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# Direct synthesis of sulfonated poly(phthalazinone ether) for proton exchange membrane via N–C coupling reaction

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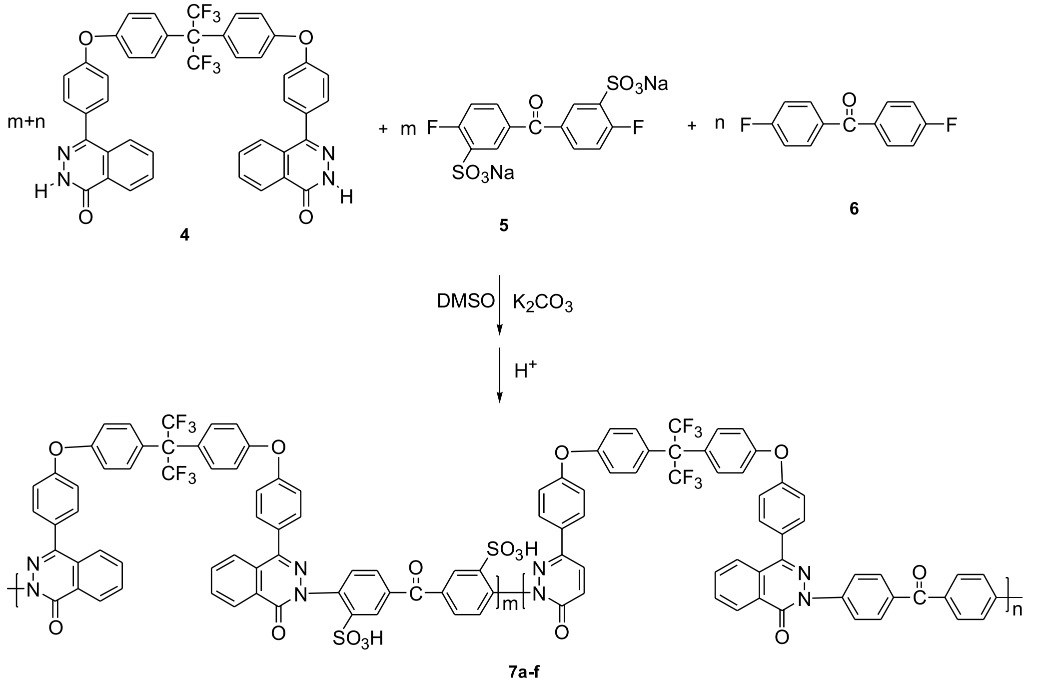
## Abstract

Sulfonated poly(phthalazinone ether)s **7a–f** were directly synthesized by aromatic nucleophilic polycondensation of bisphthalazinone **4** with the mixture of sulfonated dihalide **5** and non-modified dihalide **6** via N–C coupling reaction. The sulfonated polymers were characterized by $^1$H NMR, elemental analysis and other technologies. Because of their specially designed molecular structure, the novel sulfonated polymers showed excellent thermal and oxidative stability. The sulfonated polymers also had reasonable water affinity and moderate proton conductivity for the usage in proton exchange membrane fuel cells.



*Keywords:* Sulfonation; Polyaromatics; Polycondensation

## 1. Introduction

Recently, polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attention because they are considered to be a promising future power source for

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vehicular transportation and for other applications, which require cleaning, quiet, and portable power [1]. The most important integral part of a PEMFC has been well documented to be polymer electrolyte membrane itself. The current state-of-the-art resin used for PEMFC is DuPont's Nafions, [2] owing to their good mechanic strength, electrochemical and chemical stabilities, as well as high proton conductivity. However, some well-known demerits of these perfluorinated ionomers (PFI), including high cost of production, low conductivity at low humidity or high temperature (above 100 °C due to loss of water) and high methanol permeation in direct methanol fuel cell (DMFC), strongly constrain their practicable application [3,4]. This stimulated a number of approaches in the development of alternative proton conducting polymers.

Poly(arylene ether)s (PAE)s are a class of high-performance polymers due to their high glass transition temperatures, good mechanical properties, excellent thermal, oxidative and chemical stability [5–7]. The conversion of these materials to sulfonated polymers used as PEM could be achieved in two ways: postsulfonation [8,9] as well as other modification reactions [10,11] and direct polymerization [12–15] from sulfonated monomers. Many research papers have been published on treating PAE in concentrated sulfuric acid, fuming sulfuric acid or chlorosulfonic acid to afford sulfonated PAE [16–20]. However, unfavorable side reactions, such as crosslinking or degradation, may occur during the modification.

In this paper, herewith, a new approach is presented for the direct synthesis of high-molecular-weight sulfonated poly(-phthalazinone ether)s **7a–f** from bisphthalazinone **4** with sulfonated 4,4′-difluorobenzophenone **5** and 4,4′-difluorobenzophenone **6** in different ratios. The careful characterization of the sulfonated polymers **7a–f** by $^1$H NMR and elemental analysis confirmed the structures that were designed. The membranes prepared from the polymers with different sulfonation degrees exhibited reasonable water affinity and moderate proton conductivity. More importantly, the membrane was highly resistant to oxidation.

## 2. Experimental

### 2.1. Materials

2-(4-Chlorophenyl) benzoic acid was prepared from phthalic anhydride and chlorobenzene via a Friedel–Crafts reaction. 4,4′-(Hexafluoroisopylidene) diphenol (6F-BPA), 4,4′-difluorobenzophenone, dimethyl sulfoxide (DMSO) were purchased from Aldrich Chemical Co. and used as received. Sulfonated 4,4′-difluorobenzophenone (SDFBP) **5** was obtained by the sulfonation of 4,4′-difluorobenzophenone (DFBP) **6** according to the literature [12]. Reagent-grade *N*,*N*′-dimethylacetamide (DMAc), toluene, methanol, anhydrous potassium carbonate, were obtained from commercial sources used without further purification.

### 2.2. Measurements

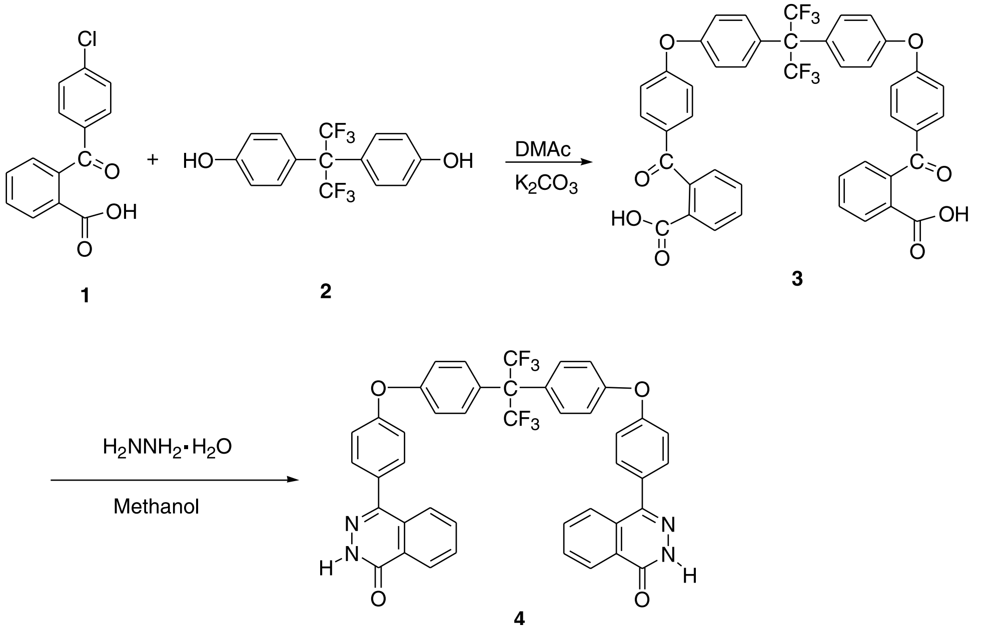
$^1$H NMR spectra were recorded on a Bruker NMR instrument (Model: DRX 400 MHz) using dimethyl-$d_6$ sulfoxide (DMSO-$d_6$) as a solvent. For spectroscope results, chemical shifts are given in ppm against tetramethylsilane as an internal standard. Elemental analyses were performed on a Varios EL elemental analyzer for C, H, N, and S determination. Melting points were taken on a melting-point testing apparatus. The thermal stability of the polymers was determined with a Seiko SSC-5200 thermogravimetric analyzer [thermogravimetric analysis (TGA)/differential thermal analysis (DTA)] under a protective nitrogen atmosphere (200 mL/min). The heating rate was 20 °C/min. The glass transition temperatures ($T_g$'s) were determined on a Seiko 220 DSC instrument at a heating rate of 20 °C/min under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature. Inherent viscosity was determined for solution of 0.5 g/dL in DMAc at 25 °C with a calibrated Ubbelohde viscometer. The water uptake of the prepared membrane was evaluated by measuring the weight change between dried and humidified states at 80 °C. Proton conductivity measurement was performed on hydrated film samples by a Solartron 1255B frequency response analyzer functioning with an oscillating voltage of 10 mV using two probes with the frequency between 1 MHz and 5 KHz. The measurement of proton conductivity was conducted at 20 °C and 100% relative humidity. The cell assembly was similar to that used in the literature [21].

### 2.3. Monomer synthesis

#### 2.3.1. Preparation of dicarboxylic acid **3** containing 6F-BPA moiety [5]

Dicarboxylic acid **3** was prepared as depicted in Scheme 1. A 100 mL three-necked round-bottom flask equipped with a Dean-stark trap, a condenser, nitrogen inlet/outlet and magnetic stirrer was charged with 2-(4-chlorophenyl)benzoic acid **1** (10.4268 g, 40 mmol), 6F-BPA **2** (6.7246 g, 20 mmol), anhydrous $K_2CO_3$ (6.0812 g, 44 mmol), DMAc 30 mL and toluene 30 mL. Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was kept at 140 °C for 2 h. After the produced water was azeotroped off with toluene, the mixture was heated up to 175 °C and kept at this temperature for another 20 h. Upon cooling, the resulting mixture was diluted with 200 mL of water and then concentrated HCl was dropped with stirring to precipitate the product. By filtering, the residue was washed with water for three times. After dried, 14.99 g (yield 96%) of product was collected and directly used to prepare bisphthalazinone. Part of the pure compound was obtained by crystallizing the crude product from water/methanol for characterization. Mp 103–104 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.14$ (d, 4H), 7.20 (d, 4H), 7.40 (m, 6H), 7.62–7.73 (m, 8H), 7.98 (d, 2H).



Scheme 1. Synthesis of bisphthalazinone monomer **4**.

### 2.3.2. Preparation of bisphthalazinone **4** containing 6F-BPA moiety [5]

Bisphthalazinone was synthesized via the ring closure reaction of bicarboxylic acid **3** with hydrazine monohydrate in methanol (Scheme 1). To a 500 mL round-bottom flask equipped with a condenser containing 14.92 g of bicarboxylic acid **3** and 250 mL of methanol was slowly introduced 2 g (40 mmol) of hydrazine monohydrate. The clear solution was heated to reflux. The product precipitated out of the solution as the reaction proceeded. After 24 h, the heat was removed and the mixture was allowed to cool to room temperature. The precipitates were collected by filtration. The crude product was recrystallized from DMAc as white powders **4** (13.73 g, Yield 93%). Mp 314 °C.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.22$ (d, 4H), 7.27 (d, 4H), 7.42 (d, 4H), 7.65 (d, 4H), 7.73 (m, 2H), 7.90 (m, 4H), 8.33 (m, 2H), 12.86 (s, 2H).

$C_{43}H_{26}F_6N_4O_4$ (776.69): Calcd C 66.50, H 3.37, N 7.21; Found C 65.38, H 4.15, N 7.37.

## 2.4. Preparation of sulfonated polymer **7** via direct polymerization

### 2.4.1. Preparation of sulfonated polymer **7a**

To a 25 mL three-necked round-bottomed fitted with a Dean-stark trap, a condenser, a nitrogen inlet/outlet and magnetic stirrer were added bisphthalazinone monomer **4** 0.7767 g (1 mmol), SDFBP **5** 0.4223 g (1 mmol), anhydrous potassium carbonate 0.1935 g (1.4 mmol), 5 mL of DMSO and 6 mL of toluene. Nitrogen was purged through the reaction mixture with stirring for 10 min, and then the mixture was slowly heated to 140 °C with stirring for 2 h. After the produced water was azoetroped off with toluene. The temperature was slowly increased to 175 °C, followed by maintaining at this temperature for 20 h. The resulting viscous solution was cooled to 100 °C followed by diluting with 2 mL of DMSO and, thereafter, precipitated into 100 mL of 1:1 methanol/water. The precipitates were filtered and washed with water for three times. The fibrous residues were collected and dried at 110 °C under vacuum for 24 h. A total of 1.1093 g of polymer **7a** was obtained in high yield of 96%.

Proton-form polymer **7a** was obtained by precipitating the 5% solution of sodium-form polymer **7a** in DMAc out of 100 mL of 10% hydrogen chloride aqueous solution followed by keeping at 60 °C for 6 h. The precipitated polymer **7a** was dialyzed to remove inorganic salts. The final polymer **7a** was filtered off, washed with water for three times, and then dried at 110 °C for 24 h.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.66 (d, 2H), 7.82–7.93 (m, 12H), 8.38 (m, 4H).

$(C_{56}H_{32}F_6N_4O_{11}S_2 \cdot 6H_2O)_n$ $(1223.10)_n$: Calcd C 54.99, H 3.63, N 4.58, S 5.24; Found C 55.48, H 4.66, N 6.10, S 5.62.

### 2.4.2. Preparation of sulfonated polymer **7b**

The polymerization was carried out following the same procedure as the synthesis of polymer **7a**. The mixture of 0.3378 g (0.8 mmol) SDFBP **5** and 0.0436 g (0.2 mmol) DFBP **6** was used as the activated dihalide instead of neat sulfonated difluoride ketone **5**. After workup, 1.0753 g of polymer **7b** was obtained in a high yield of 96%.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.66 (d, 1.6H), 7.76 (d, 0.8H), 7.82–7.95 (m, 12.4H), 8.38–8.46 (m, 3.6H).

$(C_{56}H_{32}F_6N_4O_{9.8}S_{1.6} \cdot 4H_2O)_n$ $(1155.04)_n$: Calcd C 58.23, H 3.49, N 4.85, S 4.44; Found C 58.13, H 4.52, N 6.82, S 4.49.

### 2.4.3. Preparation of sulfonated polymer **7c**

The polymerization was carried out with the same procedure as the synthesis of polymer **7a**. The mixture of 0.2534 g

(0.6 mmol) SDFBP **5** and 0.0873 g (0.4 mmol) DFBP **6** was used as the activated dihalide instead of neat sulfonated difluoride ketone **5**. After workup, 1.0461 g of polymer **7c** was obtained in a high yield of 97%.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.66 (d, 1.2H), 7.76 (d, 1.6H), 7.82–7.95 (m, 12.8H), 8.37–8.45 (m, 3.2H).

$(C_{56}H_{32}F_6N_4O_{8.6}S_{1.2}\cdot 3H_2O)_n$ $(1105.00)_n$: Calcd C 60.87, H 3.49, N 5.07, S 3.48; Found C 60.60, H 4.19, N 6.89, S 3.56.

### 2.4.4. Preparation of sulfonated polymer 7d

The polymerization was carried out with the same procedure as the synthesis of polymer **7a**. The mixture of 0.2111 g (0.5 mmol) SDFBP **5** and 0.1091 g (0.5 mmol) DFBP **6** was used as the activated dihalide instead of neat sulfonated difluoride ketone **5**. After workup, 1.0192 g of polymer **7d** was obtained in a high yield of 96%.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.65 (d, 1H), 7.74 (d, 2H), 7.82–7.95 (m, 13H), 8.78–8.44 (m, 3H).

$(C_{56}H_{32}F_6N_4O_8S\cdot 4H_2O)_n$ $(1107.00)_n$: Calcd C 60.76, H 3.64, N 5.06, S 2.90; Found C 61.13, H 4.26, N 6.63, S 3.19.

### 2.4.5. Preparation of sulfonated polymer 7e

The polymerization was carried out with the same procedure as the synthesis of polymer **7a**. The mixture of 0.1689 g (0.4 mmol) SDFBP **5** and 0.1309 g (0.6 mmol) DFBP **6** was used as the activated dihalide instead of neat sulfonated difluoride ketone **5**. After workup, 1.0146 g of polymer **7e** was obtained in a high yield of 98%.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.66–7.74 (m, 3.2H), 7.82–7.95 (m, 13.2H), 8.38–8.46 (m, 2.8H).

$(C_{56}H_{32}F_6N_4O_{7.4}S_{0.8}\cdot 5H_2O)_n$ $(1109.01)_n$: Calcd C 60.65, H 3.82, N 5.05, S 2.31; Found C 60.57, H 4.39, N 6.79, S 2.52.

### 2.4.6. Preparation of sulfonated polymer 7f

The polymerization was carried out with the same procedure as the synthesis of polymer **7a**. The mixture of 0.0845 g (0.2 mmol) SDFBP **5** and 0.1746 g (0.8 mmol) DFBP **6** was used as the activated dihalide instead of sulfonated difluoride ketone **5**. After workup, 0.9458 g of polymer **7f** was obtained in a high yield of 95%.

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 7.20$ (d, 4H), 7.26 (d, 4H), 7.39 (d, 4H), 7.66–7.74 (m, 3.6H), 7.82–7.95 (m, 13.6H), 8.38–8.46 (m, 2.4H).

$(C_{56}H_{32}F_6N_4O_{6.2}S_{0.4}\cdot 2H_2O)_n$ $(1022.92)_n$: Calcd C 65.75, H 3.55, N 5.48, S 1.25; Found C 65.11, H 4.02, N 6.07, S 1.49.

### 2.5. Preparation of membrane

Membranes of the polymers **7a–f** were prepared by casting a 5–10% solution of polymers **7a–f** in DMAc on a glass plate in a dust-free environment. Membranes were dried at 60 °C for 12 h and then at 110 °C under vacuum for 48 h.

## 3. Results and discussion

### 3.1. Monomer synthesis

The bisphthalazinone monomer **4** was synthesized from 2-(4-chlrorophenyl) benzoic acid **1** and 6F-BPA **2** in two steps as shown in Scheme 1. First, the dicarboxylic acid **3** was prepared by the nucleophilic substitution reaction of **1** with **2** under the same conditions as the general formation of poly(arylene ether)s. Then dicarboxylic acid **3** was converted to bisphthalazinone **4** by refluxing with hydrazine monohydrate in methanol. The overall yield of two steps was quite high, implying that the reactions were readily carried out and easily controlled to be free of side reaction. The desirable bisphthalazinone **4** was confirmed by both elemental analysis and $^1$H NMR spectrum. Fig. 1 showed the $^1$H NMR spectrum of bisphthalazinone **4**. The peaks at 7.73, 7.90, 8.33 and 12.86 were the feature peaks of the phthalazinone moiety.

### 3.2. Synthesis and properties of sulfonated polymers 7a–f

As depicted in Scheme 2, the sulfonated polymers **7a–f** were synthesized by the reaction of bisphthalazinone monomer **4** with the mixture of sulfonated dihalo monomer **5** and

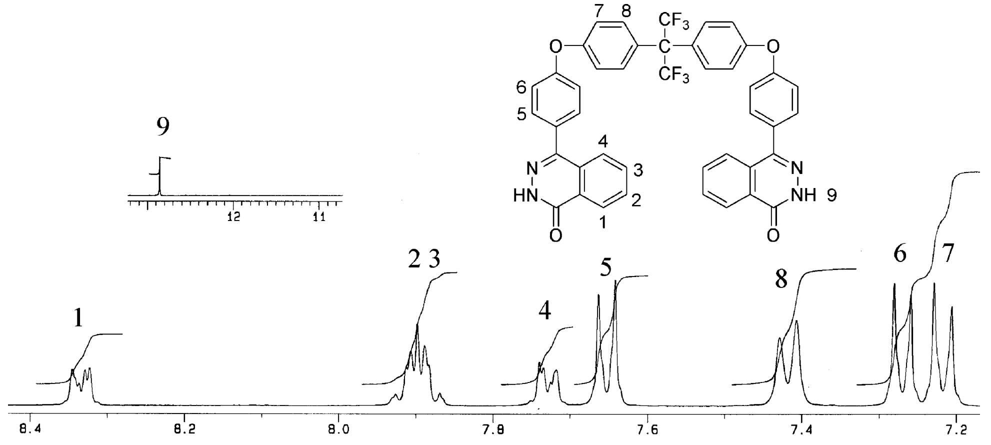
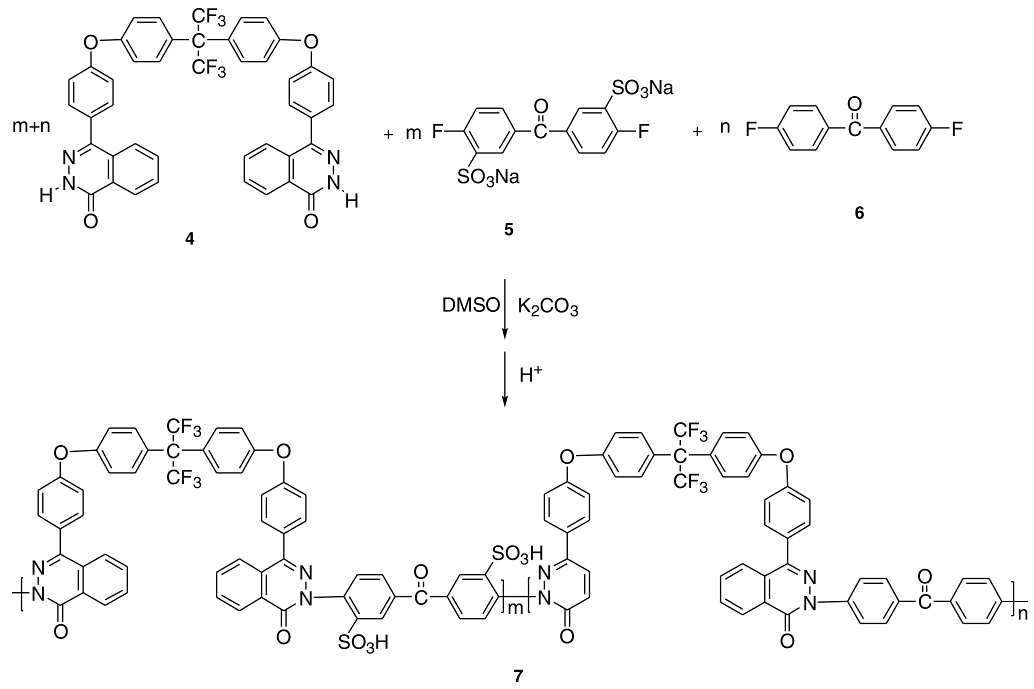


Fig. 1. $^1$H NMR spectrum of bisphthalazinone **4**.



Scheme 2. Synthesis of sulfonated poly(phthalazinone ether) **7**.

un-sulfonated dihalo monomer **6** in a dipolar aprotic solvent of DMSO. The sulfonated polymers **7a–f** with different sulfonation degrees can be readily afforded by adjudging the molar ratio of **5** to **6** (Table 1). The reaction had to be performed for a long time to obtain high molecular weight. In this regard, the reaction mixture should be carefully protected under a nitrogen flow. The inherent viscosities ($\eta_{\text{inh}}$) of the sulfonated polymers **7a–f** ranged from 0.87 to 1.22 dL/g, indicating the very high molecular weights of the resulting polymers. The structure of sulfonated polymers **7a–f** as given in Scheme 2 was confirmed by $^1$H NMR spectra and elemental analysis. Regarding the elemental analysis, the results deviated from the formula to some extent. Like other report concerning the sulfur content measurement for hydrated polymers [22], the data of the sulfur contents for polymers **7** are in good agreement with the proposed structures in case that the absorbed water was taken into account except for polymer **7f**. Presumably, the lower sulfur content of polymer **7f** resulted from the measurement

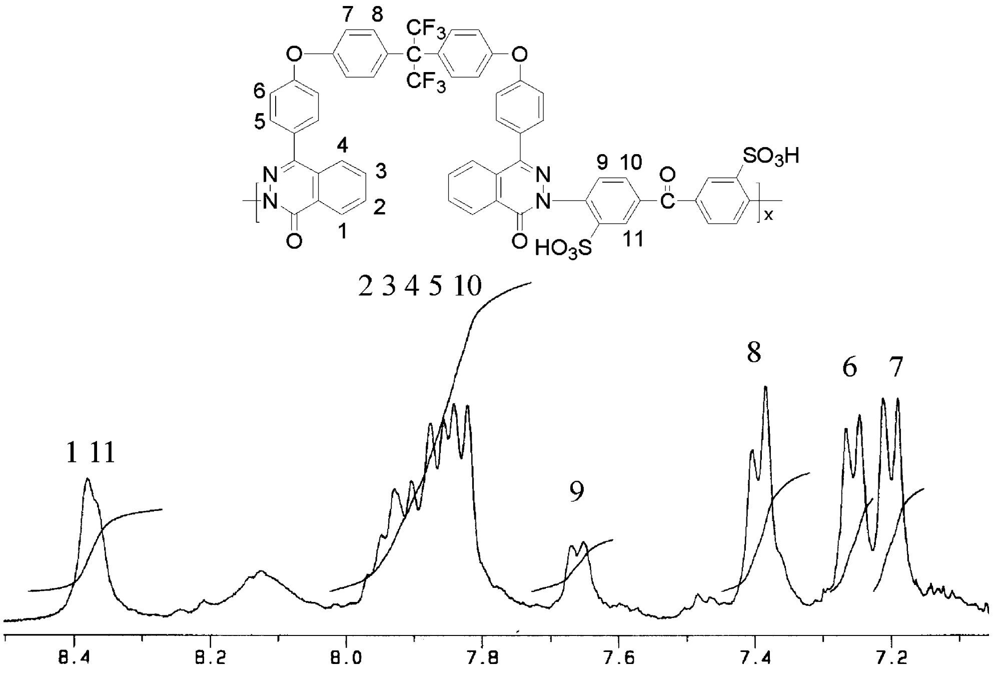


Fig. 2. $^1$H NMR spectrum of polymer **7a**.

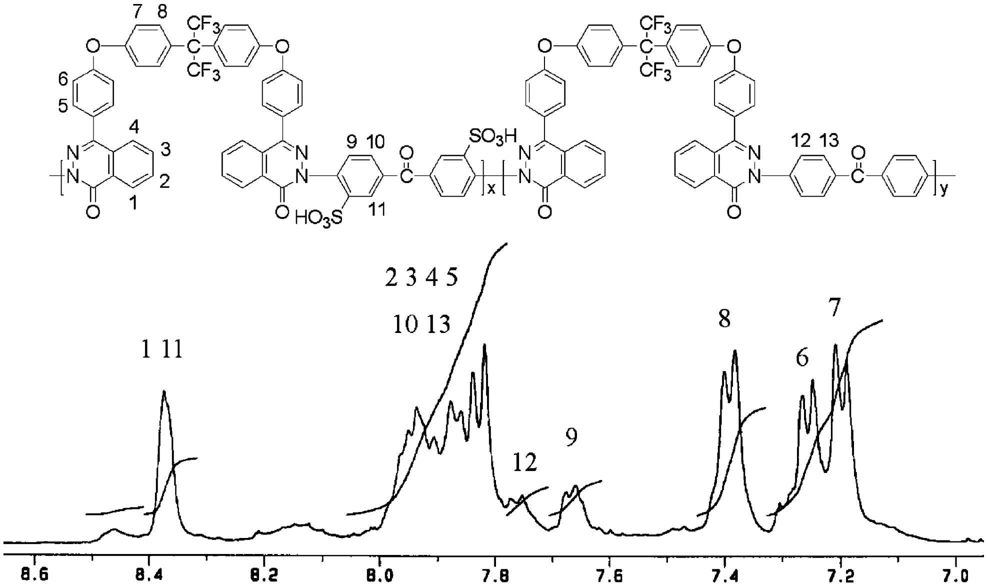


Fig. 3. $^1$H NMR spectrum of polymer **7b**.

Table 1

Polymerization results and analytical data for polymer **7a–f**

| | m/n | Yield (%) | $\eta_{inh}$[a] (dL/g) | Degree of sulfonation[b] | |
|---|---|---|---|---|---|
| | | | | Calculated | Measured by elemental analysis |
| **7a** | 10/0 | 96 | 1.22 | 2.00 | 2.14 |
| **7b** | 8/2 | 96 | 0.93 | 1.60 | 1.62 |
| **7c** | 6/4 | 97 | 0.87 | 1.20 | 1.23 |
| **7d** | 5/5 | 96 | 1.02 | 1.00 | 1.10 |
| **7e** | 4/6 | 98 | 0.95 | 0.80 | 0.87 |
| **7f** | 2/8 | 95 | 0.91 | 0.40 | 0.48 |

[a] Measured in 0.5 g/dL solution in DMAc at 25 °C.

[b] Number of sulfonic acid groups per repeating unit.

derivation. Figs. 2 and 3 showed $^1$H NMR spectra of polymer **7a** and **7b**, respectively. Although the spectra are complicated due to the overlap of the peaks of arylene proton, the assignment can be done by the comparison with corresponding monomers. A new peak at 7.76 attributed to un-sulfonated dihalo monomer. The peaks of proton on the dihalide moiety for all the polymers moved down field dramatically due to the strong electron withdrawing effect of the phthalazinone moiety.

The thermal stabilities of polymers **7a–f** were investigated using TGA and DSC. Similar to other sulfonated polymer, [23] a two-step degradation profile was observed for these polymers as shown in Fig. 4. The first weight loss at about 250 °C was attributed to the elimination of sulfonic acid groups, whereas the second weight loss peak at about 450 °C was due to the main-chain degradation of the polymers. This implies that the new polymer is much thermally stable than Nafion. From Table 2, it can be seen that the weight loss temperatures of polymers **7a–f** decreased with increasing the ratio of sulfonated monomer **5** to un-sulfonated monomer **6** in polar solvents because of the increase of sulfonic acid groups on polymer backbones. The sulfonic acid group on phenylene ring behaves un-stable when compared to the one without sulfonic acid group. There was no glass transition temperature observed from the DSC measurement of the polymers ranging from 30 to 300 °C due to their ionomer nature. The stability of the proton exchange membranes against oxidation was assessed by soaking the film in Fenton's reagent (30 ppm $FeSO_4$ in 30% $H_2O_2$) at 25 °C. It took 46 h before the film

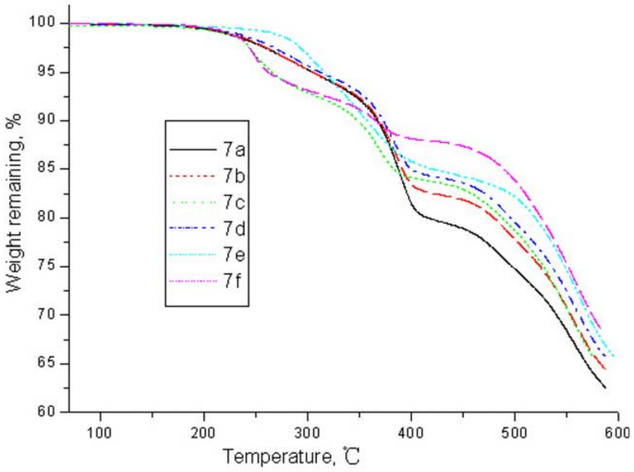


Fig. 4. TGA thermogram of sulfonated poly(phthalazinone ether) **7**.

Table 2
Physical properties for polymer **7a–f**

| | EW[a] | Resistence to oxidation[b] (h) | | Water uptake[c] (%) | $T_{d5\%}$[d] (°C) | Conductivity[e] (S/cm) |
|---|---|---|---|---|---|---|
| | | $t_1$ | $t_2$ | | | |
| **7a** | 558 | 46 | 52 | 36 | 305 | $4.32\times10^{-3}$ |
| **7b** | 677 | 60 | 132 | 22 | 306 | $1.81\times10^{-3}$ |
| **7c** | 876 | 69 | 153 | 19 | 266 | $1.07\times10^{-3}$ |
| **7d** | 1035 | 86 | 240 | 16 | 314 | $7.46\times10^{-4}$ |
| **7e** | 1274 | 130 | 300 | 14 | 309 | $1.08\times10^{-4}$ |
| **7f** | 2468 | –[f] | –[f] | 9 | 263 | $2.88\times10^{-5}$ |

[a] Equivalent weight per sulfonic acid group.
[b] $t_1$ and $t_2$ refer to the expended time that the membrane began to rupture and disappeared in the solution.
[c] Measured at 80 °C.
[d] Five percent weight loss temperature under nitrogen.
[e] Measured at 20 °C, 100% relative humidity for hydrate membrane samples, Nafion 117 was 2.03 $\times10^{-2}$ S/cm under the same condition.
[f] Undegradable.

started to break into pieces and 52 h for the polymer **7a** before it disappeared into the solution. The resistant-to-oxidation properties were improved with decreasing the sulfonation degree of the sulfonated polymers as can be seen in Table 2. These new polymers exhibited much better property of resistance to oxidation when compared with other sulfonated polymers [21,24–25]. This merit was attributed to the specially designed molecular structure of the polymer. If the sulfonic groups were located at *ortho* position to the phenyl ether bond, the strong electron withdrawing effect of sulfonic acid group will lead to that the ether bond can be easily attacked by the nucleophilic agent followed by the degradation of the polymer. As shown in Scheme 2, the sulfonated polymers synthesized in this work were prepared from bisphthalazinone monomer via N–C coupling reaction. As a result, the sulfonic groups were adjacent to the more stable aromatic C–N bond, and led to a kind of more stable polymer. The above-said properties endow the new polymer as a promising proton exchange membrane used for PEMFC, especially for high temperature PEMFC.

It is well known that incorporation of 4,4′-(hexafluoroisopropylidene) diphenol moiety (6F-BPA) in polymers is of great help to improve the solubility of rigid aromatic polymers in organic solvents [26,27]. Good solubility of polymers **7a–f** containing 6F-BPA moiety prepared in this work was also evidenced by being easily dissolved in DMSO, DMAc, dimethylformamide (DMF) or *N*-methylpyrroridone (NMP) to yield clear solutions. Tough and smooth films can be obtained by evaporating the used solvent(s) at a programmed temperature profile ranging from 60 to 120 °C. The solubility of polymers **7a–f** increased with increasing the ratio of sulfonated monomer **5** to un-sulfonated monomer **6** in polar solvents because of the increase of sulfonic acid groups on polymer backbones.

The water uptakes of the membranes were evaluated by measuring the weight change between dried and humidified forms at 80 °C. The results were tabulated in Table 2. Polymer **7a** bearing two sulfonic acid groups per repeating unit had the best hydrophilic ability. The water uptakes of the membrane increased with increasing the sulfonation degree of polymers. It should be noted that the membranes became slight brittle with the decrease of sulfonation degree due to the decrease in absorbed water. The proton conductivities of the membranes determined at 20 °C and 100% relative humidity indicated a good ability of proton transport for these new polymers (Table 2). The values increased gradually from $2.88\times10^{-5}$ S/cm for polymer **7f** to $4.32\times10^{-3}$ S/cm for polymer **7a**, with increasing sulfonation degree. For polymer **7a** with the highest proton conductivity, the conductivity value was very close to that of Nafion 117 membrane under the same determination conditions.

## 4. Conclusion

Novel poly(phthalazinone ether)s **7a–f** with different sulfonation degrees were synthesized by using bisphthalazinone **4** with sulfonated 4,4′-difluorobenzophenone **5** and 4,4′-difluorobenzophenone **6** by direct polymerization via N–C coupling reaction. Very high molecular weight polymers can be readily obtained. The synthesized polymers are soluble in dipolar aprotic solvents, and therefore, can be cast into tough and transparent films from a dilute solution of these new polymers. The new polymers exhibited a much highly thermal stable nature when compared with Nafion films. It also showed a greatly improved oxidation property than other reported sulfonated poly(arylene ether)s. Both reasonable water affinity and high proton conductivity together with good oxidative stability of the sulfonated polymers demonstrated the potential application of the polymers as a proton-exchange membrane for fuel cells.

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