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(54) **POLY(IONIC LIQUID)S AS NEW MATERIALS FOR CO_2 SEPARATION AND OTHER APPLICATIONS**

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PCT Pub. Date: **Mar. 9, 2006**

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B01D 53/22 (2006.01)
B01D 53/02 (2006.01)

(52) **U.S. Cl.**
USPC **95/51**; 95/92; 95/139; 96/4; 96/153

(58) **Field of Classification Search**
USPC 95/51, 92, 236, 139, 148; 528/289, 528/394; 502/402
See application file for complete search history.

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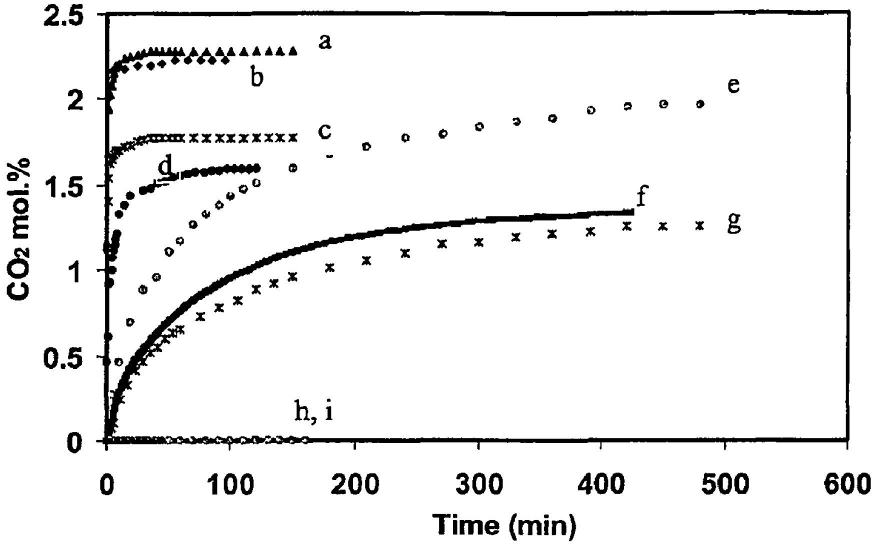
(74) *Attorney, Agent, or Firm* — Davis, Brown, Koehn, Shors & Roberts, P.C.; Kent A. Herink

(57) **ABSTRACT**

Polymerizable ionic liquid monomers and their corresponding polymers (poly(ionic liquid)s) are created and found to exhibit high CO2 sorption. The poly(ionic liquid)s have enhanced and reproducible CO2 sorption capacities and sorption/desorption rates relative to room-temperature ionic liquids. Furthermore, these materials exhibit selectivity relative to other gases such as nitrogen, methane, and oxygen. They are useful as efficient separation agents, such sorbents and membranes. Novel radical and condensation polymerization approaches are used in the preparation of the poly(ionic liquids).

3 Claims, 11 Drawing Sheets



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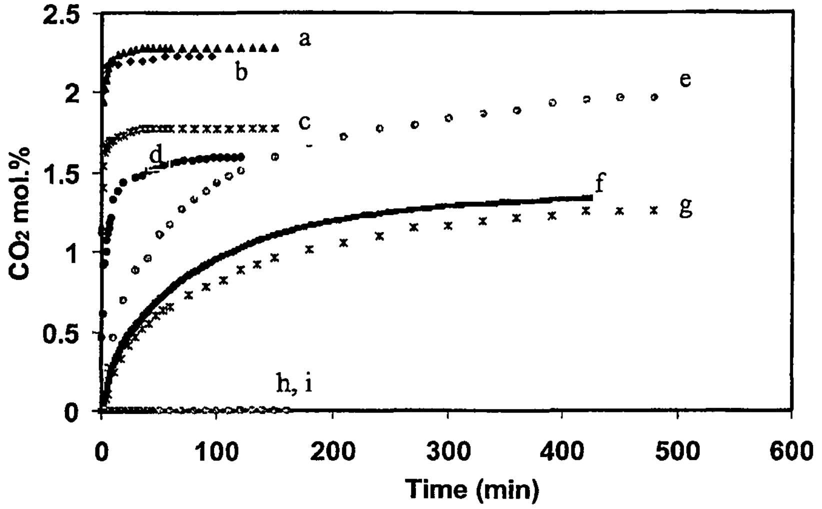

2.5
2
1.5
1
0.5
0
CO2 mol.%
0
100
200
300
400
500
600
Time (min)
a
b
c
d
e
f
g
h, i

FIG. 1

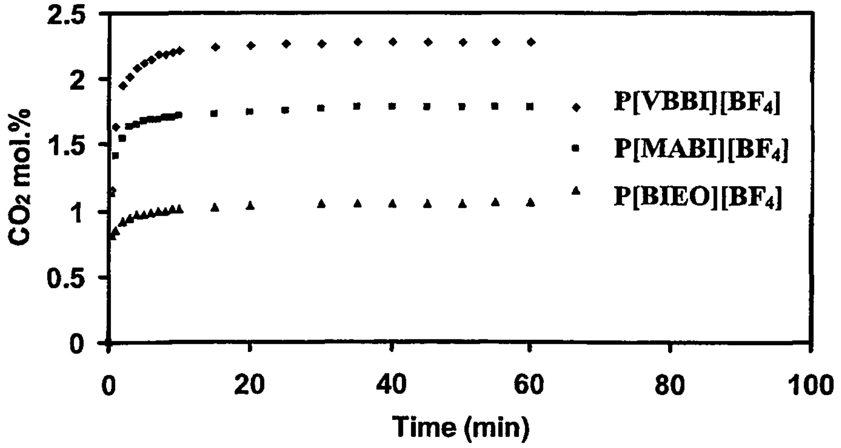

2.5
2
1.5
1
0.5
0
CO2 mol.%
0
20
40
60
80
100
Time (min)
◆ P[VBBI][BF4]
▪ P[MABI][BF4]
▲ P[BIEO][BF4]

FIG. 2

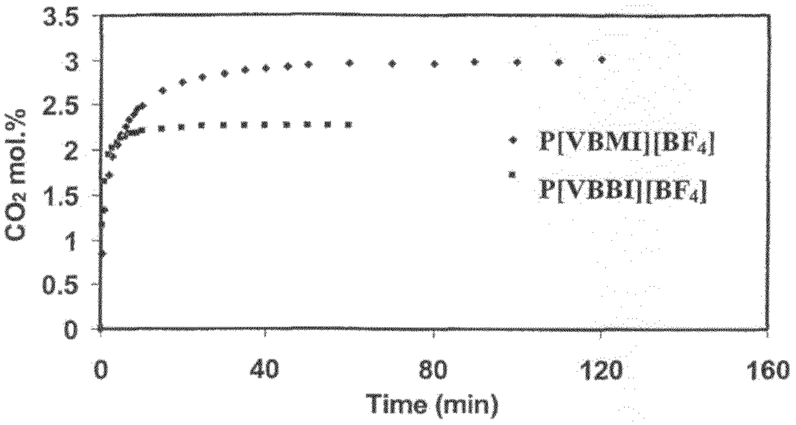

3.5
3
2.5
2
1.5
1
0.5
0
CO₂ mol.%
0
40
80
120
160
Time (min)
P[VBMI][BF₄]
P[VBBI][BF₄]

FIG. 3

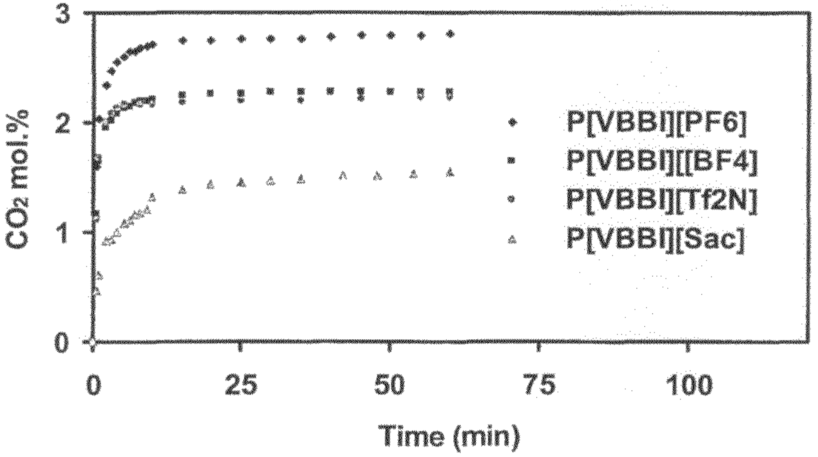

3
2
1
0
CO₂ mol.%
0
25
50
75
100
Time (min)
P[VBBI][PF6]
P[VBBI][[BF4]
P[VBBI][Tf2N]
P[VBBI][Sac]

FIG. 4

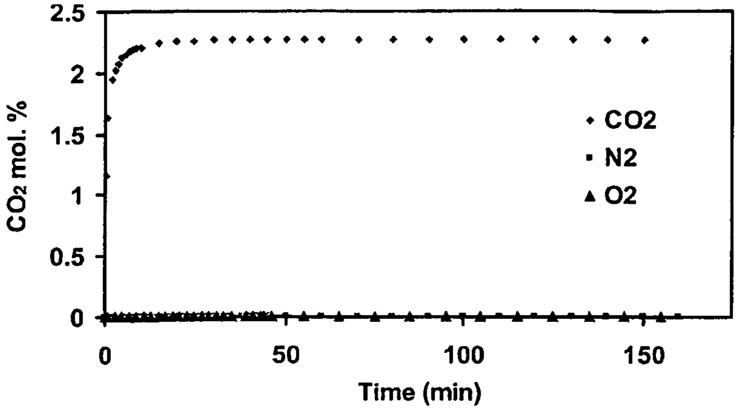


FIG. 5

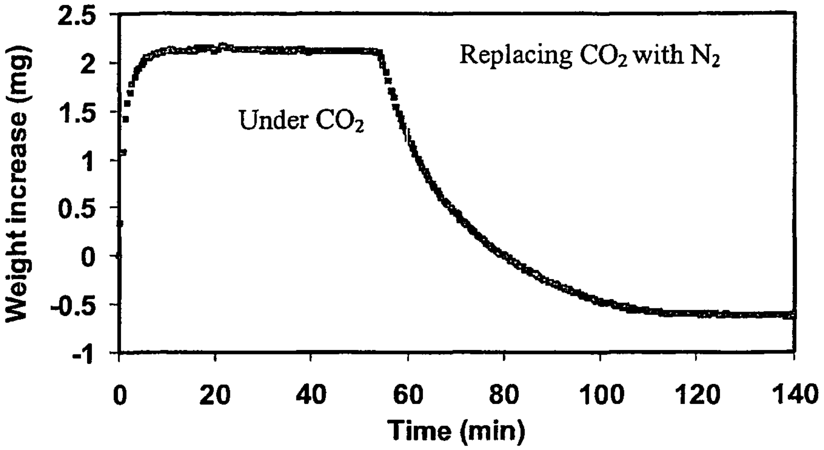

2.5
2
1.5
1
0.5
0
-0.5
-1
Weight increase (mg)
0
20
40
60
80
100
120
140
Time (min)
Under CO2
Replacing CO2 with N2

FIG. 6

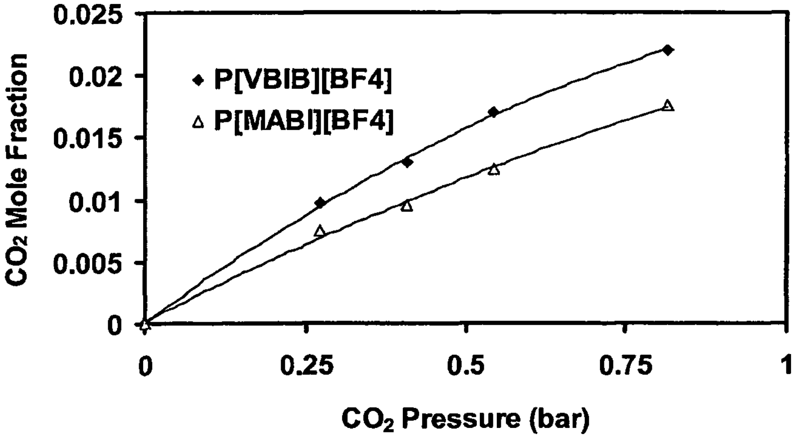
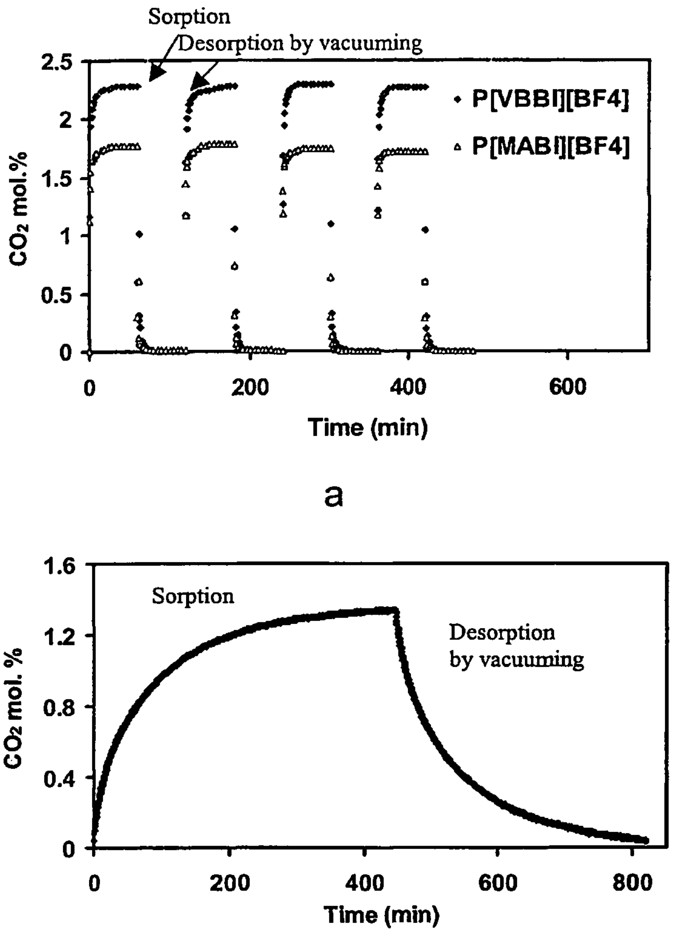

0.025
0.02
0.015
0.01
0.005
0
CO2 Mole Fraction
◆ P[VBIB][BF4]
△ P[MABI][BF4]
0
0.25
0.5
0.75
1
CO2 Pressure (bar)

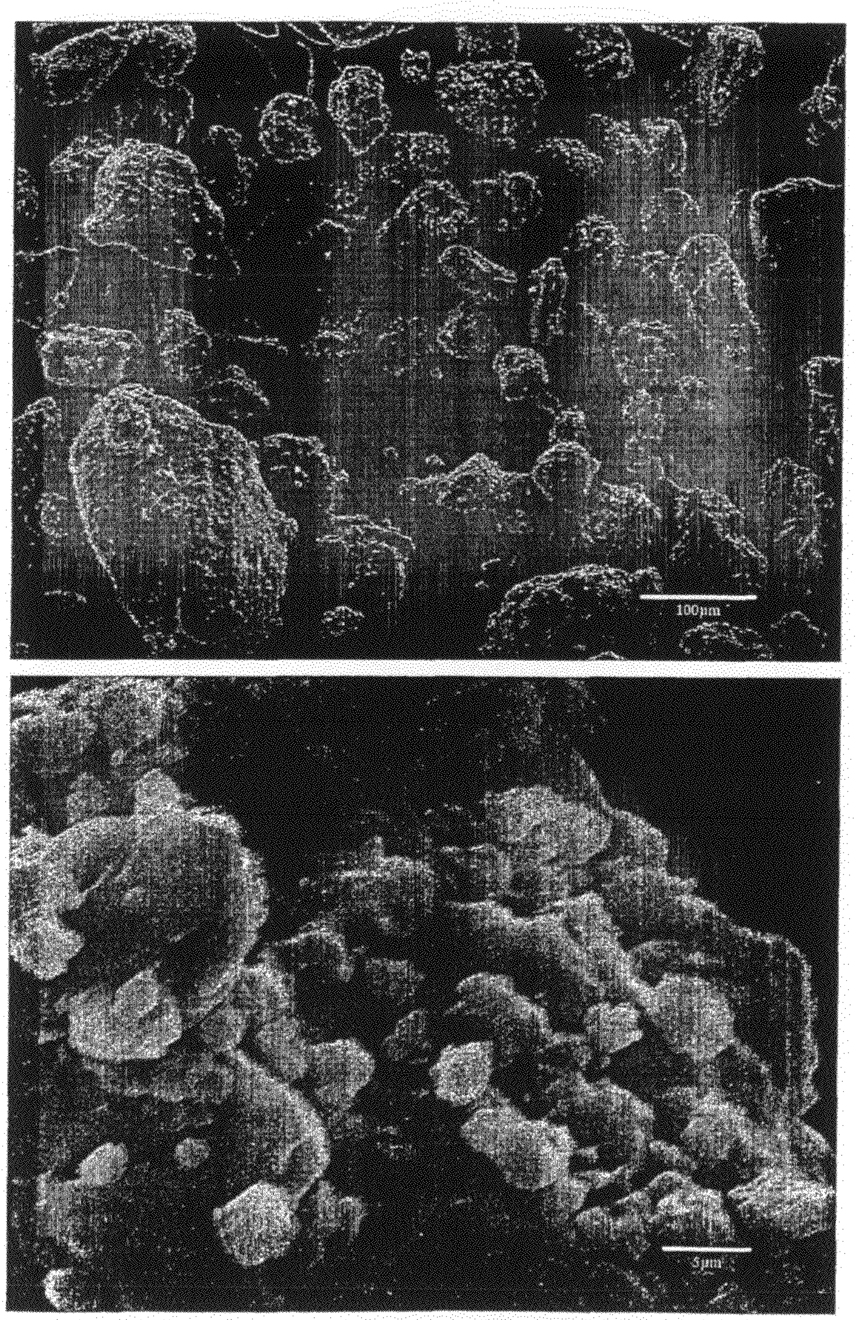
FIG. 7


Sorption
Desorption by vacuuming
2.5
2
1.5
1
0.5
0
CO₂ mol.%
0
200
400
600
Time (min)
P[VBBI][BF4]
P[MABI][BF4]
1.6
1.2
0.8
0.4
0
CO₂ mol. %
Sorption
Desorption
by vacuuming
0
200
400
600
800
Time (min)

a

b

FIGS. 8



FIGS. 9A, B

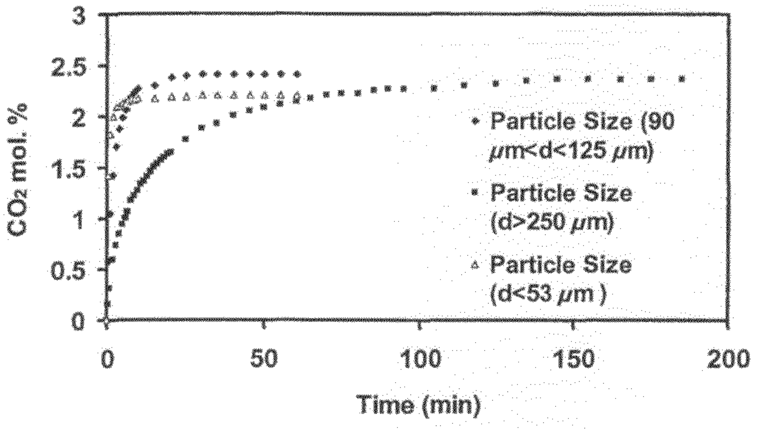

3
2.5
2
1.5
1
0.5
0
CO_2 mol. %
0
50
100
150
200
Time (min)
◆ Particle Size (90 μm<d<125 μm)
■ Particle Size (d>250 μm)
△ Particle Size (d<53 μm)

FIG. 10

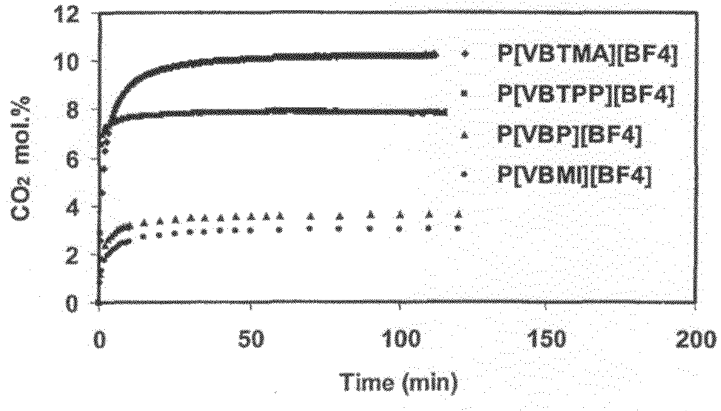

12
10
8
6
4
2
0
CO_2 mol.%
0
50
100
150
200
Time (min)
◆ P[VBTMA][BF4]
■ P[VBTPP][BF4]
▲ P[VBP][BF4]
● P[VBMI][BF4]

FIG 11

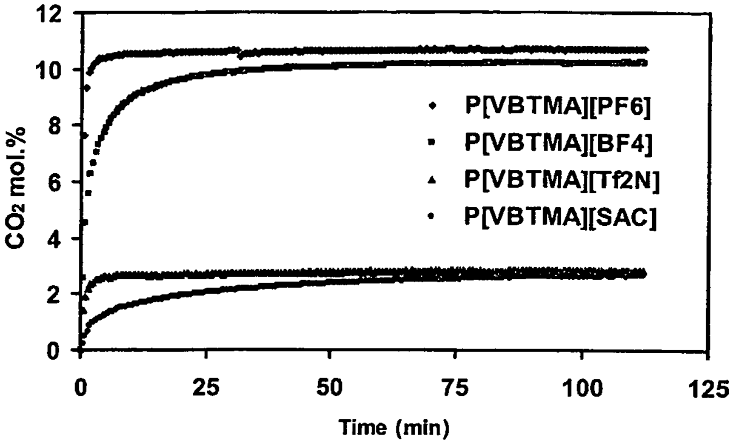

12
10
8
6
4
2
0
CO2 mol.%
0
25
50
75
100
125
Time (min)
◆ P[VBTMA][PF6]
■ P[VBTMA][BF4]
▲ P[VBTMA][Tf2N]
● P[VBTMA][SAC]

FIG 12

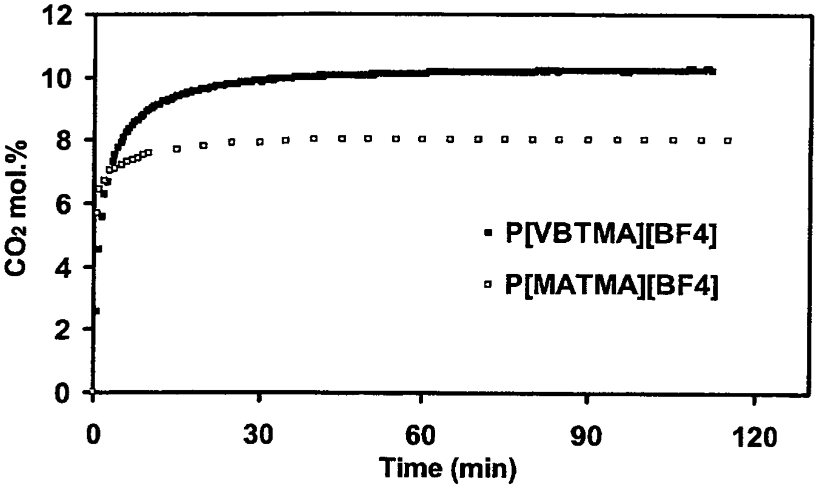

12
10
8
6
4
2
0
CO2 mol.%
0
30
60
90
120
Time (min)
■ P[VBTMA][BF4]
□ P[MATMA][BF4]

FIG 13

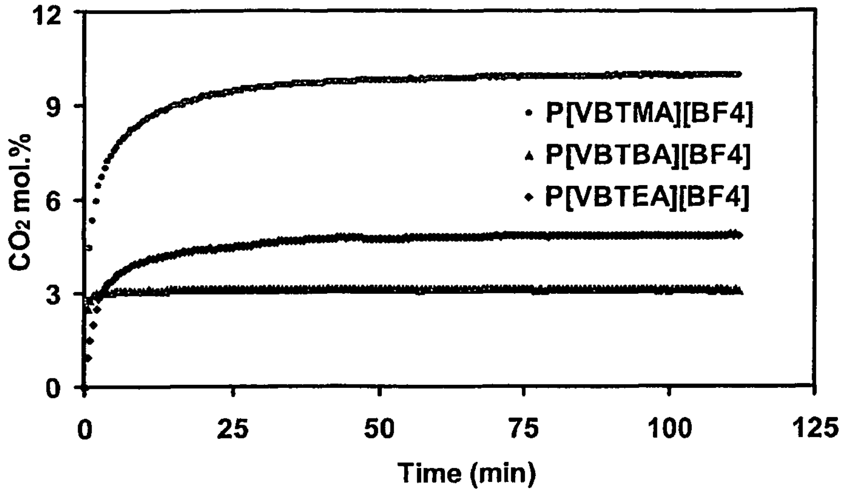

12
9
6
3
0
CO2 mol.%
0
25
50
75
100
125
Time (min)
• P[VBTMA][BF4]
▲ P[VBTBA][BF4]
◆ P[VBTEA][BF4]

FIG 14

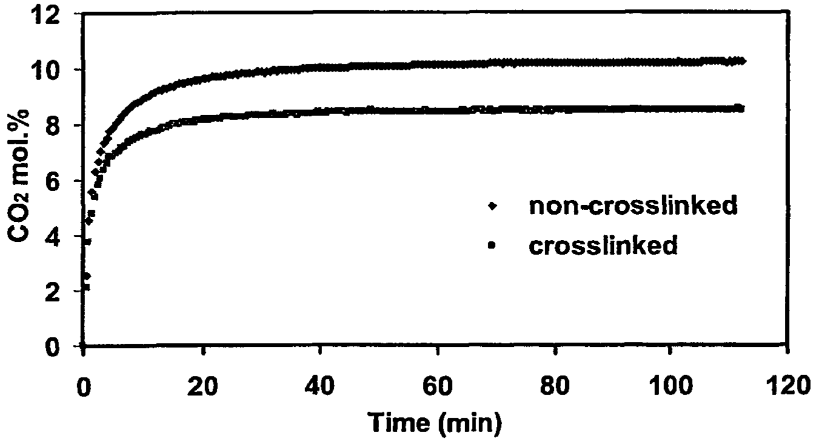

12
10
8
6
4
2
0
CO2 mol.%
0
20
40
60
80
100
120
Time (min)
◆ non-crosslinked
■ crosslinked

FIG. 15

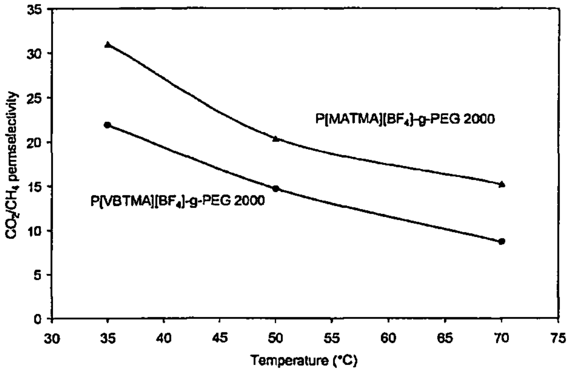

35
30
25
20
15
10
5
0
30
35
40
45
50
55
60
65
70
75
Temperature (°C)
CO_2/CH_4 permselectivity
P[MATMA][BF_4]-g-PEG 2000
P[VBTMA][BF_4]-g-PEG 2000

FIG. 16

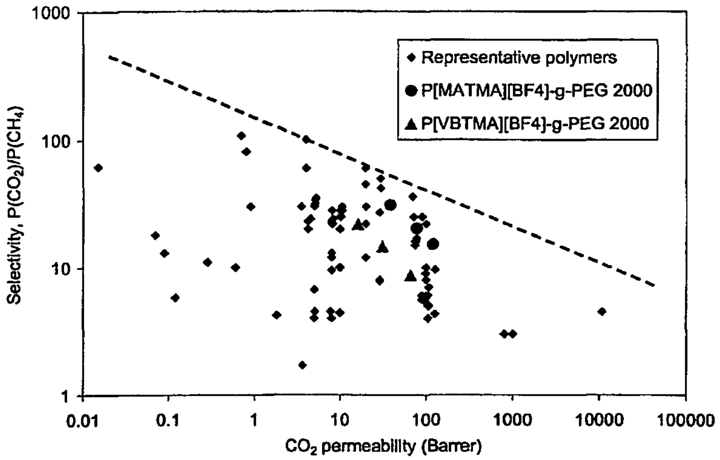

1000
100
10
1
0.01
0.1
1
10
100
1000
10000
100000
CO_2 permeability (Barrer)
Selectivity, $P(CO_2)/P(CH_4)$
◆ Representative polymers
● P[MATMA][BF4]-g-PEG 2000
▲ P[VBTMA][BF4]-g-PEG 2000

FIG. 17

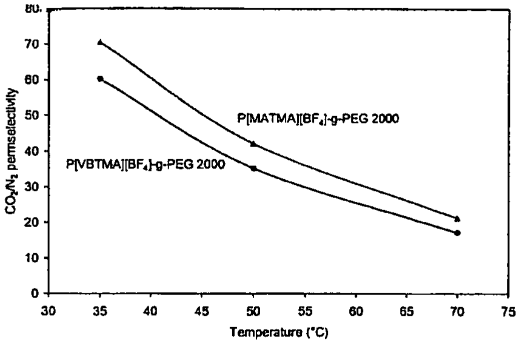

80
70
60
50
40
30
20
10
0
CO_2/N_2 permselectivity
P[MATMA][BF_4]-g-PEG 2000
P[VBTMA][BF_4]-g-PEG 2000
30
35
40
45
50
55
60
65
70
75
Temperature (°C)

FIG. 18

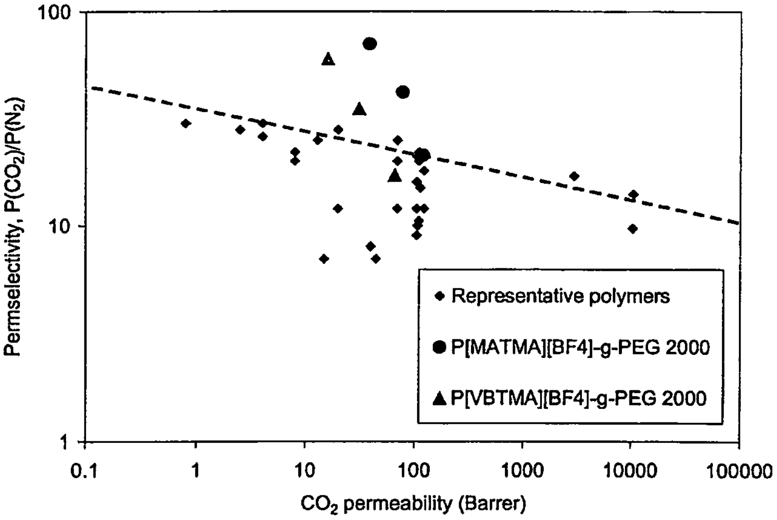

100
10
1
Permselectivity, $P(CO_2)/P(N_2)$
◆ Representative polymers
● P[MATMA][BF4]-g-PEG 2000
▲ P[VBTMA][BF4]-g-PEG 2000
0.1
1
10
100
1000
10000
100000
CO_2 permeability (Barrer)

FIG. 19

POLY(IONIC LIQUID)S AS NEW MATERIALS FOR CO_2 SEPARATION AND OTHER APPLICATIONS

BACKGROUND OF THE INVENTION

The invention relates generally to novel materials, namely polymers made from ionic liquids, referred to herein as poly (ionic liquid)s, and, more specifically, to poly(ionic liquid)s for separating gases, particularly carbon dioxide (CO_2).

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

Ionic liquids, which are organic salts that become liquids usually below about 200° C., have attracted attention because of their unique chemical and physical properties and wide application potentials.[6-12] Recently, CO_2 was found to be remarkably soluble in ionic liquids, and thus ionic liquids have been explored as non-volatile, and reversible absorbents for CO_2 separation.[13-21] 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. %.[19] The CO_2 solubility in the ionic liquids is dependent on their cations and substituents, and especially on their anions.[19] For example, fluorine-containing anions (e.g. bis(trifluoromethyl-sulfonyl)imide, Tf_2N),[19] or cations,[22] or amine groups[23] tend to increase the CO_2 solubility. Ionic liquids have also been impregnated into porous materials for developing supported liquid membranes. Such membranes have high CO_2 selectivity and permeance because of the selective sorption of CO_2 in ionic liquids.[24-26]

We have found that poly(ionic liquid)s, the polymers prepared from ionic liquid monomers, have higher CO_2 sorption capacity than room temperature ionic liquids. Most importantly, the CO_2 sorption and desorption of the polymers are much faster than those of ionic liquids and the sorption/desorption is completely reversible. These poly(ionic liquid)s are thus promising as sorbent and membrane materials for CO_2 separation.

SUMMARY OF THE INVENTION

The invention consists of a class of new materials consisting of novel ionic liquids and polymers made from ionic liquids. The poly(ionic liquid)s are polymerized ionic liquid monomers and have been found to have a CO_2 absorption rate and/or a CO_2 absorption capacity higher than that of the ionic liquid monomer. Certain of the poly(ionic liquid)s have a CO_2 absorption capacity almost ten times that of the ionic liquid monomer from which they are made. The sorption/desorption rates of the poly(ionic liquid)s are much faster than those of the corresponding ionic liquid monomers, and the poly(ionic liquid)s retain their sorption/desorption properties after going through sorption/desorption cycling. The polymers are made primarily through radical polymerization, but other methods of polymerization may also be used.

The ionic liquid monomers include: (a) Imidazolium-based ionic liquids, such as (a) 1-[2-(methacryloyloxy) ethyl]-3-butyl-imidazolium tetrafluoroborate ([MABI] [BF_4]), 1-(p-vinylbenzyl)-3-butyl-imidazolium tetrafluoroborate ([VBBI][BF_4]), 1-(p-vinylbenzyl)-3-methyl-imidazolium tetrafluoroborate [VBMI][BF_4], 1-(p-vinylbenzyl)-3-butyl-imidazolium hexafluorophosphate [VBBI][PF_6], 1-(p-vinylbenzyl)-3-butyl-imidazolium o-benzoic sulphimide ([VBBI][Sac]), 1-p-vinylbenzyl)-3-butyl-imidazolium trifluoromethane sulfonamide([VBBI] [BF_4]), and (1-butylimidazolium-3)methyl-ethylene oxide ([BIEO][BF_4]); (b) Ammonium-based ionic liquids, such as p-vinylbenzyl)trimethyl ammonium tetrafluoroborate ([VBTMA][BF_4]), (p-vinylbenzyl)triethyl ammonium tetrafluoroborate ([VBTEA][BF_4]), (p-vinylbenzyl)tributyl ammonium tetrafluoroborate ([VBTBA][BF_4]), 2-(methacryloyloxy)ethyltrimethylamnonium tetrafluoroborate ([MATMA][BF_4]), (p-vinylbenzyl)trimethyl ammonium hexafluorophosphate ([VBTMA][PF_6]), (p-vinylbenzyl)trimethyl ammonium o-benzoic sulphimide ([VBTMA][Sac]), and (p-vinylbenzyl)trimethyl ammonium trifluoromethane sulfonamide ([VBTMA][Tf_2N]); (c) Phosphonium-based ionic liquids, such as p-vinylbenzyl)triethyl phosphonium tetrafluoroborate ([VBTEP][BF_4]), and (p-vinylbenzyl) triphenyl phosphonium tetrafluoroborate ([VBTPP][BF_4]); (d) Pyridinium-based ionic liquids, such as 1-(p-vinylbenzyl) pyridinium tetrafluoroborate ([VBP][BF_4]); and (e) Condensation polymerization ionic monomers, such as bis(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate ([BHEDMA][BF_4]), 2,2-bis(methylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BMIMP][BF_4]), and 2,2-bis(butylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BBIMP][BF_4]).

The invention also consists of a process for the separation and recovery of gases that are soluble in the ionic liquid monomers and have sorption capacities and/or rates in the poly(ionic liquid)s that are higher than those in the corresponding ionic liquid monomer. In the specific example of CO_2, the process includes the steps of contacting a CO_2-containing gas mixture with a solid sorbent that includes at least one poly(ionic liquid) compound under such conditions as to obtain a gas product having a lower concentration of CO_2 than the initial gas mixture and a solid sorbent containing absorbed carbon dioxide which has been removed from said gas mixture. Preferably, the solid sorbent is treated under conditions as to substantially desorb the CO_2 contained in the solid sorbent so as to obtain a regenerated solid sorbent.

BRIEF DESCRIPTION OF THE FIGURES

FIG. **1** is a graphical representation of the CO_2 sorption of the poly(ionic liquids)s (P[VBBI][BF_4](a), P[VBBI][Tf_2N] (b), P[MABI][BF_4](c), P[VBBI][Sac](d)), with their corresponding monomers ([VBBI][Tf_2N](e), [MABI][BF_4](g), [VBBI][BF_4](h), [VBBI][Sac](i)), and an ionic liquid [bmim][BF_4] (f) as a function of time (592.3 mmHg CO_2, 22° C.).

FIG. **2** is a graphical representation of the CO_2 sorption of poly(ionic liquid)s with different polymer backbones (592.3 mmHg of CO_2 and 22° C.).

FIG. **3** is a graphical representation of the CO_2 sorption of poly(ionic liquid)s with different substituents (592.3 mmHg of CO_2 and 22° C.).

FIG. **4** is a graphical representation of the CO_2 sorption of poly(ionic liquid)s with different anions (592.3 mmHg of CO_2 and 22° C.).

FIG. **5** is a graphical representation of the gas (CO_2, O_2, N_2) sorption of P[VBBI][BF_4] as a function of time at 592.3 mmHg, 22° C.

FIG. **6** is a graphical representation of the weight change of P[VBBI][BF_4] (1 g) (without buoyancy correction) after introducing CO_2 into the system, and then replacing CO_2 with N_2 (total pressure 592.3 mmHg, 22° C.).

FIG. **7** is a graphical representation of the isothermal sorption of P[VBBI][BF_4] and P[MABI][BF_4] at different CO_2 pressures (22° C.).

FIG. **8** is a graphical representation of the (a) cycles of CO_2 sorption (592.3 mmHg CO_2, 22° C.) and desorption of P[VBBI][BF_4] and P[MABI][BF_4] under vacuum; (b) CO_2 sorption (592.3 mmHg CO_2, 22° C.) and desorption of a typical ionic liquid [bmim][BF_4] under vacuum.

FIGS. **9**A and **9**B are scanning electron micrographs of P[VBBI][BF_4] particles.

FIG. **10** is a graphical representation of the CO_2 sorption of P[VBBI][BF_4] with different particle sizes (592.3 mmHg, 22° C.).

FIG. **11** is a graphical representation of the CO_2 sorption of poly(ionic liquid)s with different types of cation.

FIG. **12** is a graphical representation of the CO_2 sorption of poly(ionic liquid)s with different types of anion.

FIG. **13** is a graphical representation of the CO_2 sorption in poly(ionic liquid)s with different backbones

FIG. **14** is a graphical representation of the CO_2 sorption in poly(ionic liquid)s with different substituents.

FIG. **15** is a graphical representation of the effect of crosslinking on CO_2 sorption in poly(ionic liquid)s.

FIG. **16** is a graphical representation of the CO_2/CH_4 selectivity for P[VBTMA][BF_4]-co-PEG and P[MATMA][BF_4]-co-PEG.

FIG. **17** is a graphical representation of the CO_2/CH_4 selectivity for representative polymers and poly(ionic liquids) (◆: representative polymers; ●: P[MATMA][BF_4]-co-PEG at 35° C., 50° C. and 70° C.; ▲: P[VBTMA][BF_4]-co-PEG at 35° C., 50° C. and 70° C.)

FIG. **18** is a graphical representation of the CO_2/N_2 selectivity for P[VBTMA][BF_4]-co-PEG and P[MATMA][BF_4]-co-PEG

FIG. **19** is a graphical representation of the CO_2/N_2 selectivity for representative polymers and poly(ionic liquids) (◆: representative polymers; ●: P[MATMA][BF_4]-co-PEG at 35° C., 50° C. and 70° C.; ▲: P[VBTMA][BF_4]-co-PEG at 35° C., 50° C. and 70° C.)

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In this description, each material is introduced by its full chemical name followed by a shortened name in parenthesis, for example, 1-[2-(methacryloyloxy)ethyl]-3-butyl-imidazolium tetrafluoroborate ([MABI][BF_4]). Following the initial introduction, only the shortened name is used.

Ionic liquids are organic salts with melting points usually below 200° C., often below room temperature. They can be substitutes for the traditional organic solvents in chemical reactions. The most common examples are imidazolium and pyridinium derivatives, but phosphonium or tetralkylammonium compounds have also been explored.

Ionic liquid monomers of the present application are ionic liquids that are suitable for polymerization of the ionic liquid monomers to form poly(ionic liquid)s. Specific examples of ionic liquid monomers of the present application have a double bond that forms a radical when broken. The ionic liquid monomers may include an inorganic moiety. Specific examples of ionic liquid monomers used for polymer synthesis and other applications include but are not limited to:

(1) Ionic liquid monomers based on imidazolium, such as 1-[2-(methacryloyloxy)ethyl]-3-butyl-imidazolium tetrafluoroborate ([MABI][BF_4]), 1-p-vinylbenzyl)-3-butyl-imidazolium tetrafluoroborate ([VBBI][BF_4]), 1-(p-vinylbenzyl)-3-methyl-imidazolium tetrafluoroborate ([VBMI][BF_4]), 1-(p-vinylbenzyl)-3-butyl-imidazolium hexafluorophosphate ([VBBI][PF_6]), 1-(p-vinylbenzyl)-3-butyl-imidazolium o-benzoic sulphimide ([VBBI][Sac]), 1-(p-vinylbenzyl)-3-butyl-imidazolium trifluoromethane sulfonamide([VBBI][BF_4]), (1-butylimidazolium-3)methyl-ethylene oxide ([BIEO][BF_4]);

(2) Ionic liquid monomers based on ammonium, such as (p-vinylbenzyltrimethyl) ammonium tetrafluoroborate ([VBTMA][BF_4]), (p-vinylbenzyl)triethyl ammonium tetrafluoroborate ([VBTEA][BF_4]), p-vinylbenzyl)tributyl ammonium tetrafluoroborate ([VBTBA][BF_4]), [2-(methacryloyloxy)ethyl]trimethyl ammonium tetrafluoroborate ([MATMA][BF_4]), (p-vinylbenzyl)trimethyl ammonium hexafluorophosphate ([VBTMA][PF_6]), p-vinylbenzyl)trimethyl ammonium o-benzoic sulphimide ([VBTMA][Sac]), (p-vinylbenzyltrimethyl) ammonium trifluoromethane sulfonamide ([VBTMA][Tf_2N]);

(3) Ionic liquid monomers based on phosphonium, such as (p-vinylbenzyl)triethyl phosphonium tetrafluoroborate ([VBTEP][BF_4]), (p-vinylbenzyl)triphenyl phosphonium tetrafluoroborate ([VBTPP][BF_4]);

(4) Ionic liquid monomers based on pyridinium, such as 1-(p-vinylbenzyl)pyridinium tetrafluoroborate ([VBP][BF_4]);

(5) Ionic liquid monomers for condensation polymerization, such as bis(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate ([BHEDMA][BF_4]), 2,2-bis(methylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BMIMP][BF_4]), and 2,2-bis(butylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BBIMP][BF_4]).

Poly(ionic liquid)s as used in this specification means polymers formed using ionic liquids as monomers via radical polymerization or other kind of polymerization. Certain of the poly(ionic liquid)s have a gas sorption capacity and/or rate that is greater than that of the corresponding ionic liquid monomer for the corresponding gas.

Radical polymerization is a common and useful reaction for making polymers from vinyl monomers, that is, from small molecules containing carbon-carbon double bonds. Polymers made by radical polymerization include polystyrene, poly(methyl methacrylate), poly(vinyl acetate) and branched polyethylene. Radical polymerization begins with a molecule called an initiator; common initiators are benzoyl peroxide or 2,2'-azo-bis-isobutyrylnitrile (AIBN).

EXAMPLE 1

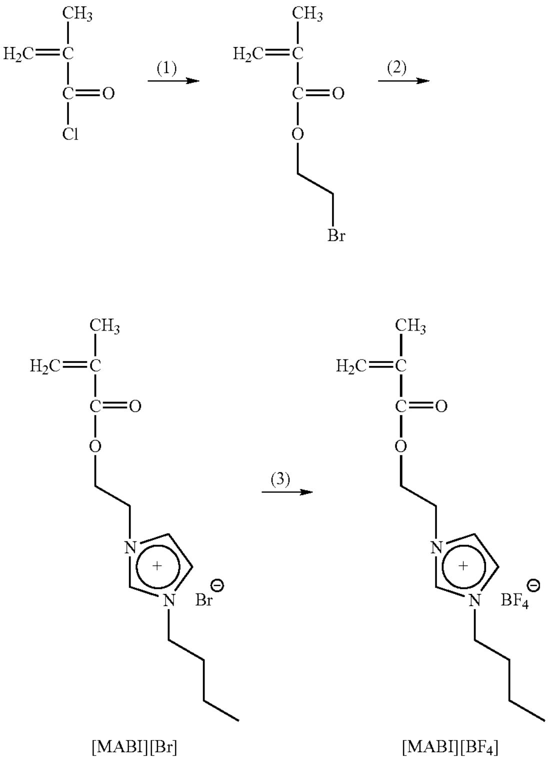
Materials

4-Vinylbenzyl chloride, methacryloyl chloride, 1-butylimidazole, 2-bromoethanol, lithium trifluoromethane sulfonimide, potassium hexafluorophosphate, sodium tetrafluoroborate, 2,6-di-tert-butyl-4-methyl phenol (DBMP), 2,2'-azobisisobutyronitrile (AIBN), aluminum isopropoxide, epichlorohydrin, N,N-dimethylformamide (DMF), acetonitrile, and acetone were purchased from Aldrich. 1-Methylimidazole, and o-benzoic sulphimide sodium salt hydrate were purchased from Lancaster Synthesis Inc. These chemicals were used without further purification.

Synthesis and Characterization

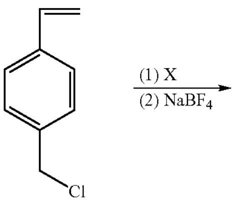
1-[2-(Methylacryloyloxy)ethyl]-3-butyl-imidazolium tetrafluoroborate ([MABI][BF_4]) and 1-(p-vinylbenzyl)-3-butyl-imidazolium tetrafluoroborate ([VBBI][BF_4]) were synthesized according to our published reports,[27,28] as shown in Schemes 1 and 2. 1-(p-Vinylbenzyl)-3-butyl-imidazolium hexafluorophosphate ([VBBI][PF_6]), 1-(p-vinylbenzyl)-3-butyl-imidazolium o-benzoic sulphimide ([VBBI][Sac]), 1-(p-vinylbenzyl)-3-butyl-imidazolium trifluoromethane sulfonamide ([VBBI][Tf_2N]) were synthesized by a similar procedure except using $NaPF_6$, o-benzoic sulphimide sodium salt hydrate (NaSac) or lithium trifluoromethane sulfonamide ($LiTf_2N$) for anion exchange reactions. The yields were 93.0%, 49.6%, 39.9%, respectively.

Scheme 1

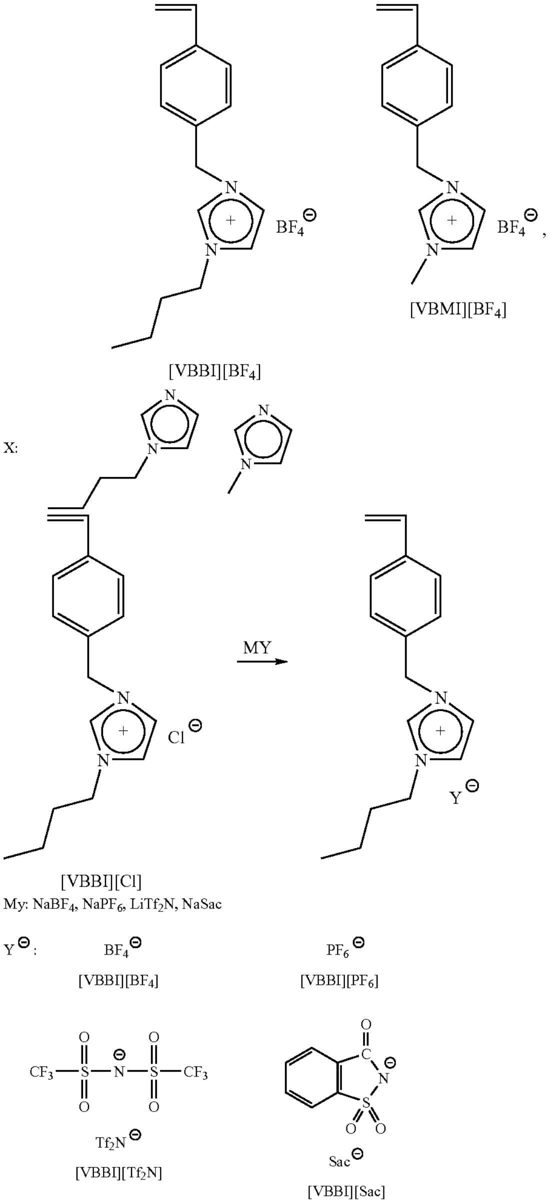


(1) 2-bromoethanol
(2) 1-butyl imidazole
(3) $NaBF_4$

Scheme 2



-continued



1-p-Vinylbenzyl)-3-methyl-imidazolium tetrafluoroborate ([VBMI][BF_4]) was synthesized as follows: To a 50 ml flask, p-vinylbenzyl chloride (10 ml, 0.064 mole), a small amount of DBMP, and 1-methylimdazole (5.14 ml, 0.064 mole) were added and heated at 45° C. overnight. The solution became gradually viscous. $NaBF_4$ (5.2 g, 0.47 mole) and dry acetone (30 ml) were added. The mixture was stirred at room temperature. The viscous liquid dissolved gradually while a white solid precipitated. After 12 h reaction, the precipitate was removed by filtration. The solvent was removed under vacuum. The solid was washed with water and ether, and dried by vacuuming at room temperature, producing 14 g of white crystals (yield 76.5%).

[VBBI][BF_4]: ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 9.24 (1H, s), 7.80 (2H, s), 7.51 (2H, d) 7.35 (2H, d), 6.73 (1H, m), 5.89 (1H, d) 5.27 (1H, d), 5.40 (2H, s), 4.14 (2H, t), 1.78 (2H, m), 1.24 (2H, m), 0.88 (3H, t). mp: 67-68° C.

[VBBI][PF$_6$] ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm): δ 9.22 (1H, s), 7.80 (2H, s), 7.48 (2H, d) 7.35 (2H, d), 6.73 (1H, m), 5.89 (1H, d), 5.30 (1H, d), 5.46 (2H, s), 4.14 (2H, t), 1.79 (2H, m), 1.22 (2H, m), 0.87 (3H, t). mp: 87-88.5° C.

[VBBI][Sac] ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm) δ 9.38 (1H, s), 7.80 (2H, s) 7.66 (1H, d), 7.61 (1H, d), 7.59 (2H, d), 7.49 (2H, d), 7.40 (2H, d), 6.72 (1H, m) 5.84 (1H, d), 5.42 (2H, s), 5.26 (2H, d) 4.16 (2H, m) 1.73 (2H, m), 1.21 (2H, m), 0.84 (3H, m). mp: −36-−38° C.

[VBBI][Tf$_2$N] ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm): δ 8.83 (1H, s), 7.44 (2H, s), 7.34 (2H, d) 7.27 (2H, d), 6.70 (1H, m), 5.79 (1H, d) 5.33 (1H, d), 5.31 (2H, s), 4.17 (2H, t), 1.84 (2H, m), 1.35 (2H, m), 0.94 (3H, t). mp: −61-−62° C.

[VBMI][BF$_4$]: ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm): 9.13 (1H, s), 7.71 (1H, s), 7.63 (1H, s), 7.52 (1H, d), 7.42 (2H, d), 6.75 (1H, m), 5.88 (1, d), 5.41 (2H, s), 5.26 (1H, d), 3.86 (3H, s). mp: 42-44° C.

Poly(ionic liquid)s were prepared from above ionic liquid monomers by free radical polymerization. A typical example is as the following: [VBBI][BF$_4$] (3 g), AIBN (30 mg) and DMF (3 ml) were charged into a reaction tube. The tube was tightly sealed, and degassed. It was immersed in an oil bath at 60° C. for 6 h. The solution was poured into methanol to precipitate out the polymer. The polymer was dried under vacuum at 100° C. The yield was 2.3 g (75%).

Poly[1-(p-Vinylbenzyl)-3-butyl-imidazolium tetrafluoroborate] (P[VBBI][BF$_4$]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.12 (s, 1H), 7.8 (br, 1H), 7.4 (br, 1H), 7.1 (br, 2H), 6.4 (br, 2H), 5.6-4.9 (br, 2H), 4.1 (br, 2H), 2.1-1.0 (m, 7H), 0.8 (s, 3H). Anal. Calcd for ($C_{16}H_{21}BF_4N_2$)n: C, 58.56%; H, 6.45%; N, 8.54%. Found: C, 58.35%; H, 6.43%; N, 8.50%.

Poly[1-(p-Vinylbenzyl)-3-butyl-imidazolium hexafluorophosphate] (P[VBBI][PF$_6$]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.16 (s, 1H), 7.72 (br, 1H), 7.47 (br, 1H), 7.04 (br, 2H), 6.42 (br, 2H), 5.23 (br, 2H), 4.15 (br, 2H), 2.1-0.8 (m, 10H) Anal. Calcd for $(C_{16}H_{21}F_6N_2P)_n$: C, 49.75%; H, 5.48%; N, 7.25%; Found: C, 49.70%; H, 5.37%; N, 7.12%.

Poly[1-(p-Vinylbenzyl)-3-butyl-imidazolium o-benzoic sulphimide] (P[VBBI] [Sac]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.44 (s, 1H), 7.5-7.9 (br, 6H), 7.19 (br, 2H), 6.35 (br, 2H), 5.35 (br, 2H), 4.15 (br, 2H), 1.9-0.5 (m, 10H) Anal. Calcd for $(C_{23}H_{25}N_3O_3S)_n$: C, 65.25; H, 5.91; N, 9.93. Found: C, 64.11; H, 6.05; N, 9.68.

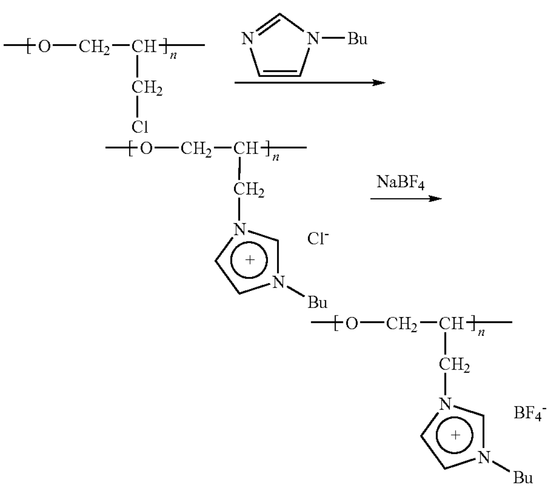
Poly[1-(p-Vinylbenzyl)-3-butyl-imidazolium trifluoromethane sulfonamide] (P[VBBI][Tf$_2$N]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.20 (s, 1H), 7.73 (br, 1H), 7.44 (br, 1H), 6.94 (br, 2 H), 6.33 (br, 2H), 5.19 (br, 2H), 4.13 (br; 2H), 2.0-1.0 (m, 7H), 0.81 (s, 3 H). Anal. Calcd for $(C_{18}H_{21}N_3F_6O_4S_2)_n$: C, 41.46; H, 4.03; N, 8.06. Found: C, 41.46; H, 4.13; N, 7.94.

Poly {1-[2-(Methylacryloyloxy)ethyl]-3-butyl-imidazolium tetrafluoroborate} (P[MABI][BF$_4$]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.1 (br, 1H), 7.9-7.6 (d, 2H), 4.8-3.8 (m 6H), 2.0-0.2 (m, 12H). Anal. Calcd for $(C_9H_{18}BF_4NO_2)_n$: C, 48.17 H, 6.49; N, 8.65. Found: C, 47.68; H, 6.48; N, 6.48.

Poly[1-(p-vinylbenzyl)-3-methyl-imidazolium tetrafluoroborate] (P[VBMI][BF$_4$]): ^{1}H NMR (DMSO-d$_6$, 400 MHz, ppm): δ 9.10 (1H, br), 7.60-7.30 (2H, br), 7.10 (2H, br), 6.40 (2H, br), 5.30 (2H, br), 3.70 (2H, br) 2.1-0.5 (3H, br). Anal. Calcd for $(C_{13}H_{15}BF_4N_2)_n$: C, 54.58; H, 5.25; N, 9.80. Found: C, 52.74; H, 5.33; N, 9.38.

The poly(ionic liquid) with poly(ethylene oxide) backbone was synthesized from poly(epichlorohydrin) (Scheme 3). Aluminum isopropoxide (0.18 g, 0.88 mmol) was added into a 100 mL flask. The flask was degassed by repeated vacuum/nitrogen purging (5 cycles). Degassed THF (25 mL) and epichlorohydrin (5.0 mL, 66 mmol) was added by degassed syringes. After the reaction flask was immersed into a 40° C. oil bath for 12 hours, the poly(epichlorohydrin) was precipitated out by adding a large amount of hexane. 3.3 g of poly (epichlorohydrin) was dissolved in 50 mL of DMF. N-butylimidazole (5.0 g, 40 mmol) was added to the DMF solution. This solution was stirred at 80° C. for 5 days, and then NaBF$_4$ (4.4 g, 40 mmol) was added. After the mixture was stirred at room temperature for 2 days, sodium chloride precipitate was removed by filtration. Anhydrous ethyl ether was added to the filtrate to precipitate the poly(ionic liquid). The obtained P[BIEO][BF$_4$] was washed with ethyl ether and dried in vacuum oven at 50° C. for one day. ^{1}H-NMR (acetone-d$_6$): δ 8.86 (1H, s), 7.69 (2H, br), 4.44-4.31 (4H, br), 3.97 (1H, br), 3.67 (2H, br), 1.88 (2H, br), 1.34 (2H, br), 0.93 (3H, br). Anal. Calcd for $(C_{10}H_{17}BF_4N_2O)_n$: C, 44.80; H, 6.34; N, 10.46. Found: C, 44.66; H, 6.26; N, 10.11.

Scheme 3



The syntheses of ionic liquid monomers are shown in Schemes 1-3. Two steps were generally involved in the preparations: the quaternization reaction of 1-butylimidazole or 1-methylimidazole with 4-vinylbenzyl chloride or 2-bromoethyl methacrylate, and the anion exchange reaction of the halide ions with tetrafluoroborate, hexafluorophosphate, Sac or Tf$_2$N anions.

The quaternization with 4-vinylbenzyl chloride was fast with a high yield. The anion exchange of the resulting chloride [VBBI][Cl] and [VBMI][Cl] with BF$_4^-$ produced the monomers, [VBBI][BF$_4$] and [VBMI][BF$_4$], as crystalline solids, which are soluble in acetone, acetonitrile, dichloromethane, DMF, and DMSO, but insoluble in diethyl ether. [VBBI][PF$_6$] is also a solid with similar solubility. [VBBI] [Sac] and [VBBI][Tf$_2$N] are liquid at room temperature and soluble in acetone, acetonitrile, DMF, and DMSO. [VBBI] [Tf$_2$N] is also soluble in ethyl ether.

The quaternization of N-butylimidazole with 2-bromoethyl methacrylate was slow and difficult to get high yield of [MABI][Br]. After the anion exchange, [MABI][BF$_4$] is also a liquid at room temperature and soluble in above polar solvents but insoluble in ethyl ether and other nonpolar solvents.

All above ionic liquid monomers, unlike their corresponding chloride salts, are insoluble in water. So unreacted chloride salts could be easily removed by washing with water. Silver nitrate test indicated that no chloride was present in all the ionic liquid monomers.

The poly(ionic liquid)s, except for P[BIEO][BF_4] which was synthesized by the polymer reaction shown in Scheme 3, were prepared by free radical polymerization of the ionic liquid monomers using AIBN as initiators. DMF was used as solvent because all poly(ionic liquid)s are soluble in it. All these ionic liquid monomers are easily polymerized with high conversions. Poly(ionic liquid)s were precipitated in methanol to remove unreacted monomers. DMF residue in polymers was removed by drying at 100° C. under vacuum. All poly(ionic liquid)s can dissolve in DMF, DMSO, acetonitrile, but are insoluble in water, dichloromethane and toluene. H^1 NMR and element analysis indicated the poly(ionic liquid)s were pure.

CO_2 Sorption and Desorption

The CO_2 sorption of the poly(ionic liquid)s was measured using a Cahn 1000 Electrobalance. The sample pan and the counterweight of the balance were configured symmetrically to minimize buoyancy effects. The microbalance has 100 g capacity and 1.0 μg sensitivity and is suitable for study of sorption and diffusion of gases on/in solid or liquid materials. CO_2 gas (99.995%) was dried by passing two drying columns (length×diameter: 15 in×2 in) packed with P_2O_5. The fine powder of the ionic liquid polymer was dried and degassed at 70° C. under vacuum for 12 h to remove moisture or other volatile contaminants. It was further dried in the balance by evacuating the chamber at high vacuum until its weight reached constant for at least 30 min. CO_2 was introduced into the chamber and the sample weight increase was recorded until the weight did not change significantly in 30 min. The buoyancy effects in these measurements were corrected according to the literature.[29] The system was validated by measuring the CO_2 sorption of an ionic liquid, 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF_4]). The measured CO_2 sorption capacity of [bmim][BF_4] was identical to the reported.[19]

CO_2 has remarkable solubility in imidazolium-based ionic liquids because of its interactions with the anions and cations of ionic liquids.[19] The CO_2 sorption of (P[VBBI][BF_4](a), P[VBBI][Tf_2N](b), P[MABI][BF_4](c), P[VBBI][Sac](d)), with their corresponding monomers ([VBBI][Tf_2N](e), [MABI][BF_4](g), [VBBI][BF_4](h), [VBBI][Sac](i)), and an ionic liquid [bmim][BF_4] (f) as a function of time (592.3 mmHg CO_2, 22° C.) is shown in FIG. **1**. The CO_2 solubility of [bmim][BF_4] was tested first and found consistent with that reported in the literature,[19] which validated the setup of the apparatus.

At the equilibrium, P[VBBI][BF_4], P[VBBI][Tf_2N], P[MABI][BF_4] and P[VBBI][Sac], respectively, took up 2.27 mol %, 2.23 mol %, 1.78 mol % and 1.55 mol % of CO_2 in terms of their monomer units. In comparison, room temperature ionic liquid [bmim][BF_4] absorbed 1.34 mol % of CO_2 under the same conditions. [VBBI][BF_4] monomer had no measurable sorption of CO_2 because of its crystalline structure. [MABI][BF_4], [VBBI] [Sac] and [VBBI][Tf_2N] monomers are liquid at room temperature. [MABI][BF_4] had the same CO_2 sorption capacity as [bmim][BF_4]. [VBBI][Tf_2N] had a CO_2 sorption capacity of 1.96 mol %, higher than that of [bmim][BF_4], which is consistent with the report that the ionic liquid with Tf_2N anions had higher capacity than ionic liquids with BF_4 anions.[14] [VBBI][Sac] did not take up any CO_2 when it was exposed to CO_2 (FIG. **1**). This comparison shows that polymerizing ionic liquids can increase the CO_2 sorption capacity.

Meanwhile, the CO_2 sorption of the ploy(ionic liquid)s was much faster than that of ionic liquids. It takes only several minutes for the poly(ionic liquid)s to reach their 90% capacity and less than 30 minutes to reach their equilibrium capacity. In contrast, room temperature ionic liquids [MABI][BF_4] and [bmim][BF_4] needed more than 400 min to reach their equilibrium capacity (FIG. **1**).

The CO_2 sorption of poly(ionic liquid)s with different backbones, cations, and anions was compared to understand the factors affecting the CO_2 sorption. The CO_2 sorption kinetics of poly(ionic liquid)s with different backbones are shown in FIG. **2**. At the equilibrium, the polymers sorbed 2.27 mol % (P[VBBI][BF_4]), 1.78 mol % (P[MABI][BF_4]) and 1.06 mol % (P[BIEO][BF_4]), respectively, in terms of their monomer units at 592.3 mmHg of CO_2 and 22° C. With the same butylimidazolium cation and BF_4^- anion, the polymer with polystyrene backbone had a higher CO_2 sorption capacity than those with polymethylmethacrylate and polyethylene glycol backbones. The polymer with polyethylene glycol backbone had the lowest capacity.

The effect of substituent of the imidazolium cation on the CO_2 sorption is shown in FIG. **3**. P[VBMI][BF_4], which has a methyl substituent on its imidazolium cation, had a higher capacity (3.05 mol. %) than P[VBBI][BF_4] (2.27 mol. %) with butyl group. This indicates that a large substituent on the imidazolium cation may block the CO_2 sorption.

The effect of the anions on the CO_2 sorption capacity of the poly(ionic liquid)s is shown in FIG. **4**. The CO_2 sorption capacity the P[VBBI]-based polymers depends on the type of the anions: it was 2.80 mol. % for P[VBBI][PF_4], 2.27 mol % for P[VBBI][BF_4], 2.23 mol. % for P[VBBI][Tf_2N] and 1.55 mol. % for P[VBBI][Sac], respectively, in terms of their monomer units at 592.3 mmHg of CO_2 and 22° C. This trend is different from that of ionic liquids. The CO_2 solubility in ionic liquids with Tf_2N^- anions is much higher than those with PF_6^- or BF_4^- anions. [19] By contrast, the poly(ionic liquid) with PF_6— anions ([PVBBI][PF_6]) had the highest sorption capacity, and those with BF_4^- and Tf_2N^- anions had a similar capacity. The poly(ionic liquid) with Sac^- anions could take up 1.55 mol % of CO_2 even though the anion contains no fluorine atoms. These results indicate that for poly(ionic liquid)s, fluorine-atoms are not a decisive factor for CO_2 sorption but fluorine-atoms in the anions indeed enhance the CO_2 sorption.

The CO_2 sorption of the polymers is very selective, as shown in FIG. **5**. There was no weight increase when the polymers were exposed to N_2 or O_2 under the same conditions, which means that poly(ionic liquid)s can selectively absorb CO_2.

The selective CO_2 sorption of the poly(ionic liquid)s was also confirmed by a gas-replacement experiment. The CO_2 sorption of P[VBBI][BF_4] (1 gram) and desorption by replacing CO_2 with N_2 are shown in FIG. **6**. After introducing CO_2 into the balance, the sample weight increased rapidly until it became constant after 12 min. The weight increase was 2.1 mg, and the actual weight increase was 3.10 mg after a buoyancy correction. When N_2 was introduced into the chambers while maintaining the total pressure in the chambers at ambient pressure (592.3 mmHg), the sample weight decreased gradually, and finally reached −0.56 mg, which was equal to the buoyancy of the sample under N_2. This experiment indicates that the poly(ionic liquid) does not take up N_2. Similar experiments conformed that there was no O_2 sorption.

The sorption isotherms of P[VBBI][BF_4] and P[MABI][BF_4] at different CO_2 partial pressures and 22° C. are shown in FIG. **7**. The different CO_2 partial pressures were obtained by adjusting the N_2/CO_2 ratio of the mixed gas charged to the balance chambers because P[VBBI][BF_4] and P[MABI][BF_4] had no N_2 sorption. As shown in FIG. **7**, the CO_2 mole fraction in the polymers increased with the increase of CO_2 partial pressure.

Henry's constant is defined as

$$H = \lim_{x \to 0} \frac{p}{x}$$

where H is Henry's constant, x is the mole fraction of gas sorbed in the polymer in term of monomeric unit, and P is the CO_2 partial pressure Since the x vs. P plots were not linear in the entire pressure range, Henry's constants were calculated by fitting the data and extrapolating the slope to the zero CO_2 partial pressure.[16] Henry's constant was 26.0 bar for P[VBBI][BF_4] and 37.7 bar for P[MABI][BF_4], which is lower than that of room temperature ionic liquid [bmim][PF_6] (38.7 bar at 10° C. and 53.4 bar at 25° C.).[16]

Stable sorption capacity after repeated sorption/desorption is important for materials used for CO_2 separation. Four cycles of CO_2 sorption and desorption of P[VBBI][BF_4] and P[MABI][BF_4] were tested by filling the chambers with CO_2 and then vacuuming (FIG. **8***a*). The sorption and desorption of P[VBBI][BF_4] and P[MABI][BF_4] were all very fast. It took only about 30 min to take up CO_2 and to have a complete desorption of CO_2. The desorption was complete, suggesting that the sorption/desorption was reversible. No change in sorption/desorption kinetics and sorption capacity was observed after the four cycles. By contrast, the desorption of CO_2 from room temperature ionic liquids [bmim][BF_4] was very slow (FIG. **8***b*)

The enhanced sorption capacity and fast sorption/desorption rates of the poly(ionic liquid)s were unexpected because all polymers are solid at room temperature. An immediate question is whether the sorption occurred on the surface (adsorption) or in the bulk (absorption) or both. The BET surface area of P[VBBI][BF_4] was measured by nitrogen sorption and its morphology was examined by SEM. The measured BET surface area of P[VBBI][BF_4] sample was 0.295 m^2/g, The calculated CO_2-adsorption assuming a monolayer of CO_2 on this surface was only 0.0128 wt %, much less than the measured CO_2 sorption capacities. The SEM (FIGS. **9**A, B) indicated that the particles had a nonporous structure, and the average diameter of the particles was about 100 μm.

The CO_2 sorption of P[VBBI][BF_4] samples with different particle sizes was tested (FIG. **10**). The particle size did not significantly affect the capacity of CO_2 sorption and the sample with a big size even had a slightly higher sorption capacity. However, the particle size affected the rate of CO_2 sorption. The CO_2 sorption of the sample with big particle sizes (>250 μm in diameter) was slow, and needed about 120 minutes to reach its full sorption capacity, while those with the particle diameters less than 125 μm in diameter only needed less than 30 mins.

Without being bound to any particular theory, it appears that the CO_2 sorption of the polymer particles involves more absorption (the bulk) but less adsorption (the surface). Their CO_2 sorption capacity mainly depends on the chemical structure of poly(ionic liquid)s, while the rate of CO_2 sorption depends on the particle size due to the CO_2 diffusion in the polymers.

EXAMPLE 2

Materials

4-vinylbenzyl chloride (90%), 1-methylimidazole (98%), lithium trifluoromethane sulfonimide 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+%), aqueous [2-(methacryloyloxy)ethyl]trimethyl ammonium chloride solution (75 wt. %), (p-vinylbenzyl)trimethylammonium chloride (98%), triethylamine (99.5%), tributylamine (99.5%) triphenylphosphine 99%, α,α'-azobis(isobutyrobitrile)(AIBN) (98%) were purchased from Aldrich. 1-methyl imidazole 99%, o-Benzoic sulphimide sodium salt hydrate (97%) were purchased from Lancaster Synthesis Inc. Pyridine was purchased from Fisher scientific. All chemicals were used as received.

Synthesis and Characterization

(p-vinylbenzyl)trimethyl ammonium tetrafluoroborate ([VBTMA][BF_4]) and 2-(methacryloyloxy)ethyltrimethylamnonium tetrafluoroborate ([MATMA][BF_4]) were synthesized as described previously[30] using (p-vinylbenzyl)triethyl phosphonium tetrafluoroborate ([VBTEP][BF_4]), (p-vinylbenzyl)triphenyl phosphonium tetrafluoroborate ([VBTPP][BF_4]).

The synthesis of p-vinylbenzyl)triphenyl phosphonium tetrafluoroborate ([VBTPP][BF_4]), 1-(p-vinylbenzyl)pyridinium tetrafluoroborate ([VBP] [BF_4]) and 1-(p-vinylbenzyl)-3-methyl-imidazolium tetrafluoroborate ([VBMI] [BF_4]) is similar to 1-(p-vinylbenzyl)-3-butyl-imidazolium tetrafluoroborate ([VBBI][BF_4]) [VBBI][BF_4] (VBIT), as reported previously,[28] using triphenylphosphine, pyridine and 1-methyl imidazole instead of 1-butylimidazole, respectively.

The synthesis of (p-vinylbenzyl)triethylammonium tetrafluoroborate [VBTEA][BF_4] and (p-vinyl benzyl)tributylammonium tetrafluoroborate [VBTBA][BF_4] was follows: In a 50 ml flask, 4-vinylbenzyl chloride (6.1 g, 0.04 mol) and triethylamine (4.2 g, 0.042 mol) mol were mixed and heated at 50° C. under N_2 atmosphere for 2 days. The formed solid was washed with diethyl ether. The resultant white solid (8.5 g, 0.033 mol) was mixed with $NaBF_4$ (3.8 g, 0.035) in 50 acetonitrile and stirred at room temperature for 2 days. The salt precipitate was removed by filtration. The filtrate was concentrated and poured into 200 ml diethyl ether to precipitate out product. White crystal precipitate was formed, collected by filtration, and dried under vacuum. The total yield was 9.2 g (75%). [VBTBA][BF_4] was synthesized according to a similar procedure with yield of 64%.

In the synthesis of bis[p-vinylbenzyl)dimethylammonium] ethane, [BVDEA][BF_4], which is an ionic liquid crosslinker, tetramethylethylenediamine (5.8 g, 0.05 mol), 4-vinylbenzyl chloride (16.0 g, 0.105 mol) and 0.1 g DBMP were mixed in 50 ml DMF. The resulting solution was heated at 50° C. for 2 days. The solution was poured into 400 ml diethyl ether to precipitate out the product. After filtration and drying under vacuum, 15.8 g white crystal product was obtained. The product was 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 product was collected by filtration and dried under vacuum. The overall yield was 16.7 g (63.7%).

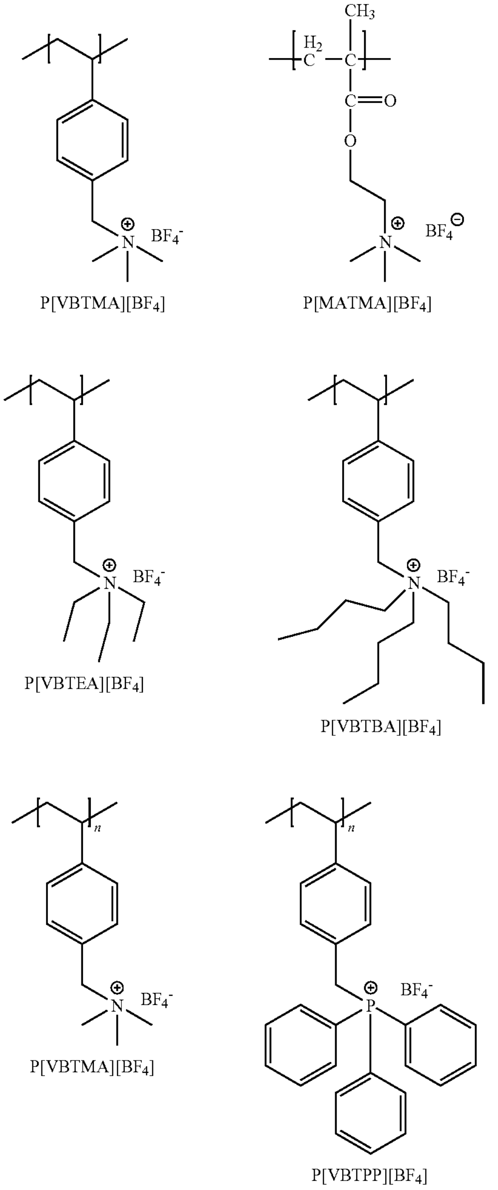
Poly(ionic liquid)s were synthesized by free radical polymerization using AIBN as initiator in DMF as described previously.[30] The crosslinked P[VBTMA][BF_4] was synthesized in the same way except for adding 5 wt % of the crosslinker.

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 structures of poly(ionic liquid)s are shown in Schemes 4 and 5. Two steps were generally involved in the preparation 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 solvents, such as DMF, acetone, or acetonitrile. All monomers based on ammonium except for P[VBTMA][Tf_2N] are soluble in H_2O. The ionic liquid monomers based on phosphonium, pyridium, imidazolium are insoluble in H_2O. The poly(ionic liquid)s are soluble in DMF.

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

Scheme 4



P[VBTMA][BF_4]

P[MATMA][BF_4]

P[VBTEA][BF_4]

P[VBTBA][BF_4]

P[VBTMA][BF_4]

P[VBTPP][BF_4]

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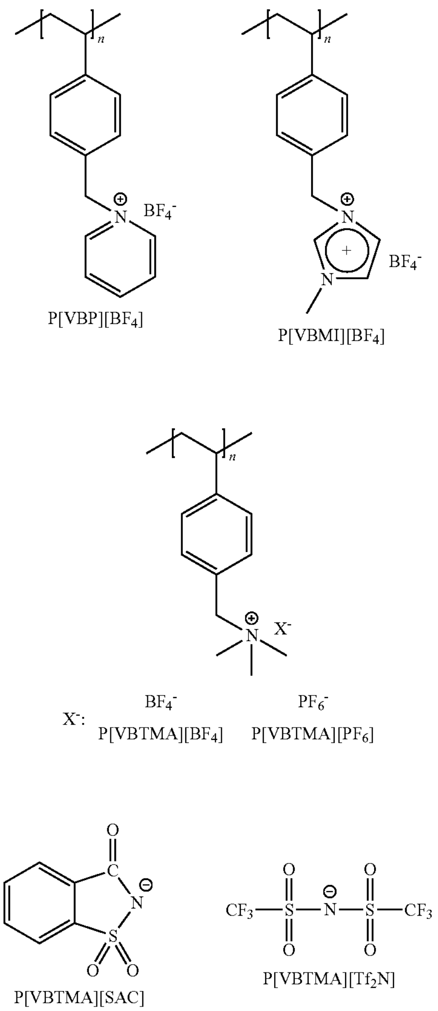


P[VBP][BF_4]

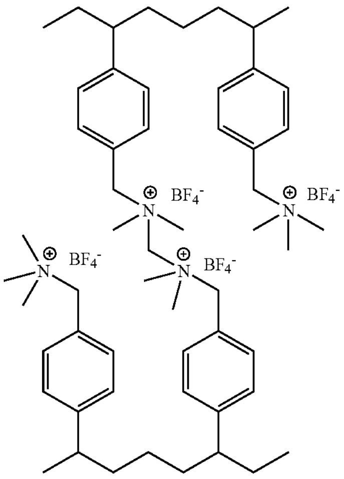
P[VBMI][BF_4]

X^-: BF_4^- P[VBTMA][BF_4] PF_6^- P[VBTMA][PF_6]

P[VBTMA][SAC]

P[VBTMA][Tf_2N]

Scheme 5 - Structure of crosslinked P[VBTMA][BF_4]



CO_2 Sorption and Desorption

FIG. **11** shows the effect of cation types on CO_2 sorption of poly(ionic liquid)s. The CO_2 sorption capacity of poly(ionic liquid)s with different cations is as follows: 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 increasing cation polarity. The polymer based on ammonium has the highest solubility because of its highest cation polarity. The polymer based on imidazolium, with the lowest cation polarity, has the lowest solubility.

FIG. **12** shows the effect 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][BF_6] and P[VBTMA][BF_4] have a similar CO_2 solubility of 10.7 mol. % and 10.2 mol. %, respectively. P[VBTMA][[Sac] and P[VBTMA][Tf_2N] have a solubility of 2.8 mol. % and 2.7%, respectively. The two poly(ionic liquid)s with inorganic anion have much higher solubility than the two with an organic anion, which can be explained in terms of the anion polarity effect on the interaction between the poly(ionic liquid)s with CO_2; the higher the anion polarity, the higher the affinity to CO_2. As a result the poly(ionic liquid) with high anion polarity exhibit a higher CO_2 solubility.

The CO_2 sorption kinetics of poly(ionic liquid)s with different backbones are shown in FIG. **13**. At the equilibrium, the polymers took up 10.22 mol % (P[VBTMA][BF_4]), 7.99 mol % (P[MATMA][BF_4]), respectively, in terms of their monomer units at 592.3 mmHg of CO_2 and 22° C. With the same ammonium cation and BF_4^- anion, the polymer with polystyrene backbone had a higher CO_2 sorption capacity than that with polymethylmethacrylate backbone.

The effect of substituent of the ammonium cation on the CO_2 sorption is shown in FIG. **14**. Their CO_2 sorption capacities are as follows: P[VBTMA][BF_4] (10.2 mol. %)>P [VBTEA][BF_4] (4.85 mol. %)>P[VBTBA][BF_4] (3.1 mol. %). Obviously, the CO_2 sorption capacity decreases with increasing length of the substituent, which indicates that a large substituent on the ammonium cation blocks CO_2 sorption.

FIG. **15** shows the effect of crosslinking on CO_2 sorption of poly(ionic liquid). Compared with P[VBTMA][BF_4] without crosslinking, the CO_2 sorption capacity of 5%-crosslinked P[VBTMA][BF_4] decreased by 17.3%.

EXAMPLE 3

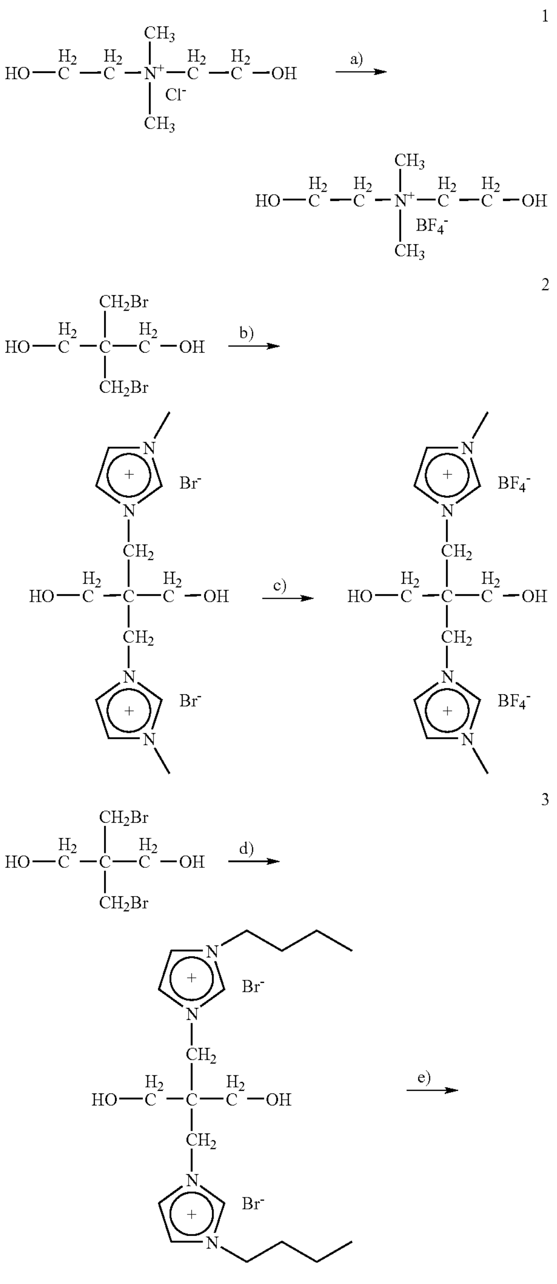
Materials

Bis(2-hydroxyethyl)dimethyl ammonium chloride (Acros, 99%), 2,2-Bis(bromomethyl)-1,3-propanediol (Aldrich, 98%), 1-Methylimidazole (Lancaster, 99%), 1-Butylimidazole (Aldrich, 98%), 1,1-Carbonyldiimidazole (Aldrich, reagent grade), terephthaloyl chloride (Aldrich, 99+%), sodium tetrafluoroborate (Aldrich, 98%, $NaBF_4$), dimethyl sulfoxide (Aldrich, 99.9+%, DMSO) and methanol (A.C.S. reagent) were used as received. Acetonitrile (Aldrich, 99.5+ %), N,N-Dimethylformiamide (Aldrich, 99.8%, DMF) and triethylamine (EMD, 99.5%, Et_3N) were used after removing water by molecular sieves.

Synthesis and Characterization

The synthesis of the monomers, Bis(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate ([BHEDMA][BF_4]) 1, 2,2-Bis(methylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BMIMP][BF_4]) 2 and 2,2-Bis(butylimidazolium methyl)-1,3-propanediol tetrafluoroborate ([BBIMP] [BF_4]) 3 is shown in Scheme 6. The reagents and conditions were: a) $NaBF_4$, acetonitrile, room temperature, 48h, 96%; b) 1-Methylimidazole, N_2, 60° C., 24h, 98%; c) $NaBF_4$, acetonitrile, room temperature, 48h, 96%; d) 1-Butylimidazole, N_2, 80° C., 24h, 97%; d) $NaBF_4$, acetonitrile, room temperature, 48h, 96%. Monomer 1 is an ammonium-based ionic liquid, while 2 and 3 are imidazolium-based ionic liquids.

Scheme 6



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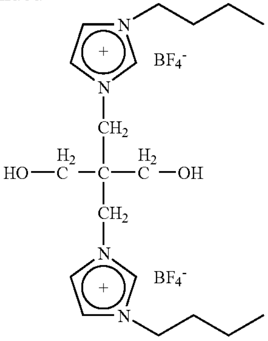
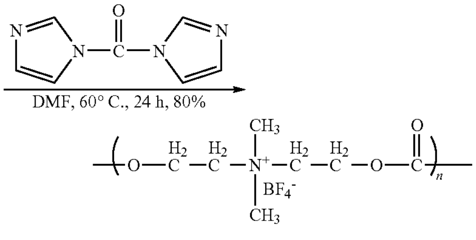


1: [BHEDMA][BF4]
2: [BMIMP][BF4]
3: [BBIMP][BF4]

The synthesis of polycarbonate (PC) and polyethylene terephthalate (PET) types of ionic liquid polymers by condensation polymerization is as follows. The PC type of ionic liquid polymers can be synthesized using the monomers 1 (2 or 3) reacted with 1,1-carbonyldiimidazole. The PET type of ionic liquid polymers can be synthesized using the monomers 1 (2 or 3) reacted with terephthaloyl chloride, respectively. Both kinds of condensation polymerizations required a strict 1:1 ratio of the reagents with different difunctional groups. All the reactions were carried out in DMF at 60° C. for 24 h. All the polymers were precipitated by methanol after polymerization and dried under vacuum at 50° C.

The ionic liquid monomer **1** is colorless, while 2 and 3 have a light yellow color. Synthesis of 2 and 3 in a N_2 atmosphere is necessary because the imidazole group is liable to be oxidized by the O_2 in the air, which will make the product have a brown color. For the 1 methylimidazole is more active than 1-butylimidazole, it will react with 2,2-Bis(bromomethyl)-1,3-propanediol at a lower temperature (60° C.) than that of the 1-Butylimidazole (80° C.). All the monomers (1, 2 and 3) are viscous liquids, and they all absorb moisture quickly when contacting air, so all of them need to be dried in a rotating evaporator before the polymerization.

The polycondensation synthesis of the PC type polymers, poly(bis(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate) carbonate (P[BHEDMA][BF$_4$]C) 4, poly(2,2-Bis (methylimidazolium methyl)-1,3-propanediol tetrafluoroborate) carbonate (P[BMIM][BF$_4$]C) 5, and poly(2,2-Bis (butylimidazolium methyl)-1,3-propanediol tetrafluoroborate) carbonate (P[BBIMP][BF$_4$]C) **6** is shown in Scheme 7. Polymer 4 is white, while 5 and 6 have a light yellow color. At room temperature, all polymers are easily crashed into fine powders. Polymer 4 is soluble in acetonitrile, and polymer 5 and 6 are soluble in chloroform. They all can be cast into membranes for CO_2 separation using a solvent evaporation method.



1

DMF, 60° C., 24 h, 80%

4

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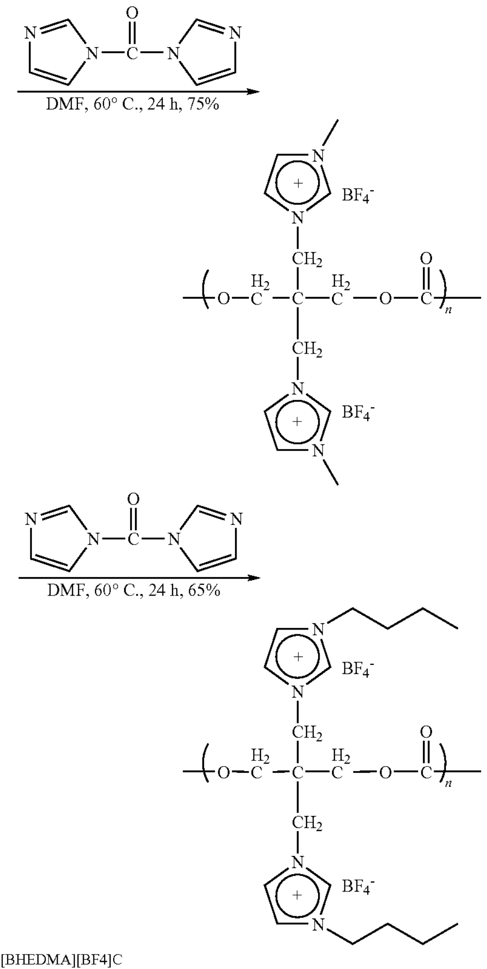


2

DMF, 60° C., 24 h, 75%

5

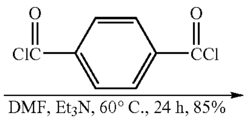
3

DMF, 60° C., 24 h, 65%

6

4: P[BHEDMA][BF4]C
5: P[BMIMP][BF4]C
6: P[BBIMP][BF4]C

The synthesis of the PET type polymers, poly(Bis(2-hydroxyethyl)dimethyl ammonium tetrafluoroborate) terephthalate (P[BHEDMA][BF$_4$]T) 7, poly(2,2-Bis(methylimidazolium methyl)-1,3-propanediol tetrafluoroborate) terephthalate (P[BMIMP][BF$_4$]T) 8 and poly(2,2-Bis(butylimidazolium methyl)-1,3-propanediol tetrafluoroborate) terephthalate (P[BBIMP][BF$_4$]T) 9, is shown in Scheme 8. Triethylamine was added to the reaction system slowly to remove the hydrogen chloride. The obtained three polymers (7, 8 and 9) are all white powders. But the solubilities of them are not as good as those for the corresponding PC types because their phenyl groups increase the rigidity of the polymer chains greatly. Because they are only soluble in solvents with strong polarity and high boiling points, such as DMSO and DMF, it is difficult to fabricate them into membranes using the solvent evaporation method.



1

DMF, Et3N, 60° C., 24 h, 85%

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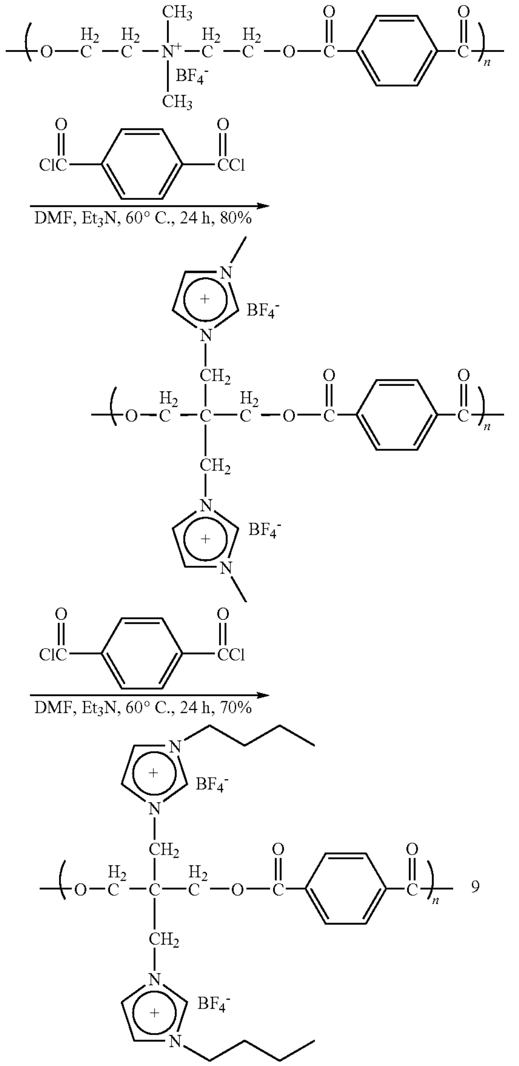

7: P[BHEDMA][BF4]T
8: P[BMIMP]]BF4]T
9: P[BBIMP][BF4]T

EXAMPLE 4

Poly(ionic liquid) Membranes for CO_2/CH_4 and CO_2/N_2 Separations[31]

Copolymers of ionic liquid and polyethylene glycol (PEG), for example P[VBTMA][BF$_4$]-co-PEG and P[MATMA][BF$_4$]-co-PEG were synthesized as follows: Ionic liquid monomer ([VBTMA][BF$_4$] or [MATMA][BF$_4$]) (2 gram), poly(ethylene glycol)methyl ether methacrylate (Mn=2000) (2 g), AIBN (40 mg) and DMF (8 ml) are charged into a reaction tube. The tube is tightly sealed, degassed, and immersed in an oil bath at 60° C. for 12 h to get complete polymerization. These copolymer solutions were used to cast membranes for CO_2/CH_4 and CO_2/N_2 separations at 35° C., 50° C. and 70° C., all at 40 psig. These membranes were tested for permeability and selectivity. FIG. **16** shows the CO_2CH_4 selectivity. FIG. **17** shows that our copolymers have better properties than the previously studied representative polymers for CO_2/CH_4 separation. FIG. **18** shows the selectivity of CO_2/N_2 for both P[VBTMA][BF$_4$]-co-PEG and P[MATMA][BF$_4$]-co-PEG at 35° C., 50° C. and 70° C. FIG. **19** illustrates that both P[VBTMA][BF$_4$]-co-PEG and P[MATMA][BF$_4$]-co-PEG membranes exhibit better ideal separation performance than the representative polymers because the data lie well above the upper limit bound curve, particularly for P[MATMA][BF$_4$]-co-PEG.

The foregoing description and drawings comprise illustrative embodiments of the present inventions. The foregoing embodiments and the methods described herein may vary based on the ability, experience, and preference of those skilled in the art. Merely listing the steps of the method in a certain order does not constitute any limitation on the order of the steps of the method. The foregoing description and drawings merely explain and illustrate the invention, and the invention is not limited thereto, except insofar as the claims are so limited. Those skilled in the art who have the disclosure before them will be able to make modifications and variations therein without departing from the scope of the invention.

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We claim:

1. A process for the separation of a gas, comprising the steps of:

(a) contacting a mixture containing the gas with a solid sorbent comprising at least one poly(ionic liquid) compound under such conditions as to obtain a product having a lower concentration of the gas than the mixture and a solid sorbent containing absorbed gas which has been removed from the mixture; and

(b) treating the solid sorbent under conditions as to substantially desorb the gas contained in the solid sorbent so as to obtain a regenerated solid sorbent wherein the treatment step is one or more steps selected from the group consisting of heating, depressurizing, and displacing the gas.

2. A process as defined in claim **1**, wherein the gas is carbon dioxide.

3. A process for the separation of carbon dioxide, comprising the step of contacting a gas mixture containing carbon dioxide with a membrane comprising at least one poly(ionic liquid) compound under such conditions as to obtain a CO_2-rich gas product that permeates through the membrane and a CO_2-lean gas product that does not permeate through the membrane.

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