[Supporting Information]

# Reentrant phase behavior and coexistence in asymmetric block copolymer electrolytes

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#### **Experimental Section**

#### Polymer Synthesis and Characterization

The polystyrene-b-poly(ethylene oxide) (SEO) copolymers in this study were synthesized via anionic living polymerization. The polystyrene (PS) blocks were grown first from a *sec*-butylithium initiator in benzene. The poly(ethylene oxide) (PEO) blocks were then synthesized using P4 *tert*-butylphosphazene as a catalyst and terminated with methanol. Both syntheses were done in benzene. The copolymers were purified using three rounds of precipitation in ice cold (0 °C) hexanes and subsequent dissolution in benzene. They were then passed through a column of neutral alumina and 1 µm nylon filters to remove residual reaction byproducts until they were no longer seen in <sup>1</sup>H Nuclear Magnetic Resonance (NMR) spectroscopy. The copolymers were freeze-dried in a Millrock LD85 lyophilizer. The molecular weights and polydispersity indices of the PS blocks were obtained from aliquots taken of the copolymers before EO addition by gel permeation chromotopgraphy (GPC) using a tetrahydrofuran (THF)-based Viscotek OmiSEC separations module and triple detection system calibrated with PS standards. The polydispersity indices of the final SEO copolymers were also obtained by GPC using a THF-based Viscotek OmiSec separations module. The volume fractions of each block of the copolymers were determined by <sup>1</sup>H NMR spectroscopy and are given by

$$f_{EO} = \frac{\nu_{EO}}{\nu_{EO} + \frac{M_{PS}M_{EO}}{M_S M_{PEO}}\nu_S}$$

where  $v_{EO}$  and  $v_S$  are the molar volumes of ethylene oxide and styrene monomer units, respectively, and  $M_{EO}$  and  $M_S$  are the molar masses of ethylene oxide (44.05 g mol<sup>-1</sup>) and styrene (104.15 g mol<sup>-1</sup>), respectively.  $M_{PS}$  and  $M_{PEO}$  are the number averaged molecular weights of the PS and PEO blocks in kg mol<sup>-1</sup>, respectively. Molar volumes were calculated by  $v = M/\rho$ . In this study,  $\rho_{PEO} = 1.139-7.31 \times 10^{-4} \times T$ 

and  $\rho_{PS} = 1.0865 - 6.19 \times 10^{-4} \times T + 1.36 \times 10^{-7} \times T^2$  for the densities of the PEO and PS blocks, respectively. The overall degree of polymerization, *N*, was calculated by  $N = N_{PS} + N_{PEO}$  where

$$N_i = \frac{M_i}{\rho_i(T)N_A \nu_{ref}}$$

and  $N_A$  is Avogadro's number and  $v_{ref}$  was fixed at 0.1 nm<sup>3</sup>. The properties of the three copolymers used in this study can be found in Table 1. The neat copolymers are completely transparent and colorless.

#### Small Angle X-Ray Scattering (SAXS) Measurements

SAXS samples were prepared and thermally pre-treated as described in the main text. SAXS measurements were conducted at the Advanced Light Source beamline 7.3.3 at Lawrence Berkeley National Lab and Stanford Synchrotron Radiation Lightsource beamline 1-5 at SLAC National Accelerator Laboratory. Measurement correction was completed as outlined in the main text. In order to compare data collected at each beamline, temperature calibrations were conducted to measure the absolute temperature of the samples by making separate high-density polyethylene samples with a thermocouple running through the sample holder. The data presented in the main text reflects the corrected temperatures of the samples. There was no temperature dependence on phase behavior seen for any of the studied copolymers. Figure SI1 shows the scattering profiles of the electrolytes at the lowest temperature measured, 75 °C. All of the qualitative SAXS features obtained at 132 °C and reported in the main text are also seen at 75 °C (and at all temperatures between these two limits).



Figure SI1: SAXS profiles at 75 °C for a) SEO (9.4-4.0) b) SEO (17.4-3.9) and c) SEO (9.4-2.4) at varying salt concentrations. The symbols marking the primary peaks and higher order reflections match those used in the main text.

### **Electron Tomography**



Figure SI2: Sector-averaged FFT of tomogram slice 10 (red triangles), 20 (blue circles), and 30 (green squares) showing overall intensity as a function of *q*. The arrows indicate the primary peak positions of each BCC lattice detected in SAXS. There is good agreement in sphere-to-sphere spacing between TEM and SAXS throughout the tomogram.

## **References:**

1 D. M. Pesko, K. Timachova, R. Bhattacharya, M. C. Smith, I. Villaluenga, J. Newman and N. P. Balsara, *J. Electrochem. Soc.*, 2017, **164**, E3569–E3575.