Carbon Dioxide Absorption of Poly(Ionic Liquid)s With Different Ionic Structures

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INTRODUCTION

Global warming resulting from the increasing CO_2 concentration in the atmosphere due to emissions of CO_2 from fossil fuel combustion has become one of most important environmental issues[1-2]. Recently, CO_2 capture and sequestration are receiving significant attention.[3,4,5] For carbon sequestration, it is critical to develop cost-effective methods for separation and capture of CO_2 from flue gas because the cost of capture and separation are estimated to make up three-fourths of total costs of ocean or geologic sequestration.[3,4,5]

CO_2 was found remarkably soluble in ionic liquids, and thus ionic liquids have been explored as non-volatile, and reversible absorbents for CO_2 separation.[6-12] Recently, we found that poly(ionic liquid)s, the polymers from ionic liquid monomers, had higher CO_2 absorption capacity than room temperature ionic liquids and their absorption is selective, fast and completely reversible.[13,14] These poly(ionic liquid)s are thus very promising as sorbent and membrane materials for CO_2 separation. In this paper, a series of new poly(ionic liquid)s are synthesized and the relationship of their structures with CO_2 solubility is discussed.

EXPERIMENT

Materials. 4-Vinylbenzyl chloride (90 %), lithium trifluoromethane sulfonamide ($LiTf_2N$, 99.95%), potassium hexafluorophosphate (98%), sodium tetrafluoroborate (98%), 2, 6-di-tert-butyl-4-methyl phenol (98%) (DBMP), N,N-Dimethylformamide (99.8%, DMF), acetonitrile (99.5+%), acetone (99.5+%), triphenylphosphine (99%), α,α'-azobis(isobutyrobitrile)(AIBN) (98%) were purchased from Aldrich. 1-Methylimidazole (99%), o-benzoic sulphimide sodium salt hydrate (NaSac) 97% were purchased from Lancaster synthesis Inc. Pyridine was purchased from Fisher scientific. All chemicals were used as received.

Syntheses of Ionic Liquid Monomers. Synthesis of [VBTMA][BF_4] and other ammonium-based monomers will be published elsewhere.[14] The syntheses of [VBTPP][BF_4], [VBP][BF_4] and [VBMI][BF] is similar to that of [VBBI][BF_4] (VBIT)[13], except for using triphenylphosphine, pyridine and 1-methylimidazole instead of 1-butylimidazole, respectively.

Syntehesis of Ionic Liquid Crosslinker. N,N,N`,N`-tetramethylethylenediamine (5.8 g, 0.05 mol), 4-vinylbenzyl chloride (16.0 g, 0.105 mol) and a small amount of DBMP were mixed in 50 ml of DMF. The resulting solution was heated at 50 ^oC for 2 days. The solution was poured into 400 ml diethyl ether to precipitate out the product. After filtration and drying under vacuum, a white crystal (15.8 g) was obtained. The product reacted with $NaBF_4$ (4.3 g, 0.04 mol) in 50 ml dried acetonitrile for 2 days. After the reaction, the insoluble chloride salt was removed by filtration. The filtrate was concentrated and poured into diethyl ether to precipitate out the product. A white crystal was collected by filtration and dried under vacuum. The overall yield was 63.7%.

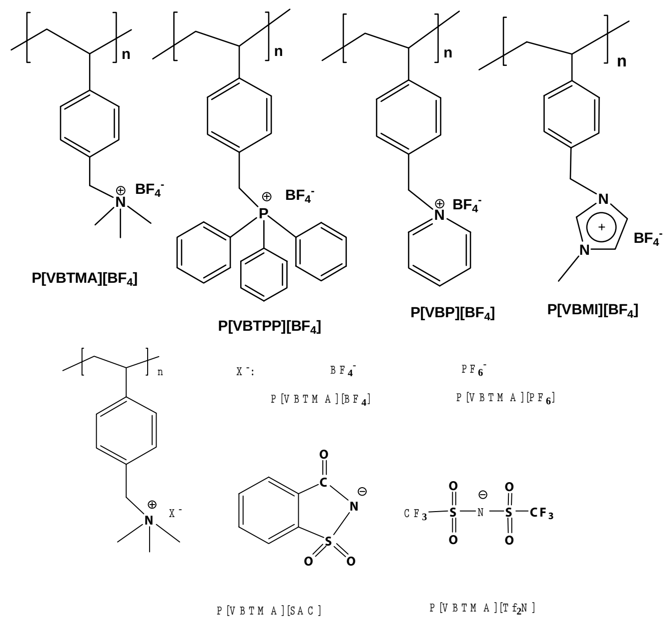
Synthesis of Poly(ionic liquids)s. Poly(ionic liquid)s were synthesized by free radical polymerization using AIBN as initiator in DMF following our previous report.[13] The crosslinked P[VBTMA][BF_4] was synthesized in the same way except for adding 5 w.% crosslinker.

Measurement. The polymers were characterized by ^1H NMR on a Bruker Advance DRX-400 spectrometer using d^6-dimethylsulfoxide (DMSO-d_6) as solvent. The elemental analyses of polymers were tested by Midwest Microlab LLC (US). The CO_2 sorption of the poly(ionic liquid)s was measured using a CAHN 1000 Electrobalance, the details of the measurement were described in our previous reports.[13,14]

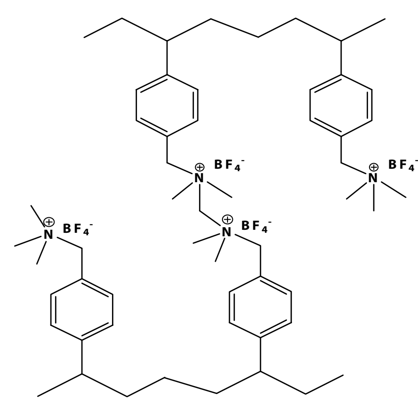
RESULTS AND DISCUSSION

Synthesis of Ionic Liquid Monomers and Poly(ionic liquid)s. The structures of poly(ionic liquid)s are shown in Scheme 1. Two steps were generally involved in the preparations of ionic liquid monomers: the quaternization reaction and the anion exchange reaction of the halide ions with tetrafluoroborate, hexafluorophosphate, Sac or Tf_2N anions. The resulting monomers are soluble in polar solvent such as DMF, acetone, acetonitrile. All ammonium-based monomers except for [VBTMA][Tf_2N] are soluble in H_2O. Ionic liquid monomers based on phosphonium, pyridium, imidazolium are insoluble in H_2O. All poly(ionic liquid)s are soluble in DMF.

The ^1H NMR and elemental analyses indicated the ionic liquid monomers and poly(ionic liquid)s were pure.



Scheme 1. Structures of poly(ionic liquid)s with different structures.



Scheme 2. Structure of crosslinked P[VBTMA][BF_4].

CO_2 Absorption of Poly(ionic liquid)s With Different Types of Cations. Figure 1 shows the effects of cation types on CO_2 absorption of poly(ionic liquid)s.. CO_2 absorption capacity of Poly(ionic liquid)s with different cations is as fellows: P[VBTMA][BF_4] (10.2 mol.%) < P[VBTPP][BF_4] (7.8 mol.%) < P[VBP][BF_4] (3.6%) < P[VBMI][BF_4] (3.0 %). The solubility increases with the increase of polarity of the cations. The ammonium-based polymer has the highest solubility because of the high polarity of its cation. The imidazolium-based polymer with the low polar cation has the lowest solubility. This phenomenon indicate that the polarity of the cation can affect the interaction between the cation and CO_2.

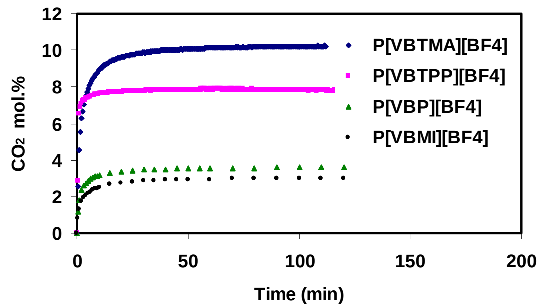


Figure 1. CO_2 absorption of poly(ionic liquid)s with different types of cations (592 mmHg CO_2, 22°C).

CO_2 Absorption of Poly(ionic liquid)s With Different Types of Anions. **Figure 2** shows the effects of anion types on the CO_2 solubility of poly(ionic liquid)s. The four polymers have the same cation structure, but different anions. P[VBTMA][PF_6] and P[VBTMA][BF_4] had the same CO_2 solubility of 10.2 mol.%. P[VBTMA][[Sac] and P[VBTMA][Tf_2N] had a solubility of 2.8 mol.% and 2.7% respectively. The two poly(ionic liquid)s with inorganic anions had much higher solubility than the two with organic anion. This can also be explained by the polarity of anions, which affects the interaction between the poly(ionic liquid)s with CO_2.

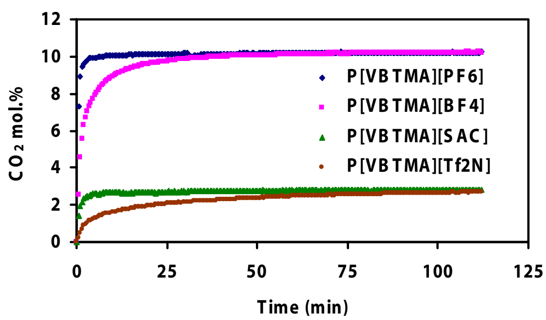


Figure 2. CO_2 absorption of poly(ionic liquid)s with different anions (592 mmHg CO_2, 22 °C).

Effect of Crosslinking on the CO_2 Absorption. **Figure 3** shows the CO_2 absorption of crosslinked poly(ionic liquid). Compared with P[VBTMA][BF_4] without crosslinking, the CO_2 absorption capacity of crosslinked P[VBTMA][BF_4] decreased by 17.3%. This may be due to that crosslinking causes a decrease in free volume of the polymer.

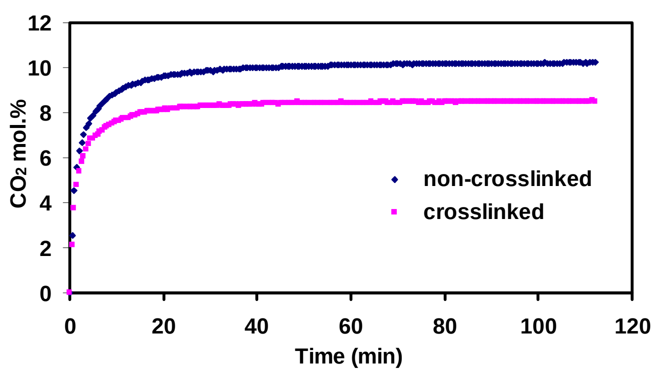


Figure 3. The crosslink effect on CO_2 absorption poly(ionic liquid)s (592 mmHg CO_2, 22 °C).

CONCLUSION

A series of ionic liquid monomers and their polymers with different cation and anion structures were synthesized and characterized. Their CO_2 absorption capacities range from 2.7 mol.% to 10.2 mol.%. Poly(ionic liquid)s with higher polar cations and anions have higher CO_2 solubility. Crosslinking of the polymer decreases the CO_2 absorption capacity of poly(ionic liquid).

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