Tetrahydrosalen-Stabilized, Chloride-Containing Rare-Earth Complexes: Facile Initiator Precursors for the Preparation of Hydroxytelechelic Poly(ε-caprolactone)s

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ABSTRACT: End-capped poly(ε-caprolactone)s (PCLs) have been prepared elsewhere by various initiators. However, hydroxytelechelic PCLs have been reported less frequently, although there are two hydroxyl end groups in one polymer chain, which allows diversified functionalization. Two tetrahydrosalen-backboned chlorides containing rare-earth complexes, YbLCl(DME)$_2$ and ErLCl(DME) {where L is 6,6′-[ethane-1,2-diylbis(methylazanediyl)]bis (methylene)bis(2,4-di-*tert*-butylphenol) and DME is dimethoxyethane}, were first synthesized in this study, and they were used as initiator precursors for a ring-opening polymerization in the presence of NaBH$_4$ to afford hydroxytelechelic PCLs. The polymerization under different conditions was investigated, and a possible mechanism is proposed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 557–562, 2009

Key words: functionalization of polymers; initiators; ring-opening polymerization

INTRODUCTION

The ring-opening polymerization of lactones to afford polyester-based materials has been of great interest in recent years. As biodegradable and biocompatible materials, the synthesis of end-capped poly(ε-caprolactone)s (PCLs) by different kinds of initiators has received great attention,[1] whereas hydroxytelechelic PCLs have been reported less frequently.[2,3] In fact, the double ─OH end groups in this kind of PCL allow the further functionalization of the PCL in the preparation of triblock copolymers.[4] Rare-earth complexes in ring-opening polymerizations are an active research area for their high activity, lower toxicity, and good control over the molecular weight distribution.[5] Therefore, lanthanide borohydrides as efficient initiators in the preparation of hydroxytelechelic PCLs have received great attention for their novel initiation mechanism.[2]

Tetrahydrosalen-supported metal complexes, for their specific coordination properties, have been explored extensively in recent times. However, chemists have focused mainly on transition-metal tetrasalen complex and main-group elements.[6–9] To our surprise, there have been fewer reports of tetrahydrosalen-supported rare-earth-metal complexes. In this study, 6,6′-[ethane-1,2-diylbis(methylazanediyl)]-bis(methylene)bis (2,4-di-*tert*-butylphenol) (**T2**), as a quadridentate ligand (N$_2$O$_2$), was used as the backbone of a chloro-containing rare-earth complex through salt-metathesis between the sodium salt of **T2** and LnCl$_3$ (where Ln is Er or Yb). They were efficient initiator precursors for the ring-opening polymerization of ε-caprolactone (CL) in the presence of NaBH$_4$ in the preparation of hydroxytelechelic PCLs. Here, we report the results.

EXPERIMENTAL

Materials and measurements

Toluene was refluxed over sodium benzophenone and distilled under an argon atmosphere before use. Dimethoxyethane (DME) and hexane were freshly distilled over potassium and benzophenone. We prepared anhydrous YbCl$_3$ and ErCl$_3$ by heating a mixture of hydrated gadolinium chloride and ammonium chloride under reduced pressure.[10] NaH (60% in mineral oil) was washed with hexane several times and dried *in vacuo*. CL (Alpha product, 99%, Alfa Aesar Company, Ward Hill, MA) was distilled under reduced pressure and an argon atmosphere before use. Tetrahydrosalen ligand was prepared according to ref. 7, with modifications. Other chemicals were used as received. IR spectra were recorded with KBr discs on a Bruker
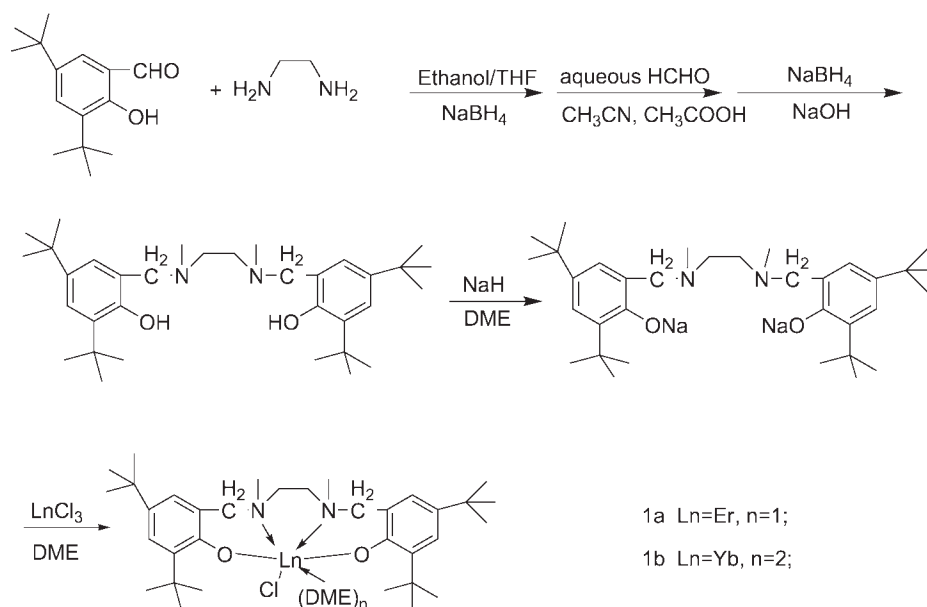
Scheme 1 Synthetic procedure of complexes **1a** and **1b**.

(Germany) Fourier transform infrared spectrometer. NMR spectra were recorded on a Bruker Avance DMX 400-MHz spectrometer in CDCl$_3$ with tetramethylsilane as the internal standard. The contents of rare earth and chloride were analyzed by ethylene diamine tetraacetic acid titration and the Volhard method. Elemental analysis was performed on a Flash EA1112 (ThermoFinnigan, Italy). Size exclusion chromatography was performed on a Waters 1525/2414 gel permeation chromatography (GPC) system (Waters Instrument Co., USA). Tetra-hydrofuran was used as the eluent with a flow rate of 1.0 mL/min at 35°C.

Preparation of T2

To a stirred solution of 3,5-di-*tert*-salicylaldehyde (14.21 g, 60.6 mmol) in 100 mL of ethanol was slowly added a solution of ethylenediamine (2.03 mL, 30.4 mmol) in 15 mL of ethanol, and the mixture was refluxed for 2 h. The mixture was cooled to 0°C; then, 50 mL of tetrahydrofuran was added to enhance the solubility. Sodium borohydride (5.75 g, 152 mmol) was then carefully added in small portions. This mixture was then slowly warmed to reflux temperature. When the mixture was nearly colorless, it was evaporated *in vacuo* and extracted several times with dichloromethane from water. The extraction was evaporated and recrystallized from ethyl acetate to afford white crystals as 6,6′-[ethane-1,2-diylbis(azanediyl)]bis(methylene)bis(2,4-di-*tert*-butylphenol) (**T1**; 11.3 g, yield = 75%).
^{1}H-NMR (400 MHz, CDCl$_3$, 25°C, δ): 10.78 (br, 2H, —OH), 7.23 (m, 2H, —Ph), 6.86 (m, 2H, —Ph), 3.97 (s, 4H, PhCH$_2$—), 2.87 (s, 4H, —NHCH$_2$—), 1.79 (b, 2H,

—NH), 1.41 [s, 18H, (CH$_3$)$_3$C—], 1.28 [s, 18H, (CH$_3$)$_3$C—].

To a solution of **T1** (6.1 g, 12.3 mmol) in acetonitrile (100 mL) and acetic acid (30 mL) was added formaldehyde (9.3 mL, 123 mmol, 37% in water), and this mixture was stirred for 30 min and cooled to 0°C. Sodium borohydride (2.78 g, 73.5 mmol) was carefully added several times, and the mixture was warmed to room temperature and stirred overnight. Acetonitrile was removed *in vacuo*, and the residue was washed with water and hydrolyzed with 2*N* NaOH, followed by extraction with dichloromethane. The organic phase was dried and recrystallized from ethanol/ethyl acetate twice to afford white needle crystals as **T2** (3.6 g, yield = 56%).
^{1}H-NMR (400 MHz, CDCl$_3$, 25°C, δ): 10.69 (br, 2H, —OH), 7.21 (m, 2H, —Ph), 6.81 (m, 2H, —Ph), 3.67 (s, 4H, PhCH$_2$—), 2.64 (s, 4H, —NHCH$_2$—), 2.27 (s, 6H, —NCH$_3$), 1.41 [s, 18H, (CH$_3$)$_3$C—], 1.28 [s, 18H, (CH$_3$)$_3$C—].

Preparation of the tetrahydrosalen-backboned ytterbium (1a) and erbium (1b) complexes

Synthesis of **1a**

The reaction was performed under an argon atmosphere. To a flamed flask purged with argon was added dry NaH (240 mg, 10 mmol) and 30 mL of fresh distilled DME, and this suspension was stirred at 0°C for 10 min. Then, the tetrahydrosalen ligand (1.581 g, 3 mmol) in 20 mL of DME was added dropwise by a syringe. This reaction mixture was warmed to room temperature and stirred overnight followed by centrifugation to remove unreacted NaH. The clear pale yellow solution was then slowly

TABLE I
Ring-Opening Polymerization of CL Initiated by 1a[a] and NaBH₄

Entry	[CL]/[I]/NaBH₄	Temperature (°C)	Time (min)	Yield (%)[b]	M_n (10³)	M_w/M_n[c]
1	200 : 0 : 4	65	120	0	—	—
2	200 : 1 : 0	65	120	0	—	—
3	200 : 1 : 4	65	120	36	7.93	1.39
4	500 : 1 : 4	65	120	63	15.9	1.37
5	1000 : 1 : 4	65	120	88	22.1	1.43
6	1500 : 1 : 4	65	120	95	28.1	1.53
7	1500 : 1 : 4	65	90	76	22.1	1.41
8	1500 : 1 : 4	65	180	94	26.6	1.44
9	1500 : 1 : 4	65	240	69	19.1	1.37
10	1500 : 1 : 4	65	300	71	19.6	1.40
11	1500 : 1 : 4	45	120	87	23.4	1.32
12	1500 : 1 : 4	55	120	90	26.7	1.51
13	1500 : 1 : 4	75	120	91	33.3	1.48
14	1500 : 1 : 4	85	120	88	31.8	1.48

[a] Polymerization conditions: 0.5 mL of CL and 1 mL of toluene.
[b] Isolated yield.
[c] Obtained from GPC analysis.

added to the slurry suspension of YbCl₃ (843 mg, 3 mmol) in 30 mL of DME and refluxed at 70°C for 24 h. The DME was evaporated *in vacuo*, and 30 mL of hexane was added to extract the complex. This yellow solution was cooled at −30°C to afford a yellow powder (2.2 g, yield = 81%).

ANAL. Calcd for $C_{42}H_{74}ClN_2O_6Yb$: C, 55.34%; H, 8.18%; Cl, 3.89%; Yb, 18.98%; N, 3.07%. Found: C, 55.78%; H, 7.78%; Cl, 4.26%; Yb, 19.03%; N, 3.59%. IR (Nujol, cm⁻¹): 3000–2700 (with Nujol); 1603, 1306, 1238, 1202, 1165, 1015, 839, 806, 767, 743, 531, 442.

¹H-NMR gave unresolved signals for its paramagnetic properties.

Synthesis of 1b

By the same procedure used for **1a**, complex **1b** was prepared from ErCl₃ as a pink solid (1.87 g, yield = 76%).

ANAL. Calcd for $C_{38}H_{64}ClErN_2O_4$: C, 55.96%; H, 7.91%; Cl, 4.35%; Er, 20.51%; N, 3.43%. Found: C, 55.35%; H, 7.91%; Cl, 4.40%; Er, 20.63%; N, 3.31%. IR (Nujol, cm⁻¹): 3000–2700 (with Nujol); 1603, 1302, 1239, 1202, 1165, 1015, 839, 806, 769, 743, 531, 440.

¹H-NMR also gave unresolved signals for its paramagnetic properties.

Polymerization

Polymerizations were carried out in a previously flamed and argon-purged 20-mL ampule at the required temperature with vacuum line techniques as described: to the toluene solution of the monomer and NaBH₄ was introduced a hexane solution of **1a** or **1b** by a syringe. The polymerization was terminated by 5% HCl in ethanol, and the polymers were dried *in vacuo*.

TABLE II
Ring-Opening Polymerization of CL Initiated by 1b[a] and NaBH₄

Entry	[CL]/[I]/NaBH₄	Temperature (°C)	Time (min)	Yield (%)[b]	M_n (10³)	M_w/M_n[c]
1	200 : 1 : 0	65	120	—	—	—
2	200 : 1 : 4	65	120	69	12.9	1.30
3	400 : 1 : 4	65	120	71	19.2	1.44
4	500 : 1 : 4	65	120	65	21.9	1.38
5	800 : 1 : 4	65	120	87	33.4	1.42
6	1000 : 1 : 4	65	120	96	36.4	1.43
7	800 : 1 : 4	65	15	61	21.8	1.15
8	800 : 1 : 4	65	25	77	23.9	1.24
9	800 : 1 : 4	65	35	83	26.2	1.20
10	800 : 1 : 4	65	60	87	34.4	1.37

[a] Polymerization conditions: 0.5 mL of CL and 1 mL of toluene at 65°C.
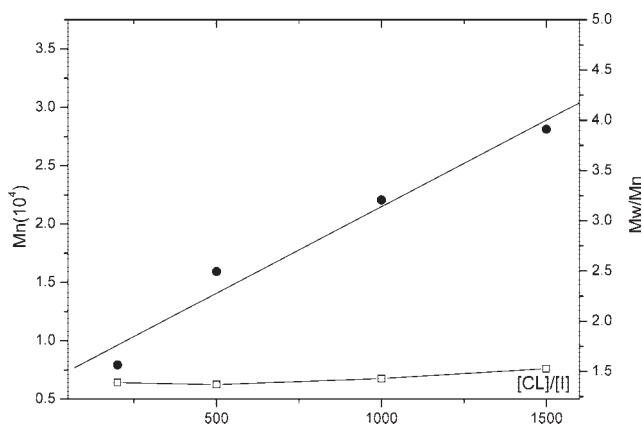[b] Isolated yield.
[c] Obtained from GPC analysis.

Figure 1 Relationship of (●) M_n and (□) M_w/M_n with the initial [CL]/[I] ratio in toluene at 65°C for **1a**.

RESULTS AND DISCUSSION

Syntheses of 1a and 1b

The ligand **T2** was synthesized in moderate yield by modification of the reported procedure. The reaction of **T2** with excess NaH in DME afforded a clear pale yellow solution after centrifugation. Salt metathesis of this sodium salt with $LnCl_3$ in DME gave the tetrahydrosalen-backboned rare-earth complexes **1a** and **1b** after extraction with hexane and cooling to −30°C. The procedures are shown in Scheme 1. However, an attempt to prepare a light rare-earth-metal-based complex ($NdCl_3$) through this salt metathesis failed, which may have been due to the relatively lower solubility of $NdCl_3$ in DME.

Ring-opening polymerization of CL from 1a/1b in the presence of NaBH₄

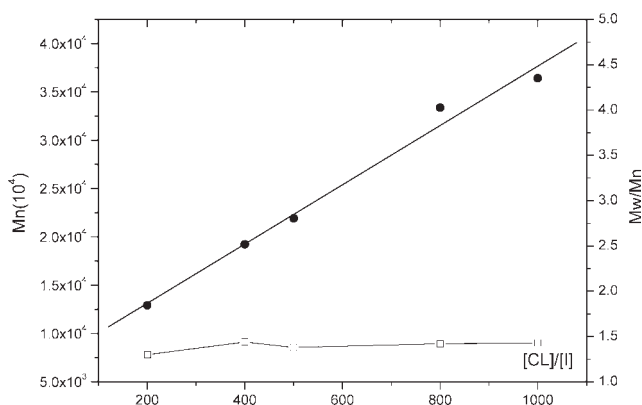Lanthanide borohydrides were reported as novel initiators for the ring-opening polymerization of CL to afford interesting hydroxytelechelic PCLs, and its initiation mechanism was different from that of traditional rare-earth initiators, as a reduction process was involved.[2] However, the formation of a gel is often observed during the polymerization, arising from the van der Waals interactions of the active end groups.[3] There are three active sites for one metal center, and the polymerization process may be affected by this complex interaction. For complexes **1a** and **1b**, two Cl atoms were substituted by the backboned O atoms in the tetrahydrosalen ligand, whereas one Ln—Cl bond remained. The feasibility of salt metathesis between Ln—Cl and $NaBH_4$[11] allowed the *in situ* generation of the active Ln—(BH_4) bond to initiate the ring-opening polymerization of CL.[12] Therefore, **1a** and **1b** were used as initiator precursors in the presence of $NaBH_4$, and the polymerization results are summarized in Tables I and II, respectively.

The polymerization of CL initiated by **1a** and $NaBH_4$ under different conditions was investigated, as listed in Table I. $NaBH_4$[12] or **1a** did not initiate the ring-opening polymerization, whereas their combination showed higher activity for the polymerization. The relationship between the number-average molecular weight (M_n) and weight-average molecular weight (M_w)/M_n and the initial ratio of [CL]/concentration of the rare-earth in solution [I] is shown in Figure 1. M_n increased linearly with increasing of [CL]/[I]. The time and temperature were then investigated. As shown from entries 7–14, the molecular weight distribution remained below 1.6, even with an extended reaction time or raised temperature. The complex van der Waals interaction resulting from the terminal —OBH_2^2 or the steric *tert*-butyl groups in the active species may account for the restrained transesterification reactions.

The polymerization activity of **1b** in the presence of $NaBH_4$ under different conditions was also investigated for comparison, as shown in Table II. The ratio effect revealed that, when the [CL]/[I] was over
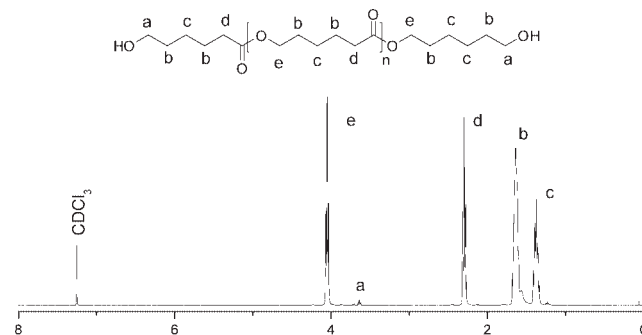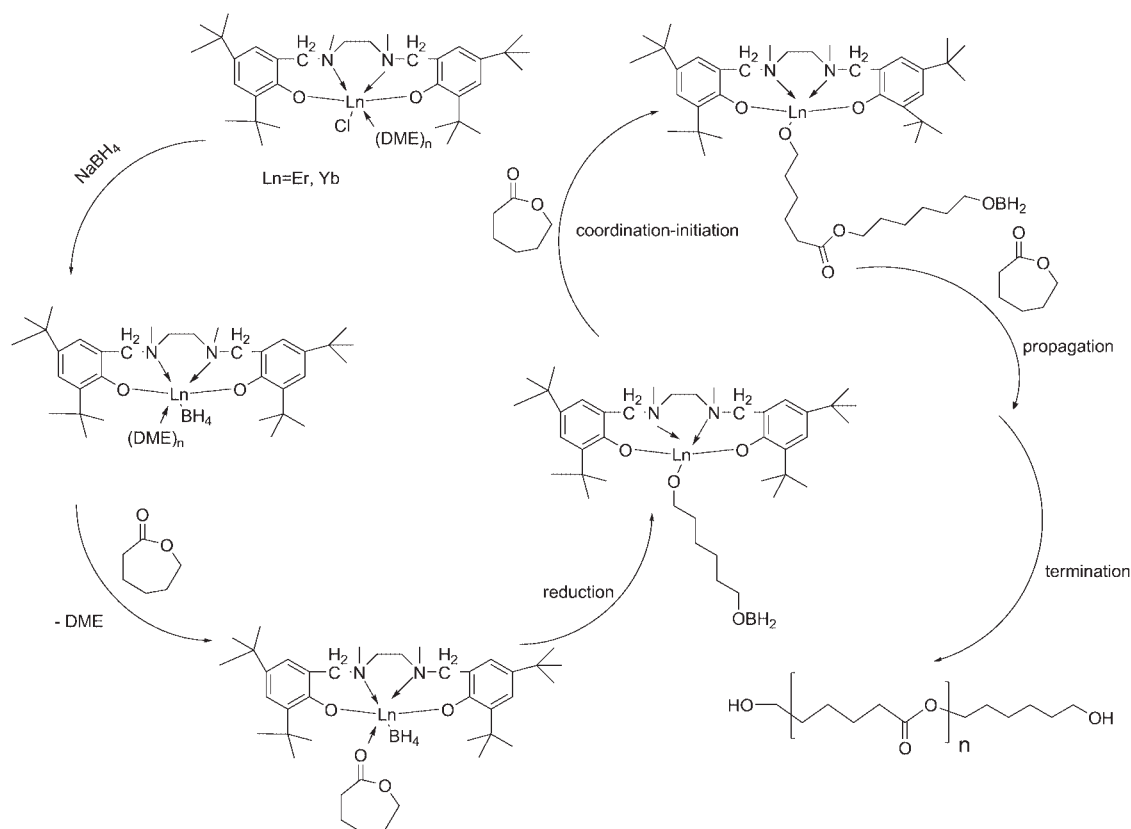

Figure 2 Relationship of (●) M_n and (□) M_w/M_n with the initial [CL]/[I] ratio in toluene at 65°C for **1b**.

Figure 3 ^{1}H-NMR analysis of the polymer terminated with isopropyl alcohol/HCl (25°C, CDCl₃).

Scheme 2 Proposed mechanism for ring-opening polymerization.

1000, the polymerization could not be initiated, which could be explained as a metal size effect (Er^{3+} > Yb^{3+}). A linear increase in M_n with increasing [CL]/[I] was also found (Fig. 2). The time effect study revealed that with increasing polymerization time, the molecular weight increased; this was accompanied by a broadening of the molecular weight distribution (entries 7–10 in Table II), which may have resulted from the intermolecular and intramolecular side reactions (back-biting and reshuffling).

Mechanistic aspects

It has been reported that the lanthanide borohydride initiated ring-opening polymerization of CL produces hydroxytelechelic PCL. The reduction-involved initiation process makes it different from those end-capped polymers, and the terminal groups are independent of the quenching agent (e.g., *i*-PrOH, PhCH$_2$OH).[2] Therefore, a polymer from a lower [CL]/[I] ratio was prepared in this study; it was terminated with *i*-PrOH/HCl and subjected to end-group analysis. As shown in Figure 3, no signal for the *i*-PrOC=O— end group was detected, which suggested that the mechanism here was similar to the reported lanthanide borohydride initiated ring-opening polymerizations.[13]

According to the previously discussed results and the commonly accepted mechanism for the ring-opening polymerization of CL from rare-earth borohydride, a mechanism for this *in situ* initiated polymerization can be depicted, as shown in Scheme 2. First, the Cl⁻ connected to Ln was substituted by BH_4^- through salt metathesis; second, a molecule of CL coordinated to the Ln center through the carbonyl group by the substitution of DME. The intramolecular reduction of the carbonyl group by BH_4^- gave the real active Ln—O initiation species. Another CL molecule was inserted into the active Ln—O bond to trigger the polymerization. This repeated insertion and propagation process produced hydroxytelechelic PCL after the hydrolysis of the —OBH$_2$ and —O—Ln end groups. It was different from the traditional ones: two —OH groups in one PCL chain rendered it with more functionalization abilities.

CONCLUSIONS

In conclusion, we prepared two tetrahydrosalen-backboned chloro-containing rare-earth complexes, **1a** and **1b**, and they were successfully used as initiator precursors for the preparation of hydroxytelechelic PCLs with a moderate molecular weight distribution (M_w/M_n = 1.15–1.53). The polymerization under different conditions was also

investigated, and a possible mechanism was proposed. Further application of the two precursors in the polymerization is underway.

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