Catalysis Science & Technology

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Coupling Reaction between CO_2 and Cyclohexene Oxide: Selective Control from Cyclic Carbonate to Polycarbonate by Ligand Design of Salen/Salalen Titanium Complexes

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Based on the mechanistic feature of metal salen catalysis system, titanium(IV) complexes from salen (salen-H_2= N, N-bis(3, 5-di-tert-butylsalicylidene)-1,2-benzenediamine) and its half saturated form salalen have been prepared, which were used as catalysts in conjugation with bis(triphenylphosphino)iminium chloride ([PPN]Cl) for coupling reaction of CO_2 and cyclohexene oxide (CHO). Salen titanium complex (Salen)Ti(IV)Cl_2 showed moderate activity producing unique *cis*-isomer of cyclic carbonate with high conversion up to 100% in 8h, however, it could not catalyze the copolymerization reaction. While salalen titanium complex (Salalen)Ti(IV)Cl was effective for the copolymerization of CO_2 and CHO, where only one chain grew on Ti during chain propagation reaction, yielding completely alternating copolymer with -OH and -Cl as terminal groups. Moreover, the nearly complete conversion of CHO indicated that (Salalen)Ti(IV)Cl might be used to synthesize multiblock poly(cyclohexene carbonate)s with controllable sequence.

Introduction

Since the pioneering work of Inoue,[1] CO_2 has been an attractive C1 resource for polymer chemistry, mainly due to its cheap and abundant feature in addition to the impending requirement on chemical utilization of CO_2. Such a reaction not only makes a net CO_2 consuming process benefitting the environment, but also provides biodegradable polymers as possible solution to the white pollution problem due to the overuse of non-biodegradable polyolefin based plastics. During the past decades, researchers have made great effort to develop various catalyst systems,[2] among which heterogeneous catalysts such as zinc dicarboxylates[3] and rare earth ternary catalysts[4] have been successfully put into use in industry due to their ease of handling and economic viability, however, the active sites of these compounds were often poorly defined. It's for this reason that homogeneous coordination complexes with well-defined active sites and controllable catalytic activity and selectivity have gained more and more attention in academic field. And up to now, (Salen)M(III)X (M=Co,[5] Cr,[6] Al,[7] Mn[8]) have stood for the most investigated catalysts due to their facile synthesis and ease of ligand modification. Especially, (Salen)Co(III)X first designed by Coates[2a] and late developed by Nozaki,[9] Lu[10] and Lee's group[11], displayed most ideal features like high catalytic activity and polymer selectivity, and producing polymer with strict alternating feature and high molecular weight. The initiation mechanisms of (Salen)M(III)X systems have been well documented, including bimetallic, monometallic, or binary initiation pathway, as summarized by Rieger and coworkers. [2a]

According to the mechanistic aspect, the axial group X acts as initiator for the copolymerization by (Salen)M(III)X systems, whether cocatalysts are brought in or not,[5, 10a] while divalent metal salen complexes like (Salen)Zn(II)[12] or (Salen)Co(II)[10b] in conjugation with cocatalysts only produce cyclic carbonates for CO_2/epoxides coupling reaction. A flexible coordination site of the metal center is also important, which may form complex with epoxides and activate epoxides during polymerization process. Therefore, an efficient metal salen catalyst for the copolymerization of CO_2 and epoxides should include a trivalent metal ion (M), a dianionic $[ONNO]^-$ tetradentate salen ligand, a monoanionic ancillary ligand (X), and a flexible coordination site. Most active metal salen catalysts have been limited to trivalent metal center up to now, however, combination of a tertravalent metal and a trianionic $[ONNO]^-$ tetradentate ligand can also form a complex following the structure of (Salen)M(III)X, such a complex might be effective for CO_2/epoxides copolymerization in case that a suitable tertravalent metal center was brought in. Nozaki and coworkers contributed the first example using tetravalent metal complex as a main component of catalyst, in particular, the copolymerization of propylene oxide with CO_2 gave the almost-completely alternating copolymers by using titanium(IV) or germanium(IV) complexes.[13] More recently, Coralie and coworkers reported that the tridentate N-heterocyclic carbene titanium(IV) complexes could effectively and selectively catalyze the copolymerization of CO_2 and CHO.[14] Actually, titanium complexes of salen analogues have shown remarkable catalytic activity for olefin polymerization,[15] ring opening polymerization of LA,[16] and enantioselective ring opening of meso-epoxides.[17] However, all these Ti complexes have a dianionic $[ONNO]^-$ tetradentate ligand and two axial groups such as -Cl or -O^{i}Pr without a flexible coordination site.

Considering the good alternating copolymerization character and good soil compostability of titanium which may fulfill the harsh requirements of biodegradable polymer, titanium complexes of salen analogues may provide promising alternatives as green catalysts for CO_2/epoxides copolymerization. This may be achieved by reasonable design of salen ligand based on mechanistic understanding. We introduced a salen ligand (salen-H_2=*N*,*N*-bis(3,5-di-tert-butylsalicylidene)-1,2-benzenediamine) and its half saturated form salalen ligand with three active hydrogen to form titanium complexes as shown in Scheme 1, where salen ligand H_2L_1 served as a dianionic $[ONNO]^-$ tetradentate ligand, and salalen ligand H_3L_2 acted as a trianionic $[ONNO]^-$ tetradentate ligand after treated with TMSLi ((trimethylsilyl)methyllithium). It was found that (Salen)Ti(IV)Cl_2 could not catalyze the copolymerization reaction of CO_2 and CHO, but it showed good activity toward cyclization reaction, while a suitable design in ligand gave (Salalen)Ti(IV)Cl mimicking the structure of (Salen)M(III)X, it was effective for the copolymerization of CO_2 and CHO in conjugation with [PPN]Cl.

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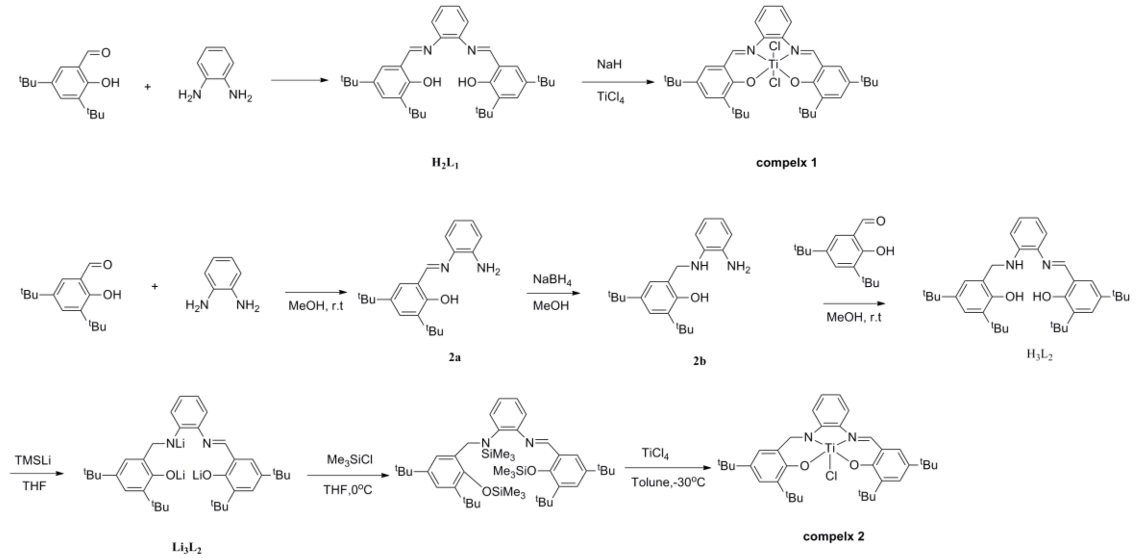
Reagents and Methods

All manipulations involving air or water sensitive compounds were carried out using standard Schlenk techniques under a dry argon atmosphere. Cyclohexene oxide (CHO) and methylene chloride (CH_2Cl_2) was distilled from calcium hydride under argon atmosphere prior to use. Tetrahydrofuran, toluene and diethyl ether were distilled under argon atmosphere from sodium/benzophenone. Carbon dioxide (99.995%) was purchased from Sipin Jianxin gas Ltd. and used as received, while 3,5-di-tert-butylsalicyaldehyde was purchased from Wuhan Yinhe Chemical plant, and purified by recrystallization in ethanol. Other reagents and chemicals were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian INOVA-400 MHz type (^{1}H, 400MHz and ^{13}C, 75MHz) spectrometer. Chemical shifts were reported in ppm from an internal standard: tetramethylsilane (0 ppm) for ^{1}H and $CDCl_3$ (77.16 ppm) for ^{13}C in $CDCl_3$, while C_6D_6 (7.16 ppm) for ^{1}H and C_6D_6 (128.06 ppm) for ^{13}C in C_6D_6. Data were presented as follows: chemical shift, multiplicity (s=singlet, d=doublet, m=multiplet and/or multiplet resonances, br=broad), coupling constant in hertz (Hz), and signal area integration in natural numbers. Mass spectra were taken with LDI-1700 mass spectrometer by matrix-assisted laser desorption/ionization-time-of-flight method. The Infrared spectra of the cyclic carbonates were obtained by directly casting the reaction mixture onto a KBr disk with a Bruker TENSOR-27 spectrophotometer, while the PCHC solution in CH_2Cl_2 was cast onto a KBr disk before testing for PCHC samples. The molecular weight and molecular weight distribution of the PCHCs were determined by gel permeation chromatography (GPC) at 35 ^oC in polystyrene standard on Waters 410 GPC instrument with CH_2Cl_2 as the eluent, where the flow rate was set at 1.0 mL/min.



Scheme 1 Detailed synthesis procedure for (Salen)Ti(IV)Cl_2 and (Salalen)Ti(IV)Cl.

Synthesis of salen ligand H_2L_1 (*N,N*-bis(3,5-di-tert-butylsalicylidene)-1,2-benzenediamine)

A 100 mL flask was charged with 20 mL of methanol, 1.08 g of 1,2-diaminobenzene (10 mmol) and 4.68 g of 3,5-di-tert-butylsalicylaldehyde (20 mmol) subsequently, the solution was stirred at room temperature for 24 h, bright yellow precipitate was generated, and then it was filtrated and dried in vacuum. Yield: 76%. ^{1}H NMR ($CDCl_3$): δ 13.55 (s, 2H), 8.66 (s, 2H), 7.44 (d, *J*=2.4 Hz, 2H), 7.29-7.35(m, 2H), 7.18-67.24(m, 4H), 6.75-6.80(m, 1H), 1.44(s, 18H), 1.32(s, 18H).^{13}C NMR ($CDCl_3$): δ 166.7, 158.6, 142.8, 140.3, 137.2, 128.2, 127.3, 126.8, 122.2, 119.8, 118.5, 118.4, 35.2, 34.2, 31.5, 29.5. Anal.Calcd for $C_{36}H_{48}N_2O_2$ (%):C, 79.96; H, 8.95; N, 5.18; Found: C, 80.00; H, 8.86; N,5.16.

Synthesis of (Salen)Ti(IV)Cl_2 (complex 1)

In a glove box, 0.54 g of H_2L_1 (1 mmol) was dissolved with 20 mL of THF in a 50 mL flame dried round bottom flask, then 0.07 g of NaH (3 eq, 60% dispersed in oil, washed with n-pentane before use) was added slowly under stirring, the mixture was filtered after 4 h at room temperature. Late 0.19 g of $TiCl_4$ (1 mmol in 3 mL toluene) was dropped into the filtrate at -30 ^oC, the mixture was then stirred for 12 h at room temperature and brown powder was obtained following the removal of volatiles under vacuum. Yield: 97%. ^{1}H NMR ($CDCl_3$): δ 8.82 (s, 2H), 7.66-7.70 (m, 2H), 7.64 (d, *J* =2.4 Hz, 2H), 7.44 (d, *J* =2.4 Hz, 2H), 7.39-7.43 (m, 2H), 1.55(s, 18H), 1.35(s, 18H). ^{13}C NMR ($CDCl_3$): δ 160.5, 158.3, 145.3, 141.2, 137.2, 132.9, 131.1, 130.0, 126.4, 116.6, 35.6, 34.6, 31.3, 29.9, Anal.Calcd for $C_{36}H_{48}N_2O_2$ (%): C, 79.96; H, 8.95; N, 5.18. Found: C, 80.00; H, 8.86; N, 5.16.

Synthesis of N-(3,5-tert-Butyl-2-hydroxybenzyl)-1,2-diaminobenzene (2b)

A 100 mL flask was charged with 20 mL of methanol and 2.70 g of 1,2-diaminobenzene (25 mmol), then 4.68 g of 3,5-di-tert-butylsalicylaldehyde (20 mmol resolved in 40 mL methanol) was slowly added. After stirring at room temperature for 24 h, the system was cooled to 0 ^{o}C before adding 2.27 g of $NaBH_4$ (60 mmol) in small portions and then it was stirred at room temperature for 4 h. 20 mL of deionized water was added to quench the reaction, grey precipitate was obtained by filtration through a G4 sand core funnel. After washed with 30 mL cold MeOH for three times, the grey precipitate turned out to be white target product with good purity. The overall yield of the two reactions was 82%. ^{1}H NMR ($CDCl_3$): δ 8.67 (s, 1H), 7.33 (d, *J* =2.4 Hz, 1H), 7.07 (d, *J* =2.4 Hz, 1H), 6.92-6.98(m, 1H), 6.85-6.90(m, 2H), 6.75-6.80(m, 1H), 4.38(s,1H), 3.71(s,1H), 3.43(s,1H), 1.45(s,1H), 1.34(s,1H).^{13}C NMR ($CDCl_3$): δ 153.3, 141.5, 136.2, 136.0, 135.4, 123.8, 123.6, 122.2, 121.6, 120.4, 116.5, 114.8, 49.0, 34.9, 34.1, 31.6, 29.6. Anal.Calcd for $C_{21}H_{30}N_2O$ (%): C, 77.26; H, 9.26; N, 8.58; Found: C, 77.76; H, 9.78; N, 8.40.

Synthesis of salalen Ligand H_3L_2

A 100 mL flask was charged with 50 mL of methanol, 3.26 g of **2b** (10 mmol) and 2.34 g of 3,5-di-tert-butylsalicylaldehyde (10 mmol), the mixture was stirred at room temperature for 24 h before it was filtrated through a G4 sand core funnel. Without painstaking chromatograph, we got 3.63 g pure product by washing the yellow solid with 20 mL petroleum ether and dichloromethane (v:v=20:1), the yield was 67.0%. ^{1}H NMR ($CDCl_3$): δ 12.93 (s, 1H), 8.60 (s, 1H), 8.44 (br, 1H), 7.46 (d, *J* =2.4 Hz, 1H),7.28 (d, *J* =2.4 Hz, 1H), 7.25-7.21 (m, 2H), 7.08-6.94 (m, 4H), 4.46 (s, 2H), 1.43 (s, 9H), 1.42 (s, 9H), 1.32 (s, 9H), 1.30 (s, 9H).^{13}C NMR ($CDCl_3$): δ 165.3, 158.0, 153.5, 141.7, 141.0, 138.7,137.2, 136.7, 128.6, 127.9, 127.1, 123.8, 123.7, 122.2, 121.0,118.8, 118.6, 114.7, 49.7, 35.3, 35.1, 34.40, 34.36, 31.8, 31.6, 29.9, 29.6. Anal. Calcd for $C_{36}H_{50}N_2O_2$ (%): C, 79.66; H, 9.28; N, 5.16. Found: C, 79.82; H, 9.27; N, 5.41.

Synthesis of (Salalen)Ti(IV)Cl (complex 2)

A 50 mL flame dried round bottom flask was charged with 0.54 g of H_3L_2 (1 mmol) and 20 mL of THF in a glove box, the flask was stored in a -30 ^{o}C fridge for 1h before 0.28 g of TMSLi (3 mmol in 3 mL THF) was slowly added. The resulting mixture was slowly warmed up to room temperature and stirred for 2h, 1 mL of the mixture was dried in vacuum for NMR characterization. $Li_3(THF)_6L_2$, ^{1}H NMR (C_6D_6): δ 8.61 (s, 1H), 7.58 (d, *J* =2.4 Hz, 1H), 7.47-7.42 (m, 2H), 7.38 (d, *J* =2.4 Hz, 1H), 7.33(m, 1H), 7.22 (d, *J* =2.4 Hz, 1H), 7.09 (d, *J* =2.4 Hz, 1H), 6.99 (m, 1H), 4.95 (d, *J* =13.8 Hz，1H), 4.43 (d, *J* =13.8 Hz，1H), 3.32(m, 24H), 1.52-1.40(m, 24H), 1.37 (s, 9H), 1.33 (s, 9H), 1.27 (s, 9H), 1.18 (s, 9H).^{13}C NMR (C_6D_6): δ 167.2, 166.3, 159.1, 156.9, 141.3, 139.7,138.4, 138.3, 136.4, 124.6, 123.3, 117.3, 111.5, 110.7, 67.9, 34.0, 34.1, 33.8, 33.4, 31.8, 31.6, 30.7, 30.1, 25.3, 22.9, 14.2.

Then 0.54 g of Me_3SiCl (5 mmol in 5 mL THF) was added to the rest mixture at 0 ^{o}C. After 12 h of reaction at room temperature, the solvent was removed and the residue was redissolved in toluene, the precipitate LiCl was removed by filtration, and the filtrate was stored in a -30 ^{o}C fridge for 1 h before 0.19 g of $TiCl_4$ (1 mmol in 3 mL toluene) was added. The reaction mixture was warmed up to room temperature gradually over 12 h. Brown product was obtained after the reaction mixture was evaporated in vacuum. For the ^{1}H NMR characterization of the complex **2** at room temperature, we got two series of peaks which stood for two isomers. However, elemental analysis and mass spectrometry were in agreement with the calculated values. Anal. Calcd for $C_{36}H_{47}ClN_2O_2Ti$ (%): C, 69.39; H, 7.60; N, 4.50. Found: C, 69.11; H, 7.87; N, 4.33. m/z for $[M\text{-}Cl^{-}\text{+}THF\text{+}H_2O]^{+}$, calcd: 677.37. Found: 677.3.

General Coupling reaction between CO_2 and CHO to generate cyclic carbonate

Typically, 0.03 mmol of complex **1** or **2** and 17.3 mg of [PPN]Cl (0.03 mmol, 1 equiv) were dissolved in CHO (30 mmol, 1000 equiv) to form red-brown solution in an argon filled glove box. The mixture solution was charged into a pre-dried 10ml autoclave equipped with a magnetic stirrer. Then the autoclave was taken out of the glove box, put into an oil bath of 120 ^{o}C and pressurized to appropriate pressure with CO_2. At the end of the reaction, the autoclave was cooled to room temperature. The crude mixture was used for ^{1}H NMR spectroscopy analysis. The total yield was calculated from the normalized integrals of the methylene resonances in the ^{1}H NMR spectra, where TON was mol CHO/mol **1** or **2**, and TOF was TON/ h.

General copolymerization reaction between CO_2 and CHO

Typically, 41.7 mg of complex **2** (0.06 mmol, 1 equiv) and 34.5 mg of [PPN]Cl (0.06 mmol, 1 equiv) were dissolved in 2.94 g of CHO (30 mmol, 500 equiv) to form red-brown solution in an argon filled glove box. The mixture solution was charged into a pre-dried 10 mL autoclave equipped with a magnetic stirrer. Then the autoclave was taken out of the glove box, put into a bath of 70 ^{o}C and pressurized to appropriate pressure with CO_2. At the end of the reaction, the autoclave was cooled to room temperature and the crude mixture was dissolved in CH_2Cl_2 (5 mL), then dried in vacuum for 20 h. No further purification of the copolymer was undertaken as the vacuum was sufficient to remove unreacted cyclohexene oxide. The copolymer was analyzed by NMR spectroscopy and GPC analysis. The reaction selectivity was determined by normalization of the integrals of the methylene protons resonances in the ^{1}H NMR spectra.

Results and discussion

Synthesis of Complexes

The salen ligand H_2L_1 with 1,2-benzenediimine as N-backbone was synthesized with high yield and purity by traditional method, while Salalen ligand H_3L_2 was prepared according to the literature in minor modification without the painstaking gel column chromatography.[18] The general synthesis procedure of the two titanium complexes involved two steps: 1) deprotonation by a strong base, followed by 2) coordination with Titanium (IV) ion. For Salen ligand, the hydrogen in phenolic hydroxyl group was relatively active, it could be deprotonated by sodium hydride (NaH). However, the acidity of hydrogen in the secondary amine of Salalen ligand was much weaker, the pKa of which was close to phenylamine, therefore, super base TMSLi was used to deprotonate instead of *n*-butyllithium, considering that the latter might react with the imine structure of Salalen ligand. Moreover, Me_3SiCl was introduced to make the reaction condition milder, thus all the manipulations could be carried out in the glove box.

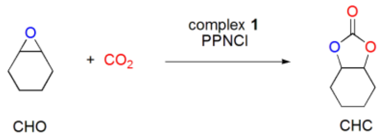
The structures of the target complexes were characterized by NMR, Element Analysis, and MALDI-TOF-MS, where (Salalen)Ti(IV)Cl showed two series of peaks in its ^{1}H NMR spectrum implying that it had two configuration at room temperature. However, the lithium salt of salalen ligand was isolated, and its formula was confirmed as (Salalen)$Li_3(THF)_6$, according to the characteristic peaks of THF in C_6D_6 as well as the relative integral areas in the ^{1}H NMR spectrum (Fig. S1, ESI†). However, the characteristic peaks of THF in C_6D_6 migrated to high field due to the coordination effect. MALDI-TOF-MS spectra were performed in THF with DCTB (2-[(2E)-3-(4-tert-buthylphenyl)-2-Methylprop-2-enylidene] malononitrile) as matrix. As for (Salen)Ti(IV)Cl_2, m/z 676.3$^+$ ([M-2Cl$^-$+THF +H_2O]$^+$, 100%) was found, while m/z 677.3$^+$ corresponding to ([M-Cl$^-$+THF+H_2O]$^+$, 100%) was found for (Salalen)Ti(IV)Cl (Fig. S2, ESI†).

Coupling reaction between CO_2 and CHO to generate cyclic carbonates

(Salen)Ti(IV)Cl_2 showed activity toward the cyclization of CO_2 and CHO in conjunction with bis(triphenylphosphino)iminium chloride ([PPN]Cl), producing cyclic cyclohexene carbonate (CHC). Table 1 summarized the coupling reactions catalyzed by complex **1**. The ring opening reaction of CHO was much slower than that of PO due to its steric hindrance, no reaction occurred by [PPN]Cl without the addition of complex **1** (Table 1, entry 1) at relatively low temperature of 70 °C, though [PPN]Cl showed moderate catalytic activity for the cyclization reaction between CO_2 and PO. However, the TON of the reaction reached 100 after 24 h at catalyst loading of 1000/1. Complex **1** exhibited high thermal stability over the temperature range 100-120 °C, its catalytic activity increased with temperature. A maximum TOF of 140 was obtained at 120 °C for 4 h (Table 1, entry 8), and above 99% conversion was acquired at 120 °C for 8 h (Table 1, entry 10). The turnover frequencies were time-dependent, decreasing with longer reaction time (Table 1, entries 8-10). Similar to other binary (Salen)M(III)X systems, its TOF increased with the loading of cocatalysts (Table 1, entries 3-5).

It should be noted that the cyclic carbonate obtained in this catalyst system was exclusively *cis*-CHC, as shown in the carbonyl stretching frequency in FTIR spectrum at 1804 cm^{-1} (*vs.* 1825 cm^{-1} for the *trans*-CHC) (Fig. S3, ESI†). Besides, the chemical shift of the methylene protons at 4.63 ppm (*vs.* 3.90 ppm for the *trans*-CHC) in the ^{1}H NMR spectrum (Fig. S4, ESI†). The *cis*-CHC formation has been reported by Kisch, where a double inversion at the epoxide carbon center was necessary.[19]

Table 1 Coupling reaction of CO_2 and CHO catalyzed by (Salen)Ti(IV)Cl_2[a]

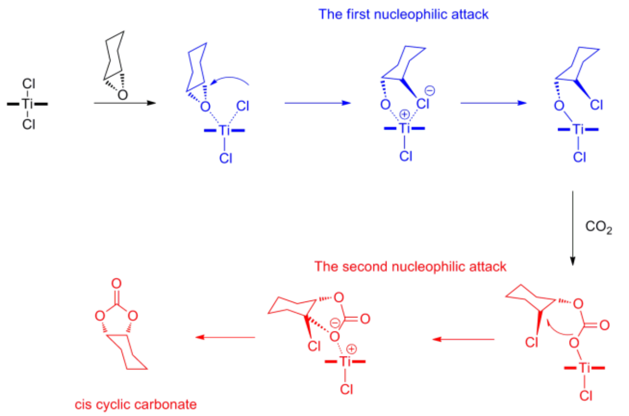


Entry	monomer	[CHO]/[**1**] /[PPN]Cl	Temp [°C]	Time [h]	Yield (%)[b]	TON	TOF [h^{-1}]
1	CHO	1000/0/1	70	3	0.0	0	0
2	CHO	1000/1/1	70	24	10.0	100	4
3	CHO	1000/1/0.5	80	24	9.5	95	4
4	CHO	1000/1/1	80	24	17.0	170	7
5	CHO	1000/1/2	80	24	26.4	264	11
6	CHO	1000/1/1	90	24	31.2	312	13
7	CHO	1000/1/1	110	24	86.4	864	36
8	CHO	1000/1/1	120	4	56.1	561	140
9	CHO	1000/1/1	120	6	80.4	804	134
10	CHO	1000/1/1	120	8	>99.0	990	125

[a] Reaction conditions: All the reactions were carried out in neat CHO under 4.0 MPa CO_2 . [b] From the normalized integrals of the methylene resonances in the ^{1}H NMR spectra.

Recently, Williams reported that bimetallic iron(III) catalyst produced dominating *cis*-CHC with high loading of [PPN]Cl as cocatalyst, and 99% *cis*-CHC formed when [PPN]Cl equivalent increased to 20.[20] Besides, Sugimoto produced *cis*-CHC as the unique form of cyclic carbonate by (Salen)Al(III)X in conjunction with equivalent cocatalysts.[21] In our work, exclusively *cis*-CHC was produced despite the change of temperature or cocatalyst loading. According to Chisholm and coworkers, transition metals like Ti(IV) may form M−OR or M-O_2CR bond with weak polarity which should disfavor the disassociation of the metal oxygen bond.[22] Therefore, we proposed a monometallic pathway for the formation of *cis*-CHC as shown in Scheme 2, including a double inversion of CHO stereochemistry in accordance with two intramolecular attacks of nucleophile. The first inversion occurred during the ring opening of CHO, the axial -Cl attacked the pre-coordinated CHO on one of the two carbons next to oxygen, and the second one occurred during the back-biting process. Due to the weak polarity of Ti-OR and Ti-O_2CR bonds, the alkyloxide and alkylcarbonate species were relatively difficult to disassociate from Ti, or at least kept close to Ti in space, resulting in steric hindrance. We assumed that both nucleophilic attacks were in transition state where the carbon under nucleophilic attack was pentacoordinate, and approximately sp^2 hybridised, thus the polarity of Ti-OR and Ti-O_2CR bonds were strengthened and easier to breakup. Moreover, due to the steric hindrance, the nucleophiles could only attack from the backside of the living group, leading to an inversion of stereochemistry when the leaving group was pushed off the opposite side.

Jing and coworkers investigated the catalytic behavior of (Salen)Sn(II) and (Salen)Sn(IV)X_2 for CO_2/PO cyclization reaction, they pointed out that dissociation of one axial ligand from parent (Salen)Sn(IV)X_2 complex could result in a cationic (Salen)XSn(IV)$^+$ complex as active species.[23] This may be true in (Salen)Ti(IV)Cl_2 system. CHO monomer could coordinate to Ti in that one of the axial -Cl was dissociated, producing the (Salen)Ti(IV) $^+$Cl species during the two intramolecular attacks of

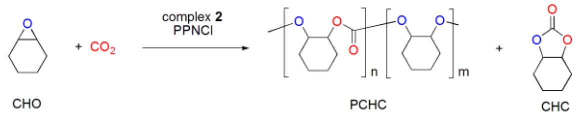


Scheme 2 Proposed mechanism for CO_2/CHO cyclization reaction (for clarity, only (S,R)-CHO was presented here, the same reaction occurred for theenantiomer, yielding a racemic mixture of *cis*-CHC).

nucleophile. Moreover, the positively charged Ti in the transition state further weakened the polarity of Ti-O_2CR, impeding the inserting of another CHO, since chain propagation proceeded via an anionic polymerization mechanism.[9b] Thus, (Salen)Ti(IV)$^+$Cl active species could not catalyze copolymerization of CHO and CO_2.

Based on the catalytic behavior and mechanistic aspect of (Salen)Ti(IV)Cl_2 system, a Ti complex of salen analogue with a nucleophilic axial group as well as a flexible coordination site should be effective for copolymerization of CO_2 and CHO. Thus an asymmetric Salalen ligand with three active hydrogen was brought in, and (Salalen)Ti(IV)Cl (complex **2)** was therefore designed and used for copolymerization of CO_2 and CHO, the results were listed in Table 2. When the reactions were conducted in neat CHO ([CHO]/[**2**]=1000/1，P(CO_2)=4.0 MPa) for 20 h, little copolymer was obtained. Considering that cocatalysts such as onium salts were effective to improve catalytic activity of (Salen)M(III)X[10a, 24], [PPN]Cl was added with complex **2,** resulted in successful production of PCHC at 60 °C with a TOF of 15, where the PCHC/CHC selectivity was 99/1. The influence of copolymerization conditions such as temperature, pressure and reaction time on copolymerization reaction was also shown in Table 2. Higher catalyst loading ([CHO]/[**2**] =500/1) gave a higher CHO conversion, while the carbonate linkage and PCHC/CHC selectivity maintained the same (Table 2, entry 2). Entries 1, 3 and 4 showed the effect of CO_2 pressure on the reaction with [CHO]/[**2**]/[[PPN]Cl] ratio of 500/1/1 at 70 °C, the TOF of the reaction increased when the pressure increased from 3.0 MPa to 4.0 MPa, however, the catalytic activity under 5.0 MPa was lower than that under 4.0 MPa, possibly due to the dilution effect of the reaction mixture by CO_2.

Table 2 CO_2/CHO reaction catalyzed by complex (Salalen)Ti(IV)Cl[a]



Entry	[CHO]/[**2**] /[[PPN]Cl]	CO_2 [MPa]	Temp [°C]	Time [h]	Yield [%][b]	PCHC /CHC[b]	TOF [h^{-1}][c]	Carbonate linkage[%][d]	M_n[e]	M_w/M_n
1	1000/1/1	4.0	60	20	23.0	98/2	12	99	4500	1.05
2	500/1/1	4.0	60	20	56.0	98/2	14	99	6300	1.07
3	1000/1/1	3.0	60	20	20.1	98/2	10	99	4150	1.13
4	1000/1/1	5.0	60	20	20.4	98/2	10	99	4300	1.12
5	500/1/2	4.0	70	10	50.0	96/4	25	98	3200	1.10
6	500/1/0.5	4.0	70	10	18.3	98/2	9	96	3800	1.10
7	500/1/1	4.0	70	7.5	36.1	98/2	24	98	3500	1.09
8	500/1/1	4.0	70	10	44.4	98/2	22	98	4200	1.09
9	500/1/1	4.0	70	12.5	49.1	98/2	20	98	4650	1.09
10	500/1/1	4.0	70	15	58.7	98/2	20	98	5500	1.11
11	500/1/1	4.0	70	25	78.5	98/2	16	98	6000	1.11
12	500/1/1	4.0	80	5	38.2	98/2	38	98	3200	1.09
13	500/1/1	4.0	80	6	44.2	98/2	37	98	3800	1.10
14	500/1/1	4.0	80	7.5	52.8	97/3	35	98	4400	1.09
15	500/1/1	4.0	80	10	62.3	97/3	31	98	5400	1.10
16	500/1/1	4.0	80	15	70.4	97/3	24	98	6100	1.12
17	500/1/1	4.0	90	8	66.0	86/14	41	98	4200	1.11
18[f]	500/1/1	4.0	70	12.5	38.2	98/2	15	98	4200	1.10
19[g]	100/1/1	4.0	70	6	>99.0	98/2	16	98	5400	1.07

[a] Reaction conditions: neat CHO. [b] Obtained from the normalized integrals of the methylene resonances in ^{1}H NMR spectra, where PCHC carbonate, ether and CHC was 4.65 ppm, 3.45 ppm, and 4.63 ppm (*cis*-CHC). [c] TOF = turnover frequency of CHO to PCHC per hour. [d] Carbonate linkage content= (carbonate linkages in copolymer)/(carbonate and ether linkages in copolymer). [e] Determined by GPC in CH_2Cl_2 solution using polystyrene standards. [f] With bis(triphenylphosphino)iminium 2,4-dinitrophenolate ([PPN][DNP]) as cocatalyst. [g] Toluene as solvent, [CHO]=5.0 mol/L.

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The effect of [catalyst]/[cocatalyst] ratio on the copolymerization reaction was investigated (Table 2, entries 5, 6 and 8), it was found that the [catalyst]/[cocatalyst] ratio of 1/1 had the best performance, a lower ratio meant lower TOF while the higher one led to more CHC. Besides, the reaction temperature had a great effect on the activity and selectivity of the copolymerization (Table 2, entries 2, 9, 15 and 17), compared to reaction at 60 °C, TOF of the reaction slightly increased at 70 °C or 80 °C, but both the carbonates linkage and the content of CHC showed no significant change, while an obviously negative effect on the PCHC/CHC selectivity at 90 °C. It should be noted that the cyclic carbonate as a side product was also proved as exclusively *cis*-isomer. Moreover, all the resulting PCHCs by complex **2** had narrow polydispersity index (PDI) ranging from 1.05-1.13, indicating quasi living copolymerization nature similar to (BDI)ZnOAc[25] (BDI =β-diiminate) or (Salen)M(III)X (M = Co[10b, 11a] or Cr[26]) catalysts. Furthermore, we carried out two series of experiments at 70 °C and 80 °C in order to understand the relationship between the number average molecular weight (M_n) and CHO conversion, where the [CHO]/[**2**]/[[PPN]Cl] ratio was set as 1000/1/1 and the CO_2 pressure as 4.0 MPa. Fig. 1 showed the linearly fitting curve between M_n and CHO conversion, and the regression coefficient R^2 of 0.997 indicated a good linear relationship. The data of entry 11 and entry 16 deviated from the linearly fitting curve in Figure 1, which might be attributed to the solidification phenomenon at high CHO conversion, such high CHO conversion showed potentiality of completely conversion of CHO under proper conditions. When toluene was used as solvent and the catalyst loading increased to [CHO]/[**2**]=100/1, the ^1H NMR spectrum showed a 99% conversion of CHO after 6 h of reaction, while the carbonate linkage stayed as 98% (Table 2, entry 19). The nearly complete conversion of CHO indicated that (Salalen)Ti(IV)Cl might be used to synthesize multiblock Poly(cyclohexene carbonate)s with controllable sequence as (BDI)ZnOAc system could.[27]

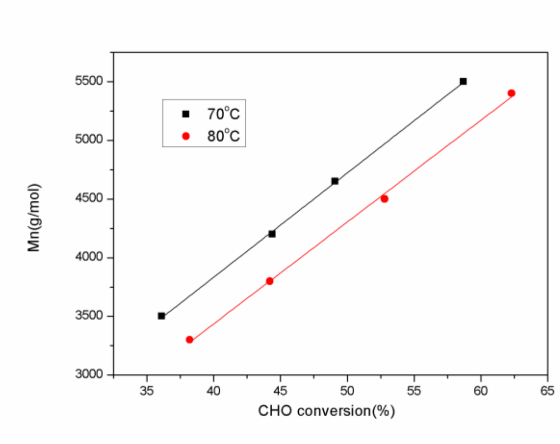
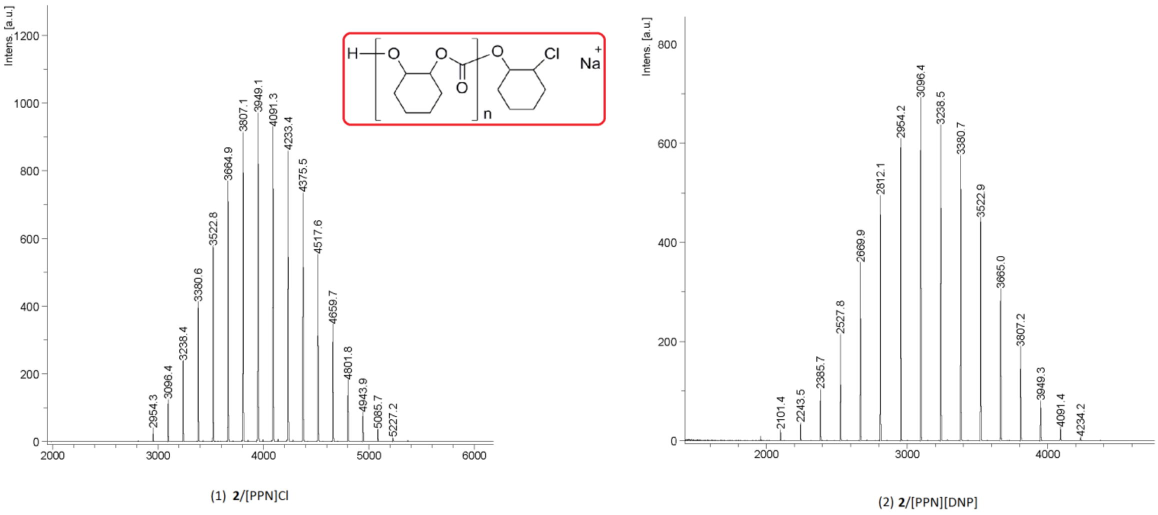


Fig. 1 Plot of PCHC M_n (GPC) *vs.* the conversion of CHO (determined by ^1H NMR) according to entries 7-10, 12-15. ■At 70 °C, ●At 80 °C.

As the molecular weight of resulting copolymer displayed a monomodal distribution with narrow PDI (1.05-1.15) (Fig. S5, ESI†), we wondered whether the (Salalen)Ti(IV)Cl system was capable of growing one or two chains in the presence of an anionic cocatalyst initiator. As for SalenCo(III)X/[PPN]Y system, Coates and Lu proposed that both axial group X and nucleophlic Y were capable of initiation, and polymer chains grew on on either side of the $SalcyCo^{III}$ plane. [24a, 28] Recently, mechanistic aspect about the role of cocatalysts in CO_2/CHO copolymerization utilizing chromium salen complex has been well explored by Darensbourg, where he found that chain propagation on one side of salen ligand was hampered due to steric hindrance, resulting in copolymer with bimodal molecular weight distribution. To explore how (Salalen)Ti(IV)Cl system worked in CO_2/CHO copolymerization, PCHCs were prepared by two different catalyst/cocatalyst combinations: (Salalen)Ti(IV)Cl/[PPN]Cl (Table 2, entry 9) and (Salalen)Ti(IV)Cl /[PPN][DNP] (Table 2, entry 18). The isolated copolymers from both systems exhibited only one series of peaks in accordance with $[HO(CHO\text{-}CO_2)_nOCHC_4H_8CHCl]Na^+$ in MALDI-TOF-MS spectra (Fig. 2), implying that axial group Cl^- acted as initiator instead of 2,4-dinitrophenolate. Thus, we believed that chain propagation only occurred on one side of $SalalenTi^{IV}$ plane. In addition, the end alkylhydroxyl group might be mainly related to the chain transfer reaction between propagating chains and trace water.

According to Williams's work, in the ^1H NMR spectrum of PCHC with -Cl as a terminal group, peaks 4.39 ppm and 3.55 ppm were assigned to the PCHC end-group methylene resonances ($OCHC_4H_8C\mathit{H}Cl$ and $OC\mathit{H}C_4H_8CHCl$, respectively), and the residual broad signal at 3.4-3.5 ppm corresponded to ether linkages in PCHC.[20] While in a typical ^1H NMR spectrum of purified PCHC by (Salalen)Ti(IV)Cl system, there were weak signals at 4.39 ppm and 3.55 ppm, but none signal at 3.4-3.5 ppm existed (Fig. S6, ESI†). Thus, we may conclude that PCHCs produced by (Salalen)Ti(IV)Cl system have completely alternating structure with -OH and -Cl as terminal groups.



(1) **2**/[PPN]Cl

(2) **2**/[PPN][DNP]

Fig. 2 he MALDI-TOF MS spectra of PCHCs produced by complex **2** at 70 °C and 4.0 MPa CO_2 pressure with different cocatalysts. (1) with [PPN]Cl; (2) with [PPN][DNP].

The stereo structure of PCHCs obtained by (Salalen)Ti(IV)Cl system was explored based on its carbonyl region (δ=153~154 ppm) of ^{13}C NMR spectrum (Fig 3). According to Nozaki's assignment, the signal at 153.7 ppm was attributed to the central carbonyl carbons of m-centered tetrad indicative of isotactic PCHC; while the signals at higher field (153.3-153.1 ppm) were assigned to the central carbonyl carbons of r-centered tetrads indicative of syndiotactic copolymer.[29] As shown in Figure 3, chemical shifts of carbonate carbon were observed at 153.7, 153.2, 153.1 and 153.0. Thus, we may conclude that the PCHCs by (Salalen)Ti(IV)Cl system have atatctic structure.

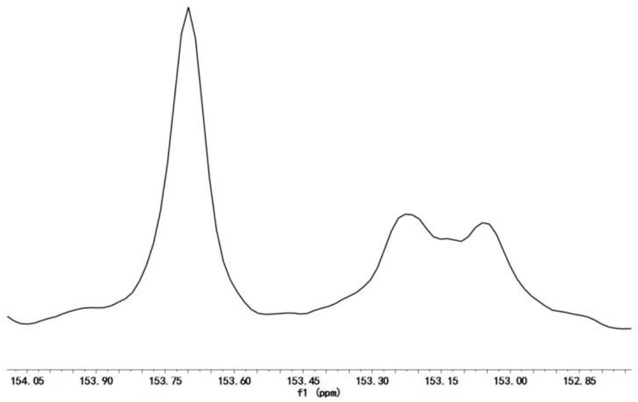
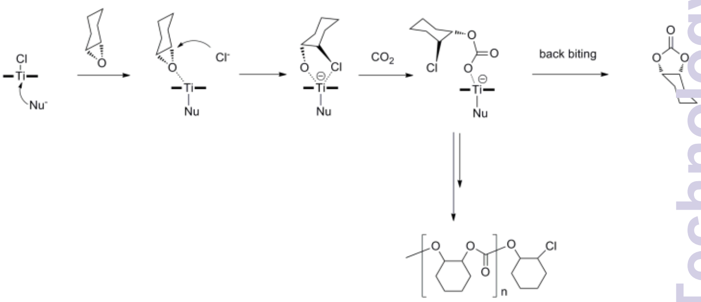


Fig. 3 The carbonyl region of the ^{13}C NMR spectrum of PCHC produced using complex **2** (Table 2, entry 11) in $CDCl_3$.

According to the exprimental results, we proposed a binary initiation mechanism for CO_2/CHO coupling reaction catalyzed by (Salalen)Ti(IV)Cl (Scheme 3). Anionic nucleophile from cocatalysts coordinated to Ti and strengthened the polarity of Ti-Cl, thus axial group Cl^- was capable of acting as an initiator. Like (Salen)Ti(IV)Cl_2 binary system, two nucleophilic attacks occurred and corresponding two inversions of stereochemistry also led to the formation of *cis*-CHC as a byproduct of the copolymerization reaction. However, during the transition state, Ti was negatively charged, enhancing the polarity of Ti-O_2CR and facilitating the inserting of another CHO. Thus, the propagation could proceed on anionic Ti center in a similar manner with (Salen)Co(III)X/onium salt binary system.



Scheme 3 Proposed mechanism for CO_2/CHO coupling reaction by (Salalen)Ti(IV)Cl system (for clarity, only (S,R)-CHO was presented here although the same reactions occurred for the enantiomer, yielding a racemic mixture of *cis*-CHC and atactic PCHC).

Conclusions

Novel titanium complexes combining Salen ligand and its half saturated form Salalen ligand have been prepared and investigated as catalyst for CO_2/epoxide coupling reaction. (Salen)Ti(IV)Cl_2 was only effective for the exclusively *cis*-cyclic cabonate with [PPN]Cl as cocatalyst. While (Salalen)Ti(IV)Cl could catalyze the copolymerization of CO_2 and CHO, producing PCHCs with completely alternating structure.

Acknowledgements

The authors thank financial support from the National Natural Science Foundation of China (Grant No. 51321062 and 21134002)

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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