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PAPER

Highly efficient conversion of carbon dioxide catalyzed by polyethylene glycol-functionalized basic ionic liquids†‡

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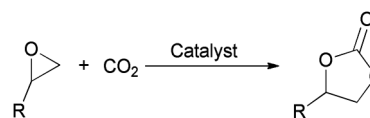
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A series of polyethylene glycol (PEG)-functionalized basic ionic liquids (ILs) were developed for efficient CO₂ conversion into organic carbonates under mild conditions. In particular, BrTBDPEG₁₅₀TBDBr was proven to be a highly efficient and recyclable catalyst for the synthesis of cyclic carbonates without utilization of any organic solvents or additives. This is presumably due to the activation of epoxide assisted by hydrogen bonding and activation of CO₂ by the ether linkage in the PEG backbone or through the formation of carbamate species with the secondary amino group in the IL cation on the basis of *in situ* FT-IR study under CO₂ pressure. In addition, the subsequent transesterification of cyclic carbonate *e.g.* ethylene carbonate (EC) with methanol to dimethyl carbonate (DMC) can also be effectively catalyzed by BrTBDPEG₁₅₀TBDBr, thanks to the activation of methanol by the secondary and tertiary nitrogen in the IL to easily form CH₃O⁻, realizing a so-called “one-pot two-stage” access to DMC from CO₂ without separation of cyclic carbonate by using one kind of single component catalyst. Therefore, this protocol represents a highly efficient and environmentally friendly example for catalytic conversion of CO₂ into value-added chemicals such as DMC by employing PEG-functionalized basic ILs as catalysts.

Introduction

Carbon dioxide from combustion of fossil fuels (coal, petroleum and natural gas) is regarded as the most significant greenhouse gas; hence, CO₂ chemistry (*e.g.* capture and conversion)¹ has attracted significant attention from the scientific community thanks to global warming. As an abundant, nontoxic, non-flammable, easily available, and renewable carbon resource, CO₂ is very attractive as an environmentally friendly feedstock for making commodity chemicals, fuels, and materials.^{1d,2} However, few industrial processes utilize CO₂ as a raw material, because CO₂ is the most oxidized state of carbon, therefore it has inherent thermodynamic stability and kinetic inertness. Accordingly, only if we understand the underlying principles of CO₂ activation, can the goal of using CO₂ as an environmentally friendly and economically feasible source of carbon be achieved.

One of the few commercial routes using CO₂ as a raw material is the insertion of CO₂ into epoxides to afford the 5-membered cyclic carbonates (Scheme 1), which can serve as electrolytes in secondary batteries, valuable monomers of polycarbonates and polyurethanes, aprotic polar solvents, and raw materials



Scheme 1 Cycloaddition reaction of CO₂ with epoxides.

in a wide range of chemical reactions.³ In the past decades, numerous catalysts have been proposed for this reaction,⁴ especially ILs which possess specific features such as high thermal stability, negligible vapor pressure, high loading capacity, easy recyclability and diverse structure/property modulation, although their preparation may involve the use of hazardous solvents or reagents.⁵ The structures of ILs are composed of cation/anion (Lewis acid and Lewis base sites) combinations especially task-specific ILs (TSILs) with various functionalized groups, which has an ability to activate CO₂ molecule and simultaneously activate the other substrates such as epoxide.⁶ For instance, hydroxyl/carboxyl group-functionalized or zinc halides-containing ILs could coordinate with the oxygen atom of epoxides and thus lead to activation of epoxide.^{5c,5d,5g,5k} We also reported efficient conversion of CO₂ catalyzed by Lewis basic ILs, which have tertiary nitrogen in the cation, having the potential with CO₂ to form the carbamate species, an activated form of CO₂.^{5a,7} Although significant advances have been made, the cycloaddition reaction of CO₂ and epoxides are commonly carried out at high pressure, which may not be economically suitable and also pose safety concerns. On the other hand,

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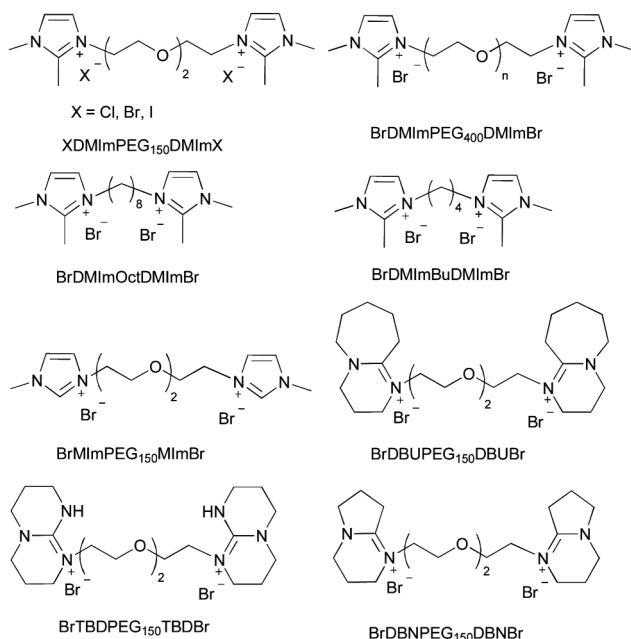
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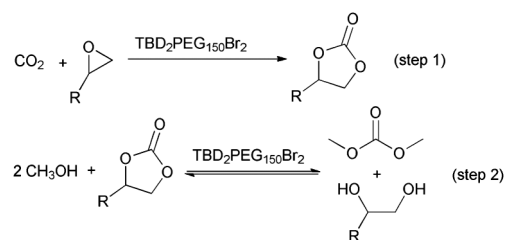
additional solvents,⁸ cocatalysts,⁹ supports¹⁰ or metals¹¹ were needed for the conversion of CO₂ into cyclic carbonates under low pressure in the published process. The challenge is to develop single component catalysts that are capable of activating CO₂ under low pressure (preferably at 1 atm), and thus incorporating CO₂ into cyclic carbonates catalytically under mild conditions.

Herein, we would like to report an efficient process for the synthesis of cyclic carbonates by employing a series of PEG-functionalized basic ILs as efficient and recyclable catalysts (Scheme 2). Interest in employing PEG stems from its distinctive properties; it is inexpensive and thermally stable, has almost negligible vapor pressure, and is toxicologically innocuous and environmentally benign. More importantly, PEG could be regarded as a CO₂-philic material. In other words, "CO₂-expansion of PEG" effect leads to changes in the physical properties of the liquid phase mixture including lowered viscosity and increased gas/liquid diffusion rates,¹² and could presumably facilitate CO₂ conversion with increasing activity. Previously, PEG₆₀₀₀ (MW = 6000 Da)-supported ammonium,¹³ phosphonium¹⁴ and guanidium salts¹⁵ have been utilized as efficient catalysts for the cycloaddition reaction of CO₂ with epoxides. In this context, the delocalized cations we used in this work have potential to stabilize the ring-opened structure of epoxide (intermediate **2**, Scheme 4), which is crucial for performing the reaction particularly at low CO₂ pressure.^{5a,10,16} We also envisioned that basic ILs could not only promote cycloaddition reaction of CO₂ with epoxides, but also catalyze transesterification of EC with methanol.

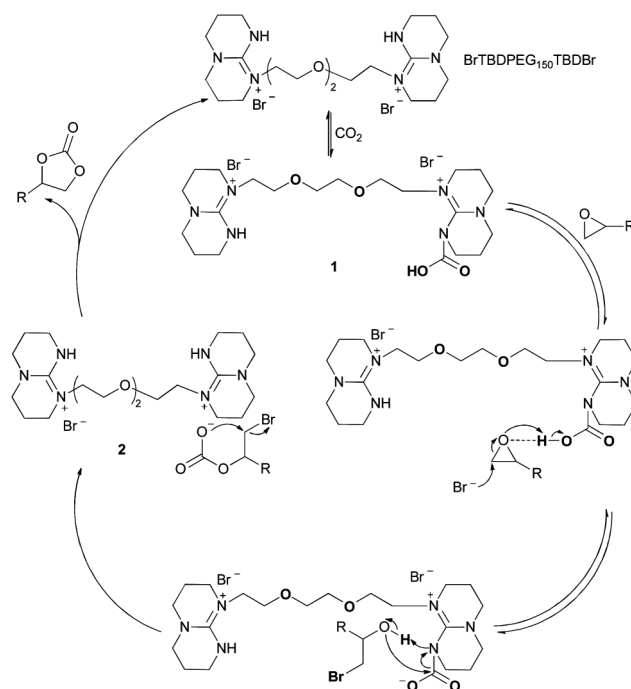


Scheme 2 PEG-functionalized ionic liquids in this study.

Indeed, the IL BrTBDPEG₁₅₀TBDBr was found to be highly efficient and recyclable catalysts with >93% yield of cyclic carbonates being obtained under atmospheric CO₂, without utilization of any solvents, or additives. The high efficiency was presumably due to activation of epoxide assisted by hydrogen bonding and activation of CO₂ by the oxygen atoms of the ether linkages of PEG,^{12b,12c} or the presence of the secondary amino



Scheme 3 Two-step process for DMC production utilizing CO₂ as a raw material.



Scheme 4 Proposed mechanism for BrTBDPEG₁₅₀TBDBr-catalyzed cycloaddition reaction of CO₂ with epoxides.

group in the cation, which has the potential to activate CO₂ molecule,^{5a,7,9e,17} on the basis of *in situ* FT-IR investigation under CO₂ pressure.

DMC has been drawing much attention as a safe, non-corrosive, and environmentally friendly building block for the production of polycarbonate and other chemical,¹⁸ an additive to fuel oil owing to a high octane number¹⁹ and an electrolyte in lithium batteries due to its high dielectric constant.²⁰ From the viewpoint of green chemistry, the two-step transesterification process utilizing CO₂ as a raw material,^{14,21} as illustrated in Scheme 3, is more attractive compared with other commercial processes^{3d,22} including methanolysis of phosgene, carbon monoxide-nitrite process, and gas-phase oxidative carbonylation of methanol using toxic, corrosive, flammable and explosive gases. However, the major disadvantages of this process are high energy consumption and investment, due to the need to separate the cyclic carbonate intermediate. Hence, it is very desirable to integrate the cycloaddition of CO₂ with epoxide and the transesterification of cyclic carbonate with methanol into a one-pot reaction.^{14,21b} Most of the catalytic systems previously reported for this two-step process include multi-component catalysts^{14,21b,23} or specifically lower catalytic activity for the cycloaddition reaction (step 1, Scheme 3).^{21n,24} Therefore,

Table 1 PC synthesis catalyzed by PEG-functionalized ILs^a

Entry	Catalyst	Yield (%) ^b	Selectivity (%) ^b
1	None	4	7
2	IDMImPEG ₁₅₀ DMImI	64	85
3	ClDMImPEG ₁₅₀ DMImCl	80	92
4	BrDMImPEG ₁₅₀ DMImBr	95	98
5	BrDMImBuDMImBr	12	29
6	BrDMImOctDMImBr	46	82
7	BrDMImPEG ₄₀₀ DMImBr	77	86
8	BrDBUPEG ₁₅₀ DBUBr	51	91
9	BrDBNPEG ₁₅₀ DBNBr	73	97
10	BrMImPEG ₁₅₀ MImBr	85	98
11	BrTBDPEG ₁₅₀ TBDBr	>99	>99

^a Reaction conditions: PO, 10 mmol, 0.5808 g; catalyst loading, 1 mol%; CO₂ pressure, 1 MPa; 120 °C; 3 h. ^b Determined by GC.

developing an efficient single-component catalyst for the one-pot two-stage process to get rid of separation of cyclic carbonate for DMC production is still highly desirable. In this context, the TSIL BrTBDPEG₁₅₀TBDBr, which bears both secondary and tertiary nitrogen in the cation and thus could have the ability to activate methanol,^{21a} delightedly displayed high activity for the transesterification of EC with methanol, 85% yield of DMC being obtained with 1:20 molar ratio of EC/methanol within 4 h. In addition, integration of the cycloaddition and transesterification reaction gave 83% yield of DMC.

Results and discussion

Propylene carbonate (PC) synthesis from CO₂ and propylene oxide (PO) was carried out in the presence of a series of PEG-functionalized ILs based on 1,2-dimethylimidazole (DMIm), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1-methylimidazole (MIm) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) under identical reaction conditions (catalyst loading, 1 mol%; CO₂ pressure, 1 MPa; 120 °C; 3 h). As shown in Table 1, almost no reaction occurred in the absence of any catalyst (Table 1 entry 1). Obviously, both the cation and anion of the investigated ILs have strong impact on the catalytic activities (entries 2–11). All the halide anions gave good results with catalytic activity increasing in the order of I⁻ < Cl⁻ < Br⁻ (entries 2–4), probably owing to good leaving ability and nucleophilicity. The cations effect on the reaction was also investigated. Notably, the

Table 2 Reaction conditions screening^a

Entry	Cat. loading/mol (%)	t/h	T/°C	CO ₂ pressure/MPa	PC Yield (%) ^b	PC Selectivity (%) ^b
1	1	3	140	1	>99	>99
2	1	3	120	1	>99	>99
3	1	3	100	1	74	>99
4	1	3	80	1	32	70
5	1	3	120	3	98	>99
6	1	3	120	5	94	97
7	1	3	120	7	86	91
8	1	3	120	12	70	82
9	1	2	120	1	84	94
10	1	1	120	1	79	93
11	0.5	3	120	1	90	>99

^a Reaction conditions: PO, 10 mmol, 0.5808 g; catalyst, BrTBDPEG₁₅₀TBDBr. ^b Determined by GC.

DMImPEG₁₅₀DMIm²⁺ cation with CO₂-philic linkages showed higher activity (entry 4), whereas, the cations containing alkyl group *i.e.* DMImOctDMIm²⁺ and DMImBuDMIm²⁺ gave much lower activity entries (5, 6). However, both PC yield and selectivity decrease markedly with PEG chain length of the cation increasing from PEG₁₅₀ to PEG₄₀₀ (entry 4 *vs.* 7), probably due to the increased mass-transport limitation. Furthermore, catalytic efficiency of cations derived from various bases decreased in the order of TBDPEG₁₅₀TBD²⁺ > DMImPEG₁₅₀DMIm²⁺ > MImPEG₁₅₀MIm²⁺ > DBNPEG₁₅₀DBN²⁺ > DBUPEG₁₅₀DBU²⁺ (entries 4, 8–11). Notably, activation of CO₂ can be achieved by adopting BrTBDPEG₁₅₀TBDBr with a secondary amino group in the cation as catalyst with formation of the carbamate species, which was detected by *in situ* FT-IR as shown in Fig. 2. Quantitative yield together with >99% selectivity of PC was obtained catalyzed by BrTBDPEG₁₅₀TBDBr. As a result, BrTBDPEG₁₅₀TBDBr was chosen as the model catalyst for further investigation. It is particularly worth mentioning that various cyclic carbonates were obtained with >93% yield under only 1 atm CO₂ pressure by adopting BrTBDPEG₁₅₀TBDBr as catalyst (Table 3).

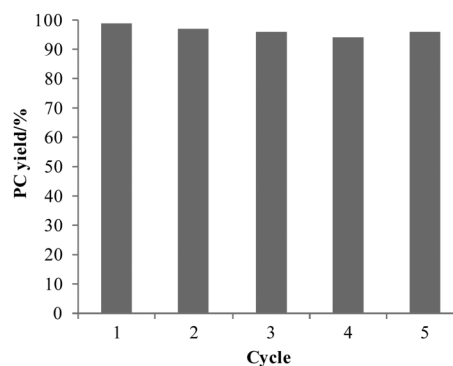




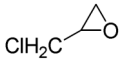
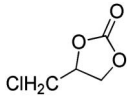

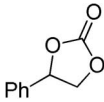
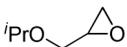
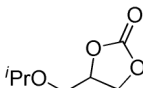
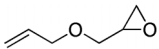
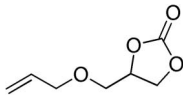

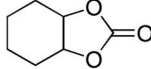


Fig. 1 Recyclability of the catalyst. Reaction conditions: propylene oxide, 10 mmol, 0.5808 g; TBD₂PEG₁₅₀Br₂, 1 mol%; CO₂ pressure, 1 MPa; 120 °C; 3 h. PC yield is determined by GC.

Influence of the reaction parameters on the reaction was then examined. As shown in Table 2, both yield and selectivity of PC were increased with temperature and thus optimal performance was achieved at 120 °C (entries 1–4). The lower selectivity at 80 °C could possibly be due to low activity for

Table 3 Various carbonates synthesis using BrTBDPEG₁₅₀TBDBr^a

Entry	Substrate	Product	Pressure/MPa	Yield/% ^d
1			1	>99
2			1	>99
3			1 0.1 ^b	98 97
4			1 0.1 ^b	94 93
5			1 0.1 ^b	>99 >99
6			1 0.1 ^b	>99 >99
7			1 ^c	95

^a Reaction conditions: epoxide, 10 mmol; BrTBDPEG₁₅₀TBDBr, 1 mol%; 120 °C; 3 h. ^b 8 h. ^c 20 h. ^d Determined by GC. Selectivities to the cyclic carbonates were >99% in this study.

PC formation but facile formation of PO isomerization by-products, such as acetone and *n*-propylaldehyde (entry 4).²⁵ In addition, the high catalytic activity can be maintained when the temperature was further increased to 140 °C (entry 1), which also could experimentally prove the excellent thermal stability of BrTBDPEG₁₅₀TBDBr. An almost quantitative yield together with excellent selectivity could be retained in the range of 1–5 MPa (entries 2, 5–6). However, CO₂ pressure over 7 MPa leads to decrease in PC yield and selectivity presumably owing to CO₂'s dilution effect (entries 7–8).^{5a,5i,5j} Notably, a reaction time of 3 h is needed to complete the reaction (entries 2, 9–10). In addition, the selectivity of PC remains constant when the catalyst loading is reduced to 0.5 mol% (entry 2 vs. 11).

To test catalyst reusability, the reaction was performed in the presence of a catalytic amount of BrTBDPEG₁₅₀TBDBr under the optimal reaction conditions. The catalyst was recovered after separation of PC from the reaction mixture by distillation under reduced pressure and then used for the next run without further purification.²⁶ The results shown in Fig. 1 indicate that the yield of PC is almost constant after five successive recycles.

The generality of this protocol was also examined and the results are summarized in Table 3. Generally, terminal epoxides with both electron-withdrawing and electron-donating groups could be transformed to the corresponding cyclic carbonates

with almost quantitative yield (>94%) within 3 h under 1 MPa CO₂ pressure (entries 1–6), but for internal cyclohexene oxide, 95% yield of the cyclic carbonate can be also reached only by prolonging the reaction time to 20 h, presumably due to the steric hindrance (entry 7). To our excitement, >93% yield of cyclic carbonates are attained under atmospheric CO₂ within 8 h, thanks to activation of epoxide assisted by hydrogen bonding and activation of CO₂ induced by the formation of carbamate species from CO₂ and BrTBDPEG₁₅₀TBDBr.

To gain a deeper insight into the reaction mechanism, *in situ* FT-IR spectroscopy under CO₂ pressure was employed to identify the possible intermediates during the reaction proceeding. The *in situ* FT-IR spectrum of BrTBDPEG₁₅₀TBDBr before and after reaction with CO₂ (at 3 MPa, 120 °C) was shown in Fig. 2(A). There are three important features in the spectrum. First, the N–H stretch observed at 3150 and 3208 cm⁻¹ decreased when CO₂ reacted with the IL. Secondly, the new peak at 2333 cm⁻¹ could correspond to physically dissolved CO₂. In addition, the bands originating from the carbamic ammonium salt between 2800–3000 cm⁻¹ and in the 2000–2800 cm⁻¹ region were not present along with addition of CO₂.²⁷ Thirdly, there is a new band centered at 1749 cm⁻¹, which could correspond to the new COOH moiety formed from the reaction of CO₂ with the IL.²⁸ As shown in Fig. 2(B), the absorption intensity of

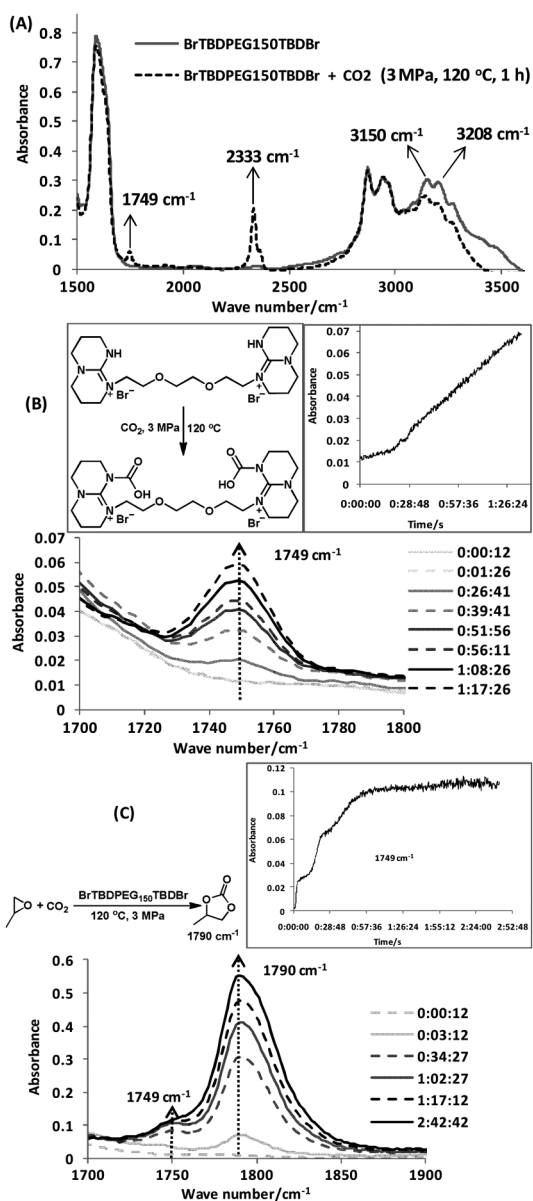


Fig. 2 Results of *in situ* IR spectroscopy under CO₂ pressure monitoring at various reaction time. Reaction conditions: (A) and (B) BrTBDPEG₁₅₀TBDBr (1 mmol), CO₂ (3 MPa), 120 °C; (C) PO (10 mmol), BrTBDPEG₁₅₀TBDBr (0.5 mmol), CO₂ (3 MPa), 120 °C. 1749 cm⁻¹ corresponds to peak for carbonyl group of carbamic acid formed between CO₂ and BrTBDPEG₁₅₀TBDBr (Scheme 4, compound 1). 1790 cm⁻¹ was the carbonyl group absorption of the product PC.

asymmetric (C=O) vibrations (1749 cm⁻¹) gradually increased in the course of the reaction between BrTBDPEG₁₅₀TBDBr and CO₂, suggesting formation of carbamic acid (1545 cm⁻¹ is characteristic of a carbamate anion).²⁹ Notably, absorption peaks of the carbonyl group at 1749 cm⁻¹ (BrTBDPEG₁₅₀TBDBr–CO₂ carbamic acid) and 1790 cm⁻¹ (PC) increased gradually along with the reaction time (Fig. 2(B)), presumably implying the activation of CO₂ by the secondary amino group in the cation of IL BrTBDPEG₁₅₀TBDBr, which leads to significant promotion of the cycloaddition reaction of PO and CO₂.

Subsequently, ¹³C NMR technique was also employed to identify the carbamic acid formation (Fig. 3). New absorption

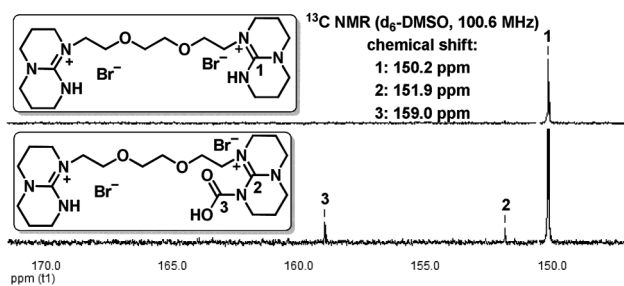


Fig. 3 The chemical shifts of quaternary carbons in BrTBDPEG₁₅₀TBDBr and carbamic acid from the reaction of BrTBDPEG₁₅₀TBDBr and CO₂. Reaction conditions: d₆-DMSO, 0.5 mL; BrTBDPEG₁₅₀TBDBr, 0.5 mmol; CO₂, 1 atm; 30 °C; 10 h.

bands at 151.9 (2) 159.0 ppm (3) upon reacting with CO₂ would also support the formation of carbamic acid between secondary amine and CO₂, being in agreement with those previously reported.²⁸

On the basis of previous reports^{5a,5d,9e,30} and the experimental results herein, a possible mechanism for the BrTBDPEG₁₅₀TBDBr-catalyzed cycloaddition of CO₂ with epoxides is proposed as shown in Scheme 4. Firstly, the secondary amino group of the IL coordinates reversibly with CO₂ to afford the carbamic acid **1**, which would be an activated form of CO₂. In parallel, epoxides could interact with TBDPEG₁₅₀TBD²⁺ or the carbamic acid **1** through hydrogen bonding, thus resulting in activation of epoxide, and simultaneously, the nucleophilic attack of bromide anion on the less sterically hindered β-carbon atom of the epoxide furnishes the bromoalkyl alcohol species HOCHRCH₂Br. Then nucleophilic attack of the bromoalkyl alcohol species on the carbamic acid **1** and the hydrogen transfer to the nitrogen atom in the cation of TBDPEG₁₅₀TBD²⁺ produces the alkyl carbonate anion **2**. Finally, the cyclic carbonate is formed by subsequent intramolecular ring-closure and the catalyst is regenerated.

Finally, catalytic efficiency of BrTBDPEG₁₅₀TBDBr on the transesterification reaction of EC with methanol was also explored (Table 4). Obviously, MeOH/EC ratio has significant impact on the transesterification. As the molar ratio of MeOH/EC

Table 4 BrTBDPEG₁₅₀TBDBr-catalyzed DMC synthesis through transesterification reaction^a

Entry	Molar ratio (EC : MeOH)	t/h	EC Conv. (%) ^b	DMC Yield (%) ^b
1	1 : 10	4	87	64
2	1 : 20	4	96	85
3	1 : 30	4	95	86
4	1 : 20	2	89	45
5	1 : 20	5	90	87
6 ^c	1 : 20	4	90	83

^a Reaction conditions: EC, 10 mmol; BrTBDPEG₁₅₀TBDBr, 1 mol% relative to EC; 70 °C. ^b Determined by GC using an internal standard technique. ^c EO : MeOH = 1 : 20. After the cycloaddition reaction of EO with CO₂ under optimal reaction conditions of (EO, 10 mmol, 10.5808 g; BrTBDPEG₁₅₀TBDBr, 1 mol%; CO₂ pressure, 1 MPa; 120 °C; 3 h), MeOH (200 mmol) was added, and then the mixture was transferred to a 25 mL flask, and refluxed for 4 h at 70 °C. The products were analyzed by GC using biphenyl as internal standard and further identified using GC-MS by comparing retention times and fragmentation patterns with authentic samples.

varying from 1 : 10 to 1 : 20, both DMC yield and EC conversion increased (Table 4, entries 1–2), being presumably attributed to the reversible nature of the transesterification.^{21a} However, DMC yield kept constant by further increasing the molar ratio of MeOH/EC to 1 : 30 (entries 2 vs. 3), owing to dilution of the catalyst. In addition, the transesterification reaction could reach equilibrium within only 4 h (entries 2 vs. 4–5), 85% yield of DMC being obtained thanks to activation of methanol assisted by the secondary and tertiary nitrogen in the cation of BrTBDPEG₁₅₀TBDBr. Notably, to realize a so-called “one-pot two-stage” access to DMC from CO₂ with no need of separation of cyclic carbonate *i.e.* EC, both cycloaddition reaction of CO₂ with EO (step 1, Scheme 3) and transesterification reaction of EC with methanol (step 2, Scheme 3) can be integrated, 83% yield of DMC being obtained by adopting BrTBDPEG₁₅₀TBDBr as a single component catalyst. Hence, TSIL BrTBDPEG₁₅₀TBDBr containing both secondary and tertiary amino group could have an ability to activate epoxides, CO₂ and methanol, particularly under low CO₂ pressure, and thus catalyze incorporating CO₂ into organic carbonates catalytically under mild conditions.

Conclusions

In summary, PEG-functionalized basic ILs, *e.g.* BrTBDPEG₁₅₀TBDBr was proved to be highly efficient and stable catalysts for the cycloaddition reaction of CO₂ to epoxides without utilization of any organic solvent or additive under modest reaction conditions. TSIL BrTBDPEG₁₅₀TBDBr used in this study can effectively activate epoxides through hydrogen bonding formation and realize activation of CO₂ through carbamic acid formation, which is also a highly efficient catalyst for the synthesis of DMC from the subsequent transesterification reaction through amine-promoted activation of methanol, thus incorporating CO₂ into industrially important organic carbonates such as DMC catalytically under atmospheric CO₂ through a “one-pot, two-stage” protocol. Therefore, this green process could show much potential application in industry. Further extending the application of PEG-functionalized basic ILs is currently under investigation in this laboratory.

Experimental

Caution: Experiments using compressed CO₂ are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Materials

Ionic liquids are synthesized according to the published procedures.^{5a,31} CO₂ with a purity of 99.99% is commercially available and epoxides are supplied from Aldrich Company. The other organic and inorganic compounds from Tianjin Guangfu Fine Chemical Research Institute are used without further purification except for the solvents, which are distilled by the known method prior to use.

General information

¹H NMR spectra is recorded at Bruker 400 spectrometer in CDCl₃ and CDCl₃ (7.26 ppm) is used as internal reference, ¹³C NMR is recorded at 100.6 MHz in CDCl₃ and CDCl₃ (77.0 ppm) is used as internal reference. ESI-MS are recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. GC analyses are performed on Shimadzu GC-2014, equipped with a capillary column (RTX-WAX, 30 m × 0.25 μm) using a flame ionization detector. *In situ* FTIR is collected on a Mettler Toledo React IR ic10, Silica ATR probe, using ic IR analysis system. Melting points are measured on an X4 apparatus and uncorrected.

Typical procedures for the synthesis of PC from PO and CO₂

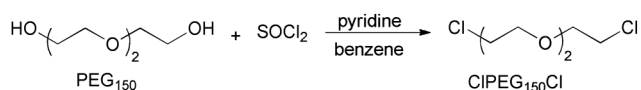
A stainless steel autoclave (25 mL inner volume) was purged with CO₂ to evacuate air, and then a PEG-functionalized ionic liquid (1 mol%), biphenyl (0.05 g, internal standard of GC) and PO (10 mmol) were added successively. CO₂ was charged in the reactor and the pressure was adjusted to 1 MPa at 120 °C. The autoclave was heated at that temperature for 3 h, and the pressure was kept constant during the reaction. After reaction, the autoclave was allowed to be cooled, and then the excess of CO₂ was vented. The product yields were determined by GC with a flame ionization detector and were further identified using GC-MS by comparing retention times and fragmentation patterns with authentic samples. The products were also isolated by column chromatography on silica gel and identified by NMR spectra as shown in the ESI†.

Typical procedure for DMC synthesis from EC and methanol

A mixture of ethylene carbonate (10 mmol), methanol (200 mmol), BrTBDPEG₁₅₀TBDBr (1 mmol%) and biphenyl (50 mg, an internal standard for GC analysis) were added to a 25 mL flask, and refluxed for 4 h. The vessel was then cooled to room temperature. The products were analyzed by GC and further identified by GC-MS (HP G1800A) by comparing retention times and fragmentation patterns with authentic samples.

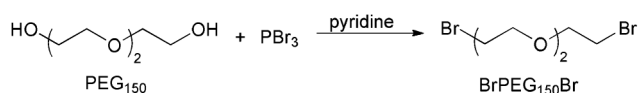
Preparation and characterization of ionic liquids

Synthesis of 1,2-bis(2-chloroethoxy)ethane (CIPEG₁₅₀Cl).^{31a}



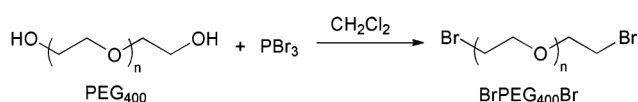
The mixture of triethylene glycol (PEG₁₅₀) (0.28 mol) and pyridine (0.61 mol) in benzene (250 mL) was heated to reflux, and then thionyl chloride (0.61 mol) was added dropwise over 3 h. The mixture was kept on reflux for another 16 h and then cooled to room temperature. Then hydrochloric acid (6.3 mL, 11.8 M) diluted with water (50 mL) was added dropwise in 15 min. The upper benzene solution was separated, and after evaporation under reduced pressure, the target compound CIPEG₁₅₀Cl was obtained as a lucid oil.

Synthesis of 1,2-bis(2-bromoethoxy)ethane (BrPEG₁₅₀Br). ^{31b}



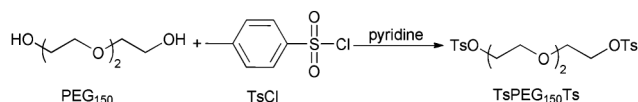
To a stirred mixture of triethylene glycol (PEG₁₅₀) (0.13 mol) and pyridine (0.51 mol) at 0 °C, phosphorus tribromide (0.103 mol, distilled) was added dropwise over 30 min. The resulting suspension was heated at 60 °C for 4 h, and then the mixture was poured into ice-water (30 mL). The lower organic layer was washed with water (5 × 20 mL), and then it was dried with MgSO₄. Finally, the target compound BrPEG₁₅₀Br was purified through distillation under reduced pressure as a light yellow liquid.

Synthesis of BrPEG₄₀₀Br. ^{31c}



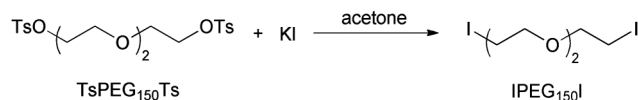
To a solution of PEG₄₀₀ (5 mmol) in CH₂Cl₂ (50 mL), freshly distilled tribromophosphine (5 mmol) was added. The mixture was stirred for 24 h at room temperature, and then 15 wt% NaOH solution was added to neutralize the excess tribromophosphine. The separated CH₂Cl₂ layer was evaporated in vacuum to give the product BrPEG₄₀₀Br as a light yellow oil.

Synthesis of triethyleneglycol disosylate (TsPEG₁₅₀Ts). ^{31d}



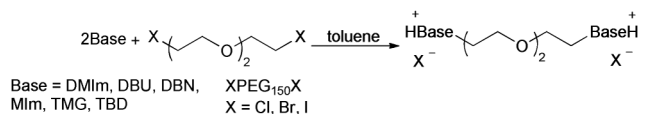
To a round-bottom flask with a magnet was added 400 mL of pyridine and 0.5 mol of triethyleneglycol (PEG₁₅₀). After cooling to <0 °C in an ice bath, 1.0 mol *p*-toluenesulfonyl chloride (TsCl) was next added to the reaction flask in several portions, keeping the reaction temperature <0 °C. Near the completion of this addition, a slurry formed. Stirring was continued for another 1.5 h after the addition has been completed. Next the slurry was poured into a solid ice and water mixture whereupon the disosylate solidified and pyridine hydrochloride salt dissolved. After filtration, TsPEG₁₅₀Ts was recrystallized from ethanol.

Synthesis of 1,2-bis(2-iodoethoxy)ethane (IPEG₁₅₀I). ^{31e}



The triethyleneglycol disosylate (TsPEG₁₅₀Ts) (13.0 mmol) was dissolved in acetone (50 mL), and KI (50.0 mmol) was added to the solution. The mixture was stirred at 40 °C for 4 days. The solvent was removed under reduced pressure, and water (10 mL) was added to the residue. The mixture was extracted with CH₂Cl₂ (4 × 50 mL), and then the combined extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (CH₂Cl₂) gave the product IPEG₁₅₀I.

Synthesis of ionic liquids used in this study. ^{5a}



Under N₂, base (1.6 mL, 20 mmol) and XPEG₁₅₀X (34.4 mmol) were added to dry toluene (2 mL) in a round-bottomed flask. The mixture was heated under reflux under N₂ for 24 h, upon which two layers had formed. The flask was allowed to cool to room temperature and was then cooled to -10 °C overnight, during which time white solid or yellow oil were formed. The excess toluene was decanted, while N₂ was being passed over the product layer. The resulting product was washed with dry Et₂O and then dried *in vacuo* for 24 h.

CIDMImPEG₁₅₀DMImCl. White solid; ¹H NMR (D₂O, 400 MHz) δ 7.34 (d, ³J = 2 Hz, 2H), 7.30 (d, ³J = 2 Hz, 2H), 4.26–4.30 (m, 4H), 3.80–3.87 (m, 4H), 3.74 (s, 6H), 3.65 (s, 2H), 3.59 (s, 2H), 2.55 (s, 6H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.8, 122.2, 120.9, 69.7, 68.5, 47.6, 34.6, 9.0; ESI-MS calcd for C₁₆H₂₈Cl₂N₄O₂ 378.16, found 154.4 [(M-2Cl)/2]⁺, 343.2, 345.2 [M-Cl]⁺.

BrDMImPEG₁₅₀DMImBr. Light yellow solid; ¹H NMR (D₂O, 400 MHz) δ 7.40 (d, ³J = 1.6 Hz, 2H), 7.36 (s, 2H), 4.33 (t, ³J = 4.8 Hz, 4H), 3.87 (t, ³J = 5.2 Hz, 4H), 3.79 (s, 6H), 3.65 (s, 4H), 2.60 (s, 6H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.9, 122.2, 120.9, 69.7, 68.5, 47.6, 34.6, 9.0; ESI-MS calcd for C₁₆H₂₈Br₂N₄O₂ 466.06, found 154.3 [(M-2Br)/2]⁺, 387.2, 389.2 [M-Br]⁺.

IDMImPEG₁₅₀DMImI. Yellow solid; ¹H NMR (D₂O, 400 MHz) δ 7.40 (d, ³J = 2 Hz, 2H), 7.37 (d, ³J = 2 Hz, 2H), 4.33 (t, ³J = 4.8 Hz, 4H), 3.88 (t, ³J = 5.2 Hz, 4H), 3.80 (s, 6H), 3.66 (s, 4H), 2.61 (s, 6H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.8, 122.1, 120.9, 69.7, 68.5, 47.6, 34.6, 9.1; ESI-MS calcd for C₁₆H₂₈I₂N₄O₂ 562.03, found 154.3 [(M-2I)/2]⁺, 435.2 [M-I]⁺, 127.2 [M-C₁₆H₂₈IN₄O₂]⁻.

BrDMImOctDMImBr. White solid; ¹H NMR (D₂O, 400 MHz) δ 7.36 (s, 2H), 7.33 (s, 2H), 4.12 (t, ³J = 7.2 Hz, 4H), 3.78 (s, 6H), 3.80 (s, 6H), 2.60 (s, 6H), 1.82 (t, ³J = 6.4 Hz, 4H), 1.34 (s, 8H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.0, 121.9, 120.6, 48.0, 34.4, 28.8, 28.0, 25.3, 8.8; ESI-MS calcd for C₁₈H₃₂Br₂N₄ 462.10, found 152.4 [(M-2Br)/2]⁺, 383.2, 385.2 [M-Br]⁺.

BrDMImBuDMImBr. White solid; ¹H NMR (D₂O, 400 MHz) δ 7.36 (d, ³J = 3.6 Hz, 4H), 4.19 (s, 4H), 3.79 (s, 6H), 2.61 (s, 6H), 1.89 (s, 4H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.3, 122.2, 120.5, 47.3, 34.5, 25.9, 8.8; ESI-MS calcd for C₁₄H₂₄Br₂N₄ 406.04, found 124.3 [(M-2Br)/2]⁺, 327.1, 329.1 [M-Br]⁺.

BrDMImPEG₄₀₀DMImBr. Light yellow oil; ¹H NMR (D₂O, 400 MHz) δ 7.40 (s, 2H), 7.33 (s, 2H), 4.32 (t, ³J = 4.8 Hz, 4H), 3.87 (t, ³J = 5.2 Hz, 4H), 3.78 (s, 6H), 3.65–3.68 (m, 30H), 2.59 (s, 6H); ¹³C NMR (D₂O, 100.6 MHz) δ 144.9, 122.2, 121.0, 69.8, 69.6, 68.6, 47.7, 34.7, 9.2; ESI-MS calcd for C₁₂H₂₀Br₂N₄(C₂H₄O)_n 378.01 + 44.03n (n = 5–12) found 220.5 (n = 5), 242.4 (n = 6), 264.4 (n = 7), 286.5 (n = 8), 308.6 (n = 9), 330.5 (n = 10), 352.6 (n = 11), 374.5 (n = 12) [(M-2Br)/2]⁺, 519.3

($n = 5$), 563.3 ($n = 6$), 607.3 ($n = 7$), 651.4 ($n = 8$), 697.4 ($n = 9$), 739.4 ($n = 10$), 785.4 ($n = 11$), 827.4 ($n = 12$) [M-Br]⁺.

BrDBUPEG₁₅₀DBUBr. Brown oil; ¹H NMR (D₂O, 400 MHz) δ 3.67–3.73 (m, 12H), 3.60–3.62 (m, 4H), 3.49–3.51 (m, 8H), 2.83 (d, ³J = 8.8 Hz, 4H), 2.04 (t, ³J = 5.2 Hz, 4H), 1.68–1.71 (m, 12H); ¹³C NMR (D₂O, 100.6 MHz) δ 167.2, 70.1, 68.0, 54.8, 52.5, 48.9, 47.2, 28.0, 25.4, 22.6, 19.6; ESI-MS calcd for C₂₄H₄₄Br₂N₄O₂ 578.18, found 210.5 [(M-2Br)/2]⁺, 499.4, 501.4 [M-Br]⁺.

BrTBDPEG₁₅₀TBDBr. Yellow oil; ¹H NMR (D₂O, 400 MHz) δ 3.68 (s, 6H), 3.48 (t, ³J = 5.2 Hz, 4H), 3.21–3.39 (m, 18H), 1.93–2.00 (m, 8H); ¹³C NMR (D₂O, 100.6 MHz) δ 151.3, 70.0, 68.2, 49.7, 47.4, 47.0, 46.8, 46.4, 38.4, 37.8, 20.6, 20.3, 20.2; ESI-MS calcd for C₂₀H₃₈Br₂N₆O₂ 552.14, found 197.3 [(M-2Br)/2]⁺, 393.3 [M-2Br-H]⁺, 473.0, 475.0 [M-Br]⁺.

BrMImPEG₁₅₀MImBr. Light brown oil; ¹H NMR (D₂O, 400 MHz) δ 7.52 (s, 2H), 7.46 (s, 2H), 4.40 (t, ³J = 4.8 Hz, 4H), 3.89–3.91 (m, 10H), 3.69 (s, 4H); ¹³C NMR (D₂O, 100.6 MHz) δ 136.1, 123.5, 122.5, 69.6, 68.5, 49.0, 35.8; ESI-MS calcd for C₁₄H₂₄Br₂N₄O₂ 438.03, found 140.3 [(M-2Br)/2]⁺, 359.1, 361.1 [M-Br]⁺.

BrDBNPEG₁₅₀DBNBr. Brown oil; ¹H NMR (D₂O, 400 MHz) δ 3.68–3.73 (m, 12H), 3.59 (s, 4H), 3.45 (s, 4H), 3.38 (s, 4H), 3.00 (t, ³J = 7.2 Hz, 4H), 2.05–2.12 (m, 8H); ¹³C NMR (D₂O, 100.6 MHz) δ 165.1, 70.1, 67.5, 54.3, 52.2, 44.8, 42.2, 30.6, 17.7, 18.0; ESI-MS calcd for C₂₀H₃₆Br₂N₄O₂ 522.12, found 182.5 [(M-2Br)/2]⁺, 443.3, 445.3 [M-Br]⁺.

Acknowledgements

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