Macromolecular Engineering of Polylactones and Polylactides. 17. Cryometric and Viscosimetric Analysis of the Species Active in the Ring-Opening Polymerization of Lactones, Lactides, and Cyclic Anhydrides as Initiated by Aluminum Triisopropoxide

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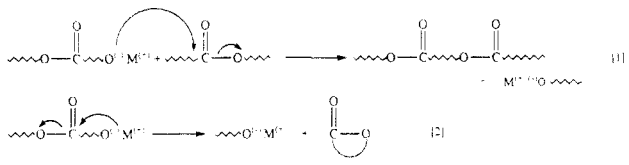
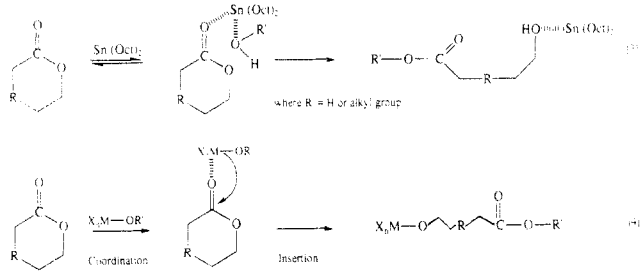
ABSTRACT: $Al(O^iPr)_3$, which is one of the most efficient initiators for the living ring-opening polymerization (ROP) of lactones, lactides, and cyclic anhydrides, is known to be coordinatively associated in apolar solvents. In the present study, the effect of cyclic monomers on the coordinative structure of $Al(O^iPr)_3$ in benzene was investigated by cryometry. γ-Butyrolactone (γ-BL), a nonpolymerizable lactone, was first studied as a model monomer. The cryometric Job diagram for the γ-BL/$Al(O^iPr)_3$ system in benzene established formation of a trisolvated six-coordinate [$Al(O^iPr)_3$·3γ-BL] complex. This is in perfect agreement with the hexacoordinated Al atoms as reported by ^{27}Al NMR. The extension of the cryometric study to a polymerizable lactone, e.g., δ-valerolactone (δ-VL), confirmed that the single [$Al(O^iPr)_3$·3M] species is the actual initiator for the ring-opening polymerization. ^{27}Al NMR shows that the same conclusion holds when other cyclic monomers, such as lactides and glutaric anhydride, are considered. The induction period of time that is usually observed in the ROP of lactones, lactides, and cyclic anhydrides may now be attributed to the dissociation of the $Al(O^iPr)_3$ aggregates upon the addition of the cyclic monomer. Toluene solutions of living poly(ε-CL) and polylactide chains as initiated by $Al(O^iPr)_3$ were also investigated by viscosimetry. The mean association degree $(\overline{DA})$ of the living chains was calculated from the intrinsic viscosity compared to the value measured for the parent hydrolyzed and purified polyester.

Introduction

Initiation of the ring-opening polymerization (ROP) of ε-caprolactone (ε-CL), lactides (LA), and cyclic anhydrides by aluminum triisopropoxide has recently proved to be a very efficient approach to the macromolecular engineering of the related polymers. Initially, ROP of these monomers was initiated with anionic and cationic species, but the polymerization could not be controlled, due to side intra- and intermolecular transesterification reactions, with formation of a mixture of linear and cyclic molecules (eqs 1 and 2 for an anionic process).[1,2]



Later, some organometallic compounds were shown to be very effective in the synthesis of high molecular weight poly(ε-caprolactone) (PCL),[3] in which the chain reaction proceeds through active covalent bonds.[4] Special attention has been paid to stannous octoate ($Sn(Oct)_2$) because of its acceptance as a food additive by the FDA.[5] Nevertheless, $Sn(Oct)_2$ and most metal derivatives, e.g., metal halides, oxides, and carboxylates, must be combined with a hydroxyl-containing compound, such as an alcohol, which is the actual initiator (eq 3).[6,7] Thus, polymerization is very sensitive to protic impurities and, accordingly, poorly reproducible. A remarkable improvement has been reported when alkoxides of metals containing free p- or d-orbitals of a favorable energy (Mg, Sn, Ti, Zr, and Zn alkoxides) have been used as an initiator (X_nM–OR′). The polymerization mechanism then relies upon a two-step insertion: monomer coordination onto the initiator followed by monomer insertion into the metal–oxygen bond.[8] The acyl-oxygen bond of the cyclic monomer is cleaved in a way which maintains the growing chain attached to the metal through an alkoxide bond (eq 4). Hydrolysis of this active bond leads to the formation of a hydroxyl end group. The second chain end is capped with an ester carrying the alkoxide radical of the initiator.



The metal has been shown to be of prime importance for the controlled synthesis of high molecular weight polyesters. Indeed, side inter- and intramolecular transesterification reactions occur easily as the metal alkoxide is a more active transesterification catalyst, i.e., $Al(OR)_3$ < $Zn(OR)_2$ < $Ti(OR)_4$ < Bu_3SnOR.[9] In agreement with these observations, some of us have reported on the "living" polymerization of ε-CL,[10] LA,[11,12] 1,5-dioxepan-2-one (DXO),[13] δ-VL,[14a] and adipic anhydride[14b] promoted by aluminum triisopropoxide ($Al(O^iPr)_3$), in toluene and tetrahydrofuran (THF).

Although the coordination–insertion polymerization of the aforementioned monomers is living, key questions about the structure and dynamics of the pseudoanionic active species are still pending. Currently, the polymerization mechanism initiated with aluminum alkoxides relies upon a series of indirect observations and nothing is known about the coordinative association and the actual

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Table 1. Polymerization of ε-CL, δ-VL, LA, DXO, and AA by Aluminum Triisopropoxide in Toluene: Polymerization Rate Constant (k), Induction Period of Time (t_i), and Average Number of Active Sites ($\bar{n}$) per $Al(O^iPr)_3$ Molecule

monomer	$[M]_0$ (mol·L^{-1})	T (°C)	k (mol·L^{-1}·min^{-1})	n	t_i (min)
ε-CL	1.0	0	36.6	0.9[b]	4
δ-VL	1.0	0	23.92	1	40
LA	0.6	70	0.6	3	40
DXO[a]	1.0	20	5.67	1	10
AA	0.6	20	0.3	1	30

[a] In THF solution. [b] n = 1.0 at 25 °C.

structure of the initiating species under the polymerization conditions. Thermodynamic and kinetic investigations have focused on the effect of the monomer structure on the activity of the living end groups (Table 1). It is, however, quite a problem to explain why the average number of growing chains per $Al(O^iPr)_3$ molecule ($\bar{n}$ = number of active isopropoxide functions per Al atom) is 1 in the presence of ε-CL, δ-VL, AA, and DXO and 3 when lactide ((L,L)- or (D,L)-LA) is the monomer. This dependence of the number of active sites per Al atom on the monomer is responsible for side homopolymerization reactions when ε-CL and LA are polymerized in a sequential way. Furthermore, some kinetic data are quite puzzling. As an example, the absolute polymerization rate constant of ε-CL in toluene at 0 °C is 60 times larger than that of LA at 70 °C, the partial order in both monomer and initiator being 1 for the two monomers. It is also worth noting that, whatever the monomer, polymerization does not start as soon as the monomer and initiator are mixed together. To date, the origin of this induction period of time (t_i) has not been elucidated.

To clear up the polymerization kinetics and the intimate mechanism of the coordination–insertion ROP, it is of the utmost importance to have an understanding of the structure and dynamics of both $Al(O^iPr)_3$ in the presence of the monomer and the propagating species in solution. In this respect, NMR spectroscopy has proved to be a very valuable tool.[15] This paper will focus on the contribution of cryometry and viscosimetry to the analysis of the actual active species in the ROP of cyclic esters and anhydrides. First, special attention will be devoted to the effect of a model monomer, i.e., γ-butyrolactone (γ-BL), on the structure of the initiator. The thermodynamic stability of γ-BL makes this monomer very well suited to cryometric measurements. With the exception of a lack of propensity to polymerization, γ-BL is quite comparable to the usually polymerized lactones, such as ε-caprolactone (ε-CL) and δ-valerolactone (δ-VL), particularly with respect to the dipole moment.[16] Moreover, cryometry is expected to explain the origin of the induction period of time which is usually observed for ROP initiated with Al alkoxides. δ-Valerolactone will then be studied as a polymerizable monomer because of its low absolute rate constant (k).[14a] Viscosimetry of living and hydrolyzed PCL and PLA chains in toluene solution will finally be investigated to calculate the mean association degree of the living polyester chains.

Experimental Section

Material. Toluene and benzene were dried by refluxing over calcium hydride and distilled just before use under nitrogen. γ-Butyrolactone (γ-BL), ε-caprolactone (ε-CL), and δ-valerolactone (δ-VL) (Aldrich) were dried over CaH_2, distilled under reduced pressure, stored under a nitrogen atmosphere, and dissolved just before use in toluene (for ^{27}Al NMR or viscosimetry) or benzene (for cryometry). Racemic (D,L)-lactide (from Boehringer) was recrystallized three times from ethyl acetate (dried over $CaCl_2$) and dried for 24 h at 35 °C under reduced pressure before polymerization. Aluminum triisopropoxide (Aldrich) was twice sublimated and then dissolved in dried toluene or benzene under nitrogen. The concentration of this solution was measured by complexometric titration of Al by EDTA.

Polymerization. ε-CL and (D,L)-LA were polymerized in solution under stirring in a previously flamed and nitrogen-purged glass reactor. The reactor was charged with the solid lactide in a glovebox under a nitrogen atmosphere. Toluene was added through a rubber septum with a stainless steel capillary or a syringe, and lactide was dissolved at 70 °C. ε-CL and $Al(O^iPr)_3$ were added into the reactor in the same way as toluene.

Polymerization was stopped by adding an excess (relative to the initiator) of 1 N HCl solution. The initiator residues were removed by repeated extractions with an aqueous EDTA solution (0.1 mol·L^{-1}) and then with water up to a neutral pH. PCL and PLA were precipitated into cold heptane and methanol, respectively, filtered, and dried for 24 h at room temperature under a reduced pressure.

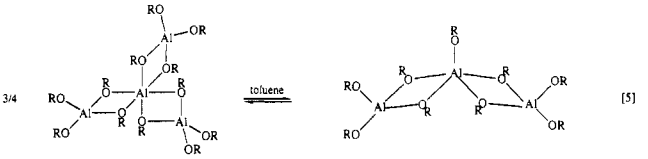
Measurements. Solutions of aluminum triisopropoxide and γ-BL or δ-VL of a well-known concentration ($[Al(O^iPr)_3]$ = [monomer] = 0.20 mol·L^{-1} = 0.23 mol·kg^{-1}) were prepared in benzene separately. A previously flame-dried and purged with nitrogen glass cryometer was charged with well-known volumes of the $Al(O^iPr)_3$ solution and the monomer solution (total volume = 15 mL). The cryometric drop, ΔT_F, was measured with a Beckman thermometer.

^{27}Al NMR spectra were recorded with an AM200 superconducting magnet system operating in the FT mode at 78.21 MHz without any lock. ^{27}Al NMR spectra were referenced to a salt solution of $Al_2(SO_4)_3$ in water (^{27}Al signal at 0 ppm).

The inherent viscosity of living and hydrolyzed PCL (or PLA) chains in toluene was measured in a previously flame-dried and purged with nitrogen glass Ubbelohde viscosimeter at 25 °C.

Results and Discussion

Many studies have focused on the structure of aluminum alkoxides $[Al(OR)_3]_m$[17-19] and have concluded that most alkoxides exist as dimers, trimers, and tetramers, depending on the nature of the alkoxy groups. Aluminum triisopropoxide, which is one of the most efficient initiators for ROP, has recently been studied by ^{27}Al NMR spectroscopy.[15] An equilibrium between trimeric and tetrameric structures has been reported as shown by eq 5.



[5]

This aggregation equilibrium depends on the aluminum triisopropoxide concentration, temperature, and addition of external ligands such as 2-propanol. Moreover, the addition of a nonpolymerizable lactone or cyclic anhydride is responsible for the complete dissociation of $Al(O^iPr)_3$.[15] The single $Al(O^iPr)_3$ species, however, consists of a hexacoordinated Al atom as a result of the monomer coordination to the metal. The structure of the actual [$Al(O^iPr)_3$·x monomers] six-coordinate complex, i.e., the actual initiator, could be elucidated by cryometry (x value), as reported hereafter.

Cryometric Analysis of $Al(O^iPr)_3$/γ-BL Mixtures in Benzene Solution. It is well known that the melting temperature of a pure solvent ($T_{F,0}$) is decreased upon the addition of a solute ($T_{F,0} - T_F = \Delta T_F$). ΔT_F is known as the cryometric decrease and directly depends on the solute concentration (C, mol·kg^{-1} of solvent) according to

$$\Delta T_F = K_C C = K_C \frac{C'}{M} \qquad (6)$$

where K_C is the cryometric constant, C' is the concentration

Table 2. Time Dependence of the Cryometric Decrease (ΔT_F) for $Al(O^iPr)_3/\gamma$-BL Mixtures of a Constant Molar Concentration (0.2 mol·L^{-1}) in Benzene

		ΔT_F (°C)							
entry	F_{Al}[a]	0.5 h	1 h	1.5 h	2.5 h	3 h	3.5 h	4 h	24 h
1	1.0	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
2	0.87	0.39	0.39	0.39	0.39	0.39	0.39	0.56	0.56
3	0.75	0.48	0.48	0.48	0.48	0.48	0.61	0.61	0.61
4	0.66	0.54	0.54	0.54	0.54	0.66	0.66	0.66	0.66
5	0.50	0.65	0.65	0.65	0.76	0.76	0.76	0.76	0.76
6	0.40	0.79	0.79	0.82	0.82	0.82	0.82	0.82	0.82
7	0.33	0.82	0.86	0.86	0.86	0.86	0.86	0.86	0.86
8	0.27	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89
9	0.20	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.96
10	0.13	1.02	1.02	1.02	1.02	1.02	1.02	1.02	1.02
11	0.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07
12	0.00	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.15

[a] $F_{\gamma\text{-BL}} = 1.0 - F_{Al}$.

in g/kg, and M is the molecular weight of the solute. Benzene is a commonly used solvent in cryometry (K_C = 5.12 mol·°C·kg^{-1}). Its melting temperature ($T_{F,0}$ = 5.533 °C) is close to the polymerization temperature of ϵ-CL (0 °C). It also has the advantage of having a structure similar to that of the usually used polymerization solvent, i.e., toluene. Table 2 shows that ΔT_F for $Al(O^iPr)_3$ in benzene (molar fraction of $Al(O^iPr)_3$:F_{Al} = 1.0) is stable over a period of time as long as 24 h. ΔT_F is equal to 0.3 °C for a 0.23 mol·kg^{-1} $Al(O^iPr)_3$ solution in benzene. The apparent molecular weight of $[Al(O^iPr)_3]_m$ as calculated from eq 6 (M_{calc} = 801) gives credit to an aggregation equilibrium (eq 5) dominated by the tetrameric species (M_{theor} = 816 for m = 4). The cryometric decrease of a 0.23 mol·kg^{-1} γ-BL solution in benzene (F_{Al} = 0 or $F_{\gamma\text{-BL}}$ = 1.0) has also been measured (Table 2, entry 12). ΔT_F is then 1.15 °C, in very good agreement with the value predicted from eq 6 (M_{theor} = 86 and ΔT_{theor} = 1.18 °C).

To know whether the monomer is able to perturb the association of $[Al(O^iPr)_3]_m$ in solution, the cryometric decrease was measured versus time (t) at various $Al(O^iPr)_3/\gamma$-BL molar ratios, i.e., in the range of F_{Al} from 0 to 1.0 (Table 2). Solutions of aluminum triisopropoxide and γ-BL of the same concentration ($[Al(O^iPr)_3]$ = $[\gamma\text{-BL}]$ = 0.2 mol·L^{-1} = 0.23 mol·kg^{-1}) in benzene were prepared. Appropriate volumes of these solutions were combined so that the expected composition was reached while the volume (15 mL) and the number of individual molecules (3×10^{-3} mol) were kept constant.

As a rule, ΔT_F is time-dependent to an extent that depends on the molar fraction of $Al(O^iPr)_3$. Changes in ΔT_F versus time are reported 0.5 h after the monomer and initiator mixing. Within the range of high $Al(O^iPr)_3$ molar fractions ($0.33 \leq F_{Al} \leq 0.87$), the period of time necessary to reach a stable ΔT_F value decreases with the relative content of $Al(O^iPr)_3$ (Table 2, entries 2–7). In a parallel way, this ΔT_F value increases, which indicates a progressive dissociation of the $Al(O^iPr)_3$ aggregates with increasing amounts of γ-BL. At the lowest molar fractions of $Al(O^iPr)_3$ ($F_{Al} < 0.33$) (Table 2, entries 8–11), the initiator is definitely dissociated when the first measurement of ΔT_F is carried out. Actually, the dissociation period of time of $Al(O^iPr)_3$ mixed with γ-BL is less than 15 min at $F_{Al} < 0.33$. This time increases from 30 to 240 min when the $Al(O^iPr)_3$ molar fraction is further increased beyond 0.33. It is thus clear that the monomer triggers a rearrangement of the $Al(O^iPr)_3$ aggregates in solution over a period of time which depends on the relative amount of these two compounds. From the cryometric measurements, a striking parallelism is emerging between the

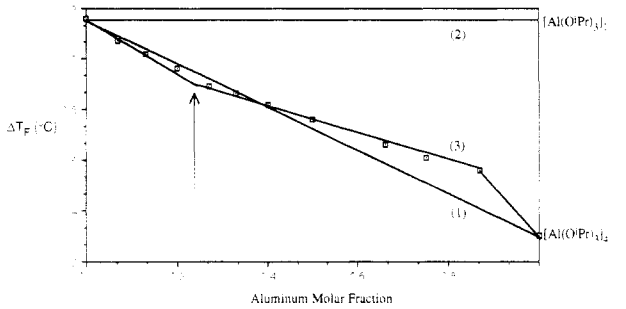


Figure 1. Job diagram for $Al(O^iPr)_3/\gamma$-BL mixtures in benzene (0.23 mol·kg^{-1}). Dependence of the cryometric decrease (ΔT_F) on the Al molar fraction. ΔT_F was measured 24 h after the γ-BL and $Al(O^iPr)_3$ mixing.

induction period of time usually reported in the ROP of lactones, lactides, and cyclic anhydrides and the period of time necessary for the cyclic monomer to dissociate the $[Al(O^iPr)_3]_m$ aggregates in solution. ROP might thus proceed through dissociated $Al(O^iPr)_3$ molecules possibly solvated by monomer molecules. Formation of a [$Al(O^iPr)_3$·$x$monomers] six-coordinate complex has indeed been suggested by previously reported spectroscopic data.[15]

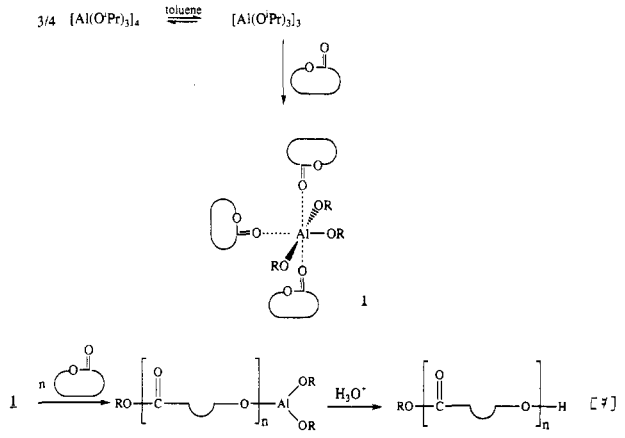
The composition of the six-coordinate complex was determined by plotting the equilibrium cryometric decrease (thus the value measured after a 24 h mixing time in Table 2) versus the $Al(O^iPr)_3$ molar fraction with respect to the monomer. The total concentration in γ-BL and $Al(O^iPr)_3$ is systematically equal to 0.2 mol·L^{-1}. This cryometric Job diagram is shown in Figure 1.

In addition to the experimental curve, theoretical curves have been calculated for two extreme situations: (i) no dissociation of the $Al(O^iPr)_3$ aggregates (m = 4) and no interaction with γ-BL (curve 1) and (ii) complete dissociation of the $Al(O^iPr)_3$ aggregates (m = 1) in the presence of γ-BL and no specific coordination with it (curve 2).

Changes in the slope of the experimental curve (curve 3) are clearly observed at F_{Al} = 0.25 and 0.86, respectively. Compared to curve 1, the sharp experimental increase in ΔT_F that occurs when γ-BL is added to tetrameric $Al(O^iPr)_3$ ($0.86 < F_{Al} < 1.0$) is the signature of the trimer (m = 3)–tetramer (m = 4) aggregation equilibrium, which has been observed to occur in toluene at 25 °C.[15] Furthermore, ^{13}C and ^{27}Al NMR spectroscopic studies have shown that the addition of γ-BL to the $Al(O^iPr)_3$ solution in toluene is responsible for a shift of this equilibrium toward the formation of an octahedral Al species that has been assigned to the $[Al(O^iPr)_3$·3γ-BL] six-coordinate complex.[15] This previous observation is in very good agreement with Figure 1. Indeed, if no interaction occurs between γ-BL and the Al compounds, then the ΔT_F versus F_{Al} experimental curve cannot cross curve 1 in the range of $F_{Al} < 0.86$. The change in slope at F_{Al} = 0.86 thus reflects the dissociation of $Al(O^iPr)_3$ tetramers into trimers combined with a solvation effect by γ-BL. It is worth noting that the second change in slope at F_{Al} = 0.25 is observed at a composition that fits the composition of the octahedral $[Al(O^iPr)_3$·3γ-BL] complex proposed on the basis of the NMR analysis. Nevertheless, the experimental cryometric decrease observed at F_{Al} = 0.25 (ΔT_F = 0.925 °C) is higher than the value calculated for the pure $[Al(O^iPr)_3$·3γ-BL] complex (ΔT_F = 0.3 °C), which might indicate that formation of the trisolvated six-coordinate complex is an equilibrated process. This conclusion also agrees with NMR, since the butyrolactone complex of aluminum has been observed to coexist with $Al(O^iPr)_3$ tetramers, the external tetrahedral Al atoms of which are coordinated with extra γ-BL molecules.[15] Furthermore, the relative

percentage of the butyrolactone complex of aluminum compared to the solvated $[Al(O^iPr)_3]_4$ tetramers increases with the amount of γ-BL.[15] This observation indicates that pure octahedral $[Al(O^iPr)_3{\cdot}3\gamma\text{-BL}]$ complex might be obtained by adding γ-BL to $[Al(O^iPr)_3]_3$ trimers rather than to tetramers. The assessment of this hypothesis is straightforward since $Al(O^iPr)_3$ is known to be trimeric when freshly sublimated.[17] Figure 2a confirms that only one compound consisting of an octahedral Al atom is formed at $F_{Al} = 2.5 \times 10^{-2}$ (δ = 5.6 ppm) when $Al(O^iPr)_3$ is originally trimeric. For the sake of comparison, Figure 2b illustrates the ^{27}Al NMR spectrum for a solution of the same composition but prepared from essentially tetrameric $Al(O^iPr)_3$. In addition to the signal at 5.6 ppm, assigned to the $[Al(O^iPr)_3{\cdot}3BL]$ mixed tetramer, signals at 2.4 and 59.5 ppm are observed which are characteristic of the $[Al(O^iPr)_3]_4$ tetramers.

A set of ^{27}Al NMR data show that the actual initiator in the ROP of lactones, lactides, and cyclic anhydrides is a trisolvated $[Al(O^iPr)_3{\cdot}3M]$ octahedral complex which results from the complete dissociation of $[Al(O^iPr)_3]_m$ aggregates in the presence of a carbonyl-containing cyclic monomer (eq 7). When δ-valerolactone, (D,L)-lactide, and glutaric anhydride[15] are considered, a new hexacoordinated ^{27}Al signal is observed in relation to the "$Al(O^iPr)_3{\cdot}3M$" active species.



In contrast to (D,L)-lactide and glutaric anhydride, which are solid at 25 °C, δ-valerolactone is a monomer that can be used as a solvent for $Al(O^iPr)_3$. Quite interestingly, a trisolvated $[Al(O^iPr)_3{\cdot}3\delta\text{-VL}]$ octahedral complex is identified by ^{27}Al NMR (Figure 3) as the only Al-containing compound when freshly sublimated $Al(O^iPr)_3$ is dissolved in pure δ-VL ($F_{Al} = 7.5 \times 10^{-2}$).

Cryometric Analysis of $Al(O^iPr)_3$/δ-VL Mixtures in Benzene. The assumption that the induction period of polymerization time is nothing but the time required for the monomer to dissociate the $Al(O^iPr)_3$ aggregates was assessed by replacing the thermodynamically stable γ-BL by a monomer that can be polymerized slowly enough at 0 °C. Lactides and cyclic anhydrides were disregarded for insolubility in benzene at a low temperature. ε-Caprolactone might have been a convenient monomer, except for an induction period of time (t_i) too short to be measured by cryometry (Table 1, first entry). δ-Valerolactone (δ-VL) was finally selected because of a living ROP that proceeds at a low polymerization rate and that shows a long induction period of time (Table 1, second entry).[14a]

Actually, 30 min after the mixing of $Al(O^iPr)_3$ and δ-VL in benzene ($[\delta\text{-VL}]/[Al(O^iPr)_3] = 6.5$ or $F_{Al} = 0.13$), no change in ΔT_F is measured ($\Delta T_{F,0.5h} = 0.69$ °C, Table 3). One hour later, ΔT_F has increased ($\Delta T_{F,1h} = 0.73$ °C), which

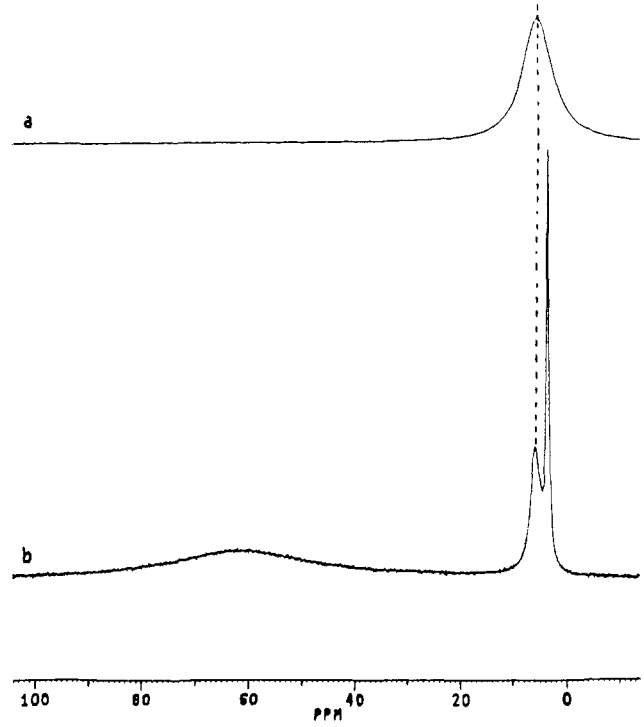


Figure 2. ^{27}Al NMR spectra at 297 K for (a) pure $[Al(O^iPr)_3{\cdot}3\gamma\text{-BL}]$ mixed tetramers as prepared by dissolution of freshly sublimated $Al(O^iPr)_3$ (mainly trimers) into pure γ-BL ($F_{Al} = 2.5 \times 10^{-2}$) and (b) $[Al(O^iPr)_3]_4$ tetramers and $[Al(O^iPr)_3{\cdot}3\gamma\text{-BL}]$ mixed tetramers as prepared by dissolution of aged $Al(O^iPr)_3$ (mainly tetramers) into pure γ-BL ($F_{Al} = 2.5 \times 10^{-2}$).

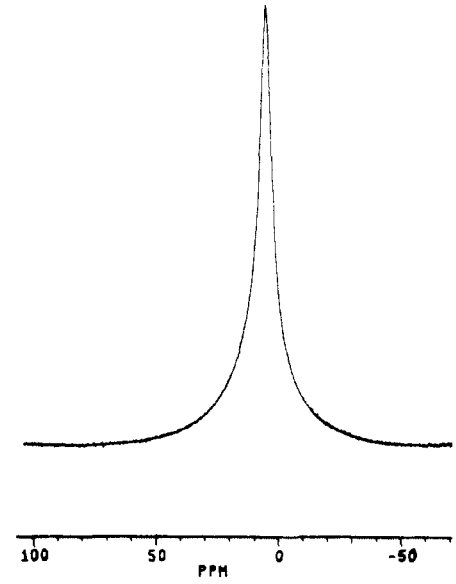


Figure 3. ^{27}Al NMR spectrum at 297 K for pure $[Al(O^iPr)_3{\cdot}3\delta\text{-VL}]$ mixed tetramers as prepared by dissolution of freshly sublimated $Al(O^iPr)_3$ (mainly trimers) into pure δ-VL ($F_{Al} = 2.5 \times 10^{-2}$).

Table 3. Time Dependence of the Cryometric Decrease (ΔT_F) for an $Al(O^iPr)_3$/δ-VL Mixture in Benzene (F_{Al} = 0.13 or $[\delta\text{-VL}]/[Al(O^iPr)_3]$ = 6.5)

t (h)	ΔT_F (°C)	t (h)	ΔT_F (°C)
0.25	0.69	4	0.65
0.5	0.69	24	0.57
1	0.73	36	0.57

clearly indicates a partial dissociation of the initiator within the interval of 30 and 60 minutes. For longer periods of time, ΔT_F decreases to a constant value of 0.57 °C after 24 h. This decrease in the freezing temperature is the expected result of the monomer conversion, the polym-

erization being indeed complete after 24 h. It is worth noting that the molecular weight calculated by eq 6 for a ΔT_F value of 0.57 °C (M_{calc} = 580) is in good agreement with the value anticipated from the living ROP of δ-VL on the basis of the initial monomer/initiator molar ratio (M_{theor} = 650).

The induction period of time (t_i) can thus be attributed to a rearrangement of the coordinative aggregates of Al(O^{i}Pr)$_3$ in toluene or THF upon the addition of the polar monomer (eq 7).

Solution Viscosity of Living and "Dead" PCL and PLA Chains As Initiated by Al(O^{i}Pr)$_3$. The living polymerization of ε-CL and racemic (D,L)-LA by Al(O^{i}Pr)$_3$ in toluene at 0 and 70 °C, respectively, relies upon a series of experimental observations, such as polymerization resumption experiments, and a linear relationship between the mean degree of polymerization ($\overline{DP}$) at complete monomer conversion and the initial monomer/initiator molar ratio.[10,12] From the slope of this linear dependence, it has been calculated that each alkoxide group of Al(O^{i}Pr)$_3$ participates in the lactide polymeriation (n = 3). This is in sharp contrast to the ROP of ε-CL, since only one alkoxide group is then active (n = 1). A direct consequence of this situation is that an average of three PLA chains are growing per Al atom, compared to only one chain when PCL is concerned. If this was the case, the solution viscosity of living PLA chains in toluene should drop upon the hydrolysis of the active aluminum alkoxide species, in contrast to the solution viscosity of living PCL chains, which should remain unchanged. Comparison of the intrinsic viscosity of the living PLA chains after and before hydrolysis is an easy way to calculate the average association degree of the growing chains in solution.

Living PCL and PLA chains with a molecular weight of 25 000 were synthesized in toluene by using Al(O^{i}Pr)$_3$ as an initiator at 0 and 70 °C, respectively. The specific viscosity of the living polyester solutions was measured under N_2 at 25 °C when the monomer conversion was complete, i.e., for a polymerization time of 2 and 26 h for ε-CL and LA, respectively. Actually, 5 mL of the polymerization medium was transferred into a previously flame-dried and nitrogen-purged viscosimeter while avoiding any contact with the atmosphere. The viscosimeter is designed in such a way that the initial solution can be diluted by increasing amounts of dry toluene. For the sake of comparison, an additional aliquot of the reaction medium was hydrolyzed by 0.1 N HCl, purified by complexometric extraction of Al salts with EDTA, and finally recovered by selective precipitation. Molecular weight and molecular weight distribution of the recovered ω-hydroxy PCL and PLA chains were analyzed by size exclusion chromatography (SEC) in reference to a universal calibration curve. The molecular parameters are as follows: $\bar{M}_n$ = 25000 and $\bar{M}_w/\bar{M}_n$ = 1.1 for PCL and $\bar{M}_n$ = 25500 and $\bar{M}_w/\bar{M}_n$ = 1.2 for PLA. The specific viscosity (η_{sp}) of the "dead" chains was also measured in toluene at 25 °C for the same concentrations as the living chains. Table 4 summarizes the viscosimetric data for both the living and the hydrolyzed polyester chains. Reduced viscosity ($\eta_{red} = \eta_{sp}/C$) was plotted versus polymer concentration and extrapolated to zero concentration, in agreement with the Huggins relationship: $\eta_{red} = \eta_{sp}/C = [\eta] + k[\eta]^2C$ (Figure 4a,b). The intrinsic viscosity ([η]) data are compiled in Table 5. The mean association degree of the living chains ($\overline{DA}$), i.e., the average number of growing chains per initiating species, is the actual ratio of the molecular weight for the living chains and the hydrolyzed counterparts, respectively.[20] This molecular weight ratio can be transformed into the intrinsic viscosities ratio on the assumption that the (viscosity) expansion coefficient is the same for both the aggregated and the single chains (eq 8).[20]

$$\overline{DA} = \frac{M_{living}}{M_{dead}} = \left(\frac{[\eta]_{living}}{[\eta]_{dead}}\right)^2 \quad (8)$$

As shown by data in Tables 1 and 5, there is perfect agreement between the mean association degree of the living chains in toluene ($\overline{DA}$ = 1 for PCL and $\overline{DA}$ = 3 for PLA) and the mean number of active alkoxide groups ($\bar{n}$) per Al atom in the same solvent.[10,12] Therefore and whatever the monomer, no *inter*molecular coordinative aggregation occurs in toluene.

From the intrinsic viscosity data, it is thus obvious that aluminum triisopropoxide remains completely dissociated in toluene during the whole ROP process. Thus, polymerization is initiated by monomer-trisolvated Al(O^{i}Pr)$_3$ species that remain independent of each other even when the monomer conversion is complete. Depending on the

Table 4. Specific Viscosity (η_{sp}) for the Living and Hydrolyzed PCL and PLA Chains in Toluene at 25 °C

	η_{sp}			
	PCL		PLA	
concn (g/dL)	living	hydrolyzed[a]	living	hydrolyzed[b]
5.0	8.60	8.60	2.68	1.31
3.3	3.45	3.40	1.38	0.75
2.5	2.13	2.12	0.95	0.52
2.0	1.56	1.53	0.72	0.40
1.65			0.57	0.32

[a] $\bar{M}_n$ = 25000, $\bar{M}_w/\bar{M}_n$ = 1.1 [b] $\bar{M}_n$ = 25500, $\bar{M}_w/\bar{M}_n$ = 1.2.

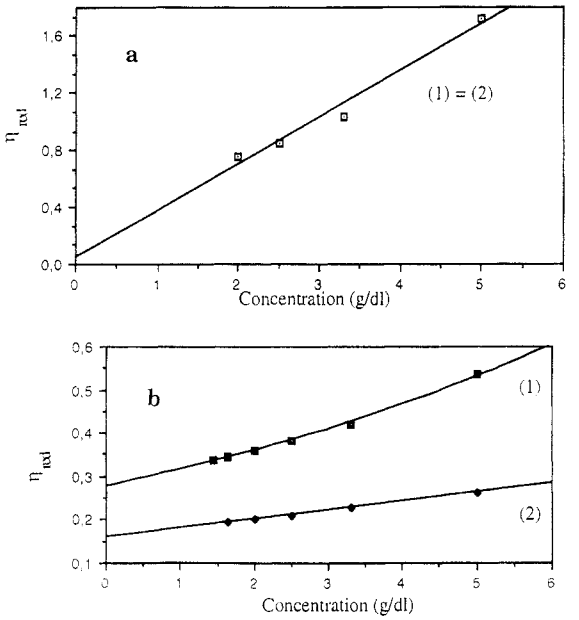


Figure 4. Reduced viscosity (η_{red}) against polymer concentration (g/dL) in toluene at 297 K for (a) living (1) and hydrolyzed (2) PCL chains and (b) living (1) and hydrolyzed (2) PLA chains.

Table 5. Viscosity Data for Living and Hydrolyzed PCL and PLA Chains in Toluene at 25 °C[a]

	PCL		PLA	
	living	hydrolyzed	living	hydrolyzed
[η] (dL/g)	0.049	0.049	0.28	0.16
$\overline{DA}$	1	1	3	3

[a] Intrinsic viscosity ([η]) and mean degree of association ($\overline{DA}$) as determined from eq 8.

monomer, either individual linear $^{i}PrO-PCL-OAl(O^{i}Pr)_2$ chains or individual three arm star shaped $(^{i}PrO-PLA)_3Al$ chains exist in solution. In the case of independent living PCL chains, ^{27}Al and ^{13}C NMR studies have shown that *intra*molecular coordinative interactions between the polyester chain and the active aluminum end group are responsible for tetrahedral and octahedral Al atoms. Investigation of this intramolecular aggregation in relation to the solvent polarity (toluene or THF) will be the topic of a forthcoming paper.

Conclusions

Aluminum triisopropoxide has proved to be a very effective initiator for the ROP of lactones (ϵ-Cl, δ-VL, β-PL, and DXO), lactides (LA), and cyclic anhydrides (AA) in toluene. The ring opening proceeds through a general coordination–insertion mechanism which involves the insertion of the monomer into an "Al–O" bond of the initiator. This mechanism, which assumes the coordination of the monomer to the initiator, is in agreement with IR observations reported by Feijen et al.[21] These authors have indeed shown that aluminum tribromide and aluminum triisobutyl form complexes with lactide and glycolide through coordinative bonds between Al and the acyl oxygen of the cyclic monomers. These coordinative interactions have recently been investigated by ^{13}C and ^{27}Al NMR using γ-BL as a nonpolymerizable lactone.[15] Although NMR of $Al(O^{i}Pr)_3$ in toluene proves an aggregation equilibrium between tetramers and trimers (eq 5), addition of the monomer is responsible for the formation of monomer-solvated $[Al(O^{i}Pr)_3{\cdot}x\text{monomer}]$ octahedral aluminum triisopropoxide. From cryometry, the actual initiator in the ROP of lactones and, by extension, of lactides and cyclic anhydrides is $Al(O^{i}Pr)_3$ solvated by three ($x = 3$) monomer molecules (eq 7).

It is interesting to note that Evans et al.[22] have recently reported the crystal structure of a six-coordinate yttrium trichloride complex of caprolactone that was prepared by crystallization from a saturated solution of YCl_3 in ϵ-caprolactone. The molecular structure of this complex is in perfect agreement with the structure proposed for the trisolvated $[Al(O^{i}Pr)_3{\cdot}3\text{monomer}]$ octahedral aluminum triisopropoxide in this study. The yttrium-based complex was shown to be a trisolvated meridional octahedral complex in which each caprolactone is coordinated as a monodentate ligand through its carbonyl oxygen.

From the results reported in this paper, several pending questions may now be answered. The dissociation of the $[Al(O^{i}Pr)_3]_m$ aggregates by the cyclic monomer may account for the induction period of time usually observed before the polymerization starts. Therefore, this period of time should depend on the ability of the monomer to solvate the initiator and it is actually so, since the induction period of time (t_i) for the ϵ-CL polymerization ($t_i = 4$ min) is approximately 10 times shorter than for LA ($t_i = 40$ min), in agreement with the less electron-donating capability of LA compared to ϵ-CL (IR data in Table 6).

It has been previously discussed that the difference in the average number of active alkoxides ($\bar{n}$) per Al atom in the presence of ϵ-CL and LA (Table 1) cannot be attributed to a difference in the polymerization temperature, i.e., 0 °C for ϵ-CL and 70 °C for LA. Indeed $\bar{n}$ does not exceed 1.4 when the polymerization temperature for ϵ-CL is increased from 0 to 100 °C. A pertinent explanation might be found[23] in the molecular structure of the six-coordinate $[Al(O^{i}Pr)_3{\cdot}3\epsilon\text{-CL}]$ aluminum triisopropoxide complex of ϵ-caprolactone, a model of which has shown that two isopropoxides are sterically hindered, in contrast to the third one which might favorably contribute to the ROP of ϵ-CL ($n = 1$). Substitution of the cyclic monomer by two methyl groups, as occurs in lactide, creates a comparable steric hindrance around each isopropoxide. Moreover, IR data in Table 6 indicate a weaker coordinative interaction between $Al(O^{i}Pr)_3$ and the less electron-donating LA compared to ϵ-CL. Thus, a combination of coordinative interaction and steric effects is more likely responsible for an increase in the average number of active isopropoxy groups per Al atom and for the parallel decrease in the polymerization rate when lactide is polymerized instead of ϵ-CL (Table 1).

Table 6. Polymerization of ϵ-CL and LA Initiated with $Al(O^{i}Pr)_3$ in Toluene at 0 and 70 °C, Respectively: Induction Period of Time (t_i), Average Number of Active Sites (n) per $Al(O^{i}Pr)_3$ Molecule, and Coordination Ability of the Related Monomers

monomer	T (°C)	t_i (min)	n	IR [$\nu_{C=O}$ (cm^{-1})]	K_B[a] ($mol{\cdot}L^{-1}$)
ϵ-CL	0	4	0.9	1725	7.8
LA	70	40	3.0	1770	2.9

[a] Equilibrium constant ($CH_3OD + O{=}C{\frown}O \rightleftharpoons CH_3O{\cdots}D{\cdots}O{=}C{\frown}O$) calculated from the optical density of the oxygen–deuterium bond in the presence of (D,L)-LA and ϵ-CL ($K_B = 0$ for CH_3OD + poly[(D,L)-LA]).[22]

The effect of experimental parameters, such as the nature of the solvent, initiator, and ligand, on the structure and activity of the active aluminum alkoxide species is currently being investigated by multinuclear NMR and viscosimetry. It will be the purpose of a forthcoming paper to focus on the relationship between the aggregation behavior of the initiator and the polymerization kinetics.

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