Synthesis and Characterization of Biodegradable Homopolymers and Block Copolymers Based on 1,5-Dioxepan-2-one

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ABSTRACT: Homopolymers of 1,5-dioxepan-2-one (DXO) and block copolymers of DXO and ϵ-caprolactone (ϵ-CL) have been synthesized with aluminum isopropoxide as an initiator in toluene and tetrahydrofuran (THF). The homopolymerization is first order with respect to both monomer and initiator, and the end-group analysis agrees with a coordination insertion mechanism based on the acyl–oxygen cleavage of the DXO ring. Living poly(ϵ-caprolactone) (PCL) and poly(1,5-dioxepan-2-one) (PDXO) chains are very efficient macroinitiators for the polymerization of DXO and ϵ-CL, respectively, with formation of block copolymers of a narrow molecular weight distribution. Size-exclusion chromatography (SEC) and ^{13}C NMR confirm the blocky structure of the copolymers, in agreement with DSC that shows a melting endotherm for the PCL block and two glass transitions characteristic of the amorphous phases of PDXO and PCL. Because of the crystallinity of the PCL block (T_m = 60 °C) and the low glass transition temperature of the amorphous PDXO block (T_g = −39 °C), poly(ϵ-CL-*b*-DXO-*b*-ϵ-CL) triblocks have the potential of thermoplastic elastomers. Block copolymers of ϵ-CL and DXO are also sensitive to hydrolysis which makes them possible candidates for biomedical applications. Initiation of the DXO polymerization with functional diethylaluminum alkoxides is also discussed.

Introduction

For a number of years, A.-C. Albertsson and collaborators have investigated different ways of polymerizing 1,5-dioxepan-2-one (DXO).[1-3] The homopolymer of DXO is an amorphous material with a low glass transition temperature (T_g) of approximately −36 °C. This polymer undergoes hydrolysis in vitro[3] and is therefore a possible candidate in the design of bioabsorbable materials. Copolymerization has been investigated as one route to modify and improve the usually poor mechanical properties of poly(DXO) at and above T_g.[2] Statistical copolymers of DXO with, e.g., lactides have shown interesting properties on degradation rates and stiffness which could be easily varied.[2]

The scientific literature reports on the synthesis of bioabsorbable block copolymers either from prepolymers[4,5] or by a sequential living polymerization technique.[6,7] The latter method, which, however, requires more elaborate working conditions, gives a much better molecular control and possibilities of tailoring the final product. So, it has been shown that, e.g., ϵ-caprolactone (ϵ-CL) and lactide can be polymerized with aluminum alkoxides as initiators in a controlled way to yield high molecular weight block copolymers with a narrow molecular weight distribution (MWD).[7] Statistical copolymers of DXO and ϵ-CL have also been synthesized in bulk with stannous octoate as an initiator.[8,9] This paper deals with the polymerization of DXO initiated with various aluminum alkoxides and the synthesis and characterization of new bioabsorbable block copolymers made from DXO and ϵ-CL. A special attention will be paid to triblocks consisting of a soft inner poly(DXO) block associated with outer semicrystalline poly(ϵ-caprolactone) (PCL) blocks of a high strength. These triblock copolymers should yield original biodegradable thermoplastic elastomers that might have interesting potentialities in the biomedical field.

Experimental Section

Materials. Synthesis of 1,5-dioxepan-2-one (DXO) was described elsewhere.[1] Prior to polymerization, DXO was dried by azeotropic distillation of toluene under reduced pressure (10^{-2} mmHg) and then recrystallized twice from dry diethyl ether. The ϵ-CL (Janssen, Belgium) was dried over CaH_2 (Aldrich, Germany) for 48 h and then distilled under reduced pressure before use. Aluminum triisopropoxide (Aldrich, Germany) 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 according to the following procedure: 1 mL of the initiator solution was added to 20 mL of H_2O and 0.5 mL of 2 M HCl. The mixture was heated until a clear solution was obtained. A total of 25 mL of EDTA (0.1 M) was added, and the solution was heated to 100 °C during a period of 10 min. Acetic acid sodium salt was added to buffer the solution at a pH of 4.8 using a standard pH meter. The excess EDTA was titrated with a 0.1 M solution of $ZnSO_4$, using xylenol orange sodium salt as an indicator. The change in color from yellow to pink was used. The mean value of three samples was used to calculate the concentration of the $Al(O^iPr)_3$ solution.

The 2-bromoethanol (Aldrich, Germany) was washed with a saturated aqueous solution of sodium carbonate, dried over P_2O_5, and distilled under reduced pressure before use. Triethylaluminum (Fluka, Switzerland) was used as received and dissolved in dry toluene, and the solution concentration was determined by complexometric titration of Al with EDTA.

Pyridine, toluene, and THF were dried by refluxing over KOH, CaH_2, and a sodium benzophenone complex, respectively, and distilled in a nitrogen atmosphere right before use.

Preparation of the Initiator. Diethylaluminum 2-bromoethoxide was prepared by reaction of triethylaluminum in toluene with 1 mol equiv of dry bromoethanol. The alcohol was slowly added dropwise to the stirred triethylaluminum solution in a previously flame-dried glass reactor, purged with nitrogen, and

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chilled in an acetone/CO_2(s) bath. The reactor was fitted to an oil valve so that the ethane formed as a reaction byproduct could escape. The solution was allowed to attain room temperature and left under stirring for an extra 3 h.

Polymerization Procedure. DXO and ϵ-CL were polymerized in toluene or THF under stirring, in a previously flamed and nitrogen-purged glass reactor. DXO was charged into the reactor in a glovebox, under a nitrogen atmosphere. Solvent and ϵ-CL were then added to the reactor through a rubber septum using stainless steel capillaries or syringes.

The initial monomer concentration was consistently at 1 mol/L. Polymerization was stopped by adding a 3-fold molar excess (compared to the amount of initiator used) of HCl (0.5 M solution). Initiator residues were removed by two successive extractions with an aqueous solution of EDTA (0.1 M) 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.

Esterification of PDXO-OH. A poly(DXO) solution in dry THF was added consecutively with a 5-fold molar excess of acetic anhydride, with triethylamine, and finally with a catalytic amount of 4-(dimethylamino)pyridine (DMAP; 0.2 equiv). The solution was kept under stirring for 24 h at 50 °C. The polymer was precipitated in cold diethyl ether and dried under reduced pressure.

Characterization. A size-exclusion chromatograph HP 1090 (Hewlett Packard, U.S.A.) was used to analyze the molecular weight distribution and to estimate the molecular weight of homo- and copolymers. The apparatus operated in THF at 25 °C and was calibrated with polystyrene standards. The universal calibration method was used for homoPCL since the related viscosimetric relationships were known.[10] The molecular weight of short-length homopolymers ($M_n < 15\,000$) was also calculated by ^{1}H NMR from the relative intensity of signals of the isopropyl ester end group and the methylene groups of the ester subunits. From the overall composition of the diblock copolymers (^{1}H NMR) and M_n of the first polymerized block (SEC and/or ^{1}H NMR), the molecular weight of the second block was calculated. The knowledge of composition of the intermediate diblock and final triblock together with the molecular weight of the first block allowed the molecular weights of the second and third blocks to be calculated.

Copolymer composition and monomer conversion were analyzed by ^{1}H NMR. Spectra were recorded in $CDCl_3$ at 25 °C with a Bruker AM400 apparatus (Bruker, Germany). The same apparatus was used to record ^{13}C-NMR spectra of the copolymers.

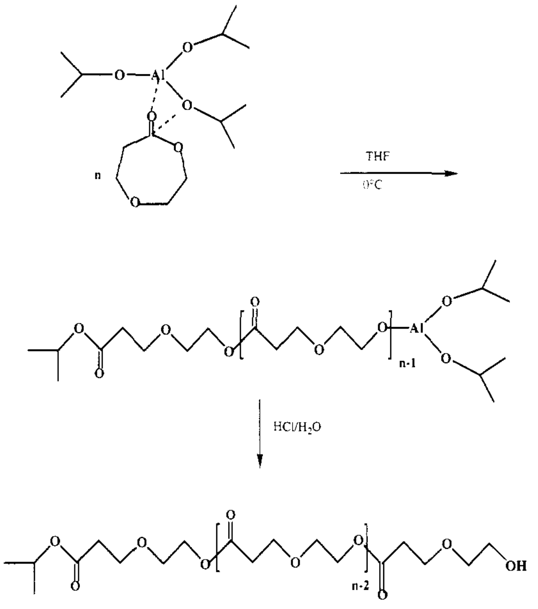
Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC-7 (Perkin-Elmer, U.S.A.), equipped with a Perkin-Elmer 7700 computer and calibrated with an indium standard (T_{onset} = 156.6 °C and ΔH_f = 28.45 J/g^{-1}). The melting temperature was measured after cooling the sample down to −70 °C and heating it up to +100 °C. The glass transition temperature was measured the same way except for a premelting at 100 °C for 5 min. The heating and cooling rates were 20 °C min^{-1}.

Infrared spectroscopy was performed with a Perkin-Elmer 1725X FT-IR spectrometer (Perkin-Elmer, U.S.A.).

Results and Discussion

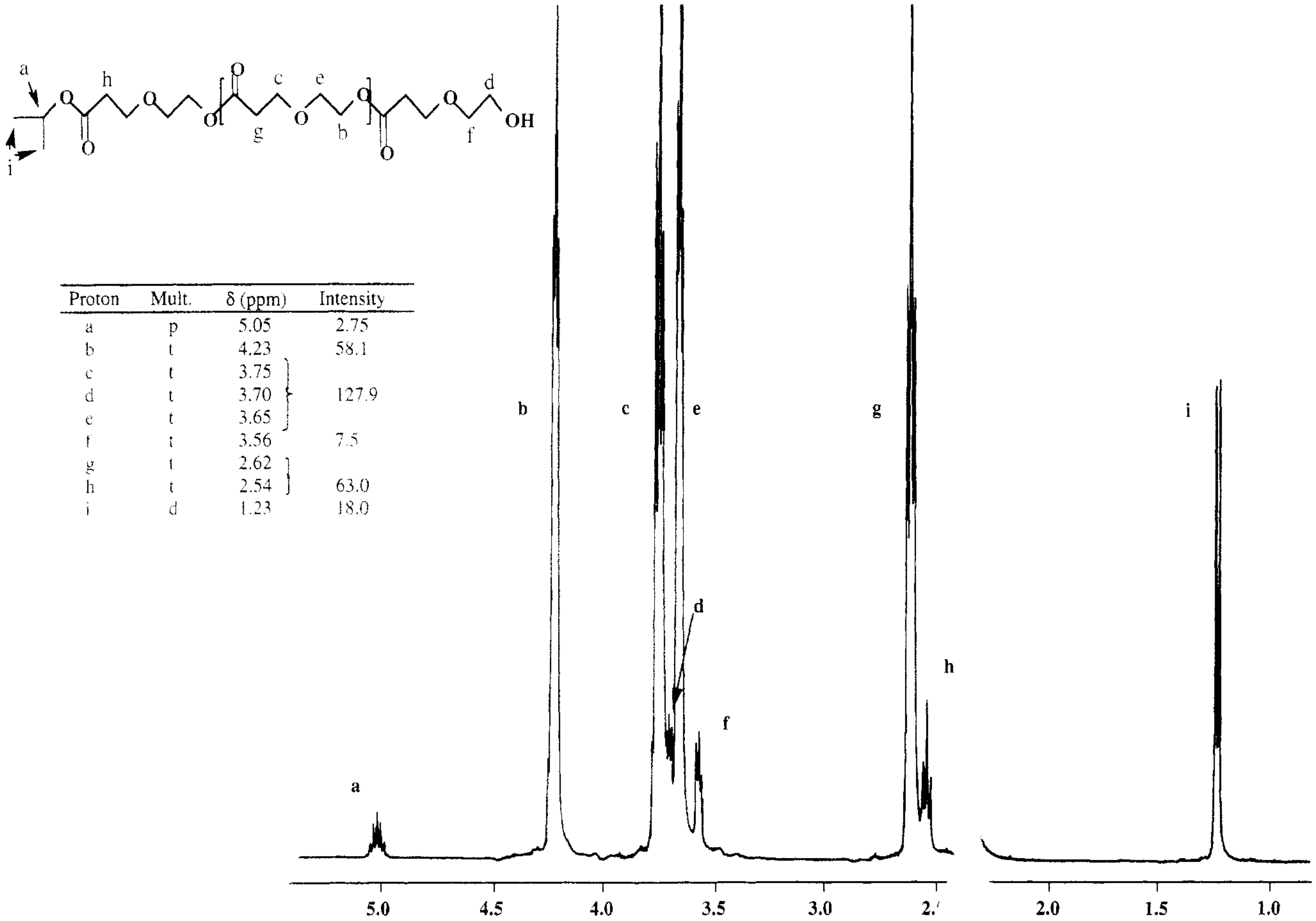
Homopolymerization of DXO with Aluminum Isopropoxide. To the best knowledge of these authors, it is the first time that polymerization of DXO is initiated with an aluminum alkoxide, and particularly with aluminum isopropoxide in solution. Polymerization has been first conducted in toluene, but, because of the limited solubility of poly(DXO) in this solvent, THF has ultimately been used. Structural similarities of DXO and ϵ-CL led us to believe that polymerization of DXO might proceed by a mechanism similar to that known for ϵ-CL, i.e., a coordination–insertion mechanism.[11] ^{1}H-NMR analysis of the end groups of low molecular weight poly(DXO) initiated with $Al(O^iPr)_3$ confirms this hypothesis. Indeed $Al(O^iPr)_3$ coordinates to the exocyclic carbonyl oxygen, and the acyl–oxygen cleavage yields an isopropyl ester end group, observed as a multiplet at 5.05 ppm ($-C(O)OCH(CH_3)_2$) together with a doublet at 1.23 ppm ($-OCH(CH_3)_2$) in a 1:6 ratio (Figure 1). Termination of the growing poly(DXO) chains with dilute HCl transforms the second end group, i.e., an aluminum alkoxide, into a hydroxyl group. The methylene protons (H_d) of this CH_2OH end group are barely observed as a triplet at 3.70 ppm between two characteristic resonance peaks of the polymer. In contrast, the signal of the $-CH_2CH_2OH$ protons (H_f) is well resolved at 3.57 ppm (Figure 1). In order to assess the peak assignment, the hydroxyl end group of poly(DXO) has been esterified with an excess of acetic anhydride with formation of an acetate end group. After polymer purification, ^{1}H NMR shows the complete disappearance of the H_d and H_f peaks in favor of the H_b and H_e peaks, respectively. Furthermore, a new sharp singlet at 2.07 ppm emerges, which is characteristic of the $-OCOCH_3$ protons. By analogy with ϵ-CL, the DXO polymerization mechanism is shown in Scheme 1.

Scheme 1



Living Character of the Polymerization. The linear relationship between the number-average degree of polymerization ($\overline{DP}_n$) and the monomer to initiator molar ratio ([M]/[I]), shown in Figure 2, indicates a living polymerization under the experimental conditions of this study. Furthermore, the molecular weight distribution (MWD) of the poly(DXO) is narrow (1.03–1.16), in agreement with a fast initiation compared to propagation. Earlier studies[10] have shown that an increase in temperature and/or a longer polymerization time have a deleterious effect on the living polyaddition of ϵ-CL. Therefore, the effect of these parameters on the DXO polymerization has been considered. A poly(DXO) of $\bar{M}_n$ = 17 500 has been prepared in THF at 0 °C. When the monomer conversion has been ascertained to be complete by ^{1}H NMR, the living polymer solution has been allowed to reach room temperature and kept under stirring for 95 h. In the meantime, samples have regularly been withdrawn and the polymer has been characterized by SEC and ^{1}H-NMR spectrometry.

The number-average molecular weight ($\bar{M}_n$) remains essentially unchanged for the whole period of time, although the MWDs increase very quickly, as shown in Figure 3. No oligomer is formed, at least according to SEC, which indicates that the broadening of the MWD more likely results from intermolecular transesterification



Proton	Mult.	δ (ppm)	Intensity
a	p	5.05	2.75
b	t	4.23	58.1
c	t	3.75	127.9
d	t	3.70	
e	t	3.65	
f	t	3.56	7.5
g	t	2.62	63.0
h	t	2.54	
i	d	1.23	18.0

Figure 1. ^{1}H-NMR spectrum of α-isopropyl ester–ω-hydroxypoly(1,5-dioxepan-2-one), in $CDCl_3$ ($\bar{M}_n$ = 1350).

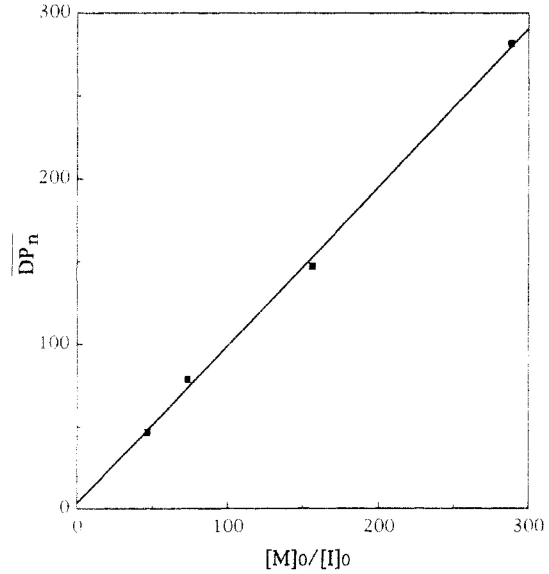


Figure 2. Degree of polymerization ($\overline{DP}_n$) as a function of the monomer/initiator ([M]/[I]) molar ratio for the DXO polymerization initiated with $Al(O^iPr)_3$ in THF at 0 °C.

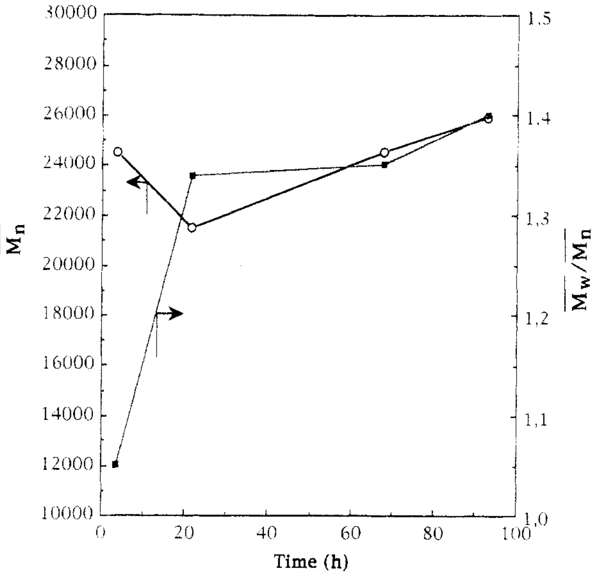


Figure 3. Time dependence of the number-average molecular weight ($\bar{M}_n$) and the molecular weight distribution (MWD) when a solution of living PDXO chains is kept at 25 °C.

reactions. Therefore, all the subsequent polymerization experiments have been conducted at 0 °C.

Number of Active Sites. From the slope of the linear relationship between the degree of polymerization ($\overline{DP}_n$) and the monomer/initiator molar ratio ([M]/[I]) (Figure 2), it appears that only one of the three potentially active sites in $Al(O^iPr)_3$ participates in the initiation process. This behavior is exactly the same as that observed when ε-CL is polymerized with $Al(O^iPr)_3$.[11] It has been accounted for by the solvation of the initiator with the monomer in solution.[12] Indeed, $Al(O^iPr)_3$ is aggregated as tetramer and/or trimer in solution.[13] Upon the monomer addition (ε-CL), the aggregates are dissociated and the individual $Al(O^iPr)_3$ molecules are solvated with an average of three monomers in such a way that all the Al–OR bonds are not equivalent in terms of electronic and steric environment and that only one of the three OR groups is active in the polymerization process.[14] Nevertheless, when the ε-CL polymerization is initiated with $Al(O^iPr)_3$ in the presence of a dissociating agent, all three isopropoxy groups of the initiator contribute to the monomer conversion.[7] DXO would accordingly have the

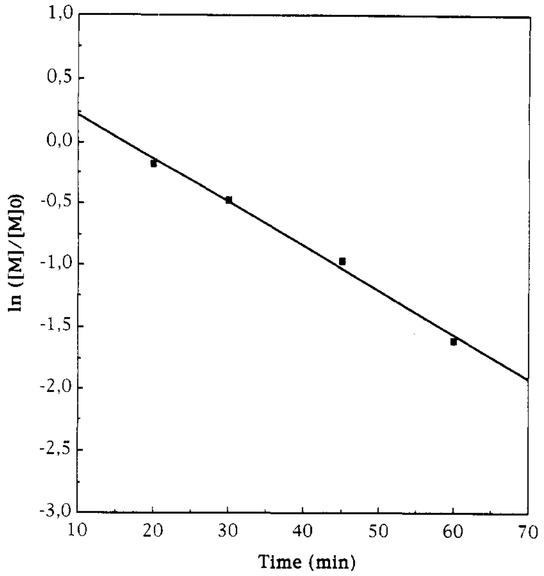


Figure 4. Linear dependence of the monomer consumption on the polymerization time. $[M]_0$ = initial monomer concentration, and [M] = monomer concentration at time *t*.

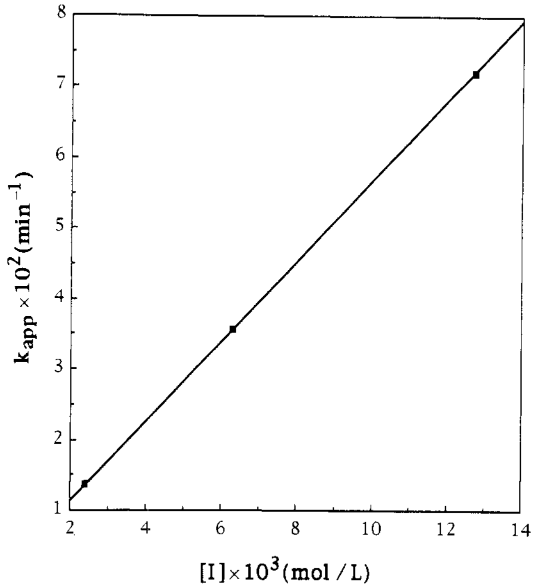


Figure 5. Linear dependence of the apparent rate constant (k_{app}) on the initiator concentration ([I]).

same effect as ϵ-CL on the solution behavior of the $Al(O^iPr)_3$.

Kinetics of the Polymerization. The kinetics of the DXO polymerization has been studied in THF at 0 °C. Figure 4 shows a linear relationship between monomer consumption and time which is in agreement with a living polymerization of a first order in monomer. The same kinetic feature has previously been reported for the ϵ-CL polymerization initiated with $Al(O^iPr)_3$.[15] An induction period of ca. 5–15 min is observed when monomer and initiator are mixed together, so that the straight line does not go through the origin of the $\ln([M]/[M]_0)$ vs time plot. This induction period actually corresponds to the time required for the dissociation of the $Al(O^iPr)_3$ aggregates.[16]

A linear relationship is also observed when the apparent rate constant ($k_{app} = (\ln[M]/[M]_0)/t$, min^{-1}) is plotted as a function of the initiator concentration ([I]) (Figure 5); thus, the DXO polymerization is first order with respect to the initiator. As a rule, the kinetics of this polymerization obeys the following equation: $R_p = k[M][I]$, where R_p is the propagation rate and k the absolute rate constant equal to 5.65 L min^{-1} mol^{-1} (Table 1). This equation is the same as that for the ϵ-CL and lactide (LA) polymerization in toluene at 0 and 70 °C, respectively. k values are then 36.6 L mol^{-1} min^{-1} for ϵ-CL[10] and 0.6 L mol^{-1} min^{-1} for LA.[15]

Table 1. Kinetic Data for the DXO Polymerization Initiated with $Al(O^iPr)_3$ in THF at 0 °C ($[M]_0$ = 1 mol/L)

[M]/[I]	$\bar{M}_n$	k_{app} (min^{-1}) × 10^3	k_{app}/[I] (L min^{-1} mol^{-1})
77	9 000	72.0	5.65
156	18 000	35.7	5.70
293	34 000	13.6	5.65

Table 2. Data Characteristic of the DXO Polymerization Initiated with $Br(CH_2)_2OAlEt_2$ ([M]/[I] = 86)

solvent	temp (°C)	polym time (h)	conv (%)	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	k_{app} (min^{-1})
THF	25	120	35	5 000	1.55	5.3×10^{-5}
THF	40	120	96	12 000	1.95[b]	2.4×10^{-4}
	40[c]	48	80	12 500	1.25	5.6×10^{-4}
toluene	70	20	100	9 500	1.75[b]	3.2×10^{-3}

[a] Molecular weight as measured by SEC (calibration with PS standard). [b] Formation of oligomers. [c] Addition of pyridine (1 equiv with respect to Al).

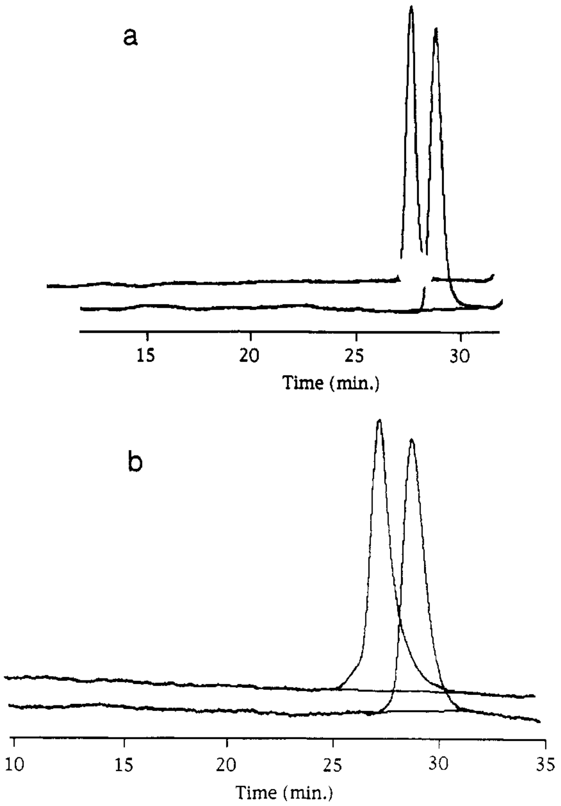
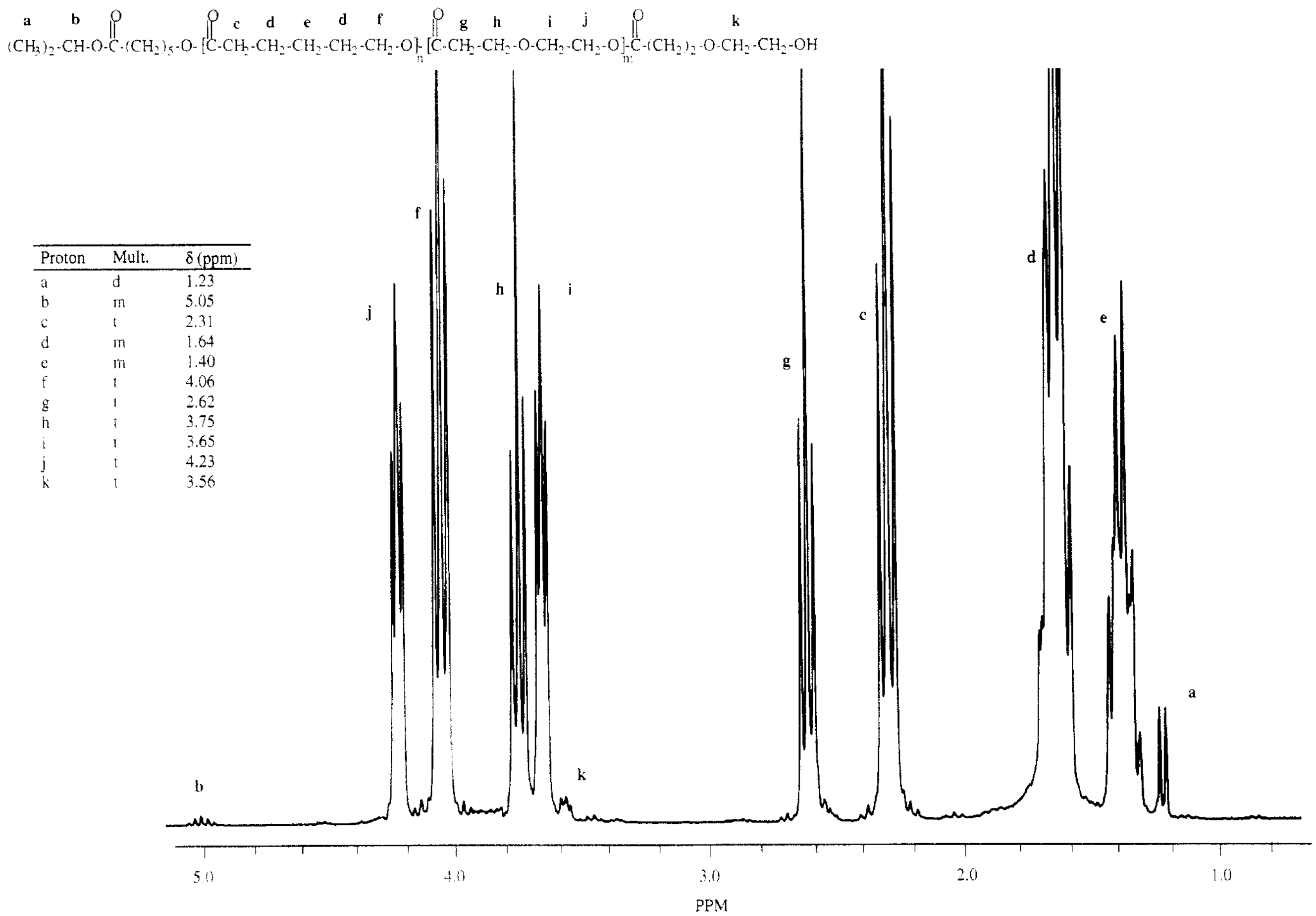


Figure 6. (a) SEC chromatogram of the PCL block (lower curve) and the poly(ϵ-CL-*b*-DXO) copolymer (upper curve). $M_{n,PCL}$ = 5400; wt % PCL = 53%. (b) SEC chromatogram of the PDXO block (lower curve) and the poly(DXO-*b*-ϵ-CL) copolymer (upper curve). $M_{n,PDXO}$ = 5500; wt % PDXO = 57%.

Polymerization of DXO with Dialkylaluminum Alkoxides. The homopolymerization of DXO with a functional dialkylaluminum alkoxide has been investigated. It is worth recalling that this type of initiator (Et_2AlOCH_2X with X = $-CH_2Br$, $-(CH_2)_2-CH{=}CH_2$, or $-CH_2C(O)OC(CH_3){=}CH_2$) is less reactive than the trialkoxide counterparts ($Al(OCH_2X)_3$) in agreement with a much slower polymerization, as reported for ϵ-CL.[17] These dialkylaluminum functional alkoxides have the advantage of leading to the formation of α-functional polyesters.[17]



Proton	Mult.	δ (ppm)
a	d	1.23
b	m	5.05
c	t	2.31
d	m	1.64
e	m	1.40
f	t	4.06
g	t	2.62
h	t	3.75
i	t	3.65
j	t	4.23
k	t	3.56

Figure 7. ^{1}H-NMR spectrum of a poly(ϵ-CL-*b*-DXO) copolymer in $CDCl_3$. $M_{n,PCL}$ = 5400; wt % PCL = 53%.

Table 3. Diblock Copolymerization Initiated with $Al(O^iPr)_3$ in THF or Toluene at 0 °C

block copolyester	polym time (h)	conv (%)	$\bar{M}_n$ theor[c]	$\bar{M}_n$ ^{1}H NMR	$\bar{M}_n$ SEC[d]	$\bar{M}_w/\bar{M}_n$
PCL[a]	2.5	>99	5300	4900	10 500[e]	1.03
PCL/PDXO	2.0	95	5300/5200	4900/5400	21 000	1.02
PDXO[b]	1.5	>99	4500	5500	8 500	1.10
PDXO/PCL	3.0	>99	4500/4500	5500/4200	16 000	1.15

[a] In toluene. [b] In THF. [c] Theoretical molecular weight = ([M]/[I])MMx, where [M]/[I] = monomer to initiator molar ratio, MM = molecular weight of the monomer, and x = monomer conversion. [d] Molecular weights measured by SEC (calibration with PS standards). [e] Absolute $M_{n,PCL}$ = 5400 (universal calibration).

Table 4. DSC Data for PCL and Poly(ϵ-CL-*b*-DXO)

sample	ϵ-CL (mol %)	$M_{n,SEC}$	$\bar{M}_w/\bar{M}_n$	$T_{m,peak}$ (°C)	ΔH_f (J/g)	T_g (°C)
PCL[a]	100	66 000	1.55	57.5	61.5	−65
P(ϵ-CL-*b*-DXO)	63	43 500	1.20	59.0	40.5	−55 and −40

[a] PCL (Union Carbide; tone polymer 767E).

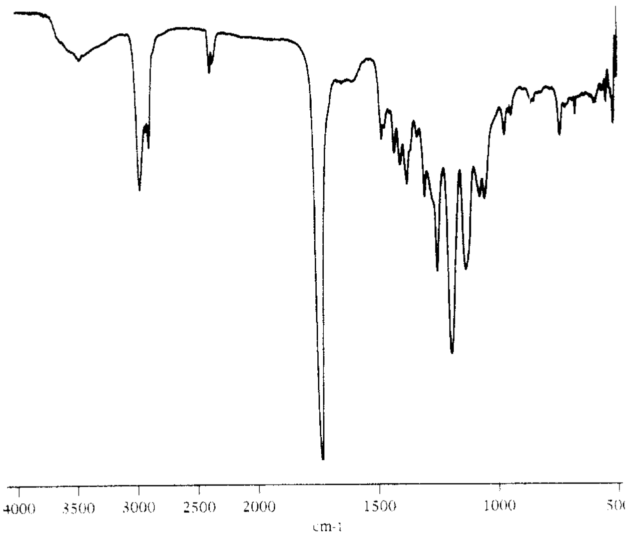


Figure 8. FTIR spectrum of a poly(ϵ-CL-*b*-DXO) copolymer. Film: $M_{n,PCL}$ = 5400; wt % PCL = 53%.

We can also visualize an alternative pathway for the synthesis of an ABA triblock copolymer. This is the polymerization of monomer B with a difunctional initiator (e.g., $Et_2AlO(CH_2)_4OAlEt_2$) followed by addition of monomer A. This method is thus more attractive since it is a two-step synthesis compared to the method of sequential monomer addition where three steps are necessary.

$Et_2AlO(CH_2)_2Br$ has been prepared and used to initiate the DXO polymerization in THF and toluene at different temperatures. Conditions and results are summarized in Table 2.

The apparent rate constants expectedly show that the polymerization rate is slower by a factor of ca. 10^3 at 25 °C compared to polymerization with $Al(O^iPr)_3$ at 0 °C. Increasing the polymerization temperature up to 40 and 70 °C, respectively, results in an increased polymerization rate. However, the MWD becomes broader as the temperature is increased, and at 70 °C an oligomer formation is clearly observed by SEC. Obviously, side reactions of an inter- and intramolecular nature occur at higher temperatures. As discussed elsewhere the oligomer formation at 70 °C is due to an intramolecular backbiting reaction, whereas the broader MWD is the result of intermolecular transesterification reactions.[15] In agreement with observations previously reported by some of us,[18] addition of 1 equiv of pyridine with respect to Al is able not only to increase the apparent propagation rate

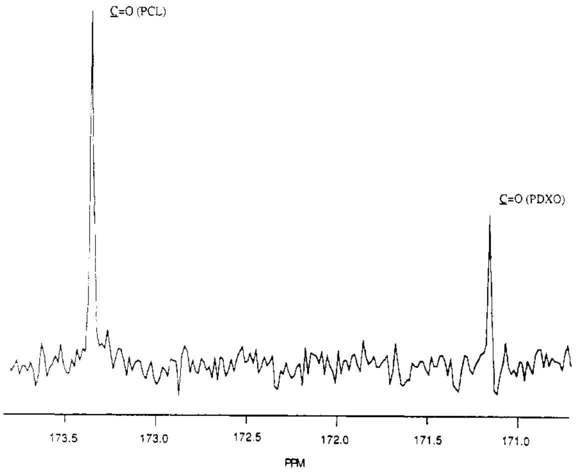


Figure 9. ^{13}C-NMR spectrum of a poly(ϵ-CL-*b*-DXO) copolymer in $CDCl_3$. $M_{n,PCL}$ = 5400; wt % PCL = 53%.

but also to prevent the occurrence of transesterification reactions, as shown by a rather narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.25) compared to the value observed in the absence of pyridine (1.95), while all other conditions are the same. Controlled ring-opening polymerization of DXO promoted by diethylaluminum monoalkoxide in the presence of a Lewis base is currently under investigation.

Diblock Copolymerization of DXO and ϵ-CL. With the synthesis of the poly(ϵ-CL-*b*-DXO-*b*-ϵ-CL) triblocks in view, it is essential to start the sequential addition with ϵ-CL and to ascertain that living PCL chains can initiate the DXO polymerization and vice versa for poly(DXO) chains with respect to ϵ-CL. For this purpose, diblock copolymers have been prepared with either living PDXO or living PCL chains as macroinitiators. Parts a and b of Figure 6 compare the SEC chromatograms of the first block and the final diblock copolymer when ϵ-CL is first polymerized (Figure 6a) and for the reverse situation (Figure 6b). MWD of the first block is narrow and does not change significantly upon the second monomer conversion. In a parallel way, the molecular weight of the macroinitiators is shifted toward higher values, in close agreement with the theoretical value. Results and conditions for the diblock copolymerization are reported in Table 3.

Figures 7 and 8 show the ^{1}H-NMR and IR spectra of a typical poly(ϵ-CL-*b*-DXO) diblock copolymer. In order to assess that the copolymerization product is a pure diblock, i.e., that no transesterification has occurred between the PDXO and PCL blocks, a ^{13}C-NMR spectrum has been recorded. Transesterification reactions should result in mixed sequences, easily detected as an additional resonance in between the homodiad peaks in the carbonyl region. Figure 9 confirms the absence of new intermediate peaks in this region; only the two homodiad peaks are observed at the chemical shifts characteristic of each homopolymer (171.2 ppm for PDXO and 173.3 ppm for PCL, respectively).

The DSC thermogram of a poly(ϵ-CL-*b*-DXO) containing 63 mol % ϵ-CL shows a melting endotherm for the crystalline PCL block (Figure 10a). Figure 10b emphasizes two glass transitions (T_g) in close proximity to each other. The experimental thermal data are listed in Table 4. T_g of the PCL block in the copolymer is higher than that of the PCL homopolymer. Conversely, T_g of the PDXO block is slightly lower than that of the PDXO homopolymer (T_g ≈ −36 °C). The moving closer of the two glass transitions might be indicative of some miscibility of the amorphous phases of PCL and PDXO at least in the copolymer and the molecular weight range under consideration.

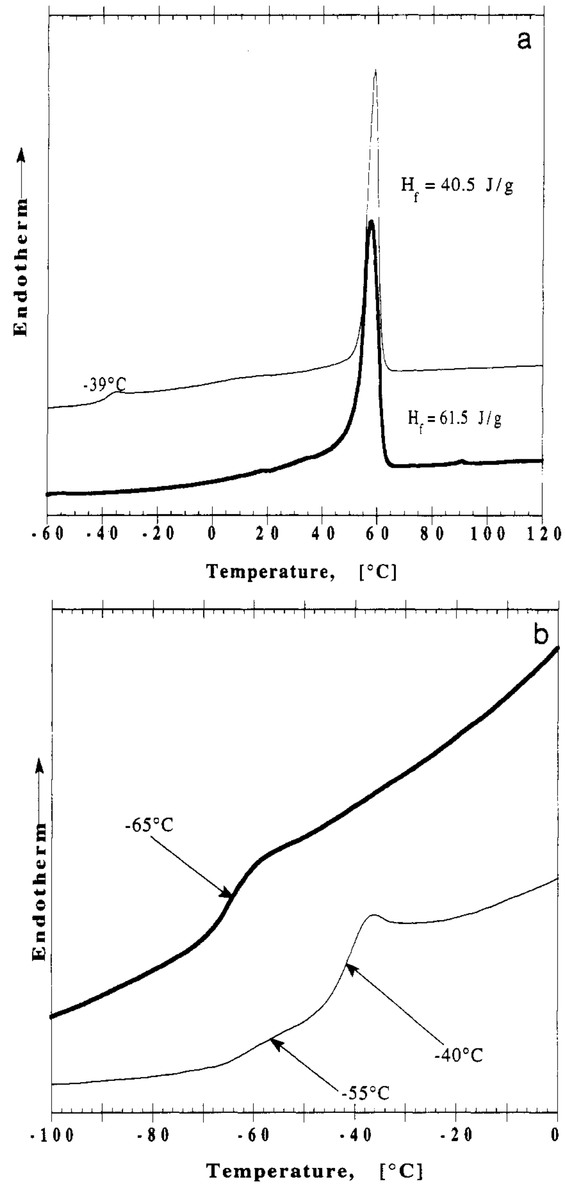


Figure 10. (a) DSC thermogram of a poly(ϵ-CL-*b*-DXO) copolymer [$M_{n,PCL}$ = 18 000; wt % PCL = 63% (upper curve)] a PCL homopolymer [$M_{n,PCL}$ = 38 300 (lower curve)] (first heating). (b) DSC thermogram of a poly(ϵ-CL-*b*-DXO) copolymer [$M_{n,PCL}$ = 18 000; wt % PCL = 63% (lower curve)] and a PCL homopolymer [$M_{n,PCL}$ = 38 300 (upper curve)] in the glass transition region (second heating run).

Triblock Copolymerization of DXO and ϵ-CL. Synthesis of triblock copolymers of ϵ-CL and DXO has been successful. According to Table 5 (first entry), it is clear that the purification of the monomers is of the utmost importance for the third polymerization step to reach completion. When DXO is purified as reported elsewhere,[1] no living polymerization is observed. The purification method reported in the Experimental Section, allows for the DXO polymerization to be living. Nevertheless, when conversion of the last PCL block and sometimes of the middle PDXO block happens to be incomplete, the presence of hydroxyl impurities in the DXO monomer might be suspected. Further studies are currently under investigation in order to further improve the purification procedure. Polydispersity of the triblock copolymers is relatively narrow, and no homopolymer formation can be detected by SEC. This observation is of course in good agreement with results reported in Table 3, according to which each monomer can be quantitatively initiated with living chains of the second comonomer. Experimental data

Table 5. Triblock Copolymerization Initiated with Al(O^{i}Pr)$_3$ in Toluene at 0 °C

block copolyesters	polym time (h)	conv (%)	$\bar{M}_n$ theor[a]	$\bar{M}_n$ ^{1}H NMR	$\bar{M}_n$ SEC[b]	$\bar{M}_w/\bar{M}_n$
PCL block	2.5	>99	8200	8100	15 500[c]	1.18
PCL/PDXO	2.5	99	8200/9000	8100/8300	26 500	1.15
PCL/PDXO/PCL	2.0	37	8200/9000/3400	8100/8300/3600	31 500	1.18
PCL block	1.0	>99	5500	5500	10 500[d]	1.15
PCL/PDXO	1.0	98	5500/6100	5500/5300	16 500	1.20
PCL/PDXO/PCL	3.3	90	5500/6100/5000	5500/5300/4100	26 000	1.21

[a] Theoretical molecular weight = ([M]/[I])MMx, where [M]/[I] = monomer to initiator molar ratio, MM = molecular weight of the monomer, and x = monomer conversion. [b] Molecular weight measured by SEC (calibration with PS standard). [c] Absolute $M_{n,PCL}$ = 8100 (universal calibration). [d] Absolute $M_{n,PCL}$ = 5500.

for the triblock copolymerization are reported in Table 5.

Conclusions

Homopolymerization of 1,5-dioxepan-2-one (DXO) initiated with aluminum isopropoxide in THF at 0 °C yields a polymer of a predictable molecular weight and a narrow MWD. Polymerization proceeds through a coordination–insertion mechanism with selective cleavage of the acyl–oxygen bond of the monomer. Kinetics is first order with respect to both the monomer and the initiator, with an absolute rate constant of 5.5 L mol^{-1} min^{-1}.

Transesterification reactions are responsible for the broadening of the MWD when a solution of living chains is kept at room temperature for 20 h and more.

Polymerization of DXO with a dialkylaluminum alkoxide is markedly slower compared to polymerization initiated with Al(O^{i}Pr)$_3$. Side reactions also broaden the MWD, and backbiting reactions with formation of oligomers occur at higher temperatures (70 °C).

Block copolymers have successfully been synthesized in THF at 0 °C with Al(O^{i}Pr)$_3$ as an initiator. Monomers A (ϵ-CL) and B (DXO) have sequentially been polymerized, so that AB, BA, and ABA block copolymers have been prepared. It is worth noting that a careful purification of DXO is required for conversion of the monomer (DXO) and the comonomer (ϵ-CL) to be complete. ^{13}C NMR and SEC have confirmed the absence of side reactions and the actual formation of the expected block copolymers. DSC thermograms of block copolymers show the melting point of PCL and the glass transition of the amorphous PCL and PDXO phases. A more detailed analysis of these multiphase block copolymers is under current investigation.

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References and Notes

(1) Mathisen, T.; Masus, K.; Albertsson, A.-C. *Macromolecules* **1989**, *22*, 3842.

(2) Albertsson, A.-C.; Löfgren, A. *Makromol. Chem., Macromol. Symp.* **1992**, *53*, 221.

(3) Albertsson, A.-C.; Palmgren, R. *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30* (12), 919.

(4) Deng, X. M.; Xiong, C. D.; Cheng, L. M.; Xu, R. P. *J. Polym. Sci., Part C* **1990**, *28*, 411.

(5) Cohn, D.; Younes, H. *J. Biomed. Mater. Res.* **1988**, *22*, 993.

(6) Kurcok, P.; Penczek, J.; Franek, J.; Jedlinski, Z. *Macromolecules* **1992**, *25* (9), 2285.

(7) Jacobs, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24* (11), 3027.

(8) Shalaby, S. W. (Ethicon Inc.). U.S. Patent 4 190 720, 1980; *Chem. Abstr.* **1980**, *93*, 73629s.

(9) Shalaby, S. W.; Kafrawy, A. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 4423.

(10) Heushen, J.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 242.

(11) Ouhadi, T.; Stevens, C.; Teyssié, Ph. *Makromol. Chem.* **1975**, Suppl. 1, 191.

(12) Ropson, N.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph., submitted to *Macromolecules*.

(13) Ropson, N.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 6378.

(14) Ropson, N.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph.; Parente, V.; Bredas, J. L., to be published.

(15) Dubois, Ph.; Jacobs, C.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 2266.

(16) Ropson, N.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph., submitted to *Macromolecules*.

(17) Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 103.

(18) Dubois, Ph.; Barakat, I.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1993**, *26*, 4407.