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Synthesis and Structural Studies of Heterobimetallic Alkoxide Complexes Supported by Bis(phenolate) Ligands: Efficient Catalysts for Ring-Opening Polymerization of L-Lactide

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A series of heterobimetallic titanium(IV) complexes [$LTi(O^iPr)(\mu\text{-}O^iPr)_2Li(THF)_2$], [$LTi(O^iPr)(\mu\text{-}O^iPr)_2Na(THF)_2$], [$LTi(\mu\text{-}O^iPr)_2Zn(O^iPr)_2$], and [$LTi(\mu\text{-}O^iPr)_2Mg(O^iPr)_2$] (where L = bidentate bisphenol ligands) have been synthesized and characterized including a structural determination of [$L^1Ti(\mu_2\text{-}O^iPr)_2(O^iPr)Li(THF)_2$] (**1a**). These complexes were investigated for their utility in the ring-opening polymerization (ROP) of L-lactide (LA). Polymerization activities have been shown to correlate with the electronic properties of the substituent within the bisphenol ligand. In contrast to monometallic titanium initiator **1e**, all the heterobimetallic titanium initiators (Ti—Li, Ti—Na, Ti—Zn, and Ti—Mg) show enhanced catalytic activity toward ring-opening polymerization (ROP) of L-LA. In addition, the use of electron-donating methoxy or methylphenylsulfonyl functional ligands reveals the highest activity. The bisphenol bimetallic complexes give rise to controlled ring-opening polymerization, as shown by the linear relationship between the percentage conversion and the number-average molecular weight. The polymerization kinetics using **2c** as an initiator were also studied, and the experimental results indicate that the reaction rate is first-order with respect to both monomer and catalyst concentration with a polymerization rate constant, $k = 81.64\ M^{-1}\ min^{-1}$.

Introduction

As a biodegradable and biocompatible polymeric material derived from annually biorenewable natural resources poly(L-lactide) (PLLA) has attracted considerable attention as a promising alternative to synthetic petrochemical-based polymers.[1] Mechanical and physical properties of PLLAs, along with their biodegradable and biocompatible nature, make them prospective thermoplastics with broad applications such as single-use packaging materials, medical sutures, and drug delivery systems.[2] Ring-opening polymerization (ROP) of lactide, for example, by metal initiators, proved to be the most efficient method for the preparation of PLAs with controlled molecular weight and narrow molecular-weight distribution.[3,4] Over the past few decades, there has been a particular emphasis on the synthesis of discrete, well-defined metal complexes as active ring-opening polymerization initiators.

Among the variety of initiators, a large number of metal alkoxide complexes of aluminum,[5] zinc,[6] magnesium,[7] iron,[8] lanthanide,[9] lithium,[10] and titanium[11] have been active as LA polymerization catalysts affording polymers with controlled molecular weights and narrow molecular weight distribution. Despite the fact that several excellent initiators have been

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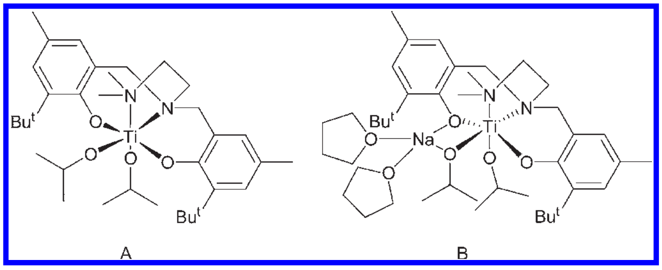
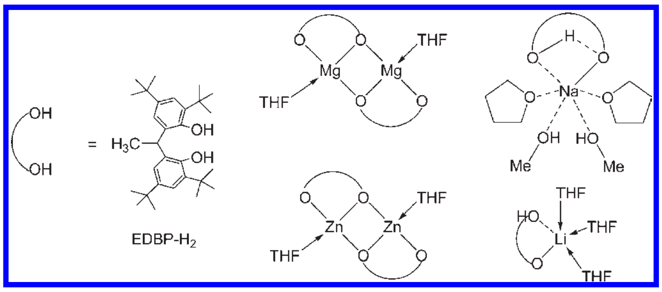
reported for the polymerization of LA, the search for new catalysts remains of keen interest in order to improve catalyst activity and control of microstructure of polyesters. Among these metal initiators, tin(II) compounds are employed commercially with approval by the U.S. Food and Drug Administration (USFDA),[12] in spite of the difficulties of removing the catalyst residues from the resultant polymer.

Although titanium is an eco-friendly and nontoxic metal which the human body can tolerate in large doses[13] and there are similarities in properties of tin and titanium, only a limited number of investigations are reported on the titanium alkoxide complexes as potential ROP catalysts.[11b,13−15] A series of the biphenoxy ligand supported titanium alkoxide initiators was recently reported which shows catalytic ring-opening polymerization of L-lactide in bulk phase with narrow dispersities.[16] Living ring-opening polymerization of ε-caprotactone was achieved using well-defined titanium alkoxide complexes.[17]

Scheme 1. Titanium Complexes **A** and **B**[11h]



Scheme 2. Bisphenol Ligand EDBP-H_2 and its Metal Complexes[6e,7e,h,10e,18]



However, titanium alkoxides have low activity toward ROP because of their high positive charges and strong π bonding effect between Ti and alkoxides and consequently decreases the rate of polymerization. To overcome this barrier, Bochmann et al. developed heterobimetallic complex of titanium−sodium supported by a multidentate amino-bis(phenol) ligand (Scheme 1, B).[11h] This complex revealed a higher reactivity for ROP of ε-captorlactone than the monomeric complex **A**. The higher activity of bimetallic complex **B**, which achieves almost complete conversion of 200 equiv of CL over 2 h, is probably due to the coordination of sodium metal reducing the electron density on alkoxo Ti−O bond and therefore decreases π donor ability.

On the other hand, alkali metal alkoxide complexes have shown excellent catalytic activity toward ROP of lactones and lactide when the complexes are supported by sterically demanding ligands. We reported Li,[10e] Na,[18] Mg,[7e,h] and Zn[6e] complexes supported by 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H_2) ligands as shown in Scheme 2, and all of them demonstrated excellent catalytic activity for the ROP of L-lactide.

On the basis of the experiences in synthesis and ROP activity of the alkali metal complexes, Mg, and Zn-alkoxide complexes and the scope of development of the titanium based initiators, we thus believed it would be interesting to

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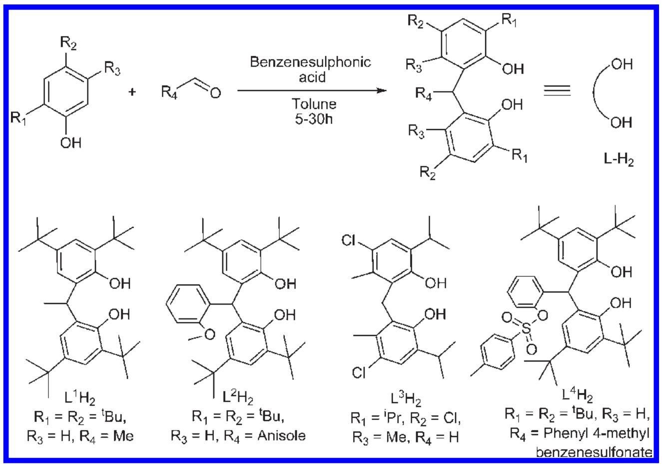
synthesize a series of titanium based heterobimetallic complexes supported by sterically protected bis(phenolate) ligands with a systematic variation of substitutents as alkyl, halide, and sulfonate on the ligand and subsequently varying the other metal with Li, Na, Mg, and Zn. Such well-defined heterobimetallic species can then be examined for their ROP activity of L-lactide, and the results can be analyzed in terms of the electronics of the ligand and the effect of the four different metals (Li, Na, Mg, and Zn) on the polymerization activity.

Results and Discussion

Synthesis of Bisphenol Supported Mixed Metal Complexes. Bisphenol ligands L^n-H_2 (n = 1−4) were synthesized by the condensation of 2 equiv of the substituted phenol with the appropriate aldehyde under reflux conditions (Scheme 3).[5d] The ligands were obtained as white crystalline powder and in good yield (> 70%). They were characterized by ^1H NMR spectroscopy and in the case of the reported ligands, the data was in accord with the literature reports. The ^1H NMR signals for the corresponding aromatic rings, as well as the *tert*-butyl and methine protons of L^2-H_2 and L^4-H_2 appeared at δ 1.37 (18H, s, $C(CH_3)_3$), 1.16 (18H, s, $C(CH_3)_3$), 5.92 (1H, s, CH) and (18H, s, $C(CH_3)_3$), 1.16 (18H, s, p-$C(CH_3)_3$), and 6.11 (1H, s, $HCPh_3$), respectively, supporting the identical chemical environments of these groups and structure of the ligands.

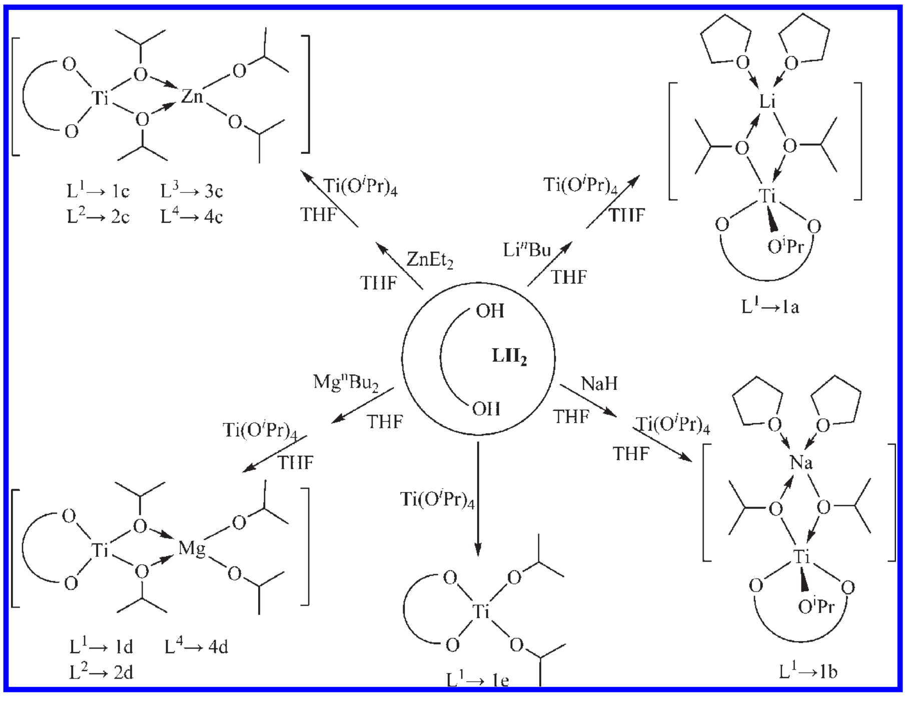
Scheme 3. Synthesis of Bisphenol Ligands L-H_2 (**1**−**4**)



Synthesis of L^1-ligand supported magnesium(II), sodium(I), lithium(I), and zinc(II) complexes and their ROP activity have been reported in the literature.[6e,7e,h,10e,18] Herein, we extended the chemistry of L^1 for the preparation of monometallic titanium(IV) complex **1e** following the literature methods.[11,13] Further, we attempted the synthesis of the heterobimetallic titanium(IV) alkoxide complexes using L^1-L^4-H_2 ligands. The synthesis was carried out in two steps: first, condensation of the proligand L^n-H_2 with equivalent metal alkyl or hydride to produce the monometallic complexes followed by the treatment of the monometallic complexes with $Ti(O^iPr)_4$ in 1:1 ratio to produce heterobimetallic complexes with reasonable yields. In the reaction of the bis(phenolate) ligands with Li^nBu, NaH, Mg^nBu_2, and $ZnEt_2$ in THF readily generated corresponding tetracoordinated complexes $[(L\text{-}H)Li(THF)_3]$, $[(L\text{-}H)Na(THF)_3]$, $[LMg]_2$, and $[LZn]_2$, respectively (Scheme 4). For all the bimetallic complexes, pale yellow crystals were obtained from white suspension in THF; recrystallization gives moderate to good yields. These bimetallic complexes **1a**−**1d**, **2c**−**2d**, **3c**, and **4c**−**4d** were fully characterized by NMR spectral and elemental analysis.

The ^1H NMR resonances indicate that chemical environments of aromatic rings, as well as two bridging isopropoxide groups are identical in complexes **1a** and **1b**. The chemical shifts corresponding to the methine and methyl protons of the metal bound isopropoxide in

Scheme 4. Synthesis of Metal Complexes



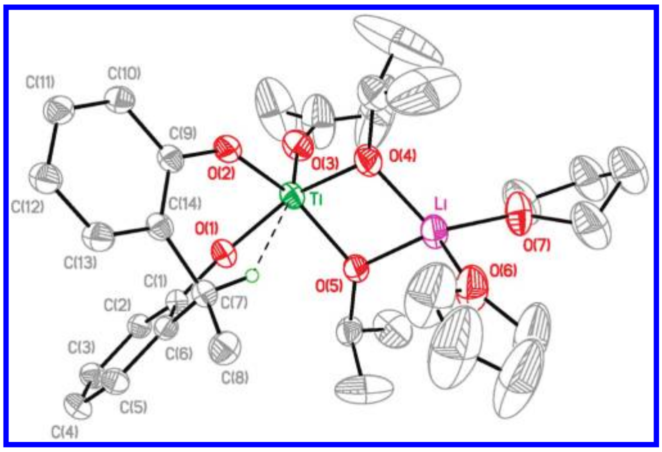


Figure 1. Molecular structure of EDBPTi(μ-OPr^i)$_3$Li(THF)$_2$ **1a** as 20% ellipsoids (hydrogen atoms and ^{t}Bu groups are omitted for clarity). Selected bond lengths (Å): Ti−O(1) 1.876(3), Ti−O(2) 1.898(3), Ti−O(3) 1.760(3), Ti−O(4) 1.932(3), Ti−O(5) 1.924(3), Ti−H(7A) 2.55(4), Li−O(4) 1.891(9), Li−O(5) 1.922(9), Li−O(6) 1.990(10), Li−O(7) 1.989(9). Bond angles (deg): O(1)−Ti−O(2) 90.0. (2), O(1)−Ti−O(3) 99.7(2), O(1)−Ti−O(5) 89.7(2), O(2)−Ti−O(3) 105.2(2), O(2)−Ti−O(4) 88.7(2), O(3)−Ti−O(4) 101.9(2), O(3)−Ti−O(5) 109.8(2), O(4)−Li−O(5) 80.0(3), O(4)−Li−O(6) 116.5(5), O(4)−Li−O(7) 122.5(5), O(5)−Li−O(6) 115.7(5), O(5)−Li−O(7) 120.5(5), O(6)−Li−O(7) 101.9(4), O(3)−Ti−H(7A) 166.8(10).

complex **1a** appeared at δ 5.11 and 1.28, respectively, which is identical to that of **1b**'s at δ 5.11 and 1.25 ppm, respectively.

In contrast, complexes **1c** and **1d** containing two bridging and two terminal iso-propoxide groups exhibit different ^{1}H NMR resonances from that of **1a** and **1b**. Two sets of methine proton resonances appeared at δ 4.86 and 4.34 for **1c** and δ 4.82 and 4.19 for **1d** suggesting inequivalent chemical environments for the bridging isopropoxides. Similarly, the methine signals of the bridging isopropoxide appeared at δ 5.02 and 4.31 for **2c** and δ 4.99 and 4.20 for **2d**. For compound **3c**, an unusual ^{1}H NMR pattern was recorded showing three sets of methine signals of the coordinated isopropoxide at δ 4.93, 4.55, and 4.25 ppm. More strangely, four separate methine signals were observed at δ 5.14, 4.35, 4.03, 3.49 and δ 5.10, 4.25, 4.11, 3.41 for **4c** and **4d**, respectively, which is probably due to the highly fluxional nature of the terminal and bridging isopropoxides. The ^{1}H NMR data analysis revealed that complexes **1c**−**2c**, and **1d**−**2d**, contain two diastereotopic methine protons in each isopropoxide group and the twelve methyl protons (−OCH(CH_3)$_2$) resonated at one signal whereas the other twelve of the methyl protons resolved as two separate multiplets of dq pattern indicating that the bulky *ortho*-tert-butyl substituents restricted the free rotation of the phenyl moiety on the NMR time scale.

Molecular Structure of Bimetallic Complex 1a. Single crystals of the bimetallic titanium−lithium complex **1a** [L^{1}Ti(μ_2-O^{i}Pr)$_2$(O^{i}Pr)Li(THF)$_2$] suitable for X-ray diffraction measurement were obtained by the slow cooling of a hot hexane solution. The molecular structure of **1a** and selected bond lengths and angles are shown in Figure 1. The titanium atom bears a distorted octahedral geometry having a terminal isopropoxide group lying on the axial position and the other four oxygen atoms on the basal position with the bond angles ranging from 88.7 to 109.8°. However, two oxygen atoms from isopropoxides are also involved in μ-oxo bridges between the lithium and titanium atoms. The lithium is four-coordinate with coordination of THF molecules and two bridging oxygen atoms with distorted tetrahedral geometry. Two mean bond lengths of titanium−oxygen (aryloxide) [Ti−O(1) and Ti−O(2) type bonds are 1.876(3) and 1.898(3) Å] and titanium−oxygen (bridging isopropoxide) [Ti−O(4) and Ti−O(5) type bonds are 1.932(3) and 1.924(3)Å] in **1a** are significantly longer than that of titanium−oxygen (terminal isopropoxide) bond of 1.762(3) Å. This difference is due to significant π-bonding in Ti−O (terminal isopropoxide), while in the case of bridging isopropoxide groups, reduction in the extent of the π-bonding resulted in longer Ti−O distances. This is corroborated by a much wider Ti−O−C angle in **1a** in the case of the terminal OPr^i ligand [mean Ti−O(3)−C(32) is 159.7(5)° against Ti−O-(4)−C(35) 128.7(3)° and Ti−O(5)−C(38) 130.9(3)°]. Similar structural features were reported for a titanium−sodium bimetallic complex.[11h] Interestingly, a closer inspection of the 3D structure of **1a** reveals close association of the hydrogen atom at C(7)of the EDBP ligand in the Ti empty coordination site, making the titanium acquire a distorted octahedral geometry in which the Ti····H(7A) distance is 2.550 Å and the C(7)−H(7A)−Ti angle is 132.2°. It could be argued that the EDBP ligand is rocked in a direction that would essentially increase the Ti···H agostic type of interaction. Such movement of hemilabile EDBP ligand could accommodate an incoming monomer for coordination to the Ti center.

Table 1. Polymerization of L-Lactide in Toluene (15 mL) Using Complexes **1a**−**1d** (0.05 mmol) as Initiators at 30 °C

entry	cat	[M]/ [cat]	time (h)	conv (%)[a]	M_n (calcd)[b]	M_n (obs)[c]	M_n (NMR)[d]	PDI
1	**1a**	150	94	74	5400	9100(5300)	5300	1.07
2	**1b**	150	94	80	5800	10600(6100)	6000	1.05
3	**1c**	100	0.5	91	6600	15200(8800)	6800	1.27
4	**1d**	100	3.5	89	6500	10800(6300)	6900	1.28
5[e]	**1d**	100	1.5	94	6800	13600(7900)	5900	1.18
6	**1e**	100	11	27	f	f	f	f
7	**1e**	100	94	76	5500	9300(5400)	5900	1.08

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA $\times$ $[M]_0/[O^iPr^-]_0$ $\times$ conversion yield + M_w(^{i}PrOH). [c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[19] [d] Obtained from ^{1}H NMR analysis. [e] The reaction temperature is 70 °C. [f] Not available.

Ring-Opening Polymerization of L-Lactide. Ring-opening polymerization of L-lactide initiated by bimetallic alkoxide complexes **1a**−**1e**, **2c**−**2d**, **3c**, and **4c**−**4d** were carried out in toluene at a range of temperatures of 30−70 °C, and the polymerization results are deposited in Tables 1 and 2. It is evidenced that the heterobimetallic complexes are stable in toluene within this temperature range and remain intact during the course of polymerization process. All complexes displayed high activities in ring-opening polymerization with narrow molecular weight distribution and great control of molecular weights. From the careful analysis of the polymerization, runs performed in Tables 1 and 2, several structure−activity trends can be drawn. Complexes **1a**−**1e** as initiator in toluene at 30 °C (Table 1, entries 1 and 2) show no difference in activity when replacing lithium **1a** with

Table 2. Polymerization of L-Lactide in Toluene (15 mL) Using Complexes **1c**, **1d**, **2c**, **2d**, **3c**, **4c**, **4d** (0.05 mmol) as Initiators

entry	ini	[M]/ [ini]	temp (°C)	time (h)	conv (%)[a]	M_n (calcd)[b]	M_n (obs)[c]	M_n (NMR)[d]	PDI
1	**1c**	100	30	0.25	27				
2	**1c**	100	30	0.5	91	6600	8800	6800	1.27
3	**1d**	100	70	1.5	94	6800	7900	5900	1.18
4	**1d**	100	30	3.5	89	6500	6300	6900	1.28
5	**1d**	100	50	1	56				
6	**2c**	50	30	0.5	89	3300	3600	3700	1.13
7	**2c**	100	30	0.5	94	6800	7800	7200	1.15
8	**2c**	150	30	0.5	94	10200	11400	10500	1.16
9	**2c**	200	30	0.5	95	13700	14800	14000	1.15
10	**2d**	100	30	1	13				
11	**2d**	50	50	1	85	3100	3900	3300	1.23
12	**2d**	100	50	1	92	6700	8700	6800	1.19
13	**2d**	150	50	1	91	9900	12200	10600	1.15
14	**2d**	200	50	1	91	13200	16200	13600	1.12
15	**3c**	100	30	0.25	5				
16	**3c**	100	30	0.5	94	3400	3800	3700	1.17
17	**4c**	100	30	0.25	93	6800	7700	7900	1.29
18	**4d**	100	30	1	32				
19	**4d**	100	50	0.5	47				
20	**4d**	100	50	1	95	6900	5000	5100	1.29

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA $\times$ $[M]_0/[O^iPr^-]_0$ $\times$ conversion yield + $M_w(^iPrOH)$. [c] Obtained from GPC analysis and calibrated by polystyrene standard.[19] [d] Obtained from ^{1}H NMR analysis.

sodium **1b**. In contrast, when the magnesium was introduced in place of lithium or sodium (Table 1 entries 1 and 2) in **1d**, the polymerization rate drastically enhanced (Table 1, entry 4). Remarkably faster reaction was noted when magnesium was replaced with zinc in complex **1c** (Table 1, entry 3). This is probably due to the difference in electronic configurations and charge density of zinc and magnesium, which controls the interactions and electron transfer process in the formation of the metal−lactide complexes. It is known that the charge density of magnesium is higher than that of zinc, resulting in a stronger Mg−OR bond and therefore making it more difficult to cleave the Mg−O bond causing decrease in the polymerization rate and resulting in longer reaction time.

Expected molecular weights (M_n) of the polymer obtained from GPC analysis calibrated by polystyrene standard for all the entries in Table 1. Similarly, molecular weights M_n(NMR) of the polymers were obtained from the ^{1}H NMR data analysis by integrating methine and methyl signals of the polymer chain end-capped with an isopropyl ester group.[19] The obtained M_n(NMR) showed good agreement with the calculated M_n(calcd) and M_n(obs). By analysis of the ROP results of the bimetallic complexes **1a**−**1e** in Table 1, we found that Ti−Zn or Ti−Mg mixed metal complexes are more effective in polymerization of L-LA in comparison to the bimetallic Ti−Li, Ti−Na or monometallic Ti complexes. Polymerization of L-lactide using complexes **2c**, **2d**, **3c**, **4c**, and **4d** as an initiator was systematically investigated in toluene (Table 2). In the case of the complex **2c**, the polymerization completed within 30 min at 30 °C. On the basis of the molecular weight of poly(L-lactide) (PLLA) and $[LA]_0/[\mathbf{2c}]$ ratio, we believed that two of these four $^iPrO^-$ groups could be involved in initiation. The linear increase in M_n with conversion and the low polydispersity index (PDI, M_w/M_n) of the polymers revealed controlled nature of polymerization (Figure 2). The ^{1}H NMR spectrum of PLLA (Figure 3) indicated that the polymer chain is capped with one isopropyl ester and one hydroxyl end due to the insertion of an isopropyl alkoxy group into the lactide in PLLA. The integration of the methine and methyl protons of the isopropyl end-capped polyester reveals the molecular weight M_n(NMR) which has good agreement with the calculated molecular weights and GPC (M_n(obs)) analysis. The complex **2d** also polymerized L-lactide with molecular weight control and narrow molecular weight distribution, but the polymerization rate was slower than that of **2c**.

From entries 1, 5, 7, and 12 in Table 2, we found that the Ti−Zn and Ti−Mg complexes supported by the L^2-H_2 ligand were more effective than L^1-H_2. When the methyl was replaced with the methylphenylsulfonyl group, the reactivity of complexes **4c** or **4d** increased due to the high electron donor ability of the ligand (Table 2, entries 17 and 20). Summarized here from the results in Table 2, a prominent decrease in catalytic activity is found in the order **4c** > **2c** > **1c** > **3c** for Ti−Zn complexes and **4d** > **2d** > **1d** for Ti−Mg complexes, indicating that electron-donating substituents at the *ortho*-position are the advantage to the polymerization process.

The comparative ROP activity of the heterobimetallic complexes of Ti with the main group metal initiators shows the introduction of the Mg and zinc has enhanced the rate of the reaction to a large extent. The results showed Ti−Zn isopropoxide systems are quite comparable to the BDI (2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene) supported Coates Zn-isopropoxide initiators in terms of rate and conversion.[20] The rate of the reaction of L-LA using Ti−Mg and Ti−Zn complexes was slower than the highly active homobimetallic Mg and Zn initiators supported by Schiff base ligands.[7h,21,6d,21,22] The ROP of the L-LA using isopropoxy bridged heterobimetallic Ti−Li complexes was very slow for a 70−80% conversion. However, lithium forms dimeric complexes supported by the bis(phenolate) ligand which are more active for the ROP of lactide.[10e]

Kinetic Studies of Polymerization of L-Lactide by 2c. Kinetic studies were performed to establish the reaction order with respect to monomer and initiator for the polymerization of L-lactide using **2c**. Conversion of L-lactide ([LA] = 0.167 M in 10 mL of toluene) with time was monitored by ^{1}H NMR for various concentrations of **2c** ([**2c**] = 3.33, 2.57, and 2.09 mM, respectively) at 30 °C. Plots of $\ln[LA]_0 - \ln[LA]$ vs time for a wide range of [**2c**] were linear as shown in Figure 4a, indicating the first-order dependence on monomer concentration. Thus, the rate expression can be written as $-d[LA]/dt = k_{obs}[LA]^1 = k[\mathbf{2c}]^x[LA]^1$, where $k_{obs} = k[\mathbf{2c}]^x$ and k = polymerization rate constant. A plot of $\ln(k_{obs})$ vs $\ln[\mathbf{2c}]$ (Figure 4b) allows

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[19] M_n(GPC) is multiplied by a factor of 0.58, giving the actual M_n of poly(lactide). Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325–333.

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[21] Wu, J.; Huang., B.-H.; Hsueh, M.-L.; Lai, S.-L.; Lin, C.-C. *Polymer* **2005**, *46*, 9784–9792.

[22] Hung, W.-C.; Lin, C.-C. *Inorg. Chem.* **2009**, *48*, 728–734.

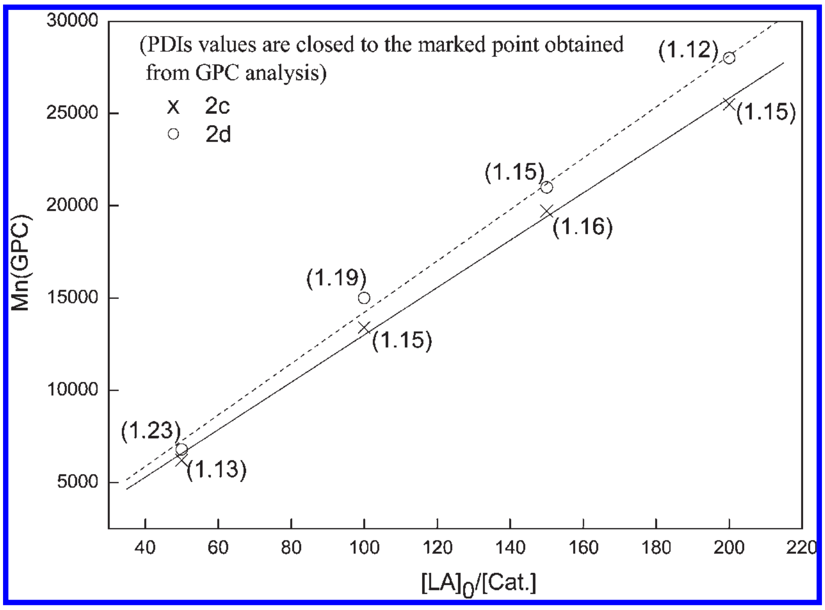

Figure 2. Plot of M_n(GPC) vs [LA]/[**2c**] and [LA]/[**2d**]. The values in parentheses are PDI values obtained from GPC analysis.

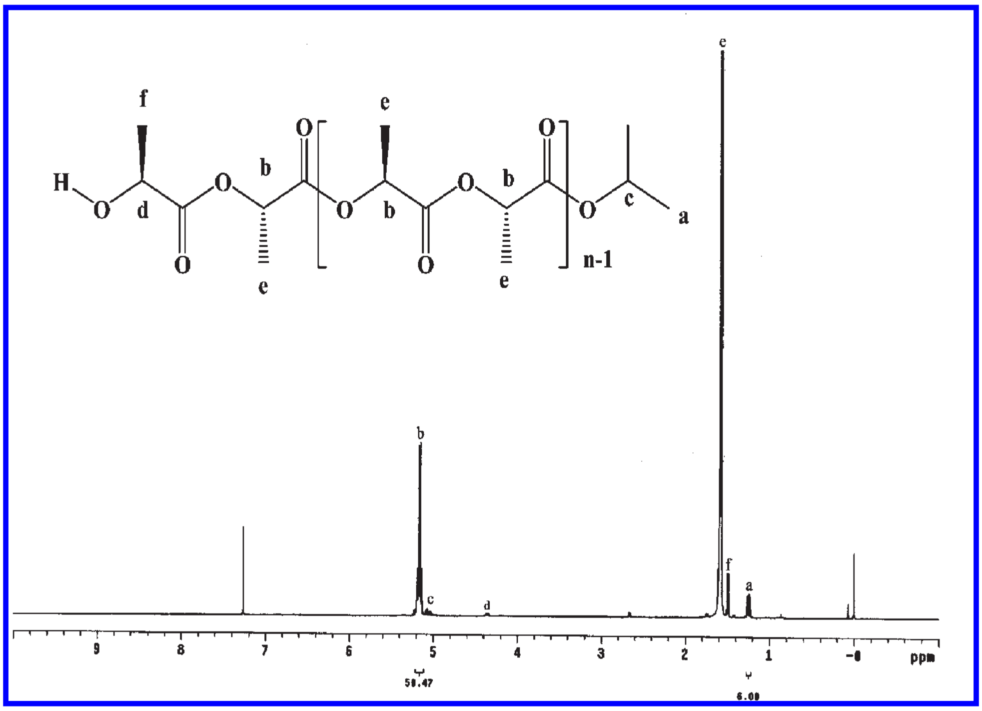

Figure 3. ^{1}H NMR spectrum of PLLA-50 (50 indicates $[LA]_0/[\mathbf{2c}]_0 = 50$).

the determination of k and x (the order in [**2c**] concentration). From the calculation of the y-intercept of the regression line, polymerization rate constant k is calculated to be 81.64 M^{-1} min^{-1}. The slope (x) of the fitted line calculated to be one nearest whole number and thus the reaction is first order in catalyst **2c** suggesting that one molecule is involved in the transition state for the propagation event.

Thus, the overall rate expression is $-d[LA]/dt = k[LA]^1[\mathbf{2c}]^1$. Also from Figure 4, we found that the reaction was at rest in initial 10 min, and then, polymerization started quickly. This may be due to the formation of a new active species by the mixing of catalyst with LA which needs a certain time to develop, and the process can be monitored by the ^{1}H NMR studies. We recorded the ^{1}H NMR of the mixture of **2c** and LA from 10 to 60 min at regular intervals at 30 °C and a stack plot of the spectra is shown in Figure 5. It is interesting to note that the rate law $-d[LA]/dt = k[LA]^1[\mathbf{2c}]^1$ is in good agreement with the previously described Mg and Zn-dimeric initiators reported by us.[7d,e,8]

A slow polymerization rate with long reaction time (from 4 to 15 h) was reported for the well-defined titanium alkoxide initiators.[23] Less than 50% conversion of L-LA to PLA using $Ti(O\text{-}i\text{-}Pr)_4$, $TiCl(O\text{-}i\text{-}Pr)_3$, $TiCl_2(O\text{-}i\text{-}Pr)_2$,

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(23) Kim, Y; Janeshwara, G. K.; Verkade, G. *Inorg. Chem.* **2003**, *42*, 1437–1447.

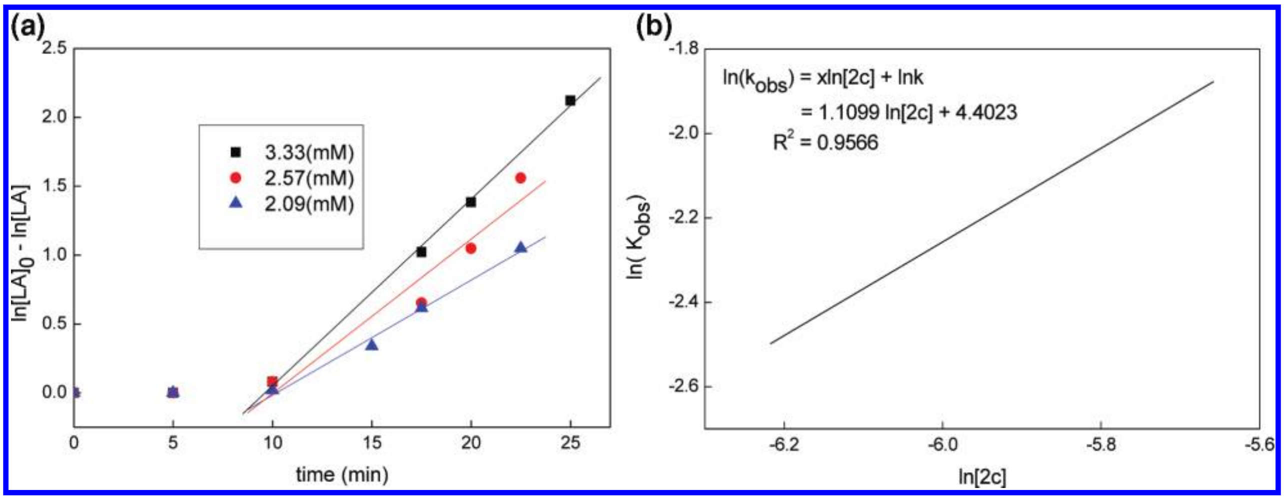

Figure 4. (a) First-order kinetic plots for L-lactide polymerizations with time in toluene with different concentration of [**2c**] as an initiator. (b) Linear plot of ln k_{obs} vs ln[**2c**] with $[LA]_0 = 0.167$ M in toluene.

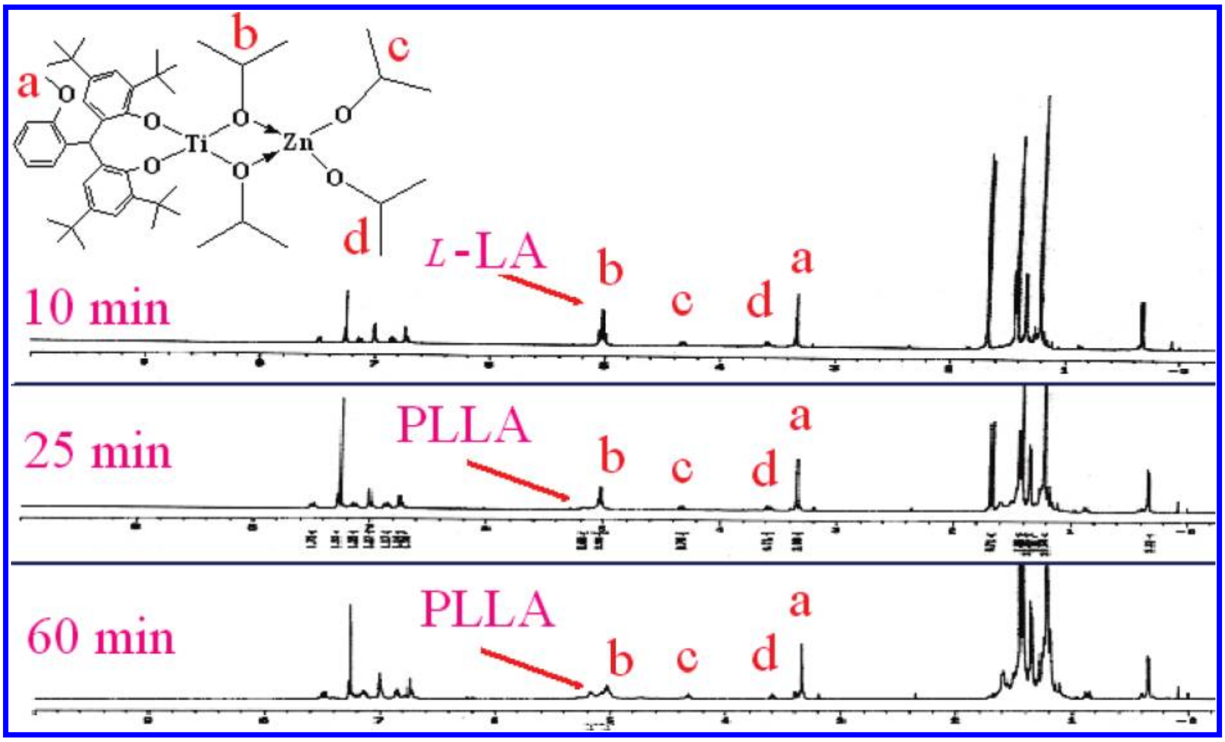

Figure 5. ^{1}H NMR spectrum of a mixture of LA and **2c** in $CDCl_3$ with time.

and $TiCl_3$(O-*i*-Pr) as initiator requires 30 min at 130 °C. In our systems, a dramatic increase in ROP reactivity is observed when zinc or magnesium is introduced in bimetallic Ti−Zn and Ti−Mg (**1c**, **1d**) at room temperature. Comparatively, a slow conversion rate of L-LA to PLA using bimetallic Ti−Li/Na complexes (**1a**, **1b**) is recorded which resembles the conversion rate for the bis(phenolate) ligand supported Li and Na alkoxides with aggregates as initiators.[10e,18,24] Coates and co-workers previously reported remarkable reactivity of the well-defined Zn(O-*i*-Pr) complexes for the ROP of lactide.[19] Similarly, we observed the notable enhancement of the rate of reaction on introduction of Zn in titanium based heterobimetallic initiators. Similarly, Okuda and co-workers have reported that yttrium−lithium heterometallic complexes are efficient initiators for the ROP of L-lactide and ε-caprolatone where a mechanism similar to radical chain polymerization is tentatively assumed based on the kinetic results.[25]

Conclusion

In conclusion, we have synthesized a series of bisphenol ligands (L^1-H_2~L^4-H_2) and their titanium-based heterobimetallic complexes. These complexes all show good activities for the controlled ring-opening polymerization of L-lactide.

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(24) Huang, B.-H.; Ko, B.-T.; Athar, T.; Lin, C.-C. *Inorg. Chem.* **2006**, *45*, 7348–7356.

(25) (a) Hultzsch, K. C.; Okuda, J. *Macromol. Rapid Commun.* **1997**, *18*, 809–815. (b) Beckerle, K.; Hultzsch, K. C.; Okuda, J. *Macromol. Chem. Phys.* **1999**, *200*, 1702–1707.

Among this series of bimetallic complexes, Ti−Zn and Ti−Mg systems have demonstrated high activities toward the controlled polymerization of LA as compared with the other titanium initiators reported in the literature. This is probably a convenient synthetic strategy to increase the ROP ability of titanium based complexes. Furthermore, complexes with ligands bearing electron donating groups such as L^2-H_2 or L^4-H_2 show significantly higher activities than others because these ligands stabilize higher oxidation states of titanium. We have also found that the polymerization reaction proceeds with first-order rate dependence on both the monomer and initiator concentrations. Mechanistic studies of polymerization in order to elucidate the role of the metals are continued in our laboratories.

Experimental Section

General Conditions. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, L-lactide, and deuterated solvents were purified before used. 2, 2′-Ethylidenebis (4,6-di-*tert*-butylphenol), 2,4-di-*tert*-butylphenol, 2-methoxybenzaldehyde, 4-chloro-2-isopropyl-5-methylphenol, formaldehyde, 2-hydroxybenzaldehyde, and 4-methylbenzene-1-sulfonyl chloride were purchased and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury-400 spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Postnova PN1122 solvent delivery system with TriSEC GPC software using THF (HPLC grade) as an eluent. Molecular weight and molecular weight distributions were calculated using polystyrene as the standard. 2, 2′-Methylenebis (4-chloro-6-isopropyl-3-methylphenol) (L^3-H_2)[5d] were prepared by acid-catalyzed condensation following literature procedures.

Synthesis of 6,6′-((2-Methoxyphenyl)methylene)bis(2,4-di-*tert*-butylphenol) (L_2-H_2). A mixture of 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol), *o*-anisaldehyde (1.45 mL, 10 mmol), and benzenesulfonic acid (0.40 mL) in hexane (50 mL) was refluxed for 30 h. After neutralization with aqueous NaOH solution (0.1 N, 20 mL), the organic layer was extracted with water (30 mL) twice. The hexane layer was then dried over $MgSO_4$ and concentrated to 15 mL. White crystalline solids were obtained after 2 days at −20 °C. Yield: 3.97 g (75%). Anal calcd for $C_{36}H_{50}O_3$: C, 81.46; H, 9.49%. Found: C, 81.16; H, 9.74%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.31−6.71 (8H, m, Ph-*H*), 5.92 (1H, s, C*H*), 4.95 (2H, br, O*H*), 3.80 (3H, s, OC*H*$_3$), 1.37 (18H, s, C(C*H*$_3$)$_3$), 1.16 (18H, s, C(C*H*$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 156.78, 150.70, 142.28, 136.50, 130.46, 128.65, 128.63, 126.96, 123.96, 122.80, 121.19, 110.92 (*Ph*), 55.75 (O*C*H$_3$), 39.66, 31.52 (*C*(CH$_3$)$_3$), 34.98, 34.29 (C(*C*H$_3$)$_3$), 29.84 (*C*H). Mp: 152−154 °C.

Synthesis of 2-(Bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)methyl)-phenyl-4-methyl Benzenesulfonate (L^4-H_2). Triethylamine (40 mL) was added to a rapidly stirred solution of 2-hydroxybenzaldehyde (12.20 g, 100 mmol) in 40 mL of CH_2Cl_2. The mixture was cooled to 0 °C, and a solution of 4-methylbenzene sulfonyl chloride (19.0 g, 100 mmol) in 20 mL of CH_2Cl_2 was added dropwise over 20 min. After the addition was complete, the mixture was allowed to warm to room temperature and stirred overnight. The resulting solution was washed with water (60 mL) three times, and the solvent was removed at reduced pressure. 2-Formylphenyl-4-methylbenzenesulfonate was isolated in 95% yield (26.22 g, 95 mmol). Then, a mixture of 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol), 2-formylphenyl-4-methylbenzenesulfonate (2.76 g, 10 mmol), and benzenesulfonic acid (0.40 mL) in toluene (30 mL) was refluxed for 12 h. After neutralization with aqueous NaOH solution (0.1 N, 20 mL), the organic layer was extracted with water (30 mL) twice. The toluene layer was then dried over $MgSO_4$ and concentrated to 10 mL. White crystalline solids were obtained after 3 days at −20 °C. Yield: 4.69 g (70%). Anal calcd for $C_{42}H_{54}O_5S$: C, 75.19; H, 8.11%. Found: C, 74.60; H, 7.90%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.87 (2H, d, *J* = 7.6 Hz, *o*-SPh-*H*), 7.34 (2H, d, *J* = 8.0 Hz, *m*-SPh-*H*), 7.28 (4H, br, HOPh-*H* + 2,4-SOPh-*H*), 7.08 (1H, br, 3-SOPh-*H*), 7.00 (1H, br, 1-SOPh-*H*), 6.50 (2H, s, HOPh-*H*), 6.11 (1H, s, *H*CPh$_3$), 5.23 (2H, s, *H*OPh), 2.45 (3H, s, PhC*H*$_3$), 1.44 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.16 (18H, s, *p*-C(CH$_3$)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.36, 147.38, 145.64, 142.17, 136.64, 135.74, 132.51, 130.69, 129.89, 128.52, 128.43, 127.52, 126.23, 124.24, 122.83, 122.76 (*Ph*); 40.18 (*C*HPh$_3$), 34.95 (*p*- Ph*C*(CH$_3$)$_3$), 34.17 (*o*-Ph*C*-(CH$_3$)$_3$), 31.38 (*o*-PhC(*C*H$_3$)$_3$), 29.87 (*p*-PhC(*C*H$_3$)$_3$), 21.65 (Ph*C*H$_3$).

Synthesis of [$L^1Ti(\mu_2$-$O^iPr)_2(O^iPr)Li(THF)_2$] (1a). ^{n}BuLi (4.4 mL, 2.5 M in hexane, 11.0 mmol) was added slowly to an ice cold (0 °C) solution of L^1-H_2 (4.386 g, 10.0 mmol) in THF (40 mL). The mixture was stirred for 3 h, and then titanium(IV) isopropoxide (2.84 g, 10.00 mmol) was added and stirred for 12 h at room temperature. Volatile materials were removed under vacuum to yield a red oil. The oil was washed with hexane (30 mL), and a light yellow powder was obtained after filtration. Yield: 4.69 g (58%). Anal calcd for $C_{47}H_{81}LiO_7Ti$: C, 69.44; H, 10.04%. Found: C, 69.81; H, 10.06%. ^{1}H NMR (C_6D_6, ppm): δ 7.48, 7.30 (4H, s, Ph-*H*), 5.11 (2H, m, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.72 (1H, q, *J* = 6.8 Hz, PhC*H*(CH$_3$)Ph), 3.37 (8H, t, *J* = 4.8 Hz, O(C*H*$_2$CH$_2$)$_2$), 1.98 (3H, d, *J* = 6.8 Hz, PhCH(C*H*$_3$)Ph), 1.72, (18H, s, PhC(C*H*$_3$)$_3$), 1.38 (26H, br, O(CH$_2$C*H*$_2$)$_2$ + PhC-(C*H*$_3$)$_3$), 1.28 (12H, d, *J* = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, ppm): δ 161.15, 137.55, 137.07, 121.38, 120.46, 120.24, (*Ph*), 73.23 (O*C*H(CH$_3$)$_2$), 67.99 (O(*C*H$_2$CH$_2$)$_2$), 36.41 (Ph*C*H(CH$_3$)Ph), 35.64 (*p*-Ph*C*(CH$_3$)$_3$), 34.53 (*o*-Ph*C*(CH$_3$)$_3$), 32.07 (OCH(*C*H$_3$)$_2$), 30.60 (O(CH$_2$*C*H$_2$)$_2$), 27.27 (*p*-PhC-(*C*H$_3$)$_3$), 26.60 (PhCH(*C*H$_3$)Ph), 25.48 (*o*-PhC(*C*H$_3$)$_3$). Mp: 173−174 °C.

Synthesis of [$L^1Ti(\mu_2$-$O^iPr)_2(O^iPr)Na(THF)_2$] (1b). A mixture of L^1-H_2 (4.386 g, 10.0 mmol) and NaH (5.00 g, 60%, 11.0 mmol) was stirred in a mixed solvent of THF (40 mL) at room temperature for 3 h. Residual NaH was removed by filtration and then titanium(IV) isopropoxide (2.84 g, 10.00 mmol) was added to be stirred for 12 h at room temperature. Volatile materials were removed under vacuum to yield red solid. The solid was washed with hexane (30 mL) and a yellow powder was obtained after filtration. Yield: 2.50 g (30%). Anal calcd for $C_{47}H_{81}NaO_7Ti$: C, 68.09; H, 9.85%. Found: C, 68.92; H, 9.62%. ^{1}H NMR (C_6D_6, ppm): δ 7.46, 7.28 (4H, s, Ph-*H*), 5.11 (3H, q, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.74 (1H, q, *J* = 6.8 Hz, PhC*H*(CH$_3$)Ph), 3.38 (8H, t, *J* = 5.2 Hz, O(C*H*$_2$CH$_2$)$_2$), 1.97 (3H, d, *J* = 6.8 Hz, PhCH(C*H*$_3$)Ph), 1.72, (18H, s, PhC(C*H*$_3$)$_3$), 1.38 (18H, s, PhC-(C*H*$_3$)$_3$), 1.30 (8H, m, *J* = 5.2 Hz, O(CH$_2$C*H*$_2$)$_2$), 1.25 (12H, d, *J* = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, ppm): δ 161.17, 138.62, 137.04, 121.348, 120.43, 120.22, (*Ph*), 73.24 (O*C*H(CH$_3$)$_2$), 68.02 (O(*C*H$_2$CH$_2$)$_2$), 35.80 (Ph*C*H(CH$_3$)Ph), 35.63 (*p*-Ph*C*(CH$_3$)$_3$), 34.53 (*o*-Ph*C*CH$_3$), 32.08 (OCH(*C*H$_3$)$_2$), 30.80 (O(CH$_2$*C*H$_2$)$_2$), 27.25 (*p*-PhC(*C*H$_3$)$_3$), 26.61 (PhCH(*C*H$_3$)Ph), 25.48 (*o*-PhC-(*C*H$_3$)$_3$). Mp: 178−179 °C.

Synthesis of [$L^1Ti(\mu_2$-$O^iPr)_2Zn(O^iPr)_2$] (1c). A diethylzinc solution (5.5 mL, 1.0 M in hexane, 5.50 mmol) was added slowly to an ice cold solution (0 °C) of L^1-H_2 (2.193 g, 5.00 mmol) in THF (40 mL). The mixture was stirred for 3 h at room temperature and then titanium(IV) isopropoxide (1.42 g, 5.00 mmol) was added and stirred for 12 h at room temperature. Volatile materials were removed under vacuum to yield an orange red solid. The solid was washed with hexane (40 mL), and a yellow powder was obtained after filtration. Yield: 2.59 g (66%). Anal calcd for $C_{42}H_{72}O_6TiZn$: C, 64.16; H, 9.23%. Found: C, 64.26; H, 8.84%. ^{1}H NMR ($CDCl_3$, ppm): δ 7.28−7.01 (4H, m, Ph-*H*), 4.90 (1H, q, *J* = 6 Hz, PhC*H*-(CH$_3$)Ph), 4.86 (2H, m, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.34 (2H, m, *J* = 6 Hz, OC*H’*(CH$_3$)$_2$), 1.62 (3H, d, *J* = 6 Hz, PhCH(C*H*$_3$)Ph), 1.41, 1.27 (36H, s, PhC(C*H*$_3$)$_3$), 1.44 (6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 1.29 (12H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 0.76(6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 160.55, 141.59, 136.19, 133.89, 120.82, 120.27 (*Ph*), 79.84, 71.85 (O*C*H(CH$_3$)$_2$), 66.74 (Ph*C*H(CH$_3$)Ph), 35.26, 34.43 (Ph*C*(CH$_3$)$_3$), 31.66, 30.52 (PhC(*C*H$_3$)$_3$), 29.31 (PhCH(*C*H$_3$)Ph), 27.18, 25.33, 21.56 (OCH(*C*H$_3$)$_2$). Mp: 170−172 °C.

Synthesis of [L^{1}Ti(μ_2-O^{i}Pr)$_2$Mg(O^{i}Pr)$_2$] (1d). To an ice cold solution (0 °C) of L^1-H$_2$ (2.193 g, 5.0 mmol) in THF (40 mL) was slowly added a Mg^{n}Bu$_2$ (5.50 mL, 1.0 M in heptane, 5.50 mmol) solution. The mixture was stirred for 3 h at room temperature and then titanium(IV) isopropoxide (1.42 g, 5.00 mmol) was added and stirred for 12 h at room temperature. Volatile materials were removed under vacuum to yield an orange yellow solid. The solid was washed with hexane (40 mL), and an orange powder was obtained after filtration. Yield: 2.01 g (54%). Anal calcd for C$_{42}$H$_{72}$O$_6$TiMg: C, 67.69; H, 9.74%. Found: C, 67.63; H, 9.64%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.34−7.04 (4H, m, Ph-*H*), 4.96 (1H, q, J = 6 Hz, PhC*H*(CH$_3$)Ph), 4.82 (2H, m, J = 6 Hz, OC*H*(CH$_3$)$_2$), 4.19 (2H, m, J = 6 Hz, OC*H′*(CH$_3$)$_2$), 1.62 (3H, d, J = 6 Hz, PhCH(C*H*$_3$)Ph), 1.41, 128 (36H, s, PhC(C*H*$_3$)$_3$), 1.38 (6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 1.31 (12H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 0.63(6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 160.80, 141.66, 135.55, 133.73, 120.97, 120.27 (*Ph*), 79.57, 70.94 (O*C*H(CH$_3$)$_2$), 63.51 (Ph*C*H(CH$_3$)Ph), 35.26, 34.43 (Ph*C*(CH$_3$)$_3$), 31.66, 30.56 (PhC(*C*H$_3$)$_3$), 29.59 (PhCH(*C*H$_3$)Ph), 27.16, 25.13, 21.94 (OCH(*C*H$_3$)$_2$). Mp: 182−184 °C.

Synthesis of [L^{1}Ti(O^{i}Pr)$_2$] (1e). **1e** were prepared by the reaction of L^1-H$_2$ and titanium(IV) isopropoxide following literature procedures.[6a]

Synthesis of [L^{2}Ti(μ_2-O^{i}Pr)$_2$Zn(O^{i}Pr)$_2$] (2c). The procedures are similar to that for **1c** with L^2-H$_2$ (2.654 g, 5.00 mmol) being used. Yield: 2.39 g (54%). Anal calcd for C$_{48}$H$_{76}$O$_7$TiZn: C, 65.63; H, 8.72%. Found: C, 65.60; H, 8.72%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.50−6.72 (8H, m, Ph-*H*), 6.74 (1H, s, PhC*H*Ph), 5.02 (2H, m, J = 6 Hz, OC*H*(CH$_3$)$_2$), 4.31 (1H, m, J = 6 Hz, OC*H*(CH$_3$)$_2$), 3.57 (1H, m, J = 6 Hz, OC*H*(CH$_3$)$_2$), 3.34 (3H, s, OC*H*$_3$), 1.41, 1.22 (36H, s, PhC(C*H*$_3$)$_3$), 1.46 (6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 1.34 (12H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 0.33 (6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 162.19, 158.30, 140.94, 134.59, 133.06, 131.52, 128.81, 126.48, 124.48, 119.49, 119.29, 111.44 (*Ph*), 78.87, 72.36, 66.71 (O*C*H(CH$_3$)$_2$), 55.12 (O*C*H$_3$), 35.25 (Ph*C*HPh), 36.01, 34.25 (Ph*C*(CH$_3$)$_3$), 31.63, 30.74 (PhC(*C*H$_3$)$_3$), 29.49, 27.13, 24.69 (OCH(*C*H$_3$)$_2$). Mp: 214−216 °C.

Synthesis of [L^{2}Ti(μ_2-O^{i}Pr)$_2$Mg(O^{i}Pr)$_2$] (2d). The procedures are similar to that for **1d** with L^2-H$_2$ (2.654 g, 5.00 mmol) being used. Yield: 2.18 g (52%). Anal calcd for C$_{48}$H$_{76}$O$_7$TiMg: C, 68.86; H, 9.15%. Found: C, 68.38; H, 8.73%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.50−6.72 (8H, m, Ph-*H*), 6.77 (1H, s, PhC*H*Ph), 4.99 (2H, m, J = 6 Hz, OC*H*(CH$_3$)$_2$), 4.20 (1H, m, J = 6 Hz, OC*H′*(CH$_3$)$_2$), 3.47 (1H, m, J = 6 Hz, OC*H″*(CH$_3$)$_2$), 3.34 (3H, s, OC*H*$_3$), 1.41, 1.22 (36H, s, PhC(C*H*$_3$)$_3$), 1.37 (6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 1.35 (12H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$), 0.31(6H, d, J = 6 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 162.40, 158.37, 140.99, 134.71, 133.04, 131.52, 128.84, 126.51, 124.52, 119.53, 119.32, 115.53 (*Ph*), 78.76, 71.38, 63.49 (O*C*H(CH$_3$)$_2$), 55.11 (O*C*H$_3$), 35.26 (Ph*C*HPh), 36.12, 34.27 (Ph*C*(CH$_3$)$_3$), 31.64, 30.81 (PhC(*C*H$_3$)$_3$), 29.71, 27.17, 24.72 (OCH(*C*H$_3$)$_2$). Mp: 214−216 °C.

Synthesis of [L^{3}Ti(μ_2-O^{i}Pr)$_2$Zn(O^{i}Pr)$_2$] (3c). The procedures are similar to that for **1c** with L^3-H$_2$ (3.814 g, 10.00 mmol) being used. Yield: 5.15 g (71%). Anal calcd for C$_{33}$H$_{52}$Cl$_2$O$_6$TiZn: C, 54.37; H, 7.19%. Found: C, 54.21; H, 7.19%. ^{1}H NMR (CDCl$_3$, ppm): δ 6.99 (2H, s, Ph-*H*), 4.93 (1H, m, J = 6.8 Hz, OC*H*(CH$_3$)$_2$), 4.55 (2H, m, J = 6.4 Hz, OC*H*(CH$_3$)$_2$), 4.25 (1H, m, J = 6.8 Hz, OC*H*(CH$_3$)$_2$), 4.17 (1H, d, J = 15 Hz, PhC*H*H'Ph), 3.70 (1H, d, J = 15 Hz, PhCH*H'*Ph), 3.41 (2H, q, J = 6 Hz, PhC*H*(CH$_3$)$_2$), 2.33 (6H, s, PhC*H*$_3$), 1.31 (6H, d, J = 6 Hz, PhCH(C*H*$_3$)$_2$), 1.26 (6H, d, J = 6 Hz, PhCH(C*H*$_3$)$_2$), 1.16 (12H, J = 6.4 Hz, OCH(C*H*$_3$)$_2$), 1.15 (12H, d, J = 6.8 Hz, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 161.67, 134.34, 131.59, 130.93, 125.50, 123.63 (*Ph*), 71.30, 66.82 (O*C*H(CH$_3$)$_2$), 28.78, 28.12 (OCH(*C*H$_3$)$_2$), 26.86, 26.76 (Ph*C*H(CH$_3$)$_2$), 25.71 (Ph*C*H$_2$Ph), 23.15, 22.90 (PhCH(*C*H$_3$)$_2$), 17.34 (Ph*C*H$_3$). Mp: 204−206 °C.

Synthesis of [L^{4}Ti(μ_2-O^{i}Pr)$_2$Zn(O^{i}Pr)$_2$] (4c). The procedures are similar to that for **1c** with L^4-H$_2$ (6.700 g, 10.00 mmol) being used. Yield: 8.12 g (80%). Anal calcd for C$_{54}$H$_{80}$O$_9$STiZn: C, 63.68; H, 7.92%. Found: C, 62.39; H, 7.15%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.52 (2H, d, J = 7.2 Hz, *o*-SPh-*H*), 7.26−6.92 (10H, m, Ph-*H*), 5.14 (1H, m, OC*H*(CH$_3$)$_2$), 5.08 (1H, br, *H*CPh$_3$), 4.35 (1H, m, OC*H*(CH$_3$)$_2$), 4.03 (1H, m, OC*H*(CH$_3$)$_2$), 3.49 (1H, m, OC*H*(CH$_3$)$_2$), 2.37 (3H, s, PhC*H*$_3$), 1.47 (18H, s, *o*-C(C*H*$_3$)$_3$), 1.38 (12H, d, J = 3.2, OCH(C*H*$_3$)$_2$), 1.20 (18H, s, *p*-C(CH$_3$)$_3$), 0.86 (6H, br, OCH(C*H*$_3$)$_2$), 0.30 (6H, d, J = 6.0, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 162.53, 149.90, 143.82, 141.07, 135.62, 134.25, 134.05, 130.75, 130.31, 129.45, 127.99, 126.65, 124.67, 123.95, 120.25, 117.29 (Ph), 78.83, 72.79, 66.78 (O*C*H(CH$_3$)$_2$), 36.31 (*C*HPh$_3$), 35.37 (*p*- Ph*C*(CH$_3$)$_3$), 34.26 (*o*-Ph*C*(CH$_3$)$_3$), 31.59 (*o*-PhC(*C*H$_3$)$_3$), 30.93 (*p*-PhC(*C*H$_3$)$_3$), 29.51, 27.22, 26.99, 24.64, 22.63, 21.49, 14.07 (OCH(*C*H$_3$)$_2$). Mp: 220−221 °C.

Synthesis of [L^{4}Ti(μ_2-O^{i}Pr)$_2$Mg(O^{i}Pr)$_2$] (4d). The procedures are similar to that for **1d** with L^4-H$_2$ (6.700 g, 10.00 mmol) being used. Yield: 2.83 g (29%). ^{1}H NMR (CDCl$_3$, ppm): δ 7.52 (2H, br, *o*-SPh-*H*), 7.25−6.94 (10H, m, Ph-*H*), 5.10 (1H, br, OC*H*(CH$_3$)$_2$), 5.07 (1H, br, *H*CPh$_3$), 4.25 (1H, br, OC*H*(CH$_3$)$_2$), 4.11 (1H, br, OC*H*(CH$_3$)$_2$), 3.41 (1H, br, OC*H*(CH$_3$)$_2$), 2.34 (3H, s, PhC*H*$_3$), 1.45 (24H, s, *o*-C(C*H*$_3$)$_3$), 1.42 (6H, br, OCH(C*H*$_3$)$_2$), 1.28 (6H, br, OCH(C*H*$_3$)$_2$), 1.22 (18H, s, *p*-C(CH$_3$)$_3$), 0.89 (6H, br, OCH(C*H*$_3$)$_2$), 0.31 (6H, br, OCH(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, ppm): δ 162.66, 149.90, 143.79, 141.05, 135.62, 134.32, 133.98, 130.74, 130.25, 129.43, 127.97, 126.62, 124.67, 123.92, 120.25, 117.24 (Ph), 78.65, 71.67, 63.50, 63.28 (O*C*H(CH$_3$)$_2$), 35.34 (*p*-Ph*C*(CH$_3$)$_3$), 34.24 (*o*-Ph*C*(CH$_3$)$_3$), 31.58 (*o*-PhC(*C*H$_3$)$_3$), 30.94 (*p*-PhC(*C*H$_3$)$_3$), 30.45 (*C*HPh$_3$) 29.69, 29.02, 27.20, 26.99, 24.64, 22.62, 21.47, 14.05 (OCH(*C*H$_3$)$_2$). Mp: 220−221 °C.

Typical Polymerization Procedure. A typical polymerization procedure was exemplified by the synthesis of PLA-100 using **2c** as an initiator at 30 °C. The conversion yield (95%) of PLA was analyzed by ^{1}H NMR spectroscopic studies. A mixture of **2c** (0.0439 g, 0.05 mmol) and L-lactide (1.44 g, 10 mmol) in toluene (15 mL) was stirred at 30 °C for 30 min. Volatile materials were removed in vacuo, and the residue was redissoved in THF (10 mL). The mixture was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL), and the polymer was precipitated on pouring into *n*-hexane (40 mL) to give a white crystalline solid. Yield: 1.04 g (72%).

X-ray Crystallographic Studies. Suitable crystals for X-ray structural determination were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[26] The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[27] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used

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(26) Sheldrick, G. M. *SADABS*; University of Gottingen: Gottingen, Germany, 1998.

(27) Sheldrick, G., Sheldrick, G. M., *SHELXTL-Plus, NT Crystallographic System*, release 5.1; Bruker Analytical X-ray Systems: Madison, WI, 1998.

for H atoms. Due to the disorder of THF and the *t*-Bu group of the EDBP ligand, the bond lengths within THF and the *t*-Bu groups are not reliable.

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Supporting Information Available: Summary of X-ray crystallography data and crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.