Macromolecules **2005,** *38,* 2037−2039 **2037**

Enhanced CO_2 Absorption of Poly(ionic liquid)s

Jianbin Tang,[†,‡,§] Weilin Sun,[‡] Huadong Tang,[†] Maciej Radosz,[†] and Youqing Shen*[,†]

Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, Wyoming 82071, and Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, China

Received November 23, 2004
Revised Manuscript Received January 26, 2005

The global warming due to the increased atmospheric CO_2 concentration resulting from increasing consumption of fossil fuel is becoming an important environmental issue today.[1,2] Carbon sequestration, which captures CO_2 from large point sources such as fossil-fuel-fired electrical power-generation plants and stores it in geological formations, has been proposed as a solution to this problem.[1,2] Efficient separation of CO_2 is key to the economically viable sequestration efforts.[1] The existing commercial CO_2 capture facilities are based on the wet scrubbing process using aqueous alkanolamine solutions.[1] It has disadvantages of energy intensive (i.e., high-energy penalty) amine loss and degradation, release of volatile organic compounds, and equipment corrosion. Therefore, there is a pressing need for new materials for efficient CO_2 separation.

Recently, ionic liquids, organic salts that are liquids at low temperatures (<100 °C), have been explored as nonvolatile and reversible CO_2 absorbents for CO_2 separation because of their high CO_2 solubility.[3−9] Supported liquid membranes using ionic liquids have also been developed.[10,11] The CO_2 solubility and selectivity can be tuned by choice of cation, anion, and substituents of the ionic liquids.[3,6] For example, Bates et al. developed a task-specific ionic liquid for CO_2 capture by introducing an amine group to the ionic liquid. The CO_2 solubility was substantially increased.[6]

Very unexpectedly, we found that the polymers from ionic liquid monomers had higher CO_2 absorption capacity than room temperature ionic liquids. To our best knowledge, this is first observation that the polymers have higher CO_2 absorption than their monomers. Most importantly, the CO_2 absorption and desorption of the polymer particles are much faster than those of ionic liquids, and the sorption/desorption is completely reversible. These poly(ionic liquid)s are thus very promising as sorbent and membrane materials for CO_2 separation.

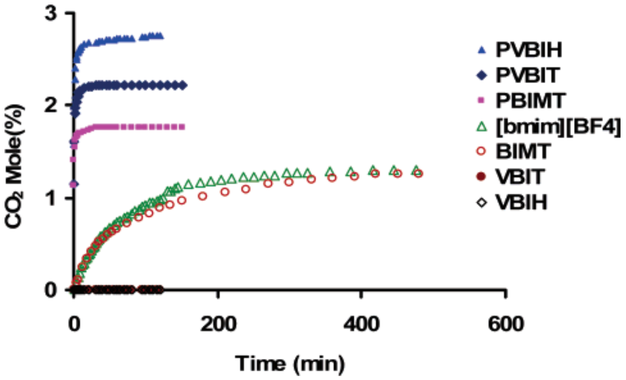

Figure 1. CO_2 absorption of the polymers (PVBIT, PVBIH, PBIMT), corresponding monomers (VBIT, VBIH, BIMT), and an ionic liquid [bmim][BF_4] as a function of time (592.3 mmHg CO_2, 22 °C).

The polymers poly[1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate] (PVBIT), poly[(1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate] (PVBIH), and poly[2-(1-butylimidazolium-3-yl)ethyl methacrylate tetrafluoroborate] (PBIMT) were prepared from their corresponding ionic liquid monomers by free radical polymerization using AIBN as initiator in DMF at 60 °C (see Supporting Information). PVBIT (M_n = 32 000, PDI = 3.56), PVBIH (M_n = 38 600, PDI = 3.2), and PBIMT (M_n = 19 000, PDI = 2.9) have glass transition temperatures at 76, 86, and 56 °C, respectively. The X-ray diffraction and DSC data show that they are amorphous and very stable. For example, the TGA showed that PVBIT could be stable up to 300 °C. At room temperature, the polymers are brittle and easily crashed into fine powders. SEM indicated the average diameter of the particles was about 100 μm, and the particles had a nonporous structure. The specific surface area of the particles measured by BET was 0.29 m^2/g.

Figure 1 shows the CO_2 sorption kinetics of the polymers and their corresponding monomers as well as a room temperature ionic liquid [bmim][BF_4]. The CO_2 absorption capacity of [bmim][BF_4] was 0.256 wt % (1.30 mol %) at 592.3 mmHg CO_2 and 22 °C, consistent with the value reported.[3] When 1.0 g of the polymer samples was exposed to dry CO_2 for 1.5 h under the same conditions, a mass gain was 3.22 mg (0.322 wt %, 2.75 mol % of VBIH units) for PVBIH, 3.05 mg (0.305 wt %, 2.22 mol % of VBIT units) for PVBIT, and 2.41 mg (0.241 wt %, 1.77 mol % of BIMT units) for PBIMT. This is about 2.1 (PVBIH), 1.7 (PVBIT), and 1.4 (PBIMT) times (in moles) of the capacity of [bmim][BF_4]. Surprisingly, VBIT and VBIH monomers did not absorb CO_2 at all probably because of their crystalline structures (mp: 68 °C of VBIT and 87.5 °C of VBIH), and the liquid BIMT monomer had the same absorption capacity as [bmim][BF_4] (Figure 1).

Very significantly, the CO_2 sorption of the polymers was much faster than that of room temperature ionic liquids, as shown in Figure 1. It took only 4 min for PVBIT and PVBIH and 3 min for PBIMT to reach their 90% sorption capacities and about 30 min to reach their full capacities. In contrast, it took more than 400 min for room temperature ionic liquids BIMT and [bmim][BF_4] to reach their equilibrium (Figure 1).

The sorption/desorption of the polymers was tested by filling the chambers with CO_2 first and then vacuuming for four cycles (Figure 2a). The sorption and desorption of PVBIT and PBIMT were all very fast. It took only about 30 min to take up CO_2 and 15 min to have a complete desorption of CO_2. The desorption was complete, suggesting that the absorption/desorption was reversible. No change in sorption/desorption kinetics and sorption capacity was observed after four cycles.

[†] University of Wyoming.
[‡] Zhejiang University.
[§] Visiting Ph.D. student to the University of Wyoming.
* Corresponding author: e-mail sheny@uwyo.edu, Fax 307 766 6777.

10.1021/ma047574z CCC: $30.25 © 2005 American Chemical Society
Published on Web 02/18/2005

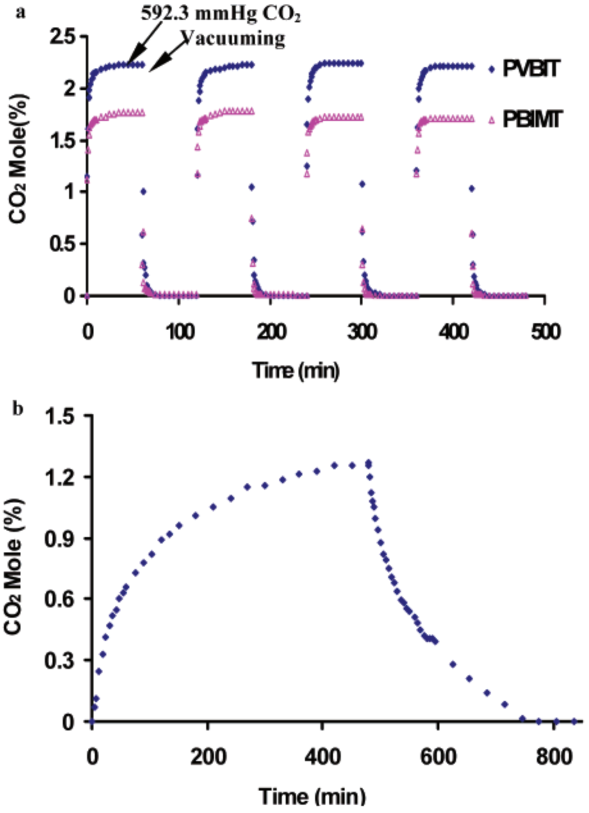

Figure 2. (a) Cycles of CO_2 adsorption (592.3 mmHg CO_2, 22 °C) and desorption by vacuuming of PVBIT and PBIMT. (b) CO_2 absorption (592.3 mmHg CO_2, 22 °C) and desorption by vacuuming of the liquid BIMT monomer.

The absorption and desorption of CO_2 from room temperature ionic liquid BIMT, in contrast, were slow (Figure 2b).

The enhanced absorption capacity and fast sorption/desorption rates of the poly(ionic liquid)s are unexpected because both polymers are solids at room temperature. The calculated CO_2 adsorption assuming a monolayer of CO_2 on the polymer particles surface was 0.0128 wt %, only 4% of the measured CO_2 sorption capacities. This indicates that the bulk of the polymer particles played a major role in the CO_2 sorption, and the diffusion of CO_2 in the polymers was very fast. Therefore, the sorption of CO_2 of the polymer particles involves more absorption (the bulk) but less adsorption (the surface). Our recent experiments show that the CO_2 absorption of the polymers is due to the interaction of the imidazolium tetrafluoroborate moiety with CO_2, and the cation plays a more important role in absorption. At present, the exact mechanism is still under investigation.

The CO_2 absorption of the polymers is very selective, as shown in Figure 3. There was no weight increase when the polymers were exposed to N_2 or O_2 under the same conditions, indicative of that they selectively absorb CO_2. In N_2/CO_2 mixed gas, only CO_2 was absorbed.

In summary, we demonstrate that the poly(ionic liquid)s are a new type of polymer materials that selectively absorb CO_2 with higher absorption capacity than room temperature ionic liquids. Most significantly, their sorption and desorption are very fast, and the desorption by vacuuming is completely reversible. These characters make the polymers exceptionally promising as solid absorbent and membrane materials for CO_2 separation. The studies on the underlying mechanisms of CO_2 absorption and synthesis of poly(ionic liquid)s with even higher absorption capacity are underway.

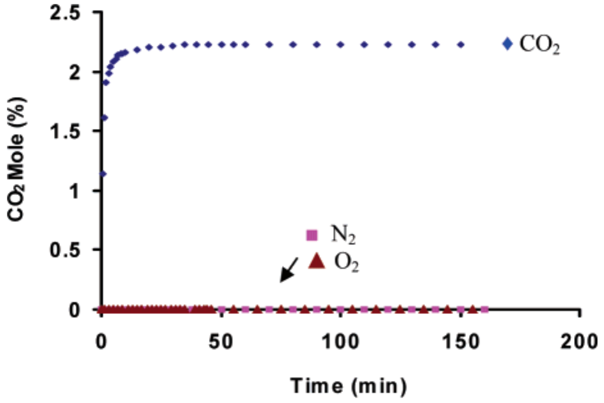

Figure 3. Gas (CO_2, O_2, N_2) sorption of PVBIT as a function of time at 592.3 mmHg and 22 °C.

Experimental Section. The ionic liquid monomers 1-(4-vinylbenzyl)-3-butylimidazolium tetrafluoroborate (VBIT) and 1-(4-vinylbenzyl)-3-butylimidazolium hexafluorophosphate (VBIH) were prepared by the reaction of vinylbenzyl chloride with 1-butylimidazole and subsequent anion exchange with $NaBF_4$ or $NaPF_6$ (see the Supporting Information). 2-(1-Butylimidazolium-3-yl)-ethyl methacrylate tetrafluoroborate (BIMT) was synthesized according to our previous report.[12]

The gas sorption of the polymers was measured using Cahn 1000 electrobalance under ambient atmosphere pressure (592.3 mmHg or 0.78 standard atmosphere pressure at Laramie, WY). The sample used was 1.0 g. A detailed description of this apparatus and the experimental procedures are given in the Supporting Information. The buoyancy effects were corrected according to the reported method.[13] The gas was dried by passing through two columns of phosphorus peroxide (P_2O_5). A layer of P_2O_5 was also put on the bottoms of the two chambers of the microbalance. The system was validated by measuring the CO_2 absorption of an ionic liquid, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]). The measured CO_2 absorption capacity of [bmim][BF_4] was consistent with that reported.[3]

Acknowledgment. We thank the State of Wyoming (EORI) and University of Wyoming for financial support.

Supporting Information Available: Experimental details of the synthesis and characterization of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffman, J. S.; Pennline, H. W. *J. Air Waste Manage. Assoc.* **2003**, *53*, 645–715.
(2) Herzog, H.; Drake, E.; Adams, E. CO_2 Capture, Reuse and Storage Technologies for Mitigating Global Climate Change. Report No. DOE/DE-AF22-96PC01257, Pittsburgh, PA, 1999.
(3) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. *J. Am. Chem. Soc.* **2004**, *26*, 5300–5308.
(4) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. *J. Phys. Chem. B* **2001**, *105*, 2437–2444.

(5) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.

(6) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 926−927.

(7) Kamps, A. P.-S.; Tuma, D.; Xia, J.; Maurer, G. *J. Chem. Eng. Data* **2003**, *48*, 746−749.

(8) Camper, D.; Scovazzo, P.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 3049−3054.

(9) Scovazzo, P.; Camper, D.; Kieft, J.; Poshusta, J.; Koval, C.; Noble, R. *Ind. Eng. Chem. Res.* **2004**, *43*, 6855−6860.

(10) Scovazzo, P.; Visser, A. E.; Davis, J. H., Jr.; Rogers, R. D.; Koval, C.; DuBois, D. L.; Noble, R. *ACS Symp. Ser.* **2002**, *818*, 69−87.

(11) Scovazzo, P.; Kieft, J.; Finan, D. A.; Koval, C.; DuBois, D. L.; Noble, R. *J. Membr. Sci.* **2004**, *238*, 57−63.

(12) Ding, S.; Tang, H. D.; Radosz, M.; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5794−5801.

(13) Macedonia, M. D.; Moore, D. D.; Maginn, E. J. *Langmuir* **2000**, *16*, 3823−3834.

MA047574Z