

## **In Situ Crosslinkable Sulfonated Polyaromatic Ionomers for the Polyelectrolyte Used in Proton Exchange Membrane Fuel Cell**

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**ABSTRACT:** Two series of sulfonated poly(arylene ether nitrile ketone) ionomers containing potential crosslinkable nitrile groups were synthesized in high yield by direct aromatic nucleophilic polycondensation of 1,4-bis-(4-hydroxyphenyl)-2,3-dicyano-naphthalene (**3**) with different molar ratio of disodium 5,5'-carbonyl-bis-(2-fluorobenzene-sulfonate) (**4**) to 5,5'-carbonyl-bis-(2-fluorobenzene) (**5**) or 4,4'-biphenol (**7**). Subsequently, the sulfonated polymeric ionomers were *in situ* crosslinked when cast into membranes from solution at 180°C under nitrogen protection. The structure of the synthesized polymers was characterized by <sup>1</sup>H-nuclear magnetic resonance (NMR), Fourier-transform infrared spectra, and elemental analysis. Comparing with the original polymeric membranes, the cross-linked membranes showed much better thermal and hydrolytic stabilities and superior mechanical properties as well as much lower swelling behavior, which were even better than Nafion 117 membrane. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** fuel cell; proton exchange membrane (PEM); crosslinkable; ionomer

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### **INTRODUCTION**

Proton exchange membrane fuel cells (PEMFCs) have been considered as promising clean power sources for vehicular transportation, resident and institution, and also for computers, mobile communications equipment, and etc.<sup>1</sup> Proton exchange membrane is a key component of PEMFCs, which serves as a separator to prevent reactants from mixing and provide a pathway for proton transportation. During the last decades, the most commonly used proton exchange membrane were perfluorinated copolymers with pendant sulfonic acid group, such as Nafion (Dupont), Dow membrane, and Flemion membrane (Asahi Glass Co. Ltd.),<sup>2</sup> which combine high conductivity (<80°C) and excellent chemical stability as well as superior mechanical strength. However, the high price and limited operating temperature have limited the perfluorinated sulfonated membranes applications in large scale. In addition, the high methanol permeation restrains their use in DMFC. To surmount these disadvantages and as a response to the commercial need for less expensive and more versatile polymer electrolytes, many efforts have been devoted to searching for new alternative materials during the past decades.<sup>3–7</sup> Among these materials, modification of aromatic polymers through sulfonation is one of the main approaches due to their excellent thermal and mechanical properties as well as resistance to oxidation and stability under acidic conditions. Poly(aryl ether sulfone), poly(aryl ether

ketone), poly(ether imide), polybenzimidazole, poly(phthalazinone ether ketone), etc., are well known for their excellent physical and chemical properties. After modification, they show rather high proton conductivities and become promising PEM materials. Generally, there are two approaches to introduce the sulfonate groups onto polymer chain, postsulfonation of polymer and direct copolymerization with sulfonated monomers. In the postsulfonation, the sulfonate groups can be easily attached onto polymer chains by using appropriate sulphonating agents and many sulfonated polymers have been obtained by this method, such as sulfonated poly(arylene ether ether ketone), sulfonated poly(arylene ether sulfone). Wang et al.<sup>8,9</sup> for example, reported the synthesis and properties of sulfonated poly(arylene ether) containing tetraphenylmethane moieties for proton exchange membrane through postsulfonation. Unfortunately, crosslinking and degradation side reactions sometimes occurred and the degree of sulfonation (DS) was rather difficult to control; however, the side reactions can be avoided in direct polymerization and the DS can be precisely controlled. Furthermore, the polymers synthesized by direct polymerization have higher acidity and thermal stability due to the effect of the electron-withdrawing group and possess more sulfonate groups per repeating unit. For example, Wang et al. reported the synthesis of biphenyl-based poly(arylene ether sulfone) containing sulfonic acid groups by direct polymerization reactions,<sup>10</sup> and Chen et al. reported the synthesis of poly(phthalazinone ether

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ketone) containing sulfonate group via novel —C—N coupling reaction.<sup>11,12</sup> However, the earlier-mentioned sulfonated polymers have a tendency to swell at high humidity and elevated temperature, especially for the polymers with high sulfonic acid content. As a consequence, the membranes lose the mechanical strength, and their ability to function under PEMFC conditions becomes impossible.

Poly(aryl ether nitrile) are a new class of high-performance thermoplastic polymers that exhibit good mechanical and chemical properties and have already been used as matrices in advanced composites in aerospace industries.<sup>13,14</sup> Poly(aryl ether nitrile) have strongly polar nitrile groups appended on aromatic rings, which can promote the adhesion between the polymers with substrates via interaction with other polar chemical groups. The enhanced adhesion of poly(aryl ether nitrile) to inorganic compounds is beneficial for the adhesion of catalyst to PEM. Recently, it was reported<sup>15</sup> that nitrile groups were introduced into poly(aryl ether sulfone) containing sulfonic acid groups with the aim at decreasing the swelling degree of membrane materials via enhanced intermolecular interaction. Moreover, the nitrile groups on polymer chains can act as a potential crosslinking site. In this work, we report the synthesis and characterization of the sulfonated poly(arylene ether nitrile ketone) containing dicyanoarylene moiety. Subsequently, the above precursor polymers were *in situ* crosslinked when cast from solution at 180°C under nitrogen protection resulting in proton exchange membrane. Finally, the properties of the membranes were evaluated as PEMFC electrolytes.

## EXPERIMENTAL

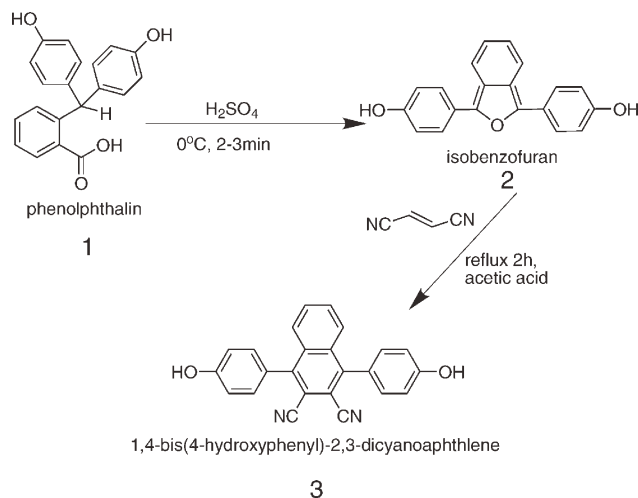
### Materials

5,5-Carbonyl-bis-(2-fluorobenzene) (5) was purchased from Aldrich, disodium 5,5-carbonyl-bis-(2-fluorobenzene sulfonate) (4) was obtained by the sulfonation of 5,5-carbonyl-bis-(2-fluorobenzene) according to the literature.<sup>16</sup> Fumaronitrile and 4,4'-biphenol (6) was purchased from TCI. Phenolphthalein and other chemicals were obtained from commercial sources. All chemicals above were purified according to the standard method prior to use.

### Preparation of 1,4-bis-(4-hydroxyphenyl)-2,3-dicyanonaphthalene (3)

1,4-Bis-(4-hydroxyphenyl)-2,3-dicyanonaphthalene (3) was prepared according to the literature<sup>17-19</sup> (Scheme 1). To a dry 25-mL round-bottom flask equipped with a mechanical stirrer, 2 g (6.24 mmol) of dry, finely powdered reduced phenolphthalein (1) was added. The flask was immersed in an ice-acetone bath for 10 min and then concentrated sulfuric acid (6.5 mL, also cooled to 0°C) was poured into the flask. The mixture was vigorously stirred for 2–3 min to dissolve the solids. The mixture was then stirred for another 7–8 min at this temperature. The resulting yellow-brown slurry (isobenzofuran, coded as 2) was quickly poured into a 500-mL beaker containing 120 mL of ice-water. The solids (2) were separated by filtration, and washed with 20 mL cold water (0°C) and dried on the filter paper for 5–15 min before being used directly in the following Diels–Alder reaction.

To a 50-mL round-bottom flask containing 2.0 g (20.41 mmol) of fumaronitrile in 13 mL of acetic acid the compound 2 was



**Scheme 1.** Preparation of 1,4-bis-(4-hydroxyphenyl)-2,3-dicyanonaphthalene (3).

added. The mixture was quickly heated to the temperature of reflux. After 15–20 min, a yellow product, 1,4-bis-(4-hydroxyphenyl)-naphtha-2,3-dicarbonitrilen (coded as 3) precipitated out from the reaction mixture. The reaction was continued at this temperature for another 2 h to complete the reaction. The product was isolated by filtration and washed twice with a minimum amount of acetic acid. The final product powder 3 was obtained in 64% yield as light gray powder.

### Synthesis of Sulfonated Polymers

A typical example for polymer 6a is given as follows. To a 25-mL three-neck round-bottomed flask fitted with a Deanstark trap, a condenser, a nitrogen inlet/outlet and a magnetic stirrer were charged with (3) 0.3624 g (1 mmol), (4) 0.4223 g (1 mmol), anhydrous potassium carbonate 0.1935 g (1.4 mmol), 6 mL of DMSO, and 8 mL toluene. The reaction mixture was slowly heated to 140°C after the nitrogen being purged through the system with stirring for 10 min, and then maintained at this temperature for another 2 h to dehydrate the reaction system. Subsequently, the system was quickly heated to 160°C and maintained at this temperature for 16 h to complete the reaction. The resulting viscous solution was cooled to 100°C followed by diluting with 2 mL of DMSO, and then precipitated out by pouring into 100 mL mixture of methanol/water (1 : 1). The precipitates were filtered off and washed twice with deionized water. The fibrous products were collected and dried at 110°C under vacuum for 12 h. A total of 0.7455 g of polymer 6a was obtained in high yield of 95%.

All polymers 6a–6d were prepared from monomers (3), (4), and (5) and polymers 8a–8d from monomers (3), (4), and (7) in different ratios (Table I). The general procedure was always the same.

### Membrane Preparation of Polymers 6a–6d and 8a–8d

Sodium-form membranes of polymers 6a–6d and 8a–8d were prepared by casting 5%–10% solution of polymers 6a–6d and 8a–8d in DMSO on a glass tray in a dust-free environment. Membranes were dried at 80°C for 15 h, and then at 110°C

**Table I.** Polymerization Results of Polymers **6a–6d** and **8a–8d**

Polymer	Monomer feed ratio (m/n)	$\eta_{inh}$ (dL/g)	EW	Yield (%)	DS	
					Calculated	Found <sup>a</sup>
<b>6a</b>	10/0	1.82	388	95	2.00	1.92
<b>6b</b>	8/2	2.33	487	91	1.60	1.39
<b>6c</b>	6/4	1.76	598	97	1.20	1.34
<b>6d</b>	5/5	1.80	769	89	1.00	0.79
<b>8a</b>	3/7	1.13	300	93	2.00	1.92
<b>8b</b>	4/6	1.23	293	90	2.00	2.03
<b>8c</b>	5/5	1.32	309	92	2.00	1.98
<b>8d</b>	6/4	1.35	314	96	2.00	2.01

<sup>a</sup>Measured by elemental analysis.

under vacuum for 20 h. Acid-form polymeric membranes **6a–6d** and **8a–8d** were obtained by immersing the sodium-form ones **6a–6d** and **8a–8d** in 0.5M boiling sulfuric acid solution for 3 h, followed in boiling deionized for another 3 h, and then dried at 110°C under vacuum for 24 h.

#### In Situ Crosslinking of Polymers

A typical example for the *in situ* crosslinking of polymer **6a** is given as follows. One gram of transparent light-yellow polymer **6a** in acid form was dissolved in 40 mL of DMSO, then the dilute solution was filtered off and the filtrate was poured onto a glass tray. Subsequently, the glass tray was put in an oven at 80°C for 15 h, then 120°C for 2 h, and thereafter the oven was purged with nitrogen for 30 min. Finally, the temperature was increased to 180°C and kept at this temperature for 15 h. After workup, 1 g of dark-yellow polymer **9a** was obtained. The general *in situ* crosslinking procedure of all polymers **6a–6d** and **8a–8d** was always the same. The resulting crosslinked polymers were **9c–9d** and **10a–10d** correspondingly.

#### Characterization

<sup>1</sup>H-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker NMR instrument (Model: DRX 400MHz) using dimethyl-d<sub>6</sub> sulfoxide as solvent. For spectroscopy results, chemical shifts were given in ppm against tetramethylsilane as an internal standard. Elemental analyses were performed on an elemental analyzer (Model Varios EL) for C, H, N, and S determination. Fourier-transform infrared (FTIR) spectra were measured on a Perkin-Elmer Spectrum 100 Fourier transform spectrometer with membrane samples. Melting point was taken on a digital micro melting-point testing apparatus. The thermal stability of the polymers was analyzed using a Perkin-Elmer Pyris Diamond TG/DTA analyzer under a protective nitrogen atmosphere (200 mL/min) from 50°C to 600°C with a heating rate of 20°C/min. Inherent viscosity was determined for a solution of 0.5 g/dL in DMSO at 30°C with a calibrated Ubbelohde viscometer.

The proton conductivity was measured on a Solartron 1255B frequency response analyzer coupled with a Solartron 1287 electrochemical interface in the frequency range of 1 Hz to 1 MHz.

The measurement of proton conductivity was conducted at 25°C and 100% relative humidity.

Tensile properties of the samples were examined by SANS (Shenzhen, China) electromechanical universal test machine (model CMT-4014) at 25°C and 100% relative humidity. The specimens with thickness of 110–125 μm and size of 20 mm × 2 mm were used for testing. Three specimens were tested and average value was reported for each sample.

The swelling ratio was described as the linear expansion rate of wet membrane. They were determined at 30°C after being immersed in deionized water for 48 h and calculated according to the following equation.

$$\text{Swelling ratio} = \frac{L_1 - L_0}{L_0} \times 100\% \quad (1)$$

where  $L_0$  and  $L_1$  are the lengths of dry and wet membranes, respectively.

Oxidative stability was tested by soaking the membrane in Fenton's reagent (30 wt % H<sub>2</sub>O<sub>2</sub> + 30 ppm FeSO<sub>4</sub>) at 30°C. The results were reported by the time that the membrane took to become brittle. DS is defined as number of sulfonic acid groups per repeating unit. DS is calculated from the monomer feed ratio and determined by elemental analysis. Equivalent weight (EW) of the sulfonated polymer is described as EW per sulfonic acid group. EW is calculated from the feed ratio and molecular weights of the structure units. The values of DS and EW are calculated by the following equations:

$$\text{DS of polymer } \mathbf{6a - 6d} = 2m/(m + n) \quad (2)$$

$$\text{DS of polymer } \mathbf{8a - 8d} = 2(m + n)/(m + n) = 2 \quad (3)$$

$$\text{EW of polymer } \mathbf{6a - 6d} = (M1 \times m + M2 \times n)/2m \quad (4)$$

$$\text{EW of polymer } \mathbf{8a - 8d} = (M1 \times m + M2 \times n)/2(m + n) \quad (5)$$

where  $m$  and  $n$  are the numbers of the structure unit in one repeating unit as depicted in Schemes 2 and 3,  $M1$  and  $M2$  are the molecular weights of the structure units as depicted in Schemes 2 and 3.

## RESULTS AND DISCUSSION

### Syntheses of Sulfonated Polymers **6a–6d** and **8a–8d**

As depicted in Schemes 2 and 3, the sulfonated polymers **6a–6d** and **8a–8d** were synthesized by the polycondensation of monomer (3) with the mixture of sulfonated dihalide (4) and unsulfonated monomer (5) or (7) in a dipolar aprotic solvent of DMSO. The syntheses of sulfonated polymers **6a–6d** and **8a–8d** with different sulfonation degrees and EW values can be readily achieved by adjusting the molar ratio of 4–5 or 7. The polycondensation generally took a long time of 16 h to give high molecular weight of **6a–6d** and **8a–8d**, so the reaction mixture must be protected carefully under nitrogen purge. The molecular structure of the sulfonated polymers **6a–6d** and **8a–8d** was confirmed by <sup>1</sup>H-NMR spectra and elemental analysis. Regarding the elemental analysis, the results deviated from the formula to some extent. When the absorbed water was taken into



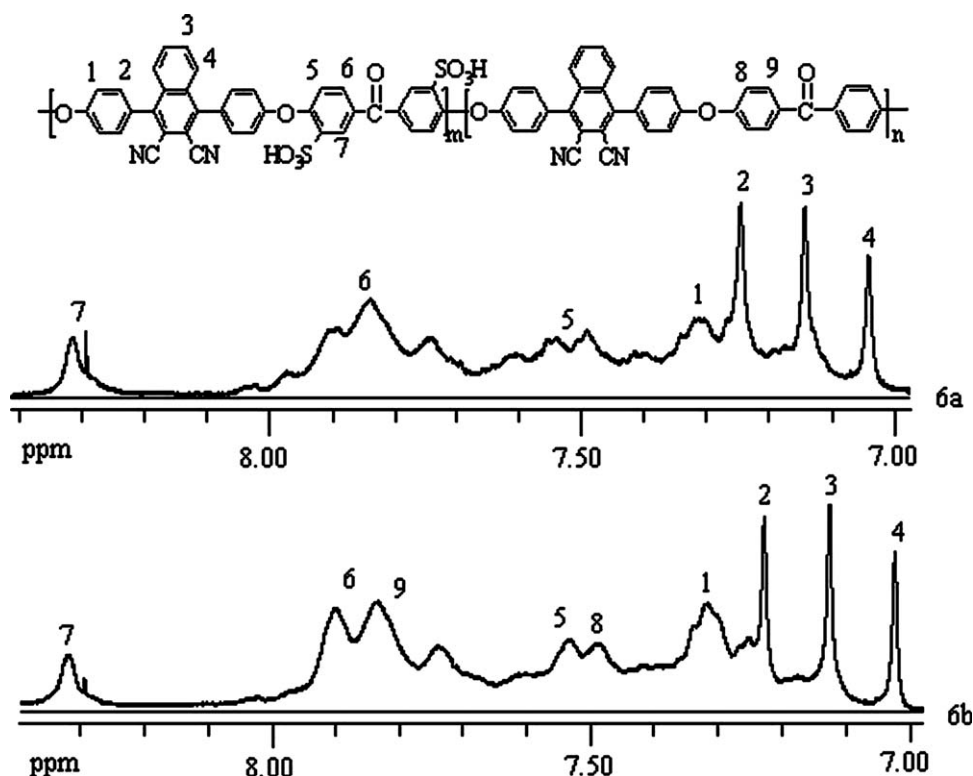


Figure 1.  $^1\text{H-NMR}$  spectrum of sulfonated polymers **6a** and **6b**.

consideration, the earlier-mentioned data can be in good agreement with the proposed molecular structures. Figure 1 shows the  $^1\text{H-NMR}$  spectrum of the aromatic protons on highly sulfonated polymers **6a** ( $m/n = 10/0$ ) and **6b** ( $m/n = 8/2$ ). Because of its special configuration, the chemical shifts of all the aromatic protons can not completely be separated. Sulfonated polymers **6a** and **6b** are assigned by their aromatic protons (Figure 1). The accurate analysis of the  $^1\text{H-NMR}$  spectrum<sup>18</sup> of monomer (3) can greatly simplify the assignment of the complicated homopolymer spectrum, and in turn, the complicated copolymer spectrum. However, it is rather difficult to assign all the peaks of the sulfonated polymer spectrum owing to the partially overlapped proton peaks on naphthalene ring of bis-phenol units with the proton peaks on dihalide units. Polymers **8a–8d** were characterized by both  $^1\text{H-NMR}$  and elemental analysis. As shown in Figure 2, the intensity of peak 1 and peak 2 increases with the increase of the feeding ratio of monomer (3).

$^1\text{H-NMR}$  and elemental analysis results of polymers **6a–6d** as follows:

**Polymer 6a:**  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 8.32\text{--}8.29$  ( $d$ , 1.09H), 8.02–7.69 ( $m$ , 6.24H), 7.60–7.49 ( $m$ , 4.47H), 7.31–7.25 ( $d$ , 4.29H), 7.14 ( $s$ , 2.42H), 7.04 ( $s$ , 1.25H). ( $\text{C}_{37}\text{H}_{20}\text{O}_9\text{N}_2\text{S}_2\cdot 6\text{H}_2\text{O}$ )<sub>*n*</sub> (800.78)<sub>*n*</sub>; Calcd: C, 56.30; H, 4.248; N, 2.684; S, 8.268. Found: C, 54.95; H, 3.99; N, 3.46; S, 7.93.

**Polymer 6b:**  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 8.32\text{--}8.29$  ( $d$ , 1.00H), 8.02–7.69 ( $m$ , 8.20H), 7.60–7.49 ( $m$ , 2.96H), 7.31–7.25 ( $d$ , 5.60H), 7.14 ( $s$ , 1.78H), 7.04 ( $s$ , 0.92H). ( $\text{C}_{37}\text{H}_{20}\text{O}_{7.8}\text{N}_2\cdot$

$\text{S}_{1.6}\cdot 5\text{H}_2\text{O}$ )<sub>*n*</sub> (758.74)<sub>*n*</sub>; Calcd: C, 58.57; H, 3.99; N, 3.69; S, 6.76. Found: C, 60.89; H, 4.15; N, 3.36; S, 6.83.

**Polymer 6c:**  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 8.32\text{--}8.29$  ( $d$ , 0.99H), 8.02–7.69 ( $m$ , 6.34H), 7.60–7.49 ( $m$ , 3.94H), 7.31–7.25 ( $d$ , 4.58H), 7.14 ( $s$ , 2.66H), 7.04 ( $s$ , 1.13H). ( $\text{C}_{37}\text{H}_{20}\text{O}_{5.3}\text{N}_2\cdot \text{S}_{1.2}\cdot 3\text{H}_2\text{O}$ )<sub>*n*</sub> (669.89)<sub>*n*</sub>; Calcd: C, 66.34; H, 3.91; N, 4.18; S, 4.54. Found: C, 67.13; H, 4.02; N, 3.85; S, 4.54.

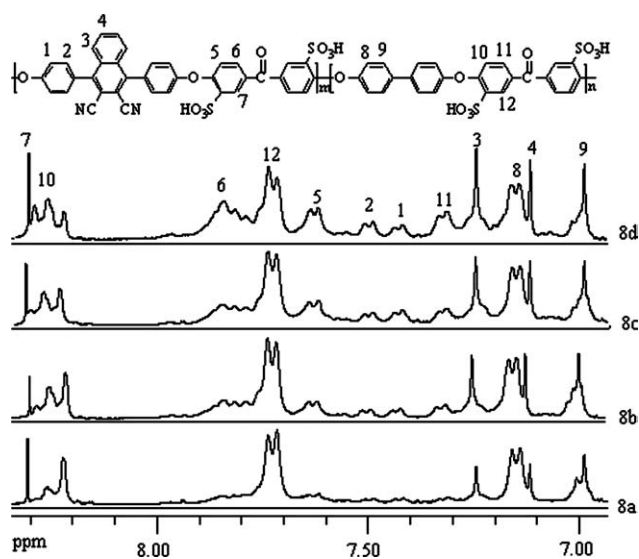
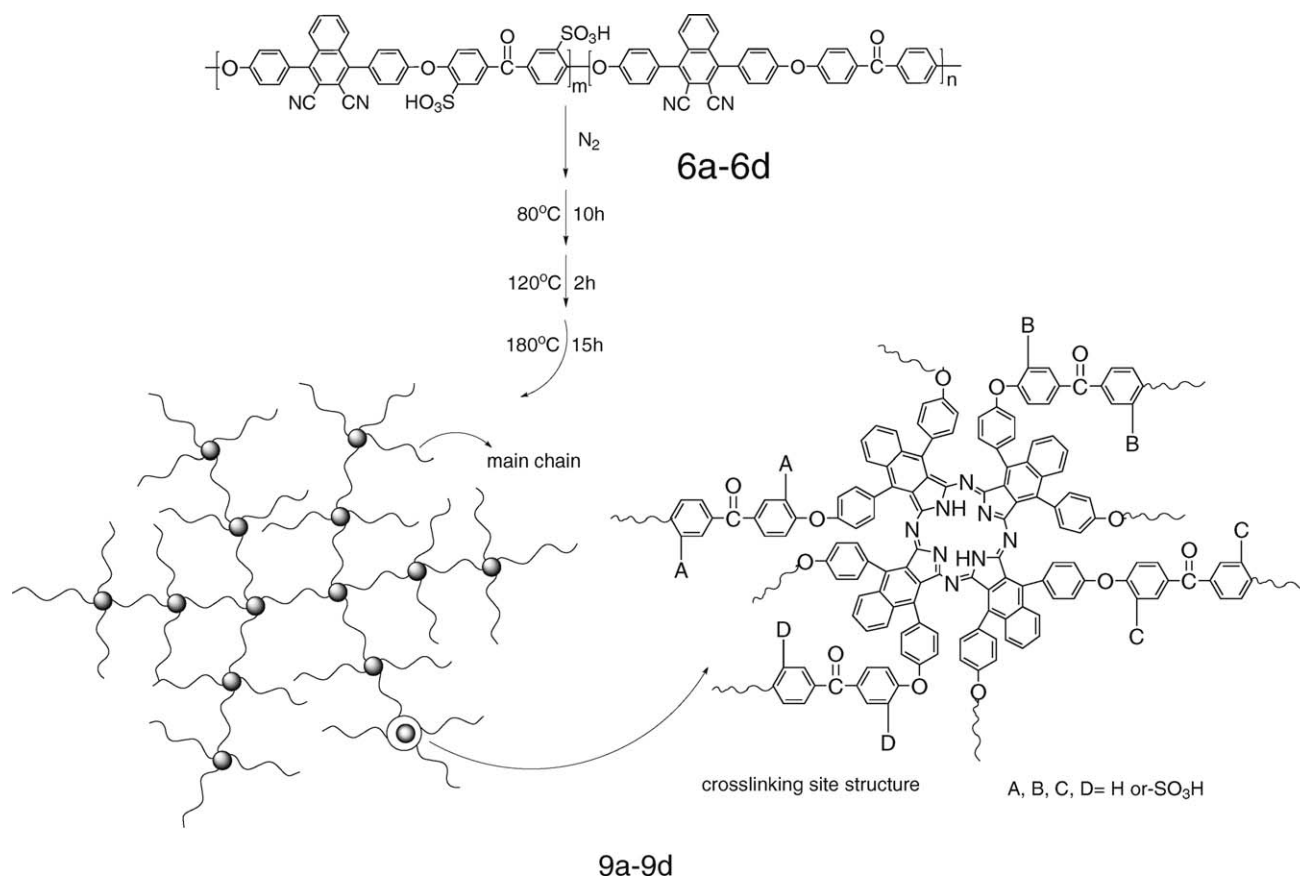


Figure 2.  $^1\text{H-NMR}$  spectrum of sulfonated polymers **8a–8d**.



**Scheme 4.** Schematic diagram for the crosslinking structure of polymers **9a–9d**.

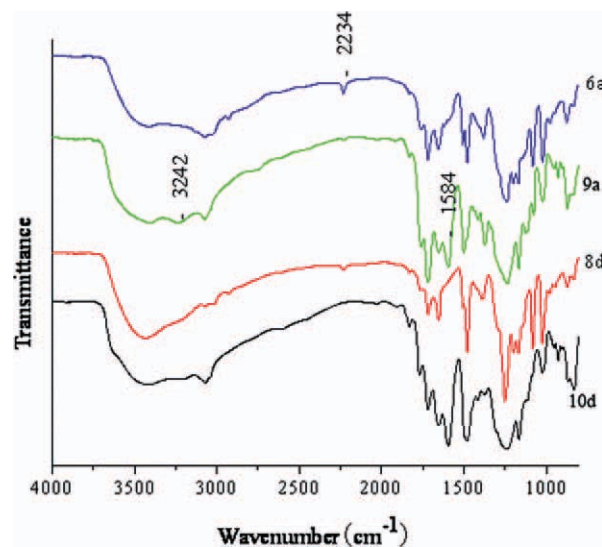
**Polymer 6d:**  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 8.32\text{--}8.29$  (*d*, 0.90H), 8.02–7.69 (*m*, 6.34H), 7.60–7.49 (*m*, 3.94H), 7.31–7.25 (*d*, 4.60H), 7.14 (*s*, 2.64H), 7.04 (*s*, 1.01H). ( $\text{C}_{37}\text{H}_{20}\text{O}_6\text{N}_2\cdot\text{S}\cdot 3\text{H}_2\text{O}$ )<sub>*n*</sub> (674.68)<sub>*n*</sub>; Calcd: C, 65.87; H, 3.88; N, 4.15; S, 4.75. Found: C, 66.65; H, 4.53; N, 3.66; S, 4.53.

**Polymer 9a**  $\nu$  ( $\text{cm}^{-1}$ ): 3408 (–OH); 3236 (stretching –NH); 3073 (Ar–H); 1654 (C=O); 1594 (C=N); 1500–1422 (aromatic C=C); 1235–1168 (Ar–O–Ar); 1126 (bending –NH); 1085, 1024 (–SO<sub>3</sub>H); 930; 874; 764.

#### **In Situ Crosslinking of Polymers 6a–6d and 8a–8d**

Polymers **6a–6d** and **8a–8d** were *in situ* crosslinked during casting membrane from solution at 180°C under nitrogen protection according to the procedures above-mentioned. The proposed crosslinking mechanism and the chemical structures of the formed polymers **9a–9d** are shown in Scheme 4. Polymers **6a**, **9a**, **8d**, and **10d** were selected as typical examples. In the FTIR spectra of **6a**, **9a**, **8d**, and **10d** as shown in Figure 3, the spectra of **9a** and **10d** is obviously different from those of **6a** and **8d** except for the similar characteristic absorbance of aromatic main chain. The appearance of a new absorbance at 3236  $\text{cm}^{-1}$  (the stretching vibration of N–H) and the disappearance of the typical absorbance at 2232  $\text{cm}^{-1}$  (stretching vibration of –CN) demonstrated the formation of polymers **9a** and **10d**. The appearance of a new resonance at 1594  $\text{cm}^{-1}$  (the stretching vibration of C=N) and 1126  $\text{cm}^{-1}$  (the bending of –NH) were in good agreement with the proposed structures of **9a** and **10d**.

FTIR Spectra: Polymer **6a**  $\nu$  ( $\text{cm}^{-1}$ ): 3409 (–OH); 3072 (Ar–H); 2232 (–CN); 1507–1481 (aromatic C=C); 1656 (C=O); 1239–1170 (Ar–O–Ar); 1083, 1022 (–SO<sub>3</sub>H); 980; 877; 768.



**Figure 3.** FTIR spectrum of sulfonated polymers **6a**, **9a**, **8d**, and **10d**.

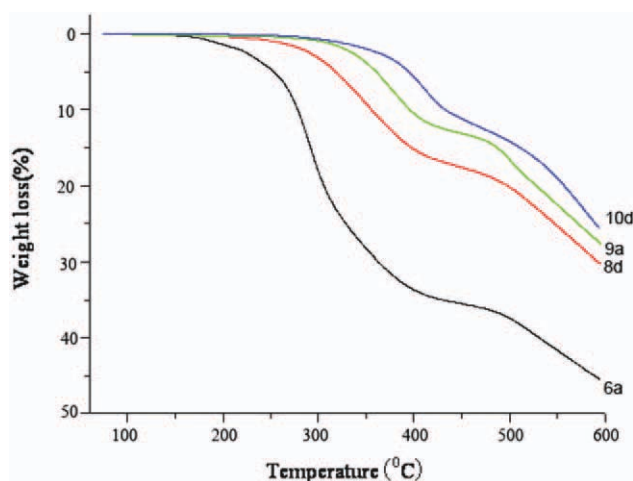


Figure 4. TGA traces of acid-form polymers 6a, 9a, 8d, and 10d.

#### Properties of Sulfonated Polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d

The solubility of polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d was widely divergent. Polymers 6a–6d and 8a–8d were easily soluble in dipolar aprotic solvent such as DMSO, DMF, DMAc, or *N*-methylpyrrolidone (NMP), but polymers 9a–9d and 10a–10d were insoluble because of their crosslinked structure as presented in Scheme 4. Tough and smooth films from polymers 6a–6d and 8a–8d can be obtained by removing the used solvent at a programmed temperature profile ranging from 80°C to 120°C followed by acidification. The inherent viscosities ( $\eta_{inh}$ ) of sulfonated polymers 6a–6d and 8a–8d were measured and listed in Table I, indicating the high molecular weights.

The thermal stabilities of the acid-form sulfonated polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d were investigated using TGA. As shown in Figure 4, a two-step degradation profile was observed for these acid-form sulfonated polymers, which is similar to other sulfonated poly(aryl ether nitrile).<sup>15</sup> The first weight loss was at  $\sim 280^\circ\text{C}$  for polymer 9a and about  $250^\circ\text{C}$  for polymer 6a. Polymer 9a is more stable than polymer 6a due to the effect of crosslinking. The degradation rate of the acid-

form polymers increased gradually with the increase of the sulfonation degree and temperature. It should be noted, correspondingly, that polymer 6a and 9a were less stable than 8d and 10d, which may be related to the difference of the nitrile content. There was no glass transition temperature observed for the sulfonated polymers ranging from  $30^\circ\text{C}$  to  $300^\circ\text{C}$  due to their ionomer nature. The two series of polymers showed good oxidation stability, especially for the polymers 6c and 6d.

The swelling degree of the membranes from polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d were evaluated and listed in Tables II and III. The swelling degree of the membranes from polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d increased with increasing the sulfonation degree. Polymers 6a–6d and 8a–8d were more swelled than Nafion 117 under the same condition. Polymer 6a and 8a–8d became a little brittle owing to excessive hydration. Unlike other sulfonated polymers,<sup>20–22</sup> the synthesized polymers were normally insoluble in water even at high DS. However, the swelling degree of polymers 9a–9d and 10a–10d was notably decreased because of crosslinking, which was smaller than Nafion 117. The proton conductivities of the membranes indicated a good ability of proton transport for these sulfonated polymers as listed in Table II. The proton conductivity increased gradually with increasing sulfonation degree, while the conductivity of the crosslinked polymers 9a–9d and 10a–10d decreased a little due to the decrease of the water uptake. Polymers 9a and 10a–10d were comparable with Nafion 117 with the conductivity  $\sim 10^{-2} \text{ S cm}^{-1}$ .

The mechanical properties of the membranes from the polymers 6a–6d, 8a–8d, 9a–9d, and 10a–10d were tested and listed in Tables II and III. The tensile strength was equivalent to Nafion 117 for both series of the polymers 6a–6d and 8a–8d, especially for the polymers 9a–9d and 10a–10d which was remarkably strengthened by crosslinking.

#### CONCLUSIONS

Two series of high molecular weight of sulfonated poly(arylene ether nitrile ketone) containing dicyanoarylene moiety were synthesized by direct polycondensation, subsequently the precursor

Table II. Properties of Polymers 6a–6d and 9a–9d

Polymer	Tensile strength(MPa)	Antioxidation (h)	Conductivity (s/cm)	$T_{-5\%}^a$ ( $^\circ\text{C}$ )	Swelling (%)	Residual <sup>b</sup> (%)
6a	21.30	64	$2.84 \times 10^{-2}$	292	21.30	0
6b	22.49	69	$2.08 \times 10^{-2}$	346	15.78	0
6c	21.30	240	$1.05 \times 10^{-2}$	400	14.15	0
6d	41.03	288	$1.77 \times 10^{-3}$	387	12.48	0
9a	48.42	108	$1.04 \times 10^{-2}$	386	1.37	96.09
9b	32.57	130	$4.33 \times 10^{-3}$	387	2.72	95.40
9c	33.38	>300	$9.36 \times 10^{-4}$	372	0.626	92.37
9d	43.15	>300	$3.53 \times 10^{-4}$	362	0.784	89.92
SPPEK <sup>c</sup>	25.86	51	$1.07 \times 10^{-3}$	266	12.51	– <sup>d</sup>
Nafion117	21.88	>300	$4.25 \times 10^{-2}$	– <sup>d</sup>	2.89	– <sup>d</sup>

<sup>a</sup>Five percent weight loss temperature under nitrogen protection, <sup>b</sup>The residual weight percentage of the polymer after immersed in DMSO at  $100^\circ\text{C}$  for 10 h, <sup>c</sup>Sulfonated poly(phthalazinone ether ketone) membrane (SPPEK) prepared in our laboratory<sup>11,12</sup>, <sup>d</sup>Not detected.

**Table III.** Properties of Polymers **8a–8d** and **10a–10d**

Polymer	Tensile strength (MPa)	Antioxidation (h)	Conductivity (s/cm)	T <sub>d5%</sub> <sup>a</sup> (°C)	Swelling (%)	Residual <sup>b</sup> (%)
<b>8a</b>	17.56	50	$1.80 \times 10^{-1}$	267	53.2	0
<b>8b</b>	16.98	55	$2.91 \times 10^{-1}$	252	48.8	0
<b>8c</b>	18.37	60	$2.05 \times 10^{-1}$	262	44.4	0
<b>8d</b>	19.26	60	$2.07 \times 10^{-1}$	259	40.0	0
<b>10a</b>	35.06	72	$6.81 \times 10^{-2}$	334	23.6	55.5
<b>10b</b>	35.74	85	$5.05 \times 10^{-2}$	325	15.9	67.8
<b>10c</b>	38.25	90	$2.37 \times 10^{-2}$	356	8.90	74.9
<b>10d</b>	40.83	105	$2.11 \times 10^{-2}$	322	6.85	80.3

<sup>a</sup>Five percent weight loss temperature under nitrogen protection, <sup>b</sup>The residual weight percentage of the polymer after immersed in DMSO at 100°C for 10 h.

polymers were crosslinked through potential crosslinkable dicyanoarylene, and characterized by <sup>1</sup>H-NMR, elemental analysis and FTIR, TGA as well as other technologies available. It demonstrated that both series of crosslinked sulfonated polymers possessed excellent thermal stability, mechanical strength and smaller swelling degree compared with their corresponding mother polymers. Although proton conductivity of polymers **9a–9d** and **10a–10d** decreased a little due to the crosslinking, the proton conductivities of polymer **9a** and **10a–10d** with high DS were still comparable with that of Nafion 117 under the same conditions. In this regard, the synthesized crosslinkable polymer materials could be promising candidates using in PEMFC as proton exchange membrane, especially for polymers **9a** and **10a–10d**.

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#### REFERENCES

- Steele, B. C. H.; Heinzl, A. *Nature* **2001**, *414*, 345.
- Chikashige, Y.; Chikyu, Y.; Miyatake, K.; Watanabe, M. *Macromolecules* **2005**, *38*, 7121.
- Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.
- Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.
- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.
- Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896.
- Rusanov, A. L.; Likhatchev, D. Y.; Mullen, K. *Russ. Chem. Rev.* **2002**, *71*, 761.
- Wang, L.; Meng, Y. Z.; Hay, S. A. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 6411.
- Wang, L.; Meng, Y. Z.; Wang, S. J.; Shang, X. Y.; Li, L.; Hay, A. S. *Macromolecules* **2004**, *37*, 3151.
- Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J. Membr. Sci.* **2002**, *197*, 231.
- Chen, Y. L.; Meng, Y. Z.; Li, X. H.; Hay, A. S. *Macromolecules* **2005**, *38*, 3564.
- Chen, Y. L.; Meng, Y. Z.; Li, X. H.; Hay, A. S. *Macromolecules* **2005**, *38*, 10007.
- Kricheldorf, H. R.; Berghahn, M. *Macromol. Chem. Rapid Commun.* **1991**, *12*, 529.
- Gao, Y.; Guiver, M. D. *Macromolecules* **2005**, *38*, 3237.
- Sumner, M. J.; McGrath, J. E. *J. Membr. Sci.* **2004**, *239*, 199.
- Liu, S.; Wang, F.; Chen, T. L. *Macromol. Rapid Commun.* **2001**, *22*, 579.
- Paventi, M.; Chan, K. P. *Pure Appl. Chem.* **1996**, *A33*, 133.
- Wan, W.; Meng, Y. Z. *Polymer* **2003**, *44*, 575.
- Meng, Y. Z.; Imad, A. A.; Hay, A. S. *Macromolecules* **2000**, *33*, 9185.
- Mitsuru, U.; Hidetsugu, T.; Takao, O. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 853.
- Wang, F.; Hickner, M.; Ji, Q.; McGrath, J. E. *J. Membr. Sci.* **2001**, *175*, 387.
- Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *Macromolecules* **2004**, *37*, 7960.