RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/cOxxOOOOOx

www.rsc.org/xxxxxx

PAPER

Magnesium Complexes Bearing N, N-Bidentate Phenanthrene Derivatives for the Stereoselective Ring-Opening Polymerization of *rac*-Lactides

Bo Gao[*1,2], Dehai Zhao[1,2], Xiang Li[2], Yuan Cui[*1,2], Ranlong Duan[2], Xuan Pang[2]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Three unreported magnesium complexes bearing N, N-bidentate phenanthrene derivatives derived from Schiff base were synthesized. These complexes were characterized by ^{1}H, ^{13}C NMR and elemental analyses and employed for *rac*-lactide and L-lactide polymerization. Complex **1** uncovered the highest activity among these Mg complexes for the ring-opening polymerization (ROP) of L-lactide, and complex **3** showed the highest stereoselectivity for the ROP of *rac*-lactide achieving partially heterotactic polylactide (PLA) with a P_r of 0.76. The polymerization kinetics utilizing **2** as a catalyst was researched in detail. The kinetics of the polymerization data revealed that the rate of polymerization was first-order as to monomer, and had an order of 0.97 as to catalyst. There was a linear relationship between the L-lactide conversion and the number-average molecular weight of PLA.

Introduction

Biodegradable and biocompatible polymers have been exploited for a wide field of applications such as sutures, disposal containers, bone fracture fixation devices, controlled release drug carriers, scaffolds, textiles and tissue engineering.[1, 2] Especially, polylactide (PLA) derived from lactic acid, which is a renewable resource, has proved to be one of the most promising polyesters exhibiting having biological degradation.[2] Presence of two chiral centers in the lactide monomer results in the different lactide stereoisomers, namely L-lactide (L-LA), D-lactide (D-LA) and meso-lactide (Fig. 1). The stereochemistry of the polymer chains influence PLA's physical and chemical properties.[1b] Commonly, PLA is synthesized by the ring-opening polymerization (ROP) of lactide that initiated by metal complexes, such as some alkoxides of Sn,[3] Al,[4, 13, 14] Zn,[5] Mg,[6] Fe,[7] Ti,[8] In,[9] rare-earth metals,[10] organo-catalysts,[11] and enzymes.[12] Among them, biocompatible zinc and magnesium provoke researchers' attentions because they are essential nutrients and minerals for plants and humans.[1h] Moreover, zinc and magnesium catalysts were highly effective initiators employed for ROP of PLA[5]. In this context, our group had reported some zinc complexes derived from β-diketone ligands.[5i] These complexes proved to be highly effective single-site living initiators for the well-controlled ROP of lactides. Furthermore, the more sterically hindered zinc catalysts offered effective control of the polymer microstructures in the ROP of *rac*-lactide. In the past twenty years, many efforts had been made for the selection of proper ancillary ligands for enhancing the performance of initiators in polymerizations. A number of research workers had tried to expound the relation among *rac*-lactide (*rac*-LA), the metal complexes and tacticity of polymers (see Fig. 2). [13, 14]

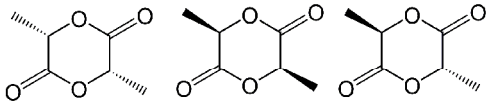


Figure 1. Stereoisomers of lactides.

However, to our knowledge, few researches on magnesium complexes bearing diamido derivatives derived from phenanthrene Schiff base derivatives (see Scheme 1) have been investigated for the stereoselective ROP of *rac*-LA. Based on the efficient uses of magnesium complexes,[1h, 6b, 6d, 6e] we believed this magnesium complex brearing N, N-bidentate diamido ligands might be potential catalyst for the ROP of *rac*-LA. In this work, the preliminary results of preparation of magnesium complexes bearing phenanthrene derivatives and their use as initiators to polymerize *rac*-LA in a controlled measure were reported.

Result and discussion

Synthesis of the pro-ligands

As shown in Scheme 1, pro-ligands $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$ were prepared in middling yields (35.2 − 64.7%) by the condensation reaction between phenanthraquinone and modified aniline *via* catalysis with titanic chloride and dabco in toluene according to the literature.[15] The ^{1}H NMR spectra of pro-ligands displayed that there were two sets of signals that can be assigned to two different *ortho* substituents at the phenyl rings. For example, the resonances δ 1.07 and 0.74 ppm in the ^{1}H NMR spectrum of pro-ligand $\mathbf{L_2}$ were assigned

to the two sets of primary protons from the ethyls (see Fig. 3) It revealed that these ligands possess *Z/E* configuration.[16] A similar situation was also reported in the Ar', Ar-BIAN ligands.[17]

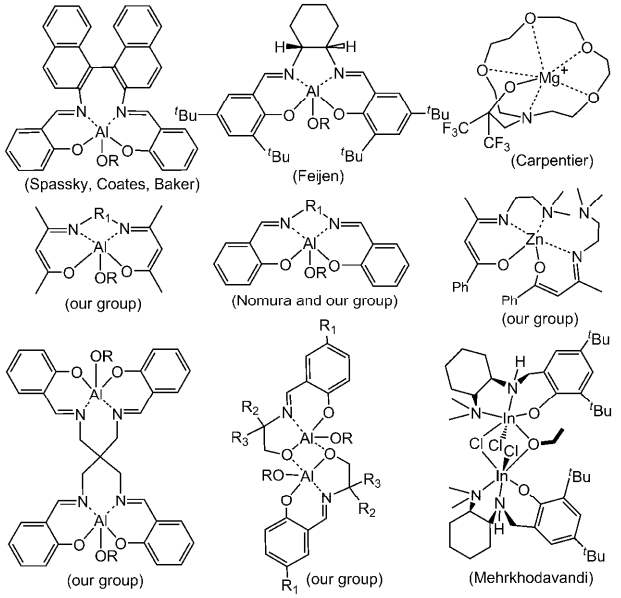
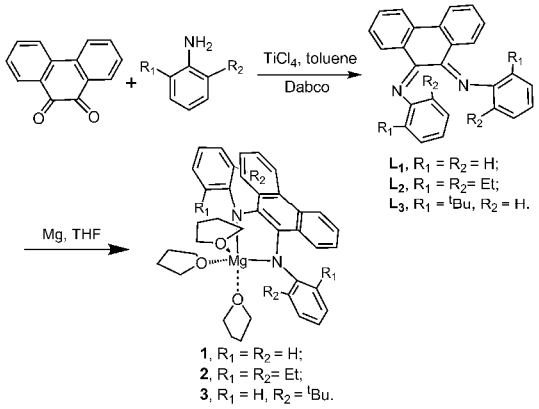


Figure 2. Initiators for stereoselective ROP of lactide.



Scheme 1. Synthesis of pro-ligands and Mg complexes.

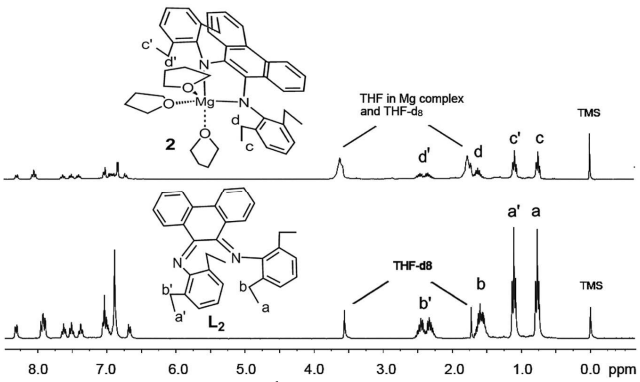


Figure 3. Stacked 400 MHz ^{1}H NMR spectra of pro-ligand $\mathbf{L_2}$ and complex **2**, in THF-d_8.

Synthesis of magnesium complexes

As shown in Scheme 1, Mg complexes **1** − **3** were prepared easily in high yields (84.7 − 95.6%) by combining magnesium with corresponding pro-ligands in a glovebox and were isolated as red solids from THF. The magnesium was activated by iodine and rinsed with THF for three times. All three complexes were sensitive to air and moisture. Complexes **1** − **3** were characterized by ^{1}H and ^{13}C NMR in THF-d_8 at room temperature and elemental analysis. The ^{1}H and ^{13}C NMR spectra of complexes **1** − **3** showed one ligand and three THF molecules were coordinated to magnesium in these complexes. For instance, the resonances (δ 3.58 and 1.73 ppm) in the ^{1}H NMR spectrum of complex **2** were assigned to the secondary protons in three THF molecules coordinating to complex **2** (see Fig. 3). Interestingly, the ^{1}H NMR spectra of **1**–**3** revealed that the phenyl groups of the ligands in these complexes were inequivalent. For example, two groups of resonances from ethyls (δ 2.52 – 2.18, 1.58, 1.05, 0.71 ppm) are observed in the ^{1}H NMR spectrum (see Fig. 3). It appeared the geometry of **2** in solution was "b" rather than "a" possibilities (Fig. S1), *i.e.* the Mg atom in **2** exhibits a trigonal bipyramidal geometry and the two N donors occupied axial and equatorial positions. It was consistent with the single crystal structure of **2** in solid state. Similar configurations also appeared in salan aluminium complexes.[13e] The geometry of complex **2** in solid state was confirmed *via* X-ray diffraction analysis. The molecular structure is depicted in Fig. 4. The selected bond distances and angles and other crystallographic data are listed in Table 1 and Table S1, respectively. X-ray structural analysis revealed that complex **2** was mononuclear and the central magnesium atom was coordinated by two N atoms and three O atoms. In complex **2** (see Table 1), the Mg1–O1 bond length, 2.161(2) (Å), was the longest among these bond lengths; N1–Mg1–O2, N1–Mg1–N2, N2–Mg1–O3 and O2–Mg1–O3 angles were 116.10(10), 80.60(10), 96.62(10) and 110.67(9) °, respectively. The quantity of the distortion can be calculated by structural index parameter τ.[18] The τ values range from 0 (perfectly square pyramidal) to 1 (perfectly trigonal bipyramidal). For complex **2**, the τ value was 0.59, which suggested the magnesium was in distorted trigonal bipyramidal environment. The C–N bond average distance of 1.397 Å for **2** (see Table 1) approximated that of 1.390 Å in BIAN magnesium complex **1** [19] reported previously. It showed that the ligand bonded in a dianionic diamino manner. In other words, the pro-ligand was a Schiff base, but upon reaction with Mg, oxidative addition occured where Mg (0) was oxidized to Mg (2+) and the Schiff base was reduced to a diamido ligand. Hence, the Mg complex should be referred to as diamido magnesium complex.

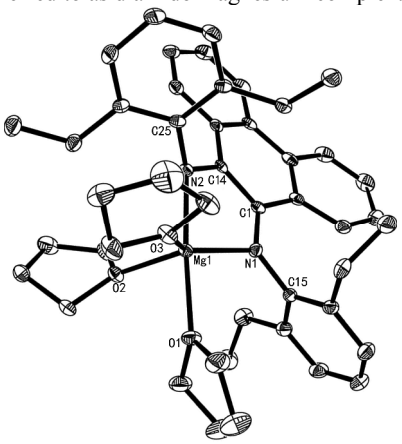


Figure 4. Perspective view of **2** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

Lactide Polymerization

All magnesium complexes were studied as catalysts for the ROP of L-LA or *rac*-LA. The polymerization reactions were performed in tetrahydrofuran or toluene, and the representational polymerization data were recorded in Table 2. These magnesium complexes showed moderate to high activities (87.8 – 97.7% monomer conversion) with the co-catalysis of isopropanol at 70 °C. ^{1}H NMR and GPC were used to confirm the M_n values of the PLA. The number-averaged molecular weights (measured by ^{1}H NMR [20]) were close to theoretical values (calculated from the monomer/ magnesium complexes molar ratio). The activities of these complexes declined accompanying the raise of substituent bulk on the phenyl rings. Among the three complexes, the monomer conversion for complex **1** was the highest under the same conditions (see Fig. 5, Table 2, Entries 1, 2, 3, 4, 5 and 6).

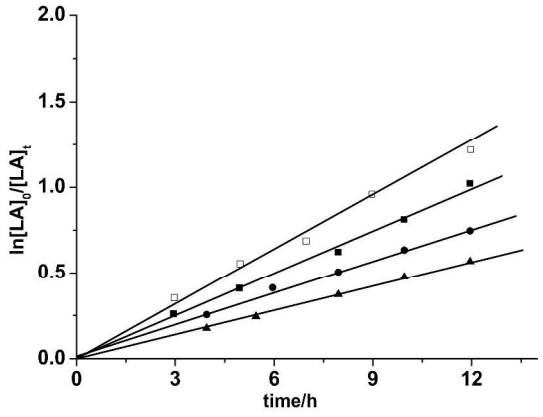


Figure 5. Kinetics of the ROP of L-LA by **2** with isopropanol at 40 °C in THF with ([LA]$_0$ = 0.5 mol L^{-1}; $k_p = k_{app}$/[cat.]$_0$. ■: L-LA, [cat.]$_0$ = 0.005 mol L^{-1}, k_{app} = 82.5 × 10^{-3} h^{-1}; □: L-LA, [cat.]$_0$ = 0.0067 mol L^{-1}, k_{app} = 107.6 × 10^{-3} h^{-1}; ●: L-LA, [cat.]$_0$ = 0.004 mol L^{-1}, k_{app} = 65.8 × 10^{-3} h^{-1}; ▲: L-LA, [cat.]$_0$ = 0.0033mol L^{-1}, k_{app} = 53.7 × 10^{-3} h^{-1}.

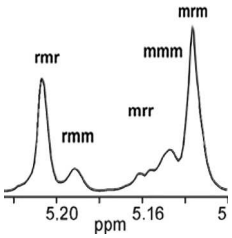


Figure 6. Homonuclear decoupled ^{1}H NMR spectrum of the methine part of poly(*rac*-LA) by complex **3** at 25 °C, P_r = 0.76, (Table 2, Entry 16, 400 MHz, $CDCl_3$).

Stereoselective polymerization

We have also studied the poly(*rac*-LA) (Table 2, Entry 16) with the homonuclear decoupled ^{1}H NMR spectrum of the methane fragment[21] (see Fig. 6). The P_r[22] value, 0.76, certified that these polymer chains were heterotactic enriched. The results indicated that the P_r selectivities increased from 0.51 to 0.58 with the raise of the bulk of the substitutes on pro-ligands (from hydrogen atoms to *tert*-butyls on phenyl rings) at 70 °C (see Table 2, Entries 10, 12). The stereo-regularity of the poly(*rac*-LA) was also affected by the reaction temperature. For complex **3**, reducing the temperature from 70 to 25 °C, the P_r value increased from 0.58 to 0.76 (Table 2, Entries 12, 16).

Kinetics of lactide polymerization

The kinetics of ROP of L-LA in some conditions such as monomer/initiator ratios were researched in THF employing **2**. The molecular weight (M_n) of the polymers increased linearly with increasing monomer conversion. The PDI values of these polymers remained low (1.05 – 1.10). This illustrated the living characteristic of the catalytic systems (Fig. 7). In order to calculate the order in initiator, k_{app} value was plotted versus the concentration of complex **2** (see Fig. 8). In each condition, first-order kinetics in monomer was surveyed (see Fig. 8). So the ROP of LA by **2** speculatively agreed with the formula:

$$-d[LA]/dt = k_{app}[LA] \qquad (1)$$

where $k_{app} = k_p[cat.]^x$, and k_p is the propagation speed constant. In order to calculate the order in catalyst, lnk_{app} was plotted versus ln[cat.]$_0$ (Figure 9). The order in catalyst was calculated 0.97 ~ 1. So the ROP of LA by **2** followed the entire kinetic equation:

$$-d[LA]/dt = k_p[cat.]^{0.97}[LA] \qquad (2)$$

In addition, complexes **1** – **3** were also examined as catalysts in high [LA]$_0$/[cat.]$_0$ mole ratio ([LA]$_0$/[cat.]$_0$ = 400) for the ROP of L-LA in toluene solution at 90 °C, where high degree of monomer conversions (87.5% – 98.0%) were achieved (Table 2, Entries 17 – 19).

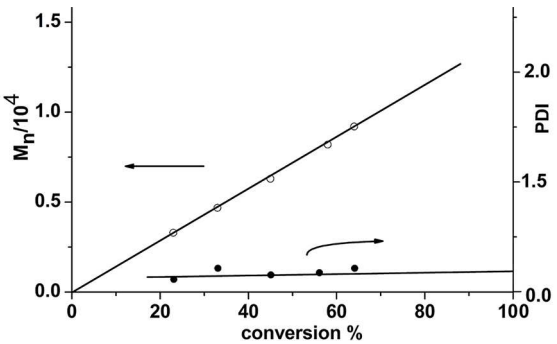


Figure 7. Plots of PLA' s M_n and PDI in the light of L-LA conversion employing complex **2**/isopropanol, [LA]$_0$/[cat.]$_0$ = 100, at 40 °C in THF.

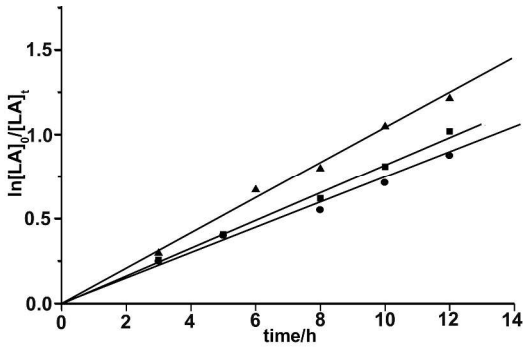


Figure 8. Kinetics of the ROP of L-LA by **1** – **3** with isopropanol at 40 °C in toluene with $[LA]_0 = 0.5$ mol L^{-1}, $[cat.]_0 = 5 \times 10^{-3}$ mol L^{-1}, $[LA]_0/[cat.]_0 = 100$, ▲: **1**, $k_{app} = 103.2 \times 10^{-3}$ h^{-1}; ■: **2**, $k_{app} = 82.5 \times 10^{-3}$ h^{-1}; ●: **3**, $k_{app} = 72.4$ $h^{-1} \times 10^{-3}$ h^{-1}.

Mechanism of lactide polymerization

Chain end analysis of the oligomer of L-LA, which was prepared by the polymerization of the L-LA at low monomer/initiator ratio ($[LA]_t$: $[\mathbf{2}]_t$ = 41 : 1) (Fig. 10) was measured by ^{1}H NMR. Integral ratio of the two peaks at δ 1.24 ppm (assigned to the methyl protons from the isopropoxycarbonyl end-group, "**a**" in Fig. 10) and δ 4.34 ppm (was assigned to the methine proton neighboring the hydroxyl end-group, "**d**" in Fig. 10) approximated 6 : 1. It meant the aggregating chain was end-capped by an isopropyl ester with an hydroxyl.[14a, 14d] In other words, the magnesium complex had transformed isopropoxy magnesium reactive species at the initiation of the aggregation, so the genuine initiator might be the isopropoxy magnesium species. This ROP of lactitde using magnesium complexes adopted coordination insertion mechanism.[6a]

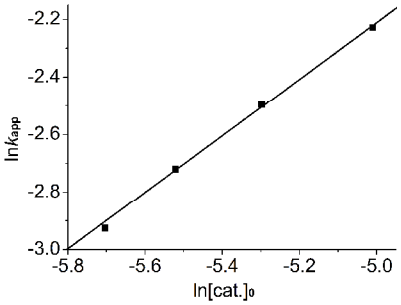


Figure 9. lnk_{app} versus the ln[cat.]$_0$ of **2**/isopropanol initiator for the L-LA polymerization at 40 °C in THF.

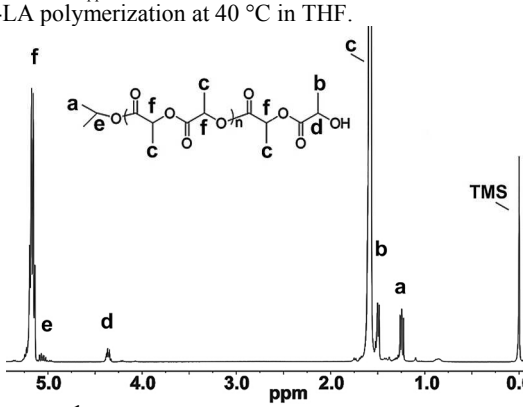


Figure 10. ^{1}H NMR spectrum of oligomer of L-LA at low monomer/initiator ratio ($[LA]_t$: $[\mathbf{2}]_t$ = 41 : 1) in $CDCl_3$.

Experiment Section

General

All experimental operations were performed using Schlenk line techniques.[23, 24] Elemental analysis were accomplished by a Varian EL microanalyzer; ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker AV 400M or 300M instruments at RT in THF-d_8 or $CDCl_3$ with TMS for compounds and polymers. Gel permeation chromatography (GPC) measurements were conducted with a Waters 515 GPC with $CHCl_3$ as the eluant (flow rate: 1 mL/min, at 35 °C). The molecular weight was adjusted through PS standard. Crystallographic data were gathered and analyzed by according to the experiment sections of references. [14b, 14c, 14d, 25] Magnesium, titanic chloride, isopropanol, 9,10-phenanthrenequinone, 1,4-diazabicyclo[2.2.2]octane (dabco), aniline, 2,6-diethyl-aniline and 2-tert-butylaniline were purchased from J&K Scientific Ltd.

Synthesis of pro-ligands (general procedure)

To the stirring solution of aniline (50 mmol) and dabco (150 mmol) in toluene (130 mL), $TiCl_4$ (50 mmol) in toluene (25 mL) was added dropwise at 90 °C, then 9, 10-phenanthrenequinone (25 mmol) was added. The reaction was maintained at 140 – 145 °C for 20 – 24 h and then was cooled to ca. 80 °C. The insoluble substance was removed by hot filtration and then the solvent was removed under vacuum. The product was isolated as deep red solid by silica-gel columnchromatography ($V_{petroleum}$: $V_{ethyl\ acetate}$ = 6 : 1).

L_1: Yield 64.7%. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.42 (d, J = 7.2 Hz, 1H, Ar*H*), 8.28 (d, J = 7.9 Hz, 2H, Ar*H*), 8.20 (t, J = 7.6 Hz, 1H, Ar*H*), 7.56 (t, J = 7.4 Hz, 1H, Ar*H*), 7.46 (t, J = 7.5 Hz, 1H, Ar*H*), 7.21 – 6.84 (m, 11H, Ar*H*), 6.69 (d, J = 7.8 Hz, 1H, Ar*H*). ^{13}C NMR (100MHz, THF-d_8, δ, ppm): 162.2, 158.5, 149.1, 147.8, 136.0, 132.4, 133.6, 131.9, 131.8, 129.4, 128.6, 128.0, 127.4, 127.0, 126.8, 125.5, 124.6, 124.3, 123.6, 123.3, 122.7. Anal. Calcd for $C_{26}H_{18}N_2$ (%): C, 87.12; H, 5.06; N, 7.82. Found: C, 87.15; H, 5.10; N, 7.86. HRMS (m/z): calcd for $C_{26}H_{18}N_2$: 358.15; Found: 358.20 [M + H]+.

L_2: yield 45.3%. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.32 (d, J = 7.4 Hz, 1H, Ar*H*), 7.93 (m, 2H, Ar*H*), 7.49 (t, J = 7.4 Hz, 1H, Ar*H*), 7.36 (t, J = 7.6 Hz, 1H, Ar*H*), 7.09 – 6.94 (m, 3H, Ar*H*), 6.92 – 6.84 (m, 5H, Ar*H*), 6.68 (d, J = 7.9 Hz, 1H, Ar*H*), 2.36 (ddt, J = 36.5, 15.0, 7.6 Hz, 4H, C*H*$_2$CH$_3$), 1.72 – 1.50 (m, 4H, C*H*$_2$CH$_3$), 1.07 (t, J = 6.0 Hz, 6H, CH$_2$C*H*$_3$), 0.74 (t, J = 6.0 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, THF-d_8, δ, ppm): 159.04,134.86, 134.15, 133.62, 131.91, 131.40, 130.77, 130.43, 129.08, 128.78, 128.12, 127.41, 127.27, 125.42, 124.66, 123.61, 123.55, 122.80, 24.82, 23.39, 14.89, 13.36. Anal. Calcd for $C_{34}H_{34}N_2$ (%): C, 86.77; H, 7.28; N, 5.95. Found: C, 86.66; H, 7.27; N, 5.90. HRMS (m/z): calcd for $C_{34}H_{34}N_2$: 470.27; Found: 470.30 [M + H]+.

L_3: yield 35.2 %. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.26 (d, J = 7.4 Hz 1H, Ar*H*), 7.88 (dd, J = 13.2, 7.9 Hz, 2H, Ar*H*), 7.59 (m, 1H, Ar*H*), 7.51 (t, J = 7.5 Hz, 1H, Ar*H*), 7.30 (m, 1H, Ar*H*), 7.09 – 7.01 (m, 4H, Ar*H*), 6.96 – 6.81 (m, 5H, Ar*H*), 6.63 (d, J = 7.9 Hz, 1H, Ar*H*), 1.25 (s, 9H, C(C*H*$_3$)$_3$), 1.13 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, THF-d_8, δ, ppm): 159.82, 146.57, 144.91, 135.56, 135.40, 135.11, 134.76, 124.49, 131.78, 131.05, 129.42, 129.10, 128.77, 127.40, 127.04, 124.07, 123.47, 123.41, 123.37, 122.50, 58.23, 54.59, 28.30, 27.25. Anal. Calcd for $C_{34}H_{34}N_2$ (%): C, 86.77; H, 7.28; N, 5.95. Found: C, 86.69; H, 7.23; N, 5.89. HRMS (m/z): calcd for $C_{34}H_{34}N_2$: 470.27; Found: 470.20 [M + H]+.

Synthesis of Mg Complexes

The mixture of pro-ligand (10 mmol) and magnesium powder (50 mmol) activated with iodine in tetrahydrofuran (50 mL) was stirred for ca. 1h in glovebox at RT. The deep red solid complex was isolated through filtering and removing the solvent under vacuum.

1: yield 94.5%. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.38 (d, J = 7.4 Hz, 1H, Ar*H*), 8.25 (t, J = 7.6 Hz, 2H, Ar*H*), 7.62 (t, J = 7.5 Hz, 1H, Ar*H*), 7.58 – 7.45 (m, 2H, Ar*H*), 7.39 (t, J = 7.9 Hz, 1H, Ar*H*), 7.12 – 6.95 (m, 9H, Ar*H*), 6.91 – 6.82 (m, 2H, Ar*H*), 3.61 (bs, 12H, α-C*H*$_2$(THF)), 1.75 (bs, 12H, β-C*H*$_2$(THF)). ^{13}C NMR (100 MHz, THF-d_8, δ, ppm): 162.00, 135.21, 134.05, 132.77, 130.56, 129.85, 129.43, 129.22, 128.87, 128.33, 127.92, 127.80, 127.64, 126.39, 125.91, 125.72, 124.98, 124.40, 124.03, 123.88, 123.44, 69.02 (α-*C*H$_2$ (THF)), 26.43 (β-*C*H$_2$(THF)). Anal. Calcd for $C_{38}H_{42}MgN_2O_3$ (%): C, 76.19; H, 7.07; N, 4.68. Found: C, 76.24; H,7.11; N, 4.75. M.p. 189 °C.

2: yield 91.0%. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.26 (d, J = 7.5 Hz, 1H, Ar*H*), 8.01 (t, J = 8.1 Hz, 2H, Ar*H*), 7.59 (t, J = 7.4 Hz, 1H, Ar*H*), 7.53 – 7.42 (m, 2H, Ar*H*), 7.36 (t, J = 7.5 Hz, 1H, Ar*H*), 6.99 (d, J = 7.4 Hz, 2H, Ar*H*), 6.94 – 6.64 (m, 3H, Ar*H*), 3.58 (bs, 12H, α-C*H*$_2$ (THF)), 2.52 – 2.18 (m, 4H, C*H*$_2$CH$_3$), 1.73 (bs, 12H, β-C*H*$_2$(THF)), 1.58 (dt, J = 15.3, 7.7 Hz, 4H, C*H*$_2$CH$_3$), 1.05 (t, J = 7.4 Hz, 6H, CH$_2$C*H*$_3$), 0.71 (t, J = 7.4 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, THF-d_8, δ, ppm): 159.65, 132.49, 132.11, 131.12, 129.92, 129.44, 128.89, 128.55, 128.27, 128.07, 127.83, 127.7, 127.55, 126.10, 125.81, 125.42, 124.43 124.15, 123.91, 123.26, 122.95, 68.34 (α-*C*H$_2$(THF)), 28.73, 26.05 (β-*C*H$_2$(THF)), 23.96, 13.39, 13.32. Anal. Calcd for $C_{46}H_{58}MgN_2O_3$ (%): C, 77.68; H, 8.22; N, 3.94. Found: C, 77.65; H, 88.19; N, 3.89. M.p. 213 °C. Crystal of **2** suitable for X-ray structural determination was grown in tetrahydrofuran solution. CCDC: 1029408.

3: yield 87.3%. ^{1}H NMR (400 MHz, THF-d_8, δ, ppm): 8.24 (d, J = 7.8 Hz, 1H, Ar*H*), 7.94 (t, J = 7.9 Hz, 2H, Ar*H*), 7.57 (m, 1H, Ar*H*), 7.50 – 7.38 (m, 2H, Ar*H*), 7.36 (t, J = 7.8 Hz, 1H, Ar*H*), 6.96 – 6.60 (m, 5H, Ar*H*), 3.55 (bs, 12H, α-C*H*$_2$(THF)), 1.70 (bs, 12H, β-C*H*$_2$(THF)), 1.23 (s, 9H, C(C*H*$_3$)$_3$), 1.10 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, THF-d_8, δ, ppm): 159.45, 133.00, 132.54, 131.03, 129.83, 129.35, 128.71, 128.48, 128.12, 128.00, 127.56, 127.66, 127.48, 126.01, 125.59, 125.33, 124.37, 124.26, 123.75, 123.11, 122.77, 66.87 (α-*C*H$_2$(THF)), 29.02, 28.95, 26.05 (β-*C*H$_2$(THF)). Anal. Calcd for $C_{44}H_{54}MgN_2O_3$ (%): C, 77.35; H, 7.97; N, 4.10. Found: C, 77.41; H, 8.00; N, 4.14. M.p. 227 °C.

General procedure for lactide polymerization

In a typical polymerization reaction: magnesium complex (0.4 mmol) and isopropanol (0.4 mmol) in toluene (80 mL) were added in a flame-dried ampules including a magnetic stir bar. The ampules was placed in an oil bath at 70 °C. The solution was stirred for ca. 10 min, when the catalyst was activated by isopropanol and whereafter the selected quantity of lactide was added. The polymer was isolated by precipitating with cold methanol or refrigerated centrifuge, after required quantity of reaction time. The solid was attained and dried in vacuo at 30 °C for 40 h.

Conclusions

In conclusion, three magnesium complexes **1** – **3** were synthesized in moderate yields from the reactions of magnesium with Schiff base containing phenanthrene derivatives. These complexes were employed as catalysts for the polymerization of L-LA and *rac*-LA. The bulky substituents on the ligand affect the tacticities of the polymers. Microstructural analysis of the polymers catalyzed by these complexes revealed that the Schiff base ligands have certain ability to affect the tacticity of the polymer, and this ability varies according to ligand bulk. In addition, kinetic analysis indicated that polymerizations of lactide by complex **2** was first-order as to monomer, and had an order of 0.97 as to catalyst.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21204082, 51173183, 51021003, 51321062); the Ministry of Science and Technology of China (No. 2011AA02A202); Jilin Science & Technology Department, Science and Technology Development Project (No. 20140204017GX); Science and Technology Bureau of Changchun City (No. 2013060).

Notes and references

1. *School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China. Tel: +86-431-85583016, Fax: +86-431-85583016. E-mail: cuiyuancust@163.com; gaobo@ciac.ac.cn.*
2. *Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun 130022, China.*

† Electronic Supplementary Information (ESI) available: X-ray crystallographic datum and refinement for complex **2** in CIF format.See DOI: 10.1039/b000000x/

1. (a) R. Langer, J. P Vacanti, *Science* 1993, **260**, 920–926. (b) K. E. Uhrich, S. M. Cannizzaro, R. S. Langer, K. M. Shakesheff. *Chem. Rev.* 1999, **99**, 3181–3198. (c) A. M. DiCiccio, G. W. Coates, *J. Am. Chem. Soc*. 2011, **133**, 10724–10727. (d) M. J. Stanford, A. P. Dove, *Chem. Soc. Rev*. 2010, **39**, 486–494. (e) C. M. Thomas, *Chem. Soc. Rev*. 2010, *39*, 165–173. (f) D. Q. Wu, X. Z. Zhang, C. C. Chu. *Am. J. Drug. Deliv.* 2004, **3**, 253–267. (g) R. M. Thomas, P. C. Widger, S. M. Ahmed, R. C. Jeske, W. Hirahata, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc*. 2010, **132**, 16520–16525. (h) M. H. Chisholm, J. C. Gallucci, and K. Phomphrai, *Inorganic Chemistry*, 2005, **44**, 22.
2. (a) W. Chen, H. C. Yang, R. Wang, R. Cheng, F. H. Meng, W. X. Wei, Z. Y. Zhong, *Macromolecules* 2010, **43**, 201–207. (b) A. Kowalski, A. Duda, S. Penczek, *Macromolecules* 2000, **33**, 689–695. (c) R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater*. 2000, **12**, 1841–1846. (d) D. Sykes and M. D. Ward, *Chem. Commun.*, 2011, **47**, 2279–2281. (e) X. Song, F. Ling, X. S. Chen. *Acta Polymerica Sinica*, 2013, **1**, 95–101. (f) R. J. Cox and P. S. H. Wang, *J. Chem. Soc., Perkin Trans.* 2001, **1**, 2006–2008.
3. (a) E. E. Schmitt, R. A. Polistina, U.S. Patent 3,463, **158**, 1969. (b) K. M. Stridsberg, M. Ryner, A. C. Albertsson, *Adv. Polym. Sci*. 2002, **157**, 41–65. (c) M. Lahcini, P. M. Castro, M. Kalmi, M. Leskelä, T. Repo, *Organometallics* 2004, **23**, 4547–4549. (d) A. Tullo, *Chem. Eng. News.* 2000, **3**, 13–15. (e) W. Chen, H. C. Yang, R. Wang, R. Cheng, F. H. Meng, W. X. Wei, Z. Y. Zhong, *Macromolecules* 2010, **43**, 201–207.
4. (a) R. K. Iha, K. L. Wooley, A. M. Nyström, D. J. Burke, M. J. Kade, C. J. Hawker, *Chem. Rev.* 2009, **109**, 5620–5686. (b) J. M. Leiston-Belanger, T. P. Russell, E. Drockenmuller and C. J. Hawker, *Macromolecules* 2005, **38**, 7676–7683. (c) A. Alaaeddine, C. M. Thomas, T. Roisnel, J. F. Carpentier, *Organometallics* 2009, **28**, 1469–1475. (d) C. -T. Chen, C. -A. Huang, B. -H. Huang, *Dalton Trans*. 2003*,* 3799–3803. (e) N. Iwasaa, M. Fujiki, K. Nomura, *J Mol Catal A: Chem.* 2008, **292**, 67–75. (f) Y. Wang, H. Y. Ma, *Chem. Commun*. 2012, *48*, 6729–6731. (g) W. J. Zhang, Y. H. Wang, W. -H. Sun, Lin Wang, C. Redshaw, *Dalton Trans*. 2012, **41**, 11587–11596. (h) Z. Liu, W. Gao, J. Zhang, D. M. Cui, Q. Wu, Y. Mu, *Organometallics* 2010, **29**, 5783–5790. (i) C. Robert, F. Montigny, C. M. Thomas, *Nature Commun.* 2011, **2**, 586.
5. (a) G. Labourdette, D. J. Lee, B. O. Patrick, M. B. Ezhova, P. Mehrkhodavandi, *Organometallics* 2009, **28**, 1309–1319. (b) C. A. Wheaton, B. J. Ireland, P. G. Hayes, *Organometallics* 2009, **28**, 1282–1285. (c) V. Poirier, T. Roisnel, J. -F. Carpentier, Y. Sarazin, *Dalton Trans*. 2009, 9820–9827. (d) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, Jr., M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc*. 2003, **125**, 11350–11359. (e) E. L. Whitelaw, G. Loraine, M. F. Mahon and M. D. Jones, *Dalton Trans.* 2011, **40**, 11469–11473. (f) A. J. Nijenhuis, D. W. Grijpma, and A. J. Pennings, *Macromolecules,* 1992, **25**, 6419–6424. (g) J. Ejfler, S. Szafert, K. Mierzwicki, L. B. Jerzykiewicz and P. Sobota, *Dalton Trans.*, 2008, 6556–6562. (h) R. R. Gowda, D. Chakraborty, *Journal of Molecular Catalysis A: Chemical*, 2010, **333**, 167–172. (i) X. Pang, X. S. Chen, X. L. Zhuang, X. B. Jing, *J Polym Sci Part A: Polym Chem*. 2008, **46**, 643–649. (j) Y. -E. Tai, C. -Y. Li, C. -H. Lin, Y. -C. Liu, B. -T. Ko, Y. -S. Sun, *Journal of Polymer Science Part A: Polymer Chemistry* 2011, **49**, 4027–4036.
6. (a) H. -Y. Tang, H. -Y. Chen, J. -H. Huang, C. -C. Lin, *Macromolecules* 2007, **40**, 8855–8860. (b) J. -C. Wu, Y. -Z. Chen, W. -C. Hung, C. -C. Lin, *Organometallics* 2008, **27**, 4970–4978. (c) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Organometallics* 2006, **25**, 1012–1020.（d） I. J. Blackmore, V. C. Gibson, P. B. Hitchcock, C. W. Rees, D. J. Williams, and A. J. P. White. *J. Am. Chem. Soc*. 2000, **122**, 11845–11854. (e) I. L. Fedushkin, A. G. Morozov, V. A. Chudakova, G. K. Fukin, and V. K. Cherkasov, *Eur. J. Inorg. Chem*. 2009, 4995–5003. (f) L. Wang, H. Ma, *Macromolecules*, 2010, **43**, 6535–6537.
7. (a) J. B. Chen, J. L. Gorczynski, G. Q. Zhang, C. L. Fraser, *Macromolecules* 2010, **43**, 4909–4920. (b) D. S. Mcguinness, E. L. Marshall, V. C. Gibson, J. W. Steed, *J Polym Sci Part A: Polym Chem.* 2003, **41**, 3798–3803.
8. (a) D. Takeuchi, T. Aida, *Macromolecules* 2000, **33**, 4607–4609. (b) Y. Kim, J. G. Verkade, *Organometallics* 2002, **21**, 2395–2399. (c) Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, H. Yasuda, A. Harada, J. Okuda, *Macromolecules* 2002, **35**, 7538–7544. (d) Y. Kim, J. G. Verkade, *Macromol. Rapid Commun*. 2002, **23**, 917–921. (e) Y. Kim, P. N. Kapoor, J. G. Verkade, *Inorg. Chem*. 2002, **41**, 4834–4838. (f) H. Y. Chen, M. Y. Liu, A. K. Sutar, C. -C. Lin, *Inorg. Chem.* 2010, **49**, 665–674. (g) J. Okuda, I. L. Rushkin, *Macromolecules* 1993, **26**, 5530–5532. E. L. Whitelaw, M. D. Jones, M. F. Mahon, G. Kociok-Kohn, *Dalton Trans*. 2009, 9020–9025.
9. (a) A. F. Douglas, B. O. Patrick, P. Mehrkhoda-vandi, *Angew. Chem. Int. Ed*. 2008, **47**, 2290–2293. (b) I. Yu, A. Acosta-Ramírez, P. Mehrkhodavandi, *J. Am. Chem. Soc*. 2012, **134**, 12758–12773. (c) A. Pietrangelo, S. C. Knight, A. K. Gupta, L. J. Yao, M. A. Hillmyer, and W. B. Tolman *J. Am. Chem. Soc*. 2010, **132**, 11649–11657.
10. (a) B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, Y. Sarazin, *Chem. Eur. J.* 2013, **19**, 3986–3994 (b) S. Marks, J. G. Heck, M. H. Habicht, P. OñaBurgos, C. Feldmann, P. W. Roesky, *J. Am. Chem. Soc*. 2012, **134**, 16983–16986. (c) P. Benndorf, J. Kratsch, L. Hartenstein, C. M. Preuss, P. W. Roesky, *Chem. Eur. J*. 2012, 14454–14463. (d) J. Wang, Y. Yao, Y. Zhang, Q. Shen, *Inorg. Chem*. 2009, **48**, 744–751. (e) H. Ma, T. P. Spaniol, J. Okuda, *Inorg. Chem*. 2008, **47**, 3328–3339. (f) B. Liu, D. Cui, J. Ma, X. Chen, X. Jing, *Chem. Eur. J*. 2007, **13**, 834–845. (g) X. Liu, X. Shang, T. Tang, N. Hu, F. Pei, D. Cui, X. Chen, X. Jing, *Organometallics* 2007, **26**, 2747–2757. (h) I. Westmoreland and J. Arnold, *Dalton Trans.*, 2006, 4155–4163. (i) G. Giesbrecht, G. D. Whitener, J. Arnold. *Dalton Trans*. 2001, **11**, 923–927.
11. R. H. Platel, L. M. Hodgson, C. K. Williams, *Polym. Rev.* 2008 , **48** ,11−63.
12. (a) R. A. Gross, A. Kumar, B. Kalra, *Chem. Rev*. 2001, **101**, 2097−2124. (b) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* 2004, **104**, 6147−6176. (c) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* 2007, **107**, 5813−5840.
13. (a) N. Spassky, M. Wisniewski, C. Pluta, A. L. Borgne, *Macromol. Chem. Phys.* 1996, **197**, 2627. (b) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* 2002, **124**, 1316. (c) C. P. Radano, G. L. Baker, M. R. Smith, *J. Am. Chem. Soc.* 2000, **122**, 1552. (d) Z. Y. Zhong, P. J. Dijkstra, J. Feijen, *Angew. Chem.* 2002, 114, 4692; *Angew. Chem. Int. Ed.* 2002, **41**, 4510; (e) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. S. Chen, and J. Feijen, *Chem. Eur. J.* 2009, **15***,* 9836 – 9845. (f) N. Nomura, R. Ishii, M. Akakura, K. Aoi, *J. Am. Chem. Soc.* 2002, **124**, 5938; (g) N. Nomura, R. Ishii, Y. Yamamoto T. Kondo, *Chem.–Eur. J.* 2007, **13**, 4433. (h) K. Majerska, A. Duda, *J. Am. Chem. Soc.* 2004, **126**, 1026. (i) Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J. -F. Carpentier, *J. Am. Chem. Soc*. 2011, **133**, 9069–9087. (j) I. Yu, A. Acosta-Ramírez, and P. Mehrkhodavandi, *J. Am. Chem. Soc*. 2012, **134***,* 12758−12773.

14. (a) H. Du, A. H. Velders, P. J. Dijkstra, Z. Y. Zhong, X. S. Chen, J. Feijen, *Macromolecules* 2009, **42**, 1058–1066. (b) Z. H. Tang, X. S. Chen, X. Pang, Y. K. Yang, X. F. Zhang, X. B. Jing, *Biomacromolecules* 2004, **5**, 965–970. (c) X. Pang, H. Z. Du, X. S. Chen, X. Wang, X. B. Jing, *Chem. – Eur. J.* 2008, **14**, 3126–3136. (d) Z. H. Tang, X. S. Chen, Y. K.Yang, X. Pang, J. R. Sun, X. F. Zhang, X. B. Jing, *J Polym Sci Part A: Polym Chem*. 2004, **42**, 5974–5982. (e) X. Pang, H. Z. Du, X. S Chen, X. L. Zhuang, D. M. Cui, X. B. Jing, *J Polym Sci Part A: Polym Chem*. 2005, **43**, 6605–6612. (f) X. Pang, R. L. Duan, X. Li, X. S. Chen, *Polym. Chem*, 2014, **5**, 3894–3900. (g) X. Pang, R. L. Duan, X. Li, Z. Sun, H. Zhang, X. H. Wang, X. S. Chen, *Polym. Chem*. DOI: 10.1039/c4py00734d. (h) X. Pang, R. L. Duan, X. Li, B. Gao, Z. Sun, X. H. Wang, X. S. Chen, *RSC Adv.* 2014, **4**, 22561–22566.
15. (a) H. K. Jr. Hall, A. B. Padias, P. A. Williams, J. Gosau, H. W. Boone, and D. Park, *Macromolecules*, 1995, **28**, 1–8. (b). M. Jeon and S.Y. Kim. *Polym. Journal*, 2008, **40**, 409–413.
16. (a) A. W. Addison, T. N. Rao, J. Reedijk, J. Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1984, 1349.
17. (a) A. Scarel, M. R. Axet, F. Amoroso, F. Ragaini, C. J. Elsevier, A. Holuigue, C. Carfagna, L. Mosca and B. Milani, *Organometallics*, 2008, **27**, 1486; (b) M. Gasperini, F. Ragaini, E. Gazzola, A. Caselli and P. Macchi, *Dalton Trans.*, 2004, 3376.
18. M. -A. Munoz-Hernandez, T. S. Keizer, P. Wei, S. Parkin, D. A. Atwood, *Inorg. Chem*. 2001, **40**, 6782–6787.
19. I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, S. Dechert, H. Schumann, *Eur. Inorg. Chem.*, 2003, 3336.
20. J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun.* 1997, **18**, 325–333.
21. K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lingren, M. A. Doscotch, J. I. Siepmann, E. J. Munson, *Macromolecules* 1997, **30**, 2422–2428.
22. P_r is the probability of racemic linkages between monomer units and is determined from the methane region of the homonuclear decoupled ^{1}H NMR spectrum ($P_r + P_m = 1$). The expressions for the tetrad concentrations in terms of P_r, assuming Bernoullian statistics and the absence of transesterification, are as follows: [mmm] = $(2(1 - P_r)^2 + P_r (1 - P_r))/2$; [mrm] = $(P_r^2 + P_r(1 - P_r))/2$; [mmr] = [rmm] = $(P_r(1 - P_r))/2$; [rmr]= $P_r^2/2$. See: B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc*. 2001, **123**, 3229–3238.
23. (a) R. J. Cox, D. J. Ritson, T. A. Dane, J. Berge, J. P. H. Charmant and A. Kantacha, *Chem. Commun.*, 2005, 1037–1039. (b) A. Fahad, A. Abood, K. M. Fisch, A. Osipow, J. Davison, M. Avramović, C. P. Butts, J. Piel, T. J. Simpson, R. J. Cox, *Chem. Sci.*, 2014, **5**, 523–527. (c) A. Yakasai, J. Davison, Z. Wasil, L. M. Halo, C. P. Butts, C. M. Lazarus, A. M. Bailey, T. J. Simpson R. J. Cox, *J. Am. Chem. Soc.*, 2011, **133**, 10990–10998. (d) R. J. Cox, A. Al-Fahad, *Current Opinion in Chemical Biology*, 2013, **17**, 532–536. (e) R. J. Cox, T. S. Hitchman, K. J. Byrom, I. S. Findlow, J. A. Tanner, J. Crosby, T. J. Simpson. *EBS Letters*, 1997, **405**, 267–272. (f) R. J. Cox. *Natural Product Reports* 1996, **13**, 29–43.
24. (a) I. S. Tidmarsh, T. B. Faust, H. Adams, L. P. Harding, L.Russo, W. Clegg and M. D. Ward. *J. Am. Chem. Soc.*, 2008, **130**, 15167–15175. (b) M. Whitehead, S. Turega, A. Stephenson, C. A. Hunter and M. D. Ward, *Chem. Sci.*, 2013, **4**, 2744–2751. (c) A. Stephenson, D. Sykes and M. D. Ward, *Dalton Trans.* 2013, **42**, 6756–6767. (d) A. H. Shelton, I. V. Sazanovich, J. A. Weinstein and M. D. Ward, *Chem. Commun*. 2012, **48**, 2749–2751. (e) D. Sykes, I. S. Tidmarsh, A. Barbieri, I. V. Sazanovich, J. A. Weinstein and M D. Ward, *Inorg. Chem.* 2011, **50**, 11323–11339. (f) A. Stephenson, S. P. Argent, T. Riis-Johannessen, I. S. Tidmarsh and M. D. Ward, *J. Am. Chem. Soc.* 2011, **133**, 858–870.
25. G. M. Sheldrick, SHELXTL, Version 5. 1, Siemens Industrial Automation, Inc., 1997.

Table 1. Selected bond lengths (Å) and angles (deg) for complex **2**.

Mg1–N1	2.051(3)	N1–Mg1–O2	116.10(10)
Mg1–N2	2.071(3)	N1–Mg1–N2	80.60(10)
Mg1–O1	2.161(2)	N2–Mg1–O3	96.62(10)
Mg1–O2	2.078(2)	O2–Mg1–O3	110.67(9)
Mg1–O3	2.085(2)		
C1–N1	1.384(4)		
C14–N2	1.409(4)		

Table 2. Polymerization data of LA with complexes **1**– **3**.[a]

Entry	Cat.	Monomer	Temp (°C)	*t* (h)	[LA]/[cat.]	Conv.[b] (%)	$M_{n(calcd)}$[c] $\times 10^{-4}$	M_{nGPC}[d] $\times 10^{-4}$	PDI[d]	K_{app}(h^{-1}) $\times 10^{-3}$	P_r
1	**1**	L-LA	70	6	100	97.7	1.41	2.52	1.30	n.a.	0
2	**2**	L-LA	70	6	100	93.6	1.35	2.40	1.17	n.a.	0
3	**3**	L-LA	70	6	100	89.4	1.29	2.26	1.21	n.a.	0
4	**1**	L-LA	40	12	100	71.3	1.03	1.72	1.15	103.2	0
5	**2**	L-LA	40	12	100	64.0	0.92	1.54	1.10	82.5	0
6	**3**	L-LA	40	12	100	58.3	0.84	1.45	1.13	72.4	0
7	**2**	L-LA	40	12	75	70.5	1.05	1.71	1.11	107.6	0
8	**2**	L-LA	40	12	125	55.9	1.01	1.74	1.12	65.8	0
9	**2**	L-LA	40	12	150	51.7	1.12	1.94	1.10	53.7	0
10	**1**	*rac*-LA	70	6	100	95.6	1.38	2.31	1.35	n.a.	0.51
11	**2**	*rac*-LA	70	6	100	92.2	1.33	2.17	1.22	n.a.	0.55
12	**3**	*rac*-LA	70	6	100	87.8	1.26	2.21	1.28	n.a.	0.58
13	**1**	*rac*-LA	40	12	100	69.2	1.00	1.53	1.21	n.a.	0.56
14	**2**	*rac*-LA	40	12	100	61.9	0.89	1.57	1.13	n.a.	0.65
15	**3**	*rac*-LA	40	12	100	56.9	0.82	1.44	1.14	n.a.	0.71
16	**3**	*rac*-LA	25	20	100	52.4	0.75	1.29	1.13	n.a.	0.76
17	**1**	L-LA	90	16	400	98.0	5.64	9.85	1.40	n.a.	0
18	**2**	L-LA	90	18	400	92.3	5.32	9.77	1.33	n.a.	0
19	**3**	L-LA	90	18	400	87.5	5.04	8.82	1.38	n.a.	0

[a] The polymerization reactions were carried out in toluene solution except that several actions processed in THF at 25 and 40 °C, $[LA]_0 = 0.5$ mol L^{-1}, [isopropanol]/[cat.] = 1.0 [b] Measured by ^1H NMR. [c] Computed from the 144 × $[LA]_0/[cat.]_0$ × conversion + $M_w^{isopropanol}$. [d] Get from GPC analysis and calibrated against polystyrene standard. The veritable value of $M_{n(calcd)}$ could be computed according to formula $M_n = 0.58 M_{nGPC}$.[20]