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Modified polyether glycols supported ionic liquids for CO_2 adsorption and chemical fixation



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ABSTRACT

Hydroxyl polyether-grafted imidazolium ionic liquids (HPEG_nRIMX) have been synthesized by a chemical stoichiometric method, which were applied into strengthening CO₂ accessibility and conversing CO₂ into cyclic carbonates. The structure was determined by FT-IR, NMR, TGA and MS. Under the optimum reaction conditions of 1.0 mol% HPEG_nRIMX, 2.0 MPa CO₂ pressure, 130 °C and 1.5 h, it could achieve excellent catalytic activities. The performance was over than that of PEG₄₀₀DEIMBr with double terminal ending-capped ILs functional groups due to its multifunctional synergestic roles including the long polyether chains, hydrogen-bonding between hydroxyl groups on HPEG_nILs and oxygen atoms on cyclo-epoxides, and the halide anionic nuclephilicity. The mechanism was further investigated by IGA and *in-situ* NMR spectrum.

1. Introduction

 CO_2 as the aboundant C1 resource from combustion of fossil fuels (coal, petroleum and natural gas) has drawn much more attraction to convert into some useful main chemicals such as cyclic carbonate [1–3], cyclic acids [4], formic acid [5,6], methanol [7], polycarbonate [8,9], diethyl carbonate [10], dimethyl carbonate [11] and diphenyl carbonate [12]. Cyclic carbonate [13,14] has been considering as the most versatile, usable compounds or intermediates in the fields of organic synthesis [15], electrolytes [16,17], polycarbonates [18], and polyurethanes [19].

Homogeneous catalysts including alkali-metal salts [20], salen metal complexes [8,21], amino acids [22], quaternary ammoniums [23], phosphonium salts [24], and the solid heterogeneous catalysts such as metal oxide [25], organic-inorganic hybrid catalyst [26], in-soluble ion-exchange resins [27] or polymeric ILs [2,28] have been developed and successfully applied into cycloaddition of CO_2 with cyclo epoxides for cyclic carbonates. These homogeneous catalysts were difficultly recovered and recycled, and cyclic carbonates were usually through some tedious prufication process, for example distillation and solvent extraction [29]. During the process, much high energy consumption or some organic solvents were often cost and wasted. Heterogeneous catalysts could resolve the separation and reusability problem. However, they usually encountered the loss of catalytic active species or withdrawal problem from the large-scaled fixed-bed reactor.

Polyether glycols(PEGs)-supported ILs as the good CO₂ soluble catalysts [30] containing with double ammonium-based ILs [31], phosphonium-based ILs [32] and others special-tasked ILs catalysts [33], which not only performed lower vapor pressure and easily being withdrawn through simple filtration, but also could show good recyclability like those conventional heterogeneous catalysts. Up to this date, Yang group [34] has reported glycol-based di-cationic ILs, for XDMImPEG₁₅₀DMImX, BrDBUPEG₁₅₀DBUBr example and BrTBDPEG₁₅₀TBDBr, which could catalyze the chemical fixation of CO₂ to cyclic carbonates with 74-99% yields within the longer reaction time of 3-4h under the conditions of 80-120°C, 1.0-3.0 MPa [35]. PEG₆₀₀₀-supported ammonium salts transformed CO₂ into cyclic carbonates under the harsh supercritical condition (> 8 MPa CO₂ pressure) [36,37].

Hydrogen-bonding between hydroxyl groups on catalysts and oxygen atom of cyclo-epoxides could enhance producing cyclic carbonates from CO_2 over task-specific ILs catalysts [38,39]. For example, hydroxyl-functionalized micro-porous organic polymer (HF-MOP) [40], 1-(2-hydroxylethyl)-imidazolium-based ionic liquid functionalized graphene oxide (GO-HEIMBr) [41], polystyrene-supported 1-(2-hydroxyl-ethyl)-imidazolium bromide (PS-HEIMBr) [42] and polymer nanoparticles grafted hydroxyl-functionalized phosphonium-based ionic liquids (PNP-HPILs) [43] generally performed highly efficient catalytic activities in conversion of CO_2 into cyclic carbonates because of the hydrogen-bonding's synergistic facilitation role.

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In this work, a series of hydroxyl polyethylene ether-grafted imidazolium ionic liquids (HPEG_nRIMX) have been synthesized through a chemical stoichiometric method, and determined their structures by FT-IR, NMR, TGA and MS (seeing in Figure S1, S5-S7). The conversion of CO₂ into cyclic carbonates was used as the model reaction to evaluate HPEG_nRIMX's catalytic activities. Compared with polyethylene ether ending-capped di-imidazolium ILs (PEGsDIMBr), HPEG_nRIMX with mono-hydroxyl group and terminal ending-capped ILs exhibited an obvious promoted catalysis, which might be resulted from the multifunctional facilitated roles including the improved CO₂-solubilities of catalysts, hydrogen-bondings between hydroxyl group and oxygen atom on cyclo-epoxides, and bromine anionic nuclephilicity for attacking the C₂ sites of cycloepoxides. The mechanism formation process on the chemical fixation of CO₂ into cyclic carbonates has been proposed and further investigated by IGA and *in-situ* NMR spectroscopy.

2. Experimental

2.1. Materials

Halogenated hydrocarbons and polyethylene glycols (PEG_n, M_w or n = 200, 400, and 600) as the post-modified supports were purchased from the J&K (Beijing) CHEMICA Ltd. and directly utilized without any purification process. Other chemicals containing with sulphuric dichloride, sodium ethylate, pyridine and imidazole were obtained from the Beijing Chemical Reagent Co., Ltd. and directly used to synthesize HPEG_nILs. Ethanol, acetonitrile, toluene and ethyl ether were dried over 4A molecular sieve and then refined under N₂ atmosphere by using Schlenk technique. 99.5 wt% purity of CO₂ was the commercial product, and all epoxides were purchased from Aldrich Company and directly used as received.

2.2. Synthesis of monochlorinated polyethylene glycols (HPEG_nCl, n = 200,400,600) [44,45]

$$HO(\bigcirc n)^n OH + SOCI_2 \xrightarrow{pyridine} HO(\bigcirc n)^n CI$$

 $PEG_n HPEG_nCI$
 $n = 200, 400, 600$

Monochloridated HPEG_nCl were synthesized through the chemical stoichiometric method as the below procedure: 0.10 mol of PEG_n (Mw = 200,400,600), 0.20 mol of pyridine and dried toluene (200 mL) were subsequently added into a 500 mL three-neck round bottle at the room temperature. After the mixture was stirred for half an hour by using the magnetic stirrer, it was warmed to the refluxing temperature

successively rotary concentration process, and dried over vacuum for 4-6 h. The yollowish HPEG_nCl was obtained with the isolated yield of above 80%, and determined by ¹H NMR (Figure S2-S4), MS spectrum (Figure S5) and TGA (seeing in Figure S11).

HPEG₂₀₀Cl. Pale yellow oily liquid; ¹H NMR (D₂O, 600 MHz) δ 3.76 - 3.74 (m, 4H, CH₂CH₂Cl), 3.67 - 3.62(m, 19H, CH₂OH), 3.57 - 3.55(m, 2H, CH₂).

HPEG₄₀₀**Cl.** Pale yellow oily liquid; ¹H NMR (D₂O, 600 MHz) δ 3.76 - 3.74(m, 4H, -CH₂Cl), 3.65 - 3.62(m, 39H, CH₂OH), 3.60 - 3.55(m, 2H, CH₂).

HPEG₆₀₀**Cl.** Pale yellow oily liquid; ¹H NMR (D₂O, 600 MHz) δ 3.76 – 3.74(m, 4H, –CH₂), 3.67 – 3.64(m, 61 H, CH₂OH), 3.57 – 3.56 (m, 2H, CH₂).

2.3. Synthesis of hydroxyl polyethylene ether-grafted imidazole (HPEG_nIM) [46]

$$HO(\bigcirc n \bigcirc CI + \sqrt{NH} \xrightarrow{EtONa} HO(\bigcirc n \bigcirc n \bigcirc N \bigcirc N$$

$$HPEG_nCI \qquad HPEG_nIM$$

$$n = 200, 400, 600$$

Imidazole (50 mmol, 3.40 g) and 75 mL dried ethanol were added into a 250 mL round bottomed flask with the spherical reflux condenser. The obtained solution was magnetically stirred and refluxed for 1.0 h, and then 20 mL of 21 wt% sodium ethylate in dried ethanol was dripped slowly. After refluxing for 8 h, HPEG_nCl (0.05 mol) was added into the mixture solution for reacting another 12 h. Finally, it was cooled to r.t. and filtrated off precipitations. The obtained filtrate was washed with anhydrous ether (50 mL \times 3), and then concentrated by using rotary evaporator. After drying over vacuum at 45 °C for 12 h, HPEG_nIM with the yellowish colour was obtained and determined by using NMR (Figure S8 – 10), MS (Figure S6) and TGA (Figure S12), and its yield was 72%.

HPEG₂₀₀**IM**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 7.83(s, 1H, CH), 7.05 (s, 2H, CH), 3.75 - 3.67(m, 2H, CH₂N), 3.59 - 3.42(m, 13H, CH₂OH).

HPEG₄₀₀**IM**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 7.73(s, 1H, NCHN), 7.07(s, 2H, 2CH), 3.75 - 3.59(m, 33H, CH₂OH).

HPEG₆₀₀IM. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 7.76(s, 1H, NCHN), 7.07(s, 2H, 2CH), 3.74 – 3.55(m, 65H, CH₂OH).

2.4. Synthesis of polyethylene glycols grafted imidazolium ionic liquids (HPEG_nRIMX) [47,48]

$$HO(\underbrace{O}_{n}, N, N + RX \xrightarrow{CH_{3}CN} HO(\underbrace{O}_{n}, N, N, N, RX \xrightarrow{CH_{3}CN} HO(\underbrace{O}_{n}, N, N, N, R \xrightarrow{\Theta} X^{\Theta}$$

$$HPEG_{n}IM \qquad HPEG_{n}RIMX$$

$$n = 200, 400, 600$$

$$R = ethyl, propyl, butyl.$$

$$X = Cl, Br, l.$$

and reacted for 1.0 h. Then, 1.00 equiv. of sulphuric dichloride as the chloride reagent was slowly dripped into the mixture solution within 45 min. The solution was refluxed for 48 h until completing the reaction. The precipitated pyridine salts were filtrated off, and the mixture solution was washed with toluene (100 mL \times 3) and CH₂Cl₂ (50 mL \times 3), and dried over anhydrous sodium sulphate. Finally, after removing off the organic solvents within, the obtained crude HPEG_nCl was further purified by liquid-liquid extraction from diethyl ether and

The solution of HPEG_nIM (0.02 mol), acetonitrile (50 mL) and 1bromoethane (0.03 mol, 3.30 g) was added into a 250 mL round bottome flask equipped with the reflux condenser and the magnetic stirrer. After refluxing for 24 h, the reaction was completed and then the mixture solution was warmed to the room temperature. Inorganic precipitation was removed off by filtration, and the filtrate was washed with diethyl ether (40 mL × 5) for further purifying the crude products. Finally, HPEG_nRIMX with the yellowish colour was obtained with the yields of 71–86% and dried over vacuum atmosphere. Its structure was determined by NMR spectrum depicted in Figure S15, S16.

HPEG₂₀₀**EIMBr.** Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.80 – 8.63 (m, 1H, CH), 7.51 – 7.38 (m, 2H, CH), 4.38 – 4.18 (m, 2H, CH₂), 3.68 – 3.51 (m, 13H, OCH₂), 1.45 – 1.41 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 134.70, 122.16, 69.87, 60.38, 45.02, 14.76.

HPEG₄₀₀EIMBr. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.80 – 8.62 (m, 1H, CH), 7.51 – 7.37 (m, 2H, CH), 4.38 – 4.14 (m, 2H, CH₂), 3.85 – 3.51 (m, 36H, OCH₂), 1.43 – 1.40 (m, 3H, CH₃); ¹³C NMR (D₂O. 151 MHz) δ 135.58, 120.74, 69.67 – 69.17, 60.52, 44.68, 14.51.

HPEG₄₀₀**PIMBr**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 7.91 – 7.80 (m, 1H, CH), 7.19 – 7.02 (m, 2H, CH), 4.70 – 4.01 (m, 2H, CH₂), 3.79 – 3.56 (m, 36H, OCH₂), 1.83 – 1.68 (m, 2H, CH₂), 1.24 – 1.19 (m, 2H, CH₂), 0.86 – 0.80 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 135.10, 122.07, 71.44 – 69.02, 60.01, 49.79, 22.99, 9.75.

HPEG₄₀₀**BIMBr**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.75 – 8.70 (m, 1H, CH), 7.51 – 7.42 (m, 1H, CH), 7.41 – 7.29 (m, 1H, CH), 4.36 – 4.31 (m, 1H, CH), 4.18 – 4.10 (m, 2H, CH₂), 3.84 – 3.56 (m, 36H, OCH₂), 1.83 – 1.68 (m, 2H, CH₂), 1.42 – 1.10 (m, 2H, CH₂), 0.86 – 0.82 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 135.08, 122.35, 69.57 – 68.49, 60.29, 49.20, 30.93, 18.61, 14.59.

HPEG₄₀₀**BIMCI**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.68 – 8.62 (m, 1H, CH), 7.51 – 7.42 (m, 2H, CH – CH), 4.21 – 4.11 (m, 2H, CH), 3.56–3.66 (m, 36H, OCH₂), 2.04 – 1.63 (m, 2H, CH₂), 1.41 – 1.11 (m, 2H, CH₂), 1.10 – 1.07 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 135.28, 120.99, 69.56 – 69.22, 60.24, 47.02, 31.82, 12.68.

HPEG₄₀₀**BIMI**. Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.01 – 7.91 (m, 1H, CH), 7.37 – 7.01 (m, 2H, CH – CH), 4.20 – 3.42 (m, 3H, OCH₂), 3.87 – 3.83 (m, 1H, CH), 3.63 – 3.56 (m, 55H, OCH₂), 1.46 – 1.41 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 135.15, 122.31, 69.45 – 69.27, 60.16, 49.19, 31.10, 18.57, 12.63.

HPEG₆₀₀**EIMBr.** Yellowish oil; ¹H NMR (D₂O, 600 MHz) δ 8.75 – 8.62 (m, 1H, CH), 7.50 – 7.40 (m, 1H, CH), 7.39 – 7.37 (m, 1H, CH), 4.21 – 4.19 (dd, J = 6.0, 18.0 Hz, 1H, CH), 4.16 – 4.12 (dd, J =6.0, 18.0 Hz, 2H, CH₂), 3.75 – 3.50 (m, 67H, OCH₂), 1.45 – 1.41 (m, 3H, CH₃); ¹³C NMR (D₂O, 151 MHz) δ 134.50, 122.03, 69.68 – 69.46, 60.37, 44.77, 14.59.

2.5. General procedure for cycloaddition



R = H, -CH₃, -CH₂Cl, -cyclohexenyl, -phenyl, -CH₂OPh.

All cycloadditions of CO2 with epoxides were conducted within a 25 mL stainless steel autoclave. Typical procedure for the reaction was depicted as below: 0.014 mol of epoxide and 1.00 mol% HPEG_nRIMX were successively added into a 75 mL stainless steel autoclave with a magnetic stirring. After the autoclave was sealed, CO₂ was charged into the reactor and adjusted to the reaction pressure and reacted at presetted temperature. After completing the reaction, the mixture solution was cooled to r.t. and CO₂ residue was given off slowly. The mixture was warmed to r.t. and stirred for completing the reaction residue of CO₂ was given off slowly. The catalyst was recovered by using a simple extraction process and then washed with anhydrous diethyl ether for the next recycle. Finally, the reaction solution was collected and determined by GC analysis using diphenyl as the internal standard material. All crude products were purified by using the silica gel's flash chromatograph with EtOAc/Hexane (volume ratio = 1:20), and their chemical structures were characterized by ¹H NMR (data listed in below and spectrum seeing in Figure S15-S20).

1,3-Dioxolan-2-one[49a]. White solid; ¹H NMR (CDCl₃, 600 MHz) δ 4.50 (s, 4H, OCH₂).

4-methyl-1,3-dioxolan-2-one[49b]. White solid; ¹H NMR (CDCl₃, 600 MHz) δ 4.85 – 4.81 (m, 1H, OCH), 4.53 (t, *J* = 8.0 Hz, 1H, CH₂), 4.01 (t, *J* = 8.01 Hz, 1H, CH₂), 1.46 (d, *J* = 6.2 Hz, 3 H, CH₃).

4-Chloromethyl-1,3-dioxolan-2-one[49c]. Yellowish solid; ¹H NMR (CDCl₃, 600 MHz) δ 4.99 – 4.95 (m, 1H, CH), 4.60 (t, *J* = 12.0, 6.0 Hz, 1H, CH), 4.42 (dd, *J* = 6.0 Hz, 1H, CH), 3.75 (m, 2 H, CH₂).

1,2-cyclohexyl carbonate[49d]. White solid; ¹H NMR (CDCl₃, 600 MHz) δ 4.70 – 4.67 (m, 2H, 2 × CH), 1.92 – 1.89 (m, 4H, 2CH₂), 1.66 – 1.60 (m, 2H, CH₂), 1.46 – 1.40 (m, 2H, CH₂).

4-Phenyl-1,3-dioxolan-2-one[49d]. White solid; ¹H NMR (CDCl₃, 600 MHz) δ 7.45 – 7.35 (m, 5H, Ph), 5.67 (t, *J* = 8.0 Hz, 1H, OCH), 4.79 (t, *J* = 8.4 Hz, 1H, CH), 4.34 (t, *J* = 8.4 Hz, 1H, CH).

4-Phenoxy-1,3-dioxolan-2-one[49e]. White solid; ¹H NMR (CDCl₃, 600 MHz) δ 7.30 (t, J = 8.0 Hz, 2H, m-Ph), 7.00 (t, J = 7.4 Hz, 1H, p-Ph), 6.90 (d, J = 8.2 Hz, 2H, o-Ph), 5.04 – 5.00 (m, 1H, OCH), 4.61 (t, J = 8.5 Hz, 1H, CH), 4.53 (t, J = 5.8 Hz, 1H, CH), 4.23 (dd, J = 10.5, 4.3 Hz, 1H, =CHO), 4.15 (dd, J = 10.5, 3.2, 1H, =CHO).

2.6. Characterization

FT-IR was conducted by using KBr as a standard material on the Thermo Corp. Nicolet 380 FT-IR 6700 (thermo, CO. Let.) spectrometer. Thermogravimetric analysis (TGA) was carried out on Shimadzu Corp. DTG-60H Thermal Analysis System at a heating rate of 10 °C/min from 25 to 650 °C. The NMR spectra of samples were recorded on JNM-ECA600 spectrometer. The CO₂ solubility in the supported ILs was analyzed by using the intelligent gravimetric analyser (IGA, Haliga 165 IGA-001, HIDEN Company, British) after treating the sample at 400 for 10 h under 10 - 4 Pa vacuum environment. GC yields were determined by GC-7890A, Agilent Technology using biphenyl as the standard material.

3. Results and discussion

3.1. FT-IR analysis

FT-IR spectra of PEG₄₀₀, HPEG₄₀₀Cl, HPEG₄₀₀IM and HPEG₄₀₀EIMBr were depicted in Fig. 1. The peak at 3361 cm⁻¹ in Fig. 1b belonged to OH stretching vibrations of HPEG₄₀₀Cl, and it was narrower and a little weaker than that of OH stretching vibration on PEG₄₀₀ in Fig. 1a due to the substitution of chloro-group on the long chains of polyethylene glycols. The peak of 664 cm⁻¹ in the curve of Fig. 1b attributed to the stretching vibration of C-Cl in HPEG₄₀₀Cl. The C–H stretching vibrations at 2880 and 1460 cm⁻¹ in Fig. 1a–c didn't perform any shifts.



Fig. 1. FT-IR spectra of (a) $\text{PEG}_{400},$ (b) $\text{HPEG}_{400}\text{Cl},$ (c) $\text{HPEG}_{400}\text{IM}$ and (d) $\text{HPEG}_{400}\text{EIMBr}.$



Fig. 2. TGA graph of HPEG₄₀₀EIMBr.

While HPEG₄₀₀EIBr was analyzed by FT-IR, the C–H stretching vibration at the peak of 1400 cm⁻¹ resulted into the obvious redshift to lower wavenumber in Fig.1d. In addition, the O–H bond's stretching vibration at above 3600 cm⁻¹ also gave the similar varying tendency (Fig. 1d) because of the interaction between the task-functional imidazolium-based ILs moieties and hydroxyl group on HPEG₄₀₀EIMBr. Furthermore, their structures were further determined by ESI-MS as shown in Figure S1, S5-S7, and the molecular weights of HPEG₄₀₀Cl, HPEG₄₀₀IM and HPEG₄₀₀EIMBr were 434, 456 and 493, respectively. The results indicated that HPEG₄₀₀EIMBr could be successfully synthesized by chemical stoichiometric method.

Thermal stability of HPEG₄₀₀EIMBr was investigated by TGA analysis as depicted in Fig. 2, and its thermal stable temperature was below 200 °C. The curve of HPEG₄₀₀EIMBr ranging from 200 to 300 °C appeared the first weight loss stage for the thermal decomposition of bromo-ethane moieties on HPEG₄₀₀EIMBr. The second decomposed thermal stage was from 300 to 450 °C as the result of the thermal degradation of polyether long chains of the reported catalyst. Thus, the catalyst could maintain thermal stability of structure below the temperature of 200 °C.

 CO_2 adsorption properties of HPEG_nRIMX with different molecular weights were analyzed by using IGA instrument, and their comparative curves were listed in Fig. 3. As the increased CO_2 pressures from 0 to 1.5 MPa at r.t. (25 °C), the adsorption capacities of HPEG_nRIMX showed the obvious increasing trends. Moreover, the lower molecular weights of HPEG_nRIMX, the higher CO_2 adsorption capacities might be approached as the result of higher concentration of functionalized IIs moieties and lower concentration of Lewis acidic hydroxyl groups on them. When CO_2 adsorption capacity of HPEG₂₀₀EIMBr reached to



Fig. 3. $\rm CO_2$ adsorption curves of HPEG_{200}EIMBr, HPEG_{400}EIMBr and HPEG_{600}EIMBr at r.t..



Fig. 4. Effect of CO₂ pressures on the catalytic activities under reaction conditions of propyl oxide (14 mmol), 1.0 mol% of HPEG₄₀₀EIMBr, 130 $^\circ$ C and 1.5 h.

72.8 mg/g under the conditions of 1.5 MPa and 25 °C; HPEG₄₀₀EIMBr attained 77.6 mg/g; HPEG₆₀₀EIMBr only had 40.3 mg/g. Among the three curves in Fig. 3, HPEG₄₀₀EIMBr shown the best solubility for CO₂ within the ranges from 0 to 1.5 MPa at r.t., which could be attributed to the higher content of ILs functional moieties on HPEG₄₀₀EIMBr and their CO₂-philicity of polyether's long chains.

The reaction pressure played an important role for the chemical fixation of CO_2 with epoxides, and their results were depicted in Fig.4. Under the lower reaction pressure, the gaseous CO_2 at the upper of reaction solution was the CO_2 -rich phase. As CO_2 pressure increased to 1.5 MPa, the catalysis in the reaction might be improved and easily benefited from the raised CO_2 concentration at the bottom of the mixture solution. When cycloadditions between CO_2 and propyl oxide were conducted under the pressures ranging from 0.5 to 2.0 MPa, the catalytic activities could attain the most excellent catalytic activity with the yield of 99%, and reach the highest selectivity of 98%. While the reaction pressure was increased to 2.5 MPa, HPEG₄₀₀EIMBr exhibited the decreased catalytic activity with propyl carbonate's yield of 96% and 97% selectivity within the shorter reaction time of 1.5 h. 2.0 MPa CO_2 pressure was chosen as the best pressure for HPEG₄₀₀EIBr in the cycloaddition of CO_2 with propyl epoxides.

The reaction parameters containing with the types of catalysts, temperature and reaction time were also very important to evaluate the catalysis of HPEG_nRIMX in the chemical fixation of CO₂ with epoxides. Under the optimum CO₂ pressure of 2.0 MPa, these parameters were screened and the corresponding results were listed in Table 1. When PEG_{400} was directly used to the cycloaddition between propyl oxide and

Table 1										
Screening	reaction	conditions	for	the	chemical	fixation	of	CO_2	by	using
HPEG _P RIMX ^[a] .										

- 11 -					
Entry	Cat.	T (°C)	<i>T</i> (h)	Yield (%) ^[b]	Sel. (%)
1	PEG400	100	3.0	2.0	3.5
2	HPEG ₄₀₀ EIMBr	100	1.5	67	97
3	HPEG ₄₀₀ EIMBr	110	1.5	81	97
4	HPEG400EIMBr	120	1.5	93	96
5	HPEG400EIMBr	130	1.5	99	98
6	HPEG ₂₀₀ EIMBr	130	1.5	≥99	98
7	HPEG ₆₀₀ EIMBr	130	1.5	96	85
8	HPEG400PIMBr	130	1.5	99	97
9	HPEG400BIMBr	130	1.5	99	98
10 ^[c]	HPEG400EIMBr	130	1.5	67	83
11 ^[d]	HPEG400EIMBr	130	1.5	83	84

^[a]Reaction conditions: propylene oxide (14 mmol), 1.0 mol% of catalyst and CO_2 pressure(2.0 MPa). ^[b]GC yield with biphenyl as the standard material. ^[c] 0.25 mol% of HPEG₄₀₀EIMBr. ^[d]0.5 mol% of HPEG₄₀₀EIMBr.

Table 2Substrates' tolerance[a]

Entry	Epoxides	Products	Yield (%) ^[b]	Sel. (%)
1			99	≥99
2			97	≥99
3	ci		97	97
4	O		42	97
5			97	≥99
6			99	≥99

^[a]Reaction conditions: epoxides (14 mmol), HPEG₄₀₀EIMBr (1.0 mol%), CO₂ (2.0 MPa), 130 °C and 1.5 h. ^[b]Isolated yield.

CO₂ and without any functionalization, the yield of propylene carbonate was only 2% within 3 h (Entry 1, Table 1). Under the same reaction conditions of 1.0 mol% of catalyst, 2.0 MPa CO2 pressure, 100 °C and 1.5 h, HPEG₄₀₀EIMBr was applied into the reaction, the yield was increased to 67% (Entry 2, Table 1). As the reaction temperatures were increased to 130 °C from 100 °C, the yields of propylene carbonate reached to 99% and its selectivity attained 98% (Entries 2-5, Table 1). By contrast, under the same reaction conditions, the both catalysts of HPEG₄₀₀EIMBr (Entry 5, Table 1) and HPEG₂₀₀EIMBr (Entry 6, Table 1) preferred to exhibit higher catalytic activities over than that of HPE-G₆₀₀EIMBr with 96% yield and 85% selectivity (Entry 7, Table 1). From the experimental results, it was also found that the lower molecular weights of HPEG_nRIMX, the higher catalytic activities easily attained. It could be attributed to their higher CO₂-philicity of HPEG_nRIMX (seeing in Fig. 3) and the weaker steric hindrance from short alkyl chains on imidazolium cation units (Entries 8 and 9, Table 1). Under the conditions of 2.0 MPa CO₂ pressure, 130 °C and the reaction time of 1.5 h, the utilized amount of HPEG400EIMBr affected its catalytic activities in cycloaddition between propyl epoxide and CO2. When the amount of HPEG400EIMBr was 0.25 mol%, the yield was only 67% and the selectivity reached to 83% (Entry 10, Table 1). While 0.50 mol% HPE-G400EIMBr was used to catalyze the reaction, it gave the yield of 83% and 84% selectivity (Entry 11, Table 1). As the amount of catalyst was increased to 1.0 mol%, the yield of cyclic carbonate approached the highest value of 99% and the selectivity of propyl carbonate was 98% (Entry 5, Table 1). 1.0 mol% of HPEG_{400} EIMBr could smoothly catalyze the transformation of CO₂ into cyclic carbonates.

HPEG₄₀₀EIMBr's substrate tolerance had been conducted under the best optimized reaction conditions of 1.0 mol% catalyst, 2.0 MPa CO_2 pressure, 130 °C and 1.5 h, and the datum were listed in Table 2. The steric hindrance of cyclo-epoxides easily resulted into the lower

products' yield in the reaction. When cyclohexyl epoxide as the substrate was applied into the chemical fixation of CO₂, HPEG₄₀₀EIMBr gave the yield of 42% with 97% selectivity (Entry 4, Table 2). However, when ethylene epoxide was used as the substrate, the reported catalyst exhibited the excellent catalytic activity with the yield of 99% and above 99% selectivity (Entry 1, Table 2). Moreover, it was noteworthy that the substrates of cyclo-epoxides with the withdrawing or donating electronic group at the C₃ site of cyclo- epoxides were nearly all converted into their corresponding cyclic carbonates. When propylene epoxide was used as the substrate, propyl carbonate achieved 97% yield and more than 99% selectivity (Entry 2, Table 2). Chloro-cyclopropyl epoxide gave its corresponding product with the excellent yield of 97%



Fig. 5. Recyclability of HPEG₄₀₀EIMBr. Reaction conditions: propylene oxide (14 mmol), CO₂ (2.0 MPa), 1.0 mol% of catalyst, 130 °C and 1.5 h.



Fig. 6. Comparative activities of HPEG₄₀₀EIMBr and PEG₄₀₀DEIMBr under the conditions of propylene oxide (14 mmol), CO₂ (2.0 MPa), 1.0 mol% of catalyst and 130 °C.

(Entry 3, Table 2), phenyl ethylene oxide gave 97% yield with above 99% selectivity (Entry 5, Table 2), and phenyl ether propylene oxide shown 99% yield and \geq 99% selectivity (Entry 6, Table 2). HPE-G₄₀₀EIMBr easily performed better tolerance for different cyclo-epoxides.

Under the optimum reaction conditions, the recyclability of HPEG₄₀₀EIMBr in cycloaddition between CO_2 and propylene epoxide was investigated as depicted in Fig. 5. The catalyst was recovered by a simple extraction with diethyl ether as the solvent, and it could be recycled or reused five times without any loss of catalytic activity and decreased selectivity during being recycled. The decrease of catalytic activities might be resulted from the lose weight of HPEG₄₀₀EIMBr during its recovering process. The catalyst could be reused for several times with highly catalytic activities and remained stabilities being used before and after (seeing in Figure S21). Moreover, when the run time was decreased to 1.0 h, HPEG₄₀₀EIMBr could be recycled seven times without the loss of catalytic activities, and remained cyclic carbonate's yield more than 91.0% and the selectivity of 97% (Figure S22).

By comparison with the catalysis of $PEG_{400}DEIMBr$ in the chemical fixation of CO_2 with propylene epoxides, $HPEG_{400}EIMBr$ exhibited excellent catalytic activities, and the results were depicted in Fig. 6. As the increased reaction time varying from 0.5 to 2.5 h, $PEG_{400}DEIMBr$ gave the yields of propyl carbonate with 8.0–82%. Within the same reaction



Fig. 7. Proposed mechanism for the chemical fixation of CO₂.



Fig. 8. ¹H NMR spectra of propylene oxide (PO) with $PEG_{400}EIMBr$ at different concentrations of (a) 0.0045 M, (b) 0.0081 M and (c) 0.014 M (¹³CDCl₃, 600 MHz). The symbol "•" indicates the hydroxyl signal.

time, the reported catalyst exhibited the higher catalysis than that of $PEG_{400}DEIMBr$, which shown the excellent yield of 98% for 1.5 h. The improved catalytic activities of $HPEG_{400}EIMBr$ might be ascribed to the synergism of hydrogen-bonding between hydroxyl group in HPE- $G_{400}EIMBr$ and oxygen atom of cyclo-epoxides like the reported catalysts of HBD/TBAI[50] and [EvimOH][Cl]/DBU [51]. Moreover, HPE- $G_{400}EIMBr$ behaved the properties of metal-free, lower loading, easily accessibility and recoverability, which could easily chemically absorb much more CO_2 moleculars from the upper gaseous atmosphere and then acted them by nucleophilic attack to efficiently generate the aim products of cyclic carbonates.

The mechanism for HPEG_nRIMX in the chemical fixation of CO₂ with cyclo-epoxides was proposed as shown in Fig. 7. Firstly, hydrogen bonding between hydroxyl group on HPEG_nRIMX and oxygen atom of epoxides induced the opening-ring process of cycloepoxide and played the synergistic promotion for the conversion of CO₂ into cyclic carbonates, which was similar like the reported hydrogen bonding's facilitation roles[16,43]. According to our experimental on ¹H NMR spectra of PO with HPEG400EIMBr at the different concentrations within ¹³CDCl₃ (Fig. 8, S4 and S5), it could be found that the chemical shifts of hydroxyl group on HPEG400EIMBr were easily detected and could be observed in the lower fields with the increased concentrations of HPEG400EIMBr. Hydrogen bonds including intermolecular or intramolecular function were possibly enhanced and further facilitated the nucleophilic attack of the bromide anion with the epoxide ring of PO through reducing the barriers, which were similar like the reported literatures of [52,53]. As a result, the cyclo-rings of cyclo-epoxide might be easily opened and possibly swiftly activated CO₂ to form cyclic carbonates.

Secondly, bromide anion on HPEG₄₀₀EIMBr nucleophilic attacked C₂ site on the cyclo-ring of propylene oxide to generate the intermediate of compound (I), and then opened the cyclo-ring of epoxide to form the compound (II). Then, compound (II) as Lewis base chemisorpted free CO₂ to produce the new compound (III). During the process, HPEG_nRIMX probably adsorbed much more CO₂ molecules around the active centers because of the CO₂-philic property from their long polyether chains. The CO₂ adsorption capacity of HPEG₄₀₀EIMBr was 77.6 mg/g under the conditions of 25 °C and 1.5 MPa, which was higher than the CO₂ adsorption ability of PEG₄₀₀DEIMBr with double imidazolium-based ILs ending-capped polyethylene ether (seeing in Table S1). The result indicated that the diffusion of CO₂ molecules in the upper gaseous phase into the lower phase around the active species of HPEG_nRIMX could be facilitated by the CO₂-philic property of HPEG_nRIMX behaving the long polyether chains and imidazolium-

based ILs functional moieties. Subsequently, the activated CO_2 molecules were swiftly converted into the products of cyclic carbonates.

4. Conclusion

HPEG_nRIMX (n = 200,400,600) with the long polyether chain and bifunctional ending-capped moieties of hydroxyl group and task-specific ionic liquids have been synthesized by the chemical stoichiometric method. The supported catalysts could be recovered and reused five times without any loss of catalytic activity, which swiftly attained the excellent catalytic activity with the highest yield of 99% and 97% selectivity within shorter reaction time of 1.5 h. The catalytic activity was obviously more than that of PEG₄₀₀DEIMBr with double terminal ending-capped ILs functional groups due to its multifunctional synergetic role of the easy accessibility of polyether long chains for CO₂, hydrogen bonding inducing ring-opening of hydroxyl group on HPEG_nRIMX with oxygen atom on cycloepoxides, and nuclephilicity of halide anion attacking C₂ site of epoxide, which has been investigated by IGA and NMR spectrum.

The work shows a types of attractive catalysts behaving free-metal, easy accessibility for CO_2 , lower active species' loading of active species and excellent catalytic activities for chemical fixation of CO_2 through designing the complex multifunctional properties including polyether long chains, hydrogen bonding from hydroxyl group with epoxides and task-specific ILs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Ying Liu: Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing - original draft, Writing - review & editing. Yan Song: Formal analysis. Jianhua Zhou: Supervision. Xiangping Zhang: Supervision.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111008.

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