

Guanidinium Salt Functionalized PEG: An Effective and Recyclable Homogeneous Catalyst for the Synthesis of Cyclic Carbonates from CO₂ and Epoxides under Solvent-Free Conditions

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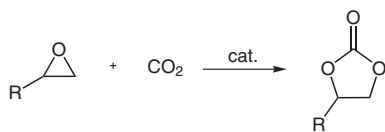
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Abstract: A guanidinium bromide covalently bound to CO₂-philic polyethylene glycol (PEG) is proved to be a highly effective homogeneous catalyst for the eco-friendly synthesis of cyclic carbonates from carbon dioxide and epoxides under mild conditions, which requires no additional organic solvents or co-catalyst. Notably, it has been found that there is a pronouncedly cooperative effect between the catalyst part and the support part. Moreover, the catalyst is able to be reused with retention of high catalytic activity and selectivity. This process looks promising as a strategy for homogeneous catalyst recycling.

Key words: guanidinium bromide, functionalized polyethylene glycol, carbon dioxide, epoxide, cycloaddition

Carbon dioxide is considered as an abundant, nontoxic, nonflammable and cheap C₁ building block in organic synthesis as well as being the main greenhouse gas.¹ Therefore, chemical fixation of CO₂ is a very attractive subject from the viewpoint of sustainable chemistry and environment protection.

One of the most promising methodologies in this area is the synthesis of cyclic carbonate via the coupling of CO₂ and epoxide (Scheme 1).² This high atom economical reaction has seen significant progress, since cyclic carbonates have widely been used for various purposes, such as polar aprotic solvents, intermediates in organic synthesis, monomers for synthesizing polycarbonate, agricultural chemicals, alkylating agents, electrolytic elements of lithium secondary batteries and chemical ingredients for preparing medicines.³⁻⁷



Scheme 1 Cycloaddition of epoxide with CO₂

Numerous homogeneous catalysts have already been developed for the synthesis of cyclic carbonates from CO₂ and epoxides.²⁻⁴ Unfortunately, homogeneous catalysts are undesirably dissolved in a phase containing cyclic carbonates, which inevitably results in difficulty in separat-

ing the reaction product from the catalyst and reaction solvent. In order to circumvent this problem, a lot of solid catalysts⁸ have been proposed for this reaction. However, solid catalysts generally suffer from insufficient activity and an additive or co-catalyst is necessary for maintaining good catalyst performance.

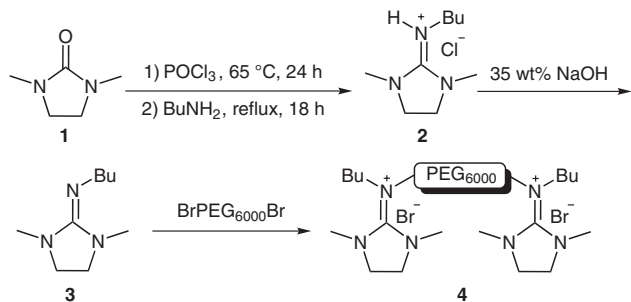
In order to preserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst, one strategy is that the active species can be chemically or physically attached to an insoluble support such as silica,^{8o,r,s} natural or synthesized polymers,^{8a,b,k,m,t,u} zeolite,^{8v} and other materials.^{8o} Generally, the supported catalysts can easily be separated from the products. It is worth noting that a large cooperative acceleration between both catalytic species and support like silica has been found by immobilization of homogeneous catalyst on the support.^{8s} Another strategy is to employ a CO₂-philic support to design such a supported catalyst that can homogeneously dissolve during the reaction and precipitate quantitatively in the separation stage. The most commonly used parameters to induce the precipitation are temperature, solvent polarity and pH of the solution. In this context, polyethylene glycol (PEG) should be an excellent candidate, being regarded as an environmentally benign media for chemical reactions.⁹ It is particularly noteworthy that PEG as a CO₂-philic support demonstrates a synergistic effect for the catalyst activity presumably due to 'CO₂-expansion of a liquid' effect.^{9a,j}

Ionic liquids being recognized as green media and catalysts for organic reactions have recently attracted considerable attention due to their versatile properties such as nonvolatility, tunable polarity, high stability and so on.^{10a-j} Guanidinium salt can be regarded as a kind of ionic liquid with special properties of high thermal and chemical stability, the tunable groups of the three N atoms in the molecular structure and excellent catalytic activity for typical organic reactions. Extensive research has been devoted to the design, synthesis and application of guanidinium-based ionic liquids.^{10k-o} Recently, hexaalkylguanidinium salts have been found to be active catalysts for cycloaddition of CO₂ and epoxides to produce cyclic carbonate.^{8p,10k,o}

In the present work, we envisioned that a functionalized PEG, with hexaalkylguanidinium bromide being covalently tethered to PEG ($M_w = 6000$), could be utilized as an active homogeneous catalyst for the synthesis of cyclic

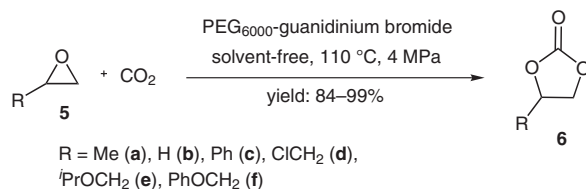
carbonates from CO₂ and epoxide with almost quantitative yield and excellent selectivity.

As shown in Scheme 2, the preparation of PEG₆₀₀₀-supported guanidinium bromide **4** was accomplished via the reaction of pentaalkylguanidine **3** with polyethylene glycol bromide which was easily prepared according to the literature.¹¹ Pentaalkylguanidine **3** was synthesized from 1,3-dimethylimidazolidin-2-one (**1**), POCl₃ and BuNH₂.^{12,13} The supported catalyst was characterized by the FTIR, ¹H NMR and ¹³C NMR spectroscopy.¹⁴



Scheme 2 The synthesis of PEG₆₀₀₀-supported guanidinium bromide

For cycloaddition reaction¹⁵ of CO₂ with epoxide catalyzed by PEG functionalized with guanidinium bromide **4**, isopropyl glycidyl ether (**5e**) was chosen as the standard substrate to investigate suitable reaction conditions for the desired reaction (Scheme 3). The results are summarized in Table 1. Without a catalyst, or in the presence of PEG alone, the reaction barely took place (entries 1 and 2), whereas guanidinium bromide exhibited a moderate catalytic activity under the reaction conditions (entry 3). The guanidinium bromide functionalized PEG **4** demonstrated higher activity than the supported guanidinium bromide, even more effective than a simple physical mixture of PEG and guanidinium salt (entries 3, 4 vs. 10). Consequently, supporting guanidinium salt on a CO₂-philic polymer enhances the catalytic activity. The enhancement of catalyst performance is presumably attributed to the benefits from changes in the physical properties of the reaction mixture, such as lower melting points, lower viscosity, higher diffusion rates, and increased solubility for epoxide and CO₂ through the so-called ‘CO₂-expansion of liquid’ effect.^{9a} Such a phenomenon was judged by visual inspection through a window-equipped high-pressure reactor.^{9k}



Scheme 3 Synthesis of various carbonates catalyzed by PEG₆₀₀₀-supported hexaalkylguanidinium bromide

The results also show that the catalyst loading has a significant influence on the catalytic activity. When the catalyst amount was increased from 0.1 mol% to 0.5 mol% (Table 1, entries 5, 6 and 9), the yield increased from 16% to 98%. The reaction temperature also has a remarkable effect on the cycloaddition reaction as shown in Table 1. As the temperature was increased from 90 °C to 110 °C, the yield of product increased from 55% to 97% (entries 10 and 11). When the temperature was raised to 130 °C, a high yield of 97% was obtained even at low catalyst loading 0.25 mol% (entry 6). From a practical point of view,

Table 1 Synthesis of Cyclic Carbonate from CO₂ and Epoxide Catalyzed by Guanidinium Bromide Functionalized PEG^a

Entry	Catalyst (mol%) ^b	Time (h)	Temp. (°C)	Pressure (MPa)	Yield (%) ^c
1	–	4	110	4	trace
2	PEG ^d	4	110	4	trace
3	HAGB ^e	4	110	4	80
4	HAGB + PEG ^f	4	110	4	84
5	0.1	4	130	4	16
6	0.25	4	130	4	97
7	0.25	4	110	4	74
8	1	4	130	4	99
9	0.5	4	130	4	98
10	0.5	4	110	4	97
11	0.5	4	90	4	55
12	0.5	2	110	4	79
13	0.5	3	110	4	86
14	0.5	4	110	2	99
15 ^g	1	4	110	4	99
16 ^h	1	4	110	4	97
17 ⁱ	1	4	110	4	94
18 ^j	1	4	110	4	90

^a Reaction conditions: isopropyl glycidyl ether (2 mL, 15.8 mmol); catalyst amount refers to molar percentage with respect to the initial amount of the substrate.

^b Catalyst: PEG₆₀₀₀-supported guanidinium bromide (**4**), unless otherwise noted.

^c Yields of the product 4-isopropoxy-1,3-dioxolan-2-one were determined by GC using an internal standard technique.

^d PEG (MW = 6000): 474 mg.

^e HAGB: di-*n*-butyl(1,3-dimethylimidazolidin-2-ylidene)ammonium bromide (48 mg, 1 mol%).

^f Physical mixture of HAGB (48 mg) and PEG (474 mg).

^g The first run of the catalyst.

^h The second run of the catalyst.

ⁱ The third run of the catalyst.

^j The fourth run of the catalyst.

0.5 mol% and 110 °C are the appropriate catalyst loading and reaction temperature, respectively.

Table 1 (entries 10, 12 and 13) shows the reaction time dependence on the yield and selectivity of 4-isopropoxy-methyl-1,3-dioxolan-2-one (**6e**). A yield of 79% could be obtained in two hours at 110 °C (entry 12). The yield experienced a further increase to 97% within four hours (entries 12, 13 and 10), while the selectivity of the product remained almost unchanged during the whole reaction course. Consequently, a reaction time of four hours was required for complete epoxide conversion. A significant drawback associated with using CO₂ as a reagent or reaction medium in organic synthesis is the potential danger of operating at high temperature and pressure. We were gratified to find that the reaction proceeded smoothly even under the pressure as low as 2 MPa (entry 14).

A series of catalytic cycles was subsequently examined to test the catalyst recycling (entries 15–18, Table 1). The workup of the reaction was performed by extraction with diethyl ether.¹⁶ The recovered catalyst was then subjected to a second run of the reaction without replenishment of fresh catalyst by charging with the same substrate. The yield of the product was over 90% after the fourth recycling process. It has been demonstrated that the catalyst could be reused with retention of high catalytic activity. The leaching of the active ingredient of the catalyst was also tested. The solidified catalyst¹⁶ was thoroughly filtered from the product solution, and the content of bromide ion in the resulting filtrate was measured by ion chromatography with a DIONEX DX-120 Ion Chromatographic instrument. The content of bromide ion was at the level of 60 ppm, demonstrating the thermal stability of the catalyst. Conclusively, the recyclability of the catalyst makes the reaction economically and potentially viable for commercial applications.

The scope of the substrates was further explored as depicted in Scheme 3. A series of epoxides was chosen to be tested for the synthesis of the corresponding carbonates in the presence of the catalyst (0.5 mol% relative to epoxide) under the optimal reaction conditions. The results are listed in Table 2. Delightedly, the catalyst was found to be applicable to a variety of terminal epoxides **5**, providing the corresponding cyclic carbonates **6** in high yields and selectivities. Propylene oxide (**5a**), ethylene oxide (**5b**), styrene oxide (**5c**), isopropyl glycidyl ether (**5e**), and glycidyl phenyl ether (**5f**) were all good substrates to give the corresponding cyclic carbonates, while epichlorohydrin (**5d**) exhibited relatively low activity among the terminal epoxides surveyed.

In conclusion, a guanidinium bromide functionalized PEG is shown, for the first time, to be an efficacious catalyst for the synthesis of cyclic carbonates from CO₂ and epoxides under mild conditions without utilizing any solvent or co-catalyst. Supporting guanidinium bromide on CO₂-philic polymer enhances the catalytic activity. Notably, the catalyst can be reused with retention of high catalytic activity and selectivity. This environmentally

Table 2 Synthesis of Various Carbonates Using Guanidinium Bromide Functionalized PEG as a Catalyst^a

Entry	Epoxide	Product	Yield (%) ^b	Selectivity (%)
1			99	99
2			99	99
3			97	99
4			84	93
5			97	99
6			95	99

^a Reaction conditions: epoxides (15.8 mmol), catalyst **4** (0.498 g, 0.5 mol%), 110 °C, 4 MPa, 4 h.

^b Determined by GC using an internal standard technique.

friendly protocol offers ease of operation and enables recyclability of homogeneous catalyst and synthesis of a variety of cyclic carbonates.

Acknowledgment

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- (13) The pentaalkylguanidine **3** was synthesized from 1,3-dimethylimidazolidin-2-one(**1**), POCl₃ and BuNH₂ by the methods reported in the literature;^{12b} colorless liquid; yield: 71% (lit.^{12b} 85%). ¹H NMR (300 MHz, CDCl₃): δ = 0.91 (t, *J* = 14.4 Hz, 3 H, Me), 1.33–1.41 (m, 2 H, CH₂), 1.48–1.58 (m, 2 H, CH₂), 2.79 (s, 6 H, Me), 3.14 (s, 4 H, NCH₂), 3.34 (s, 2 H, CH₂).
- (14) **Procedure for the Synthesis of PEG-Supported Guanidinium Bromide 4:** To a solution of polyethylene glycol bromide (12 g, 0.002 mol) in toluene (150 mL), pentaalkylguanidine **3** (3.38 g, 0.02 mol) was added, and the resulting solution was stirred at 65 °C for 72 h. After the reaction was completed, the solvent was removed under reduced pressure, and then anhyd Et₂O (40 mL) was added. The product was precipitated and isolated by filtration, then washed by anhyd Et₂O and dried to obtain the product **4** (94%); white powder; mp 53–55 °C. IR: 1638 (C=N) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, *J* = 14.7 Hz, 6 H, 2 × Me), 1.29–1.36 (m, 4 H, 2 × CH₂), 1.62–1.72 (m, 4 H, 2 × CH₂), 3.11 (s, 6 H, 2 × Me), 3.60 (m, 4 H, OCH₂CH₂O). ¹³C NMR (75 MHz, CDCl₃): δ = 13.08, 19.13, 31.69, 34.85, 43.08, 49.02, 69.90, 158.72.
- (15) **Representative Procedure for the Cycloaddition Reaction of Epoxide with CO₂:** In a 25-mL inner volume stainless-steel autoclave equipped with a magnetic stirrer, isopropyl glycidyl ether (15.8 mmol) and PEG-supported hexaalkylguanidinium bromide (0.5 mol%) were added, and CO₂ (liquid, 3.0 MPa) was charged into the reactor at r.t. The initial pressure was generally adjusted to 4 MPa at 110 °C. The reactor was heated at that temperature for 4 h. After cooling, the products were separated by adding Et₂O and analyzed by a gas chromatograph (Shimadzu GC-2014) equipped with a capillary column (RTX-5, 30 m × 0.25 μm) using a flame ionization detector and the side-products were detected by GC-MS. All of the products were further identified using GC-MS by comparing the retention times and fragmentation patterns with authentic samples. The structures of the isolated products were also characterized by ¹H NMR and ¹³C NMR spectroscopy. Spectral characteristics of cyclic carbonates shown in Table 2 are as follows:
- 4-Methyl-1,3-dioxolan-2-one (6a):** ¹H NMR (400 MHz, CDCl₃): δ = 1.43 (d, *J* = 6.0 Hz, 3 H, Me), 3.98 (t, *J* = 8.4 Hz, 1 H, OCH₂), 4.51 (t, *J* = 8.4 Hz, 1 H, OCH₂), 4.82 (m, 1 H, CHO). ¹³C NMR (100.4 MHz, CDCl₃): δ = 19.15, 70.53, 73.49, 154.95. **1,3-Dioxolan-2-one (6b):** ¹H NMR (400

MHz, CDCl₃): δ = 4.50 (s, 4 H, OCH₂). ¹³C NMR (100.4 MHz, CDCl₃): δ = 64.62, 155.55. **4-Phenyl-1,3-dioxolan-2-one (6c)**: ¹H NMR (400 MHz, CDCl₃): δ = 4.35 (t, *J* = 8.4 Hz, 1 H, OCH₂), 4.80 (t, *J* = 8.4 Hz, 1 H, OCH₂), 5.70 (t, *J* = 8.0 Hz, 1 H, OCH), 7.36 (d, *J* = 7.6 Hz, 2 H, Ph), 7.44 (d, *J* = 6.4 Hz, 3 H, Ph). ¹³C NMR (100.4 MHz, CDCl₃): δ = 71.12, 77.95, 125.83, 129.22, 129.71, 135.78, 154.76.

4-Chloromethyl-1,3-dioxolan-2-one (6d): ¹H NMR (400 MHz, CDCl₃): δ = 3.71 (dd, *J* = 3.2, 12.0 Hz, 1 H, ClCH₂), 3.80 (dd, *J* = 5.2, 12.0 Hz, 1 H, ClCH₂), 4.39 (dd, *J* = 6.0, 8.4 Hz, 1 H, OCH₂), 4.58 (t, *J* = 8.4 Hz, 1 H, OCH₂), 4.98 (m, 1 H, CHO). ¹³C NMR (100.4 MHz, CDCl₃): δ = 43.84, 66.83, 74.29, 154.28. **4-Isopropoxy-1,3-dioxolan-2-one (6e)**: ¹H NMR (400 MHz, CDCl₃): δ = 1.08 (t, *J* = 6.4 Hz, 6 H, 2 × Me), 3.51–3.62 (m, 3 H, CHO, CH₂O), 4.30 (dd, *J* = 8.0, 15.6 Hz, 1 H, OCH₂), 4.42 (dd, *J* = 8.0, 15.6 Hz, 1 H, OCH₂), 4.74 (m, 1 H, CHO). ¹³C NMR (100.4 MHz, CDCl₃): δ = 21.53, 21.65, 66.16, 66.89, 72.59, 75.18, 155.03.

4-Phenoxymethyl-1,3-dioxolan-2-one (6f): ¹H NMR (400 MHz, CDCl₃): δ = 4.15 (dd, *J* = 4.4, 10.8 Hz, 1 H, OCH₂), 4.24 (dd, *J* = 3.6, 10.8 Hz, 1 H, OCH₂), 4.55 (dd, *J* = 6.0, 8.4 Hz, 1 H, PhOCH₂), 4.62 (t, *J* = 8.4 Hz, 1 H, PhOCH₂), 5.03 (m, 1 H, OCH), 6.91 (d, *J* = 8.0 Hz, 2 H, Ph), 7.02 (t, *J* = 7.4 Hz, 1 H, Ph), 7.31 (t, *J* = 8.0 Hz, 2 H, Ph). ¹³C NMR (100.4 MHz, CDCl₃): δ = 66.17, 68.84, 74.11, 114.57, 121.92, 129.63, 154.65, 157.71.

- (16) **Extraction Procedure with Et₂O**: After addition of Et₂O (3 × 4 mL) to the resulting mixture upon completion of the reaction, the PEG-guanidinium bromide was solidified when cooled to –20 °C to –10 °C, followed by simple decantation of the Et₂O phase containing the products, thus allowing the catalyst to be recycled. The combined extracts were dried over MgSO₄ and concentrated in vacuo to give the product cyclic carbonate. We conducted further reaction by the addition of successive portions of the epoxide to the recovered catalyst under identical reaction conditions.

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