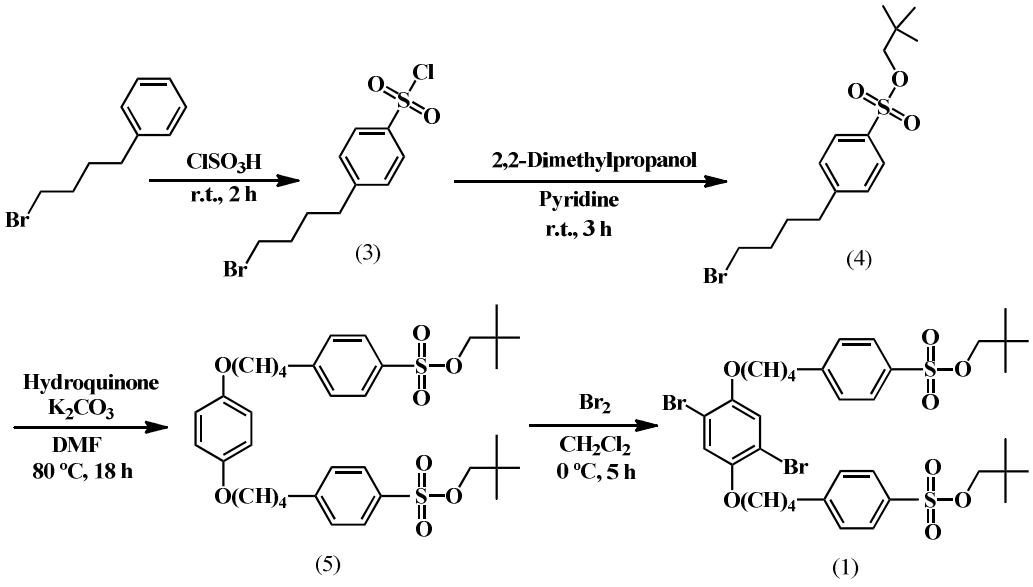
Supporting Information

Materials.

Hydroquinone, potassium carbonate, pyridine, tetrahydrofuran (THF for organic synthesis) were purchased from Wako Pure Chemical Industries Ltd and used as received. Chlorosulfuric acid was purchased from Kanto Chemical Ltd and used as received. *iso*-Propyl magnesium chloride lithium chloride complex THF solution (^{i}PrMgCl·MgCl, 1.3 M) was purchased from Aldrich Ltd and used as received. Chloroform, carbon tetrachloride, *N,N*-dimethylformamide (DMF), 1,2-dichloroethane, dichloromethane, and 1-methyl-2-pyrrolidone (NMP) were purchased and purified by the conventional ways. 1-Bromobutane was purified by distillation, and 1-bromohexane, 1-bromodecane, and 4-phenylbutyl bromide were purified by reduced-pressure distillation. *N,N*-diethylamine hydrobromide (Wako) was dried at 40 °C overnight.

Synthesis of hydrophilic monomer, 1,4-dibromo-2,5-di[4-(2,2-dimethylpropoxysulfonyl)phenyl]butoxybenzene (Scheme 1).



Scheme 1. Synthesis of hydrophilic monomer.

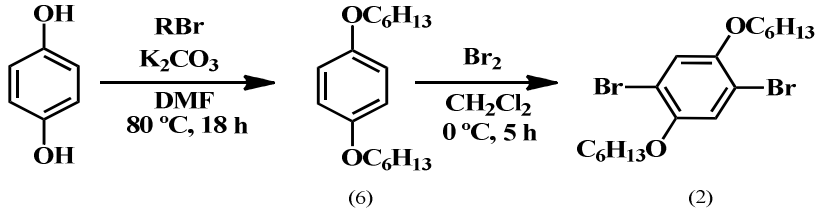
4-(4-Bromo-butyl)-benzenesulfonic acid 2,2-dimethyl-propyl ester (4). Chlorosulfonic acid (40.0 g, 602 mmol) was added to a 4-phenylbutyl bromide (50.2 g, 236 mmol), and the reaction mixture was stirred at room temperature for 2 h. After addition of water, the mixture was extracted with dichloromethane. The organic layer was washed with 5 wt% aqueous NaOH and water, and dried over anhydrous $MgSO_4$. Filtration and evaporation gave 4-(4-bromo-butyl)-benzenesulfonyl chloride **(3)** as a colorless oil (60.0 g, 77.6%). **3** (57.0 g, 183 mmol) was added to a solution of 2,2-dimethylpropanol (20.0 g, 227 mmol) in pyridine (20.0 ml), and the reaction mixture was stirred at room temperature for 3 h. After addition of water, the mixture was extracted with dichloromethane. The organic layer was washed with 5 wt% aqueous HCl solution, 5 wt% aqueous NaOH solution, and water, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by silica gel column chromatography (THF/hexane = 9/1) to give 4-(4-bromo-butyl)-benzenesulfonic acid 2,2-dimethyl-propyl ester **(4)** as a white solid (34.2 g, 51.7%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.80 (d, *J* = 8.7 Hz, 2 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 3.65 (s, 2 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 1.93-1.77 (m, 4 H), 0.882 (s, 9 H) ; ^{13}C NMR (125 MHz, CD_2Cl_2) δ 149.1, 134.0, 129.6, 128.4, 80.0, 35.3, 33.9, 32.6, 31.9, 29.8, 26.1. EIMS: *m/z* 364 (M^+). Anal. Calcd for $C_{15}H_{20}SO_3Br$: C, 49.59; H, 6.38; S, 8.83. Found: C, 50.45; H, 6.50; S, 9.28.

1,4-Di[4-(2,2-dimetylpropoxysulfonyl)phenyl]butoxybenzene (5). **4** (12.6 g, 34.7 mmol) was added to a mixture of hydroquinone (1.81 g, 16.4 mmol) and K_2CO_3 (5.03 g, 36.4 mmol) in dry *N,N*-dimethylformamide (DMF) (7 mL), and the reaction mixture was stirred at 80 ºC for 18 h. After addition of water, the mixture was extracted with dichloromethane. The organic layer was washed with water, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by recrystallization from methanol to give 1,4-di[4-(2,2-dimetylpropoxysulfonyl)phenyl]butoxybenzene **(5)** as a white solid (8.13 g, 73.4%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 4 H), 7.37 (d, *J* = 8.5 Hz, 4 H), 6.81 (s, 4 H), 3.99 (t, *J* = 5.6 Hz, 4 H), 3.68 (s, 4 H), 2.80 (t, *J* = 7.3 Hz, 4 H), 1.95-1.80 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 153.5, 149.5, 133.8, 129.6, 128.3, 115.6, 79.9, 68.5, 35.9, 31.8, 29.3, 27.9, 26.1. EIMS: *m/z* 674 (M^+). Anal. Calcd for $C_{36}H_{50}S_2O_6$: C, 64.07; H, 7.47; S, 9.50. Found: C, 64.18; H, 7.38; S, 9.81.

1,4-Dibromo-2,5-di[4-(2,2-dimetylpropoxysulfonyl)phenyl]butoxybenzene (1).

Bromine (6.98 g, 43.7 mmol) was added to a solution of **5** (14.2 g, 21.0 mmol) in dichloromethane (70.0 ml) at 0 ºC, and the reaction mixture was stirred for 5 h. After addition of 30 wt% aqueous Na_2SO_3 the mixture was extracted with dichloromethane. The organic layer was washed with water, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by recrystallization from ethanol to give **1** as a white solid (15.8 g, 90.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 4 H), 7.39 (d, *J* = 8.3 Hz, 4 H), 7.08 (s, 2 H), 3.93 (t, *J* = 5.7 Hz, 4 H), 3.67 (s, 4 H), 2.77 (t, *J* = 7.3 Hz, 4 H), 1.90-1.75 (m, 8 H); ^{13}C NMR (125 MHz, CD_2Cl2_3) δ 150.5, 149.4, 133.8, 129.6, 128.3, 118.8, 111.5, 80.1, 70.3, 35.8, 31.9, 29.0, 27.7, 26.1. EIMS: *m/z* 832 (M^+). Anal. Calcd for $C_{36}H_{48}S_2O_6Br_2$: C, 51.93; H, 5.81; S, 7.70. Found: C, 52.03; H, 5.66; S, 8.18.

Synthesis of hydrophobic monomer, 1,4-dibromo-2,5-dihexyloxybenzene (Scheme 2)



Scheme 2. Synthesis of hydrophobic monomer.

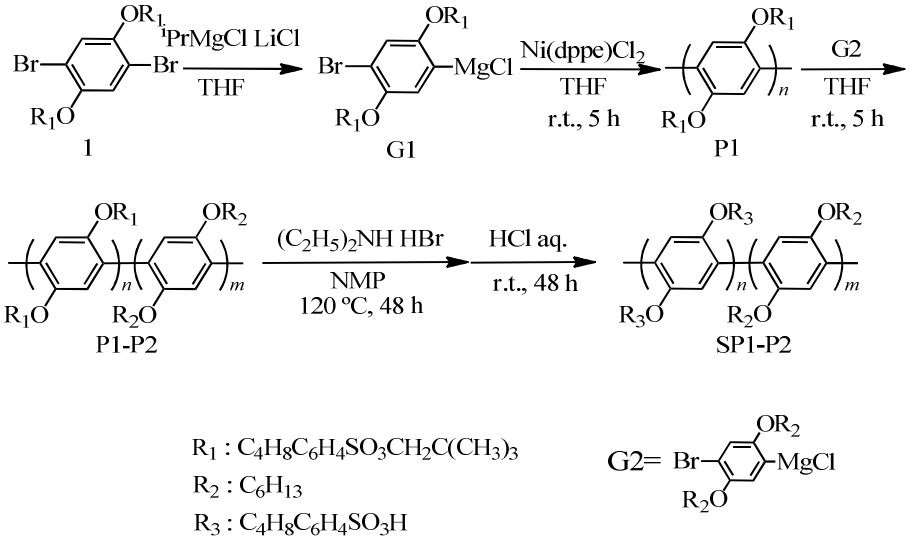
1,4-Dihexyloxybenzene (6). 1-Bromohexane (100 g, 110 mmol) was added to a mixture of hydroquinone (37.8 g, 343 mmol) and K_2CO_3 (91.1 g, 659 mmol) in dry *N,N*-dimethylformamide (DMF) (130 mL), and the reaction mixture was stirred at 80 ºC for 18 h. After addition of water, the mixture was extracted with dichloromethane. The organic layer was washed with water, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by recrystallization from methanol to give **6** as a white solid (60.9 g, 63.7%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 4H), 3.90 (t, *J* = 6.5 Hz, 4H), 1.75 (q, *J* = 7.1 Hz, 4H), 1.47-1.42 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 153.7, 115.7, 69.0, 32.1, 29.8, 26.1, 23.0, 14.2, EIMS: *m/z* 278(M^+). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 78.22; H, 11.39.

1,4-Dibromo-2,5-dihexyloxybenzene (2). Bromine (95.5 g, 598 mmol) was added to a solution of **6** (60.7 g, 218 mmol) in dichloromethane (15.5 ml) at 0 ºC, and the reaction mixture was stirred for 5 h. After addition of 30 wt% aqueous Na_2SO_3, the mixture was extracted with dichloromethane. The organic layer was washed with water, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by recrystallization from ethanol to give **2** as a white solid (86.1 g, 90.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 2 H), 3.95 (t, *J* = 6.5 Hz, 4 H), 1.80 (q, *J* = 7.0 Hz, 4 H), 1.51.1.46 (m, 4 H), 1.37.1.32 (m, 8 H), 0.90 (t, *J* = 7.0 Hz 6 H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 150.5, 118.8, 111.4, 70.7, 31.9, 29.5, 26.0, 23.0, 14.2. EIMS: *m/z* 436 (M^+). Anal. Calcd for $C_{18}H_{28}O_2Br_2$: C, 49.56; H, 6.47. Found: C, 49.66; H, 6.47.

General polymerization procedure of diblock copolymer ionomer SP1-P2(n-m) by catalyst transfer polymerization.

Synthesis of P1-P2

Isopropylmagnesium chloride lithium chloride complex (^{i}PrMgCl·LiCl, 1.3 M solution in THF) was added via a syringe to a solution of **1** in THF at room temperature in an argon-filled gloved box, and the reaction mixture was stirred at 40 ºC for 5 h. The mixture was added to a



Scheme 3. Synthesis of SP1-P2.

suspension of Ni(dppe)Cl_2 in THF at room temperature, and stirred for 5 h. To this reaction solution, the second monomer, **2** treated with ^{i}PrMgCl·LiCl complex (1.3 M solution in THF) was added and stirred for 5 h. After addition of 20 vol.% MeOH solution of HCl, the insoluble material was washed well with MeOH and collected by suction filtration to give P1-P2(*n*-*m*). The synthetic conditions of **P1-P2(28-262)**, **P1-P2(44-178)**, and **P1-P2(74-164)** were displayed in Tables 1 to 3.

Table 1 Synthesis condition of P1-P2 (28-262)

	Monomer / g (mmol)	^{i}PrMgCl·LiCl / ml (mmol)	Ni(dppe)Cl_2 / g (mmol)	THF / ml	Monomer/ Ni(dppe)Cl_2	Yield g (%)
1st polymerization step (Monomer 1)	2.78 (3.33)	2.33 (3.03)	0.0400 (0.0758)	13.2	40	-
2nd polymerization step (Monomer 2)	6.18 (14.2)	9.91 (12.9)	0.0400 (0.0758)	300	170	2.89 (51.6)

Table 2 Synthesis condition of P1-P2 (44-178)

	Monomer / g (mmol)	^{i}PrMgCl·LiCl / ml (mmol)	Ni(dppe)Cl_2 / g (mmol)	THF / ml	Monomer/ Ni(dppe)Cl_2	Yield g (%)
1st polymerization step (Monomer 1)	5.00 (6.00)	4.20 (5.46)	0.0453 (0.0858)	48.0	64	-
2nd polymerization step (Monomer 2)	5.38 (12.3)	8.63 (11.2)	0.0453 (0.0858)	300	131	2.76 (40.7)

Table 3 Synthesis condition of P1-P2 (74-164)

	Monomer / g (mmol)	^{i}PrMgCl·LiCl / ml (mmol)	Ni(dppe)Cl_2 / g (mmol)	THF / ml	Monomer/ Ni(dppe)Cl_2	Yield g (%)
1st polymerization step (Monomer 1)	7.63 (9.17)	6.41 (8.33)	0.0400 (0.0758)	37.2	110	-
2nd polymerization step (Monomer 2)	3.42 (7.84)	5.48 (7.13)	0.0400 (0.0758)	300	94	4.57 (60.3)

Synthesis of SP1-P2

The neopentyl protected sulfonyl group in **P1-P2(n-m)** was cleaved with an *N*-methylpyrrolidone solution of diethylamine hydrobromide at 120 ℃ for 48 h to obtain the acid form of the copolymer SP1-P2. After cooling to room temperature, the dark brown viscous reaction solution was poured into diethyl ether. Insoluble material was collected by suction filtration. The reddish brown product was stirred in 1 M HCl aq. for 48 h, and in water for 24 h to give **SP1-P2(n-m)** as a brown solid. The synthetic conditions of **SP1-P2(28-262)**, **SP1-P2(44-178)**, and **SP1-P2(74-164)** were displayed in Table 4.

Table 4 Synthetic condition of SP1-P2

Sample name	P1-P2 / g	$(C_2H_5)_2NH$ HBr / g (mmol)	NMP / ml	Yields g (%)
P1-P2(28-262)	4.57	5.45 (35.4)	40	3.49 (72.1)
P1-P2(44-178)	2.76	3.16 (20.5)	40	2.41 (92.6)
P1-P2(74-164)	2.89	1.40 (9.09)	40	2.29 (83.8)

Characterization of block copolymers. All ^{1}H NMR (500, 300 MHz) and ^{13}C NMR (75 MHz) spectra of monomers and polymers were acquired with Lambda 500 and 300 (JEOL) instruments, respectively. Elemental analysis was obtained with a PE2400-II (PerkinElmer Inc.) at 975 °C. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) equipped with two Shodex LF-804 columns, and measurements were made at 40 °C with THF eluent at a flow rate of 1.0 mL/min. Molecular weights were estimated with a calibration curve constructed using polystyrene standards.

P1-P2(28-262)

^{1}H NMR (300 MHz, THF-d_8) δ 7.72, 7.32, 7.11, 7.07, 3.94, 3.81, 3.64, 2.60, 1.69, 1.61, 1.42, 1.32, 0.90, 0.84; ^{13}C NMR (125 MHz, THF-d_8) δ 151.2, 150.0, 135.0, 130.1, 128.8, 118.0, 79.9,

70.2, 36.2, 32.7, 32.3, 30.6, 30.0, 28.6, 26.8, 26.3, 23.6, 14.5. IR ν cm^{-1} 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. Anal. Found: C, 73.78; H, 8.86; S, 2.85.

SP1-P2(28-262)

^{1}H NMR (300 MHz, THF-d_8) δ 7.74, 7.30, 7.07, 4.84, 3.94, 2.61, 1.69, 1.61, 1.41, 1.31, 0.90, ^{13}C NMR (125 MHz, THF-d_8) δ 151.2, 148.4, 138.5, 129.7, 128.7, 127.6, 118.0, 70.2, 36.1, 32.7, 30.6, 29.8, 28.6, 26.8, 23.6 14.5. IR ν cm^{-1} 3226, 3087, 3065, 2946, 2920, 2858, 1600, 1492, 1473, 1424, 1402, 1377, 1340, 1286, 1205, 1123, 1067, 1033, 1006, 846, 815, 788, 723, 692, 676. Anal. Found: C, 72.35; H, 8.65; S, 3.07.

P1-P2(44-178)

^{1}H NMR (300 MHz, THF-d_8) δ 7.72, 7.32, 7.11, 7.07, 3.94, 3.87, 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 151.2, 150.0, 135.0, 130.1, 128.8, 118.1, 79.9, 70.2, 69.7, 36.2, 32.7, 32.3, 30.6, 30.0, 28.5, 26.8, 26.4, 23.6, 14.5. IR ν cm^{-1} 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. Anal. Found: C, 70.88; H, 8.42; S, 4.66.

SP1-P2(44-178)

^{1}H NMR (300 MHz, THF-d_8) δ 7.72, 7.26, 7.07, 3.94, 2.60, 1.68, 1.60, 1.42, 1.31, 0.90, ^{13}C NMR (125 MHz, THF-d_8) δ 151.2, 148.5, 139.2, 129.7, 128.8, 127.5, 118.0, 70.2, 36.1, 32.7, 30.6, 29.9, 28.5, 26.8, 23.6 14.5. IR ν cm^{-1} 3226, 3087, 3065, 2946, 2920, 2858, 1600, 1492, 1473, 1424, 1402, 1377, 1340, 1286, 1205, 1123, 1067, 1033, 1006, 846, 815, 788, 723, 692, 676. Anal. Found: C, 68.68; H, 8.00; S, 5.42.

P1-P2(74-164)

^{1}H NMR (300 MHz, THF-d_8) δ 7.72, 7.32, 7.11, 7.07, 3.94, 3.87, 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 151.2, 150.0, 135.0, 130.1, 128.8, 118.1, 79.9, 70.2, 69.6, 36.2, 32.7, 32.3, 30.6, 30.0, 28.5, 26.8, 26.3, 23.6, 14.5. IR v cm^{-1} 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. Anal. Found: C, 68.64; H, 8.01; S, 6.51.

SP1-P2(74-164)

^{1}H NMR (300 MHz, THF-d_8) δ 7.74, 7.31, 7.07, 6.50, 3.94, 2.61, 1.68, 1.60, 1.42, 1.31, 0.90, ^{13}C NMR (125 MHz, THF-d_8) δ 151.1, 147.8, 140.0, 129.5, 128.8, 127.5, 118.1, 71.0, 70.2, 35.7, 32.7, 30.6, 29.3, 27.8, 26.8, 23.6 14.5. IR v cm^{-1} 3226, 3087, 3065, 2946, 2920, 2858, 1600, 1492, 1473, 1424, 1402, 1377, 1340, 1286, 1205, 1123, 1067, 1033, 1006, 846, 815, 788, 723, 692, 676. Anal. Found: C, 65.21; H, 7.26; S, 7.76.

Preparation and characterization of SP1-P2(n-m) membranes

SP1-P2(n-m) membranes were prepared by cast method using *N*-methylpyrrolidinone as a solvent. Dried sulfoated block polymers **SP1-P2(n-m)** membranes were placed in a humidified chamber at 90% RH and 80 °C to prepare hydrated samples. Water uptakes (W) were estimated from the weights of dried (W_{dry}) and hydrated (W_{wet}) membranes as W = (Wwet - W_{dry})/W_{dry} × 100%, and hydration numbers (λ) were calculated as λ = (number of sorbed water molecules)/(number of sulfo groups). The *IEC* was determined by ^{1}H NMR, back titration, and also by elemental analysis. Proton conductivity values of polymer membranes were measured with an electrochemical impedance analyzer SI-1260 (Solartron). Samples were clamped between Pt electrodes and placed on a home-made Teflon four-probe cell. Cells were set in a thermo-hygrostat that was electrically shielded and grounded to ensure accurate measurements.

AC-conducted atomic force microscopy (AFM) images were obtained using a JSPM-5400 (JEOL) with a humidity control unit. A Pt-coated cantilever (TAP-300E, Budgetsensors) with a force constant of 40 N/m and a resonance frequency of 300 kHz was used. The membrane samples were placed on a gold-plated conductive sample stage with Nafion dispersion (DE-2020, DuPont) as adhesive. Bias voltage was applied to the sample stage during the observations. Topography, phase, and current-mapping images were simultaneously obtained.