



The sulfonated poly(phenylene) membranes containing multi-phenylrings prepared by nickel catalyst



Hohyoun Jang^a, Taehoon Hong^a, Jiho Yoo^a, Jaeseung Pyo^a, Jaeseong Ha^a, Chaekyun Lee^a, Kunyoung Choi^a, Taewook Ryu^a, Whangi Kim^a, Heung-Seok Jeon^{b,*}

^a Department of Applied Chemistry, Konkuk University, Chungju 380-701, Republic of Korea

^b Department of Computer Engineering, Konkuk University, Chungju 380-701, Republic of Korea

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ABSTRACT

The poly(phenylene)s containing multi-pendant phenyl were prepared by Ni-catalyzed reaction of 1,2-bis(4-chlorobenzoyl)-3,4,5,6-tetraphenylbenzene and 1,4-dichloro-2,5-dibenzoylbenzene. 1,4-Dichloro-2,5-dibenzoylbenzene is very reactive moiety to increase high molecular weight. These polymers without any ether linkages on polymer backbone were presumably stable against nucleophilic attack by hydrogen peroxide, hydroxide anion, and radical generated in PEMFC operation system. The phenyl rings on side chain were selectively sulfonated, but phenyl rings on main chain were deactivated by strong electron-withdrawing groups and steric hindrance. The structure of membranes was studied by ¹H NMR spectroscopy and properties were measured by ion exchange capacity, water uptake, Fenton test and proton conductivity.

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Introduction

Over the few years, proton exchange membrane fuel cells (PEMFCs) are focused on great interests due to their attractive technologies for their high energy efficiency and pro-environment [1,2]. The polymer membrane is one of key components of PEMFC and influence the performance and durability of fuel cell system [3]. Generally, commercial membranes, Nafion[®] and Flemion[®] which are perfluorinated copolymer membranes, are used to PEM materials because they have good chemical, mechanical stability, and high proton conductivity [4–6]. However, the demerit of the perfluorosulfonic acid polymers, such as high methanol permeability and low operation temperature (<100 °C) disrupt their applications [7–9]. In recent years, researcher's interest about aromatic hydrocarbon polymer materials with degrees of sulfonation [10–12]. Wang et al. [13] reported the correlation between dimensional stability and proton conductivity of polymer membranes are important factor, because mechanical properties of polymer are shown good or poor according to the sulfonation level. However, the chemical stabilities of ether sulfone polymers are unapproachable to Nafion, because of ether linkage with acid functional groups was

easily attacked by nucleophiles at operating PEMFC system [14]. In order to redeem the fault, many researcher, Ghassemi and co-workers [15], Zhang and co-workers [16], Linivin and co-workers [17], Si and co-workers [18] were studied carbon-carbon coupling reaction with metal catalyst. Chemical degradation of membranes is considered as a major concern for fuel cell performance. To improve the long term stability, the carbon-carbon backbone structured polymers were studied. Generally, sulfonated poly(p-phenylene)s were synthesized by Ni(0)-catalyzed coupling copolymerization and Diels-Alder polymerization [19–22]. These carbon-carbon backbone based polymer membranes have excellent chemical stability and good performances. Specially, polymer membranes containing benzoyl groups on monomer unit have a great of advantages, such as good durability, high ion conductivity, thermooxidative stability, excellent chemical, and physical properties as well. Moreover, Parmax is one of commercially useful inventions containing side benzoyl group. It affects the surface properties including the surface morphology and other properties [15,23]. The sulfonic acid groups on the pendant phenyl rings in polymer side chain were showed a well phase-separated morphology compared to the sulfonic acid on phenyl ring of main chain. These membranes have good chemical and mechanical properties compared with generally hydrocarbon membrane [24–27].

Our research group has studied polymer structures without ether linkage using nickel catalyst [20–22]. But this work was difficult to

* Corresponding author. Tel.: +82 43 840 3621.
E-mail address: hsjeon@kku.ac.kr (H.-S. Jeon).

enhance its molecular weight and form random unit. This research is an attempt to institute monomer, 1,4-dichloro-2,5-dibenzoylbenzene, which has a symmetrical structure and excellent reactivity due to electron-withdrawing group along with chlorine [21]. In this article, we have synthesized polyphenylene without ether group by Ni/Zn catalyzed polymerization with multi pendant phenyl rings and benzoyl moieties. The sulfonation reaction was controlled by chlorosulfuric acid and reaction time. The introduced multi pendant phenyl rings effect on the improvement of morphology and properties. Moreover, polymers with pendant benzoyl group improve molecular weight due to symmetrical monomer and have some advantages, such as good solubility, durability and thermo-oxidative stability [10,15–18]. The proposed polymer membranes containing no-ether linkage, multi-phenyl, and benzoyl structures were desirable monomer units to good chemical stability, morphology, and proton conductivity. Polymer membranes were studied by ^1H NMR spectroscopy, thermogravimetric analysis, water uptake, ion exchange capacity, proton conductivity, and also by the investigation of atomic force microscopic (AFM) images.

Experimental

Materials

1,2-Bis(dichlorobenzoyl)-3,4,5,6-tetraphenylbenzene and 2,5-dichloro-1,4-dibenzoylbenzene was synthesized as reported previously [24,28]. 2,5-dichloro-p-xylene, potassium permanganate, pyridine, thionyl chloride, aluminum chloride, fumaryl chloride, chlorobenzene, tetraphenylcyclopentadiene, triethylamine, bromine, dimethyl acetamide, nickel bromide, triphenylphosphine, zinc dust, hydrogen chloride, and chlorosulfuric acid were purchased from Sigma-Aldrich and TCI. DMAc and DMSO was dried over calcium hydride and distilled prior to use. Common solvents, such as toluene, acetone, carbon disulfide, dichloromethane, and methanol were used without any further purification.

Preparation of polyphenylene tetraphenyl benzophenone (PPTPB)

In a typical polymerization procedure (Scheme 1), dried DMAc (5 mL) was poured into to a three-neck 100 mL flask under nitrogen atmosphere. Under the flow of nitrogen atmosphere, zinc-dust

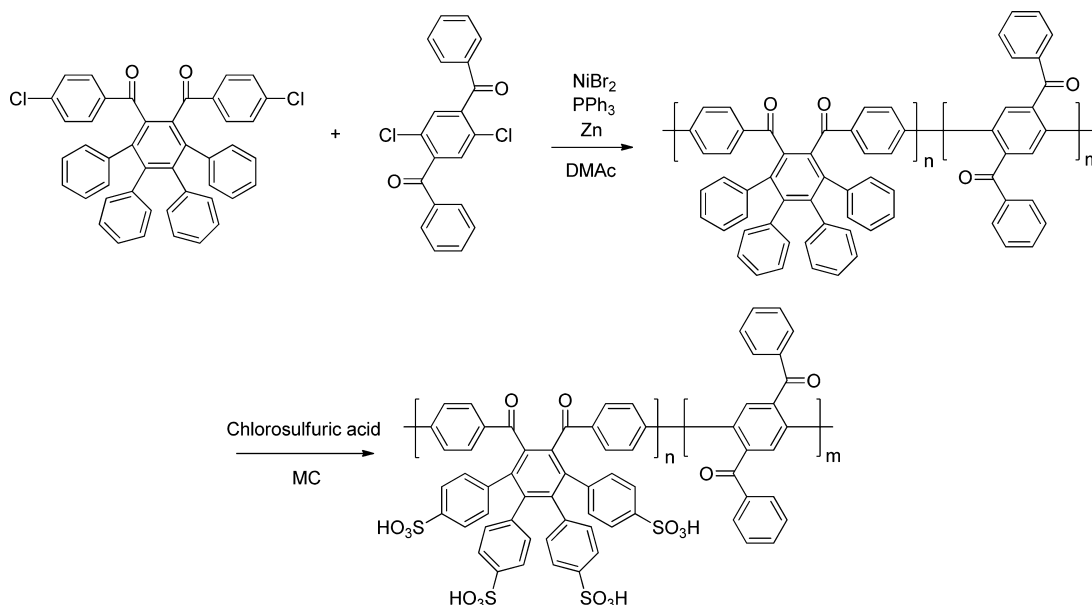
(2.7 g, 41 mmol), nickel bromide (0.15 g, 69 mmol), and triphenylphosphine (1.45 g, 5.5 mmol) were added into solution. The mixture was stirred at 80 °C for 15 min and became dark-red in color. Thereafter, a solution of 1,2-bis(4-chlorobenzoyl)-3,4,5,6-tetraphenylbenzene (1 g, 1.5 mmol) and 1,4-dichloro-2,5-dibenzoylbenzene (2.15 g, 6.1 mmol) in dried DMAc (20 mL) were added via a syringe under nitrogen condition. The mixture was reacted at 110 °C for 12 h until highly viscous solution came out. After the reaction, the solution was diluted with DMAc, and then the solution was poured into a 10% HCl aqueous solution. The obtained polymer was filtered, washed methanol, and dried in at 80 °C. Polymer was washed several time in the same way for remove residual catalyst, and dried at 80 °C in a vacuum oven.

Synthesis of sulfonated PPTPB (SPPTPB)

Chlorosulfonic acid (0.47 mL) in dichloromethane (3 mL) solution was added into a solution of copolymer (0.5 g) in dichloromethane (10 mL) at 0 °C. After added chlorosulfonic acid, the reaction was maintained for 3 h at room temperature. The solution was slowly poured into water giving fibrous precipitate. The precipitate was washed with deionized water for several times to remove residual acid until neutral condition. The polymer was dried under vacuum oven at 80 °C for 24 h.

Characterization of membranes

Membranes (25 μm) were prepared by the 20 wt% filtrated polymer in DMSO to afford transparent film on a flat glass plate (5 cm \times 5 cm) through the ambient temperatures of 60, 80, 100, 120 °C. The ^1H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses were used Scinco TGA-N 1000 analyze under the condition of a heating rate of 10 °C min^{-1} , from 30 to 600 °C. The analysis was the dry and wet measurements of 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 water uptakes of membranes were measured by three samples, and calculated as the ratio of adsorbed water on the dry sample as follows; water uptake (%) = $[(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100$, where W_{wet} and W_{dry} are the weights of the wet and dry



Scheme 1. Synthesize of PPTPB and SPPTPB.

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