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Rigid-Rod Poly(phenylenesulfonic acid) Proton Exchange Membranes with Cross-Linkable Biphenyl Groups for Fuel Cell Applications

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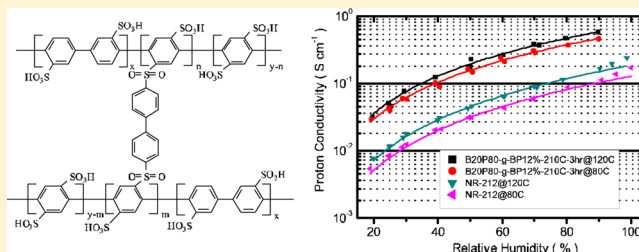
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S Supporting Information

ABSTRACT: Biphenyl was grafted on rigid-rod aromatic poly(*p*-phenylenesulfonic acids) (IEC ~ 8 mequiv g⁻¹) to generate cross-linkable polyelectrolytes. Cross-linking conditions and film properties before and after cross-linking were studied. Films equilibrated between 20 and 30% relative humidity (RH) had tensile moduli of 2 to 1 GPa and broke at 5 to 9% elongation. The moduli decreased as RH increased and dropped drastically at high humidity if the films were not cross-linked. Grafted films had conductivities at 80 °C 4–5 times that of Nafion NR-212 over the whole relative humidity range even after cross-linking. The sample reported in detail here had a conductivity of 0.10 S cm⁻¹ at 120 °C and 30% RH. As is usual for this class of materials, even after the loss of 24% of starting sulfonic acid groups by grafting and cross-linking, ionic conductivity was high at low humidity. A membrane electrode assembly (MEA) prepared with this rigid-rod poly(phenylenesulfonic acid) proton exchange membrane and tested in a fuel cell exhibited performance and properties similar to those of Nafion NR-212 films. The power density was $\sim 95\%$ of that of the Nafion MEA over the operating range in spite of relatively high hydrogen crossover due to the presence of nanocracks in the membrane.



1. INTRODUCTION

Proton exchange membranes (PEMs) are key components of low-temperature fuel cells (PEMFCs). The membranes serve to transfer protons from anode to cathode but act as barriers for fuel gas, oxidant, and electrons. Currently, perfluorinated polymers, such as Nafion and Flemion, are widely used as PEM materials due to their excellent physical and chemical stability and high proton conductivity.^{1–3} However, their disadvantages, such as high price, high fuel crossover, and loss of water at high temperature and low humidity that seriously decreases conductivity, restrict their practical use in PEMFCs. Therefore, the development of less expensive PEMs with better high-temperature conductivity is needed for the large-scale commercialization of PEMFCs.

In the past two decades, many hydrocarbon-based PEMs have been suggested as alternatives to the perfluorinated polymer membranes,⁴ such as polysulfones,^{5,6} poly(ether ether ketone)s,^{7,8} polyimides,^{9–11} poly(phenylene)s,^{12–14} and poly-benzimidazoles.^{15–21} While they could be less expensive, most of them lose conductivity at low relative humidity (RH) and perform poorly above 100 °C. We have studied a new class of

PEMs based on rigid-rod, nematic liquid crystalline poly-(aromatic sulfonic acid) polymers and copolymers over the past 10 years.^{11,14,22–32} Since chains in these polymers are packed parallel, incorporation of bulky comonomers forces chains apart and generates long nanopores lined with sulfonic acid groups that hold water very tightly. Water retention and conductivity at low RH increase compared to Nafion and poly(arylene ether sulfonic acid) structures. We call this “frozen-in free volume”.²² Initially, we studied poly(naphthalene bis-imide)s.^{11,26,30–32} They were unstable in the acid state due to slow hydrolysis of the imide groups. Research over the past 8 years has focused on poly(phenylenesulfonic acid)s, which cannot hydrolyze.

A new synthetic method was developed to make the rigid-rod polymers, poly(*p*-biphenylene disulfonic acid) and poly(*p*-phenylene disulfonic acid), using the Ullmann reaction.^{14,22–25,27} Their conductivity at low RH was remarkable compared to other PEMs. It met or exceeded US Department

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of Energy objectives for 2010 and later. However, the homopolymers had two major problems; they were water-soluble and had poor break elongation. Alkylbenzene groups were grafted to confer water insolubility, but the resultant copolymer became very soft at high humidity and the membrane broke into a colloidal dispersion in water.³³

Normally, block copolymers are made to generate dimensionally stable, water-insoluble materials. This is relatively easy to accomplish with solution polymerization of A–A, B–B, and C–C monomers. In our case, when polymerizing a single monomer, the chain length could not be controlled by monomer ratios. In addition, the Ullmann reaction is not a solution reaction since it requires monomer or end-group adsorption on a metallic copper surface to proceed. We found that the reaction is strongly affected by monomer stereochemistry and polarity. No sulfonated ester or sulfone comonomer that we made could be copolymerized or homopolymerized. Any factor that raised electron density at the aromatic bromide site decreased reactivity. We could not make random copolymers, much less block copolymers.

In the present study, we describe a new approach to generate dimensionally and mechanically stable materials through grafting biphenyl onto poly(*p*-phenylene disulfonic acid) homopolymer and copolymers and its subsequent cross-linking. Such grafting yields the much less reactive biphenyl 4-sulfone. Heating the grafted polymers at 170 °C or higher cross-linked them. Cross-linking was almost complete after 1 h at 210 °C. They were studied before and after cross-linking. Cross-linked membranes were made into membrane electrode assemblies (MEAs) and tested at the Florida Solar Energy Center.

2. EXPERIMENTAL SECTION

2.1. Materials and Instrumentation. All chemicals were purchased from Sigma-Aldrich. Copper powder (99%, 400 mesh) was activated according to a previously reported procedure,³⁴ vacuum-dried, and used immediately. *N*-Methylpyrrolidinone (NMP) was dried by calcium hydride and distilled under vacuum before use. 1,4-Dibromobenzene (98%), 4,4'-dibromobiphenyl (98%), fuming sulfuric acid (12–17% SO₃), and other solvents and reagents were used as received. ¹H and ¹³C NMR spectra of monomers, polymers, copolymers, and their grafts were recorded on a Varian Inova NMR spectrometer operating at a proton frequency of 600 MHz and a carbon frequency of 150 MHz. Deuterium oxide or deuterated methanol was used to dissolve samples, with added dioxane or solvent residual peak (CD₂H) as chemical shift reference.

4,4'-Dibromobiphenyl 3,3'-disulfonic acid (DBBPDSA) was synthesized from 4,4'-dibromobiphenyl using fuming sulfuric acid.²⁷ NMR data are listed here: ¹H (Li salt in D₂O, δ , ppm) 8.17 (d, 2H), 7.73 (d, 2H), 7.45 (dd, 2H). ¹³C (Li salt in D₂O, δ , ppm): 143.0 (C–SO₃H), 138.6 (C–C), 136.2 (CH–CBr), 131.2 (CH–C), 127.7 (CH–CSO₃H), 119.4 (C–Br). 1,4-Dibromobenzene 2,5-disulfonic acid (DBBDSA) was synthesized from 1,4-dibromobenzene using fuming sulfuric acid.²⁴ NMR data are listed here: ¹H (Li salt in D₂O, δ , ppm): 8.34 (s, 2H). ¹³C (Li salt in D₂O, δ , ppm): 145.4 (C–SO₃H), 135.6 (C–H), 118.7 (C–Br). The corresponding NMR spectra are provided in Figures S1 and S2 of the Supporting Information.

2.2. Synthesis of Polymers and Copolymers. DBBDSA-Li salt (16.1 g, 0.04 mol) and freshly activated and predried copper powder (25.4 g, 0.40 mol) were placed in a 1000 mL three-neck heavy-duty flask with a magnetic stirring bar and dried at 135 °C under high vacuum (0.03 Torr) for 48 h. Freshly distilled NMP (750 mL) was added to the system using a double-tipped needle under argon pressure. The mixture was degassed by bubbling with argon for 30 min and then polymerized at 140 °C for 36 h under vigorous stirring.

After polymerization, the mixture was filtered. The solid was extracted at room temperature by stirring with 800 mL of DI water for

24 h and filtered to remove insoluble copper powder and CuBr. The aqueous solution was concentrated to ~50 mL and purified by ultrafiltration using 0.01 M HCl solution (2000 mL). The solution was passed through an H⁺ ion exchange column to remove any strongly bound cations. After water was evaporated, the polymer was dried under vacuum at 90 °C for 48 h to give poly(*p*-phenylene 2,5-disulfonic acid) (PPDSA) (7.8 g, yield = 84%). Poly(*p*-biphenylene 3,3'-disulfonic acid) (PBPDSA) and poly(biphenylene disulfonic acid-*co*-phenylene disulfonic acid) copolymers were made following similar procedures. The copolymers are denoted as BxP100-*x* (e.g., B20P80, B40P60), where “*x*” is the mole percent of biphenyl comonomer in the copolymer.

Polymer molecular weight was characterized by viscosity measurements. GPC spectra were taken using DMF as solvent. However, these are rigid-rod polymers and they reached the exclusion limit (5 000 000 Da polystyrene calibration) at very low reduced viscosity.

2.3.1. Grafting Biphenyl Groups on Polymers. PPDSA (1.06 g, 0.004 mol) and H₃PO₄ (16.84 g, 0.150 mol) were placed in a 100 mL three-neck round-bottom flask, heated to 80 °C, and stirred at 100 rpm. After 60 min, a homogeneous solution formed. Biphenyl (BP) (1.30 g, 0.004 mol) was added to the solution. P₂O₅ (22.5 g, 0.160 mol) was then added in batches of 0.5 g in order to keep the reaction mixture temperature below 100 °C. After the P₂O₅ addition was complete, an argon inlet and a condenser were fitted to the flask; the temperature was raised to 125 °C, and the mixture was stirred vigorously for 60 min.

After the mixture cooled to room temperature, ice water (50 mL) was added with vigorous stirring. The acid solution was neutralized with NaOH, and unreacted BP was removed by filtration. The neutralized solution was purified by ultrafiltration with DI water. The concentrated Na form polymer solution was passed through an ion exchange column to acidify it. After water evaporation, the purified product was dried under vacuum at 90 °C for 48 h; 0.94 g of purified graft polymer was obtained. A grafting degree of 12% was determined by ¹H NMR; the grafted polymer is denoted as PPDSA-g-BP12% (yield = 78%). Grafted polymer PPDSA-g-BP16% and copolymers B20P80-g-BP12% were made using this procedure but increasing the heating time to 2 h. Lower grafting degree copolymers, B20P80-g-BP03% and B20P80-g-BP07%, were obtained when the temperature while P₂O₅ was added was kept below 75 °C, with reaction times of 30 and 90 min, respectively.

2.3.2. Cross-Linking. Grafted polymer was dissolved in isopropanol to make a ~20 wt % solution and cast in a 7 cm diameter Teflon dish. The dish was covered by filter paper and stored in a closed cabinet for 24 h at room temperature to evaporate the isopropanol; it was then dried by heating for 48 h at 90 °C under vacuum (10 Torr). The dried membrane could be removed easily from the dish.

The effect of time and temperature on degree of cross-linking was studied. Strips (1 × 4 cm) were cut from the membranes and heated in ACE-8648 tubes in a Buchi TO-51 glass oven at 170–210 °C for predetermined times under high vacuum (~0.04 Torr). The cross-linked membranes are named by adding the cross-linking temperature and time as a suffix to the corresponding grafted polymer's name. One set of membranes was also heated at 225 and 250 °C.

2.4. Membrane Characterization. Cross-linked and un-cross-linked polymer membranes were characterized by ATR-FTIR spectroscopy. ATR-FTIR data were collected with a Nexus 870 FTIR bench coupled to a Continuum microscope (Thermo Nicolet, Madison, WI). The microscope utilized an attenuated total reflectance (ATR) slide-on attachment with a germanium crystal. Spectra were collected at a resolution of 2 cm⁻¹ for 32 scans with a sampling area of 150 μ m × 150 μ m.

Grafting degree was determined by NMR and titration. Cross-linking degree was determined by titration and maximum swelling ratios. Because some water was always held in the polymer, elemental analysis could not be used to determine the cross-linking content as presented further in the Results and Discussion.

The equivalent weights (EW) and ion-exchange capacities (IEC) of the cross-linked and un-cross-linked membranes were determined by titration of three or more samples of each material. Film strips in the

acid form were dried in vacuum (10 Torr) at 90 °C for 24 h, weighed, and placed in an aqueous 2 M NaCl solution for at least 24 h. The solutions were then titrated with a 0.01 M NaOH solution using bromothymol blue as indicator. The NaOH solution was calibrated by potassium hydrogen phthalate immediately before use. The EW [g mol^{-1}] and IEC [mequiv g^{-1}] of the membranes, including the bound water, were calculated according to the following equations:

$$\text{EW} = \frac{W_{\text{dry}}}{V_{\text{NaOH}} M_{\text{NaOH}}} \quad (1)$$

$$\text{IEC} = \frac{1000}{\text{EW}} \quad (2)$$

where W_{dry} is the weight of the dried membrane in grams, M_{NaOH} is the molarity of the NaOH solution, and V_{NaOH} is the volume (in liters) of NaOH required to reach the end point.

Membrane swelling and water uptake was measured as follows. Grafted, as cast and after cross-linking, polymer membranes were dried under vacuum (10 Torr) at 90 °C for 24 h. These membranes are referred to as "dry". Its length (L_{dry}), width (W_{dry}), thickness (T_{dry}), and weight (W_{dry}) were measured. Our titration and NMR studies showed that such membranes still contained about one water molecule per sulfonic acid group.^{22,23}

Dried membranes in open weighing bottles were put into each of nine humidity control saturated salt solution chambers at room temperature.^{35,36} LiCl (11.3%), KAc (23.1%), MgCl_2 (33.1%), K_2CO_3 (43.2%), $\text{Mg}(\text{NO}_3)_2$ (54.4%), NaNO_2 (66.0%), NaCl (75.9%), KCl (85.1%), K_2SO_4 (97.6%). After equilibration (48 h), the membranes were removed for characterization; this is called the "wet" membrane. Its weight (W_{wet}) was measured immediately. The drying/wetting procedure was repeated twice, and the measured values were averaged. The water content of "wet" un-cross-linked grafted polymers was also measured by ^1H NMR. The fractional water uptake (WU) of the membrane is defined as

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (3)$$

The number of water molecules per sulfonic acid, λ , is given by

$$\lambda = \frac{(W_{\text{wet}} - W_{\text{dry}})\text{EW}}{W_{\text{dry}} M_{\text{H}_2\text{O}}} + 1 \quad (4)$$

where EW is the equivalent weight of the polymer defined by eq 1 and $M_{\text{H}_2\text{O}}$ the molecular weight of water, 18 g mol^{-1} . Lengths (L_{wet}), widths (W_{wet}), and thicknesses (T_{wet}) were also measured for membranes equilibrated at 97.6% RH (saturated K_2SO_4 solution) and room temperature. The fractional dimensional changes, ΔL , ΔW , ΔT , and ΔV , are defined as

$$\Delta L = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}}$$

$$\Delta W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$

$$\Delta T = \frac{T_{\text{wet}} - T_{\text{dry}}}{T_{\text{dry}}}$$

and

$$\Delta V = (1 + \Delta L)(1 + \Delta W)(1 + \Delta T) - 1$$

The state of water in cross-linked and un-cross-linked membranes was determined using a Modulated TA Instruments Q2000 differential scanning calorimeter (DSC). Typically, 2–4 mg of a membrane equilibrated at 98% RH was hermetically sealed in an aluminum pan and analyzed by DSC. A temperature scan of 10 °C min^{-1} from 30 to –90 °C and from –90 to 30 °C was used. The cooling and heating cycle was repeated, and the ice melting endotherms near 0 °C were

averaged. The content of freezable water is defined as the ratio of the endothermic peak area recorded for the wet film to the endothermic heat of melting of pure water (333.6 J/g),³⁷ referenced to the total weight of water in the sample. Here the total weight of water is the weight difference between the wet and dried sample plus the weight of water in the "dried" sample (one water molecule per sulfonic acid group). The nonfreezable water content is defined as total water minus the freezable water content in the sample. The freezable and nonfreezable water weights were converted to lambdas for clarification and comparison purpose.

Stress–strain tests were performed using a TA Instruments DMA 2980 Q800 apparatus (dynamic mechanical analysis) in the extension mode. Sample strips of approximately 3 × 15 mm width and length, and 50 μm thicknesses, were cut from a membrane cast in a Teflon dish. The strips were equilibrated for 6 h at laboratory RH (17–29%) before measurement.

In-plane conductivity at 80 °C for all materials was measured at CWRU by electrochemical impedance spectroscopy (EIS) using a four-electrode cell connected to a Solartron 1260 frequency response analyzer (FRA) and a Solartron 1287 potentiostat. The custom-made PTFE cell with four graphite electrodes was enclosed in a stainless steel humidity chamber and placed in a heating oven with built-in temperature controller. The cell temperature was set to 80 °C, and the relative humidity was controlled by placing a small container with a saturated salt solution inside the humidity chamber. The following saturated salt solutions at 80 °C were employed for humidity control:³⁶ LiCl (10.5%), KAc (15.1%), MgCl_2 (26.1%), K_2CO_3 (41.1%), NaBr (51.4%), NaNO_2 (57.4%), NaNO_3 (65.4%), KCl (78.9%), K_2SO_4 (94.1%). After the sample was equilibrated at a given humidity (~12 h), ac impedance scans were performed over a frequency range of 1 Hz to 20 kHz. Repeated measurements showed that the membranes equilibrated within 12 h. The real (Z') and imaginary (Z'') impedance components were plotted, and the resistance (R) was taken as the value of Z' when the curve was extrapolated to $Z'' = 0$ in the high-frequency region. The humidity was increased by changing the saturated salt solution, starting with the lowest relative humidity container. Conductivity was calculated using the equation

$$\sigma_p = \frac{L}{RWT} \quad (5)$$

where σ_p is the proton conductivity (S cm^{-1}), L the distance between the reference electrodes (cm), R the membrane resistance (Ω), W the membrane width (cm), and T the membrane thickness (cm).

In-plane proton conductivity of Nafion NR-212 and cross-linked B20P80-g-BP12% membrane was also measured in a four-electrode cell system (BekkTech LLC) using ac electrochemical impedance spectroscopy (EIS). An Espec SH-241 environmental chamber that could operate at superatmospheric pressures was employed to control humidity and temperature of the samples. Testing temperatures were, 30 (for Nafion NR-212), 80, and 120 °C. Conductivity tests at 30 and 80 °C were performed at atmospheric pressure (~101 kPa_{abs}), while testing at 120 °C was performed at 230 kPa_{abs} . The testing started at 70% RH; it was lowered to 20% and then raised to 90% RH at 10% intervals with a 15 min equilibration time after each step. At a given RH, the conductivities measured as the RH was decreased or increased agreed to within 15%, showing that the samples were reasonably equilibrated. The in-plane proton conductivity of the membranes was calculated using eq 5.

Through-plane conductivity of cross-linked B20P80-g-BP12% was determined at 30, 80, and 120 °C via two-electrode, four-terminal impedance spectroscopy in a Model 740 Membrane Test System (MTS, Scribner Associates, Inc.) that could operate at superatmospheric pressures. For through-plane measurements, the membrane was compressed between gas diffusion electrodes (GDE) media (E-TEK ELAT GDE 140-HT) that were attached to solid platinum backing electrodes with conductive carbon paint. The contact pressure was 2.15 MPa (312 psi). The sample was conditioned for 2 h at 70% RH, followed by stepping through the RH cycle: 70 to 20 to 90% at 10% intervals followed by 95%, with a 15 min equilibration time at

each RH before measuring the membrane resistance. A Solartron 1260 FRA (ac frequency 2 MHz to 1 Hz, 10 steps/decade, and 10 mV_{ac} at 0 V_{dc}) with ZPlot and ZView software (Scribner Associates, Inc.) was used to control the impedance measurement parameters and to analyze the impedance spectra, respectively. At a given RH, the conductivities measured as the RH was decreased or increased agreed to within 10%, showing that the samples were reasonably equilibrated. At each temperature and RH, the through-plane resistance was taken as the high-frequency resistance (R_{hf} , Ω) where $Z'' = 0$ which was obtained from an equivalent circuit model fit to the impedance spectra. This resistance was used in the calculation of the through-plane conductivity (σ_v , S cm⁻¹):

$$\sigma_t = \frac{T_t}{R_{hf}A} \quad (6)$$

where the thickness (T_t , cm) of the 1.0 × 3.0 cm sample was taken as the average of five measurements at ambient conditions (~50% RH) obtained using a calibrated, high-precision film thickness gauge (Brunswick Instruments, contact pressure 15 kPa) and the active area (A) was 0.5 cm².

2.5. MEA Fabrication and Single Cell Performance. MEAs were prepared and tested at the Florida Solar Energy Center (FSEC). The MEA was prepared by spraying catalyst ink directly onto the anode and the cathode sides of the 60 μ m thick cross-linked membrane. Carbon-supported Pt (46 wt %)-Co (4.6 wt %) (Tanaka Kikinzokou Kogyo, Tokyo, Japan) was used for the anode and cathode catalysts. The catalyst ink was prepared by dispersing the catalyst powder (0.72 g) in deionized water (DI) (3.17 g), isopropanol (4.49 g), and methanol (20.08 g) mixture; the solution was then ultrasonically mixed with 3 M ionomer (1.57 g, 18% dispersion). The membrane B20P80-g-BP12%-210C-3h was sandwiched between two Teflon gaskets that served as a structural support and mounted into a spraying frame. The spraying frame was placed into the spray box, and the above-prepared catalyst ink was applied to the membrane with a Badger Airbrush 150 mounted on computer-controlled X-Z motor axes. The final loading of platinum was estimated to be 0.38 mg cm⁻² on each electrode.

The catalyst-coated membrane (CCM) was assembled into conventional 5 cm² fuel cell hardware, with SGL 10 BC gas diffusion layers (GDLs), and a pinch of 254 μ m (10 mil), using Teflon gaskets. The membrane developed a tear during MEA preparation, which was patched with a few drops of 3 M ionomer dispersion at the tear area (see Figure S5 in Supporting Information). During assembly, the thickness of the CCM was measured. The cell performance was evaluated by testing at 80 °C/100% RH at ambient and 7 psig pressure, 95 °C/83% RH at 7 psig pressure, and 120 °C/35% RH at 7 psig pressure for 5 consecutive days. Polarization curves were recorded from low to high current density; resistance was also measured. It had a very high H₂ crossover due to the tear (not possible to calculate a meaningful crossover) and low electrochemically active surface area (ECA) (18 m²/gPt for day 1). Only one curve, taken at 80 °C/100% RH and ambient pressure, is shown in the Results and Discussion section.

3. RESULTS AND DISCUSSION

3.1. Membrane Preparation. 1,4-Dibromobenzene and 4,4'-dibromobiphenyl were sulfonated using fuming sulfuric acid to obtain the DBBDSA and DBBPDSA monomers. DBBDSA polymerization and DBBDSA:DBBPDSA copolymerization at a 4:1 mole ratio were run at 140 °C in *N*-methylpyrrolidinone (NMP) using copper as the coupling reagent (Ullmann reaction). Reasonably high molecular weight polymers were obtained. The reduced viscosities at ~0.5 g dL⁻¹ concentration in DMF for PPDSA and B20P80 were about 0.6 and 0.7 dL g⁻¹, respectively (Figure 1).

Biphenyl (BP) grafted on PPDSA and B20P80 forms biphenyl 4-sulfone groups attached to the polymer backbones, as illustrated in Scheme 1. Only one grafted biphenyl is shown

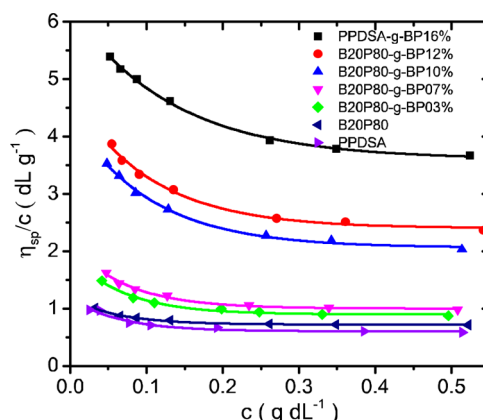


Figure 1. Reduced viscosity as a function of concentration for protonated PPDSA, B20P80, and selected BP grafted polymers in DMF at 35.0 °C (Cannon-Ubbelohde viscometer, type OC C453).

for simplicity. Certainly both residues react, but we could not determine their relative reactivity. Grafting was done in P₂O₅/H₃PO₄ (poly(phosphoric acid), PPA). The grafting degree was controlled by varying the reaction time and temperature. As shown in Figure 1, grafting increased reduced viscosities of polymers from 0.6 to 2–3.5 dL g⁻¹ at 0.5 g dL⁻¹, depending on the degree of BP grafting. Grafted polymers were cross-linked under high vacuum at elevated temperature (Scheme 1). The cross-linking degree as a function of heating time and temperature was studied. Cross-linking, as determined by titration, was complete within experimental error after heating at 210 °C for 1 h (Table 1).

There is a literature report where cross-linking was accomplished by casting a film of sulfonated polyether containing diphenoxybenzene and doubly reacting it by dipping the film into a methanesulfonic acid/P₂O₅ solution.³⁸ We tried this approach using biphenyl, but our polymers are so polar that biphenyl formed a separate phase when the solvent evaporated. This is the smallest cross-linker that can be used; larger organic molecules would be even less compatible.

3.2. Membrane Characterization. In order to quantify degrees of grafting and cross-linking, attenuated total reflectance (ATR) FTIR spectra were obtained for several samples before and after grafting and after cross-linking. Unfortunately, sulfonic acids have a large peak at ~700 cm⁻¹ that obscured the expected peak from the dangling phenyl group (5 Hs). The changes due to grafting and subsequent cross-linking were too small to be observed (see Figure S6). Grafting degree could be determined by NMR and titration. Rough estimates of degree of cross-linking were made by titration and maximum swelling ratios. The degree of cross-linking could not be determined accurately by titration. Titration and weighing errors were 3%, and the change in equivalent weight from the starting material to complete cross-linking was ~15%. In addition, the polymers contained about 1 equiv of adsorbed water. Since we wanted fully cross-linked membranes for use in fuel cells, a reasonable criterion was the degree of swelling at 98% relative humidity after treatment. If longer heating did not decrease swelling, we concluded that the material had completely reacted; this agreed with the titration results. Heating the membranes for more than 1 h at 210 °C gave essentially complete reaction.

Scheme 1. Preparation of Cross-Linked PPDSA and B20P80 Membranes

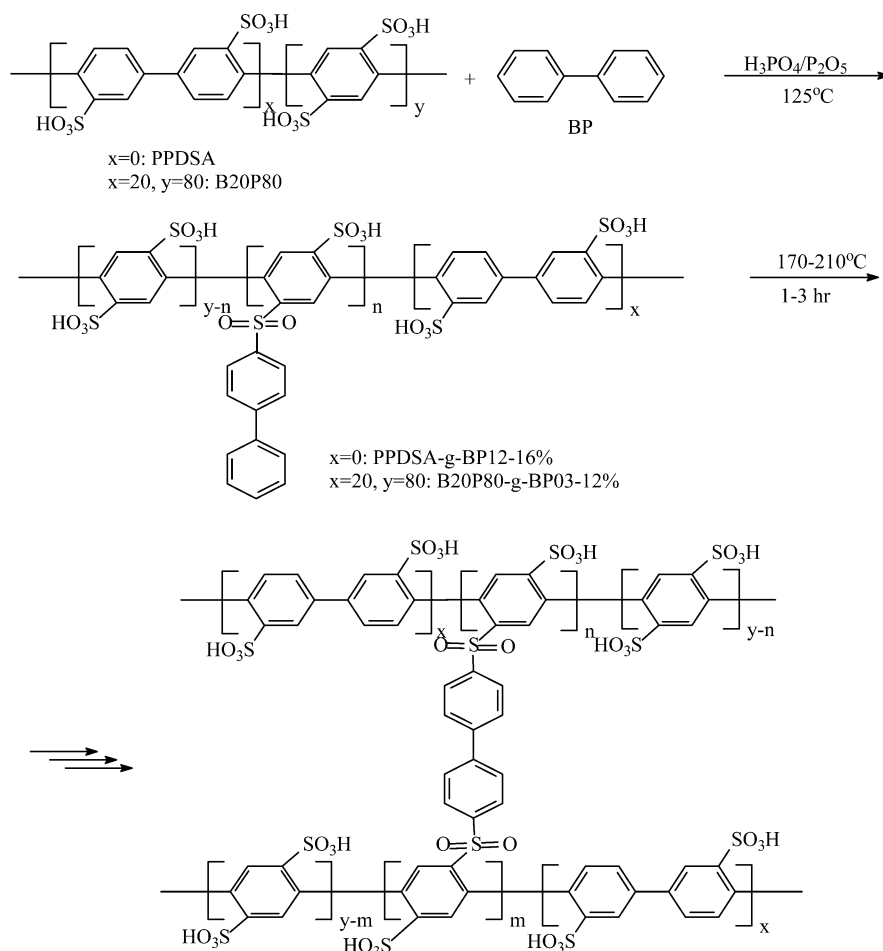


Table 1. Equivalent Weights (EW) and Water Content for Selected Dried Cross-Linked and Un-Cross-Linked Membranes Determined by Titration

sample	EW (g mol ⁻¹)		λ^b
	expt	calc ^a	
PPDSA	138	118	1.1
B20P80	146	126	1.1
PPDSA-g-BP12%	176	153	1.1
B20P80-g-BP10%	183	155	1.6
B20P80-g-BP12%	179	161	1.0
PPDSA-g-BP12%-170C-1h	184		
PPDSA-g-BP12%-190C-2h	181		
PPDSA-g-BP12%-210C-1h	203	174 ^c	1.6
B20P80-g-BP12%-210C-1h	204	184 ^c	1.1
B20P80-g-BP12%-210C-2h	199	184 ^c	0.8
B20P80-g-BP12%-210C-3h	207	184 ^c	1.1

^aCalculated equivalent weight based on the chemical structure. ^b λ was calculated as the difference between the experimental equivalent weight and the calculated equivalent weight divided by 18. ^cCalculated equivalent weight assuming complete cross-linking and no water.

Because some water was always held in the polymer, elemental analysis could not be used to determine the cross-linking extent.

All grafted polymers in the acid form were dried in vacuum (10 Torr) at 90 °C for 24 h and analyzed by ¹H NMR with methanol-*d*₄ as solvent. The spectra were used to determine the

extent of grafting and the water content of the dried material. The solvent was run at the same time to measure its OH to CD₂H ratio. Peaks between 7.2 and 7.5 ppm are from the three terminal hydrogens in the dangling phenyl ring of the grafted biphenyl (Figure S3). Twice their area was subtracted from the rest of the aromatic area, between 7.5 and 8.6 ppm, to give the signal area due to backbone hydrogens. This was normalized by dividing by the number of backbone hydrogens per sulfonic acid plus sulfone groups, 1 for PPDSA and 1.4 for B20P80. The ratio of one-third the 7.2 to 7.5 ppm area to the normalized backbone area is the degree of grafting. Once this was known, the aromatic backbone area per sulfonic acid could be calculated. The solvent OH contribution to the OH peak area was subtracted from the total area, and the remainder was divided by the backbone area per sulfonic acid. This ratio represents the hydrogen from the acid plus water per acid group. λ was calculated by subtracting 1.0 and dividing by 2. Above analysis of ¹H NMR spectra of dried films confirmed our earlier findings that they retained about one water molecule per acid group.²²

Equivalent weights (EW) of un-cross-linked and cross-linked membranes were determined by titration with 0.01 N NaOH solution; the results are given in Table 1. Earlier studies showed that vacuum-dried (10 Torr, 90 °C) PPDSA membranes still contained ~1 water per sulfonic acid group. The listed λ values were calculated by subtracting the theoretical equivalent weight from the experimental equivalent weight and dividing the difference by 18. The un-cross-linked membranes had λ

between 0.9 and 1.6, averaging 1.2, agreeing with our results based on NMR analysis.

When heated at high vacuum (0.04 Torr) and temperature above 190 °C, the grafted polymer starts losing its residual water. Now, the nonsolvated SO₃H groups can sulfonate the free phenyl tails of the biphenyl 4-sulfone groups to form twice-reacted biphenyl cross-links. Because the completely dried membrane absorbs water very rapidly during weighing, it was not titrated immediately after cross-linking but was analyzed after following the drying procedure used for the un-cross-linked polymers. The calculated equivalent weight of completely cross-linked B20P80-g-BP12% is 184 g mol⁻¹; when one water molecule per SO₃H group is included, the equivalent weight is 202. Table 1 shows that cross-linking is basically complete after 1 h at 210 °C, with a λ of 1.1. The equivalent weight data show that, within experimental error, the membranes lost no free acid after 3 h at 210 °C. When the PEMs were heated at lower temperatures, the measured equivalent weights show that there was very little cross-linking. Based on the data, PPDSA-g-BP-12%-210C-1h also seems to be completely cross-linked. λ for these polymers ranges from 0.8 to 1.6. The spread is probably mainly due to experimental error; a combined 3% error in weighing and titration could lead to ± 0.4 variation in λ . Membranes of B20P80-g-BP07% were heated at 225 and 250 °C for 2 h (Figure 2). After heating at

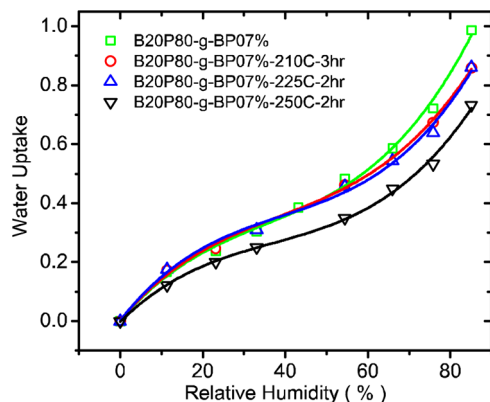


Figure 2. Effect of cross-linking temperature on B20P80-g-BP07% membranes: fractional water uptake at room temperature as a function of relative humidity.

225 °C, its titration (data not shown) and water uptake were identical to that of the copolymer heated at 210 °C for 3 h. Heating at 250 °C for 2 h increased its equivalent weight by ~50%, estimated from the decrease in water uptake with the assumption that λ was unchanged. These polymers are exceptionally thermally stable.

3.3. Water Uptake and Dimensional Changes. Proton conductivity of sulfonic acid polymer membranes depends on the proton carrier concentration which is related to the number of available acid groups, their dissociation degree, and the extent of hydration. Water is the transport medium for protons; therefore, the water uptake is an important parameter in studying PEMs. Higher water uptake leads to higher proton conductivity. However, excessive water uptake reduces the effective charge density of the membranes and can also result in poor dimensional stability and a loss of mechanical strength. Figure 3 shows the fractional water uptake and λ as a function of RH at room temperature for B20P80, B20P80-g-BP12%, and B20P80-g-BP12%-210C-3h membranes. The fractional water

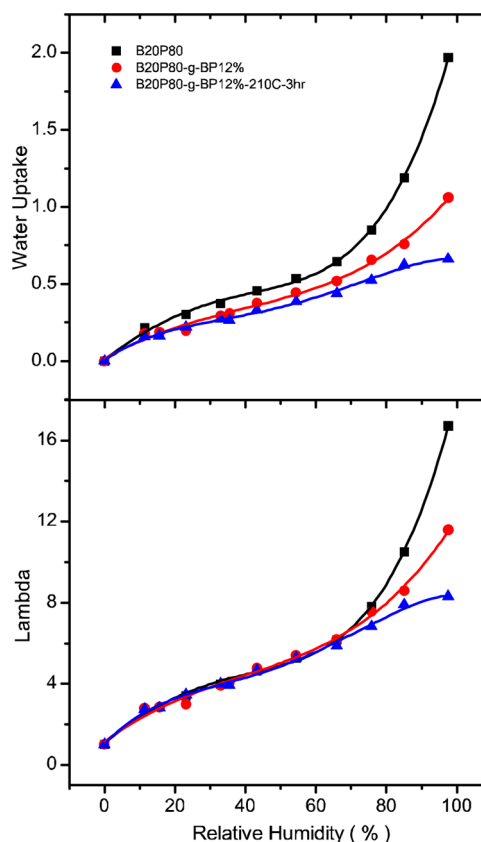


Figure 3. Fractional water uptake (top) and λ (bottom) as a function of relative humidity at room temperature for B20P80, B20P80-g-BP12%, and B20P80-g-BP12%-210C-3h.

uptake of B20P80 increased with increasing RH, reaching 1.97 at 98% RH, corresponding to a λ of 16.7. The water uptake of B20P80-g-BP12% also increased with increasing RH but reached only 1.06 ($\lambda = 11.6$) at 98% RH, possibly due to hydrophobic bonding of the grafted biphenyl 4-sulfone groups. The 98% RH water uptake of the fully cross-linked B20P80-g-BP12% further decreased to 0.66 ($\lambda = 8.3$), one-third that of pristine B20P80. The water absorption and dimensional changes of some cross-linked and un-cross-linked membranes are summarized in Table 2.

The decrease in water uptake after cross-linking resulted in decreased membrane swelling. Un-cross-linked PPDSA, B20P80, and B20P80-g-BP07% membranes absorbed 1.5–2 times their dry weight of water at 98% RH and became very soft, making it impossible to measure their dimensional changes. Within the experimental error, all membranes tested swelled equally in length and width, but the extent of the lateral expansion was significantly smaller than the through-plane swelling. Both un-cross-linked and cross-linked membranes were anisotropic. Probably almost all polymer molecules are in domains with their backbones parallel to the membrane surface. As the membrane absorbs water, chain separation increases. Swelling in the plane is hindered by other domains with chains oriented perpendicular to the swelling direction. Since few if any chains are oriented perpendicular to the film surface, swelling in the thickness direction is restricted only by cross-linking. Cross-linking forms a 3-D network, which has a larger effect on the swelling in the thickness direction than on its lateral directions. This is understandable since thickness swelling was unhindered before cross-linking.

Table 2. Fractional Water Uptake and Dimensional Changes from 0 to 98% RH for Selected Cross-Linked and Un-Cross-Linked Membranes

sample	EW ^a (g mol ⁻¹)	water uptake	dimensional change				λ_{FFV}^c
			ΔL^b	ΔW^b	ΔT^b	ΔV^b	
PPDSA	118	2.13					
B20P80	126	1.97					
B20P80-g-BP07%	140	1.50					
B20P80-g-BP07%-210C-3h	150	1.11	0.15	0.15	0.42	0.88	3.8
B20P80-g-BP10%	155	1.20	0.15	0.17	0.53	1.06	3.4
B20P80-g-BP10%-210C-3h	170	0.81	0.11	0.12	0.33	0.65	3.3
B20P80-g-BP12%	160	1.06	0.14	0.12	0.42	0.81	4.2
B20P80-g-BP12%-210C-3h	185	0.66	0.07	0.11	0.34	0.59	2.5
PPDSA-g-BP12%	156	1.37	0.19	0.17	0.52	1.12	4.4
PPDSA-g-BP12%-210C-3h	177	1.00	0.14	0.14	0.43	0.86	3.4
PPDSA-g-BP16%	167	1.13	0.16	0.18	0.49	1.04	3.1
PPDSA-g-BP16%-210C-3h	196	0.77	0.13	0.14	0.33	0.71	2.6

^aEW is the equivalent weight determined by titration and confirmed by NMR for un-cross-linked membranes. ^b ΔW , ΔL , ΔT , and ΔV are the relative width, length, thickness, and volume increases of the membranes from 0 RH to 98% RH. ^c λ_{FFV} is the frozen-in free volume in moles of water per sulfonic acid, calculated using eq 7.

Since the absorbed water generates the volume increase, we can calculate the absorbed water density by dividing the weight increase by the volume increase. The calculated water density is in the range 1.1–1.3 g cm⁻³ for the membranes that hold their shape at 98% RH. This high water density indicates that there is frozen-in free volume²² that is filled by water molecules without swelling the film.

Frozen-in free volume can be understood as follows. Two sulfonic acid groups per benzene ring plus the lack of conformational mobility generates much steric hindrance; the polymer chains cannot pack well. This leads to a segmental packing volume that is much larger than its van der Waals volume. Drying forces the molecules into close contact, raising their internal energy by distorting the bond angles. Water absorption at low relative humidity is facilitated since it separates the polyelectrolyte molecules, relieving the compressive stress. Further water absorption fills the remaining free volume and separates the chains more. This was studied by Litt, Granados-Focil, and Kang.²² They found that PPDSA density in water was ~ 2.0 g cm⁻³ compared to a measured “dry” density of 1.15 g cm⁻³. The frozen-in free volume was estimated as 63 cm³ per mole of SO₃H, $\lambda = 3.5$. This can be seen in Figure 3; λ rises from 1 (dry) to ~ 4 by 30% RH.

The frozen-in free volume plays an important role, holding water tightly at low RH. It can be estimated as follows. We postulate that the first water is absorbed with no change in volume; it is held very tightly. This has been seen in many polar polymers. The frozen-in free volume, as moles of water per mole acid, λ_{FFV} , was calculated using eq 7.

$$\lambda_{\text{FFV}} = \frac{\left(\text{WU} - \frac{\rho_{\text{H}_2\text{O}}}{\rho_{\text{dry}}} \Delta V \right) \text{EW}}{M_{\text{H}_2\text{O}}} \quad (7)$$

WU is the water uptake per gram of “dry” polymer; $\Delta V/\rho_{\text{dry}}$ is the volume change per gram of “dry” polymer; EW is the equivalent weight defined in eq 1, including one water per sulfonic group; $M_{\text{H}_2\text{O}}$ is the molecular weight of water, 18 g mol⁻¹; and $\rho_{\text{H}_2\text{O}}$ is the density of pure water, 1.0 g mL⁻¹. ρ_{dry} is the density of dry membranes, estimated to be close to the density of “dry” PPDSA, 1.15 g mL⁻¹,²² for these cross-linked

and un-cross-linked membranes. The calculated frozen-in free volumes are listed in Table 2. The values of λ_{FFV} range from 2.5 to 4.4, averaging 3.4, close to the value of 3.5 for PPDSA reported previously.²²

3.4. The State of Water Characterized by DSC. The DSC curve of B20P80-g-BP07% equilibrated at 98% RH is shown in Figure 4. There is an exothermic peak near -24 °C

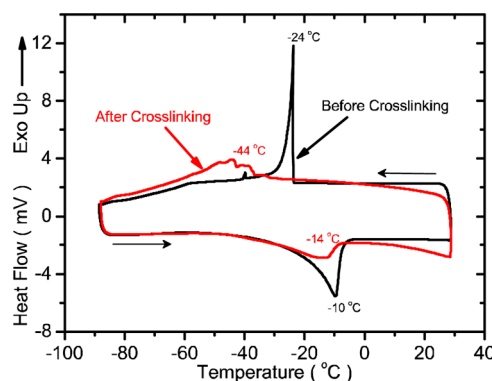


Figure 4. Low-temperature DSC thermograms of B20P80-g-BP07% membrane before (black curve) and after (red curve) cross-linking (heating rate: 10 °C min⁻¹). Samples were equilibrated at 98% RH prior to measurements.

when cooling and an endothermic peak near -10 °C when heating. The peak areas are very close; they average about 75 J g⁻¹. Since the heat of fusion of pure water is about 333.6 J g⁻¹,³⁷ the freezable water in B20P80-g-BP07% is calculated to be 0.23 g per gram of equilibrated sample. The fractional water uptake was 1.50 for B20P80-g-BP07% equilibrated at 98% RH, which corresponds to 0.65 g of water per gram of equilibrated sample. The freezable water determined by DSC was about 35% of the total water content. The rest, 65%, was nonfreezable water, strongly bound to the sulfonic acid groups. From eq 4, λ was calculated as 14.1 for B20P80-g-BP07%. Thus, there were about 5 freezable water molecules and 9 nonfreezable water molecules per sulfonic acid. Table 3 lists the total water, freezable, and nonfreezable water contents for the materials tested.

Table 3. Ion-Exchange Capacity (IEC) of Selected Cross-Linked and Un-Cross-Linked Membranes and State of Water in These Membranes after Equilibration at 98% RH and Room Temperature

samples	IEC ^a (mequiv g ⁻¹)	freezable water			$\lambda(\text{H}_2\text{O}/\text{SO}_3\text{H})$		
		T_c^b (°C)	T_m^c (°C)	peak area (J g ⁻¹)	λ_{total}^d	λ_{fr}^d	λ_{nfr}^d
PPDSA	8.3	-36	-5	114	17.1	8.1	9.0
B20P80	7.9	-29	-7	111	16.7	7.9	8.8
B20P80-g-BP07%	7.1	-24	-10	75	14.1	5.0	9.1
B20P80-g-BP07%-210C-3h	6.7	-44	-14	36	11.2	2.1	9.1
B20P80-g-BP10%	6.5	-30	-10	65	12.5	4.3	8.2
B20P80-g-BP10%-210C-3h	5.9	-58	-23	16	9.5	0.9	8.6
B20P80-g-BP12%	6.3	-33	-14	45	11.6	2.8	8.8
B20P80-g-BP12%-210C-3h	5.4			0	8.3	0.0	8.3
PPDSA-g-BP12%	6.4	-23	-7	74	14.3	4.7	9.6
PPDSA-g-BP12%-210C-3h	5.6	-41	-12	26	11.8	2.1	9.7
PPDSA-g-BP16%	6.0	-27	-8	73	12.6	4.1	8.5
PPDSA-g-BP16%-210C-3h	5.1	-43	-14	28	10.2	1.8	8.4

^aCalculated from titration and confirmed by NMR for un-cross-linked polymers. ^b T_c defined as the temperature of the maximum in ΔH , determined by DSC. ^c T_m defined as the freezable water melting temperature at maximum ΔH determined by DSC. ^d λ_{total} defined as the total absorbed water in the membrane equilibrated at 98% RH, determined by weighing. λ_{fr} defined as the freezable water determined by DSC and λ_{nfr} the nonfreezable water ($\lambda_{\text{nfr}} = \lambda_{\text{total}} - \lambda_{\text{fr}}$).

The DSC curve of the cross-linked copolymer, B20P80-g-BP07%-210C-3h, equilibrated at 98% RH is also shown in Figure 4. Both the endothermic and exothermic peak areas are much smaller than those of the un-cross-linked polymer. The peak positions also move to lower temperatures compared to the un-cross-linked ones. This is expected since the proton concentration (impurity) is greater, lowering the melting point. The melting endotherms are complete below 0 °C for both the un-cross-linked and cross-linked copolymers, showing that there is no region of bulk water in the polymers.

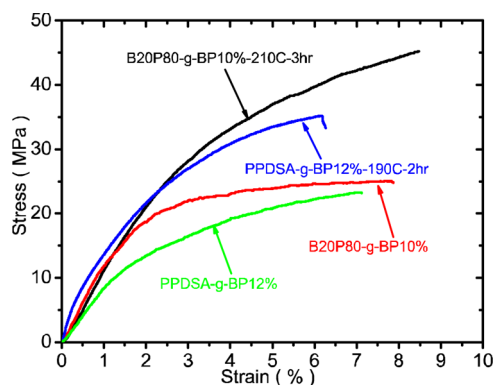
The fractional water uptake is 1.11 for wet B20P80-g-BP07%-210C-3h. Lambda of B20P80-g-BP07%-210C-3h at 98% RH is calculated as 11 using the above analysis, with 2 freezable water molecules and 9 nonfreezable water molecules per sulfonic acid.

From Table 3 it can be seen that the nonfreezable water content (λ_{nfr}) for all membranes is the same within the experimental error, ~ 9 water molecules per sulfonic acid. Further absorbed water is loosely bound and freezes and melts during the low-temperature DSC cooling/heating cycles. Cross-linking decreases the freezable water uptake; this is expected since cross-linking limits the swelling. At 98% RH, B20P80-g-BP07% membrane has about 5 freezable water molecules per sulfonic acid. After cross-linking, this drops to 2. Similarly, B20P80-g-BP12% equilibrated at 98% RH has about 3 freezable water molecules per sulfonic acid. After cross-linking, all absorbed water ($\lambda = 8.3$) is nonfreezable; no endotherm was seen in the DSC thermograms. PPDSA membranes act similarly. There are about 5–4 freezable and 8–9 nonfreezable water molecules in PPDSA-g-BP12% and PPDSA-g-BP16% equilibrated at 98% RH. After cross-linking, the membranes still have 8–9 nonfreezable water molecules but contain only 2 freezable water molecules due to the swelling limitation.

Cross-linked PPDSA grafts swell more than the copolymer grafts at 98% RH, even with a higher percentage of grafting. This is probably due to inhomogeneous grafting. Biphenyl is insoluble in poly(phosphoric acid), and the polymer precipitates slowly after the P_2O_5 has been added. Reaction can only occur at the interface between the two phases, and homogeneity would depend strongly on mixing efficiency. It is worth noting that B20P80-g-BP12%-210C-3h swelled less than the corresponding PPDSA graft (0.66 vs 1.0). Even

PPDSA-g-16%BP-210C-3h swelled more than this copolymer (0.77). We think that the copolymer may be somewhat more soluble in poly(phosphoric acid) than the homopolymer; this could make its grafting more homogeneous and result in more efficient cross-linking. We are looking for procedures that would give homogeneous grafts. Homogeneous grafting should produce cross-linked films with less swelling, better mechanical properties and higher conductivity at a lower grafting fraction.

3.5. Mechanical Properties. Stress–strain curves for some cross-linked and un-cross-linked membranes are given in Figure 5. All the curves fit exactly a simple three-element, linear

**Figure 5.** Stress–strain curves for selected cross-linked and un-cross-linked membranes at $\sim 25\%$ relative humidity.

viscoelastic model: a spring in series with a parallel spring and dashpot. The initial Young's moduli were taken from these analyses. (This will be the subject of a separate paper.) The maximum stress and elongation at maximum stress were also recorded for the listed materials (Table 4). The mechanical properties of membranes composed of rigid-rod poly(sulfonic acid)s are very sensitive to the RH. All stress–strain tests reported here were performed at room temperature with a room relative humidity in the range 17–29%. The Young's moduli for the un-cross-linked samples ranged from 1 to 2 GPa, at RHs of 20–29%. This is very low for a biaxially oriented rigid-rod system; it shows that the absorbed water is acting as a

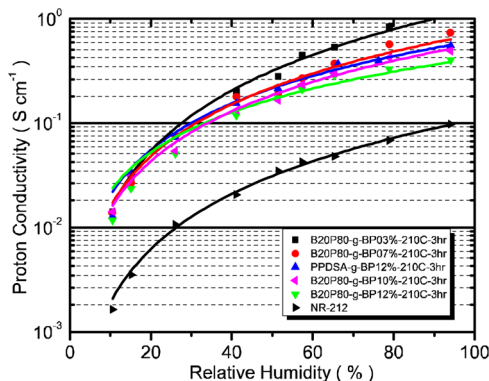
Table 4. Stress–Strain Properties of Selected Cross-Linked and Un-Cross-Linked Membranes at House Relative Humidity (17–29%)

film sample	RH ^a (%)	Young's modulus (GPa)	tensile strength (MPa)	elongation (%)
B20P80-g-BP10%	29	1.78	24.7	7.9
B20P80-g-BP12%	29	1.11	27.4	5.1
B20P80-g-BP12%	17	8.29	53.6	4.0
B20P80-g-BP10%-190C-5h	20	1.89	40.8	6.2
B20P80-g-BP10%-210C-3h	29	1.56	45.4	8.5
PPDSA-g-BP12%	22	1.16	23.2	7.1
PPDSA-g-BP12%-190C-2h	20	1.76	35.0	6.2

^aRH is the laboratory relative humidity during the test period.

plasticizer. At 17% RH, Young's modulus increased to 8.3 GPa. Cross-linked membranes had about the same moduli as the un-cross-linked ones but broke at higher tensile stress. Most membranes broke at 6–8% elongation, indicating some modest ductility, which is reasonable for rigid-rod polymers. Nafion membranes usually break at about 100% elongation, but their ultimate strength is low.

3.6. Conductivity and Fuel Cell Performance. Proton conductivity is very important for fuel cell performance. High proton conductivity is needed to achieve high power densities in PEMFCs. In-plane proton conductivity at 80 °C was measured in house as a function of relative humidity for cross-linked BP grafted polymers (Figure 6). As a comparison, the

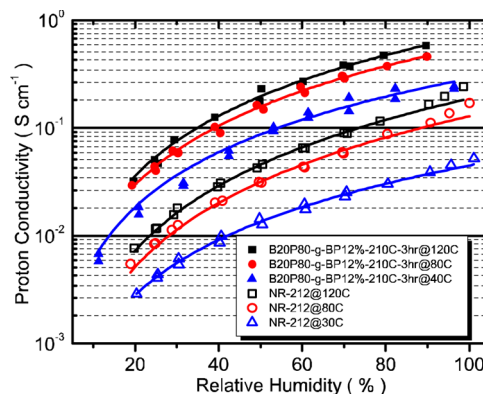
**Figure 6.** In-plane proton conductivity at 80 °C as a function of relative humidity for selected grafted, cross-linked B20P80 and PPDSA polymers and Nafion NR-212.

data of Nafion NR-212 are also included. As can be seen, the conductivities of all cross-linked polymers are very high over the whole humidity range, about 5–11 times higher than that of Nafion NR-212. Conductivities were calculated using the dry dimensions. Obviously, the membrane swells at higher humidity; this increases the cross-sectional area which could decrease conductivity, but higher λ increases proton mobility. The maximum possible decrease can be easily estimated. Table 2 shows the dimensional increases for various films at 98% relative humidity. We have observed that the lengths and widths change identically and stop increasing above ~40% relative humidity, while the thickness keeps increasing. Equation 5 shows that uniform changes in the length and width cancel; only the thickness change is important. The maximum increase in thickness for the polymers studied is 50%; the maximum for the cross-linked polymers is 40%. Thus,

at the highest RH, a recalculated conductivity would be lowered by 30% (cross-linked) to 40% (un-cross-linked). This change is insignificant for fuel cell use. Figure 3 shows that swelling of cross-linked B2P8-gBP12% stops increasing above 80% RH and drops rapidly with lower RH. At low RH where high conductivity is important for fuel cell operation, the conductivity would be very close to the value based on dry dimensions.

After cross-linking, B20P80-g-BP03%, with the highest IEC (7.2 mequiv g⁻¹), has the highest conductivity, about 10–12 times that of Nafion NR-212. Cross-linked B20P80-g-BP12% (IEC = 5.5 mequiv g⁻¹) still has 5–6 times higher conductivity than Nafion NR-212. Interestingly, the cross-linked polymers have almost the same conductivity as the corresponding un-cross-linked ones (Figures S7 and S8), even though the cross-linking reaction consumes sulfonic acid groups, lowering the IEC. Un-cross-linked polymers deformed easily at high RH, making conductivity measurement impossible above 75% RH, but the cross-linked polymers were dimensionally stable up to at least 95% RH.

The in-plane conductivity of a B20P80-g-BP12%-210C-3h membrane was measured at different temperatures (Figure 7).

**Figure 7.** In-plane proton conductivity for B20P80-g-BP12%-210C-3h and Nafion NR-212 as a function of relative humidity at different temperatures, done at FSEC (except that data at 40 °C were done at CWRU).

As a comparison, the data for Nafion NR-212 are also provided. B20P80-g-BP12%-210C-3h proton conductivity is about 5 times higher than that of Nafion NR-212 at 80 °C throughout the whole relative humidity range but drops to about 4 times at 120 °C. High conductivity at high humidity is expected for a PEM with such a high IEC, but the relatively high conductivity at low humidity is probably due to the “frozen-in free volume”. The Arrhenius activation energy (E_a) for proton conduction is estimated to be 10–11 kJ mol⁻¹ for membrane B20P80-g-BP12%-210C-3h at 20 to 50% RH and 12–13 kJ mol⁻¹ at 60–95% RH. On the other hand, E_a is about 11–14 kJ mol⁻¹ for Nafion NR-212 at 20 to 50% RH and 14–16 kJ mol⁻¹ at 60–95% RH. The lower energy barrier for proton transport in the B20P80-g-BP12%-210C-3h membrane is probably due to the very high concentration of sulfonic acid groups plus the higher water content and a short proton traveling distance, so proton movement becomes less hindered energetically. Even at this high level of cross-linking, conductivity at 30% RH and 120 °C reached ~100 mS cm⁻¹, the US Department of Energy 2017 target.³⁹

Through-plane conductivity at 30, 80, and 120 °C was also measured for membrane B20P80-g-BP12%-210C-3h; the results are given in Figure 8. These resistance data were not

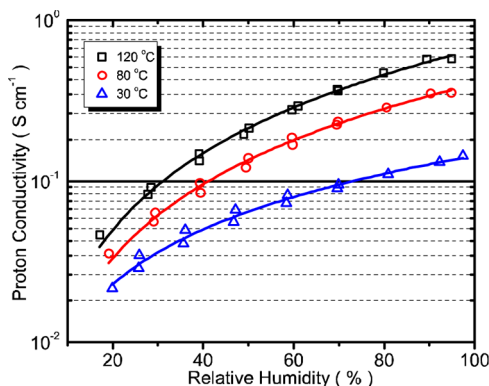


Figure 8. Through-plane proton conductivity for B20P80-g-BP12%-210C-3h as a function of relative humidity at different temperatures, done at Scribner Associates Inc.

corrected for the interfacial resistance, while the four-point probe in-plane conductivity measurements were free from the interfacial resistance effects. Therefore, the actual membrane conductivity should be somewhat higher than the reported through-plane values. It was observed that the through-plane conductivity was slightly higher than the in-plane conductivity in the lower RH range. However, as humidity rises and membrane conductivity increases (resistance decreases), through-plane conductivity dropped below in-plane conductivity above 40% RH at 80 °C and above 60% RH at 120 °C. This implies that membrane conductivity at low RH is anisotropic, slightly higher in the thickness direction than in the lateral directions.

If one postulates that the ratio of in-plane to through conductivity is independent of relative humidity at high RH where λ is almost constant, since we are measuring the same material, the interfacial electrode “resistivity” and the real through-plane conductivity at high RH can be estimated fairly well from the data.

We have the following definitions: σ_p , in-plane conductivity, $S\ cm^{-1}$; σ_{tp} , true through-plane conductivity, $S\ cm^{-1}$; R_e , interfacial electrode area resistance, $\Omega\ cm^2$; σ_v , measured through-plane conductivity, $S\ cm^{-1}$; T_v , the membrane thickness used for the through-plane measurements. The conductivity ratio, γ , is defined as

$$\gamma = \frac{\sigma_p}{\sigma_{tp}}$$

The total area specific membrane resistance in the through-plane measurements can be written as

$$\frac{T_t}{\sigma_t} = \frac{T_t}{\sigma_{tp}} + R_e$$

Substituting for $\sigma_{tp} = \sigma_p/\gamma$ and dividing by T_v we obtain eq 8:

$$\frac{1}{\sigma_t} = \frac{\gamma}{\sigma_p} + \frac{R_e}{T_t} \quad (8)$$

Plots of $1/\sigma_t$ vs $1/\sigma_p$ for the 80 and 120 °C measurements at 50–90% RH are shown in Figure S9. The high RH plots are linear. There is a slight decrease in slope with lower humidity.

The change in slope at low humidity could be due to increasing R_e , decreasing γ , or both. The slope and intercept at low resistivity (high RH) where γ should be constant can be equated respectively to the ratio of in-plane to through conductivity and the interfacial area resistance. The measured average membrane thickness (T_t) was 0.006 06 cm. The values for γ are 1.17 (80 °C) and 0.86 (120 °C) while R_e is 2.2 (80 °C) and 2.0 (120 °C) $m\Omega\ cm^2$.

The interfacial resistance R_e is very low. The 80 °C high humidity value of 2.2 $m\Omega\ cm^2$ can be compared to those of wet Nafion. Pivovar and Kim⁴⁰ found R_e of 8 for Nafion 117 and 57 $m\Omega\ cm^2$ for recast Nafion, respectively. Cooper⁴¹ reported that for Nafion 117 at 80 °C R_e was $\sim 15\ m\Omega\ cm^2$ and relatively independent of RH over the range 20–95%, whereas at 120 °C, R_e increased from 18 $m\Omega\ cm^2$ at 95% RH to 175 $m\Omega\ cm^2$ at 20% RH. The plots show that there is only a slight rise for our material. Probably the fact that these polyelectrolytes have no nonpolar regions is responsible for the low interfacial resistance. Considering that we are comparing two sets of measurements done using two different experimental procedures and two different instruments in two laboratories, the results are gratifying. However, the values obtained must be checked by other methods to confirm them.

Several membrane electrode assemblies (MEAs) were made from the polymers and tested at the Florida Solar Energy Center (FSEC). The low elongation to break and large change in modulus with humidity caused problems; the procedures used for attaching electrodes and pressing gas diffusion layers can generate stresses that could locally tear the membranes. During preparation of the MEA from B20P80-g-BP12%-210C-3h a tear developed. It was patched with a low equivalent weight 3 M ionomer (see Figure S5). There may have been other, undetected tears. The MEA was not hot-pressed because it was felt that that could cause more tearing. Hydrogen permeation was very high for most of the testing, especially at lower humidity. Results for an 80 °C run compared with a hot-pressed NR-212 MEA are shown in Figure 9. The open-circuit

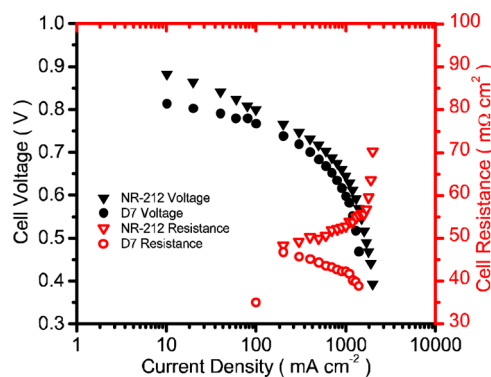


Figure 9. Single-cell performance of an MEA using B20P80-g-BP12%-210C-3h (D7) compared to that of Nafion NR-212 at 80 °C, 100% RH, H_2 /air, ambient pressure.

voltage (OCV) was 0.835 V, compared to Nafion NR-212 at 0.942 V; it was low due to the hydrogen leakage. Later runs using MEAs with no tears gave OCVs of 0.94–0.98 V (to be reported in another paper). The effect of hydrogen permeation shows clearly in the low current density region, where voltage for the B20P80-g-BP12%-210C-3h membrane is significantly lower than that of the Nafion membrane. Above 100 $mA\ cm^{-2}$, the curves follow each other closely, with the power output for

the B20P80-g-BP12%-210C-3h membrane cell about 95% that of the Nafion cell. The test membrane resistance was lower than that of the Nafion membrane and decreased at higher currents. A possible reason is that as current increases, the temperature rises due to resistive heating. However, the greater amount of water produced keeps the film near saturation so the higher temperature could lower the resistance. Nafion loses water more easily as RH drops with increasing temperature, which might explain its rise in resistance at higher currents. No long-term durability studies were run since this was the first membrane tested; it had tears and high hydrogen crossover. However, there was little change in performance after seven days of testing from 35 to 100% relative humidity (120 to 80 °C).

Considering that this was the first fuel cell test on a new material with very different mechanical properties from the normal PEMs, such good performance is remarkable. A defect-free MEA fabricated from these materials will probably have very low hydrogen and oxygen permeability; the highly polar aqueous phase is a very poor solvent for the nonpolar gases while the organic phase consists of rigid aromatic rings that could not dissolve the gases. An analogous membrane had extremely low permeability; this will be reported in the next paper.

4. CONCLUSIONS

We have made novel, very high IEC, polyelectrolytes using a relatively novel synthetic method, the Ullmann reaction. Under the correct grafting conditions, one phenyl group of biphenyl could be reacted with a sulfonic acid to generate a dangling biphenyl sulfone. The grafted polymers could be cross-linked at elevated temperatures to make high-conductivity membranes.

These cross-linked polymers with “frozen-in free volume” maintain high conductivity at low RH (i.e., λ remains relatively high since water is strongly absorbed), with reasonable mechanical characteristics and dimensional stability at high RH. The main difficulty is that the rigid-rod structure generates high modulus, low elongation membranes which are difficult to process into defect free MEAs. However, the first fuel cell tests were very encouraging. In spite of high hydrogen crossover, the cell had about 95% of the power of the Nafion NR-212 reference fuel cell at higher currents. Membranes with no defects should give much better fuel cell performance at low currents.

In order to get better mechanical properties, the molecular weight needs to be raised; this should increase break elongation and decrease membrane defects. It should also decrease swelling at a given percentage of grafting. The grafting method also needs improvement. With one of four acid groups involved in cross-linking (on average, every other or every third benzene ring has a cross-link), a water swelling of 60% or more is probably due to grafting inhomogeneity. Cross-linked PPDSA grafts swelled much more than the corresponding B20P80 grafts. However, some of the swelling may be because the doubly reacted biphenyl groups could reorient perpendicular to the backbone as water is absorbed, increasing the backbone spacing. We are working to solve these problems.

■ ASSOCIATED CONTENT

■ Supporting Information

¹H and ¹³C NMR spectra of monomers and polymers, photographs of B20P80-g-BP12% membrane before and after cross-linking and during MEA preparation, ATR-FTIR and in-

plane proton conductivity of selected PPDSA and B20P80 grafted polymers (un-cross-linked and cross-linked), and plots of reciprocal in-plane proton conductivity vs reciprocal through-plane conductivity of the B20P80-g-BP12%-210C-3h membrane.²² This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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