Unprecedented Polymerization of ε-Caprolactone Initiated by a Single-Site Lanthanide Borohydride Complex, [Sm(η-C_5Me_5)$_2$(BH_4)(thf)]: Mechanistic Insights

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Abstract: The monoborohydride lanthanide complex [Sm(Cp*)$_2$(BH_4)(thf)] (**1a**) (Cp* = η-C_5Me_5), has been successfully used for the controlled ring-opening polymerization of ε-caprolactone (ε-CL). The organometallic samarium(III) initiator **1a** produces, in quantitative yields, α,ω-dihydroxytelechelic poly(ε-caprolactone) displaying relatively narrow polydispersity indices (<1.3) within a short period of time (30 min). The polymers have been characterized by ^{1}H and ^{13}C NMR, SEC, and MALDI-TOF MS analyses. Use of the single-site initiator **1a** allows a better understanding of the polymerization mechanism, in particular with the identification of the intermediate compound [Sm(Cp*)$_2$(BH_4)(ε-CL)] (**1b**). Indeed, one molecule of ε-CL initially displaces the coordinated THF in **1a** to give **1b**. Then, ε-CL opening (through cleavage of the cyclic ester oxygen–acyl bond) and insertion into the Sm–HBH_3 bond followed by reduction of the carbonyl function by the BH_3 end-group ligand, leads to the samarium alkoxyborane derivative [Sm(Cp*)$_2${O(CH_2)$_6$O(BH_2)}] (**2**). This compound subsequently initiates the polymerization of ε-CL through a coordination–insertion mechanism. Finally, upon hydrolysis, α,ω-dihydroxypoly(ε-caprolactone), HO(CH_2)$_5$C(O){O(CH_2)$_5$C(O)}$_n$O(CH_2)$_6$OH (**4**) is recovered. The stereoelectronic contribution of the two Cp* ligands appears to slow down the polymerization and to limit transesterification reactions.

Keywords: borohydride · hydroxytelechelic · lactones · rare-earth metal · ring-opening polymerization

Introduction

Aliphatic polyesters are of major interest by virtue of their biodegradability and biocompatibility properties.[1,2] In this field, we have focused our investigations on poly(ε-caprolactone), poly(lactide), and poly(carbonate), synthesized by ring-opening polymerization initiated by rare-earth complexes.[3–8] Indeed, rare-earth derivatives are now well recognized as efficient initiators for the polymerization of a wide variety of monomers, including both polar and nonpolar species, olefinic and vinylic compounds, cyclic esters, and amides.[9–16] This has resulted from the developments associated with lanthanide organometallic chemistry, which have revealed Group 3 metal derivatives to be valuable and versatile reagents. The highly electropositive nature of the lanthanide leads to predominantly ionic compounds in which ligand exchange and insertion is favored,[17] thereby making rare-earth complexes suitable initiators for polymerization reactions.[12]

To date, most polymerization studies have involved the use of homoleptic trivalent rare-earth species LnX_3 (Ln = rare-earth metal, X = R, OR, NR_2), which are readily accessible either commercially or by synthetic means.[3–16] However, the major drawback in using such trifunctional initiators is that several chains may grow on a single metal center. This results in a lower degree of control over the polymerization reactions; in particular, the kinetics is difficult to determine, the polymerization mechanism is not straightforward, and polymer mixtures displaying various molecular weights and microstructures are obtained. Besides, compounds such as the tris(alkoxide)s, $Ln(OR)_3$, have been shown to be aggregated, thereby further complicating the understanding of the overall polymerization process.[4–6]

In this regard, single-site catalysts, L_xMX (L = spectator ligand, X = functional group), as the name implies, can constitute uniform polymerizing species that enable control of the molecular weight, the molecular weight distribution, and stereochemistry and the end-group structure of the polymer, as well as co-monomer incorporation.[12,19] The role of the ancillary ligand set L_x, which remains bound to the metal center during the whole process, is not only to maintain a

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single type of active polymerization site X, but also to modify the reactivity of the metal throughout the polymerization. Eventually, it may also allow the characterization of the initiator precursor or of the active species and thus further enable detailed structural and mechanistic studies.

Polymerization by single-site trivalent rare-earth initiators, supported or unsupported, has been essentially developed with olefinic monomers.[18,19] With lactones, monohapto mono-alkoxide,[20–24] -amide,[24–29] -hydride,[23] -alkyl,[23,30–35] -halide,[24,36,37] and -phosphorane iminato[38] organo-rare-earth derivatives have been used as effective initiators. These incorporated spectator ligands as varied as halide,[20,37,38] alkyl,[22] cyclopentadienyl,[23,26,30,31,33–35] bridged fluorenyl cyclopentadienyl,[28] phospholyl,[20] cyclooctatetraenyl,[25,37] pyrrolyl,[27] phenolato,[29] acetate,[21] amide,[36,37] amidinate,[24,25] guanidinate,[32] and phosphorane iminato,[26,38] as well as mono- or dinuclear and even "ate"[22,24] complexes.

Following our initial work on the polymerization of lactones by novel rare-earth derivatives such as borohydride complexes,[3] we investigated the use of a lanthanocene monoborohydride complex, $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) ($Cp^* = \eta$-C_5Me_5; thf = tetrahydrofuran) in the ring-opening polymerization of ε-caprolactone (ε-CL). Indeed, while the versatility of borohydride complexes has been revealed by organolanthanide chemistry, borohydride species are known to be less aggregated, and thus more soluble, than the corresponding alkoxides.[39–47] Moreover, the borohydride ligand can be characterized by NMR and IR spectroscopy,[39–47] enabling accurate identification of its derivatives and thus allowing a deeper understanding and consequently a better control of the polymerization process.

Herein, we present experimental and mechanistic features of the ring-opening polymerization of ε-CL initiated by the samarium(III) monosite complex **1a**. Within 30 min, total conversion to α,ω-dihydroxytelechelic poly(ε-caprolactone)s is achieved, with controlled molecular weights, relatively narrow polydispersities, and limited side reactions. The use of pentamethylcyclopentadienyl ligands, which are known to provide solubility and to impart crystallinity,[12,17] allowed verification of the polymerization process.[3] To the best of our knowledge, this is the first report of polymerization of a cyclic ester using a monosite transition-metal complex with a borohydride ligand.

Results and Discussion

Synthesis of $[Sm(Cp^*)_2(BH_4)(thf)]$ (1a): The initial synthesis of $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) from $[SmCl_3(thf)_2]$, NaCp*, and $NaBH_4$ in THF (59% yield) was reported by Schumann et al.[48] However, this one-pot approach requires reflux temperature and the prior preparation and characterization of the THF-solvated samarium trichloride precursor $[SmCl_3(thf)_2]$, an associated difficulty in this case being the quantification of the number of coordinated THF molecules. We have isolated compound **1a** in similar yields from the direct reaction of $[Sm(BH_4)_3(thf)_3]$ with NaCp* in toluene at room temperature. $[Sm(BH_4)_3(thf)_3]$ is easily prepared and can be characterized by NMR spectroscopy, the THF being directly quantified by comparison of its ^{1}H NMR integrals with that of the BH_4 group.[39,40] Moreover, the formation of **1a** is instantaneous at room temperature.

Polymerization features: Various ε-CL polymerizations were performed in CH_2Cl_2/toluene under homogeneous conditions with a monomer concentration of 1.13 mol L^{-1} and an initiator concentration $[\mathbf{1a}]_0$ ranging from 2.0 to 27.8 × 10^{-3} mol L^{-1} (Table 1, Table 2). Under such conditions, the monosite borohydride samarium(III) complex **1a** is able to initiate the ring-opening polymerization of ε-CL at room temperature to directly afford α,ω-dihydroxytelechelic poly(ε-caprolactone).

Table 1. Polymerization of ε-CL initiated by $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) (temperature: 21 °C; $[\varepsilon\text{-CL}]_0$ = 1.13 mol L^{-1}; solvent: CH_2Cl_2/toluene (30:70)).

$[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$	$[\mathbf{1a}]_0$ [10^{-3} mol L^{-1}]	Reaction time [min]	Monomer conv.[a] [%]
50	22.7	3	74
41	27.8	30	100
135	8.4	5	84
126	9.0	30	100
342	3.3	20	71
305	3.7	30	100

[a] Calculated from ^{1}H NMR analyses.

Table 2. Polymerization of ε-CL initiated by $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) (temperature: 21 °C; $[\varepsilon\text{-CL}]_0$ = 1.13 mol L^{-1}; solvent: CH_2Cl_2/toluene (30:70); polymerization time: 30 min).

$[\varepsilon\text{-CL}]_0/[BH_4]_0$	$[\mathbf{1a}]_0$ [10^{-3} mol L^{-1}]	Monomer conv.[a] [%]	$\bar{M}_{n(theo)}$ [g mol^{-1}]	$\bar{M}_{n(exp)}$[b] [g mol^{-1}]	PDI[c]	N_n[d] (chain/Sm)
72	15.6	100	8218	7893	1.3	1.04
126	9.0	100	14382	11381	1.3	1.26
177	6.4	100	20203	13707	1.3	1.47
305	3.7	99	34465	22676	1.3	1.52
565	2.0	99	63844	39146	1.3	1.63
283[e]	4.0	85	27456	16404	1.2	1.67

[a] Calculated from ^{1}H NMR analyses. [b] SEC values of precipitated polymer samples corrected with the coefficient 0.56. [c] Polydispersity indices calculated from SEC chromatogram traces. [d] Calculated from $\bar{M}_{n(theo)}/\bar{M}_{n(exp)}$. [e] In the presence of 2,6-di-*tert*-butylpyridine; reaction time: 6 h.

The polymerization is relatively fast since, whatever the $[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$ ratio, the monomer conversion is quantitative within 30 min. Moreover, the monomer conversion increases, as expected, with time and initiator concentration values $[\mathbf{1a}]_0$ (Table 1).

For a monosite initiator, the concentration in active site is supposed to be equal, in the absence of termination or transfer reactions, to the initiator concentration $[BH_4] = [\mathbf{1a}]$; theoretical molecular weights $\bar{M}_{n(theo)}$ were thus calculated from the initial concentration in samarium initiator

$[\mathbf{1a}]_0$. As reported in Table 2, relatively high molecular weight polyesters with relatively narrow polydispersities (~1.3) were obtained in good yields. The experimental $\bar{M}_n$ values increased linearly with $[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$ as illustrated in Figure 1. However, while $\bar{M}_{n(exp)}$ are in good agreement with $\bar{M}_{n(theo)}$ at low $[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$ ratios, a deviation is observed when this ratio increases: the higher the ratio, the larger the divergence. Such behavior has previously been reported for the polymerization of ε-CL initiated by a samarium phosphorane iminato derivative.[38]

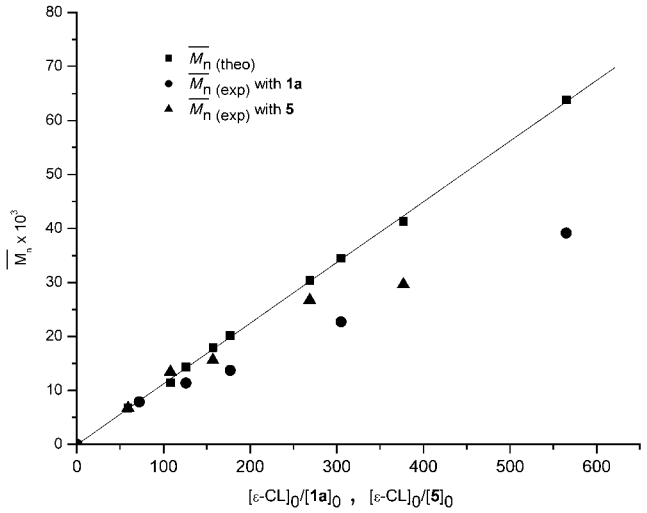


Figure 1. Plots of $\bar{M}_{n(exp)}$ or $\bar{M}_{n(theo)}$ versus $[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$ or $[\varepsilon\text{-CL}]_0/[\mathbf{5}]_0$.

The deviation observed in Figure 1 might result either from common side reactions (inter- and intramolecular transesterifications) occurring simultaneously with the propagation in the ring-opening processes, or from specific transfer reactions.

Regarding the occurrence of conventional transesterification reactions, although SEC (SEC = size-exclusion chromatography) analysis of the polymerization medium shows no other detectable signals besides that of the polymer in the low molecular weight region, cyclic and linear oligomers were however detected by MALDI-TOF MS analyses of the soluble polymerization residues (recovered after polymer precipitation). Nevertheless, the amount of residue recovered was always negligible (<5%) relative to the polymer conversion and the PDI (polydispersity index) values remained constant and relatively narrow throughout the polymerization (Table 3). Therefore, even though some inter- and intramolecular transesterification reactions take place, their contribution to the actual deviation should remain negligible.

Since the experimental average molecular weight values are lower than the theoretical ones, it may be assumed that more than one polymer chain is formed per initiator molecule. Thus, transfer reactions might account for the discrepancy between $\bar{M}_{n(exp)}$ and $\bar{M}_{n(theo)}$. Considering the nature of the active polymer chain $[Sm(Cp^*)_2(\{O(CH_2)_5C(O)\}_{n+1}\text{-}O(CH_2)_6O(BH_2))]$ (**3**) (vide infra, Scheme 2), these transfer reactions might stem from polymerizations initiated by the $\text{-}O(BH_2)$ chain end. To assess this possibility, we first attempted to inhibit any transfer reaction due to a putative hydride species arising from **1a** by adding 2,6-di-*tert*-butylpyridine as a proton trap; the same $\bar{M}_{n(exp)}/\bar{M}_{n(theo)}$ divergence was observed (Table 2). We then tried to initiate the polymerization of ε-CL using a model compound for the $\text{-}O(BH_2)$ chain end. Given that, to the best of our knowledge, no $(RO)BH_2$ compound is known or available, we attempted to synthesize poly(ε-CL) from the resulting product of the reaction of BH_3·THF with HO*t*Bu. We also tested BH_3·THF and $B(OEt)_3$ as potential initiators. In no case was any polymer formed.

Thus, to date, the reasons for the observed difference between $\bar{M}_{n(exp)}$ and $\bar{M}_{n(theo)}$ values are not clear and further comprehensive investigations are in progress.[49]

Polymerization mechanism: One of the major reasons for using a monosite initiator such as **1a** for the polymerization of ε-CL, besides allowing the growth of only one polymer chain per lanthanide center, is to facilitate deeper insights into the process. Indeed, mechanistic studies on the polymerization of ε-CL with trifunctional borohydride lanthanide complexes have involved initiation by $[Nd(BH_4)_3(thf)_3]$ (Nd-**1a**).[3] The presence of permethylated cyclopentadienyl ligands as spectator groups on the samarium center provides a different stereoelectronic environment at the metal, which is likely to result in an overall slightly different reactivity.[12,21] In fact, slower formation, improved stability, and/or better solubility of the intermediates might enable their better isolation and/or identification.

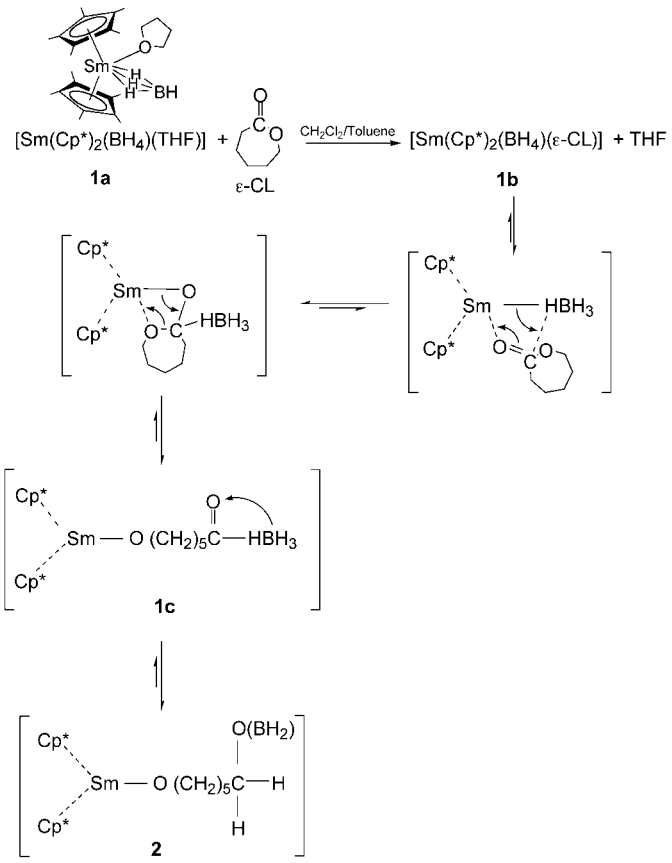
Initiation of the polymerization of ε-caprolactone by $[Sm(Cp^*)_2(BH_4)(thf)]$ (1a): In the complexes referred to hereafter, the samarium is likely to have Lewis base molecules (THF, ε-CL, γ-butyrolactone (γ-BL)) coordinated to it to satisfy stereoelectronic factors; for the sake of clarity, these have been omitted in the schemes and discussion, and the species are represented in square brackets. Furthermore, the BH_4 ligand bonded to the samarium in **1a**, which is most likely tridentate in the solid-state structure ($[Sm(\mu_2\text{-}H)_3BH]$) as illustrated in Scheme 1,[48] is written as $H{-}BH_3$ for clarity, and the Cp* ligands, which are pentahapto (η^5-C_5Me_5), are illustrated as Cp*–––Sm.

First, we studied by NMR spectroscopy the equimolar reaction of $[Sm(Cp^*)_2(BH_4)(thf)]$

Table 3. Polymerization of ε-CL initiated by $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) (temperature: 21°C; $[\varepsilon\text{-CL}]_0$ = 1.13 mol L^{-1}; solvent: CH_2Cl_2/toluene (30:70)).

$[\varepsilon\text{-CL}]_0/[\mathbf{1a}]_0$	$[\mathbf{1a}]_0$ [10^{-3} mol L^{-1}]	Reaction time [min]	Monomer conv.[a] [%]	$\bar{M}_{n(theo)}$ [g mol^{-1}]	$\bar{M}_{n(exp)}$[b] [g mol^{-1}]	PDI[c]
135	8.4	5	84	12943	12794	1.3
126	9.0	30	100	14382	12065	1.3

[a] Calculated from ^{1}H NMR analyses. [b] SEC values of crude polymer samples corrected with the coefficient 0.56. [c] Polydispersity indices calculated from SEC chromatogram traces.



Scheme 1. Proposed mechanism for the initiation step of the polymerization of ε-caprolactone initiated by $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**).

(**1a**) with ε-CL in CD_2Cl_2, which, through Lewis base exchange, gave $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**). Indeed, the displacement of THF by ε-CL is to be expected based on previous studies highlighting the stronger coordinating strength of the lactone over the ether.[3,36,37,50] Although **1b** could not be isolated since it rapidly evolved towards the formation of **2** (vide infra), it could be characterized in situ by its ^1H NMR (Figure 2) and $^{11}B\{^1H\}$ NMR spectra. The ^{11}B NMR chemical shift of **1b** is similar to that of **1a**.

The analogous γ-butyrolactone adduct, $[Sm(Cp^*)_2(BH_4)(\gamma\text{-BL})]$, **1b**/γ-BL, was prepared from **1a** and γ-BL to corroborate the formation of the intermediate **1b**. Since the γ-BL monomer has a positive standard polymerization enthalpy, it cannot be polymerized and the preparation of **1b**/γ-BL is thus eased by its impossible evolution towards the formation of **2**/γ-BL. For both compounds **1b** and **1b**/γ-BL, the borohydride signal is shifted downfield by 4.5 ppm relative to that observed in **1a**, the signals of the liberated THF appear in the diamagnetic region, and the signals of ε-CL or γ-BL coordinated to Sm^{III} are slightly shifted upfield relative to the free monomer signals (Figure 2, Figure 3). Since the most downfield resonance of γ-BL overlaps with one of the THF peaks, more than 1 equivalent of γ-BL (4 equiv, **1b**/3γ-BL) is required in order to displace and resolve the γ-butyrolactone signals, which, in fact, then correspond to the averaged peaks of free and coordinated γ-BL (Figure 3). The γ-BL peaks were then assigned on the basis of a 2D ^1H-^1H COSY NMR spectrum of **1b**/γ-BL, which also confirmed the coordination of the lactone to the samarium center through the carbonyl oxygen atom in a C=O→Sm interaction. Indeed, this induces the largest shielding on the signal of the $CH_2C(O)$ unit adjacent to the samarium, while both the more distant groups OCH_2 and OCH_2CH_2 are similarly affected by the paramagnetic metal, the methylene group in the α-position to the oxygen giving rise to the most downfield peak. The signals of the coordinated ε-CL in **1b** were then assigned on the same basis (Figure 2).

Once the first ε-CL molecule is coordinated through its carbonyl to the samarium center in **1b**, it inserts into the Sm–HBH_3 bond as depicted in Scheme 1. This involves conventional oxygen–acyl bond rupture,[3,12,13] as evidenced by NMR analysis of the final polymer chain ends. Indeed, the spectra display the presence of only one type of end group, a hydroxyl one, indicative of nucleophilic attack at the lactone carbon atom followed by oxygen–acyl bond cleavage (Figure 4, Figure 5). After this insertion, the carbonyl function immediately reacts with the adjacent borohydride to form a $CH_2O(BH_2)$ unit in the alkoxyborane intermediate $[Sm(Cp^*)_2\{O(CH_2)_6O(BH_2)\}]$ (**2**) (Scheme 1).

Finally, to gain further confirmation of the identities of the intermediates $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**) and

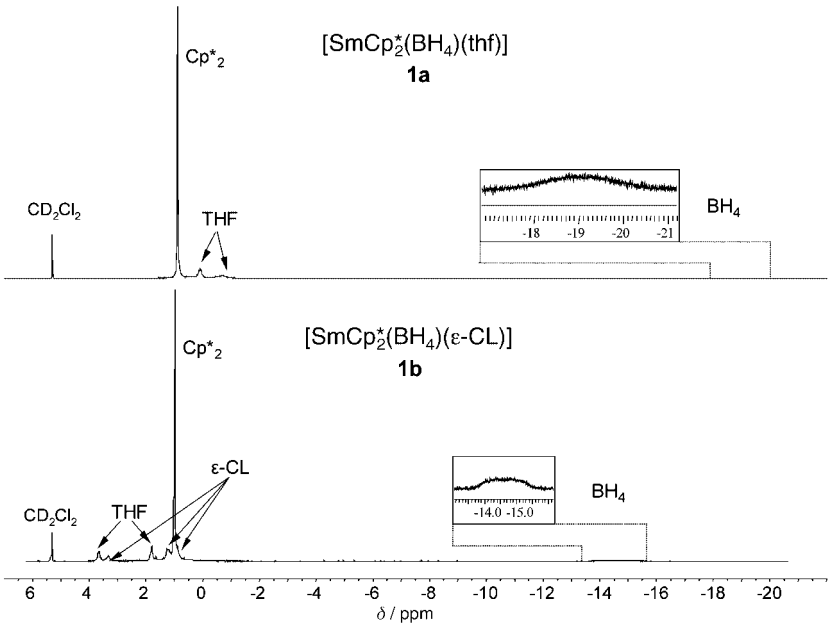


Figure 2. ^1H NMR spectra of $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) and $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**) in CD_2Cl_2.

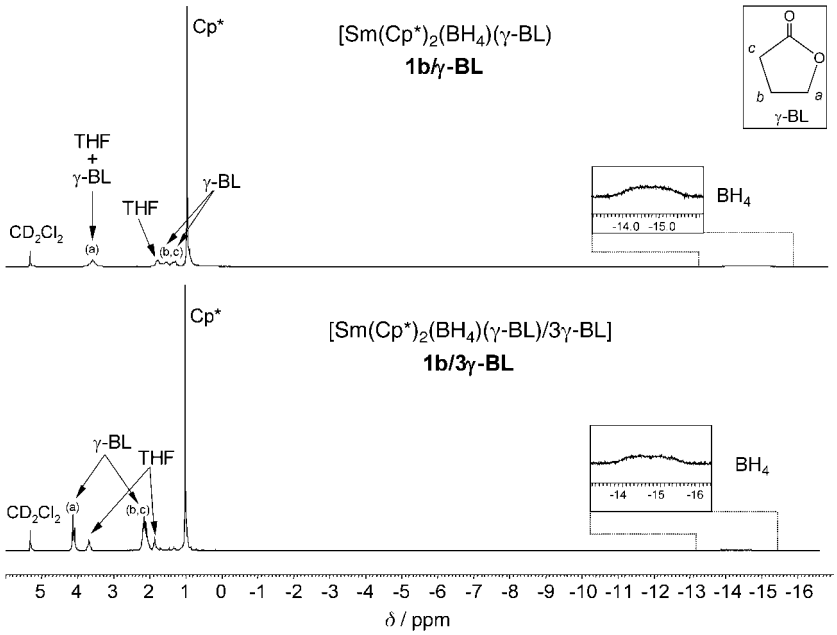


Figure 3. ^{1}H NMR spectra of [Sm(Cp*)$_2$(BH$_4$)(γ-BL)] (**1b**/γ-BL) and [Sm(Cp*)$_2$(BH$_4$)(γ-BL)/3γ-BL] (**1b**/3γ-BL) in CD_2Cl_2.

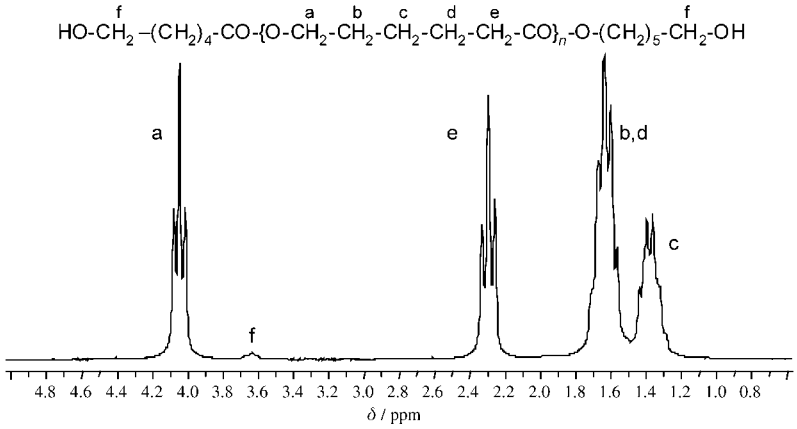


Figure 4. ^{1}H NMR spectrum of $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_{39}O(CH_2)_6OH$ in $CDCl_3$.

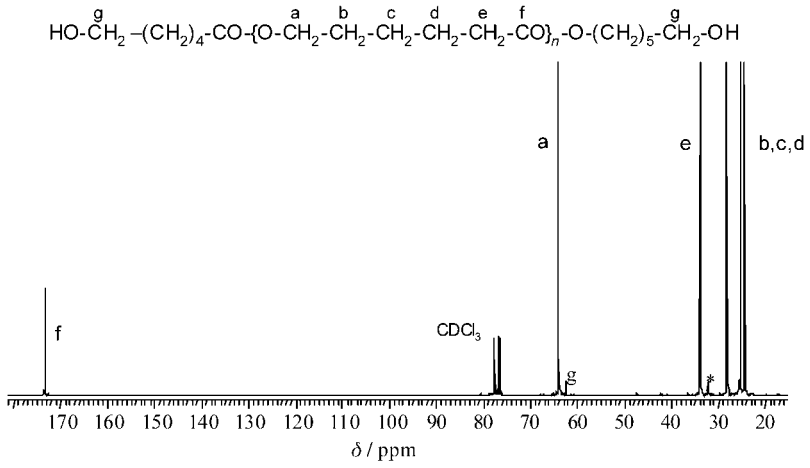
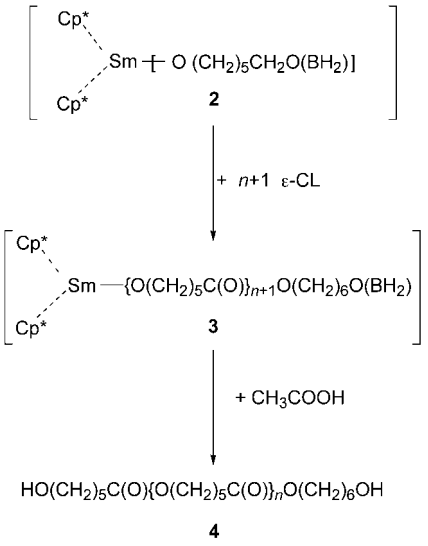


Figure 5. ^{13}C NMR spectrum of $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_{39}O(CH_2)_6OH$ in $CDCl_3$.

[Sm(Cp*)$_2${O(CH$_2$)$_6$O(BH$_2$)}] (**2**) each of these two products was independently hydrolyzed; a mixture of ε-CL and 1,6-hexanediol was obtained from both compounds. In either experiment, the ε-CL can only result from the coordinated ε-CL of **1b** and not from any excess lactone previously eliminated by washing. Similarly, recovered 1,6-hexanediol can only come from the intermediate **2** and not from **1b** or **1c**. Thus, the results strongly support the rapid conversion of **1c** into **2**, that is, the rapid reaction of BH_3 with the carbonyl group. Formation of this alcohol as a hydrolysis product also confirms that oxygen–acyl bond cleavage occurs in the monomer instead of an oxygen–alkyl bond cleavage, since no HOC(O) linkage is observed in the NMR spectra of the hydrolyzed samples. Furthermore, these results might also suggest the existence of an equilibrium between **1b** and **2**. One would expect this equilibrium to be displaced towards the formation of **2**, as this species is less soluble than **1b**. Similarly, the addition of an excess of ε-CL favors the formation of **2**. These findings further support the identities of intermediates [Sm(Cp*)$_2$(BH$_4$)(ε-CL)] (**1b**) and [Sm(Cp*)$_2${O(CH$_2$)$_6$O(BH$_2$)}] (**2**) and are fully consistent with the proposed mechanism for the initiation process of the polymerization of ε-caprolactone initiated by [Sm(Cp*)$_2$(BH$_4$)(thf)] (**1a**) as depicted in Scheme 1.

Propagation of the polymerization of ε-CL by the alkoxide complex [Sm(Cp*)$_2$ {O(CH$_2$)$_6$O(BH$_2$)}] (2): Analysis of the structures of low molecular weight polymers by ^{1}H and ^{13}C NMR spectroscopy, SEC, and MALDI-TOF MS allowed the ε-CL chain growth process from [Sm(Cp*)$_2$-{O(CH$_2$)$_5$CH$_2$O(BH$_2$)}] (**2**) to be established.

The alkoxide complex **2**, as generated in the initiation step, undergoes insertion of ε-CL through a coordination–insertion (or pseudo-anionic) type mechanism to form the active polymer chain $[Sm(Cp^*)_2[\{O(CH_2)_5C(O)\}_{n+1}O(CH_2)_6O(BH_2)]]$ (**3**) (Scheme 2). Subsequent addition of



Scheme 2. Proposed mechanism for the propagation step of the polymerization of ε-caprolactone initiated by $[Sm(Cp^*)_2\{O(CH_2)_5(CH_2)O(BH_2)\}]$ (**2**).

acetic acid to **3** results in hydrolysis of the Sm–O bond at one end and of the -$O(BH_2)$ group at the other, to finally afford a polymer capped at each end by a hydroxy group (**4**) (Scheme 2). Indeed, we have verified experimentally that the polymerization of ε-CL initiated by previously isolated compound **2** successfully gives dihydroxy-poly(ε-caprolactone).

In addition, the ^1H and ^{13}C NMR spectra display, besides the polymer chain peaks, single signals at $\delta = 3.62$ and $\delta = 62.10$ ppm, respectively, attributable to the -CH_2OH chain end (Figure 4, Figure 5). Also, no other chain end signal is observed and there is no evidence of a -C(O)OH linkage; again, this supports the view that the ring-opening process occurs via an oxygen–acyl bond cleavage and that both chain ends of the polymers, prepared from initiator **1a**, are hydroxyl groups.[3]

Influence of the spectator ligands on the polymerization of ε-CL: Through the use of a monoinitiator, $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**), in which the two Cp* ligands provide a modified stereoelectronic environment at the lanthanide, the first intermediate of the initiation step $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**), as well as the real initiator $[Sm(Cp^*)_2\{O(CH_2)_5CH_2O(BH_2)\}]$ (**2**) could be characterized; this represents a significant improvement on our initial study in terms of available information.[3] Although the metal (Nd) was different in the previous work, the stereoelectronic contribution of the two Cp* ligands in **1a** seems to be significant and sufficient to render the caprolactone intermediate $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**) more stable than the neodymium analogue $[Nd(BH_4)_3(\varepsilon\text{-CL})_3]$ (Nd-**1b**)), thus making it easier to characterize. Indeed, with the Cp* ligands (as in **1a** and **1b**) being bulkier and more electron-donating than the two BH_4 groups (as in $[(BH_4)_2Nd(BH_4)(thf)_3]$ (Nd-**1a**) and $[(BH_4)_2Nd(BH_4)(\varepsilon\text{-CL})_3]$ (Nd-**1b**), the samarium center in organometallic compounds **1a** and **1b** is more electron-rich than the neodymium center in the corresponding species Nd-**1a** and Nd-**1b**, which are thus less stable.

To truly evaluate the influence of the two ancillary Cp* ligands in **1a**, we have compared the features of polyesters formed upon polymerizing ε-CL with the two distinct samarium derivatives **1a** and $[Sm(BH_4)_3(thf)_3]$ (**5**). Results related to the polymerization of ε-CL with **5** are gathered in Table 4. Within 10 min, the monomer conversion is quantitative. Therefore, for a similar concentration in active sites ($[BH_4]_0$), the rate of polymerization is faster with **5** (10 min) than with **1a** (30 min). Indeed, with the samarium being more electron-rich in **1a** compared to **5**, complex **1a** is less reactive than **5** toward the incoming ε-CL during both the coordination and insertion steps. Moreover, compounds **1b** and **2** will react more slowly with ε-CL than the analogous $[Sm(BH_4)_3(\varepsilon\text{-CL})_3]$ and $[Sm\{O(CH_2)_5CH_2O(BH_2)\}_3]$ derivatives. Similar results have been obtained with other tris(borohydride) rare earth complexes $[Ln(BH_4)_3(thf)_3]$ (Ln = La, Nd, Sm).[49]

Table 4. Polymerization of ε-CL initiated by $[Sm(BH_4)_3(thf)_3]$ (**5**) (temperature: 21 °C; $[\varepsilon\text{-CL}]_0 = 1.13\ mol\,L^{-1}$; solvent: CH_2Cl_2/toluene (30:70); reaction time: 10 min).

$[\varepsilon\text{-CL}]_0/[BH_4]_0$[a]	$[\mathbf{5}]_0$ [10^{-3} mol L^{-1}]	Monomer conv.[b] [%]	$\bar{M}_{n(theo)}$ [g mol^{-1}]	$\bar{M}_{n(exp)}$[c] [g mol^{-1}]	PDI[d]
59	6.4	100	6734	7343	1.3
108	3.5	93	11464	13455	1.4
157	2.4	100	17920	15604	1.5
269	1.4	99	30397	26716	1.4
377	1.0	96	41310	29614	1.4

[a] $[\mathbf{5}]_0 = [Sm(BH_4)_3(thf)_3]_0 = 3[BH_4]_0$. [b] Calculated from ^1H NMR analyses. [c] SEC values of precipitated polymer samples corrected with the coefficient 0.56. [d] Polydispersity indices calculated from SEC chromatogram traces.

As with the monosite initiator **1a**, a deviation between $\bar{M}_{n(exp)}$ and $\bar{M}_{n(theo)}$ is also observed with the tris(borohydride) initiator **5** (Figure 1). The polydispersity indices are, however, generally higher in the case of **5** (Table 2, Table 4).

Further support of the positive impact of the Cp* ligands on the polymerization process is gained by considering the transesterification reactions. As already mentioned, in ring-opening polymerization of cyclic esters, especially for processes involving anionic and cationic initiators, back-biting and reshuffling side reactions are commonly observed along with a broadening of the molecular weight distribution.[12–14,21] With our initiator **1a**, we have shown that such transesterification reactions are largely suppressed and that PDI values remain relatively low. Taking into account the fact that the volume of the polymer chain is greater than that of the monomer, the steric hindrance around the active center provided by the two permethylated cyclopentadienyl

rings in **1a** may subsequently better shield the lanthanide polymerization site from any potential coordination of the polymer chains; consequently, this might improve the overall control of the process. Such a phenomenon, by which transesterification reactions are kinetically suppressed, has been reported previously.[12,21] Therefore, in searching for a monofunctional initiator, the influence of the ancillary ligand set should not be underestimated. Indeed, even if these ligands do not initiate polymerization, which is the reason for their designation as "spectator" ligands, they have a significant stereoelectronic effect on the polymerization process, in agreement with previous reports.[29]

Conclusion

The monosite samarium borohydride complex $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) has been shown to be an efficient initiator for the ring-opening polymerization of ε-caprolactone. As an organometallic derivative, **1a** offers the possibility of comprehensively investigating the polymerization mechanism. The present study confirms and provides further support for the mechanism previously reported for the polymerization of ε-CL by rare-earth borohydride initiators, based on the use of $[Nd(BH_4)_3(thf)_3]$ as initiator.[3] Following initial coordination of the ε-CL monomer to the metal to give $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (**1b**), the propagation proceeds from $[Sm(Cp^*)_2\{O(CH_2)_6O(BH_2)\}]$ (**2**) as the active species, which results from the insertion of ε-CL into the Sm–H bond followed by an intramolecular reaction of the borohydride end-group with the adjacent carbonyl function. In addition, the use of bulky inactive Cp* ligands contributes to an overall better control of the polymerization process. Further investigations on the polymerization of cyclic esters initiated by lanthanide borohydride complexes are part of our ongoing research.[49]

As a borohydride species, **1a** provides an easy and direct synthesis of α,ω-dihydroxytelechelic poly(ε-caprolactone)s, which may further act as macroinitiators to prepare novel macromolecular architectures, as is presently being investigated in our research group.

Experimental Section

Materials: All manipulations were performed under an inert atmosphere (argon, <3 ppm O_2) by using standard Schlenk, vacuum line, and glovebox techniques.[51] Solvents were thoroughly dried and deoxygenated by standard methods and distilled before use.[52] CD_2Cl_2, $CDCl_3$, and $[D_8]$toluene were dried over a mixture of 3 and 4 Å molecular sieves. NaCp* was obtained by drying THF solutions purchased from Aldrich. All other reagents were commercially available (Aldrich). ε-Caprolactone (ε-CL, Lancaster) was successively dried over CaH_2 (for at least one week) and then over 4,4′-methylenebis(phenylisocyanate); ^{1}H NMR (CD_2Cl_2): δ = 4.18 (t, J(H,H) = 4.6 Hz, 2H), 2.57 (t, J(H,H) = 5.1 Hz, 2H), 1.77 ppm (m, 6H). γ-Butyrolactone (γ-BL; Aldrich) was dried over CaH_2; ^{1}H NMR (CD_2Cl_2): δ = 4.29 (t, J(H,H) = 7.0 Hz, 2H), 2.42 (t, J(H,H) = 8.1 Hz, 2H), 1.25 ppm (q, J(H,H) = 7.6 Hz, 2H). $[Sm(BH_4)_3(thf)_3]$ was synthesized from $SmCl_3$ (Aldrich) following the literature procedure.[39,40]

Instrumentation and measurements: ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker AC200 instrument at 25 °C and were referenced internally using the residual protic solvent resonance relative to tetramethylsilane (δ = 0 ppm). ^{11}B NMR (128 MHz) spectra were recorded on a Bruker AC400 instrument at 25 °C and were referenced to an external standard of BBr_3 (1.0 M in hexane, δ = +40.0 ppm). 2D HSQC and 2D ^{1}H-^{1}H COSY spectra were recorded on a Bruker Advance DPX 300 instrument.

Molecular weight ($\bar{M}_n$) and polydispersity index (PDI) determinations were performed in THF at 20 °C (flow rate 0.8 mL min^{-1}) on a Varian apparatus equipped with a refractive index detector and four TSK gel columns with respective pore sizes of 250, 1500, 10^4, and 10^5 Å and 5 μm bead size. The polymer samples were dissolved in THF (2 mg mL^{-1}). Average molar mass values were calculated from the linear polystyrene calibration curve using the previously reported correction coefficient ($\bar{M}_{n(exp)} = \bar{M}_{n(SEC)}$ 0.56);[5] the absolute $\bar{M}_n$ values of our polymers determined by osmometry were in agreement with this coefficient. Low molecular weights (<10000) were also calculated from ^{1}H NMR analyses; the values were determined from the integration ratio of the main chain signal (OCH_2, 2nH) at δ = 4.05 ppm relative to the end group methylene proton signal (CH_2OH, 4H) at δ = 3.64 ppm. The monomer conversion was calculated from the ^{1}H NMR spectra from the crude polymer sample and the polymer conversion was obtained by gravimetric measurements of the precipitated polyester.

MALDI-TOF MS experiments were carried out on a TOF-SPEC apparatus (Micromass) equipped with a pulsed N_2 laser (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and an accelerating voltage of 20 kV. Polymer samples were dissolved in THF (40 mg mL^{-1}) and solutions of ditranol/THF (10 mg mL^{-1}) and NaI/MeOH (10 mg mL^{-1}) were prepared as matrix and cation source, respectively. All three solutions were then mixed in a 1:10:1 volume ratio, respectively, deposited on the sample target, and then air-dried.

Synthesis of $[Sm(Cp^*)_2(BH_4)(thf)]$ (1a): $[Sm(BH_4)_3(thf)_3]$ (1.62 g, 3.94 mmol) and NaCp* (1.25 g, 7.90 mmol) were placed in a reaction flask. Toluene (60 mL) was condensed into the flask and the resulting mixture, which rapidly became dark orange, was stirred at room temperature for 15 h. After drying, the complex was thoroughly extracted with pentane to afford an orange crystalline powder, which was identified by ^{1}H and ^{13}C NMR analyses as $[Sm(Cp^*)_2(BH_4)(thf)]$ (**1a**) and isolated in 60% yield (0.99 g, 1.95 mmol); ^{1}H NMR (CD_2Cl_2): δ = 0.88 (s, 30H; C_5Me_5), 0.04 (br s, $w_{1/2}$ = 30 Hz, 4H; THF), −0.90 (br s, $w_{1/2}$ = 70 Hz, 4H; THF), −19.05 ppm (v br s, $w_{1/2}$ = 560 Hz, 4H; BH_4; see Figure 3); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 115.2 (C_5CH_3), 67.9 (THF), 22.7 (THF), 19.0 ppm (C_5CH_3). These NMR data are in agreement with those reported for this complex in C_6D_6 solution by Schumann.[48] ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = −51.0 ppm (br s, $w_{1/2}$ = 285 Hz; BH_4).

Typical polymerization procedure: Under vacuum, a 1.5 M solution of ε-CL (0.5 mL, 4.5 mmol) in toluene (2.5 mL) was added via a burette to a stirred solution of the pre-initiator **1a** (4–6 mg, 8–11 μmol) in CH_2Cl_2 (1 mL) at room temperature. A yellow gel was consistently formed within 10 min. The polymerization was then stopped after 30 min by the addition of a large excess, relative to **1a**, of a solution of acetic acid (16.5×10^{-3} mol L^{-1}) in toluene, and then the resulting mixture was dried. The crude polymer obtained was redissolved in CH_2Cl_2, purified by precipitation from a large amount of cold pentane followed by centrifugation, and finally dried under dynamic vacuum. The resulting polymers were then characterized by ^{1}H and ^{13}C NMR, SEC, and MALDI-TOF MS analyses.

Attempted polymerization of ε-CL initiated by BH_3·THF, $B(OEt)_3$ or BH_3·THF/HOtBu: A solution of ε-CL (0.5 mL, 4.5 mmol) in toluene (2.5 mL) was added under argon to a solution of BH_3·THF (1 M in THF, 3 μL, 3 μmol) or $B(OEt)_3$ (4 μL, 23.5 μmol) in CH_2Cl_2 (1 mL) or to a mixture of BH_3·THF (1 M in THF, 150 μL, 150 μmol) and HOtBu (14 μL, 146 μmol), initially placed in a Schlenk tube. After 30 min, the reaction was stopped by the addition of an acetic acid solution (16.5×10^{-3} mol L^{-1}) in toluene; the resulting mixture was dried and analyzed by ^{1}H NMR spectroscopy, which showed only unreacted monomer.

Stoichiometric reaction of 1a with ε-CL: a) Formation of $[Sm(Cp^*)_2(BH_4)(\varepsilon\text{-CL})]$ (1b): In an NMR tube, ε-CL (4.4 μL, 39.7 μmol) was added to a solution of **1a** (19.8 mg, 39.0 μmol) in CD_2Cl_2 (0.3 mL). The tube was then placed in an ultrasound bath at room temperature for

5 min resulting in a bright-orange solution (lighter than the solution of **1a** in CD_2Cl_2), which was then analyzed. ^1H NMR (CD_2Cl_2): δ = 3.64 (s, 4H; THF), 3.26 (br s, $w_{1/2}$ = 30 Hz, 2H; -OCH_2), 1.78 (s, 4H; THF), 1.17 (br s, $w_{1/2}$ = 44 Hz, 2H; $CH_2C(O)$), 0.98 (s, 30H; C_5Me_5), 0.88 (s overlap with C_5Me_5, 6H; $CH_2CH_2CH_2$), −14.75 ppm (br q, $w_{1/2}$ = 545 Hz, 4H; BH_4) (Figure 2). These signals were assigned on the basis of their integrals and by comparison with the corresponding peaks of [Sm(Cp*)$_2$(BH_4)(γ-BL)] (**1b**/γ-BL) (see below). A ^{13}C NMR spectrum could not be recorded for the sample rapidly proceeded towards the formation of **2**. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −46.6 ppm (s, $w_{1/2}$ = 265 Hz; BH_4). Compound **1b** was then hydrolyzed by the addition of H_2O to an equimolar solution of **1a** and ε-CL in toluene, which had been previously stirred for 5 min and carefully washed with pentane to remove any excess reactants. Based on NMR and gas chromatographic analyses, ε-CL was recovered in >80% yield along with 1,6-hexanediol.

b) Formation of [Sm(Cp*)$_2${O(CH_2)$_6$O(BH_2)}] (2): ε-CL (44.3 mg, 43.0 μL, 387.9 μmol) and **1a** (198.9 mg, 391.7 μmol) were placed in a reaction flask with toluene (40 mL), and the resulting solution was stirred at room temperature for 30 min. After removal of the solvent, the recovered product was thoroughly washed with pentane (to remove the excess **1a**) to afford a yellow solid in 97% yield (208.9 mg, 379.9 μmol); elemental analysis calcd (%) for $C_{26}H_{44}BO_2Sm$: C 56.80, H 8.07, B 1.97; found: C 56.53, H 7.93, B 1.84. The ^1H NMR spectrum of this sample could not be acquired because the product could not be solubilized in common organic solvents. In situ hydrolysis of this yellow solid with H_2O followed by careful washings to remove remaining reactants gave, based on NMR and gas chromatographic analyses, 1,6-hexanediol (>75%) and ε-CL.

Reaction of 1a with γ-butyrolactone: Formation of [Sm(Cp*)$_2$(BH_4)(γ-BL)] (1b/γ-BL): Compound **1b**/γ-BL was prepared in a similar manner to **1b**. Aliquots (up to 4 equiv) of γ-BL (1 equiv = 1.6 μL, 20.6 μmol) were added to a solution of **1a** (10.5 mg, 20.6 μmol) in CD_2Cl_2 (0.3 mL), which thus became lighter, and the stepwise addition was monitored by ^1H NMR analyses. **1b**/γ-BL: ^1H NMR (CD_2Cl_2): δ = 3.56 (br s, $w_{1/2}$ = 27 Hz; 4H + 2H; THF + γ-BL-OCH_2), 1.74 (s, 4H; THF), 1.52 (br s, $w_{1/2}$ = 32 Hz, 2H; γ-BL-$CH_2CH_2CH_2$), 1.25 (br s, $w_{1/2}$ = 32 Hz, 2H; γ-BL-$CH_2C(O)$), 0.93 (s, 30H; C_5Me_5); −14.72 ppm (br s, $w_{1/2}$ = 310 Hz, 4H; BH_4; Figure 3).

[Sm(Cp*)$_2$(BH_4)(γ-BL)] + 3γ-BL (1b/3γ-BL): ^1H NMR (CD_2Cl_2): δ = 4.10 (t, 8H; γ-BL-OCH_2), 3.66 (s, 4H; THF), 2.09 (m, 16H, γ-BL-$CH_2CH_2C(O)$), 1.79 (s, 4H; THF), 0.94 (s, 30H; C_5Me_5); −14.62 ppm (br s, $w_{1/2}$ = 300 Hz, 4H; BH_4).

Polymerization of ε-CL by [Sm(Cp*)$_2${O(CH_2)$_5$$CH_2$O($BH_2$)}] (2): In a glove box, a 1.5 M solution of ε-CL (0.5 mL, 4.5 mmol) in toluene (2.5 mL) was added to **2** (7.4 mg, 13.5 μmol) placed in a Schlenk tube with CH_2Cl_2 (1 mL). The suspension was stirred at room temperature for 30 min and then a solution of acetic acid (16.5×10^{-3} mol L^{-1}) in toluene was added. ^1H NMR analysis of the resulting product showed the formation of **4**.

Characterization of HO(CH_2)$_5$C(O){O(CH_2)$_5$C(O)}$_n$O(CH_2)$_6$OH: The polyester HO(CH_2)$_5$C(O){O(CH_2)$_5$C(O)}$_n$O(CH_2)$_6$OH was prepared by ring-opening polymerization of ε-CL (in toluene, 2.5 mL; [ε-CL] = 1.13 mol L^{-1}) initiated by **1a** (in CH_2Cl_2, 1 mL; 55.86 mg, 0.11 mmol), with [ε-CL]$_0$/[**1a**]$_0$ = 41 (n = 39). ^1H NMR ($CDCl_3$): δ = 4.04 (t, J(H,H) = 7 Hz, (2n+2)H; OCH_2), 3.62 (t, J(H,H) = 7 Hz, 4H; HOCH_2), 2.28 (t, J(H,H) = 7.5 Hz, (2n+1)H, $CH_2C(O)$), 1.63 (m, J(H,H) = 7 Hz, (4n+2)H, $CH_2CH_2CH_2$), 1.35 ppm (m, J(H,H) = 7.5 Hz, (2n+2)H, $CH_2CH_2CH_2$) (Figure 4); ^{13}C NMR ($CDCl_3$): δ = 173.5 (CH_2CO), 77.0 ($CDCl_3$), 64.0 (OCH_2), 62.1 ($HOCH_2$), 34.0 (CH_2CO), 28.3, 25.4, 24.5 ppm ($CH_2CH_2CH_2$) (Figure 5). The small signal (marked *) at δ = 32.4 ppm could be attributed to an impurity, as indicated by the absence of coupling with any other peaks in a $^1H\{^{13}C\}$ HSQC experiment.

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