

Supplementary Information

Poly(Ionic Liquid) ABC Triblock and ABCBA Pentablock Terpolymer Electrolytes for Lithium Metal Batteries

*Dohyun Kim^a, Rui Sun^a, Roger Tocchetto^b, Carl Willis^b, Bert Krutzer^b, Frederick L. Beyer^c, and
Yossef A. Elabd^{a,*}*

^a Department of Chemical Engineering, Texas A&M University, College Station, TX, 77843,
United States

^b Kraton Polymers, LLC, Houston, TX, 77032, United States

^c U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 21005, United States

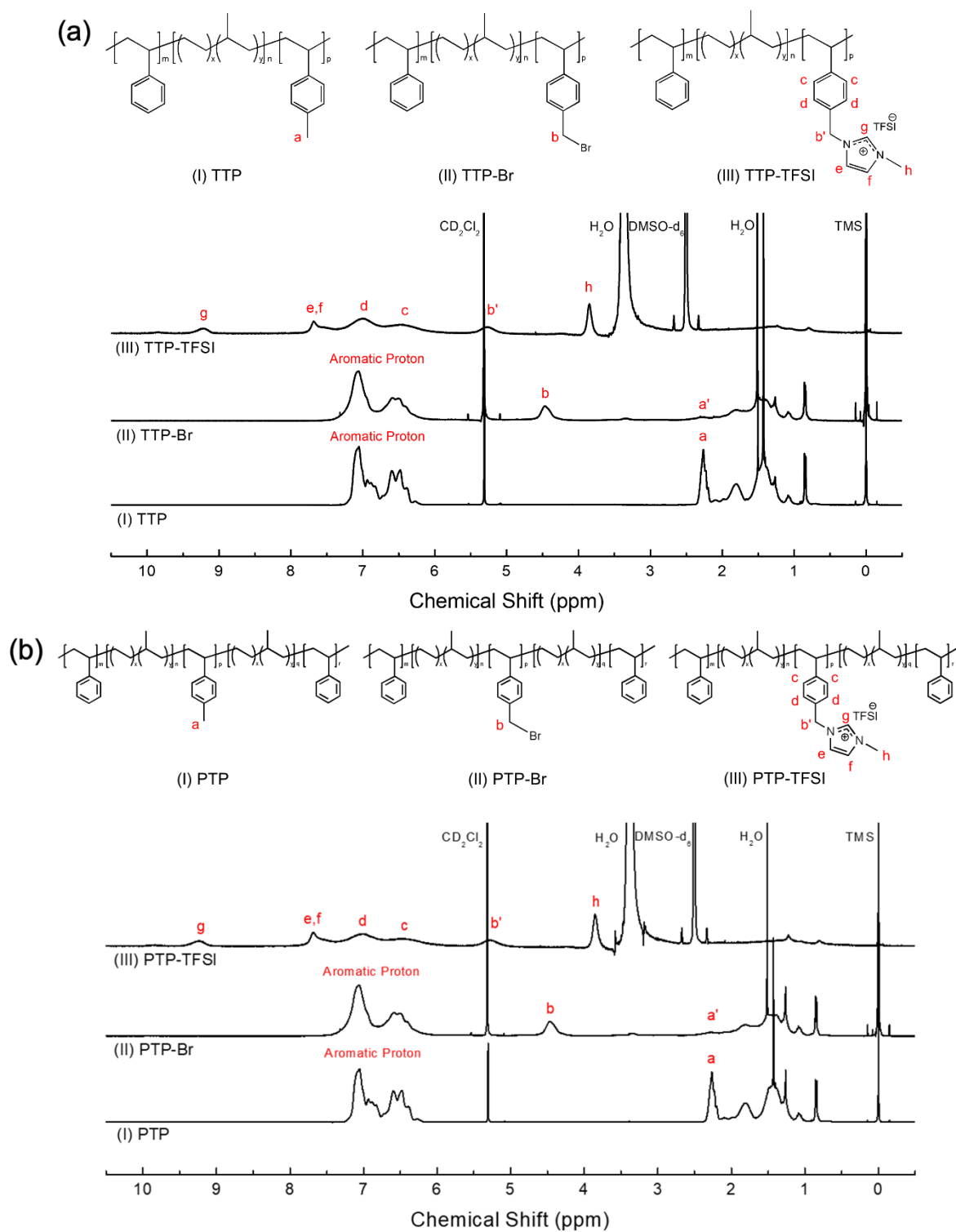


Figure S1. Chemical structures and ^1H NMR spectra of precursor, brominated, and anion exchanged triblock and pentablock terpolymers: (a) TTP, TTP-Br, and TTP-TFSI, (b) PTP, PTP-Br, and PTP-TFSI.

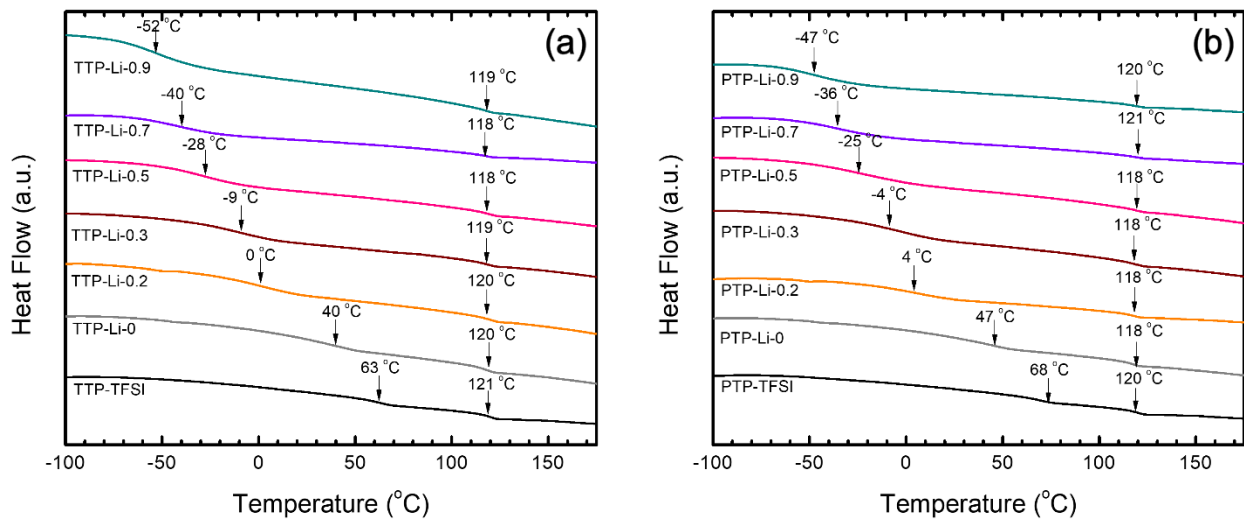


Figure S2. DSC heating thermograms of (a) TTP-TFSI and TTP-Li-r and (b) PTP-TFSI and PTP-Li-r at different r ([IL]/[PIL]) ratios.

Table S1. VFT and Arrhenius parameters for TTP-Li-r and PTP-Li-r SPEs.

SPE	Arrhenius		VFT		
	E_a (kJ mol ⁻¹)	R^2	T_0 (K)	$T_g - T_0$ (K)	R^2
TTP-Li-0.3	84.3	0.974	229.0	35.5	0.996
TTP-Li-0.5	63.4	0.984	220.7	24.0	0.997
PTP-Li-0.2	111.4	0.968	232.6	44.9	0.990
PTP-Li-0.3	77.5	0.978	225.8	43.7	0.998
PTP-Li-0.5	63.3	0.989	200.0	48.1	0.999
PTP-Li-0.7	54.0	0.994	170.0	67.0	0.999
PTP-Li-0.9	37.9	0.997	144.7	81.1	0.999

SI.1. Small Angle X-ray Scattering

Under the assumption that resulting features were Bragg diffraction maxima, they were compared to the diffraction peak positions for the equilibrium morphologies observed in block copolymers to verify the morphology of the TTP-TFSI and PTP-TFSI with IL concentration ($r = 0.3$ and 0.5). The resulting diffraction peaks for all samples do not correspond to those of known morphologies, suggesting that higher-order scattering features result from form factor scattering. Figure S3 shows SAXS profiles for TTP-TFSI and PTP-TFSI with their respective regression with sphere model. The sphere form factor and hard sphere structure factor (Percus-Yevick) represent well the scattering features for both polymers, suggesting that the polymer shares a morphology of microphase separated spheres.

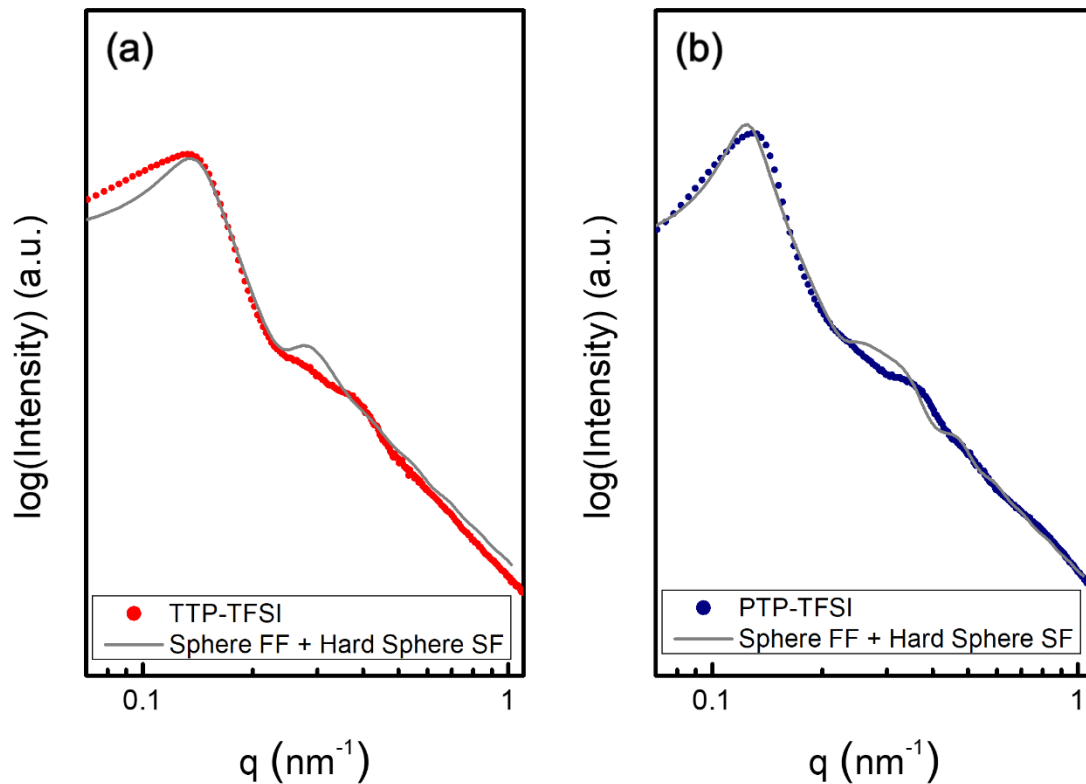


Figure S3. SAXS profiles of (a) TTP-TFSI and (b) PTP-TFSI. The regression with sphere model (sphere form factor and hard sphere structure factor) for each polymer is indicated by gray line, respectively.

The SAXS profiles for TTP-Li-0.5 and PTP-Li-0.5 SPEs with sphere regression models are shown in Figure S4. Similar to the result in Figure S3, both SPEs have a morphology of microphase separated spheres, indicating that the morphology of TTP-TFSI and PTP-TFSI is retained with addition of IL. The results from Figure S3 and Figure S4 indicate that ABC triblock and ABCBA pentablock terpolymer-based SPEs have similar morphologies regardless of IL concentration, suggesting that the effect of chain architecture (ABC vs. ABCBA) does not lead to a significant change in morphology.

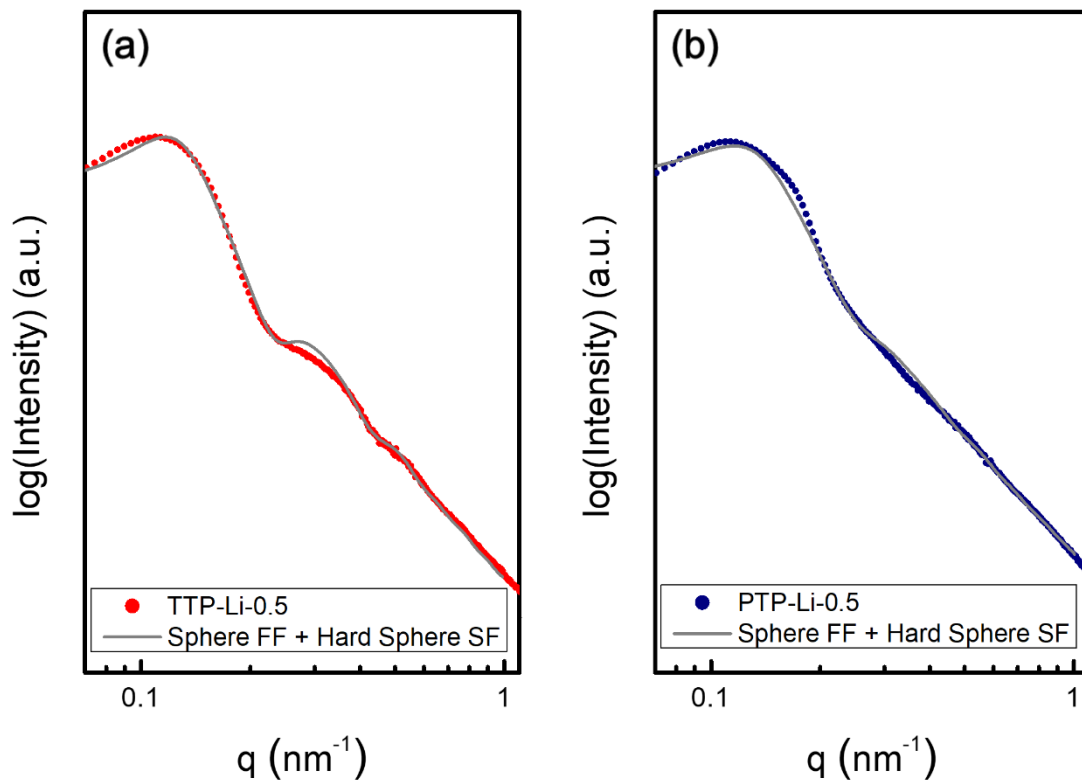
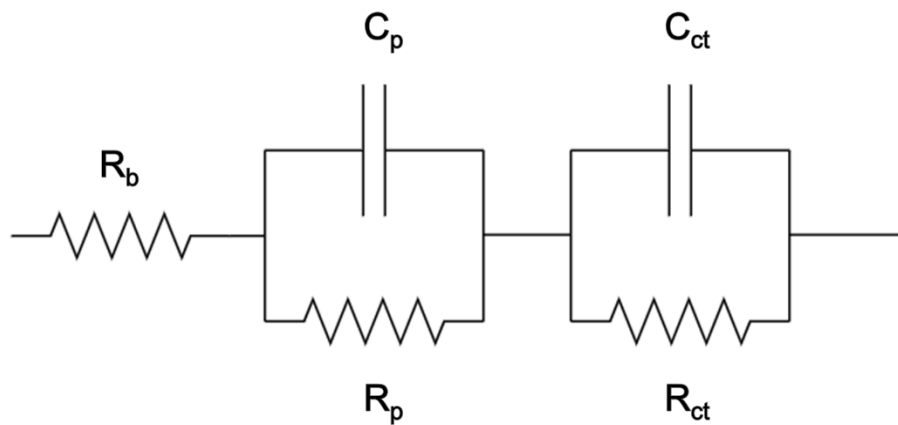


Figure S4. SAXS profiles of (a) TTP-Li-0.5 and (b) PTP-Li-0.5 SPEs. The regression with sphere model (sphere form factor and hard sphere structure factor) for each polymer is indicated by gray line, respectively.



R_b : bulk resistance
 R_p : passivation layer resistance C_p : constant phase element of passivation layer
 R_{ct} : charge transfer resistance C_{ct} : constant phase element of electric double layer

Figure S5. Equivalent circuit model for regressing impedance spectra of Li symmetric cells.