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Highly Conductive Aromatic Ionomers with Perfluorosulfonic Acid Side Chains for Elevated Temperature Fuel Cells

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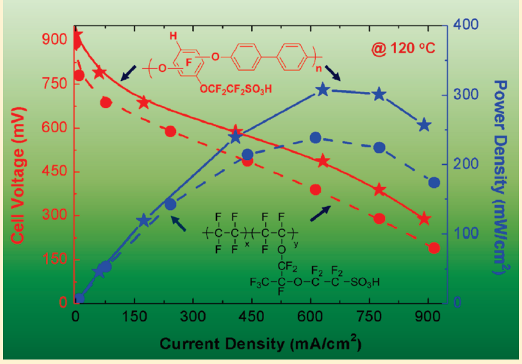
S Supporting Information

ABSTRACT: A versatile and facile synthetic approach to a new class of ionomers with rigid aromatic backbone and pendant perfluorinated sulfonic acid groups is described. Characterization of the prepared polymers has been carefully carried out by ^{1}H and ^{19}F NMR, elemental analysis, intrinsic viscosity, TGA and DSC. It is shown that the perfluorosulfonic acids greatly enhance the proton conductivity of ionomers under high temperature and low humidity conditions. The aromatic ionomers exhibit comparable proton conductivity to Nafion over a wide humidity range at elevated temperatures, while maintaining other outstanding properties of aromatic polymers, e.g. low gas permeability, excellent thermal and chemical stability and good mechanical properties. It is also demonstrated that the maximum power density and current density of the aromatic ionomers are 30% and 43% higher, respectively, than those of Nafion in initial fuel cell tests at 120 °C.



With combined advantages of low environment impact, high energy density and good conversion efficiency, polymer electrolyte membrane (PEM) fuel cells have been considered one of the next-generation power technologies for automotive, stationary, and portable applications.[1,2] PEMFC commercialization has been hampered by the lack of inexpensive, high performance PEM materials in spite of decades of intensive research.[3] Perfluorinated polymers, such as Nafion, so far stand as the state-of-the-art PEM materials.[4] These types of PEMs are highly proton conductive when hydrated and possess excellent chemically stability. However, Nafion suffers from some significant drawbacks including high synthesis and processing costs, modest thermal durability due to its relatively low glass transition temperature, and high gas permeability. Acid-functionalized aromatic hydrocarbon polymers have thus been extensively investigated as alternative membranes.[3,5] These polymers have rigid, aromatic backbones that confer high thermal stability, mechanical strength, and reasonable chemical durability. Most examples of aromatic ionomers rely on aryl or alkyl sulfonic acid groups to induce high proton conductivity in these materials; however, these moieties have lower acidity compared to superacidic groups such as perfluoroalkyl sulfonic acids. Therefore, rarely do aromatic ionomers show proton conductivity that competes with Nafion, particularly under conditions of high temperature and low humidity.[6] There are a number of attractive benefits associated with fuel cells operating in a low humidity and elevated temperature environment, including improved tolerance of the catalyst to carbon monoxide, simplification of the cooling system, possible use of cogenerated heat, and improved electrode reaction kinetics.[7] More recently, there are a few elegant studies on the introduction of perfluoroalkyl sulfonic acids into aromatic ionomers using the copper-catalyzed Ullmann coupling reaction.[8] However, none of these alternative membranes exhibited higher proton conductivity than Nafion at elevated temperatures and low humidities.

In this Communication, we describe the synthesis of a new series of aromatic ionomoers with perfluorinated sulfonic acid side chains and demonstrate comparable or even superior proton conductivity and fuel cell performance to Nafion under high temperature and low humidity conditions.

Scheme 1 illustrates our synthetic approach which involves the preparation of halogen-substituted aromatic monomers with perfluoroalkyl sulfonate groups and subsequent condensation polymerizations to afford polyaromatic ionomers. Attempts to generate similar aromatic polymers with fluorinated side chains generally involved postfunctionalization of aromatic polymers to attach perfluorosulfonate moieties via nucleophilic substitution or dehalogen coupling reactions,[8] allowing little control of the polymer structure and position of acid groups. The method reported herein provides facile synthetic access to a broad range of new aromatic ionomers with precisely designed chemical structures as illustrated in Scheme 1. Moreover, the structural characteristics of the aromatic ionomers can be readily tailored by adjusting monomer composition and polymerization conditions, which permits the optimization of molecular weight and acid concentration for PEM applications.

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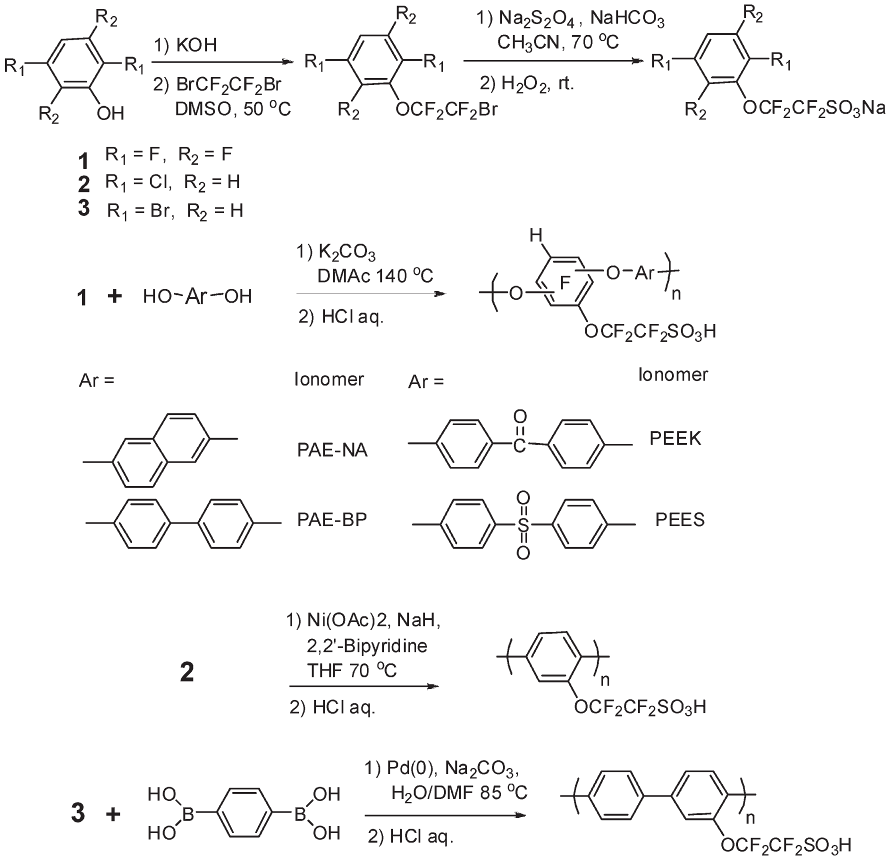
Scheme 1. Synthesis of the Monomers and Aromatic Polymers with Perfluoroalkyl Sulfonate Groups



As shown in Scheme 1, the monomer synthesis includes the nucleophilic substitution of 1,2-dibromotetrafluoroethane with phenols carrying halide groups and subsequent reduction reaction of perfluoro-alkyl bromide by sodium dithionite followed by oxidation with hydrogen peroxide to yield perfluorinated sulfonate groups.[9] The chemical structures of the intermediates and monomers were confirmed by NMR and elemental analysis. The overall synthetic route toward new monomers is facile, safe, and potentially low cost due to excluding the use of explosive chemicals as in the cases of monomer synthesis for Nafion and other perfluorosulfonate ionomers that employ tetrafluoroethylene.[4] On the basis of the monomers prepared in Scheme 1, various aromatic ionomers based on poly(arylene ether) (**PAE**), poly(ether ether ketone) (**PEEK**), poly(ether ether sulfone) (**PEES**) and poly(*p*-phenylene) backbones with pendant perfluorosulfonic acids can be synthesized. The focus of this Communication is on the ionomers with **PAE** backbones, including **PAE-NA** and **PAE-BP**, which were prepared from the polycondensation of monomer **1** with 2,6-dihydroxynaphthalene and 4,4′-biphenol, respectively, while the properties of the other ionomers will be reported elsewhere. The reaction conditions of polymerization were carefully controlled to avoid the formation of highly branched or cross-linked structures, since the phenyl ring of monomer **1** has four active fluorines that can undergo nucleophilic attack by phenolate group. Temperature was found to have essential control on the sequential fluorine-substitution process. While the first two fluorines on the phenyl ring were highly reactive and could be substituted below 145 °C, the remaining fluorines showed much lower reactivity and only reacted above 160 °C. This is presumably due to the loss of the activating effect of the two electron-withdrawing fluorines after substitution and the electron-donating effect from the newly formed ether oxygen. The chemical structures and compositions of the resulting polymers have been fully analyzed by NMR and elemental analysis (see the Supporting Information). For instance, as shown in Figure 1, the ^{19}F NMR spectrum of **PAE-BP** clearly featured multiple peaks between −125 and −160 ppm ascribed to two unsubstituted fluorines on the phenyl ring, and the integral ratio of the sum of these peaks to the $-CF_2-$ peak at −81 ppm is nearly to 1:1 as expected for the linear structures. Elemental analysis of **PAE-BP** revealed 22.8% F and 48.9% C, which are in good agreement with theoretical values of 23.1% and 48.7%, respectively. The aromatic ionomers are soluble in polar aprotic solvents such as DMF, NMP and DMAc.

As summarized in Table 1, **PAE-NA** and **PAE-BP** possess ion exchange capacities (IECs) of 2.09 and 1.96 mequiv/g, respectively. Ionomers with such high ionic content are typically water-soluble or swell excessively in water. High molecular weight polymers are thus desired to combat high swelling in water and provide mechanical support to accommodate high acid contents. Enabled by the active monomers, high molecular weights were obtained in the prepared polymers as indicated by their intrinsic viscosities of around 2.1−2.2 dL/g measured in DMAc/0.05 M LiBr at 25 °C. The thermal properties of these new ionomers were evaluated by DSC and TGA. It was found that the aromatic ionomers have considerably higher glass transition temperatures (T_g) than Nafion (∼110 °C), following a trend as **PAE-NA** (T_g: 142 °C) < **PAE-BP** (T_g: 160 °C). In addition, the ionomers

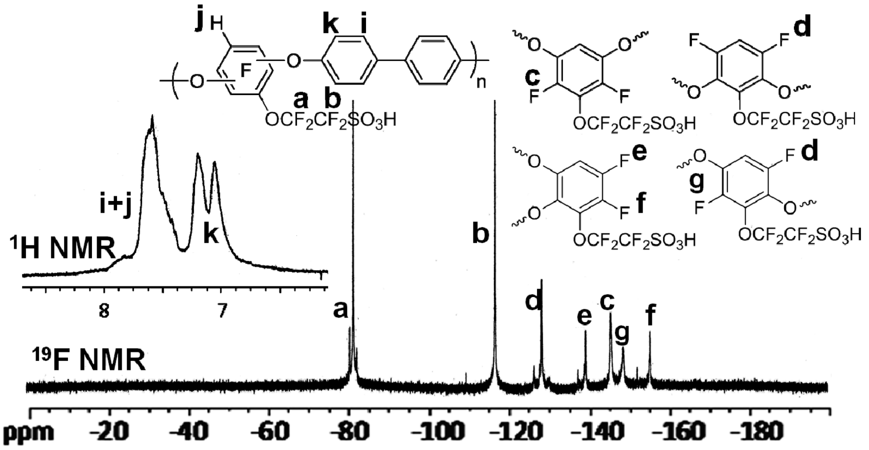


Figure 1. NMR spectra of ionomer **PAE-BP**.

Table 1. Water Uptake and Transport Properties of the Membranes

membrane	IEC [mequiv/g][a]	water uptake [wt %][b]	λ	proton conductivity [mS/cm][b]	proton diffusion coefficient [cm^2/s]
PAE-NA	2.09	45	14.6	107	1.18×10^{-5}
PAE-BP	1.96	28	7.9	89	1.01×10^{-5}
Nafion 115	0.91	29	17.7	83	1.51×10^{-5}

[a] Calculated from the elemental analysis. [b] Measured after equilibration with deionized water at 30 °C.

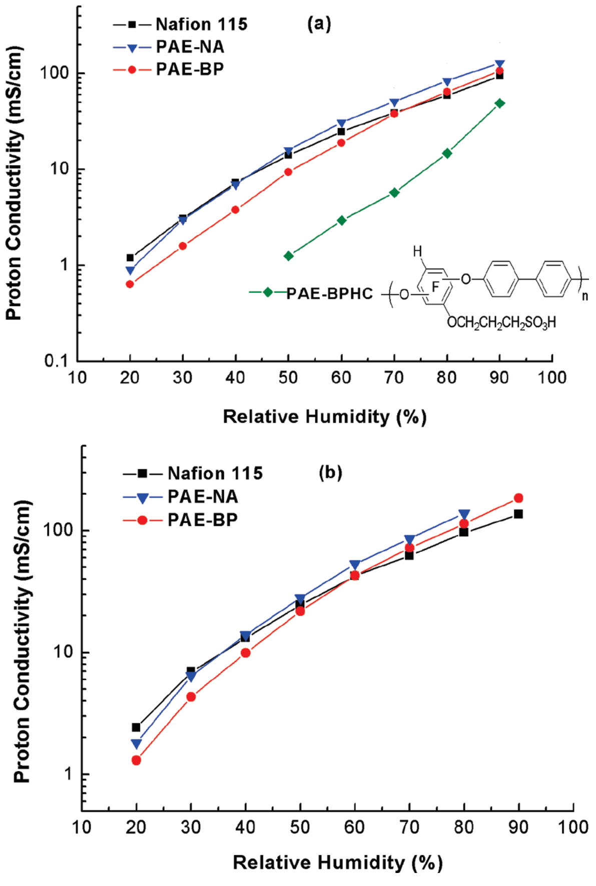


Figure 2. Humidity dependence of proton conductivity for the ionomer membranes at (a) 80 °C and (b) 120 °C.

showed excellent thermal stability as indicated by high degradation onset temperatures (T_d > 270 °C), which is requisite for elevated temperature applications. The chemical durability of the ionomers was examined in the hydrolytic and oxidative stability tests. Markedly, both **PAE-NA** and **PAE-BP** exhibited outstanding chemical resistance to the hydrolytic and oxidative conditions, and retained more than 95% of its original weight after the tests. The mechanical properties of ionomer membranes in both dry and hydrated states were investigated and are summarized in Table S1 (Supporting Information). It is worth mentioning that the **PAE-BP** membrane is a very tough and robust polymer film, showing high maximum strength (~34 MPa) and tensile modulus (~0.94 GPa) and reasonable elongation at break (~20%) in the hydrated state. The difference in the mechanical properties between the **PAE** ionomers presumably arises from the effect of the varied bisphenol monomer structure in the polymers, e.g. enhanced intramolecular interactions ($\pi-\pi$ stacking) between polymer main-chains and reduced water absorption by the presence of 4,4′-diphenoate in the polymer backbone in the case of **PAE-BP**.

The morphology of the lead acetate-stained membranes was probed by transmission electron microscopy (TEM). It was found that **PAE** membranes exhibited ionic clusters with relatively uniform size (ca. ~3 nm in diameter) that are markedly smaller than those observed in Nafion (see the Supporting Information).

Table 1 outlines the water uptake characteristics and transport properties of the fully hydrated ionomer membranes at 30 °C. Interestingly, Nafion 115 and **PAE-BP** absorbed a similar amount of water (~28 wt %), although **PAE-BP** has more than double the IEC. The relatively low hydration number (λ ~ 7.9) of **PAE-BP** gave comparable conductivity (89 mS/cm) to Nafion (83 mS/cm) in spite of its much higher IEC. On the other hand, **PAE-NA** displayed much higher proton conductivity of 107 mS/cm, in accordance with its high water uptake and IEC. High proton mobility in the aromatic ionomers is further substantiated by their high values of proton diffusion

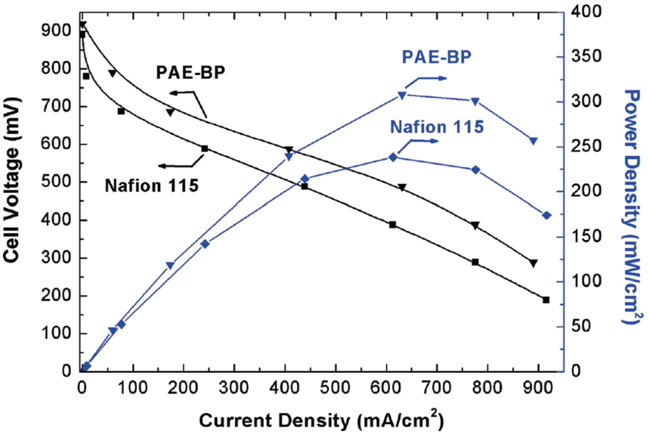


Figure 3. H_2/air fuel cell performance of **PAE-BP** and Nafion 115 at 120 °C with anode and cathode gas streams humidified to 80% RH.

coefficient ($>10^{-5}$ cm^2/s, Table 1), which are on a par with that of Nafion. The proton diffusion coefficient (D) was calculated by the following equation, $D = RT\sigma/F^2C(H^+)$, where R is the gas constant, T is the absolute temperature, σ is proton conductivity, F is the Faraday constant, and $C(H^+)$ is the concentration of the proton ions.[10]

The humidity dependence of proton conductivity was determined at 80 and 120 °C. As depicted in Figure 2, **PAE-BP** and **PAE-NA** possessed conductivities comparable (<50% RH) or superior (>50% RH) to Nafion 115. For instance, a proton conductivity of 116 mS/cm was measured for **PAE-BP** at 80% RH and 120 °C, while Nafion 115 showed a value of 95 mS/cm. For comparison, we also prepared and measured the conductivity of an aromatic ionomer with the same backbone as **PAE-BP** and hydrocarbon alkyl sulfonate side chain (**PAE-BPHC**, inset of Figure 2a). The proton conductivity of **PAE-BPHC** was almost 1 order of magnitude lower than the conductivity of the aromatic ionomers with perfluoroalkyl sulfonic acid groups and Nafion. Furthermore, the conductivity of **PAE-BPHC** declined precipitously with decreasing RH, which is a common trend for conventional aromatic ionomers.[2b,5] This observation further proves the benefit of perfluorosulfonic acid groups on the proton conduction of the ionomer membranes.

Membrane–electrode assemblies (MEAs) of these new aromatic ionomers are now under investigation to evaluate their potential application in hydrogen/air fuel cell devices at elevated temperatures. The initial fuel cell performance was tested at 120 °C with reactant gases humidified at 113 °C. To isolate only the effect of the membrane, MEAs of **PAE-BP** employed the Pt/C catalyst layers without using Nafion binders. Figure 3 presents the polarization and power density curves for **PAE-BP** and Nafion 115 membranes with similar thickness (~125 μm). Encouragingly, it was found that **PAE-BP** membrane outperformed Nafion under the test conditions. The maximum power density and current density at 0.5 V of **PAE-BP** were 30% and 43% higher, respectively, than those of Nafion. Another notable feature of the new aromatic membranes is their low gas permeability. The measured hydrogen crossover current density of 0.7 mA/cm^2 from **PAE-BP** was half that observed for Nafion 115 (1.6 mA/cm^2). Further work is ongoing to optimize MEA fabrication and evaluate the long-term performance of new ionomer membranes in elevated temperature fuel cells.

In summary, we have developed a versatile and facile approach for the preparation of a family of new ionomers with rigid aromatic backbones and pendant perfluoroalkyl sulfonic acid side groups. These ionomers exhibited comparable or even superior proton conductivity to Nafion over a wide humidity range at elevated temperatures, while maintaining other outstanding properties of aromatic polymers, e.g., high T_g, low gas permeability, excellent thermal and chemical stability, and good mechanical properties. The prepared membranes showed better performance than Nafion in initial fuel cell tests at 120 °C without any optimization, indicating the potential of the aromatic ionomers to meet the demands of elevated temperature PEM fuel cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details pertaining to the synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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