Fabrication and properties of cross-linked sulfonated fluorene-containing poly(arylene ether ketone) for proton exchange membrane

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Abstract

The cross-linkable sulfonated ploy(arylene ether)s derived from 3,3′-diallyl-4,4′-dihydroxybiphenyl, 9,9′-bis(3,5-dimethyl-4-hydroxypheyl) fluorene (DMHPF), 4,4′-difluorobenzophenone (DFBP) and sulfonated 4,4′-diflourobenzophenone (SDFBP) were synthesized over a wide range of DFBP/SDFBP molar ratios. The resulting sulfonated poly(arylene ether)s with high inherent viscosity (0.87–1.46 $dl\,g^{-1}$) are soluble in polar organic solvents and can form flexible and transparent membranes by casting from their solution. The cross-linking reaction was carried out using a thermal activated radical cross-linking agent (TARC) at 100 °C. The comprehensive properties of the virgin and the cross-linked membranes were characterized and compared accordingly. The results showed that the cross-linked membranes had better mechanical, oxidative and dimensional stabilities together with high proton conductivity (5.41×10^{-2} $S\,cm^{-1}$) at 80 °C under 100% relative humidity when compared with previously synthesized and similar membranes. These improvements were raised from the cross-linking structure and the fabrication procedure of the membranes.
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1. Introduction

Proton exchange membrane fuel cells (PEMFC) have received widely investigated as a promising new power source for vehicles and portable devices, due to their low emissions and high conversion efficiency [1–3]. Proton exchange membrane (PEM), as proton conductive material, is a key component of the PEM fuel cells for transferring protons from the anode to cathode as well as providing a barrier to the fuel cross-leaks between the electrodes. For a fuel cell to work effectively and to be widely adapted, the PEM must have a portfolio of properties including acceptable costs, high proton conductivity, good chemical and thermal stability, good mechanical strength, and low fuel crossover [4].

As the gold standard PEM material, Nafion has many desirable properties such as good chemical and thermal stability, high proton conductivity under conditions of high water availability and reasonable mechanical properties. However, Nafion has several shortcomings that limit its utility and performance such as the high cost, low conductivity at low humidity or high temperature and high methanol permeability [5]. The need for the alternatives of the copolymers containing perfluorosulfonic acid groups has led to the development of a number of aromatic sulfonated polymers as membrane candidates [6–15]. Poly(ary ether)s (PAE)s are high performance polymers that possess good mechanical properties and excellent thermal, oxidative, and chemical stability, and therefore they have been extensively studied as a base for new ionomeric materials. Much effort has devoted to develop sulfonated PAEs (SPAEs) by direct polymerization, of which the sulfonic acid groups are attached onto the deactivated aromatic rings [16–18]. These sulfonated aromatic polymer membranes require a high sulfonation level to achieve sufficient proton conductivity. Unfortunately, for linear polymers, such a high sulfonation level makes them excessively water-swollen or soluble in water. In this case, highly sulfonated polymer membranes lose their mechanical properties and become unavailable in PEMFC applications.

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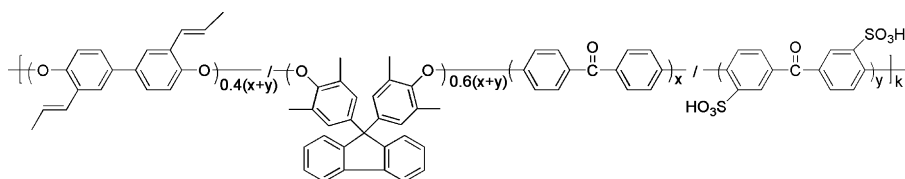
Scheme 1. The structure of sulfonated fluorene-containing poly(arylene ether ketone).

To achieve high proton conductivity without the challenges associated with linear polymers, chemically cross-linkable ionomeric systems were proposed with few systems studied. Important cross-linking methods included electron beam [19] or γ-irradiation [20–22] of preformed membranes and cross-linking through inter/intra chain bridging links [23–25] through the sulfonic acid groups. However, irradiation cross-linking can result in PEMs with no uniform properties, and the consumption of sulfonic acid groups results in a decrease in ion content of the membrane, which will result in lower proton conductivity.

In the previous work [18], we have had synthesized the sulfonated poly(fluorenyl ether ketone)s base on the monomer 9,9-bis(4-hydroxyphenyl)fluorene, sulfonated 4,4′-diflourobenzophenone and the 4,4′-difluorobenzophenone. The highest proton conductivity reached 4.43×10^{-2} S cm^{-1}, while the proton conductivity of the Nafion 117 was 4.18×10^{-2} S cm^{-1} under the same conditions at 20 °C 100% relative humidity. Unfortunately, some membranes of these SPAEs were strongly swelled or soluble in the water higher than 60 °C. In this work, we present a cross-linkable sulfonated fluorene-containing poly(arylene ether ketone) with unsaturated propenyl group. The propenyl groups can be cross-linked using usual thermal activated radical cross-linking agent without consumption of sulfonic acid groups, giving a PEM with excellent proton conductivity, long durability and high dimensional stability (Scheme 1).

2. Experimental

2.1. Materials

Fluorenone, 2,6–dimethylphenol, betamercaptopropionic acid, 4, 4′-difluorobenzophenone (DFBP), 4,4′-dihydrodphenyl and allylbromid were purchased from Aldrich Chemical Co. and used as received. Benzoyl peroxide (BPO) (AR) was provided by Guangzhou Chemical Co. China and was recrystallized twice from the mixture of CHCl$_3$/CH$_3$OH. Sulfonated 4,4′-difluorobenzophenone 5 (SDFBP) were synthesized as outlined in reference [26], Reagent-grade N,N'-dimethylacetamide (DMAc), toluene, methanol, anhydrous potassium carbonate were obtained from commercial sources used without further purification. DMAc was dried over 4 Å molecule sieves and toluene was dried over sodium wire prior to use.

2.2. Instrumentation

The ^{1}H NMR spectra were recorded on a Bruker NMR instrument (model DRX 400 MHz); chemical shifts were given in ppm against tetramethylsilane as an internal standard. Elemental analyses were performed on an Elemetar elemental analyzer (model Varios EL). Melting points were taken on a XT4A melting point apparatus. Inherent viscosity was determined for a solution of 0.5 g dl^{-1} in DMAc at 30 °C with a calibrated Ubbelonhde viscometer. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 Fourier transform spectrometer using film sample.

2.3. Membrane characterization

2.3.1. Ion exchange capacity (IEC)

The IEC of the membranes were determined by titration according to the literature [15]. A dry weight of 0.5–1.0 g of the polymer membrane in the acid form was immersed into saturated NaCl solution to replace the protons of sulfonic acid groups with sodium ions. The replaced protons were titrated using 0.1 M NaOH solution, with phenolphthalein as indicator. The moles of the proton are equal to the moles of sulfonic group and the IEC was calculated from the titration data using following Eq. (1):

$$ICE = \frac{\Delta V_{NaOH} C_{NaOH}}{W_s} (mol\ g^{-1}) \tag{1}$$

where ΔV_{NaOH} is the consumed volume of NaOH solution, C_{NaOH} the concentration of NaOH solution, and W_s is the weight of the membrane sample.

2.3.2. Water uptake and swelling ratio [18,27]

The membrane was dried under vacuum at 80 °C for 24 h. The weighed membrane was immersed in deionized water at 80 °C for 24 h. Wet membrane was weighed quickly upon wiping up its surface water with tissue paper. The water uptake of membrane was calculated according to the following Eq. (2):

$$water\ uptake\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{2}$$

where W_{wet} and W_{dry} are wet and dry the weights of the membrane, respectively.

The dimensional stability of the membrane was characterized by the swelling ratio. The swelling ratio was calculated from the following Eq. (3):

$$swelling\ ratio = \frac{L_w - L_d}{L_d} \tag{3}$$

where L_w and L_d are the lengths of the cross of the wet membrane and dry membrane (test area 1 cm × 2 cm), respectively.

2.3.3. Proton conductivity

Proton conductivity measurement was performed on fully hydrated film samples at temperature 30 °C at 100% relative humidity with a Solartron 1255B frequency response analyzer at an oscillating voltage of 10 mV, using a two probe method at frequency ranging from 1 MHz to 5 KHz. The cell assembly was similar to that used in the literatures [28,29]. The proton conductivity (σ) of the specimen in the transverse direction (across the membrane) was calculated from the impedance data according to following Eq. (4):

$$\sigma = \frac{d}{RS} \tag{4}$$

where d and S are the thickness and the face area of the specimen, respectively, and R is derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re (Z') axis.

2.3.4. Oxidative and hydrolytical stability

Oxidative stabilities were determined using Fenton's reagent (3 wt.% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C. The membranes were immersed in Erlenmeyer flask containing Fenton's reagent. The flask was shaken vigorously once every 10 min until the membrane began to break. The hydrolytic stability was also investigated by treating membrane samples in boiling water for more than 100 h.

2.3.5. Thermal stability

The thermal stability of the sulfonated PAEs was determined with a Seiko SSC-5200 thermal gravimetric analyzer under a nitrogen atmosphere (200 ml min^{-1}) at temperature range of 70–600 °C. The heating rate was 20 °C min^{-1}. Specimens were heated to 150 °C and held at this temperature for 20 min to remove absorbed moisture. They were then cooled to 70 °C and heated again to 600 °C at 20 °C min^{-1}.

2.3.6. Mechanical properties

The tensile properties were determined at 25 °C and 50% relative humidity by SANS (Shenzhen, China) electromechanical universal test machine (model CMT-4014). The samples were cut into a size of 5 mm × 50 mm. The cross-head speed was set at a constant speed of 10 mm min^{-1}. For each testing reported, at least three measurements were taken and average value was calculated.

2.3.7. Gel content

The gel content of the cross-linked samples was determined according to ASTM D2765 method using a Soxhlet extractor, DMAc was used as solvent. Samples were refluxed in DMAc for at least 48 h, until the sample attained a constant weight. The residue after extraction was taken as the gel component, and the gel content was calculated according to the following equation.

$$\text{Gel content (\%)} = \frac{W_2}{W_1} \times 100 \tag{5}$$

where W_1 and W_2 are the weights of the samples before and after refluxed in DMAc for 48 h.
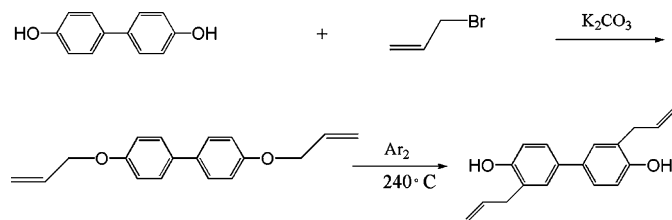
Scheme 2. Synthesis of 3,3′-diallyl-4,4′-dihydroxybiphenyl (monomer **2**).

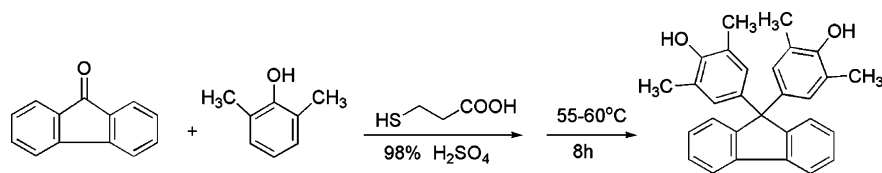### 2.3.8. Preparation of 3,3′-diallyl-4,4′-dihydroxybiphenyl 2 [30]

To a 50 ml three-necked round-bottom flask equipped with a Dean-stark trap, a condenser, nitrogen inlet/outlet and a magnetic stirrer, 4,4′-dihydrodphenyl (9.31 g, 50 mmol), anhydrous K_2CO_3 (7.60 g, 55 mmol), DMAc (20 ml), and toluene (20 ml) were charged. The reaction is depicted as in Scheme 2. Nitrogen was purged through the reaction mixture with stirring for 15 min, and then the mixture was heated to 150 °C and kept at this temperature for 3 h. After the produced water was azeotroped off with toluene, the temperature was cooled to 110 °C and the Dean-stark trap was removed. A 14.52g Allyl-bromide (120 mmol) was added to the reaction mixtures. After 8 h, water was added and the crystalline powders were collected, washed for several times with boiling 95% ethanol, finally filtered and dried in oven to give **1** (mp 154 °C, yield 92%). Following the Claisen rearrangement procedure, the compound **1** was kept at 240 °C under argon for 30 min, upon cooling to room temperature, the precipitates were filtered off and recrystallized in boiling heptane to obtain **2** (yield 76%); mp: 82–83 °C.

^{1}H NMR (400 MHz, CDCl$_3$)δ:(ppm) 3.45 (d, 4H), 4.99 (s, 2H), 5.13–5.25 (m, 4H), 5.97–6.14 (m, 2H), 6.87 (d, 2H), 7.27–7.30 (q, 2H), 7.30–7.31(d, 2H). Elem. Anal. For (C$_{18}$H$_{18}$O$_2$) (266.33): Calcd C, 81.17%; H, 6.81%; Found C, 80.94%, H, 6.84%.

2.3.9. Preparation of 9,9′-Bis(3,5-dimethyl-4-hydroxyphenyl)fluorene (DMHPE)

DMHPF was synthesized in-house from fluorenone and 2,6-dimethlyphenol according to a modified method appeared in the literature [31] (Scheme 3). To a 500 ml four-necked flask equipped with a mechanic stirrer, a condenser, a nitrogen inlet/outlet and a thermometer was charged 45 g (0.25 mol) of fluorenone, 122 g (1 mol) of 2,6-dimethylphenol, 60 ml of toluene, 0.2 ml of beta-merapto propionic acid. The temperature was set at 30 °C for 30 min. Then 8 ml of 95–98% sulfuric acid was added drop wise to assure the temperature was below 50 °C. After the addition, the temperature was raised to 55 °C and kept at 55–60 °C. The resulting product precipitated out of the reaction mixture during the reaction. After 8 h, the reaction mixture was cooled to room temperature and then was poured into excess amount of deionized water (500 ml). The precipitates were filtered, washed with water and dried. The crude product was crystallized from toluene twice to give DMHPE (mp = 290–292 °C).Yield: 67%. 1H NMR(400 MHz, CDCl$_3$, ppm): 2.11(s, 12H), 6.78(s, 4H), 7.24(t, 2H), 7.32(t, 2H), 7.38(d,

Scheme 3. Synthesis of DMHPE.

2H), 7.73(d, 2H). Elem. Anal. for $C_{29}H_{26}O_2$, 406.52: Calcd.: C, 85.71%, H, 6.40%. Found: C, 85.42%, H, 6.27%.

2.3.10. Synthesis of spaes 6a–f

The typical procedure for the synthesis of SPAEs **6a–f** is as follows (Scheme 4): to a 25 ml three-neck flask equipped with a Dean-Stark trap, an nitrogen inlet/outlet, a condenser, and a magnetic stirrer was added previously synthesized monomer **2** 3,3′-diallyl-4,4′-dihydroxybiphenyl (0.213 g, 0.8 mmol), monomer **3** DMHPE (0.488 g, 1.2 mmol), the mixture of monomer **4** (4,4′-difluorobenzophenone) and monomer **5** (sulfonated 4,4′-diflourobenzophenone) (2 mmol), the sulfonation degree (SD), which is the number of sulfonated groups per repeating unit was controlled by adjusting the ratio of monomer **4** to monomer **5** as 4/1, 3/2, 1/1, 2/3, 1/4, 0, respectively, anhydrous potassium carbonate (3.50 g, 2.5 mmol), 8 ml of DMAc and 9 ml of toluene. The mixture was refluxed for 3 h at 140 °C to azeotrope off the formed water with toluene. After distilling off the excess toluene, the temperature was slowly raised to 165 °C and maintained at this temperature for 15 h. Before cooling down the reaction mixture 5 ml DMAc was added to dilute the reaction solution. The result viscous polymer solution was poured into the mixture of methanol/water (l:1, v/v) to precipitate out the polymer. The precipitates were filtered off and washed with water. The recovered polymers were dried at 110 °C under vacuum for 24 h.

2.3.11. Preparation of membranes

The SPAEs **6a–f** in sodium salt form were transformed to proton form by the process as follows: the 10 wt.% DMAc solutions of the 1 g SPAEs **6a–f** were added to the 50 ml 2 M H_2SO_4 solution and maintained at 50 °C for 10 h. The fibrous polymers were filtered off and washed with water. The proton form SPAEs were immersed in the water that

was changed several times for 24 h to remove H_2SO_4 residual.

Membranes of the SPAEs **6a–f** (proton form) were prepared by casting their 10% solutions in DMAc on a glass plate and dried at 60 °C for 12 h and then at 80 °C under vacuum for 2 d. Membranes of cross-linked polymers **6a^c–f^c** (proton form) were prepared by casting 30% DMAc solutions of the virgin SPAEs **6a–f** on a glass plate with 5% BPO of the SPAEs, then annealing at 100 °C under nitrogen protection for 3 h [32]. Finally BPO resisual in the cross-linked membranes was removed by immersing the membranes in ethanol.

3. Results and discussion

3.1. Synthesis of SPAEs 6a-f

The SPAEs **6a–f** with different sulfonation degree were prepared from aromatic nucleophilic polycondensation of **2** (0.8 mmol) and **3** (1.2 mmol) with various contents of DFBP **4** and SDFBP **5** (Scheme 4). In this work, **DMHPE** was selected as the monomer but 9,9-bis(4-hydroxyphenyl)fluorene. This is because the electron donor methyl groups on **DMHPE** make the hydroxyl groups more reactive, therefore, the polycondensation can be preceded at the temperature of below 170 °C. At this temperature, the unsaturated propenyl groups can be free from cross-linking. The resulting polymers were all soluble in polar organic solvents, such as DMSO, DMF, DMAc and NMP. The cross-linking density can then be readily controlled by adjusting the ratio of monomer **2** to monomer **3**, while the sulfonation degree can be altered by changing the ratio of monomer **4** to monomer **5**. In this sense, the desired properties such as the proton conductivity, the water uptake and the mechanical strength of the synthesized SPAE **6** can be achieved accordingly. The
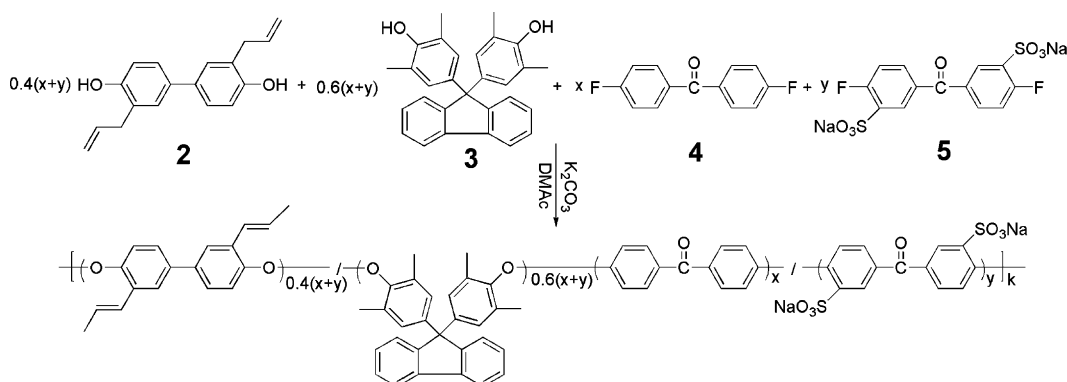
Scheme 4. Synthesis of SPAEs.

Table 1
The polymerization results of SPAEs **6a–6f**

Polymer	Monomer 4 mmol	Monomer 5 mmol	$[\eta]^a$ dl g^{-1}	Yield %	IEC[b] ($\times 10^{-3}$ mol g^{-1})	IEC[c] ($\times 10^{-3}$ mol g^{-1})
6a	1.6	0.4	1.53	98	0.66	0.61
6b	1.2	0.8	1.87	97	1.24	1.18
6c	1.0	1.0	1.48	93	1.51	1.46
6d	0.8	1.2	1.39	96	1.76	1.68
6e	0.4	1.6	1.26	94	2.22	2.19
6f	0	2.0	1.51	95	2.64	2.57
Nafion 117	–		–	–	0.91[d]	0.83

  [a] Tested in 0.5 g dl^{-1} solution in DMAc at 30 °C.
  [b] Calculated IEC of the PAEs.
  [c] Measured IEC of the PAEs.
  [d] Ref. [33].

polymerization results of SPAEs **6a–f** are listed in Table 1.The inherent viscosity of the synthesized polymers ranged from 1.26 to 1.87 dl g^{-1}, demonstrating very high molecular weight of the resulted polymers in high yield of ≥93%. The IEC of the sulfonated SPAEs determined by titrating was in good agreement with the expected values within the experimental deviation. This implies that the pendant sulfonic acid groups were quantitatively attached onto the polymer chains. The ^{1}H NMR spectrum of SPAE **6b** is shown in Fig. 1, with all the peaks assigned to the molecular structure shown in the figure. The integration ratios of these peaks are well in accordance with the proposed molar ratios of each component (the feed molar ratio of monomers) of the copolymer. Moreover, we can find that ally group of 3,3′-diallyl-4,4′-dihydroxybiphenyl was rearranged into propenyl group by comparing ^{1}H NMR data of bisphenol **2** with those in Fig. 1. This is because that the potassium carbonate in the reaction mixture acted as the base-catalysis of isomerization of allyl group to propenyl group [36,37]. The rearrangement arise from the stable product nature. Finally, the resulted double bond containing sPAEs can be easily thermally cross-linked.

3.2. Preparation of the membranes

The sodium salt form SPAEs can be transformed to the proton form completely by this method. Because of the good soluble nature of the polymers in sodium salt form, water can easily move into the polymer domains and N$_a^+$ ions can be easily exchanged by H$^+$ ions.

The BPO initiator initiated the propenyl groups to cross-link at about 100 °C. At this temperature, DMAc vaporized at a moderate rate and highly quality cross-linked membranes can be obtained. By this process, tough and transparent membranes with thickness in the range of 100–130 μ were easily fabricated, such as the **6e^c** showed in Fig. 2. All the cross-linked membranes were tested to be insoluble in polar organic solvents, and the gel contents of the cross-linked **6a^c–e^c** are listed in Table 2. The FTIR spectra of the virgin SPAEs **6d** and the cross-linked SPAEs **6d^c** are showed in Fig. 3. The bands at 1650 cm^{-1}, 970 cm^{-1} and 680 cm^{-1} represent the characteristics of C=C stretch, the conjugated =C–H out-of –plane deformations for the trans (970 cm^{-1}) and *cis* (680 cm^{-1}) alkene of the propenyl groups. The intensity
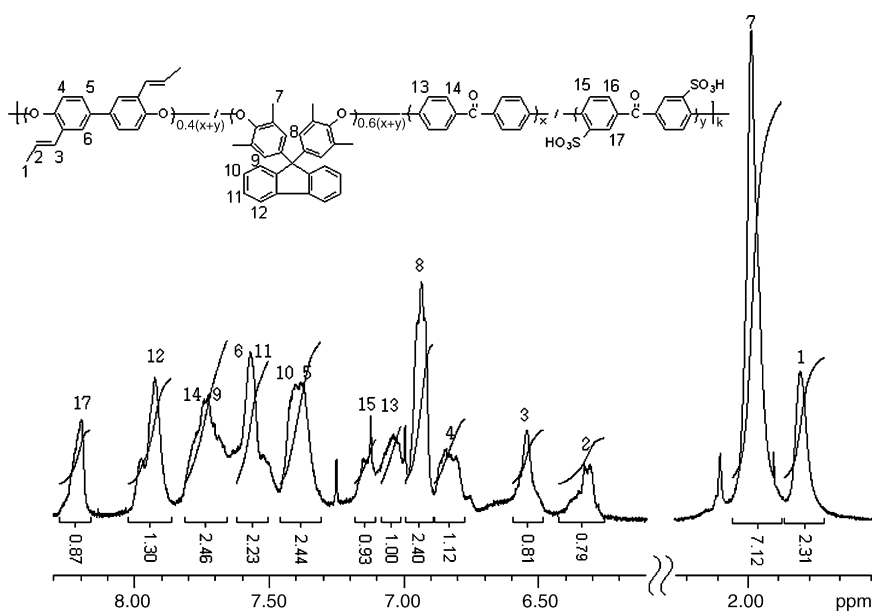

Fig. 1. ^{1}H NMR spectrum of polymer **6b**.

Table 2
The properties for the virgin polymers and the cross-linked polymers

Sample	Mechanical property		Water uptake (%)	Swelling ratio (%)	Oxidative stability (h:min)	Proton conductivity ($\times 10^{-2}$ S cm^{-1})		Gel content (wt.%)
	Tensile strength (Mpa)	Elongation at break (%)				30 °C	80 °C	
6a	68.46	50.25	5.2	2.6	3:40	0.26	0.41	–
6b	70.31	33.74	12.6	6.8	2:10	0.85	1.10	–
6c	65.72	46.21	30.1	16.2	1:50	1.52	2.38	–
6d	59.89	28.56	56.2	28.3	1:00	2.84	4.06	–
6e	46.13	22.19	87.3	38.9	0:40	3.46	4.53	–
6f	42.56	23.82	128.6	62.4	0:30	4.27	6.32	
6a[a]	97.47	12.78	3.1	1.8	5:50	0.12	0.16	98
6b[a]	89.56	8.61	6.8	4.8	4:40	0.67	1.02	96
6c[a]	84.39	11.36	18.9	6.2	4:30	1.32	2.18	94
6d[a]	74.22	9.53	38.5	12.1	3:20	2.29	3.24	91
6e[a]	72.83	6.85	49.8	31.6	2:10	3.16	4.08	91
6f[a]	64.72	5.76	68.3	42.1	1:20	3.69	5.41	84
Nafion 117	24.82	180.8	42.3	23.6	[b]	3.48	5.26	–

[a] The crossed-SPAEs.
[b] After 10 h, it is undegrdable.

of these bands decreased obviously after cross-linking, indicating that the propenyl groups of the virgin polymers had been cross-linked. Moreover the gel content decreased with increasing the sulfonation degree of these SPAEs. This implies that the sulfonated groups influenced on the cross-linking reaction. Presumably, this resulted from the less solubility of BPO in the polymer solution and the moving ability of the segments of the SPAEs decreased with the increasing sulfonation degree.

3.3. Mechanical properties

The mechanical properties of the membranes **6a–f** and **6a^c–f^c** are summarized in Table 2. The tensile strengths of the virgin SPAEs **6a–f** were lower than those of the cross-linked ones **6a^c–f^c**, while the elongations at break of the original SPAEs were greater than those of the cross-linked polymers. This is due to that the cross-linkages within the polymer can reinforce the tensile strength but decrease the toughness of the polymer. Concerning the inherent viscosity (molecular weight), both tensile strength and the elongation at the break decreased with increasing sulfonic acid group content. This is because the presence of sulfonic acid groups on the backbone can decrease the covalent nature while increase the ionic nature of the sulfonated polymer. The IEC and the proton conductivity increased with increasing the sulfonation degree, while the mechanical properties decreased with increasing the sulfonation degree. It can also be seen that the tensile strength in dry state of the membranes can be enhanced greatly upon the cross-linking. It is believed that the wet strength of these membranes should be much higher than that of the virgin polymers. Moreover, these phenomena demonstrated that the cross-linking reaction had taken place. The tensile strengths of these SPAEs were higher than that of Nafion 117, but the elongation at the break was smaller than that of Nafion 117.
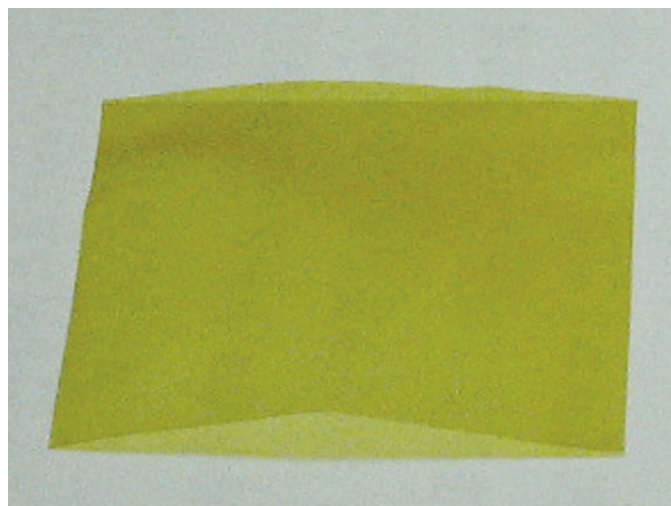

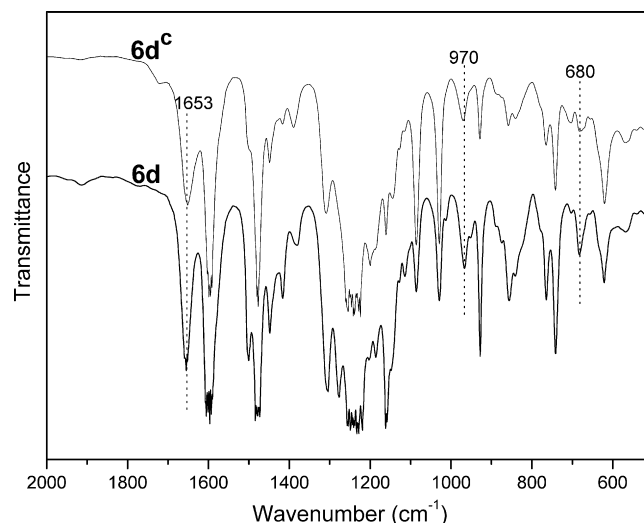Fig. 2. Appearance of the **6e^c** membrane.

Fig. 3. FTIR spectra of virgin SPAE **6d** and cross-linked SPAE **6d^c**.

3.4. Water uptake and swelling ratio

The water content and water state in sulfonated polymers are very important factors that directly affect proton transport across the membranes. Generally, protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H_3O+, $H_5O_2^+$, and $H_9O_4^+$ in the water medium [34–36]. In a fully hydrated state, sulfonated polymers may dissociate immobile sulfonic acid groups and mobile protons in aqueous solution. Then, the free protons move through a localized ionic network within fully water-swollen sulfonated polymer membranes. Accordingly, the proper water content level should be maintained in sulfonated polymer membranes in order to guarantee high proton conductivity. The water uptake was strongly dependent upon the content of sulfonic acid groups and also related to IEC values. However, when the content of protonic acid group to be introduced increase, hydrophilicity and water absorption of the sulfonated polymer increase, resulting in the increase of water-soluble and dimensional unstable characteristics. The water uptake of the SPAEs membranes from liquid water is presented in Table 2 as the weight percentage of the dry samples. The swelling ratio of the membranes was measured at 80 °C in water for 24 h (Table 2). Analogous to water uptake, dimensional change also strongly depended on IEC values, and almost linearly correlated with the water uptake of the membrane. The increase in the cross-linking density reduced the free volume of the membranes to hold the water, showing a lower water uptake and a smaller swelling ratio.

3.5. Oxidative and hydrolytical stabilities

The oxidative stability to peroxide radical attack was investigated by measuring the elapsed times that a membrane began to break after immersion of each sample in Fenton's reagent (3 wt.% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C. The results are listed in Table 2. It can be seen that the oxidative stabilities decreased with increasing sulfonation degree. The sulfonic acid groups on the backbone of the polymers seemed to decrease the oxidative stability toward peroxide radical attack. Because of the cross-linking, the membranes of cross-linked SPAEs exhibited superior oxidative stability compared with virgin SPAEs. The hydrolytic stability was also investigated by treating membrane samples in boiling water for more than 100 h. No obvious change was observed in both the membrane's shape and appearance, demonstrating that no hydrolysis occurred during the treatment. Nafion is a perfluronated polymer, and F is the strongest electron withdrawing group, leading to a more oxidative stability than the C–H linkages of the most SPAEs. The cross-linked SPAEs synthesized in this work were more oxidatively stable than the reported SPAEs with same IEC under same conditions [12,37].

3.6. Thermal stabilities

The thermal stabilities of the sPAEs were investigated by both TGA and DSC techniques. A two-step degradation profile of the polymers was observed as showed in Figs. 4 and 5. The first step occurred at around 250 °C and the second thermal
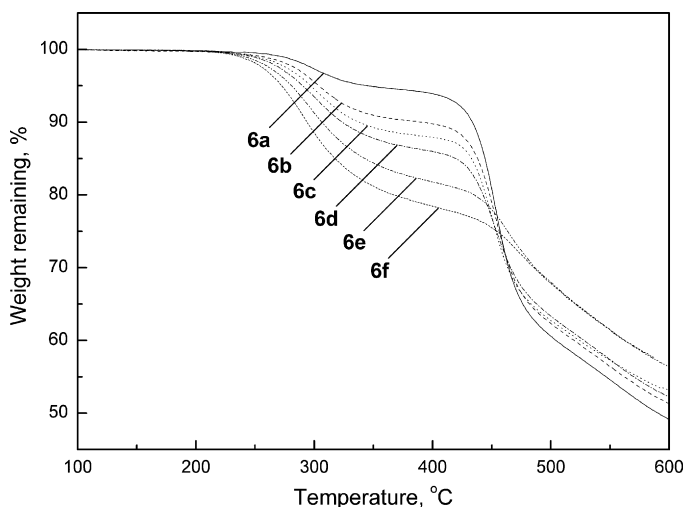

Fig. 4. TGA curves of SPAEs **6a–f**.

degradation took place at about 450 °C. The degradation of first step was assigned to the sulfonic acid groups, propenyl groups or the cross-linkages decomposition, while the second weight loss peak was due to main-chain degradation. It can be seen from Figs. 4 and 5 that the percentage of the first weight loss increased with the increase of sulfonation degree. From DSC curves of the polymers, there was no glass transition temperature observed in the range of 50–250 °C before thermal decomposition. This is the inherent nature of highly sulfonated polymers or ionomer. The T_g of these polymers were higher than the first decomposition temperature. The increase in $T_g s$ is believed to result from the intermolecular reactions of sulfonic acid groups.

3.7. Proton conductivity

The proton conductivity of the synthesized polymers membrane is also tabulated in Table 2. The water content and water state in the sulfonated polymers are very important factors that directly affect proton transport across the mem-
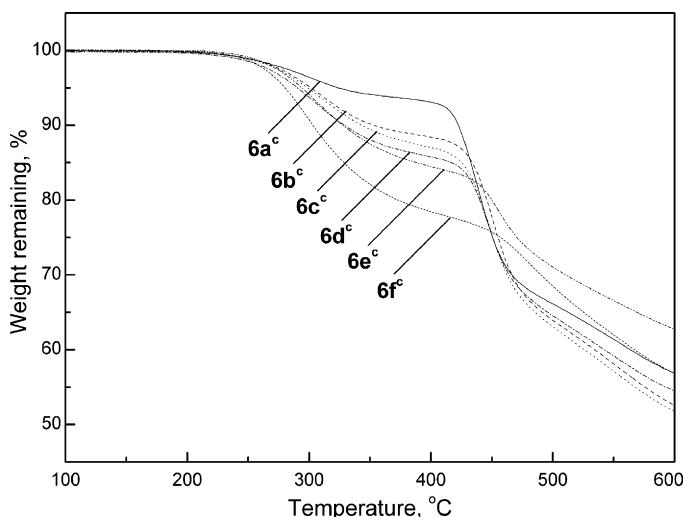

Fig. 5. TGA curves of cross-linked SPAEs **6a^c^–6f^c^**.

branes [34–36]. Generally, protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H_3O+, $H_5O_2^+$, and $H_9O_4^+$ in the water medium. In a fully hydrated state, sulfonated polymers may dissociate immobile sulfonic acid groups and mobile protons in aqueous solution. Then, the dissociated protons move through a localized ionic network within the fully water-swollen sulfonated polymer membranes. Accordingly, a proper water content level should be maintained in sulfonated polymer membranes in order to guarantee high proton conductivity. Moreover water uptake are strongly dependent upon the content of sulfonic acid groups and IEC values. It can also be seen that from Table 2 the cross-linking can constrain the water-uptake to a limited level, and then improve the dimensional and oxidative stability. Because the IECs of the membranes were not changed during cross-linking, therefore, the proton conductivity was not affected. The polymers **6e^c** and **6f^c** had proton conductivities of 3.16×10^{-2} S cm^{-1}, 3.69×10^{-2} S cm^{-1} at temperature of 30 °C, and 4.08×10^{-2} S cm^{-1}, 5.41×10^{-2} S cm^{-1} at temperature of 80 °C under 100% relative humidity, respectively. The proton conductivity of Naffion 117 under the same conditions was 3.48×10^{-2} S cm^{-1} and 5.26×10^{-2} S cm^{-1}. Therefore, the membranes from **6e^c** and **6f^c** showed potential application as an alternative membrane used in PEM fuel cell, in terms of water uptake, the mechanical property, oxidative stability as well as proton conductivity.

4. Conclusions

Cross-linked sulfonated poly(arylene ether)s were successfully synthesized by introducing cross-linkable propenyl group onto sulfonated poly(phathalazinone ether ketone), followed by thermal cross-linking. The cross-linking reaction was verified by FTIR technique. Because of the cross-linked structure, the synthesized polymers could fulfill the contradiction of the high sulfonation degree and the dimensional stability. The cross-linked membrane obtained from above polymer had equivalent IEC (2.57×10^{-3} mol g^{-1}) and proton conductivity (5.41×10^{-2} S cm^{-1}) when compared with Nafion 117 (5.26×10^{-2} S cm^{-1}) at 80 °C and under 100% humidity. Moreover, the cross-linking reaction can greatly improve the oxidative and dimensional stabilities of the prepared membranes without the loss of proton conductivity. The cross-linking methodology is an effective way to increase the oxidative and hydrolytical properties of the sulfonated polyarylenes membrane.

Acknowledgements

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