Controlled Ring-Opening Polymerization of ϵ-Caprolactone Promoted by "in Situ" Formed Yttrium Alkoxides

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ABSTRACT: The ring-opening polymerization of ϵ-caprolactone has been initiated by [tris(hexamethyldisilyl)amide]yttrium in the presence of an excess of 2-propanol. This initiating system is very active even at high alcohol-to-Y molar ratio. Polymers with controlled molecular parameters (M_n, end groups) and low dispersity are formed as result of fast alkoxide/alcohol exchange. At molar excess of 2-propanol higher than 100, this exchange is no longer quantitative. The in situ formed active species involved in this new initiating system are different from those ones present in the commercial yttrium oxo-isopropoxide $Y_5(\mu\text{-O})(O^iPr)_{13}$ cluster. Evidence is provided by ^1H NMR spectroscopy.

Introduction

Poly(ϵ-caprolactone) (PCL) is one of the most attractive aliphatic polyesters, because of widely recognized biodegradability[1] and unique compatibility with large range of polymers, including poly(vinyl chloride) (PVC), poly(styrene-*co*-acrylonitrile), nitrocellulose, poly(epichlorohydrin), and bisphenol A polycarbonate.[2]

For the past two decades, great attention was paid to the controlled polymerization of ϵ-caprolactone (ϵ-CL). In contrast to the anionic polymerization initiated by for example alkali metal alkoxides, which is perturbed by intra- and intermolecular transesterification reactions,[3,4] the use of less reactive aluminum alkoxides is an efficient way to impart "livingness" to the ring-opening polymerization (ROP) of ϵ-CL.[5−7] Well-defined PCL (containing) chains have accordingly been made available, which include ω- and α,ω-functional PCL, PCL macromonomers, and PCL containing block, random, and graft copolymers. As a result of the reduced ionicity of the "O−Al" bond of the aluminum alkoxide initiators, the polymerization mechanism is no longer anionic, but it fits a "coordination-insertion" process, which is favorably conducted in solvents of a low polarity. In these solvents aluminum alkoxides however form aggregates, whose size controls the activity.[8]

Quite recently, ROP of ϵ-CL and other lactones, including lactides, has been successfully initiated by rare earth alkoxides.[9−11] These compounds show exceptionally high reactivity, and some of them give rise to "living" polyaddition.[12,13] Yttrium oxo-isopropoxide has been more extensively studied, being commercially available. It forms $Y_5(\mu\text{-O})(O^iPr)_{13}$ clusters, in which five yttrium atoms are linked to a single central oxygen atom. This clustering is responsible for sterically crowded polymerization sites and more complex kinetic behavior.[12,14] Moreover, transesterification reactions occur rapidly when the monomer conversion is close to completion, which results in the broadening of the molecular weight distribution.

To overcome these drawbacks, Stevels et al. have initiated the ϵ-CL polymerization by yttrium isopropoxide prepared by reaction of bulky tris(2,6-di-*tert*-butylphenoxy)yttrium with 3 equiv of 2-propanol.[14] A well-defined kinetics is then observed, with first-order dependence on both the monomer and the initiator concentrations. Shen et al.[15,16] have also reported on the living polymerization of ϵ-CL initiated by lanthanide isopropoxides, such as isopropoxy rare earth diethyl acetoacetate and donor adducts of neodynium isopropoxide. The bulky coordinate groups of the metal prevent polymer chains from having access to the actives sites, which is detrimental to the occurrence of transesterification reactions. Block copolymerization of ϵ-CL with either trimethylene carbonate (TMC) or lactide has also been carried out by the same authors. However, compared with commercially available yttrium oxo-isopropoxide, all the other mentioned rare earth alkoxides require more or less time-consuming synthesis.[14−16]

This paper deals with the solution polymerization of ϵ-CL initiated by a novel system based on yttrium isopropoxide. The alkoxide is actually formed "in situ" by the fast reaction of the commercially available [tris(hexamethyldisilyl)amide]yttrium (**1**) with excess of 2-propanol. A rapid exchange between the formed Y alkoxide and the alcohol allows the average number of active initiation sites to be controlled, while maintaining the yttrium content low and preventing the alkoxide from clustering. To our best knowledge, these characteristic features have not been reported yet, as far as rare earth initiators are concerned.

Experimental Section

Materials. ϵ-CL (Janssen Chimica) and 2-propanol (Labotec) were dried over CaH_2 at room temperature for 48 h and distilled under reduced pressure (10^{-2} mmHg). [Tris(hexamethyldisilyl)amide]yttrium, $Y[N(SiMe_3)_2]_3$ (Strem Chemicals), was used as received. Toluene was dried by refluxing over benzophenone−Na complex 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 for 48 h and distilled under reduced pressure just prior to use. $CDCl_3$ (Aldrich) was used as received.

Polymerization Procedure. ϵ-CL was polymerized in toluene under stirring in a round-bottom flask previously

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Table 1. Polymerization of ϵ-Caprolactone Promoted by [Tris(hexamethyldisilyl)amide]yttrium (1) in the Presence of 2-Propanol in Toluene ($[^iPrOH]_0/[Y]_0 = 10$, $[\epsilon\text{-CL}]_0 = 1$ M)

entry	T (°C)	react. time (min)	conv (%)	$M_{n,calc}$ (g/mol)[b]	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n
1	20	1	99	2000	2300	2400	1.2
2	20	1	100	5000	4500	5000	1.2
3	20	1.6	100	10000		11000	1.15
4	40	3	100	20000		22000	1.1
5[a]	20	1.6	97	9700		10000	1.1
6	40	60	100	2000	2100	2200	1.55

[a] $HN(SiMe_3)_2$ removed under vacuum prior to ϵ-CL polymerization. [b] $M_{n,calc} = [\epsilon\text{-CL}]_0 \times 114.14 \times Q/[^iPrOH]_0$.

flame-dried and purged with nitrogen. The reactor was initially charged with solid [tris(hexamethyldisilyl)amide]yttrium under nitrogen atmosphere in a glovebox. Toluene and 2-propanol (4% solution in toluene) were added through rubber septa by using flame-dried stainless steel capillaries and syringes. The amount of 2-propanol was calculated on the basis of the desired alcohol-to-Y molar ratio. After stirring for 20 min at 40 °C, ϵ-CL was added with a syringe. Polymerization reaction was stopped by adding an excess (with respect to the alkoxide species) of 1 M HCl solution, and the catalytic residues were extracted with 0.1 M EDTA aqueous solution followed by water up to neutral pH. The polymer was then precipitated by pouring the organic solution in an excess of heptane, recovered, and dried under vacuum up to constant weight.

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. The universal calibration method was used based on the previously reported viscosimetric relationships.[17]

The ^{1}H NMR spectrum was recorded at 25 °C with Bruker 250 and 400 MHz spectrometers. $CDCl_3$ was used as solvent for the polyester characterization whereas NMR studies on the active species were carried out in either $C_6D_5CD_3$ or C_6D_6. Chemical shifts are quoted relative to tetramethylsilane (TMS).

Results and Discussion

As mentioned in the Introduction, the catalyst system investigated in this study for the ring-opening polymerization of ϵ-caprolactone results from the reaction of the commercially available [tris(hexamethyldisilyl)amide]yttrium, $Y[N(SiMe_3)_2]_3$ (**1**), with excess of 2-propanol. Yttrium−nitrogen bonds are known for reactivity toward protic compounds in acid−base type reaction.[18] Therefore, the amide ligands of **1** rapidly react with the alcohol molecules and release "in situ" yttrium alkoxides, which are well-known active species for the polymerization of lactones, lactides, and oxiranes.[14,19,20] For each yttrium isopropoxide molecule formed, three $HN(SiMe_3)_2$ molecules are also released in toluene solution. Compared to rare earth initiators previously reported in the open scientific literature,[14−16] the implementation of the present system is straightforward, since time-consuming synthesis is not required.

For the sake of comparison, yttrium triamide **1** has been first used to initiate the polymerization of ϵ-CL in toluene at 25 °C. This derivative, which is nonassociated in toluene solution,[21] shows a high activity. Indeed, the ϵ-CL conversion is complete within less than 5 min, in good agreement with the observations reported by Agarwal et al.[22] in the case of ROP of ϵ-CL intiated by $Sm[N(SiMe_3)_2]_3$ and $(Sm[N(SiMe_3)_2]_2(\epsilon\text{-CL})THF)_2$. However, the polymerization is completely out of control as attested by broad molecular weight distribution and number-average molecular weight much higher than the value calculated on the assumption that each amide ligand initiates the polymerization ($M_{n,calc} = 1500$ g/mol; $M_{n,SEC} = 8000$ g/mol; $M_w/M_n = 3.1$). Furthermore, no characteristic end group could be detected in the recorded ^{1}H NMR spectra.

ϵ-CL has then been polymerized by [tris(hexamethyldisilyl)amide]yttrium (**1**) previously added with 2-propanol, with an initial alcohol-to-Y molar ratio [ROH]/[Y] of 10 (Table 1). The monomer conversion was determined by weighing the polymer precipitated into heptane (see Experimental Section), and M_n was calculated by assuming that all the alcohol molecules contribute to polymerization.

Addition of excess of 2-propanol to **1** allows the polymerization to be controlled at least within the time required for the monomer conversion to be complete (entries 1−5). This initiating system has very high activity toward the ϵ-CL polymerization. Indeed, the monomer conversion is quantitative within a very short period of time. For instance (Table 1, entry 3: initial $[^iPrOH]/[Y]$ molar ratio = 10), PCL of 10 000 g/mol M_n is prepared at room temperature within less than 100 s, the molecular weight distribution being symmetric and narrow ($M_w/M_n = 1.15$). This observation is consistent with the absence of transesterification reactions all along the propagation step. Nevertheless, longer reaction time results in the broadening of the molecular weight distribution (Table 1, entry 6), as was reported elsewhere for the ROP of lactones initiated by other rare earth based initiators.[12,14]

The very good agreement between the molecular weight measured by SEC and the calculated value indicates that the 2-propanol is the actual initiator of the ring-opening polymerization. Consistently, no trace of unreacted 2-propanol is detected by ^{1}H NMR analysis of the final reaction mixture.

The end groups of the polyester chains have been analyzed by ^{1}H NMR (Figure 1), leading to the conclusion that the PCL chains are capped by an isopropoxy ester at one end and an alcohol at the second extremity, which results from the hydrolytic deactivation of the yttrium alkoxide growing species. This structural feature agrees with the "coordination−insertion" mechanism reported in the case of aluminum alkoxide initiators[5−7] and yttrium alkoxides[14,19] as well. Briefly, the coordination of the polar yttrium alkoxide group onto the lactone carbonyl group activates the selective acyl−oxygen cleavage of the ϵ-CL ring followed by its insertion in the yttrium−oxygen bond in a way that maintains the growing chain bound to the yttrium through an active alkoxide bond. Interestingly enough, the number-average molecular weight of short-length PCL chains ($M_n < 5000$ g/mol) has also been calculated from the ^{1}H NMR spectrum, i.e., from the relative intensity of the methylene protons of the PCL chains, e.g., $-CH_2-O-C(O)-$, and the protons of the end groups, either of the α-hydroxy methylene or the iso-

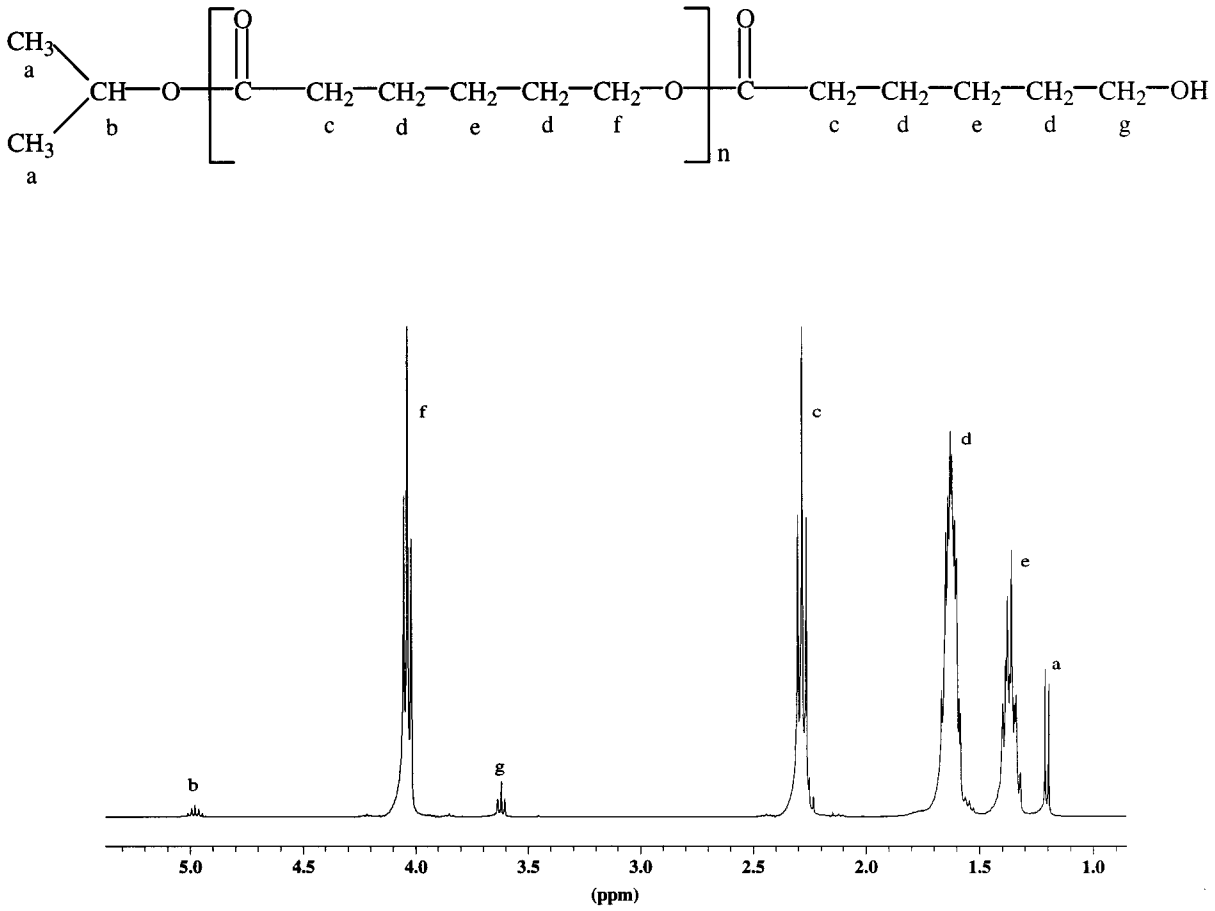


Figure 1. ^{1}H NMR spectrum of PCL synthesized in toluene at 20 °C, the initiator being [tris(hexamethyldisilyl)amide]yttrium (**1**) added with 2-propanol ($[^i\text{PrOH}]_0/[\text{Y}]_0 = 10$). Solvent: $CDCl_3$.

propoxy ester. The good agreement between $M_{n,NMR}$ and $M_{n,calc}$ confirms that the chain end-capping is quantitative at both ends.

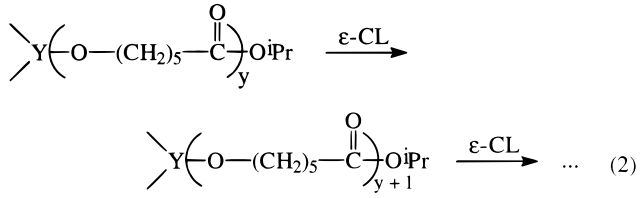
Thus, although part of the alcohol molecules are consumed by the formation of yttrium alkoxides, the molecules in excess are rapidly exchanged with the growing alkoxide species during the polymerization process and act as effective chain transfer agents. Since the PCL polydispersity is low, this exchange reaction between alkoxides and free alcohol molecules is fast with respect to the chain propagation.

From these observations, the mechanism for the ϵ-CL polymerization initiated by the [tris(hexamethyldisilyl)amide]yttrium (**1**)/2-propanol catalyst system can be schematized by eqs 1−3.

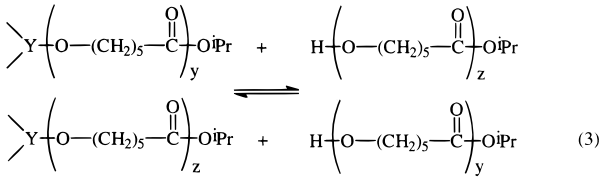
Formation of the active species

$$\text{Y}[\text{N}(\text{SiMe}_3)_2]_3 + x\,^i\text{PrOH} \rightarrow \text{Y}(\text{O}^i\text{Pr})_3 + 3\text{HN}(\text{SiMe}_3)_2 + (x-3)\,^i\text{PrOH} \quad (1)$$

ϵ-CL polymerization



Alkoxide/alcohol exchange



First, alcohol reacts with the [tri(hexamethyldisilyl)amide]yttrium with formation of the yttrium alkoxide and 1,1,1,3,3,3-hexamethyldisilazane $HN(SiMe_3)_2$ (eq 1). Although the yttrium alkoxide is the actual initiator, the number of growing chain is fixed by the original molar amount of alcohol as a result of rapid exchange with the active alkoxide functions (eq 3). The polymer molecular weight is therefore predictable from the monomer-to-alcohol molar ratio (Table 1).

The role of 2-propanol as chain transfer agent has recently been observed when ROP of ϵ-caprolactone is initiated by the yttrium oxo-isopropoxide $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$ cluster.[14] In this case, the number-average molecular weight of PCL agrees with the initial concentrations of free 2-propanol and the 2-propoxide functions of $Y_5(\mu\text{-O})(O^i\text{Pr})_{13}$. The polymer is also of narrow polydispersity. However, only a small excess of 2-propanol ($[^i\text{PrOH}]_0/[Y_5(\mu\text{-O})(O^i\text{Pr})_{13}]_0 < 20$) is consumed by the polymerization, whose kinetics is adversaly affected by increased alcohol concentration. Although the polymerization is complete after ca. 1 min when initiated by the commercially available yttrium oxo-isopropoxide cluster at

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

entry	$[^iPrOH]_0/[Y]_0$	react. time (min)	conv (%)[b]	$M_{n,calc}$ (g/mol)[a]	$M_{n,NMR}$ (g/mol)	$M_{n,SEC}$ (g/mol)	M_w/M_n	α (%)[c]
1	30	3	100	2000	2100	2150	1.25	0
2[d]	50	3	99	2000	2300	2100	1.25	0
3	100	12	100	2000	2600	2300	1.2	15
4[e]	100	13	100	2000	2400	1800	1.3	18
5	150	10	75	1500	2300	1600	1.3	25

[a] $M_{n,calc} = [\epsilon\text{-CL}]_0 \times 114.14 \times Q/[^iPrOH]_0$. [b] Determined by gravimetric measurements. [c] Unreacted 2-propanol measured by ^1H NMR (see text). [d] Initial ϵ-CL concentration = 0.75 M. [e] Reaction carried out at 0 °C

Table 3. ^1H NMR Spectroscopic Data for the Different Compounds Involved in the [Tris(hexamethyldisilyl)amide]yttrium/2-Propanol Catalytic System and for Commercial $Y_5(\mu\text{-O})(O^iPr)_{13}$ (at Room Temperature)

		^1H NMR δ (ppm)[a] (intensity ratio, type of multiplet)		
		"O−CH(CH$_3$)$_2$"		"Si(CH$_3$)$_3$"
analyzed compound	solvent	CH[d]	CH$_3$[d]	CH$_3$[d]
^iPrOH	$C_6D_5CD_3$	3.84 (d)	1.08 (sp)	/
$HN(SiMe_3)_2$	$C_6D_5CD_3$	/	/	0.07 (s)
$Y[N(SiMe_3)_2]_3$ (**1**)	$C_6D_5CD_3$	/	/	0.25 (s)
(**1**)/2-propanol system [b]	$C_6D_5CD_3$	4.43, 4.66 (1(sp):1(sp))	1.62, 1.67, 1.88 (1(d):1(d):1(d))	0.07 (s)
	C_6D_6	4.45, 4.71 (1(sp):1(sp))	1.65, 1.70, 1.93 (1(d):1(d):1(d))	0.10 (s)
$Y_5(\mu\text{-O})(O^iPr)_{13}$[c]	C_6D_6	4.35−4.7[e]	1.36, 1.4, 1.48, 1.65 (1(d):4(d):4(d):4(d))	

[a] Chemicals shifts are quoted relative to TMS. [b] With 2-propanol-to-yttrium molar ratio of 3. [c] Data from ref 21. [d] s = singulet, d = doublet, sp = septet. [e] Cluster of septets.

monomer-to-initiator molar ratio of 150, the ϵ-CL conversion is limited to 16% after 30 min when 18 equiv of ^iPrOH (with respect to $Y_5(\mu\text{-O})(O^iPr)_{13}$) is added, all the other experimental conditions being kept unchanged.

In the system under consideration in this study, the 2-propanol-to-yttrium molar ratio has been increased up to 150 (Table 2). α is the percentage of the 2-propanol molecules left unreacted when the reaction is stopped. In fact, α was determined by ^1H NMR analysis of the crude polymerization medium after hydrolytic deactivation of the yttrium alkoxide propagating species.

At least up to a 50-fold molar excess with respect to Y, all the 2-propanol molecules have initiated the polymerization of ϵ-CL in toluene at room temperature (Table 2, entries 1 and 2), and the monomer conversion is quantitative after 3 min polymerization time. Moreover, the agreement between the experimental M_n's and the monomer-to-alcohol molar ratio (at complete monomer conversion) is very good. 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 commercially available yttrium oxo-isopropoxide $Y_5(\mu\text{-O})(O^iPr)_{13}$ cluster.[14] This difference in the polymerization kinetics has to reflect differences in the structure of the active species (isopropoxide groups) in solution. To confirm this expectation, the structure of these species in the **1**/2-propanol system has been analyzed by ^1H NMR in $C_6D_5CD_3$ and C_6D_6 and compared with the species observed in the same solvents for the pentanuclear oxo-isopropoxide $Y_5(\mu\text{-O})(O^iPr)_{13}$[21] (Table 3).

Actually, the structure of the clusters of commercial yttrium isopropoxide was studied and fully characterized several years ago,[21,23] which led to the $Y_5(\mu_5\text{-O})(\mu_3\text{-}O^iPr)_4(\mu_2\text{-}O^iPr)_4(O^iPr)_5$ expanded formula. Thus, in the ^1H NMR spectrum in C_6D_6, four doublets were discerned for the different sets of methyl groups whereas a broad hump was typically observed for the associated methine groups (Table 3). However, Bradley et al. reported that the doublets for the methyl groups in C_6D_6 at 25 °C generally collapsed into two broad peaks and one resolved peak in a 5:4:4 ratio.[21] In $C_6D_5CD_3$, this 5:4:4 spectrum was maintained. This coalescence was explained by exchange reactions caused by traces of 2-propanol. Such a peak broadening by exchange was clearly pointed out elsewhere.[23]

The product formed by the reaction of $Y[N(SiMe_3)_2]_3$ (**1**) with 3 equiv of 2-propanol in $C_6D_5CD_3$ has been analyzed by ^1H NMR spectroscopy in this work. In the recorded spectrum, the signal characteristic of **1** (singlet at 0.25 ppm) disappears in favor of a singlet at 0.07 ppm, typical of $HN(SiMe_3)_2$ (Table 3). This observation confirms the complete substitution of the amide ligands of **1** by isopropoxide ligands. The accordingly formed yttrium isopropoxides are identified by three separate doublets of equal intensity (δ = 1.62, 1.67, 1.88, CH_3) and two septets (δ = 4.43, 4.66, CH) in a 1:1 ratio, which are clearly shifted downfield with respect to the signals of 2-propanol. Integration of these signals leads to a doublet/septet intensity ratio of 6. This fine structure is completely different from that one previously reported for the commercial $Y_5(\mu\text{-O})(O^iPr)_{13}$ cluster. Indeed, the methine septets are well-resolved, and the 5:4:4 intensity ratio and the coalescence of the signals for the methyl groups are no longer observed. It is worth noting that the ^1H NMR spectrum for the **1**/2-propanol mixture in $C_6D_5CD_3$ remains unchanged even after several days at 25 °C.

Very similar observations have been achieved for the **1**/2-propanol system in C_6D_6 (Table 3). In addition, the methyl and methine protons were characterized by chemical shifts slightly downfield shifted compared to the related signals for the isoproxide ligands in the yttrium oxo-isopropoxide cluster in the same solvent.

More interestingly, when an excess of alcohol (initial [^{i}PrOH]/[Y] ratio >3) is used, the ^{1}H NMR spectrum for the **1**/2-propanol system is maintained except for the observation of two additional broad peaks characteristic of free ^{i}PrOH molecules at 1.2 (CH_3) and 4.0 ppm (CH) in $C_6D_5CD_3$, whose intensity increases with the excess. So, under the studied reaction conditions, the nature of the active species is independent of the initial 2-propanol-to-yttrium molar ratio. In contrast, the ^{1}H NMR spectrum of $Y_5(\mu\text{-O})(O^iPr)_{13}$ is extremely sensitive to the addition of ^{i}PrOH.[23] Indeed, the ^{i}PrOH molecules trigger the coalescence of the terminal and μ_2-bridging Y isopropoxide doublets and the broadening of the associated methine signals.

From all these ^{1}H NMR results, it appears that the active species involved in the $Y[N(SiMe_3)_2]_3$ (**1**)/2-propanol catalytic system are quite different from the species that are active in the commercially available $Y_5(\mu\text{-O})(O^iPr)_{13}$ and are likely free from covalently bridging atoms. The observations reported in this work are in very good agreement with a previous study on rare-earth alkoxides.[21] Indeed, the addition of an excess of 2-propanol to $Y[N(SiMe_3)_2]_3$ (**1**) was observed to form the yttrium oxo-isopropoxide $Y_5(\mu\text{-O})(O^iPr)_{13}$ only upon heating the solution at the reflux temperature of alcohol for several hours, and the release of diisopropyl ether was then reported. It is important to note that, under the conditions used in this work, no traces of diisopropyl ether have been detected. Note finally that a more detailed interpretation of the ^{1}H NMR spectra of the **1**/2-propanol system is difficult since the resulting yttrium trialkoxides more likely form reversible self-association in a nonpolar solvent as already observed with other metal alkoxides[8,24] or can be coordinated by remaining ^{i}PrOH molecules as also reported for other lanthanide alkoxides.[25]

Interestingly enough, Stevels et al. reported on the initiation of the polymerization of ϵ-CL and lactide by the reaction product of bulky tris(2,6-di-*tert*-butylphenoxy)yttrium with 3 equiv of 2-propanol.[14,19] This initiator was analyzed by ^{1}H NMR in CD_2Cl_2.[19] A multiplet at 1.2−1.7 ppm was observed for the methyl protons of isopropoxide groups and a broad peak at 4.4 ppm for the related methine protons. However, the comparison with the initiator used in this work is not straightforward, because solvents of different polarity were used for their analysis. A more detailed comparison would require further investigation.

When the initial alcohol-to-Y molar ratio is 100 and 150 (Table 2, entries 3−5), part of the alcohol molecules ($15 \le \alpha \le 25\%$) do not contribute to the complete ϵ-CL conversion, α increasing with the initial ^{i}PrOH-to-Y molar ratio. A similar observation has also been reported for the ϵ-CL polymerization initiated by aluminum isopropoxide.[26,27] 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 2 illustrates the time dependence of α when the ^{i}PrOH/Y molar ratio is 100. After a rapid drop within the first 2 min of polymerization, α tends slowly to a plateau value (18%). So, it seems that after some time, the metal center is "encaged" by the growing polymer chains, in such a way that only the hydroxyl end group of these chains can participate in the alcohol−yttrium alkoxide exchange excluding the not yet converted 2-propanol. Had the exchange of this alcohol excess been merely slowed down, formation of shorter chains would be observed, which is not the case (even for 8 min reaction time).

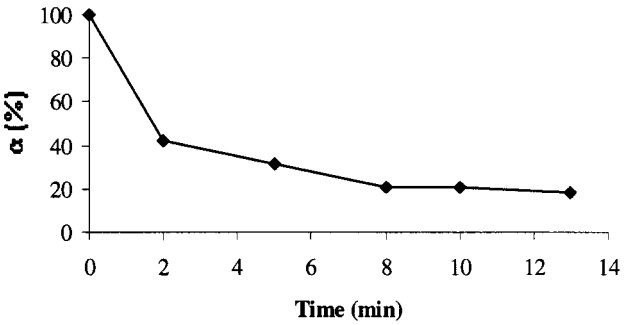


Figure 2. Time dependence of unreacted 2-propanol (α) in the ϵ-CL polymerization initiated by [tris(hexamethyldisilyl)-amide]yttrium (**1**) added with 2-propanol Solvent: toluene, $[\epsilon\text{-CL}]_0 = 1$ M, $[^i\text{PrOH}]_0/[Y]_0 = 100$, $T = 0$ °C.

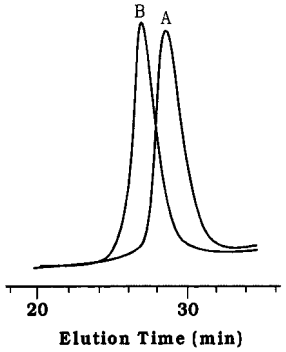


Figure 3. Size exclusion chromatograms of PCL initiated by [tris(hexamethyldisilyl)amide]yttrium (**1**) added with 2-propanol (solvent: toluene, $[\epsilon\text{-CL}]_0 = 1$ M, $[^i\text{PrOH}]_0/[Y]_0 = 30$, $T = 20$ °C): (A) first ϵ-CL feed, $t_P = 3$ min, 100% conversion ($M_{n,calc} = 2000$, $M_{n,SEC} = 2150$, $M_w/M_n = 1.25$); (B) second ϵ-CL feed, $t_P = 2$ min, 100% conversion ($M_{n,calc} = 5200$, $M_{n,SEC} = 4900$, $M_w/M_n = 1.25$).

To prove that the chains preserve their capacity of growing after the complete ϵ-CL conversion, a second monomer feed has been added to a completely polymerized solution. Size exclusion chromatograms (Figure 3) show that the symmetric peak observed at the end of the first step is completely shifted toward higher MW as result of the polymerization resumption. The molecular weight has increased proportionally to the molar amount of ϵ-CL added in the second step ($M_{n,calc} = 5200$, $M_{n,SEC} = 4900$, $M_{n,RMN} = 5100$), while keeping the molecular weight distribution narrow. This conclusion is confirmed by the number-average molecular weight determined by ^{1}H NMR analysis. Moreover, the high activity is preserved since the conversion of the second monomer feed is at least as fast as the first one. These observations raise optimistic forecasts for the synthesis of block copolymers. Furthermore, this initiating system is very versatile, since changing the structure of the alcohol is a straightforward way to prepare a large range of α-functional PCL, including macromonomers, asymmetric telechelic polymers, and block or graft copolymers (in the case of polymeric alcohols).

In conclusion, combination of [tris(hexamethyldisilyl)-amide]yttrium (**1**) and alcohol is a very efficient catalytic system to initiate the ring-opening polymerization of ϵ-CL. Polymerization proceeds through competition between chain propagation ("coordination−insertion" of ϵ-CL into a yttrium−alkoxide bond) and alkoxide/alcohol exchange. When the 2-propanol-to-Y molar ratio is

smaller than 50, the chain transfer to the alcohol is quantitative, and the molecular weight of the polymer chains can be predicted by the monomer-to-alcohol molar ratio. Transesterification reactions do not occur rapidly, so that polymers of narrow molecular weight distribution can be synthesized with very high monomer conversion (>99%).

From the practical viewpoint, the control and the high rate of the polymerization being maintained at high alcohol-to-Y molar ratios has the advantage to produce polymers contaminated by only small amounts of catalytic residues.

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