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New poly(ethylene oxide) soft segment-containing sulfonated polyimide copolymers for high temperature proton-exchange membrane fuel cells

He Bai [a,b], W.S. Winston Ho [a,b,*]

[a] Department of Chemical and Biomolecular Engineering, The Ohio State University, 140 West 19th Avenue, Columbus, OH 43210-1180, USA
[b] Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210-1178, USA

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Abstract

The synthesis and characterization of a series of new poly(ethylene oxide) (PEO) soft segment-containing six-member ring sulfonated polyimide (SPI) copolymers are described in this paper. One-step high temperature polymerization method was used to prepare the SPI copolymers from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4′-diaminostilbene-2,2′-disulfonic acid (DSDSA), and diamine-terminated poly(ethylene oxide) (PEO-diamine, MW = 1000). The relative ratio of the sulfonic acid-containing hard segments to the PEO-containing soft segments was controlled through varying the molar ratio of DSDSA to PEO-diamine. Flexible, transparent, and mechanically strong free-standing membranes were successfully obtained. The membranes were characterized with ion-exchange capacity, Fourier transform infrared spectra, thermogravimetric analysis, water sorption, proton conductivity, and fuel cell performance measurements. The results showed that the new SPI membranes exhibited desirable mechanical properties and thermal stability as well as better proton conductivities than Nafion® 115 at high relative humidity (RH) levels (>50%) at both 70 and 120 °C. The results from the fuel cell performance measurements indicated that the SPI membrane containing 5 mol% (12.4 wt.%) PEO soft segments had similar fuel cell performance as Nafion® 112 at 70 °C and 80% RH, but better fuel cell performance than Nafion® 112 when the current density was higher than 0.32 A/cm^2 at 120 °C and 50% RH.

Keywords: Sulfonated polyimide (SPI); Poly(ethylene oxide) (PEO) soft segments; Copolymer; Proton-exchange membrane (PEM); High temperature; Proton conductivity; Fuel cell performance; Fuel cell

1. Introduction

In recent years, great progress has been made on the development of proton-exchange membrane fuel cells (PEMFCs) for both mobile and stationary applications, particularly for fuel cell vehicles. Dupont's Nafion® and other perfluorinated sulfonic acid membranes are currently popular to use for low temperature PEMFCs due to their high proton conductivity as well as desirable mechanical strength and chemical stability. However, some disadvantages, such as high cost, relatively low conductivity at high temperatures (above 100 °C) and low humidities, and high dependence of proton conduction on the water content, seriously limit the industrial application of these membranes. High temperature operations can increase the anode's tolerable level of CO in the fuel and accelerate the reaction rates at the anode and cathode. Low humidity operations can facilitate the water management of the fuel cell system. Therefore, it is desirable for a PEMFC to operate at high temperatures (above 100 °C) and low relative humidities (below 50% RH). As a result, the development of competitive and less expensive PEMs that have efficient performance at high temperatures is crucial for fuel cell applications.

Many efforts have been initiated to synthesize cost-effective and thermally stable alternative membranes, including sulfonated poly(arylene ether sulfone) copolymers [1–3], sulfonated poly(aryl ether ketone) copolymers [4,5], phosphoric acid-soaking polybenzimidazole (PBI) [6,7], and radiation-grafted membranes [8,9]. Several membranes have continued to attract interest.

Recently, sulfonated polyimides (SPIs) have been shown to be promising materials for PEMs mainly because of their excellent mechanical and thermal properties as well as their chemical

* Corresponding author at: Department of Chemical and Biomolecular Engineering, The Ohio State University, 140 West 19th Avenue, Columbus, OH 43210-1180, USA. Tel.: +1 614 292 9970; fax: +1 614 292 3769.
E-mail address: ho@chbmeng.ohio-state.edu (W.S.W. Ho).

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stability. Pineri and his coworkers first synthesized five-member and six-member ring SPIs from 4,4′-diaminobiphenyl-2,2′-disulfonic acid (BDSA), 4,4′-oxydianiline (ODA), and two types of dianhydrides—oxydiphthalic dianhydride (OPDA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) [10]. Fuel cell experiments performed with the six-member ring NTDA-based SPI membrane revealed reasonably good performance (similar to Nafion® 117 at 70 °C and a fully hydrated state) and the stability of at least 3000 h. In contrast, the five-member ring OPDA-based SPI membrane was not stable during fuel cell measurements, which was due to the hydrolysis of imide rings from the sulfonated imide sequence, thus leading to chain scissions.

McGrath et al. also prepared a series of five-member and six-member ring SPIs using different sulfonated diamines, two commercially available sulfonated diamines—BDSA and 2,5-diamino benzene sulfonic acid (DABSA) [11,12] and two self-synthesized sulfonated diamines—sulfonated bis(3-aminophenyl)phenyl phosphine oxide (SBAPPO) and 3,3′-disulfonic acid-bis[4-(3-aminophenoxy)phenyl]sulfone (SA-DADPS) [13,14]. The SA-DADPS-based six-member ring SPI membranes with the IEC values of about 1.6 mmol/g showed lower conductivities than Nafion® 1135 at 80 °C and all RH levels [15]. The membranes were also used for direct methanol fuel cell (DMFC) measurements, with the results showing similar fuel cell performance as Nafion® 117 at 80 °C with the methanol feed concentration of 0.5 M [15]. However, no high temperature H_2/O_2 fuel cell performance data were reported.

Okamoto and his coworkers successfully synthesized two types of six-member ring SPIs (main-chain type and side-chain type) to study the "structure–property" relationship of SPIs systematically. They synthesized aromatic sulfonated diamines, such as 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) [16], 9,9′-bis(4-aminophenyl) fluorene-2,7-disulfonic acid (BAPFDS) [17], 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) [18], and 2,2′-bis(4-aminophenoxy)biphenyl-5,5′-disulfonic acid (oBAPBDS) [19], and prepared several series of main-chain type sulfonated polyimides by their copolymerization with NTDA and common diamines. They also synthesized a new type of side-chain SPIs using their self-developed sulfonated diamines, such as 2,2′-bis(3-sulfopropoxy)benzidine (2,2′-BSPB) [20–22], 3,3′-bis(3-sulfopropoxy)benzidine (3,3′-BSPB) [21,22], 3-(2′,4′-diaminophenoxy)propane sulfonic acid (DAPPS) [23], 3,5-diamino-3′-sulfo-4′-(4-sulfophenoxy) benzophenone (DASSPB) [24], 3,5-diamino-3′-sulfo-4′-(2,4-disulfophenoxy)benzophenone (DASDSPB) [24], and bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPS-BPS) [25]. The results showed that at low temperatures (i.e., 50 or 60 °C), the conductivities of these new SPI membranes were lower than Nafion® 117 at low RH levels and similar or higher than Nafion® 117 at high RH levels. Moreover, at the same RH value, the membrane conductivity improved with the increase of temperature due to the activation energy effect.

Further research in Okamoto's group showed that the BAPBDS-based main-chain type and BSPB-based side-chain type SPI membranes displayed fairly good conductivities [18,20–22] and excellent water stability (more than 1000 h in boiling water) [26]. So they were more suitable for the real fuel cell applications, particularly for direct methanol fuel cells (DMFCs) because of their low methanol permeabilities [27]. The BAPBDS-based SPI membranes showed comparable fuel cell performance to Nafion® 112 at 90 °C and nearly 100% RH and the short-term stability up to 50 h in the H_2/O_2 fuel cell measurements [28]. Okamoto et al. also prepared a series of branched/crosslinked SPI membranes by using their self-synthesized 1,3,5-tris(4-aminophenoxy)benzene (TAPB) as a crosslinker, and the resulting membranes showed similar conductivities and fuel cell performance as the BAPBDS-based SPI membranes but much improved water stability and mechanical properties under the accelerated aging treatment [29,30].

In this article, we report the synthesis of a series of new soft segment-containing six-member ring SPI copolymers using NTDA, DSDSA, and PEO-diamine. Hydrophilic soft segments of PEO were copolymerized into SPIs to not only increase water retention in the membranes (particularly at high temperatures and low RHs), but also improve the membrane mechanical properties. The resulting free-standing membranes were characterized with ion-exchange capacity, Fourier transform infrared spectra, thermogravimetric analysis, water sorption, proton conductivity, and fuel cell performance measurements, and their potential applications for high temperature PEMFCs were explored.

2. Experimental

2.1. Materials

Triethylamine (TEA, 99.5%), *m*-cresol (99%, bp = 203 °C, *d* = 1.034 g/ml), and benzoic acid (99.5+%), all from Aldrich (Milwaukee, WI), were used as received without further purification. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA, 99+%, Aldrich) and 4,4′-diaminostilbene-2,2′-disulfonic acid (DSDSA, 94+%, TCI America (Portland, OR)) were dried in a vacuum oven at 150 °C overnight before the reaction. Diamine terminated poly(ethylene oxide) (PEO-diamine, MW = 1000, 100%) was donated by Kawaken Fine Chemicals Co., Ltd. (Tokyo, Japan), and was dried in vacuum at 120 °C overnight prior to use.

2.2. Synthesis of new soft segment-containing six-member ring SPI copolymers

A typical procedure for preparation of new soft segment-containing six-member ring sulfonated polyimide copolymers is described below using the copolymer of NTDA/DSDSA-Et_3N (95 mol%)/PEO-diamine (5 mol%) as an example. In the preparation, 3.744 g (9.5 mmol, 94+%) of DSDSA, 2.307 g (22.8 mmol) of TEA, and 44 g of *m*-cresol were charged into a 250-ml, completely dried 4-neck flask equipped with a mechanical stirring device and a nitrogen inlet. The mixture was heated to 80 °C under stirring with a nitrogen flow until DSDSA-Et_3N was completely dissolved, and a transpar-