# **Supporting information for:**

# High Modulus, High Conductivity Nanostructured Polymer Electrolyte Membranes via Polymerization-Induced Phase Separation

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#### **Experimental Procedures**

#### Synthesis of End-functionalized Poly(ethylene oxide) Precursors

Asymmetrically end-capped poly(ethylene oxide) was synthesized by anionic polymerization from a potassium *tert*-butoxide initiator (1.0 M in THF, Sigma Aldrich) using standard Schlenck techniques ( $M_n = 28 \text{ kg mol}^{-1}$ , D = 1.03). Poly(ethylene glycol) methyl ether was purchased from Sigma Aldrich ( $M_n = 5 \text{ kg mol}^{-1}$ , D = 1.11). The chain transfer agent, (*S*)-1-dodecyl-(*S'*)-( $\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate, was prepared as previously reported,<sup>1</sup> and coupled to the hydroxyl-terminus of each polymer via an acid chloride intermediate to produce macromolecular PEO-CTA.<sup>1</sup> SEC traces of linear PS-*b*-PEO block copolymers prepared and initiated from PEO-CTA in the bulk polymerization of styrene monomer had narrow molecular weight distributions. This result supported complete end-functionalization of PEO and agreed with the quantitative end-group analysis performed using <sup>1</sup>H-NMR spectroscopy.

#### Synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI) was prepared following established procedures.<sup>2,3</sup> A 10% molar excess of 4-chlorobutane was mixed with 1-methylimidazole in a round bottom flask, and cyclohexane was added to the reagents at a volumetric ratio of 10/1. The mixture was heated to reflux conditions and stirred vigorously overnight. Cyclohexane was removed via rotovap and the product, 1-butyl-3-methylimidazole chloride (BMICl), was dried at 60 °C under dynamic vacuum overnight. Lithium bis(trifluoromethylsulfonyl)imide was added to BMICl at 10% molar excess, assuming complete conversion in the first step. DI water was added at a volumetric ratio of 10/1, and the mixture was heated to 70 °C and stirred vigorously for 24 h. The resulting solution phase-separated into BMITFSI and an aqueous phase containing LiCl. BMITFSI was washed with distilled water three times and purified by passing through an

alumina column. <sup>1</sup>H-NMR spectroscopy was used to confirm the final product. The ionic liquid was dried at elevated temperature under dynamic vacuum for 2 d before use.

## **Preparation of Polymer Electrolyte Membranes**

Typical reactions to produce polymer electrolyte membranes were performed in a glass vial without degassing. Styrene (99%, Sigma Aldrich) and divinylbenzene (80%, tech., Sigma Aldrich) were passed through activated alumina columns prior to use. A solution maintained at 30 vol% PEO-CTA was prepared by the sequential addition of macro-CTA, styrene, and divinylbenzene, where the monomer molar ratio was maintained at 4/1, respectively. BMITFSI was added to a predetermined concentration, and the entire solution was well-mixed prior to heating to 120 °C to auto-initiate styrene. The use of AIBN as an external initiator (0.05 *eq* to PEO-CTA) was necessary for the uniform generation of radicals to prevent density inhomogeneities that would otherwise induce cracks during polymerization. The resulting transparent, solid monolith could be sanded to a flat surface of ca. 500  $\mu$ m thickness for additional analysis.

#### **Transmission Electron Microscopy**

Bulk samples were microtomed at room temperature on a Leica UC6 Ultramicrotome to obtain sections with a nominal thickness of 70 nm. Sample sections were collected on a 300 mesh copper grid and were stained with the vapor of a 0.5 wt% RuO<sub>4</sub> aqueous solution for 5 min. On this time-scale, RuO<sub>4</sub> preferentially stains poly(ethylene oxide), which appears dark in TEM images. Sections were imaged at room temperature on an FEI Tecnai G2 Spirit Bio-TWIN using an accelerating voltage of 120 kV. Images were collected by a 2048 × 2048 pixel CCD. ImageJ software was used to generate Fourier transforms (FTs) of TEM images and then azimuthally integrate pixel intensity to generate 1D plots of intensity versus the wave vector, *q*.

#### **Small-Angle X-ray Scattering**

Small-angle X-ray scattering (SAXS) experiments were performed at the Argonne National Lab Advanced Photon Source beamline 5-ID-D, which is maintained by the DuPont-Northwestern-Dow Collaborative Access Team. Samples were exposed at room temperature to synchrotronsource X-rays with a nominal wavelength of 0.729 Å. Scattered X-rays were collected on a 2D MAR CCD detector located at a sample-to-detector distance of 5680 mm. The sample-to-detector distance was calibrated using a silver behenate standard, and intensity was calibrated with glassy carbon. 2D SAXS intensity was reduced to a function of the magnitude of the wave vector, q, by azimuthally integrating the 2D data. q is given by  $q = 4\pi \sin(\theta/2)/\lambda$ , where  $\lambda$  is the X-ray wavelength and $\theta$  is the scattering angle.

## Impedance Spectroscopy

Ionic conductivity was measured using 2-point probe impedance spectroscopy on a Solartron 1255B frequency response analyzer connected to a Solartron SI 1287 electrochemical interface. Bulk polymer electrolyte membrane samples were sanded to uniform thickness (ca. 0.5 mm) and sandwiched between stainless steel electrodes. Impedance was measured over the frequency range from  $10^6$ –1 Hz using a voltage amplitude of 100 mV. Bulk resistance, *R*, was determined from the frequency-independent plateau of the real part, *Z'*, of impedance. Ionic conductivity,  $\sigma$ , was calculated as  $\sigma = l/(Ra)$ , where *l* is the sample thickness and *a* is the superficial area. Thickness was measured with a Mitutoyo micrometer (1  $\mu$ m resolution) and area was measured using ImageJ software. Samples were stored in either an Ar-filled glovebox or under dynamic vacuum. Each sample was heated under dynamic vacuum (100 mTorr) for at least one day prior to running impedance experiments. Impedance measurements were performed in an open atmosphere at temperatures from 30 to 150 °C in 10 degree increments. Each temperature was maintained for 1 h prior to measurement to ensure thermal equilibration. Replicate measurements were performed in series to observe the

effect of possible water absorption on the conductivity for temperatures below 100 °C. The reproducibility of conductivity measurements over the entire temperature range for polymer electrolyte membranes that contained only ionic liquid indicated that these samples do not exhibit a strong affinity for water. Repeated measurements of the conductivity of LiTFSI-containing samples, however, indicated that these samples were highly absorptive. For this reason, these samples were heated to 100 °C for 3 h prior to measurement and temperatures were restricted to 100–150 °C.

## Rheology

Mechanical response was measured in the linear viscoelastic regime using an RSA-G2 Solids Analyzer (TA Instruments). Samples prepared for mechanical response measurements were polymerized in Teflon molds to produce samples with the appropriate geometry. These tensile bars measured approximately  $50 \times 10 \times 1$  mm. To generate time-temperature superposition (tTS) master curves, samples were heated to a series of increasing temperatures and thermally equilibrated at a given temperature for at least 10 min. Strain sweeps were performed at a radial frequency of 10 rad/s to determine the limit of linear viscoelastic response, followed by a frequency sweep performed at fixed strain over the frequency range from 100–0.1 rad/s. Raw data were shifted horizontally by visual alignment of the elastic modulus, *E'*.

## **Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments Discovery DSC. Samples for measurement were prepared using standard aluminum T-zero pans with standard or hermetic lids. Each sample was annealed at 200 °C for 5 min. Subsequent cooling and heating ramps were applied at 5 °C/min. Heats of fusion were estimated from the

endotherm of the second heating and the weight fraction of PEO incorporated into the crosslinked block polymer. Percent crystallinity was calculated in reference to the enthalpy of fusion of 213.4 J/g for pure crystalline PEO.<sup>4</sup>



Figure S1: Small angle X-ray scattering data of polymer electrolyte membrane samples prepared with (a) 5 and (b) 28 kg mol<sup>-1</sup> PEO-CTA and various concentrations of the ionic liquid BMITFSI. Domain size increases (the primary scattering peak shifts to lower q) with increasing PEO-CTA molar mass and increasing ionic liquid content (reported as overall vol%).



Figure S2: (a) Transmission electron micrographs of polymer electrolyte membrane samples prepared from 28 kg mol<sup>-1</sup> PEO-CTA without ionic liquid and 21 vol% BMITFSI. RuO<sub>4</sub> staining of the PEO/ionic liquid phase was used to enhance contrast. The scale bars represent 100 nm. (b) The corresponding Fourier transform (FT) analysis of the TEM image above. Pixel intensity in the FTs was integrated azimuthally and plotted versus wavevector q in the inset. The upper curve is the integrated FT and the lower curve is the small-angle X-ray scattering (SAXS) data of the sample. The red arrow points to the feature in the FT that appears as a peak in the inset. The close agreement between peaks in the integrated FT and the SAXS data confirms that the TEM images accurately represent the bulk morphology.



Figure S3: Differential scanning calorimetry thermograms (exo down) for polymer electrolyte membranes prepared with (a) 5 kg mol<sup>-1</sup> and (b) 28 kg mol<sup>-1</sup> PEO-CTA and various concentrations of the ionic liquid BMITFSI. The presented traces were collected during the second heating at a ramp rate of 5 °C/min.



Figure S4: Conductivity in a heterogeneous PEM sample ( $\Box$ ) is reduced relative to a PEO/ionic liquid homogeneous electrolyte ( $\bigcirc$ ) of the same composition. The conductivity of pure BMITFSI (dashed line) is also shown for reference. The homogeneous electrolyte was prepared from an 8 kg mol<sup>-1</sup> PEO homopolymer/BMITFSI mixture (50 vol%), and the heterogeneous PEM sample was prepared with 28 kg mol<sup>-1</sup> PEO-CTA and BMITFSI at 21 overall vol%. In the conducting phase of the heterogeneous electrolyte, the resulting concentration of ionic liquid is 46 vol%. In both cases, only segmental motion contributes to ion transport.<sup>5</sup> The red region is defined by a tortuosity of 1.5 (upper bound) and 3 (lower bound).



Figure S5: Linear viscoelastic master curves of representative polymer electrolyte membranes prepared from 5 kg mol<sup>-1</sup> (upper) and 28 kg mol<sup>-1</sup> (lower) PEO-CTA (a) without ionic liquid and (b) with 21 vol% BMITFSI. Frequency sweeps were collected from room temperature up to ca. 200 °C. Colored numbers indicate the temperature of the corresponding frequency sweep. Data of (a) and (b) show the elastic modulus, E' ( $\Box$ ), and the viscous modulus, E'' ( $\bigcirc$ ), versus reduced frequency,  $a_{T}\omega$ , for samples without ionic liquid and samples containing 21 vol% BMITFSI, respectively. The inset graphs display the temperature-dependent shift factors,  $a_{T}$ , for the sample without ionic liquid ( $\triangle$ ) and the sample with 21 vol% BMITFSI ( $\diamondsuit$ ).



Figure S6: Photographs of the macrophase separation observed in samples that are (a) the product of polymerization of styrene and divinylbenzene in the presence of free CTA and no PEO-CTA and (b) the product of polymerization of styrene and divinylbenzene in the presence of free CTA and 5 kg mol<sup>-1</sup> PEO-OH. These experiments indicate that domain connectivity achieved in the *in situ* synthesis of a diblock copolymer is necessary to produce a homogeneous structure. Sample sizes are of order 1 cm.



Figure S7: Scanning electron micrographs comparing a PIPS PEM sample prepared with 28 kg  $mol^{-1}$  PEO-CTA and 21 vol% BMITFSI, before (inset) and after (main panel) etching out PEO/IL with 57 wt% hydroiodic acid. Both samples were freeze-fractured to expose a fresh surface and were coated with 1–2 nm of Pt prior to imaging. Both scale bars represent 500 nm.

Composition (vol%) <sup>a</sup>							
$M_{\rm n}$ PEO-CTA (kg mol <sup>-1</sup> )	type of salt	salt <sup>b</sup>	$PEO + salt^{c}$	salt in PEO + salt domain <sup>d</sup>	$T_{g}$ (°C)	$ riangle H_{\rm m}  ({ m J g}^{-1})$	crystallinity (%)
5	BMITFSI	0	32	0	-52	17.2	25
5	BMITFSI	5	35	15	-58	18.2	28
5	BMI/LiTFSI	7	36	18	-	-	-
5	BMITFSI	21	47	45	-58	-	-
5	BMI/LiTFSI	21	47	45	-	-	-
5	BMITFSI	30	52	57	-61	-	-
5	BMITFSI	40	59	67			
28	BMITFSI	0	32	0	-	28.7	42
28	BMITFSI	4	32	12	-	28.1	43
28	BMITFSI	21	47	46	-66	16.5	32
28	BMITFSI	30	52	59	-64	10.9	25

# Table S1: Properties of polymer electrolyte samples

<sup>a</sup>Composition was calculated using the known mass incorporated into the sample and the following densities (in g cm<sup>-3</sup>):  $\rho_{PSDVB} = 1.05$ ,  $\rho_{PEO} = 1.064$ ,  $\rho_{BMITFSI} = 1.328$ ,  $\rho_{LiTFSI} = 1.334$ <sup>b</sup>Overall volume percent of ionic liquid or a mixture of ionic liquid and LiTFSI <sup>c</sup>Volume percent of the conducting phase

<sup>d</sup>Volume percent of salt in the conducting phase

Table S2:	VFT Para	meters for	the co	onductivit	y profiles	in F	Figure 2
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Composition (vol%)								
salt	PEO + salt	salt in PEO + salt domain	$\sigma_0$ (S/cm)	<i>B</i> (K)	$T_0(\mathbf{K})$			
40	59	67	0.59	884	178			
21	47	45	0.85	1333	152			
21	47	45	1.0	1467	136			
5	35	15	0.0064	749	223			
36	7	18	0.026	841	204			
	salt 40 21 21 5 36	Composition           salt         PEO + salt           40         59           21         47           21         47           5         35           36         7	Composition (vol%)saltPEO + saltsalt in PEO + salt domain4059672147452147455351536718	Composition (vol%)saltPEO + saltsalt in PEO + salt domain $\sigma_0$ (S/cm)4059670.592147450.852147451.0535150.0064367180.026	Composition (vol%)saltPEO + saltsalt in PEO + salt domain $\sigma_0$ (S/cm)B (K)4059670.598842147450.8513332147451.01467535150.0064749367180.026841			

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