

**Anomalous Thermal Characteristics of Poly(ionic liquids)
Derived from 1-Butyl-2,3-Dimethyl-4-Vinylimidazolium Salts**

*Fan Yangⁱ, Meng Zhaoⁱⁱ, Darren Smithⁱⁱⁱ, Peggy Cebe^{iv}, Sam Lucisano^v, Thomas Allston^{vi}, and Thomas W. Smith,^{vi} **

Versick Analytics, ⁱ Jersey City, NJ

BOE Technology Group, ⁱⁱ Beijing China

Experimental Therapeutics Branch, Walter Reed Army Institute of Research, ⁱⁱⁱ

Silver Spring, MD 20910

Physics and Astronomy Department, Tufts University, ^{iv} Medford, MA, 02155

Xerox Corporation, ^v Webster, NY

School of Chemistry & Materials Science, Rochester Institute of Technology ^{vi}

**Correspondence to: twssch@rit.edu*

Supplementary Information

Thermal gravimetric analysis (TGA) was carried out under a nitrogen atmosphere with a TA Instruments TGA 2050. The temperature was increased from 25-600°C at 20°C/min under a nitrogen atmosphere, and then held at 600°C for 10 minutes under an air atmosphere. TGA mass loss profiles for triflate and TFSI⁻ salts of poly(1-butyl-2,3-dimethylimidazolium) are shown in Figure S1. The thermal stability of the triflate and TFSI⁻ salts is similar. Significant mass loss in the TFSI⁻ salt occurs between 430 and 505 °C; that in the triflate salt occurs between 440 and 505°C.

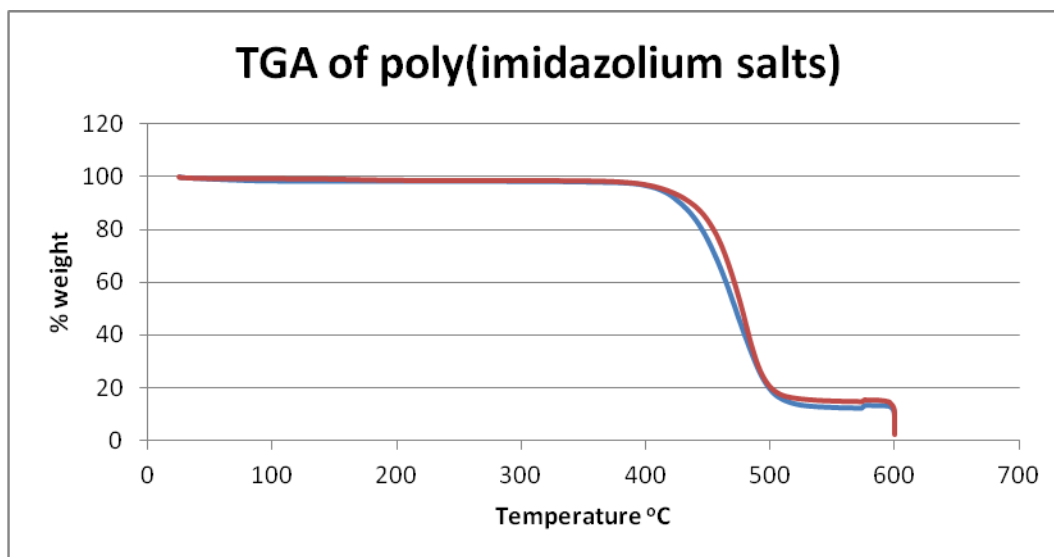


Figure S1 - TGA of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate)(red) and poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI)(blue).

Glass transition characteristics of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) triflate, hexafluorophosphate and trifluoromethylsulfonylimide salts were evaluated by differential scanning calorimetry. DSC thermograms for the triflate polymer are shown in **Figure S2** where plots of change in heat capacity in 20 °C/min heating and cooling cycles and an auxiliary 40 °C/min rapid heating cycle are shown.

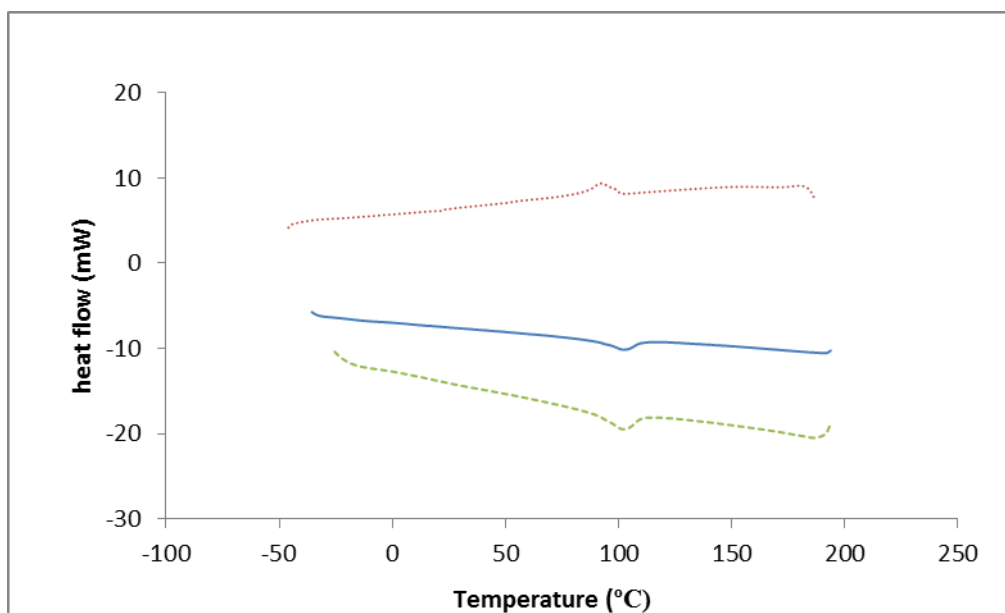


Figure S2 - DSC scans of P23DMVIm⁺ Tf⁻ : solid blue line (20°C/min – heating cycle), dotted red line (20°C/min – cooling cycle), dashed green line (40°C/min – rapid heating cycle).

Thermograms for the TFSI and hexafluorophosphate polymer salts are displayed in Figure S3 and S4, respectively.

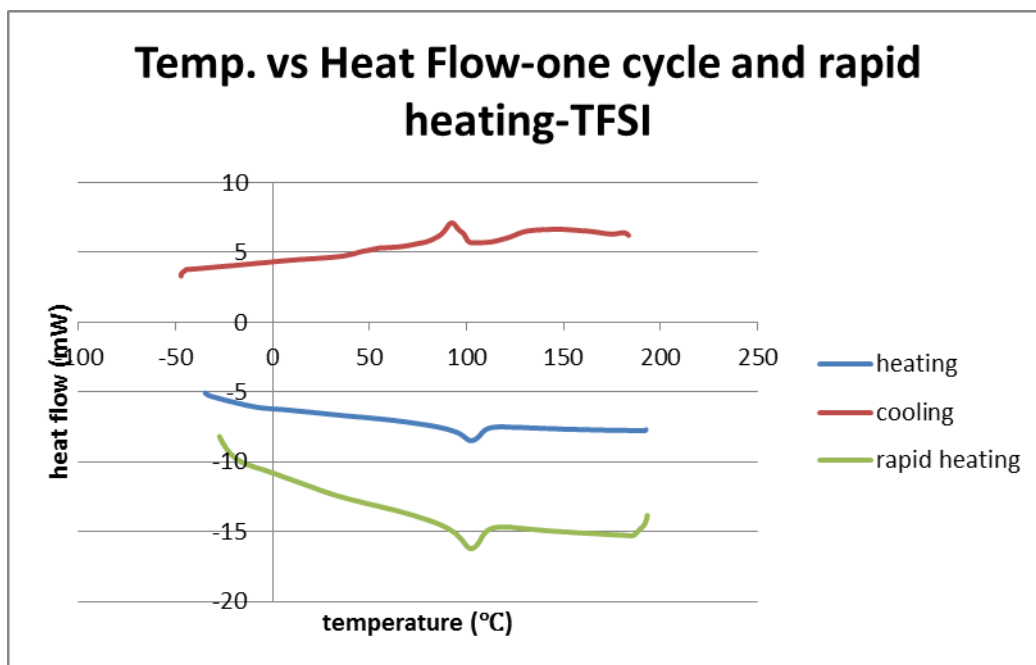


Figure S3 - DSC scans of P23DMVIm⁺TFSI⁻ during heating and subsequent cooling. The green line is from a final heating cycle at 40° per min.

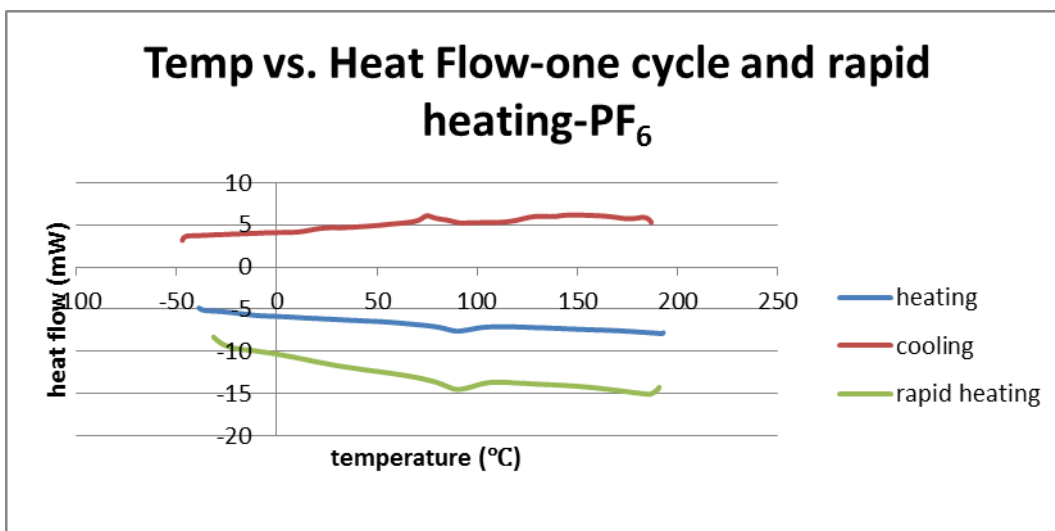


Figure S4 - DSC scans of P23DMVIm⁺PF₆⁻: solid blue line (20°C/min – heating cycle), dotted red line (20°C/min – cooling cycle), dashed green line (40°C/min – rapid heating cycle).

The TFSI⁻ salt exhibited a T_g of 96°C – 102°C in the heating cycle and 92 °C – 84 °C in the cooling cycle. The hexafluorophosphate anion is less solvating and smaller than TFSI⁻, yet it exhibits a somewhat lower T_g than that of the TFSI⁻ salt.

The ^1H NMR of 2-methyl-4-vinylimidazole is shown in **Figure S5**.

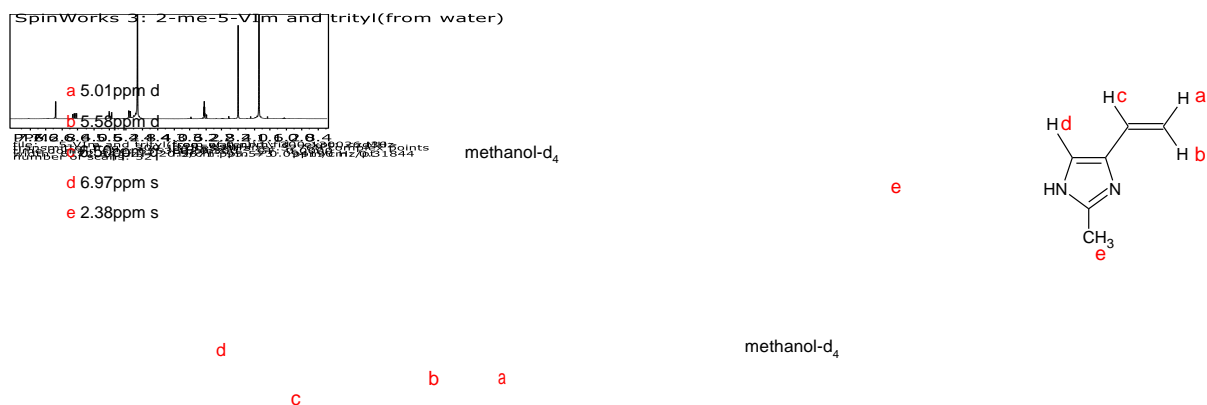


Figure S5. ^1H NMR of 2-methyl-4-vinylimidazole

H_a and H_b are in different chemical environments and they are coupled with each other and with H_c to yield split doublets. H_c is also a pair of split doublets, a result of coupling to both H_a and H_b. H_d on the imidazole ring shows a singlet at 6.97ppm and the methyl hydrogens at the 2-position exhibit a chemical shift of 2.38ppm. The sharp singlet at around 1.9 ppm is due to residual cyclohexane, which was the solvent of n-butyl lithium.

The ^1H NMR of 1-butyl-2-methyl-4-vinylimidazole is shown in **Figure S6**.

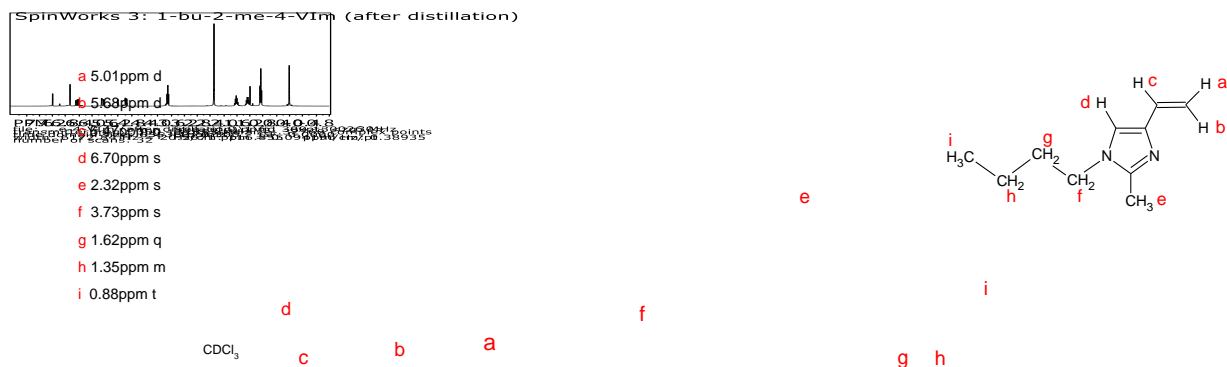


Figure S6. ^1H NMR of 1-butyl-2-methyl-4-vinylimidazole

The ^1H NMR of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate is shown in **Figure S7**. The 3-position methyl hydrogen has a chemical shift of 3.73ppm. Hf is more up field than Hg because hydrogens on the methyl group are shielded by the cone of the pi-cloud of the vinyl group.

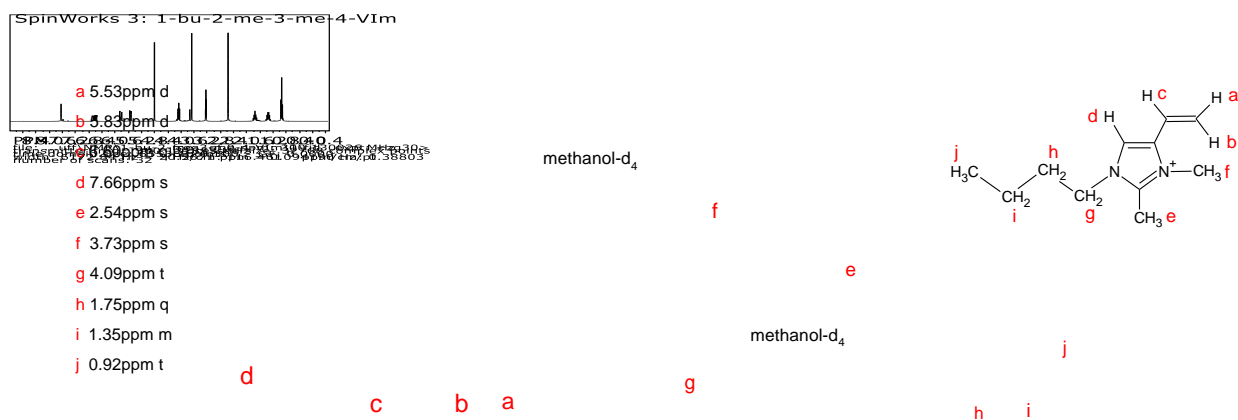


Figure S7. ^1H NMR of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate

The ^1H NMR spectrum of Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) triflate is displayed in **Figure S8**

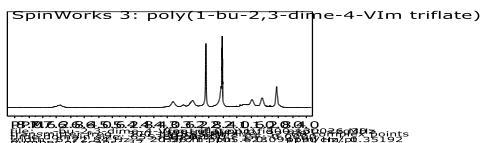


Figure S8 ^1H NMR spectrum of Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) triflate

Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) was ion-exchanged with $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ and PF_6^- . The efficacy of the ion-exchange process described in the Experimental Section of the paper was verified by the comparative ^{19}F NMR spectra of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) (**Figure S9**) and poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate) (**Figure S10**), respectively, in which the ^{19}F NMR spectrum of the fully ion-exchanged hexafluorophosphate polymer shows no trace of a peak at ~ 78 ppm corresponding to ^{19}F in CF_3SO_3^- .

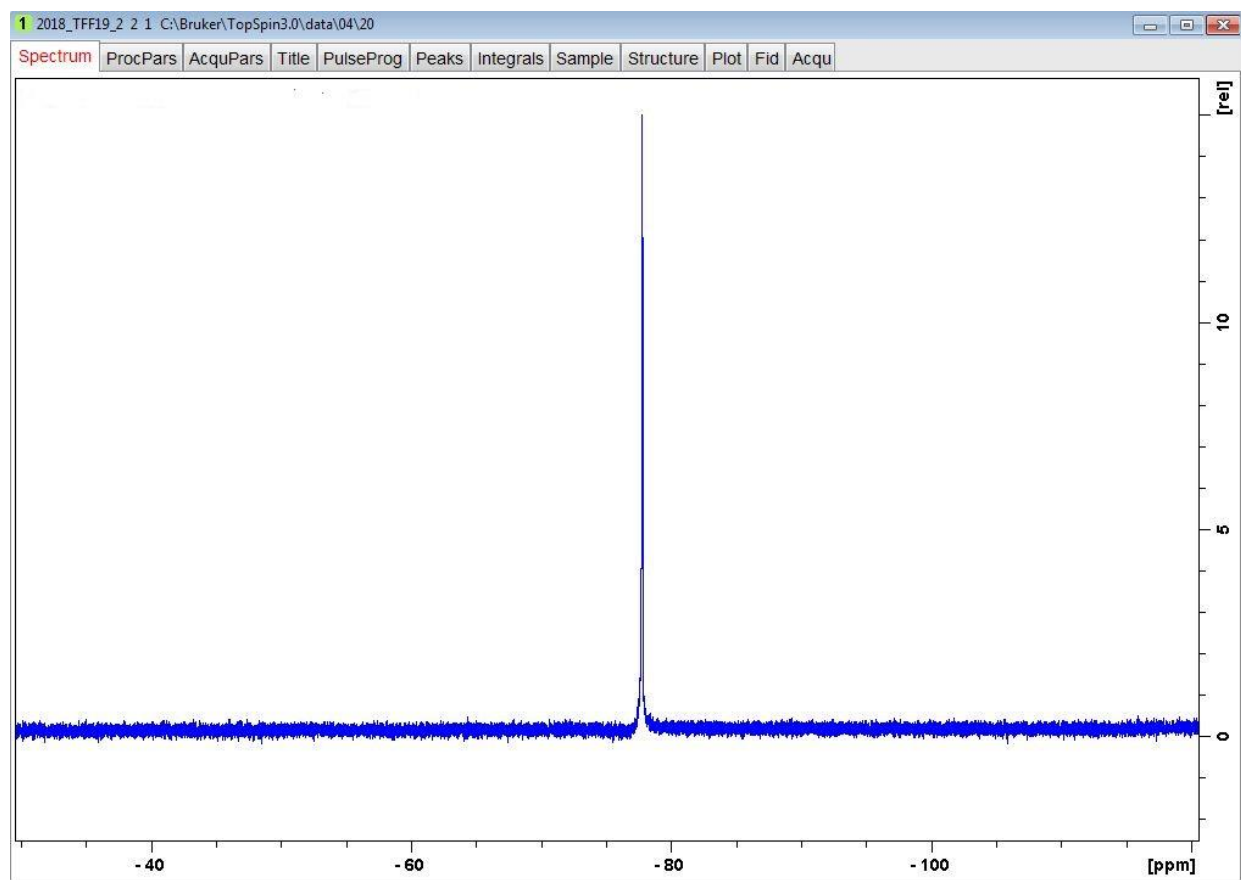


Figure S9 - ^{19}F NMR spectrum of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate)

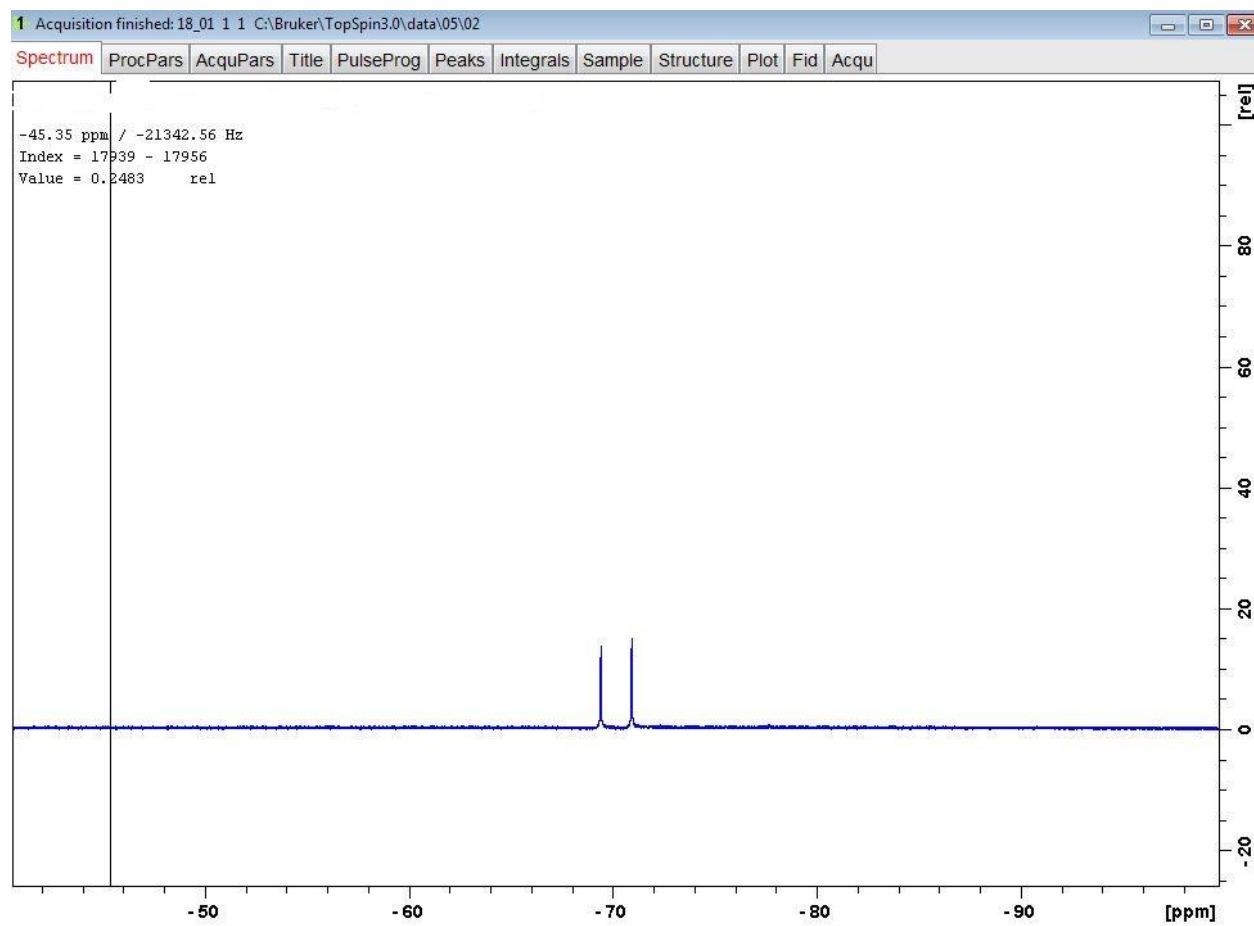


Figure S10 - ^{19}F NMR Spectrum of Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate)