


# Perfectly Alternating Copolymerization of CO<sub>2</sub> and Epichlorohydrin Using Cobalt(III)-Based Catalyst Systems

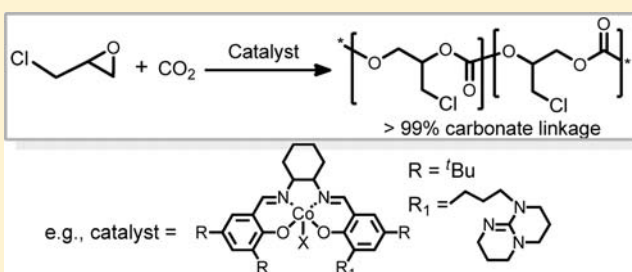
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 Supporting Information

**ABSTRACT:** Selective transformations of carbon dioxide and epoxides into biodegradable polycarbonates by the alternating copolymerization of the two monomers represent some of the most well-studied and innovative technologies for potential large-scale utilization of carbon dioxide in chemical synthesis. For the most part, previous studies of these processes have focused on the use of aliphatic terminal epoxides or cyclohexene oxide derivatives, with only rare reports concerning the synthesis of CO<sub>2</sub> copolymers from epoxides containing electron-withdrawing groups such as styrene oxide. Herein we report the production of the CO<sub>2</sub> copolymer with more than 99% carbonate linkages from the coupling of CO<sub>2</sub> with epichlorohydrin, employing binary and bifunctional (salen)cobalt(III)-based catalyst systems. Comparative kinetic studies were performed via in situ infrared measurements as a function of temperature to assess the activation barriers for the production of cyclic carbonate versus copolymer involving two electronically different epoxides: epichlorohydrin and propylene oxide. The relative small activation energy difference between copolymer versus cyclic carbonate formation for the epichlorohydrin/CO<sub>2</sub> process (45.4 kJ/mol) accounts in part for the selective synthesis of copolymer to be more difficult in comparison with the propylene oxide/CO<sub>2</sub> case (53.5 kJ/mol). Direct observation of the propagating polymer-chain species from the binary (salen)CoX/MTBD (X = 2,4-dinitrophenoxide and MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) catalyst system by means of electrospray ionization mass spectrometry confirmed the perfectly alternating nature of the copolymerization process. This observation in combination with control experiments suggests possible intermediates involving MTBD in the CO<sub>2</sub>/epichlorohydrin copolymerization process.



## INTRODUCTION

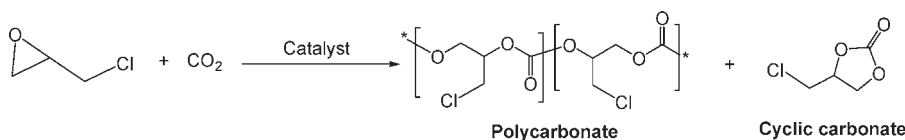
It has been over 40 years since the seminal discovery of polycarbonate synthesis from the coupling of CO<sub>2</sub> and epoxides was reported initially in a patent by Stevens and followed in the open literature by Inoue and co-workers.<sup>1</sup> In contrast to the alternative route of condensation polymerization involving the use of toxic phosgene or its derivatives, this process represents an environmentally benign approach for the synthesis of polycarbonates. Polycarbonates have potential applications as ceramic binders, adhesives, coatings, and packaging materials, as well as in the synthesis of engineering thermoplastics and resins.<sup>2</sup> A wide variety of catalytic systems have been developed for this transformation.<sup>3</sup> These include heterogeneous metal catalysts based on diethylzinc combined with diprotic sources,<sup>4</sup> dicarboxylic acid derivatives of zinc,<sup>5</sup> double metal cyanide complexes,<sup>6</sup> and rare-earth-metal coordination ternary catalysts.<sup>7</sup> In addition, numerous homogeneous metal derivatives have been employed as effective catalysts for this coupling process which consists of discrete zinc-based<sup>8</sup> as well as aluminum,<sup>9</sup> manganese,<sup>10</sup>

chromium,<sup>11–13</sup> and cobalt<sup>14–17</sup> complexes. Prominent among these are single-site homogeneous metal catalysts with well-defined structures which are active under mild reaction conditions and in some instances provide regio- and/or stereoselective copolymer synthesis. Importantly, being distinct from heterogeneous catalysts which lack active-site control, these well-defined structures of single-site homogeneous catalysts are beneficial for mechanistic investigations.<sup>12,18</sup>

Although these reported studies are very significant and impressive, they are generally associated with polycarbonate formation from aliphatic terminal epoxides or cyclohexene oxide derivatives. Very limited literature exists concerning the synthesis of CO<sub>2</sub> copolymers from epoxides with electron-withdrawing groups such as styrene oxide and epichlorohydrin. Furthermore, these reported processes generally suffered from poor copolymer selectivity and the concomitant production of ether linkage units

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Table 1. Coupling Reaction of Epichlorohydrin with CO<sub>2</sub> by salenCoX Complexes<sup>a</sup>

entry	cat.	cocat.	temp (°C)	time (h)	TOF <sup>b</sup> (h <sup>-1</sup> )	selectivity <sup>c</sup> (polymer %)	carbonate linkages <sup>c</sup> (%)	M <sub>n</sub> <sup>d</sup>	PDI <sup>d</sup> (M <sub>w</sub> /M <sub>n</sub> )	T <sub>g</sub> (°C)
1	1	PPNY	25	1	300	10				
2	1	PPNY	0	12	31	61	>99	4.7	1.22	
3	1	MTBD	25	1	246	10				
4	1	MTBD	0	24	15	65	>99	4.4	1.21	
5	2		25	1	640	72	>99	8.6	1.10	27
6	2		0	24	36	>99	>99	22.3	1.12	31
7	3		25	1	580	75	>99	7.9	1.09	27
8	3		0	24	37	>99	>99	25.9	1.07	31

<sup>a</sup>The coupling reaction was performed in neat epichlorohydrin in a 25 mL autoclave at 2.0 MPa of CO<sub>2</sub> pressure. Catalyst/cocatalyst/epichlorohydrin = 1/1/1000 (molar ratio) for entries 1–4; catalyst/epichlorohydrin = 1/2000 (molar ratio) for entries 5–8. <sup>b</sup>Turnover frequency of epichlorohydrin to products (polycarbonate and cyclic carbonate). <sup>c</sup>Based on <sup>1</sup>H NMR spectroscopy. <sup>d</sup>Determined by gel permeation chromatography in THF, calibrated with polystyrene.

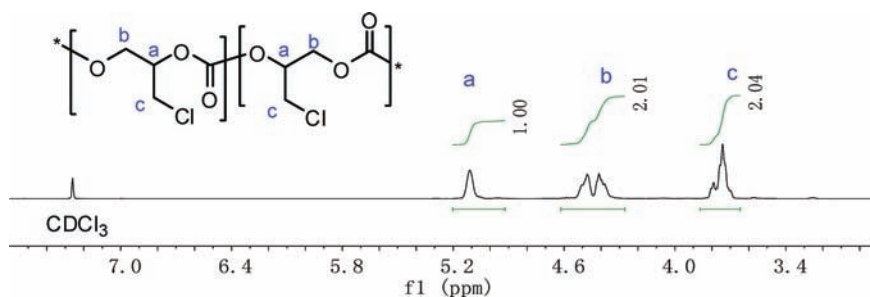
in the resulting polymers.<sup>1,19–22</sup> As an important functionalized epoxide, epichlorohydrin has had widespread use in the chemical industry such as epoxy resins, adhesive, and starting material for organic synthesis.<sup>23</sup> It has been used in the random copolymerization with maleic anhydride in the presence of coordination catalysts such as rare-earth-metal complexes, producing copolymers with low molecular weights.<sup>24</sup> Although epichlorohydrin is a highly reactive epoxide in the coupling reactions with CO<sub>2</sub>, the corresponding cyclic carbonate rather than the polycarbonate usually is the sole product. For example, well-defined zinc  $\beta$ -diiminato complexes, which present excellent activity and polymer selectivity in catalyzing cyclohexene oxide or propylene oxide/CO<sub>2</sub> copolymerization, when applied to the coupling of CO<sub>2</sub> and epichlorohydrin, only produce cyclic carbonate at various temperatures and pressures.<sup>20</sup> A similar situation was also observed for catalyst systems based on the much-studied Cr(III) complexes.<sup>21</sup> As early as 1969, Inoue and co-workers attempted to synthesize copolymer from epichlorohydrin and CO<sub>2</sub> using ZnEt<sub>2</sub>/H<sub>2</sub>O (1:1) as the catalyst under 5–6 MPa of CO<sub>2</sub> pressure. After a prolonged reaction time of 48 h, less than 1% of the epoxide was transformed into copolymer with low carbonate content.<sup>1</sup> A heterogeneous catalyst system based on rare-earth phosphonates and triisobutylaluminum was reported by Shen and co-workers for the copolymerization of epichlorohydrin and CO<sub>2</sub>, but the strong Lewis acidity of the catalyst systems resulted in the formation of polymers having more than 70% ether linkages.<sup>22</sup> Therefore, the development of a selective synthesis of a completely alternating copolymer from CO<sub>2</sub> and epichlorohydrin would be highly desirable.

In the present report, we communicate studies aimed at a selective synthesis of a perfectly alternating copolymer between CO<sub>2</sub> and epichlorohydrin utilizing cobalt-based catalyst systems. The investigation provided herein also involves a temperature-dependent kinetic study of the relative propensity of these catalyst systems for producing copolymer versus cyclic carbonate as a function of the nature of the epoxide (epichlorohydrin and propylene oxide). Furthermore, direct observation of the propagating polymer-chain species, along with single-crystal X-ray

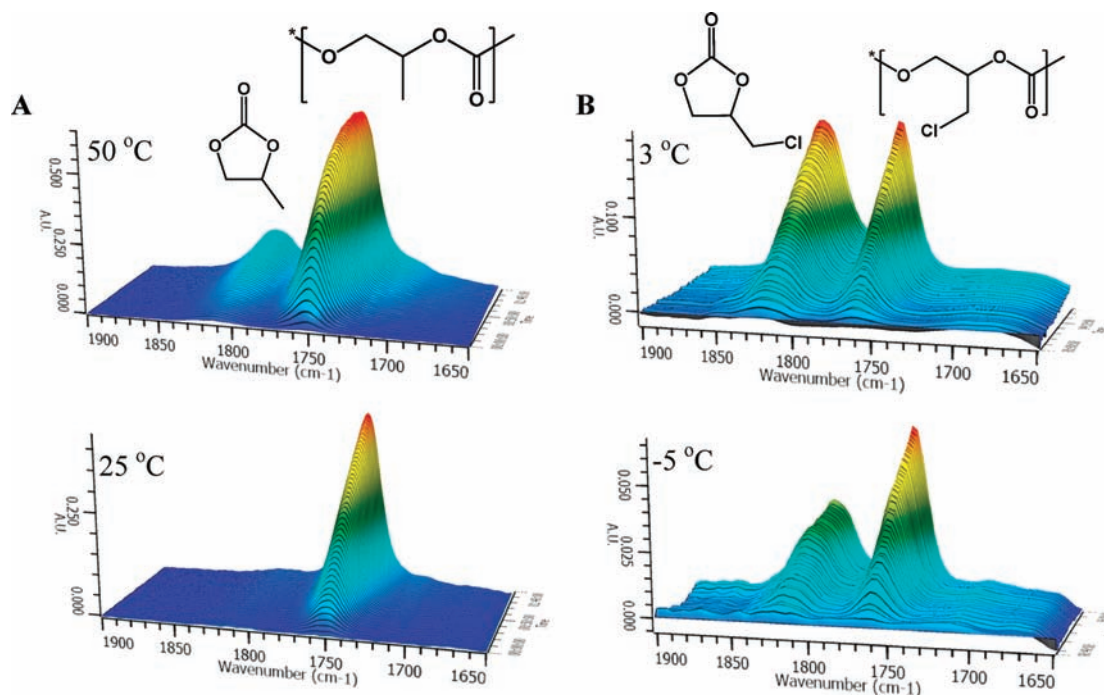
diffraction studies of key intermediates, provide insight into understanding the mechanistic aspects of the CO<sub>2</sub>/epichlorohydrin copolymerization process.

## RESULTS AND DISCUSSION

Generally, for the metal-catalyzed coupling of CO<sub>2</sub> and epoxides bearing an electron-withdrawing group, it is very difficult to avoid significant formation of thermally stable cyclic carbonates by intramolecular cyclic elimination via two concurrent back-biting mechanisms: one aided by the central metal ion and one taking place on the free anionic polymer chain.<sup>25,26</sup> Because of the electron-withdrawing nature of the group such as the chloromethyl group of epichlorohydrin, it is possible that cyclic carbonate is predominantly produced via back-biting of the propagating polycarbonate anion to the chloromethyl carbon of the adjacent carbonate unit. Stimulated by the success of the alternating copolymerization of CO<sub>2</sub> and styrene oxide using a binary catalyst system consisting of complex **1** and PPNY (Y = 2,4-dinitrophenoxide),<sup>26</sup> we investigated the activity of this system for catalyzing the coupling reaction of epichlorohydrin with CO<sub>2</sub> (Table 1). It was gratifying to find that the binary catalyst system at 0.1 mol % loading showed an excellent activity for this coupling process with a TOF of 300 h<sup>-1</sup> at 25 °C; however, the selectivity for copolymer formation was only 10%. Alternatively, a reduction in the reaction temperature suppressed the formation of cyclic carbonate and concomitantly increased the selectivity for copolymer formation. A similar temperature dependence for product selectivity was observed in the binary catalyst system of complex **1** in conjunction with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, a sterically hindered strong organic base). During the optimization of the catalyst systems, it was found that the cobalt-based catalyst **2** with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (designated as TBD) anchored to the ligand framework and bifunctional catalyst **3** bearing an appended quaternary ammonium salt were highly active for catalyzing CO<sub>2</sub>/epichlorohydrin copolymerization to selectively



**Figure 1.** Representative  $^1\text{H}$  NMR spectrum of  $\text{CO}_2$  copolymer from epichlorohydrin in  $\text{CDCl}_3$ .

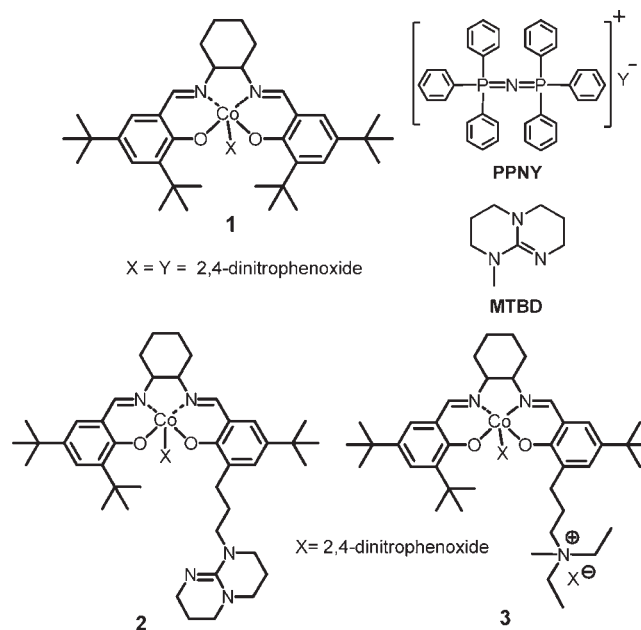


**Figure 2.** Three-dimensional stack plots for the epoxide/ $\text{CO}_2$  coupling reactions utilizing complex **1** and PPNY as catalysts (see Table S1): (A) propylene oxide and  $\text{CO}_2$ ; (B) epichlorohydrin and  $\text{CO}_2$ .

give the corresponding polycarbonates even at a low catalyst loading (Table 1, entries 6 and 8).

Notably, the resulting polycarbonates have more than 99% carbonate content, as confirmed by  $^1\text{H}$  NMR (Figure 1) and MALDI-TOF spectroscopy (Supporting Information, Figure S1). As shown in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of the resultant copolymer in Figure 1, the signals at  $\delta$  3.6–3.8 ppm are assigned to the hydrogens of the  $\text{CH}_2\text{Cl}$  group, while the signals at 5.1 and 4.5 ppm originate from the resonances of the methine CH and the methylene  $\text{CH}_2$  of the carbonate unit, respectively. Although only one peak at 3.7 ppm was observed in the  $^1\text{H}$  NMR spectrum of the homopolymer of epichlorohydrin, the well-proportional relationship of the CH,  $\text{CH}_2$ , and  $\text{CH}_2\text{Cl}$  integrated areas (1/2.01/2.04), as well as MALDI-TOF and ESI-MS (vide infra) analyses, confirmed the perfectly alternating nature of the copolymer.

It was also of interest to study the microstructure of poly( $\text{CO}_2$ -*alt*-epichlorohydrin) by  $^{13}\text{C}$  NMR spectroscopy. Unfortunately, the failure to synthesize model compounds of the three carbonate linkages (head-to-head, head-to-tail, and tail-to-tail linkages) of this  $\text{CO}_2$  copolymer made it difficult to assign the



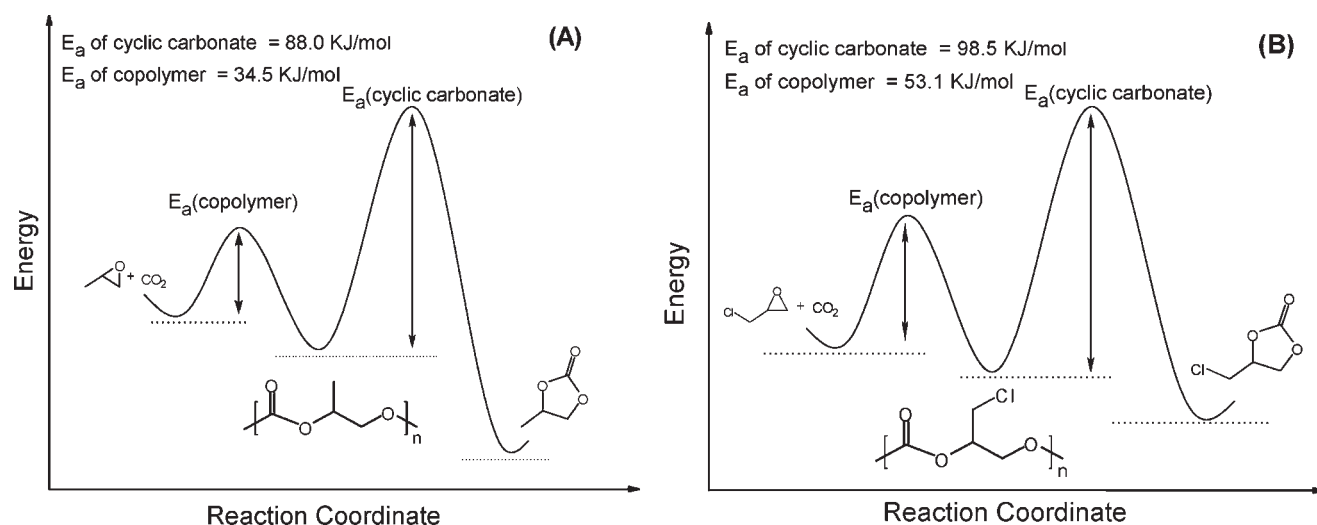


Figure 3. Reaction coordinate diagrams for (A)  $\text{CO}_2$ /propylene oxide and (B)  $\text{CO}_2$ /epichlorohydrin coupling reactions.

signals of  $^{13}\text{C}$  NMR spectrum in the carbonyl region to the corresponding configuration sequences. In order to investigate the effect of the chloromethyl group on the position of nucleophilic ring opening of epichlorohydrin, the coupling of  $\text{CO}_2$  and (*R*)-epichlorohydrin was performed using the single-component catalysts of the optically active complexes (1*S*,2*S*)-2 and (1*S*,2*S*)-3. The resulting polycarbonates displayed about 80% enantioselectivity for the *R* configuration on the basis of its hydrolysis product, indicating 20% of (*R*)-epichlorohydrin was ring-opened at the methine C–O bond during the copolymerization with  $\text{CO}_2$ : i.e., a change in stereochemistry at the methine carbon center with inversion occurred.

In order to better ascertain the influence of the chloromethyl group of epichlorohydrin on the catalytic activity and selectivity for copolymer versus cyclic carbonate formation, comparative kinetic experiments between epichlorohydrin and propylene oxide were conducted for the copolymerization with  $\text{CO}_2$ , using the binary catalyst system of complex 1 and PPNY ( $\text{Y} = 2,4$ -dinitrophenoxide). Table S1 gives the initial reaction rates for production of copolymer and cyclic carbonate for both epoxide monomers as a function of temperature (see the Supporting Information). Figure 2 illustrates the reaction profiles for the propylene oxide/ $\text{CO}_2$  and epichlorohydrin/ $\text{CO}_2$  copolymerization processes at two different temperatures as monitored by in situ infrared spectroscopy. Even at the very low temperature of  $-5^\circ\text{C}$  for epichlorohydrin/ $\text{CO}_2$  copolymerization, cyclic carbonate was produced to a significant extent. In contrast, only weak  $\nu_{\text{CO}_2}$  absorptions at  $1800\text{ cm}^{-1}$  assigned to cyclic propylene carbonate were detected at an enhanced temperature of  $40^\circ\text{C}$  in the copolymerization of  $\text{CO}_2$  and propylene oxide. The energies of activation for copolymer and cyclic carbonate formation for both propylene oxide and epichlorohydrin derived from the plots of  $\ln(\text{initial rate})$  vs  $1/T$  are illustrated in Figure S4. Using these activation parameters, we obtained the reaction coordinate diagrams for each process as depicted in Figure 3. It is important to note that although the diagrams in Figure 3 present the production of cyclic carbonates via pathways involving a metal-bound copolymer chain, the energy of activation barriers measured for cyclic carbonate formation actually reflects a composite of mechanistic pathways. That is, we are not able to resolve the energy barriers for the three routes to cyclic carbonate

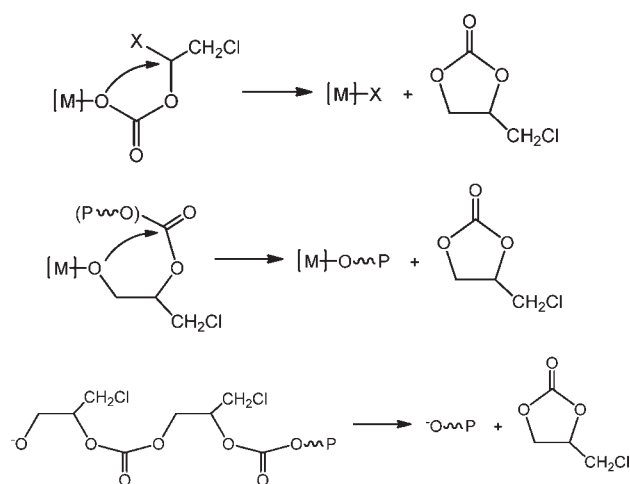
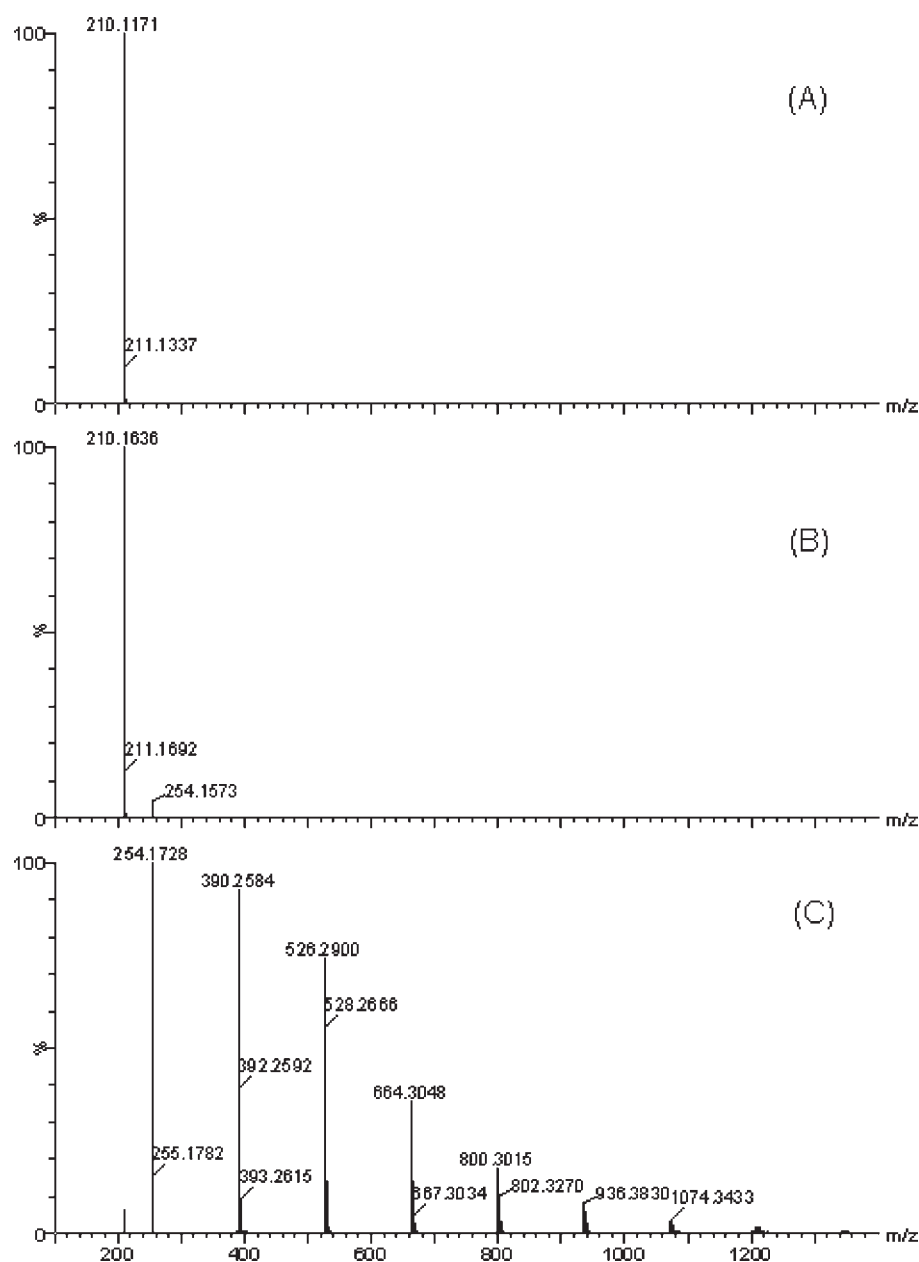


Figure 4. Three modes for cyclic carbonate production.  $\text{O}\sim\text{P}$  = growing polymer chain.

production as depicted in Figure 4. The difference in activation energy barriers employing this catalyst system for cyclic carbonate vs copolymer formation for the epichlorohydrin process is less than that of propylene oxide:  $45.4$  vs  $53.5$  kJ/mol. In addition, the relative rates of production of cyclic carbonate vs copolymer become greater than 1 for epichlorohydrin/ $\text{CO}_2$  coupling above  $5^\circ\text{C}$ , whereas this is projected to occur at a much higher temperature ( $>80^\circ\text{C}$ ) for the propylene oxide/ $\text{CO}_2$  process (see Figure S5). In other words, cyclic carbonate formation during the epichlorohydrin/ $\text{CO}_2$  coupling process is *entropically* favored as well over the corresponding process involving propylene oxide and  $\text{CO}_2$ , with the former case being under thermodynamic control at temperatures above  $5^\circ\text{C}$ . This explains the tendency to produce large quantities of cyclic carbonate in the coupling reaction of epichlorohydrin and  $\text{CO}_2$  even at rather low temperatures.

Electrospray ionization (ESI) is a soft ionization method that leaves weakly bound ligand intact in a complex ion.<sup>27</sup> For example, ESI in combination with tandem mass spectrometry (ESI-MS), has been employed to study mechanistic aspects of metal-mediated homogeneous polymerizations.<sup>28,29</sup> In a previous





**Figure 5.** ESI-Q-TOF mass spectra of the reaction mixture resulting from the systems of MTBD and complex **1** (1/MTBD/epichlorohydrin = 1/1/1000, molar ratio) at 0 °C and 2.0 MPa CO<sub>2</sub> pressure. (A) 30 min; (B) 45 min; (C) 60 min.

study, we reported a continuous determination of a polymer end group (initiating and chain growth species) at various times by *in situ* ESI-MS method and directly observed the perfect alternating nature of copolymer formation during the Co(III)-mediated CO<sub>2</sub>/propylene oxide copolymerization using MTBD as cocatalyst.<sup>15b</sup> In order to confirm the alternating nature of the polymers from the epichlorohydrin/CO<sub>2</sub> copolymerization with cobalt(III)-based catalyst systems, ESI-MS was performed in the positive-mode for continuous determination of the transient cationic species in the reaction mixture catalyzed by binary **1**/MTBD system under 0 °C at various time periods (Figure 5). Different from the propylene oxide/CO<sub>2</sub> copolymerization with binary **1**/MTBD catalyst system, in which the chain initiator species {[MTBD + H<sup>+</sup>], [<sup>-</sup>OCH-(CH<sub>3</sub>)CH<sub>2</sub>-MTBD<sup>+</sup> + H<sup>+</sup>], and [<sup>-</sup>OCH(CH<sub>3</sub>)CH<sub>2</sub>-(CO<sub>2</sub>-*alt*-PO)<sub>*n*</sub>-MTBD<sup>+</sup> + H<sup>+</sup>]} (PO = propylene oxide) were clearly found,

we did not observe the species of [MTBD + H<sup>+</sup>], [<sup>-</sup>OCH-(CH<sub>2</sub>Cl)CH<sub>2</sub>-MTBD<sup>+</sup> + H<sup>+</sup>], and [<sup>-</sup>OCH(CH<sub>2</sub>Cl)CH<sub>2</sub>-(CO<sub>2</sub>-*alt*-ECH)<sub>*n*</sub>-MTBD<sup>+</sup> + H<sup>+</sup>] (ECH = epichlorohydrin), but unexpectedly detected only one species of *m/z* 210.1 within 30 min, and two species of *m/z* 210.1 and 254.1 at 45 min point. When the reaction was carried out about 60 min, the relative abundance of *m/z* 254.1 significantly increased while the species at *m/z* 210.1 was negligible. Meanwhile, a series of species based on *m/z* 254.1 at an interval of 136 (which is equivalent to a repeat unit of CO<sub>2</sub>-*alt*-ECH) were also observed in the positive-mode ESI-MS spectrum. The species of *m/z* 210.1 was characterized by collision-induced dissociation (CID). This analysis did not result in any scission even *via* CID experiments up to 15 V, indicating that the species at *m/z* 210.1 is highly stable (Supporting Information, Figure S6).

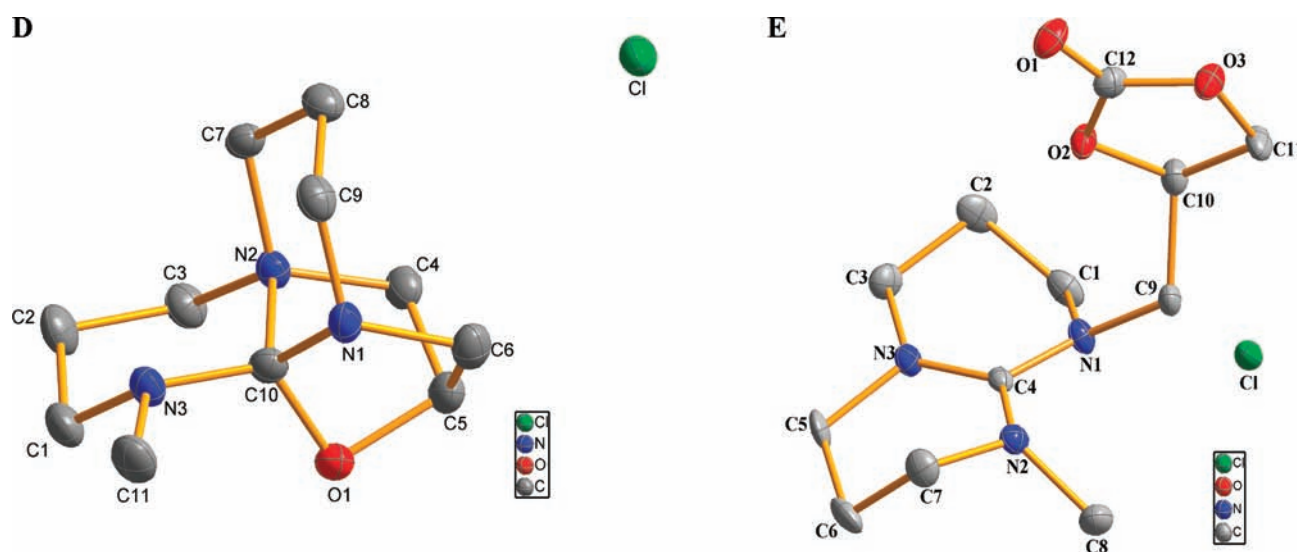


Figure 6. Thermal ellipsoid representation of the species at  $m/z$  210.1 (left) and 254.1 (right) at the 30% probability level. H atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the Species at  $m/z$  210.1 and 254.1

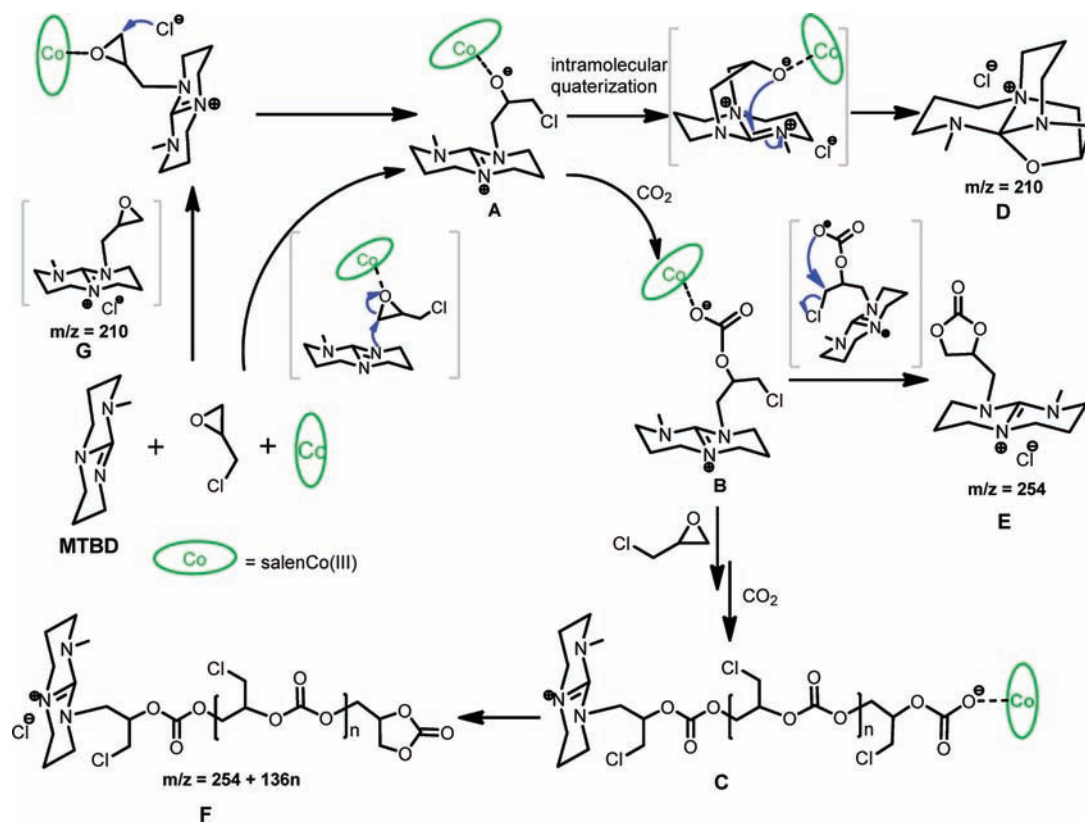
species at $m/z$ 210.1				species at $m/z$ 254.1			
N(1)–C(6)	1.486(4)	C(10)–O(1)–C(5)	96.3(2)	O(1)–C(12)	1.183(8)	O(1)–C(12)–O(3)	125.8(6)
O(1)–C(10)	1.410(4)	N(1)–C(6)–C(5)	100.3(3)	O(2)–C(10)	1.464(8)	O(1)–C(12)–O(2)	122.7(6)
O(1)–C(5)	1.462(4)	O(1)–C(5)–C(4)	102.5(2)	N(1)–C(9)	1.473(8)	C(9)–N(1)–C(1)	118.1(5)
C(5)–C(6)	1.517(5)	C(3)–N(2)–C(7)	109.9(2)	O(2)–C(12)	1.344(8)	O(3)–C(12)–O(2)	111.4(6)
C(4)–C(5)	1.523(5)	C(3)–N(2)–C(4)	109.5(2)	O(3)–C(12)	1.330(8)	O(2)–C(10)–C(11)	103.9(5)
N(2)–C(7)	1.512(4)	C(10)–N(1)–C(9)	114.8(2)	O(3)–C(11)	1.430(9)	O(2)–C(10)–C(9)	109.1(5)
N(2)–C(4)	1.524(4)	C(10)–N(1)–C(6)	105.2(2)	N(1)–C(4)	1.354(8)	C(11)–C(10)–C(9)	112.9(6)
N(1)–C(9)	1.470(4)	N(1)–C(10)–N(2)	108.9(2)	N(1)–C(1)	1.487(8)	C(4)–N(1)–C(9)	120.6(5)

To further investigate the  $m/z$  210.1 species, the reaction of complex **1**, MTBD, and epichlorohydrin in the absence of  $\text{CO}_2$  was examined by ESI-MS spectroscopy. Two species of  $m/z$  154.1 and 210.1 were detected. The former species, assigned to  $[\text{MTBD} + \text{H}^+]$ , rapidly disappeared with time. This suggests that the formation of the species of  $m/z$  210.1 is a relatively fast reaction (Supporting Information, Figure S7). It is worth while noting here parenthetically that the species at  $m/z$  210.1 is also easily formed in the system consisting of MTBD and epichlorohydrin without complex **1**, indicating a quaternization occurred in solution. With the aid of a column chromatogram, the species  $m/z$  210.1 was isolated from the reaction system consisting of complex **1** and MTBD with epichlorohydrin in the absence of  $\text{CO}_2$  (1/MTBD/epichlorohydrin = 1/1/20, molar ratio). The solid-state structures and crystallographic data of the resultant species at  $m/z$  210.1 obtained by X-ray diffraction studies are provided in Figure 6 and Table 2. As illustrated in Figure 6, the cationic ion of the quaternary ammonium salt consists of three six-membered rings and one five-membered ring. Although the isolated quaternary ammonium salt in conjunction with complex **1** proved to be active in catalyzing the  $\text{CO}_2$ /epichlorohydrin copolymerization to provide the corresponding polycarbonate along with some cyclic carbonate, we did not observe the propagating polymer chain with the cationic ion based on

MTBD. When the anion  $\text{Cl}^-$  of the compound in Figure 6 was changed to  $\text{BF}_4^-$ , the resulting binary catalyst system completely lost activity for copolymer formation. These results demonstrate that the species at  $m/z$  210.1 is stable and initiates the coupling of  $\text{CO}_2$  and epichlorohydrin with difficulty.

Furthermore, an organic compound including a species at  $m/z$  254.1 was isolated in a very low yield from the reaction system consisting of complex **1** and MTBD with epichlorohydrin in the presence of  $\text{CO}_2$  (1/MTBD/epichlorohydrin = 1/1/10, molar ratio). The compound was well characterized by FTIR and NMR spectroscopy, and its solid-state structure was obtained by single-crystal X-ray diffraction studies (Figure 6). The results demonstrate it is a quaternary ammonium salt with a bulky cationic ion including a cyclic carbonate unit. Interestingly, in the presence of complex **1**, the bulky cationic ion of the quaternary ammonium salt did not initiate the copolymerization of epichlorohydrin and  $\text{CO}_2$ . These results indicate that the compounds shown in Figure 6 (D and E) are not intermediates in the MTBD-initiated copolymer-chain growth process as illustrated in Scheme 1.

Consistent with the mechanistic aspects previously noted for the binary 1/MTBD-mediated  $\text{CO}_2$ /propylene oxide copolymerization process, possible intermediates involving MTBD during the  $\text{CO}_2$ /epichlorohydrin copolymer formation are proposed

Scheme 1. Possible Intermediates Involving MTBD during the CO<sub>2</sub>/Epichlorohydrin Copolymerization with the Binary 1/MTBD Catalyst System

as summarized in Scheme 1. In the initial step, the epoxide first coordinates to the active metal center trans to the axial anion and is ring-opened by nucleophilic attack of MTBD to afford intermediate A. The intermediate A can also be formed by nucleophilic ring opening by the chloride ion to the coordinated epoxide G, which is formed by the quaternization reaction of MTBD and epichlorohydrin. The fast insertion of CO<sub>2</sub> into the Co–O bond provides the carbonate intermediate B. Continuous alternating incorporation of epichlorohydrin and CO<sub>2</sub> produces linear polycarbonate C. When the intermediate A is isolated from the reaction system, it isomerizes into the stable quaternary ammonium salt D with a cation of  $m/z$  210.1 via intramolecular quaternization and nucleophilic ring closing. If the carbonate intermediate B is isolated, it can be transferred into organic compound E with a cation of  $m/z$  254.1 via a back-biting reaction caused by the nucleophilic attack of the carbonate end group at the carbon atom of the chloromethyl of the adjacent carbonate unit. A similar transformation can also take place with the intermediate C, thereby producing the stable quaternary ammonium salt F with a cation of  $m/z$  254.1 + 136*n*, through a back-biting reaction to afford a five-membered cyclic carbonate at the terminal position with simultaneous release of chloride ion. The cations of these stable quaternary ammonium salts are responsible for the species at  $m/z$  210.1 and 254.1 and species based on  $m/z$  254.1 at an interval of 136 in Figure 5C. It is noteworthy that, apart from the propagating polymer chains with respect to MTBD, the nucleophilic axial anion of complex 1 and the chloride ion formed by intramolecular quaternization can also serve as initiators for this copolymerization process.

## CONCLUSIONS

In summary, we have reported perfectly alternating copolymerization of CO<sub>2</sub> and epichlorohydrin using cobalt(III)-based catalyst systems. Single-component cobalt(III)-based complexes bearing an appended TBD or quaternary ammonium salt on the ligand framework have been shown to be highly active for catalyzing CO<sub>2</sub>/epichlorohydrin copolymerization to selectively provide the corresponding polycarbonates with more than 99% carbonate linkages even at a low catalyst loading. A more sensitive temperature-dependent product distribution, with cyclic carbonate readily formed at enhanced temperatures, was observed in the coupling reaction of CO<sub>2</sub> and epichlorohydrin in comparison with the propylene oxide/CO<sub>2</sub> process. In part, this is ascribed to the lower activation energy barrier for cyclic carbonate production via the back-biting mechanism for epichlorohydrin versus propylene oxide.

Direct observation of the propagating polymer-chain species from the binary complex 1/MTBD system by means of electrospray ionization mass spectrometry confirmed the perfectly alternating nature of the copolymer, wherein a series of species  $m/z$  210.1 and 254.1 and that based on  $m/z$  254.1 at an interval of 136 were observed. The compounds ascribed to the species  $m/z$  210.1 and 254.1 were isolated, and their solid-state structures were determined by X-ray crystallography. The species at  $m/z$  210.1 is assignable to the bulky cation of a stable quaternary ammonium salt, consisting of three six-membered rings and one five-membered ring, formed by the isomerization of the active species via intramolecular quaternization and nucleophilic ring closing. The species at  $m/z$  254.1 and that based on  $m/z$  254.1 at



an interval of 136 are also assigned to various bulky cations of the corresponding quaternary ammonium salts originating from the true intermediates via a back-biting reaction caused by the nucleophilic attack of the carbonate end group at the carbon atom of chloromethyl of the adjacent carbonate unit.

## ■ ASSOCIATED CONTENT

Supporting Information. Text, figures, tables, and CIF files giving general experimental procedures and characterization data for CO<sub>2</sub> copolymers, as well as X-ray crystallographic data for the structure determination of two compounds with a cation of *m/z* 210.1 and 254.1, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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