

Supplementary information for

Block poly(arylene ether sulfone ketone)s containing densely sulfonated linear hydrophilic segments as proton conductive membranes

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Measurements.

^1H and ^{19}F NMR spectra were obtained on a JEOL JNM-ECA 500 using deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$) as solvent and tetramethylsilane (TMS) as internal reference. Ion exchange capacity (IEC) of the membranes was measured by back-titration. A piece of the membrane (ca. 30 mg) was equilibrated in a large excess of 5 M NaCl for 1 day. The released HCl by the ion exchange was titrated with standard 0.01 N NaOH at 25 °C. Apparent molecular weight was measured with gel permeation chromatography (GPC) with a Jasco 805 UV detector. DMF containing 0.01 M LiBr was used as eluent. Two Shodex K-805L columns were used for polymers and a Shodex SB-803HQ column was used for oligomers, respectively. Molecular weight was calibrated with standard polystyrene samples. For scanning transmission electron microscopy (STEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution, rinsed with deionized water, and dried in vacuum for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 90 nm thickness with Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi HD-2300C STEM with an accelerating voltage of 200 kV. Water uptake and proton conductivity were measured with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature and humidity controllable chamber. Weight of the membranes was measured by magnetic suspension balance at given humidity, and then water uptake ($(\text{weight of hydrated membrane}) - (\text{weight of dry membrane}) / \text{weight of dry membrane} \times 100$) was calculated. Vacuum drying for 3 h at 80 °C gave the weight of dry membranes and exposure to a given humidity for at least 2 h gave the weight of hydrated membranes. Proton conductivity was measured using four-probe conductivity cell attached with impedance spectroscopy (Solartron 1255B and 1287) simultaneously in the same chamber. Ion conducting resistances (R) were determined from the impedance plot obtained in the frequency range from 1 to 10 kHz. The proton conductivity (σ) was calculated from the equation $\sigma = l / (A \times R)$, where A and l are the conducting area and the membrane thickness, respectively. Dynamic mechanical analysis (DMA) was carried out with an ITK DVA-200 dynamic viscoelastic analyzer.

Humidity dependence of E' (storage modulus), E'' (loss modulus), and $\tan \delta$ was obtained at 80 °C at a humidification rate of 1% RH/min for samples cut into a rectangular shape (5 mm × 30 mm). Oxidative stability of the membranes was tested by immersing the membrane samples in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h. After the stability test, residual samples were subjected to gravimetry and GPC measurements.

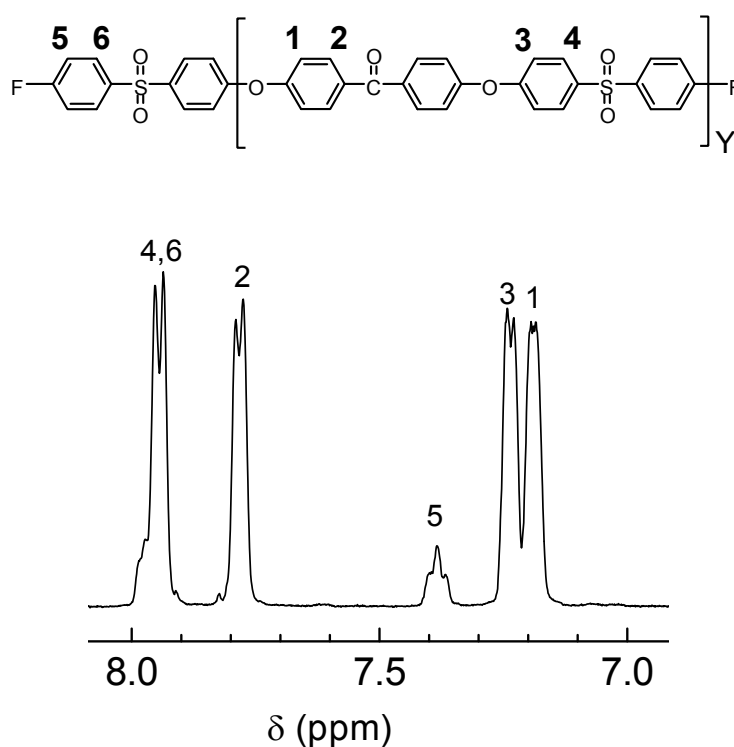


Fig. S1 1H NMR spectrum 1 (Y = 4).

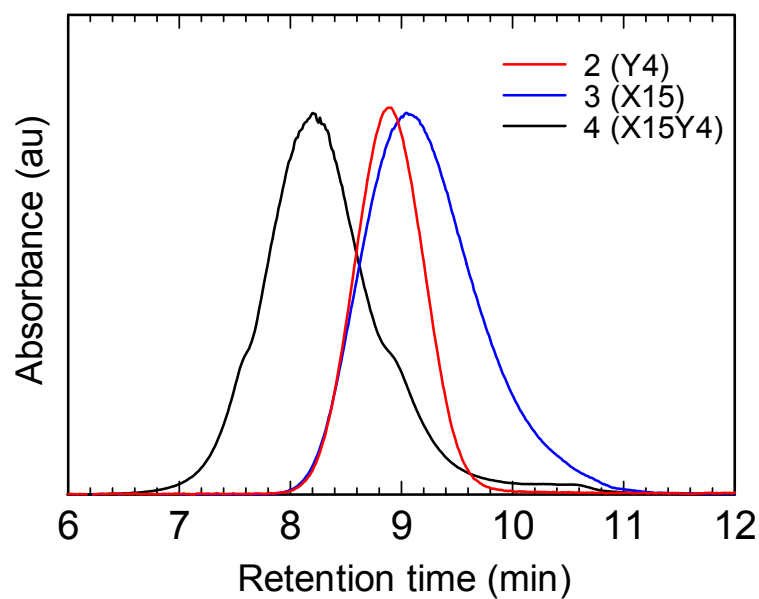


Fig. S2 GPC profiles of 2 (Y = 4), 3 (X = 15), and 4 (X15Y4).

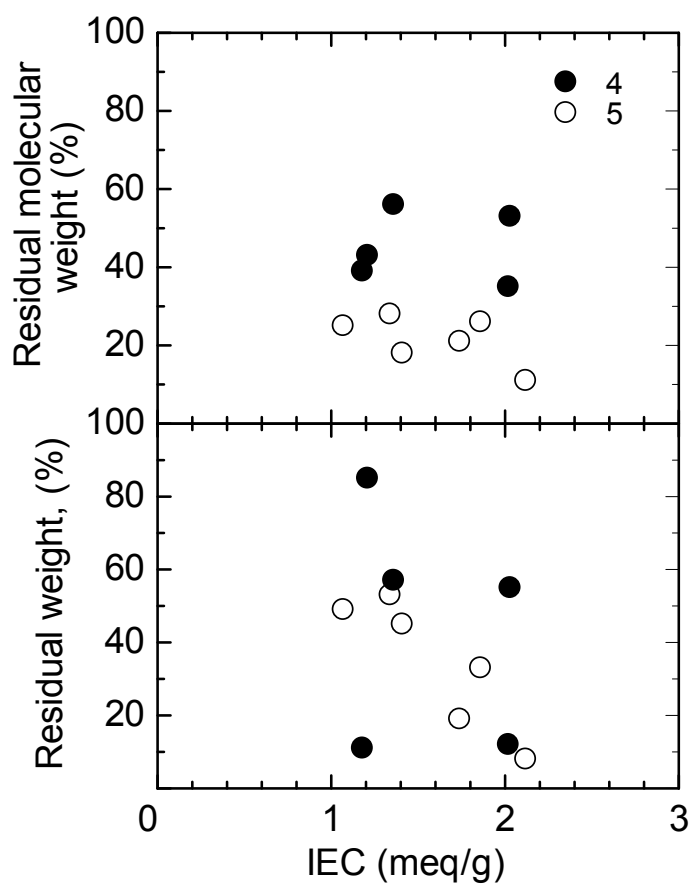


Fig. S3 Residual molecular weight and weight of 4 and 5 membranes after the oxidative stability test as a function of the IEC obtained by titration.