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Concerning the Deactivation of Cobalt(III)-Based Porphyrin and Salen Catalysts in Epoxide/CO_2 Copolymerization

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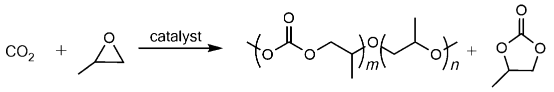
Abstract: Functioning as active catalysts for propylene oxide (PO) and carbon dioxide copolymerization, cobalt(III)-based salen and porphyrin complexes have drawn great attention owing to their readily modifiable nature and promising catalytic behavior, such as high selectivity for the copolymer formation and good regioselectivity with respect to the polymer microstructure. Both cobalt(III)–salen and porphyrin catalysts have been found to undergo reduction reactions to their corresponding catalytically inactive cobalt(II) species in the presence of propylene oxide, as evidenced by UV/Vis and NMR spectroscopies and X-ray crystallography (for cobalt(II)–salen). Further investigations on a TPPCoCl (TPP = tetraphenylporphyrin) and NaOMe system reveal that such a catalyst reduction is attributed to the presence of alkoxide anions. Kinetic studies of the redox reaction of TPPCoCl with NaOMe suggests a pseudo-first order in cobalt(III)–porphyrin. The addition of a co-catalyst, namely bis(triphenylphosphine)iminium chloride (PPNCl), into the reaction system of cobalt(III)–salen/porphyrin and PO shows no direct stabilizing effect. However, the results of PO/CO_2 copolymerization by cobalt(III)–salen/porphyrin with PPNCl suggest a suppressed catalyst reduction. This phenomenon is explained by a rapid transformation of the alkoxide into the carbonate chain end in the course of the polymer formation, greatly shortening the lifetime of the autoreducible PO-ring-opening intermediates, cobalt(III)–salen/porphyrin alkoxides.

Introduction

Following the initial discovery of the epoxide/CO_2 copolymerization by Inoue and co-workers in 1969 (Scheme 1),[1] this particularly interesting reaction has attracted significant attention for its utilization of the nontoxic, low-cost greenhouse gas, carbon dioxide. The afforded copolymers exhibit biodegradability that meets the current environmental considerations. Numerous heterogeneous and homogeneous catalysts have been hitherto developed to improve the overall catalytic activities and the selectivity for copolymer formation, against that of byproducts such as cyclic carbonate, and to further tailor the polymer microstructure for the fulfillment of specific mechanical properties.[2] In 2003, Coates and co-workers introduced the first cobalt(III)-based catalyst active for such a copolymerization.[3] Since then, various cobalt(III)-based organic metal complexes, mainly with porphyrin[4] or salen (salen = 2,2′-ethylenebis(nitrilomethylidene)diphenol)[3,5] as the ligand, have been investigated and cobalt(III)-based catalysts have become among the most important catalytic species. A highest reported TOF value of 26 000 h^{-1} was achieved for poly(propylene carbonate) (PPC) formation by using a cobalt(III)–salen catalyst bearing four onium-salt arms on its periphery designed by Lee and co-workers.[5b] Cobalt(III) tetraphenylporphyrin complex (TPPCoCl) has also been proven active for poly(propylene carbonate) formation with either bis(triphenylphosphine)iminium chloride (PPNCl)[4a] or 4-dimethylaminopyridine (DMAP)[4b] as a co-catalyst. A phenomenon of the catalyst deactivation via reduction to cobalt(II) species, however, was briefly mentioned in earlier publications for both cobalt(III)–salen[5a] and –porphyrin[4d,e] catalysts. Herein a systematic evaluation on this unfavorable side reaction is presented, aiming to gain a deeper insight into the catalyst behavior in PO/CO_2 copolymerization.



Scheme 1. The copolymerization of propylene oxide and CO_2.

Results and Discussion

Reduction of a cobalt(III)–porphyrin catalyst in PO/CO_2 copolymerization

During investigations on the cobaltoporphyrin catalyst in propylene oxide (PO) and CO_2 copolymerization in our laboratory, the reduction of $TPPCo^{III}Cl$ to $TPPCo^{II}$ in the presence of PO

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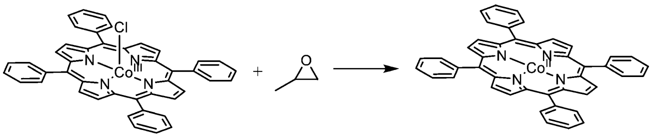


Scheme 2. The reduction of TPPCo^{III}Cl in the presence of propylene oxide.

was evaluated and monitored by both UV/Vis and ^{1}H NMR spectroscopies (Scheme 2).

The UV/Vis spectrum of TPPCoCl in dichloromethane (DCM) solution exhibits a Soret band at 406 nm and a broad Q band at 543 nm. If a small amount of a coordinating solvent, such as tetrahydrofuran (THF), is added, a 20 nm red shift of the Soret band is observed and the Q band becomes narrower. Such a change of spectrum is assigned to the transformation of a pentacoordinate TPPCoCl species (in DCM) to a hexacoordinate one (in DCM + THF).[6]

In contrast, the UV/Vis spectra of TPPCo^{II} in non-coordinating (DCM, Soret band: 410 nm, Q band: 525 nm) and coordinating (DCM + THF, Soret band: 411 nm, Q band: 525 nm) solvents are very similar (see the Supporting Information, Figure S1). Therefore, given the sufficiently distinguishable UV/Vis spectra of cobalt porphyrins with different metal oxidation states, the redox reaction between cobalt(III) and cobalt(II) species can be successfully monitored in situ.

A series of time-resolved UV/Vis measurements of TPPCo^{III}Cl in pure propylene oxide were carried out at room temperature (Figure 1). A continuing decrease of the TPPCo^{III} Soret band (436.9 nm) with a simultaneous increase of the TPPCo^{II} Soret band (412.6 nm) was observed, indicating the occurrence of the reduction of TPPCo^{III} to TPPCo^{II} in the presence of PO (Scheme 2).[7]

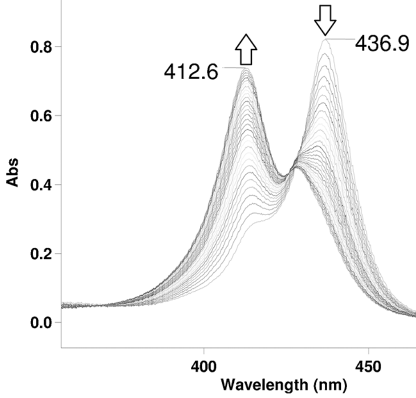


Figure 1. Time-resolved UV/Vis spectra of TPPCo^{III}Cl in propylene oxide.

Onium salts, such as PPNCl, are commonly used as co-catalysts in PO/CO_2 copolymerization and are assumed to have a stabilizing effect on the catalyst.[5a] Hence, we subsequently examined the potential influence of PPNCl towards the TPPCo^{III} reduction in a PO solution. As indicated by the time-resolved UV/Vis spectra (see the Supporting Information, Figure S2), the addition of 1 equivalent of PPNCl into the TPPCoCl and PO system (0.75 mM) did not completely prevent the catalyst from reduction, as a shift of the TPPCo^{III} Q band (542.9 nm) towards lower wavelengths (TPPCo^{II} Q band: 525 nm) was detected.

For a quantitative evaluation, this reduction reaction is further investigated by ^{1}H NMR spectroscopy, taking advantage of the readily identifiable signals of the paramagnetic TPPCo^{II} (see the Supporting Information, Figure S3). The found marginal shift of these proton resonances, compared with the literature,[8] is probably due to the presence of PO.

Time-resolved ^{1}H NMR spectra were subsequently collected for a system containing TPPCo^{III}Cl (5 mg, 10.8 mM) and PO (0.15 mL) in CD_2Cl_2 (0.5 mL). Conversion of TPPCo^{III} to TPPCo^{II} was determined and the initial rate of this reduction was calculated to be 0.97 ± 0.06 mM h^{-1} (Figure 2, triangles). Moreover, the addition of PPNCl was proven to have no noticeable influence [TPPCoCl (5 mg), PPNCl (0.3 equiv), PO (0.3 mL)], as the rate of reduction was nearly identical compared with that acquired in the absence of onium salts (Figure 2).

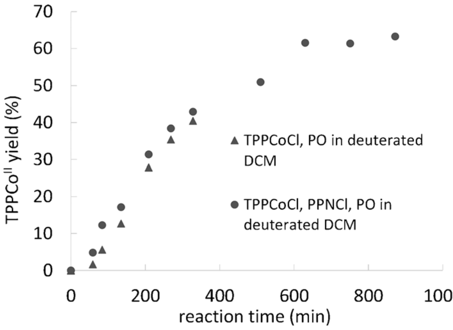


Figure 2. The formation of TPPCo^{II} monitored by ^{1}H NMR spectroscopy.

Taking into consideration the initial ring opening of PO by TPPCoCl as demonstrated in our previous study (Scheme 4, step 1; see below),[6] the reduction of TPPCo^{III} to TPPCo^{II} in PO solution most probably proceeds via a cobalt(III)–porphyrin alkoxide. Therefore, an attempt to further explore the nature of such a reduction was made by investigating the simplest cobalt(III)–porphyrin alkoxide, TPPCo–methoxide.

Time-resolved UV/Vis measurements were then performed on TPPCoCl (1 equivalent, 5×10^{-6} M) and NaOMe (3000 equivalents) in a 9:1 DCM/methanol (10 mL) solution (Figure 3) and, in the absence of PO, the reduction of TPPCo^{III} to TPPCo^{II} still occured (Scheme 3). After the determination of the molar absorptivity of TPPCo^{II} in a DCM solution ($\varepsilon = 2.3 \times 10^5$ M^{-1}cm^{-1}) at 411 nm), the initial reduction rate was calculated to be $(3.11 \pm 0.06) \times 10^{-7}$ M h^{-1}.

Additionally, the formation of paramagnetic TPPCo^{II} was also detected by ^{1}H NMR spectroscopy of a solution of TPPCoCl (5 mg) and NaOMe (23 mg, 60 equivalents) in $CDCl_3$ (0.5 mL) and methanol (0.05 mL; see the Supporting Information, Figure S11). After this NMR sample had been left to stand overnight, quantities of TPPCo^{II} precipitate had formed, further confirming the reduction of TPPCo^{III}Cl in the presence of the methoxide anion.

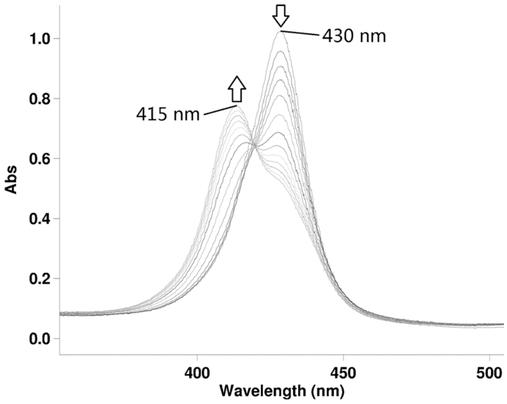
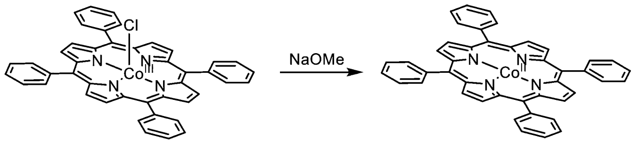


Figure 3. Time-resolved UV/Vis spectra of TPPCoCl (1 equiv), NaOMe (3000 equiv) in DCM/MeOH (9:1 v/v).



Scheme 3. The reduction of $TPPCo^{III}Cl$ to $TPPCo^{II}$ in the presence of sodium methoxide.

For a deeper insight into the mechanism of such a redox reaction between TPPCoCl and sodium methoxide, the reaction order of the cobalt(III)–porphyrin complex, as monitored by UV/Vis spectroscopy, was tentatively explored by varying the initial TPPCoCl concentration (2×10^{-5} м, 1.25×10^{-5} м, 5×10^{-6} м, and 2.5×10^{-6} м in a 9:1 DCM/methanol solution).

An induction period[9] was evident, with a continuous decrease in the intensity of the $TPPCo^{III}$ Soret band prior to the catalyst reduction (Figure 3). This observation is attributed to an axial ligand exchange on the cobalt(III)–porphyrin complex. After the exclusion of this induction period, the double logarithmic plot of the TPPCoCl concentration versus the initial reaction rate shows a linear fit with a slope of 0.95 ± 0.04 (Figure 4), suggesting a reaction that is pseudo-first order in the cobalt(III)–porphyrin species.

This value is supportive of our postulated mechanism of the reduction of TPPCoCl with sodium methoxide, in that an electron transfer from the coordinated methoxide anion to the $TPPCo^{III}$ cation should be involved. To our knowledge, such a reduction of cobalt(III)–porphyrin complexes in the presence of alkoxides has not to date been reported, although similar behavior has been observed for both cobalt(III)[10] and iron(III)[11] porphyrins with certain other axial ligands.

Interestingly, in the reaction system of TPPCoCl and propylene oxide, the formation of acetaldehyde was detected by ^{1}H NMR spectroscopy (see the Supporting Information, Figure S8 and S9), alongside the catalyst reduction. A carbon–carbon bond cleavage in PO or its derivatives must be involved in this additional chemical transformation. If our hypothesis of a homolytic fission of cobalt(III) alkoxides holds true (Scheme 4, step 2), this byproduct (acetaldehyde) may thus come from a β-fragmentation of the alkoxy radicals (a common reaction of alkoxy radicals, which has often been reported[12]; Scheme 4, step 3).

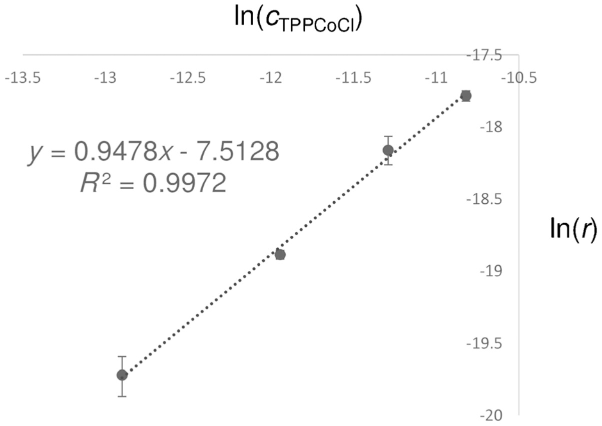
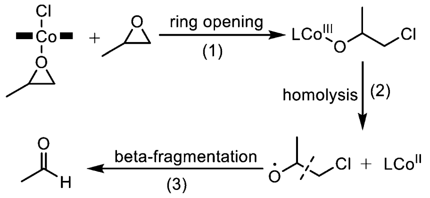


Figure 4. The double logarithmic plot of the TPPCoCl concentration versus the initial rate in the reduction of TPPCoCl with NaOMe.



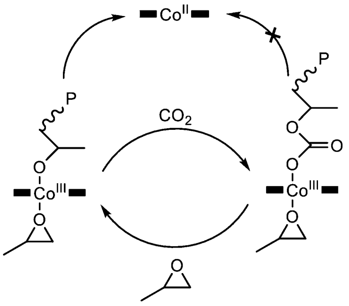
Scheme 4. A postulated mechanism of the formation of acetaldehyde in the cobalt(III)–salen/porphyrin and PO system (L = TPP/salen and axial ligands).

Contrary to the observed reduction of $TPPCo^{III}Cl$ in PO, the in situ IR graphic of PO/CO_2 copolymerization catalyzed by TPPCoCl/PPNCl implied a suppression of the catalyst reduction (see the Supporting Information, Figure S4). This is reflected in nearly no loss of the catalytic activity even after a 16-hour reaction, as the reduction product of the catalyst ($TPPCo^{II}$) is known to produce cyclic carbonate rather than polymer.

This catalyst protection during PO/CO_2 copolymerization is attributed to a consistently formed carbonate chain end, which greatly shortens the lifetime of the autoreducible cobalt(III)–porphyrin alkoxides (Scheme 5). This hypothesis is further supported by the fact that CO_2 insertion is not the rate-determining step (within the CO_2 pressure range of 20–30 bar) in TPPCoCl/PPNCl-catalyzed PO/CO_2 copolymerization (see below).

As suggested in previous publications,[13] the ring opening of the epoxide rather than CO_2 insertion is, in most cases, the rate-determining step (RDS) in the chain propagation, especially under high CO_2 pressure (>25 bar). Only very few examples of a shift of the RDS from the epoxide ring opening to the CO_2 insertion have been hitherto reported.[14]

In this study, an increase of the applied CO_2 pressure from 20 bar to 30 bar, while keeping the rest conditions of polymerization unaltered, did not induce a noticeable change in the reaction rate, as reflected in the same TOF values obtained under these two conditions (Table 1). This result is indicative of a faster CO_2 insertion during polymer formation within the ex-



Scheme 5. CO$_2$ insertion stabilizes cobalt(III) catalysts from deactivation during the chain propagation (P = the growing polymer chain; the coordinating ligands on the cobalt(II) complex are not specified).

Table 1. PO/CO$_2$ copolymerization catalyzed by TPPCoCl/PPNCl.[a]

Entry	Pressure [bar]	PPC [%][b]	CC [%][c]	TON[d]	TOF[e] [h^{-1}]	Carbonate content [%][f]
1	20	21	< 1	420	420	> 99
2	30	21	< 1	420	420	97

[a] Polymerization conditions: PO/TPPCoCl/PPNCl ratio = 2000:1:1, 25 °C, 1 hour; [b] PPC (poly(propylene carbonate)) yield, determined by weighing the isolated copolymer; [c] CC (cyclic carbonate) yield, determined by ^{1}H NMR spectroscopy; [d] TON (turnover number) = PPC % × n(PO)/n(TPPCoCl); [e] TOF (turnover frequency) = TON/t (h); [f] determined by ^{1}H NMR spectroscopy.

amined pressure range, compared with the epoxide ring opening. Therefore, the mechanism of the catalyst protection proposed in Scheme 5 is supported, as the growing polymer chain mostly stays at a carbonate end group and the carbonate-coordinated cobalt(III)–porphyrin complex is not able to undergo an autoreduction to TPPCo^{II}. The stability of TPPCo^{III}-carbonate is demonstrated in the reaction system of TPPCoCl with NaCH$_3$CO$_3$, in that no reduction is observed after a three-day reaction under identical conditions compared with the TPPCoCl/NaOMe system.[5c]

Reduction of a cobalt(III)–salen catalyst in PO/CO$_2$ copolymerization

A similar reduction reaction to that of TPPCoCl in PO was observed for a cobalt(III)–salen complex in PO/CO$_2$ copolymerization in the absence of a co-catalyst (Scheme 6).[5a] A red precipitate was isolated after a polymerization reaction catalyzed by dark-green-colored (R,R)-salenCo^{III}Cl (PO/(R,R)-salenCo^{III}Cl ratio = 1000:1, 50 bar CO$_2$ pressure, 30 °C, 4 h). This precipitate was subsequently crystalized and characterized by X-ray crystallography to be the catalytically inactive (R,R)-salenCo^{II} (see the Supporting Information, Figure S5).[15]

Table 2. PO/CO$_2$ copolymerization catalyzed by (R,R)-salenCo^{III}Cl.[a]

Entry	Reaction Time [h]	PPC [%][b]	CC [%][c]	TON[d]	TOF[e] [h^{-1})]	Carbonate content [%][f]
1	2	25	1	250	125	> 98
2	4	23	1	230	57.5	> 98

[a] polymerization conditions: PO:(R,R)-salenCo^{III}Cl ratio = 1000:1, 30 °C, 50 bar CO$_2$ pressure. [b] PPC yield, determined by ^{1}H NMR spectroscopy; [c] CC yield, determined by ^{1}H NMR spectroscopy; [d] TON (turnover number) = PPC % × n(PO)/n((R,R)-salenCo^{III}Cl); [e] TOF (turnover frequency) = TON/t (h); [f] determined by ^{1}H NMR spectroscopy.

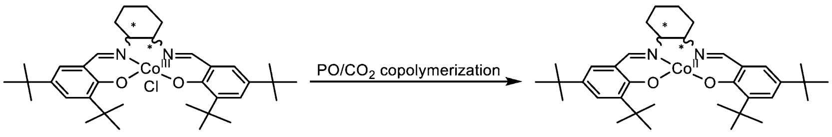
This catalyst reduction was further reflected in the unchanged PPC yield when the polymerization was carried out with a longer reaction time (Table 2). This phenomenon is indicative of nearly complete deactivation of the catalyst after a 2-hour polymerization.

However, when 0.5 equivalents of PPNCl were introduced into the polymerization system, the yield of the copolymer showed a correlation with the polymerization time (Figure 5). This result implies a suppressed catalyst reduction when the polymerization is performed in the presence of a co-catalyst.

To test whether PPNCl itself has a direct stabilizing effect on the cobalt(III)–salen or the above-discussed phenomenon[16] results from a change in the polymerization mechanism due to the presence of a co-catalyst (PPNCl), as has often been reported in previous publications,[17] we subsequently investigated the redox reaction of (R,R)-salenCo^{III}Cl (4 mg, 7.8 mM) in PO (0.3 mL), both in the absence and presence of PPNCl (0.5 and 1 equivalent), by using ^{1}H NMR spectroscopy.

For all three reactions examined (without PPNCl and with 0.5 or 1 equivalent of PPNCl), a gradual increase of a series of broad proton resonances, caused by the formation of a paramagnetic (R,R)-salenCo^{II}, with time is detected (see the Supporting Information, Figure S6). The assignment of these proton signals to salenCo^{II} is also supported by previous reports.[18] This observation confirms the reduction of cobalt(III)–salen in the presence of PO, which is consistent with the reduction of TPPCoCl in PO (see above).

To establish whether PPNCl has a direct stabilizing effect on the cobalt(III)–salen complex, the reduction rates of (R,R)-salenCo^{III}Cl in PO for the reactions performed with and without PPNCl were calculated and were compared with each other. Under exactly the same reaction conditions, the initial reduction rates for the experiments with 0.5 and 1 equivalent of PPNCl, as well as that without PPNCl, were 0.62 ± 0.07 mM h^{-1}, 0.82 ± 0.11 mM h^{-1} and 0.71 ± 0.05 mM h^{-1}, respectively (Figure 6). These values imply that PPNCl does not directly prevent the catalyst from reduction.



Scheme 6. The observed reduction of (R,R)-salenCo^{III}Cl to (R,R)salenCo^{II} in PO/CO$_2$ copolymerization in the absence of a co-catalyst.

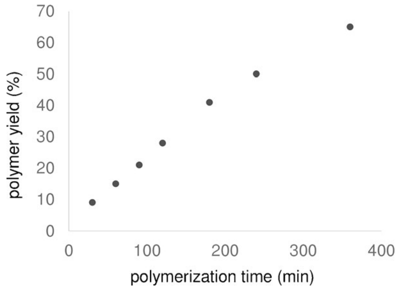


Figure 5. The plot of polymer yield (%) versus reaction time (min) in the copolymerization of PO and CO_2 in the presence of PPNCl (polymerization conditions: PO/(*R*,*R*)-salenCo^{III}Cl/PPNCl ratio = 1000:1:0.5, 30 °C, 30 bar CO_2 pressure).

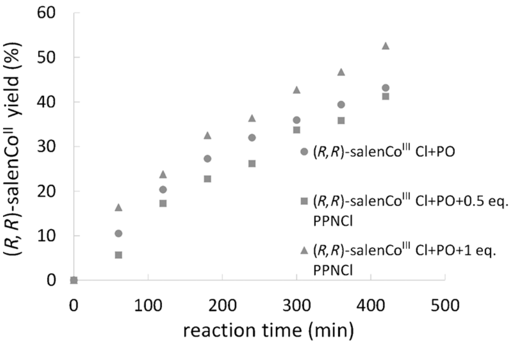
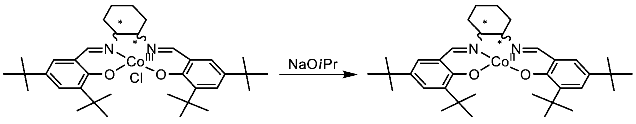


Figure 6. The formation of (*R*,*R*)-salenCo^{II} in PO, monitored by ^{1}H NMR spectroscopy, both in the absence and presence of PPNCl.

As cobalt(III)–salen is also able to catalyze the ring opening of PO,[19] the reduction of cobalt(III)–salen in PO is considered most likely to proceed via a salenCo^{III}–alkoxide intermediate. Indeed, resembling the reduction of the cobalt(III)–porphyrin with sodium methoxide, a transformation from the cobalt(III)–salen into the cobalt(II) species with sodium isopropoxide was also demonstrated by ^{1}H NMR spectroscopy (Scheme 7 and Figure S7 in the Supporting Information). This result is evidential for our hypothesis that the reduction of salenCo^{III}Cl during the copolymerization very likely results from the homolytic bond cleavage of the ring-opening intermediates, cobalt(III)–salen alkoxides (Scheme 4, step 2).

Interestingly, a substitution of NaO*i*Pr with NaOMe led to nearly no reduction of the salenCo^{III}Cl, even after a three-day reaction. This observation is explained by distinct reduction potentials between cobalt(III)–porpyrin and salen complexes.[15,20] Moreover, the formation of acetaldehyde was also detected by ^{1}H NMR spectroscopy in the reaction system of cobalt(III)–salen and PO (see the Supporting Information, Figure S10). Since this byproduct was also found in the reaction system of TPPCoCl and PO, the same reaction pathway is thus proposed, whereby a β-fragmentation of alkoxy radicals (produced from the homolysis of cobalt(III) alkoxides) takes place (Scheme 4, step 3).



Scheme 7. The reduction of (*R*,*R*)-salenCo^{III}Cl to (*R*,*R*)salenCo^{II} with sodium isopropoxide.

A brief summary of the above-discussed phenomena for the reduction of salenCo^{III}Cl is listed below:

1) The catalyst is reduced nearly completely after a 2-hour polymerization if no co-catalyst (PPNCl) is utilized.
2) If 0.5 equivalents of PPNCl is introduced into the polymerization system, the catalyst reduction is significantly suppressed.
3) There exists no direct stabilizing effect of PPNCl on the catalyst in a PO solution.
4) The autoreduction of salenCo^{III}–isopropoxide was demonstrated.

Therefore, after a careful consideration of these facts, the catalyst protection in the course of polymerization is most probably due to a constantly formed carbonate chain end, which shortens the lifetime of the autoreducible salenCo^{III}–alkoxides, as shown in Scheme 5. However, the mechanism behind the enhancement of CO_2 insertion during the copolymerization via a co-catalyst addition has not to date been fully confirmed, although such a behavior was also observed by Chisholm and co-workers when using an aluminum(III)–porphyrin alkoxide/DMAP system.[21]

Conclusions

In summary, we reported herein a systematic investigation on the deactivation of cobalt(III)-based porphyrin and salen catalysts via reduction to cobalt(II) species in the copolymerization of PO and CO_2. We found that both catalysts underwent reduction in PO solution. Taking into consideration their capabilities towards PO ring opening, the initially formed cobalt(III) alkoxides were shown to account for this catalyst deactivation, as evidenced by UV/Vis and ^{1}H NMR spectroscopies. The addition of a co-catalyst, namely PPNCl, into the PO solution of cobalt(III)–salen/porphyrin displayed no direct stabilizing effect. Thereby, a faster CO_2 insertion, compared with the epoxide ring opening, during the chain propagation keeps the polymer chain end mostly at a carbonate group and consequently protects the catalysts (Scheme 5).

Experimental Section

Methods and materials

NMR spectra were collected on Bruker AVIII-300 and AVIII-500 spectrometers. Mass spectra were collected on a Varian LC-MS 500 (50–2000 Da) spectrometer. UV/Vis spectra were collected with a Varian Cary 50-Scan UV/Vis spectrophotometer. Elemental analysis was performed at the microanalytic laboratory of the Department of Inorganic Chemistry at the Technical University of Munich. GPC (gel-permeation chromatography) measurements were performed using a PolymerLaboratoriesGPC50 Plus chromatograph (calibrated with polystyrene standards) at 35 °C with THF as the eluent. DSC (differential scanning calorimetry) measurements were performed on a TA DSC Q2000 calorimeter. Single crystal X-ray crystallography was carried out at the Department of Inorganic Chemistry at the Technical University of Munich. Most of the chemicals and solvents were utilized as received from commercial suppliers unless otherwise stated. Propylene oxide applied in copolymerization reactions was distilled with CaH_2 and stored under argon atmosphere prior to use.

Synthetic procedures

[5,10,15,20-Tetraphenylporphyrin]cobalt(III) chloride: Tetraphenylporphyrin ligand (100 mg, 0.14 mmol) was dissolved in DMF (30 mL) in a 500 mL flask, and the solution was heated up to 110 °C. Cobalt(II) acetate tetrahydrate (61 mg, 0.25 mmol) was then added as a solid, and the reaction system was stirred at 110 °C for one hour. After removal of the solvent under reduced pressure, the remaining solid ($TPPCo^{II}$) was utilized directly for the oxidation of the metal center. Methanol (250 mL) was poured into the flask containing $TPPCo^{II}$, and concentrated aqueous HCl (ca. 7 mL) was added. Afterwards, the reaction mixture became a dark red solution and was allowed to stir under air atmosphere overnight. After removal of methanol under reduced pressure, the remaining suspension in water was filtered, and the filtration cake was washed with water (3×20 mL) and saturated aqueous $NaHCO_3$ (3×20 mL), followed again by water (5×20 mL). The purple porphyrin complex product was air dried in the fume hood overnight and then redissolved in acetone (30 mL) and filtered. After removing the volatiles under reduced pressure, the final product was obtained as a purple solid. ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C): $\delta = 8.79$ (br), 8.26 (br), 7.81 ppm (br); $^{13}C\{^1H\}$ NMR ([D_8]THF, 75.5 MHz, 25 °C): $\delta =$ 135.1, 126.6, 125.4, 118.4, 115.6, 114.1, 113.8 ppm; MS (ESI) *m/z*: 671.5 ($TPPCo^+$); UV/Vis (DCM): $\lambda_{max} = 406.0$, 542.9 nm (br); elemental analysis calcd (%) for $C_{44}H_{28}N_4CoCl$: C 74.74, H 3.99, N 7.92; found: C 74.21, H 4.04, N 7.93.

(*R*,*R*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine [(*R*,*R*)-salenH$_2$]: A three-necked flask fitted with a reflux condenser and a dropping funnel was loaded with (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (5 g, 18.9 mmol), K_2CO_3 (5.2 g, 37.6 mmol), and distilled water (10 mL) and the reaction mixture was stirred at room temperature until full dissolution had occurred, followed by addition of ethanol (100 mL). The reaction system was heated to 80 °C, and a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (8.9 g, 37.6 mmol) in ethanol (50 mL) was added dropwise. The dropping funnel was then rinsed with small amounts of ethanol (20 mL in total), and the yellow slurry was stirred at 80 °C for an additional 2 h. Afterwards, the reaction mixture was allowed to cool to ambient temperature followed by further cooling in an ice water bath with vigorous stirring for 2 h. The product was collected by vacuum filtration and the filtration cake was washed with ethanol (100 mL). The crude solid was again dissolved in CH_2Cl_2 (100 mL) and washed with water (2×100 mL) and brine solution (100 mL). After drying over anhydrous Na_2SO_4, the solution was filtered and all volatiles were removed from the filtrate under reduced pressure to afford the product as a yellow powder (10.9 g, 98% yield). M.p. 207–208 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 13.74$ (s, 2H), 8.33 (s, 2H), 7.33 (d, $J = 2.5$ Hz, 2H), 7.01 (d, $J = 2.5$ Hz, 2H), 3.36–3.33 (m, 2H), 1.98–1.48 (m, 8H), 1.44 (s, 18H), 1.26 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta =$ 165.94, 158.13, 139.99, 136.45, 126.86, 126.17, 117.97, 72.56, 35.09, 34.17, 33.42, 31.57, 29.58, 24.5 ppm; elemental analysis calcd (%) for $C_{36}H_{54}N_2O_2$: C 79.07, H 9.95, N 5.12; found: C 79.32, H 9.43, N 5.10.

(*R*,*R*)-SalenCo^{II}: A two-necked Schlenk flask fitted with a reflux condenser was loaded with (*R*,*R*)-salenH$_2$ (1.29 g, 2.4 mmol) in dry toluene (10 mL). A solution of $Co(OAc)_2$ (0.41 g, 2.4 mmol) in dry methanol (20 mL) was then transferred via a cannula under argon atmosphere to the Schlenk flask to afford a red precipitate. The mixture was heated at reflux with stirring at 90 °C for 1 h. After the reaction mixture was allowed to cool to 40 °C, the red precipitate was filtered and washed with MeOH until the filtrate turned colorless. The final product was dried at 40 °C under vacuum to a constant weight, yielding the product as a red powder (1.2 g, 83% yield). Elemental analysis calcd (%) for $C_{36}H_{52}CoN_2O_2$: C 71.62, H 8.68, N 4.64; found: C 71.68, H 8.42, N 4.53.

(*R*,*R*)-SalenCo^{III}OTs: The synthetic procedure was adopted from previous publications with a slight modification.[18b,22] A round-bottom flask was loaded with a mixture of (*R*,*R*)-salenCo^{II} complex (6.0 g, 9.9 mmol) and *p*-toluenesulfonic acid monohydrate (1.89 g, 9.9 mmol) in CH_2Cl_2 (200 mL) and the solution was stirred under dry oxygen atmosphere at room temperature for 3 h. Afterwards, all volatiles were removed using rotary evaporation and the remaining solid was further dried under vacuum. The resulting solid was suspended in hexane, re-collected by filtration, and washed with a CH_2Cl_2/hexane (25:75) mixture. After drying at 40 °C under vacuum to a constant weight, the product was obtained as a dark green solid (6.6 g, 86% yield). ^1H NMR ([D_6]DMSO, 500 MHz, 25 °C): $\delta = 7.82$ (s, 2H), 7.46–7.41 (m, 6H), 7.07 (d, $J = 7.5$ Hz, 2H), 3.57–3.56 (m, 2H), 3.05–3.03 (m, 2H), 2.24 (s, 3H), 1.97–1.96 (m, 2H), 1.88–1.84 (m, 2H), 1.71 (s, 18H), 1.57–1.53 (m, 2H), 1.27 ppm (s, 18H); $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 125 MHz, 25 °C): $\delta = 163.79$, 161.21, 140.87, 136.63, 134.93, 128.43, 127.90, 127.18, 124.67, 117.64, 68.38, 34.93, 32.69, 30.64, 29.54, 28.65, 23.41, 19.95 ppm; elemental analysis calcd (%) for $C_{43}H_{59}CoN_2O_5S$: C 66.65, H 7.67, N 3.61, S 4.14; found: C 64.45; H,7.57, N 3.39, S 4.81.

(*R*,*R*)-SalenCo^{III}Cl: The synthetic procedure was adopted from previous publications with a slight modification.[18b,22] (*R*,*R*)-SalenCo^{III}OTs (5.68 g, 7.33 mmol) was dissolved in CH_2Cl_2 (200 mL) and transferred into a 500 mL separating funnel. The solution was washed with saturated brine solution (3×400 mL) and the organic layer was collected and dried over anhydrous Na_2SO_4 powder followed by removal of the volatiles under reduced pressure. The remaining solid was suspended in hexane under vigorous stirring and a precipitate was formed and isolated. After repeating the above hexane wash, the collected solid was dried at 40 °C under vacuum to a constant weight, affording the product as a dark green solid (3.98 g, 85%). ^1H NMR ([D_6]DMSO, 300 MHz, 25 °C): $\delta =$ 7.83 (s, 2H), 7.44 (s, 2H), 7.32 (s, 2H), 3.84–3.63 (m, 2H), 3.09–3.06 (m, 2H), 2.02–1.97 (m, 2H), 1.97–1.83 (m, 2H), 1.72 (s, 18H), 1.63–1.52 (m, 2H), 1.31 ppm (s, 18H); elemental analysis calcd (%) for $C_{36}H_{52}ClCoN_2O_2$: C 67.65, H 8.20, N 4.38; found: C 67.25, H 8.26, N 4.28.

Sodium methyl carbonate: In an autoclave, a solution of sodium methoxide (5 g) in methanol (30 mL) was pressurized with CO_2 gas (20 bar). After stirring the reaction mixture overnight at room temperature, the CO_2 pressure was released and all volatiles were removed via rotary evaporation under reduced pressure, affording the product as a white solid (quantitative yield).

General procedure for PO/CO$_2$ copolymerization

A 100 mL or 200 mL autoclave was dried in the oven at 102 °C overnight prior to use. The autoclave was allowed to cool to room temperature under vacuum and filled with argon gas, then the catalyst, co-catalyst, and propylene oxide were added in the required amounts and the stirring rate was set to 500 rpm. The autoclave was moved into an oil bath and heated to the appointed temperature (if required) and CO_2 gas was incorporated to the appointed pressure level. After the required reaction time, the CO_2 pressure was carefully released and dichloromethane (ca. 10 mL) was poured into the autoclave to dissolve the reaction mixture. A small amount of solution was taken out for NMR spectroscopic analyses and the remainder was added dropwise into methanol (200 mL) to precipitate out the polymer product. After removing the supernatant, the remaining red polymer (due to residual catalyst) was redissolved in chloroform (50 mL) and activated charcoal (ca. 7 g) was added, yielding a suspension that was heated at reflux for 1 hour. After filtration, chloroform was removed using a rotary evaporator and the purified polymer product was obtained as a slightly yellow solid.

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Keywords: carbon dioxide · catalyst deactivation · cobalt · epoxides · ring-opening polymerization

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FULL PAPER

Polymerization Catalysis

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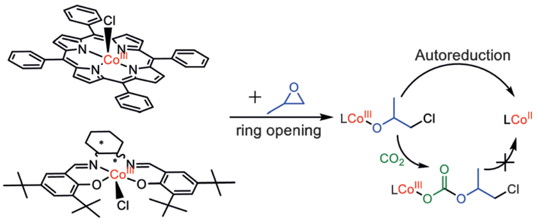
Concerning the Deactivation of Cobalt(III)-Based Porphyrin and Salen Catalysts in Epoxide/CO_2 Copolymerization



CO_2 saves: The deactivation of cobalt(III)–porphyrin and salen catalysts in propylene oxide/carbon dioxide copolymerization is systematically investigated, revealing a proposed mechanism for the catalyst reduction (see scheme).