



Poly(arylene ether)s with pendant sulfoalkoxy groups prepared by direct copolymerization method for proton exchange membranes

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ARTICLE INFO

Article history:

Received 28 April 2008

Received in revised form 9 June 2008

Accepted 10 June 2008

Available online 20 June 2008

Keywords:

Sulfonated polymers

Poly(arylene ether)s

Proton exchange membrane

Fuel cells

ABSTRACT

A novel sulfonated monomer sodium-3-(4-(2,6-difluorobenzoyl)phenoxy)propane-1-sulfonate was designed and synthesized. Based on above monomer, a series of sulfonated poly(arylene ether) copolymers containing aliphatic acid groups between aromatic backbones and sulfonic acid groups (PSOA-SPA-E) were successfully prepared by direct copolymerization. Ion exchange capacity (IEC) of the copolymers could be mediated in the range of 1.07–1.61 meq g⁻¹ by the monomer ratios used in the copolymerization. These copolymers exhibited good oxidative and dimensional stability. The proton conductivities of copolymer films increased with the increase of IEC and temperature. The conductivity of PSOA-SPA-E-80 was 4.94 × 10⁻² S cm⁻¹ at room temperature, and was up to 1.35 × 10⁻¹ S cm⁻¹ at 100 °C, which was close to that of Nafion 117. These copolymers may be promising proton exchange membranes (PEMs) due to their high proton conductivity and good oxidative and dimensional stability.

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1. Introduction

Perfluorosulfonic acid ionomers, such as Nafion, are commonly employed as the electrolytes in proton exchange membrane (PEM) fuel cells [1,2]. Although almost half of a century has passed since DuPont developed Nafion membranes, they are still state-of-the-art because of their high proton conductivity and excellent stability. However, the practical applications of the perfluorosulfonic acid PEMs in large scale are limited to some extent due to their high methanol permeability, low conductivity at high temperature, and high cost [3–5]. Recently, great efforts have been made to design and synthesize alternative PEM materials to the perfluorosulfonic acid ones. One possible approach is to make hydrocarbon polymers bearing acid groups. Aromatic polymers have been extensively studied due to their excellent stability and high susceptibility to electrophilic sulfonation reactions. A number of aromatic polymers, such as poly(arylene ether)s [6,7], polyimides [8,9], polybenzimidazoles [10], and others have been sulfonated or doped with mineral acids.

The sulfonated poly(arylene ether)s can be divided into two types, main-chain-style and side-chain-style, according to the position of the attached sulfonic acid groups. Main-chain-style polymers, in which the sulfonic acid groups are attached to the

polymer backbone, sometimes show an intensive water uptake over a critical temperature or sulfonate degree, resulting in unfavorable excess water swelling of the membranes. A strategy to lower the water-swelling ratio is to separate the hydrophilic sulfonic acid groups from the hydrophobic polymer main chain [11]. Recently, polymers with sulfonic acid groups on pendent side chains (side-chain-style) have been reported by several research groups [11–15]. Polymers with pendent acid groups on side chains keep the polymer chain in a hydrophobic environment, which may contribute to improve dimensional, thermal and oxidative stability of the membranes. Miyatake and coworkers reported that polymers with flexible side chains exhibited improved dimensional stability and enhanced conductivity [16,17]. Ding and Guiver et al. synthesized comb-shaped polymers that had rigid aromatic main chains and flexible side chains [18]. These polymers displayed advantageous conductivity and membrane hydrodynamic properties compared to most of sulfonated main-chain-style polymers. It appears that the unique polymer chemical structure that is helpful to micro-phase separation between hydrophobic and hydrophilic domains is responsible for the high proton conductivity.

In the previous study, we presented several kinds of poly(arylene ether)s with sulfonic acid group on side chains [19–21]. In this paper, we successfully prepared a series of poly(arylene ether)s with sulfonic acid groups on pendent flexible sulfoalkoxy side chains via a nucleophilic substitution polycondensation reaction of sodium-3-(4-(2,6-difluorobenzoyl)phenoxy)propane-1-sulfonate (SFPOPS), 4,4'-dihydroxydiphenylether (DHDPE) and 4,4'-dichlorodiphenyl sulfone (DCDPS). Different from previous

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work [20,21], more flexible sulfoalkoxy side chains were incorporated into aromatic ether backbones. The properties, such as proton conductivity, thermal stability, dimensional change and oxidative stability, were fully investigated.

2. Experimental

2.1. Materials

2,6-Difluorobenzoyl chloride, 1-bromo-3-phenoxypropane and DHDPE were purchased from Aldrich Ltd. DCDPS and tetramethylene sulfone (TMS) were purchased from Shanghai Chemical Factory. Other chemicals were purchased from Beijing Chemical Reagent and were purified by conventional method. K_2CO_3 was dried at 120°C for 24 h before polymerization.

2.2. Synthesis of (4-(3-bromophenoxy)(2,6-difluorephenyl)methanone (BPOFPM)

A 250-mL three-neck flask equipped with a mechanical stirrer, addition funnel, and nitrogen inlet was charged with $AlCl_3$ (14.6 g, 0.11 mol), CH_2Cl_2 (75 mL), and 2,6-difluorobenzoyl chloride (17.6 g, 0.1 mol). The solution was cooled to 0°C and stirred for 10 min. 1-Bromo-3-phenoxypropane (21.5 g, 0.1 mol) was then added dropwise over 10 min. After stirring for 4 h at 0°C , the mixture was poured into 100 mL of ice water that contained 10 mL of concentrated hydrochloric acid. The organic phase was washed with 10% NaOH (1×100 mL) and H_2O (4×100 mL) and dried with anhydrous $MgSO_4$. After evaporating the solvent under vacuum, the residue was recrystallized in petroleum ether and 30.1 g of white crystals were obtained (85% yield).

$^1\text{H NMR}$ ($CDCl_3$): $\delta = 2.35$ (q, $J = 6$ Hz, 2H, H_f), 3.61 (t, $J = 6.3$ Hz, 2H, H_g), 4.19 (t, $J = 5.8$ Hz, 1H, H_e), 6.95 (d, $J = 8.8$ Hz, 2H, H_b), 6.99 (t, $J = 8.9$ Hz, 2H, H_d), 7.43 (m, 1H, H_a), 7.81 (d, $J = 8.6$ Hz, 2H, H_c).

2.3. Synthesis of sodium-3-(4-(2,6-difluorobenzoyl)phenoxy)propane-1-sulfonate (SFPOPS)

BPOFPM (35.5 g, 0.1 mol) and Na_2SO_3 (37.8 g, 0.3 mol) were refluxed for 2 days in a mixture of H_2O and ethanol (100 mL, 1:1, v/v). The solution was concentrated by vacuum distillation, followed by diluting with 100 mL of water and hot filtering. After the solution was cooled to 4°C , the SFPOPS was separated as powders. Recrystallized the products in anhydrous ethanol to afford 28.7 g of pure white crystals (76% yield).

$^1\text{H NMR}$ (ppm, $DMSO-d_6$): $\delta = 2.01$ (q, $J = 7.1$ Hz, 2H, H_f), 2.54 (t, $J = 7.7$ Hz, 2H, H_g), 4.19 (t, $J = 6.4$ Hz, 2H, H_e), 7.08 (t, $J = 8.9$ Hz, 2H,

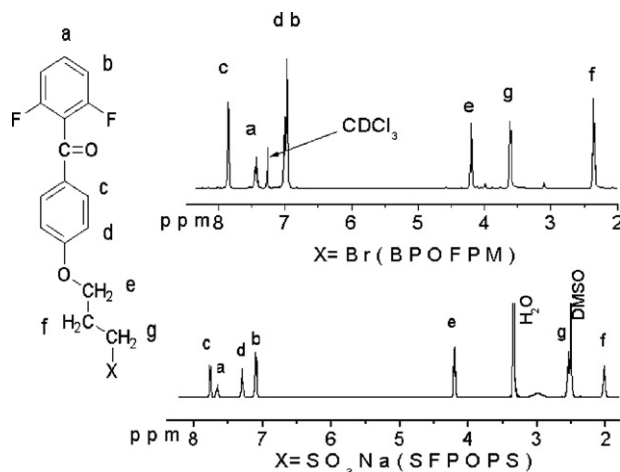


Fig. 1. $^1\text{H NMR}$ spectra of BPOFPM and SFPOPS.

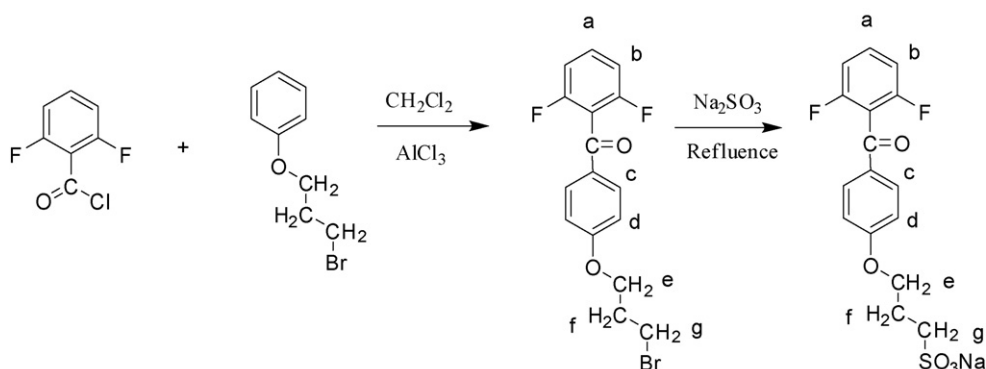
H_b), 7.29 (t, $J = 8.1$ Hz, 2H, H_d), 7.66 (m, 1H, H_a), 7.75 (d, $J = 8.7$ Hz, 2H, H_c).

2.4. Synthesis of sulfoalkoxy acid groups in side-chain of sulfonated poly(arylene ether) copolymers (PSOA-SPEAs)

The polymers were prepared by copolymerization polycondensation dihalo- and bisphenol monomers in TMS at the presence of an excess of anhydrous potassium carbonate. SDPOPS and DCDPS (1.0 mmol), DHDPE (1.0 mmol), and potassium carbonate (1.1 mmol) were added into a 50 mL three-neck flask equipped with a Dean-Stark trap and a nitrogen inlet. TMS (21 mL) and toluene (10 mL) were used as solvents. The mixture was refluxed for 2 h at 135°C until water was removed from mixture by azeotropic distillation. After removed the excess toluene, the temperature of the reaction mixture was slowly raised to 185°C and maintained at that temperature for 18 h. Before stopping the reaction, 5 mL of TMS was added to dilute the reaction solution, and the polymer was recovered by precipitating into water and then washed with hot deionized water and ethanol for several times, respectively. The resulting product was dried in vacuum oven at 120°C for 15 h.

2.5. Film formation and proton exchange

Sodium-form copolymer (1.0 g) was dissolved in 10 mL of *N*-methyl-2-pyrrolidinone (NMP) overnight. Then the solution was filtered with a fine glass frit filter funnel and cast directly onto



Scheme 1. Synthesis of sulfonated monomer.

clean glass plates. After carefully dried at 60 °C for 10 h and then at 120 °C for 12 h in vacuum oven, tough and flexible sodium-form film (thickness: ~80–100 μm and size: ~100 cm²) was obtained. The sodium-form membrane was transformed to its acid form by proton exchange in 1.0 M H₂SO₄ for 24 h at room temperature. Then the acidified film was soaked and thoroughly washed with deionized water.

2.6. Measurements

2.6.1. Copolymer analysis and measurements

The viscosities of the obtained copolymers were determined using an Ubbelohde viscometer in thermostatic container with the polymer concentration of 0.5 g dL⁻¹ in DMAc at 25 °C. FT-IR spectrum (film) was measured on a Nicolet Impact 410 Fourier transform infrared spectrometer. ¹H NMR experiments were carried out on a Bruker 510 spectrometer (¹H, 500 MHz) using DMSO-*d*₆ as solvent.

2.6.2. Thermal properties of membranes

Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating

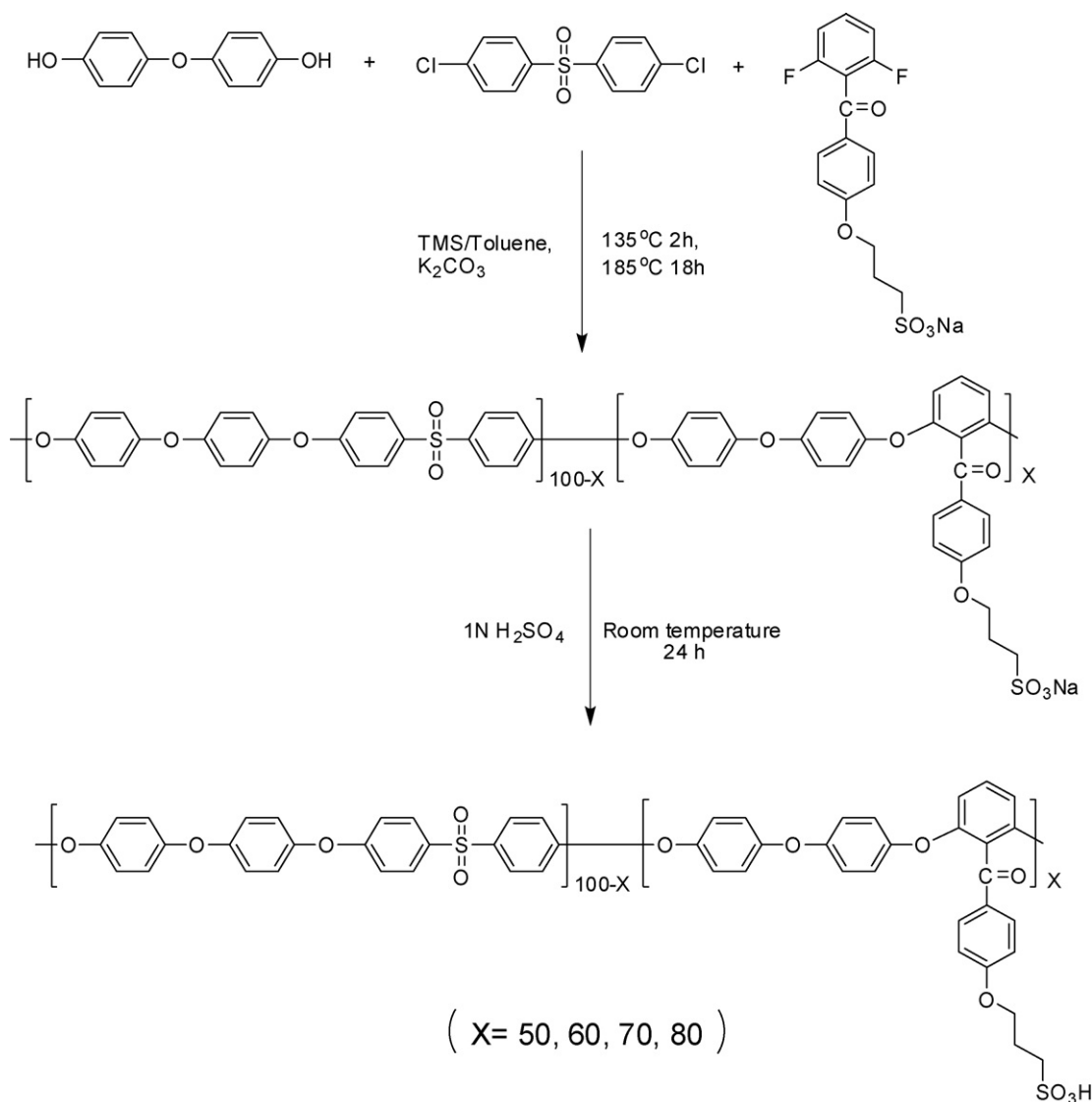
rate of 10 °C min⁻¹ from 50 to 300 °C under nitrogen. The glass-transition temperatures (*T*_g) of the copolymers were reported as the midpoint of the step transition in the second heating run. Thermogravimetric analysis (TGA) was employed to assess thermal stability of membranes with a PerkinElmer Pyris 1 thermal analyzer system. Before running, the films were dried and kept in the TGA furnace at 120 °C under an air atmosphere for 20 min to remove water. The samples were evaluated over the range of 100–800 °C with a heating rate of 10 °C min⁻¹ in air.

2.6.3. Water uptake and swelling ratio measurements

The sample films were soaked in deionized water to reach equilibrium at desired temperature. Then the films were dried at 120 °C for 24 h. Weights or lengths of dry and wet membranes were measured. The water uptake content was calculated by

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where *W*_{dry} and *W*_{wet} are the weights of dry and wet samples, respectively. The swelling ratio was calculated from the change of



Scheme 2. Synthesis of PSOA-SPA-E-X polymers.

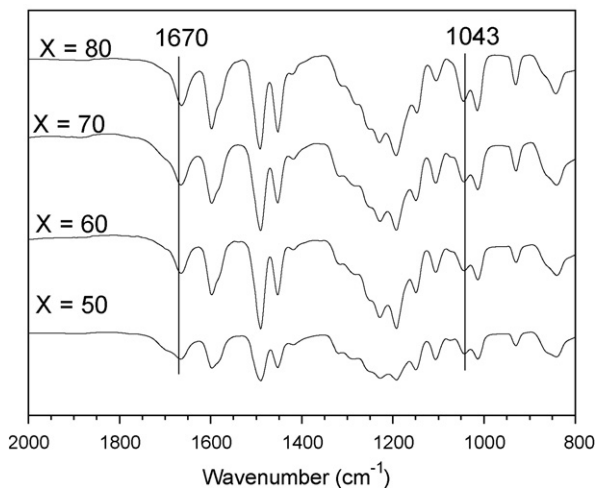


Fig. 2. FT-IR spectra of PSOA-SPAE-X.

film length by

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100$$

where L_{wet} and L_{dry} are the lengths of the wet and dry membrane, respectively.

2.6.4. Oxidative stability

A small piece of membrane sample was soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm FeSO_4) at 80°C . The stability was evaluated by recording the time when membranes began to dissolve and dissolved completely.

2.6.5. Proton conductivity

Proton conductivity measurements were conducted using ac impedance spectroscopy (Solatron-1260/1287 impedance analyzer) over a frequency range of $10\text{--}10^7$ Hz with 50–500 mV oscillating voltage. A sheet of sulfonated membrane ($15\text{ mm} \times 10\text{ mm}$) was

placed in a test cell similar with that in previous reports [15]. Before measurement, the films were full hydrated in water for 48 h. Temperature was controlled through a wrap-around resistance heater with a feedback temperature controller. The impedance measurements were performed in water vapor with 100% relative humidity (RH) at desired temperature. The conductivity (σ) of the films in the transverse direction was calculated from the following equation:

$$\sigma = \frac{D}{LBR}$$

where D is the distance between the two electrodes and L and B are the thickness and width of the film samples.

2.7. Transmission electron microscopy (TEM)

TEM images were determined by JEM-2000EX. Before test, the polymers were first converted into Ag^+ forms (PSOA-SPAE-Ag) by dissolving the polymers in AgNO_3 solutions for 24 h. The SPEKK-Ag in DMF solutions was then cast onto copper grids for TEM use. All the tests were carried out in the unhydrated condition.

3. Results and discussion

3.1. Synthesis of monomer

The comb-shaped polymers containing hydrophobic aromatic backbones and hydrophilic aliphatic pendants were considered to be helpful to form distinct micro-phase separation between the opposing domains in the membrane [18]. The micro-phase separation serves to compartmentalize water into the hydrophilic polymer side chain domains, resulting in effective membrane water management and excellent proton conductivities. As an attempt of enhancing the trend of micro-phase separation of the membranes, polymers bearing a $-\text{SO}_3\text{H}$ group on the end of a more flexible side chain would be prepared. We firstly synthesized a difluoride-monomer (SFPOPS), which had a more flexible side chain than the one reported by us [20,21]. A two-step synthetic route was adopted, as shown in Scheme 1(a). Monomer SFPOPS was prepared by an anhydrous aluminum chloride-catalyzed Friedel-Crafts acylation of

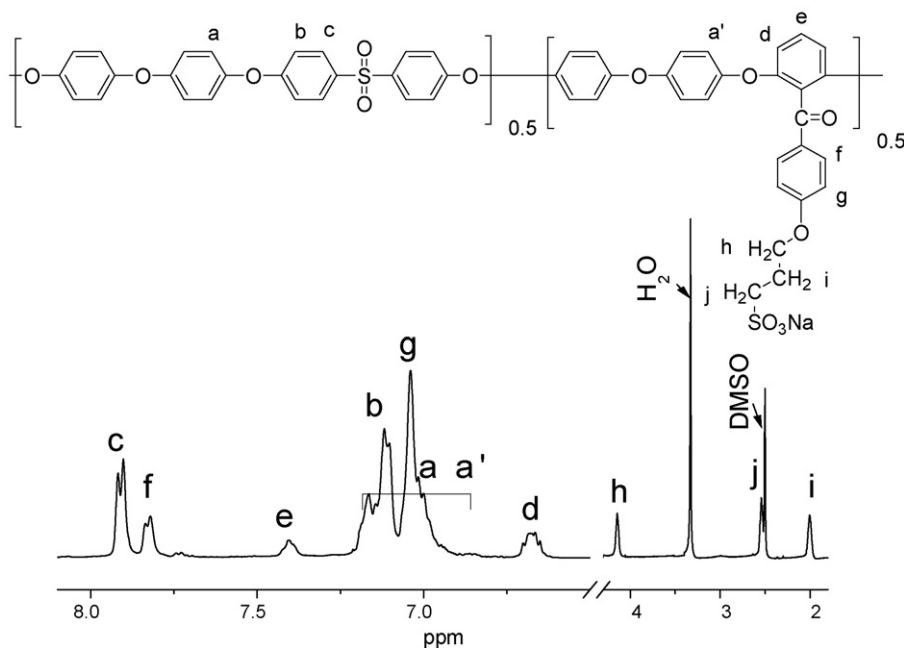


Fig. 3. ^1H NMR spectrum of PSOA-SPAE-50 in $\text{DMSO-}d_6$.

1-bromo-3-phenoxypropane with 2,6-difluorobenzoyl chloride to yield BPOFPM and followed by sulfonation with Na_2SO_3 . Its structure was confirmed by ^1H NMR spectrum (Fig. 1).

3.2. Synthesis of polymers

As shown in Scheme 2, the sulfonated poly(arylene ether)s with pendant sulfoalkoxy groups (PSOA-SPA-E-X) were synthesized by polycondensation using various feed ratios of SFPOPS/DCDPS, so that polymers with different molar percentage of pendant sulfoalkoxy groups (Scheme 2) were obtained. The polymerization reactions proceeded smoothly, and no crosslinking was evident when the system was carefully purged with nitrogen and the temperature was well controlled by oil bath (less than 185°C). TMS was used as the reaction solvent, and toluene was used to remove the water during the copolymerization. After copolymerization about 20 h at 185°C , the solutions became highly viscous, and the reaction solution was cooled before precipitation into water. Table 1 shows the nomenclatures used in this paper for the prepared copolymers. In all cases, the yields were obtained as evidenced by the high η_{inh} values of above 0.8 dL g^{-1} in NMP. The successful introduction of the sodium sulfonated groups was confirmed by FT-IR spectra (Fig. 2), where characteristic peaks at 1043 cm^{-1} assigned to stretching of the sodium sulfonate groups and at 1670 cm^{-1} assigned to double bond of benzoyl stretching were observed for all sulfonated copolymers from PSOA-SPEA-50 to PSOA-SPEA-80. ^1H NMR spectroscopy was used as the principal method for structural characterization of the polymers in the sodium salt form. As an example, ^1H NMR spectrum of PSOA-SPA-E-50 is shown in Fig. 3. The protons were assigned according to its ^1H - ^1H COSY spectrum. The aromatic region and aliphatic region of ^1H - ^1H COSY spectrum are also shown in Fig. 4(a) and (b), respectively. On the basis of their correlation signals, the proton was assigned easily. All the protons were well assigned to the protons of the supposed chemical structure. The ^{13}C NMR spectrum of PSOA-SPA-E-50 is shown in Fig. 5. The signal at $\delta = 191.6 \text{ ppm}$ was assigned to the carbonyl carbon atom of side chain. The signal from $\delta = 15 \text{ ppm}$ to $\delta = 75 \text{ ppm}$ was assigned to the carbon of aliphatic groups, and the peak at $\delta = 48.5 \text{ ppm}$ could be assigned to the carbon attached $-\text{SO}_3\text{Na}$ group. We used mathematical function and ratio of spectral line intensities (integral values) to assess the IEC values of the sulfonated polymers. The observed IEC values were in agreement with the expected IEC derived from the monomer ratios (see Table 1). Particular calculate method according to the following formula:

$$\text{IEC} = \frac{\text{Sa}}{\text{Sa} \times \text{Ma} + (\text{Sb}/2) \times \text{Mb}}$$

where Sa and Sb were the integral values of the H_f and H_c . Ma and Mb denoted molecular weights of the sulfonated segment and nonsulfonated segment in a repeat unit, separately.

3.3. Thermal analysis

The introduction of sulfonate groups into polymers has two effects on their glass transition temperatures: one is the increased intermolecular interaction by pendant ions, i.e. ionomer effect;

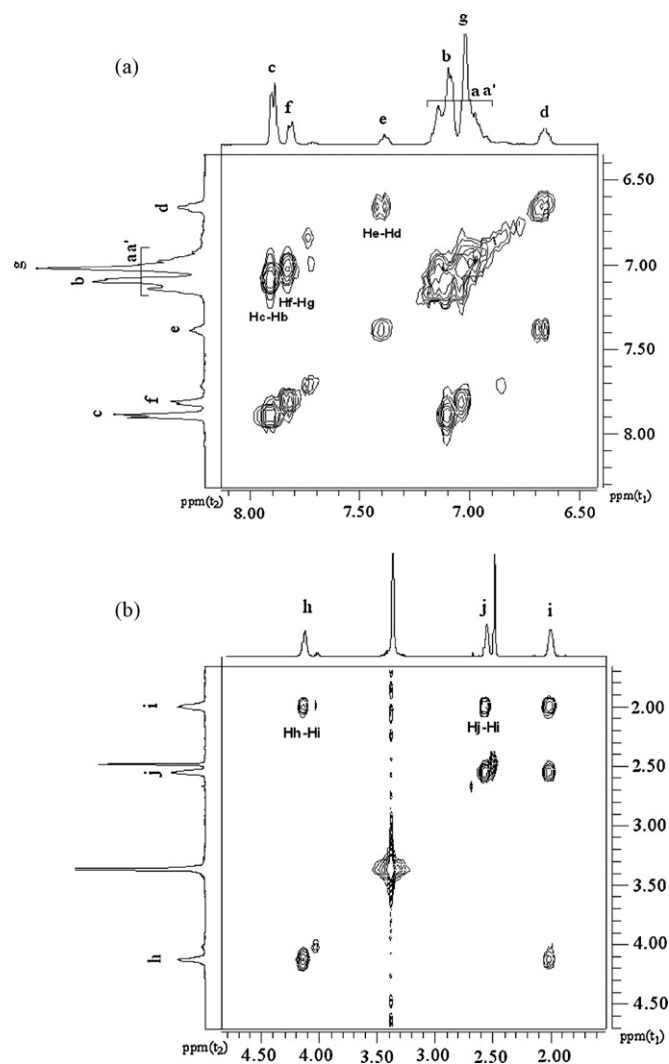


Fig. 4. ^1H - ^1H COSY spectrum of PSOA-SPA-E-50: (a) aromatic region and (b) aliphatic region.

and the other is the increased molecular bulkiness. Both effects hinder internal rotation, leading to the higher glass transition temperatures for sulfonated polymers [22]. Glass transition temperatures (T_g s) of the copolymers PSOA-SPA-E-X were evaluated using DSC by heating the samples from 50 to 300°C at $10^\circ\text{C min}^{-1}$. As shown in Fig. 6, the T_g s of PSOA-SPA-E-X increased substantially when the mole fraction of sulfonation was increased. And T_g values increased from 173°C (for the copolymer containing 50% sulfonated repeat units) to 207°C (for the copolymer containing 80% sulfonated repeat units). The thermal stabilities of this series of polymers were studied by TGA in air. Table 2 lists the TGA data for the polymers in the acid form and sodium form. All of the sulfonated copolymers in acid form exhibited good thermal stability up to 210°C where weight loss was observed. The PSOA-SPA-E-X

Table 1

Some properties of PSOA-SPEA-X polymers (where X is the number of sulfonated unit per 100 repeat units in the polymers)

Polymer	SFPOPS/DCDPS	DS	IEC expected from monomer feed ratio	IEC from ^1H NMR	η_{inh} (dL g^{-1})
PSOA-SPEA-80	4.0	0.8	1.61	1.60	0.90
PSOA-SPEA-70	2.3	0.7	1.44	1.43	0.88
PSOA-SPEA-60	2.0	0.6	1.26	1.26	0.82
PSOA-SPEA-50	1.0	0.5	1.07	1.06	0.79

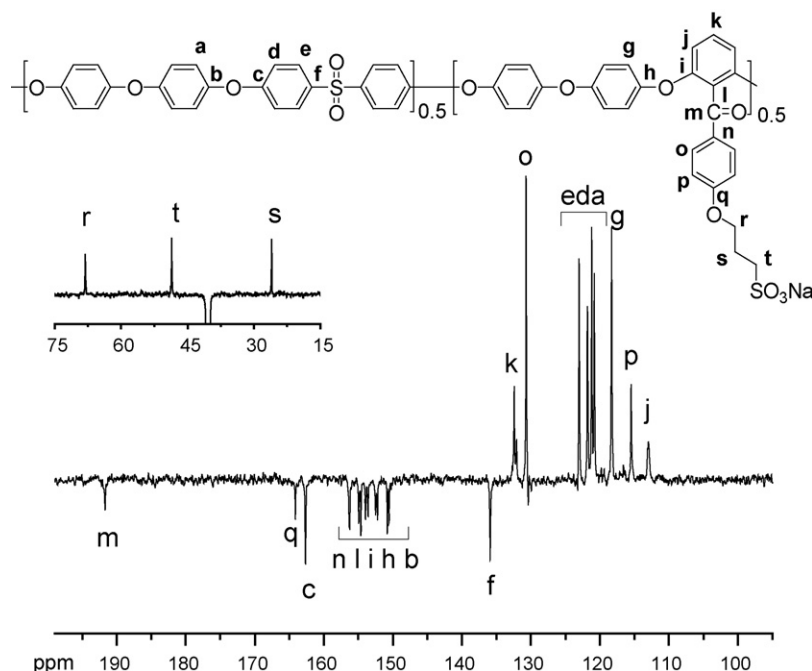


Fig. 5. ^{13}C NMR spectrum of PSOA-SPAE-50.

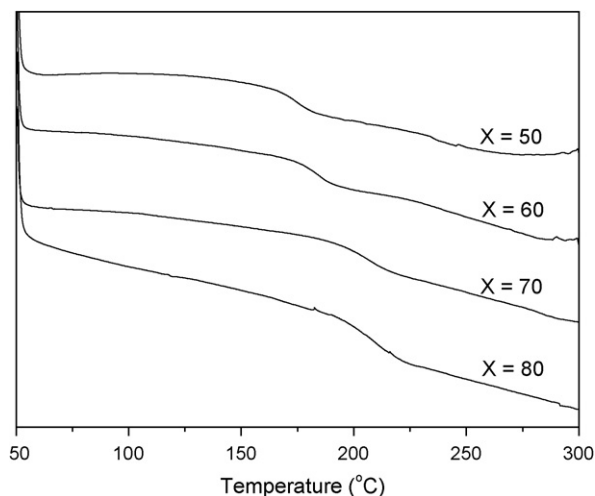


Fig. 6. DSC curves of the PSOA-SPAE-X polymers in sodium form.

in acid form exhibited two distinct thermal degradation steps, as shown in Fig. 7. The initial weight loss between 210 and 230 °C was assigned to the loss of $-\text{SO}_3\text{H}$ groups. The second thermal degradation above 390 °C was assigned to the degradation of the main chains.

Table 2
Thermal properties of PSOA-SPEA polymers

Polymer	T_g (°C)	$T_{d_{\text{onset}}}$ (°C)		$T_{d_{10\%}}$ (°C)	
		Acid form	Sodium form	Acid form	Sodium form
PSOA-SPEA-80	207	212	243	292	387
PSOA-SPEA-70	203	216	252	295	387
PSOA-SPEA-60	182	212	238	299	389
PSOA-SPEA-50	173	227	219	307	399

3.4. Oxidative stability

Oxidative stability of PSOA-SPAE-X membranes was examined by observing the dissolving behavior in Fenton's reagent at 80 °C. Both the initially dissolving and dissolved time became shorter by increasing the sulfonated degree. All membranes did not show any dissolution before 2 h and afterward, PSOA-SPAE-80, PSOA-SPAE-70 and PSOA-SPAE-60 began to dissolve in succession. After 8 h in Fenton's reagent at 80 °C, above membranes completely dissolved. These results demonstrated that PSOA-SPAE membranes had acceptable oxidative stability.

3.5. Water uptake and swelling ratio

We prepared sulfonated copolymers (PSOA-SPAE-X) containing aromatic main chain and flexible side chain. Our intention is to avoid disadvantage for main-chain-style sulfonated poly(aryl ether)s [11,23,24] and to improve micro-phase separation of the

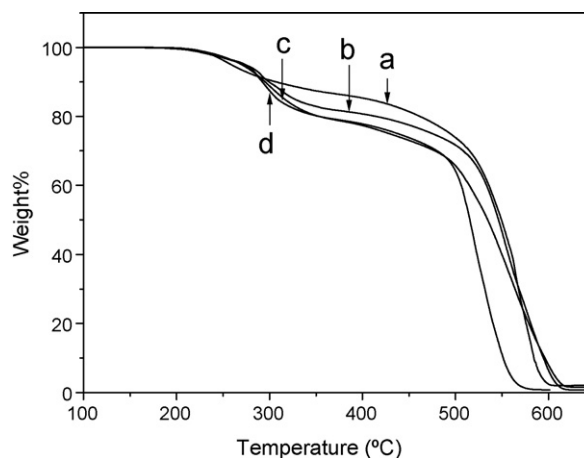


Fig. 7. TGA curves of the polymers in acid form: (a) PSOA-SPAE-50, (b) PSOA-SPAE-60, (c) PSOA-SPAE-70 and (d) PSOA-SPAE-80.

Table 3
Swelling ratio, λ value and conductivity of the copolymers

polymer	Room temperature			80 °C			100 °C		
	ΔL (%)	λ	σ (S cm ⁻¹)	ΔL (%)	λ	σ (S cm ⁻¹)	ΔL (%)	λ	σ (S cm ⁻¹)
PSOA-SPEA-80	14.6	14.5	4.84×10^{-2}	21.0	23.0	9.94×10^{-2}	26.6	41.1	1.35×10^{-1}
PSOA-SPEA-70	10.0	10.8	3.26×10^{-2}	14.0	17.3	6.89×10^{-2}	21.4	23.7	1.18×10^{-1}
PSOA-SPEA-60	6.0	7.5	1.30×10^{-2}	7.9	12.3	3.12×10^{-2}	9.1	15.4	6.91×10^{-2}
PSOA-SPEA-50	4.6	6.7	2.67×10^{-3}	4.6	9.3	7.39×10^{-2}	5.9	11.4	1.67×10^{-2}
PSA-SPAE-80	5.3	8.7	3.5×10^{-2}	12.0	15.1	9.48×10^{-2}	26.3	26.1	1.44×10^{-2}
PSA-SPAE-70	5.1	7.9	1.8×10^{-2}	10.2	14.3	6.61×10^{-2}	21.0	22.4	1.01×10^{-2}
SPAEEK-6F-60 ^[7]	19	14	4.6×10^{-2}	52	45	1.1×10^{-1}	–	–	–
M-60 ^[25]	15	11	6.3×10^{-2}	50	41	8.5×10^{-2}	–	–	–
Nafion 117	13.1	12.0	6.7×10^{-2}	20.2	18.0	9.6×10^{-2}	23.1	21.0	1.45×10^{-1}

ΔL (%): swelling ratio; λ : ($\text{H}_2\text{O}/\text{SO}_3\text{H}$).

sulfonated polymer membranes by adjusting molecular structure of polymer. The water uptake and swelling ratio were measured from the ratio of the weight and length before and after immersed in water. Water uptake can also be expressed as the number of H_2O molecules per sulfonic acid group ($\lambda = \text{H}_2\text{O}/\text{SO}_3\text{H}$). The swelling ratio (ΔL %) and λ value (Table 3) of the copolymers exhibited generally change trend, which increased with the increasing of temperature and IEC. At 100 °C, the swelling ratio of PSOA-SPAE-50, -60, -70, -80 membranes ranged from 5.9% to 26.0%. The swelling ratio of PSOA-SPAE-80 is similar to Nafion 117 when they retained the same conductivity. Compare with main-chain-style bisulfonated poly(arylene ether)s (SPAEEK-6F-60 [7], M-60 [25]) PSOA-SPAE-X copolymer films exhibited appropriate water absorption and smaller swelling ratio in hot water in a range of comparable proton conductivity. Compared with the previous work [20,21], the PSOA-SPAE copolymer films exhibited higher λ value and swelling ratio than PSA-SPAE copolymer films at low temperature. At high-elevated temperature, the λ value and swelling ratio of PSOA-SPAE membranes became to approach that of PSA-SPAE membranes (Table 3). Due to the ether bond was introduced between aromatic main chains and flexible aliphatic sulfonated side chain, flexible ether linkage in side chain of PSOA-SPAE copolymer might make the sulfonic acid groups move easily, which would be helpful for sulfonic acid groups to aggregate actively and to form continuous hydrophilic domains. Figs. 8 and 9 show the temperature-dependence of water uptake and swelling ratio of PSOA-SPAE-X membranes, respectively. For the membranes with low sulfonate content (IEC < 1.43), the water

uptake and swelling ratio increased mildly with the increase of temperature. The membranes with high sulfonate content (IEC \geq 1.43) exhibited a sharp increase in water uptake and swelling ratio at high temperature (above 80 °C). The water uptake and swelling ratio are associated with the micro-phase separation. The pendant flexible sulfoalkoxy chains of PSOA-SPAE-X copolymers may be helpful to assemble sulfonic acid groups and form distinct steady hydrophilic and hydrophobic phase region. Therefore, the water uptake and swelling ratio of PSOA-SPAE copolymer film exhibited low temperature-dependence that was distinct before 80 °C. After 80 °C, both water uptake and swelling ratio values increased sharply due to the hydrophilic phase expansion.

3.6. Proton conductivity

Water absorption of the membranes was considered to explain this conductivity difference in terms of polymer structure. Table 3 demonstrates the effect of ether bond on conductivity at specific temperature. Surprisingly, the proton conductivity yielded similar trend to water absorption behavior. Fig. 10 displays the Arrhenius plots of the conductivity of the analyzed membranes in the range of 30–100 °C. The activation energy (E_a) of conductivity was calculated by fitting the Arrhenius equation $\sigma = \sigma^0 \exp(-E_a/RT)$. Curves were fitted linearly for E_a determination. PSOA-SPAE-80's E_a was 15.2 kJ mol^{-1} . This value was smaller than PSA-SPAE-80 (18.2 kJ mol^{-1}). From E_a , the proton conductivity of PSOA-SPAE membranes also showed lower temperature-dependence. The conductivity values of the membranes were above $10^{-2} \text{ S cm}^{-1}$ except

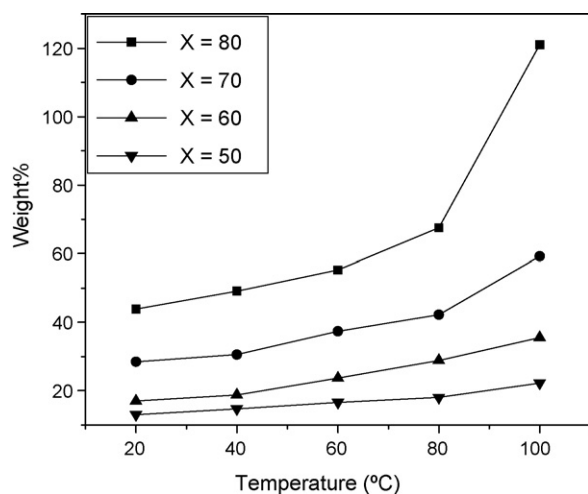


Fig. 8. Water uptake of PSOA-SPAE-X polymers in acid form as a function of temperature.

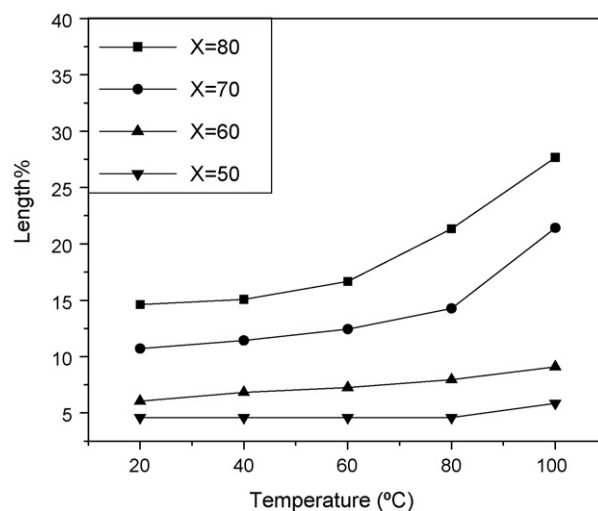


Fig. 9. Water-swelling ratio of PSOA-SPAE-X polymers in acid form as a function of temperature.

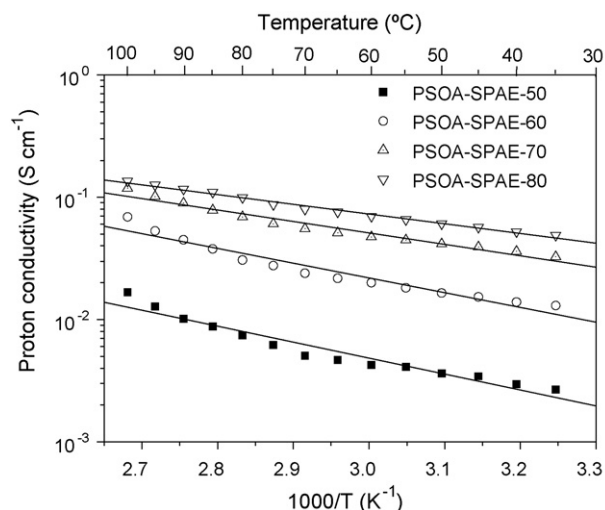


Fig. 10. Proton conductivity of the membranes as function of temperature under 100 RH.

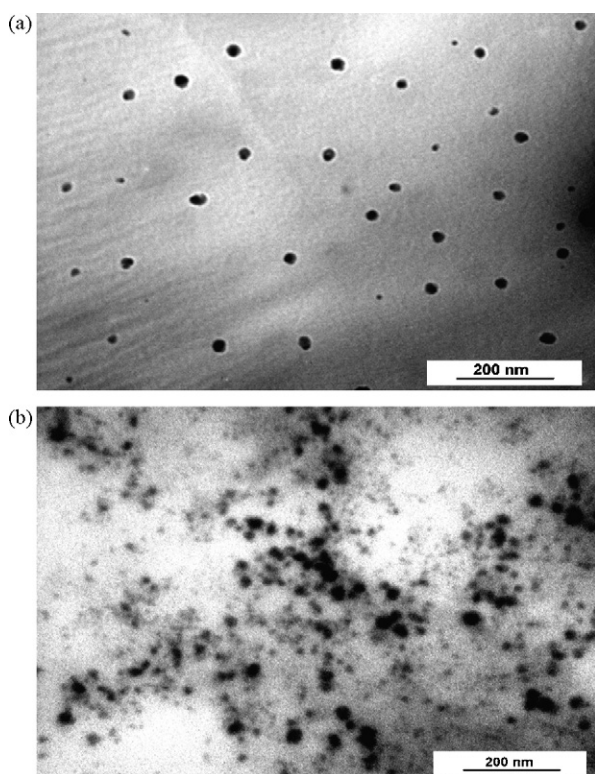


Fig. 11. TEM images of (a) PSOA-SPAE-50 and (b) PSOA-SPAE-80.

that PSOA-SPAE-50, and the proton conductivities of some membranes were comparable to that of Nafion 117.

3.7. Transmission electron microscopy (TEM)

Proton conductivity and dimensional stability of the membranes are closely related to their morphology. Wide ion channels formed by hydrophilic domains are helpful to the movement of protons but are possibly detrimental to mechanical properties and dimensional

stability in hot water. In order to observe microcosmic morphology of PSOA-SPAE membranes, the TEM analysis was performed on Ag^+ stained PSOA-SPAE ultrathin films on the carbon grid under ambient humidity. Two micrographs corresponding to the morphologies of PSOA-SPAE-50 and PSOA-SPAE-80 are shown in Fig. 11. The dark regions represented localized ionic domains and the light regions referred to the domains formed by hydrophobic polymer backbones. The images exhibited that the silver ionic groups dispersed within polymers. With the increase of DS, the silver clusters became more obvious and their density and average sizes increased. This result indicated that a higher degree of sulfonation resulted in more and larger ionic domains, and thus a larger channel for proton transport.

4. Conclusion

Novel difluoro-monomer bearing a sulfoalkoxy group, SFPOPS, was synthesized successfully. A series of PSOA-SPAE derived from this monomer were prepared. Tough and transparent membranes were obtained from solution casting. The novel PSOA-SPAE displayed good solubility in common aprotic solvents and high thermal stability up to 210 °C in air. Being different from the PSA-SPAE copolymers, the proton conductivity of PSOA-SPAE membranes also showed lower dependence on temperature. PSOA-SPAE copolymers showed good thermal, dimensional and oxidative stability, which suggested a potential feasibility of this family of PSOA-SPAE membranes for PEMFC applications.

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