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Design of Highly Active Binary Catalyst Systems for CO_2/Epoxide Copolymerization: Polymer Selectivity, Enantioselectivity, and Stereochemistry Control

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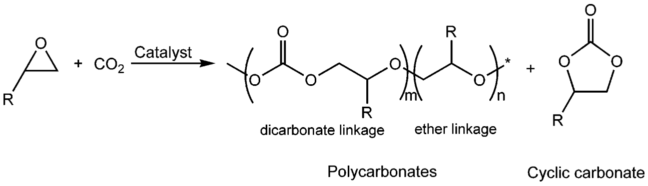
Abstract: Asymmetric, regio- and stereoselective alternating copolymerization of CO_2 and racemic aliphatic epoxides proceeds effectively under mild temperature and pressure by using a binary catalyst system of a chiral tetradentate Schiff base cobalt complex [SalenCo^{III}X] as the electrophile in conjunction with an ionic organic ammonium salt or a sterically hindered strong organic base as the nucleophile. The substituent groups on the aromatic rings, chiral diamine backbone, and axial X group of the electrophile, as well as the nucleophilicity, leaving ability, and coordination ability of the nucleophile, all significantly affect the catalyst activity, polymer selectivity, enantioselectivity, and stereochemistry. A bulky chiral cyclohexenediimine backbone complex [SalcyCo^{III}X] with an axial X group of poor leaving ability as the electrophile, combined with a bulky nuclephile with poor leaving ability and low coordination ability, is an ideal binary catalyst system for the copolymerization of CO_2 and a racemic aliphatic epoxide to selectively produce polycarbonates with relatively high enantioselectivity, $>$95% head-to-tail connectivity, and $>$99% carbonate linkages. A fast copolymerization of CO_2 and epoxides was observed when the concentration of the electrophile or/and the nucleophile was increased, and the number of polycarbonate chains was proportional to the concentration of the nucleophile. Electrospray ionization mass spectrometry, in combination with a kinetic study, showed that the copolymerization involved the coordination activation of the monomer by the electrophile and polymer chain growth predominately occurring in the nucleophile. Both the enantiomorphic site effect resulting from the chiral electrophile and the polymer chain end effect mainly from the bulky nucleophile cooperatively control the stereochemistry of the CO_2/epoxide copolymerization.

Introduction

Scheme 1. Reaction of CO_2 and Aliphatic Epoxides To Form Linear Polycarbonates and Cyclic Carbonates



Conversion of carbon dioxide to desirable, economically competitive products has received much attention because of its potential use as an abundant carbon resource and its indirect role as an environmental pollutant.[1] One of the most promising green reactions in this area is the alternating copolymerization of CO_2 and epoxides to make polycarbonates (Scheme 1),[2] which was first reported by Inoue et al. in the late 1960s.[3] This might provide an alternative to condensation polymerization involving phosgene and diols.[4] These polycarbonates have potential applications as ceramic binders, adhesives, coatings, and packaging materials, as well as in the synthesis of engineering thermoplastics and resins.[5] In recent decades, numerous catalyst systems, including zinc, aluminum, cadmium, manganese, cobalt, chromium, and rare-earth-metal complexes or in combination with other reagents, have been developed for this transformation.[6−13] Although the advances have been significant, high catalyst loading, elevated CO_2 pressure, and long reaction time are usually prerequisites for obtaining appreciable amounts of polymer, which are often not perfectly

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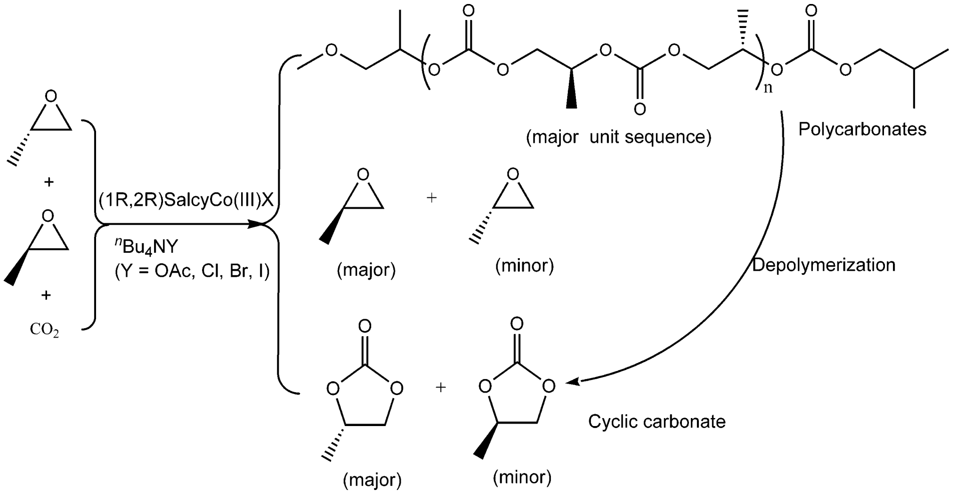
Scheme 2. Direct Synthesis of Optically Active Cyclic PC or Linear PPC from *rac*-PO and CO_2 by a Catalytic Kinetic Resolution Process



alternating and exhibit broad molecular weight distributions. Recently, several efficient catalyst systems associated with discrete zinc-based complexes for the copolymerization of CO_2 and alicyclic epoxides such as cyclohexene oxide (CHO) have been reported that offer significant advantages over traditional heterogeneous catalysts.[14] Unfortunately, these catalysts are much less effective when aliphatic epoxides such as propylene oxide (PO) are employed as substrates; even those which are active generally suffer from the concomitant production of cyclic carbonates. For example, Coates et al. reported on the first highly active zinc β-diiminate catalysts bearing electron-withdrawing groups for the synthesis of poly(propylene carbonate) (PPC) with carbonate linkages up to 99%, but along with the formation of cyclic propylene carbonate (PC) from 7% to 25%.[15] Simply reducing the reaction temperature and increasing the CO_2 pressure suppressed the formation of PC and increased the selectivity for PPC. A similar effect has been observed in the systems of chiral Salen chromium chloride alone or in conjunction with *N*-methylimidazole (*N*-MeIm) or 4-(dimethylamino)-pyridine (DMAP) as catalysts for this reaction.[16] Stimulated by the ground-breaking work of Jacobsen and co-workers, who employed chiral SalcyCo^{III} complexes for the asymmetric ring-opening and kinetic resolution of aliphatic epoxides,[17] our group has proposed a convenient route to optically active cyclic carbonates by a catalytic kinetic resolution process resulting from the coupling reaction of CO_2 and racemic epoxides (Scheme 2) using simple chiral SalcyCo^{III}X/quaternary ammonium halide catalyst systems.[18] During our optimization studies of this process, we unexpectedly found that simple changes in the axial X group of chiral SalcyCo^{III}X and the anion of quaternary ammonium salts drastically affect the polymer/cyclic product selectivity. It seems that the use of a cobalt complex with an electron-withdrawing axial X group and a quaternary ammonium salt, the anion of which having low leaving ability, is more beneficial for increasing the selectivity for polycarbonates.[19] Notably, these resulting polymers not only show completely alternating nature, but also have an unprecedented head-to-tail content of >95%, which is in contrast to polymers made using zinc glutarate (~60% head-to-tail linkages) and (BDI)ZnOAc (~54% head-to-tail linkages).[15,20] However, the mechanism involving the real active species and polymer stereochemistry control is not clear. Prior to our work, Coates et al. reported the use of chiral cobalt complexes alone as catalysts for CO_2/racemic PO (*rac*-PO) copolymerization, and ~80% head-to-tail linkages was observed in the resulting

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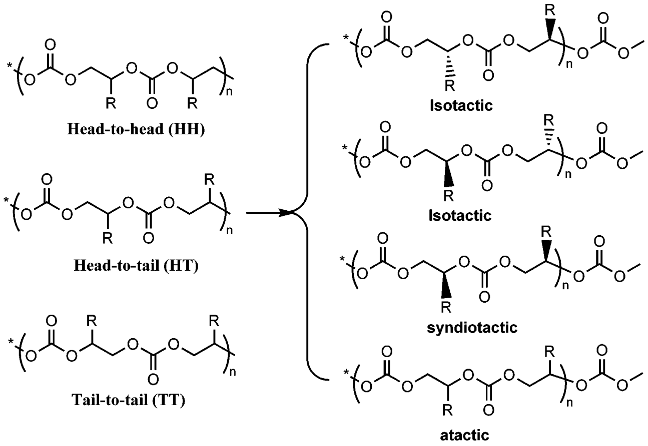
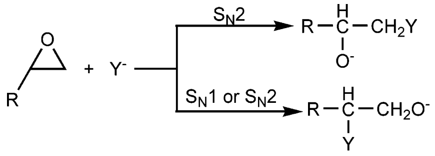


Figure 1. Regio- and stereochemistry of polycarbonates.

Scheme 3. Nucleophilic Ring-Opening Mechanisms of the Aliphatic Epoxides



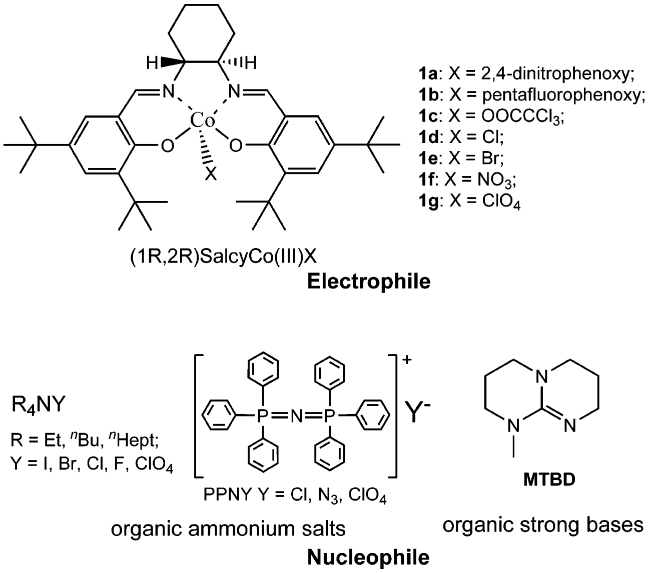


Figure 2. Binary electrophile−nucleophile catalyst systems for CO_2/*rac*-PO copolymerization.

polymer, but these complexes are inactive at low CO_2 pressure.[21] More recently, they further discovered the synthesis of syndio-enriched PPC generated from *rac*-PO/CO_2 with the catalyst *rac*-SalcyCoBr.[22]

On the other hand, the simultaneous control of the polymer chain length and relative stereochemistry remains an important goal in polymerization catalysis.[23] For CO_2/aliphatic epoxide copolymerization, there exists much interesting information, such as the polymer/cyclic product selectivity, ether and dicarbonate linkages, regiochemistry of epoxide ring-opening (Scheme 3), and stereochemistry of the carbonate unit sequence in a polymer (Figure 1), which bears a memory of the reaction pathway leading to its formation.[24]

Herein, we will describe the design principle of highly active binary catalyst systems for CO_2/epoxide copolymerization by outlining optimized systems and elucidate fully the synthetic potential of this reaction by establishing its substrate scope. Continuous determination of a polymer chain end group (initiating and chain growth species) at various times was first achieved by in situ electrospray ionization mass spectrometry (ESI-MS), which in combination with a kinetic study gave us an insight into the mechanistic understanding of CO_2/epoxide copolymerization in the presence of a binary electrophile−nucleophile catalyst system.

Results and Discussion

Alternating Copolymerization of *rac*-PO and CO_2 with Binary Electrophile−Nucleophile Catalyst Systems. Although (1*R*,2*R*)-SalcyCoX (X = OAc, Br, Cl) complexes with a nucleophilic axial X group could catalyze the copolymerization of CO_2 and PO to yield PPC with high selectivity and ∼80% head-to-tail linkages at a very high CO_2 pressure of up to 800 psig (∼5.5MPa),[21,22] these cobalt complexes were proved to be inactive at low CO_2 pressure or at elevated temperature (∼50 °C) and unexpectedly reduced to Co(II) derivatives as a red solid precipitate, which were ineffective in producing the copolymer. On the contrary, some (1*R*,2*R*)-SalcyCoX complexes with a low nucleophilic or/and sterically hindered axial X group (such as ClO_4^-, NO_3^-, 2,4-dinitrophenoxy, etc.) alone cannot catalyze this reaction. However, in the presence of a quaternary ammonium halide, all soluble SalcyCo^{III}X complexes exhibited unprecedented activity and increased regio- and stereoselectivity of ∼95% head-to-tail linkages for the resulting PPC, even at a 0.2 MPa CO_2 pressure.[19] Our further research found that most nucleophiles in connection with any of the (1*R*,2*R*)-SalcyCoX complexes (Figure 2) could effectively catalyze the coupling of CO_2 and PO at extremely mild conditions. Also, these binary catalyst systems based on chiral (1*R*,2*R*)-SalcyCoX complexes all preferentially consume (*S*)-PO over (*R*)-PO with $K_{rel} = 1.9-5.5$ (Tables 1 and 2). Interestingly, the properties of the nucleophile, such as nucleophilicity, coordination, and leaving ability, significantly affect the catalytic activity and polymer selectivity, as well as the enantioselectivity and stereochemistry of the resulting polymer.

With ionic ammonium salts as the cocatalyst, both the anion and cation of the ionic salt influence the *rac*-PO/CO_2 copolymerization (Table 1). Anions with higher nucleophilicity and better leaving ability, such as I^-, Br^-, and N_3^-, are beneficial for improving the activity of the binary catalyst system, but have a negative effect on the selectivity for PPC. The use of a nucleophilic anion with poor leaving ability, such as Cl^- and F^-, can effectively suppress cyclic PC formation and increase the selectivity for the polymer as well as the enantioselectivity of the resulting PPC, while decreasing the catalytic activity to a certain extent. In contrast, if the anion of the used ionic ammonium salt has no nucleophilicity, the binary catalyst system is found to be ineffective for this reaction (entries 5 and 11). Surprisingly, the cation of the ionic organic salt also significantly affects the *rac*-PO/CO_2 copolymerization in reaction rate and PPC enantioselectivity. For example, ^{n}Hept$_4$NBr substituted for Et$_4$NBr with complex **1a** results in a TOF from 156 h^{-1}

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Table 1. Effect of the Nucleophile: *rac*-PO/CO_2 Copolymerization Catalyzed by Complex **1a** Combined with Various Nucleophiles[a]

entry	cocatalyst	time (h)	TOF[b] (h^{-1})	selectivity[c] (% PPC)	carbonate linkages[c] (%)	head-to-tail linkages[d] (%)	M_n[e]	PDI[e] (M_w/M_n)	ee[f] (%)	K_{rel}[g]
1	^{n}Bu$_4$NI	3.0	243	63	>99	94	15900	1.32	39.8	2.9
2	^{n}Bu$_4$NBr	3.0	291	74	>99	94	20400	1.35	43.5	3.5
3	^{n}Bu$_4$NCl	3.0	249	99	>99	95	25700	1.24	51.6	4.2
4	^{n}Bu$_4$NF	3.0	97	99	>99	95	10900	1.27	63.5	4.6
5	^{n}Bu$_4$NClO$_4$	10.0	<5							
6	Et$_4$NBr	3.0	156	65	>99	94	10400	1.25	46.7	3.2
7	^{n}Hept$_4$NBr	3.0	314	74	>99	95	19600	1.29	53.1	4.4
8	18-crown-6/KI	3.0	182	41	>99	92	4700	1.43	27.6	1.9
9	(PPN)Cl	1.5	530	>99	>99	96	30900	1.20	54.2	4.7
10	(PPN)N$_3$	1.5	554	96	>99	94	29200	1.21	51.9	4.5
11	(PPN)ClO$_4$	3.0	<5							

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; **1a**:cocatalyst:PO = 1:1:2000, molar ratio) in a 75 mL autoclave at 25 °C and a 1.5 MPa CO_2 pressure. [b] Turnover frequency of PO to products (polycarbonate and cyclic carbonate). [c] Determined by using ^{1}H NMR spectroscopy. [d] Determined by using ^{13}C NMR spectroscopy. [e] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [f] Based on the enantiomeric excess of cyclic PC given after complete degradation of PPC. [g] $K_{rel} = \ln[1 - c(1 + ee)]/\ln[1 - c(1 - ee)]$, where c is the conversion and ee is the enantiomeric excess of the resulting PPC based on the value of PC after degradation.

Table 2. Alternating Copolymerization of *rac*-PO and CO_2 Catalyzed by **1a**/Lewis Base Systems[a]

entry	cocatalyst	time (h)	TOF (h^{-1})	M_n	PDI (M_w/M_n)	ee (%)	K_{rel}
1	MTBD	1	75	6900	1.22	68.9	5.6
2	MTBD	2	77	12300	1.16	68.3	5.6
3	MTBD	3	73	18400	1.15	67.2	5.5
4	MTBD	5	69	31300	1.18	66.5	5.7
5	*N*-MeIm	5	<5				

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; **1a**:cocatalyst:PO = 1:1:2000, molar ratio) in a 75 mL autoclave at 25 °C and a 0.6 MPa CO_2 pressure. Entries 1−4: Both the selectivity for PPC over cyclic PC and carbonate linkages of the resulting PPC are ≥99%, determined by using ^{1}H NMR spectroscopy. Other notes are the same as those for Table 1.

Table 3. Effect of the Coordination Agent: *rac*-PO/CO_2 Copolymerization Catalyzed by Complex **1a** Combined with Various Nucleophiles[a]

entry	cocatalyst	coordination agent (amt, equiv)	time (h)	TOF (h^{-1})	selectivity (% PPC)	M_n	PDI (M_w/M_n)
1	MTBD	*N*-MeIm (1.0)	4	9	0		
2	MTBD	*N*-MeIm (2.0)	4	0			
3	^{n}Bu$_4$NCl	H$_2$O (2.0)	4	118	88	7200	1.39
4	^{n}Bu$_4$NCl	H$_2$O (10.0)	4	54	5		
5	(PPN)Cl	*N*-MeIm (2.0)	3	<5	0		
6	(PPN)Cl	*N*-MeIm (0.5)	3	229	93	11800	1.61

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; **1a**:cocatalyst:PO = 1:1:2000, molar ratio) in a 75 mL autoclave at 25 °C and a 1.5 MPa CO_2 pressure. Other notes are the same as those in Table 1.

increasing to 314 h^{-1} and a K_{rel} from 3.2 to 4.4 (entries 6 and 7). Similar increases in activity and enantioselectivity also occur in the substitution of (PPN)Cl {PPN = bis(triphenylphosphine)-iminium} for ^{n}Bu$_4$NCl or ^{n}Bu$_4$NI for the 18-crown-6/KI complex as the cocatalyst.[25] In general, an ionic ammonium salt consisting of a bulky cation and a nucleophilic anion with poor leaving ability as the cocatalyst is more beneficial for improving the activity, polymer selectivity, and enantioselectivity.

We were gratified to discover that sterically hindered strong organic bases, such as 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) (Figure 2), combined with complex **1a** also effectively catalyzed the *rac*-PO/CO_2 copolymerization to selectively form PPC with improved enantioselectivity (Table 2).[26] Also, the resulting PPC has a narrow molecular weight distribution and a high head-to-tail content of up to 96%. A prolonged reaction time resulted in a linear increase in the polymer molecular weight, consistent with a controlled polymerization, and M_n values close to the expected values, which indicates a living polymerization nature. The results are different from those of the binary system with an ionic ammonium salt as the cocatalyst, in which unexpected chain transfer appears during the reaction. Surprisingly, with replacement of MTBD with a nonsterically hindered strong organic base, such as *N*-MeIm, the resulting binary system was found to be inactive (entry 5). As anticipated, in the presence of *N*-MeIm, the MTBD/**1a** system shows no or very low activity for this reaction (Table 3, entries 1 and 2). These results are not in agreement with the SalenCr^{III}Cl/*N*-MeIm system reported by Darensbourg group.[16] The difference only in the central metal ion in the two similar catalyst systems resulting in a contrary tendency indicates different reaction pathways for CO_2/epoxide copolymerization. We further found that, in the presence of any coordination agent such as water, all binary catalyst systems show substantial losses in activity, polymer selectivity, and molecular weight (entries 3−6).

It is interesting that the molar ratio of MTBD to **1a** in the binary catalyst system significantly affects the reaction rate and polymer molecular weight, rather than the polymer selectivity and molecular weight distribution, enantioselectivity, and stereochemistry of the resulting polymer (Table 4, entries 1−3). Increasing the ratio results in an unexpected decrease in the polymer molecular weight, but has a pronounced positive effect on the rate. It is worthy of note that the number of PPC chains is independent of the initial cobalt complex concentration but is only determined by the MTBD concentration. This finding suggests that MTBD should play an important role in polymer chain growth during the reaction. For the binary (PPN)Cl/**1a** system, increasing the ratio of the ionic ammonium salt to **1a** also increases the rate, but causes a substantial decrease in the polymer molecular weight and the concomitant formation of cyclic PC to a certain extent (entries 4−6).

It is generally known for CO_2/epoxide copolymerization that elevated CO_2 pressure benefits suppressing the formation of cyclic carbonate and increasing the selectivity for the polymer.

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(25) During the course of our work, Coates et al. reported that (*R*,*R*)-SalcyCoOBzF$_5$ (OBzF$_5$ = pentafluorobenzoate) in combination with (PPN)-Cl showed very high activity for CO_2/PO copolymerization; see ref 22.

(26) More recently, the Nguyen group reported a binary system of the (*R*,*R*)-SalenCo^{III} complex combined with *N*,*N*-dimethylaminoquinoline (DMAQ) as the catalyst for the copolymerization of CO_2 and PO: Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251−6253.

Table 4. Effect of the Cocatalyst Concentration: *rac*-PO/CO_2 Copolymerization Catalyzed by Complex **1a**/(PPN)Cl and Complex **1a**/MTBD Systems[a]

entry	cocatalyst	cocatalyst amt (equiv)	pressure (MPa)	time (h)	TOF (h^{-1})	selectivity (% PPC)	head-to-tail linkages (%)	M_n	PDI (M_w/M_n)	K_{rel}
1	MTBD	1	0.6	2	77	>99	96	12300	1.16	5.6
2	MTBD	2	0.6	2	152	>99	96	12800	1.20	5.6
3	MTBD	4	0.6	2	205	>99	96	9700	1.24	5.9
4	(PPN)Cl	1	1.5	1	504	>99	96	20300	1.16	4.7
5	(PPN)Cl	2	1.5	1	770	97	96	14100	1.28	4.9
6	(PPN)Cl	4	1.5	1	844	91	95	7400	1.33	4.9

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; **1a**:PO = 1:2000, molar ratio) in a 75 mL autoclave at 25 °C. All resulting PPC contains ≥99% carbonate linkages as determined by ^1H NMR spectroscopy. Other notes are the same as those in Table 1.

Table 5. Effects of Reaction Pressure and Temperature: *rac*-PO/CO_2 Copolymerization Catalyzed by Complex **1a**/(PPN)Cl and Complex **1a**/MTBD Systems[a]

entry	cocatalyst (amt, equiv)	temp (°C)	pressure (MPa)	time (h)	TOF (h^{-1})	selectivity (% PPC)	head-to-tail linkages (%)	M_n	PDI (M_w/M_n)	K_{rel}
1	(PPN)Cl (1)	25	1.5	1.5	530	>99	96	30900	1.20	4.7
2	(PPN)Cl (1)	25	0.1	3.0	175	98	96	18200	1.12	4.6
3	(PPN)Cl (1)	35	2.0	1.0	940	99	92	31600	1.14	4.4
4	(PPN)Cl (1)	45	2.0	0.7	1400	97	89	25900	1.08	4.3
5	MTBD (2)	25	0.6	2.0	152	>99	96	12800	1.20	5.6
6	MTBD (2)	25	0.1	4.0	75	>99	96	13400	1.18	5.1
7	MTBD (2)	0	0.6	15.0	22	>99	96	14300	1.19	6.2
8	MTBD (2)	35	0.6	2.0	223	>99	94	19200	1.18	5.1
9	MTBD (2)	60	2.0	1.0	518	98	91	19100	1.17	4.7

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; **1a**:PO = 1:2000, molar ratio) in a 75 mL autoclave at 25 °C. All resulting PPC contains ≥99% carbonate linkages as determined by ^1H NMR spectroscopy. Other notes are the same as those in Table 1.

Table 6. Effect of the Axial X Group of the Cobalt Complexes: *rac*-PO/CO_2 Copolymerization Catalyzed by (1*R*,2*R*)-SalcyCoX in Conjunction with (PPN)Cl or MTBD[a]

entry	catalyst	cocatalyst	TOF (h^{-1})	selectivity (% PPC)	head-to-tail linkages (%)	M_n	PDI (M_w/M_n)	ee (%)	K_{rel}
1	**1a**	(PPN)Cl	530	>99	96	30900	1.20	54.2	4.7
2	**1b**	(PPN)Cl	545	>99	96	24800	1.17	53.0	4.6
3	**1c**	(PPN)Cl	568	>99	96	28100	1.14	54.5	5.0
4	**1d**	(PPN)Cl	427	>99	95	21500	1.16	52.6	4.1
5	**1e**	(PPN)Cl	450	88	95	18700	1.22	46.2	3.4
6	**1f**	(PPN)Cl	434	>99	96	28000	1.16	56.1	4.6
7	**1g**	(PPN)Cl	<5						
8[b]	**1g**	(PPN)Cl	432	>99	95	22100	1.20	53.4	4.2
9	**1d**	MTBD	72	>99	95	32900	1.19	62.6	5.0
10	**1 g**	MTBD	61	>99	90	29500	1.17	63.0	4.9

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; catalyst:cocatalyst:PO = 1:1:2000, molar ratio) in a 75 mL autoclave at 25 °C and a 1.5 MPa CO_2 pressure. Polymerization time: 1.5 h for entries 1−8 and 5.0 h for entries 9 and 10. All resulting PPC contains ≥99% carbonate linkages as determined by ^1H NMR spectroscopy. Other notes are the same as those in Table 1. [b] In the presence of 2 equiv of (PPN)Cl.

We were delighted to find that the binary catalyst system of complex **1a** with MTBD or (PPN)Cl can operate very efficiently at a low temperature of 0 °C and with CO_2 at atmospheric pressure (Table 5). To the best of our knowledge, it is the first example of *rac*-PO/CO_2 copolymerization under an atmospheric pressure of CO_2 with excellent activity, high polymer selectivity, >99% carbonate linkages, and >95% head-to-tail linkages. An increase in the temperature between 0 and 60 °C results in a dramatic increase in activity, but the variation of temperature or CO_2 pressure does not lead to an observable decrease in selectivity for PPC formation (entries 7 and 9). A change in the reaction temperature from 25 to 60 °C only causes slight decreases in the enantioselectivity and microstructure of the resulting polymer (Figure 3).

Indeed, the structure of the electrophile—SalcyCoX—also significantly affects the catalytic activity and polymer selectivity, as well as the enantioselectivity and stereochemistry of the resulting polymer (Table 6). The nucleophilicity and leaving ability of the axial X group of SalcyCoX have similar influences on the *rac*-PO/CO_2 copolymerization process. It seems that the use of a nucleophilic axial X group with poor leaving ability can effectively suppress cyclic PC formation and increase the selectivity for the polymer as well as the enantioselectivity of the resulting PPC. In the presence of 1 equiv of (PPN)Cl, replacement of **1a** with **1b** or **1c** has little effect on the reaction rate, while with replacement with **1g** results in a complete loss in activity (entry 7). Interestingly, if the loading of (PPN)Cl is increased to 2 equiv while 1 equiv of **1g** is maintained (entry 8), the system shows activity similar to that of the binary **1d**/(PPN)Cl system. However, if the loading of complex **1g** is increased, the binary system gradually losses its activity. We suspect that complex **1g** easily reacts with (PPN)Cl to predominately form **1d** and (PPN)ClO_4, due to the high leaving ability of the nonnucleophilic ClO_4^- anion.

For the binary systems with MTBD as the cocatalyst, the situation is very different. In the presence of MTBD, the SalcyCoX complexes as illustrated in Figure 2 all show a certain activity, and there is no obvious trend in the relationship between

Table 7. Effects of the Chiral Diamine Backbone and Substituent Groups on the Aromatic Rings of the Cobalt Complexes: *rac*-PO/CO_2 Copolymerization Catalyzed by the (1*R*,2*R*)-SalenCo•$OOCCCl_3$/(PPN)Cl System[a]

entry	catalyst	time (h)	TOF (h^{-1})	selectivity (% PPC)	head-to-tail linkages (%)	M_n	PDI (M_w/M_n)	ee (%)	K_{rel}
1	**1c**	1.5	568	>99	96	28100	1.14	54.5	5.0
2	**2c**	2.0	233	>99	95	16300	1.17	35.4	2.3
3	**3c**	2.0	328	>99	95	25400	1.14	14.6	1.4
4	**4c**	1.5	549	>99	96	30100	1.15	48.0	3.9
5	**5c**	2.0	235	>99	96	15500	1.18	57.7	4.4
6	**6c**	10.0	48	97	89	9600	1.22	41.9	2.8

[a] The reaction was performed in neat *rac*-PO (14 mL, 200 mmol; catalyst:(PPN)Cl:PO = 1:1:2000, molar ratio) in a 75 mL autoclave at 25 °C and a 1.5 MPa CO_2 pressure. All resulting PPC contains ≥99% carbonate linkages as determined by ^1H NMR spectroscopy. Other notes are the same as those in Table 1.

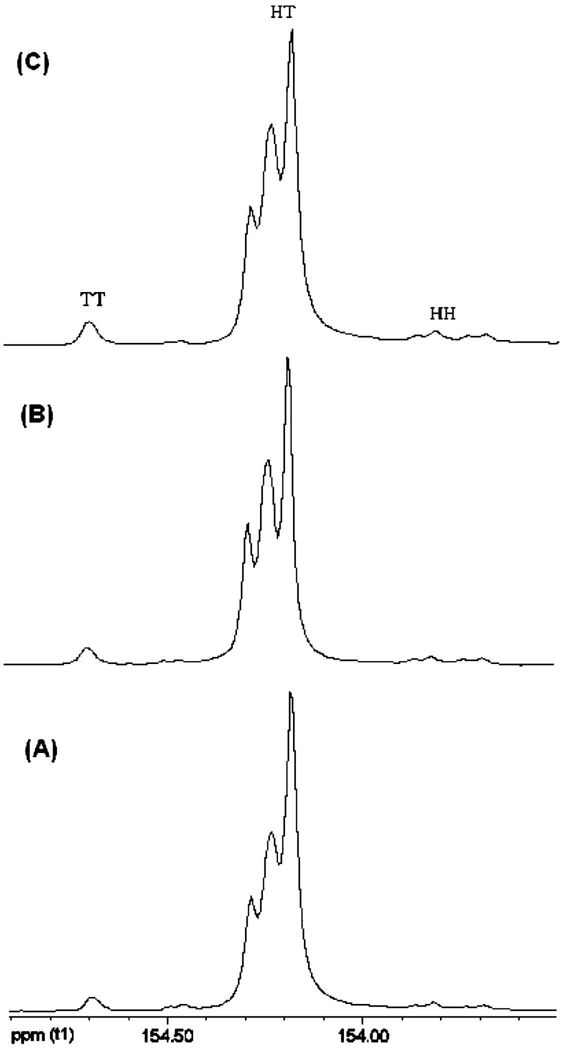
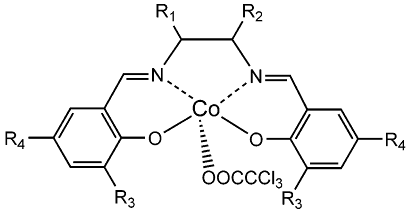


Figure 3. Carbonyl region of the ^{13}C NMR spectra of PPC obtained at various temperatures with the **1a**/MTBD binary system: (A) 25, (B) 45, and (C) 60 °C.

the catalyst activity and the axial X group, even for the nonnucleophilic ClO_4^- anion with a high leaving ability (entries 9 and 10). However, a relatively low head-to-tail linkage was observed in the PPC obtained from the **1g**/MTBD system as compared with the **1a**/MTBD system.

With (PPN)Cl as the cocatalyst, several $SalenCo^{III}OOCCl_3$ complexes with varying chiral diamine backbones and substituent groups on the aromatic rings (Figure 4) were investigated as the catalyst for CO_2/*rac*-PO copolymerization (Table 7). For the same axial X group, changing the Salen ligand framework to a noncyclic diamine backbone had no observable effect on the polymer head-to-tail linkages, but resulted in significant decreases in the catalyst activity and polymer enantioselectivity. A K_{rel} of 5.0 was obtained with the (1*R*,2*R*)-cyclohexyl backbone, whereas the (1*R*,2*R*)-diphenyl and (*R*)-propyl backbones of catalysts **2c** and **3c** gave K_{rel} values of only 2.3 and 1.4, respectively (entries 1−3). With the (1*R*,2*R*)-cyclohexyl backbone, substitution of H for the ^{t}Bu group on the 5-position of the aromatic rings had little effect on the catalyst activity, but caused a decrease in the polymer enantioselectivity (entry 4), while the substitution on the 3-position resulted in significant decreases in the activity, polymer enantioselectivity, and head-to-tail linkages (entry 6). Also, it was found that electron-withdrawing substituents on the aromatic rings (complex **5c**) led to decreased activity for CO_2/PO copolymerization.



2c: (*1R,2R*)-trans, $R_1 = R_2 =$ Ph, $R_3 = R_4 = {}^t$Bu;
3c: $R_1 =$ (*R*)-CH_3, $R_2 =$ H; $R_3 = R_4 = {}^t$Bu;
4c: R_1 and $R_2 =$ (*1R,2R*)-trans-$(CH_2)_4$-, $R_3 = {}^t$Bu, $R_4 =$ H;
5c: R_1 and $R_2 =$ (*1R,2R*)-trans-$(CH_2)_4$-, $R_3 = {}^t$Bu, $R_4 =$ Br;
6c: R_1 and $R_2 =$ (*1R,2R*)-trans-$(CH_2)_4$-, $R_3 =$ H, $R_4 = {}^t$Bu

Figure 4. Tetradentate Schiff base cobalt complexes with varying chiral diamine backbones and substituent groups on the aromatic rings.

In summary, for binary catalyst systems of a chiral tetradentate Schiff base cobalt complex [$SalenCo^{III}X$] as the electrophile in conjunction with an ionic organic salt or a sterically hindered strong base as the nucleophile, the substituent groups on the aromatic rings, chiral diamine backbone, and axial X group of the electrophile, as well as the nucleophilicity, leaving ability, and coordination ability of the nucleophile all significantly affect the catalyst activity, polymer selectivity, enantioselectivity, and stereochemistry (Figure 5). Generally, a bulky chiral $SalcyCo^{III}X$ with an axial X group of poor leaving ability as the electrophile, in conjunction with a bulky ionic ammonium salt consisting of a bulky cation and a nucleophilic anion with poor leaving ability as the nucleophile, composes the ideal binary catalyst system for CO_2/*rac*-PO copolymerization to selectively produce PPC with excellent activity, relatively high enantioselectivity, >95% head-to-tail connectivity, and >99% carbonate linkages. A sterically hindered strong organic base with low coordination ability (also a bulky nucleophile) and a bulky electrophile of chiral $SalcyCo^{III}X$ compose the ideal binary catalyst system for

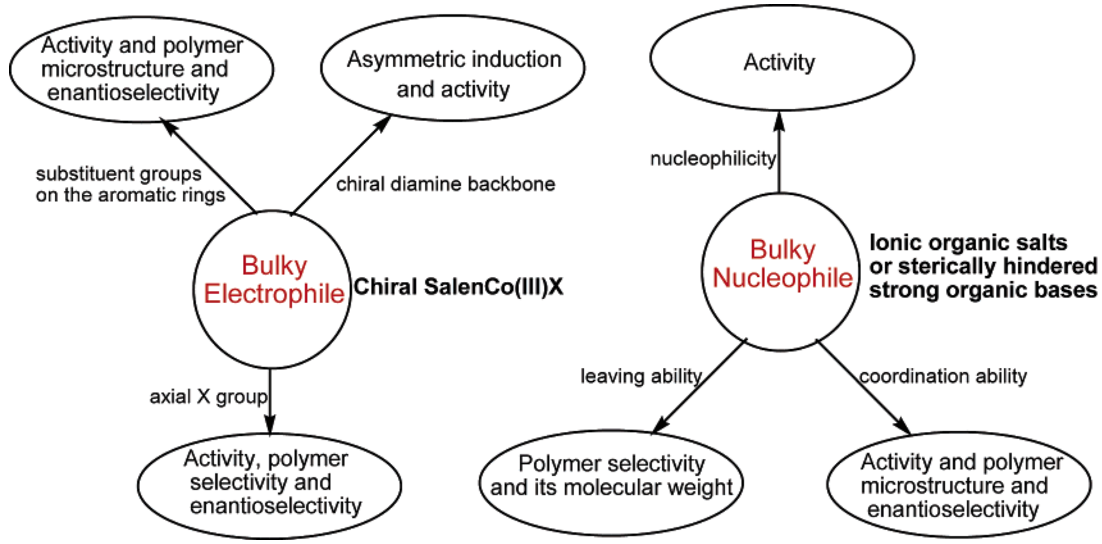


Figure 5. Effects of the electrophile and the nucleophile of the binary catalyst system on the CO_2/*rac*-PO copolymerization.

Table 8. Alternating Copolymerization of Various Epoxides and CO_2 with the **1a**/(PPN)Cl System[a]

entry	epoxide	catalyst:epoxide molar ratio	temp (°C)	time (h)	TOF (h^{-1})	selectivity (% polymer)	carbonate linkages (%)	M_n	PDI (M_w/M_n)
1	1,2-BuO[b]	1:1500	25	3.0	196	99	>99	14400	1.23
2	1,2-HO[c]	1:500	40	3.0	75	98	99	8200	1.28
3	1,2-OctO[d]	1:500	40	4.0	41	97	98	5100	1.19
4	CHO[e]	1:1000	25	4.0	85	>99	99	16600	1.25
5	CHO[f]	1:1000	40	1.5	298	>99	99	18300	1.20

[a] The reaction was performed in neat epoxide (100 mmol; catalyst:(PPN)Cl = 1:1, molar ratio) in a 75 mL autoclave at a 1.5 MPa CO_2 pressure. Other notes are the same as those in Table 1. [b] 1,2-Butene oxide. [c] 1,2-Hexene oxide. [d] 1,2-Octene oxide. [e] CHO = cyclohexene oxide; ee = 36.6%, measured by hydrolyzing the poly(cyclohexene carbonate) and analyzing the resultant diol by chiral GC. [f] ee = 33.9%.

CO_2/*rac*-PO asymmetric living copolymerization with improved enantioselectivity.

Alternating Copolymerization of Other Epoxides and CO_2 with a Binary Catalyst System. Chiral SalcyCo^{III}X in conjunction with an ionic organic salt is also a highly efficient catalyst system for the copolymerization of CO_2 and various terminal epoxides with a long aliphatic chain under solvent-free conditions. The longer the aliphatic chain of the epoxide, the slower the CO_2/epoxide copolymerization proceeds. The binary **1a**/(PPN)Cl system was applicable to the copolymerization of CO_2 with various aliphatic epoxides to provide the corresponding optically active polycarbonates (Table 8, entries 1−3). All the isolated polymers have a narrow molecular weight distribution and ≥98% carbonate linkages. Of importance, the ^{13}C NMR spectra in the carbonyl region show that these polycarbonates all have an unprecedented head-to-tail content of >98% (See the Supporting Information, Figure 20).

Copolymerization of CO_2 and an alicyclic epoxide such as CHO is usually carried out at elevated temperature, and has great selectivity for polycarbonate formation due to the increased strain in forming the five-membered carbonate ring imposed by the conformation of the alicyclic group.[27] Because the ring-opening of a *meso*-epoxide proceeds with inversion at one of the two chiral centers, a successful asymmetric ring-opening by a chiral catalyst can give optically active polycarbonates with an (*R*,*R*)- or (*S*,*S*)-*trans*-1,2-diol unit. On the basis of this idea, Nozaki and co-workers first reported the asymmetric synthesis catalyzed by Et_2Zn−chiral amino alcohol to produce optically active poly[cyclohexene oxide-*alt*-CO_2] of ∼70% ee,[28] and then the Coates group reported the use of a well-defined chiral Zn−imine oxazoline complex as the catalyst for this reaction, which showed similar enantioselectivity, but higher activity and controlled molecular weight.[29] We were gratified to discover that the binary system of **1a**/(PPN)Cl could operate very efficiently at ambient temperature for CHO/CO_2 copolymerization to provide optically active polycarbonates with >99% carbonate linkages (Supporting Information, Figure 21). Entries 4 and 5 in Table 8 show the strong influence of reaction temperature on the rate. An increase in the temperature from 25 to 40 °C resulted in a TOF from 85 h^{-1} rapidly increasing to 298 h^{-1} and a polymer enantioselectivity from 36.6% ee slightly decreasing to 33.9% ee, respectively.

Mechanism of the Copolymerization of CO_2 and Epoxides catalyzed by the Binary Electrophile−Nucleophile System. Recently, an elegant mechanistic study on the stereochemistry and kinetics of the initial ring-opening event of PO has been conducted in the copolymerization of CO_2 and PO catalyzed by porphyrin and Salen complexes of Al(III) and Cr(III) alone or in the presence of a Lewis base cocatalyst.[24] Prior to this study, Darensbourg and co-workers performed elegant kinetics studies on the copolymerization of CO_2 and epoxides catalyzed by binary SalenCr^{III}X (X = Cl^-, N_3^-)/Lewis base (such as *N*-MeIm) systems, and proposed a copolymerization mechanism

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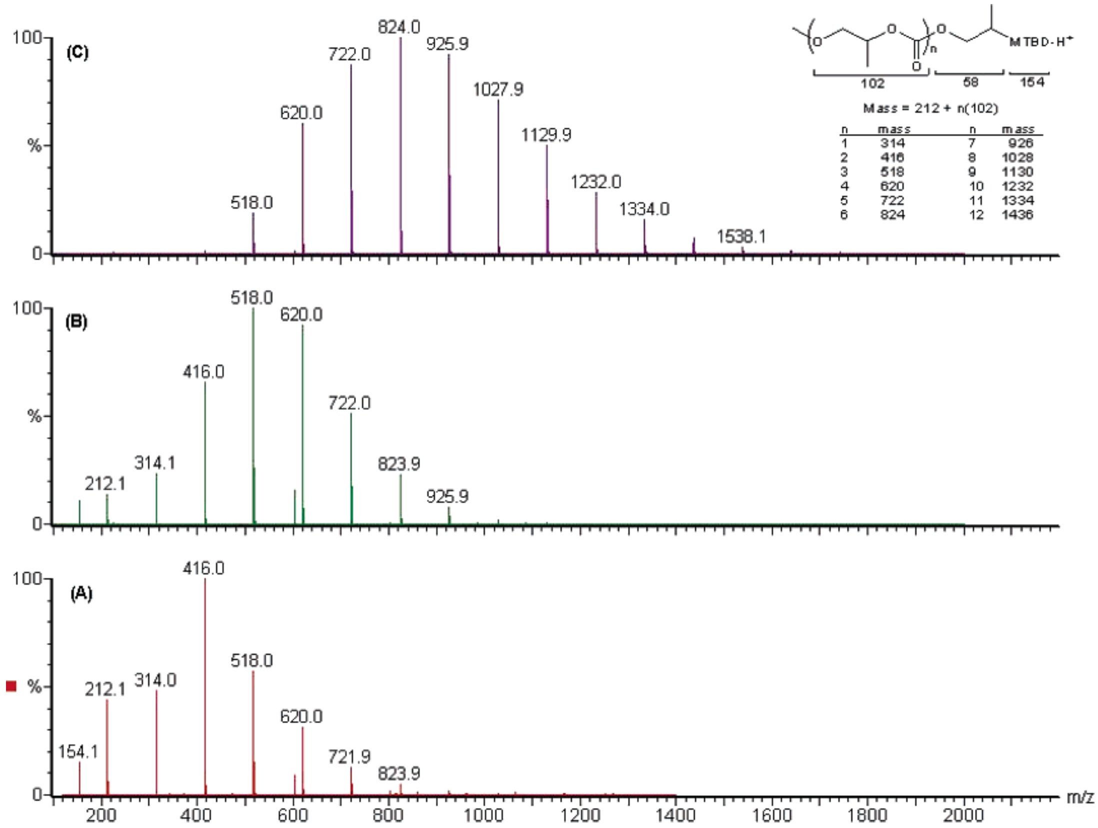
(27) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622−4629.

(28) (a) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 1, 11008-11009. (b) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501−5510. (c) Xiao, Y.; Wang, Z.; Ding, K. *Chem.−Eur. J.* **2005**, *11*, 3668−3678.

(29) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007−2008.



n	mass	n	mass
1	314	7	926
2	416	8	1028
3	518	9	1130
4	620	10	1232
5	722	11	1334
6	824	12	1436

Figure 6. ESI-Q-TOF mass spectra of the reaction mixture resulting from the systems of MTBD and complex **1a** with different ratios at 10 °C and a 0.6 MPa CO_2 pressure. MTBD:**1a** molar ratio: (A) 1:1, 20 min; (B) 3:1, 20 min; (C) 3:1, 30 min.

with initiation occurring by a bimetallic process and propagation operating by monometallic enchainment of epoxides.[16] These studies all have suggested that the Lewis base coordinates to the active metal center *trans* to the propagating metal−polymer chain, thereby labilizing the propagating alkoxide or carboxylate ligand and promoting the insertion of CO_2 into the metal−alkoxide bond. However, with the binary catalyst system composed of an electrophile and a bulky nucleophile with no or low coordination ability, the CO_2/epoxide copolymerization process with enhanced rate may operate via a different reaction pathway.

As previously described, in the copolymerization of CO_2 and *rac*-PO catalyzed by the (1*R*,2*R*)-SalcyCoX complexes in conjunction with various loadings of the MTBD cocatalyst, the number of PPC chains is independent of the initial cobalt complex concentration but is only determined by the MTBD concentration. This finding suggests that MTBD should play an important role in polymer chain growth during the reaction. For clarifying the mechanistic aspects of the copolymerization process, we have performed in situ ESI-MS for investigating the mode of polymer chain growth and the real active species of the binary catalyst systems with various ratios of MTBD to **1a** (Figure 6). To our surprise, the two systems both exhibit perfectly alternating and living polymerization characteristics in the measurable range of the instrument. In the ESI-Q-TOF mass spectra in the positive ion mode, we observe the species [MTBD + H^+], [MTBD + PO + H^+], and [$^-OCH(CH_3)CH_2$-(CO_2-*alt*-PO)$_n$-MTBD$^+$ + H^+], but with time the two former species gradually disappear and the latter species moves to the high *m*/*z* region. On the other hand, no polymer chain species involving the dinitrophenol ion of the cobalt complex **1a** was observed in the negative ion mode (see the Supporting Information, Figure 5). Hence, it can be concluded that in the copolymerization process MTBD prodominately plays an initiator role for polymer chain growth, and the propagating species can easily dissociate from the metal center during the copolymerization. Moreover, the narrow molecular weight distribution of polycarbonates proves that the dissociation rate of the active species should be significantly faster than that of polymer chain growth. Further MALDI-TOF-MS studies also confirmed these results (see the Supporting Information, Figure 6). However, we cannot affirm that the dissociated species is [$^-OCH(CH_3)CH_2$-(CO_2-*alt*-PO)$_n$-MTBD$^+$] or [$^-OOCOCH(CH_3)CH_2$-(CO_2-*alt*-PO)$_n$-MTBD$^+$], due to the low stability of the latter species in the absence of free CO_2.

To examine further the copolymerization mechanism, we also obtained in situ infrared spectra of the complex **1a**/MTBD/neat PO system at ambient temperature and a 0.1 MPa CO_2 pressure with time (see the Supporting Information, Figures 11 and 12). An increasing intensity in the $\nu(CO_2)$ region of 1660−1710 cm^{-1}, arising from the C−O stretching vibration, appeared in the IR spectra after CO_2 was bubbled through the solution. However, the removal of free CO_2 by bubbling N_2 resulted in a decrease in the $\nu(CO_2)$ region intensity and an unexpected formation of cyclic PC, originating from intermolecular cyclic elimination of the propagating polymer species. These results indicate that free CO_2 in the copolymerization process helps to stabilize the propagating carboxylate against decomposition to CO_2 and a long-chain alkoxide, which easily degrades into cyclic PC. Therefore, we suspect that the species [$^-OCH(CH_3)CH_2$-(CO_2-*alt*-PO)$_n$-MTBD$^+$] observed in ESI-MS spectra originates from the decomposition of [$^-OOCOCH(CH_3)CH_2$-(CO_2-*alt*-

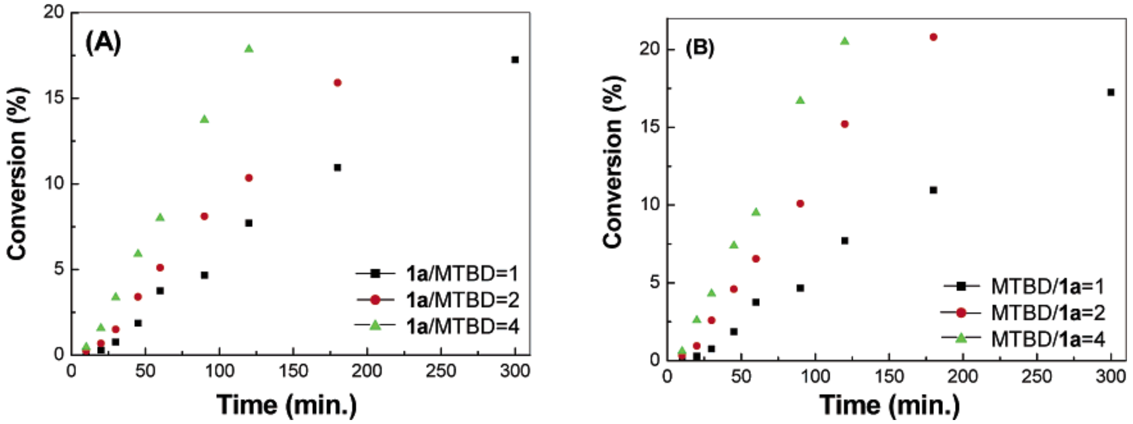


Figure 7. Conversion vs time curves of CO_2/*rac*-PO copolymerization catalyzed by (A) MTBD in the presence of increasing amounts of **1a** and (B) **1a** in the presence of increasing amounts of MTBD at 25 °C and 0.6 MPa.

PO)$_n$-MTBD$^+$], the real dissociated species, due to its low collision dissociation energy and the effect of the ESI gas N_2. More recently, the Rieger group reported the mechanism is based on the formation of aliphatic polycarbonates from aliphatic epoxides and CO_2 copolymerization with chromium(III) and aluminum(III) metal−Salen complexes by a DFT theoretical calculation method, in which they also proposed the propagating carboxylate easily dissociates from the metal center during the copolymerization.[30] However, in sharp contrast to that of our system, the formation of cyclic carbonate from the polymer chain in the catalyst system of chromium(III) or aluminum(III) metal−Salen complexes would involve attack of a free propagating carboxylate rather than an alkoxide at the last unit of the growing chain.

It is worthy of note that when MTBD and complex **1a** are used separately as the initiator or catalyst, the CO_2/PO copolymerization does not proceed even after 24 h at 25 °C and a 0.6 MPa CO_2 pressure, whereas their combination for this reaction shows high activity. Interestingly, in the presence of an excess of **1a** with respect to MTBD, a fast copolymerization of CO_2 and PO takes place and the number of PPC chains is only dependent on the initial MTBD concentration (Table 4). These results suggest an important activating effect of complex **1a** on the copolymerization, which can be postulated monomer activation through complexation. The fact that the addition of a coordination reagent such as *N*-MeIm resulted in a complete loss in activity for the binary **1a**/MTBD system also supports this hypothesis.

The activating role of cobalt complex **1a** was further investigated by studying the polymerization kinetics at various amounts of **1a**. Conversion vs time curves for a series of experiments performed at increasing **1a** concentration and constant MTBD and PO concentration, or at increasing MTBD concentration and constant **1a** and PO concentration, under a 0.6 MPa CO_2 pressure are shown in Figure 7. One may notice first the presence of an important induction period, which becomes shorter with increasing **1a** or/and MTBD concentration (Table 9). A similar situation also prevails when the molar ratio of **1a** to MTBD to PO changes from 1:1:2000 to 1:1:500. It can be tentatively assumed that the nucleophilic attack of MTBD or the propagating carboxylate species at the activating PO by its coordination to the metal center of **1a** is similar to a bimolecular process. Therefore, the rate is proportional to the concentration of the propagating species consistent with MTBD and the activating PO with regard to the **1a** concentration.

Table 9. Kinetic Data of CO_2/*rac*-PO Copolymerization Initiated by MTBD in the Presence of Various Amounts of Complex **1a**[a]

entry	**1a**:MTBD:PO molar ratio	polymerization induction time[b] (min)	R_p[c] (min^{-1})	10% conversion time[d] (min)
1	1:1:2000	12	0.07	163
2	2:1:2000	8	0.10	114
3	4:1:2000	6	0.15	70
4	1:2:2000	7	0.13	86
5	1:4:2000	5	0.18	59
6	1:1:500	4	0.41	25

[a] The reaction was performed in neat PO (14 mL, 200 mmol) in a 75 mL autoclave at 25 °C and a 0.6 MPa CO_2 constant pressure. [b] Estimated time of the induction period corresponding to the intersection of the linear PO conversion law at 0% conversion with the time axis. [c] Slope of conversion vs time curves calculated for the linear part. [d] Time for 10% conversion of PO.

Table 10. Kinetic Data of CO_2/*rac*-PO Copolymerization Initiated by (PPN)Cl in the Presence of Various Amounts of Complex **1a**[a]

entry	**1a**:(PPN)Cl:PO molar ratio	polymerization induction time[b] (min)	R_p[c] (min^{-1})	20% conversion time[d] (min)
1	1:1:2000	6	0.45	48
2	2:1:2000	4	0.64	33
3	4:1:2000	3	0.76	28
4	1:2:2000	4	0.68	31
5	1:4:2000	3	0.75	28
6	1:1:500	3	2.10	11

[a] The reaction was performed in neat PO (14 mL, 200 mmol) in a 75 mL autoclave at 25 °C and a 1.5 MPa CO_2 constant pressure. [b] Estimated time of the induction period corresponding to the intersection of the linear PO conversion law at 0% conversion with the time axis. [c] Slope of conversion vs time curves calculated for the linear part. [d] Time for 20% conversion of PO.

On the basis of the facts described above, a reaction mechanism, in which the epoxide is activated by its coordination to the metal center of the cobalt complex and MTBD plays an initiator role in polymer chain growth, is proposed and shown in Scheme 4. The mechanism also suggests that the activation of CO_2 is generally initiated by nucleophilic attack of the $^{-}OCH(CH_3)CH_2$-MTBD$^+$ species at the Lewis acid carbon atom of CO_2 and weak interaction between the central metal ion of the cobalt complex and the lone pairs of one oxygen atom of CO_2.

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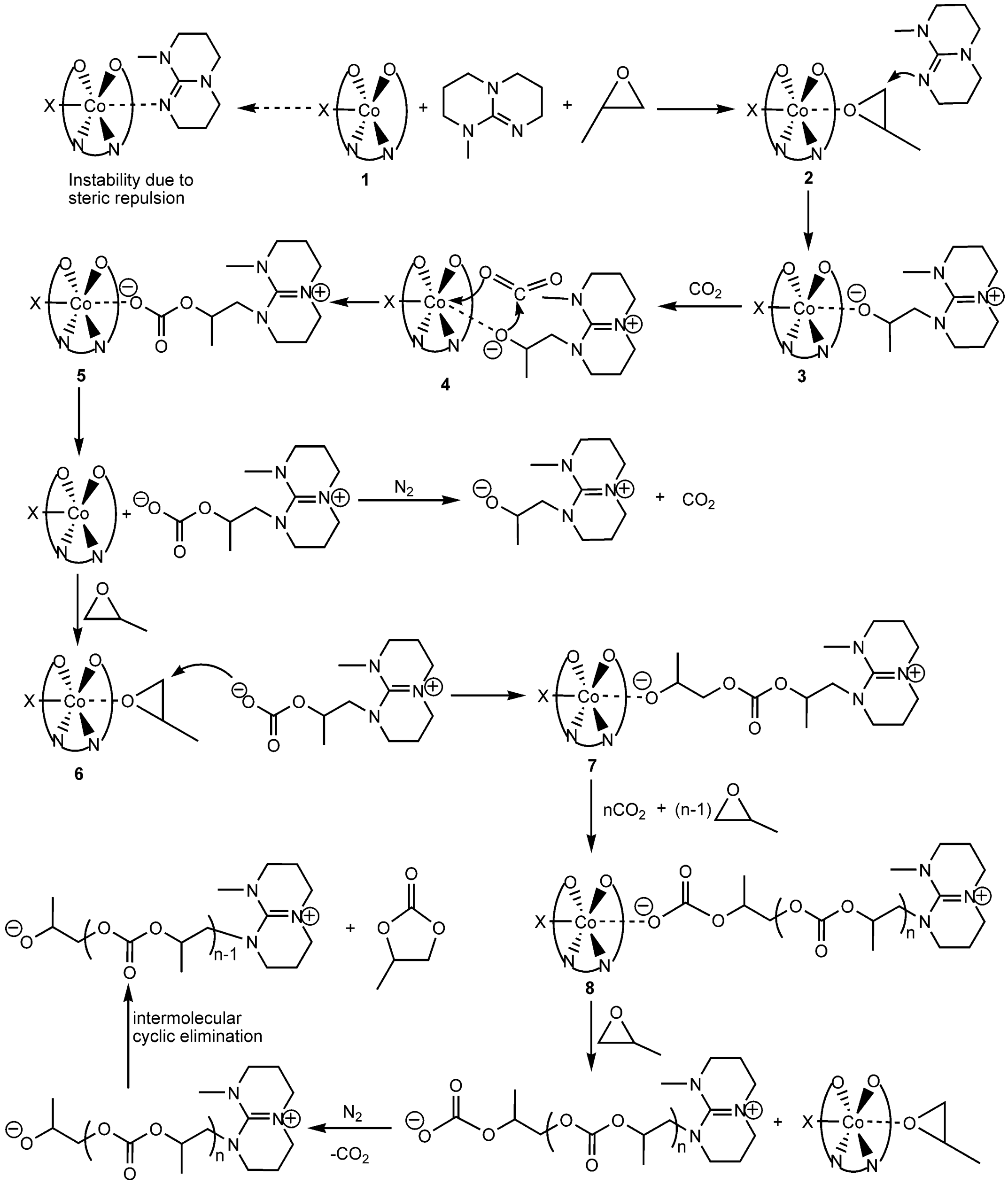
(30) Luinstra, G. A.; Hass, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.*−*Eur. J.* **2005**, *11*, 6298−6314.

Scheme 4. Proposed Mechanism of CO_2/PO Copolymerization Catalyzed by the Binary **1a**/MTBD System



The dissociation of the propagating carboxylate from the metal center is a much faster process than propagation, and the free propagating carboxylate can also act as a nucleophile for attack at a cobalt-coordinated epoxide during the copolymerization.

Furthermore, we also investigated the kinetics of CO_2/PO copolymerization with the binary catalyst system of **1a**/(PPN)Cl (Table 10). Similar to the binary **1a**/MTBD system, a fast copolymerization of CO_2 and PO takes place with increasing **1a** or/and (PPN)Cl concentration, and the number of PPC chains is proportional to the concentration of the cocatalyst (PPN)Cl. These results have led us to tentatively assume a mechanism similar to that of the **1a**/MTBD system for the binary system of a cobalt complex as the electrophile and an ionic ammonium salt as the nucleophile. On the other hand, for the binary systems of SalcyCoX with a nucleophilic but low sterically hindered axial X group combined with an ionic ammonium salt, we suspect that the nucleophilic axial X group of the cobalt complex is also capable of initiation and thus polymer chain propagation occurs simultaneously on either side of the $SalcyCo^{III}$ plane, which has been previously reported by the Coates group[22] and is similar to that proposed by Inoue et al. using aluminum porphyrins combined with an ionic ammonium or phosphonium salt.[7b] However, it is difficult to understand why the binary **1d**/(PPN)ClO_4 (1:1 molar ratio) or **1d**/*N*-MeIm system cannot effectively catalyze the CO_2/PO copolymerization.

It is generally known that both the ligand set of a single-site catalyst and the propagating polymer chain influence the stereochemistry of the polymerization reaction.[31] As previously discussed, the substituent groups on the aromatic rings, chiral diamine backbone, and axial X group of the cobalt complexes (electrophile) significantly affect the polymer enantioselectivity and microstructure. Also, the properties of the cocatalyst (nucleophile) consistent with polymer chain growth affect the polymer enantioselectivity and microstructure to a certain extent.

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(31) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252.

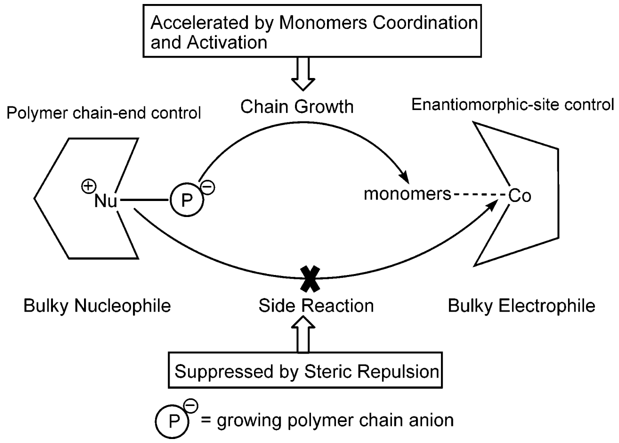

Figure 8. Schematic representation of high-speed asymmetric copolymerization of CO_2 and *rac*-epoxide by a synergistic catalysis of the binary electrophile−nucleophile system.

Therefore, we tentatively assume that both the enantiomorphic site effect resulting from the chiral electrophile and the polymer chain end effect mainly from the bulky nucleophile cooperatively control the stereochemistry of the CO_2/epoxide copolymerization process (Figure 8), but the former effect should be predominant. A detailed investigation on how to precisely control polymer regio- and stereochemistry is in progress.

Conclusions

We have reported the asymmetric alternating copolymerization of CO_2 and racemic epoxides by using a binary catalyst system of a chiral tetradentate Schiff base cobalt complex as the electrophile in conjunction with an ionic organic ammonium salt or sterically hindered strong organic base as the nucleophile at mild conditions, even at an atmospheric pressure of CO_2. Both properties of the electrophile and the nucleophile significantly affect the catalyst activity, polymer selectivity, enantioselectivity, and stereochemistry. A bulky chiral SalcyCo^{III}X with an axial X group of poor leaving ability as the electrophile and a bulky ionic ammonium salt (consisting of a bulky cation and a nucleophilic anion with poor leaving ability) or a sterically hindered strong organic base with low coordination ability as the nuclephile compose the ideal binary catalyst system for the copolymerization of CO_2 and racemic aliphatic epoxide to selectively produce polycarbonates with relatively high enantioselectivity, >95% head-to-tail connectivity, and >99% carbonate linkages. The copolymerization rate increases with the concentration of the electrophile or/and the nucleophile, and the number of polymer chains is independent of the electrophile concentration but is only proportional to the nucleophile concentration. Also, the binary system was found to be effective for the asymmetric alternating copolymerization of CO_2 and cyclohexene oxide to give optically active polycarbonates with 36.6% ee and >99% carbonate linkages at ambient temperature. Furthermore, continuous determination of a polymer end group (initiating and chain growth species) at various times was first achieved by in situ ESI-MS, which in combination with a kinetic study reveals a copolymerization mechanism, in which the electrophile plays an important role in activating epoxides and the nucleophile plays an initiator role in polymer chain growth during the copolymerization. Both the enantiomorphic site effect resulting from the chiral electrophile and the polymer chain end effect mainly from the bulky nucleophile cooperatively control the stereochemistry of the CO_2/epoxide copolymerization.

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Supporting Information Available: General experimental procedures, detailed ESI-Q-TOF mass spectra at various times, and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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