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Sulfonated polybenzophenone/polyimide copolymer as a novel proton exchange membrane

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A sulfonated polybenzophenone/polyimide block copolymer membrane exhibited high proton conductivity, good dimensional and mechanical stabilities, and low gas permeability, which are attractive for fuel cell applications.

Polymer electrolyte fuel cells (PEFCs) have received considerable attention as clean energy devices because of their high efficiencies and low pollution levels. PEFCs are especially attractive for automotive and stationary applications. Fuel cell electric vehicles have recently been commercialized. However, there still remain technical issues for widespread commercialization of PEFCs. One of the important challenges in the current fuel cell research is to develop polymer electrolyte membranes (PEMs) that are more proton conductive and durable, and less gas permeable than the existing PEMs. While state-of-the-art PEMs, perfluorosulfonic acid (PFSA) ionomers such as Nafion, exhibit high proton conductivity and stability, non-fluorinated alternative PEMs are in great demand in terms of environmental compatibility and cost effectiveness.

Hydrocarbon-based fluorine-free PEMs have been extensively investigated in the last decade or two due to their flexibility in molecular design and synthesis and low gas permeability. Acid-functionalized aromatic polymers such as poly(arylene ether)s,[1-7] polybenzimidazoles,[8] polyimides,[9-11] polyphenylene derivatives[12-15] have been proposed in the literature. It is well-known that block copolymers composed of sulfonated and unsulfonated blocks are much more proton-conductive than the random copolymer equivalents, because the former are likely to form well-developed hydrophilic/hydrophobic phase separation with interconnected ionic channels.[16] We have developed block copolymers composed of highly sulfonated benzophenone groups as hydrophilic components.[17] The block copolymer (SPK-bl-1, Fig. 1) membranes are highly proton-conductive at high temperature (120 °C) and low relative humidity (30% relative humidity (RH)) and exhibit fuel cell performance comparable to that of Nafion membranes over a wide range of humidity. In order to achieve such high performance, the SPK-bl-1 membrane needs to have relatively high ion exchange capacity (IEC = 2.57 meq g^{-1}), which causes large water uptake and swelling under fully hydrated conditions and may cause mechanical failure when experiencing frequent wet/dry cycling. Our idea to improve the dimensional stability, without compromising the high proton conductivity and low gas permeability, is to combine the above-mentioned hydrophilic component with a rigid aromatic hydrophobic component.[8] Polyimides are attractive for this purpose, since they have a planar main chain structure with polar imide groups to enhance the intermolecular interactions. We have previously reported that a sulfonated polyimide (SPI-8, Fig. 1) membrane exhibited high mechanical stability.[18] McGrath et al. reported block copolymers composed of polyimide and sulfonated poly(arylene ether sulfone), whose morphology and thermal transition were well-investigated.[19,20] We report herein a novel copolymer containing a sulfonated benzophenone as a hydrophilic component and a polyimide as a hydrophobic component. The properties of the copolymer membrane are compared with those of SPK-bl-1 and SPI-8 membranes.

The hydrophilic monomer, bis(3-sulfo-4-chlorophenyl) ketone **1**, was synthesized according to the literature.[17] The chlorine-terminated hydrophobic oligomers **2**, oligo(imide ether sulfone), were prepared by polycondensation of bis[4-(3-aminophenoxy)phenyl]sulfone and a slight excess of 1,4,5,8-naphthalenetetracarboxylic dianhydride, followed by end-capping with 4-chloroaniline (Scheme 1). The main chain and telechelic chemical structures of **2** were confirmed by the ^{1}H NMR spectrum (Fig. S1†), in which the peaks were well-assigned. The degrees of oligomerization of **2** were estimated from the integral ratios in the ^{1}H NMR spectra to be *ca.* 10.8 and 16.9, which were in fair agreement with those (8 and 16) calculated from the feed comonomer ratios. The molecular weights of **2** were determined by gel permeation chromatography (GPC) to be M_n = 11,700, 17,900 (M_w/M_n = 2.9, 3.0), respectively. The degrees of oligomerization estimated from M_n were 16.9, 26.2. These values were higher than those mentioned above obtained from the ^{1}H NMR spectra and feed comonomer compositions probably because the oligomers eluted faster than the standard polystyrene samples from the GPC columns due to the rigid rod-like structure of the oligoimide.

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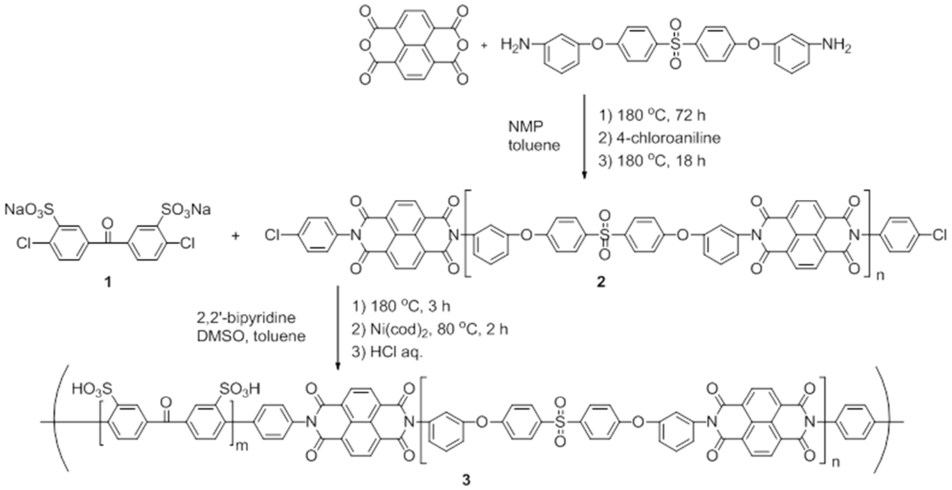

Scheme 1 Synthesis of copolymer **3**.

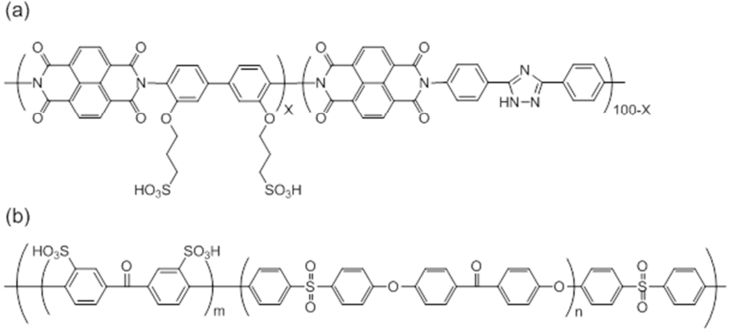

Fig. 1 Structures of (a) SPI-8 and (b) SPK-bl-1.

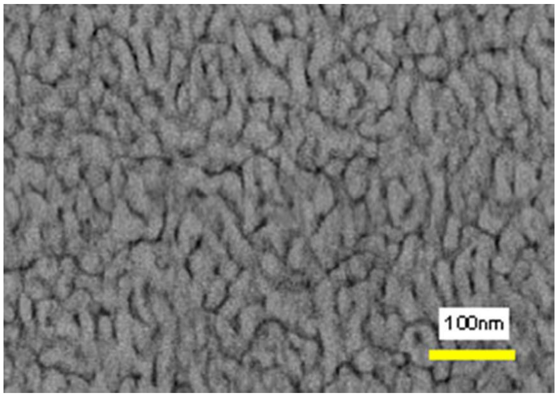

Fig. 2 TEM image of **3** membrane (IEC = 1.01 meq g^{-1}) in lead ion form.

The copolymers **3** were synthesized from **1** and **2** by Ni-mediated coupling reaction. The block copolymerization was complete within 2 h at 80 °C to give **3** as high-molecular-weight (M_w = 150 - 313 kDa) products with reasonable polydispersity indices (M_w/M_n = 3.4 - 7.1). Copolymers **3** were soluble in polar aprotic solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylacetamide (DMAc) and were characterized by NMR spectra. In the ^{1}H NMR spectrum of **3** (Fig. S2†), the peaks at 7.60-7.80 and 8.28-8.40 ppm were assigned to the sulfonated benzophenone groups, and the peaks at 7.00-7.40, 7.48-7.68, 7.80-8.05, and 8.48-8.80 ppm were assigned to the oligoimide blocks. The results suggest the successful formation of the targeted block copolymer. Two samples of copolymer **3** with different length of hydrophobic block (n = 8, 16) were prepared. The IEC values were estimated to be 1.89 and 1.33 meq g^{-1} from the integral ratios in the ^{1}H NMR spectra. The IEC values were also measured by titration to be 1.57 and 1.01 meq g^{-1}, which were slightly lower than that obtained from the ^{1}H NMR spectra and much lower than that calculated from the feed comonomer/oligomer composition (3.13 meq g^{-1}). There are two plausible reasons for the lower IEC of the obtained copolymers: 1) the hydrophilic monomer **1** was not as reactive as the hydrophobic oligomer **2** due to steric hindrance; and 2) the higher IEC portions of the copolymers were soluble in water and were lost during the purification procedure. The copolymer yields were 53 - 64%, which supports these assumptions.

The obtained copolymers **3** provided brown transparent membranes by solution casting. The morphology of the **3** membrane was observed by transmission electron microscopy (TEM) with the sample in lead ion form (Fig. 2). The dark areas represent hydrophilic domains containing lead sulfonate groups. The hydrophilic domains in black and the hydrophobic domains in white were both belt-like structures and well-interconnected. The belts were *ca.* 5-10 nm wide (hydrophilic) and *ca.* 25-40 nm wide (hydrophobic), respectively. Compared to our previous version of the block copolymer (SPK-bl-1, IEC = 2.57 meq g^{-1}) membrane sharing the same hydrophilic component,[17] the hydrophobic domains were larger in the **3** membrane due to the latter's lower IEC value.

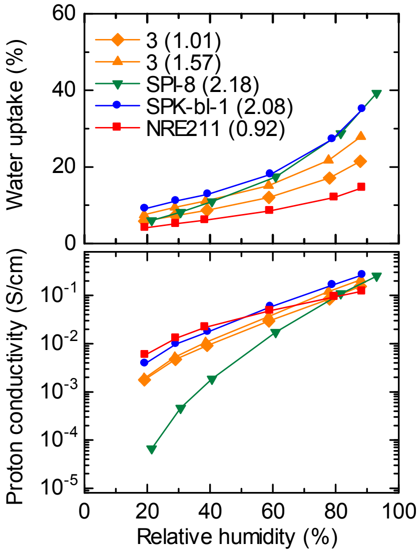

Fig. 3 Humidity dependence of water uptake and proton conductivity of **3** (orange diamonds, IEC = 1.01 meq g^{-1}), **3** (orange triangles, IEC = 1.57 meq g^{-1}), SPI-8 (green inverted triangles, IEC = 2.18 meq g^{-1}), SPK-bl-1 (blue circles, IEC = 2.08 meq g^{-1}) and Nafion NRE211CS (red squares, IEC= 0.92 meq g^{-1}) membranes at 80 °C.

Fig. 3 compares the water uptake and proton conductivity of **3**, SPI-8, SPK-bl-1, and Nafion NRE211CS membranes at 80 °C. The water uptake approximately followed the order of the IEC values at all RH. The proton conductivity at high RH (*ca.* 90% RH) showed a similar tendency, i.e., membranes with higher IEC values were more proton-conductive. This result is reasonable since most sulfonic acid groups would be dissociated at high water content, and ionic channels would be formed and interconnected with water molecules regardless of the polymer structures. On the other hand, the proton conductivity at low RH (e.g., 20% RH) was more complex and contained the effects of multiple parameters, e.g., acidity,[21] IEC value, and morphology. The proton conductivity decreased in the order Nafion NRE211 (estimated pK_a = -14 for $-CF_2CF_2SO_3H$ and IEC = 0.92 meq g^{-1} with well-developed morphology) > SPK-bl-1 (estimated pK_a = -2.5 for $-ArSO_3H$ and IEC = 2.08 meq g^{-1} with well-developed morphology) > **3** (estimated pK_a = -2.5 for $-ArSO_3H$ and IEC = 1.01 meq g^{-1} with well-developed morphology) > SPI-8 (estimated pK_a = -0.6 for $-(CH_2)_3SO_3H$ and IEC = 2.18 meq g^{-1} with no phase-separated morphology). The acidity seemed more crucial than the other parameters for the proton conductivity at low humidity. SPI-8 membrane exhibited less-developed morphology with isolated ionic domains, which accounted for significantly lower proton conductivity. It is noteworthy that λ (number of absorbed water molecules per sulfonic acid group) of the **3** membrane was higher than those of the other membranes (Table S1). The higher λ should also contribute to higher proton conductivity of the **3** membrane at low RH than that of the SPI-8 membrane despite the former's much lower IEC.

Table 1 Properties of the membranes

PEMs	M_w (M_n)[a] / kDa	IEC[b] / meq g^{-1}	Swelling ratio[c], %		Gas permeability[d] / cm^3(STD) cm cm^{-2} s^{-1} cmHg^{-1}	
			Δl	Δt	O_2	H_2
3	313 (44)	1.01	5	47	2.0×10^{-10}	6.5×10^{-10}
3	150 (44)	1.57	6	69	1.0×10^{-10}	3.8×10^{-10}
SPI-8	363 (89)	2.18	2	157	5.1×10^{-10}	8.2×10^{-10}
SPK-bl-1	335 (65)	2.08	35	33	8.5×10^{-11}	3.4×10^{-10}
NRE-211	- (-)	0.92	18	15	2.7×10^{-9}	5.2×10^{-9}

[a] Determined by GPC analyses (calibrated with polystyrene standards). [b] Determined by titration. [c] In water at r.t. (Δl: in-plane, Δt: through-plane). [d] At 80 °C and 95% RH.

Dimensional stability of the **3** membranes were measured after treatment in water at r.t. for 15 h and is summarized in Table 1 with those of the other membranes. The in-plane and through-plane dimensional changes of **3** membranes (1.01 and 1.57 meq g^{-1}) were 5 and 6%, and 47 and 69%, respectively. Comparison between **3** and SPK-bl-1 membranes suggested that the introduction of polyimide groups as hydrophobic components contributed to lowering the in-plane swelling. The anisotropic swelling behaviour of the **3** membranes were similar to that of the SPI-8 membrane (Δl = 2%, Δt = 157%, respectively), probably reflecting the orientation of the imide planes parallel to the membrane surface.[22] Hydrogen and oxygen permeabilities of **3** membranes were between those of SPK-bl-1 and SPI-8 membranes. The four aromatic ionomer membranes showed much lower gas permeabilities than those of Nafion, and the differences among the aromatic ionomer membranes were rather minor.

In Fig. 4 are shown *E'* (storage moduli), *E"* (loss moduli), and tan δ of **3**, SPI-8, and SPK-bl-1 membranes at 80 °C as a function of RH. SPK-bl-1 and **3** membranes, having the same hydrophilic component, showed similar viscoelastic properties and corresponding humidity dependences, i.e., they showed clear peaks at *ca.* 60% RH in the *E''* and tan δ curves, possibly ascribed to the glass transition. The *E'* values decreased above this humidity. The changes in *E''* and tan δ curves of the **3** membrane were smaller than those of the SPK-bl-1 membrane because of the lower IEC values and/or rigid hydrophobic polyimide blocks. SPI-8 retained high *E'* values up to 90% RH, with no distinct peaks in the *E''* and tan δ curves, suggesting that the rigid, robust polyimide components contributed to the improvement in the viscoelastic properties under both dry and wet conditions.

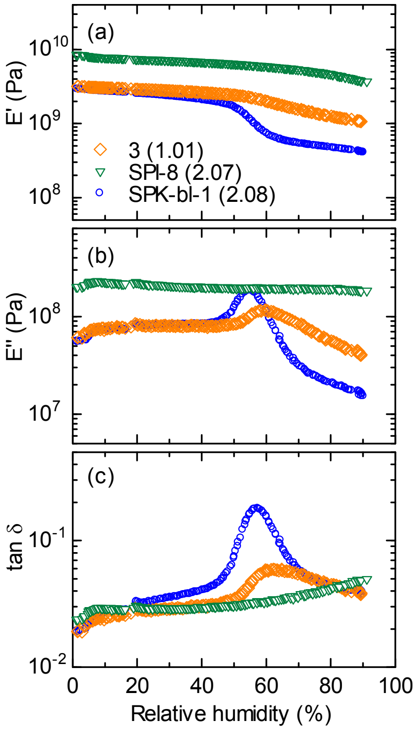

Fig. 4 DMA analyses of the membranes; (a) *E′* (storage modulus), (b) *E′′* (loss modulus), and (c) tan *δ* at 80 °C as a function of RH.

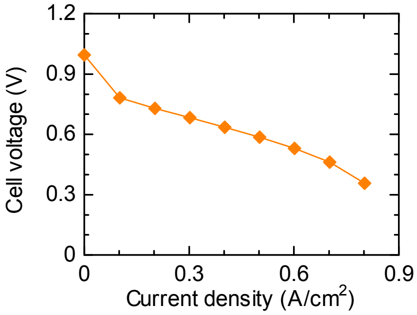

Fig. 5 Steady state H_2/air fuel cell performance of the **3** membrane (IEC = 1.01 meq g^{-1}) at 80 °C and 100% RH for both electrodes.

Fig. 5 shows fuel cell performance of the **3** membrane (IEC = 1.01 meq g^{-1}) with hydrogen and air at 80 °C and 100% RH. The open circuit voltage (OCV) was 1.00 V suggesting low gas permeation through the membrane in good accordance with the above mentioned gas permeability data. Reasonably good fuel cell performance was obtained despite its low IEC value. It is well-known that the OCV hold test, holding the cell voltage at OCV under low humidity conditions, provides information about the oxidative stability of membranes since membranes have high chances to be attacked by hydrogen peroxide and the resulting oxidative radical species under the circumstances. We have demonstrated the OCV hold test of the **3** membrane (IEC = 1.01 meq g^{-1}) at 80 °C and 20% RH (Fig. S3). The OCV was initially 0.98 V and decreased to 0.77 V after 386 h. The **3** membrane was much more durable than Nafion (0.97 V to 0.60 V after 140 h) due to the low gas permeability and the robust chemical structure.

In summary, we have synthesized a novel aromatic ionomer membrane **3** containing sulfonated benzophenone groups as hydrophilic components and oligoimide groups as hydrophobic blocks. Despite its low IEC value (1.01 meq g^{-1}) for aromatic ionomers, the **3** membrane exhibited well-developed phase-separated morphology with interconnected ionic channels, low water uptake and good swelling stability, high proton conductivity at low humidity, low gas permeabilities, and reasonable viscoelastic properties. The rigid and planar oligoimide moieties functioned effectively in the aromatic ionomer membrane.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure and characterisation data of oligomers and polymers. See DOI: 10.1039/c000000x/

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Graphical Abstract

Sulfonated polybenzophenone/polyimide copolymer as a novel proton exchange membrane

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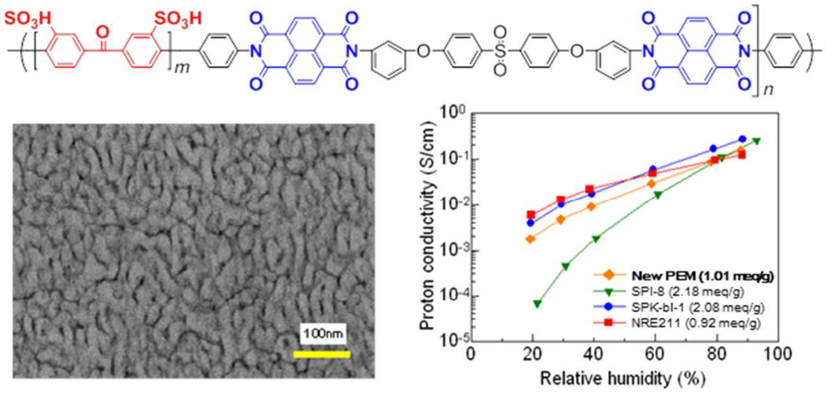

Supplementary information

Sulfonated polybenzophenone/polyimide copolymer as a novel proton exchange membrane

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[d] Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu, Yamanashi 400-8510, Japan.

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% SO$_3$, 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

^{1}H 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 N_2 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 10^5 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} cm^3 (STD) cm/cm^2 cm mmHg), was calculated by eq 1:

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

where T (K) is the absolute temperature, A (cm^2) is the permeation area, B (cm^3) 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 δ of **3** membrane were obtained from an ITK DVA-200 dynamic viscoelastic analyzer. Humidity dependence of E', E'', and tan δ 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-*bl*-1	2.43	7.28
NRE211	2.47	7.26

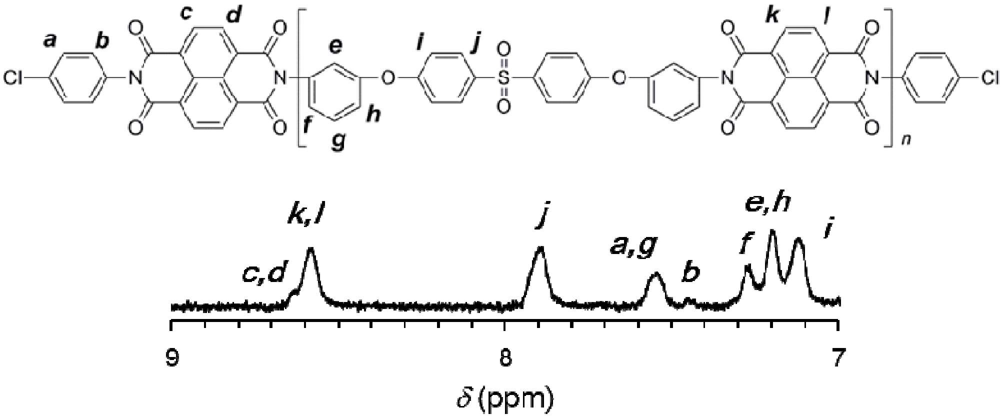

Fig. S1 ^{1}H NMR spectrum of hydrophobic oligomer **2**.

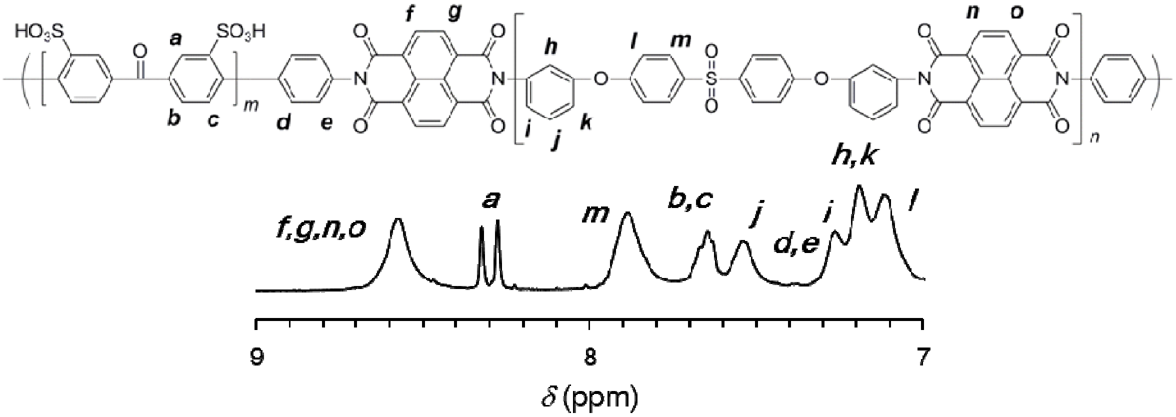

Fig. S2 ^{1}H NMR spectrum of block copolymer **3**.

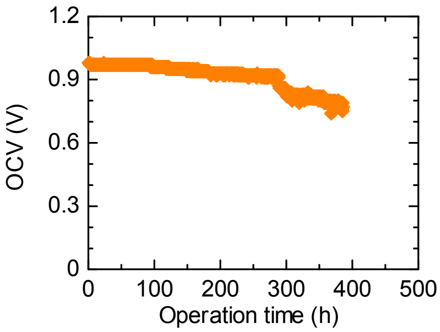

Fig. S3 OCV hold test of the **3** membrane (IEC = 1.01 meq g^{-1}) at 80 °C and 20% RH.