Supplementary Material (ESI) for Journal of Materials Chemistry
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Supporting information

S1. Solvent uptake studies.

The membrane solvent uptake was determined in equilibrium with water and water-methanol mixture (30% Methanol), separately, using the following equation:

$$Water\ uptake\left(\varphi_w\right)= {W_{wet}-W_{dry}}\Big/{W_{dry}} \times 100\% \qquad (1)$$

where W_{wet} and W_{dry} is the mass of membrane in wet and dry condition.

Number of water molecules associated per ionic sites (λ_w) was calculated according to the following relationship:

$$\lambda_w = \frac{\left(W_h - W_d\right)\big/MW_{H_2O}}{IEC \times W_d} = \frac{\varphi_w}{IEC \times MW_{H_2O}} \qquad (2)$$

where MW_{H2O} is the molecular weight of water.

S2. Water retention studies.

The water retention ability of the developed membranes was evaluated by measuring water mobility during the dynamic deswelling test. Fully swollen membranes were placed in desiccators containing silica gel (drying agent) at 35 ºC and were weighed after regular intervals. The weight of fully swollen membranes (W_{wet}), weight of membrane at time t (W_{t}), and weight of dry membrane (W_{dry}) were recorded. The deswelling profile can be obtained by plotting (M_t/M_0)-time curves using the following equation:

$$M_t\big/M_0 = 4\left(\frac{D\,t}{\Pi\, l^2}\right)^{1/2} \qquad (3)$$

where M_0 is the initial amount of water in membrane ($M_0 = W_{\mathrm{wet}} - W_{\mathrm{dry}}$), and M_t is the amount of water remaining in the membrane at any given time ($M_t = W_t - W_{\mathrm{dry}}$), D is water diffusion coefficient, and l is the membrane thickness.

S3. Ion-exchange capacity (IEC) measurements.

IEC indicates the number of mili equivalents of exchangeable charge in 1.0 g of the dry polymer matrix. For *IEC* measurements, the dry membrane samples were equilibrated with acid and base, repeatedly to ensure conversion of sulfonate to sulfonic acid groups. The membranes were then washed with deionized water to remove last trace of acidity. Afterwards, equilibrated membrane samples were immersed in 50 cm^3 0.1 M NaCl solution for 24 h under random stirring at ambient temperature. Then 10 cm^3 of sample solution was titrated against standard NaOH solution. The sample was regenerated with 1.0M hydrochloric acid, washed to free of acid with deionized water and dried to a constant weight. The *IEC* was calculated according to the equation:

$$IEC\left(mequiv.g^{-1}\,dry\,membrane\right) = \frac{C_{Na^+} V_{sol}}{W_{dry}} \qquad (4)$$

Where W_{dry} is the weight of the membrane sample under dry condition.

S4. Dimensional, oxidative and hydrolytic stabilities.

Dimensional stability was examined by immersing the square pieces of the membranes in to room temperature water and 50% water-methanol for 24 h. The dimensional changes in the membranes due to their swelling in water or methanol-water solution were determined by measuring the variation in length, width and thickness. A change in the ratio of the ‘swollen’ length to the ‘dry’ length of the membranes was calculated by using the following relationship:

$$\Delta L_x = \left(L_x - L_{xo}\right) \big/ L_{xo} \qquad (5)$$

where L_x may be the length/width/thickness of the swollen membrane and subscript 'o' denotes the dimensions in the ambient conditions. Changes in volume fraction (Φ) of different synthesized membranes were estimated by following equation:

$$\Phi = \frac{\left(L_x L_y L_z - L_{xo} L_{yo} L_{zo}\right)}{L_x L_y L_z} \qquad (6)$$

Oxidative stability was evaluated by immersing the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 3 ppm $FeSO_4$) at 80 ºC for 1 h. For hydrolytic stability test, a small piece of membrane was boiled in water for 24 h at 140 ºC in a pressurized closed vial. The loss in weight due to oxidative and hydrolytic treatment was recorded and termed as oxidative and hydrolytic weight loss.

S5. Membrane conductivity measurement.

Membrane conductivity measurements were carried out in equilibration with water using a potentiostat/galvanostat frequency response analyzer (Auto Lab, Model PGSTAT 30). The membranes were sandwiched between two in-house made stainless steel circular electrodes (4.0 cm^2). Direct current (DC) and sinusoidal alternating currents (AC) were supplied to the respective electrodes for recording the frequency at a scanning rate of 1 μA/s within a frequency range of 10^6 to 1 Hz. The spectrum of the blank short-circuited cell was also collected and this data was subtracted (as a series circuit) from each of the recorded spectra of the membranes to eliminate cell and wiring resistances and inductances. The corrected spectra were viewed as complex impedance plots with the imaginary component of Z'' on the y-axis and the real component of Z' on the x-axis ($Z = Z' - iZ''$); the ionic resistance of each membrane was estimated to be the intersection of the x-axis with the extrapolation of the low frequency linear component of each plot. The membrane resistances were obtained from Nyquist plots. The proton conductivity (κ^m) was calculated from eq:

$$\kappa^m(S/cm) = L(cm) \Big/ \left[R(\Omega) \times A(cm^2)\right] \qquad (7)$$

where, L is the distance between the electrodes used to measure the potential, R is the resistance of the membrane, and A is the surface area of the membrane.

S6. Methanol permeability measurements.

Methanol permeability of the composite membranes was determined in a diaphragm diffusion cell, consisting of two compartments (80 cm^3) separated by a vertical membrane with 20 cm^2 effective area. The membrane was clamped between both compartments, which were stirred during the experiments. Before the experiment, membranes were equilibrated in water-methanol mixture for 12 h. Initially, one compartment (A) contained 30 or 50% (v/v) methanol-water mixture while other (B) double distilled water. Methanol flux arises across the membrane as a result of concentration difference between two compartments. The increase in methanol concentration with time in compartment B was monitored by measuring the refractive index using a digital refractometer (Mettler Toledo RE40D refractometer). The methanol permeability (P) finally was obtained by the equation given below:

$$P \;=\; \frac{1}{A}\,\frac{C_{B(t)}}{C_A(t-t_0)}\,V_B\,l \qquad (8)$$

where A is the effective membrane area, l the thickness of the membrane, $C_{B(t)}$ the methanol concentration in compartment B at time t, $C_A(t - t_0)$ the change in the methanol concentration in compartment A between time 0 and t, and V_B the volume of compartment B. All experiments were carried out at room temperature, and the uncertainty of the measured values was less than 2%.

S7 Solubility of the cross-linked membrane

Solubilities of the PES, SPES, and CPES-100 membranes were tested in common organic solvents and boiling water (neutral pH). Relevant observations are listed below.

Solvents	PES	SPES	CPES-100	Remarks
N,N-Dimethylformamide	Y	Y	Y	Soluble at room temperature
N,N-Diethylacetamide	Y	Y	Y	Soluble at room temperature
N-methyl-2-pyrolidone	Y	Y	Y	Soluble at room temperature
Dimethyl sulfoxide	Y	Y	Y	Soluble at room temperature
Chloroform	Y	N	N	Some swelling was observed in SPES and CPES-100
Water (under boiling condition at pH 7)	N	PS	N	SPES showed more swelling compared to CPES-100
Methanol	N	PS	PS	SPES was more soluble compared to CPES-100
Acetone	N	N	N	CPES-100 showed some amount of swelling
Tetrahydrofuron	N	N	N	No swelling was observed
Hexane	N	N	N	No swelling was observed

Y=soluble; N=insoluble; and PS=partially soluble

Figure S1. Peak assignment of ^{1}H NMR of BAPBDS.

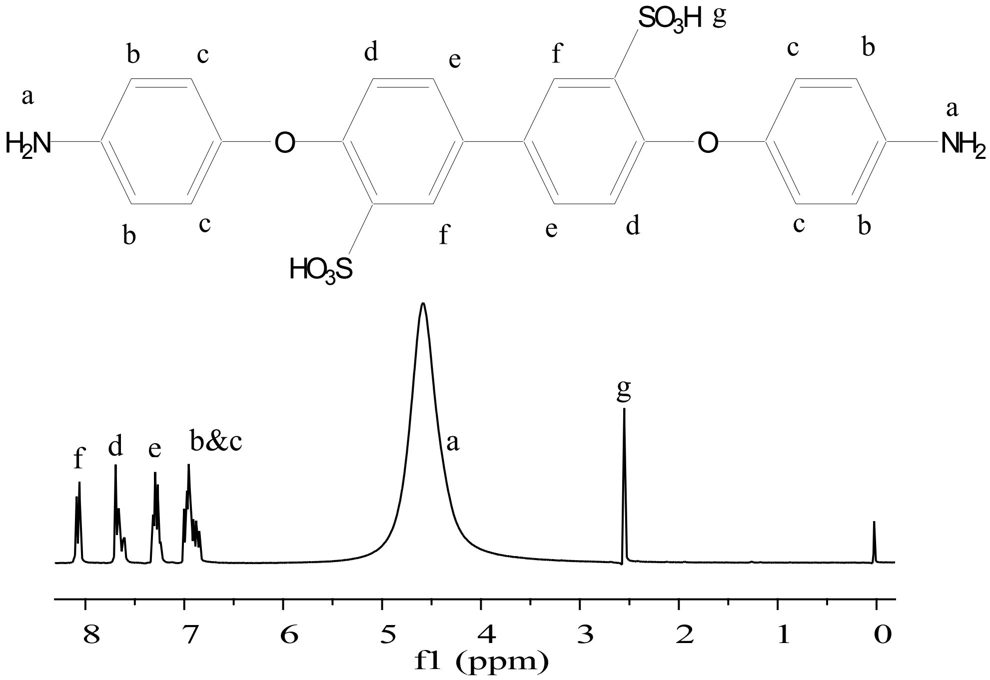

Figure S2. Peak assignment of ^{13}C NMR of BAPBDS.

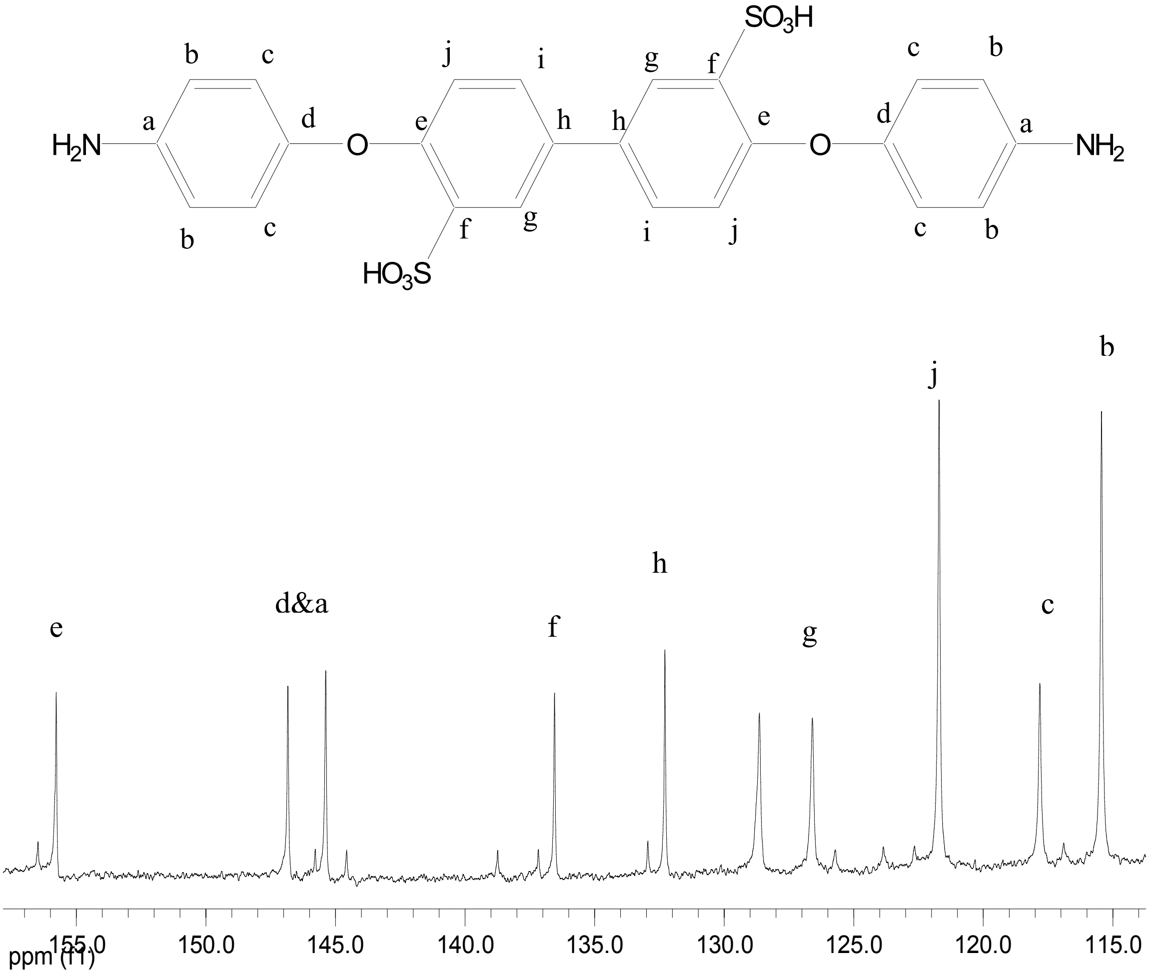

Figure S3. The bound water content comparison of the uncross-linked and cross-linked sulfonated poly(ether sulfone) based membranes.

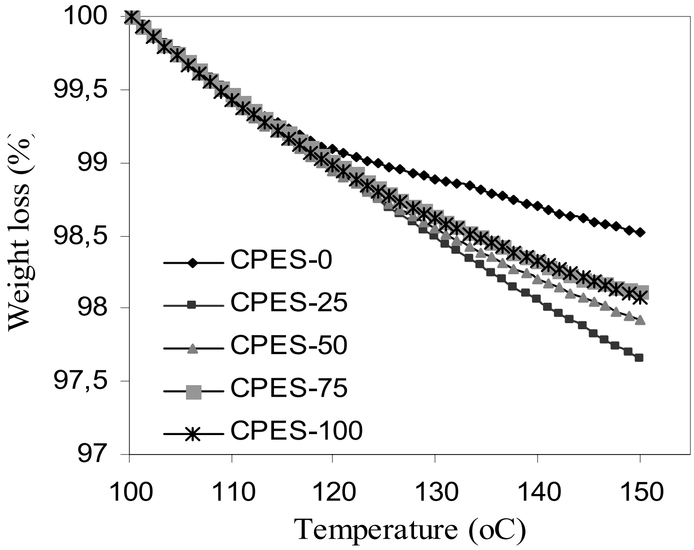

Figure S4. Water desorption profile for all the developed membranes: (A) isotherm at 35 ^{o}C; (B) Higuchi's model fit of deswelling behavior.