

CO₂ Copolymers from Epoxides: Catalyst Activity, Product Selectivity, and Stereochemistry Control

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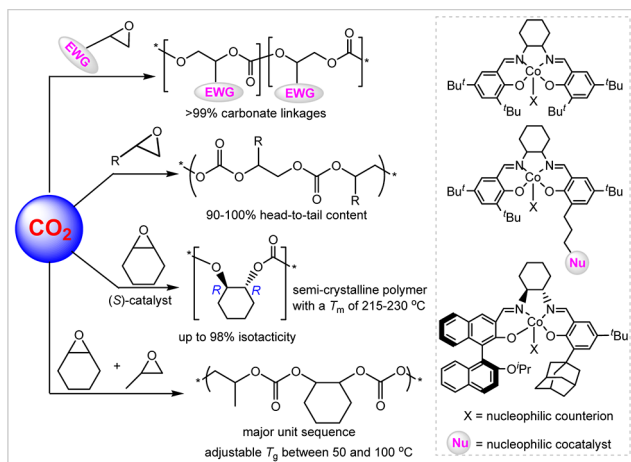
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CONSPECTUS

The use of carbon dioxide as a carbon source for the synthesis of organic chemicals can contribute to a more sustainable chemical industry. Because CO₂ is such a thermodynamically stable molecule, few effective catalysts are available to facilitate this transformation. Currently, the major industrial processes that convert CO₂ into viable products generate urea and hydroxybenzoic acid. One of the most promising new technologies for the use of this abundant, inexpensive, and nontoxic renewable resource is the alternating copolymerization of CO₂ and epoxides to provide biodegradable polycarbonates, which are highly valuable polymeric materials. Because this process often generates byproducts, such as polyether or ether linkages randomly dispersed within the polycarbonate chains and/or the more thermodynamically stable cyclic carbonates, the choice of catalyst is critical for selectively obtaining the expected product.

In this Account, we outline our efforts to develop highly active Co(III)-based catalysts for the selective production of polycarbonates from the alternating copolymerization of CO₂ with epoxides. Binary systems consisting of simple (salen)Co(III)X and a nucleophilic cocatalyst exhibited high activity under mild conditions even at 0.1 MPa CO₂ pressure and afforded copolymers with >99% carbonate linkages and a high regiochemical control (~95% head-to-tail content). Discrete, one-component (salen)Co(III)X complexes bearing an appended quaternary ammonium salt or sterically hindered Lewis base showed excellent activity in the selectively alternating copolymerization of CO₂ with both aliphatic epoxides and cyclohexene oxide at high temperatures with low catalyst loading and/or low pressures of CO₂. Binary or one-component catalysts based on unsymmetric multichiral Co(III) complexes facilitated the efficient enantioselective copolymerization of CO₂ with epoxides, providing aliphatic polycarbonates with >99% head-to-tail content. These systems were also very efficient in catalyzing the terpolymerization of cyclohexene oxide, propylene oxide and CO₂. The resulting terpolymer had a single glass-transition temperature and a single thermolysis peak.

This Account also provides a thorough mechanistic understanding of the high activities, excellent selectivities, and unprecedented stereochemical control of these Co(III)-based catalysts in the production of CO₂ copolymers. The catalysis occurs through a cooperative monometallic mechanism, in which the Lewis acidic Co(III) ion serves as electrophile to activate then epoxide and the nucleophilic counterion or cocatalyst serves as a nucleophile to initiate polymer-chain growth. The high activity and excellent regioselectivity observed in the epoxide ring-opening reactions results from epoxide activation through the moderate electrophilicity of the Co(III) ion, the fast insertion of CO₂ into the Co–O bond, and the facile dissociation of the propagating carboxylate species from the central metal ion. The reversible intra- or intermolecular Co–O bond formation and dissociation helps to stabilize the active Co(III) species against reversion to the inactive Co(II) ion. We also describe our laboratory's recent preparation of the first crystalline CO₂-based polymer via highly stereospecific copolymerization of CO₂ and *meso*-cyclohexene oxide and the selective synthesis of perfectly alternating polycarbonates from the coupling of CO₂ with epoxides bearing an electron-withdrawing group.



Introduction

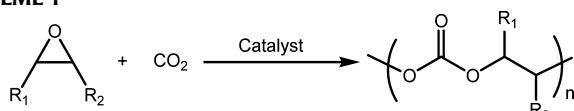
Selective transformation of CO₂ into degradable polycarbonates by the alternating copolymerization with epoxides represents a green polymerization process for potential large-scale utilization of CO₂ in chemical synthesis.^{1–4} Scheme 1 depicts the reaction which generally occurs in the presence of a metal catalyst. This process is often accompanied by the generation of undesired byproducts. One side-reaction is consecutive epoxide ring-opening resulting in the formation of polyether or ether linkages randomly dispersed in the polycarbonate chains (Scheme 2, path A). Another is to form cyclic carbonate, a more pervasive byproduct, originating from intramolecular cyclic elimination by either of two concurrent backbite mechanisms, one aided by the central metal ion and the other involving the dissociated linear carbonate anion or growing polymer-chain (paths B and C).⁵

For the alternating copolymerization of CO₂ with terminal epoxides, there is much interesting information: regiochemistry of epoxide ring-opening (Scheme 3), and

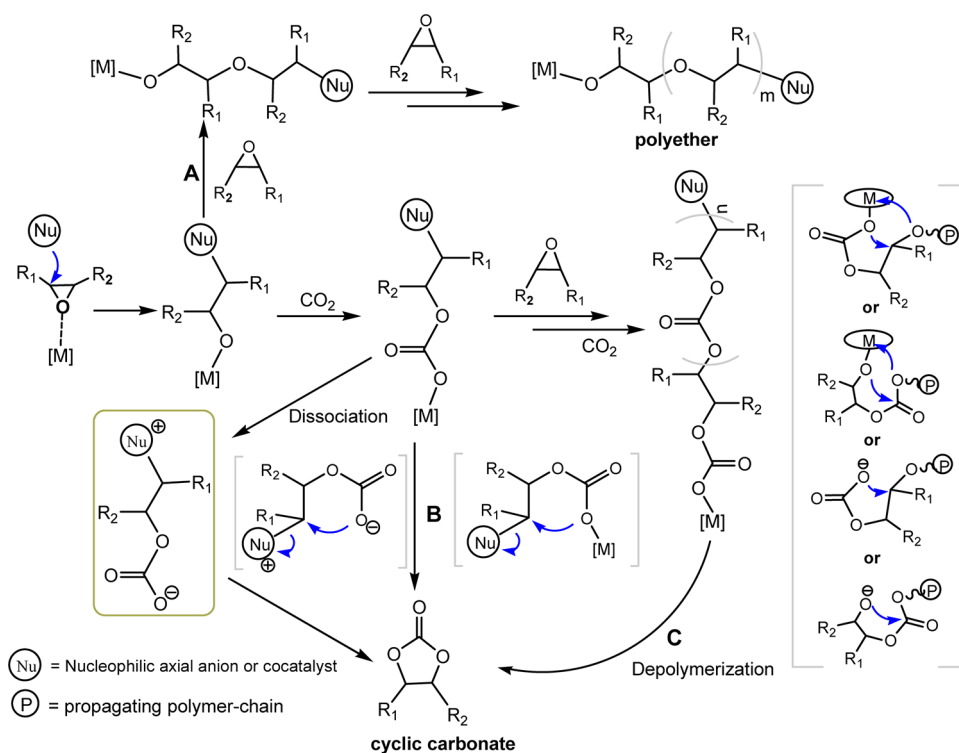
stereochemistry of carbonate unit sequence in a polymer (Scheme 4), which bears a memory of the reaction pathway leading to its formation.⁶ Regioselectivity in ring-opening position of the epoxide significantly affects the stereochemistry of the resultant polymer. Ring-opening occurring at the methylene C–O bond normally retains the stereochemistry at the methine carbon of the epoxide incorporated into polycarbonate. Contrarily, ring-opening at the methine C–O bond may cause a change in stereochemistry at the methine carbon with inversion. There are three possible linkages for neighboring carbonate units in the alternating copolymer, dependent on the regioselectivity in epoxide ring-opening. Head-to-tail carbonate linkage is produced concerning successive epoxide ring-opening at either the methylene or methine C–O bond, while the formation of head-to-head or tail-to-tail linkage involves alternating ring-opening at the methylene C–O bond of one epoxide and the methine C–O bond of the following epoxide.

In this Account, we summarize the recent progress from our laboratory on developing highly active catalysts for the synthesis of CO₂ copolymers from various epoxides. In particular, we focus on well-defined cobalt(III) complexes that serve as homogeneous catalysts for producing stereoregular CO₂-based polycarbonates.

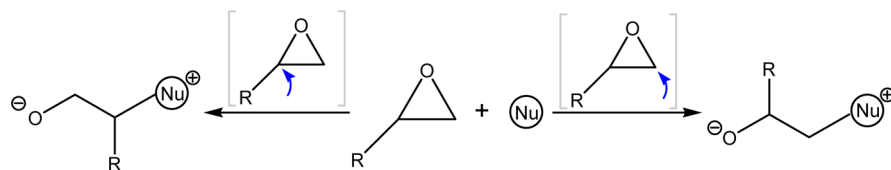
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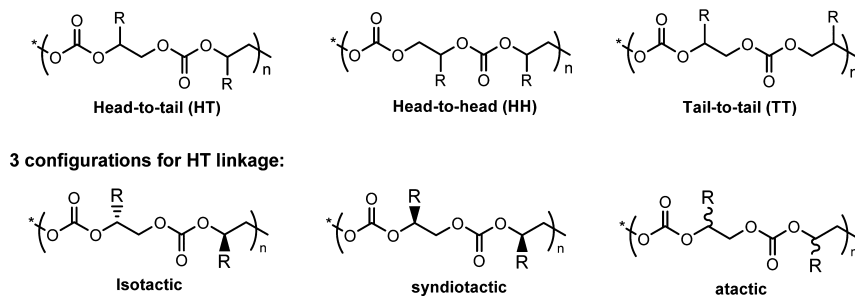
SCHEME 2



SCHEME 3



SCHEME 4



Historical Background

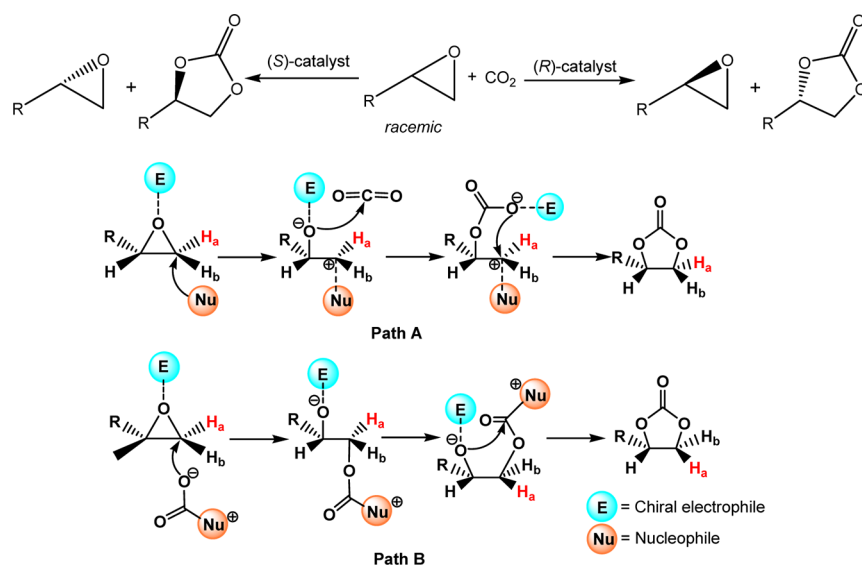
Inoue's discovery of CO₂/epoxide copolymerization with a heterogeneous catalyst derived from diethyl zinc and equivalent water opened up a new field of CO₂-based polymers.⁷ Following this study, numerous heterogeneous zinc-based catalysts have been developed for this transformation.¹ However, high catalyst loading, elevated CO₂ pressure, and long reaction time are usually prerequisites for obtaining appreciable amounts of polymer, and the produced polymers often have high ether content and exhibit broad molecular weight distributions. Additionally, these systems generally suffered from the concomitant production of cyclic carbonates, especially with regard to aliphatic epoxides.

Being distinct from heterogeneous catalysts which lack active-site control, the well-defined homogeneous catalysts are beneficial for mechanistic investigations. In 1983, Inoue and colleagues reported the first single-site catalyst for CO₂/epoxide copolymerization.⁸ The aluminum–porphyrin complex operated at a very low rate even at a high catalyst loading, thereby providing copolymers with low molecular weight. Inoue's early discovery has also propelled the design of various discrete zinc-phenoxide derivatives⁹ and β -diiminate-zinc catalysts for this reaction.¹⁰ These studies resulted in significantly improved catalytic activity, selectivity, and importantly a better mechanistic understanding of the copolymerization process. The next significant study came with the use of chromium-salen derivatives by Darensbourg et al. This kind of catalyst was widely investigated for the

selective formation of CO₂ copolymers from both alicyclic and aliphatic epoxides by systematically altering ligand structure, cocatalyst, and reaction conditions.¹¹

The most significant development in this area was uncovered in 2003 by the Coates group, demonstrating that (salen)Co(III)X with a nucleophilic counterion was an effective catalyst for selectively producing poly(propylene carbonate) from the copolymerization of CO₂ and propylene oxide at 55 bar and room temperature.¹² The isolated copolymers have 90–99% carbonate linkages and ~80% head-to-tail content. Turnover frequencies (TOFs) extended over a range of 17–81 h^{−1}, depending on reaction conditions and the substituent groups on the salen ligand. Unfortunately, low CO₂ pressures or elevated temperatures led to the nearly complete loss in activity. However, our group delightedly found that the addition of a nucleophilic cocatalyst such as quaternary ammonium halide significantly enhanced the activity of (salen)Co(III)X, even at low CO₂ pressures and/or elevated temperatures, affording copolymers with >99% carbonate linkages and an increased stereochemistry control (~95% head-to-tail content).¹³ Recently, we succeeded in synthesizing poly(propylene carbonate) with >99% head-to-tail content, using multichiral cobalt complexes.¹⁴ Catalytic activity reached a pinnacle when Lee and co-workers¹⁵ designed bifunctional Co(III)-based catalysts bearing quaternary ammonium salts. These complexes displayed a significant improvement in activity at high temperatures and high [epoxide]/[catalyst] ratios, with a maximum TOF of

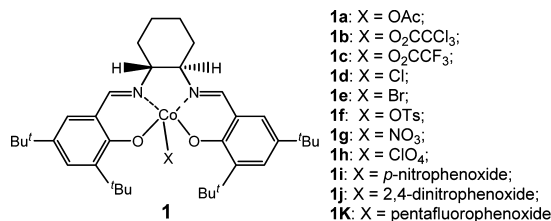
SCHEME 5



16 000 h⁻¹ at 80 °C. Prior to this study, the Nozaki group utilized a salen-type cobaltate complex with a piperidinium end-capping arm as catalyst for selectively preparing CO₂ copolymers from aliphatic epoxides, and first succeeded in synthesizing a block terpolymer from CO₂, propylene oxide, and 1-hexene oxide.¹⁶

Discovery of Highly Active Binary Co(III)-Based Catalyst Systems

At the start of our studies involving CO₂/epoxide coupling, our interests mainly focused on the selective production of cyclic carbonates.¹⁷ Pursuant to our own efforts toward the development of highly efficient metal–salen catalysts for CO₂/epoxide coupling, we became interested in developing a method for direct synthesis of chiral cyclic carbonates from *racemic* epoxides by a catalytic kinetic resolution process with CO₂ as reagent (Scheme 5).

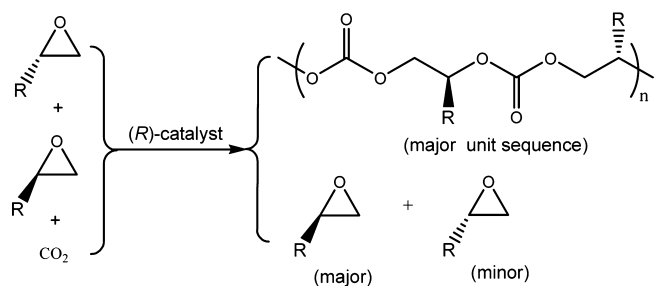


Chiral Co(III)-salen complexes proved to be highly efficient and enantioselective catalysts for the hydrolytic kinetic resolution of terminal epoxides.¹⁸ Based on the fact, we designed binary nucleophile–electrophile catalyst systems consisting of an enantiopure (salen)Co(III)X and a quaternary ammonium salt for the asymmetric coupling of CO₂ with

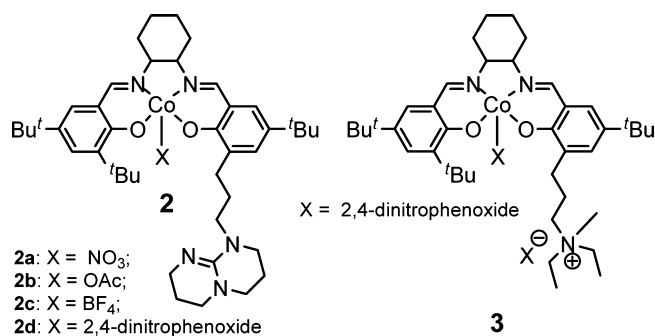
racemic epoxides.¹⁹ In this system, (salen)Co(III)X was proposed to serve as an electrophile for selectively complexing one enantiomer of the *racemic* epoxides, while the anion of the quaternary ammonium salt served as a nucleophile. The regioselective attack of either the nucleophile or activated CO₂ at the methylene carbon of the coordinated epoxide leads to enantioselective ring-opening of the epoxide with subsequent formation of chiral cyclic carbonate through intramolecular cyclic elimination (Scheme 5). We found that, in the presence of 0.1 mol % **1b** and equimolar ⁿBu₄NBr, the solvent-free reaction of *racemic* propylene oxide with 0.55–0.60 equiv of CO₂ at room temperature in 2 h afforded a mixture of unreacted epoxide and propylene carbonate with moderate enantioselectivity. The formation rate of propylene carbonate was up to 245 h⁻¹, the highest TOF record for CO₂/epoxide coupling at that time. Unfortunately, the asymmetric coupling only gave a *k*_{rel} (kinetic resolution coefficient) of less than 10. Additionally, a certain amount of polycarbonate with low molecular weight was also detected in the resultant mixture, though this could be easily depolymerized to yield cyclic propylene carbonate. Since this time, our subsequent studies have revealed that the selectivity for copolymer increased significantly if the adventitious water in the reaction system was carefully removed.²⁰

During the course of this work, Coates and co-workers reported the first set of discrete cobalt complexes which would act as catalysts for selective copolymer formation at enhanced CO₂ pressures.¹² This work led us to believe that synthesizing CO₂ copolymers from epoxides was more important than focusing on cyclic carbonates.

SCHEME 6



Thus, our research interest gradually shifted to the synthesis of optically active polycarbonates from *racemic* epoxides by a catalytic kinetic resolution process with CO₂ as reagent (Scheme 6). Careful screening revealed that simple changes in the axial counterion of (salen)Co(III)X and the anion of quaternary ammonium salt drastically affected the polymeric/cyclic product selectivity.¹³ The use of a bulky nucleophilic cocatalyst with low leaving ability is more beneficial for increasing the selectivity for polycarbonate. The binary system consisting of complex **1j** or **1k** and very hydrophobic PPNCl {PPN = bis(triphenylphosphoranylidene)ammonium} exhibited the highest catalytic activity with a TOF of 530–620 h⁻¹ for CO₂/propylene oxide copolymerization at room temperature, with >99% selectivity for polycarbonate.^{21,22} Notably, these resulting polymers not only show completely alternating nature, but they also have an unprecedented head-to-tail content of ~95%. Systematic studies showed that many aspects of catalyst, including substituent groups on the salen ligand, chiral diamine backbone, and axial counterion of (salen)Co(III)X, as well as nucleophilicity, leaving ability, and coordination ability of the cocatalyst, significantly affected the catalytic activity, polymer selectivity, and enantioselectivity.²²



Driven by the desire for mechanistic understanding of binary Co(III)-based catalyst systems, as well as the success of elegant one-component catalyst design of Nozaki et al.¹⁶

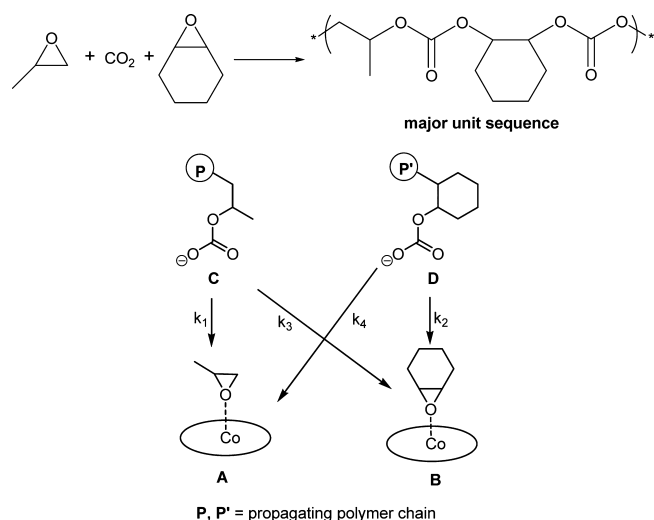
and Lee et al.,¹⁵ we prepared thermally stable catalyst **2** with an appended 1,5,7-triabicyclo[4.4.0]dec-5-ene (TBD) and bifunctional catalyst **3** bearing a quaternary ammonium salt.²³ These catalysts all showed excellent activities for the copolymerization of CO₂ with both aliphatic epoxides and cyclohexene oxide at high temperatures and low catalyst loading, or/and low CO₂ pressures. For example, complex **2b** was used for copolymerizing CO₂ and propylene oxide to selectively afford poly(propylene carbonate) with a TOF of 10 880 h⁻¹ at 100 °C, 0.01 mol % catalyst loading, and 2.5 MPa CO₂ pressure. It was also found to operate at high efficiency with a TOF of 612 h⁻¹ at room temperature, as well as under just 0.1 MPa CO₂ pressure, giving a TOF up to 265 h⁻¹ for producing copolymer with >99% selectivity. Catalyst **3** operated very efficiently for the copolymerization of CO₂ and cyclohexene oxide at 120 °C, selectively affording poly(cyclohexene carbonate) in completely alternating nature with a TOF of 6105 h⁻¹.²⁴

Moreover, an unprecedented success was achieved in the terpolymerization of cyclohexene oxide, propylene oxide and CO₂ using these Co(III)-based catalysts.^{24,25} The resultant terpolymers possess a single glass-transition temperature (*T_g*) and one thermolysis peak, and their *T_g*'s could be tuned from 50 to 100 °C by controlling the relative proportions of the two epoxides loaded into the reaction mixture. This method provides a possible route for improving the heat-resistant property of aliphatic polycarbonates with low *T_g*'s. Although propylene oxide is more reactive than cyclohexene oxide during the copolymerization with CO₂, a matched reactivity for both epoxides was observed in this terpolymerization. An alternating nature of the two different carbonate units predominantly existing in the resulting terpolymers was proposed, indicating that *k*₃ and *k*₄ are main pathways (Scheme 7). This was ascribed to (1) the relatively high basicity and coordination ability of cyclohexene oxide significantly inhibited the reactivity of propylene oxide, and (2) the relatively low reactivity and steric hindrance of cyclohexene oxide retarded the formation of successive cyclohexene carbonate linkages. Thus, the relatively high reactivity of propylene oxide was lowered, resulting in a matched reactivity for both epoxides during the terpolymerization with CO₂.

Selective Synthesis of CO₂ Copolymers from Epoxides with an Electron-withdrawing Group

The scope of epoxides used in the production of CO₂ copolymers is very narrow, and the much-studied epoxides

SCHEME 7



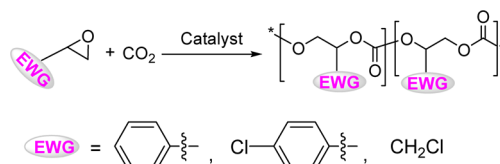
are aliphatic terminal epoxides or cyclohexene oxide derivatives. The selective synthesis of polycarbonates from epoxides with electron-withdrawing groups such as styrene oxide was thus highly desirable (Scheme 8). Being distinct from propylene oxide, the nucleophilic ring-opening of styrene oxide predominantly occurs at the methine C_α–O bond rather than the methylene C_β–O bond due to the electron-withdrawing nature of the aromatic ring (Scheme 9). This favors the formation of cyclic styrene carbonate via backbiting of the propagating polycarbonate anion to the benzyl carbon of the adjacent carbonate unit (Scheme 10, paths B and D).

After a comprehensive screening, we delightedly found that complex **1j** in conjunction with PPNY (Y = 2,4-dinitrophenoxide) was a more effective binary catalyst for selectively providing poly(styrene carbonate) in perfectly alternating nature.²⁶ The resultant copolymer has a relatively high *T_g* of 80 °C. Furthermore, with the use of 4-chloro-styrene oxide, the produced CO₂ copolymer has a *T_g* of 92 °C.²⁷

Although epichlorohydrin is a highly reactive epoxide in the coupling reaction with CO₂, cyclic carbonate usually is the sole product. It was gratifying to find that complexes **2d** and **3** were highly active for catalyzing CO₂/epichlorohydrin copolymerization to selectively give the corresponding polycarbonate.²⁸ A temperature-dependence for product selectivity was observed in the system, and the reduced reaction temperature significantly increased the selectivity for copolymer.

ESI-MS was performed for continuous determination of the transient cationic species in the reaction system regarding **1j**/MTBD catalyzed CO₂/epichlorohydrin coupling at 0 °C. Only one species of *m/z* 210.1 was detected within

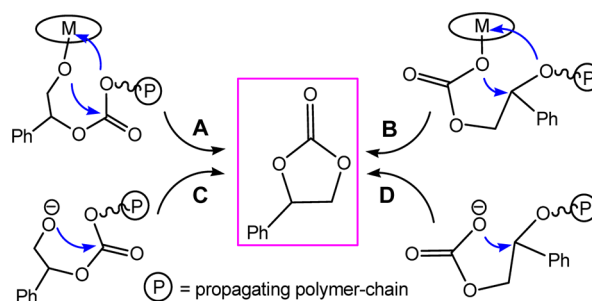
SCHEME 8



SCHEME 9



SCHEME 10



30 min, and two species of *m/z* 210.1 and 254.1 at the 45 min point. When the reaction was carried out to ~60 min, a series of species based on *m/z* 254.1 at an interval of 136 (which is equivalent to a repeat unit of CO₂-*alt*-epichlorohydrin) were observed in the ESI-MS spectrum (Figure 1). Single-crystal X-ray diffraction analysis revealed that the species at *m/z* 210.1 was assignable to the bulk cation of a quaternary ammonium salt, consisting of three six-membered rings and one five-membered ring, formed by the isomerization of the active species via intramolecular quaterization and nucleophilic closing-ring (Scheme 11). The species at 254.1 and based on *m/z* 254.1 at an interval of 136 were also assigned to the bulk cations of various quaternary ammonium salts originated from the intermediates via a backbiting reaction caused by the nucleophilic attack of carbonate end group at the carbon atom of chloromethyl of the adjacent carbonate unit.

Regio- and Stereochemistry Control of CO₂ Copolymers

The control of polymer microstructure is one of the most important goals in coordination polymerization catalysis. For metal–complex catalyzed terminal epoxide/CO₂

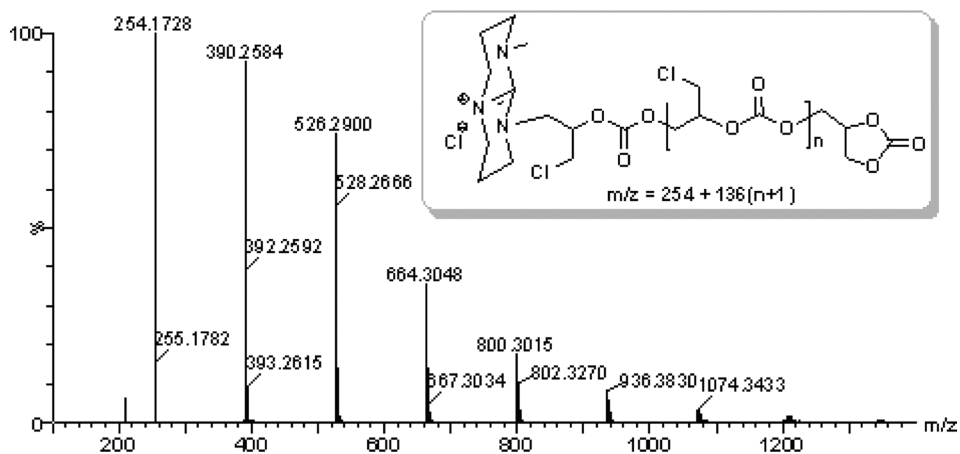
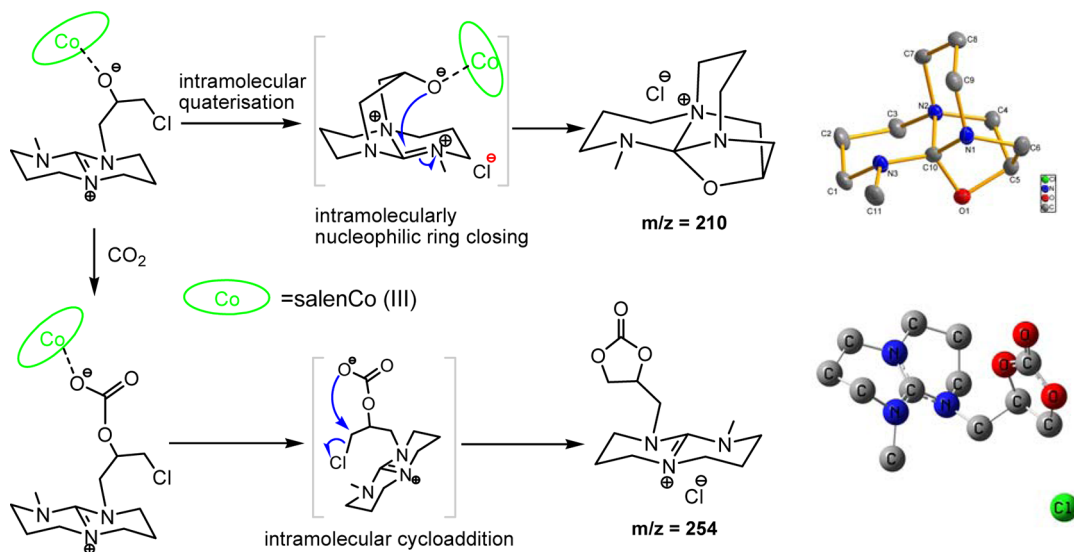


FIGURE 1. ESI-Q-TOF of the reaction mixture resulting from the system of **1j**/MTBD catalyzed CO₂/epichlorohydrin coupling at 0 °C for 60 min.

SCHEME 11

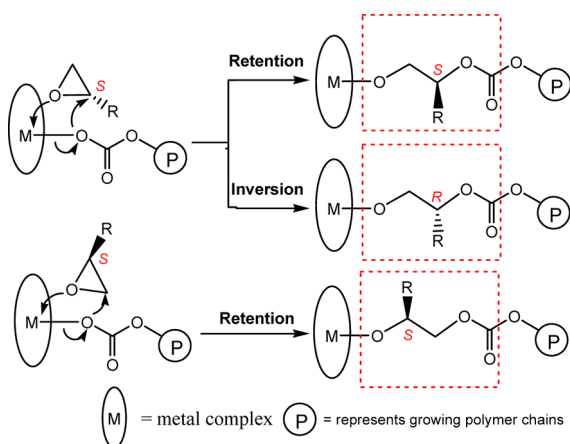


copolymerization, highly regioselective ring-opening of the epoxide is a prerequisite for obtaining stereoregular polycarbonates. Specifically, ring-opening at the methylene C–O bond of the epoxide retains the stereochemistry at the methine carbon of the epoxide incorporated into copolymer. Contrarily, ring-opening at the methine C–O bond may cause a change in stereochemistry at the methine carbon with inversion (Scheme 12).

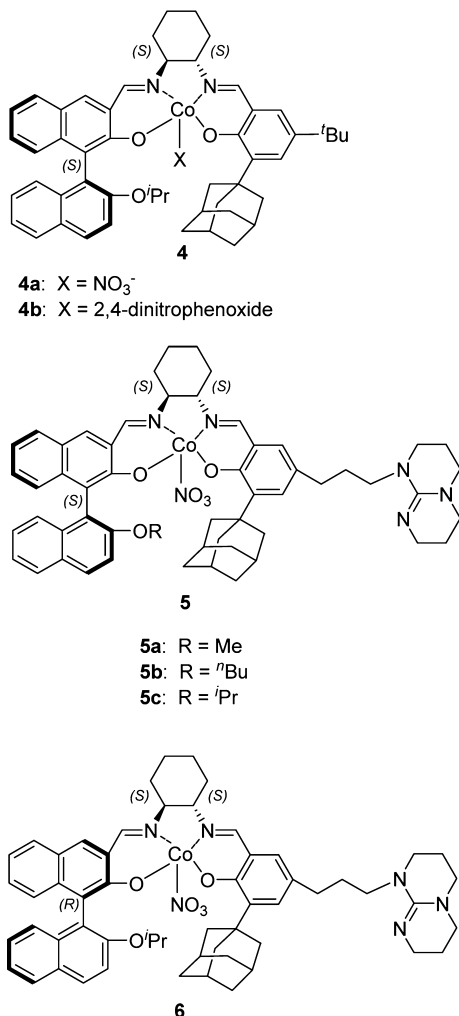
The discovery of highly regioselective catalyst stems back from the use of (salen)Co(III)X as catalyst for CO₂/propylene oxide coupling to afford copolymers with ~80% head-to-tail content.¹² Soon after, our study revealed that in the presence of a quaternary ammonium salt, enantiopure (salen)Co(III)X exhibited unprecedented stereochemistry control (~95% head-to-tail content) during the asymmetric

copolymerization of CO₂ with *racemic* propylene oxide.¹³ These binary catalysts based on (1*R*,2*R*)-(salen)Co(III)X all preferentially consumed (*S*)-propylene oxide over its (*R*)-configuration enantiomer with a *k*_{rel} of 2.8–5.9. Recently, we designed a series of multichiral (*S,S,S*)-Co(III) catalysts **4** and **5**. Both the (1*S*,2*S*)-1,2-diaminocyclohexane backbone and *S* configured 2'-isopropoxy-1,1'-binaphthyl of the ligand cooperatively provide a chiral environment around the central metal ion.^{14,29} With complex **5c** as catalyst, a *k*_{rel} of 24.3 was obtained. Notably, epoxide ring-opening occurred preferentially at the methylene carbon, resulting in the copolymer with >99% head-to-tail content (Figure 2). Interestingly, complex **6** with (*S,S*)-1,2-diaminocyclohexane backbone and *R* configured 2'-isopropoxy-1,1'-binaphthyl also exhibited excellent regioselectivity for

SCHEME 12



epoxide ring-opening with the polymeric product having 99% head-to-tail content, but the k_{rel} of only 1.4 resulted in a low copolymer enantioselectivity.



Far different from the highly regioselective ring-opening of propylene oxide during the copolymerization with CO₂,

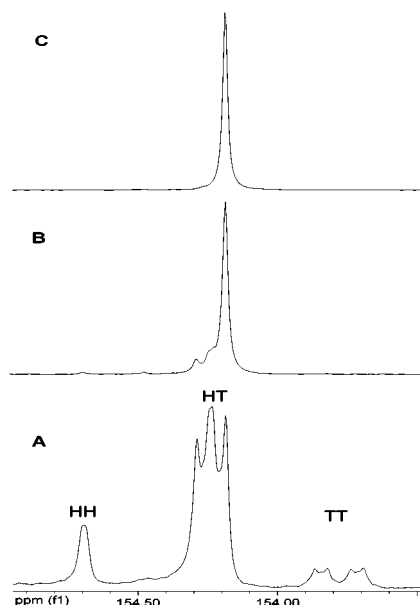
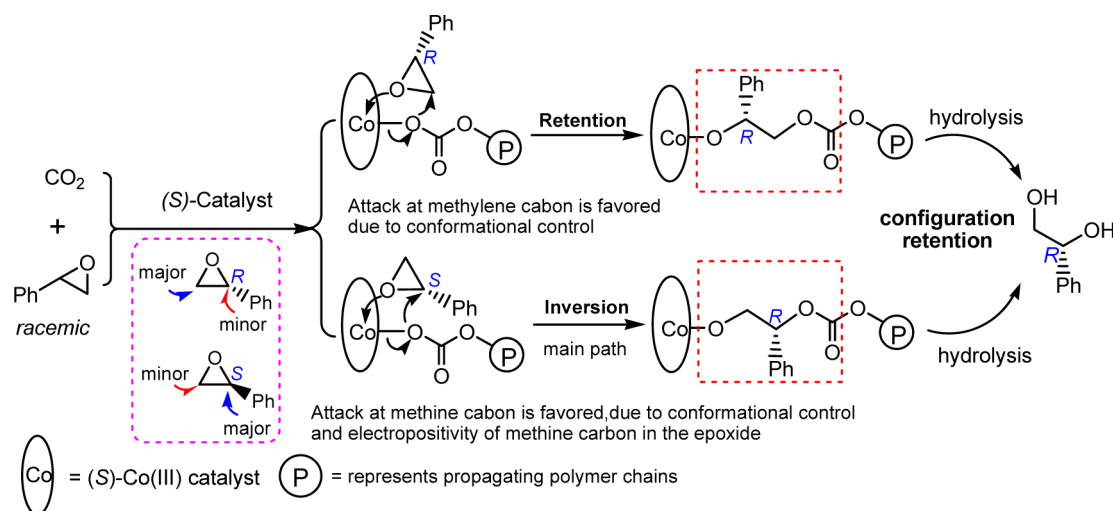


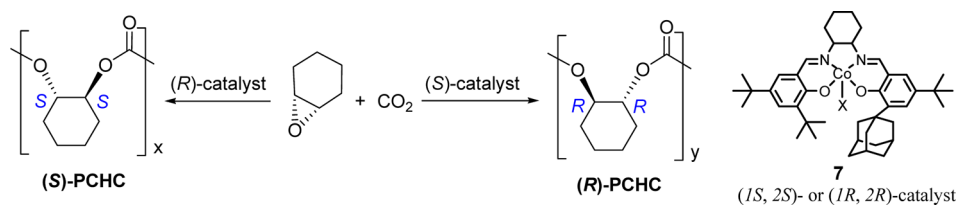
FIGURE 2. Carbonyl region of the ¹³C NMR spectra of poly(propylene carbonate)s obtained with different systems: (A) 70% Head-to-tail linkages, (B) **5c** and *racemic* propylene oxide, and (C) **5c** and (*R*)-propylene oxide.

binary **1j**/PPNY (Y = 2,4-dinitrophenoxide) catalyst for styrene oxide case afforded regio-irregular copolymer with a head-to-tail content of 51%, indicating that epoxide ring-opening occurs almost equally at both C_α-O and C_β-O bonds.²⁶ When enantiopure (1*S*,2*S*)-**1j** was applied to the copolymerization of CO₂ and *racemic* styrene oxide, a kinetic resolution was observed with a k_{rel} of 1.6 at ambient temperature. The catalyst preferentially consumed (*R*)-styrene oxide over its (*S*)-configuration. Surprisingly, in comparison with the low k_{rel} , an enhanced enantioselectivity for (*R*)-configuration with a selective factor of 4.3 was found in the resulting copolymer. Because of the low k_{rel} , a significant amount of (*S*)-styrene oxide should be incorporated into the polycarbonate. Therefore, the increase in poly(styrene carbonate) enantioselectivity for (*R*)-configuration was ascribed to the preferential configuration inversion occurred at the methine carbon of (*S*)-styrene oxide caused by chiral induction of (1*S*,2*S*)-**1j** (Scheme 13).²⁷ To confirm this assumption, (*S*)-styrene oxide/CO₂ copolymerization was carried out in the presence of binary catalyst based on (1*S*,2*S*)-**1j**. The resulting copolymer has an enantioselectivity of 32% with (*R*)-configuration excess, implying that the reaction proceeded with 66% inversion at the benzyl carbon. Moreover, the chiral environment around the central metal ion significantly influences the regioselectivity of epoxide ring-opening. With complex (*S,S,S*)-**4b** as catalyst, a k_{rel} of 3.3 was observed in the asymmetric copolymerization of CO₂ and

SCHEME 13



SCHEME 14



racemic styrene oxide.²⁷ Upon replacing *racemic* styrene oxide with (*R*)-styrene oxide, the resultant copolymer has an enantioselectivity of 92% with (*R*)-configuration excess, indicative of retaining 96% of the stereochemistry at the methine carbon of (*R*)-styrene oxide incorporated into the polycarbonate.

Because the nucleophilic ring-opening of *meso*-epoxide proceeds with inversion at one of the two chiral centers, the successful asymmetric ring-opening by a chiral catalyst or reagent can give optically active polycarbonates with main-chain chirality containing an (*R,R*)- or (*S,S*)-*trans*-1,2-diol unit. In 1999, Nozaki and co-workers described the first example of the asymmetric copolymerization of CO₂ and cyclohexene oxide using equimolar Et₂Zn and (*S*)- α,α -diphenyl-(pyrrolidin-2-yl)methanol as catalyst, affording polycarbonate with moderate enantioselectivity (30–70% ee).³⁰ Subsequently, the Coates group reported the use of hybrid β -imine-oxazoline zinc catalysts, showing similar enantioselectivity but higher activity and controlled molecular weight.³¹ Although the binary (1*R*,2*R*)-**1b**/PPNCl catalyst could operate very efficiently for this reaction at room temperature, the resultant copolymer showed a relatively low enantioselectivity with a (*S,S*)-configuration.²⁵ Recently,

we designed a series of unsymmetric (salen)Co(III) complexes, and the screening revealed that enantiopure Co(III) complexes **4** and **7** were more effective in the stereospecific copolymerization of CO₂ and cyclohexene oxide, affording highly isotactic poly(cyclohexene carbonate)s up to 96% ee (Scheme 14 and Figure 3B). Notably, this stereoregular copolymer is a typical semicrystalline thermoplastic (*vide infra*).³²

Making Crystalline CO₂ Copolymer

All of the previously reported CO₂-based polycarbonates are amorphous, and their corresponding low thermal deformation resistance makes them difficult to use as structural materials. In a recent study, our group succeeded in synthesizing the first crystalline CO₂-based polymer by highly stereospecific copolymerization of CO₂ and cyclohexene oxide using enantiopure Co(III) catalysts. The stereoregular poly(cyclohexene carbonate) possesses a high melting point (*T_m*) of 215–230 °C and one decomposition temperature of ~310 °C.³²

In a manner reminiscent of poly(lactide), the isotacticity of poly(cyclohexene carbonate) has the critical influence on its crystallinity (Figure 4).³³ It was found that the samples with

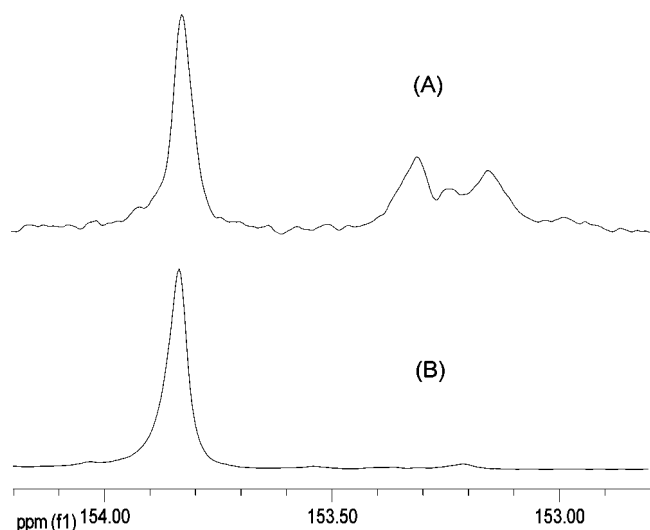


FIGURE 3. Carbonyl region of ¹³C NMR spectra of (A) atactic and (B) highly stereoregular (with 98% isotacticity) poly(cyclohexene carbonate)s.

less than 80% isotacticity did not show any crystallization. The sample (R)-PCHC-92 (RR:SS ratio in the polycarbonate is 92:8) gave a T_g of 122 °C and a very small melting endothermic peak at 207 °C with the melting enthalpy of (ΔH_m) 3.92 J/g, indicating a very low degree of crystallinity. Regarding highly isotactic polymer (R)-PCHC-98 (RR:SS = 98:2), a sharp and high crystallization endothermic peak appears at 216 °C with ΔH_m = 22.50 J/g. Surprisingly, the crystallization endothermic peak of the (R)-PCHC-98/(S)-PCHC-98 (RR:SS = 2:98) blend (1/1 mass ratio) increases to 227 °C with ΔH_m = 29.70 J/g using the same crystallization conditions, indicating that the blend with two opposing configurations forms a stereocomplex with a new and distinct crystalline structure.

Figure 5 shows the wide-angle X-ray diffraction (WAXD) profiles of various poly(cyclohexene carbonate)s. No diffraction was observed for atactic polycarbonate, confirming its amorphous feature. Contrarily, for (R)-PCHC-98 sample, sharp diffraction peaks were observed at 2θ values of 12.2, 17.9, 19.0, and 20.4°, demonstrating that isotactic poly(cyclohexene carbonate) is a typical semicrystalline polymer. Surprisingly, the blend of (S)-PCHC-98/(R)-PCHC-98 (1/1 mass ratio) has different diffraction peaks appearing at 2θ equal to 8.6, 17.9, and 21.5°, while the 2θ values at 12.2, 19.0, and 20.4° have disappeared, indicating that the stereocomplex possesses a new crystalline structure, being different from that of the sole configuration polymer. The unique crystallization behavior was further revealed by atomic force microscopy (AFM) observations (Figure 6). For (S)-PCHC-98, the lamellae or lamellar aggregates preferentially bend anticlockwise. Conversely, a clockwise rotated

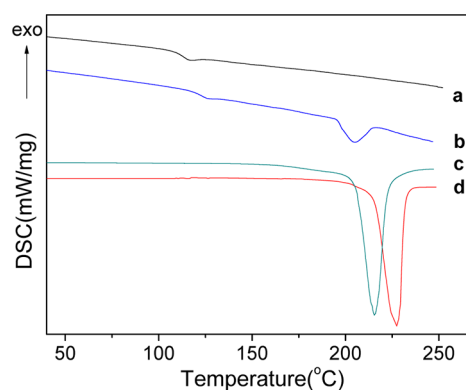


FIGURE 4. DSC thermograms of various poly(cyclohexene carbonate)s: (a) atactic PCHC; (b) (R)-PCHC-92; (c) (R)-PCHC-98; (d) (R)-PCHC-98/(S)-PCHC-98 blend, 1/1 mass ratio.

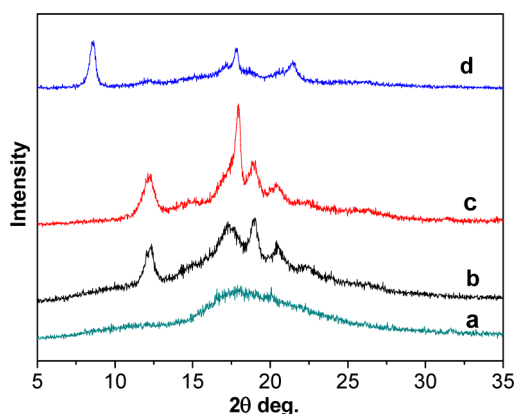


FIGURE 5. WAXD profiles of various poly(cyclohexene carbonate) samples: (a) atactic PCHC; (b) (R)-PCHC-92; (c) (R)-PCHC-98; (d) (R)-PCHC-98/(S)-PCHC-98 blend, 1/1 mass ratio.

spherulite can be clearly observed in (R)-PCHC-98 sample. To our surprise, the morphological feature of the stereocomplex of (S)-PCHC-98/(R)-PCHC-98 (1/1 mass ratio) changes dramatically. Unlike its parent polymers, the stereocomplex presents a lath-like dendritic crystal, which is very different from the bending features observed for both (S)-PCHC-98 and (R)-PCHC-98.

Mechanistic Aspects of Co(III)-Complex-Mediated Formation of CO₂ Copolymers

A detailed mechanistic description on Co(III)-complex catalyzed CO₂/epoxide coupling has been covered in our recent review,³⁴ and will not be duplicated herein. However, we will reiterate some key-points for the integrity of the present Account. To ascertain the role of nucleophilic cocatalyst in binary Co(III)-based catalyst systems, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), a sterically hindered Lewis base with low coordination ability and excellent ion

intensity in ESI-MS, was chosen as cocatalyst in conjunction with complex **1j** for examining the CO₂/propylene oxide copolymerization process.²² A series of polymer chain-growth species based on MTBD were clearly observed in the high-resolution mass spectra, and with time these species moved to the high *m/z* region. The similar tendency was also found in the system of excess MTBD with regard to the cobalt complex, indicating that all MTBD participated in this reaction (Figure 7). This research confirmed that in the copolymerization process MTBD predominately played an initiator role for polymer chain-growth, and the propagating species easily dissociated from the metal center.

Generally, simple (salen)Co(III)X alone as catalyst for CO₂/epoxide copolymerization is easily reduced to inactive Co(II) derivatives, while the addition of a nucleophilic cocatalyst significantly improves its stability and greatly enhances the catalytic activity. For a thorough understanding of the role of the nucleophilic cocatalyst in binary or bifunctional Co(III)-based catalysts, we designed (salen)Co(III)X **2a–c** with an

appending TBD, and performed mechanistic studies using in situ ESI-MS and FT-IR methods.²³ These studies suggested that the initiation involved two carbonate species: (1) at 1750 cm^{−1} assigned to the linear carbonate involving the axial X counterion, and (2) at 1719 cm^{−1} assigned to a TBD-carbonate adduct (Scheme 15). With a low catalyst loading, no propagating polymer-species consistent with the appended-TBD was observed, while only one species of *m/z* 784.5 was clearly detected in the ESI-MS spectra of all samples at various time-points. The species originates from the dissociation of the real species, the TBD-carbonate adduct, due to its low collision dissociation energy and the effect of ESI gas of N₂. The carboxylate intermediate regarding the tethered TBD was proposed to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversibly intramolecular Co–O bond formation and dissociation, which allows copolymer chain-growth to occur at the *trans* position. The cobalt complex with an iminium moiety regarding the appended TBD can maintain the dissociated anion nearby by Coulombic interaction, resulting in higher stabilizing ability and catalytic activity (Scheme 16). The sole initiating anion of the cobalt complex is beneficial for maintaining polymer selectivity and narrow molecular-weight distribution even under highly diluted solution conditions and/or at high reaction temperatures.

Furthermore, combined with the previous ESI-MS studies, we are able to propose a reason for the excellent activities of binary or bifunctional Co(III)-based catalysts. In these

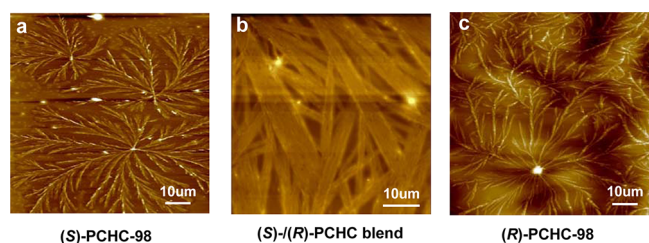


FIGURE 6. AFM height images of (a) (S)-PCHC-98; (b) (R)-PCHC-98/(S)-PCHC-98 blend (1/1 mass ratio); (c) (R)-PCHC-98.

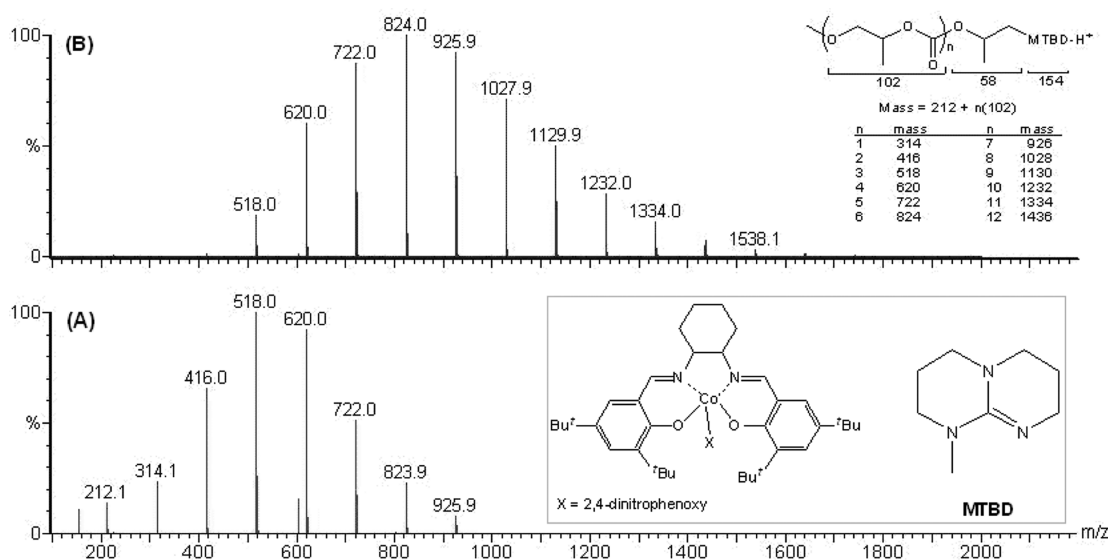
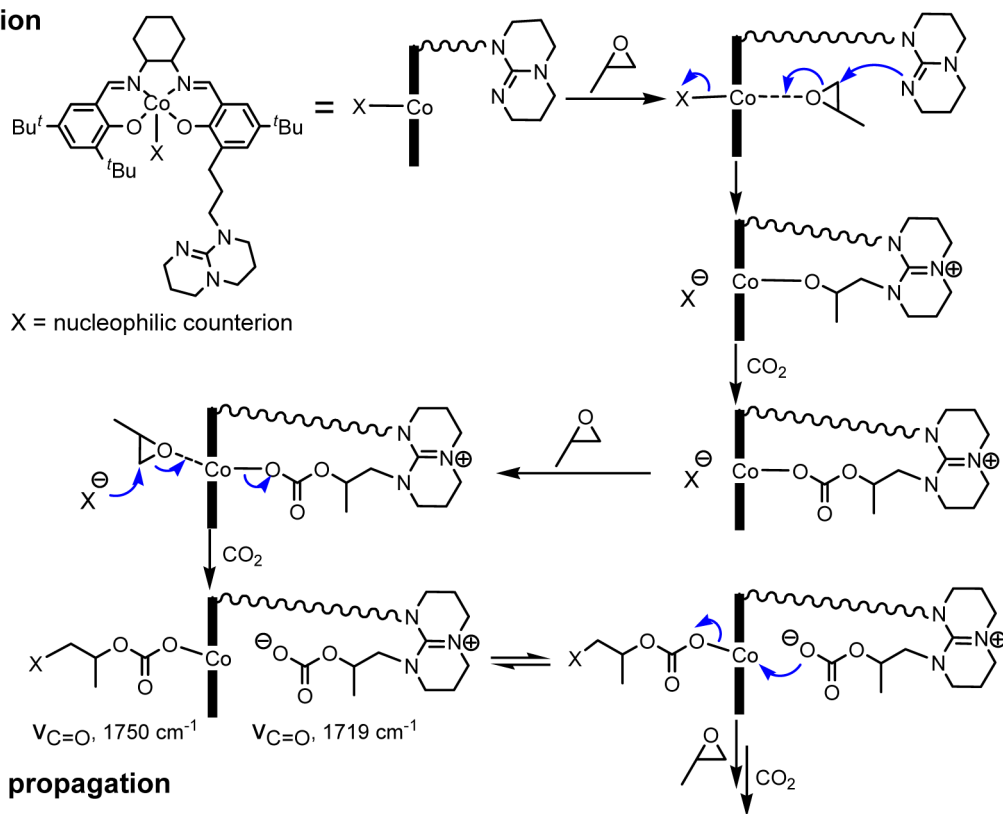


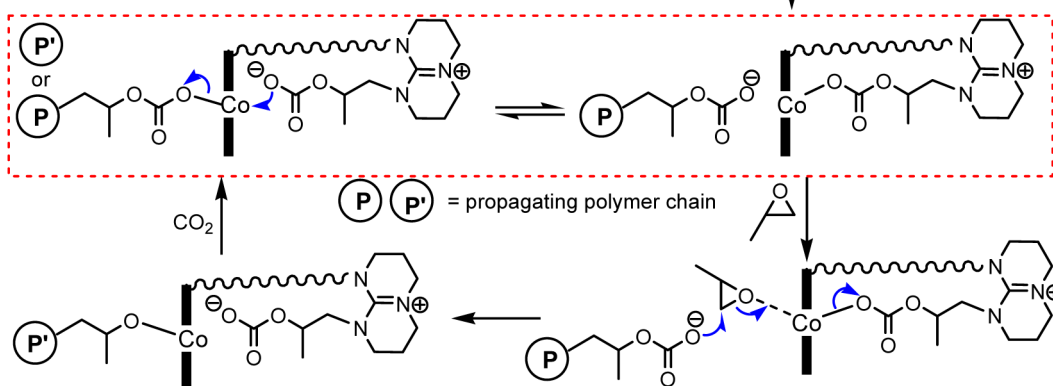
FIGURE 7. ESI-Q-TOF of the reaction mixture resulted from the systems of MTBD/**1j**/propylene oxide (3/1/2000, molar ratio) at 10 °C and 0.6 MPa CO₂ pressure with different time points: (A) 20 min; (B) 30 min.

SCHEME 15

Initiation



Chain propagation



systems, epoxide is activated by coordination to the metal center, and both the nucleophilic counterion and cocatalyst play initiator roles in polymer-chain growth. This mechanism also suggests that the propagating carboxylate anion easily dissociates from the metal center, and the free propagating carboxylate can act as a nucleophile for attack at a cobalt-coordinated epoxide throughout the copolymerization process (Scheme 17). The alternating chain-growth and dissociation of propagating carboxylate species derived from the nucleophilic axial counterion and cocatalyst take turns at both sides of the Co(III)-salen plane. This arrangement significantly increases reaction rate and also helps to stabilize the active Co(III) species against decomposition to

inactive Co(II) even at low CO₂ pressures and/or relatively high temperatures. It is important to note here that being different from the free cocatalyst in the binary systems, the cation of the appended quaternary ammonium salt in bifunctional catalyst **3** keeps the dissociating anionic copolymer growth-chains easily close to the metal center through Coulombic interaction (Scheme 16).

The high activity of the Co(III)-based catalysts originates from (1) the moderate electrophilicity of Co(III) ion being suitable for epoxide activation and the insertion of CO₂ into Co–O bond, which is not a rate-determining step but a fast process, and (2) the facile dissociation of the propagating carboxylate species from the cobalt center.



complexes operate under a mechanism in which the Co(III) complex serves as an electrophile (Lewis acidic metal ion) to activate the epoxide, and the nucleophilic counterion or cocatalyst as a nucleophile to initiate polymer-chain growth. Their high catalytic activity results from the moderate electrophilicity of Co(III) ion being suitable for epoxide activation and the fast insertion of CO₂ into Co–O bond as well as the facile dissociation of propagating carboxylate species from the central metal ion. The reversible intra- or intermolecular Co–O bond formation and dissociation helps to stabilize the active Co(III) species against decomposition to inactive Co(II).

The discovery of the first semicrystalline CO₂-based polycarbonate, highly isotactic poly(cyclohexene carbonate), is a good start to develop a more environmentally benign route for producing polycarbonates with excellent properties. We anticipate further efforts will lead to discoveries of highly stereoregular catalysts and the development of new CO₂-based crystalline polymers with improved thermal and mechanical properties comparable to that of polyolefins. The economical production of CO₂ copolymers capable of crystallization should become an important goal of both academic researchers and polymer manufacturers who focus on biodegradable polymers derived from renewable resources.

Computational methods have been used to study the mechanism of some reactions catalyzed by chiral salen complexes. It is anticipated that this approach will play an increasing important role in understanding the features that account for the unique catalytic performance of the Co(III)-based catalysts for CO₂/epoxide coupling and thus aid in developing new privileged catalysts with a tolerance of trace water and no need to separate from polymeric products. Additionally, it will be greatly welcomed to further broaden the scope of epoxides capable of copolymerizing with CO₂ as well as the terpolymerization with other functional monomers to provide polymers with improved properties competitive with those of the traditional bisphenol-A-derived polycarbonates and some polyolefin products.

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FOOTNOTES

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