

Synthesis and characterization of carbon-bridged bis(phenolate) lanthanum alkoxides and their catalytic behavior for the polymerization of *L*-lactide

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Received December 23, 2011; accepted March 6, 2012; published online July 10, 2012

Four lanthanum alkoxides stabilized by a carbon-bridged bis(phenolate) ligand were synthesized and their catalytic behavior for the ring-opening polymerization of *L*-lactide was explored. Reactions of [(MBMP)LaCp(THF)₂] (MBMP²⁻ = 2,2'-methylene-bis(6-*tert*-butyl-4-methyl phenoxo)) with HOCH₂Ph, HOCH₂CF₃, HOCH(CH₃)₂, and HOCH₂CH₂N(CH₃)₂, respectively, in a 1:1 molar ratio in THF gave the dimeric lanthanum alkoxo complexes [(MBMP)Ln(μ-OR)(THF)₂]₂ (OR = OCH₂Ph (**1**), OCH₂CF₃ (**2**), OCH(CH₃)₂ (**3**), OCH₂CH₂N(CH₃)₂ (**4**)). These complexes were well characterized, and the definitive molecular structure of complex **1** was determined. It was found that complexes **1** to **4** are efficient initiators for the ring-opening polymerization of *L*-lactide. The structure of the alkoxo groups has a significant effect on the catalytic behavior, and complex **2** can initiate *L*-lactide polymerization in a controlled manner.

organolanthanide complex, bis(phenolate) ligands, alkoxide, lactide, synthesis, polymerization

Citation: Li B X, Qi R P, Yao Y M, et al. Synthesis and characterization of carbon-bridged bis(phenolate) lanthanum alkoxides and their catalytic behavior for the polymerization of *L*-lactide. *Chin Sci Bull*, 2012, 57: 4442–4447, doi: 10.1007/s11434-012-5330-9

In recent years, bridged bis(phenolate) ligands have become among the most attractive chelating systems in organolanthanide chemistry, because of their ease of preparation from inexpensive and readily available starting materials and sample modification of both steric and/or electronic properties. Moreover, some of the lanthanide complexes stabilized by bridged bis(phenolate) ligands exhibit exciting reactivity in homogeneous catalysis, such as the ring-opening polymerization of cyclic esters [1–7] and organic transformations [8,9]. Recently, we became interested in studying the synthesis and reactivity of organolanthanide complexes stabilized by bridged bis(phenolate) ligands [6,7]. It was found that the ionic radii of the lanthanide metals have a profound effect on the polymerization activity of the corresponding lanthanide complexes, and the activity increases with the increase of ionic radius of the lanthanide metals. On the other hand, the initiating groups in bridged bis

(phenolate) lanthanide complexes also have an obvious effect on their catalytic behavior for the polymerization of cyclic esters [4,5]. For example, bis(phenolate) lanthanide alkoxides showed better controllability for the polymerization of cyclic esters in comparison with the corresponding lanthanide amides and alkyls, giving polymers with high molecular weight and narrow molecular weight distributions [10]. However, the effect of the structures of alkoxo groups on the catalytic behavior has seldom been studied to date. In our continuous study in this area, four new lanthanum alkoxo complexes stabilized by a carbon-bridged bis(phenolate) ligand were synthesized and their catalytic behavior for the ring-opening polymerization of *L*-lactide was examined. Here we report these results.

1 Experimental

Since the lanthanum complexes are sensitive to moisture

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and air, all manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk technique or in glovebox.

1.1 Materials

THF and toluene were degassed and distilled from sodium benzophenone ketyl under argon prior to use. (MBMP)LaCp(THF)₃ (MBMP²⁻ = 2,2'-methylene-bis(6-*tert*-butyl-4-methyl phenoxo)) was prepared according to the literature [11]. All alcohols were predried, and distilled before use. *L*-Lactide was recrystallized twice from dry toluene and then sublimed under vacuum at 50°C.

1.2 Synthesis

(i) Synthesis of complex **1**. To a THF solution (30 mL) of (MBMP)LaCp(THF)₃ (2.22 g, 2.92 mmol) was added HOCH₂Ph (0.76 mL, 2.92 mmol). The mixture was stirred overnight at 50°C, and then precipitate formed gradually. The precipitate was separated from the solution by centrifugation. The powder was washed twice with THF, and then dried under vacuum (1.75 g, 82%). Colorless crystals suitable for X-ray structure determination were obtained by the slowly cooling of a hot THF solution. mp. 180–182°C (dec). Anal. Calcd. for C₇₆H₁₀₆La₂O₁₀ (%): C, 62.63; H, 7.33; La, 19.06. Found (%): C, 62.21; H, 7.34; La, 19.21. ¹H NMR: 1.26 (br, 16H, THF), 1.78 (s, 36H, C(CH₃)₃), 2.20 (s, 12H, Ar-CH₃), 3.62 (br, 16H, THF), 3.80 (m, 4H, CH₂), 4.36 (s, 4H, OCH₂Ph), 7.00 (m, 4H, Ar), 7.07 (m, 10H, Ph), 7.18 (m, 4H, Ar). IR (KBr, cm⁻¹): 2956(s), 2918(s), 1646(w), 1463(s), 1388(m), 1233(m), 1050(m), 868(m).

(ii) Synthesis of complex **2**. The synthesis of complex **2** was carried out in the same way as that described for complex **1**, but HOCH₂CF₃ (3.80 mL, 3.50 mmol) was used instead of HOCH₂Ph. Colorless powder was obtained (1.97 g, 78%). Colorless microcrystals were obtained by the slowly cooling of a hot THF solution. mp. 220–222°C. Anal. Calcd. for C₆₆H₉₆F₆La₂O₁₀ (%): C, 55.00; H, 6.71; La, 19.27. Found (%): C, 55.21; H, 6.69; La, 19.50. ¹H NMR: 1.33 (br, 16H, THF), 1.63 (s, 36H, C(CH₃)₃), 2.29 (s, 12H, Ar-CH₃), 3.56 (m, 4H, CH₂), 3.70 (br, 16H, THF), 4.21 (s, 4H, OCH₂CF₃), 7.01 (m, 4H, Ar), 7.40 (m, 4H, Ar). IR (KBr, cm⁻¹): 2953(s), 2912(s), 1645(w), 1443(s), 1435(s), 1362(m), 1274(m), 1026(m), 863(m).

(iii) Synthesis of complex **3**. The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but HOCH(CH₃)₂ (0.16 mL, 2.08 mmol) was used instead of HOCH₂Ph. Colorless powder was obtained (1.21 g, 85%). Colorless microcrystals were obtained by the slowly cooling of a hot THF solution. mp. 171–173°C. Anal. Calcd. for C₆₈H₁₀₆La₂O₁₀ (%): C, 59.99; H, 7.84; La, 20.40. Found (%): C, 59.72; H, 7.57; La, 20.13. ¹H NMR: 0.92 (12H, OCH(CH₃)₂), 1.45 (48H, Ar-C(CH₃)₃), 1.60 (16H, THF), 2.30 (12H, Ar-CH₃), 3.58 (16H, THF), 3.58 (2H,

OCH(CH₃)₂), 3.76 (4H, Ar-CH₂), 7.01 (4H, Ar-H), 7.41 (4H, Ar-H). IR (KBr, cm⁻¹): 2955(s), 2916(m), 2870(m), 1605(w), 1464(s), 1433(s), 1385(m), 1252(s), 1137(w), 1050(w), 861(w), 790(w).

(iv) Synthesis of complex **4**. The synthesis of complex **4** was carried out in the same way as that described for complex **1**, but HOCH₂CH₂N(CH₃)₂ (3.08 mL, 3.20 mmol) was used instead of HOCH₂Ph. Colorless powder was obtained (1.77 g, 78%). Colorless microcrystals were obtained by the slowly cooling of a hot THF solution. mp. 217–219°C. Anal. Calcd. for C₇₀H₁₁₂La₂N₂O₁₀ (%): C, 59.23; H, 7.95; N, 1.97; La, 19.57. Found (%): C, 58.89; H, 7.85; N, 1.92; La, 20.01. ¹H NMR: 1.37 (br, 16H, THF), 1.79 (s, 36H, C(CH₃)₃), 2.21 (s, 12H, Ar-CH₃), 2.31 (s, 12H, N(CH₃)₂), 2.36 (m, 4H, CH₂N), 3.63 (m, 16H, THF), 3.85 (m, 4H, CH₂), 4.27 (m, 4H, OCH₂), 6.90 (m, 4H, Ar), 7.08 (m, 4H, Ar). IR (KBr, cm⁻¹): 3394(s), 2954(s), 2916 (s), 1630(w), 1467(s), 1431(s), 1259(m), 1029(s), 860(m).

(v) Polymerization procedure. The procedures for the polymerization of *L*-lactide initiated by complexes **1–4** are similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of *L*-lactide and toluene. The contents of the flask were then stirred at 70°C until *L*-lactide was dissolved, and then a solution of the initiator in hot toluene was added to this solution by syringe. The mixture was stirred vigorously at 70°C for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

1.3 Analyses

¹H NMR spectrum was recorded in THF-*d*₈ solution for the lanthanum complexes with a Unity Varian-400 spectrometer. Melting point was determined in a sealed argon-filled capillary and was uncorrected. Metal analysis was carried out using complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on an EA-1110 instrument, and quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 FTIR spectrometer as KBr pellets. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40°C.

1.4 Crystal structure determination

Suitable single crystal of complex **1** was sealed in a thin-walled glass capillary for determining the molecular structure. Intensity data were collected with a Rigaku Mercury

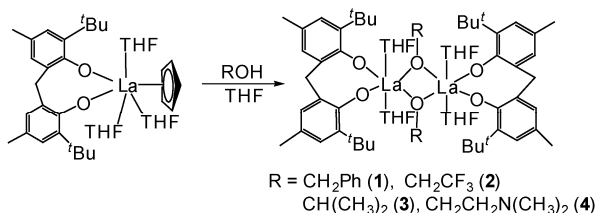
CCD area detector in ω scan mode using Mo $K\alpha$ radiation ($\lambda = 0.07107$ nm). The diffracted intensity was corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.098 nm for methylene, 0.097 nm for methyl and 0.094 nm for aromatic rings). The structure was solved and refined using SHELEXL-97 programs.

2 Results and discussion

Well-defined lanthanum alkoxo complexes stabilized by the carbon-bridged bis(phenolate) ligand can be conveniently prepared using (MBMP)LaCp(THF)₃ as the starting material, which was synthesized by the reaction of Cp₃La(THF) with one equivalent of bis(phenol) (MBMP)_{H₂} [11]. When alcohol (HOCH₂Ph, HOCH₂CF₃, HOCH(CH₃)₂, HOCH₂CH₂N(CH₃)₂) was added to a THF solution of (MBMP)LaCp(THF)₃ in a 1:1 molar ratio at 50°C, a precipitate gradually formed. After workup, a colorless powder of the final products [(MBMP)Ln(μ -OR)(THF)₂]₂ (OR = OCH₂Ph (1), OCH₂CF₃ (2), OCH(CH₃)₂ (3), OCH₂CH₂N(CH₃)₂ (4)) was obtained in high isolated yields as summarized in Scheme 1.

Table 1 Crystallographic data for complex 1

Complex 1		Complex 1	
Formula	C ₇₆ H ₁₀₆ La ₂ O ₁₀	D_c (mg m ⁻³)	1.346
M_w	1457.43	μ (mm ⁻¹)	1.228
T (K)	213(2)	$F(000)$	3024
Crystal system	Monoclinic	θ_{max} (°)	25.3
Space group	$C2/c$	Collected reflections	34468
a (nm)	3.3187(6)	Unique reflections	6580
b (nm)	1.3536(2)	Observed reflections	5417
c (nm)	1.8095(3)	$[I > 2.0\sigma(I)]$	
β (°)	117.809(4)	No. of variables	415
V (nm ³)	7.190(2)	GOF	1.155
Z	4	R	0.0579
		wR	0.0975



Scheme 1

The compositions of complexes 1–4 were established as (MBMP)Ln(μ -OR)(THF)₂ by elemental analysis and ¹H NMR spectroscopy. Definitive molecular structure determination of complex 1 revealed that these complexes have solvated dimeric structures [(MBMP)Ln(μ -OR)(THF)₂]₂ in the solid state. All of these complexes are sensitive to air and moisture. Complexes 1–3 are slightly soluble in THF and hot toluene and insoluble in hexane; whereas complex 4 is soluble in THF and slightly soluble in toluene.

Crystals suitable for an X-ray structure analysis of complex 1 were obtained by slowly cooling a hot THF solution. The molecular structure of complex 1 is shown in Figure 1, and its selected bond lengths and bond angles are provided in Table 2. Complex 1 has a centrosymmetric dimeric structure containing La₂O₂ core, and possess bridging oxygen atoms from benzyloxy groups, which are similar to those found in the lanthanide alkoxides stabilized by carbon-bridged bis(phenolate) ligands [12,13]. The metal centers in this complex are six-coordinated with six oxygen atoms from one bis(phenolate) ligand, two benzyloxy groups, and two THF molecules, respectively. Each of the metal centers has a distorted octahedral coordination geometry, in which O(1), O(3), O(3A) and O(4) can be considered

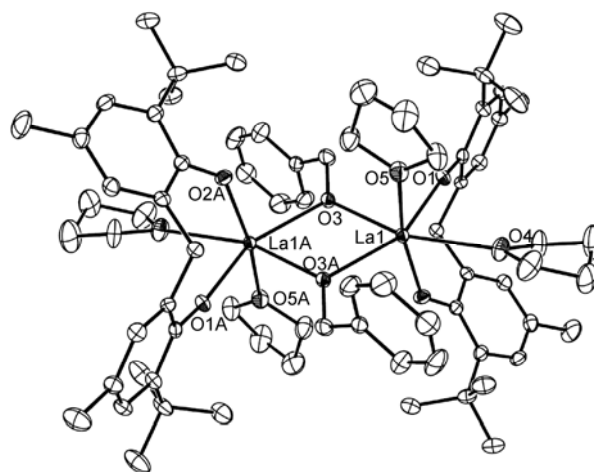


Figure 1 ORTEP diagram of complex 1. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (nm) and bond angles (°) of complex 1

Bond distances		Bond angle	
La(1)–O(1)	0.2246(3)	O(1)–La(1)–O(3)	84.4(1)
La(1)–O(3)	0.2406(3)	O(3A)–La(1)–O(4)	127.8(1)
La(1)–O(4)	0.2647(4)	O(2)–La(1)–O(5)	163.1(1)
C(1)–O(1)	0.1345(6)	La(1)–O(2)–C(7)	140.1(3)
La(1)–O(2)	0.2270(3)	O(3)–La(1)–O(3A)	68.8(1)
La(1)–O(3A)	0.2442(3)	O(4)–La(1)–O(1)	78.9(1)
La(1)–O(5)	0.2624(4)	La(1)–O(1)–C(1)	159.8(3)
C(7)–O(2)	0.1342(6)	O(1)–La(1)–O(2)	93.1(1)

to occupy equatorial positions within the octahedron about the lanthanum ion with $\sum \text{O-La-O} = 359.9^\circ$, O(2) and O(5) occupy axial positions, and the O(2)-La-O(5) angle is distorted away from the idealized 180° to $163.1(1)^\circ$. In complex **1**, two benzyloxy groups are unsymmetrically coordinated to the lanthanum atom with a deviation of 0.004 nm. The average Ln-O(Ar) and Ln-O(benzyloxy) bond lengths are 0.2258(3) and 0.2428(3) nm, respectively, which are comparable with the corresponding bond lengths in carbon-bridged bis(phenolate) lanthanide alkoxides mentioned above, when the difference in ionic radii is considered [12,13].

The catalytic behavior of the lanthanum alkoxo complexes **1–4** for the ring-opening polymerization of *L*-lactide was examined. The polymerization results are summarized in Table 3. It can be seen that all of these lanthanum alkoxo complexes can initiate *L*-lactide polymerization in toluene, and all of the polymers obtained have high molecular weights and relatively narrow molecular weight distributions (PDIs). These lanthanum alkoxides showed apparently higher activity for the polymerization in comparison with the corresponding neodymium methoxy complex [12]. For example, using complex **1** as the initiator, the yield reaches 100% after 1 h at 60°C when the molar ratio of monomer to initiator is 700 (Table 3, entry 3); whereas the yield is 93% in 2 h using the carbon-bridged bis(phenolate) neodymium methoxy complex as the initiator when the molar ratio of initiator to *L*-lactide is 200. The observed activity order is in agreement with the order of ionic radii, which is consistent with the active trend for the polymerization of cyclic esters initiated by the lanthanide-based complexes [14,15]. Polymerization medium played an important role in

influencing the catalytic activity. These complexes show higher activity in toluene than in THF. Using complex **2** as the initiator, complete polymerization was achieved in toluene in 1 h at 60°C when the molar ratio of monomer to initiator ($[\text{M}]_0/[\text{I}]_0$) is 600; whereas the yield is 86% in THF under the same polymerization conditions, even when the molar ratio of monomer to initiator decreases to 100 (Table 3, entries 7 and 10).

The structure of the alkoxo groups has a profound effect on the polymerization controllability. The resultant polymers initiated by the lanthanum trifluoroethanoxo complex have apparently narrow molecular weight distributions (PDIs) in comparison with those polymers initiated by other lanthanum alkoxides. A further study revealed that the molecular weights of the resultant polymers increased linearly when the molar ratio of monomer to initiator was increased, whereas the molecular weight distributions remained almost unchanged using complex **2** as the initiator (Table 3, entries 4–8, Figure 2). This is a characteristic feature of controlled polymerization. To further confirm the controlled character initiated by complex **2**, the polymerization kinetics at room temperature (27°C) in THF were measured when the molar ratio of monomer to initiator is 100. The conversion increases with time and the pseudo first order kinetic plot of $\ln([\text{M}]_0/[\text{M}])$ versus polymerization time was observed as shown in Figure 3. The linear semilogarithmic plots indicated that the concentration of the active species remained constant throughout the polymerization. The number average molecular weights (M_n) of the resultant polymers increased proportionally to the monomer conversion, whereas the molecular weight distributions (PDIs) of the polymers remained narrow ($\text{PDI} \leq 1.20$, Table 4) and intact irrespective

Table 3 Polymerization of *L*-lactide initiated by complexes **1–4**^{a)}

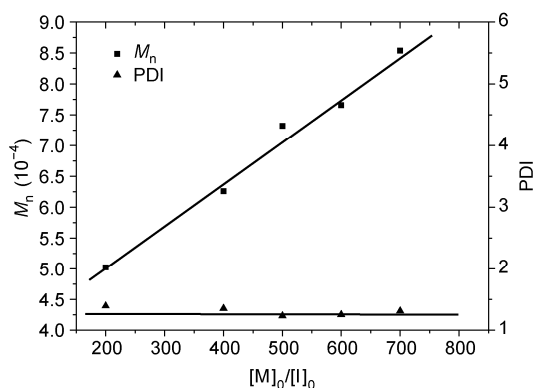
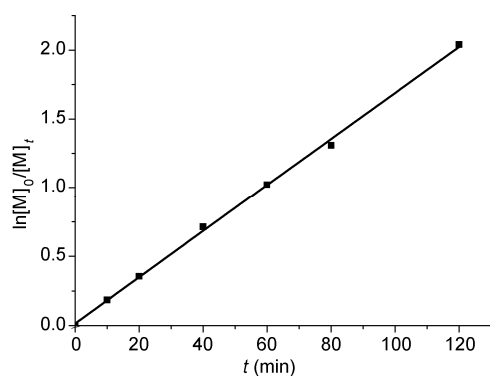
Entry	Initiator	$[\text{M}]_0/[\text{I}]_0^{\text{b)}$	Solvent	T_p ($^\circ\text{C}$)	t (h)	Yield (%) ^{c)}	M_n (10^{-4}) ^{d)}	PDI ^{d)}
1	1	500	Toluene	60	1	100	5.93	1.56
2	1	600	Toluene	60	1	100	7.47	1.71
3	1	700	Toluene	60	1	100	9.59	1.67
4	2	200	Toluene	60	1	97	5.02	1.39
5	2	400	Toluene	60	1	95	6.26	1.35
6	2	500	Toluene	60	1	98	7.32	1.23
7	2	600	Toluene	60	1	95	7.66	1.25
8	2	700	Toluene	60	3	95	8.54	1.31
9	2	800	Toluene	60	5	70	7.68	1.26
10	2	100	THF	60	1	86	1.82	1.23
11	3	500	Toluene	60	1	100	9.25	1.54
12	3	600	Toluene	60	1	96	11.22	1.57
13	3	700	Toluene	60	1	92	12.18	1.46
14	4	500	Toluene	60	1	95	5.46	1.52
15	4	600	Toluene	60	1	98	7.56	1.44
16	4	700	Toluene	60	1	78	4.86	1.40

a) Polymerization conditions: $V_{\text{sol}}/V_{[\text{M}]} = 1:1$; b) $[\text{M}]_0/[\text{I}]_0 = [\text{monomer}]/[\text{initiator}]$; c) yield: weight of polymer obtained/weight of monomer used; d) measured by GPC calibrated with standard polystyrene samples.

Table 4 Polymerization of *L*-lactide initiated by complex **2** in THF^{a)}

Entry	Initiator	[M] ₀ /[I] ₀ ^{b)}	T _p (°C)	t (min)	Yield (%) ^{c)}	M _n (10 ⁻⁴) ^{d)}	PDI ^{d)}
1	2	100	27	10	17	0.45	1.13
2	2	100	27	20	30	0.65	1.16
3	2	100	27	40	51	1.10	1.15
4	2	100	27	60	64	1.51	1.17
5	2	100	27	80	73	1.62	1.16
6	2	100	27	120	87	1.97	1.12

a) Polymerization conditions: V_{sol}/V_[M] = 1:1; b) [M]₀/[I]₀ = [monomer]/[initiator]; c) yield: weight of polymer obtained/weight of monomer used; d) measured by GPC calibrated with standard polystyrene samples.

**Figure 2** Polymerization of *L*-lactide initiated by complex **2** in toluene at 60°C. Relationship between the number-averaged molecular weight (*M_n*) and the molar ratio of monomer to initiator.**Figure 3** Semilogarithmic plot of ln[M]₀/[M]_t vs. time for the polymerization of *L*-lactide in THF initiated by complex **2**.

of the conversion during the polymerization of *L*-lactide. All these results indicated that the polymerization of *L*-lactide initiated by the carbon-bridged bis(phenolate) lanthanum trifluoroethanoxide proceeded in a controlled fashion.

3 Conclusions

In summary, four new lanthanum alkoxo complexes stabilized by a dianionic carbon-bridged bis(phenolate) ligand

were synthesized via simple protonolysis exchange reactions using LaCp₃(THF) as the starting material, and the structural features were characterized by X-ray diffraction study. These lanthanum alkoxo complexes are efficient initiators for the ring-opening polymerization of *L*-lactide to give polymers with high molecule weights and narrow molecule weight distributions. It was found that the structure of the alkoxo groups has a profound effect on the polymerization controllability, and that the lanthanum trifluoroethanoxide can initiate *L*-lactide polymerization in a controlled manner.

This work was supported by the National Natural Science Foundation of China (20972108, 21174095 and 21132002), the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the Qing Lan Project.

- 1 Amgoune A, Thomas C M, Ilinca S, et al. Highly active, productive, and syndiospecific yttrium initiators for the polymerization of racemic β-butyrolactone. *Angew Chem Int Ed*, 2006, 45: 2782–2784
- 2 Ma H Y, Spaniol T P, Okuda J. Highly heteroselective ring-opening polymerization of *rac*-lactide initiated by bis(phenolato)samarium complexes. *Angew Chem Int Ed*, 2006, 45: 7818–7821
- 3 Kramer J W, Treitler D S, Dunn E W, et al. Polymerization of enantiopure monomers using syndiospecific catalysts: A new approach to sequence control in polymer synthesis. *J Am Chem Soc*, 2009, 131: 16042–16044
- 4 Liu X L, Shang X M, Tang T, et al. Achiral lanthanide alkyl complexes bearing N, O multidentate ligands. Synthesis and catalysis of highly heteroselective ring-opening polymerization of *rac*-lactide. *Organometallics*, 2007, 26: 2747–2757
- 5 Dyer H E, Huijser S, Susperregui N, et al. Ring-opening polymerization of *rac*-lactide by bis(phenolate)amine-supported samarium borohydride complexes: An experimental and DFT study. *Organometallics*, 2010, 29: 3602–3621
- 6 Zhang Z J, Xu X P, Sun S, et al. Facile synthesis of bimetallic ytterbium bisamides stabilized by a flexible bridged bis(phenolate) ligand and the high activity for the polymerization of *L*-lactide. *Chem Commun*, 2009, 7414–7416
- 7 Luo Y J, Li W Y, Lin D, et al. Lanthanide alkyl complexes supported by a piperazine-bridged bis(phenolato) ligand: Synthesis, structural characterization, and catalysis for the polymerization of *L*-lactide and *rac*-lactide. *Organometallics*, 2010, 29: 3507–3514
- 8 Xu B, Huang L L, Yang Z J, et al. Synthesis and structural diversity of heterobimetallic lanthanide-potassium complexes and catalytic activity for amidation of aldehydes with amines. *Organometallics*, 2011, 30: 3588–3595
- 9 Pang M L, Yao Y M, Zhang Y, et al. Synthesis, characterization of amine-bridged bis(phenolate) yttrium alkyl complex and its catalytic

- behavior for the Tishchenko reaction. *Chin Sci Bull*, 2008, 53: 1978–1982
- 10 Ma H Y, Okuda J. Kinetics and mechanism of *L*-lactide polymerization by rare earth metal silylamido complexes: Effect of alcohol addition. *Macromolecules*, 2005, 38: 2665–2673
- 11 Qi R P, Liu B, Xu X P, et al. Synthesis, characterization and reactivity of heteroleptic rare earth metal bis(phenolate) complexes. *Dalton Trans*, 2008, 5016–5024
- 12 Xu X P, Yao Y M, Zhang Y, et al. Well-defined bis(phenolate) lanthanide methoxides as efficient initiators for the polymerization of cyclic carbonate and lactide. *Chin Sci Bull*, 2007, 52: 1623–1628
- 13 Xu X P, Yao Y M, Hu M Y, et al. Homopolymerization of cyclic esters initiated by lanthanide isopropoxides supported by 2,2'-ethylene-bis(4,6-di-*tert*-butylphenolate) ligands. *J Polym Sci Pol Chem*, 2006, 44: 4409–4419
- 14 Han X Z, Wu L L, Yao Y M, et al. Synthesis and characterization of *N*-aryloxo-functionalized β -ketoiminate rare-earth complexes and their catalytic activity for the polymerization of ϵ -caprolactone. *Chin Sci Bull*, 2009, 54: 3795–3800
- 15 Xu B, Han X Z, Yao Y M, et al. Synthesis and structural characterization of lanthanide amides stabilized by an *N*-aryloxo functionalized β -ketoiminate ligand. *Chin J Chem*, 2010, 28: 1013–1018

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