## Supporting Information for

# Effect of Morphology of Nanoscale Hydrated Channels on Proton Conductivity in Block Copolymer Electrolyte Membranes

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This file includes: experimental information on the synthesis of material, water uptake and conductivity measurements, small angle X-ray scattering and scanning transmission electron microscopy measurements.

**Synthesis and characterization of polymer:** Polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer was synthesized by sequential anionic polymerization of styrene and butadiene, using sec-butyl lithium as the initiator, followed by the coupling of polystyrene-*block*-polybutadiene using dibromoethane to yield a symmetric polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer.[S1] The use of a nonpolar solvent (cyclohexane) resulted in approximately 93% 1,4-addition of the butadiene monomers. SBS was hydrogenated using p-toluenesulfonyl hydrazide in the presence of equimolar tri-n-propyl amine, to yield polystyrene-*block*-polyethylene-*block*-polystyrene (SES). SES copolymers were purified by precipitation into hydrochloric acid/methanol mixtures, followed by redissolving in *o*-xylene at 100 °C and precipitating into hydrochloric acid/methanol mixture for two more times, then washed in a separatory funnel with excess deionized water for three times, and subsequently redissolved in *o*-xylene at 100 °C and precipitated in pure methanol for three times. Finally it was dried under vacuum at 80 °C for 10 days.

The molecular weights of PS and polybutadiene (PB) blocks of the SBS copolymer were obtained by measuring aliquots of the reaction mixture extracted during synthesis, with a Viscotek GPC Max VE-2001 equipped with a TDA 302 triple-detector system, calibrated using PS standards with tetrahydrofuran (THF) as the eluent. The volume fractions of PS and PB of the SBS copolymer and the ratio of 1,4-addition over 1,2-addition in the PB blocks of the copolymer were determined using $^1$H nuclear magnetic resonance (NMR) spectroscopy ($CDCl_3$, 25 °C). High temperature NMR (toluene-$d_8$, 90 °C) was used to ensure the complete saturation of the vinyl groups in the polybutadiene block of SBS to yield SES. The polydispersity indices of the PS and PB components of SBS were both 1.02. The physical characterizations of SES are described in Table S1.

**Table S1** Physical characteristics of SES.

| Polymer | PS $M_n$ (kg/mol) | PE $M_n$ (kg/mol) | PS volume fraction |
|---|---|---|---|
| SES | 13.8 | 37.4 | 0.41 |

**Membrane preparation and sulfonation:** SES was dissolved in *o*-xylene and gently stirred at 100 °C for 4 hours. The solution was then casted on ultraclean aluminum foil on a custom-built solvent caster heated to 80 °C, using a doctor blade. The concentration of the solution and the height of the doctor blade were adjusted to obtain a membrane with a thickness of 40 ± 5 µm. The membrane was then dried in vacuum at 80 °C for 24 hours. After drying, the aluminum foil was removed by immersing in 1M hydrochloric acid. Resulting free-standing membrane was washed with deionized water several times and dried in vacuum for overnight. We did not attempt to investigate the effect of annealing temperature on the water uptake, proton conductivity and morphology of the membranes.

SES membrane was sulfonated as one piece in a custom-designed three-neck reactor. Specifically, a circular membrane of 2 inch in diameter was punched out and held in place with a Teflon clamp inside the reactor. 90 mL of 1, 2-dichloroethane (Sigma-Aldrich) was added to the reactor. The mixture was heated to 40 °C and stirred under dry $N_2$ environment for an hour. Acetic sulfate was prepared by injecting 4.8 mL of acetic anhydride (Sigma-Aldrich) and 14.4 mL of 1,2-dichloroethane into a sealed $N_2$ purged round bottom flask in an ice bath. The solution was allowed to cool to 0 °C before injecting 1.6 mL of 96% sulfuric acid (Sigma-Aldrich) into the flask. The mixture was immediately transferred to the reactor through an addition funnel. After 4 hours, the reaction was terminated with 20 mL of methanol. The sulfonated SES (S-SES) membrane was washed with methanol several times and then soaked in deionized water for 5 days, replaced with fresh deionized water every day. Membranes were kept in deionized water prior to measurements.

**Sulfonation level determination:** The sulfonation level (SL) of S-SES, specified in equation S1, where SSA is styrene sulfonic acid and S is styrene, was determined using an ion exchange capacity (IEC) measurement method.

$$\mathrm{SL} = \frac{\mathrm{mol\ SSA}}{\mathrm{mol\ S} + \mathrm{mol\ SSA}} \tag{S1}$$

IEC, defined as the milliequivalents of sulfonic acid groups per dry gram of polymer (mmol/g), was measured using the following procedure: [S2] a piece of water-equilibrated membrane was immersed in 1M NaCl solution, gently stirred overnight. Membrane was subsequently removed from solution. The solution was titrated with standard volumetric NaOH solution to the phenolphthalein endpoint. The membrane was then soaked in 0.1 M hydrochloric acid for 2 hours, washed with deionized water several times and soaked in deionized water for overnight. Finally the membrane was dried in vacuum at room temperature for 24 hours and then at 80 °C for two hours. It was allowed to cool down in a desiccator before the dry weight, $W_{\mathrm{dry}}$, was measured. IEC is calculated using equation S2.

$$\mathrm{IEC\ (mmol/g)} = \frac{\text{volume of NaOH solution (mL)}\times\text{concentration of NaOH solution (M)}}{W_{\mathrm{dry}}\ \mathrm{(g)}} \qquad (S2)$$

**Water uptake:** Water uptake of water equilibrated S-SES was obtained by measuring the wet weight, $W_{\mathrm{wet}}$, of a piece of water equilibrated membrane after dabbing off the surface water with Kimwipe. The membrane was subsequently dried in vacuum at room temperature for 24 hours and then at 80 °C for two hours. It was allowed to cool down in a desiccator before $W_{\mathrm{dry}}$ was measured. Water uptake is given by equation S3.

$$\text{water uptake} = \frac{W_{wet}-W_{dry}}{W_{dry}} \times 100\% \qquad \text{(S3)}$$

Hydration number, $\lambda$, specified as the number of water molecules per sulfonic acid group, can thus be calculated from water uptake and IEC of S-SES, given by equation S4.

$$\lambda = \frac{water\ uptake\ (\%) \times 10}{MW_{H2O}\ \times IEC} \qquad \text{(S4)}$$

Where $\mathrm{MW_{H2O}}$ = 18.02 g/mol.

Water uptake of S-SES equilibrated in humid air was measured in a humidity-controlled environmental chamber (SH-241, Espec. Corp). A small piece of water-equilibrated membrane was placed in a quartz pan which was hooked on the end of a quartz spring (Deerslayer) in the humidity chamber. The membrane was equilibrated at each humidity level for 48 hours. $W_{\mathrm{wet}}$ was obtained by measuring spring length through a port on the wall of the humidity chamber by a cathetometer equipped with an optical zoom telescope located outside the chamber. Care was taken to minimize the time when the port was opened (typically 10 s). The spring was calibrated with standard masses at experimental temperatures and relative humidity in the chamber before use (spring constant was about 0.5 mN/mm). $W_{\mathrm{dry}}$ of humid air-equilibrated membranes was measured following the same procedure as described above. Water uptake and $\lambda$ were calculated from equation S3 and S4, respectively.

**Conductivity:** Free-standing membranes of S-SES with dimension 3 cm × 0.5 cm were prepared for conductivity measurements by cutting from the bulk water-equilibrated membrane using a razor blade. The membrane was soaked in 1M HCl for overnight and washed with deionized water for a few times. It was then allowed to soak in deionized water for 24 hours with frequent changing of water. Thickness of the membranes was measured using a micrometer. In-plane proton conductivity of water-equilibrated membranes was measured in deionized water by ac impedance spectroscopy using platinum electrodes in the standard four-probe configuration using a BekkTech sample clamp. Data were collected over a frequency range of 1 Hz-100 kHz. Proton conductivity measurements of S-SES equilibrated in humid air were performed in the same humidity chamber for water uptake measurements. Membrane was allowed to equilibrate at each humidity level for 48 hours before a measurement was taken. Conductivity, $\sigma$, is given by:

$$\sigma = \frac{l}{w \times h \times R} \tag{S5}$$

where $w$ and $h$ are width and thickness of the membrane, respectively, $R$ is the touchdown of the Nyquist semicircle on the real axis, and $l$ is the distance between the inner platinum electrodes.

**Morphology of the membranes:** Morphology of the membranes was characterized with synchrotron small angle X-ray scattering (SAXS) and scanning transmission electron microscopy (STEM).

**SAXS:** Samples equilibrated in liquid water were prepared by sealing a small piece of water-equilibrated membrane in a Teflon washer filled with water. The Teflon washer was sandwiched between two pieces of kapton films and sealed with heat resistant sealant. Samples equilibrated in humid air was measured in a custom designed humidity stage as reported previously.[S3] Samples were equilibrated for 30 minutes at each relative humidity level before measurements were taken. Synchrotron SAXS was performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). [S4] The original two-dimensional scattering images were azimuthally averaged to generate one-dimensional scattering intensity profiles, $I(q)$. The scattering wave vector $q = 4\pi\sin(\theta/2)/\lambda$, where $\theta$ is scattering angle and $\lambda$ is the wavelength of the incident beam.

**STEM:** Thin sections of dry S-SES with thickness of approximately 70 nm were obtained by cryo-microtoming using a Leica EM FC6 and picked up on a lacey carbon supported copper grid (Electron Microscopy Sciences). Hydrated samples were prepared by annealing dry microtomed samples in a humidity-controlled FEI Vitrobot. Water-equilibrated samples were annealed by casting 300 µL of water on the both sides of copper grid placed inside the Vitrobot, with an environmental relative humidity (RH) of 100%. Samples equilibrated in humid air were annealed inside the Vitrobot with a controlled RH of 95%, without applied water. It's worth mentioning that the control of RH in the Vitrobot is less accurate than that used in water uptake, conductivity and SAXS measurements. After equilibration with water or humid air, samples were quickly plunged into liquid ethane and transferred into liquid nitrogen. STEM experiments were performed on a Tecnai F20 UT FEG, equipped with a high angle annular dark field (HAADF) detector, using 200 keV acceleration voltage. Dry samples were imaged at room temperature. Hydrated samples were imaged at −184 °C, using a Gatan 914 high tilt cryo-stage. Images were analyzed in Digital Micrograph and ImageJ. Domain spacings obtained from FFT analysis were averaged from at least 9 images on different areas of each sample. Domain spacings calculated from line scans were averaged from 5-9 images with 6-8 lines per image.

## References

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