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Synthesis and property of sulfonated poly(methylisatin biphenylene) containing diphenyl ether by polyhydroalkylation reaction

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ABSTRACT

A series of poly(methylisatin biphenylene) were prepared by superacid-catalyzed polyhydroxyalkylation reaction of N-methyl isatin, 2,2'-dihydroxybiphenyl and diphenyl ether. These polymers have some ether linkages on polymer backbone that render softness and make more elastic. And sulfonic acid groups were introduced by sulfonation reaction with potassium-3-bromopropane sulfonic acid. Their sulfonic acid groups with functionalization and the measurement of apposite parameters for proton exchange membranes (PEMs) were described. The membranes showed comparable IEC (1.59–1.98 meq./g), water uptake (32.72–57.30%), proton conductivity (72.1–109.2 mS/cm), and high thermal stability, and also proton conductivity measurement compared with Nafion 211®.

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Introduction

Polymer electrolyte membrane fuel cell (PEMFC) can efficiently generate high power densities, and thereby making it an attractive technology for automobile and portable applications. At present, perfluorinated polymer membranes, such as Nafion® and Flemion® are widely used for PEM materials because of their excellent physical & chemical stability, and high proton conductivity at high relative humidity and low temperature [1–3]. However, they suffer from such disadvantages as limited operation temperature (0–80 °C), high cost, and high fuel permeability. This has stimulated the development of research focused on hydrocarbon

membranes with low cost and high performance [4–6]. To overcome the drawbacks, a certain number of polymer families, such as polyphosphazenes [7,8], polybenzimidazole [9], poly(ether sulfone)s, and poly(ether ketone)s [10,11], were used to prepare membranes for fuel cell applications. Research in the field of hydrocarbon membranes has made great strides throughout the years. The recent advances in the development of PEM materials reveal that the performances (like-proton conductivity, power density etc.) of hydrocarbon membranes are close to those of perfluorinated sulfuric acid membranes, and also their production and processing cost is lower [12]. However, the durability is unapproachable to Nafion®. Their characteristics are derived from fluoro atoms and carbon–carbon bonded chemical structures which

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attribute relatively long lifetime compare to hydrocarbon membranes. Most hydrocarbon membranes are susceptible to oxidative or acid-catalyzed degradation than Nafion[®] by structural ether linkage [4,11]. Chemical degradation of membranes is considered as a major concern for fuel cell performance. To improve the long term stability, the carbon–carbon backbone structured polymers were studied. Generally, Sulfonated poly(p-phenylene)s were synthesized by Ni(0)-catalyzed coupling copolymerization and Diels–Alder polymerization [13]. These carbon–carbon backbone based polymer membranes have excellent chemical stability and good performances [14]. But, they are very expensive regarding the processing of monomers, catalyst, and demanding reaction conditions. Since Olah and co-workers explain the high reactivity of electrophilic species in superacid media, numerous reactions have been carried out using superacid as a reaction medium. And this reaction needs low cost, and easy control of reaction condition by insensitivity from water molecule [15,16].

Nafion[®] is consisted of a perfluorocarbon backbone, to which carbon–carbon main structure and fluorocarbon side chains are attached. These side chains carry a sulfonic acid group at their ends. It has been argued frequently in the literature that Nafion[®] is owed for its good proton conductivity at relatively low water uptake to its morphology [17]. In previous research, the use of side chain structures with flexible pendant sulfonic acid group, high density sulfonic acid group, and high IEC values resulted in good performance [18]. Particularly chemical modification to flexible sulfoalkyl groups attached to a polymer's side chain structure afforded better stability due to less reactivity of the nucleophile substitution reaction, and good proton mobility by good phase separation.

The purpose of this work is to design and synthesized bis-2,6-dimethylphenoxyphenylsulfone, which is structured the meta position steric hindrance by two methyl groups, because this structure minimized crosslinking reaction during superacid catalyzed polymerization, and also grafted sulfonic acid for improving proton mobility, low water uptake and good solubility in polar solvent. Most hydrocarbon membranes are the fully aromatic structures in which sulfonic acid groups are directly attached to the phenyl rings of the polymer backbone. These acidic groups cannot aggregate as freely as those of Nafion[®] because for a group attached in this way, a segment of the polymer backbone needs to move, and not just an independent side chain. Clearly, attaching the acidic groups to the backbone via side chains can be expected to be beneficial [19].

This work is an attempt to synthesize polymer from isatin, dihydroxy biphenyl and diphenyl ether with trifluoromethane sulfonic acid as a superacid catalyzed, and the sulfonated polymer was followed by grafting reaction with 3-bromo-1-propanesulfonic acid potassium salt which was prepared from propanesultone. The sulfonated membrane has some characteristics of bicontinuous morphology and high proton conductivity. The synthesized copolymers were characterized by ¹H NMR spectroscopy, thermogravimetric analysis (TGA), proton conductivities, water uptake, and ion exchange capacity (IEC) measurement.

Experimental

Materials

Trifluoroacetic acid (TFA, 99%), 1,3-propane sultone (99%), potassium bromide ($\geq 99.5\%$), potassium carbonate, anhydrous (99.5%) dimethylsulfoxide (99%), dimethylacetamide (99%) and isatin (98%) were purchased from Aldrich. Trifluoromethanesulfonic acid (TFSA, 98%), 2,2'-dihydroxybiphenyl (99%) were purchased from Alfa Aesar. Diphenyl ether (99%) was from Acros. Common solvents, such as dichloromethane, methanol and ethanol were also used with or without further purification.

Synthesis of 3-bromo-1-propanesulfonic acid potassium salt

A solution of 1,3-propane sultone (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 1 h. The reaction mixture was evaporated to remove the water. The residue was washed with cool ethanol. After purification by recrystallization of the residue from ethanol and water (3:1 v/v), a white solid (8.88 g, 90%) was obtained.

Synthesis of poly(*N*-propylsulfonic acid isatin dihydroxy biphenylene) (PPSIDB 1)

A typical polyhydroxyalkylation procedure was as follows: TFSA (15 mL) was added to an ice-cooled mixtures of isatin (2.90 g, 19.73 mmol), dihydroxy biphenyl (0.92 g, 4.93 mmol), diphenyl ether (1.78 g, 11.51 mmol) and trifluoroacetic acid (25 mL) in a 100 mL two-neck round bottomed flask equipped with a mechanical stirrer. After addition, ice bath was removed. Thereafter, the temperature was gradually raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 24 h to afford a highly viscous dark-purple solution. The resulting mixture was poured slowly into methanol. The precipitate, white fibrous polymer was filtered, washed with methanol and dried overnight in a vacuum oven at 80 °C. After drying, white fiber like polymer was obtained. A mixture of polymer (1 g), potassium carbonate (0.68 g, 4.93 mmol) and 3-bromo-1-propanesulfonic acid potassium salt (0.29 g, 1.18 mmol) in dimethylacetamide (20 mL) was stirred at 60 °C for 24 h. The resulting mixture was decanted slowly into distilled water. The precipitate was washed with water for several times until residual water was pH neutral. The polymer product was collected by filtration and dried under vacuum at 80 °C for 24 h.

Synthesis of poly(*N*-propylsulfonic acid isatin dihydroxy biphenylene) (PPSIDB 2)

PPSIDB 2 was synthesized by following the same procedure as that for PPSIDB 1. TFSA (15 mL) was added to an ice-cooled mixtures of isatin (2.90 g, 19.68 mmol), dihydroxy biphenyl (1.07 g, 5.74 mmol), diphenyl ether (1.81 g, 10.66 mmol) and trifluoroacetic acid (25 mL) in a 100 mL two-neck round bottomed flask equipped with a mechanical stirrer. After reaction, white fibre like polymer was obtained. A mixture of

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