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Supporting Information

Synthesis and characterization of crosslink-free highly sulfonated multi-block poly(arylene ether sulfone) multi-block membranes for fuel cells

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1. Synthesis of oligomers and polymers

1.1 Synthesis of hydrophilic oligomers

Potassium hydroquinone sulfonate (HQS; TCI) and 3,3'-disulfonated-4,4'-difluorophenyl sulfone (DSDFPS; Yanjin) were used as monomers. HQS and DSDFPS were recrystallized and used after drying in a vacuum oven for more than one day at 120 °C. Dimethyl sulfoxide (DMSO) from Aldrich was used as a solvent. Potassium carbonate (K₂CO₃, Aldrich) was used after drying in a vacuum oven for more than 24 h at 100 °C. The molecular weight was measured by gel permeation chromatography (GPC; YL9100, Younglin, Korea) with a UV detector based on the molecular weight relative to a polystyrene standard. *N,N*-Dimethylacetamide (DMAc) with 0.05 M LiBr was used as the eluent and KF-805L (Shodex) was used as the column. ¹H and ¹⁹F NMR spectra were obtained using a Bruker Avance 600 MHz. Spectra of the hydrophilic oligomers were obtained from a DMSO-d₆ solution.

Fluorine-terminated hydrophilic oligomers were synthesized by nucleophilic aromatic substitution under a nitrogen atmosphere [Figure S1]. A three-necked flask with a condenser and mechanical stirrer was charged with HQS, DSFDPS, K_2CO_3 , and DMSO. The reaction temperature was slowly increased to 120 °C. The progress of the experiment was monitored by GPC every hour and the reaction was carried out for 8 h until a targeted molecular weight was reached. Celite[®] was poured on the reacted solution to remove the catalyst and then filtered. The solution was poured dropwise onto a large amount of IPA to remove the unreacted monomers. Finally, dialysis (Spectrum[®], Spectra/Por[®] Dialysis membrane, 1 kDa) was applied to remove any trace of residual sulfonated monomers.

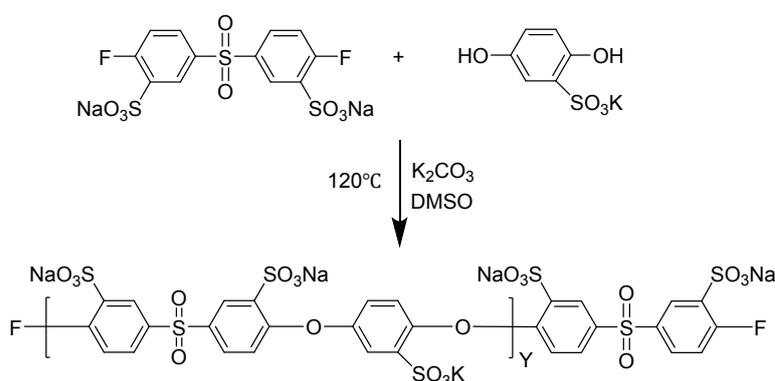


Figure S1. Synthesis of sulfonated hydrophilic oligomers.

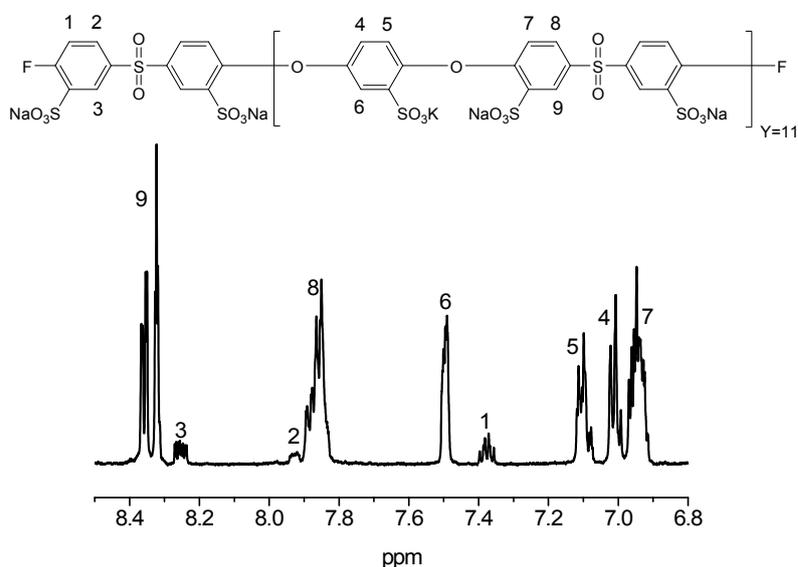


Figure S2. ^1H NMR spectrum of the hydrophilic oligomer in dimethyl sulfoxide (DMSO-d_6).

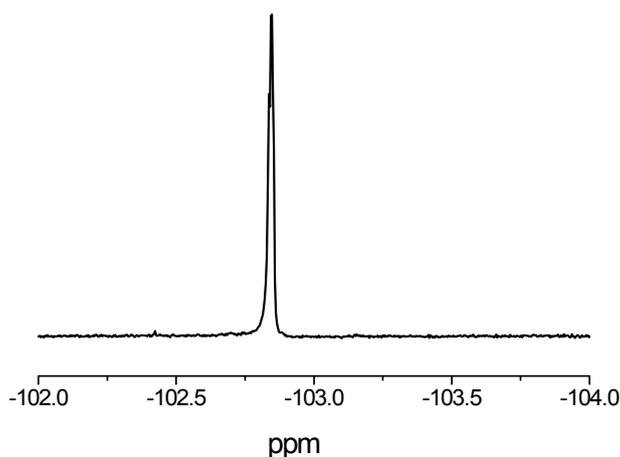


Figure S3. ^{19}F NMR spectrum of the hydrophilic oligomer in dimethyl sulfoxide (DMSO-d_6).

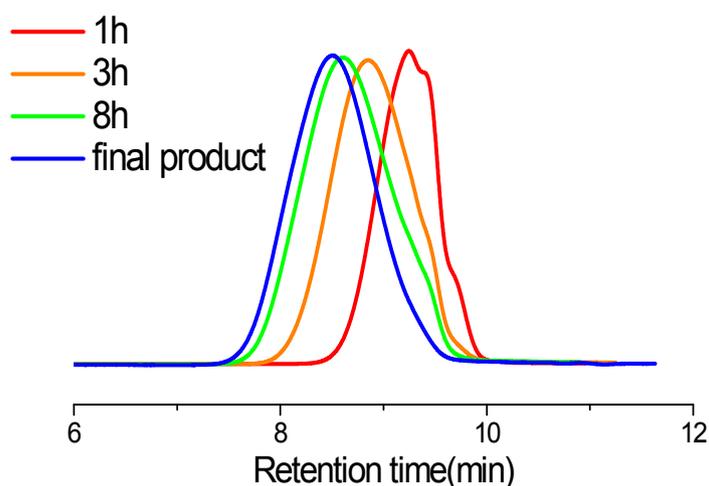


Figure S4. GPC profiles of the hydrophilic oligomer according to reaction time.

1.2 Synthesis of hydrophobic oligomers

4,4'-Dihydroxybiphenyl (BP; Aldrich) and 4-fluorophenyl sulfone (FPS; Aldrich) were recrystallized and used as monomers. DMAc was used as a solvent instead of DMSO. Synthesis of the hydroxyl-terminated hydrophobic oligomer [Figure S5] also progressed via the same method as that for the hydrophilic oligomer except without dialysis. The reaction was monitored by GPC and conducted for 4 h. Hydrophobic oligomer sampling was used with a solvent mixture of dimethylformamide (DMF) containing 0.05M LiBr as the eluent. A GPC column was used SB-803HQ from Shodex.

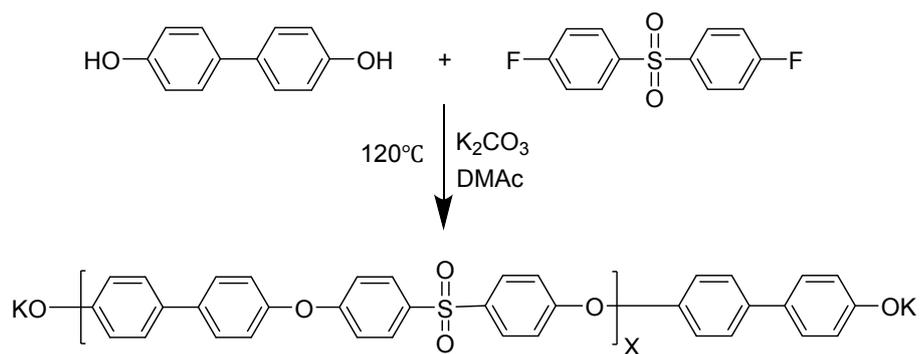


Figure S5. Synthesis of the hydrophobic oligomer.

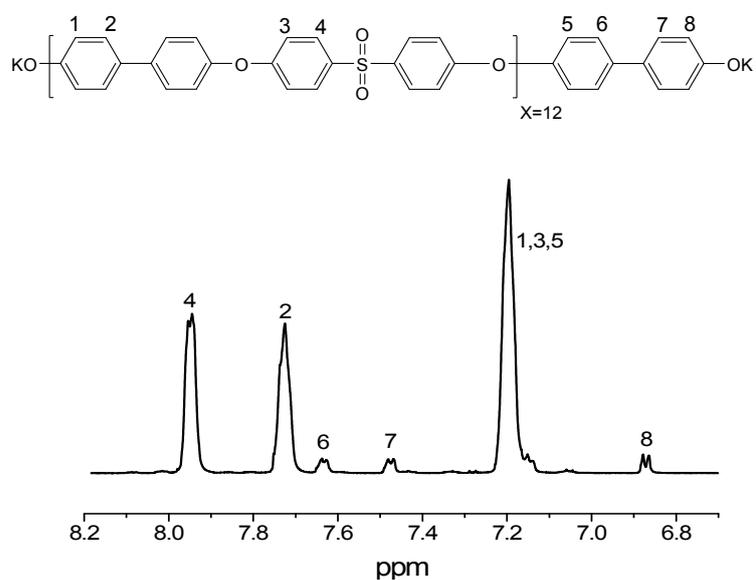


Figure S6. 1H NMR spectrum of the hydrophobic oligomer in dimethyl sulfoxide (DMSO- d_6).

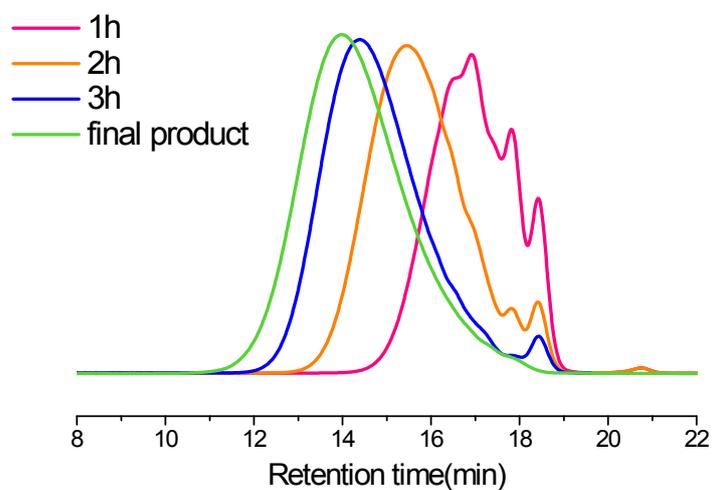


Figure S7. GPC profiles of the hydrophobic oligomer according to reaction time.

1.3 Synthesis of multi-block copolymers (SPAES)

Multi-block copolymers were synthesized by nucleophilic aromatic substitution reactions between the hydroxyl- and fluorine-terminated [Figures S1 and S5] oligomers [Figure 1(b)]. The hydrophobic oligomer dissolved in DMAc was mixed with a DMSO solution of the hydrophilic oligomer. The coupling reaction was conducted for 9–12 h at 130 °C and the polymerization progress was monitored by GPC [Figure S8]. After polymerization, excess DMSO was added to lower the viscosity, and then the polymer solution was added dropwise in deionized water. The precipitate was filtered and dried in a vacuum oven at 100 °C overnight.

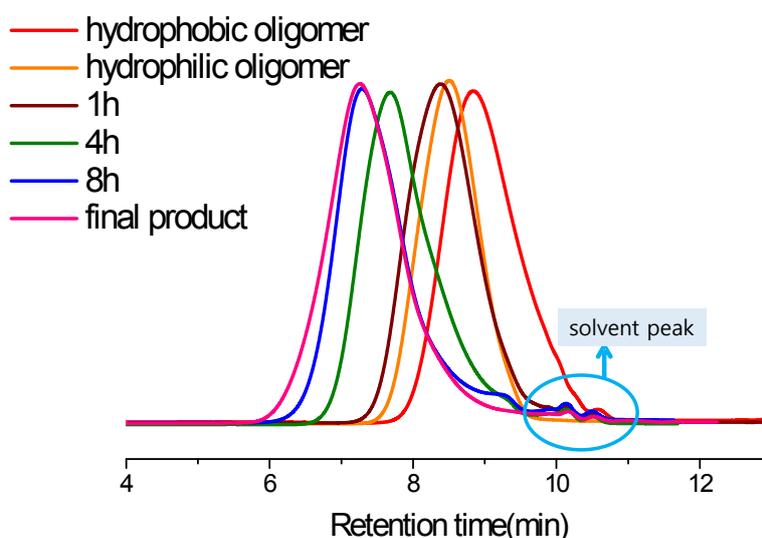


Figure S8. GPC profiles of block SPAES according to reaction time.

2. Characterization of membranes

A membrane film was obtained by solution casting. The salt form of SPAES was dissolved in NMP and filtered through a 0.45 μm filter before casting. The solution was poured on clean glass and dried at 80 °C for 24 h. The membrane was changed to the acid form by boiling in a 3 M HCl solution for 8 h; this was repeated twice, followed by washing with deionized water several times. Finally, a transparent, flexible film was obtained.

The ion-exchange capacity (IEC) was calculated from both the ^1H NMR spectra and back-titration experiments. The membrane film was converted to the sodium form by treatment with a 5 M NaCl solution for 24 h. Then, the IEC measurement was determined by titration with a 0.01 M NaOH solution. The ion-exchange capacity value was 2.9 meq/g; this result correlated with the NMR results.

The proton conductivity of the SPAES was determined using a Solatron impedance analyzer (SI 1260 + 1287) with pressure- and temperature-control devices from Bekktech. The proton conductivity of the SPAES membranes showed humidity dependence at 80 °C.

To observe the phase separation of the hydrophilic and hydrophobic segments, transmission electron microscopy (TEM) was used. H^+ was substituted with Pb^+ using a 0.5 M lead acetate solution and pretreated with a microtome.

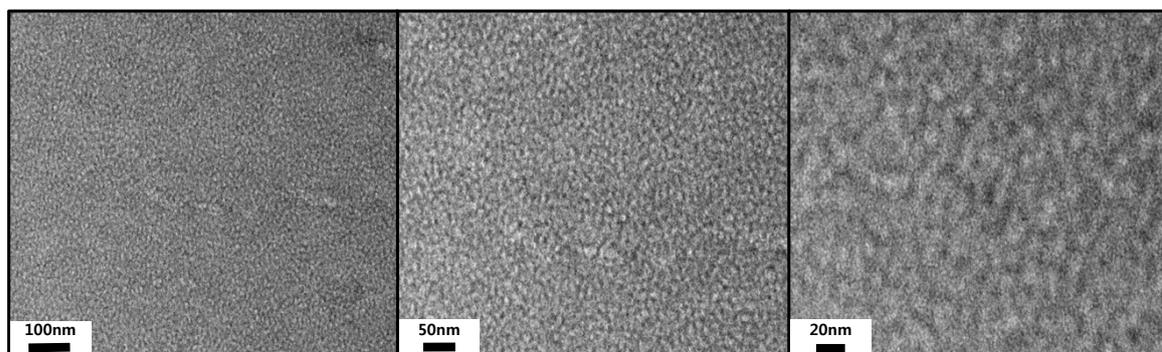


Figure S9. TEM images of an SPAES membrane (100 nm, 50 nm, and 20 nm).

A slurry of Pt catalyst supported on ordered mesoporous carbon (Pt/OMC, 60 wt%-Pt, homemade) containing Nafion ionomer with ionomer/(Pt/OMC) = 0.2 was mixed in a planetary ball-mill for 30 min. The obtained paste was uniformly coated on MPL directly by tape casting method and then dried at 120°C overnight under vacuum. The geometric area and the Pt loading amount of all electrodes were 10 cm² and 0.4 mg/cm², respectively. The membrane-electrode assemblies (MEA) were prepared by pressing block SPAES membrane (40 μm thick) or Aquivion (R79-02S) sandwiched between two above-mentioned MPL-coated CPs (25BC, SGL Japan) at 160 °C under 25 kg_f/cm² for 30 min and then 100 kg_f/cm² for 3 min.

3. Solubility test of hydrophobic and hydrophilic oligomers

Single solvent system with DMAc or DMSO didn't give high molecular weights of block SPAES due to a precipitation during the polymerization. Solubility of each oligomers at 130°C was tested for optimum polymerization.

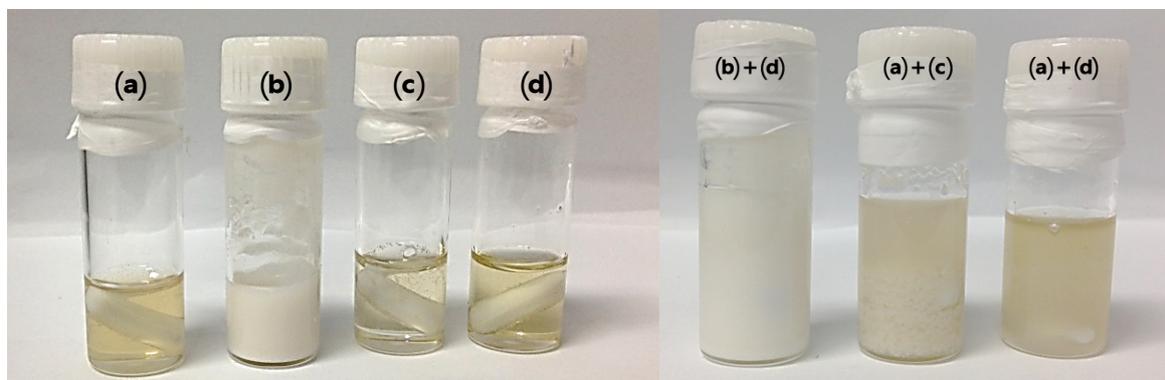


Figure S10. Solubility test at 130°C of (a) hydrophilic oligomer in DMSO, (b) Hydrophilic oligomer in DMAc, (c) hydrophobic oligomer in DMSO, (d) Hydrophobic oligomer in DMAc, and mixed solution of (a), (b), (c), and (d). Concentration of solution was controlled to be same as polymerization.

Table S1. Summary of solubility test of oligomers under same concentration as polymerization

Oligomers	DMAc	DMSO	DMAc + DMSO
Hydrophilic	- (b)	+ (a)	N/A
Hydrophobic	++ (d)	++ (c)	N/A
Hydrophilic + Hydrophobic	-, (b)+(d)	-, (a)+(c)	+, (a)+(d)

++: completely soluble, + : partially soluble, - : insoluble.

Figure S10 shows solubility test of hydrophilic and hydrophobic oligomers in each solvent and their mixtures. Table 1 summarized its results. (b)+(d) represents solubility of both oligomers in. It showed lots of precipitation, which didn't allow successful polymerization. As a similar way, DMSO was tested as polymerization solvent as shown in (a)+(c). This combination also didn't show good solubility. Only mixed solvent system gave a good solubility toward both oligomers as shown in (a)+(d).