

Electronic Supplementary Information

**Intrapolymer Heck reaction for
proton conductive ladder-type aromatic block copolymers**

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Experimental Section

Materials

N,N-Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), toluene (dehydrated), 30% oleum, sulfuric acid (96%), nitric acid (60%), hydrochloric acid (35%), potassium carbonate (K_2CO_3), calcium carbonate ($CaCO_3$), lead(II) acetate ($Pb(OAc)_2$) trihydrate, sodium chloride (NaCl), and activated carbon (powder) were purchased from Kanto Chemical Co. and used as received. 4,4'-Dihydroxybenzophenone (DHBP), bis(4-fluorophenyl)sulfone (FPS), 4,4'-biphenol (BP), N-bromosuccinimide (NBS), cesium carbonate (Cs_2CO_3), sodium diphenylphosphino benzene-3-sulfonate ($sPPh_3$), palladium(II) acetate ($Pd(OAc)_2$) were purchased from TCI Inc. and used as received. Methanol was purchased from Wako and used as received. Methyl sulfoxide- d_6 (for NMR, with 0.03% TMS, 99.9 atom% D) and 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2 , for NMR, 99 atom% D) were purchased from Acros Organics and used as received. Spectra/Por 6 dialysis tubing (1,000 Da MWCO) was purchased from Spectrum Laboratories, Inc. and used as received. 4,4'-Sulfonylbis(2-bromo-1-fluorobenzene) (BrFPS) was prepared by the reaction of FPS with NBS according to the literature method.^[S1]

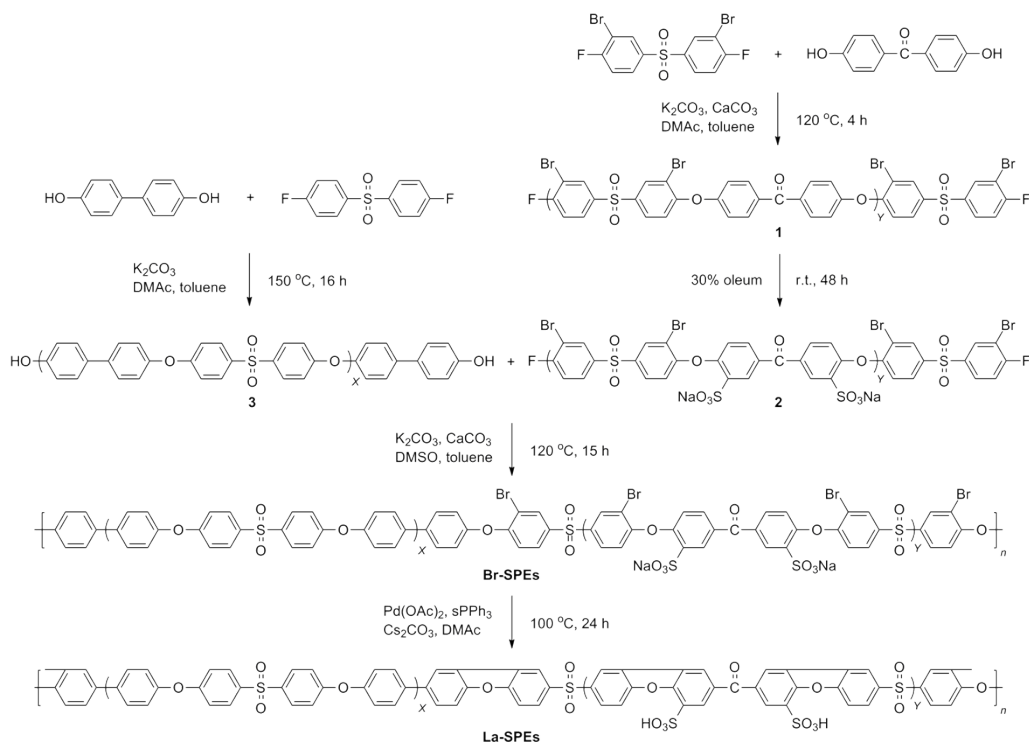
Measurements

^1H (500 MHz), ^{19}F (471 MHz), and ^{31}P (202 MHz) NMR spectra were obtained on a JEOL JNM-ECA 500 at 80 °C using $\text{TCE-}d_2$ and $\text{DMSO-}d_6$ as solvents, and tetramethylsilane (TMS) as an internal reference. Apparent molecular weights were measured at 50 °C with gel permeation chromatography (GPC) with a Jasco 805 UV detector. DMF containing 0.01 M LiBr was used as eluent. A Shodex K-805L column was used for sulfonated compounds (oligomer **2**, Br-SPEs, and La-SPEs) and a Shodex SB-803HQ column was used for unsulfonated compounds (oligomers **1** and **3**), respectively. Molecular weights were calibrated with standard polystyrene samples. Ion exchange capacity (IEC) of the membranes was measured by back-titration. A piece of the membrane (*ca.* 20 mg) was equilibrated in a large excess of 2 M NaCl aqueous solution for 24 h at room temperature. The released HCl by the ion exchange was titrated with standard 0.01 *N* NaOH aqueous solution at room temperature. For transmission electron microscope (TEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M $\text{Pb}(\text{OAc})_2$ aqueous solution, rinsed with deionized water, and dried in vacuum oven at 80 °C for 24 h. The stained membranes were embedded in epoxy resin, sectioned to 50 nm thickness with Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi H-9500 TEM with an accelerating voltage of 200 kV. Water uptake and proton conductivity were measured at 80 °C and 120 °C 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 10⁵ Hz. The proton conductivity (σ) was calculated from the equation $\sigma = l / (A \times R)$, where l and A are the distance between the two inner platinum wires ($l = 1$ cm) and the conducting area, respectively. Dynamic mechanical analyses (DMA) were carried out with an ITR DVA-225 dynamic viscoelastic analyzer. Humidity dependence of the storage moduli (E'), loss moduli (E''), and $\tan \delta$ was measured at 80 °C for the membranes (5 mm \times 30 mm) at a humidification rate of 1% relative humidity (RH) per minute. Tensile strength was measured with a Shimadzu AGS-J 500N universal test machine attached to a Toshin Kogyo Bethel-3A temperature and humidity controllable chamber. Stress versus strain curves were obtained for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm \times 6 mm (total) and 12 mm \times 2 mm (test area)). The measurement was conducted at 80 °C and 60% RH at a stretching rate of 10 mm min⁻¹.

Synthetic strategy

Scheme S1 shows the synthetic route to the target polymers; (i) Hydrophilic oligomer precursors **1** were designed to be Br-containing, F-terminated, and chain length-controlled ($Y = 5, 10$) structure, (ii) hydrophilic oligomers **2** were obtained by the sulfonation reaction of oligomers **1** in 30% oleum at r.t., (iii) hydrophobic oligomer **3** was designed to be OH-terminated and chain length-controlled ($X = 5$) structure, (iv) Br-SPEs were obtained by polycondensation of oligomers **2** and **3**, and (v) Pd-catalyzed intramolecular Heck reaction of Br-SPEs provided ladderized polymers (La-SPEs).



Scheme S1. Overall synthetic route to the target block copolymers.

Synthesis and characterization of oligomers **1**

Oligomers **1** were prepared by nucleophilic substitution polymerization of BrFPS and DHBP with a controlled feed monomer ratio in the presence of K_2CO_3 and $CaCO_3$ in DMAc/toluene solution. Slight excess of BrFPS was used to be F-terminated and chain length-controlled oligomers. The chemical structure of **1** was confirmed by 1H and ^{19}F NMR spectra (Figure S1). Both spectra were well-assigned and verified the chemical structure of **1** with controlled chain length ($Y = 5, 10$).

A detailed procedure for **1a** (Y_5) is as follows. A 100 mL round-bottom flask was charged with BrFPS (2.210 g, 5.364 mmol), DHBP (0.919 g, 4.291 mmol), K_2CO_3 (1.480 g, 10.71 mmol), $CaCO_3$ (8.580 g, 85.70 mmol), DMAc (10 mL), and toluene (1 mL). After heated at 120 °C for 4 h with a Dean Stark trap, the reaction mixture was cooled to room temperature and diluted with 10 mL of DMAc. The mixture was poured into a large excess of 1 M hydrochloric acid solution (1 L) to precipitate a white powder. The crude product was washed with hot deionized water and hot methanol several times. Drying in a vacuum oven at 80 °C for 12 h gave **1a** (Y_5 , 2.591 g, 89% yield).

1b (Y_{10} , 3.552 g, 89% yield) was obtained under the conditions similar to those for oligomer **1a**. BrFPS (2.720 g, 6.60 mmol), DHBP (1.285 g, 6.00 mmol), K_2CO_3 (2.073 g, 15.0 mmol), $CaCO_3$ (6.606 g, 66.0 mmol), DMAc (15 mL), and toluene (1 mL) were used.

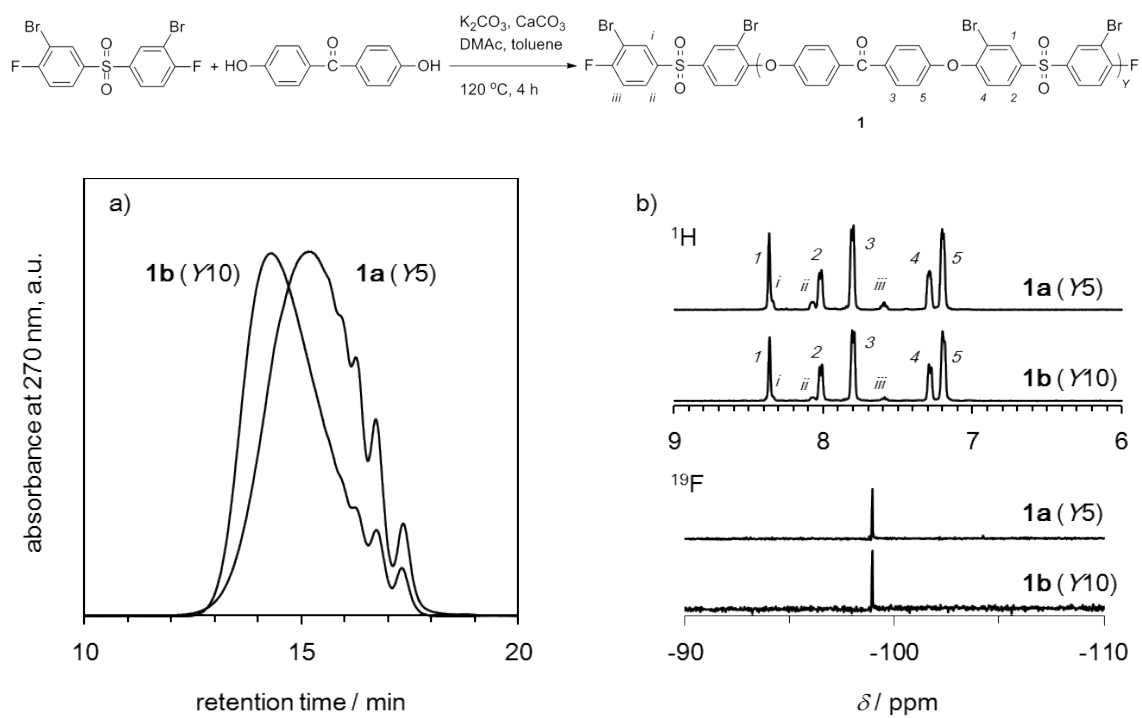


Figure S1. a) GPC profiles with a Shodex SB-803HQ column at $50\text{ }^\circ\text{C}$ (DMF containing 0.01 M LiBr was used as eluent), b) ^1H and ^{19}F NMR spectra in $\text{DMSO-}d_6$ at $80\text{ }^\circ\text{C}$.

Synthesis and characterization of oligomers **2**

Hydrophilic oligomers **2** were synthesized by selective sulfonation reaction of oligomers **1** in 30% oleum at room temperature. The amount of 30% oleum was calculated to be 5 excess equimolar of SO₃ to phenylene rings in the oligomers **1**. The GPC profiles and ¹H, ¹⁹F NMR spectra of the sulfonated oligomers **2** (*Y* = 5, 10) are shown in Figure S2, which support selective sulfonation at the ortho position to ether bonds without detectable degradation. Further, ¹⁹F NMR spectra of oligomers **2** showed a singlet at almost the same position with precursor oligomers **1**, meaning no sulfonation reaction occurred at the chain end.

A detailed procedure for **2a** (*Y*5) is as follows. A 100 mL round-bottom flask was charged with oligomer **1a** (1.50 g) and 30% oleum (8.3 mL). After stirred at room temperature for 48 h, the mixture was poured into a large excess of cold water (500 mL). The solution was basified with NaOH aqueous solution, dialyzed, evaporated, and dried in a vacuum oven at 80 °C for 12 h to obtain **2a** (*Y*5, in sodium ion form, 0.921 g).

2b (*Y*10, in sodium ion form, 3.49 g) was obtained under the conditions similar to those for oligomer **2a**.

Oligomer **1b** (3.50 g) and 30% oleum (20 mL) were used.

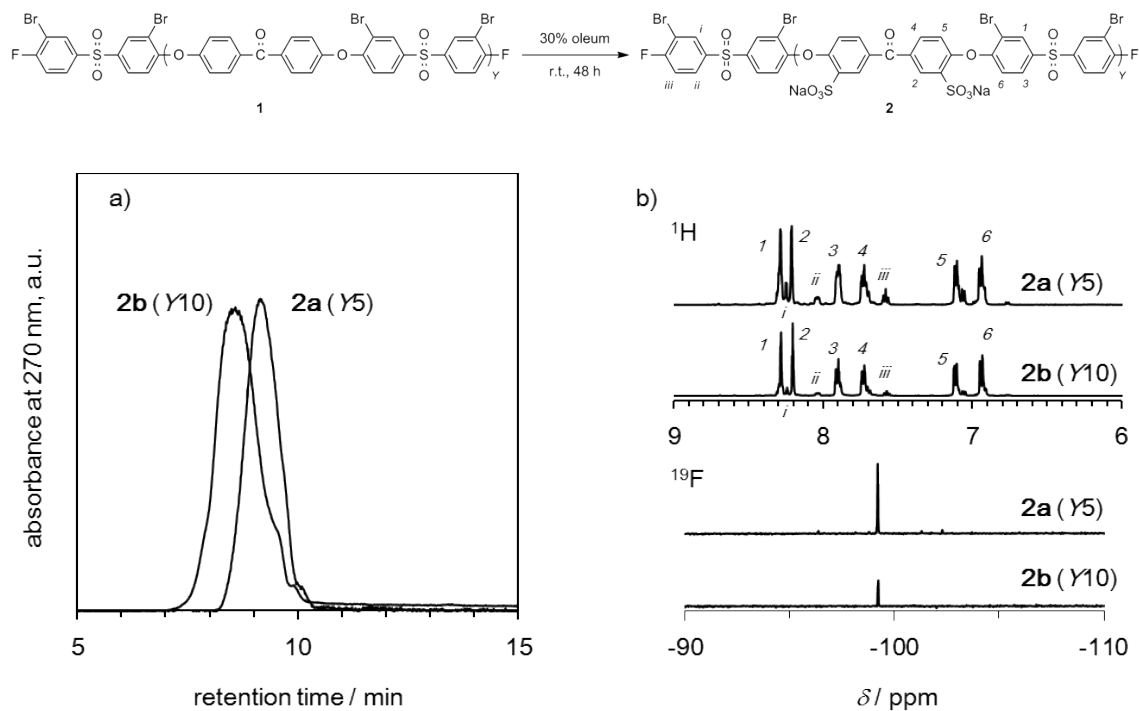


Figure S2. a) GPC profiles with a Shodex K-805L column at 50 °C (DMF containing 0.01 M LiBr was used as eluent), b) ^1H and ^{19}F NMR spectra in $\text{DMSO}-d_6$ at 80 °C.

Synthesis and characterization of oligomer **3**

Oligomer **3** was prepared by nucleophilic substitution polymerization of BP and FPS with a controlled feed monomer ratio in the presence of K_2CO_3 in DMAc/toluene solution. Slight excess of BP was used to be OH-terminated and chain length-controlled oligomer. ^1H and ^{19}F NMR spectra of **3** showed the targeted chemical structure of **3** with controlled chain length ($X=5$, Figure S3).

A detailed procedure for **3** ($X5$) is as follows. A 100 mL round-bottom flask was charged with

BP (1.862 g, 10.0 mmol), FPS (1.907 g, 7.50 mmol), K_2CO_3 (3.455 g, 25.0 mmol), DMAc (20 mL), and toluene (1 mL). After heated at 150 °C for 16 h with a Dean Stark trap, the reaction mixture was cooled to room temperature and diluted with 20 mL of DMAc. The mixture was poured into a large excess of 1 M hydrochloric acid solution (1 L) to precipitate a white powder. The crude product was washed with 1 M hydrochloric acid solution, hot deionized water, and hot methanol several times. Drying in a vacuum oven at 80 °C for 12 h gave **3** (X_5 , 2.853 g, 76% yield).

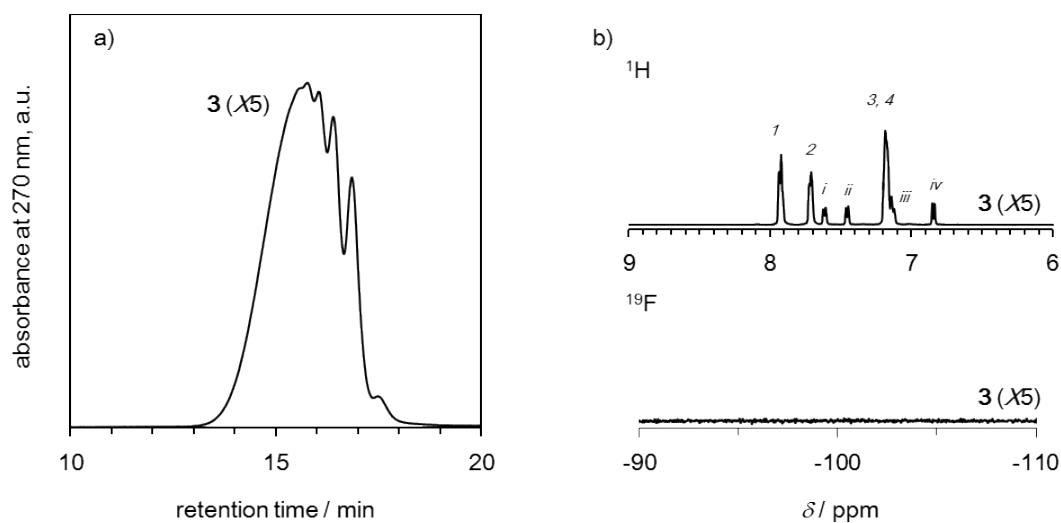
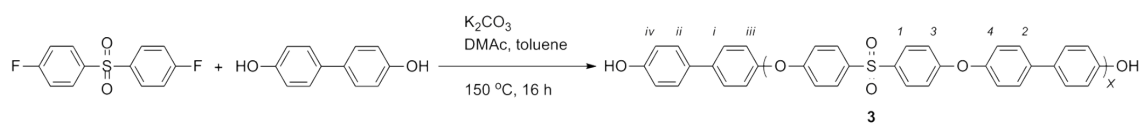


Figure S3. a) GPC profile with a Shodex SB-803HQ column at 50 °C (DMF containing 0.01 M LiBr was used as eluent), b) 1H and ^{19}F NMR spectra in $DMSO-d_6$ at 80 °C.

Table S1. Molecular weight and number of repeat unit of oligomers.

oligomer	<i>X</i> or <i>Y</i>				M_n [kDa]		M_w / M_n	
	feed	$^1\text{H NMR}$	GPC ^a	GPC ^b	GPC ^a	GPC ^b	GPC ^a	GPC ^b
1a (Y5)	4.0	4.5	4.9	3.6	3.3	2.5	2.8	1.6
1b (Y10)	10	9.0	8.2	5.9	5.2	3.9	2.2	1.6
2a (Y5)	4.0	5.0	-	-	-	-	-	-
2b (Y10)	10	10	-	-	-	-	-	-
3 (X5)	3.0	4.8	6.4	4.0	2.7	1.8	1.9	1.6

^a Determined by M_n values (calibrated with polystyrene standards).

^b Determined by M_n values (calibrated with oligomers **1a**, **1b** and **3**, Figure S4).

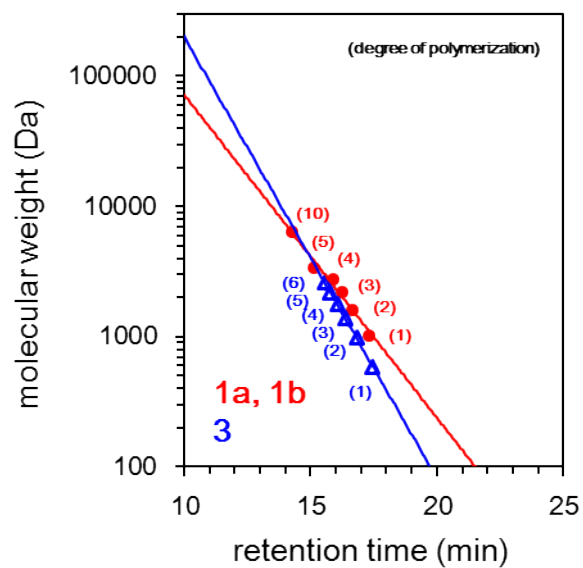


Figure S4. GPC calibration curves obtained by oligomers **1a**, **1b** and **3** (Shodex SB-803HQ column at 50 °C, DMF containing 0.01 M LiBr eluent).

Synthesis and characterization of Br-containing block copolymers (Br-SPEs)

Br-containing block copolymers (Br-SPEs) were synthesized under conditions similar to those for the oligomers. The use of equimolar amount of oligomers **2** and **3** provided high molecular weight polymers without detectable chain end. Figure S4b displays ^1H NMR spectra, in which signals derived from both hydrophilic and hydrophobic segments, and no signals of end groups were observed. Further, the absence of ^{19}F signals (Figure S4b) also supported the polymers without chain end.

A detailed procedure for Br-SPE (*X5Y5*) is as follows. A 100 mL round-bottom flask was charged with oligomer **2a** (0.4857 g, 0.120 mmol), oligomer **3** (0.2549 g, 0.120 mmol), K_2CO_3 (0.0415 g, 0.300 mmol), CaCO_3 (0.1201 g, 1.20 mmol), DMSO (3 mL), and toluene (0.5 mL). After heated at 120 °C for 15 h with a Dean Stark trap, the mixture was cooled to r.t. Then, 1 M HCl_{aq} solution (50 mL) was poured into the mixture and stirred for 6 h. The precipitate was filtered, washed with 1 M HCl_{aq} solution, brine, deionized water, and dried in a vacuum oven at 80 °C for 12 h to obtain Br-SPE (*X5Y5*) (in sodium ion form, 0.6633 g, 90% yield).

Br-SPE (*X5Y10*) (in sodium ion form, 0.7726 g, 82% yield) was obtained under the conditions similar to those for polymer Br-SPE (*X5Y5*). Oligomer **2b** (0.7484 g, 0.090 mmol), oligomer **3** (0.1912 g, 0.090 mmol), K_2CO_3 (0.0311 g, 0.225 mmol), CaCO_3 (0.0901 g, 0.900 mmol), DMSO (4.5 mL), and toluene (0.5 mL) were used.

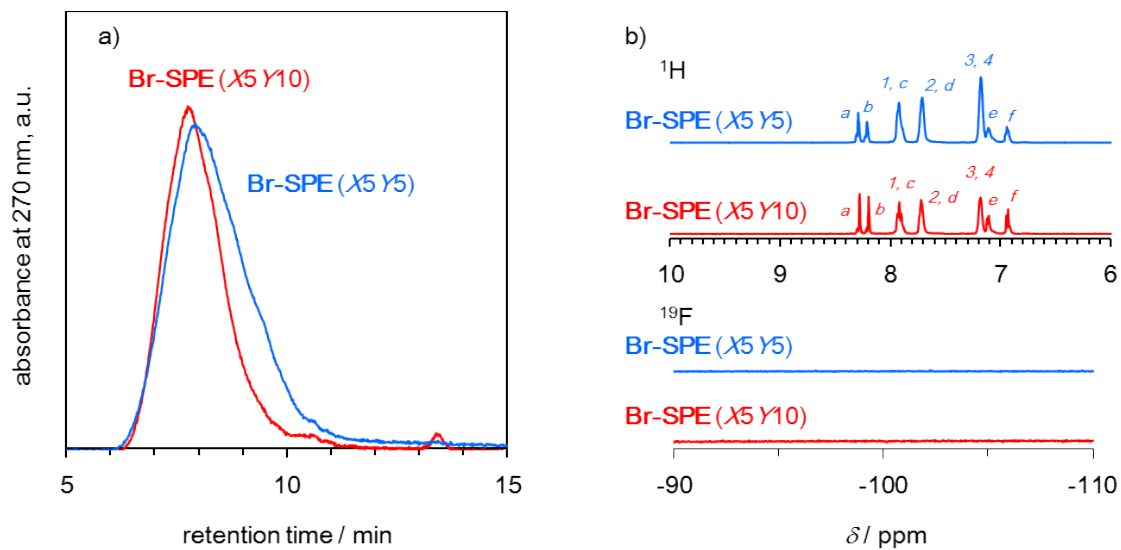
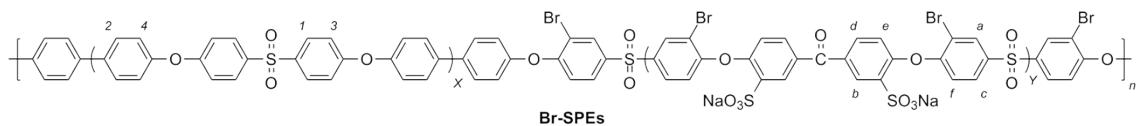


Figure S5. a) GPC profiles with a Shodex K-805L column at 50 °C (DMF containing 0.01 M LiBr was used as eluent), b) ^1H and ^{19}F NMR spectra in DMSO- d_6 at 80 °C.

Synthesis and characterization of fused block copolymers (La-SPEs)

A detailed procedure for La-SPE (*X5Y5*) is as follows. A 200 mL round-bottom flask was charged with polymer Br-SPE (*X5Y5*) (0.600 g) and DMAc (100 mL) under a nitrogen atmosphere. After heated at 80 °C for 1 h to obtain homogeneous solution, the mixture was cooled to room temperature. Then, sPPh₃ (0.0339 g, 0.0932 mmol) and Cs₂CO₃ (1.165 g, 3.576 mmol) were added, and stirred for 1 h. Pd(OAc)₂ (0.0105 g, 0.0467 mmol) in DMAc (20 mL) solution was added to the mixture. After heated at 100 °C for 24 h under a nitrogen atmosphere, the reaction mixture was cooled to room temperature. The mixture was filtered and the filtrate was poured into 1 M nitric acid solution (400 mL), and stirred with activated carbon at room temperature for 12 h. The mixture was filtered and the filtrate was stirred with activated carbon at room temperature for 12 h. This procedure was repeated twice. Then, the filtrate was dialyzed and evaporated to obtain a solid product. The crude product was stirred in brine for 3 h, then washed with deionized water and dried in a vacuum oven at 80 °C for 12 h to obtain La-SPE (*X5Y5*) (in sodium ion form, 0.2933 g, 57% yield). La-SPE (*X5Y10*) (in sodium ion form, 0.303 g, 61% yield) was obtained under the conditions similar to those for La-SPE (*X5Y5*). Br-SPE (*X5Y10*) (0.6244 g), sPPh₃ (0.0720 g, 0.1977 mmol), Cs₂CO₃ (1.6291 g, 5.00 mmol), Pd(OAc)₂ (0.0222 g, 0.0988 mmol), and DMAc (190 mL) were used.

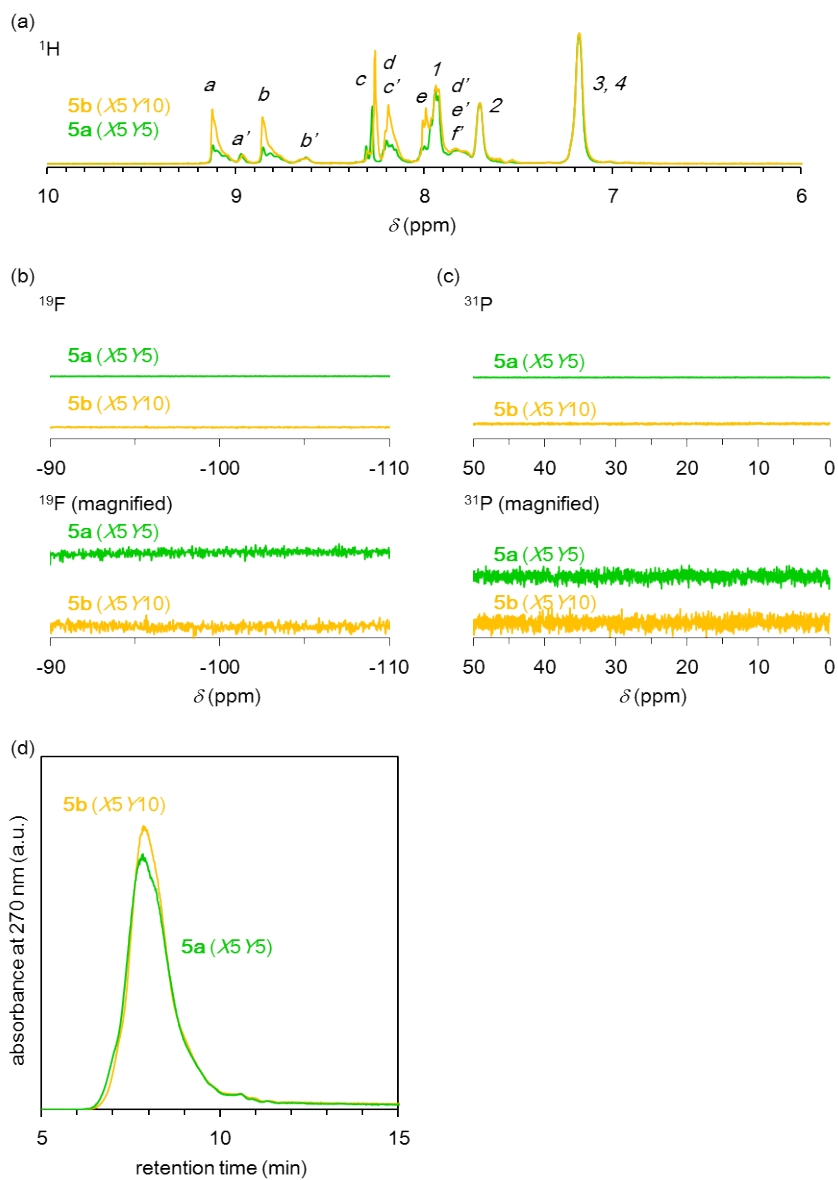
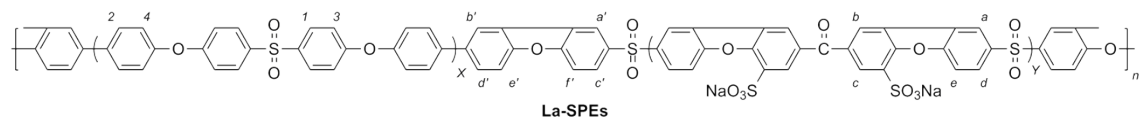


Figure S6. a) ^1H , b) ^{19}F , c) ^{31}P NMR spectra (DMSO- d_6 at 80 °C), and d) GPC profiles with a Shodex

K-805L column at 50 °C (DMF containing 0.01 M LiBr was used as eluent).

Membrane preparation

Block copolymers (*ca.* 0.2 g) were dissolved in solvents (*ca.* 3 mL) and cast onto a flat glass plate.

Drying the solvents (DMAc at 50 °C for Br-SPEs and DMSO at 80 °C for La-SPEs, respectively) for 48

h gave *ca.* 50 μm thick, transparent, and tough membranes. The membrane was further dried at 80 °C in

a vacuum oven for 6 h. The membranes were treated with 1 M H₂SO₄ for 24 h at room temperature,

washed with deionized water several times, and dried at room temperature.

Intramolecular Heck reaction of oligomer 2a (Y5) (model reaction)

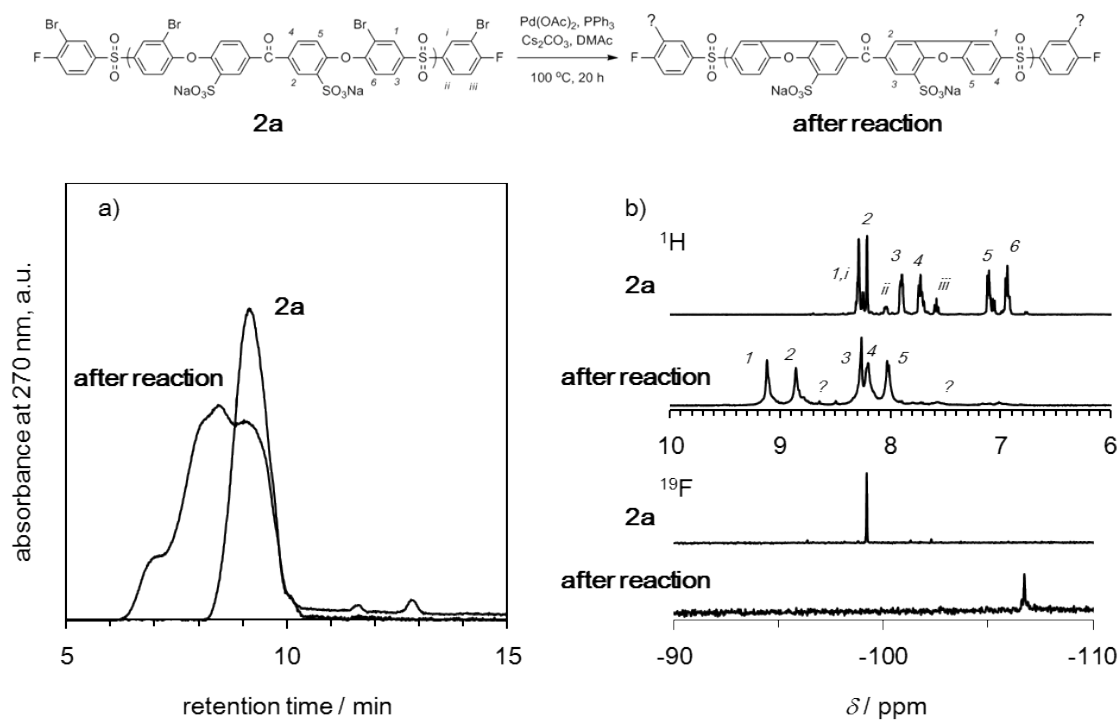


Figure S7. a) GPC profiles with a Shodex K-805L column at 50 °C (DMF containing 0.01 M LiBr was used as eluent), b) ¹H and ¹⁹F NMR spectra in DMSO-*d*₆ at 80 °C.

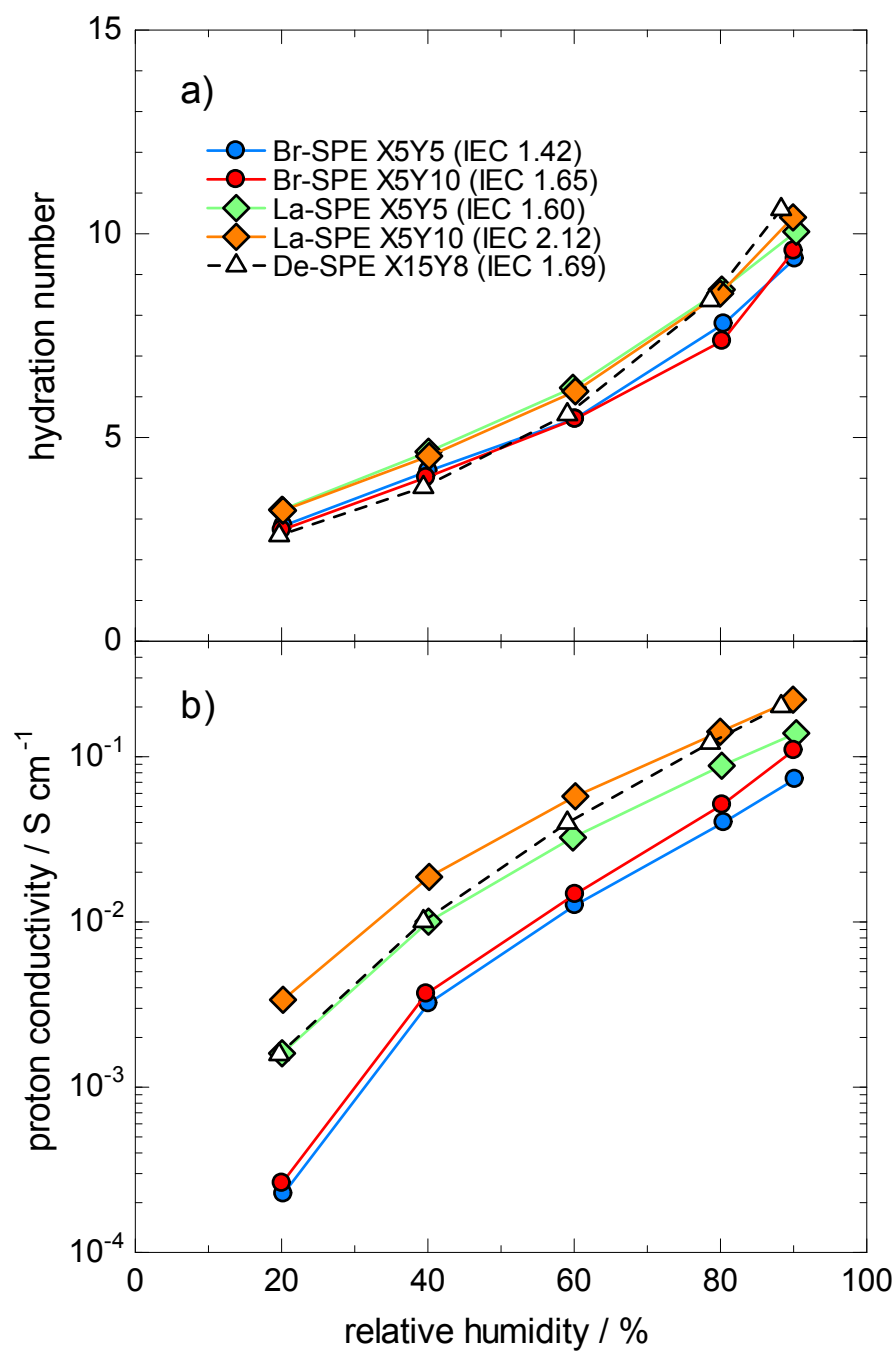


Figure S8. a) Hydration number (λ) and b) proton conductivity of membranes at 80 °C as a function of relative humidity (RH). The IEC values are given in meq g⁻¹.

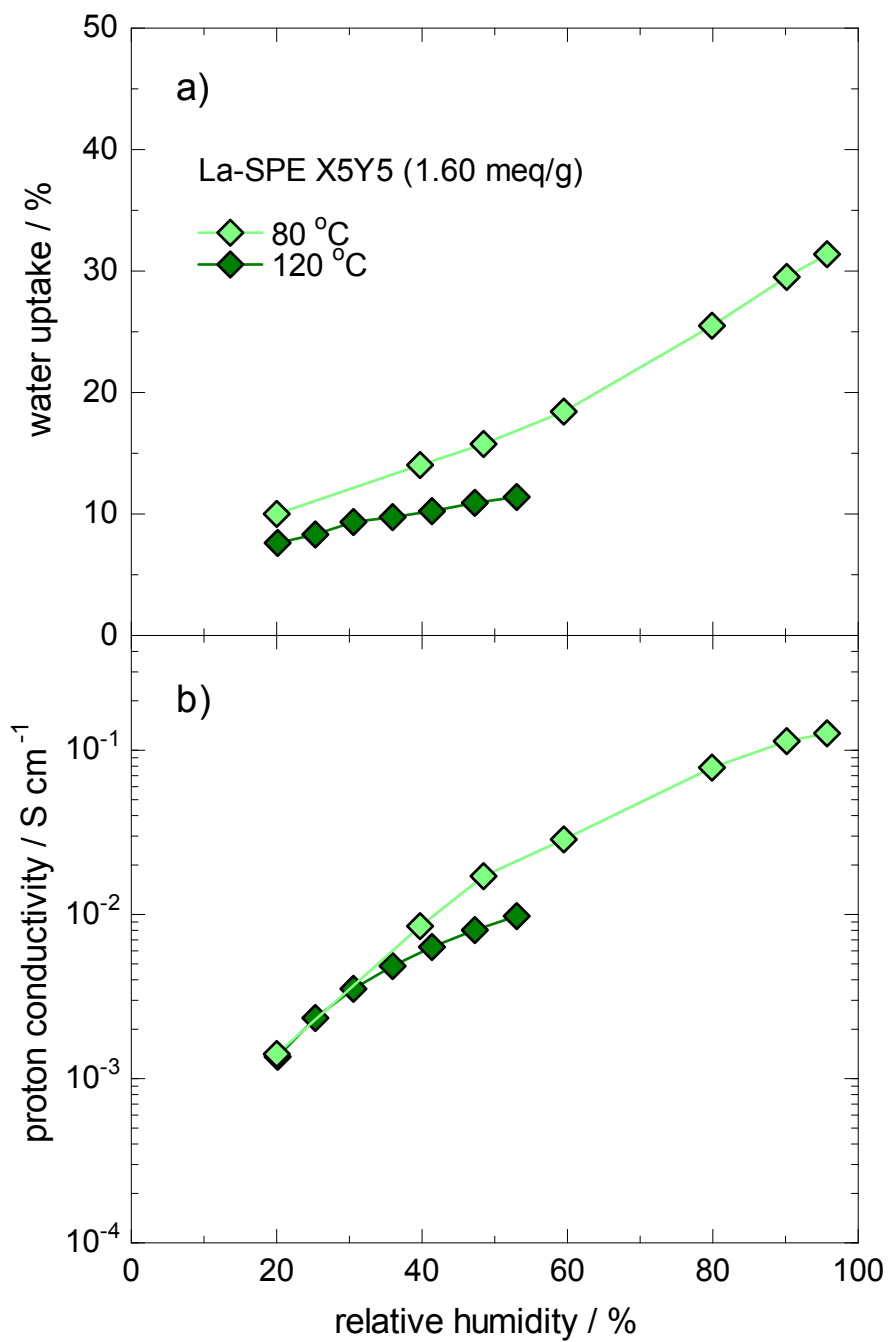


Figure S9. a) Water uptake and b) proton conductivity of La-SPE (X5Y5) membrane at 80 °C and 120

°C as a function of relative humidity (RH).

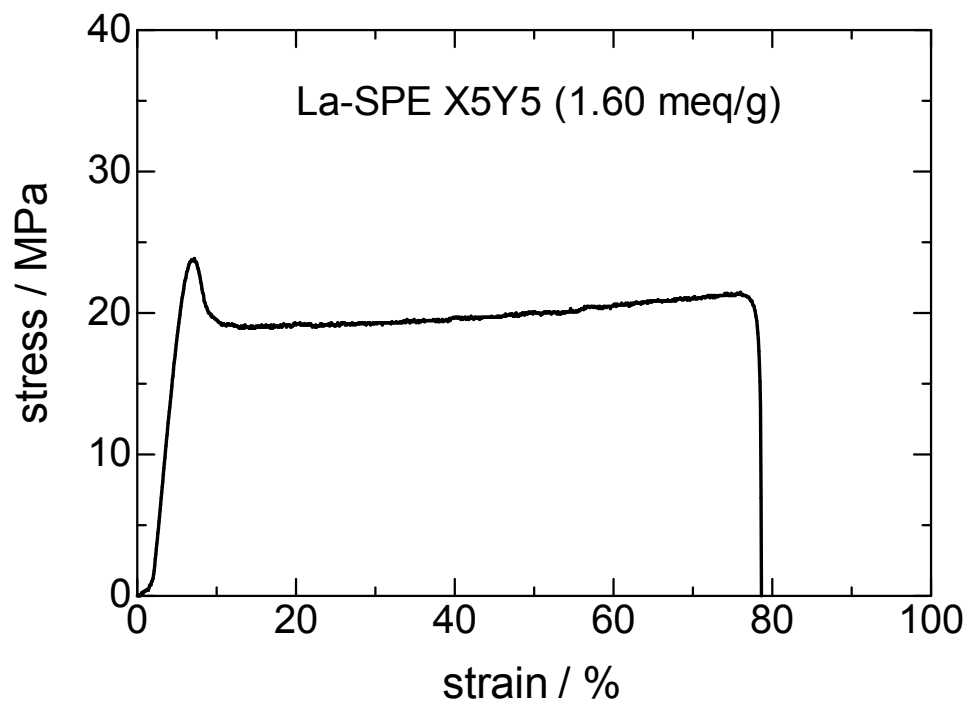


Figure S10. Stress vs strain curve of La-SPE (X5Y5) at 80 °C and 60% RH.

Reference

[S1] N. Li, D. W. Shin, D. S. Hwang, Y. M. Lee and M. D. Guiver, *Macromolecules*, 2010, **43**, 9810.