Magnesium Complexes Incorporated by Sulfonate Phenoxide Ligands as Efficient Catalysts for Ring-Opening Polymerization of ε-Caprolactone and Trimethylene Carbonate

PO-SHENG CHEN, YI-CHANG LIU, CHIA-HER LIN, BAO-TSAN KO

Department of Chemistry, Chung Yuan Christian University, Chung-Li 320, Taiwan, Republic of China

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ABSTRACT: Two novel sulfonate phenol ligands—3,3′-di-*tert*-butyl-2′-hydroxy-5,5′,6,6′-tetramethyl-biphenyl-2-yl 4-X-benzenesulfonate (X=CF_3, $\mathbf{L^{CF3}}$-H, and X=OCH_3, $\mathbf{L^{OMe}}$-H)—were prepared through the sulfonylation of 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-biphenyl-2,2′-diol with the corresponding 4-substituted benzenesulfonyl chloride (1 equiv.) in the presence of excess triethylamine. Magnesium (Mg) complexes supported by sulfonate phenoxide ligands were synthesized and characterized structurally. The reaction of Mg^nBu_2 with L-H (2 equiv.) produces the four-coordinated monomeric complexes $(\mathbf{L^{CF3}})_2$Mg (**1**) and $(\mathbf{L^{OMe}})_2$Mg (**2**). Complexes **1** and **2** are efficient catalysts for the ring-opening polymerization of ε-caprolactone (ε-CL) and trimethylene carbonate (TMC) in the presence of 9-anthracenemethanol; complex **1** catalyzes the polymerization of ε-CL and TMC in a controlled manner, yielding polymers with the expected molecular weights and narrow polydispersity indices (PDIs). In ε-CL polymerization, the activity of complex **1** is greater than that of complex **2**, likely because of the greater Lewis acidity of Mg^{2+} metal caused by the electron-withdrawing substitute trifluoromethyl (—CF_3) at the 4-position of the benzenesulfonate group. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3564–3572, 2010

KEYWORDS: ε-caprolactone; catalysts; magnesium; polycarbonates; polyesters; ring-opening polymerization; sulfonate phenoxide; trimethylene carbonate

INTRODUCTION

Because of their biodegradable, biocompatible, and permeable properties, aliphatic polyesters and polycarbonates such as poly(ε-caprolactone) (PCL), polylactide (PLA), and poly(trimethylene carbonate) (PTMC), as well as their copolymers, have attracted considerable attention and have been widely used in the biomedical, pharmaceutical and environmental fields.[1] A common chemical synthetic route to PCL, PLA, and PTMC is the ring-opening polymerization (ROP) of cyclic esters and carbonates using metal-alkoxide initiators or catalysts derived from various main-group metal complexes,[2] such as lithium,[3] calcium,[4] zinc,[5] tin(II),[6] and aluminium[7] as well as magnesium complexes.[8] These metal complexes are efficient initiators and catalysts for the preparation of polyesters with controlled molecular weight and its narrow distribution. Among these metals, magnesium is nontoxic and essential for human life[9]; therefore, magnesium complexes are worthy candidates as catalysts and initiators of ROP for biomedical purposes.

So-called single-active-site metal complexes supported by various ligands such as β-diketiminate,[5(c,d,g)] Schiff base,[10] anilido-aldiminate,[11] and many others have been developed to achieve great activity with effective molecular weight in a controlled manner. In particular, the bisphenolate system receives increasing attention because of easy modification and functionalization. Many bisphenolato ligands (Type **I**, Chart 1) have been modified on introducing various functional groups, and their metal complexes have shown to have promising catalytic activities for ROP.[7(f,j,l),12] Magnesium complexes supported by monovalent phenols derived from 2,2′-ethylidene-bis(4,6-di-*tert*-butylphenol) (EDBP-H_2), including EDBP-RTs-H (Type **II**, Chart 1)[13] and EDBP-(Me)-H (Type **III**, Chart 1),[14] have been synthesized and structurally characterized; these complexes bearing bidentate monovalent phenoxide ligands have proved to be effective initiators for ROP of lactides and demonstrated that their catalytic activities were greatly increased relative to the bisphenol system. Encouraged by these results from the modified EDBP system, we are interested in developing the sulfonate phenol ligand derived from another bisphenol—3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-biphenyl-2,2′-diol—to investigate the catalytic behavior of these complexes bearing such a ligand. As a result, a novel 4-substituted benzenesulfonate phenol ligand (**L**-H, Chart 1) has been designed and synthesized. Herein, we describe the synthesis, characterization, and ROP catalytic studies of magnesium derivatives supported by novel sulfonate phenoxide ligands of this kind.

EXPERIMENTAL

General

All manipulations were carried out under a dry nitrogen atmosphere. Solvents and reagents were dried by refluxing for

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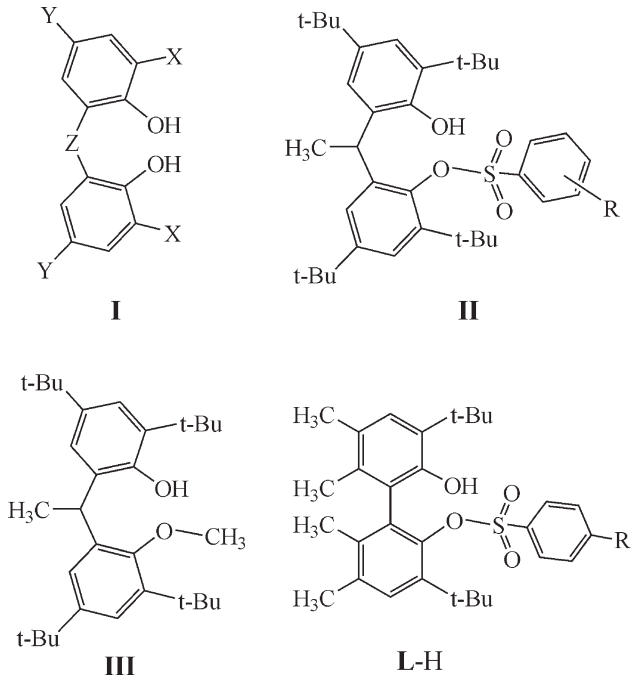


CHART 1

at least 24 h over sodium/benzophenone (hexane, toluene, and tetrahydrofuran [THF]), or over calcium hydride (CH_2Cl_2). Deuterated solvents, triethylamine, and ε-caprolactone (ε-CL) were dried over 4 Å molecular sieves. Trimethylene carbonate (TMC) was purchased from Boehringer Ingelheim (http://www.boehringer-ingelheim.com) and was recrystallized from a toluene solution before use. 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol (Strem), 4-(trifluoromethyl)benzenesulfonyl chloride (Acros), 4-methoxybenzene-1-sulfonyl chloride (Acros), 9-anthracenemethanol (9-AnOH) (Acros), 1-pyrenebutanol (Acros), and 4-dimethylaminopyridine (Alfa) were purchased and used without further purification. Mg^{n}Bu$_2$ (1.0 M in heptane) was purchased from Aldrich (http://www.sigmaaldrich.com) and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer with chemical shifts given in parts per million (ppm) from the peak of internal tetramethylsilane. Microanalyses were performed using a Heraeus CHN—O—RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a JASCO PU-2080 plus system equipped with a RI-2031 detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5 μ 103 Å, and the calibration curve used to calculate Mn(GPC) was produced from polystyrene standards. The GPC results were calculated using the Scientific Information Service Corporation (SISC) chromatography data solution 3.1 edition.

General Procedures for Synthesis of the Sulfonate Phenol Ligands

3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol (1.24 g, 3.50 mmol), 4-(trifluoromethyl)-benzenesulfonyl chloride (0.87 g, 3.50 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.069 g, 0.57 mmol, catalyst) were dissolved in 50 mL of freshly distilled CH_2Cl_2 and the resulting solution cooled to 0 °C. Neat triethylamine (NEt_3, 0.6 mL, 3.85 mmol) was added dropwise to the solution, which was then stirred at ambient temperature for 48 h. The solution was filtered, and the filtrate was washed with 50 mL of water three times. The dichloromethane layer was collected and dried over anhydrous $MgSO_4$ and filtered through Celite again to remove $MgSO_4$. The resulting filtrate was then dried under vacuum, and the residue was recrystallized from an acetonitrile solution.

L^{CF3}-H: Yield: 1.59 g (81%).^{1}H NMR (298 K, $CDCl_3$, 300 MHz, ppm): δ 6.63–7.51 (6H, m, Ar*H*), 4.94 (1H, s, O*H*), 2.33 (3H, s, CH_3), 1.75 (3H, s, CH_3), 1.72 (3H, s, CH_3), 1.52 (3H, s, CH_3), 1.61 (9H, s, C(CH_3)$_3$), 1.44 (9H, s, C(CH_3)$_3$). ^{13}C NMR (298 K, $CDCl_3$, 75 MHz, ppm): δ 150.63, 147.00, 141.30, 141.11, 136.83, 136.27, 133.72, 133.33, 133.29, 132.71, 130.62, 129.94, 128.24, 127.27, 125.60, 125.46, 125.10(CF_3), 35.07, 34.35, 31.17, 29.58, 20.75, 19.67, 16.04, 15.90. Anal. calcd for $C_{31}H_{37}F_3O_4S$: C, 66.17; H, 6.63. Found: C, 66.55; H, 6.68%.

L^{OMe}-H: Yield: 1.47g (80%). ^{1}H NMR (298 K, $CDCl_3$, 300 MHz, ppm): δ 6.67–7.35 (6H, m, Ar*H*), 5.02 (1H, s, O*H*), 3.86 (1H, s, OCH_3), 2.31 (3H, s, CH_3), 2.01 (3H, s CH_3), 1.84 (3H, s, CH_3), 1.52 (3H, s, CH_3), 1.58 (9H, s, C(CH_3)$_3$), 1.45 (9H, s, C(CH_3)$_3$). ^{13}C NMR (298 K, $CDCl_3$, 75 MHz, ppm): δ 162.39, 150.81, 146.73, 141.08, 136.63, 135.70, 133.41, 132.84, 131.26, 129.92, 129.87, 127,96, 127.67, 127.34, 126.46, 113.27, 55.54, 35.19, 34.40, 31.35, 29.71, 20.78, 19.89, 16.15, 15.93. Anal. calcd for $C_{31}H_{40}O_5S$: C, 70.96; H, 7.68. Found: C, 70.69; H, 7.98%.

Synthesis of Magnesium Complexes

[(**L^{CF3}**)$_2$Mg] (**1**): ^{n}Bu$_2$Mg (1.0 mL, 1.0 M in heptane, 1.0 mmol) was added slowly to an ice cold solution (0 °C) of **L^{CF3}**-H (1.12 g, 2.0 mmol) in 30.0 mL of toluene under a dry nitrogen atmosphere. The mixture was then stirred for 24 h while the temperature was slowly increased to ambient temperature. Volatile materials were removed under vacuum and the residue was recrystallized from a hexane solution to give white solids. Yield: 0.84 g (73%). The resulting solids were crystallized from the saturated hexane solution to yield colorless crystals.

^{1}H NMR (298 K, $CDCl_3$, 300 MHz, ppm): δ 6.45–7.56 (6H, m, Ar*H*), 2.29 (3H, s, CH_3), 1.74 (3H, s, CH_3), 1.66 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.47 (9H, s, C(CH_3)$_3$), 1.31 (9H, s, C(CH_3)$_3$). ^{13}C NMR (298 K, $CDCl_3$, 75 MHz, ppm): δ 160.81, 147.21, 139.16, 139.05, 138.19, 136.62, 135.01, 134.94, 133.92, 131.44, 128.41, 127.98, 126.93, 125.51, 125.47, 124.77, 120.30, 34.73, 34.33, 31.21, 29.37, 21.08, 19.52, 16.12, 15.96. Anal. calcd for $C_{62}H_{72}F_6MgO_8S_2$: C, 64.89%; H, 6.32%. Found: C, 64.79%; H, 6.70%.

[(**L^{OMe}**)$_2$Mg] (**2**): To an ice cold solution (0 °C) of **L^{OMe}**-H (1.05 g, 2.0 mmol) in 30.0 mL of toluene was slowly added a ^{n}Bu$_2$Mg (1.0 mL, 1.0 M in heptane, 1.0 mmol) under a dry

nitrogen atmosphere. The mixture was then stirred for 24 h while the temperature was slowly increased to ambient temperature. Volatile materials were removed under vacuum and the residue was recrystallized from a hexane solution to give white solids. Yield: 0.75 g (70%). The resulting solids were crystallized from the saturated hexane solution to yield colorless crystals.

^{1}H NMR (298 K, $CDCl_3$, 300 MHz, ppm): δ 6.61–7.21 (6H, m, Ar*H*), 3.87 (3H, s, OCH_3), 2.29 (3H, s, CH_3), 1.77 (3H, s, CH_3), 1.75 (3H, s, CH_3), 1.45 (9H, s, C(CH_3)$_3$), 1.34 (12H, s, CH_3 + C(CH_3)$_3$). ^{13}C NMR (298 K, $CDCl_3$, 75 MHz, ppm): δ 162.94, 161.22, 146.58, 139.25, 137.96, 136.04, 135.45, 134.99, 131.54, 128.40, 127.64, 127.46, 127.41, 119.90, 113.82, 113.66, 55.59, 34.88, 34.39, 31.40, 29.57, 21.10, 19.73, 16.20, 16.00. Anal. calcd for $C_{62}H_{78}MgO_{10}S_2$: C, 69.48% ; H, 7.34%. Found: C, 69.71%; H, 7.29%.

Polymerization of ε-CL Catalyzed by the Sulfonate Phenoxide Magnesium Complex

A typical polymerization procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed $[CL]_0/[9\text{-AnOH}]_0$). To a rapidly stirring solution of [($\mathbf{L^{CF3}}$)$_2$Mg] (**1**) (0.057 g, 0.05 mmol) and 9-anthracenemethanol (9-AnOH, 0.021 g, 0.1 mmol) in toluene (15 mL) was added ε-caprolactone (0.55 mL, 5.0 mmol). The reaction mixture was stirred at 25 °C for 5 min. The conversion yield (99%) of PCL-50 was analyzed by ^{1}H NMR spectroscopic studies. After the reaction was quenched by the addition of excess water (1.0 mL), the polymer was precipitated into hexane (100 mL). The white precipitate was purified by redissolving the polymer in THF (5.0 mL) and then precipitated into MeOH (60 mL). Finally, the white polymer was dried under vacuum giving white solids. Yield: 0.45 g (79%).

Polymerization of TMC Catalyzed by the Sulfonate Phenoxide Magnesium Complex

A typical polymerization procedure was exemplified by the synthesis of PTMC-100 (the number 100 indicates the designed $[TMC]_0/[9\text{-AnOH}]_0$). To a rapidly stirring solution of [($\mathbf{L^{CF3}}$)$_2$Mg] (**1**) (0.057 g, 0.05 mmol) and 9-anthracenemethanol (9-AnOH, 0.021 g, 0.1 mmol) in CH_2Cl_2 (10 mL) was added TMC (1.02 g, 10 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at 0 °C for 60 min. The conversion yield (98%) of PTMC-100 was analyzed by ^{1}H NMR spectroscopic determinations. After the reaction was quenched by the addition of excess water (1.0 mL), the polymer was precipitated into hexane (100 mL). The white precipitate was purified by redissolving the polymer in THF (5.0 mL) and then precipitated into MeOH (60 mL). Yield: 0.92 g (90%).

Synthesis of PCL-*b*-PTMC Diblock Copolymer Catalyzed by the Sulfonate Phenoxide Magnesium Complex

A typical polymerization procedure was exemplified by the synthesis of PCL(100)-*b*-PTMC(50) (the number 100 or 50 indicates the designed $[CL]_0/[9\text{-AnOH}]_0$ or $[TMC]_0/[9\text{-AnOH}]_0$). The living prepolymer PCL-100 was synthesized by a similar approach as described above, but ε-CL (1.10 mL, 10.0 mmol) in CH_2Cl_2 (15.0 ml) was used. After prepolymerization for 15 min, TMC (0.51 g, 5.0 mmol) in CH_2Cl_2 (5.0 mL) was added. After another 30 min, the reaction was quenched using the procedures described previously. Yield: 1.35 g (82%).

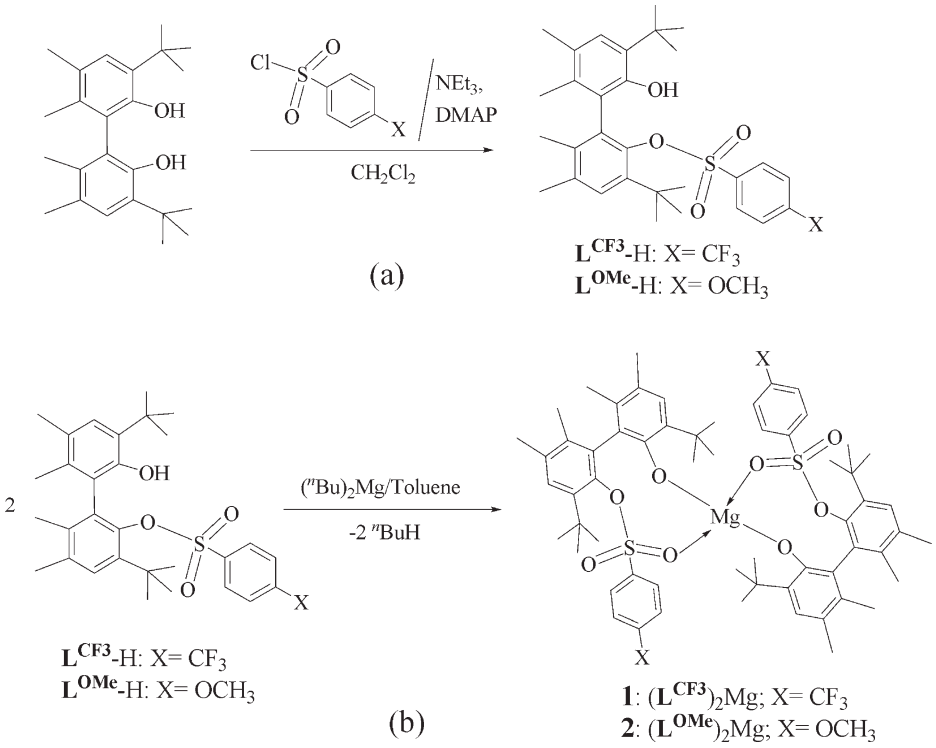
X-Ray Crystallographic Studies

Suitable crystals of complexes **1** and **2** were sealed in thin-walled glass capillaries under nitrogen atmosphere and were mounted on Brucker SMART APEX2 or Oxford Gemini R Ultra diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.3° per frame). The absorption correction was based on the symmetry-equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absence and was confirmed using the structure solution. The structures were solved with 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.

RESULTS AND DISCUSSION

Syntheses and Crystal Structure Determination

The synthetic routes of sulfonate phenol ligands ($\mathbf{L^{CF3}}$-H and $\mathbf{L^{OMe}}$-H) and their Mg complexes (**1** and **2**) are outlined in Scheme 1. These 4-substituted benzenesulfonate phenol derivatives (3,3′-di-*tert*-butyl-2′-hydroxy-5,5′,6,6′-tetramethylbiphenyl-2-yl 4-X-benzenesulfonate) were prepared in high yield (80%) on the reaction of 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol with the corresponding 4-substituted benzenesulfonyl chloride (4-X—$C_6H_4SO_2Cl$, X=CF_3 or OCH_3, 1 molar equiv.) in the presence of excess triethylamine, using 4-dimethylaminopyridine (DMAP) as catalyst and dichloromethane as solvent at ambient temperature.[15] These ligands ($\mathbf{L^{CF3}}$-H and $\mathbf{L^{OMe}}$-H**)** were isolated as white solids and easily purified on recrystallization from acetonitrile or hexane solution. These two ligands were characterized by ^{1}H and ^{13}C NMR spectra and microanalyses. The ^{1}H NMR spectrum of the ligands exhibited resonances approximately δ 5.0 ppm for the only hydroxyl proton of the phenol group, and signals of methyl or *tert*-butyl group on biphenyl backbone in two sets, indicating the formation of the desired monobenzenesulfonylate phenol ligand. For instance, four resonance peaks corresponding to methyl protons (δ = 1.52, 1.72, 1.75, 2.33 ppm, 3H each) and two peaks arising from *tert*-butyl groups (δ = 1.44, 1.61 ppm, 9H each) were observed for $\mathbf{L^{CF3}}$-H. Compounds **1** and **2** were further synthesized via alkane elimination in toluene. Treatment of the ligand ($\mathbf{L^{CF3}}$-H or $\mathbf{L^{OMe}}$-H, two equiv.**)** with Mg^{n}Bu$_2$ affords the tetra-coordinated monomeric complex [$\mathbf{L}_2$Mg] (**1**: ($\mathbf{L^{CF3}}$)$_2$Mg; **2**: ($\mathbf{L^{OMe}}$)$_2$Mg) in 73% and 70% yields, respectively. Attempts to obtain the butylmagnesium complexes modified by the sulfonate phenolate ligand were unsuccessful. Complexes **1** and **2** were obtained as white crystalline solids after recrystallization from hexane solution and have been fully characterized by spectroscopic studies and X-ray structural determinations.



SCHEME 1 Synthetic routes for (a) ligands L^{CF3}-H & L^{OMe}-H and (b) complexes (**1**)–(**2**).

Single crystals of complexes **1** and **2** suitable for X-ray structural determinations were obtained on cooling a saturated hexane solution. Oak Ridge Thermal Ellipsoid Plot drawings displaying selected bond lengths and angles of the molecular structure of **1** and **2** appear in Figures 1 and 2, respectively. The molecular structures of compound **1** and **2** are *isostructural*, except either a trifluoromethyl (—CF_3) or a methoxy (—OCH_3) substituent at the 4-position of the benzenesulfonate group. Both exhibit the homoleptic and monomeric feature with a four-coordinated magnesium center supported by oxygen atoms of sulfonate phenoxide ligands, forming two nine-membered chelating rings. The bond angles around Mg in **1** in a range 97.12(10)–135.61(11)° and around Mg in **2** in the range 97.08(6)–136.88(6)° all show a distorted tetrahedral geometry. The average bond lengths of Mg–O(phenoxy oxygen) are 1.876(2) Å for **1** and 1.883(1) Å for **2**, respectively, which are within a normal range for the four-coordinated magnesium phenoxide complexes.[13,14] The oxygen atoms of the sulfonate groups coordinate the magnesium ion with an average Mg—O(sulfonate oxygen) bond distance of 2.028(2) Å for **1** and 2.003(1) Å for **2**, greater than the covalent Mg–O(phenoxy oxygen) bond. The slightly shorter

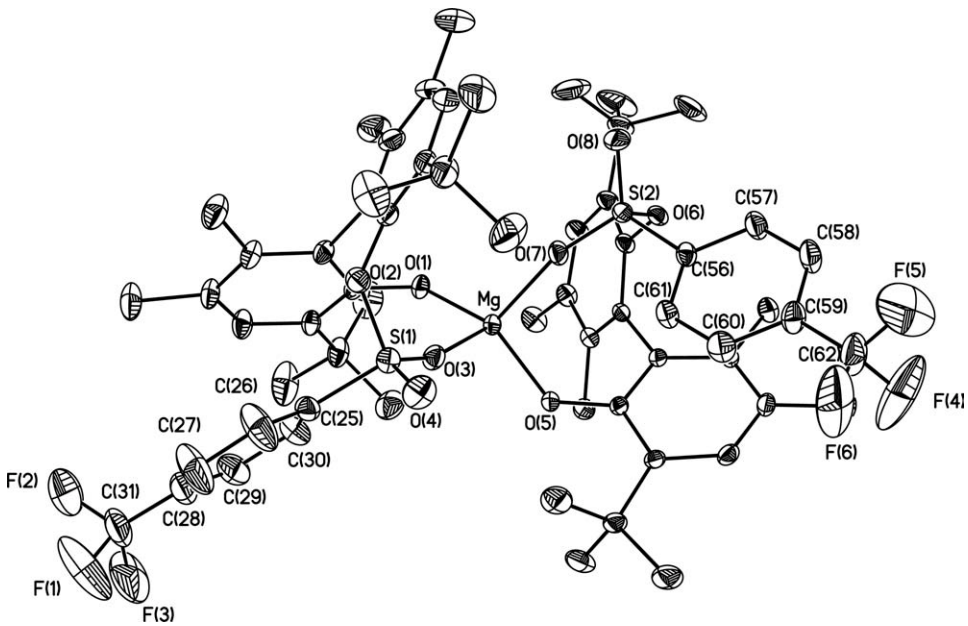


FIGURE 1 Oak Ridge Thermal Ellipsoid Plot drawing of complex **1** with probability ellipsoids drawn at the 20% level. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and angles/deg: Mg—O(1) 1.867(2), Mg—O(5) 1.884(2), Mg—O(7) 2.013(2), Mg—O(3) 2.042(2), O(1)—Mg—O(5) 135.61(11), O(1)— Mg—O(7) 113.62(10), O(5)—Mg— O(7) 101.97(9), O(1)—Mg—O(3) 97.12 (10), O(5)—Mg—O(3) 100.05 (10), O(7)—Mg—O(3) 102.80(10).

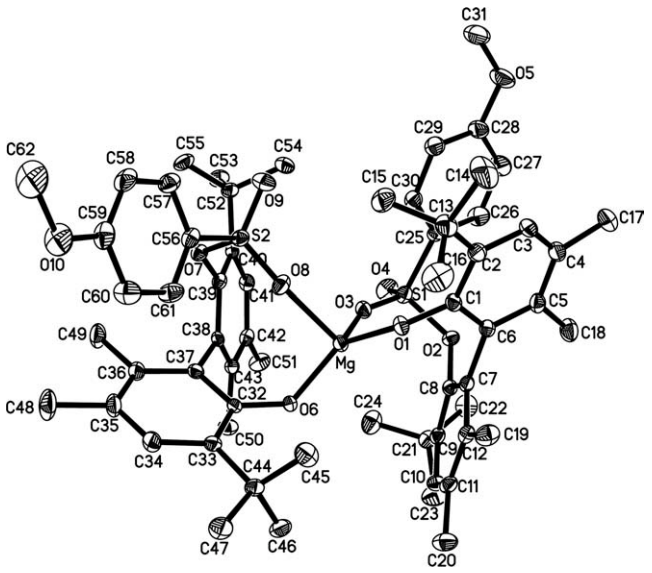


FIGURE 2 Oak Ridge Thermal Ellipsoid Plot drawing of complex **2** with probability ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths/Å and angles/deg: Mg—O(1) 1.8929(14), Mg—O(3) 1.9987(14), Mg—O(6) 1.8739(14), Mg—O(8) 2.0077(14), O(6)—Mg—O(1) 136.88(6), O(1)—Mg—O(8) 98.84(6), O(1)—Mg—O(3) 106.36(6), O(6)—Mg—O(3) 109.93(6), O(6)—Mg—O(8) 97.08(6), O(3)—Mg—O(8) 99.97(6).

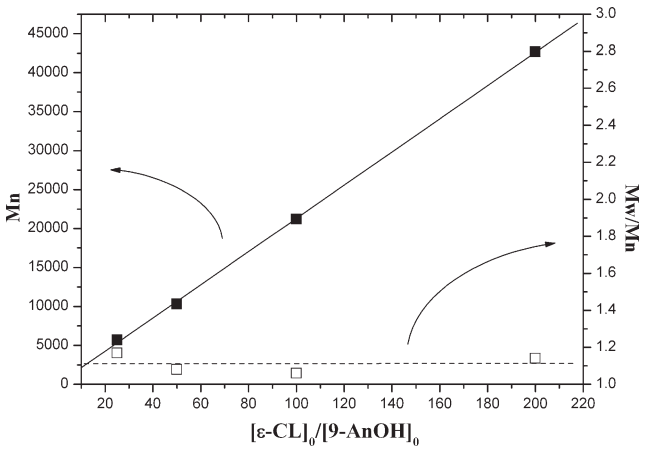
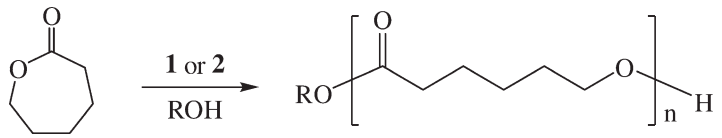


FIGURE 3 Polymerization of ε-CL catalyzed by **1** in toluene at 25 °C. The relationship between M_n(■)/(PDI(□) of polymer and the initial molar ratio $[CL]_0/[9\text{-AnOH}]_0$ is shown.

Mg—O(sulfonate oxygen) bond in **2** is consistent with the effective electron-donating group, —OCH_3 on the sulfonate group, that increases the electron density to form a stronger dative bond. These Mg—O(sulfonate oxygen) bond distances of bis(sulfonate phenoxide) Mg complexes in this work are somewhat smaller than those (~2.090(2) Å) found in alkyl Mg complexes, but are similar to those (~2.010(2) Å) of Mg alkoxide complexes with EDBP-*R*T ligands.[13]

TABLE 1 Ring-Opening Polymerization of ε-Caprolactone (ε-CL) Catalyzed by Complexes **1** and **2** in the Presence of ROH[a]



Entry	Catalyst	$[CL]_0/[Mg]_0/[ROH]_0$	Conversion yield (%)[b]	*t* (min)	M_n (calcd.)[c]	M_n (obsd.)[d]	M_n (NMR)[b]	PDI[d]
1	**1**	25/1/0	99	5	2,800[e]	37,000(20,700)	–[f]	1.77
2	**1**	25/1/1	99	5	3,000	7,000(3,900)	5,500	1.06
3	**1**	50/1/2	98	5	3,000	5,700(3,200)	3,200	1.17
4	**1**	100/1/2	99	5	5,900	10,300(5,800)	6,400[f]	1.08
5	**1**	200/1/2	99	5	11,500	21,200(11,900)	15,000	1.06
6	**1**	400/1/2	99	5	22,800	42,700(23,900)	33,700	1.14
7	**2**	25/1/0	99	15	2,800[e]	17,800(10,000)	–[f]	2.05
8	**2**	50/1/2	99	15	3,000	5,300(3,000)	3100	1.14
9	**2**	100/1/2	99	15	5,900	11,000(6,200)	6,700	1.06
10	**2**	200/1/2	99	15	11,500	20,600(11,500)	13300	1.14
11	**2**	400/1/2	92	15	21,200	32,400(18,100)	27,100	1.18
12[g]	**1**	50/1/2	96	5	3,000	6,900(3,900)	3,300	1.07

[a] 0.05 mmol complexes, 25 °C, 15 mL of toluene, 9-AnOH was used as the alcohol.
[b] Obtained from ^{1}H NMR determination.
[c] Calculated from the molecular weight of ε-caprolactone × times $[CL]_0/[ROH]_0$ × conversion yield plus the molecular weight of ROH.
[d] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC × 0.56.[17]
[e] Calculated from the molecular weight of ε-caprolactone × 25 × conversion yield.
[f] Not available.
[g] 1-pyrenebutanol was used as the alcohol.

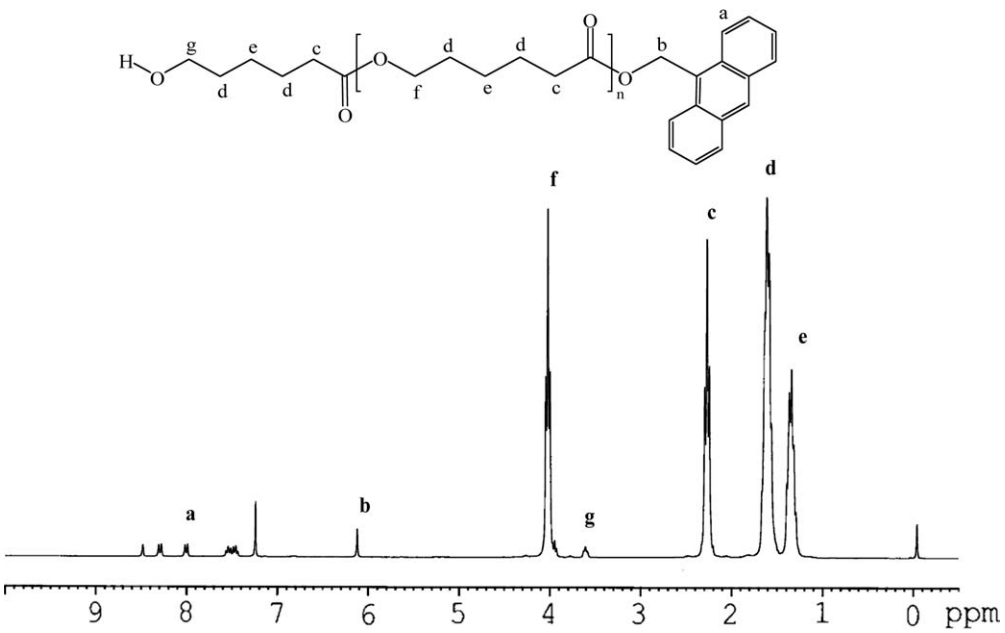
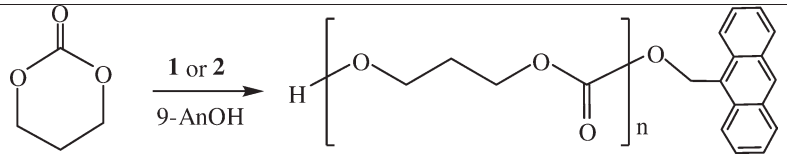


FIGURE 4 ^{1}H NMR spectra of PCL-25 (Table 1, entry 3) in $CDCl_3$.

Ring-Opening Polymerization of ε-Caprolactone

Based on some successful lactone polymerizations catalyzed by calcium bis(NNO tridentate Schiff-base),[16(a)] magnesium bis(amido-oxazolinate)[16(b)] or magnesium/zinc bis(phenolate) derivatives,[12(f,i,k)] the bis(sulfonate phenoxide) Mg complexes **1** and **2** were expected to behave as catalysts toward the ROP of ε-caprolactone (ε-CL) in the presence of alcohol. In general, polymerizations were performed in toluene (15 mL) with a prescribed equivalent ratio on the catalyst (0.05 mmol), monomers, and 9-anthracenemethanol (9-AnOH) for the prescribed duration. After the reaction was quenched with the addition of water, the polymer was precipitated into hexane. The results of the polymerization of ε-CL catalyzed by **1** or **2** under varied conditions are listed in Table 1. The

TABLE 2 Ring-Opening Polymerization of Trimethylene Carbonate (TMC) Catalyzed by Complexes **1** and **2** in the Presence of 9-AnOH, and Copolymerization of PCL-*b*-PTMC Catalyzed by Complex **1**



Entry	Catalyst	$[M]_0/[Mg]_0$ /[9-AnOH]$_0$	Conversion yield (%)[a]	Temperature (°C)	t (min)	M_n (calcd.)[b]	M_n (obsd.)[c]	M_n (NMR)[a]	PDI[c]
1[d]	**1**	200/1/2	97	25	10	10100	21,900	7,500	1.46
2[e]	**1**	200/1/2	81	25	30	8,500	11,500	9,500	1.74
3[f]	**1**	200/1/2	87	25	20	9,100	19,800	14,800	1.44
4[f]	**1**	200/1/2	98	0	60	10,200	24,700	13,900	1.30
5[f]	**1**	150/1/2	91	0	60	7,200	14,700	9,300	1.30
6[f]	**1**	100/1/2	89	0	80	4,700	9,200	5,100	1.30
7[f]	**1**	50/1/2	87	0	120	2,400	5,800	3,800	1.27
8[f]	**2**	200/1/2	99	0	60	10,300	20,400	14,700	1.66
9[g]	**1**	100/1/2; 100/1/2	>99; 90	25	15; 30	10,500[h]	22,900	10,300	1.18
10[g]	**1**	200/1/2; 100/1/2	>99; 95	25	15; 30	16,500[h]	34,100	16,100	1.19

[a] Obtained from ^{1}H NMR determination.
[b] Calculated from the molecular weight of TMC × $[TMC]_0/[9\text{-AnOH}]_0$ × conversion yield plus the molecular weight of 9-AnOH.
[c] Obtained from GPC analysis and calibrated by polystyrene standard.
[d] 0.05 mmol complexes, 10 mL of CH_2Cl_2.
[e] 10 mL THF was used as the solvent.
[f] 20 mL of CH_2Cl_2 was used as the solvent.
[g] Prepolymerization of CL in CH_2Cl_2 (15 mL) for 15 min followed by the addition of TMC in CH_2Cl_2 (5 mL) for another 30 min.
[h] Calculated from the molecular weight of CL × $[CL]_0/[9\text{-AnOH}]_0$ plus the molecular weight of TMC × $[TMC]_0/[9\text{-AnOH}]_0$ × conversion yield plus the molecular weight of 9-AnOH.

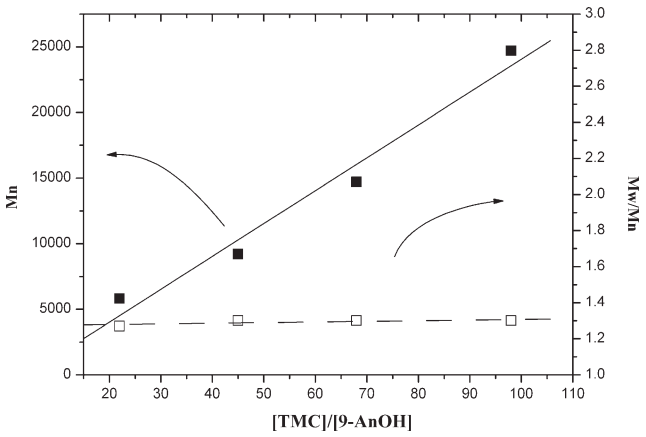


FIGURE 5 Polymerization of TMC catalyzed by **1** in CH_2Cl_2 at 0 °C. The relationship between M_n(■)/(PDI(□) of polymer and the initial molar ratio $[TMC]_0/[9\text{-AnOH}]_0$ × the conversion yield is shown.

results indicate that both complexes **1** and **2** show a great catalytic activity for the ROP of ε-CL in the presence of 9-AnOH, whereas polymerizations with uncontrollable behaviors are observed in the absence of 9-AnOH (Table 1, entries 1 and 7). Complex **1** was chosen to investigate the effects of polymerization conditions in detail because it showed greater catalytic activity than complex **2**. The effect of the ratio of 9-AnOH to the catalyst was examined; a great catalytic activity and the "controlled" character were obtainable with a Mg: 9-AnOH molar ratio of 1:2 (Table 1, entries 2 vs. 3). Polymerizations of ε-CL under these optimal conditions were then systematically investigated (Table 1, entries 3–6). The conversion yield attained >98% in toluene within 5 min at 25 °C with the ratio $[M]_0/[9\text{-AnOH}]_0$ in a range 25–200. The "living" character of the polymerization is demonstrated by a linear relationship between the number-averaged molecular weight (M_n) and the ratio ($[CL]_0/[9\text{-AnOH}]_0$) of monomer to initiator as shown in Figure 3, and the produced PCL with narrow polydispersity indices (PDIs), ranging from 1.06 to 1.17. The ^{1}H NMR spectrum of PCL-25 ("25" indicates the designed $[CL]_0/[9\text{-AnOH}]_0$ ratio; Fig. 4) indicates that the polymer chain is capped with one 9-anthracenemethyl ester and one hydroxyl chain end. This result indicates that the Mg(sulfonate phenoxide)$_2$/9-AnOH system might undergo an "activated-monomer" path, whereas monomer or 9-AnOH are activated by **1** and 9-AnOH behaves as a nucleophile.[12(l,k),16(b)] Relative to complex **1**, ε-CL polymerization catalyzed by complex **2** shows similar activities and a "controlled" manner (Table 1, entries 8–11), but with duration of polymerization up to 15 min to attain conversion >92%. According to the literature,[12(f,i,k),14] magnesium catalyst **1** reveals the greatest catalytic activity and "controlled" character toward ROP of ε-CL among magnesium or zinc complexes bearing bisphenoxide derivative ligands. The catalytic activities are little affected when the 1-pyrenebutanol is altered as initiator. As expected, the synthesized PCL with the 1-pyrenebutyl ester end group displayed the desired molecular weight and low PDI (Table 1, entry 12).

Ring-Opening Polymerization of TMC

Encouraged by the excellent catalytic activities of ROP of ε-CL catalyzed with bis(sulfonate phenoxide) Mg catalysts, we explored the catalytic activity in the ROP of TMC. In this context, the ROP of TMC using **1** or **2** as catalyst in the presence of 9-AnOH under dry N_2 was systematically examined as shown in Table 2; Mg complex **1** is an effective catalyst for the polymerization of TMC. The conversion yield >95% of polymerization was achieved within 10 min at 25 °C in CH_2Cl_2 (Table 2, entry 1). To obtain the optimal catalytic condition, we investigated the effects of solvent, concentration, and temperature on the TMC polymerization. After several trials of polymerization with THF as solvent, decreased concentration and decreased temperature using **1** as the catalyst, optimum conditions were found to be CH_2Cl_2 (20 mL, 0 °C) in the presence of 9-AnOH (Table 2, entries 2–4). According to these results for the optimal conditions (Table 2, entries 4–7), the PDIs of poly(TMC)s produced are narrow

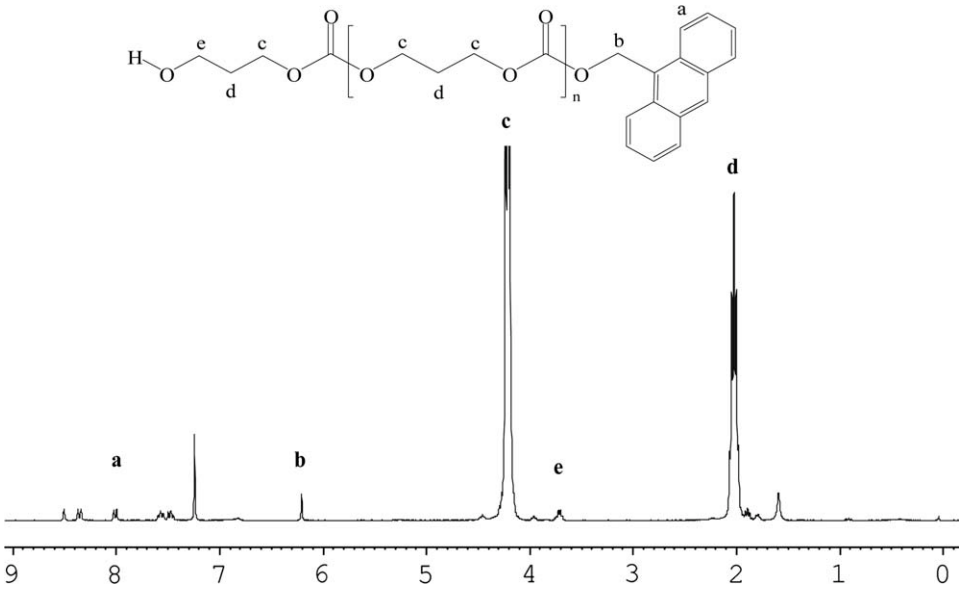


FIGURE 6 ^{1}H NMR spectra of PTMC-25 (Table 2, entry 7) in $CDCl_3$.

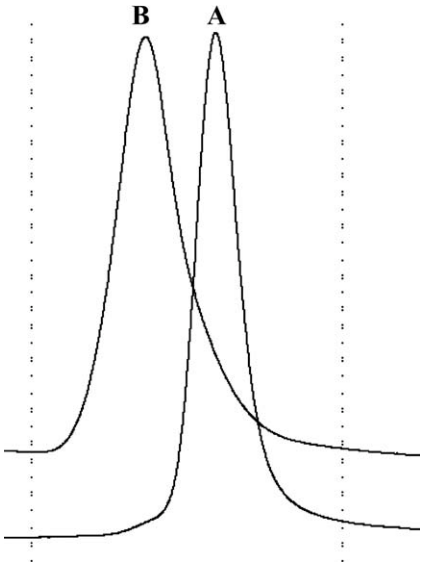


FIGURE 7 GPC profiles of copolymerization of PCL-*b*-PTMC catalyzed by complex **1**: (line A) after prepolymerization of CL (100 equiv to 9-AnOH, 15 min, M_n = 19700 (PDI = 1.06)); (line B) after block copolymerization of PCL-*b*-PTMC ($[CL]_0/[9\text{-AnOH}]_0/[TMC]_0$ = 100/1/50, M_n = 34100 (PDI = 1.19)).

(1.27–1.30) and a linear relationship between M_n (determined from GPC) and [TMC]/[9-AnOH] exists (Fig. 5), but the number-averaged molecular weight (M_n determined from ^{1}H NMR) of the obtained polymers are all slightly greater than the molecular weight calculated from the molar ratio of monomer to 9-AnOH. The ^{1}H NMR spectrum of PTMC-25 (Fig. 6) exhibits that the polymer chain is capped with one 9-anthracenemethyl ester and one hydroxyl chain end, indicating that significant intra-transesterification leading to the formation of macrocycles does not occur. In comparison, complex **2** demonstrated a similar activity but poor PDI control toward the ROP of TMC (Table 2, entry 8 vs. 4) under the optimal conditions of complex **1**. To further demonstrate the versatility of complex **1** for the ROP of CL and TMC, we prepared their copolymer, PCL-*b*-PTMC, using sequential addition (Table 2, entries 9–10).[7(f,j,l)] For instance, the PCL-*b*-PTMC block polymer (M_n = 34100, M_w/M_n = 1.19, entry 10) was synthesized through the sequential ROP of CL ($[CL]_0/[9\text{-AnOH}]_0$ = 100) and TMC monomer ($[TMC]_0/[9\text{-AnOH}]_0$ = 50) in the presence of **1** at 25 °C; the GPC profile is shown in Figure 7.

CONCLUSION

Two Mg complexes supported by sulfonate phenoxide ligands were synthesized and fully characterized. Complexes **1** and **2** are efficient catalysts for the ring-opening polymerization of ε-CL and TMC in the presence of 9-anthracenemethanol. The polymerizations of ε-CL and TMC catalyzed by complex **1** are demonstrated in a controlled manner with narrow PDI. The catalytic activity of complex **1** is greater than that of complex **2** for ε-CL polymerization. The electron-withdrawing substitute —CF_3 at the 4-position of the benzenesulfonate group seems to increase the Lewis acidity of Mg^{2+} metal, so that the harder Mg^{2+} center of complex **1** provides a superior combination of monomer activation and alkoxide nucleophilicity, producing an improved catalytic performance for polymerization. These catalysts demonstrate a new family of ROP catalytic system and show the highest catalytic activity (25 °C, 5 min) and "controlled" character (PDI<1.2) toward ROP of ε-CL among magnesium complexes bearing the bisphenoxide derivatives. The controlled character of complex **1** also enabled preparation of PCL-*b*-PTMC copolymers.

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