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Bridged Bis(amidinate) Ytterbium Alkoxide and Phenoxide: Syntheses, Structures, and Their High Activity for Controlled Polymerization of L-Lactide and ε-Caprolactone

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Bridged bis(amidinate) ytterbium alkoxide and phenoxide with diverse molecular structures were synthesized in high yields and confirmed by X-ray crystal structural analysis. The reaction of $LYbCl(THF)_2$ ($L = Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$) with 1 equiv of NaOAr (ArO = 2,6-diisopropylphenoxo) afforded the mononuclear complex LYb(OAr)DME **1** with a seven-coordinated ytterbium atom surrrounded by one chelating bis(amidinate) ligand, one phenoxo group, and one DME (dimethoxyethane) molecule. The same reaction with 1 equiv of NaO^iPr yielded the binuclear complex $Yb(\mu_2\text{-}L)_2(\mu_2\text{-}O^iPr)_2Yb$, **2**, with two equivalent six-coordinate metal centers connected by two linked bis(amidinate)s and two O^iPr bridges formed via a ligand redistribution reaction that occurred during the metathesis reaction. Both **1** and **2** initiated the ring-opening polymerization of L-lactide, as well as ε-caprolactone (ε-CL), in a controlled manner with high reactivity, as indicated by a linear relationship between M_n and conversion and by narrow molecular weight distributions (PDI = 1.15−1.25) up to 100% conversion. The differences in catalytic performance between complexes **1** and **2** are discussed.

Introduction

There is continuing interest in the synthesis of aliphatic polyesters, particularly, of polylactide, due to their biodegradable and biocompatible characteristics and the renewable nature of their feedstock.[1] Controlled ring-opening polymerization of lactones is a convenient route for the synthesis of aliphatic polyesters with predictable molecular weight, low polydispersity indices, and control over end groups. Lanthanide alkoxides are known to be highly active initiators. However, not all of the alkoxides are capable of initiating the polymerization in a living fashion.[2] Consequently, significant effort over the past few decades has been placed toward the design and synthesis of well-characterized single-site lanthanide alkoxides by use of an appropriate ancillary ligand to improve their performance. Various ligand sets, such as bulky cyclopentadienyl[3] and noncyclopentadienyl ligands,[4−7] have been developed. Among them, heteroatom-containing tetradentated bis(phenolate) ligands are of particular interest for this aim. Diverse lanthanide alkoxides and other derivatives bearing these “ONNO”, “ONOO”, or “OSSO” ligands allow provision of the polymerization in a living fashion[5−7] and even production of the polylactides (PLAs) with high stereoselectivity.[5,6]

Bridged bis(amidinate) dianions can be viewed as another kind of noncyclopentadienyl tetradentated “NNNN” ligand,

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(1) (a) Okada, M *Prog. Polym. Sci.* **2002**, *27*, 87. (b) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (c) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602. (d) O’Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.

(2) (a) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923. (b) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132. (c) Stevels, M. W.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 8296. (d) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 1320. (e) Nishiura, M.; Hou, Z. M.; Koizumi, T.; Imamoto, T.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 8245. (f) Shen, Z. Q.; Chen, X. H.; Shen, Y. Q.; Zhang, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 597. (g) Shen, Y. Q.; Shen, Z. Q.; Zhang, Y. F.; Yao, K. M. *Macromolecules* **1996**, *29*, 8289. (h) Shen, Y. Q.; Shen, Z. Q.; Zhang, Y. F.; Yao, K. M. *Macromolecules* **1996**, *29*, 3441. (i) Shen, Y. Q.; Shen, Z. Q.; Zhang, F. Y.; Zhang, Y. F. *J. Appl. Polym. Sci.* **1997**, *64*, 2131. (j) Ling, J.; Shen, Z. Q. *Macromolecules* **2001**, *34*, 7613. (k) Ling, J.; Zhu, W. P.; Shen, Z. Q. *Macromolecules* **2004**, *37*, 758. (l) Yao, Y.; Ma, M.; Xu, X.; Zhang, Y.; Shen, Q.; Wong, W.-T. *Organometallics* **2005**, *24*, 4014. (m) Sheng, H.; Zhou, L.; Zhang, Y.; Yao, Y.; Shen, Q. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1210. (n) Kerton, F. M.; Whitwood, A. C.; Willans, C. E. *Dalton Trans.* **2004**, 2237. (o) Yu, C.; Zhang, L.; Ni, X.; Shen, Z.; Tu, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6209.

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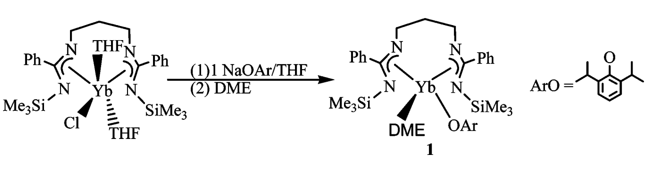
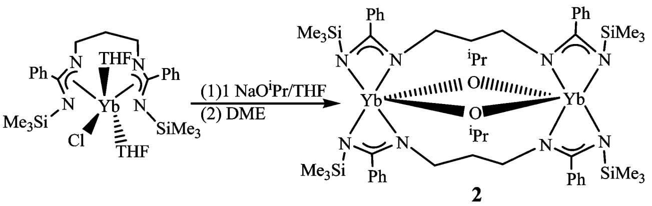
which has the advantage of tunable electronic and steric effects. These tetradentated "NNNN" groups were first introduced in lanthanide chemistry by Hessen et al. in 2001.[8] However, their usage in the design of lanthanide catalysts as a supporting ligand has not attracted more attention yet, although alkoxide and amide derivatives of yttrium supported by unbridged arylamidinated were reported to be active catalysts for the polymerization of D,L-lactone.[9] Very recently, we reported successful catalyst systems of ytterbium amides supported by a bis(amidinate) L (L = $Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$) for the controlled polymerization of L-lactide.[10] Further study revealed that the ytterbium amide complex LYb(NHAr)(DME) (Ar = 2,6-$^iPr_2C_6H_3$) can also serve as an efficient catalyst for the addition of amines to nitriles affording, selectively, monosubstituted *N*-arylamidinates.[11] These results promoted us to design well-defined lanthanide alkoxides using these ligands for the controlled polymerization of lactones.

In this contribution, we describe the synthesis and characterization of a new ytterbium alkoxide and phenoxide with the bridged bis(amidinate) ligand L, and their high activity for the controlled ring-opening polymerization of L-lactide, as well as ε-caprolactone, presenting the first example for a well-characterized binuclear lanthanide alkoxide-catalyzed, well-controlled polymerization of lactones. Moreover, the difference in performance between the two complexes is also discussed.

Scheme 1



Scheme 2



Results and Discussion

Syntheses of Complexes 1 and 2. The reaction of $LYbCl(THF)_2$, which was prepared by a published procedure,[12] with 1 equiv of NaOAr (OAr = 2,6-diisopropylphenoxo) was conducted in THF. The reaction went smoothly, and the chlorine can be simply replaced by the OAr group to give the corresponding aryloxide LYb(OAr)(DME), **1**, as colorless crystals upon the addition of DME (dimethoxylethane) in good yield. The monomeric nature of **1** was indicated by an X-ray diffraction study (Scheme 1).

In contrast, the reaction of $LYbCl(THF)_2$ with 1 equiv of NaO^iPr afforded the binuclear complex $Yb(\mu_2\text{-}L)_2(\mu_2\text{-}O^iPr)_2Yb$, **2**, which was confirmed by a crystal structure determination, instead of the mononuclear complex LYb(O^iPr), as the case of aryloxide (Scheme 2). The reaction is reproducible with the yields ranging from 48 to 53%, and no mononuclear complex LYb(O^iPr) has ever been isolated, indicating that **2** is more thermodynamically stable than expected for LYb(O^iPr). The formation of **2** demonstrated that a ligand redistribution reaction occurred concomitantly during the metathesis reaction. Such a ligand redistribution reaction with a binuclear complex was seen previously for the related reaction of $LYbCl(THF)_2$ with $NaN(TMS)_2$[10] and Li_2L.[13] Here, the occurrence of a ligand redistribution may be attributed to the encapsulation of two O^iPr bridges, which makes the complex more stable. The reaction pathway for the formation of **2** can be supposed as follows: the attack of NaO^iPr results in the cleavage of one of the linked bis(amidinate)−Yb bonds, followed by redistribution to another Yb atom.

Both complexes **1** and **2** are soluble in THF, DME, and even in toluene. A strong absorption of the C═N stretch at approximately 1640 cm^{-1} was observed for both complexes in their IR spectra, indicating the delocalized double bond

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(3) (a) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798. (b) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097. (c) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.

(4) (a) Xue, M.; Sun, H.; Zhou, H.; Yao, Y.; Shen, Q.; Zhang, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1147. (b) Yao, Y. M.; Xu, X. P.; Zhang, Y.; Shen, S.; Wong, W. T. *Inorg. Chem.* **2005**, *44*, 5133. (c) Simic, V.; Spassky, N.; Hubert-Pfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338. (d) Simic, V.; Girardon, V.; Spassky, N.; Hubert-Pfalzgraf, L. G.; Duda, A. *Polym. Degrad. Stab.* **1998**, *59*, 227. (e) Save, M.; Schappacher, M. le; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889. (f) Spassky, N.; Simic, V.; Montaudo, M. S.; Hubert-Pfalzgraf, L. G. *Macromol. Chem. Phys.* **2000**, *201*, 2432. (g) Agarwal, S.; Mast, C.; Dehnike, K.; Greiner, A. *Macromol. Rapid Commun.* **2000**, *21*, 195. (h) Chamberlain, B. M.; Jazdzewski, B. A.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2000**, *33*, 3970. (i) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 3332. (j) Alaaeddine, A.; Amgoune, A.; Thomas, C. M.; Dagorne, S.; Bellemin-Laonnaz, S.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2006**, 3652.

(5) (a) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (b) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169. (c) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328. (d) Yao, Y. M.; Xu, X. P.; Zhang, Y.; Shen, Q.; Wong, W. T. *Inorg. Chem.* **2005**, *44*, 5133.

(6) (a) Cai, C.-X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem.Commun.* **2004**, 330. (b) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *118*, 7982. (c) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046. (d) Amgoune, A.; Thomas, C. M.; Hinca, S.; Roisnel, T.; Carpentier, J.-F. *Angew. Chem., Int. Ed.* **200645**, 2782. (e) Amgoune, A.; Thomas, C. M.; Carpentier, J.-F. *Macromol. Rapid Commun.* **2007**, *28*, 693. (f) Ma, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818.

(7) (a) Liu, X.; Shang, X.; Tang, T.; Hu, N.; Pei, F.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 2747. (b) Kerton, F. M.; Whitwood, A. C.; Willams, C. E. *Dalton Trans.* **2004**, 2237. (c) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665. (d) Ma, H.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770. (e) Ma, H.; Melillo, G.; Oliva, L.; Okuda, J. *Dalton Trans.* **2005**, 721. (f) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124. (g) Gribkov, D. V.; Hultzch, K. C.; Hampel, F. *Chem.—Eur. J.* **2003**, *9*, 4796.

(8) Bambirra, S.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2001**, *20*, 782.

(9) Aubrecht, K. B.; Chang, K.; Hillmyer, M. A.; Tolman, W. B. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 284.

(10) Wang, J.; Cai, T.; Yao, Y.; Zhang, Y.; Shen, Q. *Dalton Trans.* **2007**, 5275.

(11) Wang, J.; Xu, F.; Cai, T.; Shen, Q. *Org. Lett.* **2008**, *10*, 445.

(12) Wang, J. F.; Yao, Y. M.; Cheng, J. L.; Pang, X. A.; Zhang, Y.; Shen, Q. *J. Mol. Struct.* **2005**, *743*, 229.

(13) Wang, J.; Sun, H.; Yao, Y.; Zhang, Y.; Shen, Q. *Polyhedron* **2008**, *27*, 1977.

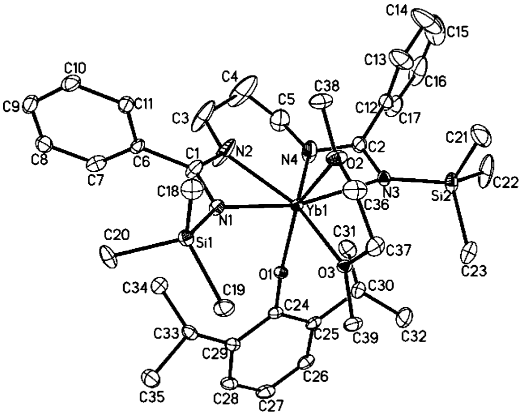

Figure 1. Molecular structure of complex **1** drawn with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Bond Angles in **1**

Yb(1)−N(1)	2.485(4)	Yb(1)−C(2)	2.782(6)
Yb(1)−N(2)	2.283(5)	N(1)−C(1)	1.326(7)
Yb(1)−N(3)	2.477(4)	N(2)−C(1)	1.309(7)
Yb(1)−N(4)	2.296(5)	N(3)−C(2)	1.326(7)
Yb(1)−C(1)	2.805(5)	N(4)−C(2)	1.331(8)
Yb(1)−O(1)	2.075(3)		
N(2)−Yb(1)−N(1)	55.66(16)	N(4)−Yb(1)−N(3)	56.01(17)
O(1)−Yb(1)−O(2)	150.75(14)		

of N−C−N linkage.[14] The acceptable NMR spectra for them are difficult to obtain because of the paramagnetic behavior of ytterbium.

X-Ray Crystal Structures of Complexes 1 and 2. Single crystals of **1** and **2** suitable for X-ray diffraction were obtained by cooling a mixture of DME and toluene. The X-ray diffraction analysis confirmed complex **1** being a monomer (Figure 1). The selected bond lengths and angles are listed in Table 1. The central metal coordinated to one chelating bis(amidinate) ligand and three oxygen atoms from one −OAr group and one DME molecule, forming a distorted trigonal bipyramid, if each amidinate ligand is considered to occupy one coordination vertex. Each center of the two amidinate groups and one oxygen atom (O3) occupy equatorial positions, while two oxygen atoms (O1 and O2) locate on axial sites. The coordination geometry around the central metal in **1** is similar to those of the related alkyl,[8] amide,[10] chloride, and cyclopentadienyl derivatives[12] reported previously. The bond parameters within the two amidinate ligands are not dramatically different. But there is a substantial difference in Yb−N(amidinate) distance for the amidinate nitrogens attached to the bridge compared to those attached to the $SiMe_3$ group (the former being 0.202 Å and 0.181 Å shorter), which is similar to those found in the related derivatives.[8,10,12] The bond parameters within Yb−N−C−N fall in the normal range of those found in the published complexes. The C−N bond distances within the chelating N−C−N unit are nearly equal, and the average value, 1.33 Å, reflected the delocalization of the π bond in the N−C−N unit. Because no aryloxide analogous with the related ligand was reported, the bond length of Yb−O(OAr) can only be compared with those of other lanthanide aryloxide complexes. The Ln−O(OAr) bond length of 2.075(3) Å in **1** is somewhat shorter than the corresponding values observed in L^1Yb (OAr)Cl(THF) [L^1 = N,N′-bis(2,6-dimethylphenyl)-2,4-pentanediiminato, OAr = 2,6-ditert-butylphenoxo-], 2.039(3) Å,[4a] and unbridged bis(amidinate) aryloxide $L_2^{TMS}Y(OC_6H_2{}^tBu_2Me)$ (L^{TMS} = bis[*N*,*N*′-bis(trimethylsilyl-)benzamidinate]), 2.075(2) Å,[9] when taking into account the difference in ionic radii of the metals and the different coordination numbers of the Yb complexes.

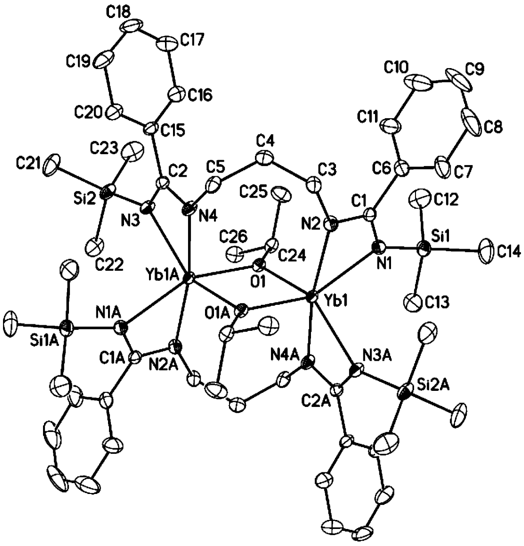

Figure 2. Molecular structure of complex **2** drawn with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths and Bond Angles in **2**

Yb(1)−N(1)	2.337(3)	Yb(1A)−N(3)	2.352(3)
Yb(1)−N(2)	2.346(3)	Yb(1A)−N(4)	2.304(3)
Yb(1)−N(3A)	2.352(3)	Yb(1A)−N(1A)	2.337(3)
Yb(1)−N(4A)	2.304(3)	Yb(1A)−N(2A)	2.346(3)
Yb(1)−O(1)	2.212(2)	Yb(1A)−O(1)	2.186(2)
Yb(1)−O(1A)	2.186(2)	Yb(1A)−O(1A)	2.212(2)
N(1)−Yb(1)−N(2)	57.88(10)	N(1A)−Yb(1A)−N(2A)	57.88(10)
N(4A)−Yb(1)−N(3A)	57.83(10)	N(4)−Yb(1A)−N(3)	57.83(10)

The molecular structure of **2** is shown in Figure 2. The selected bond lengths and angles are listed in Table 2. Complex **2** has a centro-symmetric bimetallic structure in which the coordination sphere around each Yb center is composed of two amidinate groups from two bridged bis(amidinate) ligands and two bridged oxygen atoms from O^iPr groups forming a distorted tetrahedron, if each amidinate ligand is considered to occupy a single coordination vertex. In the Yb_2O_2 core, the two bridging oxygen atoms and two lanthanide atoms are exactly coplanar, as required by the crystallographic symmetry. The dihedral angle of the Yb_2O_2 plane and the plane defined by Yb1−N2−N4−Yb1A equals 84.10°. Two O^iPr groups are unsymmetrically coordinated to the central metals, but the bond lengths of Yb−O^iPr are equivalent within the error limits. The mean bond length of Yb−O^iPr is 2.199(2) Å, which is comparable with the values reported in $[(C_5H_5)_2Lu(\mu\text{-}OCH_2CH_2CH_2CH_2Ph)]_2$,[15a] $[(Me_3CC_5H_4)_2Ce(\mu\text{-}O^iPr)]_2$,[15b] $(C_5H_5)_2Yb(\mu\text{-}O^iPr)]_2$,[15c] and $[(MBMP)Yb(\mu\text{-}O^iPr_2)(THF)_2]_2$ [MBMP = 2,2-methylenebis(6-

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(14) Giesbrecht, G. R.; Sharfir, A.; Arnold, J. *Dalton Trans.* **1999**, 3601.

(15) (a) Stults, S. D.; Anderson, R. A.; Zalkin, A. *Organometallics* **1990**, *9*, 1623. (b) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C49. (c) Wu, Z. Z.; Xu, Z.; You, X. Z.; Zhou, X. G.; Jin, Z. S. *Polyhedron* **1992**, *11*, 2673.

Table 3. Polymerization of L-Lactide Initiated by **1** and **2**[a]

run	init.	temp. (°C)	$[M]_0/[I]_0$	*t* (min)	conv. (%)[b]	M_n (10^4)[c]	M_n (10^4)[d]	M_n (10^4)[e]	PDI
1	1	70	200	10	100	7.42	4.30	2.88	1.19
2	1	70	300	60	trace				
3[f]	1	70	200	10	trace				
4	1	90	200	5	100	7.35	4.26	2.88	1.22
5	2	70	200	1	100	1.40	0.81	1.44	1.26
6	2	70	500	1	100	3.40	1.97	3.61	1.21
7	2	70	800	5	100	5.80	3.36	5.75	1.22
8	2	70	1500	20	100	10.8	6.26	10.8	1.26
9[f]	2	70	1500	20	trace				
10	2	100	1500	10	100	10.3	5.97	10.8	1.29
11	2	100	2000	120	29	4.71	2.73	4.18	1.25

[a] General polymerization conditions: in toluene, [LLA] = 1 mol L^{-1}. [b] Yield: weight of polymer obtained/weight of monomer used. [c] Measured by GPC relative to polystyrene standards. [d] Measured by GPC relative to polystyrene standards with Mark−Houwink corrections[17] for M_n [$M_n(\text{obsd}) = 0.58M_n(\text{GPC})$]. [e] Calculated value = 144.13 × $[M]_0/[I]_0$ × conv. (for initiator **1**), and = 144.13 × $[M]_0/[I]_0$ × 0.5 × conv. (for initiator **2**). [f] In THF.

tert-butyl-4-methylphenoxo)][4b] when the difference in ionic radii of the metals and the different coordination number of these metals are considered. It is worth noticing that the distance of Yb−Yb is 3.45 Å in complex **2**, which is much shorter than the 6.54 Å in $[\text{YbN(TMS)}_2]_2(\mu\text{-L})_2$ that has been published.[10] Such a short distance may be attributed to the existence of two oxygen bridges. However, the value is longer than that estimated from twice the single bond radius of the Yb atom. In the present spanning ligation, the bonding parameters within the amidinate ligands are comparable to those found in $[\text{YbN(TMS)}_2]_2(\mu\text{-L})_2$.[10]

Polymerization of L-Lactide Initiated by 1 and 2. The polymerization of L-lactide with complexes **1** and **2** was examined. The results obtained under various conditions are listed in Table 3. Both complexes were found to be efficient initiators to give a complete conversion in a short time in toluene at 70 °C. The complex with alkoxide group **2** is more active than the complex with a bulky phenoxide group **1**, as isopropoxide is usually a better initiating group than the phenoxide group.[4i] For example, complete conversion of 200 equiv of monomer was achieved in only 1 min for **2** (Table 3, entry 5), but in 10 min for **1** (Table 3, entry 1). Furthermore, the yield reached still as high as 100% when the molar ratio of monomer to initiator (M/I) increased to 1500 for **2** (Table 3, entry 8). To the best of our knowledge, such a high reactivity for lactide polymerization shown by a well-defined lanthanide alkoxide has never been reported yet. However, polymerization with **1** went sluggishly, when M/I increased to 300 (Table 3, entry 2). The experiment was reproducible. Such a dramatic decrease in activity with the increasing of M/I from 200 to 300 for **1** (the same situation was also found for the system with **2** (entries 10 and 11)) may be attributed to the existence of a trace of lactide acid contaminated in the monomer and moisture in the solvent, since **1** and **2** are highly sensitive to any proton source. Thus, the catalyst will be decomposed if the loading of the catalyst is too low to tolerate this impurity.

The polymerizations with **1** and **2** proceeded much more slowly in THF than in toluene; only trace polymers were obtained in THF (Table 3, entries 3 and 9), presumably because of competitive coordination of the coordinating solvent.[16]

All of the PLAs obtained with complexes **1** and **2** showed monomodal GPC traces with narrow polydispersity values (M_w/M_n = 1.15−1.29). In the case of **2**, the experimental (uncorrected) number-average molecular mass (M_n) values are very close to the theoretical ones (calculated on the assumption that each O^iPr group initiates the polymerization), and the corrected values with Mark−Houwink corrections[17] are proportionately lower (Figure 3a). In addition, the larger experimental values for both uncorrected and corrected M_n related to calculated ones were observed for the case of **1** (Figure 3b). Most likely it is because some transfer occurred in the system with **2** and both the difficulty of initiation by the hindered aryloxide and some transfer reaction for **1**. Although there is deviation in M_n between corrected experimental and calculated values for both systems, the polymerization occurs in a living fashion over the entire conversion range, as confirmed by narrow polydispersities of the polymers. The same situation was also found for the lactide polymerization with the catalysts published.[6c,7c] The living character was further confirmed by a proportional increase in number averaged molecular weight (M_w) with the ratio of monomer to initiator for complex **2** (Table 3, entries 5−8) and a linear increase in M_n with monomer conversion recorded with both **1** and **2**, while the molecular weight distributions (M_w/M_n) of the resulting polymers were kept narrow ($M_w/M_n \leq 1.29$) and intact, as shown in Figure 3. Polymerization kinetics at 70 °C in toluene with a molar ratio of monomer/initiator of 200 for **1** and 1500 for **2** were further measured. The pseudo first-order kinetic plots of $\ln([M]_0/[M])$ versus polymerization time were observed for both systems, as shown in Figure 4. The linear semi logarithmic plots indicate that the concentration of the catalytic active species kept constant throughout the polymerization.

It is worth noticing that the polydispersity index of the resulting polymers keeps narrow and almost unchanging, even when the polymerization temperature is raised from 70 to 100 °C (Table 3, entries 1 and 4; 8 and 10).

Prereacting phenoxide complex **1** with 2-propanol, to generate in situ the corresponding isopropoxide complex, was

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(16) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J.-F. *J. Mol. Catal. A* **2007**, *268*, 163.

(17) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.

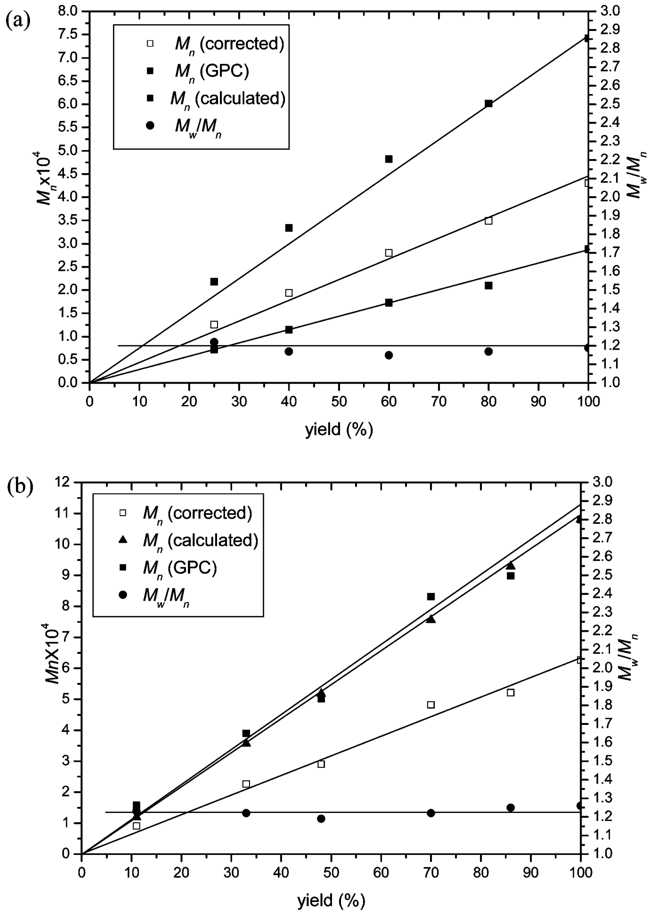

Figure 3. M$_n$ and M_w/M_n versus conversion plots for PLAs obtained using complexes **1** (a) and **2** (b). Conditions: $[M]_0/[I]_0 = 200$ (for complex **1**) and $[M]_0/[I]_0 = 1500$ (for complex **2**), $[LA]_0 = 1$ mol/L, 70 °C, toluene.

tried since the treatment of amide complexes with 2-propanol is well-known to be a useful strategy for improving the reactivity and control of polymerization. Surprisingly, the pretreatment led to the deactivation of **1**, and almost no polymerization was observed under the same conditions. The reason for it may be that **1** was decomposed by free 2-propanol via the protonolysis of the amidinate−metal bond. Attempts to isolate the product from the reaction of **1** with 2-propanol failed.

NMR spectroscopy has been used to identify the stereosequence in PLAs. ^{1}H NMR spectra of the PLAs obtained with **2** showed a nearly ideal quartet for the methine proton at δ 5.17 ppm and a doublet for the methyl proton at δ 1.58 ppm, indicating no inversion of the configuration of asymmetric carbon atoms of the monomer under the reaction conditions.

The end groups of the oligomer have been analyzed by ^{1}H NMR, leading to the conclusion that the PLA chains are capped by an isopropoxyester (δ 5.07 ppm) at one end and an alcohol at the other end (δ 4.30 and 2.70 ppm) assigned to the methine proton,[2n,18] which results from the hydrolytic deactivation of the ytterbium alkoxide growing species.

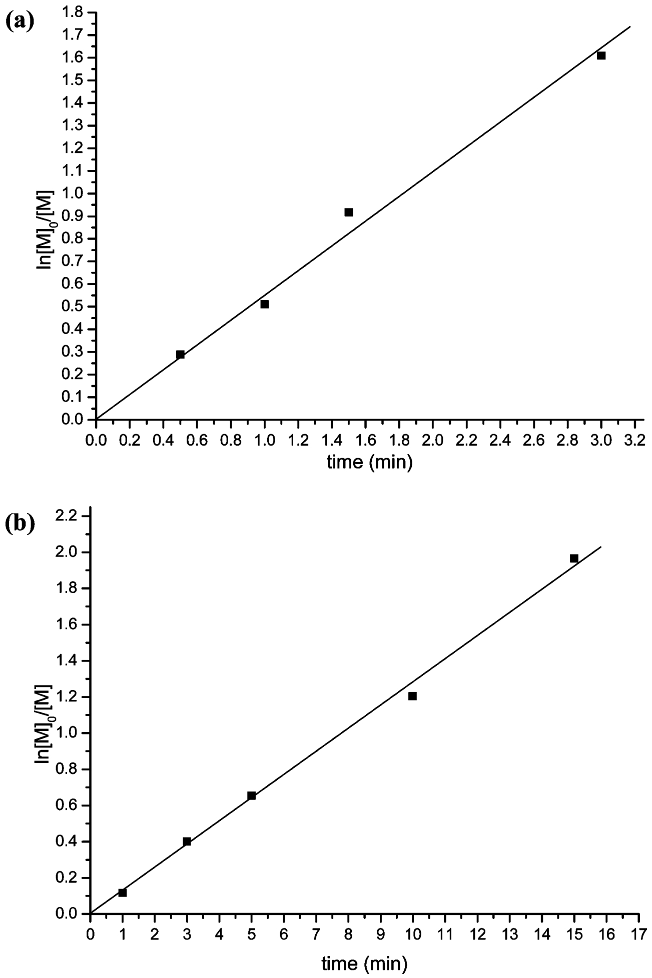

Figure 4. Polymerization time vs ln$[M]_0/[M]$ plots for the polymerization of L-lactide initiated with complexes **1** (a) and **2** (b). Conditions: $[M]_0/[I]_0 = 200$ (for complex **1**), $[M]_0/[I]_0 = 1500$ (for complex **2**), $[LA]_0 = 1$ mol/L, 70 °C toluene.

Polymerization of ε-CL Initiated by 1 and 2. The ring-opening polymerizations of ε-CL were examined by usage of **1** and **2** as initiators. The representative results are listed in Table 4. For both catalysts, the polymerization depends upon the solvent greatly, and the activity in toluene is much higher than that in THF (Table 4, entries 3 and 4, and 7 and 9).[15] As shown in Table 4, the polymerization with **1** proceeded rapidly at room temperature in toluene: complete conversions of 800 equivalents of ε-CL to polymers were achieved within 20 min, and the resulting polymer with narrow molecular weight distributions was obtained ($M_w/M_n = 1.37$, Table 4 entry 3). However, the polymerization with **2** is not so efficient at room temperature, as confirmed by the low activity and the rather broad polydispersity of the resulting polymer: only 50% of the conversion of 400 equivalents of the monomer to polymers was reached in 90 min, and the M_w/M_n of the polymer was as high as 1.79 (Table 4, entry 5). Surprisingly, raising the polymerization temperature to 40 °C led to a dramatic increase in the activity of **2**: complete conversion of as high as 2000 equivalents of ε-CL was reached within 60 min, and the resulting polycaprolactone had a high molecular weight with a narrow molecular weight distribution of 1.29 (Table 4 entry 8). In contrast, raising the temperature is not favorable for the

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(18) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem. Phys.* **1995**, *196*, 1153.

Table 4. Polymerization of ε-CL initiated by **1** and **2**[a]

run	init.	temp. (°C)	$[M]_0/[I]_0$	t (min)	conv. (%)[b]	M_n (10^4)[c]	M_n (10^4)[d]	M_n (10^4)[e]	PDI
1	1	40	1000	90	100	8.57	4.80	11.41	1.77
2	1	40	1000	15	85	7.10	3.98	9.70	1.67
3	1	rt	800	20	100	14.5	8.12	9.13	1.37
4[f]	1	rt	800	20	trace				
5	2	rt	400	90	50	4.21	1.32	2.28	1.79
6	2	40	1000	20	100	10.2	5.71	11.41	1.25
7	2	40	1500	50	100	15	8.40	17.12	1.26
8	2	40	2000	60	100	23.0	12.88	22.83	1.29
9[f]	2	40	1500	50	trace				

[a] General polymerization conditions: in toluene. [b] Yield: weight of polymer obtained/weight of monomer used. [c] Measured by GPC relative to polystyrene standards. [d] Measured by GPC relative to polystyrene standards with Mark−Houwink corrections for M_n [M_n(obsd) = $0.56M_n$(GPC)]. [e] Calculated value = $114.14 \times [M]_0/[I]_0 \times$ conv. (for initiator **1**), and = $112.17 \times [M]_0/[I]_0 \times 0.5 \times$ conv. (for initiator **2**). [f] In THF.

polymerization with **1**: the polymerization is out of control at 40 °C, as confirmed by the fact that the polymers have much lower molecular weights than the theoretical one and broad molecular weight distributions of 1.77 and 1.67 (entries 1 and 2). These differences in activity and control of the polymerization between **1** and **2** may be attributed to a crucial influence on the catalytic behavior resulting from the coordinated environment around the central metal. The difficulty of initiation by the hindered aryloxide group, resulting in slower initiation in comparison with the propagating reaction and a faster transesterification reaction at 40 °C compared to that at room temperature, may be the reason for the uncontrolled polymerization of **1** at 40 °C. The bridged O^{i}Pr group was supposed to remain in **2** at room temperature, and the μ-O^{i}Pr group is less active in the polymerization of ε-CL. Thus, the polymerization with **2** proceeded at room temperature sluggishly. The bridged O^{i}Pr group of **2** was supposed to change to a terminal group under the attack of the monomer at 40 °C, and a the terminal O^{i}Pr group is highly active. So far, we were not able to isolate any pure complex, but the suggestion seems reasonable.

Both **1** and **2** were capable of initiating controlled polymerization of ε-CL under their own optimizing conditions, as shown by linear increases of M_n with conversion for both **1** and **2** (Figure 5), and also by a proportional increase of M_n with the monomer-to-initiator ratio for **2** (Table 4, entries 6−8) and narrow molecular weight distributions. The polymerization kinetics at room temperature in toluene with an M/I of 800 for **1** and at 40 °C with an M/I of 1500 for **2** gave the pseudo first-order kinetic plots of $\ln([M]_0/[M])$ versus polymerization time, as shown in Figure 6.

End-group analysis of the oligomer obtained by polymerization at an M/I of 10 with **2** revealed the existence of an isopropoxyester (δ 5.07 ppm) and an alcohol (δ 3.57 ppm) in ^{1}H NMR. The results indicated the participation of only the isopropoxy group in initiation.

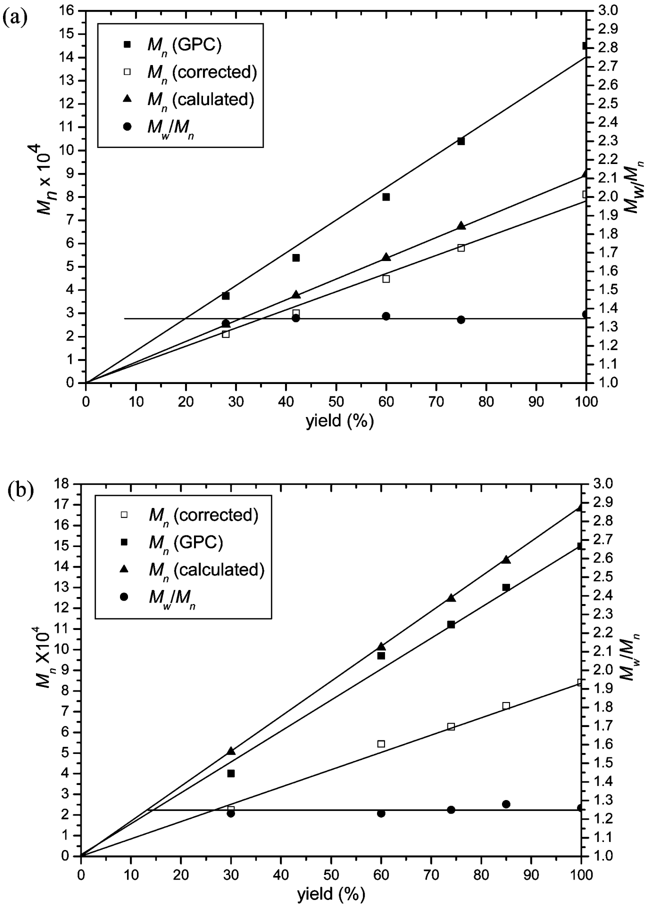

Figure 5. M_n and M_w/M_n vs conversion plots for poly(ε-CL) obtained using complexes **1** (a) and **2** (b). Conditions: $[M]_0/[I]_0$ = 800, toluene, rt (for complex **1**); $[M]_0/[I]_0$ = 1500, toluene, 40 °C (for complex **2**).

Conclusion

We have synthesized ytterbium phenoxide complex **1** and isopropoxide complex **2** supported by a bridged bis(amidinate) ligand. X-ray structural analysis showed that **1** is a mononuclear complex with a chelating bis(amidinate) group, while **2** is a binuclear complex in which two Yb atoms are connected by two bridged bis(amidinate) groups and two bridged O^{i}Pr groups. Both **1** and **2** were found to initiate the polymerization of L-lactide and ε-CL in a controlled manner. The most notable feature of the binuclear ytterbium isopropoxide initiator described in this report is high polymerization activity in conjunction with good controllability for the polymerization of both L-lactide and ε-CL. It can be anticipated that the best combination of a bridged bis(amidinate) with an active group in group 3 metal complexes should provide new and interesting reactivity. Work to develop new catalysts with this kind of ligand set is proceeding in our laboratory.

Experimental Section

General Procedures. All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from

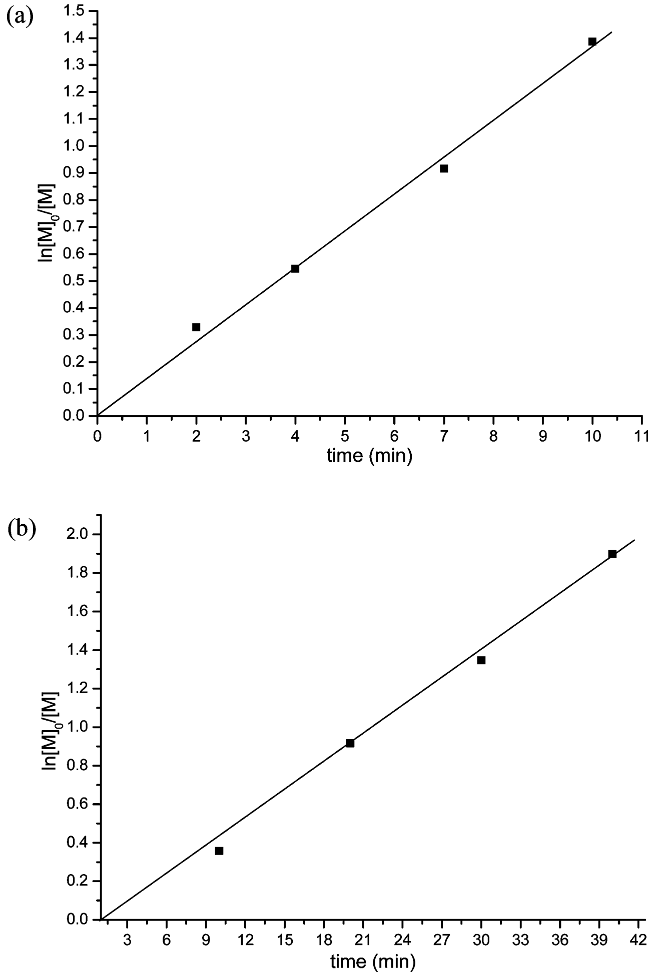

Figure 6. Polymerization time versus ln[M]$_0$/[M] for the polymerization of ε-CL initiated by complexes **1** (a) and **2** (b). Conditions: $[M]_0/[I]_0 = 800$, toluene, rt (for complex **1**); $[M]_0/[I]_0 = 1500$, toluene 40 °C (for complex **2**).

Table 5. Details of the Crystallographic Data and Refinements for **1** and **2**[a]

	1	**2**
formula	$C_{39}H_{61}N_4O_3Si_2Yb$	$C_{52}H_{82}N_8O_2Si_4Yb_2$
M_r	863.14	1309.70
temp/K	213(2)	193(2)
cryst size/mm	0.50 × 0.30 × 0.30	0.30 × 0.20 × 0.10
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a/Å	24.764(2)	10.5426(3)
b/Å	8.7551(6)	10.7834(5)
c/Å	20.0979(16)	15.2118(6)
α/deg	90	109.501(9)
β/deg	106.648(2	99.684(9)
γ/deg	90	104.004(12)
V/Å^3	4174.7(6)	1521.96
Z	4	1
D_{calcd}/g cm^{-3}	1.373	1.429
μ/mm^{-1}	2.336	3.174
F(000)	1780	662
θ range for collection/deg	3.08−25.35	3.02−25.35
no. of reflns collected	39562	15165
no. of independent reflns	7645	5525
R [$(I > 2\sigma(I))$]	0.0431	0.0269
wR	0.0798	0.0618
GOF	1.165	1.091

[a] The structures were 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, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the H 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 program.

sodium benzophenone ketyl before use. ε-CL and L-lactide were purchased from Acros and purified by distillation in CaH_2 for ε-CL and recrystallization from a mixture of THF and toluene for L-lactide. LYbCl(THF)$_2$[11] was prepared according to the literature procedure. All other reagents were purchased from Acros and were used as received without further purification. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets. Melting points were determined in sealed Ar-filled capillary tubes and are uncorrected. Lanthanide analyses were carried out by a complexometric titration. Carbon, hydrogen, and nitrogen analyses were preformed by direct combustion using a Carlo-Erba EA 1110 instrument. Molecular weight and molecular weight distributions were determined against a polystyrene standard by gel permeation chromatography on a Waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4) at 30 °C; THF was used as an eluent.

LYb(OAr)(DME) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1). A solution of NaOAr (2 mmol, 1 M) in THF was added to a stirring solution of LYbCl(THF)$_2$ (1.55 g, 2 mmol) in THF (30 mL). The reaction mixture was stirred for 48 h at room temperature. The volatiles were removed under reduced pressure, and the residue was extracted with DME (2 × 25 mL) and reduced to 20 mL. Cooling the solution to 0 °C afforded the colorless crystals (0.86 g, 50% based on Yb). Mp: 149−151 °C. Anal. calcd for $C_{39}H_{61}N_4O_3Si_2Yb$: C, 54.27; H, 7.12; N, 6.49; Yb, 20.05%. Found: C, 54.18; H, 7.02; N, 6.58; Yb, 20.23%. IR (KBr, cm^{-1}): 2957 (m), 1637 (s), 1624 (s), 1436 (m), 1252 (m), 1127 (s), 1084 (s), 1003 (w), 833 (w), 750 (m), 700 (m).

Yb(μ_2-L)$_2$(μ_2-O^{i}Pr)$_2$Yb (2). A solution of NaO^{i}Pr (2 mmol, 1 M) in THF was added to a stirring solution of LYbCl(THF)$_2$ (1.55 g, 2 mmol) in THF (30 mL). The reaction mixture was stirred for 48 h at room temperature. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (2 × 80 mL). The volume of the extract was reduced to 10 mL, followed by an addition of 1 mL of DME. Cooling the solution to 0 °C afforded the product as colorless crystals (0.69 g, 53% based on Yb). Mp: 92−95 °C. Anal. calcd for $C_{52}H_{82}N_8O_2Si_4Yb_2$: C, 47.69; H, 6.31; N, 8.56; Yb, 26.42%. Found: C, 47.84; H, 6.01; N, 8.85; Yb, 26.33%. IR (KBr, cm^{-1}): 2955 (m), 1635 (s), 1566 (s), 1489 (m), 1381 (m), 1250 (m), 1157 (w), 1003 (w), 918 (w), 833 (m), 779 (m), 748 (m), 702 (m).

General Procedure for the Polymerization of ε-CL and L-Lactide. The procedures for the polymerization of ε-CL and L-lactide initiated by complexes **1** and **2** are similar, and a typical polymerization procedure is given below. To a stirred solution of ε-CL or L-lactide in toluene was added a toluene solution of the initiator using a syringe. The polymerization mixture was stirred for a definite time at the desired temperature and then quenched with an ethanol solution containing a small amount of hydrochloric acid (5%). The polymer was precipitated from ethanol and washed with ethanol three times and dried under a vacuum.

Oligomer for End Group Analysis. The oligomerization of ε-CL (L-lactide) was carried out with **2** in toluene at 25 °C under a [ε-CL]/[initiator] ([L-lactide]/[initiator]) molar ratio of 10. The reaction was terminated by adding 1 mL of 5% HCl/hexane after 2 h. The oligomer was precipitated from ethanol. The product was dissolved in THF, followed by precipitation in ethanol. After filtration, the white product was dried in a vacuum.

X-Ray Crystallography. Crystals suitable for X-ray diffraction of complexes **1** and **2** were sealed in a thin-walled glass capillary filled with argon for structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector in the ω scan mode using Mo Kα radiation ($\lambda = 0.71070$ 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 5.

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Supporting Information Available: Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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