

# Synthesis and properties of sulfonated poly(phosphazene)-graft-poly(styrene-co-*N*-benzylmaleimide) copolymers via atom transfer radical polymerization for proton exchange membrane

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**ABSTRACT:** A series of sulfonated poly(phosphazene)-graft-poly(styrene-co-*N*-benzylmaleimide) (*PP-g-PSN*) copolymers were prepared via atom transfer radical polymerization (ATRP), followed by regioselective sulfonation which occurred preferentially at the poly(styrene-co-*N*-benzylmaleimide) sites. The structures of these copolymers were confirmed by Fourier transform infrared (FTIR) spectroscopy, <sup>1</sup>H-NMR, and <sup>31</sup>P-NMR, respectively. The resulting sulfonated *PP-g-PSN* membranes showed high water uptakes (WUs), low water swelling ratios (SWs), low methanol permeability coefficients, and proper proton conductivities. In comparison with non-grafting sulfonated poly(bis(phenoxy)phosphazene) (SPBPP) membrane previously reported, the present membranes displayed higher proton conductivity, significantly improved the thermal and oxidative stabilities. Transmission electron microscopy (TEM) observation showed clear phase-separated structures resulting from the difference in polarity between the hydrophobic polyphosphazene backbone and hydrophilic sulfonated poly(styrene-co-*N*-benzylmaleimide) side chains, indicating effective ionic pathway in these membranes. The results showed that these materials were promising candidate materials for proton exchange membrane (PEM) in direct methanol fuel cell (DMFC) applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42251.

**KEYWORDS:** batteries and fuel cells; copolymers; grafting; membranes; ring-opening polymerization

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## INTRODUCTION

During the last decades, DMFCs have attracted increasing attention by virtue of their low emission of pollutants, stable and simple operating conditions at a relatively low temperature.<sup>1,2</sup> The PEM is the critical component in DMFC that acts as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport.

Perfluorosulfonated membranes, such as Nafion membranes, are the most common PEMs used in DMFCs due to their high proton conductivities and excellent thermal as well as chemical stabilities.<sup>3</sup> However, the expensive cost, high methanol crossover and difficulty in preparation have limited their widespread commercial application.<sup>4,5</sup> In particular, the high methanol crossover causes not only catalyst poisoning but also fuel consumption and energy efficiency loss.<sup>6,7</sup> To overcome these problems, many efforts have been devoted to improve Nafion-based membrane or to develop new PEMs.<sup>8,9</sup>

Among the alternative materials, sulfonated polymers, such as sulfonated poly(ether ether ketone)s,<sup>10,11</sup> sulfonated polysul-

phones,<sup>12,13</sup> and sulfonated polyphosphazenes,<sup>14,15</sup> have been considered as candidates as alternative PEM materials due to their high thermal and chemical stability, high proton conductivity and low cost. To obtain high proton conductivity, these sulfonated polymers should have high degree of sulfonation (DS). However, the sulfonic acid groups in these polymers with high DS are located on the main chain, which consequently leads to high SW and poor oxidative stability.<sup>16</sup>

Among these materials, sulfonated polyphosphazenes are attracting a great deal of attention. These materials have been widely investigated as PEM materials for their low cost, high proton conductivity, and low methanol crossover.<sup>14,15</sup> In our previous study, the preparation and properties of SPBPP membranes have been reported.<sup>17</sup> However, inadequate thermal and oxidative properties of these membranes limit their practical application in PEMs.

The main aim of this study is to enhance the thermal and oxidative properties of sulfonated polyphosphazene while maintaining the high proton conductivity and low methanol

permeability. The introduction of rigid moieties to polymer backbone as side-chain structure has been considered as strategy to improve thermal and chemical property of polymer.<sup>18</sup> In order to achieve the objective, the poly(styrene-co-*N*-benzylmaleimide) has been prepared and grafted on the side chain of polyphosphazene. Poly(styrene-co-*N*-benzylmaleimide) exhibits excellent thermal and chemical stability. Because *N*-substituted maleimide (MI) monomer contains a rigid planar ring and can effectively enhance the glass transition temperature ( $T_g$ ) and degradation temperature of copolymers.<sup>19–22</sup> Therefore, introduction of poly(styrene-co-*N*-benzylmaleimide) onto polyphosphazenes is reasonable to prepare the PEM with better performance. In addition, sulfonation of the poly(styrene-co-*N*-benzylmaleimide) moiety may be helpful to form phase separation structures, and in turn to improve proton conductivity.<sup>23</sup>

Here, we report the graft of poly(styrene-co-*N*-benzylmaleimide) on the side chain of polyphosphazenes by ATRP. The properties of these membranes possessing different degrees of sulfonation, such as proton conductivity, methanol permeability, WU, thermal stability, and oxidative stability were investigated.

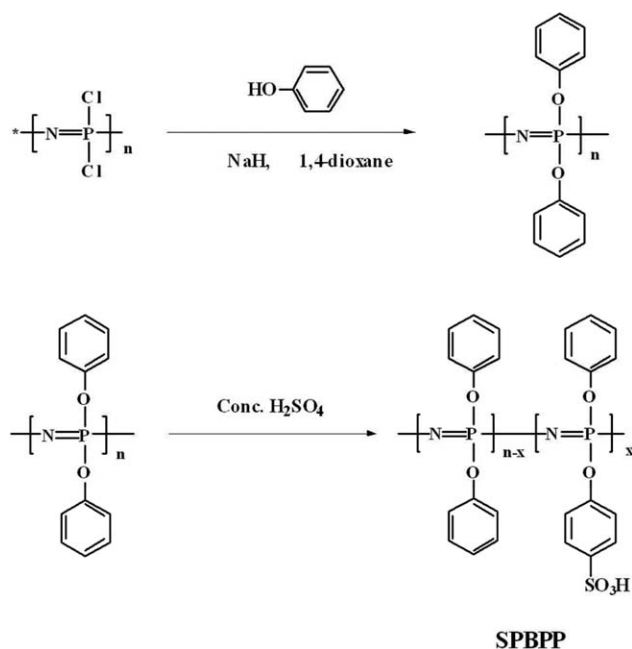
## EXPERIMENTAL

### Materials

The synthesis and characterization of SPBPP were reported by our previous work.<sup>17</sup> The structure of SPBPP was shown in Scheme 1. Hexachlorocyclotriphosphazene (( $\text{NPCl}_2$ )<sub>3</sub>) was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), Dioxane, Dimethylacetamide (DMAc), and concentrated sulfuric acid (98%), were purchased from Aldrich Chemical Co. ( $\text{NPCl}_2$ )<sub>3</sub> was purified by two recrystallizations from hexane and vacuum sublimation prior to use. Dioxane and THF were freshly distilled from sodium benzophenone ketyl. Copper (I) bromide (CuBr, AR grade, from Shanghai Chemical Reagent Corporation) was purified by stirring in acetic acid, washing with methanol, and then drying under vacuum. Styrene (St) (AR; Beijing Chemicals Co.) was distilled under reduced pressure. 2,2'-Bipyridine (bipy; AR; Beijing Chemicals) *N*-benzylmaleimide (NBMI, Shanghai Ziyi Chemical Factory) was recrystallized twice from dry ethanol and dried under vacuum. Other chemical reagents and the organic solvents were purchased from Beijing Chemical Reagent and were purified by conventional methods.

### Synthesis of (NP(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p)<sub>2</sub>)<sub>n</sub>(1)

Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of ( $\text{NPCl}_2$ )<sub>3</sub> at 250°C in a sealed tube.<sup>24,25</sup> The resultant linear PDCP (5 g, 43 mmol) was dissolved in 80 mL dry 1,4-dioxane. 4-Methylphenoxide (20.6 g, 190 mmol) was dissolved in 100 mL 1,4-dioxane and added dropwise to a suspension of sodium hydride (7.27 g, 182 mmol) and tetra-*n*-butyl ammonium bromide (0.33 g, 1 mmol) in 50 mL of 1,4-dioxane. The resultant sodium aryloxide was added to the solution of polydichlorophosphazene. The reaction mixture was refluxed for 55 h. The mixture was cooled to room temperature, then it was poured into distilled water and the polymer was collected. The resulting polymer 1 was purified by successive reprecipitation from THF to hexane. The obtained polymer was dried in a vacuum oven at 60°C overnight. <sup>1</sup>H-NMR (400



Scheme 1. Synthetic route of SPBPP.

MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.067 (s, 3H,  $\text{CH}_3$ ), 6.539–6.681 (m, 4H, ArH).

**Synthesis of (NP(OC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Br-p)<sub>0.16</sub>NP(OC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p)<sub>1.84</sub>)<sub>n</sub>(2)**  
 Polymer 1 (1 g, 3.8 mmol) was added into 80 mL  $\text{CCl}_4$  in a round-bottomed flask, under nitrogen by stirring at 40°C temperature for 3 h. Then *N*-bromosuccinimide (NBS) (0.09 g, 0.5 mmol) and benzoyl peroxide (BPO) (0.009 g, 0.038 mmol) were added into the mixture solution. The solution was shielded from light and brought rapidly to reflux for 3 h. After the reaction, the mixture was filtered by pinhole filter (0.8  $\mu\text{m}$ ). The mixture was then evaporated under vacuum. After removal of  $\text{CCl}_4$ , the mixture was poured into hexane. The resulting polymer was washed with hexane. The polymer was dried in vacuum at room temperature for 24 h to give polymer 2. <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.071 (s, 3H,  $\text{CH}_3$ ), 4.150 (s, 2H,  $\text{CH}_2\text{Br}$ ), 6.537–6.709 (m, 4H, ArH). <sup>31</sup>P-NMR (162 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -19.547 (s, 1P, -N=P-).

### Synthesis of PP-g-PSN Copolymers (3)

The bulk polymerization was conducted in a sealed glass tube. Polymer 2 (1 g), a controlled amount of styrene (4.05 g, 39 mmol), *N*-benzylmaleimide (7.30 g, 39 mmol) and 2,2-bipyridine (Bpy, 0.5 g, 3.2 mmol) were dissolved in 15 mL dry dioxane under inert atmosphere. After cooled by liquid nitrogen under inert atmosphere, CuBr (0.125 g, 1.3 mmol) was added into the mixture under the inert atmosphere quickly. The polymerization reaction was carried out at 105°C for 24 h. The polymerization was terminated by cooling to room temperature. The resulting mixture was diluted with THF and then passed through a column filled with neutral alumina, followed by precipitation into excess methanol/HCl aqueous solution (1 : 1). Finally, the obtained precipitate was immersed in cyclohexane overnight to remove homopolymer of polystyrene, and then dried under vacuum at 60°C. The polymers obtained were

yellow fine elasticity.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.070 (s, 3H,  $\text{CH}_3$ ), 4.433 (s, 1H,  $-\text{N}-\text{CH}_2-$ ), 6.534–6.680 (m, 6H, ArH), 6.904–7.168 (m, 4H, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3030.7, 1704.

#### Sulfonation Reaction of PP-g-PSN Copolymers (4)

About 1.0 g of polymer 3 was dissolved in 1,2-dichloroethane (20 mL) in a round-bottomed flask at  $50^\circ\text{C}$  under inert atmosphere. Acetyl sulfate was freshly prepared by injecting acetic anhydride (3 mL) and dichloroethane (10 mL) into nitrogen-purged vial. The solution was cooled to  $0^\circ\text{C}$  in an ice bath after 95% sulfuric acid (1 mL) was added. The resulting acetyl sulfate solution was immediately added to the polymer solution dropwise at  $55^\circ\text{C}$  under stirring. Then the solution was stirred at  $55^\circ\text{C}$  for 7 h, 8 h, and 9 h, respectively. The reaction was terminated by cooling to room temperature. The resulting mixture was precipitated in hexane and the obtained precipitate was washed with water until  $\text{pH}=7$ . The obtained residue was dried under vacuum at  $70^\circ\text{C}$  overnight to give sulfonated copolymer 4.  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ): 4.391 (s, 1H,  $-\text{N}-\text{CH}_2-$ ), 6.582–7.220 (m, 8H, ArH). IR (KBr,  $\text{cm}^{-1}$ ): 3452.1, 1174.8, 1034.8.

#### Membrane Preparation and Proton Exchange

Sulfonated polymer 4 was dissolved in DMAc (5% wt) overnight. The filtered solution was cast onto a clean glass plate. After being dried at  $60^\circ\text{C}$  for 10 h and vacuum-dried at  $120^\circ\text{C}$  for 24 h, the clean and transparent membranes were obtained. The membranes were transformed to the acid forms by proton exchange in 1M  $\text{H}_2\text{SO}_4$  for 24 h at room temperature. Finally, the membranes were soaked and washed thoroughly with deionized water. The thickness of the membranes was 100–150  $\mu\text{m}$ .

#### Characterization and Measurements

$^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-400 spectrometer. FTIR spectra of the membranes were measured on a Horiba FT-720 spectrometer. Molecular weight measurements were performed via Viscotek I-MBHMW-3078 gel permeation chromatography (GPC) equipped with Viscotek VE 1122 solvent delivery system. The GPC system was calibrated with polystyrene standards.  $T_g$  were determined using a differential scanning calorimeter (DSC) Q 200 at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen in the range of  $-20$ – $150^\circ\text{C}$ . Thermogravimetric analysis (TGA) was performed with TGA-Q500 at a heating rate of 10 K/min under nitrogen in the range of 25– $700^\circ\text{C}$ . The ratios of S to P of sulfonated polymers were determined by Axios-Advanced X-ray fluorescence spectrometer (XRF) analysis.

#### 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 ( $\sigma$ ) 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<sup>16</sup> was carried out using a liquid diffusion cell composed of two compartments containing solutions A and B. A ( $V_A = 50$  mL) was 1 mol/L methanol solution, and B ( $V_B = 50$  mL) was deionized water. 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 ( $\text{cm}^2 \text{s}^{-1}$ ),  $k$  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 ( $\text{mol L}^{-1}$ ),  $A$  is the membrane areas ( $\text{cm}^2$ ), and  $h$  is the thickness of wet membrane (cm), respectively.

#### Water Uptake (WU) Measurements

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. The weight and volume based WU is reported as a percentage using the following equations:

$$\text{WU (wt \%)} = [(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}] \times 100\%$$

$$\text{WU (vol \%)} = [(W_{\text{wet}} - W_{\text{dry}}) / \delta_w] / (W_{\text{dry}} / \delta_m) \times 100\%$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of the wet and dry membranes, respectively;  $\delta_m$  is the membrane density in the dry state, membrane densities were determined according to previously reported method,<sup>26</sup> and the  $\delta_w$  is the density of water ( $1 \text{ g/cm}^3$ ). The weights of dried membranes were measured after drying in vacuum at  $70^\circ\text{C}$  for 8 h.

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:

$$\text{SW(\%)} = [(L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}}] \times 100\%$$

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

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

$$SV(\text{vol } \%) = \frac{[(L_{\text{wet}} \times L_{\text{wet}} \times T_{\text{wet}}) - (L_{\text{dry}} \times L_{\text{dry}} \times T_{\text{dry}})]}{(L_{\text{dry}} \times L_{\text{dry}} \times T_{\text{dry}})} \times 100\%$$

where  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the lengths of wet and dry membranes, respectively.  $T_{\text{wet}}$  and  $T_{\text{dry}}$  are the thickness 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%  $\text{H}_2\text{O}_2$  containing 2 ppm  $\text{FeSO}_4$ ) at  $80^\circ\text{C}$  for 1 h.<sup>25</sup>

### 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  $2 \text{ mol L}^{-1}$  for 24 h at room temperature. The amount of the  $\text{H}^+$  released from the membranes was determined by titration of  $0.01 \text{ mol L}^{-1}$  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:

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

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

### Scanning Electron Microscopic (SEM) Observations

The morphology of the membranes was investigated using a SHIMADZU SSX-550 SEM at an accelerating voltage of 5 kV. The samples were fractured in liquid nitrogen and the fractured surfaces were coated by Au prior to SEM measurements.

### Transmission Electron Microscopic (TEM) Observations

The membranes were stained with lead by ion exchange of the sulfonic acid groups by immersing it in a large excess of  $\text{Pb}(\text{NO}_3)_2$  aqueous solution for 24 h and then rinsed with water, and dried at room temperature. The stained membranes were embedded in polystyrene and sectioned to give 70 nm thick membranes. TEM observations were performed with a JEOL JEM-2010 TEM.

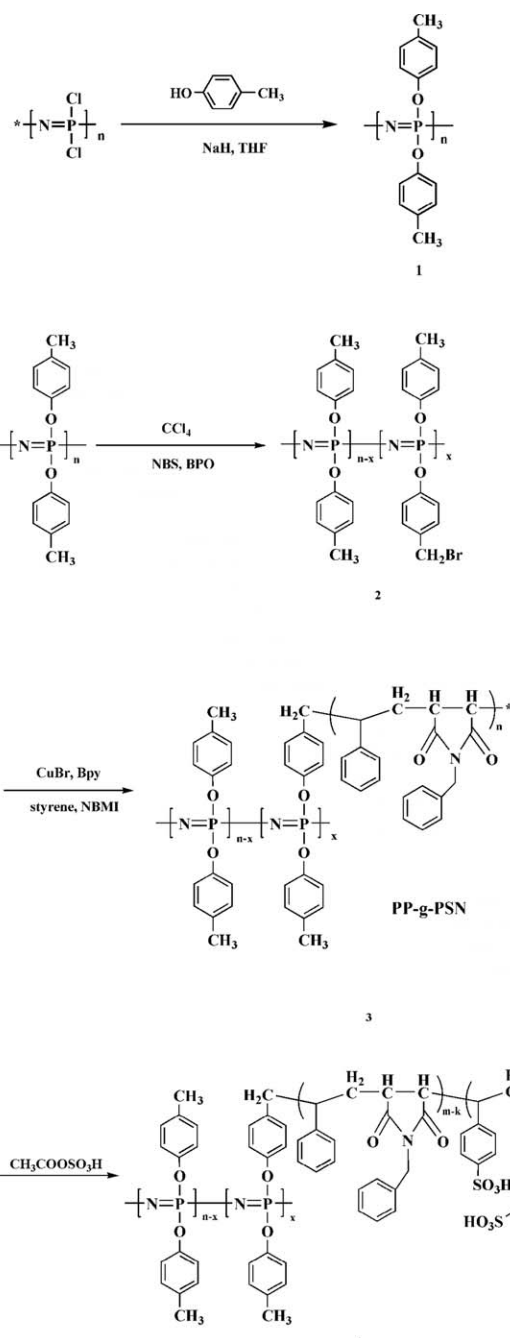
## RESULTS AND DISCUSSIONS

### Synthesis of Bromomethylation of Poly(bis(4-methylphenoxy)phosphazene) (2)

The polymer **2** was prepared via bromination of the benzylic methyl groups in the polymer **1** with NBS (Scheme 2).<sup>27,28</sup> The reaction flask was shielded from light to avoid crosslinking reaction. The degree of bromination in polymer **2** can be controlled by the amounts of NBS/BPO and calculated by  $^1\text{H-NMR}$ .<sup>16</sup> Polymer **2** having bromination degree of 8% was chosen as the macromolecular initiator.

### Synthesis of Copolymers via ATRP

Generally, the copolymerization of styrene with *N*-substituted MIs, i.e., *N*-(2-acetoxy ethyl) and *N*-phenylmaleimides can be initiated by radical initiator such as AIBN (azodiisobutyronitrile) or by UV-light irradiation, but the polymerization process is difficult to control.<sup>29</sup> However, ATRP, one of the most popular methods of controllable polymerization, has already been widely

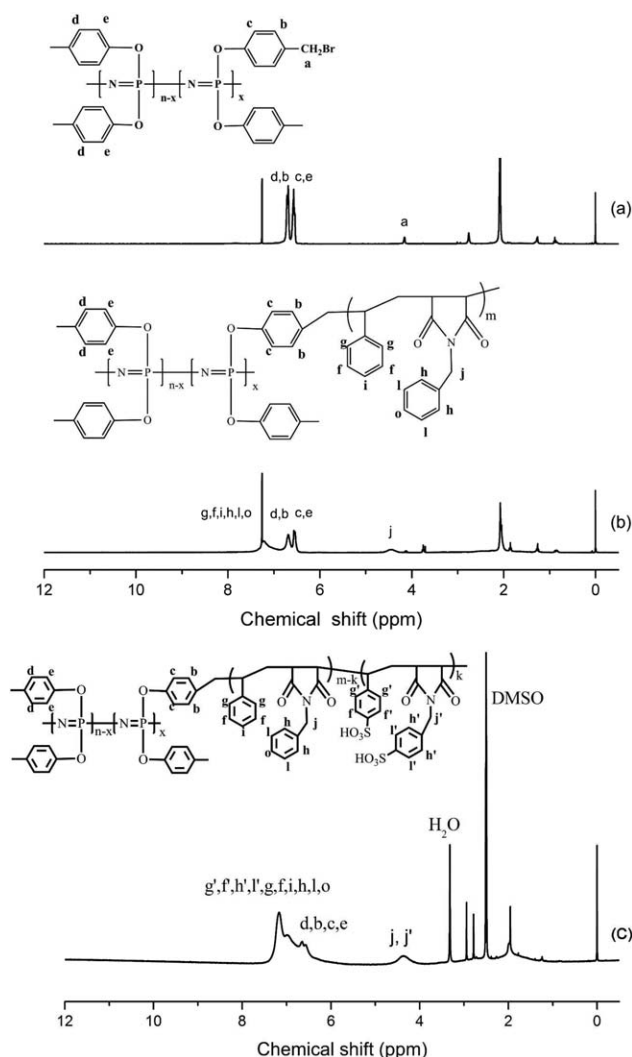


Scheme 2. Synthetic route of polymers 3 and 4.

used for the synthesis of block, graft, and star copolymers and polymers with complex structures based on a wide variety of monomers.<sup>30,31</sup>

In the present study, we used ATRP as the controllable and precision polymerization method.<sup>32</sup> The reaction of macroinitiator **2** with styrene and *N*-benzylmaleimide by CuBr-catalyzed ATRP yielded PP-g-PSN copolymers **3**. The graft chain length of poly(styrene-co-*N*-benzylmaleimide) [Figure 1(b)] was calculated by the  $^1\text{H-NMR}$  spectra data. Compared with the  $^1\text{H-NMR}$  spectra of macroinitiator **2** [Figure 1(a)], the  $^1\text{H-NMR}$  spectra of polymer **3** exhibits the appearance of signals (g, f, i, l,





**Figure 1.**  $^1\text{H-NMR}$  spectra of synthetic polymers: (a) macroinitiator **2**, (b) *PP-g-PSN* copolymer **3** in  $\text{CDCl}_3$ , (c) Sulfonated *PP-g-PSN* copolymer **4** in  $\text{DMSO-}d_6$ .

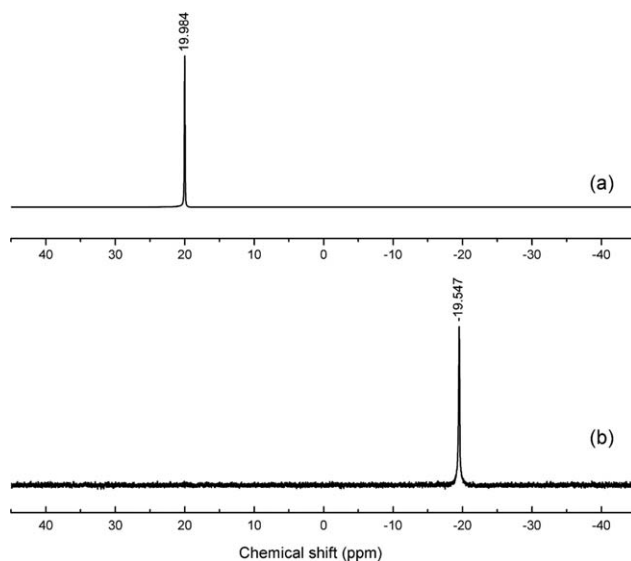
h, and o) at  $\delta = 6.904\text{--}7.168$  corresponding to aromatic protons of poly(styrene-co-*N*-benzylmaleimide) grafted to the main chain,<sup>33</sup> and the disappearance of the  $\text{Ph-CH}_2\text{Br}$  signal at  $\delta = 4.150$  indicates the consumption of almost all the benzyl bromide groups during the reaction. This demonstrates the formation of the *PP-g-PSN* copolymers **3** (Scheme 2).

The average chain length of the grafted poly(styrene-co-*N*-benzylmaleimide) was calculated by the ratio of peak integrals in the  $^1\text{H-NMR}$  spectra of polymer **3** [Figure 1(b)] as given by the following equation:

**Table I.** Molecular Weights of *PP-g-PSN* Copolymers

NO.	Graft length	$*M_n \times 10^5$ (Da)	$*M_w \times 10^5$ (Da)	$M_w/M_n$
<b>2</b>	–	4.0	7.6	1.9
<b>3</b>	8	5.2	6.6	1.3

Determined at  $25^\circ\text{C}$  using THF as a solvent and polystyrene as a standard.



**Figure 2.**  $^{31}\text{P-NMR}$  spectra of (a)  $(\text{NPCL}_2)_3$  and (b) macroinitiator **2**.

$$\text{Graft-length} = [4 \times (G + F + I + H + L + O)] / [5 \times (B + C + D + E) \times \text{Br}\%]$$

where B, C, D, E, G, F, I, H, L, and O represent the peak integrals of b, c, d, e, g, f, i, h, l, and o, respectively.

The comparison (Tables I–III) shows that the copolymer **3** shows increased molecular weights after the ATRP and lower polydispersity index ( $\text{PDI} = M_w/M_n$ ).

### Sulfonation of Copolymers

Sulfonation of copolymer **3** using acetyl sulfate gave sulfonated *PP-g-PSN* copolymers **4** (Scheme 2). XRF analysis was used to monitor the sulfonation, showing that the ratio, S/P (Table II) in the sulfonated copolymer **4** increased with longer sulfonation reaction time. The IEC values (Table II) of the products are dependent on the different sulfonation reaction time. We observed that longer reaction time led to the higher IEC value.

The copolymers **3** and **4** were characterized by the FTIR spectroscopy (Figure 3). The characteristic absorption of carbonyl groups in MI was observed at  $1704\text{ cm}^{-1}$ , indicating the polymerization of styrene-co-*N*-benzylmaleimide [Figure 3(a)].<sup>20</sup> Upon sulfonation of copolymer **3**, we obtained copolymer **4** and measured the FTIR [Figure 3(b)] which showed a broad absorption band at  $3452.1\text{ cm}^{-1}$ , corresponding to the O–H in the sulfonic acid group ( $\text{HO-SO}_2\text{--}$ ) or absorbed moisture (HO–H). The characteristic symmetric and asymmetric stretch bands of the  $\text{O}=\text{S}=\text{O}$  appear [Figure 3(b)] at  $1034.8\text{ cm}^{-1}$  and  $1174.8\text{ cm}^{-1}$ , demonstrating the formation of *PP-g-PSN* copolymer **4**. The structure of the copolymer **4** was further confirmed by the  $^1\text{H-NMR}$  spectroscopy [Figure 1(b,c)]. After sulfonation, the peaks around  $6.904\text{--}7.168$  ppm become broad due to the electron withdrawing effect on the protons adjacent to the sulfonic acid groups. The XRF, FTIR, and  $^1\text{H-NMR}$  analysis confirmed the synthesis of copolymer **4**.

The sulfonation reaction occurred on aromatic rings of poly(styrene-co-*N*-benzylmaleimide) segments due to relatively less hindrance. The sulfonated *PP-g-PSN* copolymers were soluble in

**Table II.** Sulfonated PP-g-PSN Copolymers and Membrane Properties

Copolymers	Sulfonation Time (h)	IEC <sup>a</sup> (mmol g <sup>-1</sup> )	S/P <sup>b</sup>	Density (g cm <sup>-3</sup> )	WU <sup>c</sup> (wt %)	WU <sup>c</sup> (vol %)	SW <sup>c</sup> (%)	SV <sup>c</sup> (vol %)	Excess volume <sup>d</sup> (vol %)
SPBPP	-	1.1	-	0.93	30	27.9	12.4	34.4	6.5
PPN-S7	7	1.1	0.578	1.20	37	44.4	17.4	50.3	5.9
PPN-S8	8	1.3	0.694	1.23	51	62.7	18.6	70.5	7.8
PPN-S9	9	1.5	0.795	1.25	66	82.5	23.1	91.6	9.1
SPEEK <sup>e</sup>	-	1.81	-	-	36.6	-	8.7	-	-
Nafion 117	-	0.9	-	1.98	35	69.3	24	75.4	6.1

<sup>a</sup> Determined by titration.<sup>b</sup> XRF results.<sup>c</sup> Determined at 25°C.<sup>d</sup> Excess volume (vol %) = SV (vol %) - WU (vol %).<sup>e</sup> Na *et al.*<sup>34</sup>

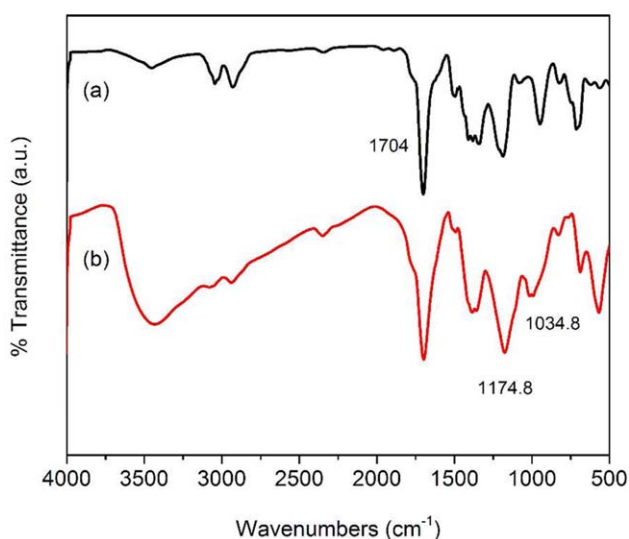
polar aprotic solvents such as DMAc, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

### IEC, Water Uptake (WU), and Swelling Ratio (SW)

The IEC indicates the number of protons per ionomer unit mass that can be replaced by other cations, which is responsible for their WU and proton conductivity. The IEC values of the membranes were measured by titration and the results were listed in Table II. As expected, the IEC values observed for sulfonated PP-g-PSN membranes varied from 1.1 to 1.5 mmol g<sup>-1</sup> when the sulfonation time was increasing.

The WU of PEM is another factor that decides proton conductivity of the membrane because water molecules behave as proton transportation carriers in membranes. However, water SW should be considered because high WU always leads to dimensional change or even soluble of membranes. Therefore, the preparation of the sulfonated polymers with ideal WUs and SW is one of the critical demands for their application as PEMs. As

shown in Table II, the sulfonated PP-g-PSN membranes showed relatively high WUs in the hydrated state. All membranes showed an increase in WU proportional to the IEC values. The PPN-S9 exhibited the highest WU due to its highest IEC value. Compared with SPBPP, the sulfonated PP-g-PSN membranes exhibited higher WUs, indicating their better water-retention capacity (Table II). However, as shown in Table II, the rise of SWs of sulfonated PP-g-PSN membranes was not as large as that of the WUs. From PPN-S7 to PPN-S9, small increase in SW was observed. The swelling volume of the membranes is primarily contributed by the WU. The excess volume of the PPN-Sx showed an increase with the increasing IEC values. Moreover, the excess volume of PPN-S7 is lower than that of SPBPP with the similar IEC value, indicating that the PPN-S7 with sulfonic acid units on side chains may be more effective in suppressing the swelling behavior of the membrane. These results are suggested that the structure of the graft copolymers has good water swelling stability because the water molecules may be restricted to special hydrophilic domains of the side chains, and separated from the hydrophobic domains of the polyphosphazene backbone.<sup>1</sup>

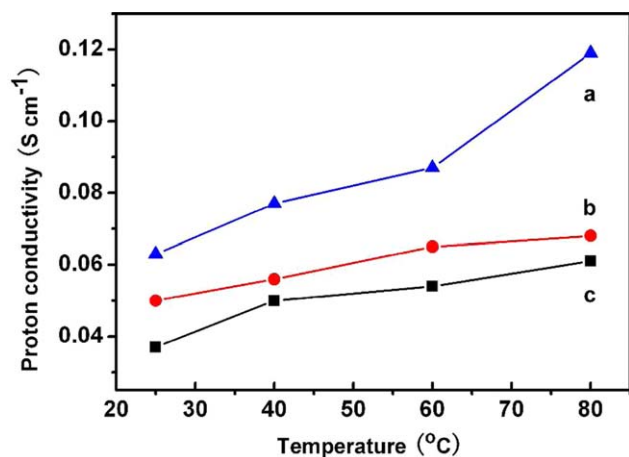


**Figure 3.** FT-IR spectra of the (a) copolymer 3 and (b) copolymer 4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table III.** Methanol Permeability and Selectivity of Membranes

Membranes	Proton conductivity (S cm <sup>-1</sup> )		Methanol permeability <sup>a</sup> (cm <sup>2</sup> s <sup>-1</sup> ) × 10 <sup>-7</sup>	Relative selectivity
	25°C	80°C		
SPBPP	0.035	NA <sup>e</sup>	2.86	1.64
PPN-S7	0.037	0.061	1.37	3.63
PPN-S8	0.05	0.068	2.15	3.13
PPN-S9	0.063	0.119	5.01	1.69
SPEEK <sup>b</sup>	0.058	0.119	19.5	0.40
Nafion 117	0.09	0.17	12.1	1.00

<sup>a</sup> Not applicable: membrane was broken in water.<sup>b</sup> Determined at 25°C.Na *et al.*<sup>34</sup>

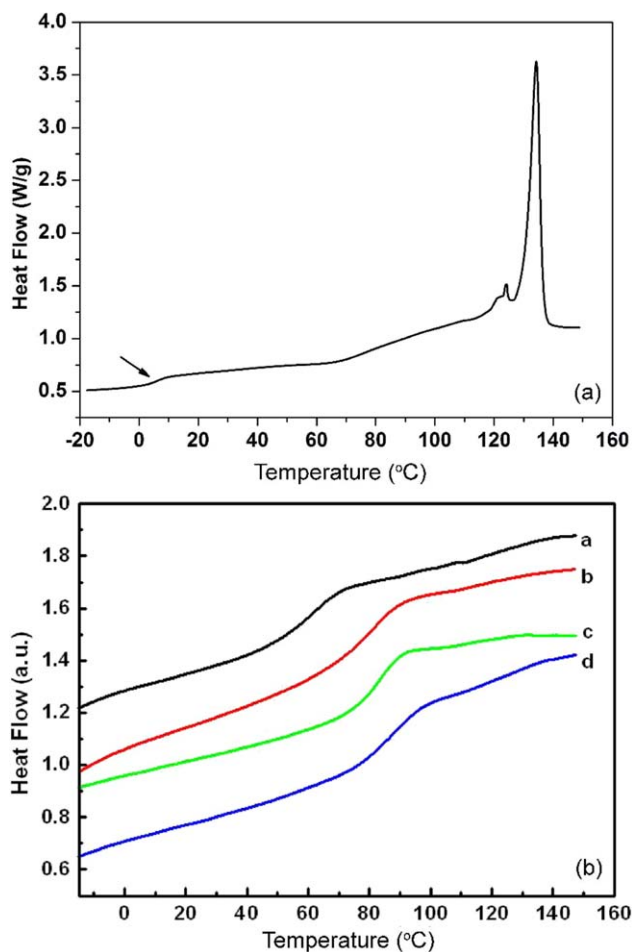


**Figure 4.** Proton conductivity of *PPN-Sx* at elevated temperature (25–80°C) (a) *PPN-S9*, (b) *PPN-S8*, and (c) *PPN-S7*. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Proton Conductivity and Methanol Permeability

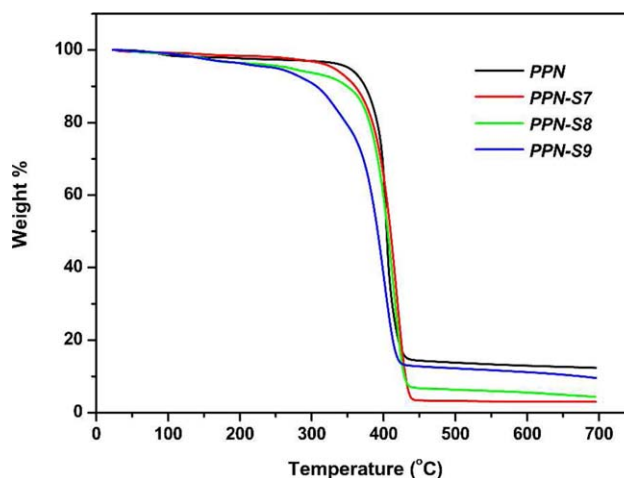
The proton conductivities of the membranes were measured by varying the temperatures and were given in Table III. The proton conductivities of the membranes increased with the rise of IEC values. The proton conductivity values increased for all the sulfonated *PP-g-PSN* membranes (Figure 4) with the increasing temperature. The proton conductivity of *PPN-S9* increased more sharply than the other membranes due to its high IEC value. All of the obtained membranes exhibited reasonable proton conductivities under fully hydrated condition. The *PPN-S7* with IEC value of 1.1 mmol g<sup>-1</sup>, its proton conductivity reached 0.061 S cm<sup>-1</sup> at 80°C. When the IEC value increases to 1.5 mmol g<sup>-1</sup> (*PPN-S9*), the proton conductivity increased to 0.119 S cm<sup>-1</sup> at 80°C, which was suitable for application as PEMs in fuel cell. In addition, all the sulfonated *PP-g-PSN* membranes have higher proton conductivities than the SPBPP membrane. Compared with the SPBPP membrane, the proton conductivities of the *PPN-Sx* membranes were improved, and especially, the *PPN-S9* membrane with the highest IEC value could achieve excellent proton conductivity.

For DMFCs, the methanol permeability coefficient is an important parameter as methanol crossover can cause catalyst poisoning and thus serious reduction of DMFC voltage. The sulfonated *PP-g-PSN* membranes exhibited methanol permeability (Table III) coefficients in the range of 1.37 × 10<sup>-7</sup> to 5.01 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>. These values are lower than the Nafion 117 (12.1 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>). The methanol permeability coefficients of *PPN-Sx* membranes increased from 1.37 × 10<sup>-7</sup> to 5.01 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup> with the increasing IEC values (1.1–1.5 mmol g<sup>-1</sup>). This tendency follows the results of WU and suggests that higher IEC value (more hydrophilic sulfonic acid groups) allows formation of more water absorption channels, resulting in the enhanced WU and methanol permeability coefficient. Furthermore, compared with the SPBPP membrane, the *PPN-S7* with similar IEC value shows much lower methanol permeability, indicating that the grafted structure could provide an effective barrier against the diffusion of aggregated methanol molecules.



**Figure 5.** DSC curves of copolymers. (a) macroinitiator 2. (b) (a) *PP-g-PSN*, (b) *PPN-S7*, (c) *PPN-S8*, and (d) *PPN-S9*. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The ratio of proton conductivity to the methanol permeability coefficient (selectivity) is a crucial factor to evaluate the performance of DMFCs. While the relative selectivity value (the ratio of copolymer membranes to Nafion 117) can be used to



**Figure 6.** TGA curves of *PPN-Sx* membranes. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Thermal Property and Oxidative Stability of Membranes

Copolymers	$T_{d5\%}$ (°C) <sup>a</sup>	$T_g$ (°C)	Oxidative stability
			RW <sup>b</sup> (%)
<b>2</b>	-	5.44	-
<i>PP-g-PSN</i>	353.0	59.51	-
<i>PPN-S7</i>	331.0	76.74	100
<i>PPN-S8</i>	270.6	82.54	100
<i>PPN-S9</i>	251.5	85.44	99
<i>SPBPP</i>	83.2	ND <sup>c</sup>	NA <sup>d</sup>
Nafion 117	306.0	64.4	97

<sup>a</sup> 5% weight loss temperature in N<sub>2</sub> gas.<sup>b</sup> Retained weight of membranes after treating in Fenton's reagent for 1 h.<sup>c</sup> Not detectable.<sup>d</sup> Not applicable: membrane was broken in water.

evaluate the relative performance of the copolymer. The series of sulfonated *PP-g-PSN* membranes (Table III) show high selectivity values. Among these membranes, the selectivity value of *PPN-S7* is three times higher than that of Nafion 117. As shown in Tables II and III, compared with reported SPEEK membrane with similar proton conductivity,<sup>34</sup> the IEC value and the methanol permeability coefficient of *PPN-S9* (1.5 mmol g<sup>-1</sup>, 5.01 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>) are lower than those of SPEEK (1.8 mmol g<sup>-1</sup>, 19.5 × 10<sup>-7</sup> cm<sup>2</sup> s<sup>-1</sup>) at 25°C. Moreover, the selectivity value of *PPN-S9* is four times higher than that of SPEEK. These results indicate that the *PPN-Sx* membranes could be potentially used for DMFCs application.

### Thermal Property

The thermal properties of the sulfonated *PP-g-PSN* membranes were evaluated by their  $T_g$  (DSC, Figure 5) and weight losses (TGA, Figure 6) analysis. The  $T_g$  values of the membranes are listed in Table IV. The  $T_g$  value of *PP-g-PSN* showed an increase after grafting block groups because the grafted block groups can hinder polymer chain rotation and enhance the chain rigidity. The  $T_g$  values of *PPN-S7* to *PPN-S9* showed gradual increase with the increasing IEC values, likely due to the increasing hydrogen bonding between the polymer chains which reduces the reorientational freedom of the macromolecular phosphazene

backbone.<sup>35</sup> Moreover, in comparison with Nafion 117, the  $T_g$  values of the *PPN-Sx* were higher than the Nafion 117, indicating that they could operate better in high temperature fuel cells.<sup>36</sup>

The thermal stabilities of *PP-g-PSN* and sulfonated *PP-g-PSN* copolymers evaluated by the TGA (Figure 6) showed a three-step weight loss. The first weight loss of all copolymers below 200°C is due to the evaporation of the residual water that reflects the hygroscopic nature of the sulfonated copolymers.<sup>16</sup> In the second stage, the weight loss occurring in the range of 200–350°C is due to the decomposition of the sulfonic acid groups.<sup>19</sup> The third stage starts at about 350°C, corresponding to the degradation of the poly(styrene-co-*N*-benzylmaleimide) segments and the polyphosphazene backbone.<sup>16,19</sup> The 5% weight loss temperatures of the obtained copolymers (Table IV), show that the  $T_d(5\%)$ s of *PPN-Sx* are higher than the SPBPP. This indicates that the grafted block groups can significantly enhance the thermal stabilities of the membranes. The TGA and DSC studies revealed that the membranes were thermally stable enough for the fuel cell application.

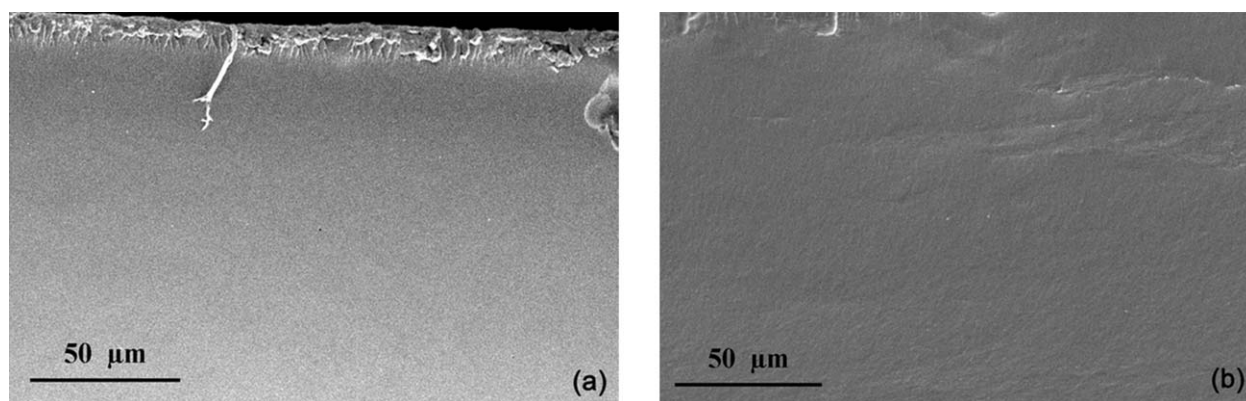
### Oxidative Stability

The oxidative stability has a strong effect on the lifetime of DMFC. Commonly, the oxidative stabilities of the membranes were evaluated in hot Fenton's reagent (80°C) for 1 h.<sup>25,37</sup> The results are displayed in Table IV, for all the sulfonated *PP-g-PSN* membranes, no obvious weight losses were observed after the test, indicating excellent oxidative stability. Compared to the non-grafting sulfonated polyphosphazene membrane, the sulfonated *PP-g-PSN* membranes exhibited a significant improvement in the oxidative stability.

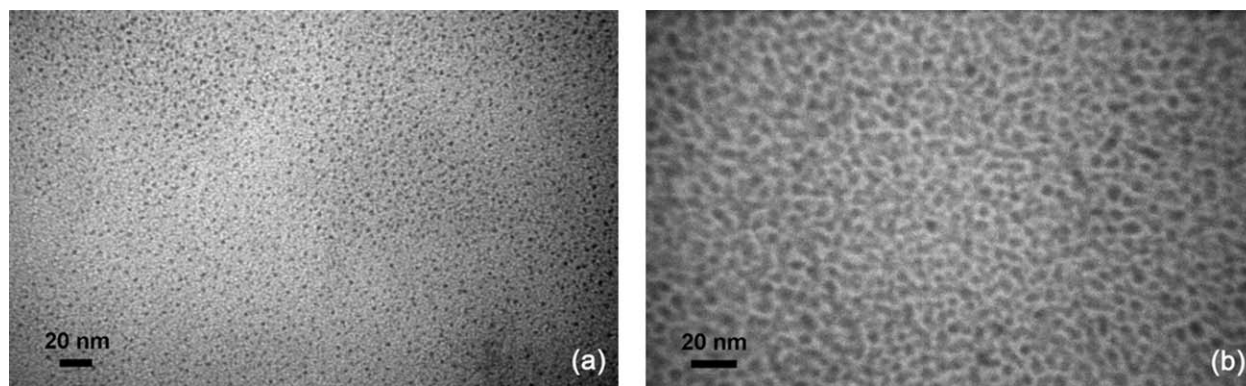
Generally, the oxidative degradation of typical sulfonated aromatic polymers mainly occurred on the main chains, and large weight losses were observed for membranes with high IEC values.<sup>38</sup> The high oxidative stabilities of sulfonated *PP-g-PSN* membranes could be considered to be derived from their moderate IEC values and the relatively short poly(styrene-co-*N*-benzylmaleimide) chains, which might provide shield for the backbone against the oxidative reagents.<sup>16,37</sup>

### Morphology

Two-phase separation morphology of the sulfonated *PP-g-PSN* membranes were observed by the SEM (Figure 7) and the TEM

**Figure 7.** Cross-sectional SEM images of (a) *PPN-S7* membrane and (b) *PPN-S9* membrane.





**Figure 8.** TEM images of (a) *PPN-S7* membrane and (b) *PPN-S9* membrane.

(Figure 8). Proton conductivities of the membranes are closely related to their morphology. Wide ion channels formed by hydrophilic domains can help the movement of protons in water. Figure 7(a,b) shows the cross-sectional SEM images of *PPN-S7* and *PPN-S9* membranes. From the two images, no obvious difference could be observed at low resolution, indicating the dense membranes. The dark and bright regions (Figure 8) correspond to the hydrophilic and hydrophobic domains, respectively. A clear phase separation of hydrophilic domains surrounded by the hydrophobic domains was observed for the *PPN-S7*. Compared with the *PPN-S7*, the hydrophilic ionic clusters in *PPN-S9* increased in density due to higher  $-\text{SO}_3\text{H}$  content. Therefore the *PPN-S9* shows higher WU and proton conductivity than *PPN-S7*. These morphological characteristics indicate the formation of ionic channels for proton conduction inside the sulfonated *PP-g-PSN* membranes.

## CONCLUSIONS

A series of *PP-g-PSN* membranes were prepared for PEM applications in DMFC. When compared with the previously studied non-graft sulfonated polyphosphazenes membranes, our sulfonated *PP-g-PSN* membranes had significantly lower water SW, methanol permeability and enhanced proton conductivity. These membranes showed higher thermal and oxidative stabilities due to the introduction of the poly(styrene-co-*N*-benzylmaleimide) groups. Among these membranes, the *PPN-S7* could be considered as the most promising candidate for the PEM material for DMFCs due to its high selectivity value, which is three times higher than that of Nafion 117. TEM observation showed that well defined phase separation, favorable for the effective proton transportation. These results demonstrate that sulfonated membranes can be promising candidates for fuel cell applications.

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