Ring-Opening Polymerization of Trimethylenecarbonate by the Bridged Diphenoxo Ytterbium (II) Complex

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ABSTRACT: A novel ytterbium (II) complex **2** supporting by a bridged bisphenolate ligand H_2L^{OC4H7} (L = $C_4H_7OCH_2N(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}Bu^t_2)_2$) with a tetrahydrofuran donor on side-arm was synthesized in high yield and characterized by elementary analysis, IR, ^{1}H-NMR, and ^{13}C-NMR. Ring-opening polymerization of 1,3-trimethylenecarbonate (TMC) was carried out using complex **2** and a known complex $[Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2(Bu^t)_2)_2]Yb$ **1** as the initiators, respectively. It was found that both complexes **1** and **2** can alone initiate the ring-opening polymerization of TMC, and complex **1** showed higher activity than complex **2**. The activity of both complexes **1** and **2** was found to be higher than that of monodentate phenoxo ytterbium (II) complex $(2,6\text{-}Bu^t_2\text{-}C_6H_3O)_2Yb(THF)_3$. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2693–2698, 2011

Key words: trimethylenecarbonate; bridged diphenoxo ytterbium (II) complex; polymerization

INTRODUCTION

Poly(trimethylene carbonate) (PTMC) is one of the widely investigated aliphatic polycarbonates, owing to its high biocompatibility, facile biodegradation, low toxicity, and superior mechanical properties,[1–9] which are of great interest for use in medical applications as well as ecological applications, such as sutures, dental devices, orthopedic fixation devices, drug-delivery systems, and tissue engineering.[10–13] Up to date, aliphatic polycarbonates can be prepared mainly by three routes: (1) condensation polymerization of diols and carbonates;[14] (2) copolymerization of epoxides with carbon dioxide;[15–18] and (3) ring opening polymerization (ROP) of suitable cyclic carbonates. Among them, the ROP method is currently receiving much attention due to the mild polymerization condition, handy control of the structure of polymer, the purity of polymer, and the use of low toxic and easy-removed catalyst. Various cyclic carbonates, such as trimethylenecarbonate (TMC), 2,2-dimethyl trimethylenecarbonate, 1-methyltrimethylene carbonate, and 2,2-(2-pentene-1,5-diyl)trimethylene carbonate, have been found to polymerize chemically or enzymatically.[19–34] Lanthanide metal catalysts have received increasing interest as they are structurally characterized and can be used as an efficient single-component catalyst to yield the polymers with high-molecular weights and low-polydispersity indices.

Hard, electronegative π-donor ligands such as aryloxides are particularly attractive as they offer strong metal-oxygen bonds that are expected to stabilize complexes of those electropositive lanthanide metals. A series of lanthanide alkoxides (phenoxides) have been explored to be the efficient catalysts for ROP reaction.[33–39] Recently, bridged bisphenolate ligands have become popular in *d*-block transition metals and lanthanide metals (III) chemistry. Especially, the tetradentate side-arm donor-bridged bisphenolate ligands, where the donor atoms are those capable of binding to the metal but the type of bond is not defined, therefore called a hemilabile functional group, have shown great potential applications in catalytic reactions promoted by groups 4 and 3 and lanthanide (III) metals complexes. For example, alkoxyaminobisphenolate group 3 and lanthanide metal catalysts are highly active in the synthesis of heterotactic and sydiotactic poly(lactide) from *rac*- and *meso*-lactide, respectively,[40,41] and syndiospecific poly(β-butyrolactone) from racemic β-butyrolactone.[42] The amine bisphenolate lanthanide methyl and amido complexes are efficient initiators for the ring-opening polymerization of ε-caprolactone.[43] However, the application of these tetradentate bridged bisphenolate ligands in lanthanide (II) chemistry has been seldom explored to date.[44–46] The first ytterbium (II) complex supported by a diaminobisphenolate ligand $[Me_2NCH_2CH_2N\text{-}(CH_2\text{-}2\text{-}OC_6H_2\text{-}$

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3,5-Bu^t_2)$_2$]$_2$Yb **1** was found to exhibit extremely high activity for the ROP of ε-CL. The activity is much higher than those found for complexes Yb(ArO)$_2$(THF)$_2$, [Yb(MBMP)(THF)$_2$]$_2$[47] and Yb($C_5H_9C_9H_6$)(THF)$_2$.[48] The activity is even comparable with that of Sm(ArO)$_2$(THF)$_3$.[49] To extend the application of complex **1** in polymerization of lactones, the polymerization of TMC by it was studied in this article. Moreover, a new Yb(II) complex [$C_4H_7OCH_2N$(CH_2-2-OC_6H_2-3,5-Bu^t_2)$_2$]$_2$Yb **2** supported by a bridged bisphenolate ligand with a tetrahydrofuran donor on sidearm was synthesized and its activity for TMC polymerization was examined, in an attempt to understand the influence of ligand on the activity. It was found that both complexes **1** and **2** can alone initiate the ring-opening polymerization of TMC, and complex **1** showed higher activity than complex **2**. The activity of complexes **1** and **2** was found to be higher than that of monodentate phenoxo ytterbium (II) complex (2,6-Bu^t_2-C_6H_3O)$_2$Yb(THF)$_3$. Herein, we report the results.

EXPERIMENTAL

Materials

Because all lanthanide complexes described here are air- and moisture-sensitive, all manipulations were performed under argon atmospheres using typical Schlenk techniques. The starting complex Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$[50,51] and the aminobisphenol ligands[52] were synthesized according to the published methods. A known diaminobisphenolate Yb(II) complex [$Me_2NCH_2CH_2N$(CH_2-2-OC_6H_2-3,5-Bu^t)$_2$]$_2$Yb(THF)$_2$ was prepared according to the literature.[44] The synthesis of YbI_2(THF)$_2$ was performed by the reaction of ytterbium metal with iodine in THF. TMC was prepared by the exchange reaction of 1,3-propandiol and diethyl carbonate, recrystallized, and dried before use.[53] All solvents were analytical grade and were distilled from Na/benzophenone ketyl before use.

Measurements

Lanthanide metal analyses were performed by ethylenediaminetetraacetic acid titration with a xylenol orange indicator and a hexamine buffer.[54] Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. The IR spectra were recorded on a Nicolet-550 Fourier transform IR spectrometer as KBr pellets. ^{1}H-NMR spectra were recorded at 400 MHz, and ^{13}C-NMR spectrum was recorded at 100 HMz in d_8-THF (unless otherwise indicated) with tetramethylsilane as internal standard on a Unity Inova-400 spectrometer. Number–(M_n) and weight–average molecular weight (M_w) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC) and calibrated to commercial polystyrene standards on a PE PL-GPC50 apparatus with two PL gel 10-μm MIXED-B columns in THF (1.0 mL/min) at 40°C.

Synthesis of [$C_4H_7OCH_2N$(CH_2-2-OC_6H_2-3,5-Bu^t_2)$_2$]Yb 2

Into a deep orange toluene solution of Yb(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ (3.00 mmol) was added a colorless toluene solution of H_2L^{OC4H7} (1.61 g and 3.00 mmol) at room temperature. The color change to deep red was immediately observed, and the mixture was stirred for 4 h. A fine orange-red powder precipitated from the solution. Isolation of the powder and recrystallization from toluene afforded crystals of **2** (1.33 g, 62.74%). Anal. Calcd for $C_{35}H_{53}NO_3Yb$ (708.05): C, 59.32; H, 7.49; N, 1.98; Yb, 24.44. Found: C, 58.98; H, 7.72; N, 1.61; Yb, 23.98; ν (KBr, cm^{-1}): 2956 (m), 2895 (w), 2863 (w), 1604 (w), 1538 (w), 1476 (m), 1305 (m), 1240 (m), 1203 (w), 1054 (w), 839(w); δ_H: 7.08 (2H, s, ArH), 6.85 (1H, s, ArH), 6.75 (1H, s, ArH), 4.19 (2H, m, $ArCH_2N$), 3.74 (1H, s, CH), 3.60 (2H, s, OCH_2), 3.02 (2H, m, $ArCH_2N$), 2.30 (2H, s, NCH_2-THF), 1.72 (4H, s, CH_2 in THF), 1.39 (18H, s, Bu^t), 1.23 (18H, s, Bu^t); δ_C: 165.7 (arom-CO), 137.9 (arom-CCH_2N), 129.2 (arom-CBu^t), 128.4 (arom-CH), 125.6 (arom-CBu^t), 122.7 (arom-CH), 79.2 ($ArCH_2N$), 64.2 (CH), 63.6 (OCH_2), 54.0 (NCH_2-THF), 33.8 (CMe_3), 31.5 (CMe_3), 29.7 (CMe_3), 29.6 (CMe_3), 28.0 (CH_2 in THF), and 25.3 (CH_2 in THF).

A typical polymerization of TMC procedure

All polymerizations were carried out under dry argon atmosphere with a similar procedure. A typical polymerization reaction is given below: a 50-mL Schlenk flask equipped with a magnetic stir bar was charged with a solution of 1,3-trimethylenecarbonate (TMC; 0.306 g and 3 mmol) in toluene (2.7 mL), which was kept at the polymerization temperature. A toluene solution of catalyst **1** (5.0×10^{-2} mol L^{-1}, 1.5×10^{-2} mmol) was added to this solution using a rubber septum and syringe. The mixture was vigorously stirred for a certain time, quenched by methanol with 2% HCl, and the polymers precipitated from methanol. The polymers PTMC were washed with methanol, filtered, and dried under vacuum to constant weight. The polymer yield was determined gravimetrically.

Oligomers for end-group analysis

The oligomerization of TMC was carried out with catalyst **1** in toluene at room temperature under the condition of [TMC]/[**1**] (molar ratio) of 10. The reaction was terminated by adding 1 mL of 2%

TABLE I
Ring Opening Polymerization of TMC Catalyzed by Ytterbium (II) Complexes[a]

Entry	Initiator	[M]/[I][b]	Temperature (°C)	Yield (%)[c]	M_n (10^4)[d]	M_w/M_n[d]
1	**1**	1000	25	43	1.63	1.46
2	**1**	700	25	68	2.23	1.76
3	**1**	500	25	74	2.08	1.78
4	**1**	200	25	85	1.20	1.91
5	**2**	500	25	15	0.81	1.13
6	**2**	200	25	74	1.65	1.70
7	$(2,6\text{-}Bu^t_2C_6H_3O)_2Yb(THF)_3$	200	25	54	3.48	2.07
8	$(2,6\text{-}Bu^t_2C_6H_3O)_2Sm(THF)_3$	500	40	65	4.55	2.51

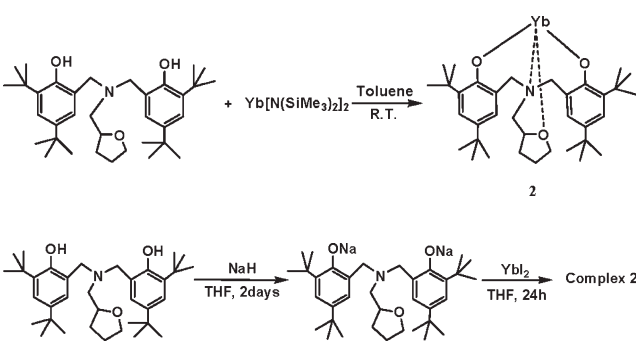
[a] Conditions: [TMC] = 1 mol L^{-1}, 25°C, time = 30 min, toluene.
[b] [M] = monomer concentration; [I] = initiator concentration.
[c] Yield = weight of the obtained polymer/weight of the used monomer.
[d] Measured by gel permeation chromatography calibrated with standard polystyrene samples.

HCl/MeOH after 1 h. The oligomer was precipitated from methanol. The product was dissolved in THF, followed by precipitation in methanol. After filtration, the white product was dried *in vacuo*.

RESULTS AND DISCUSSION

Synthesis of $[C_4H_7OCH_2N(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}Bu^t_2)_2]Yb$ 2

The reaction of the ligand H_2L^{OC4H7} with $Yb[N(SiMe_3)_2]_2(THF)_2$ in a 1 : 1 molar ratio in toluene at room temperature was conducted, and the orange-red crystals were obtained after workup. The crystals were characterized by elemental analysis, IR spectral analysis, ^{1}H-NMR, and ^{13}C-NMR analyses to be complex **2** [eq. (1)]. The satisfied elemental analysis for unsolvated complex **2** can be obtained by careful treatment of the sample. The IR spectrum showed the typical signals for the ligand. ^{1}H-NMR and ^{13}C-NMR spectra indicated a symmetrical arrangement of the bisphenolate ligand. Complex **2** can also be synthesized by treatment of the ligand H_2L^{OC4H7} with NaH, followed by the addition of an equivalent amount of YbI_2 in THF [eq. (2)]. Complex **2** is soluble in THF, slightly soluble in toluene. Attempts to isolate the crystals of **2** suitable for X-ray structural analysis were unsuccessful.



To understand the effect of the side-arm-donor on a tetradentate-bridged bisphenolate ligand on the activity of divalent ytterbium complex for the polymerization of TMC, the known complex **1** $[Me_2NCH_2CH_2N(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}Bu^t_2)_2]Yb$ was also synthesized by the published method.[44]

Homopolymerization of TMC

The homopolymerization of TMC was first tried by use of complexes **1** and **2**, respectively, as single-component catalysts [eq. (3)]. The polymerizations went smoothly at the molar ratio of monomer to initiator of 200, and the results are presented in Table I. Both complexes exhibited high activity in toluene. However, the dependence of polymerization activity greatly on the ligand was observed, with the sequence of **2** < **1**. For example, the ROP with complex **1** can be conducted at 25°C in toluene and gave the polymer in 85% yield (Table I, entry 4) after 30 min, while the system with complex **2** generated the polymer in 74% yield (Table I, entry 6). Even the molar ratio of monomer to initiator increased to 700, the polymer yield can still reach to 68% for **1** after 30 min (Table I, entry 2), and the system still showed desired activity when the molar ratio increased to 1000 (Table I, entry 1). In comparison with the activity of **1** and **2** with those of divalent unbridged bisaryloxo ytterbium complexes published,[33] it was obviously found that both **1** and **2** were higher active catalysts than $(2,6\text{-}Bu^t_2C_6H_3O)_2Yb(THF)_3$. Normally, an active sequence of Yb(II) < Sm(II) in reactivity was often observed in the homogeneous catalyzes catalyzed by lanthanide metal (II) complexes. The reason for it may be contributed to the lower oxidation potentials of Sm related to Yb.

TABLE II
Homopolymerization of TMC Catalyzed by Complexes 1 and 2

Entry	Initiator	[M] (mol L^{-1})	[M]/[I][a]	Sol.	T (°C)	Time (min)	Yield (%)[b]	M_n[c] (10^4)	M_w/M_n[c]
1	**1**	0.5	500	Toluene	25	2	25	1.30	1.43
2	**1**	1	500	Toluene	25	2	49	1.44	1.51
3	**1**	1.2	500	Toluene	25	2	69	1.86	1.89
4	**1**	1	500	Toluene	20	30	70	0.81	2.02
5	**1**	1	500	Toluene	40	30	67	1.03	1.87
6	**1**	1	500	Toluene	60	30	68	1.17	1.75
7	**1**	1	1000	THF	25	30	72	1.01	1.74
8	**1**	1	500	THF	25	30	80	0.91	1.69
9	**1**	1	500	THF	40	30	74	0.74	1.72
10	**1**	1	500	THF	60	30	75	0.71	1.67
11	**2**	1	100	Toluene	25	30	78	2.21	1.41
12	**2**	1	100	Toluene	60	30	69	3.44	1.26

[a] [M] = monomer concentration; [I] = initiator concentration.
[b] Yield = weight of the obtained polymer/weight of the used monomer.
[c] Measured by GPC calibrated with standard polystyrene samples.

Here, we can see that the activity of complex **1** was even comparable to those of Sm(II) complex (Table I, entry 8). The results indicate that improved catalytic behavior for the ytterbium(II) complex can be obtained by a tetradentate bisphenolate ligand bearing a side-arm donor.

Then the effects of reaction conditions on polymerization were studied with complex **1** as the initiator. The decrease in the initiator concentration led to the decrease in polymer yield, the increase of *Mn* of the resulting polymer, while the polydispersity of PTMC remained relatively broad ranging from 1.46 to 1.91 (Table I, entries 1–4). The increasing monomer concentration from 0.5 mol L^{-1} to 1.2 mol L^{-1} resulted in the increase both in polymer yields and molecular weights of the resulting polymers (Table II, entries 1–3). However, the polydispersities of the polymers became broader. This may be because of the increase of transesterification reaction.

The influence of the solvent on polymerization was observed. The polymerization gave higher yields and lower molecular weights of the resulting polymers in THF than in toluene. For example, the polymer with the molecular weight 1.01×10^4 in the yield of 72% could be gained in THF at the molar ratio of [M]/[I] of 1000 for 30 min (Table II, entry 7), while the polymer with the molecular weight 1.63×10^4 in only 43% yield was obtained in toluene (Table I, entry 1). The polydispersity of the polymers obtained in THF is relatively narrower (1.67–1.74) than those of the polymers resulted in toluene (1.46–2.02).

It was unexpected that reaction temperature has almost no influence on the polymerization for both systems with **1** and/or **2**: neither polymer

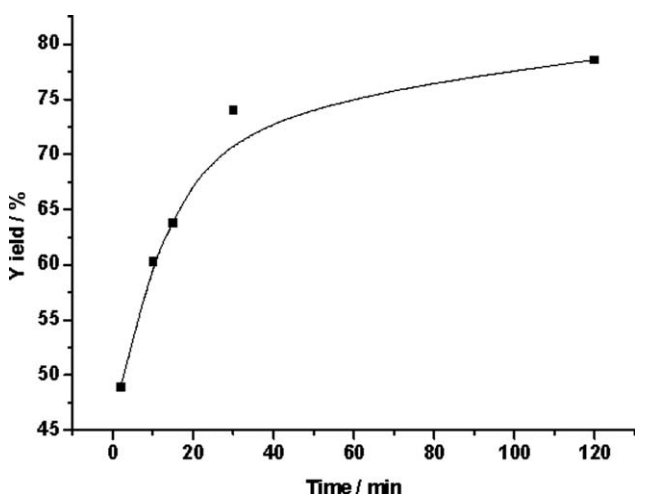


Figure 1 Plot of PTMC yield versus the polymerization time with complex **1** as the initiator in toluene at 25°C, [M] = 1.0 mol/L, [M]/[I] = 500.

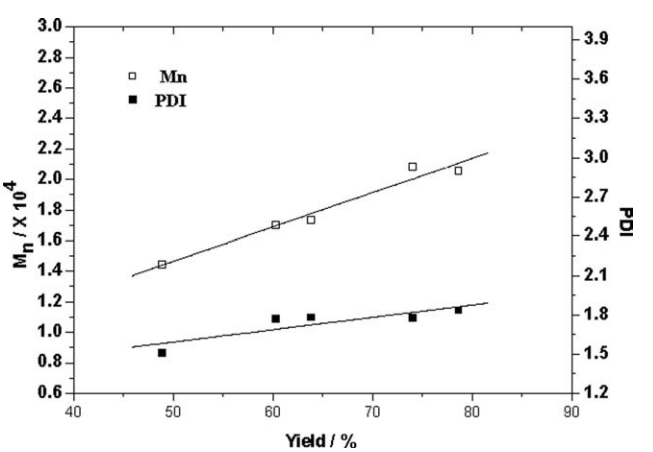
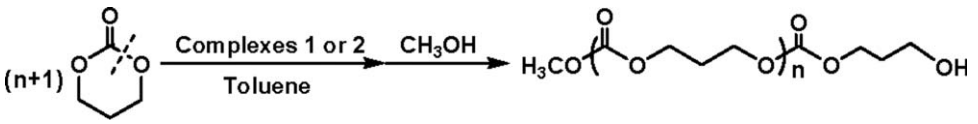


Figure 2 Dependence of number-average molecular weight (M_n) and polydispersity (PDI) on yield for the polymerization of TMC with complex 1 as initiator. The reaction conditions were identical with those of Figure 1.



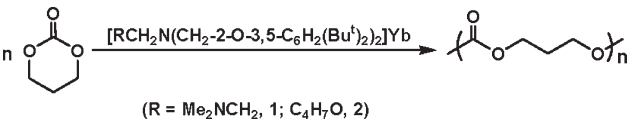
Scheme 1

yields nor molecular weights and molecular weight distributions of the resulting polymers have changed with the increasing temperature from 20 to 60°C. The reason for it has not been cleared yet.

Figures 1 and 2 depict the dependence of yields on polymerization time, and the relationship between the polymer yields and molecular weights and molecular weight distributions of the polymers, respectively. The yields increased with the polymerization time, and the molecular weights of the polymers increased with the increase of the yields; however, the molecular weight distributions of the polymers became gradually broader (M_w/M_n = 1.51–1.78), indicating that transesterification reaction may be accompanied with the ring-opening polymerization.

Mechanism assumption

It has been reported the ROP of cyclocarbonate by lanthanide metal (III) catalysts takes place according to a coordination–insertion mechanism.[38] To clarify the mechanism of the ROP of TMC catalyzed by the tetradentate bridged bis(phenolate) ytterbium(II) complexes **1** and **2**, the end-group analyses were carried out, and oligomers of TMC terminated by CH_3OH were prepared. Careful examinations of these low-molecular weight PTMC samples by ^{1}H-NMR spectroscopy in $CDCl_3$ revealed that the oligomers contained the esterified methyl end groups, because the characteristic signal at δ3.7 was observed. Obviously, the methoxy groups in the oligomers were derived from the corresponding quenching methanol. The acylation of methanol apparently required the presence of an electrophilic acyl end group in the original polymer chain.[49] Therefore, it could be concluded that the ROP of TMC undergoes the acyl-oxygen bond cleavage (Scheme 1), following by the coordination–insertion mechanism, which is content with our previous work.[33] It was observed that the color of the initiators solution turned from red to yellow as soon as the initiators were injected into the system, which was apparent that the Yb(II) ion was oxidized at the early stage, and the polymerization should be catalyzed by a Yb(III) species.[33] However, attempts to gain structural information on the real active species or the end group of the oligomer species before alcoholysis were not successful. The detailed study on the mechanism is proceeding in our laboratory.



CONCLUSIONS

A new divalent ytterbium complex $[C_4H_7OCH_2N(CH_2\text{-}2\text{-}OC_6H_2\text{-}3,5\text{-}Bu^t_2)_2]_2Yb$ **2** supported by a tetradentate-bridged bisphenolate ligand with a tetrahydrofuran donor on side-arm was synthesized. The catalytic activity of **2** and a known complex **1**, respectively, for polymerization of TMC was studied. It was found that both complexes exhibited high activity and **1** was more active than **2**, indicating that the side-arm donors have distinct effects on the activity of bridged bisphenolate divalent ytterbium complexes. The activity of both complexes **1** and **2** was higher than that of monodentate phenoxo ytterbium (II) complex $(2,6\text{-}Bu^t_2\text{-}C_6H_3O)_2Yb(THF)_3$. The polymerization behavior of complex **1** was studied in detail, and the mechanism was supposed.

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