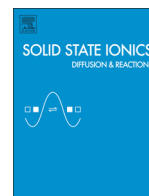




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Synthesis of high molecular weight sulfonated poly(arylene ether sulfone) copolymer without azeotropic reaction

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ABSTRACT

Currently, most sulfonated poly(arylene ether sulfone) (s-PAES) polymers are synthesized using a solvent mixture consisting of toluene and dimethylacetamide (DMAc) by two successive reactions, namely azeotropic water removal, followed by nucleophilic substitution. In this study, a novel method for the synthesis of s-PAES polymers has been developed, where alcohols such as methanol, ethanol, or 2-propanol are used along with DMAc as the co-solvent in the place of toluene that is used in the conventional synthesis of s-PAES. Moreover, the synthesis method used in this study involves only one step, namely the polymerization at 160 °C and does not require the azeotropic water distillation step at 140 °C. The new synthesis method was found to yield s-PAES polymers with a higher molecular weight in a shorter reaction time compared to the conventional polymerization method. Further, membrane electrode assemblies (MEA) were fabricated using the synthesized s-PAES polymer membranes, in order to evaluate the performance of the membranes in polymer electrolyte membrane fuel cells (PEMFCs). The results indicate that the s-PAES membranes synthesized using the method proposed in this study have a great potential for use as PEMFC membranes.

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1. Introduction

The desired properties for the electrolyte membranes used in polymer electrolyte membrane fuel cells (PEMFCs) include high proton conductivity, good mechanical strength, low fuel permeability, high dimensional stability, high chemical inertness, and low cost [1,2]. Nafion-type perfluorosulfonated polymers have been traditionally used in the fabrication of the electrolyte membranes for PEMFCs. Although Nafion has high proton conductivity, high chemical inertness, and excellent mechanical properties, it suffers from high fuel permeability and low proton conductivity under high temperature and low humidity conditions. In addition, it is also expensive [3].

Owing to the disadvantages associated with Nafion, non-fluorinated and partially fluorinated cation exchange membranes such as sulfonated poly(phenylene oxide), poly(phenylene sulfide), poly(para-phenylene), polystyrene, poly(ether ether ketone), polyimide, and poly(arylene ether sulfone) based polymers have been investigated as alternatives [4,5]. In particular, several studies have been conducted on the sulfonated poly(arylene ether sulfone) (s-PAES) based polymers, which were developed by James E. McGrath and coworkers in 2002 [6], as a potential replacement for fluorocarbon-based polymers. These polymers have advantages in terms of cost and structural diversity, which results in high ionic

conductivity, high chemical stability, and excellent mechanical properties [7–10].

In general, s-PAESs are prepared by direct condensation polymerization via a nucleophilic aromatic substitution reaction with sulfonated monomers, in the presence of a catalyst such as K_2CO_3 . These direct condensation polymerization methods require a dehydration process to form ether linkages between the monomers. To carry out the dehydration process, a combination of polar organic solvents with high boiling points (such as dimethylacetamide (DMAc), N-methyl-2-pyrrolidone (NMP), or dimethyl sulfoxide (DMSO)) and low boiling point solvents that can be distilled azeotropically with water (such as benzene, toluene, or cyclohexane) are used [11–13]. The conventional polymerization procedure involves two steps, namely the azeotropic removal of water at 120–140 °C using the low boiling point solvents to synthesize an active intermediate, followed by polymerization with the active intermediate and another monomer at 160–190 °C in the presence of high boiling point organic solvents. However, the use of such mixed solvent systems decreases the solubility of the monomer and the intermediate used in the polymerization, leading to difficulties in homogeneous polymerization and the reproducibility of the polymer synthesis. Moreover, the synthesis is complicated since the polymerization process proceeds in two stages [11].

In order to solve the above-mentioned problems, a method that uses only DMAc as the solvent instead of using a mixture of solvents was developed [14,15]. Moreover, this method does not require a special step for removing water at 120–140 °C, and the polymers can be

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synthesized at a single polymerization temperature (130–160 °C). However, according to the researchers who developed this method, an excess amount of catalyst, an expensive monomer, and a lengthy reaction time are required to obtain high molecular weight polymers. Therefore, this method needs to be refined further.

In this study, *s*-PAES polymers were synthesized by a novel single step polymerization method. Instead of using a mixture of toluene and DMAc as the solvent for the polymerization reaction, an alcohol such as methanol, ethanol, or 2-propanol was mixed with DMAc, and the polymerization temperature was immediately raised to 160 °C for the synthesis of high molecular weight *s*-PAES, without performing the first step of removing water azeotropically at 120–140 °C for 3–6 h. In addition, membrane electrode assemblies (MEA) were fabricated using the polymers synthesized by this method and the performance of the MEA was evaluated to ensure that the polymer was suitable for applications in PEMFC membranes.

2. Experimental section

2.1. Materials

The monomers, 4,4'-dichlorodiphenylsulfone (DCDPS) and 4,4'-dihydroxybiphenyl (BP), used in the synthesis of the poly(arylene ether sulfone) random copolymer were purchased from Sigma Aldrich Co. and were used after recrystallization from ethanol and vacuum drying for 24 h at 120 °C. The monomer, 3,3'-disulfonated DCDPS (SDCDPS) was synthesized by the method used in the previous study [16]. DMAc (Aldrich Chemical Co., Madison, WI, USA) was used as the solvent for the synthesis and the casting of the polymers. K₂CO₃ was purchased from Aldrich Chemical Co., whereas methanol, ethanol, and 2-propanol were purchased from J.T. Baker.

2.2. Synthesis of sulfonated poly(arylene ether sulfone)s

To a 250 mL four-neck flask equipped with a mechanical stirrer, thermometer, Dean–Stark trap, and a condenser in an Ar atmosphere, SDCDPS (1.97 g, 4 mmol), DCDPS (1.72 g, 6 mmol), and BP (1.88 g, 10 mmol) were added. The quantities of the monomers were chosen so as to maintain the degree of sulfonation of the resulting polymer at 40%. A mixture consisting of 22 mL of DMAc and 11 mL of ethanol was used as the solvent and approximately 1.67 g of K₂CO₃ (the molar ratio of K₂CO₃ and BP was 1.2) was used as the catalyst. The reaction was performed at 160 °C. When the temperature was increased to 160 °C, water, which is a byproduct of the polymerization reaction, accumulated on the Dean–Stark trap along with ethanol. In order to monitor the change in the molecular weight of the polymers with time, the reactions were carried out for different durations namely, 5 h, 10 h, 15 h, and 20 h.

Further, polymers were synthesized by replacing ethanol with methanol and 2-propanol, using the same procedure described above. In addition, the effect of the presence of water on the polymer condensation reaction was studied by adding water (the volume ratio of water and DMAc was 0.5) instead of alcohols. For this purpose, the polymers were prepared by pouring a highly viscous copolymer solution into a mixture of 2-propanol and water (7:3, v/v) and the resulting polymers were filtered and dried in vacuum at 120 °C for 24 h. Furthermore, conventional polymerization using DMAc and toluene was also conducted according to the method published in the literature, for comparison [6].

2.3. Preparation of sulfonated poly(arylene ether sulfone) membranes

Each polymer sample (2 g) was dissolved in DMAc (18 g, 10 wt.%) and cast on a glass plate. The cast polymer membranes were dried in an oven, followed by drying at 80 °C for 4 h, and finally at 120 °C in vacuum for 24 h. The thickness of the prepared membrane in each

case was 50 μm. Each membrane was immersed in 1 M H₂SO₄ solution at 60 °C for 2 h, followed by 2 h of washing in distilled water, thereby converting the membrane into the free sulfonic acid form.

2.4. Characterization

The ¹H NMR spectra of the polymers were measured using a Varian 300 MHz Bruker AV300 spectrometer. DMSO-*d*₆ was used as the solvent to characterize the polymers. The molecular weight of the polymers was measured using a gel permeation chromatography (GPC) instrument (Waters 2414 refractive index detector equipped with Styragel HR 3 and 4 columns), and a mixture of 0.05 M LiBr in NMP was used as the solvent. Standard poly(methyl methacrylate) (PMMA) was used for molecular weight calibration. The elongation and the tensile strength of the membranes were measured using a universal test machine (Cometech, QC-508E, Japan) at a temperature of 30 °C and a relative humidity (RH) of 45%, following the ASTM D882 method.

2.5. Membrane electrode assembly (MEA) and cell performance evaluation

The MEA was prepared by spraying the catalyst slurry on the membranes. The catalyst slurry was prepared by dispersing a 45 wt.% Pt/C (BASF Fuel Cells, Somerset, NJ, USA) and a 5 wt.% Nafion dispersion solution (DE 521, DuPont, Wilmington, DE, USA) in a mixture of 2-propanol and water. The total amounts of Pt catalyst on the anode and the cathode were 0.4 mg cm⁻² and the Nafion content of the electrodes was 20 wt.%. The prepared MEA was dried at 60 °C in an oven for 1 h. The unit cell experiments were conducted using H₂ and air supplied in a stoichiometric ratio of 1.5:2.0, at 65 °C and an RH of 90%.

3. Results and discussion

The molecular weights of the *s*-PAES polymers as a function of various polymerization conditions such as the type of solvents, the presence of a water removal process, the presence or absence of a Dean–Stark trap, and reaction time are listed in Table 1. The various *s*-PAES samples are named in the general form of BPS-*x*-*yy*, where *x* refers to the co-solvent used along with DMAc (m, e, i, t, and w correspond to methanol, ethanol, 2-propanol, toluene, and water, respectively, whereas o indicates that DMAc was used as the only solvent) and *yy* refers to the total reaction time. For example, BPS-t-25 represents the polymer prepared by the conventional method, where toluene was used as the azeotropic solvent (the volume ratio of water and DMAc was 0.5) and the reactants were refluxed for 5 h at 140 °C and polymerized for 20 h at 160 °C. In the case of BPS-*x*-20, the polymerization was carried out for 20 h at 160 °C, without a preceding reflux procedure. Furthermore, if the *s*-PAES sample was prepared in the absence of the Dean–Stark trap in the reaction setup, the term “nt” was appended to the sample name.

As confirmed by the ¹H NMR results (Fig. 1(a)), BPS-t-25 polymers were successfully synthesized using the procedure described and the BPS-t-25 polymer showed a 41.1% degree of sulfonation, according to the calculations based on the ¹H NMR results reported by Y. Li et al. [17]. Further, the GPC results confirmed the formation of a polymer with a high molecular weight (*M_w*) of over 160,000.

The BPS-o-20 polymer synthesized without toluene also showed a high molecular weight of 120,000. This is probably because water, which is formed along with potassium phenoxide as a byproduct during the polymerization reaction [15], evaporated along with a small amount of DMAc at the polymerization temperature of 160 °C even in the absence of toluene and was then removed by the Dean–Stark trap, resulting in relatively high molecular weight copolymers. Further, as shown in Fig. 1(b), no significant differences in the ¹H NMR spectra were observed in the case of BPS-o-20 compared to that of BPS-t-25 (Fig. 1(a)). However, in the case of BPS-t-20-nt, where the Dean–Stark trap was not used in the equipment setup, the water formed as the

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