Macromolecular Engineering of Polylactones and Polylactides. 20. Effect of Monomer, Solvent, and Initiator on the Ring-Opening Polymerization As Initiated with Aluminum Alkoxides

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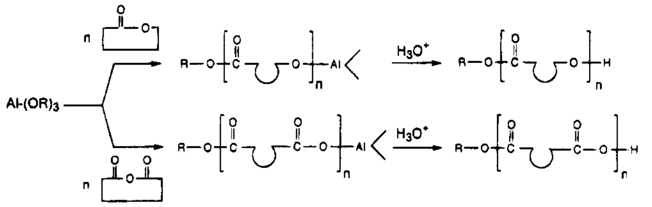
ABSTRACT: Structure and coordinative association of the propagating species have been studied by ^{1}H, ^{27}Al, and ^{13}C NMR and viscosimetry in case of ϵ-caprolactone (ϵ-CL) and lactides (LA) polymerization initiated by aluminum alkoxides. In toluene, aluminum triisopropoxide, a commonly used initiator, forms tetrameric (A_4) and/or trimeric (A_3) aggregates, which are dissociated upon the addition of the cyclic monomer. Actually, LA is responsible for the complete deaggregation of both A_3 and A_4 into single species (A_1) trisolvated by the monomer (Al coordination number, CN = 6), whereas A_3 is selectively deaggregated by ϵ-CL. This behavior is consistent with the higher stability of A_4 compared to A_3. Whatever the monomer, three chains are initiated by the active A_1 species. When conversion of ϵ-CL is complete, the active aluminum trialkoxide sites are solvated by one (CN = 4) and more probably three (CN = 6) carbonyl groups of the attached poly-ϵ-caprolactone chains. At the complete LA conversion, only one carbonyl group of the polylactide chains is coordinated to Al (CN = 4). In THF, there is a competition between monomer and solvent for coordination to Al, which explains why polymerization is slower in THF than in toluene. In both toluene and THF, diethylaluminum monoalkoxide forms cyclic trimers that are solvated by the monomer (ϵ-CL) at least on the NMR time scale. Nevertheless, a fractional kinetic order in initiator is observed which gives credit to a fast reversible dissociation of the ϵ-CL-solvated trimers.

Introduction

Depending on the initiator, the ring-opening polymerization (ROP) of lactones and lactides is known to be living. In this respect, the commercially available aluminum triisopropoxide ($Al(O^iPr)_3$) has proved to be a very effective initiator for the living ROP of ϵ-caprolactone (ϵ-CL),[1] lactides (LA),[2,3] glycolide,[4] and cyclic anhydrides.[5,6] In agreement with kinetic and structural data, the ROP mechanism fits a "coordination–insertion" mechanism, consistent with the monomer insertion into an active "Al–O" bond of the initiator. Since the ring-opening proceeds through the scission of the acyl oxygen bond of the monomer, the final chains are end-capped with an ester group carrying the radical of the initiator (R = ^{i}Pr for $Al(O^iPr)_3$) and with a hydroxyl (or carboxyl) end group that results from the hydrolysis of the polyester (or polyanhydride) growing species, respectively (eq 1). The great versatility of aluminum alkoxides, functional or not, has opened the way to the macromolecular engineering of polyesters and polyanhydrides, as supported by the perfectly controlled synthesis of telechelic polymers, block copolymers and macromonomers, i.e. promoters of graft copolymers.[3–8]



[1]

Although ROP is under control, the actual structure of the pseudoanionic active species is still a pending question. Nevertheless, a study from our laboratory has recently focused on the coordinative structure and dynamics of $Al(O^iPr)_3$ in toluene, before and after the addition of a carbonyl-containing cyclic monomer.[9] According to ^{27}Al NMR, an aggregation equilibrium occurs between tetramers (A_4) and trimers (A_3) of $Al(O^iPr)_3$ in toluene. Upon the addition of a model nonpolymerizable lactone, i.e. γ-butyrolactone (γ-BL), this equilibrium is altered and ultimately leads to additional aluminum alkoxide monomeric species. Actually, single $Al(O^iPr)_3$ species are solvated by the monomer with formation of a trisolvated six-coordinate "$Al(O^iPr)_3(monomer)_3$" complex in which each monomer is assumed to be coordinated as a monodentate ligand through its carbonyl oxygen.[10] This aggregation is in agreement with infrared observations by Feijen et al.[11] about the complexation of aluminum tribromide (or triisobutyl) with lactide (or glycolide) through coordinative interactions between Al and the acyl oxygen of the cyclic monomer.

Cryometric measurements have confirmed that ROP of lactones does not start as soon as monomer and initiator are mixed together.[10] This observation has been accounted for by the slow rearrangement of the coordinative aggregates of $Al(O^iPr)_3$ in toluene, as triggered by the addition of the polar monomer. The induction period of time for ROP of lactones and lactides (t_i) clearly depends on the ability of the monomer to coordinate to the initiator. Indeed, t_i is much longer for lactides (40 min at 70 °C) than for ϵ-CL (4 min at 0 °C) in toluene, in good agreement with the weaker electron-donating capability of lactides.

From kinetic data listed in Table 1, it is clear that the nature of the monomer (entries 1 and 2), solvent (entries 2 and 3, and 4 and 5), and initiator (entries 3 and 5–8) has a deep effect on the activity of the

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Table 1. Kinetics of the ϵ-CL ($[\epsilon\text{-CL}]_o$ = 1 mol/L) and Lactide ($[\text{LA}]_o$ = 0.6 mol/L) Polymerization Initiated by Aluminum Triisopropoxide and Distilled Dialkylaluminum Monoalkoxides

entry	monomer	solvent	temp (°C)	initiator	partial order in initiator[a]	k (L mol^{-1} min^{-1})	n_{OR}/Al	m[c]
1	LA[d]	toluene	70	$Al(O^iPr)_3$	1.0	0.60	3.0	1.0
2	ϵ-CL[d]	toluene	0	$Al(O^iPr)_3$	1.0	36.6	1.0	1.0
3	ϵ-CL	THF	0	$Al(O^iPr)_3$	–[e]	–[e]	1.0	–[e]
4	ϵ-CL[b]	toluene	25	$Et_2AlOCH_2CH_3$	1/3	8.40	1.0	1.0
5	ϵ-CL[b]	THF	25	$Et_2AlOCH_2CH_3$	1/3	2.34	1.0	3.0
6	ϵ-CL	THF	25	$Et_2AlO(CH_2)_2Br$	1/3	1.68	1.0	3.0
7	ϵ-CL[b]	THF	25	$Et_2AlOCH_2CH{=}CH_2$	1/3	2.40	1.0	3.0
8	ϵ-CL[b]	THF	25	$(^iBu)_2AlOCH_3$	1/2	2.52	1.0	2.0

[a] The partial order in monomer is systematically 1.0. [b] Results reported by Penczek et al.,[25,26] $[\epsilon\text{-CL}]_o$ = 2.0 mol/L. [c] m is the aggregation degree of the growing aluminum alkoxide species, as calculated from eq 7. [d] The induction period of time for the ϵ-CL and LA polymerization is 4 and 40 min, respectively. [e] Half-polymerization time ($t_{1/2}$) = 8.7 min ($[\epsilon\text{-CL}]_o/[I]$ = 200).[20]

propagating species. Indeed, when aluminum triisopropoxide is used as an initiator for the ROP of ϵ-CL and LA in toluene, the polymerization rate constant is 60 times higher for ϵ-CL at 0 °C compared to LA at 70 °C, the partial order in monomer and initiator being the same (Table 1, entries 1 and 2).[12]

When the initiator of the ϵ-CL polymerization is a dialkylaluminum monoalkoxide, the partial order in initiator depends on the alkyl group of the dialkylaluminum monoalkoxide (Table 1, entries 5–8). Again, the ROP proceeds faster in less polar medium (Table 1, entries 4 and 5) whereas the nature of the alkoxide substituents has no significant effect on the activity of the growing species (entries 5–7).

In order to account for the aforementioned kinetic data, it is of prime importance to analyze the structure of the propagating species and to focus on the coordinative association of these species in relation to the experimental conditions: monomer, solvent, and initiator. ^{1}H, ^{27}Al, and ^{13}C NMR spectroscopy and viscosimetry have been used as the main investigation techniques for this purpose.

Viscosimetry allows the mean degree of association ($\overline{DA}$) of the living chains to be measured. Interestingly enough, comparison of $\overline{DA}$ with the aggregation degree of the propagating aluminum alkoxide species[12] (m; see eq 7) can give some information about the intermolecular coordinative aggregation of these living end groups. ^{27}Al and ^{13}C NMR are expected to probe the possible coordination of the polyester chains to Al, at complete monomer conversion. Actually, NMR and viscosimetry complement each other, since NMR is suitable for short length chains, in contrast to viscosimetry, which is sensitive to high molecular weight chains.

An aluminum trialkoxide ($Al(O^iPr)_3$) and two dialkylaluminum monoalkoxides [Et_2AlO^iPr and $Et_2AlO(CH_2)_2Br$] will be used as initiators for the ϵ-CL and LA polymerization, in toluene or THF.

Experimental Section

I. Materials. Toluene and benzene-d_6 were dried by refluxing over calcium hydride and distilled under nitrogen just before use. Tetrahydrofuran (THF) was refluxed over a benzophenone–sodium complex and freshly distilled before use. γ-Butyrolactone and ϵ-caprolactone (from Aldrich) were dried over CaH_2, distilled under a reduced pressure, and then stored under a nitrogen atmosphere and dissolved, just before use, in toluene or THF (for ^{27}Al NMR or viscosimetry) or in benzene-d_6 (for ^{13}C NMR). 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 a reduced pressure before polymerization. Aluminum triisopropoxide (from Aldrich) was twice sublimated and then dissolved in toluene under nitrogen. Diethylaluminum isopropoxide and diethylaluminum bromoethoxide were synthesized by reaction of a triethylaluminum solution in toluene with 1 equiv of 2-propanol and 2-bromoethanol, respectively. Synthesis and purification of the aluminum alkoxides were detailed elsewhere.[3,12] The concentration of their solutions was measured by complexometric titration of aluminum with a standard solution of EDTA.

II. 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. Solvent was then added through a rubber septum with a stainless steel capillary or a syringe and LA was dissolved at 70 °C. Since ϵ-CL was soluble (in toluene or THF) at 25 °C, it was added as a solution into the reactor. A solution of the initiator was ultimately added, and the polymerization was carried out at 0 °C for ϵ-CL and at 70 °C for LA, under vigorous stirring.

After the complete monomer conversion, polymerization was stopped by adding an excess (compared to the initiator) of 1 N HCl solution. The initiator residues were repeatedly extracted with an aqueous EDTA solution (0.1 mol L^{-1}) and then with water up to a neutral pH. Poly-ϵ-caprolactone (PCL) and polylactide (PLA) were precipitated into cold heptane and methanol, respectively, filtered, and dried for 24 h at room temperature under a reduced pressure.

III. Measurements. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AM400 superconducting magnet system respectively operating in the FT mode at 400.13 or 100.6 MHz with a deuterium lock (benzene-d_6). Quantitative ^{13}C NMR measurements were carried out by using the "INV-GATE" sequence[13] with a pulse width of 30°, an acquisition time of 0.7 s, and a delay of 3 s between pulses. ^{13}C chemical shifts were referred to the low field resonance of benzene-d_6, the chemical shift of which was measured to be 77.7 ppm in reference to $(CH_3)_4Si$. ^{27}Al NMR spectra were recorded with a Bruker AM200 apparatus operating at 78.21 MHz with a deuterium lock (toluene-d_8 or THF-d_8). ^{27}Al NMR were referred to a $Al(acac)_3$ solution in toluene-d_8 or THF-d_8 (^{27}Al signal at 0 ppm).

Solution viscosity was measured with a modified Ubbelohde viscosimeter in a thermostated bath at 25 ± 0.1 °C. The previously flame-dried and nitrogen-purged glass viscosimeter had caps to prevent evaporation of solvent and exposure to air. Measurements were repeated until the relative error of three successive measurements was less than 0.5%.[14,15]

Molecular weight and molecular weight distribution were measured with a gel permeation chromatograph (Waters 200) operating with tetrahydrofuran and calibrated with polystyrene standards. The universal calibration method was used for P-D,L-LA and PCL using the previously reported viscosimetric relationships.[3,16]

Results and Discussion

I. Structure of the Propagating Species as Initiated with an Aluminum Trialkoxide. I.1. Monomer Effect.

Polymerization of ϵ-CL and LA is perfectly living when initiated by $Al(O^iPr)_3$ in toluene at 0 and 70 °C, respectively.[1–3] From the slope of the linear relationship between the mean degree of polymerization ($\overline{DP}$) at complete monomer conversion and the initial monomer/initiator molar ratio, it appears that each alkoxide group of $Al(O^iPr)_3$ participates in the

Table 2. Viscosity Data and Mean Degree of Association ($\bar{D}\bar{A}$) at 25 °C for Living and Deactivated PCL and PLA Chains Initiated by Al(O^{i}Pr)$_3$ (A_3/A_4 mixture) in Toluene at 0 and 70 °C, Respectively

	PCL				PLA	
	A_3/A_4 (45/55)		A_3/A_4 (90/10)		A_3/A_4 (45/55)	
	living	deactivated[a]	living	deactivated[b]	living	deactivated[c]
$[\eta]$	0.875	0.26	0.51	0.305	0.28	0.16
$\bar{D}\bar{A}$	11.3		2.75		3.1	

[a] $\bar{M}_n = 28\,000$ $\bar{M}_w/\bar{M}_n = 1.1$ [b] $\bar{M}_n = 29\,000$ $\bar{M}_w/\bar{M}_n = 1.1$. [c] $\bar{M}_n = 25\,500$ $\bar{M}_w/\bar{M}_n = 1.2$.

lactide polymerization ($n_{OR}/Al = 3$). This is in sharp contrast to the ROP of ϵ-CL since only one alkoxide group is then active ($n_{OR}/Al = 1$) (Table 1, entries 1 and 2). As a result, three PLA chains are growing from each Al atom whereas, in case of PCL, there is either one PCL chain per Al atom or only part of the Al(O^{i}Pr)$_3$ molecules initiates and propagates three PCL chains per Al atom. In order to discriminate these two proposals, the intrinsic viscosity of the living PLA and PCL chains has been measured before and after deactivation, in toluene at 25 °C, which allows the average association degree of the growing chains to be calculated.

The mean degree of association ($\bar{D}\bar{A}$) of the living chains has been estimated from the Huggins equation (eq 2):[17]

$$\eta_{\mathrm{red.}} = \eta_{\mathrm{sp}/C} = [\eta] + K'[\eta]^2C \qquad (2)$$

where η_{sp} is the specific viscosity, $[\eta]$ the intrinsic viscosity, $\eta_{\mathrm{red.}}$ the reduced viscosity, C the polymer concentration, and K' the Huggins constant. From the $\eta_{\mathrm{red.}}$ vs C plot, $[\eta]$ and K' have been calculated for the deactivated polyester chains. The value of K' has then been used in eq 3 in order to calculate the apparent intrinsic viscosity of the aggregated living chains, $[\eta]_{agg}$, at various concentrations. This procedure implies that the molecular aggregates formed at concentration C persists down to infinite dilution. $[\eta]_{agg}$ can thus be inferred to be expressed by eq 3.[14,15]

$$[\eta]_{\mathrm{agg}} = \frac{-1 + (1 + 4K'C\eta_{\mathrm{red.}})^{0.5}}{2K'C} \qquad (3)$$

The association degree, DA, is expressed by eq 4:

$$\bar{D}\bar{A} = \frac{M_{\mathrm{agg}}}{M_{\mathrm{o}}} \qquad (4)$$

where M_{agg} and M_o are the average molecular weight of the living and the deactivated chains, respectively.

According to Flory,[18] the intrinsic viscosity depends on the polymer molecular weight, as follows (eq 5)

$$[\eta] = KM^{1/2}\alpha^3 \qquad (5)$$

where K is the Mark–Houwink constant and α is the (viscosity) expansion coefficient.

On the assumption that K and α are the same for both the living and the deactivated chains, eq 6 results from eqs 4 and 5

$$\bar{D}\bar{A} = ([\eta]_{\mathrm{agg}}/[\eta]_0)^2 \qquad (6)$$

The intrinsic viscosity and association degree data are compiled in Table 2. When LA polymerization is initiated by an Al(O^{i}Pr)$_3$ solution in toluene, be it freshly prepared or not, there is a good agreement between the mean association degree of the living PLA chains ($\bar{D}\bar{A} = 3$) and the mean number of active alkoxide groups ($n_{OR}/Al = 3$) per Al atom. In case of the ϵ-CL polymerization, $\bar{D}\bar{A} = 11.3$ is substantially higher than $n_{OR}/Al = 1$ when an aged Al(O^{i}Pr)$_3$ solution is used, that contains ca. 45 mol % A_3 in the A_3/A_4 mixture. However, $\bar{D}\bar{A}$ decreases down to 2.75 when Al(O^{i}Pr)$_3$ is freshly distilled and then contains ca. 90 mol % A_3. It must be noted that a $\bar{D}\bar{A}$ value of 1 has been erroneously reported by us in a previous paper.[10] The origin of this problem is more likely a nonsuspected deactivation of the living PCL chains prior to or during the viscosimetry measurement. It is clear now that the A_3/A_4 equilibrium has a deep effect on the mean association degree of the PCL chains in toluene. Furthermore, intermolecular coordinative association in which the active aluminum growing species would be involved may be precluded on the basis of a kinetic study by Penczek and colleagues,[19] who proposed the following linear relationships (eqs 7 and 8):

$$\ln\left\{(1/t)\ln\left(\frac{[\mathrm{M}]_0}{[\mathrm{M}]}\right)\right\} = 1/m \ln[\mathrm{Al}]_{\mathrm{o}} + \ln\left\{\left(\frac{1}{m}\right)^{1/m} k_{\mathrm{p}}K_{\mathrm{m},1}{}^{1/m}\right\} \qquad (7)$$

$$\ln k_{\mathrm{app}} = 1/m \ln[\mathrm{Al}]_{\mathrm{o}} + C^{\mathrm{ste}} \qquad (8)$$

where k_p is the propagation rate constant (L mol^{-1} s^{-1}), $K_{m,1}$ is the association equilibrium constant for the growing end group, and m is the aggregation degree of these active end groups. Plots of the left hand side of eq 8 as a function of ln[Al]$_o$ give the reciprocal aggregation degree under the same polymerization conditions as for the viscosimetric study (T (°C), $[M]_o$, $[M]/[I]$, and solvent and initiator). Value of m is 1 for both PCL at 0 °C and PLA at 70 °C (Figure 1). It is thus clear that the living aluminum trialkoxide growing centers do not associate in toluene whatever the monomer. The value of the $\bar{D}\bar{A} = 3$ for living PLA chains, as calculated from viscosity data, thus originates from three-armed star-shaped [^{i}PrO-PLA-O]$_3$Al growing chains. The same conclusion may hold for the living PCL chains provided that the persistency of the unreactive tetrameric A_4 aggregates is taken into account. The much higher stability of the Al(O^{i}Pr)$_3$ tetramers compared to the trimeric A_3 counterparts has been recently confirmed by semiempirical calculations,[28] making reasonable the hypothesis that the trimers A_3 are the active species and that three PCL chains are growing from each Al atom of these aggregates. So the estimated average association degree of 2.75 (Table 2) when Al(O^{i}Pr)$_3$ is freshly distilled is consistent with a composition of 90 mol % A_3 for the initiator. Al atoms of the inactive A_4 aggregates could however be coordinated to carbonyl groups of PCL chains and be responsible for an additional interchain association. This effect might explain the sharp increase in the solution viscosity and the "apparent" $\bar{D}\bar{A}$ (=11.3) when the A_4 content of the aged initiator solution is as high as 55 mol % A_4 (Table 2). In order to assess the unreactivity of the A_4 aluminum alkoxides, the living PCL chains have been precipitated into dried n-heptane and filtered out under an inert atmosphere, and the n-heptane filtrate has been evaporated to dryness. The solid residue has been dissolved in dry deuterated benzene for ^{1}H NMR analysis (Figure 2). In addition to a low amount of (unfiltrated) PCL chains, the unreacted [Al(O^{i}Pr)$_3$]$_4$ tetramers are easily identified by the characteristic

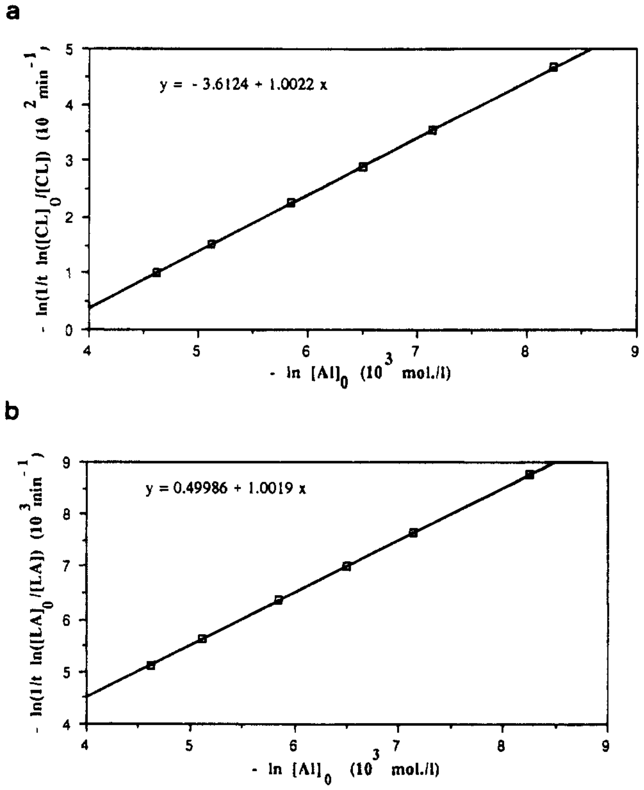


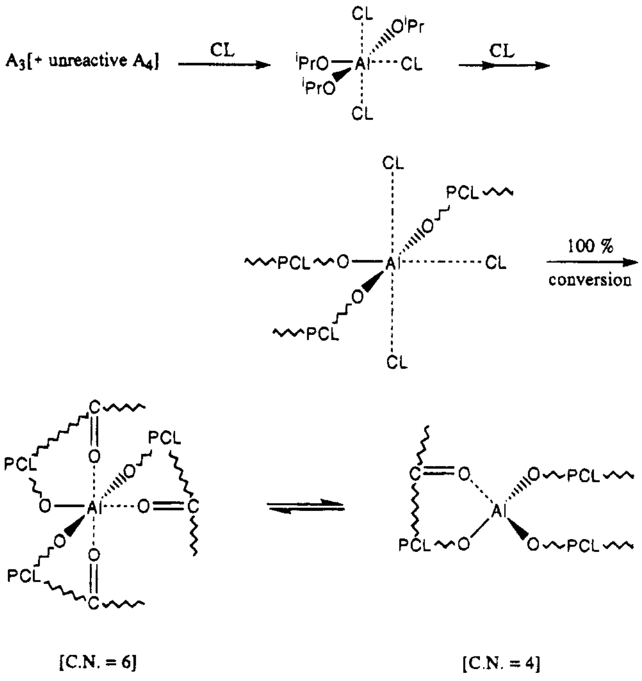
Figure 1. Dependence of the polymerization rate on the initial $Al(O^iPr)_3$ concentration in toluene. (a) ϵ-CL polymerization at 0 °C. $[M]_o = 1$ mol/L. (b) LA polymerization at 70 °C. $[M]_o = 0.6$ mol/L.

chemical shifts at 4.69 and 4.41 ppm for the nonequivalent methine protons, and at 1.69, 1.40, and 1.33 ppm for the methyl protons.[29] No trimeric $[Al(O^iPr)_3]_3$ can be detected as supported by the complete lack of signals at 4.38, 4.32, and 4.26 ppm, characteristic of the A_3 methine protons. This experimental observation confirms that when a mixture of A_3 and A_4 is used to initiate the ϵ-CL polymerization, the A_3 component is completely consumed, in contrast to the A_4 fraction that remains unreacted. In the light of these results, the original statement based on viscosimetric data that only one of the three isopropoxy groups of $Al(O^iPr)_3$ participates to the ϵ-CL polymerization has to be revised. Actually the A_3/A_4 composition of the aged $Al(O^iPr)_3$ solution is such that the activity of all the isopropoxy groups of the A_3 aggregates corresponds to a number of growing chains which by chance agrees with an average of one chain per Al when the whole amount of $Al(O^iPr)_3$ is considered. It is worth point out that this conclusion completely confirms the very recent work by Duda and Penczek,[30] who reported about the much higher reactivity of A_3 compared to A_4 toward ϵ-CL ($k_{i3}/k_{i4} \approx 10^3$, with k_{i3} and k_{i4} being the initiation rate constants of A_3 and A_4, respectively). They also interestingly proved that the A_3/A_4 interconversion was very slow in dilute solutions (≤ 0.1 mol L^{-1}) in C_6D_6 with added ϵ-CL or not.

Polymerization of less reactive monomers, such as lactides, requires longer polymerization times and higher temperatures (70 °C), which may give A_4 enough time to be completely consumed. All the aluminum alkoxide functions are then active ($\overline{DA} = 3$) as observed in the LA homopolymerization[2,3] and in the random copolymerization of LA and ϵ-CL,[13] both in toluene at 70 °C.

Since ^{27}Al NMR has shown that $Al(O^iPr)_3$ in toluene is solvated by the monomer (ϵ-CL or LA) with formation of trisolvated single Al trialkoxide species $[Al(OR)_3\cdot(M)_3]$,[9,10] the question of the coordination structure of Al is addressed, particularly when the monomer conversion is complete. For this purpose, short living PCL and PLA chains (theoretical molecular weight of 2000) have been synthesized by using $Al(O^iPr)_3$ as an initiator, in toluene at 0 and 70 °C, respectively. Polymerization has proved to be complete after 30 min and 20 h for ϵ-CL and LA, respectively.

Figure 3a illustrates the ^{27}Al spectrum of the active PCL chains in toluene and shows two types of aluminum atoms. In reference to the chemical shift of the $Al(acac)_3$ salt, the sharp line at high field (2.0 ppm) is due to hexacoordinated aluminum atoms (CN = 6), whereas the broad line at ca. 60.0 ppm is usually assigned to tetracoordinated Al atoms (CN = 4).[9] Coordination numbers (CN) of 4 and 6 may not be attributed to the monomer coordination due to the complete polymerization. The solvent may also be precluded since toluene is not prone to solvate Al. The only way to account for the coordination numbers of the Al atoms is to accept an inter- and/or intramolecular coordination of carbonyl groups of the polyester chains on the metal. Indeed, although viscosimetry indicated the absence of intermolecular association between the Al alkoxide end groups of living PCL chains, one cannot preclude fastly exchanging Al–carbonyl intermolecular interactions as well as interaction between the living PCL chains and the remaining unreacted A_4 if present. Therefore, the single active aluminum trialkoxide sites appear to be stabilized by a coordinative aggregation with one (CN = 4) and more probably three (CN = 6) main chain ester groups. Equation 9 schematizes the situation that prevails in the presence and absence of monomer (M) for the living PCL chains (only intramolecular coordination is shown for clarity).



[9]

When LA is substituted for ϵ-CL, Figure 3b shows that after complete monomer conversion, all the aluminum atoms are tetrahedral (CN = 4). A slightly smaller

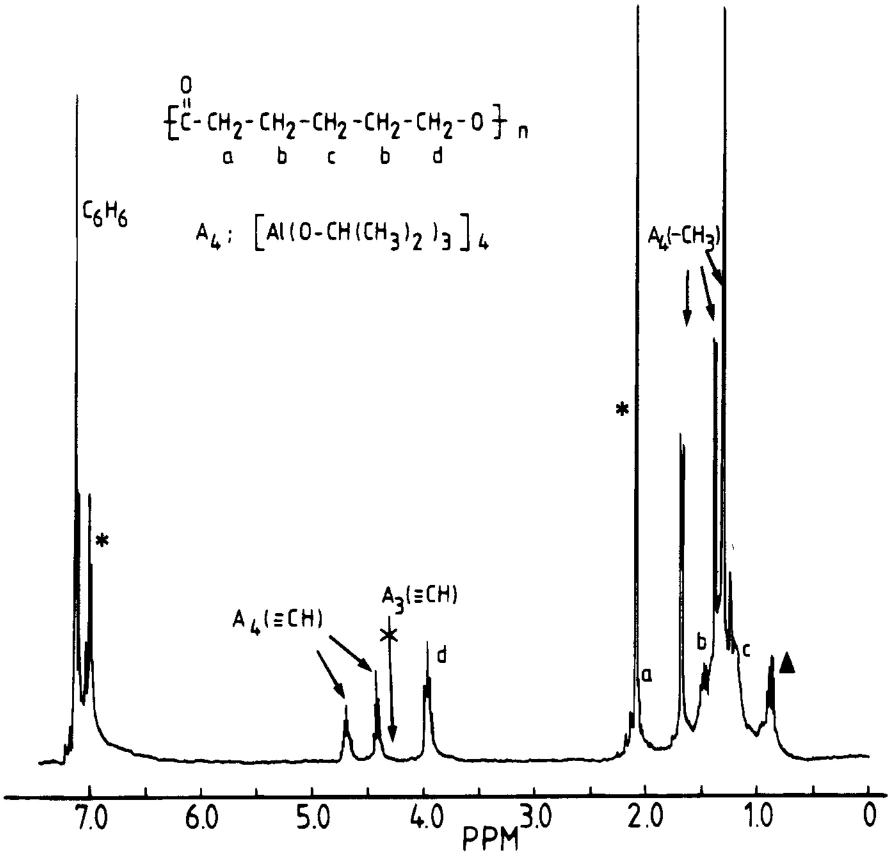
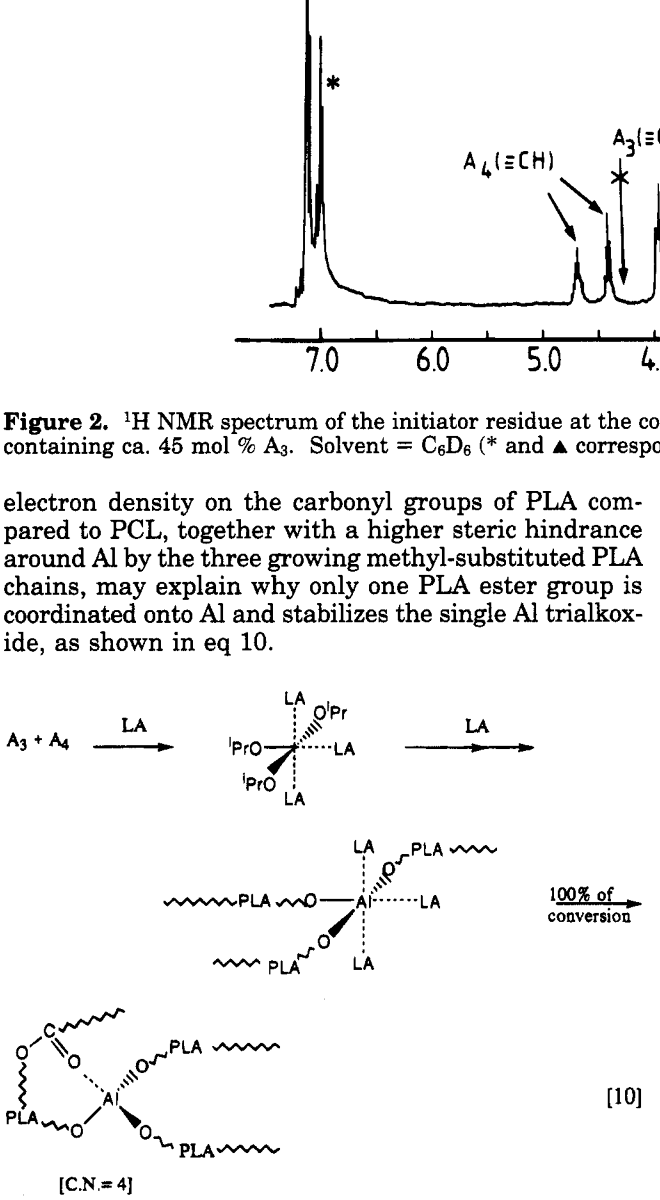


Figure 2. ^{1}H NMR spectrum of the initiator residue at the complete ε-CL conversion. The original initiator is a A_3/A_4 mixture containing ca. 45 mol % A_3. Solvent = C_6D_6 (* and ▲ correspond to residual toluene and *n*-heptane, respectively).

electron density on the carbonyl groups of PLA compared to PCL, together with a higher steric hindrance around Al by the three growing methyl-substituted PLA chains, may explain why only one PLA ester group is coordinated onto Al and stabilizes the single Al trialkoxide, as shown in eq 10.



[10]

These experimental observations are in direct line with the intramolecular transesterification reactions, known as back-biting reactions, that occur under well-defined experimental conditions (long polymerization time, high polymerization temperature, etc.).[3]

I.2. Solvent Effect. Substitution of THF for toluene as the ε-CL polymerization solvent does not modify the average number of active isopropoxide groups per Al (n_{OR}/Al = 1) (Table 1).[20,21] When kinetics is concerned, beyond the similarity in the partial order in monomer and initiator (1 in the two solvents),[12] there is a deep discrepancy in the polymerization rate, which is significantly smaller in THF than in toluene. Indeed, the half-polymerization time ($t_{1/2}$) is 3.5 min in toluene and 8.7 min in THF when ε-CL is polymerized ([ε-CL] = 1 mol/L and $[\epsilon\text{-CL}]_0/[I] = 200$) at 0 °C.[20] Multinuclear NMR has been used in order to account for this solvent effect on the activity of the living PCL end groups.

In order to know whether substitution of THF for toluene perturbs the previously observed dissociation of $Al(O^iPr)_3$ by the monomer with formation of trisolvated six-coordinate $Al(O^iPr)_3 \cdot (\epsilon\text{-CL})_3$ species, $Al(O^iPr)_3$ has been dissolved in γ-BL, a nonpolymerizable monomer analogue of ε-CL, and analysed by ^{27}Al NMR. Although γ-BL is stable toward $Al(O^iPr)_3$ tetramers, it is opened by the trimers, as will be detailed in a forthcoming paper.[31] The molar fraction in Al (F_{Al} = 2.5 × 10^{-2}) has been kept small in order to mimic the polymerization conditions, whereas an Al concentration of 8 × 10^{-2} M has been selected so as to avoid problems due to the limited sensitivity of Al NMR spectrometry.[9] At this concentration, the A_4 content is higher than 95% and γ-BL is stable at 25 °C for more than 2 days. In the absence of solvent, three resolved ^{27}Al signals are observed (Figure 4a). The two signals at 2.4 and 59.5 ppm are characteristic of the tetrameric $[Al(O^iPr)_3]_4$ species, the central six-coordinate Al of which is observed at 2.4 ppm and the external four-coordinate Al atoms at 59.5 ppm.[9] The additional signal at 5.6 ppm has previously been attributed to single $Al(O^iPr)_3$ species, trisolvated with lactone molecules.[9,10] Addition of a small amount of toluene (25 wt %) to the $Al(O^iPr)_3$ solution in γ-BL (F_{Al} = 2.5 10^{-2}) is responsible for a sharp increase in intensity of the ^{27}Al signal at 5.6 ppm (Figure 4b). In contrast, addition of a small amount of

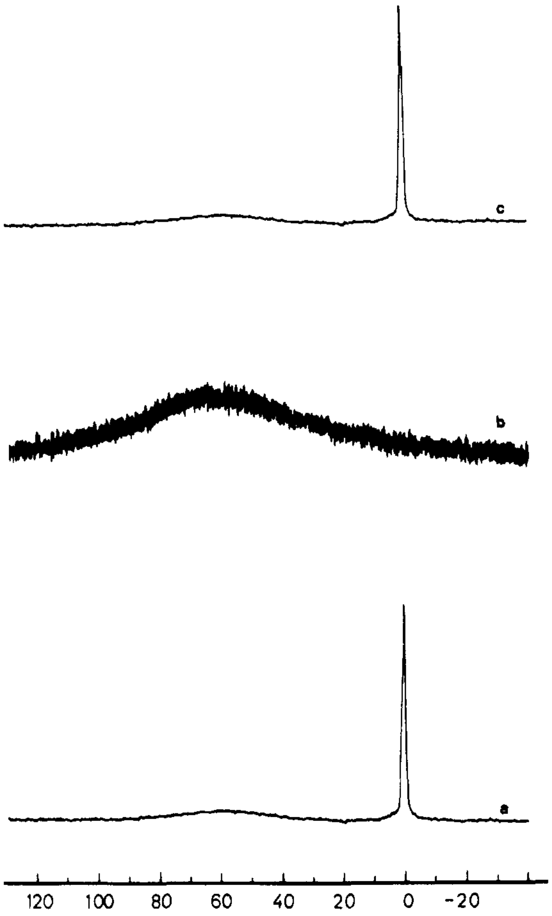


Figure 3. ^{27}Al NMR spectra (297 K) for the active aluminum trialkoxide end groups of (a) PCL chains, as initiated by Al(O^{i}Pr)$_3$ in toluene at 0 °C; (b) PLA chains, as initiated by Al(O^{i}Pr)$_3$ in toluene at 70 °C; (c) PCL chains, as initiated by Al(O^{i}Pr)$_3$ in THF at 0 °C.

THF (25 wt %) triggers a sharp decrease in the signal (5.6 ppm) intensity of the octahedral Al atoms characteristic of the single Al(O^{i}Pr)$_3$ molecules coordinated with three cyclic monomers in favor of the aggregated [Al(O^{i}Pr)$_3$]$_4$ species (2.4 and 59.5 ppm) (Figure 4c). Undoubtedly, THF competes with γ-BL for coordination to tetrameric Al(O^{i}Pr)$_3$, which is consistent with the longer half-polymerization time observed in THF (Table 1).

THF is a well-known solvating agent, the ether oxygen of which is able to compete with the carbonyl group of γ-BL for coordination onto aluminum. These competitive interactions might account for the unfavorable formation of the single Al(O^{i}Pr)$_3$·(lactone)$_3$ initiating species, which agrees very well with the longer induction time for the ϵ-CL polymerization in THF compared to toluene.[20] All in all, the experimental observations confirm that the structure of the initiating species is independent of the solvent, although the solvent has a decisive effect on the kinetics of formation of these species.

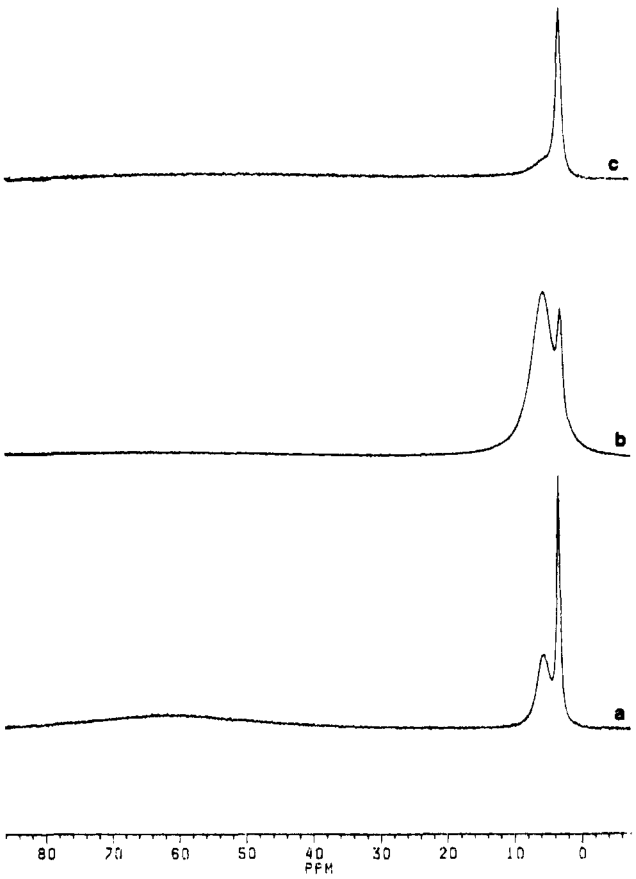


Figure 4. ^{27}Al NMR of the Al(O^{i}Pr)$_3$ (mainly A_4 species)/γ-BL system (F_{Al} = 2.5 10^{-2}): (a) no solvent, (b) addition of toluene (25 wt %), (c) addition of THF (25 wt %).

^{27}Al NMR analysis of the living PCL chains formed when the monomer conversion is complete has confirmed that the active species consist of tetracoordinated and hexacoordinated Al atoms (Figures 3a,c), whatever the solvent. In toluene, coordination numbers of 4 and 6 have been attributed to intramolecular coordinative interactions between the polymer ester groups and the Al atom, rather than to a solvent coordination effect. This situation might however change when toluene is replaced by a more polar solvent and a well-known solvating compound, such as THF. It is thus important to know whether the coordination structure of Al in toluene persists in THF as a result of persistent coordinative associations or due to a solvation process. In this respect, living PCL chains have been prepared in toluene ($\bar{M}_n$ = 1800) and recovered by solvent distillation. Part of them has been dissolved in pure deuterated benzene and the second part in benzene-d_6 added with 10 molar equiv of THF compared to the living Al sites. These solutions have been analyzed by quantitative ^{13}C NMR spectroscopy by using a special "INVGATE" sequence, as reported in the Experimental Section. The quantitative ^{13}C NMR spectrum (Figure 5) allows calculation of the percentage of the carbonyl groups in PCL chains that are free (F) and coordinated (C) to the Al atom of the active species, respectively. In benzene-d_6, which is representative of the living PCL chains in toluene, two signals are observed for the ^{13}CO carbonyl resonance (Figure 5a). Resonance at 172.6 ppm is characteristic of the free carbonyl groups (^{13}CO$_F$ signal) and largely predominates over the resonance at 172.2 ppm, which corresponds to the coordinated carbonyl groups (^{13}CO$_C$ signal). This observation confirms the hypothesis—inferred from ^{27}Al NMR analysis—that coordinative interactions stabilize the active Al sites (as shown in eq 9). When a small amount of THF is added to benzene-d_6, the two ^{13}CO resonances are still observed at the same chemical shift (Figure 5b). The relative intensity of these two signals is however modified in such a way that 2% of the carbonyl groups are coordinated to Al compared to 5% in the absence of THF (Table 3). It is thus clear that THF competes with the ester carbonyl groups for coordination to Al. This observation has been completed by recording the quan-

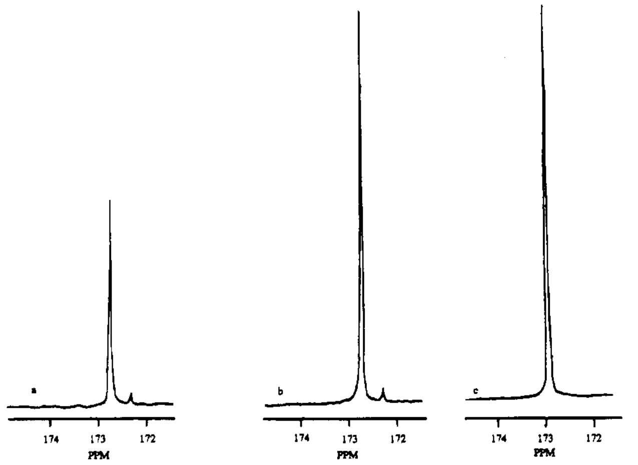


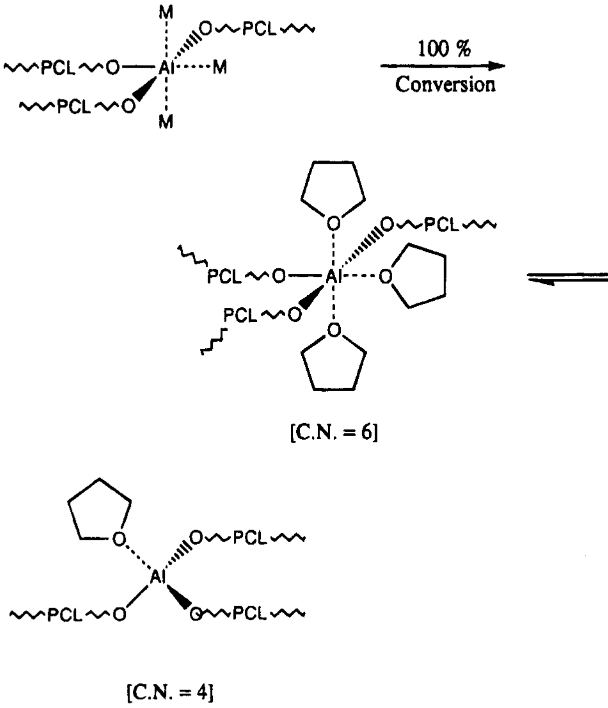
Figure 5. Quantitative ^{13}C NMR spectra (297 K) for living PCL chains initiated by $Al(O^iPr)_3$ in toluene at 0 °C. Spectra recorded in (a) pure benzene-d_6, (b) a benzene-d_6/THF mixture (10 equiv of THF with respect to Al), (c) pure THF-d_8.

Table 3. ^{13}C NMR of the Carbonyl Signals for the Living PCL Chains, Initiated by $Al(O^iPr)_3$ at 25 °C ($\bar{M}_n$ = 1800; $\bar{M}_w/\bar{M}_n$ = 1.1)

	relative intensity in % of the carbonyl signal	
solvent	free at 172.6 ppm	coordinated at 172.2 ppm
C_6D_6	95.0	5.0
C_6D_6 + THF[a]	98.0	2.0
THF-d_8	100.0	0.0

[a] 10 equiv of THF relative to Al.

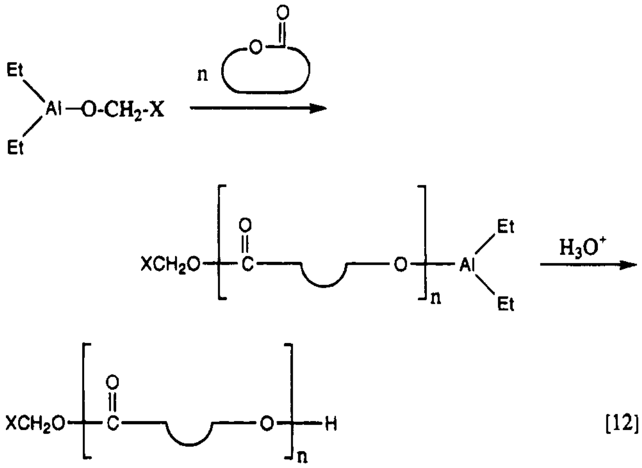
titative ^{13}C NMR spectrum of the living PCL chains dissolved in pure THF-d_8. Figure 5c shows that the carbonyl group is not coordinated anymore, since only the $^{13}CO_F$ signal at 172.6 ppm is observed (Table 3). Accordingly, eq 11 schematizes that the living aluminum



[11]

trialkoxide species are solvated by THF in competition with the monomer, which also explains why the half-polymerization time is higher in THF than in toluene.

II. Structure of the Propagating Species As Initiated by a Dialkylaluminum Alkoxide. Diethylaluminum alkoxides (Et_2AlOCH_2X, where X is a functional group) have been investigated as potential initiators for the ROP of ϵ-CL and LA[7,8,19–21] (eq 12).



[12]

With X = CH_2-Br

= $(CH_2)_2$-CH=CH_2

= CH_2-O-C(O)-C(CH_3)=CH_2

The absolute propagation rate constant, k_p, has been found to be independent of the functional alkoxy groups (R = CH_2X), whatever the solvent: toluene or THF.

Dialkylaluminum alkoxides (R'_2AlOR) are known to be coordinatively associated as dimers or trimers in apolar solvents and in the solid state.[22] Actually, the alkyl substituent R′ affects the mean aggregation degree of these aluminum monoalkoxides. For instance, trimers are formed when R′ is an ethyl substituent, whereas formation of dimers is reported when R′ is a more sterically hindered isobutyl group.[23]

Whatever the monomer, ϵ-CL or LA, the alkoxy group of each dialkylaluminum alkoxide participates in the ring-opening polymerization at 25 °C for ϵ-CL and 70 °C for LA (n = 1) in contrast to the alkyl groups that are inactive under anhydrous conditions (Table 1, entries 4–8).[7,8] The monomer has only a minor effect on k_p in relation to a different propensity to polymerization.[6,8]

Consistent with a "coordination–insertion" polymerization mechanism and in agreement with observations reported for aluminum trialkoxides, substitution of toluene by a more polar solvent, such as THF, is responsible for a decrease in the polymerization rate (Table 1, entries 4 and 5).[20,24] A first partial order in monomer and a fractional partial order in initiator have been reported when the ϵ-CL polymerization is initiated by distilled R'_2AlOR in toluene or in THF at 25 °C (Table 1, entries 4–8).[20,24,25]

Penczek et al.[19] have proposed a kinetic model based on an aggregation–deaggregation equilibrium of the dialkylaluminum alkoxides and on the hypothesis that only the nonaggregated species are active and contribute to the chain propagation (eq 13).

$$\begin{aligned} &(P_n{}^*)_m \underset{}{\overset{K_{m,1}}{\rightleftharpoons}} mP_n{}^* && \text{aggregation–deaggregation} \\ &P_n{}^* + CL \overset{k_p}{\rightleftharpoons} P_{n+1}{}^* && \text{propagation} \end{aligned} \qquad (13)$$

where $K_{m,1}$ denotes the equilibrium constant of deaggregation of the growing end groups, k_p the rate constant

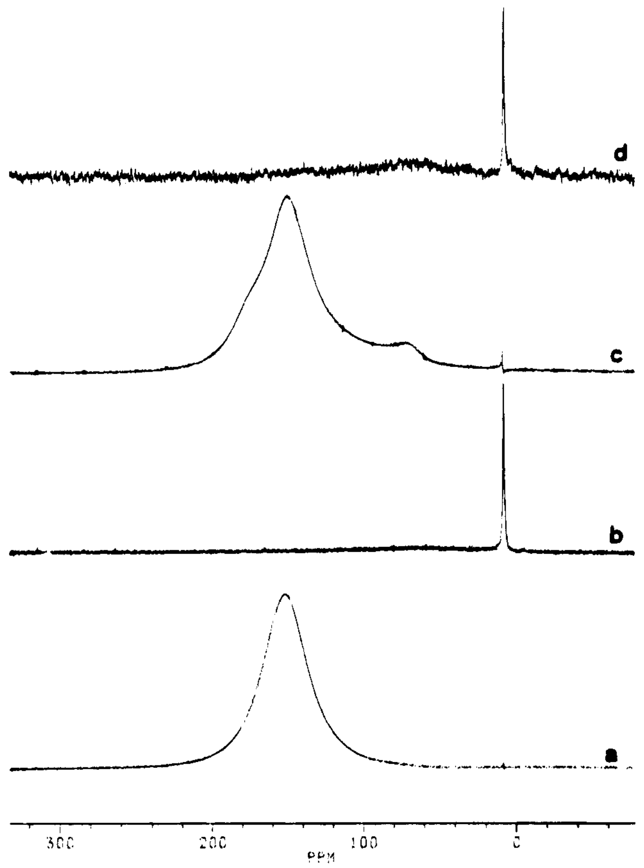


Figure 6. ^{27}Al NMR of the active $Et_2AlO(CH_2)_2Br$ species at 297 K: (a) in toluene, (b) in γ-BL (10 wt % toluene), (c) in THF, (d) in γ-BL (10 wt % THF).

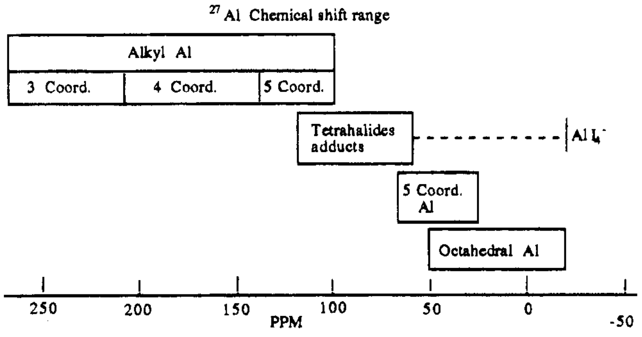


Figure 7. Dependence of the ^{27}Al chemical shift on the coordination number of aluminum. Al–C bonds are observed at low fields, on contrast to the bonding of Al to elements of the VA, VIA, and VIIA groups, which appears at high fields.

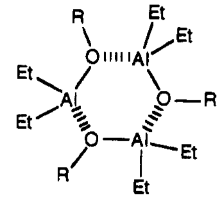
of propagation, m the degree of aggregation, P_n^* the growing macromolecule.

In order to explain the kinetic discrepancy between toluene and THF, the structure of the initiating and propagating dialkylaluminum monoalkoxide sites has been analyzed by viscosimetry and ^{27}Al NMR in toluene and in THF.

II.1. Viscosimetric and NMR Analysis in Toluene. Diethylaluminum bromoethoxide ($Et_2AlO(CH_2)_2Br$) has been analyzed by ^{27}Al NMR in pure toluene and in the presence of γ-butyrolactone (Figure 6).

In pure toluene (Figure 6a), the initiator shows only one ^{27}Al signal centered at ca. 152 ppm. This chemical shift, which is related to the coordination number and to the chemical environment of Al (Figure 7), agrees with tetracoordinated alkylated aluminum atoms.

As previously mentioned, the alkyl substituents (R′) have an effect on the aggregation of the dialkyl monoalkoxide. Formation of trimers has been reported for ethyl substituents (m = 3).[22] This $^{27}Al_{CN=4}$ signal for the $Et_2AlO(CH_2)_2Br$ initiator in toluene has accordingly been assigned to the cyclic trimer, shown below:



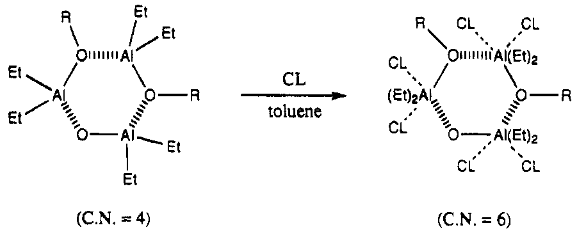
(m = 3)

An equilibrium between cyclic trimers and dimers may however not been precluded because ^{27}Al NMR cannot discriminate these two aggregated species that consist of identical tetrahedral (CN = 4) Al atoms.

In a second experiment, freshly distilled $Et_2AlO(CH_2)_2Br$ has been dissolved in γ-BL and added with a small amount of toluene. γ-BL has a deep effect on the structure of $Et_2AlO(CH_2)_2Br$ since the signal observed in toluene at 152 ppm has completely disappeared in favor of a new ^{27}Al signal at 7.4 ppm (Figure 6b). This new signal is characteristic of octahedral (CN = 6) Al atoms, which might be attributed to (1) the solvation of each aluminum atom of the $[Et_2AlO(CH_2)_2Br]_3$ cyclic trimers by two γ-BL molecules (CN = 6) or (2) the complete dissociation of the cyclic trimers with formation of single $Et_2AlO(CH_2)_2Br$ species (m = 1) solvated with three γ-BL molecules (CN = 6), by analogy with the structure of aluminum trialkoxides under the same conditions.

In order to discriminate these two hypotheses, the solution viscosity of the living PCL chains initiated by a diethylaluminum monoalkoxide in toluene has been compared to that of the parent deactivated chains. These viscosity data are summarized in Table 4 and show that the association degree ($\overline{DA}$) of the living PCL chains is close to 3 in toluene. This $\overline{DA}$ value is in agreement with the number of active alkoxide groups per dialkylaluminum alkoxide molecule ($n_{OR}/Al = 3$) and supports that the Al monoalkoxide remains associated all along the ROP in toluene.

From ^{27}Al NMR and viscosimetry, it may thus be concluded that the addition of lactone to the diethylaluminum monoalkoxide cyclic trimers in toluene is responsible for solvation of the Al atoms (CN = 6 for all the Al atoms), as schematized by eq 14.



[14]

The living PCL chains initiated by $Et_2AlO(CH_2)_2Br$ in toluene have also been analyzed by ^{27}Al NMR (Figure 8a). There is a complete similarity with the structure previously reported for the living chains initiated with $Al(O^iPr)_3$ (Figure 3a). Since the active aluminum alkoxide end groups are kept aggregated, eq 9, which is valid for aluminum trialkoxide, may be extended to the structure of the living aluminum monoalkoxide species in toluene with formation of pentacoordinated (CN = 5) and hexacoordinated (CN = 6) Al atoms.

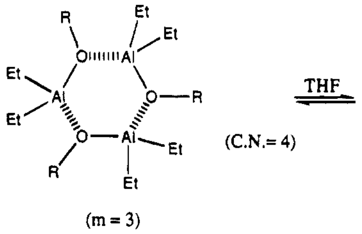
Table 4. Viscosity Data and Mean Degree of Association ($\bar{D}\bar{A}$) for Living and Deactivated PCL Chains Initiated with Distilled Et_2AlO^iPr and $Et_2AlO(CH_2)_2Br$ in Solution, at 25 °C

	$(CH_3)_2CHOAlEt_2$ in toluene		$Br(CH_2)_2OAlEt_2$ in THF[a]	
	living	deactivated[b]	living	deactivated[c]
$[\eta]$	0.17	0.10	0.42 to 0.36[d]	0.24
$\bar{D}\bar{A}$	2.85		3.0–2.0[d]	

[a] Viscosity data are unchanged when 10 equiv of γ-BL (compared to Al) are added to PCL in THF. [b] $\bar{M}_n$ = 12 000 ($\bar{M}_w/\bar{M}_n$ = 1.2). [c] $\bar{M}_n$ = 25 000 ($\bar{M}_w/\bar{M}_n$ = 1.1). [d] $[\eta]$ of PCL chains decreases with dilution.

I.2. Viscosimetric and NMR Analysis in THF. ^{27}Al NMR analysis of diethylaluminum bromoethoxide in pure THF (Figure 6c) shows a major difference compared to the ^{27}Al NMR spectrum recorded in pure toluene (Figure 6a). Indeed, in addition to the signal observed at 152 ppm in toluene, two new well-resolved signals are reported at 75 and 7.4 ppm. These three signals support that tetrahedral (δ = 152 ppm), pentacoordinated (δ = 75 ppm), and octahedral (δ = 7.4 ppm) Al atoms coexist, in possible agreement with an exchange between the $[Et_2AlO(CH_2)_2Br]_3$ cyclic trimers (CN = 4) and the same species solvated with one THF molecule per Al atom (CN = 5), i.e. $[Et_2AlOR]_3 \cdot 3THF$ or with two THF molecules per Al (CN = 6), i.e. $[Et_2AlOR]_3 \cdot 6THF$.

Moreover, when freshly distilled $Et_2AlO(CH_2)_2Br$ is dissolved in γ-BL and added with a small amount of THF, the ^{27}Al NMR spectrum (Figure 6d) shows two ^{27}Al signals, the chemical shift of which agrees with pentacoordinated (CN = 5) (δ = 75 ppm) and octahedral (CN = 6) (δ = 7.4 ppm) Al atoms. The presence of only these two ^{27}Al signals results from a higher electron-donating capability of γ-BL compared to THF, since now all the original cyclic trimers are solvated. This certainly implies a competition between THF and γ-BL for the solvation of the aluminum atoms of $[Et_2AlO(CH_2)_2Br]_3$ (eq 15).



$$[Et_2\,Al\text{-}OR]_3\,.\,3\text{ (or 6) THF} \underset{}{\overset{M}{\rightleftharpoons}} [Et_2\,Al\text{-}OR]_3\,.\,3\text{ (or 6) M} \quad [15]$$

(C.N.= 5 or 6) (C.N.= 5 or 6)

(m=3) (m=3)

Now the question is whether the $[Et_2AlO(CH_2)_2Br]_3$ trimeric structure persists upon the extensive solvation by γ-BL in THF. Table 4 shows that the degree of association ($\bar{D}\bar{A}$) of the living PCL chains (M_n = 25 000) in THF decreases with the polymer concentration as previously reported by Penczek et al.[24] Nevertheless, when the concentration of the living chains is higher than ca. 2.0 g/dL (i.e. $[Al]_o \geq 8 \times 10^{-4}$ mol/L for $\bar{M}_n$ = 25 000), $\bar{D}\bar{A}$ = 3 which is in agreement with the aggregation degree of the active end groups as calculated from kinetic data (Table 1, entries 5 and 6, m = 3) in the investigated initiator concentration, i.e. $[Al]_o \geq 10^{-3}$ mol/L ($[\epsilon\text{-CL}] \geq 1.0$ mol/L).[20,24]

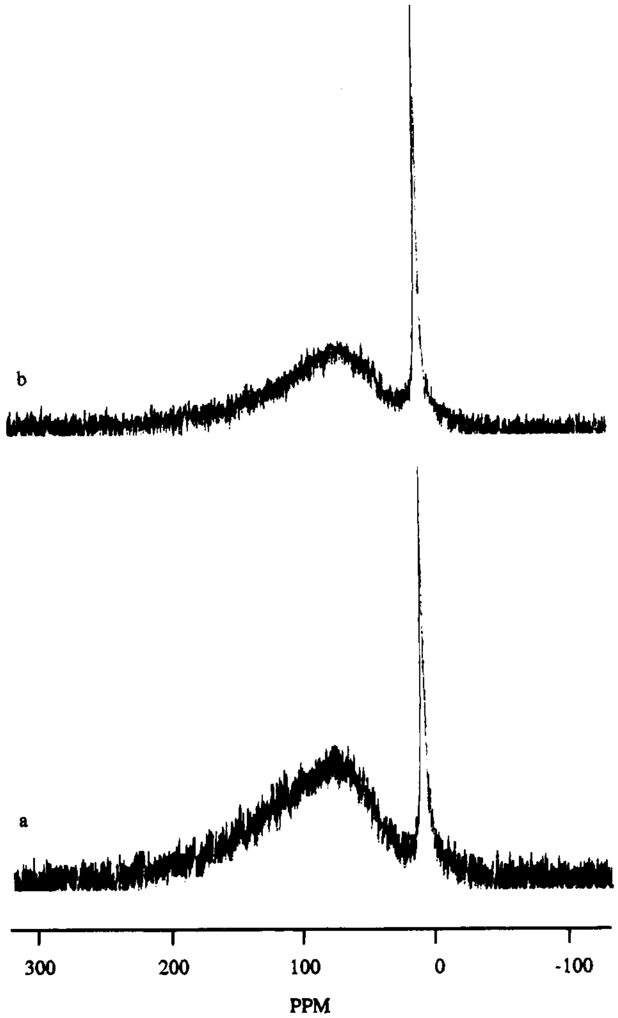


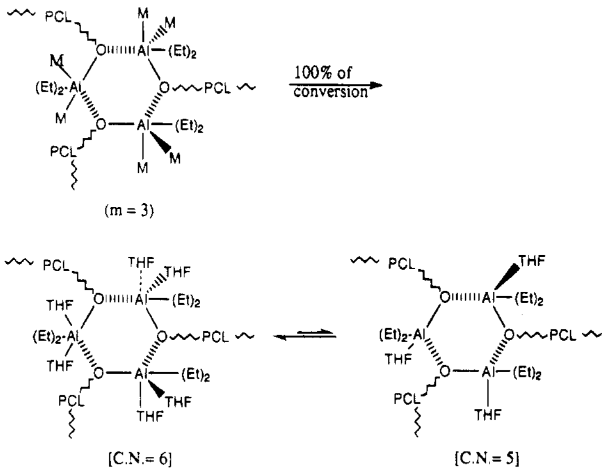
Figure 8. ^{27}Al NMR spectra (297 K) for living PCL chains initiated by $Et_2AlO(CH_2)_2Br$ at 25 °C, in toluene (a) and in THF (b).

It has also been observed (Table 4) that the addition of γ-BL does not change the specific viscosity of living (and "dead") PCL chains in THF [M_n = 25 000, 25 °C, initiator $Et_2AlO(CH_2)_2Br$]. The intermolecular coordinative aggregation is thus not disturbed by the presence of the model monomer.

So, the active aluminum monoalkoxide species in THF, in the presence or absence of cyclic monomers, would participate in a dynamnic aggregation equilibrium. When the monomer (M) is added to the solution of diethylaluminum monoalkoxide in THF, a cyclic trimeric (m = 3) monomer-solvated "$[Et_2AlO(CH_2)_2Br]_3 \cdot 3$- or -6 M" aggregate is expected to be formed, as schematized by eq 15.

Again, and thus whatever the solvent, the ϵ-CL insertion requires a fast reversible dissociation of the "$[Et_2AlO(CH_2)_2Br]_3 \cdot 3$- or -6 ϵ-CL" monomer-solvated aggregates (m = 3) ($K_{m,1} \ll 1$), in agreement with the fractional kinetic order in initiator ($1/m$).

The ^{27}Al NMR spectrum of living PCL chains initiated by $Et_2AlO(CH_2)_2Br$ in THF shows a major octahedral signal (CN = 6) at 2 ppm and a weak signal at 60 ppm (Figure 8b). In reference to Figure 7, a chemical shift of 60 ppm, for the living PCL chains initiated by $Et_2AlO(CH_2)_2Br$, agrees with pentacoordinated alkylated Al atoms. The actual propagating aluminum monoalkoxide sites should thus be stabilized by intermolecular coordinative associations (cyclic trimers) and an extra solvatation effect by THF, as shown by eq 16.



[16]

Conclusions

Although aluminum triisopropoxide is coordinatively associated in toluene, single trisolvated monomer species are formed in the presence of ϵ-CL and lactide that all remain unassociated during the propagation step. At the complete monomer conversion, the single Al trialkoxide entities are solvated by carbonyl groups of the main chain, so that the coordination number of Al (CN) is 4 and predominantly 6 in case of PCL and only 4 for PLA chains. In THF, there is competition between monomer and solvent for coordination to Al, which explains why polymerization is slower in THF than in toluene. Diethylaluminum monoalkoxide forms cyclic trimers in toluene and THF and remains associated all along the ϵ-CL polymerization. A fast reversible dissociation of the monomer (or THF) solvated trimers would explain that a fractional order in initiator (1/3) is observed.

Acknowledgment. ^{13}C and ^{27}Al NMR data were collected from the facilities at the CREMAN Center and the Laboratory of Physical Organic Chemistry (University of Liège). The authors express their sincere appreciation to Dr. J. Grandjean for his skillful assistance and discussions. They are also grateful to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" ("Poles d'Attraction Interuniversitaires: Polymères") and to FNRS (Brussels, Belgium) for financial support. The authors are also very grateful to O. Halleux for skillful technical assistance.

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