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Ring-opening polymerization of six-membered cyclic esters catalyzed by tetrahydroborate complexes of rare earth metals

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ABSTRACT

Catalytic behavior of tetrahydroborate complexes of rare earth metals, $Ln(BH_4)_3(THF)_x$ (**1**: Ln = La, $x = 3$; **2**: Ln = Pr, $x = 2$; **3**: Ln = Nd, $x = 3$; **4**: Ln = Sm, $x = 3$; **5**: Ln = Y, $x = 2.5$; **6**: Ln = Yb, $x = 3$), for ring-opening polymerization (ROP) of six-membered cyclic esters, δ-valerolactone (VL) and D,L-lactide (D,L-LA), was studied. The controlled polymerization of VL with **1**–**6** proceeded in THF at 60 °C. The catalytic activities of these complexes for the ROP of VL were observed to be in order of the ionic radii of the metals: **1**(La) ≥ **2**(Pr) ≥ **3**(Nd) > **4**(Sm) > **5**(Y) > **6**(Yb). The obtained polymers were demonstrated to be hydroxy-telechelic by ^1H NMR and MALDI-TOF MS spectroscopy. The controlled ROP of D,L-LA also proceeded by these complexes. The activities of these complexes for the D,L-LA ROP were also in order of the ionic radii of the metals.

1. Introduction

Ring-opening polymerization (ROP) of cyclic esters such as ϵ-caprolactone (CL) and L-lactide (L-LA) is an important procedure to produce aliphatic polyesters with high molecular weights. Many catalysts and/or initiators have been extensively studied for this process [1–4]. One of the most common catalysts for ROP of cyclic esters is tin 2-ethylhexanoate, ($Sn(Oct)_2$) [1,2,5–9], which possesses good stability, availability, and moderate activity. Moreover, $Sn(Oct)_2$ has been approved as a food additive by U.S. Food and Drug Administration. On the other hand, ROP catalysts based on rare earth metals have been developing due to their high activity. Simple rare earth metal alkoxides such as $Ln_5O(O^iPr)_{13}$ (Ln = rare earth metals) and $Y(OCH_2CH_2NMe_2)_3$ exhibit high activity for ROP of cyclic esters to give polyesters with controlled molecular weight [10–14]. Aryloxo complexes, $Ln(OAr)_3$ (OAr = 2,6-di-*tert*-butylphenoxide, 4-*tert*-butylphenoxide) [15–17] and an amide complex $Y\{N(SiMe_3)_2\}_3$ [18] are also effective ROP catalysts in the presence or absence of suitable initiators. Metallocene type complexes have been reported to promote living ROP of cyclic esters [19–21], and realized block copolymerization of cyclic esters with α-olefins [22–25]. Rare earth metal complexes having multidentate nitrogen and/or oxygen donor ligands have been reported to promote well-controlled ROP of LA and CL [26–35].

Several tetrahydroborate-type complexes of rare earth metals with or without other ligands have also been reported to catalyze polymerization of CL [36–39], and L-LA [37,40]. Guillaume and coworkers reported an unique catalytic behavior of tris(tetrahydroborate) complexes of rare earth metals, $Ln(BH_4)_3(THF)_x$ (Ln = rare earth metals), which polymerize CL very rapidly in living fashion [36,38,39]. The preparation of $Ln(BH_4)_3(THF)_x$ from one-step reaction of relatively cheap and easily available sources $LnCl_3$ with $NaBH_4$ is rather easy in comparison with metallocene type complexes. In addition, $Ln(BH_4)_3(THF)_x$ has a mononuclear structure and relatively good solubility in comparison with simple alkoxides. Moreover, the obtained poly(CL)s were proved to be hydroxy-telechelic polymers, $HO(CH_2)_5CO\{O(CH_2)_5CO\}_nO(CH_2)_6OH$, resulting from the reduction of carbonyl group by hydroborate functionality. We applied this catalyst system to the preparation of hydroxy-telechelic poly(L-LA)s, which were connected with the hydroxy-telechelic PCLs by using hexamethylene diisocyanate to synthesize multiblock poly(ester-urethanes) [40].

In the polymerization system with rare earth metal tetrahydroborates, $Ln(BH_4)_3(THF)_x$, the kind of the metal center should be the key factor to control the catalytic behavior because they have no ancillary ligand on the metal. The polymerization of CL catalyzed by the complexes $Ln(BH_4)_3(THF)_3$ (Ln = La, Nd, and Sm) has been studied, however, their relative activities were not clearly described possibly due to their too high activity for the polymerization of CL [38,39]. In order to evaluate relative activities of the rare earth complexes, we adopted six-membered cyclic esters as monomers because of their lower ring strain in comparison with

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the seven-membered cyclic ester, CL. In this study, we systematically investigated the activities of a series of $Ln(BH_4)_3(THF)_x$ for the ROP of δ-valerolactone (VL) and D,L-Lactide (D,L-LA).

2. Experimental section

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (400 MHz and 100 MHz for ^{1}H and ^{13}C nuclei, respectively). Chemical shifts of ^{1}H NMR were calibrated by using residual chloroform ($\delta = 7.26$ ppm) in chloroform-*d*, and those of ^{13}C NMR were determined with the reference to the carbon resonance of chloroform-*d* ($\delta = 77.0$ ppm). Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) measurements on a Tosoh GPC system (SC-8010) equipped with both RI and multi angle laser light scattering (MALS) (DAWN DSP Laser Photometer Purchased from Watto Technology Corporation, $\lambda = 632.8$ nm as light source) detectors. THF was used as an eluent at a flow rate of 1.0 ml/min at 40 °C. The data from MALS detector were processed by MASS method. The GPC curves of low molecular weight polymers were calibrated using standard polystyrenes. MALDI-TOF MS experiments were carried out on a SHIMADZU KRATOS ANALYTICAL KOMPACT MALDI equipped with a pulsed N_2 laser (337 nm, 3 ns, pulse width). Spectra were recorded in positive-ion mode. Polymer samples were dissolved in chloroform (1 mg/ml). 2,5-Dihydroxybenzoic acid was dissolved in a 1:1 mixture of aqueous 0.1% TFA solution and ethanol as a matrix solution. The polymer solution was deposited on the sample slide with the matrix solution, and the solvents were evaporated before measurements.

2.2. Materials

Solvents such as tetrahydrofuran and *n*-hexane were distilled from Na/K–benzophenone under argon prior to use. Toluene was purified by distillation from sodium–benzophenone. All the solvents were stored over sodium. δ-Valerolactone (Aldrich) was purified by distillation from calcium hydroxide under reduced-pressure. D,L-Lactide (Aldrich) was recrystallized from THF, and then sublimed twice at 70 °C under vacuum. $LnCl_3(THF)_3$ (Ln = Nd, Sm, and Y) were donated from Rhodia Researches and used as-received. $LnCl_3$ (Ln = La, Pr, and Yb) and $NaBH_4$ were purchased from Aldrich and Katayama Chemical, respectively, and used without further purification.

2.3. Synthesis of $Ln(BH_4)_3(THF)_x$ (1–6) [36,38,41–43]

A typical procedure: a round bottom flask was charged with $LaCl_3$ (2.21 g, 8.99 mmol), $NaBH_4$ (1,12 g, 29.7 mmol, 3.3 equiv.), and THF (150 ml). The suspension was stirred at 60 °C for 48 h. Then the suspension was centrifuged to remove precipitates. The solution was concentrated and cooled to −20 °C to give $La(BH_4)_3(THF)_3$ (**1**) as colorless plate crystals (65% yield). Other complexes, $Ln(BH_4)(THF)_x$ (**2**: Ln = Pr, $x = 2$; **3**: Ln = Nd, $x = 3$; **4**: Ln = Sm, $x = 3$; **5**: Ln = Y, $x = 2.5$; **6**: Ln = Yb, $x = 3$), were synthesized by the similar procedure from the reaction of $LnCl_3(THF)_3$ or $LnCl_3$ with $NaBH_4$ in THF, except that the Pr complex **2** was finally recrystallized from toluene. The yields of **2**–**6** were 48%, 46%, 63%, 47%, and 55%, respectively. **1**: Anal. Calcd. for $C_{12}H_{36}B_3LaO_3$: C, 36.05; H, 9.08. Found: C, 35.76; H, 9.17. **2**: Anal. Calcd. for $C_8H_{28}B_3PrO_2$: C, 29.15; H, 8.56. Found: C, 29.25; H, 7.94. **3**: Anal. Calcd. for $C_{12}H_{36}B_3NdO_3$: C, 35.58; H, 8.96. Found: C, 35.29; H, 9.05. **4**: Anal. Calcd. for $C_{12}H_{36}B_3SmO_3$: C, 35.05; H, 8.82. Found: C, 34.12; H, 8.01. **5**: Anal. Calcd. for $C_{10}H_{32}B_3YO_{2.5}$: C, 38.29; H, 10.28. Found: C, 38.07; H, 11.00. **6**: Anal. Calcd. for $C_{12}H_{36}B_3YbO_3$: C, 33.22; H, 8.36. Found: C, 32.31; H, 7.42.

$$LnCl_3(THF)_y \quad + \quad 3\ NaBH_4 \xrightarrow[\text{THF}]{60\ ^\circ\text{C},\ 48\ \text{h}} Ln(BH_4)_3(THF)_x$$

1: Ln = La, x = 3
2: Ln = Pr, x = 2
3: Ln = Nd, x = 3
4: Ln = Sm, x = 3
5: Ln = Y, x = 2.5
6: Ln = Yb, x = 3

Scheme 1.

2.4. Polymerization of δ-valerolactone or D,L-lactide by $Ln(BH_4)_3(THF)_x$

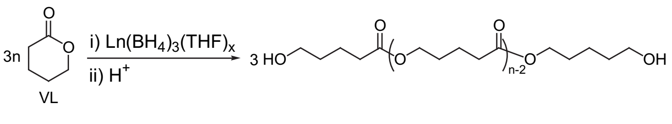
A given amount of the obtained complex was dissolved in THF. This solution was added to a prescribed amount of δ-valerolactone or D,L-lactide in the same solvent at a prescribed temperature. The resulting solution was stirred for a given time. The reaction was quenched by addition of a small amount of hydrochloric acid. The mixture was dissolved in chloroform and poured into hexane/ether (70 vol%/30 vol%) mixture or methanol. The precipitated polymer was collected by centrifugation and dried in vacuo.

3. Results and discussion

A series of tetrahydroborate complexes of rare earth metals, $Ln(BH_4)_3(THF)_x$ (**1**: Ln = La, $x = 3$; **2**: Ln = Pr, $x = 2$; **3**: Ln = Nd, $x = 3$; **4**: Ln = Sm, $x = 3$; **5**: Ln = Y, $x = 2.5$; **6**: Ln = Yb, $x = 3$), was prepared from the reaction of $LnCl_3$ or $LnCl_3(THF)_3$ with three equivalents of $NaBH_4$ in THF according to literature (Scheme 1) [36,38,41–43]. The numbers of THF in these complexes were estimated by elemental analysis. Polymerizations of cyclic esters by the rare earth complexes **1**–**6** were performed under different $[M]_0/[I]_0$ ratio typically in THF at 60 °C.

3.1. Polymerization of VL

The results for the polymerization of VL by the rare earth tetrahydroborates **1**–**6** (Scheme 2) are summarized in Table 1. In comparison with the polymerization of CL with **3**, in which more than 100 equiv. of CL was quantitatively polymerized within 5 min at r.t. [36,38,39], the polymerization of VL was considerably slower as expected, due to smaller ring strain of VL than that of CL. For example, the polymerization of 150 equiv. of VL with **1** took 30 min to reach 72% yield (run 1). The estimated number of the produced polymer chains per one initiator (*n*) was close to three in THF (runs 1–6), suggesting all the three tetrahydroborate groups on the metal initiated the polymerization of VL. Comparing runs 5 and 11–15 in Table 1, the catalytic activities of the rare earth tetrahydroborate complexes for VL polymerization were found to apparently depend on the kind of the metal center, in order of **1**(La) ≥ **2**(Pr) ≥ **3**(Nd) > **4**(Sm) > **5**(Y) > **6**(Yb). This tendency is in good relationship with ionic radii of these metals (ionic radii (Å) of six-coordinated ions: La^{3+} 1.17, Pr^{3+} 1.13, Nd^{3+} 1.12, Sm^{3+} 1.10, Y^{3+} 1.04, and Yb^{3+} 1.01 Å) [44]. Similar tendency



Scheme 2.

Table 1
Polymerization of δ-valerolactone catalyzed by $Ln(BH_4)_3(THF)_x$ (**1**–**6**) in THF.

Run	Complex	$[M]_0/[I]_0$ mol/mol	Time (min)	Yield%	M_n[a] 10^3	M_w/M_n[a]	n[b]
1	**1**	150	30	72.2	5.0[c]	1.5[c]	2.2
2	**1**	300	10	55.0	7.2	1.3	2.3
3	**1**	300	30	79.4	9.9	1.3	2.4
4	**1**	300	60	85.3	10.5	1.3	2.4
5	**1**	600	60	57.5	10.6	1.3	3.3
6	**1**	600	180	80.9	15.0	1.4	3.2
7[d]	**1**	600	10	83.1	14.7	1.4	3.4
8[d]	**1**	900	30	93.8	10.5	1.7	8.0
9[e]	**1**	600	10	82.5	10.5	1.5	4.7
10[e]	**1**	900	30	85.4	6.4	1.6	12.0
11	**2**	600	60	55.0	8.1	1.4	5.2
12	**3**	600	60	54.8	7.3	1.5	4.5
13	**4**	600	60	25.7	4.8	1.5	3.2
14	**5**	600	60	3.3	4.3	1.6	0.5
15	**6**	600	60	No polymer			

Polymerization conditions: $[M]_0 = 1.00$ mol/L, Solvent = 5.0 ml of THF, Temp. = 60 °C.

[a] Determined by SEC-MALS in THF.

[b] n: The estimated number of the produced polymer chains per one initiator; $n = 100.12 \times ([M]_0/[I]_0) \times (\mathrm{Yield}/100)/M_n$.

[c] Determined by SEC in THF calibrated with polystyrene standard.

[d] $[M]_0 = 1.00$ mol/L, Solvent = 2.5 ml of toluene, Temp. = 60 °C.

[e] $[M]_0 = 1.00$ mol/L, Solvent = 2.5 ml of toluene, Temp. = 90 °C.

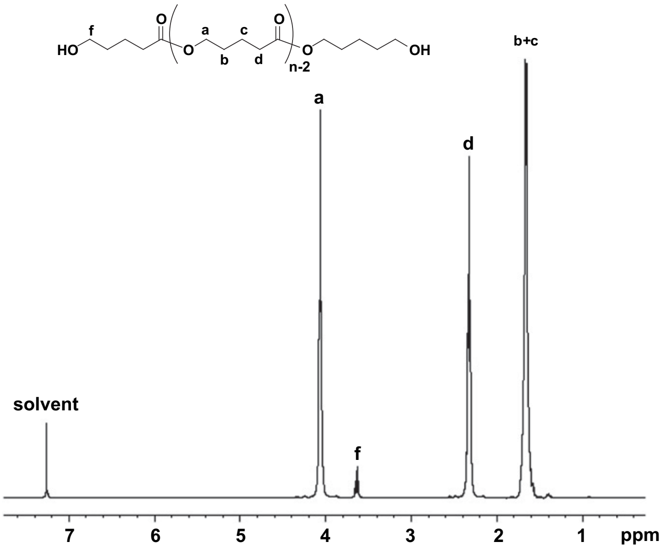


Fig. 2. ^1H NMR Spectrum (400 MHz, $CDCl_3$, r.t.) of poly(δ-valerolactone) ($M_n = 5{,}500$, $M_w/M_n = 1.5$) synthesized with $La(BH_4)_3(THF)_3$ (**1**).

was observed in the polymerization of D,L-LA by $Ln_5O(O^iPr)_{13}$ (activities: Ln = La > Sm > Y > Yb) [13,14], methyl methacrylate by $(C_5Me_5)_2LnMe(THF)$ (activities: Ln = Sm > Y > Yb > Lu) [45], and ethylene by $[(C_5Me_5)_2LnH]_2$ (activities: Ln = La ≥ Nd > > Lu) [46]. Larger ionic radii should allow faster access of the monomers to the metal center to enhance polymerization activity. The varying n values in runs 11–14 could be partly attributed to relatively low molecular weights of the polymers which are close to lower limitation of SEC-MALS analysis.

The M_n and M_w/M_n of the resulting polymers prepared by **1** in THF are plotted vs. polymer yield as shown in Fig. 1. Linear relationship between M_n and polymer yield and relatively narrow molecular weight distribution ($M_w/M_n \sim 1.2$) were observed in the polymerization of VL, indicating the controlled polymerization of VL with **1**. The M_w/M_n values tend to decrease with increasing polymer yield, suggesting that the broadening of the molecular weight distribution mainly comes from relatively slow initiation. As observed in the case of the CL polymerization by **3** [36], the use of toluene as a polymerization solvent (runs 7–10) instead of THF brought higher activity to produce polymers with lower molecular weights (higher n values) and broader molecular weight distributions, suggesting that both the rates of propagation and chain transfer such as back-biting [47] were higher in toluene than those in THF.

Fig. 2 shows the ^1H NMR spectrum of the poly(VL) obtained with **1**. The signal at 3.6 ppm can be assigned to the methylene protons at α-position to terminal hydroxy group. No other signals assignable to any other terminal groups were observed. The MALDI-TOF MS spectrum of the poly(VL), which was prepared from the ROP of VL with **1** at $[VL]_0/[La] = 10$ for the ease of detection, is shown in Fig. 3. Polymer ions were observed as repeating sets of Na^+- and K^+- adducts. The observed peaks are in good agreement with the calculated values for the hydroxy-telechelic structure, e.g., m/z (obs.) = 2029.3 vs. m/z (th.) = 2029.3 for $HO(CH_2)_4CO\{O(CH_2)_4CO\}_{18}O(CH_2)_5OH] + Na^+$. These results supported the production of hydroxy-telechelic poly(VL).

We speculate that the mechanism for the formation of hydroxy-telechelic poly(VL) by the $Ln(BH_4)_3(THF)_x$ should be similar to that for hydroxy-telechelic poly(CL) [36,38,39,48]. A VL monomer was first inserted to metal–hydride(borate) bond to

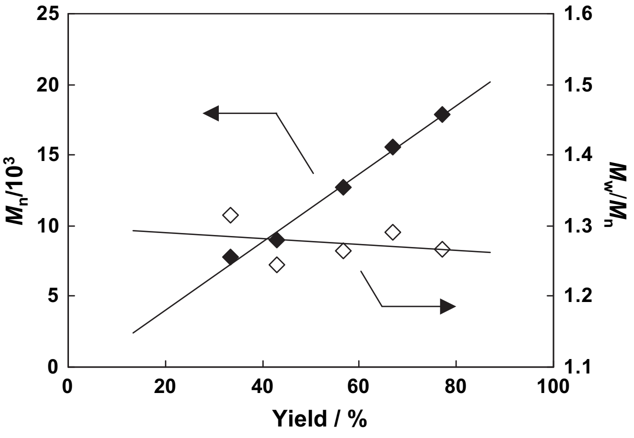


Fig. 1. Plots of M_n and M_w/M_n vs. Yield in the polymerization of δ-valerolactone with complex **1** (◆ = M_n, ◇ = M_w/M_n). Polymerization conditions: $[M]_0/[I]_0 = 600$, $[M]_0 = 1.00$ mol/L, Solvent = 5.0 ml of THF, Temp = 60 °C.

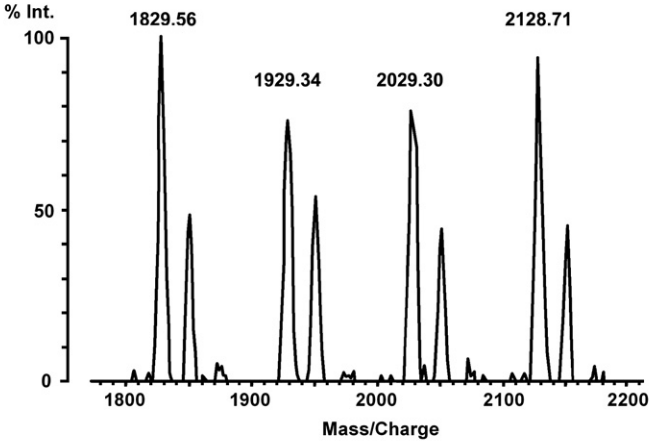
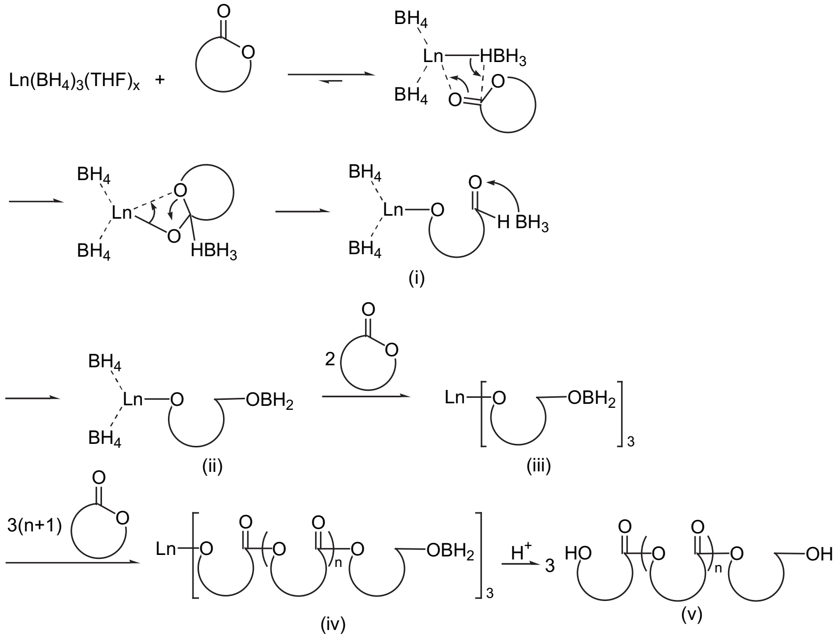


Fig. 3. MALDI-TOF MS Spectrum of poly(δ-valerolactone) obtained by using **1** in THF.



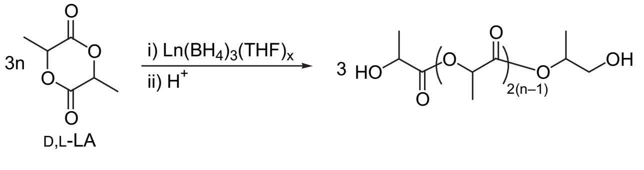
Scheme 3.

form $Ln–O(CH_2)_4C(O)HBH_3$ ((i) in Scheme 3). Immediate attack of the terminal BH_3 group to the neighboring carbonyl group could yield $Ln–O(CH_2)_5OBH_2$ ((ii) in Scheme 3). Other $Ln–HBH_3$ bonds undergoes similar reaction with the monomers to generate $Nd\{O(CH_2)_5OBH_2\}_3$ ((iii) in Scheme 3). Successive insertion of the monomer forms polymers having neodymium and boron alkoxide ends ((iv) in Scheme 3). Protonolysis of (iv) affords hydroxy-telechelic poly(VL) ((v) in Scheme 3).

3.2. *Polymerization of D,L-LA*

The polymerization of L-lactide (L-LA) by the neodymium complex **3** has been reported to proceed smoothly [40]. In this polymerization system, production of hydroxy-telechelic poly(L-LA) was supported by MALDI-TOF MS spectroscopy and by the fact that the resulting polymers could be chain extended with hexamethylene diisocyanate. Our purpose in this study is to evaluate the effect of the metal center on their catalytic activity, and here we adopted D,L-LA as a monomer for the ease of manipulation due to the better solubility of the monomer and the resulting polymer (Scheme 4). The results of the D,L-LA polymerizations are summarized in Table 2. The ROP of D,L-LA proceeded in THF to produce high molecular weight polymers as observed in the ROP of L-LA with **3** [40]. From runs 18 and 22–26, the catalytic activities of the rare earth tetrahydroborate complexes for D,L-LA polymerization were also found to be in order of **1**(La) > **2**(Pr) ≥ **3**(Nd) > **4**(Sm) > **5**(Y) > **6**(Yb), as observed in the polymerization of VL. This could be attributed to the similarity of active species.

By using the most active lanthanum complex **1** among them, effects of solvent and temperature on D,L-LA polymerization were further studied. The polymerization of D,L-LA rapidly proceeded at 60 °C both in THF and in toluene, whereas significantly slower at room temperature in THF (run 19). The polymerization of D,L-LA (600 equiv.) by the lanthanum complex **1** in THF at 60 °C was almost completed within 1 h (run 21). Thus, the complex **1** is significantly more active than $Sn(Oct)_2$ [49], although still less active than the most active zinc [50] and some other rare earth-based systems [15]. The M_n and M_w/M_n of the resulting polymers prepared in THF are plotted vs. polymer yield as shown in Fig. 4. Linear relationship between M_n and polymer yield and relatively narrow molecular weight distribution (M_w/M_n ~1.2) indicate controlled polymerization of D,L-LA with **1**. The M_w/M_n values tend to decrease with increasing polymer yield as observed in the VL polymerization, suggesting that the broadening of the molecular weight distribution mainly comes from relatively slow initiation. The estimated number of the polymer chains per one initiator (n) was 2.7–3.2 for the samples produced in THF at 60 °C, which is close



Scheme 4.

Table 2
Polymerization of D,L-Lactide catalyzed by $Ln(BH_4)_3(THF)_x$ (**1**–**6**) in THF.

Run	Complex	$[M]_0/[I]_0$ mol/mol	Time (h)	Yield%	M_n[a] 10^3	M_w/M_n[a]	n[b]
16	**1**	100	1	92.4	4.8[c]	1.6[c]	2.8
17	**1**	200	1	98.8	11.4	1.2	2.7
18	**1**	400	1	91.1	16.3	1.3	3.2
19[d]	**1**	400	6	43.8	6.9[c]	1.5	3.7
20[e]	**1**	400	1	91.8	30.1	1.2	1.8
21	**1**	600	1	89.6	24.0	1.2	3.2
22	**2**	400	1	65.1	12.7	1.3	3.0
23	**3**	400	1	64.1	12.2	1.4	3.0
24	**4**	400	1	59.4	12.1	1.3	2.8
25	**5**	400	1	23.7	3.8	1.7	3.6
26	**6**	400	1	No polymer			

Polymerization conditions: $[M]_0 = 1.39$ mol/L, Solvent = 2.5 ml of THF, Temp. = 60 °C.

[a] Determined by SEC-MALS in THF.

[b] n: The number of polymer chain per one initiator; $n = 144.13 \times ([M]_0/[I]_0) \times (\mathrm{Yield}/100)/M_n$.

[c] Determined by SEC in THF calibrated with polystyrene standard.

[d] Polymerization was performed at room temperature.

[e] $[M]_0 = 0.50$ mol/L, Solvent = 6.0 ml of toluene.

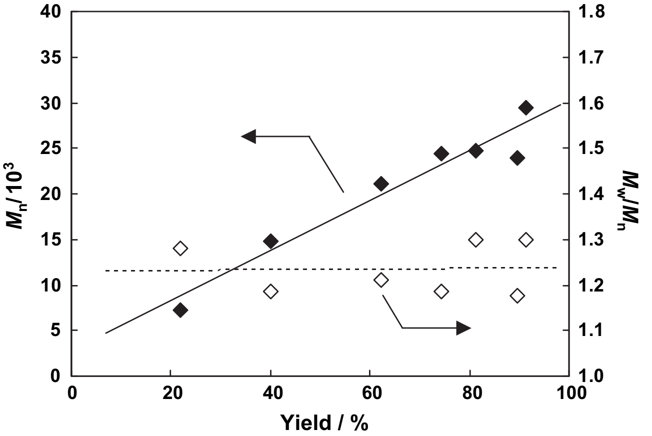


Fig. 4. Plots of M_n and M_w/M_n vs. Yield in the polymerization of D,L-LA with complex **1** (◆ = M_n, ◇ = M_w/M_n). Polymerization conditions: $[M]_0/[I]_0 = 600$, $[M]_0 = 1.39$ mol/L, Solvent = 2.5 ml of THF, Temp. = 60 °C.

to three as observed in the polymerization of VL (*vide supra*). The use of toluene as a solvent instead of THF resulted in similar activity and lower initiation efficiency, where the *n* value was decreased to 1.9 (run 20).

3.3. Copolymerization of VL with L-LA or CL

Because the complex **1** is effective for the polymerization of VL and L-LA [37,40], we tried random copolymerization of VL and L-LA (Table 3). However, VL was little incorporated in the resulting polymer (Table 3), as in the copolymerization of CL and L-LA [40]. Preliminary experiments for block copolymerization by sequential addition of VL and then L-LA were also unsuccessful, in which the second monomer polymerization was too slow similarly to that of CL and L-LA [40].

The complex **1** is also effective for the polymerization of CL [36–39], so we also tried random copolymerization of VL and CL (Table 4). The complex **1** showed high activity for the homopolymerization of CL (run 33), in which monomer conversion reached ca. 50% within 5 min. The observed activity of **1** in this study is lower than that in Guillaume's reports (100% conversion within 5 min) [38,39], which might come from lower monomer concentration in this study. In contrast, copolymerization of VL and CL (runs 30–32) was much slower than both homopolymerizations of VL and CL. The CL contents of the resulting copolymers were slightly lower than the VL contents. The polymer obtained at the early stage of the polymerization exhibited bimodal molecular weight distribution (run 30). Although we do not have a good explanation for these observations, we could consider that the rare earth tetrahydroborate complex system is significantly sensitive to the kind of used monomer.

Table 3
Random copolymerization of L-LA and VL catalyzed by $La(BH_4)_3(THF)_3$ (**1**).

Run	Time (h)	Molar ratio[a] (L-LA/VL)		Yield %	M_n[b] 10^3	M_w/M_n[b]
		Feed	Observed			
27	3	50/50	96.1/3.9	46.5	10.0	1.3
28	6	50/50	95.1/4.9	51.7	11.1	1.3
29	12	50/50	93.8/6.2	61.3	11.9	1.3

Polymerization conditions: $[L\text{-}LA]_0 = 0.5$ mol/L, $[VL]_0 = 0.5$ mol/L, $([L\text{-}LA]_0 + [VL]_0)/[I]_0 = 300$, Solvent = 5 ml of THF, Temp. = 60 °C.
[a] Determined by ^{1}H NMR.
[b] Determined by GPC in THF calibrated with polystyrene standard.

Table 4
Random copolymerization of CL and VL catalyzed by $La(BH_4)_3(THF)_3$ (**1**).

Run	Time (min)	Molar ratio[a] (CL/VL)		Yield%	M_n[b] 10^3	M_w/M_n[b]
		Feed	Observed			
30	5	50/50	42/58	2.4	17.9 (Bimodal)	2.5 (Bimodal)
31	30	50/50	37/63	9.1	13.3	1.5
32	60	50/50	39/61	16.5	11.9	1.5
33[c]	5	100/0	100/0	49.7	1.0	1.5

Polymerization conditions: $[CL]_0 = 0.5$ mol/L, $[VL]_0 = 0.5$ mol/L, $([CL]_0 + [VL]_0)/[I]_0 = 150$, Solvent = 5 ml of THF, Temp. = 60 °C.
[a] Determined by ^{1}H NMR.
[b] Determined by GPC in THF calibrated with polystyrene standard.
[c] $[CL]_0 = 0.5$ mol/L, $[CL]_0/[I]_0 = 75$, Temp. = r.t.

4. Conclusions

A series of tris(tetrahydroborate) complexes of rare earth metals, $Ln(BH_4)_3(THF)_x$ (Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Y (**5**), Yb(**6**)), was demonstrated to be active catalyst/initiator for the ring-opening polymerization of six-membered cyclic esters, VL and D,L-LA. The catalytic activities of these rare earth metals were found to be in order of La > Pr > Nd > Sm > Y > Yb for both VL and D,L-LA, which is in good agreement with the order of ionic radii of the metal center. Thus, the catalytic activity of these tetrahydroborate complexes without ancillary ligands was demonstrated to be highly dependent on the kind of metal center. The molecular weights of the resulting polymers were linearly increased with conversion and the molecular weight distributions remained relatively narrow ($M_w/M_n \approx 1.2$–1.4), indicating controlled polymerization proceeding in these systems. The obtained poly(VL) was revealed to be hydroxytelechelic by ^{1}H NMR and MALDI-TOF MS spectroscopy.

References

[1] O'Keefe BJ, Hillmyer MA, Tolman WB. J Chem Soc Dalton Trans 2001:2215–24.
[2] Dechy-Cabaret O, Martin-Vaca B, Bourissou D. Chem Rev 2004;104(12):6147–76.
[3] Chisholm MH, Zhou Z. Stereoselective polymerization of lactide. In: Baugh LS, Canich LAM, editors. Stereoselective polymerization with single-site catalysts. Boca Raton: CRC Press; 2007. p. 363–397.
[4] Dubois P, Coulembier O, Raquez J-M. Handbook of ring-opening polymerization. Weinheim: Wiley; 2009.
[5] Degee P, Dubois P, Jerome R, Jacobsen S, Fritz H-G. Macromol Symp 1999;144:289.
[6] Schwach G, Coudane J, Engel R, Vert M. J Polym Sci Part A Polym Chem 1997;35(16):3431–40.
[7] Kricheldorf HR, Kreiser-Saunders I, Stricker A. Macromolecules 2000;33(3):702–9.
[8] Kowalski A, Duda A, Penczek S. Macromolecules 2000;33(20):7359–70.
[9] Penczek S, Duda A, Kowalski A, Libiszowski J, Majerska K, Biela T. Macromol Symp 2000;157(1):61–70.
[10] McLain SJ, Drysdale NE. Polym Prep (Am Chem Soc Div Polym Chem) 1992;33(2):174.
[11] McLain SJ, Ford TM, Drysdale NE. Polym Prep (Am Chem Soc Div Polym Chem) 1992;33(2):463.
[12] McLain SJ, Ford TM, Drysdale NE, Shreeve JL, Evans WJ. Polym Prep (Am Chem Soc Div Polym Chem) 1994;35(2):534.
[13] Stevels WM, Ankoné MJK, Dijkstra PJ, Feijen J. Macromol Chem Phys 1995;196(4):1153–61.
[14] Simic V, Spassky N, Hubert-Pfalzgraf LG. Macromolecules 1997;30(23):7338–40.
[15] Stevels WM, Ankoné MJK, Dijkstra PJ, Feijen J. Macromolecules 1996;29(9):3332–3.
[16] Stevels WM, Ankoné MJK, Dijkstra PJ, Feijen J. Macromolecules 1996;29(26):8296–303.
[17] Yu C, Zhang L, Ni X, Shen Z, Tu K. J Polym Sci Part A Polym Chem 2004;42(24):6209–15.
[18] Martin E, Dubois P, Jérôme R. Macromolecules 2000;33(5):1530–5.
[19] Evans WJ, Katsumata H. Macromolecules 1994;27(8):2330–2.
[20] Evans WJ, Katsumata H. Macromolecules 1994;27:4011.
[21] Yamashita Y, Takemoto Y, Ihara E, Yasuda H. Macromolecules 1996;29(5):1798–806.

[22] Yasuda H, Furo M, Yamamoto H, Nakamura A, Miyake S, Kibino N. Macromolecules 1992;25:5115.
[23] Desurmont G, Tanaka M, Li Y, Yasuda H, Tokimitsu T, Tone S, et al. J Polym Sci Part A Polym Chem 2000;38:4095–109.
[24] Desurmont G, Tokimitsu T, Yasuda H. Macromolecules 2000;33(21):7679–81.
[25] Yasuda H, Desurmont G. Polym Int 2004;53:1017–24.
[26] Chamberlain BM, Sun Y, Hagadorn JR, Hemmesch EW, Young J VG, Pink M, et al. Macromolecules 1999;32(7):2400–2.
[27] Chamberlain BM, Jazdzewski BA, Pink M, Hillmyer MA, Tolman WB. Macromolecules 2000;33(11):3970–7.
[28] Ovitt RM, Coates GW. J Am Chem Soc 1999;121(16):4072–3.
[29] Giesbrecht GR, Whitener GD, Arnold J. J Chem Soc Dalton Trans 2001:923–7.
[30] Noss H, Oberthür M, Fischer C, Kretschmer WP, Kempe R. Eur J Inorg Chem 1999:2283–8.
[31] Shen Y, Shen Z, Zhang Y, Yao K. Macromolecules 1996;29(26):8289–95.
[32] Gröb T, Seybert G, Massa W, Weller F, Palaniswami R, Greiner A, et al. Angew Chem Int Ed 2000;39(23):4373–5.
[33] Cai C-X, Amgoune A, Lehmann CW, Carpentier J-F. Chem Commun 2004;3:330–1.
[34] Yao Y, Xu X, Liu B, Zhang Y, Shen Q, Wong W-T. Inorg Chem 2005;44(14):5133–40.
[35] Amgoune A, Thomas CM, Ilinca S, Roisnel T, Carpentier J-F. Chem Commun 2006;45(17):2782–4.
[36] Guillaume SM, Schappacher M, Soum A. Macromolecules 2003;36(1):54–60.
[37] Bonnet F, Cowley AR, Mountford P. Inorg Chem 2005;44(24):9046–55.
[38] Palard I, Soum A, Guillaume SM. Macromolecules 2005;38(16):6888–94.
[39] Palard I, Schappacher M, Soum A, Guillaume SM. Polym Int 2006;55(10):1132–7.
[40] Nakayama Y, Okuda S, Yasuda H, Shiono T. React Funct Polym 2007;67(9):798–806.
[41] Mirsaidov U, Rotenberg TG, Dymova TN. Dokl Akad Nauk Tadzhikskoi SSR 1976;19(2):30–3.
[42] Cendrowski-Guillaume SM, Nierlich M, Lance M, Ephritikhine M. Organometallics 1998;17(5):786–8.
[43] Cendrowski-Guillaume SM, Gland GL, Nierlich M, Ephritikhine M. Organometallics 2000;19(26):5654–60.
[44] Shannon RD. Acta Crystallogr 1976;A32:751.
[45] Yasuda H, Yamamoto H, Yamashita M, Yokota K, Nakamura A, Miyake S, et al. Macromolecules 1993;26(26):7134–43.
[46] Jeske G, Lauke H, Mauermann H, Swepston PN, Schumann H, Marks TJ. J Am Chem Soc 1985;107(26):8091–103.
[47] Takashima Y, Nakayama Y, Watanabe K, Itono T, Ueyama N, Nakamura A, et al. Macromolecules 2002;35(20):7538–44.
[48] Barros N, Mountford P, Guillaume SM, Maron L. Chem Eur J 2008;14(18):5507–18.
[49] Nijenhuis AJ, Grijpma DW, Pennings AJ. Macromolecules 1992;25(24):6419–24.
[50] Chamberlain BM, Cheng M, Moore DR, Ovitt TM, Lobkovski EB, Coates GW. J Am Chem Soc 2001;123(14):3229–38.