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Effects of imidazolium salts as cocatalysts on the copolymerization of CO_2 with epoxides catalyzed by (salen)Cr^{III}Cl complex

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Abstract

Imidazolium salts, most of which are room temperature ionic liquids (ILs), have been introduced as effective and tunable cocatalysts in the copolymerization of CO_2 with epoxides catalyzed by (salen)Cr^{III}Cl complex for the first time. Effects of imidazolium salts with different alkyl chains as well as with different anions on the copolymerization were investigated. The results showed that the copolymerization was influenced obviously by the property of anion. In addition, the cation of imidazolium salts with longer alkyl chain length such as *n*-dodecyl (TOF, 242.5 h^{-1}, carbonate linkages >99%) displays better activities and selectivity in the copolymerization as compared with *N*-MeIm (TOF, 72.5 h^{-1}, carbonate linkages 94%). These results are instructive for further design of task-specific ILs as effective cocatalysts to improve the copolymerization of CO_2 with epoxides.

Keywords: Imidazolium salts; Carbon dioxide; Copolymerization

1. Introduction

A series of investigations have been focused on the attractive role of CO_2 as this substance is an economical and environment benign C1 feedstock. One particularly growing area in CO_2 chemistry is the copolymerization of CO_2 with epoxides to prepare polycarbonates announced in 1960s by Inoue [1], which have displayed great potential as biodegradable polymeric materials [2]. Since then, numerous metal-based catalyst systems, involving heterogeneous and homogeneous zinc-based complex [3–13], porphyrin and bis(salicylaldimine) derivatives of aluminum [14–17], manganese [18], cobalt [19–23], chromium [24–28], and rare-earth metals [29], have been extensively studied directing to the development of catalyst systems of improved selectivity and activity.

By analyzing all of these investigations mentioned herein, such a noticeable conclusion can be drawn definitely, that is, activities and selectivity of the copolymerization catalyzed by tetradentate ligand complexes can be remarkably enhanced in the presence of cocatalysts, some of which are alkylammonium [30] and phosphate salts [31]. Though studies concerning the effects of these ionic salts with different kinds of anionic structures on the resulting copolymerization have been carried out previously, other related research involving the relationship between the structure modification of cations of the cocatalysts and the corresponding copolymerization results has not been reported until now. On the other hand, the study on the effects of amount of ionic salts on the copolymerization is absent in the literature, which is important for CO_2 copolymerization. This analysis has thus inspired us to introduce the imidazolium salts (Scheme 1), most of which are room temperature ionic liquids (ILs), as cocatalyst for the copolymerization of CO_2 with epoxides. Since the ionic liquids, so-called designer solvents, can behave differently just by changing the structure of the component ions, this can allow

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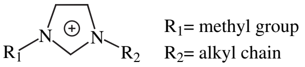
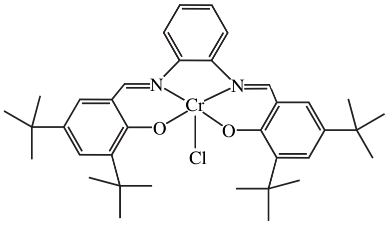
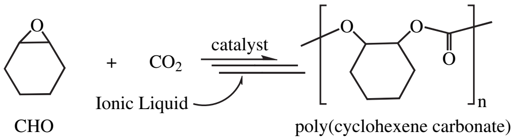


Scheme 1. Typical cation structure of 1,3-dialkylimidazolium salt.

a wide range of applications in the coupling process [32,33]. On the other hand, they have performed well in a series of reactions as cocatalysts and displayed great potential in solubility of CO_2 as reported earlier [34–40]. In this communication, a series of experiments were elaborately conducted using different imidazolium salts and (salen)Cr^{III}Cl (**1**) (Scheme 2) as dual catalytic system (Scheme 3) for the copolymerization. The effects of structure–activities of imidazolium salts as cocatalyst on the copolymerization were studied for the first time.



Scheme 2. (Salen)Cr^{III}Cl (**1**) used in copolymerization.



Scheme 3. Alternating copolymerization of CO_2 with cyclohexene oxide (CHO).

2. Experimental section

2.1. Materials

All aqueous solutions were dried by distillation over sodium/benzophenone and stored over 4 Å molecular sieves under dry nitrogen. Cyclohexene oxide and 1-methylimidazole (*N*-MeIm) (Aldrich) were freshly distilled over CaH_2 under a nitrogen atmosphere. CO_2 (Gas station in Zhejiang University, 99.99%) supplied in a high-pressure cylinder equipped with a liquid dip-tube was used as received.

2.2. Synthesis of catalyst and cocatalyst

H_2Salen ligand of *N*,*N*′-bis(3,5-di-*tert*-butyl-salicylidene)-phenylenediimine was synthesized according to the literature [41] starting from 3,5-di-*tert*-butylsalicylaldehyde and 1,2-diaminobenzene. Synthesis of (salen)Cr^{III}Cl (**1**) was described as follows: H_2Salen ligand (1.0 equiv) and chromium^{II} chloride (1.1 equiv) were dissolved in anhydrous ethanol and stirred under argon at 75 °C for 24 h. The reaction mixture was then exposed to air and stirred for an additional 24 h. After diluting the reaction mixture with diethyl ether, the organic layer was washed with aqueous saturated NH_4Cl and brine solutions followed by drying with Na_2SO_4. After filtration the solvent was removed in vacuum, yielding a dark brown powder.

The synthesis of imidazolium salts was followed by the previous literature [42]. It was carried out in a 250 ml round-bottomed flask, which was immersed in a recirculating heated water bath and fitted with a reflux condenser. In a typical reaction, 0.5 mol *N*-MeIm was dropped into the appropriate 1-bromobutane (0.6 mol) at 80 °C in 2 h. After the addition, the reaction mixture was stirred for another period of 6 h at 80 °C to ensure that the reaction had proceeded to completion. 1-Bromobutane was removed by heating the residue at 80 °C under high vacuum until the weight of the residue remained constant. Pure [bmim]Br can be obtained by recrystallization in ethyl acetate. The preparation of [bmim]PF_6 was followed by the reaction of [bmim]Br with KPF_6 in acetone at 20 °C for 48 h. The residue was filtrated to remove potassium bromide. Acetone was removed by heating the residue to 70 °C under vacuum. The residue was filtrated to further remove potassium bromide. After that, the product was dissolved in chloroform and kept in refrigerator for 24 h. The solid was filtrated to remove the remaining potassium bromide. Solvent was removed under vacuum. The product [bmim]PF_6 was colorless liquid. The synthesized salts were submitted to ^1H NMR and did not contain any detectable impurities. All of these products are kept in an inert environment.

2.3. Cyclohexene oxide/CO_2 copolymerization

A typical copolymerization of CO_2 with cyclohexene oxide was conducted in a 250 ml autoclave that had been previously under vacuum at 80 °C overnight. The (salen)Cr^{III}Cl complex and imidazolium salts were dissolved in freshly distilled cyclohexene oxide. The solution was then added via injection port into the autoclave. The autoclave was heated to 80 °C and charged to a final pressure of 55 bar. After a designed reaction time of 4 h, the autoclave was quickly cooled to room temperature and vented the residual CO_2 to a fume hood. The polymer was extracted from a dichloromethane solution and dried under vacuum at 100 °C overnight. The isolated polycarbonate was weighted to calculate the yields and analyzed by ^1H NMR (500 Hz) in $CDCl_3$ to determine the percentage of carbonate linkage. Molecular weight was determined through GPC in tetrahydrofuran (THF) (5 wt‰) and was calculated relative to polystyrene.

3. Results and discussion

It is generally accepted that copolymerization of CO_2 with epoxides is greatly enhanced in the presence of *N*-MeIm as cocatalyst [43]. Herein the question may emerge: whether this kind of *N*-containing imidazolium salts can be readily used in the copolymerization? If the answer is positive, what is the role of anion in this process? In order to answer the first question, we initially focused on some anions representing different classes of commonly used imidazolium salts, including chloride, bromide, tetrafluoroborate and hexafluorophosphate. To study the influence of imidazolium salts with different anions, the fixed cation structure 1-butyl-3-methylimidazolium (bmim) was employed here.

From the entries 2 to 5 in Table 1, it showed that bmim cation combined with varying anions can effectively catalyze this copolymerization (55 bar, 80 °C). More importantly, the results differed distinctly according to the property of anion used here. It is readily apparent that bmim cation combined with Cl^- and Br^- showed higher activities and better selectivity than their BF_4^- and PF_6^- analogues. The utility of [bmim]C1 as cocatalyst produced a turnover frequency (TOF) of 130.1 h^{-1} (entry 4 in Table 1), which is more than two times as compared with TOF of 54.7 h^{-1} for [bmim]PF_6 (entry 3 in Table 1). In addition, carbonate linkages is dramatically reduced to 53% for [bmim]PF_6 as compared with 95% for [bmim]Cl. It seems that anions with higher nucleophilicity and better leaving ability, such as Cl^- and Br^- are of benefit for improving the activities and increasing the percentage of carbonate linkages than BF_4^- and PF_6^-, which is consistent with the previous reports [44–46]. When compared with *N*-MeIm (entry 1 in Table 1), these imidazolium salts showed better performance, which indicates the positive effect of anions of imidazolium salts on this copolymerization except [bmim]PF_6.

It is reasonable to figure out that the increasing nucleophilicity of anions of imidazolium salts can effectively improve the copolymerization in a certain degree. However, what about the effect of cation structure in this process? As reported earlier, the relationship has been established between the alkyl chain length of cation structure of imidazolium ionic liquid and its performance in several other reactions, such as Stille cross-coupling [47,48]. Does this relationship also exist in the CO_2 copolymerization? In order to answer these questions, the research on the impact of the cation core structure was conducted using the following imidazolium salts: 1-butyl-3-methylimidazoliumbromide (bmimBr), 1-octyl-3-methylimidazolium bromide (C_8mimBr), 1-decyl-3-methylimidazoliumbromide (C_{10}mimBr), 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) while varying the alkyl chain at position R_2 with a fixed methyl group at R_1 (Scheme 1).

An inspiring correlation between alkyl chain length of R_2 and the copolymerization results is observed in Table 2. As illustrated, the rates of copolymer production are gradually enhanced and catalytic activities of (salen)$Cr^{III}Cl$ are over 2-fold upon increasing the alkyl chain length from *n*-butyl to *n*-dodecyl (TOF 108.8 h^{-1} versus TOF 242.5 h^{-1}). The regular change of polydispersity index (M_w/M_n) with alkyl chain length is also prominent from 1.60 to 1.11. It indicates that imidazolium salts with longer alkyl chain length can dramatically result in enhanced activities, better selectivity, and lower polydispersity index. This may be related to the enhanced nucleophilicity of an anion with increasing alkyl chain length [49,50], which could well improve the catalytic activities. In addition, the hydrophobicity of imidazolium salts was increased with longer alkyl chain. Finally, it may be due to the tunable properties of imidazolium-based ionic liquid, such as enhanced solubility of CO_2 with increasing alkyl chain length, which are of benefit for the copolymerization. These imidazolium salts produce slightly smaller turnover frequency (TOF) as compared with Bu_4NCl (TOF, 249.6 h^{-1}) in the same condition and other related cocatalyst, such as phosphonium salts [31]. However, these preliminary experimental results are still informative for the further design of the task-specific ILs to improve the copolymerization.

The observed results also showed a pronounced dependence on the cocatalyst loading when keeping the concentration of catalyst (**1**) constant. As indicated in Table 3, the activities were substantially enhanced upon initially increasing

Table 1
Effect of imidazolium salts with varying structures of anions

Entry[a]	Cocatalyst	TOF[b] (g of polym/g of Cr)	Carbonate linkages[c] (%)	$\overline{M}_w/\overline{M}_n$[d]	$\overline{M}_n$[d]
1	*N*-MeIm	72.5 (61.3)	94	1.35	4515
2	[bmim]BF_4	91.2 (73.1)	93	1.49	2379
3	[bmim]PF_6	54.7 (36.9)	53	1.34	2366
4	[bmim]Cl	130.1 (93.2)	95	1.56	4625
5	[bmim]Br	108.8 (76.8)	96	1.60	4896

[a] All reactions were conducted in the presence of 2.25 equiv of cocatalysts with 500 mg catalyst (**1**) (0.1 mol%) in 80 ml of neat cyclohexene oxide at 80 °C under 55 bar of CO_2 pressures after a reaction time of 4 h.

[b] Mol of CHO consumed/(mol of Cr h).

[c] Estimated by ^1H NMR.

[d] Determined through GPC in THF (5 wt‰).

Table 2
Effect of imidazolium salts with varying structures of cations

Entry[a]	Cocatalyst	TOF[b] (g of polym/g of Cr)	Carbonate linkages[c] (%)	$\overline{M}_w/\overline{M}_n$[d]	$\overline{M}_n$[d]
1	[bmim]Br	108.8 (76.8)	96	1.60	4896
2	[C_8mim]Br	219.1 (155.3)	98	1.18	5998
3	[C_{10}mim]Br	230.0 (160.8)	98	1.16	6286
4	[C_{12}mim]Br	242.5 (169.0)	>99	1.11	6025
5	Bu_4NCl	249.6 (184.3)	>99	1.20	7582

[a] Copolymerization conditions: 500 mg catalyst (**1**) (0.1 mol%), 80 ml of neat cyclohexene oxide, 2.25 equiv of cocatalysts, 55 bar of CO_2 pressure, 80 °C after a designated reaction time of 4 h.

[b] Mol of CHO consumed/(mol of Cr h).

[c] Estimated by ^1H NMR.

[d] Determined through GPC in THF (5 wt‰).

Table 3
Copolymerization results of different [C_8mim]Br loadings

Entry[a]	Equiv of cocatalyst	TOF[b]	Carbonate linkages[c] (%)
1	0	–	–
2	2.25	219.1	98
3	13.5	286.3	94
4	20	86.2	56

[a] 500 mg catalyst (**1**) (0.1 mol%) was dissolved in 80 ml of neat cyclohexene oxide, 55 bar of CO_2 pressure, 80 °C after 4 h.

[b] Mol of CHO consumed/(mol of Cr h).

[c] Estimated by ^1H NMR.

the concentration of imidazolium salts like [C_8mim]Br. However, there was a dramatic decrease in the activities of catalyst (**1**) as well as an increase in polyether linkages at a higher cocatalyst loading (20 equiv). It means that excess loading of imidazolium ionic liquid could hind the formation of active species for the copolymerization.

4. Conclusion

In summary, a series of common imidazolium salts were used as cocatalysts for CO_2 fixation catalyzed by (salen)-Cr^{III}Cl complex for the first time, which will greatly enrich the catalytic system in terms of its tunable property. More importantly, the cation of imidazolium salt with longer alkyl chain length and a more nucleophilic anion displays better reactivity, selectivity and lower polydispersity index in the copolymerization. This pronounced regularity between structural modification of imidazolium salts and the corresponding coupling results may enlighten us to devise novel types of task-specific ILs and therefore put a new emphasis on the role of ILs in the field of CO_2 chemistry as well as other similar reactions applying nitrogen-containing compounds as cocatalysts.

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