Supporting Information for:

Enhanced Conductivity *via* Homopolymer-Rich Pathways in Block Polymer Blended Electrolytes

Melody A. Morris,[a] Seung Hyun Sung,[a] Priyanka M. Ketkar,[a] Joseph A. Dura,[b] Ryan C. Nieuwendaal,[c] and Thomas H. Epps, III[a,d,]*

[a]Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, Delaware 19716, United States

[b]NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

[c]Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

[d]Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, United States

Table S1: Blend compositions. All poly(*oligo*-oxyethylene methacrylate) [POEM]-containing blends consist of 20 wt% homopolymer.

Sample name	**Polystyrene-*block*-POEM [PS-*b*-POEM] M_n (g mol^{-1})**	**$M_{n,\ POEM}$ in PS-*b*-POEM (g mol^{-1})**	**$M_{n,\ homopolymer\ POEM}$ (g mol^{-1})**
Unblended-17.8	43,100	17,800	N/A
Wet brush-17.8	43,100	17,800	8,000
Dry brush-17.8	43,100	17,800	24,100
Unblended-23.9	42,200	23,900	N/A
Wet brush-23.9	42,200	23,900	8,000
Dry brush-23.9	42,200	23,900	24,100

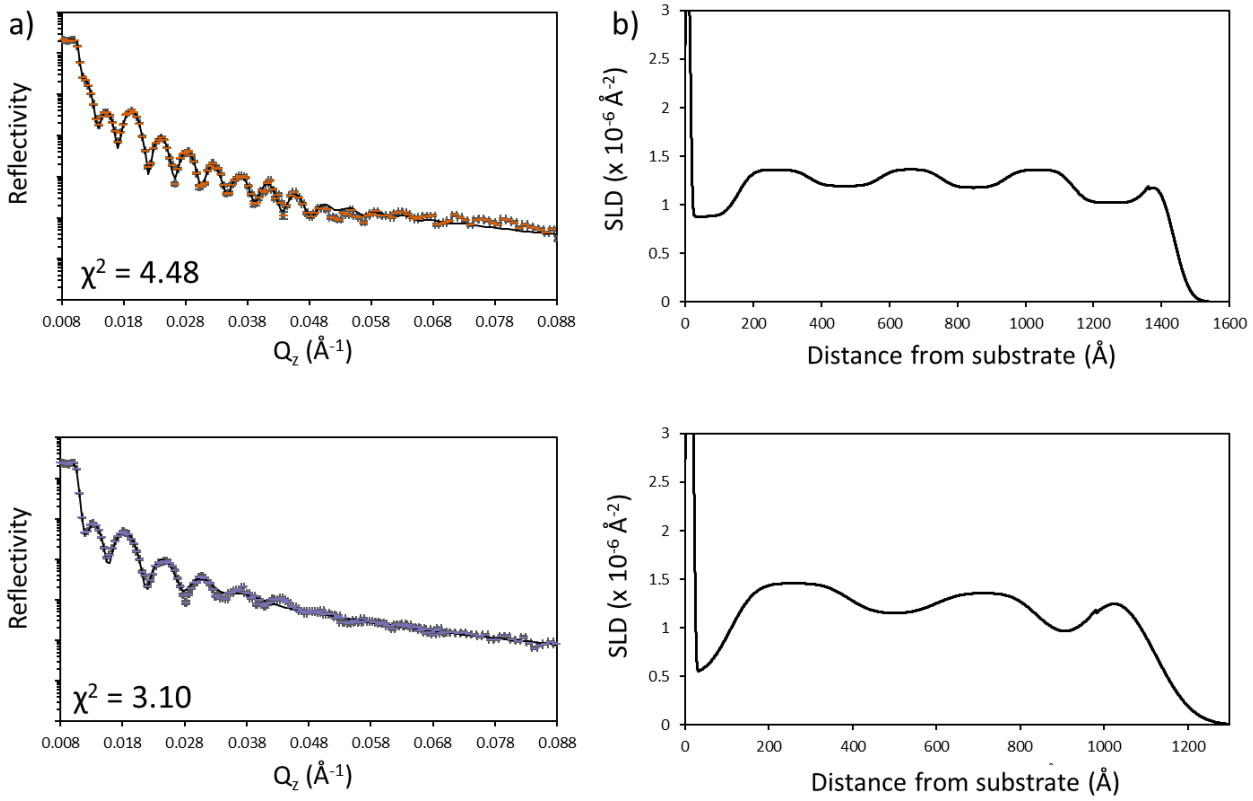

Figure S1: a) Neutron reflectometry (NR) multilayer model fits (black lines) for Wet brush-17.8 (orange points) and Dry brush-17.8 (purple points) doped with lithium trifluoromethanesulfonate (Li triflate) at [EO]:[Li] = 24:1 and b) corresponding scattering length density (SLD) profiles. We note that the statistical χ^2 reported in all reflectivity figures is unrelated to the Flory-Huggins parameter χ_{eff} discussed elsewhere in this document and the associated manuscript. Furthermore, the χ^2 reported in the NR fits is normalized by the error in each data point. Throughout the supporting information, error bars represent one standard error.

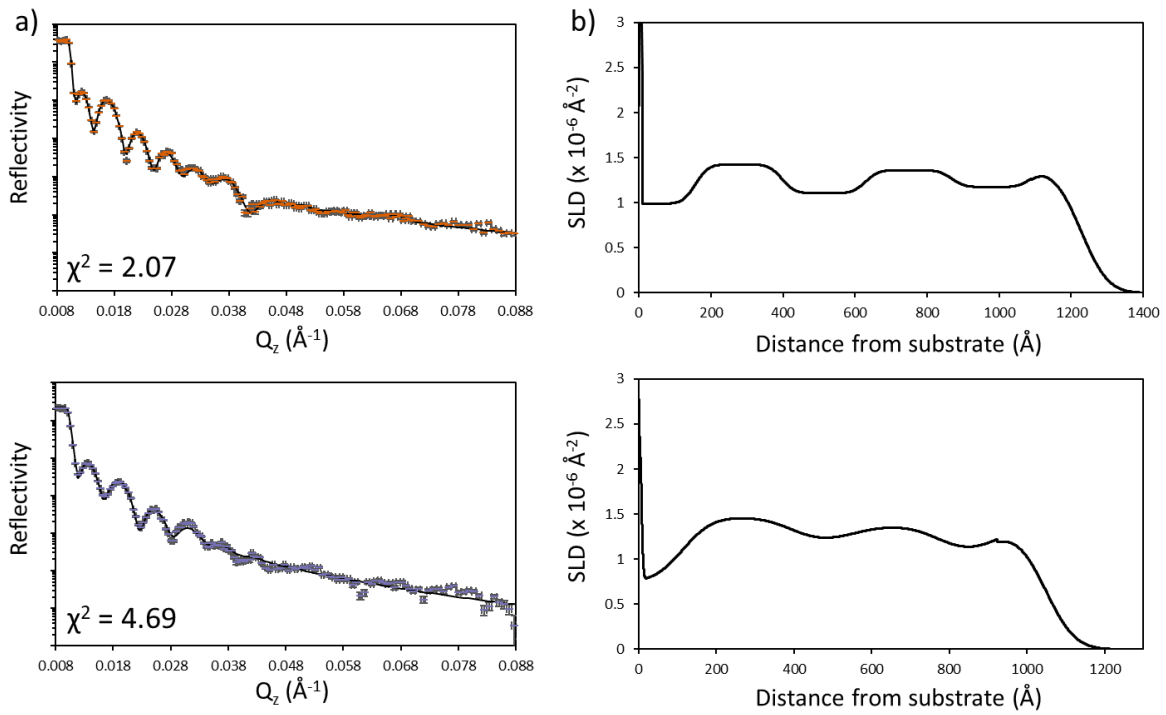

Figure S2: a) NR multilayer model fits (black line) for Wet brush-17.8 (orange points) and Dry brush-17.8 (purple points) doped with Li triflate at [EO]:[Li] = 8:1 and b) corresponding SLD profiles.

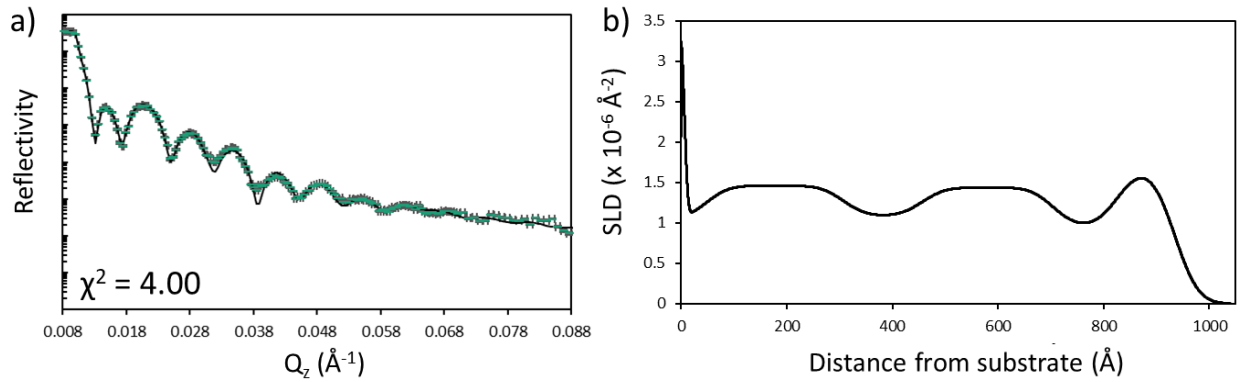

Figure S3: a) NR multilayer model fit (black line) for Unblended-17.8 (green points) doped with Li triflate at [EO]:[Li] = 18:1 and b) corresponding SLD profile.

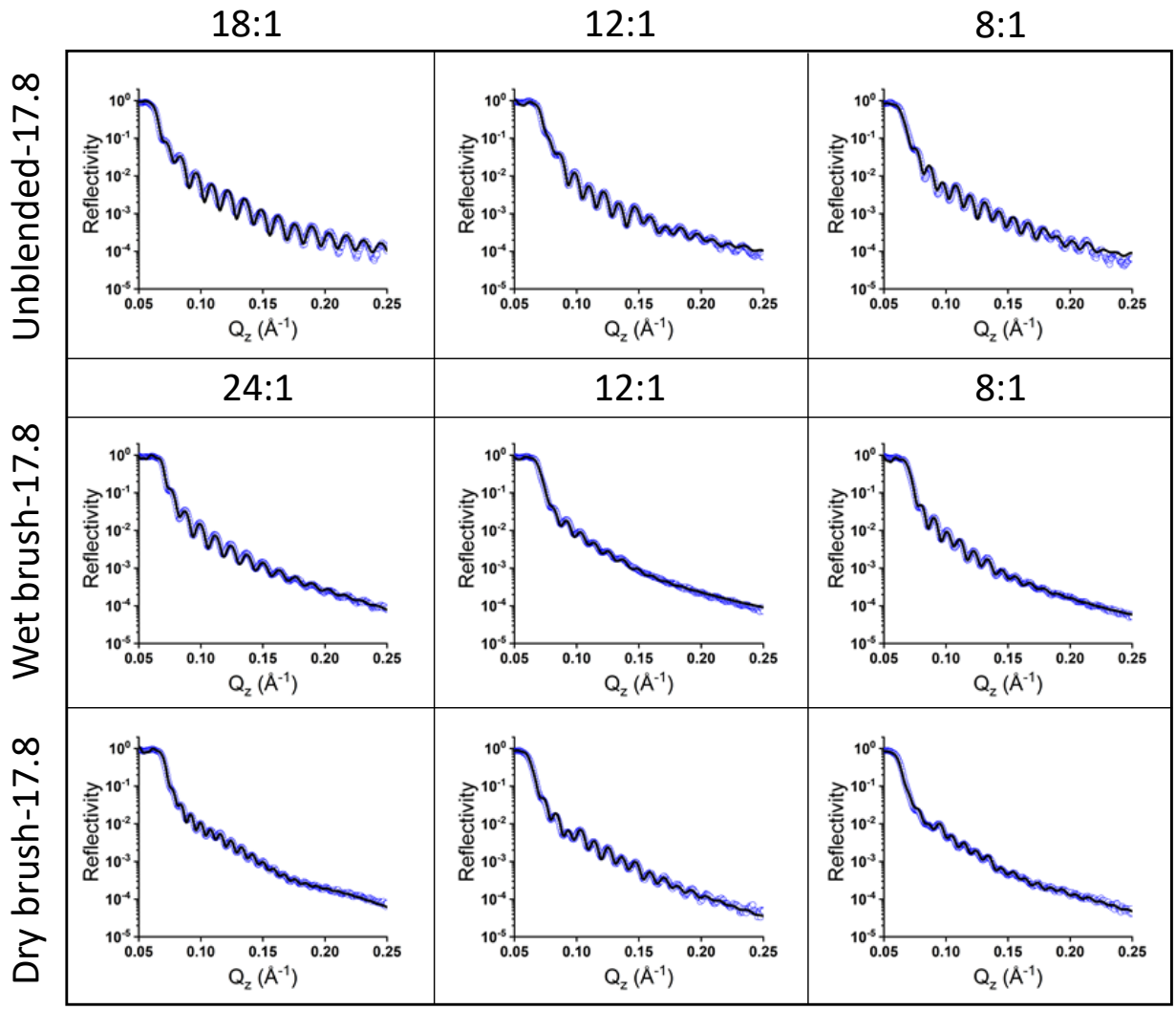

Figure S4: X-ray reflectivity (XRR) profiles (blue circles) and fits (black lines) for Unblended-17.8, Wet brush-17.8, and Dry brush-17.8 for [EO]:[Li] = 24:1 (18:1 for Unblended-17.8), 12:1, and 8:1. All fits had fitting parameter χ^2 approaching 0.001. We note that the χ^2 reported for XRR corresponds to a Pearson's χ^2 test.[1]

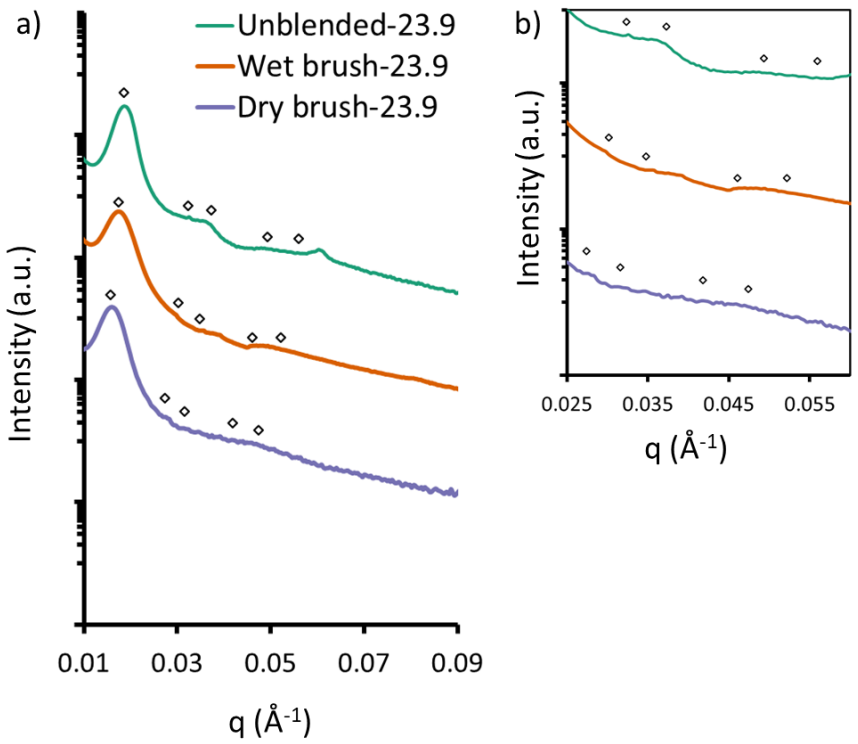

Figure S5: a) Small-angle X-ray scattering (SAXS) profiles of homopolymer-blended block polymer (BP) composite electrolytes Unblended-23.9 (green), Wet brush-23.9 (orange), and Dry brush-23.9 (purple) with b) inset of higher order peaks. White diamonds indicate peak positions of $q/q^* = 1, \sqrt{3}, 2, \sqrt{7}$, and 3, which correspond to a hexagonally-packed cylindrical morphology. Curves are shifted vertically for clarity.

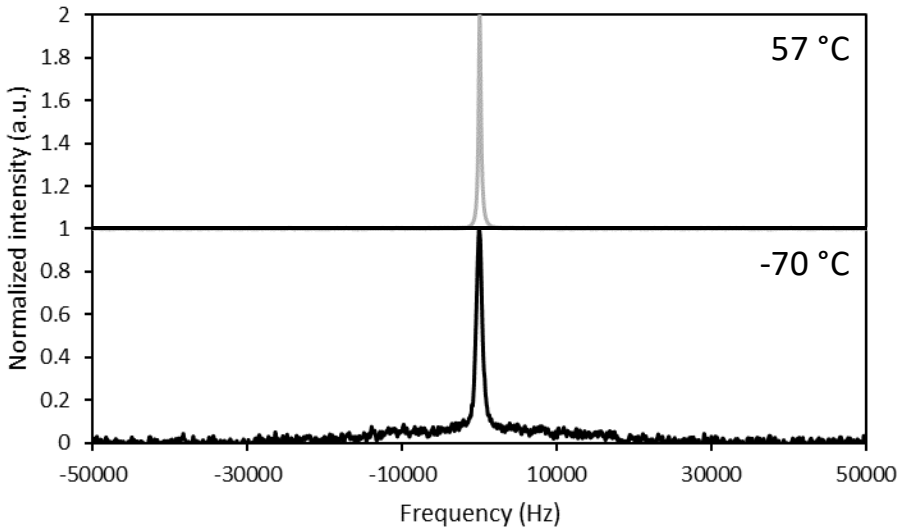

Figure S6: Representative spectra of ^{7}Li linewidth nuclear magnetic resonance (NMR) spectroscopy of Dry brush-23.9 at -70 °C (black) and 57 °C (gray), shifted vertically for clarity. At low temperatures, the spectrum has two peaks: one peak is broader (fit with a Gaussian), and the other is very narrow (fit with a Lorentzian). At high temperatures, the spectrum has only a single, narrower Lorentzian-fittable peak.

Alternating current (AC) impedance spectroscopy fitting:

AC impedance spectroscopy (details of experimental procedure are provided in the Materials and Methods section of the manuscript) was used to determine the ionic conductivity as a function of temperature for samples doped with Li triflate at [EO]:[Li] = 16:1. These data were fit to the Vogel-Fulcher-Tammann (VFT) equation[2] (equation S1)

$$\sigma = \sigma_o e^{\frac{-B}{T-T_o}} \tag{S1}$$

in which σ is the conductivity, σ_o is the pre-exponential factor, B is the effective activation energy, T is the temperature, and T_o is the reference temperature, chosen as $T_o = T_{g,POEM} - 50$ K. Throughout the SI, error bars and uncertainty figures represent one standard error.

Table S2: VFT fitting parameters.

Material	***B* (K)**	**σ_o (S cm^{-1})**
Unblended-23.9	1167 ± 9	$7.6 \times 10^{-3} \pm 4 \times 10^{-4}$
Wet brush-23.9	1108 ± 5	$1.06 \times 10^{-2} \pm 3 \times 10^{-4}$
Dry brush-23.9	1122 ± 18	$2.2 \times 10^{-2} \pm 2 \times 10^{-3}$

Dry brush homopolymer distribution modeling:

To calculate the dry brush homopolymer distribution, equations from reference 3 were used. Briefly, equation S2 defines the homopolymer fraction (Φ_H) as a function of the molecular weights of the BP components ($M_{n,POEM}$ and $M_{n,PS}$) and the mass fraction of homopolymer (x_H) in the system.

$$\Phi_H = \frac{(M_{n,POEM}+M_{n,PS})x_H}{M_{n,PS}+M_{n,POEM}x_H} \tag{S2}$$

The radius of gyration (R_g) of the POEM in the BP was calculated using equation S3 with the calculated values of the statistical segment length (b_{POEM}) from XRR and the volumetric degree of polymerization (N_{POEM}).

$$R_g = \frac{N_{POEM}^{\frac{1}{2}} b_{POEM}}{\sqrt{6}} \tag{S3}$$

With these calculated values, the overlap parameter (w_{OL}) was calculated as detailed in equation S4, using the average value of the POEM domain spacings (l_{POEM}) obtained from the XRR fit.

$$w_{OL} = 1.09 R_{g,POEM} + \frac{3.15 R_{g,POEM}^2}{l_{POEM}(1-\Phi_H)} \tag{S4}$$

Finally, the homopolymer distribution was calculated as a function of position across the POEM domain (x) as shown in equation S5.

$$Homopolymer\ fraction = 0.5(\tanh\left(\frac{\Phi_H l_{POEM} + 2x}{w_{OL}}\right) + \tanh\left(\frac{\Phi_H l_{POEM} - 2x}{w_{OL}}\right)) \tag{S5}$$

Because the NR results suggested that the salt distribution mirrored the POEM distribution throughout the POEM domain, for the 12:1 sample, the salt concentration [EO]:[Li] in the homopolymer was calculated as shown in equation S6.

$$[EO]:[Li]_{homopolymer} = \frac{[EO]:[Li]_{overall}}{Homopolymer\ fraction} \tag{S6}$$

REFERENCES

1. Pearson, K., X. On the criterion that a given system of deviations from the probable in the case of a correlated system of variables is such that it can be reasonably supposed to have arisen from random sampling. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1900,** *50* (302), 157-175.
2. Fulcher, G. S., Analysis of Recent Measurements of the Viscocity of Glasses. *J. Am. Ceram. Soc.* **1925,** *8* (6), 339-355.
3. Shull, K. R.; Winey, K. I., Homopolymer distributions in lamellar copolymer/ homopolymer blends. *Macromolecules* **1992,** *25* (10), 2637-2644.