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CO_2/Propylene Oxide Copolymerization with a Bifunctional Catalytic System Composed of Multiple Ammonium Salts and a Salen Cobalt Complex Containing Sulfonate Anions

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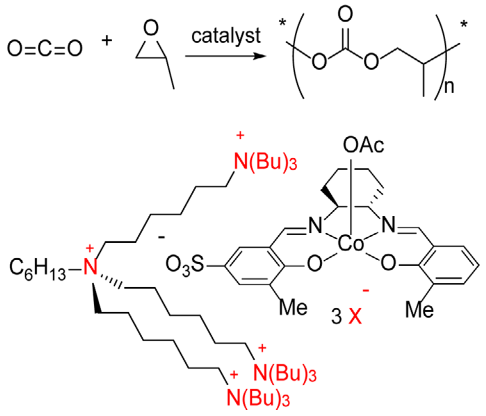
Abstract: A (Salen)Co(III) complex tethering four quaternary ammonium salts with covalent bonds is one of the most highly active catalysts for CO_2/epoxide copolymerization. In this work, we aimed to prepare similar (Salen)Co(III) complexes to which quaternary ammonium salts are linked *via* ionic interactions. Thus, multiple ammonium salts containing 2-5 quaternary ammonium salt units and (Salen)Co(III) complexes containing one or two -SO_3^-[$PhNH_3$]$^+$ moieties were prepared. A binary catalytic system composed of the prepared multiple ammonium salts and the prepared (Salen)Co(III) complex containing -SO_3^-[$(nBu)_4N$]$^+$ moieties showed high activity (TOF, 1500-4500 h^{-1}) for CO_2/propylene oxide (PO) copolymerization, whereas a combination of the multiple ammonium salts and the conventional (Salen)Co(III) complex not containing -SO_3^-[$(nBu)_4N$]$^+$ moieties was inactive under the identical polymerization conditions of [PO]/[Co] = 20000. However, a substantial amount of cyclic carbonate was concomitantly generated, especially when a (Salen)Co(III) complex containing two -SO_3^-[$(nBu)_4N$]$^+$ moieties was used (25-30%). This side-reaction could be mitigated by ca. 50% by employing a (Salen)Co(III) complex containing one -SO_3^-[$(nBu)_4N$]$^+$ moiety. Cyclic carbonate generation can reasonably be ascribed to ammonium salts ([$(nBu)_4N$]$^+$[carbonate]$^-$) not linked to the (Salen)Co(III) complex formed in the binary catalytic system.



Keywords: CO_2/propylene oxide copolymerization, bifunctional catalyst, multiple quaternary ammonium salt, salen cobalt complex.

1. Introduction

The carbon dioxide (CO_2)/epoxide coupling reaction is one of the most valuable tools in the field of CO_2 utilization. The coupling reaction converts CO_2 into either aliphatic polycarbonates or cyclic carbonate compounds.[1-8] Poly(ethylene carbonate) and poly(propylene carbonate), which are generated by CO_2/ethylene oxide or CO_2/propylene oxide (PO) copolymerization are especially attractive materials; the CO_2 content is 50 wt% in the former and 44 wt% in the latter. Poly(ethylene carbonate) is known to be biodegradable whereas poly(propylene carbonate) is not. They both burn cleanly without emission of toxic materials, whereas most commodity polymers burn with emission of large amounts of tar and toxic materials. A catalyst is essential for the copolymerization reaction. The first catalyst, discovered a half century ago by Inoue, was a heterogeneous catalyst formed by mixing dimethylzinc and water.[9] The heterogeneous catalyst has eventually evolved into zinc glutarate, which, however, shows low activity (typically, less than 100 g/g-cat).[10-14] Regardless of this, it has been actively investigated in attempts to achieve commercial production of poly(propylene carbonate), with the merit of low catalyst cost. Another type of heterogeneous catalyst, currently used in industry, is a double metal cyanide complex formed by mixing $ZnCl_2$ and $K_3Co(CN)_6$.[15-18] This shows fairly high activity (more than 1 kg/g-cat) but the product generated by the catalyst is not a strictly alternating copolymer but a copolymer containing some ether linkages.

Homogeneous catalysts based on Co, Cr, and Zn complexes have also been actively developed,[19-22] and we have previously synthesized a (Salen)Co(III) complex tethering four quaternary ammonium salts (**I** in Scheme 1), which exhibited extremely high activity (TOF, ~20000 h^{-1}) as well as almost perfect selectivity (>99%).[23-26] One company attempted its commercialization with construction of a continuous-process pilot plant. Even though the activity of the catalyst developed for CO_2/epoxide copolymerization is exceptionally high, it is substantially inferior to that of the catalysts used in olefin polymerizations. The activity

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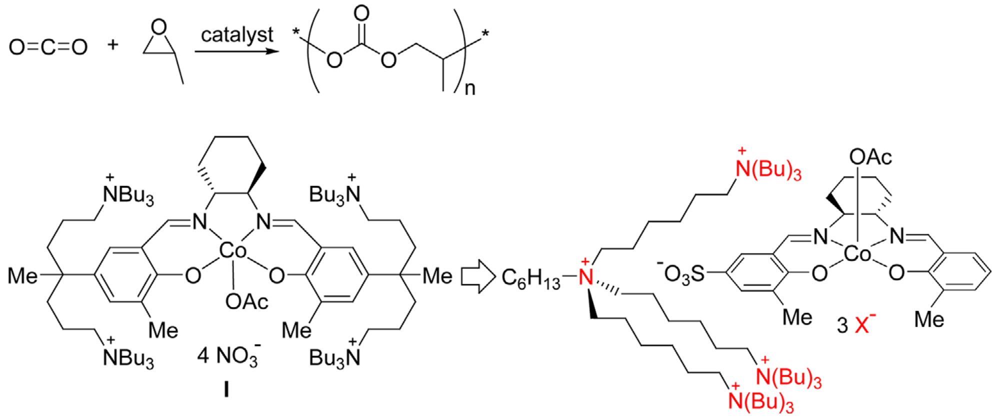


Scheme 1. CO_2/PO copolymerization catalysts (the current study objective).

of the polyolefin catalyst is typically more than 100 kg-PE/g-catalyst, and with this level of productivity, the catalyst cost is not a burden. Furthermore, the resin can be used still containing the catalyst residue.[27] The productivity of **I** is ~3 kg polymer/g-cat, and, with this lower productivity, the catalyst cost is a severe burden in commercialization. Although many obstacles to the large scale preparation of **I** have been overcome, it is prepared by a lengthy 7-step process, intrinsically burdening commercialization.[28,29] Moreover, it is necessary to remove the catalyst after polymerization. Although the catalyst could be removed *via* filtration over a short pad of silica gel, this is a burden in largescale operation.

As a strategy to overcome the intrinsic problem of low catalyst productivity, we envisaged fixing the catalyst in high-swelling polystyrene (PS) beads. The cobalt catalyst is scarcely deactivated, and it can be used for a long time when confined in a reactor and fixed to an insoluble support while CO_2, epoxide, and a chain-transfer agent diol are fed in continuously, and the low-molecular-weight macrodiols generated are continuously extracted from the reactor.[30] However, fixing **I** inside PS beads was not achieved synthetically. Instead, we aimed to realize the concept by linking the (Salen)Co(III) complex to multiple ammonium salts by means of ionic interactions rather than the conventional covalent bonds (Scheme 1). Before proceeding to a fixed catalyst system, we aimed to investigate whether the bifunctional catalytic system constructed with ionic interaction works well. The catalyst is still a bottleneck in commercialization of the attractive CO_2/epoxide copolymers, and much research on catalyst development is still actively underway in both academia and industry.[31-37]

2. Experimental

2.1. General Remarks

CO_2 gas (99.999% purity) was dried by storage in a column of molecular sieve 3A at a pressure of 50 bar. PO was dried by stirring over CaH_2 and then vacuum-transferred to a reservoir. ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded using a JEOL ECZ 600 spectrometer. Gel permeation chromatograms (GPCs) were obtained at 40 ℃ with $CHCl_3$ as an eluent using a Shodex GPC HK-400 with polystyrene standards. Silver (2,4-dinitrophenolate) (AgDNP)[38] and compounds **18**, and **19** (Scheme 3) were prepared according to the methods reported in the literatures.[39]

2.2. Preparation of 1

Tributylamine (2.19 g, 11.8 mmol) and sodium carbonate (0.627 g, 5.92 mmol) were successively added to a solution of 2,6-diiodohexane (20.0 g, 59.2 mmol) in acetonitrile (50 mL). The resulting mixture was refluxed for 1 day, and after cooling to room temperature the reaction mixture was filtered over Celite. The filter cake was washed with acetonitrile (20 mL), the filtrates were combined, and the solvent was removed by evaporation with a rotary evaporator. The excess of 2,6-diiodohexane remaining unreacted was washed out with hexane (3 × 20 mL), leaving a dark orange viscous oil, which was purified by column chromatography on silica gel, eluting first with CH_2Cl_2 and then with CH_2Cl_2/CH_3OH (v/v, 10 : 1). A dark yellow oil was obtained (5.33 g, 86%). ^1H NMR (600 MHz, $CDCl_3$): δ 3.42 (m, 2H, NCH_2), 3.34 (m, 6H, NCH_2), 3.17 (t, J = 7.2 Hz, 2H, ICH_2), 1.80 (quintet, J = 7.2 Hz, 2H, CH_2), 1.78-1.72 (br, 2H, CH_2), 1.68 (m, 6H, CH_2), 1.54-1.49 (br, 4H, CH_2), 1.46 (sextet, J = 7.2 Hz, 6H, CH_2), 1.01 (t, J = 7.2 Hz, 9H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 58.9 (nBu and hexylene), 32.8, 29.6, 25.0, 24.0 (nBu), 22.1, 19.5 (nBu), 13.5 (nBu), 6.87 ppm. HRMS(EI): m/z calcd ($[M-I]^+$ $C_{18}H_{39}NI$) 396.2127. Found: 396.2127.

2.3. Preparation of 2 [X = I]

Tributylamine (0.942 g, 5.08 mmol) and sodium carbonate (0.673 g, 6.35 mmol) were successively added to a solution of 2,6-diiodohexane (0.715 g, 2.12 mmol) in acetonitrile (10 mL). The resulting mixture was refluxed for 1 day, and after cooling to room temperature the reaction mixture was filtered over Celite. The filter cake was washed with acetonitrile (5 mL), the filtrates were combined, and the solvent was removed by evaporation with a rotary evaporator. The excess of tributylamine remaining unreacted was washed out with hexane (3 × 5 mL). The residue was dissolved in CH_2Cl_2 (5 mL) and the insoluble portion was removed by filtration. The solvent was removed using a vacuum line to obtain a white solid (1.32 g, 88%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.47 (m, 4H, NCH$_2$), 3.39-3.27 (m, 12H, NCH$_2$), 2.03-1.93 (br, 4H, CH$_2$), 1.74-1.59 (m, 16H, CH$_2$), 1.46 (sextet, J = 7.2 Hz, 12H, CH$_2$), 1.01 (t, J = 7.2 Hz, 18H, CH$_3$) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 59.2, 58.7 (nBu), 25.1, 23.8 (nBu), 21.8, 19.2 (nBu), 13.2 (nBu) ppm. HRMS(EI): m/z calcd ([M - I]$^+$ $C_{30}H_{66}N_2I$) 581.4265. Found: 581.4271.

2.4. Preparation of 3 [X = I]

Dibutylamine (0.206 g, 1.59 mmol) and sodium carbonate (0.506 g, 4.78 mmol) were successively added to a solution of **1** (2.00 g, 3.82 mmol) in acetonitrile (12 mL). The resulting mixture was refluxed for 2 days, and after cooling to room temperature, the reaction mixture was filtered over Celite. The solvent in the filtrate was removed using a vacuum line. The residue was purified by column chromatography on silica gel, eluting first with CH$_2$Cl$_2$/CH$_3$OH (v/v, 10 : 1) and then with CH$_2$Cl$_2$/CH$_3$OH (v/v, 20 : 1). A white solid was obtained (0.930 g, 56%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.43-3.26 (br, 8H, NCH$_2$), 3.26-3.07 (br, 16H, NCH$_2$), 1.87-1.66 (br, 8H, CH$_2$), 1.65-1.38 (br, 16H, CH$_2$), 1.38-1.99 (br, 16H, CH$_2$), 0.922-0.781 (br, 24H, CH$_3$) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 59.9, 59.7, 59.2 (nBu), 25.6, 25.5, 24.4 (nBu), 22.3, 22.2, 19.9 (nBu), 13.9, 13.8 (nBu) ppm. HRMS(EI): m/z calcd ([M - I]$^+$ $C_{44}H_{96}N_3I_2$) 920.5694. Found: 920.5694.

2.5. Preparation of 4 [X = I]

It was prepared by the same procedure and conditions as those employed for **3** using n-hexylamine (0.135 g 1.34 mmol), **1** (2.52 g, 4.82 mmol), and sodium carbonate (0.638 g, 6.02 mmol). A white solid was obtained (1.16 g, 61%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.50-3.39 (m, 12H, NCH$_2$), 3.36-3.25 (m, 20H, NCH$_2$), 1.95-1.84 (br, 12H, CH$_2$), 1.74-1.66 (br, 20H, CH$_2$), 1.65-1.55 (br, 12H, CH$_2$), 1.46 (sextet, J = 7.2 Hz, 18H, CH$_2$), 1.42-1.28 (br, 6H, CH$_2$), 1.02 (t, J = 7.2 Hz, 27H, CH$_3$), 0.891 (t, J = 7.2 Hz, 3H, CH$_3$) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 59.6 (hexylene), 59.4 (hexylene), 59.3 (n-hexyl), 59.0 (nBu), 31.1 (n-hexyl), 26.0 (n-hexyl), 25.4 (hexylene), 24.2 (nBu), 22.4 (n-hexyl), 22.3 (n-hexyl), 22.1 (hexylene), 22.0 (hexylene), 19.7 (nBu), 13.8 (n-hexyl), 13.7 (nBu) ppm. HRMS(EI): m/z calcd ([M - I]$^+$ $C_{60}H_{130}N_4I_3$) 1287.7430. Found: 1287.7430.

2.6. Preparation of 5 [X = I]

Compound **1** (3.14 g, 6.00 mmol) and sodium carbonate (0.795 g, 7.50 mmol) were dissolved in acetonitrile (15 mL), and then ammonia (2.27 mL, 0.55 M solution in dioxane, 1.25 mmol) was added. After stirring at room temperature for 1 day, the resulting solution was refluxed for 2 days. After filtration over Celite, the solvent was removed using a vacuum line. The residue was purified by column chromatography on silica gel, eluting first with CH$_2$Cl$_2$/CH$_3$OH (v/v, 10 : 1) and subsequently with CH$_2$Cl$_2$/CH$_3$OH (v/v, 20 : 1). A white solid was obtained (1.35 g, 63%). ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.49-3.34 (br, 8H, NCH$_2$), 3.34-3.23 (br, 24H, NCH$_2$), 3.23-3.10 (br, 8H, NCH$_2$), 2.00-1.73 (br, 16H, CH$_2$), 1.74-1.62 (br, 24H, CH$_2$), 1.61-1.49 (br, 16H, CH$_2$), 1.43 (sextet, J = 7.8 Hz, 24H, CH$_2$), 0.981 (t, J = 7.2 Hz, 36H, CH$_3$) ppm. ^{13}C NMR (150 MHz, CDCl$_3$): δ 59.6 (hexylene), 59.3 (hexylene), 59.1 (nBu), 25.7 (hexylene), 25.2 (hexylene), 24.2 (nBu), 22.8 (hexylene), 22.0 (hexylene), 19.7 (nBu), 13.7 (nBu) ppm. HRMS(EI): m/z calcd ([M - I]$^+$ $C_{72}H_{156}N_5I_4$) 1598.8534. Found: 1598.8539.

2.7. Conversion of 4 [X = I] to 4 [X = DNP]

A solution of **4** (0.150 g, 0.106 mmol) in acetonitrile (1.9 mL) was added to a solution of AgDNP (136 mg, 0.466 mmol) in acetonitrile (0.87 mL). The mixture was stirred at room temperature for 1 day, and the precipitated AgI was removed by filtration. The solvent in the filtrate was removed using a vacuum line, the residue was dissolved in CH$_2$Cl$_2$ (2.0 mL), and the excess of AgDNP was removed by filtration. A yellow solid was obtained (0.168 g, 97%). ^{1}H NMR (600M Hz, CD$_3$CN): δ 8.69 (d, J = 3.6 Hz, 4H), 7.83 (dd, J = 9.6, 3.6 Hz, 4H), 6.39 (d, J = 9.6 Hz, 4H), 3.06 (m, 30H, NCH$_2$), 3.00-2.89 (br, 2H, NCH$_2$), 1.68-1.49 (br, 32H, CH$_2$), 1.41-1.17 (m, 36H, CH$_2$), 0.943 (t, J = 6.6 Hz, 27H, CH$_3$), 0.905-0.828 (br, 3H, CH$_3$) ppm.

2.8. Preparation of 6

2-Hydroxy-3-methylbenzaldehyde (1.60 g, 11.7 mmol) and aniline (1.10 g, 11.8 mmol) were dissolved in ethanol (44 mL). Anhydrous MgSO$_4$ (0.270 g) was added and the resulting solution was stirred overnight. After filtration, the solvent in the filtrate was removed using a rotary evaporator to obtain a yellow oily product. The flask containing the yellow oil was cooled with an ice bath, and sulfuric acid (14 mL, 95%) was slowly added while stirring. The resulting orange solution was then heated to 105-110 ℃ for 3 h. The solution was allowed to cool to room temperature, and ice (14 g) was added to induce crystallization. The peach-colored solids precipitated were collected by filtration, washed with ice-cold water, and dried with a vacuum line (2.50 g, 69%). ^{1}H NMR (600M Hz, D$_2$O): δ 9.87 (s, 1H, CHO), 7.94 (d, J = 1.8 Hz, 1H), 7.82 (d, J = 1.8 Hz, 1H), 7.50 (m, 3H, *m*-H and *p*-H), 7.38 (m, 2H, *o*-H), 2.25 (s, 3H, CH$_3$) ppm. ^{13}C NMR (150 MHz, D$_2$O): δ 198, 161, 134, 130, 129, 128, 123, 119, 14.4 ppm.

2.9. Preparation of 7.[40]

This was prepared by the same procedure and conditions as those employed for **6,** using 3-*tert*-butyl-2-hydroxybenzaldehyde (1.50 g, 8.42 mmol), aniline (0.788 g, 8.46 mmol), and sulfuric acid (9.8 mL, 95%). Peach-colored solids were obtained (0.918 g, 31%). ^{1}H NMR (600M Hz, D$_2$O): δ 9.87 (s, 1H, CHO), 7.96 (d, J = 1.8 Hz, 1H), 7.94 (d, J = 1.8 Hz, 1H), 7.50 (m, 3H, *m*-H and *p*-H), 7.39 (m, 2H, *o*-H), 1.39 (s, 9H, CH$_3$) ppm. ^{13}C NMR (150 MHz, D$_2$O): δ 199, 162, 139, 134, 131, 130, 129, 123, 120, 34.5, 28.3 ppm.

2.10. Preparation of 8

Compound **6** (2.44 g, 7.88 mmol) and [(nBu)$_4$N]Cl (2.65 g, 9.52 mmol) were dissolved in CH$_2$Cl$_2$ (18 mL), and 2 N aqueous HCl solution (20 mL) was added. The resulting two-phase solution was stirred vigorously for a few minutes, and the lower organic phase was collected and washed with distilled water (5 × 10 mL). After drying with anhydrous $MgSO_4$, the solvent was removed to obtain a yellow solid (2.28 g, 63%). ^{1}H NMR (600M Hz, CD_2Cl_2): δ 11.3 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.92 (d, J = 1.8 Hz, 1H), 7.86 (d, J = 1.8 Hz, 1H), 3.24-3.13 (m, 8H, NCH_2), 2.25 (s, 3H, CH_3), 1.67-1.55 (m, 8H, CH_2), 1.40 (sextet, J = 7.2 Hz, 8H, CH_2), 0.990 (t, J = 7.2 Hz, 12H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 197, 160, 140, 136, 129, 126, 119, 59.1, 24.2, 20.0, 15.0, 13.7 ppm.

2.11. Preparation of 9

This was prepared by the same procedure and conditions as those employed for **8,** using **7** (0.718 g, 2.04 mmol) and $[(nBu)_4N]Cl$ (0.688 g, 2.47 mmol). A yellow solid was obtained (0.717 g, 81%). ^{1}H NMR (600M Hz, CD_2Cl_2): δ 11.9 (s, 1H, OH), 9.87 (s, 1H, CHO), 7.98 (d, J = 1.8 Hz, 1H), 7.93 (d, J = 1.8 Hz, 1H), 3.27-3.13 (m, 8H, NCH_2), 1.68-1.57 (m, 8H, CH_2), 1.42 (s, 9H, CH_3), 1.41 (sextet, J = 7.2 Hz, 8H, CH_2), 0.989 (t, J = 7.2 Hz, 12H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 198, 162, 140, 138, 132, 130, 120, 59.1, 35.2, 29.2, 24.2, 20.0, 13.7 ppm.

2.12. Preparation of 10

Compound **8** (0.250 g, 0.546 mmol) and (±)-*trans*-1,2-diaminocyclohexane (0.0312 g, 0.273 mmol) were dissolved in CH_2Cl_2 (2.0 mL) and molecular sieve (4A, 0.15 g) was added. After stirring overnight at room temperature, the liquid was filtered to remove the molecular sieve. The solvent was removed using a vacuum line to obtain a yellow solid (0.260 g, 96%). ^{1}H NMR (600M Hz, CD_2Cl_2): δ 8.23 (s, 2H, N=CH), 7.56 (s, 2H, C_6H_2), 7.48 (s, 2H, C_6H_2), 3.34 (m, 2H, cyclohexyl-CH), 3.07-2.92 (m, 16H, NCH_2), 2.19 (s, 6H, CH_3), 1.96-1.79 (m, 4H, cyclohexyl-CH_2), 1.78-1.65 (br, 2H, cyclohexyl-CH_2), 1.56-1.44 (br, 2H, cyclohexyl-CH_2), 1.38 (m, 16H, CH_2), 1.24 (sextet, J = 7.2 Hz, 16H, CH_2), 0.904 (t, J = 7.2 Hz, 24H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 165, 160, 139, 131, 127, 126, 117, 72.9, 58.8, 33.6, 24.5, 24.1, 19.9, 15.6, 13.8 ppm. HRMS(EI): m/z calcd ([M^+] $C_{54}H_{96}N_4O_8S_2$) 993.6670. Found: 993.6743.

2.13. Preparation of 11

This was prepared by the same procedure and conditions as those employed for **10,** using **9** (0.911 g, 1.82 mmol) and (±)-*trans*-1,2-diaminocyclohexane (0.104 g, 0.911 mmol). A yellow solid was obtained (0.854 g, 87%). ^{1}H NMR (600M Hz, CD_2Cl_2): δ 8.29 (s, 2H, N=CH), 7.69 (d, J = 1.8 Hz, 2H), 7.51 (d, J = 1.8 Hz, 2H), 3.39 (m, 2H, cyclohexyl-CH), 3.08 (m, 16H, NCH_2), 1.92 (m, 2H, cyclohexyl-CH_2), 1.83 (m, 2H, cyclohexyl-CH_2), 1.78-1.61 (m, 2H, cyclohexyl-CH_2), 1.47 (m, 18H, cyclohexyl-CH_2 and CH_2), 1.37 (s, 18H, CH_3), 1.24 (sextet, J = 7.2 Hz, 16H, CH_2), 0.884 (t, J = 7.2 Hz, 24H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2): δ 165, 161, 138, 137, 128, 127, 118, 72.3, 58.9, 35.1, 33.7, 29.5, 24.5, 24.1, 19.3, 13.7 ppm. HRMS(EI): m/z calcd ([M^+] $C_{60}H_{108}N_4O_8S_2$) 1076.7609. Found: 1076.7614.

2.14. Preparation of a mixture of 12 and 10

A solution of **8** (0.200 g, 0.437 mmol) and 2-hydroxy-3-methylbenzaldehyde (0.120 g, 0.881 mmol) dissolved in CH_2Cl_2 (3.0 mL) was added to (±)-*trans*-1,2-diaminocyclohexane (0.0760 g, 0.667 mmol) and subsequently molecular sieve (4A, 0.120 g) was added. After stirring overnight at room temperature, the liquid was filtered to remove the molecular sieve, and the solvent was removed using a vacuum line. Neutral compounds not containing sulfonate salt moiety were removed by extraction with diethyl ether (3 × 6 mL) to obtain a yellow solid. Analysis of the ^{1}H NMR spectrum indicated that the solid obtained was a mixture of **12** and **10** in 1.0 : 0.65 mole ratio (0.180 g, 34%). ^{1}H NMR (600M Hz, CD_2Cl_2) major set: δ 8.29 (s, 1H, N=CH), 8.27 (s, 1H, N=CH), 7.57-7.54 (br, 1H), 7.48-7.50 (br, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 6.70 (t, J = 7.2 Hz, 1H), 3.38-3.31 (m, 2H, cyclohexyl-CH), 3.12-3.01 (m, 8H, NCH_2), 2.19 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 1.98-1.79 (m, 4H, cyclohexyl-CH_2), 1.78-1.64 (m, 2H, cyclohexyl-CH_2), 1.55-1.38 (m, 10H, cyclohexyl-CH_2 and CH_2), 1.30 (sextet, J = 7.2 Hz, 8H, CH_2), 0.933 (t, J = 7.2 Hz, 12H, CH_3) ppm. ^{1}H NMR (600M Hz, CD_2Cl_2) minor set: δ 8.24 (s, 2H, N=CH), 7.60-7.57 (br, 2H, *m*-H), 7.50-7.48 (br, 2H, *m*-H), 3.38-3.31 (m, 2H, cyclohexyl-CH), 3.12-3.01 (m, 16H, NCH_2), 2.20 (s, 6H, CH_3), 1.98-1.79 (m, 4H, cyclohexyl-CH_2), 1.78-1.64 (m, 2H, cyclohexyl-CH_2), 1.55-1.38 (m, 18H, cyclohexyl-CH_2 and CH_2), 1.30 (sextet, J = 7.2 Hz, 16H, CH_2), 0.933 (t, J = 7.2 Hz, 24H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2) major: δ 165, 164, 160, 159, 138, 133, 131, 129, 127, 126, 125, 118, 117, 73.0, 72.7, 58.8, 33.6, 33.5, 24.5, 24.1, 19.9, 15.5, 15.4, 13.7 ppm. ^{13}C NMR (150 MHz, CD_2Cl_2) minor: δ 164, 160, 138, 131, 127, 125, 117, 72.8, 58.8, 33.6, 24.5, 24.1, 19.9, 15.6, 15.5, 13.7 ppm.

2.15. Preparation of a mixture of 13 and 11

This was prepared by the same procedure and conditions as those employed for a mixture of **12** and **10**, using **9** (0.150 g, 0.300 mmol), 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.143 g, 0.609 mmol), (±)-*trans*-1,2-diaminocyclohexane (0.0520 g, 0.456 mmol) and CH_2Cl_2 (2.6 mL). A yellow solid was obtained, which ^{1}H NMR spectrum analysis showed to be a mixture of **13** and **11** in 1.0 : 0.65 mole ratio (0.170 g, 41%). ^{1}H NMR (600M Hz, CD_2Cl_2) major set: δ 8.35 (s, 1H, N = CH), 8.31 (s, 1H, N = CH), 7.68 (d, J = 2.4 Hz, 1H, *m*-H), 7.52 (d, J = 2.4 Hz, 1H, *m*-H), 7.28 (d, J = 3.0 Hz, 1H, *m*-H), 7.02 (d, J = 3.0 Hz, 1H, *m*-H), 3.36 (m, 2H, cyclohexyl-CH), 3.12 (m, 8H, NCH_2), 2.01-1.82 (br, 4H, cyclohexyl-CH_2), 1.79-1.61 (br, 2H, cyclohexyl-CH_2), 1.60-1.44 (m, 10H, cyclohexyl-CH_2 and CH_2), 1.39 (s, 9H, CH_3), 1.38 (s, 9H, CH_3), 1.30 (sextet, J = 7.2 Hz, 8H, CH_2), 1.22 (s, 9H, CH_3), 0.919 (t, J = 7.2 Hz, 12H, CH_3) ppm. ^{1}H NMR (600M Hz, CD_2Cl_2) minor set: δ 8.30 (s, 2H, N=CH), 7.70 (d, J = 2.4 Hz, 2H, *m*-H), 7.52 (d, J = 2.4 Hz, 2H, *m*-H), 3.36 (m, 2H, cyclohexyl-CH), 3.12 (m, 16H, NCH_2), 2.01-1.82 (br, 4H, cyclohexyl-CH_2), 1.79-1.61 (br, 2H, cyclohexyl-CH_2), 1.60-1.44 (m, 18H, cyclohexyl-CH_2 and CH_2), 1.40 (s, 18H, CH_3), 1.30 (sextet, J = 7.2 Hz, 16H, CH_2), 0.919 (t, J = 7.2 Hz, 24H, CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2) major: δ 166, 165, 161, 158, 140, 138, 137, 136, 127, 126, 118, 117, 73.2, 71.9, 59.0, 35.2, 35.1, 34.3, 33.7, 33.5, 33.4, 31.5, 29.6, 29.4, 24.7, 24.6, 24.2, 19.9, 13.7 ppm. ^{13}C NMR (150 MHz, CD_2Cl_2) minor: δ 165, 161, 138, 137, 128, 118, 72, 59.0, 35.1, 33.7, 29.5, 24.5, 24.2, 19.9, 13.7 ppm.

2.16. Preparation of 14

$Co(OAc)_2$ (0.0267 g, 0.151 mmol) was added to **11** (0.150 g, 0.151 mmol) dissolved in CH_2Cl_2 (2.3 mL). After stirring for a few minutes, glacial acetic acid (0.0453 g, 0.755 mmol) was added dropwise. The resulting solution was stirred overnight under an atmosphere of O_2. The solvent was removed using a vacuum line to obtain a dark brown solid (0.164 g, 98%), which was used for the copolymerization reaction. The signals in the ^1H NMR spectrum of the product were broad and too complicated to clearly interpret (Figure S15).

2.17. Typical procedure for CO_2/PO copolymerization

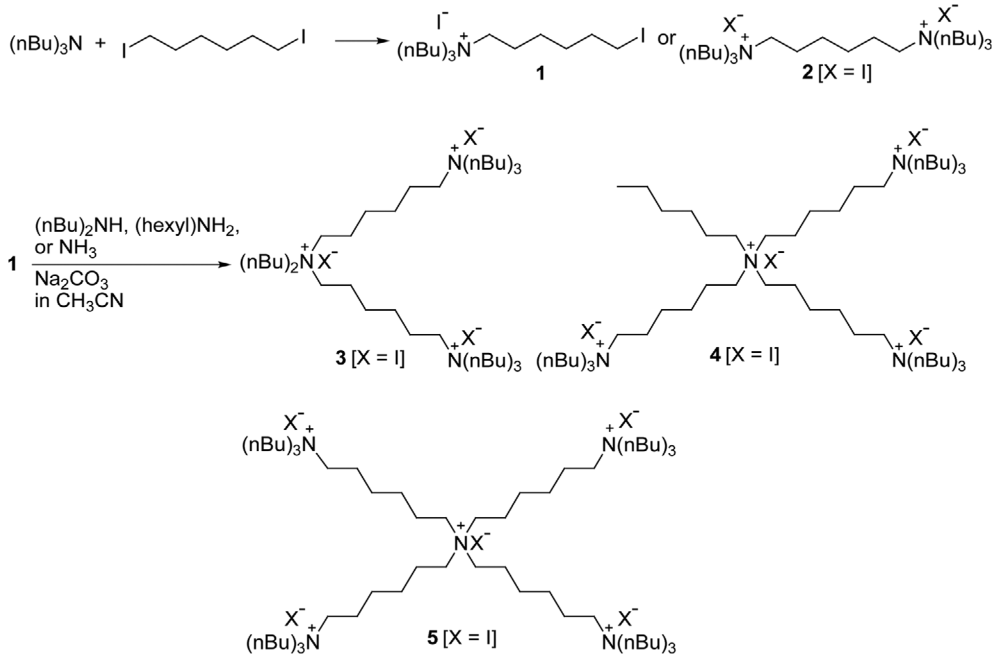
A bomb reactor (75 mL) was assembled after charging with a magnetic stirring bar, **14** (14.0 mg, 12.9 μmol), PO (15.0 g, 258 mmol, [PO]/[**14**] = 20000) and **4** [X = DNP] (21.2 mg, 12.9 μmol). The bomb was pressurized with CO_2 gas to 25 bar at room temperature, and then immersed in an oil bath at 90 ℃. As the solution temperature gradually increased to 88 ℃ over 60 min, the reactor pressure correspondingly increased, reaching 37 bar. While the temperature was maintained at 88 ℃, the pressure slowly decreased, reaching 35 bar during the reaction time of 60 min. The reactor was cooled to room temperature using an ice bath, and the CO_2 gas was released. The polymerization solution was filtered over a short pad of silica gel to remove catalyst residue. The silica gel pad was washed with methylene chloride (2 × 10 mL), and all volatiles were removed using a rotary evaporator, leaving a waxy solid.

3. Results and discussion

3.1. Preparation of multiple quaternary ammonium salts

Compounds containing 2-5 quaternary ammonium salt units were prepared (Scheme 2). Reacting $(nBu)_3N$ with excess 1,6-diiodohexane (5.0 eq) in CH_3CN at 80 ℃ for 1 day afforded the desired $[(nBu)_3N(CH_2)_6I]^+I^-$ (**1**), but the product was contaminated with some other ammonium salt, the removal of which was impossible. The contaminant was assigned as $[(nBu)_3NH]^+I^-$ generated *via* a b-elimination side reaction. By the addition of further Na_2CO_3 (0.5 eq/$(nBu)_3N$), $[(nBu)_3N(CH_2)_6I]^+I^-$ could be obtained without the contaminant; the action of the additional Na_2CO_3 was to convert the generated $[(nBu)_3NH]^+I^-$ back to the reactant $(nBu)_3N$, which eventually reacted with 1,6-diiodohexane to give the desired $[(nBu)_3N(CH_2)_6I]^+I^-$. The excess unreacted 1,6-diiodohexane could be removed by extraction with hexane, in which the product ammonium salt was completely insoluble. Finally, the isolated compound could be further purified by column chromatography on silica gel, eluting with CH_2Cl_2/CH_3OH (v/v, 10 : 1). In ^1H NMR spectrum of **1**, $NCH_2(CH_2)_5I$, $NCH_2(CH_2)_2CH_3$, and ICH_2 signals were clearly observed at 3.42, 3.36, and 3.21 ppm with intensity ratios 1 : 3 : 1 (Figure S1). In the ^{13}C NMR spectrum, signals due to carbons in $NCH_2(CH_2)_5I$ and $NCH_2(CH_2)_2CH_3$ fragments were observed at 58.9, 32.8, 29.6, 25.0, 22.1, 6.87 ppm and 58.9, 24.0, 19.5, 13.5 ppm, respectively.

A compound containing two quaternary ammonium salt units (**2** [X = I]) was prepared by reacting 1,6-diiodohexane with excess $(nBu)_3N$ (2.4 eq). In this case also, addition of Na_2CO_3 was required to obtain the desired compound cleanly. In the ^1H NMR spectrum, two signals corresponding to NCH_2 were observed at 3.47 and 3.34 ppm in a 1 : 3 intensity ratio (Figure S2). A compound containing three quaternary ammonium salt units (**3** [X = I]) was prepared by reacting $(nBu)_2NH$ with excess **1** (2.4 eq) in CH_3CN at 80 ℃ for 2 days. In this case, Na_2CO_3 (1.25 eq per $(nBu)_2NH$) was necessary to convert $(nBu)_2N^+(H)(CH_2)_6N^+(nBu)_3$ (formed in the reaction of $(nBu)_2NH$ with **1**) to $(nBu)_2N(CH_2)_6N^+(nBu)_3$, which reacted further with **1** to afford the desired **3** [X = I]. Some mono-ammonium salts (**1** remaining unreacted owing to the excess addition, and probably $[(nBu)_3N(CH_2)_4CH{=}CH_2]^+I^-$



Scheme 2. Synthesis of multiple quaternary ammonium salts.

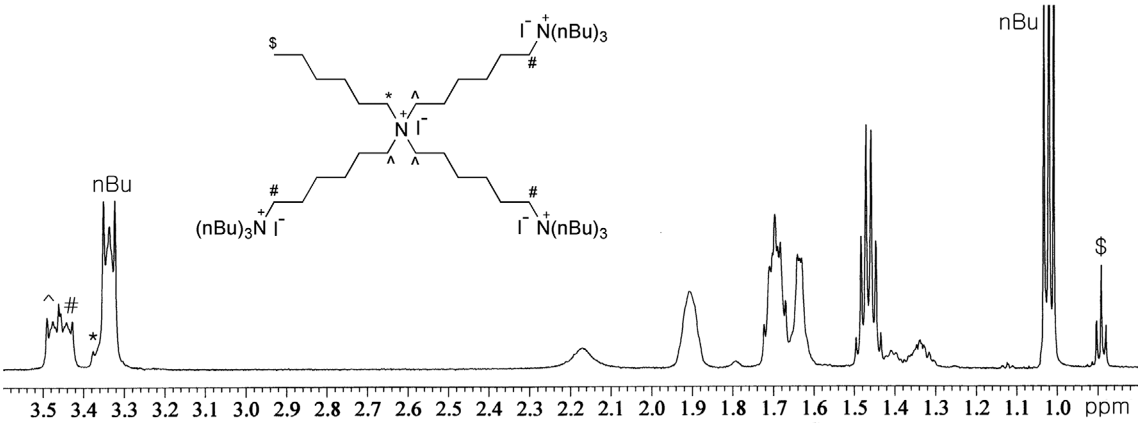
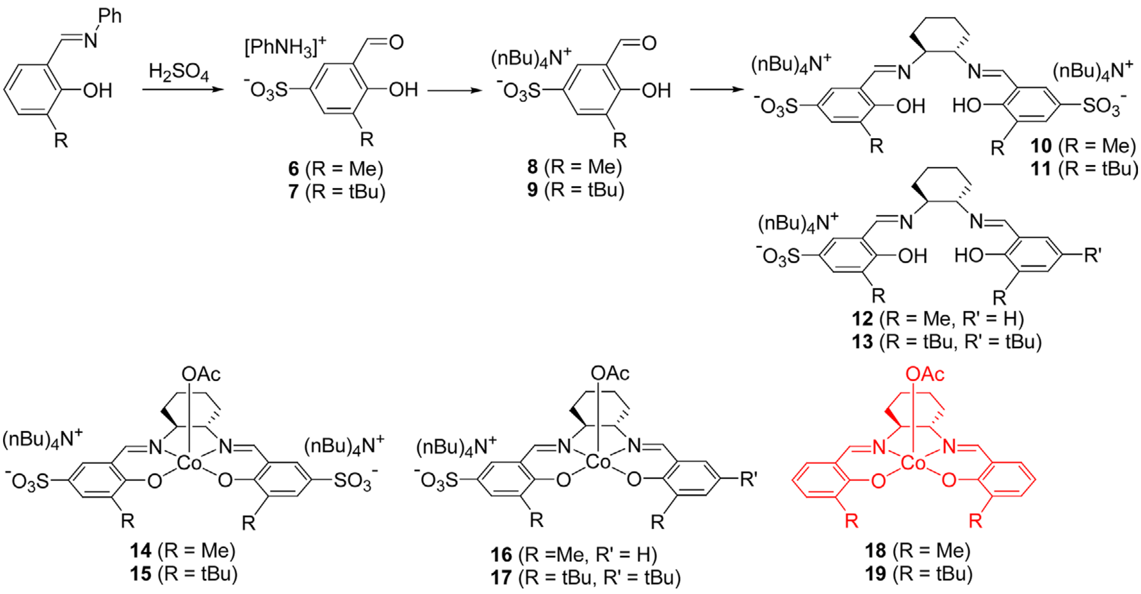


Figure 1. ^{1}H NMR spectrum of **4** [X = I].

generated by a side b-elimination reaction) could be separated from the product **3** [X = I] by column chromatography. In the ^{1}H NMR spectrum, the NCH_2 signals were observed at 3.45 and 3.33 ppm in a 1 : 2 intensity ratio (Figure S3). In the ^{13}C NMR spectrum, signals due to carbons in $(nBu)_3N$ and $N(CH_2)_6N$ fragments were observed at 59.2, 24.4, 19.9, 13.8 ppm and 59.9, 59.7, 25.5, 22.4, 22.2 ppm, respectively. Employing the same synthetic and purification method and conditions, **4** [X = I] and **5** [X = I] containing, respectively, 4 and 5 quaternary ammonium salt units were also successfully prepared using (1-hexyl)NH_2 or NH_3 as reactant (Scheme 2). In the ^{1}H NMR spectrum of **4** [X = I], three NCH_2 signals were observed at 3.45, 3.42, 3.36, 3.32 ppm in 3 : 3 : 1 : 9 intensity ratios and two CH_3 signals were observed at 1.00 and 0.88 ppm in a 9 : 1 intensity ratio (Figure 1).

3.2. Preparation of (Salen)Co(III) complexes containing sulfonate anion groups

Sulfonation of *N*-phenyl-salicylaldimine was reported.[40] Thus, *N*-phenyl-salicylaldimine containing a methyl or *tert*-butyl substituent (i.e., 3-R-2-(HO)-C_6H_3CH=NPh, R = Me or tBu) was treated with concentrated H_2SO_4 at a high temperature (100-110 ℃) to generate salicylaldehyde with a sulfonate salt group $-SO_3^-[PhNH_3]^+$ attached at the 5-position (**6** or **7**). The products were isolated as peach-colored solids. (In the previous report, the structure of the isolated solid was assigned as *N*-phenyl-5-sulfonato-3-(*tert*-butyl)-salicylaldimine, 3-*tert*-Bu-2-(HO)-5-(HO_3S)C_6H_3CH=NPh). Typical aldehyde (-C(O)H) signals were observed at 9.87 ppm in the ^{1}H NMR spectra; the aldehyde signals were also observed at 198 ppm in the ^{13}C NMR spectra. The Salen-type ligand was not obtained when **6** or **7** was treated with *trans*-1,2-diaminocyclohexane; the anilinium cation $[PhNH_3]^+$ (pK_a, 4.6) in **6** or **7** reacted with *trans*-1,2-diaminocyclohexane (pK_a, 10.7) to generate $PhNH_2$ and the ammonium salt of *trans*-1,2-diaminocyclohexane ($C_6H_{10}(NH_2)(N^+H_3)$), consequently hampering the formation of a Salen-type ligand. The anilinium cation $[PhNH_3]^+$ in **6** or **7** was therefore replaced with $(nBu)_4N^+$ by mixing **6** or **7** with $(nBu)_4NCl$ in CH_2Cl_2 and extracting $[PhNH_3]Cl$ with 2 N aqueous HCl solution. In the ^{1}H NMR spectra, signals at 7.55-7.38 ppm corresponding to $[PhNH_3]^+$ completely disappeared and signals corresponding to $(nBu)_4N^+$ were observed at 3.19, 1.61, 1.40 ppm and 0.990 ppm with exact agreement of integration values.



Scheme 3. Synthesis of (Salen)Co(III) complexes tethering sulfonate anions.

The desired Salen-type ligands (**10** and **11**) were obtained when *trans*-1,2-diaminocyclohexane was reacted with the salicylaldehyde compounds **8** or **9** containing -SO$_3^-$[(nBu)$_4$N]$^+$. We also attempted to prepare Salen-type ligands containing one -SO$_3^-$[(nBu)$_4$N]$^+$ unsymmetrically (**12** and **13**), but all trials were unsuccessful.[41] Even though the preparation of **12** and **13** as pure single compounds failed, they could be prepared admixed with some proportion of **10** and **11**, respectively. When *trans*-1,2-diaminocyclohexane was reacted with a mixture of **8** and 3-methylsalicylaldehyde in 1 : 2 mole ratio, three compounds, **12**, **10**, and a Salen-type ligand not containing any sulfonate salt (i.e., [3-Me-2-(HO)-C$_6$H$_3$CH=N]$_2$C$_6$H$_{10}$), were generated. The neutral compound [3-Me-2-(HO)-C$_6$H$_3$CH=N]$_2$C$_6$H$_{10}$ could be removed by extraction with diethyl ether, and a mixture of **12** and **10** in 1.0 : 0.65 mole ratio could be obtained. In the ^{1}H NMR spectrum, two sets of aldehyde and aromatic proton signals, corresponding to **12** (at 8.29 (s), 8.27 (s), 7.56 (s), 7.50 (s), 7.10 (d), 7.03 (d), and 6.70 (t) ppm) and **10** (at 8.24 (s), 7.59 (s) and 7.49 (s) ppm), were observed in a 1.0 : 1.3 intensity ratio (Figure S13). By use of the same method, a mixture of **13** and **11** in the same 1.0 : 0.65 mole ratio was also prepared (Figure S14).

Metalation was performed according to the reported method.[39] The prepared Salen-type ligands were reacted with Co(OAc)$_2$ in CH$_2$Cl$_2$ for 15 min, upon which the solution color changed to red, and then the resulting solution was stirred overnight under an O$_2$ atmosphere with addition of 5.0 eq. of acetic acid, during which the color gradually changed from red to brown. The ^{1}H NMR signals were typically complicate because of the variety of binding modes.[39] In the ^{1}H NMR spectrum of the neutral compound **19** with tBu substituents and no -SO$_3^-$[(nBu)$_4$N]$^+$ moieties, sharp signals showing clear splitting patterns were observed, which, however, could not be assigned simply to a single compound but were interpreted as due to a mixture of two compounds with the cis-b binding mode and trans binding mode in a 1.0 : 0.37 mole ratio (Figure 2(a)). In the ^{1}H NMR spectrum of **18** with Me substituents and no -SO$_3^-$[(nBu)$_4$N]$^+$ moieties, a set of signals assignable to the trans binding mode was observed, but the signals were very broad (Figure S19). Signals in ^{1}H NMR spectra of **14-17** containing -SO$_3^-$[(nBu)$_4$N]$^+$ moieties were either broad or too complicated to be clearly interpreted (Figure 2(b) and Figure S15-S20). Due to variety of binding mode as well as containing fluxional sulfate salt, it was impossible to purify and characterize fully the newly prepared (Salen)Co complexes, which was used for the copolymerization as was prepared according to the well-established method. The signals in the ^{1}H NMR spectrum of the highly active species **I** (Scheme 1) were also too complicate to be clearly assigned.[25]

3.3. CO$_2$/propylene oxide copolymerization

Binary catalytic systems composed of the (Salen)Co(III) complex **14** containing methyl and -SO$_3^-$[(nBu)$_4$N]$^+$ substituents and the quaternary ammonium salts **2-5** ([**14**]/[**2-5**] = 1.0) were screened for CO$_2$/PO copolymerization at the fairly high [PO]/[Co] ratio of 20000. Iodide anions in the multiple ammonium salt were replaced with 2,4-dinitrophenolate (DNP) by treatment with Ag(DNP), because quaternary ammonium salts with the iodide anion have been reported not to be good for CO$_2$/epoxide copolymerization.[42] As the number of ammonium salt units was increased from 2 to 3 and 4, the activity gradually increased, with the highest activity attained with the quadruple ammonium salt **4** [X = DNP] (TOF, 3500 h^{-1}); the activity was reduced when the number of ammonium salt units was further increased to 5 (Table 1, entries 1-4). A thick viscous solution was obtained, the

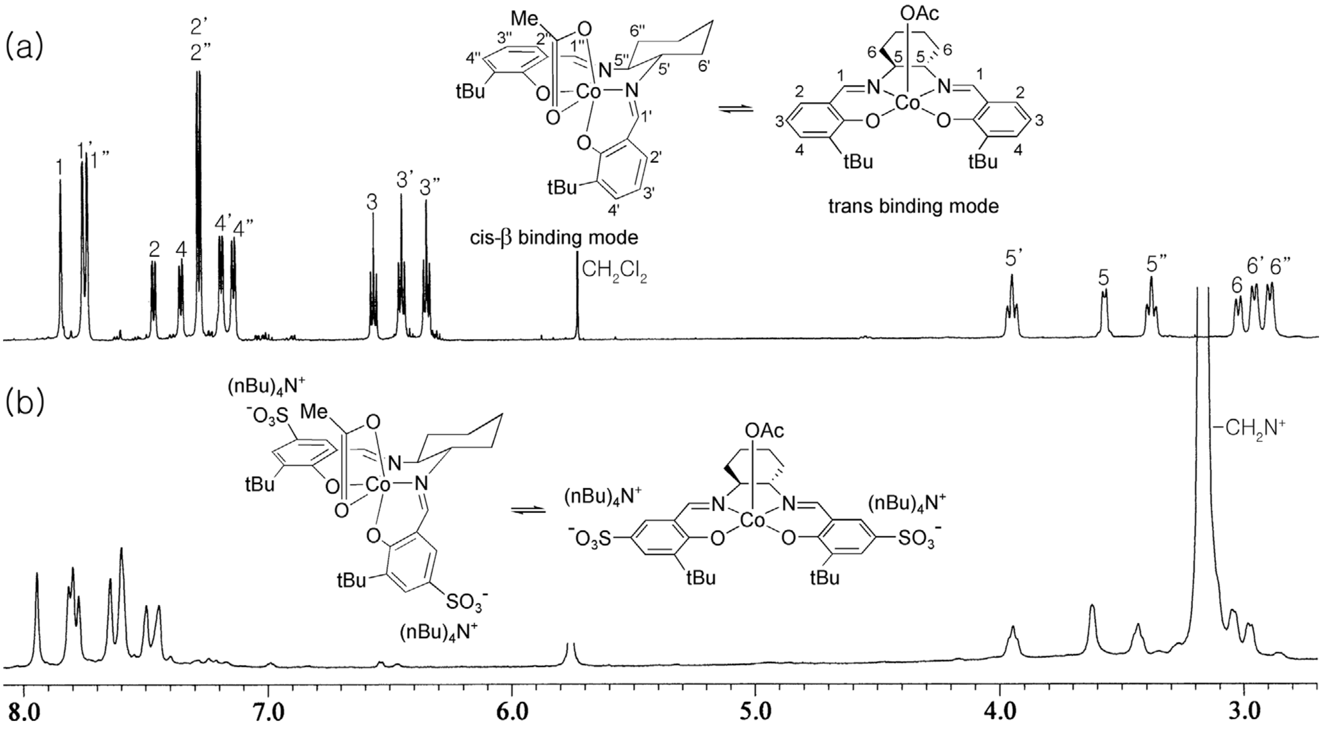


Figure 2. ^{1}H NMR spectra of **19** (a) and **15** (b).

Table 1. CO_2/PO copolymerization results.[a]

Entry	Catalyst	Ammonium salt	Yield[b] (g)	TOF[b] (h^{-1})	Cyclic carbonate[c] (%)	M_n[d] (kDa)	M_w/M_n
1	14	**2** [X = DNP]	2.0	1500	31	29	1.42
2	14	**3** [X = DNP]	3.9	2900	25	52	1.28
3	14	**4** [X = DNP]	4.6	3500	29	35	1.29
4	14	**5** [X = DNP]	3.4	2600	26	31	1.26
5	14	**4** [X = nitrate]	2.3	1700	50	33	1.71
6	14	**4** [X = acetate]	1.8	1400	67	15	1.82
7	15	**4** [X = DNP]	2.9	2200	38	27	1.42
8	**16** + **14** (1.0 : 0.65)	**2** [X = DNP]	2.5	1900	15	44	1.26
9	**16** + **14** (1.0 : 0.65)	**3** [X = DNP]	4.0	3000	9.3	66	1.27
10	**16** + **14** (1.0 : 0.65)	**4** [X = DNP]	5.3	4000	16	45	1.31
11	**16** + **14** (1.0 : 0.65)	**5** [X = DNP]	5.8	4400	17	47	1.27
12	**17** + **15** (1.0 : 0.65)	**5** [X = DNP]	5.9	4500	19	66	1.29
13	**18** or **19**	**4** [X = DNP]	~0	-	-	-	-

[a]Polymerization conditions: PO 15.0 g, 258 mmol, catalyst 13 mol, [catalyst]/[ammonium salt] = 1.0, temperature 90 °C, pressure 40-35 bar, polymerization time 1.0 h. [b]Including cyclic carbonate. [c]Determined by analysis of ^1H NMR spectra. [d]Determined on GPC using a polystyrene standard.

generated polymer being dissolved in excess PO (ca., 30 wt%). Replacement of the DNP anions with either nitrate or acetate anions substantially lowered the activity (entries 5-6).[43] Replacement of the methyl substituents in **14** with tBu substituents (i.e., replacement of the combination of **14** and **4** [X = DNP] with that of **15** and **4** [X = DNP]) also reduced the activity (entry 7). Under the identical polymerization conditions of [PO]/[Co] ratio 20000, the binary catalytic system composed of **18** or **19** (containing no $-SO_3^-[(nBu)_4N]^+$) and **4** [X = DNP] showed negligible activity. Quaternary ammonium salts should be located close to the (Salen)Co(III) complex for catalysis, a situation absent in the binary systems of **18** or **19** and **4** [X = DNP] especially at a high [PO]/[Co] ratio (i.e., at a low catalyst concentration), which consequently exhibit negligible activity. In the binary systems of **14** or **15** containing $-SO_3^-[(nBu)_4N]^+$ moieties and multiple ammonium salts **2-5**, an ion-exchange reaction occurs between **14** or **15** and **2-5** [X = DNP], positioning the ammonium salt units in **2-5**, with ionic interaction, close to the (Salen)Co(III) complex even at a low catalyst concentration, thus rendering the catalyst active (Scheme 1). However, the activity attained in this work was substantially lower than that attained with **I** (Scheme 1) in which the ammonium salts and (Salen)Co(III) complex are connected *via* covalent bonds (TOF, 4500 h^{-1} vs. ~20000 h^{-1}).[24]

Unfortunately, a substantial amount of a cyclic carbonate (propylene carbonate) was concomitantly generated; 30 wt% of cyclic carbonate was formed with the binary system of **14** and **4** [X = DNP], which demonstrated the highest activity. Not polycarbonate but cyclic carbonate is usually generated when a quaternary ammonium salt is used solely as a catalyst in the absence of metal complexes.[44]

When **14** and **4** [X = DNP] are mixed in PO, salt metathesis (ion exchange) occurs to form $[(nBu)_4N]^+[DNP]^-$, from which cyclic carbonate might be generated. By using the unsymmetrical (Salen)Co(III) complex **16** containing one $-SO_3^-[(nBu)_4N]^+$, which was obtained admixed with **14** containing two $-SO_3^-[(nBu)_4N]^+$ moieties in a 1.0 : 0.65 mol ratio, the generation of cyclic carbonate was mitigated by almost half, e.g., from 29% to 16% (entry 3 vs. entry 10); the amount of $[(nBu)_4N]^+$ cations was reduced by using a mixture of **16** and **14** instead of **14**, and a smaller amount of $[(nBu)_4N]^+[DNP]^-$ was formed, hence reducing the amount of cyclic carbonate. In the case of a mixture of **16** and **14**, the activity was also increased gradually by an increase in the number of ammonium salt units, the highest activity being attained with **5** containing five ammonium salt units (4400 h^{-1}, entry 12).

Fairly narrow molecular weight distributions (M_w/M_n, ~1.3) were observed in the GPC studies, although all the GPC curves showed a bimodal distribution; the high molecular weight portion was assigned to the polymer chains grown from H_2O, while the low molecular weight portion was assigned to those grown from DNP in ammonium salts **2-5** and grown from the acetate and acetic acid contained in cobalt complexes **14-17**.[25] Polymers with M_n values in the range of 30-66 kDa were generated. In the ^1H NMR spectra of the polymers, ether linkage signals were not detected, indicating that perfect alternating copolymers were generated in all cases.

Encouraged by the polymerization results, we attempted, in various ways, to prepare cobalt complexes containing $-SO_3^-$ groups that are charge-balanced not with $[(nBu)_4N]^+$ but with one of the quaternary ammonium cations in **4** or **5**, as shown in Scheme 1. However, these attempts were unsuccessful with insoluble complexes being deposited in most cases. Furthermore, we attempted to insert the multiple ammonium salts into high-swelling polystyrene beads but these trials were also unsuccessful; high swelling polystyrene is not a porous material with large pores but a network polymer, and such large molecules as the multiple ammonium salts **2-5** probably cannot penetrate through the net into the PS beads.

4. Conclusion

Multiple ammonium salts containing 2-5 quaternary ammonium salt units and a (Salen)Co(III) complex containing $-SO_3^-[PhNH_3]^+$ moieties were prepared. The combination of these two components exhibited high activity in CO_2/PO copolymerization (TOF, 1500-4500 h^{-1}), whereas combination of the multiple ammonium salts and a (Salen)Co(III) complex not containing $-SO_3^-$

$[(nBu)_4N]^+$ moieties was inactive under the identical polymerization conditions. In the binary catalytic system, species in which a (Salen)Co(III) complex is linked with multiple ammonium salts *via* ionic interaction is formed, with concomitant formation of $[(nBu)_4N]^+[DNP]^-$; the desired polymer was generated from the former while the undesired cyclic carbonate was generated from the latter. Hence, (Salen)Co(III) complexes containing $-SO_3^-$ that is charge-balanced with one of the quaternary ammonium cations in the multiple quaternary ammonium salts can form a highly active and highly selective catalytic system, and a combination of (Salen)Co(III) complexes containing $-SO_3^-$ and multiple ammonium salts anchored on some insoluble support can function as a useful catalytic system, even though attempts to realize those concepts have been unsuccessful up to now.

Supporting information: Information is available regarding ^{1}H NMR and ^{13}C NMR spectra of new compounds *via* the Internet at http://www.springer.com/13233.

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