

Supplementary information

Polybenzimidazole block sulfonated poly(arylene ether sulfone) ionomers

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Chemicals. 3,3'-Diaminobenzidine (> 97%), isophthalic acid (> 99%), 4,4'-biphenyldicarboxylic acid (> 97%), 2,2'-bis(4-carboxyphenyl)hexafluoropropane (> 98%), 4,4'-dicarboxydiphenyl sulfone (> 95%), poly(phosphoric acid) (83 % P₂O₅), bis(4-fluorophenyl)sulfone (> 99%), 9,9-bis(4-hydroxyphenyl)fluorene (> 98%), 4-hydroxybenzoic acid (> 98%) were purchased from TCI Inc. and used as received. Potassium carbonate (> 99.5%), potassium *tert*-butoxide (97%), dimethylacetamide (> 99%), dimethylsulfoxide (> 99%), toluene (> 99.5%), chlorosulfonic acid (> 99%), dichloromethane (> 99.5%) were purchased from Kanto Chemical Co.

Synthesis of hydrophilic oligomer.

Oligomerisation: Into a 100 mL flask equipped with a dean stark trap and a nitrogen inlet/outlet, bis(4-fluorophenyl)sulfone (4.53 g, 17.8 mmol), 9,9-bis(4-hydroxyphenyl)fluorene (5.00 g, 14.3 mmol), K₂CO₃ (3.95 g, 28.6 mmol) were mixed with 30 mL of DMAc and 15 mL of toluene. The obtained dispersion was heated at 145 °C for 3 h and at 160 °C for another 3 h. After the reaction, the mixture was slowly poured into 1 L of water to precipitate a product. The crude product was washed with water and methanol. The fluorine-terminated telechelic oligo(arylene ether sulfone) (OE) was then dried at 60 °C for 16 h (92% yield as a white solid).

Sulfonation procedure. Into a 300 mL three-neck flask, chlorosulfonic acid (4.4 mL, 64.0 mmol) was added to 100 mL of dichloromethane. The oligomer OE (2.00 g, 0.662 mmol) was dissolved in 60 mL of dichloromethane and slowly added into the solution of chlorosulfonic acid by the dropping funnel. The mixture was stirred for 24 h at room temperature, and was slowly poured into 500 mL of cold water. The organic layer was removed by evaporation under reduced pressure, and the aqueous layer containing the product was successively treated with NaCl and NaOH until neutralisation. Dialysis of the mixture allowed removal of salts. After evaporation of water by evaporation, the crude product was washed several times with ethanol to remove residual water. The obtained sulfonated oligo(arylene ether sulfone) (sOE) was dried at 60 °C for 16 h under vacuum oven (86 % yield as a yellow solid).

End-capping reaction: Into a 100 mL flask equipped with a dean stark trap and a nitrogen inlet/outlet, 4-hydroxybenzoic acid (0.120 g, 0.871 mmol) and potassium *tert*-butoxide (0.20 g, 1.74 mmol) were mixed with 10 mL of DMSO. The sOE (2.000 g, 0.436 mmol) was slowly added. The mixture was heated at 120 °C for 3 h and was slowly poured into 500 mL of 0.5 M HCl in ethanol to precipitate a product. The obtained carboxylic-terminated telechelic oligo(arylene ether sulfone) (**1**) was dried at 60 °C for 24 h (94 % yield as a white solid).

Block copolymerisation. A general procedure is as follows. Into a 100 mL three-necked round-bottom flask equipped with a nitrogen inlet/outlet and a mechanical stirrer, 15 g of poly(phosphoric acid) was charged and heated at 80 °C. Isophthalic acid (0.459 g, 2.76 mmol) and 3,3'-diaminobenzidine (0.740 g, 3.45 mmol) were added and dissolved at 90 °C. The temperature was gradually increased to 190 °C for 50 h to obtain a brown clear solution. After

cooling down at 90 °C, **1** (2.784 g, 0.691 mmol) was dissolved into the reaction mixture, which was gradually heated to 160 °C for 35 h to obtain an opaque brown mixture. The viscous mixture was slowly poured into 1 L of water to precipitate the product. The obtained block copolymer was filtered, stirred in 500 mL of 1 M of NaOH aqueous solution for 24 h, washed with water until the filtrate became neutral, and dried at 100 °C for 48 h.

Membrane preparation. Powdered block copolymers were dissolved in dimethylsulfoxide to give 5 wt% homogenous and viscous solutions, which were cast onto a glass substrate. The solvent was evaporated at 80 °C in air under reduced pressure. The dried membranes were removed from the substrate and treated with 2 mol L⁻¹ sulfuric acid at room temperature for 24 h to ensure acidification. The membranes were washed with water until the filtrate became neutral and dried between two filter papers.

Characterisation.

Oligomers and block copolymers were characterised by FTIR and by ¹H/¹⁹F NMR, in order to confirm block copolymer structure and the degree of sulfonation. FTIR spectra were obtained in the range of 4000 – 500 cm⁻¹ for KBr pellet samples using a JASCO FT/IR 6100 spectrometer. ¹H NMR spectra were recorded on a JEOL JNM-ECA 500 MHz spectrometer for deuterated dimethyl sulfoxide (DMSO-d₆) solutions with tetramethylsilane (TMS) as an internal reference. Ion exchange capacities (IEC) of membranes were obtained by back-titration. A piece of membranes (ca. 80 mg) was immersed into a large excess of saturated NaCl aqueous solution at room temperature for at least 24 h. The solution was diluted in order to obtain a 5 M NaCl aqueous solution and the released HCl was titrated with standard 0.01 N NaOH aqueous solution. Apparent molecular weight was determined by gel permeation chromatography with a Jasco 805 UV detector from the soluble part of the copolymer in DMSO/DMF (1/10) mixture, which was eluted by a 0.01 M LiBr DMF solution. Shodex KF-805 and Shodex SB-803HQ columns were used for the polymers and the oligomers, respectively. Molecular weight was calibrated with standard polystyrene samples. The thermal properties were examined by a Rigaku Thermo Mass thermogravimetric / differential thermal analyser equipped with a mass spectrometer (TG/DTA-MS) under argon atmosphere (heating rate of 10 °C min⁻¹).

Tensile strength was measured by universal test machine (AGS-J 500N, Shimadzu) attached with a temperature and humidity controllable chamber (Bethel-3A, Toshin Kogyo). Stress vs strain curves were obtained for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)). The measurement was conducted at 60% RH and 80 °C at a stretching rate of 1 mm min⁻¹.

For scanning transmission electron microscopy (STEM) observations, the membranes were emerged into a 0.5 M lead acetate aqueous solution at room temperature for 24 h to exchange sulfonic acid groups to lead form, rinsed three times with deionized water and dried at 80 °C under vacuum for 16 h. The lead 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 ((weight of hydrated membrane - weight of dry membrane)/weight of dry membrane × 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, Solartron

Inc.) simultaneously in the same chamber. Ion conducting resistances (R) were determined from the impedance plot obtained in the frequency range from 1 to 105 Hz. 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.

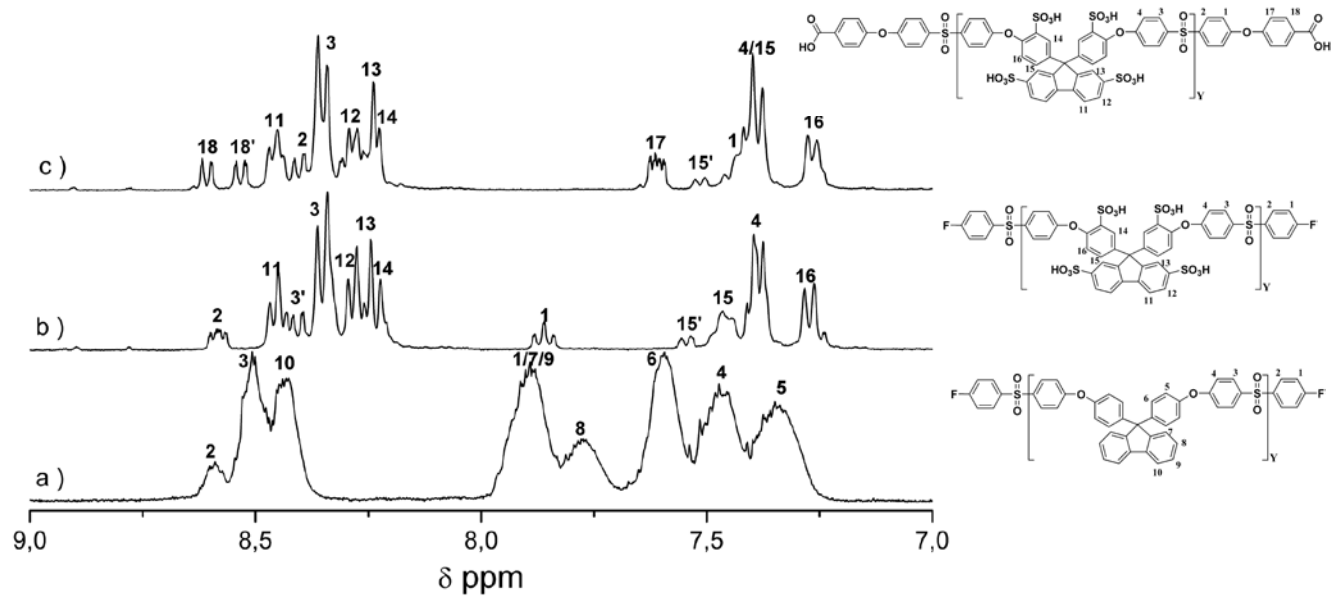


Figure S1 ^1H NMR spectra of Y4 oligomers; (a) OE, (b) sOE, and (c) 1.

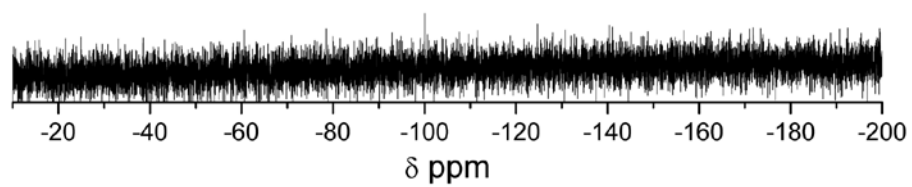


Figure S2 ^{19}F NMR spectrum of **1**.

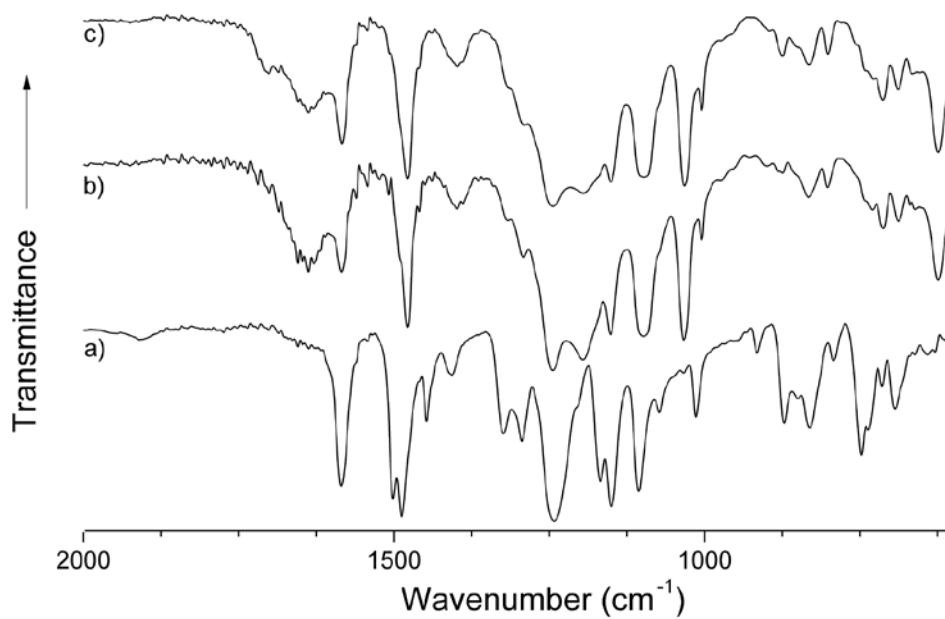


Figure S3 FTIR spectra of Y4 oligomers; (a) OE, (b) sOE, and (c) **1**.

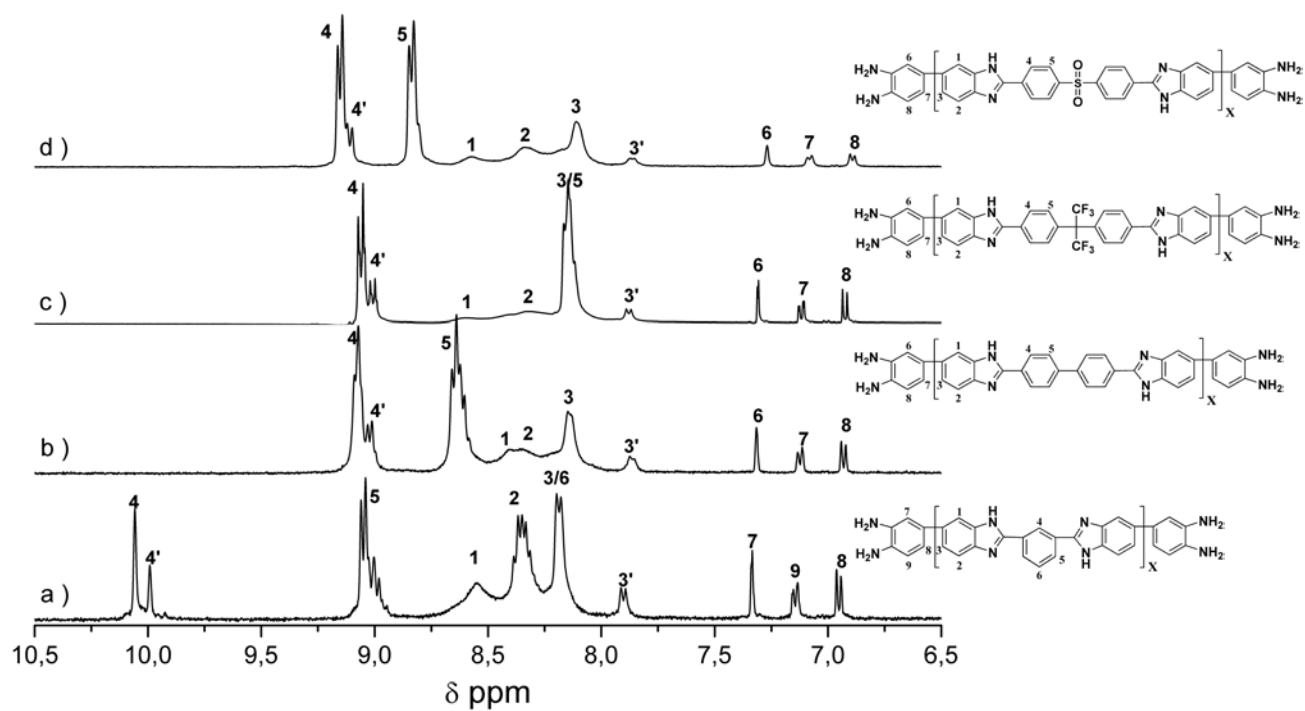


Figure S4 ^1H NMR spectra of diamine-terminated telechelic X4 oligomers; (a) mOBI, (b) BPOBI, (c) HFOBI, and (d) SuOBI.

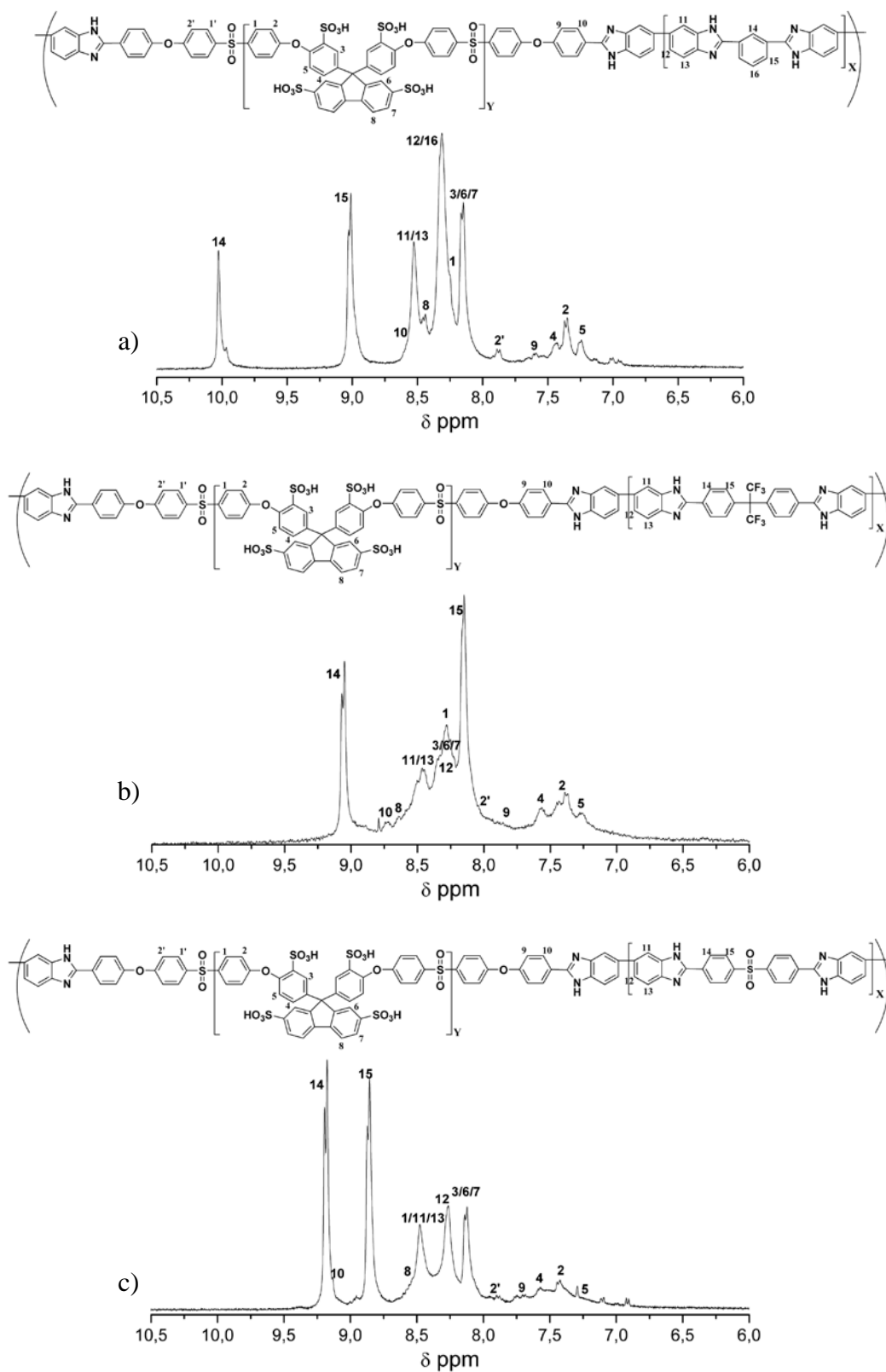


Figure S5 ^1H NMR spectra of OBI-sOE block copolymers; (a) mOBI-sOE (3a), (b) HFOBI-sOE (3c), (c) SuOBI-sOE (3d).

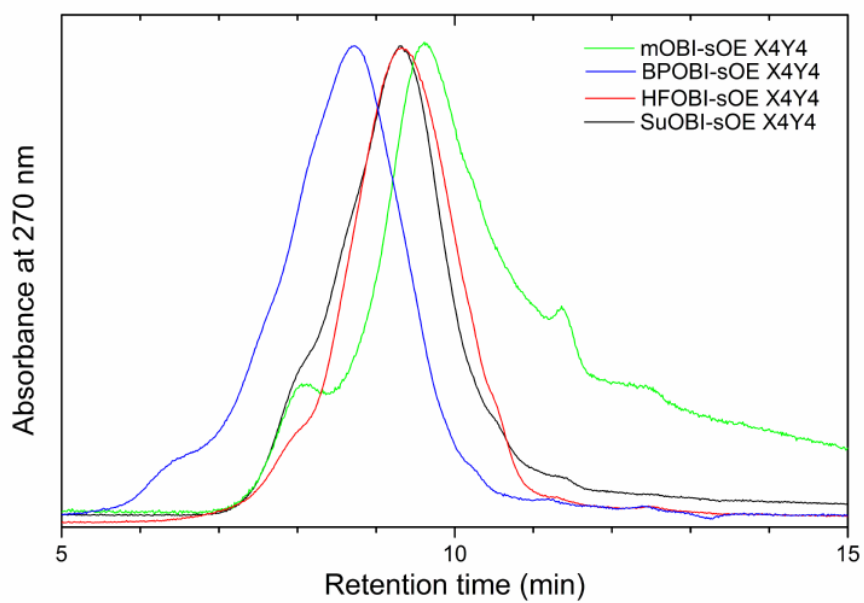


Figure S6 GPC curves of OBI-sOE block copolymers eluted by DMF/LiBr (0.01 M).

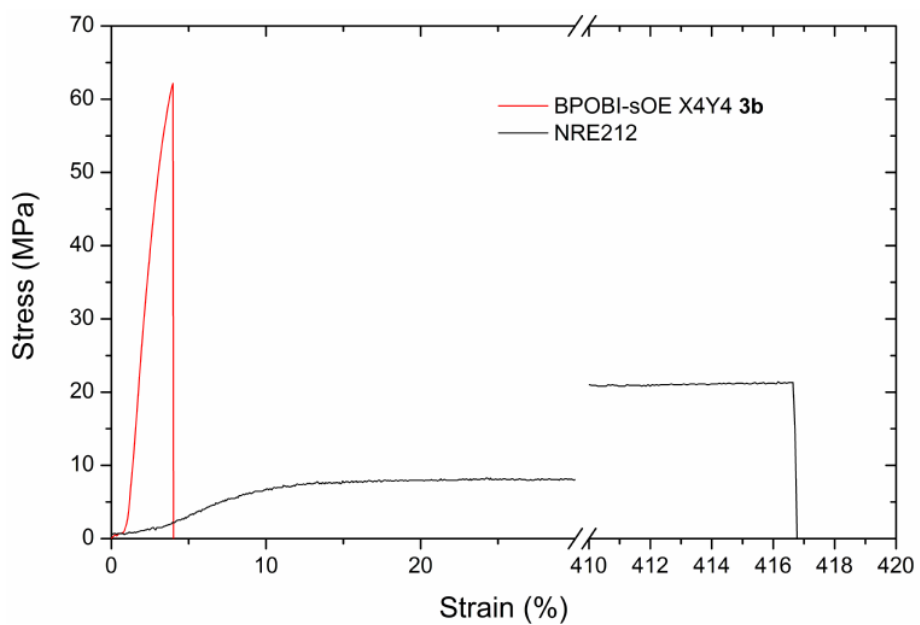


Figure S7 Stress versus strain curves of BPOBI-sOE block copolymer **3b** and Nafion NRE212 at 60% RH and 80 °C at a stretching rate of 1 mm min⁻¹.

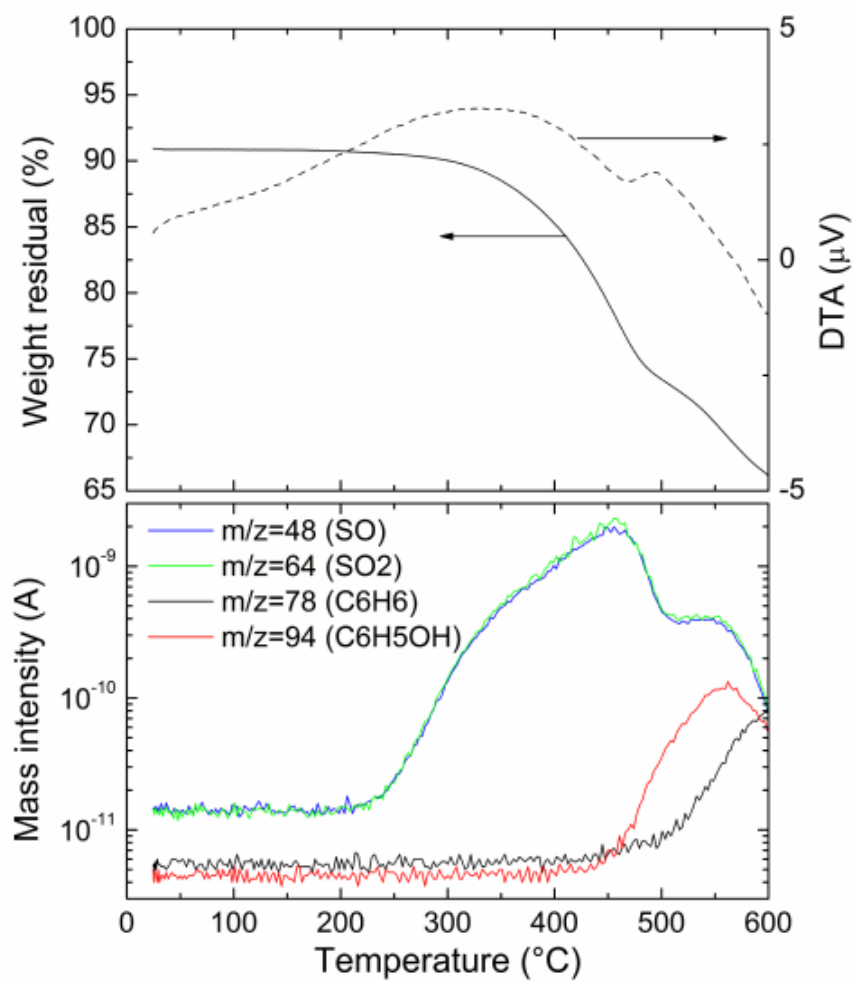


Figure S8 TG/DTA-MS curves of **3b** (IEC = 2.20 meq/g) membrane under Ar at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.