JOURNAL OF THE CHINESE
CHEMICAL SOCIETY

Copolymerization of Carbon Dioxide and Propylene Oxide by Binary Cobalt Salen Complexes with Various Anion Groups

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(Received: January 1, 2017; Accepted: February 19, 2017; DOI: 10.1002/jccs.201700001)

A series of salen–Co(III)(X) complexes tethering quaternary ammonium salts are designed to investigate the influence of the axial group X in the complex and the anion Y of quaternary ammonium salt on the copolymerization of CO_2 and PO. By copolymerization, the complex **9**, where X and Y are both 2,4-dinitrophenolate, has the highest catalytic efficiency. When X is OAc and Y is BF_4^-/NO_3^-, the complexes **11/12** have lower catalytic efficiency. For the complex **10**, where X and Y are both OAc, the catalytic efficiency is the lowest. At the same time, complex **9** can produce the copolymer with the highest carbonate fraction and M_n. And the best copolymerization conditions were as follows: reaction temperature 30°C, copolymerization time 24 h, and CO_2 pressure 2 MPa with complex **9**. The thermal properties of the copolymers are also studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

Keywords: Salen–cobalt complexes; Quaternary ammonium salt; Carbon dioxide.

INTRODUCTION

In recent years, more and more attention is being paid to the problem of global warming. CO_2 is currently regarded as the culprit for greenhouse effect, which causes the global climate to become complex and changeable. Control and use of CO_2 has attracted the attention of scientists.[1] Since Inoue and coworkers first reported the conversion of carbon dioxide and epoxide to polycarbonate in 1969,[2] many studies are being carried out around the world.[3] The copolymerization process is often accompanied by the formation of polyether and five-membered cyclic carbonates, which is attributed to the use of different catalysts and different reaction conditions.

Among the different comonomers, the most attractive one is PO.[4–6] The copolymerization of CO_2 and PO produces poly(propylene carbonate) (PPC), which burns without emitting any toxic materials and is biodegradable.[7] The other product by copolymerization is cyclic carbonate.[8–11] Cyclic carbonate is an important industrial raw material. It is widely used in textiles, printing, dyeing, battery, and other applications. As the same time, it is also an excellent solvent and organic synthesis intermediate.

For the copolymerization reaction, various catalysts including heterogeneous and homogeneous metal-based complexes have been developed.[12–16] Even though the chemical or crystal structures of heterogeneous catalysts are not clear, they are convenient for synthesis and handling, showing more potentiality for industrial use. Meanwhile, a homogeneous catalyst is interesting in academic research, and different catalysts have different catalytic effects. Through slight changes of the catalyst structures, the copolymerization can be tuned to favor the formation of the desired product. Among of them, metal–salen complexes has gained considerable attention over the past decade,[17–22] which is due to their advantages of simple preparation, high catalytic activity, and easy-to-change structure. More recently, functional metal–salen-complex-based catalysts have received much attention, especially using single-component bifunctional metal–salen complexes instead of binary catalysts.

In the present work, we have synthesized a novel salen ligand. A schematic of the synthetic steps is shown in Scheme 1. On this basis, a series of salen–Co (III)(X) complex tethering quaternary ammonium salts were synthesized through variations of the axial group

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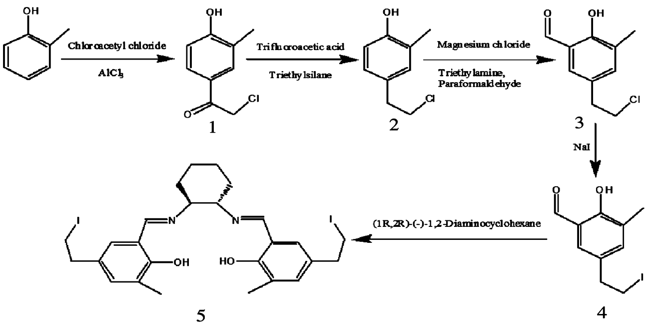


Scheme 1. Syntheses of compounds **1–5**.

X of the complexes and the anion Y of quaternary ammonium salts. In this study, the objective was to understand the differences in copolymerization of these salen complexes with different axial groups X and different anions Y of quaternary ammonium. At the same time, it can throw light on the effect of reaction conditions on the copolymerization of CO_2 with PO.

RESULTS AND DISCUSSION

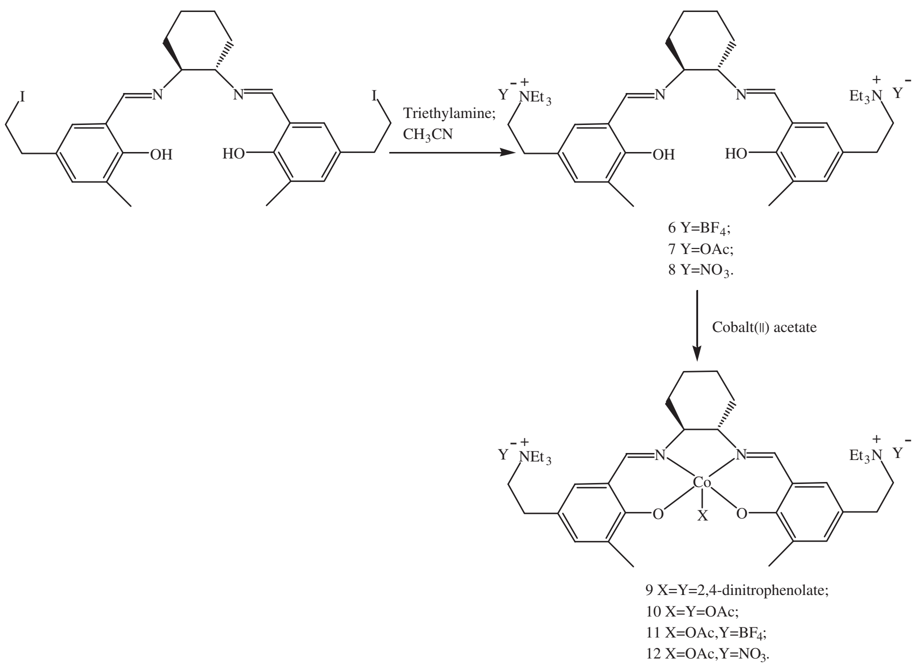
Synthesis and characterization

As stated above, salen–cobalt(III) complexes were used as catalysts for the copolymerization of CO_2 and PO. Suitable ligands should be beneficial for this purpose.[23] This motivates us to synthesize new ligands on the basis of previous studies.[24–28]

In the first step, the acylation reaction of *o*-cresol and chloroacetyl chloride was allowed to progress using $AlCl_3$ as the catalyst and CH_2Cl_2 as the solvent under N_2 atmosphere. And a part of the desired products was further acylated on the OH groups,[24] which were hydrolyzed to give compound **1**. The ^{1}H-NMR signal at δ values 4.65 indicated the presence of the methylene group, which confirmed the successful synthesis of compound **1**. In the second step, the carbonyl group of compound **1** was reduced to a methylene group using triethylsilane and trifluoroacetic acid to obtain compound **2**. ^{1}H-NMR indicated the presence of a new methylene group (δ = 2.96). Because the carbonyl group was reduced to the methylene group, the peak of original methylene changed from δ = 4.65 to δ = 3.65. In the third step, *para*-formaldehyde was used to provide the aldehyde group with magnesium chloride as catalyst, triethylamine as the acid-binding agent, and THF as the solvent under reflux conditions to gain compound **3**. ^{1}H-NMR of compound **3** indicated the presence of aldehyde group (signal at δ = 9.87). In the next step, the chlorine group of compound 3 was substituted with the iodine group using CH_3CN as solvent under reflux conditions to get compound **4**. Because the electronegativity of iodine is less than that of chlorine, the chemical shift of the methylene group attached to the iodine group moved toward high field (δ = 3.71 to δ = 3.34). The desired salen ligand was obtained by the condensation of compound **4** with (1*R*,2*R*)(−)-1,2-diaminocyclohexane. The results showed that the presence of N=CH (δ = 8.15) and cyclohexyl-H (δ = 3.24–3.22; 1.88–1.79; 1.42–1.37) in the ^{1}H-NMR showed that the salen ligand was successfully synthesized. The salen ligand tethering quaternary ammonium salt was obtained from the ligand with triethylamine. Subsequently, with $AgBF_4$ for ion exchange, the iodine ion was exchanged with BF_4^- to get a new ligand. The presence of new methylene group signal (δ = 3.11) and methyl group signal (δ = 1.18) in the ^{1}H-NMR showed that quaternary ammonium salt was successfully synthesized. Metalation of the new ligand with $Co(OAc)_2$ under an inert atmosphere gave the salen–Co(II) complex, and then salen–Co(III) complex **9** was obtained under O_2 atmosphere using sodium 2,4-dinitrophenolate by ion exchange. The salen–Co(III) complexes **10–12** were obtained using similar approach. Signals of three hydrogens on 2,4-dinitrophenolate (^{1}H-NMR signal at δ = 8.67; 8.06; 6.75) appeared, and at the same time the ^{1}H-NMR signal of the phenolic hydroxyl disappeared, which indicated the successful synthesis of compound **9**. The ^{1}H-NMR signal of the phenolic hydroxyl disappeared, and a new methyl group (signal at δ = 2.07) was found, which indicated that compounds **10–12** were successfully synthesized.

Polymerization studies

Four kinds of salen–Co(III) complex **9–12** were used as catalyst to investigate the influence of the axial group X in the complex and the anion Y of the quaternary ammonium salt on the copolymerization of CO_2 and PO (Scheme 2). The copolymerization results are listed in Table 1. In order to compare the different catalytic efficiencies of the four catalysts, the copolymerization was carried out at 2 MPa and 24 h with different temperatures (30–80°C). From entries 1–16 in Table 1, it can be seen that the four catalysts follow different



Scheme 2. Syntheses of complexes **9–12**.

catalytic trends with temperature variation. For complex **9**, the catalytic efficiency increases with decreasing temperature (entries 1–4). The decrease of polymer yield at higher temperature may be due to the selectivity for PPO and the decomposition of the copolymer at the higher temperature. When the temperatures was 30°C, the copolymerization had the highest turnover number (TON) of 816.0, which is also the highest in the whole table. At the same time, it can be seen that entry 1 has the high carbonate fraction (fco2c) of 0.583 in the whole table, which can also be seen in Figure 3. The characteristic peaks for PPC are as follows: ^{1}H-NMR ($CDCl_3$), δ(ppm) 1.34 (d, 3H, CH_3, J = 5.5 Hz), 4.17 (m, 2H, CH_2), and 5.00 (m, 1H, CH). The peaks for polypropylene ether(PPO) are at δ(ppm) 1.16 (d, 3H; CH_3), 3.58 (2H; CH_2), and 3.45 (1H; CH). The peaks for cyclic propylene carbonate(CPO) are at δ(ppm) 1.49 (d, 3H; CH_3), 4.03(1H; CH_2), 4.56(1H; CH_2), and 4.86 (1H; CH). As shown in Figure 3, the peak value of 5.00 ppm in the ^{1}H-NMR for the synthesized product at the temperature of 30°C was the highest, which indicates that the product has the highest content of PPC under 30°C. The peak value of 4.86 ppm in ^{1}H-NMR for the synthesized product at the temperature of 40°C was the highest, which indicated that the CPO content in the synthesized product was the highest under 40°C. When the temperature was greater than 40°C, the peaks at 5.00 and 4.86 ppm were almost absent, indicating that PPO is the main content of the synthesized products at temperatures >40°C. This may be due to the decomposition of the copolymer at higher temperatures. These data indicate that when both X and Y were 2,4-dinitrophenolate, the complex had the highest catalytic efficiency.

When both X and Y were OAc, the copolymerization was carried out for the complex **10** (entries 5–8). It can be seen that copolymerization did not change obviously with temperature. In addition, the copolymerization had the lowest catalytic efficiency (both TON and fco2c). These results indicate that the OAc is not a good cocatalyst.

When X is OAc and Y is BF_4^- or NO_3^-, the copolymerization was carried out for the complexes **11** and **12** (entries 9–16). It can be seen that these two complexes follow similar catalytic laws, and the catalytic efficiency increases with increasing temperature. When temperature reaches 80°C, the TON is 628.4 for complex **11** and 547.3 for complex **12**. Besides, in the case of complex **11** it can be seen that when temperature is 80°C, the carbonate fraction reaches 0.455. For the complex **12**, the highest carbonate fraction is 0.414 when the temperature reaches 40°C.

Table 1. CO_2/(propylene oxide) copolymerization results[1]

Entry	Cat	*T* (°C)	*P* (MPa)	*t* (h)	TOF[2] (h^{-1})	TON	f_{CO_2}[3]	M_n[4]$\times10^{-3}$	M_w/M_n
1	**9**	30	2	24	34.0	816.0	0.583	56.1	1.58
2	**9**	40	2	24	18.3	440.3	0.462	53.0	1.80
3	**9**	60	2	24	13.5	324.6	0.008	52.0	1.72
4	**9**	80	2	24	12.8	308.1	0.051	53.7	1.68
5	**10**	30	2	24	12.7	304.5	0.012	36.9	1.58
6	**10**	40	2	24	10.4	249.3	0.011	23.1	1.32
7	**10**	60	2	24	13.2	318.0	0.030	32.9	1.33
8	**10**	80	2	24	11.5	276.2	0.011	33.7	1.71
9	**11**	30	2	24	7.4	177.4	0.017	45.4	1.95
10	**11**	40	2	24	8.0	192.4	0.029	43.3	1.49
11	**11**	60	2	24	20.2	485.5	0.058	46.8	1.63
12	**11**	80	2	24	26.2	628.4	0.455	39.7	1.43
13	**12**	30	2	24	14.3	343.2	0.009	42.8	1.47
14	**12**	40	2	24	10.3	246.0	0.414	38.3	1.39
15	**12**	60	2	24	15.5	372.5	0.023	29.4	1.48
16	**12**	80	2	24	22.8	547.3	0.033	51.9	1.85
17	**9**	30	1	24	7.8	187.8	0.030	26.1	1.55
18	**9**	30	3	24	12.8	308.1	0.030	36.4	1.47
19	**9**	30	4	24	12.1	291.5	0.047	29.6	1.37
20	**9**	30	2	12	15.5	186.3	0.008	27.6	1.51
21	**9**	30	2	36	13.1	471.9	0.018	31.3	1.46
22	**9**	30	2	48	9.3	444.8	0.022	33.1	1.53

[1] Polymerization condition: PO 10 g, cat : PO = 1:15 000 molar ratio.
[2] Turnover frequency: mole of PO consumed by per mole of catalyst per hour.
[3] Carbonate fraction determined by ^1H NMR spectroscopy ($CDCl_3$, 400 MHz).
[4] Determined using GPC using a polystyrene standard.

At the same time, M_n and M_w/M_n of the copolymers produced by these four complexes were investigated by gel permeation chromatography (GPC). It can be seen from Table 1 that the complex **9** can give copolymers with the highest M_n, the next one is complex **11**, and the lowest is the complex **10**.

Because complex **9** has the highest catalytic efficiency, the effects of time and pressure on copolymerization were also studied. It can be seen from entries 1 and 17–19 that when the CO_2 pressure increases gradually from 1 to 4 MPa, the TON increases from 187.8 for 1 MPa, peaked at 816.0 for 2 MPa, and then dropped to 291.5 for 4 MPa. When pressure increased from 1 to 2 MPa, the ratio of CPO/PPC decreased with an increase of the ratio of PPC/PPO. When the pressure was increased from 2 to 4 MPa, conversely, the ratio of CPO/PPC increased while the ratio of the ratio of PPC/PPO decreased. The effects of time follow a similar trend (entries 1 and 20–22). When the time increased from 12 to 48 h, the TOF increased from 15.5 for 12 h, peaked at 34.0 for 24 h, and then dropped to 9.3 for 48 h. The GPC test made clear that the sample with entry 1 had the highest M_n.

In summary, the best catalyst was the complex **9**. And the best copolymerization condition was as follows: reaction temperature 30°C, copolymerization time 24 h, and CO_2 pressure 2 MPa.

Thermal properties

The DSC curves of the copolymers (entries 1, 5, 9, and 13) by the four different catalyst **9**, **10**, **11**, and **12** are shown in Figure 4. They show that the copolymer with entry 1 has the glass transition temperature (T_g) of −70°C. For those copolymers with entries 5, 9, and 13, the T_g's were all −74°C. The reason may be that the content of the carbonate fraction in these copolymers is very low, which leads to a lower T_g. For the

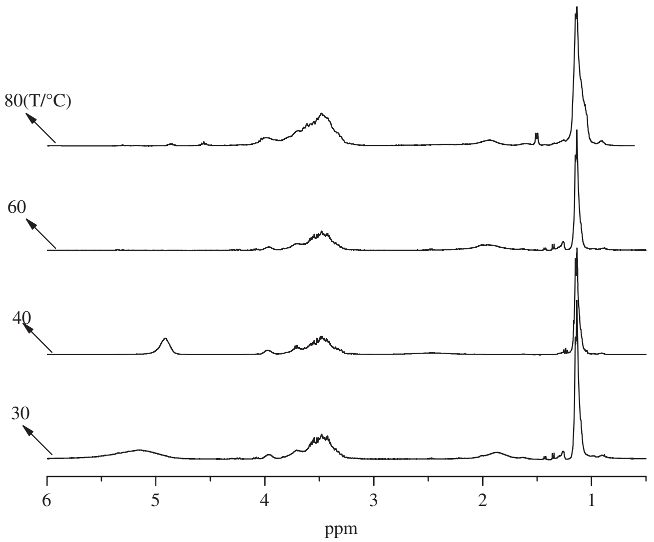


Fig. 1. ^{1}H NMR spectrum of polymers synthesized at different temperatures using complex **9** as catalyst in $CDCl_3$.

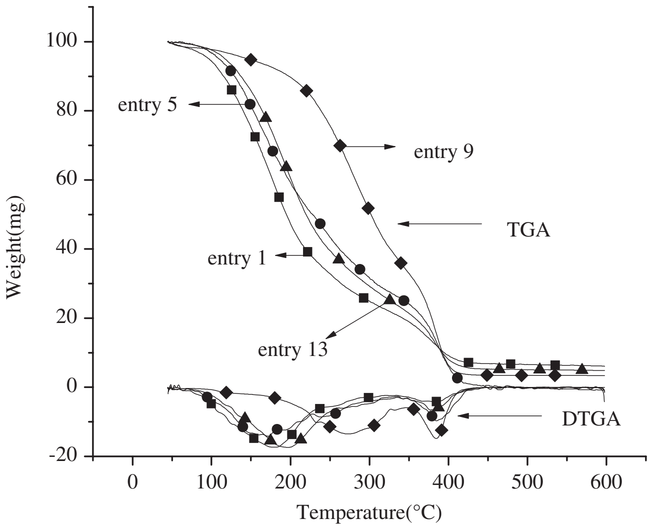


Fig. 3. TGA and DTGA curves of the copolymers with entries 1, 5, 9, and 13 synthesized by the four catalysts (complexes **9**, **10**, **11**, **12**).

copolymer with entry 1, owing to the highest carbonate fraction of 0.583, T_g is also the highest.

The typical TGA/DTGA curves of the copolymers (entries 1, 5, 9, and 13) by the four different catalysts **9**, **10**, **11**, and **12** are shown in Figure 3. The 50 wt% weight loss temperature (T_d) from TGA appeared at 194.8, 227.6, 302.2, and 220.2°C, respectively. The DTGA curves show two thermal degradation peaks for these copolymers, which are at 180.3 and 384.8°C for entry 1. For entry 5, the peaks are at 169.7 and 384.1°C. For those of entry 9, the peaks are at 273.2 and 384.7°C. For those of entry 13, the peaks are at 199.2 and 382.2°C. The first peak may be due to the thermal degradation of ester/ether bond of PPC/PPO, and the second peak to the breaking of the C—C bond which needs higher energy. The results from DSC and TGA/DTGA indicate that the synthesized copolymers are suitable as sealants.

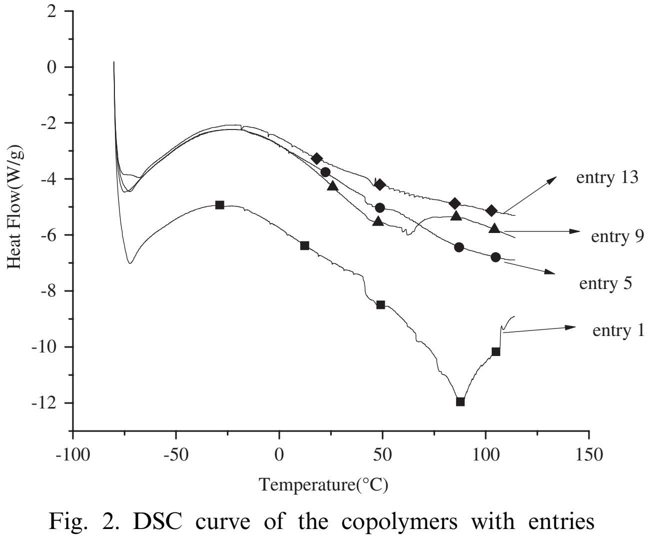


Fig. 2. DSC curve of the copolymers with entries 1, 5, 9, and 13 synthesized by four catalysts (complexes **9**, **10**, **11**, and **12**).

EXPERIMENTAL

Materials and instrumentation

All manipulations were performed under an inert atmosphere using a standard glove box and Schlenk techniques. Ethanol was dried using sodium and diethyl phthalate. THF, PO, CH_3CN, CH_2Cl_2, and cyclohexane were dried by stirring over CaH_2, and were subsequently vacuum-transferred to reservoirs. ^{1}H-NMR (400 MHz) was recorded on a Varian Mercury Plus 400. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet MAGNA-IR750 apparatus using a thin film with the ratio of sample to KBr as 1: 100 by mass. The TGA profiles were obtained on a Shimadzu TGA-50H thermoanalyzer under a nitrogen flow rate of 6×10^{-5} m^3/min and a scan rate of 20°C/min. The glass transition temperatures were determined on a Perkin-Elmer 7 DSC instrument at a heating rate of 20°C/min under nitrogen flow. GPC curves were obtained at room temperature in THF using a Waters Millennium instrument with polystyrene standards.

Synthesis and characterization of compounds 1–8

Synthesis of compound 1 $AlCl_3$ (38.94 g, 0.292 mol) was added to a four-neck flask and combined with CH_2Cl_2 (200 mL). And then chloroacetyl chloride (32.90 g, 0.291 mol) and *o*-cresol (31.40 g, 0.291 mol) were added dropwise under a N_2 atmosphere. The suspension was stirred for 24 h. The solution was then extracted using CH_2Cl_2 (3 × 50 mL). The collected organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel, eluting with petroleum ether and ethyl acetate (v/v, 10:1). The product was obtained as a gray white solid. The yield was 12 g (46.77%). IR (KBr): 3373 (OH), 1697 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$):δ 7.79 (s, 1H, m-H), 7.75 (d, J = 8.4 Hz, 1H, m-H), 6.84 (d, J = 8.4 Hz, 1H, o-H), 5.45 (s, 1H, Ar-OH), 4.65 (s, 2H, CH_2), 2.30 (s, 3H, CH_3) ppm.

Synthesis of compound 2 Compound **1** (10 g, 0.054 mol) and trifluoroacetic acid (10 mL) were weighed into a one-neck flask. And then triethylsilane (6.24 g, 0.054 mol) was added. After the solution was stirred for 12 h at room temperature, and the pH value was adjusted to 8. The compound was extracted using petroleum ether (3 × 50 mL). The organic layers were combined, and the resulting solution was dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give an oily residue, which was purified by column chromatography on silica gel, eluting with petroleum ether and ethyl acetate (v/v, 10:1). The product was obtained as a light yellow oil. The yield was 6.9 g (74.68%). IR (KBr): 3403 (OH) cm^{-1}. ^1H-NMR ($CDCl_3$):δ 6.96 (s, 1H, m-H), 6.91 (d, J = 8.0 Hz, 1H, m-H), 6.70 (d, J = 8.1, 1H, o-H), 4.99 (s, 1H, Ar-OH), 3.65 (t, J = 7.4 Hz, 2H, CH_2-Cl), 2.96 (t, J = 7.4 Hz, 2H, Ar-CH_2), 2.23 (s, 3H, CH_3) ppm.

Synthesis of compound 3 Compound **2** (6.00 g, 0.352mol) was dissolved in THF (50 mL). Magnesium chloride (13.43 g, 0.141 mol), triethylamine (14.98 g, 0.148 mol), and paraformaldehyde (4.23 g, 0.141 mol) were added under a N_2 atmosphere. The suspension was stirred at 80°C for 4 h, after which the solvent was removed with a rotary evaporator. And then the product was extracted using ethyl acetate (3 × 80 mL). The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel, eluting with petroleum ether and ethyl acetate (v/v, 5:1). The product was obtained as a light yellow solid. The yield was 4.6 g (65.90%). IR (KBr): 3462 (OH), 1639 (C=O) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 11.18 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.26 (s, 1H, m-H), 7.21 (s, 1H, m-H), 3.71 (t, J = 7.0 Hz, 2H, CH_2Cl), 3.03 (t, J = 7.3 Hz, 2H, benzyl-CH_2), 2.27 (s, 3H, CH_3) ppm.

Synthesis of compound 4 Compound **3** (4.60 g, 0.0232 mol) was dissolved in CH_3CN (80 mL), and NaI (3.47 g, 0.0232 mol) was added. The suspension was stirred at 80°C for 24 h and cooled to room temperature. The product was extracted using CH_2Cl_2 (3 × 50 mL). The solvent was removed with a rotary evaporator to give a residue, which was purified by column chromatography on silica gel, eluting with petroleum ether and ethyl acetate (v/v, 5:1). The product was obtained as a light yellow solid. The yield was 5.4 g (80.36%). IR (KBr): 3462 (OH), 1639 (CHO) cm^{-1}. ^1H-NMR ($CDCl_3$):δ 11.18 (s, 1H,OH), 9.87 (s, 1H, CHO), 7.26 (s, 1H, m-H), 7.21(s, 1H, m-H), 3.34 (t, J = 7.5 Hz, 2H, CH_2I), 3.13 (t, J = 7.5 Hz, 2H, benzyl-CH_2), 2.27 (s, 3H, CH_3) ppm.

Synthesis of compound 5 (1*R*,2*R*)(−)-1,2-Diaminocyclohexane L-tartrate (1.41 g, 0.00535 mol) was dissolved in the saturated solution of KOH (20 mL). Subsequently, the solution was extracted using CH_2Cl_2. The resulting solution and compound **4** (3.10 g, 0.0107 mol) were added to a flask containing cyclohexane (50 mL). The solution was refluxed for 24 h under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under reduced pressure to give a yellow solid. The yield was 2.3 g (65.71%). IR (KBr): 3432 (OH), 1639 (C=N) cm^{-1}. ^1H-NMR ($CDCl_3$):δ13.45 (s, 2H, OH), 8.15 (s, 2H, N=CH), 6.87 (s, 2H, m-H), 6.74 (d, J = 1.7 Hz, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, J = 7.6 Hz, 4H, CH_2I), 2.93 (t, J = 7.8 Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2) ppm.

Synthesis of compound 6 Compound **5** (0.2 g, 0.304 m mol) was dissolved in CH_3CN (50 mL). Triethylamine (0.122 g, 1.216 mmol) was added under a N_2

atmosphere. The solution was stirred at 81°C for 2 days and cooled to room temperature. And then the solvent was removed with a rotary evaporator to give a residue, which was subsequently titrated in diethyl ether. The residue was dissolved in CH_3CN (50 mL). $AgBF_4$ (0.118 g, 0.608 mmol) was added under a N_2 atmosphere. The solution was stirred overnight. The solution was filtered and then the solvent was removed under reduced pressure to give a yellow solid. The yield was 0.213 g (88.75%). IR (KBr): 3464 (OH), 1645(C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$):δ13.45 (s, 2H, OH), 8.15 (s, 2H, N=CH), 6.87 (s, 2H, m-H), 6.74 (d, J = 1.7 Hz, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, J = 7.6 Hz, 4H, CH_2), 3.11 (q, J = 7.3 Hz, 12H, CH_2), 2.93 (t, J = 7.8 Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, J = 7.3 Hz, 18H, CH_3) ppm.

Synthesis of compound 7 Compound **5** (0.2 g, 0.304 mmol) was dissolved in CH_3CN (50 mL). Triethylamine (0.122 g, 1.216 mmol) was added under a N_2 atmosphere. The solution was stirred at 81°C for 2 days and cooled to room temperature. And then the solvent was removed with a rotary evaporator to give a residue, which was subsequently titrated in diethyl ether. The residue was dissolved in CH_3CN (50 mL). AgOAc (0.101 g, 0.608 mmol) was added under a N_2 atmosphere. The solution was stirred overnight. The solution was filtered and then the solvent was removed under reduced pressure to give a yellow solid. The yield was 0.194 g (88.18%). IR (KBr): 3431 (OH), 1628 (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$):δ13.45 (s, 2H, OH), 8.15 (s, 2H, N=CH), 6.87 (s, 2H, m-H), 6.74 (d, J = 1.7 Hz, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, J = 7.6 Hz, 4H, CH_2), 3.11 (q, J = 7.3 Hz, 12H, CH_2), 2.93 (t, J = 7.8 Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, J = 7.3 Hz, 18H, CH_3) ppm.

Synthesis of compound 8 Compound **5** (0.2 g, 0.304 mmol) was dissolved in CH_3CN (50 mL). Triethylamine (0.122 g, 1.216 mmol) was added under a N_2 atmosphere. The solution was stirred at 81°C for 2 days and cooled to room temperature. And then the solvent was removed with a rotary evaporator to give a residue, which was subsequently titrated in diethyl ether. The residue was dissolved in CH_3CN (50 mL). $AgNO_3$ (0.103 g, 0.608 mmol) was added under a N_2 atmosphere. The solution was stirred overnight. The solution was filtered and then the solvent was removed under reduced pressure to give a yellow solid. The yield was 0.195 g (87.84%). IR (KBr): 3430 (OH), 1632 (C=N) cm^{-1}. ^{1}H-NMR ($CDCl_3$):δ13.45 (s, 2H, OH), 8.15 (s, 2H, N=CH), 6.87 (s, 2H, m-H), 6.74 (d, J = 1.7 Hz, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, J = 7.6 Hz, 4H, CH_2), 3.11 (q, J = 7.3 Hz, 12H, CH_2), 2.93 (t, J = 7.8 Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, J = 7.3 Hz, 18H, CH_3) ppm.

Synthesis and characterization of complexes 9–12

Synthesis of complex 9 Compound **6** (0.3 g, 0.384 mmol) and cobalt(II) acetate (0.068 g, 0.384 mmol) were dissolved in methanol under a N_2 atmosphere. After stirring for 2 h at room temperature, the solvent was removed, and the residue was titrated in diethyl ether. The solid was dissolved in CH_2Cl_2, and 2,4-dinitrophenol (0.071 g, 0.384 mmol) was added. The resulting solution was stirred for 2 h under an O_2 atmosphere. After sodium 2,4-dinitrophenolate (0.237 g, 1.152 mmol) was added, the resulting suspension was stirred overnight at room temperature. The solution was filtered and then the solvent was removed under reduced pressure to give a brown solid. The yield was 0.4 g (85.84%). ^{1}H-NMR (DMSO-d_6):δ8.67 (s, 3H, $(NO_2)_2C_6H_3O$), 8.06 (d, J = 6.8 Hz, 3H, $(NO_2)_2C_6H_3O$), 7.61 (s, 2H, N=CH), 7.23 (s, 2H, m-H), 7.15 (s, 2H, m-H), 6.75 (d, J = 9.0 Hz, 3H, $(NO_2)_2C_6H_3O$), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, J = 7.6 Hz, 4H, CH_2), 3.11 (q, J = 7.3 Hz, 12H, CH_2), 2.93 (t, J = 7.8 Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, J = 7.3 Hz, 18H, CH_3) ppm. Anal. Calc.($C_{56}H_{69}CoN_{10}O_{17}$): C, 55.44; H, 5.73; N, 11.55%. Found: C, 55.41; H, 5.84; N, 11.44%. The ^{1}H NMR spectrum of **9** is shown in Figure 4.

Synthesis of complex 10 Compound 7 (0.3 g, 0.414 mmol) was dissolved in CH_2Cl_2. Cobalt(II) acetate (0.073 g, 0.414 mmol) was added under a N_2 atmosphere. The resulting solution was stirred for 12 h

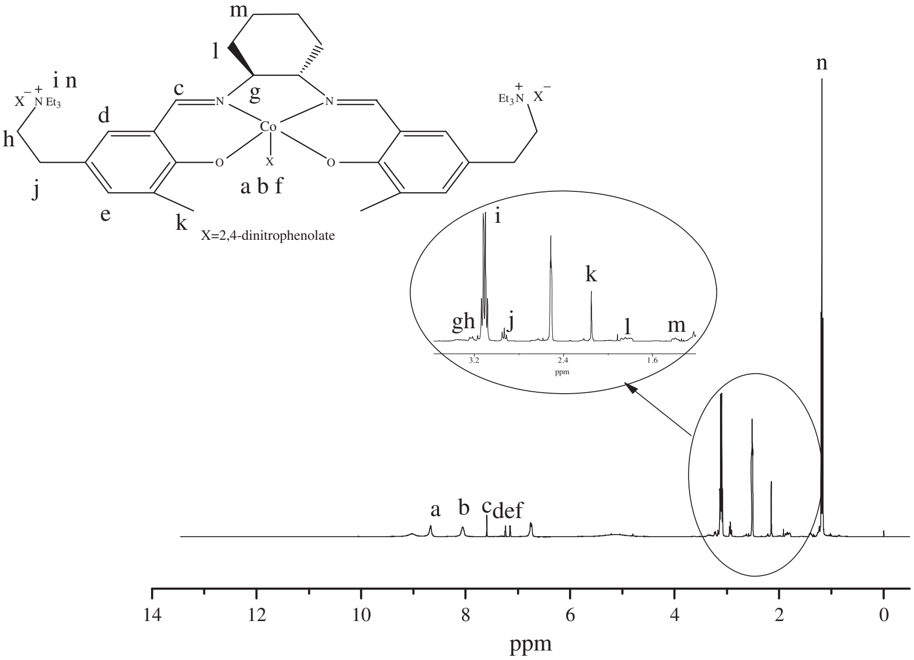


Fig. 4. ^1H NMR spectrum of the complex **9** in DMSO-d_6.

at room temperature. AgOAc (0.069 g, 0.414 mmol) was added, and then the solution was stirred for 12 h. After the solution was stirred for 2 h under an O_2 atmosphere, it was filtered and the solvent was removed under reduced pressure to give a brown solid. The yield was 0.3 g (86.21%). ^1H-NMR (DMSO-d_6):δ7.83 (s, 2H, N═CH), 7.21 (s, 2H, m-H), 7.03 (s, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, $J = 7.6$ Hz, 4H, CH_2), 3.11 (q, $J = 7.3$ Hz, 12H, CH_2), 2.93 (t, $J = 7.8$ Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 2.07 (s, 9H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, $J = 7.3$ Hz, 18H, CH_3) ppm. Anal. Calc.($C_{44}H_{69}CoN_4O_8$): C, 62.84; H, 8.27; N, 6.66%. Found: C, 62.95; H, 8.24; N, 6.56%.

Synthesis of complex 11 This complex was synthesized using the same conditions and procedure as for **10**, starting with compound **6**. A brown solid was obtained .The yield was 0.29 g (84.06%). ^1H-NMR (DMSO-d_6):δ7.83 (s, 2H, N═CH), 7.21 (s, 2H, m-H), 7.03 (s, 2H, m-H), 3.24–3.22 (m, 2H, cyclohexyl-CH), 3.15 (t, $J = 7.6$ Hz, 4H, CH_2), 3.11 (q, $J = 7.3$ Hz, 12H, CH_2), 2.93 (t, $J = 7.8$ Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 2.07 (s, 3H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, $J = 7.3$ Hz, 18H, CH_3) ppm. Anal. Calc. ($C_{40}H_{63}CoF_8N_4O_4$): C, 53.59; H, 7.08; N, 6.25%. Found: C, 53.81; H, 7.06; N, 6.21%.

Synthesis of complex 12 This complex was synthesized using the same conditions and procedure as for **10**, starting with compound **8**. A brown solid was obtained. The yield was 0.3 g (86.21%). ^1H-NMR (DMSO-d_6):δ7.83 (s, 2H, N═CH), 7.21 (s, 2H, m-H), 7.03 (s, 2H, m-H), 3.24 (t, $J = 7.6$ Hz, 4H, CH_2), 3.22–3.16 (m, 2H, cyclohexyl-CH), 3.11 (q, $J = 7.3$ Hz, 12H, CH_2), 2.93 (t, $J = 7.8$ Hz, 4H, benzyl-CH_2), 2.15 (s, 6H, CH_3), 2.07 (s, 3H, CH_3), 1.88–1.79 (m, 4H, cyclohexyl-CH_2), 1.42–1.37 (m, 4H, cyclohexyl-CH_2), 1.18 (t, $J = 7.3$ Hz, 18H, CH_3) ppm. Anal. Calc. ($C_{40}H_{63}CoN_6O_{10}$): C, 56.73; H, 7.50; N, 9.92%. Found: C, 56.91; H, 7.47; N, 9.87%.

CO_2/PO copolymerization

An autoclave was heated to 60°C under vacuum for 24 h and was then cooled to room temperature under vacuum. The catalysts **9–12** (0.0139 g, 0.012 mmol; 0.0097 g, 0.012 mmol; 0.0103 g, 0.012 mmol; 0.0097 g, 0.012 mmol) were added to the autoclave, which was heated to 60°C under vacuum for 24 h. After the autoclave was cooled to room temperature, PO (10 g) was injected into the autoclave equipped with an electric mixer under a CO_2 atmosphere. The autoclave was heated to the desired temperature (30, 40, 60, 80°C) and the appropriate pressure (1, 2, 3, 4 MPa) of CO_2. The mixture was stirred for the allotted reaction time (12, 24, 36, 48 h), after which it was cooled to room temperature. After the CO_2 pressure was released, the autoclave was opened. The resulting yellow solution was filtered through a short pad of silica gel to separate the product from the metal complexes. The silica gel pad had been wetted with CH_2Cl_2. After the filtered solution evaporated, and the residual PO and CH_2Cl_2 reached a constant weight, the polymer yield was determined. The conversion of PO was determined from NMR analysis.

CONCLUSIONS

A series of salen–Co(III)(X) complexes tethering quaternary ammonium salts were designed and synthesized for the copolymerization of CO_2 with PO. Among these four complexes, complex **9**, where X and Y are both 2,4-dinitrophenolate, showed the highest catalytic efficiency. When X and Y were both OAc, complex **10** had the lowest catalytic efficiency. At the same time, complex **9** could produce the copolymer with the highest carbonate fraction and M_n. For complex **9**, the best copolymerization conditions were as follows: reaction temperature of 30°C, copolymerization time of 24 h, and CO_2 pressure of 2 MPa.

DSC curve indicated that, owing to the highest carbonate fraction of 0.583, the sample of entry 1 had also the highest T_g of −70°C. DTGA curves showed that there were two thermal degradation peaks. The first peak might be due to the thermal degradation of ester/ether bond of PPC/PPO, and the second peak to the breaking of the C—C bond. The results from DSC and TGA/DTGA indicate that the synthesized copolymers are fit for application as sealants.

ACKNOWLEDGMENT

The authors acknowledge the financial support from the 211 Project of Anhui University (J18520210).

Supporting information

The citation and the caption have been provided at supporting information.

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