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Macromolecular Engineering of Polylactones and Polylactides. 19. Kinetics of Ring-Opening Polymerization of ϵ-Caprolactone Initiated with Functional Aluminum Alkoxides

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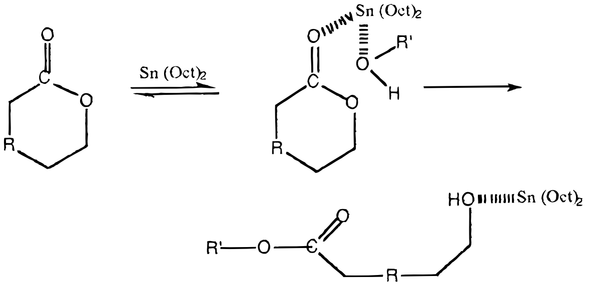
ABSTRACT: End-functional aliphatic polyesters have been synthesized by ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) and lactides (LA). Polymerization initiated with any of the functional aluminum alkoxides of the general structure $Et_{3-p}Al(OCH_2X)_p$, where $p = 1$ and 3, obeys a living "coordination−insertion" mechanism, under suitable conditions (temperature, concentration, and solvent), with the formation of α-functional chains of a predictable molecular weight. A kinetic study has emphasized the importance of the cyclic monomer (ϵ-CL or LA) and the key role of the initiator structure: the number of functional alkoxides per aluminum and the nature of the functional group (X = CH_2Br, $(CH_2)_2CH{=}CH_2$, $(CH_2)_2NEt_2$). Activation enthalpy and entropy have been calculated for the ϵ-CL polymerization initiated by several aluminum alkoxides at various temperatures. The effects of solvent (toluene or tetrahydrofuran) and purification of the aluminum monoalkoxides by distillation under reduced pressure have also been considered.

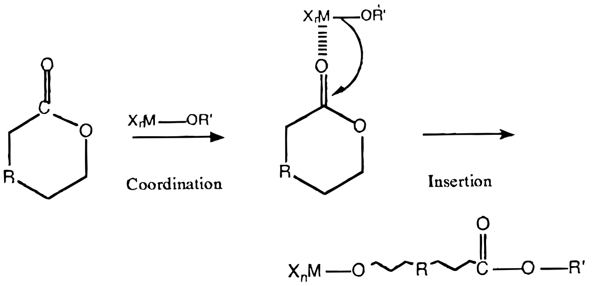
Introduction

The discovery that some organometallic compounds, such as alkylmetals and metal halides, oxides, carboxylates, and alkoxides, are very effective initiators for the synthesis of high molecular weight aliphatic polyesters has renewed interest in the ring-opening polymerization (ROP) of lactones.[1,2] Metal compounds were first used as ionic initiators,[1,3] although it is clear now that most metal derivatives initiate the chain reaction through an activated covalent bond.[4] Polymerization is usually assumed to proceed through an insertion process, the intimate mechanism of which depends on the metal compound. For instance, metal halides, oxides, and carboxylates act as Lewis acid catalysts in the ROP initiated with hydroxyl-containing compounds, e.g., water and alcohols (eq 1 for tin octanoate).[5−7] ROP is then very sensitive to the relative content of hydroxyl impurities, which explains why polyester chains cannot be synthesized in a well-controlled manner.[6,8] When metal alkoxides containing free p- or d-orbitals of a favorable energy (Mg, Sn, Ti, Zr, Zn, and Al alkoxides) are used as initiators, a two-step "coordination−insertion" mechanism is proposed, which consists of lactone complexation to the initiator followed by monomer insertion into the metal−oxygen bond (eq 2).[5,9,10] Hydrolysis of the active metal−alkoxide bond leads to the formation of a hydroxyl end group. The second chain end is capped with an ester carrying the alkoxy radical of the initiator.



where R' = H or alkyl group

[1]



[2]

The controlled synthesis of high molecular weight polyesters requires the complete absence, or at least severe limitation, of side inter- and intramolecular transesterification reactions, which perturb chain propagation and broaden the molecular weight distribution. In this respect, the nature of the metal is of prime importance, as supported by the relative reactivity of some metal alkoxides toward linear PCL chains already formed (back-biting or intermolecular side reactions): $Bu_2Sn(OR)_2 > Bu_3SnOR > Ti(OR)_4 > Zn(OR)_2 > Al(OR)_3$.[11] On this basis, some of us have reported on the "living" polymerization of ϵ-caprolactone (ϵ-CL) initiated by aluminum alkoxides, particularly bimetallic (Zn, Al) μ-oxo alkoxides[12,13] and aluminum triisopropoxide, $Al(O^iPr)_3$.[14,15,27] When the ϵ-CL polymerization is initiated by aluminum alkoxides at 0 or 25 °C,[16] the average degree of polymerization of the linear polyester chains is in very close agreement with the monomer to initiator molar ratio, at least within the time required for the complete monomer conversion. Indeed, the molecular weight distribution becomes broader when living chains are kept in the reaction medium beyond this time. Thus, ROP of ϵ-CL has to be kinetically controlled to prevent any deleterious effect of side reactions on the molecular characteristic features of PCL chains. The extent of these side reactions, mainly back-biting reactions, has recently been studied by Penczek and Duda, who have quantitatively described the tendency toward back-biting by the so-called selectivity parameter (β),

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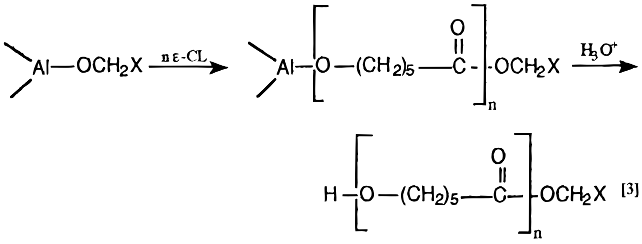
defined as the ratio of the rate constant of propagation to the rate constant of back-biting ($\beta = k_p/k_{bb}$).[17]

The kinetic control of PCL molecular parameters has been successfully extended to ROP of lactides,[18] glycolide,[19] and cyclic anhydrides[20] initiated with $Al(O^iPr)_3$ in toluene or THF. More recently, the selective end-functionalization of poly(ϵ-caprolactone) (PCL),[21,22] polylactides (PLA),[23,24] poly(glycolide) (PGA),[19] and poly(adipic anhydride)[20] has been investigated by using functional aluminum alkoxides as initiators: $(C_2H_5)_{3-p}Al(OCH_2X)_p$, where for **1**, $p = 1$, and for **2**, $p = 3$, with **a** CH_2Br, **b** $(CH_2)_2CH{=}CH_2$, and **c** $(CH_2)_2NEt_2$. In agreement with eq 2, the functional group (OCH_2X) of the active aluminum alkoxides is selectively attached to one chain end:



The purpose of this paper is to investigate the kinetics of ϵ-CL polymerization initiated by functional aluminum alkoxides in toluene. Propagation rate constant and enthalpy and entropy of activation will be determined. The kinetic study will be extended to several aluminum alkoxides in relation to the number of alkoxy groups per Al atom and the structure of the alkoxy groups, particularly functional ones (OCH_2X). The effect of solvent polarity will also be considered by substituting tetrahydrofuran (THF) for toluene. The kinetics of ϵ-CL polymerization will be compared to kinetic data previously reported for D,L-lactide ROP under similar experimental conditions.[24]

Experimental Section

Materials. ϵ-CL (Janssen Chimica), 4-penten-1-ol (Aldrich), 2-propanol (Janssen Chimica), and 3-(diethylamino)-1-propanol (Aldrich) were dried over calcium hydride for 48 h at room temperature and distilled under reduced pressure just before use. 2-Bromoethanol (Aldrich) was treated repeatedly with a saturated aqueous solution of K_2CO_3, dried over P_2O_5, and freshly distilled under reduced pressure. Previously distilled aluminum isopropoxide (Aldrich) and triethylaluminum (Fluka) were dissolved in dry toluene. Concentration of these solutions was measured by complexometric titration of Al with a standard solution of EDTA. 1,4-Dibromobutane (Aldrich) and 1,4-dichloro-2-butene (Aldrich) were treated with a saturated aqueous solution of $NaHCO_3$, washed with H_2O, dried over $CaCl_2$, and freshly distilled under reduced pressure. Toluene and tetrahydrofuran (THF) were dried by refluxing over calcium hydride and a sodium−benzophenone complex, respectively.

Preparation of the Initiators. The main experimental details were published elsewhere.[18,20,21,23,24] Diethylaluminum alkoxides **1** were prepared by slowly adding a toluene solution of a selected alcohol into a flask containing $AlEt_3$ (1.05 equiv) at −78 °C (eq 4). The glass reactor was equipped with a rubber septum connected through an oil valve to a gas buret and was previously purged with nitrogen. The reaction equilibrium was favorably displaced by the formation and elimination of ethane (eq 4). The temperature was slowly raised to 0 or 25 °C, and the reaction proceeded under vigorous stirring. It was followed by volumetric measurement of ethane. When the emission of ethane stopped, the initiator solution was allowed to stir for an extra hour before being used to initiate the ϵ-CL polymerization at 0 or 25 °C.

$$Et_3Al + HOCH_2X \xrightarrow{\text{toluene}} \underset{\mathbf{1}}{Et_2AlOCH_2X} + C_2H_6 \qquad (4)$$

$$(^iPrO)_3Al + 3HOCH_2X \xrightleftharpoons{\text{toluene}} \underset{\mathbf{2}}{(XCH_2O)_3Al} + 3^iPrOH \qquad (5)$$

Kinetic and thermodynamic parameters of ϵ-CL polymerization were first determined by using these *in situ* prepared initiators **1a**−**c** and compared to those from the ROP promoted by initiators **1** further purified by distillation under reduced pressure (10^{-2} mmHg) and dissolved in dry toluene. Indeed, the *in situ* prepared initiators might be contaminated by unreacted reagents and/or by aluminum di- and trialkoxides, although, under the aforementioned conditions, no aluminum di- or trialkoxide was observed by ^1H NMR.[36]

Aluminum trialkoxides **2** were synthesized by the reaction of $Al(O^iPr)_3$ with 3 equiv of the appropriate alcohol (eq 5) in a carefully dried and nitrogen purged distillation apparatus. The toluene/isopropyl alcohol azeotrope was continuously distilled off, which favorably displaced the reaction equilibrium. The expected structures of initiators **2** were confirmed by ^1H NMR, complexometric titration of Al, and gas chromatography.[28,36]

Polymerization Procedure. Polymerization was carried out under stirring, in toluene or THF, in a previously flamed and nitrogen-purged glass reactor, at a constant temperature for a suitable period of time. Solvent, ϵ-CL, and initiator were successively added through a rubber septum with a syringe or a stainless steel capillary.

Samples of a well-known volume were picked from the reaction medium after different periods of time, hydrolyzed, and precipitated in cold *n*-heptane. After filtration and drying under vacuum to a constant weight, PCL samples were weighed, making the time dependence of monomer conversion available (gravimetric method).

Characterization. Molecular weights and molecular weight distributions were determined by using a gel permeation chromatograph (GPC Hewlett-Packard 1090) operating in THF at 30 °C and calibrated with polystyrene (PSt) standards. The universal calibration curve was used for PCL on the basis of the following viscosimetric relationship:[16] $M_{PCL} = 0.259M_{PSt}{}^{1.073}$

Low molecular weights ($\bar{M}_n < 15\,000$) were also measured by ^1H NMR in $CDCl_3$ and dried C_6D_6 with a Bruker AM400 apparatus at 25 °C. $\bar{M}_n$ (^1H NMR) was calculated from the relative intensities of the signals corresponding to the functional ester end group and the methylene ester groups within the polyester chain, respectively.[21] Good agreement was usually observed for $\bar{M}_n$'s measured by SEC and ^1H NMR.

The inherent viscosity of living and deactivated PCL chains in toluene was measured in a previously flame-dried, nitrogen-purged glass Ubbelohde viscosimeter at 25 °C.

Results and Discussion

ϵ-CL Polymerization in Toluene. A "living" mechanism is observed when the polymerization of ϵ-CL is initiated in toluene at 25 °C by any of the functional aluminum alkoxides of the **1a**−**c** and **2a**−**c** series. This is supported by the close agreement between the number-average molecular weight ($\bar{M}_n{}^{exp}$) at total monomer conversion and the monomer to initiator molar ratio.[9] This relationship holds even for the synthesis of very high molecular weight polyesters ($\bar{M}_n = 110\,000$).[21] From the slope of the linear dependence of $\bar{M}_n$ vs $[\epsilon\text{-CL}]_0/[Al]$, it appears that the average number of active alkoxy groups per aluminum molecule ($\bar{n}$) is equal to 1 at 25 °C when the initiator is a diethylaluminum monoalkoxide of the **1a**−**c** series (Table 1). In contrast, when the aluminum trialkoxides of the **2a**−**c** series are concerned, the value of $\bar{n}$ depends on the functional OCH_2X radical (Table 1).

When the functional alkoxides **1** and **2** are used to initiate the ϵ-CL polymerization in toluene at 25 °C,

Table 1. Average Number of Active Alkoxy Groups per Initiator Molecule ($\bar{n}$) and Induction Period of Time (t_i) in the ϵ-CL Polymerization Initiated by the *in Situ* Prepared Et_2AlOR 1a−c and $Al(OR)_3$ 2a−c[a]

	$\bar{n}$		t_i (min)	
initiator	at 0 °C	at 25−30 °C	at 0 °C	at 25−30 °C
$Et_2AlO(CH_2)_2Br$ (**1a**)	0.8	1.0	9	2
$Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**)	0.7	1.0	7	2
$Et_2AlO(CH_2)_3NEt_2$[b] (**1c**)	0.85	1.0	30	8
$Al(O^iPr)_3$	0.9	1.0		
$Al[O(CH_2)_2Br]_3$ (**2a**)	3.0[c]	3.0	5	2
$Al[O(CH_2)_3CH{=}CH_2]_3$ (**2b**)	0.7	0.8	4	2
$Al[O(CH_2)_3NEt_2]_3$ (**2c**)	1.8	1.8	8	3

[a] $[M]_0 = 1.06$ mol L^{-1} for the aluminum monoalkoxides **1** and $Al(O^iPr)_3$ and $[M]_0 = 0.86$ mol L^{-1} for the aluminum trialkoxides **2** in toluene. [b] $[M]_0 = 0.90$ mol L^{-1}. [c] For $[I]_0 > 1.2 \times 10^{-2}$ mol L^{-1}.

Table 2. Reaction Yield of Triethylaluminum with 1 equiv of HORX in Toluene

HORX	yield (%) at 22 °C[a]	T (°C) (yield = 100%)[b]
$HO(CH_2)_2Br$	95	30
$HO(CH_2)_3NEt_2$	87 ± 3	30
$HO(CH_2)_2OC(O)C(Me){=}CH_2$	80 ± 3	40
$[HO(CH_2)_2]_2NMe$	59 ± 6	60
$HO(CH_2)_3CH{=}CH_2$	55 ± 4	75
$HO(CH_2)_4OH$[c]	55 ± 2	
$HOCH(CH_3)_2$	46 ± 4	90

[a] Average value for two volumetric measurements. [b] Lower temperature necessary to reach a quantitative substitution (100% = yield). [c] Substitution carried out in THF.

samples of a rather narrow molecular weight distribution are obtained ($\bar{M}_w/\bar{M}_n = 1.05-1.2$). Quite clearly, that distribution is broadened substantially when the polymerization time exceeds the time required for complete monomer conversion. This is likely due to the occurrence of intra- and intermolecular transesterification reactions. Interestingly enough, GPC, IR, and ^1H NMR studies have unambiguously shown that the function X associated to the alkoxy groups of the initiator is selectively and quantitatively attached to one chain end and that the second end group is systematically a hydroxyl function resulting from the hydrolysis of the living growing site.[9]

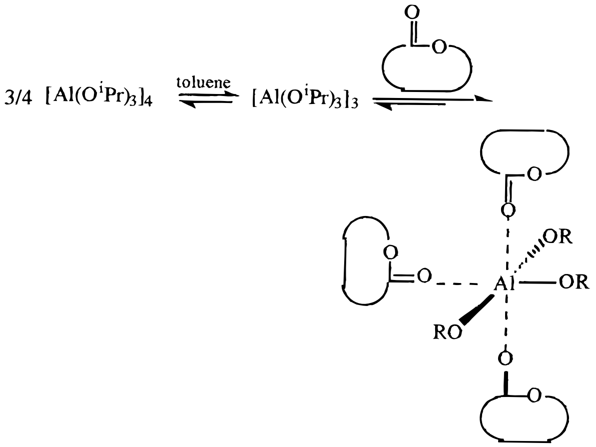
The ϵ-CL polymerization is also living, when initiated by the aluminum trialkoxides of the **2a−c** series in toluene, at a lower temperature (0 °C). It is worth noting that the average number of the growing chains per initiator molecule ($\bar{n}$) is less than 1 when polymerization is initiated by the *in situ* prepared aluminum monoalkoxides of the **1a−c** series in toluene at 0 °C (Table 1). This observation means that the initiation step is not quantitative, which is more likely due to an incomplete *in situ* reaction of Et_3Al with the functional alcohol (XCH_2OH) at 0 °C (eq 4). Actually, the initiation efficiency increases with temperature and is 1 at 25 °C (Table 1).

The volumetric measurement of ethane shows that synthesis of the diethylaluminum monoalkoxides depends on the acidity of the alcohol. Indeed, when this acidity is increased, the reaction is more complete and the temperature required for a quantitative reaction is lower (Table 2). For instance, reaction of Et_3Al with 1-bromo-2-ethanol is complete at 30 °C, although a 55% conversion is observed at 22 °C when the alcohol is 4-penten-1-ol (Table 2).

It must also be pointed out that initiation of the ϵ-CL polymerization by the *in situ* prepared diethylaluminum alkoxides **1** in toluene at 0 °C leads to a broad molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.4-1.8$). An exchange reaction between the aluminum alkoxy groups of the initiator and the unreacted alcohol might be responsible for this effect. This type of reaction has indeed been shown to occur when 2 or 3 equiv of isopropyl alcohol is added to aluminum triisopropoxide used as an initiator in the ϵ-CL and lactides ROP.[28,29]

Kinetics of the ϵ-CL polymerization initiated by the aluminum alkoxides **1** and **2** has been investigated, in toluene at 0 or 25 °C, under "living" conditions and is discussed in relation to the number of alkoxy groups per Al atom, the nature of the functional groups, and the purification of the initiators **1** by distillation.

Initiation by Al Trialkoxides 2. The ϵ-CL polymerization is *first order in monomer* when initiated in toluene by the aluminum trialkoxides **2a−c** at 0 and 25 °C. Indeed, a linear relationship between the monomer conversion [ln([M]/[M]$_0$] and the polymerization time is systematically observed, as illustrated by Figure 1A, in the particular case of the initiator **2c**. Nevertheless, an induction period is systematically observed when polymerization of ϵ-CL and LA is initiated by aluminum alkoxides.[9,14,18] This feature has recently been attributed to a rearrangement of the coordinative aggregates of the initiator in toluene upon monomer addition, as schematized for $Al(O^iPr)_3$ in eq 6.[25,26,37]



[6]

Aluminum alkoxides are indeed known to be aggregated in solution.[38,39] For instance, there is an equilibrium between trimers and tetramers when $Al(O^iPr)_3$ is dissolved in toluene.[25] Due to the much lower reactivity of the tetramers toward ϵ-CL and the low rate of conversion of tetramers into trimers and vice versa, ϵ-CL polymerization is essentially promoted by the trimers.[27] The effective active species in living ROP of ϵ-CL has recently been proposed as a monomer trisolvated octahedral complex, e.g., $Al(O^iPr)_3\cdot(\epsilon\text{-CL})_3$, more likely resulting from the selective deassociation of the trimeric species in the presence of the cyclic monomer.[26,37]

When functional aluminum alkoxides **2** are used in toluene, the induction period is usually smaller than 10 min and largely independent of the initiator (Table 1). Due to the induction period, the polymerization rate constant has to be determined from the slope of the linear dependence of ln([M]/[M]$_0$) vs time rather than from the half-reaction time. The kinetic equation thus is as follows:

$$-d[M]/dt = k_{app}[M] \qquad (7)$$

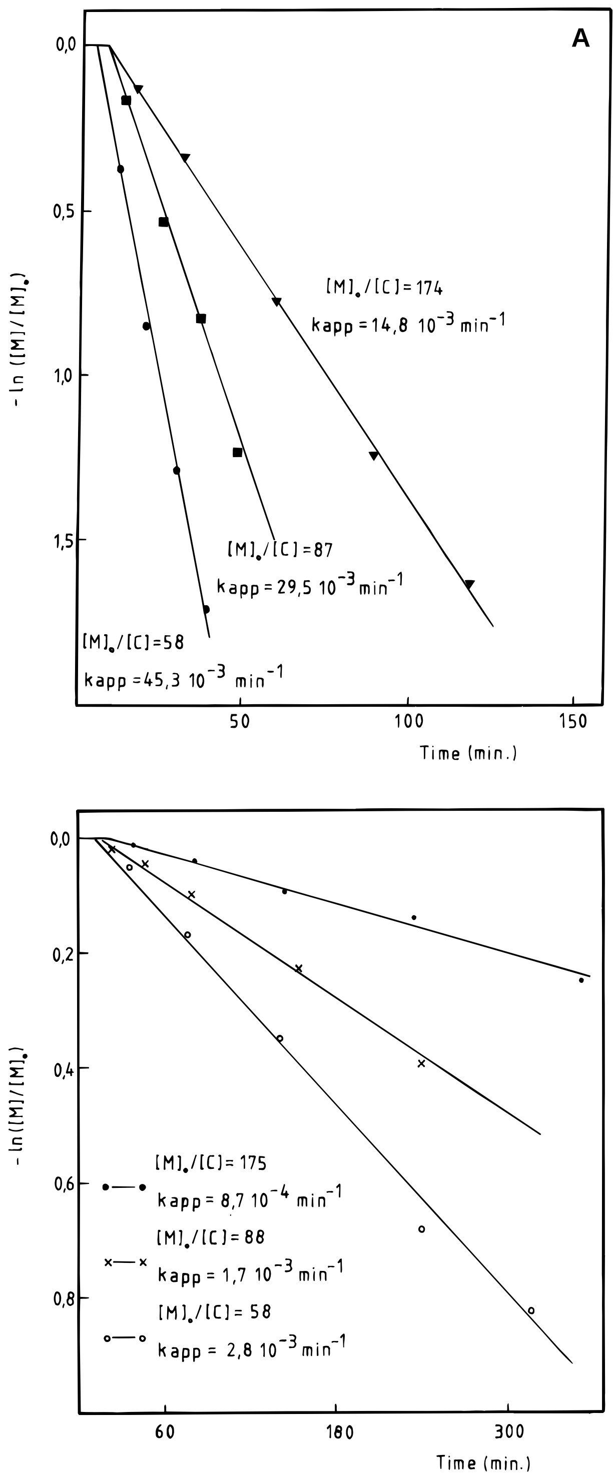


Figure 1. Kinetics of the ϵ-CL polymerization in toluene at 0 °C, initiated by (A) $Al[O(CH_2)_3NEt_2]_3$ (**2c**) ($[M]_0 = 0.86$ mol L^{-1}) and (B) *in situ* prepared $Et_2AlOCH_2CH_2Br$ (**1a**) ($[M]_0 = 1.06$ mol L^{-1}).

where k_{app} is the apparent rate constant calculated from the slope of the $\ln([M]/[M]_0)$ vs time curves (see Figure 1 as an example).

This is the reason why it is more realistic to consider the kinetic order in the active alkoxy groups rather than in the aluminum derivative. The average number of active sites per Al ($\bar{n}$) can be calculated from the number-average molecular weight ($\bar{M}_n$) of polyester chains formed at complete monomer conversion. The molar concentration in polymer chains ([P], mol L^{-1}) is expressed by

$$[P] = 114[M]_0/\bar{M}_n \tag{8}$$

Since the polymerization is living,[21-23] [P] is nothing but the molar concentration in active sites ([C], mol L^{-1}), and the [P]/[C] molar ratio is the number of growing chains—and thus active alkoxy groups—per Al atom ($\bar{n}$). The number-average molecular weight of PCL ($\bar{M}_n$), molar concentration of polymer chains ([P]), mean number of active sites per Al, and k_{app}/[C] are reported in Table 3.

If the ϵ-CL polymerization is assumed to be first order in initiator, the k_{app}/[C] ratio must be constant as long as the number of active sites is independent of the initiator concentration. Except for the ϵ-CL polymerization with $Al[O(CH_2)_2Br]_3$ (**2a**), the k_{app}/[C] ratio and the average number of active sites per Al ($\bar{n}$) are independent of the initiator concentration [C] and thus provide evidence for a first order in initiator (Table 3). The absolute polymerization rate constant (k) has been calculated from the slope of these k_{app} vs [C] plots:

$$k = k_{app}/[C] = -\frac{(\ln[M]/[M]_0)/t}{[C]} \quad (\mathrm{L\ mol^{-1}\ min^{-1}}) \tag{9}$$

Aluminum tribromoethoxide ($Al[O(CH_2)_2Br]_3$, **2a**) is an exception, since the first order in initiator is only observed when [C] is higher than 1.2×10^{-2} mol L^{-1}, at an initial monomer concentration $[M]_0$ of 0.86 mol L^{-1} (Figure 2A). There is a parallel decrease in the mean number of active alkoxy groups per Al atom ($\bar{n}$) and the initiator concentration below 1.2×10^{-2} mol L^{-1} (Table 3).

Number of Active Sites for the $Al(OCH_2CH_2Br)_3$ Initiator (2a). Figure 3 shows the dependence of the k_{app}/[C] ratio on the initiator concentration for ϵ-CL polymerization initiated by the brominated aluminum alkoxides **1a** and **2a**. In case of the *in situ* prepared $Et_2AlOCH_2CH_2Br$ monoalkoxide **1a** (see the following section), k_{app}/[C] is independent of [C] in contrast to the $Al[OCH_2CH_2Br]_3$ trialkoxide **2a**, since the independence is then only observed at [C] higher than 1.2×10^{-2} mol L^{-1}. Nevertheless, when k_{app} is plotted vs the polymer concentration [P], a linear relationship with a slope of 0.74 L mol^{-1} min^{-1} is observed (Figure 4). As previously discussed, [P] is the actual concentration of the active sites. Thus, the kinetic equation for the aluminum trialkoxide **2a** is first order in the active sites, and the mean number of active alkoxy groups is in the range of 2–3, depending on [C].

The dependence of $\bar{n}$ on the concentration of $Al[O(CH_2)_2Br]_3$ (**2a**) is surprising. One may suspect that the bromine atoms interfere in the initiation process by promoting the partial coordinative association of $Al[O(CH_2)_2Br]_3$. This is the reason why the ϵ-CL polymerization in toluene at 0 °C has been revisited by using the initiator **2a** in the same concentration range as before, but in the presence of a halogenated compound such as 1,4-dibromobutane (DBB) or 1,4-dichloro-2-butene (DCB) (Table 4). Under these experimental conditions, the k_{app}/[C] ratio is now independent of the initiator **2a** concentration and all of the alkoxy groups are active ($\bar{n} = 3$) even at concentrations smaller than 1.2×10^{-2} mol L^{-1}. It is thus clear that halogen atoms play a key role in the solution behavior of the initiator **2a**. It is proposed that bromine or chlorine efficiently competes with the alkoxy groups for coordination to aluminum as schematized by eq 10. As a

Table 3. Polymerization of ε-CL Initiated by the Aluminum Trialkoxides 2a–c and the *in Situ* Prepared Aluminum Monoalkoxides 1a–c in Toluene at 0 °C ([M]$_0$ = 0.86 and 1.06 mol L^{-1} for 2a–c and 1a–c, respectively)

initiator	[C] ($\times 10^3$ mol L^{-1})	k_{app} (min^{-1})	k_{app}/[C] (mol L^{-1} min^{-1})	$\bar{M}_n$	[P] ($\times 10^3$ mol L^{-1})	$\bar{n}$
$Al[O(CH_2)_2Br]_3$ (**2a**)	20.5	48.0×10^{-3}	2.3	1500	65.4	3.2
	15.4	37.0×10^{-3}	2.4	2000	49.0	3.2
	8.25	17.0×10^{-3}	2.1	4500	21.8	2.65
	5.15	8.2×10^{-3}	1.6	9500	10.2	2.0
$Al[O(CH_2)_3CH{=}CH_2]_3$ (**2b**)	12.6	11.0×10^{-2}	8.7			
	8.4	7.3×10^{-2}	8.7	16500	5.7	0.7
	4.3	3.6×10^{-2}	8.4	33500	3.0	0.7
$Al[O(CH_2)_3NEt_2]_3$ (**2c**)	14.85	45.3×10^{-3}	3.05	11200	25.2	1.7
	9.9	29.5×10^{-3}	3.0			
	4.95	14.8×10^{-3}	3.0	11200	8.9	1.8
$Et_2AlO(CH_2)_2Br$ (**1a**)	24.2	3.5×10^{-3}	1.45×10^{-1}	6300	19.2	0.8
	18.5	2.8×10^{-3}	1.5×10^{-1}			
	12.0	1.7×10^{-3}	1.4×10^{-1}	14100	8.5	0.7
	6.0	8.7×10^{-4}	1.45×10^{-1}	10000[a]	4.8	0.8[a]
$Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**)	24.2	3.5×10^{-3}	1.5×10^{-1}	7250	16.9	0.7
	12.0	1.9×10^{-3}	1.6×10^{-1}	13500	9.1	0.75
	6.1	9.6×10^{-3}	1.6×10^{-1}	28500	4.3	0.7
$Et_2AlO(CH_2)_3NEt_2$[b] (**1c**)	20.6	6.4×10^{-3}	3.1×10^{-2}	5800	17.6	0.85
	10.3	3.0×10^{-3}	2.9×10^{-2}	11750	8.7	0.85

[a] As determined at 40% conversion. [b] [M]$_0$ = 0.90 mol L^{-1}.

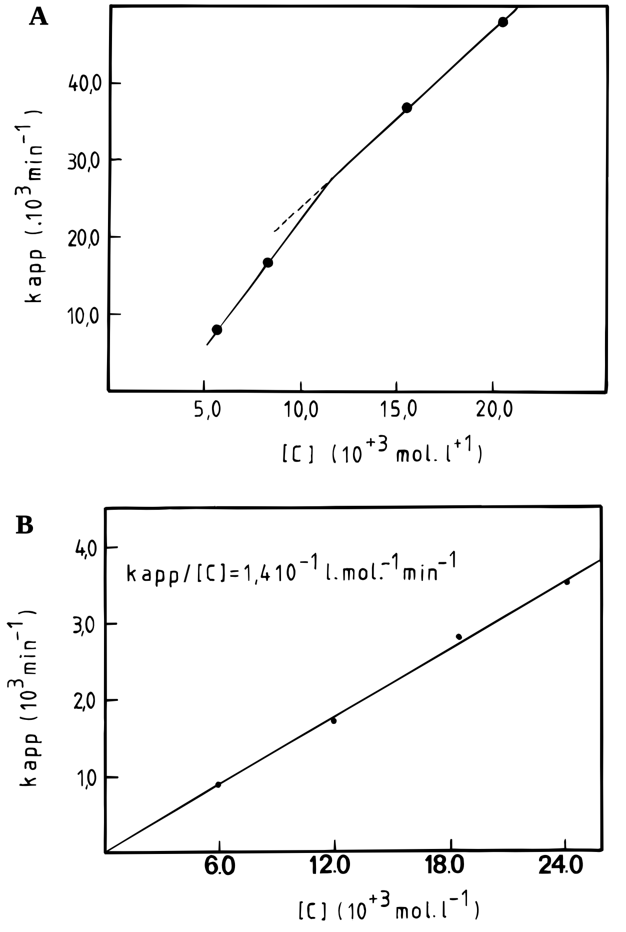
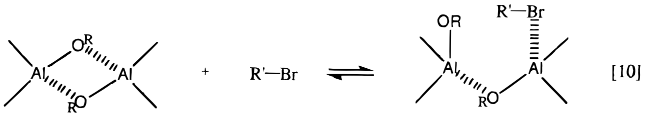


Figure 2. Dependence of k_{app} on the initiator concentration [C] for the ε-CL polymerization initiated by (A) $Al[O(CH_2)_2Br]_3$ (**2a**) and (B) *in situ* prepared $Et_2AlO(CH_2)_2Br$ (**1a**). Same conditions as in Figure 1.

result, alkoxy groups remain available to the ε-CL polymerization.



[10]

In eq 10, R′Br may represent $Al(OCH_2CH_2Br)_3$, and the equilibrium is then shifted toward the right upon increasing concentration of the brominated trialkoxide. It is worth pointing out that increasing the temperature also perturbs the association of the functional aluminum trialkoxide **2a**. For instance, $\bar{n}$ amounts to 3 at 30 °C, even for [C] < 1.2×10^{-2} mol L^{-1}. This behavior is also specific to the brominated trialkoxide **2a** and proves that the halogen–aluminum interactions are more favorable at higher temperatures, in agreement with the endothermicity of the competitive coordination reaction (eq 10). The driving force for this reaction must be a

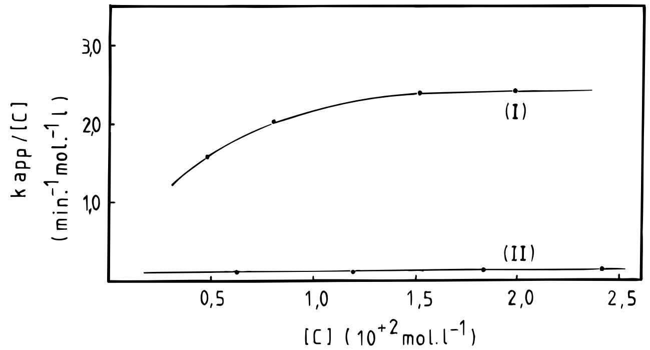


Figure 3. Dependence of k_{app}/[C] on [C] for the ε-CL polymerization initiated by (I) $Al(OCH_2CH_2Br)_3$ (**2a**) and (II) *in situ* prepared $Et_2AlOCH_2CH_2Br$ (**1a**). Same conditions as in Figure 1.

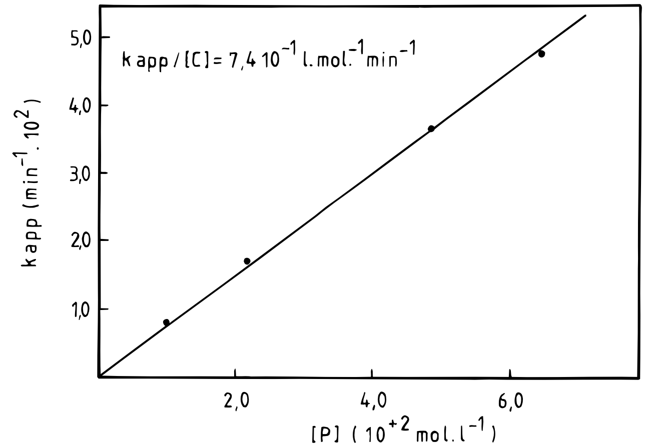


Figure 4. Dependence of k_{app} on the polymer concentration [P] for the ε-CL polymerization initiated by $Al(OCH_2CH_2Br)_3$ (**2a**) in toluene at 0 °C ([M]$_0$ = 0.86 mol L^{-1}).

Table 4. Polymerization of ϵ-CL Initiated by $Al[O(CH_2)_2Br]_3$ (2a) in Toluene at 0 °C in the Presence of DBB and DCB

HALO compound	[C] ($\times 10^3$ mol L^{-1})	$[M]_0$ ($\times 10^1$ mol L^{-1})	[HALO] ($\times 10^2$ mol L^{-1})	k_{app} ($\times 10^3$ min^{-1})	k_{app}/[C] (mol L^{-1} min^{-1})	$\bar{M}_n$	[P] ($\times 10^3$ mol L^{-1})	$\bar{n}$
DBB	15.4	8.6	15.8	36.0	2.3	2000	49.0	3.2
DBB	10.3	8.6	15.8	24.0	2.3	3200	30.3	3.0
DCB	5.15	8.6	18.0	12.4	2.4	6300	15.6	3.0

Table 5. Polymerization of ϵ-CL and D,L-LA Initiated by the Aluminum Trialkoxides 2a−c and the *in Situ* Prepared Aluminum Monoalkoxides 1a−c in Toluene

	$\bar{n}$		k (L mol^{-1} min^{-1})	
initiator	ϵ-CL (25 °C)	D,L-LA (70 °C)	ϵ-CL (0 °C)	D,L-LA (70 °C)
$Al[O(CH_2)_2Br]_3$ (**2a**)	3.0	3.0	2.3[a]	1.9×10^{-1}
$Al[O(CH_2)_3CH{=}CH_2]_3$ (**2b**)	0.8	3.0	8.6	1.3×10^{-1}
$Al[O(CH_2)_3NEt_2]_3$ (**2c**)	1.8		3.0	
$Et_2AlO(CH_2)_2Br$ (**1a**)	1.0	1.0	1.4×10^{-1}	1.1×10^{-2}
$Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**)	1.1	1.0	1.6×10^{-1}	1.0×10^{-2}
$Et_2AlO(CH_2)_3NEt_2$ (**1c**)	1.0		3.0×10^{-2}	

[a] [C] > 1.2×10^{-2} mol L^{-1} or in the presence of DBB or DCB.

Table 6. Polymerization of ϵ-CL in THF and Benzene ($[M]_0 = 2.0$ mol L^{-1}) at 25 °C (from refs 27, 28, and 32)

initiator	solvent	k_p (L mol^{-1}, s^{-1})	K_{da} (mol $L^{-1})^{m-1}$	m
$Et_2AlO(CH_2)_2Br$[a]	THF	2.8×10^{-2}	8.9×10^{-7}	3
$Et_2AlOCH_2CH{=}CH_2$	THF	4.0×10^{-2}	1.2×10^{-7}	3
$(^iBu)_2AlOCH_3$	THF	4.2×10^{-2}	6.7×10^{-3}	2
$Et_2AlOC_2H_5$	benzene	1.4×10^{-1}	1.2×10^{-6}	3

[a] $[M_0] = 1.06$ mol L^{-1}.

positive change in entropy, which may be found in the dissociation of the aluminum aggregates with the release of active alkoxy groups.

As a rule, ϵ-CL polymerization in toluene obeys eq 11, regardless of the aluminum alkoxide **2a−c**, as long as the mean number of active sites per aluminum atom ($\bar{n}$) is independent of the initiator concentration [C].

$$-d[M]/dt = k[M][C] \tag{11}$$

k is the absolute rate constant expressed in liters mole^{-1} minute^{-1}. The same kinetic equation has been reported for the lactide polymerization initiated with aluminum alkoxides in toluene at 70 °C.[24] All of the kinetic data (k and $\bar{n}$) pertinent to the ϵ-CL and D,L-LA polymerizations are listed in Table 5. In agreement with the experimental observations reported for $Al(O^iPr)_3$,[18] rate constants are higher for ϵ-CL than for D,L-LA, regardless of the functional aluminum alkoxides **2**.

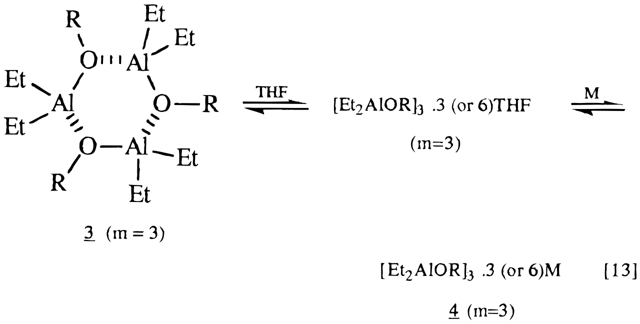
Furthermore, the rate constant also depends on both the functional group and the average number of active sites per Al ($\bar{n}$). When $\bar{n} < 3$, the inactive functional alkoxide(s) strongly affects the reactivity of the propagating species, i.e., $[PCLO]_nAl(OCH_2X)_{3-n}$. An increase in the electron-donating ability of the functional radical (CH_2X) results in a slower polymerization. When all of the alkoxides are active ($n = p$), the mild influence of X might be explained by a coordinative interaction with the active sites.

Initiation by Aluminum Monoalkoxides 1. The ϵ-CL polymerization initiated by dialkylaluminum monoalkoxides has been discussed by Duda and Penczek.[31−35] In THF at 25 °C ($[M]_0 = 2.0$ mol L^{-1}), although polymerization is again first order in monomer, the order in initiator is fractional (Table 6). This unexpected observation has been confirmed at lower monomer concentrations in THF ($[M]_0 = 1.06$ mol L^{-1}) with $Et_2AlO(CH_2)_2Br$ (**1a**) as an initiator[28] and more recently in an apolar solvent such as benzene (Table 6).[32] In agreement with a coordination mechanism, the polymerization rate increases upon substitution of an apolar solvent (benzene) for THF. Duda and Penczek[31,33] proposed a kinetic model based on a dynamic equilibrium between nonaggregated active species, P_n^*, and aggregated dormant species, $(P_n^*)_m$. Quite recently, these authors analyzed the experimental dependence of $\ln(k_{app})$ on ln[C] [where $\ln(k_{app}) = \ln([\epsilon\text{-CL}]_0/[\epsilon\text{-CL}])/t$ and $[C] = [P_n^*] + m[(P_n^*)_m]$] by the straight linear correlation method and numerical curve fitting, respectively. Equation 12 has been derived that is valid for polymerization in which a fast reversible activation of the active centers takes place:

$$(k_{app})^{1-m} = -m/K_{da}(k_{app})^{m-1} + k_p[C]_0(k_{app})^{-m} \tag{12}$$

where m is the association degree of the alkoxide, k_p is the propagation rate constant (liters mole^{-1} second^{-1}), and K_{da} is the association equilibrium constant of the growing end groups.

This model has recently been confirmed by ^{27}Al NMR and viscosimetric analysis of the active centers for ϵ-CL polymerization initiated by $Et_2AlO(CH_2)_2Br$ (**1a**) in THF and toluene.[37] When the monomer is added to solvated cyclic trimers ($m = 3$), $[Et_2AlOR]_3$ **3**, e.g., in THF, a cyclic trimeric "mixed" aggregate **4** is formed preferably (eq 13).[37] Therefore, ϵ-CL insertion requires partial and



fast reversible deassociation of **4** ($K_{da} \ll 1$), which accounts for the fractional kinetic order in initiator (1/m). As previously reported, the association degree of the aluminum alkoxides is also dependent on the alkyl substituents.[38,39] For instance, ethyl and isobutyl, which are known to form cyclic trimers ($m = 3$) and dimers ($m = 2$), respectively, are responsible for 1/3 and 1/2 partial orders in initiator (Table 6).

In all of these kinetic studies, the dialkylaluminum monoalkoxides were previously purified by distillation. Nevertheless, some functional initiators, such as $Et_2AlO(CH_2)_2OC(O)C(Me){=}CH_2$[23] and the reaction product of Et_3Al with an ω-hydroxy prepolymer,[29,40] cannot be distilled at all, so that the ϵ-CL polymerization must be initiated by *in situ* prepared aluminum monoalkoxides **1**. If the formation reaction of these initiators is not complete, an exchange reaction between the monoalkoxide and the unreacted alcohol can take place, which does not prevent molecular weight and chain-end-functionalization from being controlled. The unreacted

Table 7. Viscosity Data for Living and Hydrolyzed PCL Chains in Toluene at 25 °C with Initiation by Et_2AlO^iPr Formed *in Situ* and Purified by Distillation, Respectively

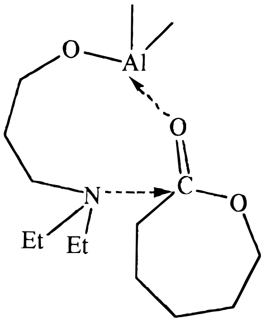
	initiator			
	in situ		purified	
	living	deactivated	living	deactivated
$[\eta]$ (dL/g)	0.055	0.105	0.102	0.170
$\overline{DA}^a$	3.6		2.8	

[a] Mean degree of association ($\overline{DA}$) calculated from eq 8.

alcohol can, however, slow down the polymerization reaction and possibly modify the overall kinetic equation.

Initiation by the *in Situ* Prepared Aluminum Monoalkoxides 1. Although the ε-CL polymerization remains first order in monomer when initiated in toluene at 0 °C by the diethylaluminum monoalkoxides **1a**−**c** that have been prepared *in situ* (Figure 1B), the fractional order in initiator is no longer observed (Table 3). Indeed, Figure 2B is representative of the linear dependence of k_{app} on the concentration of the initiators **1a**−**c** and thus provides evidence for an external first order in initiator. The polymerization rate constants (k), as calculated from the slope of the k_{app} vs [C] plots (eq 9), are compiled in Table 5.

Similar to the lactide polymerization (Table 5), the functional group (X) has no significant effect on the polymerization kinetics. The rate constant is smaller in the presence of the initiator **1c**, most likely due to competition between the alkoxy group and the tertiary amine for complexation to the monomer:

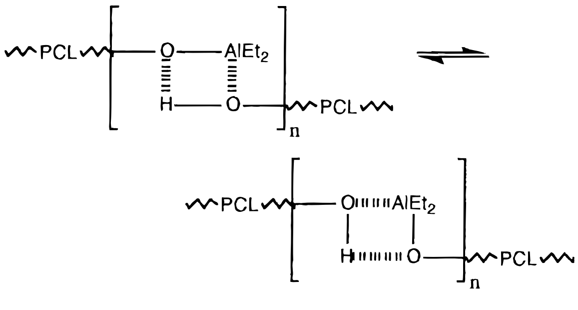


This hypothesis is supported by previous observations reported for ε-CL polymerization initiated by a primary amine in the presence of an alkylaluminum.[28] The alkylaluminum favors nucleophilic attack of the amine on the carbonyl group of the monomer, with the formation of an amide linkage and a propagating aluminum alkoxy group, respectively.[30] It is worth pointing out that a longer induction period is observed when ε-CL polymerization is initiated by **1c** (t_i = 30 min at 0 °C, Table 1). The smaller rate constant might also result from competition between the amino group and the lactone carbonyl for coordination to the Al atom of either the initiator or propagating alkoxide species.

The aforementioned exchange reaction between the *in situ* prepared aluminum monoalkoxides **1** and the unreacted alcohol might account for the kinetic discrepancy observed when the aluminum monoalkoxide has been previously purified by distillation. These exchange reactions have already been reported, e.g., between alcohol and aluminum trialkoxides[29,41] and tetraphenyl(porphinato)aluminum alkoxides.[42] The external first order in initiator observed for the *in situ* prepared diethylaluminum monoalkoxides **1** could result from the complete deassociation of the aluminum alkoxide trimeric aggregates by the unreacted alcohol. To support this hypothesis, toluene solutions of living poly(ε-CL) chains initiated by $Et_2AlO\text{-}^iPr$ *in situ* formed and previously distilled, respectively, have been investigated by viscosimetry. The mean association degree ($\overline{DA}$) of the living chains has been calculated from the intrinsic viscosity compared to the value measured for the parent hydrolyzed and purified chains:[26,37]

$$(\overline{DA}) = ([\eta]_{living}/[\eta]_{deactivated})^2 \qquad (14)$$

Table 7 shows that the mean degree of association of the living chains initiated by the purified diethylaluminum isopropoxide ($\overline{DA}$ = 2.8) is in good agreement with the trimeric aggregation of the dialkylaluminum monoalkoxides (m = 3, Table 6). However, when the polymerization is initiated by the *in situ* prepared monoalkoxide that contains ca. 46% unreacted 2-propanol at 25 °C, the aggregation of the living polyesters is clearly maintained ($\overline{DA}$ = 3.6). Since deassociation of the living species can be precluded, participation of the ω-hydroxyl PCL chains in the aggregation process must be taken into account to explain the external first order in initiator. This is the reason why ^1H NMR spectroscopy has been used to probe possible interactions between the growing aluminum alkoxide groups and the hydroxyl end groups of shortly inactive chains. Figure 5A shows the ^1H NMR spectrum for PCL chains ($M_n \approx$ 1500) initiated by previously distilled Et_2AlO^iPr. In addition to the typical PCL protons, H_{a-e} (see also the ω-OH-PCL in Figure 5C), two types of aluminum α-methylene protons ($H_{g,g'}$), and $H_{f,f'}$ protons shifted upfield with respect to the main signal H_e are observed. These signals, together with those of protons a′, d′, and b′, are in agreement with the trimeric aggregation and intramolecular coordination between the Al atom and the carbonyl group(s) of the PCL chains, as previously observed by ^{13}C and ^{27}Al NMR.[37] When polymerization has been initiated by the *in situ* prepared alkoxide (Figure 5B), a new signal appears at 3.65 ppm, whereas the signals $H_{a'}$, $H_{b'}$, $H_{d'}$, and $H_{f'}$ observed in Figure 5A have completely disappeared. The signal at 3.65 ppm has been tentatively attributed to the α-hydroxymethylene protons (H_k), which are, however, shifted downfield compared to ω-OH-PCL chains recovered after hydrolysis and purification (δH_1 = 3.37 ppm). All of these observations are consistent with a specific interaction between the PCL hydroxyl end groups and the aluminum alkoxide chain ends, which preserves the overall aggregation. A very fast exchange reaction between the coordinated alcohol end groups and the active aluminum alkoxides must occur so that only one signal is observed at 3.65 ppm for both the H_k and $H_{k'}$ protons, in agreement with an external first order in initator (eq 15).



[15]

Effect of Temperature. Increasing the temperature does not change the overall kinetics reported in toluene

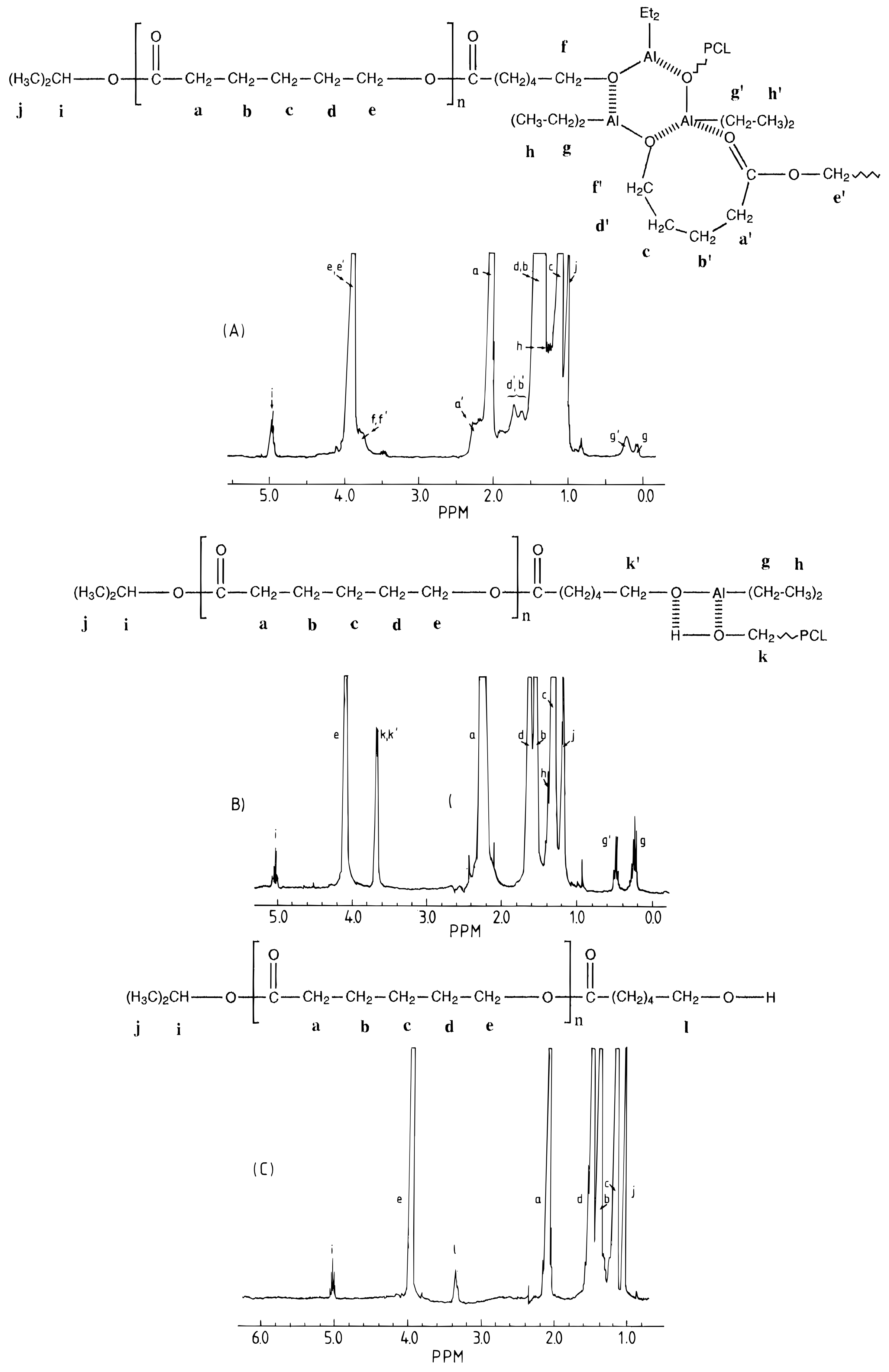


Figure 5. ^{1}H NMR spectra in C_6D_6 of living PCL chains initiated by (A) the previously distilled Et_2AlO^iPr, (B) the *in situ* prepared Et_2AlO^iPr, and (C) after deactivation of the active species.

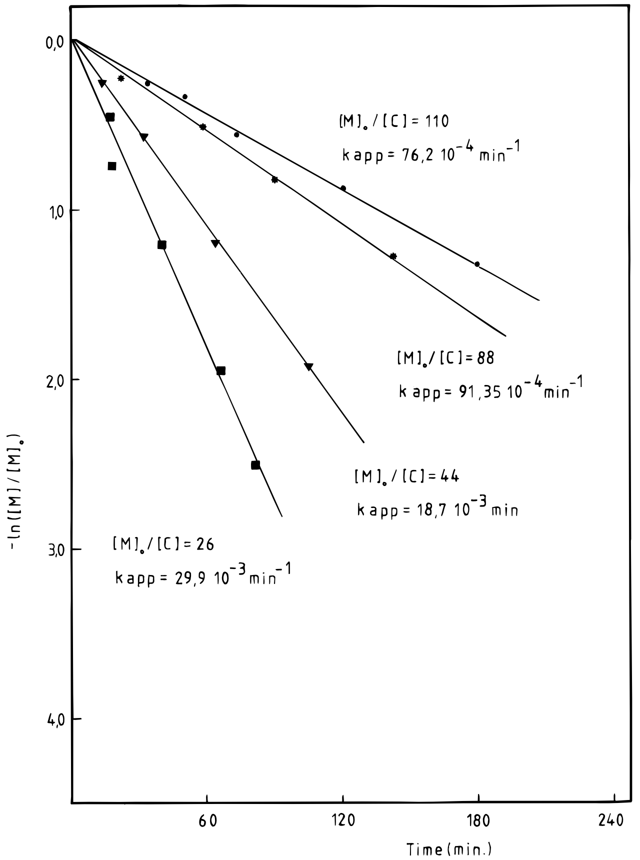


Figure 6. Kinetics of the ϵ-CL polymerization initiated by the *in situ* prepared $Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**) ($[M]_0 = 1.06$ mol L^{-1}) in toluene at 25 °C.

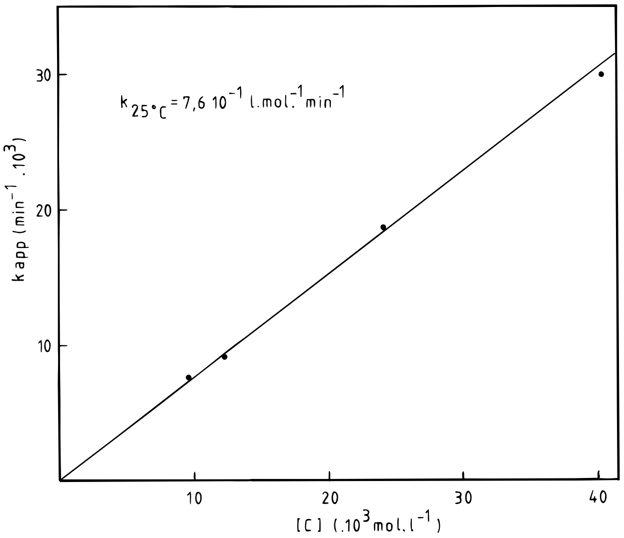


Figure 7. Determination of *k* for the ϵ-CL polymerization initiated by the *in situ* prepared $Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**) in toluene at 25 °C ($[M]_0 = 1.06$ mol L^{-1}).

at 0 °C (eq 11). Regardless of the initiator, aluminum trialkoxides **2** or *in situ* prepared aluminum monoalkoxides **1**, a partial first order in monomer and in initiator is observed. Figures 6 and 7 illustrate this observation in the particular case of $Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**) in toluene at 25 °C. Moreover, the activation energy (E_a) has been calculated from the Arrhenius equation and the thermal dependence of *k* values. As an example, Figure 8 shows how *k* changes with temperature when $Et_2AlOCH_2CH_2Br$ (**1a**) is used as the initiator in toluene. Figure 9 is the related Arrhenius plot that allows the activation energy to be calculated. The thermodynamic parameters of activation have also been calculated by reference to the theory of the activated complex:

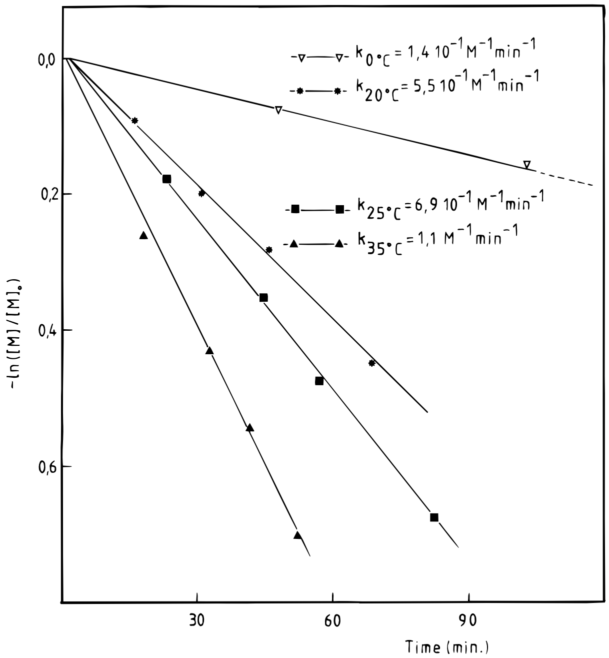


Figure 8. Kinetics of the ϵ-CL polymerization initiated by $Et_2AlOCH_2CH_2Br$ (**1a**) in toluene ($[M]_0 = 1.06$ mol L^{-1}, $[C] = 12.1 \times 10^{-3}$ mol L^{-1}) at various temperatures.

$$k = (k'T/h)e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R} \qquad (16)$$

where *k*′ is the Boltzmann constant, *h* is the Planck constant, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively. $\Delta S^{\ddagger}$ is also calculated from E_a and *k* at the appropriate temperature (*T*) from

$$\Delta S^{\ddagger}/4.576 = \log k - 10.573 - \log T + E_a/4.576T \qquad (17)$$

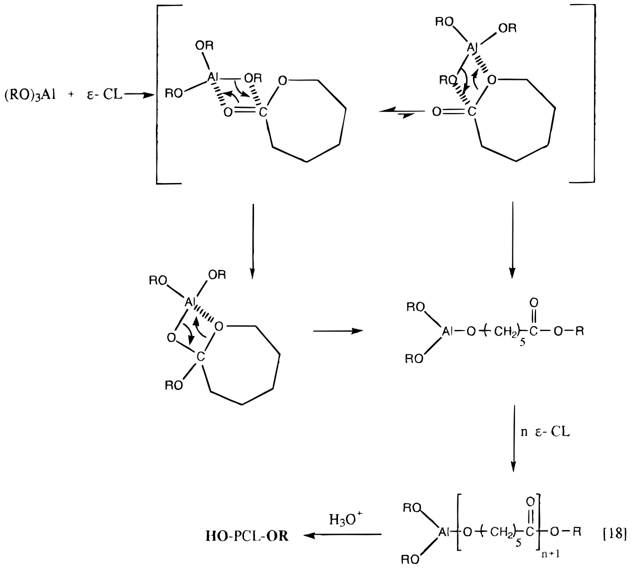
The activation energy and thermodynamic parameters, i.e., $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$, are listed in Table 8 for the ϵ-CL polymerizations initiated with the aluminum mono- and trialkoxides **1a**–**c** and **2a**–**c** in toluene at 25 °C. The activation energy and enthalpy of activation for the ϵ-CL polymerization initiated with diethylaluminum monoalkoxides **1a**–**c** are slightly higher than those reported for the aluminum trialkoxide counterparts **2a**–**c**. The origin for a smaller activation energy in the case of aluminum trialkoxides **2** might be found in the ionicity of the Al–O bonds, which is higher for the $Al(ORX)_3$ initiators than for the Et_2AlORX counterparts. Monomer insertion should, thus, be easier into the less stable alkoxide bonds of the trialkoxides **2** than those of the parent monoalkoxides **1**. Similarly, the rate constant depends on the structure of the aluminum alkoxide (mono- or trialkoxides) and decreases from an aluminum trialkoxide **2** to the diethylaluminum monoalkoxide counterpart **1**. In addition to an electronic effect, there might also be a difference in the structure of the active species and, thus, in the steric hindrance around the active Al–O bond when $Al(ORX)_3$ and Et_2AlORX are compared.

The negative values for $\Delta S^{\ddagger}$ indicate a sterically hindered mechanism for the ring-opening reaction of the

Table 8. Activation Energy, Enthalpy, Entropy, and Free Energy for the ϵ-CL Polymerization in Toluene at 25 °C, Initiated by Aluminum Trialkoxides 2a–c and the *in Situ* Prepared Aluminum Monoalkoxides 1a–c

initiator	E_a (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})
$Et_2AlO(CH_2)_2Br$ (**1a**)	10.3	9.7	−26.7	16.5
$Al[O(CH_2)_2Br]_3$ (**2a**)	8.3	7.7	−33.5	17.7
$Et_2AlO(CH_2)_3CH{=}CH_2$ (**1b**)	10.1	9.6	−27.0	17.6
$Al[O(CH_2)_3CH{=}CH_2]_3$ (**2b**)	6.4	5.8	−32.6	15.5
$Et_2AlO(CH_2)_3NEt_2$ (**1c**)	13.7	13.1	−17.3	18.2
$Al[O(CH_2)_3NEt_2]_3$ (**2c**)	10.0	9.4	−21.7	15.9

lactone, which agrees with the mechanism previously proposed by some of us[18] and by Penczek and Duda[33] (eq 18). It is worth pointing out that Penczek and Duda



have recently reported the entropy and enthalpy of activation for the ϵ-CL polymerization initiated with distilled $Et_2AlOCH_2CH{=}CH_2$ in THF at 25 °C. The reported data ($\Delta S^{\ddagger} = -19.4$ cal mol^{-1} K^{-1} and $\Delta H^{\ddagger} =$ 13.1 kcal mol^{-1}) are on the same order of magnitude as the values reported in Table 8, meaning that distillation of the initiators **1** does not strongly modify the activation parameters.

Since the active sites are more sterically crowded, the entropy of activation is higher for the aluminum trialkoxides **2** than for the corresponding aluminum monoalkoxides **1**. The tertiary amine-containing alkoxides (**1c** and **2c**) differ from the other functional alkoxides investigated by a relatively higher enthalpy of activation and relatively lower entropy of activation. These figures support the hypothesis that tertiary amine and aluminum alkoxide are in a competition for coordination to the carbonyl of the lactone. This competition can explain why $\Delta H^{\ddagger}$ of the ring-opening reaction with the alkoxide is higher. Furthermore, an initial state in which the amine of the initiator interacts with the monomer is consistent with a decrease in $\Delta S^{\ddagger}$.

In conclusion, functional aluminum alkoxides, $Et_{3-p}Al(OCH_2X)_p$ **1** and **2** are very effective initiators for the ring-opening polymerization of lactones and lactides and for the synthesis of asymmetric α-X, ω-hydroxy functional polyesters. The great versatility of their structure has opened the way to the macromolecular engineering of the polylactones and polylactides. The kinetic study reported in this paper has confirmed the coordination–insertion mechanism for the ROP promoted by aluminum alkoxides, and it has brought up the following key points.

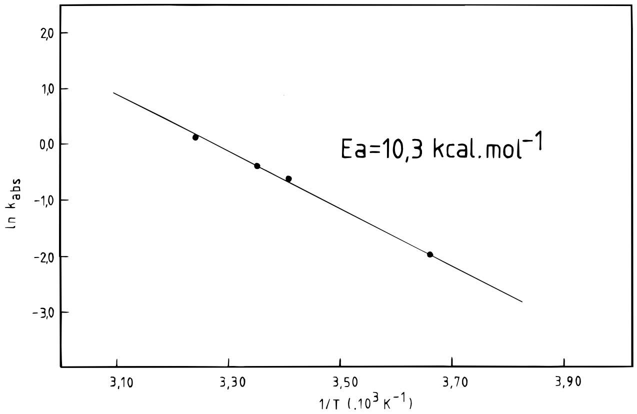


Figure 9. Determination of the energy of activation for the ϵ-CL polymerization initiated by $Et_2AlO(CH_2)_2Br$ (**1a**) in toluene at 0, 20, 25, and 35 °C ($[M]_0 = 1.06$ mol L^{-1}, $[C] = 12.1 \times 10^{-3}$ mol L^{-1}).

The rate of ϵ-CL polymerization is enhanced when an aluminum trialkoxide **2** is used instead of the monoalkoxide counterpart **1**.

As far as the aluminum monoalkoxides **1** are concerned, the kinetic equation strongly depends on the purification method of the initiators. Although a first order in monomer is systematically observed, the order in initiator is first or fractional, depending on whether the monalkoxide **1** has been prepared *in situ* or previously purified by distillation. NMR spectroscopy and viscosimetry have shown that living chains initiated by the *in situ* formed monoalkoxides **1** participate in a very fast exchange reaction with hydroxyl-terminated chains, so that the chain aggregation persists and an external first order in initiator is observed. This exchange process does not prevent the molecular weight and chain-end-functionalization from being controlled.

The organic function attached to the alkoxy group has a kinetic effect when the mean number of active sites ($\bar{n}$) is less than the total number of alkoxides (p). An increase in the electron-donating capability of the functional radical results in a slower polymerization.

In agreement with the coordination mechanism, the polymerization rate decreases upon the substitution of a polar solvent, e.g., THF, for toluene.

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