Supplementary Material for Chemical Communications

SUPPORTING INFORMATION

1. SYNTHESIS OF THE MONOMERS

2-(Methylacryloyloxy)ethyl-trimethylammonium tetrafluoroborate ([MATMA][BF_4]) and *p*-vinylbenzyltrimethylammonium tetrafluoroborate ([VBTMA][BF_4])

Aqueous 2-(methylacryloyloxy)ethyl-trimethyl ammonium 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 mole) 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 in ether. The white crystal was collected and dried in vacuum at room temperature (28 g, 90%). Similarly, [VBTMA][BF_4] was synthesized from p-vinylbenzyltrimethylammonium chloride in a yield of 93%.

[MATMA][BF_4]: ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) : δ 6.09 (1H, s), 5.75(1H, m), 4.53 (2H, m), 3.70 (2H, m), 3.14 (9H, s), 1.91 (3H, s).

[VBTMA][BF_4]: ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) : δ 7.59 (2H, d, J=8.2), 7.49(2H, d, J=8.2), 6.78 (1H, m), 5.94 (1H, d, J=17.7), 5.36 (H, d, J=11.2) , 4.47 (2H, s), 3.00 (9H, s)

1-(*p*-Vinylbenzyl)-3-butyl imidazolium chloride ([VBBI][Cl])

To a dry 250 mL flask were added *N*-butylimidazole (12.4 g, 0.10 mol), 4-vinylbenzyl chloride (16.7 g, 0.11 mol) and inhibitor 2.6-di-tert-butyl-4-methylphenol (DBMP) (0.10 g). The 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. A transparent viscous liquid was obtained in a yield of 83%. ^{1}H NMR (D_2O,400 MHz, ppm): *δ* 8.80 (1H, s), 7.56 (2H, d, J=8.2), 7.40 (2H, d, J=8.2), 7.27 (2H, d, J=17.6), 6.70 (1H, m), 5.81 (1H, d, J=11.3), 5.28 (3H, m), 4.12 (2H, t), 1.78 (2H, m), 1.24 (2H, m), 0.84 (3H, t).

1-(*p*-Vinylbenzyl)-3-butyl imidazolium tetrafluoroborate ([VBBI][BF_4])

[VBBI][Cl] (13.8 g, 0.050 mol) and inhibitor 2.6-di-tert-butyl-4-methylphenol (DBMP) (0.10 g) were dissolved in 100 mL of dry acetone. Sodium tetrafluoroborate (6.0 g, 0.055 mol) (Aldrich) was 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 a white waxy solid. This solid was washed with an excess of water to remove trace of [VBBI][Cl]. Silver nitrate testing indicated no chloride present. The yield was 15.6 g (95%). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): *δ* 9.24 (1H, s), 7.80 (2H, s), 7.51 (2H, d, J=8.2) 7.35 (2H, d, J=8.2), 6.73 (1H, m), 5.89(1H,d, J=17.6) 5.27 (1H, d, J=11.1), 5.40 (2H, s), 4.14 (2H, t), 1.78 (2H, m), 1.24 (2H, m), 0.88 (3H, t). 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%. mp: 67–68 °C.

1-(*p*-Vinylbenzyl)-3-butyl imidazolium bis(trifluoromethyl-sulfonyl)imide ([VBBI][Tf_2N])

[VBBI][Cl] (6.9 g, 0.025 mol) and inhibitor 2.6-di-tert-butyl-4-methylphenol (DBMP) (0.10 g) were dissolved in 100 mL of dry acetone. Lithium trifluoromethane sulfonamide (7.9 g, 0.028 mol) (Aldrich) was added to the acetone solution and the reaction mixture was stirred at room temperature for 2 days. The turbid solution was filtered and the filtrate was evaporated under reduced pressure to yield a yellowish oil. The oil was washed with an excess of water, then dissolved in 25 ml acetone, and precipitated in hexane. The viscous oil layer was collected and dried under vacuum. Silver nitrate testing indicated no chloride present. The yield was 5.2 g (39.9%) ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.83 (1H, s), 7.44 (2H, d, J=8.1), 7.34 (2H, d, J=8.5) 7.27 (2H, s), 6.70 (1H, m), 5.79(1H,d, J=17.61) 5.33 (1H, d, J=9.3), 5.31 (2H, s), 4.17 (2H, t), 1.84 (2H, m), 1.35 (2H, m), 0.94 (3H, t). mp: -61.5 °C

2-Bromoethyl Methacrylate To a solution of 2-bromoethanol (14.0 g, 0.11 mol) in 50 mL of methylene chloride, a solution of (10.4 g, 0.10 mol) methacryloyl chloride (Aldrich) in 10 mL of methylene chloride was added gradually in 10 min at 0 °C. After the addition, the reaction mixture was continuously stirred for 30 min. Triethylamine (11.0g, 0.11 mol) in 10 mL of methylene chloride was added dropwise in 15 min at 0 °C. The solution became slurry after several minutes. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed thoroughly by 3 ×100 mL of deionized H_2O and dried by anhydrous magnesium sulfate. The solvent was removed under vacuum at less than 30 °C. The product 2-bromoethyl methacrylate was obtained in a yield of 80%. ^{1}H NMR($CDCl_3$, 400 MHz, ppm): δ 6.17 (s, 1H), 5.62 (s, 1H), 4.45 (t, 2H), 3.56 (t, 2H), 1.96 (s, 3H).

1-[2-(Methylacryloyloxy)ethyl]-3-butyl imidazolium tetrafluoroborate ([MABI][BF_4])

1-Butylimidazole (4.96 g, 0.040mol), 2-bromoethyl methacrylate (7.72 g, 0.040mol), a small amount of 2,6-di-tert-butyl-4-methylphenol (DBMP) were added in a 250 mL flask. The reaction mixture was stirred at 40 °C for 48 hours, yielding a very viscous liquid, 1-[2-(methylacryloyloxy)ethyl]-3-butyl imidazolium bromide. The salt (12.68g, 0.040mol) was dissolved in 24 mL of anhydrous acetonitrile and added to a suspension of $NaBF_4$ (5.27 g, 0.048 mol) in 50 mL of anhydrous acetonitrile. After the mixture was stirred for 48 hours at room temperature, the sodium bromide precipitate was removed by filtration and the filtrate was concentrated by removal of the solvent. The concentrated filtrate was diluted with methylene chloride (200 mL) and filtered through a silica gel column. Removal of methylene chloride yielded the ionic liquid monomer as a viscous oil. ^{1}H NMR (DMSO-d6, 400 MHz, ppm): δ 9.23 (s, 1H), 7.80 (m, 2H), 6.02 (s, 1H), 5.71 (m, 1H), 4.51 (t, 2H), 4.46 (t, 2H), 4.18 (t, 2H), 1.83 (s, 3H), 1.76 (m, 2H), 1.21 (m, 2H), 0.88 (t, 3H). mp: -46 °C

2. SYNTHESIS AND CHARACTERIZATION OF THE POLYMERS:

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].

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, 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).

P[VBBI][Tf_2N]: ^{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 $C_{18}H_{21}N_3F_6O_4S_2$: C, 41.46; H, 4.03; N, 8.06. Found: C, 41.46; H, 4.13; N, 7.94.

P[MABI][BF_4]: ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 9.1 (br, 1H), 7.9-7.6 (br, 2H), 4.8-3.8 (m 6H), 2.0-0.2 (m, 12H). Anal. Calcd for $C_9H_{18}NO_2BF_4$: C, 48.17 H, 6.49; N,8.65. Found: C, 47.68; H, 6.48; N, 6.48.

P[MATMA][BF_4]: ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): 9.1 (br, 1H), 7.9-7.6 (br, 2H), 4.8-3.8 (m 6H), 2.0-0.2 (m, 12H). Anal. Calcd for $C_9H_{18}NO_2BF_4$: C, 41.7 H, 7.0; N, 5.4. Found: C, 40.45; H, 6.80; N, 5.12.

P[VBTMA][BF_4]: ^{1}H NMR (DMSO-d_6, 400 MHz, ppm) 7.08 (br, 2H), 6.50 (br, 2H), 4.30 (br, 2H) 2.87 (br, 9H), 1.81 (br, 1H), 1.48(br, 2H) Anal. Calcd for $C_{12}H_{18}NBF_4$: C, 54.8; H, 6.8; N, 5.3. Found: C, 55.21; H, 6.1; N, 5.4.

3. INSTRUMENTS

^{1}H and ^{13}C-NMR spectra were measured 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 Kα radiation. Differential scanning calorimetric (DSC) experiments were performed on a TA Instruments DSC 2920 differential scanning calorimeter. The samples were scanned at a heating rate of 10 °C min^{-1}. 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). The BET surface areas of the powders were determined by nitrogen adsorption (Tristar 3000, Micromeritics Instruments Corp.)

4. SOME CHARACTERIZATIONS OF THE MONOMERS AND POLYMERS

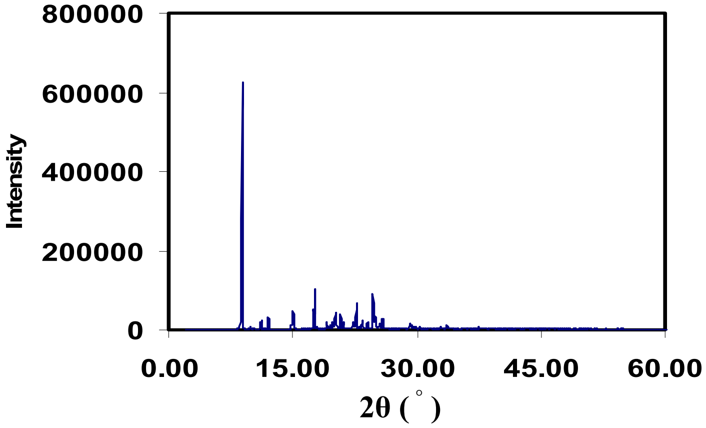


Figure 1. XRD pattern of **[VBBI][BF$_4$]**

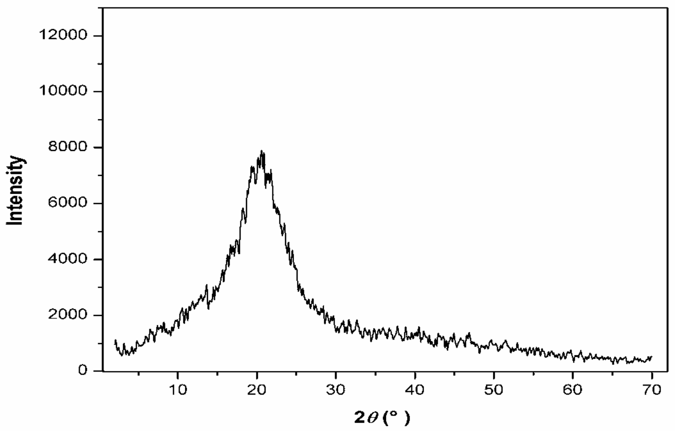


Figure 2. XRD pattern of P[VBBI][BF$_4$]

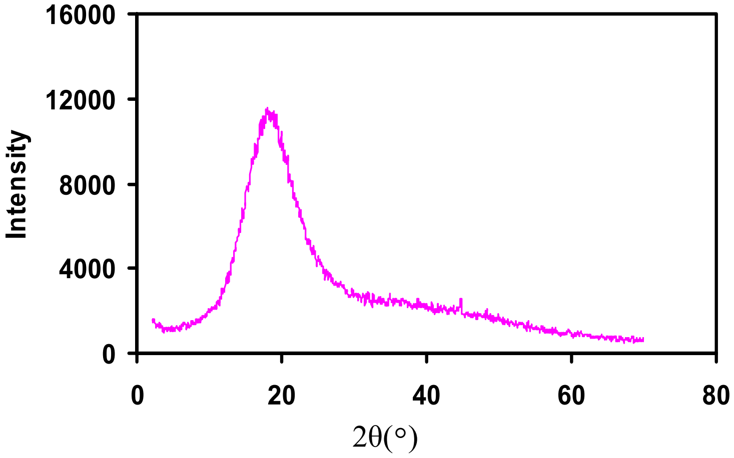


Figure 3. XRD pattern of P[VBTMA][BF_4]

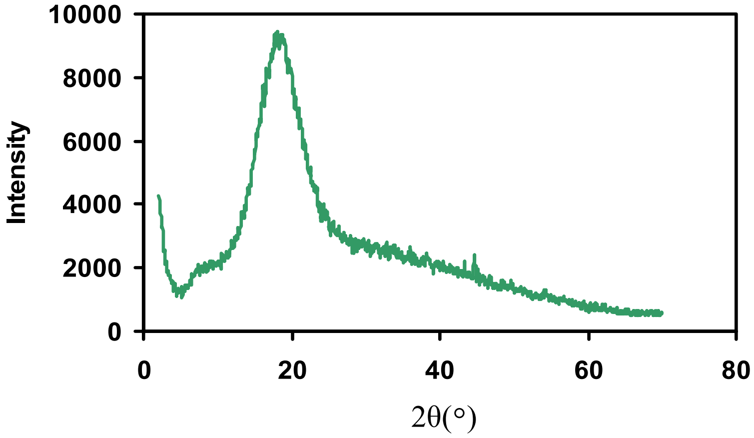
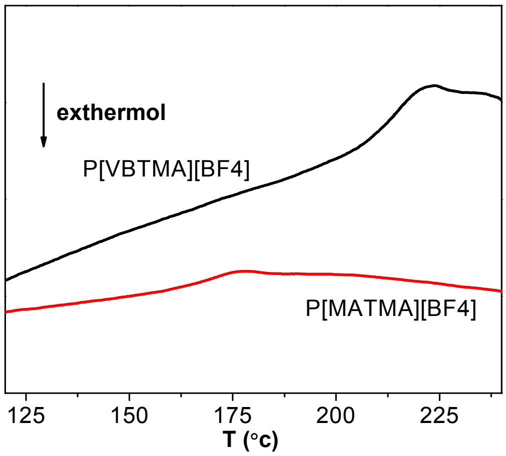


Figure 4. XRD pattern of P[MATMA][BF_4]



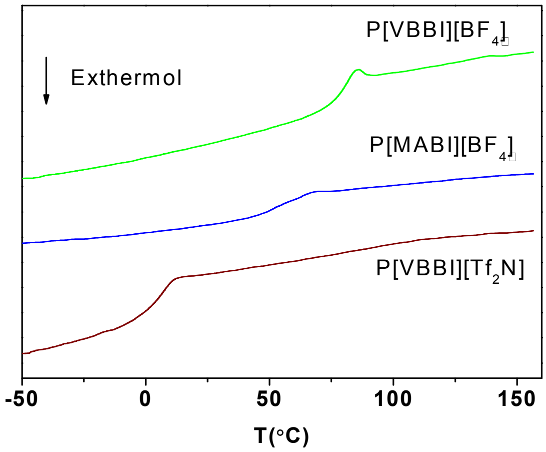


Figure 5. DSC curves of the polymers

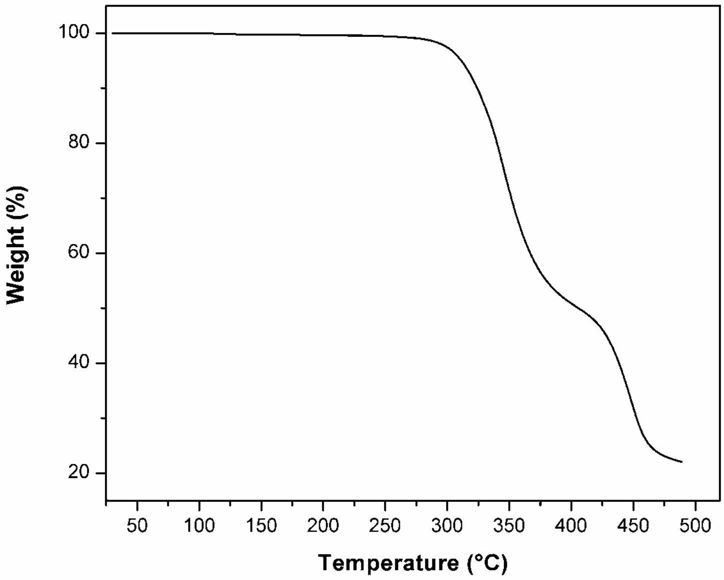


Figure 4. TGA profile of polymer P[VBBI][BF_4]

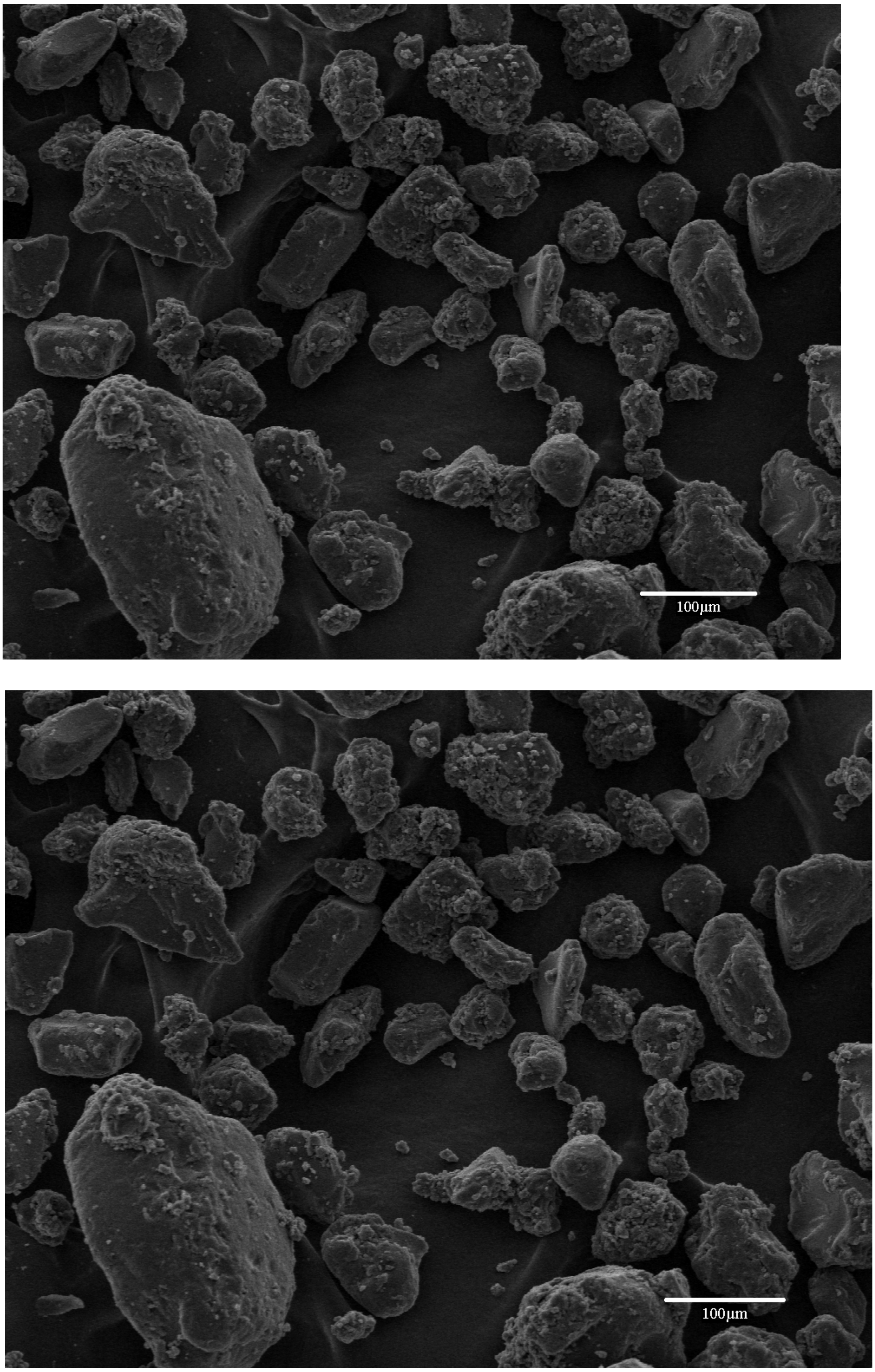


Figure 5 SEMs of particles of P[VBBI][BF_4].

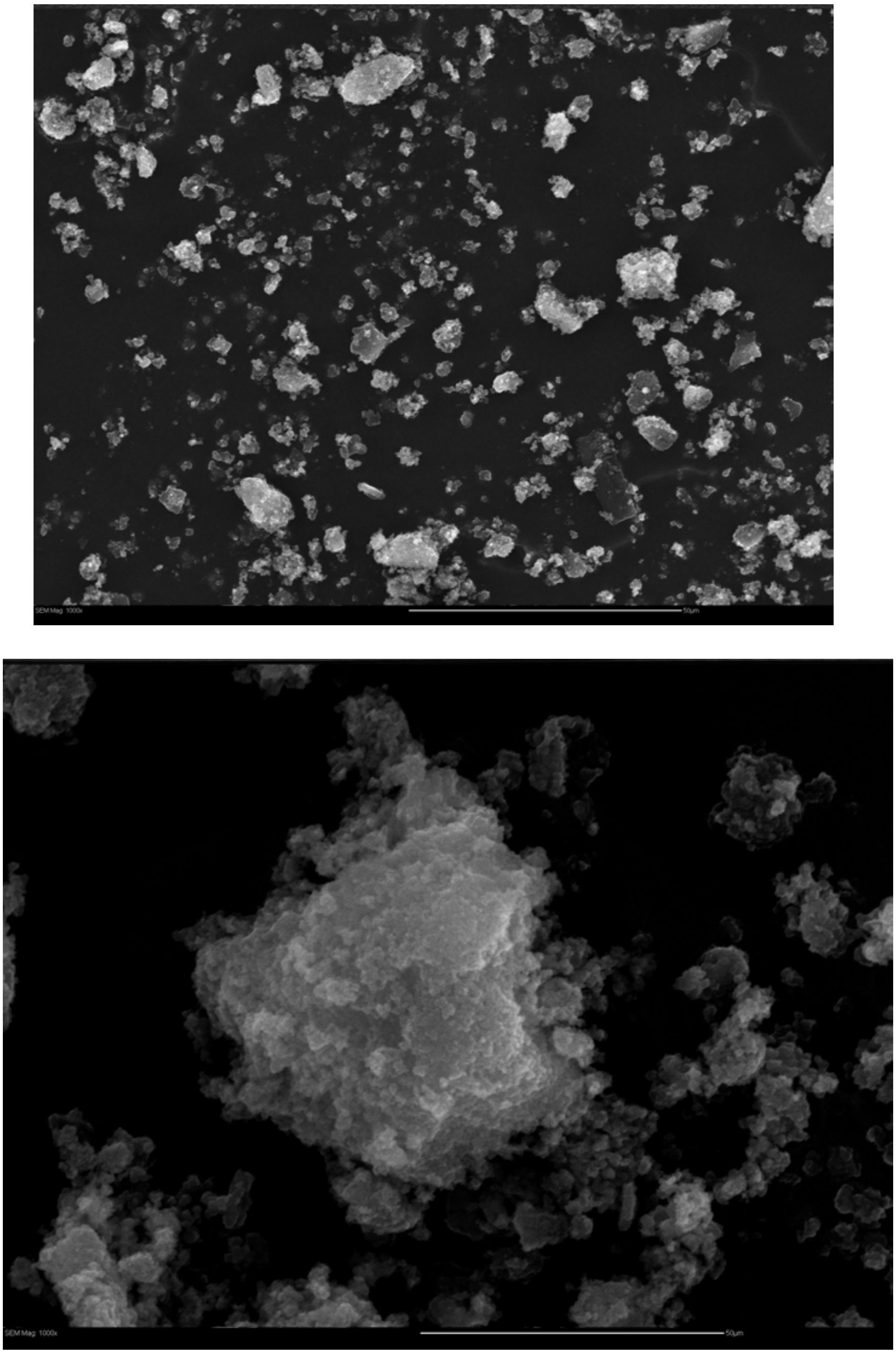


Figure 6 SEMs of particles of P[MATMA][BF_4]

CO_2 Absorption and Desorption Measurements.

The CO_2 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. The experimental apparatus is shown in Scheme 1. 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 powders of the polymers were dried at 70 °C under vacuum for 12 h to remove moisture or other volatile contaminants. Before the measurements, they were further dried in the balance by evacuating the chambers at high vacuum until the weights were constant for at least 30 min. CO_2 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.[1] 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 the reported.[2]

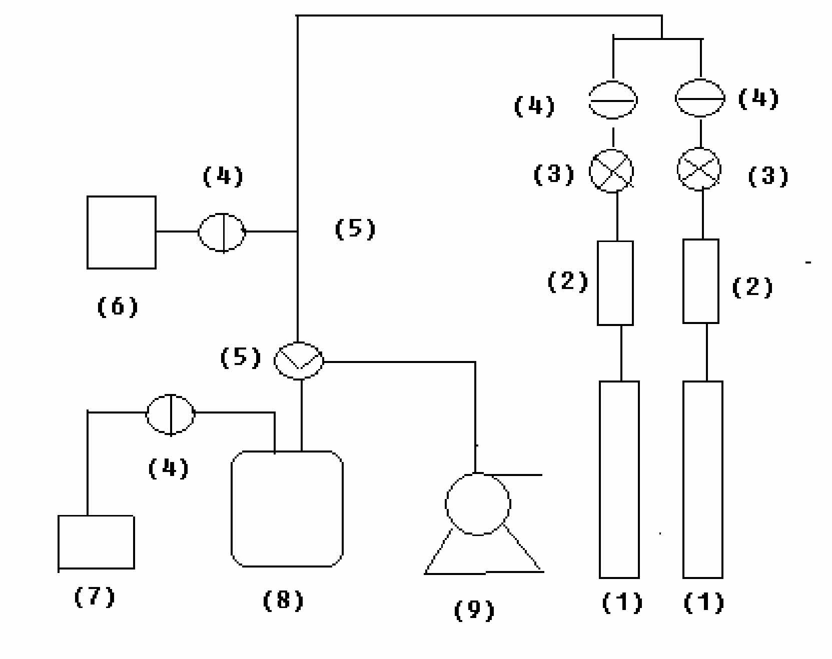


Figure 1. Schematic diagram of experimental apparatus

(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:

[1] Macedonia, M. D.; Moore, D. D. and Maginn, E. J. Langmuir 2000, 16, 3823-3834
[2] 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