Preparation, Characterization, and Catalytic Studies of Magnesium Phenoxides: Highly Active Initiators for Ring-Opening Polymerization of L-Lactide

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A series of sterically bulky phenols (**1a**−**f**; EDBP-*R*Ts-H = 2,4-di-*tert*-butyl-6-(1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)ethyl)phenyl benzenesulfonate) were synthesized. Their related *n*-butylmagnesium complexes [(μ-EDBP-*R*Ts)Mg^{n}Bu]$_2$ (**2a**−**f**) and magnesium alkoxides [(EDBP-*R*Ts)Mg(μ-OBn)]$_2$ (**3a**−**f**) were prepared and structurally characterized. In the presence of THF, coordination of [(EDBP-*R*Ts)Mg-(μ-OBn)]$_2$ (**3e**) with THF gave the pentacoordinated magnesium complex [(EDBP-*R*Ts)Mg(μ-OBn)(THF)]$_2$ (**4**). Crystal structures of **2a**−**c**,**e**, **3a**−**c**,**f**, and **4** have been determined. Experimental results show that magnesium alkoxides (**3a**−**f**) are very reactive initiators toward ROP of L-lactide, with a quantitative yield of polymer (1000 equiv) in less than 4 min.

Introduction

Over the past three decades, polylactide (PLA) has attracted considerable attention due to its wide applications in biomedical and pharmaceutical fields.[1] Though many strategies have been developed for the preparation of PLA, the most effective method to synthesize PLA is the ring-opening polymerization (ROP) of lactide. As a result, a variety of so-called single active site metal complexes coordinated with sterically bulky ligands such as β-diketiminate, salen, diol, etc., have been developed and used as catalytic/initiating systems for the ROP of lactide.[2] Metal complexes such as metal alkyls,[3] amides,[4] thiolates,[5] aryloxides,[6] and alkoxides[7] in the presence/absence of alcohol have been used as initiators. Among them, metal alkoxides with a single active site have proven to bear the highest activity along with good molecular weight controlled manner.

Recently, many lithium,[8] magnesium,[9] and aluminum[10] complexes coordinated with a variety of sterically bulky diols (L-H_2) have been developed as initiators for the ROP of lactide. These diols are potentially economically useful because they can be easily prepared and are rather cheap. Furthermore, magnesium is nontoxic and is essential for life;[11] thus, it has attracted considerable interest in terms of biomedical purposes.

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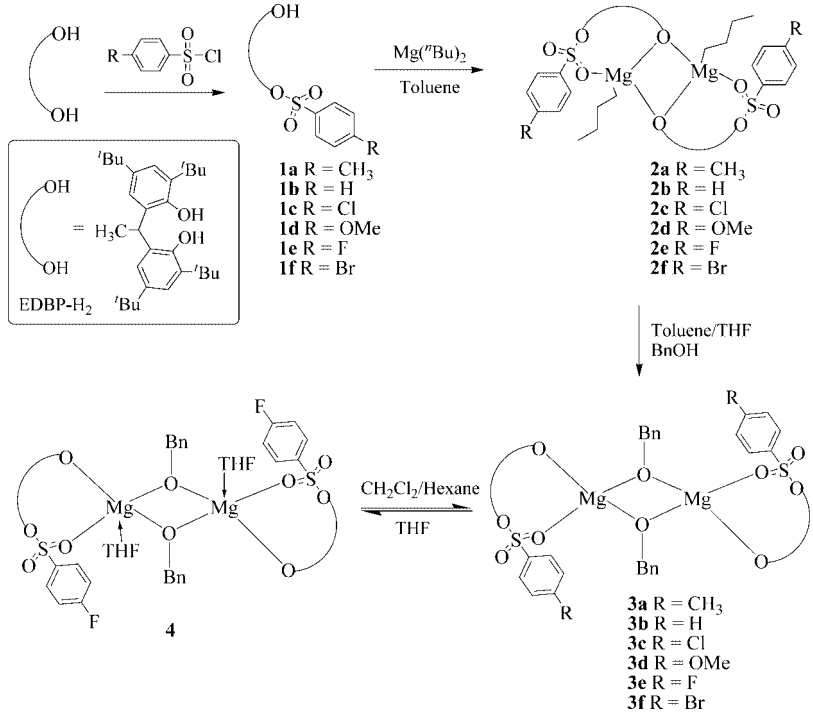
Scheme 1



However, these diols are divalent, making the activities of $[LMg(THF)]_2$ toward the ROP of lactides in the presence of alcohol relatively low. We report herein the preparation of a series of novel monovalent phenols derived from EDBP-H_2. The activity of their magnesium complexes is also presented.

Results and Discussion

Syntheses of Ligands and Complexes. A series of benzenesulfonate phenol derivatives (EDBP-*R*Ts-H, **1a**−**f**; EDBP-Ts-H = 2,4-di-*tert*-butyl-6-(1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)ethyl)phenyl benzenesulfonate) were prepared in an almost quantitative yield by the reaction of EDBP-H_2 (EDBP-H_2 = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)) with 1 molar equiv of the corresponding 4-substituted benzenesulfonyl chloride (*R*TsCl) in the presence of excess triethylamine, using dichloromethane as a solvent at room temperature (Scheme 1). These ligands, EDBP-*R*Ts-H, were easily purified by recrystallization from an acetonitrile or hexane solution. Further reaction of ligands **1a**−**f** with a stoichiometric amount of Mg^nBu_2 in toluene or hexane gave the tetracoordinated dimeric magnesium complexes $[(\mu\text{-EDBP-}R\text{Ts})Mg^nBu]_2$ (**2a**−**f**) in very high yields, respectively. All of these six ligands (**1a**−**f**) and their magnesium complexes (**2a**−**f**) were fully characterized. Unlike other magnesium alkyls, complexes **2a**−**f** remained rather stable toward heat even in a hot toluene solution. No disproportionation product $[(EDBP\text{-}R\text{Ts})_2Mg]$ was observed. However, a disproportionation reaction was found in many magnesium alkoxides and magnesium alkyl systems.[12] Treatment of the butylmagnesium complexes **2a**−**f** with 1 molar equiv of benzyl alcohol resulted in the release of *n*-butane along with the formation of the magnesium alkoxides **3a**−**f** in moderate to high isolated yields, respectively. These six magnesium alkoxides were also rather thermally stable. No disproportionation was detected, even in the refluxing toluene solution. All of these complexes could be purified using recrystallization from a hot toluene solution or from a mixed dichloromethane/hexane solution.

It is interesting to note that in the presence of THF, the coordination of THF to **3e** yielded the pentacoordinated magnesium complex **4**. However, no similar products were able to be isolated when compounds **3a**−**d**,**f** were recrystallized from THF. The reason for the difference is believed to be due to the high electron-withdrawing ability of the F group, decreasing the electron density of magnesium and therefore requiring an extra electron donor from THF.

X-ray Single-Crystal Structure Studies. Single crystals of **2a**−**c**,**e** suitable for X-ray structural determination were obtained by cooling hot hexane solutions. The ORTEP drawings of the molecular structures of **2a**−**c**,**e** are given in Figures 1−4, respectively. The molecular structures of these four *n*-butylmagnesium complexes are similar, with a dimeric character. The geometry around the magnesium atoms in **2a** is distorted tetrahedral, with coordination to two bridging phenolate oxygen atoms, one oxygen atom of the sulfonyl group, and a methylene carbon atom of the *n*-butyl group. The oxygen atom of the sulfonyl group is fixed firmly on the magnesium ion with an average Mg−O bond distance of 2.093(3) Å. The molecular structures of **2b**,**c**,**e** are all similar to that of **2a** with average Mg−O bond distances of 2.087(4), 2.103(3), and 2.105(2) Å for **2b**,**c**,**e**, respectively.

Single crystals of **3a**−**c**,**f** suitable for X-ray structure determination were obtained from mixed solutions of dichloromethane and hexane. The ORTEP drawings of **3a**−**c**,**f** are given in Figures 5−8. The molecular structures of these compounds show that all four of these magnesium benzyl alkoxides have dimeric features, bridging through the oxygen atoms of the benzyl alkoxy group with similar structures. The geometry around Mg is distorted tetrahedral, with coordination by an oxygen atom of the sulfonyl group, an oxygen atom of the phenoxy group, and two bridging oxygen atoms of the benzyl alkoxy groups. In these four dimeric structures, two magnesium atoms are bridged by two oxygen atoms of the benzyl alkoxy group instead of phenolate in *n*-butylmagnesium

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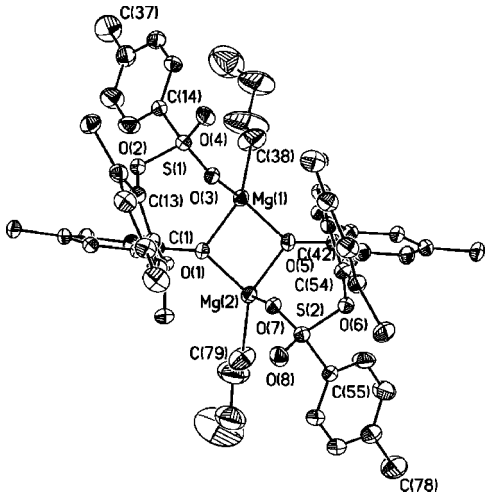


Figure 1. Molecular structure of **2a** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(5) = 1.980(3), Mg(1)−O(1) = 2.013(3), Mg(1)−O(3) = 2.097(3), Mg(1)−C(38) = 2.110(5), Mg(2)−O(1) = 1.968(2), Mg(2)−O(5) = 2.010(3), Mg(2)−O(7) = 2.088(3), Mg(2)−C(79) = 2.123(5); O(5)−Mg(1)−O(1) = 82.41(10), O(1)−Mg(1)−O(3) = 88.23(10), O(1)−Mg(2)−O(5) = 82.77(10), Mg(1)−O(1)−Mg(2) = 97.44(11), Mg(1)−O(5)−Mg(2) = 97.17(11).

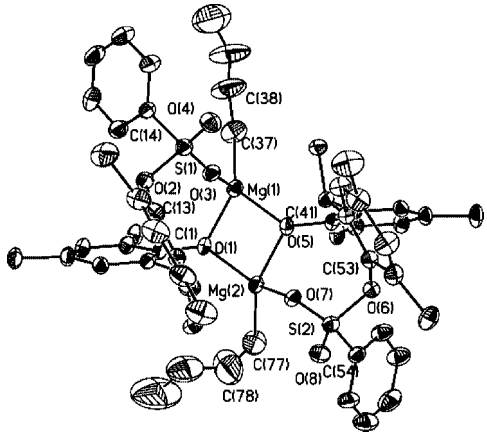


Figure 2. Molecular structure of **2b** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(5) = 1.969(4), Mg(1)−O(1) = 2.016(5), Mg(1)−C(37) = 2.077(12), Mg(1)−O(3) = 2.097(5), Mg(2)−O(1) = 1.977(4), Mg(2)−O(5) = 1.986(5), Mg(2)−O(7) = 2.079(5), Mg(2)−C(77) = 2.110(10); O(5)−Mg(1)−O(1) = 81.79(18), O(1)−Mg(2)−O(5) = 82.33-(18), Mg(1)−O(5)−Mg(2) = 98.49(19), Mg(2)−O(1)−Mg(1) = 97.23(19).

complexes, and the separations are 2.862(2), 2.881(2), 2.872(2), and 2.872(4) Å for **3a**−**c**,**f**, respectively. In comparison to the *n*-butylmagnesium complexes, the two ligands in the same dimeric molecules had different chiralities, forming pure meso complexes. The oxygen atom of the sulfonyl group is fixed on the magnesium ion more firmly than in the related *n*-butyl complexes, as evidenced by the short Mg(1)−O(3) bond distances of 2.009(2), 2.019(2), 2.008(2), and 2.013(4) Å for **3a**−**c**,**f**, respectively.

The molecular structure of complex **4** also revealed a dimeric character. Unlike compounds **3a**−**c**,**f**, the geometry around the magnesium atoms in **4** was pentacoordinate (Figure 9), with bonding to two oxygen atoms of the bridging benzyl alkoxy group, one oxygen atom of the sulfonyl group, an oxygen atom

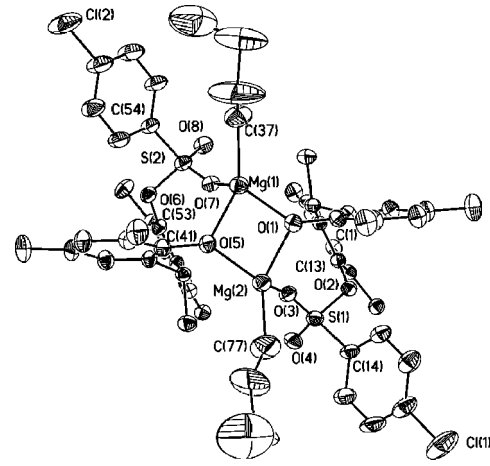


Figure 3. Molecular structure of **2c** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.974(3), Mg(1)−O(5) = 1.999(3), Mg(1)−C(37) = 2.108(6), Mg(1)−O(7) = 2.111(3), Mg(2)−O(5) = 1.983(3), Mg(2)−O(1) = 2.007(3), Mg(2)−C(77) = 2.090(7), Mg(2)−O(3) = 2.095(3); O(1)−Mg(1)−O(5) = 82.50(13), O(5)−Mg(2)−O(1) = 82.06(13), Mg(1)−O(1)−Mg(2) = 97.47(14), Mg(1)−O(5)−Mg(2) = 97.43(15).

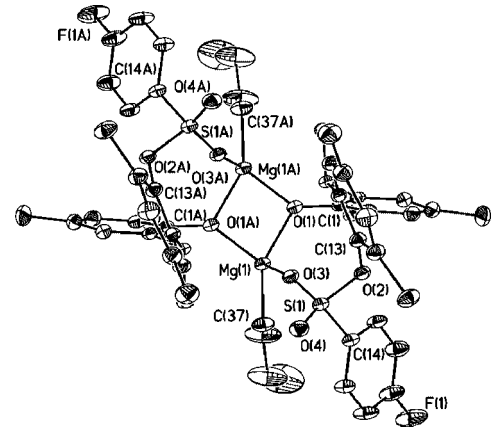


Figure 4. Molecular structure of **2e** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1A) = 1.979(2), Mg(1)−O(1) = 2.015(2), Mg(1)−O(3) = 2.102(2), Mg(1)−C(37) = 2.119(3); O(1A)−Mg(1)−O(1) = 82.51(9), Mg(1A)−O(1)−Mg(1) = 97.36(9).

of phenol, and the oxygen atoms of THF. Because of the presence of excess THF, the distance between the magnesium and the oxygen atoms of the sulfonyl group was somewhat longer than that in the tetracoordinated complexes **3a**−**c**,**f** with a Mg(1)−O(3) bond distance of 2.1693(17) Å for **4** as compared to the aveage of 2.010 Å for **3a**−**c**,**f**. The oxygen atom of THF was only weakly coordinated to magnesium with a Mg−O(6) bond distance of 2.1250(17) Å in **4**, which is somewhat longer than the Mg−O(THF) distance of 2.027(2) Å found in $[(EDBP)Mg(THF)]_2$.[9a]

Ring-Opening Polymerization of L-Lactides. In this context, the ROP of L-lactide employing **3a**−**f** (0.0125 mmol) as initiators is systematically examined in CH_2Cl_2 (10 mL), as shown in Table 1. Complex **3a** was an efficient initiator for the ROP of L-lactide, and the polymerization went to completion within 4 min at 25 °C at a monomer-to-initiator ratio of 200 (entry 1). Because the reaction was too rapid and the molecular weight of the polymer obtained was somewhat higher than the

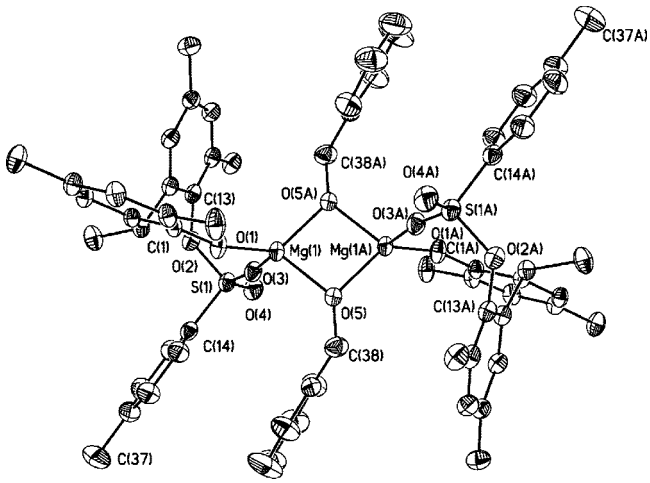


Figure 5. Molecular structure of **3a** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.831(2), Mg(1)−O(5A) = 1.925(2), Mg(1)−O(5) = 1.946(2), Mg(1)−O(3) = 2.009(2); O(1)−Mg(1)−O(5A) = 127.73(11), O(1)−Mg(1)−O(5) = 121.45(10), O(5)−Mg(1)−O(5A) = 84.64(9), O(1)−Mg(1)−O(3) = 105.91(10), O(5A)−Mg(1)−O(3) = 106.92-(10), O(5)−Mg(1)−O(3) = 107.93(9), Mg(1)−O(5)−Mg(1A) = 95.35(9).

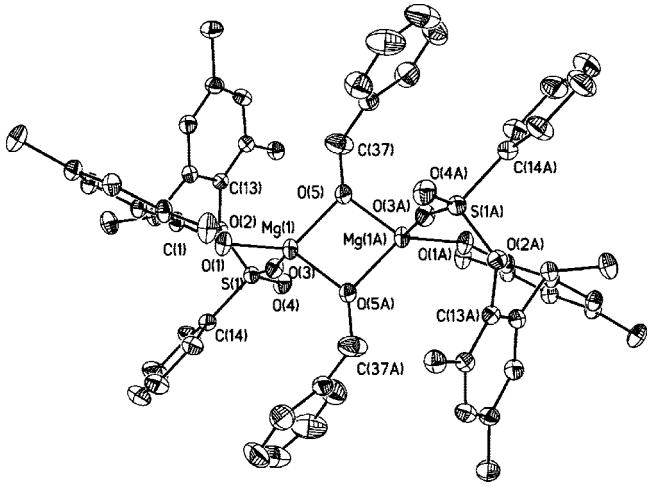


Figure 6. Molecular structure of **3b** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.833(2), Mg(1)−O(5A) = 1.929(3), Mg(1)−O(5) = 1.935(2), Mg(1)−O(3) = 2.019(2); O(1)−Mg(1)−O(5A) = 124.04(12), O(1)−Mg(1)−O(5) = 125.00(12), O(5A)−Mg(1)−O(5) = 83.57(11), O(1)−Mg(1)−O(3) = 103.31(11), O(5A)−Mg(1)−O(3) = 110.74-(10), O(5)−Mg(1)−O(3) = 109.17(11), Mg(1A)−O(5)−Mg(1) = 96.43(11).

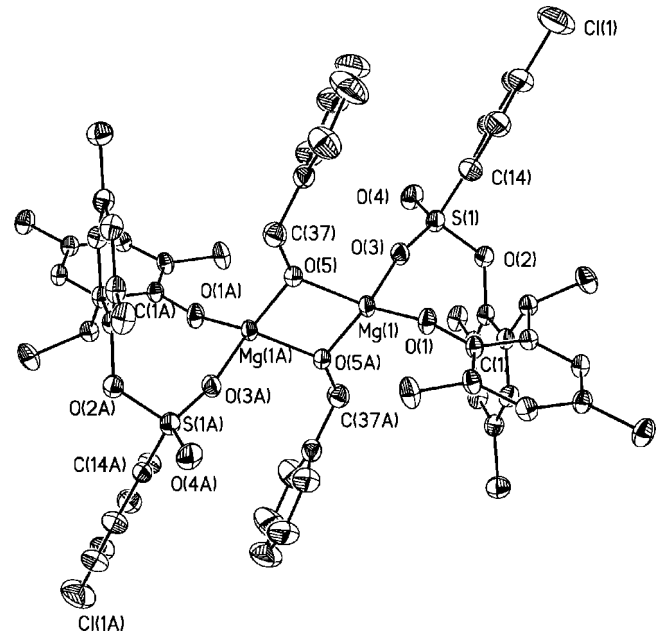


Figure 7. Molecular structure of **3c** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.8257(19), Mg(1)−O(5A) = 1.932(2), Mg(1)−O(5) = 1.9410(19), Mg(1)−O(4) = 2.0079(19); O(1)−Mg(1)−O(5A) = 127.74(9), O(1)−Mg(1)−O(5) = 122.46(9), O(5A)−Mg(1)−O(5) = 84.34(8), O(1)−Mg(1)−O(3) = 103.77(9), O(5A)−Mg(1)−O(3) = 107.82(9), O(5)−Mg(1)−O(4) = 109.18(8).

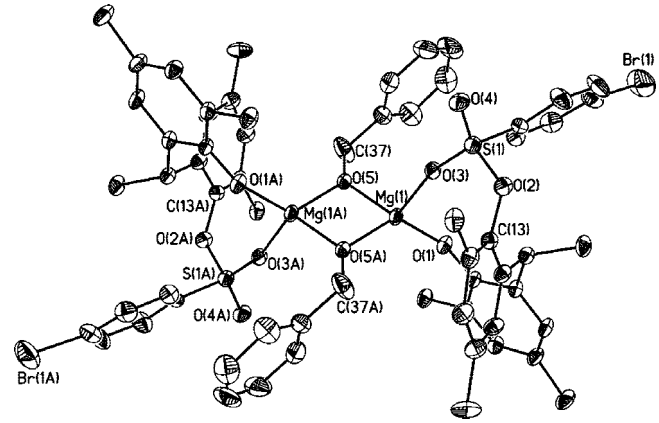


Figure 8. Molecular structure of **3f** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.835(4), Mg(1)−O(5) = 1.926(4), Mg(1)−O(5A) = 1.940(4), Mg(1)−O(3) = 2.013(4), Mg(1)−Mg(1A) = 2.872(4); O(1)−Mg(1)−O(5) = 123.5(2), O(1)−Mg(1)−O(5A) = 127.61(19), O(5)−Mg(1)−O(5A) = 84.01(18), O(1)−Mg(1)−O(3) = 102.66(18), O(5)−Mg(1)−O(3) = 109.08(18), O(5A)−Mg(1)−O(3) = 108.68(18), Mg(1)−O(5)−Mg(1A) = 95.99.

expected value, this indicates that side reactions may have occurred at high temperatures. Therefore, systematic studies for the polymerization of L-lactide were performed at 0 °C. Experimental results showed that conversions up to 95% could be achieved within 5 min at 0 °C when the monomer-to-initiator ratio was 200 (entry 2). The polydispersity indexes (PDIs) of poly(L-lactide)s obtainted at 0 °C were quite narrow, ranging from 1.07 to 1.14, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio (M to complex) existed (entries 2, 4, and 6−8 and Figure 10), implying the controlled character of the polymerization process, which was further confirmed by the polymerization resumption experiment (entry 9). Complexes **3b**−**f** also proved to be good initiators for the ROP of L-lactide, with polymers having the expected molecular weights and narrow PDIs (entries 11−15). The ^{1}H NMR spectrum (Figure 11) of PLA showed one benzyl ester and one hydroxyl chain end with an integral ratio of 5:1 between H_e and H_c, suggesting that the initiation occurred through the insertion of the benzyl alkoxy group from complexes **3a**−**f** into L-lactide and the backing reactions did not occur under our conditions.[9a,13] This was further verified by the following experimental results. First, the homonuclear

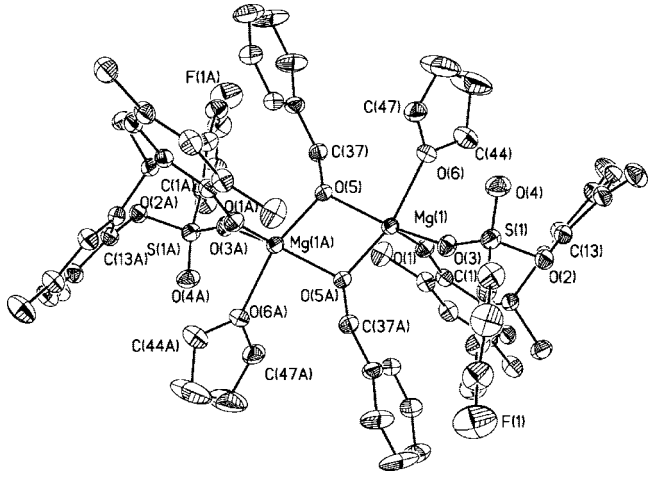


Figure 9. Molecular structure of **4** (methyl carbons of the *tert*-butyl group and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Mg(1)−O(1) = 1.8848(17), Mg(1)−O(5) = 1.9829(15), Mg(1)−O(5A) = 1.9851(16), Mg(1)−O(6) = 2.1250(17), Mg(1)−O(3) = 2.1693(17); O(1)−Mg(1)−O(5) = 116.42(7), O(1)−Mg(1)−O(5A) = 113.68(7), O(5)−Mg(1)−O(5A) = 80.06(6), O(1)−Mg(1)−O(6) = 96.52(8), O(5)−Mg(1)−O(6) = 90.17(7), O(5A)−Mg(1)−O(6) = 149.57-(8), O(1)−Mg(1)−O(3) = 100.77(7), O(5)−Mg(1)−O(3) = 142.65(7), O(5A)−Mg(1)−O(3) = 88.52(6), O(6)−Mg(1)−O(3) = 81.93(7), Mg(1)−O(5)−Mg(1A) = 99.94(6).

decoupled ^{1}H NMR spectrum revealed only one resonance at δ 5.16 ppm in the methane region (Figure S1, Supporting Information). Second, if cyclization occurred during polymerization, the PDIs of the PLA obtained could not have fallen in so narrow a range. Furthermore, epimerization of the chiral centers in PLA did not occur, as observed by the homonuclear decoupled ^{1}H NMR studies in the methane region.[15]

It is interesting to note that complex **3a** also could be used to initiate high monomer-to-catalyst ratios, with a high conversion of LA even up to $[LA]_0/[\mathbf{3a}]_0$ ratios of 1000, yielding PLA with a molecular weight as large as 84 800 in a very short time (less than 4 min). Although the molecular weight was lower than expected, which may have resulted from cyclization (PDI = 1.41) due to the bad solubility of PLLA, we have found no other report of a magnesium alkoxide that is so effective. Although diketiminate magnesium alkoxides are also very highly active, no large molecular weight polylactides have been reported.

Electron Effect on Ring-Opening Polymerization of L-Lactides. Because all of these complexes **3a**−**f** were too active toward the ROP of L-lactide in CH_2Cl_2, it was difficult to compare their activities in CH_2Cl_2. However, the reaction rate decreased dramatically while the polymerization was performed in THF (Table 1, entry 3). It was found that different polymerization yields could be achieved when the reaction time was kept at 12 min using complexes **3a**−**f** as initiators (Table 2). Experimental results indicated that the electron-withdrawing group on the phenyl ring of the Ts fragment decreased the reaction rate, as evidenced by the polymerization yield ranging from 31% to 77% to 96% for F, Cl, and Br, respectively.

Ring-Opening Polymerization of *rac*-Lactide. Polymerizations of *rac*-lactide by complexes **3a**−**e** were also performed, as shown in Table 3. The homonuclear decoupled ^{1}H NMR spectrum at the methine region of the PLA derived from **3a**−**e** reveals atatic to little heterotatic predominance. The probabilities of racemic linkages, Pr, were estimated from the relative intensity of the *rmr* and *mrm* tetrads vs other tetrads (*rmm*/*mmr*, *mmm*).[7a,16] When using CH_2Cl_2 as solvent, only atatic polymers were obtained. When the solvent was THF, heterotactic polymer was achieved with Pr = 0.59, 0.59, 0.65, 0.58, and 0.64 for **3a**–**e**, respectively. The low selectivity may result from the insufficient bulk of the ligand; the modification of this type of ligand is now in progess in our laboratory.

Conclusions

A series of magnesium alkoxides were designed and used as initiators for the ring opening polymerization of lactides. The reactivity of these magnesium benzyl alkoxides were highly active toward ring opening polymerization of lactides at 0 °C in CH_2Cl_2. Polylactides with a high molecular weight were prepared in a very short period of time.

Experimental Section

General Considerations. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, L-lactide, *rac*-lactide, and benzyl alcohol were purified before use. $Mg(^nBu)_2$ (1.0 M in heptane) was purchased from Aldrich and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-700 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent running at 1 mL/min. Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

General Procedures for Synthesis of the Ligands EDBP-*R*Ts-H (1a−f). EDBP-H_2 (4.38 g, 10 mmol) and triethylamine (14 mL, 100 mmol) were dissolved in 100 mL of dichloromethane. 4-Methylbenzene-1-sulfonyl chloride (2.09 g, 11 mmol) in dichloromethane (20 mL) was added dropwise into the above solution at 0 °C for about 1 h. The resulting mixture was then stirred for 24 h while the temperature was increased to room temperature. The solution was filtered, and the filtrate was washed with 50 mL of water three times. The dichloromethane layer was collected and dried over anhydrous $MgSO_4$ and filtered through Celite again to remove $MgSO_4$. The resulting filtrate was then dried under vacuum, and the residue was recrystallized by slow cooling of a hexane or acetonitrile solution.

1a: yield 5.45 g (92%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.99 (2H, d, J = 8.0 Hz, Ar*H*), 7.39 (2H, d, J = 8.0 Hz, Ar*H*), 7.34 (1H, d, J = 2.0 Hz, Ar*H*), 7.27 (1H, d, J = 2.0 Hz, Ar*H*), 7.10 (1H, d, J = 2.0 Hz, Ar*H*), 6.54 (1H, d, J = 2.0 Hz, Ar*H*), 5.95 (1H, b, O*H*), 4.49 (1H, q, J = 6.8 Hz, C*H*), 2.47 (3H, s, CH_3), 1.46 (9H, s, $C(CH_3)_3$), 1.40 (9H, s, $C(CH_3)_3$), 1.31 (9H, s, $C(CH_3)_3$), 1.28 (3H, d, J = 6.8 Hz, CH_3), 1.08 (9H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.73, 149.17, 145.13, 143.83, 142.85, 141.14, 139.23, 135.93, 129.93, 127.88, 127.32, 124.80, 123.71, 122.10, 121.88, 35.96, 35.05, 34.51, 34.40, 31.82, 31.70, 31.03, 29.73, 21.67, 19.95.

(13) Wu, J.; Huang, B. H.; Hsueh, M. L.; Lai, S. L.; Lin, C. C. *Polymer* **2005**, *46*, 9784.

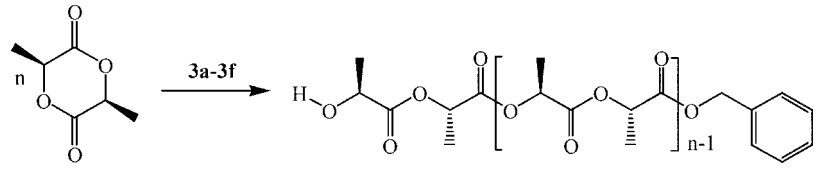
(14) The M_n (GPC) value is multiplied by a factor of 0.58, giving the actual M_n of the polylactide. (a) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325. (b) Biela, T.; Duda, A.; Penczek, S. *Macromol. Symp.* **2002**, *183*, 1. (c) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.

(15) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665.

(16) (a) Kasperczyk, J. E. *Macromolecules* **1995**, *28*, 3937. (b) Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; Academic Press: San Diego, CA, 1996.

(17) See the Supporting Information.

Table 1. Ring-Opening Polymerization of L-Lactide using Complexes 3a−f[a]



					M_n			
entry	[ini]	$[M]_0/[complex]_0$	solvent	t (min)	PDI	GPC[b]	calcd[c]	NMR[d]	conversn (%)
1[e]	**3a**	200	CH_2Cl_2	4	1.08	32 300	28 300	30 200	98
2	**3a**	200	CH_2Cl_2	5	1.09	26 900	27 500	26 400	95
3	**3a**	200	THF	12	1.20	34 800	27 800	29 200	96
4	**3a**	25	CH_2Cl_2	20	1.14	4 300	3 500	4 000	93
5	**3a**	150	CH_2Cl_2	5	1.10	16 500	17 400	18 100	80
6	**3a**	150	CH_2Cl_2	8	1.08	21 000	20 600	17 700	95
7	**3a**	250	CH_2Cl_2	5	1.08	33 200	34 000	29 000	95
8	**3a**	300	CH_2Cl_2	5	1.07	42 900	42 000		97
9	**3a**	150 (150)	CH_2Cl_2	8 (8)	1.09	47 100	42 000		97
10[e]	**3a**	1000	THF	4	1.41	84 800	142 700		99[f]
11	**3b**	200	CH_2Cl_2	5	1.08	24 000	28 000	24 300	97
12	**3c**	200	CH_2Cl_2	5	1.06	25 400	27 200	23 900	94
13	**3d**	200	CH_2Cl_2	5	1.05	27 000	28 000	26 500	97
14	**3e**	200	CH_2Cl_2	5	1.05	28 800	26 600	23 700	92
15	**3f**	200	CH_2Cl_2	5	1.09	30 000	26 900	28 400	93

[a] Conditions: 0.025 mmol of complex, 10 mL of solvent, 0 °C. [b] Obtained from GPC analysis times 0.5.[14] and calibrated by polystyrene standard. [c] Obtained from ^{1}H NMR analysis. [d] Calculated from the molecular weight of L-lactide times $[M]_0/[complex]_0$ times conversion yield plus the molecular weight of BnOH. [e] At 25 °C. [f] 15 mL of THF was used.

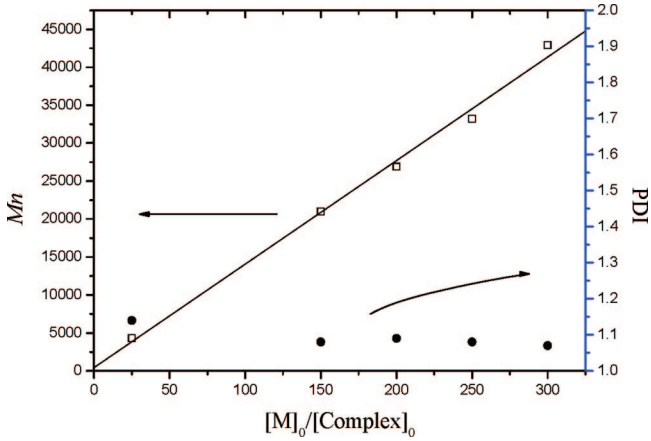


Figure 10. Polymerization of L-LA catalyzed by **3a** in CH_2Cl_2 at 0 °C. The relationship between M_n(□) (PDI (•)) of the polymer and the initial mole ratio $[M]_0$/[complex] is shown.

Anal. Calcd for $C_{37}H_{52}O_4S$: C, 74.96; H, 8.84; S, 5.41. Found: C, 74.82; H, 8.78; S, 5.21.

1b: yield 5.44 g (94%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.11 (2H, d, J = 8 Hz, Ar*H*), 7.71 (1H, m, Ar*H*), 7.58 (2H, m, Ar*H*), 7.34 (1H, d, J = 2.4 Hz, Ar*H*), 7.27 (1H, d, J = 2.4 Hz, Ar*H*), 7.09 (1H, d, J = 2.0 Hz, Ar*H*), 6.54 (1H, d, J = 2.0 Hz, Ar*H*), 5.91 (1H, b, O*H*), 4.47 (1H, q, J = 6.8 Hz, C*H*), 1.46 (9H, s, C(CH_3)$_3$), 1.40 (9H, s, C(CH_3)$_3$), 1.31 (9H, s, C(CH_3)$_3$), 1.26 (3H, d, J = 6.8 Hz, CH_3), 1.08 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.68, 149.28, 143.90, 142.84, 141.21, 139.12, 137.53, 135.96, 133.99, 129.34, 127.85, 127.30, 124.83, 123.77, 122.13, 121.87, 35.94, 35.06, 34.53, 34.44, 34.41, 31.77, 31.69, 31.01, 29.74, 19.89. Anal. Calcd for $C_{36}H_{50}O_4S$: C, 74.70; H, 8.71; S, 5.54. Found: C, 74.33; H, 8.69; S, 5.44.

1c: yield 5.94 g (97%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.05 (2H, d, J = 6.8 Hz, Ar*H*), 7.58 (2H, d, J = 6.8 Hz, Ar*H*), 7.34 (1H, d, J = 1.6 Hz, Ar*H*), 7.27 (1H, d, J = 1.6 Hz, Ar*H*), 7.09 (1H, d, J = 2.4 Hz, Ar*H*), 6.57 (1H, d, J = 2.4 Hz, Ar*H*), 5.78 (1H, b, O*H*), 4.45 (1H, q, J = 7.2 Hz, C*H*), 1.45 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.31 (9H, s, C(CH_3)$_3$), 1.29 (3H, d, J = 7.2 Hz, CH_3), 1.08 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.57, 149.49, 143.89, 142.82, 141,38, 140.76, 138.97, 136.04, 135.96, 129.71, 128.77, 127.80, 124.94, 123.85, 122.23, 121.87, 35.94, 35.05, 34.55, 34.47, 34.41, 31.77, 31.68, 31.01, 29.74, 19.95. Anal. Calcd for $C_{36}H_{49}O_4ClS$: C, 70.50; H, 8.05; S, 5.23. Found: C, 70.26; H, 8.21; S, 5.24.

1d: yield 5.96 g (98%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.03 (2H, d, J = 9.2 Hz, Ar*H*), 7.34 (1H, d, J = 2.0 Hz, Ar*H*), 7.28 (1H, d, J = 2.0 Hz, Ar*H*), 7.12 (1H, d, J = 2.0 Hz, Ar*H*), 7.04 (2H, d, J = 9.2 Hz, Ar*H*), 6.56 (1H, d, J = 2.0 Hz, Ar*H*), 5.99 (1H, b, O*H*), 4.55 (1H, q, J =, C*H*), 3.88 (3H, s, O CH_3), 1.46 (9H, s, C(CH_3)$_3$), 1.40 (9H, s, C(CH_3)$_3$), 1.32 (9H, s, C(CH_3)$_3$), 1.31 (3H, d, J =, CH_3), 1.09 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 163.89, 150.74, 149.11, 143.84, 142.85, 141.17, 139.30, 135.92, 129.65, 128.88, 127.94, 124.81, 123.67, 122.09, 121.89, 114.50, 55.71, 35.98, 35.07, 34.51, 34.43, 31.84, 31.70, 31.03, 29.75, 19.96. Anal. Calcd for $C_{37}H_{52}O_5S$: C, 72.99; H, 8.61; S, 5.27. Found: C, 72.88; H, 8.89; S, 5.30.

1e: yield 5.84 g (98%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.14 (2H, m, Ar*H*), 7.35 (1H, d, J = 1.6 Hz, Ar*H*), 7.28 (3H, m, Ar*H*), 7.09 (1H, s, Ar*H*), 6.57 (1H, d, J = 1.6 Hz, Ar*H*), 5.82 (1H, b, O*H*), 4.47 (1H, q, J = 6.9 Hz, C*H*), 1.45 (9H, s, C(CH_3)$_3$), 1.40 (9H, s, C(CH_3)$_3$), 1.32 (9H, s, C(CH_3)$_3$), 1.29 (3H, d, J = 6.9 Hz, CH_3), 1.09 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.59, 149.44, 143.86, 142.82, 141.37, 139.03, 136.02, 130.33, 130.33, 127.84, 124.94, 123.82, 122.21, 121.87, 116.87, 116.65, 35.95, 35.05, 34.54, 34.47, 34.41, 31.77, 31.68, 31.00, 29.74, 19.93. Anal. Calcd for $C_{36}H_{49}O_4FS$: C, 72.45; H, 8.28; S, 5.37. Found: C, 72.11; H, 8.19; S, 5.25.

1f: yield 5.91 g (90%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.97 (2H, d, J = 8.8 Hz, Ar*H*), 7.74 (2H, d, J = 8.8 Hz, Ar*H*), 7.35 (1H, d, J = 2.4 Hz, Ar*H*), 7.28 (1H, d, J = 2.4 Hz, Ar*H*), 7.09 (1H, d, J = 2.4 Hz, Ar*H*), 6.56 (1H, d, J = 2.4 Hz, Ar*H*), 5.78 (1H, b, O*H*), 4.43 (1H, q, J = 6.8 Hz, C*H*), 1.45 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.31 (9H, s, C(CH_3)$_3$), 1.28 (3H, d, J = 6.8 Hz, CH_3), 1.08 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 150.58, 149.50, 143.89, 142.84, 141,41, 138.98, 136.53, 136.06, 132.70, 129.31, 128.80, 127.84, 124.94, 123.86, 122.23, 121.89, 35.95, 35.07, 34.57,

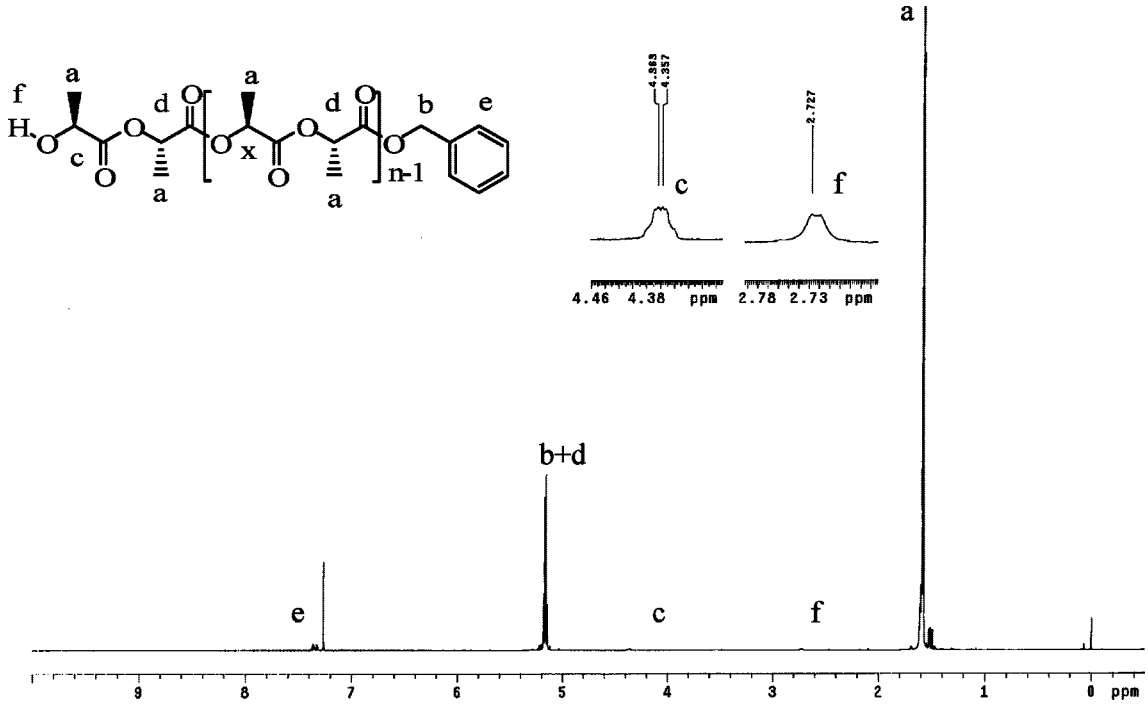


Figure 11. ^{1}H NMR PLA-25 (from entry 4) in $CDCl_3$.

Table 2. Comparison of Reaction Rates of 3a−f[a]

				M_n			
entry	initiator	*t* (min)	PDI	GPC[b]	calcd[c]	NMR[d]	conversn (%)
1	**3a**	12	1.19	51 400	26 700	26 600	91
2	**3b**	12	1.25	41 800	25 500	23 200	88
3	**3c**	12	1.14	40 700	22 600	20 700	77
4	**3d**	12	1.10	52 600	26 400	25 400	92
5	**3e**	12	1.11	15 700	8 700	8 900	31
6	**3f**	12	1.08	45 700	27 800	28 300	96

[a] Conditions: 0.025 mmol of complex, 15 mL of THF as solvent, 0 °C. [b] Obtained from GPC analysis and calibrated by polystyrene standard. [c] Obtained from ^{1}H NMR analysis. [d] Calculated from the molecular weight of L-lactide times $[M]_0/[complex]_0$ times conversion plus the molecular weight of BnOH.

34.49, 34.43, 31.78, 31.70, 31.02, 29.77, 19.98. Anal. Calcd for $C_{36}H_{49}O_4BrS$: C, 65.74; H, 7.51; S, 4.88. Found: C, 65.81; H, 7.12; S, 4.86.

General Preparation Procedures for [(EDBP-RTs)Mg(^{n}Bu)] (2a−f). Mg(^{n}Bu)$_2$(2.2 mmol) was added slowly to an ice cold toluene (30 mL) solution of ligand (**1a**) (1.15 g, 2.0 mmol) in toluene (30 mL). The mixture was stirred for 12 h while the temperature was slowly increased to room temperature. Volatile materials were removed under vaccum and the residue was recrystalled from a hexane solution.

2a: yield 1.21 g (90%). ^{1}H NMR (C_6D_6, ppm): δ 7.78 (1H, s, Ar*H*), 7.59 (1H, s, Ar*H*), 7.45 (1H, s, Ar*H*), 7.07 (2H, d, J = 8.0 Hz, Ar*H*), 6.95 (1H, s, Ar*H*), 6.82 (2H, d, J = 8.0 Hz, Ar*H*), 5.57 (1H, q, J = 6.0 Hz, C*H*), 1.97 (3H, d, J = 6.0 Hz, CH_3), 1.89 (9H, s, C(C*H*$_3$)$_3$), 1.77 (3H, s, C*H*$_3$), 1.57 (9H, s, C(C*H*$_3$)$_3$), 1.35 (9H, s, C(C*H*$_3$)$_3$), 1.23 (9H, s, C(C*H*$_3$)$_3$) 0.85−1.67 (7H, m,C*H*$_2$C*H*$_2$C*H*$_3$), −0.65 (2H, m, MgC*H*$_2$). ^{13}C NMR (C_6D_6, ppm): δ 153.47, 149.35, 146.05, 142.75, 142.18, 140.61, 139.37, 139.18, 138.80, 133.03, 129.79, 126.84, 124.76, 123.01, 121.21, 115.22, 36.37, 36.17, 34.91, 34.26, 33.50, 32.61, 31.87, 31.46, 26.33, 22.98, 21.22, 14.28, 14.16, 10.10, 1.34. Anal. Calcd for $C_{82}H_{120}Mg_2O_8S_2$: C, 73.14; H, 8.98; S, 4.76. Found: C, 73.52; H, 8.90; S, 4.62.

2b: yield 1.17 g (89%). ^{1}H NMR (C_6D_6, ppm): δ 7.76 (1H, s, Ar*H*), 7.56 (1H, d, J = 2.4 Hz, Ar*H*), 7.44 (1H, d, J = 2.4 Hz, Ar*H*), 7.04 (1H, s, Ar*H*), 6.90−6.95 (5H, m, Ar*H*), 5.51 (1H, q, J = 6.0 Hz, C*H*), 1.96 (3H, d, J = 6.0 Hz, C*H*$_3$), 1.86 (9H, s, C(C*H*$_3$)$_3$), 1.31 (9H, s, C(C*H*$_3$)$_3$), 1.21 (9H, s, C(C*H*$_3$)$_3$), 1.12 (9H, s, C(C*H*$_3$)$_3$), 0.80−1.85 (7H, m, C*H*$_2$C*H*$_2$C*H*$_3$), −0.74 (2H, m, MgC*H*$_2$). ^{13}C NMR (C_6D_6, ppm): δ 153.38, 149.46, 142.79, 141.95, 140.73, 139.44, 139.06, 138.77, 135.83, 134.63, 129.11, 126.89, 125.64, 124.89, 123.13, 121.19, 36.39, 36.21, 34.92, 34.26, 33.51, 32.63, 31.86, 31.46, 26.39, 22.99, 14.31, 14.21, 9.86, 1.35. Anal. Calcd for $C_{80}H_{116}Mg_2O_8S_2$: C, 72.87; H, 8.87; S, 4.86. Found: C, 73.10; H, 8.78; S, 5.02.

2c: yield 1.32 g (95%). ^{1}H NMR (C_6D_6, ppm): δ 7.69 (1H, s, Ar*H*), 7.46 (1H, s, Ar*H*), 7.40 (1H, s, Ar*H*), 7.07 (2H, d, J = 7.6 Hz, Ar*H*), 6.87 (1H, s, Ar*H*), 6.85 (2H, d, J = 7.6 Hz, Ar*H*), 5.40 (1H, q, J = 6.0 Hz, C*H*), 1.85 (3H, d, J = 6.0 Hz, C*H*$_3$), 1.81 (9H,

Table 3. Ring-Opening Polymerization of *rac*-Lactide Initiated by Complexes 3a−f[a]

				M_n					
entry	initiator	*t*	PDI	GPC[b]	calcd[c]	NMR[d]	conversn (%)	yield (%)	Pr
1[e]	**3a**	16 min	1.12	43 100 (25 000)	23 100	24 900	79	55	0.59
2	**3a**	1 h	1.16	50 100 (29 100)	26 600	29 000	92	70	0.59
3	**3b**	1 h	1.23	43 700 (25 300)	28 000	25 700	97	81	0.59
4	**3c**	1 h	1.13	40 300 (23 400)	26 900	23 500	93	84	0.65
5	**3d**	1 h	1.14	43 300 (25 100)	27 200	25 400	94	82	0.58
6	**3e**	1.5 h	1.15	39 200 (22 700)	25 500	23 500	88	70	0.64

[a] Conditions: 0.025 mmol of complex, 15 mL of THF, 0 °C. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[14] [c] Calculated from the molecular weight of L-lactide times $[M]_0/[complex]_0$ times conversion yield plus the molecular weight of BnOH. [d] Obtained from ^{1}H NMR analysis. [e] 10 mL of THF.

Table 4. Summary of Crystallographic Data

	2a·0.5C_6H_{14}	**2b**	**2c**·2C_6H_{14}	**2e**·C_7H_8	**3a**·1.5C_7H_8	**3b**·0.5C_6H_{14}	**3c**·C_6H_{14}·0.5C_7H_8	**3f**·0.5C_6H_{14}	**4**·THF
empirical formula	$C_{85}H_{127}Mg_2O_8S_2$	$C_{80}H_{116}Mg_2O_8S_2$	$C_{92}H_{128}Cl_2Mg_2O_8S_2$	$C_{47}H_{65}FMgO_4S$	$C_{54.5}H_{70}MgO_5S$	$C_{46}H_{63}MgO_5S$	$C_{52.5}H_{72.5}ClMgO_5S$	$C_{46}H_{62}BrMgO_5S$	$C_{51}H_{71}FMgO_7S$
formula wt	1389.61	1318.47	1545.58	761.30	849.38	736.21	861.31	831.24	863.38
color	colorless	colorless	colorless	colorless	colorless	colorless	colorless	colorless	colorless
cryst syst	monoclinic	rhombohedral	monoclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$R\bar{3}$	$P2_1/c$	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	15.5879(18)	19.5642(12)	23.1133(16)	24.988(3)	14.1759(11)	35.524(2)	13.9706(11)	13.406(3)	14.8665(12)
b (Å)	19.530(2)	19.5642(12)	22.8161(15)	20.691(2)	14.8279(12)	18.9707(13)	14.9301(12)	13.949(4)	22.4247(17)
c (Å)	28.960(3)	19.5642(12)	19.1247(13)	20.122(2)	15.2796(11)	14.2179(9)	15.4703(13)	14.944(4)	15.9899(13)
α (deg)	90.00	101.0230(10)	90.00	90.00	104.389(2)	90.00	103.167(2)	99.659(5)	90.00
β (deg)	102.972(2)	101.0230(10)	109.3990(10)	115.113(2)	116.6980(10)	110.5490(10)	116.353(2)	110.113(5)	100.390(2)
γ (deg)	90.00	101.0230(10)	90.00	90.00	98.7810(10)	90.00	100.663(2)	109.958(5)	90.00
Z	4	3	4	8	2	8	2	2	4
V (Å^3)	8591.4(17)	7010.1(7)	9512.9(11)	9420.1(19)	2646.5(4)	8971.9(10)	2659.8(4)	2334.3(10)	5243.3(7)
D_{calcd}(g/cm^3)	1.074	2.499	1.079	1.074	1.066	1.090	1.075	1.183	1.094
μ(Mo Kα) (mm^{-1})	0.126	0.113	0.174	0.124	0.115	0.126	0.164	0.979	0.122
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
2θ range (deg)	1.70−26.05	1.72−25.99	1.87−26.09	1.80−26.03	1.75−26.05	1.24−26.05	2.22−26.02	1.64−26.05	1.58−26.03
no. of rflns collected	46 275	38 824	51 501	25 229	14 433	24 407	14 602	12 877	28 201
no. of indep rflns	16 823	13 488	18 764	9245	10 261	8 832	10 328	9 076	10 307
R1[a]	0.0767	0.0853	0.0773	0.0816	0.0818	0.0616	0.0613	0.0885	0.0612
wR2[b]	0.1804	0.1973	0.1962	0.2554	0.2465	0.1627	0.1640	0.2095	0.1761
GOF[c]	1.341	1.041	1.137	1.098	1.477	0.990	1.004	0.996	1.286

[a] $R1 = |\sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$; $w = 0.10$, except $w = 0.20$ for **2e**·C_7H_8. [c] $GOF = [\sum w(F_o^2 - F_c^2)^2]/(N_{rflns} - N_{params})]^{1/2}$.

s, C(CH_3)$_3$), 1.30 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$), 0.87−1.8 (7H, m, $CH_2CH_2CH_3$), −0.81 (2H, m, MgCH_2). ^{13}C NMR (C_6D_6, ppm): δ 153.22, 149.66, 142.75, 141.89, 141.73, 140.93, 139.63, 138.91, 138.56, 134.20, 129.60, 129.37, 126.82, 125.00, 123.14, 121.13, 36.33, 36.21, 34.91, 34.22, 33.39, 32.60, 31.94, 31.80, 31.40, 22.99, 14.29, 14.10, 10.05, 1.34. Anal. Calcd for $C_{80}H_{114}Mg_2O_8Cl_2S_2$: C, 69.26; H, 8.28; S, 4.62. Found: C, 68.94; H, 7.95; S, 4.37.

2d: yield 1.24 g (90%). ^{1}H NMR (C_6D_6, ppm): δ 7.72 (1H, s, ArH), 7.50 (1H, d, J = 2.4 Hz, ArH), 7.40 (1H, d, J = 2.4 Hz, ArH), 7.10 (2H, d, ArH), 6.89 (1H, d, J = 8.8 Hz, ArH), 6.53 (2H, d, J = 8.8 Hz, ArH), 5.55 (1H, q, J = 6.0 Hz, CH), 2.95 (3H, s, OCH_3), 1.93 (3H, d, J = 6.0 Hz, CH_3), 1.84 (9H, s, C(CH_3)$_3$), 1.35 (9H, s, C(CH_3)$_3$), 1.19 (9H, s, C(CH_3)$_3$), 1.09 (9H, s, C(CH_3)$_3$), 0.82−1.35 (7H, m, $CH_2CH_2CH_3$), −0.66 (2H, m, MgCH_2). ^{13}C NMR (C_6D_6, ppm): δ 164.65, 153.54, 149.29, 142.77, 142.36, 140.62, 139.41, 139.26, 138.85, 130.28, 127.28, 126.80, 124.71, 123.03, 121.27, 114.46, 54.96, 36.40, 36.21, 34.92, 34.26, 33.52, 33.02, 32.64, 32.23, 31.87, 31.49, 26.33, 14.21, 10.19, 1.36. Anal. Calcd for $C_{82}H_{120}Mg_2O_{10}S_2$: C, 71.44; H, 8.77; S, 4.65. Found: C, 71.53; H, 8.70; S, 4.21.

2e: yield 1.23 g (91%). ^{1}H NMR (C_6D_6, ppm): δ 7.76 (1H, s, ArH), 7.53 (1H, d, J = 2.4 Hz, ArH), 7.47 (1H, d, J = 2.4 Hz, ArH), 7. 02 (2H, m, ArH), 6.69 (2H, t, J = 6.0 Hz, ArH), 6.25 (1H, m, ArH), 5.47 (1H, q, J = 6.0 Hz, CH), 1.93 (3H, d, J = 6.0 Hz, CH_3), 1.84 (9H, s, C(CH_3)$_3$), 1.34 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 1.18 (9H, s, C(CH_3)$_3$), 1.65, 1.53, 1.17, 0.89 (7H, m, $CH_2CH_2CH_3$), −0.67 (2H, m, MgCH_2). ^{13}C NMR (C_6D_6, ppm): δ 167.72, 165.16, 153.24, 149.61, 142.78, 141.84, 140.91, 139.59, 138.64, 131.00, 130.91, 126.87, 125.00, 123.14, 121.15, 116.73, 116.50, 36.35, 36.15, 34.92, 34.22, 33.44, 32.63, 31.81, 31.43, 26.31, 25.13, 14.11, 13.93, 9.95, 1.34. Anal. Calcd for $C_{80}H_{114}Mg_2O_8F_2S_2$: C, 70.94; H, 8.48; S, 4.73. Found: C, 71.21; H, 7.99; S, 4.83.

2f: yield 1.33 g (90%). ^{1}H NMR (C_6D_6, ppm): δ 7.73 (1H, s, ArH), 7.50 (1H, s, ArH), 7.43 (1H, s, ArH), 7.23 (2H, d, J = 8.4 Hz, ArH), 6.91 (1H, s, ArH), 6.83 (2H, d, J = 8.4 Hz, ArH), 5.46 (1H, q, J = 6.4 Hz, CH), 1.90 (3H, d, J = 6.4 Hz, CH_3), 1.81 (9H, s, C(CH_3)$_3$), 1.30 (9H, s, C(CH_3)$_3$), 1.21 (9H, s, C(CH_3)$_3$), 1.08 (9H, s, C(CH_3)$_3$), 0.81−1.59 (7H, m, $CH_2CH_2CH_3$), −0.87 (2H, m, MgCH_2). ^{13}C NMR (C_6D_6, ppm): δ 153.24, 149.68, 142.76, 141.94, 140.94, 139.64, 138.95, 138.55, 134.71, 132.62, 130.46, 129.34, 126.81, 124.99, 123.16, 121.14, 36.33, 36.21, 36.12, 34.91, 34.23, 33.40, 32.89, 32.60, 32.11, 31.82, 31.42, 26.21, 14.15, 10.08, 1.36. Anal. Calcd for $C_{80}H_{114}Mg_2O_8Br_2S_2$: C, 65.09; H, 7.78; S, 4.34. Found: C, 64.57; H, 7.34; S, 3.65.

General Procedures for the Preparation of [(EDBP-RTs)Mg(μ-OBn)]$_2$ (3a−e). Benzyl alcohol (0.21 mL, 2 mmol) was added to an ice-cold solution of **2a** (2.692 g, 2 mmol) in toluene (25 mL) (in the case of **3e**, 25 mL of THF was used). The mixture was stirred for 24 h, during which time the temperature was raised to room temperature. The mixture was then filtrated through Celite and the filtrate was dried in vacuo to give a white solid. The residue was dissolved in 5 mL of CH_2Cl_2, and about 30 mL of hexane was added to the CH_2Cl_2 solution, yielding a white precipitate.

3a: yield 2.46 g (90%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.47 (2H, d, J = 4.0 Hz, ArH), 7.14−7.27 (4H, m, ArH), 6.95 (2H, m, ArH), 6.94 (1H, s, ArH), 6.80 (2H, m, ArH), 6.70 (1H, t, J = 4.0 Hz, ArH), 6.56 (1H, d, ArH), 4.32 (1H, q, J = 7.2 Hz, CH), 4.05 (1H, d, J = 12.4 Hz, CH_2Ph), 3.07 (1H, d, J = 12.4 Hz, CH_2Ph), 2.43 (3H, s, CH_3), 1.58 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.83 (3H, d, J = 7.2 Hz, CH_3), 0.66 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 158.66, 149.90, 145.31, 145.11, 144.78, 142.19, 141.99, 136.54, 133.97, 132.25, 130.06, 129.95, 127.72, 127.20, 126.81, 124.59, 123.73, 121.67, 121.25, 64.69, 35.88, 34.99, 34.21, 34.09, 31.97, 31.85, 30.61, 30.07, 21.69,

21.45, 18.99. Anal. Calcd for $C_{88}H_{116}Mg_2O_{10}S_2$: C, 73.06; H, 8.08; S, 4.43. Found: C, 72.95; H, 8.21; S, 4.62.

3b: yield 2.41 g (85%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.59 (3H, m, Ar*H*), 7.39 (2H, m, Ar*H*), 7.20 (1H, d, J = 2.0 Hz, Ar*H*), 7.14 (1H, s, Ar*H*), 6.94 (3H, m, Ar*H*), 6.80 (2H, m, Ar*H*), 6.56 (1H, m, Ar*H*), 6.56 (1H, d, J = 2.0 Hz, Ar*H*), 4.30 (1H, q, J = 7.6 Hz, C*H*), 4.03 (1H, d, J = 12.4 Hz, CH_2Ph), 3.07 (1H, d, J = 12.4 Hz, CH_2Ph), 1.58 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.80 (3H, d, J = 7.6 Hz, CH_3), 0.65 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 158.60, 150.02, 145.19, 144.69, 142.17, 141.89, 136.50, 135.14, 134.04, 129.99, 129.39, 127.75, 127.12, 126.85, 126.28, 124.62, 123.75, 121.68, 121.28, 64.69, 35.85, 34.97, 34.21, 34.08, 31.95, 31.82, 30.58, 30.06, 22.63, 18.85. Anal. Calcd for $C_{86}H_{112}Mg_2O_{10}S_2$: C, 72.82; H, 7.96; S, 4.52. Found: C, 72.56; H, 7.87; S, 4.18.

3c: yield 2.55 g (86%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.72 (1H, s, Ar*H*), 7.45 (1H, s, Ar*H*), 7.34 (2H, m, Ar*H*), 7.20 (1H, d, J = 2.8 Hz, ArH), 7.15 (1H, d, J = 2.8 Hz, ArH), 6.95 (2H, m, Ar*H*), 6.84 (2H, m, Ar*H*), 6.73(1H, m, Ar*H*), 6.70 (1H, t, J = 2.8 Hz, Ar*H*), 6.56 (1H, d, J = 2.8 Hz, Ar*H*), 4.19 (1H, q, J = 7.2 Hz, C*H*), 4.02 (1H, d, J = 12.8 Hz, CH_2Ph), 3.02 (1H, d, J = 12.8 Hz, CH_2Ph), 1.58 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.81 (3H, d, J = 7.2 Hz, CH_3), 0.65 (9H, s, C(CH_3)$_3$).^{13}C NMR ($CDCl_3$, ppm): δ 158.45, 150.29, 145.35, 144.63, 142.21, 141.69, 140.93, 136.51, 134.31, 133.57, 129.78, 129.70, 128.52, 127.77, 126.91, 126.37, 124.61, 123.85, 121.73, 121.40, 64.71, 35.84, 35.01, 34.97, 34.23, 34.09, 31.93, 31.79, 30.58, 30.10, 19.02. Anal. Calcd for $C_{86}H_{110}Mg_2O_{10}Cl_2S_2$: C, 69.44; H, 7.45; S, 4.31. Found: C, 70.01; H, 7.67; S, 4.59.

3d: yield 2.30 g (78%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.52 (2H, d, Ar*H*), 7.19 (1H, s, Ar*H*), 7.12 (1H, s, Ar*H*), 6.93 (3H, m, Ar*H*), 6.79 (4H, m, Ar*H*), 6.72 (1H, m, Ar*H*), 6.53 (1H, s, Ar*H*), 4.31 (1H, q, J = 6.8 Hz, C*H*), 4.04 (1H, d, J = 12.4 Hz, CH_2Ph), 3.87 (3H, s, OCH_3),3.06 (1H, d, J = 12.4 Hz, CH_2Ph), 1.57 (9H, s, C(CH_3)$_3$), 1.48 (9H, s, C(CH_3)$_3$), 1.26 (9H, s, C(CH_3)$_3$), 0.83 (3H, d, J = 6.8 Hz, CH_3), 0.64 (9H, s, C(CH_3)$_3$).^{13}C NMR ($CDCl_3$, ppm): δ 163.9, 158.67, 149.86, 145.24, 144.85, 142.24, 142.00, 136.55, 134.03, 130.14, 129.62, 127.72, 126.80, 126.46, 126.11, 124.58, 123.71, 121.74, 121.28, 114.59, 64.68, 55.75, 35.91, 35.00, 34.21, 34.11, 31.98, 31.88, 30.62, 30.08, 18.85. Anal. Calcd for $C_{88}H_{116}Mg_2O_{12}S_2$: C, 71.48; H, 7.91; S, 4.34. Found: C, 71.20; H, 7.68; S, 4.03.

3e: yield 2.32 g (80%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.58 (2H, m, Ar*H*), 7.14−7.25 (2H, m, Ar*H*), 7.21 (1H, d, J = 2.0 Hz, Ar*H*), 7.05 (2H, m, Ar*H*), 6.94 (2H, m, Ar*H*), 6.81 (2H, m, Ar*H*), 6.73 (1H, m, Ar*H*), 6.57 (1H, d, J = 2.0 Hz, Ar*H*), 4.27 (1H, q, J = 6.8 Hz, C*H*), 4.05 (1H, b, CH_2Ph), 3.09 (1H, b, CH_2Ph), 1.58 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.81(3H, d, J = 6.8 Hz, CH_3), 0.65 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 158.50, 150.26, 145.32, 144.68, 142.27, 141.76, 136.52, 134.31, 131.15, 130.23, 130.13, 129.85, 127.77, 126.89, 126.33, 124.62, 123.86, 121.74, 121.40, 116.94, 116.71, 64.72, 35.87, 35.04, 34.98, 34.24, 34.24, 34.11, 31.95, 31.82, 30.56, 30.11, 18.99. Anal. Calcd for $C_{86}H_{110}Mg_2O_{10}F_2S_2$: C, 71.01; H, 7.62; S, 4.41. Found: C, 71.28; H, 7.34; S, 4.33.

3f: yield 2.70 g (86%). ^{1}H NMR ($CDCl_3$, ppm): δ 7.50 (2H, d, J = 8.0 Hz, Ar*H*), 7.39 (2H, d, J = 8.0 Hz, Ar*H*), 7.20 (2H, d, J = 2.4 Hz, Ar*H*), 7.15 (2H, d, J = 2.4 Hz, Ar*H*), 6.94 (2H, m, Ar*H*), 6.82 (1H, t, Ar*H*), 6.73 (1H, m, Ar*H*), 6.57 (1H, d, J = 2.4 Hz, Ar*H*), 4.19 (1H, q, J = 6.8 Hz, C*H*), 4.01 (1H, d, J = 12.4 Hz, CH_2Ph), 3.03 (1H, d, J = 12.4 Hz, CH_2Ph), 1.58 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.81 (3H, d, J = 6.8 Hz, CH_3), 0.65 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 158.46, 150.31, 145.35, 144.61, 142.21, 141.70, 136.53, 134.34, 134.14, 132.70, 129.78, 128.80, 128.50, 127.84, 126.86, 126.40, 124.62, 123.86, 121.73, 121.41, 64.78, 35.85, 35.03, 34.97, 34.25, 34.10, 31.95, 31.80, 30.60, 30.12, 19.05. Anal. Calcd for $C_{86}H_{110}Mg_2O_{10}Br_2S_2$: C, 65.53; H, 7.03; S, 4.07. Found: C, 65.15; H, 7.33; S, 4.17.

Alternative Synthetic Procedures for 3f. 1f (1.31 g, 2 mmol) was dissolved in 25 mL of toluene, and the solution was cooled to 0 °C. Benzyl alcohol (0.21 mL, 2 mmol) was added to the above solution with continuous stirring, and 2.2 mmol Mg(^{n}Bu)$_2$ was then added. The mixture was stirred for 24 h at room temperature and then filtered through Celite. Data for **4e**·THF are as follows. ^{1}H NMR ($CDCl_3$, ppm): δ 7.56 (2H, m, Ar*H*), 7.20 (1H, d, J = 2.8 Hz, Ar*H*), 7.15 (1H, d, J = 2.8 Hz, Ar*H*), 7.04 (2H, m, Ar*H*), 6.96−6.91 (2H, m, Ar*H*), 6.93 (1H, d, J = 2.8 Hz, Ar*H*), 6.81 (2H, m, Ar*H*), 6.73 (1H, m, Ar*H*), 6.57 (1H, d, J = 2.8 Hz, Ar*H*), 4.25 (1H, q, J = 7.2 Hz, C*H*), 3.74 (4H, s, OCH_2CH$_2$), 1.85 (4H, s, OCH$_2$CH_2), 1.56 (9H, s, C(CH_3)$_3$), 1.49 (9H, s, C(CH_3)$_3$), 1.27 (9H, s, C(CH_3)$_3$), 0.83(3H, d, J = 7.2 Hz, CH_3), 0.67 (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 158.57, 150.23, 145.23, 144.74, 142.23, 141.84, 136.56, 134.31, 130.26, 130.17, 129.94, 127.78, 126.90, 126.30, 124.66, 123.89, 121.74, 121.38, 116.92, 116.69, 67.97, 64.76, 35.88, 35.04, 35.00, 34.26, 34.12, 31.96, 31.84, 30.63, 30.16, 25.60, 19.04. Anal. Calcd for $C_{94}H_{126}Mg_2O_{12}F_2S_2$·THF: C, 70.62; H, 7.94; S, 4.01. Found: C, 70.42; H, 7.64; S, 3.54.

Typical Polymerization Procedures. A typical polymerization procedure was exemplified by the synthesis of PLLA-200 (the number 200 indicates the designed $[M]_0/[complex]_0$) at 0 °C (Table 1, entry 2). The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. L-Lactide (0.360 g, 2.5 mmol) was added to an ice-cold solution of complex **3a** (0.0180 g, 0.0125 mmol) in CH_2Cl_2 (10 mL). After the solution was stirred at 0 °C for 5 min, the reaction was then quenched by the addition of an aqueous acetic acid solution (0.35 N, 10 mL). *n*-Hexane (40 mL) was then added to the above mixture to give a white crystalline solid. The resulting solid was washed with water twice and then dried under vacuum. Yield: 0.342 g (95%).

X-ray Crystallographic Studies. A summary of the crystallographic data is given in Table 4. Suitable crystals of **2a**−**c**,**e**, **3a**−**c**,**f**, and **4** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and were 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 program SADABS. The space group determination was based on a check of the Laue symmetry and systematic absence and was confirmed using the structure solution. The structures were solved by direct methods using the SHELXTL package. 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 for H atoms.

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Supporting Information Available: A figure giving the homonuclear decoupled ^{1}H NMR spectrum of PLLA-200 and CIF files giving crystallographic data for **2a**−**c**,**e**, **3a**−**c**,**f**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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