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Synthesis and investigation of random-structured ionomers with highly sulfonated multi-phenyl pendants for electrochemical applications

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ABSTRACT

Poly(*p*-phenylene)-based random copolymers with locally and densely sulfonated multi-phenyl pendants, which are promising candidates for hydrocarbon-based electrolyte membrane materials for fuel cells, were synthesized using Ni(0)-catalyzed cross-coupling polymerization. The synthesized ionomers, SPPFPB-o, showed outstanding dimensional changes and proton conductivity. The SPPFPB-5.5 membrane in particular had the highest ion exchange capacity (IEC) (2.58 meq/g) among the SPPFPB-o series. It exhibited smaller dimensional changes toward the in-plane direction (Δl) than that of the Nafion[®] 212 membrane, in spite of a higher water uptake (WU) value, which seemed to be derived from the rigid backbone structure. Moreover, the SPPFPB-5.5 membrane showed excellent fuel cell performance and long-term stability comparable or superior to those of Nafion[®] 212 under fully and partially hydrated conditions.

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1. Introduction

International interest in the development of sustainable and renewable energy technologies as alternatives for the current fossil fuel-based energy technologies has been increasing. Among a variety of candidate technologies, such as solar cells, wind power, hydropower, etc., fuel cells have been regarded as promising candidates due to their environmentally friendly characteristics, highly mature technology, and outstanding energy conversion ratio [1–4]. Polymer electrolyte membrane fuel cells (PEMFCs), a typical fuel cell technology, have been vigorously studied because they have a wide scope of application, from portable electronics (\sim W) such as mobile phones, laptop computers, etc., to motor vehicles (\sim kW) and energy plants (\sim MW).

PEMFCs are not only a green energy technology that generates electricity and water through a redox reaction of hydrogen and oxygen but also a core technology for practical utilization of hydrogen energy. Generally, proton exchange membranes (PEMs), a core component of PEMFCs, act not only as a proton conductor but also as a separator that divides the hydrogen fuel from the oxidant

in fuel cells [5,6].

Among various ionomers developed up to now, Nafion[®], a perfluorinated ionomer membrane, is the most widely used electrolyte membrane material in fuel cells owing to its high proton conductivity and mechanical/chemical stability [7]. However, well-known limitations such as high cost, high fuel permeability, restricted thermal stability, etc., hamper their practical application in PEMFCs [8–10]. Especially, the high cost of perfluorinated ionomers is a critical issue that needs to be resolved for widespread use of PEMFCs. This limitation has resulted in increased attention toward developing alternative ionomer materials with low cost, high performance, and high stability. Many candidate ionomers, including Nafion[®]-modified ionomers [11–15], partially fluorinated ionomers [16–20], and hydrocarbon-based ionomers [21–25], have been used in development of practical electrolyte membrane materials in PEMFCs for several decades. Among them, hydrocarbon-based ionomers have been considered as the most effective solution toward low-cost materials. Nevertheless, hydrocarbon-based ionomers have many drawbacks, such as low proton conductivity and large dimensional variation. Accordingly, a variety of structural concepts such as crosslinked copolymers [26–28] and block copolymers [29–35] have been investigated to address the drawbacks of hydrocarbon-based ionomers.

The crosslinking process has been regarded as a valuable

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method for improving mechanical and dimensional stability. However, typically, proton conductivity and fuel cell performance continuously decrease as the degree of crosslinking increases due to the consumption of functional groups or a decrease of backbone mobility during the crosslinking reaction. Additionally, a high degree of crosslinking interrupts the fabrication of high-quality membranes.

In contrast to crosslinking, the synthesis of hydrocarbon-based blocks or multi-block structured ionomers are efficient methods to improve proton conductivity and membrane durability by inducing effective nanoscale phase separation between the hydrophilic and hydrophobic domains. Nonetheless, these strategies also might not be ultimate solutions for the fabrication of practical polymer electrolyte membranes because of synthetic problems. In other words, the complicated synthetic roots of block copolymers not only obstruct large-scale polymerization but also increase the cost of the electrolyte membrane. Moreover, because purification of monomers and oligomers is difficult, the synthesis of high molecular weight copolymers is challenging. On the other hand, random copolymers have simple synthetic roots, the synthetic process is inexpensive, and adjusting the molecular weight is simple. Thus, if it is possible to improve the electrochemical and morphological properties through a structural supplement, it is expected that the development of random-structured ionomers would be the best choice for alternative ionomer materials.

In this study, we present a promising candidate ionomer material for PEMFCs with a rigid poly(*p*-phenylene)-based backbone and locally and densely sulfonated multi-phenylene pendant groups. It is expected that the rigid poly(*p*-phenylene) structure would lead to an increase of hydrolysis and oxidation stability due to the high bond dissociation energy between phenyl groups, as well as a decrease of dimensional variation [36,37]. For last two decades, poly(*p*-phenylene)-based multi-block copolymers have been investigated for their excellent oxidative stability and outstanding electrochemical property [38–45]. In particular, since Goto et al. have developed multi-block copolymer membranes consisting of sulfonated poly(*p*-phenylene) and poly(arylene ketone) as hydrophilic and hydrophobic segments, respectively, sulfonated poly(*p*-phenylene)-based ionomers have been drawing great attention as promising polymer electrolyte materials for fuel cell [46]. A CF₃ group is introduced to improve the hydrophobicity, which should enhance the nanoscale phase separation between the hydrophilic and hydrophobic domains. In order to compensate for the disadvantages of random copolymers, densely and locally sulfonated multi-phenyl pendant groups are also introduced via a nucleophilic substitution reaction because this strategy can typically induce block-like nanoscale phase-separated morphology. According to these synthetic strategies, we synthesized five proton conduction polymers, which are denoted as SPPFPB-o, through a Ni(O)-catalyzed cross-coupling reaction, and the properties were compared with those of Nafion[®] 212.

2. Experimental

2.1. Materials

2,5-Dichlorobenzotrifluoride (DCBTF), nickel bromide (NiBr₂), triphenylphosphine (TPP), and zinc were purchased from Sigma Aldrich. DCBTF was used without further purification. TPP was purified by recrystallization from *n*-hexane and completely dried under vacuum prior to use. Zinc was stirred into 1.0 M hydrogen chloride in diethyl ether for 5 min, followed by washing with anhydrous diethyl ether and drying at 110 °C under vacuum using an Abderhalden drying apparatus. Potassium carbonate (K₂CO₃) was purchased from Sigma Aldrich and dried at 80 °C before

polymerization. 2,5-Dichlorobenzoyl chloride (2,5-DCBC) was bought from TCI Chemical. 2,5-Dichlorobenzophenone (2,5-DCBP), 2,5-dichloro-4'-fluorobenzophenone (2,5-DCFBP), and 1-(4-hydroxyphenyl)-2,3,4,5,6-pentaphenyl benzene (HPPPB) were synthesized according to a previously reported method [47–49]. All other reagents were used as received.

2.1.1. 2,5-Dichlorobenzophenone (2,5-DCBP)

In a round-bottomed flask, 2,5-dichlorobenzoyl chloride (150 g, 0.716 mol) was added to excess benzene, and then anhydrous AlCl₃ (95.488 g, 0.716 mol) was added to the solution at 0 °C. After stirring for 3 h, the temperature was increased to room temperature and the reaction was allowed to proceed for 24 h. The evolved hydrogen chloride was collected in a water gas trap. The reaction mixture was poured into 2 L of 10% hydrochloric acid in ice water. The crude product was decolorized with activated charcoal and recrystallized from ethanol to obtain 151.028 g of 2,5-DCBP (yield: 84%). ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 7.77 (s, 1H), 7.74 (m, 2H), 7.73–7.69 (m, 1H), 7.67 (m, 2H), 7.61–7.59 (d, 1H), 7.59–7.56 (d, 1H). ¹³C-NMR (75 MHz, DMSO-*d*₆) δ (ppm): 193.00, 139.74, 135.26, 134.45, 132.23, 131.53, 131.41, 129.65, 129.11, 128.51, 128.33.

2.1.2. 2,5-Dichloro-4'-fluorobenzophenone (2,5-DCFBP)

A solution of anhydrous AlCl₃ (31.831 g, 0.238 mol), nitromethane (80 mL), and excess fluorobenzene (33.5 mL) were introduced into a round-bottomed flask equipped with a dropping funnel, a magnetic bar, and a gas inlet and outlet at 0 °C. 2,5-Dichlorobenzoyl chloride (50 g, 0.238 mol) was added dropwise to the reaction solution. The reaction was held at room temperature under argon atmosphere for 24 h. The hydrogen chloride that evolved was collected in a water gas trap. The reaction mixture was poured into 2 L of 10% hydrochloric acid in ice water. The precipitate was collected by suction filtration, decolorized with activated charcoal, and recrystallized from *n*-hexane and ethyl acetate (4:1). The white crystal was dried under vacuum at room temperature for 24 h to obtain 48.03 g 2,5-DCFBP (yield: 75%). ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 7.83 (d, 2H), 7.41 (m, 2H), 7.35 (d, 1H), 7.15 (d, 2H). ¹³C-NMR (75 MHz, DMSO-*d*₆) δ (ppm): 192.1, 166.3, 139.6, 133.0, 132.8, 132.3, 131.3, 131.2, 129.4, 128.8, 116.0.

2.1.3. 1-(4-hydroxyphenyl)-2,3,4,5,6-pentaphenylbenzene (HPPPB)

A 1 M BBr₃ solution in dichloromethane (27.635 mL, 27.635 mmol) was added dropwise to a solution of 1-(4-methoxyphenyl)-2,3,4,5,6-pentaphenylbenzene (14.187 g, 25.123 mmol) in dichloromethane (200 mL) at –78 °C under argon atmosphere. After stirring for 3 h, the resulting mixture was warmed to room temperature slowly over a period of 16 h with continuous stirring. The reaction product was poured into water (200 mL), and the dichloromethane was removed from the product in vacuum. The white precipitate was washed with water and dried in vacuum at 40 °C for 24 h. The crude product was recrystallized from acetone and tetrahydrofuran (THF) to obtain 12.6 g of HPPPB as white crystals. ¹H-NMR (300 MHz, DMSO-*d*₆) δ (ppm): 8.65 (s, H), 6.88–6.78 (m, 25H), 6.66 (d, 2H), 6.21 (d, 2H). ¹³C-NMR (75 MHz, DMSO-*d*₆) δ (ppm): 140.8–139.4, 131.7, 130.8, 126.1, 124.9, 113.4.

2.1.4. Typical synthesis of PPF-o

Two fully dried 250 mL three-necked flasks were prepared. In one flask, DCBP, DCFBP, and DCBTF were completely dissolved in anhydrous DMAc. After degassing the solution, the resulting solution was heated in an oil bath to 80 °C. The other flask was charged with NiBr₂ (0.07 eq. to DCBP, DCFBP, and DCBTF), TPP (7 eq. to NiBr₂), zinc (60 eq. to NiBr₂), and DMAc. The mixture was heated in an oil bath to 80 °C with continuous stirring. The color of the catalyst mixture changed from yellowish-brown to blood-red. After the appearance of the blood-red color of the catalyst, a

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