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Synthesis and characterization of block copolymer and comparative study with random copolymer via superacid– catalyzed reaction

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ABSTRACT

The grafted block copolymer based polymer electrolyte membrane (PEM) was successfully synthesized by the superacid-catalyzed polyhydroxyalkylation reaction from biphenyl, 2,2'-biphenol and isatin and the performance of the block copolymer were compared in conjunction with the random copolymer. These polymers have all carbon-carbon structure on polymer backbone without ether linkage. The bromoalkylsulfone potassium salt was prepared from 1,3-propane sultone and potassium bromide. Particularly, the attached alkyl sulfone groups were afforded better stability due to less reactivity towards nucleophilic substitution reaction. Moreover, the block copolymer exhibited better proton conductivity (76.84 mS/cm under 90% relative humidity at 80 °C), water resistivity, chemical, and thermal stability compared to the random copolymer, because block copolymer membranes showed good hydrophilic/hydrophobic phase separation and wide ionic channels. The structures of the resultant PEMs were confirmed by ¹H NMR spectroscopy and thermogravimetric analysis (TGA). These membranes were studied by proton conductivity, water uptake (WU), and ion exchange capacity (IEC). Fenton test was attended by Fenton's reagent (4 ppm Fe²⁺, 3% H₂O₂) for confirmation of the polymer degradation and the surface morphology of membranes was also analyzed by atomic force microscope.

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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]. DuPont's Nafion is widely studied as good fuel cell membranes because of its

high proton conductivity combined with oxidative and chemical stability. However, some drawbacks of Nafion, such as high methanol crossover and high cost, hinder its widespread commercial use in PEMFCs [2]. Recently, much progress has been made to develop novel hydrocarbon PEMs based on sulfonated aromatic copolymers as alternatives to perfluorosulfonic acid (PFSA) polymers. Numerous examples of

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randomly sulfonated aromatic copolymers based on polyphosphazenes, polybenzimidazole, poly (ether sulfone)s and poly (ether ketone)s, were used to prepare membranes for fuel cell applications [3–8]. Although random polymer-based membranes have certain good properties, they exhibit several drawbacks such as weak mechanical properties, low proton conductivity, and low fuel cell performance. Moreover, the chemical stability is unapproachable to Nafion, because of ether linkage with acid functional groups is attacked by hydrogen peroxide or peroxide radicals generated during PEMFC operation [9]. To overcome low conductivity and durability, researchers were studied block copolymer and polyphenylene. Actually, sulfonated block copolymer based membranes offer a number of benefits for fuel cell application, including, high proton conductivity at low relative humidity, mechanical stability, and better cell performance compared to homo polymer and random polymer [10–12]. In these membranes, one block (sulfonated part) of the copolymer facilitates proton conductivity while the second block (e.g., polyethylenes, polypropylenes, polybutylenes, polyarylenes, polyimides, and polybenzimidazoles) maintains the mechanical stability of the membrane during operation [13–16]. Furthermore, the block copolymer membranes show good hydrophilic/hydrophobic phase separation and wide ionic channels in conjunction with the random copolymer [17].

Nowadays Chemical stability of membranes is considered as a major concern for PEMFC application. Many polymers with carbon-carbon backbone structured, derived from Diels–Alder and Ni/Zn catalyze reactions, were reported to overcome this problem [18–22]. These carbon-carbon backbones based polymer membranes have excellent chemical stability and good performances [23]. But, they are very expensive regarding the processing of monomers, catalyst, and demanding reaction conditions. Furthermore, Diels–Alder polymerization has a limitation of high molecular weight and desirable monomer synthesis. Ni/Zn catalyze and super acid catalyze reactions deserve the most attention in future membrane development. Since Olah and co-workers explain the high reactivity of electrophilic species in super acid media, numerous reactions have been carried out using super acid as a reaction medium. And this reaction needs low cost and easy control of reaction condition by insensitivity from water molecule [24]. Our research group has studied polymer structures without ether linkage using super acid [25].

The purpose of this work is to improve conductivity and durability applying merits of the block copolymer and polyphenylene. In this research, we have prepared grafted block copolymer by the superacid-catalyzed polyhydroxyalkylation reaction from biphenyl, 2,2'-biphenol and isatin. The grafting reaction was conducted with 3-bromo-1-propane sulfonic acid potassium salt which was prepared from propane sulfone. The membranes were characterized by ^1H NMR spectroscopy and the results demonstrated that the PEMs were formed with high purity. The suitability of these PEMs for the development of fuel cell was investigated by measuring WU, IEC, chemical stability, and proton conductivity. The results revealed that the block copolymer is better than random copolymer as PEMs.

Experimental

Materials

2,2'-Biphenol, isatin, biphenyl, trifluoroacetic acid (TFA), trifluoromethanesulfonic acid (TFSA), 1,3-propane sulfone, potassium bromide, hydrochloric acid and potassium carbonate were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Alfa Aesar (Ward Hill, USA). Other commercially available solvents such as acetone, toluene, dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), methanol (MeOH), ethanol (EtOH), and water (H_2O) were used as received without any further purification.

Synthesis of block co-polyphenylene (BPPIB)

Two 100 mL two-necked round-bottomed flask was equipped with mechanical stirrers and ice-baths. To synthesis oligomer-1 (PIBP), in the first flask, TFSA (50.8 mL) was added to an ice-cooled mixture of isatin (1.00 g, 6.8 mmol), biphenyl (1.05 g, 6.8 mmol) and trifluoroacetic acid (17 mL). To prepare oligomer-2 (PIBPOH), in the second flask, similar to previous one (first flask) but in this case, 2, 2'-biphenol (1.27 g, 6.8 mmol) was added instead of biphenyl. Ice-bath was removed when the addition was finished. After 2 h, the solution of the second flask was poured into the first flask. After that, the temperature was raised up to 20 °C over a period of 30 min and the reaction was continued at this temperature for 15 h to afford a highly viscous solution. The resulting mixture was poured slowly into methanol and the white fibrous precipitate was obtained. Then the white fibrous polymer was filtered and washed with methylene chloride (MC), methanol, and water, respectively. After that, the polymer was dried in vacuum oven at 80 °C for 24 h and finally obtained a white fiber-like polymer.

Synthesis of 3-bromopropane-1-sulfonate potassium salt (BPSK)

3-bromopropane-1-sulfonate potassium salt was synthesized, shown in (Scheme 2). A solution of 1,3-propane sulfone 5 g (40.94 mmol) and potassium bromide 5.85 g (49.12 mmol) in distilled water (75 mL) was stirred at 60 °C for 2 h. After that, H_2O was evaporated via distillation. The residue was washed with cool ethanol and recrystallized from ethanol and water (3:1 v/v) mixture, a white solid 8.88 g (90%) was obtained.

Pendant sulfonation of BPPIB (SBPPIB-30)

A typical alkylation procedure follows (Scheme 1). A 100 mL three-neck round bottom flask fitted with dean-stark trap, condenser, nitrogen inlet/outlet, and magnetic stirrer. At first, as-synthesized polymer (BPPIB) (1 g, 3.34 mmol), an excess amount of BPSK (1.61 g, 6.68 mmol), potassium carbonate (0.92 g 6.68 mmol) were taken and added toluene (10 mL) and DMAc (10 mL), respectively. The mixture was refluxed for 3 h at 130 °C. After that, the produced water was azeotroped off with toluene, the mixture was heated at 160–180 °C for about 2 h. After the reaction, the reaction mixture was diluted three more times with DMAc, and then the viscous solution

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