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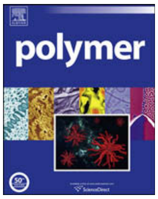

Novel side-chain-type sulfonated poly(arylene ether ketone) with pendant sulfoalkyl groups for direct methanol fuel cells

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ABSTRACT

Novel side-chain-type sulfonated poly(arylene ether ketone) with pendant sulfoalkyl groups (SPAEK-xx) were synthesized by post-sulfonation method. Their structures were confirmed by FT-IR and NMR spectra. The all obtained membranes had excellent thermal stability and mechanical properties. The side-chain-type SPAEK films showed good dimensional stability, and their water uptake and swelling ratio were lower than those of the main-chain-type SPAEK with similar ion exchange capacity (IEC) value. It should be noted that the most highly sulfonated copolymer, SPAEK-100 (DS = 1.0) with IEC of 1.54 meq./g, showed proton conductivity of 0.083 S/cm and water swelling ratio of only 9.74% at 80 °C. Moreover, the methanol permeability of SPAEK-100 membrane was 3.95×10^{-7} cm^2/s, which was much lower than 23.80×10^{-7} cm^2/s of Nafion 117.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted much attention as alternative sources of electricity due to their low emission and high conversion efficiency [1–3]. As one of the key components of DMFCs, proton exchange membrane (PEM) functions as an electrolyte for transferring protons as well as providing a barrier to the gases or fuel cross-leaks between the electrodes. Perfluorosulfonic acid membranes, such as Nafion®, are the current state-of-the-art PEM materials, because of their excellent mechanical properties, chemical stability, and high proton conductivity [4,5]. However, their high cost, low operating temperature (dehydration and loss of proton conductivity >80 °C) and high methanol permeability hinder their applications in fuel cells. Hence, great efforts have been devoted to the development of alternative PEMs [6–9].

In recent years, many kinds of sulfonated derivatives, such as sulfonated poly(arylene ether ketone) (SPAEK), sulfonated poly(ether sulfone) (SPES), sulfonated polyimide (SPI), sulfonated polybenzimidazole (SPBI) and sulfonated poly(aryl ether) have been investigated as candidates for PEM materials [10–18]. Generally, these polymers show suitable conductivities only at high ion exchange capacities (IECs). However, high IEC usually leads to high water uptake and loss of mechanical properties. Kreuer et al. reported that these sulfonated polymers are unable to form defined hydrophilic domains, as the rigid polyaromatic backbone prevents continuous ionic clustering from occurring [19]. One promising way to provide more distinct phase separation between hydrophilic and hydrophobic domains as well as connectivity between hydrophilic domains is locating the sulfonic acid groups on side chains grafted onto the polymer main chain. Up to now, a variety of side-chain-type sulfonated polymers has been prepared by chemical grafting method or by post-sulfonation on the activated pendants of the corresponding parent polymers [20], including benzylsulfonated substituted poly(benzimidazole) [17], polysulfone with sulfonated aromatic side chains, sulfonated derivatives of poly(p-phenylene) [21]. Guiver synthesized novel comb-shaped sulfonated poly(arylene ether sulfone) derivatives with proton conductivity in the range of 0.063–0.125 S/cm [22]. Jannasch prepared side-chain-type sulfonated polysulfones via lithiation of polysulfone and anionic reaction with sulfobenzoic acid cyclic anhydride [23]. Compared to chemical grafting and post-sulfonation methods, direct copolymerization method allows close control of sulfonation content and the polymer structure. However, the process for the preparation of the monomer with pendant sulfonic acid groups is very complicated. Thus, very few reports have presented the side-chain-type sulfonated polymers prepared by direct copolymerization method. Miyatake and Yin synthesized some side-chain-type SPI with higher proton conductivity and better water stability than main-chain-type ones prepared from novel sulfonated diamine monomer by direct copolymerization [24,25]. Pang reported sulfonated poly(arylene ether ketone) with pendant sulfonic acid groups by direct copolymerization of sulfonated monomer with other nonsulfonated

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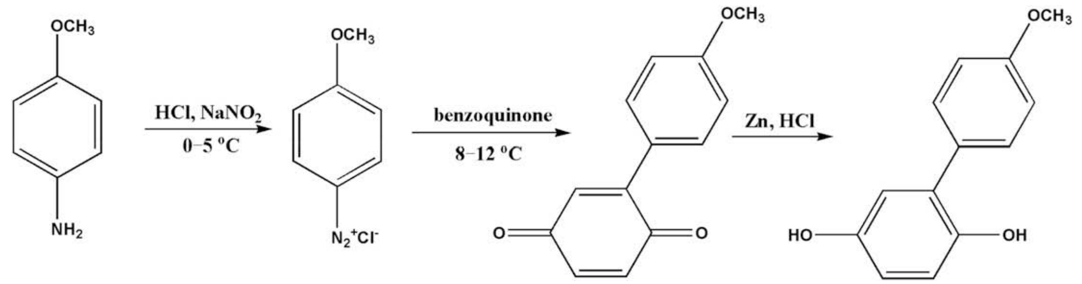


Scheme 1. Synthesis of Me-HQ monomer.

monomers, and they also suggested that sulfonated polymers showed lower water swelling and appropriate conductivity [26].

Herein, we report on a series of sulfonated poly(arylene ether ketone) copolymers with sulfonic acid groups on flexible aliphatic side chains by post-sulfonation method. Poly(arylene ether ketone) copolymers containing methoxy groups were first prepared, and then the methoxy groups were converted to reactive hydroxyl groups, similar to a procedure reported previously [27]. Subsequently, hydroxyl groups reacted with 1,4-butanesultone to obtain the sulfonated copolymers with pendant sulfonic acid groups. The flexibility of the side chain of the resulting copolymers allows for the aggregation of the sulfonic acid sites into channels, which conduct protons well. Then some important properties of these resulted copolymers were investigated.

2. Experimental

2.1. Materials

1,4-Butanesultone, (4-methoxy)aniline and 1,4-benzoquinone were purchased from Aldrich. 4,4′-difluorobenzophenone was purchased from Longjing Chemical Plant. 2,2′-Di(4-hydroxyphenyl)propane (DHP) was obtained from Shanghai Chemical Factory. Other solvents and reagents were obtained from Beingjing chemical company and used without further purified.

2.2. Monomer synthesis

2.2.1. Synthesis of (4-methoxy)phenylbenzoquinone (Me-BQ)

(4-methoxy)aniline (61.5 g, 0.5 mol), hydrochloric acid (169.5 mL, 11.8 M) and 200 mL water were added into a 1000 mL breaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer. Then, concentrated water solution (90 mL) of sodium nitrite (34.5 g, 0.5 mol) was added dropwise. The mixture was stirred at 0–5 °C for 2 h and a purple solution was obtained. The resulting solution was filtered and added dropwise into a mixture of 1,4-benzoquinone (43.2 g, 0.4 mol), sodium bicarbonate (168 g, 2 mol) and deionized water (200 mL). The reaction mixture was stirred at 8–10 °C for 2 h, and then at room temperature for another 2 h. The resulting mixture was filtered and the precipitate was washed with deionized water for several times. Then, the obtained red solid was dried at 60 °C in the vacuum oven for 24 h.

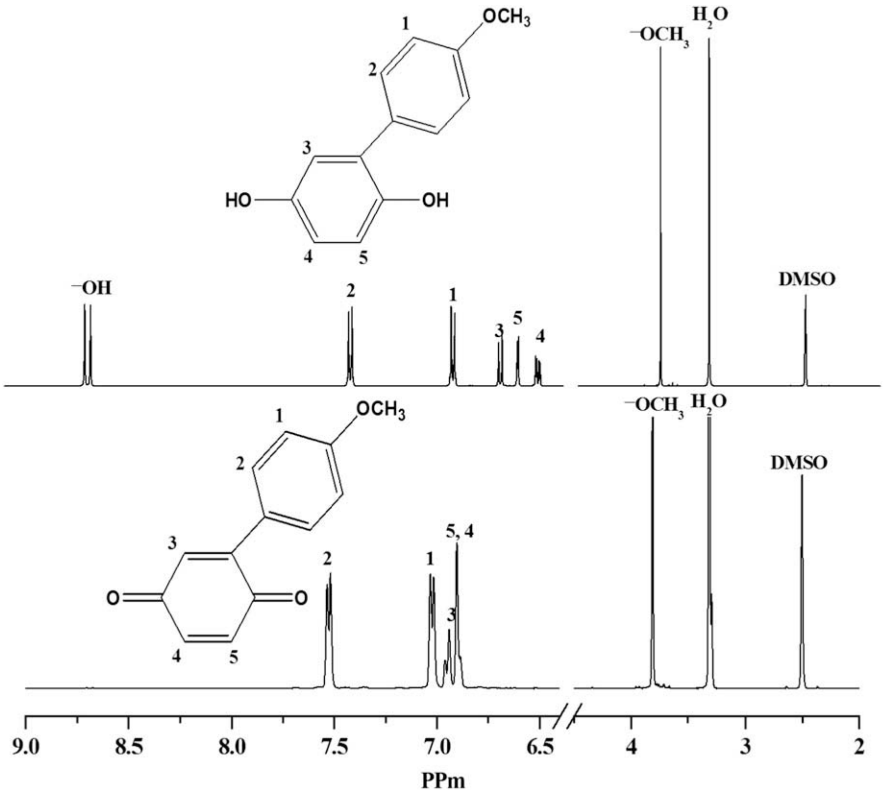


Fig. 1. ^{1}H NMR spectra of Me-BQ and Me-HQ monomer, respectively.

Yield: 90%. *M*p: 114–115 °C; *m*/*z*: 214. IR (KBr, cm^{-1}): 1651 (C=O), 2970 ($-OCH_3$). ^1H NMR (DMSO, δ, ppm): 7.54 (d, 2H), 7.02 (d, 2H), 6.94 (d, 1H), 6.89 (d, 2H), 3.81 (s, 3H).

2.2.2. *Synthesis of (4-methoxy)phenylhydroquinone (Me-HQ)*

(4-methoxy)phenylbenzoquinone (64 g, 0.3 mol), Zn power (58.9 g, 0.9 mol), and deionized water (550 mL) were added into a 1000 mL three-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. When the mixture was heated to 90 °C, 72 mL HCl (11.8 M) was added dropwise into the reaction flask. The mixture was refluxed for another 3 h. After the hot mixture was filtered, the obtained precipitate was recrystallized from toluene.

Yield: 62%. *M*p: 113–114 °C; *m*/*z*: 216. IR (KBr, cm^{-1}): 3385 (–OH), 2974 ($-OCH_3$). ^1H NMR (DMSO, δ, ppm): 8.73 (s, 1H), 8.70 (s, 1H), 7.44 (d, 2H), 6.94 (d, 2H), 6.71 (d, 1H), 6.62 (d, 1H), 6.51–6.53 (m, 1H), 3.77 (s, 3H).

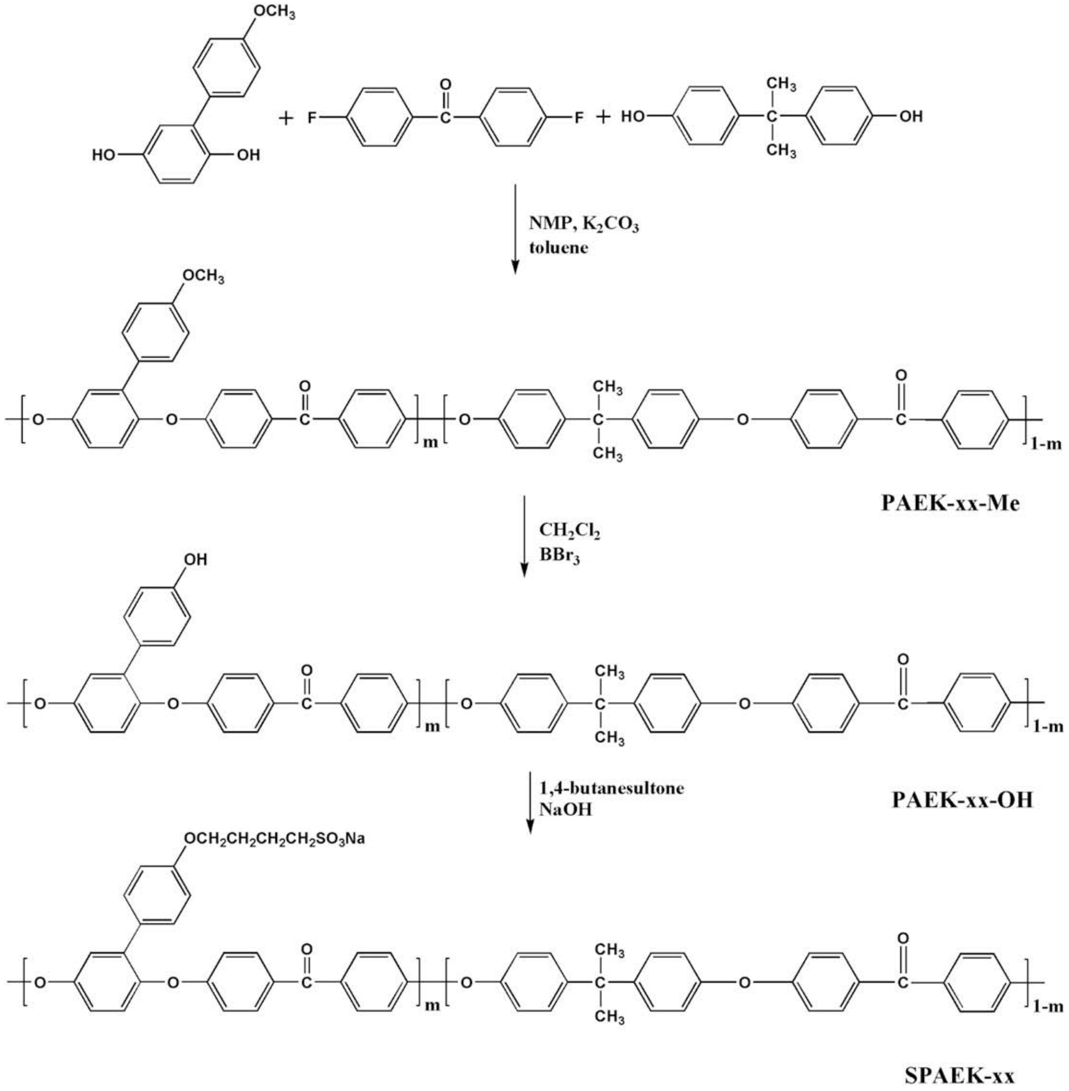
2.3. *Copolymer synthesis*

2.3.1. *Synthesis of poly(arylene ether ketone) containing methoxy group (PAEK-xx-Me)*

A typical synthetic procedure, illustrated by the preparation of PAEK-70-Me copolymer (xx: Me-HQ/DHP = 70/30), is described as follows. 3.024 g (14 mmol) Me-HQ, 1.368 g (6 mmol) DHP, 4.36 g (20 mmol) 4,4′-difluorobenzophenone and 3.036 g (22 mmol) K_2CO_3 were added into a 100 mL three-neck flask equipped with a magnetic stirrer, a Dean-Stark trap and a nitrogen inlet. Then, 25 mL NMP and 15 mL toluene were charged into the reaction flask under a nitrogen atmosphere. The reaction mixture was heated to 140 °C and maintained at this temperature for 2 h. After dehydration and removal of toluene, the reaction temperature was increased to 170 °C. When viscosity was observed to increase dramatically, the mixture was slowly poured into deionized water and stirred vigorously. The resulting fibrous copolymer was washed with hot methanol and deionized water several times, and dried at 100 °C under vacuum for 24 h.

2.3.2. *Conversion of methoxy (PAEK-xx-Me) to hydroxyl group (PAEK-xx-OH)*

1.0 g PAEK-70-Me was dissolved into 20 mL CH_2Cl_2 in a 100 mL three-neck flask equipped with a magnetic stirrer and a nitrogen inlet. The solution was cooled down to 0 °C (ice bath) and 1 mL BBr_3 dissolved in 10 mL CH_2Cl_2 was added dropwise. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. Then the copolymer was filtered and washed with methanol and deionized water. The resulting copolymer (PAEK-70-OH) was dried under vacuum at 100 °C for 24 h.



Scheme 2. Synthesis of side-chain-type SPAEK copolymers.

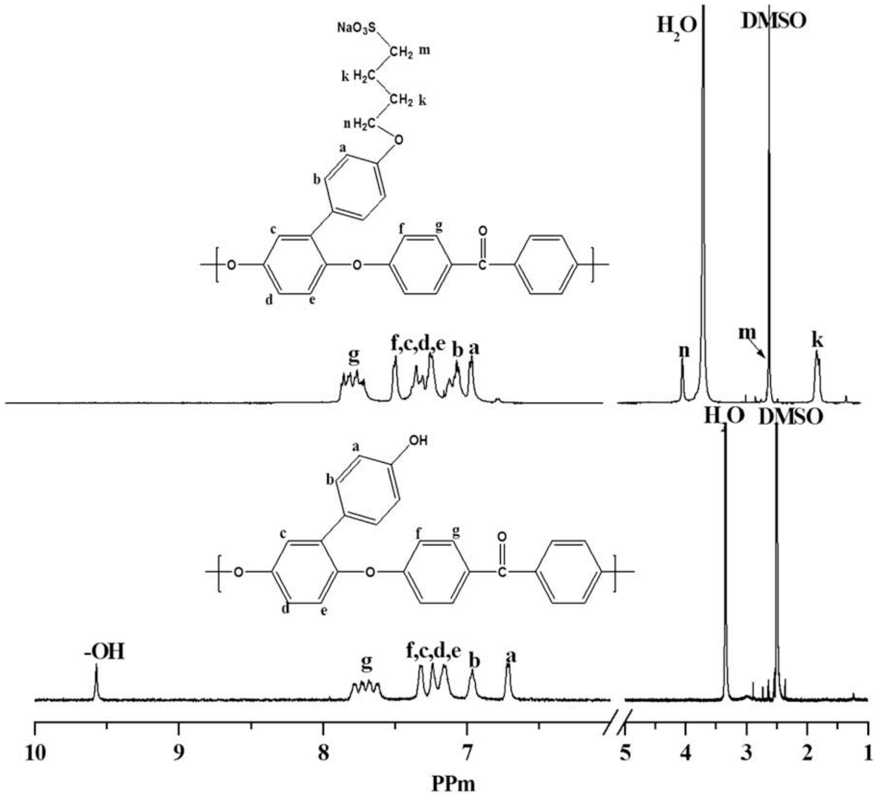


Fig. 2. ^{1}H NMR spectra of SPAEK-100 and PAEK-100-OH, respectively.

2.3.3. Preparation of sulfonated copolymer (SPAEK-xx)

1.0 g PAEK-70-OH was dissolved into 15 mL DMSO in a 100 mL three-neck flask equipped with a magnetic stirrer, condenser and a nitrogen inlet. Then 1 mL 1,4-butanesultone and 0.12 g NaOH were added into the flask. The mixture was heated to 100 °C and kept at this temperature for 6 h. The mixture was poured into 500 mL deionized water and washed with boiling water for several times. The resulting copolymers were dried under vacuum at 100 °C for 24 h.

2.4. Membrane preparation

The dried sulfonated copolymers were first dissolved in NMP to form 10–15% solutions and then filtered. The filtrates were casted onto glass substrates and dried in vacuum at 70 °C for 48 h. The membranes were immersed into 1.0 M HCl solution for 24 h and washed with deionized water to get H^+ form membranes. The thickness of the resulting membranes was in the range of 50–60 μm.

2.5. Copolymer characterization

2.5.1. Measurements

FT-IR measurements were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer. NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz) using deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. The thermogravimetric analyses (TGA) were carried out in nitrogen with a Pyris 1 TGA (Perkin Elmer). Before testing, all the copolymers were preheated to 150 °C and kept at this temperature for 10 min to remove any residual water or solvent. Then the copolymers were cooled to 100 °C and reheated to 700 °C with a heating rate of 10 °C min^{-1} under N_2 flow.

2.5.2. Degree of functionalization

The degree of functionalization of these copolymers can be estimated by their ^{1}H NMR. The signal at 9.57 ppm was characteristic resonances of the hydrogen atoms (H_h) of hydroxyl groups. The signals around 6.71 ppm were assigned to the hydrogen atoms (H_a) at the ortho position to the hydroxyl groups. After sulfonation, the new peak at 3.93 ppm was attributed to the hydrogen atoms (H_n) of aliphatic side chain connecting to SO_3Na. The degree of hydroxyl groups (DH) and sulfonation (DS) was calculated by the following equation, respectively:

$$\mathrm{DH} = \frac{2A_h}{A_{H_a}} \tag{1}$$

$$\mathrm{DS} = \frac{A_{H_n}}{A_{H_a}} \tag{2}$$

where A_h is the peak area of H_h, A_{H_a} and A_{H_n} correspond to the peak area of H_a and H_n, respectively.

2.5.3. Water uptake and swelling ratio

The membranes were dried at 120 °C for 24 h until constant weight was obtained. Then the films were immersed in deionized

Table 1
Degree of functionalization and mechanical properties of the copolymers.

Membranes	DH[a]	DS[b]	Tensile strength (MPa)	Elongation (%)	Tensile modulus (MPa)
SPAEK-70	97	81	58.07	13.26	1199.71
SPAEK-80	91	82	51.27	7.85	1275.27
SPAEK-90	95	80	47.23	6.09	1102.35
SPAEK-100	96	85	57.06	8.10	1576.23

[a] Denotes to the attachment efficiency (conversion from OCH_3 to OH).
[b] Denotes to the attachment efficiency (conversion from OH to the side chain).

water at desired temperatures for 24 h. The films were taken out, wiped with tissue quickly, and the weights or lengths of the wet membranes were measured. The water uptake (WU) was calculated by the following equation:

$$\mathrm{WU}(\%) = \frac{W_\mathrm{S} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\% \qquad (3)$$

where W_s and W_d are the weights of wet and dried samples, respectively. The swelling ratio was calculated from the change of film length as the following equation:

$$\text{Swelling ratio } (\%) = \frac{l_\mathrm{w} - l_\mathrm{d}}{l_\mathrm{d}} \times 100\% \qquad (4)$$

where l_w and l_d are the lengths of the wet membrane and dry membrane, respectively.

2.5.4. Ion exchange capacity

Ion exchange capacity (IEC) was determined by titration. Membrane samples in acid form were immersed in 1 M NaCl solution for 48 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). Then the H^+ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The IEC was calculated from the following formula:

$$\mathrm{IEC} = \frac{\text{Consumed NaOH(mL)} \times \text{molality NaOH}}{\text{weight of dry membrane}} (\text{meq./g}) \qquad (5)$$

2.5.5. Mechanical properties

The mechanical properties of the membranes were measured by SHIMADU AG-I 1KN at the test speed of 2 mm/min. The size of the films was 15 mm × 4 mm. For each measurement, at least three samples were used and their average value was calculated.

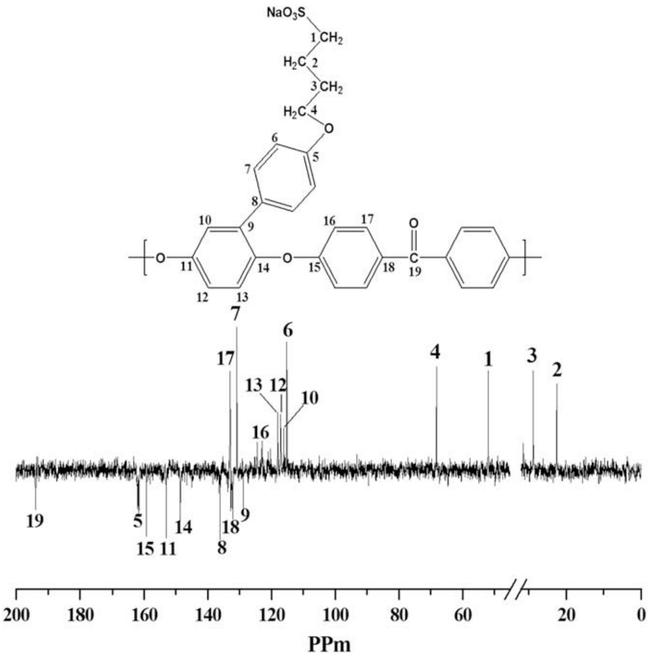


Fig. 4. ^{13}C NMR spectra of SPAEK-100.

2.5.6. Methanol permeability

Methanol permeability was measured using a liquid permeability cell with a solution containing 1.0 M methanol on one side and pure water on the other side described in the literature [11,28]. Magnetic stirrers were used in each compartment to ensure uniformity. Methanol concentrations in the water were determined by using a SHTMADU GC-8A chromatograph. The methanol permeability was calculated from:

$$C_\mathrm{B}(t) = \frac{A}{V_\mathrm{B}} \frac{\mathrm{DK}}{L} C_\mathrm{A}(t - t_0) \qquad (6)$$

where A and L are the membrane area and thickness, respectively. C_A and C_B are the methanol concentration in feed and in permeate, respectively. DK denotes the methanol permeability.

2.5.7. Proton conductivity

Proton conductivity was measured using ac impedance spectroscopy using Solatron-1260/1287 impedance analyzer, where the ac frequency range was scanned from 10 Hz to 1 MHz. Before the test, the films were soaked in deionized water for at least 24 h. The membranes were sandwiched between two pairs of gold-plate

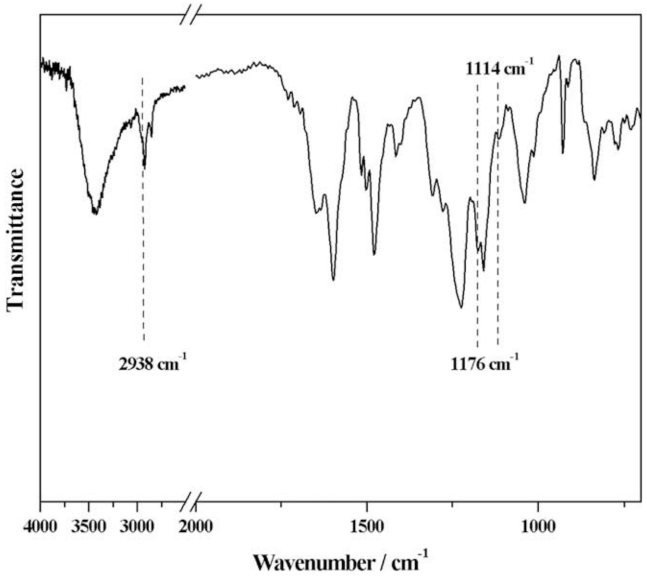


Fig. 3. FT-IR spectra of SPAEK-100 copolymer.

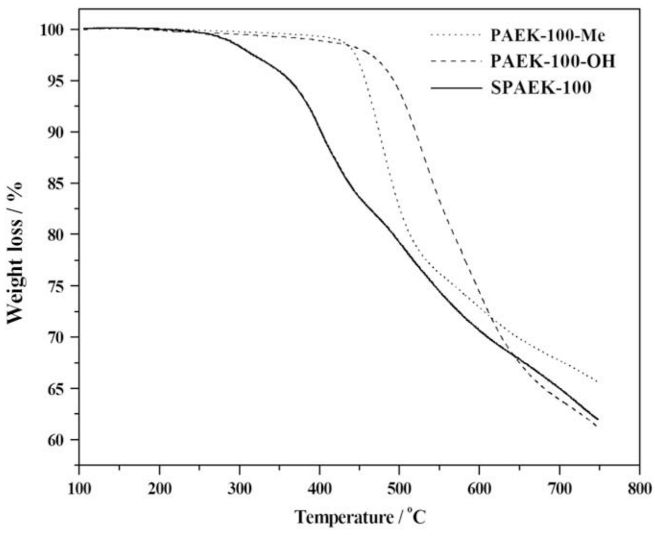


Fig. 5. TGA thermodiagram of the copolymers.

electrodes. Then the membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. The conductivity (σ) was calculated by the following equation:

$$\sigma = L/RS \tag{7}$$

where L is the distance between the two electrodes, R is the membrane resistance and S is the cross-sectional area of the membrane.

3. Results and discussion

3.1. Monomer synthesis

As shown in Scheme 1, the bisphenol monomer was synthesized in a three-step synthetic process which was similar to the method reported by Yue previously [29]. The structure of the bisphenol monomer was identified by mass spectrometry, FT-IR and ^{1}H NMR spectroscopies. In the FT-IR spectra, (4-methoxy)phenylbenzoquinone showed an absorption at around 1651 cm^{-1} attributed to the symmetric stretching vibration of carbonyl groups. After reduction, this characteristic absorption disappeared, and the characteristic band of hydroxyl group at around 3385 cm^{-1} was identified. Fig. 1 shows the ^{1}H NMR spectra of (4-methoxy)-phenylbenzoquinone and (4-methoxy)phenylhydroquinone, respectively. The signals at 8.70 and 8.73 ppm were assigned to the hydrogen atoms of hydroxyl group, which could not be observed in the spectra of the corresponding quinone. The peaks at around 3.81 ppm were assigned to the hydrogen atoms of methoxy group.

3.2. Preparation of poly(arylene ether ketone)s (PAEK-xx-ME, PAEK-xx-OH)

Poly(arylene ether ketone)s containing pendant methoxy groups (PAEK-xx-Me, xx: mole ratio (%) of Me-HQ) were synthesized by polycondensation using various feed ratios of Me-HQ/DHP, so that copolymers with different molar percentage of pendant methoxy group were obtained (Scheme 2). Because methoxy groups are reactive under high temperature using K_2CO_3, which was reported by Guiver [22], so the polymerization temperature was controlled below 170 °C in order to avoid the occurrence of crosslinkable reaction.

The conversion of the methoxy groups to reactive hydroxyl groups using BBr_3 was conducted in CH_2Cl_2. The PAEK-xx-Me copolymers were soluble in CH_2Cl_2. However, due to the polar nature of the hydroxyl groups, the PAEK-xx-OH copolymers were not soluble in CH_2Cl_2. Therefore, the PAEK-xx-Me were converted to PAEK-xx-OH copolymers and the resulting copolymers precipitated from CH_2Cl_2 solvent. Fig. 2 shows the ^{1}H NMR spectra of PAEK-100-OH copolymer. The peaks around 9.57 ppm corresponded to the hydrogen atom of hydroxyl group, and no peaks around 3.80 ppm were observed. The conversion efficiency (from OCH_3 to OH) was estimated by ^{1}H NMR spectra and the values were above 90% (Table 1).

3.3. Preparation of poly(arylene ether ketone) copolymers with pendant sulfonic acid group (SPAEK-xx)

To demonstrate the reactivity of the hydroxyl group as a grafting side on PAEK-xx-OH and prepare the sulfonated copolymer, PAEK-xx-OH was further reacted with 1,4-butane-sultone (Scheme 2). Fig. 3 shows the FT-IR spectra of SPAEK-100 copolymer. The typical absorption bands for aliphatic side chain ($-CH_2-$) were found around 2938 cm^{-1}. Furthermore, the bands around 1176 cm^{-1} and 1114 cm^{-1} were assigned to the stretching vibration of sulfonic acid groups. The ^{1}H NMR spectra of SPAEK-100 copolymer are also shown in Fig. 2. The peaks around 3.93 ppm (H_n) and 1.72 ppm (H_k) were assigned to the hydrogen atom of aliphatic side chain. According to the report previously, the peak of the hydrogen atom of aliphatic side chain connecting to sulfonic acid group was around 2.50 ppm [30]. Thus, H_m may be covered by the peak of solvent (DMSO) and it was not be observed in Fig. 2. However, ^{13}C NMR spectra of SPAEK-100 showed four signals in the 20–70 ppm region, which corresponded to the carbons of aliphatic side chain (Fig. 4), respectively. Thus, both FT-IR and NMR spectra indicated the SPAEK bearing aliphatic sulfonic acid groups were synthesized as desired. The conversion efficiency (from OH to side chain) was also estimated by their ^{1}H NMR spectra, and the degree of sulfonation (DS) is listed in Table 1.

3.4. Thermal stability and mechanical properties

The thermal stability of the copolymers was investigated by the thermogravimetric analysis (TGA). Fig. 5 shows the thermal stability of the copolymers. PAEK-100-Me and PAEK-100-OH all showed only one-step degradation pattern, which was observed around 430 °C and 450 °C, respectively. SPAEK-100 exhibited two-step degradation pattern. The first weight loss from 250 °C to 400 °C was closely associated with the thermal degradation of the sulfonic acid groups. The second degradation step was observed around 450 °C, which was attributed to the main-chain decomposition.

Table 2
IEC, water uptake, swelling ratio, methanol permeability and proton conductivity of the SPAEK membranes.

Samples	IEC[a] meq./g	IEC[b] meq./g	WU (%)		Swelling ratio (%)		DK (10^{-7} cm^2/s)	σ (S/cm)		Relative selectivity[c]
			25 °C	80 °C	25 °C	80 °C		25 °C	80 °C	
SPAEK-70	1.45	1.00	5.86	18.50	2.13	3.75	0.28	0.011	0.026	12.32
SPAEK-80	1.61	1.17	15.59	25.50	2.78	4.08	0.67	0.021	0.038	9.86
SPAEK-90	1.78	1.37	20.63	28.14	8.25	9.20	2.26	0.025	0.063	3.47
SPAEK-100	1.94	1.54	22.00	32.87	9.13	9.74	3.95	0.036	0.083	2.86
SPAEEKK-B90[d]	–	1.59	32.80	87.00	11.20	46.50	–	–	0.032	–
SPAEK-6F-50[e]	–	1.63	32.00	68.00	12.00	24.00	–	0.039	0.080	–
Nafion 117	–	0.92	18.33	27.92	10.58	17.22	23.80	0.076	0.146	1.00

[a] Measured by theoretical calculation.
[b] Determined by acid–base titration.
[c] Relative selectivity = membrane selectivity/Nafion 117 selectivity (selectivity = [proton conductivity]/[methanol permeability]) at 25 °C.
[d] Data adapted from Ref. [31].
[e] Data adapted from Ref. [32].

The mechanical properties of the SPAEK membranes are summarized in Table 1. The SPAEK membranes had tensile stress at maximum load of 47.23–58.07 MPa, tensile modulus of 1102.35–1576.23 MPa, and elongations at break of 6.09–13.26%. The results indicated the side-chain-type SPAEK membranes were tough enough for potential use as PEM materials.

3.5. IEC, water uptake and swelling ratio

IEC is usually defined as the moles of fixed SO_3 sites per gram of polymer, which plays a crucial role in deciding the water uptake and proton conductivity of the membranes. Table 2 lists the IEC values of the membranes ranged from 1.00 to 1.54 meq./g. As expected, IEC values of the side-chain-type copolymer increased with the increasing of DS which was controlled by varying the mole ratio (%) of Me-HQ.

The water uptake and swelling ratio of the membranes are very important to determine their proton conductivity and mechanical properties. Fig. 6 shows the temperature dependence of water uptake values. As expected, water uptake increased with increasing both temperature and IEC. On the whole, the side-chain-type SPAEK membranes showed moderate water uptake and a much lower swelling ratio (Table 2) than other main-chain-type SPAEK with similar IEC values, which was attributed to their different molecule structure. In general, main-chain-type highly sulfonated PAEK membranes characteristically start to excessively swell in water at a certain temperature, which results in the disintegration of the membranes. Compared to main-chain-type SPAEKs, side-chain-type SPAEKs contained short flexible side chains which separate hydrophilic sulfonic acid groups from hydrophobic polymer main chain. Therefore, water molecules can be restricted to hydrophilic domains in the membrane and separated from hydrophobic domains which may suppress the water swelling [19,33].

3.6. Proton conductivity and methanol permeability

Proton conductivities of all the hydrated membranes were measured in the temperature range of 25–80 °C. In general, the conductivity above 10^{-2} S/cm is required for proton exchange membrane materials in fuel cells. From Fig. 7, it can be seen that all the obtained membranes showed conductivities above 10^{-2} S/cm at 25 °C and their conductivities increased with increasing temperature and IEC values. SPAEK-100 with the highest IEC value (1.54 meq./g) showed proton conductivity of 0.083 S/cm at 80 °C, which was lower than Nafion 117 (0.146 S/cm). This was probably due to the unique ion-rich channels in Nafion membrane, which allow the ions to transport more easily. Furthermore, perfluorosulfonic acid is highly acidic, which also leads to higher conductivity for Nafion. As compared to other main-chain-type SPAEKs, these side-chain-type SPAEKs with similar IEC values showed much lower water uptake but similar or higher proton conductivity (as compared SPAEK-100 with SPAEEKK-B90 and SPAEK-6F-50) (Table 2). Considering these sulfonated copolymers possessed similar main-chain structure and IEC value, we think the difference of their conductivity may result from the position of sulfonic acid groups in the polymers. Sulfonic acid groups on the flexible aliphatic side chain of the polymers could decrease the limitation of main-chain rigidity on the mobility of sulfonic acid groups, making ionic network more readily and thus enhancing proton conductivity [34].

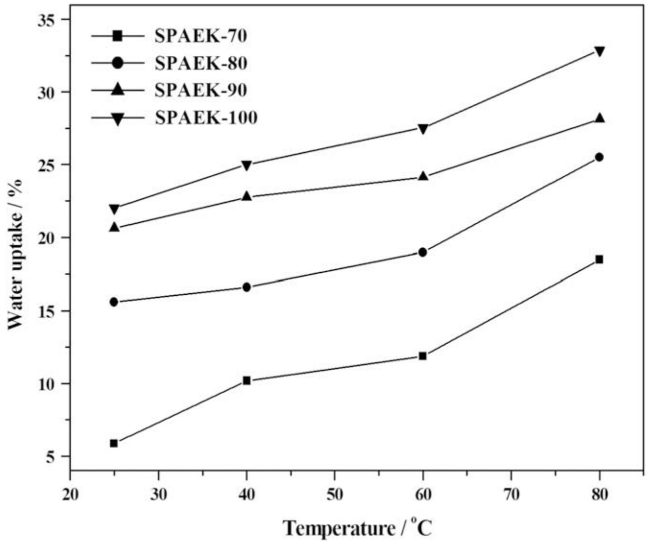


Fig. 6. Water uptake of SPAEK membranes dependence on temperature.

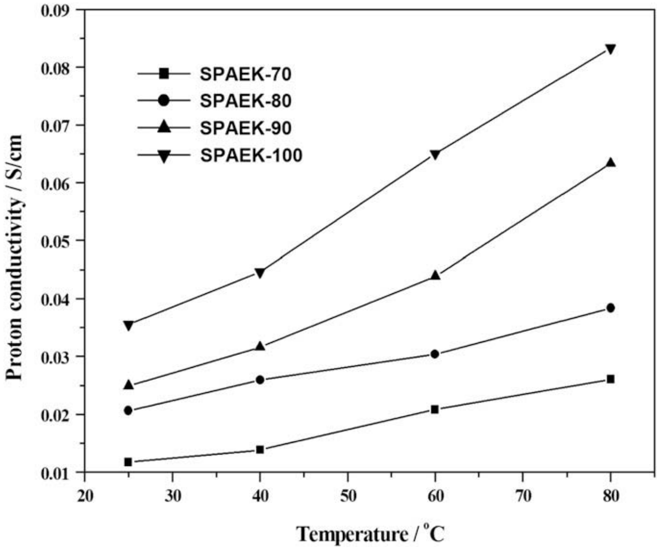


Fig. 7. Proton conductivity of SPAEK membranes at different temperatures under fully hydrated conditions.

Table 2 lists the methanol transport behavior of the side-chain-type SPAEK membranes. The methanol permeability increased with increasing IEC values and water uptake. This indicated the methanol transport across the membranes was strongly dependent on the water uptake content, and the methanol permeates through the membranes in complex forms such as $CH_3OH_2^+$. Due to their low water uptake, SPAEK membranes showed methanol permeability in range from 2.8×10^{-8} to 3.95×10^{-7} cm^2/s, which were much lower than Nafion 117 (2.38×10^{-6} cm^2/s). Although SPAEK-90 and SPAEK-100 have lower proton conductivity than Nafion 117, it was sufficient to achieve improved DMFC performance through its low methanol permeability. The selectivity, which is the ratio of the proton conductivity to the methanol permeability, is often used to evaluate the potential performance of DMFC membranes. The relative selectivity of the resulting SPAEK membranes was higher than that of Nafion 117 as listed in Table 2.

4. Conclusions

A series of novel sulfonated poly(arylene ether ketone) copolymers containing sulfonic acid groups on aliphatic side chains has been prepared as proton conductive materials. The resulting membranes exhibited low water uptake, low swelling ratio as well as appropriate conductivity. SPAEK-100 film, with the highest IEC among the obtained copolymers, showed proton conductivity of 0.083 S/cm and only 9.74% swelling ratio at 80 °C. While, the methanol permeability of SPAEK-100 membrane was 3.95×10^{-7} cm^2/s, which was several times lower than that of Nafion 117. Combined with its good thermal stability and high mechanical properties, it shows potential application as a PEM material in fuel cells.

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