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Poly(lactones). 9.[†] Polymerization Mechanism of Metal Alkoxide Initiated Polymerizations of Lactide and Various Lactones

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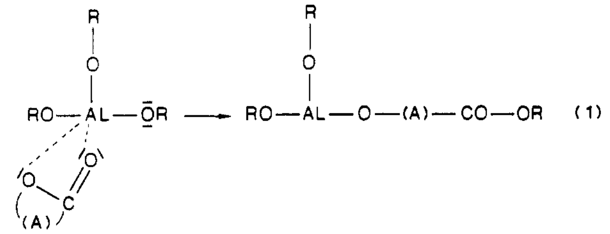
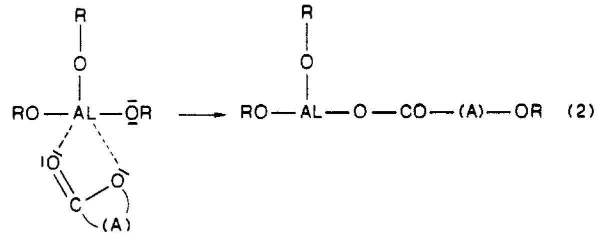
ABSTRACT: Four different lactones, namely, β-propiolactone, D,L-β-butyrolactone, ε-caprolactone, and L,L-lactide, were polymerized in bulk or in solution at temperatures between 50 and 150 °C. Various metal alkoxides, such as magnesium ethoxide, aluminum isopropoxide, zinc or titanium *n*-butoxide, zirconium *n*-propoxide, and dibutyl- or tributyltin methoxide, were used as initiators. Both ^{1}H and ^{13}C NMR spectroscopy clearly prove that in all cases the same initiation and propagation mechanisms take place. The ring opening of the lactones involves cleavage of the acyl–oxygen bond, and the alkoxide groups of the initiator form alkyl ester end groups. It is demonstrated that this so-called insertion mechanism is different from both cationic and anionic mechanisms. ^{1}H NMR end-group analyses also demonstrate that all alkoxide groups of an initiator are active, at least at temperatures above 50 °C. Despite a living character with regard to end-group activities these insertion mechanisms do not yield narrow molecular weight distributions, partially because initiation is not faster than propagation and partially because most initiators cause transesterification. Whereas aluminium isopropoxide does not effect back-biting up to temperatures around 150 °C, other initiators, in particular butyltin methoxides, are so active that cyclic oligomers are formed by degradation of the polylactones even after few hours at 100 °C.

Introduction

Aluminum alkoxides are known to be effective initiators of the polymerization of lactones. Teyssiē and co-workers have demonstrated that aluminum isopropoxide[1] and also μ-oxo bimetallic aluminum alkoxides[2,3] initiate the polymerization in such a way that the acyl–oxygen bond of the lactone is cleaved (eq 1) and not the alkyl–oxygen bond (eq 2). It is characteristic of this mechanism (eq 1) that the alkoxide group of the initiator forms the dead end of the growing chain end. Polymerizations conducted with ε-caprolactone at 0 °C also showed that only one alkoxide group per aluminum is active as an initiating species.


(1)


(2)

In the first part of this series[4] the copolymerization of glycolide and ε-caprolactone by means of aluminum isopropylate (and other initiators) was investigated. The ring-opening mechanism of eq 1 was confirmed; yet at polymerization temperatures ≥100 °C all three alkoxide group were found to be active, obviously because at high temperatures aluminum isopropoxide does not undergo self-association in dilute solution. Furthermore, it was found that aluminum isopropoxide does not cause *inter*molecular transesterification up to a temperature of 150 °C in contrast to alkyltin alkoxides.[5] On the basis of these results the purpose of the present work was threefold:

I. It should clarify whether the ring-opening mechanism of eq 1 is valid for all heavy metal alkoxides or whether the alternative mechanism, eq 2, may also be operating.

II. It should analyze whether all or only one alkoxide group per initiator is active in the initiating process. This information is important for the calculation of the average degree of polymerization ($\overline{\mathrm{DP}}$) from the monomer/initiator ratio (M/I).

III. It should elucidate whether the metal alkoxides cause transesterification of polyester chains under the polymerization conditions. A clear answer to this question is important for the course of copolymerizations, because initiators with high transesterification activity are useful for the preparation of amorphous copolyesters with random sequences, whereas initiators without transesterification activity are worthwhile for the preparation of crystalline block copolymers.

Experimental Section

Initiators. Magnesium ethoxide and aluminum isopropoxide were purchased from Lancaster Chemicals (UK). Potassium *tert*-butoxide, titanium *n*-butoxide, and zirconium *n*-propoxide

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[†] Part 8: Kricheldorf, H. R.; Dunsing, R. *Makromol. Chem.* **1986**, *197*, 1611.

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Table I
^{1}H NMR Chemical Shifts δ (ppm Relative to Internal TMS) of Metal Alkoxide Initiators Measured in $CDCl_3$

initiator	chem shifts, δ 1	2	3
$\mathrm{Al(O\overset{1}{CH}(\overset{2}{CH_3})_2)_3}$	4.24 (sept)	1.12 (d)	
$\mathrm{(\overset{1}{CH_3}\overset{2}{CH_2}\overset{2}{CH_2}\overset{2}{CH_2})_2Sn(O\overset{3}{CH_3})_2}$	0.94 (t)	1.22–1.87 (m)	3.56 (s)
$\mathrm{Ti(O\overset{1}{CH_2}\overset{2}{CH_2}\overset{2}{CH_2}\overset{3}{CH_3})_4}$	4.31 (t)	1.17–1.76 (m)	0.92 (t)
$\mathrm{Zn(O\overset{1}{CH_2}\overset{2}{CH_2}\overset{2}{CH_2}\overset{3}{CH_3})_4}$	3.65 (m)	1.21–1.56 (m)	0.87 (t)
$\mathrm{Zr(O\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_3})_4}$	3.60 (t)	1.57 (m)	0.92 (t)

were purchased from Aldrich Chemicals (St. Louis, MO). All these initiators were used without further purification. Butyltin trimethoxide, dibutyltin dimethoxide, and tributyltin methoxide were prepared from the corresponding butyltin chlorides and sodium methoxide in dry methanol. These tin methoxides were purified by distillation in vacuo. Zinc di-*n*-butoxide was prepared by addition of 1-butanol to an 1.1 M solution of diethylzinc in toluene. This solution was used immediately after the evolution of ethane had ceased.

Monomers. L,L-Lactide was a gift of Boehringer & Sohn (Ingelheim, FRG), it was recrystallized from dry ethyl acetate and dried over phosphorous pentoxide in vacuo. D,L-β-Butyrolactone, β-propiolactone, and ϵ-caprolactone (Aldrich Co., St. Louis, MO) were distilled under nitrogen over oligomeric bis(4-isocyanatophenyl)methane in vacuo.

Polymerizations (General Procedure). All polymerizations were carried out in Erlenmeyer flasks with ground-glass joints. The inner glass walls were silanized with dimethylchlorosilane, and the reagents were weighed into these reaction vessels under nitrogen. Then the Erlenmeyer flasks were closed with glass stoppers and steel springs and completely immersed into the thermostated heating bath, to prevent distillation of monomers to colder parts of the reaction vessel.

Polymerizations of Lactide and ϵ-Caprolactone (Tables VII and VIII). L,L-Lactide (or ϵ-caprolactone), 50 mmol, was weighed into the reaction vessel and the initiator was added in the form of a freshly prepared 1 M solution in dry methylene chloride. After the polymerization was complete, the reaction product was dissolved in ca. 60 mL of methylene chloride and poured into ca. 1 L of cold methanol.

Polymerizations of β-Propiolactone (Table IX). Solutions of various metal alkoxides (1 M) in dry dioxane were added to a solution of 50 mmol of β-propiolactone in 25 mL of dry dioxane. The reaction mixtures were thermostated at 95 °C for 24 or 48 h (see Table IX) and finally poured into 400 mL of ice-cold methanol. The precipitated poly(β-propiolactone) was isolated by filtration and dried at 50 °C in vacuo.

Polymerizations of D,L-β-Butyrolactone (Table X). D,L-β-Butyrolactone, 50 mmol, was weighed into a 25-mL Erlenmeyer flask equipped with a ground-glass joint. The initiators were added in the form of 1 M solutions in dry dioxane, and the reactions mixtures were thermostated at 50, 75, or 100 °C (see Table X). After certain time intervals small samples of the reaction mixtures were subjected to IR and ^{1}H NMR spectroscopic analyses, to determine the conversion and to identify the end groups (see Figure 4). Finally, the reaction product was dissolved in 25 mL of dichloromethane and precipitated into 400 mL of a 1:1 mixture (by volume) of diethyl ether and ligroin. The precipitated syrups were dried at 50 °C in vacuo and then subjected to ^{1}H NMR end-group analyses in $CDCl_3$.

Degradation of Poly(ϵ-caprolactone) (Table XI). Poly(ϵ-caprolactone), 50 mmol, was dissolved in 50 mL of dry toluene (or 1,2,4-trichlorobenzene) and 0.5 mmol of an initiator was added in the form of a 1 M solution. After the desired reaction time had past, the reaction mixture was poured into ca. 600 mL of cold methanol and the precipitated polyester was isolated by filtration. Since the molecular weight has a strong influence on the apparent rate of degradation, all experiments of Table VIII were conducted with poly(ϵ-caprolactone) of one batch (T_m = 60, Aldrich Co, St. Louis, MO).

Measurements. The 100-MHz ^{1}H NMR spectra were obtained on a Bruker AC 100 FT spectrometer. All measurements were conducted in $CDCl_3$ as solvent, containing TMS as internal standard. Solutions of 50 mg of polyester in 1 mL of solvent were measured in 5-mm-o.d. sample tubes.

The 90.5-MHz ^{13}C NMR spectra were obtained on a Bruker AM 360 FT spectrometer in 10-mm-o.d. sample tubes containing 300 mg of polyester dissolved in 2.5 mL of $CDCl_3$. Acquisition was conducted with the following parameters: pulse width 45°; relaxation delay 2 s; 32K data points/20000-Hz spectral width; 1000–10 000 transients.

Results and Discussion

Spectroscopic End-Group Analyses. A differentiation between a propagation involving acyl–oxygen cleavage (eq 1) and alkyl–oxygen cleavage (eq 2) is difficult to achieve via kinetic methods, whereas clear-cut end-group analyses should enable a reliable distinction of both mechanisms. The two methods best suited for a reliable qualitative and even quantitative end-group analysis of various kinds of end groups are ^{1}H and ^{13}C NMR spectroscopy. In order to a avoid confusion of end-group signals with signals or unreacted initiator ^{1}H and ^{13}C NMR spectra of all initiators used in this work were measured (Table I). Furthermore, a series of model compounds of ester end groups was synthesized and measured (Tables II and III) alone with an analogous series of models of ether end groups (Tables IV and V). The alkoxy groups of these model compounds were varied according to those of the initiators used in this work. For completion of the NMR data the ^{1}H and ^{13}C chemical shifts of the lactones and polylactones (including δ-valerolactone) were summarized in Table VI.

The polymerizations studied in this work were designed to vary the following three structural parameters: (I) the metal atom of the initiator; (II) the alkoxy groups of the initiator; (III) the nature of the lactone.

According to the initiators in Tables II and III the models of end groups must contain methoxy, ethoxy, *n*-propoxy, isopropoxy, *n*-butoxy, and phenoxy groups.

Table II
^{1}H NMR Chemical Shifts δ (ppm, Relative to Internal TMS) of Models of Ester End Groups Measured in $CDCl_3$

models	chem shifts, δ 1	2	3	4	5
$\mathrm{Br\overset{1}{CH_2}COO\overset{2}{CH_3}}$	3.84	3.78			
$\mathrm{HO\overset{1}{CH}(\overset{2}{CH_3})COO\overset{3}{CH_2}\overset{4}{CH_3}}$	4.26 (q)	1.2 (d)	4.24 (q)		
$\mathrm{Cl\overset{1}{CH_2}COO\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_3}}$	4.07	1.15 (t)	1.4–1.8 (m)	0.96 (t)	
$\mathrm{Cl\overset{1}{CH_2}COO\overset{2}{CH}(\overset{3}{CH_3})_2}$	4.03	5.08 (m)	1.28 (d)		
$\mathrm{Cl\overset{1}{CH_2}COOC(\overset{2}{CH_3})_3}$	3.95	1.48			
$\mathrm{Cl\overset{1}{CH_2}COO\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_3}}$	4.06	4.19 (t)	1.2–1.8 (m)		0.94 (t)
$\mathrm{Cl\overset{1}{CH_2}COO\overset{2}{C_6H_5}}$	4.30	7.1–7.3 (m)			

Table III

^{13}C NMR Chemical Shifts δ (ppm, Relative to Internal TMS) of Models of Ester End Groups Measured in $CDCl_3$

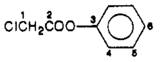
models	chem shifts, δ 1	2	3	4	5	6
$Br\overset{1}{C}H_2\overset{2}{C}OO\overset{3}{C}H_3$	25.5	167.9	53.2			
$H_3\overset{7}{C}\overset{6}{C}O_2\overset{1}{C}H(\overset{2}{C}H_3)\overset{3}{C}OO\overset{4}{C}H_2\overset{5}{C}H_3$	68.7	16.9	170.9	61.3	14.1	170.3
$Cl\overset{1}{H}_2COO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$	40.7	167.2	67.5	21.7	10.0	
$Cl\overset{1}{H}_2\overset{2}{C}OO\overset{3}{C}H(\overset{4}{C}H_3)_2$	41.1	166.7	70.0	21.5		
$Cl\overset{1}{H}_2\overset{2}{C}OO\overset{3}{C}(\overset{4}{C}H_3)_3$	41.9	166.3	82.8	27.9		
$Cl\overset{1}{C}H_2\overset{2}{C}OO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$	40.7	167.3	65.9	30.4	18.8	13.5
	40.9	165.8	150.4	121.2	129.6	126.4

Table IV

^1H NMR Chemical Shifts δ (ppm, Relative of Internal TMS) of Models of *Ether* End Groups Measured in $CDCl_3$

models	chem shifts, δ 1	2	3	4	5	6
$\overset{1}{C}H_3O\overset{2}{C}H_2CH_2OCH_3$	3.38	3.53				
$\overset{1}{C}H_3\overset{2}{H}_2OCH_2CH_3$	1.16 (t)	3.36 (q)				
$(\overset{1}{C}H_3)_2\overset{2}{C}HO\overset{3}{C}H_2CO_2\overset{4}{C}H_2\overset{5}{C}H_3$	1.45 (d)	3.6 (m)	4.06	4.19 (q)	1.28 (t)	
$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2O\overset{4}{C}H(\overset{5}{C}H_3)CO_2H$	0.75 (t)	1.22 (m)	3.31 (t) 3.41 (t)	4.75 (q)	1.28 (d)	
$(\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2)_2O$	0.91 (t)	1.20–1.65 (m)		3.40 (t)		
$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2O\overset{5}{C}H_2CO_2\overset{6}{C}H_2\overset{7}{C}H_3$	0.92 (t)	1.20–1.65 (m)		3.5 (t)	4.05	4.20 (q)
$(\overset{1}{C}H_3)_3CO\overset{2}{C}H_2CO_2C(\overset{3}{C}H_3)_3$	1.21	3.89	1.47			1.28 (t)
$\overset{1}{C}_6H_5O\overset{2}{C}H(\overset{3}{C}H_3)CO_2\overset{4}{C}H_3$	6.7–7.3	4.73 (q)	1.56 (d)	3.66		

Table V

^{13}C NMR Chemical Shifts δ (ppm, Relative to Internal TMS) of Models of *Ether* End Groups Measured in $CDCl_3$

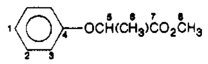
models	chem shifts, δ 1	2	3	4	5	6
$\overset{1}{C}H_3O\overset{2}{C}H_2CH_2OH$	58.8	61.4	74.2			
$\overset{1}{C}H_3\overset{2}{C}H_2OCH_2CH_3$	14.6	65.2				
$(\overset{1}{C}H_3)_2\overset{2}{C}HO\overset{3}{C}H_2\overset{4}{C}O_2\overset{5}{C}H_2\overset{6}{C}H_3$	21.8	65.9	72.6	170.9	60.7	14.2
$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2O\overset{4}{C}H(\overset{5}{C}H_3)\overset{6}{C}O_2\overset{7}{C}H_3$	13.8	31.8	70.3	74.6	18.5	178.8
$(\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2)_2O$	14.0	19.5	31.7	70.8		
$\overset{1}{C}H_3\overset{2}{C}H_2CH_2\overset{3}{C}H_2\overset{4}{C}H_2O\overset{5}{C}H_2\overset{6}{C}O_2\overset{7}{C}H_2\overset{8}{C}H_3$	13.7	19.2	31.7	68.4	71.7	170.8
$(\overset{1}{C}H_3)_3\overset{2}{C}O\overset{3}{C}H_2\overset{4}{C}O_2\overset{5}{C}(\overset{6}{C}H_3)_3$	27.3	74.2	61.3	170.6	81.0	28.1
	115.2	121.7	129.6	157.7	115.5	18.5

Table VI

^1H and ^{13}C NMR Chemical Shifts δ (ppm, Relative to Internal TMS) of Mono- and Polylactones Measured in $CDCl_3$

	chem shifts, δ												
	^{13}C						^1H						
lactone	C=O	C_α	C_β	C_γ	C_δ	C_ϵ	CH_α	$C_\alpha H_2$	$C_\beta H_2$	$C_\gamma H_2$	$C_\delta H_2$	$C_\epsilon H_2$	CH_3
β-propiolactone	169.3	39.2	59.0					3.51 (t)	4.25 (t)				
poly(β-propiolactone)	170.3	33.6	60.1					2.56 (t)	3.84 (t)				
	168.3	44.2	68.0	20.3			4.7 (m)			3.55 (q)			1.57 (d)
									3.07 (q)				
poly(D,L-β-butyrolactone)	169.3	40.9	67.7	19.8			5.28 (m)		2.70 (m)				1.27 (d)
									2.50 (m)				
δ-valerolactone	171.4	29.9	19.1	22.4	69.5			2.49 (m)	1.89 (m)	1.89 (m)	4.36 (m)		
poly(δ-valerolactone)	173.3	33.8	21.5	28.2	64.0			2.35 (m)	1.69 (m)	1.69 (m)	4.08 (m)		
ϵ-caprolactone	176.2	34.6	28.9	23.0	29.4	69.3		2.63 (t)	1.80 (m)	1.80 (m)	1.80 (m)	4.20 (t)	
poly(ϵ-caprolactone)	173.5	34.1	25.6	24.6	28.4	64.2		2.31 (t)	1.53 (m)	1.53 (m)	1.53 (m)	4.06 (t)	
L,L-lactide	167.9	15.7	72.5				1.66 (d)						5.09 (q)
poly(L,L-lactide)	169.5	16.7	69.1				1.56 (d)						5.17 (q)

Table VII
Reaction Conditions and Results of Bulk Polymerization of L,L-Lactide by Means of Various Metal Alkoxides at 100 °C

	initiator	M/I	time, h	yield, %	$\overline{DP}_n$ (calcd)[a]	$\overline{DP}_n$ (NMR)[b]	$\overline{DP}_n$ (VPO)[c]	$\overline{DP}_n$ (visc)[d]
1	$Al(O\text{-}i\text{-}Pr)_3$	150/1	24	96	96	101		55
2	$Al(O\text{-}i\text{-}Pr)_3$	300/1	3	82	164	179	83	94
3	$Ti(OBu)_4$	100/1	24	94	47	51	51	43
4	$Ti(OBu)_4$	200/1	24	85	85	98	85	74
5	$Ti(OBu)_4$	400/1	48	93	186	194	107	104
6	$Zr(OPr)_4$	100/1	24	94	47	53	52	43
7	$Zr(OPr)_4$	200/1	24	89	89	97	86	70
8	$Zr(OPr)_4$	400/1	48	97	194	194	118	103
9	$(n\text{-}Bu)_3SnOMe$	50/1	3	95	95	110	71	79
10	$(n\text{-}Bu)_3SnOMe$	100/1	4	94	188	212	85	101
11	$(n\text{-}Bu)_3SnOMe$	200/1	24	97	376	405	198	178
12	$(n\text{-}Bu)_2Sn(OMe)_2$	100/1	24	94	94	94	65	65

[a] Calculated from the M/I ratio x conversion, considering that all akoxide groups are active. [b] Determined from ^1H NMR spectra. [c] Vapor pressure osmometry in chloroform. [d] From viscosity measurements in benzene according to $[\eta] = 5.72 \times 10^{-4} \bar{M}_n^{0.72}$.[9]

Table VIII
Reaction Conditions and Results of Bulk Polymerizations of ε-Caprolactone by Means of Various Metal Alkoxides at 100 °C

	initiator	M/I	time, h	yield, %	$\overline{DP}_n$ (calcd)[a]	$\overline{DP}_n$ (NMR)[b]	$\overline{DP}_n$ (visc)[c]
1	$Al(O\text{-}i\text{-}Pr)_3$	300/1	24	90	90	100	208
2	$Ti(OBu)_4$	400/1	24	93	92	95	161
3	$Zr(OPr)_4$	400/1	24	92	92	103	156
4	$(n\text{-}Bu)_3SnOMe$	100/1	24	92	90	90	154
5	$(n\text{-}Bu)_2Sn(OMe)_2$	200/1	24	92	93	100	165
6	$Nz(OBu)_2$	200/1	24	93	93	95	170

[a] Calculated according to eq 3, considering that all alkoxide groups were active. [b] Determined by ^1H NMR end-group analyses. [c] From viscosity measurement in benzene according to $[n] = 9.94 \times 10^{-5} \bar{M}_w^{0.82}$.[10]

Ethers and esters synthesized from chloroacetic acid or α-chloropropionic acid served as models of end groups in poly(lactide), whereas compounds with longer aliphatic chains, such as esters of *n*-butyric acid or di-*n*-butyl ether, served as models of end groups in poly(ε-caprolactone). However, it was found that end groups of poly(glycolide) and poly(lactide), on the one hand, and poly(lactones) on the other hand, show nearly identical chemical shifts. In contrast, the chemical shifts of ether and ester derivatives of the same alkoxy group differ significantly, so that ether and ester groups are easy to distinguish regardless of the polyester under investigation. The ^1H NMR signal of the O–CH fragment in ether groups absorb 0.5–0.6 ppm upfield of ester groups, whereas the ^{13}C NMR signal of the ether groups absorb 5–8 ppm downfield from that of the ester groups. In the case of *tert*-butoxy and phenoxy groups ^1H NMR spectroscopy was, of course, not helpful and our conclusions are exclusively based on the ^{13}C NMR signals of the quarternary carbons.

Polymerization of L,L-Lactide and ε-Caprolactone. The homopolymerizations of L,L-lactide and ε-caprolactone with various metal alkoxides were conducted in bulk at 100 °C (Tables VII and VIII). In the case of L,L-lactide the monomer/initiator ratio was varied in addition to the initiator (Table VII). Yields and NMR spectra were measured after precipitation from methanol. Both ^1H and ^{13}C NMR spectra agree in that all polymerizations listed in Tables VII and VIII yielded polylactones with alkyl ester end groups. Alkyl ether end groups were never detectable. It is well-known[6-8] that polymerizations of ε-caprolactone initiated by alkali metal alkoxides in the presence or absence of alcohols again yield ester end groups. Thus, it is obvious that the chain growth of metal alkoxide initiated polymerization of six- and seven-membered lactones proceeds via acyl–oxygen cleavage regardless of which sort of metal alkoxide is used. Yet it should by emphasized that this conclusion does not include β-lactones (see discussion below).

A quantitative evaluation of the ^1H NMR end-group signals should clarify whether all alkoxide groups of the initiators under investigation participate in the initiation and propagation processes. The results listed in Table VII indicate that nearly complete conversions are obtainable regardless of the monomer/initiator (M/I) ratio. This result and the degradation studies discussed below demonstrate that the metal alkoxide initiated polymerizations have a "living character" with regard to the reactivity of the active chain ends. When moisture and electrophilic impurities are excluded, the metal alkoxide bonds forming the active end groups are insensitive to termination steps at least at temperatures ≤150 °C. Thus, in the absence of "back-biting" reactions the average degree of polymerization ($\overline{DP}$) should obey eq 1, if only one alkoxide group per initiator is active.

$$\overline{DP} = \frac{M}{I}\frac{\%\ \text{conversion}}{100} \qquad (3)$$

Tri(*n*-butyl)tin methoxide meets this requirement as demonstrated by the ^1H NMR measurements of Tables VII and VIII. However, in the case of di(*n*-butyl)tin dimethoxide the $\overline{DP}$ should be around $^1/_2$, in the case of aluminum isopropoxide $^1/_3$, and for titanium and zirconium alkoxides $^1/_4$ of the M/I ratio, if all alkoxide groups are equally active. The NMR measurements indeed confirm that all alkoxide groups of an initiator molecule are active enough to initiate a growing chain. This result is not trivial, because the three or four alkoxide groups attached to aluminum, titanium, or zirconium certainly do not simultaneously react with lactones. Thus, the beginning growth of one or two chains should sterically hinder the initiation step of a neighboring alkoxide group. Obviously this effect is not detectable at high conversions. However, as demonstrated by Teyssiê et al.[1-3] association of the initiators may reduce the reactivity of individual alkoxide groups at low temperatures (<25 °C). In this

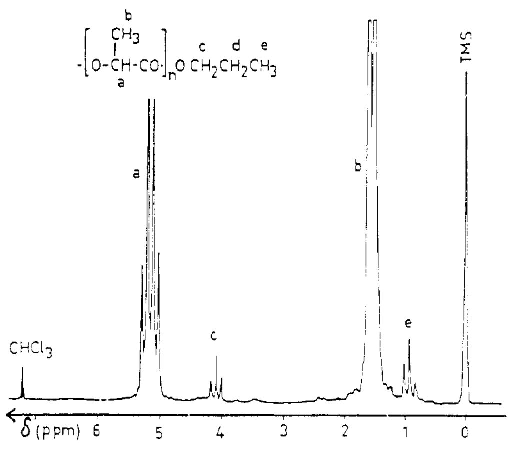


Figure 1. ^{1}H NMR spectrum, 100 MHz, of isolated poly(L-lactide) initiated with zirconium tetrapropoxide (entry 6, Table VII) measured in $CDCl_3$ with internal TMS.

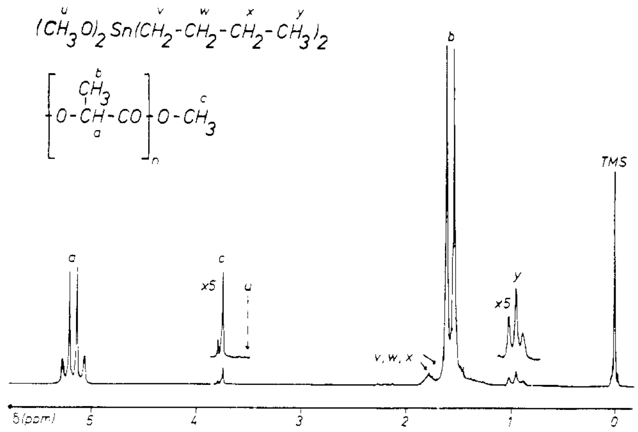


Figure 2. ^{1}H NMR spectrum (measured in $CDCl_3$, 100 MHz) of the reaction mixture of L-lactide and dibutyltin dimethoxide (M/I = 100:1) after 24 h at 100 °C.

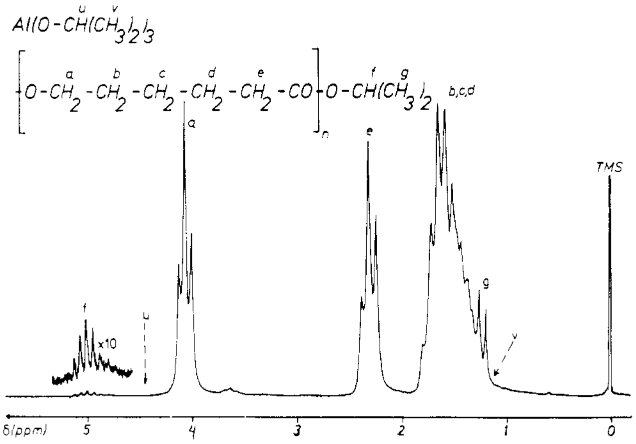


Figure 3. ^{1}H NMR spectrum (measured in $CDCl_3$, 100 MHz) of the reaction mixture of ε-caprolactone and aluminum isopropoxide (M/I = 150:1) after 24 h at 100 °C.

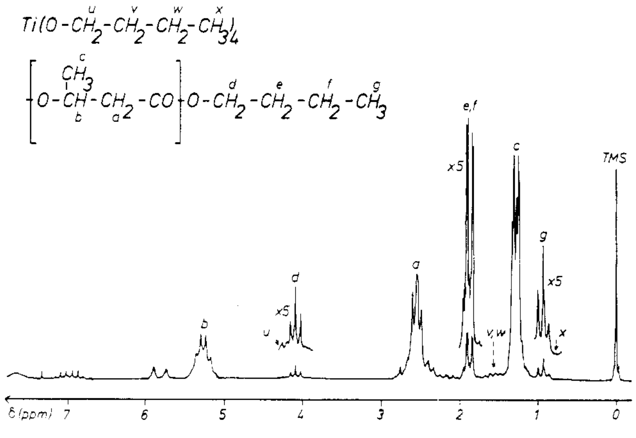


Figure 4. ^{1}H NMR spectrum (measured in $CDCl_3$, 100 MHz) of the reaction mixture of D,L-β-butyrolactone and titanium tetrabutoxide (M/I = 200:1) after 126 h at 100 °C.

connection it is noteworthy that also a magnesium ethoxide initiated bulk polymerization of L,L-lactide was conducted at 100 °C. In agreement with the corresponding experiment of Table IX (entry 1), ethyl ester end groups were found by both ^{1}H and ^{13}C NMR spectroscopy. However, this polymerization is not listed in Table VII because a quantification of the end-group signal was not reasonable due to the insolubility of magnesium ethoxide in the reaction mixture.

$$[\eta] = 5.72 \times 10^{-4} \bar{M}_n^{0.72} \qquad (4)$$

The quantitative ^{1}H NMR end-group analyses raise the question whether the apparent degrees of polymerization ($\overline{\mathrm{DP}}$'s) calculated from the monomer/end group ratios are true $\overline{\mathrm{DP}}$'s. Hence, in the case of poly(L-lactide), number-average molecular weights ($\bar{M}_n$'s) were determined by two independent methods, namely, vapor pressure osmometry and viscosimetry in combination with the Mark–Houwink equation (4).[9] Interestingly both methods gave $\bar{M}_n$ values significantly below than those calculated from ^{1}H NMR end-group analyses. This finding may be explained in two ways. First, the true $\bar{M}_n$'s (or $\overline{\mathrm{DP}}$'s) are lower than those calculated from end-group analyses, because or partial degradation due to back-biting of the active chain ends. Second, the $\bar{M}_n$'s obtained by VPO and viscosimetry are incorrect, i.e., too low.

The study of back-biting degradation presented below indeed confirms that most initiators used in this work cause back-biting, so that the true $\overline{\mathrm{DP}}$'s must be lower than those calculated from end-group analyses. However, this conclusion does not hold for aluminum isopropoxide. Thus, the $\bar{M}_n$ values derived from VPO and viscosities[4] are obviously lower than the true $\bar{M}_n$'s. In the case of VPO it is obvious that low molecular weight contaminents strongly reduce the experimental values. The "Mark–Houwink" equation (4), on the other hand is based on end-group titrations[9] and includes two negative aspects. First, the usefulness of eq 4 is highly sensitive to variations of the molecular weight distribution. Second, the basic titration might have caused partial saponification of the polylactide samples.

Regardless of whether these assumptions are correct or not, the $\bar{M}_n$ measurements along with the succeeding study of back-biting processes allow, two important conclusions: (I) End-group analyses of polylactones overestimate the true $\overline{\mathrm{DP}}_n$'s, when the metal alkoxides used as initiators are good transesterification catalysts. In this connection it is worth noting that the $\overline{\mathrm{DP}}$'s calculated from viscosities in Table VIII are based on weight-average molecular weights. Therefore, it is reasonable that these $\overline{\mathrm{DP}}_w$'s are higher by a factor of 1.5–2.0 than the $\overline{\mathrm{DP}}_n$'s. (II) All alkoxide groups of an initiator are active at higher temperatures (e.g., above 50 °C) as indicated by the good agreement between calculated $\overline{\mathrm{DP}}_n$'s and those derived from end-group analyses.

In order to obtain independent evidence for conclusion II, several polymerizations (e.g., entries 3 and 12 of Table VII, entries 1 and 4 of Table VIII, and entries 5 and 8 of Table X) were repeated. The reaction mixtures were

Table IX
Reaction Conditions and Results of Solution Polymerization of β-Propiolactone Initiated by Various Metal Alkoxides

	initiator	M/I	solvent	temp, °C	time, h	yield,[a] %	end groups as revealed by ^{1}H and ^{13}C NMR spec
1	$Mg(OEt)_2$	5/1	diethylene glycol methyl ether	95	24	77	ethyl ester
2	$(n\text{-}Bu)_3SnOMe$	100/1	dioxane	95	48	43	methyl ester
3	$(n\text{-}Bu)_3SnO\text{-}t\text{-}Bu$	25/1	dioxane	25	24	21	*tert*-butyl ester
4	$(n\text{-}Bu)_3SnOPh$	50/1	dioxane	95	48	45	phenyl ester (+acrylate)
5	$Al(O\text{-}i\text{-}Pr)_3$	150/1	dioxane	95	24	59	isopropyl ester
6	$Ti(O\text{-}n\text{-}Bu)_4$	200/1	dioxane	95	48	53	*n*-butyl ester
7	$Zr(O\text{-}n\text{-}Pr)_4$	200/1	dioxane	95	48	48	*n*-propyl ester
8	$Zn(O\text{-}n\text{-}Bu)_2$	200/1	dioxane	95	48	55	*n*-butyl ester

[a] After precipitation from cold methanol.

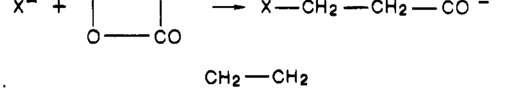
Table X
Bulk Polymerization of D,L-β-Butyrolactone with Various Metal Alkoxides

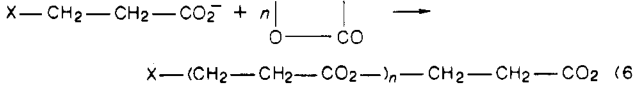
	initiator	M/I	temp, °C	time, h	conv,[a] %	end groups[b]
1	$Al(O\text{-}i\text{-}Pr)_3$	300/1	50	300	0	
2	$Al(O\text{-}i\text{-}Pr)_3$	300/1	75	400	100	isopropyl ester
3	$Al(O\text{-}i\text{-}Pr)_3$	300/1	100	48	100	isopropyl ester
4	$Ti(O\text{-}n\text{-}Bu)_4$	400/1	50	400	0	
5	$Ti(O\text{-}n\text{-}Bu)_4$	400/1	75	300	100	*n*-butyl ester
6	$Ti(O\text{-}n\text{-}Bu)_4$	400/1	100	120	100	*n*-butyl ester
7	Bu_3SnOMe	100/1	50	48	50	methyl ester
8	Bu_3SnOMe	100/1	75	48	100	methyl ester
9	Bu_3SnOMe	100/1	100	24	100	methyl ester
10	Bu_3SnOPh	100/1	75	24	20	phenyl ester[c]
11	Bu_3SnOPh	100/1	100	24	70	phenyl ester[c]

[a] Determined by means of IR and ^{1}H NMR spectroscopy. [b] As determined from 100- or 300-MHz ^{1}H NMR spectra. [c] As indicated by the ^{13}C signal of the quaternary carbon (at 144.9 ppm).

dissolved in $CDCl_3$ and directly subjected to ^{1}H NMR measurements. In all cases complete transformation of metal-bound alkoxide groups into alkyl ester end groups was found (Figures 2–4). As indicated by dotted arrows in Figures 2–4 (compare Table I and II), the shift differences of initiators and alkyl ester groups are sufficiently large to enable a clear-cut distinction. Thus, the ^{1}H NMR spectroscopic characterizations of reaction mixtures perfectly agree with end-group analyses of isolated polylactones.

Polymerization of β-Lactones. The results obtained with L,L-lactide and ε-caprolactone (Tables VII and VIII) suggest that both initiation and propagation step of polymerizations initiated by covalent metal alkoxides have a uniform mechanism which is characterized by cleavage of the acyl–oxygen bond. In this regard five-membered and higher membered lactones and glycolide react analogously with various nucleophiles including water and alcohols,[6,11] amines,[12] or anions.[6,8,13] Hence, anionic polymerizations initiated by alkoxide ions yield polylactones with alkyl ester end groups, and thus, end-groups analyses of the dead chain ends do not allow a differentiation between an anionic mechanism or an insertion mechanism. In contrast β-lactones react with nucleophiles, including anions, mainly or even exclusively by cleavage of the alkyl–oxygen bond.[14,15] Therefore, the reaction of β-propiolactone with an excess of highly nucleophilic anions enables the synthesis of β-substituted propionic acids in good yields[16] (eq 5). The alkylation of nucleophilic sites in proteins or DNS is also the reason for the carcinogenic property of β-propiolactone.


$$X^- + \underset{O\text{——}CO}{\overset{CH_2\text{—}CH_2}{|\qquad|}} \rightarrow X\text{—}CH_2\text{—}CH_2\text{—}CO^- \quad (5)$$


$$X\text{—}CH_2\text{—}CH_2\text{—}CO_2^- + n\underset{O\text{——}CO}{\overset{CH_2\text{—}CH_2}{|\qquad|}} \rightarrow X\text{—}(CH_2\text{—}CH_2\text{—}CO_2\text{—})_n\text{—}CH_2\text{—}CH_2\text{—}CO_2 \quad (6)$$

When β-lactones are treated with anions at high monomer/initiator ratios, an anionic polymerization is initiated which involves cleavage of the alkyl–oxygen bond by carboxylate ions (eq 6). A nucleophilic attack of the initiator at the carbonyl group may occur, but it is a minor side reaction.[15] Thus, end-group analyses of metal alkoxide initiated polymerizations should enable an unambiguous distinction between an anionic and an insertion mechanism. The results obtained from polymerizations of β-propiolactone in dioxane solution are summarized in Table IX. ^{1}H and ^{13}C NMR end-group analyses clearly indicated that all covalent and metal alkoxides yielded alkyl ester end groups and never alkyl ether groups.

A second series of polymerizations was conducted with D,L-β-butyrolactone in the absence of a solvent. β-Butyrolactone is rather insensitive to anionic initiators, because the methyl group in the β-position reduces the electrophilicity of the β-carbon for both steric and electric reasons. Nevertheless, all covalent metal alkoxides polymerized this β-lactone at temperatures above 50 °C. In contrast to poly(β-propiolactone), atactic poly-(D,L-β-butyrolactone) is difficult to precipitate completely. Therefore, the conversions of these polymerization (Table X) were determined by IR and ^{1}H NMR spectroscopy. IR spectroscopy is well suited for this purpose in the case of β-lactones, because their carboxyl band appears at 1825 cm^{-1}, whereas the carbonyl band of the polyesters absorbs at significantly lower wavenumbers (1730 cm^{-1}). Nonetheless, a fraction of the resulting poly(D,L-β-butyrolactone) was precipitated and subjected to NMR spectroscopic end-group analyses. Regardless of whether the original reaction mixture was examined (Figure 4) or the isolated polyester, alkyl ester end groups were found and never ether end groups. Thus, the polymerizations of β-lactones clearly demonstrate that covalent metal alkoxides initiated the insertion mechanism outlined in eq 1. This result is not only backed by the covalent nature of the initiators themselves, it is also

Table XI
Degradation of Poly(ε-caprolactone) by Means of Various Metal Alkoxides in Organic Solvents

	catalyst	temp, °C	solvent	yields (%) after			
				1 day	2 days	3 days	4 days
1	$Al(O\text{-}i\text{-}Pr)_3$	100	toluene	100	100	100	100
2	$Al(O\text{-}i\text{-}Pr)_3$	150	1,2,4-TCB[a]	100	100	100	100
3	$Ti(OBu)_3$	100	toluene	98	97	95	93
4	$Ti(OBu)_3$	150	1,2,4-TCB	98	90	90	85
5	$Zr(OPr)_3$	100	toluene	94	90	90	88
6	$Zr(OPr)_3$	150	1,2,4-TCB	94	62	50	46
7	$(n\text{-}Bu)_3SnOMe$	100	toluene	92	86	84	78
8	$(n\text{-}Bu)_3SnOMe$	150	1,2,4-TCB	50	47	45	43
9	$(n\text{-}Bu)_2Sn(OMe)_2$	100	toluene	61	58	49	42
10	$(n\text{-}Bu)_2Sn(OMe)_2$	150	1,2,4-TCB	50	46	30	27

[a] 1,2,4-Trichlorobenzene.

supported by the observation that covalent metal alkoxides enable a razemization-free polymerization of L,L-lactide at temperatures up to 150 °C (and even 180 °C).[17] At such high temperatures, basic metal salts cause considerable racemization.[18]

The Role of Transesterifications. It is well-known from anionic and cationic polymerizations of δ-valerolactone and ε-caprolactone that the ionic chains ends cause transesterification even at moderate temperatures (e.g., 50 °C).[7,15,19,20] *Intra*molecular transesterification, i.e., "back-biting", causes degradation and formation of cyclic oligomers. *Inter*molecular transesterification modifies the sequences of copolylactones and prevents the formation of block copolymers, and both *intra-* and *inter*molecular transesterification broaden the molecular weight distribution. All these effects were described for ionic polymerizations of lactones, whereas information on the transesterification activity of covalent metal alkoxides is scarce, at least when polymerization of lactones is considered.

On the other hand, it is also known that covalent metal alkoxides such as titanium or zirconium propoxides are good transesterification catalysts under conditions used for the technical production of polyesters, such as poly(ethylene terephthalate) and related copolyesters. However, the reaction temperatures of these condensation processes usually fall into the range 250–350 °C and, thus, do not give reliable information on their transesterification activities at temperatures between 50 and 150 °C, where most polymerizations of lactones are conducted. Because the results summarized in Table VII suggest that polymerizations of lactones initiated by covalent metal alkoxides may be affected by back-biting degradation even at 100 °C, a separate study on the transesterification activity of the metal alkoxides was undertaken. In a first series of experiments, commercially available, high molecular weight poly(ε-caprolactone) ($\bar{M}_w$ ~50 000) was combined with covalent metal alkoxides in an inert solvent and heated to 100 or 150 °C. After reaction times of 1, 2, 3, or 4 days the fraction of methanol-insoluble poly(ε-caprolactone) was determined. Because cyclic oligomers are soluble in methanol, this simple procedure allows the detection and quantification of degradation resulting from back-biting transesterification. The results listed in Table XI allow the following conclusions. With exception of aluminum isopropylate, all catalysts induce degradation by back-biting at 100 °C. The order of reactivity is $Al(O\text{-}i\text{-}Pr)_3 < Zr(O\text{-}n\text{-}Pr) < Ti(O\text{-}n\text{-}Bu)_4 < Bu_3SnOMe < Bu_2Sn(OMe)_2$.

In a second series of transesterification experiments the least reactive catalyst, $Al(O\text{-}i\text{-}Pr)_3$, and the most reactive catalyst, $Bu_2Sn(OMe)_2$, were added to a melt of poly(ε-caprolactone). The reaction mixtures were thermostated at 100 and 150 °C and were then analyzed after 4 h, 1 day, 2 days, and 4 days by means of GPC under conditions allowing the detection of monomer and oligomers. In agreement with the results of Table XI, no degradation was found with aluminum isopropoxide neither at 100 nor at 150 °C. In contrast, the reaction mixture containing dibutyltin dimethoxide displayed in the GPC curve not only a considerable broadening of the molecular weight distribution but also the peak of an oligomer (Figure 5).

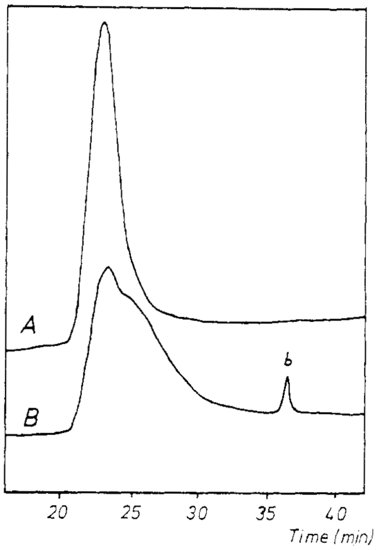


Figure 5. GPC curves of (A) original poly(ε-caprolactone) and a (B) poly(ε-caprolactone)/$Bu_2Sn(OCH_3)_2$ mixture (M/I = 100:1) after 4 h at 100 °C.

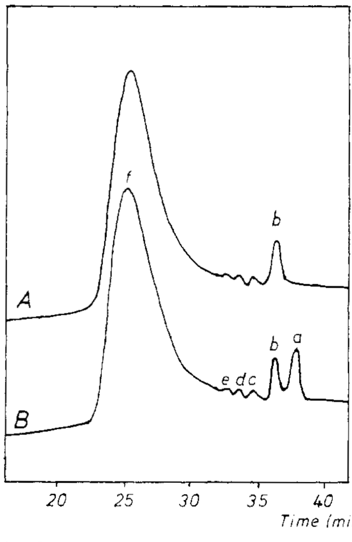


Figure 6. GPC curves of (A) a mixture of poly(ε-caprolactone)/$Bu_2Sn(OCH_3)_2$ (M/I = 100:1) after 96 at 150 °C and (B) the same sample as (A) with ε-caprolactone added.

After 24 h at 150 °C even peaks of four oligomers could be resolved (b–e in Figure 6). A comparison with the elution curve of ϵ-caprolactone (a in Figure 6) revealed that the most prominent peak of the degradation products (b in Figure 6) does not represent the monomer but the cyclic dimer. Obviously, the peaks c, d, and e represent the cyclic trimer, tetramer, and pentamer of ϵ-caprolactone. This conclusion is supported by two observations. First, when the reaction mixtures were analyzed by means of ^{1}H NMR spectroscopy, ϵ-caprolactone could not be detected, although the ^{1}H NMR signals allow a clear-cut distinction between monomer and polymer (including oligomers) (Table VI). Second, the GPC curves (Figures 5 and 6) perfectly agree with those of Yamashita and co-workers[7] who investigated the effect of degradation in anionic polymerizations of ϵ-caprolactone. These authors unambiguously identified the cyclic oligomers and confirmed that the cyclic dimer is the favored degradation product. In summary, the present results clearly demonstrate that not only ionic chain ends but also the covalent bonds of various metal alkoxides are active enough to cause rapid transesterification and back-biting at temperatures around 100 °C.

Conclusions

The present results along with those of previous investigations[1–4] suggest the following conclusions. All covalent metal alkoxides with free p or d orbitals react as coordination (or complexation) initiators and not as anionic or cationic initiators. The first step of their reaction with lactones is a complexation of these monomers at the carbonyl oxygen which is the most basic and most nucleophilic site of a lactone. IR spectroscopic evidence for such a complexation was recently presented by Kohn et al.[21] using various tin and aluminum compounds as complexing reagents. The next step is a cleavage of the acyl–oxygen bond of the lactone or, in other words, the insertion of the lactone into the metal–oxygen bond (eq 1). Therefore, this kind of polymerization mechanism is best called an "insertion mechanism" to enable a clear-cut distinction from mechanisms involving free ions or ion pairs. All alkoxide groups of an initiator may participate in the mechanism at least at temperatures above 50 °C. This insertion mechanism is valid for all kinds of alkoxide (and probably phenoxide) groups and it is operating for all classes of lactones. Furthermore, it is noteworthy that covalent metal alkoxides may cause transesterification, in particular degradation by back-biting, at temperatures around or even below 100 °C. The transesterification activity is high for tin alkoxides and low for aluminum alkoxides. Thus, tin alkoxides are useful initiators when copoly(lactones) with random sequences are to be synthesized, wheres aluminum isopropoxide is best suited for the synthesis of block copolyesters. NMR spectroscopic results confirming this conclusion for copolymerizations of ϵ-caprolactone and L,L-lactide were presented in a previous part of this series.[5]

Registry No. Magnesium ethoxide, 2414-98-4; aluminum isopropoxide, 555-31-7; potassium *tert*-butoxide, 865-47-4; titanium *n*-butoxide, 5593-70-4; zirconium *n*-propoxide, 23519-77-9; butyltin methoxide, 1067-59-0; dibutyltin dimethoxide, 1067-55-6; tributyltin methoxide, 1067-52-3; zinc di-*n*-butoxide, 13422-22-5; (L,L)-lactide, 4511-42-6; (L,L)-lactide (homopolymer), 33135-50-1; (L,L)-lactide (SRU), 26161-42-2; (DL)-β-butyrolactone, 36536-46-6; (DL)-β-butyrolactone (homopolymer), 36521-53-6; (DL)-β-butyrolactone (SRU), 35038-21-2; β-propiolactone, 57-57-8; β-propiolactone (homopolymer), 25037-58-5; β-propiolactone (SRU), 24938-43-0; ϵ-caprolactone, 502-44-3; ϵ-caprolactone (homopolymer), 24980-41-4; ϵ-caprolactone (SRU), 25248-42-4; tributyltin phenoxide, 3587-18-6.

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