Alternating copolymerization of carbon dioxide and cyclohexene oxide catalyzed by salen Co$^{III}$(acetate) complexes

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Abstract A series of Co$^{III}$ carboxylate based upon N,N,O,O-tetradentate Schiff base ligand framework have been prepared. X-ray diffraction analysis confirms that these Schiff base Co$^{III}$ carboxylate are all monomeric species with a six-coordinated central Co in their solid structures. The activities and polycarbonate selectivity of these complexes toward the copolymerization of epoxide (cyclohexene oxide and propylene oxide) and carbon dioxide have been investigated in the presence of bis(triphenylphosphine)iminium chloride. Copolymerization experiments indicate that [bis(α-methyl-3,5-di-tert-butyl-salicylaldehyde) ethylenediaminato] Co$^{III}$OOC$\text{H}_3$ exhibits the highest activity and polycarbonate selectivity among these Co$^{III}$ carboxylate. The resultant copolymer contained almost 100 % carbonate linkages with the molecular weight up to 71.8 kg mol$^{-1}$ as well as narrow polymer dispersity index (polymer dispersity index=1.5). The substituents and the mode of the bridging part between the two nitrogen atoms both exert significant influences upon the progress of the copolymerizations, influencing both the polycarbonate selectivity and the rate of copolymerization.

Keywords Biodegradable · Carbon dioxide · Copolymerization · Polycarbonates · Poly(cyclohexene oxide)

Introduction

The transition metal complexes with Schiff bases as ligands are promising systems for application in the coupling of CO$_2$ with epoxide to aliphatic polycarbonates because the copolymerization of CO$_2$ and epoxide [such as cyclohexene oxide (CHO), propylene oxide (PO)] with discrete metal complex has been well documented [1]. Copolymers of CHO with CO$_2$ are important product with favorable property in comparison to homopoly(cyclohexene oxide), which is also one of the most promising routes for the chemical fixation of carbon dioxide [2–4]. For another, introduction of a CO$_2$ comonomer to the poly(cyclohexene oxide) chain changes the structure, and consequently, the properties of the polymer product are obtained. The effect is dependent on the type of catalytic system used and polymerization conditions [5].

Metal salen complexes have been used for the copolymerization of CO$_2$ with certain monomers to form polycarbonates [6–9]. A particular feature of these complexes is that polymers tend to be isolated with very narrow molecular weight distributions and that the molecular weights of the produced copolymer can be controlled. Typically, these complexes are tolerant toward water and air, so that extensive drying and purification of reagents are unnecessary. (Salen)Cr$^{III}$X or (salen)Co$^{III}$X complexes (salen=N,N'-bis(salicylidene)-1,2-diaminalkane), which exhibit outstanding performance and can obtain the carbonate contents reach almost 100 %, are composed of zinc acetate complexes [10], tetrakis(pentafluorophenyl)porphyrin chromium(III) chloride [11] and β-diaminate zinc complexes [12, 13]. (Salen)Cr$^{III}$X [14–18] or (Salen)Co$^{III}$X [19–25] complexes [salen=N,N'-bis(salicylidene)-1,2-diaminalkane] exhibit outstanding performance, and the carbonate contents reach almost 100 %. These studies should be very important for designing a highly efficient complex and for understanding the scope and the limitation of these types of transition metal complexes as CHO/CO$_2$ copolymerization catalysts.

Metal salen complexes have received increasing attention for their unusually high catalytic activity on the copolymerization of CO$_2$ with epoxide [1]. The influence of the
phenolate ortho and para substituents as well as the axial group epoxide/CO₂ copolymerization has been studied widely [6, 26, 27]. The cobalt Schiff base complex with axial acetate ligand has been employed to the carbon dioxide fixation field. However, some thought one cobaltate axial acetate ligand has been employed to the carbon dioxide in the direction of the axial ligand. Recently, we reported with Co located slightly above the plane of the salen ligand coordinated cobalt complex is pseudo square-pyramidal 28 hexane, and chloroform were distilled from CaH₂ under distilled from sodium benzophenone. Methylene chloride, Special Gases and used as received. Diethyl ether was

diluted with THF at 25 °C (515 HPLC pump) equipped with a Wyatt interferometric measurements were carried out with a Waters instrument (nitrogen laser, λ=337 nm) were accelerated through 20 kV, and detection voltage was set at 1.60 kV. The laser was adjusted by the experiments slightly above the threshold, and the mass spectra were obtained from the results of 35 laser shots in positive mode. The matrix, trans-3-indoleacrylic acid, was dissolved in purified THF (0.1 mol l⁻¹), and the solution was mixed with the polymer solution in THF (5 mg ml⁻¹) in a 1:1 v/v ratio. Crystallographic data were collected on a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at 293 K. The structure was refined by the full-matrix least-squares method on F² using the SHELXTL-97 crystallographic software package. Anisotropic thermal parameters were used to refine all nonhydrogen atoms. Hydrogen atoms were located in idealized positions.

Synthesis of complexes 1–6

Synthesis of complex 1 To a stirred mixture of salen CoII complex (1.16 g, 2.0 mmol) in CH₂Cl₂ (150 ml), the mixture of CH₃COOH (0.12 g, 2.0 mmol, 1 equiv.) and CH₂Cl₂ (20 ml) was added. The solution was stirred under dry oxygen atmosphere at room temperature for 60 min. The solvents were removed in vacuum to leave a crude green dark solid in near 100 % yield. The resulted solid was further treated with the mixture of diethyl ether and hexane, and then dried at 60 °C in vacuum for 24 h. Yield: 89 %. Elemental analysis calcd (%) for C₃₂H₄₆N₂O₄: C, 74.63; H, 8.39; N, 4.40. Found: C, 74.67; H, 8.39; N, 4.43. ¹H NMR (1,4-Dioxane-δ8): 1.12 (s, 6H), 1.32 (s, 18H), 1.71 (s, 18H), 2.14 (s, 2H), 4.13 (m, 4H), 7.41 (s, 2H), 7.49 (s, 2H). ¹³C NMR (1,4-Dioxane-δ8): δ 19.02, 27.14, 30.35, 31.46, 32.48, 40.71, 124.06, 121.22, 126.48, 128.98, 137.48, 142.41, 163.69, 176.27. ESIMS (m/z, M⁺+H): 577.3201; Calcd. for [C₃₄H₅₀N₂O₄Co]⁺: 577.3204.

Synthesis of complex 2 It was synthesized according to the literature method [35]. Yield: 91 %. Elemental analysis calcd (%) for C₃₃H₄₆N₂O₄: C, 74.69; H, 8.11; N, 4.60. found: C, 74.65; H, 8.04; N, 4.55. ¹H NMR (1,4-Dioxane-δ8): 1.31 (s, 18H), 1.73 (s, 18H), 2.09 (s, 3H), 4.12 (m, 4H), 7.39 (s, 2H), 7.45 (s, 2H). ¹³C NMR (1,4-Dioxane-δ8): δ 24.56, 30.75, 30.27, 31.48, 33.49, 58.25, 122.16, 125.42, 127.37, 137.72, 142.41, 151.35, 162.69, 168.70. ESIMS (m/z, M⁺+H): 549.2890; Calcd. for [C₃₃H₄₆N₂O₄Co]⁺: 549.2891.

Experimental section

General methods

All manipulations involving air- and/or water-sensitive compounds were carried out using standard Schlenk techniques under dry argon. CHO was refluxed over CaH₂, and fractionally distilled under an argon atmosphere prior to use. CO₂ (99.995 %) was purchased from Qingdao Institute of

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Synthesis of complex 3. It was synthesized as a similar procedure of complex 1. Yield: 85 %. Elemental analysis calcd (%) for C_{28}H_{35}CoI_{2}N_{2}O_{4}: C, 43.32; H, 4.54; N, 3.61; found: C, 43.28; H, 4.51; N, 3.60. 'H NMR (1,4-Dioxane-d8): 1.10 (s, 6H), 1.37 (s, 18H), 2.09 (s, 3H), 4.02 (m, 4H), 7.49 (s, 2H), 7.55 (s, 2H). 13C NMR (1,4-Dioxane-d8): δ 20.56, 29.67, 30.15, 32.17, 125.16, 128.42, 138.37, 137.12, 151.35, 163.59, 169.71. ESIMS (m/z, M' + H): 716.9882; Calcd. for [C_{28}H_{35}I_{2}N_{2}O_{2}Co]^+: 716.9885.

Synthesis of complex 4. It was synthesized as a similar procedure of complex 1. Yield: 88 %. Elemental analysis calcd (%) for C_{28}H_{35}CoI_{2}N_{2}O_{4}: C, 43.32; H, 4.54; N, 3.61; found: C, 43.29; H, 4.50; N, 3.59. 'H NMR (1,4-Dioxane-d8): 1.06 (s, 6H), 1.31 (s, 18H), 2.07 (s, 3H), 4.05 (m, 4H), 7.45 (s, 2H), 7.51 (s, 2H). 13C NMR (1,4-Dioxane-d8): δ 20.16, 25.63, 30.25, 31.45, 40.15, 89.16, 125.92, 126.37, 139.98, 144.34, 163.13, 164.59, 169.78. ESIMS (m/z, M' + H): 716.9880; Calcd. for [C_{28}H_{35}I_{2}N_{2}O_{2}Co]^+: 716.9885.

Synthesis of complex 5. It was synthesized as a similar procedure of complex 1. Yield: 87 %. Elemental analysis calcd (%) for C_{20}H_{17}CoI_{4}N_{2}O_{4}: C, 26.23; H, 1.87; N, 3.06; found: C, 26.20; H, 1.85; N, 3.07. 'H NMR (1,4-Dioxane-d8): 1.08 (s, 6H), 2.09 (s, 3H), 4.07 (m, 4H), 7.76 (s, 2H), 7.79 (s, 2H). 13C NMR (1,4-Dioxane-d8): δ 21.34, 24.63, 29.24, 89.16, 91.21, 128.12, 136.37, 139.98, 147.74, 1661.31, 165.59, 169.89. ESIMS (m/z, M' + H): 856.6564; Calcd. for [C_{18}H_{14}I_{4}N_{2}O_{2}Co]^+: 856.6566.

Synthesis of complex 6. It was synthesized according to the literature method [35]. Yield: 89 %. Elemental analysis calcd (%) for C_{37}H_{55}CoN_{2}O_{4}: C, 68.29; H, 8.52; N, 4.30; found: C, 67.32; H, 8.67; N, 4.51. 'H NMR (1,4-Dioxane-d8): 1.35 (s, 18H), 1.37 (s, 18H), 1.65 (s, 6H), 2.09 (s, 3H), 7.64 (s, 2H). 13C NMR (1,4-Dioxane-d8): δ 24.54, 30.13, 31.25, 32.46, 31.66, 62.71, 128.12, 128.56, 137.37, 139.88, 145.94, 154.54, 164.37, 170.45. ESIMS (m/z, M' + H): 591.3363; Calcd. for [C_{35}H_{52}N_{2}O_{2}Co]^+: 591.3366.

Representative copolymerization procedure

A 100-ml stainless steel autoclave equipped with a magnetic stirring bar was heated to 120 °C under vacuum for 2 h. After cooled to room temperature, the autoclave was charged with CO_{2}. A mixture of complex and [PPN]Cl was dissolved in 1,4-dioxane under CO_{2} atmosphere. The mixture solution was injected into the autoclave with a syringe under CO_{2} atmosphere, followed by the addition of CHO. The autoclave was heated to a desired temperature in an oil bath and the 1.5 MPa pressure of CO_{2}. The mixture was stirred for the allotted reaction time, then quickly cooled to room temperature and vented in a fume hood. A small aliquot of the resultant copolymerization mixture was removed from the reactor for 'H NMR analysis. The remaining copolymerization mixture was then dissolved in chloroform, quenched with 5 % HCl solution in methanol, and precipitated from methanol. The copolymer was collected and dried in vacuum to constant weight, and the copolymer yield was determined. The carbonate linkages were determined from the relative intensity of the cyclohexyl methine proton signals (4.6 ppm for carbonate linkages and 3.4 ppm for ether linkages) in the 'H NMR spectrum of the polymer. The molar mass and the molar mass distribution of the resulting polymer were determined by GPC.

**Results and discussion**

Syntheses of complexes

Substituted derivatives of the parent ligand salen were prepared by condensation of salicylaldehyde derivatives with ethylenediamine. Substituted salicylaldehydes were prepared via the Reimer–Tiemann reaction or through lithium aluminum hydride reduction followed by manganese dioxide oxidation of a substituted salicylic acid [37–39]. Stirring the Schiff base ligands with cobaltII acetate tetrahydrate under aerobic conditions afforded the requisite Co^{III} complexes [38]. The nature of the R_1, R_2, and R_3 substituents, the hydrocarbonated chain R, and their abbreviations are also shown in Fig. 1.

![Fig. 1 Salen Co^{III} acetate complexes for cyclohexene oxide/CO_{2} copolymerization](image-url)
The product was sufficiently dried under reduced pressure. Complexes 1–6 were isolated as a solid powder. Numerous attempts to isolate complexes 1–5 in a mixture of methylene chloride and hexane or other solvents were proved to be unsuccessful. Fortunately, the structure of a closely related complex 6 could be elucidated by single crystal X-ray analysis. Crystal suitable for X-ray diffraction was grown from a mixture of methylene chloride and hexane at 20 °C. A single crystal was selected for X-ray analysis (Table 1). As shown in Fig. 2, the structure is indeed a six-coordinate octahedral as the structure of the salen CoIII(2,4-dinitrophenoxy) [35, 36]. X-ray diffraction data showed that the crystal was analogous monomeric structures. The overall geometry around the metal cobalt was a triblock with the two carbon atoms superseeded by that with the three carbon atoms, the catalytic activity is dramatically decreased. The catalytic activity is influenced markedly by the nature of the substituents grafted on the ligands molecules and the length of the diimine bridges between the two nitrogen atoms in the ligands, respectively. These results might be mainly ascribed to the steric bulk effect of the substituents R on the phenolates of the ligand. This agrees well with the literature data [5]. These differences in ligands framework and the length of the diimine bridges between the two nitrogen atoms in the ligands also reflect on the selectivity formation of poly(cyclohexenylene carbonate) (PCHC) over cyclohexene carbonate (CHC) and the resulting copolymer number average molecular weights (\(M_n\)). Complex 1 displays the highest PCHC/CHC selectivity and yields polymer with the highest \(M_n\). However, complex 6 presents the lowest PCHC/CHC selectivity and produces polymer with the lowest \(M_n\). Both the length of the diimine bridges and the substituents on the ligands do not have a clear effect on the microstructure of the resultant polymer. With complexes 1–6 the copolymerization affords products possessing >99% carbonate linkages.

The mole ratio of [PPN]Cl to the complex 1 played an important role in the copolymerization of CHO with CO₂, as

| Table 1 Crystal data and structure refinement parameters for complex 6 |
|---------------------------------------------------------------|
| **Empirical formula**                                           | \(C_{37}H_{55}CoN_2O_4\) |
| **Formula weight**                                             | 650.76                  |
| **Temperature (K)**                                            | 293(2)                  |
| **Wavelength (Å)**                                             | 0.71073                 |
| **Crystal system**                                             | Monoclinic              |
| **Space group**                                                | C2/c                    |
| **Unit cell dimensions**                                       |                          |
| \(a\) (Å)                                                      | 25.197(3)               |
| \(b\) (Å)                                                      | 14.7486(17)             |
| \(c\) (Å)                                                      | 23.101(3)               |
| \(\alpha\) (°)                                                | 90                      |
| \(\beta\) (°)                                                 | 108.344(2)              |
| \(\gamma\) (°)                                                | 90                      |
| **Volume (Å³)**                                                | 8148.8(16)              |
| **Z**                                                          | 8                       |
| **Calculated density(Mg m⁻³)**                                 | 1.061                   |
| **Absorption coefficient (mm⁻¹)**                             | 0.455                   |
| **\(F(000)\)**                                                | 2,800                   |
| **Crystal size (mm)**                                         | 0.48×0.18×0.13          |
| **Theta range for data collection (°)**                        | 1.62–25.39              |
| **Limiting indices \((hkl\) range)**                          | –30 ≤ h ≤ 19, –17 ≤ k ≤ 17, –26 ≤ l ≤ 27 |
| **Reflections collected**                                     | 21,475                  |
| **Independent reflections**                                    | 7,465                   |
| **\(R_{int}\)**                                               | 0.0380                  |
| **Data/restraints/parameters**                                 | 7,465/0/412             |
| **Goodness-of-fit on \(F^2\)**                                | 1.024                   |
| **Final \(R\) indices**                                      | \(R_1=0.0593, wR_2=0.1619\) |
| **\(R\) indices (all data)**                                  | \(R_1=0.0815, wR_2=0.1752\) |
| **Largest difference in peak and hole (e Å⁻³)**                | 0.542 and –0.274        |
listed in Table 4 (entries 1–4). Although almost negligible yield was observed in the absence of cocatalyst (see entry 1 in Table 4), the addition of cocatalyst [PPN]Cl resulted in the production of the alternating copolymer (see entries 2–4, in Table 4). Optimization of the molar ratio between complex 1 and [PPN]Cl revealed that the highest yield was achieved using 1 equiv. of [PPN]Cl. However, the increase in the ratio of [PPN]Cl to complex 1 above 2 equiv. could increase the reaction activities. The CHC only was obtained. The CHC formation might be based on the presence of a depolymerization reaction that is promoted at higher [PPN]Cl concentrations. It is most likely due to a backbiting reaction starting from an alcoholate chain end that is displaced from the CoIII center in a coordination equilibrium with [PPN]Cl after epoxide ring opening [18].

The influence of reaction temperature on the copolymerization of CHO and CO2 was investigated using complex 1/[PPN]Cl (see entries 3 and 5–7, in Table 4). Dramatic increase in catalytic activity with temperature was observed, and the turnover frequency (TOF) at 80 °C (48.7 h⁻¹) almost doubles that at 60 °C (25.6 h⁻¹) (see entries 3 and 5, in Table 4), which reaches to 52.2 h⁻¹ when the copolymerization is performed at 100 °C (see entry 6, in Table 4). The highest catalytic activity (54.5 h⁻¹) is achieved at 120 °C (see Entry 7, in Table 4). While the yield of copolymer increases with increasing temperature up to about 80 °C, and then decreases with the further increase. Similar results have been observed previously [33]. In agreement with the increase in yield, $M_n$ of the obtained copolymer increases

![Molecular structure of complex 6](image-url)
correspondingly from 21.6 kg mol$^{-1}$ at 60 °C to 38.7 kg mol$^{-1}$ at 80 °C. In the meantime, polymer dispersity index remains narrow and almost constant (PDI=1.2). 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 [10]. Moreover, the polycarbonates obtained at the range of 60–120 °C all have >99 % carbonate linkages. Obviously, the mole ratio of monomer to complex plays an important role on the TOF of copolymerization, as listed in Table 4 (entries 3 and 8–10). For example, in the experiment of entry 3, TOF (10 h) is 48.7 h$^{-1}$ when 1,000 equiv. of CHO are used. As the ratio of CHO to complex decreases to 200 equiv. in entry 8, the reaction activity decreases by almost thrice, compared with entry 3. Meanwhile, PDI also slightly decreases from 1.2 to 1.1, 

| Entry | Complex | [CHO]/[Cat] | Time (h) | [CHO] (mol l$^{-1}$) | Temperature (°C) | Yield$^a$ | TOF$^b$ (h$^{-1}$) | Selectivity$^c$ (% PPC) | $M_n^d$ (kg mol$^{-1}$) | PDI$^d$ |
|-------|---------|-------------|---------|---------------------|------------------|----------|------------------|---------------------|-----------------|--------|
| 1     | 1       | 1,000       | 10      | 50                  | 60               | 25.6     | 25.6             | >99                 | 21.6            | 1.2    |
| 2     | 2       | 1,000       | 10      | 50                  | 60               | 10.4     | 12.2             | 85                  | 9.3             | 1.4    |
| 3     | 3       | 1,000       | 10      | 50                  | 60               | 17.0     | 17.5             | 97                  | 14.4            | 1.2    |
| 4     | 4       | 1,000       | 10      | 50                  | 60               | 18.9     | 19.7             | 96                  | 17.1            | 1.2    |
| 5     | 5       | 1,000       | 10      | 50                  | 60               | 15.8     | 16.6             | 95                  | 14.5            | 1.3    |
| 6     | 6       | 1,000       | 10      | 50                  | 60               | 0.44     | 2.2              | 20                  | 2.1             | 1.5    |

Copolymerizations run in neat cyclohexene oxide (CHO) with [Co]/([PPN]Cl]=1:1 at 1.5 MPa of CO$_2$ in 1,4-dioxane (7 ml)

$^a$ Based on isolated poly(cyclohexene carbonate) yield
$^b$ Turnover frequency: mol CHO mol Co$^{-1}$ h$^{-1}$
$^c$ Determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz)
$^d$ Determined by gel permeation chromatography calibrated with polystyrene standards in tetrahydrofuran at 40 °C

| Entry | [PPN]Cl/complex 1 | [CHO]/[complex 1] | Time (h) | [CHO] (mol l$^{-1}$) | Temperature (°C) | Yield$^a$ | TOF$^b$ (h$^{-1}$) | Selectivity$^c$ (% PPC) | $M_n^d$ (kg mol$^{-1}$) | PDI$^d$ |
|-------|-----------------|-------------------|---------|---------------------|------------------|----------|------------------|---------------------|-----------------|--------|
| 1     | 0               | 1,000             | 10      | 50                  | 80               | Trace    | –                | –                   | –               | –      |
| 2     | 0.5             | 1,000             | 10      | 50                  | 80               | 10.4     | 12.2             | 99                  | 10.3            | 1.2    |
| 3     | 1               | 1,000             | 10      | 50                  | 80               | 48.2     | 48.7             | 99                  | 38.7            | 1.2    |
| 4     | 2               | 1,000             | 10      | 50                  | 80               | Trace    | –                | –                   | –               | –      |
| 5     | 1               | 1,000             | 10      | 50                  | 60               | 25.6     | 25.6             | >99                 | 21.6            | 1.2    |
| 6     | 1               | 1,000             | 10      | 50                  | 100              | 48.0     | 52.2             | 92                  | 37.1            | 1.4    |
| 7     | 1               | 1,000             | 10      | 50                  | 120              | 46.3     | 54.5             | 85                  | 33.9            | 1.5    |
| 8     | 1               | 200               | 10      | 50                  | 80               | 85.6     | 17.3             | 99                  | 14.9            | 1.1    |
| 9     | 1               | 800               | 10      | 50                  | 80               | 56.7     | 45.8             | 99                  | 35.6            | 1.2    |
| 10    | 1               | 1,200             | 10      | 50                  | 80               | 39.4     | 47.8             | 99                  | 37.7            | 1.2    |
| 11    | 1               | 1,000             | 10      | 30                  | 80               | 27.4     | 27.7             | 99                  | 23.1            | 1.3    |
| 12    | 1               | 1,000             | 10      | 40                  | 80               | 39.6     | 40.2             | 99                  | 30.1            | 1.2    |
| 13    | 1               | 1,000             | 10      | 60                  | 80               | 43.9     | 46.2             | 95                  | 35.7            | 1.3    |
| 14    | 1               | 1,000             | 5       | 50                  | 80               | 29.2     | 58.4             | 99                  | 23.8            | 1.2    |
| 15    | 1               | 1,000             | 20      | 50                  | 80               | 70.7     | 36.1             | 98                  | 57.8            | 1.3    |
| 16    | 1               | 1,000             | 40      | 50                  | 80               | 85.2     | 22.2             | 96                  | 71.8            | 1.5    |

$^a$ Copolymerizations run in neat cyclohexene oxide (CHO) with [Co]/([PPN]Cl]=1:1 at 1.5 MPa of CO$_2$ in 1,4-dioxane (7 ml)
$^b$ Based on isolated poly(cyclohexene carbonate) yield
$^c$ Turnover frequency: mol CHO mol Co$^{-1}$ h$^{-1}$
$^d$ Determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz)
$^e$ Determined by gel permeation chromatography calibrated with polystyrene standards in tetrahydrofuran at 40 °C
and $M_n$ decreases significantly from 38.7 to 14.9 kg mol$^{-1}$. However, the further increases in the ratio of CHO to complex I above 1,000 equiv. could reduce the reaction activities (see entries 3 and 10, in Table 3). Especially, when over 1,000 equiv. of CHO are selected, both drops in catalytic activity and yield of the resultant product are observed (entry 10), which could be attributed to the lowering of the catalytic concentration when overloading monomer.

Besides operation temperature and ratio of monomer to complex, initial CHO concentration is another important issue for the reaction. In our results, it is observed that the catalytic activity increases as the initial CHO concentration increases from 30 to 50 mol l$^{-1}$ (see entries 3, 11, and 12, in Table 4) and decreases then with the further increase in CHO concentration (entry 13 in Table 4). The prolonged reaction does not lead to an observable decrease in selectivity for PCHC formation, which can be explained by the so-called solvent effect. A similar solvent effect was reported for the copolymerization with binary catalyst systems [32, 42].

$^{13}$C NMR spectroscopy has been extensively used to investigate CHO incorporation into polymer backbones, which can be used to estimate the tacticity of the copolymer [2, 14]. Figure 3 presents a $^{13}$C NMR spectrum of the PCHC which can be used to estimate the tacticity of the copolymer investigated CHO incorporation into polymer backbones, especially when overloading monomer (Table 3). The spectrum is very similar to those of PCHC prepared with (salen)CoX catalysts [5]. Clearly, the carbonyl regions at $\delta=153.80–153.66$ and 153.25–153.30 ppm can be assigned to the isotactic and syndiotactic structures of the PCHC chain, respectively [2]. The peaks at 153.25–153.30 ppm are assigned to the central carbonyl carbons of $r$-centered tetrads, whereas the peaks at 153.80–153.66 ppm are attributed to the central carbonyl carbons of $m$-centered tetrads [2, 14]. PCHCs revealed a strong contribution correlating to $r$-centered tetrads (78 %), indicative of syndiotactic PCHC.

MALDI-TOF mass spectrometry is specifically suitable for structural and end-group analysis [5]. Figure 4 displays a spectrum of the resultant PCHC obtained (entry 3 in Table 4). At least two series of signals with regular repeat intervals (repeating units of 142.2 mass units) were observed in the mass spectra. For the first series of peaks at the $m/z$ of 1,931.6, 2,073.8, 2,216.0, 2,358.2, 2,500.4, and 2,642.6, there was a difference of 142.2 in $m/z$ between every two neighboring peaks, which was also seen in the second series at the $m/z$ of 1,947.7, 2,089.9, 2,232.1, 2,374.3, 2,516.5, and 2,658.7. Moreover, in the second series peaks in $m/z$ were correspondingly 16 larger than those in the first series. Additionally, the weight number of propylene carbonate unit is 142.2. Thus, it could be known by calculation that the first series peaks resulted from the copolymerization reaction was initiated by insertion of CHO into a Co-acetate bond of the catalytic species attached to a Co center, and terminated with acetate groups and Na$^+$ ions, and K$^+$ ions instead of Na$^+$ ions for the second series.

On the basis of the information presented so far, some proposed mechanism illustrated that the monomer was inserted to the cobalt–oxygen bond of the propagating end, as shown in Scheme 1. [PPN]Cl coordinated to the metal center in the axial site transferred to the propagating metal–polymer chain, thereby labilizing the metal alkoxide bond and facilitating the insertion of CO$_2$ [3, 6, 17, 18, 21, 24]. The CHO monomer might be first favorably inserted into the Co–OR bond of the Schiff base cobalt complex, followed by the insertion of the CO$_2$ monomer. Subsequent alternating copolymerization of CHO and CO$_2$ affords the alternating repeating unit structure to yield the polycarbonate. The side reaction to yield the cyclic carbonate could take place through the backbiting degradation of the growing polymer–catalyst complex, which may lead to the lower polymer yield. A mechanism similar to that proposed by Darenbourg and Yarbrough using chromium salen and N-MeIm in the copolymerization of CO$_2$ and cyclohexene oxide [14].
Copolymerization of PO and CO$_2$

By use of complex 1 and [PPN]Cl catalyst system, the copolymerization of CO$_2$ and PO ([PO]$_0$/[[PPN]Cl]$_0$/[complex 1]$_0$ = 500/1/1) selectively gave the alternating copolymer in 1,4-dioxane at 60 °C in 24 h (carbonate linkages=99 %, polycarbonate/cyclic carbonate=99/1, $M_n$=6,400, $M_w/M_n$=1.21; Table 5, run 2), although the reaction proceeded rather slowly (36.8 % yield). Also at 80 °C, the copolymerization proceeded more rapidly to attain 42.1 % polymer yield in the same reaction time, slightly lowering the selectivity (carbonate linkages=95.8 %, polycarbonate/cyclic carbonate=92/8, $M_n$=7,800, $M_w/M_n$=1.31; Table 5, run 3). When the copolymerization was conducted at an elevated temperature, such as

**Table 5** Copolymerization of PO and CO$_2$

| Entry | Temperature (°C) | Time (h) | Yield$^a$ | Selectivity$^b$ (% PPC) | $M_n$ (kg mol$^{-1}$) | PDF$^c$ |
|-------|-----------------|----------|-----------|------------------------|----------------------|--------|
| 1     | 40              | 24       | 17.7      | 99                     | 5.3                  | 1.12   |
| 2     | 60              | 24       | 22.8      | 99                     | 6.4                  | 1.21   |
| 3     | 80              | 24       | 42.1      | 92                     | 7.8                  | 1.31   |
| 4     | 100             | 24       | 16.7      | 30                     | 6.9                  | 1.52   |
| 5     | 60              | 48       | 76.7      | 93                     | 13.9                 | 1.26   |

The reaction was performed in neat PO (14 ml, 200 mmol; [PO]$_0$/[[PPN]Cl]$_0$/[complex 1]$_0$=500:1:1) in a 100-ml autoclave at 1.6 MPa of CO$_2$ in in 1,4-dioxane (5 ml)

$^a$ Based on isolated poly(propylene carbonate) yield
$^b$ Determined by $^1$H NMR spectroscopy (CDCl$_3$, 300 MHz)
$^c$ Determined by gel permeation chromatography calibrated with polystyrene standards in tetrahydrofuran at 40 °C
100 °C, a significant amount of cyclic carbonate (polycarbonate/cyclic carbonate=30/70) was generated under otherwise similar conditions (Table 5; run 3).

The high selectivity of polycarbonate over cyclic carbonate at 60 °C was maintained after a longer reaction time to attain quantitative formation of the alternating copolymer. The alternating copolymerization of CO₂ and PO by using complex 1 and [PPN]Cl catalyst system was carried out at 60 °C for 48 h and afforded the alternating copolymer almost quantitatively (polycarbonate/cyclic carbonate = 93/7, carbonate linkages = 99 %, $M_n = 13,900$, $M_w/M_n = 1.26$, Table 5, run 5).

Conclusions

In summary, a series of cobalt/Schiff base complexes 1–6 were investigated for the alternating copolymerization of CO₂ with epoxide (CHO and PO) to afford completely alternating polycarbonates with good activity in presence of [PPN]Cl. The resultant polymer has high molecular weight and high carbonate linkages as well as narrow molar mass distribution. The molecular weight of the copolymers is also sensitive to the concentration of CHO in the feed for the complexes. In addition, the solid-state structure of complex 6 was characterized, providing valuable information about the mechanism of the catalytic polymerization reaction. This strategy allows considerable scope for ligand modification and thus might lead to the design of new, efficient, and practical catalysts for the copolymerization of epoxides with CO₂.

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