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Synthesis and catalytic application of magnesium complexes bearing pendant indolyl ligands†

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Three novel indole-based ligand precursors [HIndPh^{R}, R = methoxy, HIndPh^{OMe} (**2a**); thiomethoxy, HIndPh^{SMe} (**2b**); and *N*,*N*′-dimethylamino, HIndPh^{NMe2} (**2c**)] have been synthesized *via* Sonogashira and cyclization reactions with moderate to high yield. Reactions of these ligand precursors with 0.6 equivalent of Mg^{n}Bu$_2$ in THF afforded the magnesium bis-indolyl complexes **3a–3c**, respectively. All the ligand precursors and related magnesium complexes have been characterized by NMR spectroscopy and elemental analyses. The molecular structures are reported for compounds **3a** and **3b**. Under optimized conditions, compound **3a** demonstrates efficient catalytic activities towards the ring opening polymerization of L-lactide and ε-caprolactone in the presence of BnOH.

Introduction

Environmentally friendly polyesters, such as poly(ε-caprolactone) (PCL) or polylactide (PLA), are the most important synthetic biodegradable polymers, and these polymers have attracted great interest for various applications, especially in the drug delivery or biomedical field based on their biocompatible properties.[1] The main method to synthesize the polyesters is the ring opening polymerization (ROP) reaction using metal complexes.[1c] Although a number of excellent catalysts have been examined for the ROP,[2] chemists are still interested in the development of novel efficient metal catalysts to produce polymers which contain the properties of a precise molecular weight, narrow polydispersity index (PDI), efficient rate and high *enantio*- or regio-selectivity under mild conditions. Recently, the metal complexes supported by N-heterocyclic-containing anionic ligands, such as pyrrole,[3] pyridine,[3i,4] pyrazole,[5] imidazole,[3i,6] oxazoline,[7] quinoline,[4a–d,8] benzotriazole,[9] and carbazole,[10] have been shown to exhibit catalytic activities towards the ROP of cyclic esters. We also previously reported some metal complexes bearing pendant monoanionic anilido-pyrazolate[5m] or anilido-oxazolinate[7b–d] ligands which worked as catalysts/initiators in catalyzing the ROP of cyclic esters. Some metal complexes supported by indolyl ligands have been reported and applied in many catalytic reactions,[11] such as olefin polymerization,[11a–h] hydroarylation,[11i–j] cross-coupling reactions[11k–l] and others.[11m–p] Although the investigation of organo-catalyzed ROP using indole as the organocatalyst has been reported;[12a,b] the indole-containing metal complexes used in the ROP of cyclic esters are rare. Bildstein's group reported the enantioselective chiral indole-imino chromium(III) complexes for the conversion of propylene oxide and CO to enantioenriched β-butyrolactone that is the key monomer for the production of PHB by ring-opening polymerization.[12c] Recently, Lamberti's group designed anilidopyridyl-indolyl yttrium complexes which demonstrated moderate stereoselectivity and efficient activities in the ROP of *rac*-lactide.[12d] Herein, we report the synthesis and characterization of magnesium complexes incorporating pendant functionalized indolyl ligands. To our knowledge, no analogous magnesium complexes derived from substituted indolyl ligands have been reported. Their application towards the ROP of L-lactide (L-LA) and ε-caprolactone (ε-CL) will be examined.

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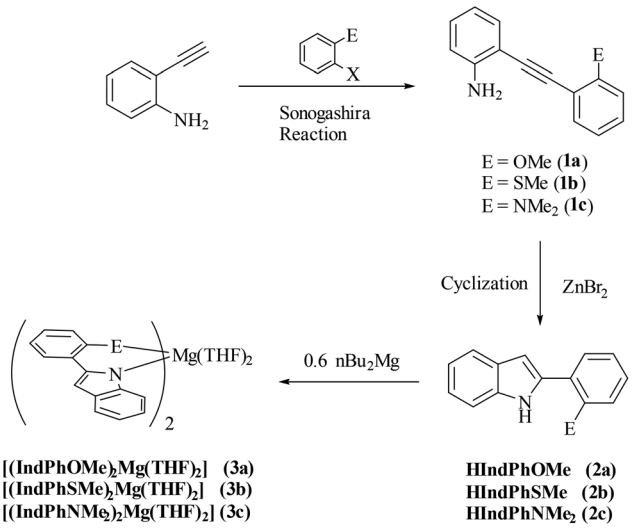
Results and discussion

Preparation of ligand precursors and magnesium complexes

The synthesis of indole compounds has been reported through many strategies, such as Fischer indole synthesis or Pd/Cu-catalyzed cyclization.[13] According to experimental operation and for a cost-effective procedure, our strategy focused on the Sonogashira reaction[14] and Zn-mediated cyclization,[15] as shown in Scheme 1. The acetylene ligand precursors **1a–1c** were prepared *via* Pd/Cu-catalyzed Sonogashira reaction [$PdCl_2(PPh_3)_2$/CuI/$HNEt_2$ for **1a** and **1b**, and $PdCl_2$/dppf/CuI/$HNEt_2$ for **1c**] from the reactions of 2-ethynylaniline with aryl halides (2-iodoanisole for **1a**, 2-iodothioanisole for **1b** and 2-bromo-*N*,*N*-dimethylaniline for **1c**) under mild conditions,



Scheme 1

respectively.[14c] Compounds **1a** and **1b** were prepared in high yields without further purification for the cyclization. However, compound **1c** had to be purified *via* column chromatography before cyclization. For these acetylene compounds, the signals of $-NH_2$ on ^1H NMR spectra were found to be around δ 4.5 ppm (4.50 ppm for **1a** and 4.54 ppm for **1b**) and acetylene functionality on $^{13}C\{^1H\}$ NMR spectra was found to be between δ 90–93 ppm (90.6 and 91.3 ppm for **1a**, and 92.1 and 92.7 ppm for **1b**). The NMR spectra of **1a** and **1c** are consistent with those reported in the literature.[16] Treatment of acetylene compounds **1a–1c** with 0.5 equivalent $ZnBr_2$ in refluxing toluene resulted in the formation of related indole ligands **2a–2c** in moderate to high yields, respectively. The signals of –NH on the ^1H NMR spectrum for indole **2c** were observed at δ 10.75 ppm. The NMR spectra of **2a** and **2b** are consistent with those reported in the literature.[17,18] Compounds **1a**, **1b** and **2c** were characterized by elemental analyses as well.

Treatment of pendant indole ligand precursors **2a–2c** with 0.6 equivalent $^nBu_2Mg$ in THF affords the desired bis-indolyl magnesium complexes **3a–3c** (room temperature for **3a** or 60 °C for **3b** and **3c**) in moderate yields. Compounds **3a–3c** were characterized by NMR spectroscopy as well as by elemental analyses. The disappearance of the N–H signal of indole and the appearance of coordinated THF (1.02, 3.23 ppm for **3a**, 1.17, 3.35 ppm for **3b** and 1.42, 3.57 ppm for **3c** in C_6D_6) are consistent with the structures proposed in Scheme 1. The NMR spectroscopy indicates that these compounds are highly symmetric species in solution. The elemental analysis data are also consistent with a complex containing two coordinated THF.

Suitable crystals for the structural determination of **3a** or **3b** were obtained from THF/*n*-hexane solution. The molecular structures are depicted in Fig. 1 and 2. The structure of **3a** reveals that the Mg centre adopts an approximate octahedral

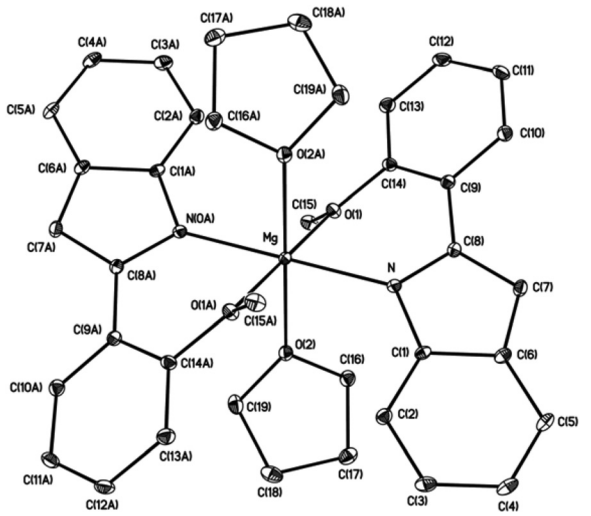


Fig. 1 Molecular structure of one of the crystallographically independent molecules of **3a**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mg–N, 2.091(2); Mg–O(1), 2.149(1); Mg–O(2), 2.228(1); N–C(8), 1.381(2); C(8)–C(9), 1.478(3); C(9)–C(14), 1.400(3); O(1)–C(14), 1.406(2); O(1)–C(15), 1.447(2); O(1)–Mg–O(1A), 180.00(10); O(2)–Mg–O(2A), 180.00(10); N–MgN(0A), 180.00(12); O(1)–Mg–O(2), 83.98(5); N–Mg–O(2), 86.34(6); N–Mg–O(1), 83.01(6); Mg–N–C(8), 125.66(13); Mg–O(1)–C(14), 121.67(11).

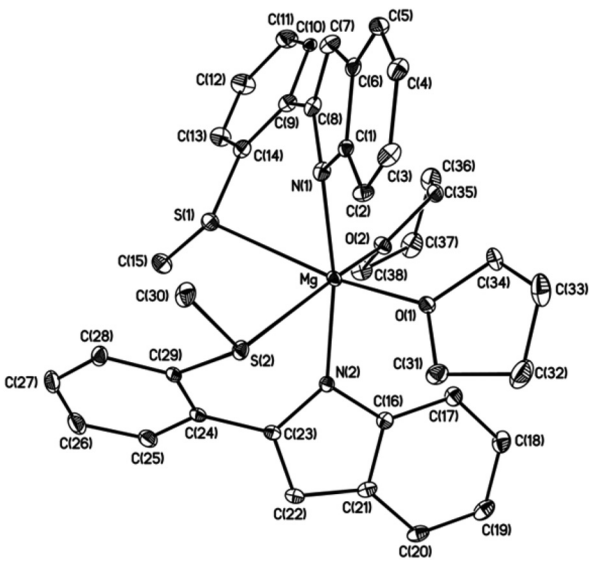


Fig. 2 Molecular structure of one of the crystallographically independent molecules of **3b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Mg–N(1), 2.138(2); Mg–N(2), 2.126(2); Mg–O(1), 2.078(2); Mg–O(2), 2.053(2); Mg–S(1), 2.769(1); Mg–S(2), 2.763(1); N(1)–C(8), 1.398(3); C(8)–C(9), 1.488(4); C(9)–C(14), 1.386(4); S(1)–C(14), 1.777(3); S(1)–C(15), 1.780(3); N(2)–C(23), 1.389(3); C(23)–C(24), 1.469(3); C(24)–C(29), 1.402(4); S(2)–C(29), 1.778(3); S(2)–C(30), 1.796(3); O(1)–Mg–O(2), 99.21(8); S(1)–Mg–S(2), 83.76(3), N(1)–Mg–N(2), 169.17(9); O(1)–Mg–S(1), 164.32(6); O(2)–Mg–S(2), 164.80(6); N(1)–Mg–O(1), 93.89(8); N(1)–Mg–O(2), 95.65(8); N(1)–Mg–S(1), 72.10(6); N(1)–Mg–S(2), 95.14(7); N(2)–Mg–O(1), 90.96(8); N(2)–Mg–O(2), 93.12(8); N(2)–Mg–S(1), 101.70(6); N(2)–Mg–S(2), 75.10(6); Mg–N(1)–C(8), 129.53(17); Mg–S(1)–C(14), 101.86(9); Mg–N(2)–C(23), 133.04(16); Mg–S(2)–C(29), 97.78(8).

geometry [O_{THF}–Mg–O_{THF} ~ 180°] with the metal centre chelated by two nitrogen atoms of the indole ring, two oxygen atoms of methoxy and two oxygen atoms of coordinated THF. The structure of **3b** reveals that the Mg centre adopts a distorted octahedral geometry [N(1)–Mg–N(2), 169.17(9)°, O(1)–Mg–S(1), 164.32(6)° and O(2)–Mg–S(2), 164.80(6)°] with the metal centre chelated by two nitrogen atoms of the indole ring, two sulfur atoms of thiomethoxy and two oxygen atoms of coordinated THF. The positions of coordinated THF molecules are different between **3a** (*trans*- configuration) and **3b** (*cis*-configuration) in the solid state. This difference might result from the soft properties of the sulfur atoms *trans* to the THF molecules. However, only one set of signals corresponding to THF molecules has been observed on the ^{1}H NMR for **3b** (Fig. S2†), even though the temperature was cooled down to 183 K (Fig. S4†). This demonstrates the fluxional behaviour of coordinated THF molecules in solution. According to the coordinated THF positions of related magnesium complexes reported in the literature,[19] the *trans*- and *cis*-configurations are observed for **3a** and **3b** [O_{THF}–Mg–O_{THF}, 180.00(10)° for **3a** and 99.21(8)° for **3b**], respectively. The Mg–O_{THF} bond length of **3a** [2.228(1) Å] is longer than that of **3b** [2.053(2) and 2.078(2) Å], and this tendency is also consistent with the literature data [Mg–O_{THF}, 2.141(4)–2.230(4) Å for *trans*-form[19a,b] and 2.066(1)–2.136(5) Å for *cis*-form[19c,d]]. The Mg–N_{indole} bond lengths [2.091(2) Å for **3a**, and 2.126(2) and 2.138(2) Å for **3b**] are close to those found in magnesium anilido complexes [1.994(2)–2.131(2) Å].[7c,20] The Mg–$O_{methoxy}$ bond length [2.149(1) Å] for **3a** is close to that found in magnesium complexes bearing methoxy functionality [2.109(2)–2.239(2) Å].[7c,21] The Mg–$S_{thiomethoxy}$ bond length [2.769(1) and 2.763(1) Å] for **3b** is shorter than that for anilido-oxazolinate magnesium complexes containing thiomethoxy functionality [2.8613(9) and 2.8215(9) Å].[7c] The chelate 6-membered rings of **3a** and **3b** have a half-chair conformation as evidenced by the dihedral angles between the planes defined by N–Mg–O(1)/N–C(8)–C(9)–C(14)–O(1), which is 33.1° for **3a**, N(1)–Mg–S(1)/N(1)–C(8)–C(9)–C(14)–S(1) and N(2)–Mg–S(2)/N(2)–C(23)–C(24)–C(29)–S(2), which are 55.1° and 51.7° for **3b**.

Ring-opening polymerization

Several magnesium complexes containing auxiliary ligands have been reported as initiators/catalysts for the ROP of cyclic esters,[4f,5a,g,h,o,s,6e,7c,22] especially for those complexes bearing β-diketiminate (BDI)[22a–d] or amino-phenolate[22e–l] ligands. Although attempts to synthesize related magnesium benzyl oxide complexes have been proved unsuccessful, the efficient catalytic activities demonstrated by magnesium di-substituted complexes[7c,23c–d] towards the ROP of cyclic esters encouraged us to examine the magnesium bis-indolyl complexes **3a–3c** in catalyzing the ROP of cyclic esters. Representative results are shown in Tables 1 and 2.

The catalytic activities employing these complexes as catalysts are examined under a dry nitrogen atmosphere. The reactions were run in 2.5 mL solvent at 0 °C or 30 °C for the prescribed time with the prescribed equivalent ratios of the catalyst (0.0125 mmol), L-LA and alcohol, as shown in Table 1. Optimized conditions (entry 1) were found to be dichloromethane at 0 °C in the presence of benzyl alcohol (BnOH) after several trials of running the polymerization with various solvents (dichloromethane, tetrahydrofuran or toluene) and alcohols [BnOH, 2-propanol (^{i}PrOH) and 9-anthracenemethanol (9-AnOH)] for polymerization of L-LA (entries 1–5). Poor conversions were observed in the absence of benzyl alcohol or **3a** under the optimized conditions (entries 6 and 7). The same optimized conditions were applied to examine the catalytic activities of the other two catalysts. Therefore a clear decreasing tendency of catalytic activity was found for these magnesium complexes in the order **3a** > **3b** > **3c** (entries 1, 8 and 9). The interaction between the pendant methoxy group and

Table 1 Polymerisation of L-LA using compounds **3a–3c** as catalysts in CH_2Cl_2 if not stated otherwise[a]

Entry	Catalyst	$[LA]_0:[Mg]_0:[ROH]$	T (°C)	t (min)	M_n[b] (obsd)	M_n[c] (calcd)	Conv.[d] (%)	Yield[e] (%)	M_w/M_n[b]
1	**3a**	300 : 1 : 1	0	3	40 300	37 300	86	82	1.35
2[f]	**3a**	300 : 1 : 1	0	3	—	—	11	—	—
3[g]	**3a**	300 : 1 : 1	0	3	—	—	<5	—	—
4[h]	**3a**	300 : 1 : 1	0	3	40 000	31 600	73	68	1.24
5[i]	**3a**	300 : 1 : 1	0	3	—	—	12	—	—
6	**3a**	300 : 1 : 0	0	3	—	—	<5	—	—
7	**3a**	300 : 0 : 1	0	3	—	—	<5	—	—
8	**3b**	300 : 1 : 1	0	3	29 800	22 500	52	47	1.91
9	**3c**	300 : 1 : 1	0	3	—	—	17	—	—
10	**3a**	200 : 1 : 1	30	1	26 600	28 400	98	89	1.31
11	**3a**	300 : 1 : 1	30	1	35 000	41 200	95	93	1.29
12	**3a**	400 : 1 : 1	30	1	43 100	55 500	96	94	1.31
13	**3a**	500 : 1 : 1	30	1	47 400	69 300	96	95	1.23
14	**3a**	600 : 1 : 1	30	3	50 400	81 400	94	91	1.24
15	**3a**	400 : 1 : 2	30	1	35 100	28 400	98	94	1.28
16	**3a**	500 : 1 : 5	30	2	18 900	14 100	97	87	1.13

[a] $[Mg]_0$ = [BnOH] = 0.005 M in 2.5 mL CH_2Cl_2. [b] Obtained from GPC analysis values time 0.58. [c] Calculated from [M(monomer) × $[LA]_0/[Mg]_0$ × conversion yield/$([ROH]_{eq})$] + M(ROH). [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield. [f] In toluene. [g] In THF. [h] ROH = ^{i}PrOH. [i] ROH = 9-AnOH.

Table 2 Polymerisation of ε-CL using compound **3a** as the catalyst in toluene if not stated otherwise[a]

Entry	$[CL]_0:[Mg]_0:[BnOH]$	T (°C)	t (min)	M_n [b] (obsd)	M_n [c] (calcd)	Conv.[d] (%)	Yield[e] (%)	M_w/M_n [b]
1[f]	500 : 1 : 1	0	1	—	—	<5	—	—
2[g]	500 : 1 : 1	0	1	—	—	46	—	—
3	500 : 1 : 1	0	1	64 800	56 600	99	90	1.33
4	500 : 1 : 0	0	1	142 500	46 200	81	70	1.14
5	500 : 0 : 1	0	1	—	—	<5	—	—
6	100 : 1 : 1	0	0.5	28 900	11 400	99	91	1.27
7	300 : 1 : 1	0	0.75	49 500	33 700	98	93	1.32
8	700 : 1 : 1	0	7	82 300	77 600	97	90	1.26
9	100(100) : 1 : 1	0	0.5(1)	32 400	22 700	99(99)	92	1.29
10	250 : 1 : 2.5	0	3	20 300	11 400	99	92	1.15
11	500 : 1 : 5	30	7	17 400	11 300	98	91	1.17

[a] $[Mg]_0 = [BnOH] = 0.0083$M in 1.875 mL toluene. [b] Obtained from GPC analysis values time 0.56. [c] Calculated from $[M(\text{monomer}) \times [CL]_0/[Mg]_0 \times \text{conversion yield}/([BnOH]_{eq})] + M(BnOH)$. [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield. [f] In CH_2Cl_2. [g] In THF.

the magnesium center might affect the activities of this catalytic system. The linear relationship (R^2 value = 0.957) between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[L\text{-LA}]_0/[Mg]_0$ = 200–600) is demonstrated in Fig. 3 (Table 1, entries 10–14, PDIs = 1.23–1.31). The gap between calculated molecular weight [M_n(calcd)] and observed molecular weight [M_n(obsd)] was easily obtained with a higher monomer-to-initiator loading ratio. This means that the catalyst demonstrates poor living and controlled behaviors in catalyzing polymerization reactions. The end group analysis is demonstrated by the ^{1}H NMR spectrum of polylactide (PLA-100), as shown in Fig. 4. Peaks are assignable to the corresponding protons in the proposed structure. However, the ESI-MS spectrum (Fig. S5†) shows that serious *trans*-esterification could happen in this system.[23a,b] With reference to the mechanism reported for magnesium complexes bearing an *N*,*N* di-anionic ligand or a bis(*N*,*O*-chelate) ligand, the active magnesium alkoxide species might form first, followed by the coordination–insertion mechanism.[23c,e] The immortal behavior was demonstrated using benzyl alcohol as the chain transfer agent (entries 15 and 16) resulting in the reasonable M_n values (comparing with entry 10). The ROP of *rac*-lactide (*rac*-LA) employing **3a** or **3b** at 0 °C under the optimized conditions was examined. Based on the homonuclear decoupled ^{1}H NMR spectra, the atactic polylactides (Pr = 0.51 for **3a**; Pr = 0.43 for **3b**) were produced. Comparing with other structure-related magnesium complexes, the catalytic activity of **3a** was more than magnesium complexes bearing anilido-oxazolinate ligands,[7c] benzotriazole phenoxide ligands,[9d] or amino-phenolate ligands.[22c,h]

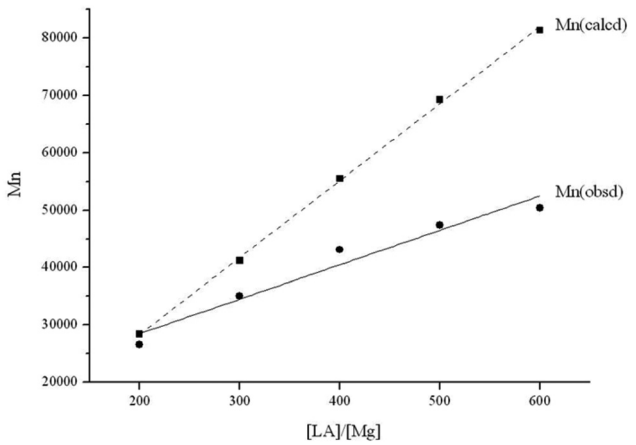


Fig. 3 Polymerization of L-LA catalyzed by **3a** in CH_2Cl_2 at 30 °C.

Optimized catalyst **3a** was introduced for examining the catalytic activities in the ROP of ε-CL under a dry nitrogen atmosphere. The prescribed equivalent ratios of the catalyst (0.0156 mmol), ε-CL and BnOH were employed in 1.875 mL solvent at 0 °C for the prescribed time, as shown in Table 2. Toluene seems to be the right choice at 0 °C in the presence of BnOH for the ROP of ε-CL after running the polymerization reactions with various solvents (dichloromethane, tetrahydrofuran or toluene) (entries 1–3). Compound **3a** showed efficient activities in the presence of BnOH, however lower activity and higher molecular weight were observed in the absence of BnOH (entries 3 and 4). The polymerization reaction might be initiated by a ligand in the absence of BnOH. Trace amount of polymers was observed in the absence of **3a** under the optimized conditions (entry 5). The linear relationship (R^2 value = 0.996) between the number-average molecular weight and monomer-to-initiator ratio ($[\varepsilon\text{-CL}]_0/[Mg]_0$) exhibited by **3a** implies the "living" character of the polymerization process under optimized conditions (entries 3, 6–8; PDIs = 1.26–1.33). Representative results catalyzed by **3a** are shown in Fig. 5. The "living" character was also confirmed by the resumption experiment (entry 9). The end group analysis is demonstrated by the ^{1}H NMR spectrum of polycaprolactone (PCL-100), as shown in Fig. 6. Peaks are assignable to the corresponding protons in the proposed structure, indicating that a similar mechanism as discussed above might happen in the polymerization of ε-CL. The "immortal" character was examined using 2.5 or 5 equivalents of BnOH as the chain transfer agent to produce the polymers with a lower molecular weight at 0 °C or 30 °C (entries 10 and 11). Compound **3a** showed better cata-

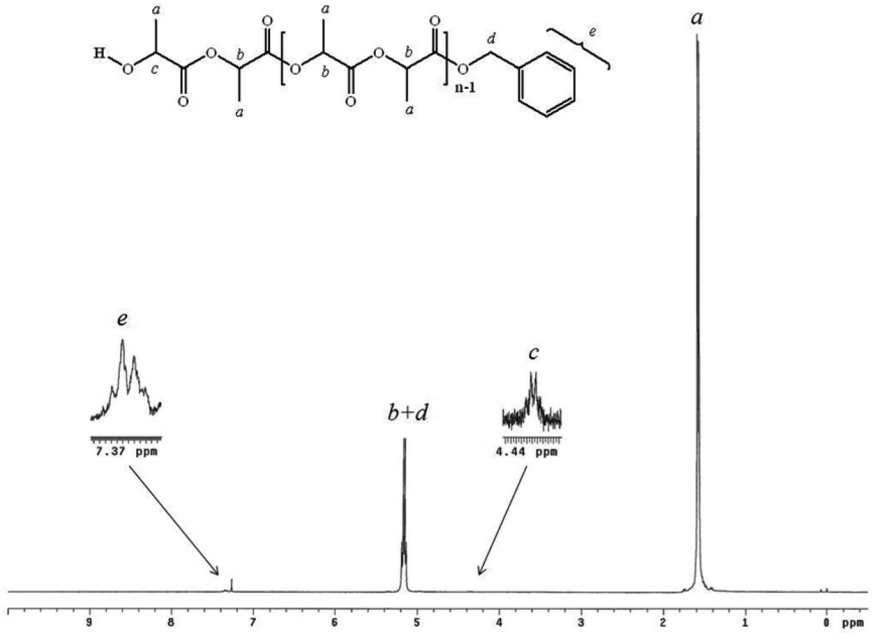


Fig. 4 ^{1}H NMR spectrum of PLA-100 initiated by **3a** in the presence of BnOH in CH_2Cl_2 at 0 °C.

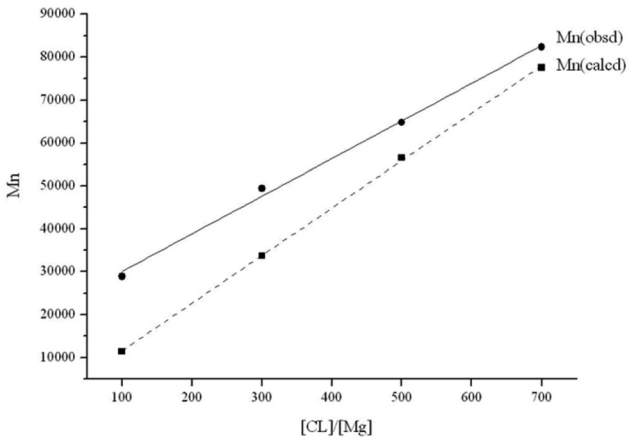


Fig. 5 Polymerization of ε-CL catalyzed by **3a** in toluene at 0 °C.

lytic activity than that demonstrated by magnesium complexes bearing sulfonate phenoxide ligands.[22u]

Conclusions

Three novel magnesium bis-indolyl complexes **3a–3c** have been synthesized and fully characterized. They all show two coordinated THF molecules in the NMR spectroscopic studies and elemental analyses. The molecular determination by single-crystal X-ray crystallography for **3a** and **3b** is also consistent with this result. Under optimized conditions, complex **3a** shows catalytic activities for the ROP of L-LA in the presence of benzyl alcohol with "immortal" behaviour, however, producing lower molecular weights and moderate PDIs (~1.3) meaning in a poorly controlled fashion. The mass spectrum of the produced polymers reveals that serious *trans*-esterification could happen during polymerization. Complex **3a** also demonstrated activities in catalyzing the ROP of ε-CL efficiently, producing the expected molecular weights and narrow PDIs (~1.2). Preliminary studies on fine-tuning the modification of indole ligands with different substituents and their application in the synthesis of metal complexes are currently underway.

Experimental

General conditions

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* or benzene-d_6 at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by an Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and a Waters styragel column (HR4E). Molecular weights (M_n) and molecular weight distributions (PDIs) were calculated using polystyrene as the standard. The electrospray ionization mass spectrometry (ESI-MS) analyses were carried

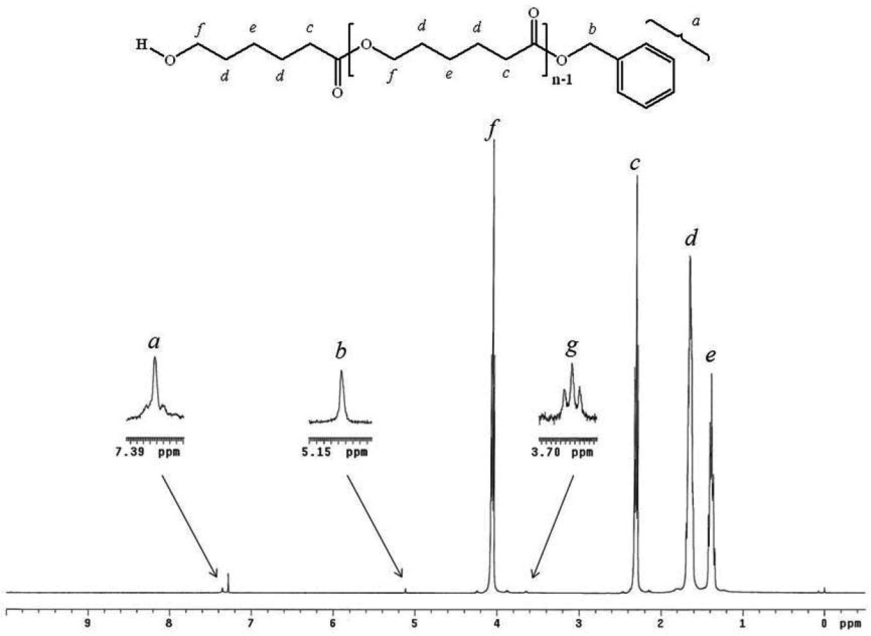


Fig. 6 ^{1}H NMR spectrum of PCL-100 initiated by **3a** in the presence of BnOH in toluene at 0 °C.

out with a Thermo Finnigan TSQ Quantum Triple Quadrupole Mass Spectrometer.

2-Bromo-*N*,*N*-dimethylaniline (TCI), 2-iodoanisole (Alfa Aesar), 2-iodothioanisole (Alfa Aesar), bis(triphenylphosphine)-palladium(II)chloride (Acros), copper(I) iodide (Strem), palladium(II) chloride (UR Chemical), 1,1′-bis(diphenylphosphino)-ferrocene (Strem), diethylamine (Acros), zinc(II) bromide (Acros), 9-anthracenemethanol (Acros) and di-*n*-butyl magnesium (1.0 M in heptane, Aldrich) were used as supplied. *N*,*N*-Dimethylforamide (TEDIA) was dried over molecular sieves before use. Benzyl alcohol (TEDIA) and ε-caprolactone (Acros) were dried over CaH_2 and distilled before use. L- or *rac*-lactide (Bio Invigor) were recrystallized from dry toluene prior to use. 2-Ethynylaniline was prepared by the modification of methods reported in the literature.[14]

Preparations

2-[(2-Methoxyphenyl)ethynyl]aniline (1a). To a flask containing $PdCl_2(PPh_3)_2$ (0.0175 g, 2.5 mol%), CuI (0.0095 g, 5 mol%), 2-iodoanisole (1.17 g, 5 mmol) and 2-ethynylaniline (0.703 g, 6 mmol), 5 mL DMF and $HNEt_2$ (4.14 mL, 40 mmol) were added at room temperature under nitrogen. The reaction mixture was heated at 50 °C for 14 hours and the conversion was monitored by ^{1}H NMR spectrum. The reaction mixture was allowed to cool to room temperature. Then the mixture was extracted with a mixed solution of 20 mL ethyl acetate and 50 mL de-ionized water. The organic layer was separated and dried over magnesium sulphate. The solution was passed through a pad of silica gel. The filtrate was pumped to dryness to afford green oil, **1a**. Compound **1a** was pure enough without the need for further purification for the next step, otherwise it was purified *via* column chromatography (ethyl acetate : *n*-hexane = 1 : 5). Yield, 1.12 g, 99%. ^{1}H NMR (400 MHz): δ(ppm) 3.89 (s, –OCH_3, 3H), 4.50 (b, –N*H*, 2H), 6.67–6.72 (overlap, Ar-*H*, 2H), 6.90 (d, J = 8.4 Hz, Ar-*H*, 1H), 6.94 (td, J = 7.6 & 0.8 Hz, Ar-*H*, 1H), 7.12 (m, Ar-*H*, 1H), 7.29 (m, Ar-*H*, 1H), 7.45 (dd, J = 7.6 & 1.6 Hz, Ar-*H*, 1H), 7.36 (dd, J = 7.6 & 1.6 Hz, Ar-*H*, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ(ppm) 52.6 (–O*C*H$_3$), 110.4, 114.0, 117.5, 120.5, 129.4, 129.5, 131.2, 132.3 (Ar-*C*), 90.6, 91.3, 108.0, 112.6, 148.1, 159.6 (*tert-C*). Anal. Calc. for $C_{15}H_{13}NO$ (M.W. 239.34): C, 80.69; H, 5.87; N, 6.27. Found: C, 80.50; H, 5.90; N, 6.30%. The NMR spectra are consistent with the literature report.[16]

2-[(2-Thiomethoxyphenyl)ethynyl]aniline (1b). The procedure for the preparation of **1b** was similar to that used for **1a**, using $PdCl_2(PPh_3)_2$ (0.0175 g, 2.5 mol%), CuI (0.0095 g, 5 mol%), 2-iodothioanisole (1.25 g, 5.0 mmol), and 2-ethynylaniline (0.703 g, 6 mmol), 5 mL DMF and $HNEt_2$ (4.14 mL, 40 mmol) for 2.5 hours. The crude product was pumped to dryness to afford a green oil, **1b**. Compound **1b** was pure enough without the need for further purification for the next step, otherwise it was purified *via* column chromatography (ethyl acetate : *n*-hexane = 1 : 5). Yield, 1.20 g, 99%. ^{1}H NMR (400 MHz): δ(ppm) 2.49 (s, –SCH_3, 3H), 4.54 (b, –N*H*, 2H), 6.68–6.71 (overlap, Ar-*H*, 2H), 7.09–7.14 (overlap, Ar-*H*, 2H), 7.18 (d, J = 8.0 Hz, Ar-*H*, 1H), 7.28 (td, J = 7.6 & 1.1 Hz, Ar-*H*, 1H), 7.38 (dd, J = 8.0 & 1.6 Hz, Ar-*H*, 1H), 7.48 (dd, J = 7.6 & 0.8 Hz, Ar-*H*, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ (ppm) 15.1 (–S*C*H$_3$), 114.1, 117.5, 124.3, 124.4, 128.4, 129.8, 131.7, 131.7 (Ar-*C*), 92.1, 92.7, 107.4, 121.6, 148.1, 140.4 (*tert-C*). Anal. Calc. for $C_{15}H_{13}NS$ (M.W. 239.34): C, 75.28; H, 5.47; N, 5.85. Found: C, 75.70; H, 5.84; N, 6.05%.

2-{[2-(*N*,*N*-dimethylamino)phenyl]ethynyl}aniline (1c). The procedure for the preparation of **1c** was similar to that used for **1a**, using $PdCl_2$ (0.0177 g, 10.0 mol%), DPPF (0.111 g, 20 mol%), CuI (0.038 g, 20 mol%), 2-bromo-*N*,*N*-dimethylaniline (0.800 g, 4 mmol) and 2-ethynylaniline (0.609 g, 5.2 mmol), 5 mL DMF and $HNEt_2$ (3.30 mL, 32 mmol) for 24 hours at 80 °C. The conversion of ^{1}H NMR spectrum was monitored up to about 70%. The crude product was purified by column chromatography (ethyl acetate : *n*-hexane = 1 : 5) to afford a pale-yellow solid, **1c**. Yield, 0.60 g, 63%. ^{1}H NMR (400 MHz): δ(ppm) 2.94 (s, –N(C*H*$_3$)$_2$, 6H), 4.43 (b, –N*H*, 2H), 6.68–6.72 (overlap, Ar-*H*, 2H), 6.91–6.98 (overlap, Ar-*H*, 2H), 7.12 (td, *J* = 7.8 & 1.2 Hz, Ar-*H*, 1H), 7.25 (td, *J* = 7.8 & 1.6 Hz, Ar-*H*, 1H), 7.35 (m, Ar-*H*, 1H), 7.48 (dd, *J* = 7.8 & 1.6 Hz, Ar-*H*, 1H). The NMR spectrum is consistent with literature reports.[16]

2-(2-Methoxyphenyl)-1*H*-indole (2a). To a flask containing $ZnBr_2$ (0.563 g, 2.5 mmol), a toluene solution of **1a** (1.12 g, 5.0 mmol) was added at room temperature under nitrogen. The reaction mixture was heated at 100 °C for 1.5 hours. After cooling, the mixture was passed through a pad of silica gel and the filtrate was pumped to dryness to afford a dark brown oil. The crude product was purified by column chromatography (ethyl acetate : *n*-hexane = 1 : 3) to afford the product as a pale-yellow solid. Yield, 1.05 g, 94%. ^{1}H NMR (400 MHz): δ (ppm) 3.98 (s, –OC*H*$_3$, 3H), 6.89 (b, Ar-*H*, 1H), 6.99–7.11 (overlap, Ar-*H*, 3H), 7.17 (t, *J* = 7.2 Hz, Ar-*H*, 1H), 7.26 (t, *J* = 7.8 Hz, Ar-*H*, 1H), 7.40 (d, *J* = 7.6 Hz, Ar-*H*, 1H), 7.63 (d, *J* = 7.2 Hz, Ar-*H*, 1H), 7.83 (d, *J* = 7.6 Hz, Ar-*H*, 1H), 9.64 (b, –N*H*, 1H). The NMR spectrum is consistent with the literature.[17]

2-(2-Thiomethoxyphenyl)-1*H*-indole (2b). The procedure for the preparation of **2b** was similar to that used for **2a** with **1b** (1.20 g, 5.0 mmol) and $ZnBr_2$ (0.563 g, 2.5 mmol). The reaction mixture was heated at 100 °C for 1 hour. The crude product was purified by column chromatography (ethyl acetate : *n*-hexane = 1 : 6) to afford the product as a pale-brown solid. Yield, 1.13 g, 94%. ^{1}H NMR (400 MHz): δ (ppm) 2.38 (s, –SC*H*$_3$, 3H), 6.79 (d, *J* = 2.0 Hz, Ar-*H*, 1H), 7.12 (t, *J* = 7.8 Hz, Ar-*H*, 1H), 7.18–7.33 (overlap, Ar-*H*, 3H), 7.40 (m, Ar-*H*, 1H), 7.58 (dd, *J* = 7.8 & 1.8 Hz, Ar-*H*, 1H), 7.65 (d, *J* = 8.0 Hz, Ar-*H*, 1H), 9.09 (b, –N*H*, 1H). The NMR spectrum is consistent with the literature report.[18]

2-[2-(*N*,*N*-Dimethylamino)phenyl]-1*H*-indole (2c). The procedure for the preparation of **2c** was similar to that used for **2a** with **1c** (0.853 g, 3.6 mmol) and $ZnBr_2$ (0.406 g, 1.8 mmol). The reaction mixture was heated at 100 °C for 14 h. The crude product was purified by column chromatography (ethyl acetate : *n*-hexane = 1 : 8) to afford the product as a pale-yellow solid. Yield, 0.52 g, 61%. ^{1}H NMR (400 MHz): δ (ppm) 2.65 (s, –N(C*H*$_3$)$_2$, 6H), 6.80 (m, Ar-*H*, 1H), 7.07–7.25 (overlap, Ar-*H*, 5H), 7.38 (dd, *J* = 8.0 & 0.8 Hz, Ar-*H*, 1H), 7.62 (d, *J* = 7.6 Hz, Ar-*H*, 1H), 7.73 (dd, *J* = 7.6 & 1.6 Hz, Ar-*H*, 1H), 10.75 (b, –N*H*, 1H). ^{13}C{^{1}H} NMR (100 MHz): δ (ppm) 44.5 (s, –N(*C*H$_3$)$_2$), 99.6, 110.9, 119.5, 119.6, 120.2, 121.7, 123.2, 128.2, 129.3 (Ar-*C*), 126.0, 128.3, 136.1, 137.8, 150.5 (*tert*-*C*). Anal. Calc. for $C_{16}H_{16}N_2$ (M.W. 236.31): C, 81.32; H, 6.82; N, 11.85. Found: C, 81.14; H, 6.93; N, 11.54%.

Bis[2-(2-methoxyphenyl)indolyl]magnesium·2THF (3a). To a flask containing **2a** (0.893 g, 4.0 mmol) in 6 mL THF, di-*n*-butyl magnesium (2.4 mL, 2.4 mmol) was added at 0 °C. The reaction mixture was allowed to warm up to room temperature. After 1 hour of stirring, a pale-orange suspension was formed. Then the orange solution was removed by filtration and the off-white solid obtained was washed with 3 mL cool THF twice. The residue was pumped to dryness to afford a white solid. Yield, 0.90 g, 74%. ^{1}H NMR (C_6D_6, 600 MHz): δ (ppm) 1.02 (b, –C*H*$_2$–, 8H), 2.99 (s, –OC*H*$_3$, 6H), 3.23 (b, –OC*H*$_2$–, 8H), 6.79 (d, *J* = 7.8 Hz, Ar-*H*, 1H), 6.96 (td, *J* = 7.8 & 1.6 Hz, Ar-*H*, 1H), 7.01 (m, Ar-*H*, 1H), 7.26 (s, Ar-*H*, 1H), 7.32–7.38 (overlap, Ar-*H*, 2H), 7.46 (d, *J* = 7.8 Hz, Ar-*H*, 1H), 8.06 (dd, *J* = 7.8 & 1.8 Hz, Ar-*H*, 1H), 8.13 (d, *J* = 7.2 Hz, Ar-*H*, 1H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ(ppm) 25.2 (–*C*H$_2$–), 59.9 (–OCH$_3$), 68.7 (–O*C*H$_2$–), 101.3, 114.5, 116.7, 118.1, 120.0, 120.8, 125.0, 127.0, 130.76 (Ar-*C*), 129.1, 132.5, 143.8, 147.0, 153.5 (*tert*-*C*). Anal. Calc. for $C_{38}H_{40}MgN_2O_4$ (M.W. 613.04): C, 74.45; H, 6.58; N, 4.57. Found: C, 73.99; H, 6.49; N, 4.39%.

Bis[2-(2-thiomethoxyphenyl)indolyl]magnesium·2THF (3b). To a flask containing **2b** (0.359 g, 1.5 mmol) in 2 mL THF, di-*n*-butyl magnesium (0.9 mL, 0.9 mmol) was added at 0 °C. The reaction mixture was allowed to warm up to room temperature and reacted at 60 °C. After 1 hour of stirring, the volatiles were removed under reduced pressure. The residue was washed with 3 mL cool THF three times and pumped to dryness to afford a pale-yellow solid. Yield, 0.23 g, 48%. ^{1}H NMR (C_6D_6, 600 MHz): δ(ppm) 1.17 (b, –C*H*$_2$–, 8H), 1.62 (s, –SC*H*$_3$, 6H), 3.35 (b, –OC*H*$_2$–, 8H), 6.69–6.70 (overlap, Ar-*H*, 4H), 6.93 (m, Ar-*H*, 2H), 7.03 (s, Ar-*H*, 1H), 7.22 (m, Ar-*H*, 2H), 7.31 (t, *J* = 6.9 Hz, Ar-*H*, 2H), 7.52 (d, *J* = 8.4 Hz, Ar-*H*, 2H), 7.59 (d, *J* = 7.2 Hz, Ar-*H*, 2H), 8.05 (d, *J* = 7.8 Hz, Ar-*H*, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ(ppm) 16.2 (–S*C*H$_3$), 25.3 (–*C*H$_2$–), 68.7 (–O*C*H$_2$–), 103.5, 114.9, 118.2, 120.2, 120.8, 126.4, 128.4, 129.5, 131.6 (Ar-*C*), 129.8, 132.4, 139.2, 145.9, 147.2 (*tert*-*C*). Anal. Calc. for $C_{38}H_{40}MgN_2O_2S_2$ (M.W. 645.17): C, 70.74; H, 6.25; N, 4.34. Found: C, 70.43; H, 6.25; N, 4.29%.

Bis{2-[2-(*N*,*N*-dimethylamino)phenyl]indolyl}magnesium·2THF (3c). To a flask containing **2c** (0.226 g, 1.0 mmol) in 10 mL THF, di-*n*-butyl magnesium (0.6 mL, 0.6 mmol) was added at 0 °C. The reaction mixture was allowed to warm up to room temperature and reacted at 60 °C for 2 hours. After cooling, the orange solution was stirred at room temperature for further 12 hours to form a suspension. The reaction mixture was filtered and the residue was washed with 5 mL cool THF twice to afford a pale-yellow solid. Yield, 0.11 g, 35%. ^{1}H NMR (C_6D_6, 600 MHz): δ (ppm) 1.42 (p, *J* = 2.9 Hz, –C*H*$_2$–, 8H), 1.81 (b, –N(C*H*$_3$)$_2$, 12H), 3.57 (t, *J* = 6.0 Hz, –OC*H*$_2$–, 8H), 6.35 (m, Ar-*H*, 2H), 6.82 (m, Ar-*H*, 2H), 7.00 (td, *J* = 7.5 & 1.0 Hz, Ar-*H*, 2H), 7.15–7.16 (overlap with C_6D_6, Ar-*H*, 2H), 7.30–7.36 (overlap, Ar-*H*, 4H), 7.57 (d, *J* = 8.4 Hz, Ar-*H*, 2H), 7.89 (m, Ar-*H*, 2H), 8.07 (dd, *J* = 7.2 & 0.6 Hz, Ar-*H*, 2H). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ(ppm) 25.8 (–*C*H$_2$–), 44.1 (b, –N(*C*H$_3$)$_2$), 67.9 (–O*C*H$_2$–), 103.4, 115.7, 118.2, 119.0, 120.6,

121.3, 126.86, 126.9, 132.6 (Ar-*C*), 132.2, 132.8, 144.4, 144.6, 147.7 (*tert-C*). Anal. Calc. for $C_{40}H_{46}MgN_4O_2$ (M.W. 639.12): C, 75.17; H, 7.25; N, 8.77. Found: C, 75.29; H, 7.72; N, 9.06%.

Polymerization procedure of L- or *rac*-lactide. Typically, to a flask containing the prescribed amount of monomers (L- or *rac*-lactide) and 0.0125 mmol catalyst, was added 2.5 mL solvent containing 0.0125 mmol alcohol. The reaction mixture was stirred at the prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 1.5 mL acetic acid solution (0.35 N), the resulting mixture was poured into 15 mL *n*-hexane to precipitate polymers. Crude products were recrystallized from THF/hexane and dried *in vacuo* up to a constant weight.

Polymerization procedure of ε-caprolactone. Typically, to a flask containing the prescribed amount of monomers (ε-caprolactone) and 0.015625 mmol catalyst was added 1.875 mL solvent containing 0.015625 mmol alcohol. The reaction mixture was stirred at the prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 1.5 mL acetic acid solution (0.35 N), the resulting mixture was poured into 15 mL *n*-hexane to precipitate polymers. Crude products were recrystallized from THF/hexane and dried *in vacuo* up to a constant weight.

Crystal structure data

Crystals were grown from a THF/hexane solution for **3a** or **3b**, and isolated by filtration. Suitable crystals were mounted onto Mounted CryoLoop (HAMPTON RESEARCH, size: 0.5–0.7 mm) using perfluoropolyether oil (Aldrich, FOMBLIN®Y) and cooled rapidly in a stream of cold nitrogen gas using an Oxford Cryosystems Cryostream unit. Diffraction data were collected at 100 K using an Oxford Gemini S diffractometer. Empirical absorption correction was based on spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm from CrysAlis RED, Oxford Diffraction Ltd. 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.[24] 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. Some details of the data collection and refinement are given in Table 3. CCDC reference numbers 1044567–1044568 for **3a** and **3b**.

Table 3 Summary of crystal data for compounds **3a** and **3b**

	3a	**3b**
Formula	$C_{38}H_{40}MgN_2O_4$	$C_{38}H_{40}MgN_2O_2S_2$
Fw	613.03	645.15
T, K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*n*
a, Å	21.2856(16)	14.9449(4)
b, Å	7.6356(6)	14.0155(3)
c, Å	18.3690(12)	15.4168(4)
α, °	90	90
β, °	93.092(6)	93.830(2)
γ, °	90	90
V, Å^3	2981.1(4)	3221.99(14)
Z	4	4
ρ_{calc}, Mg m^{-3}	1.366	1.330
μ(Mo Kα), mm^{-1}	0.107	0.223
Reflections collected	6238	12 852
No. of parameters	205	406
R_1[a]	0.0527	0.0555
wR_2[a]	0.1489	0.1571
GoF[b]	1.000	1.000

[a] $R_1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, w = 0.10. [b] GoF $= [\sum w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

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