Macromolecules

Aromatic Ionomers with Highly Acidic Sulfonate Groups: Acidity, Hydration, and Proton Conductivity

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Supporting Information

ABSTRACT: A novel sulfonation method that involves iridiumcatalyzed aromatic C—H activation/borylation and subsequent Suzuki— Miyaura coupling with sulfonated phenyl bromides was developed for the preparation of aromatic ionomers. Superacidic fluoroalkyl sulfonic acid and less acidic aryl and alkyl sulfonic acids were efficiently incorporated into the aromatic ring of model polystyrene, and the resulting sulfonated ionomers were characterized for their properties as proton-conducting membranes. The membrane properties of ionomers containing sulfonic acid groups with different acidity strengths were compared to study the effect of acidity on the water properties, proton conductivity, and morphology. The superacidic fluoroalkyl sulfonated ionomer (sPS-S₁) exhibited a significantly higher proton conductivity than that of the less acidic aryl and alkyl sulfonated ionomers (sPS-S₂ and



 $sPS-S_3$, respectively) at low relative humidity, despite a lower ion exchange capacity and lower water uptake. Hydration behaviors of the ionomers as a function of relative humidity were studied to correlate the acid strength of the sulfonates and water uptake properties. Morphology studies of the sulfonated ionomers show that $sPS-S_1$ has a larger hydrophilic domain than that of $sPS-S_3$. Molecular dynamic simulations were performed to understand the origin of the improved proton conductivity of the superacidic ionomer at the molecular level. These simulations suggest that the enhanced proton conductivity of $sPS-S_1$ is due to the cumulative effect of higher acidity of the sulfonate, which leads to increased dissociation to hydronium ions and a higher degree of ionic character in the sulfonate, and better solvation of the sulfonate with water molecules.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are considered one of the most promising clean energy conversion technologies for alleviating environmental problems associated with burning fossil fuels.^{1–5} The proton exchange membrane (PEM), an important component of PEMFCs, functions as a proton conductor and separates hydrogen fuel from the oxidant in PEMFCs. State-of-the-art PEMFC technology currently relies on perfluorosulfonic acid (PFSA) membranes, such as Nafion.^{6,7} It is generally believed that the high proton conductivity of PFSAs in PEMFCs, especially at low relative humidity (RH), is related to the strong acidity of their perfluorosulfonic acid groups and a distinct nanoscale phase-separated morphology derived from extremely hydrophobic perfluorinated polymer backbone and flexible, hydrophilic fluoroalkyl sulfonic acid groups.^{2,3,7,8} Although Nafion has been the most commonly used PEM during recent decades, its properties need to be improved for broader fuel cell applications. The drawbacks of Nafion include its high cost, the rare availability of fluorine-containing precursors, high methanol permeability in direct methanol fuel cells, and poor mechanical stability at high temperatures (>100 °C). Furthermore, the lack of reactive sites in the perfluorinated structure of Nafion makes modifications to overcome these shortcomings difficult.

Compared with perfluorinated polymers, aromatic-based polymers are less expensive, more readily available, and easier to modify.¹ Considerable efforts have therefore been devoted to

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the development of aromatic PEMs as Nafion alternatives. Numerous examples of randomly sulfonated aromatic copolymers based on polybenzimidazoles,⁹ poly(ether ether ketone)s,¹⁰ poly(arylene ether sulfone)s,^{11–13} polyimides,^{14–16} and polyphenylenes¹⁷ have been prepared by either electrophilic postsulfonation of aromatic polymers or direct copolymerization of sulfonated monomers and investigated as alternative PEM materials. Some examples of aromatic PEMs show promising performance in fuel cell operations. However, these types of PEMs generally have achieved high proton conductivity only at fully hydrated conditions and their conductivities drop sharply when RH is decreased. Because PEMFC operation under reduced RH gives increased system efficiency, the development of PEMs that are highly conductive at reduced RH is critical for successful adoption of fuel cell technology in automobile transportation applications.⁴

Recently, studies of the relationship between morphology and proton conductivity have drawn considerable attention to increase proton conductivity at low RH in the design of new PEMs.^{18–25} Accordingly, sulfonated multiblock copolymers composed of hydrophilic and hydrophobic aromatic units have been investigated to provide continuous proton conduction pathways through self-assembled domain structures at low RH. Although multiblock copolymer ionomers can achieve enhanced proton conductivity at low RH in comparison to that of the corresponding randomly sulfonated ionomers, the conductivity at low RH has not reached the level needed for practical low RH PEMFC operations. Molecular weight control and sequence length of multiblock copolymer synthesis is also complicated, which hinders their widespread adoption.

In addition to unique nanoscale phase separation, another characteristic feature of PFSA ionomer is its strong acidity. Owing to the strong electron-withdrawing effect of fluorine, the fluorinated sulfonic acid in PFSA is an extremely acidic group (also called a superacid). Although accurate measurement of the strength of this group is difficult because reliable methods for assessing solid acids are lacking, the acidity range is expected to be similar to that of perfluoroalkyl sulfonic acid (approximate $pK_a =$ -14.1).²⁶ Except for a few recent examples of superacidic PEMs,²⁷⁻³⁴ most aromatic ionomers contain much less acidic aryl sulfonic acid or alkyl sulfonic acid groups as protonconducting moieties. Although those perfluoroalkyl-sulfonated (superacidic) aromatic ionomers have exhibited better proton conductivity at reduced RH compared with typical sulfonated aromatic PEMs, most superacidic ionomers are still restricted in their synthetic generality; when less efficient Ullmann coupling was used, low ion-exchange capacity (IEC; <1.5 mequiv/g) was obtained.²⁷⁻³¹ Importantly, there have been no comprehensive studies exploring the effect of acidity on fuel cell membrane properties, such as how increased acidity affects proton conductivity, morphology, and water transport behavior within a PEM.

Herein, we report a highly efficient synthetic method that allows the incorporation of fluoroalkyl, aryl, and alkyl-tethered sulfonate groups with various acidities into a model aromatic polymer and a detailed study of the effects of acidity on PEM properties, particularly its hydration and proton conductivity at low RH. Although polystyrene is not considered an ideal material for PEM application owing to its poor oxidative stability of the benzylic C-H bond,¹ we selected syndiotactic polystyrene (sPS) as the model PEM material for our study because of its simple chemical structure, which allows expeditious computational modeling and convenient spectroscopic characterization (see the Results and Discussion for details). By comparing the properties of aromatic PEMs with different acidity strengths, we sought to understand the relationship between the chemical structures of ionic groups and the property of PEMs at the molecular level. We also conducted molecular dynamics studies of the synthesized PEMs to more fully understand the mechanism underlying acid group interactions with water molecules within the membrane.

RESULTS AND DISCUSSION

A. Experimental Studies of sPS lonomers. Synthetic Strategy for Sulfonated lonomers. The synthesis of sulfonated sPS ionomers functionalized with different sulfonic acid groups is summarized in Scheme 1. The synthetic strategy is based on sequential reactions of (i) iridium-catalyzed borylation of the aromatic C-H bonds of sPS, (ii) palladium-catalyzed Suzuki-Miyaura cross-coupling reactions of borylated sPS (sPS-Bpin) with phenyl bromides that contain different sulfonate precursor groups $(S_1, S_2, S_3$ in Scheme 1), and (iii) removal of the protecting group from the sulfonates and subsequent acidification. Three examples of sulfonated sPS ionomers containing fluoroalkyl sulfonic acid ($sPS-S_1$), aryl sulfonic acid ($sPS-S_2$), and alkyl sulfonic acid $(sPS-S_3)$ were prepared using this synthetic method. Detailed synthetic procedures for ionomers and sulfonated phenyl bromides are described in the Experimental Section and the Supporting Information.

Synthesis of Sulfonated Phenyl Bromides. To introduce sulfonate groups with different acidity strengths into sPS via the Suzuki—Miyaura coupling reaction, we prepared three types of phenyl bromides functionalized with sulfonate groups: fluoroalkyl sulfonated S_1 , aryl sulfonated S_2 , and alkyl sulfonated S_3 (Scheme 2). All three sulfonated phenyl bromides were capped with a 3,5-dimethylphenol protecting group at the end and conveniently prepared from readily available chemicals in high yields using traditional organic synthetic methods.

Nucleophilic substitution reaction of 4-bromophenol with 1,2dibromotetrafluoroethane under basic conditions produces an ether covalent bond between oxygen and CF2CF2Br.35 The terminal bromide was converted first to its sodium sulfinate form $(-SO_2Na)$ via reaction with sodium dithionite and sodium bicarbonate and then to its sulfonyl chloride form $(-SO_2Cl)$ by bubbling chlorine. The sulfonyl chloride was transformed to 3,5dimethylphenol-protected sulfonate S1 via reaction with 3,5dimethylphenol in the presence of N,N-dimethylaminopyridine. Ring-opening of 1,3-propane sultone with 4-bromophenol under basic conditions, subsequent conversion of sodium sulfonate to sulfonyl chloride, and protection with 3,5-dimethylphenol afforded S₃ in good yield. S₂ was prepared from a condensation reaction of 4-bromobenzenesulfonyl chloride with 3,5-dimethylphenol in one step. All three protected sulfonates were air- and moisture-stable and could be stored under ambient conditions.

Synthesis and Characterization of Sulfonated Polymers. We recently reported a highly effective borylation of aromatic polymers using bis(pinacolato)diboron (B_2pin_2) as a borylation reagent in the iridium-catalyzed activation of aromatic C–H bonds.^{36,37} Because sPS gives a ¹H NMR spectrum that is more finely resolved than that of atactic polystyrene, owing to the high stereoregularity of the phenyl rings along the polymer main chain (see Figure 1a), we chose sPS for postfunctionalization in this study. The iridium-catalyzed borylation substitutes aromatic C–H bonds to C–B bonds under mild conditions while tolerating various functional groups.^{38,39} As reported elsewhere,³⁶ the

Scheme 1. Synthesis of Syndiotactic Polystyrene Ionomers Functionalized with Different Sulfonic Acid Groups^a



^{*a*} Reagents and conditions: (i) B_2pin_2 , [IrCl(COD)]₂ (1.5 mol %), dtbpy (3 mol %), cyclooctane, 150 °C, 6 h; (ii) S_1 , S_2 , or S_3 (2 equiv), Pd(PPh₃)₄ (4 mol %), K_3PO_4 (4.5 equiv), THF/H₂O (10/1), 80 °C, 12 h; (iii) NaOH (8 equiv), dioxane/H₂O, 100 °C, 4 h; and (iv) 1 M H₂SO₄.





C–H borylation of sPS [weight-average molecular weight (M_w) = 140.9 kg/mol; polydispersity index (M_w/M_n) = 2.90] was conducted in cyclooctane solvent at high temperature (150 °C).

After borylation of the polymer, a new proton signal corresponding to the four methyl groups of the pinacolboronic ester (Bpin) appeared at 1.16 ppm (Figure 1b). Integrals of the resonances of methylene at 1.49 ppm and methine at 2.09 ppm in the sPS main chain maintained a ratio of 2:1 in the ¹H NMR spectrum, suggesting that the main-chain structure of sPS remained intact during the borylation. Thus, the molar concentration of the attached Bpin group in the borylated polymer was estimated by comparing the resonance integrals of the methyl group at 1.16 ppm and the methine proton of the polymer main chain at 2.09 ppm. The incorporated Bpin concentration was well controlled up to ~50 mol % simply by changing the loading amount of B_2pin_2 relative to the polymer repeating unit. In this work, we focused on borylated sPS with 40 mol % Bpin concentration.

The palladium-catalyzed Suzuki—Miyaura cross-coupling reaction of aryl boron compounds and aryl halides⁴⁰ has been a powerful method for biaryl C–C bond formation because of its high efficiency and good tolerance of functional groups. Thus, we conducted Suzuki—Miyaura coupling reactions of the borylated polymer with sulfonated phenyl bromides (S₁, S₂, and S₃ in Scheme 1) to incorporate the corresponding sulfonate groups into sPS. After the coupling reactions, the Bpin resonance of sPS-Bpin at 1.16 ppm disappeared completely in the ¹H NMR spectra, and a new signal at 1.97 ppm appeared and was assigned to the two methyl groups of the 3,5-dimethylphenol structure of the sulfonated sPS (Figure 1c).



Figure 1. ¹H NMR spectra of (a) sPS, (b) sPS-Bpin, (c) sPS-S₃ in the 3,5-dimethylphenol protected form, and (d) sPS-S₃ in the $-SO_3Na$ form.

Similar to that in the sPS-Bpin characterization, the concentration of 3,5-dimethylphenol-protected sulfonate groups in the polymers was calculated based on the integral ratio of the methine proton of the sPS main chain (at 2.09 ppm) and the terminal methyl groups in the side chain of sulfonated sPS (at 1.97 ppm). The molar concentration of the sulfonate group matched well with that of the borylated group in the precursor polymer (i.e., 40 mol %). In the case of the coupling reaction with S₃, the resulting polymer also showed the characteristic propylene group of S₃ at 3.52, 3.08, and 2.12 ppm with the expected molar concentrations. Successful incorporation of the fluoroalkyl sulfonate group after the coupling reaction with S₁ was further confirmed by two clean resonances at -80.3 ppm ($-OCF_2-$) and -111.9 ppm ($-CF_2SO_3-$) in the ¹⁹F NMR spectrum (Figure 2a). Unlike electrophilic sulfonation of aromatic polymers using chlorosulfonic acid or sulfuric acid, in which polymer gelation frequently occurs because of undesired side reactions (cross-linking) in the polymer chains,⁴¹ the borylation and the subsequent coupling reaction caused no gelation.

Removal of 3,5-dimethylphenol from the protected sulfonate groups of sPS using basic hydrolysis and subsequent acidification with sulfuric acid yielded the final sPS ionomers functionalized with fluoroalkyl, aryl, or alkyl sulfonic acid groups (sPS-S₁, sPS-S₂, and sPS-S₃, respectively, in Scheme 1). Basic hydrolysis of the protected sulfonated sPS was conducted with sodium hydroxide in a mixture of dioxane and water. Upon completion of the reaction, the sPS ionomers in the sodium salt form precipitated owing to a dramatic solubility change in the medium. The ionic polymers were stirred in a refluxing solution of water and methanol to remove salt and organic impurities and filtered. After the deprotection step, the ¹H NMR resonance of the methyl side groups at 1.97 ppm disappeared, and the ¹⁹F NMR resonance of $-CF_2SO_3$ - in sPS-S₁ shifted to -116.2 ppm (Figure 2b). A small amount of desulfonation was also detected during the deprotection of the 3,5-dimethylphenol group of sPS-S₁.



Figure 2. 19 F NMR spectra of sulfonated sPS-S₁ before (a) and after (b) deprotection of the 3,5-dimethylphenol group.

In addition to the expected resonances of -CF2CF2SO3Na at -80.4 and -116.2 ppm, two small resonances were observed at -86.9 ppm and -137.2 ppm in the ¹⁹F NMR spectrum of deprotected sPS-S₁, and they were identified as $-CF_2CF_2H$ and $-CF_2CF_2H_1$, respectively (Figure 2b). Confirmation of the desulfonated side chain structure was made from its anticipated chemical shift range and the splitting pattern of CF_2CF_2H in the ¹⁹F NMR spectrum (doublet; J = 59 Hz). The ¹⁹F NMR resonance integral of the desulfonated structure was less than 5% of that of $-CF_2CF_2SO_3Na$. In a related experiment of basic deprotection of S₁, a small amount of Br-C₆H₄-OCF₂CF₂H was also detected in GC-MS and ¹⁹F NMR. In contrast, no similar desulfonation was observed when we examined the ¹H and ¹³C NMR spectra of sPS-S₃ and the reaction mixture of deprotected S₃ with GC-MS. These results indicate the desulfonation that occurred during the deprotection step of the sPS-S1 synthesis might be related to the presence of the strong electronwithdrawing fluoroalkyl group. Although further study is needed to confirm this hypothesis, it was encouraging to observe that only a small fraction of the sulfonate group in sPS-S₁ underwent the undesired side reaction.

Membrane Properties. All sPS ionomers (-SO₃Na forms) prepared using this method had a good solubility in polar aprotic solvents, such as dimethyl sulfoxide (DMSO), and high molecular weights, as reflected in their intrinsic viscosities (Table 1). Although all sulfonated sPSs have different (weight-based) IECs, they have the same parent polymer backbone and the same sulfonation level (i.e., 40 mol %). Thus, the higher viscosity of sPS-S₁ compared to two other polymers in Table 1 is believed to be derived from properties of superacidic sulfonate group, such as degree of dissociation. Superacidic sPS-S1 would have the highest dissociation degree. Thus, in spite of having the lowest IEC, it showed the highest viscosity. A similar conclusion was drawn by Lundberg and Makowski that due to stronger association and greater polarization present in sulfonate groups than those of carboxylate groups, melt viscosities of sodium sulfonated polystyrene ionomers at a given functional level are significantly higher than their corresponding carboxylated ionomers.⁴² All sPS ionomer membranes were readily prepared as transparent films using a solution casting method and further acidified with 1 M H₂SO₄ to yield their acid forms. The IECs of the sPS ionomers were measured by titration and compared to the calculated values determined from ¹H NMR. At a given degree of sulfonation, the

Table 1. Properties of sPS Ionomers and Nafion

ionomer ^a	IEC^{b}	IV^c	water uptake ^d	λ^e
sPS-S ₁	1.64 (1.87)	1.41	22	7.5
sPS-S ₂	2.29 (2.39)	1.01	32	7.8
sPS-S ₃	2.01 (2.10)	0.85	21	5.8
Nafion 112	0.86 (0.90)	_	16	9.6

^{*a*} All sPS ionomers contain 40 mol % sulfonate in the repeating unit based on the ¹H NMR spectra of 3,5-dimethylphenol-protected sulfonate group. ^{*b*} IEC (mequiv/g) measured by titration. Calculated IEC values are shown in parentheses. ^{*c*} Intrinsic viscosity of sodium salt form ionomer in 0.1 M NaI/DMSO at 30 °C. ^{*d*} Water uptake (%) = (W_{wet} – W_{dry})/W_{dry} measured at 98% RH and 30 °C during dynamic RH scans used for conductivity. ^{*c*} Number of water molecules per sulfonic acid moiety (hydration number).

IEC values decreased in the order of $sPS-S_2 > sPS-S_3 > sPS-S_1$ because of the increasing sizes of the pendant sulfonate tethers.

Proton conductivity (σ_{H+}) is the primary property that determines PEM performance, and high proton conductivity at low RH is highly desired for the successful adoption of PEMFC technology in vehicle applications. The proton conductivity of sPS-S₂ followed the typical proton conductivity pattern of aromatic PEMs randomly functionalized with aryl sulfonic acid groups. Although it exhibited high proton conductivity when fully hydrated, its conductivity dropped sharply at lower RH. In contrast, sPS-S1 demonstrated proton conductivity that was higher than that of sPS-S₂ below 90% RH despite its lower water uptake, lower IEC, and similar hydration number (λ). Notably, the relative slope of the conductivity (on a log scale) vs RH of the superacidic sPS-S₁ was less steep than those of sPS-S₂ and sPS-S₃ and was almost parallel to that of Nafion: 0.020 for Nation, 0.022 for sPS-S₁, 0.029 for sPS-S₂, and 0.030 for sPS-S₃ (see Figure 3a). This conductivity behavior is unique when compared with typical aromatic PEMs. The order of the proton conductivities at reduced RH follows the same order of the acidities of the pendant sulfonic acid groups: $-CF_2CF_2SO_3H$ (estimated $pK_a =$ $-14)^{25,43} > -C_6H_4 - SO_3H$ (estimated $pK_a = -2.5)^{27,44} > -(CH_2)_3SO_3H$ (estimated $pK_a = -0.6)^{43,45}$ Among the sPS ionomers studied, sPS-S₃ had the lowest conductivity across the entire RH range, possibly resulting from the combined effect of the weaker acidity of the sulfonic acid and lower WU.

The water uptake (WU) properties of PEMs have a strong influence on their proton conductivity. The WU of sPS-S₂ is the greatest among the samples studied due to its high IEC (Figure 3b). Interestingly, the superacid-containing sPS-S₁ has a similar bulk WU to that of sPS-S₃, even though the IEC of sPS-S₃ is 20% greater than that of sPS-S₁. This difference in the WU of the fluoroalkyl sulfonate sample compared to the alkyl sample can be attributed to the increased hydration of the superacid as discussed later. The λ of the alkyl sulfonate sample is lower than those of two other ionomers, likely due to its lower acidity and a hydrophobicity effect of the alkyl tether (Figure 3c). Interestingly, sPS-S₁ and sPS-S₂ had similar hydration numbers, but clearly the sulfonate moiety of the former is more effective in promoting conductivity, even at equivalent hydration. Nafion which has the same fluoroalkyl sulfonate group as sPS-S₁ shows the highest λ across all RHs, which suggests that other factors such as backbone structure may impact the hydration of the ionic groups.

lonic Domain Morphology. The morphological characteristics of sulfonated sPS ionomers were investigated using tapping-mode



Figure 3. (a) Proton conductivity (σ_{H+}) , (b) water uptake (WU), and (c) hydration number (λ) of Nafion and sPS ionomers under different relative humidity conditions.

AFM after exposure of the PEMs to ambient conditions for >6 h. In the AFM images (Figure 4), domains having higher phase lag angle appear as dark areas (hydrophilic domains) and domains having lower phase lag angle appear as bright areas (hydrophobic domains). All three sPS ionomers exhibited a phase separated morphology with slightly different hydrophilic and hydrophobic domain sizes, but no obvious connectivity among the hydrophilic domains was observed. The hydrophilic domain size of sPS-S₁



250 nm 250 nm 0 250

Figure 4. Morphology of Nafion and sPS ionomers studied by AFM.



Figure 5. Morphology of Nafion and sPS ionomers studied by TEM.

was ~10 nm which was larger than that of sPS-S₂ (~8 nm) and sPS-S₃ (~6 nm). The hydrophilic domain size does not seem to be strongly related to the acid strength of sulfonated group as superacidic fluoroalkyl sPS-S₁ has a similar domain size as the aryl sulfonated sPS-S₂. These data on the hydrophilic domain sizes of our ionomers by AFM are supported by measurements of the hydrophilic domains in other random sulfonated poly(arylene ether sulfone)s with a similar IEC (1.5–2.2 mequiv/g).^{19,46} Compared to Nafion, all three sPS ionomers demonstrated a low degree of phase separation with smaller isolated hydrophilic domains. Of the sPS ionomers, the AFM image of sPS-S₂ exhibited a somewhat higher degree of phase mixing between the hydrophobic and hydrophilic domains. By introducing a

sulfonic acid group at the terminal position of flexible pendant side chains (i.e., $sPS-S_1$ and $sPS-S_3$), improved phase separation was achieved.

The TEM images of the sPS ionomers showed morphological features similar to those observed with AFM (Figure 5): indistinct phase separation with poor connectivity among hydrophilic domains. Because the TEM images were obtained under vacuum and there are no tip sharpness artifacts as with AFM, the hydrophilic domains of the PEMs were observed to be much smaller in TEM than what was obtained using AFM. While sPS ionomers demonstrated a low level of phase separation with significantly smaller hydrophilic domains, Nafion showed distinctive nanoscale phase-separated hydrophilic domains (2-4 nm in TEM). Considering that Nafion and sPS-S₁ have a terminal sulfonate group with the same acidity strength, the larger size and better continuity of the hydrophilic domains in Nafion strongly suggest that other structural differences (i.e., more hydrophobic polymer backbone, longer and more flexible side chain of Nafion) might play critical roles in enhancing the aggregation of ionic groups and formation of water channels within the PEM. Although Nafion has a lower IEC than sPS-S₁, the former still achieved a comparable proton conductivity of the latter at the entire RH possibly due to the higher λ created by the favorable morphology effect.

The morphological study by AFM and TEM confirmed that the hydrophilic and hydrophobic domain structures depend on several other factors besides acidity, such as polymer architecture, concentration and distribution of sulfonated groups, difference in hydrophobicity/hydrophilicity of backbone and sulfonated side chain, and backbone/side chain stiffness. It is difficult to completely decouple the acidity effect from other factors in the model polymer systems we used. However, it is interesting to note that sPS-S₁ exhibited high proton conductivity at low RH even with somewhat undesirable domain structure (i.e, little observed domain connectivity), which is in stark contrast with previous multiblock copolymer approach that endeavor to form highly connected hydrophilic domains to improve low RH conductivity.

B. Computational Simulation Studies of sPS lonomers. The experimental data above demonstrate differences in membrane properties but provide no mechanistic insight into their cause. Thus, we investigated the effect of acidity strength on proton conductivity and water properties using molecular dynamic simulations. We selected two sulfonated sPS ionomers containing short ponytail side chains, sPS-S₁ and sPS-S₃, as model polymers. Because these ionomers have an identical polymer backbone structure, an identical concentration of sulfonic acid groups, and a similar flexibility along their side chains, we believe that a comparison of their properties by computational studies provides a theoretical understanding of the acidity effect on PEM properties. All calculations were conducted for hydrated membranes with 10 and 20 wt % water contents at 80 °C. The molecular parameters of the computational simulation are listed in Table 2.

Dissociation and Solvation of Sulfonate Groups. Previous theoretical PEM studies on Nafion,⁴⁷ dendrion,^{48,49} and sulfonated poly(ether ether ketone)⁵⁰ suggest that nanoscale phase-segregation of hydrated PEMs can form well-connected water phases within a PEM and that this process requires the solvation of the hydrophilic sulfonate groups with water molecules in the first step.

To investigate the relationship between acidity and interactions of sulfonate with water molecules, we analyzed the pair

 Table 2. Composition of Hydrated sPS Membranes and

 Simulation Conditions

ionomers	sPS-S ₁	sPS-S ₃
molecular weight per chain (Da)	7756	6624
equivalent weight (g/mmol)	554	473
degree of polymerization	35	35
degree of sulfonation	40	40
number of polymer chains	4	4
total number of sulfonate groups	56	56

correlations of sulfonate—hydronium pair, ρg_{S-O} (hydronium), and sulfonate—water pair, ρg_{S-O} (water), for sPS-S₁ and sPS-S₃ with 10 and 20 wt % water contents. The definition of pair correlation function, $g_{A-B}(r)$, is the probability density of finding B atoms at a distance r from A atoms averaged over the equilibrium trajectory as shown in eq 1:

$$g_{A-B}(r) = \left(\frac{n_B}{4\pi r^2 \Delta r}\right) / \left(\frac{N_B}{V}\right) \tag{1}$$

where n_B is the number of B particles located at a distance r in a shell of thickness Δr from particle A, N_B is the number of B particles in the system, and V is the total volume of the system. Therefore, $g_{A-B}(r)$ is equivalent to the ratio of the number density of particle B in a thin shell to the global number density at a distance r from the position of particle A.

The pair correlation function for the sulfonate—hydronium pair clearly shows an acidity effect (Figure 6a). The stronger acid group of sPS-S₁ can more readily dissociate into the ionized form and has a lower pair correlation intensity. This is because sPS-S₁ can stabilize the ionized sulfonate form with the adjacent electron-withdrawing CF₂ group, whereas sPS-S₃ does not have these strong electron-withdrawing groups for stabilizing the negative charge on the sulfonate.

As shown in Figure 6b, the intensity of $[\rho g_{S-O(water)}(r)]$ increased with increasing water content for both ionomers, indicating that more water molecules gathered around the hydrophilic sulfonate groups. Between the two sPS ionomers, sPS-S₁ had a higher pair correlation intensity than that of sPS-S₃ at both water contents. To quantitatively assess the difference in pair correlation, we calculated the average number of water molecules that surrounded each sulfonate group, or the hydration number (λ), by integrating the first peak in Figure 6b. The hydration numbers for sPS-S1 were 1.78 and 3.91 at 10 and 20 wt % water content, respectively, and the corresponding hydration numbers for sPS-S₃ were 1.35 and 3.61. These results suggest that the sulfonate groups in sPS-S₁ attracted more water molecules than did those of sPS-S₃, and this can be explained by that a stronger acid group has a greater tendency to exist in an ionized form and requires solvation with more water molecules. Overall, the data of Figure 6 suggest that more hydronium ions are dissociated from the sulfonate groups in sPS-S1 because of its stronger acidity, and the resulting higher degree of ionic character of the sulfonate group attracts more water molecules for solvation. The superior solvation of the sulfonate groups in sPS-S₁ compared with that of sPS-S₃ may account for the larger hydrophilic domains of the former observed on the AFM images and contribute to its enhanced proton conductivity at low RH. This phenomenon is also observed in the hydration data where sPS-S₁ absorbs more water molecules per sulfonic acid group than sPS-S₃.



Figure 6. Calculated pair correlation functions of (a) sulfonatehydronium ion and (b) sulfonate-water in hydrated sPS ionomers.

Transport Properties of Water and Protons. We also investigated the transport properties of water molecules and protons within the sPS ionomer membranes. The water diffusion coefficient (D_{water}) was calculated from the mean squared displacement of water using the following equation:

$$D_{water} = \lim_{t \to \infty} \frac{1}{6t} \langle (r(t) - r(0))^2 \rangle$$
(2)

where r(t) and r(0) are the positions of water at a certain time (t) and at the beginning (t = 0), respectively. The results shown in Table 3 suggest that water diffusion increases with increasing water content, and this relationship is attributed to the better development of a water phase in hydrophilic domains. As the sulfonate groups become surrounded by more water molecules, the local water concentration increases and eventually these water domains coalesce and enhance water transport. Comparison of sPS-S₁ and sPS-S₃ showed that the former achieved greater water diffusion. This result can be understood by considering the aforementioned discussion of $\rho g_{S-O(water)}(r)$: more water molecules that are attracted to the acid groups of sPS-S₁ enhance the possibility of better solvated sulfonate groups and facilitate water transport in the hydrophilic phase.

We also investigated the proton diffusion of $sPS-S_1$ and $sPS-S_3$ under 10 and 20 wt % water contents. Proton diffusion can occur via vehicular diffusion and hopping mechanisms. Through the vehicular diffusion mechanism, protons are transported as water molecules carrying protons diffuse through the membrane,

Table 3. Calculated Diffusion Coefficients of Water and Protons of sPS Ionomers at 80 $^\circ \rm C$

			proton	proton diffusion		
	water content	water diffusion D _{water}	vehicular D _{vehicular}	hopping D _{hopping}		
ionomer	(wt %)	($\times ~10^{-5}~cm^2/s)$	($\times ~10^{-5}~cm^2/s)$	($\times ~10^{-5}~cm^2/s)$		
sPS-S ₁	10	0.0908	0.0029	0.2511		
	20	0.4441	0.0221	0.4272		
$sPS-S_3$	10	0.0584	0.0012	0.0820		
	20	0.2626	0.0214	0.3303		

whereas in the hopping mechanism, protons are transported by transfer from one water molecule (proton donor) to another (proton acceptor). The proton diffusion coefficient under the vehicular mechanism ($D_{vehicular}$) can be described by the classical molecular dynamics simulation in eq 2. However, calculating proton diffusion coefficient of the hopping mechanism ($D_{hopping}$) requires a quantum mechanical treatment because intermolecular distances between water molecules will change dynamically during the proton conduction. Therefore, we applied quantum mechanical transition state theory using eq 3 as described in previous studies:^{49,51,52}

$$k_{ij}(r) = \kappa(T, r) \frac{k_{\rm B}T}{h} \exp\left(-\frac{E_{ij}(r) - 1/2h\omega(r)}{RT}\right)$$
(3)

where $\kappa(T,r)$ and $\omega(r)$ are the tunneling factor and the frequency for zero point energy correction (adopted from literature^{50,51}), respectively, and E(r) is the energy barrier for a proton to be transferred from donor to acceptor in water when they are at a distance of r. We first calculated the proton hopping energy barrier, E(r), for fixed distances between donor and acceptor oxygen atoms using quantum mechanics (B3LYP with the 6-311G^{**} basis) to see how energy varies as a function of the distance between the proton and the donor oxygen. We then used the Poisson–Boltzmann self-consistent reaction field model^{53,54} to correct the solvent effect along the reaction path, and we recalculated the energy barrier. From the results obtained from eq 3 and the distances between all pairs of donors and acceptors determined with the equilibrium molecular dynamics trajectory, we calculated the proton hopping diffusion coefficient as follows:

$$D_{hopping} = \frac{1}{6Nt} \int_0^{t \to \infty} \sum_{i}^N \sum_{j}^M k_{ij} r_{ij}^2 P_{ij} dt$$
(4)

where *N* is the number of protons and P_{ij} is the probability that a proton will jump from hydronium *i* to water *j* defined as $P_{ij} = k_{ij}/\sum_j k_{ij}$. Here r_{ij} is the distance between all pairs of donors and acceptors measured from the equilibrium molecular dynamics trajectory.

Table 3 summarizes the calculated proton diffusion coefficients of hydrated sPS ionomers. Similar to water diffusion, proton diffusion became greater as water content increased, and sPS-S₁ has a proton diffusion coefficient higher than that of sPS-S₃ under both mechanisms. Especially at 10 wt % water content, the proton diffusion coefficient of sPS-S₁ is almost three times larger than that of sPS-S₃. At 20 wt % water content, however, the proton diffusion coefficient of sPS-S₁ is only 1.3 times larger than that of sPS-S₃. Thus, the computational results strongly suggest

Table 4.	Computed	Proton	Cond	uctivity	of sPS	Ionomer	s at
80 °C							

ionomer	water content (wt %)	proton conductivity (σ) (mS/cm)
sPS-S ₁	10	14.4
	20	24.6
sPS-S ₃	10	4.7
	20	19.5

that the effect of strong acidity on proton conduction is more significant at lower water content.

Lastly, we calculated proton conductivity (σ) based on the proton diffusion coefficient ($D_{proton,total} = D_{vehicular} + D_{hopping}$) using the following Nernst–Einstein equation:

$$\sigma = \frac{D_{proton, total} cz^2 F^2}{RT}$$
(5)

where *c* and *z* denote the proton concentration and the charge carried by the proton, respectively, and *F* and *R* denote the Faraday constant and the gas constant, respectively. *T* is temperature in Kelvin. The computed proton conductivity results are summarized in Table 4. The difference in computed proton conductivities between sPS-S₁ and sPS-S₃ becomes larger as the water content decreases, which is consistent with the results of proton diffusion coefficient calculations: the ratio of the calculated proton conductivities of sPS-S₁ and sPS-S₃ increased from 1.3 to 3.1 as the water content decreased from 20 wt % to 10 wt %. Therefore, the more robust proton conductivity of sPS-S₁ compared to the other sPS ionomers at low RH is due primarily to the stronger acidity of the superacidic ionomer and its resulting higher diffusions of water and protons within the membrane.

CONCLUSIONS

We have developed a novel, efficient sulfonation method for aromatic polymers using a combination of transition metalcatalyzed borylation of aromatic C-H bonds and Suzuki-Miyaura coupling reactions. The new polymer functionalization method allows for convenient attachment of a variety of sulfonate groups with different acidities onto the aromatic polymer. We prepared polystyrene-based sulfonate ionomers by attachment of superacidic fluoroalkyl sulfonic acid and less acidic aryl sulfonic and alkyl sulfonic acids to the backbone, and evaluated their fuel cell membrane properties. With these systematic series of polymers, we performed a comprehensive study on the effect of acid strength on the proton conductivity of the sulfonated ionomers. Despite its lower water uptake and IEC, the fluoroalkyl sulfonated superacidic ionomer $(sPS-S_1)$ maintained higher proton conductivity at low RH compared with the less acidic aryl and alkyl sulfonated ionomers (sPS-S2 and sPS-S3), and this difference in proton conductivity gradually increased as the RH decreased. The water uptake behavior as a function of RH and the morphology studies show that compared to less acidic ionomers sPS-S₃, the superacidic sulfonate groups of sPS-S₁ attract more water molecules and create enlarged hydrophilic domains that could provide more facile transports of hydronium ions and water and afford higher proton conductivity. Comparison of properties of two superacidic sulfonated ionomers with different polymer backbones, Nafion and sPS-S1, suggests that creation of favorable morphology with larger-sized and better-connected

hydrophilic domains also plays an important role in enhancing proton conduction.

We conducted comparative computational studies of $sPS-S_1$ and $sPS-S_3$ under hydrated conditions to investigate acidity effects at a molecular level. By analyzing the solvation of sulfonate groups with water in each system, we confirmed that the sulfonate groups in $sPS-S_1$ are better solvated than those in $sPS-S_3$. Thus, the acidity effect not only induces more effective dissociation of protons (in the form of hydronium ion) from the sulfonate but also develops better solvated sulfonate groups by surrounding them with more water molecules. Because of the superacid solvation effect, $sPS-S_1$ has higher calculated water diffusion coefficient and proton diffusion coefficient (under both vehicular and hopping mechanisms) than $sPS-S_3$, and their difference in proton diffusion coefficient was greater at lower water content.

Overall, our studies on the effect of acidity strength on fuel cell membrane properties suggest a clear relationship between acidity strength and proton conductivity: the enhanced proton conductivity of the more acidic ionomer is due to the cumulative effects of better dissociation of the superacidic sulfonic acid to hydronium ion and better solvation of the sulfonates through increased water concentration. We believe that the results reported herein are a significant step toward the development of highly conductive hydrocarbon-based ionomers and offer an alternative approach to morphology-driven high-performance multiblock copolymer ionomers.

EXPERIMENTAL SECTION

Materials and Methods. 4,4'-Di-*tert*-butyl-2,2'-dipyridyl (d*t*bpy), chloro-1,5-cyclooctadiene iridium(I) dimer ([IrCl(COD)]₂), tetrakis-(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), 4-dimethylaminopyridine (DMAP), Na₂S₂O₄, 3,5-dimethylphenol, and 4-bromobenzene-sulfonyl chloride were reagent grade and used without further purification. Bis(pinacolato)diboron (B₂pin₂) from Frontier Scientific Co., ICF₂CF₂I from Oakwood Products, Inc., BrCF₂CF₂Br from SynQuest Laboratories, Inc., Chlorine gas from Praxair Inc., CFC-113 from ChemNet were used as received. Cyclooctane was dried using sodium and benzophenone, distilled under vacuum, and stored in a nitrogen-filled glovebox. sPS ($M_w = 140.9 \text{ kg/mol}$ with $M_w/M_n = 2.90$) was obtained from LG Chemical Ltd., Daejeon, S. Korea and used as received. Anhydrous tetrahydrofuran (THF) was obtained from EMD Chemicals and collected from the container using a positive pressure of nitrogen.

¹H, ¹⁹F, and ¹³C NMR spectra were obtained using a Varian NMR spectrometer (400 MHz for ¹H, 376 MHz for ¹⁹F, and 100 MHz for ¹³C) at room temperature and chemical shifts were referenced to TMS (¹H and ¹³C) and CFCl₃ (¹⁹F). GC/MS analysis was conducted using a Shimadzu QP2010S equipped with a 30 m \times 0.25 mm SHR-XLB GC column and an EI ionization MS detector. FT-IR spectra were recorded on a Shimadzu IR Prestige-21.

Ion Exchange Capacity (IEC). The calculated IECs of sPS ionomers were estimated from the mol % of 3,5-dimethylphenol protected sulfonated sPS (i.e., sPS-S₁—Ph, sPS-S₂—Ph, and sPS-S₃—Ph in Scheme S3 of the Supporting Information) in the ¹H NMR spectra. The experimental IECs of sPS ionomers were determined using a titration method. Membranes were equilibrated in 2 M NaCl solution at room temperature for 3 days before titration. The protons released into the aqueous solution were titrated with 0.025 M NaOH solution using phenolphthalein as an indicator. The experimental IEC values of the sPS ionomer membranes were calculated according to the equation below:

Here M_{NaOH} and V_{NaOH} are the molar concentration and volume (mL) of the aqueous NaOH solution used in titration, $W_{\text{dry}}(g)$ is the weight of dry membrane.

Water Uptake and Hydration Number (λ). Water uptake was measured as a function of relative humidity at 30 °C using a TA Instruments Q5000SA dynamic vapor sorption analyzer. The relative humidity steps and equilibration times were the same those used in the conductivity experiments. Hydration number (λ) was calculated from

$$\lambda = \left(rac{W_{RH} - W_{dry}}{18.01}
ight) \left(rac{1000}{W_{dry} imes IEC}
ight)$$

where W_{RH} is the sample mass at a given RH, W_{dry} is the dry mass of the sample, and IEC is the ion exchange capacity of the sample in milliequivalents of sulfonate group per gram of polymer.

Proton Conductivity. To measure the proton conductivity of sPS ionomers, the membrane in sulfonic acid form was immersed in deionized water for at least 24 h. The proton conductivity of the membrane was measured using a four-electrode method with a BT-512 membrane conductivity test system (BekkTech LLC). The proton conductivity was measured by changing the relative humidity from 20 to 100% at 80 °C. RH control started from 70%, stabilized for 2 h, decreased to 20% at a rate of 10% RH/20 min, then increase to 100% at a rate of 10% RH/20 min. The proton conductivity data was collected from the cycle of 20% RH to 100% RH. The proton conductivity was calculated according to the following equation:

$$\sigma (\mathrm{mS/cm}) = \frac{L}{R \times W \times T}$$

where L is the distance between the two inner platinum wires (0.425 cm), R is the resistance of the membrane, and W and T are the width and the thickness of the membrane in centimeters, respectively.

Membrane Morphology. Membranes in acid form were stained by soaking in 0.5 M lead acetate solution at room temperature for 1 day, then rinsed with deionized water and dried under vacuum at room temperature overnight. The stained membranes were cut into small pieces and embedded in Spurr's epoxy resin and cured overnight at 70 °C. The samples were sectioned to yield slices of 100 nm thickness using Leica EM UC6 ultramicrotome and placed on copper grids. Transmission electron microscopy images were taken by TECNAI-F30 Supertwin TEM using an accelerating voltage of 300 kV. The phase segregation of membranes was characterized by AFM. Acid form of membranes were soaked in water for 12 h, dried at 60 °C for 30 min, and then exposed to ambient conditions for >6 h before the characterization. A Veeco Metrology D3000 microscope with a Nanoscepe IIIa controller with standard commercially available SFM 125 μ m long silicon cantilevers with a spring constant of about 40 N/m was used to obtain all images. Identical operating conditions, i.e., cantilever drive amplitude and set point, were employed for all aromatic membranes.

Synthesis of 3,5-Dimethylphenyl 2-(4-Bromophenoxy)tetrafluoroethanesulfonate Ester (S₁). 3,5-Dimethylphenol (3.10 g, 25.4 mmol, 1.1 equiv) and CH₂Cl₂ (70 mL) were added to a 250 mL two-neck flask filled with nitrogen and was cooled to 0 °C. 2-(4-Bromophenoxy)tetrafluoroethanesulfonyl chloride (8.57 g, 23.1 mmol), which was prepared from 4-bromophenol in 61% overall yield using a literature method,³⁵ and DMAP (3.38 g, 27.7 mmol, 1.2 equiv) were added in sequence and the mixture was stirred at 0 °C for 2 h and room temperature for 12 h. The reaction mixture was diluted with CH₂Cl₂ (80 mL), washed with 2 M HCl (40 mL × 3), saturated NaHCO₃ (40 mL) and brine (30 mL), and combined organic layer was dried over MgSO₄. After evaporation of solvent, resulting crude product was purified by column chromatography (hexane/ethyl acetate=10:1) to give 9.66 g of S₁ as an yellowish oil (92% yield). ¹H NMR (CDCl₃): δ 7.52 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.99 (s, 1H), 6.92

IEC (mequiv/g) =
$$M_{\rm NaOH} \times V_{\rm NaOH}/W_{\rm dry}$$

(s, 2H), 2.25 (s, 6H). ¹⁹F NMR (CDCl₃): δ –81.4 (t, *J* = 4.3 Hz, OCF₂), –112.5 (t, *J* = 4.3 Hz, CF₂SO₃). ¹³C NMR (CDCl₃): δ 150.0, 147.5, 140.4, 133.1, 129.9, 123.8, 120.7, 119.2, 115.8 (tt, ¹*J*_{CF} = 277 Hz, ²*J*_{CF} = 28.6 Hz), 113.9 (tt, ¹*J*_{CF} = 298 Hz, ²*J*_{CF} = 39.1 Hz), 21.4. GC/MS: 458, 456, 392, 192, 143, 121 (100%), 91, 77. HRMS (*m*/*z*) (CI, NH₃): calcd for C₁₆H₁₃O₄BrF₄S (M + NH₄)^{+,} 473.9992; found, 473.9996.

Synthesis of 3,5-Dimethylphenyl 4-Bromobenzenesulfonate Ester (S₂). 4-Bromobenzenesulfonyl chloride (20.0 g, 78.3 mmol), 3,5-dimethylphenol (9.56 g, 78.3 mmol), and DMAP (10.5 g, 86.1 mmol, 1.1 equiv) were placed in a 500 mL two-neck flask under nitrogen. CH₂Cl₂ (250 mL) was added, and the resulting mixture was stirred overnight at room temperature. The reaction solution was washed with 2 M HCl solution (50 mL \times 2), saturated NaHCO₃ solution (50 mL) and brine (50 mL), dried over Na₂SO₄, and evaporated. Crude product was purified by column chromatography (ethyl acetate/hexane: 1/10 to 3/ 10) to give 26.4 g of S_2 as an off-white solid product (94% yield). ¹H NMR (CDCl₃): δ 7.69 (distorted doublet, I = 8.0 Hz, 2H), 7.58 (distorted doublet, J = 8.0 Hz, 2H), 6.89 (s, 2H), 6.61 (s, 1 H), 2.25 (s, 6H). ¹³C NMR (CDCl₃): δ 149.3, 139.7, 134.7, 132.3, 129.9, 128.3, 128.9, 119.6, 21.1. GC/MS: 342, 340, 248, 221, 155, 121 (100%), 109, 91, 77, 65, 50, 41. HRMS (m/z) (CI, NH₃): calcd for C₁₄H₁₃O₃BrS $(M + NH_4)^+$, 358.0107; found, 358.0115.

Preparation of 3,5-Dimethylphenyl 3-(4-Bromophenoxy)propanesulfonate Ester (S₃). 4-Bromophenol (5.0 g, 28.9 mmol) and K₂CO₃ (12.0 g, 86.7 mmol, 3 equiv) were placed in a 100 mL two-neck flask under nitrogen, and DMF (50 mL) and 1,3-propane sultone (4.59 g, 37.6 mmol, 1.3 equiv) were added. The mixture was stirred at 110 °C overnight and cooled to room temperature, and the resulting precipitate was filtered. The filtered solid was stirred with water (200 mL) for 1 h at room temperature, filtered and dried in air to give 5.83 g of potassium 3-(4-bromophenoxy)propanesulfonate as a white solid (61% yield). ¹H NMR (DMSO- d_6): δ 7.42 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.6 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H), 1.98 (m, 2H). ¹³C NMR (DMSO- d_6): δ 157.9, 132.1, 116.8, 111.7, 67.0, 47.8, 25.1. Potassium 3-(4-bromophenoxy)propanesulfonate (1.73 g, 5.46 mmol) was added to a 50 mL two-neck flask under nitrogen, and acetonitrile (17 mL) and phosphorus oxychloride (4.18 g, 27.3 mmol, 5 equiv) were added subsequently. The reaction mixture was stirred at 85 °C overnight, cooled to room temperature, poured into ice water (~60 g), and extracted with CH_2Cl_2 (30 mL × 3). Combined organic layer was dried over Na2SO4, and evaporation of solvent gave 1.45 g of 3-(4-bromophenoxy)propanesulfonyl chloride as an off-white solid (85% yield). ¹H NMR (DMSO- d_6): δ 7.42 (d, J = 9.2 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.64 (t, J = 7.6 Hz, 2H), 2.00 (m, 2H). ¹³C NMR (DMSO- d_6): δ 158.0, 132.2, 116.9, 111.9, 66.7, 48.0, 24.9. 3-(4-Bromophenoxy)propanesulfonyl chloride (1.44 g, 4.59 mmol) and 3,5-dimethylphenol (0.51 g, 4.17 mmol, 0.91 equiv) were added to a 50 mL two-neck flask under nitrogen and CH₂Cl₂ (15 mL) and DMAP (0.56 g, 4.59 mmol, 1 equiv) were added in sequence. The resulting solution was stirred overnight at room temperature, diluted with CH_2Cl_2 (50 mL), washed with 2 M HCl (20 mL \times 2), and dried over Na2SO4. After evaporation of solvent, crude product was purified by column chromatography (ethyl acetate/hexane: 1/10 to 2/10) to give 1.65 g of S₃ as a white solid (99% yield). ¹H NMR (CDCl₃): δ 7.39 (d, J = 8.8 Hz, 2H), 6.94 (s, 1H), 6.88 (s, 2H), 6.77 (d, J = 8.8 Hz, 2H),4.11 (t, J = 5.6 Hz, 2H), 3.47 (t, J = 7.6 Hz, 2H), 2.45 (m, 2H), 2.32 (s, 6H). ¹³C NMR (CDCl₃): δ 157.6, 149.2, 140.2, 132.6, 129.2, 119.6, 116.4, 113.6, 65.5, 47.4, 24.1, 21.4. GC/MS: 400, 398, 227, 185, 174, 157, 134, 121 (100%), 105, 91, 77, 65, 41.

Preparation of sPS-Bpin (40 mol %). In a nitrogen-filled glovebox, sPS (700 mg, 6.73 mmol polystyrene repeating unit), B_2pin_2 (1.37 g, 5.38 mmol, 0.8 equiv), [IrCl(COD)]₂ (54.2 mg, 3 mol % iridium based on the amount of B_2pin_2), dfbpy (43.3 mg, 3 mol % based on the amount of B_2pin_2), cyclooctane (4.30 g, 0.40 mol, 60 equiv), and a magnetic stirring bar were placed into a 30 mL vial, which was capped with a Teflon-lined septum. The vial was removed from the glovebox and placed in an oil bath at 150 °C for 6 h. After cooling to room temperature, the solution was diluted with chloroform (60 mL) and filtered through a short plug of silica gel to remove the catalyst. The filtrate was concentrated by a rotary evaporator to about 10 mL, and cold methanol (100 mL) was added to precipitate polymer. The dissolution and precipitation process was repeated one more time. The borylated polymer was isolated as a white solid and dried under vacuum at 80 °C (1.04 g, 148% yield based on polymer weight). ¹H NMR (benzene-*d*₆): δ 8.00 (H_{arom} from C₆H₄–Bpin), 7.73 (H_{arom} from C₆H₄–Bpin), 7.08 (H_{arom}), 6.71 (H_{arom}), 2.09 (CH of sPS backbone), 1.49 (CH₂ of sPS backbone), 1.16 (CH₃ of Bpin). On the basis of analysis of ¹H NMR spectrum, an average of 40% of polymer repeating unit contains Bpin group.

Preparation of 3,5-Dimethylphenyl-Protected Sulfonate of sPS-S₁, sPS-S₂, and sPS-S₃. sPS-Bpin (100 mg of 40 mol % Bpin-functionalized sPS, 0.250 mmol Bpin) and K₃PO₄ (0.240 g, 1.13 mmol, 4.5 equiv) were placed in a 25 mL vial. which was capped with a Teflon-lined septum. Tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol, 4 mol %) and THF (4 mL) were added to the vial in a nitrogen-filled glovebox and the vial was removed from the glovebox. Compound S_1 (230 mg, 0.50 mmol, 2 equiv) and water (0.4 mL) were added using syringes. The solution was stirred at 80 °C for 12 h, cooled to room temperature, diluted with chloroform (40 mL), and filtered through a short pad of silica gel. The filtrate was concentrated to about 3 mL and cold methanol (10 mL) was added to precipitate the polymer. Another cycle of dissolution in chloroform and precipitation with cold methanol provided 140 mg of 3,5-dimethylphenol protected sulfonate form of sPS-S1 as a white solid. ¹H NMR (benzene- d_6): δ 6.62–7.20 (multiple H_{arom}), 2.18 (CH of sPS backbone), 1.97 (CH₃), 1.59 (CH₂ of sPS backbone). 19 F NMR (benzene- d_6): δ -80.3 (s, 2F, -OCF₂), -111.9 (s, 2F, $CF_2SO_3-)$

The same procedure above with compound S₂ produced sPS-S₂ in 3,5-dimethylphenol protected sulfonate form. ¹H NMR (benzene-d₆): δ 6.56–8.00 (multiple H_{arom}), 2.03 (CH of sPS backbone), 1.93 (CH₃), 1.55 (CH₂ of sPS backbone).

The same procedure above with compound S₃ produced sPS-S₃ in 3,5-dimethylphenol protected sulfonate form. ¹H NMR (benzene-d₆): δ 6.56–7.50 (multiple H_{arom}), 3.53 (OCH₂CH₂CH₂SO₃), 3.09 (OCH₂-CH₂CH₂SO₃), 2.12 (CH of sPS backbone and OCH₂CH₂CH₂SO₃), 1.97 (CH₃), 1.52 (CH₂ of sPS backbone).

Preparation of the Sodium Sulfonate Form of sPS-S₁, sPS-S₂, and sPS-S₃. Above 3,5-dimethylphenol protected sulfonate form of sPS-S₁ (100 mg of 40 mol % sulfonated sPS; 0.158 mmol of sulfonate) was dissolved in dioxane (4 mL) with gentle heating and NaOH (50.6 mg, 1.26 mmol, 8 equiv) and H₂O (40 µL) were added. The resulting solution was stirred at 100 °C for 4 h. After cooling to room temperature, solvent was evaporated and residue was dissolved in methanol, filtered through a short plug of silica gel. After concentration of the filtrate, addition of H₂O (20 mL) caused precipitation of polymer which was filtered and washed with a refluxing solution of water/methanol (3/1, v/v) for 2 h. Drying under vacuum at 80 °C for 12 h gave 87 mg of polymer product. ¹H NMR (DMSO-*d*₆) δ: 6.80–8.10 (multiple H_{arom}), 1.61 (CH of sPS backbone), 1.23 (CH₂ of sPS backbone). ¹⁹F NMR (DMSO-*d*₆) δ: -80.4 (s, OCF₂), -116.2(s, CF₂SO₃).

The above procedure was used for preparation of sodium salt form of sPS-S₂. The obtained polymer product was purified by stirring in hot methanol for 2 h. Yield: 87% based on recovered polymer weight. ¹H NMR (DMSO-*d*₆): δ 6.43–7.64 (multiple H_{arom}), 1.63 (CH of sPS backbone), 1.28 (CH₂ of sPS backbone).

The above procedure was used for preparation of sodium salt form of sPS-S₃. The obtained polymer product was purified by stirring in hot methanol for 2 h. Yield: 86% based on recovered polymer weight.

¹H NMR (DMSO-*d*₆): δ 6.30–7.50 (multiple H_{arom}), 4.00 (OCH₂-CH₂CH₂SO₃), 2.54 (OCH₂CH₂CH₂SO₃), 1.98 (OCH₂CH₂CH₂SO₃), 1.62 (CH of sPS backbone), 1.22 (CH₂ of sPS backbone).

Acid Form Membrane Preparation of $sPS-S_1$, $sPS-S_2$, and $sPS-S_3$. The sodium sulfonate form of sPS ionomers (300 mg) was dissolved in DMSO (3 mL) and cast on a glass plate. The film was dried at 40 °C under a positive air flow for 24 h and then at 80 °C under vacuum for 12 h. The acid form membrane was obtained by immersing the membrane in 1 M H₂SO₄ for 3 days (during which time the solution was changed every day) at room temperature, followed by immersing in deionized water for 1 day (water was changed several times). FT-IR (cm⁻¹, film) (Figure S1 in Supporting Information) 3450 (O–H), 3025 (aromatic C–H), 2920 (alkyl C–H), 1600 and 1490 (aromatic C–H), 1198, 1172 (S=O), 962 (C–F).

COMPUTATIONAL MODELS AND METHODS

Using a full atomistic simulation method, we investigate the nanophase-segregated structure and transport properties of the hydrated sulfonated syndiotactic polystyrene membrane with 10 and 20 wt % water contents at 353.15 K.

Force Field and Simulation Parameters. To perform molecular dynamics (MD) simulations, we used the DREIDING⁵⁵ force field, which has been used for other fuel cell studies such as Nafion,⁴⁷ Dendrion,^{48,49} and sulfonated poly(ether ether ketone)⁵⁰ as well as for various molecular systems such as hydrogels,^{56,57} liquid–liquid and liquid–air interfaces,^{58,59} and molecular self-assembly.^{60,61} The F3C force field was employed to describe the water molecules.⁶² These force field parameters are described in the original paper and our previous study on hydrated Nafion.⁴⁶ The form of the potential energy used, therefore, is

$$E_{total} = E_{vdW} + E_Q + E_{bond} + E_{angle} + E_{torsion} + E_{inversion}$$
(6)

where $E_{totab} E_{vdW} E_{Q} E_{bond} E_{angle} E_{torsion}$ and $E_{inversion}$ are total energies, van der Waals, electrostatic, bond stretching, angle bending, torsion, and inversion components, respectively. The individual atomic charges of the copolymer were assigned by Mulliken population analysis with B3LYP and 6-31G** basis set. The atomic charges of the water molecule were from the F3C water model.⁶¹ The particle – particle particle – mesh (PPPM) method⁶³ was used to calculate the electrostatic interactions.

The annealing MD and equilibrium MD simulations were performed using the MD code LAMMPS (large-scale atomic/molecular massively parallel simulator) from Plimpton at Sandia⁶⁴ with modifications to handle our force fields.⁴⁷ The equations of motion were integrated using the velocity Verlet algorithm⁶⁵ with a time step of 1.0 fs. The Nose– Hoover temperature thermostat^{66,67} for the NVT and NPT MD simulations used a damping relaxation time of 0.1 ps and a dimensionless cell mass factor of 1.0.

Construction and Equilibration of Amorphous Membrane. The simulated hydrated membrane systems consist of four chains of sPS ionomers and water molecules with 10 and 20 wt % as summarized in Table 2. The degree of polymerization and the degree of sulfonation were set to 35 and 40, respectively. Thus, the number of sulfonate group per chain is 14. The sulfonated units were selected randomly from 35 repeating units in the backbone and all of the sulfonic acid groups are assumed to be ionized as assumed in the previous studies.^{47–49}

The initial amorphous structures of hydrated sPS ionomers were constructed using the Amorphous Builder of Cerius2.⁶⁸ Since such initial structures of polymeric materials may include unstable conformations, they were equilibrated using the annealing procedure as used in the previous studies of Nafion,⁴⁷ Dendrion,^{48,49} and sulfonated poly(ether ether ketone)⁵⁰ membranes, which accelerates the attainment of equilibrium by driving the system repeatedly through 5 cycles of thermal

annealing (between 300 and 600 K) and volume annealing (between densities of 0.5 to 1.1 times the expected density). This procedure aims to help the system escape from various local minima and promote the migration of species required for phase-segregation in heterogeneous systems, whose detailed steps are described in the previous publications.^{47–50} After finishing the *annealing cycles*, a 100 ps *NVT* MD simulation and a subsequent 5 ns *NPT* MD simulation were performed at 353.15 K to finalize the annealing procedure. Then, another 15 ns *NPT* simulation was performed at 353.15 K for data collection.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, synthesis schemes, and FT-IR, GC/MS and NMR spectra (¹H, ¹⁹F and ¹³C). This material is available free of charge via the Internet at http://pubs.acs.org.

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