"In Situ" Formation of Yttrium Alkoxides: A Versatile and Efficient Catalyst for the ROP of ϵ-Caprolactone

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ABSTRACT: [Tris(hexamethyldisilyl)amide] yttrium is a catalyst for the controlled ring-opening polymerization of ϵ-caprolactone when reacted with an excess of alcohol. Up to an alcohol-to-yttrium molar ratio of 50, the chain transfer to the alcohol is quantitative, and the molecular weight of the chains can be predicted from the monomer-to-alcohol molar ratio. At alcohol-to-yttrium ratios higher than 100, the alcohol is quantitatively consumed provided that 1,1,1,3,3,3-hexamethyldisilazane, which is formed as a byproduct, is removed from the reation medium. Depending on the structure of the alcohol, end-functional polyesters can be prepared (e.g., with *N*-pyrrolyl and 3-thienyl end groups). Well-defined block and random copolymers of ϵ-CL with lactides and γ-bromo-ϵ-caprolactone, respectively, have also been synthesized. Compared to aluminum alkoxides, the in situ formed yttrium alkoxides have the advantage of a much faster polymerization kinetics while preserving control.

Introduction

Nowadays, the ultimate goal of the polymer chemist is to tailor macromolecules at will, so making pieces of a construction set available for the design of new polymeric materials.[1,2] Block and graft copolymers are representative examples of well-controlled macromolecular architectures that lead to original materials, e.g., thermoplastic elastomers, polymeric stabilizers, surface and interface modifiers, etc.

In a previous paper, we reported on the efficiency of the $Y[N(SiMe_3)_2]_3$ (**1**)/2-propanol system to control the ring-opening polymerization of ϵ-CL.[3] Aliphatic polyesters with predictable molecular parameters (M_n, end groups) and low polydispersity were prepared as result of fast alkoxide/alcohol exchange and absence of side reactions, such as irreversible chain transfer, chain termination and formation of macrocyclic oligomers. This paper aims at the macromolecular engineering of poly(ϵ-caprolactone) (PCL) by the (**1**)/2-propanol catalyst, particularly at high 2-propanol-to-yttrium molar ratios. Substitution of alcohols containing functional groups or polymerizable groups for 2-propanol is a straightforward way to α-functional PCL, including PCL macromonomers and block copolymers with lactide and γ-functional ϵ-caprolactone. The substantial advantages of this catalyst compared to the largely used Al alkoxides are "in situ" formation from commercially available compounds and a much faster polymerization kinetics while preserving control.

Experimental Section

Materials. ϵ-CL (Janssen Chimica), 2-propanol (Labotec), *n*-butanol (Acros), 1-phenyl-2-propanol (Aldrich), and 1,1,1,3,3,3-hexamethyldisilazane (HMDS; Aldrich) were dried over CaH_2 at room temperature for 48 h and distilled over reduced pressure (10^{-2} mmHg). D,L-Lactide (Boeringher), γ-bromo-ϵ-caprolactone (γBrCL), 2-(3-thienyl)ethanol (Aldrich), and *N*-pyrrolyl-2-ethanol were dried by repeated (three times) azeotropic distillation of toluene just before use. γBrCL and *N*-pyrrolyl-2-ethanol were synthesized as reported elsewhere by Detrembleur et al.[4] and Bidan,[5] respectively. [Tris(hexamethyldisilyl)amide]yttrium, $Y[N(SiMe_3)_2]_3$ (Strem Chemicals), was used as received. Toluene was dried by refluxing over a benzophenone−Na mixture and distilled under nitrogen atmosphere just prior to use. $C_6D_5CD_3$ and C_6D_6 (Aldrich) were dried by stirring over CaH_2 at room temperature for 48 h and distilled under reduced pressure just prior to use. $CDCl_3$ (Aldrich) was used as received.

(Co)polymerization. ϵ-CL was polymerized in toluene under stirring in a round-bottom flask previously flame-dried and purged with nitrogen. The reactor was initially charged with solid [tris(hexamethyldisilyl)amide]yttrium under nitrogen in a glovebox. Toluene and alcohol were added through rubber septa by using flame-dried stainless steel capillaries and syringes. The amount of alcohol was calculated on the basis of the desired alcohol-to-Y molar ratio. After this mixture was stirred for 20 min at 40 °C and before the monomer (or mixture of comonomers in the case of random copolymerization) was added, the temperature was fixed at 20 °C. Polymerization was stopped by addition of an excess (with respect to the alkoxide species) of 1 M HCl solution. After this reaction was stirred for 30 min, the polymer was precipitated by pouring the organic solution in a large excess of heptane, recovered and dried under vacuum up to constant weight. It was then weighed and characterized. In the case of block copolymerization, a small volume of the polymerization medium was withdrawn in order to determine the monomer conversion and to analyze the first block by SEC. The polymer solution was then added with the required amount of the second monomer. Copolymerization was also stopped by HCl.

Characterization. Molecular weight and molecular weight distribution were determined by size exclusion chromatography (SEC) using a HP1090 liquid chromatograph (columns: Plgel 10^2, 10^3, 10^4, 10^5 Å) operating in THF and calibrated with polystyrene standards and the previously reported viscometric relationships.[6]

^{1}H NMR spectra were recorded at 25 °C with Bruker 250 and 400 MHz spectrometers. $CDCl_3$ was used as solvent for the (co)polyester characterization, whereas the active species were analyzed by ^{1}H NMR in either $C_6D_5CD_3$ or C_6D_6.

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Chemical shifts were quoted with respect to tetramethylsilane (TMS). Unreacted 2-propanol was determined during polymerization by ^{1}H NMR spectroscopy with the 400 MHz spectrometer. Indeed, the methyl protons of the unreacted alcohol were observed as a doublet at 1.10 ppm, whereas the doublet characteristic of the same protons attached as an end group [$(CH_3)_2-CH-O$] of the growing chains was observed at 1.20 ppm without overlapping. The relative intensities of these two doublets allowed the percentage of unreacted 2-propanol to be determined. Practically, a 1−2 mL sample of the polymerization medium was hydrolyzed, added to $CDCl_3$, and analyzed.

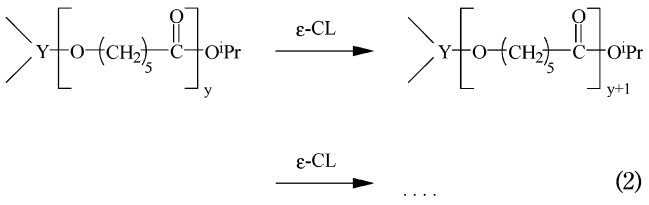
Results and Discussion

The Catalytic System. The homogeneous catalyst under consideration consists of the combination of yttrium amide $Y[N(SiMe_3)_2]_3$ with an excess of 2-propanol. In addition to the active yttrium alkoxide species formed "in situ", 1,1,1,3,3,3-hexamethyldisilazane, $HN(SiMe_3)_2$ (HMDS), is released in the reaction medium. As previously demonstrated,[3] the alkoxide is exchanged with 2-propanol in excess and with hydroxyl end group of growing chains. These exchange reactions compete with monomer propagation, which proceeds through coordination of the monomer on the Lewis metal vacancy followed by insertion into the metal−oxygen bond. The whole mechanism is schematized by eqs 1−3.

Formation of the Active Species

$$Y[N(SiMe_3)_2]_3 + x\,^iPrOH \rightarrow Y(O^iPr)_3 + 3HN(SiMe_3)_2 + (x-3)\,^iPrOH, \quad \text{with } x > 3 \qquad (1)$$

ϵ-CL Polymerization



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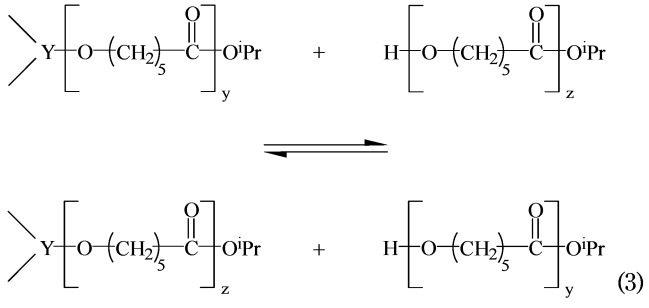
Alkoxide/Alcohol Exchange



(3)

with $z = 0$ or higher.

1,1,1,3,3,3-Hexamethyldisilazane, HMDS, is a well-known silylating agent, commonly used for the protection of primary amines,[7,8] and quantitative silylation of primary and secondary alcohols.[8,9] Reaction with alcohols usually occurs under mild conditions ($T = 50-60$ °C, [HMDS]/[Alcohol] = 2, reaction time depending on the alcohol) and is catalyzed by amines, such as triethylamine, pyridine, ... Therefore, the released HMDS molecules might react with 2-propanol or the hydroxyl end groups in solution, as schematized by eq 4.

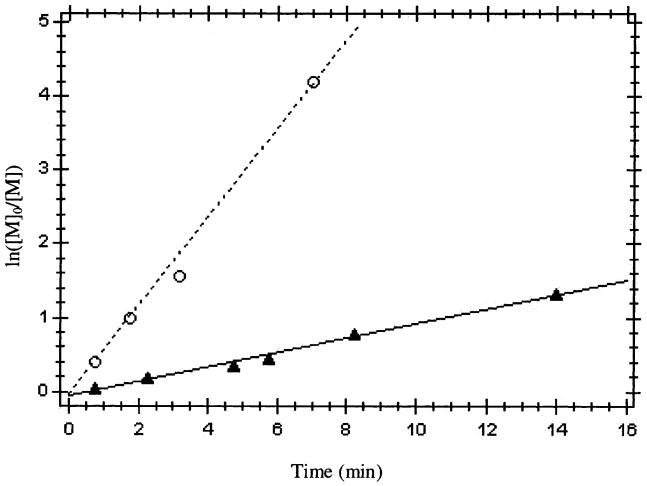


Figure 1. Semilogarithmic plot of ϵ-CL conversion vs time for the ϵ-CL polymerization initiated by the (**1**)/2-propanol system (solvent, toluene; $T = 0$ °C; $[\epsilon\text{-CL}]_0 = 0.5$ M; $[Y]_0 = 0.22$ mM; $[^iPrOH]_0/[Y]_0 = 5$). Key: (▲) in the presence of HDMS; (○) in the absence of HDMS.

$$HN(SiMe_3)_2 + 2\,^iPrOH \rightarrow 2\,^iPrOSiMe_3 + NH_3 \qquad (4)$$

To know whether the HMDS/alcohol reaction takes place under the experimental conditions used in this study, HMDS was added to 2-propanol ([HMDS]/[^{i}PrOH] = 3/20), in toluene at 50 °C, all the chemicals being previously dried. A small amount of *m*-xylene, which is inert toward the reactants, was also added to the solution as an internal standard. The solution composition was indeed analyzed by gas chromatography (GC). Over a period of 25 h, the intensity (with respect to the internal standard) of the GC peaks for HMDS and 2-propanol remained constant indicating that no reaction occurs between HMDS and 2-propanol. Consistently, no additional peak was detected on the chromatograms. These observations were confirmed by ^{1}H NMR analysis. Moreover, an increase in the reaction temperature up to 80 °C, and the addition of NEt_3 to the reaction medium did not change the situation.

Kinetics of the ϵ-CL Polymerization. Polymerization of ϵ-caprolactone initiated by the (**1**)/2-propanol system is very fast.[3] To follow the progress of the ϵ-CL conversion, the kinetics was slown down by decreasing both the polymerization temperature ($T = 0$ °C) and the monomer and initiator concentrations ($[\epsilon\text{-CL}]_0 = 0.5$ M, $[Y]_0 = 0.22$ mM). The initial $[^iPrOH]_0/[Y]_0$ molar ratio was fixed at 5. The monomer conversion was monitored by ^{1}H NMR analysis of samples withdrawn from the reaction mixture and immediately quenched.

Equation 5 is commonly valid to the polymerization of ϵ-CL in solution, e.g., when initiated by aluminum alkoxides[10,11]

$$\ln([M]_0/[M]) = k_{app}t \qquad (5)$$

where k_{app} is the apparent rate constant; $[M]_0$ and $[M]$ are the monomer concentrations at time zero and t, respectively.

Figure 1 shows that eq 5 fits the kinetics of the ϵ-CL polymerization initiated by the (**1**)/2-propanol system in toluene.

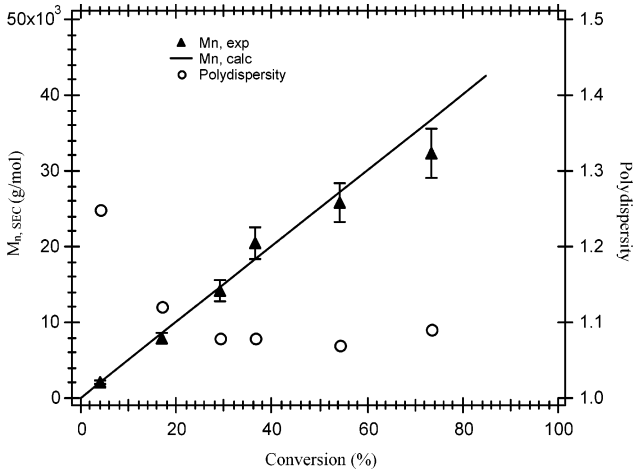


Figure 2. $M_{n,SEC}$ vs monomer conversion for the ϵ-CL polymerization initiated by the (**1**)/2-propanol system (solvent, toluene; $T = 0$ °C; $[\epsilon\text{-CL}]_0 = 0.5$ M; $[Y]_0 = 0.22$ mM; $[^i\text{PrOH}]_0/[Y]_0 = 5$) in the presence of HDMS.

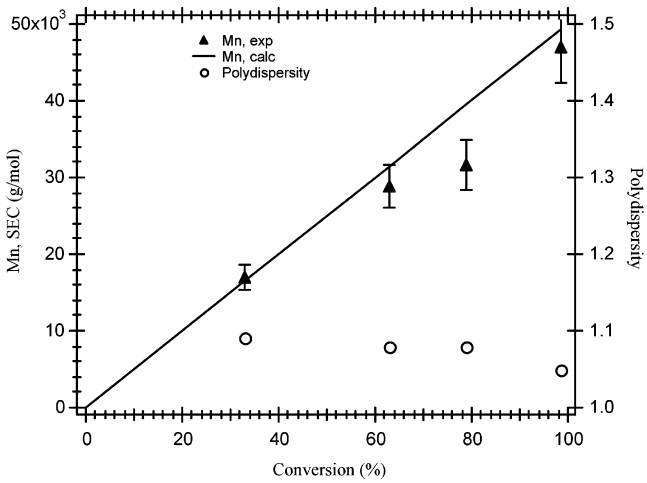


Figure 3. $M_{n,SEC}$ vs monomer conversion for the ϵ-CL polymerization initiated by the (**1**)/2-propanol system (solvent, toluene; $T = 0$ °C; $[\epsilon\text{-CL}]_0 = 0.5$ M; $[Y]_0 = 0.22$ mM; $[^i\text{PrOH}]_0/[Y]_0 = 5$) in the absence of HDMS.

The linear time dependence of $\ln([M]_0/[M])$ demonstrates that the polymerization is first order in monomer under the conditions used in this study. This linear relationship is thought to persist at high ϵ-CL conversion (>85%). Indeed, no data are available in this range, because the high viscosity of the polymerization medium prevents samples from being picked out. The value of k_{app}, i.e., the slope of the straight line, has been calculated by linear regression (Figure 1) and found to be 0.091 min^{-1}.

Moreover, no induction period is observed, which indicates that no substantial rearrangement of the species is required before the polymerization starts. Thus, the alcohol molecules in excess are immediately exchanged with the alkoxides, as confirmed by the complete disappearance of 2-propanol from the very first stage of the polymerization (no ^{1}H NMR doublet characteristic of the methyl group at 1.2 ppm is recorded after a 1 min reaction). This result completely contrasts with observations reported by Stevels et al.,[12] who initiated ROP of ϵ-caprolactone in dichloromethane by the commercially available yttrium oxoisopropoxide cluster in the presence of 2-propanol. In this case, the polymerization is initially very slow and becomes faster with time. A similar inhibiting effect of the alcohol was reported in the case of aluminum alkoxide initiators.[13,14] The explanation is that the alcohol molecules reversibly coordinate to the active species and form dormant species. However, the alcohol molecules are converted into alkoxides by exchange reaction, and the oligomeric poly(ϵ-CL) chains derived from them are in turn transformed into hydroxyl-terminated chains. These end groups engage themselves in intra- and/or intermolecular hydrogen bonding with the ester groups of the polyester chains at the expense of complexation with the growing species. The monomer molecules can then access the active species without suffering from competition, which increases the polymerization rate.[13] Clustering of the commercially available yttrium alkoxide is the main reason for the slower kinetics compared to the nonassociated alkoxide formed in situ in this study.

As shown in Figure 2, the experimental number-average molecular weight measured by SEC increases linearly with the monomer conversion in close agreement with the calculated values, which indicates that propagation and fast exchange reactions are operative all along the polymerization. The polydispersity rapidly decreases as the monomer conversion increases, and finally reaches small values in the 1.05−1.1 range. The size exclusion chromatograms are monomodal and quite symmetrical. All these observations confirm that no intramolecular and/or intermolecular transesterification reactions occur during the polymerization process.

The addition of an equimolar amount of a Lewis base, such as pyridine and picoline to aluminum alkoxide, increases the ϵ-CL polymerization rate.[6,15] An excess of Lewis base has, however, a detrimental effect on the polymerization rate.[10] Because hexamethyldisilazane (HMDS), which is formed in situ simultaneously with a yttrium alkoxide species (eq 1), is a Lewis base, it is interesting to know whether it interferes with the polymerization rate. For this purpose, the polymerization of ϵ-CL was carried out in toluene under the same conditions as before ($T = 0$ °C, $[Y]_0 = 0.22$ mM, $[^i\text{PrOH}]_0/[Y]_0 = 5$, $[\epsilon\text{-CL}]_0 = 0.5$ M), except for HMDS that was eliminated. Actually, the yttrium amide was reacted with an excess of 2-propanol in toluene. After 20 min at 40 °C, HMDS, toluene, and unreacted 2-propanol were eliminated under vacuum. The solid residue was dissolved in toluene and added successively with the required amounts of 2-propanol and ϵ-CL at the polymerization temperature. Figure 1 compares the kinetic plots recorded in the presence and in the absence of HMDS, respectively. In both the cases, the $\ln([M]_0/[M])$ vs reaction time relationship is linear up to very high ϵ-CL conversion (>98%) and is thus first-order in monomer. However, the 3 equiv of HMDS formed per Y have a detrimental effect on the polymerization rate. From the slope of the curves in Figure 1, the apparent rate constant k_{app} is increased by a factor of 6.5 when $HN(SiMe_3)_2$ is removed from the medium ($k_{app} = 0.596$ min^{-1}). This observation is comparable to that one reported when an excess of pyridine was added to $Al(O^iPr)_3$ in the polymerization of ϵ-CL. Thus, an excess of Lewis base no longer activates the metal alkoxide but rather prevents it from being accessible to the monomer. Figures 2 and 3 show that the number-average molecular weight determined by SEC increases linearly with conversion independently of the formation of HMDS. Therefore, the (**1**)/2-propanol system allows PCL of high

Table 1. Effect of the $[^i\text{PrOH}]_0/[Y]_0$ Molar Ratio on the ϵ-CL Polymerization Initiated by the [Tris(hexamethyldisilyl)amide]yttrium/2-Propanol Catalytic System (Toluene, $T = 20$ °C, $[\epsilon\text{-CL}]_0 = 1$ M)

entry	$[^i\text{PrOH}]_0/[Y]_0$	reacn time (min)	convn[a] (%)	$M_{n,calcd}$[b] (10^3 g/mol)	$M_{n,RMN}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	M_w/M_n	α[c] (%)
1	30	3	100	2	2.1	2.15	1.25	0
2[d]	50	3	99	2	2.3	2.1	1.25	0
3	100	12	100	2.3	2.6	2.3	1.2	15
4[e]	100	13	100	2.4	2.4	1.8	1.3	18
5[f]	100	16	87	1.8	2.9	2.7	1.15	4
6	150	10	75	2	2.3	1.6	1.3	25

[a] Determined by ^{1}H NMR. [b] $M_{n,calcd} = [\epsilon\text{-CL}]_0 \times 114.14 \times \text{convn}/(1 - \alpha/100) \times [^i\text{PrOH}]_0$. [c] Unreacted 2-propanol measured by ^{1}H NMR (see text). [d] $[\epsilon\text{-CL}]_0 = 0.75$ M. [e] Reaction carried out at 0 °C. [f] Reaction carried out without HMDS at 0 °C.

molecular weight to be synthesized in a well-controlled manner.

The role of 2-propanol as chain transfer agent was recently reported in ROP of ϵ-caprolactone initiated by the commercially available $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$ yttrium oxo-isopropoxide cluster.[12] The number-average molecular weight of PCL was in agreement with the initial concentrations of 2-propanol and 2-propoxide functions of $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$. The polymer was also of a low polydispersity. However, only a small excess of 2-propanol ($[^i\text{PrOH}]_0/[Y_5(\mu\text{-O})(O^i\text{Pr})_{13}]_0 < 20$) participated to the polymerization, whose the kinetics was unfavorably influenced by increased alcohol concentration. Although the polymerization was complete after ca. 1 min, at a monomer-to-initiator molar ratio of 150 in the absence of alcohol, the ϵ-CL conversion was limited to 16% after 30 min when 18 equiv of ^{i}PrOH (with respect to $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$) were added, all the other experimental conditions being the same. In the system under consideration, the 2-propanol-to-yttrium molar ratio has been increased up to 150 (Table 1). α is the percentage of 2-propanol left unreacted when the polymerization is stopped. It is determined by ^{1}H NMR analysis of the crude polymerization medium after the hydrolytic deactivation of the yttrium alkoxide propagating species (see the Experimental Section). At least up to a 50-fold molar excess with respect to Y, all of the 2-propanol molecules contribute to the polymerization of ϵ-CL in toluene at room temperature (Table 1, entries 1 and 2), and the monomer conversion is quantitative after only 3 min of polymerization. Moreover, the agreement between the experimental M_n's and the monomer-to-alcohol molar ratio (at complete monomer conversion) is excellent. This very high activity is in sharp contrast to the very deleterious effect of 2-propanol on the kinetics of the ϵ-CL polymerization initiated by the $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$ cluster.[12] This difference in the polymerization kinetics more likely results from differences in the structure of the active species in solution, as shown by ^{1}H NMR analysis in $C_6D_5CD_3$ and C_6D_6.[3] When the initial alcohol-to-Y molar ratio is 100 and higher (Table 1, entries 3−6), part of the alcohol molecules ($15 \leq \alpha \leq 25\%$) do not contribute to the complete ϵ-CL conversion. Similar observation was reported for the ϵ-CL polymerization initiated by aluminum isopropoxide.[13,16] Polymerization at lower temperature, i.e., 0 °C instead of 20 °C (entry 4), has only a slight influence on α and the PCL polydispersity. Figure 4 illustrates the time dependence of α when the ^{i}PrOH/Y molar ratio is 100. Surprisingly, after a rapid drop within the two first minutes of polymerization, α decreases very slowly and tends to 18% at complete monomer conversion. So, it seems that the metal center becomes rapidly "encaged" by growing chains, in such a way that only the hydroxyl end group of these chains can participate to the alcohol-yttrium alkoxide exchange excluding the not yet converted 2-propanol.

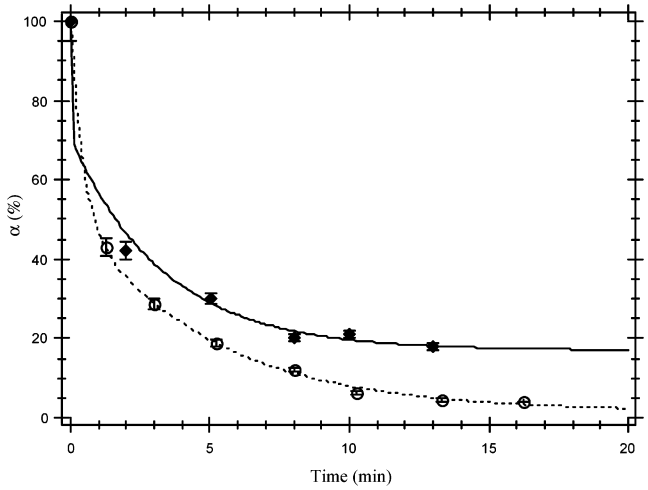


Figure 4. Reaction time dependence of α for the ϵ-CL polymerization initiated by the $Y[N(SiMe_3)_2]_3$/2-propanol catalyst in the presence (◆) and in the absence (○) of HMDS (solvent, toluene; $[\epsilon\text{-CL}]_0 = 1$ M; $T = 0$ °C; $[^i\text{PrOH}]_0/[Y]_0 = 100$).

To know whether the HMDS molecules have an effect on this phenomenon, the same experiment has been repeated in the absence of amine (Table 1, entry 5). HDMS was removed from the reaction mixture just after formation of the active species as previously mentioned. In this case, α decreases regularly all along the polymerization at a rate which decreases with the effective alcohol concentration (Figure 4). The alcohol consumption is more rapid and more complete than in the presence of 3 equiv of HMDS/equiv of Y. For example, at a monomer conversion of ca. 90%, only 4% of the initial alcohol molecules are left unreacted (although the molecular weight expected at complete monomer conversion is very low; $M_n = 2000$), which indicates that competition between monomer insertion and alcohol/alkoxide exchange is in favor of the latter process. Figure 5 shows that the ϵ-CL polymerization is consistently slowed down when carried out in the absence of HMDS. Clearly all the alcohol molecules can initiate polymer chains of a high enough molecular weight.

Small amounts of PCL have been sampled all along the polymerization and characterized by SEC and ^{1}H NMR. In the absence of HMDS, the experimental molecular weight slightly exceeds the value expected from initial $[\epsilon\text{-CL}]_0/[^i\text{PrOH}]_0$ ratio, α, and monomer conversion (Table 1). SEC profiles are monomodal but show a very small tailing at high elution times (particularly for PCL prepared in the presence of $HN(SiMe_3)_2$)), which is characteristic of a delayed initiation. Moreover, molecular weight distribution is very narrow, and

Table 2. Polymerization of ϵ-Caprolactone Promoted by the Alcohol/[Tris(hexamethyldisilyl)amide]yttrium Catalytic System (Toluene, T = 20 °C, $[\epsilon\text{-CL}]_0$ = 1 M)

entry	alcohol ROH	$[ROH]_0/[Y]_0$	reacn time (min)	convn[b] (%)	$M_{n,calcd}$[c] (10^3 g/mol)	$M_{n,NMR}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	M_w/M_n
1	methanol	8	3.5	99	5	4.8	5.1	1.2
2	*n*-butanol	7	1.5	100	2.5	2.5	2.5	1.2
3[a]	1-phenyl-2-propanol	10	3	100	4.9	4.5	4.1	1.3
4	2-(3-thienyl)ethanol	7	3.5	100	3	3.4	3.7	1.15
5	N-pyrrolyl-2-ethanol	8	3.5	100	3	3.6	3.3	1.15

[a] $[\epsilon\text{-CL}]_0$ = 0.75 M. [b] Determined by gravimetric measurements. [c] $M_{n,calcd} = [\epsilon\text{-CL}]_0 \times 114.14 \times convn/[ROH]_0$

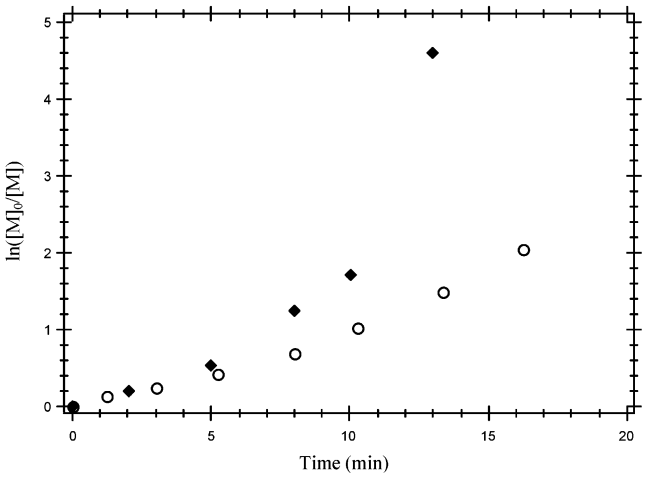


Figure 5. Ln($[M]_0/[M]$) vs reaction time for the ϵ-CL polymerization initiated by the $Y[N(SiMe_3)_2]_3$/2-propanol catalyst in the presence (◆) and in the absence (○) of HMDS (solvent, toluene; $[\epsilon\text{-CL}]_0$ = 1 M; T = 0 °C; $[^iPrOH]_0/[Y]_0$ = 100).

polydispersity is smaller in the absence of HMDS, particularly at high monomer conversion (1.15 instead of 1.3, respectively). All these results are in agreement with the time dependence of α (Figure 4).

As a rule, HMDS acts as Lewis base, which competes with the alcohol and the monomer for coordination to the metal. Because of a stronger coordination, the amine is a brake for the alcohol/alkoxide exchange reaction. However, when used in large excess, the coordination of the alcohol to the yttrium alkoxide is thermodynamically favored and the amine effect is less pronounced, in agreement with the sharp decrease in α at the very first stage of the ϵ-CL polymerization (Figure 4).

Control of the ϵ End Group of PCL. Poly(ϵ-caprolactone) chains formed by the $Y[N(SiMe_3)_2]_3$ (**1**)/2-propanol catalytic system are systematically capped by an isopropoxy ester $(CH_3)_2CHOC(O)-$ end group in direct relation to the structure of the alcohol used. So, changing the alcohol is a straightforward way to modify the α end group and to contribute to the macromolecular engineering of PCL, as was reported in the case of aluminum alkoxides.[4,17,18] Quite recently, a similar approach was reported for the ROP of L-lactide by using the sterically crowded tris(2,6-di-*tert*-butylphenoxy)-yttrium precursor.[19] This Y derivative is indeed basically inactive in the ROP of lactide, as result of the limited access of the metal−oxygen bond. It is however easily converted into active yttrium alkoxide by substitution of the sterically hindered phenolate by a variety of alcohols, such as ethylene glycol and *N*,*N*-dimethyl-2-hydroxyethylamine (Me_2NEtOH). With poly(ethylene glycol) as a co-initiator, a PLA−PEO−PLA triblock copolymer was prepared.

Poly(ϵ-caprolactone) capped by different end groups have been prepared in toluene by combining **1** with excess of various alcohols (Table 2, entries 1−4). The structure of these alcohols can influence the reactivity of the initiating alkoxide species and the kinetics of the exchange reaction. This aspect is however out of the scope of this paper, which aims at highlighting the versatility of the catalytic system under consideration. Table 2 shows that the **1**/ROH catalyst remains highly active whatever the alcohol used. In all the cases, the monomer conversion is quantitative within very short period of time.

The α end group of PCL has been analyzed by ^1H NMR spectroscopy. The methyl protons of the end group derived from methanol and *n*-butanol are observed as a singlet at 1.7 ppm and a triplet at 0.95 ppm, respectively. Figures 6−8 show the ^1H NMR spectra from PCL co-initiated by 1-phenyl-2-propanol, 2-(3-thienyl)ethanol, and *N*-pyrrolyl-2-ethanol, respectively. In addition to the hydroxyl end group formed by hydrolysis of the growing yttrium alkoxide species, the α end group has the structure expected from the alcohol used as precursor of the active species. The number-average molecular weight has been calculated from the relative intensity of the methylene protons of the polymer chains, e.g., $-CH_2-O-C(O)-$, and the protons characteristic of the α end groups ($M_{n,NMR}$). It is in very close agreement with the theoretical value ($M_{n,calcd}$) calculated from the initial monomer-to-alcohol molar ratio and the monomer conversion (Table 2), which confirms that all the alcohol molecules initiate ROP of ϵ-CL and participate in a fast exchange with the alkoxides compared to chain propagation. Moreover, the molecular weight distribution is monomodal, symmetric, and narrow (Table 2).

When 1-phenyl-2-propanol is the precursor of the active species (Table 2, entry 3), a small tailing is observed on the low molecular weight side, which accounts for a slightly higher polydispersity and a not as good agreement between calculated and experimental molecular weights. It must however be noted that all the chains are end-capped by a phenyl group, because the same SEC chromatogram is reported by dual refractive index and UV (at 254 nm) detectors. Therefore, formation of cyclic oligomers by intramolecular transesterification can be precluded. Interestingly enough, whenever ϵ-CL is polymerized in the presence of *N*-pyrrolylethanol or 2-(3-thienyl)ethanol, PCL macromonomers are formed because the pyrrolyl and thienyl end groups are polymerizable by oxidation. These macromonomers have been successfully copolymerized with pyrrole and thiophene by electropolymerization, respectively, as will be reported in a forthcoming paper.

Synthesis of Block Copolymers. The successful resumption of the ϵ-CL polymerization proved that the chains initiated by the $Y[N(SiMe_3)_2]_3$/2-propanol catalytic system preserve their activity at the end of the process.[3] Therefore, the addition of a second monomer is an easy way to prepare block copolymers. The sequential polymerization of ϵ-CL and comonomer poly-

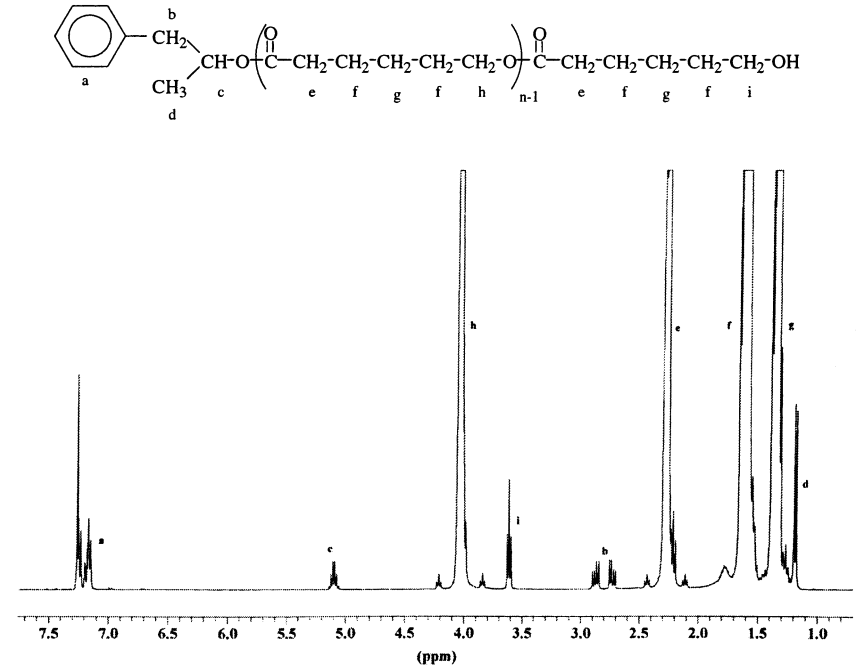


Figure 6. ^{1}H NMR spectrum in $CDCl_3$ for PCL prepared by the [tris(hexamethyldisilyl)amide]yttrium (**1**)/1-phenyl-2-propanol catalytic system in toluene at 20 °C (Table 2, entry 3).

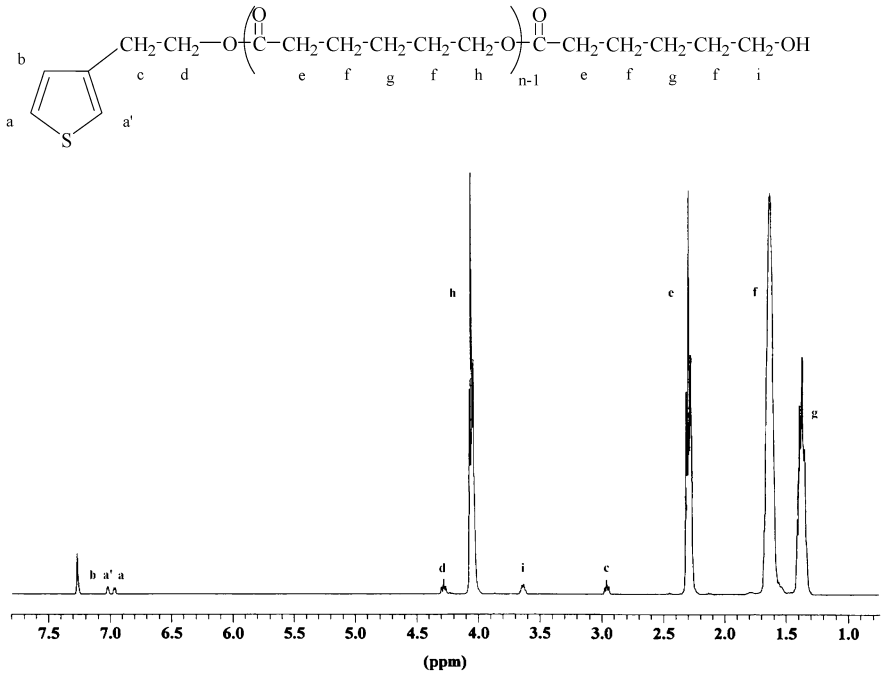


Figure 7. ^{1}H NMR spectrum in $CDCl_3$ for PCL prepared by the [tris(hexamethyldisilyl)amide]yttrium (**1**)/2-(3-thienyl)ethanol catalytic system in toluene at 20 °C (Table 2, entry 4).

merizable by the same mechanism has been initiated by the $Y[N(SiMe_3)_2]_3$/2-propanol catalyst. Table 3 reports on the complete polymerization of ϵ-CL, followed by the addition of D,L-lactide (D,L-LA) (entry 1) and γ-bromo-ϵ-caprolactone (γBrCL) (entry 2), respectively. In both the cases, polymerization of the second monomer has been stopped before complete conversion. SEC analysis shows that the elution peak of PCL is shifted toward higher molecular weight as result of copolymerization and that the molecular weight distribution of the copolymer is monomodal and at least as narrow as that one of the first block (Table 3). ^{1}H NMR analysis of the samples collected after hydrolysis of the growing species confirm that the signal for the $-CH_2OH$ end groups of PCL chains (δ = 3.6 ppm) have disappeared at the benefit of a resonance assigned to the $-CH(CH_3)OH$ proton of the lactide end group (δ = 4.3 ppm) in the case of the PCL-*b*-P(D,L-LA) diblock and the $-CH(Br)CH_2CH_2$-OH proton of the end group of the PCL-*b*-γBrCL diblock (δ = 3.8 ppm), respectively. Therefore, all the polymer chains formed in the first polymerization step have initiated the polyaddition of the second comonomer. Moreover, the experimental molecular weight determined for each block by ^{1}H NMR is in agreement with the value expected at the actual monomer conversion.

The poly(γBrCL-*b*-ϵ-CL) diblock copolymer has also been prepared by reversing the addition order of the comonomers (Table 3, entry 3). As observed for the ϵ-CL

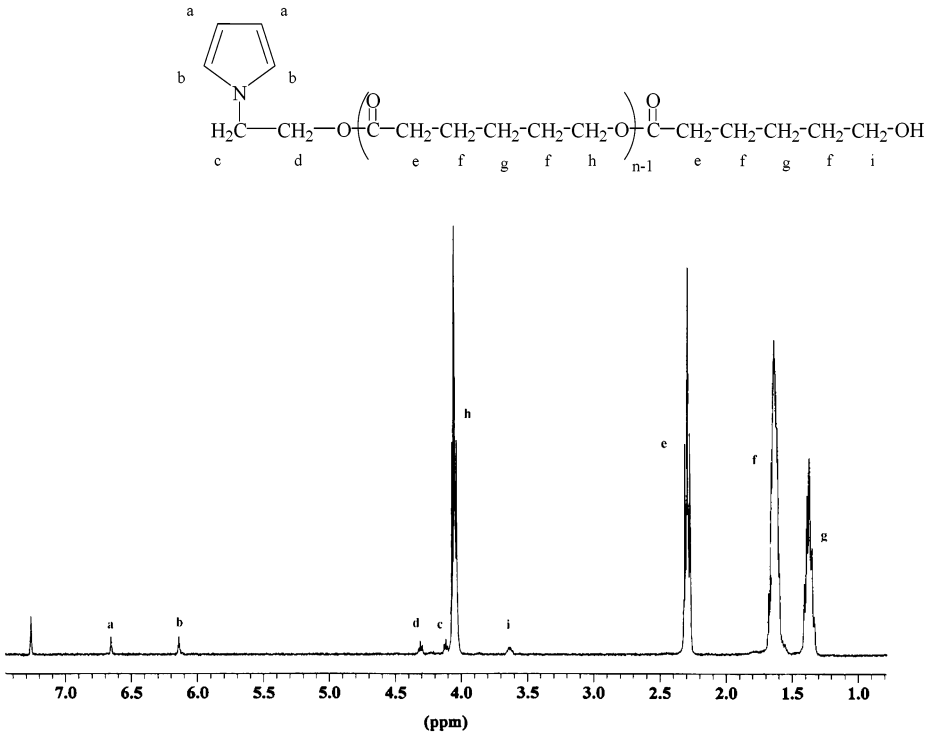


Figure 8. ^{1}H NMR spectrum in $CDCl_3$ for PCL prepared by the [tris(hexamethyldisilyl)amide]yttrium (**1**)/*N*-pyrrolylethanol catalytic system in toluene at 20 °C (Table 2, entry 5).

Table 3. Block Copolymerization of ϵ-Caprolactone in Toluene Initiated by the 2-Propanol/ [Tris(hexamethyldisilyl)amide]yttrium Catalytic System (Toluene, T = 20 °C, $[^i\text{PrOH}]_0/[\text{Y}]_0$ = 10)

	1st block			2nd block			$M_{n,calcd}$ (0.10^3 g/mol)		$M_{n,RMN}$ (0.10^3 g/mol)		M_w/M_n	
entry	M_1	t[a] (min)	Q_1[b] (%)	M_2	t[a] (min)	Q_2[b] (%)	1st block[c]	copolym[d]	1st block	copolym	1st block	copolym
1	ϵ-CL	1.6	100	D,L-LA	2	25	10	10.5	9.1	9.7	1.1	1.1
2	ϵ-CL	3.5	100	γ-BrCL	10	79	5.2	9.3	5.5	9.8	1.25	1.2
3	γ-BrCL	6.5	100	ϵ-CL	3	100	2	8.2	1.8	8.0	1.25	1.1

[a] Polymerization time. [b] Conversion determined by weighing the polymer formed. [c] $M_{n,calcd} = [M_1]_0 \times Fw_{M_1} \times Q_1/[^i\text{PrOH}]_0$ where Q_i is the conversion of monomer i and Fw_{M_i} the molecular weight of the M_i repeating unit. [d] $M_{n,calcd} = ([M_1]_0 \times Fw_{M_1} \times Q_1 + [M_2]_0 \times Fw_{M_2} \times Q_2)/[^i\text{PrOH}]_0$.

homopolymerization, γBrCL is polymerized quantitatively within a short period of time, i.e., a few minutes (Table 3). There is again a close agreement between the theoretical molecular weight, based on the initial monomer-to-2-propanol molar ratio and the monomer conversion, and the experimental value (^{1}H NMR analysis), consistent with a well-controlled process. Molecular weight distribution of the poly(γBrCL) block is monomodal and narrow, which indicates fast initiation and fast alcohol/alkoxide exchange with respect to chain propagation. This molecular weight distribution is actually narrower than that one reported for poly(γBrCL) of comparable molecular weight prepared in solution with $Al(O^iPr)_3$ as the initiator (M_w/M_n = 1.25 instead of 1.35).[4] The addition of ϵ-CL to "living" brominated polyester chains results in a well-defined poly(γBrCL-*b*-ϵ-CL) diblock copolymer, as confirmed by SEC analysis and ^{1}H NMR (Table 3). Figure 9 compares the SEC traces for the first poly(PγBrCL) block and the poly(γBrCL-*b*-ϵ-CL) diblock. The elution peak for the macroinitiator is clearly shifted toward higher molecular weight, and no trace of unreacted poly(PγBrCL) homopolymer can be detected. Molecular weight distribution of the copolymer is very narrow and quite symmetrical.

Random copolymerization of γ-bromo-ϵ-caprolactone and ϵ-CL has been initiated by the $Y[N(SiMe_3)_2]_3$/2-propanol catalyst in toluene at 20 °C ($[^i\text{PrOH}]_0/[\text{Y}]$ = 10). The apparent molecular weight (SEC analysis; PCL calibration) agrees with the value calculated from the monomer-to-initiator molar ratio (7.7×10^3 vs 7.8×10^3), and the molecular weight distribution is very narrow (M_w/M_n = 1.15). The molar fraction of the comonomers in the copolymer ($F_{\gamma BrCL}$ = 0.26 as measured by ^{1}H NMR) fits the comonomer feed composition ($f_{\gamma BrCL}$ = 0.24), consistent with the quantitative conversion. Random copolymerization of ϵ-CL and γBrCL is thus also well-controlled. Similar results were reported with $Al(O^iPr)_3$ as an initiator.[4] The superiority of the Y-based catalyst over the Al counterpart has to be found in a higher reactivity. Quantitative monomer conversion is observed within minutes compared to hours in the case of the Al initiator.

Because the Y-based catalyst proposed in this work allows for the well-controlled polymerization of γ-substituted ϵ-CL, the way is paved for the preparation of functional polyesters. Indeed, the alkyl bromide can be converted into unsaturation and ammonium cation by dehydrohalogenation and quaternization, respectively.[17] Double bonds in the polyester chains can make the polymer cross-linkable, and combination of double bonds and cationic groups can lead to degradable hydrogels. Quaternization of poly(CL-*b*-γBrCL) copolymer is a possible way to prepare potentially degradable surfactants.

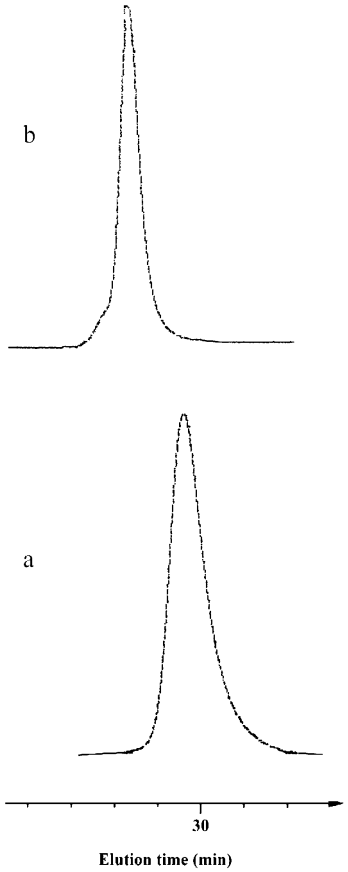


Figure 9. Size exclusion chromatograms for the PγBrCL precursor and the poly(γBrCL)-*b*-PCL diblock copolymer: (a) poly(γBrCL) macroinitiator, $M_n = 2000$, $M_w/M_n = 1.25$; (b) diblock $M_n = 2000/8200$, $M_w/M_n = 1.1$ (Table 3, entry 3).

Conclusions

The versatility of the $Y[N(SiMe_3)_2]_3$/2-propanol catalytic system has been illustrated. The ϵ-CL polymerization is well-controlled, even at high initial alcohol-to-yttrium molar ratio. Up-to-a ratio of 50, the chain transfer to the alcohol is quantitative, and the molecular weight of the polymer chains can be predicted from the monomer-to-alcohol molar ratio. Because part of the actual initiator can be replaced by alcohol molecules without sacrificing the control of the chain length, the system has a catalytic attribute, which allows the amount of metal residues to be substantially decreased. At initial alcohol-to-yttrium molar ratio higher than 100, the alcohol consumption is quantitative provided that HMDS formed as a byproduct is removed from the reaction medium. This secondary amine acts as a Lewis base, which competes with both the alcohol and the monomer for coordination to the metal. As result, the extent of the alcohol/alkoxide exchange reaction is restricted.

Depending on the structure of the alcohol used, end-functional polymers can be prepared, including macromonomers. Synthesis of well-defined block and random copolymers of ϵ-CL with lactides or other lactones, such as γ-bromo-ϵ-caprolactone (γBrCL) has also been reported. In all of the cases, the $Y[N(SiMe_3)_2]_3$/alcohol catalyst is highly reactive, such that the macromolecular engineering of the aliphatic polyesters reported in the case of aluminum alkoxides can be extended to yttrium alkoxides although with a faster kinetics.

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