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N-Heterocyclic Carbene Functionalized Polymer for Reversible Fixation−Release of CO_2

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Reversible fixation−release of CO_2 has attracted much attention during the last decades due to the economic and environmental benefits arising from the utilization of renewable resources and the growing concern on the greenhouse effect.[1−3] Numerous systems based on liquid primary or secondary amines have been developed for this process, in which CO_2 is chemically converted into ammonium carbamates or zwitterionic adducts at ambient temperature[4−6] and the fixed CO_2 is released upon heating.[7,8] Likewise, amino-functionalized synthetic polymers or mesoporous materials were also proved to be efficient in CO_2 capture.[9−11] Notably, ethylenimine functionalized mesoporous molecular sieve MCM-41 has higher absorption capacity than either pure polyethylenimine or MCM-41 alone and could be used as highly CO_2-selective adsorbent for gas mixtures without the preremoval of moisture.[10] Endo and co-workers reported a new type of reversible CO_2 fixation by amidine derivatives and by polymers bearing an amidine moiety both in solution and solid state.[12] The cyclic amidine-functionalized copolymers exhibited better ability to retain CO_2 than corresponding low-molecular weight amidine at ambient temperature and could be applied to reversible fixation−release of CO_2. The CO_2 fixation by polymers in the solid state may be one of the most simple, economic and effective methods for CO_2 recovery, though the fixing efficiency is relatively low.

During the past decade, *N*-heterocyclic carbenes were studied extensively as versatile ligands[13] and effective organocatalysts.[14] Because of their high basicity,[15] *N*-heterocyclic carbenes can react rapidly with CO_2 to afford zwitterionic adducts (designated as NHC−CO_2), even at very low CO_2 concentrations.[16] In recent studies, we found that both the formation of NHC−CO_2 adducts at 20−50 °C in nearly 100% yield and their complete decomposition into free *N*-heterocyclic carbenes and CO_2 at elevated temperatures were very fast (Figure 1).[17] These observation stimulated us to explore the feasibility of *N*-heterocyclic carbenes as highly CO_2-selective adsorbent at low CO_2 concentration. Herein, we report a *N*-heterocyclic carbene-functionalized synthetic polymer for reversible fixation−release of CO_2.

The synthetic route of zwitterionic NHC−CO_2 adduct-functionalized copolymer (designated as **P-NHC-CO_2**) is shown in Scheme 1. Formation of quaternary ammonium by reaction of 1-(2,6-diisopropylphenyl) imidazole with styrene-4-vinylbenzyl chloride copolymer afforded imidazolium-modified copolymer **P-NHC-HCl**. Similar to the synthesis of 1-(2,6-diisopropylphenyl)-3-benzyl imidazolium-2-carboxylate (see Supporting Information), **P-NHC-CO_2** was readily prepared by deprotonation of **P-NHC-HCl** using $KN(SiMe_3)_2$, and followed by reaction with CO_2. The IR spectrum of the resulted polymer showed a broad absorption peak around 1649 cm^{-1}, which is assigned to the asymmetric $\nu(CO_2)$ vibrations of NHC−CO_2 adduct moiety. The content of immobilized *N*-heterocyclic carbene sites could be calculated from the nitrogen content determined by elemental analysis.

Although 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), a heterocyclic nitrogen Lewis base, has been utilized for its intrinsic ability to absorb one molecule of CO_2, and thereby serving as a quantitative method for the CO_2 addition,[18] the thermogravimetric analysis of the amidine−CO_2 carbamic complex suggested that the zwitterion was probably associated with one molecule of water by a hydrogen-bond interaction.[19] Heldebrant and co-workers have reported that they were unable to spectroscopically observe adduct formation between DBU and CO_2 under moderate CO_2 pressure and at ambient temperature,[20] while single crystals of the bicarbonate salt of DBU were isolated in the presence of adventitious water.[19,21] Recently, Endo et al. optimized the geometries of the hypothetical amidine−CO_2 complexes by DFT B3LYP/6-31G* calculations, and found a very weak interactigon by the almost straight O−C−O bonds (Figure 2, C and D).[12b] In sharp contrast to the very weak interaction in amidine-CO_2 complexes, the angle of the O−C−O bond in NHC−CO_2 adducts (Figure 2, A and B) is close to 130°, which indicates a strong affinity of CO_2 to NHC.

The stability of the fixed CO_2 in **P-NHC-CO_2** was studied by thermogravimetric analysis (TGA). The polymer **P-NHC-CO_2** began losing weight at 120 °C, and a total weight of 6.22% was lost between 120 and 160 °C (Figure S3). The CO_2 adduct immobilized in **P-NHC-CO_2** is seem to exhibit higher thermal stability than the corresponding free NHC−CO_2 adduct. The CO_2 released from **P-NHC-CO_2** at elevated temperatures was also confirmed by FTIR analysis. When **P-NHC-CO_2** was heated at 140 °C for 30 min, the absorption intensity at 1649 cm^{-1} significantly decreased and the absorption at 2400 cm^{-1} ascribed to free CO_2 appeared in IR spectrum. When the system was cooled below 100 °C, the absorption intensity at 1649 cm^{-1} obviously increased. On the basis of these facts, it is possible that **P-NHC** obtained from decarboxylation of **P-NHC-CO_2** at elevated temperature could be used as an efficient absorbent for reversible fixation−release of CO_2.

TGA is an effective method for evaluating reversible CO_2 fixation−release capability of **P-NHC** in the solid state. When **P-NHC** powder was exposed to CO_2 atmosphere with a CO_2 flow (10 mL/min) at 40 °C for 60 min, 57% CO_2 fixing efficiency

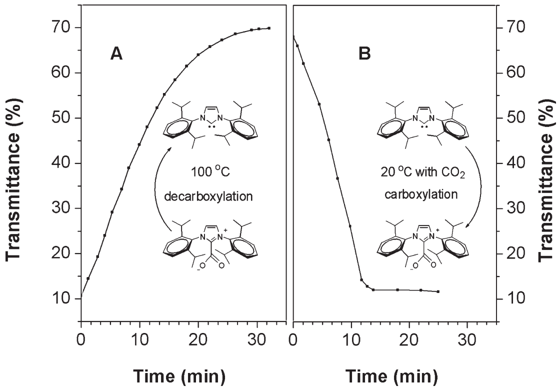

Figure 1. Plots of transmittance at 1692 cm^{-1} versus time for (A) the decomposition of the NHC−CO_2 adduct at 100 °C, and (B) the formation of the NHC−CO_2 adduct at 20 °C.

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(mol of CO_2/mol of *N*-heterocyclic carbene) was observed on the basis of the weight increase. After trapped CO_2 was removed by a N_2 flow (40 mL/min) at 140 °C for 30 min, 42% CO_2 fixing efficiency was obtained for the second CO_2 capture (Figure 3). No obvious decrease in CO_2 fixing efficiency was observed in the third and fourth reversible CO_2 fixation−release experiments. We tentatively assume that the decrease of CO_2 fixing efficiency in the second CO_2 capture cycle in comparison to the first cycle was attributed to trace quantities of water in **P-NHC**. It is generally known that free *N*-heterocyclic carbenes are sensitive to moisture at elevated temperatures. When **P-NHC-CO$_2$** released CO_2 upon heating after first cycle, part of formed *N*-heterocyclic carbenes were decomposed by the trace quantities of water. This resulted in a significant decrease of CO_2 fixing efficiency in the second CO_2 capture cycle. In comparison to the free *N*-heterocyclic carbenes dissolved in organic solvent, **P-NHC** in the solid state exhibited relatively low CO_2 fixing efficiency and capture rate, due to the difficult diffusion of CO_2 into the *N*-heterocyclic carbene units buried in the polymer matrix. Prior to this research, Endo and co-workers have reported a polymer bearing DBN moieties was more efficient in CO_2 capture than other amidine-functionalized copolymers, and its CO_2 fixing efficiency could reach 27% at 25 °C for 500 min under CO_2 flow of 200 mL/min.[12] Therefore, as compared with the previously reported amine-functionalized polymers, **P-NHC** exhibited higher CO_2 fixing efficiency in the much shorter time.

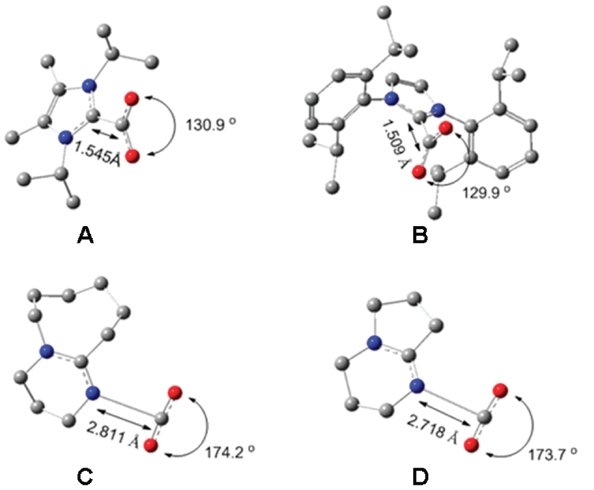


Figure 2. (A) DFT B3LYP/6-31G optimized geometry of 1,3- diisopropyl-4,5-dimethylimidazolium-2-carboxylate by calculation; (B) crystal structure of IPr−CO_2;[16a] (C) DFT B3LYP/6-31G optimized geometry of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)-CO_2;[12b] (D) DFT B3LYP/6-31G optimized geometry of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN)−CO_2.[12b] Hydrogen atoms on the carbon atoms are omitted for clarity.

In the conventional industrial process for recovering CO_2 from flue gas stream, the energy was predominantly consumed in the procedure that the flue gas was cooled to ambient temperature prior to the removal of CO_2. Therefore, an ideal CO_2 absorbent candidate should be promising to be operated at elevated temperatures, typically the temperature of flue gas stream. Due to the strong affinity of CO_2 to *N*-heterocyclic carbenes, **P-NHC** also exhibits good capability to capture CO_2 at higher temperatures (Figure 4). When **P-NHC** was exposed to CO_2 atmosphere with a CO_2 flow (10 mL/min) for 30 min, the CO_2 fixing efficiency at 100 and 120 °C are 22.5% and 6.4%, respectively.

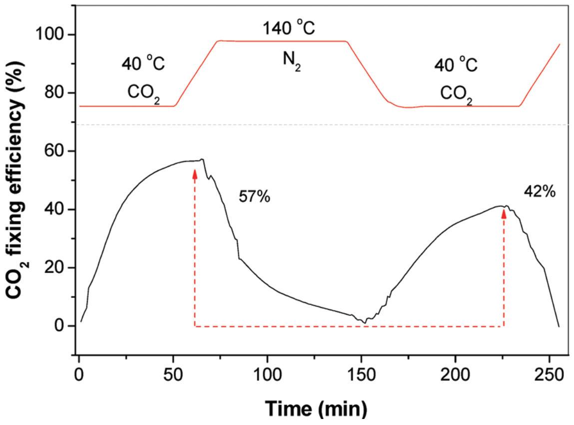
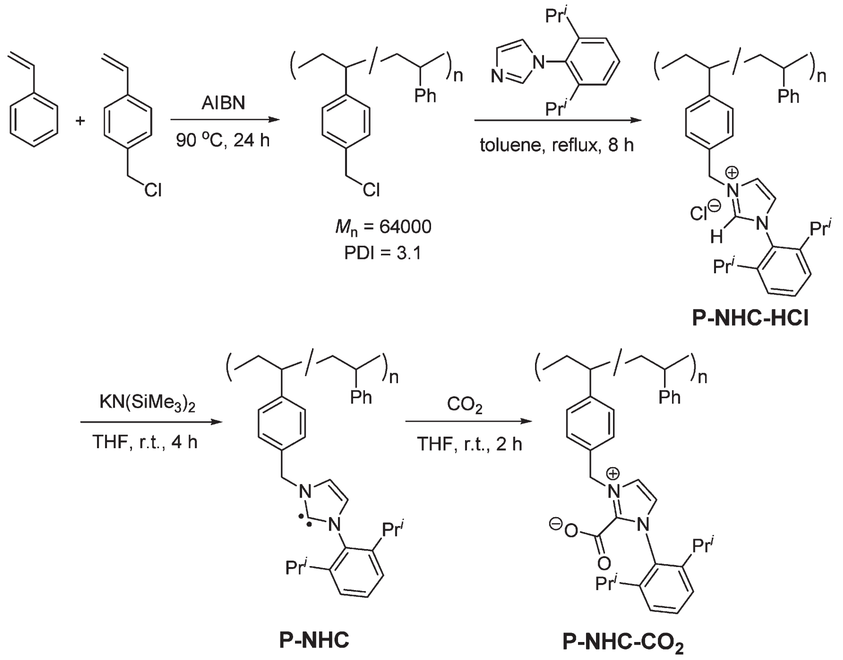


Figure 3. Reversible CO_2 trap−release of **P-NHC**.

Scheme 1. Synthesis of Copolymer Bearing *N*-Heterocyclic Carbene



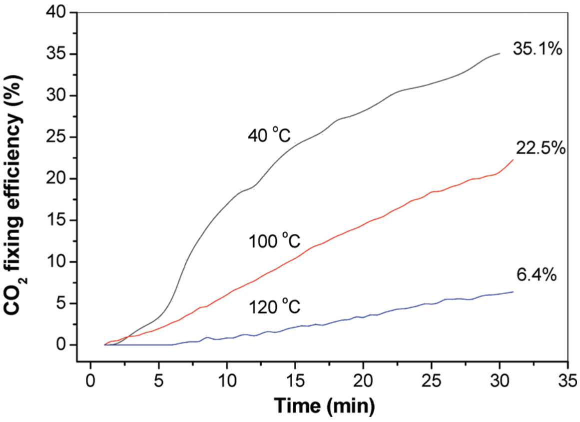


Figure 4. CO_2 capture capability of **P-NHC** at different temperatures.

In summary, we have developed a highly efficient CO_2-selective adsorbent based on *N*-heterocyclic carbene-functionalized polymer. The immobilized *N*-heterocyclic carbenes could react rapidly with CO_2 to afford zwitterionic adducts under temperatures of 20−100 °C and the trapped CO_2 was quantitatively released by a N_2 flow at 140 °C. This result demonstrates the potential application of *N*-heterocyclic carbene-functionalized polymers as a highly efficient adsorbent for reversible fixation−release of CO_2 with higher fixing efficiency and faster capture rate. Further study on increasing fixing capacity and exploration on the transformation of the trapped CO_2 to organic compounds is in progress in our laboratory.

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Supporting Information Available: Text giving the experimental procedures, synthesis, and characterization of 1-(2,6-diisopropylphenyl)-3-benzyl imidazolium-2-carboxylate and copolymers, schemes showing the reactions involved, and figures showing a TG plot, IR spectra, and a TGA curve. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Falkowski, P.; Scholes, R. J.; Boyle, E.; Canadell, J.; Canfield, D.; Elser, J.; Gruber, N.; Hibbard, K.; Hogberg, P.; Linder, S.; Mackenzie, F. T.; Moore, B.III; Pedersen, T.; Rosenthal, Y.; Seitzinger, S.; Smetacek, V.; Steffen, W. *Science* **2000**, *290*, 291–296.

(2) (a) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939–943. (b) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

(3) For recent reviews on CO_2 transformation, see: (a) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410. (b) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365–2387. (c) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618–6639. (d) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561–5573.

(4) Song, C. S. *Catal. Today* **2006**, *115*, 2–32.

(5) Belli Dell'Amico, D.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857–3898.

(6) (a) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H.Jr. *J. Am. Chem. Soc.* **2002**, *124*, 926–927. (b) Hampe, E. M.; Rudkevich, D. M. *Tetrahedron* **2003**, *48*, 9619–9625. (c) Bonenfant, D.; Mimeault, M.; Hausler, R. *Ind. Eng. Chem. Res.* **2007**, *46*, 8968–8971. (d) Tobiesen, F. A.; Svendsen, H. F.; Mejdell, T. *Ind. Eng. Chem. Res.* **2007**, *46*, 7811–7819.

(7) (a) Liu, Y. X.; Jessop, P. G.; Cunningham, M.; Eckert, C. A.; Liotta, C. L. *Science* **2006**, *313*, 958–960. (b) Jessop, P. G.; Heldebrant, D. J.; Li, X. W.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102.

(8) (a) Yamada, T.; Lukac, P. J.; George, M.; Weiss, R. G. *Chem. Mater.* **2007**, *19*, 967–969. (b) George, M.; Weiss, R. G. *Acc. Chem. Res.* **2006**, *39*, 489–497.

(9) (a) Filburn, T.; Helble, J. J.; Weiss, R. A. *Ind. Eng. Chem. Res.* **2005**, *44*, 1542–1546. (b) Diaf, A.; Garcia, J. L.; Beckman, E. J. *J. Appl. Polym. Sci.* **1994**, *53*, 857–875. (c) Li, P. Y.; Zhang, S. J.; Chen, S. X.; Zhang, Q. K.; Pan, J. J.; Ge, B. Q. *J. Appl. Polym. Sci.* **2008**, *108*, 3851–3858.

(10) (a) Xu, X.; Song, C. S.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. *Energy Fuels* **2002**, *16*, 1463–1469. (b) Xu, X.; Song, C. S.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. *Microporous Mesoporous Mater.* **2003**, *62*, 29–45.

(11) Yue, M. B.; Sun, L. B.; Cao, Y.; Wang, Y.; Wang, Z. J.; Zhu, J. H. *Chem.—Eur. J.* **2008**, *14*, 3442–3451.

(12) (a) Endo, T.; Nagai, D.; Monma, T.; Yamaguchi, H.; Ochiai, B. *Macromolecules* **2004**, *37*, 2007–2009. (b) Ochiai, B.; Yokota, K.; Fujii, A.; Nagai, D.; Endo, T. *Macromolecules* **2008**, *41*, 1229–1236.

(13) (a) Hermann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (b) Crabtree, R. H. *Coord. Chem. Rev.* **2007**, *251*, 595.

(14) (a) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606–5655. (b) Marion, N.; Dķez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000.

(15) (a) Alder, R. H.; Allen, P. R.; Williams, S. J. *Chem. Commum.* **1995**, 1267–1268. (b) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717–8724.

(16) (a) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112–113. (b) Voutchkova, A. M.; Feliz, M.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 12834–12846.

(17) (a) Zhou, H.; Zhang, W. Z.; Liu, C. H.; Qu, J. P.; Lu, X. B. *J. Org. Chem.* **2008**, *73*, 8039–8044. (b) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 4194–4197.

(18) Pérez, E. R.; da Silva, O. M.; Costa, V. C.; Rodrigues-Filho, U. P.; Franco, D. W. *Tetrahedron Lett.* **2002**, *43*, 4091–4093.

(19) Pérez, E. R.; Santos, R. H. A.; Gambardella, M. T. P.; de Macedo, L. G. M.; Rodrigues-Filho, U. P.; Launay, J. -C.; Franco, D. W. *J. Org. Chem.* **2004**, *69*, 8005–8011.

(20) Heldebrant, D. J.; Jessop, P. G.; Thomas, C. A.; Eckert, C. A.; Liotta, C. L. *J. Org. Chem.* **2005**, *70*, 5335–5338.

(21) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026–14038.