Thiazolium poly(ionic liquid)s: synthesis and application as binder for lithium-ion batteries

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Experimental

Chemicals

4-Methyl-5-vinylthiazole (≥ 97 %, Sigma Aldrich), potassium hexafluorophosphate (99 %, Alfa Aesar), lithium bis(trifluoromethylsulfonyl) imide (99 %, Io-li-tec), silver tetrafluoroborate (98 %, Aldrich), methyl iodide (99 %, Alfa Aesar), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Wako Chemicals) were used without further purification. 2,2′-Azobis(2-methylpropionitrile) (Sigma Aldrich, 98%) was recrystallized from methanol. All used organic solvents were of analytic grade.

Instrumentation

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. The heteronuclear multiple bond correlation (^{1}H-^{13}C HMBC) NMR spectrum was recorded at room temperature on a VARIAN 400-MR (400 MHz) spectrometer. DMSO-d_6 and DMF-d_7 were used as solvents for performed measurements.

Thermogravimetric analysis (TGA) experiments were performed under nitrogen flow at a heating rate of 10 K·min^{-1} using a Netzsch TG209-F1 apparatus.

Fourier-transform infrared (FT-IR) spectroscopy was performed at room temperature with a BioRad 6000 FT-IR spectrometer equipped with a Single Reflection Diamond ATR.

Gel permeation chromatography (GPC) was performed using NOVEMA Max linear XL column with a mixture of 80% of aqueous acetate buffer and 20% of methanol. Conditions: flow rate 1.00 mL min^{-1}, PEO standards using RI detector - Optilab-DSP-Interferometric Refractometer (Wyatt-Technology).

Differential scanning calorimetry (DSC) measurements were done under nitrogen flow using Mettler-Toledo DSC-1 STAR^e System instrument.

Solubility test was performed by mixing 10 mg of samples with different solvents (1 wt% and 0.1 wt%) in glass vials. After 24 hours of shaking vials, the presence of solid inside vials was checked. Non-dissolved samples were heated in order to examine solubility at elevated temperatures.

Electrochemical analysis

The electrodes were prepared by casting slurry of acetylene black (AB), polymer binder and lithium iron phosphate ($LiFePO_4$) in NMP on an aluminum foil current collector. The weight ratio of all components was kept constant (80% $LiFePO_4$, 10% AB, and 10% binder material). The electrodes were dried at 80 $^{\circ}$C for 3 h followed by drying at 120 $^{\circ}$C for 24 h. The loading mass of the mixture was controlled at ~2.5 mg. The electrodes were assembled in two-electrode Swagelok-type cells. The assembly process was performed inside a glovebox, in argon atmosphere. Metallic lithium foil was used as counter electrode and glass fiber membrane was used as a separator. 1 M lithium hexafluorophosphate ($LiPF_6$) in mixture of ethylene carbonate and dimethyl carbonate (1:1 v/v) was used as the electrolyte. The cells were cycled in a potential window between 2.0 and 4.0 V *vs.* Li/Li^+ using multichannel potentiostatic / galvanostatic system (VMP-3, Bio-Logic). The C-rate was calculated on the basis of $LiFePO_4$ assuming a theoretical specific capacity of 170 mAh/g.

Monomer synthesis

Synthesis of 3,4-dimethyl-5-vinylthiazol-3-ium iodide (MVTh+I-):

4-Methyl-5-vinylthiazole (20.0 g, 0.155 mol) and 2,6-ditertbutylo-4-methylphenol (100 mg, 0.45 mmol) were charged into a 250 mL round bottom flask. Methyl iodide (0.31 mol, 19.5 mL) was added dropwise under vigorous stirring. The flask was closed with a stopper and placed for 20 h in an oil-bath thermostated at 40 °C. Afterwards the solid product was dissolved in 200 mL dimethyl sulfoxide followed by precipitation in 4.0 L of 1:1 volume mixture of diethyl ether and tetrahydrofuran. The precipitate was filtered off on a Buchner funnel, washed with 1:1 volume mixture of diethyl ether and tetrahydrofuran and dried overnight at 40 °C, at high vacuum to the constant weight (37.6 g, 88% yield). ^{1}H-NMR (400 MHz, DMF-d_7) δ 10.38 (s, 1H), 7.19 (dd, *J* = 17.2, 11.1 Hz, 1H), 6.02 (d, *J* = 17.2 Hz, 1H), 5.66 (d, *J* = 11.1 Hz, 1H), 4.36 (s, 3H), 2.69 (s, 3H); ^{13}C-NMR (101 MHz, DMF) δ 158.38, 144.50, 135.92, 125.98, 121.95, 41.81, and 12.50.

Synthesis of 3,4-dimethyl-5-vinylthiazol-3-ium bis(trifluoromethylsulfonyl) imide:

3,4-Dimethyl-5-vinylthiazol-3-ium iodide (40,0 g, 150 mmol) was dissolved in 1.0 L of water. Lithium bis(trifluoromethylsulfonyl) imide (52.11 g, 180 mmol) was dissolved in 500 mL water and added dropwise under vigorous stirring to the solution of 3,4-dimethyl-5-vinylthiazol-3-ium iodide. The mixture was stirred for 2 h, followed by vacuum filtration on the Buchner funnel and washing with water. The product was dried overnight at 40 °C at high vacuum to the constant weight (36.96 g, 59 % yield). ^{1}H-NMR (400 MHz, DMF-d_7) δ 10.28 (s, 1H), 7.17 (dd, *J* = 17.2, 11.1 Hz, 1H), 6.03 (d, *J* = 17.3 Hz, 1H), 5.69 (d, *J* = 11.1 Hz, 1H), 4.33 (s, 3H), 2.68 (s, 3H); ^{13}C-NMR (101 MHz, DMF) δ 158.29, 144.43, 136.07, 125.98, 122.78, 121.96, 119.59, 116.39, 41.40, and 12.04.

<u>Synthesis of 3,4-dimethyl-5-vinylthiazol-3-ium tetrafluoroborate:</u>

3,4-Dimethyl-5-vinylthiazol-3-ium iodide (4.0 g, 15.0 mmol) was dissolved in a mixture of 30.0 g of MiliQ water ad 90.0 g of acetone. Silver tetrafluoroborate (2.95 g 15.0 mmol) was dissolved in a mixture of 10.0 g of MiliQ water and 30.0 g of acetone, following by adding dropwise under vigorous stirring to a solution of 3,4-dimethyl-5-vinylthiazol-3-ium iodide. After half an hour, the yellow precipitate was centrifuged out. The supernatant was collected and dried by evaporation of acetone under reduced pressure followed by lyophilization. (3,20 g, 94 % yield). ^{1}H NMR (400 MHz, DMF-d_7) δ 10.23 (s, 1H), 7.17 (dd, *J* = 17.3, 11.1 Hz, 1H), 6.03 (d, *J* = 17.3 Hz, 1H), 5.68 (d, *J* = 11.1 Hz, 1H), 4.32 (d, *J* = 0.8 Hz, 3H), 2.67 (s, 3H), ^{13}C NMR (101 MHz, DMF) δ 158.07, 144.40, 135.94, 125.81, 121.90, 41.32, 11.95.

Polymer synthesis

<u>Synthesis of poly(3,4-dimethyl-5-vinylthiazol-3-ium iodide):</u>

3,4-Dimethyl-5-vinylthiazol-3-ium iodide (4.0 g, 15.0 mmol), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (0.10 g, 0.35 mmol) and 8.0 mL of MiliQ water were loaded into a 50 mL Schlenk flask and stirred. The flask was 5 times degassed and back-filled with argon and the reaction was carried out under argon at 90 °C for 20 h. The mixture was diluted with 5.0 mL of MiliQ water and precipitated in 300 mL of acetone. The product was collected by filtration and dried overnight at 80 °C, at high vacuum (2,9 g, 73 % yield).

<u>Synthesis of poly(3,4-dimethyl-5-vinylthiazol-3-ium bis(trifluoromethylsulfonyl) imide):</u>

3,4-Dimethyl-5-vinylthiazol-3-ium bis(trifluoromethylsulfonyl) imide (2.0 g, 4.8 mmol) and 2,2′-azobis(2-methylpropionitrile) (40 mg, 0.24 mmol) were loaded into a 50 mL Schlenk flask together with a stirring bar. The flask was 5 times degassed and back-filled with argon and the bulk polymerization was carried out under argon at 120 °C for 6 h. The crude product was dissolved in 5.0 mL of acetone followed by precipitation in 100 mL of chloroform. The product was collected by filtration and dried overnight at 100 °C, at high vacuum (1.8 g, 90 % yield).

Synthesis of poly(3,4-dimethyl-5-vinylthiazol-3-ium tetrafluoroborate).

Poly(3,4-dimethyl-5-vinylthiazol-3-ium tetrafluoroborate) [P(MVT^{+}BF$_{4}^{-}$)]: MVT^{+}BF$_{4}^{-}$ (1.0 g, 4.4 mmol) was loaded into a 50 mL Schlenk flask together with a stirring bar. The flask was 5 times degassed and back-filled with argon and the bulk polymerization was carried out under argon at 170 °C for 8 h. The crude product was dissolved in 10 mL of DMF followed by precipitation in 100 mL of acetone. The product was collected by centrifugation and dried overnight at 80 °C, at high vacuum (0.83 g, 83 % yield);

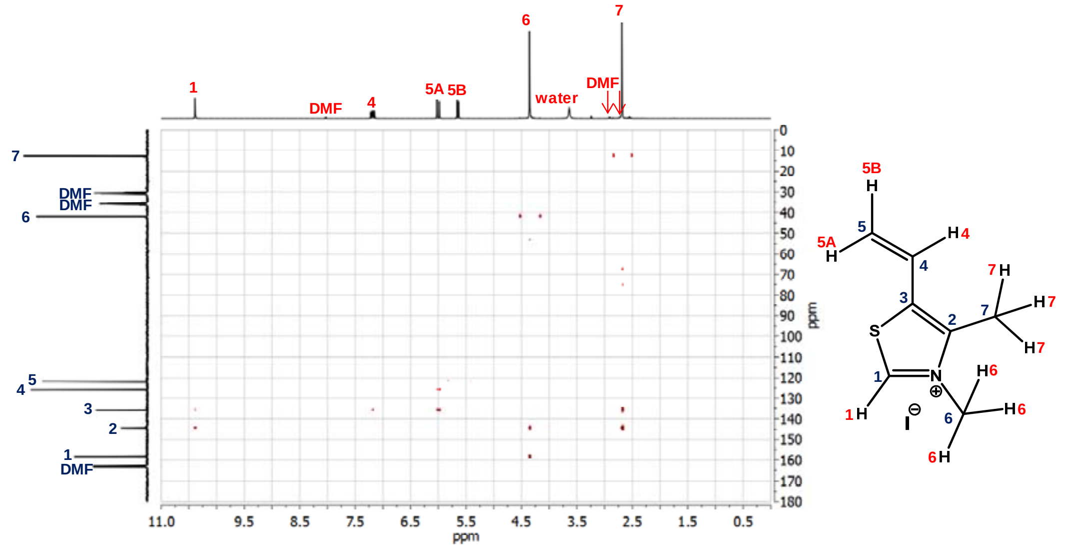

Figure S1. ^{1}H-^{13}C HMBC correlation spectrum of MVTh^{+}I^{-}.

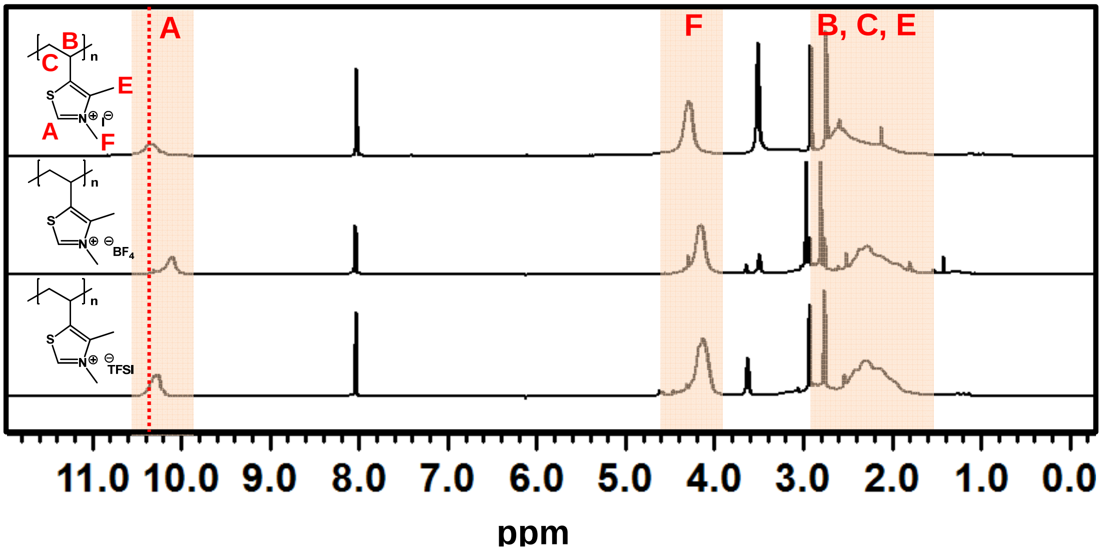

Figure S2. ^{1}H-NMR of P(MVTh^{+}I^{-}), P(MVTh^{+}BF$_{4}^{-}$), and P(MVTh^{+}TFSI^{-}) [red line – position of the peak A" in the ^{1}H-NMR spectrum of P(MVTh^{+}I^{-})]

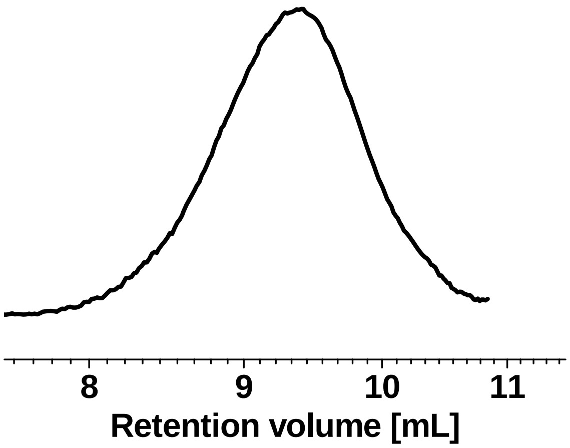

Figure S3. GPC trace of the polymer sample PMVTh$^+$I$^-$.

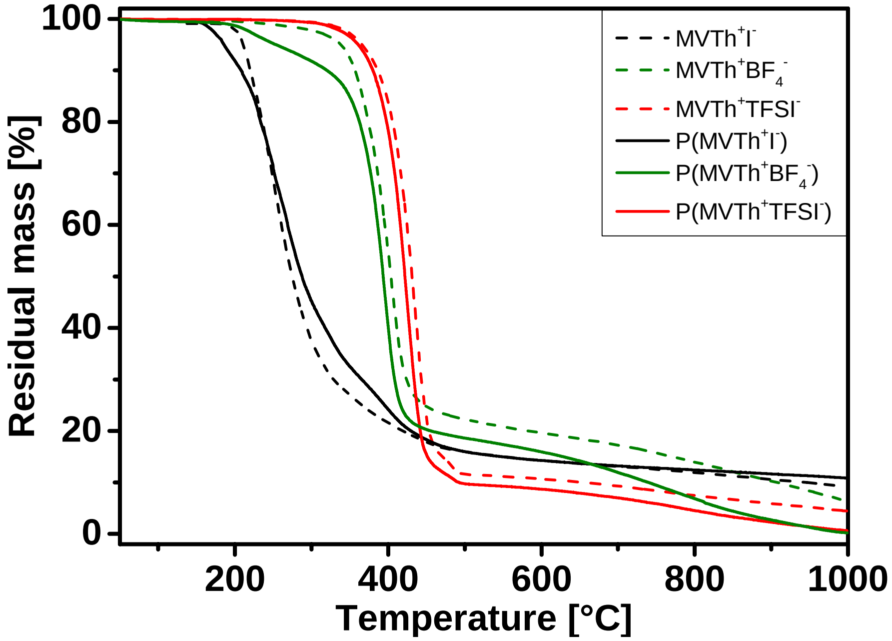

Figure S4. TGA thermograms of all synthesized monomers and polymers.