Proton exchange membrane based on crosslinked sulfonated polyphosphazene containing pendent perfluorosulfonic acid groups with sulfonated poly(ether ether ketone)

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ABSTRACT: A series of crosslinked membranes based on new sulfonated polyphosphazene bearing pendent perfluorosulfonic acid groups (PMFP-g-PS) and sulfonated poly (ether ether ketone) were prepared and evaluated as proton exchange membranes for direct methanol fuel cells (DMFCs). The structure of PMFP-g-PS was characterized by Fourier transform infrared spectroscopy, ^{1}H and ^{19}F NMR spectra. In comparison with the pristine PMFP-g-PS membrane, the crosslinked membranes showed improved water uptakes and proton conductivities. The methanol permeability values of the membranes were in the range of 1.32×10^{-7} to 3.85×10^{-7} cm^2/s, which were lower than Nafion 117 (12.1×10^{-7} cm^2/s). The selectivity of all the membranes was much higher compared with Nafion 117. Furthermore, transmission electron microscopy observation revealed that clear phase-separated structures were well dispersed and connected to each other in the membranes. These membranes displayed high water uptakes and low swelling ratios, high proton conductivities, low methanol permeability values, good thermal, and oxidative stabilities. The results indicate that these membranes are potential candidate proton exchange membrane materials for DMFCs. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43492.
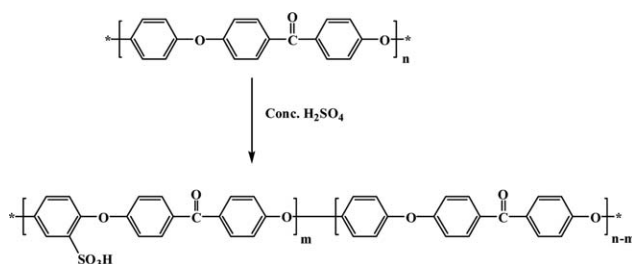
INTRODUCTION

The proton exchange membranes (PEMs) are key components of direct methanol fuel cells (DMFCs) which are of great interest due to their widely potential applications, especially in the area of portable power generation.[1,2] At present, Nafion has been considered as the most promising PEM for DMFC because of its high proton conductivity and chemical stability. However, some drawbacks such as high methanol permeability and high cost of Nafion severely limit its application in DMFCs.[3] In order to obtain high proton conductivity, low methanol permeability and low cost alternative PEMs, many kinds of sulfonated polymers with high ion exchange capacity (IEC) values have been developed as alternative materials to Nafion in the past decades, including sulfonated polyimide (SPI),[4–6] sulfonated polysulfones (SPSFs),[7] sulfonated polyphenylenes,[8] sulfonated poly(ether ether ketone) (SPEEK),[9,10] and sulfonated polyphosphazene.[11,12] Among them, sulfonated polyphosphazenes are considered to be one of the most promising candidates because of their low methanol permeability, good chemical stability, and facile preparation process.[11–14] Although these

membranes with high IEC values can achieve sufficient conductivities, such membranes usually result in high water swelling and methanol permeability, making them impractical for use in DMFC applications.

One of the approaches to improve the performance is to design polymer structure composed of hydrophilic and hydrophobic segments which are expected to improve proton conductivity and reduce the water swelling of membranes due to the defined phase-separated structure between hydrophilic and hydrophobic domains.[15–21] In addition, several research groups proved that flexible pendent perfluoroalkyl sulfonic acid groups in the side chains of polymers could effectively form the phase separation and enhance the proton conductivity.[22,23] Ken and coworkers reported a series of poly(ether sulfone) membranes with flexible pendent perfluoroalkyl sulfonic acid side chain and hydrophobic main chain, showing the increased proton conductivities with relatively low IEC values.[24] Ueda's group prepared poly (phenylene ether)s membranes with pendent perfluoroalkyl sulfonic acid side chains, which exhibited low water swelling and high proton conductivities

Scheme 1. Synthetic route of SPEEK.

due to the flexibility and high acidity of the side chains.[25] Moreover, introduction of high conductive polymers into polymer structure by crosslinking is thought to be an attractive method to enhance proton conductivity while maintains low methanol permeability of membranes. Na group prepared a series of crosslinked membranes by crosslinking SPEEK and (2-acrylamido-2-methyl propane sulfonic acid). Their results showed that these membranes exhibited increased proton conductivities and low methanol permeability values.[26]

With the aim to obtain the PEMs with high proton conductivity, low methanol permeability and water swelling, we synthesized a novel sulfonated grafted polyphosphazene bearing pendent perfluorosulfonic acid groups (PMFP-*g*-PS) to promote the separation of hydrophilic and hydrophobic phases, finally to improve the proton conductivity. Then, a series of crosslinked membranes based on PMFP-*g*-PS and sulfonated poly(ether ether ketone) (SPEEK) were designed and prepared. SPEEK is chosen because of its good proton conductivity and low methanol permeability properties.[27–32] These membranes showed high proton conductivities and low methanol permeability values. The membrane properties, such as water uptake, swelling ratio, thermal stability, oxidative stabilities were also investigated in detail.

EXPERIMENTAL

Materials
Poly(ether ether ketone) (PEEK) 450G Victrex, provided by ICI Corp, was dried in a vacuum at 130 °C for at least 12 h prior to sulfonation. Hexachlorocyclotriphosphazene (NPCl$_2$)$_3$ was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), Dioxane, Concentrated sulfuric acid (98%) were purchased from Aldrich Chemical Co. 4-methylphenol, N-bromosuccinimide (NBS), benzoyl peroxide (BPO), CuBr and 2,2-bipyridine (bpy) were purchased from Aldrich Chemical Co. Styrene was purchased from TCI Chemical Co. Copper (I) bromide (CuBr, AR grade) was purified by stirring in acetic acid, washing with methanol, and then drying under vacuum. Styrene was passed through a column of basic aluminium prior to use. (NPCl$_2$)$_3$ was purified by two recrystallizations from hexane and vacuum sublimation prior to use. 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethanesulphonic acid sultone was purchased from Sigma-Aldrich. Dioxane and THF were freshly distilled from sodium benzophenone ketyl. 2,6-*Bis*(hydroxymethyl)−4-methylphenol (BHMP) was prepared by hydroxymethylation of *p*-cresol according to a reported procedure.[33] Other chemical reagents

and the organic solvents were purchased from Beijing Chemical Reagent and were purified by conventional methods.

Characterizations and Measurements
Fourier transform infrared (FTIR) spectra of the membranes were measured on a Nicolet Nexux 470. Nuclear magnetic resonance (NMR) spectra were recorded on a AVANCE-300 spectrometer. Number- and weight-average molecular weights (M_n and M_w) were measured by Waters-515 gel permeation chromatography (GPC) instrument (tetrahydrofuran as eluent and polystyrene as standard). The molecular weight distribution (PDI) of copolymers was obtained from GPC. Thermogravimetic analysis (TGA) was performed with TGA-Q500 at a heating rate of 10 °C/min under nitrogen in the range of 25–700 °C. Transmission electron microscopic (TEM) observations were performed with a JEOL JEM-2010 transmission electron microscope.

### Synthesis of Sulfonated Poly(ether ether ketone) (SPEEK)
PEEK (3.0 g) was slowly added to sulfuric acid (98 wt %, 60 mL) at room temperature under a N$_2$ atmosphere. After the complete dissolution of PEEK, the solution was stirred at 70 °C under vigorous mechanical stirring for 2 h. The polymer solution was then cooled in ice water bath to terminate the reaction and poured into excess cold water to give a fibrous type SPEEK polymer. The precipitated polymer was filtered and washed several times with distilled water until the pH was neutral and dried under vacuum at 100 °C for 24 h, as shown in Scheme 1. According to previous report,[9] the degree of sulfonation (DS) of the polymer was 70%.

Synthesis of Poly[(4-methylphenoxy)(4-methoxyphenoxy)phosphazene] (PMMP)
Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene (NPCl$_2$)$_3$ at 250 °C in a sealed tube.[34,35] 4-methylphenol (4.65 g, 43 mmol) was added to a suspension of NaH (60% by weight, 1.72 g, 43 mmol of NaH) and tetra-(*n*-butyl) ammonium bromide (0.33 g, 1 mmol) in 1,4-dioxane (60 mL). The mixture was refluxed overnight to form the sodium salt. The salt solution was added slowly dropwise to a rapidly stirred solution of PDCP (5.0 g, 43 mmol) in 1,4-dioxane (80 mL) under an inert atmosphere in a 250 mL three-neck flask equipped with a reflux condenser, magnetic stirrer and N$_2$ inlet/outlet. The reaction mixture was refluxed for 24 h, and then a solution of sodium 4-methoxyphenoxide in 1,4-dioxane was added dropwise. The sodium 4-methoxyphenoxide was prepared by adding 4-methoxyphenoxide (10.66 g, 86 mmol) to a suspension of NaH (60% by weight, 3.44 g, 86 mmol of NaH) in 1,4-dioxane (60 mL), and the mixture was refluxed overnight. The reaction mixture was stirred at 100 °C for 24 h. Then it was poured into distilled water and the polymer was collected. The resulting polymer was purified by successive reprecipitation from THF to hexane. The obtained polymer PMMP was dried in vacuum oven at 60 °C overnight (Scheme 2). ^{1}H-NMR (300 MHz, CDCl$_3$, δ): 6.251–6.725 (m, —OC$_6$H$_4$), 3.470 (s, —OCH$_3$), 2.077 (s, —CH$_3$). ($M_n = 2.07 \times 10^5$ Da, $M_w = 5.37 \times 10^5$ Da, PDI = 2.59).

Synthesis of PMMP-Br Initiator
To a 200 mL round-bottom flask, equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet/outlet, the polymer
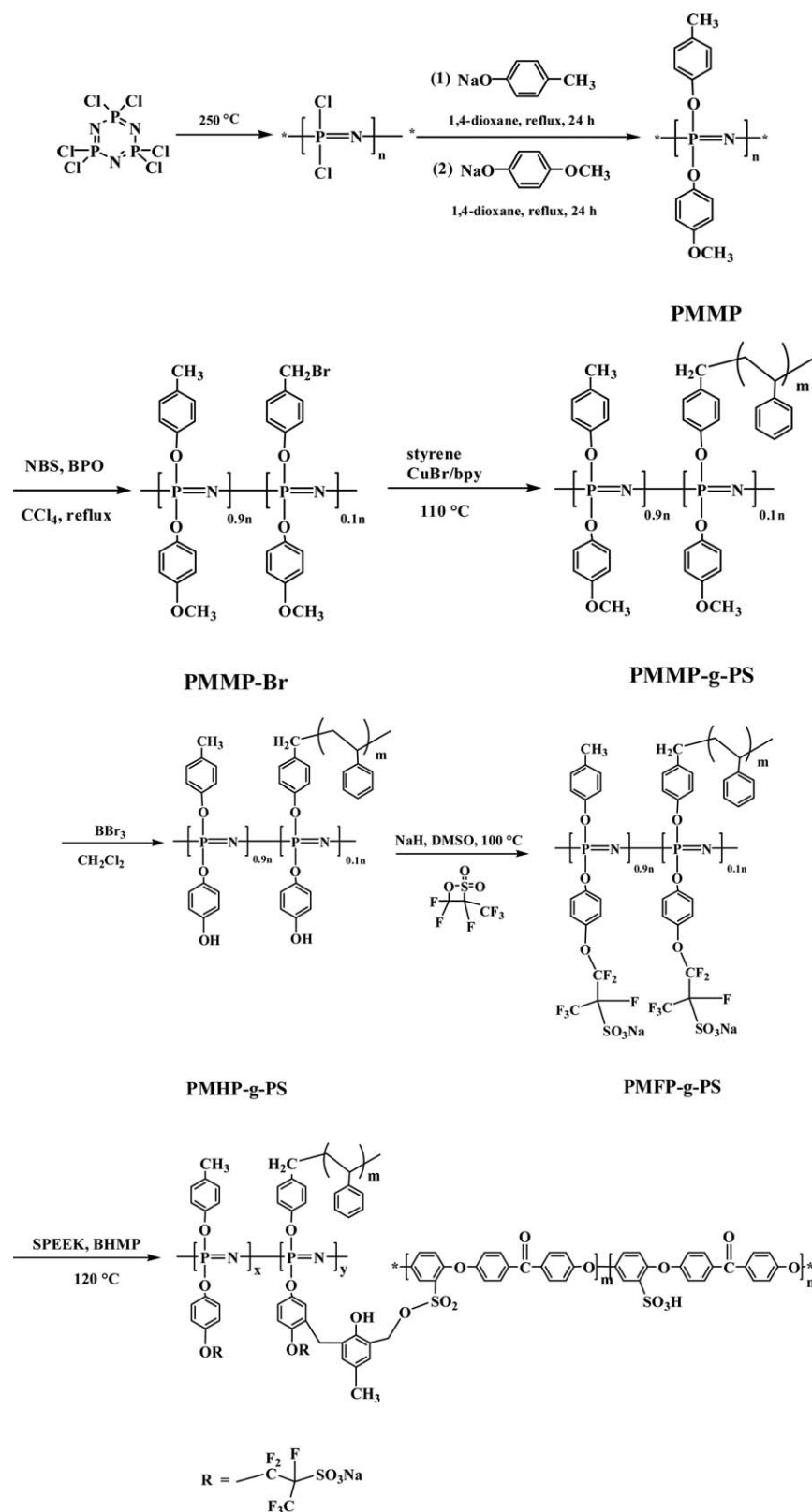
Scheme 2. Synthetic routes for the copolymers.

PMMP (1.0 g, 3.6 mmol), NBS (0.128 g, 0.72 mmol), BPO (0.017 g, 0.072 mmol), and carbon tetrachloride (100 mL) were added. The solution was shielded from light and brought rapidly to reflux at 80 °C for 3 h. Then, the mixture was cooled and filtered. The filtrate was concentrated under reduced pressure and precipitated into hexane to give crude product, which

was re-precipitated from THF to hexane for two additional times and then dried at 50 °C under vacuum for 24 h. ^{1}H-NMR (300 MHz, CDCl$_3$, δ): 6.277–6.705 (m, —OC$_6$H$_4$), 4.171 (s, CH$_2$Br), 3.479 (s, —OCH$_3$), 2.081 (s, —CH$_3$).

Synthesis of PMMP-*g*-Polystyrene (PMMP-*g*-PS)

PMMP-*g*-polystyrene copolymer was synthesized using an atom transfer radical polymerization (ATRP).[12,14] The macroinitiator PMMP-Br (0.72 g, 2.6 mmol), styrene (1.083 g, 10.4 mmol), Bpy (3.65 g, 23.4 mmol), and CuBr (1.12 g, 7.8 mmol) were added to a dried reaction tube equipped with a stopcock and a magnetic stirrer. Three freeze-pump–thaw cycles were performed to remove oxygen. The polymerization reaction was carried out at 115 °C for 24 h under a nitrogen blanket and then resulting mixture was diluted with THF, purified by passing through a column of alumina, and then precipitated into methanol. ^{1}H-NMR (300 MHz, CDCl$_3$, δ): 6.976–7.182 (m, —C$_6$H$_5$), 6.247–6.705 (m, —OC$_6$H$_4$), 3.471 (s, —OCH$_3$), 2.076 (s, —CH$_3$), 1.256–1.852 (m, —CH$_2$, —CH,). (M_n = 4.36 × 10^5 Da, M_w = 11.67 × 10^5 Da, PDI = 2.68).

Synthesis of Poly[(4-methylphenoxy)(4-hydroxyphenoxy)phosphazene]-*g*-Polystyrene (PMHP-*g*-PS)

PMMP-*g*-polystyrene (1.24 g, 3.6 mmol) and CH$_2$Cl$_2$ (50 mL) were added into a 50 mL dried flask, and excess BBr$_3$ (2.0 mL) was added dropwise. The reaction mixture was magnetically stirred under nitrogen at room temperature for 5 h. The resulting mixture was precipitated in water, and the residue was washed with water several times and dried under vacuum at 60 °C for 24 h to give the product. ^{1}H-NMR (300 MHz, DMSO-d_6, δ): 9.015 (s, —OH), 6.701–7.032 (m, —C$_6$H$_5$), 6.323–6.609 (m, —OC$_6$H$_4$), 2.034 (s, —CH$_3$), 1.234–1.847 (m, —CH$_2$, —CH,).

Synthesis of Poly[(4-methylphenoxy)(4-perfluoroalkyloxyphenoxy)phosphazene] (PMFP)-*g*-Polystyrene (PMFP-*g*-PS)

NaH (0.052 g, 2.16 mmol) was added into the solution of PMHP-*g*-PS (0.60 g, 1.8 mmol) in DMSO (10 mL). The reaction mixture was magnetically stirred at 40 °C for 24 h, and 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethanesulphonic acid sultone (0.23 g, 1 mmol) was added dropwise into the reaction system. The resulting mixture was magnetically stirred under nitrogen at 100 °C for 24 h, and then was precipitated in isopropanol. The isolated polymer was dried at 80 °C for 10 h in vacuum. ^{1}H-NMR (300 MHz, DMSO-d_6, δ): 6.861–7.041 (m, —C$_6$H$_5$), 6.317–6.861 (m, —OC$_6$H$_4$), 2.014 (s, —CH$_3$), 1.235–1.860 (m, —CH$_2$, —CH,). ^{19}F-NMR (282 MHz, DMSO-d_6, δ): δ: −64.033, −139.199, −184.272.

Preparation of the Membranes

Membranes were prepared by a solution casting method according to previous report.[13,36–39] The PMFP-*g*-PS copolymer, dried SPEEK and the crosslinker BHMP (5 wt %) were dissolved in DMSO to give a 10 w/v % solution overnight, then a drop pf methanesulfonic acid was added. The solutions were cast on to clean Teflon plates, and dried at 120 °C for 1 h and vacuum dried at 70 °C for 24 h. The membrane was immersed into water to remove the residual solvent. The resulting membranes were immersed into 2.0 mol/L H$_2$SO$_4$ for 48 h, and then rinsed with deionized water for another 24 h to obtain the H$^+$ form membranes. The membranes thus prepared were designated as PMFP-*g*-PS/SPEEK X, where X is the SPEEK content (wt %) in the membrane. The SPEEK content is from 0 to 30% in the membranes. All membranes were approximately 100–150 μm thick.

Proton Conductivity

The proton conductivity of the membrane was determined using electrochemical impedance analyzer (CHI660D) over the frequency from 1 Hz to 100 MHz. A four-point-probe cell with two pairs of platinum plate electrodes pressed with a sample membrane was mounted in a sealed Teflon cell. The distance between two electrodes was 1 cm. The cell was placed in deionized water for measurement. The membranes were hydrated in deionized water at room temperature for 1 day prior to the measurement.

The conductivity (σ) of the samples was calculated from

$$\sigma = L/RS$$

where L is the distance between the electrodes to measure the potential. R is the membrane resistance, and S is the cross sectional area of the membrane sample.

Methanol Permeability

Methanol permeability (P) measured through a reported method was carried out using a liquid diffusion cell composed of two compartments containing solutions A and B. A (V_A = 50 mL) is 1 mol/L methanol solution, and B (V_B = 50 mL) was deionized water.[12,14] The membrane under test was immersed in deionized water for hydration before measurements and then vertically placed between the two compartments by a screw clamp. Both solutions were stirred during testing to keep them homogenous. A gas chromatograph (Shimadzu, GC-14B) was used to monitor the concentration of methanol diffusion from compartment solution A to B across the membrane over time. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability coefficient was calculated by the following equation:

$$P = (k \times V_B \times h)/(A \times C_A)$$

where P is the methanol permeability (cm^2/s), k is the slope of the straight-line plot of methanol concentration in solution B versus testing time, V_B is the volume of solution B (mL), C_A is the concentration of methanol in A (mol/L), A is the membrane areas (cm^2), and h is the thickness of wet membrane (cm), respectively.

Water Uptake Measurements

Water uptake (WU) was measured by immersing the membrane into deionized water for 24 h. Then, the membrane was taken out, wiped with a tissue paper, and quickly weighed on a microbalance. Water uptake was calculated from

$$\text{Water uptake }(\%) = \left[\left(W_{\text{wet}} - W_{\text{dry}} \right)/W_{\text{dry}} \right] \times 100\%$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. The weights of dried membranes were measured after drying in vacuum at 70 °C for 8 h.

Swelling ratio (SW) was determined by immersing membranes samples into water for 24 h and measuring the change in length before and after the swelling according to the following equation:

$$\text{Swelling ratio (\%)} = \left[\left(L_{\text{wet}} - L_{\text{dry}} \right) / L_{\text{dry}} \right] \times 100\%$$

where L_{wet} and L_{dry} are the lengths of wet and dry membranes, respectively.

Oxidative Stability

Oxidative stability of the membranes was tested by immersing the membrane into hot Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h.[14]

Ion Exchange Capacity (IEC)

IEC of the sulfonated polymers was measured using a typical titration method. The membranes in acid form were equilibrated with 50 mL NaCl solution of 2 mol/L for 24 h at room temperature. The amount of the H^+ released from the membranes was determined by titration of 0.01 mol/L NaOH aqueous solution using pH meter to monitor the end points. The moles of the proton were equal to those of sulfonic groups and the IEC was calculated from the titration data using the following equation:

$$\text{IEC} = \left(C_{\text{NaOH}} \times V_{\text{NaOH}} \right) / W_s$$

where C_{NaOH} is the concentration of NaOH solution, V_{NaOH} is the consumed volume of NaOH solution, and W_s is the weight of the dry membrane sample.

TEM Observations

The membranes were stained with lead by ion exchange of the sulfonic acid groups by immersing it in a large excess of $Pb(NO_3)_2$ aqueous solution for 24 h and then rinsed with water, and dried at room temperature. The stained membranes were embedded in epoxy resin and sectioned to give 70 nm thick membranes. TEM observations were performed with a JEOL JEM-2010 transmission electron microscope.

RESULTS AND DISCUSSION

Synthesis and Characterization of Copolymers

The polyphosphazene copolymer poly[(4-methylphenoxy)(4-methoxyphenoxy) phosphazene] (PMMP) was prepared by the substitution reaction on poly(dichlorophosphazene) with sodium phenolates (Scheme 2). The Bromination of the benzylic methyl group of PMMP produced the macroinitiator PMMP-Br with the bromination degree (Br %) of 10% calculated according to our previous studies.[12,14] The reaction of macroinitiator PMMP-Br with the styrene yielded the graft copolymer by the CuBr-catalyzed atom transfer radical polymerization (ATRP). In the ATRP reaction, the feed molar ratio of macroinitiator/CuBr/bpy in the reaction was set to 1:3:9. The resulting unit number of styrene (S_x) in the graft side chains of the product PMMP-g-PS was calculated from ^{1}H-NMR, and the length of the grafted side chain in copolymer was approximate 7 in this study.[35,38]

The chemical structures of the synthesized copolymers were characterized by IR and ^{1}H-NMR spectroscopy. The structure of poly[(4-methylphenoxy) (4-methoxyphenoxy)phosphazene] (PMMP) was confirmed by ^{1}H-NMR analysis, as shown in Figure 1(a), the signals in the spectrum at about 2.077 and 3.47 ppm were contributed to the chemical shifts of methyl group and methoxy group, respectively. Figure 1(b) shows the ^{1}H-NMR spectrum of PMMP-g-PS. The signal at 3.471 ppm was assigned to the methoxy protons. Meanwhile, the signals at 6.976 and 7.182 ppm were assigned to the aromatic protons of

polystyrene grafting to the side chain. PMMP-g-PS was then converted to the copolymer with phenolic hydroxyl groups (PMHP-g-PS) by treatment with BBr_3 in CH_2Cl_2. As shown in the FT-IR spectra (Figure 2), in comparison with PMMP-g-PS, PMHP-g-PS showed a new characteristic band at 3405.9 cm^{-1} that can be assigned to the stretching vibration of the phenolic hydroxyl group. In the ^{1}H-NMR of PMHP-g-PS [Figure 1(c)], the signal at 9.015 ppm was assigned to the hydroxyl group compared with PMMP-g-PS [Figure 1(b)]. Further, PMFP-g-PS with perfluoroalkyl sulfonic acid groups was obtained by the ring-opening reaction, as shown in Scheme 2. As shown in PMFP-g-PS [Figure 2(c)], the absorption peak at 1124.4 cm^{-1} can be due to symmetric O=S=O stretching vibration of the sulfonic acids. As shown in Figure 1, there was remarkable change in the ^{1}H-NMR spectrum of PMFP-g-PS [Figure 1(d)] compared to that of PMHP-g-PS [Figure 1(c)]. The disappearance of the hydroxyl signal indicated that the perfluoroalkyl sulfonic acid groups were grafted onto PMHP-g-PS.

The structure of PMFP-g-PS was also analyzed by ^{19}F NMR to examine the structures. As shown in Figure 3, three ^{19}F signals at −184.272, −139.199, and −64.033 ppm were due to the —CF, —CF$_2$, and —CF$_3$ fluorine moieties, respectively. The results indicated the successful introduction of pendent sulfonic acid groups in the polymers.

Thermal and Oxidative Stabilities

The thermal stabilities of the membranes were investigated by thermogravimetric analysis (TGA). Figure 4 showed the TGA curves of the membranes, which appeared to have three distinct decomposition steps. The first decomposition stage before 200 °C was possibly associated with the loss of absorbed water. The second stage (200–390 °C) arose from the decomposition of pendent sulfonic acid groups. The last stage, which started around 390 °C, was mainly due to main-chain decomposition. As shown in Table I, the 10% weight loss temperature ($T_{d10\%}$) of the obtained copolymers was comparable with the Nafion 117. Among the membranes, the $T_{d10\%}$ of PMFP-g-PS and PMFP-g-PS/SPEEK 10 were higher than Nafion 117, suggesting both PMFP-g-PS and PMFP-g-PS/SPEEK 10 have higher thermal stabilities than Nafion 117. These results indicated that the obtained membranes were thermally stable within the temperature range for DMFC applications.

The oxidative stability of the membranes was evaluated by remaining weight in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C for 1 h. The results were listed in Table I, all the membranes exhibited good oxidative stability. Compared to the reported main-chain type sulfonated polyphosphazene membrane with the similar IEC value, weight retention for all samples was above 92% after treatment in Fenton's reagent at 80 °C for 1 h, showing the improved oxidative stabilities.[12] This might be contributed to the highly stable grafted polyphosphazene backbone and crosslinking structures of copolymers, which could effectively suppress the attack of oxidative radicals and improve the oxidative stabilities of membranes.[40,41]

Ionic Exchange Capacity (IEC), Water Uptake, and Swelling Ratio Measurements

The ionic exchange capacity (IEC) is a key parameter for evaluating membrane performance. The IEC values of the membranes
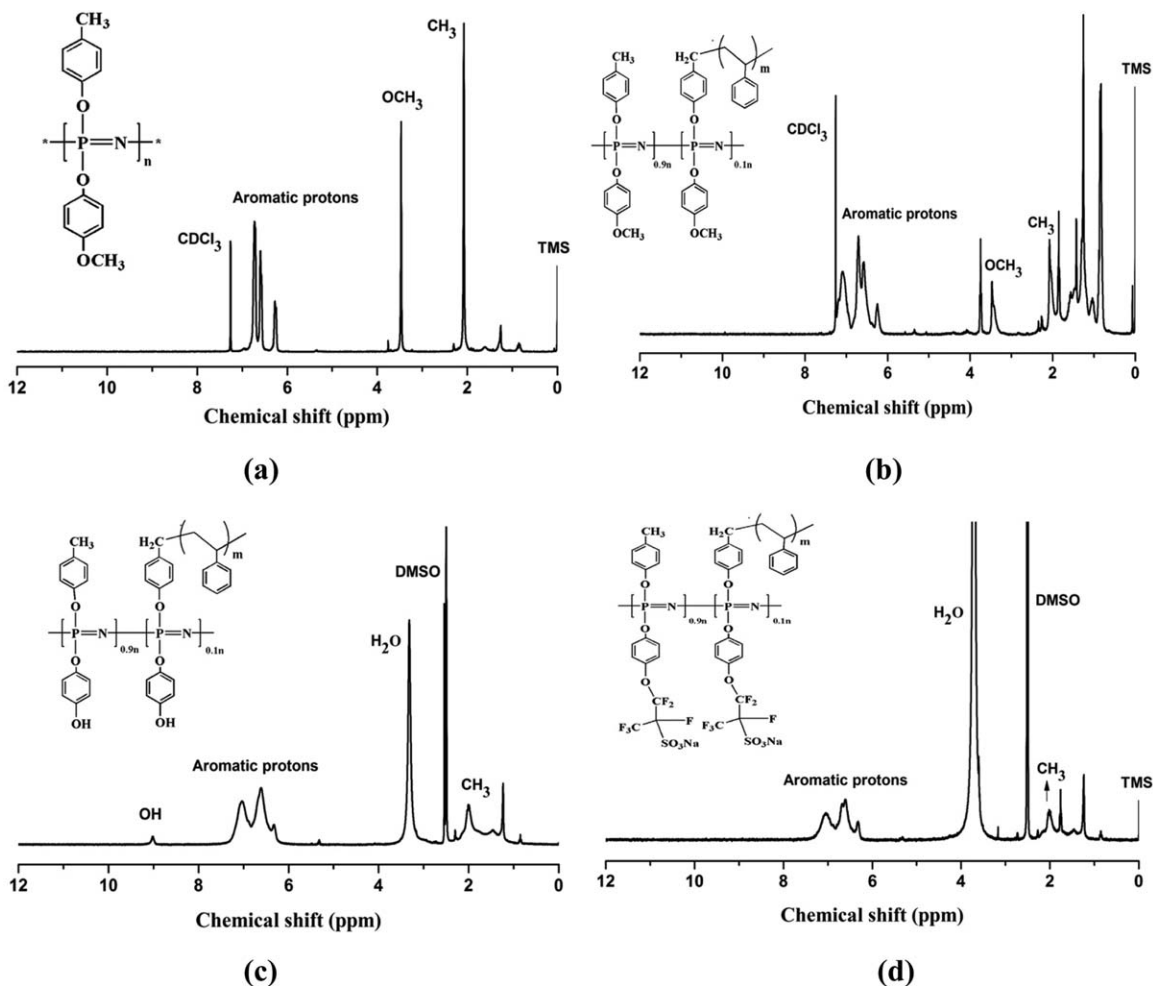
Figure 1. ^{1}H-NMR spectra of copolymers: (a) PMMP, (b) PMMP-*g*-PS, (c) PMHP-*g*-PS, (d) PMFP-*g*-PS.

were measured by titration and the results were listed in Table I. The IEC values of the PMFP-*g*-PS/SPEEK membranes showed an increase from 1.21 to 1.42 mmol/g with increasing SPEEK content from 0 to 30%.
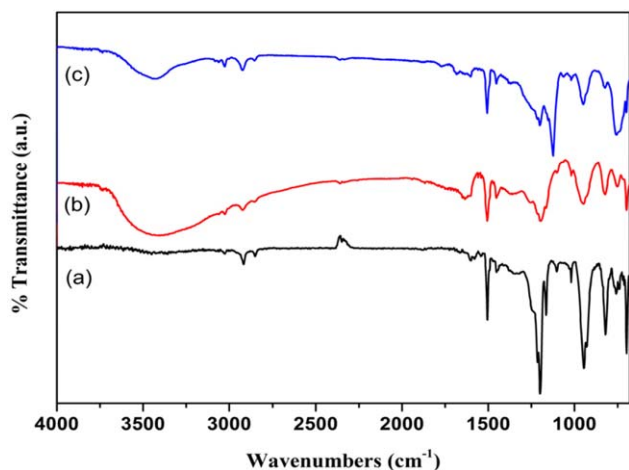

Figure 2. FT-IR spectra of (a) PMMP-*g*-PS, (b) PMHP-*g*-PS, (c) PMFP-*g*-PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water uptakes of membranes are known to have a profound effect on proton and methanol permeability.[42] For most proton conductive polymers, water acts as the carrier for the proton transportation through the polymer membrane. However, high water uptake in the membrane usually leads to high methanol permeability and poor dimensional stability. Thus an optimum water uptake is needed for application for PEMs. As shown in Table I, the water uptakes and swelling ratios of the membranes increased with increasing temperature and IEC value. The water
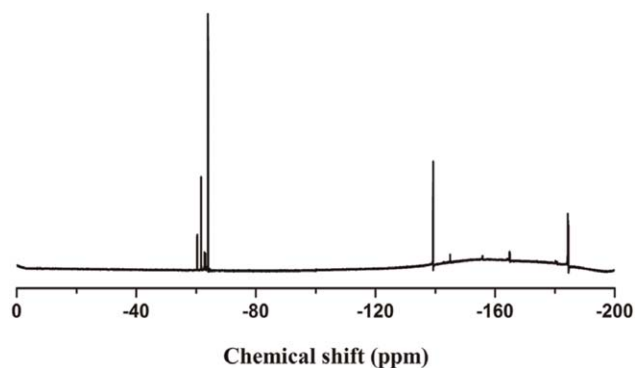

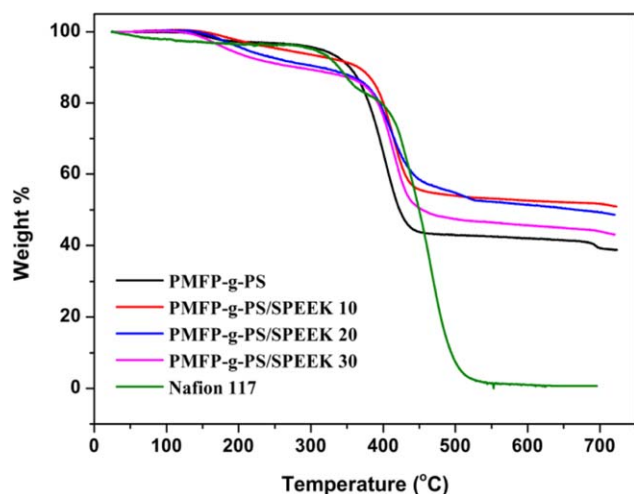**Figure 3.** ^{19}F-NMR spectra of copolymer PMFP-*g*-PS.

Figure 4. TGA curves of the membranes and Nafion 117. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
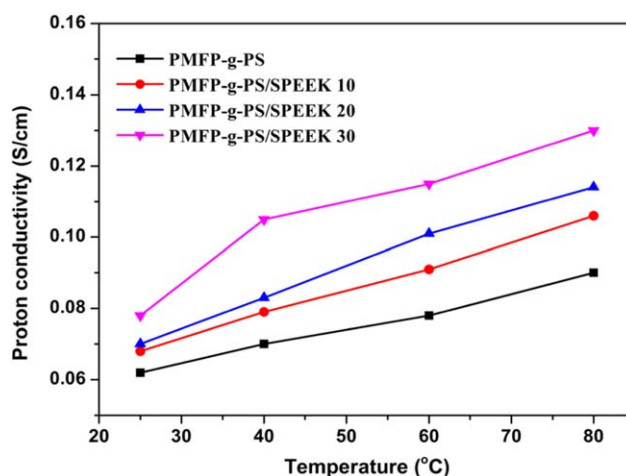

Figure 5. Proton conductivities of membranes at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

uptakes of PMFP-g-PS/SPEEK membranes were found to increase with the rise of SPEEK content. This can be attributed to the incorporation of more sulfonic acid groups from the SPEEK increases the water absorption capacity. In this experiment, when the content of SPEEK was increased to approximate 35%, the membrane could be broken in hot water. Hence, in this study, we chose 30% as the maximum of the SPEEK content.

All of the membranes exhibited lower swelling ratios than that of Nafion (Table I). Among them, the PMFP-g-PS exhibited good resistance to water since the swelling ratio of PMFP-g-PS was only 3.6% at 25°C, the comparatively low water uptake and swelling ratio might be attributed to the existence of short hydrophobic chain between the sulfonic acid groups and polymer main chain, which could favor the phase separation in the sulfonated polymer and suppress the swelling behavior.[43–45]

Proton Conductivity and Methanol Permeability
Proton conductivity is considered to play an important role in the performance of fuel cells. In general, the proton conductivity depends on the number of available sulfonic acid group and their acidity in water.[46] Figure 5 shows the proton conductivities of

copolymers as a function of temperature ranging from 25 to 80°C under fully hydrated condition. As shown in Figure 5, the proton conductivities of all the membranes increased with increasing temperature or the IEC values.

Methanol permeation through the membrane is another key factor that affects fuel cell performance, because the permeated methanol will poison the cathode catalyst, and reduce the fuel efficiency.[47] Polyphosphazene has been chosen as structure base for the design and preparation of new PEM material for DMFC in our work because of its excellent methanol resistance.[12,14] As shown in Table II, all the membranes showed low methanol permeability in the range of $1.32–3.85 \times 10^{-7}$ cm²/s at room temperature, which was lower than the Nafion 117 (12.1×10^{-7} cm²/s). This suggested the polyphospahzene skeleton and crosslinked structures have effectively suppressed the methanol permeability. The methanol permeability of the membranes increased as the IEC values increased. The methanol permeability value of the PMFP-g-PS/SPEEK 30 (IEC = 1.42 mmol/g) was higher than that of PMFP-g-PS (IEC = 1.21 mmol/g). The increased methanol permeability values of PMFP-g-PS to PMFP-g-PS/SPEEK 30 might be attributed to: (1) the addition of SPEEK caused the high IEC

Table I. Compositions of Membranes and their Thermal Properties, IEC, Water Uptake and Swelling Ratio

Membrane	PMFP-g-PS (wt %)	SPEEK (wt %)	$T_{d10\%}$ (°C)	Oxidative stability RW[a] (%)	IEC (mmol/g)	Water uptake (wt %)		Swelling ratio (%)	
						25°C	80°C	25°C	80°C
PMFP-g-PS	100	0	353.49	99	1.21	14.6	44.3	3.6	10.3
PMFP-g-PS/ SPEEK 10	90	10	365.28	98	1.27	16.5	46.7	4.1	12.4
PMFP-g-PS/ SPEEK 20	80	20	312.50	96	1.34	22.1	55.6	9.5	16.2
PMFP-g-PS/ SPEEK 30	70	30	279.84	92	1.42	27.5	63.8	11.6	20.9
Nafion 117	0	0	338.49	98	0.90	34.5	40.3	23.5	32.4

[a] Remaining weights of membranes after treating in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80°C for 1 h.

Table II. Proton Conductivities, Methanol Permeability and Selectivity of Membranes

Membrane	Proton conductivity (S/cm)		Methanol permeability coefficient[a] (cm^2/s) $\times 10^{-7}$	Selectivity $\times 10^5$ (Ss/cm^3)
	25 °C	80 °C		
PMFP-g-PS	0.062	0.090	1.32	4.70
PMFP-g-PS/SPEEK 10	0.068	0.106	1.58	4.30
PMFP-g-PS/SPEEK 20	0.070	0.114	2.35	2.98
PMFP-g-PS/SPEEK 30	0.078	0.131	3.85	2.03
Nafion 117	0.090	0.170	12.1	0.74

[a] Determined at 25 °C.

values and water uptakes, which could enhance the high methanol permeation; (2) the well-developed hydrophilic domains that were easier to form channel for methanol to pass, which was supported by TEM observation.[47]

The selectivity (the ratio proton conductivity to methanol permeability) was also calculated to evaluate the potential performance of direct methanol fuel cell membranes. The higher selectivity of the membrane is, the better the membrane can perform as both a good conductor and a good separator in DMFC. As shown in Table II, the selectivity ratio values of the membranes were higher than that of Nafion. Compared with reported SPEEK membrane with similar IEC value,[48] the proton conductivity of the PMFP-g-PS/SPEEK 30 was higher than that of SPEEK in the range of 25–80 °C. The methanol permeability value of PMFP-g-PS/SPEEK 30 (3.85×10^{-7} cm^2/s) was lower than that of SPEEK (7.3×10^{-7} cm^2/s) at 25 °C. Moreover, the selectivity value of PMFP-g-PS/SPEEK 30 was three times higher than that of SPEEK. These results indicated that these membranes could be potentially used for DMFCs application.

TEM Observation

The morphology of membranes was investigated by TEM observation. Proton conductivity of the membrane is closely related to their morphology. The TEM images of membranes PMFP-g-PS and PMFP-g-PS/SPEEK 30 were shown in Figure 6. As shown in Figure 6, both the PMFP-g-PS and PMFP-g-PS/SPEEK 30 showed well-defined phase separated structures. The dark regions in the image were assigned to the hydrophilic sulfonate groups. The bright regions in the images were attributed to the hydrophobic polymer matrix. Compared to PMFP-g-PS, crosslinked

membranes PMFP-g-PS/SPEEK X showed improved proton conductivities and water uptakes with the SPEEK content increased. According to TEM observation, more hydrophilic domains were observed for PMFP-g-PS/SPEEK 30. That might be because the incorporation of SPEEK could result in higher water absorption capacity to create additional hydrophilic channels through sulfonic acid groups, which would lead to more obvious hydrophilic/hydrophobic separation and improve proton conductivity.[49]

CONCLUSIONS

A series of crosslinked membranes based on sulfonated polyphosphazene containing flexible pendent perfluorosulfonic acid groups and SPEEK have been prepared. The obtained membranes exhibited suitable water uptake, low swelling ratios and high proton conductivities. The methanol permeability values of the membranes were in the range of 1.32–3.85×10^{-7} cm^2/s, which were much lower than Nafion 117 (12.1×10^{-7} cm^2/s). The crosslinked membranes showed higher water uptakes and proton conductivities than the pristine PMFP-g-PS membrane. Among them, the PMFP-g-PS/SPEEK 30 displayed a high proton conductivity of 0.131 S/cm at 80 °C and a low methanol permeability value which was only one third of Nafion 117. Moreover, these membranes show not only good thermal and oxidative stabilities but also higher selectivity values compared with Nafion 117. TEM observations suggested that these membranes showed obvious phase separation, favorable for the effective proton transportation via the membrane. These results indicated that the membranes were promising candidates for proton exchange membranes.
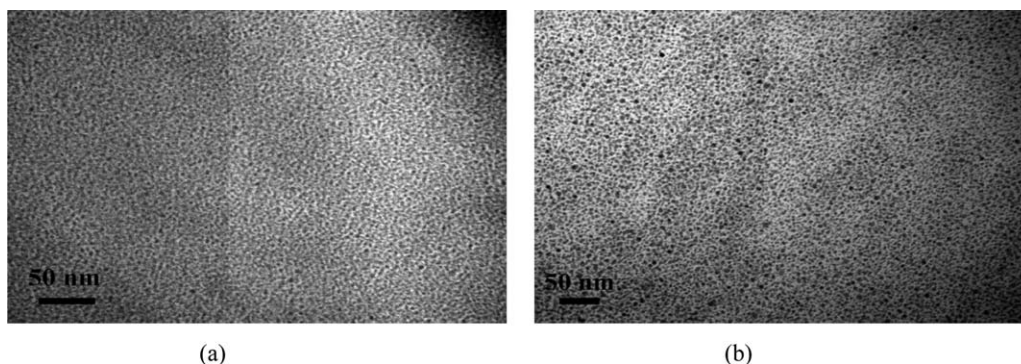

(a)

(b)

Figure 6. TEM images of (a) PMFP-g-PS, (b) PMFP-g-PS/SPEEK 30.

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