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Sulfonated Polybenzophenone/Poly(arylene ether) Block Copolymer Membranes for Fuel Cell Applications

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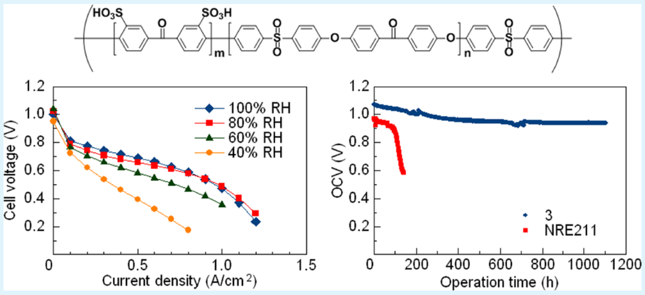
Supporting Information

ABSTRACT: Sulfonated polybenzophenone/poly(arylene ether) block copolymers were designed and synthesized via Ni-mediated coupling polymerization. The block copolymers were obtained as high-molecular-weight (M_n = 70−110 kDa, M_w = 150−230 kDa) with low polydispersity index (M_w/M_n = 2.0−2.3). The block copolymer membranes showed well-developed hydrophilic/hydrophobic phase separation and high proton conductivity and low gas permeability. The membrane showed better fuel cell performance and durability compared with those with Nafion, state-of-the-art proton conducting membrane.



KEYWORDS: *fuel cells, polymer electrolyte membranes, proton conduction, block copolymers, poly(benzophenone)s, poly(arylene ether)s*

INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have received much attention as alternative energy converting devices because of their high efficiency and environmental affinity. Major car companies have announced that they will commercialize fuel cell vehicles from 2015. For the development of advanced PEFCs, component materials, such as electrocatalysts, polymer electrolyte membranes (PEMs), and bipolar plates need improvement. With respect to PEMs, perfluorosulfonic acid (PFSA) ionomers such as Nafion are state-of-the-art; however, high cost, low glass-transition temperature, high gas permeability, and environmental incompatibility are issues for the PFSA membranes and would impede widespread commercialization of PEFCs. Therefore, alternative PEMs with no fluorine atoms are in great demand.

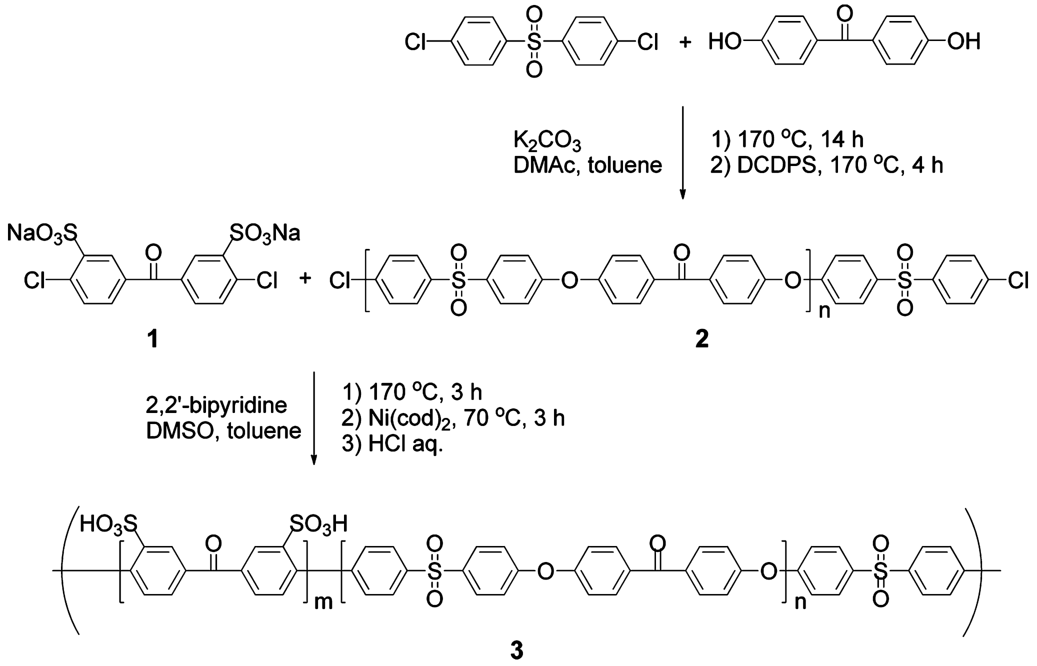
Hydrocarbon-based PEMs are attractive candidates because of their flexibility in molecular design and synthesis. Aromatic polymers such as poly(arylene ether sulfone)s,[1,2] poly(arylene ether ketone)s,[3,4] polyimides,[5,6] polyphenylene derivatives,[7,8] and others have been investigated as base skeletons for sulfonation. Block copolymers have been claimed to show improved proton conductivity compared with random copolymers.[9] Recently, we have reported a series of aromatic block copolymers composed of highly sulfonated fluorenyl groups in the hydrophilic blocks.[10,11] The block copolymer membranes contained high density of sulfonic acid groups in the hydrophilic component and showed unique phase-separated morphology with well-interconnected proton transport pathways. The membranes were highly proton conductive at high temperature (110 °C) and low relative humidity (30% relative humidity (RH)) and showed fuel cell performance comparable to that with a Nafion membrane.[12] The long-term stability of the membrane was tested under fuel cell operation at a constant current density of 200 mA/cm^2 at 80 °C and 53% RH for 2000 h. Although the post-test membrane retained ion exchange capacity (IEC), minor oxidative degradation occurred in the hydrophilic blocks. ^{1}H NMR and IR spectra suggested that the sulfonated fluorenyl groups and ether linkages were likely to experience oxidative degradation.[13] In this communication, we report advanced version of our sulfonated block copolymers, which contain sulfonated benzophenone units with no fluorene and ether groups. The electron-withdrawing carbonyl groups are expected to improve the oxidative stability and enhance the acidity of sulfonic acid groups attached onto the same phenylene rings. Synthesis and properties of the novel sulfonated block copolymer membranes are described.

RESULTS AND DISCUSSION

The hydrophilic monomer **1** was prepared by sulfonation of 4,4′-dichlorobenzophenone (see the Supporting Information). The chlorine-terminated telechelic hydrophobic oligomer **2** was synthesized by nucleophilic substitution polymerization of 4,4′-dihydroxybenzophenone and slight excess of 4,4′-dichlorodiphenylsulfone (Scheme 1). ^{1}H NMR spectrum of **2** confirmed its chemical structure (see Figure S2 in the Supporting Information). The degree of polymerization was estimated

Received: May 10, 2012
Accepted: June 12, 2012
Published: June 12, 2012

Scheme 1. Synthesis of Multiblock Copolymers 3



from the integral ratio in the ^{1}H NMR spectrum to be ca. 10.7, which was in fair agreement with the one (10) calculated from the feed monomer ratio. The molecular weight of **2** was determined by gel permeation chromatography (GPC) to be M_n = 7600 (M_w/M_n = 2.6). The degree of polymerization of **2** was then estimated from M_n to be 17.0, which was higher than those calculated from the monomer composition and the ^{1}H NMR spectrum probably due to the rigid rod-like structure of the main chain.

The block copolymer was synthesized from **1** and **2** by Ni-mediated coupling reaction. The block copolymerization completed within 3 h at 70 °C to give **3** as high-molecular-weight (M_n = 70-110 kDa, M_w = 150-230 kDa) with low polydispersity index (M_w/M_n = 2.0−2.3). Block copolymer **3** was soluble in polar aprotic solvents such as dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMAc), and were characterized by NMR spectra. In the ^{1}H NMR spectrum of **3** (see Figure S3 in the Supporting Information), the peaks at 7.60−7.75 and 8.30-8.40 ppm were assigned to the sulfonated benzophenone groups, and the peaks at 7.25, 7.81, and 8.00 ppm were assigned to the hydrophobic blocks. The results suggest successful formation of the targeted block copolymer. Two samples of **3** were prepared, of which ion exchange capacity (IEC) values were estimated to be 2.37 and 2.67 mequiv/g, respectively, from the integral ratios in the ^{1}H NMR spectra. Block copolymers **3** provided self-standing and bendable membranes by solution casting. The IEC values of the two membranes were also determined by titration to be 2.08 and 2.57 mequiv/g, respectively, which were in good agreement with the ones obtained from the NMR spectra.

Block copolymer **3** membranes showed well-developed hydrophilic/hydrophobic phase separation as confirmed by transmission electron microscopic (TEM) images with the samples in lead ion form. A typical TEM image is shown in Figure 1. The dark areas represent hydrophilic domains containing lead sulfonate groups. The hydrophilic domains were ca. 5−10 nm wide and interconnected. The phase separated morphology is similar to that of our previous block copolymers sharing the same hydrophobic blocks.[10,11] The results indicate that the hydrophilic components were sequenced to some extent although the hydrophilic monomer **1** was used for the copolymerization. A 3D TEM image was also taken (see the Supporting Information), which further confirmed the interconnectivity of the hydrophilic ionic domains.

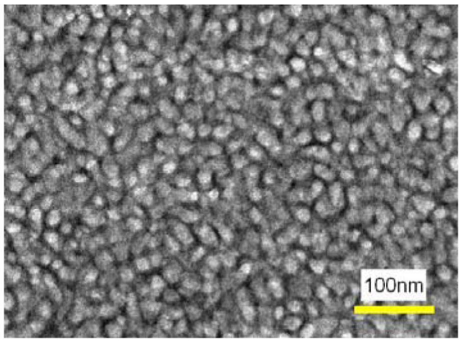


Figure 1. TEM image of **3** membrane (IEC = 2.57 mequiv/g) in lead ion form.

Figure 2 compares water uptake and proton conductivity of **3** and Nafion membranes at 80 °C as a function of relative humidity (RH). The **3** membranes showed higher water uptake than that of Nafion because of the formers' higher IEC values. The **3** membrane with higher IEC (2.57 mequiv/g) showed higher proton conductivity than that of Nafion at wide humidity range between 20 and 90% RH. The dimensional change of **3** membrane (IEC = 2.57 mequiv/g) was 22% (in-plane) and 53% (through-plane) in water at 25 °C. The conductivity of **3** membrane was 0.45 S/cm at 90% RH, which was 3.7 times higher than that of Nafion. The **3** membranes showed smaller humidity dependence of the proton conductivity compared with conventional aromatic sulfonated polymers. The conductivity of **3** membrane was 6.5 mS/cm at 20% RH and comparable to that of Nafion (5.9 mS/cm).

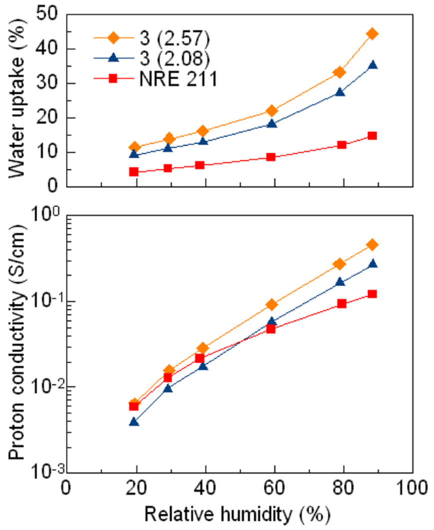


Figure 2. Water uptake and proton conductivity of **3** (orange diamond, IEC = 2.57; blue triangle, 2.08 mequiv/g) and Nafion NRE211 (red square, IEC = 0.92 mequiv/g) membranes. Error limits are ±0.7% (relative humidity), ±1.1% (water uptake), and ±2.0% (proton conductivity), respectively.

Highly acidic sulfonic acid groups, due to the presence of carbonyl groups attached on the same phenylene rings, would be responsible for the high proton conductivity at low humidity. The **3** membrane retained its high proton conductivity at higher temperature (100 and 120 °C) (see Figure S4 in the Supporting Information). It is noticeable that although the water uptake slightly decreased as increasing the temperature, the proton conductivity stayed nearly the same between 80 and 120 °C. It is considered that the lower water content is counteracted by the increased mobility of hydronium ions at higher temperature. In other words, **3** membrane could utilize water more efficiently at higher temperature.

Gas permeability of **3** membrane was much lower than that of Nafion (Figure 3). The O_2 and H_2 permeability of **3** membrane was 9 and 7 times lower than that of Nafion under dry (0% RH) conditions. It is noticeable that the O_2 and H_2 permeability of **3** membrane showed little dependence on the humidity despite its large water uptake at high humidity. The trend is different from our previous aromatic ionomer membranes with similar hydrophobic blocks[11] and from Nafion, in which gas permeability increases with the humidity. The rigid rodlike structure of the hydrophilic blocks is probably responsible for the low gas permeability of **3** membrane under humidified conditions.

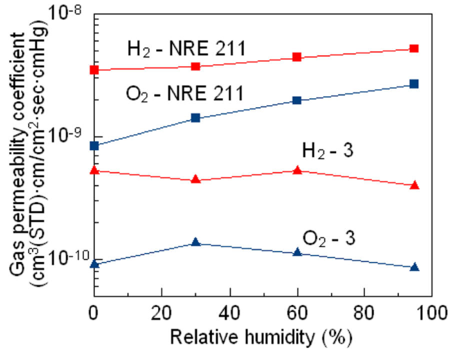


Figure 3. Humidity dependence of hydrogen and oxygen permeability coefficient of **3** (red and blue triangles, IEC = 2.57 mequiv/g) and Nafion NRE 211 (red and blue squares) membrane at 80 °C.

In Figure 4 are shown *E*′ (storage modulus), E” (loss modulus), and tan *δ* of **3** membrane. The **3** membrane showed higher *E*′ than 1 × 10^8 Pa at wide range of humidity. In the *E*″ and tan *δ* curves, obvious peaks were observed at ca. 60% RH, which might be ascribed to the glass transition. The results explain a significant increase in the water uptake of **3** membrane (IEC = 2.57 mequiv/g) above 60% RH in Figure 2.

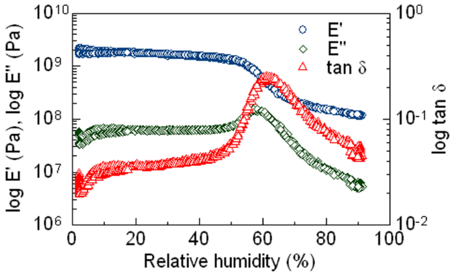


Figure 4. DMA analyses of **3** membrane (IEC = 2.57 mequiv/g); *E*′ (storage modulus), *E*″ (loss modulus), and tan *δ* as a function of RH at 80 °C.

The **3** membrane (IEC = 2.57 mequiv/g) was sandwiched by two gas diffusion electrodes and subjected to fuel cell operation with hydrogen and air at 80 °C (Figure 5). The open circuit voltage (OCV) was 0.95 V at 40% RH, 1.04 V at 60% RH, 1.02 V at 80% RH, and 1.00 V at 100% RH, suggesting that gas permeation through the membrane was negligible. Reasonably good fuel cell performance was obtained at high humidity (80 and 100% RH), however, the performance became worse with decreasing humidity because of the decreased proton conductivity. Nevertheless, humidity dependence of the fuel cell performance of **3** membrane was smaller than that of Nafion (see Figure S5 in the Supporting Information). The cell voltage at the current density of 0.5 A/cm² decreased from 0.69 V (100% RH) to 0.39 V (40% RH) for **3** membrane and from 0.70 V (100% RH) to 0.33 V (40% RH) for Nafion.

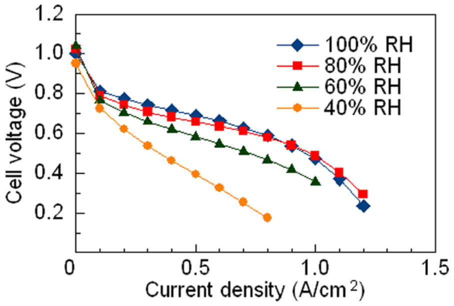


Figure 5. Steady state H_2/air fuel cell performance of **3** membrane (IEC = 2.57 mequiv/g) at 80 °C with humidification at 40, 60, 80, and 100% RH for both electrodes.

It is well-known that the holding the cell voltage at OCV under low humidity conditions accelerates membrane degradation because of the increased formation of hydrogen peroxide and the resulting oxidative radical species.[14,15] We have demonstrated the OCV test of **3** and Nafion membranes at 80 °C and 20% RH (Figure S6). The OCV was initially 1.07 V for **3** membrane and decreased slightly to 0.94 V after 1100 h.

Such high oxidative stability should be ascribed to the robust chemical structure of the hydrophilic component and the low gas permeability of **3** membrane. In contrast, Nafion was much less durable and the OCV decreased from 0.97 V to 0.60 V after 140 h under the same conditions.

■ CONCLUSIONS

We have designed and synthesized novel sulfonated polybenzophenone/poly(arylene ether) block copolymers via Ni-mediated coupling polymerization from the corresponding hydrophilic monomer and hydrophobic oligomer. The block copolymer **3** membranes showed well-developed hydrophilic/hydrophobic phase separation and high proton conductivity at high temperature. Good fuel cell performance was obtained. The humidity dependence of the fuel cell performance of **3** membrane was smaller than that of Nafion. The **3** membrane was durable in the OCV test at low humidity for 1100 h with minor losses in the cell voltage. Robust hydrophilic blocks and low gas permeability are considered to be responsible for such high oxidative stability of **3** membrane.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed preparation of monomer **1**, oligomer **2**, and block copolymer **3** and their NMR spectra. Temperature dependence of water uptake and proton conductivity of **3** membrane. Humidity dependence of steady state H_2/air fuel cell performance of Nafion NRE212CS membrane. Time cource of open circuit voltage (OCV) of a fuel cell with **3** and Nafion NRE211 membranes. 3D TEM image of **3** membrane in lead ion form. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO) through the HiPer-FC Project.

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