



# Preparation and evaluation of crosslinked sulfonated polyphosphazene with poly(aryloxy cyclotriphosphazene) for proton exchange membrane

Yan Dong<sup>a</sup>, Hulin Xu<sup>b</sup>, Fengyan Fu<sup>a</sup>, Changjin Zhu<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Beijing Institute of Technology, Beijing 100081, China

<sup>b</sup> Beijing Qintian Science & Technology Development Co., Beijing 100070, China

## ARTICLE INFO

### Article history:

Received 9 September 2015

Revised 16 November 2015

Accepted 16 November 2015

Available online 16 March 2016

### Keywords:

Polyphosphazene

Proton exchange membrane

Phase separation

Direct methanol fuel cell

## ABSTRACT

Several crosslinked proton exchange membranes with high proton conductivities and low methanol permeability coefficients were prepared, based on the sulfonated poly[(4-fluorophenoxy)(phenoxy)] phosphazene (SPFPP) and newly synthesized water soluble sulfonated poly(cyclophosphazene) (SPCP) containing clustered flexible pendant sulfonic acids. The structure of SPCP was characterized by fourier transform infrared spectroscopy (FTIR) and <sup>1</sup>H NMR spectra. The membranes showed moderate proton conductivities and much lower methanol permeability coefficients when compared to Nafion 117. Transmission electron microscopy (TEM) results indicated the well-defined phase separation between the locally and densely sulfonated units and hydrophobic units, which induced efficient proton conduction. In comparison with SPFPP membrane, the proton conductivities, oxidative stabilities and mechanical properties of crosslinked membranes remarkably were improved. The selectivity values of all the crosslinked membranes were also much higher than that of Nafion 117 ( $0.74 \times 10^5 \text{ S} \cdot \text{s}/\text{cm}^3$ ). These results suggested that the cSPFPP/SPCP membranes were promising candidate materials for proton exchange membrane in direct methanol fuel cells.

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## 1. Introduction

In these years, direct methanol fuel cells (DMFCs) have gained great attention as candidate for future portable power devices for their advantages, such as low emission and simple system [1,2]. The proton exchange membrane (PEM), which transfers protons from the anode to the cathode to produce electricity and prevents the passage of electrons and a fuel gas crossover between the electrodes, is a key component of DMFCs [3].

Perfluorosulfonate membranes, such as Nafion membranes, have been widely applied in DMFCs, because they have high proton conductivities and excellent thermal as well as chemical stabilities [4]. However, there are still several technical problems limiting their applications, such as expensive cost, high methanol crossover and difficulty in preparing. One major obstacle is the high methanol crossover, which causes not only catalyst poisoning but also fuel consumption and energy efficiency loss [4,5]. To overcome these problems, many efforts have been devoted to improving Nafion-based membrane or developing new proton ex-

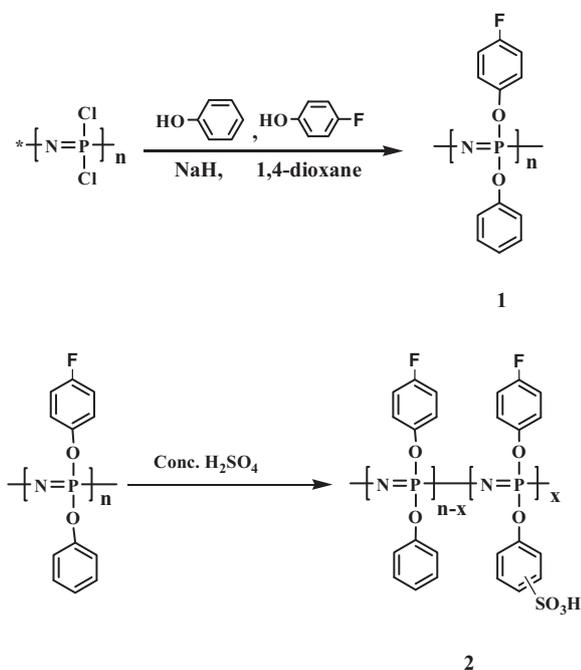
change membranes [6,7]. In recent years, many polymeric membranes have been examined for use in fuel cells, including sulfonated poly(phenylene)s [8], sulfonated polysulfones (SPSFs) [9], sulfonated poly(ether ether ketone)s (SPEEKs) [10,11], sulfonated polyimides (SPIs) [12,13] and sulfonated polyphosphazenes [14]. Among these materials, sulfonated polyphosphazenes have attracted considerable attention because of their low cost, acceptably high proton conductivities and low methanol permeability coefficients [15,16]. In the case of sulfonated polyphosphazene, adequate acidic groups are required to obtain sufficient proton conductivity. However, high degree of sulfonation (DS) always results in the increase of water uptake and methanol crossover, and solubility in methanol/water solution [17,18].

Crosslinking of polymer membrane has been thought to be an effective approach to overcome these problems, which can not only suppress excess water uptake, methanol permeability and swelling ratio but also improve the chemical stability [19,20]. Many research groups have made great progress on the crosslinking of sulfonated polymers [21–23]. Self-crosslinked sulfonated polyphosphazene-based PEMs show relatively low proton conductivity and poor thermal stability [24].

In the present study, to achieve the PEM with sufficient proton conductivity and thermal property while maintaining the low

\* Corresponding author. Tel: +86 10 68918506.

E-mail address: [zcj@bit.edu.cn](mailto:zcj@bit.edu.cn) (C. Zhu).



**Scheme 1.** Synthetic route of polymers **1** and **2** (SPFPP).

water swelling and methanol crossover, we designed a new sulfonated poly(aryloxy cyclotriphosphazene) copolymer and combined it with the sulfonated polyphosphazenes by crosslinking in the membrane preparation. As a result, the obtained membranes showed higher proton conductivities than sulfonated polyphosphazene (SPFPP) membrane and oxidative stabilities and mechanical properties were improved. Additionally, the properties of the crosslinked membranes such as water uptake, swelling ratio, methanol permeability, oxidative stability and thermal stability are also discussed in detail.

## 2. Experimental

### 2.1. Materials

The synthesis and characterization of sulfonated poly[(4-fluorophenoxy)(phenoxy)] phosphazene (SPFPP) were reported by our previous work with minor modification [25]. The structure of SPFPP **2** was shown in Scheme 1. 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) was prepared according to the previous report [26]. Hexachlorocyclotriphosphazene ( $\text{N}_3\text{P}_3\text{Cl}_6$ ) was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), dioxane, dimethylsulfoxide (DMSO), concentrated sulfuric acid (98%), were purchased from Aldrich Chemical Co. ( $\text{N}_3\text{P}_3\text{Cl}_6$ ) was purified by two recrystallizations from hexane and vacuum sublimation prior to use. 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA), boron tribromide ( $\text{BBr}_3$ ), 1,4-butanediol were purchased from Sigma-Aldrich. Dioxane and THF were freshly distilled from sodium benzophenone ketyl. Other chemical reagents and the organic solvents were purchased from Beijing Chemical Reagent and were purified by conventional methods.

### 2.2. Characterizations and measurements

Fourier transform infrared (FTIR) spectra of the membranes were measured on a Nicolet Nexux 470 (Nicolet, USA).  $^1\text{H}$  and  $^{31}\text{P}$  nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE-300 spectrometer (Bruker Biospin International AG, Switzerland). Mass spectrum (MS) was collected using a Micromass

Quattro-II triple quadrupole mass spectrometer (WATERS, USA). Molecular weight measurements were performed via Viscotek I-MBHMW-3078 gel permeation chromatography (GPC) equipped with Viscotek VE 1122 solvent delivery system (Tetrahydrofuran was used as a solvent at 25 °C.  $M_n$  and  $M_w$  were calibrated by standard polystyrene samples). Thermogravimetric analysis (TGA) was performed with TGA-Q500 (TA, USA) 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 JEM-2010 (JEOL, Japan) transmission electron microscope.

#### 2.2.1. Synthesis of tetra-substituted cyclotriphosphazene monomer ( $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{OCH}_3)_4\text{Cl}_2$ ) (**3**)

( $\text{N}_3\text{P}_3\text{Cl}_6$ ) (3.5 g, 0.0101 mol) was dissolved in 15 mL of THF. 4-Methoxyphenol (5.01 g, 0.0404 mol) was dissolved in 50 mL of THF and then the solution was added dropwise to the suspension of NaH (1.04 g, 0.0424 mol) in 10 mL of THF. This reaction mixture was stirred at room temperature for 24 h under the nitrogen atmosphere. The resultant sodium phenoxide solution was added dropwise to the stirred solution of ( $\text{N}_3\text{P}_3\text{Cl}_6$ ) in THF at 0 °C. This mixture was warmed to room temperature to perform the reaction for 12 h. After the reaction was completed, the solvent was evaporated at reduced pressure, and then the oily resultant was dissolved in 50 mL of  $\text{CH}_2\text{Cl}_2$ . This solution was washed three times with 50 mL of 3% aqueous  $\text{NaHCO}_3$ , dried over  $\text{Na}_2\text{SO}_4$ , and concentrated by rotary evaporation. Column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ :n-hexane = 7:5) was carried out for further purification to give off-yellow oil as **3** (4.434 g, 63.0 wt% yield). IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1234.6.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 3.756 (m, 3H,  $\text{OCH}_3$ ), 6.795–7.178 (m, 4H, ArH). MS:  $m/z$  697.81,  $[\text{M} + \text{H}]^+$ .

#### 2.2.2. Synthesis of cyclolinear poly(aryloxy cyclotriphosphazene) containing methoxy groups (**4**)

A mixture of 6F-BPA (1.736 g, 0.0076 mol) and NaH (0.382 g, 0.0156 mol) in THF (20 mL) was stirred and refluxed at room temperature for 12 h, and afterward a solution of **3** (5.305 g, 0.0076 mol) in 10 mL of freshly distilled THF was added dropwise to this reaction mixture to perform the reaction with vigorous stirring at room temperature for 24 h under a nitrogen atmosphere. Then the yellow precipitate was filtered off, and the solution was poured in to 50 mL of deionized water with vigorous stirring. The resulting copolymer was washed with deionized water and hot methanol three times and dried at 70 °C under vacuum for 24 h.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 3.734 (m, 1H,  $\text{OCH}_3$ ), 6.776–7.071 (m, 2H, ArH).  $^{31}\text{P}$ -NMR (162 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 9.475 (s, 2P,  $\text{P}-\text{OC}_6\text{H}_4\text{OCH}_3$ ), 9.601 (s, 1P,  $\text{P}-\text{OC}_6\text{H}_4\text{C}(\text{CF}_3)_2\text{OC}_6\text{H}_4$ ).

#### 2.2.3. Synthesis of cyclolinear poly(aryloxy cyclotriphosphazene) containing hydroxyl groups (**5**)

A sample of 2.0 g of **4** was dissolved into 50 mL of  $\text{CH}_2\text{Cl}_2$  in a 100 mL three-neck flask equipped with mechanical stirrer and a nitrogen inlet.  $\text{BBr}_3$  (2 mL) was mixed with  $\text{CH}_2\text{Cl}_2$  (20 mL), and the resulting solution was added dropwise to the **4** solution at 0 °C (ice bath). After 12 h, the mixture was poured into water with stirring, the polymer was washed with boiling water, recovered, and then dried under vacuum at 70 °C for 24 h. IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3166.5.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  = 6.596–7.264 (m, 6H, ArH), 9.448 (m, 1H, OH). ( $M_n$  = 68069 Da,  $M_w$  = 103772 Da,  $M_w/M_n$  = 1.525).

#### 2.2.4. Synthesis of sulfonated poly(cyclophosphazene) (SPCP) (**6**)

2.0 g of sample **5** and NaH (0.382 g, 0.0156 mol) were dissolved into 30 mL of DMSO at room temperature and stirred for 24 h under nitrogen atmosphere. 1 mL of 1,4-butanediol was added, the reaction temperature rise to 100 °C and kept at the temperature for another 24 h. The viscous solution was precipitated into 50 mL of

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