

ALTERNATING COPOLYMERIZATION OF CYCLOHEXENE OXIDE AND CARBON DIOXIDE UNDER COBALT PORPHYRIN CATALYST*

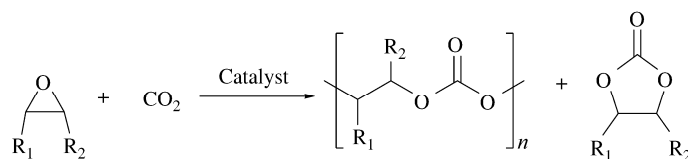
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Abstract Cobalt porphyrin complexes (TPPCo^{III}X) (TPP = 5,10,15,20-tetraphenyl-porphyrin; X = halide) in combination with bis(triphenylphosphine) iminium chloride (PPNCl) were used for the copolymerization of cyclohexene oxide and CO₂. The highest turnover frequency of 67.2 h⁻¹ was achieved after 13 h at 20°C, and the obtained poly(1,2-cyclohexylene carbonate) (PCHC) showed number average molecular weight (*M_n*) of 10 × 10³. Though the obtained PCHC showed atactic structure, the *m*-centered tetrads content reached 58.1% at CO₂ pressure of 1.0 MPa, and decreased to 51.9% at CO₂ pressure of 6.0 MPa, indicating that it was inclined to form atactic polymer at high CO₂ pressure.

Keywords: Carbon dioxide; Cobalt porphyrin; Cyclohexene oxide; Poly(1,2-cyclohexylene carbonate); Stereochemistry; Copolymerization.

INTRODUCTION

Carbon dioxide is an attractive feedstock for synthetic chemistry, not only because it is abundant and inexpensive, but also low toxic and renewable. The efficient catalyst for transformation of CO₂ into economically competitive products is of great importance, which has been a long-standing goal in the past decades^[1–4]. One of the most promising processes for CO₂ utilization is shown in Scheme 1, *i.e.*, the alternating copolymerization of CO₂ and epoxides to form polycarbonate^[5–9], as first reported by Inoue in 1969^[10, 11].



Scheme 1 Copolymerization of carbon dioxide and epoxide

Subsequent to Inoue's initial discovery, many active catalysts with improved product selectivity have been developed. The earlier catalysts were mainly based upon heterogeneous catalysts systems^[10, 12–14], however, in the past two decades, some well-defined homogeneous metal complexes have been reported to be highly active and selective catalysts, mainly including metal complexes with phenoxide^[15], β -diiminate^[16], salen^[17–19] or salan ligands^[20–22] and porphyrin ligands^[23–28].

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20634040 and 50903084).

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Received October 9, 2010; Revised December 1, 2010; Accepted December 7, 2010

doi: 10.1007/s10118-011-1073-3

Aluminum porphyrin is the first discrete homogeneous catalyst for the copolymerization of CO₂ and epoxides^[23] to obtain an alternating copolymer with a very narrow molecular weight distribution. However, the molecular weight of the polymers was low and reaction time was long. In 2003, Inoue developed a new porphyrin system utilizing manganese as the active metal center^[25], copolymerization of cyclohexene oxide (CHO) and CO₂ under 5 MPa at 80°C produced PCHC with 99% carbonate linkages in a moderate turnover frequency (TOF) of 16.3 h⁻¹, the M_n of PCHC was 6.7×10^3 with polydispersity of 1.3.

Recently, Sugimoto reported the use of cobalt porphyrin ((TPP)CoCl) in combination with dimethylaminopyridine (DMAP) for the copolymerization of CO₂ and epoxides (CHO and PO)^[29], alternating copolymer of CO₂ and CHO was prepared under 5 MPa at 25°C, but the catalytic activity was still not high (TOF = 2.29 h⁻¹). The (TPP)CoCl/DMAP system could also catalyze the copolymerization of CO₂ and propylene oxide (PO) with TOF of 8.33 h⁻¹, but the obtained poly(1,2-propylene carbonate) (PPC) showed low M_n of 14.9×10^3 . Recently, we reported a cobalt porphyrin catalyst system (TPPCo^{III}X/PPNCl) for copolymerization of CO₂ and PO^[27], which showed not only high catalytic activity (TOF = 188 h⁻¹) during 10 h of copolymerization, but also displayed high product selectivity with the byproduct propylene carbonate (PC) below 1%, and high molecular weight ($M_n = 115 \times 10^3$) regio-regular PPC with head-to-tail (H-T) linkage of 93% was obtained.

Stimulated by the success in the copolymerization of CO₂ and PO using cobalt porphyrin catalyst system, it is natural to use this catalyst system for the copolymerization of CO₂ and CHO to prepare high molecular weight copolymer with improved stereo-structure.

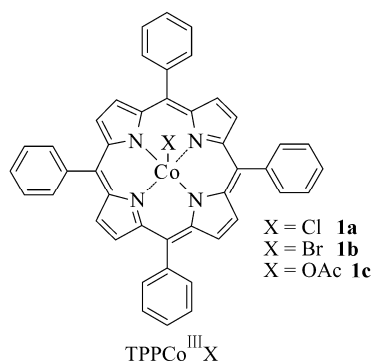
EXPERIMENTAL

General Procedure

CHO and other solvents were dried over calcium hydride and distilled before use. Bis(triphenylphosphine) iminium chloride was provided by Aldrich and dried under vacuum before use. Commercial CO₂ (99.99% pure) was used without further purification. ¹H-NMR spectra of the copolymers were recorded at room temperature on a Unity-400 NMR spectrometer using tetramethylsilane as internal reference. ¹³C-NMR spectra of the copolymers were recorded at room temperature on a Bruker AV-300 NMR spectrometer. The molecular weight and polydispersity of the polymer were determined on Waters 410 gel permeation chromatography (GPC) at 30°C using CH₂Cl₂ as eluent. The GPC profile was calibrated by monodisperse polystyrene from 500 Da to 400000 Da.

Synthesis of Cobalt Porphyrin Complexes

The structure of cobalt porphyrin complexes TPPCo^{III}X is shown in Scheme 2, which was synthesized according to the literature^[30].



Scheme 2 Structure of cobalt porphyrin complex

Synthesis of complex 1a

To a solution of TPPCo^{II} (0.60 g, 0.89 mmol) in CHCl₃/MeOH (400 mL, 1:1) was added 4.5 mL of aqueous 37% HCl solution, the mixture was stirred for 5 h to give a purple solution. At the end of the reaction, 100 mL

of CHCl_3 was added, and the CHCl_3 layer was washed with water. Then the CHCl_3 solution was dried by MgSO_4 and filtered. The solution was concentrated under reduced pressure at about 42°C to give a purple residue. The resulted solid was further treated with a mixture of CHCl_3 and petroleum ether to yield a purple solid, and then dried at 80°C in vacuum for 48 h^[31]. The product was obtained in 98% yield. UV-Vis (CH_2Cl_2) λ_{max} : 545 nm, 422 nm. Anal. Calcd for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{CoCl}$: C, 74.738; H, 3.991; N, 7.923. Found: C, 74.912; H, 3.879; N, 7.881. ESIMS (m/z) calc. ($\text{C}_{44}\text{H}_{28}\text{N}_4\text{Co}^+$): 671.666, found: 671.658.

Synthesis of complex 1b

Complex **1b** was synthesized similar to the complex **1a**, except that HBr was used instead of HCl. The complex was obtained in 98% yield. UV-Vis (CH_2Cl_2) λ_{max} : 538 nm, 405 nm. Anal. Calcd for $\text{C}_{44}\text{H}_{28}\text{N}_4\text{CoBr}$: C, 70.317; H, 3.755; N, 7.455. Found: C, 70.174; H, 3.902; N, 7.391. ESIMS (m/z) calc. ($\text{C}_{44}\text{H}_{28}\text{N}_4\text{Co}^+$): 671.666, found: 671.654.

Synthesis of complex 1c

To a suspension of TPPCo^{II} complex (0.671 g, 1 mmol) in 100 mL CHCl_3 was added glacial acetic acid (2.8 mL, 40 mmol). The solution was stirred at room temperature for 8 h. The solvent and unreacted glacial acetic acid were removed under reduced pressure to leave a purple solid in 95% yield. UV-Vis (CH_2Cl_2) λ_{max} : 529 nm, 415 nm. Anal. Calcd for $\text{C}_{46}\text{H}_{31}\text{N}_4\text{O}_2\text{Co}$: C, 75.612; H, 4.276; N, 7.667. Found: C, 75.581; H, 4.392; N, 7.604. ESIMS (m/z) calc. ($\text{C}_{44}\text{H}_{28}\text{N}_4\text{Co}^+$): 671.666, found: 671.660.

General Copolymerization Procedure

A 500 mL autoclave was heated to 80°C under vacuum for 5 h, then cooled under vacuum to 20°C . $\text{TPPCo}^{\text{III}}\text{Cl}$ (0.3358 g, 0.5 mmol), PPNCl (0.3537 g, 0.5 mmol), and CHO (54 mL, 0.75 mol) were added into the autoclave, and the autoclave was pressurized to 4.0 MPa by CO_2 and stirred at 20°C for 24 h. The reactor was then vented, and a small aliquot of the resultant polymerization mixture was transferred from the reactor for ^1H -NMR and GPC analysis. The remaining polymerization mixture was then dissolved in methylene chloride, and quenched with 5 wt% HCl solution in methanol. The as-polymerized crude product was dried in vacuum to constant weight, and the yield was determined after subtracting the catalyst weight. The as-polymerized product was purified by dichloromethane dissolving and hydrochloride/methanol precipitating process.

RESULTS AND DISCUSSION

Copolymerization of CHO and CO_2 Using $\text{TPPCo}^{\text{III}}\text{X}$ and Cocatalyst System

The copolymerization of CHO and CO_2 was carried out using $\text{TPPCo}^{\text{III}}\text{X}$ and cocatalyst system at 20°C . Negligible activity was observed in the absence of cocatalyst, the addition of cocatalyst $[\text{PPN}]\text{Cl}$ resulted in the formation of the alternating copolymer. The ^1H -NMR spectrum of a typical PCHC is shown in Fig. 1, where the carbonate unit content was about 99%. The influence of the axial X group in $\text{TPPCo}^{\text{III}}\text{X}$ on the catalytic activity

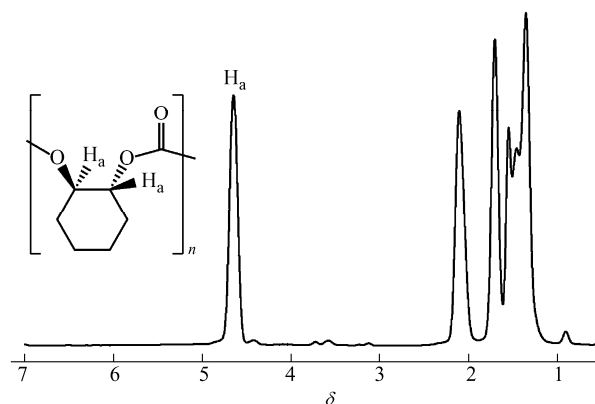


Fig. 1 ^1H -NMR spectrum of PCHC (Table 1 entry 2)

and polymer selectivity is summarized in Table 1, $\text{TPPCo}^{\text{III}}\text{Br}$ (**1b**) complex in combination with PPNCl exhibited the highest catalyst activity ($\text{TOF} = 67.2 \text{ h}^{-1}$), while the copolymerization catalyzed by $\text{TPPCo}^{\text{III}}\text{Cl}/\text{PPNCl}$ proceeded much slower. When $\text{TPPCo}^{\text{III}}\text{OAc}$ and PPNCl were used, no PCHC was formed, and PC became the only product. It seemed that incorporation of an electron-withdrawing axial group X could enhance the catalytic activity and the selectivity for PCHC. It can be assumed that the axial group with poor leaving ability is beneficial to the successive insertion of $\text{CO}_2/\text{epoxide}$ towards the $\text{Co}-\text{O}$ bond as compared with the formation of cyclic carbonates by intermolecular cyclic elimination^[19].

Table 1. Copolymerization of CHO and CO_2 by $\text{TPPCoX}/\text{cocatalyst}^{\text{a}}$

Entry	Catalyst	Cocatalyst	Time (h)	TOF ^b (h^{-1})	$M_n \times 10^{-3}$	PDI ^c (M_w/M_n)	Selectivity (%PCHC)
1	$\text{TPPCo}^{\text{III}}\text{Cl}$	—	24	1.3	5.7	1.27	42
2	$\text{TPPCo}^{\text{III}}\text{Cl}$	PPNCl	24	31.7	9.5	1.11	99
3	$\text{TPPCo}^{\text{III}}\text{Br}$	PPNCl	13	67.2	10.0	1.12	99
4	$\text{TPPCo}^{\text{III}}\text{OAc}$	PPNCl	24	—	NA ^d	NA	NA

^a Copolymerization was carried out at 20°C in neat CHO (54 mL, 500 mmol; catalyst/co-catalyst/epoxide = 1:1:1000); CO_2 pressure: 2.0 MPa; ^b Turnover frequency of CHO to products; ^c Determined by gel permeation chromatography in CH_2Cl_2 at 30°C , calibrated with polystyrene standards; ^d No polymer was found.

The influence of molar ratio of PPNCl to **1a** in the binary catalyst system on the reaction rate, PCHC selectivity and polymer molecular weight was also investigated. As listed in Table 2, the optimal activity as well as PCHC selectivity occurred when 2 equiv. of PPNCl was used. The TOF was 31.7 h^{-1} when 1 equiv. of PPNCl was used, while increase of PPNCl to 2 equiv. led to much higher TOF (70.4 h^{-1}), further raising the amount of PPNCl led to a decrease in catalytic activity as well as M_n of PCHC. For example, when the molar ratio of PPNCl to **1a** was raised from 2 to 6, the TOF dropped from 70.4 h^{-1} to 27.0 h^{-1} , and the M_n of PCHC decreased from 9.1×10^3 to 6.0×10^3 .

Table 2. Effects of the cocatalyst amount on copolymerization of CHO and CO_2^{a}

Entry	$\text{PPNCl}/\text{1a}$	Time (h)	Yield (%)	TOF (h^{-1})	$M_n \times 10^{-3}$	PDI (M_w/M_n)
1	1:1	24	76	31.7	9.5	1.11
2	2:1	12	84	70.4	9.1	1.11
3	4:1	13	51	39.0	6.9	1.12
4	6:1	24	65	27.0	6.0	1.10

^a Copolymerization conditions and determinations see Table 1 except for the molar ratio of cocatalyst to cobalt porphyrin complex **1a** ($\text{PPNCl}/\text{1a}$).

Copolymerization temperature is an important factor for the copolymerization. In sharp contrast to most catalyst system, when the copolymerization temperature increased from 20°C to 60°C , as listed in Entry 1–3 of Table 3, TOF decreased from 31.7 h^{-1} to 17.6 h^{-1} , and the M_n of PCHC decreased from 9.5×10^3 to 4.0×10^3 , indicating that high temperature was not beneficial to the catalytic activity, probably due to that the cobalt complexes lost activity at elevated temperatures, since the Co(III) may be reduced to Co(II) as red solid precipitate at high temperatures, which was ineffective for producing PCHC. In fact, when the copolymerization was carried out under high temperatures, red brown solid was observed, indicating that inactive TPPCo(II) was really produced.

Table 3. Effects of reaction temperature on copolymerization of CHO and CO_2^{a}

Entry	Temperature ($^\circ\text{C}$)	Selectivity (%PCHC)	TOF (h^{-1})	$M_n \times 10^{-3}$	PDI (M_w/M_n)
1	20	99	31.7	9.5	1.11
2	40	98	22.3	5.5	1.05
3	60	98	17.6	4.0	1.04

^a Catalyst system: complex **1a**/ PPNCl ; Reaction time: 24 h; Other copolymerization conditions see Table 1.

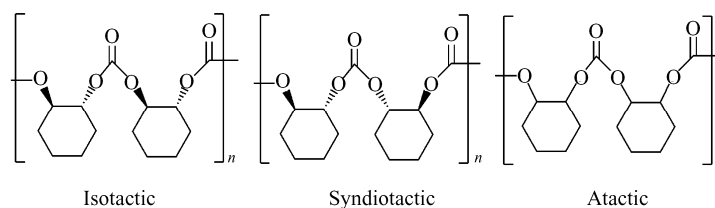
The influence of CO₂ pressure on the catalytic activity and M_n of PCHC was summarized in Table 4. Optimal TOF of 36.4 h⁻¹ occurred at 4.0 MPa, and it decreased to 28.2 h⁻¹ at 1.0 MPa, in the meanwhile, the carbonate content of PCHC dropped from 99% to 96%. Copolymerization of CHO and CO₂ at low CO₂ pressure generally resulted in decrease of M_n . Raising the pressure above the optimal level had insignificant influence on PCHC selectivity as well as carbonate content in PCHC, but the catalytic activity showed a slight decrease, which was attributed to the dilution effect of excess CO₂ diffusing into the liquid phase^[32].

Table 4. Effects of reaction pressure on copolymerization of CHO and CO₂^a

Entry	Pressure (MPa)	TOF (h ⁻¹)	Selectivity (%PCHC)	Carbonate linkages (%)	$M_n \times 10^{-3}$	PDI (M_w/M_n)
1	1.0	28.2	98	96	4.5	1.23
2	2.0	31.7	99	98	9.5	1.11
3	3.0	35.2	99	99	11.0	1.11
4	4.0	36.4	99	99	11.5	1.14
5	6.0	34.0	99	99	8.9	1.15

^a Catalyst system: complex **1a**/PPNCl; Reaction time: 24 h; Other copolymerization conditions see Table 1.

As shown in Scheme 3, the structure of PCHC can be divided into isotactic, syndiotactic and atactic from the perspective of stereochemistry. Stereoregular PCHC has been classified according to the relative stereochemistry of the carbons on the cyclohexane unit at which the main chain enters^[33, 34] (Fig. 2).



Scheme 3 Stereochemistry of PCHC

Nozaki has assigned the resonance peaks corresponding to [mmm] and [rrr] tetrad sequences based on model cyclohexene carbonate oligomers^[34]. In each case, all [mmm], [mmr] and [rmr] tetrads were correlated to one central resonance at $\delta = 153.7$ and the remaining *r*-centered tetrads resided in the $\delta = 153.3$ –153.1 range. Isotactic PCHC was therefore characterized by a strong resonance at $\delta = 153.7$ with a smaller series of resonances from $\delta = 153.3$ –153.1 due to stereoerrors. Coates found that the CO₂ pressure has dramatic effects on

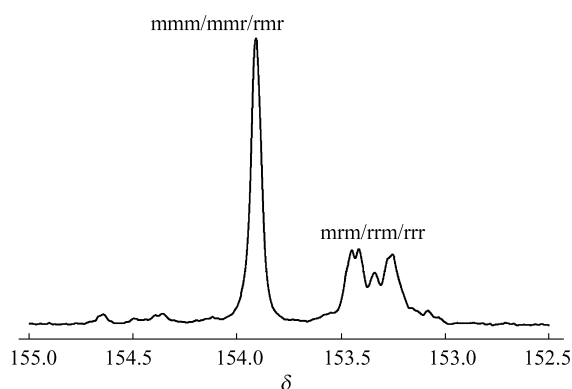


Fig. 2 ¹³C-NMR spectrum of PCHC (reaction pressure: 3.0 MPa)

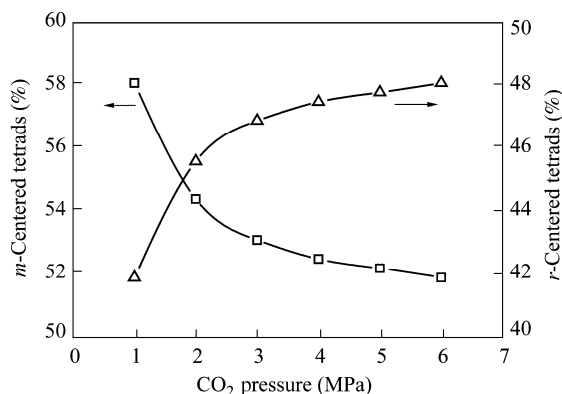


Fig. 3 The effect of CO₂ pressure on stereoselectivity of PCHC using TPPCo^{III}/PPNCl catalyst

the resultant PCHC tacticity^[35], where copolymerization at high CO₂ pressures generally resulted in improvements in syndiospecificity, PCHC with as high as 81% *r*-centered tetrads was obtained at 5.4 MPa CO₂ pressure using *rac*-(salen)CoOBzF₅ catalyst. To investigate the effect of CO₂ pressure on syndiospecificity, we studied the copolymerization of CHO and CO₂ using TPPCo^{III}Cl/PPNCl at different CO₂ pressures. As shown in Fig. 3, increasing the CO₂ pressure from 1.0 MPa to 6.0 MPa caused the decrease of *m*-centered tetrads from 58.1% to 51.9%. Although *m*-centered tetrads constituted the major part of the PCHC main chain structure, the copolymerization was inclined to form atactic polymer at high CO₂ pressure in this catalyst system.

CONCLUSIONS

A series of TPPCo^{III}X/PPNCl catalysts were synthesized for the alternating copolymerization of CHO and CO₂. TPPCo^{III}Cl alone gave low catalytic activity, while both TPPCo^{III}Cl/PPNCl and TPPCo^{III}Br/PPNCl systems showed higher activity than other ever reported in metal porphyrin catalyst at ambient temperature. The structure of the obtained PCHC was also studied. The *m*-centered tetrads corresponding to isotactic units constituted the major part of the PCHC main chain structure, and they decreased with increasing CO₂ pressure.

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