

Synthesis and Characterization of Sulfonated Polyphosphazene-graft-Polystyrene Copolymers for Proton Exchange Membranes*

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Abstract A novel series of polyphosphazene-graft-polystyrene (PP-g-PS) copolymers were successfully prepared by atom transfer radical polymerization (ATRP) of styrene monomers and brominated poly(bis(4-methylphenoxy)phosphazene) macroinitiator. The graft density and the graft length could be regulated by changing the bromination degree of the macroinitiator and the ATRP reaction time, respectively. The PP-g-PS copolymers readily underwent a regioselective sulfonation reaction, which occurred preferentially at the polystyrene sites, producing the sulfonated PP-g-PS copolymers with a range of ion exchange capacities. The resulting sulfonated PP-g-PS membranes prepared by solution casting showed high water uptake, low water swelling and considerable proton conductivity. They also exhibited good oxidative stability and high resistance to methanol crossover. Morphological studies of the membranes by transmission electron microscopy showed clear nanophase-separated structures resulted from hydrophobic polyphosphazene backbone and hydrophilic polystyrene sulfonic acid segments, indicating the formation of proton transferring tunnels. Therefore, these sulfonated copolymers may be candidate materials for proton exchange membranes in direct methanol fuel cell (DMFC) applications.

Keywords: Atom transfer radical polymerization; Direct methanol fuel cell; Graft copolymers; Proton exchange membrane; Polyphosphazenes.

INTRODUCTION

During the last decades, polymer electrolyte membrane fuel cells (PEMFCs) have received much attention, for their significant advantages such as: high efficiencies, renewable fuels and low environmental cost. Advances in this field have come primarily from the design of cheap and stable electro-catalysts that is the most challenge of developing PEMFCs^[1–3], and have also come from the significant improvements of membrane assembly fabrication strategies and cell system engineering. Apart from Nafion, new ion conducting polymeric materials have played only a minor role in significantly increasing cell performance. Perfluorinated polymers represented by Nafion have been the benchmark materials because of the chemical, physical stability and high proton conductivity^[4, 5]. However, they suffer from drawbacks such as low upper operational temperature limit, specifically high production cost and significant methanol permeability, which constrains their application in direct methanol fuel cells (DMFCs)^[6–8]. Therefore, new polymer electrolyte membrane (PEM) materials are required for the development of PEMFCs. In recent years, efforts to develop sulfonated poly(ether ether ketone)s^[9], poly(phenylenes) and poly(arylene ethers)^[10] as alternative PEM materials have been proven fruitful.

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However, a general problem with these sulfonated polymers is that they swell strongly when exceeding a certain degree of sulfonation. More recently, block and graft copolymer systems have been extensively employed because they possess regular structure and show low swelling at reasonable conductivities^[11–18]. However, most of these copolymers are built up from backbones based on carbon-carbon polymers, which tend to suffer from poor oxidative stability.

Polyphosphazenes provide a way to construct different graft copolymers as they are hybrid organic-inorganic polymers with a phosphorus-nitrogen chain backbone $-(RR'P=N)_n-$ and have valuable qualities as structural and functional materials. The potential uses of polyphosphazenes include membranes, biomedical materials, optical and electro-optical materials, solid polymer electrolytes and elastomers because of their many different chemical and physical properties depending on the tunable structure, which results from the two side-groups attached to each phosphorus atom^[19]. Most polyphosphazenes are synthesized *via* the macromolecular replacement of chlorine atoms in poly(dichlorophosphazene) with the use of various nucleophiles as the side-groups. Copolymerization of polyphosphazenes with different systems of polymers may further enlarge structural diversity and functional versatility, and it then may give rise to the production of new materials. Growing of polystyrenes on the side-groups of polyphosphazenes resulting in the formation of graft copolymers may offer different sulfonation sites and structural features for the polyphosphazene sulfonic acids as PEM materials. Previously, Wisian-Neilson and coworker produced poly(methylphenylphosphazene)-graft-polystyrene by anionic polymerization styrene from deprotonated methyl groups of the phosphazene chain^[20] and Gleria *et al.* reported the preparation of poly(bis(4-isopropylphenoxy)phosphazene)-graft-polystyrene using a radical initiation process by which styrene was polymerized from the peroxidized isopropyl groups of poly(bis(4-isopropylphenoxy)phosphazene)^[21].

Herein, we report an efficient method for the preparation of polyphosphazene-graft-polystyrene (PP-g-PS) copolymers from poly(bis(4-methylphenoxy)phosphazene) by atom transfer radical polymerization (ATRP), and we also describe the subsequent sulfonation of the graft copolymers with acetyl sulfate and their membrane properties.

EXPERIMENTAL

Materials

All chemicals were reagent grade and used as received unless specially mentioned. Hexachlorocyclotriphosphazene (LanYin Chemical, China) was purified by double recrystallizations from hexane and then by vacuum sublimation. Tetrahydrofuran (THF) and dioxane (Aldrich) were freshly distilled from sodium benzophenone ketyl. All reactions were carried out under a stream of dry argon using standard Schlenk techniques. Sample of Nafion 117 was pretreated as described elsewhere^[22].

Polymer Structure Characterization and Instruments

¹H- and ³¹P-NMR spectra were recorded on a Bruker AM-400 spectrometer, which provided the composition information of the polymers. 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. Glass transition temperatures (*T_g*) were determined using a differential scanning calorimeter (DSC) Q 200 at a heating rate of 10 K/min under nitrogen in the range of –20–150 °C. Glass transition temperatures are reported as onset and the transition midpoint during the second or third heat. FTIR spectra were measured on a Horiba FT-720 spectrometer. Thermogravimetric analysis was performed with TGA-Q500 at a heating rate of 5 K/min under nitrogen.

Experimental Methods and Procedures

Synthesis of $(NP(OC_6H_4CH_3-p)_2)_n(I)$

The precursor poly(dichlorophosphazene) (5 g, 43 mmol) prepared from hexachlorocyclotriphosphazene according to reported method^[23], was dissolved in 80 mL of pre-dried 1,4-dioxane. 4-Methylphenol (20.6 g,

190 mmol) was dissolved in 100 mL of 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 polydicholophosphazne. The reaction mixture was refluxed for days. Then, the mixture was cooled to room temperature and the contents precipitated into a large excess of acidified H₂O. The resulting precipitate was purified by successive reprecipitation from THF to water, and dialyzed against THF using dialysis tubing (MWCO 40 kDa) to obtain polymer **1**, which was dried under vacuum (50 °C, 13.3 Pa) overnight. ¹H-NMR, δ 2.1 (s, $-\text{C}_6\text{H}_4\text{CH}_3$), δ 6.5–6.9 (multiple, $-\text{OC}_6\text{H}_4\text{CH}_3$). ³¹P-NMR δ –19.25 (br, $-\text{P}=\text{N}-$).

Preparation of $(\text{NP}(\text{OC}_6\text{H}_4\text{CH}_2\text{Br}-p)_{0.13}-\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3-p)_{1.87})_n$ (**2**)

A sample of polymer **1** (1 g, 3.8 mmol) was dissolved in carbon tetrachloride (80 mL). *N*-Bromosuccinimide (0.09 g, 0.5 mmol) and benzoyl peroxide (0.009 g, 0.038 mmol) were added into the polymer solution. Then, the solution was shielded from light and brought rapidly to reflux for 3 h. After finishing the reaction, the solution 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 into hexane for two additional times and then dried at < 13.3 Pa for 24 h at 40 °C to yield a solid final polymer **2**. ¹H-NMR, δ 2.1 (s, $-\text{OC}_6\text{H}_4\text{CH}_3$), δ 4.2 (s, $-\text{CH}_2\text{Br}$); δ 6.5–6.9 (multiple, $-\text{OC}_6\text{H}_4\text{CH}_3$). ³¹P-NMR δ –19.07 (br, $-\text{P}=\text{N}-$).

Preparation of PP-g-PS copolymers (**3**)

A typical procedure for the synthesis of PP-g-PS is as follows: A sample of polymer **2** (1 g) together with CuBr (125 mg, 1.3 mmol) was dissolved in dioxane (40 mL) under an inert atmosphere. A controlled amount of styrene (6.76 g, 65 mmol) was injected into the polymer solution. Separately, 2,2-bipyridine (BPy, 500 mg, 3.2 mmol) was dissolved in 30 mL of dioxane, which was transferred into the polymer mixture under an inert atmosphere. The polymerization reaction was carried out at 105 °C for 16 h under an argon blanket. The polymerization was terminated by cooling to room temperature and exposing to air. 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 at 60 °C in a vacuum oven for 2 days. ¹H-NMR, δ 1.8–2.1 (br, $-\text{OC}_6\text{H}_4\text{CH}_3$, $-\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CHAr}-$); δ 1.2–1.5 (br, $-\text{CH}_2\text{CHAr}-$); δ 6.5–6.9 (multiple, $-\text{OC}_6\text{H}_4\text{CH}_3$); δ 7.1–7.3 (br, $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)-$).

Sulfonation reaction of PP-g-PS copolymers

A typical sulfonation reaction was carried out as follows: A sample of **3** (1 g) was dissolved in 1,2-dichloroethane (20 mL) at 50 °C under an 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 °C in an ice bath after 95%–97% sulfuric acid (1 mL) was added. The resulting acetyl sulfate solution was immediately added to the polymer solution at 40 °C, using a dropping funnel. After 2 h, 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 the residual water had a pH = 7. The obtained residue was dried under vacuum at 45 °C overnight to give sulfonated copolymer **4**^[24]. The ¹H-NMR spectrum of sulfonated PP-g-PS copolymers **4** showed similar signature peaks to that of pristine PP-g-PS copolymers, except an additional peak at δ = 7.3–7.6, corresponding to aromatic protons adjacent to sulfonic group on the styrene ring was observed.

Membrane Preparation

A dimethylacetamide (DMAc) (5 W/V %) solution of sulfonated PP-g-PS copolymers **4** was filtered and cast onto a Teflon plate. The solvent was evaporated under vacuum at 65 °C for 24 h to form membranes, which were dried subsequently at 80–100 °C overnight.

Ion Exchange Capability

Ion exchange capacity (IEC) was obtained by titration. The membrane in acid form was immersed in 50 mL of 2 mol/L NaCl solutions for 24 h at room temperature to replace the protons of sulfonic acid groups with sodium

ions, and then the released protons in solution were titrated with 0.01 mol/L NaOH using pH meter to monitor the end points. The moles of the proton were equal to those of sulfonic group 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_{NaOH} is the concentration of NaOH solution, V_{NaOH} is the consumed volume of NaOH solution, and W_s is the weight of the membrane sample.

Water Uptake and Swelling Ratio

The water uptake (WU) was determined by the weight difference between the fully hydrated membrane and dried membrane. The membranes were first equilibrated in water at 25 °C for 24 h, and then removed from water, subsequently wiped with blotting paper and weighed quickly. The water uptake of the membrane was calculated by the following equation:

$$\text{WU} = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$$

where W_{wet} and W_{dry} were the weight of the wet and dry membranes, respectively^[25].

Swelling ratio (SW) was determined by immersing membrane samples into water at 25 °C for 24 h and measuring the change in length before and after the swelling according to the following equation:

$$\text{SW} = (L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}}$$

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

Proton Conductivity

Proton conductivity (σ) was measured using CHI660D impedance analyzer over the frequency ranging from 100 Hz to 0.1 MHz. It was calculated from the impedance data using the following equation:

$$\sigma = l / (R \times A)$$

where l and A were distance between two Ag electrodes and cross-sectional area of the membrane perpendicular to the current flow and R was derived from the high frequency intercept with the Re (Z) axis on a complex impedance plane plot^[25].

Methanol Permeability

Methanol permeability (P) measured through a reported method^[26] 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 diffused 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 area (cm^2) and h is the thickness of wet membrane (cm), respectively.

Oxidative Stability

The oxidative stability of the membranes was evaluated in a hot Fenton's reagent (3% H_2O_2 , 2×10^{-6} mol/L FeSO_4 , 80 °C) for 1 h as an accelerated test^[27].

Transmission Electron Microscopic Observations

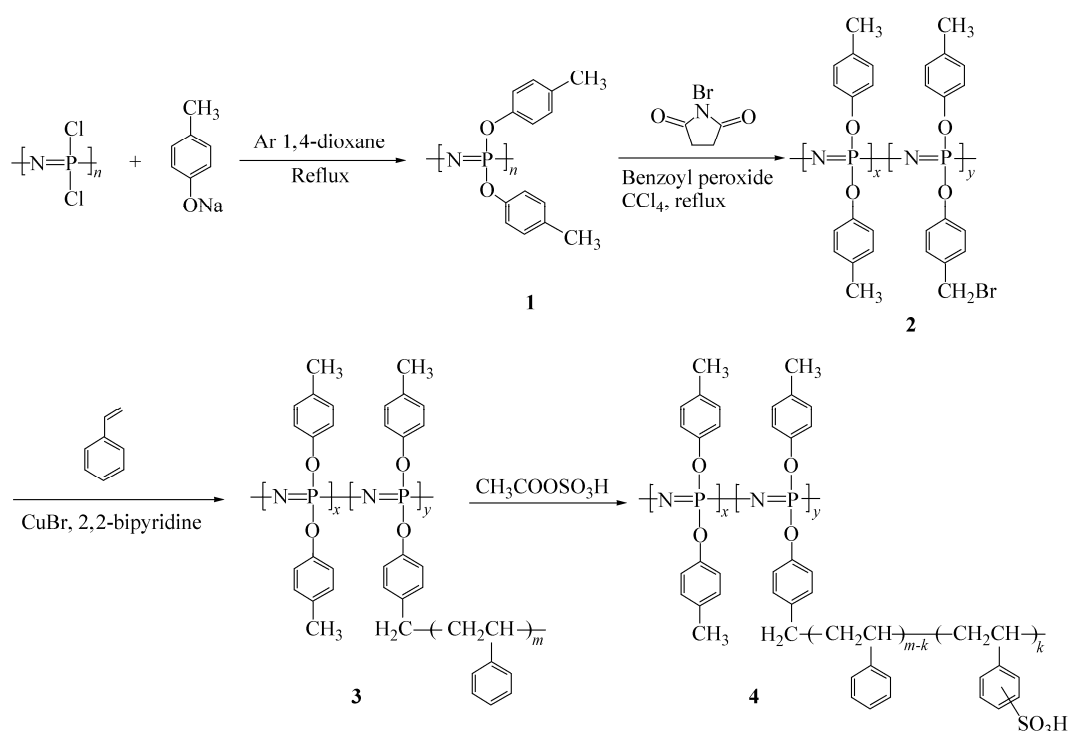
The membrane was stained with lead by ion exchange of the sulfonic acid groups by immersing it in a large

excess of PbNO_3 aqueous solution for 3 days and then rinsed with water. The stained membrane was embedded in epoxy resin and sectioned to give a 70 nm thick sample. Transmission electron microscopic (TEM) observations were performed with a JEOL JEM-2010 transmission electron microscope.

RESULTS AND DISCUSSION

Synthesis and Sulfonation of PP-g-PS Copolymers

As illustrated in Scheme 1, PP-g-PS copolymer was prepared from poly(dichlorophosphazene) *via* the formation of macroinitiator (**2**) by bromination of poly(bis(4-methylphenoxy)phosphazene) (**1**), and then grafting process by ATRP reaction with styrene. Chemical structures of all synthetic polymers were confirmed by $^1\text{H-NMR}$ and FTIR spectra.



Scheme 1 Synthetic scheme for sulfonated PP-g-PS copolymers

Initially, poly(bis(4-methylphenoxy)phosphazene) (**1**) was prepared from poly(dichlorophosphazene) (Scheme 1) as described by Allcock^[28]. A large excess of sodium 4-methylphenoxide was used to react with polydichlorophosphazene to ensure the complete chlorine replacement. The produced polymer **1** was soluble in chloroform, THF and polar aprotic solvents.

Bromination of the benzylic methyl groups in the polymer **1** with *N*-bromosuccinimide to give **2**, according to the reported method^[29]. The reaction was shielded from light to avoid crosslinking reaction because of the highly reactive benzylic bromide groups formed in this step. The bromination was confirmed by $^1\text{H-NMR}$ spectra of **2** as shown in Fig. 1(b), in which protons of the $\text{Ph}-\text{CH}_2\text{Br}$ groups were observed at $\delta = 4.2$ (peak **a**). The bromination degree ($\text{Br}\%$) for the polymer **2** could be controlled by reactant ratio, and was calculated by the following equation:

$$\text{Br}\% = 2A/(C + D + C' + D')$$

where *A*, *C*, *C'*, *D*, and *D'* represent the integrals of peaks **a**, **c**, **c'**, **d**, and **d'** in the $^1\text{H-NMR}$ spectra, respectively.

Polymer **2** that has bromination degree of 6.5% was used as the macromolecular initiator and was brought

into the graft polymerization reaction step. The polymer with bromination degree higher than 6.5% was found to be not very stable and to readily crosslink into insoluble product as it was described previously^[30].

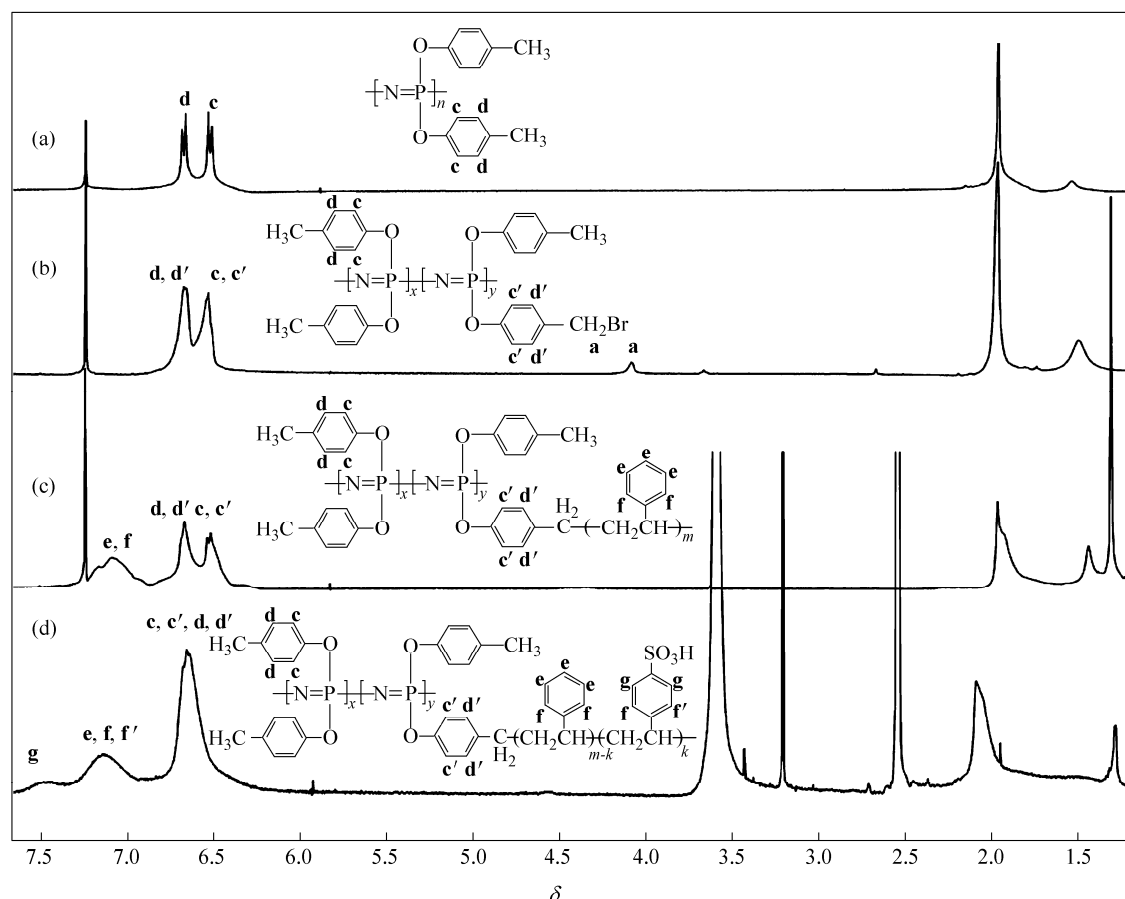


Fig. 1 ^1H -NMR spectra of synthetic polymers: (a) polymer **1**, (b) macroinitiator **2**, (c) PP-g-PS copolymer **3** in d_6 -chloroform, and (d) sulfonated PP-g-PS copolymer **4** in d_6 -DMSO

Extension of the macroinitiators **2** with styrene by CuBr-catalyzed ATRP reaction yielded three series of PP-g-PS copolymers (**3**) as listed in Table 1. They had different polystyrene graft chain lengths calculated by data of the ^1H -NMR spectra as shown in Fig. 1(c), and all had narrow polydispersities determined by GPC (Table 1). Comparison of the ^1H -NMR spectra of the products with that of the macroinitiator **2** (Fig. 1c and Fig. 1b) shows the appearance of signals (e and f) at $\delta = 7.1\text{--}7.3$ corresponding to aromatic protons of polystyrene grafting to the side chain^[30], and the disappearance of the $\text{Ph}-\text{CH}_2\text{Br}$ signal at $\delta = 4.2$ indicating the consumption of almost all the benzyl bromide groups during the ATRP process. This not only strongly demonstrates the formation of the PP-g-PS copolymers **3** but also points out that the graft density of the PP-g-PS copolymers is identical to the bromination degree of the initiator **2**.

Table 1. ATRP Reaction Conditions and Properties of **2** and PP-g-PS

Series	ATRP time (h)	Graft density (%)	Graft length	$M_n^a \times 10^5$ (Da)	$M_w^a \times 10^5$ (Da)	M_w/M_n	T_g ($^{\circ}\text{C}$)
2	—	—	—	0.872	1.07	1.23	5
S	16	6.5	5	1.07	1.35	1.26	34.4
M	24	6.5	7	1.25	1.55	1.24	37.1
L	31	6.5	8	1.57	1.61	1.03	38.5

^a Determined by GPC based on polystyrene standards

The average chain lengths of the grafted polystyrenes were controlled by reaction time and determined by the ratio of peak integrals in the ^1H -NMR spectra of **3** (Fig. 1c) as given by the following equation:

$$\text{graft-length} = [4 \times (E + F)]/[5 \times (C + D + C' + D') \times \text{Br}\%]$$

where C , C' , D , D' , E and F represent the integrals of peaks **c**, **c'**, **d**, **d'**, **e** and **f**, respectively. The produced PP-g-PS copolymers displayed a gradual increase in both number-average and weight-average molecular weights over time indicating the growing of the graft chains. The temperature for the ATRP reaction was carefully controlled at 105 °C to avoid crosslinking reaction and homopolymerization. Higher temperature would result in the homopolymerization of styrene monomers and crosslinking of copolymers, while lower temperature would be insufficient for the ATRP reaction.

The results of DSC analysis also indicated the formation of these series of PP-g-PS copolymers as their glass transition temperature (T_g) values were much higher than that of initiator **2** and heightened as the reaction time increasing (Table 1).

Sulfonation of the PP-g-PS copolymers **3** with acetyl sulfate produced sulfonated copolymers **4** as membrane materials. The sulfonation products were demonstrated by ^1H -NMR spectra (Fig. 1d). Comparing with the spectrum of the precursor **3** (Fig. 1c), the spectrum of **4** showed an additional signal (peak g) at $\delta = 7.3$ – 7.6 corresponding to protons adjacent to the sulfonic group on the polystyrene rings.

Table 2 shows the sulfonation conditions and the consequently identified ion exchange capacity (IEC) values for sulfonated PP-g-PS copolymers. These copolymers including S1, S2, M1, M2, L1, and L2 with various IEC values were prepared from the three series of corresponding PP-g-PS copolymers S, M, and L (Table 1), respectively, by adjusting the sulfonation reaction time. The IEC value depends both on the sulfonation reaction time and the graft chain length of the PP-g-PS copolymers **3**. Longer reaction time resulted in higher IEC values. In addition, the larger the graft chain length of the copolymer, the higher the IEC value yielded in the sulfonation reaction, as deduced from the comparison of IEC values for the sulfonated copolymers ($L1 > M1 > S1$ and $L2 > M2 > S2$). This graft chain length dependence of IEC value suggests that the sulfonation reaction preferred to occur on aromatic rings of the polystyrene segments because of the relatively low steric hindrance. It was also evidenced by an additional investigation in which no sulfonation was observed with poly(bis(4-methylphenoxy)phosphazene) (**1**) when it was treated in the same way as the precursors **3**. Further evidences come from the observation on water uptake and water swelling of the sulfonated PP-g-PS membranes shown in Table 2 and described in the following section. The sulfonated PP-g-PS copolymers were soluble in polar aprotic solvents such as DMAc, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

Table 2. Sulfonation of PP-g-PS copolymers and membrane properties

Series	Graft density/length	IEC (mmol/g)	Sulfonation time (h)	Weight ratio of SPS blocks ^a (%)	Membrane properties				
					σ^b (S/cm)	$P \times 10^{-7}$ (cm ² /s)	Selectivity $\times 10^5$ (Ss/cm ³)	SW (%)	WU (%)
S1	6.5/5	0.95	2	17.5	0.025	1.34	1.87	17	36
S2	6.5/5	1.05	2.5	19.3	0.036	1.6	2.25	17.6	38
M1	6.5/7	1.2	2	22.1	0.054	2.08	2.6	18.2	46
M2	6.5/7	1.4	2.5	25.8	0.056	2.32	2.41	19	53
L1	6.5/8	1.5	2	27.6	0.058	5.34	1.09	22	66
L2	6.5/8	1.6	2.5	29.4	0.059	6.18	0.955	25	80
Nafion	—	0.9	—	—	0.09	0.121	0.744	17	35

^a The weight ratio of sulfonated styrene blocks to the copolymer, calculated from IEC values

^b The proton conductivity measured at room temperature

The preparation of the sulfonated PP-g-PS copolymers **4** from the polyphosphazenes **1** via the intermediates **2** and **3** was further characterized by the FTIR spectra as displayed in Fig. 2. Comparing with the FTIR data of **2** (Fig. 2b), the relative intensity of the absorption bands assigned to C—H stretch (3026 cm⁻¹) of the aromatic

rings and C—H stretch ($2920, 2850\text{ cm}^{-1}$) in the spectra of **3** (Fig. 2c) increased, indicating the polymerization of styrene^[31]. Upon sulfonating **3** (Fig. 2d), a broad absorption band was observed at 3410 cm^{-1} corresponding to the O—H stretching of $\text{—SO}_3\text{H}$ and absorbed moisture. The characteristic band of SO_3^- groups which resulted from the symmetric stretching vibration, emerged at around 1040 cm^{-1} and 1126 cm^{-1} , demonstrating the formation of the sulfonated PP-g-PS copolymers **4**.

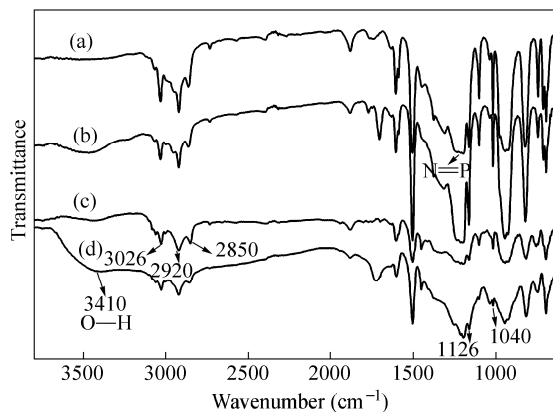


Fig. 2 FTIR spectra of (a) **1**, (b) **2**, (c) **3** and (d) **4**

Properties of Sulfonated PP-g-PS Membranes

Six series of membranes were prepared from the corresponding sulfonated PP-g-PS copolymers listed in Table 2 by casting DMAc solution of the copolymers. The properties of these membranes were shown in Table 2 and Fig. 3 to Fig. 5.

Water uptake, water swelling and proton conductivity

Water uptake and swelling ratio for all series of sulfonated PP-g-PS membranes and their comparisons are shown in Table 2. First, it was found that both water uptake and water swelling of these membranes increased obviously as their graft chain growing, confirming that the sulfonation sites positioned on the graft polystyrene chain moieties as discussed before. Furthermore, all membranes showed an increase in water uptake proportional to the IEC value. The S (S1 and S2) series gave water uptake similar to that of Nafion 117 (Table 2), while M and L series exhibited much higher water uptake. However, the rise of swelling ratio for sulfonated PP-g-PS membranes was not as large as that of the water uptake. Only slight increases in swelling ratio were observed for S and M series which were swollen very close to Nafion 117, and moderate increases were observed for L series (Table 2). Therefore, it is suggested that the structure of the sulfonated side-chains has good water swelling stability as the water molecules might be restricted to a specific hydrophilic domain of the side chains, and separated from the hydrophobic domain of the polyphosphazene backbone which might retain its cohesion and suppress the water swelling^[32]. This mild swelling behavior provides morphological stability for the proton exchange membranes.

It has been known that sulfonated aromatic polymers usually require high IEC values to attain suitable proton conductivity because of the low flexibility of the polymer skeleton chain, and the small hydrophilic/hydrophobic difference^[32]. In the present work, these problems could be alleviated by the special devise of PP-g-PS copolymer structure. The highly flexible polyphosphazene chain was employed as the backbone to keep the flexibility of the graft copolymers, and the difference in polarity between the sulfonated polystyrene blocks and the hydrophobic polyphosphazene segments was expected to produce clear phase-separated structures. Figure 3(a) reveals the correlation between the proton conductivity and the IEC value of PP-g-PS membranes at $25\text{ }^{\circ}\text{C}$. The proton conductivity soared with IEC in the range of $0.905\text{--}1.2\text{ mmol/g}$, while it showed only small rise in the IEC range of higher than 1.2 mmol/g indicating less IEC-dependence of proton conductivity at elevated IEC levels. At high temperatures, all the sulfonated PP-g-PS membranes showed

enhanced proton conductivities. However, the proton conductivity for the lower IEC-possessing PP-g-PS membranes is likely to grow more rapidly than that for the higher IEC-possessing PP-g-PS membranes (Fig. 3b). For example, the membrane S2 with IEC value of 1.05 mmol/g showed proton conductivity of 0.081 S/cm at 80 °C, close to those of membranes M1, M2 and L1 which have much higher IECs. In addition, the sulfonated PP-g-PS copolymer membranes could have higher conductivity than non-grafting polyphosphazene membranes when comparing the sulfonated PP-g-PS membrane M2 (proton conductivity = 0.056 S/cm) with sulfonated poly(bis(3-methylphenoxy)phosphazene) membrane (proton conductivity = 0.04 S/cm)^[33] at 25 °C at a IEC level of 1.4 mmol/g. These results suggest that the sulfonated PP-g-PS graft copolymers could be good candidate materials for proton exchange membranes.

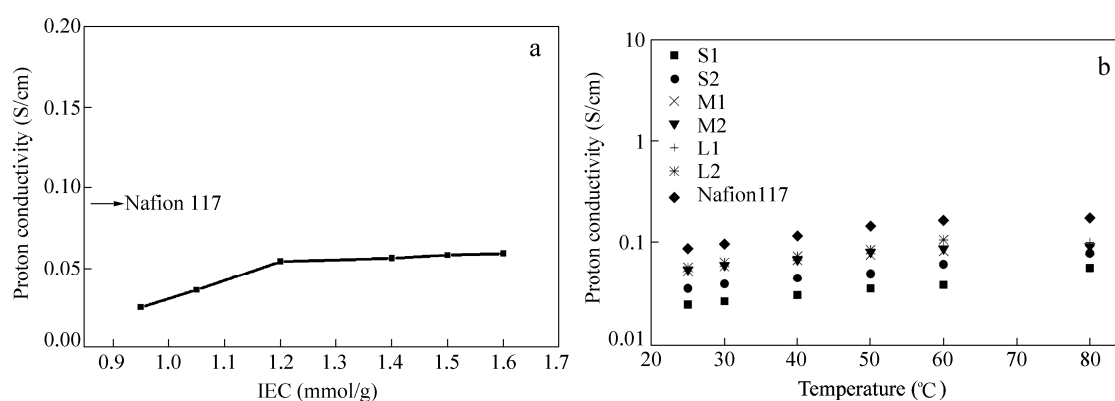


Fig. 3 (a) Proton conductivity (determined at room temperature) versus IEC and (b) proton conductivity versus temperature for PP-g-PS membranes and Nafion

TEM observation

The improved proton conduction of the sulfonated PP-g-PS membranes was further evidenced by investigations on the morphology of the membranes by transmission electron microscopy (TEM). The cross-section TEM images of membranes S2, M2 and L2 stained with lead nitrate are shown in Fig. 4. The dark and bright regions correspond to hydrophilic and hydrophobic domains, respectively. As can be seen, the hydrophilic ionic clusters in the membranes S2, M2 and L2 gradually increased in density. Furthermore, regularly distributed ionic clusters and well-defined hydrophilic/hydrophobic nanophase-separated structures were observed in these membranes, and the sizes of the ionic clusters were less than 10 nm. These morphological characteristics indicate the formation of ionic channels for proton conduction inside the sulfonated PP-g-PS membranes.

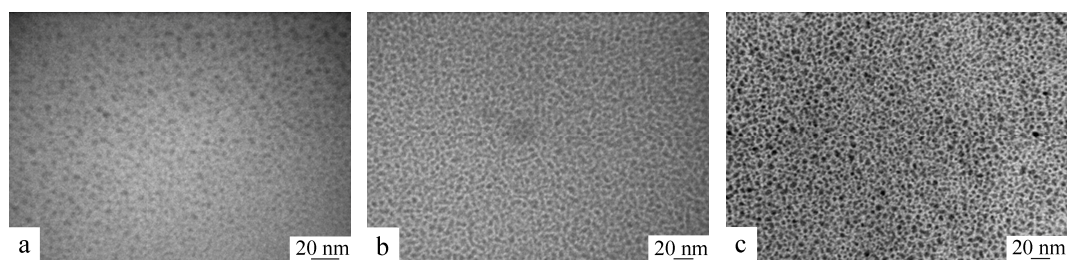


Fig. 4 TEM images of (a) membrane S2, (b) membrane M2 and (c) membrane L2

Oxidative and thermal stabilities

The oxidative stability of the membranes was evaluated in a hot Fenton's reagent (80 °C) for 1 h for accelerating purpose. For all series of sulfonated PP-g-PS membranes, no weight loss was observed and the film properties such as flexibility and transparency were maintained even after the test, indicating excellent chemical stability. Generally, the oxidative degradation of typical sulfonated aromatic polymers mainly occurs on the main

chains^[34]. However, in the present study, the attacks of the oxidative radicals might be effectively suppressed by the highly chemical stable polyphosphazene employed as the backbone in the sulfonated PP-g-PS membranes. Moreover, the relatively short polystyrene side chains might provide shield for the backbone against the oxidative reagents.

Figure 5 shows the thermogravimetric analysis of the sulfonated PP-g-PS membranes S2, M2 and L2. Profiles of the three membranes appeared similar in shape, and four stages of weight loss were observed for each curve. The initial weight loss of all copolymers below 200 °C is due to the evaporation of the residual water that reflects the hydroscopic nature of the sulfonated copolymers. In the second stage, the weight loss occurring in the range of 250–325 °C is mainly attributed to the decomposition of sulfonic acid groups in accordance with the reported data^[35]. The third thermodegradation stage in the range of 325–400 °C may be imputable to the cleavage of polystyrene segments, while the final weight loss started at 400 °C may result from the degradation of the polyphosphazene backbone. The TGA studies reveal that these membranes were thermal stable enough for fuel cell application because their initial decomposition temperatures were above 250 °C.

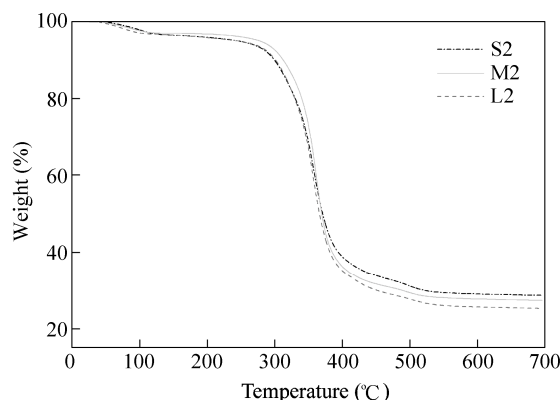


Fig. 5 Thermograms of membranes S2, M2 and L2

Methanol permeability

For direct methanol fuel cells (DMFCs), the methanol permeability coefficient is an important parameter as significant methanol crossover would cause catalyst poisoning and thus serious reduction of DMFC voltage. The methanol permeability coefficients of the sulfonated PP-g-PS membranes and Nafion 117 are listed in Table 2. Significantly, all sulfonated PP-g-PS membranes showed lower crossover of methanol in comparison to Nafion 117, although they have even much higher water uptake than Nafion 117 (Table 2) and their methanol permeability rises with IEC. Furthermore, comparing with the counterpart membrane of sulfonated poly(bis(phenoxy)phosphazene) prepared in our previous work as a non-grafting polymer membrane (IEC = 1.1 mmol/g, methanol permeability = 1.72×10^{-6} cm²/s), the sulfonated PP-g-PS membranes S2 (IEC = 1.05 mmol/g) and M1 (IEC = 1.2 mmol/g) showed a significantly reduced methanol permeability at 1.6×10^{-7} cm²/s and 2.08×10^{-7} cm²/s, respectively (Table 2). These results suggest a much obstructed movement of the methanol molecules in the sulfonated PP-g-PS membranes in which the graft structure might provide an effective barrier against the diffusion of aggregated methanol molecules. Besides, the S and M series of sulfonated PP-g-PS membranes exhibited good selectivity (Table 2), determined by the ratio of proton conductivity to methanol permeability coefficient. The highest selectivity value of 2.6×10^5 Ss/cm³ which is almost 4 times higher than that of Nafion 117, comes from the M1 membrane, indicating that it is a promising candidate for PEM materials for DMFCs.

CONCLUSIONS

Polystyrenes were successfully grafted from the side aromatic groups of polyphosphazenes by ATRP reaction leading to a new series of PP-g-PS graft copolymers possessing narrow polydispersities. During the synthesis,

the formation of macroinitiators from polyphosphazenes and the ATRP process could be well controlled to produce certain density and length of the grafted pendant polystyrene side chains, which in turn readily underwent selective sulfonation reaction to yield polystyrene sulfonic acid moieties as hydrophilic units of the sulfonated PP-g-PS copolymers. The sulfonated copolymers showed the graft-depending IEC values ranging from 0.905 mmol/g to 1.6 mmol/g and were prepared into according membranes by solution casting. Studies of the membrane properties revealed that the sulfonated PP-g-PS membranes had significantly reduced water swelling and methanol permeability, and enhanced proton conductivity as compared to non-grafting polyphosphazene membranes. These membranes also showed excellent chemical stability. Moreover, well defined nanophase-separated structures were found in the membranes and they might be resulted from the difference in polarity between the sulfonated polystyrene acid moieties and the hydrophobic polyphosphazene segments. Overall, the results of the present study have pronounced implications for the development of novel method and materials of PEM for DMFCs.

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