* **1996**, *34*, 401.
(21) in't Veld, P. J. A.; Dijkstra, P. J.; Feijen, J. *Clin. Mater.* **1993**, *13*, 143.

MA961569G