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Membranes from Poly(aryl ether)-Based Ionomers Containing Randomly Distributed Nanoclusters of 6 or 12 Sulfonic Acid Groups

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ABSTRACT: We report on the dependence of the properties on the morphologies of sulfonated polymers **3a** and **3b** ($\eta_{inh} = 0.65-1.18$) with segments containing clusters of 6 and 12 sulfonic acid groups, respectively. The larger sulfonated clusters in polymers **3b** resulted in higher proton conductivity and much better cell performance than polymers **3a**. The highest power density of a fuel cell using **3a-1** (IEC = 1.16 mequiv/g) and Nafion 117 was 0.23 and 0.21 W/cm^2, respectively, at the effective work potential of 0.5 V, whereas that of **3b-1** (IEC = 1.16 mequiv/g) was 0.29 W/cm^2 at even higher effective work potential of 0.6 V. The morphological structure of **3a-1** and **3b-1** was investigated by transmission electron microscopy (TEM) and compared with that of Nafion. TEM images of **3a-1** and **3b-1** revealed a phase separation similar to that of Nafion, which may explain their higher proton conductivities compared to those of randomly sulfonated copolymers.

Introduction

The proton exchange membrane (PEM) is a critical component in proton exchange membrane fuel cells (PEMFCs) that acts as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport. Therefore, they require both good proton conductivity and mechanical strength. Up to now, perfluorinated polymer membranes, such as Dupont's Nafion, are the major membranes used in PEMFC due to their outstanding properties.[1] However, these membranes still have a number of drawbacks especially for large-scale applications, such as high cost, high methanol permeability, and poor performance at temperatures above 80 °C, which calls for the development of new membrane materials.[2,3]

As is well-known, Nafion exhibits high proton conductivity at low IEC values due to ion-rich channels that formed by phase separation between hydrophilic sulfonic acid groups and hydrophobic domains.[4,5] There have been significant advances in the synthesis of sulfonated aromatic polymers as alternative proton exchange membrane.[6] Unfortunately, it is difficult to obtain an ideal balance between high proton conductivity and low water uptake. The randomly distributed sulfonic acid groups in the main chains result in dead end ionic channels in the membranes, and these polymers require much higher ion exchange capacity (IEC) to get proton conductivity comparable with Nafion. High IEC can result in high water uptake and the loss of mechanical properties. Research efforts have been aimed at the development of novel sulfonated aromatic polymers with pronounced hydrophilic/hydrophobic separation as in Nafion.[7−17] McGrath et al.[9] prepared multiblock sulfonated−fluorinated poly(arylene ether)s with a promising morphological structure by a two-step polycondensation. Membranes with low IEC of 0.95 mequiv/g had water uptake of 40% but high proton conductivity of 80 mS/cm. We have designed and prepared novel branched poly(ether−ketone)s (PEKs) bearing six sulfonic acid groups on each hexaphenylbenzene end-group of the copolymers or with 3,6-ditrityl-9*H*-carbazole end-groups.[12,13] Obvious phase separation was observed, and proton conductivity comparable to Nafion was obtained with IEC values as low as Nafion. We have previously reported thermally and hydrolytically stable sulfonated poly(arylene ether)s containing four sulfonic acid groups on pendant phenyl groups.[18] These results encouraged us to further investigate the effect of the morphology of sulfonated membranes on properties including water uptake, proton conductivity, and cell performance.

In this research we synthesized ionomers containing randomly distributed clusters of 6 or 12 sulfonic acid groups derived from two bisphenol monomers, **a** and **b**, with different molecular lengths containing pendant phenyl groups as shown in Figure 1. Two series of copolymers were synthesized by the polycondensation of 4,4′-difluorobenzophenone and bis(4-hydroxyphenyl)sulfone with monomers **a** and **b**, respectively. The pendant phenyl rings of the monomers **a** and **b** in the main chain of the copolymers were selectively sulfonated since the main chain containing the sulfone and ketone groups that are strong electron-withdrawing groups is stable toward sulfonation. The monomers **a** and **b** have 6 and 12 potential sites for selective sulfonation, respectively, which after sulfonation of the polymers gave two different sized clusters of sulfonic acid groups. We investigated the effect of the different sized hydrophilic block segments in the main chain on the morphology of membranes as well as the relationship between the morphology

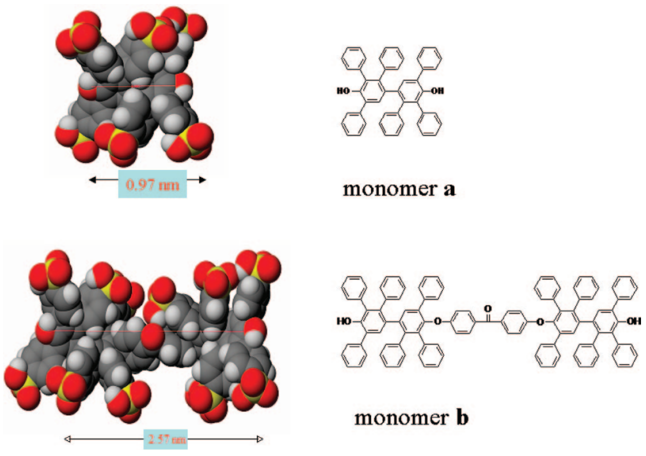

Figure 1. Molecular model of monomer **a** and monomer **b**.

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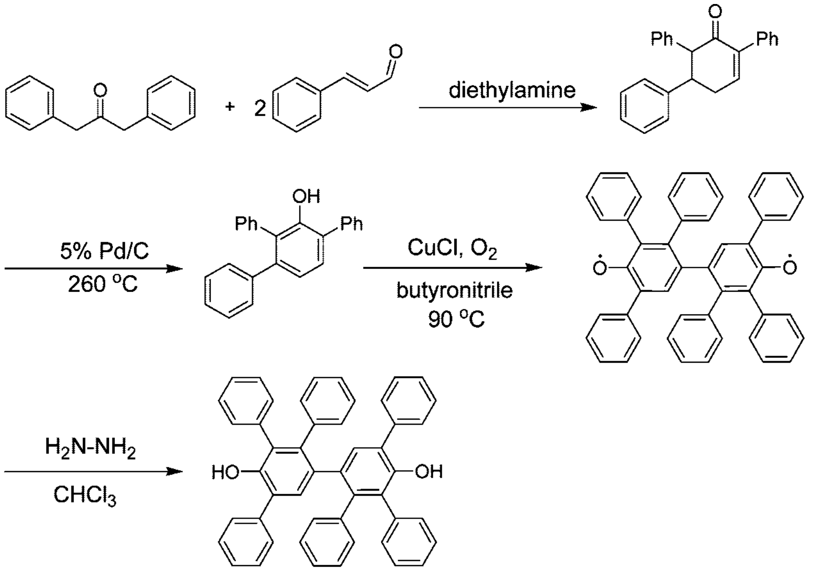
Scheme 1. Synthesis of 2,2′,3,3′,5,5′-Hexaphenyl-4,4′-dihydroxybiphenyl (Monomer a)



2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl (monomer **a**)

and the proton conductivity, water uptake, and fuel cell performance.

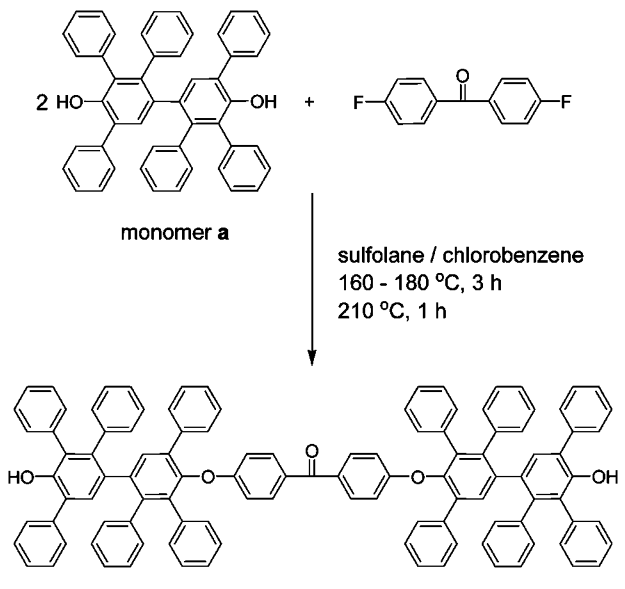
Experimental Section

Materials. 2,2′,3,3′,5,5′-Hexaphenyl-4,4′-dihydroxybiphenyl (**a**) was synthesized as described previously (Scheme 1).[19] Commercial 4,4′-difluorobenzophenone (DFBP) was recrystallized from ethanol. Bis(4-hydroxyphenyl) sulfone (BHPS), chlorosulfonic acid, *tert*-butylamine, and pyridine were purchased from Sigma-Aldrich Ltd. and used directly. K_2CO_3 was purchased from OMEGA Chemical Co. Inc. Commercial grade sulfolane, dichloromethane, DMAc, toluene, NMP, and pyridine were dried overnight over calcium hydride and distilled prior to use. Other commercially available materials and solvents were used without further purification.

Characterization. The ^{1}H NMR spectra were recorded on a NMR instrument (model: Bruker DRX 400 MHz or Varian Mercury 400) using CD_2Cl_2, CD_3Cl, or DMSO-d_6 as a solvent. Chemical shifts are given in ppm against tetramethylsilane as an internal standard. Number-average molecular weight (M_n) and molecular weight distribution (MWD) were measured by gel permeation chromatography (GPC) on a Waters 510 system equipped with three consecutive polystyrene gel columns eluted with chloroform at a flow rate of 1.0 mL/min calibrated with standard polystyrenes. Matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass spectra were recorded on a Kratos-Kompact MALDI III TOF mass spectrometer with the instrument set in the positive reflection mode. Lithium bromide and dithranol were used as cationization reagent and matrix, respectively. The thermal stability of the polymers from 150 to 600 °C was determined by a Perkin-Elmer 6300 thermogravimetric analyzer [thermogravimetric analysis (TGA)/differential thermal analysis (DTA)] under a protective nitrogen atmosphere (200 mL/min) at the heating rate of 10 °C/min. The glass-transition temperature (T_g) was determined on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen protection. T_g is reported as the temperature at the middle of the thermal transition from the second heating scan. The inherent viscosity of polymer was determined in the 0.5 g/dL DMAc solution at 25 °C with a calibrated Ubbelohde viscometer. The water uptake of the membrane was evaluated by measuring the weight change between dried and humidified state at different temperatures. Proton conductivity measurements were performed on film samples with a Solartron 1255B frequency response analyzer functioning with an oscillating voltage of 10 mV using two probes with the frequency between 0.1 Hz and 5 kHz. The film samples were cut into a circle with the diameter of 1 cm and soaked in deionized water for 24 h prior to each test. Each sample was clamped between the two gold electrodes and placed above liquid water in the temperature-controlled vessel that afforded a saturated water vapor environment. After the membrane was equilibrated with saturated water vapor at 35 or 75 °C, the measurement of proton conductivity was performed. Melting points were determined on a Fisher-Johns melting point apparatus. The ionic exchange capacity (IEC) was determined by titration. The dried membrane was weighed and immersed in 1.0 M HCl solution for 24 h to protonize the sulfonic groups and was then washed thoroughly with deionized water until pH was neutral. The membrane was then immersed in a 2.0 M solution of NaCl for 5 h to replace the protons of sulfonic acid groups with sodium ions. The solutions were titrated using 0.02 M NaOH solution, with phenolphthalein as indicator. The active area of the MEA used in the fuel cell tests was 5 cm^2. A single PEMFC was operated at different temperatures as described, 100% relative humidity, and a back gas pressure of 0 MPa with pure hydrogen and oxygen as reactant gases. In order to provide adequate oxidant to the fuel, the flow rates of the gases were fixed at 1.5 times the stoichiometry of hydrogen and twice the stoichiometric value of oxygen. The polarization curves were measured by applying a constant current for 3 min at each point using a fuel cell test station (Arbin Instruments, 160269).

Synthesis of Monomer b. A typical polycondensation procedure follows (Scheme 2): 2,2′,3,3′,5,5′-hexaphenyl-4,4′-biphenol (**a**) (8.9411 g, 13.92 mmol), 4,4′-difluorobenzophenone (0.8475 g, 3.88 mmol), K_2CO_3 (1.656 g, 12 mmol), sulfolane (28 mL), and chlorobenzene (20 mL) were charged into a 125 mL three-necked round-bottomed flask, fitted with a Dean−Stark trap, a condenser, a nitrogen inlet/outlet, and a magnetic stirrer. Nitrogen was sparged through the reaction mixture with stirring for 10 min, and then the mixture was refluxed for 3 h at 160−180 °C. After the water produced was azeotroped off with chlorobenzene, the mixture was heated at 210 °C for 1 h. The resulting mixture was cooled, diluted with DMSO, and then poured into a mixture of methanol (80 mL)/water (80 mL) to precipitate a white powder, which was collected by filtration, washed with water, and dried in a vacuum at 80 °C for 24 h. The crude product was purified by chromatography (silica gel, ethyl acetate/hexane = 1:10) to give 1.5224 g (22.4%) of monomer **b**; mp 218 °C. MALDI-TOF-MS: calcd for $C_{109}H_{74}O_5$ M^+ *m*/*z* 1463.75; found *m*/*z* 1464. ^{1}H NMR (CD_2Cl_2, 400 MHz, ppm): 7.6−6.6 (68H, m, Ar−H), 6.4−6.3 (4H, d, Ar−H^1), 5.49 (2H, s, OH^2).

Scheme 2. Synthesis of Monomer b



Synthesis of Copolymers 1a. A typical polycondensation procedure follows (Scheme 3): To a 25 mL three-necked round-bottomed flask, fitted with a Dean−Stark trap, a condenser, a nitrogen inlet/outlet, and a magnetic stirrer, were charged monomer **a** (0.2571 g, 0.4 mmol), 4,4′-difluorobenzophenone (0.8728 g, 4 mmol), bis(4-hydroxyphenyl)sulfone (0.9010 g, 3.6 mmol), K_2CO_3 (0.6624 g, 4.8 mmol), sulfolane (6.5 mL), and chlorobenzene (12 mL). Nitrogen was sparged through the reaction mixture with stirring for 10 min, and then the mixture was refluxed for 3 h at 160−180 °C. After the produced water was azeotroped off with chlorobenzene, the mixture was heated at 210 °C for about 1 h until a highly viscous solution was obtained. The resulting mixture was cooled, diluted with DMSO, and then poured into a mixture of methanol (20 mL)/water (20 mL) to precipitate a white fibrous polymer. The precipitated fibrous polymer was stirred in dilute hydrochloric acid, collected by filtration, and washed with water. The crude polymer was purified by reprecipitation from chloroform solution into methanol, and the polymer collected by filtration was dried in vacuo at 80 °C for 24 h. A total of 1.9506 g of copolymer **1a-1** ($m = 1$, $n = 9$) was obtained in 96% yield. ^{1}H NMR (CD_3Cl-d_6): 8.0−6.6 (m, 1800H), 6.5−6.2 (m, 40H). **1a-2** ($m = 1.3$, $n = 8.7$); yield 89%. ^{1}H NMR (CD_3Cl-d_6): 8.0−6.6 (m, 1860H), 6.5−6.2 (m, 52H). **1a-3** ($m = 1.6$, $n = 8.4$); yield 95%. ^{1}H NMR (CD_3Cl-d_6): 8.0−6.6 (m, 1920H), 6.5−6.2 (m, 64H).

Synthesis of Copolymers 1b. A typical polycondensation procedure follows (Scheme 3): To a 25 mL three-necked round-bottomed flask, fitted with a Dean−Stark trap, a condenser, a nitrogen inlet/outlet, and a magnetic stirrer, were charged monomer **b** (0.0732 g, 0.05 mmol), 4,4′-difluorobenzophenone (0.1964 g, 0.9 mmol), bis(4-hydroxyphenyl)sulfone (0.2127 g, 0.85 mmol), K_2CO_3(0.149 g, 1.08 mmol), sulfolane (1.5 mL), and chlorobenzene (3 mL). Nitrogen was sparged through the reaction mixture with stirring for 10 min, and then the mixture was refluxed for 3 h at 160−180 °C. After the produced water was azeotroped off with chlorobenzene, the mixture was heated at 210 °C for about 1 h until a high-viscosity solution was obtained. The resulting mixture was cooled, diluted with DMSO, and then poured into a mixture of methanol (20 mL)/water (20 mL) to precipitate a white fibrous polymer. The precipitated fibrous polymer was stirred in diluted hydrochloric acid, collected by filtration, and washed with water. The crude polymer was purified by reprecipitation from chloroform solution into methanol, and the polymer collected by filtration was dried in vacuo at 80 °C for 24 h. A total of 0.4341 g of copolymer **1b-1** ($m = 1$, $n = 18$) was obtained in 90% yield. ^{1}H NMR (CD_3Cl-d_6): 8.2−6.6 (m, 3600H), 6.5−6.2 (m, 80H). **1b-2** ($m = 1$, $n = 13.4$); yield: 87%.^{1}H NMR (CD_3Cl-d_6): 8.2−6.6 (m, 2864H), 6.5−6.2 (m, 80H). **1b-3** ($m = 1$, $n = 10.5$); yield: 92%. ^{1}H NMR (CD_3Cl-d_6): 8.2−6.6 (m, 2400H), 6.5−6.2 (m, 80H).

Sulfonation of Copolymers. [13] A typical sulfonation procedure follows (Scheme 4). To a solution of copolymer **1a-1** ($m = 1$, $n = 9$, 0.203 g, 0.043 mmol of polymer, M_n = 33 600) in dichloromethane (4 mL) at room temperature was added, dropwise, 0.8 M chlorosulfonic acid solution in dichloromethane (1.9 mL, containing chlorosulfonic acid, 1.55 mmol (6 equiv for each phenyl ring on HPDB). The reaction mixture was stirred for 3−24 h and then poured into ice water. The formed precipitate was filtered off, washed thoroughly with water, and then dried in vacuo at room temperature overnight to give **2a-1**. To a solution of the resulting polymer **2a-1** in DMSO (6 mL) at room temperature was added 3% NaOH aqueous solution (6 mL), and stirring was continued overnight. The resulting solution was acidified with concentrated HCl solution (1.2 mL) and then purified by means of dialysis for 3 days (regenerated cellulose membrane tubing MWCO 1000, Spectrum Laboratories). Water was removed under vacuum from the purified suspension, and residue was dried in vacuo at 80 °C to afford **3a-1** in 94% yield (0.2239 g) as a light yellow powdery polymer. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1783H). **3a-2**: yield 94%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1839H). **3a-3**: yield 96%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1896H). **3b-1**: yield 91%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 3570H). **3b-2**: yield 93%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 2838H). **3b-3**: yield: 97%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 2372H).

Copolymers Bearing *tert*-Butylsulfonamide Groups.[13] A typical procedure follows (Scheme 4): To a solution of the sulfonyl chloride intermediate **2a-1** in NMP (1 mL) was added, dropwise, *tert*-butylamine (0.2 mL, 1.9 mmol) and pyridine (0.05 mL, 0.6 mmol). The mixture was stirred at room temperature overnight, and then NMP, excess *tert*-butylamine, and pyridine were removed from the resulting mixture in a vacuum. The residue was washed thoroughly with boiling water and then boiling methanol and dried in a vacuum at 40 °C overnight to afford **4a-1** in 98% yield (0.051 g) as a white powdery polymer. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1783H), 1.35−0.65 (m, 513H). **4a-2**: yield 96%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1839H), 1.35−0.65 (m, 655H). **4a-3**: yield 92%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 1896H), 1.35−0.65 (m, 792H). **4b-1**: yield 95%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 3570H), 1.35−0.65 (m, 990H). **4b-2**: yield 91%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 2838H), 1.35−0.65 (m, 954H). **4b-3**: yield 90%. ^{1}H NMR (400 MHz, DMSO-d_6): 8.3−6.3 (m, 2372H), 1.35−0.65 (m, 972H).

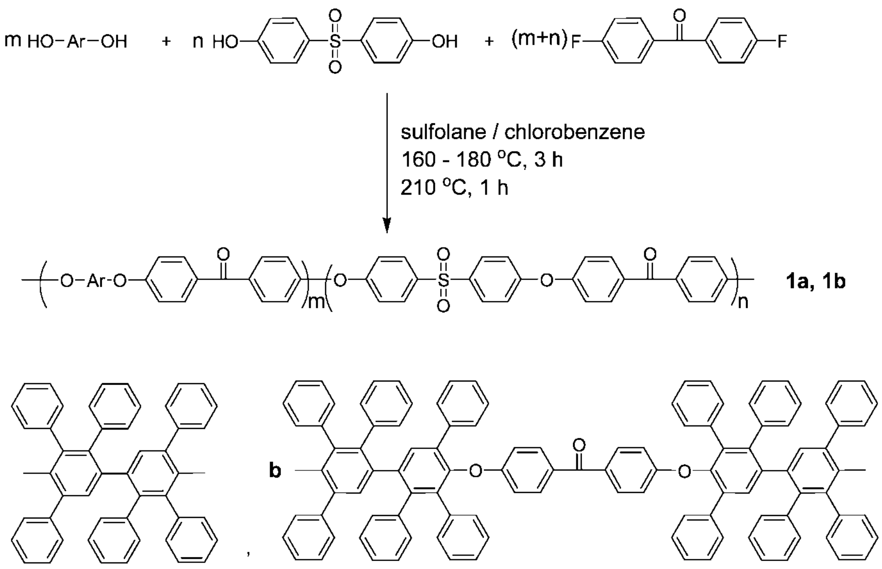
Preparation of Polymer Membrane. The membrane was prepared by casting from a 5% sulfonated copolymer solution in DMSO on a glass plate and dried under vacuum at 80 °C for 24 h and then dried at 110 °C under vacuum for 48 h. The film was removed from the glass plate and immersed in a 0.5 N solution of H_2SO_4 at 80 °C over 2 h, followed by treatment with deionized water at 80 °C for about 2 h.

MEA Preparation. MEAs were prepared from standard catalyst inks using a known procedure.[20] Carbon-supported platinum catalyst (0.5 mg/cm^2 Pt) was used for the PEMFC anode and cathode (Johnson Matthey-Platinum 40% on Vulcan XC-72R carbon). TGP-H-120 carbon paper (Toray) with a thickness of 330 μm was used for gas diffusion media (GDM). All the electrodes were made in the same way and have the same parameters. All the MEAs tested were prepared by the same procedure.

Results and Discussion

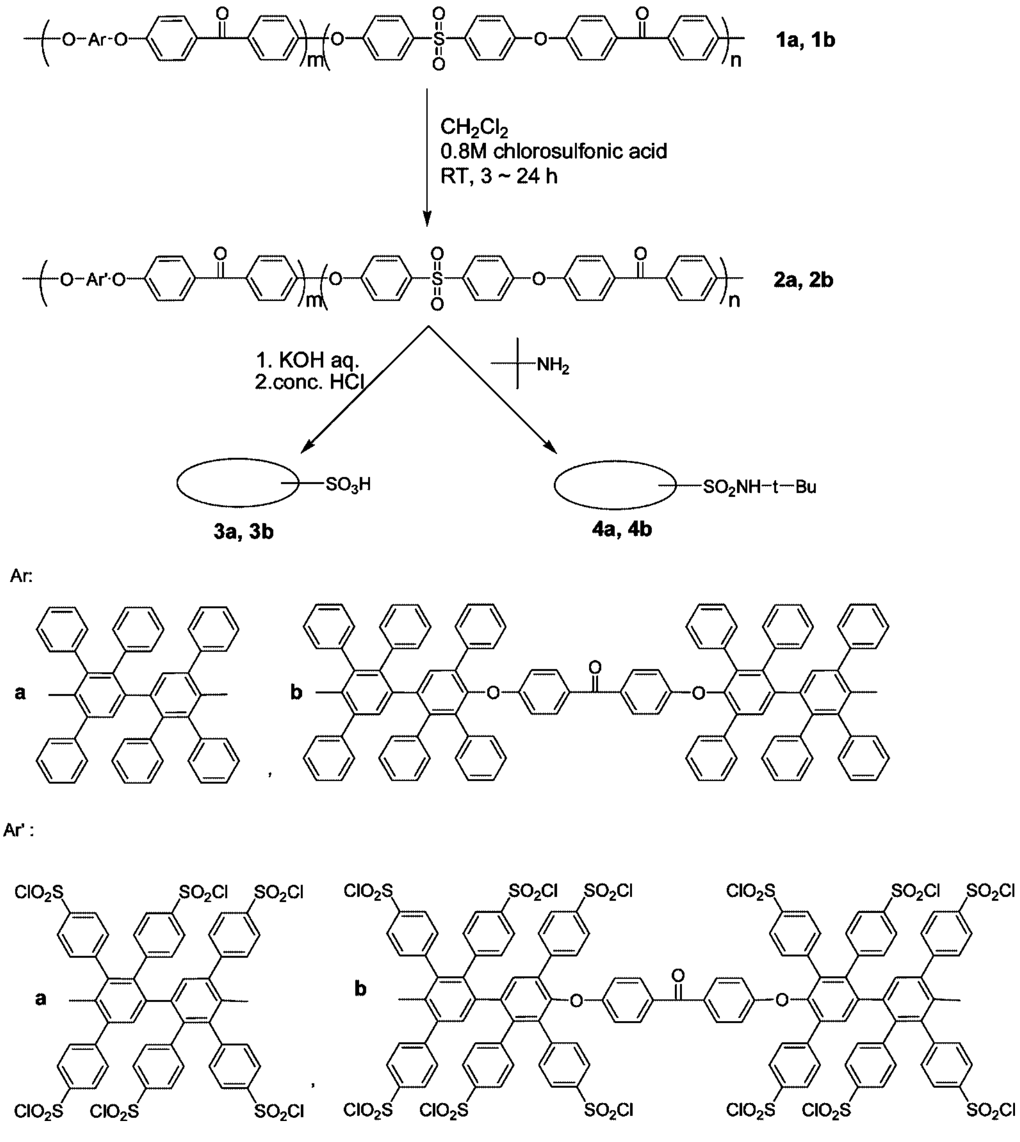
Synthesis and Characterization of Polymers. Monomer **b** was successfully synthesized via an aromatic nucleophilic substitution reaction of monomer **a** with 4,4′-difluorobenzophenone by heating at 160−180 °C for 3 h to remove water and then at 210 °C for 1 h (Scheme 1). The products were a series of oligomers. The amounts of dimer and trimer can be controlled by varying the feed ratio of monomer **a** and 4,4′-difluorobenzophenone.

Scheme 3. Synthesis of Copolymers 1a and 1b[a]



[a] **1a-1** (m = 1, n = 9), **1a-2** (m = 1.3, n = 8.7), **1a-3** (m = 1.6, n = 8.4), **1b-1** (m = 1, n = 18), **1b-2** (m = 1, n = 13.4), **1b-3** (m = 1, n = 10.5).

Scheme 4. Sulfonation of Copolymers 1a and 1b



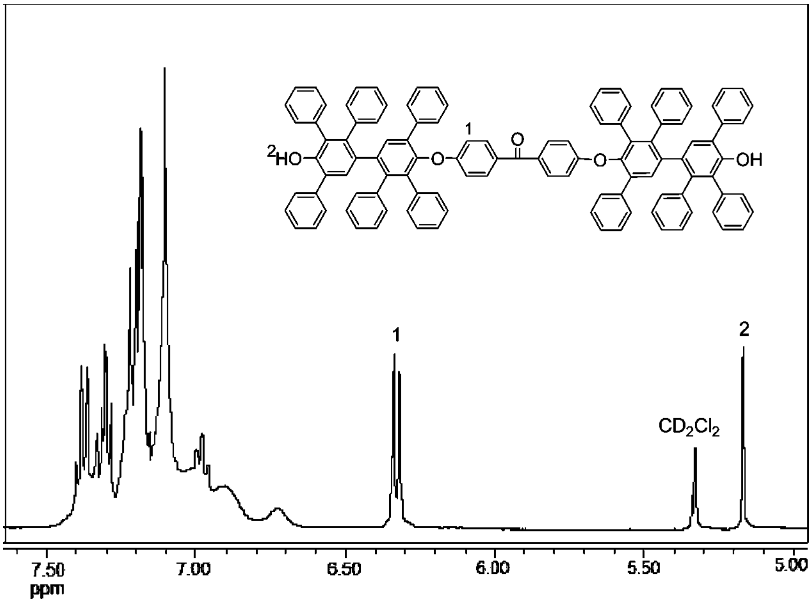


Figure 2. ^{1}H NMR spectrum of monomer **b**.

Table 1. Properties of Sulfonated Copolymers 3a and 3b

polymer	M_n (MWD)[a]	η_{inh}[b]	designed (calcd 1[c], calcd 2[d]) IEC (mequiv/g)	T_g[e]	T_g[f]	water uptake (%) 35 °C	water uptake (%) 75 °C	proton conductivity[g] (mS/cm) 35 °C	proton conductivity[g] (mS/cm) 75 °C
3a-1	33 600(1.56)	0.83	1.16 (1.11, 0.97)	208.1	199.5	20.3	27.1	16.5	20.8
3a-2	50 400(1.55)	1.18	1.44(1.35, 1.25)	209.3	212.6	42.8	53.6	39.9	53.8
3a-3	35 100(1.52)	0.99	1.69 (1.57, 1.42)	210.1	209.3	60.4	70.2	78.5	98.9
3b-1	34 300(1.68)	0.82	1.16 (1.07, 0.99)	203.1	198.9	29.2	35.4	24.4	39.6
3b-2	26 400(1.50)	0.73	1.44 (1.29, 1.23)	197.0	199.8	54.8	66.9	55.4	88.3
3b-3	39 800(1.55)	0.80	1.69 (1.54, 1.43)	203.9	207.1	88.1	108.8	85.4	123.4
Nafion 117						18.5	24.9	52.9	60.8

[a] M_n and MWD of unsulfonated copolymers **1a** and **1b** measured by GPC. [b] Inherent viscosity of sulfonated copolymers **3a** and **3b**. [c] Calculated by titration. [d] Calculated from ^{1}H NMR. [e] T_g of unsulfonated copolymers **1a** and **1b**. [f] T_g of sulfonated copolymers **3a** and **3b**. [g] Measured at 100% RH.

At a feed ratio of 3.6:1, that is, an 80% excess of monomer **a**, the isolated yield of dimer **b** was 22.4%. The melting point was 218 °C and very sharp. The unreacted monomer **a** could be recycled. Monomer **b** was characterized by ^{1}H NMR and MALDI-TOF-MS. In the ^{1}H NMR spectra (Figure 2), the protons located at about 6.35 ppm (Ar−H^1) were assigned to the 4,4′-difluorobenzophenone moiety, but protons adjacent to the 2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl (**a**) moiety in the following copolymers **1a** and **1b** were also located around 6.4 ppm.

All the copolymers were successfully synthesized via a standard K_2CO_3-catalyzed aromatic nucleophilic substitution reaction of monomer **a** or **b** with 4,4′-difluorobenzophenone and bis(4-hydroxyphenyl)sulfone in sulfolane/chlorobenzene by heating at 160−180 °C for 3 h to remove water and at 210 °C for about 1 h to give a highly viscous reaction mixture. From the ^{1}H NMR data of all the copolymers **1a** and **1b**, the integration ratios of the peaks located from 6.3 to 6.5 ppm and all the other peaks are well in accordance with the proposed molar ratios of each component of these copolymers.

Sulfonation of Copolymers. The copolymers were sulfonated using chlorosulfonic acid in methylene chloride at room temperature. We chose 4,4′-difluorobenzophenone and bis(4-hydroxyphenyl)sulfone as the other two monomers in the copolymerization because they have strong electron-withdrawing groups, ketone or sulfone. Model reactions[12] showed that the main chain containing diphenylsulfone and benzophenone moieties has excellent stability even under the strong sulfonation conditions so that neither sulfonation nor chain cleavage occurred. Therefore, the sulfonic acid groups can be introduced solely on the pendant phenyls in the main chain. The sulfonation of **1a** was completed in a few hours, whereas that of **1b** which has the longer block required 24 h. Because of the insolubility of the sulfonated products, the chlorosulfonic acid must be added as slowly as possible with vigorous stirring. The sulfonyl chloride intermediate **2a** or **2b** was then hydrolyzed with 3% NaOH aqueous solution, followed by acidification with HCl solution (Scheme 4). An aliquot of **2a** or **2b** was converted into the corresponding sulfonamide by reaction with *tert*-butylamine in the presence of pyridine in NMP (Scheme 4) to determine by ^{1}H NMR the number of sulfonic acid groups introduced in **4a** or **4b**. The introduction of *tert*-butylsulfonamide groups on each molecule was readily confirmed by the integral ratio of protons on methyl groups with all aromatic protons. The analysis confirmed that sulfonation occurred at a maximum of 6 positions on each end-group selectively in **1a** or 12 positions in **1b**.

The polymerization and sulfonation results for copolymer **1a** and **1b** are summarized in Table 1. The introduction of increasing numbers of sulfonic acid groups onto polymers improves their ionic conductivity but also makes the polymers more hydrophilic. To obtain a suitable membrane for PEMFCs, there must be sufficient sulfonic acid groups to provide suitable proton conductivity while maintaining mechanical integrity. As the amount of monomer **a** or **b** introduced into the main chain decides the IEC of sulfonated copolymer, that affects proton

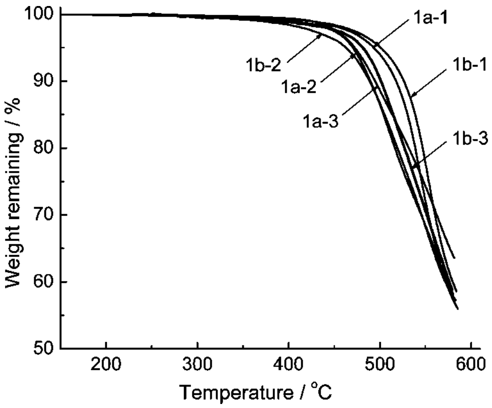


Figure 3. TGA curves of unsulfonated copolymers **1a** and **1b**.

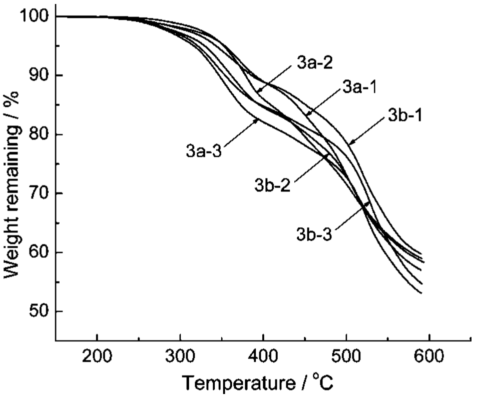


Figure 4. TGA curves of sulfonated copolymers **3a** and **3b**.

conductivity. The IEC can be tuned by varying the ratio of *m* and *n*. In order to study the influence of IEC on the properties of PEM, polymers with three IEC values, 1.16, 1.44, and 1.69 mequiv/g, were synthesized. The calculated IECs and the designed IECs were in reasonably good agreement. The M_n of all the presulfonated copolymers **1a** and **1b** ranged from 26 400 to 50 400, and the inherent viscosities (η_{inh}) of sulfonated **3a** and **3b** in DMAc at 25 °C ranged from 0.65 to 1.18 dL/g, indicating their high molecular weights. The polymers showed good solubility in polar aprotic solvents, such as DMSO, DMAc, and NMP, but were insoluble or only swollen in common solvents, such as H_2O, CH_3OH, and toluene.

Thermal Properties. The TGA curves of unsulfonated copolymers **1a** and **1b** are shown in Figure 3. The 5% weight loss temperatures are above 430 °C. In the TGA curves of sulfonated copolymers **3a** and **3b** (Figure 4), a two-step degradation profile was observed. The first weight loss at about 250 °C was attributed to the elimination of sulfonic acid groups and the small amount of absorbed water, while the second weight loss peak at about 400 °C was due to the degradation of the main chain of sulfonated polymers. The high decomposition temperature suggests that sulfonic groups attached to aromatic skeleton have high thermal stability. All the T_gs of the unsulfonated copolymers **1a** and **1b** and the sulfonated copolymers **3a** and **3b** were around 200 °C (Table 1), which is much lower than the decomposition temperature. This facilitates the preparation of the MEA by hot pressing. The T_gs of **3a-1** and **3b-1** are slightly lower than those of the corresponding parent copolymers **1a-1** and **1b-1**. However, the T_gs of **3a** and **3b** are slightly higher than that of **1a** and **1b** due to the introduction and aggregation of the polar sulfonic acid groups. The T_gs of **1a** or **1b** increase with increasing proportions of the rigid monomers **a** or **b**. These ionomers, where the hydrophilic block is a tight cluster of SO_3H groups, can be considered to behave like block copolymers. Ionomer **3b-2**, for example, has an IEC of 1.44, or an equivalent weight of 695 that is associated with each SO_3H group. In a random copolymer, only a very short hydrophobic segment is present when the equivalent weight is 695. The equivalent weight associated with the 12 SO_3H groups in the cluster is 8340. Therefore, the average hydrophobic chain segment associated with each cluster has a M_n of about 6000 Da, and the resulting copolymers show excellent microphase separation. The hydrophobic blocks are therefore large enough to show a T_g similar to the corresponding homopolymer.

Water Uptake and Proton Conductivity. As noted previously, randomly sulfonated poly(ether−ketone)s require a much higher IEC compared with Nafion to compensate for narrower and dead end channels.[4] However, high IEC usually results in high water uptake for membranes which further leads to the loss of mechanical properties.

As can be seen from Table 1, with increasing IEC of copolymers **3a** from 1.16 to 1.69 mequiv/g, the water uptakes increased from 20.3% to 60.4% at 35 °C and from 27.1% to 70.2% at 75 °C. The water uptakes of copolymers **3b** are slightly higher than those of copolymers **3a**, although both have much lower water uptake when compared with many random copolymers. The proton conductivity of copolymers **3a** increased from 16.5 to 78.5 mS/cm at 35 °C and from 20.8 to 98.8 mS/cm at 75 °C. Also, the proton conductivity of **3b** is slightly higher than the corresponding ones for copolymer **3a**. The highest proton conductivity of 123.4 mS/cm was obtained for **3b-3** at 75 °C, which is higher than that of Nafion 117 under the same conditions. Ionomers **3a-1** and **3b-1** have the same level of IECs (1.16 mequiv/g) as Nafion 117 (0.91 mequiv/g) and showed the same level of proton conductivity as Nafion 117. The low IEC of **3a** and **3b** with low water uptake and high proton

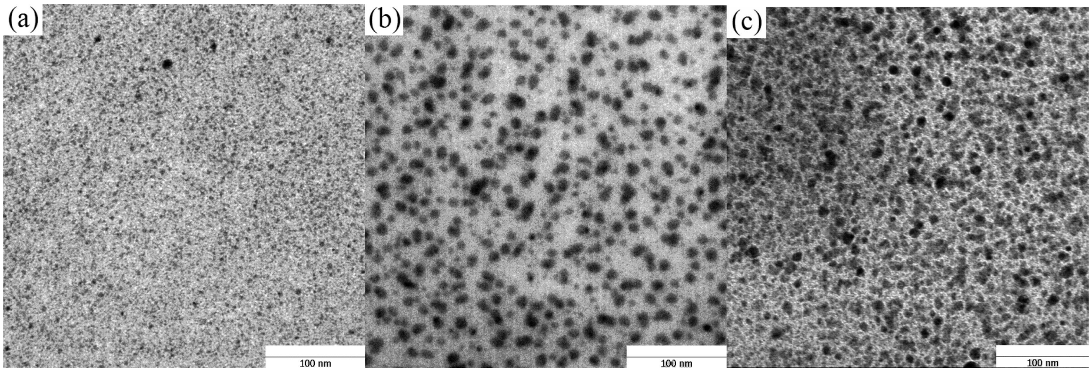


Figure 5. TEM images of (a) **1a-1**, (b) **1b-1**, and (c) Nafion 117.

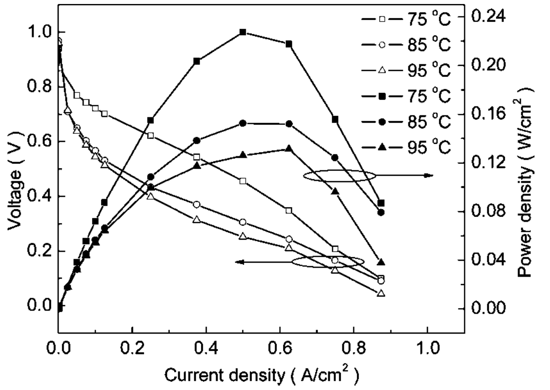


Figure 6. Polarization curves and power density of PEMFC using Nafion 117 as PEM. Operating conditions: 100% relative humidity, 0 MPa gas back-pressure, and cell temperature as noted in the figure.

conductivity suggests significant phase-separated microstructure in these membranes. Moreover, the better properties of **3b** than those of **3a** support the conclusion that longer hydrophilic segments in the main chain are more helpful in proton exchange membranes.

Morphology Investigation. The hydrophilic−hydrophobic microphase separation morphology is particularly important for PEM materials because it affects the water uptake and the proton transport pathway in the ionomer membranes.[8] The morphology of the sulfonated copolymers **3a** and **3b** was investigated by transmission electron microscopy (TEM) for the membranes stained with silver ions and compared with that of Nafion. In the TEM images, the dark areas represent the hydrophilic domains and the brighter areas represent the hydrophobic domains. As is clearly seen in Figure 5, **3a-1** and **3b-1** exhibited spherical ionic clusters with relatively uniform size that were well-dispersed throughout the membrane, similar to Nafion 117. The diameter of **3b-1** is around 12 nm, which is much larger than that of **3a-1** (around 3 nm) due to the much longer hydrophilic block segments in the main chain of **3b-1** and is also larger than that of Nafion 117 (8 nm). This kind of hydrophilic/hydrophobic microphase separation morphology may explain their higher proton conductivities and low water uptake compared to those of the random copolymers.

Fuel Cell Operation. The membranes **3a-1** (IEC = 1.16 mequiv/g) and **3b-1** (IEC = 1.16 mequiv/g) have IEC values similar to Nafion 117 (IEC = 0.91 mequiv/g). They were fabricated into a membrane electrode assembly (MEA) and evaluated in a single proton exchange membrane fuel cell (PEMFC) for comparison. Figure 6 shows the polarization curves in an H_2/O_2 single fuel cell using Nafion 117 as PEM at the cell temperature of 75, 85, and 95 °C, 100% relative humidity, and 0 MPa gas back-pressure. They have the same high current density of 0.87 A/cm^2 at the potential of 0.1 V. However, the cell performance decreased as the temperature increased from 75 to 95 °C. The best performance of a fuel cell using Nafion 117 was obtained at 75 °C, which temperature was chosen to compare with that of fuel cells using copolymers **3a-1** and **3b-1**. The cell performances using **3a-1** and **3b-1** increased with the temperature, increasing from 70 to 90 °C, as shown in Figure 7. The optimal operation temperature was at 90 °C considering current density or power density, which is 15 °C higher than that of Nafion 117. Therefore, we compared the best cell performance of these three membranes.

As is shown in Figure 8, copolymer **3a-1** has a cell performance close to that of Nafion 117. At the effective work potential of 0.5 V, the highest power density of the fuel cell using **3a-1** and Nafion 117 was 0.23 and 0.21 W/cm^2, respectively. It was very encouraging that copolymer **3b-1** exhibited much better fuel cell performance than Nafion 117 in the whole range of current density. At 0.6 V, the current density of the fuel cells using copolymer **3b-1** and Nafion 117 were 0.46 and 0.25 A/cm^2, respectively. The highest power density of a fuel cell using **3b-1** was 0.29 W/cm^2 at an even higher effective work potential of 0.6 V. These results showed that the morphology of the PEM greatly affected the cell performance and that good hydrophlilc/hydrophobic phase separation is very important in the application of the fuel cell. Considering the molecular structures of **3a** and **3b**, we can draw the conclusion that the longer hydrophilic block segments in the main chain are more beneficial for obtaining better cell performance.

Conclusions

Two series of copolymers **1a** and**1b** (M_n = 26 400−50 400) were synthesized by the polymerization of 2,2′,3,3′,5,5′-hexaphenyl-4,4′-dihydroxybiphenyl (monomer **a** or its derived dimer **b**) with 4,4′-difluorobenzophenone and bis(4-fluorophenyl)sulfone. They were then sulfonated with chlorosulfonic acid to give sulfonated polymers **3a** and **3b** (η_{inh} = 0.65−1.18). TEM images showed that **3b**, which has the larger biphenol monomer, has much larger hydrophilic clusters than **3a**. The membranes cast from polymers **3a** and **3b** show high thermal stability, low water uptake, and high proton conductivity. Polymers **3b** exhibited higher water uptake and proton conductivity than polymers **3a**. Among the membranes, **3b-1** (IEC = 1.16 mequiv/g) showed much better cell performance than both **3a-1** and

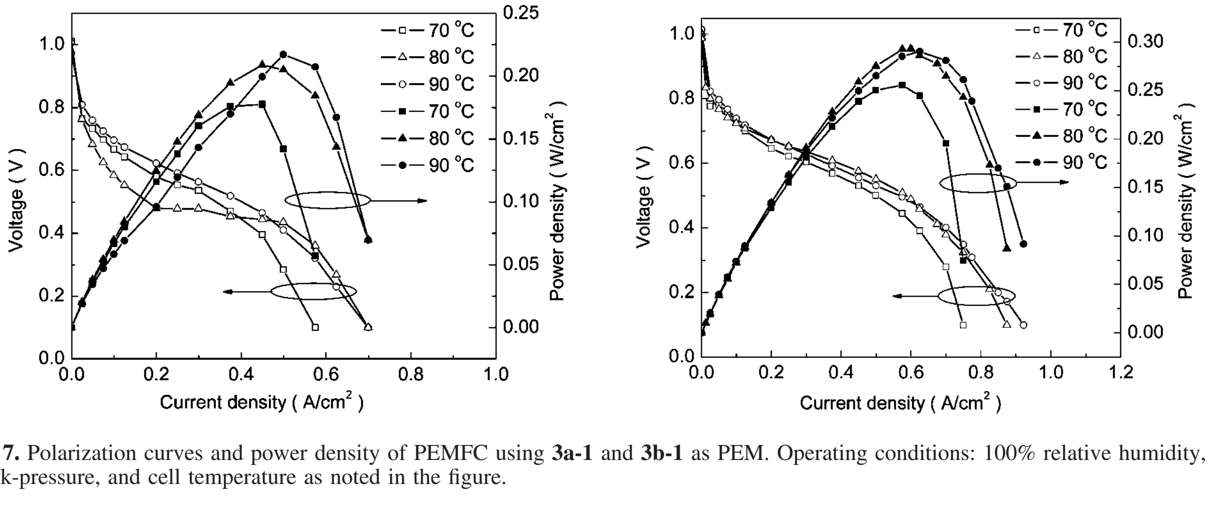


Figure 7. Polarization curves and power density of PEMFC using **3a-1** and **3b-1** as PEM. Operating conditions: 100% relative humidity, 0 MPa gas back-pressure, and cell temperature as noted in the figure.

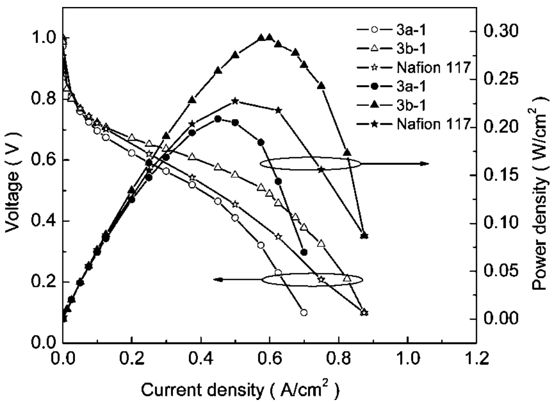


Figure 8. Polarization curves and power density of PEMFC using **3a-1**, **3b-1**, and Nafion as PEM. Operating conditions: 100% relative humidity, 0 MPa gas back-pressure.

Nafion 117. The highest power density of a fuel cell using **3a-1** (IEC = 1.16 mequiv/g) and Nafion 117 (IEC = 0.91 mequiv/g) was 0.23 and 0.21 W/cm^2, respectively, at the effective work potential of 0.5 V, whereas that of **3b-1** was 0.29 W/cm^2 at even higher effective work potential of 0.6 V. On the basis of this evidence, we can draw the following conclusions on the PEMs described in this paper: (1) Longer hydrophilic block segments in the polymer chain tend to form larger hydrophilic clusters in the membrane. (2) PEMs with better hydrophilic/hydrophobic microphase separation show higher water uptake and proton conductivity. (3) PEMs with better hydrophilic/hydrophobic microphase separation exibit much better single fuel cell performance.

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