

Supporting Information

**Azide-assisted crosslinked sulfonated poly(ether sulfone)s as
stable and highly conductive membranes with low methanol
diffusion coefficient**

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EXPERIMENTAL

1. Materials

Hydrocarbon based polymers were synthesized from commercially available 4-fluorophenyl sulfone (FPS), hydroquinone 2-potassium sulfonate (HPS), and bisphenol A (BPA). The HPS was purchased from Sigma-Aldrich and recrystallized from deionized water. The FPS and BPA were obtained from Aldrich chemicals. All the other chemicals were obtained commercially and used without further purification.

2. Synthesis of polymers

2.1. Synthesis of the hydroxy-terminated sulfonated PES-60 (1)

The typical process for synthesizing poly(ether sulfone)s (PES) is as follows. 4-Fluorophenyl sulfone (5 g, 19.6 mmol), bisphenol A (2.35 g, 10.8 mmol), hydroquinone 2-potassium sulfonate (2.24 g, 9.83 mmol) and potassium carbonate (5.57 g, 40.3 mmol) were added to a mixture of dimethyl acetamide (25 cm³) and toluene (40 cm³) in a 100 cm³ round bottom flask which was equipped with a Dean-stark apparatus. The reaction mixture was heated at 150 °C for 4 h. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled out. The temperature of the reaction mixture was then raised to 180 °C and allowed to stir at this temperature overnight under a nitrogen atmosphere. After this time, the mixture was cooled to room temperature and dissolved in DMF (30 cm³), followed by pouring into methanol (500 cm³). The product was collected by filtration and the residual inorganic materials in the polymer were extracted by treatment with deionized water several times. This was repeated twice, and dried at 60 °C under vacuum for at least 48 h to give the hydroxyl-terminated sulfonated PES-60 **1** as a

white powder (9.05 g, 94%); δ_{H} (300 MHz, d_6 -DMSO) 7.8–8.0 (10H, m, ArH), 7.3–7.5 (1.5H, m, ArH^a), 6.9–7.3 (21H, m, ArH) and 1.6 (6H, s, CH₃^b); ν_{max} (KBr)/cm⁻¹ 3454, 3104, 2970, 1590, 1473, 1301, 1156, 1028, 872 and 839.

2.2. Synthesis of the allyl-terminated PES-60 (2)

Sodium hydride (0.77 g, 19.98 mmol) was added in a DMF (50 cm³) solution of the hydroxyl-terminated PES-60 (9 g, 9.9 mmol) at 0 °C under nitrogen. This was left to stir for 1 h at this temperature before allyl bromide (0.43 cm³, 5 mmol) was added. The reaction mixture was stirred at room temperature overnight and then precipitated into 500 cm³ of methanol. The filtrate was collected, washed with deionized water several times and dried at 60 °C under vacuum to give the allyl-terminated PES-60 **2** as a white powder (8.8 g, 84%); δ_{H} (300 MHz, d_6 -DMSO) 7.8–8.0 (10H, m, ArH), 7.3–7.5 (1.5H, m, ArH), 6.9–7.3 (21H, m, ArH), 5.9–6.0 (0.2H, m, CH), 5.5–5.6 (0.4H, m, CH₂), 3.8–3.8 (0.4H, m, CH₂) and 1.65 (6H, s, CH₃); ν_{max} (KBr)/cm⁻¹ 3465, 3098, 2979, 1594, 1474, 1408, 1301, 1259, 1110, 1080, 990, 910 and 841.

3. Membrane preparation

All membranes were prepared in DMF solution of the corresponding polymers using the solution-casting method, and the film thickness was controlled by means of a doctor blade. The crosslinked PES-60 membrane was obtained by addition of the 2,6-Bis(4-azidobenzylidene)-4-methyl-cyclohexanone **4** (30 wt.% compared to polymer **2**) in a stirred DMF solution of the allyl-terminated poly(ether sulfone) **2** (20%, w/v). The solution was then poured onto a glass plate and the cast film was dried in a vacuum oven at 180 °C for 18 h to complete crosslinking. The membrane on the glass was soaked in water at room temperature to remove residual solvent, and

peeled off by immersion in deionized water. For acidification, the thermally-cured membrane was immersed in NaOH solution (15% in water) at 80 °C for 4 h, followed by HCl (10% in water) at 80 °C for 3 h, and deionized water at 80 °C for 3 h. Finally, the membrane was washed repeatedly with deionized water.

4. Membrane characterization

Structural analysis of all sulfonated poly(ether sulfone)s was carried out using Fourier transform IR using a Nicolet MAGNA 560-FTIR spectrometer.

The solubility of the prepared membranes was evaluated after vigorous stirring in various solvents mentioned at room temperature for at least 24 h.

The oxidative stability was investigated by immersing the small pieces (5 mm × 5 mm) into Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C and evaluated by recording the time that membranes began to break into pieces.

Thermogravimetric analysis measurements of the acid form membranes were performed on a TGA-2950 instrument at a heating rate of 10 °C min⁻¹ in nitrogen flow.

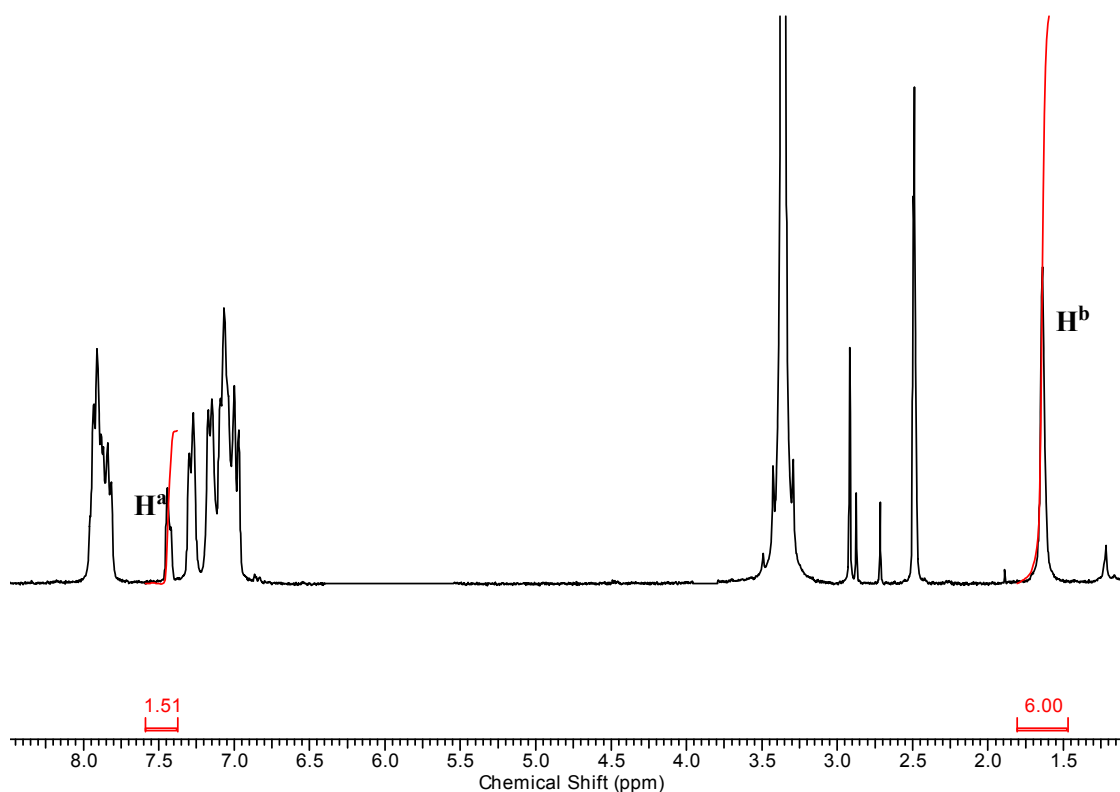
Proton conductivity (σ) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = l/RS$ (l : distance between reference electrodes, S : cross-sectional area of membrane coupon). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode systems connected with an impedance/gain-phase analyzer (SI-1260) and an electrochemical interface (SI-1287) over the frequency range from 10 to 200 kHz. Before the measurements, the acid form membranes were equilibrated with distilled deionized water for at least 24 h.

Methanol permeability of membranes was measured at room temperature using a liquid permeability cell. The cell consisted of two reservoirs, which were separated by a vertical membrane coupon (diameter 2.5 cm). 5% Methanol was placed on one side

of the cell and water was filled on the other side. The magnetic stirrers were used continuously during the measurements. Methanol concentrations in the water cell were measured by a differential refractive index (RI-750F). Prior testing, all the membranes were immersed in deionized water for 24 h.

5. $^1\text{H-NMR}$ spectra

5.1. $^1\text{H-NMR}$ spectra of the hydroxy-terminated sulfonated PES-60 (I)



5.2. $^1\text{H-NMR}$ spectra of the allyl-terminated sulfonated PES-60 (2)

