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Soluble sulfonated polybenzothiazoles containing naphthalene for use as proton exchange membranes

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ABSTRACT

Two series of sulfonated polybenzothiazoles containing naphthalene, derived from either 2,2-bis(4-carboxyphenyl) hexafluoropropane (6FA) or 2,6-naphthalene dicarboxylic acid (NA) were synthesized by polycondensation with non-sulfonated monomer 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) and sulfonated monomer 4,8-disulfonyl-2,6-naphthalene dicarboxylic acid (DSNA). The sPBT-6FA series polymers containing DSNA were soluble in polar aprotic solvents such as dimethyl sulfoxide or 1-methyl-2-pyrrolidinone, whereas sPBT-NA65 with NA was not soluble in common polar aprotic solvents. Therefore, the incorporation of both the naphthalene and flexible hexafluoroisopropylidene units enhanced the solubility of the sPBT polymer series. The polymers were evaluated as proton exchange membranes and exhibited excellent dimensional stability, high thermal and oxidative stabilities, good mechanical properties, and high proton conductivities. The proton conductivities of sPBT-6FA65 were 0.25 S cm^{-1} at 80 °C in water and 0.018 S cm^{-1} at 120 °C under 35% RH.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are attractive as an energy conversion device [1,2]. One of the most important components of PEMFCs is the proton exchange membrane (PEM) [1–3]. The most widely used commercial PEM is the perfluorinated Nafion® membrane. However, Nafion® also has a low operating temperature, high fuel permeability, and high cost, which are significant disadvantages that must be overcome. To date, non-fluorinated aromatic polymers with high proton conductivity, thermal stability, and oxidative stability have been investigated as replacements for perfluorinated PEMs [4–24].

Sulfonated polybenzothiazoles (sPBT) are a class of high performance polymers which appear promising for PEMs, as they exhibit high proton conductivity, thermal stability, oxidative stability, and good mechanical properties [10]. PBT has usually been used only as a structural material, because of its poor solubility and typically low molecular weight [7–11]. sPBT exhibits no softening or glass transition temperature (T_g) before thermal degradation occurs. Therefore, sPBT membranes can only be obtained by the solution casting method. sPBTs have rigid aromatic and heterocyclic benzothiazole backbone structures that exhibit strong intermolecular interactions. It is difficult to prepare sPBT polymers with high molecular weights that are soluble in common polar aprotic solvents [7–11]. To the best of our knowledge, only a few sPBTs have been utilized as PEMs. Yan et al. prepared soluble sPBT for PEMs for the first time, derived from bis(3-sulfonate-4-carboxyphenyl) sulfone (BSCPS), by incorporating bulky pendent groups or flexible linkages into the backbone [10]. Flexible hexafluoroisopropylidene units were incorporated into the polymer backbone to prepare more flexible sPBT polymers that were soluble in polar aprotic solvents [7–11]. In addition, the incorporation of naphthalene units into the backbone of aromatic polymers reduce water uptake and dimensional swelling of PEMs because the rigid and planar nature of the naphthalene units enhance the aggregation of the polymer chain, inducing the formation of larger and more developed hydrophilic ionic clusters [14,18]. The small hydrophobic naphthalene component is also beneficial for providing good

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mechanical properties. Thus, incorporating naphthalene units into the backbone could improve the dimensional stability, mechanical properties, and proton conductivity [14–18]. To the best of our knowledge, soluble sPBT containing naphthalene units for use in PEMs have not been reported.

In this work, the first series is named sPBT-6FAxx, while the second one is named sPBT-NAxx, where "xx" refers to the molar percentage of sulfonated monomer in the feed. The incorporation of the flexible hexafluoroisopropylidene units is expected to enhance the solubility of sPBT. sPBT-NA65, which contains additional naphthalene units but does not contain flexible hexafluoroisopropylidene units, was also synthesized for comparison. Soluble sPBT-6FAs were cast into homogeneous membranes and investigated as potential PEMs.

2. Experimental

2.1. Materials

Silicone oil was purchased from Shin-Etsu Chemical. Co. Ltd (Tokyo, Japan). DABDT was purchased from TCI (Japan). NA, polyphosphoric acid (PPA), phosphorous pentoxide, methane sulfonic acid (MSA), dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), dimethyl formamide (DMF), dimethylacetamide (DMAc), sulfolane, methanol, sodium carbonate (Na_2CO_3), fuming sulfuric acid (30% free SO_3), and other chemicals were obtained from Sigma-Aldrich Co. (St. Louis, MO, USA). All commercial reagents were used as received.

2.2. Preparation of polymers

The preparation of the sPBT-6FAs was carried out, using sPBT-6FA45 as an example: PPA (24 g) and DABDT (0.90 g, 3.6704 mmol) were placed into a 250 mL three-necked round-bottom flask equipped with a mechanical Teflon stirrer and a nitrogen inlet/outlet. The mixture was stirred at 25 °C for 12 h and 70 °C for 24 h until the evolved hydrogen chloride dissipated completely. After cooling to 25 °C, DSNA (1.0027 g, 2.3858 mmol) and 6FA (0.5039 g, 1.2846 mmol) were added to the mixture, which was then stirred at 100 °C for 12 h. Subsequently, after cooling for about 2 h, phosphorus pentoxide (3.2 g) was added to the system and then, the reaction was maintained at 120 °C for 12 h, 150 °C for 12 h, 170 °C for 12 h, 190 °C for 12 h, and 210 °C for 12 h. MSA was added into the solution under stirring for about 1 h after the mixture was cooled to 140 °C. The solution was precipitated into deionized water to obtain a brown-red fibrous polymer, which was washed with deionized water several times to remove residual acid and then soaked in a 5 wt% Na_2CO_3 solution for 24 h, washed to neutral pH, and dried in vacuo at 120 °C for 24 h.

The obtained yield was 95%. ^1H NMR (DMSO-*d*6): 9.78 (d), 9.07 (t), 8.98 (d), 8.86 (t), 8.32 (d), and 7.66 (t). FTIR (film, cm^{-1}): 1495, 1404, 1327 (benzothiazole ring stretching), 965 (benzothiazole ring bending), 1169, and 1028 (sulfonate) [10].

2.3. Membrane preparation

The sPBT-6FA polymers were dissolved in DMSO at 70 °C for 24 h, and then the solutions were filtered through 0.45 μm filters. After casting onto dust-free glass, the solutions were heated in an oven at 70 °C for 24 h, in vacuo at 100 °C for 1 h, and at 120 °C for 1 h. After cooling to room temperature, the glass plates were placed into deionized water to obtain membranes in the sodium sulfonate form. The membranes were converted to the sulfonic acid form by immersing them in 1 M HCl for 48 h followed by several washing cycles in deionized water.

2.4. Measurements

The chemical structures of sPBT-6FA polymers in the sodium sulfonate form were verified by nuclear magnetic resonance spectroscopy (^1H NMR, VNMRS 600 MHz, Varian Inc., Palo Alto, CA, USA). DMSO-d_6 and tetramethylsilane (TMS) were used as the solvent and internal standard, respectively. sPBT-6FA membranes in the sulfonic acid form were also investigated by attenuated total reflectance infrared spectroscopy (ATR-FTIR, Nicolet 6700, Thermo Scientific, Waltham, MA, USA).

The molecular weights of the sPBT-6FA salt ionomers were determined by gel permeation chromatography (GPC, Waters, Milford, MA, USA) against polymethylmethacrylate (PMMA) standards. NMP with 0.05 M LiBr was used as the eluent, where Styragel® columns and a Waters 2414 refractive index detector were used as GPC accessories.

The experimental ion exchange capacity (IEC) of the sPBT-6FA membranes was determined by a standard titration method, whereby sPBT-6FA membranes were immersed in saturated NaCl solutions for 48 h to release protons into solution, which were then titrated with 0.01 M NaOH using phenolphthalein as an indicator.

The thermal properties of the sPBT-6FA ionomers were measured by thermogravimetric analysis (TGA) using a TGA Q500 (TA Instruments, New Castle, DE, USA) in N_2. The temperature was set at 150 °C and maintained for 30 min in N_2 to remove water from the acid form sPBT-6FA polymers. Then, they were heated to 800 °C at a rate of 20 °C/min.

The thermal properties of the sPBT-6FA ionomers were also measured on a differential scanning calorimeter (DSC Q20, TA Instruments, New Castle, DE, USA). The temperature was set at 150 °C and kept for 30 min in N_2 to remove water from the acid form sPBT-6FA polymers. Then, the samples were heated in the range of 90–350 °C at a heating rate of 10 °C/min.

The in-plane proton conductivity of the sPBT-6FA membranes was measured under two different conditions. First, the resistance value was measured over the frequency range of 100 mHz to 100 kHz in water at 30, 50, 70, and 80 °C, separately. An impedance/gain-phase analyzer (Solartron 1260, Farnborough, Hampshire, UK) and an electrochemical interface (Solartron 1287) were used in the testing. The resistance value was also tested at 80 °C under 100% RH, 100 °C under 85% RH, and 120 °C under 35% RH in a two-probe type conductivity cell controlled by a fuel cell station (CNL, Seoul, Korea) under nitrogen flow at a pressure of 1.5 atm. An alternating current (AC) impedance spectrometer (Solartron 1260) was used in this analysis. Both of the proton conductivities were calculated using the following equation:

$$\sigma = \frac{L}{RS} \tag{1}$$

where *L*, *R*, and *S* represent the distance of the reference electrodes, the impedance, and the cross-sectional surface area of the membrane, respectively.

The water uptake (*WU*), in-plane dimensional swelling ($S_\parallel$), and through-plane dimensional swelling ($S_\perp$) of the sPBT-6FA membranes were obtained by measuring the changes of the ratios of the weight, length, and thickness [22–26] from the dry to wet state. Each of the sPBT-6FA membranes, which were dried in vacuo at 120 °C for 48 h, were immersed in water for 24 h at different temperatures. The *WU*, $S_\parallel$, and $S_\perp$ values were calculated using the following equations.

$$WU(\text{wt\%}) = \frac{W_\text{w} - W_\text{d}}{W_\text{d}} \times 100 \tag{2}$$

$$S_\parallel(\%) = \frac{l_\text{w} - l_\text{d}}{l_\text{d}} \times 100 \tag{3}$$