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Copolymerization of CO_2 and Epoxides Catalyzed by Metal Salen Complexes

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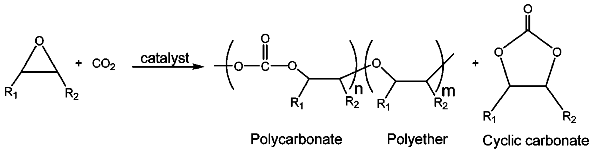
ABSTRACT
The design of efficient metal catalysts for the selective coupling of epoxides and carbon dioxide to afford completely alternating copolymers has made significant gains over the past decade. Hence, it is becoming increasingly clear that this “greener” route to polycarbonates has the potential to supplement or supplant current processes for the production of these important thermoplastics, which involve the condensation polymerization of diols and phosgene or organic carbonates. On the basis of the experiences in our laboratory, this Account summarizes our efforts at optimizing (salen)$Cr^{III}X$ catalysts for the selective formation of polycarbonates from alicyclic and aliphatic epoxides with CO_2. An iterative catalyst design process is employed in which the salen ligand, initiator, cocatalyst, and reaction conditions are systematically varied, with the reaction rates and product selectivity being monitored by in situ infrared spectroscopy.

Introduction

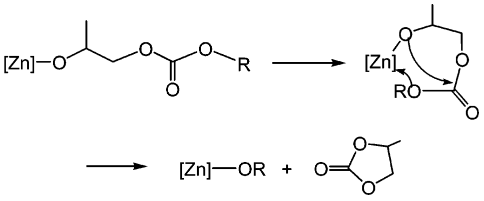
Inoue and co-workers, 35 years ago, demonstrated that it was possible to copolymerize carbon dioxide and propylene oxide in the presence of a catalyst derived from a 1:1 mixture of $(CH_3CH_2)_2Zn$ and water.[1] This process is illustrated in eq 1,



(1)

where in this instance the alternative coupling product, cyclic carbonate, is also afforded. The cyclic carbonate byproduct (1,3-dioxolan-2-ones) is proposed to result from the degradation of the growing copolymer chain, i.e., the back-biting mechanism as depicted in Scheme 1.[2] Because of the lack of an active-site control resulting from the heterogeneous nature of the catalyst, this process generally suffered from problems including inconsistent results and high polyether content in the copolymer. During the next 20 years, the design of catalysts for this process was mostly centered on derivatives of Inoue’s pioneering discovery involving different protic sources such as *tert*-butylcatechol, pyrogallol, and $(CH_3CH_2)_2Zn$.[3] It was not until 1995 when we employed well-defined zinc bis(phenoxides) as homogeneous catalysts for the copolymerization of cyclohexene oxide and carbon dioxide that a better mechanistic understanding of this catalytic process began to emerge.[4] These second generation zinc catalysts were based on 2,6-disubstituted phenols and were found to crystallize from toluene as dimeric complexes, which were easily disrupted by ether ligands to afford distorted tetrahedral species (Figure 1). These complexes exhibited enhanced catalytic activity over the first generation heterogeneous zinc catalysts, providing copolymers with very high CO_2 content and negligible quantities of cyclic carbonate. Importantly, the process involved no organic solvents; i.e., these well-characterized zinc derivatives were soluble in carbon-dioxide-expanded cyclohexene oxide. Shortly after this achievement, Beckman and co-workers reported a soluble fluorinated zinc catalyst with similar activity for the generation of copolymers from cyclohexene oxide and CO_2.[5] The most significant advancement in this area came with the contribution from Coates’s laboratory, which involved the use of monomeric and dimeric zinc catalysts containing chelating β-diiminate ligands (Figure 2).[6] Selected derivatives of this living cyclohexene oxide/carbon dioxide copolymerization system are by far the most active catalysts reported for this process.[7]

Scheme 1



Donald J. Darensbourg was born in Baton Rouge, Louisiana, in 1941. He obtained his undergraduate degree in chemistry at California State University at Los Angeles in 1964 and his Ph.D. in chemistry from the University of Illinois in 1968 under the direction of Theodore L. Brown. He has held faculty appointments at the State University of New York at Buffalo and Tulane University prior to accepting his present position as Professor of Chemistry at Texas A&M University in 1982. His research interests are in mechanistic organometallic/inorganic and polymer chemistry.

Ryan M. Mackiewicz was born and raised in and around Buffalo, New York. He obtained a B.S. in chemistry from the State University of New York at Fredonia in the spring of 2000 and currently works in the research group of Donald J. Darensbourg. His research focuses on mechanistic studies of the copolymerization of epoxides and CO_2 utilizing chromium salen complexes.

Andrea L. Phelps was born in 1978 in Fort Smith, Arkansas. She received a B.S. in chemistry from the University of Central Arkansas in 2000 and started her graduate studies at Texas A&M University in 2001 in the research group of Donald J. Darensbourg. Her research focuses on the copolymerization of CO_2 and propylene oxide using various Cr^{III}salen complexes as catalysts, as well as the copolymerization of aziridines and CO to produce polypeptides.

Damon R. Billodeaux was born in 1977 in Baton Rouge, Louisiana. He obtained a B.S. in chemistry from Louisiana State University in May 2000 and began graduate studies at Texas A&M University under the direction of Donald J. Darensbourg in August 2000. His dissertation research focuses on the use of main-group salen complexes for the copolymerization of carbon dioxide and epoxides.

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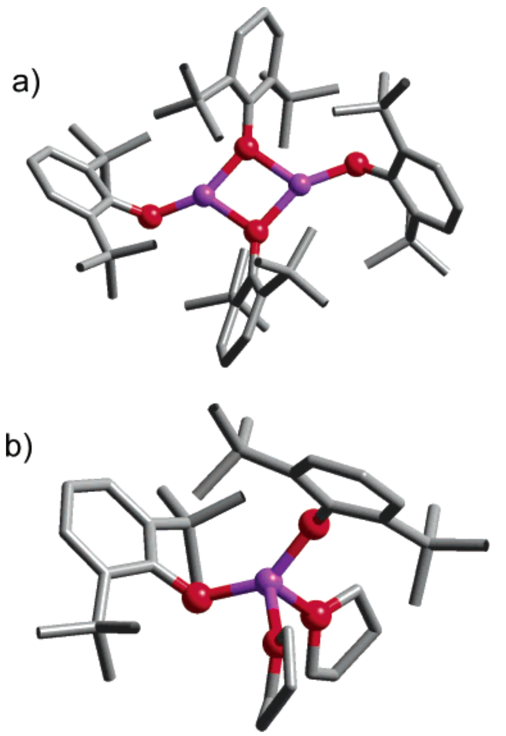


FIGURE 1. X-ray structures of (a) $[Zn(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2]_2$ and (b) $Zn(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2 \cdot THF_2$.

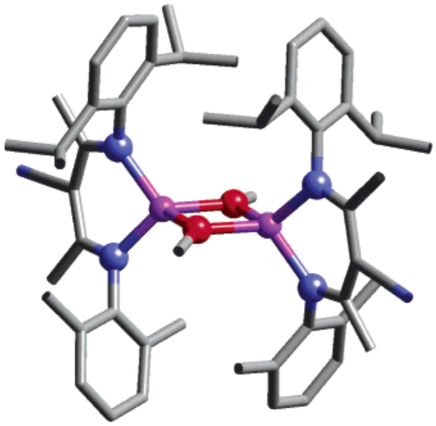


FIGURE 2. One of Coates's zinc β-diiminate complexes.

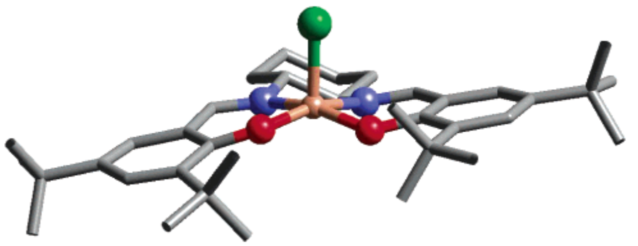
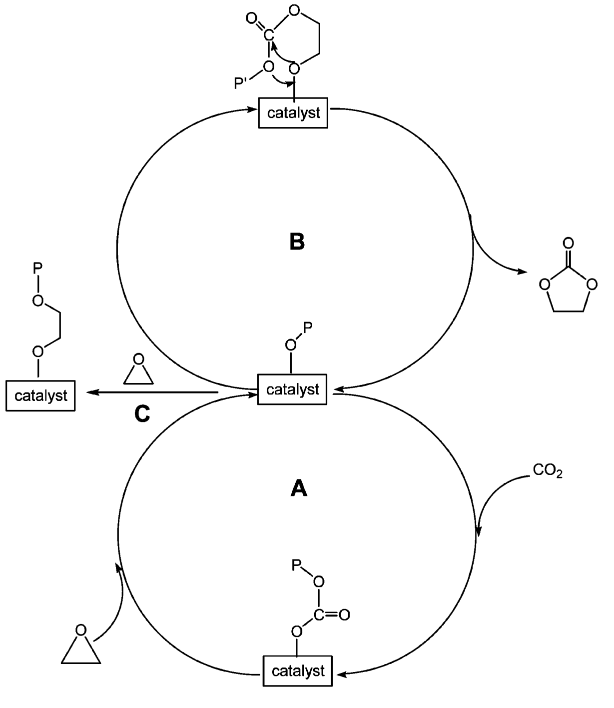


FIGURE 3. Crystallographic structure of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-(1*R*,2*R*)-(−)-1,2-cyclohexenediimine chromium chloride (**1**).

Scheme 2



P = growing polymer chain

Early studies that have inspired the work from my group that is the focus of this Account include those of Inoue,[8] Kruper,[9] and Holmes.[10] These researchers employed metal porphyrin derivatives, which are structurally similar to chlorophyll, as catalysts for the CO_2/epoxide copolymerization reaction. The rigidly planar porphyrin ligands provide metal complexes, which are structurally quite different from the previously mentioned zinc complexes, thereby offering alternative mechanistic pathways for catalysis. A common aspect in all of these investigations is that catalytic activity is significantly enhanced upon the addition of a cocatalyst, a factor which further complicates mechanistic interpretations of this chemistry. We have selected for our related studies chromium complexes containing *salen* ligands, which represent cheaper, more easily derivatized alternatives to porphyrin ligands. Although the term *salen* refers to the *N*,*N*′-bis(salicylidene)-1,2-ethylenediimine ligand, we will use it here to apply generally to bis(salicylaldimine) ligands. Specifically, our entry into catalyst systems of this type began with the chiral (salen)CrCl complex shown in Figure 3.[11] These efforts were greatly influenced by the groundbreaking work of Jacobsen and co-workers who employed this catalyst for the asymmetric ring opening (ARO) and kinetic resolution of epoxides.[12] Herein, we summarize our efforts to mechanistically understand the copolymerization of *alicyclic* and *aliphatic* epoxides with carbon dioxide in the presence of (salen)metalX catalysts to selectively produce polycarbonates.

Optimization of CO_2/Cyclohexene Oxide Copolymerization Utilizing (Salen)CrX Complexes as Catalysts

The three pathways open to reaction for the growing polymer chain are indicated in Scheme 2, and are (A) chain propagation to afford the completely alternating copolymer, (B) back biting with concomitant elimination of cyclic carbonate, and (C) consecutive epoxide enchainment leading to polyether linkages. To optimize the rate

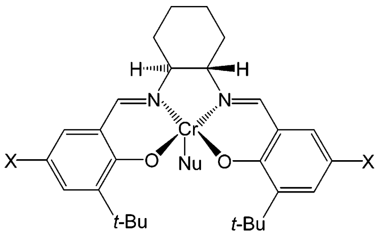
Table 1. Catalyst Variations and Their Effect on the Rate of Copolymerization of CO_2 and Cyclohexene Oxide[a]

entry	X	Nu	cocatalyst (equiv)	CO_2 pressure (Bar)	TOF[b]	% carbonate[c]	M_n	PDI
1	*t*-Bu	Cl	none	55	10.4	80		
2	*t*-Bu	Cl	*N*-MeIm (2.25)	55	35.5	99	8900	1.2
3	OCH_3	Cl	*N*-MeIm (2.25)	55	65.6	>99		
4	OCH_3	N_3	*N*-MeIm (2.25)	55	81.9	>99	23 000	1.6
5	OCH_3	N_3	PCy_3 (3)	55	346	>99		
6	OCH_3	N_3	$PPN^+N_3^-$ (1)	55	760	>99		
7	OCH_3	N_3	$PPN^+N_3^-$ (1)	35	1150	>99	50 000	1.1

[a] Each experiment was performed in 20 mL of cyclohexene oxide and with 50 mg of catalyst. [b] Moles of epoxide consumed per mole of Cr-hour. [c] Estimated by ^{1}H NMR.

of selective formation of a completely alternating copolymer of CO_2 and epoxide, it is necessary to design catalysts or define conditions to control or minimize pathways B and C, while maximizing pathway A. Catalytic studies of the copolymerization of cyclohexene oxide and CO_2 in the presence of chromium(III) complex (**1**) and derivatives thereof are summarized below with these objectives in mind.

Initially our investigations of this copolymerization process focused on the utilization of the commercially available complex **1**, as indicated in entry 1 of Table 1.



This catalyst produced *atactic* copolymer at a modest rate of 10.4 mol of epoxide consumed/mol of catalyst-hour (hereafter expressed h^{-1}) with a CO_2 incorporation of >80%.[11,13−16] The addition of a Lewis base cocatalyst, *N*-methylimidazole, increased the rate of copolymerization to 35.5 h^{-1} as well as reduced the polyether content of the copolymer to <1% (entry 2 of Table 1).[17,18] The ease of synthesizing salen derivatives, produced by a condensation reaction between diamines and salicyaldehydes, warranted an in-depth study into the effects of altering the salen structure on the activity of the catalyst in the cyclohexene oxide/CO_2 copolymerization reaction.[19] While many salen derivatives successfully catalyzed this process, the most active derivative, *N*,*N*′-bis(3-*tert*-butyl-5-methoxysalicylidene)-(1*R*,2*R*)-(−)-1,2-cyclohexenediimine (entry 3 of Table 1), contained electron-donating groups on both phenolate rings and effectively doubled the rate of copolymer production to 65.6 h^{-1}.

In situ infrared spectroscopic monitoring of the copolymerization reaction showed that these reactions were plagued by long initiation times (the time from the beginning of the reaction until the onset of the maximum rate), sometimes on the order of several hours. This was found to be partially caused by the lack of nucleophilicity of the chromium-bound chloride toward the initial epoxide ring-opening process. To overcome this, we moved toward a more nucleophilic initiator, azide. The azide adduct of complex **1** significantly reduced the initiation time to near zero, and the rate of copolymerization increased to 81.9 h^{-1} (entry 4 of Table 1). Furthermore, these studies showed that the copolymerization process may benefit from more electron-donating cocatalysts. For this purpose, phosphines were chosen because they are readily available Lewis bases with a wide variety of electronic properties. The more donating phosphine, namely, tricyclohexylphosphine, proved to be among the most active of this group of cocatalysts, increasing the rate of copolymerization to 346 h^{-1}. Notably, phosphine cocatalysts also eliminated cyclic carbonate formation, an unwanted byproduct of this reaction. Having observed that more electron-donating neutral Lewis bases enhance copolymer production, we decided to examine anionic cocatalysts. The most effective cocatalysts thus far discovered involved the noninteracting cation bis(triphenylphosphoranylidene)ammonium or PPN^+. While commercially available PPNCl was an extremely effective cocatalyst, $PPNN_3$ proved to be the most effective, producing turnover frequencies of 760 h^{-1} (entry 6 of Table 1).

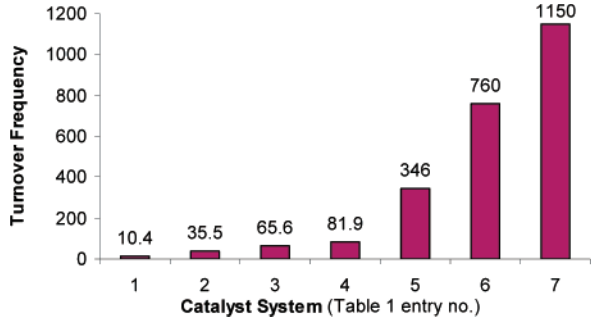


FIGURE 4. Graphical representation of the data presented in Table 1.

Modification of the reaction conditions showed that although the copolymer produced maintained a high carbonate content at CO_2 pressures as low as 1 bar, increasing the CO_2 pressure significantly enhanced the rate of copolymerization until a maximum turnover frequency of 1150 h^{-1} was observed at 35 bar. Increasing the pressure to 55 bar had the effect of decreasing the rate of copolymer production. This is most likely the result of a simple catalyst/substrate dilution effect on the reaction rate, where upon increasing the CO_2 pressure from 35 to 55 bar, there is a major volumetric expansion of the liquid phase where the catalyst and epoxide reside.[20] Figure 4 summarizes the gains made recently in the catalytic activity for the copolymerization of cyclohexene oxide and CO_2 involving (salen)CrX and various cocatalysts. As of this moment, this represents our most active and robust catalyst system, selectively producing the

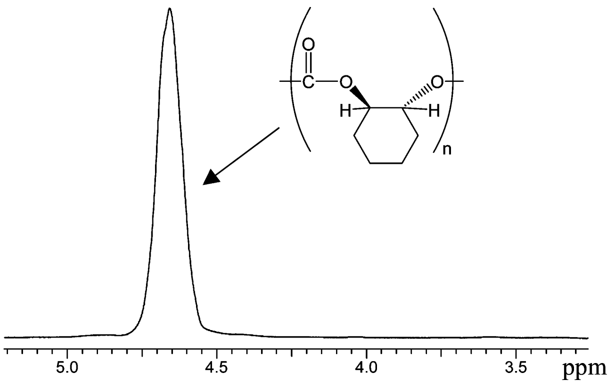


FIGURE 5. ^{1}H NMR spectrum in the methine region showing the lack of both cyclic carbonate (~4.0 ppm) and polyether linkages (~3.4–3.6 ppm) for the copolymer produced in entry 7 of Table 1.

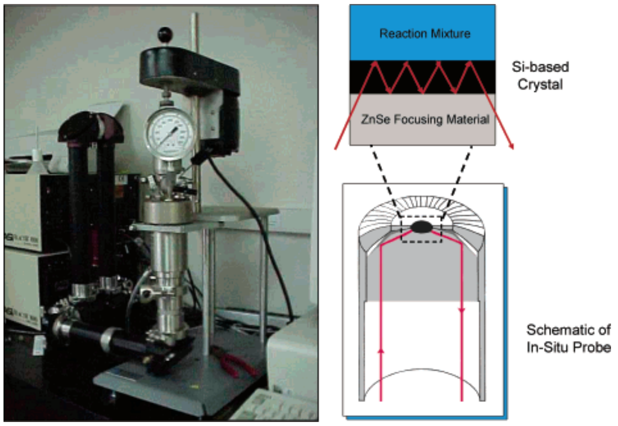


FIGURE 6. ASI ReactIR 1000 reaction analysis system with a stainless steel Parr autoclave modified with a permanently mounted ATR crystal (SiComp) at the bottom of the reactor (purchased from Mettler Toledo).

copolymer with no polyether linkages and no cyclic carbonate (Figure 5). Indeed, it is the most active system in the literature with the exception of a select group of zinc β-diiminate complexes.[7]

Mechanistic Aspects of the Cyclohexene Oxide/Carbon Dioxide Copolymerization Reactions

Concomitant with our optimization studies of this process, we have carried out kinetic investigations aimed at obtaining a better understanding of the mechanism of copolymer formation. Measurements of kinetics at high pressure were performed using a stainless steel Parr autoclave modified with a SiComp window to allow for attenuated total reflectance spectroscopy using an infrared radiation (ASI ReactIR 1000 in situ probe, as shown in Figure 6).[21] Typical data obtained for the production of poly(cyclohexylene)carbonate as monitored in the $\nu_{\text{carbonate}}$ region are illustrated in Figure 7, along with the time profile of the absorbance at ~1750 cm^{-1}. Our first study of the kinetics of the ring-opening process of cyclohexene oxide by (salen)CrCl showed that the initiation process was occurring via a pathway that was greater than first order in the metal complex.[11] This was assumed to be second order in the metal complex as previously described;[22] that is, it appeared that the mechanism of copolymerization was dictated by a second order in the [catalyst] initiation step, followed by a first-order propagation step. This latter observation is consistent with the lack of stereoregularity seen in the resulting copolymer produced from complex **1**.

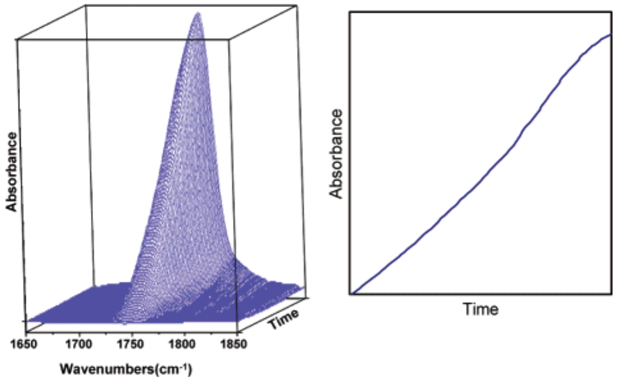
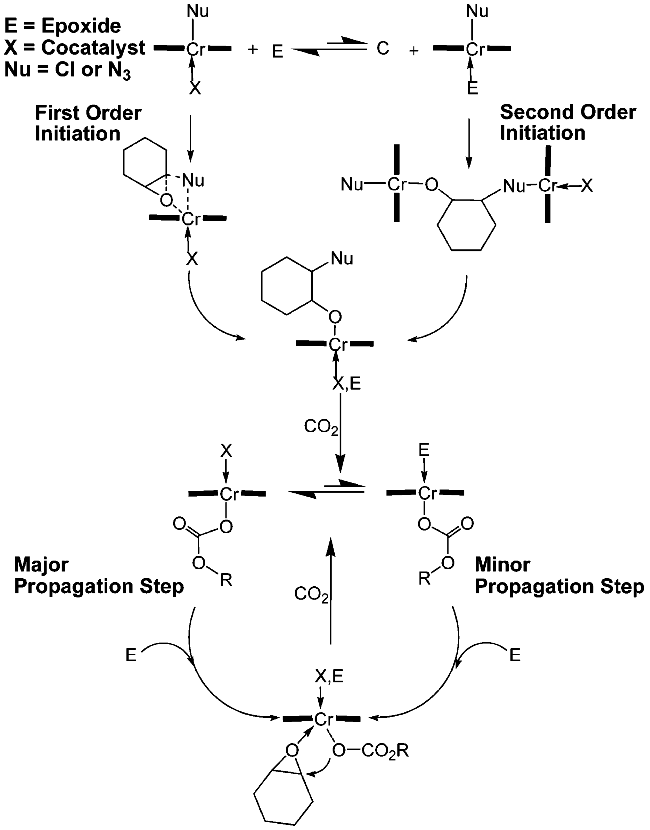


FIGURE 7. In situ infrared stack plot and peak profile of the carbonate signal produced at 1750 cm^{-1}.

Scheme 3



This initial description of the process turns out to be only partly true because this mechanism is actually being controlled by two equilibria, with different reaction pathways depending on the electronic environment around the metal center (Scheme 3). Relatively weak electron-donating Lewis base catalysts, such as *N*-methylimidazole, activate the catalyst for initiation to occur through a second order in the [catalyst] pathway. The progression down the second-order pathway makes initiation very sensitive to the amount of cocatalyst, with rate enhance-

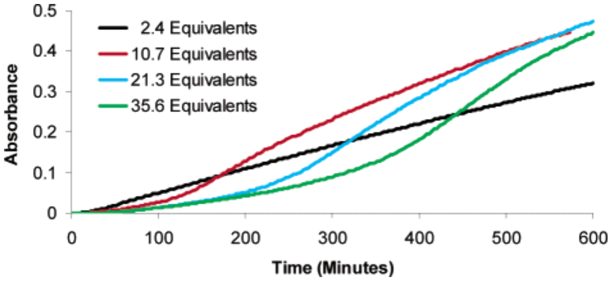


FIGURE 8. Effect of additional equivalents of *N*-methylimidazole on the rate of copolymerization.

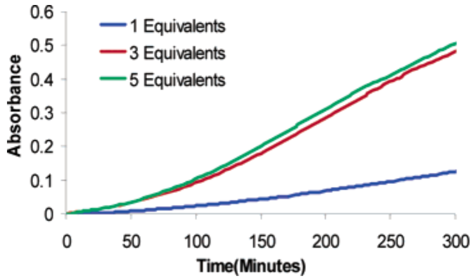


FIGURE 9. Effect of additional equivalents of tricyclohexylphosphine on the rate of copolymerization.

ment being observed at low concentrations, followed by excess cocatalyst resulting in the retardation of the initiation step (Figure 8). Contrary to this, if the cocatalyst is significantly more electron-donating, a first-order initiation step becomes possible. More donating Lewis bases such as triphenylphosphine represent the "middle of the road" case, where both pathways are possible, but with highly donating phosphines, such as tricyclohexylphosphine, the first-order pathway will dominate. This difference is best demonstrated in that the rate of copolymerization continually benefits from additional amounts of phosphine, with saturation kinetics observed above 7 equiv of cocatalyst (Figure 9). When the extreme donating case, anionic cocatalysts, is used, the initiation is decidedly first order in the [catalyst]. In this instance, a very high rate of polymerization is obtained and no change in the rate of polymerization is observed above 1 equiv of cocatalyst.

After initiation and the initial CO_2 insertion, a second equilibrium, dictating chain propagation, is observed. The difference in this step is that it is decidedly first order in the [catalyst] for *all* cocatalysts and the rate of propagation benefits from all of the catalyst being present as the cocatalyst-bound species. This allows for excess *N*-methylimidazole to increase the rate of propagation, even though it may slow the rate of initiation. The more donating phosphines and PPN salts significantly enhance the rate of copolymerization by enhancing both the initiation process and the rate of propagation.[23]

At this point, it is worth noting that the first-order epoxide ring-opening mechanism, either in the initiation step or in a subsequent chain propagation step, probably proceeds with a great deal of ionic character. This is particularly true for the initiation step involving $(salen)CrX_2^-$ systems, where one of the nucleophiles might easily be displaced by an epoxide. This is similar to the process proposed by Rieger for a related system involving DMAP as the cocatalyst.[24] Chisholm and Zhou have put forth a similar mechanism for the aluminum-porphyrin- and aluminum-salen-catalyzed reaction of propylene oxide and carbon dioxide;[25] that is, the role of the Lewis base cocatalyst is to labilize the metal−nucleophile bond of either the initiator or growing polymer chain toward heterolytic bond cleavage. Indeed, crystallographic studies clearly demonstrate that the Cr−Cl bond in (salen)CrCl is significantly lengthened upon axial ligation by a Lewis base.[19]

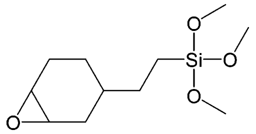


FIGURE 10. Skeletal drawing of the structure of TMSO (**2**).

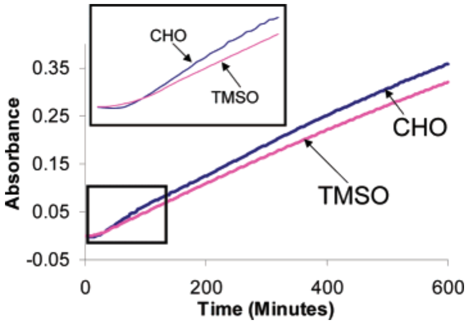


FIGURE 11. Comparison of polycarbonate formation using cyclohexene oxide and TMSO as the monomers. Inset: Initial 2 h of the reaction. Reaction conditions: 0.086 mmol of Cr(salen)Cl, 2.25 equiv of *N*-MeIm, 20 mL of epoxide, 50 bar of CO_2, and 80 °C.

Unfortunately, poly(cyclohexylene)carbonate, the copolymer most effectively produced from CO_2 and an epoxide by a variety of metal catalysts, has inferior physical properties to that of the widely used commercial polycarbonate derived from bisphenol-A.[26,27] Therefore, a current focus of our research is a search for other *alicyclic* epoxides that might lead to the production of more industrially viable polycarbonates. Thus far, we have had little success with substrates based on biorenewable resources, limonene oxide and α-pinene oxide, or those based on petroleum derivatives, *exo*-norbornene oxide or 2,3-epoxy-1,2,3,4-tetrahydronaphthalene.[28] On the other hand, we have had excellent success utilizing 2-(3,4-epoxy cyclohexyl)ethyltrimethoxysilane (TMSO, Figure 10) as a monomer for copolymerization with carbon dioxide.[29] This epoxide is beneficial in several ways. First of all, its reactivity for producing a completely alternating copolymer with CO_2 is essentially identical to that of cyclohexene oxide (Figure 11). Second, TMSO and its derived polycarbonate are completely miscible with carbon dioxide under the reaction conditions, thereby allowing for in situ infrared monitoring of the process in the absence of the multiphasic properties exhibited by cyclohexene oxide.[30] The enhanced CO_2 solubility of the polycarbonate produced from the monomer **2** has permitted the ready separation of the highly colored catalyst remains from the copolymer. Upon hydrolytic cross-linking of the trimethoxysilane tails of the copolymer, a material with a T_g higher than that of the bisphenol-A copolymer was obtained. However, this polymer was easily shattered upon forceful impact because of it being overly cross-linked. The application of monomer **2** along with cyclohexene oxide in terpolymerization processes is a continuing area of interest in our group.

Investigation of CO_2/Propylene Oxide Coupling Utilizing (salen)CrX Complexes as Catalysts. Polycarbonate versus Cyclic Carbonate Production

The wide-scale production of poly(propylene carbonate) from the *aliphatic* epoxide (propylene oxide) and carbon dioxide would be highly desirable because this copolymer currently has several industrial uses. These result from the polymer features of a low T_g (40 °C) and a sharp, clean decomposition above 200 °C. The two general application categories are destructive (evaporative pattern casting and ceramic binders) and nondestructive (adhesives and coatings). As mentioned in the Introduction, this process has been plagued by low catalyst activity and the concomitant production of propylene carbonate. Initially, we carried out comparative temperature-dependent kinetic studies of CO_2/propylene oxide versus CO_2/cyclohexene oxide coupling reactions utilizing complex **1** as the catalyst.[31] In both instances, the unimolecular pathway for cyclic carbonate formation (pathway B in Scheme 2) displayed a larger activation barrier than the bimolecular enchainment pathway A. However, the difference in the energy barrier for propylene carbonate and poly(propylene carbonate) was considerably smaller than the corresponding values for cyclohexylene carbonate and poly(cyclohexylene carbonate) production (33 kJ mol^{-1} versus 86 kJ mol^{-1}). The small energy difference in the two concurrent reactions for the propylene oxide process accounts for the large quantity of cyclic carbonate produced at higher temperatures where catalytic activity is significant.[32] Indeed, at 100 °C, the latter process is selective for the production of cyclic propylene carbonate in the presence of (salen)CrCl and 1 equiv of DMAP.[18] We have ascribed the greater selectivity for polycarbonate formation in the cyclohexene oxide instance to the increased strain in forming the five-membered carbonate ring imposed by the conformation of the cyclohexyl group. As can be seen in Figure 12, the adjacent cyclohexyl ring introduces a significant amount of twist in the five-membered carbonate ring, whereas propylene carbonate is unconstrained and perfectly planar.[33] This produces a lower energy of activation for the formation of propylene carbonate, making it much easier for polymer degradation to occur during the copolymerization reaction.

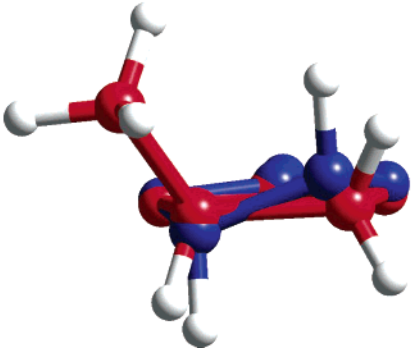
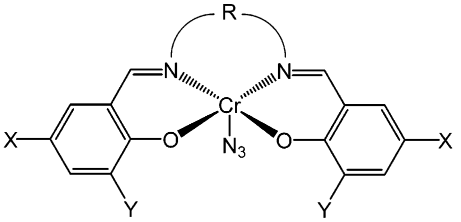


FIGURE 12. Overlay of cyclohexene carbonate (blue) and propylene carbonate (red) that depicts the differences in the ring strain between the two molecules. The cyclohexyl ring is omitted for clarity.

An experimental obstacle in obtaining detailed mechanistic information from in situ infrared monitoring of the CO_2-coupling reaction exists when utilizing propylene oxide as the comonomer;[21] that is, poly(propylene carbonate) has a very low solubility in the propylene oxide/CO_2 reaction mixture as well as in the presence of weakly interacting organic cosolvents. This leads to precipitation of the copolymer onto the crystal mounted at the bottom of the reactor, making the obtaining of useful in situ kinetic data difficult. Hence, our analysis of the propylene oxide/CO_2-coupling reaction was done with bulk reactor studies, where only the end result of the reaction was observed. Nevertheless, in our limited in situ studies done under controlled conditions, it was apparent that at low temperature (30 °C) only polycarbonate was produced, which upon raising the temperature (80 °C), degraded to cyclic carbonate.[31] The main thrust of our efforts involving propylene oxide/CO_2 coupling has been directed at optimizing copolymer production, without producing any cyclic carbonate. In related studies, zinc catalysts have demonstrated a stronger affinity for propylene carbonate over cyclic ethers (THF or propylene oxide).[4b] Therefore, these alternative products of the CO_2-coupling reaction could be expected to greatly inhibit catalytic activity.

As with our cyclohexene oxide study, many factors must be taken into consideration when optimizing the propylene oxide/CO_2 reaction for selective formation of polycarbonate. These variables include electronic and steric effects of the salen ligand, cocatalyst, initiator, and an additional concern, the temperature. On the basis of earlier results obtained by Rieger,[24] our investigation began with the *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)phenylenediimine chromium chloride complex as the catalyst.[23] However, this chromium derivative in the presence of phosphines or PPNCl cocatalysts afforded primarily propylene carbonate as the product. Upon changing the initiator to azide, selective formation of poly(propylene carbonate) resulted. Hence, we have focused our attention on Cr(salen)N_3 derivatives for an optimization of this copolymerization process (Figure 13).

As previously mentioned, this process will require reaction temperatures lower than the 75−80 °C conditions employed in our cyclohexene oxide studies. In this instance, 60 °C was found to be the ideal temperature for maximizing copolymer production while affording no cyclic carbonate byproduct. A recent report from Coates's laboratory using Co(salen)OAc as the catalyst found selective production of poly(propylene carbonate) from propylene oxide/CO_2 at 25 °C,[34] whereas other researchers using a similar cobalt(II) catalyst produced exclusive-



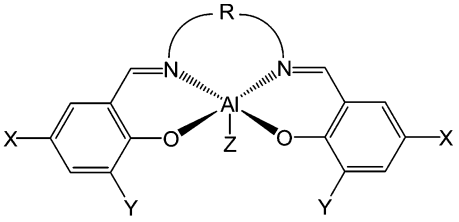
3: R = C_6H_4; X,Y= *t*-Bu
4: R = C_6H_{10}; X,Y = *t*-Bu
5: R = C_2H_4; X,Y = *t*-Bu
6: R = C_2H_4 or C_6H_4; X,Y = Cl
7: R = C_2H_4 or C_6H_4; X = H, Y = Ph

FIGURE 13. Skeletal representation of the Cr^{III}salen catalysts used in the copolymerization of propylene oxide and CO_2.

Table 2. Effect of Different Cocatalysts on the Copolymerization of PO and CO_2[a]

entry	cocatalyst (equiv)	TOF[b]	% carbonate[c]
1	PPh_3 (1)	55	86.5
2	PCy_3 (0.5)	71	89
3	PCy_3 (1)	149	94
4	PCy_3 (2)	76	96
5	$PPN^+N_3^-$ (1)	190	98
6	PPN^+Cl^- (1)	192	97

[a] Each experiment was performed in 20 mL of racemic propylene oxide and 50 mg of catalyst (**3**), at 35 bar of CO_2 and 60 °C, for 4 h. [b] Moles of epoxide consumed per mole of Cr-hour. [c] Estimated by ^1H NMR.



8: R = C_6H_{10}; X = Y = H
9: R = C_2H_4; X = NO_2, Y = *t*-Bu
10: R = C_2H_4; X = Y = Cl

FIGURE 14. Skeletal representation of (salen)AlZ complexes.

ly cyclic propylene carbonate at 100 °C.[35] Similarly, Co(salen)OAc in the presence of a cocatalyst, e.g., *n*Bu_4NBr, at 25 °C has demonstrated a high regio- and stereoselectivity for propylene oxide ring opening in the CO_2 copolymerization process.[36] The electronic effect of the salen ligand on the catalytic activity of (salen)CrX for polycarbonate production is different for the propylene oxide substrate as compared to cyclohexene oxide; that is, while the copolymerization of CO_2 and cyclohexene oxide is enhanced by electron-donating groups on the diimine backbone (complexes **4** and **5**), in the case of propylene oxide, a large quantity of cyclic carbonate is produced. On the other hand, the complex containing the electron-withdrawing phenylene diimine backbone (complex **3**) afforded exclusively the copolymer under the same reaction conditions. As was observed for the cyclohexene oxide/CO_2 copolymerization reaction, electron-withdrawing substituents on the phenolate moieties (complexes **6** and **7**) led to decreased activity for formation of either CO_2/propylene-oxide-coupled product.

Focusing on the most active catalyst (**3**) for selectively producing poly(propylene carbonate), we have investigated the dependence of the process on the nature of the cocatalyst. These data are provided in Table 2. The poly(propylene carbonate) produced is regioirregular with head−head, head−tail, and tail−tail junctions.[37,38] Of importance, Coates[34] and Wang[36] have reported independently that polymerization of (*S*)-propylene oxide with enantiomerically pure (1*R*,2*R*′)Co(salen)(OAc) provides the isotatic(*S*) polymer with a head−tail content of ≥93%. As previously noted for the cyclohexene oxide/CO_2 study, the turnover frequencies (TOFs) for polycarbonate production increase as the donating ability of the cocatalyst increases, with little cyclic carbonate produced in any instance. The most striking difference in the propylene oxide/CO_2 copolymerization process is that addition of the cocatalyst beyond 1 equiv slows polymer formation (entries 3 and 4 of Table 2); however, no attendant increase in cyclic carbonate formation was observed. A similar behavior was seen by Rieger for a (salen)CrCl/DMAP catalyzed reaction.[24] Hence, there are some subtle mechanistic aspects of the propylene oxide/CO_2 reaction that we do not fully understand at this time. Hopefully, we will soon be able to solve the technical difficulty of in situ monitoring of this process, thereby providing a more comprehensive mechanistic portrayal of this coupling reaction.

Attempts to Utilize Main-Group Salen Complexes As Catalysts for the Copolymerization of Cyclohexene Oxide and Carbon Dioxide

As a final installment in this Account, we will briefly describe our studies aimed at an assessment of main-group metal salen complexes as catalysts for the copolymerization of CO_2/epoxides. This is of particular relevance to this Account because the closely related aluminum porphyrinate complexes have an established record of reactivity for this process.[8,25] As in the chromium case, we have initially focused our efforts on optimizing the copolymerization process employing cyclohexene oxide as the substrate. It was immediately obvious that aluminum analogues of the more active chromium derivatives, i.e., those complexes containing electron-donating salen ligands along with highly donating cocatalysts, were very ineffective at producing the copolymer. Consequently, we conducted copolymerization reactions with complex **8**, where Z = Et and the anionic cocatalyst, PPNCl, resulting in a modest TOF of 8.7 h^{-1} (entry 1 of Table 3). This led us to examine the aluminum complexes containing salen ligands with less electron-donating substituents on the diimine backbone and more electron-withdrawing substituents on the phenolate groups, complexes **9** and **10**.

Two main observations are evident upon examining the results summarized in Table 3. First, the Et-Al(salen) derivatives are less reactive than their chloride analogues. Second, the most active catalyst systems were the aluminum chloride complexes along with the epoxide soluble Bu_4NN_3 cocatalyst, with complex **9** being the most active

Table 3. Copolymerization Results with (Salen)AlZ[a]

entry	salen	Z	cocatalyst	TOF[b]	% carbonate[c]
1	**8**	C_2H_5	PPNCl	8.7	94
2		C_2H_5	$PPNN_3$	17.6	98
3		Cl	$(^nBu)_4NN_3$	23.3	99
4	**9**	C_2H_5	PPNCl	11.7	97
5		C_2H_5	$PPNN_3$	14.3	98
6		C_2H_5	$(^nBu)_4NN_3$	12.3	95
7		Cl	$(^nBu)_4NN_3$	35.3	>99
8	**10**	Cl	$(^nBu)_4NN_3$	18.0	97
9		Cl	*N*-MeIm	16.9	93

[a] Each experiment was performed in 20 mL of cyclohexene oxide with 50 mg of catalyst and 1 equiv of cocatalyst [except *N*-methylimidazole (2.25 equiv)], under 50 bar of CO_2 and at 80 °C. [b] Moles of cyclohexene oxide consumed per mole of Al-h. [c] Estimated by ^1H NMR.

(TOF = 35.3 h^{-1}). Furthermore, all of these complexes afforded essentially a completely alternating copolymer with little to no polyether linkages. The order of activity was **9** > **8** > **10**, where complex **9** has more electron-withdrawing substituents on the phenolate moieties than **8** but less electron-withdrawing substituents than **10**. A similar trend in catalytic activity was observed for the analogous gallium(III) salen complexes; however, these were much less effective as catalysts when compared with their aluminum counterparts.[39]

Concluding Remarks

The production of polycarbonates from the copolymerization of CO_2 and epoxides represents a potentially less expensive and significantly "greener" route to these thermoplastics than the current commercial process, which involves the polycondensation of diols and phosgene or carbonates. As we noted earlier, our goal in this area is to find selective, facile metal-catalyzed pathways to these copolymers. Thus far, our efforts on optimizing catalyst activities of (salen)CrX derivatives for CO_2 copolymerization with select *alicyclic* epoxides have met with significant gains over the last 2 years, with the increase of TOF from 10 to 1150 h^{-1}. This has been accomplished via the judicious choice of the salen ligand, cocatalyst, initiator, and reaction conditions. Nevertheless, there is still more room for improvement. This is particularly true for the copolymerization of *aliphatic* epoxides and CO_2, as well as several less reactive *alicyclic* epoxides derived from sustainable resources, such as α-pinene oxide or limonene oxide.[40-42] As described above, *aliphatic* epoxides have a propensity for cyclic carbonate production at high temperatures (80−100 °C). It is readily apparent from these and other studies that in general the coupling reaction of epoxides and CO_2 is extremely sensitive to the electronic and steric environment about the metal center. At the same time, these requirements at the metal center differ as the epoxides is varied.

With regard to future directions, we hope to broaden the scope of epoxides capable of copolymerizing with carbon dioxide, possibly as a result of finding catalysts with increased activity. These investigations are greatly aided and guided by the ability to perform measurements of the kinetics of these reactions by in situ infrared spectroscopy. Ultimately, this should lead to an enhanced practical utility of this reaction, thereby providing for the production of copolymers with physical properties competitive with those of the bisphenol-A-derived polycarbonates.

We are most grateful to the many very talented graduate students whose names are given in the references. Without their enthusiasm, ideas, and devoted efforts, our advances outlined in this Account would not have been possible. Special acknowledgment is given to those closely associated with the specific focus of this Account, Drs. Jason C. Yarbrough, Cindy C. Fang, Jody L. Rodgers, and Cesar Ortiz. We also thank the National Science Foundation and the Robert A. Welch Foundation for their continued financial support of this project.

References

(1) Inoue, S.; Koinuma, H.; Tsuruta, T. Copolymerization of Carbon Dioxide and Epoxide. *J. Polym. Sci., Part B: Polym. Phys.* **1969**, *7*, 287−292.

(2) Kuran, W.; Listoś, T. Degradation of Poly(propylene carbonate) by Coordination Catalysts Containing Phenolatozinc and Alcholatozinc Species. *Macromol. Chem. Phys.* **1994**, *195*, 1011−1015.

(3) Darensbourg, D. J.; Holtcamp, M. W. Catalysts for the Reactions of Epoxides and Carbon Dioxide. *Coord. Chem. Rev.* **1996**, *153*, 155−174. (b) For an excellent comprehensive review of this area in general, see: Coates, G. W.; Moore, D. R. Discrete Metal-Based Catalysts for the Copolymerization of CO_2 and Epoxides: Discovery, Reactivity, Optimization, and Mechanism. *Angew. Chem., Int. Ed.* in press.

(4) Darensbourg, D. J.; Holtcamp, M. W. Catalytic Activity of Zinc(II) Phenoxides Which Possess Readily Accessible Coordination Sites. Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide. *Macromolecules* **1995**, *28*, 7577−7579. (b) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. Catalytic Activity of a Series of Zn(II) Phenoxides for the Copolymerization of Epoxides and Carbon Dioxide. *J. Am. Chem. Soc.* **1999**, *121*, 107−116.

(5) Super, M.; Berluche, E.; Costello, C.; Beckman, E. Copolymerization of 1,2-Epoxycyclohexane and Carbon Dioxide Using Carbon Dioxide as Both Reactant and Solvent. *Macromolecules* **1997**, *30*, 368−372.

(6) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. Catalytic Reactions Involving C1 Feedstocks: New High-Activity Zn(II)-Based Catalysts for the Alternating Copolymerization of Carbon Dioxide and Epoxides. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, B. W.; Coates, G. W. Single-Site β-Diiminate Zinc Catalysts for the Alternating Copolymerization of CO_2 and Epoxides: Catalyst Synthesis and Unprecedented Polymerization Activity. *J. Am. Chem. Soc.* **2001**, *123*, 8738−8749.

(7) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. Mechanism of the Alternating Copolymerization of Epoxides and CO_2 Using β-Diiminate Zinc Catalysts: Evidence for a Bimetallic Epoxide Enchainment. *J. Am. Chem. Soc.* **2003**, *125*, 11911−11924.

(8) Aida, T.; Inoue, S. Activation of Carbon Dioxide with Aluminum Porphyrin and Reation with Epoxide. Studies on (Tetraphenylporphinato)aluminum Alkoxide Having a Long Oxyalkylene Chain as the Alkoxide Group. *J. Am. Chem. Soc.* **1983**, *105*, 1304−1309. (b) Aida, T.; Inoue, S. Catalytic Reaction on Both Sides of a Metalloporphyrin Plane. Alternating Copolymerization of Phthalic Anhydride and Epoxypropane with an Aluminum Porphyrin-Quaternary Salt System. *J. Am. Chem. Soc.* **1985**, *107*, 1358−1364. (c) Aida, T.; Ishikawa, M.; Inoue, S. Alternating Copolymerization of Carbon Dioxide and Epoxide Catalyzed by the Aluminum Porphyrin-Quaternary Organic Salt or -Triphenylphosphine System. Synthesis of Polycarbonate with Well-Controlled Molecular Weight. *Macromolecules* **1986**, *19*, 8−13.

(9) Kruper, W. J.; Dellar, D. V. Catalytic Formation of Cyclic Carbonates from Epoxides and CO_2 with Chromium Metalloporphyrinates. *J. Org. Chem.* **1995**, *60*, 725−727.

(10) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. Copolymerization of CO_2 and 1,2-Cyclohexene Oxide Using a CO_2-Soluble Chromium Porphyrin Catalyst. *Macromolecules* **2000**, *33*, 303−308.

(11) Darensbourg, D. J.; Yarbrough, J. C. Mechanistic Aspects of the Copolymerization Reaction of Carbon Dioxide and Epoxides, Using a Chiral Salen Chromium Chloride Catalyst. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342.

(12) Jacobsen, E. N. Asymmetric Catalysis of Epoxide Ring Opening Reactions. *Acc. Chem. Res.* **2000**, *33*, 421−431. (b) A reviewer of this Account pointed out an observation reported in the patent literature, of which we were unaware; i.e., the copolymerization of racemic 1,2-epoxyhexane with CO^2 catalyzed by the cobalt acetate analogue of complex **1** affords polycarbonate and the *R* enantiomer of 1,2-epoxyhexane in 90% ee. Jacobsen, E. N.; Tokunaga, M.; Larrow, F. J. Stereoselective Ring Opening Reactions, U.S. Patent 6,262,278, 2001, p 69.

(13) The tacticity of poly(cyclohexylene)carbonate was determined from its ^{13}C NMR spectrum in the carbonate region based on the elegant work of Nozaki and co-workers who synthesized *syndio*- and *iso*-tetrad model carbonates and provided spectral assignments for the carbonate resonances.[14] Both Nozaki[15] and Coates[16] have reported enanioselective copolymerization of CO_2 and cyclohexene oxide to produce a highly *isotactic* copolymer with >70% ee, employing chiral zinc complexes as the catalysts.

(14) Nakano, K.; Nozaki, K.; Hiyama, T. Spectral Assignment of Poly-[cyclohexene oxide-*alt*-carbon dioxide]. *Macromolecules* **2001**, *34*, 6325−6332.

(15) Nozaki, K.; Nakano, K.; Hiyama, T. Optically Active Polycarbonates: Asymmetric Alternating Copolymerization of Cyclohexene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **1999**, *121*, 11008−11009.

(16) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. Enantiomerically Enriched Organic Reagents via Polymer Synthesis: Enantioselective Copolymerization of Cycloalkene Oxides and CO_2 Using Homogeneous, Zinc-Based Catalysts. *Chem. Commun.* **2000**, 2007−2008.

(17) While our work was in progress, Paddock and Nguyen reported that several (salen)CrCl derivatives in the presence of DMAP [(dimethylamino)pyridine] were effective catalysts for the cycloaddition of CO_2 with various epoxides. A footnote in that publication also mentioned that CO_2 and cyclohexene oxide were copolymerized under these conditions.[18]

(18) Paddock, R. L.; Nguyen, S. T. Chemical CO_2 Fixation: Cr(III) Salen Complexes as Highly Efficient Catalysts for the Coupling of CO_2 and Epoxides. *J. Am. Chem. Soc.* **2001**, *123*, 11498−11499.

(19) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. B.; Reibenspies, J. H. Cyclohexene Oxide/CO_2 Copolymerization Catalyzed by Chromium(III) Salens and *N*-Methylimidazole: Effects of Varying Salen Ligand Substituents and Relative Cocatalyst Loading. *Inorg. Chem.* **2004**, *43*, 6024−6034.

(20) Bertocco, A. Precipitation and Cyrstallization Techniques in *Chemical Synthesis Using Supercritical Fluids*; Jessop, P. G.; Leitner, W., Eds.; Wiley-VCH: Weinheim, 1999; pp 108−126.

(21) Darensbourg, D. J.; Rodgers, J. L.; Mackiewicz, R. M.; Phelps, A. L. Probing the Mechanistic Aspects of the Chromium Salen Catalyzed Carbon Dioxide/Epoxide Copolymerization Process Using In situ ATR/FTIR. *Catal. Today*, **2004**, in press.

(22) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. On the Mechanism of Asymmetric Nucleophilic Ring-Opening of Epoxides Catalyzed by (Salen)Cr^{III} Complexes. *J. Am. Chem. Soc.* **1996**, *118*, 10924−10925.

(23) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. (Salen)$Cr^{III}X$ Catalysts for the Copolymerization of Carbon Dioxide and Epoxides. Role of the Initiator and Cocatalyst. *Inorg. Chem.* **2004**, *43*, 1831−1833.

(24) Eberhardt, R.; Allendinger, M.; Rieger, B. DMAP/Cr(III) Catalyst Ratio: The Decisive Factor for Poly(propylene carbonate) Formation in the Coupling of CO_2 and Propylene Oxide. *Macromol. Rapid Commun.* **2003**, *24*, 194−196.

(25) Chisholm, M. H.; Zhou, Z. Concerning the Mechanism of the Ring Opening of Propylene Oxide in the Copolymerization of Propylene Oxide and Carbon Dioxide to Give Poly(propylene carbonate), *J. Am. Chem. Soc.* **2004**, *126*, 11030−11039.

(26) Koning, C.; Wildeson, J. R.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. Synthesis and Physical Characterization of Poly(cyclohexane carbonate), Synthesized from CO_2 and Cyclohexene Oxide. *Polymer* **2001**, *42*, 3995−4004.

(27) Thorat, S. D.; Phillips, P. J.; Semenov, V.; Gakh, A. Physical Properties of Aliphatic Polycarbonates Made from CO_2 and Epoxides. *J. Applied Polym. Sci.* **2003**, *89*, 1163−1176.

(28) Darensbourg, D. J.; Fang, C. C.; Rodgers, J. L. Catalytic Coupling of Carbon Dioxide and 2,3-Epoxy-1,2,3,4-tetrahydronapthalene in the Presence of a (Salen)$Cr^{III}Cl$ Derivative. *Organometallics* **2004**, *23*, 924−927.

(29) Darensbourg, D. J.; Rodgers, J. L.; Fang, C. C. The Copolymerization of Carbon Dioxide and [2-(3,4-Epoxycyclohexyl)ethyl]-trimethoxysilane Catalyzed by (Salen)CrCl. Formation of a CO_2 Soluble Polycarbonate. *Inorg. Chem.* **2003**, *42*, 4498−4500.

(30) Super, M.; Beckman, E. J. Copolymerization of CO_2 and Cyclohexene Oxide using CO_2 as Sole Solvent: Effects of Pressure and Concentration. *Macromol. Symp.* **1997**, *107*, 89.

(31) Darensbourg, D. J.; Yarbrough, J. C..; Ortiz, C.; Fang, C. C. Comparative Kinetic Studies of the Copolymerization of Cyclohexene Oxide and Propylene Oxide with Carbon Dioxide in the Presence of Chromium Salen Derivatives. In Situ FTIR Measurements of Copolymer vs Cyclic Carbonate Production. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591.

(32) Notably, both processes were performed at high CO_2 pressure (50 bar). As expected, at low CO_2 pressures, cyclic carbonate versus polycarbonate production is enhanced.

(33) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. Carbon Dioxide/Epoxide Coupling Reactions Utilizing Lewis Base Adducts of Zinc Halides as Catalysts. Cyclic Carbonate versus Polycarbonate Production. *Inorg. Chem.* **2003**, *42*, 581−589.

(34) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. Cobalt-Based Complexes for the Copolymerization of Propylene Oxide and CO_2: Active and Selective Catalysts for Polycarbonate Synthesis. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487.

(35) Shen, Y.-M.; Duan, W.-L.; Shi, M. Chemical Fixation of Carbon Dioxide Catalyzed by Binaphthyldiamino Zn, Cu, and Co Salen-Type Complexes. *J. Org. Chem.* **2003**, *68*, 1559−1562.

(36) Lu, X.-B.; Wang, Y. Highly Active, Binary Catalyst Systems for the Alternating Copolymerization of CO_2 and Epoxides under Mild Conditions. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574−3577.

(37) Chisholm and co-workers have provided detailed ^{13}C NMR assignments of the carbonate resonances corresponding to the different configurations of the poly(propylene carbonate) chain.[38]

(38) Chisholm, M. H.; DaVarro-Llobet, D.; Zhou, Z. Poly(propylene carbonate). 1. More about Poly(propylene carbonate) Formed from the Copolymerization of Propylene Oxide and Carbon Dioxide Employing a Zinc Glutarate Catalyst. *Macromolecules* **2002**, *35*, 6494−6504. (b) Byrnes, M. J.; Chisholm, M. H.; Hadad, C. M.; Zhou, Z. Regioregular and Regioirregular Oligoether Carbonates: A $^{13}C\{^1H\}$ NMR Investigation. *Macromolecules* **2004**, *37*, 4139−4145.

(39) Darensbourg, D. J.; Billodeaux, D. B. Five-Coordinate Schiff Base Complexes of Gallium. Potential Catalysts for the Copolymerization of Carbon Dioxide and Epoxides. *C. R. Chimie* **2004**, *7*, 755−761.

(40) A successful production of the copolymer from limonene oxide and CO_2 has recently been reported by Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004**, *126*, 11404−11405.

(41) We have also synthesized a copolymer with >99% carbonate linkages in low yield from limonene oxide and CO_2 utilizing zinc bis(phenoxide) catalysts.[42]

(42) Lewis, S. J. Ph.D. Dissertation, Texas A&M University, May 2003.

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