CO$_2$ Absorption of Polymers of Ammonium-Based Ionic Liquid Monomers

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Introduction

The topic of global warming as a result of increased atmospheric CO$_2$ concentration is becoming the most important environmental issue that the world faces today.[1] The capture and separation of CO$_2$, especially CO$_2$ from large point source, for example, fossil-fuel-fired electrical power-generation plants is critical to stabilize the atmospheric CO$_2$ concentration.[2] The existing commercial CO$_2$ capture facilities are based on the wet scrubbing process using aqueous alkanolamine compounds, and equipment corrosion.[1] Recently, ionic liquids have high energy penalty, amine loss and degradation, release of volatile organic compounds, and equipment corrosion.

The CO$_2$ absorption of the poly(ionic liquid) was determined by nitrogen adsorption (Tristar 3000, Micromeritics). The BET surface area of the powder was characterized by 1H NMR on a Bruker Advance DRX-400 spectrometer and element analysis indicated pure poly(ionic liquid) was obtained. We found that the polymers from ammonium based ionic liquids had very high CO$_2$ absorption capacity, and could be a new kind of materials for CO$_2$ capture and separation.

Experimental

Synthesis of ionic liquid monomers (Scheme 1):

[MAETA][BF$_4$] and [VBTA][BF$_4$] Water in [2-(methacryloxy)ethyl]-trimethyl ammonium chloride (75% wt) solution was removed at 40°C under high vacuum. Dried [2-(methacryloxy)ethyl]-trimethyl ammonium chloride and NaBF$_4$ were mixed in acetonitrile. The mixture was stirred overnight. The precipitated chloride salt was removed by filtration. The filtrate was concentrated and then poured in ether to precipitate out the product. The products were washed by ether and dried under vacuum. The synthesis of [VBTA][BF$_4$] was similar.

Synthesis of poly(ionic liquid)s: Ionic liquid monomer (3 g), AIBN (30 mg) in 3 ml of DMF were charged into a tube, 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 out the product. The products were washed by ether and dried under vacuum at 100°C.

Measurements: Ionic liquid monomers and poly(ionic liquids) were characterized by 1H NMR on a Bruker Advance DRX-400 spectrometer using dimethylsulfoxide (DMSO-d$_6$) as solvent and element analysis (Midwest Microlab, LLC). SEM was conducted on a Scanning Electron Microscope (Philips 505). The BET surface area of the powder was determined by nitrogen adsorption (Tristar 3000, Micromeritics Instruments Corp). The CO$_2$ absorption of the poly(ionic liquid) was measured using a Cahn 1000 Electrobalance. The buoyancy effects from these measurements were corrected according to literature.[5] 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 of [bmim][BF$_4$] was identical to that reported.[4]

Results and discussion

Synthesis of poly(ionic liquid): The two monomers were synthesized from corresponding chlorides using ion exchange reaction with NaBF$_4$. The chloride salts cannot dissolve in acetonitrile, but the ionic liquids monomers with BF$_4$ anion can dissolve in acetonitrile, acetone, DMF, DMSO. P[MAETA][BF$_4$] and P[VBTA][BF$_4$] were prepared from the two ionic liquid monomers by free radical polymerization using AIBN as initiator. 1H NMR and element analysis indicated pure poly(ionic liquids) were obtained.

Figure 1  CO$_2$ absorption of ionic liquid polymers and their monomers (592.3 mmHg CO$_2$, 22 °C).

CO$_2$ absorption kinetics of poly(ionic liquid): The CO$_2$ absorption kinetic of poly(ionic liquid) and their monomers are shown in Figure 1. There was no weight increase when the two monomers exposed to CO$_2$ which can be ascribed to their crystalline structures. When P[VBTA][BF$_4$] or P[MAETA][BF$_4$] exposed to CO$_2$, their weights increased very fast. It took only 30 min to reach the equilibrium. The polymer (1.0 g) could gain 13.6 mg (7.4 mol %) and 15.3 mg/g (8.4 mol %) for P[VBTA][BF$_4$] and P[MAETA][BF$_4$], respectively.

Figure 2  Cycles of CO$_2$ absorption (592.3 mmHg CO$_2$, 22 °C) and desorption by vacuuming of P[MAETA][BF$_4$].

CO$_2$ absorption and desorption cycles and selectivity of gas absorption: Repeated CO$_2$ absorption and desorption cycles of P[MAETA][BF$_4$] were tested by filling the chambers with CO$_2$ and then vacuuming (Figure 2). Both absorption and desorption of P[MAETA][BF$_4$] were very fast. It took only about 30 min to take up CO$_2$ or to have a complete desorption of CO$_2$. The desorption was complete, suggesting that the absorption/desorption was reversibly. No change in sorption/desorption kinetics and sorption capacity was observed after the four cycles.

Figure 3  Cycles of CO$_2$ absorption (592.3 mmHg CO$_2$, 22 °C) and desorption by vacuuming of P[MAETA][BF$_4$].

The absorption of the polymers is very selective, as shown in Figure 3. There was no weight increase when the polymers were
exposed to N₂ under the same conditions, indicative of that they selectively absorbed CO₂. In N₂/CO₂ mixed gas, only CO₂ was absorbed.

Figure 3. The selectivity of gas absorption (592.3 mmHg, 22 °C) of P[VBI][BF₄].

Conclusions

The ammonium based poly(ionic liquid)s had high CO₂ absorption capacity: 8.5 mole % and 7.4 mole %, for P[MAETA][BF₄] and P[VTBA][BF₄], respectively. The CO₂ absorption and desorption are reversibly and selectively over N₂.

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References