Macromolecular Engineering of Polylactones and Polylactides. 12. Study of the Depolymerization Reactions of Poly(ε-caprolactone) with Functional Aluminum Alkoxide End Groups

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ABSTRACT: Ring-opening polymerization of ε-caprolactone has been initiated with functional aluminum alkoxides in toluene at 25 °C. Degradation of "living" polyester chains by transesterification reactions has been studied in relation to temperature, solvent polarity, average molecular weight, and structure of the initiator, i.e., the nature of the functional group and the number of alkoxides per Al atom. Degradation products, particularly cyclic oligomers, have been isolated by supercritical fluid extraction (SFE) and characterized by GC-MS. The effect of Lewis bases on transesterification reactions has been investigated and discussed in reference to the "coordination-insertion" mechanism.

Introduction

The significance of ring-opening polymerization has been recognized since the early days of polymer science, and there have been an ever increasing number of fundamental studies devoted to various cyclic monomers such as oxiranes, thiiranes, lactams, and lactones.[1] With respect to lactones, attention has been drawn to ε-caprolactone (CL), which is readily available from petrochemical sources and easily converted into high molecular weight chains by organometallic catalysts.[2] Interest in poly(ε-caprolactone) (PCL) has also been motivated by its appealing properties, i.e., its biodegradability, biocompatibility, and unusual compatibility with a series of polymeric materials.[3]

Recent publications have focused on the synthesis of the functional aluminum alkoxides $Et_{3-p}Al[O(CH_2)_2X]_p$.[4,5] Halogen (X = Br), tertiary amine (CH_2NEt_2), carbon-carbon double bond ($CH_2CH{=}CH_2$), and methacrylic unsaturation ($CH_2OC(O)C(CH_3){=}CH_2$) are typical examples of X functional groups. Aluminum alkoxides rank among the best initiators of the ε-caprolactone polymerization.[4-7] They indeed ensure a perfect control of molecular weight and nature of the end groups (*HO*-PCL-*X*).

The thermal and chemical stability of polymers is of critical importance for practical uses. Moreover, knowledge of the degradation pathways may be most helpful in predicting the behavior of polymers exposed to various conditions. The thermal stability of poly(ε-caprolactone) has already been investigated.[3,8] For instance, a paper from this laboratory has reported on the dependence of thermal stability on catalyst residues, hydroxyl end-groups, and molecular oxygen.[9]

It is well-known that competitive degradation reactions occur in the course of the anionic ring-opening polymerization of CL.[10,11] These reactions are responsible for a decrease in the apparent rate of monomer conversion and for an increasing polymolecularity of PCL versus time. Degradation reactions are, however, not observed when the CL polymerization is initiated by aluminum alkoxides at 0 or 25 °C. Indeed, linear polyester chains are obtained with a molecular weight in very close agreement with the monomer to initiator molar ratio, at least within the time required for complete (CL) conversion. Nevertheless, molecular weight distribution is substantially broadened when the living chains are left in the reaction medium beyond the time required for complete monomer conversion.

To prevent any deleterious effect of degradation reactions, it is essential to clear up their mechanism. This is the reason why attention has been paid to conditions under which side reactions occur in the course and beyond the propagation step. The ultimate goal is to identify the most efficient conditions for circumventing any degradation of PCL and to extend these conditions to the controlled synthesis of more sensitive aliphatic polyesters such as polylactide and polyglycolide.

Experimental Section

Reagents. CL (Janssen Chimica) was dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. Triethylaluminum (TEA, Fluka) was used without further purification and dissolved in dry toluene. Diisobutylaluminum hydride in toluene (DIBAL-H, 1.0 M) was purchased from Aldrich and used without further purification. Aluminum triisopropoxide (Aldrich) was purified by distillation under reduced pressure and dissolved in dry toluene. The concentration of the catalyst solutions was determined by complexometric titration of Al by EDTA. 2-Bromoethanol (Aldrich) was washed with a saturated aqueous sodium carbonate solution, dried over P_2O_5, and distilled under reduced pressure. 4-Penten-1-ol (Aldrich) was dried over calcium hydride and distilled under reduced pressure. Pyridine, toluene, and tetrahydrofuran (THF) were dried by refluxing over KOH, CaH_2, and a benzophenone-Na complex, respectively.

Initiators. Dialkylaluminum alkoxides were prepared by slowly adding a toluene solution of the selected alcohol into a flask containing an equimolar amount of TEA or DIBAL-H. The glass reactor was equipped with a rubber septum connected to a gas buret through an oil valve. It was previously flamed and purged with nitrogen. The reaction proceeded under nitrogen and under vigorous stirring at room temperature. When the formation of ethane or hydrogen stopped, the catalyst solution was kept stirred at room temperature for an extra hour. Diethylaluminum alkoxide initiators were distilled just before used.

The synthesis of aluminum trialkoxides relied upon the reaction of $Al(O^iPr)_3$ with 3 equiv of the appropriate alcohol in a carefully dried and nitrogen-purged distillation apparatus. The toluene/2-propanol azeotrope was distilled off continuously.

Polymerization Procedure. Polymerization took place under stirring, in toluene or THF at 25 °C, in a previously flamed and nitrogen-purged glass reactor. Solvent, CL, and initiator were successively added through a rubber septum with a syringe or a stainless steel capillary. The usual polymerization temperature was 25 °C. Samples of a well-known volume were picked out of the reaction medium after different periods of time, hydrolyzed, and precipitated in cold *n*-heptane. After filtration

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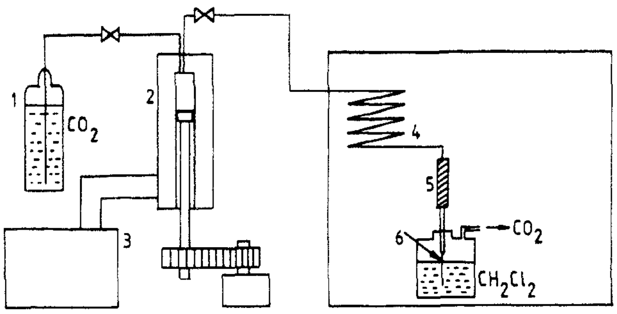


Figure 1. Schematic representation of the SFE apparatus. Components: 1, carbon dioxide cylinder; 2, high-pressure pump; 3, dry ice cooler; 4, column (length = 150 mm, diameter = 5 mm); 5, extractor containing the crude polymer; 6, restrictor plunging in CH_2Cl_2.

and drying under vacuum to a constant weight, PCL samples were weighed and analyzed by size exclusion chromatography (SEC) and ^{1}H-NMR.

Characterization. ^{1}H-NMR spectra of PCL were recorded in $CDCl_3$ using a Bruker AM 400 apparatus. SEC was performed in tetrahydrofuran at 30 °C using a Hewlett-Packard 1090 liquid chromatograph equipped with a HP 1037 A refractive index detector and four columns of various pore sizes (10^5, 10^3, 500, and 100 Å). Molecular weight and molecular weight distribution were calculated by reference to a calibration curve based on polystyrene standards. The universal calibration method was applied for PCL using the following viscosimetric relationship:[12] $M_{PCL} = 0.259 M_{PSt}^{1.073}$.

Oligomer Extraction and Identification. Oligomers present in the crude polymerization products were isolated by supercritical fluid extraction (SFE).[13,14] A modified HPLC was used for this purpose, with supercritical CO_2 as the mobile phase at 250 bar and 50 °C. The experimental device is schematized in Figure 1. Liquid CO_2 was compressed by a high-pressure pump (Varian 8500) and injected in the extractor through a thermostated column at 50 °C. Under these conditions, PCL oligomers were dissolved in the supercritical fluid and extracted from the crude polymer (~500 mg). A restrictor allowed for CO_2 expansion, and oligomers were trapped in CH_2Cl_2.

Oligomeric fractions were analyzed by ^{1}H-NMR and gas chromatography in combination with mass spectrometry (GC–MS, Hewlett-Packard 59872 C apparatus). The GC was equipped with an OV1 column (25 m; internal diameter: 250 μm) and a fid detector (T_d = 350 °C). Samples were directly injected into the column at a low temperature (40–60 °C), and hydrogen was used as the mobile phase.

Results and Discussion

Aluminum alkoxides have proved to be very effective in promoting the "living" polymerization of ϵ-caprolactone.[4-7] The polymerization mechanism is of a "coordination–insertion" type, and the reaction proceeds through insertion of the lactone in a metal–alkoxide bond. The specific cleavage of the acyl-oxygen bond of CL results in the addition of the growing chain to the catalyst through an active alkoxide bond. Hydrolysis of the active aluminum alkoxide bonds leaves a hydroxyl group on one chain end. The second end group is nothing but an ester carrying the R radical of the initial alkoxide function (eq 1).

$$>\text{Al-O-R} \xrightarrow{(n-1)\text{CL}} >\text{Al-[O(CH}_2)_5\text{CO]}_n\text{-OR} \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} \text{H-[O(CH}_2)_5\text{CO]}_n\text{-OR} \quad (1)$$

If R is a functional radical, e.g., comprising a halogen, a tertiary amine, or a methacrylic double bond, an asymmetric α-hydroxy, ω-functional polyester is formed. Within the time required for complete monomer conversion, propagation is typically "living" and yields linear polyesters of a predictable molecular weight (from the initial CL/initiator molar ratio) with a rather narrow polymolecularity ($\bar{M}_w/\bar{M}_n \leq 1.2$). Nevertheless, any increase in the reaction time has two deleterious effects: broadening of the molecular weight distribution (intermolecular transesterification reactions) and formation of cyclic oligomers (intramolecular transesterification reactions).[15] The cyclic structure of oligomers has been proved by mass spectrometry and ^{1}H-NMR as discussed in the next section.

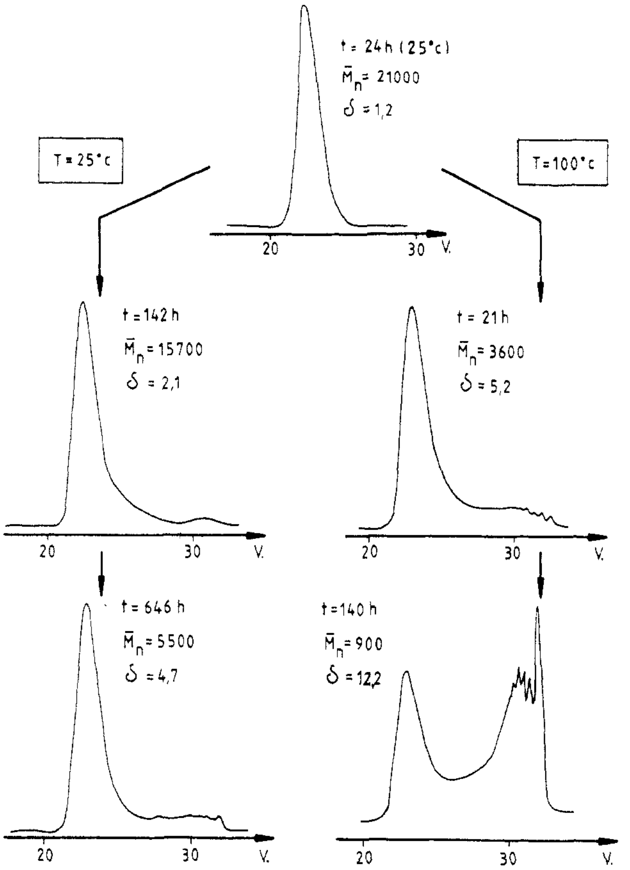


Figure 2. Size exclusion chromatograms of PCL as initiated by $Br(CH_2)_2OAlEt_2$ in toluene ($[CL]_0 = 10.6 \times 10^{-1}$ mol·L^{-1}; $[Al]_0 = 6.0 \times 10^{-3}$ mol·L^{-1}) at (a) 25 °C and (b) 25 °C (24 h) and then 100 °C.

To confirm the occurrence of transesterification reactions and to get a better insight on their mechanism, the time dependence of the molecular characteristics of living PCL chains was analyzed by size exclusion chromatography. Polymerization of CL was initiated by $Et_2AlO(CH_2)_2Br$ in toluene at 25 °C, and the temperature was raised to 100 °C after 24 h of reaction at 25 °C (Figure 2). For long reaction times at 25 °C, the molecular weight distribution became broader due to the formation of broadly dispersed oligomers. Similar to the ring-opening polymerization of lactides as initiated by $Al(O^iPr)_3$ in toluene,[15] formation of oligomers is strongly dependent on the temperature of the polymerization medium. Indeed, after 140 h at 100 °C, 62% of oligomers ($\bar{M}_n \leq 2000$) were formed, in contrast to 16% after 646 h at 25 °C.

It is worth comparing the size exclusion chromatograms of Figure 2 with chromatograms published by Penczek[16] and Yamashita[17] for PCL prepared by anionic polymerization at room temperature. Degradation is obviously more rapid when anionic propagating species are concerned. Indeed, in the presence of $(CH_3)_3SiONa$ as an initiator in THF at 20 °C, oligomers are already detected after ca. 8 h, corresponding to a monomer conversion around 50%.[16]

Table I. Transesterification Reactions in the Course of CL Polymerization Initiated by Aluminum Alkoxides ($[CL]_0 = 10.6 \times 10^{-1}$ mol·L^{-1}; $T = 25$ °C)

entry	initiator	solvent	$\bar{M}_{n\,theor}$	time (h)	$\bar{M}_{n\,GPC}$	$\bar{M}_w/\bar{M}_n$	% oligomers ($\bar{M}_n \le 2000$)
a	$Br(CH_2)_2OAlEt_2$	toluene	20000	24	21500	1.25	0
b				69	19000	1.4	3
c				142	15500	2.1	9.5
d				646	5500	4.7	15.5
e	$Br(CH_2)_2OAlEt_2$	toluene	10000	21	11000	1.2	0
f				165	9500	2.0	12
g				670	4500	3.2	16
h	$Br(CH_2)_2OAlEt_2$	THF	10000	22	10500	1.15	0
i				142	8500	2.1	15
j				650	4000	2.9	22
k	$Br(CH_2)_2OAl(^iBu)_2$	toluene	10000	22	11000	1.3	0
l				146	5500	4.7	14
m				630	8500[a]	1.6[a]	20
n	$CH_2{=}CH(CH_2)_3OAlEt_2$	toluene	10000	20	11500	1.15	0
o				118	9000	2.0	12
p				621	3500	3.1	21.5
q	$[CH_2{=}CH(CH_2)_3O]_3Al$	toluene	10000[b]	20	35500	1.5	0
r				118	23000	2.0	12.5
s				621	15500[a]	1.6[a]	20
t	$Br(CH_2)_2OAlEt_2$ + 1 equiv of pyridine	toluene	10000	27	10500	1.25	0
u				95	11500	1.3	0
v				336	10000	1.5	2
w				605	9000	1.6	5

[a] $\bar{M}_n$ and polymolecularity of PCL with high molecular weight chains ($\bar{M}_n > 2000$). [b] $\bar{M}_n = 114[CL]_0/n[Al]_0$, with $n = 3$ (number of alkoxide functions per Al atom).

Table II. Transesterification Reactions in the Course of CL Polymerization Initiated by Aluminum Alkoxides ($[CL]_0 = 10.6 \times 10^{-1}$ mol·L^{-1}; $T = 25$ °C (24 h) and then 100 °C)

entry	initiator	solvent	$\bar{M}_{n\,theor}$	time (h)	$\bar{M}_{n\,GPC}$	$\bar{M}_w/\bar{M}_n$	% oligomers ($\bar{M}_n \le 2000$)
1	$Br(CH_2)_2OAlEt_2$	toluene	20000	21	3500	5.2	17.5
2				45	18000[a]	1.4[a]	53
3				140	900	12.2	61.5
4	$Br(CH_2)_2OAlEt_2$	toluene	10000	46	1600	5.0	31
5				143	1400	5.7	39.5
6	$Br(CH_2)_2OAlEt_2$	THF	10000	26	5000	2.8	16.5
7				120	8000[a]	1.6[a]	26.5
8				192	3000	4.8	29
9	$Br(CH_2)_2OAl(^iBu)_2$	toluene	10000	144	1400	5.2	43.5
10	$CH_2{=}CH(CH_2)_3OAlEt_2$	toluene	10000	96	1700	3.4	28
11				143	1600	3.5	35.5
12	$[CH_2{=}CH(CH_2)_3O]_3Al$	toluene	10000[b]	96	1800	4.9	23.5
13				143	1900	4.3	28.5
14	$Br(CH_2)_2OAlEt_2$ + 1 equiv of pyridine	toluene	10000	68	5500	2.4	14.5
15				164	12500[a]	1.6[a]	19

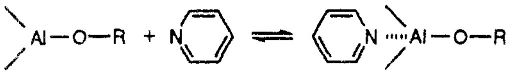
[a] $\bar{M}_n$ and polymolecularity of PCL with high molecular weight chains ($\bar{M}_n > 2000$). [b] $\bar{M}_n = 114[Cl]_0/n[Al]_0$, with $n = 3$ (number of alkoxide functions per Al atom).

Kricheldorf has recently confirmed that, in addition to anionic active sites, "covalent" bonds of metal alkoxides are also able to promote the redistribution of PCL chains at temperatures higher than 100 °C.[18] For a series of metal alkoxides, Kricheldorf has published the following reactivity scale: $Al(O^iPr)_3 < Zr(O^nPr)_3 < Ti(O^nBu)_4 < Bu_3SnOMe < Bu_2Sn(OMe)_2$.

To correlate formation of oligomers with the structure of aluminum alkoxides, several structural features of these alkoxides were changed, i.e., the number of alkoxides per Al atom, the nature of the alkyl groups associated with Al, and the nature of the functional groups attached to the alkoxy radical. Furthermore, toluene was substituted by an electro-donor solvent: tetrahydrofuran (THF). Results are reported in Tables I and II at 25 and 100 °C, respectively.

Table I clearly shows that, at 25 °C, the aluminum alkoxide structure has no significant effect on the extent of transesterification. After a reaction time of ca. 650 h at 25 °C, the final polymer contains ca. 20% of oligomers (entries d, g, j, m, p, and s). Nevertheless, when the temperature is raised to 100 °C, after a 24-h reaction time at 25 °C, the aluminum alkoxides structure is observed to affect the oligomer formation (Table II). First, the percentage of oligomers is much higher when the expected molecular weight of PCL is increased by a factor of 2, all other conditions being kept constant (entries 4 and 5 compared to entries 1–3 in Table II). This observation agrees with the randomness of the transesterification reactions: the longer the polyester chains, the higher is the probability of chain scissions. Actually, neither the functional group in the β or γ position of the alkoxide (entries 5 and 11) nor the alkyl substituent of Al (entries 5 and 9) has an effect on the oligomer formation. Initiation by aluminum trialkoxides, i.e., $[CH_2{=}CH(CH_2)_3O]_3Al$ (entries 10 and 11 compared entires to 12 and 13), or use of THF as a solvent (entries 5 and 8) decreases the extent of transesterification reactions (decrease by ca. 10% under our experimental conditions). All these observations suggest that transesterification reactions more likely proceed through coordination of carbonyl groups of the polyester chains onto the aluminum atom of the propagating species. Indeed, substitution of toluene by an electron-donor solvent, such as THF, and the use of an aluminum trialkoxide instead of a monoalkoxide are expected to decrease the electrophilicity of Al and to increase the steric hindrance of the active site. It is not surprising that these modifications have a depressive effect on intramolecular transesterification reactions, provided that the assumed coordinative interactions are operative. To confirm this hypothesis, a Lewis base was added to compete with the carbonyl groups for coordination onto Al.

Effect of Pyridine on the CL Polymerization. The first remarkable effect of pyridine is to increase the CL polymerization rate. It has been previously shown that the kinetics of CL polymerization in toluene at 25 °C is first order in $Br(CH_2)_2OAlEt_2$ used as an initiator[7,19] and that the polymerization rate constant k is 6.23 $mol^{-1}\cdot L\cdot min^{-1}$; $[CL]_0 = 10.6 \times 10^{-1}$ $mol\cdot L^{-1}$.[19] Actually, k increases to 20.0 $mol^{-1}\cdot L\cdot min^{-1}$, i.e., a threefold increase, upon addition of 1 equiv of pyridine per $Br(CH_2)_2OAlEt_2$. This kinetic effect has been accounted for by a specific coordination of pyridine and Al of the growing sites. Pyridine is indeed a ligand able to increase the ionic character of the "O–Al" bond (eq 2).

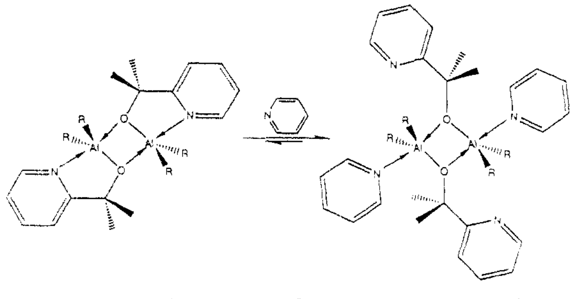


(2)

The polymerization rate enhancement by pyridine argues that the rate-determining step of the "coordination–insertion" ring-opening mechanism is the insertion of the monomer into the Al–OR bond rather than the coordination of the monomer to the initiator.[15,19] Thus the higher the ionic character of the aluminum alkoxide, the more rapid should be the monomer insertion.

Since coordination of carbonyl groups of PCL chains to Al atoms is a key feature of the transesterification reactions, addition of pyridine to the initiator (1 equiv/Al) is expected to penalize these side reactions. Indeed, after a 95-h reaction time at 25 °C, no trace of cyclic oligomers was detected (Table I, entry u). After 605 h at 25 °C, only 5% of oligomers were formed compared with 16% in the absence of pyridine (entries g and w). Similarly, at 100 °C, the cyclic oligomers were formed much more slowly when the initiator was added with pyridine (entries 4 and 5 and entries 14 and 15, Table II).

Pyridine, and expectedly a Lewis base, has a twofold benefit: it enhances the polymerization rate and it delays considerably the occurrence of the transesterification reactions. This behavior is more likely due to the specific complexation of pyridine onto the Al atom. Although the scientific literature reports on "Al–N" interactions,[20-24] the contribution by Van Koten *et al.*[25] deserves special attention. These authors focused on the binary pyridine/diorgano[(2-pyridyl)methoxy]aluminum system. A careful analysis by ^1H-, ^{13}C-, and ^{27}Al-NMR has shown that Al remains pentacoordinated even in the presence of pyridine (eq 3).



(3)

Nevertheless, the intramolecular interaction between each Al atom and the pyridiyl ring is substituted by a more favorable Al/pyridine coordination.

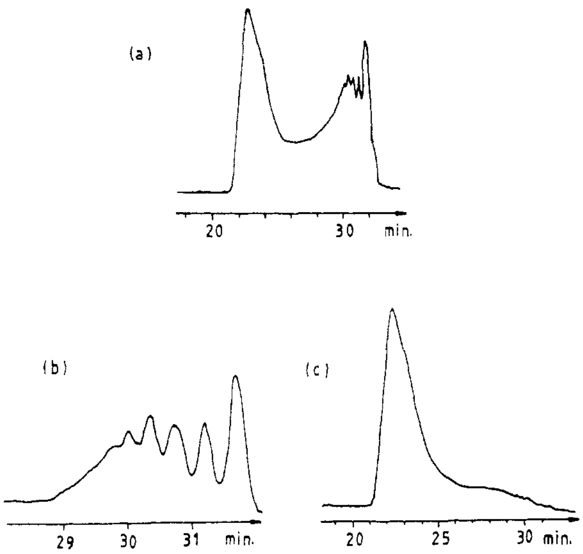


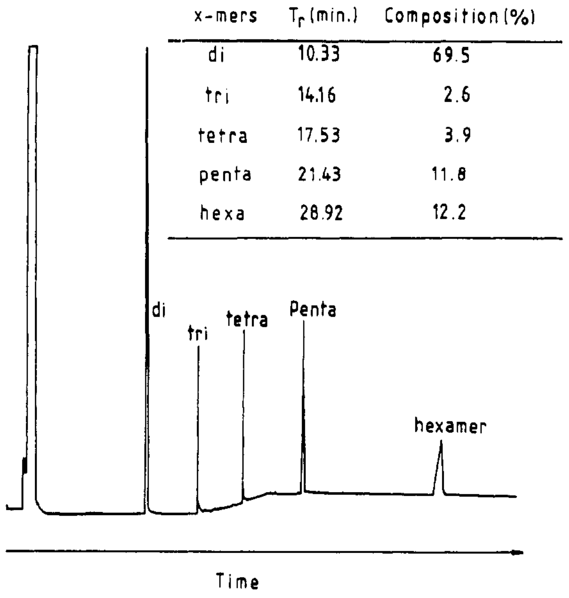
Figure 3. Size exclusion chromatograms of PCL as initiated by $Br(CH_2)_2OAlEt_2$ in toluene at 25 °C for 24 h and then at 100 °C for 45 h ($[CL]_0 = 10.6 \times 10^{-1}$ $mol\cdot L^{-1}$; $[Al]_0 = 6.0 \times 10^{-3}$ $mol\cdot L^{-1}$): (a) crude polyester; (b) soluble fraction; (c) insoluble fraction in supercritical CO_2 (SFE conditions: $P_{CO_2} = 250$ bar; $T = 50$ °C; trap = CH_2Cl_2).

It is also worth noting that the sequential polymerization of ϵ-CL and (D,L)-lactide, (D,L)-LA, has been successfully initiated by $Al(O^iPr)_3$ in the presence of 3 equiv of ^iPrOH.[26] The important point is that the usually slow (D,L)-lactide conversion has been significantly enhanced by the addition of pyridine (1 equiv) to "living" PCL chains. An additional effect, the polymolecularity of the final diblock copolymer, has been found to decrease to less than 1.25. All these results will be extensively reported in the near future, and the effect of the nature of the Lewis bases will also be considered.

Recovery and Characterization of the Cyclic Oligomers. All attempts to extract the oligomeric fraction from the crude polyester by either selective dissolution or precipitation in the current solvents have failed. This is the reason why attention has been paid to the supercritical fluid extraction (SFE) technique,[13,14] which takes advantage of the very high solvent power of supercritical fluids at temperatures and pressures near the critical point. Compared with liquid solvents, supercritical fluids have high diffusivity, low density, and low viscosity, which favor rapid extraction and phase separation. Recent experiments have shown that SFE is a very promising technique when purification and fractionation of thermolabile polymers are concerned.[13] An additional advantage of this method is that supercritical fluids can be readily separated from the extracted material by pressure reduction. Furthermore, carbon dioxide, which is most frequently used, is nontoxic and does not contaminate the extracted polymers.

Oligomers were extracted from a PCL sample (300 mg) which was initiated by $Br(CH_2)_2OAlEt_2$ in toluene (24 h at 25 °C and then 45 h at 100 °C). Figure 3a shows the size exclusion chromatogram of the crude polyester. After extraction for 40 min at 50 °C under a CO_2 pressure of 250 bar, 44 mg of oligo-PCL was trapped (CH_2Cl_2; see Figure 1), i.e., 14.5% of the initial material.

The fraction extracted in supercritical CO_2 and the insoluble material were analyzed by SEC. Chromatograms b and c of Figure 3 illustrate the high selectivity of the oligomer extraction. Although the extraction is not quantitative under the reported experimental conditions (compare chromatograms a and c of Figure 3), the amount



x-mers	T_r (min.)	Composition (%)
di	10.33	69.5
tri	14.16	2.6
tetra	17.53	3.9
penta	21.43	11.8
hexa	28.92	12.2

Figure 4. Gas chromatogram of the oligomeric fraction extracted with supercritical CO_2 (see Figure 3b).

Conditions: 40 °C (1 min) $\xrightarrow{20\ ^\circ\mathrm{C/min}}$ 300 °C $\xrightarrow{10\ ^\circ\mathrm{C/min}}$ 350 °C (20 min)

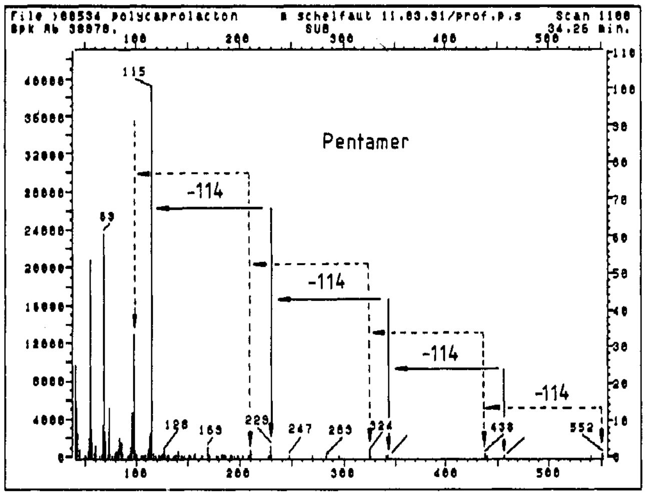
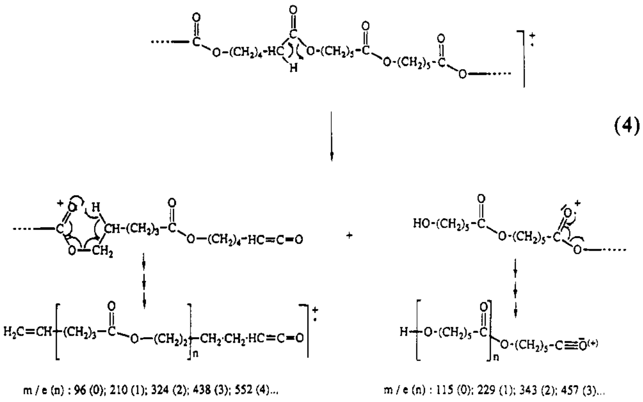


Figure 5. Mass spectrum of the pentameric compound extracted from the oligomer fraction with supercritical CO_2 (see Figure 3b) and separated by gas chromatography (see Figure 4).

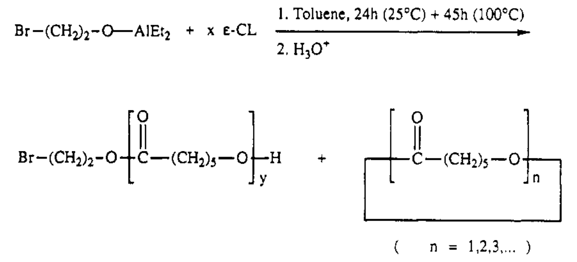
of residual oligomers is comparatively small. For the sake of completeness, it should be noted that the experimental parameters (pressure, temperature, and flow) can be selected in such a way that the percentage of extracted oligomers and their relative composition are largely controlled.[27]

PCL oligomers were analyzed by ^{1}H-NMR and no end group was identified, whether it be hydroxyl ($\delta(CH_2OH)$ = 3.64 ppm), bromide ($\delta(CH_2Br)$ = 3.52 ppm), or carboxylic acid ($\delta(COOH)$ > 8 ppm). This observation in favor of a cyclic structure for the oligomers is confirmed by the mass spectroscopy of the individual oligomers previously separated by gas chromatography (GC–MS) (Figure 4). Although the molecular ion of each oligomer cannot be identified in the mass spectrum, secondary ions are detected, the molecular weights of which are different from each other by 114, i.e., the molecular weight of the cyclic monomer (Figure 5). The secondary ions are believed to result from the fragmentation of cyclic oligomers and to be α-hydroxyl-ω-carboxonium ions or α-cetene-ω-olefinic species (eq 4). This assignment is actually in perfect agreement with studies of some linear aliphatic polylactones by direct pyrolysis–mass spectrometry (DP–MS).[28] In DP–MS, polymeric chains were directly degraded by pyrolysis in the ion source, and the resulting oligomers were isolated and detected.



(4)

In conclusion, ^{1}H-NMR and mass spectrometry show that intramolecular transesterification reactions which could compete with propagation of PCL chains lead to cyclic oligomers which range from dimer to, at least, hexamer (eq 5). In agreement with previous observations by Yamashita[29] and Megna,[30] the cyclic dimer is preferentially formed (Figure 4).



(5)

Conclusion

Functional aluminum alkoxides rank among the best initiators for the perfectly controlled polymerization of ε-caprolactone. Nevertheless, an exceedingly high temperature and/or reaction time is in favor with side degradation reactions of the linear polyester chains. Combinations of supercritical fluid extraction, gas chromatography, ^{1}H-NMR, and mass spectrometry have proved to be very successful in recovering and analyzing the structure of the individual oligomers. Addition of a Lewis base, such as pyridine, is very efficient in delaying the occurrence of the secondary transesterification reactions. Actually, pyridine has a twofold beneficial effect. It enhances the polymerization rate and it decreases the extent of the transesterification reactions. This effect is of the utmost importance, since it might improve the control of the ring-opening polymerization of lactides and glycolide, which is more sensitive to transesterification than the ε-CL polyaddition.

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References and Notes

(1) IUPAC Symposium on Ring-Opening Polymerization, Warsaw, Poland, July 7-11, 1992; *Makromol. Chem., Macromol. Symp.*, to be published.

(2) Cox, E. F.; Hostettler, F. Union Carbide Corp., U.S. Pat. 3,021,310, 1962.
(3) Brode, G. L.; Koleske, J. V. *J. Macromol. Sci., Chem.* **1972**, *A6* (6), 1109.
(4) Dubois, Ph.; Jerôme, R.; Teyssié, Ph. *Polym. Bull.* **1989**, *22*, 475.
(5) Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 977.
(6) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640.
(7) Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 103.
(8) Lundberg, R. D.; Koleske, J. V.; Wischmann, K. B. *J. Polym. Sci., Part A-1* **1969**, *7*, 2915.
(9) Ouhadi, T.; Stevens, C.; Teyssié, Ph. *J. Appl. Polym. Sci.* **1976**, *20*, 2963.
(10) Yamashita, Y. In *Anionic Polymerization: Kinetics, Mechanisms and Synthesis*; McGrath, J. E., Ed.; ACS Symposium Series 166; American Chemical Society: Washington, DC, 1981; p 199.
(11) Sosnowski, S.; Slomkowski, S.; Penczek, S. *J. Macromol. Sci., Chem.* **1983** *A20* (9), 979.
(12) Heuschen, J. Ph.D. Thesis, University of Liège, Liège, Belgium, 1977.
(13) Krukonis, V. *Polym. News* **1985**, *11*, 7.
(14) Williams, D. F. *Chem. Eng. Sci.* **1981**, *36* (11), 1769.
(15) Dubois, Ph.; Jacobs, Ch.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 2266.
(16) Sosnowski, S.; Slomkowski, S.; Penczek, S. *Makromol. Chem.* **1983**, *184*, 2159.
(17) Ito, K.; Yamashita, Y. *Macromolecules* **1978**, *11* (1), 68.
(18) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286.
(19) Dubois, Ph. Ph.D. Thesis, University of Liège, Liège, Belgium, 1991.
(20) Benn, R.; Rufinska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.
(21) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.
(22) Hendrickson, C. H.; Duffy, D.; Eyman, D. P. *Inorg. Chem.* **1968**, *7*, 1047.
(23) Beachley, O. T. J.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 210.
(24) Yasuda, H.; Araki, T.; Tani, H. *J. Organomet. Chem.* **1973**, *49*, 103.
(25) Van Vliet, M. R. P.; Buysingh, P.; Van Koten, G.; Vrieze, K. *Organometalics* **1985**, *4*, 101.
(26) Jacobs, Ch.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 3027.
(27) Unpublished results.
(28) Garozzo, D.; Giuffrida, M.; Montaudo, G. *Macromolecules* **1986**, *19*, 1643.
(29) Ito, K.; Hashizuka, Y.; Yamashita, Y. *Macromolecules* **1977**, *10* (4), 821.
(30) Megna, I. S.; Koroscil, A. *J. Polym. Sci., Polym. Lett.* **1968**, *6*, 653.