

Synthesis and Characterization of a New Degradable Thermoplastic Elastomer Based on 1,5-Dioxepan-2-one and ϵ -Caprolactone

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SYNOPSIS

A new, highly elastomeric ABA triblock copolymer made from ϵ -caprolactone (ϵ -CL) and 1,5-dioxepan-2-one (DXO) has been synthesized by sequential addition of the comonomers in THF or toluene solution initiated by aluminum isopropoxide. Careful purification of the comonomers was essential to obtain high conversion of the final amount of the added monomer. The optimal conditions were found to be polymerization in toluene solution at 25°C with the addition of 1 molar equivalent (with respect to initiator) of pyridine, which gives a slight increase in the rate of polymerization. Under these conditions, poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers of high molecular weight ($M_n > 10^5$ g/mol) with a relatively narrow molecular weight distribution were obtained. Thermal analysis shows a melting peak at 51°C and a glass transition at ca. -38°C, corresponding to the PCL block crystalline phase and the PDXO amorphous region, respectively. The mechanical properties of these materials are highly elastic and can be varied by tailoring the block lengths of the corresponding comonomers. Tensile modulus, tensile strength at break, and elongation at break were found to be 20–30 MPa, 50 MPa, and ca. 1000%, respectively. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

For some 15 years, our research group has worked with the synthesis, characterization, and hydrolysis behavior of degradable materials. From the very start, block copolymers were recognized as an interesting possibility to create new, highly flexible degradable materials.^{1,2} After an initial study with condensation polymerization,² ring-opening polymerization was used to make systematical investigations of polymers with potential use as hard and soft blocks in copolymers.^{3–6}

Block copolymers have for some 30 years contributed to the ever-growing field of new polymeric materials. Block and graft copolymers possess unique properties in that they combine the inherent natures of the polymers included. Often this results in, e.g., surface-active properties or thermoplastic

elastomeric behavior.⁷ In the field of degradable polymers, block copolymers have been synthesized,^{8,9} although few examples of well-defined triblock copolymers have been reported.¹⁰

In an earlier work,¹¹ a synthetic route to poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers was described. This method was based on the sequential addition of the different comonomers to a living polymerization system, initiated with aluminum isopropoxide in THF or toluene solution. The molecular weights obtained were, however, relatively low and it was difficult to achieve full conversion of the final added monomer.¹¹

The primary goal of this work was to synthesize a material with good elastomeric and mechanical properties. Poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers have crystalline end blocks and an amorphous middle block with a glass transition in the low-temperature region. The hydrolytically cleavable backbone of both the A and B blocks makes this copolymer to a potential degradable thermoplastic elastomer.

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EXPERIMENTAL

Materials and Methods

THF and toluene were dried by distillation over a Na/K-alloy/benzophenone complex under an inert gas. Pyridine, triethyl amine, and ϵ -CL (Aldrich) were purified by drying over CaH₂ and subsequent distillation under reduced pressure (10⁻² mbar). Hexane (Shell) was used as received unless otherwise stated. Methylene chloride (Shell) was distilled over CaCl₂ and diethyl ether (Riedel-de-Haën) was dried over sodium wire and distilled under reduced pressure. Aluminum tri-isopropoxide (Aldrich) was purified by distillation under reduced pressure and dissolved in dry toluene. The concentration of this solution was measured by complexometric titration of Al with a standard solution of EDTA. Terephthaloyl chloride was dissolved in dry hexane (dried over CaH₂ and subsequently distilled) at 70°C and the insoluble part was filtered off. The remaining solution was cooled to -20°C and the hexane was removed by a capillary under a positive pressure of an inert gas. The remaining white crystals were dried under reduced pressure. 1,4-Phenylene diisocyanate was dissolved in dry THF at ambient temperature and then stored overnight at -20°C. The insoluble impurities were filtered off and the THF was removed under reduced pressure. Dimethyl aminopyridine (DMAP) was dried twice by azeotropic distillation of toluene under reduced pressure (10⁻² mmHg).

Synthesis of 1,5-Dioxepan-2-one (DXO)

A typical synthesis procedure was carried out as follows: Sixty-seven grams of 3-chloroperbenzoic acid (70%) (Aldrich) was dissolved in 400 mL of methylene chloride and the organic phase was separated and dried with MgSO₄ (anhydrous) (Merck). After filtration, the methylene chloride solution was cooled to 0°C in an ice/water bath. Twenty grams of tetrahydro-4H-pyran-4-one (Fluka) was immersed in the peracid solution, which was allowed to attain room temperature under stirring during 15 h. After filtration, the methylene chloride phase was washed with sodium bisulfite and sodium bicarbonate to eliminate any remaining peracid and most of the 3-chlorobenzoic acid. The methylene chloride phase was evaporated to give a slightly yellow oil. This was distilled under reduced pressure (10⁻² mbar) and gave an 80% yield of DXO (55°C). The DXO monomer was recrystallized twice in anhydrous diethyl ether to remove any residual 3-chlorobenzoic acid.

Before polymerization, the DXO was dried over CaH₂ at 40°C for at least 15 h and then distilled under reduced pressure on a standard vacuum/inert gas line.

Polymerization Procedure

The polymerizations were carried out in round-bottomed glass flasks (equipped with magnetic stirring bars) which had been carefully dried by flaming under reduced pressure (10⁻² mbar) and flushing with inert gas [N₂ or Ar (g)]. Solvent and ϵ -CL were introduced via glass syringes or stainless-steel capillaries (previously flamed under purge of inert gas) through rubber septums under a positive pressure of inert gas. DXO was weighed into a similarly dried round-bottomed flask inside a glove box (MBraun MB 150B-G-I, Germany) under strictly anhydrous conditions. The DXO was dissolved in the solvent before introduction into the polymerization vessel. The reaction was terminated by the addition of a molar excess of 0.5M HCl solution compared to the amount of initiator. The block copolymer was precipitated in cold hexane and dried under reduced pressure at ambient temperature to constant weight.

Coupling of Poly(ϵ -CL-*b*-DXO) Diblock Copolymers

Diblock copolymers were dissolved in CHCl₃ and the initiator residues were removed by two successive extractions with an aqueous solution of EDTA (0.1M) followed by repeated washing of the organic phase with water. The polymer was recovered by precipitation in heptane and finally dried under reduced pressure at room temperature until no change in weight was observed. To remove any further traces of water, the polymer was dissolved in dry toluene, which was subsequently removed by azeotropic distillation under reduced pressure (10⁻² mmHg). This drying procedure was carried out twice. The hydroxy functional poly(ϵ -CL-*b*-DXO) copolymer was weighed into a dry round-bottomed flask under strictly anhydrous conditions inside a glove box. All solutions were subsequently transferred by the previously mentioned capillary technique.

Coupling reactions using 1,4-phenylene diisocyanate were performed according to the following procedure: A THF solution of the diblock copolymer was heated to 50°C. A solution of diisocyanate and NEt₃ in THF (0.575 g and 1.0 mL, respectively, in 94 mL THF) was prepared. An exact quantity of this solution corresponding to 0.45 and 0.9 molar

equivalents (compared to the hydroxyl end group) of diisocyanate and triethylamine, respectively, was added to the polymer solution. After 6 h, the diisocyanate/triethylamine solution was again added, leading to a 5% molar excess of isocyanate groups and triethylamine. The reaction mixture was left under stirring for 15 h. The reaction was terminated by the addition of a molar excess of 0.5M HCl. The polymer was precipitated in cold hexane and dried under reduced pressure to constant weight.

Coupling reactions using $\text{Et}_2\text{Al}-\text{O}-\text{PDXO}-b\text{-PCL}$ were carried out according to the following procedure: To a THF solution of the $\text{PCL}-\text{PDXO}-\text{OH}$ diblock copolymer, a 10% molar excess of AlEt_3 (0.1M solution in toluene) compared to moles of hydroxyl end groups at 0°C was added. The ethane gas emitted was allowed to escape via an oil valve and the solution was left under stirring for 30 min to attain ambient temperature. A solution of diacid chloride and pyridine (0.5 g and 0.5 mL, respectively, in 50 mL THF) was prepared. An exact quantity of this solution, corresponding to 0.45 and 0.9 molar equivalents of diacid chloride and pyridine, respectively, was added to the $\text{Et}_2\text{Al}-\text{O}-\text{PDXO}-b\text{-PCL}$ solution. The reaction mixture was left under stirring for 15 h at 25°C and the reaction was then terminated by the addition of a molar excess of 0.5M HCl. The polymer was precipitated in cold hexane and dried under reduced pressure to constant weight.

Size-exclusion Chromatography (SEC)

SEC measurements were made at 30°C with three PLgel columns (5 μm , mixed C). A Waters Model 510 apparatus was used with a differential refractometer (Waters 410) as a detector and a WISP 712. THF was used as the solvent, with a flow rate of 0.5 mL/min. To record the data and make the calculations, a Copam PC-501 Turbo unit was used. Narrow MWD polystyrene standards were used for calibration. The universal calibration method was used for homo PCL since the related viscosimetric relationships were known.¹²

Light-scattering Measurements

Data on molecular weights estimated from light scattering were obtained by a Wyatt Technology Dawn-F laser photometer, operating at a wavelength of 632.8 nm and connected to the SEC apparatus. Wyatt Technology data acquisition and processing software (ASTRA 2.11) was used to calculate the molecular weights. The differential refractive index

increment (dn/dc) of DXO and $\epsilon\text{-CL}$ in THF (25°C) was determined to be 0.065 mL/g.

Differential Scanning Calorimetry (DSC)

DSC analysis was performed with a Perkin-Elmer DSC-7. The samples were heated to 80°C and then cooled at 20°C/min to -100°C. After 2 min equilibration, the heating scan was recorded at 10°C/min to 80°C. Perkin-Elmer 7 series standard software was used for processing and calculation of the glass transition temperatures.

Nuclear Magnetic Resonance Spectrometry (NMR)

¹H-NMR and ¹³C-NMR spectra were obtained with a Bruker AC-250 spectrometer using the solvent (CDCl_3) as an internal standard. Samples were dissolved in deuteriochloroform in sample tubes 5 mm in diameter. To calculate the conversion of samples taken during polymerization, integrals of peaks corresponding to DXO and the $\epsilon\text{-CL}$ monomer and polymer were compared. Assignment of peaks was reported earlier.¹⁰

Melt Pressing of Films

Melt pressing was performed in a Schwabenthan Polystat 400S hydraulic press (Schwabenthan, Germany). A mold with dimensions 70 × 70 × 0.5 mm was used. Approximately 3.2 g of copolymer was placed into the mold between two fiber-reinforced PTFE films. The material was pressed at 70–75°C, 100 bar for 3 min, with subsequent cooling under constant pressure at 10°C/min to room temperature. SEC measurements of some triblock copolymers made before and after one and two melt pressings indicated that the molecular weight decrease was less than 10% and that the MWD was not affected.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was performed on a Polymer Laboratories MK II instrument controlled by a Mylex MSL 486 personal computer. The measurements were made in the tensile mode with an approximate distance of 10 mm between the grips. Two different temperature programs were used: -150 to 55°C and -70 to 55°C at a rate of 2°C/min. The specimens were reclamped at the low temperature with a torque wrench set at 5 Ncm. A static force of 1.3 N was applied at approximately 8°C above the start temperature. The dynamic strain displacement was

chosen to be 16 μm peak-to-peak. All measurements were performed at 1 Hz. Three samples of each triblock copolymer were measured (except for the 10K/30K/10K copolymer, where one sample only was used at a scanning rate of 1°C/min).

Tensile Testing

Tensile testing was performed on an Instron 5566, equipped with a 2663 noncontacting video extensometer, a 3119-009 temperature chamber, and pneumatic grips, controlled by a Dell 466/ME personal computer. The tensile measurements were made with a crosshead speed of 150 mm/min and the cyclic loading was performed at 10 mm/min. The strain at break was calculated using grip separation due to the large elongation of the samples.

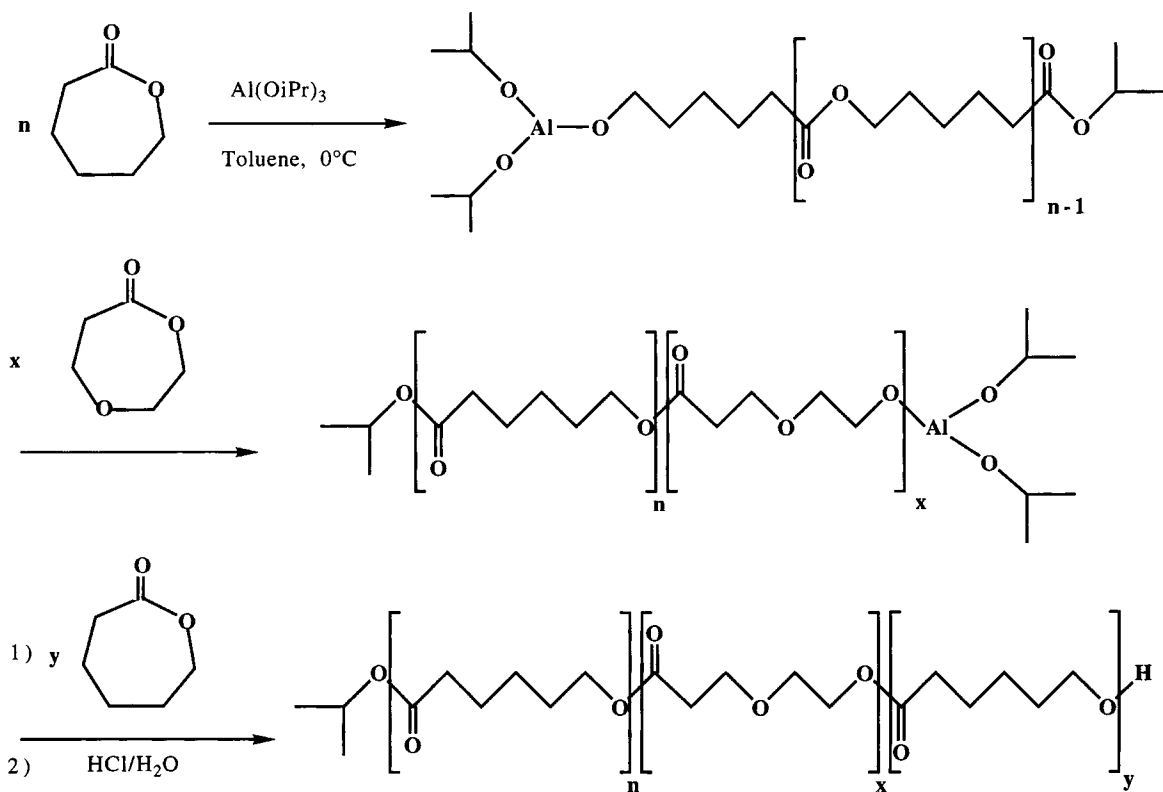
The measurements were made on preconditioned (48 h at $50 \pm 5\%$ RH and $23 \pm 1^\circ\text{C}$) samples according to ASTM D638V with a thickness of approximately 0.5 mm. Five samples, taken from the same melt-pressed film, were analyzed for each copolymer. In the cyclic loading experiment, only one sample was used.

Stress Relaxation

The stress-relaxation measurement was performed at 37°C with prior conditioning of samples as described above. The samples were mounted in a preheated temperature chamber and were allowed to equilibrate for 40 min prior to application of strain (7.0% elongation).

RESULTS AND DISCUSSION

Triblock copolymerizations of ϵ -CL and DXO were made using a sequential monomer addition according to Scheme 1. The results and conditions of triblock copolymerizations in this study are presented in Table I. In the following discussion, a poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymer with block lengths of *x* and *y* 1000 g/mol is called a (*x*K/*y*K/*x*K) copolymer. Thus, a triblock copolymer with PCL blocks of 10,000 g/mol and a PDXO block of 30,000 g/mol is abbreviated as a (10K/30K/10K) copolymer.



Scheme 1 General procedure to synthesize poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers.

Table I Triblock Copolymerization of ϵ -CL and DXO Initiated by Al(OⁱPr)₃

Sample	Solvent	Polymerization Temp (°C)		Conversion (%)	Polymerization Time (h)		$M_{n,th}$ ($\times 10^{-3}$) ^b (g/mol)	$M_{n,SEC}$ ($\times 10^{-3}$) ^d (g/mol)	$M_{n,real}$ ^e (g/mol)	$M_{n,LS}$ ^f (g/mol)	MWD
		A/B/A ^a	A/B/A ^a		A/B/A ^a	A/B/A ^a					
1	Toluene	0/0/0	0/0/0	> 99/> 99/37	2.5/2.5/2.0	10/20/24	16/27/32	8,100	—	1.18/1.15/1.18	
2	THF	0/0/0	0/0/0	> 99/> 99/15	3.0/5.5/16.5	20/40/43	32/40/44	17,500	—	1.13/1.15/1.20	
3 ^g	THF	0/25/25	0/25/25	> 99/93/96	2.0/14/21	10/38/50	17/30/51	8,900	40,000	1.13/1.15/1.15	
4 ^g	THF	0/25/25	0/25/25	> 99/95/98	1.3/17/25	10/39/50	22/42/64	11,700	55,000	1.10/1.15/1.15	
5 ^g	THF	0/25/25	0/25/25	> 99/96/62	2.0/117/17	15/63/73	28/60/68	17,700	—	1.10/1.20/1.20	
6 ^g	Toluene	0/25/25	0/25/25	> 99/97/> 99	2.0/36.5/7.0	15/64/80	29/65/90	16,000	66,300	1.10/1.20/1.25	
7 ^g	Toluene	0/25/25	0/25/25	> 99/96/> 99	1.5/17/16.5	15/82/100	26/73/87	13,700	91,300	1.10/1.25/1.30	
8	Toluene ^h	0/25/25	0/25/25	> 99/96/98	1.5/21/5.0	15/63/80	26/67/77	14,100	63,000	1.10/1.25/1.30	
9 ^g	Toluene ^h	0/25/25	0/25/25	> 99/98/> 99	1.1/17.5/5.5	15/64/80	26/68/79	14,300	79,500	1.10/1.25/1.30	

^a A/B/A corresponds to data from first, second, and third monomer addition, respectively.

^b Theoretical molecular weight = $([M]/[I]) MM_x$, where $[M]/[I]$ = monomer-to-initiator molar ratio, MM = molecular weight of the monomer, and x = monomer conversion.

^c mono/di/tri corresponds to data from 1st PCL block, PCL/PDXO diblock, and PCL/PDXO/PCL triblock, respectively.

^d Molecular weights measured by SEC (calibration with PS standards).

^e Absolute M_n (PCL) obtained by universal calibration.

^f Absolute M_n of triblock copolymer obtained by $M_{w,LS}/MWD$, where $M_{w,LS}$ is the weight-average molecular weight obtained by light-scattering measurements and $MWD = M_w/M_n$.

^g Addition of 1 molar equivalent pyridine compared to amount of initiator.

^h Toluene distilled over polystyryl-Li under reduced pressure before use.

Polymerization kinetics

Earlier studies^{11,13} have shown that the polymerization of both ϵ -CL and DXO initiated by $\text{Al}(\text{O}^i\text{Pr})_3$ follows first-order kinetics with respect to the monomer and initiator, with a rate equation of the general formula $R_p = k[M][I]$, where R_p is the propagation rate and k the absolute rate constant equal to $5.7 \text{ L min}^{-1} \text{ mol}^{-1}$ at 0°C in THF for DXO and $36.6 \text{ L min}^{-1} \text{ mol}^{-1}$ at 0°C in toluene for ϵ -CL. In a separate study¹⁴ of the DXO homopolymerization to high molecular weight in THF, it was shown that this rate constant was not valid at high molecular weight polymerizations ($M_n > 30,000 \text{ g/mol}$), probably because of the strong influence of traces of water on the polymerization kinetics. At high molecular weight, if no elaborate purification of all the components was made, the amount of water present in the system might be comparable to the amount of initiator. Traces of water led to a dramatic drop in the polymerization rate and this was also observed in these block copolymerizations.

As seen in Table I, the monomer conversion of the first PCL block was always quantitative. With the second and especially the third addition of monomer, the same situation became possible only if the DXO was dried carefully over CaH_2 . After subsequent distillation, full conversion of all three sequential additions was obtained with molecular weights exceeding 30,000–40,000 g/mol. To improve

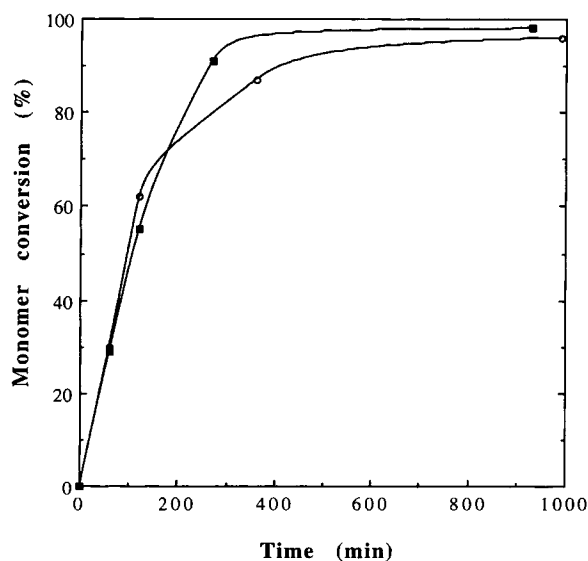


Figure 1 Monomer (DXO) conversion of second block vs. polymerization time (closed squares) with and (open circles) without 1 equivalent of pyridine.

the kinetic situation, the polymerizations of the second and third blocks were conducted at 25°C in contrast to the first block, which was polymerized at 0°C to obtain as narrow an MWD as possible.

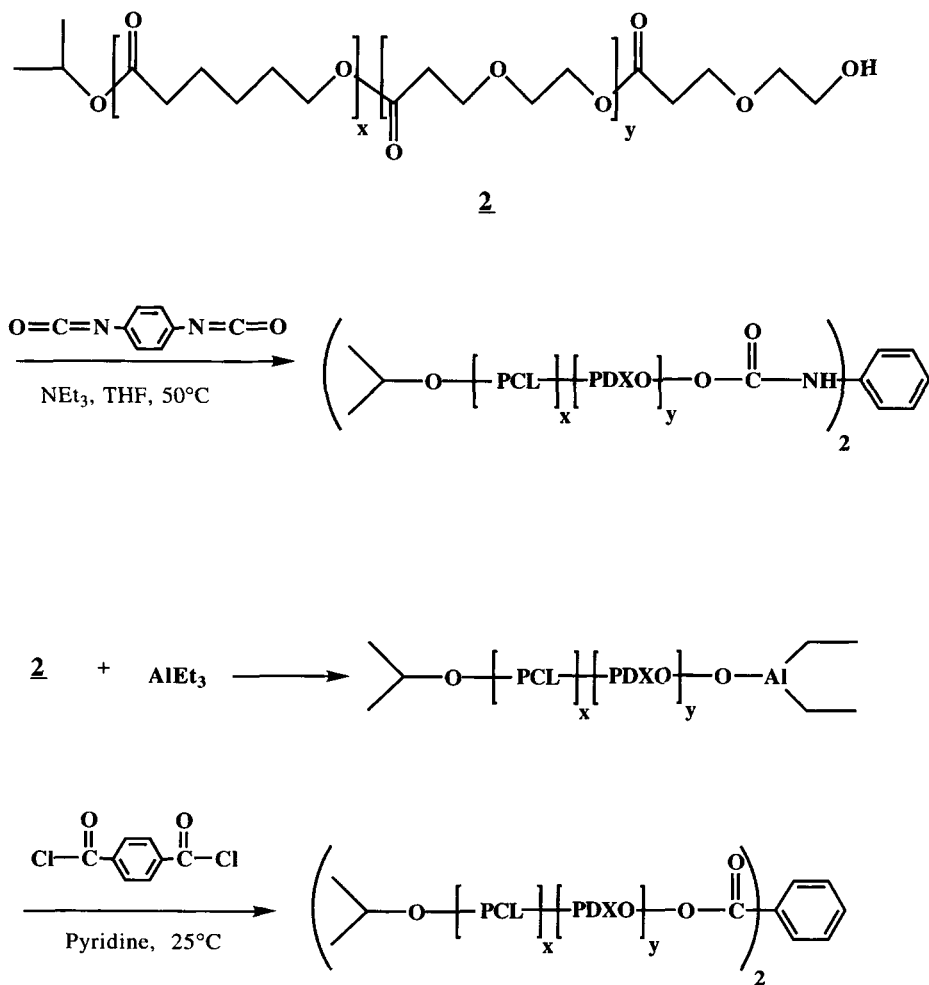
Influence of Lewis Base Addition

Dubois et al. investigated the effect of Lewis base addition (pyridine) on the polymerization of ϵ -CL, initiated by aluminum monoalkoxides in toluene.¹⁵ A twofold effect was reported: first, an acceleration of the polymerization kinetics and, second, a decrease in transesterification reactions, leading to a more narrow MWD. It was suggested that the Lewis base coordinated specifically to the Al atom, thus increasing the ionic character of the Al—O bond. This would lead to a more reactive initiating species and an accelerated polymerization rate. The decrease in rate of transesterification was explained by the steric effect of the more bulky nature of the initiator/Lewis base aggregate than of the Al monoalkoxide alone.¹⁵

In the first experiments to accelerate the polymerization kinetics of the ϵ -CL/DXO triblock copolymerization by adding pyridine, no significant effect was observed. A similar observation was made with regard to the homopolymerization of DXO under the same conditions.¹⁴ This was attributed to the generally more ionic character of the Al—O bonds in $\text{Al}(\text{O}^i\text{Pr})_3$ than in the Al—O bond in Et_2AlOR . In addition, the polar character of THF presumably results in a competing coordination of pyridine and solvent to the Al atom, thus decreasing the effect of the pyridine. When THF is replaced by toluene, a less polar solvent, a slight increase in polymerization rate was observed after the addition of 1 molar equivalent of pyridine with respect to the amount of $\text{Al}(\text{O}^i\text{Pr})_3$, especially in the later stages of the polymerization. An example of monomer conversion during the DXO block formation with and without the addition of pyridine is given in Figure 1.

Side Reactions

It is well known that intra- and intermolecular transesterification reactions occur in many ring-opening polymerizations. This also occurs in polymerizations initiated by Al alkoxides, although the influence of these side reactions can be minimized by polymerization at low temperatures and by termination of the living polymer solution as soon as full conversion has been obtained.



Scheme 2 Synthetic pathways to poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers using coupling reagents.

The triblock copolymerizations driven to high molecular weights show a broader MWD, which indicates an onset of transesterification reactions. No evidence of intramolecular “backbiting” reactions could, however, be detected by SEC measurements on the crude polymer.

Intermolecular transesterifications may lead to a mixing of initially pure blocks in the copolymer. This should be detected by, e.g., ^{13}C -NMR, which can distinguish mixed dyads of ϵ -CL and DXO from homodyad peaks. In ^{13}C -NMR spectra taken from some high molecular weight triblock copolymers, no such peaks could, however, be seen. Thus, the relatively higher value of the MWD (1.30–1.35) shown by the high molecular weight samples did not seem to induce mixing of monomer sequences to any great extent.

Use of Difunctional Coupling Reagents

An alternative method for the synthesis of poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers is to react a poly(ϵ -CL-*b*-DXO) diblock copolymer containing a hydroxyl functional chain end onto a difunctional core molecule, such as a diisocyanate, or an aluminum monoalkoxide functionalized diblock copolymer onto terephthaloylchloride (Scheme 2). This approach has been reported by Dubois et al. in the synthesis of, e.g., telechelic polyesters.¹⁶

In our preliminary experiments, however, only limited coupling efficiencies were obtained even though relatively low molecular weight poly(ϵ -CL-*b*-DXO) diblock copolymers were used (block lengths 5000–10,000 g/mol). This is possibly due to traces of water left in the diblock copolymer, which can be

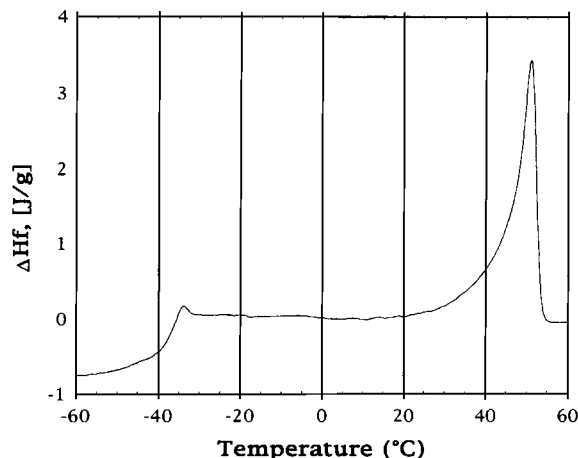


Figure 2 DSC thermogram of PCL/PDXO/PCL (15K/50K/15K) triblock copolymer.

difficult to remove. This alternative method of producing poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers must be considered less important at least when high molecular weight materials are required.

Thermal Properties

Differential scanning calorimetry (DSC) measurements of the triblock copolymers showed one glass transition and one melting peak, corresponding to the PDXO block and PCL blocks, respectively (Fig. 2). Some data relating to the thermal properties are listed in Table II.

In an earlier study,¹¹ a more detailed investigation of the glass transition region was made on a PCL/PDXO diblock copolymer (65/35 mol %). This revealed two separate glass transitions in close proximity: a large transition at -39°C corresponding to the PDXO block and a smaller one at -56°C corresponding to the amorphous fraction of the PCL block.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) measurements of the diblock copolymer discussed above indicate two separate transitions, one small at a low temperature and one large at a higher temperature (Fig. 3). DMTA of triblock copolymers, however, does not exhibit the same features: Only one transition can be detected. This may be an effect of the relatively low amount of PCL in the triblock copolymers compared to that in diblock copolymer (35 vs. 65 mol % PCL, respectively), making it dif-

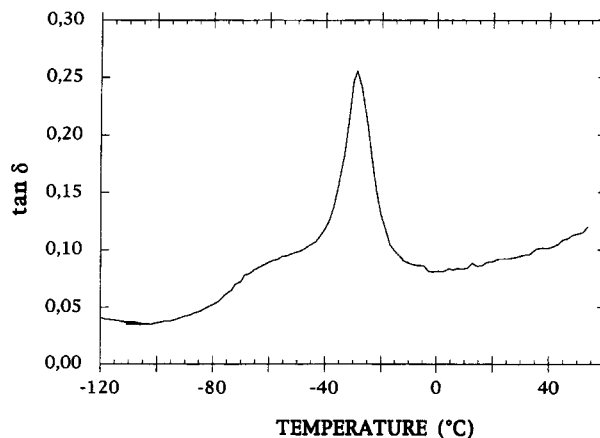


Figure 3 DMTA plot of a PCL/PDXO diblock copolymer (65/35 mol %) showing two separate transitions.

icult to observe the small transition originating from the PCL amorphous phase.

Table III shows the results of the DMTA. The storage modulus, E' , is considerably higher for the samples with lower amounts of PDXO. Mean values of the loss modulus (E'') and loss tangent ($\tan \delta$) peak temperatures show higher values with an increasing relative amount of PCL, as expected. The $\tan \delta$ peak values decrease with an increasing amount of PCL.

Figure 4 shows E' and $\tan \delta$ for PCL/PDXO/PCL triblock copolymers of different block lengths. All exhibit a single, sharp $\tan \delta$ peak, and with increasing block length of PDXO, the peak value of $\tan \delta$ increases. This is indicative of a greater relaxation strength,¹⁷ which indicates that a larger fraction of less constrained chains can participate in the relaxation. A decrease in PDXO block length gives less mobile chain segments, which, consequently, decreases the relaxation strength. A possible explanation could be that an increase in the length of the PDXO blocks gives a larger fraction of chain segments which are less constrained by PCL crystallinity.

Table II Thermal Properties of PCL/PDXO/PCL Triblock Copolymers

PCL/PDXO Molar Ratio (%)	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH (J/g)
38/62	-40.0	50.7	22.5
30/70	-36.9	51.0	22.1

Table III Data from DMTA Measurements of PCL/PDXO/PCL Triblock Copolymers; Standard Deviation in Parentheses

Block Lengths A/B/A (g/mol)	10K/30K/10K ^a	15K/50K/15K	15K/70K/15K
Storage modulus at 23°C (MPa)	110	70 (9.1)	23 (12.4)
Loss modulus peak value (MPa)	220	260 (12.4)	285 (11.7)
Loss modulus peak (°C)	-30.8	-31.2 (2.7)	-31.7 (2.9)
Loss tangent peak (°C)	-28.1	-27.9 (2.6)	-27.6 (2.1)
Loss tangent peak value	0.43	0.51 (0.02)	0.84 (0.14)

^a Single measurement at 1°/min.

The fact that the $\tan \delta$ peak temperature for the triblock copolymer lies between that of pure PCL[†] and that which could be expected for pure PDXO suggests that segments from both polymers participate in the glass transition. The increase in peak temperatures for $\tan \delta$ and E'' with increasing PDXO block length is probably due to a greater influence of the higher T_g corresponding to PDXO, which indicates that PDXO influences the unordered region to some extent.

All three materials in Table III exhibit subglass transitions illustrated for 10K/30K/10K in Figure 5. The 15K/70K/15K and 10K/30K/10K copoly-

mers exhibit what appears to be two separate relaxations at approximately -120 and -85°C. The 15K/50K/15K copolymer show two weaker transitions or possibly one broader transition in the same temperature range.

Tensile Properties

The results of tensile tests on the 15K/50K/15K and 15K/70K/15K copolymers are given in Table IV. More detailed information concerning the elastomeric properties of the materials is obtained by hysteresis testing.

The tensile modulus and stress at yield are higher for the 15K/50K/15K copolymer than for the 15K/70K/15K copolymer. The elongation at yield and break are slightly higher for the 15K/70K/15K co-

[†] Unpublished measurements (PCL: $M_n = 91900$; $M_w = 163,000$).

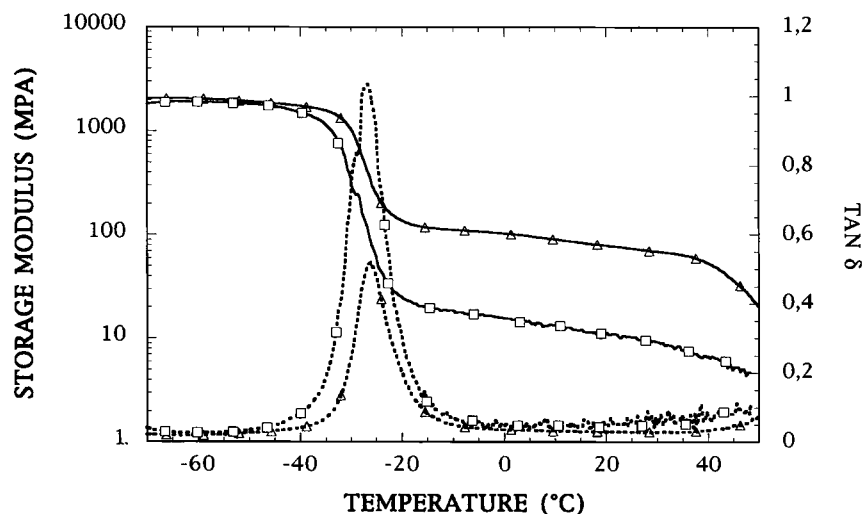


Figure 4 Storage modulus, E' , and loss tangent, $\tan \delta$, for the (open triangles) 15K/50K/15K and (open squares) 15K/70K/15K triblock copolymers.

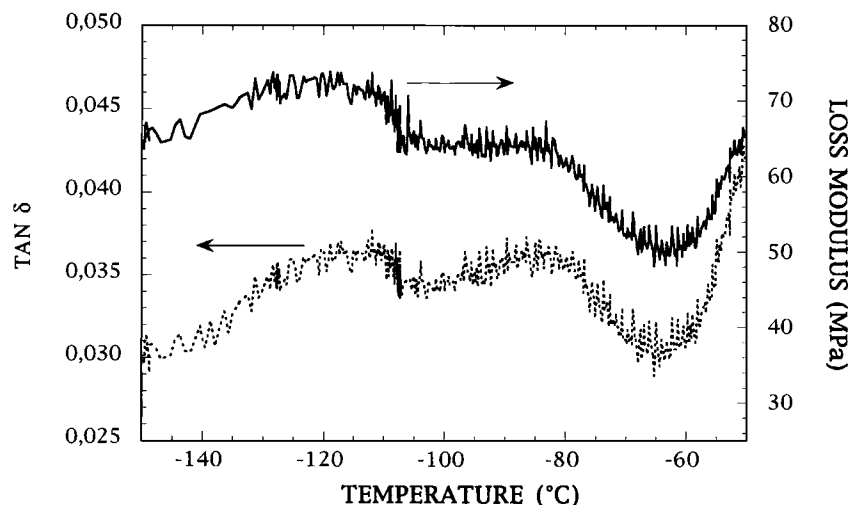


Figure 5 Loss modulus, E'' , and loss tangent, $\tan \delta$, for the 10K/30K/10K triblock copolymer at temperatures below the glass transition.

polymer than for the 15K/50K/15K copolymer. Both materials show strain-hardening effects and exhibit about the same strength at break. This behavior is probably due to the influence of the PCL, which makes the material more rigid as a consequence of its ability to crystallize and thereby reach a high degree of orientation. It is interesting that the strength at break seems to be unaffected by the length of the PDXO blocks.

The elastic properties of these materials are demonstrated in Figure 6, which shows the 15K/70K/15K copolymer strained to a grip separation of 10, 50, 100, 150, and 200% and thereafter allowed to recover after each cycle. The tensile set is about 85% after cycling to approximately 290% elongation. The

15K/50K/15K copolymer exhibits the same behavior, but with a slightly higher set per cycle, 3–5%.

Stress Relaxation

To study whether there is any difference in the time dependence of the properties of these materials, stress-relaxation measurements were carried out. The samples were strained to 7% elongation at 37°C.

The level of stress was higher for the 15K/50K/15K copolymer than for the 15K/70K/15K copolymer, as is illustrated in Figure 7. This is an effect of the more rigid behavior of the material which contains less PDXO. Table V shows that the material which contains more PDXO relaxes more

Table IV Tensile Properties of PCL/PDXO/PCL Triblock Copolymers; Standard Deviation in Parentheses

Block Lengths A/B/A (g/mol)	15K/50K/15K		15K/70K/15K	
Tensile modulus (MPa)	31	(8.8)	21	(4.2)
Stress at yield (MPa)	3.0	(0.4)	2.1	(0.1)
Elongation at yield (%)	15	(4.3)	18	(0.4)
Strength at break (MPa)	52	(6.7)	53	(3.0)
Elongation at break (%)	1070	(50)	1210	(67)

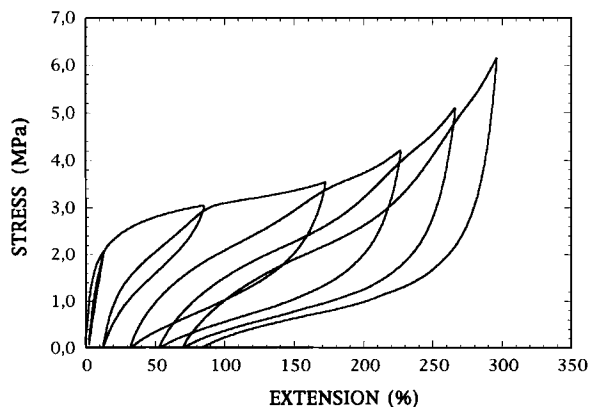


Figure 6 Hysteresis of the 15K/70K/15K triblock copolymer.

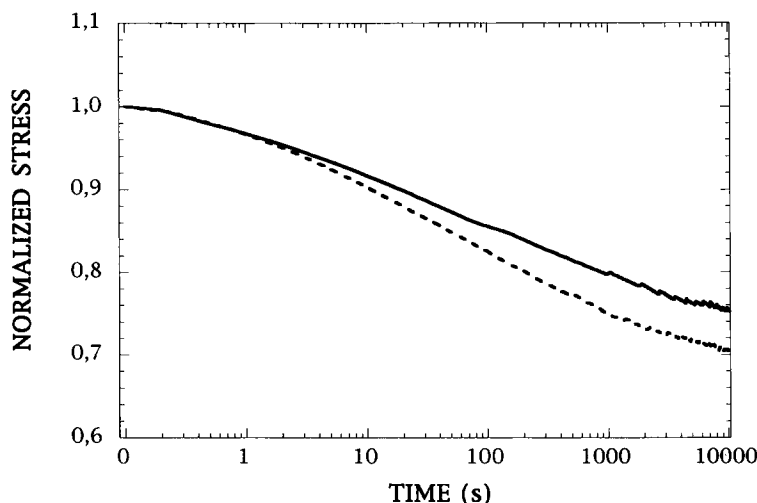


Figure 7 Comparison of the normalized stress relaxation of the (continuous line) 15K/50K/15K and (broken line) 15K/70K/15K triblock copolymers at 7.0% elongation.

rapidly, probably due to the higher fraction of less constrained chain segments.

CONCLUSIONS

Poly(ϵ -CL-*b*-DXO-*b*- ϵ -CL) triblock copolymers of high molecular weight are readily synthesized by sequential monomer addition to a living polymer, in toluene or THF solution, initiated by aluminum isopropoxide at 0–25°C. The addition of a Lewis base such as pyridine does not significantly alter the polymerization rate measured in THF. In toluene, a small increase in polymerization rate is observed especially in the later stages of the polymerization. No significant change in MWD was observed when pyridine was added. The most favorable conditions experienced so far are to carry out the polymerization in toluene solution with the addition of 1 molar equivalent of pyridine with respect to amount of Al(OⁱPr)₃. The first PCL block should be polymer-

ized at 0°C and the following two blocks at 25°C, in order to increase the polymerization rate.

A small broadening of the MWD in the block copolymers with the highest molecular weight indicates that transesterification reactions occur although not to any greater extent. Mechanical measurements reveal that the materials exhibit elastomeric properties which are dependent on block length. High tensile modulus, strength at break, and elongation at break characterize these materials as well as a high permanent set. This new type of biodegradable thermoplastic elastomer is an example of the great versatility offered to the synthetic polymer chemist using living ROP.

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Table V Stress Relaxation Data of PCL/PDXO/PCL Triblock Copolymers

Block Lengths A/B/A (g/mol)	Relaxed Modulus ^a /Initial Modulus
15K/70K/15K	70%
15K/50K/15K	75%

^a Measured after 10⁴ s.

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