Macromolecules

Sulfo-Phenylated Polyphenylenes Containing Sterically Hindered **Pyridines**

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S Supporting Information



ABSTRACT: We systematically investigated the effect of incorporating a sterically hindered pyridyl group into a sulfophenylated polyphenylene to control the polymer's physicochemical properties through acid-base interactions. Homopolymers with similar molecular weights and comparable structures that vary by only one atom (N - vs C -) per repeat unit along the polymer chain were prepared. Compared to a non-pyridyl reference membrane, incorporation of a pyridyl group improves the oxidative stability against free radicals, increases the elongation at break to 55% (from 37%), and enhances the thermal stability to 326 °C (from 246 °C). In an accelerated fuel cell degradation test, polymeric membranes containing the sterically encumbered pyridyl unit exhibited exceptional stability (0.16 mV h^{-1} degradation rate over 1000 h) and retained ~80% of their peak power density over this time.

1. INTRODUCTION

A wide variety of hydrocarbon polymers functionalized with sulfonic acid have been investigated for use in proton exchange membrane fuel cells (PEMFCs), redox-flow batteries, and PEM electrolyzers.¹⁻⁴ Among these, sulfonated polyphenylenes are attracting increased attention due to their low gas permeability, high thermal and chemical stability, and mechanical robustness.^{5–8} However, this class of polymer requires relatively high sulfonic acid content to achieve a percolation network for proton and water transport and often swells to much greater extents compared to incumbent PFSA ionomer membranes. For instance, the volumetric expansion of reported sulfonated phenylated polyphenylene (sPPP-H⁺) homopolymers in water can be as high as 300 vol % at ambient temperature, which limits their useful integration into electrochemical devices.^{5,6}

It has been well-documented that the incorporation of monomer units containing basic N-heterocycle groups in a sulfonated polymer can serve to reduce swelling due to the creation of intermolecular acid-base interactions.^{9,10} The incorporation of basic N-heterocycle groups is also reported to enhance oxidative durability and thermal stability.⁹⁻¹² For

example, Guiver and co-workers prepared poly(benzothiazoleco-benzimidazole)-based PEMs that possessed low dimensional swelling and high mechanical strength.¹² Kallitsis et al. reported an aromatic polyether bearing pyridine group that retained its mechanical integrity after exposure to Fenton's Reagent for 72 h.¹⁰ A series of basic polybenzimidazole (PBI) blend polymers with low water uptake and enhanced oxidation resistivity were investigated for high-temperature PEMs by Kerres et al.^{3,13}

Despite the aforementioned, sulfonated hydrocarbon-based polymers for PEMs incorporating N-heterocycle moieties usually suffer from reduced proton conductivity due to the Brønsted-Lowry acid-base neutralization of dissociated protons. The N-heterocycle groups (e.g., benzimidazole, pyridine, pyrazole, triazole, and imidazole) commonly employed in these acid-base polymer systems can be readily neutralized by available protons from nearby sulfonic acid groups to form the conjugate acid.4,9,14-17 The stronger the

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Scheme 1. Synthesis of Sulfo-Triphenylated Pyridylpolyphenylenes (sTPPyPP-H⁺) and Sulfo-Triphenylated Phenylpolyphenylenes (sTPPPP-H⁺)



base, the stronger the proton is bound to the resulting conjugate acid, which reduces the extent of dissociate of the proton and reduces proton conduction.^{18–20} As a result, their utility in solid polymer electrolyte electrochemical devices is compromised. Thus, the addition of basic N-heterocycle groups to a sulfonated aromatic polymer creates a paradox: the resulting acid—base interactions serve to reduce swelling and enhance the mechanical properties of the solid polymer electrolyte, but proton conductivity and their performance in electrochemical devices are reduced.

To address this dilemma, physical blending and copolymerization have been employed to control the ratio of Nheterocycle moieties to sulfonic acid groups in polymers.^{4,13,15,16} In other examples, the number of acidic groups attached to a polymer has been increased to excessive values to compensate for the presence of acid-neutralizing basic groups and to obtain a desired ion exchange capacity (IEC) based on the concentration of "free" protons.^{15,19–25} Often, the molecular structures of such polymers are not easily defined as they possess block or random structures or consist of physical mixtures of acidic and basic polymers. Because the acid-base interactions require molecular proximity of the corollary groups, a lack of control of the polymer structures translates into a lack of control of the acid-base interactions within polymer chains. Given this, it would be useful to synthesize hydrocarbon polymers that bear both acidic and Nheterocycle groups with more precise molecular control and spatial resolution so that the effect of incorporating basic groups into acidic hydrocarbon polymers could be clearly distinguished.

To this end, we designed and synthesized two novel sulfonated homopolymers (Scheme 1): a sterically hindered

triphenylated pyridine-containing polyphenylene (sTPPyPP) and the corollary all-phenylene analogue, triphenylated phenylpolyphenylene (sTPPPP). Notably, the pyridine in the TPPy molecule is congested by three attached phenyl groups to provide steric hindrance around the amine. This design was incorporated to reduce the pK_a for the conjugate acid of the pyridine moiety and facilitate proton transport, the details of which are discussed later. It is known that incorporating hydrophobic phenyl groups into proton conducting polymers decreases their ion-exchange capacity (IEC) and consequently reduces the water uptake and swelling characteristics.²⁶⁻²⁹ Therefore, to compare the pyridine-containing polymer with a non-pyridine-containing polymers, the linker TPP was synthesized, and a the novel polymer, sTPPPP, was prepared. Thus, sTPPyPP and sTPPPP are structurally identical except for one N atom per repeat unit, as shown in Scheme 1. For comparison, a first-generation sulfonated phenylated polyphenylene homopolymer prepared by our group in this series, sPPP-H⁺, is also shown.⁶

2. EXPERIMENTAL SECTION

2.1. Synthesis. The details of materials, synthetic procedures, and reaction yields can be found in the Supporting Information.

2.2. Membrane Preparation. A 6 wt % polymeric solution was prepared by dissolving the polymer in DMSO. After filtering through a sintered glass funnel, the solution was poured into a glass Petri dish and placed for 12 h into an oven set to 86 °C. Once the solvent had evaporated, water was added to the Petri dish to help desorb the polymer membrane. The membrane was then soaked in 1 M H_2SO_4 for 24 h and subsequently in water for 3 × 12 h to remove residual acid. Membranes were dried under vacuum at 80 °C overnight.

2.3. Water Uptake and Swelling. Membrane samples were predried in a vacuum oven at 80 °C for 24 h. The weight of dry

samples W_{dry} was recorded. After immersion in Milli-Q water for 24 h, fully hydrated membrane samples were blotted dry with an absorbent paper and their weights W_{wet} were recorded. The experiment was typically repeated five times to obtain average values. Water uptake was then calculated by using eq 1:

water uptake (%) =
$$\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$
 (1)

The volume expansion was calculated via the equation

volume expansion (%) =
$$\frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{dry}}} \times 100\%$$
 (2)

where V_{wet} and V_{dry} are the volume of wet membrane and dry membrane, respectively, and $V = \text{length} \times \text{width} \times \text{thickness}$.

2.4. Ion-Exchange Capacity (IEC) Measurements. A small piece of membrane was predried (vacuum oven at 80 °C for 24 h, final weight W_{dry}) was immersed in a 25 mL solution of 2 M NaCl solution for 24 h. The membrane was removed, and the displaced H⁺ ions were titrated to neutral pH using a 0.01 M NaOH standard solution with phenolphthalein indicator. The IEC of the membrane was calculated using eq 3:

$$IEC = \frac{0.01 \times V_{NaOH}}{W_{dry}}$$
(3)

wherein V_{NaOH} is the volume of the 0.01 M NaOH solution used for titrating the proton concentration in the NaCl solution.

2.5. Hydration Number (λ), Analytical Acid Concentration [-SO₃H], Proton Mobility μ_{H^*} , and Water Content. The hydration number (λ) was calculated via the equation

hydration number (
$$\lambda$$
) = $\frac{1000 \times \text{water uptake}}{18.01 \text{ g/mol} \times \text{IEC}}$ (4)

where the molecular weight of H_2O is 18.01 g mol⁻¹.

The effective acid concentration in the whole membrane and the water-rich have $[-SO_3H]_{mem}$ and $[-SO_3H]_{water}$, respectively, were calculated via the following equations:

$$[-SO_{3}H]_{mem} = \frac{m_{dry}IEC_{titr}}{V_{wet membrane}}$$
(5)

$$[-SO_{3}H]_{water} = \frac{m_{dry}IEC_{titr}}{V_{water absorbed}} = \frac{m_{dry}IEC_{titr}}{m_{wet} - m_{dry}} \times 1 \text{ g/mL}$$
(6)

where $m_{\rm dry}$ and $m_{\rm wet}$ are the mass of dry and hydrated membrane, respectively, IEC_{titr} is the experimentally determined IEC obtained from titration experiments, and $V_{\rm wet}$ is the volume of a wet membrane sample.

The proton mobility $\mu_{H^+,mem}$ and $\mu_{H^+,water}$ were calculated according to the equations

$$\mu_{\mathrm{H}^{+},\mathrm{mem}} = \frac{\sigma_{\mathrm{H}^{+}}}{F[-\mathrm{SO}_{3}\mathrm{H}]_{\mathrm{mem}}}$$
(7)

$$\mu_{\mathrm{H}^{+},\mathrm{water}} = \frac{\sigma_{\mathrm{H}^{+}}}{F[-\mathrm{SO}_{3}\mathrm{H}]_{\mathrm{water}}}$$
(8)

where F is Faraday's constant, σ_{H^+} is the proton conductivity at 30 °C and 95% RH, and $[-SO_3H]$ is the effective acid concentration.

The water content wet and water $content_{expanded}$ were calculated via the following equation:

water content_{wet} =
$$\frac{m_{wet} - m_{dry}}{V_{wet} \times 1 \text{ g/mL}}$$
 (9)

where the m_{dry} and m_{wet} are the mass of dry and hydrated membrane sample, respectively, and V_{dry} and V_{wet} are the volume of dry and hydrated membrane sample, respectively.

2.6. Density of Polymers. The density of polymers ρ was calculated via the equation

$$\rho = \frac{m}{V} \tag{10}$$

where m is the mass of a membrane sample under the desired condition and V is the volume of a membrane sample under the same conditions.

2.7. Mechanical Stress Tests. The membranes were cut into barbell shapes using a standard ASTM D638-4 cutter. The mechanical tests were performed under ambient conditions on a single column system (Instron 3344 Series) using a crosshead speed of 5 mm min⁻¹. Five specimens were tested for each polymer's mechanic properties. The determined tensile strength, Young's moduli, and elongation at break were averaged over five samples. The error reported is the standard deviation for five measurements.

2.8. TGA Measurements. Six milligrams of the polymer sample was heated under Ar at 10 °C min⁻¹ from 23 °C to reach 800 °C. The weight loss was recorded by a PerkinElmer STA6000.

2.9. Oxidative Stability Test (Fenton's Test). The oxidative stability of polymers sTPPPP-H⁺ and sTPPyPP-H⁺ was studied by immersing dry, preweighed (average 20 mg, three samples for each hour) membrane samples in Fenton's reagent $(3\% H_2O_2, 3 \text{ ppm Fe}^{2+})$ at 80 °C. Every 1 h, a membrane sample was retrieved, washed with water (24 h × 3 times), and soaked in 1 M HCl (24 h × 3 times) and again in water (24 h × 3 times). After the membrane was dried in a vacuum oven at 80 °C for 24 h, the weight loss was calculated according to the following equation:

weight loss (%) =
$$\frac{M_0 - M_1}{M_0} \times 100\%$$
 (11)

where M_0 is the initial dry mass before Fenton's test and M_1 is the dry mass after the degradation test.

2.10. Proton Conductivity Measurements. A small piece of the membrane $(1 \text{ cm} \times 0.5 \text{ cm})$ was assembled into a conductivity cell in a two-probe configuration, as previously described.⁵ The cell was placed in an Espec model SH-241 humidity chamber, which allowed for temperature and humidity modulation. The ionic conductivity (σ) was calculated from the resistance (R) and the membrane dimensions using the equation

$$\sigma = \frac{L}{R \times A} \tag{12}$$

where A is the cross-sectional area of membrane for the resistance measurement and L is the distance between the two electrodes. R was measured using an impedance analyzer (Solartron 1260 frequency response analyzer (FRA) using ac frequencies ranging from 10 MHz to 100 Hz).

2.11. MEA Fabrication. The catalyst inks for fuel cell tests were prepared via the following method: Water was used to wet Pt/C powder (TKK TEC-10E50E: 46.4 wt % Pt on graphitized carbon), after which methanol was added to achieve the desired mixture (MeOH:H₂O = 3:1). Nafion D520 ionomer was added dropwise to the stirring mixture to obtain 1% solids containing 30 wt % ionomer and 70 wt % Pt/C. The resulting catalyst ink was then deposited via a spray coater (Sono-Tek ExactaCoat SC) onto the membrane surface at 60 °C for an electrode area of 5 cm², yielding a catalyst coated membrane (CCM): 0.4 mg cm⁻² Pt/C was deposited on the cathode, and 0.2 mg cm⁻² Pt/C was deposited on the anode. The CCMs were then sandwiched between conventional GDLs (Sigracet 24BC) and laid between Teflon gaskets with thicknesses allowing for 20–30% GDL compression by a torque wrench set to 50 in.-lb.

2.12. Fuel Cell Tests and Chemical Accelerated Stress Test (AST). The fuel cell performances for membranes were evaluated using a single cell fuel cell test station at 80 °C, 100%, 95%, 90%, and 50% RH, zero back-pressure, and O_2/H_2 or air/ H_2 . After the above evaluation for sTPPyPP-H⁺, the AST experiment was followed. The conditions were: OCV was held was 90 °C, 30% RH at anode and cathode, zero back-pressure under H_2/Air for 1000 h. Then the cell

Scheme 2. Synthesis of Diene Monomer BTCS-TEA^a

Synthesis of BTCS-TEA diene monomer



"Reagents and conditions: (a) Pd(PPh₃)₂Cl₂, CuI, TEA, 50 °C, overnight; (b) I₂, DMSO, 155 °C, overnight; (c) dibenzyl ketone, KOH, reflux, 45 min; (d) TMS-OSO₂-Cl, DCE, overnight; (e) *n*-BuOH, triethylamine, THF.

Scheme 3. Synthesis of Dienophiles TPPy and TPP^a



^{*a*}Reagents and conditions: (a) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuJ, TEA, 50 °C, overnight; (b) benzaldehyde, KOH, NH₄OH, EtOH, RT, 3 days; (c) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuJ, TEA, RT, overnight; (d) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *n*-BuLi, THF, -78 °C, 1 h; (e) phenylboronic acid, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O, 90 °C, overnight; (f) **13**, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O, 90 °C, overnight; (g) K₂CO₃, Et₂O/MeOH, RT, 1 h.

was reconditioned, and a polarization was performed to examine the fuel cell recoverability after AST. The details of fuel cell experiments can be found in the Supporting Information.

2.13. X-ray Scattering Experiment. We utilized a SAXSLab Ganesha 300XL instrument for X-ray scattering measurements. This instrument operates a copper anode source at 50 kV and 0.6 mA, selecting K α radiation with a wavelength of 1.54 Å⁻¹. Measurements

were performed in four standard configurations—extremely small angle, small angle, medium angle, and wide angle—providing a usable q-range of 0.003–2.7 Å⁻¹. All samples were allowed to equilibrate with ambient conditions overnight, and hydrated samples were immersed in deionized water for 1 h and then patted dry with a tissue. Samples were measured in sealed paste cells. A transmission-corrected

background measurement of an empty sample cell was subtracted pixel-by-pixel from each measurement.

The mid-q feature in the data from the hydrated samples was fit to the broad peak model (BPM) as implemented in the NIST small-angle scattering analysis package³⁰

$$I(q) = \frac{A}{q^n} + \frac{C}{1 + (|q - q_0|\xi)^m} + B$$
(13)

where q_0 , is the peak position, ξ is the correlation length, m and n are Porod exponents, A and C are scale parameters, and B is the qindependent background. q_0 is inversely proportional to the characteristic spacing D, which is commonly approximated according to the Bragg equation:

$$D = 2\pi/q_0 \tag{14}$$

However, this may underestimate length scales in polymer systems by up to 22%. 31

3. RESULTS AND DISCUSSION

3.1. Synthesis. As shown in Scheme 1, the polymers sTPPyPP-H⁺ and sTPPPP-H⁺ were synthesized from the diene BTCS-HNEt₃⁺ and dienophiles TPPy and TPP, respectively. The presulfonated monomer BTCS-HNEt₃⁺ (Scheme 2) was synthesized according to our previous report.⁶ The detailed procedures and reaction yields can be found in the Supporting Information.

The N-heterocycle dienophile TPPy was obtained via a twostep synthesis according to literature procedures (Scheme 3).^{32,33} The procedures commenced with Sonogashira coupling between trimethylsilylacetylene and bromoacetophenone (8) to yield the acetophenone-bearing alkynyl moieties (9). Subsequently, 9 was reacted with benzaldehyde to yield the target molecule TPPy (10). During the reaction, cyclization to yield pyridine rings and the cleavage of trimethylsilyl groups were achieved via a one-pot reaction under basic conditions. The structure of TPPy (10) was confirmed by ¹H NMR, ¹³C NMR, and high-resolution MS-¹H NMR (CDCl₃, 400 MHz) δ : 8.20 (d, 4H), 7.92 (s, 2H), 7.76 (d, 4H), 7.67 (d, 4H), 7.58–7.50 (m, 3H), 3.12 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ : 156. HRMS (EI) *m/z* calculated for C₂₇H₁₈N⁺ (M + H⁺) 356.1439; found 356.1449.

The route to the fully phenylene analogue, TPP, is also depicted in Scheme 3. A Sonogashira reaction was employed to couple bromoiodobenzene (11) with trimethylsilylacetylene, affording the alkyne-functionated bromobenzene (12). A lithium-halide exchange was performed with Br of 12, followed by addition of triisopropyl borate to yield the boronate ester (13). After Suzuki cross-coupling between 14 and phenylboronic acid, the resulting product 15 was subject to another Suzuki coupling with 13, yielding trimethylsilyl-protected TPP (16). During the reaction, although an excess of Na_2CO_3 was used as the base, the trimethylsilyl groups were not completely removed. Thus, deprotection using K₂CO₃ was employed in the last step was to ensure complete removal of trimethylsilyl groups, giving the product (TPP, 17). The structures of 16 and 17 were confirmed by ¹H NMR, ¹³C NMR, and highresolution MS (see the Supporting Information for 16). TPP $(17)^{-1}$ H NMR (CDCl₃, 400 MHz) δ : 8.20 (d, 4H), 7.92 (s, 2H), 7.77 (d, 2H), 7.67 (d, 4H), 7.57-7.53 (m, 6H), 3.18 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ: 142.70, 141.54, 141.32, 140.83, 132.64, 128.88, 127.71, 127.32, 127.18, 125.43, 124.84, 121.48, 83.45, 77.92. HRMS (EI) m/z calculated for $C_{28}H_{19}^{-1}$ $(M + H^{+})$ 355.1481; found 355.1472.

As outlined in Scheme 1, polymer sTPPPP-HNEt₃⁺ was prepared by Diels-Alder polymerization of BTCS-HNEt₃⁺ and TPP at 180 °C for 72 h. ¹H NMR analysis was employed to confirm the successful polymerization. ¹H NMR (DMSO-d₆, 400 MHz) δ: 9.00 (s, 4H), 8.25-6.0 (m, 48H), 3.01 (q, 24H), 1.25 (t, 36H). The characteristic ¹H resonance signals of methyl, methylene, and aromatic protons of the polymers are observed at δ 1.10, δ 3.05, and δ 6.00–8.35 ppm, respectively (Figure S27). The integration ratios are consistent with the experimental ¹H NMR spectra (-CH₂ 36H: -CH₂- 24H: aromatic protons 48H). The HNEt₃⁺ counterions were converted to the Na⁺ form via a methanolic NaOH wash, after which they were exchanged to the acidic form (H^+) by acidification with aqueous H₂SO₄ to yield polymer sTPPPP-H⁺. Gel permeation chromatography (GPC) analysis of sTPPPP-H⁺ revealed an estimated molecular weight (M_w = 271 kDa; D = 3.0). In a similar fashion, Diels-Alder polymerization of the presulfonated monomer BTCS-HNEt₂⁺ vielded polymer sTPPyPP-HNEt3+. The structure of polymer was verified by ¹H NMR spectroscopic analysis . ¹H NMR (DMSO-d₆, 400 MHz) δ: 8.9 (s, 4H), 8.25-6.46 (m, 47H), 3.01 (q, 24H), 1.25 (t, 36H). The chemical shifts associated with the methyl, methylene, and aromatic protons occur at δ 1.10, δ 3.05, and δ 6.00–8.35, and the integration ratios are 36H, 24H, and 47H, respectively (Figure S25). After the conversion from HNEt₃⁺ to H⁺ forms, polymer sTPPyPP-H⁺ was obtained with a $M_{\rm w}$ of 295 kDa (D = 2.56). Polymer membrane FT-IR data showed minimal differences (Figure 1).



Figure 1. FT-IR spectra of sTPPPP-H⁺ and sTPPyPP-H⁺ membranes.

The spectrum obtained for sTPPPP-H⁺ was very similar to that previously reported for sPPP-H⁺.³⁴ The spectrum obtained for sTPPyPP-H⁺ showed a new signal at 1617 cm⁻¹ (vs), and greater absorbance at 1223 cm⁻¹ (m), which is characteristic of pyridine mixed ring vibrations typically observed between 1581–1590 cm⁻¹ and 1217–1218 cm⁻¹, respectively.³⁵ Shifts to higher frequencies of the skeletal vibrations of pyridine have previously been attributed to hydrogen bonding due to the presence of hydrogen bond donors such as water or methanol.³⁶ In the case of sTPPyPP-H⁺, the observed shift may be due to intermolecular hydrogen bonding with neighboring $-SO_3H$ moieties.

3.2. Physical Properties. As shown in Table 1, the experimentally derived IEC of the fully phenylated polyphenylene sTPPPP-H⁺ (IEC_{exp} = $2.90 \pm 0.04 \text{ mmol g}^{-1}$) is close to its theoretical value (IEC_{th} = 3.06 mmol g^{-1}).

Table 1. IEC, Water Uptake, and Swe	lling of sTPPyPP-H ⁺ , TPPPP-H ⁺ ,	and sPPP-H ⁺
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	theor IEC^a (mmol g ⁻¹)	theor IEC ^b (mmol g^{-1})	exptl IEC (mmol g^{-1})	water uptake (wt %)	vol expansion (%) ^c	hydration no. ^d
sTPPyPP-H ⁺	3.05	2.29	1.98 ± 0.08	54.4 ± 0.7	62.4 ± 1.9	15.2
$sTPPPP-H^+$	3.06	3.06	2.90 ± 0.04	79.8 ± 2.6	81.8 ± 2.5	15.3
sPPP-H ⁺	3.70	3.70	3.47	319.3	364.3	50.7
<i>a</i>	h_ 1	<i>"a n i n n n n n n n n n n</i>				

"Based on sulfonic acid content. "Based on "free" H⁺ calculated by taking account of acid—base neutralization (one sulfonic acid group per pyridine group) into consideration. "Volume increase ratio (length \times width \times thickness). See the Supporting Information. "Based on experimental IEC.

Compared to the previously reported homopolymer sPPP-H⁺ (IEC_{exp} = 3.47 mmol g^{-1}), the reduced IEC of sTPPPP-H⁺ is attributed to the introduction of enhanced molecular mass of the triphenylphenylene compared to phenylene. Because of its structural similarity, the theoretical IEC of sTPPyPP-H⁺ (IEC_{th} = 3.05 mmol g^{-1}) is similar to that of sTPPPP-H⁺ when based simply on the number of sulfonic acid groups present. The titration-derived IEC_{exp} of sTPPyPP-H⁺ is found to be 1.98 \pm 0.08 mmol g^{-1} . This can be explained by assuming that each basic pyridine group neutralizes a sulfonic acid, such that only three acidic protons are available per polymer repeat unit. In this case, the theoretical IEC value (i.e., the "free" H⁺) for sTPPyPP-H⁺ is reduced to 2.29 mmol g^{-1} , closer to the experimental value. This indicates that indeed the proton bound to the conjugate acid of pyridine moiety is not exchanged with Na⁺ ions in the Na⁺/H⁺ exchange process used in the titration.

The results of dimensional swelling measurements are summarized in Table 1. At ambient temperature, sTPPPP-H⁺ membranes exhibit a water uptake of $79.8 \pm 2.6\%$ and volume expansion of 81.8 \pm 2.5%. The decrease in swelling compared to previously published data on sPPP-H⁺ is attributed to the increased molecular mass of the TPP moiety and the resulting reduced IEC compared to sPPP-H⁺. In comparison, the water uptake and volume expansion of the protonated triphenylpyridyl polymer membrane, sTPPyPP-H⁺, are 54.4 \pm 0.7% and $62.4 \pm 1.9\%$, respectively, a decrease of 32% and 24%, respectively, compared to sTPPPP-H⁺. In both cases, the values are significantly lower than those measured for sPPP-H⁺ (Table 1). Direct comparison between $sTPPPP-H^+$ and sTPPyPP-H⁺ indicates that the acid-base interaction between pyridine and sulfonic acid groups reducing swelling. Both polymers sTPPPP-H⁺ (λ = 15.2) and sTPPyPP-H⁺ (λ = 15.3) display a lower hydration number λ than sPPP-H⁺ (λ = 50.7).

Thermogravimetric analyses (TGA) of sTPPPP-H⁺ and sTPPyPP-H⁺ exhibited similar mass loss patterns with three steps consistent with previous reports on sulfonated polyphenylenes.^{5,7} As shown in Figure S30, the first stage of mass loss occurs between 100 and 200 °C due to loss of residual water. Degradation of sulfonic acid groups occurs during the second stage. TGA data indicate that the -SO₃H groups of pyridyl polymer sTPPyPP-H⁺ decompose at 326 °C, much higher in temperature than sTPPPP-H⁺, which occurs at 246 °C. This is the highest thermal stability among reported sulfonated polyphenylenes. $^{5-8,37}$ During this second stage, sTPPPP-H⁺ loses 23.6% of its mass, close to the theoretical value for loss of four -SO₃H groups (24.4%). Two decomposition steps in the desulfonation stage are observed for sTPPyPP-H⁺: an 18.8% mass loss at 326 °C, corresponding to three $-SO_3H$ groups (theoretical = 18.3%), and a 6.1% mass loss at 511 °C, corresponding to the fourth -SO₃H group (theoretical = 6.4%). This two-step behavior suggests that each pyridine group may function as a protecting group for a sulfonic acid moiety during thermolysis, by virtue of it

forming an acid—base salt. The third stage of decomposition, observed at temperatures >550 °C, is attributed to the decomposition of the polyphenylene backbone.^{5,7} The TGA data show that sTPPyPP-H⁺ possesses a greater thermal stability than sTPPyPP-H⁺, which in turn is consistent with previously reported polymers based completely on phenylenes,^{5,7} indicating that incorporation of pyridine moieties into acid-bearing polymers is an effective approach to enhancing their thermal stability, which may aid their thermal processing. This phenomenon is consistent with previous reports, which also have pointed out that improved thermal stability can be ascribed to acid—base interactions.^{12,38}

As shown in Table 2 and Figure S29, the sTPPyPP-H⁺ membranes exhibit a tensile strength of 43.3 \pm 1.1 MPa,

Table 2. Mechanical Properties^{*a*} of sTPPyPP-H⁺, TPPPP-H⁺, sPPP-H⁺, and N-211

ionomers	tensile strength (MPa)	elongation at break (%)	Young's modulus (MPa)
sTPPyPP- H ⁺	43.3 ± 1.1	55.5 ± 3.1	401.8 ± 23.8
$sTPPPP-H^+$	54.8 ± 1.9	36.8 ± 1.7	584.1 ± 81.5
sPPP-H ⁺⁵	43.5 ± 1.9	29.1 ± 1.4	1059 ± 34
N-211	17.3 ± 0.4	148 ± 4	270 ± 17

^aThe mechanical analyses were performed under ambient conditions (23 °C, 50% RH).

Young's modulus of 401.8 ± 23.8 MPa, and elongation at break of 55.5 \pm 3.1% under ambient conditions. Polymer sTPPPP-H⁺ yields comparable values: 54.8 \pm 1.9 MPa, 584.1 \pm 81.5 MPa, and 36.8 \pm 1.7%, respectively. Both polymers show a higher tensile strength and Young's modulus but lower elongation at break than N-211. The N-heterocycle-containing polymer sTPPyPP-H⁺ was less strong but tougher than sTPPPP-H⁺. Membrane toughness is an important consideration for material handling, electrochemical cell construction, and durability in long-term, dynamic operation of electrochemical devices. It is commonly known that sulfonated, phenylated polyphenylenes possess a relatively high tensile strength and Young's modulus but a low elongation at break compared to that of PFSA ionomer membranes. For example, the postsulfonated polyphenylenes reported by Fujimoto et al. possessed a tensile strength of 74.0 MPa, Young's modulus of 1200 MPa, and elongation at break of 12%.⁷ The presulfonated sPPP-H⁺ reported previously listed values of 43.5 \pm 1.9 MPa, 1059 ± 34 MPa, and $29.1 \pm 1.4\%$, respectively.⁵

Both polymers sTPPPP-H⁺ and sTPPyPP-H⁺ showed tensile strength (54.8 \pm 1.9 and 43.3 \pm 1.1 MPa, respectively) comparable to that of previously reported materials.^{5,7} Despite the lower Young's moduli (584 \pm 81.5 and 401.8 \pm 23.8 MPa, respectively) as compared to sPPP-H⁺, both polymers showed improved elongation at break (36.8 \pm 1.7% and 55.5 \pm 3.1%, respectively) and generally improved membrane flexibility and robustness. The higher elongation at break observed in



Figure 2. (a) In-plane proton conductivities of sTPPyPP-H⁺, sTPPPP-H⁺, and N-211 at 30 $^{\circ}$ C (open) and 80 $^{\circ}$ C (solid) under different RH and (b) respective log plot.

Table 3. Analytical Acid Concentration ([-SO₃H]), Effective Proton Mobility (μ_{H^+}), and Water Content of sTPPPP-H⁺ and sTPPyPP-H⁺

membranes	σ^a (mS cm ⁻¹)	water $\operatorname{content}_{\operatorname{mem}}$	$\left[-SO_{3}H ight]_{mem}(M)$	$[-SO_{3}H]_{water}$ (M)	$\mu_{\text{H}^{^+},\text{mem}}{}^a~(ext{cm}^2~ ext{V}^{-1}~ ext{S}^{-1})$	$\mu_{\text{H}^{+},\text{water}}^{a}$ (cm ² V ⁻¹ S ⁻¹)
$sTPPPP-H^+$	115	0.46	1.66	3.6	0.72×10^{-3}	0.33×10^{-3}
sTPPyPP-H ⁺	85	0.41	1.48	3.6	0.60×10^{-3}	0.24×10^{-3}
^{<i>a</i>} At 30 °C and 9	95% RH.					

sTPPPP-H⁺ vs sPPP-H⁺ (+7.7%) may be due to the slightly more kinked molecular structure of the repeating unit induced by the TPP moiety, allowing for a more flexible polymer backbone. The further enhancement in elongation at break observed for sTPPyPP-H⁺ (+26.4% vs sPPP-H⁺) may also be ascribed to the kinked structure of the repeating unit due to the TPPy moiety present, together with the acid-base interactions. These data suggest that such acid-base interactions exert a role in improving membrane strain, as sTPPyPP-H⁺ exhibits the highest elongation at break among previously reported sulfonated polyphenylenes.^{5-8,37} It is noted that the densities of dry sTPPyPP-H⁺ and dry sTPPPP-H⁺ are 1.18 and 1.04 g cm⁻³, respectively, and the densities of hydrated sTPPyPP-H⁺ and hydrated sTPPPP-H⁺ are 1.15 and 1.03 g cm⁻³, respectively. That is, sTPPyPP-H is denser than sTPPPP-H⁺ by virtue of the acid-base interactions present.

3.3. Proton Conductivity. The RH-dependent proton conductivities for polymer sTPPPP-H⁺ and sTPPyPP-H⁺ were determined at 30 and 80 °C (Figures 2). At 95% RH, sTPPPP-H⁺ (155 mS cm⁻¹ at 80 °C, 115 mS cm⁻¹ at 30 °C) exhibited greater proton conductivities than sTPPyPP-H⁺ (119 mS cm⁻¹ at 80 °C, 85 mS cm⁻¹ at 30 °C) due to its higher IEC (2.90 mmol g⁻¹). Both polymers exhibited proton conductivities higher than a PFSA reference, Nafion N-211 (110 mS cm⁻¹ at 80 °C, 78 mS cm⁻¹ at 30 °C).

The ion exchange capacity of sulfonated polyphenylenebased polymers plays an important role in their proton conductivity—a small difference in IEC can lead to a large change in conductivity.^{7,39,40} For example, in the case of the sulfo-phenylated polyphenylenes reported by Cornelius and co-workers, an IEC reduction from 1.8 to 1.4 mmol g⁻¹ (a 22% decrease) resulted in a disproportionate reduction in proton conductivity in water at 80 °C, from 87 to 49 mS cm⁻¹ (44% decrease).⁷ In another report, sulfonated polyphenylene polymers prepared by Huang's group³⁹ possessed a high proton conductivity (264 mS cm⁻¹) for high IEC (2.73 mmol g^{-1}) membranes, which also decreased disproportionately (70%, to 80 mS cm⁻¹) at lower IEC (31%, 1.89 mmol g^{-1}) when measured at 95% RH and 80 °C. In contrast, while sTPPPP-H⁺ and sTPPyPP-H⁺ display a similar discrepancy in IEC (32% difference from 2.90 to 1.98 mmol g^{-1}), the associated decrease in proton conductivities is only 23% (155 to 119 mS cm⁻¹) when measured at 95% RH and 80 °C.

To explore the mechanism explaining the unusually high conductivity of sTPPyPP-H⁺ having an IEC < 2 mmol g^{-1} , we examined the water content, analytical acid concentration ([-SO₃H]), and effective proton mobility (μ_{H^+}) for the two polymers. Besides IEC, water content has an impact on proton conduction in a PEM.⁴¹ As shown in Table 3, the water contents for sTPPvPP-H⁺ and sTPPPP-H⁺ are close, 0.41 vs 0.46, respectively. For hydrocarbon-based PEMs, a higher IEC often leads to a higher water content.⁴¹ However, in our case, the slightly decreased water content of sTPPyPP-H⁺ in comparison to sTPPPP-H⁺ suggested that the water content is not significantly affected by the large IEC difference, which may be caused by the lower volume swelling of the former membrane. Because sTPPyPP-H⁺ displays a unique behavior in swelling, IEC, and proton conductivity, we calculated the volume of the absorbed water, $[-SO_3H]$, and μ_{H^+} with respect to the volume of both the hydrated membrane and the water phase (see the Experimental Section for details). In this analysis, [-SO₃H]_{mem} refers to the analytical acid concentration per the volume of wet membrane, while $[-SO_3H]_{water}$ refers to the analytical acid concentration per the volume of absorbed water. The latter recognizes that H⁺ resides in the water phase only. The $[-SO_3H]$ value of sTPPyPP-H⁺ in either case is slightly lower or identical compared to that of sTPPPP-H⁺ (1.48 M vs 1.66 and 3.6 M vs 3.6 M, respectively). According to eq 5, $[-SO_3H]_{mem}$ is dependent on both IEC_{exp}

and the volume of the wet membranes. IEC_{exp} of sTPPyPP-H⁺ is smaller than that of sTPPPP-H⁺ (1.98 mmol g^{-1} vs 2.90 mmol g^{-1}), which can decrease the $[-SO_3H]_{mem}$ value for the former. However, the volume swelling of the sTPPyPP-H⁺ in the hydrated state is smaller (62.4% vs 81.8%), which compensates for the decrease in $[-SO_3H]_{mem}$ caused by the difference in IEC. Similarly, in regards to the acid concentration in the water phase in the membrane $([-SO_3H]_{water})$, the volume of absorbed water for sTPPyPP- H^+ is also lower compared to that of sTPPPP- H^+ (eq 6), which makes up the above-mentioned decrease in $[-SO_3H]_{water}$. Thus, it explains why the sTPPyPP-H⁺ and sTPPPP-H⁺ membranes possessed similar values in $[-SO_3H]_{mem}$ or $[-SO_3H]_{water}$. Given that the proton conductivities at 30 °C and 95 RH (Table 3) and using eqs 7 and 8, we calculated the effective proton mobilities for the two membranes. The sTPPyPP-H⁺ membrane exhibited $\mu_{H^+,mem}$ (based on the volume of the wet membrane) of 0.60 \times 10^{-3} cm 2 V $^{-1}$ S $^{-1}$ and $\mu_{H^{+},water}$ (based on the volume of absorbed water) of 0.24× 10^{-3} cm² V⁻¹ S⁻¹, which are smaller than those of sTPPPP-H⁺ (0.72 × 10^{-3} cm² V⁻¹ S⁻¹ and 0.33 × 10^{-3} cm² V⁻¹ S⁻¹, respectively). Considering the large IEC difference between the two polymers, it is surprising that the proton mobility values of sTPPyPP-H⁺ are as high as they are based on previously reported correlations of IEC versus proton mobility. Because the effective proton mobility is related to acid dissociation and tortuosity in the PEM,⁴² we examined possible reasons for the high mobility in the context of pK_a of the acidic functionality, which controls the fraction of free H^+ carrier, and morphology, which controls the tortuosity.

A possible reason for this unusually high proton conductivity behavior of sTPPyPP-H⁺ with respect to its low IEC is due to the presence of the sterically hindered pyridine (TPPy). As previously mentioned, in the pyridine-containing dienophile monomer, the basic N atom is hindered by two flanking phenyl rings, resulting in a sterically hindered pyridine, which was reported to possess a lower basicity than pyridine itself.⁴³ It has been well-studied that the steric effect introduced by the pyridine limits the solvation of the resulting protonated pyridine and lowers the pK_a for sterically hindered pyridinium (H^+) .⁴³ It has been experimentally verified that the pK_a of protonated pyridine in 70% aqueous ethanol is 3.69, while the more sterically hindered protonated 2,4,6-triphenylpyridine (TPPy) is 1.84.44 According to the extrapolated equation $(pK_{a,water} - pK_{a,70\% ethanol} = 1.56)$ ⁴³ the pK_a of the conjugate acid of 2,4,6-triphenylpyridine is 3.40 in water at 25 °C, which is lower than that of pyridine (5.25).⁴⁵ On the basis of this, 1 M of the conjugated acid 2,4,6-triphenylpyridinium (H⁺) in water dissociates 2.0%. Under the same conditions, 1 M of pyridine-H⁺ will dissociate 10 times less (\sim 0.2%). Because of the reduced pK_a of TPPy, as shown in Scheme 4, the proton on TPPy may dissociate to a greater extent than a proton bound to pyridine, which will participate in proton conduction. Liu et al. demonstrated this concept by incorporating 1H-1,2,4triazole (pK_a of its conjugate acid = 2.39) in place of imidazole $(pK_a \text{ of its conjugate acid} = 7.18)$ to enhance proton conductivity of a hydrocarbon-based PEM.46 Miyatake and co-workers also reported a triazole-based polyimide possessing a high proton conductivity.⁴⁷ Thus, the reduced pK_a of TPPy-H⁺ caused by the sterically hindrance around the nitrogen may explain why the sTPPyPP-H⁺ polymer, with an IEC of <2.0 mequiv g^{-1} , exhibited a proton conductivity comparable to that

Scheme 4. Scheme Demonstrating How Steric Hindrance Leads to a Lower pK_a of the Protonated Form of TPPy Relative to Py



of the sTPPPP-H⁺ polymer, which possesses a 50% higher IEC (2.9 mequiv g^{-1}).

Another reason for the higher than expected proton conductivity of sTPPyPP-H⁺ could lie in differences between its morphology and that of sTPPPP-H⁺, given that differences in conductivity can be tied to the nanoscale organization of the polymer membrane. We performed X-ray scattering experiments to investigate the morphology of the materials. The results are shown in Figure 3. Under ambient conditions, the



Figure 3. Small-angle X-ray scattering spectra of dry and hydrated sTPPyPP-H⁺ and sTPPPP-H⁺.

X-ray scattering profiles for sTPPyPP-H⁺ (black) and sTPPPP-H⁺ (blue) are indistinguishable, suggesting that the morphologies of dry membranes are similar. However, when the two membranes are hydrated, the sTPPPP-H⁺ membrane (red) reveals a much more distinct feature in the mid-q region than sTPPyPP-H⁺ (magenta), indicating a sharper interface between the water- and polymer-rich regions of the material.

The broad peak model (BPM, eq 13) was fit to the mid-q regions of the SAXS data for the hydrated membranes to determine the distribution and extent of the water-rich regions (Figure S35); the BPM has been used to study solvation distributions in polymers.⁴⁸ Results produced similar values for the separation D of water-rich regions for both films: 36 ± 1 Å for sTPPPP and 35 ± 1 Å for sTPPyPP. However, values for

the correlation length ξ , which represents the extent of the water-rich regions, were substantially different. sTPPPP-H⁺ measured 13.8 \pm 0.3 Å, whereas sTPPyPP-H⁺ measured 6.2 \pm 0.6 Å, reflecting the broader feature in the latter. The more intense peak with larger ξ in sTPPPP-H⁺ indicates that the water-rich regions are more distinct and are of greater extent than in sTPPyPP-H⁺, while the water content by volume is similar in the two materials (Table 1).

Both hydrated samples showed a large peak at ~2 Å⁻¹, which is consistent with bulk water.⁴⁹ As this feature could correspond to tighter intermolecular packing inside the membranes *or* bulk water on the surface of the membranes or sample holders, we avoided further interpretations of the WAXS region.

3.4. Stability against Fenton's Reagent. The oxidative stability of the polymers was examined by immersing polymeric membranes in Fenton's reagent. As shown in Figure 4, in the first 3 h, sTPPyPP-H⁺ and sTPPPP-H⁺ showed a



Figure 4. Accelerated oxidative stability test of membranes sTPPPP-H⁺ and sTPPyPP-H⁺ in Fenton's reagent (3% H₂O₂, 3 ppm Fe²⁺) at 80 °C (the thickness of dry membranes used in the Fenton's test is 28 \pm 5 μ m; sTPPPP-H⁺ membrane dissolved completely at 5.3 h).

similar rate of degradation. However, after 4 h of exposure to the Fenton's reagent, sTPPyPP-H⁺ degraded more slowly. The mass loss of sTPPyPP-H⁺ was 37.5 ± 9.1 wt % after 4 h, while

sTPPPP-H⁺ lost 57.5 \pm 7.8 wt %. The sTPPPP-H⁺ membrane completely dissolved in the solution after 5.3 h while 10 wt % of sTPPyPP-H⁺ remained after 6 h. Enhanced oxidative stability of N-heterocycles is recognized in the literature.^{9,10,21} For example, to examine the antioxidation property of pyridine-containing polymers, Wang and co-workers⁵⁰ refluxed a pyridine-based compound in a mixture of H_2O_2 and glacial acetic acid. Mass spectrometric analysis indicated that pyridine had reacted with peroxide to form pyridine-N-oxide, scavenging reactive species in solution. In the case of sTPPyPP-H⁺, the pyridine moiety is believed to act as a freeradical scavenger, preventing critical chain degradation. It should be pointed out that although the hydrocarbon polymer sTPPPP-H⁺ displays a lower chemical stability than its pyridyl analogue, it is still much more resistive to oxidative degradation than sulfonated polyaromatic ethers (20% weight loss after 1 h in Fenton's reagent, 3% H₂O₂, 2 ppm Fe²⁺ at 80 °C).39

3.5. Investigation in Fuel Cells. Single cell performance of membrane-electrode assemblies incorporating sTPPPP-H⁺ and sTPPyPP-H⁺ membranes (thickness in dry state: 28 and 28 μ m, respectively) were evaluated in a fuel cell testing station operated under zero back-pressure, at 80 °C, and under fully humidified conditions. Catalyst ink containing PFSA ionomers and Pt/C was spray coated onto the membranes to form catalyst-coated membranes (CCMs) to achieve 0.4 mg cm^{-2} loading on the anode and 0.2 mg cm^{-2} on the cathode. MEAs were subjected to fuel cell conditioning and RH cycling, the duration of which was 15 h, after which polarization experiments were conducted. As shown in Figure 5a, using H_2/O_2 , the peak power densities of sTPPPP-H⁺ and sTPPyPP-H⁺ membranes are 1080 and 931 mW cm⁻², respectively. Using H_2/air , the peak power density of sTPPyPP-H⁺ is similar to that of sTPPPP-H⁺ (532 vs 521 mW cm⁻², Figure 5b). MEAs prepared from N-212 tested under the same conditions yield peak power densities of 793 mW cm⁻² using H_2/O_2 and 455 mW cm⁻² using H₂/air.⁵ For MEAs prepared from 25 μ m N-211 the maximum power densities in H_2/O_2 and H_2/air under identical conditions are 1337 and 537 mW cm⁻², respectively (Figure 5), which reflects the reduced thickness of the N-211 membranes. An electrochemical surface area (ECSA) measurement was performed via cyclic voltammetry. The ECSA values of N212 and N211 are 68.6 and 49.2 $m^2 g^{-1}$



Figure 5. In situ polarization (left axis, solid) and power density (right axis, open) under (a) H_2/O_2 and (b) H_2/air . Conditions in both cases were 80 °C, 100% RH, 0.5/1.0 slpm anode/cathode gas flows, and zero back-pressure.

Pt, respectively, while sTPPPP-H⁺ displayed an ECSA value of 34.5 m² g⁻¹ Pt and sTPPyPP-H⁺ showed that of 55.1 m² g⁻¹ Pt. The ohmic resistances (*iR*-drop method) of sTPPPP-H⁺ and sTPPyPP-H⁺ polymers are 63 and 65 mohm·cm², respectively, indicating that the two polymers exhibit high *in situ* proton conductivities.

The sTPPPP-H⁺ and sTPPyPP-H⁺ polymers displayed open circuit voltages (OCVs) of 0.966 and 0.936 V, respectively. In addition, after 15 h of fuel cell conditioning and RH cycling, fuel crossover of sTPPPP-H⁺ (0.52 mA cm⁻²) and sTPPyPP-H⁺ (0.46 mA cm⁻²) membranes determined by chronoamperometry (CA) measurements were exceptionally low, further verified by comparison to a N-211 standard (1.36 mA cm⁻²) under the same conditions. Both OCV and CA data show that both membranes possess good gas barrier properties with similar gas crossover rates, further supporting that the addition of the pyridine moiety and resulting acid—base interactions does not lead to membranes with reduced quality or performance.

Polarization studies under different RH were performed on sTPPyPP-H⁺ and sTPPPP-H⁺. The peak power densities reached 931/878/846/297 mW cm⁻² and 1083/1075/1042/ 470 mW cm⁻², respectively, under 100/95/90/50% RH using H_2/O_2 (Figures S32 and S33). After performing the fuel cell test at 50% RH, the polarization data at 100% RH were reobtained to examine the recoverability for two polymers. While sTPPPP-H⁺ experienced a decrease of 17% in peak power density (1083 to 896 mW cm⁻²) at 100% RH following polarization at 50% RH, the two IV curves of sTPPyPP-H⁺ were identical (Figure S34). Full recoverability was observed for the pyridine-containing polymeric membrane, possibly due to its tougher nature (cf. mechanical properties). Following the above polarization experiments, an in situ chemical accelerated stress test (AST) was performed to evaluate the chemical stability of sTPPyPP-H⁺ within a fuel cell device. During this test, the open circuit voltage (OCV) was held at 90 °C and 30% RH using H₂/air. It has been reported that such harsh conditions can generate hydrogen and peroxide radicals, which are highly reactive and detrimental to membrane integrity. For example, N-211 fails after 153 h under these condition.⁵ In contrast, after 1000 h of AST, an OCV of 0.733 V was observed for sTPPyPP-H⁺-a decrease of only 0.16 mV h⁻¹ was observed for the first hour, after which the degradation rate decreased to 0.11 mV h⁻¹. By comparison, N-211 degraded by 2.14 mV h⁻¹ under the same conditions (Figure 6). After the AST, the sTPPyPP-H⁺ MEA was reconditioned using the procedure described above, and a second set of polarization experiments were performed. The peak power density after 1000 h of AST was found to be 728 mW cm⁻² at 80 °C, 100% RH using H_2/O_2 . (Figure 7). That is, after 1000 h of accelerated in situ oxidative chemical degradation, sTPPyPP-H⁺ experienced a decrease in performance of only 21%, and continued to serve its function as a PEM, providing useful polarization data with no signs of cell failure. This exceptional in situ performance is attributed to a combination of increased membrane toughness, low gas crossover, and high oxidative stability.

4. CONCLUSIONS

In this work, we systematically investigated the effect of a sterically hindered pyridine moiety on the properties of proton-conducting sulfonated polyphenylenes. Two novel sulfonated, phenylated polyphenylene homopolymers,



Figure 6. Accelerated stress test (AST) of sTPPyPP-H⁺ (the thickness in the dry state: 28 μ m, plus conditioning and polarization experiments before and after the AST) and N-211 (AST only). The open circuit voltage (OCV) was held at 90 °C, 30% RH, and zero back-pressure using H₂/air. During the AST of N-211, several polarizations and gas crossover measurements were conducted, the interruption of which caused the observable spikes.



Figure 7. *In situ* polarization (left axis, solid) and power density (right axis, open) of sTPPyPP-H⁺ before and after AST. Conditions were 80 °C, 100% RH, 0.5/1.0 slpm anode/cathode gas flows, and zero back-pressure under H_2/O_2 .

sTPPPP-H⁺ and sTPPyPP-H⁺, were designed and synthesized for comparison. Both polymers possess well-defined structures with a nonrandom distribution of -SO₃H groups because of the prefunctionalization approach, and their compositions of repeating units differ by only one atom. These minimal structural variations enabled precise analysis of the effect of the pyridine moiety (N atom) on physicochemical properties such as the dimensional stability, elongation at break, and thermal and oxidative properties, which were significantly enhanced. Insitu and ex-situ electrochemical experiments revealed a minimal reduction in proton conductivity and fuel cell performance of sTPPyPP-H⁺ versus that of sTPPPP-H⁺. Notably, to the best of our knowledge, many properties of sTPPyPP-H⁺, such as the elongation at break at ambient conditions $(55.5 \pm 3.1\%)$, the initial thermal degradation temperature (326 °C via thermolysis), and chemical durability in fuel cells (0.16 mV h^{-1} degradation rate in 1000 h of AST), are exceptional among reported sulfonated aromatic polymers. The results indicate that incorporation of a sterically hindered pyridine moiety into sulfonated polyphenylenes is an efficient means of exploiting

acid—base interactions and improving the physical and chemical attributes of polyphenylenes without compromising proton conductivity. We propose two possible explanations for this: the morphological differences caused between the pyridine and non-pyridine form and the reduced pK_a of pyridinium (H⁺) caused by the sterically hindered amine structure; however, more possibilities remain to be explored. We expect this simple pyridine moiety to be of broad utility in the design and synthesis of sulfonated aromatic-based polymers for next-generation proton-conducting membranes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b02289.

Materials and instruments information, full synthetic schemes for each monomer and polymer starting from commercially available reagents, the synthetic details and NMR spectra for all compounds and polymers described, stress vs strain curves of polymers at ambient conditions, TGA profiles of polymers under nitrogen flow, additional experimental information about fuel cell setup and characterization, in situ polarization and power density curves of both polymers described compared to Nafion 211 and 212 membranes, in situ polarization and power density curves of both polymers described at different RHs using H_2/O_2 , in situ polarization of both polymers described before and after 50% RH polarization using H₂/O₂, fit small-angle X-ray scattering spectra of both polymers described in their hydrated state (PDF)

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Notes

The authors declare no competing financial interest.

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