Macromolecules **2007,** *40,* 8855−8860 **8855**

Synthesis and Structural Characterization of Magnesium Ketiminate Complexes: Efficient Initiators for the Ring-Opening Polymerization of L-Lactide

Hui-Yi Tang,[†] Hsuan-Ying Chen,[†] Jui-Hsien Huang,[‡] and Chu-Chieh Lin*,[†]

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, Republic of China, and Department of Chemistry, National Changhua University of Education, Changhua 500, Taiwan, Republic of China

Received July 11, 2007; Revised Manuscript Received September 21, 2007

ABSTRACT: A series of dinuclear magnesium complexes of the type $[LMg(\mu\text{-OBn})]_2$ (where L = NNO-tridentate ketiminate ligand) have been prepared. Their activities toward the ring-opening polymerization of L-lactide have been investigated. Experimental results indicate that the reactivity of $[LMg(\mu\text{ -OBn})]_2$ is dramatically affected by the steric and electronic effect of the substituents on the ketiminate ligand. On the basis of the melting point depression and variable-temperature ^1H NMR studies, it is believed that these magnesium complexes exist as an equilibrium between a monomeric and a dimeric species in solution in which the monomeric species is the most active species during polymerization. The polymerization probably proceeds with the coordination of the lactide to the monomeric species giving a five-coordinated magnesium complex as an intermediate.

Introduction

Poly(lactide) (PLA) and its copolymers have been studied intensively because of their potential applications in many fields.[1] Ring-opening polymerization (ROP) of lactide initiated by metal alkoxide precursors has proven to be effective.[2] Many metal complexes such as Al,[3] Li,[4] Mg,[5] Fe,[6] Sn,[7] and Zn[8] have been used as initiators/catalysts for ROP of cyclic esters in literature reports. However, in many cases, backbiting reaction/transesterification takes place as side reactions, resulting in the formation of macrocycles with a wide range of molecular weight distribution. The undesired reactions can be minimized by using a steric bulky ligand coordinatively attached to an active metal center, which provides a steric barrier for prevention of these side reactions. Recently, many coordinately bulky metal complexes have been synthesized to increase a mononuclear active site.[3,7,8]

Ketimine system has been used in a variety of applications; however, its application to ROP is rather rare.[9] Because of the lack of steric effect on one side, the ketiminate ligand is insufficient enough to protect metal complexes from forming a side reaction such as disproportionation, and therefore the so-called "single-side" metal complex containing ketiminate ligands is difficult to achieve. This problem can be compromised by the addition of a pendant functional coordination side, which can be observed in NNO-tridentate aminophenol or Schiff base system.[10] By using the above-mentioned influence on the ketiminate ligand, we report herein the preparation of a series of NNO-tridentate ketimine ligands[11] (Chart 1) and their magnesium derivatives. The catalytic activities of Mg alkoxides with different substituents of NNO-tridentate ketiminate ligand will also be discussed.

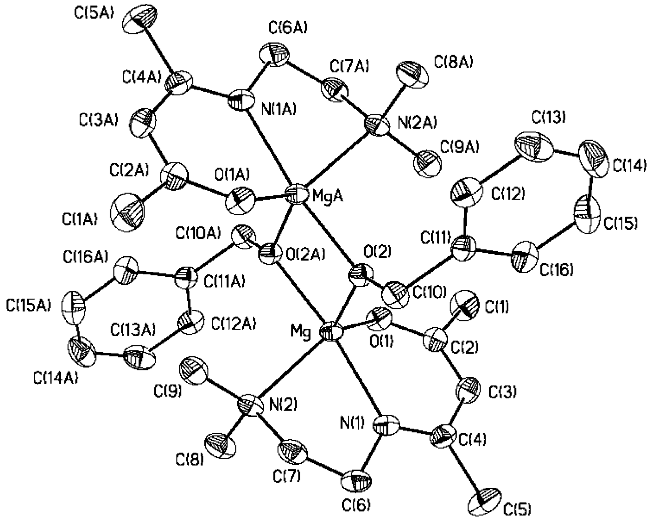
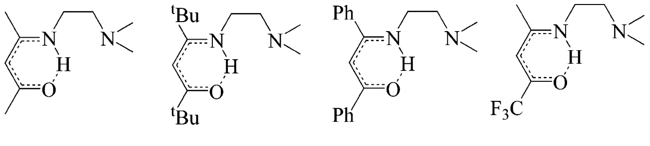


Figure 1. ORTEP drawing of $[L^1Mg(\mu\text{-OBn})]_2$ (**1**) (non-hydrogen atoms) with thermal ellipsoids drawn at the 20% probability level.

Chart 1



L^1H L^2H L^3H L^4H

Results and Discussion

Synthesis and Characterization. Four ketimines (L^1H-L^4H) have been prepared in high yield from the condensation reaction of N^1,N^1-dimethylethane-1,2-diamine with the corresponding 2,4-dione. The reaction of 4-[2-(dimethylamino)ethylamino]-pent-3-en-2-one (L^1H) with Mg^nBu_2 in THF produced a light yellow sticky colloid $[L^1Mg^nBu]_2$. Without isolation, the reaction of the sticky colloid $[L^1Mg^nBu]_2$ with a stoichiometric amount of benzyl alcohol (BnOH) leads to the formation of a magnesium alkoxide complex, $[L^1Mg(\mu\text{-OBn})]_2$ (**1**). Unlike other ketiminato magnesium complexes,[9] $[L^1Mg(\mu\text{-OBn})]_2$ is isolated as a stable complex without disproportionation. This result is probably attributed to strong coordination of the amino group on L^1H to

---

* Corresponding author. E-mail: cchlin@mail.nchu.edu.tw.
[†] National Chung Hsing University.
[‡] National Changhua University of Education.

10.1021/ma071540k CCC: \$37.00

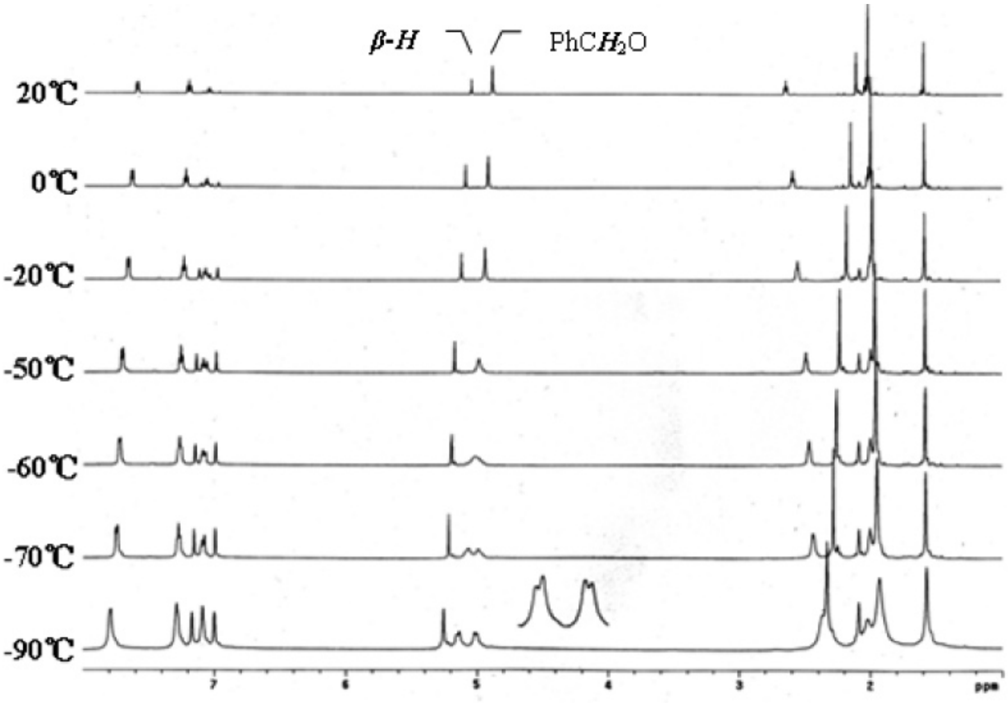
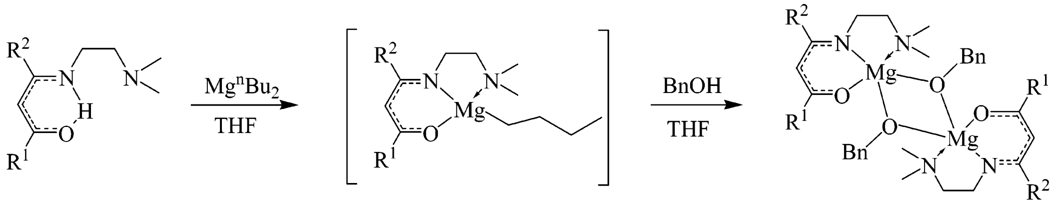


Figure 2. ^{1}H NMR spectrum of $[L^1Mg(\mu\text{-}OBn)]_2$ (**1**) in d_8-toluene with variable temperature.

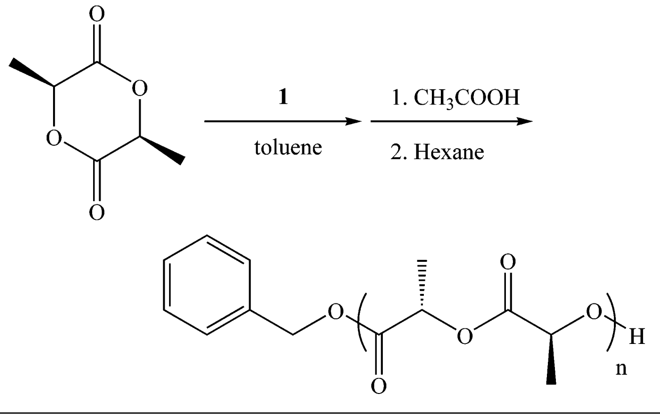
Scheme 1. Preparation of Ketiminate Magnesium Alkoxides



$L^1H : R^1 = CH_3 ;\ R^2 = CH_3$
$L^2H : R^1 = {}^tBu ;\ R^2 = {}^tBu$
$L^3H : R^1 = Ph ;\ R^2 = Ph$
$L^4H : R^1 = CF_3 ;\ R^2 = CH_3$

1 : $R^1 = CH_3 ;\ R^2 = CH_3$
2 : $R^1 = {}^tBu ;\ R^2 = {}^tBu$
3 : $R^1 = Ph ;\ R^2 = Ph$
4 : $R^1 = CF_3 ;\ R^2 = CH_3$

Table 1. Polymerization of L-Lactide Using 1 (2.5 mM) as an Initiator in Toluene (10 mL) at Room Temperature



entry	$[LA]_0/[\mathbf{1}]$	*t* (min)	conv.[a]	M_n(calcd)[b]	M_n(obs)[c]	M_n(NMR)[a]	PDI
1	50	8	97	3600	5500	3900	1.07
2	100	8	95	7000	10 600	7300	1.08
3	150	8	90	9800	16 100	9000	1.17
4	200	8	97	14 100	23 700	15 100	1.10

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA × $[LA]_0/2[\mathbf{1}]$ × conversion yield + M_w(BnOH). [c] Obtained from GPC analysis and calibrated by polystyrene standard.

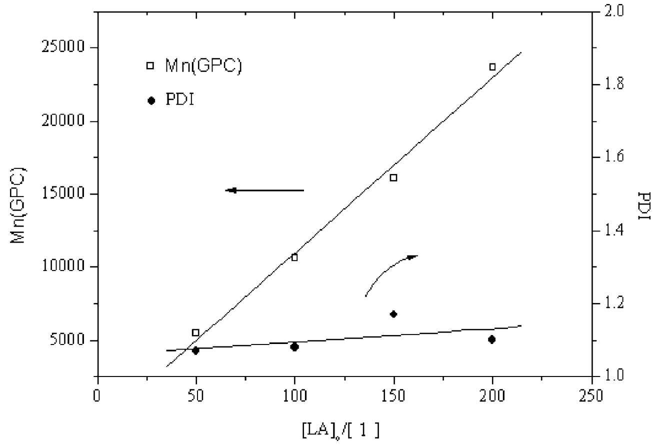


Figure 3. Plot of PLLA M_n (GPC) and molecular weight distribution versus $[LA]_0/[\mathbf{1}]$.

Mg atom and therefore stabilizes the Mg alkoxide complex. The stability of $[L^1Mg(\mu\text{-OBn})]_2$ provides us an opportunity to investigate both the steric and the electronic effect of the substituent on the ketimine toward the ring-opening polymerization of lactides. As a result, $[L^2Mg(\mu\text{-OBn})]_2$ (**2**), $[L^3Mg(\mu\text{-OBn})]_2$ (**3**), and $[L^4Mg(\mu\text{-OBn})]_2$ (**4**) have been synthesized by a method similar to that of **1**, as shown in Scheme 1.

The molecular structure of **1** (Figure 1) reveals a dimeric behavior with two symmetrical pentacoordinated Mg centers bridging through the oxygen atoms of the benzyl alkoxy groups. The geometry around Mg atoms is a distorted trigonal bipyramid with an average compressed axial O(2A)−Mg−N(1) bond angle of 171.59(7)° and equatorial O(1)−Mg−O(2), O(1)−Mg−N(2), and O(2)−Mg−N(2) bond angles of 118.03(10)°, 137.98(10)°, and 103.49(9)°, respectively. The distances from the Mg atom to O(1), O(2), O(2A), N(1), and N(2) are 1.966(2), 1.969(2), 1.990(2), 2.123(3), and 2.262(3) Å, respectively.

Melting Point Depression Study of 1 and 2. The solid-state structure of $[L^1Mg(\mu\text{-OBn})]_2$ (**1**) shows a dimeric behavior. However, whether the dimeric species is the active species during the polymerization or an equilibrium existing between a dimeric and a monomeric species in solution still remained unknown. To figure out which species is the active one, freezing point depression studies of **1** and **2** using naphthalene as the solvent have been performed. The dissociation percentage of the dimeric species can be calculated from the following equation:

$$\Delta T_f = i \times k_f \times C_m$$

in which ΔT_f is the melting point depressed (°C), i is the number of particles measured/number of particles added, k_f is 6.9 °C/m for naphthalene, and C_m is the molality of the solute (m).

Experimental results reveal the activity $i = 1.64 \pm 0.14$ for **1**, indicating the dissociation of 64% of compound **1** from the dimeric species into monomeric species at 80 °C. The activity for **2** is measured as $i = 1.83 \pm 0.04$, illustrating that the existence of compound **2** is ca. 17% as dimeric species and 83% as monomeric species in solution at 80 °C.

^{1}H NMR Variable-Temperature Studies. The ^{1}H NMR spectrum of **1** (Figure 2) in d_8-toluene at 20 °C shows only one set of resonance peaks. While the temperature increases slowly from 20 to 80 °C, the spectrum remains unchanged (Supporting Information Figure 1), indicating that rapid equilibrium between a dimeric and a monomeric species occurs. When the temperature decreases from 20 to −70 °C, the β-H of ketiminate peak remained unchanged as a singlet (only the chemical shift changes from 4.90 to 5.20 ppm). However, peaks at 5.0 ppm corresponding to PhCH_2O became broader and split into two broad peaks, and finally peaks with a doublet of doublet were observed at −90 °C. The result reveals that these two PhCH_2 protons are nonequilibrium at low temperature.

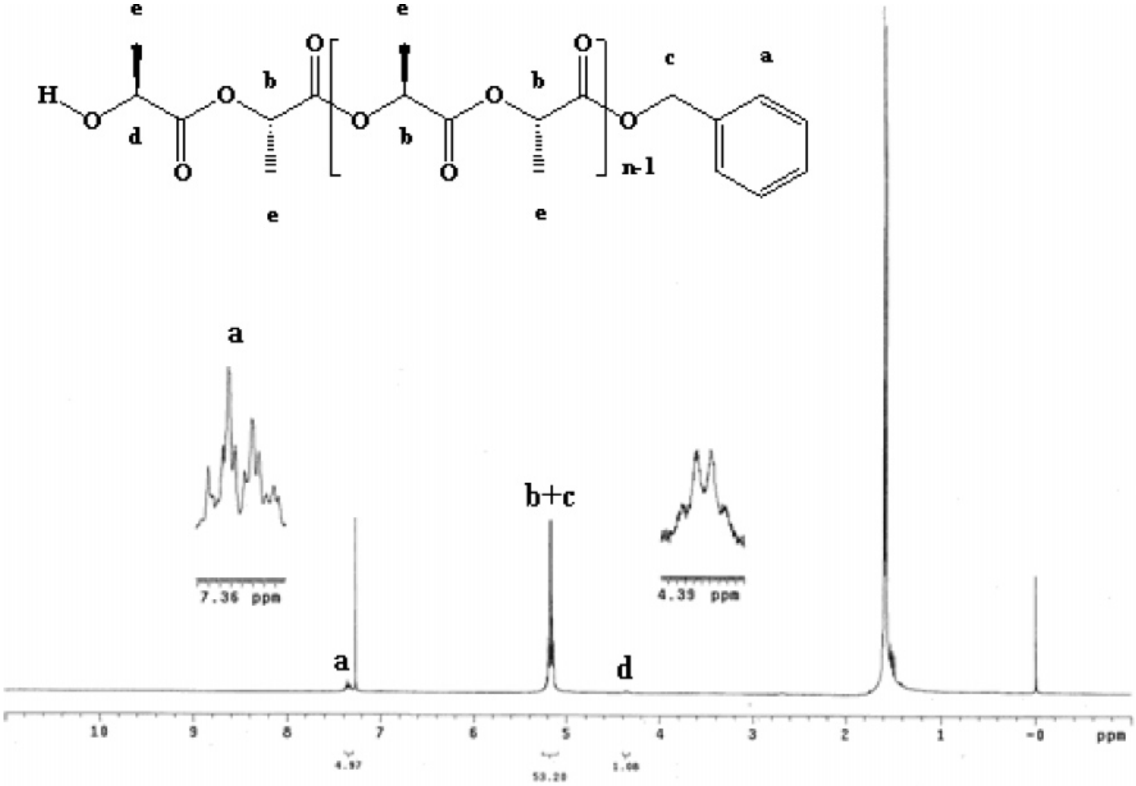


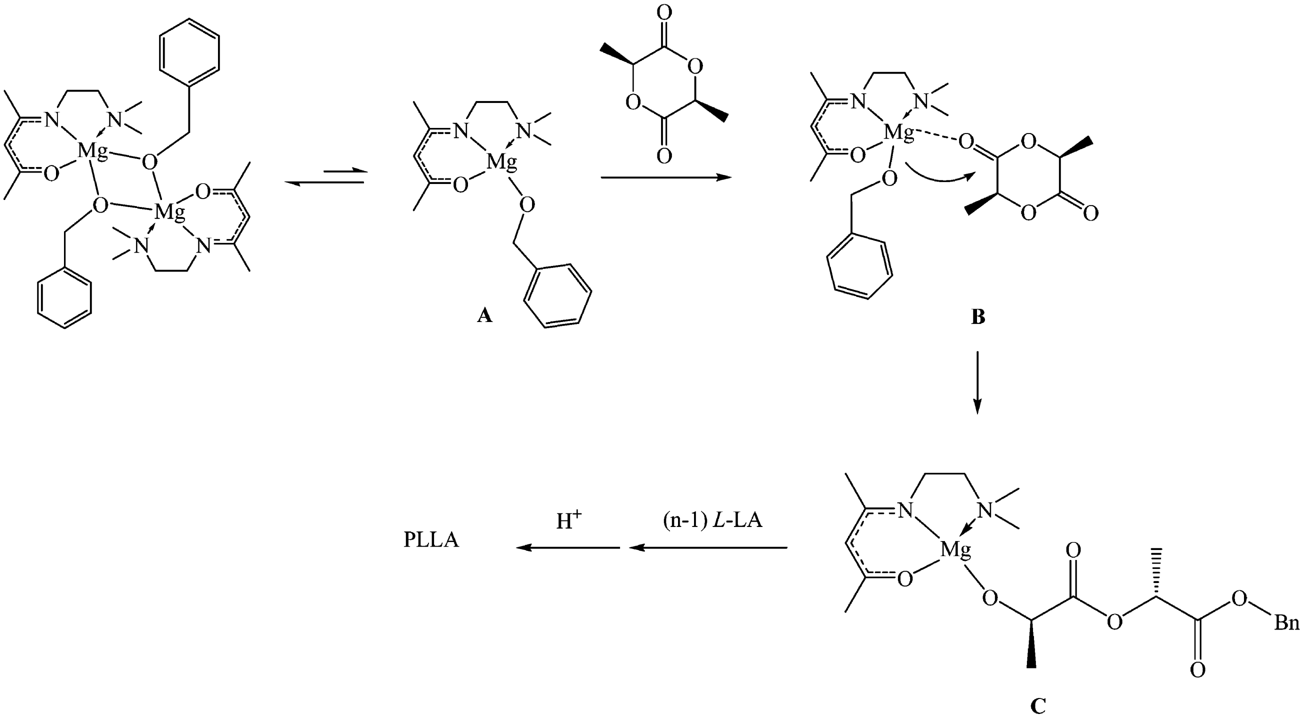
Figure 4. ^{1}H NMR spectrum of PLLA-50 (50 indicates $[LA]_0/[\mathbf{1}]_0 = 50$).

Table 2. Polymerization of L-Lactide (500 mM) Using Mg Ketiminate Complexes (2.5 mM) as an Initiator in Toluene (10 mL) at Room Temperature

entry	initiator	*t* (min)	conv. (%)[a]	M_n(calcd)[b]	M_n(obs)[c]	M_n(NMR)[a]	PDI
1	**1**	8	97	14 100	28 900	15 500	1.13
2[d]	**2**	2	>99	14 500	24 500	14 200	1.46
3	**3**	4	89	12 900	23 000	13 400	1.08
4	**4**	10 h	89	12 900	22 300	13 700	1.15

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA × $[LA]_0/2[\mathbf{1}]$ × conversion yield + M_w(BnOH). [c] Obtained from GPC analysis and calibrated by polystyrene standard. [d] The reaction condition is at 0 °C.

Scheme 2. Proposed Mechanism for the ROP of L-LA Initiated by 1



Polymerization of L-Lactide. Polymerization of L-lactide using **1** (5 mM) as an initiator was systematically investigated in toluene (Table 1). From Table 1, it is found that complex **1** is an efficient initiator for the polymerization of L-lactide. The polymerization goes to completion within 8 min at room temperature. On the basis of the molecular weight of poly(L-lactide) (PLLA) and $[LA]_0/[\mathbf{1}]$ ratio, it is believed that all of these two BnO^- groups have been used as initiators. The linear increase in M_n with conversion and the low polydispersity index (PDI, M_w/M_n) of the polymers revealed that the level of polymerization control was high (Figure 3). The ^{1}H NMR spectrum of PLLA prepared using a $[LA]_0/[\mathbf{1}]$ ratio of 50 showed one benzyl ester and one hydroxy chain end with an integral ratio of 5:1 between H_a and H_d, suggesting that the initiation occurred through the insertion of the benzyl alkoxy group from **1** into L-lactide (Figure 4). When compared to other Mg ketiminate complexes,[9] these designed NNO-type magnesium ketiminate complexes are more active and successful in the polymer molecular weight control.

To realize the steric and electronic effect of the substituent on the ketiminate ligand affecting the activity of Mg complexes, the activities of complexes **2**−**4** toward ROP of L-lactide were also examined (Table 2). Experimental results show that all of these complexes efficiently initiate the polymerization of L-lactide, and the resulting molecular weight of PLLA was obtained as expected with low polydispersity. On the basis of the experimental data, we found that the reactivity varies with different functional groups on the ligand. The reactivity in the order $\mathbf{2} > \mathbf{3} \approx \mathbf{1} \gg \mathbf{4}$ reveals that by replacing the 1,5-dimethyl groups (complex **1**) with a sterically bulkier group such as ^{t}-butyl groups (complex **2**), the reactivity increases dramatically. This can be attributed to that the steric hindrance of ^{t}butyl groups enhances the tendency of forming the monomeric complex, which can be verified by the melting point depressing experiment of **1** and **2**, and therefore increases the rate of polymerization (entry 2). On the other hand, the reactivity decreases substantially by the substitution of 1-methyl group to an electron-withdrawing group such as trifluoromethyl group (entry 4). A reasonable explanation is that ketiminate ligand with electron-withdrawing groups causes magnesium atom to be more acidic, resulting in a stronger Mg−OBn bond, and therefore retards the breaking of the Mg−OBn bond.

On the basis of the variable-temperature ^{1}H NMR studies, melting point depression experiment, and polymerization results, the mechanism for the ROP of L-LA initiated by **1** is proposed as shown in Scheme 2. Although $[L^1Mg(\mu\text{-}OBn)]_2$ is observed as a pentacoordinated dimeric compound in the solid state, it exists as an equilibrium between a dimeric and a monomeric species in solution in which the monomeric species is believed to be the most active one. The coordination of L-lactide to the tetracoordinated monomeric Mg alkoxide (**A**) yields a pentacoordinated intermediate **B**, followed by the insertion of a benzylalkoxy group into L-lactide to produce a new initiator **C**.

Conclusions

A series of NNO-tridentate ketiminate ligands (L^1H−L^4H) and their Mg alkoxide complexes have been synthesized. All of the Mg alkoxides have shown great reactivities toward the controlled polymerization of LA, and the reactivity increases with the help of the steric and electron-donating group on the ketiminate ligand.

Experimental Section

General. All manipulations were carried out under a dry nitrogen atmosphere. Solvents, benzyl alcohol, L-lactide, and deuterated solvents were purified before use. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) or a Varian Mercury-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $\mathrm{CHCl_3}$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent. Molecular weight and polydispersity of PLA were calculated using polystyrene as a standard reference.

Synthesis of [(*Z*)-4-(2-(Dimethylamino)ethylamino)pent-3-en-2-one] ($\mathbf{L^1H}$). A mixture of N^1,N^1-dimethylethane-1,2-diamine (2.2 g, 25 mmol) and 2,4-pentanedione (2 g, 20 mmol) was refluxed in absolute ethanol (100 mL) for 1 day. Volatile materials were removed under vacuum to give a yellow oil. Yield: 3.23 g (95%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 10.85 (1H, br, $\mathrm{N}H$), 4.97 (1H, s, $\mathrm{C}H$), 3.33 (2H, m, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.50 (2H, t, $J = 6.4$ Hz, $\mathrm{NHCH_2C}H_2$), 2.28 (6H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 2.00 (3H, s, $\mathrm{COC}H_3$), 1.94 (3H, s, $\mathrm{C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 194.76 ($C\mathrm{O}$), 162.60 ($\mathrm{CH_3}C\mathrm{CH}$), 95.23 ($C\mathrm{H}$), 58.72 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 45.46 ($\mathrm{N(}C\mathrm{H_3)_2}$), 41.06 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 28.66 ($\mathrm{CO}C\mathrm{H_3}$), 18.88 ($\mathrm{C}C\mathrm{H_3}$).

Synthesis of [(*Z*)-5-(2-(Dimethylamino)ethylamino)-2,2,6,6-tetramethylhept-4-en-3-one] ($\mathbf{L^2H}$). A mixture of N^1,N^1-dimethylethane-1,2-diamine (2.2 g, 25 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (5.09 g, 20 mmol), and benzenesulfonic acid (0.4 mL) was stirred and refluxed in absolute toluene (100 mL) for 3 days. The mixture was then neutralized with NaOH(aq) (0.1 N, 20 mL) and extracted. The organic extractive was dried over anhydrous $\mathrm{MgSO_4}$ and evaporated to oil. Recrystallization from hexane gave colorless crystals. Yield: 2.44 g (48%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 11.53 (1H, br, $\mathrm{N}H$), 5.32 (1H, s, $\mathrm{C}H$), 3.59 (2H, m, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.59 (2H, t, $J = 6.4$ Hz, $\mathrm{NHCH_2C}H_2$), 2.31 (6H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.29 (9H, s, $\mathrm{C(C}H_3\mathrm{)_3}$), 1.15 (9H, s, $\mathrm{CO(C}H_3\mathrm{)_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 203.56 ($C\mathrm{O}$), 173.44 ($\mathrm{(CH_3)_3C}C\mathrm{CH}$), 86.45 ($C\mathrm{H}$), 59.46 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 45.63 ($\mathrm{N(}C\mathrm{H_3)_2}$), 43.72 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 41.63 ($\mathrm{CO}C\mathrm{(CH_3)_3}$), 36.01 ($\mathrm{(CH_3)_3}C\mathrm{C}$), 29.00 ($\mathrm{(}C\mathrm{H_3)_3CC}$), 28.04 ($\mathrm{COC(}C\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{15}H_{30}N_2O}$: N, 11.01; C, 70.86; H, 11.89. Found: N, 10.58; C, 69.69; H, 12.06. Mp: 36−38 °C. Mass spectrum (EI, *m*/*e*): 254.3 ($\mathrm{M^+}$, 0.87%).

Synthesis of [(*Z*)-3-(2-(Dimethylamino)ethylamino)-1,3-diphenylprop-2-en-1-one] ($\mathbf{L^3H}$). A mixture of N^1,N^1-dimethylethane-1,2-diamine (2.2 g, 25 mmol), dibenzoylmethane (4.49 g, 20 mmol), and benzenesulfonic acid (0.4 mL) was refluxed in absolute toluene (100 mL) for 3 days. The mixture was then neutralized with NaOH(aq) (0.1 N, 20 mL) and extracted. The organic extractive was dried over anhydrous $\mathrm{MgSO_4}$, and the solution was evaporated to about 10 mL. Light yellow powder was obtained by the addition of an excess of hexane. Yield: 4.30 g (73%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 11.36 (1H, br, $\mathrm{N}H$), 7.90−7.88 (2H, m, $\mathrm{Ar}H$), 7.45−7.35 (8H, m, $\mathrm{Ar}H$), 5.76 (1H, s, $\mathrm{C}H$), 3.29 (2H, m, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.47 (2H, t, $J = 6.4$ Hz, $\mathrm{NHCH_2C}H_2$), 2.21 (6H, s, $\mathrm{N(C}H_3\mathrm{)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 188.21 ($C\mathrm{O}$), 166.35 ($\mathrm{CH_3}C\mathrm{CH}$), 144.23, 135.69, 130.46, 129.26, 128.38, 127.98, 127.52, 126.93 (Ar), 93.35 ($C\mathrm{H}$), 59.28 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 45.38 ($\mathrm{N(}C\mathrm{H_3)_2}$), 42.67 ($\mathrm{NH}C\mathrm{H_2CH_2}$). Anal. Calcd for $\mathrm{C_{19}H_{22}N_2O}$: N, 9.52; C, 77.52; H, 7.53. Found: N, 9.72; C, 77.51; H, 7.02. Mp: 84−86 °C. Mass spectrum (EI, *m*/*e*): 294.2 ($\mathrm{M^+}$, 2.17%).

Synthesis of (*Z*)-4-(2-(Dimethylamino)ethylamino)-1,1,1-trifluoropent-3-en-2-one ($\mathbf{L^4H}$). A mixture of N^1,N^1-dimethylethane-1,2-diamine (2.2 g, 25 mmol) and 1,1,1-trifluoro-2,4-pentanedione (3.08 g, 20 mmol) was stirred and refluxed in absolute diethylether (100 mL) for 1 day. Volatile materials were removed under vacuum to give a red liquid. Yield: 4.21 g (94%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 11.10 (1H, br, $\mathrm{N}H$), 5.25 (1H, s, $\mathrm{C}H$), 3.36 (2H, m, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.48 (2H, t, $J = 6.0$ Hz, $\mathrm{NHCH_2C}H_2$), 2.22 (6H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 2.03 (3H, s, $\mathrm{COC}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 169.01($C\mathrm{O}$), 119.07 ($\mathrm{CH_3}C\mathrm{CH}$), 116.20 ($C\mathrm{F_3}$), 89.07 ($C\mathrm{H}$), 57.52 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 45.11 ($\mathrm{N(}C\mathrm{H_3)_2}$), 41.50 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 19.39 ($\mathrm{CO}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_9H_{15}F_3N_2O}$: N, 12.49; C, 48.21; H, 6.74. Found: N, 12.30; C, 47.88; H, 6.62. Mass spectrum (EI, *m*/*e*): 224.1 ($\mathrm{M^+}$, 2.74%).

Synthesis of $\mathbf{[L^1MgOBn]_2}$ (1). To a rapidly stirred suspension of ($\mathrm{L^1H}$) (0.85 g, 5.0 mmol) in THF (40.0 mL) was slowly added $\mathrm{Mg}^n\mathrm{Bu_2}$ (5.5 mL, 5.5 mmol). The mixture was stirred at 0 °C for 3 h, giving a clear dark yellow solution. Volatile materials were removed under vacuum to yield an orange red oily compound, which was then redissolved in THF (40.0 mL). BnOH (0.525 mL, 5.0 mmol) was added to the THF solution, and the mixture was stirred at 0 °C for 3 h. The solution was then evaporated to dryness to yield a yellow powder. The resulting powder was redissolved in THF (15.0 mL), and 40.0 mL of hexane was added into the THF solution. Yellowish turbidity was observed while the mixture was stirred. The resulting yellow powder was collected by filtration and dried in vacuo. Yield: 1.10 g (73%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 7.43 (4H, d, $J = 4.8$ Hz, $\mathrm{Ar}H$), 7.19 (4H, t, $J = 4.8$ Hz, $\mathrm{Ar}H$), 7.09 (2H, t, $J = 4.8$ Hz, $\mathrm{Ar}H$), 4.91 (2H, s, $\mathrm{C}H$), 4.69 (4H, s, $\mathrm{OC}H_2\mathrm{Ar}$), 2.90 (4H, t, $J = 4.4$ Hz, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.22 (4H, t, $J = 4.4$ Hz, $\mathrm{NHCH_2C}H_2$), 2.15 (12H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.93 (6H, s, $\mathrm{COC}H_3$), 1.73 (6H, s, $\mathrm{C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 180.49 ($C\mathrm{O}$), 171.38 ($\mathrm{CH_3}C\mathrm{CH}$), 147.36, 127.62, 127.47, 125.62 ($\mathrm{Ar}C$), 96.98 ($\mathrm{CH_3C}C\mathrm{H}$), 66.57 ($\mathrm{O}C\mathrm{H_2Ar}$), 58.15 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 46.21 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 44.77 ($\mathrm{N(}C\mathrm{H_3)_2}$), 27.21 ($\mathrm{CO}C\mathrm{H_3}$), 21.31 ($\mathrm{C}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{32}H_{48}Mg_2N_4O_4}$: N, 9.32; C, 63.91; H, 8.05. Found: N, 9.39; C, 63.88; H, 8.02. Mp: 122−124 °C.

Synthesis of $\mathbf{[L^2MgOBn]_2}$ (2). This was done using a method similar to that for $\mathrm{[L^1MgOBn]_2}$ but $\mathrm{L^2H}$ was used as reagent and $\mathrm{[L^2MgOBn]_2}$ was obtained as a white powder. Yield: 1.57 g (84%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 7.45 (4H, d, $J = 7.2$ Hz, $\mathrm{Ar}H$), 7.19 (4H, t, $J = 7.2$ Hz, $\mathrm{Ar}H$), 7.08 (2H, t, $J = 7.2$ Hz, $\mathrm{Ar}H$), 5.27 (2H, s, $\mathrm{C}H$), 4.85 (4H, dd, $J = 11.2$ Hz, $\mathrm{OC}H_2\mathrm{Ar}$), 3.40 (4H, t, $J = 5.2$ Hz, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.26 (4H, q, $J = 5.2$ Hz, $\mathrm{NHCH_2C}H_2$), 2.16 (12H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.25 (18H, s, $\mathrm{C(C}H_3\mathrm{)_3}$), 1.07 (18H, s, $\mathrm{CO(C}H_3\mathrm{)_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 189.99 ($C\mathrm{O}$), 178.19 ($\mathrm{CH_3}C\mathrm{CH}$), 147.69, 127.53, 126.56, 125.06 ($\mathrm{Ar}C$), 88.17 ($\mathrm{CH_3}C\mathrm{CH}$), 66.04 ($\mathrm{O}C\mathrm{H_2Ar}$), 61.06 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 46.24 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 45.85 ($\mathrm{N(}C\mathrm{H_3)_2}$), 40.46 ($\mathrm{CO}C\mathrm{(CH_3)_3}$), 39.03 ($\mathrm{(CH_3)_3}C\mathrm{C}$), 30.11 ($\mathrm{(}C\mathrm{H_3)_3CC}$), 29.48 ($\mathrm{COC(}C\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{44}H_{72}Mg_2N_4O_4}$: N, 7.28; C, 68.66; H, 9.43. Found: N, 6.98; C, 68.21; H, 9.43. Mp: 180−182 °C.

Synthesis of $\mathbf{[L^3MgOBn]_2}$ (3). This was done using a method similar to that for $\mathrm{[L^1MgOBn]_2}$ but $\mathrm{L^3H}$ was used as reagent and $\mathrm{[L^3MgOBn]_2}$ was collected as a yellow powder. Yield: 1.80 g (85%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 8.04 (4H, d, $J = 6.8$ Hz, $\mathrm{Ar}H$), 7.61 (4H, d, $J = 7.6$ Hz, $\mathrm{Ar}H$), 7.44−7.25 (16H, m, $\mathrm{Ar}H$), 7.14 (2H, t, $J = 7.2$ Hz, $\mathrm{Ar}H$), 7.07 (4H, d, $J = 6.4$ Hz, $\mathrm{Ar}H$), 5.76 (2H, s, $\mathrm{C}H$), 5.05 (4H, s, $\mathrm{OC}H_2\mathrm{Ar}$), 2.96 (4H, t, $J = 5.6$ Hz, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.21 (4H, t, $J = 5.6$ Hz, $\mathrm{NHCH_2C}H_2$), 2.12 (12H, s, $\mathrm{N(C}H_3\mathrm{)_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 175.06 ($C\mathrm{O}$), 173.79 ($\mathrm{CH_3}C\mathrm{CH}$), 142.07, 141.33, 128.65, 128.48, 128.10, 127.95, 127.68, 127.62, 127.07, 126.73, 126.70, 125.78 ($\mathrm{Ar}C$), 95.47 ($\mathrm{CH_3C}C\mathrm{H}$), 66.67 ($\mathrm{O}C\mathrm{H_2Ar}$), 59.47 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 47.10 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 45.10 ($\mathrm{N(}C\mathrm{H_3)_2}$). Anal. Calcd for $\mathrm{C_{52}H_{56}Mg_2N_4O_4}$: N, 6.59; C, 73.51; H, 6.64. Found: N, 6.16; C, 72.92; H, 6.67. Mp: 264−266 °C.

Synthesis of $\mathbf{[L^4MgOBn]_2}$ (4). This was done using a method similar to that for $\mathrm{[L^1MgOBn]_2}$ but $\mathrm{L^4H}$ was used as reagent and $\mathrm{[L^4MgOBn]_2}$ was obtained as a white powder. Yield: 0.55 g (31%). ^{1}H NMR ($\mathrm{CDCl_3}$, ppm): δ 7.39 (4H, d, $J = 7.2$ Hz, $\mathrm{Ar}H$), 7.21 (4H, t, $J = 7.2$ Hz, $\mathrm{Ar}H$), 7.11 (2H, t, $J = 7.2$ Hz, $\mathrm{Ar}H$), 5.33 (2H, s, $\mathrm{C}H$), 4.65 (4H, s, $\mathrm{OC}H_2\mathrm{Ar}$), 2.95 (4H, t, $J = 6.0$ Hz, $\mathrm{NHC}H_2\mathrm{CH_2}$), 2.33 (4H, t, $J = 6.4$ Hz, $\mathrm{NHCH_2C}H_2$), 2.16 (12H, s, $\mathrm{N(C}H_3\mathrm{)_2}$), 1.83 (6H, s, $\mathrm{C}H_3$). ^{13}C NMR ($\mathrm{CDCl_3}$, ppm): δ 173.03 ($C\mathrm{O}$), 162.18 ($J_{\mathrm{C-F}} = 80.8$ Hz, $\mathrm{CH_3}C\mathrm{CH}$), 146.72, 127.85, 127.39, 125.98 ($\mathrm{Ar}C$), 120.49 ($J_{\mathrm{C-F}} = 752.4$ Hz, $\mathrm{CO}C\mathrm{F_3}$), 94.57 ($\mathrm{CH_3C}C\mathrm{H}$), 66.54 ($\mathrm{O}C\mathrm{H_2Ar}$), 57.42 ($\mathrm{NHCH_2}C\mathrm{H_2}$), 45.42 ($\mathrm{NH}C\mathrm{H_2CH_2}$), 44.79 ($\mathrm{N(}C\mathrm{H_3)_2}$), 21.66 ($\mathrm{C}C\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{33}H_{45}F_6Mg_2N_4O_4}$: N, 7.90; C, 54.19; H, 5.97. Found: N, 8.46; C, 54.07; H, 5.57. Mp: 146−148 °C.

Melting Point Depression Measurement. [$L^1Mg(\mu$-OBn)]$_2$ (**1**) (0.8 g, 1.30 mmol) was dissolved in hot naphthalene (3.2 g). The freezing point of the mixture was measured by slowly cooling the mixture, and the temperature was recorded once every 30 s using a Beckman thermometer, which was corrected prior to use. This procedure was repeated three times. Melting point depression of [$L^2Mg(\mu$-OBn)]$_2$ (**2**) (0.8 g, 1.02 mmol) was measured in a similar procedure.

Typical Polymerization Procedures. A typical polymerization procedure was exemplified by the synthesis of entry 1 (Table 1) using [$L^1Mg(\mu$-OBn)]$_2$ as an initiator at 25 °C. The conversion yield (97%) of PLA was analyzed by ^{1}H NMR spectroscopic studies. A mixture of [$L^1Mg(\mu$-OBn)]$_2$ (0.015 g, 0.025 mmol) and L-lactide (0.18 g, 1.25 mmol) in toluene (10 mL) was stirred at 20 °C for 8 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 white crystalline solids. Yield: 0.11 g (61%).

X-ray Crystallographic Studies. Suitable crystals of **1** 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 θ (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program. 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. 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.

Acknowledgment. Financial support from the National Science Council of the Republic of China is gratefully appreciated.

Supporting Information Available: Crystallographic data of **1** (Table 1) and variable-temperature ^{1}H NMR spectrum of **1** (Figure 1). This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This article was published ASAP on November 8, 2007. Schemes 1 and 2 and the Table of Contents graphic have been modified. The correct version was published on November 12, 2007.

References and Notes

(1) (a) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982. (b) Duda, A.; Florjanczyk, Z.; Hofman, A.; Slomkowski, S.; Penczek, S. *Macromolecules* **1990**, *23*, 1640. (c) Kowalski, A.; Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1998**, *19*, 567. (d) Gan, Z.; Jim, T. F.; Jim, M.; Yuer, Z.; Wang, S.; Wu, C. *Macromolecules* **1999**, *32*, 1218. (e) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G., Jr.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400. (f) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072. (g) Chen, X.; Gross, R. A. *Macromolecules* **1999**, *32*, 308. (h) Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature (London)* **1997**, *388*, 860. (i) Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskov, V.; Torchilin, V.; Langer, R. *Science* **1994**, *263*, 1600.

(2) (a) O'Keefe, B. J. M. A.; Tolman, W. B. *Dalton Trans.* **2001**, 2215. (b) Cabaret, O. D.; Vaca, B. M.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (c) Wu, J.-C.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602.

(3) (a) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (b) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. *Macromolecules* **2001**, *34*, 356. (c) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196. (d) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076. (e) Hsueh, M.-L.; Huang, B.-H.; Lin, C.-C. *Macromolecules* **2002**, *35*, 5763. (f) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291. (g) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552. (h) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (i) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026. (j) Chakraborty, D.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 1438. (k) Li, H.; Wang, C.; Bai, F.; Yue, J.; Woo, H.-G. *Organometallics* **2004**, *23*, 1411. (l) Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382. (m) Lewiński, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (n) Lewiński, J.; Horeglad, P.; Wójcik, K.; Justyniak, I. *Organometallics* **2005**, *24*, 4588. (o) Chisholm, M. H.; Patmore, N. J.; Zhou, Z. *Chem. Commun.* **2005**, 127. (p) Lewiński, J.; Horeglad, P.; Tratkiewicz, E.; Grzenda, W.; Lipkowski, J.; Kolodziejczyk, E. *Macromol. Rapid Commun.* **2004**, *25*, 1939.

(4) (a) Kricheldorf, H. R. *Makromol. Chem.* **1993**, *194*, 1665. (b) Ko, B.-T.; Lin, C.-C. *J. Am. Chem. Soc.* **2001**, *123*, 7973. (c) Chisholm, M. H.; Lin, C.-C.; Galluccia, J. C.; Ko, B.-T. *Dalton Trans.* **2003**, 406.

(5) (a) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286. (b) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845. (c) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Inorg. Chem.* **2002**, *41*, 2785. (d) Chisholm, M. H.; Phomphrai, K. *Inorg. Chim. Acta* **2003**, *350*, 121. (e) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229. (f) Marshall, E. L.; Gibson, V. C.; Rzepa, H. S. *J. Am. Chem. Soc.* **2005**, *127*, 6048 (g) Ejfler, J.; Kobyłka, M.; Jerzykiewicz, L. B.; Sobota, P. *Dalton Trans.* **2005**, 2047.

(6) (a) O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384. (b) Duda, A.; Penczek, S. In *Polymers from Renewable Resources: Biopolyesters and Biocatalysis*; Scholz, C., Gross, R. A., Eds.; ACS Symposium Series Vol. 764; American Chemical Society: Washington, DC. (c) Dobrzynski, P.; Kasperczyk, J.; Janeczek, M.; Bero, M. *Polymer* **2002**, *43*, 2595. (d) Wang, X.; Liao, K.; Quan, D.; Wu, Q. *Macromolecules* **2005**, *38*, 4611.

(7) (a) Kricheldorf, H. R.; Sumbbl, M. V.; Saunders, I. K. *Macromolecules* **1991**, *24*, 1944. (b) Aubrecht, K. B.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2002**, *35*, 644. (c) Amsden, B.; Wang, S.; Wyss, U. *Biomacromolecules* **2004**, *5*, 1399. (d) Nimitsiriwat, N.; Marshall, E. L.; Gibson, V. C.; Elsegood, M. R. J.; Dale, S. H. *J. Am. Chem. Soc.* **2004**, *126*, 13598.

(8) (a) Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Int.* **1998**, *46*, 177. (b) Bero, M.; Kasperczyk, J.; Jedliski, Z. *Macromol. Chem.* **1990**, *191*, 2287. (c) Bero, M.; Kasperczyk, J.; Adamus, G. *Macromol. Chem.* **1993**, *194*, 907. (d) Chen, H.-Y.; Tang, H.-Y.; Lin, C.-C. *Macromolecules* **2006**, *39*, 3745.

(9) (a) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450. (b) Lee, W.-Y.; Hsieh, H.-H.; Hsieh, C.-C.; Lee, H. M.; Lee, G.-H.; Huang, J.-H.; Wu, T.-C.; Chuang, S.-H. *J. Organomet. Chem.* **2007**, *692*, 1131.

(10) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.

(11) Becht, M.; Gerfin, T.; Dahmen, K.-H. *Helv. Chim. Acta* **1994**, *77*, 1288.

MA071540K