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Synthesis and Characterization of Amine-Bridged Bis(phenolate)lanthanide Alkoxides and Their Application in the Controlled Polymerization of *rac*-Lactide and *rac*-β-Butyrolactone

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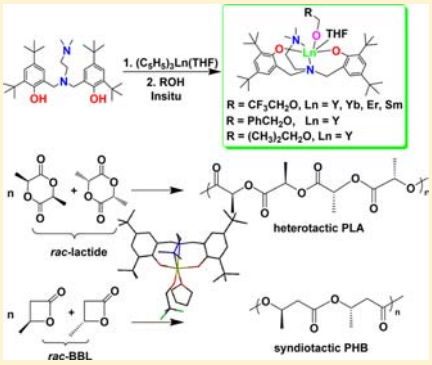
Supporting Information

ABSTRACT: A series of neutral lanthanide alkoxides supported by an amine-bridged bis(phenolate) ligand were synthesized, and their catalytic behaviors for the polymerization of *rac*-lactide (LA) and *rac*-β-butyrolactone (BBL) were explored. The reactions of $(C_5H_5)_3Ln(THF)$ with amine-bridged bis(phenol) LH_2 [L = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2Bu^t_2\text{-}3,5)\}_2$] in a 1:1 molar ratio in THF for 1 h and then with 1 equiv each of 2,2,2-trifluoroethanol, benzyl alcohol, and 2-propanol gave the neutral lanthanide alkoxides $LLn(OCH_2CF_3)(THF)$ [Ln = Y (**1**), Yb (**2**), Er (**3**), Sm (**4**)], $LY(OCH_2Ph)(THF)$ (**5**), and $LY(OPr^i)(THF)$ (**6**), respectively. These lanthanide alkoxides are sensitive to moisture, and the yttrium complex $[(LY)_2(\mu\text{-}OPr^i)(\mu\text{-}OH)]$ (**7**) was also isolated as a byproduct during the synthesis of complex **6**. Complexes **1**−**6** were well characterized by elemental analyses and IR and NMR spectroscopy in the cases of complexes **1** and **4**−**6**. The definitive molecular structures of all of these complexes were determined by single-crystal X-ray analysis. It was found that complexes **1**−**6** can initiate efficiently the ring-opening polymerization of *rac*-LA and *rac*-BBL in a controlled manner. For *rac*-LA, polymerization gave polymers with very narrow molecular weight distributions (PDI ≤ 1.12) and very high heterotacticity (P_r up to 0.99). The observed activity-increasing order is in agreement with the order of the ionic radii, whereas the order for stereoselectivity is in the reverse order. For *rac*-BBL polymerization, the resultant polymers have narrow molecular distributions (PDI ≤ 1.26) and high syndiotacticity (P_r up to 0.83). It is worth noting that the activity-decreasing order Yb > Er > Y ≫ Sm is observed for *rac*-BBL polymerization, which is opposite to the order of ionic radii and to the order of activity for *rac*-LA polymerization. The ionic radii of lanthanide metals have no obvious effect on the stereoselectivity for *rac*-BBL polymerization, which is quite different from that for *rac*-LA polymerization. End-group analysis of the oligomer of *rac*-BBL suggested that elimination side reactions occurred slowly in these systems, which led to chain cleavage and the formation of crotonate (and carboxy) end groups.



INTRODUCTION

Biodegradable polymers, such as poly(lactide) (PLA) and poly(hydroxybutyrate) (PHB), have recently gained great attention as a replacement for conventional synthetic materials because of their biodegradable, biocompatible, and permeable properties.[1] The most efficient synthesis, and the commercial route to PLA and PHB, involves the ring-opening polymerization (ROP) of the related monomers, respectively.[1d,g] Because the stereochemistry of the monomeric units in the polymer chains plays a decisive role in the mechanical, physical, and degradation properties of PLA or PHB materials, the design and synthesis of catalysts to prepare different stereospecific PLA or PHB architectures is a major topic.[2] Throughout the past decade, significant effort has been invested in the development of discrete, well-characterized metal complexes to initiate the stereocontrolled ROP of lactide (LA) and β-butyrolactone (BBL).[3−10] Among the numerous metal-based catalysts that have been disclosed for these polymerizations, organolanthanides, especially yttrium complexes, hold a special position, which is particularly efficient initiators for the preparation of unique polyesters with controlled features.[6,8c,d,9,10a,b,g]

Amine-bridged bis(phenolate)lanthanide derivatives showed high activity for the polymerization of cyclic esters, giving polymers both in high yields and with high molecular weights, and, in some cases, excellent stereoselectivity for *rac*-LA polymerization. However, the alkoxides showed good controllability for these polymerizations, in comparison with the corresponding lanthanide amides and alkyls. Almost all of the amine-bridged bis(phenolate)lanthanide alkoxides are generated in situ by alcoholysis reactions of lanthanide amido or alkyl complexes with alcohols while these lanthanide alkyl and amido complexes are extremely sensitive, and alcoholysis reactions are,

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in some cases, uncontrolled. Thus, unexpected products were usually generated, which led to termination of the active propagation species in the polymerization of cyclic esters. The structurally characterized amine-bridged bis(phenolate)-lanthanide alkoxide is scarce. To our knowledge, there is only one example of crystallographically characterized yttrium alkoxide stabilized by a tetradentate salan ligand formed by alcoholysis reaction in the literature.[10a]

Recently, we became interested in studying the synthesis and reactivity of lanthanide alkoxo complexes that are supported by the bulky bridged bis(phenolate) ligands.[11] It was found that carbon-bridged bis(phenolate)lanthanide alkoxo complexes can be conveniently synthesized by proton-exchange reactions using $(C_5H_5)_3Ln(THF)$ as the starting materials, which are efficient initiators for the controlled polymerization of ε-caprolactone.[11b,c] A further study revealed that lanthanide aryloxides stabilized by the amine-bridged bis(phenolate) ligand can be prepared in high yields by sequential proton-exchange reactions using $(C_5H_5)_3Ln(THF)$ as the precursors,[10b] but attempts to synthesize the desired amine-bridged bis(phenolate)lanthanum alkoxides by the same method were unsuccessful.[11d] We now find that both the acidity of the alcohols and the ionic radii of the lanthanide metals play crucial roles in proton-exchange reactions between amine-bridged bis(phenolate)lanthanide cyclopentadienyl complexes and alcohols, and the desired lanthanide alkoxides can be prepared under suitable reaction conditions using $(C_5H_5)_3Ln(THF)$ as the precursors. It was found that these lanthanide alkoxides are efficient initiators for the ROP of *rac*-LA and *rac*-BBL to give polymers with narrow molecular distributions and high syndio/heterotacticity. A systematic study revealed that the ionic radii of lanthanide metals have no obvious effect on the stereoselectivity for *rac*-BBL polymerization, but the activity-decreasing order is opposite to the order of the ionic radii, which is quite different from those for polymerization of other cyclic esters. Herein we report these results.

EXPERIMENTAL SECTION

General Procedures. All of the manipulations were performed under a purified argon atmosphere using standard Schlenk techniques. The solvents were degassed and distilled from sodium benzophenone ketyl under argon prior to use. $(C_5H_5)_3Ln(THF)$[12] and the ligand LH_2 [L = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2Bu^t_2\text{-}3,5)\}_2$][13] were prepared according to the procedures reported in the literature. 2,2,2-Trifluoroethanol, benzyl alcohol, and 2-propanol were dried over 4 Å molecular sieves for 1 week and then distilled before use. *rac*-Lactide (*rac*-LA) was recrystallized twice from dry toluene and then sublimed under vacuum at 50 °C. *rac*-β-Butyrolactone (*rac*-BBL) was freshly distilled from CaH_2 under nitrogen and degassed thoroughly by freeze−pump−thaw cycles prior to use. Lanthanide analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[14] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 Fourier transform IR spectrometer as KBr pellets. The ^1H and ^{13}C NMR spectra were recorded in a C_6D_6 solution for complexes **1** and **4**−**6** with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectra for the other complexes were obtained. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weight and molecular weight distribution (PDI) were determined against a poly(methyl methacrylate) (PMMA) standard by gel permeation chromatography (GPC) on a PL 50 apparatus equipped with PLgel 10 μm MIXED-B columns (300 × 7.5 mm) and a refractive index detector, and tetrahydrofuran (THF; HPLC grade, distilled and filtered under vacuum prior to use) was used as an eluent at a flow rate of 1.0 mL min^{-1} at 40 °C. The samples were prepared by dissolving a maximum weight of 5 mg of polymer in 5 mL of THF. The microstructures of PLAs and PHBs were measured by homodecoupling ^1H NMR spectroscopy at 20 °C in $CDCl_3$ and by $^{13}C\{^1H\}$ NMR spectroscopy at 40 °C in $CDCl_3$, respectively, on a Unity Varian AC-400 spectrometer.

Synthesis of $LY(OCH_2CF_3)(THF)$ (1). To a THF solution of $(C_5H_5)_3Y(THF)$ (2.41 g, 6.76 mmol) was added a THF solution of LH_2 (3.55 g, 6.76 mmol). The reaction mixture was stirred for 1 h at room temperature, and then 2,2,2-trifluoroethanol (0.49 mL, 6.76 mmol) was added via a syringe. The mixture was stirred for 24 h at 50 °C, and then THF was evaporated completely under vacuum. Toluene (15 mL) was added to extract the residue, then THF (1 mL) was added, and colorless crystals were obtained at 5 °C in several days (3.70 g, 70%). Mp: 190−192 °C. Anal. Calcd for $C_{40}H_{64}F_3N_2O_4Y$: C, 61.37; H, 8.24; N, 3.58; Y, 11.36. Found: C, 61.09; H, 8.43; N, 3.73; Y, 11.26. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 7.57 (s, 2H, ArH), 7.10 (d, 2H, J(H,H) = 11.7 Hz, ArH), 4.35 (s, 2H, OCH_2CF_3), 3.94 (br, 2H, $ArCH_2N$), 3.85 (br, 4H, α-CH_2THF), 2.89 (br, 2H, $ArCH_2N$), 2.26 (br, 2H, $N(CH_2)_2N$), 1.71 (s, 18H, $C(CH_3)_3$), 1.66 (br, 6H, $N(CH_3)_2$), 1.53 (br, 2H, $N(CH_2)_2N$), 1.43 (s, 18H, $C(CH_3)_3$), 1.26 (br, 4H, β-CH_2THF). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C): δ 161.8, 136.5, 136.4, 125.8, 124.6, 124.5 (Ar−C), 70.7 (α-CH_2, THF), 66.6 (CF_3), 65.2 (CH_2CF_3), 58.8 ($ArCH_2N$), 48.9 ($N(CH_2)_2N$), 45.6 ($N(CH_3)_2$), 35.5 ($C(CH_3)_2$), 34.3 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 30.4 ($C(CH_3)_3$), 25.3 (β-CH_2, THF). IR (KBr pellet, cm^{-1}): 2957(s), 2905(m), 2858(m), 1608(w), 1468(s), 1287(m), 1192(m), 1148(m), 1028(m), 995(w), 958(m), 922(w), 877(m), 825(m), 776(w), 739(m).

Synthesis of $LYb(OCH_2CF_3)(THF)$ (2). The synthesis of complex **2** followed a procedure similar to that described for the preparation of complex **1**, but $(C_5H_5)_3Yb(THF)$ (2.14 g, 4.86 mmol) was used instead of $(C_5H_5)_3Y(THF)$. Yellow crystals were obtained in a toluene/THF solution (3.29 g, 71%). Mp: 193−195 °C. Anal. Calcd for $C_{40}H_{64}F_3N_2O_4Yb$: C, 55.41; H, 7.44; N, 3.23; Yb, 19.96. Found: C, 55.44; H, 7.56; N, 3.37; Yb, 19.83. IR (KBr pellet, cm^{-1}): 2957(s), 2904(m), 2859(m), 1604(w), 1468(s), 1287(m), 1243(w), 1192(m), 1148(m), 1027(m), 991(w), 960(m), 922(w), 880(m), 838(m), 778(w), 744(m).

Synthesis of $LEr(OCH_2CF_3)(THF)$ (3). The synthesis of complex **3** followed a procedure similar to that described for the preparation of complex **1**, but $(C_5H_5)_3Er(THF)$ (2.29 g, 4.37 mmol) was used instead of $(C_5H_5)_3Y(THF)$. Pink crystals were obtained in the toluene/THF solution (2.52 g, 67%). Mp: 198−200 °C. Anal. Calcd for $C_{40}H_{64}F_3N_2O_4Er$: C, 55.79; H, 7.49; N, 3.25; Er, 19.42. Found: C, 55.51; H, 7.57; N, 3.49; Er, 19.56. IR (KBr pellet, cm^{-1}): 2957(s), 2904(m), 2867(m), 1608(w), 1467(s), 1286(m), 1235(w), 1192(m), 1153(m), 1026(m), 991(w), 960(m), 922(w), 879(m), 833(m), 775(w), 740(m).

Synthesis of $LSm(OCH_2CF_3)(THF)$ (4). The synthesis of complex **4** followed a procedure similar to that described for the preparation of complex **1**, but $(C_5H_5)_3Sm(THF)$ (1.40 g, 3.35 mmol) was used instead of $(C_5H_5)_3Y(THF)$. Colorless crystals were obtained in a toluene/THF solution (1.84 g, 65%). Mp: 206−208 °C. Anal. Calcd for $C_{40}H_{64}F_3N_2O_4Sm$: C, 56.90; H, 7.64; N, 3.32; Sm, 17.81. Found: C, 57.21; H, 7.47; N, 3.63; Sm, 17.77. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 8.14 (d, 4H, ArH), 7.93 (d, 2H, $ArCH_2N$), 5.45 (br, 2H, $ArCH_2N$), 4.96 (s, 2H, OCH_2CF_3), 3.28 (s, 18H, $C(CH_3)_3$), 2.32 (br, 2H, $N(CH_2)_2N$), 1.94 (br, 4H, β-CH_2THF), 1.68 (s, 18H, $C(CH_3)_3$), 1.22 (br, 4H, α-CH_2THF), 0.55 (s, 6H, $N(CH_3)_2$), 0.18 (br, 2H, $N(CH_2)_2N$). IR (KBr pellet, cm^{-1}): 2957(s), 2867(m), 1775(w), 1466(s), 1282(m), 1246(w), 1162(m), 991(w), 960(m), 922(w), 878(m), 823(m), 775(w), 742(w).

Synthesis of $LY(OCH_2Ph)(THF)$ (5). The synthesis of complex **5** followed a procedure similar to that described for the preparation of complex **1**, but benzyl alcohol (0.36 mL, 3.50 mmol) was used instead of 2,2,2-trifluoroethanol. Colorless crystals were obtained in a toluene solution (2.13 g, 77%). Mp: 177−179 °C. Anal. Calcd for $C_{45}H_{69}N_2O_4Y$: C, 68.33; H, 8.79; N, 3.54; Y, 11.24. Found: C,

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Table 1. Crystallographic Data for Complexes 1−7

	1	2	3	4	5	6	7 ·hexane
formula	$C_{40}H_{64}F_3N_2O_4Y$	$C_{40}H_{64}F_3N_2O_4Yb$	$C_{40}H_{64}ErF_3N_2O_4$	$C_{40}H_{64}F_3N_2O_4Sm$	$C_{45}H_{69}N_2O_4Y$	$C_{41}H_{69}N_2O_4Y$	$C_{77}H_{130}N_4O_6Y_2$
fw	782.84	866.97	861.19	844.28	790.93	742.89	1385.67
T/K	223(2)	223(2)	223(2)	223(2)	293(2)	223(2)	223(2)
cryst syst	triclinic	triclinic	triclinic	triclinic	orthorhombic	triclinic	orthorhombic
cryst size/mm	0.50 × 0.20 × 0.15	0.60 × 0.40 × 0.30	0.50 × 0.10 × 0.10	0.45 × 0.20 × 0.20	0.70 × 0.50 × 0.30	0.60 × 0.40 × 0.30	0.40 × 0.30 × 0.30
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_12_12_1$
a/Å	10.8358(7)	10.8072(7)	10.8288(7)	10.891(3)	13.0187(14)	10.823(3)	17.9555(10)
b/Å	11.7873(6)	11.7853(6)	11.7776(6)	11.800(3)	17.8209(18)	11.778(2)	21.0348(12)
c/Å	17.2975(11)	17.2989(12)	17.2934(11)	17.306(5)	19.477(2)	17.233(4)	21.4682(13)
α/deg	77.769(4)	77.660(4)	77.713(4)	77.981(15)		77.929(14)	
β/deg	88.802(5)	88.739(5)	88.780(4)	89.348(18)		89.923(16)	
γ/deg	76.706(4)	76.945(4)	76.773(4)	76.359(14)		77.180(13)	
V/Å^3	2100.4(2)	2096.0(2)	2097.0(2)	2112.3(9)	4518.7(8)	2092.1(9)	8108.3(8)
Z	2	2	2	2	4	2	4
D_{calcd}/g cm^{-3}	1.238	1.374	1.364	1.327	1.163	1.179	1.135
μ/mm^{-1}	1.440	2.283	2.053	1.441	1.330	1.432	1.472
F(000)	832	894	890	878	1696	800	2984
θ_{max}/deg	27.5	27.5	25.50	25.50	25.35	25.50	25.50
colld reflns	17248	17866	18104	17873	44370	17466	37951
unique reflns	7742	7717	7735	7813	8264	7745	14965
obsd reflns [I > 2.0σ(I)]	6600	7250	6812	6184	7247	6220	11698
no. of variables	462	462	438	456	402	420	730
GOF	1.101	1.070	1.093	1.074	1.112	1.091	1.125
R	0.0724	0.0388	0.0484	0.0747	0.0712	0.0603	0.0833
wR	0.1726	0.0985	0.1071	0.1904	0.1545	0.1445	0.1471
R_{int}	0.0560	0.0345	0.0497	0.0619	0.0614	0.0435	0.0790
largest diff peak, hole/e Å^{-3}	0.772, −1.132	1.286, −1.561	0.974, −1.348	1.990, −1.753	0.810, −0.458	1.209, −1.352	0.570, −0.467

68.71; H, 8.33; N, 3.25; Y, 11.49. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.74 (d, 2H, J(H,H) = 7.5 Hz, ArH), 7.63 (d, 2H, J(H,H) = 2.5 Hz, ArH), 7.39 (m, 2H, ArH), 7.18 (m, 2H, ArH), 7.15 (s, 1H, ArH), 5.37 (s, 2H, OCH_2Ph), 4.01 (d, 2H, J(H,H) = 12.3 Hz, $ArCH_2N$), 3.80 (t, 4H, α-CH_2THF), 2.96 (d, 2H, J(H,H) = 12.4 Hz, $ArCH_2N$), 2.35 (s, 2H, $N(CH_2)_2N$), 1.83 (s, 18H, $C(CH_3)_3$), 1.75 (s, 6H, $N(CH_3)_2$), 1.63 (s, 2H, $N(CH_2)_2N$), 1.47 (s, 18H, $C(CH_3)_3$), 1.18 (m, 4H, β-CH_2THF). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C): δ 162.2, 148.4, 136.3, 136.2, 128.2, 126.5, 125.9, 125.8, 124.7, 124.4 (Ar−C), 69.9 (α-CH_2THF), 65.3 (OCH_2Ph), 58.8 ($ArCH_2N$), 48.9 ($N(CH_2)_2N$), 45.7 ($N(CH_3)_2$), 35.7 ($C(CH_3)_2$), 34.3 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 30.5 ($C(CH_3)_3$), 25.4 (β-CH_2THF). IR (KBr pellet, cm^{-1}): 2955(s), 2903(m), 2869(m), 1603(w), 1464(s), 1301(m), 1246(w), 1135(m), 1020(m), 991(w), 960(m), 923(w), 876(m), 837(m), 734(w).

Synthesis of LY(OPr^i)(THF) (6). The synthesis of complex **6** followed a procedure similar to that described for the preparation of complex **1**, but 2-propanol (0.33 mL, 4.28 mmol) was used instead of 2,2,2-trifluoroethanol. Colorless crystals were obtained in a concentrated hexane solution (2.52 g, 42%). Mp: 170−172 °C. Anal. Calcd for $C_{41}H_{69}N_2O_4Y$: C, 66.29; H, 9.36; N, 3.77; Y, 11.97. Found: C, 66.12; H, 9.30; N, 3.65; Y, 12.23. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.64 (d, 2H, J(H,H) = 9.9 Hz, ArH), 7.14 (s, 2H, ArH), 4.49 (s, 1H, $OCH(CH_3)_2$), 4.01 (d, 2H, J(H,H) = 12.3 Hz, $ArCH_2N$), 3.88 (s, 4H, α-CH_2THF), 2.95 (d, 2H, J(H,H) = 12.2 Hz, $ArCH_2N$), 2.35 (s, 2H, $N(CH_2)_2N$), 1.81 (s, 18H, $C(CH_3)_3$), 1.74 (s, 3H, $N(CH_3)_2$), 1.62 (br, 2H, $N(CH_2)_2N$), 1.55 (s, 3H, $N(CH_3)_2$), 1.50 (s, 18H, $C(CH_3)_3$), 1.35 (s, 6H, $OCH(CH_3)_2$), 1.21 (br, 4H, β-CH_2THF). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ 162.4, 136.2, 136.0, 125.8, 124.8, 124.3 (Ar−C), 70.2 (α-CH_2THF), 67.3 ($OCH(CH_3)_2$), 65.4 ($ArCH_2N$), 58.9 ($N(CH_2)_2N$), 48.9 ($N(CH_2)_2N$), 45.9 ($N(CH_3)_2$), 35.6 ($C(CH_3)_2$), 34.3 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$), 30.6 ($C(CH_3)_3$), 29.9 ($OCH(CH_3)_2$), 25.4 (β-CH_2THF). IR (KBr pellet, cm^{-1}): 2956(s), 2906(m), 2868(m), 1617(w), 1466(s), 1300(m), 1245(w), 1190(m), 1166(m), 1014(m), 991(w), 960(m), 923(w), 881(m), 828(m), 771(w), 746(m).

Synthesis of [(LY)$_2$(μ-OPr^i)(μ-OH)] (7). During the synthesis of complex **6**, a small amount of colorless crystals was isolated before the hexane solution was concentrated.

Typical Procedure for the Polymerization Reaction. The procedures for polymerization of *rac*-LA and *rac*-BBL initiated by complexes **1**−**6** were similar, and a typical polymerization procedure is given as follows. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of monomer and solvent. After the monomer was dissolved, a solution of the initiator was added to this solution via a syringe. The mixture was immediately stirred vigorously for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of ethanol and then poured into ethanol to precipitate the polymer, which was dried under vacuum and weighed.

Oligomer Preparation. Oligomerization of *rac*-LA and *rac*-BBL was carried out with complex **5** as the initiator in THF and toluene, respectively, at 25 °C under the condition of a molar ratio of [monomer]/[initiator] of 20. The reaction was stirred for 0.5 h and then quenched by adding *n*-hexane and 1 drop of water. The precipitated oligomers were collected, dried under vacuum, and used for ^{1}H NMR measurement.

X-ray Crystallographic Structure Determination. Suitable single crystals of complexes **1**−**7** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. The hydrogen atoms in

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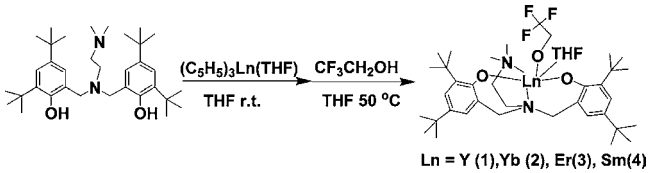
these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using *SHELEXL-97* programs.

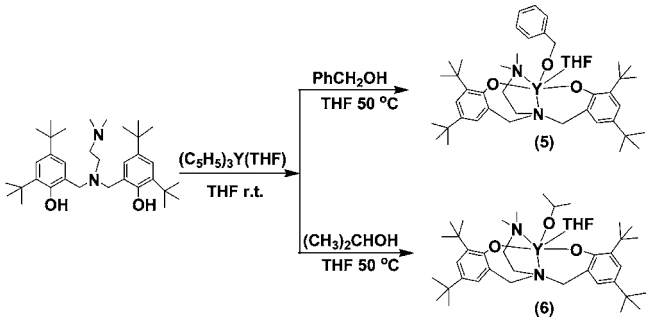
RESULTS AND DISCUSSION

Synthesis of Amine-Bridged Bis(phenolate)lanthanide Alkoxo Complexes. The lanthanide aryloxo complexes stabilized by amine-bridged bis(phenolate) ligand L [L = $Me_2NCH_2CH_2N\{CH_2\text{-}(2\text{-}OC_6H_2Bu^t_2\text{-}3,5)\}_2$] can be prepared by the reactions of amine-bridged bis(phenolate)lanthanide cyclopentadienyl complexes with phenols under mild conditions,[10b] but the corresponding lanthanum cyclopentadienyl complexes cannot react with methanol or 2-propanol even in refluxed THF or toluene to generate the desired amine-bridged bis(phenolate)lanthanum alkoxides.[11d] Taking into account the difference in acidity among cyclopentadienes, phenols, and alcohols, 2,2,2-trifluoroethanol was selected to revisit this proton-exchange reaction. The reactions of amine-bridged bis(phenolate)lanthanum and -yttrium cyclopentadienyl complexes with 2,2,2-trifluoroethanol were conducted at first. ^{1}H NMR monitoring revealed that the reaction of LYCp(THF) with 1 equiv of 2,2,2-trifluoroethanol in C_6D_6 at room temperature took place rapidly and, after a few minutes, afforded the yttrium alkoxide complex **1** as a neat product, with elimination of cyclopentadiene, because the resonance at 6.65 ppm for the cyclopentadienyl group disappeared and the characteristic signals for cyclopentadiene were observed. However, in the case of LLaCp(THF), the reaction became more complicated. When the amine-bridged bis(phenolate) lanthanum cyclopentadienyl complex reacted with 2,2,2-trifluoroethanol, the splitting peaks for the eliminated cyclopentadiene were found at 6.49, 6.30, and 2.69 ppm in the ^{1}H NMR spectrum, indicating that the exchange reaction took place. However, the proton-exchange reaction is not complete because the single sharp resonance at 6.65 ppm for the cyclopentadienyl group still existed; even after the reaction was conducted at elevated temperature, the alcohol was in excess. Furthermore, when the alcohol was in excess, two new peaks were observed at 9.85 and 8.61 ppm, indicating that some side reactions occurred. It is reasonable to postulate that there is an equilibrium between the amine-bridged bis(phenolate)lanthanum cyclopentadienyl complex and the corresponding lanthanum alkoxide. These results revealed that the ionic radii of the lanthanide metals have a significant effect on the outcome of this proton-exchange reaction. On a preparative scale, the yttrium alkoxide complex **1** can also be synthesized by the direct reaction of $(C_5H_5)_3Y(THF)$ with LH_2 in a 1:1 molar ratio and then with 1 equiv of 2,2,2-trifluoroethanol in situ in THF. A further study revealed that the analogous amine-bridged bis(phenolato)lanthanide alkoxides $LLn(OCH_2CF_3)(THF)$ [Ln = Yb (**2**), Er (**3**), Sm (**4**)] can be prepared by sequential exchange reactions using $(C_5H_5)_3Ln(THF)$ (Ln = Yb, Er, Sm) as the starting materials in THF at 50 °C in moderate isolated yields (Scheme 1). For the smaller lanthanide metal, yttrium, the proton-exchange reactions with benzyl alcohol and 2-propanol were also examined, and it was found that the yttrium alkoxides **5** and **6** can also be synthesized by the same method as that shown in Scheme 2. However, for samarium, the attempts were unsuccessful, and no pure product was isolated. This difference should be attributed

Scheme 1. Synthesis of Complexes 1−4



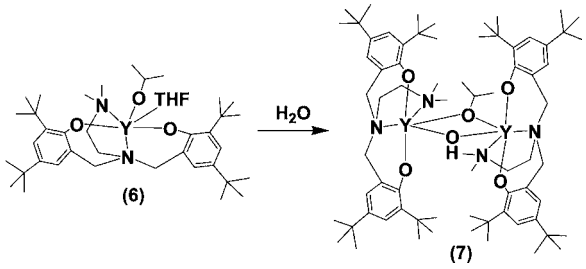
Scheme 2. Synthesis of Complexes 5 and 6



to the fact that the acidity of benzyl alcohol and 2-propanol is weaker than that of 2,2,2-trifluoroethanol. These results show that the acidity of alcohols also has a significant effect on the proton-exchange reaction.

During the synthesis of complex **6**, a small amount of **7** was concomitantly isolated as a colorless crystalline byproduct, which should be attributed to the presence of trace water in the reaction mixture (Scheme 3). The compositions of complexes

Scheme 3. Pathway for the Formation of Complex 7



1−**6** were confirmed by elemental analysis and NMR spectroscopy in the cases of complexes **1** and **4**−**6**. The definitive molecular structures of all of these complexes were determined by single-crystal structural analysis. Complexes **1**−**6** are sensitive to air and moisture. The crystals decompose in a few minutes when they are exposed to air, but both the crystals and solution are rather stable when stored under argon. All of these lanthanide complexes are freely soluble in THF and toluene and slightly soluble in hexane.

Crystal Structures. To provide complete structural information for these new amine-bridged bis(phenolate)-lanthanide species, single-crystal X-ray structural analyses were carried out for complexes **1**−**7**. Crystals suitable for an X-ray structure determination of complexes **1**−**5** were obtained from a toluene and THF solution at room temperature, whereas crystals of complexes **6** and **7** were obtained from a hexane solution. X-ray diffraction analyses show that complexes **1**−**6** have monomeric structures and **7** has a dinuclear structure.

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The structures of complexes **1**−**6** are similar, and the ORTEP diagrams of complexes **1**, **5**, and **6** are shown in Figures 1−3, respectively. The selected bond lengths and angles

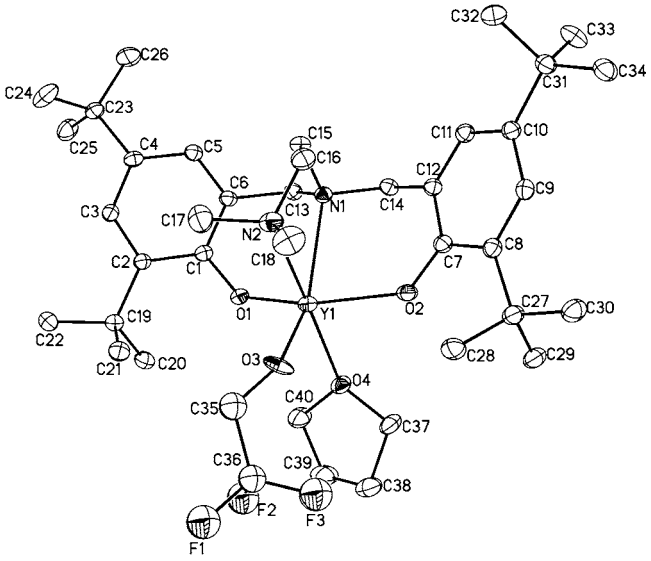

Figure 1. ORTEP diagram of complex **1** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Complexes **2**−**4** are isomorphous with complex **1**.

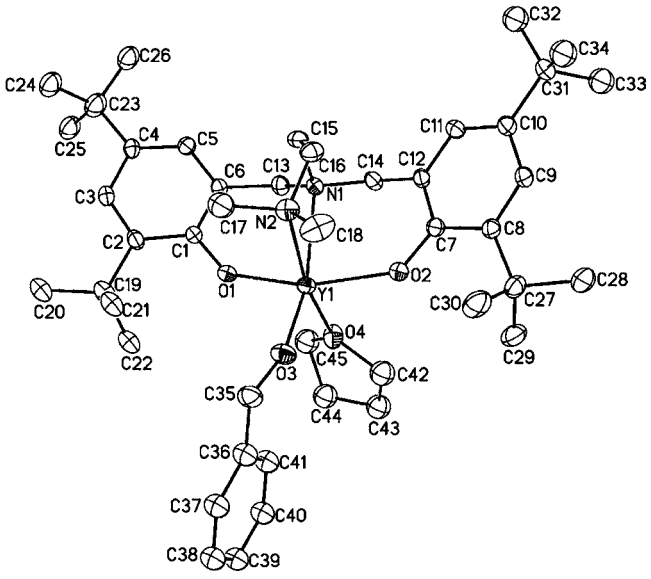

Figure 2. ORTEP diagram of complex **5** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity.

for these complexes are provided in Tables 2 and 3. Like other amine-bridged bis(phenolate)lanthanide complexes,[9a,10b,15] the side-arm amido group was found to bind to the metal center in the solid state. Each metal ion is six-coordinated to two oxygen and two nitrogen atoms from the dianionic amine-bridged bis(phenolate) ligand, one oxygen atom from the alkoxo group, and one oxygen atom from one THF molecule. The coordination geometry around the metal center can be best described as a slightly distorted octahedron, in which O1, O2, O3, and N1 can be considered to occupy equatorial positions within the octahedron. O4 and N2 occupy axial positions, and

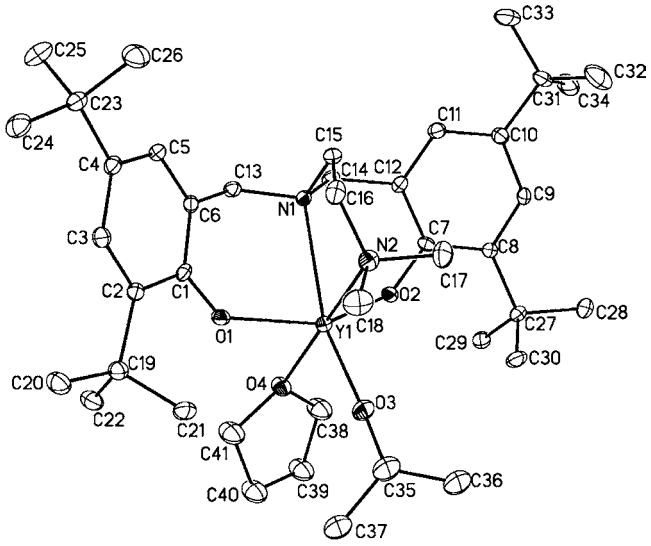

Figure 3. ORTEP diagram of complex **6** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity.

the O4−Ln−N2 angle is slightly distorted away from the idealized position of 180° to about 168° for these complexes. The overall coordination geometries of complexes **1**−**6** are similar to those of LYbCl(THF), LYb(NPh_2)(THF), LYbMe(THF),[15b] LY(CH_2SiMe_3)(THF),[9a] and LY(OC_6H_4-4-CH_3)(THF).[10b] In complexes **1**−**6**, the average Ln−O(Ar) bond lengths are 2.158(3), 2.122(3), 2.144(3), 2.214(7), 2.161(4), and 2.168(3) Å, respectively, following the trend of Sm > Y > Er > Yb, which is consistent with their ionic radii, and are comparable with the corresponding values in the complexes mentioned above, when the differences in the ionic radii are considered. Similar consequences are also observed from the Ln−N1, Ln−N2, Ln−O(CH_2CF_3), and Ln−O(THF) bond lengths in these complexes. In complexes **1**, **5**, and **6**, the Y−OR bond lengths are 2.08(2), 2.063(4), and 2.068(3) Å, respectively, which are apparently shorter than that in (SalanY-OPr^i)$_2$ [2.276(2) Å; Salan = MeN(CH_2)$_2$MeN{CH_2-(2-$OC_6H_2Bu^t_2$-3,5)}$_2$] because of the formation of a bridge bond in the latter.[10a]

The structure of complex **7** (Figure 4) shows a dinuclear feature containing a Y_2O_2 core bridging through the oxygen atoms of one O^{i}Pr group and one hydroxyl group. Each of the yttrium atoms is six-coordinated by two oxygen and two nitrogen atoms from the dianionic amine-bridged bis(phenolate) ligand, one oxygen atom from the O^{i}Pr group, and one oxygen atom from the hydroxyl group to form a distorted octahedron. The average bond length of Y1−O(Ar) [2.138(4) Å] is comparable with that of Y2−O(Ar) [2.119(4) Å], both of which are slightly shorter than the corresponding values in the amine-bridged bis(phenolate)yttrium complexes mentioned above. The O^{i}Pr group is unsymmetrically coordinated to the central metal atoms with a deviation of 0.027 Å, but the hydroxyl group is almost symmetrically coordinated to the yttrium atoms.

ROP of *rac*-LA by Complexes 1−6. To understand the effect of the lanthanide ionic radius, and the structure of the initiating group of amine-bridged bis(phenolate)lanthanide complexes on the polymerization activity, controllability, and stereoselectivity, the catalytic behavior of complexes **1**−**6** for

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes 1−6

	1	2	3	4	5	6
			Bond Lengths			
Ln1−O1	2.153(3)	2.116(3)	2.136(3)	2.197(7)	2.151(4)	2.161(3)
Ln1−O2	2.162(3)	2.127(3)	2.152(3)	2.230(7)	2.170(4)	2.175(3)
Ln1−O3	2.08(2)	2.068(18)	2.08(2)	2.09(3)	2.063(4)	2.068(3)
Ln1−O4	2.376(3)	2.352(3)	2.363(4)	2.432(7)	2.372(4)	2.379(3)
Ln1−N1	2.588(3)	2.549(3)	2.567(4)	2.652(8)	2.554(4)	2.617(3)
Ln1-N2	2.553(4)	2.516(4)	2.529(5)	2.655(9)	2.522(5)	2.561(4)
			Bond Angles			
O4−Ln1−N2	170.61(12)	170.80(11)	170.53(14)	168.9(3)	168.48(15)	172.94(11)
O1−Ln1−O3	110.6(6)	110.8(5)	111.2(6)	110.5(17)	99.94(16)	107.61(12)
O2−Ln1−O3	104.4(8)	101.3(6)	102.1(5)	108.6(19)	106.39(17)	106.86(13)
O2−Ln1−N1	79.06(10)	79.80(11)	79.47(13)	78.1(3)	79.90(13)	77.13(10)
O1−Ln1−N1	78.27(10)	79.06(11)	78.77(12)	77.6(2)	77.17(13)	78.47(10)
O3−Ln1−N1	148.5(7)	152.8(10)	152.7(12)	145.1(13)	159.46(15)	154.07(12)
O1−Ln1−O2	142.35(12)	144.09(12)	142.49(15)	138.7(3)	153.15(15)	142.42(11)
O1−Ln1−N2	103.01(12)	102.88(12)	103.46(15)	104.6(3)	96.17(16)	94.14(12)

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex 7

bond lengths		bond angles	
Y1−O1	2.117(4)	O5−Y1−N1	166.00(16)
Y1−O2	2.158(4)	O1−Y1−O2	97.11(17)
Y1−O5	2.244(4)	O1−Y1−O6	94.41(17)
Y1−O6	2.267(4)	O2−Y1−N2	85.05(17)
Y1−N1	2.494(5)	O6−Y1−N2	79.98(17)
Y1−N2	2.622(5)	O5−Y2−N3	172.73(15)
Y2−O3	2.107(4)	O3−Y2−O4	100.77(18)
Y2−O4	2.131(4)	O3−Y2−O6	96.03(18)
Y2−O5	2.271(4)	O6−Y2−N4	79.07(17)
Y2−O6	2.278(4)	O4−Y2−N4	94.08(17)
Y2−N3	2.526(5)	O5−Y1−O6	73.19(14)
Y2−N4	2.598(6)	O5−Y2−O6	72.47(14)
		Y1−O5−Y2	107.46(16)
		Y1−O6−Y2	106.46(16)

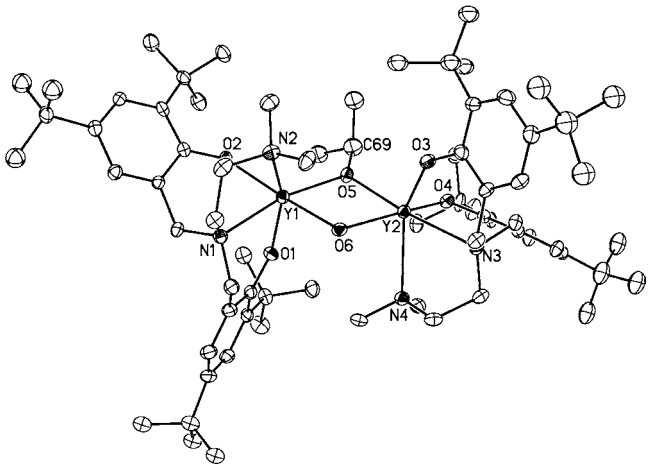

Figure 4. ORTEP diagram of complex **7** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity.

the ROP of *rac*-LA was examined. The representative polymerization data are summarized in Table 4.

All of these complexes were proven to be active initiators for the ROP of *rac*-LA and gave PLAs with high molecular weights. It was found that the number-average molecular weight (M_n) values are generally in good agreement with the calculated ones, when the molar ratio of monomer to initiator is lower than 1000 in THF. However, as the molar ratio of monomer to initiator increases, the experimental M_n values apparently deviate from the calculated ones. A similar phenomenon has been also observed by Carpentier and Coates, and this mismatch possibly arises from chain-transfer processes or poor correlation between the PMMA calibration of the gel permeation chromatograph and the actual molecular weights of the PLA chains.[3k,6b] Solvent plays a key role not only in the polymerization activity but also the stereoselectivity. Using complex **1** as the initiator (Figure 5), the yield is 98% and P_r is 0.98 (P_r: probability of racemic enchainment) in THF when the molar ratio of monomer to initiator is 400 (Table 4, entry 2), whereas the yield is 44% and P_r is 0.74 in toluene under the same polymerization conditions (Table 4, entry 3). The effects of the solvent in our cases are consistent with those observed in the alkoxyamino-bridged bis(phenolate)lanthanide systems.[6a,k]

The ionic radii of the lanthanide metals have an obvious effect on the catalytic activity and stereoselectivity but have no obvious effect on the controllability for *rac*-LA polymerization. Using complex **4** as the initiator, the yield is 96% when the molar ratio of monomer to initiator is 2000 in 1 h (Table 4, entry 17), whereas the yield is 84% using the ytterbium complex **2** as the initiator, even when the molar ratio of monomer to initiator decreased to 1500 under the same polymerization conditions (Table 4, entry 10). The activity-decreasing order of Sm > Y ≈ Er > Yb is in agreement with the order of their ionic radii, which is also consistent with the activity trend observed in the other lanthanide initiator systems for LA polymerization.[10b,i,11a] This may be attributed to the larger ionic radii resulting in a greater opening of the metal coordination sphere in the vicinity of the σ ligand, which makes insertion of *rac*-LA into Ln−O bonds easier. All of these lanthanide alkoxo complexes polymerize *rac*-LA to give highly heterotactic PLAs. The increasing order in heterotacticity follows the decreasing order of the ionic radii of the central metal: Sm (P_r = 0.93−0.94) < Y (P_r = 0.97−0.98) ≤ Er (P_r = 0.98−0.99) ≤ Yb (P_r = 0.99). This result revealed that a crowded coordination environment around the metal center is essential for higher stereoselectivity for *rac*-LA polymerization. The influence of the ionic radii of the metal center reported

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Table 4. Polymerization of *rac*-LA Initiated by Complexes 1−6[a]

entry	catalyst	$[M]_0/[I]_0$	t	yield (%)[b]	M_c[c] ($\times 10^4$)	M_n[d] ($\times 10^4$)	PDI[d]	P_r[e]
1	**1**	200	1 h	96	2.76	3.67	1.07	0.97
2	**1**	400	1 h	98	5.64	6.40	1.07	0.98
3[f]	**1**	400	1 h	44				0.74
4	**1**	600	1 h	98	8.47	9.01	1.05	0.98
5	**1**	800	1 h	98	11.29	10.15	1.06	0.98
6	**1**	1000	1 h	98	14.11	12.30	1.05	0.97
7	**1**	1500	1 h	90	19.44	14.25	1.09	0.97
8	**2**	400	1 h	95	5.47	7.82	1.03	0.99
9	**2**	1000	1 h	95	13.68	16.90	1.04	0.99
10	**2**	1500	1 h	84	18.14	19.81	1.05	0.99
11	**3**	400	1 h	93	5.36	5.83	1.07	0.98
12	**3**	1000	1 h	94	13.54	13.15	1.09	0.99
13	**3**	1500	1 h	91	19.66	14.58	1.09	0.98
14	**4**	400	10 min	95	5.47	6.09	1.09	0.94
15	**4**	1000	20 min	95	13.68	10.43	1.08	0.93
16	**4**	1500	30 min	92	19.87	12.25	1.10	0.94
17	**4**	2000	1 h	96	27.65	14.06	1.09	0.94
18	**4**	3000	2 h	73	31.54	12.57	1.12	0.93
19	**5**	400	1 h	98	5.64	5.53	1.06	0.98
20	**5**	1000	1 h	96	13.82	10.53	1.06	0.97
21	**5**	1500	1 h	88	19.01	12.11	1.09	0.98
22	**6**	400	1 h	98	5.64	5.94	1.06	0.98
23	**6**	1000	1 h	95	13.68	11.25	1.07	0.98
24	**6**	1500	1 h	89	19.22	13.43	1.07	0.97

[a]General polymerization conditions: THF as the solvent; [*rac*-LA] = 1 mol L^{-1}, at 25 °C. [b]Yield: weight of polymer obtained/weight of monomer used. [c]M_c = 144.13 × $([M]_0/[I]_0)$ × (polymer yield) (%). [d]Measured by GPC calibrated with standard PMMA samples. [e]Measured by homodecoupling ^{1}H NMR spectroscopy at 25 °C. [f]In toluene.

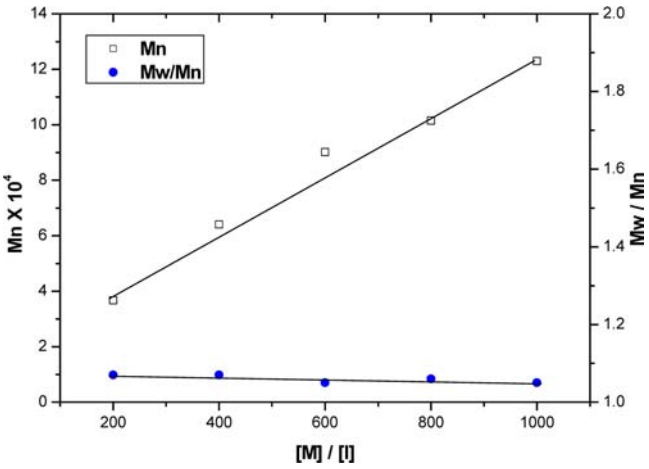

Figure 5. Polymerization of *rac*-LA initiated by complex **1** in THF at 25 °C. Relationship between the number-averaged molecular weight (M_n) and the molar ratio of monomer to initiator.

here is also in agreement with the observations reported by the Carpentier group in the alkoxyamino-bridged bis(phenolate)-lanthanide systems.[6a,k] The polymerizations initiated by complexes **1**−**6** gave polymers with very narrow PDIs (1.03−1.12), which revealed that the congestion around the metal center has no obvious effect on the controllability. To further elucidate the controlled character of the polymerization, the relationship between the number-average molecular weight (M_n) and the molar ratio of monomer to initiator ($[M]_0/[I]_0$) was measured (Table 4, entries 1, 2, and 4−6). When the molar ratio of monomer to initiator increased, the molecular weight of the resultant polymer increased linearly, whereas the PDIs remained almost unchanged (ranging from 1.05 to 1.09), indicating that the polymerization process is controlled.

The property of the initiating groups has no obvious effect on the catalytic activity but has a profound effect on the controllability for *rac*-LA polymerization. In comparison with the amine-bridged bis(phenolate)lanthanide alkyl,[9a] amido,[6a] and aryloxo complexes,[10b] these lanthanide alkoxides exhibit similar activity for *rac*-LA polymerization. However, the polymerization controllability of these lanthanide alkoxo complexes is superior to those of the lanthanide complexes mentioned above and is as good as that of the amine-bridged bis(phenolate)lanthanide alkoxo complexes generated in situ.[6a] These results can be attributed to the fact that the alkoxo groups are more nucleophilic in comparison with the alkyl and amido groups, which caused a fast initiation and gave the polymers narrow PDIs. A comparative study (polymerization by complexes **1**, **5**, and **6**) revealed that the structures of the alkoxo groups in these complexes have no obvious effect on the activity and controllability for *rac*-LA polymerization. However, for the stereoselectivity, the situation is complicated. The stereoselectivity of these yttrium alkoxo complexes for *rac*-LA polymerization is similar to those of the corresponding yttrium alkyls, amides, and aryloxides. However, the samarium alkoxo complex **4** showed better stereoselectivity than the amine-bridged bis(phenolate)samarium borohydride complex (the P_r values are 0.94 and 0.83, respectively),[8b] which indicates that the initiating group seems to have an influence on the stereoselectivity of *rac*-LA polymerization.

The initiation mechanism was elucidated by end-group analysis of the oligomer of *rac*-LA, which was prepared by the reaction of complex **5** with *rac*-LA in a 1:20 molar ratio. End-group analysis by ^{1}H NMR spectroscopy clearly showed the

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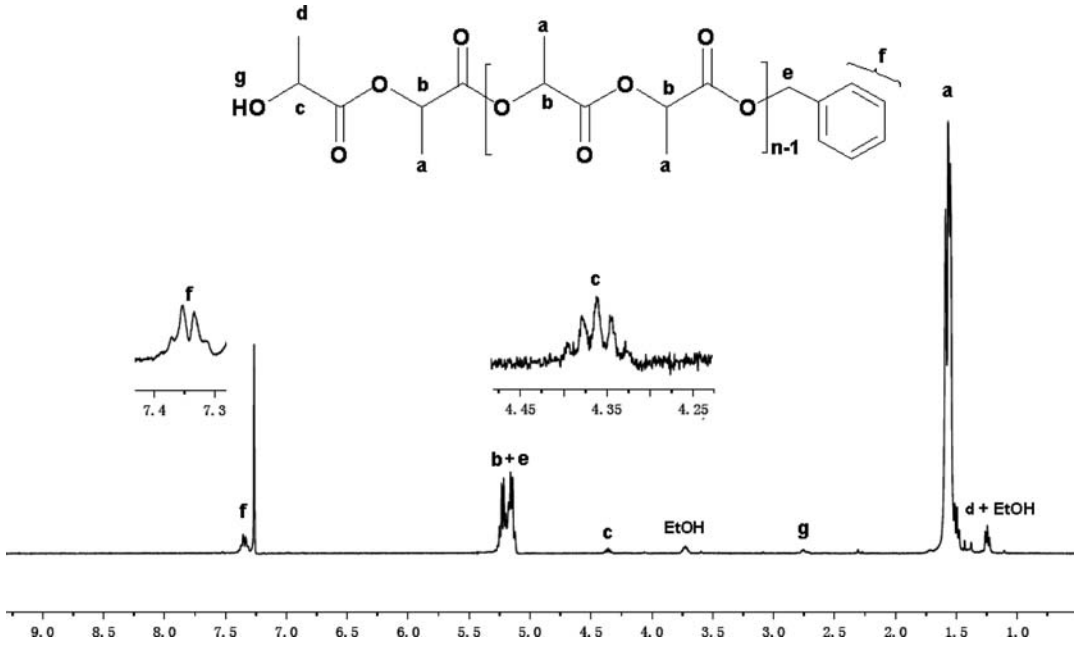

Figure 6. ^{1}H NMR spectrum of *rac*-LA oligomer initiated by complex **5** in $CDCl_3$ ([*rac*-LA]$_0$:**5** = 20:1, 25 °C).

Table 5. Polymerization of *rac*-BBL Initiated by Complexes 1−6[a]

entry	catalyst	$[M]_0/[I]_0$	t	yield (%)[b]	M_c[c] (×10^4)	M_n[d] (×10^4)	PDI[d]	P_r[e]
1	**1**	400	10 min	91	3.13	4.46	1.11	0.83
2	**1**	1000	10 min	77	6.62	8.82	1.17	0.83
3	**2**	200	2 min	100	1.72	2.12	1.25	0.83
4	**2**	400	2 min	100	3.44	4.20	1.21	0.83
5[f]	**2**	400	30 min	55				0.67
6[g]	**2**	400	2 min	87	2.99	3.36	1.20	0.82
7	**2**	600	10 min	100	5.16	5.58	1.21	0.83
8	**2**	800	10 min	100	6.88	7.42	1.19	0.83
9	**2**	1000	10 min	100	8.60	10.35	1.13	0.83
10	**2**	1500	30 min	99	12.77	15.65	1.13	0.83
11	**2**	2000	30 min	92	15.82	16.19	1.24	0.83
12	**3**	400	10 min	100	3.44	3.55	1.18	0.83
13	**3**	1000	10 min	81	6.97	6.13	1.25	0.83
14	**4**	400	5 h	57				
15	**5**	400	10 min	95	3.27	3.51	1.26	0.83
16	**5**	1000	10 min	80	6.88	7.40	1.18	0.82
17	**6**	400	10 min	95	3.27	3.44	1.21	0.83
18	**6**	1000	10 min	83	7.14	8.06	1.15	0.82

[a]General polymerization conditions: toluene as the solvent; [*rac*-BBL] = 2 mol L^{-1}, at 25 °C. [b]Yield: weight of polymer obtained/weight of monomer used. [c]M_c = 86 × ($[M]_0/[I]_0$) × (polymer yield) (%). [d]Measured by GPC calibrated with standard PMMA samples. [e]Determined from the carbonyl region of the ^{13}C NMR spectrum at 25 °C. [f]In THF. [g][*rac*-BBL] = 1 mol L^{-1}.

existence of a benzyloxy group and a $HOCH(CH_3)CO-$ group according to the resonances at about 7.35 ppm for the former and at 1.26, 2.76, and 4.36 ppm for the latter, as shown in Figure 6. Meanwhile, no proton resonance of the ligand was observed in the ^{1}H NMR spectrum of the oligomer, which revealed that the amine-bridged bis(phenolate) group was not involved in the polymerization process. Thus, polymerization proceeds via a common "coordination−insertion" mechanism.

ROP of *rac*-BBL by Complexes 1−6. Highly active and controlled ROP of BBL to produce high-molecular-weight PHB is rare[5k,6b−i] because most of the catalysts showed low activity toward β-lactone polymerizations, despite their favorable ring strain,[16] and a high prevalence of chain termination events, such as transesterification and chain transfer.[2a,6j] In this work, the polymerization behavior of complexes **1−6** for polymerization of *rac*-BBL has also been examined, and the results are summarized in Table 5. It can be seen that the polymerizations of *rac*-BBL initiated by complexes **1−6** also proceeded in a controlled fashion, resulting in PHBs with narrow PDIs ($M_w/M_n \leq 1.26$) and a good agreement of the number-average molecular weights determined by GPC with the calculated M_n values (Table 5).

The solvent also has a significant influence on both the polymerization rate and stereoselectivity. Different from that observed for *rac*-LA polymerization, toluene is a better polymerization medium than THF. For example, using complex **2** as the initiator, polymerization in toluene reached 100% conversion in less than 2 min, and P_r of the resultant polymer is

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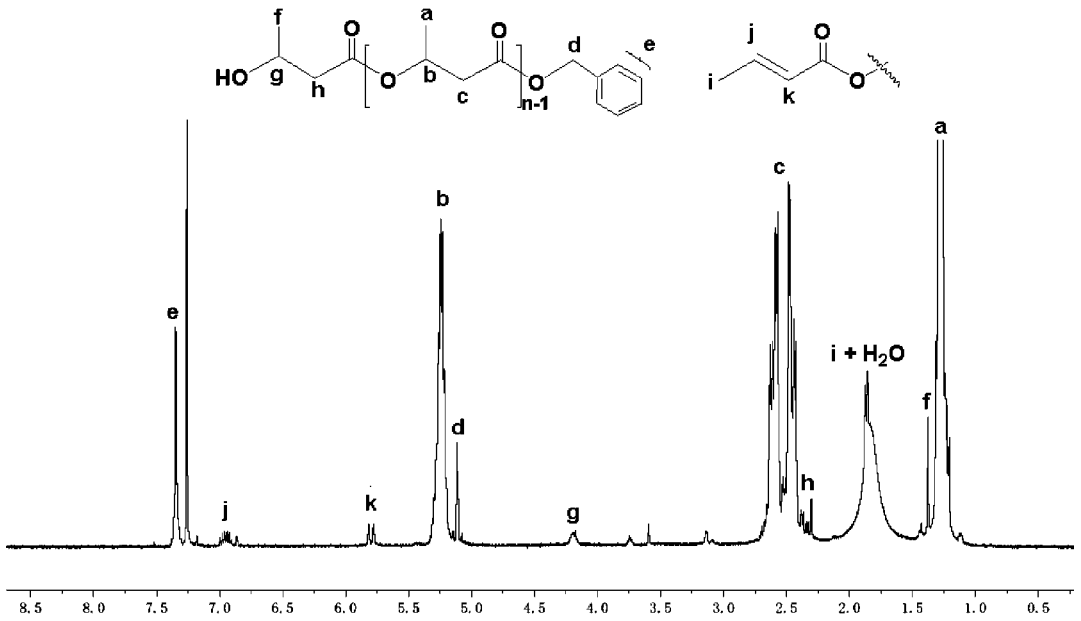

Figure 7. ^{1}H NMR spectrum of *rac*-BBL oligomer initiated by complex **5** in $CDCl_3$ ([*rac*-BBL]$_0$:**5** = 20:1, 25 °C).

0.83 (Table 5, entry 4), when the molar ratio of *rac*-BBL to complex **2** is 400, whereas polymerization in THF led to 55% conversion within 30 min, and P_r is 0.67 under the same polymerization conditions (Table 5, entry 5). It was found that decreasing the monomer concentration resulted in a slight decrease in the polymerization rate (Table 5, entries 4 and 6). The effects of the solvent and the monomer concentration in our cases are consistent with those observed in the alkoxyamino-bridged bis(phenolate)lanthanide systems.[6b,d] Therefore, all other polymerization reactions were preferably conducted in toluene at a concentration of *rac*-BBL of 2 M.

The ionic radii of the lanthanide metals have significant effect on the catalytic activity for *rac*-BBL polymerization. For example, using the ytterbium complex **2** as the initiator, the yield was 99% in 30 min, when the molar ratio of monomer to initiator was 1500 (Table 5, entry 10), whereas the yield was 57% in 5 h using the samarium complex **4** as the initiator, even when the molar ratio of monomer to initiator decreased to 400 under the same polymerization conditions (Table 5, entry 14). The activity-decreasing order Yb > Er > Y ≫ Sm is opposite to the order of the ionic radii and the activity order for *rac*-LA polymerization. Carpentier et al. found that the lanthanum amido complexes stabilized by tridentate pyridyine- and thiophene-linked bis(naphtholate) ligands showed the highest polymerization rate for *rac*-BBL polymerization, in comparison with the corresponding yttrium and scandium amido complexes.[6i] Similarly, bis(guanidinate)neodymium isopropoxide is much more active than its yttrium and lutetium congeners for the ROP of *rac*-BBL.[6g] These results indicated that the ancillary ligand can adversely affect the activity order of the ionic radii on the polymerization, although the real reason still remains unclear. It is worth noting that the ionic radii of the lanthanide metals have no obvious effect on the stereoselectivity for *rac*-BBL polymerization in this ligand system, which is quite different from that observed in *rac*-LA polymerization. All of these complexes polymerize *rac*-BBL to give syndiotactic-enriched polymers, and the P_r values are about 0.82.

The nature of the alkoxo groups does not affect the activity and stereoselectivity for *rac*-BBL polymerization. Complexes **1**, **5**, and **6** show similar activity and stereoselectivity for the polymerization. The activity and stereoselectivity of these lanthanide alkoxo complexes are also comparable with the alkoxyamino-bridged bis(phenolate)lanthanide alkoxo complexes generated in situ (P_r is about 0.81).[6b,d]

The initiation mechanism was elucidated by end-group analysis of the oligomer of *rac*-BBL, which was prepared by the reaction of complex **5** with *rac*-BBL in a 1:20 molar ratio. End-group analysis by ^{1}H NMR spectroscopy clearly showed the existence of a benzyloxy group and a $HOCH(CH_3)CH_2CO-$ group according to the resonances at about 7.34 and 5.12 ppm for the former and at 4.19, 2.30, and 1.38 ppm for the latter, as shown in Figure 7, which confirmed that the *rac*-BBL ring is opened via cleavage of the acyl−oxygen bond and then inserted into the Ln−O bond. Meanwhile, *trans*-crotonate (and carboxy) groups were also observed in the ^{1}H NMR spectrum, which indicated that the elimination side reaction exists in the polymerization progress. A similar elimination reaction in *rac*-BBL polymerization has been observed using bulky *β*-diiminatezinc alkoxides,[3k] $Al(O^iPr)_3$, and tin-based complexes as the initiators,[17] but not observed in the polymerization initiated by the alkoxyamino-bridged bis(phenolate)lanthanide alkoxo complexes formed in situ.[6b]

■ CONCLUSION

In summary, a series of neutral amine-bridged bis(phenolate)-lanthanide alkoxo complexes were successfully synthesized via proton-exchange reactions using the readily available $(C_5H_5)_3Ln(THF)$ as the precursors, and their structural features have been provided by a X-ray diffraction study. Both the acidity of the alcohols and the ionic radii of the lanthanide metals significantly affect the proton-exchange reaction. It was found that these lanthanide alkoxo complexes are efficient initiators for the ROP of *rac*-LA and *rac*-BBL. Both the ancillary ligand and the ionic radii of the lanthanide metals have a profound effect on the activity and stereoselectivity. The nature of the initiating groups has a significant effect on the

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controllability but has no obvious effect on the activity and stereoselectivity. For *rac*-LA polymerization, these complexes displayed good activity, excellent controllability, and high stereoselectivity to give highly heterotactic PLAs. The observed activity-increasing order is in agreement with the order of the ionic radii, but the heterotacticity follows the opposite sequence. The stereoselectivity is similar to those of the corresponding lanthanide alkyls, amides, and aryloxides but is better than that of the samarium borohydride. For *rac*-BBL polymerization, these complexes represented one of the best initiators in activity and stereoselectivity to give syndiotactic-enriched polymers. It was found that the activity-decreasing order of Yb > Er > Y ≫ Sm for *rac*-BBL polymerization is opposite to the order of the ionic radii for the first time, and the ionic radii of the lanthanide metals have no obvious effect on the stereoselectivity, which is quite different from that for *rac*-LA polymerization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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