ORIGINAL ARTICLE

Alternating copolymerization of CO₂ with propylene oxide and terpolymerization with aliphatic epoxides by bifunctional cobalt Salen complex

Hongchun Li and Yongsheng Niu

A novel *N,N*-[2,2'-bis(nitrilomethylidyne)]bis[α -methyl-4-(morpholin-1-ylmethyl)-6-tert-butyl phenolato]-1,2-diaminocyclohexane Co^{III} (2,4-dinitrophenoxy) complex (complex 1) was designed and used to couple carbon dioxide (CO₂) and propylene oxide (PO) as a single-component catalyst. Systematic investigation revealed that complex 1 was highly active and selective in the coupling of CO₂/PO and that complete consumption of PO was accomplished with high copolymer selectivity. A high molecular weight of up to 108.6 kg mol⁻¹ was achieved with an appropriate combination of all variables. Matrix-assisted laser desorption/ionization-time-of-flight mass spectrometer analysis implied that a chain-end control mechanism controls the copolymerization. In addition, complex 1 could operate very efficiently in the terpolymerization of PO and cyclohexene oxide (CHO) with CO₂ to provide polycarbonates with a narrow polydispersity. The *T*_g of the PO/CHO/CO₂ terpolymer can be easily adjusted between 40 and 118.9 °C.

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The transformation of carbon dioxide (CO₂) into aliphatic polycarbonates by coupling with epoxides has been studied intensively in recent decades as one of the most promising processes for the fixation of CO₂ (for reviews on the copolymerization of epoxides and CO₂, see references Darensbourg and Holtcamp,¹ Super and Beckman,² Darensbourg,³ Coates and Moore⁴). After the pioneering work by Inoue and co-workers^{5,6} in the late 1960s, a wide variety of metal catalysts were developed for this transformation.^{7–18} Among the metal complex catalysts, Co Schiff base complexes are effective catalysts for CO₂/epoxides coupling reactions,^{11,13,15–17} because these complexes can control the molecular weights and distribution of the polycarbonates produced and regulate the selective formation of alternating copolymers. However, Co Schiff base complexes are not highly active at a high monomer/catalyst mole ratio in conjunction with a Lewis base or organic salt, which prevents them from becoming commercially viable.¹⁹ Contrarily, one Co Schiff base complex showed a moderate catalytic activity at only high pressure. However, the complex was inactive at low CO₂ pressure.^{11,13} Nozaki and co-workers utilized a Salen-type cobaltate complex with a piperidinium unit as a catalyst for propylene oxide (PO)/CO₂ copolymerization.²⁰ The complex exhibited high selectivity for polycarbonate over cyclic carbonate. After this study, the quaternary ammonium salt unit was anchored by Lee *et al.*,¹⁹ and a Lewis base moiety was anchored to the Salen ligand by Wang and co-workers.²¹ Compared with the binary catalyst systems composed of a Co Schiff base complex and a Lewis

base or organic salt, the bifunctional Salen complexes displayed excellent activity and polycarbonate selectivity because the anchored units of aromatic rings had an important role in maintaining the thermal stability and high activity of the catalyst.²² On the other hand, Lu *et al.*¹⁶ reported that simple changes in the axial group X of the Salen Co^{III}X complex could drastically affect the selectivity of poly(propylene carbonate) (PPC) and cyclic carbonate in PO/CO₂ copolymerization. Recently, it was found that the axial group 2,4-dinitrophenoxy has an important role in CO₂/epoxides coupling reactions.²³ On the basis of the information presented thus far, a novel bifunctional SalcyCo^{III}(2,4-dinitrophenoxy) complex (complex 1, Salcy=*N,N*-[2,2'-bis(nitrilomethylidyne)]bis[α -methyl-4-(morpholin-1-ylmethyl)-6-tert-butyl phenolato]-1,2-diaminocyclohexane) containing a Lewis acidic Co center and two Lewis base units in one molecule was designed and used in the coupling of CO₂ and epoxides without a Lewis base or organic salt, as shown in Figure 1.

The aim of this work was to synthesize a highly active catalyst for CO₂ and epoxide copolymerization. It is assumed that the morpholine groups control the nucleophilicity of the propagating species by protonating the anionic propagating species that is released from the cobaltate center. Unlike binary catalyst systems, which can yield very high head-to-tail content PPC but with relatively low molecular weight, this study offers a new route to produce PPC with higher head-to-tail linkages while maintaining a Mn of over 100 kg mol⁻¹. Moreover, the terpolymerization of PO and cyclohexene oxide (CHO) with CO₂ using

Figure 1 Structure of complex 1.

complex 1 was studied, and cyclohexene carbonate units were used to adjust the structure of the resultant polymer, which is extremely important to improve its mechanical and thermal performances.

EXPERIMENTAL PROCEDURE

Materials

All manipulations involving air- and/or water-sensitive compounds were carried out using standard Schlenk techniques under dry argon. PO was refluxed over CaH₂ and fractionally distilled under an argon atmosphere before use. CO₂ (99.995 %) was purchased from the Qingdao Institute of Special Gases (Qingdao, China). Polymerization grade CO₂ was further purified by passage through a 5-Å molecular sieve column containing MnO. Diethyl ether was distilled from sodium benzophenone. Methylene chloride, hexane and chloroform were distilled from CaH₂ under argon. *N,N'*-[2,2'-bis(nitrilomethylidene)]bis[α -methyl-4-(morpholin-1-ylmethyl)-6-tert-butyl phenolato]-1,2-cyclohexanediamine^{24,25} and *N,N'*-[2,2'-bis(nitrilomethylidene)]bis[α -methyl-4-(morpholin-1-ylmethyl)-6-tert-butyl phenolato]-1,2-cyclohexanediamine^{26–29} Co^{II} were prepared according to methods reported in the literature.

Measurements

Nuclear magnetic resonance spectra were recorded on a Bruker AV 400M (Bruker Biospin GmbH, Rheinstette, Germany) instrument in CDCl₃ at room temperature. Chemical shifts were given in parts per million using tetramethylsilane. Matrix-assisted laser desorption/ionization–time-of-flight mass spectrometer analyses were carried out on a commercial Reflex III MALDI-TOF mass spectrometer (Bruker Daltonics, Bielefeld, Germany) equipped with delayed extraction technology. Ions formed by a pulsed UV laser beam with a 3-nm pulse (nitrogen laser, $\lambda=337$ nm) were accelerated through 20 kV, and the detection voltage was set to 1.60 kV. The laser was slightly above the threshold during the experiments, and the mass spectra were obtained from the results of 35 laser shots in the positive mode. The matrix, trans-3-indoleacrylic acid, was dissolved in purified tetrahydrofuran (0.1 mol l⁻¹), and the solution was mixed with the polymer solution in tetrahydrofuran (5 mg ml⁻¹) in a 1:1 v/v ratio. Gel permeation chromatography measurements were carried out with a Waters instrument (515 HPLC pump, Version 1.5d, Visual Solutions, Westford, MA, USA) equipped with a Wyatt interferometric refractometer. Gel permeation chromatography columns were eluted with tetrahydrofuran at 25 °C at 1 ml min⁻¹. The molecular weights were calibrated against polystyrene standards. Infrared spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer (PerkinElmer Inc., Waltham, MA, USA). The experiment was performed on a Micromass Q-ToF (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in both the positive and negative ion modes.

Synthesis of complex 1

To a stirred mixture of Salcy Co^{II} complex (1.35 g, 1.5 mmol) in CH₂Cl₂ (150 ml), the mixture of 2,4-dinitrophenol (0.276 g, 1.5 mmol, 1 equiv.) and

CH₂Cl₂ (20 ml) was added. The solution was stirred under a dry oxygen atmosphere at room temperature for 60 min. The solvents were removed in vacuum, leaving a crude green dark solid with nearly 100% yield. The solid was further treated with a mixture of diethyl ether and hexane and then dried at 60 °C in vacuum for 24 h. Yield: 91%. elemental analysis calcd (%) for C₄₄H₅₇CoN₆O₉: C, 61.32; H, 6.82; N, 9.33. Found: C, 61.35; H, 6.84; N, 9.35. UV–Vis: 261, 335 and 414 nm.

Representative copolymerization procedure

A 100-ml Parr autoclave was heated to 120 °C under vacuum for 4 h and then cooled under vacuum to room temperature. A 1,4-dioxane solution of complex 1 was loaded into the autoclave with a syringe through the injection port under the protection of CO₂ followed by the addition of PO or the mixture of PO and CHO. The solution was stirred for about 10 min and then injected into an autoclave equipped with a magnetic stirrer under a CO₂ atmosphere. The autoclave was heated to the desired temperature in an oil bath, and the appropriate pressure of CO₂ was obtained. The mixture was stirred for the allotted reaction time, then cooled to room temperature and vented in a fume hood. A small aliquot of the resultant polymerization mixture was removed from the reactor for ¹H nuclear magnetic resonance analysis. The remaining polymerization mixture was then dissolved in chloroform, quenched with 5% HCl solution in methanol and precipitated from methanol. The polymer was collected and dried *in vacuo* to a constant weight, and the polymer yield was determined.

RESULTS AND DISCUSSION

Complex 1 was synthesized by the reaction of Co^{II} acetate tetrahydrate with the ligand and subsequent oxidation in the presence of 1 equiv. 2,4-dinitrophenol and oxygen. The product was sufficiently dried under reduced pressure. Complex 1 was isolated as a solid powder. Numerous attempts to isolate complex 1 in some solvents proved to be unsuccessful. Compared with the structures of *N,N'*-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine Co^{III} 2,4-dinitrophenoxy (complex 2) and 2,2-dimethyl-1,3-propylene bis(3,5-di-tert-butylsalicylideneimino) Co^{III} 2,4-dinitrophenolate,^{26,27} complex 1 should be a stable six-coordinated central Co octahedron (Figure 1). Simple Salen Co^{III}X complexes alone have proven to be inactive under low CO₂ pressure or at elevated temperature, where they are reduced to Co^{II} derivatives.^{11,16,17,22,23,30} The key factor in the catalyst design was the use of Lewis base units as phenolate para substituents on complex 1 to stabilize the active Salen Co^{III} against decomposition to inactive Salen Co^{II}.

The copolymerization of CO₂/PO was examined with complex 1 as the catalyst under 1.5-MPa CO₂ at 25 °C in 1,2-dimethoxyethane; the results are summarized in Table 1. Complex 1 exhibited high catalytic activity (turnover frequency=120 h⁻¹), PPC in 60% polymer yield and a small amount of propylene carbonate (PC) byproducts (PPC/PC>99%, Mn=34.1 kg mol⁻¹, polydispersity indices (PDIs)=1.14; entry 1). The catalyst activity was over four times greater than that of the binary catalyst system of complex 2 in conjunction with *N*-methylmorpholine under the same conditions. In addition, the previously reported Co Salen complex as catalyst was inactive for the copolymerization of CO₂/PO at low CO₂ pressures,^{11,13,22,23} perhaps because the Lewis base anchored on the catalyst ligand framework helps to trap the dissociated anion, resulting in higher catalytic activity and stabilizing ability.

It is generally known that an elevated reaction temperature leads to increased cyclic carbonate in CO₂/epoxide copolymerization. However, complex 1 showed higher activity (turnover frequency=633 h⁻¹) without lowering the selectivity (PPC/PC=98, Mn=16.7 kg mol⁻¹, PDIs=1.11; entry 2) as the temperature was increased to 60 °C. In comparison, the binary catalyst system has shown decreased selectivity at higher reaction temperatures.^{11,16,17,30} No obvious change in copolymerization rate and polymer selectivity was observed in this

Table 1 The coupling of epoxides and CO₂ catalyzed by complex **1**^a

Entry	PO (mmol)	CHO (mmol)	Time (h)	Yield ^b (%)	TOF ^c (h ⁻¹)	Selectivity ^d (% PPC)	Mn ^e (kg mol ⁻¹)	PDI ^e (Mw/Mn)	T _g ^f (°C)	T _{d,5%} ^g (°C)
1	50	0	10	60	120	>99	34.1	1.14	37.9	234.1
2	50	0	1	31	633	98	16.7	1.11	37.8	233.5
3	50	0	30	96	64.7	99	47.8	1.17	40.0	298.5
4	100	0	40	97	99	98	89.5	1.16	42.1	318.7
5	150	0	50	96	59.4	97	108.6	1.16	41.9	316.5
6	10	40	30	96	64	—	57.3	1.17	47.7	321.9
7	25	25	30	98	65.3	—	65.2	1.17	69.5	329.8
8	40	10	30	98	65.3	—	71.7	1.15	88.5	332.7
9	0	50	30	99	66	—	78.5	1.16	118.9	356.2
10 ^h	50	0	10	12	27	92	13.7	1.24	34.9	225.7

Abbreviations: CHO, cyclohexene oxide; DME, 1,2-dimethoxyethane; DSC, differential scanning calorimetry; GPC, gel permeation chromatography; PDIs, polydispersity indices; PO, propylene oxide; PPC, poly(propylene carbonate); TGA, Thermogravimetric analysis; TOF, time-of-flight.

^aReaction conditions: $n_{\text{complex 1}} = 2.5 \times 10^{-5}$ mol, $V_{\text{DME}} = 1.0$ mL, at 25 °C (entries 1 and 3–10) or 60 °C (entry 2) with 1.5 MPa of CO₂.

^bBased on isolated PPC yield.

^cTurnover frequency of epoxide to products (polycarbonate and cyclic carbonate).

^dDetermined on the basis of ¹H nuclear magnetic resonance spectroscopy of the crude product.

^eDetermined by GPC.

^fDetermined by DSC.

^gTemperature at polymer decomposition of 5% measured by TGA.

^hReaction was performed using binary catalyst system of complex **2**/*N*-methylmorpholine with a molar ratio of 1/2.

reaction with complex **1** when the catalyst concentration was decreased (entries 3–5). These results confirm that the anchored Lewis bases on the ligand framework of complex **1** helps to stabilize the active Co^{III} species against decomposition to inactive Co^{II} by reversible intramolecular Co–O bond formation and dissociation.

To obtain the complete consumption of PO, the reaction time was prolonged. The PO was completely consumed within 30 h, and a quantitative conversion with high copolymer selectivity was obtained (PPC/PC=99, yield=96%; entry 3). The prolonged reaction did not lead to an observable decrease in selectivity for PPC formation. The result might be ascribed to the effective diffusion of the reactant by adding solvents, which is the so-called solvent effect. A similar solvent effect was reported for copolymerization with binary catalyst systems.^{12,20,30} The Mn value of the copolymer obtained increased linearly in proportion to the PO conversion, retaining a narrow but bimodal distribution (Figure 2). The Mn values were much lower than the theoretical values because of chain transfer caused by trace quantities of water in the copolymerization system. However, chain transfer did not result in chain termination, and the dissociated chains could repropagate when activated on a catalyst center. The Mn values of both the higher molecular weight and lower molecular weight copolymers increased linearly with PO conversion, and the PDIs remained narrow (PDI <1.2). Similar results have been reported before.^{12,20} To obtain copolymers with higher Mn values, copolymerization was attempted at a higher PO/complex **1** ratio of 6000. With a reaction time up to 50 h, the molecular weight reached 108.6 kg mol⁻¹, and the selectivity for PPC formation did not show an observable decrease (PPC/PC=97; entry 5). A change in the reaction time from 1 to 50 h caused only a slight decrease in the microstructure of the resulting polymer (Figure 3).

Because the structure of the PPC obtained was completely alternating, Matrix-assisted laser desorption ionization–time-of-flight mass spectrometry was the ideal tool for the end-group analysis to probe the active species responsible for the initiation of the polymerization reaction.³¹ As shown in Figure 4, at least three series of signals with regular repeat intervals (repeating units of 102 mass units) were observed in the mass spectra. A higher molecular number series of peaks at the *m/z* of 1469, 1572, 1674, 1776 and 1878 (series A, Figure 4, HO-[CH₂CH(CH₃)OC(O)O]*n*-H, Na⁺) was assigned to

Figure 2 Typical gel permeation chromatography curve of poly(propylene carbonate) produced by the alternating copolymerization of carbon dioxide/propylene oxide sample precreated by complex **1** (entry 5 in Table 1).

chains that were end-capped with hydroxyl groups. The hydroxyl end-groups are proposed to arise via a series of chain transfer reactions initiated by trace amounts of water. These end-groups are commonly observed in this polymerization reaction.^{12,20,22} A lower molecular number series of peaks was assigned to two series of peaks. For the first series of peaks at *m/z* of 1534, 1636, 1738, 1840 and 1941 (series B, Figure 4, C₆H₃(NO₂)₂O-[CH₂CH(CH₃)OC(O)O]*n*-H, Na⁺), there was a difference of 102 in *m/z* between every two neighboring peaks, which was also seen in the second series at *m/z* of 1550, 1652, 1754, 1855 and 1957 (series C, Figure 4, C₆H₃(NO₂)₂O-[CH₂CH(CH₃)OC(O)O]*n*-H, K⁺). Moreover, the second series of peaks in *m/z* were correspondingly 16 larger than those in the first series. In addition, the weight number of the propylene carbonate units was 102. Thus, it could be calculated that the first series of peaks resulting from the copolymerization reaction was initiated by the insertion of PO into a Co–O bond of the catalytic species attached to a Co center and terminated with 2,4-dinitrophenolate groups and Na⁺ ions. For the second series, K⁺ ions terminated the reaction instead of Na⁺ ions. Thus, a chain-end control mechanism exerts control on the copolymerization. The initiation step presumably occurs via Jacobsen's mechanism.³²

All the copolymers obtained had a high content of head-to-tail connectivity (>90%) according to the ¹³C nuclear magnetic

Figure 3 ¹³C spectrum (100 MHz) of the carbonyl region for PPC: (a) 1 h, (b) 10 h and (c) 50 h. TT, tail-to-tail; HT, head-to-tail; HH, head-to-head.

Figure 4 Matrix-assisted laser desorption/ionization–time-of-flight mass spectrum of poly(propylene carbonate) produced by the alternating copolymerization of carbon dioxide/propylene oxide sample proceant by complex **1** (entry 5 in Table 1).

resonance spectra of the PPCs in the carbonyl region. To understand whether the increase in *M_n* of PPC improved its thermal performance, PPC samples with different *M_n*s were chosen for differential scattering calorimetry and thermogravimetric analysis measurements. Figure 5 shows two differential scattering calorimetry curves of different PPCs. The *T_g* was 37.8 °C for PPC with a *M_n* of 16.7 kg mol^{−1}, and it increased to 41.9 °C for PPC with a *M_n* of 108.6 kg mol^{−1}. The decomposition temperatures of 5 wt% weight loss (*T_{d,5%}*) of the corresponding samples increased from 233.5 to 316.5 °C with increasing *M_n*, as shown in Figure 6. Therefore, increasing the *M_n* of PPC is one practical way to improve its thermal properties.

The possibility of using complex **1** for the terpolymerization of CO₂ with PO and CHO was explored, and it was found that complex **1** could operate very efficiently at 25 °C and 1.5-MPa CO₂ pressure in the terpolymerization of CO₂ with PO (50 mol%) and CHO (50 mol%) to selectively provide polycarbonates with narrow molecular weight distributions (PDIs=1.17; entry 7). In the ¹H nuclear magnetic resonance of this sample, the resonances in the regions of

Figure 5 Differential scanning calorimetry curves of different poly(propylene carbonate) samples: (a) entry 5 and (b) entry 2 in Table 1.

Figure 6 Thermogravimetric analysis curves of different poly(propylene carbonate) samples: (a) entry 5 and (b) entry 2 in Table 1.

Figure 7 ¹H nuclear magnetic resonance spectra of the propylene oxide/cyclohexene oxide/carbon dioxide terpolymer (entry 7 in Table 1).

4.92–5.08 p.p.m. of the two peaks can be assigned to CH in the propylene carbonate unit, and the resonances in the 4.68 p.p.m. arise from CH in the cyclohexene carbonate unit³³ (Figure 7). In addition,

terpolymerization with different PO/CHO mole ratios gave different contents of cyclohexene carbonate linkages and propylene carbonate linkages in the terpolymer. Thus, the *T_g* of the PO/CHO/CO₂ terpolymer could be easily varied between 40 and 118.9 °C.

CONCLUSIONS

In conclusion, PPC with Mn up to 108.6 kg mol⁻¹ was synthesized at room temperature using a tetradentate Schiff-base Co complex with two Lewis base units. Complete consumption of the epoxide was accomplished with high copolymer selectivity and without a significant amount of associated cyclic carbonate. In addition, the bifunctional complex proved to be very effective in the terpolymerization of CHO, PO and CO₂. The *T_g* of the PO/CHO/CO₂ terpolymer could be easily varied between 40 and 118.9 °C by controlling the proportion of cyclohexene carbonate linkages and propylene carbonate linkages in the terpolymer.

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