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Comparison of proton conducting polymer electrolyte membranes prepared from multi-block and random copolymers based on poly(arylene ether ketone)

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HIGHLIGHTS

- Multi-block and random copolymers based on poly(arylene ether ketone) with the similar IEC values are synthesized.
- While water uptake is similar, proton conductivity of multi-block copolymer membranes is higher than that of random ones.
- Multi-block copolymer membranes illustrate superior oxidation stability to random copolymer membranes.
- Ion cluster dimension of multi-block copolymer membrane is larger than that of random one from the SAXS analysis.

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ABSTRACT

Multi-block and random copolymers based on poly(arylene ether ketone) with the similar IEC values are synthesized. The chemical structure of the hydrophobic and hydrophilic oligomers and the copolymers synthesized from them is identified using ^{1}H - and ^{19}F- nuclear magnetic resonance (NMR) spectroscopy, attenuated total reflection fourier transform infrared (ATR-FTIR) spectroscopy, and gel permeation chromatography (GPC). The development of distinguished hydrophobic-hydrophilic phase separation is confirmed by small-angle X-ray scattering (SAXS) spectroscopy. The proton conductivity and water uptake along with the thermal, mechanical, oxidative stabilities are measured to investigate the effect of the copolymer structure on the membrane properties. While water uptake is similar with respect to each other, the proton conductivity of the multi-block copolymer membrane is higher than that of random one at the same levels of IEC. It results from much more distinct hydrophobic-hydrophilic phase separation formed in the multi-block copolymer membrane than the random one. The ion cluster dimension of the multi-block copolymer membranes is larger than that of the random copolymer membranes from the SAXS analysis. Also, the ion cluster dimension distribution of the block copolymer membranes is much narrower than that of random ones. The multi-block copolymer membranes illustrate superior oxidation stability to the random copolymer membrane due to the same phase separation difference.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are environmentally compatible power sources because they use hydrogen and methanol as fuel (reactant) and produce water through an electrochemical reaction. PEMFC and DMFC are characterized by an excellent energy density, a low operation temperature, and fast start and response times. It can thus be applied in a variety of fields such as for automobiles, mobile phones, laptop computers, houses, and public construction not only in a mobile but also as a stationary energy source [1–3].

A proton exchange membrane (PEM) is one of the core components in a fuel cell system. It aids in proton transfer, but not fuel, from the anode to the cathode side. In order to obtain high efficiency in a fuel cell, it is a prerequisite to use a polymer electrotype membrane with high proton conductivity; acceptable mechanical, thermal, and chemical stability; and high dimensional stability [4]. Nafion, developed by Du Pont, is a well known commercial electrolyte membrane that can be used for such an application [5], Nafion is a perflurocarbon-based membrane that is composed of a

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hydrophobic backbone and hydrophilic pendant groups. When it is in contact with water, the hydrophilic segments are aggregated together to form ionic clusters that provide a water channel where protons are transferred. The mechanical and chemical stability and the high proton conductivity are useful properties of a Nafion membrane, but the high cost and the reduced conductivity at a low humidity limits its utilization for a diversity of applications [6]. Also, the high methanol permeability of the Nafion membrane results in a loss of fuel and significant decrease of energy density in DMFC application.

A number of phase separable hydrocarbon-based polymers have been studied for their suitability to replace Nafion membranes due to the weaknesses mentioned above. Sulfonated poly(arylene ether ketone) [7–10], sulfonated poly (ether sulfone) [11,12], and sulfonated polyimide [13,14] are hydrocarbon based membranes that have been studied the most. Poly(arylene ether ketone) (PAEK) is a thermoplastic material that can be used for fuel cell membranes since it has very good thermo-mechanical and chemical stability with a low purchase cost. SPAEK is usually obtained via post-sulfonation of commercially purchasable material, ie, poly(ether ether ketone) (PEEK). Chemical degradation or crosslinking is sometimes caused by this postsulfonation [15], so a sulfonated monomer is sometimes used in the synthesis of sulfonated PAEK. The material and membrane properties are controllable mostly via the degree of sulfonation and the degree of polymerization [16].

During the past decade, our research group has tried to synthesize SPAEK membranes using sulfonated monomers and has analyzed their properties as compared to Nafion membranes [17–21]. The sulfonated hydrophilic segments and nonsulfonated hydrophobic segments were randomly distributed in a polymer molecule to form a random copolymer structure, and the prepared random copolymer membranes presented relatively low proton conductivities to that of Nafion since the phase separation was not clearly established due to the random distribution of hydrophilic segments. The ionic cluster dimension was smaller than that of Nafion, and thus a narrow water channel was formed, resulting in lower proton conductivity than for Nafion.

In this study, we synthesized SPAEK in a block copolymer structure composed of sulfonated and non-sulfonated PAEK oligomers for the first time in order to fix the weakness associated with a random copolymer structure. Since the block copolymers possibly provide a well-defined phase separation between hydrophobic and hydrophilic segments and thus large hydrophilic ionic clusters are formed in the hydrophobic polymer matrix, the enhanced proton conductivity is expected [22,23]. Membranes were prepared from the synthesized SPAEK block copolymers, and several important membrane properties including water uptake, ion conductivity, and thermal and mechanical, and chemical stability were investigated relative to those of SPAEK random copolymers. For this purpose, not only block but also random SPAEK copolymer was synthesized for their comparison.

2. Experimental

2.1. Materials

Bisphenol A, potassium carbonate (K_2CO_3), methylsulfonic acid 99.5% (MSA), decafluorobiphenyl (DFBP), sodium hydroxide (ACS reagent, 97.0%), and cyclohexane were purchased form the Aldrich Chemical Company (Aldrich, Milwaukee, WI, USA). 4,4′-difluorobenzophenone, dimethyl sulfoxide (DMSO), and N,N-dimethyl acetamide (DMAc), tetrahydrofuran (THF) were purchased from Tokyo Chemical Industry (TCI, Japan). Toluene, isopropanol, methyl alcohol (99.5%), and sulfuric acid (95.0%) were obtained from the Samchun Chemical Company (Korea). Hydrochloric acid, iron (II) sulfate, heptahydrate ($FeSO_4 \cdot 7H_2O$), and sodium chloride were supplied from Duksan Chemical Company (Korea) and Daejung Chemicals & Metals Company (Korea). Hydrogen peroxide was purchased from Yakuri Chemical Company (Japan).

2.2. Synthesis of hydrophobic arylene ether ketone oligomer (o-AEK) and hydrophilic sulfonated arylene ether ketone oligomer (o-SAEK)

Bisphenol A (0.01 mol), K_2CO_3 (0.02 mol), DMSO (60 mL), and toluene (60 mL) were placed in a 250-mL 4-neck round bottom flask, and then the mixture was stirred for 2 h at room temperature, followed by for 4 h at 145 °C under a nitrogen gas atmosphere. 4,4′-difluorobenzophenone (0.01 mol) was dissolved in 60 mL of DMSO under stirring for 4 h. The 4,4′-difluorobenzophenone solution was added to the prepared mixture to produce o-AEK at 165 °C, and the water byproduct was removed via azeotropic reflux distillation with toluene. The product was obtained as precipitates in 1000 mL IPA at room temperature and was then filtered. After the product was washed with 2000 mL distilled water for several times, it was dried in a 80 °C vacuum oven for 24 h. The synthetic scheme of the hydrophobic o-AEK is shown in Fig. 1a.

The hydrophilic o-SAEK was synthesized following the same method and procedure as the hydrophobic o-AEK using sulfonated 4,4′-difluorobenzophenone (0.01 mol) instead of 4,4′-difluorobenzophenone. 4,4′-difluorobenzophenon was first sulfonated [24] as shown in Fig. 1b. 21.8 g (0.1 mol) of 4,4′-difluorobenzophenone were dissolved in 50 mL of methylsulfonic acid (99.5%, MSA) and stirred for 12 h at room temperature under nitrogen gas in a flask equipped with a Dean-stark trap. Sulfuric acid, (95.0%, H_2SO_4) was added to the resulting solution, and then the temperature was raised to 120 °C, followed by stirring for another 24 h. After the solution was cooled down to 0 °C, it was dropped into 150 mL distilled water to obtain a precipitate. The sulfonated ketone product was a neutralized sodium hydroxide aqueous solution, and the precipitates were filtered off with a glass filter and were then dried in a 80 °C vacuum oven for 24 h. The filtered precipitates were purified by recrystallization. The precipitates were dropped into a methanol/water mixture and were then stirred for 12 h. The product was obtained via filtration and was dried in an oven at 80 °C for at least 24 h. The separation and drying processes were also the same as those used for the o-AEK mentioned above. Fig. 1b illustrates the synthetic scheme for the hydrophilic o-SPAEK.

2.3. Synthesis of PAEK block copolymers (b-CPAEK)

The synthesized hydrophobic o-AEK was end-capped with DFBP. o-AEK (0.01 mol) and K_2CO_3 (0.02 mol) were mixed with DMSO (60 mL) and cyclohexane (30 mL) in a 250 mL 4 neck flask equipped with Dean-stark trap with a nitrogen inlet and mechanical stirrer. After stirring for 4 h at 100 °C, DFBP (0.012 mol) was added and then the coupling reaction proceeded for 12 h at 105 °C while water and cyclohexane were removed via reflux distillation. The DFBP end capped o-AEK (o-AEK-DFBP) was precipitated by placing the reaction product in 1000 mL IPA. The final product was obtained after the same separation and drying processes mentioned above. The synthesis of the o-AEK-DFBP is illustrated in Fig. 2a.

The hydrophilic o-SAEK (0.001 mol) and DMSO (60 mL), K_2CO_3 (0.02 mol), and cyclohexane (30 mL) were placed in a 250-mL four-necked round bottom flask. After stirring for 2 h at room temperature, further reaction was conducted at 100 °C for 4 h the o-AEK-DFBP (0.001 mol) was dissolved in 60 mL DMSO by stirring at room temperature for 4 h, hydrophobic and hydrophilic oligomer