



Synthesis and characterization of pendant propane sulfonic acid on phenylene based copolymers by superacid-catalyzed reaction



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ABSTRACT

A series of phenylene based polyelectrolytes were synthesized from 2,2'-biphenol, biphenyl and isatin by superacid catalyzed polyhydroxyalkylation reactions. Grafted sulfonated polymers were synthesized by substitution reaction with 3-bromopropane sulfonic acid potassium salt. These polymers have all carbon-carbon structure on polymer backbone without ether linkage. Particularly, the flexible sulfoalkyl groups were attached to a 2,2'-biphenol unit and formed grafting structure which afforded better stability due to less reactive towards nucleophilic substitution reaction, and good proton mobility because of well phase separation. The structure properties of the synthesized polymers were investigated by ¹H NMR spectroscopy. The membranes were studied by ion exchange capacity (IEC), water uptake, dimensional stability, proton conductivity, and cell performance. The chemical deterioration test was performed by Fenton reagent, and compared with normal sulfonated poly(ether sulfone)s and Nafion.

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1. Introduction

Fuel cells are widely regarded as an efficient and clean energy source and as an alternative to fossil fuel. Polymer electrolyte membrane fuel cells (PEMFCs) particularly offer many advantages, such as high efficiency, high energy density, quiet operation, and environmental friendliness [1]. Most current PEM is based on perfluorosulfonic acid polymer membranes, represented by Dupont's Nafion. Nafion exhibits generally good chemical stability and proton conductivity at high relative humidity (RH) and low temperature [2,3]. 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 [4–8]. To overcome the drawbacks, a certain number of polymer families, such as polyphosphazenes [9,10], polybenzimidazole [11], poly(ether sulfone)s, and poly(ether ketone)s [12–18], were used to prepare membranes for fuel cell applications. These polymers have received much attention because of their high thermal, oxidative, and chemical stability in fuel cell environments.

Most hydrocarbon based PEM materials has good thermal stability, and closely to the Nafion's performance [19–21]. But the chemical stability is unapproachable to Nafion, because of their structure with acid functional groups attached on main chain, and ether linkage possibly attacked by nucleophiles [11,22]. To improve the long term stability, the carbon-carbon backbone structured polymers were studied. Generally, the sulfonated poly(phenylene) polyelectrolytes were synthesized by Ni(0)-catalyzed coupling copolymerization and Diels-Alder polymerization [23–26]. The resultant polymers are consisted of carbon-carbon bonded structure which is tough rigid-rod material with high chemical stability, and the backbone stiffness does not negatively affect membrane properties. However, they are very expensive process 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 superacids as a reaction medium. And this reaction need low cost, and easy control of reaction condition by insensitivity from water molecule [27,28]. 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 [30–35]. 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.

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This research is an attempt to synthesize carbon–carbon linked polymer in main chain without ether linkage by super acid catalyzed polymerization. And sulfoalkyl groups selectively attached to the OH groups on 2,2'-biphenol unit by alkylation reaction with K_2CO_3 . The proposed polymer membranes, in which sulfonic acid groups attached on side alkyl chain and backbone without ether linkage structure, were promising units to good chemically stability and proton conductivity. The polymer membranes are easily soluble in aprotic organic solvents. Polymer membranes were studied by 1H NMR spectroscopy, thermo gravimetric analysis (TGA), water uptake, ion exchange capacity (IEC), Fenton test, proton conductivity, and cell performance.

2. Experimental

2.1. Materials

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

2.2. Synthesis of co-polyphenylene (PPIB)

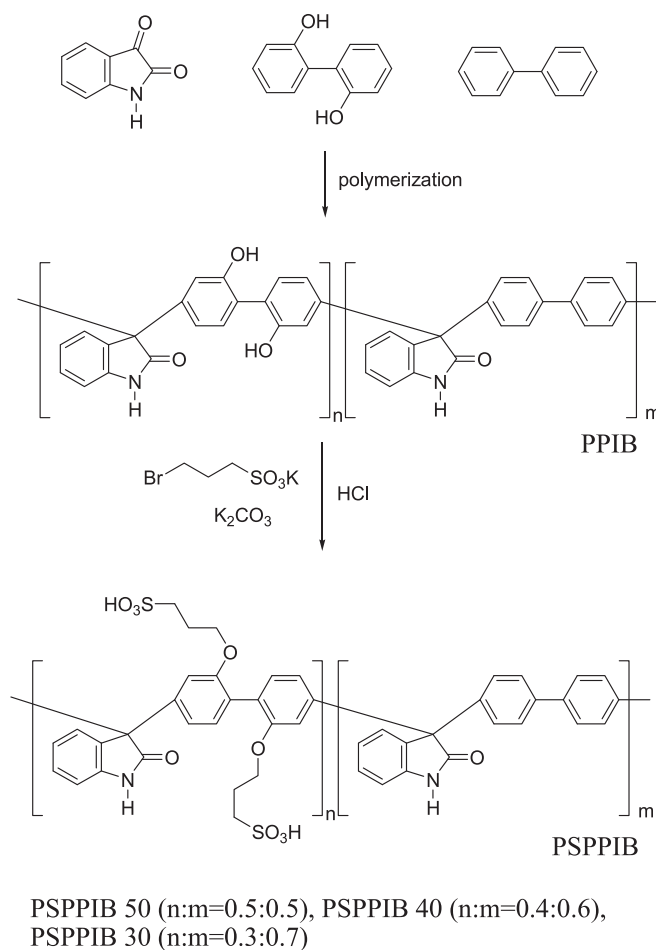
A typical polyhydroxyalkylation procedure follows (Scheme 1). To a 100 mL two-necked round-bottomed flask equipped with a mechanical stirrer and ice-bath. TFSA (15 mL) was added slowly to an ice-cooled mixture of isatin (2.00 g, 13.6 mmol), biphenyl (1.05 g, 6.8 mmol), 2,2'-biphenol (1.27 g, 6.8 mmol), trifluoroacetic acid (8.8 mL) and MC (1.2 mL). After addition, ice bath was removed. Thereafter, the temperature was raised to 20 °C over a period of 30 min and reaction was continued at this temperature for 15 h to afford a highly viscous solution was obtained. The resulting mixture was poured slowly into methanol. The precipitate, white fibrous polymer was filtered and washing with MC, methanol, and water. After that, polymer was dried in vacuum oven at 80 °C for 24 h. After drying, white fibre like polymer was obtained. 1H NMR (400 MHz; $DMSO-d_6$): 6.62–7.32 ppm (ph-H, 2H), 10.27 ppm (s, ph-OH, 2H), 10.57 ppm (s, N-H, 2H).

2.3. Synthesis of potassium 3-bromopropane-1-sulfonate (BPSK)

1,3-Propanesultone (35.1 mL, 400 mmol) was added to a solution of potassium bromide (400 mmol, 47.6 g) in water (700 mL), and heated to 60 °C. After the sultone completely dissolved (about 10 min), the water was removed via distillation. The crude residue was washed with cold ethanol (2×50 mL). The crude solid was recrystallized from 3:1 EtOH/ H_2O , giving BPSK as a white crystalline solid with a yield of 51%. 1H NMR (400 MHz; $DMSO-d_6$): 1.68–1.81 ppm (m, $CH_2-CH_2-CH_2$, 2H), 2.51–2.60 ppm (t, CH_2-CH_2-Br , 2H), 3.37–3.45 ppm (t, $CH_2-CH_2-SO_3K$, 2H).

2.4. Pendant sulfonation of PPIB (PSPPIB 50)

A typical alkylation procedure follows (Scheme 1). To a 100 mL three-neck round bottom flask, fitted with dean-stark trap, condenser, nitrogen inlet/outlet, and magnetic stirrer. Synthesized polymer (1 g, 3.34 mmol), excess amount of BPSK (1.61 g, 6.68 mmol), potassium carbonate (0.92 g 6.68 mmol), toluene and DMAc (10 mL) were charged. The mixture was refluxed for 3 h at 130 °C. After the produced water was azeotroped off with toluene,



Scheme 1. Synthesis of PSPPIB.

the mixture was heated at 160–180 °C for about 2 h. After reaction, reaction mixture was diluted three more times with DMAc, and then the viscous solution was slowly poured into 0.5 M hydrochloric acid aqueous solution and stirred vigorously. The polymer was washed in water several times and dried in 60 °C vacuum oven. 1H NMR (400 MHz; $DMSO-d_6$): 2.59 ppm (m, $CH_2-CH_2-CH_2$, 2H), 3.30 ppm (t, $S-CH_2-CH_2$, 2H), 3.85 ppm (t, $O-CH_2-CH_2$, 2H), 6.95–7.35 ppm (ph-H, 2H), 10.52 ppm (s, N-H, 2H).

2.5. Accelerated chemical membrane degradation

Membrane degradation was studied by immersion in Fenton reagent (4 ppm Fe^{2+} , 3% H_2O_2) at 75 °C. Samples were PSPPIB 50 membrane, linear sulfonated poly(ether sulfone)s (S-PES 40 (Fig. 5), and Nafion 211[®]). The initial sample weight was measured and the samples were put in to the solution of iron (II) sulfate heptahydrate in MilliQ water (45 mL) and heat to 75 °C, and 5 mL of 30% H_2O_2 added to this solution. The membrane samples were taken out regularly during the experiment for weighing. Washing the sample in distilled water quenched the degradation reaction and the exposed membranes were dried before the final weight was determined [37–39].

2.6. Membrane preparation and characterization

Membranes (25 μm) were prepared by the dissolution of the polymer in DMSO to afford 20 wt% transparent solutions and

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