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Multiblock copolymers based on poly(*p*-phenylene)-co-poly(arylene ether sulfone ketone) with sulfonated multiphenyl pendant groups for polymer electrolyte fuel cell (PEMFC) application

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ABSTRACT

Proton-conducting multiblock copolymer materials (sPPm-*b*-PAES-x) with a densely and locally sulfonated multiphenyl pendant group were investigated. The sPPm-*b*-PAES-x membranes exhibited proton conductivities comparable to or better than that of Nafion 212 in the hydrated state. The sPPm-*b*-PAES-16.6 and the sPPm-*b*-PAES-22 membranes showed outstanding PEM fuel cell performance at 80 °C under conditions of 100% relative humidity. In particular, the sPPm-*b*-PAES-22 membranes exhibited very high current density (around 1800 mA/cm^2 at 0.6 V). Among the synthesized polymers, sPPm-*b*-PAES-16.6 showed reasonable dimensional change and well-developed nanoscale phase separation morphology; the proton conductivity and cell performance were comparable to those of Nafion 212, with a promising maximum power density of 0.8 W/cm^2.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has received considerable attention owing to its high energy efficiency [1,2]. Polymer electrolyte membranes (PEMs) essentially act as a proton transport medium and as a separator of fuel and oxidant in PEMFCs. Thus, polymer electrolyte membrane materials that meet the requirements of good proton conductivity, processibility, oxidative stability, and low material cost are in demand for practical applications [3–6].

Nafion, an archetypal perfluorinated polymer, is considered as the state-of-the-art membrane because of its high chemical stability and high proton conductivity under a wide humidity range at moderate operating temperatures [7,8]. Nevertheless, the Nafion membrane suffers from general disadvantages such as high cost, high fuel permeability, and a low mechanical modulus. The Nafion membrane has a tendency to dehydrate above 80 °C, leading to lowered conductivity which is highly detrimental. Thus, it fails to meet the current industrial demands which call for high operating temperatures [9,10].

Over the last decade, extensive research effort has been directed toward developing alternative membranes based on sulfonated hydrocarbon polymers to address the limitations of Nafion [11,12]. Among these polymers, sulfonated poly(arylene ether sulfone)s (SPAESs) have been extensively investigated as membrane materials because of their

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excellent mechanical strength, high thermal/chemical stability, generally excellent solubility, and membrane-forming properties, in combination with the availability of commercial monomers and polymers [13]. However, sulfonated statistical copolymers are generally characterized by low proton conductivity and a high degree of dimensional change derived from the poor connectivity (percolation) of the proton-conducting hydrated phase domain, combined with significant retardation of the water diffusion [14].

Recently, several research groups have focused on PEMs based on sulfonated poly(*p*-phenylene)s (sPP) and their derivatives. This type of polymer may be synthesized simply using a Ni(0)-catalyzed cross-coupling reaction [15,16]. The stiff and rod-like chemical structure of the polymers confers exceptionally good mechanical toughness and chemical stability to the polymer. Moreover, the flexible hydrophobic poly(arylene ether) block gives rise to a nanophase-separated morphology [17–20].

In this study, we report the synthesis of multiblock copolymers (sPPm-*b*-PAES-x) for proton exchange membrane materials by means of Ni(0)-catalyzed coupling polymerization. sPP and poly(arylene ether sulfone ketone) (PAESK) were introduced as hydrophilic and hydrophobic segments, respectively. Sulfone and ketone groups were introduced in hydrophobic block in order to ward off electrophilic substitution attack of sulfonic acid group by improving electron deficient property of hydrophobic chain. Moreover, sulfonated multiphenyl pendant side groups were introduced in order to improve the solubility and nanophase separation between the hydrophilic sulfonic acid-containing regions and the hydrophobic polymer main chain [21,22]. The physical properties, morphology, and PEMFC performance of these polymers is presented herein.

2. Experimental

2.1. Materials

4,4′-Dihydroxybenzophenone (4,4′-DHBP), potassium carbonate (K_2CO_3), *N*,*N*-dimethylacetamide (DMAc), anhydrous toluene, 4,4′-dichlorodiphenylsulfone (4,4′-DCDPS), 4,4′-dichlorobenzophenone (4,4′-DCBP), reagent grade anhydrous $NiBr_2$, and chlorosulfonic acid (99%) were purchased from Aldrich and used without further purification unless otherwise noted. Zinc dust (Aldrich) was stirred with 2 M HCl for 5 min, filtered, then washed with ethyl ether and dried under vacuum. Triphenylphosphine (PPh_3) was purified by recrystallization from *n*-hexane. 4-(2′,3′,4′,5′,6′-Pentakis-phenylbenzen)phenol (sexyphenylene-OH) was prepared as described in the literature [23]. 2,5-Dichloro-4′-fluorobenzophenone (2,5-DCFBP) and 2,5-dichlorobenzophenone (2,5-DCBP) were prepared as described in the literature [24,25].

2.1.1. Poly(arylene ether sulfone) functional oligomer (PAES-oligomer-10K)

The desired hydroxyl-terminated poly(arylene ether sulfone) (PAES-OH) (targeted $M_n = 10{,}000$) was synthesized from 4,4′-DCDPS and 4,4′-DHBP. The PAES-OH oligomer was synthesized by using an excess of 4,4′-DHBP as the end-capping group. 4,4′-DHBP (8.00 g, 31.96 mmol) and DCDPS (8.38 g, 33.59 mmol) were added to a 300 mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and a Dean-Stark trap. K_2CO_3 (5.30 g, 38.35 mmol) was added and DMAc (120 mL) was introduced to produce a 13% (w/v) solid concentration. Toluene (50 mL) was used as an azeotropic agent. The reaction mixture was heated under reflux at 145 °C for 4 h to dry the system. The temperature was then slowly raised to 160 °C to distill off the toluene. The reaction was allowed to proceed at this temperature for another 24 h, and then at 175 °C for 12 h, during which it became viscous. Subsequently, Cl-substituted end groups were introduced by the addition of 4-chloro-4′-fluoro-benzophenone (0.90 g). The reaction mixture was cooled to room temperature and filtered without dilution to remove the salts. The oligomer was isolated by precipitation in methanol. The precipitate was filtered and washed several times with methanol, then carefully dried in a vacuum oven at 120 °C for 72 h. The yield was 98%.

2.1.2. Poly(p-phenylene)-based multiblock copolymer (polymer backbone) (PP-b-PAES-x)

2.1.2.1. PP-b-PAES-8. Zinc (3.56 g, 52.90 mmol), $NiBr_2$ (0.22 g, 1.71 mmol), and PPh_3 (1.79 g, 6.83 mmol) were combined in a previously flame-dried 100 mL four-necked flask equipped with an overhead stirrer. Addition of the catalyst mixture to the reaction flask was performed in a dry bag under argon atmosphere. The flask was then sealed with a septum and anhydrous DMAc (15 mL) was added using a syringe. The mixture was heated in an oil bath to 80 °C under Ar with continuous stirring. The color of the catalyst mixture changed from yellowish brown to deep green, and finally to blood red. After appearance of the blood-red color of the catalyst, a mixture of 2,5-DCBP (3.19 g, 12.73 mmol), 2,5-DCFBP (0.30 g, 1.12 mmol), and the PAES-oligomer (1.00 g, 0.60 mmol) dissolved in anhydrous DMAc (10 mL) were added to the flask using a syringe. The reaction was allowed to proceed for 8 h before precipitation into methanol containing 30% hydrochloric acid. After stirring for 3–4 h, the resulting yellow solid was filtered and washed several times with water and methanol before drying in a vacuum oven at 80 °C to afford the product in 96% yield. ^1H NMR (300 MHz, DMSO-d_6): 7.2–8.1 ppm.

2.1.2.2. PP-b-PAES-10.5. PP-*b*-PAES-10.5 was prepared using the same procedure as described above. The amounts of monomer and reagents used were: 2,5-DCBP (3.13 g, 12.49 mmol), 2,5-DCFBP (0.36 g, 1.14 mmol), and PAES-oligomer (1.00 g, 0.60 mmol). ^1H NMR (300 MHz, DMSO-d_6): 7.2–8.1 ppm.

2.1.2.3. PP-b-PAES-16.6. PP-*b*-PAES-16.6 was prepared using the same procedure as described above. The amounts of monomer and reagents used were: 2,5-DCBP (2.89 g, 11.54 mmol), 2,5-DCFBP (0.62 g, 2.31 mmol), and PAES-oligomer (1.00 g, 0.60 mmol). ^1H NMR (300 MHz, DMSO-d_6): 7.2–8.1 ppm.