Polymerization of ϵ-Caprolactone Initiated by $Nd(BH_4)_3(THF)_3$: Synthesis of Hydroxytelechelic Poly(ϵ-caprolactone)

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ABSTRACT: The ring-opening polymerization of ϵ-caprolactone initiated by $Nd(BH_4)_3(THF)_3$, **1a**, has been investigated. The polymerization occurs rapidly (<5 min) and quantitatively at room temperature to give, in high yields, polymers which exhibit controlled molecular weights and relatively low polydispersities. Initially, 3 mol of ϵ-caprolactone may coordinate the neodymium center to form the $Nd(BH_4)_3$(ϵ-caprolactone)$_3$ complex, **1b**. Then, ϵ-caprolactone inserts into the metal−borohydride hydrogen bond of **1a** or **1b** to give the intermediate $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]**, in which each (HBH_3) unit immediately interacts with the α-carbonyl group to form the corresponding neodymium(trisalkoxide) derivative $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**. Polymerization of ϵ-caprolactone by **2a** then proceeds via a pseudoanionic mechanism through the alkoxide attack at the monomer resulting in the oxygen−acyl bond cleavage. Further treatment of the resulting product with benzyl alcohol gives α,ω-telechelic poly(ϵ-caprolactone) diols, $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_nO(CH_2)_6OH$. The proposed mechanism is supported by ^1H and ^{13}C NMR, SEC, and MALDI−TOF analyses of the polymers.

Introduction

Biodegradable and biocompatible polyesters such as poly(ϵ-caprolactone), poly(lactide), or poly(trimethylene carbonate) are of great interest for their applications in the medical field.[1,2] These polymers are more conveniently synthesized by ring-opening polymerization of cyclic esters using anionic (and to a lesser extent cationic) or covalent initiators.[3]

Rare earth metal (lanthanide = Ln) chemistry is one of the most rapidly growing areas of inorganic/metallo-organic chemistry. Lanthanide derivatives form an emerging and promising class of polymerization initiators, especially for better understanding and developing ring-opening polymerization of lactones and lactides;[4] in particular, trivalent rare earth alkoxides have shown very high and unprecedented activities for such ring-opening reactions.[4a,5] However, in our continuing researches on controlled ring-opening polymerization of cyclic esters and their homologues, we highlighted that the major drawbacks inherent to such initiating systems is their high propensity to form aggregated clusters.[6,7]

As an alternative approach, we investigated the potential of lanthanide borohydride complexes as initiators. Indeed, these pseudohalide compounds have been confirmed as valuable and versatile precursors in lanthanide chemistry.[8] They are also more conveniently prepared and more reactive than their halides congeners; besides, they can be identified by ^1H NMR spectroscopy.[9] As opposed to alkoxide species, lanthanide borohydrides can be easily obtained as analytically pure samples which exhibit well-defined non-aggregated structures, established by infrared and X-ray diffraction analyses.[8,10] This is essential since knowledge of the initiator−structure−performances relationships is required for the better comprehension and control of the polymerization.

In this paper we present the experimental and mechanistic features of the polymerization of ϵ-caprolactone initiated by $Nd(BH_4)_3(THF)_3$, **1a** (THF = tetrahydrofuran). The initiation process consecutively involves monomer coordination to the neodymium center, insertion into the Nd−hydride bond and reaction with the (HBH_3) group. The polymerization subsequently proceeds with an alkoxide initiator to finally yield α,ω-telechelic poly(ϵ-caprolactone) with hydroxy end groups. To our knowledge, no other thorough study of cyclic esters polymerization, using a borohydride complex of a transition metal as initiator, has been reported to date.

Experimental Section

Materials. All operations were conducted under inert atmosphere (argon, <5 ppm of O_2) using standard Schlenk, vacuum line, and glovebox techniques.[11a] Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use.[11b] CD_2Cl_2, $CDCl_3$, and toluene-d_8 were dried over molecular sieves and THF-d_8 over a sodium mirror. ϵ-Caprolactone (ϵ-CL, Aldrich) was successively dried over CaH_2 (at least 1 week) and then 4,4′-methylenebis(phenylisocyanate) (1 week); finally, it was distilled under reduced pressure (0.5 mbar) before use. $Nd(BH_4)_3(THF)_3$, **1a**, was conveniently synthesized from $NdCl_3$ (Aldrich) as reported in the literature.[8a,b] ^1H NMR in THF-d_8, δ: 95.5 ppm (br s, $w_{1/2}$ = 345 Hz, 12H, BH_4), 3.50 and 1.67 (t, THF); in CD_2Cl_2, δ: 98.5 ppm (br s, $w_{1/2}$ = 370 Hz, 12H, BH_4), 4.88 and 3.92 (s, 12H, s, 12H, THF).

Instrumentation and Measurements. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were recorded on a Bruker AC200 instrument and were referenced internally using the residual protic solvent resonance relative to tetramethylsilane (δ = 0).

Elemental analyses were performed by the Analytische Laboratorien at Lindlar (Germany).

Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) using THF (1 mL/min) as eluent at 25 °C on a Varian 5500 apparatus equipped with a refractive index detector and high-speed PSS columns; the polymer samples were dissolved in THF (2 mg/

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Table 1. Polymerization of ϵ-Caprolactone Initiated by $Nd(BH_4)_3(THF)_3$, 1a (Temperature (21 °C), Reaction Time = 5 min, Solvent = 2.5 mL)

[**1a**]$_0$, 10^{-3} mol/L	[ϵ-CL]$_0$, mol/L	[ϵ-CL]$_0$/3[**1a**]$_0$[a]	solvent	$\overline{M}_n$(th),[b] g/mol	$\overline{M}_n$(exp),[c] g/mol	MWD[d]
6	2.09	116	THF	13230	10300	1.2
4.6	1.17	85	THF	9614	8300	1.4
9.2	1.65	60	THF	6700	5450	1.3
7.7	1.17	51	THF	5800	4900	1.3
12.5	1.25	33	THF	3572	3500	1.2
10	1.17	39	CH_2Cl_2	4560	4800	1.5
15	1.25	28	CH_2Cl_2	2980	3040	1.2

[a] [**1a**]$_0$ = [$Nd(BH_4)_3(THF)_3$] = [Nd]$_0$ = 3[BH_4]$_0$. [b] Calculated for three polymer chains per neodymium atom with $\overline{M}_{n(th)}$ = molar mass$_{(\epsilon-CL)}$ ([ϵ-CL]$_0$/3[**1a**]$_0$). [c] SEC values corrected with the coefficient 0.56. [d] Molecular weight distribution calculated from SEC values.

mL). Average molecular weight values were calculated from the polystyrene calibration curve using a correction coefficient ($\overline{M}_{n(exp)} = 0.56\overline{M}_{n(SEC)}$).[7a]

The molecular weights were also calculated from ^{1}H NMR analyses; the values resulted from the integration ratio of the main chain (OCH_2, 2nH) signal at δ = 3.99 ppm relative to the end group methylene proton (CH_2OH, 4H) signal at δ = 3.57 ppm.

The monomer conversion was calculated by gravimetric measurements of the recovered polymer sample.

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), and solutions of ditranol/THF (10 mg/mL) and NaI/MeOH (10 mg/mL) 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. EI mass spectra (EIMS) were recorded on a Micromass AUTOSPEC apparatus in positive mode with a beam energy of 70 keV.

Synthesis of $La(BH_4)_3(Pyr)_3$, 3, from $La(BH_4)_3(THF)_3$. $La(BH_4)_3(THF)_3$ was prepared in a similar way to **1a** according to a modified literature procedure.[8a,12] $LaCl_3$ (5.00 g, 20.39 mmol) and 3.24 equiv of $NaBH_4$ (2.50 g, 66.08 mmol, 8% excess instead of 20−100%) were placed in a flask. THF (125 mL) was condensed in, and the suspension was allowed to stir at 60 °C over 48 h (instead of 12 h at room temperature).[8a,12] After evaporation of the solvent and drying over 18 h under dynamic vacuum, the residue was thoroughly extracted with THF (75 mL). The filtrate was evaporated, leaving $La(BH_4)_3(THF)_3$ isolated in 72% as a white powder. ^{1}H NMR in toluene-d_8, δ: 1.7 (br q, $w_{1/2}$ = 300 Hz, J_{BH} = 80 Hz, 12H, BH_4), 3.79 and 1.35 (t, 12H; t, 12H, THF); in THF-d_8, δ: 0.6 ppm (br q, $w_{1/2}$ = 280 Hz, J_{BH} = 84 Hz, 12H, BH_4).

$La(BH_4)_3(Pyr)_3$ (Pyr = pyridine), **3**, was made quantitatively as a white powder upon dissolution in pyridine of $La(BH_4)_3(THF)_3$ and stirring (48 h), followed by removal of pyridine, washings with pentane, and finally drying under dynamic vacuum (10 h). ^{1}H NMR in CD_2Cl_2, δ: 1.45 (br q, $w_{1/2}$ = 280 Hz, J_{BH} = 84 Hz, 12H, BH_4), 8.77, 7.81, and 7.38 (d, 6H; t, 3H; t, 6H, Pyr).

Typical Polymerization Procedure. A THF or CH_2Cl_2 (1 mL) solution of the preinitiator **1a** (11.6 mg, 30.83 μmol) is added via a cannula to a stirred solution of ϵ-CL (538 mg, 4.71 mmol) in the same solvent (2.5 mL) at room temperature. *(The experiments were not performed in toluene in which **1a** is only slightly soluble.)* The polymerization in THF thus proceeds under homogeneous conditions with a monomer concentration of about 1 mol/L and an initiator concentration [**1a**] ranging from 4.6 × 10^{-3} to 15 × 10^{-3} mol/L. In all reactions, a white precipitate initially appears and very rapidly disappears to give a colorless "gel" (typically within 5 min). The polymerization is then stopped by the addition of a large excess, relative to **1a**, of a benzyl alcohol solution (0.1 mol/L in toluene). The polymer is then recovered from this resulting mixture by precipitation in a large volume of cold methanol followed by filtration and drying. The polymers are then analyzed by ^{1}H and ^{13}C NMR, SEC, and MALDI−TOF analyses.

Reaction of 1a with ϵ-CL Followed by Hydrolysis: Formation of 2a. A 1:3 mixture of **1a** (590 mg, 1.57 mmol) and ϵ-CL (538 mg, 4.71 mmol) is dissolved in THF (5 mL) and stirred at room temperature. A white precipitate rapidly appears (within 5 min) in a colorless solution. After 1 h, the solution is filtered, and the white powder thus obtained is thoroughly washed with THF and pentane and finally dried under vacuum. The intermediate **1b** cannot be isolated since the Nd−HBH_3 ligands immediately react with ϵ-CL to give **[i]**, **[ii]**, and finally **2a**, as demonstrated thereafter. The insolubility of this solid (identified as **2a**, wide infra) in common organic solvents precludes its characterization. However, the elemental analysis of this white product confirms its formulation as [$Nd[O(CH_2)_5CH_2(OBH_2)]_3$], **2a**. Anal. Calcd for $C_{18}H_{42}B_3NdO_6$: C, 40.70; H, 7.97; B, 6.11. Found: C, 40.68; H, 7.79; B, 5.94. This white solid is then hydrolyzed by addition of H_2O; the resulting liquid, purified on a silica gel column, is identified by ^{1}H and ^{13}C NMR, gas chromatography, and EIMS analyses as 1,6-hexanediol (42% yield). ^{1}H NMR ($CDCl_3$, δ): 3.70 (t, 7 Hz, 4H, $HOCH_2$); 2.4 (br s, 2H, $HOCH_2$); 1.64 (m, 6 Hz, 4H, $HOCH_2CH_2$); 1.45 (m, 6.5 Hz, 4H, $HOCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$, δ): 62.7 ($HOCH_2$); 32.5 ($HOCH_2CH_2$); 26.1 ($HOCH_2CH_2CH_2$). EIMS (*m*/*z*, relative intensity): 118 (M, 0.2), 88 (3.6), 82 (28.9), 67 (59.0), 55 (47.2), 41 (84.7), 31 (100).

Reaction of $La(BH_4)_3(Pyr)_3$, 3, with ϵ-CL. Aliquots of ϵ-CL (1 equiv = 2.3 mg, 20.44 μmol) were added to $La(BH_4)_3(Pyr)_3$, **3** (8.6 mg, 20.44 μmol), in an NMR tube in CD_2Cl_2 (5 mL). The stepwise addition of 1, 2, and 3 equiv of ϵ-CL was then monitored by ^{1}H NMR spectroscopy.

Results and Discussion

Polymerization Features. The trivalent homoleptic borohydride neodymium complex $Nd(BH_4)_3(THF)_3$, **1a**, is an efficient polymerization initiator for the ring-opening of ϵ-caprolactone. Table 1 summarizes the results of the reactions performed in THF or dichloromethane solutions at room temperature (21°C). Generally, the polymerizations carried out in THF give better features (especially $\overline{M}_{n(exp)}$ and MWD) than those performed in CH_2Cl_2. Nevertheless, in either solvent, **1a** appears as a highly active initiator.

In all experiments, the monomer conversion is quantitative, and the polymer is recovered in about 95% yield simultaneously with a low fraction of residual products. Polymers of molecular weights ranging from 3000 to 10 300 and displaying narrow molecular weights distributions (MWD) are isolated over a very short period (within 5 min). The theoretical molecular weights $\overline{M}_{n(th)}$ were calculated from the initial concentrations in neodymium initiator ([**1a**]$_0$) on the basis of three active sites per metal available for polymerization. The experimental average molecular weight values, $\overline{M}_{n(exp)}$, derived from size-exclusion chromatography measure-

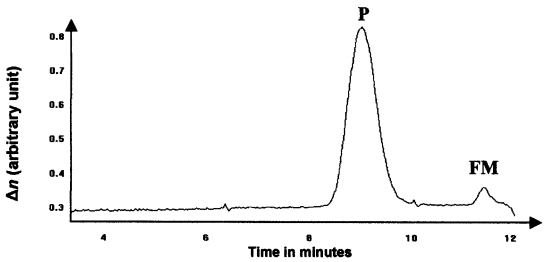


Figure 1. SEC chromatogram of a polyester prepared through ring-opening polymerization of ϵ-CL initiated by **1a** in THF with $[\epsilon\text{-CL}]_0 = 1.17$ mol/L, $[\epsilon\text{-CL}]_0/3[\mathbf{1a}]_0 = 51$; $\overline{M}_n$(SEC) = 4900, MWD = 1.3. P = polymer; FM = flow marker.

ments, generally match those determined from ^{1}H NMR analyses. In addition, these $\overline{M}_{n(exp)}$ data are also in good agreement (within experimental error) with the theoretical ones, $\overline{M}_{n(th)}$ (Table 1). Also, $\overline{M}_n$ values increase linearly with [monomer]/[initiator] ratios, suggesting the absence of significant transfer reactions, while the MWD remains constant whatever the concentration of **1a**. Moreover, the relatively narrow and symmetrical SEC elution peak of the polymer indicates a good control of the polymerization reaction (Figure 1).

Initiation Process of the Polymerization of ϵ-Caprolactone in the Presence of $Nd(BH_4)_3(THF)_3$, 1a. Throughout this paper, the borohydride mode of binding to the neodymium in $Nd(BH_4)_3(THF)_3$, **1a**, is presented, for clarity, by Nd- - -BH_4 (Schemes 1−3). However, it is well-known that the borohydride coordination mode occurs through bridging hydrogen atoms either in a monodentate, bidentate, or tridentate fashion (on the basis of infrared and X-ray diffraction studies).[9a,10,13] In complex $Nd(BH_4)_3(THF)_3$, **1a**, there are two tridentate and one bidentate BH_4 ligand, $Nd[(\mu_2\text{-}H)_3BH]_2[(\mu_2\text{-}H)_2BH_2](THF)_3$, as determined by X-ray analysis.[10a] Therefore, the bond of the neodymium borohydride complex **1a** involved in the polymerization of ϵ-CL is a neodymium-bridging hydride bond, more explicitly written as Nd−HBH_3. The same structure is also observed for the lanthanum borohydride species, **3**.[10a]

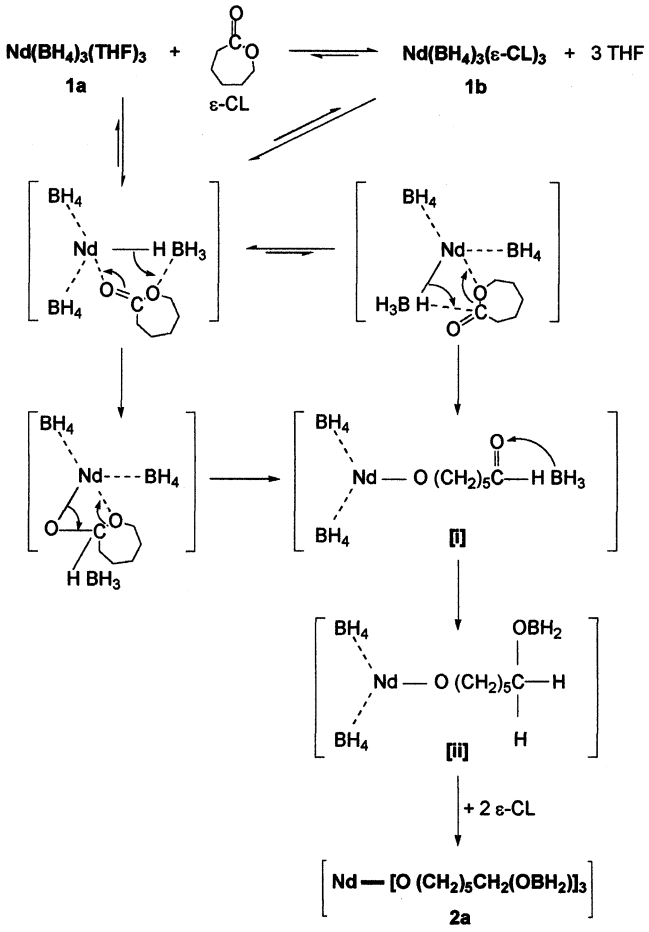
All lanthanide derivatives mentioned in this paper are likely to bear Lewis bases molecules (THF, ϵ-CL, Pyr, etc.) coordinated to the metal center to satisfy stereoelectronic factors; for the sake of clarity, these have been omitted in the schemes and discussion and the species as represented thereafter in square brackets.

Upon reaction of the first three ϵ-caprolactone molecules with $Nd(BH_4)_3(THF)_3$, **1a**, several products may be formed.

First, one might get a lactone solvated complex analogous to **1a**, $Nd(BH_4)_3(\epsilon\text{-CL})_x(THF)_{3-x}$ ($x = 0-3$), upon displacement of THF by ϵ-caprolactone which would then be, likewise to THF, coordinated in a monodentate fashion through the carbonyl oxygen atom. This would be consistent with recent results confirming that the coordinating strength of ϵ-CL toward lanthanide metals is greater than that of THF, among other oxygen-donor ligands.[14] Complex $Nd(BH_4)_3(\epsilon\text{-CL})_3$, **1b,** might subsequently behave as **1a** to give compounds **2a**, **2b**, and **2c** (see below), solvated by ϵ-caprolactone (Schemes 1 and 2).

Second, ϵ-caprolactone could coordinate the metal through its carbonyl group and then insert into one neodymium−hydride bond of **1a** or **1b** to give $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]** (Scheme 1); this is assuming an oxygen−acyl bond rupture of the monomer as will be demonstrated thereafter. Then, the (BH_3) unit located at the end of the inserted caprolactone would immediately react with the α-carbonyl group to yield the alkoxide derivative $[(BH_4)_2Nd[O(CH_2)_5CH_2(OBH_2)]]$, **[ii]**, through a well-known reduction reaction.[15] Consequently, upon reaction of three monomer units with the trivalent borohydride precursor **1a**, the neodymium trisalkoxide product $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, would be obtained (Scheme 1).

Scheme 1. Proposed Mechanism for the Initiation Process of the Polymerization of ϵ-Caprolactone Initiated by $Nd(BH_4)_3(THF)_3$, 1a

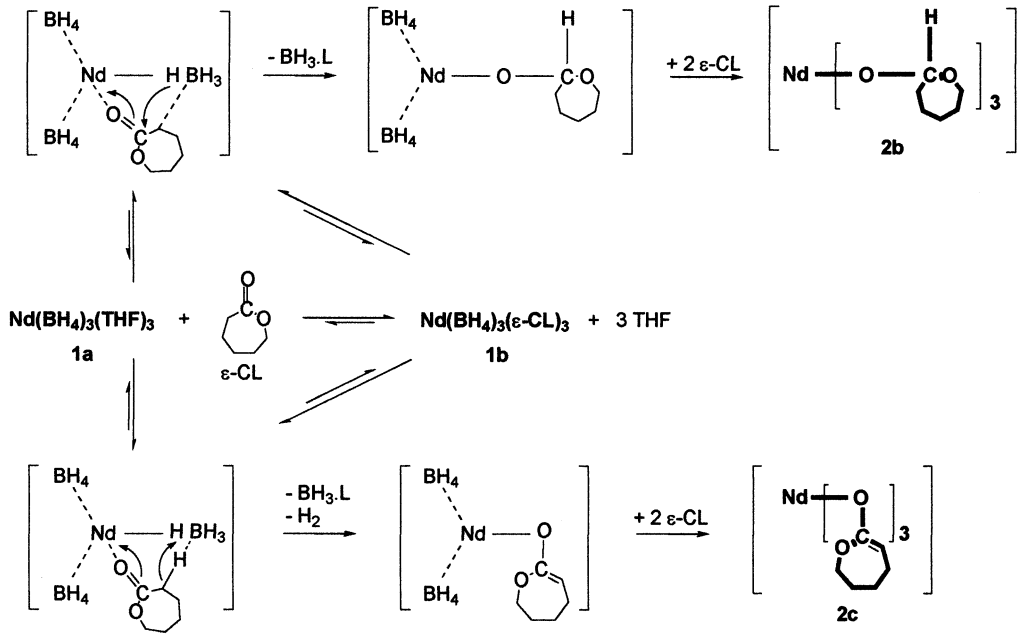


Third, in complexes such as **1a** and **1b**, the borohydride group might also add to the carbonyl group of ϵ-caprolactone to give an acetal linkage as shown in compound **2b** (Scheme 2). Such a mechanism has already been reported for the reaction of $(C_5Me_5)_2Lu(Me)(THF)$ with ϵ-caprolactone[5b] as well as during the reaction of **1a** with $Me_2C(O)$.[16]

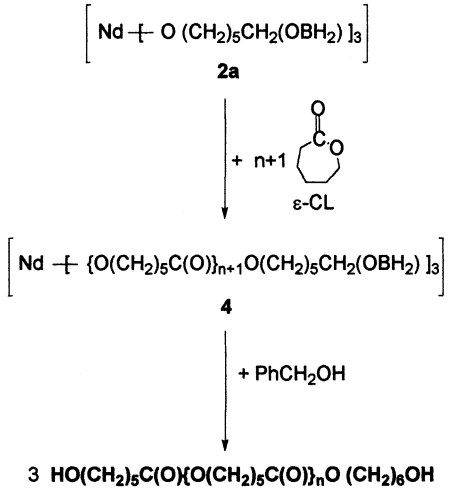
Finally, a cyclic enolate compound **2c** might be formed upon abstraction of the acidic proton in α-position of the carbonyl group by the borohydride ligand of **1a** or **1b** (Scheme 2). Although it is rather unlikely that the abstraction of the weakly acidic α-proton giving **2c** would be favored over the hydride transfer giving **2a**, cyclic enolates of other lanthanide systems have been mentioned.[17]

To better understand the initiation mechanism of the polymerization of ϵ-caprolactone by **1a** and to determine which of these neodymium derivatives—the THF solvated complex **1a**, its ϵ-caprolactone analogue **1b**, the alkoxide **2a**, the acetal **2b**, or the enolate **2c** compound—

Scheme 2. Proposed Mechanism for the Initiation Process of the Polymerization of ϵ-Caprolactone Initiated by $Nd(BH_4)_3(THF)_3$, 1a (Continued)



Scheme 3. Proposed Mechanism for the Propagation Process of the Polymerization of ϵ-Caprolactone Initiated by $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, 2a



is initially formed, we undertook NMR studies of the resulting products issued from the reaction of **1a** with ϵ-CL, with a special emphasis on chain ends analyses.

Reaction of 1a with ϵ-CL Followed by Hydrolysis. First, we attempted to follow the stepwise addition of **1a** to 3 equiv of ϵ-CL by NMR studies. However, the signals were greatly enlarged (due to the presence of paramagnetic neodymium species) and overlapped with the resonances of the **1a**-coordinated THF molecules. Thus, formation of either complex **1b**, **2a**, **2b**, or **2c** could not be observed this way.

We then performed the reaction of **1a** with ϵ-caprolactone in THF (molar ratio ϵ-CL:**1a** = 3) which gave a white solid. Careful washings (to remove any uncoordinated ϵ-caprolactone or unreacted **1a**) followed by hydrolysis and purification resulted in a liquid identified as 1,6-hexanediol by ^1H and ^{13}C NMR, gas chromatography, and mass spectrometry analyses. The ^1H and ^{13}C NMR spectra clearly showed the absence of free ϵ-caprolactone (no ($CH_2OC(O)$) proton signal at 4.06 ppm and no (C(O)) carbon resonance at 175 ppm), indicating that the monomer reacted with **1a** prior to hydrolysis, to give either **2a**, **2b**, or **2c**. Indeed, hydrolysis of **1b** would generate free ϵ-caprolactone, which was not observed.[5b] Also, if compound **1b** was formed during the first step of initiation, it would immediately react similarly to **1a** to give **2a**, **2b**, or **2c**; therefore, **1b** cannot be isolated. On the other hand, while hydrolysis of $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, would certainly generate 1,6-hexanediol, hydrolysis of the acetal **2b** or the enolate **2c** species would not. These results strongly suggested the formation of the neodymium alkoxide derivative $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, issued from the reaction of the trisborohydride precursor $Nd(BH_4)_3(THF)_3$, **1a**, with ϵ-caprolactone during the first step of the polymerization process (Scheme 1). This was further confirmed by elemental analysis of the white solid, which gave satisfactory results for the formulation as $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**. Similar behaviors upon hydrolysis have already been observed on lanthanide hydride or alkyl lactone complexes.[5b] Recovering 1,6-hexanediol from this hydrolysis experiment already suggested an oxygen−acyl bond cleavage of the monomer instead of an oxygen−akyl one, since no (HOC(O)) linkage was observed in the NMR spectra.

Therefore, it is likely that, during the initiation period, the monomer would first coordinate the metal—most certainly through its carbonyl group in an η^1 fashion—and then insert into the neodymium−borohydride hydride bond via oxygen−acyl bond cleavage to give $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]**; the (C(O)-($HBH_3$)) ligand would then rapidly react with the adjacent carbonyl to give $[(BH_4)_2Nd[O(CH_2)_5CH_2(OBH_2)]]$, **[ii]**. This would occur at the three borohydride active sites available on **1a** to finally form the homoleptic trivalent neodymium alkoxide product $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, according to Scheme 1. The postulated species **[i]** and **[ii]** cannot be isolated because of the immediate intramolecular reduction of the terminal carbonyl group by the borane to form **2a**. Compound **2a,** thereafter, would serve as the real initiator of the polymerization of ϵ-caprolactone. Such a coordination−

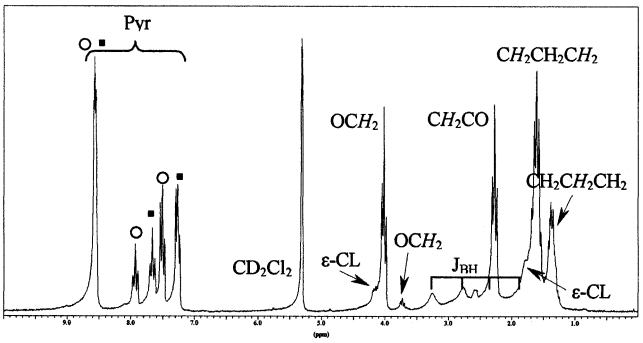


Figure 2. ^{1}H NMR spectrum in CD_2Cl_2 of $La(BH_4)_3(Pyr)_3$, **3**, in the presence of 3 mol equiv of ϵ-CL.

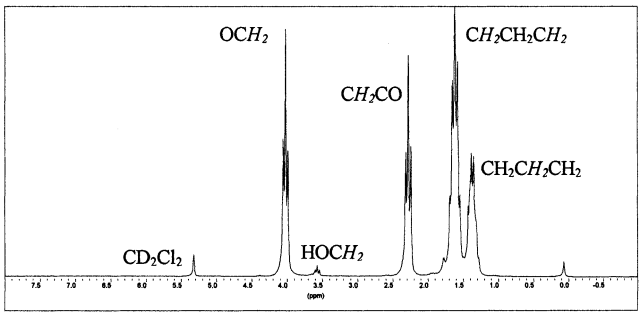


Figure 3. ^{1}H NMR spectrum in CD_2Cl_2 of a polyester prepared through ring-opening polymerization of ϵ-CL initiated by **1a** in THF with $[\epsilon\text{-CL}]_0 = 1.17$ mol/L, $[\epsilon\text{-CL}]_0/3[\mathbf{1a}]_0 = 51$. $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_nO(CH_2)_6OH$, δ (ppm): 3.99 (OCH_2); 3.57 ($HOCH_2$); 2.31 ($CH_2C(O)$); 1.61 ($CH_2CH_2CH_2$); 1.37 ($CH_2CH_2CH_2$); $\overline{M}_n$(NMR) = 4836.

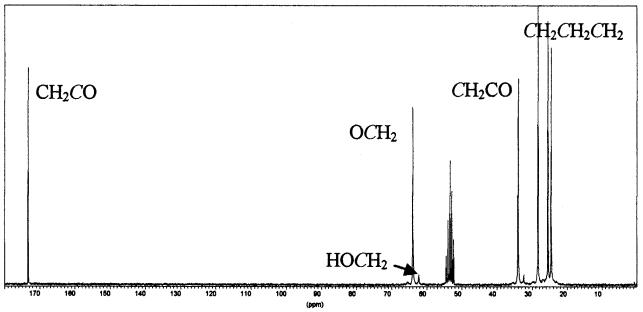


Figure 4. ^{13}C NMR spectrum in CD_2Cl_2 of a polyester prepared through ring-opening polymerization of ϵ-CL initiated by **1a** in THF with $[\epsilon\text{-CL}]_0 = 1.17$ mol/L, $[\epsilon\text{-CL}]_0/3[\mathbf{1a}]_0 = 51$. $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_nO(CH_2)_6OH$, δ (ppm): 173.6 (CH_2CO); 64.3 (OCH_2); 62.3 ($HOCH_2$); 53.7 (CD_2Cl_2); 34.3 (CH_2CO); 28.6, 25.8, 24.8 ($CH_2CH_2CH_2$).

insertion (pseudoanionic) mechanism would be similar to that reported with trivalent aluminum[3a] and lanthanide[7] alkoxides.

Reaction of $La(BH_4)_3(Pyr)_3$, 3, with ϵ-CL. To gain further insights into this initial polymerization step, we monitored by ^{1}H NMR the stepwise addition of 3 equiv of ϵ-caprolactone to $La(BH_4)_3(Pyr)_3$, **3**, a diamagnetic lanthanide complex analogous to **1a**. Thereby, the narrow signals obtained allowed unequivocal analysis of the NMR spectra (Figure 2). In addition, the monomer and oligomers peaks did not overlap with any coordinated Lewis base resonances, the pyridine peaks of **3** appearing downfield from that region. Upon addition of ϵ-CL aliquots to a CD_2Cl_2 solution of **3**, the initial borohydride quadruplet (J_{BH}) was shifted downfield while a new set of pyridine signals appeared, clearly indicating that **3** reacted with ϵ-CL which displaced the pyridine groups. Very rapidly (molar ratio ϵ-CL:**3** = 2; 20 min), both the resonances of the ϵ-CL and the oligomers were simultaneously identified with those of the oligomers quickly exceeding those of the monomer. After addition of 3 equiv of ϵ-CL, a minor amount of monomer remained besides the major oligomer species (Figure 2). In addition, a triplet corresponding to a (CH_2O) unit grew at δ = 3.73 ppm throughout the experiment.

These observations are in complete agreement with the in-situ formation of the postulated lanthanum intermediates $[(BH_4)_2La[\mathbf{O(CH_2)}(CH_2)_4\mathbf{CH_2(O}BH_2)]]$ and $[La[\mathbf{O(CH_2)}(CH_2)_4\mathbf{CH_2(O}BH_2)]_3]$ compounds analogous to the neodymium species **[ii]** and **2a**, respectively (Scheme 1). Neither the lanthanum acetal compound nor the enolate complex analogous to the neodymium species **2b** and **2c**, respectively, would generate such a unique finely resolved triplet at 3.73 ppm. These results thus further support the initial formation of the homoleptic trivalent lanthanide alkoxide product $[Ln[O(CH_2)_5CH_2(OBH_2)]_3]$ (Ln = Nd **2a**, La) during the initial step of the polymerization of ϵ-caprolactone initiated by a tris(borohydride) lanthanide complex $Ln(BH_4)_3(L)_3$ (Ln = Nd, L = THF, **1a**, ϵ-CL, **1b**; Ln = La, L = Pyr, **3**) according to Scheme 1.

Propagation Process of the Polymerization of ϵ-Caprolactone by the Alkoxide Complex $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, 2a. To confirm the ϵ-caprolactone chain growth process on $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, the molecular structure of the polymers has been investigated by ^{1}H and ^{13}C NMR, SEC, and MALDI−TOF analyses.

An end group NMR study of various low molecular weight poly(ϵ-caprolactone) samples ($\overline{M}_n$<5000) strongly indicated, as expected, a coordination−insertion type mechanism with an acyl−oxygen bond cleavage instead of an oxygen−alkyl one (Figures 3 and 4).[3a,7b] Indeed, no (HOC(O)) linkage resulting from the oxygen−alkyl bond breaking was ever noticed in the NMR spectra of the macromolecular chains. Besides the main polymer chain peaks, a (CH_2OH) resonance was clearly identified at δ = 3.57 ppm in the ^{1}H NMR spectrum (Figure 3) and at δ = 62.61 ppm in the ^{13}C NMR spectrum (Figure 4); no other end group was observed. This suggested that both ends of the polymer chain are alike and of hydroxy type. Formation of a putative neodymium−aldehyde intermediate, $[(BH_4)_2Nd[O(CH_2)_5C(O)(H)]]$, potentially resulting from the abstraction of BH_3 from $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]**, is ruled out by the absence of the benzyl group signal in the ^{1}H NMR spectra of the polymer. Indeed, upon deactivation of the aldehyde-terminated growing chain with benzyl alcohol, a ($PhCH_2O$) (Ph = C_6H_5) end group should be identified at δ = 7.31 ppm. Similarly, quenching the polymerization on alleged acetal- or enolate-terminated growing chains with $PhCH_2OH$ should generate that same ($PhCH_2O$) resonance which was never observed. These results further strongly corroborate the intramolecular reaction of the (BH_3) group with the α-carbonyl function in $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]**, to form $[(BH_4)_2Nd[O(CH_2)_5\mathbf{CH_2(O}BH_2)]]$, **[ii]**, and finally $[Nd[O(CH_2)_5\mathbf{CH_2(O}BH_2)]_3]$, **2a**, as suggested above (Scheme 1). Complex **2a** subsequently polymerizes ϵ-caprolactone to give the active polymeric chains $[Nd[\{O(CH_2)_5C(O)\}_nO(CH_2)_5CH_2(OBH_2)]_3]$, **4** (Scheme 3). The simultaneous existence of the species **[ii]** or **2a** with **4** was observed with lanthanum homo-

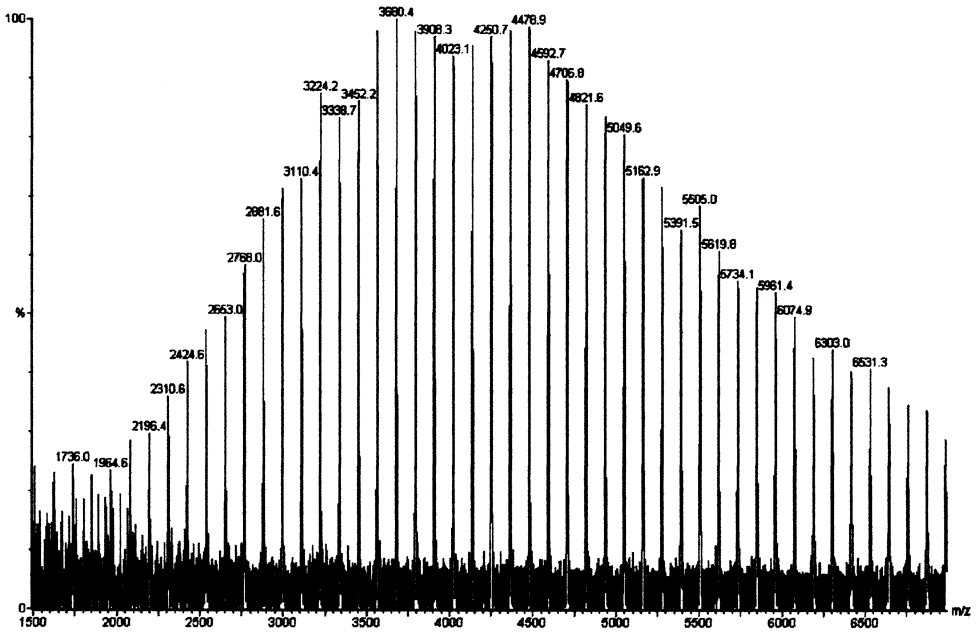


Figure 5. MALDI−TOF MS spectrum in reflectron mode of a polyester prepared through ring-opening polymerization of ϵ-CL initiated by **1a** in THF with $[\epsilon\text{-CL}]_0 = 1.17$ mol/L, $[\epsilon\text{-CL}]_0/3[\mathbf{1a}]_0 = 51$.

logues during the $La(BH_4)_3(Pyr)_3$, **3**,/ϵ-CL experiment described previously, based on NMR analyses (Figure 2).

The MALDI−TOF spectrum of the same polymer sample which NMR spectra are shown in Figures 3 and 4 clearly displays a single population of polymer molecules, unequivocally confirmed as $HO(CH_2)_5C(O)$-$[O(CH_2)_5C(O)]_nO(CH_2)_6OH$ (Figure 5). Moreover, comparison of theoretical simulations, based on this chemical formula, exhibits a perfect match with experimental MALDI values; for instance, for a polymer chain with $n = 30$, $\overline{M}_{n(th)} = 3565.1$ and $\overline{M}_{n(MALDI)} = 3566.3$. The average molecular weight $\overline{M}_n$ and the molecular weight distribution obtained from this MALDI spectrum are 3750 and 1.2, respectively.

Thus, further addition of ϵ-caprolactone to $[Nd$-$[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, results in three growing chains that remain fixed to the neodymium center through an alkoxide bond as $[Nd[\{O(CH_2)_5C(O)\}_nO$-$(CH_2)_5CH_2(OBH_2)]_3]$, **4**. Quenching the reaction by addition of benzyl alcohol results in the hydrolysis of this active Nd−O(polymer) bond that generates an hydroxy chain end. The other extremity of the polymer is also capped with an hydroxy end group resulting from the hydrolysis of the $[O(CH_2)_5CH_2(OBH_2)]$ chain end. Therefore, the α,ω-telechelic polyesters formed can thus be formulated as $HO(CH_2)_5C(O)\{O(CH_2)_5C(O)\}_nO(CH_2)_6$-OH (Scheme 3).

Conclusion

The neodymium borohydride complex $Nd(BH_4)_3$-$(THF)_3$, **1a**, serves as precursor in the initiation process of the polymerization of ϵ-caprolactone: it simultaneously opens the cyclic lactone and reduces the aldehyde group. Indeed, **1a** behaves as an hydridic compound toward the lactone to give, first by H-migration, the alkoxide derivative $[(BH_4)_2Nd[O(CH_2)_5C(O)(HBH_3)]]$, **[i]**, and then, by intramolecular reduction of the terminal carbonyl group, the trisalkoxide compound $[Nd[O(CH_2)_5CH_2(OBH_2)]_3]$, **2a**, which acts as the real initiator. The novel poly(ϵ-CL) obtained are thus depleted of any C(O) functions at their extremity and offer two OH group instead. The molecular weights and the molecular weight distributions of the α,ω-dihydroxytelechelic polyesters are well controlled, and the conversions of the monomer are quantitative.

This study highlights that rare earth derivatives, other than alkoxides, are also successful in lactone polymerization. The improved versatility of such lanthanide borohydride initiators, relative to alkoxides, lies in their ability to generate polyesters that are functionalized at each end by an OH group. These original and well-defined dihydroxytelechelic polymers may be further employed as a macroinitiators in the synthesis of multihydroxy functional ϵ-caprolactone copolymers. Indeed, ϵ-caprolactone copolymers are attracting much attention as biopolymers for biomedical applications including surgery and medicine.[1d,2,18] Such hydrophobic copolyesters may also be used for the design of amphiphilic block copolymers, thereby opening the route to the micellar domain and its diversity.[19] We are currently exploring the potential of such hydroxytelechelic poly(ϵ-caprolactone).

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