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Biometal Derivatives as Catalysts for the Ring-Opening Polymerization of Trimethylene Carbonate. Optimization of the Ca(II) Salen Catalyst System

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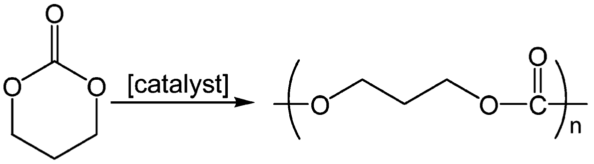
ABSTRACT: Schiff base derivatives of the biometals (Zn, Mg, Ca) in the presence of anion initiators have been shown to be very effective catalysts for the ring-opening polymerization of trimethylene carbonate (TMC or 1,3-dioxan-2-one) to poly(TMC) devoid of oxetane linkages. The order of catalytic activity as a function of metal was found to be Ca(II) ≫ Mg(II) > Zn(II). Optimization of the calcium system was achieved utilizing a salen ligand with *tert*-butyl substituents in the 3,5-positions of the phenolate rings and an ethylene backbone for the diimine along with an azide ion initiator. These conditions led to a TOF of 1286 h^{-1} for a melt polymerization carried out at 86 °C. Solution studies in tetrachloroethane demonstrated the polymerization reaction to proceed via a mechanism first order in [monomer], [(salen)Ca], and [anion initiator] and to involve TMC ring-opening by way of acyl−oxygen bond cleavage. The activation parameters were determined to be $\Delta H^{\ddagger} = 20.1$ kJ/mol and $\Delta S^{\ddagger} = -128$ J/(mol K).

Introduction

Significant developments have been accomplished over the past decade with regard to the synthesis of polycarbonates via the environmentally benign route of alternative coupling of the comonomers carbon dioxide and epoxides.[1] Nevertheless, the concomitant production of five-membered cyclic carbonates, which is exacerbated when utilizing aliphatic epoxides, remains a hindrance to the wide-scale use of this methodology.[2] This general lack of high selectivity for formation of these latter copolymers is unfortunate since these biodegradable materials are widely used as medical implants and in drug delivery and tissue engineering applications.[3]

Five-membered cyclic carbonates afforded from CO_2/epoxide are thermodynamically stable toward polycarbonate formation without loss of carbon dioxide. However, six-membered cyclic carbonates such as trimethylene carbonate (TMC) can under certain catalytic conditions provide aliphatic polycarbonates with complete retention of their CO_2 contents (eq 1). That is, for six- and seven-membered cyclic carbonates ΔH_p is negative and ΔS_p is positive; hence, unlike their five-membered analogues, the polymerization of these cyclic carbonates is spontaneous at all temperatures.[4]



(1)

Presently, the most widely employed catalysts for the anionic ring-opening polymerization of TMC are salts of aluminum and tin.[5] Our group,[6] as well as Cao and co-workers,[7] has recently reported the use of well-defined, effective salen derivatives of aluminum for the ring-opening polymerization of trimethylene carbonate. Because of the difficulty of removing trace quantities of catalyst residues from the thereby produced polycarbonates, we have chosen to investigate metal salen complexes based on biocompatible metals, i.e., salen derivatives of zinc, magnesium, and calcium as catalysts for the reaction defined in eq 1. Previously, studies have demonstrated organozinc, calcium, and magnesium compounds to be active catalysts for lactide polymerization. For example, the β-diiminate zinc complexes developed by Coates have been shown to be very effective living polymerization catalysts for *rac*-LA at ambient temperature.[8] More recently, Chisholm and co-workers have performed comparative studies of a series of monomeric amide and aryloxide tris(pyrazolyl) borate complexes of calcium, magnesium, and zinc for their efficacy at polymerizing lactides.[9] Feijan and co-workers have examined the use of in situ generated calcium alkoxides for similar types of polymerization processes.[10] Dibutylmagnesium has been used as a catalyst for the ring-opening polymerization of DMC (2,2-dimethyltrimethylene carbonate) by Keul and co-workers.[11] Also, in a recent report Dobrznski and co-workers have employed acetylacetonate derivatives of zinc, iron, and zirconium as catalysts for the polymerization of both TMC and DMC.[12]

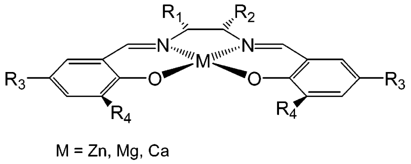


Figure 1. General structure of biometal salen complexes utilized as catalysts for the polymerization of trimethylene carbonate.

Herein, we will describe the details of our investigation of the polymerization reactions of trimethylene carbonate (1,3-dioxan-2-one) catalyzed by a series of biometal salen complexes (Figure 1). Importantly, it is necessary in these processes to employ a cocatalyst since these M(II) salen derivatives do not possess internal nucleophiles for the chain initiation step as is present in the M(III) derivatives previously reported upon, i.e., (salen)AlCl.[6] For this purpose we have generally utilized anions derived from PPN^+ (μ-nitrido-bis(triphenylphosphine)(1+)) or $n\text{-}Bu_4N^+$ salts.

Experimental Section

Methods and Materials. Unless otherwise specified, all manipulations were performed using a double-manifold Schlenk

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vacuum line under an atmosphere of argon or an argon-filled glovebox. Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone. Acetonitrile was first dried by distillation from CaH_2 onto P_2O_5 followed by distillation onto CaH_2 prior to use. Both CH_2Cl_2 and 1,1,2,2-tetrachloroethane (TCE) were freshly distilled from P_2O_5. Trimethylene carbonate was purchased from Boehringer Ingelheim. It was recyrstallized from tetrahydrofuran and diethyl ether, dried under vacuum, and stored in the glovebox. Potassium hydride was purchased from Aldrich as a mineral oil emulsion, washed with hexanes (3 × 30 mL), and dried under vacuum prior to use. Salicylaldehyde, ethylenediamine, 1,2-phenylenediamine, and 1,2-naphthylenediamine were purchased from Aldrich and used as received. The corresponding salen ligands were synthesized according to literature procedure.[13] The syntheses of magnesium and zinc salens have been previously described in the literature.[14] The methodology used for the synthesis of {*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediimine}Al(III)Et was also adapted from the literature.[15]

PPN^+Cl^- ($PPN^+ = (Ph_3P)_2N^+$) was purchased from Aldrich and recrystallized from dichloromethane/ether before use, and $PPN^+N_3^-$ was synthesized according to published procedure.[16] Tetra-*n*-butylammonium halides (Aldrich) were recrystallized from acetone/ether twice before use. Tetra-*n*-butylammonium azide (TCI) was stored in the freezer of the glovebox immediately upon arrival. ^1H NMR spectra were recorded on Unity+ 300 MHz and VXR 300 MHz superconducting NMR spectrometers. Infrared spectra were recorded on a Mattson 6021 FT-IR spectrometer with DTGS and MCT detectors. Analytical elemental analysis was provided by Canadian Microanalytical Services Ltd. Molecular weight determinations (M_w and M_n) were carried out at the New Jersey Center for Biomaterials, Rutgers University.

General Synthesis of Ca(II)(salen) Complexes. H_2Salen (1.0 equiv) and NaH (5 equiv) were dissolved in THF. After stirring at room temperature overnight, excess NaH was removed by filtration, and the sodium salt was transferred via cannula through a medium porosity frit packed with Celite to a Schlenk flask containing CaI_2 (1.1 equiv). The reaction mixture became clear and was stirred at ambient temperature overnight. THF was removed under reduced pressure, and dichloromethane was added to the reaction mixture after filtration to remove NaI. The desired complex was isolated following the removal of dichloromethane and was dried in vacuo. In general, these complexes were obtained with two to three molecules of THF as solvates. Because of the variability of the number of solvates, elemental analysis of these complexes generally is not reliable. Infrared spectra of these metal complexes in methylene chloride showed a $\nu_{C=N}$ mode (1632.6 cm^{-1} in **1** and 1600.8 cm^{-1} in **4**) very close to that observed in the free ligand, with slight variations due to the diimine backbone. In some instances it has been possible to obtain X-ray structural data which definitively characterizes these metal derivatives. This information will be published elsewhere. Nevertheless, the ^1H NMR spectra of all of these metal complexes were very clean with the exception of resonances due to solvated molecules.

Synthesis of {*N,N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine}Ca(II) (1). Using the general method, 0.492 g of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-ethylenediimine (1.0 mmol) and 0.322 g of CaI_2 (1.1 mol) were dissolved in 30 mL of THF. The final product was a pale yellow solid (0.522 g, 98% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.20 (s, CH=N, 2H), 7.26 (d, 2H), 6.94 (d, 2H), 3.81 (s, NH_2, 4H), 1.56 (s, 18H, $C(CH_3)_3$), 1.35 (s, 18H, $C(CH_3)_3$).

Synthesis of {*N,N*′-Bis(salicylidene)-1,2-phenylenediimine}Ca(II) (2). Using the general method, 0.158 g of *N*,*N*′-bis(salicylidene)-1,2-phenylenediimine (0.5 mmol) and 0.150 g of CaI_2 (0.52 mmol) were dissolved in 30 mL of THF. The final product was a yellow solid (0.18 g, 92% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.37 (s, CH=N, 2H), 7.17 (d, 2H), 7.08 (d, 2H), 6.90 (d, 2H), 6.63 (d, 2H), 6.60 (d, 2H), 6.38 (d, 2H).

Synthesis of {*N,N*′-Bis(5-*tert*-butylsalicylidene)-1,2-phenylenediimine}Ca(II) (3). Using the general method, 0.216 g of *N*,*N*′-bis(5-*tert*-butylsalicylidene)-1,2-phenylenediimine (0.5 mmol) and 0.150 g of CaI_2 (0.52 mmol) were dissolved in 30 mL of THF. The final product was a yellow solid (0.207 g, 88% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.32 (s, CH=N, 2H), 7.41 (d, 2H), 7.36 (d, 2H), 7.23 (d, 2H), 6.49 (d, 2H), 6.43 (d, 2H), 1.43 (s, 18H, $C(CH_3)_3$).

Synthesis of {*N,N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediimine}Ca(II) (4). Using the general method, 0.275 g of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediimine (0.50 mmol) and 0.162 g of CaI_2 (0.55 mol) were dissolved in 20 mL of THF. The final product was a yellow solid (0.272 g, 94% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.64 (s, CH=N, 2H), 6.94−7.27 (m, 8H), 1.43 (s, 18H, $C(CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$).

Synthesis of {*N,N*′-Bis(3,5-di-chlorosalicylidene)-1,2-phenylenediimine}Ca(II) (5). Using the general method, 0.227 g of *N*,*N*′-bis(3,5-di-chlorosalicylidene)-1,2-phenylenediimine (0.50 mmol) and 0.162 g of CaI_2 (0.55 mol) were dissolved in 20 mL of THF. The final product was a dark yellow solid (0.167 g, 68% yield). ^1H NMR (DMSO, 300 MHz): δ 8.30 (s, CH=N, 2H), 7.40 (s, 2H), 7.30 (m, 4H), 7.05 (s, 2H).

Synthesis of {*N,N*′-Bis(3-methoxy-5-*tert*-butylsalicylidene)-1,2-phenylenediimine}Ca(II) (6). Using the general method, 0.245 g of *N*,*N*′-bis(3-methoxy-5-*tert*-butylsalicylidene)-1,2-phenylenediimine (0.50 mmol) and 0.162 g of CaI_2 (0.55 mol) were dissolved in 20 mL of THF. The final product was a orange brown solid (0.227 g, 86% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.63 (s, CH=N, 2H), 7.35 (m, 4H), 7.04 (s, 2H), 6.73 (s, 2H), 3.79 (s, 6H), 1.42 (s, 18H).

Synthesis of {*N,N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-naphthylenediimine}Ca(II) (7). Using the general method, 0.304 g of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-naphthylenediimine (0.50 mmol) and 0.162 g of CaI_2 (0.55 mol) were dissolved in 20 mL of THF. The final product was a brown solid (0.292 g, 93% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 8.73 (s, CH=N, 2H), 7.08−7.92 (m, 10H), 1.45 (s, 18H, $C(CH_3)_3$), 1.35 (s, 18H, $C(CH_3)_3$).

Polymerization Runs. A typical melt polymerization run consisted of adding 1 g of the monomer to a previously flame-dried Schlenk flask. The monomer:initiator:co-initiator ratio was maintained at 350:1:1. The metal loadings may be low by as much as 10−15% due to unknown quantities of THF or other molecules of solvation associated with these metal catalysts. Hence, the catalytic activities reported are to be taken as the minimum values. The reaction was carried on at 86 °C for only 15 min under an argon atmosphere. The resulting polymer was purified by precipitation from dichloromethane, 5% HCl and methanol and then dried in vacuo. Turnover frequencies (mol of TMC consumed/(mol of the catalyst h)) were calculated following weighing of the vacuum-dried polymer.

Kinetic Studies. TMC, catalyst, and the cocatalyst were weighed out in a Schlenk flask in the desired monomer:initiator:co-initiator ratio followed by the addition of 10 mL of dry 1,1,2,2-tetrachloroethane (TCE). The reaction vessel was placed into a preheated oil bath. The percent conversion of the monomer with time was calculated by manually sampling a small aliquot of the solution, quenching it, and analyzing it by NMR.

Results and Discussion

Melt Ring-Opening Polymerization Studies. The first priority of our efforts in this area was to examine the relative effectiveness of the various biometal complexes shown in Figure 1 for polymerizing trimethylene carbonate (TMC) to poly(TMC). The common salen ligand employed in this investigation was H_2salen = *N*,*N*′-bis(di-*tert*-butylsalicylidene)-1,2-ethylenediimine. For this purpose we chose to carry out melt studies at a monomer:catalyst:initiator ratio of 350:1:1 at 86 °C for 15 min under an argon atmosphere. The results of this inquiry are summarized in Table 1, where the TOFs (mol of TMC consumed/(mol of catalyst h)) were determined by precipitating the polymer from dichloromethane, 5% HCl, and methanol, following by drying in vacuo and weighing. As revealed by ^1H NMR spectra, which exhibit a triplet at 4.23 ppm and a quintet at 2.04 ppm of intensity ratio 2:1, respectively, all polymers

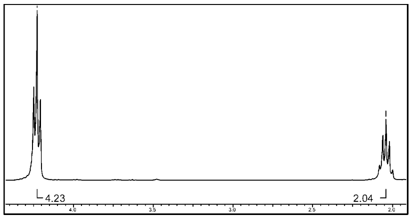


Figure 2. ^{1}H NMR spectrum of poly(trimethylene carbonate) in $CDCl_3$.

Table 1. Polymerization of TMC As Catalyzed by (salen)M Complexes in the Presence of 1 equiv of *n*-$Bu_4N^+Cl^-$ [a]

M	TOF[b]
Zn[c]	250
C_2H_5Al	485
Mg	541
Ca	1123

[a] Salen ligand contains an ethylene backbone and *tert*-butyl groups in the 3,5-positions of the phenolate rings. [b] Mol of TMC/(mol of catalyst h). [c] Shown to be dimeric by X-ray crystallography.

Table 2. Polymerization Results on Varying the Substituents in the 3,5-Positions of the Phenolate Rings for (salen)Ca(II) Complexes Containing a Phenylene Backbone[a]

entry	R_3	R_4	TOF[b]
1	H	H	416
2	H	*tert*-butyl	961
3	OMe	*tert*-butyl	1132
4	*tert*-butyl	*tert*-butyl	1175
5	Cl	Cl	756

[a] Each reaction was performed in melt maintaining a monomer:initiator: *n*-$[Bu_4N]^+Cl^-$ ratio as 350:1:1 at 86 °C for 15 min. [b] The TOF was determined by weighing the polymer after precipitating in 5% HCl and MeOH and drying in a vacuum oven and is reported as mol of TMC/(mol of Ca h).

showed a complete absence of ether linkages (Figure 2). That is, the lack of proton resonance at 1.8 and 3.4 ppm indicates that the poly(TMC)s obtained are free of polyoxetane arising from CO_2 elimination.[17] Included in Table 1 is a version of our most effective catalyst reported to date, Al(III) salen.[6] In this instance it was necessary to utilize an Al(III) salen derivative where the internal axial ligand is not involved in the catalytic process, thereby requiring an exterior initiator or cocatalyst as is needed in the other M(II) cases. Previous studies have shown that the Al$-C_2H_5$ unit does not participate in the polymerization process.[15] As is readily apparent from Table 1, calcium(II) is the most active salen derivative, displaying a catalytic activity in the presence of *n*-$Bu_4N^+Cl^-$ of about twice that of its magnesium or aluminum analogues.

Subsequent investigations have been carried out to optimize the catalytic activity of the calcium(II) salen complex by changing the nature of the diimine backbone and substituents on the phenolate rings of the salen ligands. Retaining the salen ligand with the phenylene backbone while changing the substituents in the 3,5-positions of the phenolate rings (Table 2) reveals the Ca(II) salen derivative containing the bulky di-*tert*-butyl groups to be the most active. This is consistent with our previously reported observations employing aluminum salen catalysts.[6] We have also examined the effect of altering the diimine backbone of the Ca(II) salen derivative while maintaining the di-*tert*-butyl substituents in the 3,5-positions of the phenolate rings. These results are summarized in Table 3 and indicate that an electron-withdrawing, rigid and planar backbone leads to enhanced catalytic activity. Nevertheless, as is evident in Table 3, changes in the diimine backbone do not significantly effect catalytic activity, where only an 8% increase is noted in proceeding from ethylene to naphthylene.

Table 3. Polymerization Results for Varying the Backbone for (salen)Ca(II) Complexes Where the Substituents in the 3,5-Positions of the Phenolate Ring Are *tert*-Butyl Groups[a]

entry	R_1 and R_2	TOF[b]
1	ethylene	1123
2	phenylene	1175
3	naphthylene	1270

[a] Each reaction was performed in melt maintaining a monomer:initiator: *n*-$[Bu_4N]^+Cl^-$ ratio as 350:1:1at 86 °C for 15 min. [b] The TOF was determined by weighing the polymer after precipitating in 5% HCl and MeOH and drying in a vacuum oven and is reported as mol of TMC/(mol of Ca h).

Table 4. Polymerization Results on Varying the Cocatalyst in Ca(II)(salen) Complexes Containing an Ethylene Backbone and *tert*-Butyl Groups in the 3,5-Positions of the Phenolate Ring[a]

entry	cocatalyst	TOF[b]	entry	cocatalyst	TOF[b]
1	$Bu_4N^+Br^-$	766	4	PPN^+Cl^-	1221
2	$Bu_4N^+Cl^-$	1123	5	$PPN^+N_3^-$	1286
3	$Bu_4N^+N_3^-$	1183			

[a] Each reaction was performed in melt maintaining a monomer:initiator: co-initiator ratio as 350:1:1 at 86 °C for 15 min. [b] The TOF was determined by weighing the polymer after precipitating in 5% HCl and MeOH and drying in a vacuum oven and is reported as mol of TMC/(mol of Ca h).

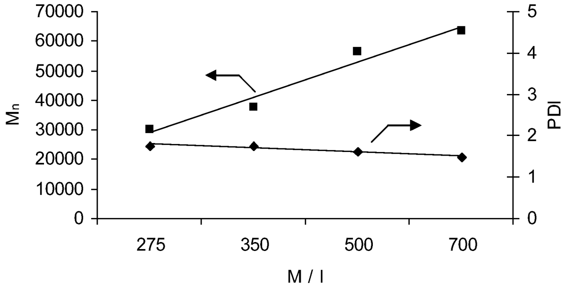
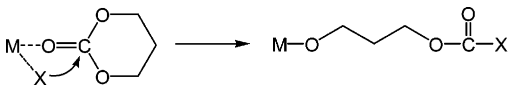


Figure 3. Plot of the dependence of molecular weight of PTMC on M/I ratios.

Our final examination of this melt polymerization process was to probe the influence of the external anionic cocatalyst (X) on the initiation step of the reaction (eq 2).[1e,9] Studies were conducted with salts of both the very bulky, weakly interacting cation, PPN^+, and the less expensive, slightly more interacting *n*-Bu_4N^+ cation. Importantly, these latter tetraalkylammonium salts have the added advantage over their PPN^+ counterparts in that they are readily soluble in a large variety of organic solvents. Table 4 lists our findings, where the PPN^+ salts were found to be only about 10% more active than their *n*-Bu_4N^+ analogues, and azide was only 5% more active than chloride.[18] On the other hand, as might be anticipated on the basis of other ring-opening processes, the bromide anion is significantly less effective at the initiation step.[19]



(2)

Catalytic reactions carried out under identical reaction conditions with *n*-$Bu_4N^+Cl^-$ or PPN^+Cl^- in the absence of the (salen)Ca catalyst provided 4.52% and 6.06% conversions or TOF of 63.3 and 84.9 h^{-1}, respectively.

The molecular weight and polydispersity of poly(trimethylene carbonate) obtained in these studies were measured by gel permeation chromatography (GPC). In general, the melt polymerizations were carried out at 88 °C using (*N,N'*-bis(3,5-di-*tert*-butylsalicylidene) phenylenediimine)Ca(II) in the presence of 1 equiv of $PPN^+N_3^-$ (Table 5). As indicated in Table 5, the molecular weights experimentally determined by GPC closely

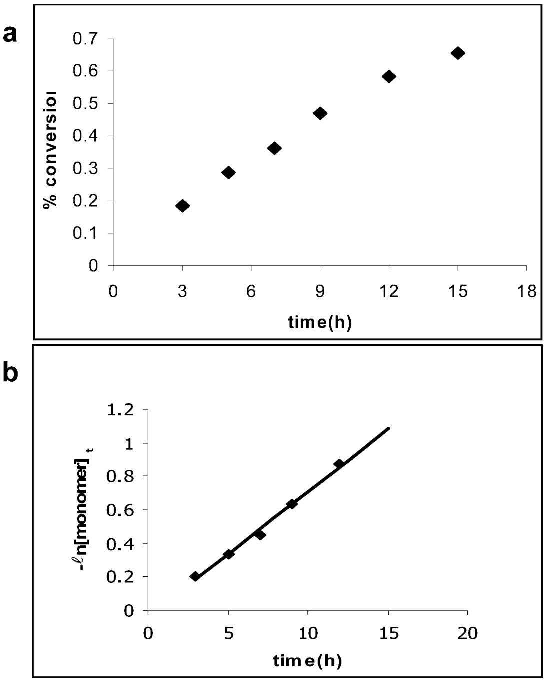


Figure 4. (a) Plot of monomer conversion vs time. (b) Semilogarithmic plot depicting a reaction order of unity with respect to monomer concentration.

Table 5. Dependence of Molecular Weights of PTMC on M/I Ratios[a]

entry	M/I	$M_n \times 10^{-4}$ GPC	$M_n \times 10^{-4}$ theoretical[b]	PDI
1	275	3.0	2.8	1.76
2	350	3.7	3.4	1.76
3	500	5.6	5.0	1.61
4[c]	700	6.3	6.7	1.48

[a] Reactions conducted at 88 °C for 30 min using (*N*,*N'*-bis(3,5-di-*tert*-butylsalicylidene)phenylene diimine)Ca(II) as catalyst and 1 equiv of $PPNN_3$ as cocatalyst. [b] *M*(theoretical) = M/I × mol wt TMC × % conversion. [c] Entry 4 run for 45 min.

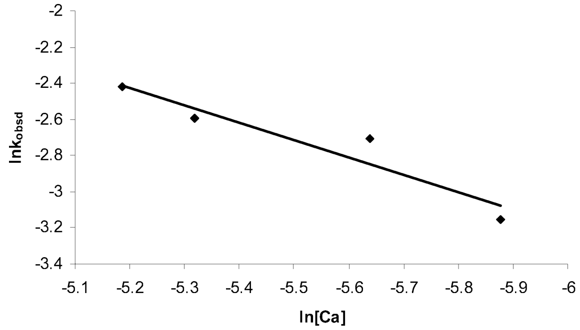


Figure 5. Plot of ln k_{obsd} vs ln[Ca] to determine the order of the polymerization reaction with respect to [catalyst]. Slope = 0.953 with $R^2 = 0.904$.

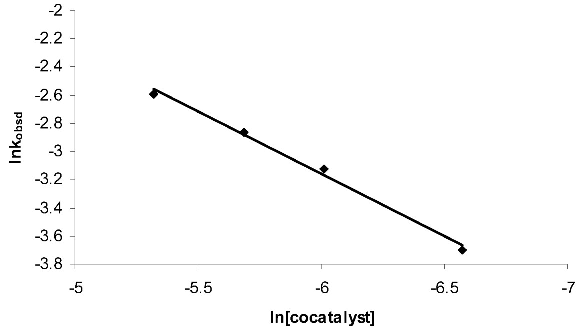


Figure 6. Plot of ln k_{obsd} vs ln[cocatalyst] to determine the order of the polymerization reaction with respect to [cocatalyst] over the range of 0.28−1.0 equiv. Slope = 0.902 with $R^2 = 0.995$.

Table 6. Rate Constant Dependence on the Concentrations of the Catalyst, Cocatalyst, and Temperature[a]

entry	[Ca] (mol/L)	equiv of *n*-$[Bu_4N]^+Cl^-$	temp (°C)	k_{obsd} (h^{-1})
1	0.0028	1.0	110	0.0426
2	0.0036	1.0	110	0.0666
3	0.0049	1.0	110	0.0749
4	0.0056	1.0	110	0.0889
5	0.0049	1.0	102	0.0625[b]
6	0.0049	1.0	125	0.0995
7	0.0049	1.0	135	0.1141
8	0.0049	0.7	110	0.0572
9	0.0049	0.5	110	0.0439
10	0.0049	0.28	110	0.0247
11	0.0049	2.0	110	0.1305
12	0.0049	3.0	110	0.1609
13	0.0049	6.0	110	0.1945

[a] Monomer concentration held constant at 0.98 M. Reactions carried out in 1,1,2,2-tetrachloroethane. [b] The k_{obsd} value calculated under these conditions for ambient temperature (25 °C) is 0.00949 h^{-1}.

parallel the theoretical molecular weights. Figure 3 illustrates the linear increase in M_n observed with conversion and the low polydispersity indices (PDI, M_w/M_n) of the product polymers. *This clearly demonstrates that the level of polymerization control is high.*

Solution Kinetic Studies of ROP Process. We have initiated kinetic measurements of the ring-opening polymerization of trimethylene carbonate in solution in the presence of the (salen)-Ca(II)/*n*-$Bu_4N^+X^-$ catalyst system. These studies were conducted employing {3,5-di-*tert*-butyl(salicylidene)-1,2-ethylenediimine}Ca(II) with 1 equiv of *n*-$Bu_4N^+Cl^-$ as cocatalyst in 1,1,2,2-tetrachloroethane (TCE). As we previously reported for the ROP of TMC utilizing (salen)AlCl as catalyst, the rate of polymerization in a weakly polar solvent like toluene (dielectric constant = 2.4) was found to be faster than in the more polar TCE solvent (dielectric constant = 10.8). This observation is characteristic of a coordination−insertion mechanism. Although the polymerization reaction is slower in TCE, it was found to be advantageous to use a high boiling chlorinated solvent for these kinetic studies because of the high solubility of both monomer and polymer in this solvent. The reactions were monitored by ^1H NMR spectroscopy.

Figure 4a displays a typical monomer consumption vs time plot, whereas the semilogarithmic plot of −ln[monomer]$_t$ vs time is illustrated in Figure 4b. Hence, as might be expected, the polymerization reaction is found to be first order in monomer (TMC) concentration. Table 6 summarizes the determined rate constants (k_{obsd}) for the ROP of TMC as a function of the [catalyst], [cocatalyst], and temperature. Figures 5 and 6 depict the log−log plots of k_{obsd} vs [catalyst] or [cocatalyst], respectively. These latter plots reveal linear relationships between ln k_{obsd} vs ln[catalyst] or ln[cocatalyst] with slopes close to unity, thereby indicative of the polymerization reaction being first order in [catalyst] or [cocatalyst]. Of course, at concentration of cocatalyst much greater than 1 equiv the polymerization rate eventually should become independent of [cocatalyst] (vide infra).

Figure 7 illustrates the effect of the number of equivalents of cocatalyst ($Bu_4N^+Cl^-$) on the rate constant of the ROP process. As would be anticipated, the initiation process ultimately becomes independent of [cocatalyst], or "saturation" kinetics is observed. A double-reciprocal plot of these data reveals a linear relationship with a limiting k_{obsd} value of 0.363 h^{-1} observed under these reaction conditions at 110 °C (see Figure 8).

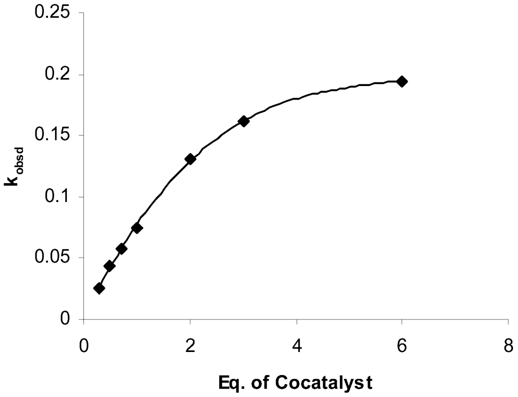


Figure 7. Rate constant for production of polymer as a function of the number of equivalents of *n*-$Bu_4N^+Cl^-$. Data take from Table 6.

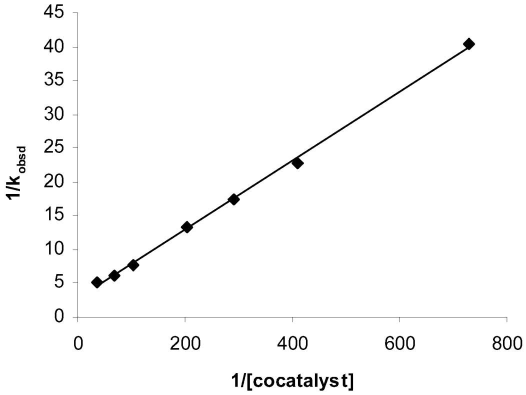


Figure 8. Double-reciprocal plot of the rate constant dependence of the ROP process with [cocatalyst]. Data taken from Table 6. Slope = 0.0511 and intercept = 2.756 with R^2 = 0.998.

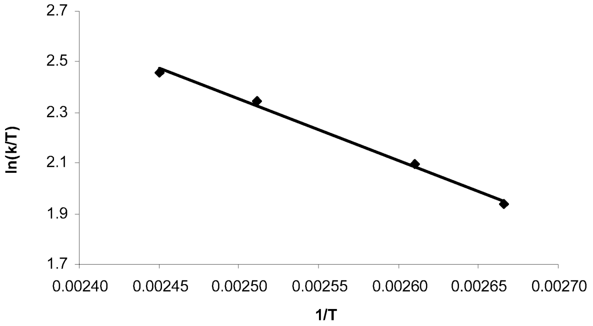


Figure 9. Eyring plot of ROP of TMC in the presence (salen)Ca/*n*-$Bu_4N^+Cl^-$ catalyst in TCE. Slope = −2415 with R^2 = 0.994.

The activation parameters for the ROP of trimethylene carbonate catalyzed by (salen)Ca(II)/*n*-$Bu_4N^+Cl^-$ in TCE were found to be $\Delta H^\ddagger = 20.1 \pm 1.0$ kJ/mol and $\Delta S^\ddagger = -128 \pm 3$ J/(mol K). These values were calculated from the temperature-dependent rate constants listed in Table 6 and the Eyring plot depicted in Figure 9. The $\Delta G^\ddagger$ value of 58.2 kJ/mol observed for the calcium catalyzed process is 24.5 kJ/mol lower in energy than that which we previously reported for the reaction catalyzed by an aluminum derivative (82.7 kJ/mol).[6] This is consistent with the latter process occurring much slower under similar reaction conditions. In both instances, these activation parameters are in accordance with a reaction mechanism involving the addition of a nucleophile to a metal-bound cyclic carbonate (vide infra).

Experimental studies were designed to better define the ring-opening process at the molecular level. As previously described for ROP of trimethylene carbonate in the presence of (salen)-AlCl catalysts, the mechanism involves an insertion of the monomer into the growing polymer chain by breaking the acyl−oxygen bond instead of the alkyl−oxygen bond.[6] This result was obtained by ^1H NMR spectroscopy on a low molecular weight polymer derived from chain termination upon reaction with 2-propanol, a procedure employed by Shen and co-workers numerous times.[20] Pertinent to the initiation process involving ring-opening of trimethylene carbonate by the anion of the cocatalyst *n*-$Bu_4N^+X^-$, we have examined the interaction of (salen)Ca (salen = *N*,*N'*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediimine) with the azide ion in TCE solution (eq 3).[21,22] The equilibrium constant for the reaction in eq 3 was determined by monitoring the ν_{N_3} vibrational modes in the metal-bound and free species. In this manner K_{eq} at ambient temperature was found to be 79 ± 21 M^{-1}.

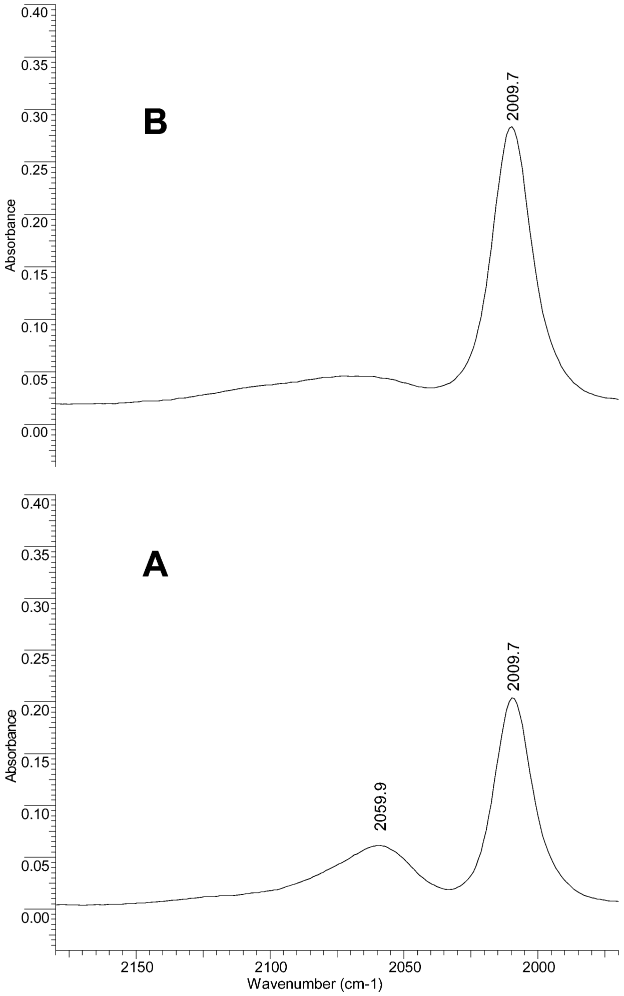
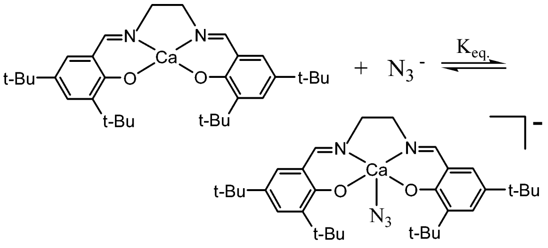


Figure 10. Infrared spectrum in ν_{N_3} stretching region in tetrachloroethane: (A) 0.025 M Ca(salen) and 1 equiv of *n*-$Bu_4N^+N_3^-$ at ambient temperature, 2009.7 cm^{-1} peak for free N_3^- and 2059.9 cm^{-1} peak for calcium bond N_3^-; (B) after addition of 50 equiv of trimethylene carbonate to the solution in (A). Note that free ν_{N_3} absorption has increased.



(3)

Although (salen)Ca complexes in the presence of 1 equiv of the cocatalyst, *n*-$Bu_4N^+N_3^-$, in tetrachloroethane exist as an equilibrium mixture of (salen)Ca and (salen)CaN_3^-, upon addition of excess trimethylene carbonate all the azide ligand is free in solution. This is best depicted in Figure 10 where the calcium bound azide vibration (2059.9 cm^{-1}) is displaced in the presence of only 50 equiv of trimethylene carbonate. Once the azide nucleophile ring opens the cyclic carbonate its infrared stretching vibrational mode shift to higher frequency, i.e., above 2100 cm^{-1}. This initiation process is fast under catalytic reaction conditions; i.e., the initial ring-opening of the monomer in TCE by azide ion at 110 °C occurs within 3 min. Hence, chain propagation is the slow step in the polymerization process, which is consistent with the narrow molecular weight distribution observed for these processes. Because our kinetic studies were generally carried out in a monomer-to-initiator ratio of 350 to 1.0, the initiation process most likely involves free or weakly associated azide (or other anion, X^-) at a metal coordinated (activated) trimethylene carbonate monomer (eq 2).

Summary Remarks

Herein we have reported on the use of biometal Schiff base derivatives along with anions derived from PPN^+ or n-Bu_4N^+ salts as catalysts for the ring-opening polymerization of trimethylene carbonate. The catalytic activity varied with metal in the order $Ca^{2+} > Mg^{2+} \approx C_2H_5Al^{2+} > Zn^{2+}$. Optimization of the calcium(II) system was achieved utilizing a salen ligand with *tert*-butyl substituents in the 3,5-positions of the phenolate rings and a ethylene backbone for the diimine grouping along with $PPN^+N_3^-$. Employing this catalytic system in a melt polymerization process provided a TOF of 1286 h^{-1} at 86 °C. Solution kinetic studies in tetrachloroethane revealed the polymerization reaction to be first order in [monomer], [(salen)-Ca], and [n-$Bu_4N^+Cl^-$], with the latter dependence reaching saturation when [n-$Bu_4N^+Cl^-$] ≫ [(salen)Ca]. The polymerization reaction was shown to be *quasi-living* as illustrated by a linear relationship between M_n and percent conversion and a low polydispensity index, clearly demonstrating that the level of polymerization control was high.

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