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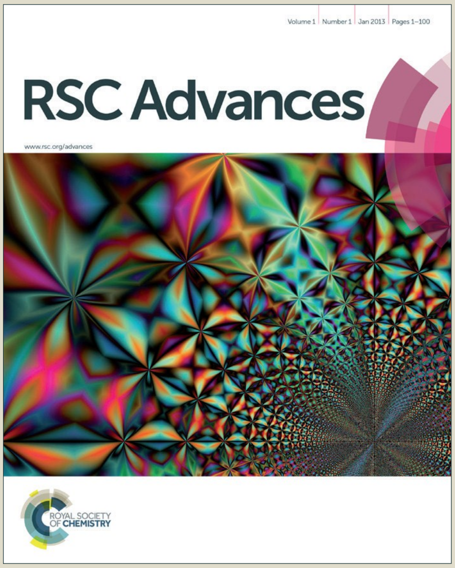

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Chromium Complexes Containing Tetradentate [OSSO]-type Bisphenolate Ligand as a Novel Family of Catalyst for the Copolymerization of Carbon Dioxide and 4-Vinylcyclohexene Oxide

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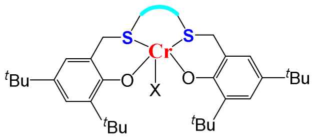
This work reports the synthesis of polycarbonates from 4-vinylcyclohexene oxide(VCHO)/carbon dioxide copolymerizations catalyzed by new homogeneous chromium complexes with [OSSO]-type bis(phenolato) dianionic ligand. Through the structure design, the ethylene-bridged ligands of the chromium complex exhibits the highest activity with the same axial anion Cl. The catalytic activity and product selectivity of these [OSSO]Cr^{III} complexes have been systematically investigated under varied conditions. ^{1}H NMR spectrum of the obtained copolymers confirmed the the resulting polycarboante with high CO_2 incorpoartion with carbonate unit above 95%. This is one of the rare examples of a well-defined metal complex with soft Lewis base as donor for the efficient copolymerization of carbon dioxide and epoxides.

Introduction

Copolymerization of epoxides and carbon dioxide (CO_2) to prepare aliphatic poly(carbonate)s (APCs) has been considered to be one of an attractive polymerization process for potential large-scale utilization of greenhouse CO_2 in chemical synthesis,[1] whose resulting APCs is a promising class of biodegradable polymers for various applications, such as integral components of engineered tissues, medical devices and drug delivery systems.[2] Since the pioneering work reported by Inoue in the late 1960s,[3] various catalysts have been explored for this reaction, of particular efforts are devoted to developing structurally well-defined metal complexes supported by different ancillary ligands [1b, 4-12,]. So far, such successful ligands employed dominantly involve hard Lewis base nitrogen and/or oxygen as coordination atoms such as salen [4c, 4d, 5] salalen[6], salan[7], porphyrinato,[8] corrole,[9] β-diketiminates,[10] etc. [11-12] Compared to considerable reports of the ligands based on the hard donors oxygen and nitrogen, there has been a few examples concerning on the metal complexes chelated with soft atoms for this transformation.[13] Duchateau and co-workers found that chromium complex having soft phosphorus atom as one coordinate donor could catalyze the cyclohexene oxide(CHO)-CO_2 copolymerization. However, this kind of chromium aminophinate complex shows low activity (turnover frequency (TOF)<30 h^{-1}) and the product is oligomeric poly(cyclohexene carbonate)s (Mn<1800 g mol^{-1}) with the appreciable ether linkages (≥6%).[13a] Capacchione and co-workers have reported that dinuclear Fe (III) complex coordinated by dithioether-triphenolate catalyzed the coupling reaction of CO_2 with epoxides, exclusively producing the formation of cyclic carbonate.[13b]

In our recent work we found that [OSSO]CrX/Lewis base binary catalyst demonstrated efficient activity for the ring opening copolymerization (ROCOP) of epoxides with anhydride.[14] Of importance, [OSSO]-type bis(phenolate) dianionic tetradentate ligands are analogous to the [ONNO]-salan ligands, in which the *N*-Me (H) donors are replaced with soft sulphur donors, *i.e.* the two phenoxide frameworks are linked to sulfur atom. As revealed by Lu and Darensbourg groups,[7] chromium salan complex has shown higher catalytic performance than the corresponding chromium salen complex in catalyzing CO2/epoxides compolymerization, regarding both activity and stereochemistry control. They proposed that such higher catalytic performance should be related to the greater electron-donating feature of amino donor of salan ligand than that of salen counterparts, and *cis*-configuration structure is also an important contribution factor. Noteworthy, sulphur is a better electron-donating atom than that of nitrogen. Moreover, an characteristics of metal complexes of the [OSSO]-type ligand possess the *cis*-geometry as similar as complexes bearing [ONNO]-type tetradentate salan ligands.[15] Furthermore, some well-defined metal complexes-based efficient catalysts for copolymerization of epoxides with CO_2 are often capable of catalyzing the ROCOP of epoxides with



	[OSSO]CrX	
C_6H_{10}	X=Cl	Complex **1**
C_6H_{10}	X=N_3	Complex **2**
CH_2CH_2	X=Cl	Complex **3**
C_6H_4	X=Cl	Complex **4**

Fig. 1 Structures of [OSSO]CrX complexes employed in this work (X=Cl or N_3).

anhydride or inverse due to the similarity of copolymerization mechanism.[16,17]

Inspired by the above-mentioned descriptions, the chromium complex containing a [OSSO]-type dianionic ligands (see Fig. 1) are, therefore, employed to test their catalytic behavior toward CO_2/VCHO copolymerization in conjugation with organic onium salts or Lewis base, which is a part of our continuous efforts in search for novel catalyst for the ROCOP of epoxides and CO_2.[18] The VCHO was selected for this work because VCHO is largely unexplored as substrate for copolymerization with CO_2 compared to substantial reports on CHO.[19-22] The focuses are paid on the influence of ligand skeleton and reaction parameters on the activity and selectivity.

Experimental Section

Reagents and measurements

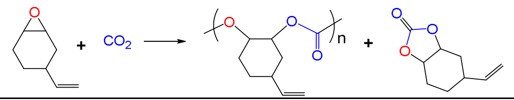
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under argon atmosphere. VCHO was stirred over powered CaH_2 at room temperature over 48h and vacuum-distilled before use. All used cocatalysts including bis(triphenylphosphine)iminium chloride (PPNCl), 4-dimethylaminopyridine (DMAP), and tetrabutylammonium chloride (TABCl) were purified by standard methods. bis(triphenylphosphine)iminium azide ($PPNN_3$), was prepared according to published procedure.[23] [OSSO]CrX complexes were synthesized as described in our previous work.[14]

All ^{1}H spectra were recorded on a Bruker-400 spectrometer at frequencies of 400 MHz. Chemical shifts are given in ppm relative to TMS. Infrared (IR) spectra were obtained on a BrukerVector 22 spectrometer at a resolution of 4 cm^{-1} (16 scans collected). The molecular weight of polymer was determined by using gel permeation chromatography (GPC) on a PL-GPC 220 instrument with a refractive index detector, calibrated with polystyrene standards. The columns used were MIXED-B 300 × 7.5 mm columns held at 40 ^{o}C, using THF as eluents at a flow rate of 1.0 mL/min. The glass transition temperatures (T_g) of polymers were determined at a heating rate of 10 °C/min on PerkinElmer Diamond differential scanning calorimetry (DSC) instrument.

General Procedure for the Copolymerization of epoxides and CO_2.

The copolymerization of CO_2 with VCHO was carried out in a 100 ml autoclave, which was equipped with a magnetic stirrer. Desired amounts of catalyst, cocatalyst and VCHO were transferred into the dried autoclave. The autoclave was heated to the target temperature in a pre-heated oil bath, filled with CO_2 to a set pressure and was kept stirring for the desired time. After the reaction, the autoclave was slowly vented CO_2, followed addition of mixture was taken for IR spectroscopic analysis. The residual mixture was added excess methanol to precipitate and filtrate. The crude copolymer was washed with methanol for several times. The resulting polymer was dried at 60 ^{o}C in vacuo overnight.

Table 1 Copolymerization of VCHO with CO_2 under [OSSO]CrX-PPNCl binary catalytic system



Entry	Complex	TOF^a	Select^b	Carbonate^c	M_n^{d}(g/mol)	PDI^d
1	1	74	73%	97.5%	15 000	1.30
2	2	82	68%	98.0%	20 000	1.35
3	3	78	71%	99.0%	19 000	1.27
4	4	13	44%	95.5%	6 000	1.26

Reaction conditions: [VCHO]: Cr: PPNCl=1000: 1: 2; VCHO=12.4g (0.1mol); 3.0MPa, 90^{o}C, 6h.^{a} Turnover frequency (TOF) for the copolymer calculated as mole of VCHO consumed per mole of catalyst per hour (h^{-1}). ^{b} Selectivity of PVCHC estimated by IR spectroscopy. ^{c} Calculated by ^{1}H NMR spectroscopy. ^{d} Determined by GPC.

Results and Discussions

To investigate the relationship between complex structure and catalytic performance, four [OSSO]CrX complexes with different skeleton of [OSSO]-type ligands and axial anion (see Fig.1) were synthesized[14] and tested for the copolymerization of VCHO with CO_2. As shown in Table 1, all the complexes were active in catalyzing the copolymerization of VCHO with CO_2 at a molar ratio of 1000/1/2 ([VCHO]/[[OSSO]CrX]/[PPNCl]) at 90 ^{o}C in an efficient way. When X=Cl, complex **3** supported by [OSSO] ligand with ethylene backbone showed the highest activity to poly(vinylcyclohexene carbonate) with TOF up to 78 h^{-1}, followed by the cyclohexylene-bridged chromium complex **1** (entry 1, TOF: 74 h^{-1}, Table 1), and the least phenylene framework complex **4** (entry 4,Table 1). While the axial anion of Cl^- was instead of N_3^- anion, the catalytic activity to the polymer is slightly enhanced by 10%. (entry 2 vs entry 1, Table 1).

The complex structure also affect the chemoselectivity of the polycarbonate vs cyclic carbonate. [OSSO] ligand with phenylene bridge complex **4** showed lowest selectivity to the polycarbonate (entry 4, Table 1), whereas complex **1** and **3** gave the comparable selectivity. Not only that, the copolymer obtained from complex **4** possessed lowest molecular weight (MW) and carbonate unit contents in the polymer chain (entry 4, Table 1). As indicated from the ^{1}H NMR spectrum (Fig.**S1** in Supporting Information) and Table 1, the copolymer achieved from complex **3** with ethylene bridge possessed the almost perfectly alternating structure and higher MW. These results indicates that [OSSO]CrX complex with electron-withdrawing framework is unfavorable for the better catalytic performance from the viewpoints of activity and resulting polymer structure. The worse selectivity to polycarbonate vs. cyclic carbonate in the case of [OSSO]CrX-based catalytic system compared to its salanCrX analogue can be attributed to weaker interaction of

Table 2 Effect of cocatalyst on the copolymerization of VCHO with CO_2 under complex **1** catalytic system

Entry	**1**/Cocatal	TOF[a]	Select[b] (%)	M_n[c] (g/mol)	PDI[c]
1	PPNCl(1/2)	58	73	9 000	1.49
2	$PPNN_3$(1/2)	61	68	12 000	1.28
3	DMAP(1/2)	15	86	6 000	1.43
4	TABCl(1/2)	30	67	10 000	1.24
5	PPNCl(1/1)	38	74	_	_
6	PPNCl(1/3)	36	52	_	_

Reaction conditions: [VCHO]: complex **1**: Cocatalyst=1000: 1: 2(entries 1-4); VCHO=12.4g (0.1mol); 2.0MPa, 90°C, 6h. [a] Turnover frequency (TOF) for the copolymer calculated as mole of VCHO consumed per mole of catalyst per hour (h^{-1}); [b] Selectivity of PVCHC estimated by IR spectroscopy. [c] Determined by GPC. "-" not measured

growing anionic polymer chain with higher electron-rich Cr center as a result of coordination to higher electron-donating soft sulfur atoms in [OSSO]CrX complexes, resulting in a higher propensity to backbite.

Pioneering works revealed that the catalytic activity in the copolymerization of epoxides with CO_2 are drastically dependent on the cocatalyst type and loading.[24] Thus, the cocatalyst often used in the salenMX catalytic system including DMAP, PPNX (X=Cl, N_3), and TABCl were selected to estimate their efficiency for the copolymerization of VCHO and CO_2 in neat VCHO at 90 °C within 6h. It is found that DMAP afforded the copolymer with the lowest yield and the copolymer with lowest MW, while PPNX (X=Cl or N_3) onium salt as cocatalyst displayed the highest catalytic activity at same conditions (Table 2). The observation of the catalytic activity consists with the metal salen complexes–based catalyst system for the copolymerization of epoxides and CO_2,[6a, 23, 24e, 24h, 25] The stronger interaction between alkylammonium cations with hard anions than their PPN counterparts could account for the less activity for the TBACl than that of PPNCl.[6a,23e,23h]

As evidenced from Table 2, an increase in catalytic activity is noted for 2 equiv of quaternary organic salts over 1 equiv (entries 1 and 5 in Table 2). This is in contrast to what is observed in previous studies[7b] utilizing its analogue of salanCrX as catalyst, where 1 equiv of cocatalyst optimizes the rate of copolymer formation. Further increase the PPNCl/complex **1** ratio to 3 result in the poor selectivity to polycarbonate. This is presumably due to the facile displacement of anionic growing polymer chain from active metal center by competitive coordination of nucleophilic cocatalyst moieties promoted at higher cocatalyst concentration, leading to a higher tendency to form cyclic carbonate via backbiting reaction.[8e]

The role of cocatalyst in salen or salan complex-based binary catalytic systems for epoxides/CO_2 copolymerization have been investigated and found that the Lewis base or anion of onium salt can coordinate to the active metal center and remarkably improve the catalytic activity of the obtained copolymers by weakening the chromium nucleophile bond with the *trans* effect, which benefits the epoxide coordination and then ring-opening via a nucleophile attack.[24e] We speculated that cocatalyst employed here play a similar function in a similar manner, that is, which could also coordinate to the central metal site of [OSSO]CrX molecule to form six-coordinated chromium species. This speculation is supported by the shift of azide stretching vibration (ν(N_3)) of $PPNN_3$ in the presence of complex **1**.

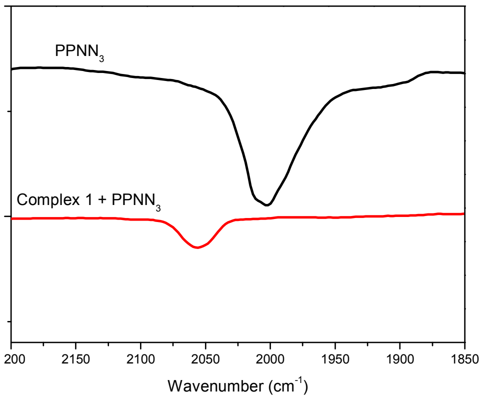
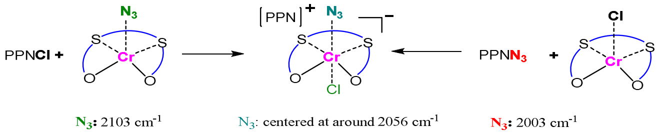
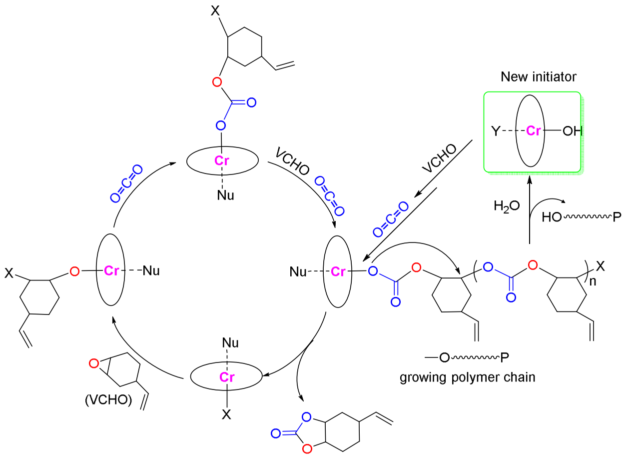


Fig. 2 IR spectra of $PPNN_3$ and the mixture of $PPNN_3$/complex (1:1)

As revealed by Fig. 2**,** it was found that ν(N_3) appeared at 2003 cm^{-1} for the $PPNN_3$, while the ν(N_3) mainly shifted to 2056 cm^{-1} when one equiv of complex **1** was added into $PPNN_3$ CH_2Cl_2 solution, indicating that the N_3^- coordinate to chromium to generate six-coordinated chromium species. The analogous interaction was occurred between PPNCl and complex **2**, where a peak at 2103 cm^{-1} characteristic of ν(N_3) of complex **2** shifted to around 2061 cm^{-1} for the mixture of one equiv of PPNCl and complex **2** (See Fig.**S2**). A proposed interaction between cocatalyst PPNY(Y=Cl or N_3) and [OSSO]CrX (X=Cl or N_3)is as shown in Scheme 1. Furthermore, a shift to a lower frequency of the ν(N_3) vibration of complex **2** occurred with the addition of DMAP.[22] All cases evidenced that both Lewis base and onium salts can coordinate to chromium sites of [OSSO]CrX complexes. Indeed, chromium (III) complexes have a tendency to form six-coordination species as demonstrated by salen,[24e,24b, 26] porphyrin,[27] tetramethyltetraazaannulene,[9] and *N*, *N′*-bis(trifluoroacetylacetone)-1, 2-diminine chromium complexes.[28] Additionally, blank experiments with complex **1** or PPNCl as the sole initiator for the copolymerization of VCHO and CO_2 have been carried out at the VCHO/initiator=1000:1, 3.0Mpa, and 90 °C for 6h. The catalytic results show that no polymeric products are produced. Nonetheless, the combinati-



Scheme 1 Proposed Mechanism of interaction of PPNY/[OSSO]CrX (X, Y=Cl or N_3)



Scheme 2. Proposed mechanism for the copolymerization of VCHO with CO_2.

on of complex **1** and one of the four co-catalysts (DMAP, PPNCl, $PPNN_3$ and *n*-Bu_4NCl) under the same reaction condition endows the effective copolymerization (entries 1-6 in Table 2) . This results further suggest that the real catalytically activity species is the six-coordinate chromium center as proposed in Scheme 1.

According to the observations above-described, a reaction pathway is presumed via a coordination–insertion mechanism as illustrated in Scheme 2. First, the epoxides coordinate to the six-coordinated chromium center and then the metal alkoxide (M-OR) intermediate is formed by ring-opening of the epoxide. Subsequently, CO_2 insert into the M-OR bond through a nucleophilic attack to form a metal carbonate intermediate. This metal carbonate intermediate will react with the epoxides to regenerate the M-OR bond again. Therefore, the copolymerization occurs by the continual cycling between the metal alkoxide and carbonate intermediates. If the presence of the active proton compound such as trace H_2O in the reaction system, chain transfer reaction will be taken place. This proposal is further evidenced by the presence of weak proton signal at 4.54 ppm and broad signals δ=3.90 and 3.75 ppm, which indicate chains end-capped with hydroxyl groups[20], arising by chain transfer reaction with the trace water in the reaction system.

To get insight of resulting PVCHC microstructure, the ^{13}C-NMR spectroscopy was recorded. As shown in Fig.3, the resulting PVCHC presents complex signals in the carbonate region ranging from 153.0ppm to 153.5 ppm of the ^{13}C NMR spectrum, which is well agreement with the observation of PVCHC prepared by the Iron complex-catalyzed the copolymerization of VCHC and CO_2.[20] As analyzed by Pescarmona *et al.*[20], the resultant polycarbonate is atactic (Fig. **3**). This speculation is further evidenced by the fact of no presence of melting point while only glass transition temperature is present at about 110.6°C (see Fig. S3).

The molecular weight (MW) values of resulting copolymers are lower than the theoretical expected MW and GPC curves show a bimodal distribution (see Fig. S4). This observation is consistent with the above proposal of the chain transfer reaction. Indeed, this phenomenon has been demonstrated to be a general one for a variety of metal complex-catalyzed the

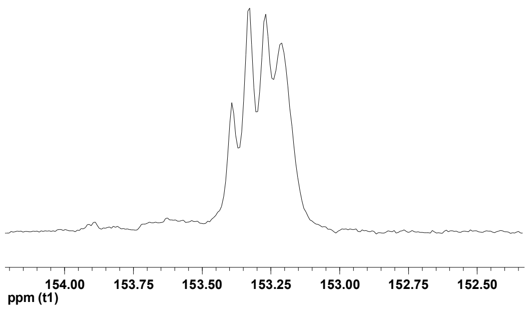


Fig. 3 The carbonate region of ^{13}C NMR spectrum of PVCHC (Table 1, entry 1)

Table 3 Copolymerization of VCHO with CO_2 under Complex 1-PPNCl binary catalytic system

Entry	P (MPa)	Temp (°C)	Molar ratio^a	T (h)	Select.^{b}(%)	TOF^c	M_n^d(g/mol)	PDI^d
1	3.0	80	1000:1	6	74	54	10000	1.26
2	3.0	90	1000:1	6	73	74	15000	1.30
3	3.0	100	1000:1	6	61	57	14700	1.30
4	3.0	90	1500:1	6	70	46	_	_
5	3.0	90	800:1	6	72	69	_	_
6	3.0	90	500:1	6	69	58	_	_
7	3.0	90	1000:1	3	71	93	9000	1.48
8	3.0	90	1000:1	2	65	114	7000	1.28
9	3.0	90	500:1	2	79	134	9800	1.21
10	1.5	90	1000:1	6	73	52	_	_
11	1.0	90	1000:1	6	68	25	6000	1.26

Reaction conditions: VCHO (12.4 g, 0.1 mol); Complex **1**: PPNCl= 1: 2 in neat VCHO; [a] VCHO]/[complex **1**; [b] Selectivity of PVCHC estimated by IR spectroscopy. [c] Turnover frequency (TOF) for the copolymer calculated as mole of VCHO consumed per mole of catalyst per hour (h^{-1}). [d] Determined by GPC. "-" not measured.

copolymerization of CO_2 and epoxides.[6a, 9, 24a, 29] Although GPC curves show a bimodal distribution, the M_n values display a linear relationship with the VCHO conversion as illustrated in Fig. S5. The case suggests that the copolymerization proceeds with a controlled manner.

To further optimize the reactivity of this catalyst system, the effect of variables including temperature, CO_2 pressure, reaction time, molar ratio of monomer to catalyst on the copolymerization were investigated in the presence of PPNCl as shown in Table 3. It is found that the temperature over or below 90 °C results in the lower polymerization rate (44%, 61% and 56% of VCHO conversion for 80°C, 90°C, and 100°C, respectively). The selectivity to copolymer varies from 74 to 61% with the temperature change from 80 to 100°C (entries 1-3, Table 3). At the identified conditions, CO_2 pressure apparently influences the catalytic activity and reaction rate, the higher pressure is beneficial for the copolymerization process (entries 2, 10, and 11, Table 3), whereas the pressure has a slight effect on the selectivity of the copolymer, especially when the pressure is above 1.5 MPa. The molar ratio of VCHO to [OSSO]CrX complex also considerably affect the copolymerization. It was found that TOF value for copolymers is up to 134 h^{-1} at a molar ratio of VCHO to complex **1** of 500:1 in 2 h (entry 9, Table 3), even at higher VCHO to complex **1** molar ratio at 1000:1, the TOF for copolymer still reaches to 114 h^{-1} (entry 8, Table 3) in a same reaction period, further increasing VCHO/complex **1** molar ratio to 1500, the reaction rate decreased (entries 2, 4-6 in Table 3). Whereas the coupling reaction of CO_2 with terminal epoxides such as propylene oxide (PO) and epichlorohydrin (ECH), exclusive cyclic carbonates were produced at 80 °C and 3.0 Mpa with TOF value of 145 h^{-1} for PO and 136 h^{-1} for ECH, respectively.

At last, it should be pointed out that [OSSO]CrCl-based catalyst show inferior catalytic activity to the polycarbonate for the copolymerization of CHO with CO_2 when compared with its salanCrCl analogue based catalyst. The TOF to copolymer is 39 h^{-1} for [OSSO]CrCl catalyst, while TOF value for salanCrCl catalyst was up to 240 h^{-1} and at the same conditions (CHO/catalyst/$PPNN_3$=1250/1/2, 60 °C, 3.4 PMa).[7b] The poorer activity presumedly results from a weaker interaction of the growing anionic polymer chain with a more electron-rich Cr^{III} center arising from the more electron-releasing sulfur donor.

Conclusions

In summary, four chromium complexes with [OSSO] ligands in combination with Lewis base and onium salt have been surveyed as the efficient catalyst for the copolymerization of CO_2 and VCHO with TOF up to 134 h^{-1} and carbonate unit in the polymer chain greater than 95%. Among the catalysts presented in this work, complex supported by [OSSO] ligand with ethylene backbone showed the superior catalytic performance than those of the cyclohexylene- or phenylene-bridged chromium complex. Further investigation are aimed at tailoring the physical and chemical properties of this polymer by free radical- mediated post-polymerization.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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

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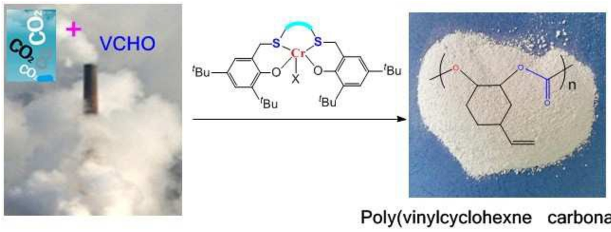
Graphical Abstract

Chromium Complexes Containing Tetradentate [OSSO]-type Bisphenolate Ligand as a Novel Family of Catalyst for the Copolymerization of Carbon Dioxide and 4-Vinylcyclohexene Oxide

Gaoshan Si, Li Zhang, Bing Han, Hongye Zhang, Xiangqing Li, and Binyuan Liu

A functional polycarbonate is efficiently prepared by new [OSSO]CrX catalyzing the copolymerization of 4-vinylcyclohexene oxide with carbon dioxide.



Poly(vinylcyclohexne carbonate)