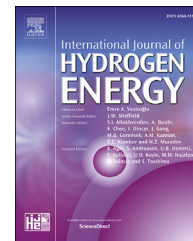




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# Comparative study of sulfonated branched and linear poly(phenylene)s polymer electrolyte membranes for fuel cells

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## ABSTRACT

Branched and linear sulfonated poly(phenylene)s (BSPs and LSPs, respectively) polymer electrolyte membranes (PEMs) containing benzophenone moiety were successfully synthesized and the performance of the LSPs and BSPs were compared in conjunction with Nafion 211<sup>®</sup>. The LSPs and BSPs were synthesized by the C–C coupling polymerization reaction between 1,4-dichloro-2,5-dibenzoylbenzene (PBP) and 1,4-dichloro-2-benzoylbenzene, and from PBP, 1,4-dichloro-2-benzoylbenzene, and 1,3,5-trichlorobenzene (branching agent), respectively. The degree of sulfonation in both LSPs and BSPs were controlled by varying the concentrations of chlorosulfonic acid and the structures of the resultant PEMs were confirmed by <sup>1</sup>H-NMR spectroscopy. The optimal LSP (LSP-2) and BSP (BSP-2) PEMs showed excellent chemical stability due to the absence of ether linkages in the polymer backbone, while the BSP-2 exhibited better proton conductivity (94.6 mS/cm under 90% relative humidity at 80 °C), water resistivity, and lower dimensional changes compared to the LSP-2, which is comparable to Nafion 211<sup>®</sup>. The maximum power density for BSP-2 and LSP-2 were 0.60 and 0.49 W/cm<sup>2</sup>, respectively, while it was 0.62 W/cm<sup>2</sup> for Nafion 211<sup>®</sup>. Membrane properties were studied with regard to ion exchange capacity, dimensional stability, proton conductivity, thermogravimetric analysis, and water uptake. The surface morphology of membranes was also analyzed by atomic force microscope.

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## Introduction

From the last few decades, fuel consumption and environment pollution have been key issues in the modern scientific research world. For this reason, researchers are giving focus to study in different sectors such as electric transportation, environmental friendly behavior, and factors of environmental pollution [1]. Recently, proton exchange membrane

fuel cells (PEMFCs) have attracted potential interest as an efficient and alternative energy sources to limited fossil fuel resources, which directly transform chemical energy into electrical energy with high efficiency, high power density, and less emission of environmental pollutants [2,3]. The PEMFC device plays an important role as an effective energy transformation system for portable, stationary power generation, and transportation applications [4,5]. The major components of PEMFC are proton exchange membrane (PEM), electro-

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catalyst, and porous gas diffusion electrodes. Among them, PEM is the key part, which conducts  $H^+$  ions from the anode to the cathode. The conductivity of  $H^+$  ions controls the rate of redox reaction at the anode and cathode, which ultimately affects the efficiency of the cell. Up to now, Dupont's Nafion, a perfluorosulfonic acid based PEM showed the highest  $H^+$  ions conductivity (104.50 mS/cm at 80 °C under 90% relative humidity (RH)) as well as cell efficiency [6]. Furthermore, Nafion PEM based fuel cell exhibited excellent physical, chemical, electrochemical, and thermal stability, and high life time (>56,000 h) [7,8]. Nevertheless, the industrial application of Nafion membranes based fuel cell is limited owing to its high price, long process of manufacturing, methanol crossover, low operation temperature ( $\leq 80$  °C), and recycling problem [9]. Thus, the improvement of Nafion properties as well as finding its alternatives based on non-fluorinated ionomers have been the key issues of research during the past decade.

Accordingly, extensive research has been demonstrated to develop the alternatives of Nafion membrane based on linear, branched, and cross-linked sulfonated/non-sulfonated aromatic hydrocarbon polymers and their derivatives with/without ether linkage including poly(phenylene ether)s [10], sulfonated poly(arylene ether)s [11–13], sulfonated poly(phenylene) [14,15], sulfonated poly(ether ketone)s [16,17], poly(arylene ether)s [18,19], disulfonated poly(arylene ether sulfone) [20], and poly(*p*-phenylene)s [21]. Recently, alternative membrane materials for PEMFCs have been extensively investigated such as sulfonated poly(*p*-phenylene)s, and poly(*para*-phenylene disulfonic acid) aromatic hydrocarbon polymers (without ether linkage). Shuqing et al. [22] prepared poly(*p*-phenylene)s polymer, which shows good proton conductivity with the value of  $3.4 \times 10^{-1}$  S/cm at 120 °C that is almost 2–3 times higher than that of Nafion and have excellent oxidative, mechanical stability, due to their fully aromatic structure extending through the backbone and pendent groups. Kun et al. [23] also synthesized water insoluble poly(*para*-phenylene disulfonic acid) copolymers. These polymers exhibited proton conductivity as much as ten times higher than that of Nafion<sup>®</sup> 212, at elevated temperature and low relative humidity. Particularly, branched sulfonated polymers (BSP) exhibited better proton conductivity and high ion exchange capacity (IEC) compared to linear sulfonated polymers (LSP), which is due to the formation of unique three-dimensional (3D) network by interconnected hydrophilic sulfonic acid groups ( $-SO_3H$ ) [24]. Nevertheless, the degree of sulfonation is significantly important in both LSP and BSP, since the high ratio of sulfonation tends to decrease the mechanical and water resistance, which ultimately decrease the life time of the cell [25]. Thus, controlling the degree of sulfonation and the introduction of hydrophobic non-sulfonated segments in the BSP backbone has been under intense investigation to increase the mechanical stability, water resistivity, and the life time of PEMs without sacrificing the proton conductivity and IEC. Furthermore, the ratio of hydrophobic branched backbone in the BSP controls the solubility of PEMs in organic solvents. It was reported that the optimal ratio of branching agent was  $\leq 0.4\%$  [25]. Hence, a wide variety of BSP containing hydrophilic and hydrophobic segments with optimized branching ratios and their phase separated structures have been reported [26–29]. For example,

Lee et al. [30] developed a highly sulfonated poly(phenylene sulfide nitrile) (XESPSN) random network copolymers, which exhibited reduced water uptake (WU) and dimensional swelling, improved mechanical, and oxidative stability due to the 3D network formation. Furthermore, the XESPSN exhibited 160% higher proton conductivity than that of Nafion 212<sup>®</sup> at 80 °C and 50% RH, which corroborated significantly high power density in fuel cells than that of Nafion 212<sup>®</sup> under partially hydrated environments. Surprisingly, in fuel cell research, it is difficult to find out a complete investigation on LSP and BSP as well as their physical and chemical properties in conjunction with Nafion by controlling ratio of sulfonation along with branching segment.

In this research, we have synthesized a series of non-fluorinated LSPs and BSPs without ether linkage containing benzophenone moiety by the dechlorination of 1,4-dichloro-2,5-dibenzoylbenzene (PBP), 1,4-dichloro-2-benzoylbenzene, and 1,3,5-trichlorobenzene (as branching agent) followed by C–C bonded coupling reaction, where chlorosulfuric acid functioned as a sulfonating precursor. The ratio of the sulfonation in both LSP and BSP were varied by controlling the amount of chlorosulfuric acid. The membranes were characterized by <sup>1</sup>H NMR spectroscopy. The thermogravimetric analysis (TGA) 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, proton conductivity, mechanical stability, and maximum power density. The results revealed that the BSP (BSP-2) with the optimal ratio of sulfonation and branching agent is better than optimal LSP (LSP-2) as PEMs.

## Experimental

### Materials

Pyridine, zinc powder (Zn), benzene, nickel bromide (NiBr<sub>2</sub>), thionyl chloride (SOCl<sub>2</sub>), dimethylacetamide (DMAc), triphenylphosphine (PPh<sub>3</sub>), chlorosulfuric acid, 2,5-dichloro-*p*-xylene, and potassium permanganate (KMnO<sub>4</sub>) were purchased from Sigma-Aldrich (St. Louis, MO, USA). 1,4-dichloro-2-benzoylbenzene and 1,3,5-trichlorobenzene were procured from Alfa Aesar (Ward Hill, USA). *N*-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO), methylene chloride (MC), acetone, methanol, hexane, ethanol, and carbon disulfide (CS<sub>2</sub>) were obtained from Sigma-Aldrich and used as received without any additional purification.

### Synthesis of 1,4-dichloro-2,5-dibenzoylbenzene (PBP)

The monomer PBP was synthesized by sequential reactions of oxidation, chlorination, and Friedel-Crafts acylation as shown in Scheme 1. In the first step, 2,5-dichloroterephthalic acid was synthesized by reacting a mixture solution of KMnO<sub>4</sub> (109 g, 0.69 mol), pyridine (324 mL, 4.0 mol), and 2,5-dichloro-*p*-xylene (20 g, 0.114 mol) in 100 mL distilled water in a round bottom flask at 90 °C for 12 h. Then, the hot mixture solution was filtered and the pH of the filtrate was adjusted to 1 by the addition of 36% HCl solution, which allows the precipitation of 2,5-dichloroterephthalic acid. The

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