Novel Sulfonated Poly(arylene ether ketone) Containing Benzoxazole Membranes for Proton Exchange Membrane Fuel Cell

Jinhuan Li, Chang Hyun Lee, Ho Bum Park, and Young Moo Lee*

School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

Abstract: Novel sulfonated poly(aryl ether ketones) containing benzoxazole were directly synthesized by aromatic nucleophilic polycondensation using various ratios of 2,2'-bi[2-(4-flurophenyl)benzoxazol-6-yl]hexafluoropropane to sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate). The copolymers were soluble in polar aprotic solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and N,N-dimethylformamide at a relatively high solid composition (>15 wt%) and formed tough, flexible and transparent membranes. The membranes exhibited a degradation temperature of above 290 °C. The exact dissolution times of these membranes at 80 °C in Fenton's reagent (3 wt% H_2O_2 containing 2 ppm $FeSO_4$) were undetectable, confirming their excellent chemical stability in fuel cell application. The membranes showed a moderate increase in water uptake with respect to increasing temperature. The proton conductivities of the membranes were dependent on the composition and ranged from 1.10×10^{-2} to 5.50×10^{-2} Scm^{-1} at 80 °C and 95% relative humidity (RH). At 120 °C without externally humidified conditions, the conductivities increased above 10^{-2} Scm^{-1} with respect to increasing benzoxazole content, which suggested that the benzoxazole moieties contributed to the proton conduction.

Keywords: fuel cell, membrane, poly(aryl ether ketone), polybenzoxazole, sulfonation.

Introduction

The proton exchange membrane (PEM) is one of the key components of the proton exchange membrane fuel cell (PEMFC).[1,2] For this type of application, the polymer membranes must meet many requirements concerning various aspects including proton conductivity, fuel gas permeability, oxidative and hydrolytic stability, strong mechanical properties and economic feasibility.[3] Advances in PEMFC technology highlight operations at high temperature and low humidity or even under anhydrous conditions, all of which are more demanding of the polymer membranes. Although the Nafion®-type perfluorosulfonated polymer membranes may be successfully used in the hydrated state under moderate conditions (below 80 °C), a large methanol crossover, high cost and a considerable deterioration in the proton conductivity at low humidity or temperatures above 80 °C make them unfit for practical PEMFC applications.[4-6]

To date, some sulfonated hydrocarbon-derivatives have been developed as alternative PEM materials.[7-15] Sulfonated poly(aryl ether ketone)s (SPAEKs) have been singled out due to their excellent mechanical properties, thermal stability and high proton conductivity for highly sulfonated membranes.[16-19]

Generally, there is a compromise among the properties for most of the homogenous sulfonated membranes. As a typical example, for efficient proton conductivity, it is necessary to maintain high sulfonation. However, this usually induces the membranes to swell dramatically in hydrated states and become very brittle in the dry state, which causes a complete loss of the membrane's mechanical properties.[20,21] From the point of view of polymer structure design, the introduction of additional functionality to the sulfonated polymer backbone is a strategy which may possibly overcome this compromise of properties and could lead to membranes with good comprehensive properties. The incorporation of basic moieties such as nitriles[22] into sulfonated polymers *via* copolymerization has yielded interesting properties as a result of their interactions with the sulfonic acid groups. This functionality may present additional structural sites that contribute to proton conduction or a potential modification which results in improved proton conduction. It is possible to attain a balance amongst the proton conductivity, mechanical properties and other properties.

Among basic polymers examined for PEMFC applications, polybenzimidazole (PBI) has been intensively investigated and has demonstrated the most attractive properties.[3,18] In particular, PBI containing impregnated acids such as phosphoric acid, hydrochloric acid, and sulfonic acid, is believed

*Corresponding Author. E-mail: ymlee@hanyang.ac.kr

to conduct protons *via* the hopping mechanism which is independent of the water content, and benefits from both high temperature and low humidity operation.[23] Polybenzoxazole (PBO) is another heterocyclic basic polymer which has a structure similar to PBI, but has even better thermo-oxidative stability, tensile properties and hydrolytic stability.[24] However, there are few investigations that have reported on the use of PBO in PEM. This is partially ascribed to the fact that PBO generally can not be dissolved in organic solvents, which increases the difficulty of designing processable polymers.

The present work reports a series of novel membranes that were made of sulfonated poly(aryl ether ketone) containing benzoxazole. PBO was incorporated into the SPAEK backbone by copolymerization through ether linkages. This approach is an advanced one that has never been reported. The copolymers were quite soluble in most of the commonly used polar aprotic solvents and could afford robust membranes. The thermal and thermo-oxidative stability, water uptake, and proton conductivity of the membranes were evaluated for PEMFC applications.

Experimental

Materials. Sodium 5,5'-carbonylbis-(2-fluorobenzenesulfonate) (**1**) was obtained by the sulfonation of 4,4'-difffluorobenzophenone.[25] 4,4'-(Hexafluoroiso-propylidene)-diphenol (Aldrich Co.) (**3**) was purified by vacuum sublimation before use. 4-Fluorobenzoic acid, *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF), fuming sulfuric acid (30 wt% SO_3), polyphosphoric acid (PPA) and toluene were purchased from Aldrich Co. and used as received. Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (6F-BAHP) was purchased from TCI Co. and used as received.

Synthesis of 2,2'-Bi[2-(4-flurophenyl)benzoxazol-6-yl] hexafluoropropane (2). A three-necked 250 mL flask was charged with 50 g of PPA, 7.326 g of 6F-BAHP (0.02 mol) and 6.164 g of 4-fluorobenzoic acid (0.04 mol) under nitrogen flow with constant stirring. The mixture was heated at 60 °C for 2 h and 120 °C for 10 h. The mixture was subsequently heated to 190 °C for 4-6 h and held at this temperature for an additional 10 h. After cooling to room temperature, the slurry was poured into an excess of water. A white precipitate resulted was neutralized by repeated washings with deionized water. The white solid was then dried at 100 °C under vacuum, and crystallized from DMF to yield a white crystalline solid.

IR (KBr): 1605, 1565, 1049 (benzoxazole), 1309, 1285, 1258, 1235, 1137 (CF_3), 1500, 1481 (C=C).

^{1}H NMR (CDCl$_3$): δ = 8.30-8.20 (m, 4H), 7.92 (s, 2H), 7.60-7.50 (d, 2H), 7.45-7.35 (d, 2H), 7.25-7.20 (m, 4H).

Polymer Synthesis. In a three-necked flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet, monomers **1** and **2** (at a combined total of 3 mmol), monomer **3**

(at 3 mmol) and potassium carbonate (at 3.6 mmol) were dissolved in a mixture of 10 mL DMAc and 10 mL toluene. The mixture was heated at 135-140 °C for 6 h under nitrogen to maintain toluene refluxing until the water was completely removed from the reaction mixture. The temperature was gradually increased to 160 °C to distill off the excess toluene, and this temperature was maintained for an additional 24 h. The polymer was coagulated in ethanol, washed with water to remove any inorganic salts and dried in a vacuum oven at 80 °C for 24 h.

IR (KBr): 1659 (C=O), 1085, 1028 (SO_3Na), 1562, 1049 (benzoxazole), 1599, 1495 (C=C).

^{1}H NMR (DMF-d_7): δ=8.60-8.52, 8.45-8.30, 8.00-7.75, 7.70-7.20, 7.15-7.00.

Membrane Fabrication. Membranes (**4a-4e**) in the sodium form were prepared by casting NMP solutions (15 wt%) onto glass plates and drying them at 60 and 100 °C under vacuum for 24 h. The acid form of the membranes was obtained by immersing the sodium salt membranes in 2.0 M HCl for 24 h, followed by subsequent washing with deionized water for 2 h to remove un-bonded free acid.

Measurements. The inherent viscosity ($[\eta]$) was measured with an Ubbelohde viscometer. ^{1}H NMR spectra were recorded on a 300 MHz Unityinova spectrometer (VARIAN, USA). IR spectra were obtained using a MAGNa-IR 760 spectrometer (Microfluidics, USA). Thermal gravimetric analyses (TGA) were measured under an air flow (heating rate: 10 °C · min^{-1}) by using a TGA 2050 thermogravimetric analyzer (TA Instruments, DE, U.S.A). The impedance of the membranes was determined by a four-point probe A.C. impedance spectroscopy technique.[26] The electrode system was connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, GU14, ONR, UK). The ion exchange capacity (IEC) of each membrane, i.e. the milliequivalents of sulfonic acid per gram of protonated membrane, was determined using a conventional titration method. Small pieces of the protonated membranes were put in 200 mL of 2 M NaCl for 48 h to exchange the sodium ions with the protons. The resulting solution was then titrated with 0.01 M NaOH, using phenolphthalein as a pH indicator. The protonated membranes were weighed after being fully dried to obtain the dry weight, W_{dry}, and then immersed in water for equilibration at 30 and 80 °C for 12 h, respectively. Any liquid water on the surface of the wetted membranes was removed with tissue paper prior to weighing to obtain the wet weight, W_{wet}. The values for the water uptake (W_{water}) were calculated as:

$$W_{water} = [(W_{wet} - W_{dry})/W_{dry}] \times 100\% \tag{1}$$

Results and Discussion

Preparation of the Monomer and the Polymer. Pristine

PBOs are known to only be soluble in some strong acids such as polyphosphoric acid and can not be processed from common organic solvents. Monomer modification by introducing flexible linkages or bulky groups to the polymer backbone is one strategy that can improve the solubility and processability of the PBOs.[27,28] Hexafluoroisopropylidene groups provided the benzoxazole containing monomer **2** with a very good solubility in most commonly used organic solvents, even acetone, which was indicative of the solubility of the final copolymers. The resulting partially fluorinated-polymer backbone is also believed to promote adhesion and the electrochemical compatibility with electrodes that contain perfluorinated polymer-based binder materials.[29]

As shown in Scheme I, the copolymers (**4**) with various sulfonation degrees (SDs) were synthesized via the nucleophilic polycondensation of a phenoxide (**3**) and different ratios of aryl fluorides (**1** and **2**) in DMAc. K_2CO_3 was used as a catalyst and toluene was used as an azeotropic solvent to remove any water molecules during the reaction. The hexafluoroisopropylidene moiety and the electron-poor benzoxazole ring activated the fluorine atoms in monomer **2** for the substitution due to their strong electron-withdrawing nature. Therefore, the copolymerization proceeded well and

Table I. Polymerization Results of 4a-4e

Polymer	Monomer **1** [mol%]	$[\eta]^a$ [dLg^{-1}]	Yield [wt%]
4a	20	1.36	97
4b	30	1.48	98
4c	40	0.80	97
4d	50	1.21	96
4e	60	0.93	96

^{a}Measured with 0.5 gdL^{-1} of the polymer nMP solution at 25 °C.

the polymer solution became highly viscous during the 24 h of reaction at 160 °C. The polymerization outcomes are depicted in Table I. In all cases, the yields were above 90 wt%, and the inherent viscosities were greater than 0.8 dLg^{-1}. Figure 1 shows the ^{1}H NMR spectra of monomer **2** and the copolymer **4d**. The absorption bands were clearly assigned and confirmed their respective structures.

All of the polymers were quite soluble in NMP, DMAc, and DMF at a high solid composition (>15 wt%). The membranes fabricated from 15 wt% NMP solutions were tough, flexible, and transparent.
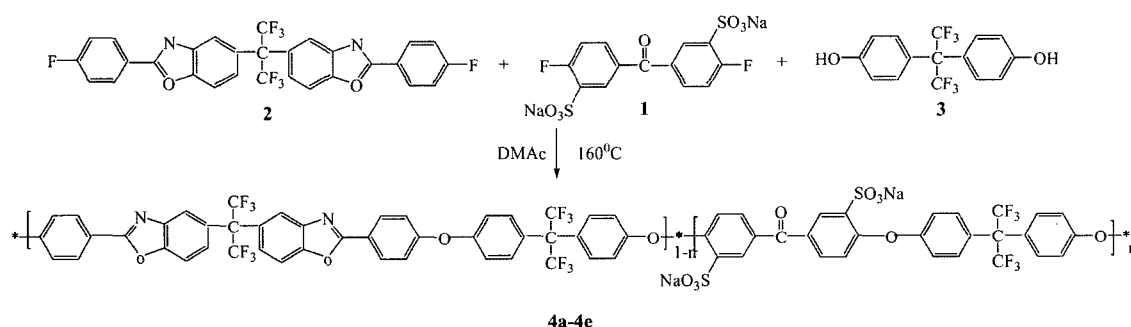
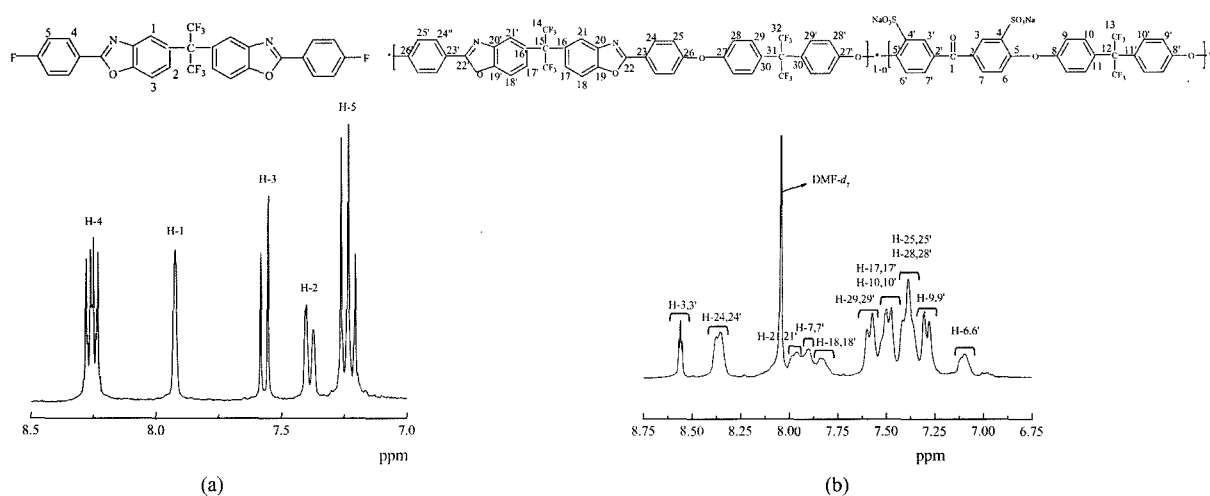**Scheme I.** Synthesis of the copolymers.

Figure 1. ^{1}H NMR spectra of the monomer **2** in CDCl$_3$ (a) and the copolymer **4d** in DMF-d_7 (b).

Membrane Properties. TGA was used to characterize the thermal behaviors of the protonated membranes in air. The thermal degradation occurred in two characteristic steps and the first weight loss was related to the decomposition of the sulfonic acid groups. As shown in Table II, all of the membrane samples began to degrade at about or just above 290 °C. This temperature was higher than that (about 250 °C) of most of the sulfonated polymers investigated in previous literature.[5] Typically, protonated hexafluoroisopropylidene containing sulfonated poly(aryl ether ketone)s (6F-SPAEKs) with the same SD degrade at 250-260 °C.[30] This implies that the ether benzoxazole rather than the ether ketone as the hydrophobic segment contributes more to the thermal stability of the membranes owing to a possible interaction between the basic benzoxazole moieties and the sulfonic acid groups.

The IEC values of the membranes determined by titration were in good agreement with the calculated values and also within the experimental error (Table II), indicating that all of the sulfonate groups were incorporated into the polymers. The water uptake trends at both 30 and 80 °C were comparable to the membranes' IEC (see Table II), and were enhanced with an increase of the IEC. For the membranes with a similar IEC range (0.70-1.60 meqg^{-1}), the water uptake of the copolymers at 80 °C was comparable with that of 6F-SPAEKs (10-68 wt%). However, in consideration of the water uptake values at 30 °C, the benzoxazole containing copolymer membranes showed a smaller increase in the water uptake with respect to the temperature than did the 6F-SPAEK membranes (about 4-12 wt%).[30]

The free radical stability of the copolymer membranes to oxidation was evaluated by immersing the films into Fenton's reagent (3 wt% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The exact dissolution time was undetectable, which indicated their excellent durability. All of the membranes retained their mechanical strength even after 2 h of above treatment, and membranes **4a** and **4b** maintained their strong and flexible state even after weight loss occurred. These results indicated that the membranes possessed a higher oxidative stability than many other hydrocarbon membranes, e.g. PBI[17] and 6F-SPAEKs.[20]

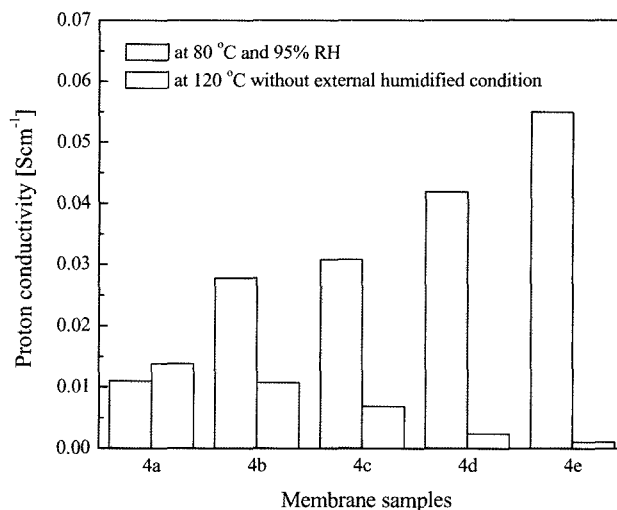The proton conductivities of the membranes under two

Figure 2. Proton conductivity of the membranes **4a-4e** under two conditions of temperature and relative humidity.

different conditions were measured to evaluate their proton conducting performances for the PEMs and was shown in Figure 2. As more sulfonic acid sites were incorporated, the proton conductivity of the membranes at 80 °C and 95% RH increased (1.10 × 10^{-2} - 5.50 × 10^{-2} Scm^{-1}), which was consistent with other sulfonated membrane systems where a high degree of sulfonation guarantees superior proton conductivity. It is worth noting that at both 120 °C and without any external humidifying conditions, the membranes showed relatively high conductivities which increased with respect to an increase of the basic benzoxazole segments. The proton conductivity of membrane **4a** reached 1.38 × 10^{-2} Scm^{-1}. This implied that the HCl-treated benzoxazole contributed the proton conductivities in high temperature and low humidity conditions, which was similar to the acid doped PBI systems. The introduction of the basic benzoxazole in the sulfonated SPAEKs allows for other potential improvements in the proton conductivity in the membranes at elevated temperatures, such as via additional doping with inorganic acids and the incorporation of heteropolyacids (HPAs).

Table II. Membrane Properties

Membrane	IEC [meqg^{-1}]		W_{water} [wt%]		$T_d{}^a$ [°C]
	Measured	Calculated	30 °C	80 °C	
4a	0.43	0.48	4.8	7.5	335
4b	0.68	0.74	7.8	12.3	321
4c	0.98	1.01	14.2	20.5	308
4d	1.26	1.29	25.4	39.4	305
4e	1.40	1.59	30.2	72.4	290

^{a}Initial degradation temperature.

Conclusions

Novel SPAEK containing benzoxazole copolymer membranes were successfully prepared to evaluate the availability as PEMs for fuel cell. All of the copolymers showed excellent thermal and chemical resistance, as well as low water swellability with respect to higher temperatures. The copolymer membranes showed high proton conductivities over a wide range of temperature and humidity conditions. Thus, the copolymer membranes are promising for PEMFC applications. More detailed studies on the proton conduction mechanism and membrane doping or the incorporation process using inorganic strong acids or HPAs are still underway for their practical applications to PEMFC.

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