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Preparation and characterization of sulfonated poly(phenylene)s membranes containing conjugated moiety via nickel catalyzed carbon–carbon coupling polymerization

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ABSTRACT

A series of sulfonated polyphenylene membranes (SPBCDPEs) containing conjugated tetraphenylethylene moieties were synthesized via Ni(0) catalyzed polymerization, and subsequent sulfonation with concentrated sulfuric acid. These membranes showed improved performance in ion exchange capacity, water uptake, proton conductivity, and thermal stability over Nafion 211[®] membranes. The membranes' thermal properties were investigated by thermo-gravimetric analysis (TGA) and also surface morphologies were assessed by atomic force microscope (AFM). SPBCDPEs may have applications as fuel cell membranes due to excellent proton conductivity.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising to the future of energy due to high power densities, efficiencies, and eco-friendliness [1]. Commercial perfluorinated copolymer membranes, such as Nafion[®] and Flemion[®] have good chemical, mechanical stability, and proton conductivity at relative humidity (RH) and low temperature [2]. However, perfluorosulfonic acid polymers have some drawbacks, such

as limited operation temperatures (0 °C–80 °C), high cost, and high methanol crossover. Hydrocarbon polymeric proton-conducting materials may be an interesting solution due to low cost and high performance [3–6]. A number of polymer families, such as polyphosphazenes [7,8], polybenzimidazole [9], poly(ether sulfone)s, and poly(ether ketone)s [10–14], have been used to prepare membranes for fuel cell applications. These polymers have received much attention because of high thermal, oxidative, chemical stability in fuel cell environments, as well as performance similar to Nafion membranes

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[15,16]. However, the chemical stability is not comparable to Nafion, specifically due to ether linkages with acid functional groups which may be attacked by hydrogen peroxide or peroxide radicals generated during PEMFC operation [17]. This research focused on polyphenylene structure without ether linkages, and leveraged advantages such as such as robust durability, high performance, amorphous thermoplasticity, thermooxidative stability, excellent chemical and physical properties, and good solubility [18].

This work demonstrates the synthesis of polyphenylene without ether moieties by Ni(0) catalyzed polymerization and the subsequent sulfonation reaction was controlled by varying the mole ratio of BCDPE monomers in synthesized copolymer. The BCDPE consisted of a 4:6 ratio of cis and trans isomers. Conjugated cis/trans BCDPE has a non-planar conformation containing four peripheral aromatic rings to facilitate π - π interactions. Moreover, polymers with pendant benzoyl groups are known to have advantages such as good solubility, durability, and thermooxidative stability [19,20]. The proposed polymer membranes, without ether linkages, demonstrated good chemical stability, proton conductivity, and solubility in aprotic organic solvents. Polymer membranes were studied by ^1H NMR spectroscopy, thermogravimetric analysis, water uptake, ion exchange capacity, proton conductivity, and atomic force microscopy (AFM).

Experimental

Materials

Nickel bromide, zinc dust, triphenylphosphine, hydrogen chloride, and sulfuric acid were purchased from Sigma–Aldrich, and TCI; used as received. Commercial grade dimethylacetamide (DMAc) was dried over calcium hydride and distilled prior to use. Other common solvents (like acetone, dichloromethane, methanol, tetrahydrofuran, and dimethylsulfoxide etc.) were used without any further purification. 2,5-Dichlorobenzophenone and cis/trans bis(4-chlorophenyl)-1,2-diphenylethylene were purchased from IS Chem Co., Korea.

Synthesis of polyphenylenes containing bis(4-chlorophenyl)-1,2-diphenylethylene (PBCDPE)

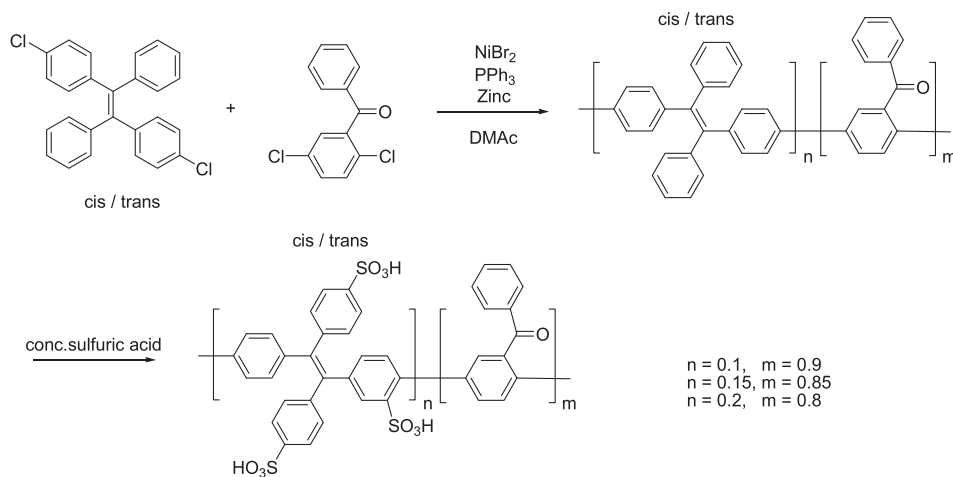
The polymers were synthesized as shown in Scheme 1. Nickel bromide (0.18 g, 0.81 mmol), zinc (3.2 g, 48.89 mmol) and triphenylphosphine (1.71 g, 6.52 mmol) were dissolved in dry DMAc (7 mL) under nitrogen atmosphere. Catalyst mixture was stirred at 80 °C for 30 min and became dark-red in color. Thereafter, a solution of monomers of BCDPE (0.56 g, 1.41 mmol) and 2,5-dichlorobenzophenone (2 g, 7.96 mmol) in dry DMAc (6 mL) were added via syringe into the catalyst flask under a vigorous flow of nitrogen. The mixture was stirred at 90 °C for 12 h to produce a highly viscous solution, and diluted with DMAc. This mixture was poured into a 10% HCl aqueous solution. Crude polymer was filtered, washed methanol, and dried in at 70 °C. Finally, polymer was dissolved in DMAc, reprecipitated in 10% HCl aqueous solution to give PBCDPE. The inherent viscosity (η_{inh}) of polymer was 0.61 for NMP. FT-IR: 3100 (aromatic C–H), 2950–2850 (–CH₃ stretch), 1630–1670 (C=O), 1600–1475 (aromatic C=C).

Synthesis of sulfonated PBCDPE(SPBCDPE)

To a 50 mL flask, 0.5 g of PBCDPE polymer and 12 mL of concentrated sulfuric acid were added and the mixture was stirred at 40 °C for 24 h. The mixture was then poured into deionized water. The polymer was thoroughly washed several times with deionized water until the residual water was pH neutral and dried in vacuum oven at 80 °C for 24 h to afford SPBCDPE. FT-IR: 3600–3400 (–OH), 3100 (aromatic C–H), 2950–2850 (–CH₃ stretch), 1630–1670 (C=O), 1600–1475 (aromatic C=C), 1350 & 1150 (S=O).

Characterization of membranes

Membranes (25 μm) were prepared by the redissolution of the polymer in DMSO to afford 20 wt% transparent solutions and casting of the solutions at elevating temperatures of 60 °C, 80 °C, 100 °C, and 120 °C. The ^1H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer using DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as an internal standard and



Scheme 1 – Synthesis of SPBCDPEs.

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