Poly(ionic liquid)s: a new material with enhanced and fast CO_2 absorption†

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Novel sorbent and membrane materials for CO_2 separation, poly(ionic liquid)s made from ionic liquid monomers, poly[*p*-vinylbenzyltrimethyl ammonium tetrafluoroborate] (P[VBTMA] [BF_4]) and poly[2-(methacryloyloxy)ethyltrimethylamnonium tetrafluoroborate] (P[MATMA][BF_4]) have absorption capacities 7.6 and 6.0 times of those of room-temperature ionic liquids, *e.g.* [bmim][BF_4], respectively, with reversible and fast sorption and desorption.

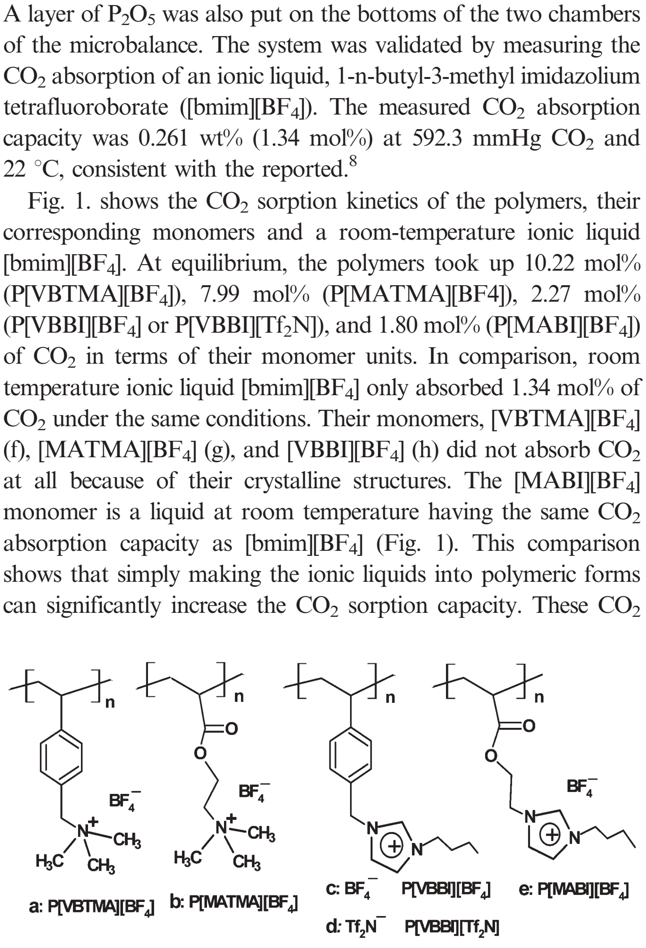
Ionic liquids are organic salts that are liquids at low temperatures.[1] Recently, CO_2 has been shown to be remarkably soluble in imidazolium-based ionic liquids.[2–11] For instance, at 15 bar of CO_2 pressure, the CO_2 solubility in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) is about 23 mol%.[3] The CO_2 solubility can be tuned by choice of cations, anions, and substituents of the ionic liquids, and anions play a major role.[8] For example, using fluorine-containing anions (*e.g.* bis(trifluoromethylsulfonyl)imide, Tf_2N)[8] or cations,[11] and introducing amine groups[12] could increase the CO_2 solubility. Ionic liquids are also impregnated on porous supports to develop supported liquid membranes (SLM). These membranes have high CO_2 selectivity and permeance.[13] Therefore, ionic liquids may be very useful in CO_2 separation for carbon sequestration.

Recently, we found that simply making the ionic liquids into polymeric forms significantly increased the CO_2 sorption capacity compared with ionic liquids. Especially, the polymers of tetraalkylammonium-based ionic liquids have CO_2 sorption capacities 6.0–7.6 times of those of room temperature ionic liquids. The CO_2 sorption and desorption of the polymer solids are very fast, and the desorption is completely reversible. These polymers are very prospective as sorbent and membrane materials for CO_2 separation.

The ionic liquid monomers were prepared by anion exchange reactions and their corresponding polymers were synthesized by free radical polymerization. The structures of the polymers, poly[*p*-vinylbenzyltrimethylammonium tetrafluoroborate] (P[VBTMA] [BF_4]), poly[2-(methacryloyloxy)ethyltrimethylammonium tetrafluoroborate] (P[MATMA][BF_4]), poly[1-(*p*-vinylbenzyl)-3-butylimidazolium tetrafluoroborate](P[VBBI][BF_4]) or bis(trifluoromethylsulfonyl)imide (P[VBBI][Tf_2N]), and poly[1-(2-methacryloyloxy)ethyl-3-butylimidazolium tetrafluoroborate] (P[MABI][BF_4]) are shown in Scheme 1. The X-ray diffraction and DSC data show that all the polymers are amorphous. They have glass transition temperatures at 215 °C (P[VBTMA][BF_4]), 166 °C (P[MATMA][BF_4]), 86 °C (P[VBBI][BF_4]), 30 °C (P[VBBI][Tf_2N]) and 69 °C (P[MABI][BF_4]), respectively. At room temperature, all polymers are easily crushed into fine powders. The specific surface areas of the particles measured by BET are 0.46 m^2 g^{-1} for P[VBTMA][BF_4], 20.5 m^2 g^{-1} for P[MATMA][BF_4], 0.29 m^2 g^{-1} for P[VBBI][BF_4], 0.77 m^2 g^{-1} for P[MABI][BF_4]. SEM shows that the particles of P[MATMA][BF_4] are porous, and the others are nonporous.

The gas sorption of the polymers was measured under local ambient pressure (592.3 mmHg, Laramie, Wyoming). A detailed description of the apparatus and the experimental procedure are given in the Supporting Information†. The buoyancy effects were corrected according to the reported method.[14] 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-methyl imidazolium tetrafluoroborate ([bmim][BF_4]). The measured CO_2 absorption capacity was 0.261 wt% (1.34 mol%) at 592.3 mmHg CO_2 and 22 °C, consistent with the reported.[8]

Fig. 1. shows the CO_2 sorption kinetics of the polymers, their corresponding monomers and a room-temperature ionic liquid [bmim][BF_4]. At equilibrium, the polymers took up 10.22 mol% (P[VBTMA][BF_4]), 7.99 mol% (P[MATMA][BF4]), 2.27 mol% (P[VBBI][BF_4] or P[VBBI][Tf_2N]), and 1.80 mol% (P[MABI][BF_4]) of CO_2 in terms of their monomer units. In comparison, room temperature ionic liquid [bmim][BF_4] only absorbed 1.34 mol% of CO_2 under the same conditions. Their monomers, [VBTMA][BF_4] (f), [MATMA][BF_4] (g), and [VBBI][BF_4] (h) did not absorb CO_2 at all because of their crystalline structures. The [MABI][BF_4] monomer is a liquid at room temperature having the same CO_2 absorption capacity as [bmim][BF_4] (Fig. 1). This comparison shows that simply making the ionic liquids into polymeric forms can significantly increase the CO_2 sorption capacity. These CO_2



Scheme 1 The structures of the poly(ionic liquid)s.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b5/b501940k/
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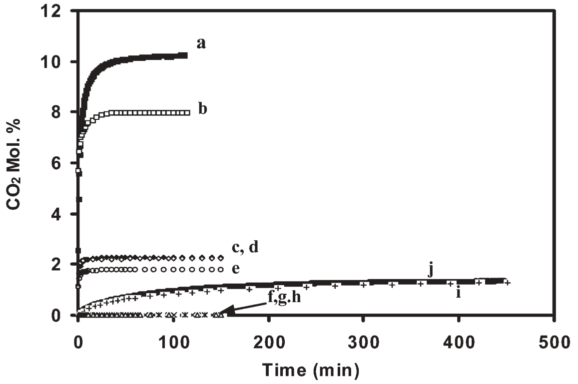

Fig. 1 CO$_2$ sorption of the polymers (a–e) in Scheme 1, their corresponding monomers [VBTMA][BF$_4$](f), [MATMA][BF$_4$](g), [VBBI][BF$_4$](h), ([MABI][BF$_4$](i), and ionic liquid [bmim][BF$_4$] (j) as a function of time (592.3 mmHg CO$_2$, 22 °C).

sorption capacities are also significantly higher than other polymer solids such as polymethacrylates, polystyrene and polycarbonates.[15–17]

The anion, cation and polymer backbone affect the CO$_2$ sorption capacity, but the type of cation plays a major role. For example, tetraalkylammonium-based poly(ionic liquid)s (a,b) had much higher CO$_2$ sorption capacity than the imidazolium-based poly(ionic liquid)s (c,d,e). This may be due to the tetraalkylammonium cation having a higher positive charge density and thus stronger interaction with CO$_2$. In contrast, the positive charge of the imidazolium is delocalized. The anions have little effects on the CO$_2$ sorption capacity. For example, P[VBBI][BF$_4$] (c) and P[VBBI][Tf$_2$N] (d) had the same CO$_2$ sorption capacity. This is in contrast to the findings in the room temperature ionic liquids, in which anion is the main parameter affecting the CO$_2$ solubility in ionic liquids, and Tf$_2$N$^-$ anions enhance the CO$_2$ solubility.[8] With the same cations and anions, the polymers with polystyrene backbone had higher CO$_2$ sorption capacity than those with polymethylmethacrylate backbones.

The sorption rates of these polymer particles are very fast (Fig. 1). It took only several minutes for the polymers to reach their 95% sorption capacities. In contrast, it took more than 400 min for room temperature ionic liquids [MABI][BF$_4$] and [bmim][BF$_4$] to reach their equilibrium. The fast sorption rates of the polymers is not solely because of their small particle sizes ($\sim$100 μm). Fig. 1 shows that the CO$_2$ sorption kinetics was not affected by their surface areas (*i.e.* particle sizes). The particles with specific areas less than 1 m^2 g^{-1} took up CO$_2$ as fast as porous P[MATMA][BF$_4$] particles having specific areas of 20 m^2 g^{-1}. Additionally, the larger particles ($\sim$500 μm) of P[VBBI][Tf$_2$N] still took up CO$_2$ very fast (Fig. 1d). In contrast, when BF$_4^-$ anions in P[VBBI][BF$_4$] were replaced with Cl$^-$ anions, the resulting poly[1-(4-vinylbenzyl)-3-butylimidazolium chloride] sorbed CO$_2$ very slowly (Supporting Information†) even with the same particle sizes. Therefore, the fast CO$_2$ sorption is characteristic of the poly(ionic liquid)s.

The desorption of the poly(ionic liquid)s is also fast (Fig. 2A). Under vacuum, the polymers released CO$_2$ in less than 15 min. The desorption was complete, and no change in sorption/desorption kinetics and sorption capacity was observed after four cycles of sorption/desorption experiments, suggesting that the sorption/desorption was completely reversible. In contrast, the desorption of ionic liquids (*e.g.*[bmim][BF$_4$]) was also very slow (Fig. 2B).

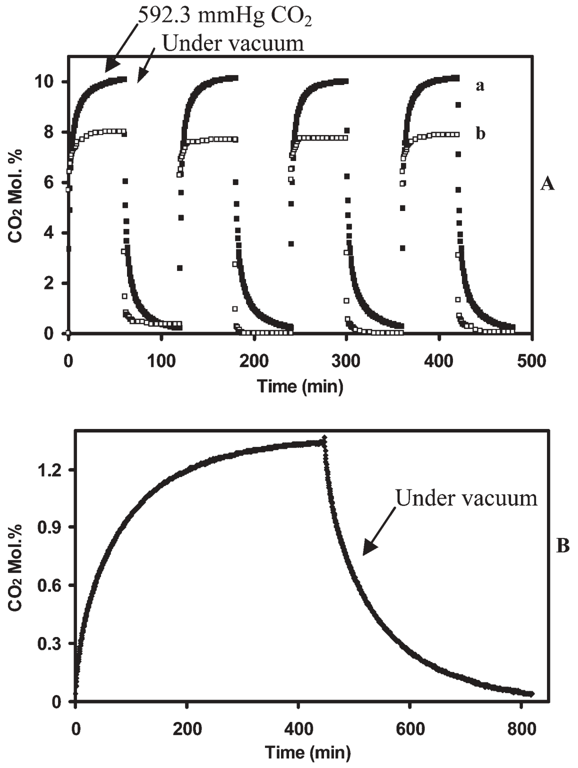

Fig. 2 (A) Cycles of CO$_2$ sorption (592.3 mmHg CO$_2$, 22 °C) and desorption under vacuum of (a) P[VBTMA][BF$_4$] and (b) P[MATMA][BF$_4$], and (B) CO$_2$ absorption (592.3 mmHg CO$_2$, 22 °C) and desorption under vacuum of [bmim][BF$_4$].

The CO$_2$ sorption of P[VBTMA][BF$_4$] as a function of pressure is shown in Fig. 3. The sorption capacity increased with the increase of the CO$_2$ pressure. For example, P[VBTMA][BF$_4$] absorbed 44.8 mol% of CO$_2$ (in terms of its monomer units) at 12 atm. of CO$_2$ pressure, much higher than that of room temperature ionic liquids.[8]

The enhanced sorption capacity and fast sorption/desorption rates of the poly(ionic liquid)s were unexpected because the polymers are solid at room temperature. The calculated

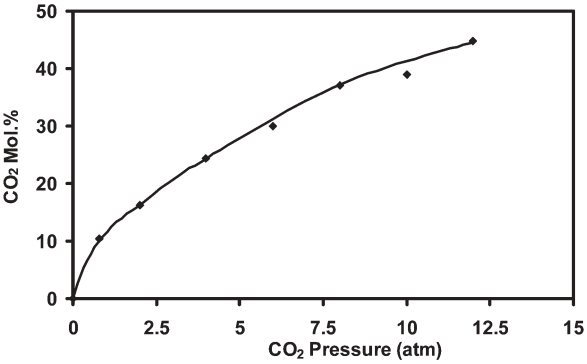

Fig. 3 CO$_2$ sorption capacities of P[VBTMA][BF$_4$] at different CO$_2$ pressures (22 °C).

CO_2-adsorption of P[VBTMA][BF_4] assuming a monolayer of CO_2 on the polymer particle surface was about 0.02 wt%, much less than the measured CO_2 sorption capacities (1.70 wt%) at 592.3 mmHg of CO_2. This indicates that the bulk of the polymer particles plays a major role in the CO_2 sorption. Therefore, the CO_2 sorption of the polymer particles involves more absorption (the bulk) but less adsorption (the surface). The fast absorption/desorption rates indicate that the diffusion of CO_2 in the polymer solids is very fast. At present, the underlying mechanism of the enhanced absorption capacity and fast sorption/desorption of the polymer solids are still under investigation.

The CO_2 absorption of the polymers is very selective. There was no weight gain when the polymers were exposed to N_2 or O_2 under the same conditions (Supporting Information†). Moisture could slightly decease the CO_2 absorption capacity. For example, wet P[VBTMA][BF_4] with 13.8 mol% water had a CO_2 absorption capacity of 7.9 mol%, lower than that of dry P[VBTMA][BF_4].

In summary, we demonstrate that the poly(ionic liquid)s are a novel polymer materials that selectively absorb CO_2 with higher absorption capacity and faster absorption/desorption rates than room-temperature ionic liquids. These characters make these polymers exceptionally promising as absorbent and membrane materials for CO_2 separation. The poly(ionic liquid) membranes for CO_2 separation will be reported soon.

The ionic liquid monomers were prepared by anion exchange reaction of the corresponding chloride salts with $NaBF_4$, $NaPF_6$ or lithium trifluoromethane sulfonamide($LiTf_2N$).† An example of the synthesis of [MATMA][BF_4] is as follows: Aqueous 2-(methylacryloyloxy)ethyltrimethylammonium chloride solution (75 wt%) (30 ml, 0.12 mol) was added into a 250 ml flask. After the water was removed under vacuum, $NaBF_4$ (14.5 g, 0.132 mol) and CH_3CN (150 ml) were added to the flask. The mixture was stirred over night. The salt dissolved gradually and a white precipitate formed. The precipitate was removed by filtration. The filtrate was concentrated, and then poured into ether. The white crystals were collected and dried under vacuum at room temperature (28 g, 90%). Similarly, [VBTMA][BF_4] was synthesized from *p*-vinylbenzyltrimethylammonium chloride in a yield of 93%.

The polymers were synthesized *via* free radical polymerization. A general procedure is as follows: Ionic liquid monomers (2 g), AIBN (20 mg) and DMF (4 ml) were charged into a reaction tube. The tube was tightly sealed and degassed. The tube was immersed in an oil bath at 60 °C for 6 h. After polymerization, the solution of polymer was poured in methanol to precipitate the polymer. The polymer was dried under vacuum at 60 °C. The yield was 75% for P[VBBI][BF_4], 68% for P[VBBI][Tf_2N], 70% for P[MABI][BF_4], 90% for P[MATMA][BF_4], 95% for P[VBTMA][BF_4].

The gas sorption of the polymers was measured using a Cahn 1000 electrobalance under ambient atmosphere pressure (592.3 mmHg or 0.78 atm, Laramie, Wyoming USA). The sample used was 1.0 g. A detailed description of this apparatus and the experimental procedures are given in the supporting information.†

In the CO_2 sorption of wet P[VBTMA][BF_4] experiment, wet N_2 saturated with moisture was first introduced to the chambers. When the amount of absorbed water reached 13.8 mol%, N_2 was changed to dry CO_2, and the CO_2 absorption was recorded.

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