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Controllable Homogeneity/Heterogeneity Switch of Imidazolium Ionic Liquids for CO_2 Utilization

Jeehye Byun[a] and Kai A. I. Zhang*[a]

Abstract: Imidazolium ionic liquids (IL) have been recognized as a promising platform for CO_2 capture and conversion owing to the structural designability through molecular combination of cationic substituents and counter anions. However, the conventional homogeneous catalysis with ILs accompanies a laborious work-up procedure to recycle the catalyst and purify product after the reaction, limiting the applicability of ILs. Herein, we optimize the molecular structure of imidazolium ILs to mediate the cycloaddition of CO_2 upon epoxides, in which the IL functions as a homogeneous catalyst but exhibits heterogeneous separation capability. By varying the length of alkyl substituent on the imidazolium ring, the conversion efficiency of the epoxide into cyclic carbonate could be accelerated owing to higher reactivity of anions with longer aliphatic chains. The conversion efficiency was further optimized by having a proper type of counter anions with suitable level of nucleophilicity. The long-chain IL exhibited temperature-responsive phase transition behavior, allowing a facile isolation of IL and products after the reaction. In addition, with the high purity of obtained cyclic carbonates, non-isocyanate poly(hydroxylurethane)s could be produced by polyaddition of diamines, promoting the utilization of CO_2 as a chemical building block.

Introduction

Large anthropogenic emission of carbon dioxide (CO_2) is revealed as a primary cause of global warming in the last decades[1]. Due to prematurity of renewable energy technologies, increasing energy demand depends on fossil fuels all the same, so that the application of carbon capture and utilization (CCS) technology has been ever highlighted[2]. The direct CO_2 capture and conversion into valuable chemicals using well-designed materials offer new opportunities to reduce CO_2 emission into the atmosphere as well as to use it as chemical feedstocks[3]. Thus, there have been tremendous attempts to develop materials for CO_2 capture and conversion, such as metal organic frameworks[4] and porous organic polymers[5]. All these advances, however, have to face a challenge upon the imbalance between efficiency and cost of materials.

Ionic liquids (ILs) have drawn much attention for chemical reactions due to their low vapor pressure, high thermal stability and structural designability, also with an affordable price tag[6]. After being first tested by Blanchard *et al.*[7], ILs have been extensively studied for direct CO_2 utilization. In particular, imidazolium-based ILs are most widely investigated and reported in the literatures owing to their availability and high CO_2 solubility[8]. The CO_2 solubility in the ILs is known to correlate with the chemical nature of cations and anions. For instance, functionalization of imidazolium cations with alkyl[9], hydroxyl[10], fluorine[11], ether[12], nitrile[13] and amino[14] groups were found to be effective for enhancing CO_2 solubility. The fluor anions on imidazolium ILs, i.e., Tf_2N^-, BF_4^- and PF_6^-, also exhibited high CO_2 solubility compared to the ILs without the fluor groups[15]. The counter anions are further involving in catalytic cycles such as CO_2 cycloaddition with epoxides, resulting in 5-membered cyclic carbonates[16]. The simple anion exchange of imidazolium ILs allows a large window of catalytic applications for CO_2 conversion, e.g. synthesis of oxazolidinone[17] and quinazoline-2,4(1H,3H)-diones[18], formylation of amine[19], etc. Hence, various combinations of cations and anions have led to the structural diversity of ILs for providing a great degree of control for catalytic CO_2 utilization.

A remaining obstacle in exploiting ILs for CO_2 utilization would be the recovery process after the homogeneous catalysis, accompanying a tedious work-up process to recycle the ILs. Whereupon, many have tried to incorporate ILs on heterogeneous substrates such as silica structures[20], polymer matrix[21], porous polymers[22], and metal organic frameworks[23] to facilitate the regeneration of materials. Nonetheless, the embedment in substrates hinders the catalytic activity of ILs, which requires high reaction pressure and temperature, consequently resulting in inevitably higher cost. Therefore, there needs a strategy to combine homogenous catalysis and heterogeneous separation of ILs for the efficient CO_2 utilization.

Herein, we report a systematic design of imidazolium ILs with controllable homogeneity/heterogeneity switch for CO_2 utilization. By simply increasing alkyl chain length of the ILs to a certain extent, the reactivity of counter anion and the solubility of IL in epoxides could be gradually enhanced, thus affecting the CO_2 conversion efficiency. The longer alkyl chain of ILs resulted into the reversible solid/liquid phase transition behavior via temperature swing, leading to easy heterogeneous separation of the IL after the homogeneous catalytic reaction under a solvent-free condition. In order to enhance the chemical fixation of CO_2 with epoxide under atmospheric pressure, the effect of the counter anions was also rationalized by altering their nucleophilicity. Additionally, with high conversion efficiency of epoxides, the obtained bis(cyclic carbonate) product was able to be polymerized into poly(hydroxylurethane), demonstrating the feasibility of CO_2 utilization over imidazolium ILs a step forward.

Results and Discussion

The CO_2 cycloaddition upon epoxide is often conducted in elevated temperature, and imidazolium IL plays a role as a homogeneous catalyst in the reaction. Therefore, in order to separate out cyclic carbonate product and recycle the IL catalyst, energy-intensive methods have been utilized such as vacuum

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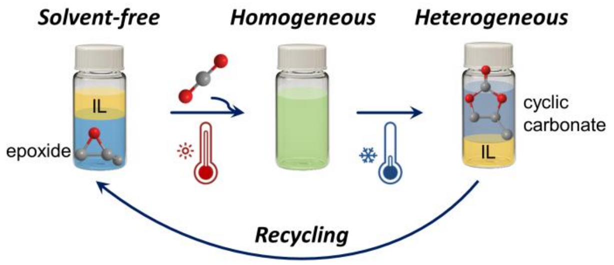
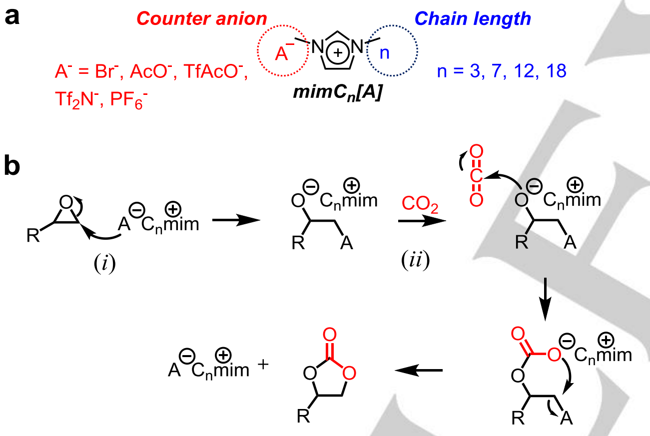
Supporting information for this article is given via a link at the end of the document.

distillation[24] and column chromatography[25], resulting in extra cost. Basic idea of homogeneity/heterogeneity switch resides in phase separation of IL catalyst by temperature change. When the homogenous solution of reaction mixture is cooled down, the IL is subjected to precipitation, thus enabling heterogeneous isolation of the IL catalyst by a simple filtration (**Scheme 1**). Therefore, structural design of imidazolium IL is a prerequisite for accomplishing the controllable homogeneity/heterogeneity switch of IL catalyst.



Scheme 1. Schematic illustration of temperature-assisted homogeneity/heterogeneity switch of imidazolium IL to catalyze CO_2 cycloaddition on epoxide.



Scheme 2. (a) Molecular design of imidazolium ionic liquid mimC$_n$[A] for CO_2 utilization. (b) Plausible mechanism of CO_2 cycloaddition upon epoxide substrates catalyzed by mimC$_n$[A].

The rational design of imidazolium ILs involves the change of alkyl chain length on imidazolium cation and counter anions in different combinations (**Scheme 2a**). Firstly, the length of alkyl chain on imidazolium ring was varied from propane to octadecane with bromide as a counter anion, giving a series of ILs, namely mimC$_n$[Br] (where n = 3, 7, 12, and 18, for propane, heptane, dodecane, and octadecane-functionalized IL, respectively). The mimC$_n$[Br]s were utilized to catalyze cycloaddition of CO_2 with epoxides, of which tert-butyl glycidyl ether (tBGE) and 1,2-epoxyoctane (EO) were tested in a typical condition of atmospheric CO_2 pressure (**Figure 1**). Time-dependent kinetics showed that the epoxide substrates were fully converted into respective cyclic carbonates in 24 h when catalyzed with mimC$_n$[Br]s at the elevated temperature. Since the rate-determining step of CO_2 fixation upon epoxide is nucleophilic ring-opening of epoxides by counter anion (**Scheme 2b**, *step i*)[26], mimC$_n$[Br] having the same bromide anion might exhibit the similar reactivity irrespective of alkyl chain length.

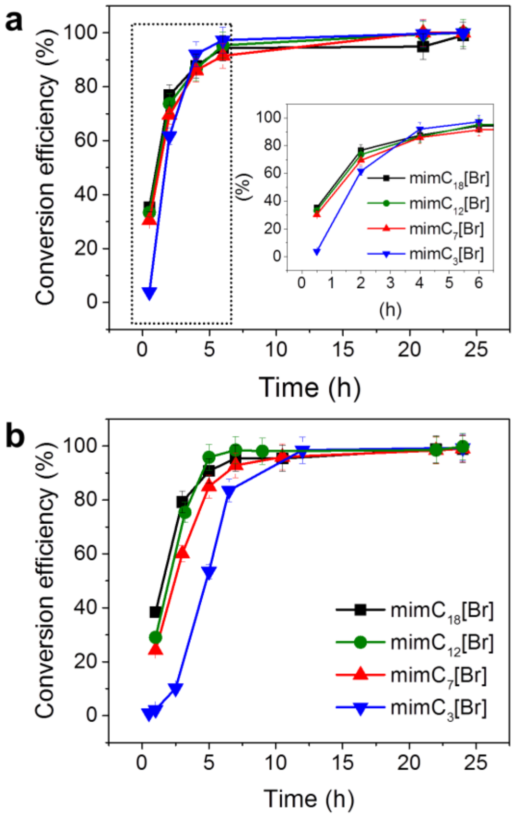


Figure 1. Time-dependent conversion of epoxide substrates (a) tert-butyl glycidyl ether (tBGE) and (b) 1,2-epoxyoctane (EO) through cycloaddition of CO_2 to form cyclic carbonates with mimC$_n$[Br]s (n = 3, 7, 12, and 18) as catalysts. Inset of (a) shows the magnified view of the first 6 h of experiment (dotted frame). Reaction condition: mimC$_n$[Br] (0.1 mmol, 1 mol%), epoxide (10 mmol), CO_2 (< 1 bar), 110 °C for (a) and 130 °C for (b).

The magnified conversion kinetics, however, clearly revealed the effect of alkyl chains on cation. As the alkyl chain length on imidazolium ring became longer, the conversion of epoxide into cyclic carbonate was faster in the first few hours. As displayed in **figure 1a**, tBGE was converted into respective cyclic carbonate upto 3.9 % and 35.3 % at the first 30 min of reaction with mimC$_3$[Br] and mimC$_{18}$[Br], respectively. The conversion of EO substrate also exhibited the similar pattern, showing 2.2 % and 38.4 % of conversion efficiency at 1 h of reaction with mimC$_3$[Br] and mimC$_{18}$[Br], respectively (**Figure 1b**). The enhancement in conversion efficiency with respect to the longer alkyl chain on imidazolium cation would be primarily attributed to weaker electrostatic interaction between cation and anion of ILs. The bulkiness of long-chain cation pushes the bromide ion away, thus making the anion more nucleophilic to attack epoxide ring[27]. Secondary reason for the increasing efficiency would be originated from the improved solubility of ILs in epoxide substrates with longer aliphatic chains, particularly for solvent-free reaction. The longer chain IL is supposed to dissolve well in non-polar solvent than the shorter chain IL[28], therefore the mimC_{18}[Br] could show enhanced catalytic efficiency owing to the higher solubility in epoxide substrate. Control experiment using inorganic LiBr salt as a catalyst showed 3% conversion of EO substrate after 24 h, implying that the solubility of catalyst in epoxide is indispensable for chemical fixation of CO_2 upon epoxide.

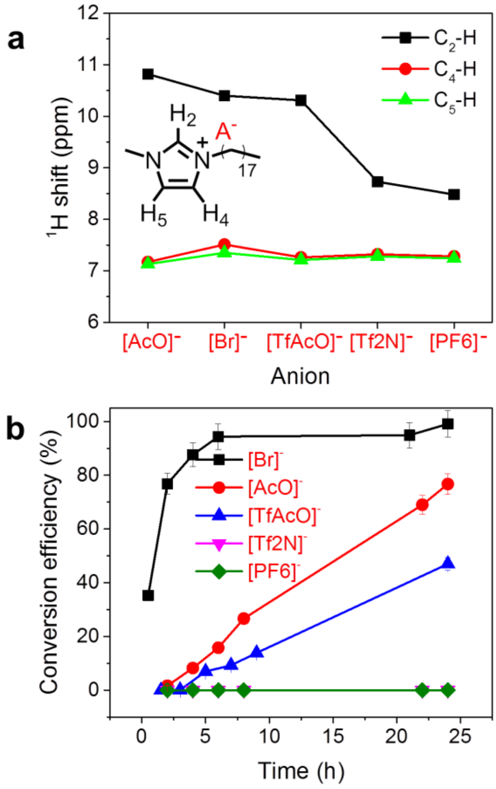


Figure 2. (a) ^{1}H NMR chemical shifts for C_2-H, C_4-H, and C_5-H on the imidazolium ring for mimC_{18}[A]s with different counter anions. The chemical shifts are relative to external TMS in $CDCl_3$. (b) Time-dependent conversion of tBGE to cyclic carbonate with CO_2 catalyzed by mimC_{18}[A]s having different anions. Reaction condition: mimC_{18}[A] (0.1 mmol, 1 mol%), epoxide (10 mmol), CO_2 (< 1 bar), 110 °C.

Along with the longest alkyl chain, the influence of counter anions on ILs was tested for CO_2 conversion. Beside mimC_{18}[Br], four additional ILs were prepared by anion exchange of bromide with common anions, giving mimC_{18}[AcO], mimC_{18}[TfAcO], mimC_{18}[Tf_2N], and mimC_{18}[PF_6], for acetate, trifluoroacetate, bis(trifluoromethylsulfonyl)imide, and hexafluorophosphate, respectively. Since the counter anions attack the electrophilic carbon on epoxide ring, higher nucleophilicity of anions would lead to the improved conversion of epoxide into cyclic carbonate. The nucleophilicity of counter anions on mimC_{18}[A]s could be probed by experimental chemical shifts of protons on imidazolium cation. The weakly acidic protons on imidazolium ring can be affected by hydrogen bonding and inductive effect of counter anions[29], in other words, the chemical shift of protons on imidazolium ring moves to downfield with increasing nucleophilicity of anions[30]. As shown in **Figure 2a**, the ^{1}H chemical shifts on 2-, 4-, and 5-position of imidazolium ring (H_2, H_4, and H_5, respectively) exhibited obvious difference depending on the type of anions (See **Figure S1** for ^{1}H NMR spectra of mimC_{18}[A]s). The ^{1}H chemical shift for 2-position showed the largest change than those for 4- and 5-position as the anions are likely to be located at around 2-position on imidazolium cation[31]. Through a relative comparison of ^{1}H chemical shift, the nucleophilicity of anion was found to follow the order of $[AcO]^- > [Br]^- \geq [TfAcO]^- > [Tf_2N]^- > [PF_6]^-$, which would correlate to their reactivity for CO_2 conversion. As displayed in **Figure 2b**, however, the conversion of tBGE was rather inconsistent with the order of nucleophilicity, in which the conversion efficiency of tBGE decreased in the following order of mimC_{18}[Br] > mimC_{18}[AcO] > mimC_{18}[TfAcO] >> mimC_{18}[Tf_2N] ≈ mimC_{18}[PF_6]. Despite the highest nucleophilicity, the IL with acetate anion showed a moderate conversion of epoxide upto 76.7 % for 24 h, while the IL with bromide anion resulted in 99 % of conversion efficiency for 24 h. Though trifluoroacetate anion exhibited similar level of nucleophilicity with bromide anion, mimC_{18}[TfAcO] showed 47 % of conversion efficiency for 24 h. Unexpected behavior of mimC_{18}[AcO] and mimC_{18}[TfAcO] may be attributed to thermal decomposition of ILs by S_N2 nucleophilic substitution of basic acetate anions upon methyl imidazolium ring[32]. In fact, mimC_{18}[AcO] and mimC_{18}[TfAcO] could not be separated and recycled after the first cycle of conversion experiment. Besides, ILs with fluorinated anions showed no reactivity to convert epoxides at the given atmospheric CO_2 condition, probably due to the relatively low nucleophilicity. The low nucleophilicity of fluorinated counter anions may thus require high pressure (~2 MPa[33]) to facilitate the chemical fixation of CO_2 on epoxides. Therefore, the structure of imidazolium ILs could be optimized with long alkyl substituent on cation and bromide as a counter anion.

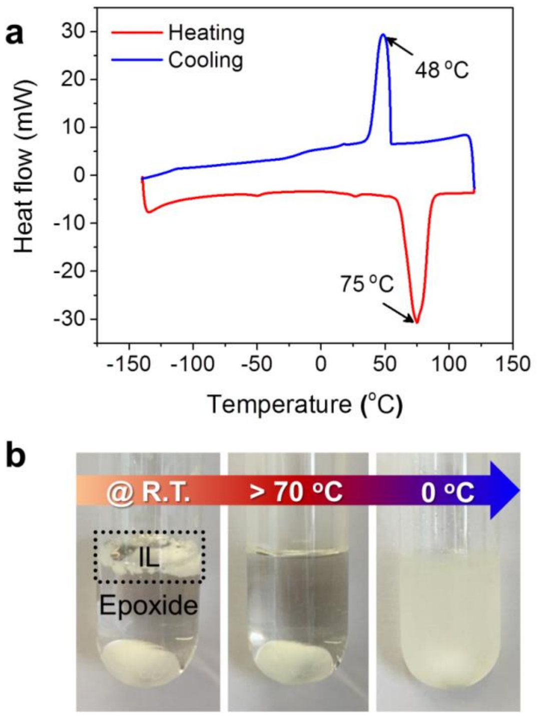


Figure 3. (a) Temperature dependence of the total heat flow monitored during the heating and cooling process for mimC$_{18}$[Br]. (b) Phase transition of mimC$_{18}$[Br] in epoxide substrate (tBGE) via a consecutive temperature change.

The optimized mimC$_{18}$[Br] exhibited phase transition behavior upon temperature change. **Figure 3a** shows the temperature-dependent total heat flow by heating and cooling mimC$_{18}$[Br]. As the temperature increased from -140 °C, a large endothermic peak appeared at 75 °C, which corresponds to the temperature for transition from crystalline solid to smectic phase as a liquid crystal[34]. By the successive cooling of mimC$_{18}$[Br], the transition from smectic phase to solid phase was observed at 48 °C. The temperature range of phase transition from solid to liquid coincides with the operation temperature of CO_2 conversion reaction (**Figure 3b**). In other words, mimC$_{18}$[Br] solid at room temperature would not fully dissolve in target epoxide substrates due to the long aliphatic chain. Once being heated over 75 °C, mimC$_{18}$[Br] is transformed into smectic liquid crystals, becoming soluble in the epoxides to catalyze the CO_2 cycloaddition reaction. When the reaction is finished, mimC$_{18}$[Br] can be separated out from liquid products by lowering down the temperature of reaction mixture e.g. to 0 °C. Therefore, the temperature-responsive phase transition of mimC$_{18}$[Br] enables heterogeneous isolation of catalyst after the reaction as well as homogeneous catalysis for CO_2 conversion.

The homogeneous catalysis and heterogeneous separation using mimC$_{18}$[Br] could be monitored by ^{1}H NMR spectroscopy (**Figure 4**). Pristine catalyst mimC$_{18}$[Br] (**Figure 4a**) and epoxide substrate tBGE (**Figure 4b**) were mixed and heated up to 110 °C in the absence of CO_2, giving no change in the substrate (**Figure 4c**). When blown with CO_2, the epoxide substrate was then able to be converted into respective cyclic carbonate, showing clear chemical shifts at 4.74, 4.43, 4.34, 3.55, and 3.48 ppm for cyclic carbonate formation (**Figure 4d**). The mimC$_{18}$[Br] was separated out from reaction medium by cooling the temperature down, and the recovered catalyst was clean and intact with identical chemical shifts from the pristine catalyst (**Figure 4e**).

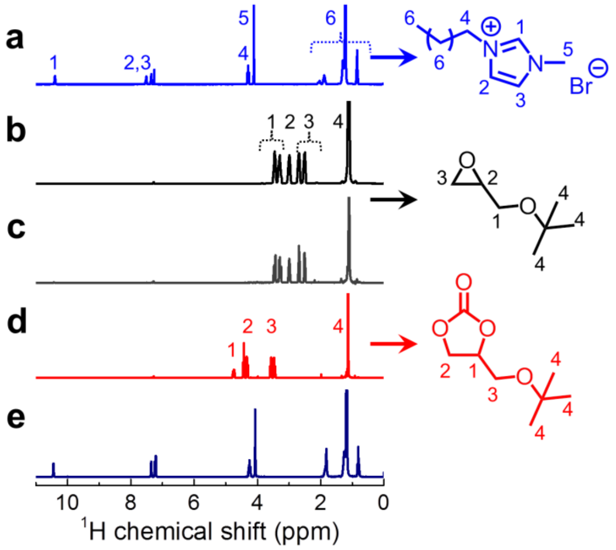


Figure 4. Temperature-assisted separation of catalyst proven by ^{1}H NMR spectra in $CDCl_3$. ^{1}H NMR spectrum of (a) pristine catalyst mimC$_{18}$[Br], (b) pure substrate of tBGE before reaction, products recovered after the reaction at 110 °C (c) without CO_2 and (d) with CO_2 injection for 24 h (< 1 bar), and (e) the separated catalyst through temperature swing after the reaction.

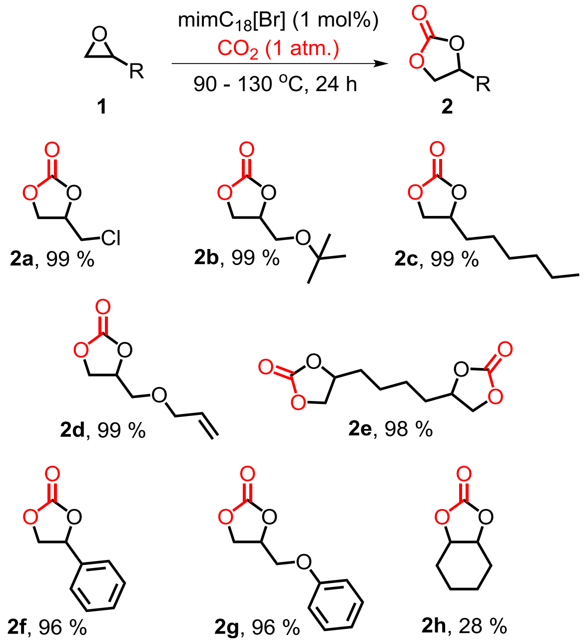


Figure 5. Substrate scope for generation of cyclic carbonates **2** by the cycloaddition of CO_2 on epoxides **1** (10 mmol). For **2a**, the reaction was done at 90 °C. For **2b** and **2f**, at 110 °C. For **2c-e** and **2g-h**, at 130 °C.

Temperature-assisted homogeneity/heterogeneity switch of IL has been applied to epoxide substrates with a variety of substituents (**Figure 5**). Regardless of the functionalities, the tested substrates have shown quantitative conversion into cyclic carbonates under atmospheric pressure of CO_2, making mimC$_{18}$[Br] comparable to efficient ILs reported recently[24, 35]. By virtue of thermal stability of mimC$_{18}$[Br] (**Figure S2**), reaction temperature could range from 90 °C to 130 °C to yield target products **2a - 2h** in 24 h (See NMR spectra of products in supporting information). Depending on the type of products, however, there was discrepancy in time to isolate the mimC$_{18}$[Br] after the reaction through lowering down the temperature. The mimC$_{18}$[Br] could be easily separated out from the reaction mixture of **2a – 2c** in ice bath, while there took few hours to isolate the catalyst out of **2d** and **2e** mixture, maybe due to high viscosity of resulting cyclic carbonates. In case of **2f – 2h**, the catalyst was separated by flash column chromatography as the reaction mixtures were solidified in low temperature. When the small amount of ethyl acetate was added into the crude reaction mixtures, the temperature-controlled separation of catalyst could be far accelerated under low temperature to afford the pure products in few minutes (See a video clip in supporting information).

Owing to the temperature-responsive separation behavior, mimC$_{18}$[Br] was able to be regenerated for the repeated use. Repeating cycles of CO_2 cycloaddition on epoxide **1c** in few gram scale revealed that mimC$_{18}$[Br] could catalyze the reaction for repeated cycles, showing 98 % of conversion efficiency in 5th cycle (**Figure S3a**). Each cycle only run for 6 h owing to the fast conversion of **1c** as described in **Figure 1b**. In order to facilitate the separation of catalyst during the repeated cycle, the isolation of mimC$_{18}$[Br] was conducted in ethyl acetate solution (~20 mL). There was no evidence of residual catalyst in product, confirmed by the addition of $AgNO_3$ solution after 5th cycle (**Figure S3a** inset). The high efficiency and low cost of mimC$_{18}$[Br] prompted us to conduct in much larger scale of CO_2 conversion. Epichlorohydrin **1a**, one of the cheapest substrate among the epoxides, was tested in 80 ml scale (1 mol) with 0.25 mol% of mimC$_{18}$[Br] (**Figure 6a**). The catalytic dose of mimC$_{18}$[Br] was optimized in a smaller scale as shown in **Figure S3b**. Large-scale production of cyclic carbonate **2a** was achieved after 70 h of the reaction, leading to 99 % of conversion efficiency (**Figure 6b**). The longer reaction time for the large-scale experiment would be associated from the slower CO_2 diffusion in the liquid substrate. Nonetheless, the product aliquot obtained through large-scale CO_2 cycloaddition reaction under atmospheric condition was clean after the separation of catalyst through a temperature swing (**Figure S4**).

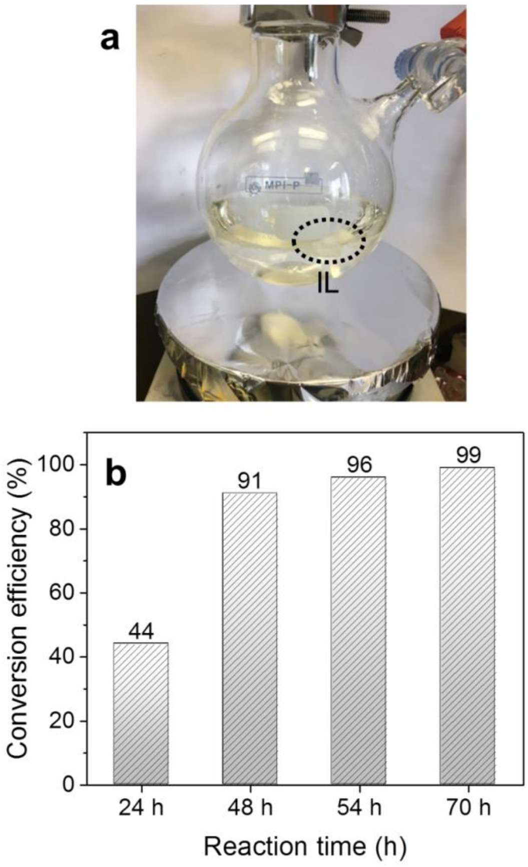


Figure 6. (a) Photograph of large-scale experiment set-up with ~80 mL of **1a** and mimC$_{18}$[Br]. (b) Large-scale production of **2a** catalyzed by mimC$_{18}$[Br]. Reaction condition: mimC$_{18}$[Br] (2.5 mmol, 0.25 mol%), epoxide **1a** (1 mol), CO_2 (< 1 bar), 90 °C.

Cyclic carbonates are known as environmentally-friendly precursor of non-isocyanate polyurethane (NIPU) by polyaddition reaction with amine group[36]. The pure cyclic carbonate afforded from CO_2 cycloaddition on epoxide was thus applied to generate NIPU for proving the feasibility of CO_2 utilization process mediated by mimC$_{18}$[Br]. Bis(cyclic carbonate) **2e** was reacted with two different diamines to form hydroxylurethane linkage at the elevated temperature, giving two NIPUs **3a** and **3b** with high yields (**Figure 7a**). The resulting NIPUs were insoluble in common organic solvents, probably due to high molecular weight after polymerization (**Figure S5a** and **b**). The fraction of NIPUs dissolved in 0.5% LiBr DMF solution at 70 °C showed molecular weight (M_w) of 3320 g mol^{-1} and 14166 g mol^{-1} for **3a** and **3b**, respectively. The formation of NIPU was able to be simply observed by FTIR spectra (**Figure 7b**). A distinct peak of **2e** at 1780 cm^{-1} from C=O stretching vibration of cyclic carbonate disappeared after the polymerization, while broad peak was evolved at 3315 cm^{-1} for both **3a** and **3b**, which is attributed to N-H and O-H stretching vibrations of amide and hydroxyl group, respectively. The peaks appeared at around 1650 cm^{-1} also correspond to the formation of secondary amide in the NIPUs. As being connected with different type of amines, thermal properties of **3a** and **3b** could be largely altered. In particular, the degree of freedom in chain fragments was verified by glass transition temperature (T_g) of NIPUs, in which **3a** and **3b** showed -30 °C and 32 °C of T_g, respectively (**Figure 7c**). Relatively low T_g of **3a** resulted from structural flexibility with alkyl chains of n-hexane, and **3b** with harder segment of *p*-xylene caused relatively higher T_g. In fact, **3a** had sticky texture owing to the free aliphatic chains, on the other hand, **3b** with rigid aromatic ring was fine powder without adhesiveness. The adhesive **3a** could carry more than 50 g of mass when the 5 mg of **3a** was sandwiched between two glass plates and one side of the plate was pulled with the mass (**Figure S5c**). The simple change in monomeric composition thus allowed a fine adjustment in properties of NIPUs. Both NIPUs exhibited high thermal stability, in which the first 5 % of mass loss occurred at 255 °C (**Figure 7d**).

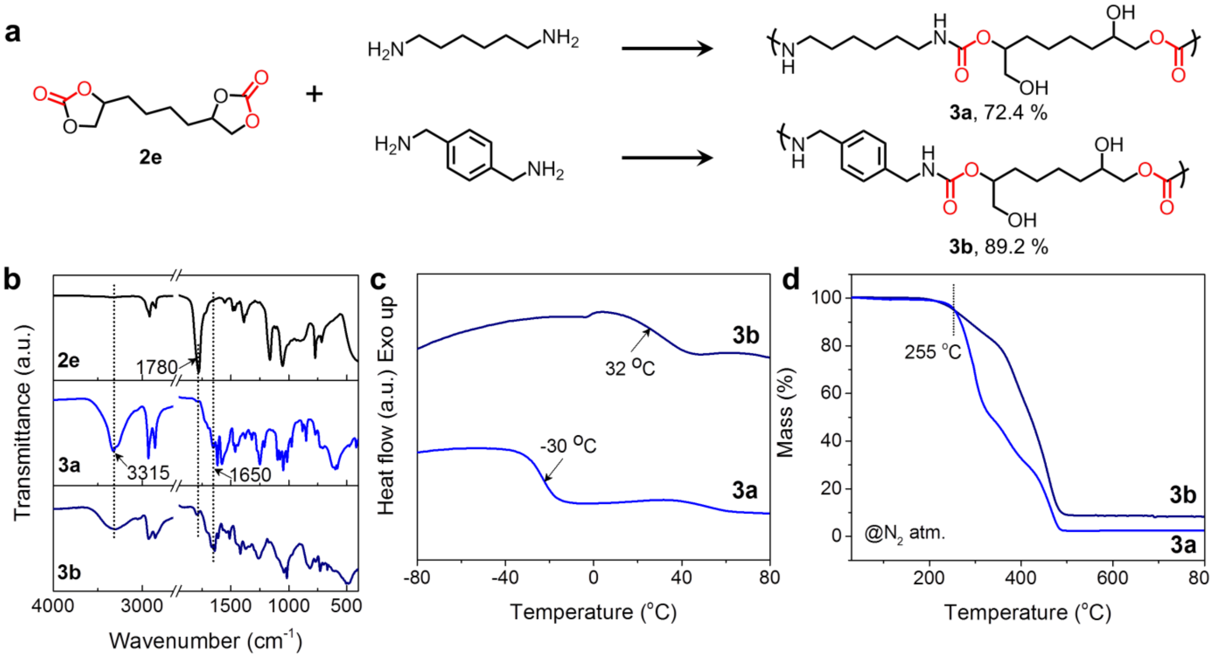


Figure 7. (a) Synthetic scheme of non-isocyanate polyurethanes **3a** and **3b** by polyaddition of bis(cyclic carbonate) **2e** and diamines. (b) FTIR spectra of **2e**, **3a** and **3b.** (c) DSC and (d) TGA thermogram of **3a** and **3b**.

Conclusions

In summary, we have optimized the structural composition of imidazolium ILs by simply altering the length of alkyl substituent on cation and type of counter anions to catalyze cycloaddition of CO_2 upon epoxides. When the IL bore long aliphatic chain of octadecane on imidazolium ring with bromide as a counter anion, the complete conversion of epoxides into cyclic carbonates could be achieved under atmospheric pressure of CO_2. The long chain structure of IL exhibited temperature-responsive solid/liquid phase transition behavior, enabling the homogeneous catalysis at high temperature and the heterogeneous separation of catalyst under low temperature after the reaction. Low cost of the ILs facilitated large-scale production of cyclic carbonate, and the IL was recyclable for the repeated use. The obtained bis(cyclic carbonate) product could be utilized to generate non-isocyanate polyurethane (NIPU) by polyaddition with diamines under the elevated temperature, proving the feasibility of imidazolium IL for CO_2 conversion. The resulting poly(hydroxylurethane) showed structural variation based on the type of diamine linkage, further providing a room to explore the production of various NIPUs by CO_2 utilization.

Experimental Section

Synthesis of mimC$_{18}$[Br]: In a typical set-up, 1-methylimidazole (1.1 mL, 13.9 mmol) and 1-bromododecane (7.12 mL, 20.85 mmol) were dispersed in absolute ethanol (7 mL). The mixture was heated at 80 ºC for 3 d under N_2 atmosphere. After the reaction, the solvent was evaporated under the reduced pressure, resulting in off-white wax-like solution. The crude product was dissolved in acetonitrile and reprecipitated with ethyl acetate. The obtained precipitate was filtered and dried *in vacuo* at 60 ºC for overnight to afford white powder as a product. The purified product was kept in moisture-free condition for further use. Yield = 84.2 %. The other mimC$_n$[Br]s (n = 3, 7, and 12) with shorter alkyl chains were produced with the similar procedure described above.

General procedure for synthesis of cyclic carbonate under atmospheric pressure of CO_2: Ionic liquid (0.1 mmol) and epoxide substrate (10 mmol) were placed in a 20 mL screw-cap vial and purged with CO_2 for 10 min. The mixture was heated at the desired temperature under CO_2 atmosphere for 24 h, in which CO_2 was injected through a Schlenk line with the pressure of ~1 bar. The reaction mixture was cooled down to room temperature and the aliquot was diluted with dichloromethane for GC-MS analysis to determine conversion efficiency. For the repeated use of the short-chain ionic liquids, mimC$_n$[Br] (n = 3, 7, 12), the reaction mixture was purified through flash column chromatography to isolate product. In the case of mimC$_{18}$[Br], temperature-assisted separation of catalyst was conducted. After the reaction, the mixture was cooled down in ice bath, leading to precipitation of the catalyst. Afterwards, the mixture was centrifuged at 3000 rpm for 10 min under low temperature (~0 ºC) to isolate the catalyst and afford pure product as supernatant. For the cyclic experiment, the reaction mixture was diluted with 20 mL of ethyl acetate and cooled down at 0 ºC to isolate mimC$_{18}$[Br] in few minute. The solution was filtered while cold, and the pure product was obtained after the evaporation of ethyl acetate. The collected catalyst was gently washed with ether and dried for next run. For the all tested substrates, the separation of catalyst from reaction media could be accelerated by the addition of ethyl acetate.

General procedure for production of poly(hydroxylurethane): Pure bis(cyclic carbonate) **2e** (1 mmol) and diamine (1.4 mmol) were placed in a 40 mL screw-cap vial and dissolved in anhydrous DMF (1 mL). The mixture was heated at 130 ºC under N_2 atmosphere for max. 2 d. The obtained product was intensively washed with dichloromethane, and dried at 80 ºC for further characterization.

Acknowledgements

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Keywords: CO_2 utilization • Ionic liquid • Cyclic carbonate • Homogeneity/heterogeneity switch • Polyhydroxylurethane.

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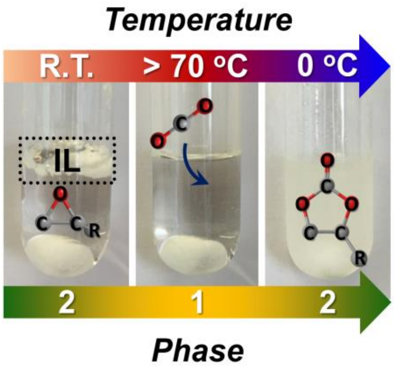
FULL PAPER

Settling ionic liquid: Long-chain imidazolium ionic liquid exhibited temperature-dependent phase transition behavior, thus enabling heterogeneous isolation of catalyst after the reaction as well as homogeneous catalysis for CO_2 conversion.



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Controllable Homogeneity/Heterogeneity Switch of Imidazolium Ionic Liquids for CO_2 Utilization