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Preparation and characterization of grafted propane sulfonic acid polyphenylene membrane via superacid-catalyzed reaction

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ABSTRACT

A series of polyphenylene-based polyelectrolytes were synthesized from 2,2'-biphenol, and isatin by superacid catalyzed polyhydroxyalkylation reactions. Grafted sulfonated polyphenylenes were synthesized via K_2CO_3 catalyzed condensation reaction with 3-bromopropane sulfonic acid potassium salt. These polymers have all carbon–carbon linkages without any ether linkage on polymer backbone, which were not attacked by nucleophiles (H_2O, hydrogen peroxide, hydroxide anion and radical). Particularly, chemical modification to flexible sulfoalkyl groups implanted to a biphenol unit afforded better stability due to less reactive towards nucleophilic substitution reaction, and good proton mobility because of well phase separation. The structural properties of the synthesized polymers were investigated by ^{1}H NMR spectroscopy. The membranes were studied by ion exchange capacity (IEC), water uptake, dimensional stability as well as proton conductivity assessment. The chemical degradation test was performed by Fenton's reagent, and compared with the usual sulfonated poly(ether sulfone)s and Nafion.

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Introduction

Polymer electrolyte membranes (PEMs) based on sulfonated perfluoropolymers, Nafion and Flemion have been widely used as polymer electrolyte membrane fuel cells (PEMFCs) because of their high proton conductivity and high durability [1,2]. Their characteristics are derived from fluoro atoms and carbon–carbon bonded chemical structures which attribute relatively long lifetime compared to the hydrocarbon membranes. Most hydrocarbon membranes generally show lower ionic conductivities at comparable ion exchange capacities than Nafion, and more susceptible to oxidative or acid-catalyzed degradation due to structural ether linkage [3,4]. Chemical degradation of membranes is commonly thought to play the most important role for the cessation of normal operation [5–7]. Research in the field of hydrocarbon membranes has made great strides throughout the years. Performances of proton conductivity, power density etc. of hydrocarbon membranes are close to those of

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perfluororinated sulfuric acid membranes and their cost is lower as well. However, the durability of hydrocarbon membranes is not as high as that of Nafion. To surmount this intrinsic drawback, the carbon–carbon backbone structured polymers were studied. Sulfonated polyphenylenes ordinarily synthesized by Ni-catalyzed polymerization and Diels-Alder polymerization [8–10]. These all carbon structured polymer backbone based polymer membranes have excellent oxidative and chemical stability and good performances [10]. However, they are very expensive with respect to the processing of monomers, catalyst, and demanding reaction conditions. Since Olah and co-workers explain the high reactivity of electrophilic species in superacid, numerous reactions have already been performed using superacids as a reaction medium [11,12]. And 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. Particularly chemical modification to flexible sulfoalkyl groups attached to a polymer's side chain with multi-phenyl structure afforded better stability due to less reactivity of the nucleophile substitution reaction, and good proton mobility by good phase separation [13–16].

This work is fabricated to prepare the carbon–carbon linked polymer in the main chain without ether group, and also contain grafting moieties for improving solubility and proton mobility. The copolymer membrane synthesized by superacid catalyzed polymerization bearing pendant sulfonic acid groups were studied by cell performance.

Experimental

Materials

2,2'-Biphenol, isatin, trifluoroacetic acid (TFA), trifluoromethanesulfonic acid (TFSA), 1,3-propanesultone, potassium bromide, hydrochloric acid and potassium carbonate were from Alfa Aesar, Sigma–Aldrich and TCI, and used as received. Other commercially available solvents – dichloromethane (MC), acetone, methanol (MeOH), ethanol (EtOH), dimethylsulfoxide (DMSO), and dimethylacetamide (DMAc) – were used without further purification.

Synthesis of isatin-based polyphenylene polymer (PPIB)

To a round-bottomed flask, trifluoromethane sulfonic acid (11 mL) was added to an ice-cooled mixture of isatin (1.59 g, 10.85 mmol), 2,2-biphenyl (1.87 g, 10.05 mmol) and trifluoroacetic acid (6.2 mL). After addition, the temperature was raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 18 h to afford a highly viscous dark-green solution. The resulting mixture was poured into methanol. The filtered polymer was washed several times with water and methanol, and dried in vacuum oven at 80 °C for 24 h.

Synthesis of bromopropane-sulfonic acid potassium salt (BPSK)

To a solution of potassium bromide (4.76 g, 40 mmol) in water (15 mL), 1,3-propanesultone (3.51 mL, 40 mmol) was added at 60 °C. After completely dissolving the sultone (about 10 min) into the water solution, the water was removed via distillation. The crude residue was washed with cold ethanol (2 × 10 mL) and purified by recrystallization from 3:1 EtOH/H_2O to give white crystalline solid, and finally dried in 80 °C vacuum oven for 24 h.

Pendant sulfonation of polymer (PSPP)

To a round-bottomed flask, synthesized polymer (1.5 g), excess amount of bromopropanesulfonic acid potassium salt (4.80 g, 19.90 mmol), potassium carbonate (2.75 g, 19.90 mmol), toluene (20 mL) and DMAc (20 mL) were charged. The mixture was refluxed for 3 h at 130 °C, dehydrayed and toluene was remved slowly. The reaction mixture was gradually heated to 160–180 °C for about 4–5 h and thence poured into 0.5 M HCl solution with vigorous stirring. The polymer was washed in water several times and dried in 60 °C vacuum oven. PSPP 1, 2, and 3 were synthesized by same procedure with different ratio of BPSK (12.3, 15.9, and 19.9 mmol each).

Accelerated chemical membrane degradation test

The membrane degradation was studied by immersion in Fenton's reagent (4 ppm Fe^{2+}, 3% H_2O_2) at 75 °C. The samples were sulfonated polyphenylene membranes, commonly used linear sulfonated poly(ether sulfone)s (SPES 40), and Nafion 211. Initiallly, sample weight was measured, and the samples were put into a solution of iron(II)sulfate heptahydrate in ultra pure water (45 mL) and heated to 75 °C, after which 5 mL of 30% H_2O_2 was added to the solution. The membrane samples were taken out regularly during the experiment to weigh. Washing the sample in distilled water quenched the degradation reaction, and the exposed membranes were dried before the final weight was determined [17,18].

Membrane preparation and characterization

Membranes (25 μm) were prepared by the dissolution of the polymer in DMSO to afford 20 wt% transparent solutions and casting of the solutions at elevating temperatures of 60, 80, 100, and 120 °C. The polymer structure was confirmed by ^1H NMR spectra recorded on a Bruker DRX (400 MHz) spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-7 analyzer. Membranes were prepared by the dissolution of the polymer in DMSO to afford 25 μm transparent films. To assess the water uptake, the membranes were vacuum-dried at 100 °C for 24 h, weighed, and immersed in deionized water at 30 °C and 80 °C for 24 h. The wet membranes were wiped dry and quickly weighed again. The water uptakes of membranes are reported in weight percent as follows: water uptake $= \{(W_{wet} - W_{dry})/W_{dry}\}\cdot 100\%$, where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. The dimensional change was investigated by immersing the membrane into water at 80 °C for 24 h, and the changes in thickness and length were calculated from the equation, $\Delta t = \{(t - t_s)/t_s\}\cdot 100\%$, $\Delta l = \{(l - l_s)/l_s\} \times 100\%$, where t_s and l_s are the thickness and diameter of the dried membrane,

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