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Highly Active, Bifunctional Co(III)-Salen Catalyst for Alternating Copolymerization of CO_2 with Cyclohexene Oxide and Terpolymerization with Aliphatic Epoxides

Wei-Min Ren, Xiao Zhang, Ye Liu, Jian-Feng Li, Hui Wang, and Xiao-Bing Lu*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, China

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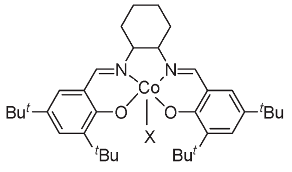
ABSTRACT: The cobalt(III) complex of a salen ligand bearing one quaternary ammonium salt on the three-position of one aromatic ring is a highly active catalyst for the alternating copolymerization of cyclohexene oxide (CHO) and CO_2 to afford the corresponding poly(cyclohexene carbonate) (PCHC) at various temperatures. The cobalt-based catalyst exhibited excellent activity and selectivity for polymer formation at high temperatures up to 120 °C and even under low CO_2 pressures of 0.1 MPa. Also, the cobalt(III)-salen complex could operate very efficiently for the terpolymerization of CHO and aliphatic epoxides with CO_2 to provide selectively polycarbonates with a narrow polydispersity at high temperatures. The polycarbonates resulting from the terpolymerization of equimolar CHO and propylene oxide (PO) with CO_2 have a close content for both cyclohexene carbonate and propylene carbonate units. This is ascribed to the presence of CHO significantly inhibiting the reactivity of PO and thereby causing a matched reactivity for both epoxides during the terpolymerization. The competition coordination of CHO and PO to the electrophilic cobalt(III) ion has no effect on regioselective ring-opening of PO in the terpolymerization.

Introduction

The development of efficient catalytic processes for CO_2 transformation to economically competitive products is of great interest and has been a long-standing goal for chemists.[1] One of the most promising ways to utilize effectively CO_2, the synthesis of polycarbonates through the metal-catalyzed coupling reactions of CO_2 and epoxides, was first reported by Inoue et al. in 1969[2] and has attracted much attention to both academic and industrial researchers. In recent decades, numerous catalyst systems have been developed for this transformation.[3] In particular, some well-defined homogeneous metal complexes have been reported to be highly active and selective catalysts, most notably zinc phenoxides,[4] β-diiminate zinc alkoxides,[5] and binary or bifunctional catalyst systems based on metal-salen or -salan complexes.[6−9]

In 2003, Coates and coworkers were the first to report the use of SalenCoX (salen, *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) complexes with a nucleophilic axial X group alone as catalysts for CO_2/propylene oxide (PO) copolymerization.[10] This approach produced poly(propylene carbonate) (PPC) with $>99\%$ selectivity and 90−99% carbonate linkages at a CO_2 pressure of 55 bar and ambient temperature. Unfortunately, low CO_2 pressures or elevated temperatures (~50 °C) led to the nearly complete loss in activity. We delightedly found that the addition of a nucleophilic cocatalyst such as quaternary ammonium halides could significantly improve the activity of SalenCo(III)X (X = 2,4-dinitrophenoxy) **1** even at low CO_2 pressures and/or elevated temperatures.[7a] Further mechanistic studies demonstrated that the nucleophilic cocatalyst functioned not only as an initiator[7d] but also in another role for stabilizing the active SalenCo(III) species against decomposition to SalenCo(II), which was ineffective in producing copolymer.[11] An elegant design of bifunctional catalyst **2** that contains a Lewis acidic metal center and quaternary ammonium salt units in a molecule was reported by Lee et al.[9b,c] The bifunctional catalyst exhibited excellent activity and polymer selectivity, even at high temperatures and high [epoxide]/[catalyst] ratios. Prior to this study, Nozaki et al. utilized a salen-type cobaltate complex with a piperidinium end-capping arm as catalyst for selectively synthesizing aliphatic polycarbonates from CO_2 and terminal epoxides and first succeeded in synthesizing a block polycarbonates terpolymer.[9a]



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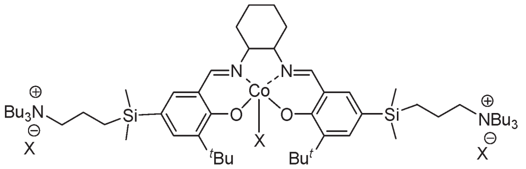

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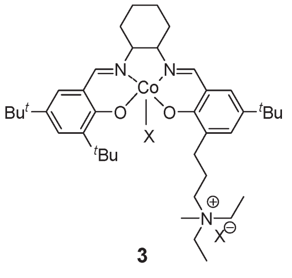

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X = 2,4-dinitrophenoxy

Stimulated by the success with bifunctional cobalt-based catalyst systems for the alternating copolymerization of CO_2 and PO, herein we apply the bifunctional Co(III)-salen complex **3**

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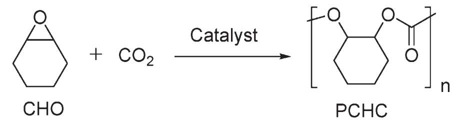
*Corresponding author. E-mail: lxb-1999@163.com.

Table 1. CHO/CO_2 Copolymerization Results[a]



entry	catalyst	[CHO]/[cat.]	pressure (MPa)	temp (°C)	time (h)	TOF (h^{-1})[b]	M_n (kg/mol)[c]	PDI M_w/M_n[c]
1	**3**	2000	1.5	25	6.0	170	52.0	1.08
2	**1**/^{n}Bu$_4$NX[d]	2000	1.5	25	8.0	87	19.1	1.17
3	**3**	5000	1.5	25	8.0	158	62.9	1.06
4	**3**	5000	2.5	25	8.0	162	64.1	1.04
5	**3**	5000	0.1	25	8.0	68	24.7	1.08
6	**3**	5000	0.1	50	5.0	263	48.2	1.12
7	**3**	5000	2.0	50	2.0	1018	68.7	1.10
8	**3**	5000	2.0	80	1.0	1924	52.7	1.14
9	**3**	5000	2.5	100	0.5	4509	43.8	1.20
10	**3**	5000	2.5	120	0.3	6105	29.3	1.23
11	**1**/^{n}Bu$_4$NX[d]	5000	2.5	100	1.0	< 5		

[a] Reaction was performed in neat cyclohexene oxide (CHO) (9.8 mL, 100 mmol) in a 75 mL autoclave. The polymer selectivity and carbonate linkages of the resulted polycarbonates are > 99% based on ^{1}H NMR spectroscopy. [b] Turnover frequency (TOF) = mole of product (PCHC)/mol of catalyst per hour. [c] Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [d] Reaction was performed using binary catalyst system of **1**/^{n}Bu$_4$NX (X = 2,4-dinitrophenoxy) with a molar ratio of 1/1.

bearing a quaternary ammonium salt on the three-position of one aromatic ring to the copolymerization of CO_2 and cyclohexene oxide (CHO) as well as terpolymerization with aliphatic epoxides at high temperatures. As distinct from the complex **2** containing two quaternary ammonium salts on the five-position of the aromatic rings, complex **3** present in this study concerns only a pendant quaternary ammonium salt on the three-position of one aromatic ring. This structure probably benefits to improving intramolecular cooperation catalysis of the electrophilic cobalt ion and the nucleophilic anion of the anchored quaternary ammonium salt. Also, we are interested in exploring the regiochemistry with regard to carbonate units sequence in the terpolymers obtained at various temperatures.

Results and Discussion

Alternating Copolymerization of CO_2 and CHO Catalyzed by the Complex 3 at Various Temperatures. The Co(III)-salen complex **3** bearing a quaternary ammonium salt on the three-position of one aromatic ring was prepared by the reported method.[11] The synthesis of enantiopure Co(III)-salen complex **3** is similar to the corresponding racemic complex only concerning the use of enantiopure 1,2-diaminocyclohexane mono(hydrogen chloride). Because complex **3** is easily dissolved in neat epoxides surveyed, the catalyzed coupling of CO_2 and epoxides does not require any organic cosolvent.

Our initial studies show that complex **3** could efficiently catalyze CHO/CO_2 copolymerization to afford selectively the corresponding copolymer with > 99% carbonate linkages at a [CHO]/[catalyst] molar ratio of 2000 under a CO_2 pressure of 1.5 MPa and at ambient temperature (Table 1, entry 1). The catalytic activity is double that of the binary catalyst system of complex **1** in conjunction with ^{n}Bu$_4$NX (X = 2,4-dinitrophenoxy) under the same conditions (entry 2). When [CHO]/[catalyst] ratio was increased to 5000, no obvious change in catalyst activity and polymer selectivity was observed in this reaction (entry 3). Notably, the bifunctional catalyst proved to be very active under 0.1 MPa CO_2 pressure under ambient temperature or elevated temperatures (entries 5 and 6). Indeed, only limited catalysts exhibit certain activities for CHO/CO_2 copolymerization at room temperature and relatively low CO_2 pressures, probably because of the more sterically hindered, less reactive CHO monomer.[12−14] For example, Williams and coworkers recently reported a novel macrocyclic dizinc catalyst for CHO/CO_2 copolymerization, and an activity with a turnover frequency (TOF) of 24 h^{-1} was achieved at 0.1 MPa CO_2 pressure and 90 °C.[13]

In sharp contrast with the copolymerization of CO_2 with aliphatic epoxides, the copolymerization of CO_2 with alicyclic CHO has great selectivity for polycarbonates formation, even at elevated temperatures, because of the increased strain in forming the five-membered carbonate ring imposed by the conformation of the alicyclic group.[14] Therefore, the development of a thermally robust catalyst is highly desirable. In a recent mechanistic study regarding a highly active and thermally stable cobalt(III)-salen catalyst with a sterically hindered organic base anchored on the ligand framework, we have demonstrated that the formed carboxylate intermediate helped to stabilize the active Co(III) species against decomposition to inactive Co(II) by reversibly intramolecular Co−O bond formation and dissociation.[11] Indeed, the addition of a nucleophilic cocatalyst could effectively stabilize the active Co(III) species and thus significantly improve the activity of Co(III)-salen complexes only at temperatures < 80 °C, whereas beyond this temperature, the binary catalyst systems usually lose their activities and predominately form the inactive Co(II)-salen. We were gratified to discover that the bifunctional catalyst **3** exhibited highly thermal stability and excellent activity at high temperatures even up to 120 °C. As anticipated, the reaction rate is highly sensitive to the reaction temperature (entries 4, 7−10). An increase in temperature from 25 to 100 °C resulted in a dramatic increase in TOF from 162 to 4509 h^{-1}. Furthermore, a TOF up to 6105 h^{-1} was achieved at 120 °C, the highest record in this copolymerization. In comparison, the binary catalyst system shows complete loss in activity at 100 °C, and Co(II) derivative as red solid precipitate was observed in the reaction mixture (entry 11). It is generally known that the homopolymerization of CHO easily takes place at elevated temperatures and is normally observed at catalyst systems with regard to much-studied zinc complexes.[4] However, in the present studies, the polycarbonates obtained at the range of 25 to 120 °C all have > 99% carbonate linkages; also, the polymer selectivity of > 99% does not change with the reaction temperature. To the best of our knowledge, this is the first example to be highly active and selective for alternating copolymerization of CHO and CO_2 at > 100 °C. It is

Table 2. Terpolymerization of CHO and Aliphatic Epoxides with CO_2 Catalyzed by the Complex 3[a]

entry	epoxide	temp (°C)	time (h)	TOF (h^{-1})[b]	M_n (kg/mol)[c]	M_w/M_n[c]	CHC linkages (mol %)[d]	T_g (°C)[e]	T_{50} (°C)[f]
1	CHO	25	8.0	158	62.9	1.06	100	118	310
2	CHO	90	0.5	3020	40.6	1.15	100		
3	PO	25	4.0	497	69.5	1.09	0	42	252
4[g]	PO	90	0.5	5160	58.8	1.22	0		
5	CHO/PO	25	8.0	202	70.5	1.04	48	77	285
6	CHO/PO	60	1.5	1246	82.1	1.14	49	78	290
7	CHO/PO	90	0.5	3590	50.9	1.12	52	79	292
8	CHO/EO[h]	90	0.5	4250	48.0	1.18	37	32	289
9	CHO/BuO[i]	90	0.5	2564	42.1	1.10	56	68	298
10	CHO/HO[j]	90	0.5	1958	39.7	1.15	65	72	302

[a] Reaction was performed in neat epoxide (**3**/epoxide = 1/5000, molar ratio) in a 75 mL autoclave. The molar ratio of CHO/aliphatic epoxide in terpolymerization is 1/1. When the reaction temperatures are 25, 60, and 90 °C, the CO_2 pressures in the corresponding systems are 1.5, 2.0, and 2.5 MPa, respectively. The resulting polymers all have >99% carbonate linkages. The selectivity for polymer formation in the CHO/aliphatic epoxide/CO_2 terpolymerization is all >99%. [b] Turnover frequency (TOF) = mole of product (polycarbonates)/mol of catalyst per hour. [c] Determined by GPC against polystyrene standards. [d] Proportion of cyclohexene carbonate linkages in the resulting polymers. [e] Glass-transition temperature determined by DSC. [f] Temperature at polymer decomposition of 50% measured by TGA. [g] About 6% of cyclic propylene carbonate was also observed. [h] EO, ethylene oxide. [i] BuO, 1,2-butene oxide. [j] HO, 1,2-hexene oxide.

worth noting here that a decrease in polycarbonate molecular weight and a slight increase in polymer molecular-weight distribution were observed at enhanced reaction temperatures.

Terpolymerization of CO_2, CHO, and Aliphatic Epoxides Catalyzed by the Complex 3. Although aliphatic epoxides are inexpensive or easily accessible from inexpensive commercial starting materials, the resulting polycarbonates by the copolymerization with CO_2 have relatively low glass-transition temperatures (T_g) < 50 °C, which limits their use as structural materials in various fields. As a result, some attention was paid to the terpolymerization of aliphatic epoxides, CHO, and CO_2 for adjusting T_g of the polycarbonates, but only limited success was achieved.[15] The main problem is that the great difference in reactivity of CHO and aliphatic epoxides during the terpolymerization with CO_2 leads to the difficulty in controlling the composition and the alternating nature of the resulting copolymer.[15] For example, bis-2,6-difluorophenoxide dimeric complexes of zinc have been reported as catalysts for the terpolymerization of PO (50 mol %) and CHO (50 mol %) with CO_2 at 55 °C and 4 to 5 MPa pressure, but the resulting polymer had 84.76 mol % cyclohexene carbonate linkages, only 11.90 mol % propylene carbonate linkages, and 3.34 mol % propylene ether linkages, with concomitant production of cyclic propylene carbonate.[15a] Inspired by our success in the use of binary cobalt-based catalyst systems for the alternating copolymerization of both PO and CHO with CO_2 under mild conditions, we also applied these catalyst systems to the terpolymerization of PO, CHO, and CO_2 and first succeeded in synthesizing the CO_2/PO/CHO terpolymer with only one T_g and one thermolysis peak.[17] Notably, the T_g is adjustable between 50 and 100 °C by controlling the relative proportions of PO and CHO. The main drawback is that the catalytic efficiency and the resulting polymer molecular weight are relatively low because the binary catalyst systems could not perform at high temperatures. Therefore, the development of a highly active, thermally stable catalyst is highly desirable for this terpolymerization.

Catalyst **3** bearing a quaternary ammonium salt on the three-position of one aromatic ring exhibited very excellent activities for both PO/CO_2 and CHO/CO_2 copolymerization with high polymer selectivity at high temperatures (Table 2, entries 1−4). As expected, complex **3** could operate efficiently for the terpolymerization of CHO (50 mol %) and PO (50 mol %) with CO_2 at various temperatures to provide selectively polycarbonates with a narrow polydispersity (M_w/M_n ratio) (Table 2, entries 5−7). In the ^{1}H NMR of the resulting terpolymers in $CDCl_3$, one ($\delta = 4.65$) of the two peaks was attributed to CH in cyclohexene carbonate unit and the other ($\delta = 4.99$) was attributed to CH in propylene carbonate unit (Supporting Information, Figure S1). No ether linkage signal at $\delta = 3.4$ to 3.5 assignable to the repeating oxy(1,2-cyclohexene) or oxy(1,2-propylene) units was observed in the ^{1}H NMR spectra of the resulting terpolymers. This verified that the terpolymers have >99% carbonate linkages. A TOF up to 3590 h^{-1} was observed for this terpolymerization at 90 °C. Although PO is a more active epoxide than CHO with copolymerization with CO_2 under the same reaction conditions, the resulting terpolymers have >48 mol % cyclohexene carbonate (CHC) units after ~20% conversion of all epoxides.

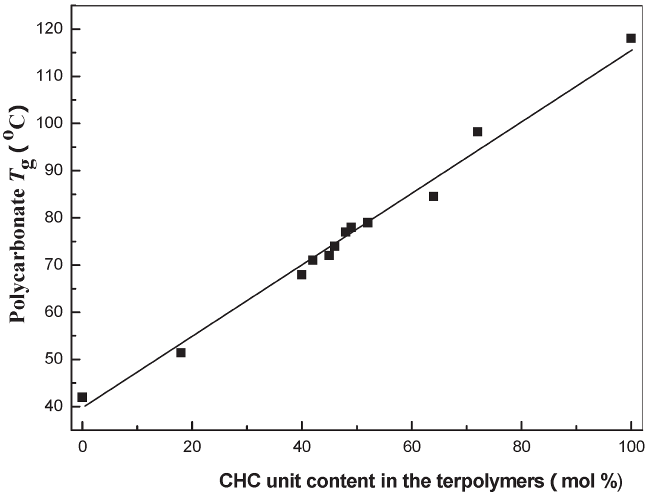


Figure 1. Plot of the T_g versus CHC units content in the CHO/PO/CO_2 terpolymers.

Surprisingly, the selectivity for polymer formation in the CHO/PO/CO_2 terpolymerization is >99% at 90 °C, whereas ~6% cyclic propylene carbonate was observed at mixture products during CO_2/PO copolymerization at the same temperature. This result indicates that the presence of CHO significantly inhibits the cyclic carbonate formation. Also, we got CHO/PO/CO_2 terpolymers with various CHC linkage content by altering the molar fraction of CHO in the mixture epoxides and found that the T_g was directly proportional to the CHC unit content (Figure 1). Usually, high CHC unit content in the CHO/PO/CO_2 terpolymers results

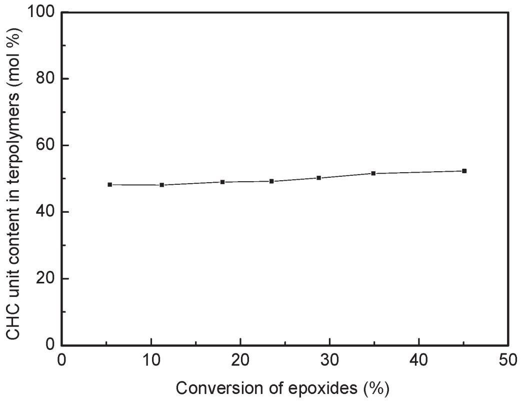


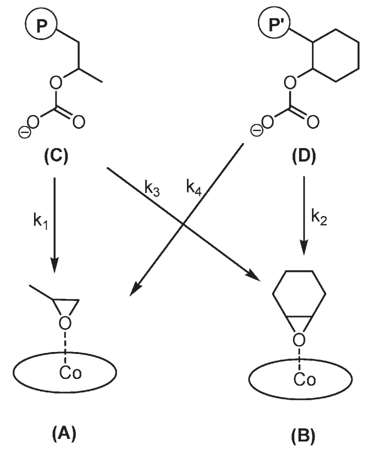
Figure 2. Plot of the CHC unit content in the resulting terpolymers versus the conversion of all epoxides in the CHO/PO/CO_2 terpolymerization catalyzed by the complex **3** (epoxides/**3** = 5000/1, CHO/PO = 1/1, molar ratio) at ambient temperature.

in enhanced thermal stability. Furthermore, the bifunctional catalyst **3** was found to be applicable to the terpolymerization of CO_2 with CHO and other aliphatic epoxides, providing the corresponding terpolymers in high activity and excellent selectivity (Table 2, entries 8−10). No ether linkage signal at $\delta = 3.4-3.6$ was observed in the ^{1}H NMR spectra of the resulting terpolymers (Supporting Information, Figures S2−S4). Ethylene oxide was found to be the most reactive epoxide, so the relative low CHC unit content was observed in the resulting terpolymer. On the contrary, 1,2-hexene oxide exhibited relatively low reactivity among the epoxides surveyed, and the resulting terpolymer has a CHC unit content up to 65%. These terpolymers all showed highly thermal stability. Also, the resulting terpolymers have only one T_g and one thermolysis peak (Supporting Information, Figure S5−S8). These results are similar to our previously reported binary catalyst systems at ambient temperature.[17]

Regiochemistry in the CHO/PO/CO_2 Terpolymerization. We are interested in exploring what factors lead to the close content for both cyclohexene carbonate and propylene carbonate units in the resulting terpolymer from the mixture epoxides of equimolar CHO and PO, whereas the reactivity of PO is about 3 times that of CHO using the complex **3** as catalyst at ambient temperature. We performed the competition polymerization of CHO and PO with CO_2 using equimolar CHO and PO. Figure 2 shows the plot of the CHC unit content of the resulting terpolymers at different time points versus the conversion of epoxides at ambient temperature. In the system of equimolar CHO and PO, the CHC unit content in the resulting terpolymers at different time points is very close to 50%. For a comparison purpose, we further performed the terpolymerization in the system of low CHO loading (CHO/PO = 1/2, molar ratio) and found that the CHC unit content in the terpolymers was 32% after ~20% conversion of all epoxides. These results indicate that the presence of CHO significantly inhibits the reactivity of PO, causing a matched reactivity for both epoxides during the terpolymerization.

In previous studies, we have demonstrated that the propagating polymer chains easily dissociated from the central cobalt ion and thus left the vacant coordination site for epoxide activation.[7d,11] Because a matched reactivity for both epoxides was observed in the terpolymerization, usually the resulting terpolymer from the system at the feed ratio of [CHO]/[PO] = 1 has ~50% PC−CHC (or CHC-PC placement) linkages in random distribution. However, the relatively high basicity and steric hindrance of CHO as well as

Scheme 1. Pathways of Epoxide Ring-Opening during CHO/PO/CO_2 Terpolymerization



P, P' = propagating polymer chain

the relatively high reactivity of PO probably lead to the enhanced content of PC−CHC or CHC-PC linkages in the terpolymer. Obviously, the relatively high basicity and coordination ability of CHO result in the concentration of the bound CHO (**B**) being higher than that of the bound PO (**A**) (Scheme 1). Because of the steric hindrance of CHO and the CHC end of the species (**D**), the ring-opening of the bound CHO (**B**) attacked by (**D**) is more difficult than that by the species (**C**). These will result in the ring-openings of the bound PO (**A**) attacked by the species (**D**) and the bound CHO (**B**) attacked by the species (**C**) being main reaction pathways. This arrangement will cause PC−CHC or CHC-PC linkage content to be higher than the total content of PC-PC and CHC−CHC linkages in the resulting terpolymer. Indeed, we have investigated ESI-Q-TOF mass spectrum of the mixture resulting from the PO/CHO/CO_2 terpolymerization catalyzed by binary SalenCoX/MTBD system in the initial stage and clearly found that the two different carbonate units in the resulting terpolymer mainly arrange in alternating fashion.[18] Of course, the PC-CHC or CHC-PC linkages distribute in random nature rather than perfect alternating mode. Unfortunately, because of the very poor ion intensity of the propagating polymer chains based on 2,4-dinitrophenoxy in ESI-Q-TOF mass spectroscopy, we failed to determine the sequence nature of carbonate units in the terpolymer with the complex **3** as catalyst.

In previous regio- and stereoselective copolymerization of CO_2 and PO, we found that the enhanced reaction temperatures caused a significant decrease in regioselective ring-opening of PO and thus had a negative effect on the stereoregularity of the resulting polycarbonates.[7d] With complex **3** as catalyst, the reaction temperature increases from 25 to 90 °C, the head-to-tail linkage content of the resulting PPC decreases from 92 to 77% (Figure 3A,B). On the contrary, the ^{13}C NMR spectra at carbonyl region of the terpolymers obtained at various temperatures are very similar (Figure 3C, D), but the reason is not clear.

To investigate the effect of the competition copolymerization of CHO on the regioselective ring-opening of PO, we performed the terpolymerization of CHO and (*R*)-PO with CO_2 catalyzed by the enantiopure complex (1*R*,2*R*)-**3**. For the copolymerization or terpolymerization concerning chiral PO, regioselective ring-opening of PO significantly affects the resulting polymer enantioselectivity because head-to-tail carbonate linkages normally retain the stereochemistry at the methine carbon as a consequence of the preferential

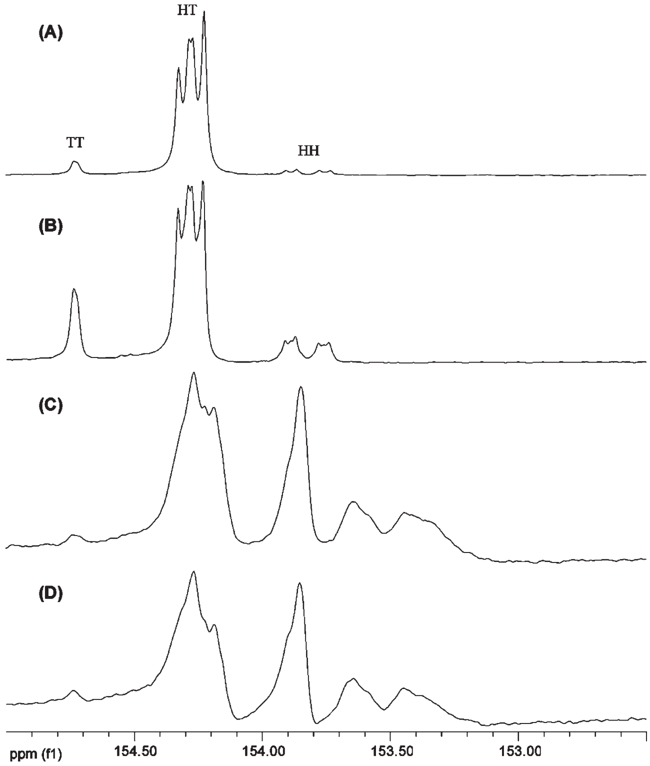


Figure 3. Carbonyl region of the ^{13}C NMR spectra of polycarbonates resulted from (A) the PO/CO_2 copolymerization at 25 °C; (B) the PO/CO_2 copolymerization at 90 °C; (C) the PO/CHO/CO_2 terpolymerization at 25 °C; and (D) the PO/CHO/CO_2 terpolymerization at 90 °C. TT, tail-to-tail carbonate linkage; HT, head-to-tail carbonate linkage; HH, head-to-head carbonate linkage.

ring-opening at the methylene carbon.[8a,19] On the contrary, the ring-opening at the methine carbon occurs by backside attack, usually leading to the formation of head-to-head or tail-to-tail carbonate linkages; this may cause a change in stereochemistry with inversion. The degradation of linear PPC to cyclic propylene carbonate by intramolecular cyclic elimination normally retains the stereochemistry at the methine carbon of PPC because the reaction involves alkoxide ion attack on the carbonate carbon rather than the methine or methylene carbon. As a result, we can easily evaluate the relationship of polymer enantioselectivity and its head-to-tail linkages in relation to regioselective ring-opening of the epoxide by determining the enantiomeric excess of the cyclic carbonate produced from the degradation of the resulting polycarbonates. Interestingly, the enantiomeric excess of cyclic propylene carbonate given after complete degradation of the polycarbonates from the terpolymerization of CHO and (*R*)-PO with CO_2 at ambient temperature is 79%, which is the same as that from (*R*)-PO/CO_2 copolymerization under the same conditions. This result clearly demonstrates that the competition coordination of CHO and PO to the electrophilic metal ion has no effect on regioselective ring-opening of PO in the terpolymerization.

Conclusions

We have developed a highly active, bifunctional Co(III)-salen catalyst bearing a quaternary ammonium salt on the three-position of one aromatic ring for the copolymerization of CO_2 and CHO as well as terpolymerization with aliphatic epoxides at high temperatures. The catalytic activity is highly sensitive to the reaction temperature, and the highest TOF up to 6105 h^{-1} was obtained at 120 °C, without sacrificing polymer selectivity. Notably, the bifunctional catalyst exhibits active under 0.1 MPa CO_2 pressure at ambient temperature or elevated temperatures, selectively affording the corresponding copolymer >99% carbonate linkages. The functionalized Co(III)-salen complex could operate very efficiently for the terpolymerization of CHO and aliphatic epoxides with CO_2 to provide selectively polycarbonates with a narrow polydispersity at various temperatures. The resulting terpolymers have only one thermolysis peak and one adjustable glass-transition temperature dependable on cyclohexene carbonate unit content. The close content for both cyclohexene carbonate and propylene carbonate units was observed in the polymers from the terpolymerization of equimolar CHO and PO with CO_2 at various temperatures. This is ascribed to the presence of CHO significantly inhibiting the reactivity of PO and thereby causing a matched reactivity for both epoxides during the terpolymerization.

Experimental Section

Synthesis of Chiral Salen Ligand Bearing a Quaternary Ammonium Salt. A flask was charged with (*R*,*R*)-1,2-cyclohexanediamine mono(hydrogen chloride) (0.30 g, 2.0 mmol), activated 5 Å molecular sieve (3.00 g), and anhydrous methanol (20 mL). 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (0.57 g, 2.4 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 2 h. A solution of 5-*tert*-butyl-3-(3-(diethylamino)propyl)-2-hydroxybenzaldehyde (0.58 g, 2.0 mmol) in anhydrous ethanol (20 mL) was then added to the reaction system, followed by the slow addition of triethylamine (0.42 mL, 3.0 mmol). After stirring at room temperature for an additional 4 h, the reaction mixture was filtered through a short pad of dry silica gel. Then, all solvents and the excessive triethylamine were removed in vacuo. The residue was purified by column chromatography on silica gel using petrol ether/ethyl acetate (5:1, 1% Et_3N) as the mobile phase to afford 3-(diethylamino)propyl appended Salen ligand as a yellow compound (0.65 g). ^1H NMR (400 MHz, $CDCl_3$, δ): 13.70 (s, 1H), 13.40 (s, 1H), 8.29 (s, 1H), 8.27 (s, 1H), 7.30 (s, 1H), 7.16 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 3.30−3.33 (m, 2H), 2.48−2.73 (m, 8H), 1.67−1.96 (m, 10H), 1.41 (s, 9H), 1.24 (s, 9H), 1.22 (s, 9H), 1.00 (t, J = 7.2 Hz, 6H). HRMS (m/z) Calcd for $[C_{39}H_{62}N_3O_2]^+$, 604.4842; found, 604.4846.

To a stirred mixture of the resulting 3-(diethylamino)propyl-appended Salen ligand (0.64 g, 1.0 mmol) in acetonitrile (20 mL) in a 50 mL flask wrapped in aluminum foil was added iodomethane (0.075 mL, 1.2 mmol). The resulting mixture solution was stirred for 24 h. The solvent was removed in vacuo; then, the residue was dissolved in ethanol (40 mL) and $AgBF_4$ (0.21 g, 1.1 mmol) was added. The mixture was stirred for 1 h and then filtered to remove the Ag byproduct. The solvent was removed in vacuo; then, the residue was purified by column chromatography on silica gel using ethyl acetate (1% Et_3N) as the mobile phase to give the afforded quaternary ammonium salt-appended salen ligand (0.58 g, 41%) as a bright-yellow solid. $[\alpha]_D^{20}$ − 312 (*c* 1.0, $CHCl_3$). ^1H NMR(400 MHz, $CDCl_3$, δ): 13.70 (s, 1H), 13.50 (s, 1H), 8.35 (s, 1H), 8.32 (s, 1H), 7.30 (s, 1H), 7.17 (s, 1H), 7.05 (s, 1H), 7.01 (s, 1H), 3.13−3.36 (m, 8H), 2.97 (s, 3H), 2.69 (m, 2H), 1.45−1.98 (m, 10H), 1.38 (s, 9H), 1.20−1.28 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 165.6, 165.2, 158.1, 157.0, 141.3, 140.2, 136.6, 130.3, 126.9, 126.8, 126.3, 126.1, 117.9, 117.8, 73.2, 71.7, 59.9, 56.8, 47.4, 35.1, 34.2, 34.0, 33.6, 33.1, 32.6, 31.5, 29.5, 27.3, 24.5, 24.4, 22.1, 7.8. HRMS (m/z) Calcd for $[C_{40}H_{64}N_3O_2]^+$, 618.4999; found, 618.4987.

Synthesis of the Complex (*R*,*R*)-3. Cobalt(II) acetate (0.18 g, 1.0 mmol) and the quaternary ammonium salt-appended Salen ligand (0.35 g, 0.5 mmol) were dissolved in methanol (10 mL). After stirring for 12 h at room temperature, LiCl (0.04 g, 1.0 mmol) was added, and the mixture was further stirred for 12 h while oxygen was bubbled through the reaction mixture. The solvent was removed in vacuo, and the residue was extracted with methylene chloride. The organic layer was washed with saturated aq $NaHCO_3$ and brine and then dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. After the removal of the solution, the residue was dissolved in methylene chloride (20 mL) in a 80 mL Schlenk vial wrapped in aluminum foil, and $AgBF_4$ was added (0.20 g, 1.0 mmol). The mixture was stirred for 24 h and then filtered to remove the Ag byproduct. To the filtrate was added sodium 2,4-dinitrophenolate (0.21 g, 1.0 mmol), and the solution was stirred for another 2 h and then filtered to remove inorganic salt. The solvent was removed in vacuo. The resulting solid was further treated with a mixture of methylene chloride and hexane to afford the enantiopure complex (*R*,*R*)-3 as a brown solid (0.47 g, 90%). ^{1}H NMR (DMSO-d_6, δ): 8.60 (s, 2H), 7.98 (s, 1H), 7.90 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H,), 7.51 (s, 1H), 7.47 (s, 1H), 7.45 (s, 1H,), 7.41 (s, 1H), 6.35 (d, J = 8.4 Hz, 2H), 3.55−3.58 (m, 2H), 3.28−3.41 (m, 6H), 3.03 (t, J = 6.8 Hz, 2H), 2.98−3.01 (m, 2H), 2.90 (s, 3H), 2.16−1.49 (m, 8H), 1.75 (s, 9H), 1.30 (s, 9H), 1.28 (s, 9H), 1.22 (t, J = 7.2 Hz, 6H). ^{13}C NMR (DMSO-d_6, δ): 169.8, 164.4, 164.1, 162.0, 160.9, 141.5, 136.9, 135.8, 132.8, 131.8, 128.8, 128.5, 127.7, 127.4, 124.7, 118.6, 118.4, 69.4, 69.0, 59.8, 55.6, 46.6, 35.4, 33.4, 33.3, 31.3, 31.2, 30.2, 29.3, 29.2, 26.8, 24.1, 22.2, 7.9. HRMS (*m*/*z*): Calcd for $[C_{46}H_{65}CoN_5O_7]^+$, 858.4216; found, 858.4235.

CO_2/CHO Copolymerization Procedure. A stirred mixture of complex **3** (0.021 g, 0.020 mmol, 1 equiv) was dissolved in CHO (9.8 mL, 100 mmol, 5000 equiv) to form red-brown solution under a nitrogen atmosphere. The mixture solution was charged into a predried 75 mL autoclave equipped with a magnetic stirrer under a CO_2 atmosphere. The autoclave was put into a bath, which had been set at a given temperature. Then, the system was pressurized to appropriate pressure with CO_2. After the allotted reaction time, the CO_2 pressure was released, and a small amount of the residue was removed for ^{1}H NMR analysis to give quantitatively the activity and selectivity of PCHC and also used for GPC analysis. The unreacted CHO was isolated under ambient temperature by vacuum (3 mmHg) transfer into a cooled (−20 °C) receiving flask. The crude polymer was dissolved in 10 mL of $CHCl_3$/MeOH (5/1, v/v) mixture and precipitated from methanol or diethyl ether. This process was repeated 3−5 times to remove completely the catalyst, and white polymer was obtained by vacuum drying.

CO_2/CHO/Aliphatic Epoxides Terpolymerization Procedure at High Temperatures. A stirred mixture of complex **3** (0.021 g, 0.020 mmol, 1 equiv.) was dissolved in CHO/aliphatic epoxide (CHO/aliphatic epoxide/catalyst, 2500/2500/1, molar ratio) to form a red-brown solution under a nitrogen atmosphere at 0 °C. The mixture solution was charged into a predried 75 mL autoclave equipped with a magnetic stirrer under a CO_2 atmosphere. After it was pressurized to 1.0 MPa pressure with CO_2, the autoclave was put into a bath whose temperature had been set at a given temperature, and the solution was stirred for 15 min to allow the solution temperature to reach the bath temperature. Then, the system was pressurized to 2.5 MPa pressure with CO_2. After the allotted reaction time, the autoclave was cooled to ambient temperature by immersion in an ice bath. After CO_2 was released, a small amount of the residue was taken and dissolved in $CDCl_3$ for ^{1}H NMR analysis to give quantitatively the activity and selectivity of polymer as well as carbonate linkage. The unreacted epoxides were isolated at ambient temperature by vacuum (3 mm Hg) transfer into a cooled (−20 °C) receiving flask. The crude terpolymer was dissolved in 10 mL of $CHCl_3$/MeOH (5/1, v/v) mixture and precipitated from methanol or diethyl ether. This process was repeated three to five times to remove completely the catalyst, and white polymer was obtained by vacuum drying.

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Supporting Information Available: General information, characterization of various terpolymers, and NMR spectra of chiral ligand and complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) We chose 7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene (MTBD, a sterically hindered strong organic bases) as a cocatalyst to be consistent with the complex **1** for the terpolymerization of CHO/PO/CO_2. In the ESI-Q-TOF mass spectra in positive ion mode, we observe the strong signals of 314, 354, 456, 558, 598, and 700, which are attributed to the species of [(H^++MTBD+PO)+PC], [(H^++MTBD+PO)+CHC], [(H^++MTBD+PO)+PC+CHC] or [(H^++MTBD+PO)+CHC+PC], [(H^++MTBD+PO)+2PC+CHC], [(H^++MTBD+PO)+PC+2CHC], and [(H^++MTBD+PO)+2(PC+CHC)], respectively. (See Figure S9 of the Supporting Information.) This result indicates that the two different carbonate units in the resulting terpolymer mainly arrange in alternating fashion (PC-CHC or CHC-PC linkage).

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