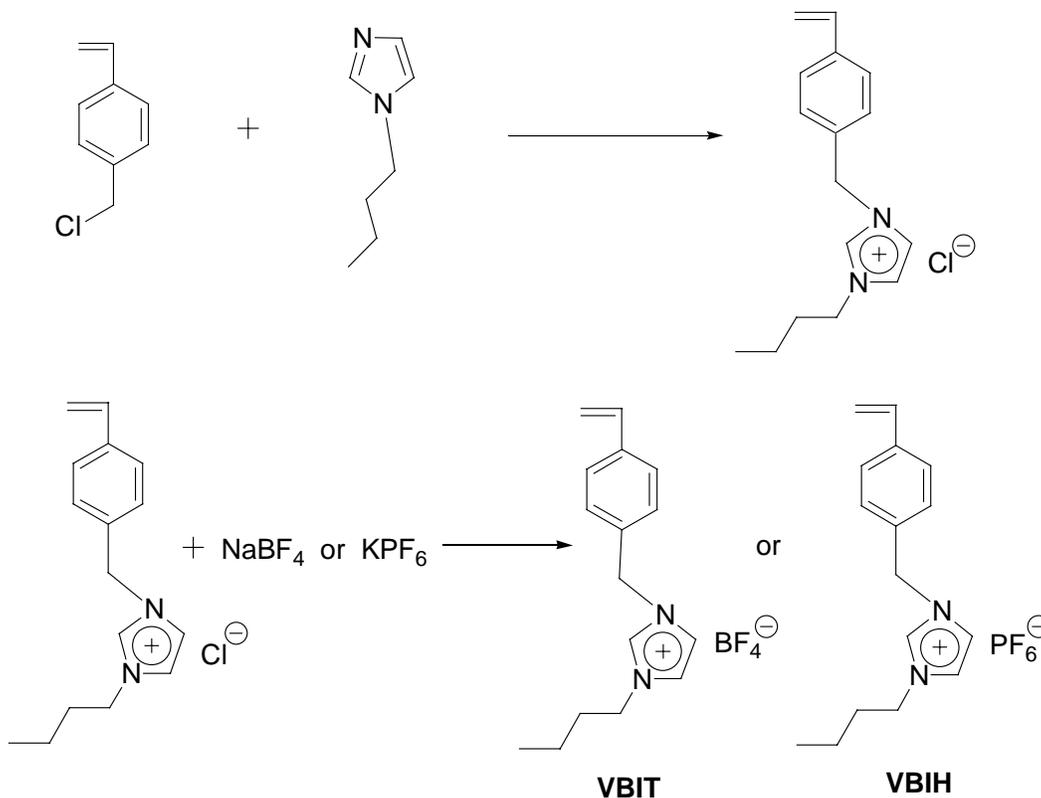


Supporting information

Synthesis and characterization of the polymers:

The BIMT monomers were synthesized according to our previous report.[1]. The VBIT and VBIH monomer are synthesized as follows (Scheme 1):



Scheme 1. Synthesis of VBIT and VBIH.

Synthesis of 1-(4-Vinylbenzyl)-3-Butyl Imidazolium Tetrafluoroborate (VBIT):.

To a dried 250 mL flask were added *N*-butylimidazole (12.4 g, 0.10 mol), 4-vinylbenzyl chloride (16.7 g, 0.11 mol) and inhibitor DBMP (0.10 g). The reaction mixture was stirred at 45 °C under nitrogen for 24 hours. The obtained viscous liquid was washed with an excess of ethyl ether, and dried under vacuum at room temperature to give the purified product as a transparent viscous liquid in a yield of 83%. ^1H NMR

(D₂O): δ 8.80 (1H, s, N-CH-N), 7.56 (2H, d, N-CH=CH-N), 7.40 (2H, d, Ph), 7.27 (2H, d, Ph), 6.70 (1H, m, CH₂=CH), 5.81 (1H, d, CH₂=CH), 5.28 (3H, m, Ph-CH₂-N and CH₂=CH), 4.12 (2H, t, N-CH₂-CH₂-CH₂-CH₃), 1.78 (2H, m, N-CH₂-CH₂-CH₂-CH₃), 1.24 (2H, m, N-CH₂-CH₂-CH₂-CH₃), 0.84 (3H, t, N-CH₂-CH₂-CH₂-CH₃).

1-(4-Vinylbenzyl)-3-butyl imidazolium chloride (13.8 g, 0.050 mol) and inhibitor DBMP (0.10 g) were dissolved in 100 mL of dry acetone. Sodium tetrafluoroborate (6.0 g, 0.055 mol) was slowly added to the acetone solution and the reaction mixture was stirred at room temperature for three days. The turbid solution was filtered and the filtrate was evaporated under reduced pressure to yield 15.6 g white waxy solid. This solid was washed with an excess of water and ethyl ether, and then stored in refrigerator. Silver nitrate testing indicated no chloride present. Mp: 67 ~ 68 °C. ¹H NMR (DMSO-d₆): δ 9.24 (1H, s, N-CH-N), 7.80 (2H, s, N-CH=CH-N), 7.51 (2H, d, Ph) 7.35 (2H, d, Ph), 6.73 (1H, m, CH₂=CH), 5.89, 5.27 (1H, 1H, d, d, CH₂=CH), 5.40 (2H, s, Ph-CH₂-N), 4.14 (2H, t, N-CH₂-CH₂-CH₂-CH₃), 1.78 (2H, m, N-CH₂-CH₂-CH₂-CH₃), 1.24 (2H, m, N-CH₂-CH₂-CH₂-CH₃), 0.88 (3H, t, N-CH₂-CH₂-CH₂-CH₃). ¹³C NMR (DMSO-d₆): δ 137.9 (N-CH-N), 136.4 (CH₂=CH), 136.3 (Ph), 134.6 (Ph), 129.0 (Ph), 127.0 (Ph), 123.1 (N-CH=CH-N-Bu), 122.9 (N-CH=CH-N-Bu), 115.6 (CH₂=CH), 52.1 (Ph-CH₂-N), 49.0 (N-CH₂-CH₂-CH₂-CH₃), 31.6 (N-CH₂-CH₂-CH₂-CH₃), 19.1 (N-CH₂-CH₂-CH₂-CH₃), 13.6 (N-CH₂-CH₂-CH₂-CH₃). Anal. Calcd for C₁₆H₂₁BF₄N₂: C, 58.56; H, 6.45; N, 8.54; F 23.16. Found: C, 58.35; H, 6.43; N, 8.50; F 23.46.

Synthesis of 1-(4-Vinylbenzyl)-3-Butyl Imidazolium Hexafluorophosphate (VBIH):

VBIH was synthesized in a similar manner from 1-(4-vinylbenzyl)-3-butyl

imidazolium chloride and potassium hexafluorophosphate (Scheme 1). To a dried flask were charged 1-(4-vinylbenzyl)-3-butyl imidazolium chloride (13.8 g, 0.050 mol), inhibitor DBMP (0.10 g), potassium hexafluorophosphate (10.1 g, 0.055 mol) and dry acetone (150 mL). After the mixture was stirred at room temperature for three days, the potassium chloride was removed by filtration and the filtrate was evaporated under reduced pressure to give 16.9 g white VBIH. It was washed with water and ethyl ether, and stored in refrigerator. Silver nitrate testing indicated no chloride present. Mp: 87 ~ 88.5 °C. ^1H NMR (DMSO- d_6): δ 9.22 (1H, s, N- $\underline{\text{C}}\text{H}$ -N), 7.80 (2H, s, N- $\underline{\text{C}}\text{H}=\underline{\text{C}}\text{H}$ -N), 7.48 (2H, d, Ph) 7.35 (2H, d, Ph), 6.73 (1H, m, $\text{CH}_2=\underline{\text{C}}\text{H}$), 5.89, 5.30 (1H, 1H, d, d, $\underline{\text{C}}\text{H}_2=\text{CH}$), 5.46 (2H, s, Ph- $\underline{\text{C}}\text{H}_2$ -N), 4.14 (2H, t, N- $\underline{\text{C}}\text{H}_2$ - CH_2 - CH_2 - CH_3), 1.79 (2H, m, N- CH_2 - $\underline{\text{C}}\text{H}_2$ - CH_2 - CH_3), 1.22 (2H, m, N- CH_2 - CH_2 - $\underline{\text{C}}\text{H}_2$ - CH_3), 0.87 (3H, t, N- CH_2 - CH_2 - CH_2 - $\underline{\text{C}}\text{H}_3$). ^{13}C NMR (DMSO- d_6): δ 138.0 (N- $\underline{\text{C}}\text{H}$ -N), 136.4 ($\text{CH}_2=\underline{\text{C}}\text{H}$), 136.3 (Ph), 134.6 (Ph), 129.1 (Ph), 127.1 (Ph), 123.1 (N- $\underline{\text{C}}\text{H}=\text{CH}$ -N-Bu), 122.9 (N- $\text{CH}=\underline{\text{C}}\text{H}$ -N-Bu), 115.6 ($\underline{\text{C}}\text{H}_2=\text{CH}$), 52.1 (Ph- $\underline{\text{C}}\text{H}_2$ -N), 49.1 (N- $\underline{\text{C}}\text{H}_2$ - CH_2 - CH_2 - CH_3), 31.6 (N- CH_2 - $\underline{\text{C}}\text{H}_2$ - CH_2 - CH_3), 19.1 (N- CH_2 - CH_2 - $\underline{\text{C}}\text{H}_2$ - CH_3), 13.6 (N- CH_2 - CH_2 - CH_2 - $\underline{\text{C}}\text{H}_3$). Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{F}_6\text{N}_2\text{P}$: C, 49.75; H, 5.48; N, 7.25; F, 29.51. Found: C, 49.70; H, 5.37; N, 7.12; F 30.65.

The polymers were synthesized via free radical polymerization. A typical synthesis is as follows:

VBIT, VBIH or BIMT (2 g), AIBN (20 mg) and DMF (4 ml) were charged into a tube. It 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 product. The products were dried under vacuum at 60 °C. The yield was about 75%.

PVBIT and PVBIH: ^1H NMR (DMSO- d_6 , ppm): δ 9.12 (s, 1H), 7.8 (br, 1H), 7.4 (br, 1H), 7.1 (br, 2 H), 6.4 (br, 2H), 5.6-4.9 (br, 2H), 4.1 (br, 2H), 2.1-1.0 (m, 7H), 0.8 (s, 3 H). ^{13}C NMR (DMSO- d_6 , ppm): δ 136.1, 132.2, 132.1, 129.0, 128.5, 122.9, 122.3, 52.1, 49.1, 31.6, 19.1, 13.5.

PBIMT: ^1H NMR (DMSO- d_6 , 400 MHz, ppm): 9.1 (br, 1H), 7.9-7.6 (d, 2H), 4.8-3.8 (m 6H), 2.0-0.2 (m, 12H). ^{13}C NMR (DMSO- d_6 , ppm): δ 176.7, 136.8, 123.2, 122.9, 63.1, 48.8, 47.8, 44.5, 31.6, 19.1, 17.1, 14.3, 13.6.

Instruments.

The polymers were characterized by ^1H and ^{13}C NMR on a Bruker Advance DRX-400 spectrometer using dimethylsulfoxide (DMSO- d_6) as solvent. The X-ray diffraction (XRD) analysis was recorded on a SCINTAG XDS2000 automated powder diffraction system operating in normal transmission mode with Ni-filtered Cu $K\alpha$ radiation. Differential scanning calorimetric (DSC) experiments were performed on a TA Instruments DSC 2920 differential scanning calorimeter. The polymer sample was first heated to 200 °C under nitrogen protection and immediately quenched with liquid nitrogen. The sample was then scanned at a heating rate of 10 °C min^{-1} , and the data was recorded from -50 °C to 200 °C. Thermal gravity analysis (TGA) was conducted on a TA Instruments TGA Q500 thermal gravity analytical center at a heating rate of 10 °C min^{-1} from 30°C to 500 °C.

SEMs were conducted on Scanning Electron Microscope (Philips 505). BET surface area was measured with a Tristar 3000 (Micromeritics Inc. Co.). The molecular weights of the polymers were determined by gel permeation chromatography (GPC) comprised of a Waters SEC equipped with two 300 mm Waters Styrgel solvent-saving

columns (molecular weight ranges: 5×10^2 - 3×10^4 , 5×10^3 - 6×10^5) and a Waters 2414 refractive index detector. The eluent was DMF containing 0.05 M lithium bromide at a flow rate of 0.3 mL min^{-1} , and the column temperature was $50 \text{ }^\circ\text{C}$. A series of poly(ethylene glycol) standards with molecular weights ranging from 970 to 270000 were employed to generate the calibration curve.

Some characterizations of the monomers and polymers

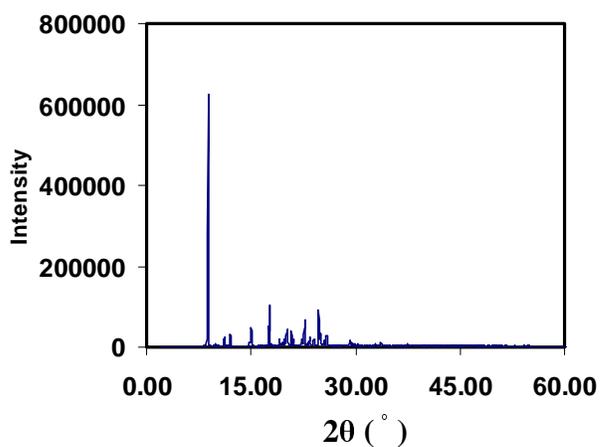


Figure 1. XRD pattern of VBIT

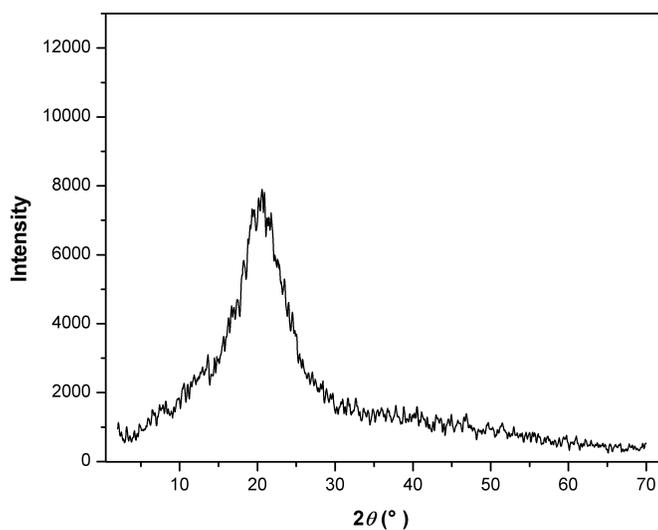


Figure 2. XRD pattern of PVBIT.

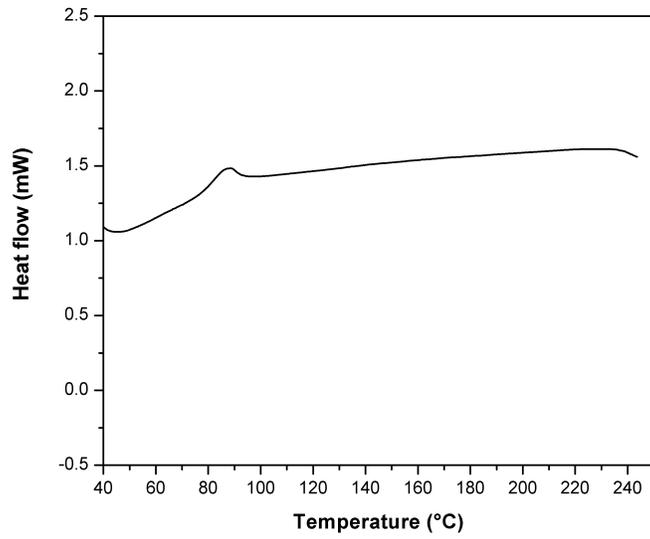


Figure 3. DSC curve of PVBIT

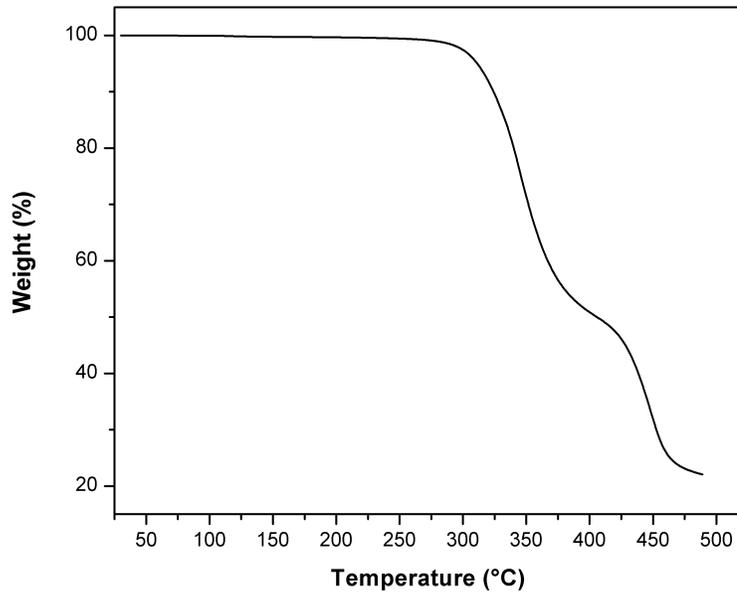
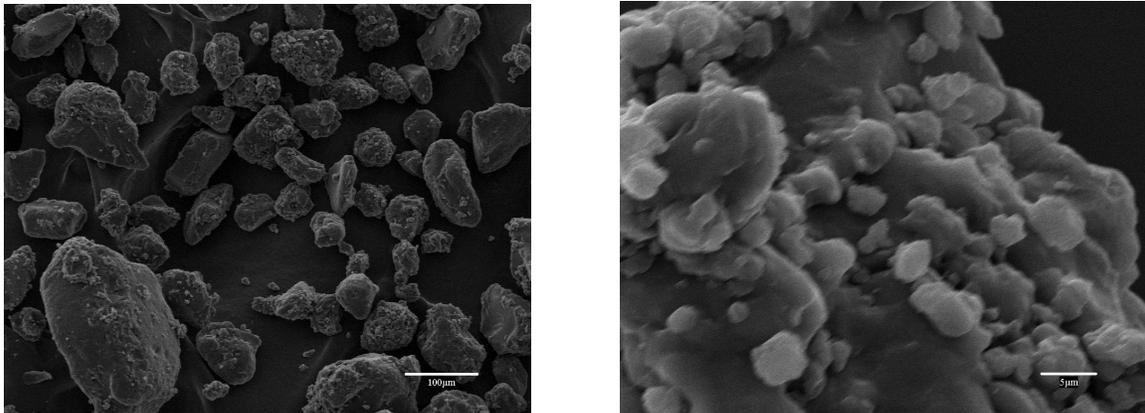


Figure 4. TGA profile of polymer PVBIT.



(a)

(b)

Figure 5 SEM of particles of PVBIT.

CO₂ Absorption and Desorption Measurements.

The CO₂ absorption of the poly(ionic liquid) 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 adsorption and diffusion of gases on/in solid or liquid materials. The experimental apparatus is shown in Scheme 1. CO₂ gas (99.995%) was dried by passing two drying column (length × diameter: 15 in × 2 in) packed with P₂O₅ and then introduced into the balance chamber. 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. CO₂ was introduced into the chamber and the absorption was recorded until the weight did not change significantly in 30 min. The buoyancy effects in these measurements were corrected according to literature.[2] The system was validated by measuring the CO₂ absorption of

an ionic liquid, 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF₄]). The measured CO₂ absorption capacity of [bmim][BF₄] was identical to that reported.[3]

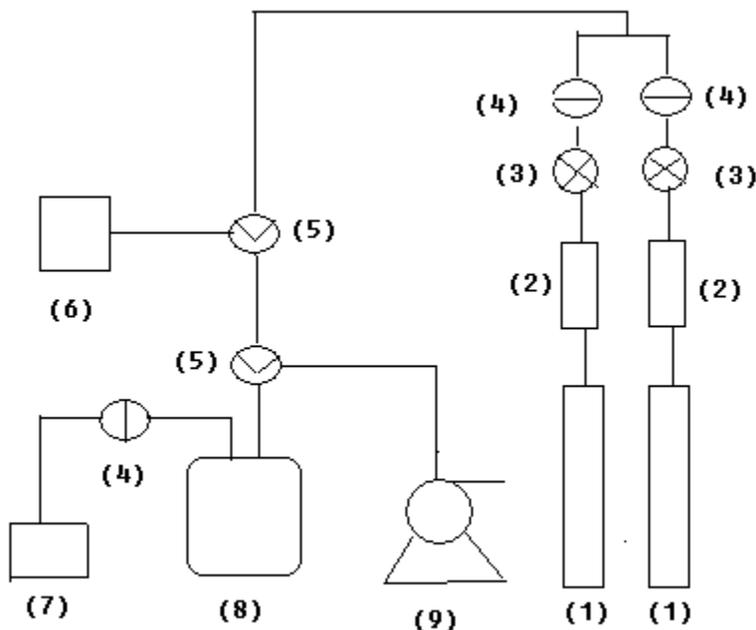


Figure 1. Schematic diagram of experimental apparatus

- (1) gas cylinder (2) dryer (3) flowmeter (4) two way valve (5) three way valve (6) gas storage (7) gas outlet (sealed with mercury) (8) equilibrium cell (electrobalance) (9) vacuum pump

References:

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- [2] Macedonia, M. D.; Moore, D. D. and Maginn, E. J. *Langmuir* **2000**, *16*, 3823-3834
- [3] Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F. and Maginn, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 5300- 5308.