

Supplementary information

Sulfonated polybenzophenone/polyimide copolymer as a novel proton exchange membrane

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Materials

4,4'-Dichlorobenzophenone (DCBP, > 99.0%, Tokyo Kasei Co. Ltd.), 1,4,5,8-naphthalenetetracarboxylic dianhydride (TCND, > 95.0%, Tokyo Kasei Co. Ltd.), bis[4-(3-aminophenoxy)phenyl]sulfone (*m*BAPS, > 97.0%, Tokyo Kasei Co. Ltd.), 4-chloroaniline (> 99.0%, Tokyo Kasei Co. Ltd.), nickel bis(cyclooctadiene) (Ni(cod)₂, > 95.0%, Kanto Chemical Co. Ltd.), 2,2'-bipyridyl (> 99.0%, Tokyo Kasei Co. Ltd.), sodium hydroxide (97.0%, Wako Co. Ltd.), sulfuric acid, fuming (30% SO₃, Kanto Chemical Co. Ltd.), hydrochloric acid (35-37%, Wako Co. Ltd.), *N*-methyl-2-pyrrolidone (NMP, 99.0%, Wako Co. Ltd.), dimethyl sulfoxide (DMSO, 99.0%, Wako Co. Ltd.), toluene (99.5%, Wako Co. Ltd.), ethanol (99.5%, Wako Co. Ltd.), *m*-cresol (98.0%, Wako Co. Ltd.), and acetone (99.0%, Wako Co. Ltd.) were commercially available grade and used as received. Monomer **1** was synthesized according to the literature.¹

Measurements

¹H NMR spectra were obtained on a JEOL JNM-ECA 500 (500MHz) using deuterated dimethyl sulfoxide (DMSO-*d*₆) as a solvent and tetramethylsilane (TMS) as an internal reference. 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 at a flow rate of 1.0 mL/min. Two Shodex KF-805 columns were used for polymers and a Shodex SB-803HQ column was used for oligomers, respectively. Column temperature was set at 35 °C. Molecular weight was calibrated with standard polystyrene samples.

Synthesis of hydrophobic oligomer **2**

A typical procedure is as follows (targeted *n* = 16). A 500-mL three-neck flask equipped with a magnetic stirring bar was charged with TCND (6.0 g, 22.4 mmol), *m*BAPS (9.1 g, 21.0 mmol), 40 mL of NMP, and 15 mL of toluene. The reaction was carried out at 180 °C for 72 h with a Dean-Stark trap. Then, 4-chloroaniline (1.0 g, 7.8 mmol) was added to the mixture. The reaction was carried out at 180 °C for 18 h. The mixture was poured into 500 mL of acetone. The precipitate was collected by filtration and dried in vacuum. The crude product was dissolved in *m*-cresol and filtered. The filtrate was poured into excess ethanol, and the precipitate was filtered and dried in vacuum to obtain **2** (*n* = 16.9) in 80% yield.

Synthesis of block copolymer **3**

A typical procedure is as follows (*n* = 16 as a hydrophobic oligomer). A 100-mL three-neck flask equipped with a magnetic stirring bar was charged with monomer **1** (3.0 g, 6.59 mmol), oligomer **2** (2.0 g), DMSO (40 mL), and toluene (15 mL). The mixture was refluxed with vigorous

stirring for 3 h at 180 °C with a Dean-Stark trap. After azeotropic removal of water by toluene, 2,2'-bipyridine (3.0 g, 19.21 mmol) and Ni(cod)₂ (5.0g, 18.18 mmol) were added at 70 °C under N₂ atmosphere. The mixture was stirred at 80 °C for 2 h. After the reaction, 10 mL of DMSO was added to the viscous mixture which was poured into 100 mL of 6 M hydrochloric acid. The mixture was stirred for 1 h, diluted with 100 mL of water, and filtered. The crude product was washed with water and dried in vacuum at 100 °C to obtain block copolymer **3** in 53% yield.

Membrane preparation

The block copolymer **3** (1.0 g) was dissolved in 20 mL of DMSO and cast onto a flat glass plate. The solution was dried at 80 °C to obtain a membrane (*ca.* 40 μm thick). The crude membrane was soaked in 6 M hydrochloric acid for 6 h twice, washed with deionized water, and dried at 100 °C under reduced pressure for 12 h.

Ion exchange capacity (IEC)

IEC of the membrane was measured by back-titration. A piece of the membrane (*ca.* 80 mg) was equilibrated in a large excess of 5 M NaCl aqueous solution for 3 days. The HCl released by the ion exchange was titrated with standard 0.01 M NaOH aqueous solution. Typical error of the titration was 1.3%.

Transmission electron microscopic (TEM) observation

For TEM observations, the membrane sample was 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 a vacuum oven 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 JEOL JEM2100F HRTEM with an accelerating voltage of 200 kV.

Water uptake and proton conductivity

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 membrane 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 membrane and exposure to a given humidity for at least 2 h gave the weight of hydrated membrane. Proton conductivity was measured using four-probe conductivity cell attached with impedance spectroscopy (Solartron 1255B and 1287, Solartron Inc.) simultaneously in the same chamber. Ionic 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 Au wires and the conducting area, respectively. Typical error of the proton conductivity was 1.3%.

Gas permeability

Hydrogen and oxygen permeability was measured with a gas permeation measurement apparatus (20XAFK, GTR-Tech Inc.) equipped with a gas chromatograph (GC, G2700T, Yanaco) with thermal conductivity detector. Argon and helium were used as the carrier for the measurement of hydrogen and oxygen, respectively. Membranes were placed in the center of the permeation cell, and the test gas was introduced onto one side of the membrane at a flow rate of 20 mL/min. Carrier gas was introduced onto the other side of the membrane at the same flow rate and was analyzed by the GC. The same humidity conditions were applied to both test and carrier gases to ensure homogeneous wetting of the membrane samples. Then, 15 mL of flow gas was sampled and subjected to the gas chromatography to quantify the test gas permeated through the membrane. The measurement was repeated until stable permeation data were obtained. The gas permeability coefficient, *Q* (barrer = 1 × 10⁻¹⁰ cm³ (STD) cm/cm² cm mmHg), was calculated by eq 1:

$$Q = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t} \times l \times \frac{1}{76 - P_{\text{water}}} \quad (1)$$

where T (K) is the absolute temperature, A (cm²) is the permeation area, B (cm³) is the volume of the test gas permeated through the membrane, t (s) is the sampling time, l (cm) is the thickness of the membrane, and P_{water} (cm Hg) is the water vapor pressure.

DMA analyses

The storage and loss moduli (E' and E'' , respectively), and $\tan \delta$ of **3** membrane were obtained from an ITK DVA-200 dynamic viscoelastic analyzer. Humidity dependence of E' , E'' , 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).

Reference

(1) T. Miyahara, T. Hayano, S. Matsuno, M. Watanabe and K. Miyatake, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2881.

Table S1 λ (number of absorbed water molecules per sulfonic acid group) of **3** (IEC = 1.01 meq g⁻¹), SPI-8 (IEC = 2.18 meq g⁻¹), SPK-*bl*-1 (IEC = 2.08 meq g⁻¹) and Nafion NRE211 (IEC = 0.92 meq g⁻¹) membranes at 80 °C

membrane	λ	
	20%RH	80%RH
3	3.19	9.40
SPI-8	1.54	7.32
SPK- <i>bl</i> -1	2.43	7.28
NRE211	2.47	7.26

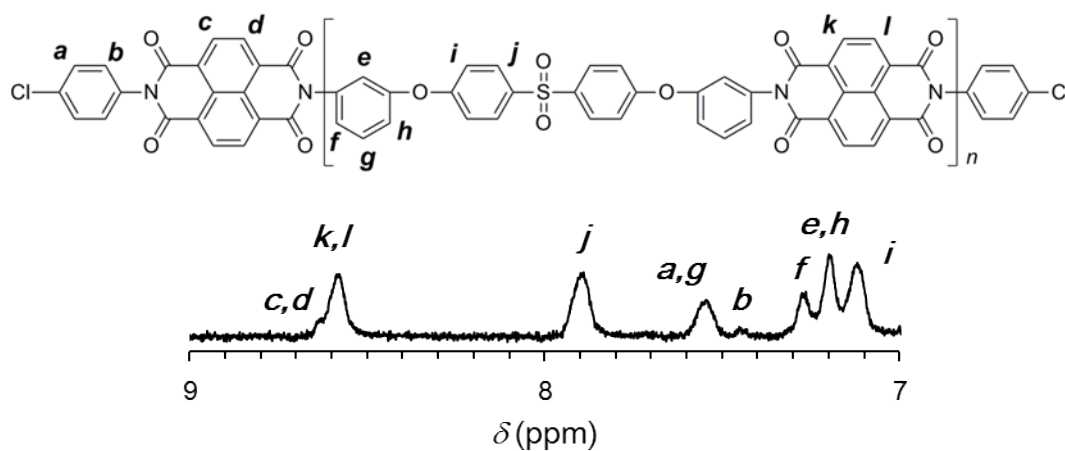


Fig. S1 ¹H NMR spectrum of hydrophobic oligomer **2**.

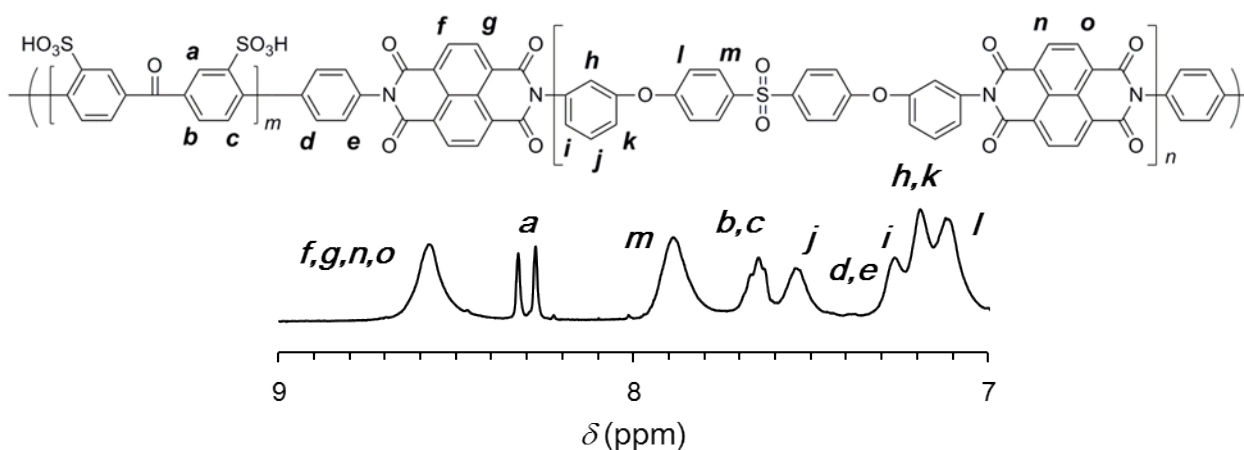


Fig. S2 ¹H NMR spectrum of block copolymer **3**.

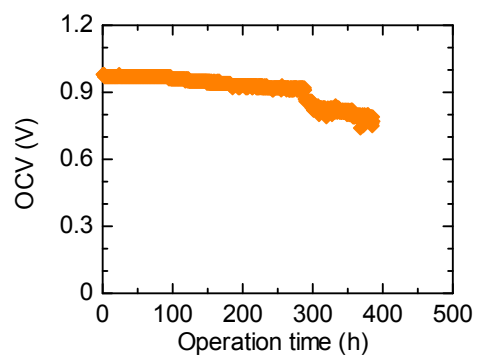


Fig. S3 OCV hold test of the **3** membrane (IEC = 1.01 meq g⁻¹) at 80 °C and 20% RH.