PII: S0032-3861(97)00115-8

Polymer Vol. 38 No. 22, pp. 5667–5676, 1997
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0032-3861/97/$17.00 + 0.00

End-functionalized poly(ϵ-caprolactone) oligomers through heterogeneous catalysis in protic conditions: a mechanistic approach

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(Received 26 November 1996; revised 27 January 1997)

An heterogeneous system constituted of aluminium alkoxides grafted on a porous silica has been used for the ring opening polymerization of lactones. Adding alcohol in excess induces a rapid exchange reaction between the grafted active centres and these free alcohol molecules present in the medium, which competes with the propagation step. The polymer chains are functionalized by end-groups issued from the alcohol and are produced in a number larger than that of metal atoms used. In addition, the active centres can be re-used for further polymerizations which brings an innovative catalytic dimension to this process.

This case was engaged in the polymerization of ϵ-caprolactone and some kinetic features are reported. The activation energy is 28 kJ mol^{-1}. The catalytic activity is strongly dependent on the alcohol concentration and exhibits some optimum. A mechanistic approach based on the share of the aluminium vacancy between the Lewis bases present in the medium was proposed to account for the experimental results. Molecular geometry calculations have been used to study the possible arrangements of the monomer–aluminium alkoxide complex. © 1997 Elsevier Science Ltd.

(Keywords: ϵ-caprolactone; anionic ring opening polymerization; heterogeneous catalysis)

INTRODUCTION

The polymerization of lactones is of great interest because of the properties of the polyesters synthesized such as no toxicity, biodegradability, biocompatibility and miscibility with other polymers[1–3]. The anionic ring-opening polymerization (AROP) of lactones provides a direct access to the related polyesters, in contrast to the traditional step-polycondensation method[4]. Using alkoxide anions as initiators gives side reactions such as backbiting, leading to macrocyclics, as well as transesterifications which broaden the molecular weight distribution[5–7].

In order to overcome this drawback, these oxygenated heterocycles are preferably polymerized with initiators based on salts of metals having Lewis acidity like Al or Zn. Several years ago, Teyssié had proposed aluminium isopropoxide and μ-oxo bimetallic alkoxides as initiators for coordinated anionic polymerization of lactones[8]. Dialkylaluminium alkoxides were also proposed as initiators[9–12]. These polymerizations are characterized by a perfectly living character and yield exclusive linear polyesters of a predictable molecular weight with a narrow molecular weight distribution[13].

In apolar or low polar solvents, these initiators display aggregate structures[14–16] which lead to a decrease of the number of the active centres and a possible distribution of their activity. For instance, it was reported that $Al(OiPr)_3$ reacts faster as a trimer than as a tetramer[16]. Dialkylaluminium ethoxide exists as an inert trimer in fast equilibrium with an active non-aggregated form[12]. Protic compounds like alcohols[17] or amines[12,18] can be added in order to dissociate the active centres, but the products have lower molecular weights because of the exchange reactions which take place between free alcohols and grafted alkoxides[19]. Another way to limit aggregation is to use either bulky substituents or supports on which the active centres are chemically grafted. The first concept is illustrated by Inoue with his catalyst based on aluminium or zinc porphyrins[20]. The aggregate state does not exist because of the steric hindrance around the metal atom. The influence of alcohols on the molecular weights was also noticed by Inoue with the aluminium porphyrins[21].

More recently, we have worked on the second concept by developing a new system based on aluminium alkoxides dispersed on a porous silica[22]. The addition of alcohol in excess induces an exchange reaction which takes place between free alcohols and grafted alcohols, that allows us to synthesize much more polymer chains than metal atoms. A consequence of this exchange reaction is the decrease of the degree of polymerization according to the [monomer]/[alcohol] ratio. That may be seen as a drawback if dealing with the synthesis of high molecular weight polymers. But it is worth noticing that the polymer chains are directly functionalized by an end-group which comes from the alcohol, which makes their synthesis easier and therefore may extend their field of application. For instance, this method was recently applied in our laboratory to the preparation of

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macromonomers containing a polymerizable end group like ω-hydroxy polycaprolactones[23]. In the same way, using diols allows us to get α–ω-dihydroxytelechelic polymer chains. The same process was also used to copolymerize ϵ-caprolactone and ethylene oxide[24]. Finally, the active centres are supported on a porous silica having an heterogeneous system which can be easily recycled and the obtained polymers are free from complexed metal residues.

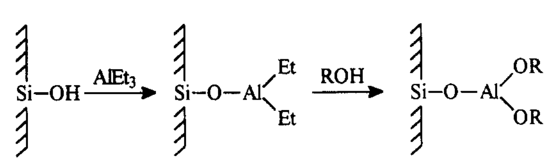
The ring opening polymerization of ethylene oxide using this new catalytic system has been previously described[22,25]. The corresponding polyethers are obtained under very mild conditions, with very satisfactory rates, high degrees of conversion and an excellent control of the length and the polydispersity of the polymeric chains. Although the composition of this system seems to be rather simple, the overall catalytic behaviour is complex, suggesting the competition of coordination on the metal of the various Lewis bases present in the reaction medium.

To understand more in depth the action of the catalyst and the mechanism of the lactones ring-opening polymerization, it was obviously important to study in detail the kinetic behaviour of the polymerization process: the influence of the alcohol (nature and concentration), the structure of the active centres and the concentration of the monomer have been studied. At the end, an interpretation in terms of share of acidic vacancies of the aluminium atom, which leads to a coordination number of five, will be proposed.

RESULTS AND DISCUSSION

Polymers synthesis

The preparation of the heterogeneous catalyst system developed for the polymerization of oxygenated heterocycles has already been reported[22,25]. The active centres are aluminium alkoxides grafted onto a porous silica. They are obtained by reaction of a trialkylaluminium on the surface silanol groups. The subsequent alcoholysis gives the aluminium alkoxides (*Scheme 1*). The amount of silanol groups is previously controlled by the thermic treatment of the silica.



Scheme 1 Grafting of the aluminium alkoxides on the silica

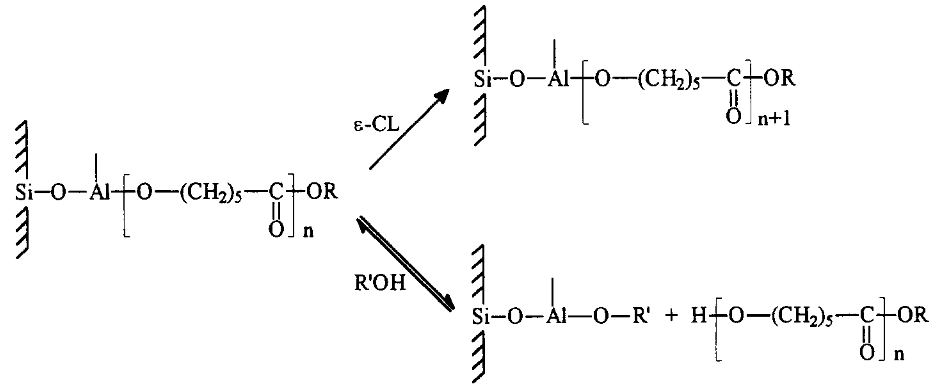
In the presence of free alcohol molecules, the polymerization proceeds through a competition of the propagation reaction (corresponding to a selective acyl–oxygen cleavage of the ϵ-caprolactone ring and insertion in the Al–O bond) and an exchange reaction between the grafted alkoxides and the free alcohols (*Scheme 2*). It was found that the monomer does not insert in the Si–O–Al bond, which allows the catalyst to be recycled several times. The inactivity of the oxygen lone pair may be due to its overlapping with silicon *d*-orbitals. This feature has been evidenced by the development of a novel continuous polymerization process[26]. In the following, stoichiometric conditions will refer to polymerizations which are carried out without any free alcohol in excess in the medium.

^{1}H n.m.r. as well as gas chromatography analysis clearly show the fast and complete consumption of the alcohol molecules during the polymerization. This point demonstrates the existence of a fast exchange reaction between free and grafted alcohols. These exchange reactions have already been mentioned by Teyssié in homogeneous medium with bimetallic μ-oxo-alkoxides[19] and by Duda with aluminium *i*-propoxide[27]. However, the transfer reaction of the alcohol is not quantitative for bulky graft alcohol[17] or at too low a temperature[1].

In addition, ^{1}H n.m.r. allows us to estimate the average molecular weight M_n from the relative intensities of protons belonging to the polymer chain and those coming from the alkoxide radical. The values are in good agreement with the s.e.c. measurement. Although this paper is dealing with functionalized low molecular weight oligomers, the production of high molecular weight products deserves some comments since we are using porous silica. The porosity is issued from the aggregation of very small elementary particles held together by the van der Waals forces. We calculated the upper limit for the degree of polymerization in the case of ethylene oxide polymerization: assuming a bulk polymerization and two polymer chains bound to one active centre, it may be expected that the increase of the degree of polymerization would be limited by the volume of the pore in which the reaction takes place:

$$\overline{DP} = \frac{\overline{M}}{44} = \frac{1}{44}\,\frac{\text{mass of polymer}}{\text{number of chains}} = \frac{V_p d}{44.2[\text{SiOH}]}$$

where V_p is the porous volume, d the density of PEO and [SiOH] the number of silanols per gram. Then, a pore



Scheme 2 The competition between the propagation step and the exchange reaction in the polymerization process

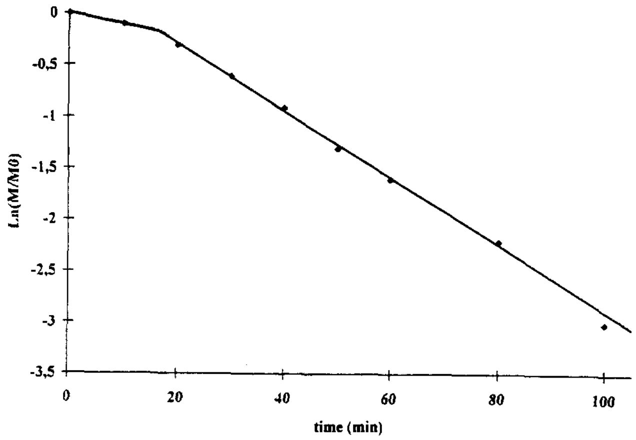


Figure 1 ε-Caprolactone consumption as a function of time. $T = 50°C$; solvent: toluene/DCE (3/1 v/v). $[Al] = 9 \times 10^{-3} mol l^{-1}$; $[M_0] = 1.8 mol l^{-1}$; $[\phi CH_2OH] = 0.18 mol l^{-1}$

would be filled by polymer chains with $\overline{DP} = 12$. Experimental data clearly show that it is actually possible to produce higher molecular weights, due to the disaggregation of silica in smaller particles: this catalytic system allows one to reach degrees of polymerization higher than 100.

The general features of the polymerization

The kinetic and thermodynamic approaches. The activity was measured by monitoring the consumption of the monomer by gas chromatography all along the reaction (*Figure 1*). The polymerization begins after an induction period. This one decreases when increasing the temperature or the alcohol concentration. These induction times were already observed by Teyssié with aluminium alkoxides as initiator in stoichiometric conditions[1,28,29]. The authors have interpreted this behaviour in terms of a rearrangement of the catalytic coordination aggregates upon the addition of the polar cyclic monomer: in nonpolar solvents, aluminium alkoxides associate by formation of intra- and intermolecular oxygen–metal coordinative bonds and the mean degree of association decreases significantly upon the increase of the dielectric constant of the solvent or upon addition of suitable ligands such as alcohols. Duda explains this behaviour by a complexation of the aluminium alkoxide active species by the alcohol molecules, hindering the approach of the monomer molecules and slowing down the propagation[27].

In our case, the active centres are grafted on a solid surface and are assumed to be isolated, so that aggregates could not arise, and particularly when working in protic conditions, in which the alcohol molecules should dissociate the possible aggregates, if any. The alcohol molecules are coordinated to the metal at the beginning of the polymerization and create a solvation sphere around the aluminium (the vacancies can be occupied by an alcohol molecule). The polymerization requires the coordination of the monomer to the metal atom to be effective, so it implies a perturbation of the solvation sphere which would lead to this induction time.

After this induction time, the monomer consumption follows a first order law with respect to the monomer, from which an apparent (experimental) rate constant is determined from the slope of the $Ln([M]/[M_0])$ vs. time curves. This rate constant depends on the active centres concentration and an absolute rate constant can be deduced according to

$$k = \frac{k_{app}}{[Al]} = -\frac{\Delta\left(Ln\frac{[M]}{[M_0]}\right)}{[Al]\Delta t}$$

The active centres concentration [Al] is calculated from the amount of silica used in the experiments, assuming each silanol group gives an active centre. As an example, a typical value will be $[Al] = 9 \times 10^{-3} M$ (0.5 g silica heated at 450°C in 50 ml toluene). The absolute rate constant for a polymerization carried out at 30°C with a $[M_0]/[ROH]$ ratio = 10 was found to be $4.4 \times 10^{-2} M^{-1} s^{-1}$.

Investigating the effect of temperature on the rate constants allows us to calculate the activation energy. It was found that this depends on the $[M_0]/[ROH]$ ratio, which means the alcohol functionality actually participates in the reaction (*Table 1*). *Figure 2* displays the Arrhenius plot of the rate constants for experiments carried out with a ratio equal to 10, from which an activation energy $E_a = 6.7 kcal mol^{-1}$ can be deduced. This value is of the same order as those reported by Dubois *et al.* ($6.4 < E_a < 10.0 kcal mol^{-1}$) when working with various functional aluminium trialkoxides in stoichiometry conditions[29]. The activation energy was found to decrease up to $3.3 kcal mol^{-1}$ when increasing the amount of alcohol. Thermodynamic parameters $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ have been deduced from the activation energy and the absolute rate constants. The main feature is the values for $\Delta S^{\#}$, which are even more negative than those reported by Dubois, which corresponds to a greater reduction of the entropy[30]. This feature may be due to the fact that the reactants have to adopt more defined orientations in the activated complex. These points will be used for discussion in the following sections.

Table 1 Thermodynamic parameters for the ε-CL polymerization in toluene at 30°C

$[M_0]/[ROH]$	E_a (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta S^{\#}$ [cal (mol/K)$^{-1}$]	$\Delta G^{\#}$ (kcal mol^{-1})
5	3.3	2.7	−41.2	15.2
10	6.7	6.1	−33.2	16.1

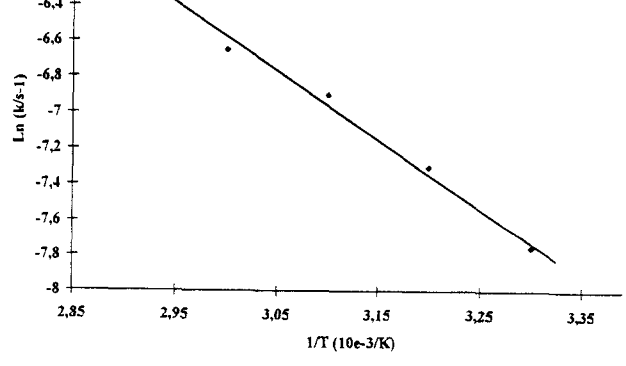


Figure 2 Determination of the activation energy. $[M_0]/[ROH] = 10$. $[Al] = 9 \times 10^{-3} mol l^{-1}$

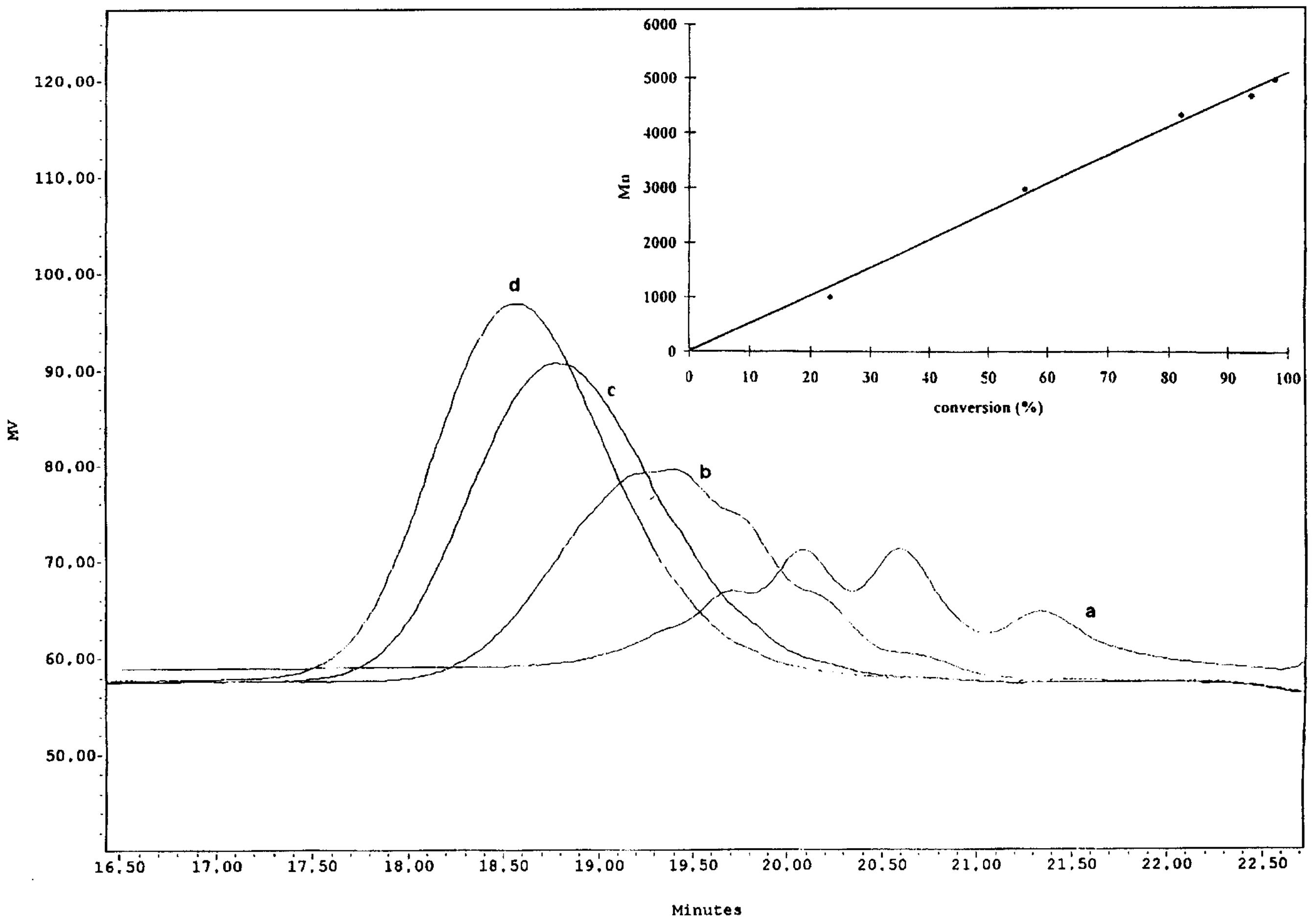


Figure 3 S.e.c. traces recorded during the polymerization. 10 min (a); 20 min (b); 30 min (c); 40 min (d). In the insert is shown the increase of the average molecular weight with conversion, using $Al(OiPr)_3$ at 50°C

The molecular weight distribution. Owing to the problem due to some residual colloidal silica that may lead to some rather questionable s.e.c. analysis, we investigated the MWD in protic conditions from homogeneous initiators, namely aluminium isopropoxide and tetraisobutylaluminoxane (TibAlOx). The reactional medium was analysed by s.e.c. at different moments during the polymerization. The spectra displayed in *Figure 3* show that the degree of polymerization increases linearly with the conversion while the polydispersity decreases simultaneously. This latter is slightly higher than that expected from a theoretical Poisson distribution. If taking into account the very low molecular weights, this fact may be due to the functional end-group, the contribution of which becomes quite important in the hydrodynamic radius, so that the molecular weight determination is somewhat inaccurate.

The linear increase of the number-average molecular weight with the conversion shows that the system displays a quasi living-like character, even in protic conditions. Strictly speaking, the reaction cannot be qualified as a living polymerization because of the transfer reactions. But it keeps the main characteristic, namely the control of the molecular weight, that is the most important from a practical point of view. Another quite interesting feature is the absence of side-reactions, such as irreversible chain transfer, chain termination or formation of macrocyclic oligomers which would broaden the MWD.

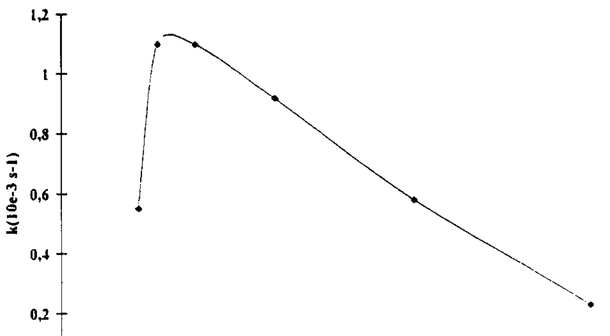


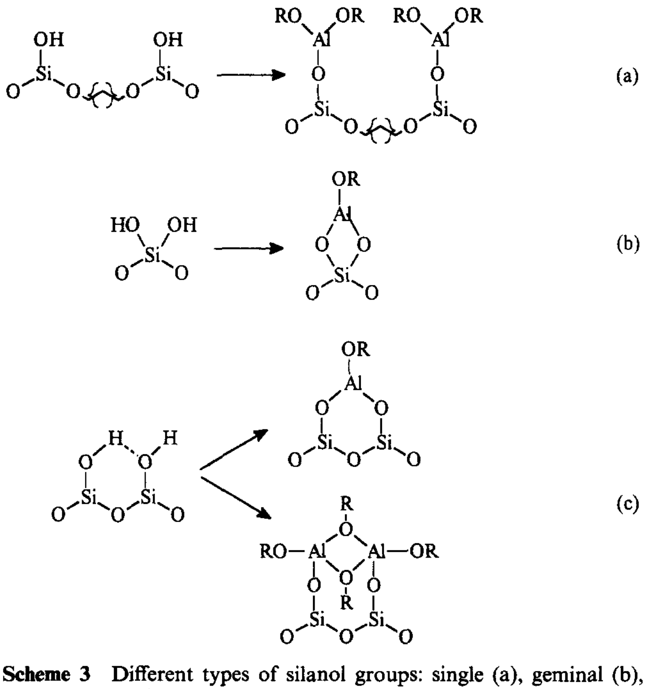
Figure 4 Alcohol dependence of the catalytic activity in ϵ-caprolactone polymerization. The [monomer]/[alcohol] is kept to a constant value in order to assure the same degree of polymerization

How do the different parameters influence the polymerization behaviour?

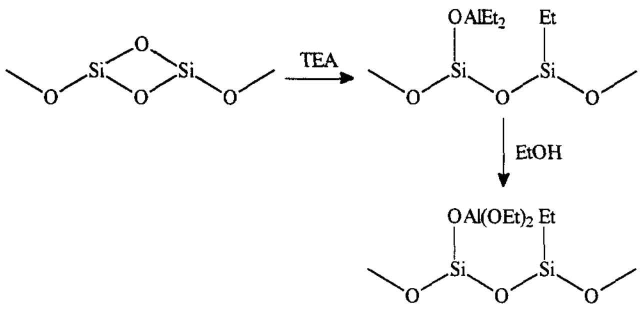
(a) *Effect of alcohol concentration on the activity.* Kinetic studies clearly show that the catalytic activity is strongly dependent on the alcohol concentration in the medium. It must be kept in mind that the experimental procedure implies first a coordination of the alcohol molecules to the active centres. When alcohol concentration varies (the other parameters being constants), the activity follows a bell-shaped curve with a maximum (*Figure 4*).

(b) *Effect of the aluminium concentration.* The aluminium concentration in the medium is a parameter which is dependent on the alcohol concentration. In fact, by increasing the aluminium concentration with a constant alcohol concentration, we decrease the [ROH]/[Al] ratio. So, the bell-shaped curve obtained for a silica being heated at 450°C must be seen as a direct consequence of the above bell-shaped curve which had previously been obtained by varying the alcohol concentration. The curve established for the silica being heated at 800°C corresponds to the first part of the precedent curve.

(c) *Influence of the structure of the active centres.* The silica surface displays different types of silanols, namely single (isolated), geminal and vicinal silanols (*Scheme 3*). Their proportion, as well as their respective nature can be changed according to specific thermic treatments[31–33]. The concentration of silanol groups decreases with increasing temperature. After heating at 450°C, it was reported by Iler that only single and geminal silanols remains at the surface[31], while the vicinal groups condense to yield strained siloxane groups. Hsieh and MacDaniel referred to single and paired hydroxyls[33], the latter being those able to react with $SiCl_4$ in a 2/1 ratio. It is important to take into account the distinction between single silanols and the others because of the subsequent reaction with the alkylaluminium. A single silanol will react with alkylaluminium in a 1/1 ratio to yield two active centres per aluminium atom while the geminal or vicinal silanols may react in a 1/1 ratio as well as in a 2/1 ratio to give only one active centre per aluminium atom.



Scheme 3 Different types of silanol groups: single (a), geminal (b), vicinal (c) and the related structures of the active centres



Scheme 4 Opening of the siloxane bridges by trialkylaluminium and formation of new active centres by reaction with EtOH

Table 2 Amount of Al and C (%) grafted on a silica previously dehydrated at 800°C. Al was brought by $AlEt_3$ and ethanol was used to form the aluminium alkoxide. Al (theor) was calculated assuming an Al/SiOH ratio = 1 with SiOH = 0.6×10^{-3} mol g^{-1}

Al (theor)	C (theor)	Al (exp)	C (exp)
1.51	2.69	2.45	4.48

The concentration of silanols is measured by using a volumetric method which consists in treating the support with triethyl aluminium in solution[34]. The results are 1.2×10^{-3} mol g^{-1} and 0.6×10^{-3} mol g^{-1} silanol groups after heating at 450°C and 800°C respectively.

The more strained bridges can be opened by adding alkylaluminium, that gives potential new active centres with a different reactivity because of their different environment (*Scheme 4*). This reaction would be similar to the opening of siloxane bridges by lithium compounds[35] or alkoxysilane[36]. Analytical procedures have shown that the Al and C contents grafted on a silica dehydrated at 800°C are higher than those expected from the silanol amount (*Table 2*). Therefore, around 50% of additional active centres can be recovered from the opening of the siloxane bridges.

In *Figure 5* are reported the influence of the thermal treatment of the silica on the polymerization rate. It is clear that heating silica at 800°C yields a better activity, but this behaviour is difficult to interpret. Because of the opening of the siloxane bridges, it is difficult to really appreciate the amount of actual active centres as well as their chemical nature. Furthermore, the bell-shaped curve is no longer observed with silica treated at 800°C, at least when using reasonable amounts of catalyst. The shape of this curve would even suggest a continuous increasing of the activity.

A mechanistic approach

Sharing the electronic vacancy. The polymerization is assumed to proceed according to an anionic coordinated process by coordination of the monomer on the aluminium vacancy followed by the insertion in the Al–O bond. The coordination of the monomer leads to a diminution of the metal acidity, that weakens the polarized C–O bond and increases the nucleophilicity of the oxygen atoms of the aluminium alkoxide. In the same way, the presence of the alcohol, which is also a Lewis base, should activate the insertion of the monomer in the Al–O bond.

Scheme 5 summarizes the possible reactional pathways when the active centre is faced with both monomer and

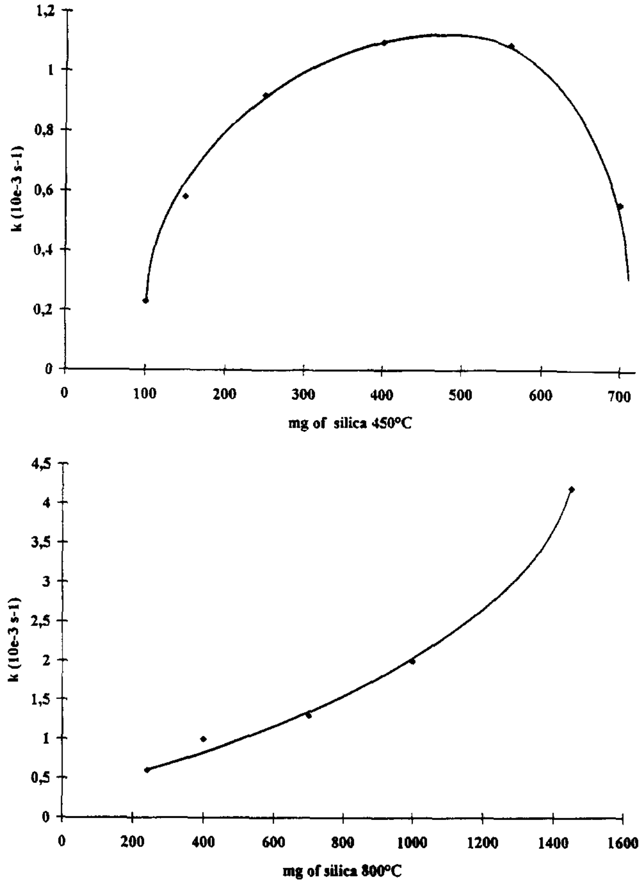
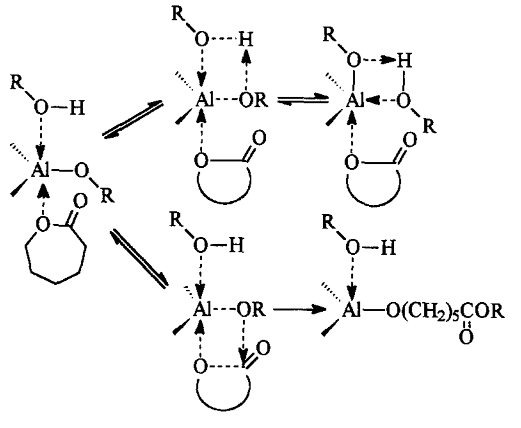
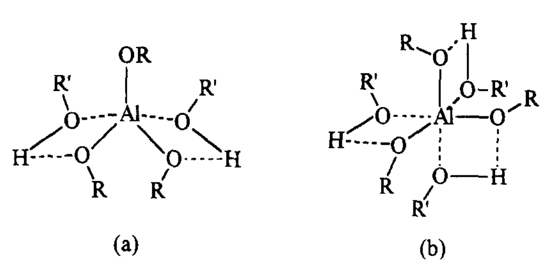


Figure 5 Influence of the silica thermal treatment on the ϵ-caprolactone polymerization. $[M]_0 = 1.8\,\mathrm{mol\,l^{-1}}$. $[ROH] = 0.18\,\mathrm{mol\,l^{-1}}$. $T = 50°C$

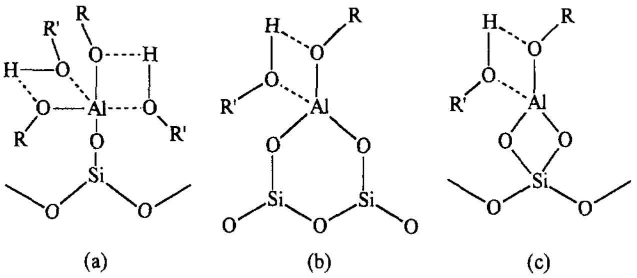


Scheme 5 Coordination followed by the insertion of the monomer

alcohol. This scheme implies that both monomer and alcohol molecules can be coordinated simultaneously to the active centre to give at least a five-coordinated state for the aluminium atom. A coordination of the alcohol on the active centres was previously assumed by Jérôme *et al.* in order to explain the dissociation of the aggregated forms of the catalysts[19] and the decrease of the polymerization rate was interpreted in terms of a competitive coordination of the alcohol and the monomer on the active centres.



Scheme 6 Complexation of aluminium alkoxide by alcohol molecules R'OH in a homogeneous system



Scheme 7 Various structures of aluminium alkoxide grafted on silica with additional alcohol complexation

When adding the alcohol to the system, hydrogen bonds take place with the oxygen atom of the alkoxide group, that may explain the alcohol exchange by switching the alkoxide ligands which are bound on the aluminium.

The important parameter to consider is in fact the [ROH]/[Al] ratio. By increasing the alcohol concentration, we favour the alcohol coordination to the aluminium. This coordination of an alcohol molecule has an activation effect on the polymerization by increasing the grafted alcohol oxygen nucleophilicity and favouring the lactone cleavage. That is why we observe both an increase of the reaction rate (*Figure 4*) and the decrease of the activation energy.

The second part of the curve corresponds to a high alcohol concentration. These alcohol molecules are competing with the monomer to coordinate to the aluminium, that leads to the exchange reactions. It was evidenced that the starting free alcohol disappears quite rapidly during the very first propagation steps[25]. This point highlights the fact that the exchange process is faster than the propagation reaction, so that all the oligomers spend the same time on the active centres. A narrow molecular weight can be expected, as confirmed by the s.e.c. chromatograms.

A too high alcohol concentration hinders the polymerization as it takes place with the first coordination of the monomer to the active centres. We found an optimum [ROH]/[Al] ratio around 17 with a rate constant equal to $1.15 \times 10^{-3}\,\mathrm{s^{-1}}$.

In the light of the structures previously reported for the aggregated forms of aluminium isopropoxide which exists as aggregated species, namely dimer (referred to as A_2, with a tetrahedrically coordinated aluminium), trimer (A_3, with a pentacoordinate metal) and tetramer (A_4, octahedrally coordinated metal) in equilibrium, some structures of the active centres may be designed which take into account a simultaneous coordination of the aluminium atom by two or more Lewis bases.

If keeping the same environment, the ligands $Al(OR)_3$ can be replaced by alcohol molecules R'OH (*Scheme 6a*, *b*). The grafting of aluminium alkoxide on silica will lead to the replacement of an Al–O–R bond with an Si–O–Al bond (*Scheme 7*). To do that, some points must be taken into account:

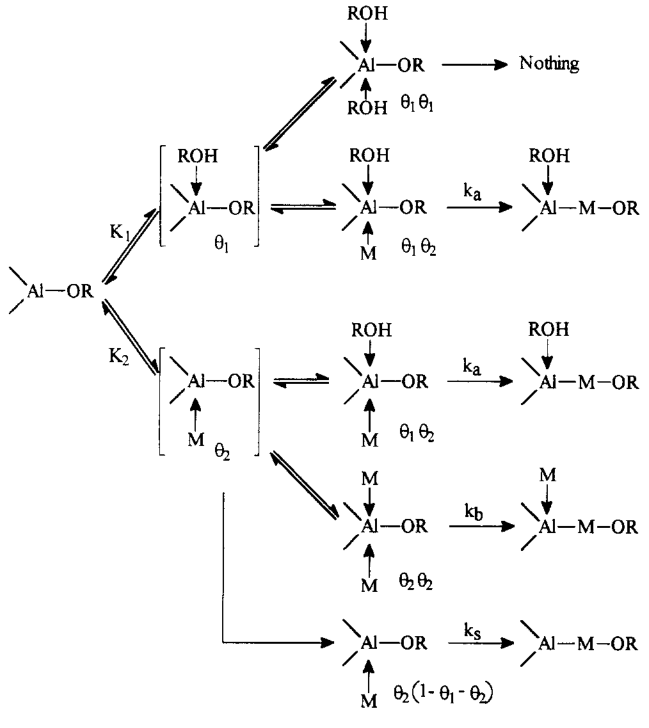
(a) the different types of silanols which may be encountered on the surface of the silica, giving rise to various ligands for the aluminium atom, as shown in *Scheme 3*;
(b) the steric hindrance due to the surface of silica;
(c) the chemical behaviour of the oxygen atom in the Si–O–Al bond which appears quite different from that in the Al–O–R groups: recycling experiments have shown there is no monomer insertion in this bond.

Based on these considerations, it may be assumed that it will be difficult for a molecule to approach the active centre in the space located between the silica surface and the aluminium atom. In addition, the inactivity of this oxygen lone pair will prevent any neighbouring alcohol molecule to establish hydrogen bonds with it. It follows that the aluminium atom would be restricted to the tetra- (*Scheme 7b, c*) and pentacoordinate states (*Scheme 7a*). This last structure is the only one which allows a simultaneous coordination by two alcohol molecules or by an alcohol and a monomer provided substitution of one or both alcohol molecules by a monomer occurs. A double coordination from the other structures would imply a coordination with an oxygen atom of the Si–O–Al bond and it was found this structure is unproductive.

Using the Langmuir–Hinshelwood model. A simple reactional scheme can be developed in order to model the different possibilities for an active centre when faced to a mixture of monomer and alcohol (*Scheme 8*). The scheme is based on the Langmuir–Hinshelwood model which has been extended to a double coordination of the active centre. All the coordinations are expected to be reversible. K_1 and K_2 are the equilibrium constants of the adsorption of the alcohol and monomer respectively. θ_1 and θ_2 are the surface coverages by the alcohol and monomer molecules respectively, defined as

$$\theta_1 = \frac{K_i[I]}{1+\sum_j K_j[J]}, \quad i,j = \text{monomer, alcohol}$$

k_a, k_b and k_s are the different rate constants involved in the reaction scheme. k_s is the rate constant of the stoichiometric reaction without any activation. k_a is the rate constant of the reaction when the active centre is also coordinated with an alcohol molecule. Finally, the rate constant k_b of the reaction involving an active centre coordinated by two monomers can be seen as an activated rate constant since the first monomer 'activates' the insertion of the second monomer (the activation by a monomer molecule will be illustrated in the following



Scheme 8 Stoichiometric vs protic and catalytic conditions for the polymerization

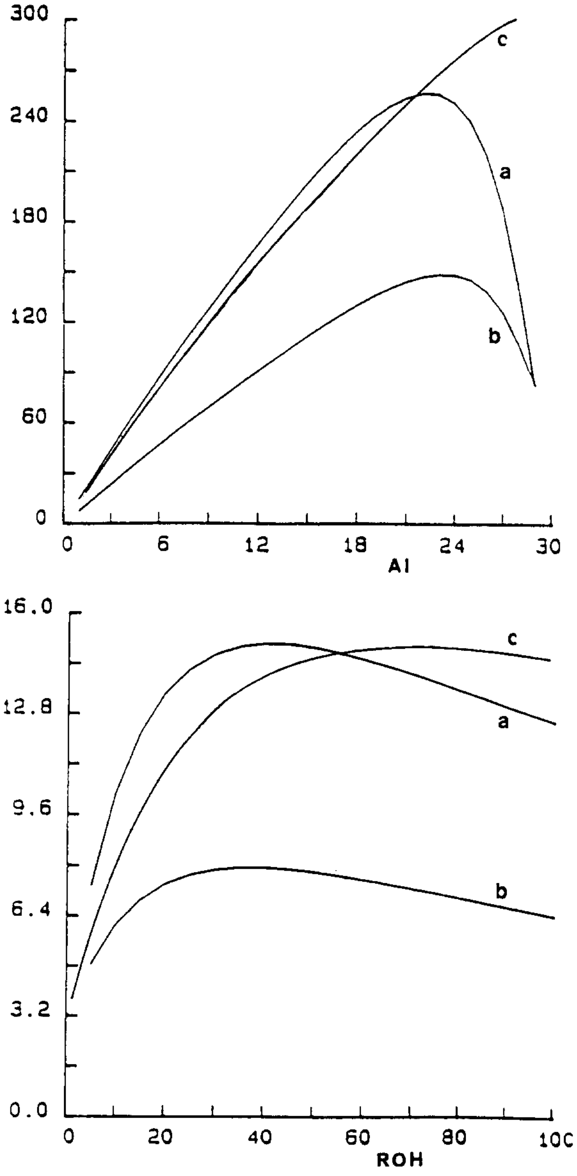


Figure 6 Simulation of the polymerization activity using the double Langmuir–Hinshelwood model according to the number of aluminium or alcohol units in the system. [Monomer] = 300 units. (a) $K_1 = 0.5 = 7K_2$. $k_{s=3}$; $k_a = 10k_s$. (b) $K_1 = 0.5 = 7K_2$. $k_s = 3$; $k_a = 5k_s$. (c) $K_1 = 0.5 = 4K_2$. $k_s = 3$; $k_a = 10k_s$

paragraph). The value of this activated rate constant has been assumed to be different from that related to an aluminium atom complexed with a monomer and an alcohol molecule ($k_s \leq k_b \leq k_a$). The expression for the reaction rate will be

$$R_p = 2k_a\theta_1\theta_2 + k_b\theta_2^2 + k_s\theta_2(1 - \theta_1 - \theta_2)$$

The computation of this rate equation gives curves, the shape of which can approach the experimental ones with the bell-shaped form (*Figure 6*). The shape can be varied by changing the θ_2/θ_1 as well as the $k_a/k_b/k_s$ ratios, with $k_s \leq k_b \leq k_a$. The two limit rate equations are

$$R_p = 2k_a\theta_1\theta_2 + k_s\theta_2(1 - \theta_2), \quad k_b = k_s$$

$$R_p = k_a\theta_2(2\theta_1 + \theta_2) + k_s\theta_2(1 - \theta_1 - \theta_2) \quad k_b = k_a$$

The higher the θ_2/θ_1 ratio, the more pronounced is the bell-shape. This case corresponds to a strong coordination of the alcohol on the active centre with respect to the monomer. Should the coordination decreases, the θ_2/θ_1 ratio also decreases and the bell-shaped tendency is reduced. The competitive coordination of the active centre by the two Lewis basis is then fully illustrated.

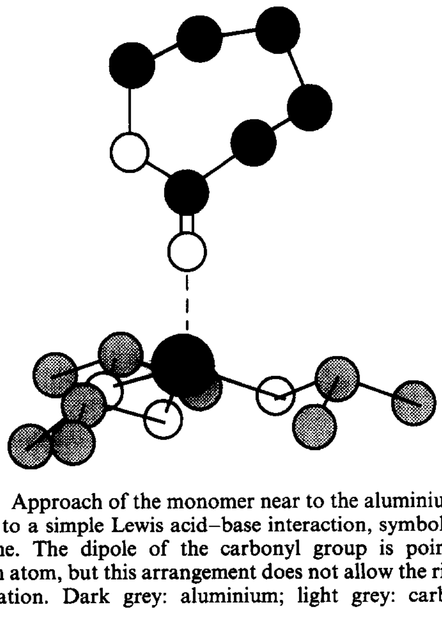
The molecular modelling. We used the SYBYL molecular modelling software[37] to carry out the molecular geometry and energy calculations in order to study the possible approaches of the monomer near the aluminium alkoxide. As a model, the approach of one and two molecules of ε-caprolactone on the electronic vacancy of aluminium isoproproxide has been examined. The energy expression includes bond stretch, angle bend, electrostatic, van der Waals and torsional potential terms.

If taking into account the partial charges in the monomer and the aluminium alkoxide, the oxygen atom of the carbonyl group (which is the most basic) might be near to the aluminium atom according to the Lewis acid and base interactions. This arrangement has been modelled and its energy is close to −13.16 kcal mol^{-1} after minimization (*Table 3*). Al(OiPr)$_3$ adopts a pyramidal conformation with the aluminium atom at the top and the monomer above the pyramid (*Scheme 9*). The dipole of the carbonyl group is pointed at the aluminium atom. Nevertheless, this arrangement does not allow any ring opening polymerization.

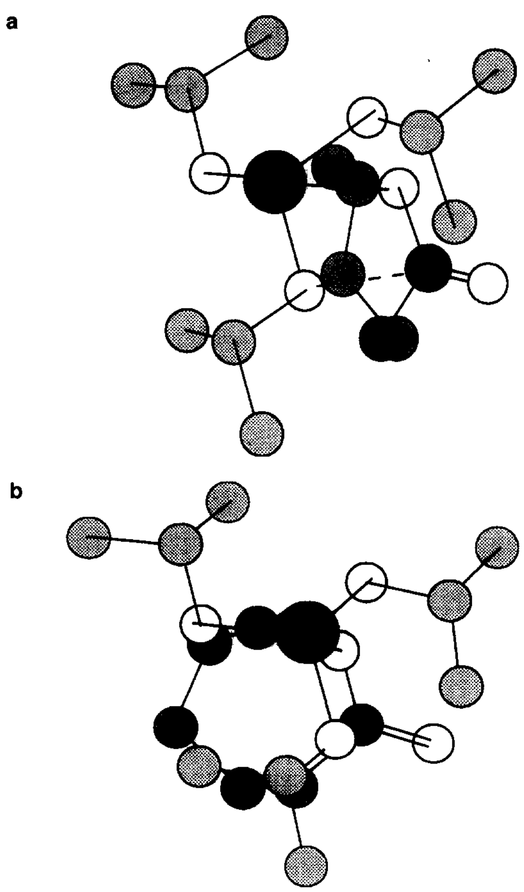
The ring opening requires an approach of the incoming monomer so that the C–O single bond of the lactone is parallel to the Al–O bond of the aluminium alkoxide. Another approach, based on this simple consideration, allowed us to find a new arrangement, the energy of which is equal to −20.52 kcal mol^{-1}, lower than the former structure (*Scheme 10a, b*). Both molecules are located in two parallel planes in order to increase the van der Waals interactions between the other adjacent atoms. It may be seen here that the aluminium alkoxide keeps its pyramidal structure, but the monomer is now located below the base of the

Table 3 Comparison of the energies for both arrangements depicted in *Scheme 9* (I) and *Scheme 10* (II) after minimization of the energy

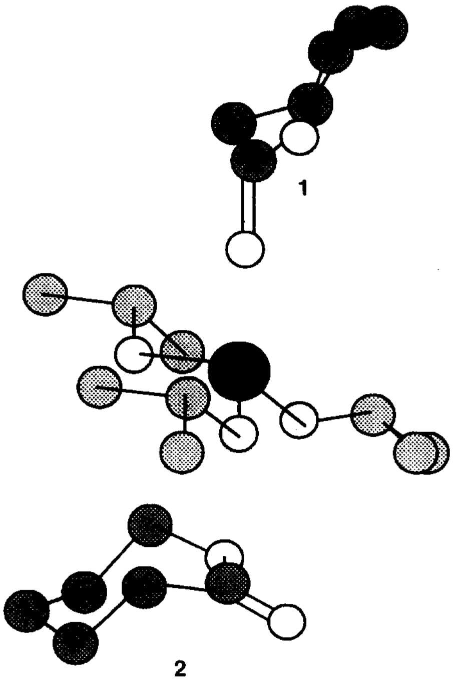
Energy (kcal mol^{-1})	(I)	(II)
Bond stretching	0.485	0.422
Angle bending	6.975	5.448
Torsional	2.552	2.517
Out of plane bending	0.001	0.002
1-4 Van der Waals	1.592	1.579
Van der Waals	−5.243	−8.356
1–4 Electrostatic	−12.283	−13.279
Electrostatic	−7.243	−8.856
	−13.164	−20.523



Scheme 9 Approach of the monomer near to the aluminium alkoxide according to a simple Lewis acid–base interaction, symbolized by the dashed line. The dipole of the carbonyl group is pointed at the aluminium atom, but this arrangement does not allow the ring opening polymerization. Dark grey: aluminium; light grey: carbon; white: oxygen



Scheme 10 Arrangement of the monomer below the aluminium alkoxide in another parallel plane. Side (a) and front (b) views. The Al–O and C–O bonds are parallel and the carbonyl group is pushed away on the outside of the structure



Scheme 11 A possible arrangement for two monomers on both sides of the aluminium alkoxide. Monomer 1 acts as an activator for the ring opening of monomer 2

pyramid. As depicted in the scheme, the Al–O and C–O bonds are in a parallel arrangement and the carbonyl group is pushed away on the outside of the structure. Such a parallel approach of the incoming monomer has been advanced in order to explain the high content of inverted units observed in poly(propylene oxide) chains when polymerized with this catalytic system[38].

One may finally conceive of a global structure consisting in two CL molecules, one above the aluminium alkoxide and the other one below the active centre (*Scheme 11*). The first one would be located according to the first structure and would increase the nucleophilicity of the oxygen atom of the Al–O bond, in order to activate the ring opening of the other monomer, located according to the second structure. This structure might be compared to that proposed by Parenté *et al.* about a theoretical investigation of the $Al(OiPr)_3$. $(\epsilon\text{-}CL)_3$ complexes[39] with a hexacoordinated aluminium atom. Nevertheless, the three ε-CL molecules appear to be coordinated through the oxygen atom of the carbonyl group. Consequently, the CH_2–O bond appears rather far from the active centre to be opened so that the question remains open. In the same way, we can imagine a complex constituted of the aluminium atom coordinated to a monomer and an alcohol molecule. The monomer would be placed in the plane parallel to the aluminium alkoxide and the alcohol on the other side. The hydrogen bond would be assured by a first oxygen atom while the other one would be used to open the lactone ring.

Conclusion

The heterogeneous catalytic system based on aluminium alkoxides grafted on a porous support working in protic conditions is a versatile tool for the synthesis of functionalized oligomers of poly(ε-caprolactone) according to a ring opening polymerization mechanism. The degree of polymerization is controlled by the [monomer]/[alcohol] ratio with a narrow molecular weight distribution.

The kinetic behaviour is complex and has tentatively been interpreted in terms of share of the electronic vacancy of the Lewis acid by external Lewis bases as ligands. The time of presence of each coordinated ligand, that is the monomer as well as the oligomers bearing an hydroxyl function as end-group, on the active centre depends on their basicity, their possible hydrogen bonds and their concentration. This behaviour has been qualitatively approached by using a 'double' Langmuir–Hinshelwood model, in order to account for the simultaneous coordination of the active centres by more than a Lewis base. Furthermore, using molecular modelling software has evidenced the stability of a system constituted by $Al(OiPr)_3$ complexed by two ε-caprolactone monomers.

These catalytic systems offer interesting potentialities towards the formation in mild conditions of polyesters derived from other lactones such as β-butyrolactone. The effect of other external Lewis bases in order to modulate the acidity of the metal atom, and therefore the nucleophilicity of the oxygen atoms, are now under investigation.

EXPERIMENTAL

Reagents

ε-Caprolactone is distilled under vacuum and dried under argon on molecular sieves 3 Å. Toluene, 1,2-dichloroethane (DCE) and benzyl alcohol are kept under argon on molecular sieves. TEA is diluted with heptane to a 1 M concentration. All the reactions are carried out in a Schlenck-type glassware under argon. All fittings are greaseless.

Preparation of the catalytic system

Porous silica (Grace 432; pore volume: $1.2\,ml\,g^{-1}$; surface area: $320\,m^2\,g^{-1}$, mean particle size ranging from $70\,\mu m$ to 1 mm) is dehydrated at 450°C for 2 h. The content of silanol groups, determined by titration with triethylaluminium, is equal to $1.2\,mmol\,g^{-1}$. Alkyl aluminium (2 ml, 1 M in heptane) is reacted at room temperature on a suspension of 500 mg silica in 50 ml of toluene. After 15 min, the excess of alkylaluminium is removed by washing three times with toluene. The desired amount of alcohol is then added to the medium and allowed to react at 50°C for 2 h. The quantity of alcohol depends on both the expected [ROH]/[Al] ratio and the degree of polymerization.

Polymer synthesis

The polymerizations are carried out in 40 ml of toluene in the Schlenck-type glassware under argon at 50°C. If necessary, 10 ml of DCE are added as reference for the kinetic monitoring.

The quantity of monomer is added according to the expected degree of polymerization and the quantity of alcohol first introduced. At the end of the polymerization, silica is allowed to decant, the solvent is removed by rotary evaporation and the recovered polymers are dried under vacuum.

Gas chromatography

The gas chromatography measurements were performed using an Intersmat IGC 112F with a FID detector. Column: SE 30 on 60/80 Chromosorb (1.80 m long). Temperatures: oven 150°C; detector 180°C; injector: 180°C. N_2 as gas vector. DCE was used as reference.

N.m.r.

^{1}H and ^{13}C n.m.r. were recorded in $CDCl_3$ on a Brücker 250 MHz spectrometer at room temperature. For several studies, benzyl alcohol was used as a chain label for ^{1}H n.m.r. spectroscopy[24]: $\delta C_6H_5{-}CH_2{-}OH = 4.70$ ppm; $\delta C_6H_5{-}CH_2{-}OCO{-} = 5.10$ ppm.

Size exclusion chromatography

S.e.c. measurements were performed on a Waters chromatograph equipped with a PSS Gel mixed B 120 cm column, a refractometer. Average molecular weights were calculated by using polystyrene standards at 30°C in THF with a correction for polycaprolactones according to the Mark–Houwink parameters: $[\eta] = 1.395 \times 10^{-4} M^{0.786}$.

Molecular modelling

We used SYBYL molecular modelling software from TRIPOS[37] and a Silicon Graphics Indigo as hardware. We used the classical TRIPOS force field data for the atoms.

ACKNOWLEDGEMENT

The authors would like to thank Dr J. P. Candy (L.C.O.M.S.-C.N.R.S. Villeurbanne) for molecular modelling with Sybyl software.

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