Polymerization of ϵ-Caprolactone Initiated by Y Alkoxide Grafted onto Porous Silica

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ABSTRACT: Ring-opening polymerization of ϵ-caprolactone has been initiated by Y isopropoxide grafted onto silica, in the presence of 2-propanol, in toluene at 40 °C. The degree of polymerization is controlled by the initial monomer/(alcohol + alkoxide) molar ratio. Deactivation of the chains by an alcohol is essential for them to be detached from the support and to be collected totally free of metal and silica residues. The alkoxide is also regenerated at the surface of the support, which allows for recycling the catalyst.

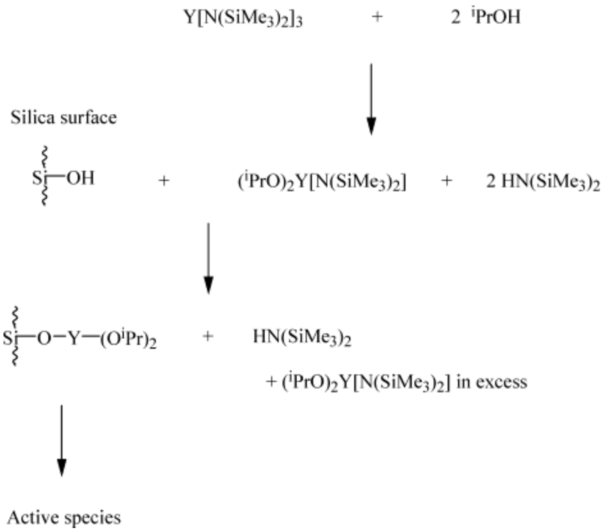
Introduction

Recently, rare earth alkoxides were shown to be highly reactive initiators for the ring-opening polymerization of ϵ-caprolactone.[1−3] A few papers reported on the "livingness" of this polymerization[2−5] that was usually conducted under homogeneous conditions, thus resulting in polymer contamination by metal residues and in loss of usually expensive catalyst. Indeed, synthesis of rare earth alkoxides may be a time-consuming and costly process, one exception being the reaction of lanthanide halides with epoxides as proposed by Shen et al.[6] Therefore, it is worth paying attention to heterogeneous catalysis, as Spitz et al. did in their study of the ϵ-caprolactone polymerization initiated by Al alkoxide grafted onto porous silica.[7] They showed that addition of alcohol molecules to the reaction medium is a way to produce more polymer chains than the active species involved in the polymerization process as a result of an alkoxide/alcohol exchange reaction. The alcohol might however decrease the catalyst activity depending on its ability to compete with the monomer for coordination to the active centers. Actually, the catalyst activity passes through a maximum, which depends on the relative concentration of these two components.

A previous paper reported on the binding of yttrium isopropoxide to the surface of porous silica.[8] The alkoxide species can be either directly formed at the surface of the support (method 1) or preformed before grafting to the support (method 2) as is the case in this work. Briefly, [tris(hexamethyldisilyl)amide]yttrium, $Y[N(SiMe_3)_2]_3$, is reacted with 2 equiv of 2-propanol with rapid and irreversible formation of the $(^iPrO)_2Y[N(SiMe_3)_2]$ yttrium dialkoxide. The reactivity of the residual amide function toward thermally pretreated silica allows the active species to be attached to the solid surface, as shown in Scheme 1.

This paper aims at testing this new type of heterogeneous catalyst in the ring-opening polymerization of ϵ-CL conducted in the presence of 2-propanol. Special attention has been paid to the quantitative separation of the support and the chains and to the recycling of the supported catalyst.

Scheme 1. Grafting of Preformed Yttrium Alkoxides to Silica Surface



Experimental Part

Materials. [Tris(hexamethyldisilyl)amide]yttrium $Y[N(SiMe_3)_2]_3$ (Strem Chemicals) and $CDCl_3$ (Aldrich) were used as received. 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). 1,1,1,3,3,3-Hexamethyldisilazane $HN(SiMe_3)_2$ (HMDS) (Aldrich) was used as received and kept under nitrogen. *m*-Xylene (Aldrich) was used as received. Toluene and THF were dried by refluxing over benzophenone−Na complex and distilled under nitrogen just prior to use. When used in the catalyst preparation, toluene and THF were further dried over living polystyryllithium oligomers and distilled. Acetonitrile was dried by refluxing over CaH_2 and distilled under nitrogen just prior to use. Silica (Grace Davison, grade M432; pore diameter = 17 nm; pore volume = 1.5 cm^3/g) was thermally treated in vacuo in order to control the surface content of the hydroxyl groups. The temperature program was 20−100 °C at 10 °C/min, 100−130 °C at 1 °C/min, and 130−800 °C at 10 °C/min, 2 h at 800 °C.

Catalyst Preparation. Preparation was carried out in round-bottom flasks, previously flame-dried and purged with nitrogen. Liquids were handled with flame-dried stainless steel

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Table 1. Polymerization of ϵ-CL by Y Isopropoxide Grafted onto Porous Silica (Conditions: Toluene; $T = 40$ °C; Termination Agent: HCl)

entry	$[Y]_0$ (10^3 M)	$[^iPrOH]_0/[Y]_0$	$[\epsilon\text{-CL}]_0$ (M)	t (h)	conv[a] (%)	$M_{n,calcd}$[b] (10^3 g/mol)	$M_{n,NMR}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	M_w/M_n
1	4.5	10	1.0	1.1	98	2.0	2.1	1.1	1.9
2	1.7	15	1.0	1.0	100	4.0	3.9	2.5	6.0
3	2.4	17	0.7	1.3	100	1.8	1.8	1.3	2.0
4[c]	2.4	17[d]	0.7	4.0	100	1.8	2.1	*e*	*e*
5	2.4	17	0.7	1.3	100	1.8	1.8	1.4	5.5
				3.3[f]	100	3.3	3.2	2.2	5.9

[a] Determined by ^{1}H NMR analysis of the crude polymerization medium. [b] $M_{n,calc} = 114.14 \times [\epsilon\text{-CL}]_0 \times \text{conv}/([^iPrOH]_0 + [^iPrO-]_0)$. [c] Polymerization initiated by Al isopropoxide grafted onto porous silica. [d] $[^iPrOH]_0/[Al]_0 = 17$. [e] SEC analysis was impossible because of the plugging of the columns. [f] Polymerization resumption.

capillaries and syringes. Typically, silica was dehydrated at 130 °C for 15 h in vacuo and suspended in dried toluene or THF. [Tris(hexamethyldisilyl)amide]yttrium, $Y[N(SiMe_3)_2]_3$ (3.47 mmol), was dissolved in toluene (45 mL) and reacted with 2 equiv of 2-propanol at 50 °C. After stirring for 20 min, this yttrium alkoxide solution was added to the suspension of silica particles (2.2 g dispersed in 80 mL of toluene) at 50 °C. After 30 min, silica was collected by filtration, washed repeatedly with fresh solvent, and added with 2-propanol for 20 min at 50 °C. After filtration, the silica particles were dried in vacuo.

Determination of the Amount of Grafted Yttrium. This analysis required to determine quantitatively the amount of HMDS released at each step of the grafting by gas chromatography (GC).

The solution collected after reaction of silica with the Y derivative contained the excess of $(^iPrO)_2Y[N(SiMe_3)_2]$ and the $HN(SiMe_3)_2$ released. These two compounds were separated by distillation under vacuum and quantitatively analyzed. The excess of Y derivative was analyzed on the basis of the HMDS released by reaction with an excess of alcohol at 40 °C. HMDS was analyzed quantitatively by gas chromatography (GC) (Perkin-Elmer 5800 gas chromatograph) on the basis of a calibration curve, *m*-xylene being used as an internal standard. In this work, silica was grafted by 8×10^{-4} mol of Y/g of silica, and each Y beared two alkoxides (within the limits of experimental errors).

Polymerization Procedure. Polymerization was carried out in dry toluene or THF under nitrogen. In a typical example, the heterogeneous catalyst (0.31 mmol of active species) was added into a round-bottom flask, followed by solvent (25 mL) and 2-propanol (4 mL, 0.4 M in toluene) according to the desired monomer concentration and the alcohol-to-Y molar ratio, respectively. The reaction medium was heated to the polymerization temperature. ϵ-CL (3.8 mL or 34 mmol for a targeted M_n of 2050) was injected into the flask, and the polymerization proceeded for a predetermined time before being stopped by an excess (with respect to the alkoxide species) of the termination agent (methanol). The silica particles were allowed to settle for 20 h, and the supernatant solution was poured in an excess of heptane for PCL to be precipitated, dried in vacuo, up to a constant weight, and characterized.

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 for PCL, based on the previously reported viscosimetric relationships.[9]

^{1}H NMR spectra were recorded at 25 °C with the Bruker 250 and 400 MHz spectrometers. $CDCl_3$ was the solvent, and the chemical shifts were quoted relative to tetramethylsilane (TMS).

Results and Discussion

A series of polymerization experiments were conducted in toluene at 40 °C. After a well-defined period of time, HCl was added to the polymerization medium in order to have the polymer chains detached from the support and analyzed by SEC and ^{1}H NMR. As systematically observed for poly(ϵ-caprolactone) (PCL) prepared in solution with Al or Y isopropoxide as initiator, as many isopropyl ester end groups (δ CH_3 at 1.2 ppm and δ CH at 4.96 ppm) as primary alcohol end groups (δ CH_2OH at 3.61 ppm) are detected, in agreement with the traditionally reported "coordination−insertion" mechanism.[10,11] The selective acyl−oxygen cleavage of the monomer is thus activated by coordination of the carbonyl to the metal, and the monomer insertion in the metal−oxygen bond maintains the growing chain bound to the metal through an active alkoxide bond. The number-average molecular weight, $M_{n,NMR}$, has been determined from the ^{1}H NMR spectrum, i.e., from the relative intensity of the methylene protons of the PCL backbone, e.g. $-CH_2-O-C(O)-$ at 4.03 ppm, and the protons of the isopropoxy end groups at 1.2 ppm (CH_3). These values are in very good agreement with the theoretical ones ($M_{n,calc}$), calculated on the assumption that all the alcohol molecules contribute to the polymerization (Table 1). Similar conclusions have already been drawn for the homogeneous polymerization initiated by the $Y[N(SiMe_3)_2]_3$/ROH system.[12] In each case, no trace of unreacted 2-propanol could be detected by ^{1}H NMR analysis of the final reaction mixture.

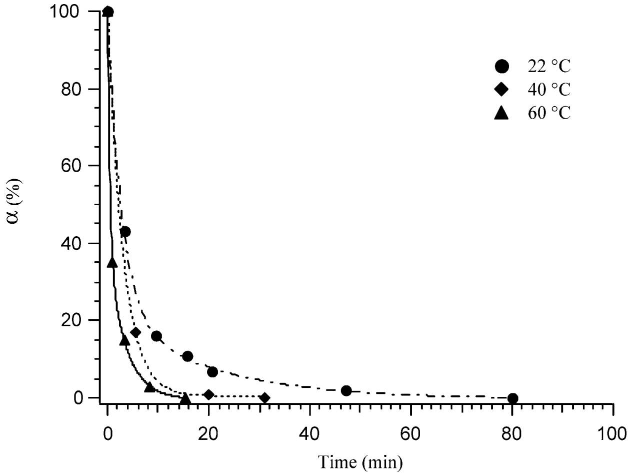


Figure 1. Time dependence of the molar fraction of unreacted 2-propanol (α) for the ϵ-CL polymerization initiated by yttrium isopropoxide grafted to porous silica (solvent: toluene, $[Y]_0 = 0.0045$ M, $[^iPrOH]_0/[Y]_0 = 10$, $[\epsilon\text{-CL}]_0 = 1$ M).

The time dependence of the molar fraction of 2-propanol left unreacted (α) has been studied at different reaction temperatures (Figure 1). α is determined by ^{1}H NMR analysis of the crude polymerization medium after deactivation of the yttrium alkoxide species.[7] Figure 1 clearly shows a rapid decrease of α with the polymerization time. The alcohol consumption is all the more rapid as the temperature is high. Whatever the

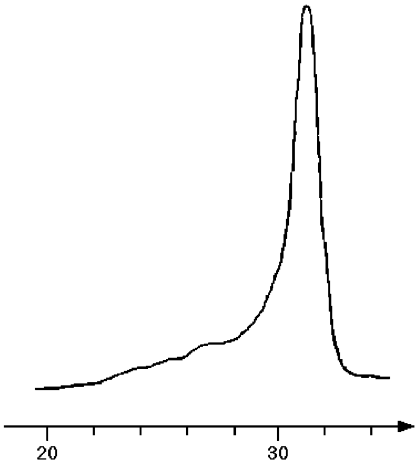


Figure 2. Size exclusion chromatogram of PCL initiated by yttrium isopropoxide grafted to porous silica in the presence of 2-propanol (solvent: toluene, $[Y]_0 = 0.0024$ M, $[^i\mathrm{PrOH}]_0/[Y]_0 = 17$, $[\epsilon\text{-CL}]_0 = 0.7$ M, $T = 40$ °C, time = 1.25 h).

polymerization temperature, the alcohol consumption is complete at least at monomer conversion lower than 50%.

Comparison of entries 3 and 4 in Table 1 shows that substitution of Y for Al greatly increases the activity of the system, as assessed by a much shorter time to reach the complete ϵ-CL conversion, all the other reaction conditions being the same. The same trend has been reported in the scientific literature for the homogeneous ROP of lactones and lactides.[13−15] The propagation rate constants are largely in favor of the lanthanide alkoxides compared to the Al counterparts.

To prove that the polymer chains preserve their capacity of growing after the complete consumption of ϵ-CL, a second monomer feed has been added to a completely polymerized medium (Table 1, entry 5). The polymerization resumption immediately occurs, and conversion of ϵ-CL is again quantitative. As confirmed by ^{1}H NMR analysis, the molecular weight of the propagating PCL chains has increased proportionally to the molar amount of ϵ-CL added in the second step. This observation is quite interesting in view of the synthesis of block copolymers.

High polydispersity indices are however observed (Table 1), which are accounted for by the SEC profiles that show a broad shoulder on the left-hand side of a very narrow peak at high elution times (Figure 2). Moreover, the PCL samples prepared by supported Al alkoxide cannot be analyzed by SEC because they plug the chromatographic columns immediately. The most reasonable explanation for these observations is the aggregation of chains by residual silica. This phenomenon leaves all the isopropyl ester end groups available to analysis (dangling chain ends), consistent with the good agreement between $M_{\mathrm{n,calc}}$ and $M_{\mathrm{n,NMR}}$. Residual silica might result from the partial burst of the original support particles by the polyester chains growing within the pores. This phenomenon is well-known in heterogeneous Phillips and Ziegler−Natta catalyses.[16] The residual particles are all the more difficult to separate from the polymer as they are small (very slow decantation) and remain attached to PCL chains.

The metal has clearly an effect on the bonding of the chains to residual silica particles. Both aluminum and yttrium ions are Lewis acids with a much larger ionic radius for yttrium (90 pm for Y^{3+}, 68 pm for Al^{3+}), which makes the alkoxide bond more ionic and thus more prone to hydrolysis. Accordingly, the amount of catalytic residue is smaller in the case of heterogeneous Y catalyst.

Table 2. XPS Analysis of Different PCL Polymers

		experimental values (%)				
entry	catalyst[a]	C	O	Si	Al	Y
1	$Y[N(SiMe_3)_2]_3/^i\mathrm{PrOH}$	76.98	22.92	0.08 ± 0.05		*b*
2	grafted Y isopropoxides	77.20	22.64	0.16 ± 0.05		*b*
3	grafted Al isopropoxides	76.03	23.74	0.23 ± 0.05	*b*	

[a] Catalyst used to prepare the PCL sample analyzed by XPS. [b] Undetected.

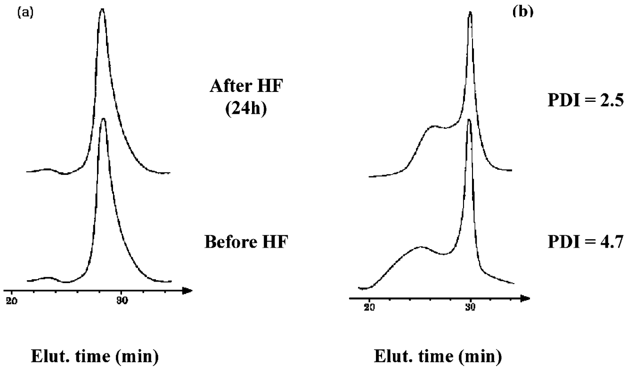


Figure 3. Effect of HF treatment on the size exclusion chromatogram of PCL ($[\mathrm{HF}]_0 = 0.5$ M, $T = 20$ °C, reaction time = 24 h). Reference PCL (a); PCL initiated by yttrium isopropoxide grafted to porous silica in the presence of 2-propanol (solvent: toluene, $[Y]_0 = 0.0024$ M, $[^i\mathrm{PrOH}]_0/[Y]_0 = 17$, $[\epsilon\text{-CL}]_0 = 0.7$ M, $T = 40$ °C) (b).

To give credit to this explanation, PCL samples have been analyzed by X-ray photoelectron spectroscopy (XPS) (Table 2). The C and O content is the same whatever the PCL sample, in reasonable agreement with the theoretical values (75% and 25%, respectively). In the case of PCL prepared under homogeneous conditions (entry 1), the experimental content of Si is below the limit of detection by XPS, which indicates absence of Si contamination. In contrast, the Si content is no longer negligible in the samples prepared by heterogeneous catalysis, in line with the suspected contamination. Consistent with previous observations, the Si content of PCL appears to be higher when grafted Al isopropoxide is used. The very low content of Si and the absence of detectable amount of Y or Al show that only trace of catalyst is left in the polyester.

If Si−O−Y−O linkages are left after deactivation of the propagating chains by HCl, a further hydrolysis treatment should decrease the relative importance of the high molecular weight fraction. So, PCL has been redissolved in THF and treated again by HCl ($T = 20$ °C, $[\mathrm{HCl}]_0 = 0.05$ M, reaction time = 1 h). The polydispersity index has accordingly decreased from 5.5 to 4.4.

Another way to tackle this problem might consist of degrading silica quantitatively by hydrofluoric acid (HF) under conditions ($[\mathrm{HF}]_0 = 0.5$ M in water, $T = 20$ °C, 0.08 mol of HF/g of silica, 10 min) that leave PCL unchanged (Figure 3a). Whenever PCL prepared by yttrium isopropoxide grafted to silica is treated by HF, the shoulder at low elution times changes in such a way that the molecular weight distribution gets narrower (Figure 3b). Only the partial degradation of residual silica that immobilizes polymer chains can explain this observation. Whatever the conditions used for the HF

Table 3. Polymerization of ϵ-CL by Y Isopropoxide Grafted to Porous Silica; Influence of the Method Used To Recover the PCL Chains (Conditions: Toluene; $T = 40$ °C)

										recovery method of PCL		
entry	$[Y]_0$ (10^3 M)	$[^i\mathrm{PrOH}]_0/[Y]_0$	$[\epsilon\text{-CL}]_0$ (M)	t (h)	conv[a] (%)	$M_{n,calcd}$[b] (10^3 g/mol)	$M_{n,NMR}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	M_w/M_n	term. agent[c]	decant.[d]	filtration[e]
1	2.4	17	0.7	1.3	100	1.8	1.8	1.4	5.5	HCl	no	no
2[f]	4.5	10	1.0	2.4	100	2.0	2.1	1.9	1.3	HCl	yes (20)	no
							1.0	0.6	1.4	acid. MeOH	yes (20)	no
3	3.3	15	1.0	2.5	100	2.0	1.8	1.3	1.5	HCl	yes (20)	no
							1.7	1.5	1.5	HCl	yes (20)	yes
4	0.7	10	0.40	1.0	g	4.9[h]	4.1	2.7	24.1	H_2O	yes (15)	no
5	4.6	10	1.0	0.1	100	2.0	2.3	1.9	1.1	MeOH	yes (20)	no

[a] Determined by ^{1}H NMR analysis of the crude polymerization medium. [b] $M_{n,calc} = 114.14 \times [\epsilon\text{-CL}]_0 \times \mathrm{conv}/([^i\mathrm{PrOH}]_0 + [^i\mathrm{PrO-}]_0)$. [c] Termination agent used for the hydrolysis of the active species. [d] Decantation of the catalyst particles after hydrolysis of the active species, for a period of time noted into parentheses (hours). [e] Filtration of the supernatant solution through a filter with pore size < 0.5 μm. [f] Polymerization carried out at 20 °C. [g] Not determined. [h] Calculated for quantitative monomer conversion (conv = 100%).

treatment, the high molecular weight fraction cannot be eliminated completely, which may suggest a problem of accessibility to the mineral residues.

Because the classical hydrolytic deactivation of the grafted yttrium alkoxide by an aqueous HCl solution is not efficient enough to separate completely the PCL chains from the silica particles, this general recipe has been modified, as reported in Table 3. As a rule, the silica particles are allowed to settle down for several hours after the hydrolysis of the growing chains. The clear supernatant solution is then withdrawn from the reactor and poured into heptane. This additional step has a very beneficial effect on the characteristics of the recovered polymer, as assessed by the comparison of entry 1 with entries 2 and 3 in Table 3. The fraction of high MW chains has almost completely disappeared, which results in a much lower polydispersity index. So, when the hydrolyzed suspension is kept at rest for 20 h, chains aggregated by silica residues have the opportunity to settle, and they are no longer recovered with the chains of the expected length. Filtration of the supernatant solution is not beneficial, as shown by entry 3 of Table 3. Finally, the termination agent was changed. Water, acidified MeOH, and pure MeOH were used instead of an aqueous HCl solution. All these agents were used in the same amount (ca. 100 equiv with respect to the active alkoxides). Water has a detrimental effect on the polymer/support separation (entry 4). A rapid (partial) degradation of the PCL chains is observed when the acidified methanol is used (entry 2). Indeed, a singlet at 3.6 ppm is detected by ^{1}H NMR which may be assigned to a terminal methyl ester group $-C(O)OCH_3$. A multiplet at ca. 2.25 ppm is also observed instead of the expected triplet, and the intensity of the triplet at 3.55 ppm is very high. All these observations are characteristic of a methanolysis reaction, as reported elsewhere in the case of the (D,L)LA polymerization initiated by homogeneous Al alkoxides.[17] The use of pure MeOH (entry 5, Table 3) allows to recover a polymer with a very narrow molecular weight distribution ($M_w/M_n = 1.1$). A symmetric monomodal elution peak is indeed observed (Figure 4), which indicates the complete absence of residual silica in the recovered polymer. The original mass of the catalyst is also recovered at the end of the process, and the experimental molecular weight determined by SEC and ^{1}H NMR is very close to the theoretical value (Table 3). So, the method used to recover the polymer chains is of the utmost importance in the case of heterogeneous catalysis. Combination of methanol as a termination agent and a period of decantation before the particles are separated from the polymer solution is ideal for the PCL chains to get rid of silica residues.

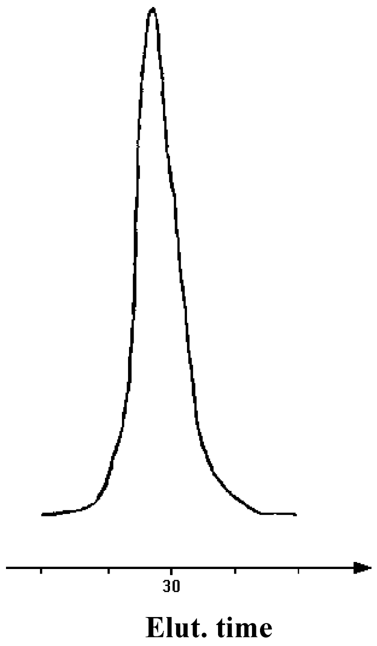


Figure 4. Size exclusion chromatogram of PCL initiated by yttrium isopropoxide grafted to porous silica in the presence of 2-propanol (solvent: toluene, $T = 40$ °C, $[Y]_0 = 0.0046$ M, $[^i\mathrm{PrOH}]_0/[Y]_0 = 10$, $[\epsilon\text{-CL}]_0 = 1$ M). Recovery method: hydrolysis with MeOH and decantation of silica.

An additional series of ϵ-CL polymerization experiments have been initiated by yttrium isopropoxide grafted onto silica or alumina, and the polymer has been systematically recovered by the optimized method, i.e., termination by methanol and settling of the support for 20 h. Table 4 shows that the ϵ-CL polymerization initiated by supported yttrium alkoxide in the presence of an alcohol is well-controlled, whatever the polymerization solvent. The agreement is good between the experimental M_n's, determined by ^{1}H NMR and SEC analysis, and M_n calculated from the initial monomer-to-alcohol molar ratio at complete conversion. Moreover, the catalytic activity is rather high, a PCL of 2000 g/mol M_n being prepared in toluene at 40 °C in less than 8.5 min (Table 4, entry 2).

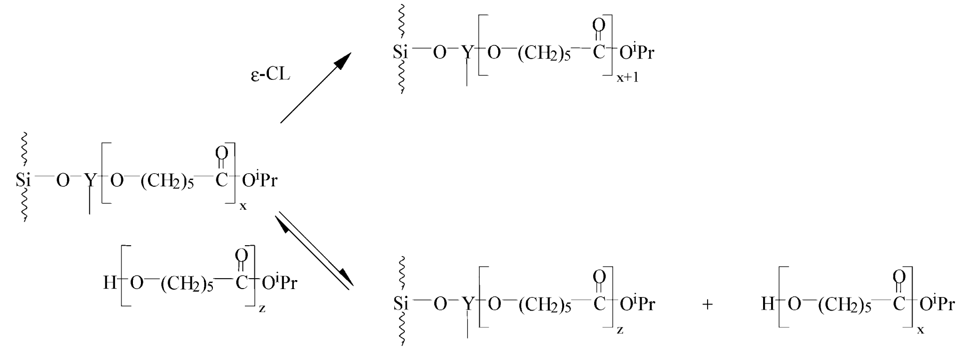
The new heterogeneous catalyst developed in this work, i.e., Y alkoxide grafted onto a mineral support, is very well-suited to the straightforward and rapid production of well-defined PCL without contamination by catalytic residues. To our best knowledge, this result has never been reported so far in the case of ROP of lactones initiated by supported aluminum and rare

Table 4. Polymerization of ϵ-CL by Y Isopropoxide Grafted to Porous Silica (Conditions: T = 40 °C; Termination Agent: MeOH)

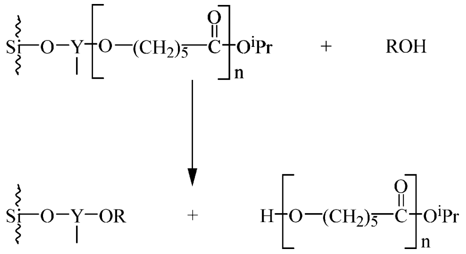
entry	catalytic support	solvent	$[Y]_0$ (10^3 M)	$[^iPrOH]_0/[Y]_0$	$[\epsilon\text{-CL}]_0$ (M)	t (min)	conv^a (%)	$M_{n,calcd}$^{b} (10^3 g/mol)	$M_{n,NMR}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	M_w/M_n
1	silica	toluene	4.6	10	1	60	100	2	*c*	1.9	1.2
2	silica	toluene	4.6	10	1	9	100	2	2.3	1.9	1.1
3	silica	THF	4.6	10	1	60	100	2	1.9	2.0	1.1

[a] Determined by ^{1}H NMR analysis of the crude polymerization medium. [b] $M_{n,calc} = 114.14 \times [\epsilon\text{-CL}]_0 \times \text{conv}/([^iPrOH]_0 + [^iPrO\text{-}]_0)$. [c] Not determined.

Scheme 2. Mechanism for the ϵ-CL Polymerization Initiated by Y Isopropoxide Grafted to a Mineral Support: Competition between Chain Propagation and Alkoxide/Alcohol Exchange



Scheme 3. Recycling of the Supported Catalyst by the Alcohol Used as the Termination Agent



earth alkoxides. The general polymerization mechanism consists of a chain propagation based on a fast alkoxide/alcohol exchange (Scheme 2). The exchange reaction must be fast indeed to account for the low polydispersity and the disappearance of the alcohol in the early stage of the polymerization (NMR analysis). Although the yttrium alkoxide is the actual initiator, the number of growing chains is dictated by the original molar amount of 2-propanol. The polymer molecular weight is thus predictable from the monomer-to-alcohol molar ratio.

Recycling of the Heterogeneous Catalyst. The alcohol, such as methanol, added to the polymerization medium when the monomer conversion is complete has a twofold role, i.e., release of the ω-hydroxypoly(ϵ-caprolactone) chains and regeneration of the alkoxide groups on the support surface (Scheme 3).

The possible recycling of the heterogeneous catalyst has been confirmed as follows. In a first step, well-defined PCL oligomers were initiated by using yttrium isopropoxide grafted onto porous silica in toluene at 40 °C (silica pretreatment at 800 °C; $[\epsilon\text{-CL}]_0 = 1$ M; $[^iPrOH]_0/[Y]_0 = 15$; $[Y]_0 = 0.0035$ M). After complete monomer conversion, 2-propanol was added to the living polyester chains in order to separate them from the support and the mineral particles were allowed to settle. The supernatant polymer solution was withdrawn from the reactor, and the catalytic support was washed two times with freshly dried solvent.

The ϵ-CL polymerization was repeated under the same conditions by using the regenerated catalyst. The polymer collected in the second experiment met the expectation in terms of molecular weight ($M_{n,calc} = 1900$ g/mol; $M_{n,NMR} = 1800$ g/mol; $M_{n,SEC} = 2000$ g/mol) and end groups. The molecular weight distribution is narrow and monomodal (M_w/M_n close to 1.1). These observations confirm that the activity of the catalyst and the number of active species available on the surface are preserved by the recycling technique and that the monomer is not inserted into the SiO−Y bonds.

It thus appears that the supported Y alkoxide can be easily and efficiently recycled, which is essential to substitute a continuous process for the batch technique used in this study. In this respect, a packed reactive column with flow characteristics comparable to those ones of a plug flow reactor might be convenient as discussed by Miola-Delaite et al.[18]

Conclusion

A new heterogeneous catalyst has been prepared by the grafting of yttrium isopropoxide onto a porous mineral support. It allows ϵ-CL to be polymerized in a controlled manner in the presence of an alcohol, which triggers an exchange reaction with the grafted active alkoxide groups. This exchange reaction is faster than the chain propagation, in agreement with a narrow molecular weight distribution (M_w/M_n close to 1.1). The alcohol/alkoxide reaction makes the system a catalytic system, since the number of growing chains exceeds the initial amount of alkoxides. As supported by SEC analysis and ^{1}H NMR spectroscopy, the degree of polymerization is controlled by the initial $[\epsilon\text{-CL}]_0/[\text{alcohol} + \text{alkoxide}]_0$ molar ratio, and all the polymer chains are end-capped by the alkyl radical of the alcohol and a hydroxyl group released by methanolysis of the growing species.

The critical importance of the method used to recover the polymer has been highlighted. Deactivation of the chains by an alcohol is a key parameter. It is also important to allow the support particles to settle until the supernatant solution is clear and finally poured into a nonsolvent for PCL. The polymer is then recovered with high purity. Y alkoxide grafted onto a mineral support is thus quite a valuable catalyst for the straightforward and rapid production of well-defined polyesters totally free of metal residues. This important achievement has never been reported until now in the case of aluminum and rare earth alkoxide based initiators and catalysts.

Last, but not least, the alcohol used in the process can have a dual role because it controls the length of the chains and it is able to regenerate the alkoxide at the surface of the support and thus to recycle the catalyst. This characteristic feature is well-suited to the conversion of a batch process to a continuous one.

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