

Synthesis and characterization of sulfonated copolyimides via thermal imidization for polymer electrolyte membrane application

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ABSTRACT

A series of soluble copoly(amic acid) precursors were synthesized with varying compositions by the conventional polycondensation of 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA) and 3,3'-sulfonyldianiline (SDA) using 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS), a sulfonated diamine, as a third component in NMP. The synthesized precursor polymers are soluble in polar aprotic solvents. The chemical structures and inherent viscosities of the copoly(amic acid)s were determined by ¹H NMR spectroscopy and viscometry, respectively. The free standing sulfonated copolyimide membranes were fabricated from solutions of the copoly(amic acid)s by a thermal imidization process and subsequent soaking in sulfuric acid solution. The chemical structure and thermal properties of the sulfonated copolyimides in the films were investigated in detail using FT-IR, DSC, and TGA. The sulfonated copolyimides show mainly three-step thermal degradation, with the degradation behavior being independent of the composition. In addition, the properties of the membranes were investigated, including their water uptake (WU), ion exchange capacity (IEC) and proton conductivity. The WU and IEC values of the sulfonated copolyimides were 8.12–38.0% and 0.18–2.05 meq/g, respectively, depending on the composition of the sulfonated diamine, and the proton conductivity of the copolyimides was dependent on the content of the sulfonated diamine. The proton conductivity values of the membranes were lower than that of Nafion 117, although their IEC values were higher.

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1. Introduction

Fuel cells are considered as one of most promising clean power sources for automotive transportation, and for both stationary and portable applications, since they do not emit any CO₂ or toxic gases, such as SO_x, NO_x, etc. The main advantage of fuel cells is their high energy density, high energy conversion efficiency, low noise, and low maintenance costs [1–3]. Among the various kinds of fuel cells, proton exchange membrane fuel cells (PEMFCs) have attracted significant attention from both the academic and industrial fields, due to the promise of commercialization, mass production and development of new materials for components [4–6]. PEMFCs use a polymer electrolyte membrane (PEM) as a proton conducting layer, which has negatively charged groups, such as sulfonic acid and phosphoric acid, attached to the polymer main chain or incorporated as a side group. The PEM acts as a separator between the anode and the cathode and a barrier to hydrogen fuel, as well as enabling the transport of protons from the anode to the cathode with minimum resistance [5,7]. Until now, perfluorinated carbon polymers bearing sulfonic acid groups at the end

of their side chains, such as Nafion, have been widely used as a PEM, because of their excellent proton conductivity, high mechanical strength, and good chemical electrochemical stability. However, PEMFCs fabricated from Nafion have an operation temperature limitation of around 80–100 °C, because of the drawbacks of perfluorinated carbon polymers, such as their low conductivity and low mechanical and electrochemical properties at high temperature [8,9].

Several high performance PEMs based on hydrocarbon polymers have been examined in an attempt to address these problems, and one of the representative approaches is based on the use of aromatic component polymers, such as poly(1,4-phenylene) [10,11], poly(oxy-1,4-phenylene) [12], polyimides (PI) [3,13–16,31], poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK) [17], poly(phenylenesulfide) [18], polybenzimidazole (PBI) [19,20], and their derivatives, for the polymer backbone with sulfonated groups. These sulfonated aromatic polymers are easily prepared by direct chemical treatment using concentrated sulfuric acid or a sulfonating agent, or by direct polymerization using designed and synthesized sulfonated monomers. These aromatic hydrocarbon polymers have attracted a great deal of attention both academically and industrially, because of their advantageous properties, which include good mechanical properties, high thermal stability, excellent chemical resistance, high water uptake over a wide temperature range, low cost, and so on.

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Among the many aromatic polymers, sulfonated polyimide (SPI) membranes are one of the potential candidates, because of their high glass transition temperature, dimensional stability, chemical resistance, and heat resistance, as well as their excellent mechanical, adhesion, and dielectric properties [3,13–16]. SPI materials with various structures were recently studied for PEMs based on five- and six-membered ring dianhydride derivatives and newly synthesized sulfonated diamines via one-spot solution polymerization [3,13–16]. However, in general, two-step methods via soluble precursor polymers, poly(amic acid)s (PAA)s, and their conversion to polyimides have been commonly used [21,22], because aromatic PIs are usually insoluble in organic solvents. For example, (PAA)s are synthesized by adding a dianhydride monomer to a solution of a diamine in a polar aprotic solvent, such as *N*-methylpyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc). The obtained PAA precursor is then converted to the corresponding insoluble PI by thermal imidization or by a chemical imidization process. However, there have been few studies concerning the preparation of SPIs by two-step polymerization for PEMs. Thus, it is important to develop high performance proton exchangeable SPIs, bearing sulfonic acid groups by the conventional thermal imidization process for PEMFCs. Furthermore, the relationship between the chemical structure of the PIs and the properties of the membranes should be clarified.

In this study, we therefore prepared a series of insoluble sulfonated aromatic copolyimides for high performance PEMs via the synthesis of soluble copoly(amic acid) precursors. A series of soluble copoly(amic acid) precursors were synthesized with varying compositions by the conventional polycondensation of 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA) and 3,3'-sufonyldianiline (SDA) using 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS), a sulfonated diamine, as a third component in NMP. The synthesized precursor polymers are soluble in polar aprotic solvents and, thus, their free standing films can be fabricated for use as membranes by means of solution casting and subsequent drying and thermal imidization processes. The chemical structure, inherent viscosity and

composition of the synthesized SPIs were determined and their membranes behaviors, such as their water uptake, ion exchange capacity, and proton conductivity, were measured and analyzed with regard to the effect of the sulfonated comonomer composition.

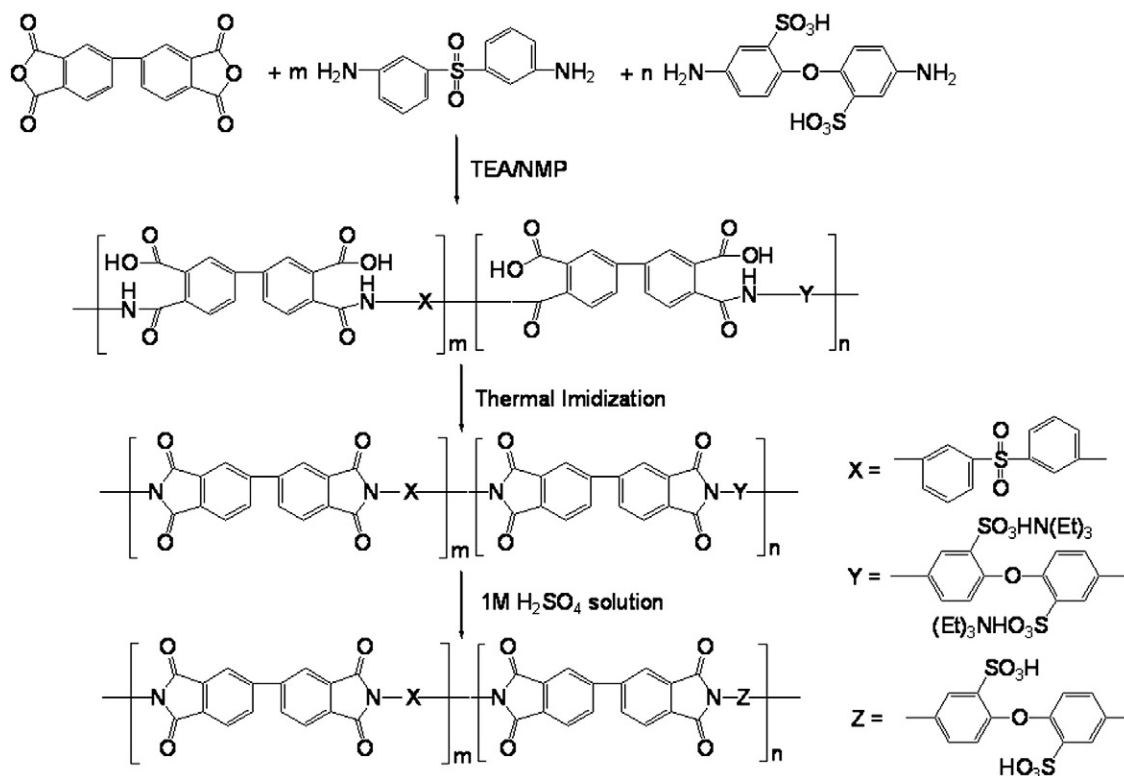
2. Experimental

2.1. Materials

3,3',4,4'-Biphenyltetracarboxylic anhydride (BPDA) was supplied by Chriskev Company and purified by recrystallization from acetic anhydride. *N*-methyl-2-pyrrolidinone (NMP) were purchased from Aldrich Company and distilled over calcium hydride under reduced pressure and under a nitrogen atmosphere, respectively. 4,4'-oxydianiline (ODA), 3,3'-sufonyldianiline (SDA) and triethylamine were purchased from Aldrich Company, and sulfuric acid and fuming sulfuric acid were purchased from Aldrich Company and used without purification.

2.2. Synthesis of 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS)

Fuming sulfuric acid (17.5 mL) was added dropwise to a solution of ODA (10.0 g, 49.9 mmol) and concentrated sulfuric acid (8.5 mL) at 0 °C under a nitrogen atmosphere with stirring [23]. The reaction mixture was stirred overnight at 0 °C for 2 h and then heated to 80 °C for 5 h. Next, the reaction mixture was poured into crushed ice and the white precipitate was filtered off. The white powder was dissolved in NaOH solution and then the precipitate was filtered off. The filtrate was acidified using HCl solution, giving 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid as a crude powder. The precipitate was filtered, washed with water and methanol successively several times, and dried at 80 °C under vacuum (14.9 g, 83% yield). ¹H NMR (DMSO-*d*₆ with a small amount of triethylamine, δ): 6.99 (d, 2H, -O-ArH-Ar), 6.75 (d, 2H, SO₃H-Ar-ArH-Ar-NH₂), 6.39 (q, 2H, -Ar-ArH-Ar-NH₂), 6.05 (s, 4H, -NH₂).



Scheme 1. Synthetic route to copoly(amic acid)s and sulfonated copolyimides.

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