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ORIGINAL PAPER

Synthesis and characterization of partially fluorinated poly(fluorenyl ether ketone)s with different degrees of sulfonation as proton exchange membranes

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Abstract Partially fluorinated poly(fluorenyl ether ketone)s with different degree of sulfonation were successfully synthesized by the sulfonation of the designed parent polymer. The sulfonation took place only at the specific (2, 7)-position on the fluorenyl groups due to the positions adjacent to the ether bond occupied by methyl groups. The sulfonated polymers are soluble in common organic solvents and can readily be cast into tough and smooth films from their solutions. The properties of proton conductivity, water uptake, thermal and oxidative stability for the membranes were investigated. It was found that the oxidative stability of the membrane decreased with increasing the degree of sulfonation. However, the partially fluorinated membrane with high degree of sulfonation exhibited better oxidative stability compared to the non-fluorinated analogy with low degree of sulfonation. The proton conductivity of the membranes increased with increasing the degree of sulfonation and temperature. Moreover, the membranes also showed good thermal and hydrolytic stabilities.

Keywords Poly(ether ketone)s · Fluoropolymers · Proton exchange membranes · Oxidative stability

Introduction

As the key component of proton exchange membrane fuel cell (PEMFC), PEM plays an important role in fuel cells, which provides the ionic pathway and acts as a

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gas separator [1]. Among all kinds of reported proton-conducting polymer electrolytes, Nafion is typically used as the polymer electrolytes in PEMFC because of its excellent chemical and mechanical stabilities, as well as its high proton conductivity [2, 3]. However, it suffers from several shortcomings. Its high cost presents a major obstacle for widespread application in fuel cell. The loss of proton conductivity above 80 °C and the low resistance toward methanol crossover of the materials impose restrictions on the operating temperature and choice of possible fuels. As a result, considerable efforts have been made to develop non-fluorinated or partially fluorinated PEM materials to overcome the drawbacks of the widely used Nafion [4–8].

The aromatic polymers have been investigated as PEM materials due to their excellent stability and high susceptibility to electrophilic sulfonation reactions. A number of aromatic polymers, such as poly(ether ether ketone)s [9, 10], poly(arylene ether)s [11, 12], polybenzimidazoles [13, 14], polyphosphazenes [15], polyimides [16–18], and polyphenylenes [19], have been sulfonated or doped with mineral acids [20] for PEM. Usually, sulfonated aromatic polymers can be obtained by post-sulfonation or by direct copolymerization of a sulfonated monomer. The sulfonated aromatic polymers can be divided into the main-chain-type and the side-chain-type according to the position of the sulfonic acid groups [21]. In general, the oxidation resistance of the side-chain-type sulfonated polymers is superior to that of the main-chain-type sulfonated polymers. Many efforts have been made to develop the side-chain-type sulfonated polymers with good properties these years [22–25].

Recently, a high proton conductivity and good durability were reported in the polymer electrolytes containing fluorenyl groups with sulfonic acid groups on pendant phenyl rings [14, 26–31]. The most exciting report was that the membranes containing fluorenyl groups prepared by Miyatake retained their strength, flexibility, and high molecular weight with an acceptable decline of proton conductivity after 10,000 h in fuel cell operation [31]. However, partially fluorinated poly(fluorenyl arylene ether)s with different degrees of sulfonation, to our knowledge, have not been investigated. In order to further enhance the chemical, thermal and hydrolytic stabilities of the membranes containing fluorenyl groups with acceptable cost, we introduced fluorinated groups to the membrane materials considering the unique properties of fluorine-containing polymers [32]. The presence of the perfluorophenylene units and fluorenyl group brings excellent mechanical strength as well as good thermal and chemical stabilities, while the presence of ether groups provides flexibility, processability, and conductivity.

We synthesized the partially fluorinated poly(arylene ether)s containing fluorenyl groups with different degrees of sulfonation and studied their properties, including the water uptake, proton conductivity, thermal and oxidation stabilities. We found that the sulfonated polymer was highly soluble in polar organic solvents and could be cast into a tough and smooth film. We would like to report it in this article.

Experimental

Materials

9-Fluorenone was purchased commercially from Tokyo Kasei Kogyo Co. Ltd. Japan (TCI). Decafluorobiphenyl and 2, 6-dimethylphenol were purchased from Aldrich Chemical. *N*, *N'*-Dimethyl acetamide (DMAc), toluene, dichloromethane, chloroform, methanol, chlorosulfonic acid, hydrochloric acid, and potassium hydroxide were obtained from commercial sources. Prior to use, the DMAc was dried with 4 Å molecule sieves, toluene was dried with sodium wire, dichloromethane was dried with anhydrous $CaCl_2$ and anhydrous potassium carbonate was dried at 200 °C for 10 h. Other chemicals were used as received.

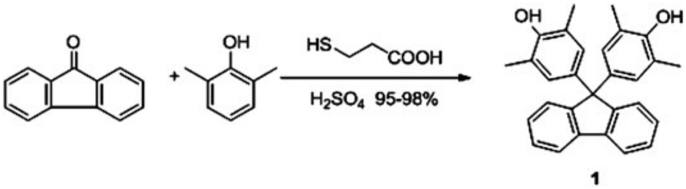
Synthesis of bis (3, 5-dimethyl-4-hydroxylphenyl) fluorene 1

The monomer **1** was synthesized in-house from 9-fluorenone and 2,6-dimethylphenol according to the method reported in literature [33], shown in Scheme 1. A 500 ml four necked flask, equipped with a mechanic stirrer, a condenser, a nitrogen inlet/outlet, and a thermometer, was used. The flask was charged with 45 g of fluorenone (0.25 mol), 91.5 g of 2, 6-dimethylphenol (0.75 mol), 60 ml of toluene, and 0.2 ml of beta-merapto propionic acid. After keeping the temperature of flask at 30 °C for 30 min, 12 ml of 60% sulfuric acid was added dropwise to assure the temperature below 50 °C. When finished the addition, the temperature was increased to 55 °C and kept at 55–60 °C. The product was precipitated from the reaction mixture during the reaction process. After the reaction of 10 h, the flask was cooled to room temperature. The product was obtained by filtering, washing the residue with deionized water, and dried. The crude product was crystallized from toluene twice to give 1 (Fig. 1). M.p.: 281–283 °C. Yield: 65%.

^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 2.01 (s, 12 H), 6.94 (s, 4 H), 7.27–7.38 (m, 6 H), 7.84 (d, 2H). *M/e*: 91, 132, 147, 179, 239, 269, 285, 332, 347, 361, 375, 391, 406 (100%, M^+).

Synthesis of polymer **2**

The synthesis process of polymer **2** is shown in Scheme 2. The mixture of 0.406 g (1 mmol) 1, 0.334 g (1 mmol) decafluorobiphenyl, 0.208 g (1.5 mmol) anhydrous potassium carbonate, and 6 mL DMAc were carefully introduced into a 25 mL three



Scheme 1 Synthesis of monomer **1**

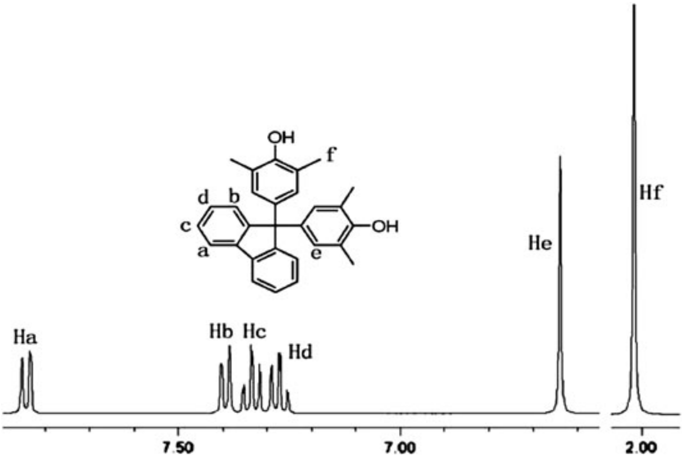
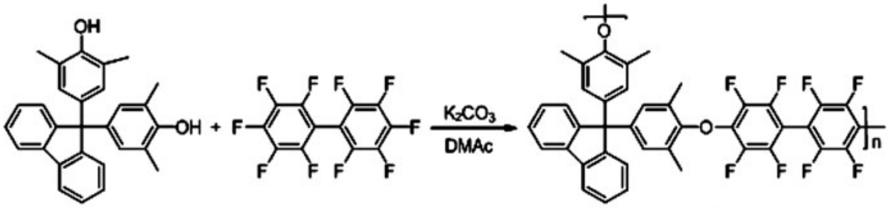


Fig. 1 ^{1}H-NMR spectrum for monomer **1**



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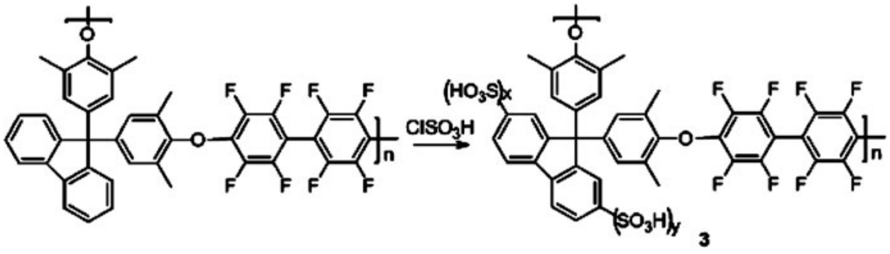
Scheme 2 Synthesis of polymer **2**

necked round bottom flask, equipped with a thermometer and a nitrogen inlet. The reaction mixture was heated to 120 °C and kept at this temperature for 4–6 h. When the solution viscosity apparently increased, it was diluted with 3 mL DMAc and then poured slowly into 100 mL methanol containing 1 mL of concentrated hydrochloric acid with stirring to precipitate the product polymer. The crude polymer was filtered and washed with water and methanol continuously, followed by dissolving in 50 mL of chloroform. The solution was filtered to remove inorganic salts. The filtrate was concentrated to about 5 mL and dropped slowly into 100 mL methanol with stirring to precipitate out the final polymer. The pure white polymer (0.65 g, 92.9% yield) in white color was obtained after dried under vacuum at 120 °C for 10 h.

^{1}H-NMR (400 MHz, DMSO-d_6, ppm): 2.14 (s, 12H), 6.84 (s, 4H), 7.26–7.42 (m, 6H), 7.76 (d, 2H).

Synthesis of sulfonated polymers 3

Sulfonated polymers **3** were synthesized by the sulfonation of polymer **2** using chlorosulfonic acid as the sulfonation agent (see Scheme 3). The degree of



Scheme 3 Synthesis of sulfonated polymers **3a–3d**

sulfonation can be altered by changing the ratio of sulfonating agent to polymer repeating unit. The typical sulfonation process is described as follows: the corresponding volume of 1 M chlorosulfonic acid in methylene chloride was added dropwise to the solution of 1.00 mmol polymer **2** in 100 mL methylene chloride at room temperature. The mixture was stirred vigorously for 3–4 h until the pale brown products precipitated from the solution. The precipitates were collected by filtering and washing with hexane three times. The precipitates redissolved in 20 mL DMAc and then added 40 mL 3 wt% potassium hydroxide aqueous solution for reaction. After 6 h reaction, the mixture was acidified with 100 mL 5 vol% hydrochloric acid. The aqueous solution was dialyzed for 2 days. The sulfonated product was recovered by evaporation of water and characterized by ^{1}H-NMR spectroscopy and elemental analysis.

Preparation of polymer film

Polymer films were prepared as follows: 0.6 g sulfonated polymer sample was dissolved in 10 mL DMAc followed by filtration. The filtrate was poured onto glass slides and dried at 60 °C to remove the solvent. The polymer film was further dried at 50 °C for about 6 h and 120 °C for 24 h under vacuum.

Measurements

The glass transition temperatures (T_gs) were determined using a Perkin-Elmer DSC-7C instrument at a heating rate of 10 °C/min under nitrogen protection atmosphere. The second scan began immediately after the sample was cooled to room temperature after 1st scan. The thermal stability of the polymers was determined with a NETZSCH STA 409 PC/PG instrument at a heating rate of 20 °C/min under following nitrogen protection atmosphere (300 mL/min). Gel permeation chromatography (GPC) analyses were carried out on a Waters 510 HPLC equipped with 5 μm Phenol gel columns (linear, 4 × 500 Å) arranged in series with chloroform as a solvent and a UV detector at 254 nm. ^{1}H-NMR data were recorded at 400 MHz on a Varian 400-Hz NMR instrument. Melting points were taken on a XT4A melting point apparatus.

Water uptake (S) was measured by weighing the water uptake during the immersion of the vacuum-dried membrane samples in deionized water for 12 h using the following equation:

$$S = (W_s - W_d)/W_d \times 100(\%)$$

where W_s and W_d are the weights of wet and dry membrane, respectively.

Proton conductivity measurements were conducted on hydrated film samples using an impedance analyzer (Solartron 1260A) functioning with an oscillating voltage of 10 mV over the frequency range from 10 MHz to 500 Hz. The cell assembly was composed of one round film and two round gold electrodes with 10 mm in diameter. Prior to the measurement, the membrane was immersed in 1 M H_2SO_4 at 80 °C for 12 h and then washed to a pH of 7 with deionized water. The membrane was kept in deionized water for over 12 h for further use. After pretreated, the membrane was tightly clamped between two round gold electrodes and placed in a closed container containing some water to keep the relative humidity of 100%. The whole container was placed in a temperature-controlled water-bath during the measurement. The proton conductivity was calculated from the impedance data according to following equation:

$$\sigma = d/RS$$

where d and S are the thickness and the face area of the specimen, respectively, and R is the membrane resistance measured by impedance analyzer.

Results and discussion

Synthesis of polymer **2**

The partially fluorinated polymer **2** belongs to the family of poly(arylene ether)s. The polymers were usually synthesized by the nucleophilic aromatic substitution of aryl halides with phenoxides. A typical procedure for the synthesis of the polymers was described as follows. A stoichiometric ratio of monomers, an excess of potassium carbonate, and dipolar solvent with 25–35% solids content was used. The reaction was first held at 140 °C for 3–4 h under nitrogen to azeotrope off water with toluene, and then heated up to 175 °C for 20–24 h to afford high molecular weight polymer. We tried to synthesize polymer **2** in the same conditions. However, the reaction was over in a short time and only gel particles being insoluble in chloroform were obtained. The results indicated that the decafluorobiphenyl and monomer **1** were so reactive that the side reactions, such as branching and crosslinking, occurred in such condition. A modification method was introduced by Ding [34], in which the reactions conducted in milder conditions thereby depressing the side reaction, but special catalyzer must be employed. In our procedure, the reaction was conducted in DMAc in the presence of K_2CO_3 at 120 °C for 4–6 h, high molecular weight polymers ($M_n = 46{,}400$, $M_w = 96{,}300$) were obtained. The polymers were very soluble in chloroform and identified by ^{1}H-NMR (see Fig. 2).

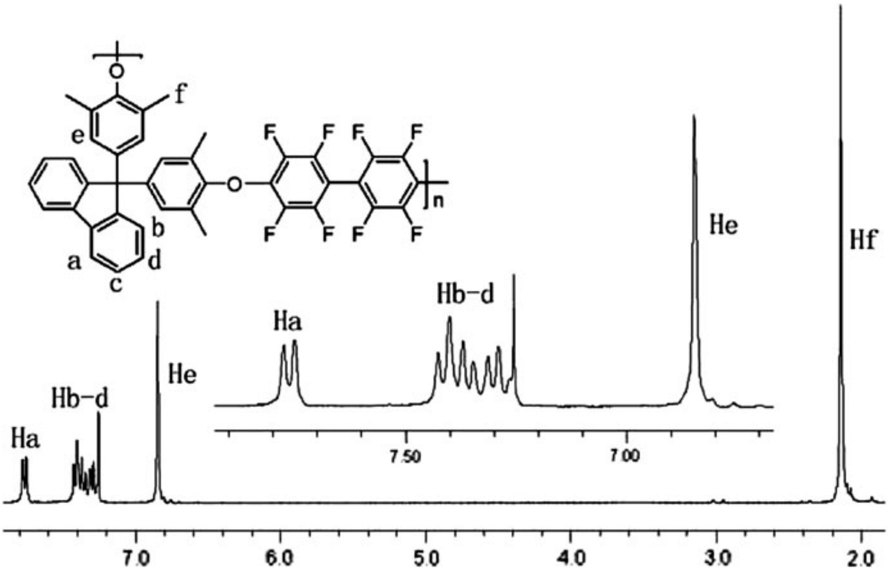


Fig. 2 ^{1}H-NMR spectrum for polymer **2**

Synthesis of sulfonated polymers 3

The polymer **2** was sulfonated using chlorosulfonic acid in methylene chloride to obtain the sulfonated polymers **3**. The sulfonation was carried out at room temperature for a few hours. The sulfonated polymers were easily collected due to their insolubility in methylene chloride. Residual sulfonyl chloride was neutralized with aqueous potassium hydroxide in DMSO. Upon treatment with hydrochloric acid followed by dialysis, light-colored polymers were obtained. When the ratio of polymer unit and chlorosulfonic acid was 1:8, it is easy to assign the peaks of the spectra between polymer **2** and sulfonated polymer **3d** (Fig. 3). Although there were some observed chemical shifts due to the different solvent used ($CDCl_3$ for 2 and DMSO-d_6 for **3d**), the peaks of polymer **2** at 2.14 ppm(s) and 6.84 ppm(s) were still found in the peaks of sulfonated polymer **3d** at 2.12 ppm(s) and 6.81 ppm(s). The two sets of peaks had the same integration ratio for the polymer **2** and sulfonated polymer **3d**, suggesting that the polymer main chain stayed intact throughout the sulfonation reaction. There were remarkable changes in the peaks of fluorenyl groups between the polymer **2** and the sulfonated polymer **3d**: the peaks of the polymer **2** at 7.26–7.42 ppm and 7.76 ppm disappeared while the peaks of the sulfonated polymer **3d** were observed at 7.62 ppm(s), 7.69 ppm(d), and 7.90 ppm(d). The integration ratio of these peaks of sulfonated polymer **3d** indicated the introduction of two sulfonic acid groups on a fluorenyl group. Elemental analyses were further performed to determine the degree of sulfonation of sulfonated polymer **3d**. The degree of sulfonation could be controlled by simply changing the amount of chlorosulfonic acid in the reaction. The ^{1}H-NMR spectra of all the sulfonated

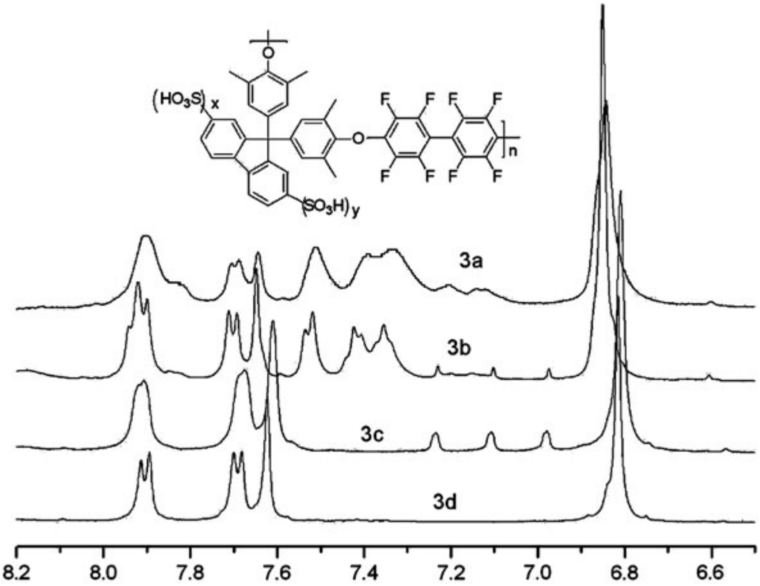


Fig. 3 ^{1}H-NMR spectrum for sulfonated polymers **3a–3d**

Table 1 Degree of sulfonation of polymers **3a–3d**

Polymer	γ[a]	Degree of sulfonation[b]	$TGA_{5\%}$ (°C)
3a	2	0.60	352
3b	4	0.90	327
3c	6	1.75	316
3d	8	2.00	313

[a] γ is the ratio of the sulfonation agent to repeating unit of polymer

[b] Number of sulfonic acid groups per repeating unit

polymers **3**, shown in Fig. 3, demonstrate that the sulfonation took place only on the pendent fluorenyl rings. The degree of sulfonation could be calculated from elemental analysis results as described in the literature [35]. The reaction conditions and the degree of sulfonation calculated from elemental analyses results are summarized in Table 1.

Thermal analysis

The thermal properties of the polymers were investigated using DSC and thermogravimetric analysis (TGA). Parent polymer **2** had a high T_g of 271 °C, while no T_g was detected for the sulfonated polymers **3** before their thermal decomposition. The T_g of the sulfonated polymers **3** may be much higher than that

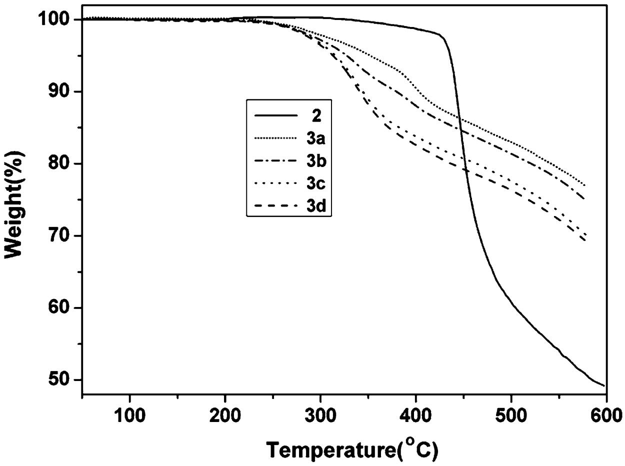


Fig. 4 TGA curves of polymer **2** and sulfonated polymers **3a**–**3d**

of the parent polymer **2** because of their ionomeric nature. The behavior was analogous to that described in the literature [35].

Figure 4 showed the TGA spectra of the polymer **2** and the sulfonated polymers **3**. Parent polymer **2** was a thermal stable polymer with 5% weight loss at temperature about 420 °C. The sharp weight loss at 400–450 °C was ascribed to the decomposition of polymer main chain. In order to ignore the effect of water, the sulfonated Polymers **3** were preheated from 50 to 200 °C and then TGA experiments were run from 50 to 600 °C at a heating rate of 10 °C/min under nitrogen. The two weight loss stages were attributed to the loss of sulfonic groups and the degradation of the polymer main chain. Polymers with higher degree of sulfonation were degraded more quickly than those with lower degree of sulfonation in the temperature range from 250 to 350 °C. The high T_g and thermal weight loss temperature of the sulfonated polymer showed potential application in high temperature (>100 °C) PEMFC.

Oxidative and hydrolytic stability

The stability of the sulfonated polymers to oxidation was investigated by immersing the membranes into Fenton's reagent (2 ppm $FeSO_4$ in 3% H_2O_2) at 80 °C. The oxidation stability of the membranes was characterized by the expended time at which membranes started to break into pieces and disappeared into solution. As can be seen in Table 2, all partially fluorinated membranes exhibited good oxidative stabilities as compared with that of the non-fluorinated membranes reported in ref. [26]. The results indicated that oxidative stability became worse with increasing the degree of sulfonation. The hydrolytic stability was also investigated by treating membrane samples in boiling water for more than 8 days. There was not any change in both the membrane's shape and appearance, implying that no hydrolysis occurred during the treatment. The results of weight loss data and proton conductivity further prove this conclusion.

Table 2 Oxidative stabilities of sulfonated polymers **3a**–**3d**

Membrane	**3a**	**3b**	**3c**	**3d**	NF2a[4]	NF2e[4]
Degree of sulfonation	0.60	0.90	1.75	2.00	0.91	1.55
T^1 (min)	>600	146	85	75	67	29
T^2 (min)	>600	360	105	97	ND[3]	ND[3]

T^1, T^2 refer to the elapsed time that the membranes started to break into pieces and disappeared into solution

ND[3] represents values not determined

NF2a[4] and NF2e[4] refer to the non-fluorinated membranes reported in the reference [26]

Water uptake and proton conductivity

It is well known that water uptake of membranes has a profound effect on proton conductivity and mechanical properties. The water uptakes for all membranes of polymers **3** in acidic form were measured at 30 and 80 °C, respectively (Table 3). It was found that the water uptake of the membranes mostly increased with increasing the degree of sulfonation and temperature, due to the strong hydrophilicity of the sulfonic acid groups. The membranes combine the hydrophobicity of the polymer backbone with the hydrophilicity of pendant sulfonic acid groups. The hydrophobic domains provide the good mechanical and morphological stability, whereas the hydrophilic domains provided the proton conductivity.

The proton conductivities of the membranes for polymers **3** are summarized in Table 3. It was found that the proton conductivities increase with increasing the degree of sulfonation and temperature. The proton conductivity of Nafion 117 was determined to be 3.9×10^{-2} S/cm at 80 °C and 100% relative humidity. The membranes from polymers **3c** and **3d** with high sulfonation degree exhibited higher proton conductivities than that of Nafion 117. Presumably, the high proton conductivity resulted from the formation of a continuous proton transport channel [36].

Mechanical strength

Table 4 listed the tensile strength, the strength at break, and the elongation at break of the membranes with the various degree of sulfonation at 30 °C and 100% relative

Table 3 Water uptake and proton conductivities of membranes **3a**–**3d**

Membrane	Water uptake (%)		Conductivity (S/cm)	
	30 °C	80 °C	30 °C	80 °C
Nafion 117	ND	ND	ND	3.9×10^{-2}
3a	14.2	22.1	3.2×10^{-5}	1.7×10^{-4}
3b	26.2	39.6	1.9×10^{-3}	4.4×10^{-3}
3c	54.6	71.9	2.1×10^{-2}	4.0×10^{-2}
3d	61.0	80.7	2.8×10^{-2}	5.7×10^{-2}

ND represents values not determined

Table 4 Mechanical properties of membranes **3a**–**3d**

Membrane	Tensile strength (MPa)	Strength at break (MPa)	Elongation at break (%)
3a	30.7	29.3	4.2
3b	26.2	25.0	8.8
3c	21.2	20.7	15.8
3d	18.8	17.8	25.6
Nafion 117	25.7	25.6	106.5

humidity. All the sulfonated polymer membranes show comparable mechanical properties with Nafion. The tensile strength increases while the elongation decreases with decreasing the degree of sulfonation due to the phase separation for the polyionomer with high sulfonic acid group content. In general, phase separation results in a poor tensile toughness, but a high stiffness, i.e., tensile strength. The comprehensive mechanical properties of the polymers **3** were believed to meet the requirement for the PEMFC assembly application.

Conclusions

The partially fluorinated poly(arylene ether)s containing fluorenyl groups with different degrees of sulfonation were successfully synthesized. The sulfonation took place only at specific (2, 7)-position on fluorenyl groups. The sulfonated polymers were soluble in common organic solvents and could be easily cast into tough membranes. These membranes exhibit very high water affinity, proton conductivity, and thermal stability, as well as oxidative and hydrolysis stabilities. These properties made them excellent candidate for polymer electrolyte membrane fuel cells.

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