

# Polyphosphazene-based copolymers containing pendant alkylsulfonic acid groups as proton exchange membranes



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## ABSTRACT

A series of polyphosphazene-based copolymers containing alkylsulfonated side chains were prepared and made into the corresponding membranes by the reaction with 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) as the cross-linking reagent. All the cross-linked membranes showed lower water uptake and dimensional swelling. They displayed significant methanol resistance ranging from 1.35 to  $7.18 \times 10^{-7}$  cm<sup>2</sup>/s and high oxidative stabilities. The individual membrane PFMPP<sub>1</sub>-r-PFSPP<sub>9</sub> showed good proton conductivity (0.14 S/cm) under fully hydrated conditions at 80 °C.

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## 1. Introduction

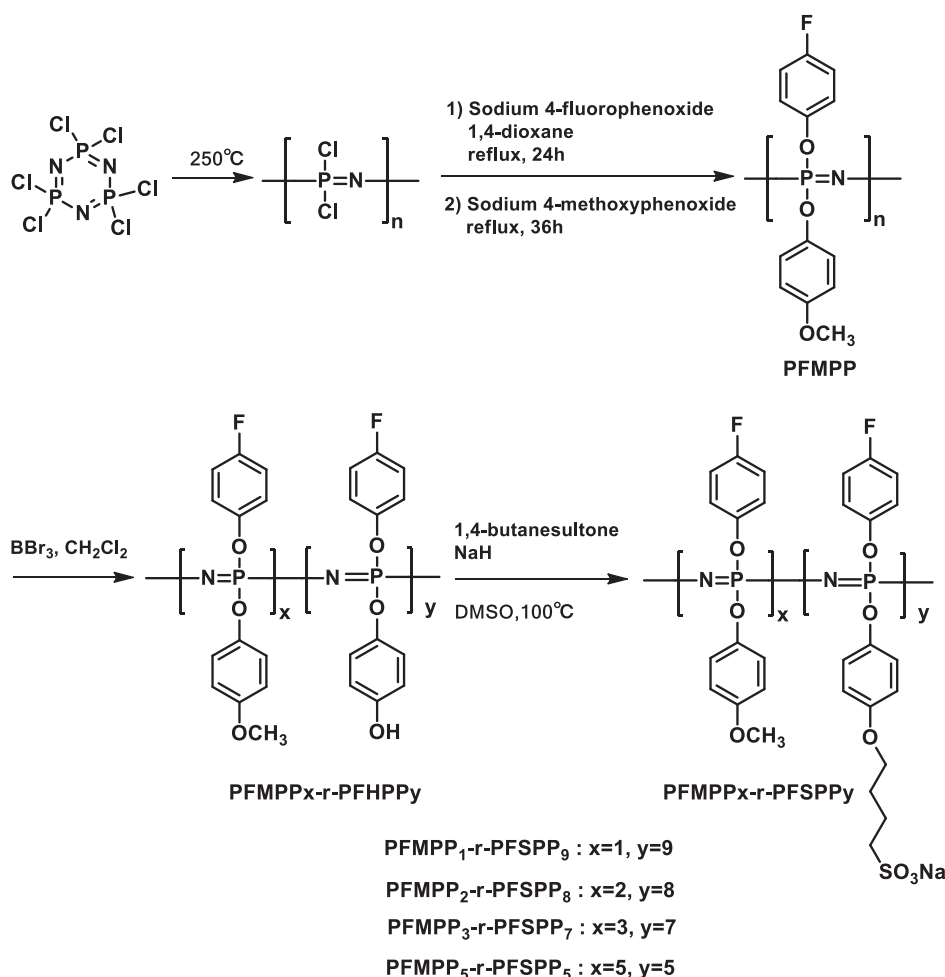
The proton exchange membrane (PEM) in fuel cell performs a number of critical functions. It separates the fuel and oxidant and provides the pathway for the protons transfer. DuPont's Nafion is widely studied as good fuel cell membranes because of its high proton conductivity combined with oxidative and chemical stability [1]. However, some drawbacks of Nafion hinder its widespread commercial use in proton exchange membrane fuel cells (PEMFCs), such as high methanol crossover and high cost [2,3].

Many efforts have been made to develop the alternative materials to Nafion in past years. Most of the acid-functionalized aromatic hydrocarbon polymers, including sulfonated poly(arylene ether sulfone) [4,5], sulfonated poly(arylene ether ketone) [6], and sulfonated polyimides [7], have been considered as promising candidates for proton exchange membranes because of their high proton conductivity, low cost. However, the sulfonated aromatic polymers which have high ion exchange capacity (IEC) result in significant swelling in water. One of the approaches to improve the performance is to design polymer structure consisted of hydrophilic and hydrophobic segments to enable the balance between the dimensional stability and proton conductivity of aromatic PEMs, and it has received increasing attention because enhanced properties in terms of proton exchange membrane performance were found in the so-designed polymers [8–13]. Recently, several research

groups found that the attachment of pendant alkylsulfonated side chains to hydrocarbon-based polymers contributed to the well-developed phase separation and thus exhibited a better balance between proton conductivity and dimensional swelling than PEMs with sulfonic acid groups attached directly onto the aromatic chain. Ueda and co-workers [9,14] reported a series of cross-linked polystyrene membranes containing a flexible pendant aliphatic sulfonic acid group and a hydrophobic main chain, which showed increased proton conductivity due to the well-developed phase separation and improved oxidative stability. Guiver and co-workers [15] reported fluorene-based poly(arylene ether sulfone)s containing clustered flexible pendant butylsulfonic acids displaying good proton conductivities with relatively low water contents.

Polyphosphazenes are hybrid organic–inorganic polymers with a phosphorus–nitrogen chain backbone and have valuable qualities as structural and functional materials. Sulfonated polyphosphazenes as proton exchange membranes for DMFCs have been reported over the past few years [16,17]. However, the sulfonated polyphosphazenes were all almost obtained by postsulfonation in which the polymers were sulfonated by using sulfonating agent such as concentrated sulfuric acid or sulfur trioxide, and this sulfonation method often caused the polymers dissolved in water at a higher level of ion exchange capacities (IECs) [18]. In our previous work, sulfonated polyphosphazene-graft-polystyrene copolymers were prepared by atom transfer radical polymerization (ATRP) of styrene and then selective sulfonation with acetyl sulfate, and exhibited good methanol-resistant ability but remained unstable at higher ion exchange capacities (IECs) [19]. In the present study,

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Scheme 1. Synthesis of PFMPP<sub>x-r</sub>-PFSPP<sub>y</sub> copolymers.

we designed and synthesized a series of cross-linked sulfonated polyphosphazene-based membranes containing hydrophobic chains and alkylsulfonated side chains with varying ion exchange capacities (IECs). We used a direct sulfonation route by which the sulfonic acid groups were incorporated into the macromolecular chain at the polymer synthesis step, and this could give better control over the membranes' properties even at higher IEC.

## 2. Experimental

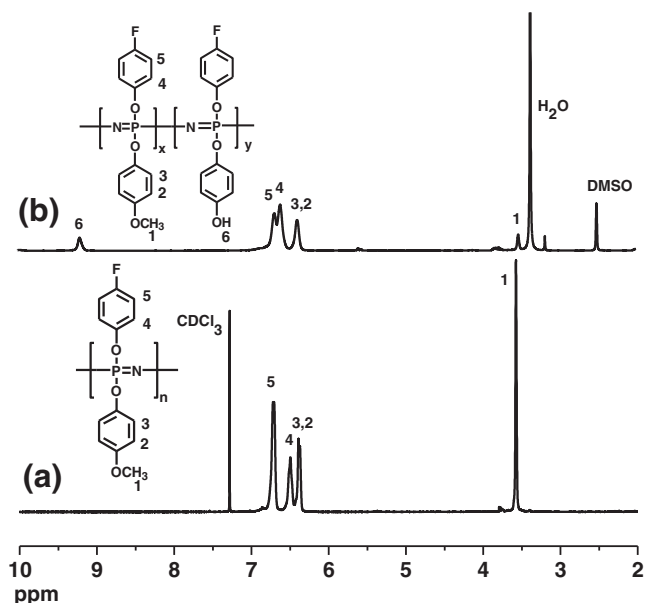
### 2.1. Materials

Hexachlorocyclotriphosphazene ( $\text{N}(\text{PCl}_2)_3$ ) was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), 1,4-dioxane, dimethylsulfoxide (DMSO), 4-methoxyphenol, 4-fluorophenol were purchased from Aldrich Chemical Co. Borontribromide ( $\text{BBr}_3$ ), 1,4-butanedisulfone were purchased from TCI Chemical Co. ( $\text{N}(\text{PCl}_2)_3$ ) was purified by two recrystallizations from hexane and vacuum sublimation prior to use. 1,4-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 [20]. Other chemicals were used as received.

### 2.2. Synthesis of poly[(4-fluorophenoxy)(4-methoxyphenoxy)phosphazene] (PFMPP)

Poly(dichlorophosphazene) (PDPCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene ( $\text{N}(\text{PCl}_2)_3$ ) at

250 °C in a sealed tube [21,22]. 4-Fluorophenol (5.33 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

Fig. 1. <sup>1</sup>H NMR spectra of (a) PFMPP and (b) PFMPP<sub>2-r</sub>-PFHPP<sub>8</sub>.

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