

Supporting Information

Hydrophilic–Hydrophobic Diblock Copolymer Based on Polyphenylenes for Cathode Ionomers of Fuel Cells

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1. Materials

Nafion[®] NR-211 membranes (1100 meq g⁻¹) and Nafion[®] D2020 solutions (1000 meq g⁻¹) were purchased from Dupont[®] Co., Ltd. SIGRACET[®] 25BC was purchased from SGL Carbon Japan Ltd. for gas diffusion layers (GDLs).

2. Polymer Preparation

2.1. Monomer Synthesis

Hydroquinone, potassium carbonate, pyridine, and tetrahydrofuran (THF, organic synthesis grade) were purchased from Wako Pure Chemical Industries Ltd. and used as received. Chlorosulfuric acid was purchased from Kanto Chemical Ltd. and used as received. Isopropyl magnesium chloride·lithium chloride complex in THF (*i*PrMgCl·LiCl, 1.3 M) was purchased from Sigma-Aldrich Co. LLC. and used as received. Chloroform, carbon tetrachloride, *N,N*-dimethylformamide (DMF, Wako Pure Chemical Industries Ltd.), dimethyl sulfoxide (DMSO, Wako Pure Chemical Industries Ltd.), 1,2-dichloroethane, dichloromethane, and 1-methyl-2-pyrrolidone (NMP, Kanto Chemical co., inc.) were purified by conventional methods. 1-Bromobutane (Wako Pure Chemical Industries Ltd.) was purified by distillation, and 1-bromohexane (Sigma-Aldrich co., ltd.) and 4-phenylbutylbromide (Tokyo Kasei Kogyo co., Ltd.) were purified by reduced-pressure distillation. *N,N*-Diethylamine hydrobromide (Wako Pure Chemical Industries Ltd.) was dried at 40 °C overnight. 1,4-Dibromo-2,5-di[4-(2,2-dimethylpropoxy sulfonyl)phenylbutoxy]benzene (**1**) and 1,4-dibromo-2,5-dihexyloxybenzene (**2**) were synthesized according to the literature.¹

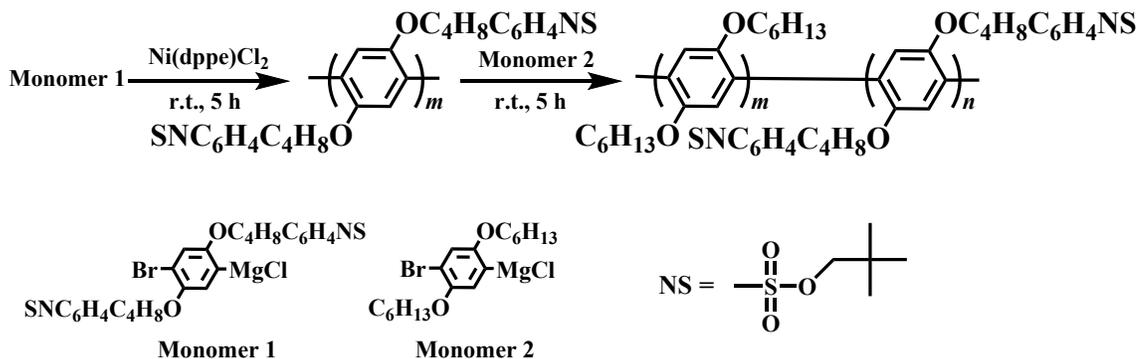
2.2. Synthesis of diblock copolymer (SBuH)

The synthesis of the diblock copolymer, SBuH, was conducted by catalyst transfer poly condensation² as described below. *i*PrMgCl·LiCl (1.3 M solution in THF: 6.36 mL, 8.27 mmol) was added to monomer **1** (7.63 g, 9.17 mmol) via a syringe at room temperature in an argon-filled glove box, and the reaction mixture was stirred at 40 °C for 5 h. The mixture was then added to a suspension of Ni(dppe)Cl₂ (0.0400 g, 0.0758 mmol) in 12 mL THF at room temperature, and stirred for 5 h to afford **P1**. Monomer **2** (3.42 g, 7.84 mmol) treated with *i*PrMgCl·LiCl (5.45 mL,

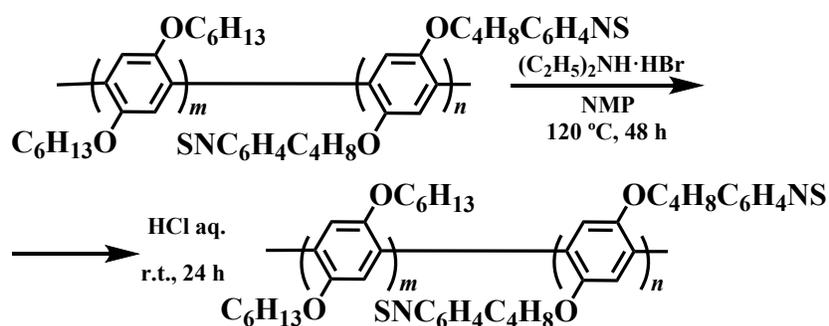
7.09 mmol) was added to the **P1** solution. THF (10 mL) was added to the mixture, and stirred at room temperature for 5 h. After addition of HCl/MeOH, the insoluble product was collected by suction filtration and washed well with MeOH. The residue was reprecipitated from chloroform solution into acetone/methanol (1/1 v/v) to give **P1-P2** (yield 53%).

^1H NMR (300 MHz, THF-*d*8): δ 7.71, 7.31, 7.11, 7.07, 3.94, 3.81, 3.64, 2.61, 1.67, 1.62, 1.41, 1.31, 0.90, 0.84. ^{13}C NMR (125 MHz, THF-*d*8): δ 151.4, 150.2, 135.2, 130.3, 129.0, 118.2, 80.1, 70.4, 69.9, 36.4, 32.9, 32.4, 30.8, 30.2, 28.7, 27.0, 26.6, 23.8, 14.7. IR ν 3064, 3050, 3032, 2946, 2921, 2866, 1598, 1474, 1402, 1355, 1300, 1251, 1208, 1189, 1174, 1131, 1116, 1098, 1067, 1038, 1019, 963, 937, 845, 788, 755, 732, 681, 659 cm^{-1} .

As previously reported,¹ the neopentyl-protected sulfonyl group in **P1-P2** was cleaved using an NMP solution of diethylamine hydrobromide at 120 °C for 48 h to provide the acid form of copolymer, **SBuH** (Scheme S2). After cooling to room temperature, the dark brown viscous reaction solution was poured into diethyl ether. The insoluble product was collected by suction filtration. The reddish-brown product was stirred in 1 M HCl aq. for 24 h and in water for 24 h to give **SBuH**.



Scheme S1. Synthesis of diblock copolymers **P1-P2**.



Scheme S2. Synthesis of diblock copolymers **SBuH**

2. Membrane preparation

SBuH membranes with a 50 μm thickness were prepared by solution casting. DMSO was used as a solvent instead of THF used in the catalyst inks because of the brittleness of membranes casted from THF solution. The SBuH solution was prepared by stirring SBuH in DMSO (5 wt.%) at 80 $^\circ\text{C}$ for 8 h. The solution was directly cast on a glass plate after the filtration, and dried at 80 $^\circ\text{C}$ under ambient pressure for 24 h, and then under vacuum for 24 h. The membranes were immersed in 1 M HCl aq. for 24 h and then washed in deionized water at r. t. These membranes were dried under vacuum at 80 $^\circ\text{C}$ for 24 h. Nafion[®] NR-211 membranes was used as received instead of Nafion[®] D2020 membranes casted from the mixture of isopropanol and water as used in the catalyst inks because of the brittleness of cast membranes.

3. Preparation of membrane electrode assemblies (MEAs)

The weight ratios of ionomer to carbon (*I/C*) for SBUH and Nafion[®] cathode CLs were 0.45 and 0.90, respectively. Nafion[®] ionomer (Nafion[®] D2020, Dupont) was used as a perfluorosulfonic acid ionomer. Graphitized carbon black was used as Pt support (29.1 wt.%) for both anode and cathode CLs.³ THF was chosen as the solvent for the cathode catalyst inks for use with the SBUH ionomer because SBUH is highly soluble in THF, and THF has a low boiling point compared to the solvents that were used with other reported aromatic ionomers, such as dimethylacetamide and DMSO. The amount of THF was adjusted such that the concentration of solid contents of the catalyst ink was 5 wt.% in THF to suppress clogging of spray nozzles and cracking of the catalyst layer surface. An SBUH ionomer solution was prepared by stirring SBUH powder in THF at 50 °C for 72 h. An adequate amount of deionized water was added to the catalyst powder to prevent its ignition before adding the ionomer solution to the catalyst powder. The catalyst ink was mixed using a planetary centrifugal mixer (ARE-250, Thinky) at 2,000 rpm for 2 min and then ground with 1.5 mm ϕ zirconia beads using a bead mill (BSG-04, Aimex) at 80 rpm for 2 min, then at 1,500 rpm for 10 min. The mixed catalyst ink was separated from the zirconia beads using a centrifuge (BuF-08, Aimex). The catalyst ink was directly sprayed onto a Nafion[®] NR-211 membrane using a pulse spray coating system[®] (V5R02, Nordson). The SBUH catalyst layers were dried at 80 °C for 3 h. A mixture of *n*-propanol and deionized water was used as the solvent for the anode CLs containing Nafion[®] ionomer. The amount of solvent was adjusted such that the solid contents corresponded to 6 wt.% in the catalyst ink. The weight ratio of water to *n*-propanol in the catalyst ink was 1.5, and the *I/C* value was 1.3. The procedure for preparation of the anode CLs was the same as for the SBUH CLs. 25BC (SGL Carbon) with micro porous layers (MPLs) was used for the GDLs. The active area of the catalyst layers was 10 cm² (2 cm \times 5 cm) for both anode

and cathode. The width and the depth of the straight gas-flow channel in the cell was 0.5 mm × 0.6 mm, respectively.³ The rib-width was 0.5 mm for both anode and cathode.³

4. Measurements

Viscoelasticity was evaluated using a dynamic mechanical analyzer (DVA[®]-220, IT Keisoku Seigyo Co. Ltd.) in a temperature and humidity-controlled chamber in tensile mode at 10 Hz with a strain of 0.01%.

Gas permeability was measured by the equal pressure method using a gas permeation measurement apparatus (GTR-30XFST, GTR Tech). The amounts of H₂ and O₂ that permeated the membranes were monitored by gas chromatography (G2700T, Yanaco), and argon and helium gases were used as the carrier gases for measurements of H₂ and O₂, respectively. H₂ and O₂ were supplied at a flow rate of 10 mL min⁻¹.

The water uptakes (WU_s) were measured using an isothermal absorption measurement system (IGAsorp, Hiden Isochema Ltd.) in a temperature and humidity controlled chamber.

The swelling volume ratio (V) was calculated from the displacement of thickness and area between dried and hydrated membranes. The membranes were dried at 80 °C for 4 h under vacuum. Hydrated membranes were prepared by immersion in deionized water at 80 °C for 24 h. The V values were calculated by the following equations:

$$\Delta A (\%) = \frac{A_w - A_d}{A_d} \times 100$$

$$\Delta T (\%) = \frac{T_w - T_d}{T_d} \times 100$$

$$V (\%) = \frac{V_w - V_d}{V_d} \times 100$$

where A and T are the area and thickness, A_w , T_w , and V_w are the wet area, thickness, and volume, and A_d , T_d , and V_d are the dry area, thickness, and volume, respectively.

The proton conductivity (σ) of the membranes was measured at 80°C from 30%RH to 100%RH by a four-point probe method. The impedance/gain-phase analyzer (SI 1260, Solartron) was used at a frequency range from 10 Hz to 1 MHz.

The contact angle of the membranes was measured using a contact angle analyzer (Drop Master 700, Kyowa Interface Science Co., Ltd.). For contact angle measurements, the membranes were fixed on a glass plate with a thermoplastic tape, covered by Teflon sheets, then hot-pressed at 100 °C and 0.90 MPa for 10 min to avoid wrinkles in the membrane surface. Deionized water (3.0 μ L) was dropped on the surface of the membranes through a syringe with a 0.4 mm diameter needle and kept on the surface for 30 s.

Cross-sectional images and pore size distributions of the catalyst layers (CLs) were obtained using a scanning electron microscope (S-4500, Hitachi Co., Ltd.) and a mercury intrusion porosimeter (AutoPore IV 9500, Micromeritics Co., Ltd.), respectively. The limiting current of the oxygen reduction reaction was measured at 80 °C and 90 %RH under a back-pressure range between 100 kPa and 200 kPa and an oxygen concentration range between 0.53 and 2.6 %. The cell voltage was scanned using a potentiostat (HZ-5000, Hokuto Denko Co., Ltd) at 10 mV s⁻¹ from open circuit voltage to 0.1 V. The cell resistance was monitored at 1 kHz. Fuel cell tests were performed at 80 °C and 90 %RH under 200 kPa by supplying hydrogen and 10 % oxygen of 4.0 L min⁻¹ and 15 L min⁻¹, respectively. The cyclic voltammetry (CV) of the MEAs were measured at 80°C and 100%RH under a potential range from 0.02 to 0.90 V vs. RHE. The potential sweep rate was 50 mV s⁻¹. Hydrogen and nitrogen was fed to the counter electrode and working electrode at 0.50 and 0.50 Nm³ min⁻¹, respectively. The inlet and the outlet valves connected to the working electrode were closed before the potential sweep.

References

- 1 K. Umezawa, T. Oshima, M. Yoshizawa-Fujita, Y. Takeoka, and M. Rikukawa, *ACS MacroLetters*, 2012, **1**, 969.

- 2 R. Miyakoshi, K. Shimono, A. Yokoyama, T. Yokozawa, *J. Am. Chem. Soc.* 2006, **128**, 16012.
- 3 Y. Ono, A. Ohma, K. Shinohara, K. Fushinobu, *J. Electrochem. Soc.*, 2013, **160** (8) F779.

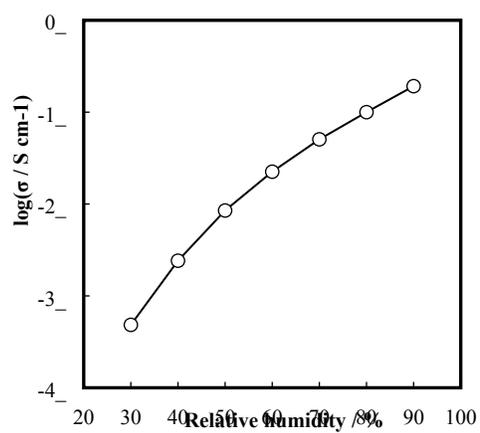


Figure S1. Proton conductivity of SBUH membranes at 80 °C as a function of relative humidity.

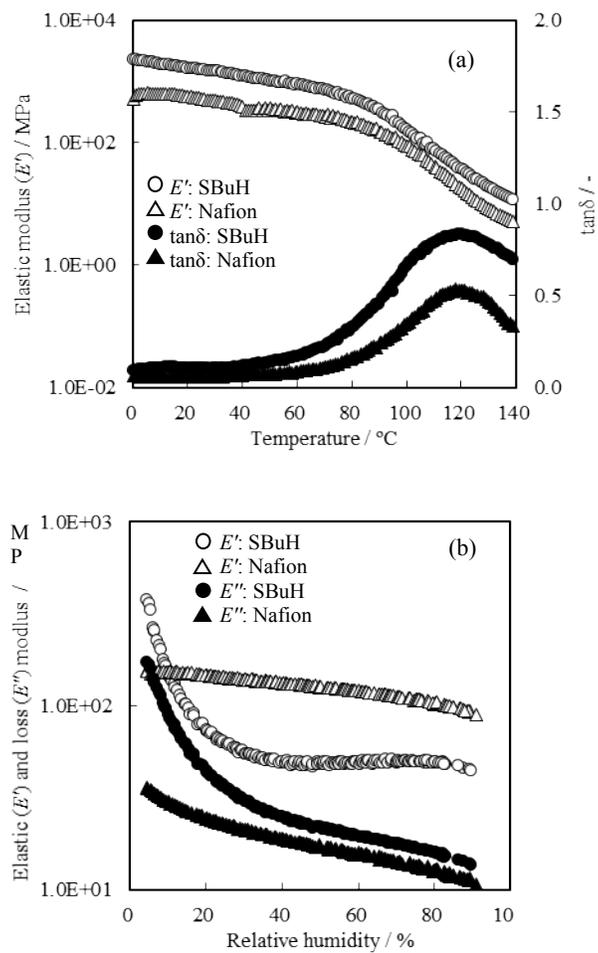


Figure S2. Viscoelasticity of SBUH and Nafion[®] membranes as a function of (a) temperature and (b) relative humidity at 80 $^{\circ}\text{C}$.

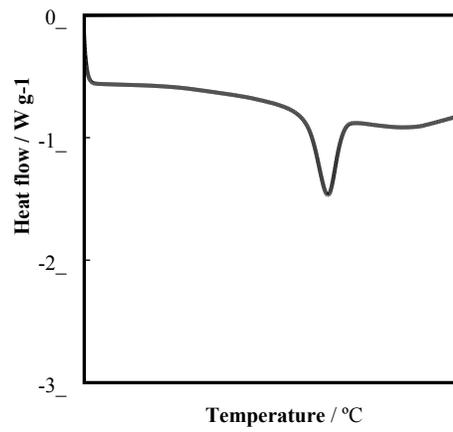


Figure S3. DCS curve of a SBUH membrane at 10 °C /min in a nitrogen atmosphere.

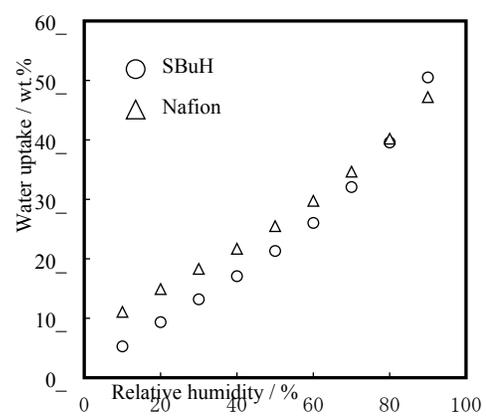


Figure S4. Water uptakes of SBUH and Nafion[®] CLs at 80 °C as a function of relative humidity.

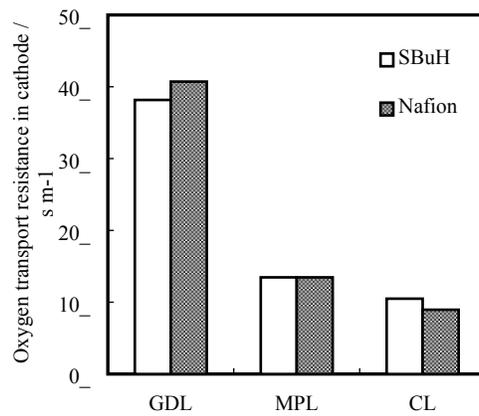


Figure S5. Breakdown of oxygen transport resistance in MEAs of SBUH CLs and Nafion[®] CLs at 80 °C and 90%RH.

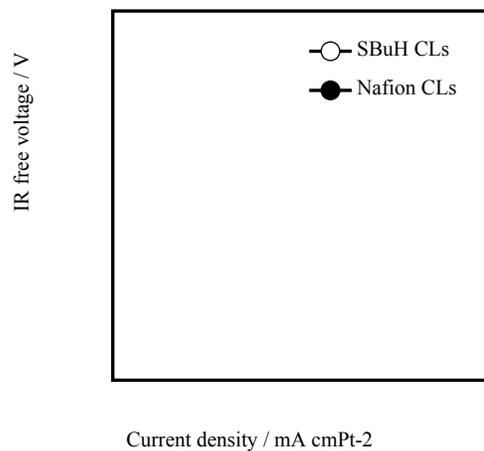


Figure S6. Tafel plots of SBuH CLs and Nafion[®] CLs at 80 °C and 100%RH at 200 kPa with hydrogen and oxygen supply.

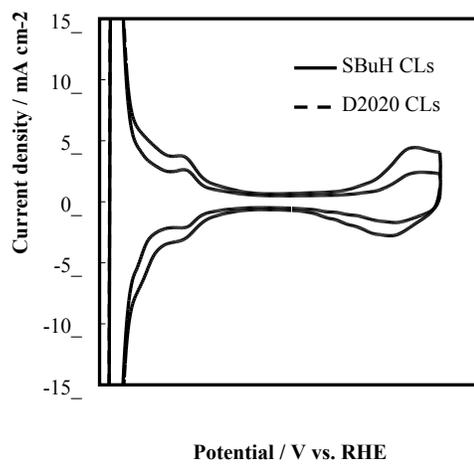


Figure S7. Cyclic voltammograms of SBUH CLs and Nafion[®] CLs at 80 °C and 100%RH at 100 kPa with hydrogen and nitrogen supply.

Table S1. Swelling ratio after immersion of water at 80 °C, and estimated λ and density of SBUH and Nafion membranes.

Sample	Area	Thickness	Volume	λ	Density
-	%	%	%	-	g/cm ³
SBUH	48.1±1.6	83.4±3.4	171.7±8.0	15.4±0.7	1.21
Nafion	37.9±6.1	24.5±10.0	71.6±9.9	20.1±2.8	1.95