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Short communication

# One-pot reaction of $CO_2$, epichlorohydrin and amine to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by ionic liquids

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ABSTRACT

Ionic liquids were firstly used as catalysts for one-pot synthesis of 4-(phenylamino)methyl-ethylene carbonate from $CO_2$, epichlorohydrin and aniline without the utilization of any solvents or additives. The effects of the ratio of epichlorohydrin and aniline, catalyst amount, reaction temperature, time and initial $CO_2$ pressure were investigated. The catalytic activity of the reaction was affected by the anions of ionic liquids and followed the order of $Cl^- > Br^- > OAc^- > BF_4^- > PF_6^-$. The possible reaction mechanism was proposed based on the reaction results.



## 1. Introduction

$CO_2$ from combustion of fossil fuels is regarded as the main greenhouse gas. Reduction of $CO_2$ emissions has attracted intense attention from governments and scientists. However, with the growth of world population and the improvement of modernization, it is apparent that atmospheric $CO_2$ concentration will continue to monotonically increase for the foreseeable future due to energy demand. Therefore, besides minimizing $CO_2$ emissions, it is significant to utilize $CO_2$ as a renewable feedstock for generating energy, material and fine chemicals [1–3].

One of the promising routes using $CO_2$ as a raw material is the production of cyclic carbonates by the cycloaddition of $CO_2$ with epoxides. This is partially because cyclic carbonates are useful as intermediates for polycarbonates, electrolytes in lithium ion batteries, green solvents and important intermediates in organic synthesis. Various catalysts have been developed for the process, including metal halides, metal oxides, metal complexes, Schiff base and so on [4–6]. With the unique properties including negligible vapor pressure, good thermal stabilities, wide liquid temperature ranges, unlimited structural variations, ionic liquids have also received much attention in the field of cycloaddition of $CO_2$ with epoxides recently [7]. The reported ionic liquids for cycloaddition of $CO_2$ with epoxides include imidazolium salts [8–10], quaternary ammonium salts [11], quaternary phosphonium salts [12], metal halide ionic liquids [13–16], supported ionic liquids [17–28].

Although significant studies have been made for synthesis of cyclic carbonates, the reports related to synthesize amino functionalized cyclic carbonate with one-pot reaction involving $CO_2$ are still very rare. Herein we report, firstly, the one-pot reaction of $CO_2$, epichlorohydrin and amine to synthesize amino functionalized cyclic carbonates in the presence of catalytic amount of ionic liquids (Scheme 1).

## 2. Experimental

### 2.1. Reagents

All chemicals were purchased commercially and used without further purification. The imidazolium ionic liquids such as 1-butyl-3-methyl-imidazolium chloride (BmimCl), 1,2-dimethyl-3-butyl-imidazolium chloride (BmmimCl), 1-butyl-3-methyl-imidazolium acetate (BmimOAc), 1,2-dimethyl-3-butyl-imidazolium acetate (BmmimOAc), 1-butyl-3-methyl-imidazolium bromide (BmimBr), 1,2-dimethyl-3-butyl-imidazolium bromide (BmmimBr), 1-butyl-3-methyl-imidazolium tetrafluoroborate ($BmimBF_4$), 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BmimPF_6$) were synthesized according to the literature.

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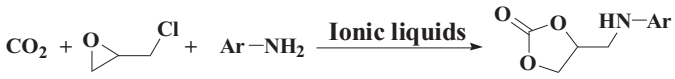



**Scheme 1.** One-pot reaction to synthesize amino functionalized cyclic carbonate.

### 2.2. A representative procedure for the reaction of $CO_2$, epichlorohydrin and aniline to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by BmimCl

The reaction of $CO_2$, epichlorohydrin and aniline was carried out in a stainless-steel autoclave reactor with an inner volume of 50 mL. BmimCl (0.1 mmol, 0.018 g), epichlorohydrin (6 mmol, 0.555 g) and aniline (2 mmol, 0.186 g) were added to the autoclave. The reactor was purged with $CO_2$ two times and pressurized with $CO_2$ to 0.5 MPa at ambient temperature. The reaction mixture was heated to 60 °C and kept for 6 h under stirring. The reactor was cooled to room temperature and depressurized to an atmospheric pressure. Dodecane was added to the reaction mixture as an internal standard for GC analysis. GC analyses were performed on a Shimadzu GC-14B equipped with a capillary column CBP1-M25-025. The yields of 4-(phenylamino)methyl-ethylene carbonate (**1**) and 1-chloro-3-phenylamino-propan-2-ol (**2**) were calculated based on the amount of aniline. The pure products were obtained by chromatography on silica gel and characterized by $^1$H NMR and GC-Mass. NMR spectra were recorded on Bruker with tetramethylsilane as the internal standard.

## 3. Results and discussion

### 3.1. One-pot reaction of $CO_2$, epichlorohydrin and aniline to synthesize 4-(phenylamino)methyl-ethylene carbonate catalyzed by various ionic liquids

Reaction of $CO_2$, epichlorohydrin and aniline in the presence catalytic amount of ionic liquids afforded amino functionalized cyclic carbonate (**1**) and the ring opening product, 1-chloro-3-phenylamino-propan-2-ol (**2**) smoothly. It is reasonably assumed that the ring opening product was formed by the aminolysis of epichlorohydrin with aniline [29,30]. Various ionic liquids with different cations and anions have been applied to catalyze the reaction and the results were summarized in Table 1. BmimCl and BmmimCl gave **1** and **2** in the combined yields of 90% and 87%, and relative higher selectivity of **1** among the various ionic liquids, respectively (Table 1 entries 1, 2). Other ionic liquids such as BmimBr, BmmimBr, BmimOAc and BmmimOAc also afforded **1** and **2** in relatively good combined yields of 72–80% (Table 1 entries 3–6). However, $BmimBF_4$ and $BmimPF_6$ showed the low catalytic activity for this reaction and gave the combined yields in 59% and 33%, respectively (Table 1 entries 7, 8). These results indicate that anions of imidazolium based ionic liquids play an important role in the reaction, and the catalytic activity follows the order of $Cl^- > Br^- > OAc^- > BF_4^- > PF_6^-$. Meanwhile, with same anions, Bmmim based ionic liquids, in which the C2-proton of imidazolium is replaced by a methyl group, gave similar catalytic activity compared with Bmim based ionic liquids. These results apparently differ from our previous works, in which C2-proton of imidazolium plays a dominating role in the reactions involving carbonates [31,32]. In addition, both BmimCl and BmmimCl had higher catalytic activity than $Bu_4NCl$ (Table 1 entries 1, 2, 9). This indicates that the imidazolium-based cations of the ionic liquids also play a momentous role in catalyzing the reaction of $CO_2$, epichlorohydrin and aniline. Conclusively, BmimCl was selected as a model catalyst for further investigation.

### 3.2. Optimization of reaction conditions

To optimize the reaction parameters, the effects of ratio of the epichlorohydrin and aniline, catalyst amount, temperature, reaction time and initial $CO_2$ pressure were investigated.

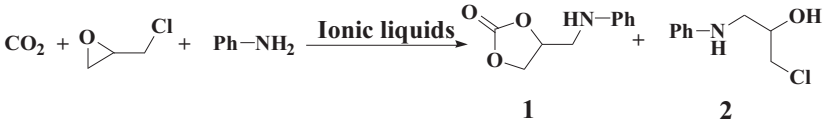
#### 3.2.1. Effect of ratio of the epichlorohydrin and aniline

The influence of the molar ratio of epichlorohydrin and aniline was shown in Fig. 1. The yield of **1** increased dramatically with increasing molar ratio of epichlorohydrin and aniline from 1 to 3 and almost leveled off with further increase of epichlorohydrin, and reached to the highest yield of 65% at the molar ratio of 8. However, the yield of **2** increased from the ratio of 1 to 2, then decreased from ratio of 2 to 8. Considering economical efficiency, the reactant molar ratio of 3 was used in the following investigation.

#### 3.2.2. Effect of catalyst amount

The influence of the catalyst amount was shown in Fig. 2. Without any catalyst, the reaction cannot go smoothly. With the increase of the amount of BmimCl from 0 to 5 mol%, the yields of

**Table 1**
Reaction of $CO_2$, epichlorohydrin and aniline catalyzed by various ionic liquids.[a]




**1** **2**

| Entry | Ionic liquid | Yield/%[b] | |
|---|---|---|---|
| | | **1** | **2** |
| 1 | BmimCl | 58 | 32 |
| 2 | BmmimCl | 53 | 34 |
| 3 | BmimBr | 31 | 49 |
| 4 | BmmimBr | 36 | 44 |
| 5 | BmimOAc | 46 | 30 |
| 6 | BmmimOAc | 44 | 28 |
| 7 | $BmimBF_4$ | 22 | 37 |
| 8 | $BmimPF_6$ | <1 | 32 |
| 9 | $Bu_4NCl$ | 36 | 32 |

[a] Reaction conditions: aniline: 2 mmol, epichlorohydrin: 6 mmol, ionic liquid: 0.1 mmol, 60 °C, 6 h, 0.5 MPa $CO_2$.
[b] GC yield.