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Ring-Opening Polymerization of Trimethylene Carbonate Using Aluminum(III) and Tin(IV) Salen Chloride Catalysts

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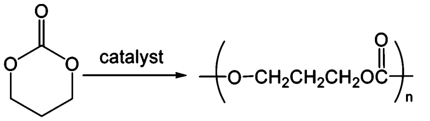
ABSTRACT: Aluminum and tin salen complexes have been shown to effectively catalyze the ring-opening polymerization (ROP) of trimethylene carbonate (TMC) to polycarbonate. The most active salen derivative in each instance contained a phenylene backbone with chloro substituents in the 3,5-positions of the phenolate rings, with the aluminum derivatives being significantly more active than their tin(IV) counterparts. Importantly, the resultant polycarbonate was shown by ^{1}H NMR to be void of ether linkages. The reaction was demonstrated to proceed via a mechanism first order in both [catalyst] and [monomer] and to involve TMC ring-opening by way of acyl oxygen bond cleavage. Consistent with a reaction pathway involving an insertion of the monomer into the metal−nucleophile bond (e.g., Al−Cl or Sn−Cl), the activation parameters were determined to be $\Delta H^‡ = 51$ kJ/mol and $\Delta S^‡ = -141$ J/(mol deg).

For several decades there has been much interest in the production of polycarbonates via the environmentally benign route of copolymerizing an epoxide and carbon dioxide.[1,2] The intensity and success of efforts in this area have been greatly enhanced with the advent of effective homogeneous catalysts.[3] Unfortunately, the concomitant formation of the thermally stable five-membered ring cyclic carbonate from aliphatic epoxides and CO_2 has hindered the wide scale use of this approach.[4] Although there have been significant strides at developing better, more selective, catalysts for the coupling of propylene oxide and carbon dioxide to poly(propylene carbonate), this still is a process which remains relatively underdeveloped.[5] An alternative pathway to aliphatic polycarbonates is the ring-opening polymerization (ROP) of six-membered cyclic carbonates such as trimethylene carbonate (eq 1). The analogous process involving five-membered cyclic carbonates affords polycarbonates with a significant quantity of ether linkages (eq 2); e.g., the thermodynamically unfavored polymerization of propylene carbonate to poly(propylene carbonate) is accompanied by a great deal of CO_2 loss.[6] On the other hand, it is possible under certain conditions to produce polycarbonates with no ether linkage, i.e., CO_2 loss, from six- and higher-membered cyclic carbonates.[7]



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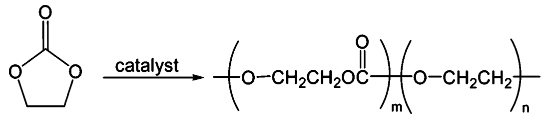

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The polycarbonate derived from trimethylene carbonate (TMC or 1,3-dioxan-2-one) has been investigated quite extensively for its potential utilization as a biodegradable polymer in important biomedical and pharmaceutical applications, such as sutures, drug delivery systems, and tissue engineering.[8,9] For the ROP of cyclic carbonates both cationic and anionic initiators have been shown to be effective.[7,10] Strong Lewis acids undergo cationic initiation to provide a polymer with ether linkages resulting from decarboxylation, where weaker Lewis acid initiate by an anionic mechanism providing polymer with 100% carbonate linkages.[11] Because of their Lewis acidic nature, aluminum and tin salts have by far been the most popular catalysts for the ring-opening polymerization of trimethylene carbonate. However, thus far there has been a marked absence of well-defined metal complexes employed as catalysts for this process.

Recently, our group has reported a variety of well-characterized metal catalysts systems for the copolymerization of cyclohexene oxide or propylene oxide and carbon dioxide. We have been able to optimize these reactions employing extremely robust metal salen complexes, with many of these systems affording copolymers with greater than 99% carbonate linkages and low polydispersity indices.[5e,12] This success has prompted us to examine the efficacy of such catalysts for the ring-opening polymerization of TMC. Relevant to our study, Cao and co-workers have recently reported the use of a novel salen aluminum alkoxide and its dimer to ring open trimethylene carbonate,[13a] and Chisholm has similarly demonstrated (salen)aluminum alkoxides to be effective catalysts for ROP of lactides.[13b] Herein, we have focused on Al(III) and Sn(IV) salen chloride compounds as catalysts for the ring-opening polymerization of trimethylene carbonate. Efforts have been made to optimize the effectiveness of these catalysts by systematic variation of the electronics of the salen ligand. Figure 1 illustrates the generic structure of the Sn(IV) and Al(III) salen chloride complexes utilized in this study.

Experimental Section

All syntheses were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Acetonitrile was first dried by distillation into CaH_2 onto P_2O_5 followed by distillation onto CaH_2 and then freshly distilled from CaH_2 prior to use. 1,1,2,2-Tetrachloroethane (TCE) was distilled over

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P_2O_5 prior to use. Salicylaldehyde, ethylenediamine, and 1,2-phenylenediamine were purchased from Aldrich and used as received. ^{1}H NMR spectra were recorded on a 300 MHz Varian Unity Plus spectrometer. The spectra was calibrated using signals from the solvent and was reported downfield from $SiMe_4$.

The methodology employed in the synthesis of the monomer was identical to that reported by Endo and co-workers using 1,3-propanediol and ethyl chloroformate.[14] The monomer was further purified by repeated crystallization in THF/diethyl ether. All aluminum salen chloride catalysts were synthesized according to known literature procedures.[12b,15]

Synthesis of *N*,*N*-Bis(3,5-dichlorosalicylidene)ethylenediimine−Sn(IV) Dichloride (1). $(Cl)_2salenH_2$ (0.406 g, 1.0 mmol) was dissolved with 20 mL of THF in a 50 mL Schlenk flask. The solution was transferred via cannula onto a 10 mL of THF suspension of KH (0.088 g, 2.1 mmol) in a separate 50 mL Schlenk flask. Immediate evolution of H_2 gas was observed, and the mixture was stirred for 1 h at room temperature to produce an orange solution of $K_2(Cl)_2salen$. A 50 mL Schlenk flask fitted with a reflux condenser was charged with $SnCl_4$ (0.286 g, 1.0 mmol) and 10 mL of THF. The potassium salt solution was transferred via cannula onto the $SnCl_4$ mixture and refluxed overnight. The reaction mixture was cooled to room temperature and filtered, and the solvent was removed in vacuo. The solid was washed with hexanes (2 × 20 mL) to yield 0.275 g of orange-yellow solid (46%). ^{1}H NMR (d_6-DMSO): $\delta = 4.18-4.29$ (m, 4H, N−CH_2CH_2−N), 7.69 (d, 2H, phenyl-*H*), 7.93 (d, 2H, phenyl-*H*), 8.86 (s, 2H, phenyl-C*H*═N).

Synthesis of *N*,*N*-Bis(3,5-dichlorosalicylidene)-1,2-phenylenediimine−Sn(IV) Dichloride (2). $(phen)(Cl)_2salenH_2$ (0.300 g, 0.66 mmol) was dissolved with 20 mL of THF in a 50 mL Schlenk flask. The solution was transferred via cannula onto a 10 mL THF suspension of KH (0.053 g, 1.32 mmol) in a separate 50 mL Schlenk flask. Immediate evolution of H_2 gas was observed and the formation of a deep red solution. The mixture was stirred for 1 h at room temperature, and a red precipitate formed. The THF slurry was transferred via cannula into a 50 mL Schlenk flask fitted with a reflux condenser and charged with $SnCl_4$ (0.172 g, 0.66 mmol) in 10 mL of THF. The mixture was refluxed for 3 h to form a dark red-orange solution and a white precipitate. The reaction mixture was cooled to room temperature and filtered, and the solvent was removed in vacuo. The solid was washed with hexanes (2 × 20 mL) to yield 0.545 g of orange solid (85%). X-ray quality crystals were grown by slow diffusion of pentane into a concentrated THF solution at −30 °C over several days. ^{1}H NMR (d_6-DMSO): $\delta = 7.31-7.39$ (m, 2H, phenyl-*H*), 7.56−7.63 (m, 2H, *N*-phenyl-*H*), 7.92 (d, 2H, *N*-phenyl-*H*), 8.21−8.24 (m, 2H, phenyl-*H*), 8.80 (s, 2H, phenyl-*H*), 9.57 (s, 2H, phenyl-C*H*═N).

Synthesis of *N*,*N*-Bis(salicylidene)-1,2-phenylenediimine−Sn(IV) *n*-Butyl Chloride (3). $(phen)salenH_2$ (0.301 g, 1.0 mmol) was dissolved with 20 mL of THF in a 50 mL Schlenk flask. The solution was transferred via cannula onto a 10 mL of THF suspension of KH (0.088 g, 2.1 mmol) in a separate 50 mL Schlenk flask. Immediate evolution of H_2 gas was observed, and the mixture was stirred for 1 h at room temperature to produce an orange solution of $K_2(phen)salen$. A 50 mL Schlenk flask was charged with $(Bu)SnCl_3$ (0.283 g, 1.0 mmol) and 10 mL of THF. The potassium salt solution was transferred via cannula onto the $(Bu)SnCl_3$, and the mixture is stirred at room temperature overnight and the solvent removed in vacuo. The crude solid was extracted with CH_2Cl_2 (2 × 20 mL). The filtrate was evaporated, and the solid was washed with hexanes (2 × 20 mL) to yield 0.460 g of yellow-orange solid (87%). ^{1}H NMR: $\delta = 0.406$ (t, 3H, CH_2−CH_3), 0.905−0.928 (m, 2H, CH_2−CH_2−CH_3), 1.21−1.23 (m, 2H, Sn−CH_2−CH_2 1.37−1.38 (m, 2H, Sn−CH_2), 6.25−6.30 (m, 4H, phenyl-*H*), 6.56−6.59 (m, 4H, phenyl-*H*), 6.85−6.86 (m, 4H, *N*-phenyl-*H*), 7.47 (s, 2H, phenyl-C*H*═N). Elemental Analysis: Calcd for $C_{24}H_{23}N_2O_2SnCl\cdot CH_2Cl$: C, 49.18%; H, 4.13%; N, 4.59%. Found: C, 49.80%; H, 4.64%; N, 4.67%.

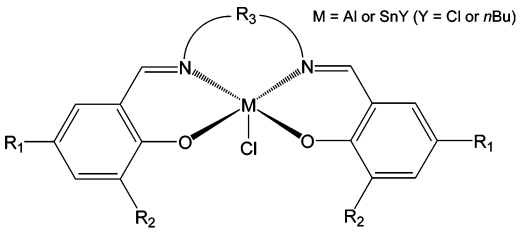

Figure 1. Generic diagram of a M salen chloride. R_1 and R_2 refers to the 3,5-positions of the phenolate rings, respectively.

Kinetic Studies. TMC and the catalyst were weighed out in a Schlenk flask in the desired monomer:initiator ratio followed by the addition of 10 mL of dry solvent. The reaction vessel was placed into a preheated oil bath. The percent conversion of the monomer in time was calculated by manually sampling a small aliquot of the solution, quenching it, and analyzing by ^{1}H NMR.

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 ratio was maintained at 350:1. The reaction was carried on at 95 °C for 3 h under an argon atmosphere unless mentioned otherwise. 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 by actually weighing the vacuum-dried polymer. Molecular weight determinations (M_n and M_w) were carried out at the New Jersey Center for Biomaterials, Rutgers University.

X-ray Crystallography. A Bausch and Lomb 10× microscope was used to identify suitable crystals from a representative sample of crystals of the same habit. Crystals were coated with mineral oil, placed on a glass fiber, and mounted on a Bruker SMART 1000 CCD diffractometer. X-ray data were collected covering more than a hemisphere of reciprocal space by a combination of three sets of exposures. Each exposure had a different φ angle for the crystal orientation, and each exposure was covered 0.3° in ω. The crystal-to-detector distance was 4.9 cm. Decay was monitored by repeating collection of the initial 50 frames collected and analyzing the duplicate reflections. Crystal decay was negligible. The space group was determined on the basis of systematic absences and intensity statistics.[1] The structure was solved by direct methods and refined by full-matrix least squares on F.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms were placed in idealized positions with fixed isotropic displacement parameters equal to 1.5 times (1.2 for methyl protons) the equivalent isotropic displacement parameters of the atom to which they are attached.

The following programs were used: data collection and cell refinement, SMART; data reduction, SAINTPLUS (Bruker); programs used to solve structures, SHELXS-97 (Sheldrick); programs used to refine structures, SHELXL-99 (Sheldrick); molecular graphics and publication materials, SHELXTL-Plus version 5.0 (Bruker).

Results and Discussion

The aluminum salen chloride catalysts were prepared, purified, and structurally characterized as previously described. Synthesis of the Sn(IV) salen complexes was achieved in good to moderate yields from the reactions of $SnCl_4$ or n-$BuSnCl_3$ and the potassium salt of the respective salen ligand. It was of interest to structurally characterize these derivatives in order to access the steric constraints about the metal center as well as the relative Sn−Cl bond distances. X-ray quality crystals were obtained from concentrated THF solutions (−30 °C) of the complexes upon slow diffusion of pentane over several days. Thermal ellipsoid representations of the three Sn(IV) salen derivatives are found in Figures 2−4, along with salient metal−ligand bond distances. Com-

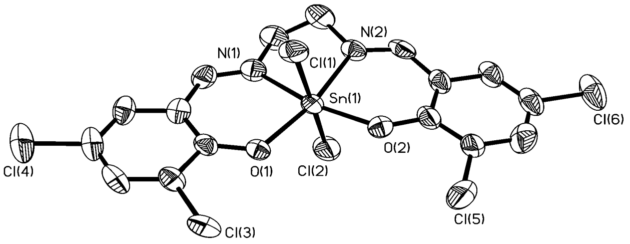

Figure 2. Molecular structure of catalyst **1-THF**. Ellipsoids are shown at 50% probability level; hydrogens are omitted for clarity. Selected distances (Å): Sn(1)−O(1), 2.005(5); Sn(1)−O(2), 2.001(5); Sn(1)−N(1), 2.144(7); Sn(1)−N(2), 2.153(6); Sn(1)−Cl(1), 2.423(2); Sn(1)−Cl(2), 2.402(2).

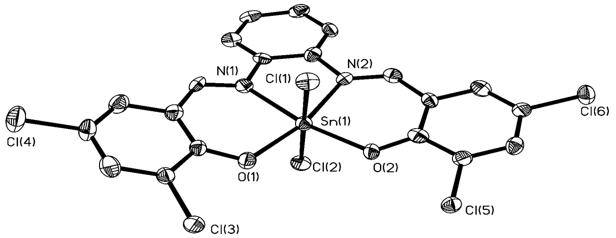

Figure 3. Molecular structure of catalyst **2-THF**. Ellipsoids are shown at 50% probability level; hydrogens are omitted for clarity. Selected distances (Å): Sn(1)−O(1), 2.032(6); Sn(1)−O(2), 2.015(6); Sn(1)−N(1), 2.160(7); Sn(1)−N(2), 2.157(7); Sn(1)−Cl(1), 2.391(2); Sn(1)−Cl(2), 2.393(2).

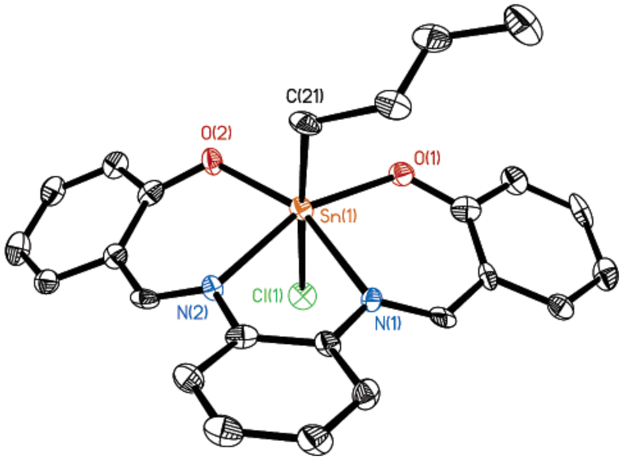

Figure 4. Molecular structure of catalyst **3**. Ellipsoids are shown at 50% probability level; hydrogens are omitted for clarity. Selected distances (Å): Sn(1)−O(1), 2.047(5); Sn(1)−O(2), 2.052(5); Sn(1)−N(1), 2.203(6); Sn(1)−N(2), 2.199(6); Sn(1)−Cl(1), 2.489(2); Sn(1)−C(21), 2.140(7).

plete molecular parameters and crystallographic details are provided as Supporting Information.

We have assayed these aluminum and tin salen derivatives for their ability to catalyze the ring-opening polymerization of trimethylene carbonate, where the salen ligand has been electronically and sterically varied in a systematic fashion. A typical melt polymerization run consisted of adding 1.0 g of TMC to a flame-dried Schlenk flask, where the monomer:initiator ratio was maintained at 350:1. The polymerization reaction was carried out at 95 °C for 3 h under argon unless otherwise specified. The resulting polymer was purified by precipitation from dichloromethane, 5% aqueous HCl, and methanol followed by drying under vacuum. Turnover frequencies (mol of TMC consumed/(mol of catalyst·h)) were calculated on the basis of the weight of dried polymer isolated. The polymers were analyzed by ^{1}H NMR and shown to be completely absent of ether linkages, even for reactions carried out at 140 °C. Molecular weights were determined by GPC, and the M_w values found were exactly what was expected on the basis of the % conversion and the monomer:initiator ratio. The polydispersity index was in general about 1.6.

Table 1. Polymerization Results on Varying the Substituents in the 3,5-positions of the Phenolate Rings for (salen)Al(III)Cl Complexes Containing a Phenylene Backbone[a]

entry	R_1	R_2	TOF[b]
1	H	H	46
2	H	phenyl	47
3	H	*tert*-butyl	50
4[c]	*tert*-butyl	*tert*-butyl	72
5	Cl	Cl	81

[a] Each reaction was performed in melt maintaining a monomer: initiator ratio (M/I) as 350:1 at 95 °C for 3 h. [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 Al·h). [c] M_w = 26 000 with a PDI of 1.66.

Table 2. Polymerization Results for Varying the Backbone for (salen)Al(III)Cl Complexes Where the Substituents in the 3,5-Positions of the Phenolate Ring Are *tert*-Butyl Groups[a]

entry	R_3	TOF[b]
1	cyclohexylene	60
2	ethylene	63
3	naphthalene	70
4	phenylene	72

[a] Each reaction was performed in melt maintaining a monomer: initiator ratio (M/I) as 350:1 at 95 °C for 3 h. [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 Al·h).

Table 1 summarizes the results of the polymerization reaction of TMC with various (salen)AlCl catalysts containing substituents in the 3,5-positions of the phenolate rings for salen ligands containing the phenylene backbone. As is evident in Table 1, the most active catalyst was found to be *N,N′*-bis(3,5-dichlorosalicylidene)phenylenediimine−aluminum(III) chloride. A steady increase in the monomer conversion was observed on substituting the 3- and 5-positions in the phenolate ring with either *tert*-butyl or chloro groups. A substantial increase, around 80%, in the catalytic activity is observed between entry 1 and 5. Similarly, studies by Gibson and co-workers have indicated that increasing the electrophilicity of the metal center by adding electron-withdrawing groups to the phenolate rings of the salen ligands increases the complexes ability to catalyze the ring-opening polymerization of DL- and L-lactide at ambient temperature.[16]

We have also attempted to optimize the catalytic activity of these derivatives by manipulating the salen backbone. An electron-withdrawing, planar, and less sterically encumbering backbone results in an increase in the activity, as shown in Table 2. Although as is evident from the trend in Table 2, changes in the backbone do not have as pronounced an effect on the performance of the catalyst as that of the substituents on the phenolate ring. Upon changing the initiator from (salen)AlCl to (salen)AlOEt afforded an increase in the effectiveness of the catalyst for the ROP process. That is, melt polymerization reactions were carried out for 2 h at 90 °C using the aluminum derivatives where the salen ligand contained *tert*-butyl substituents in the 3,5-positions of the phenolate rings and an ethylene backbone. A comparison of the results in Table 3 reveals that

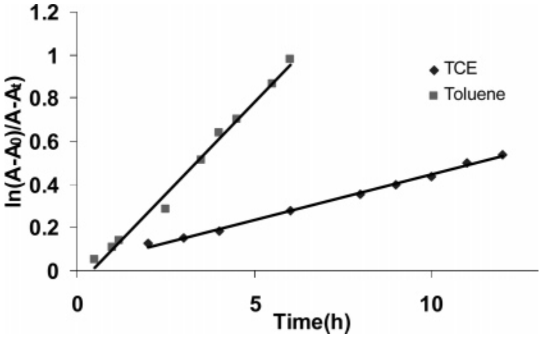

Figure 5. Rate of polymerization in toluene and 1,1,2,2-tetrachloroethane (TCE) determined by ^{1}H NMR while maintaining the monomer:catalyst as 15:1 at 80 °C.

Table 3. Polymerization Results for Varying the Initiator X for (salen)Al(III)X Complexes Contaning a Ethylene Backbone Where the Substituents in the 3,5-Positions of the Phenolate Ring Are *tert*-Butyl Groups[a]

entry	X	TOF[b]
1[c]	OEt	105
2	Cl	80

[a] Each reaction was performed in melt maintaining a monomer: initiator ratio (M/I) as 350:1 at 90 °C for 2 h. [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 Al·h). [c] M_w = 24 000 with a PDI of 1.61

Table 4. Polymerization Results for (salen)Sn(X)Y Complexes[a]

entry	R_1	R_2	backbone	Y	X	TOF[b]
1	H	H	phenylene	*n*-butyl	Cl	13
2	Cl	Cl	ethylene	Cl	Cl	17
3	Cl	Cl	phenylene	Cl	Cl	22

[a] Each reaction was performed in melt maintaining a monomer: initiator ratio (M/I) as 350:1 at 95 °C for 3 h. [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 Sn·h).

a change in the initiator from Cl to OEt significantly increases the catalytic activity of the (salen)Al derivative.

Cyclic carbonates like TMC have traditionally been polymerized using a variety of tin-based initiators such as tin(IV) tetrahalides and tin(II) octanoate. The polymerization runs employing tin(IV) salen derivatives were carried out under the same conditions as their aluminum counterparts. Though the tin compounds do ring-open trimethylene carbonate, as is apparent from Table 3, the activity is greatly reduced. *N,N′*-Bis(3,5-dichlorosalicylidene)-1,2-phenylene diimine−Sn(IV) dichloride (entry 3, Table 4), our most active tin salen, shows a turnover frequency of 22, a reduction in activity by one-fourth in comparison to the corresponding aluminum catalyst (entry 5, Table 1). It should be noted that the dependence of activity on the electronics of the salen structure follows the same trend seen for aluminum. Hence, an increase in the Lewis acidity of the metal center corresponds to an increase in the rate of polymerization. Although the sterically less encumbered phenylene backbone exhibits the fastest rate of polymerization, there is *no* correlation between the Sn−Cl bond length (bond strength) and reactivity.

At this time we wish to present preliminary kinetic data obtained in solution employing one of the catalysts, namely, *N,N′*-bis(salicylidene)-1,2-phenylene diimine−Al(III) chloride. As depicted in Figure 5, the rate of polymerization in a weakly polar solvent like toluene (dielectric constant 2.4) was found to be 4.1 times faster than in 1,1,2,2-tetrachloroethane (TCE) (dielectric constant 10.8), indicative of a coordination−insertion mechanism. The linear time dependence of the semilogarithmic plot in Figure 5 of $\ln(A - A_0)/(A - A_t)$ also clearly demonstrates that the polymerization is first order in monomer. Furthermore, a sample of low-molecular-weight polyTMC terminated by 2-propanol exhibited peaks in the ^{1}H NMR spectra consistent with this mechanism as predicted by Shen and co-workers; that is, the monomer inserts into the growing polymer chain via acyl−oxygen bond cleavage.[17]

In addition, the ring-opening polymerization reaction of trimethylene carbonate was examined kinetically in tetrachloroethane to assess the dependence of the process on [catalyst] and on temperature. These data are contained in Table 5, with respective plots illustrated in Figures 7 and 8. As is apparent from Figure

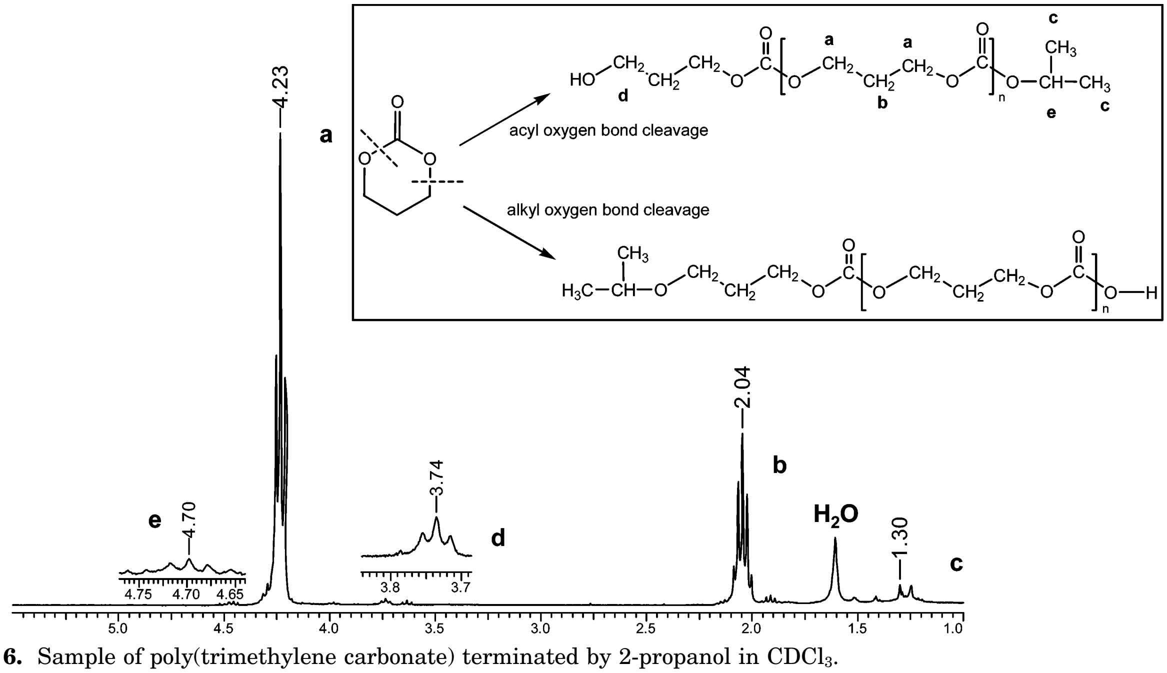

Figure 6. Sample of poly(trimethylene carbonate) terminated by 2-propanol in CDCl$_3$.

Table 5. Polymerization Rate Constants Using *N,N'*-Bis(salicylidene)-1,2-phenylenediimine−Al(III) Chloride as the Catalyst in TCE[a]

entry	[Al] (mol/L)	temp (°C)	*k* (mol/L·s)
1	0.047	95	0.0057
2	0.064	95	0.0070
3	0.082	95	0.0093
4	0.0119	95	0.0126
5	0.0135	95	0.0149
6	0.0135	80	0.0085
7	0.0135	110	0.0369
8	0.0135	125	0.0771
9	0.0135	140	0.1087

[a] Entries 1−5 contain rate constant data vs [catalyst], whereas entries 5−9 contain temperature-dependent rate constant data.

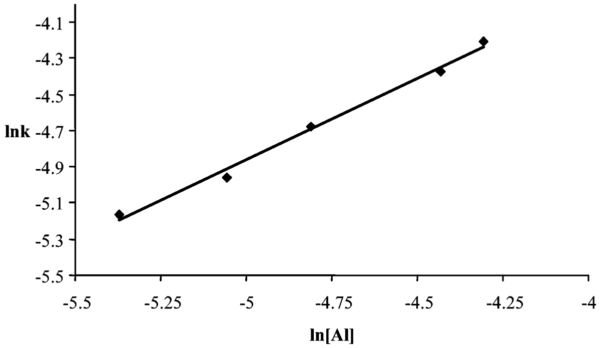

Figure 7. Plot of ln *k* vs ln[Al], where the slope = 0.90 with an R^2 value of 0.994.

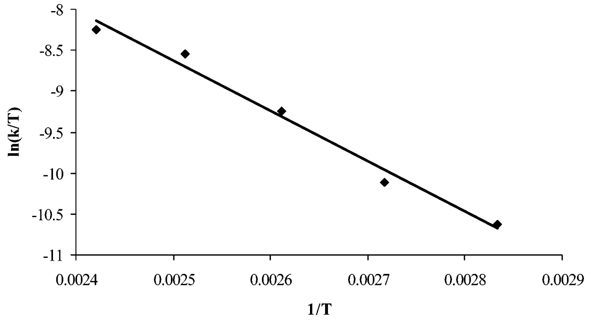

Figure 8. Eyring plot of temperature dependence of second-order rate constant with an R^2 value of 0.985.

7, the reaction is first-order in [catalyst] as well as first-order in monomer, as previously shown in Figure 5. From the Eyring plot in Figure 8, the activation parameters $\Delta H^{\ddagger} = 51$ kJ/mol and $\Delta S^{\ddagger} = -141$ J/(mol deg) were derived, which are completely consistent with a reaction mechanism involving an insertion of the monomer into the metal−nucleophile bond.

Concluding Remarks

In this article we have demonstrated that salen derivatives of Al(III) and Sn(IV) are effective catalysts for the ring-opening polymerization of trimethylene carbonate to afford polycarbonates with *no* ether linkages. We have been able to optimize the catalytic activity of these metal complexes by manipulating the salen structure. Our results indicate that an electron-withdrawing, sterically unencumbering salen backbone enhances the activity of both aluminum and tin salen derivatives. A significant decrease is observed in the performance of Sn(IV) compounds in comparison to the Al(III) complexes which can be attributed to the reduction in Lewis acidity of the metal center. Our present efforts are concentrated on developing a more detailed understanding of the mechanism of this important process, concomitantly designing more active metal catalysts based on this knowledge. Relevant to this latter point we have observed calcium(II) salen derivatives to be extremely effective toward the ROP process of trimethylene carbonate. The use of these nontoxic metal complexes (aluminum and calcium) as catalysts is of significance since these materials are widely used in biomedical/pharmaceutical applications.

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Supporting Information Available: Complete details for the crystallographic study of compounds **1-THF**, **2-THF**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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