Poly(phthalazinone ether ketone) Ionomers Synthesized via N−C Coupling Reaction for Fuel Cell Applications

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ABSTRACT: Sulfonated poly(phthalazinone ether ketone)s with different sulfonation degrees were directly polymerized via N−C coupling reaction. The resulting polymers with inherent viscosity ranging from 0.97 to 1.29 dL/g were characterized by ^{1}H NMR and elemental analysis. Membranes were obtained by casting 5% solution in DMAc (*N,N′*-dimethylacetamide) of the polymers at 60 °C. Because of their specially designed structure, the membranes of the polymer have excellent thermal and oxidative stability. TGA curves showed that the loss of sulfonic groups occurred at around 300 °C. The membranes demonstrated excellent acidic stability; their forms could be maintained for at least 47 h when subjected to Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C. For the polymer with a sulfonation degree of 2, the highest water uptake of 46% at 80 °C and the best proton conductivity of 1.77×10^{-2} S/cm at 95 °C 100% relative humidity were obtained, and a low E_a of 5.6 kJ/mol was calculated.

Introduction

Along with the progress of proton exchange membranes (PEMs), a number of approaches have been introduced to prepare novel nonfluorosulfonic polymers including polyketones,[1−4] polyimides,[5−11] poly(phenylene sulfide),[12] and polysulfones[13−16] as promising alternative materials to replace perfluorosulfonic copolymers. DuPont's Nafion, for exemple, possesses good mechanical strength, chemical stability, and high conductivity, but it has some drawbacks such as high cost, low conductivity at elevated temperature, and high methanol crossover.

There are two strategies to prepare sulfonated ionomers. The first one is postsulfonation of prepared polymers by different sulfonation agents such as concentrated sulfuric acid,[2−4,17−19] fuming sulfuric acid,[1,20] chlorosulfonic acid,[13,15,19,21] trimethylsilyl chlorosulfonate,[16] and sulfur trioxide−triethyl phosphate complex.[22] The other method is direct polymerization of modified sulfonated monomers.

In the postsulfonation reactions, the sulfonic acid groups are usually restricted to the activated position ortho to the aromatic ether bond, which might deteriorate the chemical stability of the polymer because of the cleavage of ether bond. In addition, the sulfonic acid groups are relatively easy to hydrolyze. Moreover, the degree of sullfonation is difficult to control, and too high sulfonation degree often results in solubility of functionalized polymers in water. Finally, postsulfonation might suffer from the partial degradation and cross-linking of polymers especially when strong sulfonation agents such as chlorosulfonic acid are employed.

However, the aforementioned shortcomings can be avoided and the stability of polymer can be enhanced through molecular design. More recently, Miyatake et al. have designed and reported the aromatic copolymers containing sulfonated tetraphenylphenylene, hexaphenylbiphenylene, fluorinated alkane, and perfluorobiphenylene moieties[23] and tetraphenylphenylene, perfluorobiphenylene, and tetrakis(sulfophenyl)phenylene.[24] In previous work, we reported the synthesis of poly(arylene ether sulfone)s with pendant phosphorous acid groups meta to the ether group[25] and the synthesis of poly(arylene ether)s from masked bisphenol whose ortho positions to the ether bond were occupied by methyl groups, in which the sulfonation can only take place at the para positions on the pendant phenyl rings.[26,27]

It is of great interest to develop sulfnonated polymers by direct polymerization, of which the sulfonic acid groups are attached to the deactivated aromatic rings. It is expected that such sulfonic acid groups might enhance stability and higher acidity of the resulting polymer and thus make the transportation of protons more easily.[28−34] In the present investigation, we employed bisphthalazinone, dihalide, and sulfonated dihalide monomers to directly polymerize to give high-molecular-weight sulfonated polymers via N−C coupling reaction. Since it is the heterocyclic N−C bond ortho to the sulfonic acid group but not to the aromatic ether bond, such sulfonated polymers showed excellent thermal, chemical stability, and resistance to oxidation. Moreover, the membranes of the polymers had reasonable water affinity and good proton conductivity.

Experimental Section

Materials. 2-(4-Chlorophenyl)benzoic acid was prepared from phthalic anhydride and chlorobenzene via a Friedel−Crafts reaction. 4,4′-Dihydrodiphenyl, 4,4′-difluorobenzophenone, and 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 as described in the literature.[35] Reagent-grade *N,N′*-dimethylacetamide (DMAc), toluene, methanol, and anhydrous potassium carbonate were obtained from commercial sources and used without further purification.

Instrumentation. The ^{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; 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

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points were measured on a melting point testing apparatus. The thermal stability of the polymers from 70 to 600 °C was determined with a Seiko SSC-5200 thermogravimetric analyzer [thermogravimetric analysis (TGA)/differential thermal analysis] under a 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 a solution of 0.5 g/dL in DMAc at 30 °C with a calibrated Ubbelohde viscometer. The water uptake of the membrane was evaluated by measuring the weight change between dried and humidified forms at 80 °C. The ion exchange capacity (IEC) has been determined by titration. 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 proton conductivity of the membrane was measured at temperatures ranging from 20 to 95 °C and at 100% relative humidity. The cell assembly was similar to that used in the literature.[23]

Preparation of Dicarboxylic Acid 3 Containing Biphenyl Moiety.[36] 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), 4,4′-dihydrodiphenyl, **2** (3.7242 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 150 °C for 3 h. After the produced water was azeotroped off with toluene, the mixture was heated to 170 °C and kept at this temperature for another 20 h. After cooling, the resulting mixture was diluted with water (200 mL), and then concentrated HCl was added dropwise to the stirred mixture to precipitate the product. After filtration, the residue was washed with water for three times. After dried, the desired product (12.00 g, 95%) was collected and directly used to prepare bisphthalazinone. Some pure compound was separated by crystallizing the crude product from water/methanol for characterization; mp 282−283 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: = 7.09 (d, 4H), 7.20 (d, 4H), 7.40 (d, 2H), 7.62−7.75 (m, 12H), 7.98 (d, 2H).

Preparation of Bisphthalazinone 4 Containing Biphenyl Moiety.[36] To a 500 mL round-bottom flask equipped with a condenser containing 11.77 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 mixture was allowed to cool to room temperature. The precipitates were collected by filtration. The crude product was recrystallized from DMAc to yield **4** as a white powder (11.03 g, 95%); mp 358−360 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.20−7.23 (m, 8H), 7.63 (d, 4H), 7.73−7.75 (m, 6H), 7.88−7.92 (m, 4H), 8.33 (m, 2H), 12.85 (s, 2H). $C_{40}H_{26}N_4O_4$ (626.67): Calcd C, 76.66; H, 4.18; N, 8.94. Found C, 75.86; H, 4.68; N, 8.37.

Preparation of Sulfonated Poly(phthalazinone ether ether ketone) 7a. To a 25 mL three-necked round-bottomed flask fitted with a Dean-stark trap, a condenser, a nitrogen inlet/outlet, and magnetic stirrer was added bisphthalazinone monomer **4 (**0.6267 g, 1 mmol), sulfonated difluoride ketone **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 and kept stirring for 2 h. After water generated was azeotroped off with toluene. The temperature was slowly increased to 175 °C. The temperature was maintained for 20 h, and the viscous solution was cooled to 100 °C followed by diluting with 2 mL of DMSO and, thereafter, precipitated into 100 mL of 1: 1 (v/v) 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 0.9423 g of polymer **7a** was obtained in high yield of 93%.

Proton-form polymer was obtained by precipitating the 5% solution of sodium-form polymer in DMAc out of 100 mL of 10% hydrogen chloride aqueous solution followed by keeping at 60 °C for 6 h. The precipitate polymer was dialyzed to remove inorganic salts. The treated polymer was filtered and washed with water for three times and then dried at 110 °C for 24 h. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.20 (d, 8H), 7.66 (d, 2H), 7.71 (d, 4H), 7.80 (m, 4H), 7.86−7.98 (m, 8H), 8.38 (m, 4H). $(C_{53}H_{32}N_4O_{11}S_2{\cdot}6H_2O)_n$ $(1073.08)_n$: Calcd C, 59.32; H, 4.28; N, 5.22; S, 5.98. Found C, 59.25; H, 5.15; N, 6.84; S, 6.07.

Preparation of Sulfonated Poly(phthalazinone ether ketone) 7b. The polymerization was carried out with the same procedure used for the synthesis of polymer **7a**. The mixture of 0.3378 g (0.8 mmol) of sulfonated difluoride ketone **5** and 0.0436 g (0.2 mmol) of 4,4′-difluorobenzophenone **6** was used as an activated dihalide instead of sulfonated difluoride ketone **5**. After workup, 0.9453 g of polymer **7b** was obtained (in yield of 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.19 (m, 8H), 7.65−7.72 (m, 6.4H), 7.79−7.81 (m, 3.6H), 7.86−7.96 (m, 8.8H), 8.38 (m, 3.6H). $(C_{53}H_{32}N_4O_{9.8}S_{1.6}{\cdot}6H_2O)_n$ $(1041.02)_n$: Calcd C, 61.15; H, 4.26; N, 5.44; S, 4.93. Found C, 60.66; H, 4.50; N, 5.23; S, 5.17.

Preparation of Sulfonated Poly(phthalazinone ether ketone) 7c. The polymerization was carried out with the same procedure used for the synthesis of polymer **7a**. The mixture of 0.2534 g (0.6 mmol) of sulfonated difluoride ketone **5** and 0.0873 g (0.4 mmol) of 4,4′-difluorobenzophenone **6** was used as an activated dihalide instead of sulfonated difluoride ketone **5**. After workup, 0.9046 g of polymer **7c** was obtained (in yield of 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.18 (m, 8H), 7.65−7.72 (m, 6.8H), 7.79−7.80 (m, 3.2H), 7.86−7.95 (m, 9.6H), 8.38 (m, 3.2H). $(C_{53}H_{32}N_4O_{8.6}S_{1.2}{\cdot}5H_2O)_n$ $(991.00)_n$: Calcd C, 64.24; H, 4.27; N, 5.65; S, 3.88. Found C, 64.23; H, 4.62; N, 5.30; S, 4.04.

Preparation of Sulfonated Poly(phthalazinone ether ketone) 7d. The polymerization was carried out with the same procedure used for the synthesis of polymer **7a**. The mixture of 0.2111 g (0.5 mmol) of sulfonated difluoride ketone **5** and 0.1091 g (0.5 mmol) of 4,4′-difluorobenzophenone **6** was used as an activated dihalide instead of sulfonated difluoride ketone **5**. After workup, 0.8841 g of polymer **7d** was obtained (in yield of 97%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.18 (m, 8H), 7.65−7.70 (m, 7H), 7.78−7.80 (m, 3H), 7.86−7.95 (m, 10H), 8.38 (m, 3H). $(C_{53}H_{32}N_4O_8S{\cdot}5H_2O)_n$ $(974.99)_n$: Calcd C, 65.29; H, 4.34; N, 5.75; S, 3.28. Found C, 65.90; H, 4.62; N, 5.39; S, 3.38.

Preparation of Sulfonated Poly(phthalazinone ether ketone) 7e. The polymerization was carried out with the same procedure used for the synthesis of polymer **7a**. The mixture of 0.1689 g (0.4 mmol) of sulfonated difluoride ketone **5** and 0.1309 g (0.6 mmol) of 4,4′-difluorobenzophenone **6** was used as an activated dihalide instead of sulfonated difluoride ketone **5**. After workup, 0.8537 g of polymer **7e** was obtained (in yield of 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.18 (m, 8H), 7.65−7.70 (m, 7.2H), 7.78−7.80 (m, 2.8H), 7.86−7.95 (m, 10.4H), 8.38 (m, 3H). $(C_{53}H_{32}N_4O_{7.4}S_{0.8}{\cdot}4H_2O)_n$ $(940.96)_n$: Calcd C, 66.24; H, 4.20; N, 5.83; S, 2.67. Found C, 67.93; H, 4.37; N, 5.75; S, 2.98.

Preparation of Sulfonated Poly(phthalazinone ether ketone) 7f. The polymerization was carried out with the same procedure used for the synthesis of polymer **7a**. The mixture of 0.0845 g (0.2 mmol) of sulfonated difluoride ketone **5** and 0.1746 g (0.8 mmol) of 4,4′-difluorobenzophenone **6** was used as activated dihalides instead of sulfonated difluoride ketone **5**. After workup, 0.7863 g of polymer **7f** was obtained (in yield of 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.18 (m, 8H), 7.65−7.70 (m, 7.6H), 7.78−7.80 (m, 2.4H), 7.86−7.95 (m, 11.2H), 8.38 (m, 2.4H). $(C_{53}H_{32}N_4O_{6.2}S_{0.4}{\cdot}2H_2O)_n$ $(874.91)_n$: Calcd C, 72.76; H, 4.15; N, 6.40; S, 1.47. Found C, 73.03; H, 4.26; N, 5.91; S, 1.62.

Preparation of Membranes. Membrane of the proton-form polymer was prepared by casting a 5% solution in DMAc on a glass plate in a dust-free environment. Membrane was dried at 60 °C for 12 h and then at 110 °C under vacuum for 48 h.

Scheme 1. Synthesis of Bisphalazinone Monomer 4

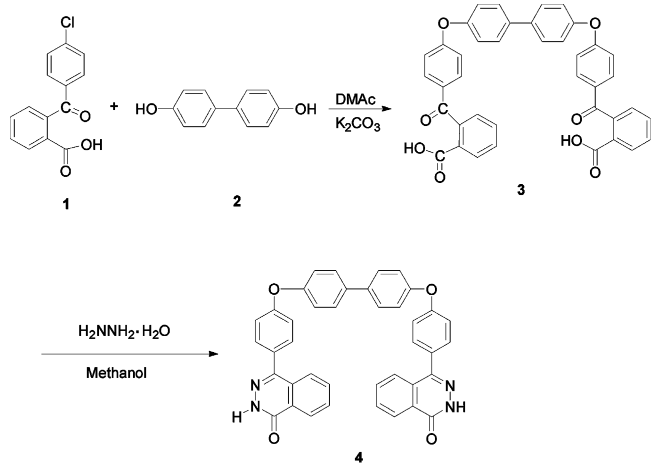


Table 1. Polymerization Results and Analytical Data of Polymers 7a−f

				SD^b	
	m/*n*	yield (%)	$\eta_{\mathrm{inh}}{}^a$ (dL/g)	calcd	measd by element analysis
7a	10/0	93	1.02	2.00	2.03
7b	8/2	98	1.22	1.60	1.67
7c	6/4	98	1.16	1.20	1.24
7d	5/5	97	0.97	1.00	1.02
7e	4/6	96	1.29	0.80	0.87
7f	2/8	93	1.03	0.40	0.44

[a] Tested in 0.5 g/dL solution in DMAc at 30 °C. [b] Degree of sulfonation, number of sulfonic acid groups per repeating unit.

Results and Discussion

Synthesis of Sulfonated Poly(phthalazinone ether ketone) 7. Bisphthalazinone monomer **4** was synthesized in a two-step sequence as shown in Scheme 1. The nucleophilic substitution reaction of **1** with **2** gave dicarboxylic acid, which was converted to bisphthalazinone **4** by refluxed with hydrazine monohydrate in methanol via the ring-closure reaction. The desired bisphthalazinone **4** was confirmed by elemental analysis and the ^{1}H NMR spectrum.

As depicted in Scheme 2, sulfonated poly(phthalazinone ether ketone) **7** was successfully synthesized via novel N−C coupling reaction. Polycondensation of the bisphthalazinone **4** with stoichiometric amounts of activated dihalides (**5** and **6**) was carried out in the presence of excess potassium carbonate as base in DMSO in a manner analogous to the conventional polyether synthesis. The degree of sulfonation was controlled by changing the ratios of monomers **5** and **6**, and the amounts of **5** and **6** were equal to that of **4**. The reaction was first held at 140 °C for 2 h under nitrogen to azeotropically remove water with toluene and then was heated to 175 °C for 20 h to afford sulfonated polymer **7**. The polymerization results and the characterization data of **7a**−**f** are displayed in Table 1. Figure 1, 2, and 3 showed the ^{1}H NMR spectra of polymers **7a**, **7b**, and **7c**, respectively. Although the systems were complicated because of the overlap of chemical shifts of aryl hydrogen, assignment was made possible by comparison with the data of the monomer and the corresponding polymers. It can be seen from the figures that because of the strong electron-withdrawing effect of the phthalazinone, the signals of hydrogen on the former dihalide aryl ring moved downfield dramatically.

Properties of Sulfonated Poly(phthalazinone ether ketone) 7. The thermal stability of the polymer was investigated using TGA and DSC. A two-step degradation profile observed for the polymers is shown in Figure 4. The first weight loss at about 300 °C was attributed to the elimination of sulfonic acid group, whereas the second weight loss peak at about 500 °C was due to main-chain degradation. It also can be seen from Figure 4 that the beginning and the end of the first weight loss were quite similar, but the curves were steeper with the increase of sulfonation degree. To minimize the effects of the absorbed water, the samples were heated to 200 °C to get rid of any water in nitrogen flow followed by cooling to 70 °C, and the trace from 70 to 600 °C was recorded. The second weight losses had the same pattern as the first one, which implied that

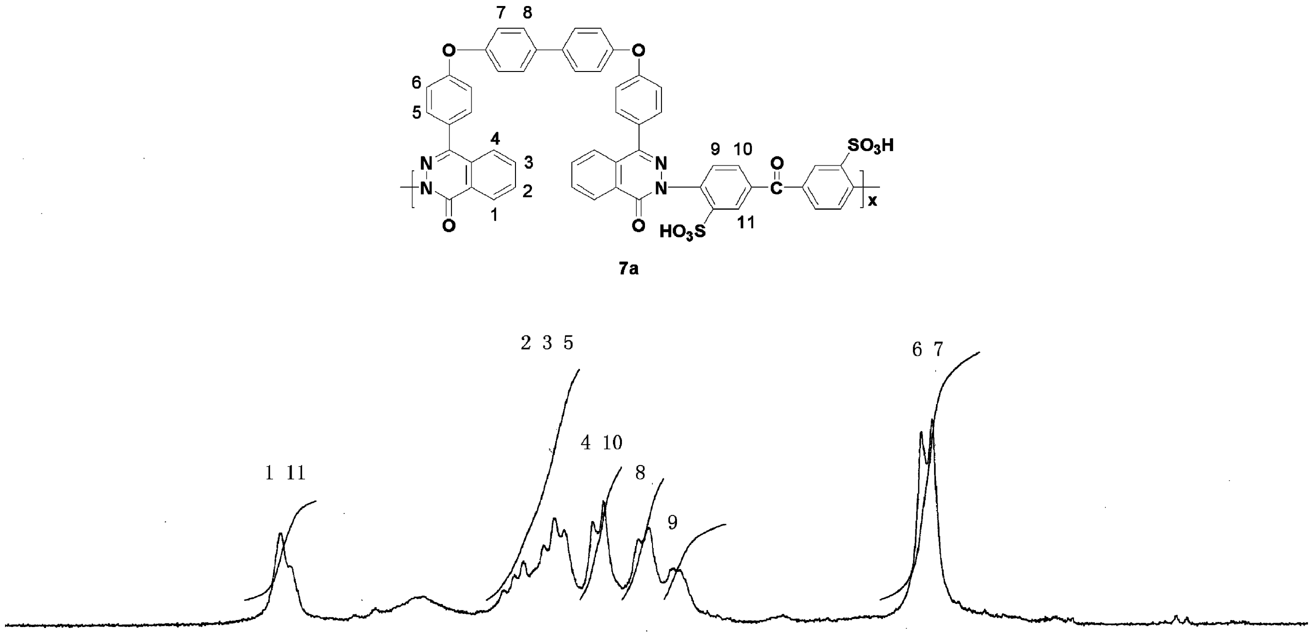


Figure 1. ^{1}H NMR spectrum of sulfonated poly(phthalazinone ether ether ketone) **7a**.

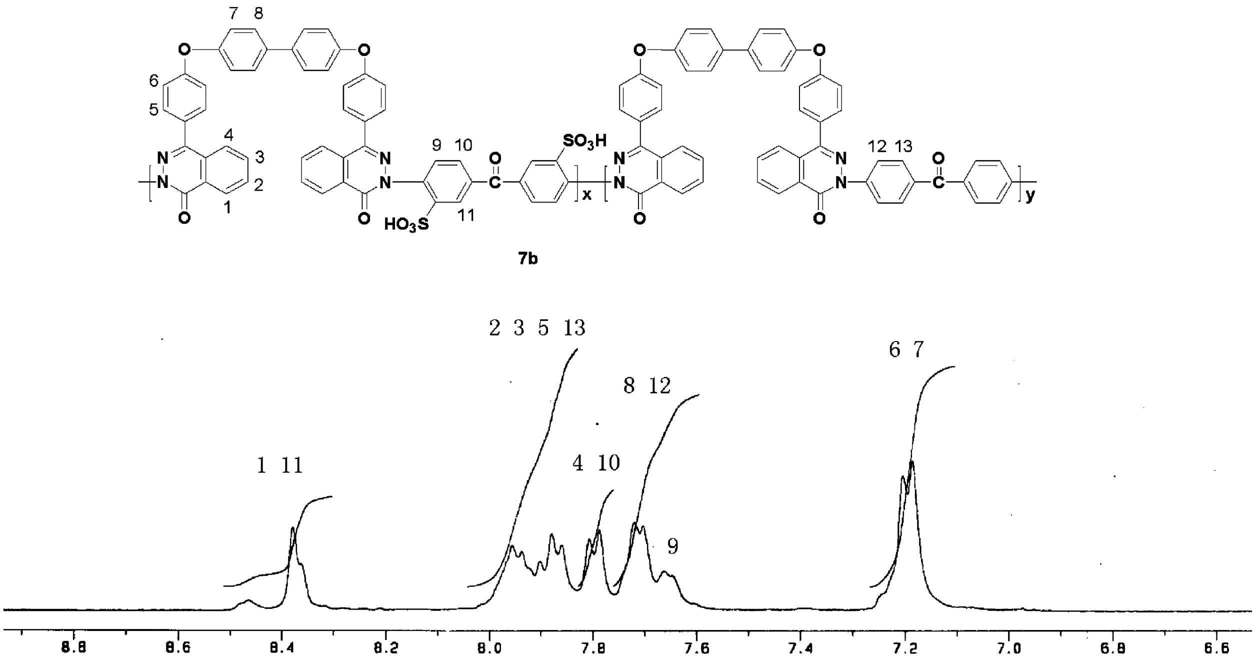


Figure 2. ^{1}H NMR spectrum of sulfonated poly(phthalazinone ether ether ketone) **7b**.

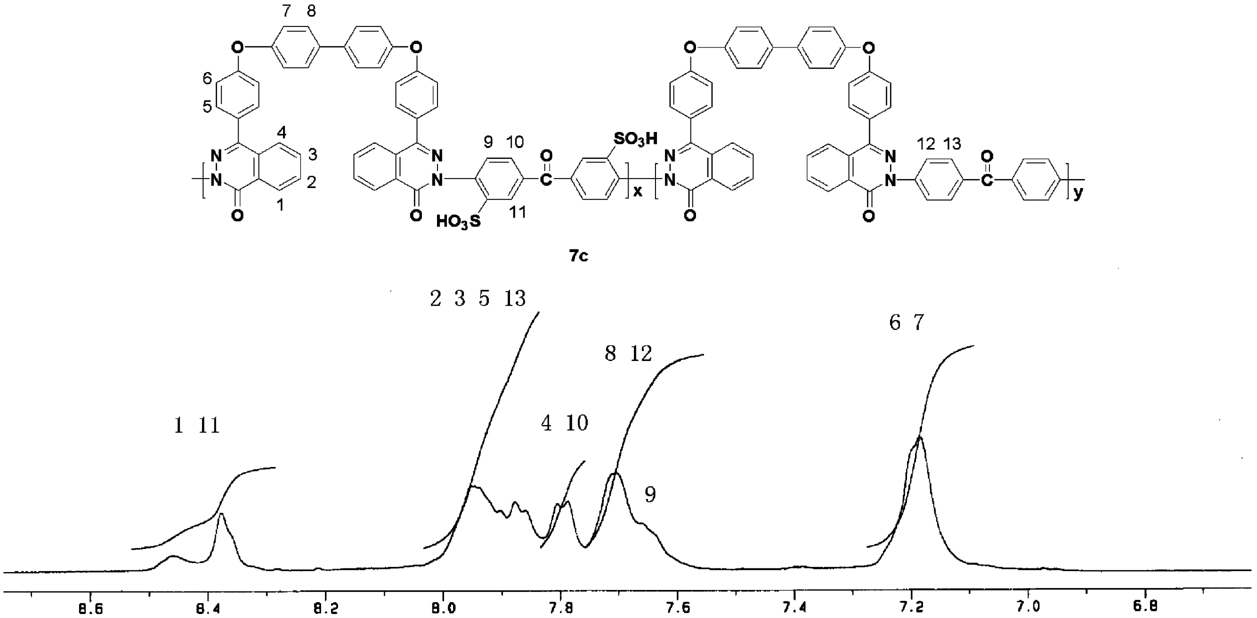


Figure 3. ^{1}H NMR spectrum of sulfonated poly(phthalazinone ether ether ketone) **7c**.

the degradation of the backbones were quite similar. DSC measurement of the polymer within a temperature from 30 to 300 °C did not reveal glass transition temperatures below thermal decomposition.

The solubility of the polymers and the properties of their membrane are shown in Table 2. All the polymers were soluble in common aprotic solvents, such as DMSO, DMAc, dimethylformamide (DMF), and *N*-methylpyrroridone (NMP). Tough and smooth film was obtained by evaporating the solvent of the 5% solution in DMAc at 60 °C in a dust-free environment.

The water uptakes of the membranes were evaluated by measuring the weight change between dried and humidified forms at 80 °C. The membrane samples were immerged in the deionized water at 80 °C for 24 h and wiped with a filter paper and immediately weighed. Then the membranes were dried at 110 °C for 24 h, and the weight of sample which was free of water was obtained. The water uptakes of membranes were reported in weight percentage of water (g) per dry membrane (g).

The ion exchange capacity (IEC) of the membrane was determined by titration. The membranes were first immerged in 2 M NaCl solution for 24 h to exchange the sodium ions for protons. The resulting solution was then titrated with 0.1 M NaOH using phenolphthalein as an indicator.

As shown in Table 2, the water uptake was dropped with the decrease of IEC which was proportional to sulfonation degree. When the sulfonation degree was 2, the highest water uptake was obtained. It dropped gradually from 46% to 13% as the sulfonation degree decreased.

Membrane stability to oxidation was investigated by soaking the film in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C. The results were reported by the

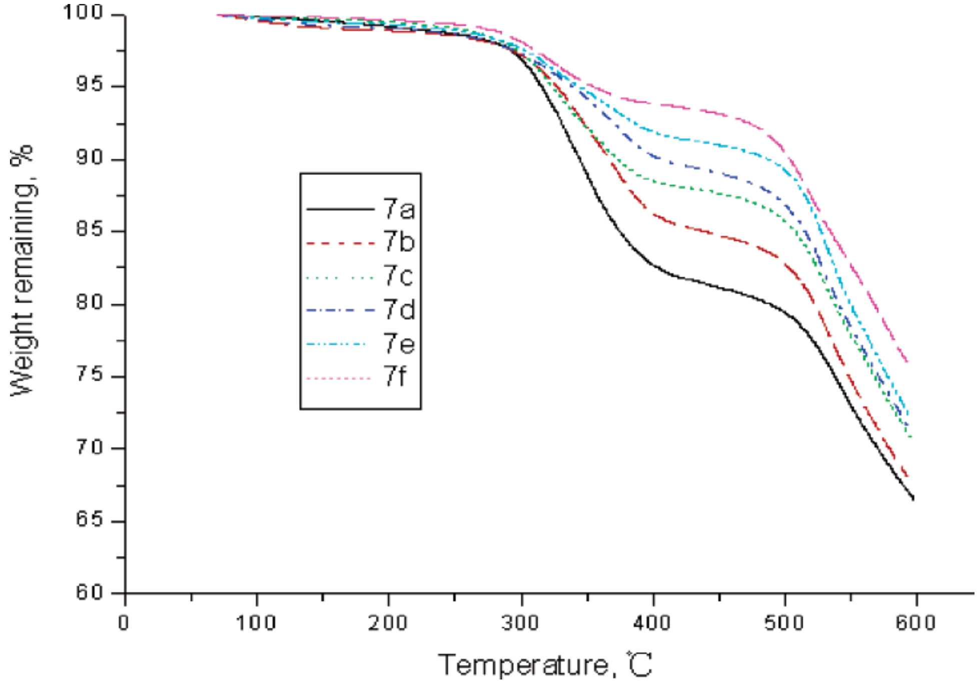


Figure 4. TGA curves of sulfonated poly(phthalazinone ether ether ketone)s **7a–f**.

Table 2. Solubility of Polymers 7a–f and Properties of Their Membranes

		resistance to oxidation,[a] h			IEC, meq/g		
	solubility	t_1	t_2	water uptake,[b] %	calcd	by titration	E_a, kJ/mol
7a		47	51	46	2.04	2.07	5.6
7b	DMF	49	63	38	1.55	1.71	13
7c	DMAc	51	250	33	1.31	1.33	15
7d	DMSO	51	250	28	1.10	1.13	19
7e	NMP	54	250	21	0.89	0.92	22
7f		-[d]	-[d]	13	0.45	0.48	26

[a] t_1 and t_2 refer to the expended time that the membrane began to rupture and disappeared in the solution. [b] Measured at 80 °C. [c] Calculated from the slope of the Arrhenius plot, Nafion 117 was 11 kJ/mol. [d] Undegradable.

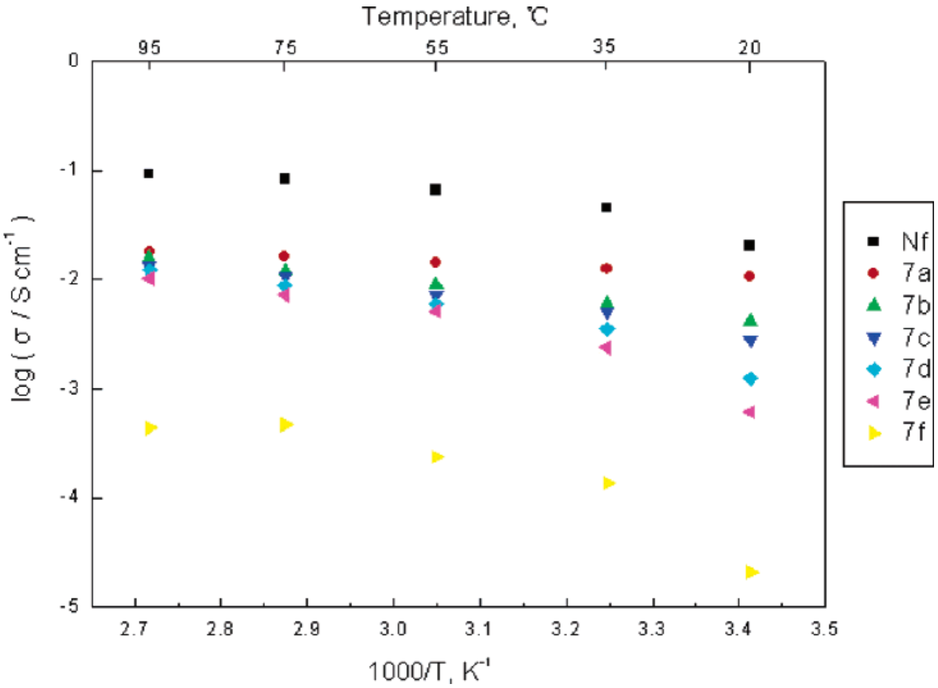
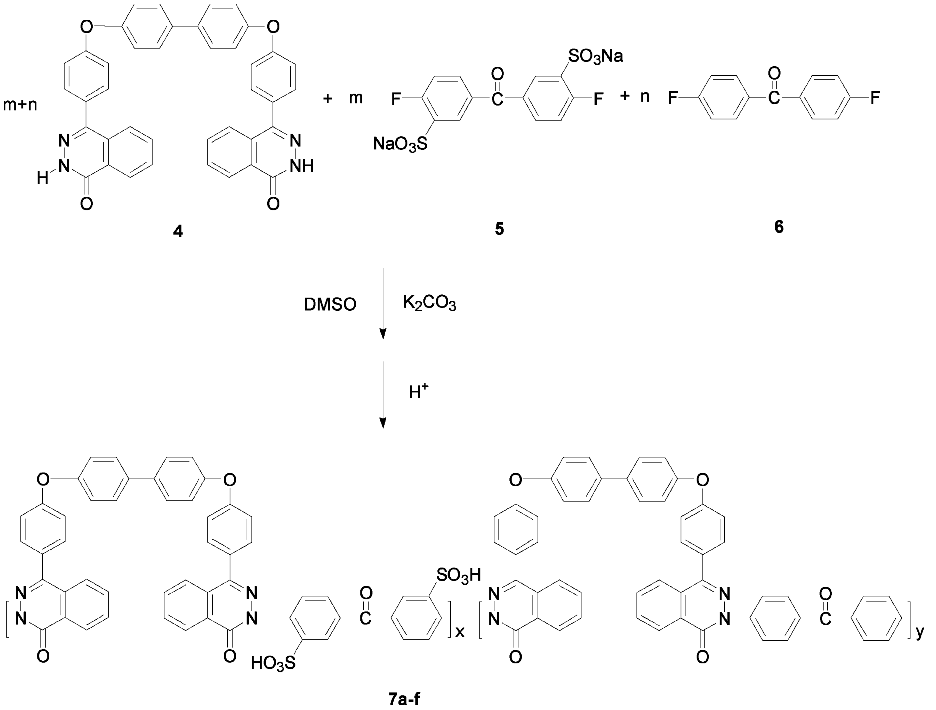
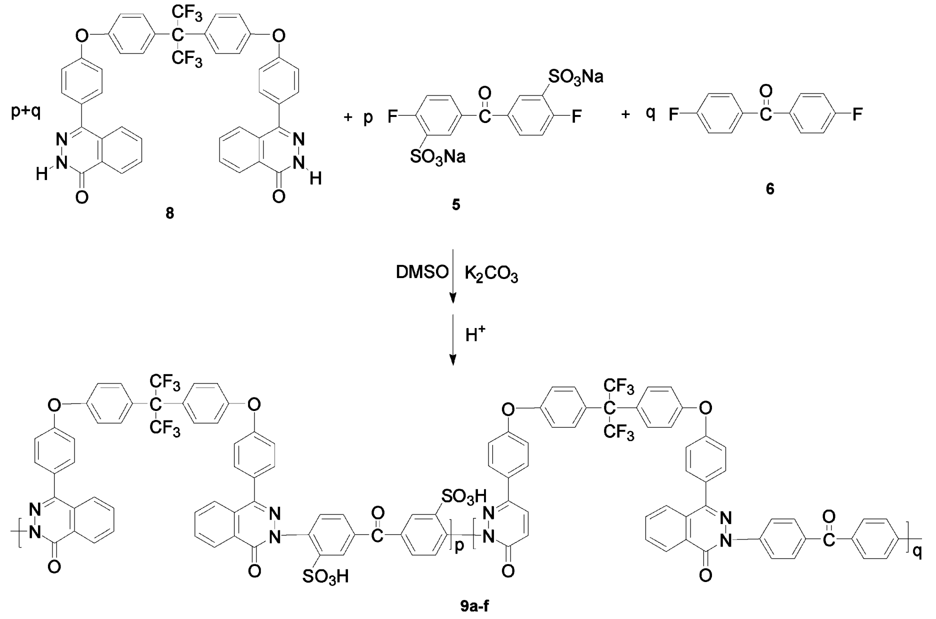


Figure 5. Temperature dependence of the proton conductivity for polymers **7a–f** with different sulfonation degrees and Nafion 117 (denoted as Nf) at 100% RH.

Scheme 2. Synthesis of Sulfonated Poly(phthalazinone ether ether ketone) 7a–f



Scheme 3. Synthesis of Sulfonated Poly(phthalazinone ether ether ketone) 9a–f



time that the membrane took to become brittle and disappear in the solution. The results listed in Table 2 indicated that the membranes were more resistant to oxidation than other sulfonated polymers.[6–7,23] The antioxidation properties of the synthesized polymers validate our assumption that the sulfonic groups on the polymers adjacent to the N–C heterocyclic bond and placed in the deactivated aromatic rings have better resistance to oxidation. Moreover, the N–C bonds exhibited much stable oxidation property due to that nitrogen atom locates on an aromatic ring, which stabilized the N–C bonds.

Proton Conductivity of Sulfonated Poly(phthalazinone ether ketone) 7. The influence of temperature on the proton conductivity of the membranes was assessed in the temperature range from 20 to 95 °C and at 100% relative humidity. Prior to the measurements, the membrane was allowed to equilibrate with the saturated water vapor at a specific temperature, and the data were collected after the proton conductivity had reached a constant value. (It usually took 2–3 h.) The experimental results are summarized in Figure 5. The proton conductivity of these membranes increased with increasing temperature with the exception of polymer **7f** which began to slightly decrease at 95 °C. Polymer **7a** with a sulfonation degree of 2 showed the highest conductivity of 1.77×10^{-2} S/cm at 95 °C. It was noteworthy that all values for polymer **7a** were higher than 10^{-2} S/cm in the test temperature range, and other copolymers **7b–e** can also surmount the value of 10^{-2} S/cm at elevated temperatures.

Table 3. Physical Properties of Polymers 9a−f

	p/q	η_{inh}[a]	SD[b]	resistance to oxidation,[c] h		water uptake,[d] %	conductivity,[e] S/cm
				t_1	t_2		
9a	10/0	1.22	2.0	46	52	36	4.32×10^{-3}
9b	8/2	0.93	1.6	60	132	22	1.81×10^{-3}
9c	6/4	0.87	1.2	69	153	19	1.07×10^{-3}
9d	5/5	1.02	1.0	86	240	16	7.46×10^{-4}
9e	4/6	0.95	0.8	130	300	14	1.08×10^{-4}
9f	8/2	0.91	0.4	*f*	*f*	9	2.88×10^{-5}

[a] Tested in 0.5 g/dL solution in DMAc at 25 °C. [b] Degree of sulfonation, number of sulfonic acid groups per repeating unit. [c] t_1 and t_2 refer to the expended time that the membrane began to rupture and disappeared in the solution. [d] Measured at 80 °C. [e] Measured at 20 °C 100% relative humidity for hydrate membrane samples, Nafion 117 was 2.03×10^{-2} S/cm under the same conditions. [f] Undegradable.

The apparent activation energies (E_a) for the conduction processes derived from the Arrhenius relation are listed in Table 2. It can be seen that the E_a values increase with the decrease in the sulfonation degree. Polymer **7a** was characterized by its low E_a value of 5.6 kJ/mol, which is presumably attributed to its regular sulfonation structure and higher sulfonation degree compared with other copolymers **7b−f**, leading to transport proton easily. The low activation energy also resulted from the low EW value for the synthesized membrane when compared with Nafion. The ionic polymers were susceptibly separated into two phases, i.e., hydrophilic ionic domain and hydrophobic polymeric matrix. The fully hydrated membrane then provides the ionic pathway for proton transportation.

Comparison of Sulfonated Poly(phthalazinone ether ketone)s 7 and 9. Bisphthalazinone **8** containing hexafluoroisopylidene diphenyl moiety could also react with activated dihalides (**5** and **6**) to offer high-molecular-weight sulfonated poly(phthalazinone ether ketone) **9** (Scheme 3). Table 3 displayed the physical properties of polymers **9a−f**. Polymers **9a−f** showed improved property of resistance to oxidation compared to polymers **8a−f** for they had higher EW (equivalent weight) values. But when the hydrophobic hexafluoroisopylidene group was introduced to the polymer, the water uptakes of their membranes decreased, which led to the decrease of proton conductivity. Furthermore, the decrease in absorbed water made the membranes become a little brittle. The results indicated that polymer **8** has an advantage over polymer **9**.

Conclusions

Sulfonated poly(phthalazinone ether ether ketone)s with different sulfonation degrees were synthesized via N−C coupling reactions using bisphthalazinone monomer, difluoride, and sulfonated difluoride. This is the first report that such strategy was employed to prepare sulfonated polymer. Because of the sulfonic groups adjacent to the N−C heterocyclic bond, the polymers were found to have better thermal and oxidative stability. The membranes of the polymers showed reasonable water affinity and good proton conductivity, which may find wide applications as proton exchange membranes for fuel cells.

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