ACS Catalysis
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Trivalent Titanium Salen Complex: Thermally Robust and Highly Active Catalyst for Copolymerization of CO_2 and Cyclohexene Oxide

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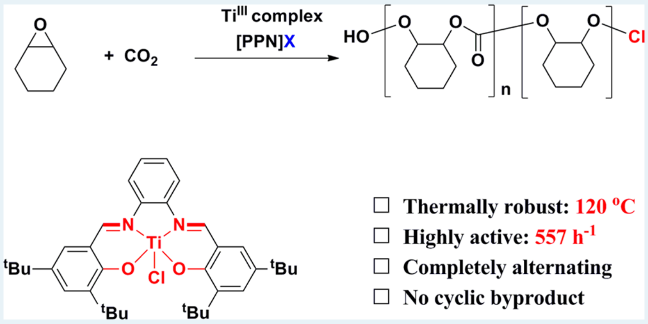
Ⓢ *Supporting Information*

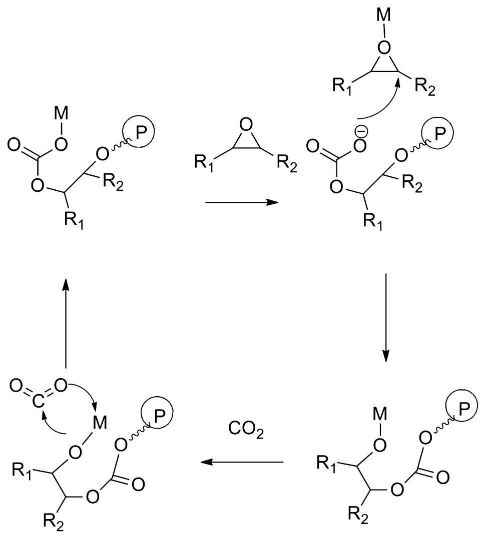
ABSTRACT: A trivalent titanium complex combining salen ligand (salen-H_2=*N*,*N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-benzenediamine) was synthesized as catalyst for copolymerization of CO_2 and cyclohexene (CHO). In combination with onium salt [PPN]Cl, (Salen)Ti(III)Cl showed impressive activity and selectivity, yielding completely alternating copolymer without the formation of cyclohexene carbonate (CHC), with turnover frequency (TOF) of 557 h^{-1} at 120 °C, which was more than 10 times higher than that of our previously reported (Salalen)Ti(IV)Cl, and close to the Cr counterparts. In addition to the biocompatibility of Ti, thermally robust character resulting from the reducibility of trivalent Ti was industrially desirable.



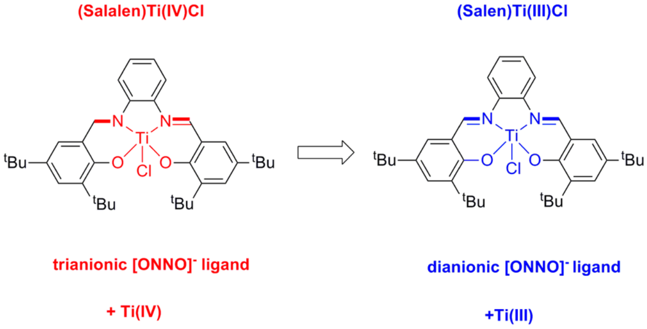
KEYWORDS: *carbon dioxide, cyclohexene oxide, copolymerization, salen, titanium, homogeneous catalysis*

Since the pioneering work by Inoue and co-workers in 1969,[1] the copolymerization of CO_2 and epoxides has become one of the most important CO_2 fixation processes, and the core issue is the development of highly active and selective catalysts.[2] Up to now, the (Salen)Co(III)X system, first introduced by Coates[3] and recently developed by Nozaki,[4] Lee[5] and Lu,[6] has displayed the most ideal features such as high catalytic activity and polymer selectivity, as well as the production of a polymer with a strict alternating feature in high molecular weight. However, a biodegradable polymer is required to be not only compostable but also nontoxic to the soil environment, and concern exists about the possible toxic cobalt residue in the copolymer. Therefore, impending research is designed to develop an environmentally friendly catalyst based on a compostable central metal. A titanium complex may be a choice, because Nozaki's contribution indicated that

Scheme 1. General Chain Propagation for the Copolymerization of CO_2 and Epoxides

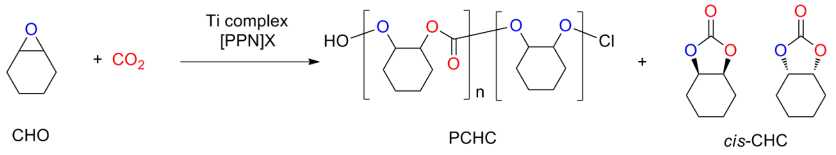


Scheme 2. Structure of (Salalen)Ti(IV)Cl (Left, Complex 2) and (Salen)Ti(III)Cl (Right, Complex 1)



Received: November 2, 2014
Revised: December 8, 2014
Published: December 9, 2014

Table 1. Copolymerization of CO_2 and CHO under Various Catalyst System[a]



entry	catalyst	cocatalyst	CHO/catalyst/cocatalyst	T (°C)	t (h)	yield (%)[b]	carbonate linkage (%)[c]	PCHC/CHC[b]	TOF[d] (h^{-1})	M_n[e]	M_w/M_n
1	**1**	[PPN]Cl	1000/1/1	70	6	50.1	99	>99/1	84	7400	1.08
2	**1**	[PPN]Cl	1000/1/1	80	2	32.2	99	>99/1	161	6300	1.09
3	**1**	[PPN]Cl	1000/1/1	90	2	46.0	99	>99/1	230	5800	1.11
4	**1**	[PPN]Cl	1000/1/1	120	1	57.7	99	>99/1	577	4200	1.06
5	**1**	[PPN]Cl	2000/1/1	120	3	29.9	99	>99/1	200	2700	1.09
6	**1**	[PPN]Cl	2000/1/2	120	1	25.1	99	94/6	502	2400	1.08
7	**1**	[PPN]Cl	2000/1/10	120	1	56.3	ND	10/90	1126	ND	ND
8	**1**	[PPN]Cl	2000/1/20	120	1	79.5	ND	0/100	1590	ND	ND
9	**1**	[PPN]Br	1000/1/1	90	3	34.5	99	64/36	115	2400	1.10
10[f]	**1**	[PPN][DNP]	1000/1/1	90	3	43.5	99	>99/1	145	4500	1.08
11	**1**	[PPN][DNP]	1000/1/1	120	1	39.6	99	>99/1	396	3600	1.07
12[g]	**2**	[PPN]Cl	500/1/1	70	10	44.4	98	98/2	22	4200	1.09
13[g]	**2**	[PPN]Cl	500/1/1	90	8	66.0	98	86/14	41	4200	1.11
14[g]	**2**	[PPN][DNP]	500/1/1	70	12.5	38.2	98	86/14	15	4200	1.10

[a] Reaction conditions: neat CHO, CO_2 pressure = 4.0 MPa. [b] Obtained from the normalized integrals of the methylene resonances in ^1H NMR spectra, where PCHC carbonate, ether, and CHC was 4.65, 3.45, and 4.63 ppm (*cis*-CHC).[14] [c] Carbonate linkage content = (carbonate linkages in copolymer)/(carbonate and ether linkages in copolymer). [d] TOF = turnover frequency of CHO to PCHC per hour. [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] According to ref 8.

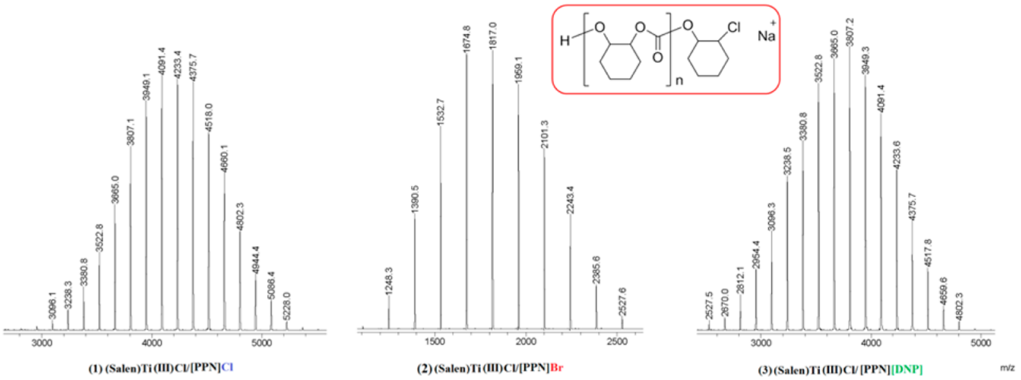
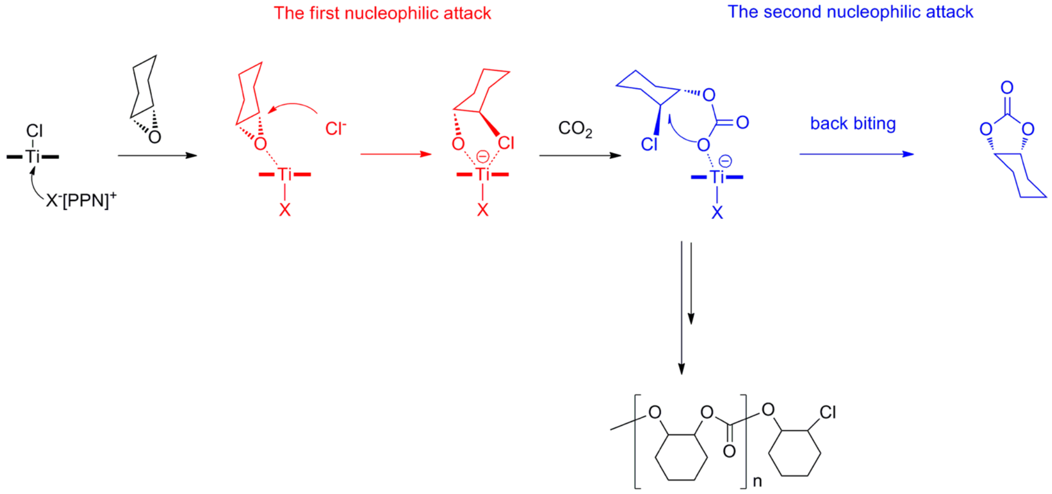


Figure 1. MALDI-TOF-MS spectra of PCHCs produced by complex **1** in combination with [PPN]X. (1) X = Cl (Table 1, entry 4); (2) X = Br (Table 1, entry 9); (3) X = DNP (Table 1, entry 11).

(BOXDIPY)Ti(IV)Cl could produce an almost completely alternating copolymer for the copolymerization of CO_2 and PO.[7] Recently, we designed (Salalen)Ti(IV)Cl as an effective catalyst for the copolymerization reaction of CHO and CO_2 based on the mechanistic aspects of (Salen)M(III)X systems, where asymmetric salalen served as trianionic $[ONNO]^-$ ligand.[8] It was found that (Salalen)Ti(IV)Cl/[PPN]X produced completely alternating PCHC with monomodal MWD (molecular weight distribution), but the TOF of the reaction under optimal condition was only 41 h^{-1}, much lower than that of cobalt or chromium salen complexes. In another consideration, higher copolymerization temperature was generally beneficial to raise activity, but when the reaction temperature was raised to 120 °C, only the formation of *cis*-CHC was observed, indicating poor catalytic performance at high temperature.

Scheme 1 shows the general chain propagation process for the copolymerization of CO_2 and epoxides, which involves two steps: (1) epoxide ring opening by anionic carboxylate intermediate, followed by (2) CO_2 insertion into a metal alkoxide.[3] However, it is apparent that both the above two steps require reversible formation and dissociation of the M-O bond, and therefore, the M-O bond with weak polarity should hamper the chain propagation for the copolymerization reaction. Wu proposed that the Ti−O bond had a covalent feature and poor polarity, which might make Ti complexes ineffective for the copolymerization.[9] Considering that Ti has strong Lewis acidity, which has been regarded to be favorable for the epoxides ring opening, it could be tentatively assumed that the much lower catalytic activity for (Salalen)Ti(IV)Cl compared with the Co and Cr counterparts resulted from the weak polarity of Ti−O bond. To solve the above problem, trivalent titanium complex (Salen)Ti(III)Cl (complex **1**) combining salen ligand was designed, utilizing $TiCl_3\cdot(THF)_3$ as starting material.[10−12] As a lower oxidation state of titanium, this trivalent Ti catalyst was likely to form Ti−O bond with stronger polarity than tetravalent Ti, it was thus expected that (Salen)Ti(III)Cl would show better catalytic activity for CO_2/

Scheme 3. Proposed Mechanism for CO_2/CHO Coupling Reaction by (Salen)Ti(III)Cl System[a]



[a] For clarity, only (S,R)−CHO was presented here, although the same reactions occurred for the enantiomer.

CHO copolymerization. Moreover, the salen ligand was symmetric in (Salen)Ti(III)Cl, whereas it was asymmetric in the tetravalent (Salalen)Ti(IV)Cl complex (complex **2**, Scheme 2). An easy synthesis may be another bonus for this catalyst system.

The copolymerization results of CO_2 and CHO are listed in Table 1 using (Salen)Ti(III)Cl (complex **1**) as catalyst and [PPN]X as cocatalyst, and corresponding results from (Salalen)Ti(IV)Cl (complex **2**) were also shown for comparison. As we have previously reported, (Salalen)Ti(IV)Cl required a high pressure of 4.0 MPa for the most favorable activity, and thus, all the experiments were carried out under 4.0 MPa. First, the reaction was carried out in the presence of [PPN]Cl (1 equiv), with CHO (1000 equiv) at 70 °C for 6 h (Table 1, entry 1), a TOF of 84 h^{-1} was obtained (Table 1, entry 1). The copolymer was obtained in almost completely alternating structure, and no production of cyclohexene carbonate was detected. The catalytic activity increased steadily with the temperature (Table 1, entries 1−5), and the TOF reached 230 h^{-1} at 90 °C; it was notable that (Salen)Ti(III)Cl produced a copolymer with a TOF of 557 h^{-1} at 120 °C and still no cyclic byproduct and ether unites were observed. It was more than 10 times higher than the maximal TOF of (Salalen)Ti(IV)Cl, and close to that of (Salen)Cr(III)X, which was the most active metal salen binary catalyst for CO_2/CHO copolymerization.[13]

These results confirmed our assumption that more polar Ti−O bond should enhance the catalytic activity of Ti complexes of salen analogues. A notable advantage of (Salen)Ti(III)Cl lied in its extremely high selectivity for polymer formation (>99/1), while generally predominant formation of cyclic carbonates was often observed at high temperature for coupling reaction of CO_2 with various epoxides, because high reaction temperature helped the dissociation of the growing polymer chain from metal center, decreasing the activation barrier for backbiting reaction.[2b,15] As far as cobalt complexes were concerned, reduction of Co^{III} to Co^{II} were commonly observed at high reaction temperature for both salen and porphyrin systems, which changed the structure of the catalysts and thus led to formation of a large amount of cyclic carbonates[6a,9,16] Here, we proposed that Ti^{IV} as the highest oxidation state of Ti also had a tendency to be reduced at high temperature like Co^{III}; Ti^{III} was stable during the reaction, and therefore, (Salen)Ti(III)Cl could keep its structure and show impressive selectivity at high temperature.

Furthermore, the effects of the nucleophilic X of the cocatalysts were explored (Table 1, entries 3, 4, 9−11). It was found that replacement of [PPN][DNP] resulted in a notable decrease in TOF, while substitution of [PPN]Br led to formation of *cis*-CHC. Lower catalyst loading ([CHO]/[**1**] = 2000/1) showed a loss in activity while the carbonate linkage and PCHC/CHC selectivity maintained (Table 1, entry 5). We noted the well-accepted trend that high loading of cocatalysts led to enhancement of catalytic activity but loss of copolymer selectivity for binary systems (entries 5−8).[17] Especially, when the ratio of [PPN]Cl/**1** was 20, only CHC formed with high TOF of 1590 h^{-1}. It was notable that the CHC produced by (Salen)Ti(III)Cl was exclusively *cis*-isomer despite the change of temperature or cocatalyst loading like the (Salalen)Ti(IV)Cl system.[8,14]

On the basis of the ^1H NMR spectrum of purified PCHCs by (Salen)Ti(III)Cl system (Figure S1), we may conclude that PCHCs produced by (Salen)Ti(III)Cl system had completely alternating structure with −OH and −Cl as terminal groups.[8,14] Moreover, Figure 1 showed typical MALDI-TOF-MS spectra by (Salen)Ti(III)Cl/[PPN]X. The isolated copolymers all exhibited only one series of peaks in accordance with $[HO(CHO{-}CO_2)_nOCHC_4H_8CHCl]Na^+$ in MALDI-TOF-MS spectra despite the cocatalysts, implying that the PCHCs by (Salen)Ti(III)Cl had completely alternating structure and monomodal MWD (molecular weight distribution). Furthermore, the absence of DNP^- or Br^- in in the copolymer revealed that axial group Cl^- acted as initiator instead of anionic nucleophile of cocatalysts. Thus, we might conclude that chain propagation only occurred on one side of $SalenTi^{III}$ plane, initiated by an axial Cl^-. As for the SalenCo(III)X/[PPN]Y system, Coates and Lu proposed that both axial group X and nucleophlic Y were capable of initiation and that polymer chains grew on either side of the $SalenCo^{III}$ plane.[6,16] Moreover, (Salen)Cr(III)Cl in combination with onium salts produced PCHCs with bimodal molecular weight distribution, implying that chain propagation on one side of the $SalenCr^{III}$ plane was partly hindered.[13b]

Because an anionic nucleophile of cocatalysts did not initiate the reaction, we wondered how they acted in the copolymerization. In order to figure this out, reactions without cocatalysts were also carried out, and no copolymer or cyclic product were detected even at [CHO]/[Cat.] loading of 250/1, implying that the carboxylate species were not able to dissociate from Ti center without cocatalysts. Thus, we assumed that the negatively charged nucleophile of the cocatalysts kept bonding to Ti during the copolymerization reaction and therefore facilitated the dissociation of Ti—O bond. On the basis of this, aspects of the mechanism for the formation of *cis*-CHC and PCHC were proposed (Scheme 3). The formation of *cis*-CHC at high cocatalysts loading included a double inversion of CHO stereochemistry in accordance with two intramolecular attacks of nucleophile. Due to the steric hindrance, the nucleophiles could only attack from the backside of the leaving group, leading to an inversion of stereochemistry when the leaving group was pushed off the opposite side.

In summary, novel trivalent titanium complex combining salen ligand has been prepared and investigated as catalyst for the copolymerization of CO_2 and CHO. Compared to our previously reported (Salalen)Ti(IV)Cl, (Salen)Ti(III)Cl was much easier to prepare and displayed superior catalytic activity and selectivity. Especially, (Salen)Ti(III)Cl/[PPN]Cl produced completely alternating PCHC without cyclic byproduct at 120 °C. Moreover, because the nucleophile of the cocatalyst did not initiate the copolymerization, a one-side propagation mechanism was proposed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501719v.

Experimental details, EPR spectra, MALDI-TOF-MS spectra, NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge financial support from the National Natural Science Foundation of China (grant nos. 51321062, 51273197, and 21134002)

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