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A clustered sulfonated poly(ether sulfone) based on a new fluorene-based bisphenol monomer†

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A new fluorene-based bisphenol monomer containing two pendant phenyl groups, 9,9-bis(3-phenyl-4-hydroxy)phenyl-fluorene, was readily synthesized in high yield by a one-step reaction from inexpensive starting materials. A series of poly(ether sulfone)s with clustered sulfonic acid groups was prepared for fuel cell applications by polycondensation of the new monomer with bis(4-hydroxyphenyl)sulfone and bis(4-fluorophenyl)sulfone, followed by sulfonation exclusively on the fluorene rings and pendant phenyl rings, using concentrated sulfuric acid at room temperature. The sulfonated polymers gave tough, flexible, and transparent membranes by solvent casting. The ionic exchange capacity (IEC), water-uptake, dimensional stabilities, mechanical properties, thermal and oxidative stabilities as well as proton conductivities and single fuel cell properties of the membranes were investigated. The membranes with high IEC values show high proton transport properties, and their proton conductivities exhibit lower dependence on relative humidity compared with typical aromatic ion exchange membranes. 4-SPES-38 with an IEC value of 2.23 mequiv. g^{-1} displays comparable fuel cell performance with Nafion 212 under low humidity conditions.

Introduction

Proton exchange membrane fuel cells (PEMFC) are of interest for their utility in automotive and portable electronic applications because of high efficiency and power density, quiet operation, and low emissions levels.[1–3] Perfluorosulfonic acid (PFSA) polymers such as Nafion® (DuPont) are the most widely used proton exchange membrane (PEM) materials in fuel cells due to their high proton conductivity and chemical stability, but limitations such as cost, fuel crossover, and restricted operation temperature have impeded their widespread adoption in PEMFC. These challenges have driven the investigation of aromatic hydrocarbon polymers as alternative PEM materials.[4–6] The most widely reported aromatic PEM include sulfonated derivatives of poly(arylene ether ketone)s,[7–9] poly(arylene ether sulfone)s,[10–12] poly(arylene ether nitrile)s,[13,14] poly(arylene sulfide sulfone)s,[15,16] poly(arylene ether)s,[17,18] and polyimides.[19,20] Aromatic sulfonated polymers have some advantages in terms of

thermal stability and low gas permeability. However, they typically require larger amounts of water and higher sulfonic acid content to achieve proton conductivities comparable to PFSA membranes. In addition, their proton conductivity is generally much lower than that of Nafion under reduced humidity conditions.[21] For example, the proton conductivity of a representative aromatic sulfonated poly(ether sulfone) (BPSH-40, IEC = 1.70 mequiv. g^{-1}) was about 1 mS cm^{-1} at 50% RH and 80 °C.[22]

Several approaches have been examined to improve aromatic PEM proton conductivity under conditions of reduced relative humidity and elevated temperatures. One of the effective strategies is the design of multiblock PEMs based on hydrophilic and hydrophobic oligomers.[23–30] The sequential block structure of these PEM promotes phase separation between hydrophilic and hydrophobic segments, resulting in much higher proton conductivity being achieved in a reduced humidity environment in comparison with random sulfonated copolymers. Some multiblock PEMs with long hydrophilic and hydrophobic block segments exhibited clear lamellar morphology with well-connected hydrophilic channels and proton conductivity comparable to that of Nafion 212 at low humidity.[27–29] The synthetic route for these multiblock copolymers often requires a multi-step reaction, and it is not easy to control the length of hydrophilic and hydrophobic block oligomers.

Another approach to enhance PEM performance can be realized by introducing locally and densely sulfonated structures into the aromatic polymer backbone.[22,31–35] The large difference in polarity between the locally and densely sulfonated units and

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hydrophobic units of the polymers results in the formation of well-defined nanophase-separated structures, which induces efficient proton conduction. Ueda and coworkers reported sulfonated poly(ether sulfone)s with ten sulfonic acid groups in each repeating unit by postsulfonation.[34] The sulfonated polymers (IEC = 1.96–2.38 mequiv. g^{-1}) exhibited good proton conductivity under low humidity conditions, which was comparable to that of Nafion 117 over a wide range of relative humidity (RH). In our previous work, we reported side-chain-type poly(arylene ether sulfone)s containing densely populated flexible butylsulfonic acid pendant units.[36] These sulfonated polymers displayed advantageous proton conductivities with relatively low water contents and good conductivity–swelling behavior.

Over the last few years, much research focus has been on fluorene-based sulfonated poly(arylene ether)s.[26,27,37–45] It has been demonstrated that fluorene-based PEM show some attractive properties, not only for chemical, thermal, and mechanical stability, but also good proton conductivities and fuel cell performance over several thousand hours.[40] However, the availability of fluorene-based monomers are limited and the resulting fluorene-based PEMs derived from the monomers often contain sulfonic acid groups directly attached to the polymer main chain. It has been demonstrated that aromatic PEMs with pendant sulfophenyl groups generally exhibited a comparatively better balance between proton conductivity and water dimensional swelling than PEM with sulfonic acid groups attached directly onto the aromatic chain. Furthermore, PEMs sulfonated on pendant phenyl groups rather than on the main chain were demonstrated to have a significantly higher thermo-oxidative stability.[46] In the present work, we report a new easily prepared and inexpensive fluorene-based monomer containing two pendant phenyl groups and resulting poly(ether sulfone)s with clustered pendant sulfonic acid groups. The membrane properties, such as thermal stability, mechanical stability, oxidative stability, water uptake, morphology, and fuel cell performance were investigated.

Experimental section

Materials

2-Phenylphenol, 9-fluorenone, mercaptopropionic acid (MPA), bis(4-hydroxyphenyl)sulfone (BHPS), and bis(4-fluorophenyl) sulfone (BFPS) were purchased from Sigma-Aldrich. N-Methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), and all other solvents and reagents were reagent grade and were used as received.

9,9-Bis(3-phenyl-4-hydroxy)phenyl-fluorene (BPHF)

To a 250 mL four necked round bottom flask, equipped with a reflux condenser, mechanical stirrer, nitrogen inlet and a dropping funnel, 7.20 g (0.04 mol) of 9-fluorenone, 17.02 g (0.1 mol) of 2-phenylphenol, 0.1 mL of MPA and 20 mL of toluene were introduced. The reaction mixture was stirred under nitrogen atmosphere at 40 °C for 30 min. 1.5 mL of 98 wt% H$_2$SO$_4$ was then added drop-wise over a period of 10 min, and the temperature was thereafter raised to 60 °C for 4–6 h with stirring. When the reaction mixture became solid, it was cooled

down and transferred into methanol. The resulting precipitate was filtered and recrystallized from toluene, and then dried in a vacuum oven at 120 °C for 10 h. 17.29 g of white solid product was obtained (yield: 86%; mp: 268–269 °C). ^{1}H NMR (300 MHz, DMSO-d$_6$; ppm): 9.37 (s, 2H, –OH), 7.88 (d, J = 7.2, 2H, H$_2$), 7.48 (d, J = 7.2, 2H, H$_5$), 7.29–7.38 (m, 12H, H$_3$, H$_{15}$, H$_{16}$, H$_4$), 7.24 (m, 2H, H$_{17}$), 7.02 (s, 2H, H$_9$), 6.97 (d, J = 8.4, 2H, H$_{13}$), 6.84 (d, J = 8.4, 2H, H$_{12}$). ^{13}C NMR (75 MHz, DMSO-d$_6$; ppm): 153.03 (C$_{11}$), 151.4 (C$_6$), 139.4 (C$_1$), 138.5 (C$_{14}$), 136.4 (C$_8$), 129.5 (C$_9$), 128.9 (C$_{15}$), 128.0 (C$_{13}$), 127.9 (C$_{16}$), 127.8 (C$_4$), 127.4 (C$_3$), 127.1 (C$_{10}$), 126.6 (C$_{17}$), 125.9 (C$_5$), 120.5 (C$_2$), 115.9 (C$_{12}$), 63.5 (C$_7$). Elemental analysis (wt%): calcd for C$_{37}$H$_{26}$O$_2$ (502.60): C 88.42, H 5.21, N 6.37; found: C 88.09, H 4.99, N 6.85.

Synthesis of poly(ether sulfone)s (4-PES-xx)

A typical synthetic procedure, illustrated by the preparation of 4-PES-38 copolymer (xx: BPHF/BHPS = 38/62), is described as follows. 1.146 g (2.28 mmol) BPHF, 0.931 g (3.72 mmol) BHPS, 1.526 g (6 mmol) BFPS, 1.076 g (7.8 mmol) K$_2$CO$_3$, 15 mL NMP and 7 mL toluene were added into a 100 mL three-neck flask equipped with a mechanical stirrer, a Dean–Stark trap and a nitrogen inlet. The solution was allowed to reflux at 140 °C while the water was azeotropically removed from the reaction mixture. After 4 h, the toluene was removed from the reaction by slowly increasing the temperature to 160 °C, and then the reaction was allowed to continue for another 10–15 h. After the reaction, 5 mL of NMP was added to the mixture to reduce the solution viscosity. The solution was poured into 500 mL deionized water with vigorous stirring. The resulting fibrous copolymer was washed with deionized water and hot methanol several times, and dried at 100 °C under vacuum for 24 h.

Sulfonation

The sulfonation reaction was conducted according to the method reported in our preceding studies.[46,47] A typical reaction for 4-SPES-38 is illustrated as follows: to a 100 mL of flask, 1 g of 4-PES-38 and 20 mL of concentrated sulfuric acid (98%) were added. After stirring at room temperature for 4 h, the clear and homogeneous viscous solution was poured into a mixture of water and ice to obtain a thread-like solid. The white solid was washed with water until the water reached neutral pH. Then the sulfonated copolymer was dried in a vacuum oven at 100 °C for 12 h.

Membrane preparation

The dried sulfonated copolymers were readily dissolved as 10–15 wt% solutions in DMAc at 60 °C. The solutions were filtered, cast onto glass plates with a doctor blade, dried at 60 °C for 12 h, and then treated in vacuum at 100 °C for 10 h. The as-cast membranes were immersed into 2.0 M H$_2$SO$_4$ solution for 24 h at room temperature and then thoroughly washed with deionized water. Tough, ductile ionomer membranes were prepared with controlled thickness in the range of 30–70 μm, depending on the solution concentration.

Measurements

^{1}H NMR spectra were measured on a 300 MHz Bruker AV 300 spectrometer using DMSO-d_6 as solvent. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. The gel permeation chromatographic (GPC) analysis was carried out with Tosoh HLC-8320 instrument (NMP as eluent and polystyrene as standard).

Ion exchange capacities (IEC) of the membranes were determined by titration. A sample membrane in proton form was immersed in 2 M NaCl aqueous solution for 48 h to exchange the H$^+$ ions with Na$^+$ ion. Released protons were titrated by 0.01 M NaOH solution using phenolphthalein as an indicator.

The humidity dependence of water uptake was measured by placing a membrane in a thermocontrolled humidity chamber for 6 h. Then, the membrane was removed and quickly weighed on a microbalance. Water uptake was calculated from: WU $= (W_w - W_d)/W_d \times 100\%$, where W_d and W_w are the weights of dry and corresponding wet membranes, respectively. The dimensional changes of the membranes were measured in the thickness and in-plane direction, which were calculated by $\Delta T = (T_{wet} - T_{dry})/T_{dry}$, $\Delta L = (L_{wet} - L_{dry})/L_{dry}$, where T_{dry}, T_{wet}, L_{dry}, and L_{wet} are the thickness and length of dry and wet samples, respectively.

The proton conductivity (σ, mS cm^{-1}) of each membrane coupon (size: 1 cm $\times$ 4 cm) was obtained using $\sigma = d/L_s W_s R$ (d: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough, Hampshire, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1.0 cm. Conductivity measurements under fully hydrated conditions were carried out in a thermo-controlled chamber with the cell immersed in liquid water.

For transmission electron microscopy (TEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution. After ion exchange, the membranes were rinsed several times with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 70 nm thickness with a RMCMTX Ultra microtome, and placed on copper grids. Electron micrographs were taken with a Carl Zeiss LIBRA 120 energy-filtering transmission electron microscope using an accelerating voltage of 120 kV.

Membrane electrolyte assemblies (MEAs) were fabricated from 4-SPES-38 (50 µm). 20 wt% Pt/C (Johnson Matthey, USA) and 20 wt% Nafion dispersion (du Pont, USA) were used as catalyst and binder. Catalyst ink was loaded on the carbon paper having a micro-porous layer (35BC, Sigracet, Germany) by the screen printing method.[48] MEAs were fabricated by hot-pressing the membrane with catalyst coated gas diffusion layers (GDLs). The active area of MEAs was 5 cm^2 with Pt catalyst loading of 0.3 mg cm^{-2}. H$_2$/O$_2$ fuel cell performance of the MEAs was evaluated using a fuel cell test station (SMART I, WonATech,

Seoul, Korea). Polarization curves were obtained at 80 °C under 50% and 100% relative humidity (RH) conditions. A comparative plot of the current density *versus* time for 4-SPES-38 and Nafion 212 based MEAs is shown in Fig. S1.†

Results and discussion

Synthesis of monomer

The monomer BPHF was synthesized from 9-fluorenone and 2-phenylphenol by a phenol condensation reaction catalyzed using MPA and sulfuric acid (Scheme 1). The reaction is facile to conduct, using inexpensive starting materials, has a high yield, and the monomer is readily purified by crystallization. The structure of BPHF was confirmed by NMR spectroscopy. As shown in Fig. 1, the –OH signal appeared at 9.37 ppm and the protons in the pendant phenyl groups (H$_{15}$, H$_{16}$ and H$_{17}$) appeared at 7.24–7.38 ppm. In the ^{13}C NMR spectrum, all the 17 carbon atoms had resonances in the region of 60–160 ppm. The unambiguous assignments of each proton and carbon in the spectra, determined by 2D NMR methods, are in complete agreement with the proposed molecular structure, which indicated the successful preparation of the target new fluorene-based monomer BPHF.

Synthesis of copolymers and sulfonation

Poly(ether sulfone) copolymers (4-PES-xx, xx: mole ratio (%) of BPHF) were synthesized by polycondensation using various feed ratios of BPHF/BHPS, resulting in copolymers with different molar percentages of BPHF, as shown in Scheme 2. The
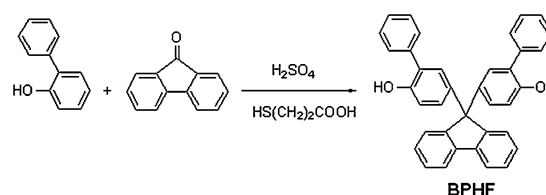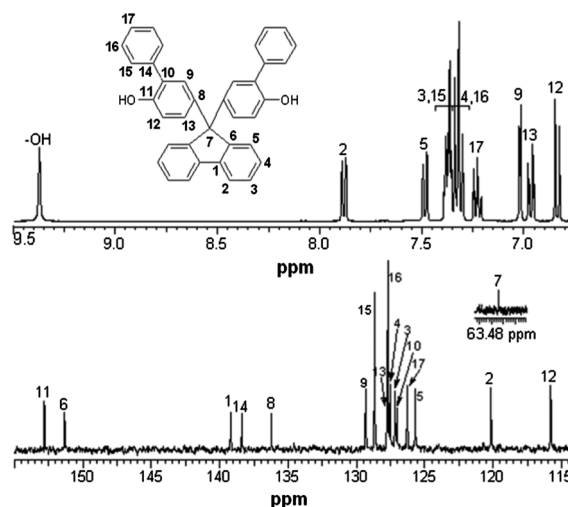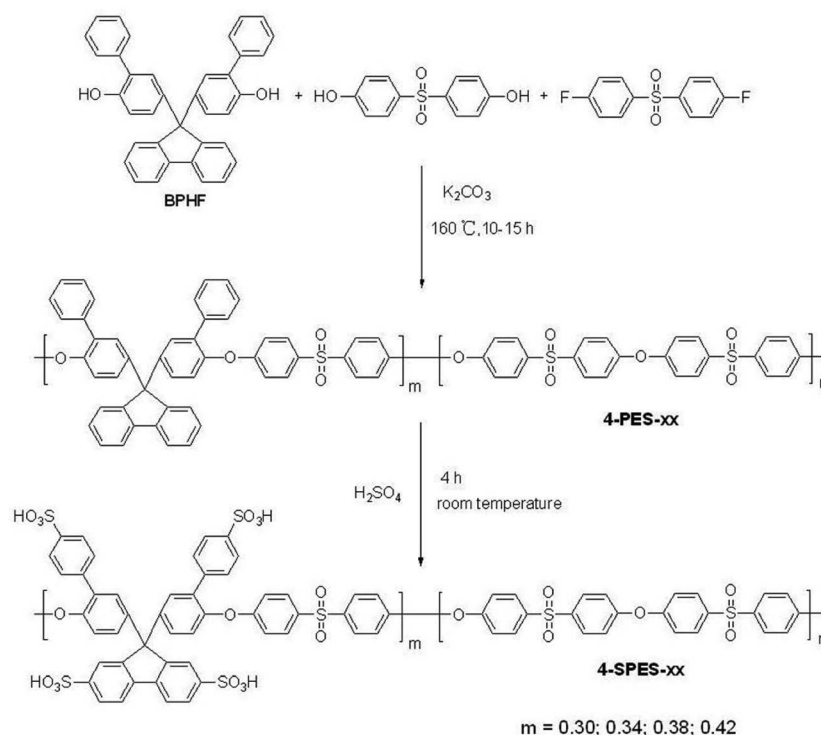

Scheme 1 Synthesis of the monomer BPHF.

Fig. 1 ^{1}H and ^{13}C NMR spectra of monomer BPHF.

Scheme 2 Synthesis of copolymers 4-PES-xx and 4-SPES-xx.

polymerization reactions proceeded smoothly to high molecular weight ($M_n > 70\,000$ g mol^{-1}) after 10–15 h reaction times. Table 1 shows the molecular weight, polydispersity index, and inherent viscosity of 4-PES-xx copolymers, which is consistent with the results of typical polycondensation reactions. The molecular weight of 4-SPES-xx showed a slight increase with increasing percentage of BPHF content, indicating that BPHF has a higher reactivity than BHPS.

In general, vigorous sulfonation conditions, such as high reaction temperatures, long reaction periods, and strong sulfonation reagents, may lead to polymer chain scission with a resulting loss of mechanical strength. Our earlier work[47] has shown that pendent phenyl rings attached to electron-donating polymer chain sites can be completely sulfonated at the para position, even under mild reaction conditions using sulfuric acid. Another group also reported polymer sulfonation by this method.[12] In the present work, the 4-PES-xx copolymers were

sulfonated at room temperature (~21 °C) by using concentrated sulfuric acid as both solvent and reagent according to our preceding studies. In all of the copolymers, full sulfonation at four substitution sites, on the pendant phenyl and fluorenyl rings, was complete in 4 h. The resulting sulfonated copolymers, denoted as 4-SPES-xx, were readily soluble in polar aprotic solvents such as NMP, DMAc and DMSO. The inherent viscosities of the sulfonated copolymers are shown in Table 1 and are higher than those of the corresponding 4-PES-xx copolymers, because of sulfonic acid hydrogen-bonding interactions between polymer chains. Flexible, tough and ductile 4-SPES-xx membranes were obtained by solvent-casting.

The structures of 4-PES-xx and 4-SPES-xx copolymers were determined by NMR spectroscopy. ^{1}H and ^{13}C NMR spectra of 4-PES-38 and 4-SPES-38 in DMSO-d$_6$ are displayed in Fig. 2 and 3, respectively. In comparison with the ^{1}H NMR spectrum of the parent copolymer 4-PES-38, the H$_3$, H$_5$ and H$_{16}$ signals of

Table 1 Physical properties of 4-PES-xx and 4-SPES-xx copolymers

| Copolymers | GPC data[a] | | | | | IEC (mequiv. g^{-1}) | |
	M_n[a] ($\times10^4$ g mol^{-1})	M_w ($\times10^4$ g mol^{-1})	PDI	η_{inh} (dL g^{-1})		Calcd[d]	Expt[e]
4-PES-30	7.25	11.54	1.59	0.51[b]	0.64[c]	1.89	1.87
4-PES-34	7.69	11.93	1.55	0.52	0.67	2.06	2.05
4-PES-38	8.52	13.72	1.61	0.55	0.72	2.23	2.23
4-PES-42	9.80	15.68	1.60	0.60	0.79	2.38	2.39

[a] Measured at 25 °C using NMP as solvent and polystyrene standards. [b] Viscosity before sulfonation; 0.5 g dL^{-1} in NMP solution at 30 °C. [c] Viscosity after sulfonation; 0.5 g dL^{-1} in NMP solution at 30 °C. [d] The theoretical IEC was calculated by the assumption of four sulfonic acid groups contained in each monomer unit. [e] The experimental IEC was determined by acid–base titration.
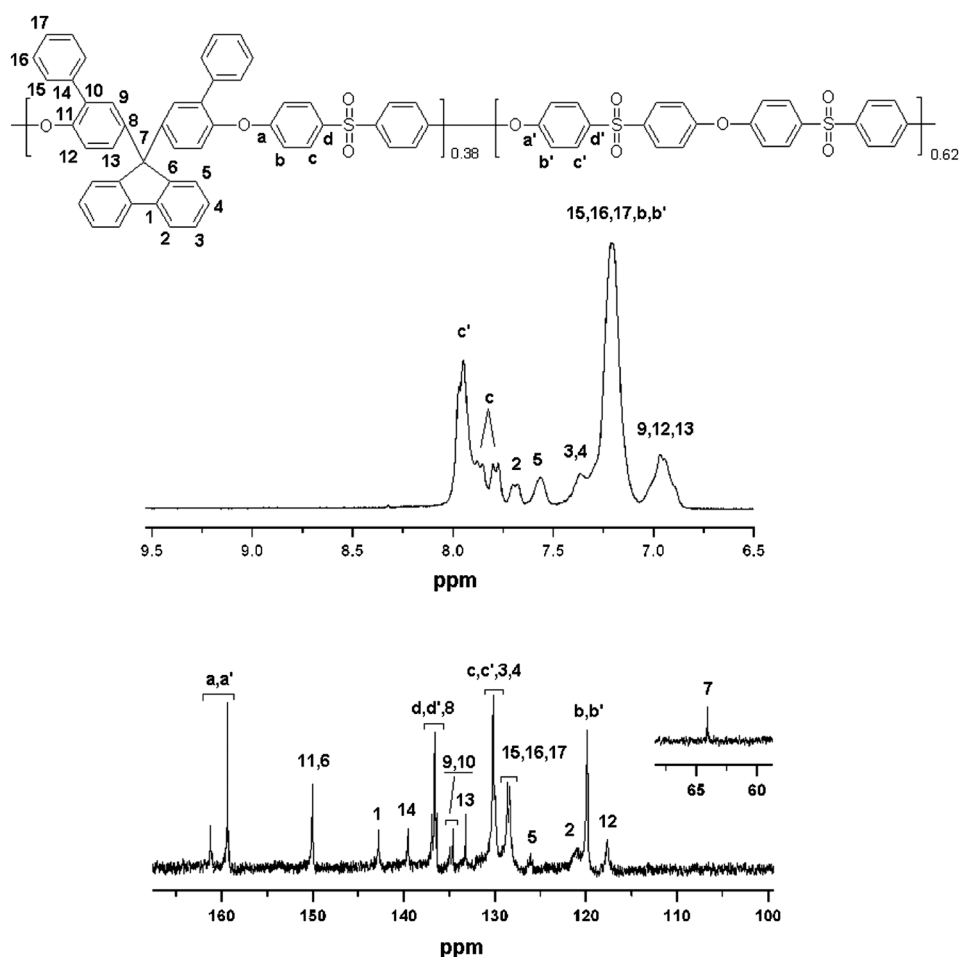
Fig. 2 ^{1}H and ^{1}C NMR spectra of 4-PES-38 copolymer.

4-SPES-38 exhibit obvious deshielding due to the strongly electron-withdrawing effects of –SO$_3$H and appear at 7.83, 7.76 and 7.50 ppm, respectively. Two new signals in the ^{1}C NMR spectrum of 4-SPES-38 are assigned to the carbon atoms (C$_4$ and C$_{17}$) attached to the sulfonic acid groups and appear at 147.99 and 146.74 ppm, respectively. No ^{1}H and ^{1}C NMR spectral evidence for partially sulfonated copolymers could be observed and the spectra are in complete agreement with the target structures of the copolymers containing tetrasulfonated units, suggesting that the sulfonation reaction was selective and complete. Furthermore, the experimental IEC values (Table 1) for all the 4-SPES-xx copolymers were close to the theoretical values, further indicating complete sulfonation.

Thermal and mechanical properties

The thermal stabilities as measured by TGA 5% weight loss temperatures are listed in Table 2. The TGA curves of all sulfonated copolymers are shown in Fig. 4. A two-step degradation profile was observed for 4-SPES-xx membranes in their acid form. There was no weight loss up to 200 °C because the samples were preheated at 150 °C for 20 min to remove absorbed water. The first weight loss, which appeared at 300–400 °C, was attributed to the desulfonation process, while the second weight loss at around 500–600 °C was related to polymer chain

degradation. The 5% weight loss temperatures ($T_{d5\%}$) decreased with increasing IEC values, which can be explained by higher initial weight losses with the presence of increasing amounts of sulfonic acid groups. The 300–400 °C decomposition temperature shows that sulfonic acid groups attached to pendent phenyl substituents have comparatively high thermal stability.

Good mechanical properties of the membranes are one of the necessary requirements for their effective use in PEMFC applications. The mechanical properties of 4-SPES-xx membranes were measured at room temperature and 50% RH. The stress–strain data are presented in Table 2. The membranes have tensile stress at maximum load of 29.6–44.8 MPa and elongation at break of 13.7–22.5% with the general trend of lower maximum stress for the higher IEC. The results indicated that the membranes were strong and tough for potential use as PEMs materials in a fuel cell.

Oxidative stability

One of the key requirements for PEMs is good oxidative-hydrolytic stability under fuel cell operating conditions. Oxidative attack by HO˙ and HOO˙ radicals mainly occurs in the hydrophilic domains, resulting in degradation of the polymer chains. The oxidative stability of 4-SPES-xx copolymers was evaluated in Fenton's reagent at 80 °C. This method is regarded
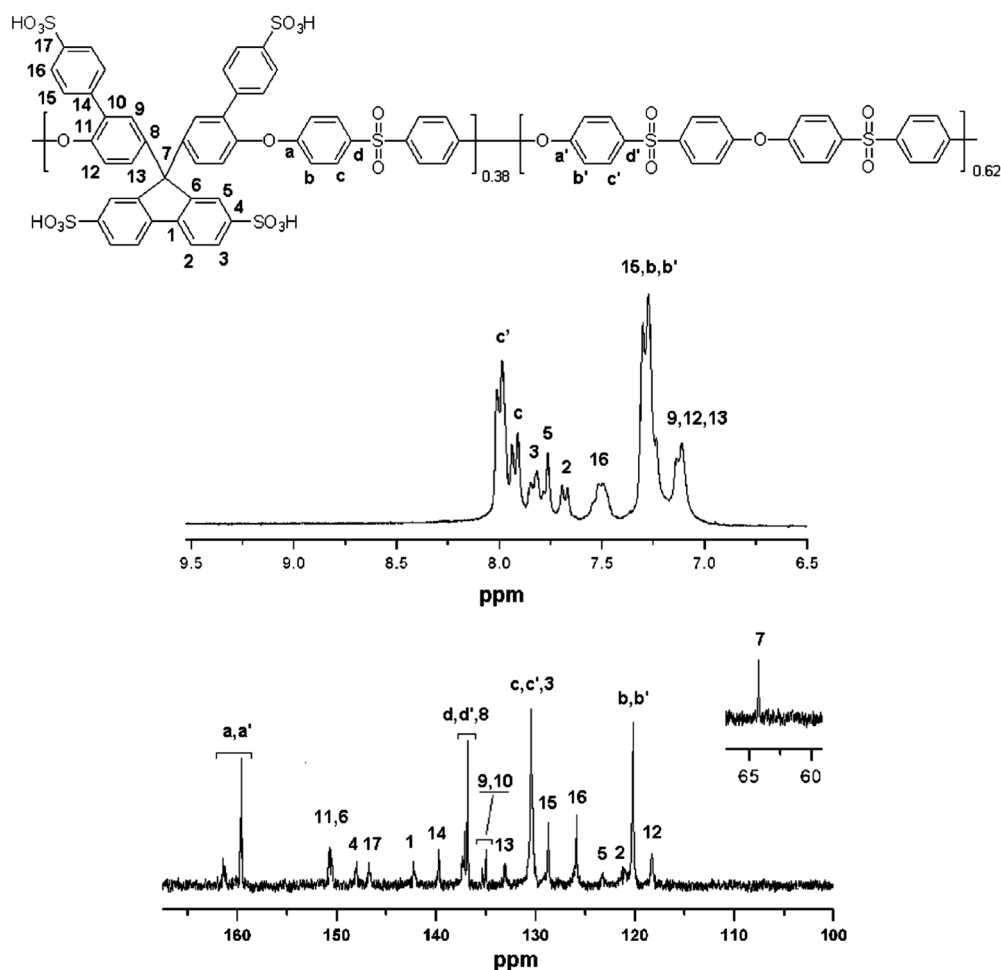
Fig. 3 ¹H and ¹C NMR spectra of 4-SPES-38 copolymer.

as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions. As shown in Table 3, over 98% copolymer weight was retained after treatment in Fenton's reagent at 80 °C for 1 h, and dissolution did not occur within 2.5 h treatment at 80 °C. The copolymers exhibited better oxidative resistance in comparison with some fluorene-based PEMs sulfonated directly on the main-chain.[37,39] The improved oxidative stability is attributed to the introduction of the sulfonic acid groups on pendant-phenyl groups on the main chain.[46]

Water uptake and dimensional stabilities

Water uptake of membranes is an important factor for proton conductivity because water molecules play an important role as
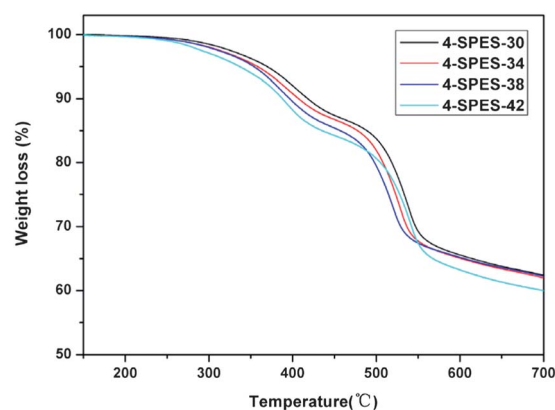

Fig. 4 TGA curves of 4-SPES-xx (acid form) membranes.

**Table 2** Thermal and mechanical properties

Copolymers	$T_{d5\%}{}^a$ (°C)	Tensile strength at break[b] (MPa)	Young's modulus (GPa)	Elongation at break (%)
4-SPES-30	369	44.8	1.03	23
4-SPES-34	358	40.6	0.83	20
4-SPES-38	354	35.9	0.67	17
4-SPES-42	337	29.6	0.55	14

[a] 5% weight loss temperature in N_2 gas (acid form membrane). [b] Measured at room temperature and 50% RH.

Table 3 Water uptake, dimensional swelling, proton conductivity and oxidative stability of the 4-SPES-xx membranes

Copolymers	Water uptake[a]	Dimensional swelling[a] (%)		Proton conductivity (mS cm^{-1}, 100% RH)		Proton conductivity (mS cm^{-1}, 80 °C)		Oxidative stability	
		Δl	Δt	25 °C	80 °C	RH 95%	RH 50%	RW[b] (%)	t^c (h)
4-SPES-30	56.8	10.5	10.9	68	147	97	8.5	100	>6.0
4-SPES-34	62.5	16.5	17.1	76	161	110	11.5	100	4.5
4-SPES-38	79.9	21.2	21.6	108	176	129	15.6	100	3.5
4-SPES-42	124.5	44.1	45.4	122	174	134	18.3	98	2.5
Nafion 212	30.6	17.7	25.3	91	182	136	21	100	>6.0

[a] In the hydrated state (80 °C and 100% RH). [b] Retained weights of membranes after treating in Fenton's reagent 1 h. [c] The dissolution time of polymer membranes.
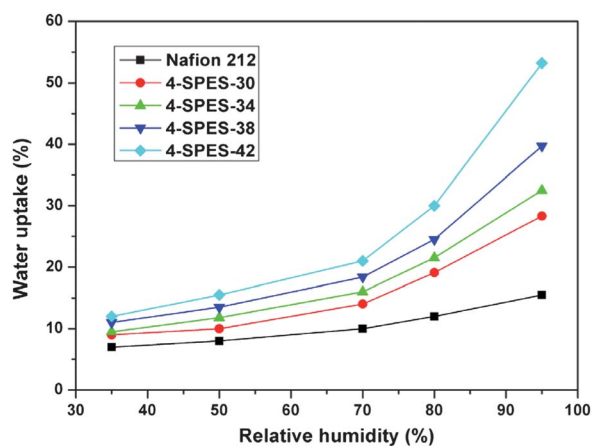
Fig. 5 Relative humidity dependence of water uptake of 4-SPES-xx membranes and Nafion 212 at 80 °C.

proton transportation carriers. However, water swelling ratio should be also considered because unrestrained swelling decreases the dimensional stability and mechanical properties of the polymer membranes.

The water uptake data of 4-SPES-xx membranes under the hydrated state is shown in Table 3, and the humidity dependence of water uptake is also shown in Fig. 5. The water uptake of 4-SPES-xx membranes is much higher than that of Nafion 212 at 35–100% RH, due to their high IEC values. It is obvious to find
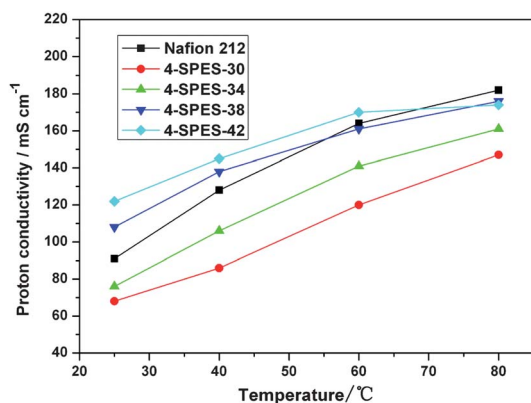
Fig. 6 Proton conductivity of 4-SPES-xx membranes and Nafion 212 at different temperatures and 100% RH.
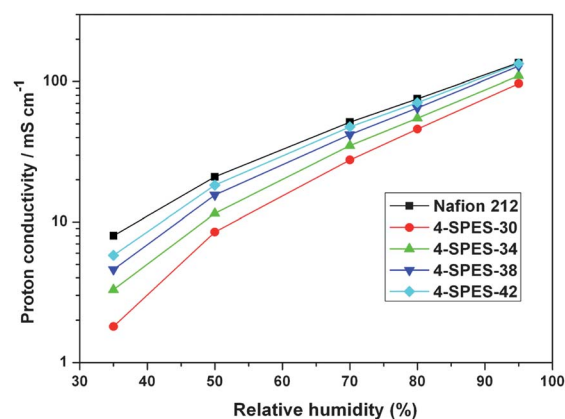
Fig. 7 Proton conductivity of 4-SPES-xx membranes and Nafion 212 at 80 °C as a function of RH.

that water uptake shows less dependence with IEC values at low humidity (<50% RH) but a much larger dependence at high humidity (80–100% RH). For the 4-SPES-30, 4-SPES-34 and 4-SPES-38 membranes, the water uptake increased modestly with increasing IEC values under the hydrated state. However, the highest IEC copolymer 4-SPES-42 shows a relative rapid increase in water uptake and attained the highest value, suggesting that 2.23 mequiv. g^{-1} (4-SPES-38) is an upper-limit IEC value. 4-SPES membranes with higher IEC values (unreported) had excessive water uptake.

The dimensional stabilities of 4-SPES-xx membranes were evaluated by comparing their hydrated state with the dry state at 80 °C (Table 3). As expected, the dimensional changes had a similar trend with water uptake. Apart from 4-SPES-42, all the membranes had lower or comparable dimensional swelling to Nafion. Considering their relatively high IEC values, 4-SPES-xx exhibited acceptable dimensional swelling, which may be attributed to the sulfonic acid groups being located on the rigid fluorene and pendant-phenyl substituents distant from the hydrophobic main chain, rendering the polymer less susceptible to water swelling. In addition, the 4-SPES-xx membranes did not exhibit marked anisotropic swelling.

Proton conductivity

The proton conductivities of 4-SPES-xx membranes and Nafion 212 were measured and some respectively data were listed in
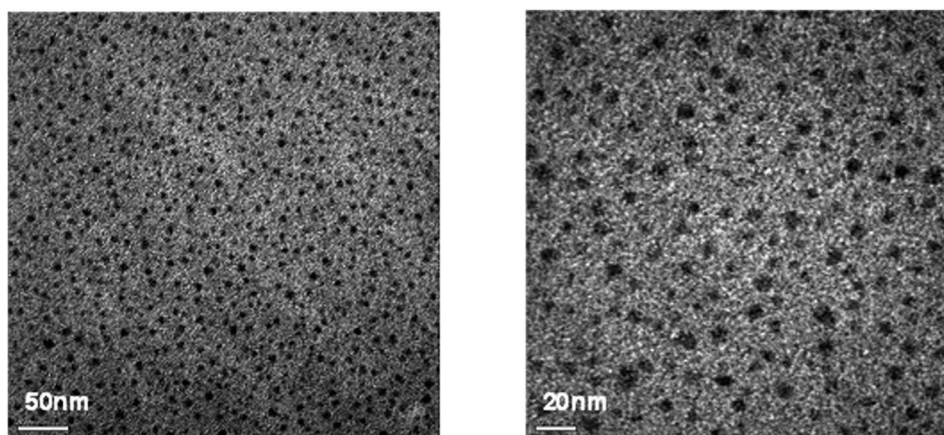
Fig. 8 TEM photographs of 4-SPES-38 membrane.

Table 3. Fig. 6 plots the proton conductivities as a function of temperature at 100% RH. 4-SPES-xx membranes show high proton transport properties and the proton conductivities were in the range of 68 to 122 mS cm^{-1} at 25 °C and 147 to 176 mS cm^{-1} at 80 °C. The proton conductivity of 4-SPES-42 with the highest IEC did not increase from 60 to 80 °C, and was lower than that of 4-SPES-38 at 80 °C, suggesting the adverse effect of excessive dimensional change on proton conductivity at 100 RH and 80 °C. Fig. 7 compares plots the humidity dependence of the proton conductivity of 4-SPES-xx and Nafion 212 membranes. It can be seen that the conductivities did not show a great dependence on humidity in the range of 50–95% RH, with 4-SPES-38 and 4-SPES-42 having a similar trend to that of Nafion 212. This is in contrast to earlier studies, which have shown that the conductivities exhibited a serious dependence on RH for some random aromatic PEMs and alternating aromatic PEMs.[21] The 4-SPES-xx membranes exhibited improved proton conductivities and lesser conductivity–RH dependence, which may be explained by the higher IEC values and the accentuated difference in polarity between clustered pendant-phenyl sulfonated groups and hydrophobic units, resulting in the formation of well-defined phase-separated morphology.

Hydrophilic–hydrophobic nanophase separation in PEMs plays an important role in proton conductivity. In order to investigate the hydrophilic–hydrophobic phase-separated morphology, 4-SPES-38 membrane was studied by TEM and the morphology is shown in Fig. 8. The dark lead-stained regions represent localized ionic domains and the light regions correspond to domains formed by the hydrophobic polymer backbone. Clear phase separation is observed, where hydrophilic domains of ~3 to 7 nm, which could assist proton conduction in the membrane, are surrounded by hydrophobic domains.

PEMFC performance

The H$_2$/O$_2$ fuel cell performance of the 4-SPES-38 membrane (50 μm) and Nafion 212 (50 μm) were tested at 80 °C. As shown in Fig. 9, 4-SPES-38 membrane displayed good performance had comparable performance to that of Nafion 212. At a cell voltage of 0.6 V, the current density of 4-SPES-38 membrane was 980 mA cm^{-2} at 100% RH and 636 mA cm^{-2} at 50% RH. At the effective working potential of 0.6 V, the maximum power density using 4-SPES-38 and Nafion 212 was 570 and 617 mW cm^{-2} at 50% RH, respectively. Although the practical fuel-cell operation of 4-SPES-38 membrane had a slightly lower maximum power density than Nafion 212, the test demonstrated that the hydrocarbon PEM could operate within the 50–100% RH range with relatively good performance.

Conclusions

A new fluorene-based bisphenol with pendant-phenyl substituents was prepared by a facile synthetic route, from which a series of sulfonated poly(ether sulfone)s with clustered sulfonic acid groups pendant to the main chain were prepared for fuel cell tests. The membranes exhibited good proton conductivity and the two highest IEC membranes had similar conductivity–humidity dependence to Nafion. They also exhibited high thermal and oxidative stability, good mechanical properties and acceptable dimensional stability. 4-SPES-38 shows a clear phase-separated morphology of ionic domains of ~3 to 7 nm size, surrounded by hydrophobic domains and a proton conductivity of 129 mS cm^{-1} at 95% RH and 15.6 mS cm^{-1} at 50% RH at 80 °C. At the effective working potential of 0.6 V, the maximum power density of the fuel cell using 4-SPES-38 (50 μm, the same thickness as Nafion 212) was 570 mW cm^{-2} at
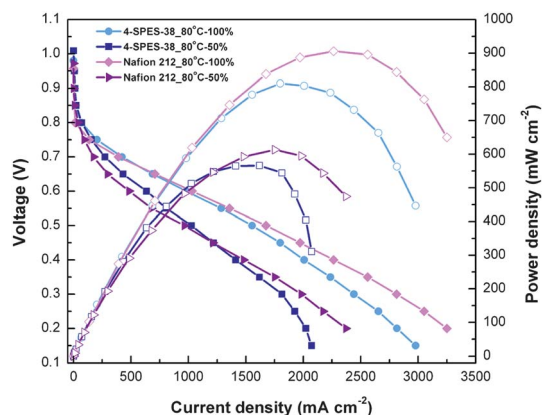

Fig. 9 H$_2$/O$_2$ PEMFC performance of 4-SPES-38 and Nafion 212 membranes at 80 °C with humidity at 50% and 100% RH.

50% RH, which is slightly less than that of Nafion 212. Considering the facile synthetic route and the overall copolymer properties, this new fluorene-based monomer and the resulting sulfonated poly(ether sulfone)s are promising for exploring larger-scale production and investigation as fuel cell membranes.

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Notes and references

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