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# Properties and morphology study of proton exchange membranes fabricated from the pendant sulfonated poly(arylene ether ketone) copolymers composed of hydrophobic and hydrophilic multi-blocks for fuel cell

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## ABSTRACT

Polymer electrolyte membranes are prepared from poly(arylene ether ketone) composed of hydrophobic and hydrophilic multi-blocks. 4,4'-bis(4-hydroxyphenyl)-valeric acid and 4,4'-difluorobenzophenone are used for the synthesis of hydrophilic oligomers, while bisphenol A and 4,4'-difluorobenzophenone are used for hydrophobic oligomers. The proton conducting property is provided by sulfonation of the pendant carboxylic groups in hydrophilic blocks. The chemical structure of the oligomers and polymer synthesized is identified using  $^1\text{H}$ - and  $^{19}\text{F}$ - nuclear magnetic resonance (NMR) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopies as well as gel permeation chromatography (GPC). The development of distinguished hydrophobic-hydrophilic phase separation is confirmed by small-angle X-ray scattering (SAXS) spectroscopy and atomic force microscope (AFM). The thermal, mechanical, and chemical stabilities are endowed by the hydrophobic segment, whereas the proton conducting and water uptake properties are provided by the hydrophilic segment. The proton conductivity of the prepared membrane is comparable to that of Nafion 115 when the hydrophobic and hydrophilic block molecular weights are  $3000 \text{ g mol}^{-1}$  and  $18,000 \text{ g mol}^{-1}$ , respectively. The block length effect on the membrane properties can be explained by the ion cluster dimension and structure examined by SAXS and AFM.

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## Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs) have drawn much attention as a potential energy

source for application in a variety of fields, such as the aerospace, military, and automobile industries [1,2]. The proton exchange membrane is a core part of PEMFCs, along with the electrode catalyst. Perfluoro-sulfonated polymer membranes such as Nafion® are widely used in industry because they have

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excellent proton conducting and chemically stable properties [3,4]. These membranes, however, have some weaknesses associated with high production cost and the reduction of proton conductivity at low humidity and high temperature, which hinder the commercialization of fuel cells.

Hydrocarbon (HC)-based polymer electrolytes are alternatives to perfluorocarbon-based ones that could resolve these problems. Poly(arylene ether sulfone), poly(arylene ether ketone), and polyimides are typical HC-based polymers that have been studied during the past decade for this purpose [5–11]. The commonly encountered problems in HC-based polymers, however, include low proton conductivity compared to perfluorocarbon-based ones at the same ion exchange capacity. When the sulfonation degree (ion exchange capacity) is increased to enhance the proton conductivity, other properties such as the mechanical, thermal, and dimensional stability are negatively affected in association with high water uptake, sometimes followed by swelling and cracking [12,13].

The proton conductivity was reported to be closely related to the dimension and structure of such water transferable ion clusters and channels [14,15]. It was reported that Nafion membranes form about 4-nm-diameter ion clusters, while HC-based polymer electrolyte membranes generally form rather smaller cluster dimensions in random copolymer structure [16–18]. In order to develop more defined ion clusters and channels, multi-block structures are more advantageous than random structures in hydrophobic-hydrophilic copolymer systems, because such multi-block structures could possibly generate much larger and distinct phase separations between hydrophobic and hydrophilic domains. According to the previous reports, multi-block-type copolymers composed of sulfonated and non-sulfonated rigid rod backbone structured oligomers showed enhanced proton conductivity and mechanical strength compared random-type ones [19–22].

In our laboratory, a series of electrolyte membranes based on poly(arylene ether ketone) polymers have been prepared and characterized for the past 10 years. As the polymers were prepared with different chemical structures such as cross-linked, pendant-sulfonated, backbone-sulfonated, and interpenetrating polymer network (IPN) structures, these polymers were basically all random copolymers composed of sulfonated and non-sulfonated monomers [10,11,23–26]. Based on this, we focused our attention on the synthesis of poly(arylene ether ketone)s composed of hydrophobic and hydrophilic multi-blocks. The hydrophilic blocks were attained by sulfonation of the pendant groups to provide strong acidity and dissociation strength. The morphology and various membrane properties were investigated according to the ratio of hydrophobic to hydrophilic block lengths.

## Experimental

### Materials

4,4'-bis (4-hydroxyphenyl)-valeric acid, 4,4'-difluorobenzophenone, bisphenol A, potassium carbonate, toluene, N,N'-dimethylacetamide (DMAc), and dimethyl sulfoxide

(DMSO) were purchased from Aldrich (Milwaukee, WI) and used for the synthesis of hydrophobic and hydrophilic oligomers. Isopropanol (IPA, Aldrich) and methanol (Aldrich) were used to remove unreacted monomers and impurities by washing. Decafluorobiphenyl (DFBP, TCI, Tokyo chemical, Japan) was used for end-capping of the hydrophobic oligomer, while dimethylformamide (DMF, TCI), and 3-amino-1,5-naphthalenedisulfonic acid disodium salt (TCI) were used for sulfonation of the hydrophilic oligomers. N,N'-dicyclohexylcarbodiimide (DCC, Aldrich), N-hydroxysuccinimide (NHS, Aldrich), and tetrahydrofuran (THF, Aldrich) were used for the synthesis of NHS end-capped poly(arylene ether ketone) (NHS-PAEK). Hydrochloric acid (HCl, Aldrich) and cyclohexane (Aldrich) were used as acidification and water-eliminating agents, respectively. Pt/C 40% (Alfa Aesar, Ward Hill), Nafion solution (5 wt%, DuPont), Gas diffusion layer (Sigracet GDL 35BC) were used to prepare MEA for PEMFC performance test.

### Synthesis of hydrophobic poly (arylene ether ketone) oligomer

Hydrophobic poly(arylene ether ketone) (PAEK) with a number average MW of 3000 g mol<sup>-1</sup> was synthesized as follows. Bisphenol A (0.01 mol), K<sub>2</sub>CO<sub>3</sub> (0.02 mol), DMSO (100 mL), and toluene (50 mL) were placed in a 250-mL three-necked round-bottom flask equipped with a Dean–Stark trap and mechanical stirrer under nitrogen gas. After about 2 h of agitation at room temperature, the reaction temperature was raised to 145 °C, followed by further reaction for 4 h under reflux distillation to remove water. After 4,4'-difluorobenzophenone (0.01 mol) was dissolved in 20 mL of DMSO, the mixture was added to the reaction flask, and then the reaction was conducted for another 5 h at 165 °C. After completion of the reaction, the temperature was reduced to room temperature, and the solution was slowly dropped into 1000 mL of IPA to obtain oligomer precipitates. After filtration, the precipitates were dried in a vacuum oven at 80 °C for 24 h. After several washing processes with 2000 mL of de-ionized (DI) water at 60 °C, the product was dried again in a vacuum oven at 80 °C for 48 h. Fig. 1(a) shows a scheme of the chemical synthesis of the OK end-capped hydrophobic PAEK oligomer (PAEK-OK).

The end groups of the hydrophobic PAEK oligomers synthesized were capped with DFBP. DFBP (0.012 mol), PAEK-OK oligomer (0.01 mol), DMAc solvent (50 mL), and cyclohexane azeotropic reagent (15 mL) were placed in a 100-mL three-necked round-bottom flask equipped with a Dean–Stark trap. After the reaction temperature was raised to 100 °C, the coupling reaction was conducted for 16 h with the reflux of water. After the reactant was cooled down to room temperature, the product was precipitated in 1000 mL of IPA. After the product was filtrated with a glass filter, it was washed and dried by the same method and procedure mentioned above. The reaction scheme for the synthesis of DFBP end-capped hydrophobic PAEK oligomer (PAEK-DFBP) is shown in Fig. 1(b).

### Synthesis of hydrophilic pendant sulfonated PAEK oligomer

Hydrophilic sulfonated poly(arylene ether ketone) (SPAEK) oligomers with different number average MWs of 5,000, 8,000, 12,000, and 18,000 g mol<sup>-1</sup> were synthesized. For an example,

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