

Synthesis of Tetrabutylphosphonium Carboxylate Ionic Liquids and Its Catalytic Activities for the Alcoholysis Reaction of Propylene Oxide

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S Supporting Information

ABSTRACT: Four tetrabutylphosphonium carboxylate ionic liquids ($[P_{4444}][CA]$) were prepared, characterized, and used as catalysts for the synthesis of propylene glycol methyl ether (PGME) from the alcoholysis reaction of propylene oxide (PO) with methanol. The effects of various parameters such as the kind of ILs, temperature, reaction time, catalyst loading, and molar ratio of the reactants on PGME yield and selectivity were also studied in detail. The results indicated that tetrabutylphosphonium butyrate ($[P_{4444}][Buty]$) exhibited the best catalytic activity in comparison to three other carboxylate ILs, and PGME was produced in nearly 94% yield under mild conditions. In addition, $[P_{4444}][Buty]$ was found to exhibit good catalytic activities and selectivities in other alcoholysis reactions of epoxides with various alcohols, such as PO with *n*-propanol, PO with *n*-butanol, 1-(allyloxy)-2,3-epoxypropane with methanol, and 1,2-epoxybutane with methanol. $[P_{4444}][Buty]$ could also be recovered easily and used repetitively at least 10 times without an obvious decrease in activity and quantity. Therefore, $[P_{4444}][Buty]$ proved to be an effective recyclable homogeneous catalyst for the synthesis of PGME and showed potential application in industry.

INTRODUCTION

Propylene glycol methyl ether (PGME) is an important intermediate in chemical and pharmaceutical industries. Due to its hydroxyl and ether groups, it is used widely as a versatile solvent for coating material, anti-icers, printing inks, leather dyeing, etc.^{1,2} And then PGME is expected to be a safe substitute for the toxic and teratogenic solvents such as ethylene glycol ether, benzene, toluene, and acetone, owing to its negligible toxicity and lower impact on the environment.³ Therefore, the production of PGME has been growing fast in the past years due to a continual demand.

Among the methods developed for the synthesis of PGME, the propylene oxide (PO) route was the most convenient and suitable scheme for industrial production in terms of atom-economy and energy-efficiency. PGME is generally synthesized by the alcoholysis reaction of PO with methanol in the presence of acid or base as catalyst, and the suggested reaction mechanism is considered as Scheme 1. As seen from Scheme 1, the epoxide ring of PO might preferentially open at the least sterically hindered position over a basic catalyst leading to most secondary alcohols, whereas an acid catalyst facilitates the formation of primary alcohols.^{4–6} However, compared to the primary alcohol (2-methoxy-1-propanol), the secondary alcohol (1-methoxy-2-propanol) has a much lower toxicity and impact on the environment.⁴ Therefore, the synthesis of 1-methoxy-2-propanol with high efficiency and selectivity in the presence of base catalysts has attracted much attention.

At present, PGME is mostly produced by using sodium hydroxide, sodium ethoxide, or triethylamine as homogeneous catalysts through the alcoholysis reaction of PO with methanol. However, these conventional base catalysts are not entirely satisfactory due to their several drawbacks such as the difficulties in separation and recovery of catalyst, relatively

low reaction selectivity, liquid waste treatment, and corrosion problems. Although solid base catalysts such as amine modified porous silica,⁷ metal oxides,⁸ and zeolites⁹ overcome some shortcomings compared with the traditional base to a certain extent, there are also other defects such as high mass transfer resistance, relatively low activity, inconvenient regeneration of catalyst, and so on, which all limited their practical applications in the synthesis of PGME. Therefore, there is an urgent need to develop environmentally friendly, highly efficient, and easily reusable novel catalysts for the PGME synthesis process.

In recent years, ionic liquids (ILs) have attracted much interest as relatively clean and promising catalysts and alternative solvents. Most ILs possess distinct physical-chemical properties such as low melting point, negligible vapor pressure, excellent thermal stability, remarkable solubility, and effortless reusability. Owing to such unique properties, ILs present a broad application prospect and have been extensively employed in catalysis,¹⁰ electrochemistry,¹¹ liquid-liquid extraction,¹² and gas separation,¹³ etc. In particular, many studies on the catalysis of ILs have been done with high catalytic activities and selectivities.^{14–16} Recently, carboxylate ILs, as a prototype of basic ILs, have received much attention and have been mainly applied to Knoevenagel condensation,¹⁷ Michael addition,¹⁸ and Henry reactions.¹⁹ In addition, ammonium carboxylate ILs are also considered to be excellent absorbent for the absorption of CO₂ and SO₂.²⁰ However, to the best of our knowledge, there are few studies in the literature on the application of phosphonium carboxylate ILs in

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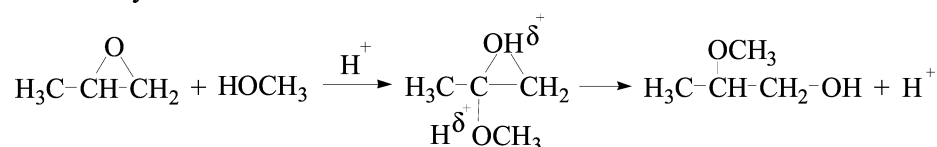
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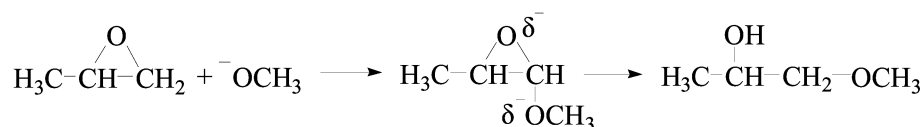
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Scheme 1. Suggested Reaction Mechanism Using Acid and Base as Catalysts

Acid-catalyzed reaction:



Base-catalyzed reaction:



alcoholysis reactions. As is well-known, phosphonium ILs are much more thermally stable at high temperatures than the corresponding ammonium and imidazolium ILs.²¹ Furthermore, acidic protons are absent in the phosphonium cation, unlike the imidazolium cation, implying that phosphonium ILs could be used in a strongly basic environment. This shows that phosphonium carboxylate ILs have potential to be efficient media for the alcoholysis reactions.

In this work, a series of tetrabutylphosphonium carboxylate ionic liquids ($[\text{P}_{4444}][\text{CA}]$) were synthesized via simple neutralization reactions, and then their catalytic behavior in the alcoholysis reaction of PO with methanol was investigated for the first time. The reaction parameters such as kind of ILs, temperature, catalyst loading, and initial molar ratio of reactants were explored in detail to obtain the optimum conditions. In addition, the reusability of $[\text{P}_{4444}][\text{CA}]$ and the alcoholysis reaction of different epoxides with alcohols in $[\text{P}_{4444}][\text{CA}]$ were also studied.

EXPERIMENTAL METHODS

Materials. Anion exchange resin Amberlite-IRA400 and Amberlite-IRA410, tetrabutylphosphonium bromide (purity $\geq 99\%$), tributylphosphonium (purity $\geq 98\%$), 1-allyloxy-2,3-epoxypropane (purity $\geq 99\%$), 1,2-epoxybutane (purity $\geq 99\%$), epichlorohydrin (purity $\geq 99\%$), styrene oxide (purity $\geq 98\%$), and cyclohexene epoxide (purity $\geq 98\%$) were purchased from Aladdin (Shanghai, China). Other reagents such as propylene oxide, triethylamine, methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, formic acid, acetic acid, propionic acid, and butyric acid were of analytical grade and used without any further purification.

Preparation and Characterization of $[\text{P}_{4444}][\text{CA}]$. Four ILs, $[\text{P}_{4444}][\text{For}]$, $[\text{P}_{4444}][\text{Ace}]$, $[\text{P}_{4444}][\text{Prop}]$ and $[\text{P}_{4444}][\text{Buty}]$ were synthesized by the procedure as follows. In the first step, $[\text{P}_{4444}]\text{OH}$ aqueous solution was obtained from the metathesis of $[\text{P}_{4444}]\text{Br}$ with anion exchange resin Amberlite-IRA400 following the method in the previous literatures.^{22,23} In the second step, $[\text{P}_{4444}]\text{OH}$ aqueous solution was then neutralized with a slight excess of carboxylic acid by stirring at room temperature for 6 h. After neutralization, water was evaporated under vacuum at 333 K. Then $[\text{P}_{4444}][\text{CA}]$ was in a vacuum oven containing P_2O_5 at 353 K for 48 h to remove the excess acid and the residual water prior to use. Four $[\text{P}_{4444}][\text{CA}]$ ILs were thus obtained with the yields of more than 80% (based on the amount of $[\text{P}_{4444}]\text{Br}$). After that, the structures of $[\text{P}_{4444}][\text{CA}]$ ILs were confirmed by ^1H NMR, FT-IR spectra, and thermal analysis, and then the density, viscosity, and

conductivity of these four $[\text{P}_{4444}][\text{CA}]$ ILs were measured. All the detailed characterization results were given in the Supporting Information. In addition, the pH values of ILs solution (0.1 mol/L IL) were measured with a PHS-3C pH-meter equipped with a recorder (Shanghai Leici instrument Inc., Shanghai, China). All the measurements were carried out in vessels externally thermostated at 25 °C with a water jacket, and then the experimental results were summarized in Table 1.

Table 1. pH Values of Different IL Solutions^a

catalyst	pH value	
	water solution	methanol solution
$[\text{P}_{4444}][\text{Buty}]$	8.37	9.51
$[\text{P}_{4444}][\text{Prop}]$	8.16	9.37
$[\text{P}_{4444}][\text{Ace}]$	8.09	9.34
$[\text{P}_{4444}][\text{For}]$	7.84	8.67
$[\text{TMG}][\text{Ace}]$	7.46	8.55
$[\text{N}_{1111}][\text{Buty}]$	7.34	8.25
$[\text{N}_{2224}][\text{HSO}_4]$	2.51	7.35
$[\text{BSEt}_3\text{N}][\text{HSO}_4]$	0.67	6.62
$[\text{BSmim}][\text{HSO}_4]$	0.68	6.71

^aSolution in water and methanol at 25 °C.

Typical Procedures for the PGME Synthesis. In a typical run, the alcoholysis reactions were carried out in a 50 mL glass stirred tank reactor immersed in a constant temperature oil bath for maintaining the required reaction temperature. PO (20 mmol) and methanol (60 mmol) were charged into the reactor fitted with a reflux condenser. When the temperature was raised to the desired value (e.g., 353 K), the catalyst $[\text{P}_{4444}][\text{Buty}]$ (0.5 mmol) was added into the reactor and the reaction mixture was then allowed to proceed for 1–8 h with vigorous stirring. Samples were taken from the reactor at regular intervals and detected by gas chromatography (GC). No byproducts were found by GC. After the reaction was completed, the reaction mixture was cooled to room temperature and extracted with diethyl ether (5 mL \times 3). Then the system forms a liquid–liquid biphasic, and the lower phase containing carboxylate ILs could be easily separated from the reaction mixture by simple decantation. After that, the catalyst carboxylate ILs was further in a vacuum oven at 363 K for 12 h to remove the residual reactants prior to reuse in the next run.

Analysis. The samples were analyzed using HP 6890 GC analyzer (Agilent) equipped with a hydrogen flame ionization detector (FID). A capillary column HP-1 (methyl polysiloxane, 30 m \times 0.32 mm \times 1 μm) was used to detect the composition

of the samples with nitrogen as the carrier gas at a flow rate of about 3 mL/min. *n*-Propanol was used as the internal standard to calculate the amount of the products. The temperature of the column, the inlet, and the detector were kept at 373, 473, and 523 K, respectively.

Definition of PGME Yield and Selectivity. The yield of PGME is defined as the ratio of the number of moles of PGME production in the reaction to the total number of moles of PO initially added. The selectivity for 1-methoxy-2-propanol is defined as the ratio of the number of moles of 1-methoxy-2-propanol to the number of moles of the two isomers.

$$\text{yield} = \frac{\text{moles of (1-methoxy-2-propanol)}}{\text{moles of propylene oxide initially added}}$$

$$\text{selectivity} = \frac{\text{moles of (1-methoxy-2-propanol)}}{\text{moles of (1-methoxy-2-propanol)} + \text{moles of (2-methoxy-1-propanol)}}$$

RESULTS AND DISCUSSION

Catalyst Selection. The alcoholysis reaction of PO with methanol in the presence of $[P_{4444}][CA]$ ILs and other base catalysts was conducted to assess their catalytic activities. As seen from Table 2, combined with the pH values from Table 1, it was obviously indicated that the catalysts $[P_{4444}][CA]$ ILs displayed various catalytic performances, and the catalytic performances of $[P_{4444}][CA]$ ILs were closely relevance to their basicities. The IL possessing strong basicity can induce a relatively high yield of PGME. For example, compared with other three carboxylate ILs, $[P_{4444}][Buty]$ shows more alkalinity

Table 2. Results of Alcoholysis of PO with Methanol in the Presence of Different Catalysts^a

entry	catalyst	yield (%)	selectivity (%)
1	$[P_{4444}][For]$	74.5	90.7
2	$[P_{4444}][Ace]$	86.8	93.6
3	$[P_{4444}][Prop]$	81.5	93.7
4	$[P_{4444}][Buty]$	93.8	95.9
5	$[TMG][Ace]$	11.4	93.1
6	$[N_{1111}][Buty]$	47.8	82.6
7	$[N_{2224}][HSO_4]$	13.4	44.5
8	$[BSmim][HSO_4]$	7.7	33.9
9	$[BSEt_3N][HSO_4]$	6.2	29.5
10 ^b	$[TMG][Ace]$	87.6	94.7
11 ^c	$[Ch][OH]$	90.3	94.6
12	blank		
13	tributylphosphine		
14	ammonium acetate		
15	sodium acetate	22.6	91.1
16	sodium butyrate	14.1	90.6
17	NaOH	87.0	90.1
18	triethylamine	84.9	84.1
19 ^d	Amberlite-IRA400	6.0	80.6
20 ^d	Amberlite-IRA410	5.2	83.7

^aReaction conditions: PO (20 mmol), methanol (60 mmol), catalyst loading (0.5 mmol), reaction temperature (353 K), reaction time (6 h), 50 mL round-bottom flask. ^bThe results were taken from ref 24. ^cThe results were taken from ref 25. ^dReaction conditions: PO (20 mmol), methanol (60 mmol), catalyst loading (0.173 g), reaction temperature (353 K), reaction time (6 h), 50 mL round-bottom flask.

and thus catalyzes the reaction to have the highest yield of 93% and selectivity of 96% at 6 h (Entries 1–4). Subsequently, we investigated the catalytic activities of other ILs such as $[TMG][Ace]$, $[N_{1111}][Buty]$, $[N_{2224}][HSO_4]$, $[BSmim][HSO_4]$, and $[BSEt_3N][HSO_4]$ in the alcoholysis reaction. It was showed that $[TMG][Ace]$ and $[N_{1111}][Buty]$, as other types of carboxylate ILs, performed good selectivity but low PGME yield because of their relatively poor basicity (entries 5 and 6). Three strong Brønsted acidic ILs $[N_{2224}][HSO_4]$, $[BSmim][HSO_4]$, and $[BSEt_3N][HSO_4]$ were found to induce very poor PGME yields and selectivities (entries 7–9). This finding demonstrates that the catalyst acidic ILs is not beneficial to the formation of PGME, whereas the strong basic ILs can facilitate relatively high yields and selectivities. Furthermore, we compared the catalytic performance of $[P_{4444}][Buty]$ with the results of other ILs which published in the literatures. Han et al.²⁴ reported that the catalysis of $[TMG][Ace]$ could obtain the PGME yield of 88% in an autoclave (entry 10). The IL choline hydroxide ($[Ch][OH]$) was reported to have the PGME yield of 90.3% (entry 11), which was the best result so far in the literature.²⁵ All in all, these results were less than or just as comparable with the catalysis performance of $[P_{4444}][Buty]$, showing that $[P_{4444}][Buty]$ performs the best catalytic performance among all the ILs investigated.

For comparison, the alcoholysis reaction of PO with methanol without catalyst or in the presence of other heterogeneous catalysts was also investigated. It was indicated that no product was detected in the blank reaction, showing that the alcoholysis reaction was very difficult to occur without catalyst (entry 12). Meanwhile, tributylphosphine and ammonium acetate were found to have no catalytic effect to the alcoholysis reaction, and low yields were also obtained using sodium acetate and sodium butyrate as catalysts (entries 13–16). This is because these inorganic salts are difficult to dissolve in the alcoholysis reactive system and thus hard to contact with the reactants, leading to the low conversions. In addition, conventional basic catalysts NaOH and triethylamine were found to induce high yields but their selectivities were not satisfied, whereas the catalysis of Amberlite-IRA400 and Amberlite-IRA410 resin resulted in relatively lower yields because of the existence of high transfer resistance (entries 17–20). Therefore, $[P_{4444}][Buty]$ was considered to be a promising catalyst with high activity and selectivity for the synthesis of PGME. $[P_{4444}][Buty]$ thus was chosen as the catalyst for further studies.

Optimization of Reaction Conditions. The effect of reaction temperature ranging from 313 to 373 K on PGME yield and selectivity was investigated using $[P_{4444}][Buty]$ as catalyst. As seen from Figure 1, the yield of PGME increased rapidly with the increase of reaction temperature. For example, the yield of PGME at 6 h increased obviously from 30% to 94% with the rise of temperature from 313 to 353 K. However, while the temperature was further increased to 363 and 373 K, a sharp decrease in the yield of PGME was observed. The yields at 363 and 373 K were reduced to 85% and 68%, respectively. It could be explained that PO and methanol were easy to be vaporized, whereas the carboxylate ILs $[P_{4444}][Buty]$ was almostly nonvolatile at high temperature. For example, at 373 K, the reactants PO and methanol were constantly volatilized and condensed, and thus they had less time for contacting with the catalyst $[P_{4444}][Buty]$, resulting in a yield drop. This demonstrated that the overhigh reaction temperature was negative to PGME yield, and it was unnecessary for this

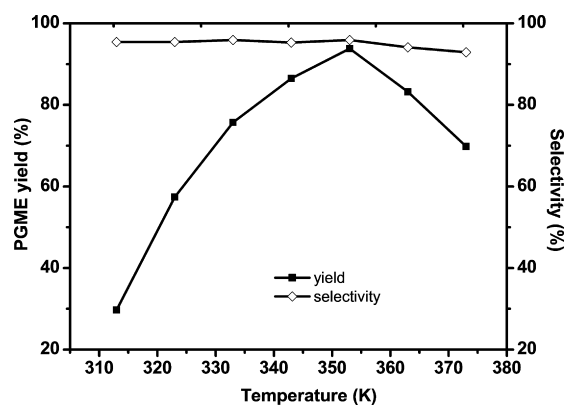


Figure 1. Effect of reaction temperature on the alcoholysis reaction. Reaction conditions: PO (20 mmol), methanol (60 mmol), catalyst loading (0.5 mmol), reaction time (6 h).

reaction. Therefore, an optimized reaction temperature for $[P_{4444}][Buty]$ should be chosen at 353 K for the synthesis of PGME, and this optimized temperature is much lower than that in the case of heterogeneous catalyst.^{26,27}

As is well-known, reaction time and catalyst loading are very important factors in performing the reaction study. The effect of reaction time on PGME yield and selectivity was evaluated, and the results were given in Figure 2. It was found that

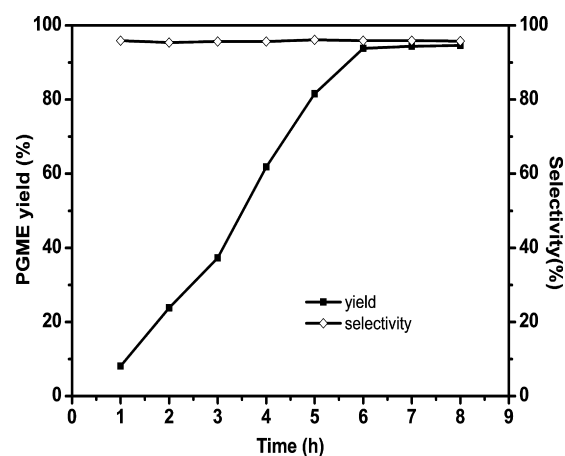


Figure 2. Effect of reaction time on the alcoholysis reaction. Reaction conditions: PO (20 mmol), methanol (60 mmol), catalyst loading (0.5 mmol), reaction temperature (353 K).

reaction time had an obvious influence on PGME yield. The yield of PGME increased rapidly via prolonged reaction time. However, while the reaction time further increased to 7 and 8 h, the yield only improved to a limited extent (from 94% to 95%). This meant that a too long reaction time was not favorable for this reaction, and an appropriate reaction time should be chosen at 6 h for the PGME synthesis process. In addition, Figure 3 shows the effect of catalyst loading on PGME yield and selectivity. With an increase in the relative amount of $[P_{4444}][Buty]$, the rate of alcoholysis reaction was enhanced, resulting in a higher reaction rate for the yield of PGME. For example, when the dosage of $[P_{4444}][Buty]$ was increased from 0.2 to 0.5 mmol, the yield significantly increased from 53% to 94% in 6 h, showing that the amount of catalyst had an obvious influence on the catalytic performance. This was attributed to the increase in alkalinity in the reaction system. However, only

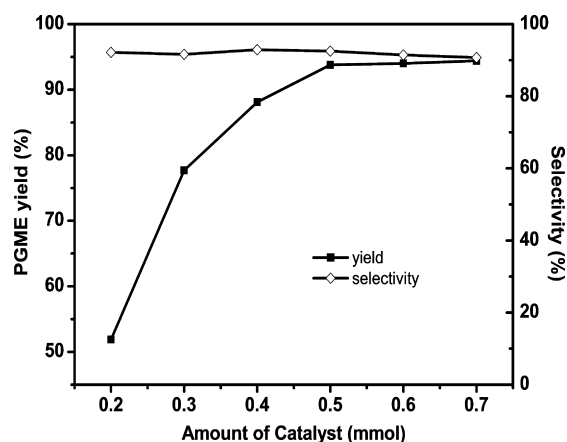


Figure 3. Effect of catalyst loading on the alcoholysis reaction. Reaction conditions: PO (20 mmol), methanol (60 mmol), reaction temperature (353 K), reaction time (6 h).

a slight increase in PGME yield and a smooth decrease in PGME selectivity were observed when the catalyst loading had been increased to 0.7 mmol. Beyond a certain catalyst loading, a further increase in the amount of catalyst was considered to be not very necessary. This experimental result was also consistent with data reported previously.²⁵ Thus, considering the reaction rate and the cost of carboxylate ILs, 0.5 mmol is taken as the optimum catalyst loading and used in most of the alcoholysis experiments.

Figure 4 shows the effect of the molar ratio of methanol to PO on the alcoholysis reaction. It was indicated that increasing

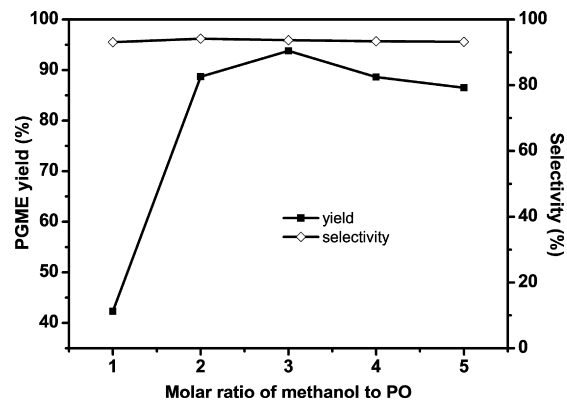


Figure 4. Effect of initial molar ratio of methanol to PO on the alcoholysis reaction. Reaction conditions: PO (20 mmol), catalyst loading (0.5 mmol), reaction temperature (353 K), reaction time (6 h).

the amount of methanol was beneficial to PGME yield, and at the same time PGME selectivity kept mostly unchangeable. The initial molar ratio of 3:1 resulted in the highest yields in comparison to the other molar ratios. Nevertheless, the yield in the initial molar ratio of 4:1 was just comparable to the case of 2:1. In the initial molar ratio of 5:1, the yield was unexpectedly decreased to 87%. This implies that an initial excess of methanol is unfavorable for PGME yield and the conversion of PO. In summary, the optimal molar ratio of methanol to PO is suggested to be 3:1.

Alcoholysis Reaction of PO with Other Alcohols. To obtain more information about other propylene glycol ethers, the alcoholysis reaction of PO with other alcohols in the

presence of $[P_{4444}][Buty]$ was also studied, and the results were listed in Table 3. It was obvious that $[P_{4444}][Buty]$ performed

Table 3. Results of Alcoholysis of PO with Other Alcohols^a

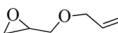




entry	alcohols	yield (%)	selectivity (%)
1	<i>n</i> -propanol	93.2	95.8
2	<i>n</i> -butanol	85.7	95.5
3	<i>n</i> -pentanol	72.2	96.5
4	<i>n</i> -hexanol	71.2	96.9
5	2-propanol	92.4	96.8
6	isopentanol	67.3	95.7
7	cyclohexanol	38.8	96.5
8	<i>tert</i> -butanol	6.7	43.3

^aReaction conditions: PO (20 mmol), alcohol (60 mmol), $[P_{4444}][Buty]$ (0.5 mmol), reaction temperature (353 K), reaction time (1 h).

well in the catalytic reactions of PO with other alcohols, such as *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, 2-propanol, and isopentanol (entries 1–6). The yield was also found to be reduced with the increase of carbon chain length of alcohol (entries 1–4). This can be explained as follows: As seen from the base-promoted reaction mechanism (Scheme 1), the key is to form the intermediate alkoxide by stripping hydrogen proton from the alcohol through the carboxylate ILs. However, with the prolonged carbon chain length of alcohol, the alkoxide is hard to form gradually due to the electron donation of the alkyl group. As a result, the alcohol with a bulk carbon chain induces relatively low yield. Moreover, low yields were obtained and resulted from the steric effect of cyclohexanol and *tert*-butanol in the alcoholysis reactions (entries 7 and 8). These results were also in good agreement with the previous findings.²⁸

Alcoholysis Reaction of Methanol with Other Epoxides. To obtain the effect of substituent on the epoxide on the reactivity, the alcoholysis reaction of methanol with other epoxides in the presence of $[P_{4444}][Buty]$ was also explored, and the results were summarized in Table 4. It was indicated

Table 4. Results of Alcoholysis of Methanol with Other Epoxides^a

Entry	Epoxides	Yield (%)	Selectivity (%)
1		83.5	86.0
2		73.8	88.5
3		13.9	87.5
4		28.5	47.5
5		51.7	54.3

^aReaction conditions: epoxide (20 mmol), methanol (60 mmol), $[P_{4444}][Buty]$ (0.5 mmol), reaction temperature (353 K), reaction time (6 h).

that 1-allyloxy-2,3-epoxypropane and 1,2-epoxybutane showed considerable reactivities (entries 1 and 2), whereas epichlorohydrin, cyclohexene epoxide, and styrene oxide were difficult to form corresponding ethers (entries 3–5). This finding demonstrates that the chloro substituent, being an electron-withdrawing group, is unfavorable for the ring-opening reaction of epoxide, and the high steric effect of phenyl and cyclohexyl group also decreases the reactivities of the epoxide.

Recycling of Catalyst. It is well-known that the stability and reusability of a catalyst system are the two key factors for the potential application in industry. $[P_{4444}][Buty]$ was therefore recycled 10 times to test its activity as well as stability. In each cycle, the catalyst was in vacuum oven before reusing in the next run. The yield and selectivity of PGME from 10 consecutive runs thus were as shown in Figure 5. The

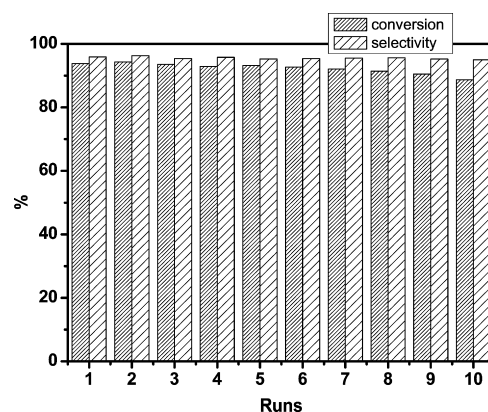


Figure 5. Recycle test of $[P_{4444}][Buty]$ catalyst. Reaction conditions: PO (20 mmol), methanol (60 mmol), catalyst loading (0.5 mmol), reaction temperature (353 K), reaction time (6 h).

experimental results indicated that obvious change in either PGME yield or selectivity was observed during these 10 successive recycles. Thus, $[P_{4444}][Buty]$ was considered to be steadily recycled for the alcoholysis reaction.

CONCLUSIONS

Four carboxylate ILs $[P_{4444}][CA]$ were prepared successfully and applied in the synthesis of PGME in this study. The experimental results showed that $[P_{4444}][Buty]$ exhibited excellent catalytic activities and selectivities in the alcoholysis of PO with methanol and other alcohols such as *n*-propanol, *n*-butanol, *n*-pentanol, and *n*-hexanol. It was also found that increasing the reaction temperature, catalyst loading, and amount of methanol could effectively improve PGME yield in the presence of $[P_{4444}][Buty]$, and the optimal condition was set as follows: temperature of 353 K, reaction time of 6 h, initial molar ratio of 3:1, and catalyst dosage of 0.05 mmol. In addition, $[P_{4444}][Buty]$ could be recovered easily and used repetitively at least 10 times without significant losses of activity and quantity. Therefore, $[P_{4444}][Buty]$ proved to be an excellent recyclable homogeneous catalyst for the synthesis of PGME and showed potential application in industry.

ASSOCIATED CONTENT

Supporting Information

Synthesis details for four CAILs $[P_{4444}][CA]$, FT-IR spectra, TGA curves, and a table of density, viscosity, and conductivity data. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

- [P₄₄₄₄]Br = tetrabutylphosphonium bromide
 [P₄₄₄₄]OH = tetrabutylphosphonium hydroxide
 [P₄₄₄₄]For = tetrabutylphosphonium formate
 [P₄₄₄₄]Ace = tetrabutylphosphonium acetate
 [P₄₄₄₄]Prop = tetrabutylphosphonium propionate
 [P₄₄₄₄]Buty = tetrabutylphosphonium butyrate
 [TMG][Ace] = tetramethylguanidinium acetate
 [N₁₁₁₁][Buty] = tetramethylammonium butyrate
 [N₂₂₂₄][HSO₄] = butyltriethylammonium hydrogen sulfate
 [BSEt₃N][HSO₄] = *N*-(4-sulfonic acid) butyltriethylammonium hydrogen sulfate
 [BSmim][HSO₄] = 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate

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