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Design of polyphosphazene-based graft copolystyrenes with alkylsulfonate branch chains for proton exchange membranes

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ABSTRACT

In order to develop efficient proton exchange membranes used for direct methanol fuel cells, we are focusing on the design and synthesis of polyphosphazene-based copolymers. In the present study, block polystyrenes were grafted onto polyphosphazenes by atom transfer radical polymerization (ATRP) of styrene and 4-acetoxystyrene, and then alkylated with 1,4-butanesultone to yield two series of graft copolymers having branch chains of alkylsulfonic acids. They were further made into the corresponding membranes with the assist of simultaneous cross-linking reaction with 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) as the cross-linker. High proton conductivities were found for the membrane series of M-PS$_x$-PSBOS$_y$ in the range of 0.184–0.266 S/cm, and for F-PS$_x$-PSBOS$_y$ in the range of 0.147–0.284 S/cm under fully hydrated conditions at 80 °C, respectively, and were supported by the nanophase-separated structures by the transmission electron microscopy (TEM) investigations. Also, the membranes showed good methanol resistance ($1.60–10.4 \times 10^{-7}$ cm^2/s) and high oxidative stabilities. These results suggest a potential of the membranes for the DMFCs application.

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1. Introduction

The proton exchange membranes (PEMs) in fuel cell perform a number of critically functions. It separates the fuel and oxidant, and provides the pathway for the proton 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, such as high methanol crossover and high cost, hinder its widespread commercial use in proton exchange membrane fuel cells (PEMFCs) [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 ketone) [4], sulfonated polyimides[5,6], and sulfonated poly(arylene ether sulfone) [7], have been considered as promising candidates for PEMs due to their thermal stabilities, low fuel permeabilities and low costs. However, the sulfonated aromatic polymer membranes have relatively low proton conductivity than that of Nafion because of the lower acidity of the aryl sulfonic acid and less distinct phase separation between hydrophilic and hydrophobic domains. One of approaches to improve the performance is to design polymer structure consisted of hydrophilic and hydrophobic segments which are expected to form ion transport channels for efficient proton conduction, and it has received increasing attention as enhanced properties in terms of PEM performance were found in the so-designed polymers [8–14]. Recent studies found that the attachment of pendant alkylsulfonated side chains to hydrocarbon-based polymers contributed to the well-developed phase separation and thus improved the proton conduction. Ueda and co-workers reported a series of cross-linked polystyrene membranes consisted of a hydrophobic main chain and flexible pendent aliphatic sulfonic acid side chains by the treatment with polyfunctional benzylic alcohol of 4,4′-methylene-bis[2,6-bis(hydroxyethyl)phenol] (MBHP) [9,14,15]. They found well-developed phase separation in the membrane structure, and a significant effect of alkylsulfonated side chains introduced to the polystyrene scaffold on membrane properties of water uptake, proton conductivity, and oxidative stability.

Polyphosphazenes are hybrid organic–inorganic polymers with a phosphorus–nitrogen chain backbone and have valuable qualities as structural and functional materials. A number of researches have focused on sulfonated polyphosphazenes as proton exchange membranes for fuel cell membranes over the past few years [16–21]. Pintauro and co-works reported that sulfonated with SO_3 and crosslinked poly[bis(3-methylphenoxy)phosphazene] membranes showed much low methanol diffusivities ($\leq 1.2 \times 10^{-7}$ cm^2/s) and also lower proton conductivity than that of Nafion 117 [17]. In our

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previous work, we have prepared sulfonated polyphosphazene-graft-polystyrene copolymers that were synthesized by atom transfer radical polymerization (ATRP) of styrene and then selectively sulfonated with acetyl sulfate, and exhibited good methanol -resistant ability but remained insufficient proton conduction [18]. Moreover, the sulfonated phosphosphazenes polymers were all almost obtained by postsulfonation with sulfonating agents such as sulfur trioxide and concentrated sulfuric acid, and this sulfonation method often led to an unstable product that later underwent degradation at a higher level of ion exchange capacity (IEC). In the present study, we designed and synthesized two series of the graft copolymer-based membranes M-PS$_x$-PSBOS$_y$ and F-PS$_x$-PSBOS$_y$, which have polyphosphazene-graft-copolystyrene and branched chains of alkylsulfonate. 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 level of IEC. The graft copolymer membranes showed excellent proton conduction even much higher than that of Nafion 117 in a range of room temperature to 80 °C. Herein, we will describe the preparations and properties of the membranes.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was purchased from LanYin Chemical, China. Tetrahydrofuran (THF), 1,4-dioxane, dimethylsulfoxide (DMSO), 4-methylphenol, 4-methoxyphenol, 4-fluorophenol, N-bromosuccinimide (NBS), benzoyl peroxide (BPO), CuBr and 2,2-bipyridine (bpy) were purchased from Aldrich Chemical Co. Styrene, 4-acetoxystyrene and 1,4-butanesultone were purchased from TCI Chemical Co. Styrene and 4-acetoxystyrene were passed through a column of basic aluminum. $(NPCl_2)_3$ was purified by recrystallizations from hexane two times and then 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 [22]. Other chemicals were used as received.

2.2. Synthesis of poly[(4-methoxyphenoxy) (4-methylphenoxy) phosphazene] (PMMPP)

Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazene ($(NPCl_2)_3$) at 250 °C in a sealed tube [23,24]. 4-Methoxyphenol (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 1,4-dioxane (60 mL). The mixture was refluxed overnight to form the sodium salt. The salt solution was added slowly dropwise to a rapidly stirred solution of PDCP (5.0 g, 43 mmol) in 1,4-dioxane (80 mL) under an inert atmosphere in a 250 mL three-neck flask equipped with a reflux condenser, magnetic stirrer and Ar inlet/outlet. The reaction mixture was refluxed for 24 h, and then a solution of sodium 4-methylphenoxide in dioxane was added dropwise. The sodium 4-methylphenoxide was prepared by adding 4-methylphenol (9.29 g, 86 mmol) to a suspension of NaH (60% by weight, 3.44 g, 86 mmol of NaH) in 1,4-dioxane (60 mL). The reaction mixture was stirred at 115 °C for 36 h. Then it was poured into distilled water and the polymer was collected. The resulting polymer was purified by successive reprecipitation from THF to hexane. The obtained polymer PMMPP was dried in a vacuum oven at 60 °C overnight. The yield was 50%. (Scheme 1).

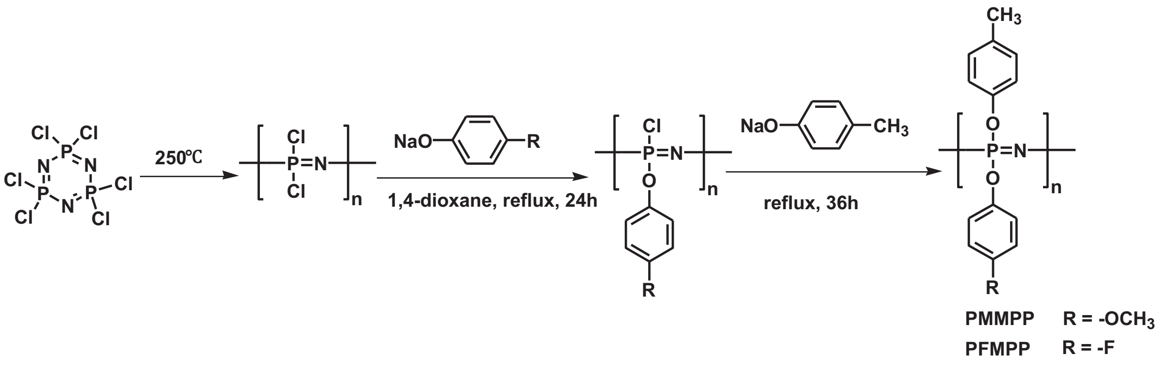
^{1}H NMR (400 MHz, $CDCl_3$; ppm): δ: 6.6–6.8 (m, $–OC_6H_4CH_3$), 6.28 (m, $–OC_6H_4OCH_3$), 3.48(s, $–OCH_3$), 2.08 (s, CH_3).

2.3. Synthesis of PMMPP–Br initiator

To a 200 mL round-bottom flask, equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet/outlet, the polymer PMMPP (1.0 g, 3.6 mmol), NBS (0.128 g, 0.72 mmol), BPO (0.017 g, 0.072 mmol), and carbon tetrachloride (100 mL) were added. The solution was shielded from light and brought rapidly to reflux at 80 °C for 3 h. Then the mixture was cooled and filtered. The filtrate was concentrated under reduced pressure and precipitated into hexane to give crude product, which was re-precipitated from THF to hexane for two additional times and then dried at 50 °C under vacuum for 24 h. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$; ppm): δ: 6.6–6.8 (m, $–OC_6H_4CH_3$), 6.28 (m, $–OC_6H_4OCH_3$), 4.2 (s, $–CH_2Br$), 3.48 (s, $–OCH_3$), 2.08 (s, CH_3).

2.4. Synthesis of PMMPP-g-poly[(styrene)$_x$-r-(4-acetoxystyrene)$_y$] (M-PS$_x$-PAS$_y$: x and y refer to the molar ratio of each unit)

PMMPP-g-poly[(styrene)$_x$-r-(4-acetoxystyrene)$_y$] copolymers were synthesized using an atom transfer radical polymerization (ATRP) [25–27]. The macroinitiator PMMPP–Br (0.5 g, 0.26 mmol), styrene (1.083 g, 10.4 mmol), 4-acetoxystyrene (1.68 g, 10.4 mmol), bpy (0.24 g, 1.56 mmol), and CuBr (0.075 g, 0.52 mmol) were added to a dried reaction tube equipped with a stopcock and a magnetic stirrer. Three freeze-pump-thaw cycles were performed to remove oxygen. The polymerization reaction was carried out at 115 °C for 24 h under a nitrogen blanket and then the resulting mixture was diluted with THF, purified by passing through a column of alumina, and then precipitated into methanol. ^{1}H NMR (400 MHz, $CDCl_3$; ppm): δ: 7.08–7.26 (m, $–OC_6H_4$), 6.6–6.8 (m,$–OC_6H_4CH_3$), 6.28 (m, $–OC_6H_4OCH_3$), 3.48 (s, $–OCH_3$), 2.26 (s, $–OOCCH_3$), 2.08 (s, CH_3), 1.2–1.9 (m, CH_2, CH).



Scheme 1. Synthesis of polymers PMMPP and PFMPP.

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