Soluble Bimetallic μ-Oxo-alkoxides. 8. Structure and Kinetic Behavior of the Catalytic Species in Unsubstituted Lactone Ring-Opening Polymerization

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ABSTRACT: The bimetallic μ-oxo-alkoxides are highly active for lactone ring-opening polymerization. These compounds are aggregated in solution and their mean degree of association depends on the nature of alkoxide groups, metals, and solvent; it is modified by addition of suitable ligands or temperature variations. The course of the lactone polymerization is strongly related to the structural features of the catalyst. The determination of the mean number of growing chains per catalyst molecule, the study of the polymerization kinetics, and the knowledge of the catalyst behavior during the monomer conversion have contributed to an understanding of the polymerization mechanism.

It is well established that some metal alkyl compounds (AlR_3, ZnR_2, . . .) are, in the presence of specific amounts of water, excellent stereospecific catalysts for methyloxirane polymerization into high molecular weight polyethers. Several fundamental studies have concluded that the catalytic sites are polynuclear[1,2] and involve several metal atoms linked together by μ-oxo bridges. Analogous catalysts have also been used for the ring-opening polymerization of other monomers such as thiiranes and lactones. However, the actual composition of the active centers remains ill-defined and their formation in the reaction medium is uncontrolled; therefore, the resulting structural and kinetic behavior of the catalytic systems cannot be easily analyzed.

Recently, an easily reproducible preparation of well-defined compounds containing several metal atoms linked together by μ-oxo bridges has been reported.[3–5] These bimetallic oxoalkoxides represent a new family of soluble catalysts having the following general formula:

$$(RO)_{p-1}\text{–}M_2{}^{p}\text{–O–}M_1{}^{II}\text{–O–}M_2{}^{p}\text{–}(OR)_{p-1}$$

The catalyst composition is easily modified by changing the nature of the metals $M_2{}^p$ (Al^{III}, Ti^{IV}, . . .) and $M_1{}^{II}$ (Zn, Co, Fe, Mo, . . .) and of the alkoxide groups (isopropoxy, *n*- or *sec*-butoxy, . . .). The structure of these catalysts in solution is also largely controlled. We have indeed demonstrated that bimetallic oxoalkoxides are associated in solution like simple alkoxides,[6–8] thanks to the formation of intra- and intermolecular oxygen–metal coordinative bonds. It is possible to control the size and shape of these coordinative aggregates by modifying principally three parameters: nature of OR groups, central metal $M_1{}^{II}$ and solvent; furthermore, specific organic ligands as alcohols, even in small amounts ($ROH/M_1 \gtrsim 3$), promote the dissociation of the aggregates into the basic trinuclear units.

With their unequivocally established composition and easily modified structure, the bimetallic oxoalkoxides represent very good models to analyze the mechanisms involved in ring-opening polymerization and to optimize the catalytic performances toward specific goals.

In a preceding paper,[9] we have studied the general features of homogeneous lactone-opening polymerization by these oxoalkoxide compounds. It has been concluded that the polymerization obeys an anionic-type coordinated insertion mechanism of the monomer into the $M_2{}^p$–OR bond and that the propagation step proceeds without transfer nor termination reactions. Furthermore, it appeared that the number of growing chains per catalyst molecule varies with the catalyst composition and mean degree of association. To better understand the catalyst behavior and the ultimate mechanism of the lactone-opening polymerization, it is important to analyze and discuss in detail the dependence of the kinetic course of the reaction on the catalyst structure in solution. The study of these structural and kinetic characteristics of the bimetallic oxoalkoxides is the main purpose of this paper.

Experimental Section

Reagents. ϵ-Caprolactone (CL). Commercial reagent (pure grade, Fluka) was dried over CaH_2 at room temperature and purified by distillation under reduced pressure (10^{-2} mm).

Toluene or benzene (practical grade) **and alcohol** (analytical grade) were dried by refluxing, the former over $LiAlH_4$ and the latter over CaH_2; they were distilled before use under argon atmosphere.

Synthesis of Bimetallic Oxoalkoxide Catalysts. Details of the preparation method of these compounds are described elsewhere.[4,5] For instance, the preparation of $ZnO_2Al_2(O\text{-}i\text{-}C_3H_7)_4$ involves a thermal condensation reaction between aluminum isopropoxide and zinc acetate at about 200 °C in decalin.

By refluxing this compound in decalin in the presence of a sufficient excess of *n*-butyl alcohol, the replacement of the isopropoxy groups by *n*-butoxy ones takes place quantitatively if the equilibrium is continuously displaced by distillation.

Polymerization Procedure. The polymerizations were carried out under stirring in toluene solution in a flask previously dried, purged with argon, and kept at constant temperature (±1 °C) for a suitable period of time. The reactions were stopped by adding a tenfold excess of a 2 N HCl solution with regard to the trinuclear catalyst units. The catalyst residues were removed by repeated extractions (four times) with a dilute acidic (0.5 N HCl) solution and the reaction medium was washed with water up to neutral pH. The polymer product was further isolated from the toluene solution by precipitation in heptane and dried for 24 h at room temperature under vacuum.

Molecular Weight Determinations. Molecular weight determinations were carried out with a vapor pressure osmometer (Knauer) in toluene at 45 °C; the precision, depending on the molecular weight range, was about 5 to 10%.

Cryoscopic Measurements. The mean degree of association was determined for different bimetallic oxoalkoxides by cryoscopic measurements. A suitable cryometer was designed to work under argon atmosphere. The mean degree of association was calculated from the slope of the straight-line plot verifying the following relationship:

$$\Delta T = K\frac{[S]}{\bar{n}}$$

where ΔT is the cryoscopic melting point depression (the temperature was measured with an accuracy of about 0.01 °C), [S] is the molar solute concentration, $\bar{n}$ the solute degree of association, and K is the molar cryoscopic constant (26.4 for cyclohexane and 5.6 for benzene).

Job's continuous variations diagrams were carried out by using stock catalyst and monomer solutions of equal concentration; for each measurement, suitable relative volumes of catalyst and monomer solutions were introduced into the cryometer, while always keeping constant the total concentration ([lactone] + [catalyst]) or (M] + [C].

Table I
Mean Association Degree of Some Bimetallic Oxoalkoxides in Benzene

Nature of metals M_2^{P}/M_1^{II}	Nature of R group	Mean association degree $\bar{n}$ and color
Al/Zn	n-C_4H_9	6.0[a] (pale-yellow)
Al/Co	n-C_4H_9	4.1 (blue)
Al/Co	i-C_3H_7	2.0 (red-violet)

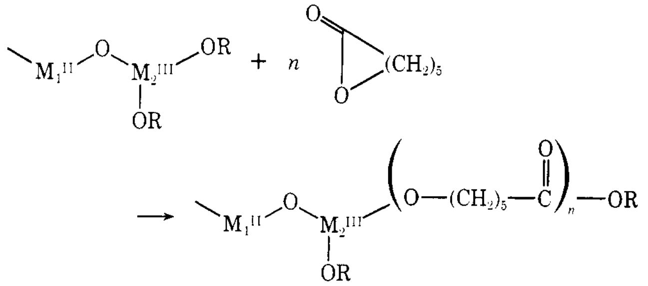
[a] $\bar{n}$ = 8.0 for a fresh solution, 6.0 for a solution aged for 2 days.

Results and Discussion

Association of the Catalyst and Its Implications on the Number of Active Polymerization Centers. As reported elsewhere,[9-11] the bimetallic oxoalkoxides are associated in solution; this phenomenon is due to the presence of electron pairs available on the oxygen atoms of the alkoxide groups, which will fulfill the vacant coordinative positions on the metal atoms of the isolated trinuclear oxoalkoxide molecules.

The coordinative association is important and depends mainly on the nature of the alkoxide groups and the central metal;[10,11] the characteristics of the catalysts used in this work are gathered in Table I.

The variation of the mean degree of reversible coordinative association ($\bar{n}$) with the nature of the alkoxide groups is probably correlated to a modification of the coordination sphere of the central metal; that change in the coordination structure is supported by the different colorations of bimetallic oxoalkoxides including the same metals: i.e., $[CoO_2Al_2(O\text{-}n\text{-}C_4H_9)_4]_{4.1}$ is blue in benzene, while the less associated $[CoO_2Al_2(O\text{-}i\text{-}C_3H_7)_4]_{2.0}$ is red-violet in the same solvent. Implication of OR groups in coordinative association is revealed by ^{13}C NMR studies which indicate that some of these groups are in different environments; in the case of $ZnO_2Al_2(O\text{-}i\text{-}C_3H_7)_4$, bridged and unbridged iso groups are observed in the 1/3 ratio.[12] In conclusion, these bimetallic oxoalkoxides in organic solution are in the form of aggregates containing a mean number of 6 to 24 metal atoms formed by the coordination of OR groups to the coordinatively unsaturated metal atoms. On the other hand, it has been demonstrated[9,13] that the OR groups play a very important role in the mechanism of the lactone-opening polymerization, which fits the following pattern:



It is accordingly evident that the catalyst association through these OR groups will exercise a determinant action on the kinetic course of the polymerization, and this phenomenon has been clearly substantiated by the measurements summarized in Table II. Thanks to the perfect living character of the propagation reaction, the mean number of growing chains per trinuclear catalyst unit can be calculated from the $\bar{M}_n$ of the polymer obtained. Thus, it can be seen (Table II) that the four OR groups of every catalyst molecule do not necessarily behave as an effective insertion site; in correlation with the mean catalyst association, the mean number of active OR groups per catalyst unit varies between 1 and 4. In the presence of four alcohol molecules per trinuclear catalyst unit, the catalyst is dissociated and the mean degree of polymerization $\overline{DP}$ corresponding to complete conversion is exactly four times lower than the theoretical $\overline{DP}$ calculated by the monomer over catalyst molar ratio; this result implies that every OR group is now available and able to start a polyester chain. Thus, with the same amount of catalyst, more polymer of a given molecular weight can now be produced, but with a slower overall rate due to competitive coordination of the alcohol on the active Al atoms (see below).

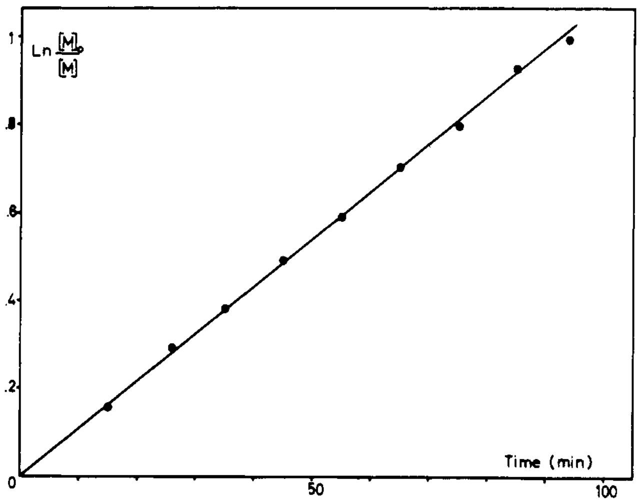


Figure 1. ϵ-Caprolactone consumption as function of time: solvent, toluene; T 20 °C; $[CL]_0$ = 1 mol/l; $[CL]_0/[Zn]$ = 150; catalyst, $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$.

Furthermore, it is also clear from Table II that any dissociative factor (branching of the R groups or temperature raise in the case of highly associated compounds) will increase the number of OR groups available for chain initiation. It will be proved hereafter that the catalyst coordinative association $\bar{n}$ measured in a pure solvent is not modified by the presence of monomer nor the polymerization process; consequently, it is justified to compare the mean degree of catalyst association $\bar{n}$ and the mean number of active OR groups per catalyst unit.

Polymerization Kinetics and Its Implications. As the coordinative association of the bimetallic oxoalkoxides in solution has a strong influence on the molecular weight control, it may be expected that the kinetics of the polymerization will also depend on that structural feature of the catalyst. Furthermore, in order to elucidate the intimate mechanism of the lactone-opening polymerization, it is important to determine the reaction order in monomer and catalyst.

The ϵ-caprolactone polymerization is first order in monomer with $CoO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ and $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ in toluene respectively at 50 and 20 °C; Figure 1 illustrates the monomer consumption as a function of time in the case of $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$.

In Table III, it is also observed that the higher the initial monomer concentration the lower seems to be the rate constant; this effect has to be attributed to an increase of the medium dielectric constant ϵ with the monomer concentration. So, when the latter is varying from 0.5 to 1.0 mol/l., the former is increasing from 3.68 to 4.96. In fact, Table IV clearly shows that, all other conditions being unchanged, the polymerization rate is decreasing (or the half-polymerization time $t_{1/2}$ is increasing) with increasing polarity of the solvent. These results strongly support a coordinated, rather than an ionic, type of reaction.

On the other hand, the initial concentration of ϵ-caprolac-

Table II
Mean Number of Active OR Groups per Trinuclear Catalyst Unit ($\overline{N}$) in ϵ-Caprolactone Polymerization with Bimetallic Oxoalkoxides in 1 M Toluene Solutions

Nature of metals M_2/M_1	Nature of R groups	T, °C	$\bar{n}$[a]	$[M]_0/[C]$[c]	Conversion, %	$\overline{DP}$	$\overline{N}$
Al/Zn	n-C_4H_9	0	8–4	100	Total	92	1.1
Al/Zn + C_4H_9OH[b]	n-C_4H_9	40	1.1	60	91.5	14	3.9
Al/Zn	i-C_3H_7	0		143	Total	48	3.0
Al/Co^{II}	i-C_3H_7	0	2.0	150	Total	49	3.1
Al/Co^{II}	n-C_4H_9	0	4.1	100	90	76	1.2
Al/Co^{II}	n-C_4H_9	50		100	Total	48	2.1

[a] Measured by cryoscopy in benzene. [b] Four alcohol molecules per trinuclear catalyst unit. [c] Initial ratio of monomer to catalyst.

Table III
Influence of Initial Monomer Concentration $[M]_0$ on the Polymerization Rate at 20 °C in Toluene[a]

$[M]_0$, mol/l.	$k \times 10^3$ min^{-1}	$[M]_0$, mol/l.	$k \times 10^3$ min^{-1}
0.5	23.6	2.0	2.45
0.8	17.2	2.06	2.4
1.0	10.9	2.12	2.4
1.92	2.6		

[a] $[ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4] = 6.6 \times 10^{-3}$ mol/l.

Table IV
Influence of the Solvent on the Polymerization Reaction Rate of ϵ-Caprolactone at 20 °C[a]

Solvent	ϵ solvent	$t_{1/2}$, min
Toluene	2.44	3
$CHCl_3$	4.80	24.5

[a] $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$, $[M]_0 = 1$ mol/l., $[M]_0/[C] = 100$, $T =$ 20 °C.

Table V
Dependence of the ϵ-Caprolactone Polymerization Rate on the Initial Monomer Concentration at Constant Medium Polarity[a]

[ϵ-Caprolactone]$_0$, mol/l.	[γ-Butyrolactone]$_0$, mol/l.	$k \times 10^3$, min^{-1}
1	0	10.9
0.5	0.5	12.9
0.5	0	23.6

[a] $[ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4] = 0.66 \times 10^{-3}$ mol/l., at 20 °C, in toluene.

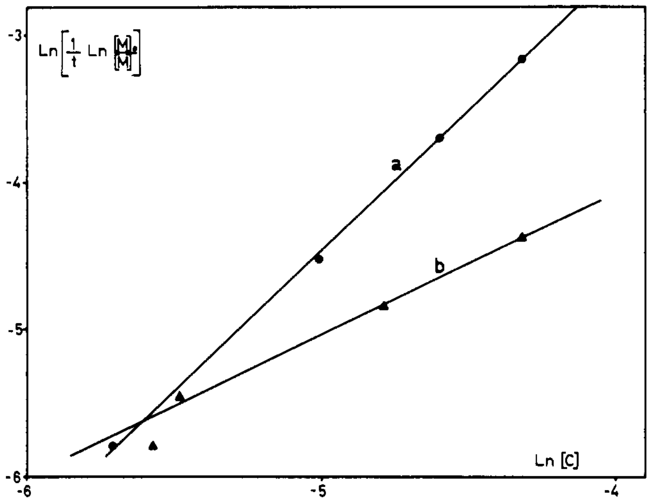


Figure 2. Order in catalyst for the ϵ-caprolactone polymerization: solvent, toluene; T, 20 °C; $[CL]_0 = 1$ mol/l; catalyst, $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$. (a) No alcohol addition; (b) alcohol addition.

tone has been changed and the medium's polarity maintained constant by adding a suitable amount of the nonpolymerizable γ-butyrolactone; these two lactones have about the same dipole moment: 4.09 for γ-butyrolactone and 4.45 for ϵ-caprolactone. Table V indicates that the polymerization rate becomes practically independent of the initial monomer concentration at constant medium polarity.

Changing the nature of the metals, alkoxide groups, solvent, and temperature does not exercise any influence on the first order in monomer.[4,14–16]

Contrary to the order in monomer, the order in catalyst is largely dependent on the structure of the oxoalkoxide used, and principally on its mean degree of association $\bar{n}$. Figure 2a illustrates second order in catalyst for the ϵ-caprolactone polymerization in toluene at 20 °C with associated $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ compound (Table II); the addition of alcohol disassociates the aggregated catalytic species (Table II), and first order in catalyst is then observed (Figure 2b). Generally, second order takes place with higher aggregates (or lower mean number of active OR groups), i.e., $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ and $CoO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$, and first order with less associated catalysts (i.e., Zn/Al and Co/Al isopropoxides) or under dissociative conditions: presence of alcohol or increasing temperature. This observation stresses the fundamental role of the catalyst association on the catalytic behavior of the bimetallic oxoalkoxide compounds.

In the presence of alcohol, the rate constant is about 17 times lower than the value calculated at the same temperature in the absence of that ligand. The decrease of the polymerization rate is undoubtedly due to the competitive coordination of the alcohol on the catalyst sites (Al atoms).

The activation energy of the polymerization reaction amounts to 11 kcal/mol for $Co^{II}O_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ in toluene and to 15 kcal/mol for $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ in the same solvent. In the latter case, the activation entropy has been evaluated to 2 μe; in other words, the geometrical requirements are not very important in the transition state. All the kinetic curves (i.e., Figure 1) are regular, no break being observed in their shape; consequently, it seems that the oxoalkoxide foreshadows exactly the actual active site and is not modified during the course of the polymerization. This conclusion has been verified by a classical method in coordination chemistry: the establishment of a Job's continuous variations diagram,[17] based on the measurement of the cryoscopic melting point depression. The results obtained with ϵ-caprolactone and $Co^{II}O_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ in benzene are gathered in Table VI and Figure 3.

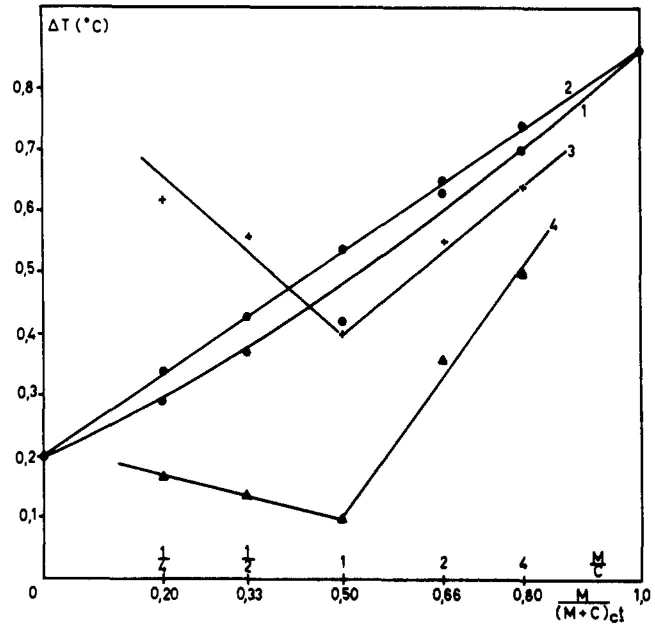


Figure 3. Job's continuous variations diagram for the interaction between ϵ-caprolactone and $Co^{II}O_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ at the beginning of the polymerization in benzene.

Table VI
Data of a Job's Continuous Variations Diagram after 100% Conversion

[M]/([M] + [C])	ΔT^a Calcd	ΔT^a Obsd
0^b	0.78	0.78
0.20	0.62	0.61
0.33	0.52	0.54
0.50	0.39	0.40
0.66	0.26	0.28

[a] Assuming no dissociation of the living catalytic aggregate.
[b] Catalyst solution containing no lactone.

Table VI clearly shows that the number of catalyst aggregates is exactly the same before polymerization and after complete monomer conversion. Figure 3 also indicates a good agreement between the experimental curve (1) measured at the beginning of the polymerization and the theoretical curve corresponding to the absence of monomer coordination on the unmodified catalyst. The small distortion observed between these two curves may be attributed to incipient polymerization which lowers the mean number of species in solution due to the high catalytic activity. The theoretical curves (3) and (4), which do not verify the experiment, correspond to the following hypothetical situations: coordination of 1 mol of monomer per catalyst unit $Co^{II}O_2Al_2(OR)_4$ with simultaneous dissociation (curve 3), and coordination of 1 mol of monomer per catalytic unit without dissociation (curve 4).

In conclusion, the coordinatively saturated aggregates are very stable, most of the monomer is in the free state, and the polymerization proceeds without catalyst rearrangement.

Mechanism of the Polymerization. As demonstrated in another paper,[9,13] the propagation step proceeds through the insertion of the monomer into a M_2–OR bond. The polymerization is probably of a coordinative, slightly anionic nature; as mentioned here above, the polymerization rate is accordingly decreased when the polarity of the reaction medium increases.

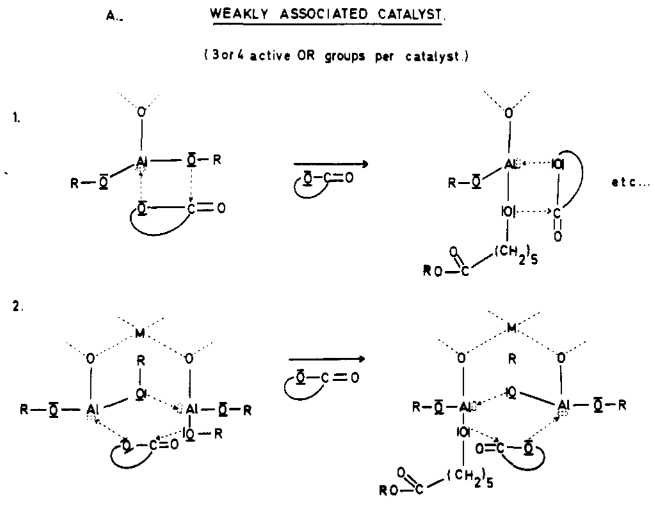


Figure 4. Lactone polymerization mechanism: (1) flip-flop on the same Al atom; (2) flip-flop on the two Al atoms of the same catalyst molecule.

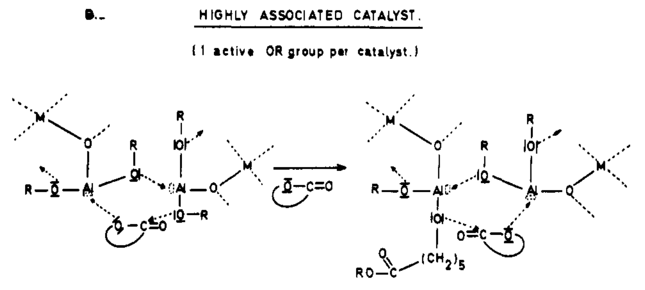


Figure 5. Lactone polymerization mechanism; flip-flop on two Al atoms (linked through an OR group) belonging to different catalyst molecules.

To take the different aspects of this lactone ring-opening polymerization into account, a flip-flop reaction scheme (Figures 4 and 5) can be proposed. This type of mechanism was previously proposed for epoxide polymerization by Vandenberg.[18]

When the catalyst is less or not associated, and characterized by three or four active (probably non-bridged) Al–OR groups per trinuclear unit, the propagation could occur by the classical flip-flop mechanism involving two vicinal coordination positions (on the same Al atom or not, but in a suitable intramolecular configuration): one carrying a coordinative vacancy to be filled by the ether oxygen of the monomer, and the other an unbridged OR group, the electron pair of which will attack the same monomer carbonyl group.

In higher aggregates (one active Al–OR group per catalyst molecule), the Al atoms carrying the active (assumed non-bridged) OR group are probably implied in the stabilization of the coordinated aggregate, and only a few of these Al atoms, the two OR groups of which are inactive (bridged), may present a coordinative site easily accessible to monomer (i.e., not stabilizing the aggregate). The probability of finding these two types of necessary sites in a favorable vicinity and accessibility, while belonging to the same catalyst molecule, must be low; under these conditions, the second order in catalyst could be expected from the necessity to first bring together these two sites in a suitable position.

Consequently, the growing species will be star-shaped entities involving four to eight chains bound to a central catalytic aggregate; this picture has been substantiated by viscometric measurements performed before and after hydrolysis of living polymers. So, the reduced viscosity of living poly(ϵ-caprolactone) obtained, at total conversion, in benzene at 30 °C with the $ZnO_2Al_2(O\text{-}n\text{-}C_4H_9)_4$ compound ([M]/[C] = 60) is 0.94 dl/g, while after hydrolysis its value falls to 0.53 dl/g.

The coordination of the monomer takes place before every insertion and is probably the rate determining step in the polymerization.

The flip–flop mechanism proposed here explains all of the basic facts described in this study and will also be useful to explain the main characteristics of oxiranes polymerization as described elsewhere.[4,5,11] The implication of two available and vicinal metal atoms in the chain growing process can account for the effect of the association degree of the catalytic coordination aggregates on the polymerization characteristics. Since the catalyst association can be controlled by specific conditions, new ways are opened to control homopolymerization and, as discussed in another paper,[19] block copolymerization processes.

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Kinetic Study of the Cationic Polymerization of *p*-Methoxystyrene Initiated by Trityl Hexachloroantimonate

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ABSTRACT: The cationic polymerization of *p*-methoxystyrene has been studied between +25 and −15 °C in dichloromethane solution, using a technique allowing the rapid consumption of monomer by calorimetry and initiator (Ph_3C^+, $SbCl_6^-$) concentration by spectrophotometry to be followed simultaneously. First orders with respect to monomer and to initiator were observed for the initiation reaction. An overall second order with respect to monomer was found for polymerization which leads to a first order for the propagation step. A kinetic scheme is proposed and rate constants of the different steps were computed assuming unimolecular termination and transfer to monomer. At +10 °C, values of initiation, propagation, transfer, and termination constants are respectively $k_i = 0.28 \pm 0.05$ M^{-1} s^{-1}, $k_p = 2.8 \pm 0.5\ 10^4$ M^{-1} s^{-1}, $k_{trm} = 53 \pm 16$ M^{-1} s^{-1}, $k_t = 0.08 \pm 0.05$ s^{-1}. Corresponding apparent activation energies were found to be $E_i = 13.3 \pm 0.6$ kcal mol^{-1}, $E_p = -6 \pm 1$ kcal mol^{-1}, $E_{trm} = 5.9 \pm 0.5$ kcal mol^{-1}. No significant variation with temperature was found for the observed low values of k_t, and apparent E_t is probably close to zero, though it was not possible to specify whether it is negative or positive. Negative E_p value may be explained by a shift of the dissociation equilibrium of propagating ion pairs into free ions, accompanied by an exothermic solvation process. An alternative explanation might be the existence of a solvation equilibrium between active species and monomer prior to the propagation step.

In most cases for cationic polymerization of ethylenic monomers the concentration of active centers remains unknown, and it is generally difficult to propose valid kinetic schemes and to determine the rate constants for the different steps of the reaction. This explains the increasing interest for initiation by stable carbocations such as triphenyl methyl carbenium ions for which a simple electrophilic addition on ethylenic double bonds is generally assumed. In addition, the concentration of trityl salts can be followed spectrophotometrically during the course of the polymerization. Kinetic schemes and propagation rate constants have been proposed for the polymerization of some ethylenic monomers, initiated in CH_2Cl_2 by stable carbocations, i.e., *N*-vinylcarbazole (NVC),[1] alkyl vinyl ethers (VE),[2–4] and cyclopentadiene (CPD).[5] In the first two cases (NVC and VE), initiation by tropylium or trityl salts is reported to be complete and rapid, leading to relatively stable active centers which are assumed to be mainly free ions. Thus propagation rate constants, obtained from a rather simple kinetic treatment,[2] are relative to free ions and the corresponding activation energies are positive.

In the case of the polymerization of cyclopentadiene, initiation by trityl salt is slower, important termination processes occur, and a nonstationary state is observed for active centers concentration. The dissociation equilibrium of propagating ends is shifted toward ion pairs on account of the strong salt effect of remaining initiator and a negative apparent activation energy is observed for propagation.

We previously reported preliminary results on the kinetics of *p*-methoxystyrene polymerization initiated by trityl hexachloroantimonate (Ph_3C^+, $SbCl_6^-$) in dichloromethane solution.[6] With the concentrations needed for monomer (10^{-2} to 10^{-1} M) and initiator (2 to 11.10^{-5} M) and the temperature range (−15 to +25 °C), observed polymerization rates were high and monomer consumption was followed by adiabatic