Macromolecular Engineering of Polylactones and Polylactides. 14. A ^{13}C and ^{27}Al NMR Study of the Effect of γ-Butyrolactone on the Structure of Aluminum Isopropoxide in Toluene

N. Ropson, Ph. Dubois,*,[†] R. Jerome, and Ph. Teyssie

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

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ABSTRACT: Solutions of Al isopropoxide in toluene have been investigated by ^{13}C and ^{27}Al NMR spectroscopy. Since $Al(O^iPr)_3$ is currently used as an initiator for the living polymerization of ϵ-caprolactone, special attention has been paid to the effect of the monomer on the coordinative structure of $Al(O^iPr_3)$ in toluene. γ-Butyrolactone (BL) has been chosen as a nonpolymerizable model, representative of ϵ-caprolactone. The NMR spectra have been recorded at various concentrations of γ-butyrolactone and temperatures. As a rule, $Al(O^iPr)_3$ is coordinatively aggregated in toluene in such a way that tetrameric and trimeric species are in equilibrium. Upon the addition of BL, this equilibrium is shifted toward the formation of an octahedric $[Al(O^iPr)_3 \cdot 3BL]$ mixed tetramer coexisting with $[Al(O^iPr)_3]_4$ tetramers, the external tetrahedric Al atoms of which are coordinated with extra BL molecules. In the presence of a large excess of BL, only the mixed tetramer persists, which suggests that the single $[Al(O^iPr)_3 \cdot 3M]$ species would be the actual initiator for the ring-opening polymerization of cyclic monomers M, such as ϵ-caprolactone, lactides, glycolide, and cyclic anhydrides.

Introduction

In the past two decades, ever increasing attention has been paid to the fine tailoring of synthetic polymers. In this respect, the availability of an initiator, the efficiency of which is close to 100%, is a key point, together with the absence of any side reactions during the propagation step. Under these conditions, the polymerization can be living, which paves the way to the macromolecular engineering of the related materials.

It is well established that some aluminum alkoxides, including the commercially available $Al(O^iPr)_3$, are very efficient initiators for the ring-opening polymerization of lactones,[1] lactides,[2] glycolide,[3] and other cyclic anhydrides.[4] Fundamental kinetic and structural investigations have confirmed the livingness of the ring-opening polymerization which fits in a "coordination-insertion" mechanism. The initiation and propagation steps proceed through the selective scission of the acyl-oxygen bond of the monomer followed by insertion into the "Al-O" bond of the active sites. This mechanism results in linear chains end-capped with an ester carrying the R "radical" of the initiator (R = ^iPr for $Al(O^iPr)_3$) and a hydroxyl or carboxylic end group, which results from the hydrolysis of the polyester or polyanhydride growing site, respectively (eq 1).

The great versatility of aluminum alkoxide, functionalized or not, allows for the macromolecular engineering of polyesters and polyanhydrides, as illustrated by the perfectly controlled synthesis of telechelic polymers, block copolymers, and macromonomers, i.e. promoters of graft copolymers.[1-4]

Although the coordination-insertion polymerization of the aforementioned monomers is living, key questions relative to the structure and dynamics of the pseudoanionic active species are still pending. Aluminum isopropoxide is known to be coordinatively associated as tetramers in apolar solvents and in the solid state. The proposed structure of the tetrameric form is shown in Figure 1 with a central octahedric aluminum atom bonded to three tetrahedric aluminum atoms through twin oxygen bridges. This structure has been first assessed by molecular weight measurements,[5] ^{27}Al NMR[6] and ^1H NMR[7] spectroscopies and finally confirmed by single crystal X-ray diffraction.[8]

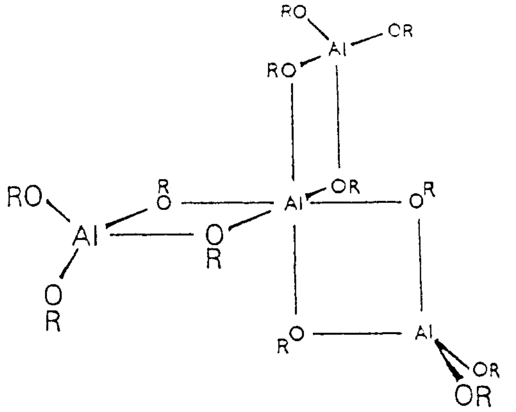

Figure 1. Structure of the aluminum isopropoxide tetramer (R = $CH(CH_3)_2$).

For the time being, the polymerization mechanism initiated by aluminum alkoxides relies upon indirect observations and nothing is known about the coordinative association and the activity of the initiating species under the polymerization conditions. Thermodynamic and kinetic investigations have emphasized the effect of the monomer structure on the activity of living end groups. It is however quite a problem to explain why the average number of growing chains per $Al(O^iPr)_3$ molecule (n, number of active isopropoxide functions per Al atom) is 1 in the presence of ϵ-caprolactone (CL), glycolide (GA), and adipic anhydride (AA), although n = 3 lactides (L,L or D,L LA) are the monomers.[1-4] Similarly, some kinetic data are quite puzzling. Indeed, the absolute polymerization rate constant of CL in toluene at 0 °C (k_{CL} = 36.6 L mol^{-1} min^{-1}) is 60 times larger than that of LA at 70 °C (k_{LA} = 0.6 L mol^{-1} min^{-1}), the partial order in both

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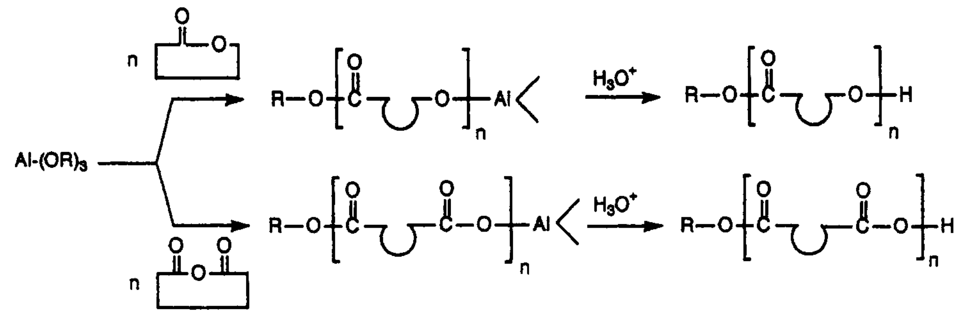


(1)

with R = ⁱPr, -(CH₂)₂-Br, -(CH₂)₃-CH =CH₂ , -(CH₂)₂-O-C(O)-C(CH₃)=CH₂

monomer and initiator being 1 for the two monomers.[2] Finally, whatever the monomer, polymerization does not start as soon as monomer and initiator are mixed together. This induction period of time has been tentatively attributed to a rearrangement of the coordinative aggregates of Al(O^{i}Pr)$_3$ in toluene upon addition of the polar monomer.[1-4]

In order to clear up the polymerization kinetics and the intimate mechanism of the coordination–insertion polymerization, it is of the utmost importance to have a deep insight on the structure and dynamics of the initiator, and accordingly of the propagating species, in solution. In this regard, NMR spectroscopy, viscosimetry, and cryometry are expected to provide basic information. This paper, which is the first of a series,[9] will focus on the contribution of ^{13}C and ^{27}Al NMR to the analysis of toluene solutions of Al isopropoxide. Special attention will be paid to the addition of model monomers, such as γ-butyrolactone (γ-BL) and glutaric anhydride (AG), to the initiator. γ-BL and AG have been selected due to nonpolymerizability under the usual experimental conditions and similarity with the currently used monomers in terms of dipole moment.[10] The ability of these cyclic compounds to be coordinated to the aluminum atom and to modify accordingly the dynamic equilibrium of the active species will be discussed.

Experimental Section

Toluene, benzene-d_6, and 2-propanol were dried by refluxing over calcium hydride and distilled just before use. Tetrahydrofuran (THF) and THF-d_8 were refluxed over a benzophenone–sodium complex and freshly distilled before use. γ-Butyrolactone (Aldrich) was dried over CaH$_2$, distilled, and then stored under nitrogen atmosphere and dissolved just before use in toluene (for ^{27}Al NMR) or benzene-d_6 (for ^{13}C NMR). Glutaric anhydride (Aldrich) was purified by sublimation, stored under nitrogen atmosphere, and dissolved just before use in THF (for ^{27}Al NMR) or THF-d_8 (for ^{13}C NMR). Aluminum isopropoxide (Aldrich) was twice sublimated and directly dissolved in toluene or benzene-d_6 under nitrogen atmosphere. The solution concentration was measured by complexometric titration of Al by EDTA.

Solutions of aluminum isopropoxide, γ-butyrolactone, and glutaric anhydride of a well defined concentration ([Al(O^{i}Pr)$_3$] = [monomer] = 2.9 M) were prepared separately. A previously flame-dried and purged with nitrogen glass vessel was then added with well-known volumes of the Al(O^{i}Pr)$_3$ solution and of a model monomer solution, respectively. An aliquot of these solutions of a well defined composition was transferred into a NMR tube which was then sealed under vacuum.

^{13}C and ^{27}Al NMR spectra were respectively recorded with a Bruker AM400 and AM200 superconducting magnet system operating in the FT mode at 100.6 MHz (^{13}C) using a deuterium lock (benzene-d_6 or THF-d_8) and at 78.21 MHz without lock. Quantitative ^{13}C NMR measurements were carried out by using the "INVGATE" sequence[2c] with a pulse width of 30°, an acquisition time of 0.7 s, and a delay of 3 s between pulses (toluene or THF). ^{13}C chemical shifts were referred to a low field resonance of benzene-d_6, the chemical shift of which was separately measured as 128.6 ppm relative to (CH$_3$)$_4$Si. ^{27}Al NMR spectra were referred to a salt solution of Al$_2$(SO$_4$)$_3$ in water (^{27}Al signal at 0 ppm).

Results and Discussion

Aluminum isopropoxide is one of the most efficient initiators for the living coordination–insertion ring-opening polymerization of lactones, lactides, and cyclic anhydrides. It is the reason why the analysis of solutions of aluminum isopropoxide in toluene deserves attention in the absence as well as in the presence of model monomers. A great deal of studies have focused on the structure of aluminum alkoxides [Al(OR)$_3$]$_n$[5-8,11] which have concluded that most alkoxides exist as dimers, trimers, and tetramers. In the particular case of Al(O^{i}Pr)$_3$, an equilibrium dominated by a tetrameric structure[8-11] has been reported (Figure 1).

The question is now addressed to know how this equilibrium is affected by the following experimental parameters: monomer, temperature, and external ligand, such as ^{i}PrOH.

^{27}Al NMR Analysis of Al(O^{i}Pr)$_3$ in Toluene. In a recent publication from this laboratory, ^{13}C and ^{7}Li NMR have been reported as powerful tools in the quantitative analysis of the coordinative aggregation of methyl α-lithioisobutyrate in THF. This organo Li compound actually foreshadows the propagating species in the living anionic polymerization of methyl methacrylate.[12] An equilibrium between a tetramer and a dimer, which slowly exchange on the ^{7}Li NMR time scale, has been clearly observed in the low temperature range. Similarly, ^{27}Al NMR spectroscopy has been used in order to analyze the coordinative aggregation of Al(O^{i}Pr)$_3$. ^{27}Al NMR spectroscopy is of steadily increasing use when structure, dynamics, and chemical properties of Al complexes are concerned, due to a strong signal of ^{27}Al of reasonable width and short relaxation times.[13] Nevertheless, the quadrupole moment of the ^{27}Al nucleus is responsible for a marked dependence of signal width on the gradient of the electrical field around Al, i.e. on the geometrical arrangement of the substituents of Al. From the chemical shift $\delta(^{27}$Al) of octahedric and tetrahedric aluminum salts,[11,13] $\delta(^{27}$Al) appears to be related to the symmetry of the metal and particularly to the coordination number (cn) of Al. On that basis, the effect of concentration, temperature, and addition of an external ligand on the aggregation of Al(O^{i}Pr)$_3$ in toluene has been investigated.

Effect of Al(O^{i}Pr)$_3$ Concentration. Figure 2 shows how the ^{27}Al NMR spectrum of Al(O^{i}Pr)$_3$ changes with concentration. At high concentrations (3.5 M), two well defined signals at 2.3 and 65 ppm, respectively, are

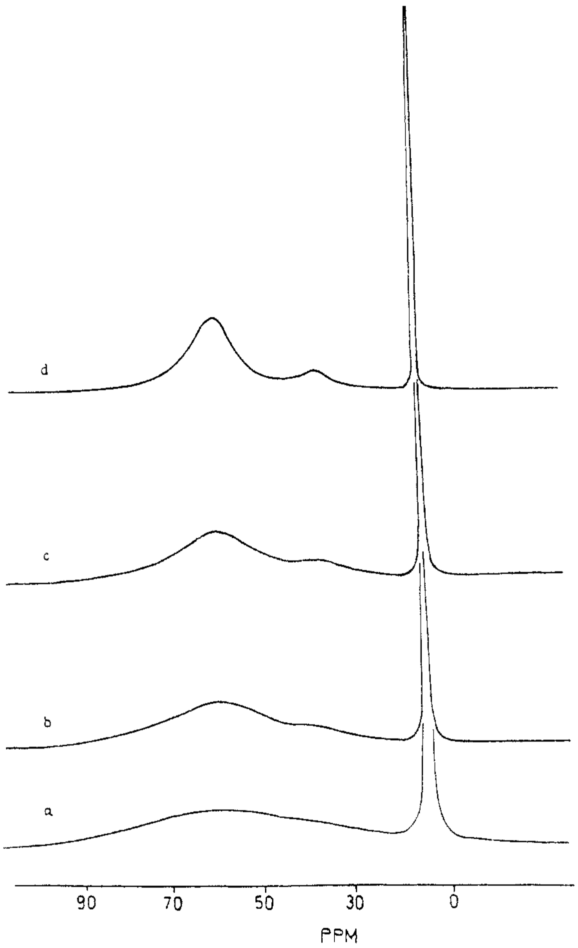


Figure 2. ^{27}Al NMR spectra of Al(O^{i}Pr)$_3$ in toluene: (a) 3.5 M at 297 K; (b) 6.2 × 10^{-1} M at 297 K; (c) 6.2 × 10^{-1} M at 309 K; (d) 6.2 × 10^{-1} M at 349 K.

Table I. Concentration in Al(O^{i}Pr)$_3$ of Tetrameric Species (δ(^{27}Al) at 2.3 ppm) and Species A (δ at 33.3 ppm) as a Function of the Total Concentration and Temperature (Solvent: Toluene)

T, K	[Al(O^{i}Pr)$_3$], M	[tetramer], M	[species A], M
297	3.5	3.5	0[a]
297	6.2 × 10^{-1}	6.0 × 10^{-1}	2.2 × 10^{-2}
297	5.4 × 10^{-2}	5.1 × 10^{-2}	3.0 × 10^{-3}
297	2.8 × 10^{-2}	25.8 × 10^{-3}	2.2 × 10^{-3}
297	6.2 × 10^{-1}	6.0 × 10^{-1}	2.2 × 10^{-2}
309	6.2 × 10^{-1}	5.6 × 10^{-1}	6.2 × 10^{-2}
319		5.0 × 10^{-1}	11.6 × 10^{-2}
329		4.6 × 10^{-1}	16.4 × 10^{-2}
339		4.4 × 10^{-1}	18.3 × 10^{-2}
349		4.0 × 10^{-1}	21.9 × 10^{-2}

[a] Not detectable in ^{27}Al NMR.

observed which support the presence of two types of aluminum atoms in a ratio close to 3:1 (Figure 2a). The sharp line at high field is due to the central octahedric aluminum whereas the broad line centered at 65 ppm is usually attributed to the external tetrahedric Al nuclei of the tetrameric structure (Figure 1). Upon dilution, a third signal appears at 33.3 ppm (Figure 2b). The resonance intensity of the new signal increases as the concentration decreases. In a parallel way, the intensity of the tetramer decreases. These results clearly indicate the formation of a different aggregated structure designated as A. The relative amount of the two types of aggregated species significantly depends on the total concentration of Al(O^{i}Pr)$_3$ (Table I). For instance, a 2.8 × 10^{-2} M solution in Al(O^{i}Pr)$_3$ contains 92.1% of the tetramers although a 6.2 × 10^{-1} M solution contains 96.7% of the same species.

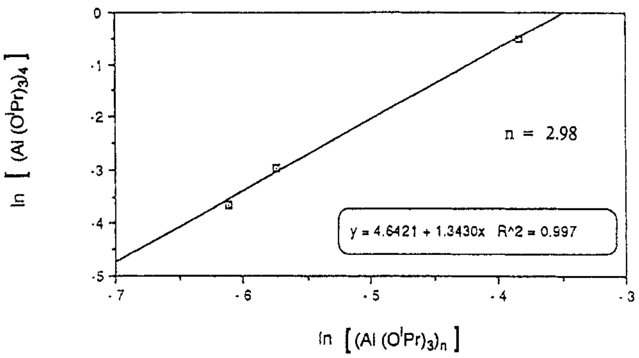


Figure 3. Plot of ln [(Al(O^{i}Pr)$_3$)$_4$] versus ln [(Al(O^{i}Pr))$_n$] for Al(O^{i}Pr)$_3$ in toluene at 297 K. Determination of the association degree (n) of Al(O^{i}Pr)$_n$ species.

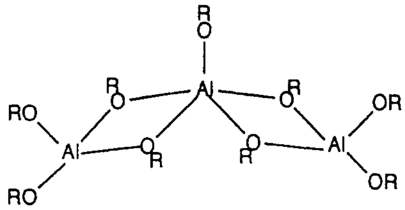


Figure 4. Structure of the aluminum isopropoxide trimer (R = CH(CH$_3$)$_2$).

This concentration dependence is consistent with an equilibrium between two differently associated forms of Al(O^{i}Pr)$_3$. The tetramer, the relative amount of which increases upon increasing concentration, must be more extensively associated than species A. In reference to the tetramer–trimer equilibrium which has been reported elsewhere,[8–11] species A may be reasonably assigned to the trimer.

The concentration of the expected trimer and tetramer at various concentrations of Al(O^{i}Pr)$_3$ has been determined from the relative peak area measured on the ^{27}Al NMR spectra (Table I). Figure 3 shows the ln [tetramer] versus ln [species A] plot for Al(O^{i}Pr)$_3$ in toluene at 297 K. An average association degree of 3 is calculated for species A in agreement with eqs 2–4.

$$\underset{\text{tetramer}}{(\mathrm{Al(O^iPr)_3})_4} \overset{K}{\rightleftharpoons} \frac{4}{n}\, \underset{\text{species A}}{(\mathrm{Al(O^iPr)_3})_n} \qquad (2)$$

with

$$K = [(\mathrm{Al(O^iPr)_3})_n]^{4/n} / [(\mathrm{Al(O^iPr)_3})_4] \qquad (3)$$

thus

$$\ln[(\mathrm{Al(O^iPr)_3})_4] = 4/n \ln\, [(\mathrm{Al(O^iPr)_3})_n] - \ln K \qquad (4)$$

This unambiguously confirms the assignment of a trimeric structure (n = 3) to the extra aggregated species A observed at 33.3 ppm. This chemical shift closely corresponds to pentacoordinated aluminum atoms,[6] in agreement with the trimeric structure previously proposed by Turova et al.[8] (Figure 4).

Effect of Temperature. ^{27}Al NMR spectra of aluminum isopropoxide in toluene (6.2 × 10^{-1} M) at various temperatures between 297 and 349 K have been recorded as shown in Figure 2b–d. Upon increasing temperature, the relative population of trimeric species (δ(^{27}Al) = 33.3 ppm) increases at the expense of octahedric Al atoms (2.3 ppm) characteristic of tetramers. Results summarized in Table I support a trimer–tetramer equilibrium of a low

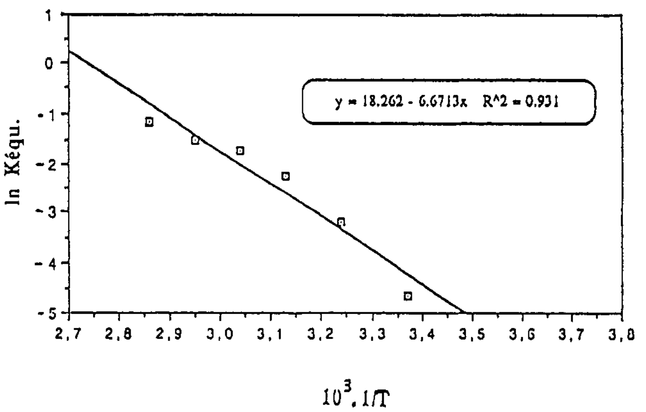


Figure 5. Van't Hoff plot for the $Al(O^iPr)_3$ tetramer–trimer equilibrium in toluene ([Al] = 6.2×10^{-1} M) (tetramer direction).

exchange rate at least on the ^{27}Al NMR time scale which allows the equilibrium constant K (see eq 2) to be calculated. Equilibrium data at different temperatures also provide the thermodynamic parameters for this equilibrium, as $\Delta H = -3.3$ kcal/mol and $\Delta S = -9.1$ cal/(mol K) (tetramer direction) (Figure 5).

The aggregation enthalpy is rather small, and negative, meaning that even in an apolar solvent, such as toluene, dissociation of aluminum alkoxide tetramers into smaller aggregates (trimers) is a favorable process at higher temperatures. A negative entropy of aggregation might reasonably be attributed to the high complexity and the associated steric hindrance of tetrameric species consisting of one octahedric Al atom surrounded with three tetrahedric Al atoms, as illustrated in Figure 1.

Effect of an External Ligand. The effect of an external ligand on the structure of organoaluminum compounds in solution, and particularly of aluminum isopropoxide, is poorly documented.[7,8,14] Worrall et al.[14] have reported that $Al(O^iPr)_3$ tetramers are insoluble in pyridine whereas soluble trimeric species are dissociated with formation of a $[Al(O^iPr)_3]_2$·(pyridine) mixed aggregate. It is also known that soluble Zn/Al μ-oxo–alkoxides are aggregated in benzene.[10,16] These catalytic species are however completely dissociated by a small amount of *tert*-butyl alcohol which deeply modifies the kinetics of CL polymerization. Similarly, the average number of active alkoxy groups per Al atom is increased from 1 to 3, when the initiator ($Al(O^iPr)_3$) of CL polymerization is added with 2-propanol. A decrease in the polymerization rate has been attributed to the competitive coordination of the monomer and the alcohol on the Al atom of $Al(O^iPr)_3$.

The effect of 2-propanol on the association degree of $Al(O^iPr)_3$ in toluene has accordingly been investigated by ^{27}Al NMR (Figure 6). Addition of only 5 equiv of alcohol, which corresponds to the amount currently used in polymerization, clearly shifts the tetramer–trimer equilibrium. At 333 K, for instance, there is 42.3% trimer in the presence of 2-propanol compared to 29.8% in pure toluene (6.2×10^{-1} M). These results are in qualitative agreement with observations by Turova *et al.*[8] who have reported that the melting point of $Al(O^iPr)_3$, as crystallized from 2-propanol, is clearly dependent on solution concentration and temperature. A correlation between melting temperature and average association degree of $Al(O^iPr)_3$ has been established, and potential interactions between $Al(O^iPr)_3$ and 2-propanol have been studied with reference to an interconversion equilibrium.

Since the tetramer–trimer equilibrium is very sensitive to the addition of an external ligand, such as an alcohol, it is of prime importance to know how the dynamic aggregation of $Al(O^iPr)_3$ is affected by the monomer itself, i.e. lactones and cyclic anhydrides. The coordination ability of these monomers has been investigated by ^{13}C and ^{27}Al NMR by using nonpolymerizable models, such as γ-butyrolactone (BL) and glutaric anhydride (AG), respectively.

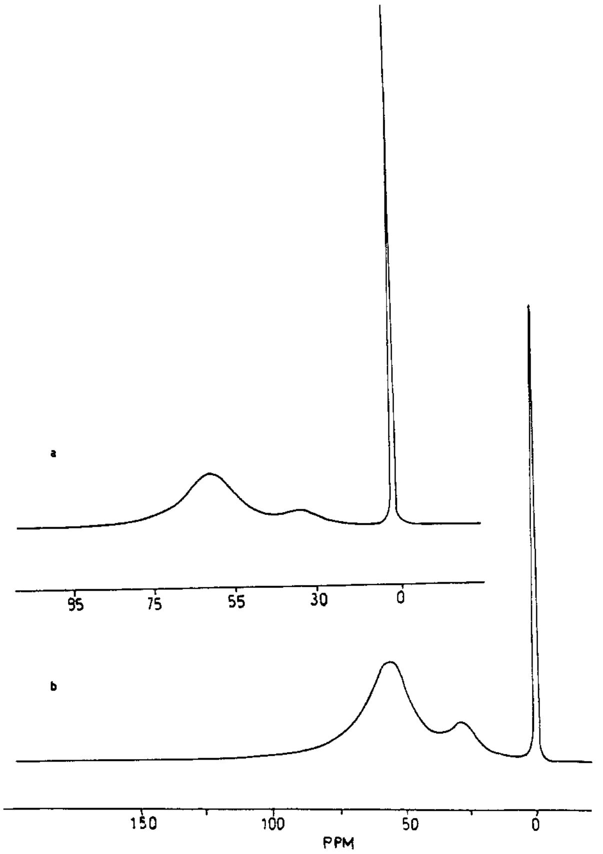


Figure 6. ^{27}Al NMR spectra of $Al(O^iPr)_3$ in toluene (6.2×10^{-1} M): (a) alone; (b) added with 5 equiv of 2-propanol ($T = 333$ K).

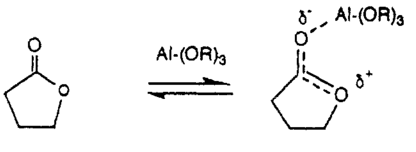
Table II. ^{13}C Chemical Shifts (δ, ppm)[a] of BL in the Presence of $Al(O^iPr)_3$ (n equiv) in C_6D_6 at Room Temperature

n equiv of $Al(O^iPr)_3$	C(O)		C_β		C_γ	
0	178		22.2		66.7	
0.1	177.8	173.3 172.2	22.2	21.9	67.7	67.5 67.3
1	177.8	173.3 172.2	22.2	21.9	67.7	67.5 67.3
10		172.2		21.9	67.7	

[a] Resonance signal of C_α ($\delta = 27.6$ ppm) appears in the same region as signals of methyl groups of isopropoxide functions, leading to confused attribution.

NMR Analysis of $Al(O^iPr)_3$ in the Presence of a Model Monomer: γ-Butyrolactone and Glutaric Anhydride. ^{13}C NMR of the BL/$Al(O^iPr)_3$ Mixture: Evidence for Coordinative Interactions. ^{13}C chemical shifts of pure BL in C_6D_6 at room temperature are reported in Table II (first entry). This table clearly shows the modification of the related chemical shifts by increasing amounts of aluminum isopropoxide. As expected, the carbonyl group is seen to interact with aluminum atoms. It is clear from Table II that the carbonyl signal (C(O)) is upfield shifted by ca. 5–6 ppm from the original position. Conversely, the signal of the γ-carbon moves to a lower field (67.7 ppm). These chemical shifts might be accounted for by some charge delocalization, as schematized in eq 5.

These NMR data are consistent with infrared observations by Feijen *et al.*[15] According to these authors, aluminum tribromide and aluminum triisobutyl form



(5)

complexes with lactide and glycolide through coordinative bonds between Al and the acyl oxygen of the cyclic monomers.

It is obvious from Figure 7 that in addition to the ^{13}C NMR signal for the free BL, two sets of coordinated carbonyl signals are mainly detected, indicating that more than one coordinated species is involved. Although the upfield shift of the (CO) signals is promoted by the addition of a low amount of $Al(O^iPr)_3$ (molar fraction of BL:F_{BL} = 0.9), the relative intensity of these signals depends on the molar fraction of $Al(O^iPr)_3$ ($0.2 < F_{BL} < 0.9$) (Table III). At the extreme low ($F_{BL} < 0.2$) and high ($F_{BL} > 0.9$) BL molar fractions, only one coordinated signal is mainly detected at 172.2 and 173.3 ppm, respectively. Such a behavior suggests the occurrence of specific interactions between BL and different $[Al(O^iPr)_3]_n$ species (n = 3 or 4), without excluding a complete dissociation of the aggregated Al alkoxide (n = 1). This hypothesis will be assessed by ^{27}Al NMR analysis of γ-BL/$Al(O^iPr)_3$ mixtures in toluene (next section).

It is worth pointing out that these observations are in favor of a dynamic exchange between free and coordinated model lactone in the ^{13}C NMR time scale. In contrast, some of us have reported on strong interactions between *tert*-butyloxirane (^tBO) and Al atoms of $(^nBuO)_4Al_2Zn_2O$ and on the absence of exchange between free and coordinated ^tBO molecules in the ^{13}C NMR time scale.[16]

Figure 8 illustrates the temperature dependence of the ^{13}C NMR spectrum of the BL/$Al(O^iPr)_3$ mixture at a constant F_{BL} = 0.3. All the carbonyl groups are coordinated to Al atoms at room temperature. A free carbonyl group (at 178 ppm) is detected at 323 K, and its relative intensity increases with increasing temperature. These observations are consistent with a dynamic equilibrium and the exothermic character of the coordinative interactions.

^{27}Al NMR of BL/$Al(O^iPr)_3$ Mixtures: Evidence for Dissociation by BL. The BL/$Al(O^iPr)_3$ mixtures, which have been previously studied by ^{13}C NMR, have also been analyzed by ^{27}Al NMR spectroscopy (Table IV). Several striking observations result from this investigation.

In the range of $F_{Al} > 0.8$, the ^{27}Al spectrum shows two well-resolved signals in a 1:3 ratio characteristic of the tetrameric structure of $Al(O^iPr)_3$ in toluene at high concentrations (see Table IV, first entry). Since ^{13}C NMR agrees with the existence of only one coordinated lactone species (carbonyl signal at 172.2 ppm, Table III), it must be concluded that BL interacts selectively with the external tetrahedric Al atoms of tetrameric species without disturbing this particular coordinative association.

In the range of $F_{Al} < 0.8$, the association degree of $Al(O^iPr)_3$ is perturbed by the addition of extra BL molecules. Then, ^{27}Al NMR spectroscopy shows an increase in the content of the octahedric Al atoms with a slight downfield shift and the presence of a very low amount of trimeric species (signal at 33.3 ppm not reported in Table IV). It is therefore obvious that tetramers of aluminum isopropoxide are unstable in the presence of a high BL content and that new aggregates selectively containing octahedric Al atoms are formed. This new coordinative structure cannot be due to a dilution effect when the $Al(O^iPr)_3$ molar fraction decreases at a constant concentration. Indeed, dilution has been previously reported to decrease the content of hexacoordinated Al species by shifting the tetramer–trimer equilibrium (eq 2). All in all these observations strongly suggest that signals of octahedric Al ranging from 2.79 to 4.83 ppm are average values of two octahedric ^{27}Al species: $[Al(O^iPr)_3]_4$ tetramer (δ = 2.3 ppm) and a new $[Al(O^iPr)_3{\cdot}xBL]$ association ($\delta > 4.83$ ppm). The interexchange of these two species is likely too fast in the ^{27}Al NMR time scale to be distinguished from each other.

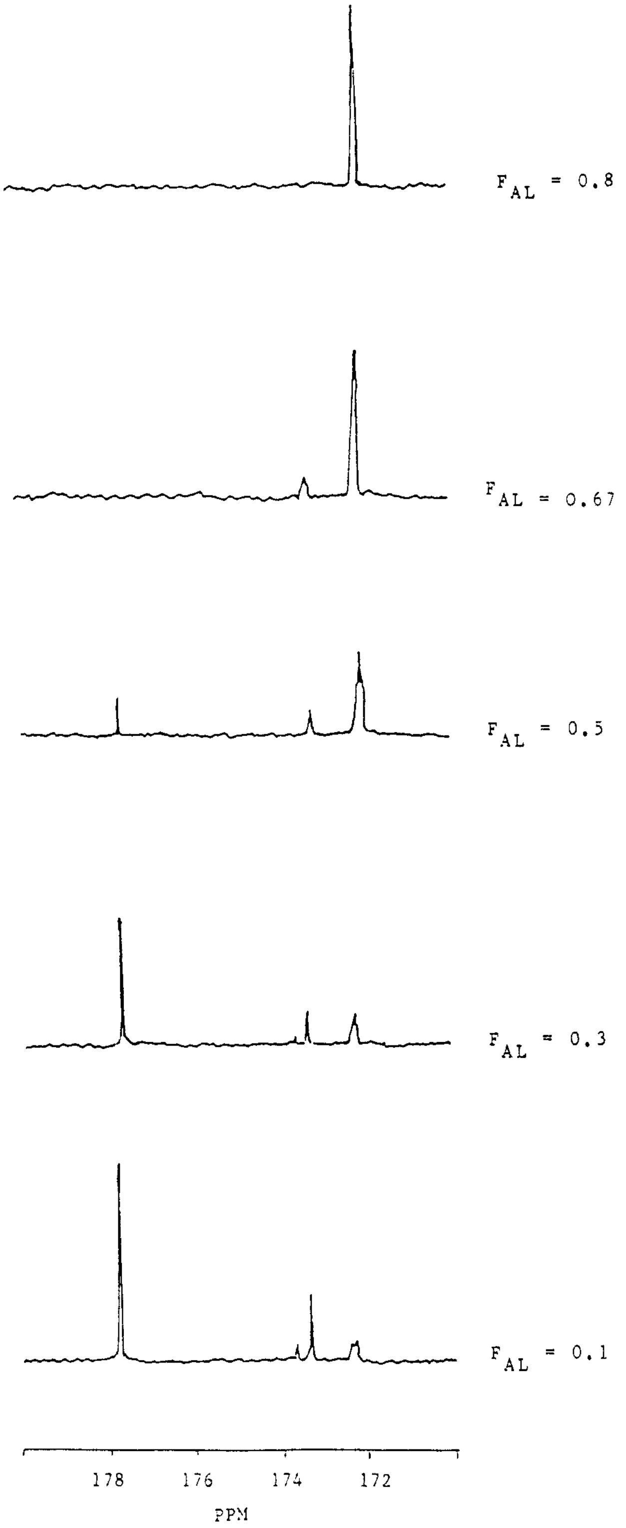


Figure 7. ^{13}C NMR spectra of the carbonyl signal of BL, in C_6D_6 at room temperature, in the presence of increasing amounts of $Al(O^iPr)_3$.

Table III. ^{13}C Chemical Shifts (δ, ppm) and Relative Contents of the Free and Coordinated Carbonyl Group of BL in a Mixture with $Al(O^iPr)_3$ in C_6D_6 at Room Temperature ([BL + $Al(O^iPr)_3$] = 2.9 M)

	relative C(O) content, %		
	free at	coordinated at	
F_{BL}[a]	~178 ppm	~173.3 ppm	~172.2 ppm
1.0	100		
0.9	72.9	20.8	6.3
0.7	51.4	11.2	37.4
0.5	13.4	15.7	70.9
0.3		3	97
0.2			100

[a] BL molar fraction in BL/$Al(O^iPr)_3$ mixture.

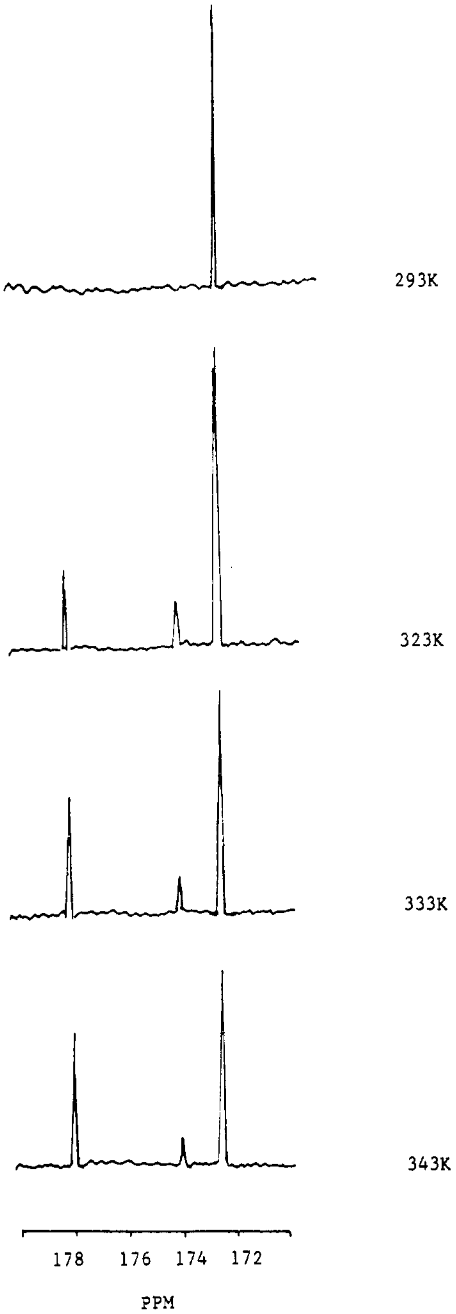


Figure 8. ^{13}C NMR spectra of the carbonyl signal of BL/$Al(O^iPr)_3$ mixtures (F_{BL} = 0.3) in C_6D_6 at various temperatures.

Table IV. ^{27}Al Chemical Shifts (δ, ppm) and Relative Content of the Hexa- and Tetracoordinated Al Atoms of $Al(O^iPr)_3$ in a Mixture with BL in C_6H_6 at Room Temperature ([$Al(O^iPr)_3$ + BL] = 2.9 M)

	$\delta(^{27}Al)$, ppm (relative content, %)	
F_{Al}[a]	cn = 6	cn = 4
1.0	2.29 (25)	65.1 (75)
0.9	2.79 (25)	63.1 (75)
0.8	2.91 (32)	63.1 (68)
0.7	3.32 (36)	63.1 (64)
0.5	4.10 (50)	63.2 (50)
0.3	4.83 (67)	47.3 (33)

[a] $Al(O^iPr)_3$ molar fraction; for $F_{Al} < 0.3$, Al content is too low to be detected in ^{27}Al.

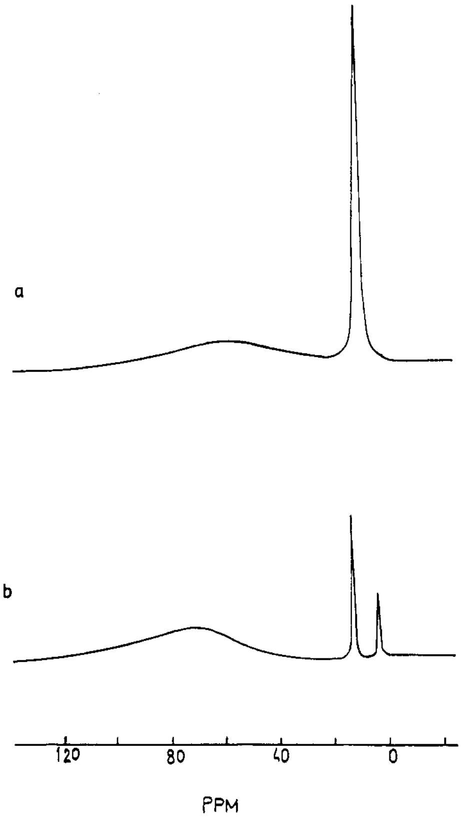


Figure 9. ^{27}Al NMR spectra of $Al(O^iPr)_3$ at 293 K in the presence of (a) BL in toluene and (b) AG in THF (F_{Al} = 0.5).

Table V. ^{27}Al NMR Chemical Shifts (δ, ppm) and Line Widths ($\Delta W_{1/2}$, Hz) of Hexacoordinated Al of $Al(O^iPr)_3$ in the Presence of BL and AG (F_{Al} = 0.5), in Toluene and THF, Respectively

	$\delta(^{27}Al$, cn = 6), ppm		
T, K	BL/$Al(O^iPr)_3$	AG/$Al(O^iPr)_3$	
281	2.28 (311.4)[a]		
293	2.29 (206.6)	2.27 (84.7)	11.74 (84.7)
303	2.35 (174.3)	2.35 (121.3)	11.84 (99.9)
313	2.37 (161.4)	2.36 (128.4)	11.94 (107.0)
323	2.41 (129.1)	2.37 (128.9)	12.00 (114.6)
333		2.38 (129.5)	12.03 (122.3)

[a] At half-height (Hz).

Substitution of BL by a nonpolymerizable cyclic anhydride, such as glutaric anhydride (AG), has allowed two signals to be resolved in the resonance range of hexacoordinated (octahedric) Al atoms (Figure 9). In order to compare the coordinative ability of the two model monomers, the effect of temperature on the chemical shifts and the line width at half-weight ($\Delta W_{1/2}$) of the octahedric aluminum nuclei has been investigated (Table V).

The BL/$Al(O^iPr)_3$ system shows only one resonance signal, even at the lowest temperature. This signal slightly shifts downfield and $\Delta W_{1/2}$ decreases with increasing temperatures.

In contrast, the AG/$Al(O^iPr)_3$ system exhibits two signals at ~2.3 and ~11.8 ppm, assigned to the $[Al(O^iPr)_3]_4$

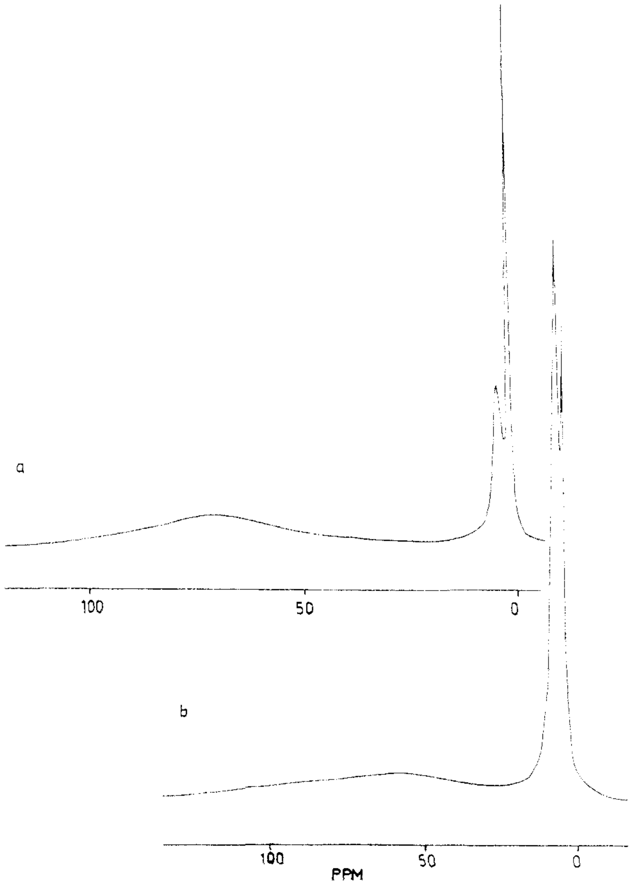


Figure 10. ^{27}Al NMR spectra of $Al(O^iPr)_3$ in BL ($F_{Al} = 2.5 \times 10^{-2}$) at 293 K (a) before and (b) after addition of toluene (25 wt %).

tetramer coordinated with cyclic anhydride and the new octahedric $Al(O^iPr)_3$ surrounded by AG, respectively. Increasing temperatures are responsible for a slight increase not only in chemical shifts but also in $\Delta W_{1/2}$. All these experimental observations support that the BL/$Al(O^iPr)_3$ pair in toluene is a *fast* exchanging coordinative system whereas the AG/$Al(O^iPr)_3$ pair is a much *slower* exchanging system in the ^{27}Al NMR time scale.

Moreover, it is worth pointing out that diethylaluminum isopropoxide, Et_2AlO^iPr, added with BL is an intermediate system, since two hexacoordinated ^{27}Al (cn = 6) signals are observed below room temperature and only one is observed at higher temperatures.[17]

^{27}Al NMR Investigations of $Al(O^iPr)_3$ in Simulated Conditions of Polymerization. The limited resolution of ^{27}Al NMR spectroscopy has prevented the content of octahedric Al atoms in $Al(O^iPr)_3$/BL mixtures in toluene ($F_{AL} < 0.3$: Table IV) from being calculated. At low $Al(O^iPr)_3$ molar fractions, a unique signal characteristic of the new octahedric $Al(O^iPr)_3{\cdot}x$BL structure would be expected to be formed. Indeed at $F_{AL} = 0.1$, ^{13}C NMR has shown that in addition to the free lactone (at 178 ppm; Figure 7) there is a main resonance signal at 173.3 ppm, that could be attributed to BL participating in the new octahedric aggregate.

Finally the signal of the new octahedric Al atoms has been resolved and identified by ^{27}Al NMR of a solution of $Al(O^iPr)_3$ in the model monomer. Use of BL as a solvent avoids limitations due to a limited sensitivity of ^{27}Al NMR and further simulates the experimental conditions of polymerization (very low F_{Al}). In these pure $Al(O^iPr)_3$/BL mixtures (no toluene), the rate of interexchange is decreased and, accordingly, the ^{27}Al NMR spectrum shows three resolved signals (Figure 10a): (a) two resonances signals at 2.4 and 59.5 ppm characteristic of the tetrameric $[Al(O^iPr)_3]_4$ species, the external tetrahedric Al atoms of which are coordinated with BL; (b) a new signal at 5.6 ppm attributed to nonaggregated $Al(O^iPr)_3$ species, however coordinated with lactone molecules.

Addition of a small amount of toluene (25 wt %) to the $Al(O^iPr)_3$/BL pair ensures a spectacular increase of the new ^{27}Al signal (Figure 10b). Since these conditions are close to the polymerization conditions, the $Al(O^iPr)_3$ species which are active in ring-opening polymerization, should expectedly be individual molecules coordinated with the cyclic monomer accounting for hexacoordinated Al atoms.

In conclusion, $Al(O^iPr)_3$ solutions in toluene have been analyzed by ^{27}Al NMR, which has revealed an aggregation equilibrium between tetramers and trimers. The addition of model monomers—nonpolymerizable lactone and cyclic anhydride—is responsible for a complete deassociation. The individual $Al(O^iPr)_3$ species consists however of a hexacoordinated Al atom that would result from the coördination of three monomer molecules per Al nucleus. As a result, the actual initiator in the ring-opening polymerization of lactones and cyclic anhydrides would be an octahedric "$Al(O^iPr)_3{\cdot}3$ monomers mixed aggregate". Such an association has recently been confirmed by cryoscopic measurements.[9]

Dissociation of $[Al(O^iPr)_3]_4$ by cyclic esters and anhydrides completely disagrees with observations previously reported for soluble bimetallic μ-oxo–alkoxides.[10] These coordinatively saturated aggregates are indeed very stable even in the presence of a large excess of monomer, and the ring-opening polymerization proceeds without any coordinative rearrangement.

The effect of experimental parameters, such as the nature of solvent, Al alkoxide, monomer, and ligands, on the structure and equilibrium of aluminum alkoxides in solution is currently investigated by multinuclear NMR, cryometry, and viscosimetry. Attempts to correlate the aggregation behavior of the initiator and the polymerization mechanism are considered and will be reported in the near future.

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