



# Investigation of using multi-hydroxyl ionic liquid polymer as catalyst to produce propylene carbonate



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## ABSTRACT

Ionic liquid with a single hydroxyl group, 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB), was prepared. It was found that HEMIMB could be an efficient catalyst for CO<sub>2</sub> cycloaddition to propylene oxide to produce propylene carbonate (PC). An ionic liquid polymer with multi-hydroxyl groups poly(1-2-hydroxyl-ethyl)-3-vinylimidazolium bromide (PHEVIMB) was also prepared. In this study, both catalytic reaction performances of HEMIMB and PHEVIMB were investigated. Results showed that product separation and catalyst recycles in the process of PHEVIMB catalytic reaction system was much more efficient with a yield of 55.5%, even after three consecutive catalyst reuses. Meanwhile, the separation was less time-efficient for homogeneous catalytic system of HEMIMB molecules with a single hydroxyl group despite of a yield of 92.4%. When it comes to practical industrial process design, the single component with multifunctional ionic liquid polymer, as catalyst, may be considered effective and friendly process.

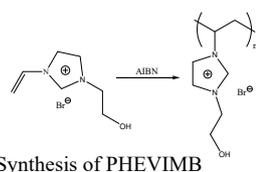
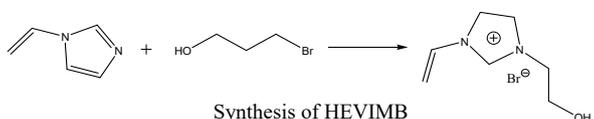
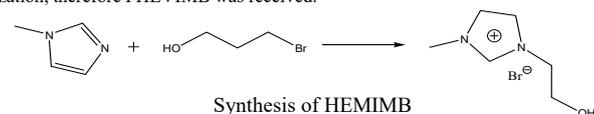
## INTRODUCTION

Cyclic carbonates are widely used in industry due to their potential applications as aprotic high-boiling point solvents, monomers, fuel additives, and intermediates in the production of pharmaceutical and fine chemicals. Cyclic carbonates are usually obtained via the reaction of an alcohol (or phenol) with phosgene as well as the reaction of an alcohol with carbon monoxide (CO). However, since phosgene and CO are extremely toxic, using carbon dioxide (CO<sub>2</sub>) as carbonyl source has recently become research of interest. Typical reactions to produce cyclic carbonates include cyclization of CO<sub>2</sub> with epoxides. CO<sub>2</sub> can be recycled from various industries, for example, fermentation industry, petrochemical industry, and metalworking industry. Hence, using CO<sub>2</sub> as a raw material to produce chemicals could potentially mitigate greenhouse gas that causes global warming.

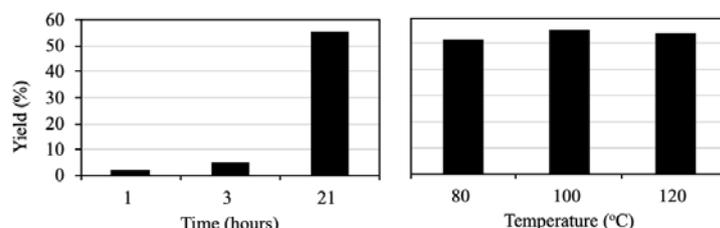
Although CO<sub>2</sub> is chemically inactive, the reactions with numerous organics are still achievable through catalysis. Numerous catalysts have been developed for these reactions. Among all catalysts, ionic liquids show a great potential as a novel class of green solvents and catalysts for CO<sub>2</sub> utilization reactions. To promote reactivity, ionic liquids are usually incorporated with other suitable catalysts, such as acid, base, and metal complex. Li et al. [1] investigated reaction performance of chemical fixation of CO<sub>2</sub> to propylene oxide (PO) producing propylene carbonate (PC), and found that conversion could reach 95% under catalysis of ionic liquid, 1-butyl-3-methylimidazolium bromide ([Bmim]Br) in conjunction with ZnCl<sub>2</sub>. Shi et al. [2] studied cyclohexylamine carbonylation to produce urea and demonstrated that conversion could reach as high as 98% by using [Bmim]Cl/CsOH as a catalyst. On the other hand, the activities of ionic liquids became very low in the absence of co-catalysts. Sun et al. [3] prepared OH-functionalized ionic liquid as simple catalyst, without co-catalyst, for synthesis of cyclic carbonates, and found that OH group was critical for the reaction to proceed efficiently due to its cooperation function of ring opening of epoxides. However, in the homogeneous system composed of reacting mixture with catalyst, reactant of propylene oxide, and product of propylene carbonate, product and catalyst are difficult to separate for reuse. From environmental and practical point of view, systems with heterogeneous catalyst are more desirable in chemical processes [4]. In this work, we prepare an ionic liquid polymer with multi-hydroxyl centers as an efficient catalyst in a heterogeneous reaction system for synthesis of propylene carbonate. This information could be very important for process design in future industrial processes.

## METHOD

Typical synthesis procedure of 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMIMB) was used based on published procedures [3]. The reaction scheme and the synthesis of ionic liquid polymers are shown below. A monomer, 1-(2-hydroxyl-ethyl)-3-vinylimidazolium bromide (HEVIMB), was obtained as follows: 2-bromidethanol (0.16 mmol) was added dropwise to the mixture of freshly distilled 1-vinylimidazole (0.14 mmol) and dry toluene (50 mL) in a three-necked glass flask, and then stirred for 3 days. The lower layer of the solution was isolated and repeatedly washed by toluene and ether, followed by solvent evaporation and then dried in vacuum for 1 hour, to obtain HEVIMB. <sup>1</sup>H-NMR of HEVIMB (300 MHz, D<sub>2</sub>O-d) was δ: 9.1(1H, s, NCHN), 7.8(1H, s, NCHCHN), 7.6(1H, s, NCHCHN), 7.1(1H, quintet, CH<sub>2</sub>CHN), 5.4(2H, d, CH<sub>2</sub>CHN), 4.4(2H, t, NCH<sub>2</sub>CH<sub>2</sub>OH), 3.9(2H, t, NCH<sub>2</sub>CH<sub>2</sub>OH), and 3.5(1H, t, NCH<sub>2</sub>CH<sub>2</sub>OH). An addition polymerization of HEVIMB was conducted by dissolving 5 g of HEVIMB in 15 mL ethanol, then adding 5 wt% of 2,2-azobisisobutyronitrile (AIBN) into the solution, followed by heating at 70°C for 1 day, and finally obtaining a yellow turbid solution. It was further treated with acetone to collect the precipitates, dried for 30 minutes in vacuum and obtain poly(1-2-hydroxyl-ethyl)-3-vinylimidazolium bromide, also known as PHEVIMB. <sup>1</sup>H-NMR showed that HEVIMB has absorbed peaks of hydrogen at δ = 7.1, 5.8 and 5.4, but PHEVIMB has no signal at δ = 5.4 to 7.1, suggesting that the bond of the ethylene monomer and hydrogen in HEVIMB were broken during polymerization, therefore PHEVIMB was received.

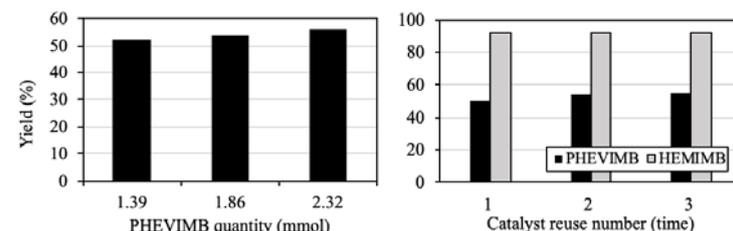


## RESULTS



Effect of time (left) and temperature (right) on PC yields

PHEVIMB was able to catalyze the cyclization of carbon dioxide and propylene oxide to obtain higher quality of propylene carbonate. However, reaction time could be longer than expected due to mass transfer resistance between reactants and catalysts, which slowed the reaction taking place on the surface of catalyst. According to reaction mechanism proposed by Sun [3], OH group and the Lewis basic site bromine anion in ionic liquid coordinately attack the different parts of epoxide molecules, resulting in epoxide ring opening and further reacting with CO<sub>2</sub> molecules. In addition, steric hindrance of long twisting polymer chains in PHEVIMB may prevent their OH groups from participating in ring opening of propylene oxide and further reacting with CO<sub>2</sub> to produce propylene carbonate.



Effect of PHEVIMB quantity and reuse of catalyst with single OH group and multiple OH groups on PC yield

The reaction yield of PHEVIMB occurred to be relatively low, since the single OH molecule in ionic liquid tended to be more active than multiple OH groups bonded in ionic liquid polymeric chains. Frequency of the single OH ionic liquid molecules collisions with reactant molecules in homogeneous mixture was higher than multiple OH ionic liquid molecules in heterogeneous mixture. Therefore, reactive capability of PHEVIMB was lower [5]. On the other hand, Figure 6 also indicated that these catalysts were still active as repeated 3 times. Also, the catalysis process of the ionic liquid polymer with multiple OH groups demonstrated in this study could be achieved on a convenient and process-friendly way. After reaction, PO was removed by evaporation, HEMIMB recycling was performed by sophisticated high vacuum distillation, and PHEVIMB catalyst could be recovered conveniently by filtration from the heterogeneous mixture for reuses. Due to the effectiveness of separation, PHEVIMB catalysis process could be further optimized to substantially increase yields with increased recycle stream of unreacted feed materials economically.

## CONCLUSIONS

Reaction and separation are inseparable in process design. The catalytic reaction performance of inserting CO<sub>2</sub> to PO and to product PC was investigated under catalysis of HEMIMB with only one single OH group, and PHEVIMB with multiple OH groups. The heterogeneous catalysis of PHEVIMB remained efficient even after three repeated uses and its yield came to 55.5%, while for homogeneous catalysis of HEMIMB the yield was up to 92.4%. However, the product separation and catalyst recycles was simpler for PHEVIMB catalytic process than for HEMIMB. From design point of view, PHEVIMB could be a valuable catalyst in the CO<sub>2</sub> insertion process.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] F. Li, L. Xiao, C. Xia, B. Hu, Chemical fixation of CO<sub>2</sub> with highly efficient ZnCl<sub>2</sub>/[Bmim]Br catalyst system, *Tetrahedron Letters*, 45(2004) 8307-8310.
- [2] F. Shi, Y. Deng, T. Sima, J. Peng, Y. Gu, B. Qiao, Alternative to phosgene and carbon monoxide: Synthesis of symmetric urea derivatives with carbon dioxide in ionic liquids, *Angew. Chem. Int. Ed.* 42(2003) 3257-3260.
- [3] Jian Sun, Suojang Zhang, Weiguo Cheng, Junyi Ren. Hydroxyl-functionalized ionic liquid: a novel efficient catalyst for chemical fixation of CO<sub>2</sub> to cyclic carbonate. *Tetrahedron Letters* 49 (2008) 3588 - 3591.
- [4] Mengshuai Liu, Jianwen Lan, Lin Liang, Jianmin Sun and Masahiko Arai. Heterogeneous catalytic conversion of CO<sub>2</sub> and epoxides to cyclic carbonates over multifunctional tri-*s*-triazine terminal-linked ionic liquids. *Journal of Catalysis* Volume 347, March 2017, Pages 138-147
- [5] Richard Horng, Shin-Ku Lee. Stepwise Inhibition Effect of Multitroxy Radicals on Styrene Polymerization. *Applied Mechanics and Materials* Vol. 440 (2014) pp 31-36