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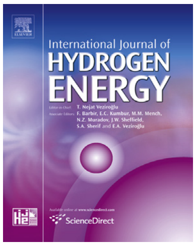

Studies of sulfonated polyphenylene containing fluorine moiety via nickel catalyzed C–C coupling polymerization

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ABSTRACT

The synthesis of polyphenylenes containing fluorine moiety (PPTF), their functionalization with sulfonic acid groups, and the measurement of apposite parameters for PEMs are described. The polymers were prepared by Ni-catalyzed carbon–carbon coupling reaction of -(2,2,2-trifluoro-1-phenylethylidene)-bis(4-chlorobenzene) (TFPECB) and 2,5-dichlorobenzophenone, followed by sulfonation reaction with chlorosulfuric acid. These polymers have all carbon–carbon linkages without any ether linkage on the polymer backbone, which was not attacked by nucleophiles (H_2O, hydrogen peroxide, hydroxide anion and radical), and sulfuric acid groups were selectively attached to the side phenyl rings of the TFPECB unit. A series of membranes was studied by ^1H NMR spectroscopy, ion exchange capacity (IEC), water uptake, and proton conductivity. The membranes' degradation was tested with Fenton reagent and compared with normal sulfonated poly(ether sulfone)s and Nafion.

Introduction

Proton exchange membrane fuel cell (PEMFC) technology has potential as a renewable energy source in the upcoming hydrogen economy owing to its high efficiency, high energy density, quiet operation, and environmental friendliness [1]. But, recent PEMs have been based on Nafion, a perfluorosulfonic acid polymer developed by Walther Grot of DuPont. Nafion generally exhibits good chemical stability and proton conductivity at high relative humidity (RH) and low temperature [2,3]. However, it has some drawbacks such as limited operation temperature (0–80 °C) due to low Tg, as well as high cost and high fuel permeability. This has stimulated research focused on hydrocarbon polymeric proton-conducting materials with low cost and high performance [4–8].

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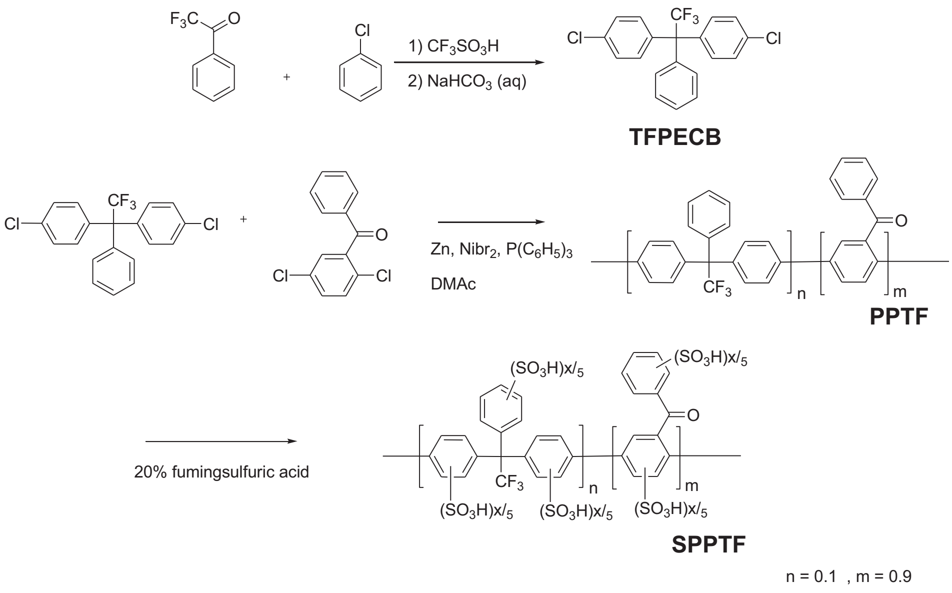

Scheme 1 – Preparation of monomer and polymers.

To overcome these obstacles, polymer families such as polyphosphazenes [9,10], polybenzimidazole [11], poly(ether sulfone)s, and poly(ether ketone)s [6,12–17] have been 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 have good thermal stability and performance close to that of Nafion [18–20]. However, their chemical stability does not approach that of Nafion, because of their structure with acid functional groups attached on the main chain, and ether linkages that are possibly attacked by nucleophiles [11,21]. So, we focused on polyphenylene structure without an ether linkage. Polyphenylene containing pendant benzoyl groups has great advantages, such as good durability, high-performance amorphous thermoplastic characteristics, thermooxidative stability, excellent chemical and physical properties, and good solubility [22,23]. A fluorine moiety with alkyl linkages is included for stability and flexibility.

This research is an attempt to synthesize polyphenylene without ether and with fluorine moieties by Ni(0) catalyzed polymerization. The sulfonation reaction was randomly done on phenyl groups of polymer. The proposed polymer membranes have fluorine moiety and no ether linkage structure, and they are promising for good chemically stability and proton conductivity. The polymer membranes are easily soluble in aprotic organic solvents. The polymer membranes were studied by ^{1}H NMR spectroscopy, thermogravimetric analysis (TGA), water uptake, ion exchange capacity (IEC), Fenton test, proton conductivity, and cell performance.

Experimental

Materials

2,2,2-Trifluoroacetophenone, chlorosulfuric acid, chlorobenzene, trifluoromethanesulfonic acid (TFSA), sodium bicarbonate, sodium chloride, silica gel 60, sodium sulfate anhydrous, zinc-dust, nickel bromide, triphenylphosphine, hydrogen chloride, fuming-sulfuric acid, and 2,5-dichlorobenzophenone were purchased from Aldrich, TCI, and Wako pure chemicals, and were used as received. Commercial-grade dimethylacetamide (DMAc) was dried over calcium hydride and distilled prior to use. Other common solvents (dichloromethane, methanol, ethyl acetate, hexane, etc.) were also used without any further purification.

Synthesis of (2,2,2-trifluoro-1-phenylethylidene) - bis(4-chlorobenzene) (TFPECB)

A typical hydroalkylation procedure is shown in Scheme 1. TFSA (26.9 g, 177.6 mmol) was added slowly to an ice-cooled mixture of 2,2,2-trifluoroacetophenone (7.0 g, 39.5 mmol) and chlorobenzene (11.1 g, 98.7 mmol) in a 100-mL two-necked round-bottomed flask equipped with a mechanical stirrer and ice-bath. After the addition, the ice bath was removed. Thereafter, the temperature was raised to 20 °C over a period of 30 min, and the reaction was continued at this temperature for 24 h. The reaction was quenched with the addition of an aqueous solution of sodium bicarbonate, and the organic layer was extracted with dichloromethane. Then, combined organic layers were washed with a saturated brine solution and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the resultant was purified by silica gel column chromatography using n-hexane and ethyl acetate. Synthesized TFPECB was dried in an 80 °C vacuum oven for 24 h. The product was attained as a white powder with a melting point of 93–94 °C.

Synthesis of polyphenylenes containing fluorine moiety (PPTF)

In a typical polymerization, zinc (2.6 g, 39.8 mmol), nickel bromide (0.3 g, 1.3 mmol), and triphenylphosphine (3.4 g,