

Electronic supplementary information for

Controlled Ionic Conductivity via Tapered Block Polymer Electrolytes

Wei-Fan Kuan^a, Roddel Remy^b, Michael E. Mackay^{a,b}, Thomas H. Epps, III^{a,b*}

^a Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

^b Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716

*Corresponding author. Email: thepps@udel.edu

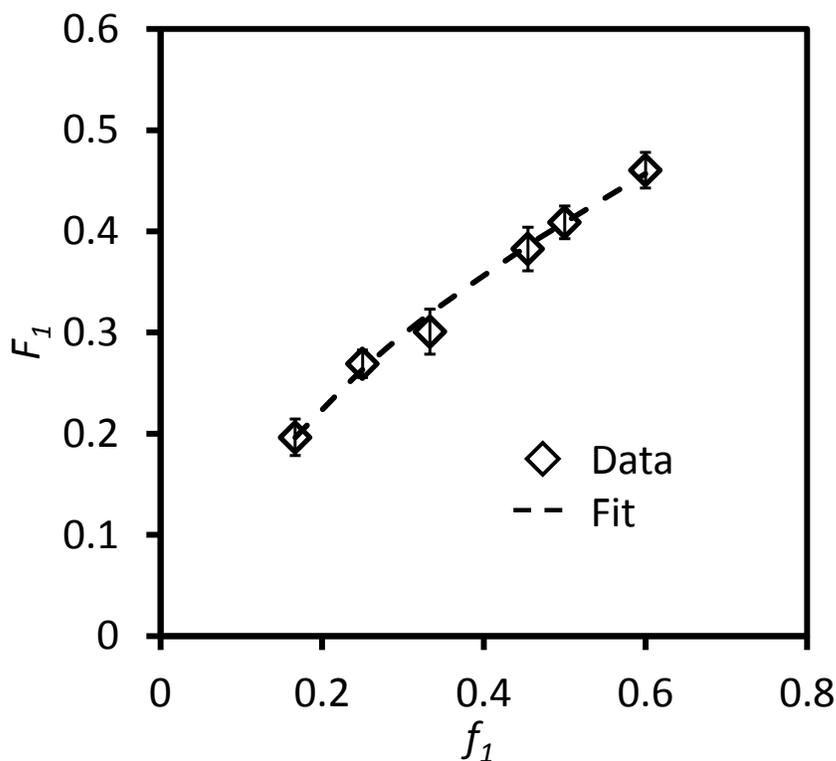


Fig. S1 Reactivity ratio data for styrene (M_1) and *oligo*-oxyethylene methacrylate (M_2) monomers from atom transfer radical polymerization (ATRP) at 90 °C in anisole and fit using the nonlinear Mayo–Lewis equation, $F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)$. f_1 and f_2 are the mole fractions of monomers (M_1 and M_2) in the feed; F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymers. The reactivity ratios from the data fit are $r_1 = k_{11}/k_{12} = 0.13$ and $r_2 = k_{22}/k_{21} = 0.64$, for which k_{11} , k_{12} , k_{22} , and k_{21} are reaction rate coefficients. Error bars represent standard deviation in proton nuclear magnetic resonance (^1H NMR) data.

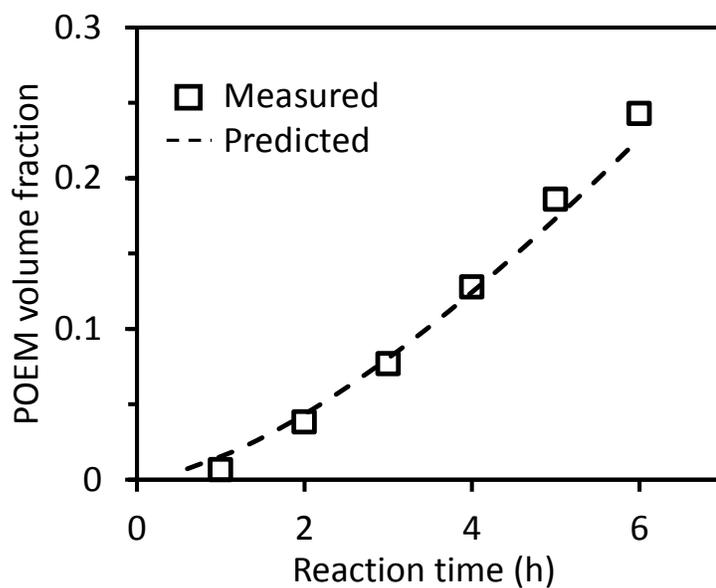


Fig. S2 Predicted (dash line) and measured (square) data for the poly(*oligo*-oxyethylene methacrylate) (POEM) volume fraction change in the taper *versus* ATRP reaction time. POEM volume fraction was determined *via* ^1H NMR. The reported data are from the synthesis of the normal-tapered $\text{P}(\text{S-SOEM-OEM})_{0.32}$ block polymer.

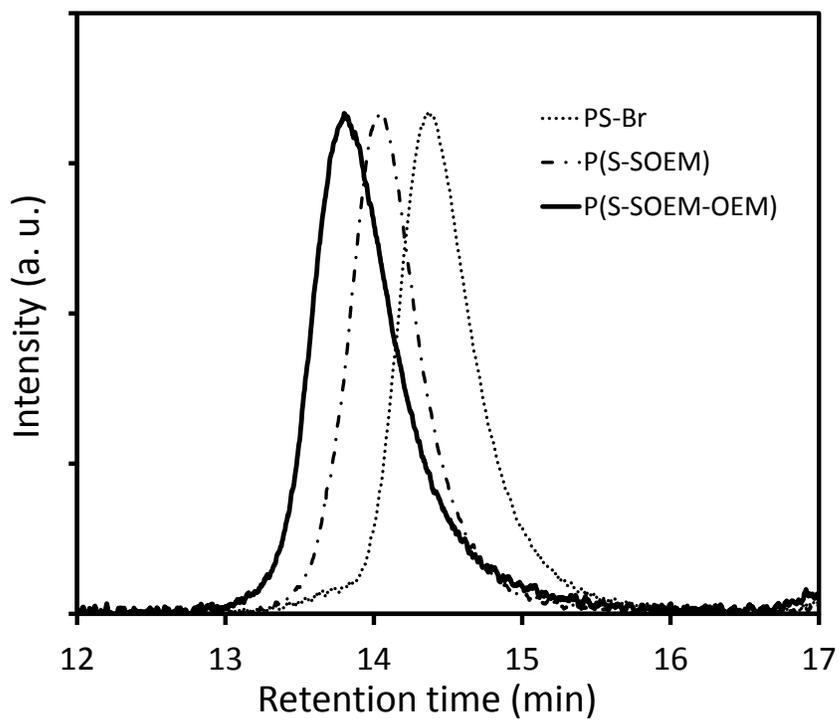


Fig. S3 Representative gel permeation chromatography (GPC) data for the PS-Br macroinitiator, P(S-SOEM) tapered polymer, and P(S-SOEM-OEM) tapered block polymer. The reported data are from the synthesis of P(S-SOEM-OEM)_{0.32}. The GPC flow rate was 1 mL/min.

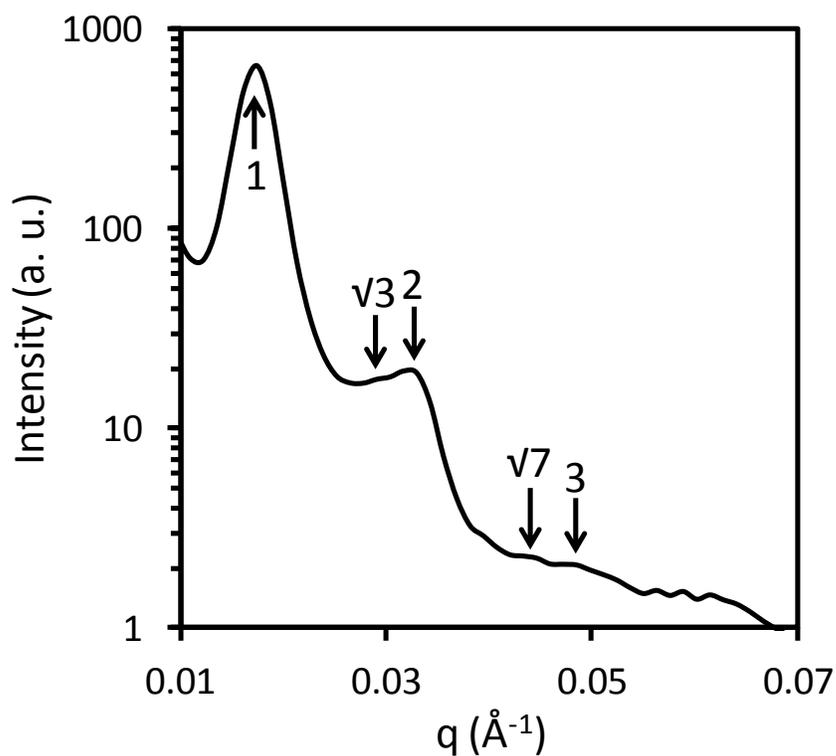


Fig. S4 Azimuthally-integrated small angle X-ray scattering (SAXS) data for LiCF_3SO_3 -doped poly(styrene-*b*-ethylene oxide) [P(S-EO)] at a salt-doping ratio of $[\text{EO}]:[\text{Li}] = 15:1$. Relative peak ratios are indicated by arrows. The domain spacing is 38.8 nm, and the peak ratios suggest a hexagonally-packed cylinder morphology. Data were collected on the lab source SAXS instrument at the University of Delaware.

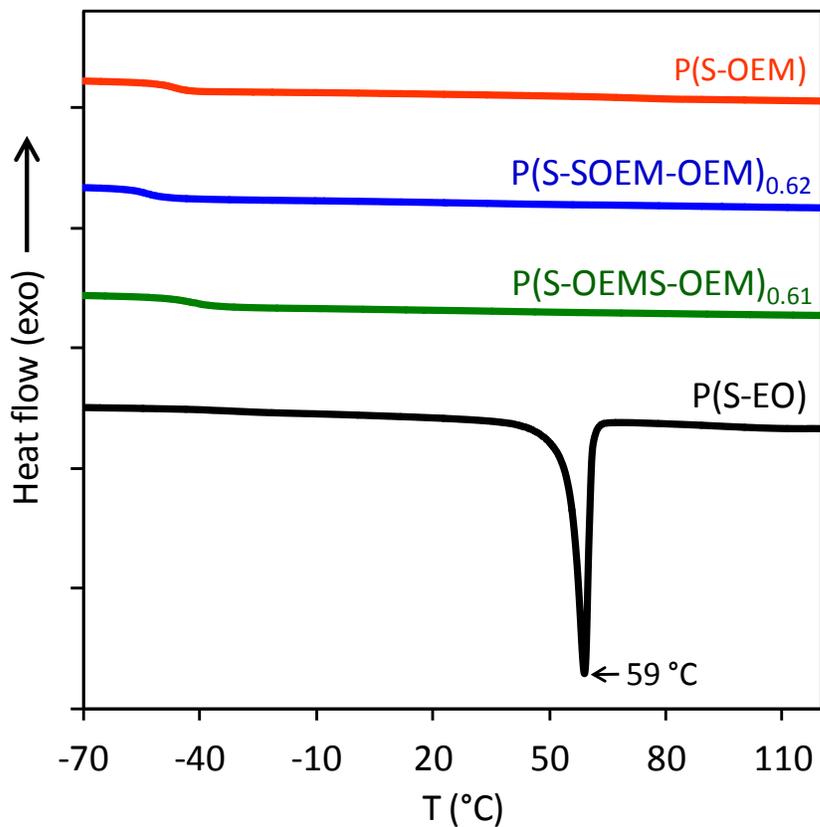


Fig. S5 Third-heating differential scanning calorimetry (DSC) traces of LiCF_3SO_3 -doped P(S-OEM), P(S-SOEM-OEM)_{0.62}, P(S-OEMS-OEM)_{0.61}, and P(S-EO) at [EO]:[Li]= 15:1. Melting peak of PEO is found only in the P(S-EO) sample, suggesting that POEM-based block polymers are amorphous over the entire experimental temperature range. The heating rate was 10 °C/min for all samples. The DSC traces were shifted vertically for clarity.

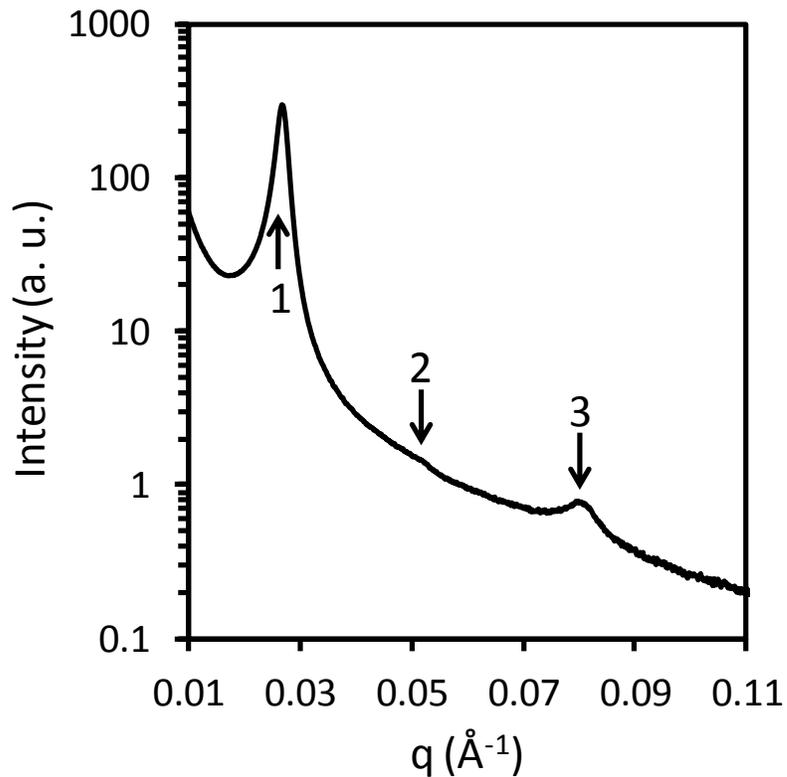


Fig. S6 Azimuthally-integrated SAXS data for LiCF_3SO_3 -doped $\text{P}(\text{S-SOEM-OEM})_{0.32}$ at a salt-doping ratio of $[\text{EO}]:[\text{Li}] = 15:1$. Relative peak ratios are indicated by arrows. The domain spacing is 23.6 nm, and the peak ratios suggest a lamellar morphology. Data were collected on the DND-CAT 5-ID-D beamline at the Advanced Photon Source of Argonne National Laboratory.