



Controllable sulfonation of aromatic poly(arylene ether ketone)s containing different pendant phenyl rings

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ABSTRACT

The sulfonation selectivity of various pendant phenyl groups in poly(arylene ether ketone) (Ph-3F-PAEK) is investigated via the postsulfonation approach. The sulfonated Ph-3F-PAEKs with different degrees of sulfonation (DS) are quantitatively synthesized by controlling the length of the segments that cannot be sulfonated. In this study, ^1H NMR and FT-IR are used to confirm the structures of the polymers and the experimentally DS values were calculated by ^1H NMR. The experimentally observed DSs are corresponding to the theoretical values expected from the monomer ratios. All the sulfonated membranes have excellent mechanical properties (with a Young's modulus >1.3 GPa, a tensile strength >55 MPa and the elongation $>10\%$). Thermogravimetric analysis (TGA) is used to characterize the thermal stability of these polymers, and all the polymers show excellent thermal properties at high temperatures. The methanol permeability values of Ph-3F-SPAEEKs in the range of 0.37×10^{-7} $\text{cm}^2 \text{s}^{-1}$ to 4.12×10^{-7} $\text{cm}^2 \text{s}^{-1}$ are much lower than that of Nafion[®] 117 (1.55×10^{-6} $\text{cm}^2 \text{s}^{-1}$). It should be noted that the polymer with highest DS, Ph-3F-SPAEEK-100 with an ion exchange capacity of 2.16 mequiv. g^{-1} , exhibits high proton conductivity of 0.187 S cm^{-1} at 80 °C, which is also higher than that of Nafion[®] 117.

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1. Introduction

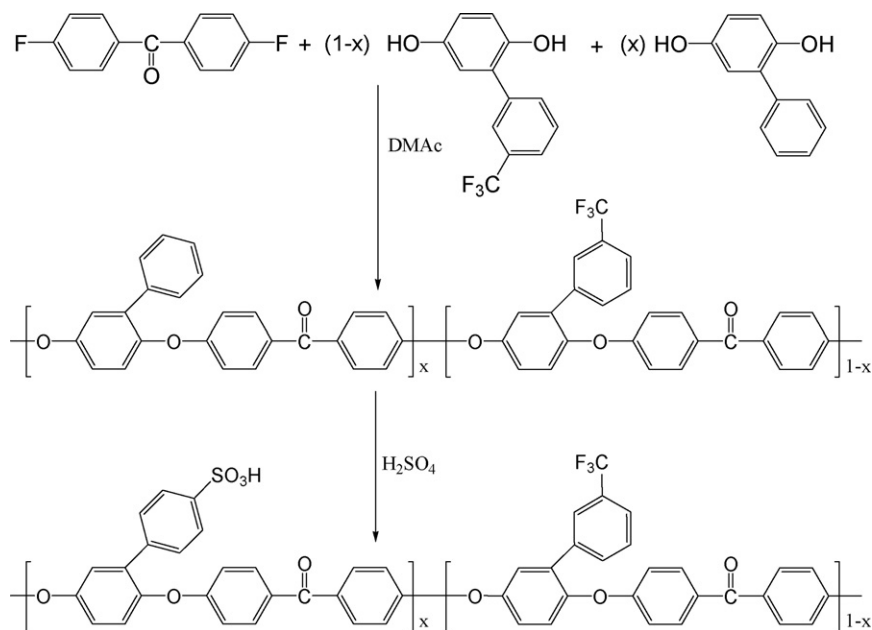
Proton exchange membrane fuel cells (PEMFCs) have been widely investigated as one of the promising clean future power sources because of their low emissions and high conversion efficiency. The key component of a PEMFC is proton exchange membrane (PEM) which is a proton conducting, electronically insulating polymer material. Traditional PEMs are perfluorinated ionomers (PFIs) such as DuPont's Nafion[®], because of their excellent mechanical and chemical stabilities as well as high proton conductivity [1–3]. However, the practical applications of PFIs PEMs in extensive scale are limited to some extent due to their high cost, low operating temperature and high methanol crossover [4,5]. Presently, many efforts have been done to design and synthesize PEMs based on fluorine free hydrocarbon ionomer membranes as alternatives to PFI membranes. The alternative materials investigated, such as polysulfones [6,7], polyimides [8,9], polybenzimidazoles [10] and so on, have been considered as promising candidates due to their outstanding thermal and chemical stabilities.

According to the position of the sulfonic acid groups attached on the polymers, the sulfonated aromatic polymers can be divided

into two types: the main-chain-type [7] and the side-chain-type [11–17]. The main-chain-type sulfonated polymers usually show an extensive water uptake above a critical temperature, or above a critical DS, which results in a dramatic loss of mechanical properties. Recently, several stereocontrolled sulfonated polymers have been reported by Kobayashi et al., and they suggested that sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP) with pendant side chain showed higher and more stable proton conductivity [16]. Jannasch and co-workers have prepared side-chain-type sulfonated polysulfones with some active properties based on lithiation reaction [18,19]. In addition, some side-chain-type sulfonated polyimides (SPIs) have been also developed by Okamoto and co-workers [20] and Watanabe and co-workers [21]. Generally, the side-chain-type sulfonated polymers are more stable to hydrolysis than those of main-chain-type polymers. Recently, aromatic poly(arylene ether ketone)s have been prepared by Liu et al. [22]. Their sulfonated polymers have shown good mechanical, thermal, and oxidative stability, along with low methanol permeability. However, they only studied the polymer with low degree of sulfonation as compared to that of Nafion[®]. Based on these properties, we prepared sulfonated poly(arylene ether ketone) via the postsulfonation method whereby the design of the polymeric structures demonstrate controllable specific sulfonation sites.

In our work, a novel series of sulfonated PAEKs with stereocontrolled sites and high DS were prepared via postsulfonation method. The DS of the copolymers were controlled by polymer chain com-

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Scheme 1. Preparation of sulfonated poly(arylene ether ketone) copolymers (Ph-3F-SPAEEK).

position that contains two types of segments: those that are readily sulfonated and those that are not. Moreover, we controlled the reaction time to obtain the anticipant position of the sulfonated groups. The properties of these sulfonated copolymers were all investigated, such as thermal stabilities, mechanical stabilities, water uptake, and proton conductivity. And the results show the polymers are promising alternatives to Nafion[®] in PEMFCs.

2. Experimental

2.1. Materials

(3-Trifluoromethyl) phenylhydroquinone and phenylhydroquinone were synthesized according to a published procedure [23,24]. 4,4'-Difluorobenzophenone (DFBP), potassium carbonate (K₂CO₃), *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), concentrated sulfuric acid (95–98%) and toluene were purchased from Aldrich Chemical Co. and used without further purification.

2.2. Synthesis of poly(arylene ether ketone)s (Ph-3F-PAEK)s

The synthetic route of the Ph-3F-PAEK is shown in Scheme 1. Poly(arylene ether ketone)s were synthesized by aromatic nucleophilic substitution step polymerization with different ratios of monomers. A typical synthesis procedure of Ph-3F-PAEK-60, where 60 refers to the feed percent of phenylhydroquinone, is as follows: to a 100 ml three-necked flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap with a condenser (3-trifluoromethyl) phenylhydroquinone (1.016 g, 0.004 mol), phenylhydroquinone (1.116 g, 0.006 mol), DFBP (2.180 g, 0.01 mol), anhydrous K₂CO₃ (1.794 g, 0.013 mol), were added into a DMAc (18 ml), and toluene (15 ml) solvent system. The mixture was kept at room temperature for a few minutes and then heated at 140 °C for 2 h and at 180 °C for 8 h in nitrogen atmosphere under magnetic stirring. Then another 15 ml DMAc was added into the mixture to lower the solution viscosity. The solution was poured into 100 ml deionized water, and the product was obtained as white flakes. The precipitated polymer was subsequently filtered out and

successively washed with deionized water and dried in vacuum at 80 °C for 15 h essentially resulted in a quantitative yield of white Ph-3F-PAEK-60 copolymer. The yield of the obtained polymer was above 90%.

2.3. Preparation of sulfonated polymers and membranes

In view of different substitution reactivity of the different pendant groups on the copolymers, a relatively mild sulfonating reagent and ambient temperature conditions were adopted. A typical reaction was shown as follows: to a 100 ml flask, 1 g of Ph-3F-PAEK and 10 ml of concentrated sulfuric acid (95–98%) were added. After stirring at room temperature for several hours, the homogeneous viscous solution was poured into a mixture of water and ice to get a silk-like solid. The raw product was washed with distilled water in order to remove the acid from its surface, until the pH of filtrate reached 7. In order to remove the acid inside the product, the polymer was then smashed to powder and washed several times until the pH reached 7. Then the sulfonated Ph-3F-PAEK was dried at 80 °C under vacuum for 2 days.

Ph-3F-SPAEEK copolymer (1.0 g) was dissolved in DMAc (10 ml) overnight. Then, the solution was filtered with a fine glass frit filter funnel and cast directly onto clean glass plates. After being carefully dried at 60 °C for 10 h and vacuum-dried at 120 °C for 24 h, tough and flexible films were obtained. The membrane was then immersed in 1 M H₂SO₄ aqueous solution for 12 h. Finally, the membrane was then washed with deionized water several times to remove acid on the surface and dried under vacuum at 60 °C for 15 h. The thicknesses of all membrane films were in the range of 50–80 μm.

2.4. Membrane characterization

2.4.1. Analysis and measurements of the copolymers

¹H NMR experiments were carried out on a Bruker 510 spectrometer by using DMSO-d₆ as solvent. FT-IR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer.

2.4.2. Thermal analysis

Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821^e instrument at a heating rate of 20 °C min⁻¹ from 50 to 300 °C under nitrogen. Thermogravimetric analysis (TGA) on a PerkinElmer Pyris-1 thermal analyzer system was employed to assess thermal stability of the membranes. Before testing, the membranes were dried and kept in the TGA furnace at 150 °C under an air atmosphere for 30 min to remove water. The samples were evaluated in the range of 100–800 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

2.4.3. Mechanical properties

Mechanical properties of the membranes were evaluated at room temperature on SHIMADZU AG-I 1KN at a strain rate of 2 mm min⁻¹, and a 500 N load cell was used. The samples were prepared by being cut into a 15 mm × 4 mm dumbbell shape. At least three measurements for each membrane were taken and average value was calculated.

2.4.4. Water uptake measurements

The membranes were immersed into deionized water at 20 °C for 7 days in order to make the membranes fully hydrated. The weight of the membranes was measured after blotting by filter paper. Then the membranes were dried at 80 °C in vacuum for 24 h and measured again. All the experimental results were based on three measurement of each testing and averages were given. The weight gained from water was calculated with reference to the weight of the dry specimen using the following equation:

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

where W_{dry} and W_{wet} stand for the masses of the dried and wet samples, respectively.

2.4.5. Ion exchange capacity (IEC) of membrane

IEC indicates the ion exchangeable groups of a polymer and reflects the proton transport action capacity of PEM from another point of view. Membrane samples were immersed in 1 M NaCl solution for at least 48 h to liberate the hydrogen ion (the H⁺ ions in the membrane were replaced by Na⁺ ions). Then the H⁺ ions were titrated by back titration with 0.01 M NaOH using phenolphthalein as an indicator. All the experimental results were based on three measurement of each testing and averages were given.

2.4.6. Methanol permeability measurement

The methanol diffusion coefficient was determined by using a home-made cell, which consisted of two compartments divided by a membrane sample. 100 ml pure methanol was placed on one side of the cell (cell A) and water was placed on the other side (cell B). The magnetic stirrers were used continuously during the measurement on both side. The concentration of methanol in the water cell with time was determined using a SHIMADZU GC-8A chromatograph. The methanol diffusion coefficient was calculated as follows:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0)$$

where A (cm²) and L (cm) stand for the effective area and the thickness of membrane, respectively. V_B (cm³) is the volume of diffusion reservoir. C_A and C_B (mol L⁻¹) are the methanol concentration in feed and in diffusion reservoir, respectively. DK is the methanol diffusion coefficient (cm² s⁻¹).

2.4.7. Proton conductivities

The proton conductivities of the membranes were measured by a four-electrode AC impedance spectroscopy technique over a frequency range of 0.1–10⁵ Hz, 10 mV ac perturbation and 0.0 V

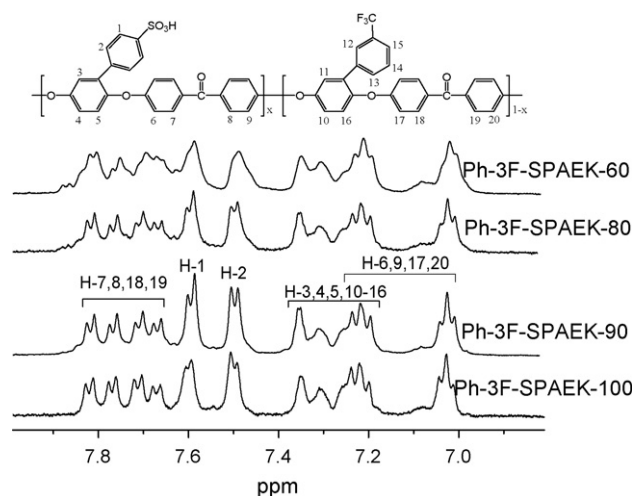


Fig. 1. ¹H NMR spectra of sulfonated polymers (Ph-3F-SPAEEK-X).

dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The samples were all immersed in deionized water for at least 24 h to completely hydrated before testing and then sandwiched between two stainless steel blocking electrodes of an open cell in 100% relative humidity. The testing temperature range of the impedance measurements was varied from 20 °C to 80 °C.

The conductivity δ of the samples was calculated using the following equation:

$$\sigma = \frac{L}{RA}$$

where L and A stand for the thickness and face area of the sample, and R is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the $\text{Re}(Z)$ axis. The impedance data were corrected for the contribution from empty and short circuited cell.

3. Results and discussion

3.1. Selectivity of sulfonation reaction and characterization of sulfonated poly(*arylene ether ketone*)s (Ph-3F-SPAEEK)

Polymers after sulfonation may possess good ionic conductivity. In general, sulfonation is an electrophilic reaction, and the positions of the sulfonic acid group depend on the substituents present on the ring. The condition of the sulfonation reaction is very important: rigorous sulfonation conditions may lead to side reactions such as destruction of the polymer chain and crosslinking reactions. In order to avoid these side reactions, we used a simple and mild sulfonation reaction condition of room temperature sulfuric acid to affect the sulfonation of the polymers. No substitution reaction was observed for pendant ring containing trifluoromethylated phenyl [22]. In our work, we prepared copolymers with certain ratios of sulfonable/un-sulfonable segments via the copolymerization method and then conducted postsulfonation to control DS.

The chemical structures of the sulfonated copolymers were confirmed by ¹H NMR spectra and the results are listed in Fig. 1. The simple NMR patterns indicate full substitution of the hydrogen at the *para*-position of the pendant group. The existence of the sulfonic acid group causes a distinct signal for the proton at the 1 position. The introduction of the sulfonic acid group results in H₁ signal shift downfield. DS was also quantitatively determined using the ¹H NMR spectrum for the Ph-3F-SPAEEK series and the results are listed in Table 1 [1,25,26].

Table 1
DS and IEC of the polymers.

Polymer	DS ^a	DS ^b	IEC ^a (mequiv. g ⁻¹)	IEC ^b (mequiv. g ⁻¹)
Ph-3F-SPAEEK-60	0.60	0.60	1.36	1.27
Ph-3F-SPAEEK-80	0.80	0.78	1.78	1.70
Ph-3F-SPAEEK-90	0.90	0.88	2.07	2.06
Ph-3F-SPAEEK-100	1.00	0.97	2.19	2.16

^a Calculative DS and IEC of the polymers.

^b Experimental DS and IEC of the polymers.

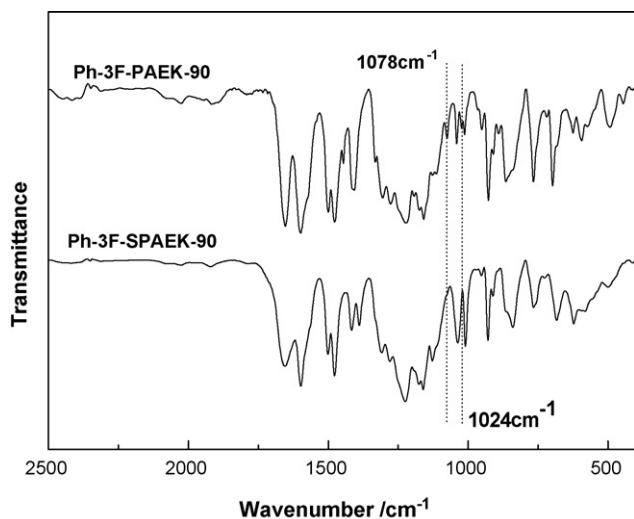


Fig. 2. Comparative FT-IR spectra of Ph-3F-SPAEEK-90 and Ph-3F-PAEK-90.

The chemical structures of the sulfonated polymers and un-sulfonated polymers were also confirmed by FT-IR spectroscopy. The spectra of Ph-3F-SPAEEK-90 and Ph-3F-PAEK-90 are listed in Fig. 2. From the FT-IR spectrum, the new absorption bands at 1078 and 1024 cm⁻¹ were assigned to stretching of the sulfonic groups in the spectra of Ph-3F-SPAEEK-90, and were not observed in the spectra of Ph-3F-PAEK-90, which exhibited successfully the introduction of sulfonic groups through postsulfonation. Both ¹H NMR and FT-IR spectrum showed that the sulfonated PAEK copolymers with different pendant phenyl ring groups were synthesized as desired.

As shown in Table 1, the calculated DS values from ¹H NMR spectra were agreement with the expected DS derived from the different monomer ratios. This result indicated that we could easily control the DS values by adjusting the ratio of the sulfonable monomer to un-sulfonable monomer.

3.2. Water uptake and IEC of the membranes

The water uptake is one of the crucial properties of PEMs, which is closely related to IEC, proton conductivity and mechanical strength. In general, the water within the membranes provides a carrier for the proton and maintains high proton conductivity [22]. However, excessive water uptake in a PEM results in loss of mechan-

Table 2
Water uptake, proton conductivities, and methanol permeabilities of Ph-3F-SPAEEKs.

Polymer	Water uptake (%)		Proton conductivity ^a σ (S cm ⁻¹)		Methanol permeability ($\times 10^{-7}$ cm ² s ⁻¹)
	RT, 48 h	80 °C, 12 h	20 °C	80 °C	
Ph-3F-SPAEEK-60	29	36	0.019	0.060	0.37
Ph-3F-SPAEEK-80	38	45	0.033	0.119	2.87
Ph-3F-SPAEEK-90	46	56	0.045	0.162	3.49
Ph-3F-SPAEEK-100	53	83	0.059	0.187	4.12

^a The proton conductivity measured at room temperature and 80 °C with 100% relative humidity.

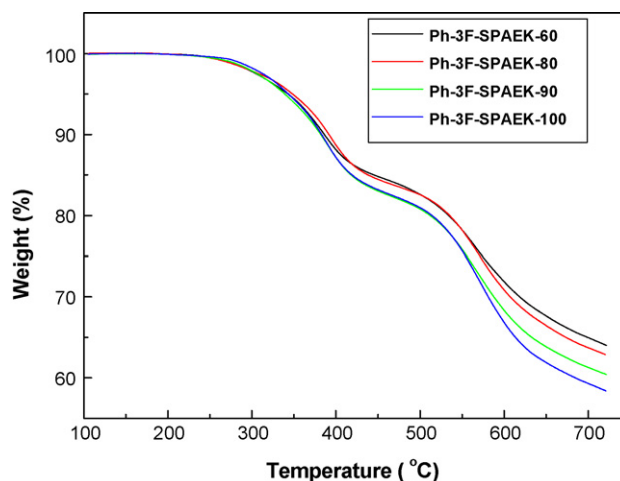


Fig. 3. TGA curves of Ph-3F-SPAEEK-X.

ically stability. The water uptakes of all membranes were measured at room temperature and 80 °C, respectively (Table 2). Table 2 shows that the water uptake of all membranes increased with the DS and temperature. This trend is due to the strong hydrophilicity of the sulfonic acid groups and the strong hydrophobicity of the polymer main chain with 3-trifluoromethyl. This separation will give the membranes higher water uptake but better mechanical property.

Ion exchange capacity (IEC) is a method to indicate the exchangeable ions of polymer membranes. The IEC values play a definitive role in determining the proton conductivity of the membranes. The IEC data from titration test and calculated by DS are listed in Table 1. The IEC data from titration test were in the range of 1.27–2.16 mequiv. g⁻¹, which were in good agreement with the theoretical values. The IEC values of the membranes increased with the DS. The IEC values of membranes were easily controlled during synthesis by adjusting the various ratios of sulfonable to un-sulfonable monomers.

3.3. Thermal properties

In order to maintain their good mechanical strength, polymer materials are usually operated below the glass-transition temperature (T_g). Higher temperature fuel cell operation requires PEM materials with high T_g [22]. Their glass-transition temperatures are listed in Table 3 and they are in the range of 210–231 °C. In general T_g increases with increment of sulfonated degree of polymer. It could be attributed to the increase in intermolecular interaction.

The thermal degradation temperatures of sulfonated polymers are shown in Table 3 and Fig. 3. From Fig. 3, we can see that sulfonated films have two step degradation pattern. The first weight loss (T₁) in all samples was due to the decomposition of sulfonic acid groups in the range of 339–348 °C. And the second weight loss (T₂) in all samples was caused by the breakdown of the polymer backbone. [27]. In general, with the sulfonic acid groups increasing, the decomposition temperature of the polymers decreased. All

Table 3
Thermal and mechanical properties of Ph-3F-SPAEEKs.

Polymer	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)	T _g (°C)	T _d (°C)	
					T ₁	T ₂
SPAEEK60	1860.69	78.89	10.2	210	338	431
SPAEEK80	1745.45	72.33	18.08	221	348	426
SPAEEK90	1382.91	57.56	33.29	226	343	412
SPAEEK100	1809.83	74.38	11.37	231	342	410
Nafion [®] 117	180.0	38.0	301.5	–	–	–

the sulfonated polymers showed excellent thermal stability at high temperatures.

3.4. Mechanical properties

Besides the excellent thermal properties, the membranes applied in fuel cells should also possess good mechanical properties. The mechanical properties of dry Ph-3F-PAEK-X membranes were measured at room temperature. A comparison of the different ratios of sulfonable/un-sulfonable segments of the polymers is listed in Table 3. The initial Young's modulus for the membranes of Ph-3F-SPAEEK-60, -80, -90 and -100 are 1.86, 1.74, 1.38 and 1.81 GPa, respectively, which were much higher than that of Nafion[®] 117 (0.18 GPa) [22]. All the high sulfonated membranes showed the elongation at break of 10.2–33.3% and tensile strength ranging from 57.56 to 78.89 MPa. Compared to Nafion[®], Ph-3F-SPAEEK-X membranes show relatively better mechanical stability at ambient condition. All the data indicate that the Ph-3F-SPAEEK-X membranes are strong and tough enough for use in PEMs.

3.5. Proton conductivities and methanol permeability

The proton conductivity is a very dominant parameter for all PEMs. All membranes were initially hydrated by immersion them in deionized water for at least 24 h at room temperature before testing. Proton conductivities of the membranes were measured at 100% RH and are depicted in Fig. 4. From Fig. 4, some general trends are observed for all membranes: the proton conductivities increase with temperature and sulfonate content. It also can be seen that all the obtained membranes showed conductivities above 10^{-2} S cm⁻¹ at 20 °C or higher temperature. Ph-3F-SPAEEK (-80, 90, 100) membranes showed conductivity higher than 0.1 S cm⁻¹ at 80 °C, which were all higher than that of Nafion[®] 117 (0.138 S cm⁻¹). But Ph-3F-SPAEEK-60 had a lower conductivity than others, due to its low sulfonate content, Ph-3F-SPAEEK-60 membrane might not

have continuous proton transport channel. The higher conductivity was also attributed to the short pendant phenyl rings and the short hydrophobic domain, and all these potentially increase the proton conductivity of the membranes.

Besides high proton conductivity, membranes intended for direct methanol fuel cell (DMFC) must also possess low methanol permeability because methanol crossover contributes to an overall decrease in the cell efficiency and life time. The methanol permeability values of the Ph-3F-SPAEEK membranes are summarized in Table 2. The Ph-3F-SPAEEK membranes exhibited extremely low methanol permeability, and the methanol permeability increased with an increment of DS. The methanol permeability values of the serial Ph-3F-SPAEEK membranes ranged from 3.7×10^{-8} to 4.12×10^{-7} cm² s⁻¹, which is much lower than that of Nafion[®] (1.55×10^{-6} cm² s⁻¹) [22]. The low methanol permeability presumably arises from a well-refined microstructure caused by regular and rigid backbone molecular structure. The series of Ph-3F-SPAEEK membranes with higher conductivity and lower methanol permeability, have the potential exhibit a high level performance as PEM materials for direct methanol fuel cells.

4. Conclusion

PAEKs with phenyl and (3-trifluoromethyl) phenyl pendant groups were synthesized successfully and were found to have controlled sulfonation sites of the pendant rings via a postsulfonation approach. It was found that this series of Ph-3F-SPAEEK had good thermal stability, good mechanical property, high proton conductivity (up to 0.187 S cm⁻¹ at 80 °C), and low methanol permeability. Combined with all these advantages, these membranes may be a potential PEM material for PEMFC applications.

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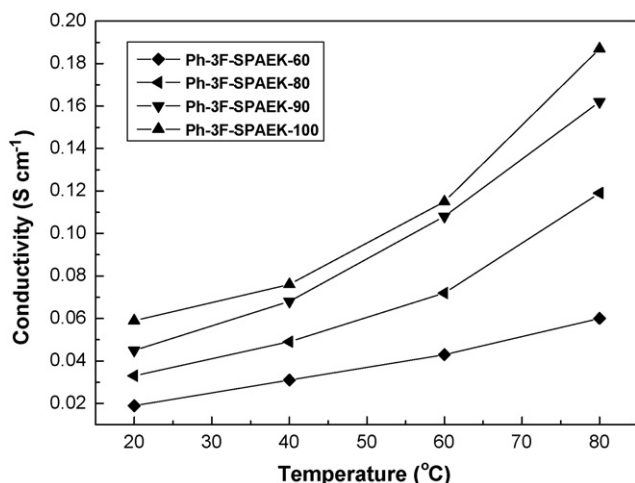


Fig. 4. Proton conductivities of Ph-3F-SPAEEK-X films as a function of temperature.

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