# Synthesis and Proton Conductivity of Sulfonated, Multi-phenylated Poly(arylene ether)s

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ABSTRACT: A series of sterically-encumbered, sulfonated, poly (arylene ether) copolymers were synthesized and their proton conductivity examined. The series was prepared by copolymerizing a novel monomer, 2",3",5",6"-tetraphenyl-[1,1':4',1"':4"',1"': quinquephenyl]-4,4""-diol, with 4,4'-difluorobenzophenone and bisphenol A. Subsequent sulfonation and solution casting provided membranes possessing ion exchange capacities of 1.9 to 2.7 mmol/g and excellent mechanical properties (Young's modulus, 0.2–1.2 GPa; tensile strength, 35–70 MPa; elongation at break, 62–231%). Water uptake ranged from 34 to 98 wt% at 80 °C/100% RH. Proton conductivities ranged between 0.24 to 16 mS/cm at 80 °C/60% RH, and 3 to 167 mS/cm at 80 °C/95% RH. TEM analysis of the polymers, in the dehydrated state, revealed isolated spherical aggregates of ions, which presumably coalesce when hydrated to provide highly conductive pathways. The strategy of using highly-encumbered polymer frameworks for the design of mechanically-robust and dimensionally-stable proton conducting membranes is demonstrated. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 2579–2587

**KEYWORDS**: fuel cells; ionomers; membranes; poly(arylene ether); polycondensation; proton conductivity

**INTRODUCTION** Polymer electrolyte membrane fuel cells (PEMFCs) are of interest because of their high fuel conversion efficiency, low noise, and the absence of toxic emissions.<sup>1–5</sup> Commercial perfluorinated sulfonic acid (PFSA) ionomers, such as Nafion, Flemion and Aciplex have been widely adopted because of their relative good mechanical/ chemical stability and high proton conductivity.<sup>6</sup> However, they suffer from a high permeability of gases, high cost, environmental inadaptability, and limited performance at higher temperatures.<sup>7</sup> As a result, alternative PEM materials, particularly those based on sulfonated aromatic polymers, are under intense investigation.<sup>8-20</sup> A feature characteristic of these materials is that a high degree of sulfonation is required to achieve highly ion-conductive membranes, which results in a high water uptake (WU),<sup>21,22</sup> a commensurate loss of mechanical strength and inferior fuel cell performance compared to PFSA ionomers.<sup>21,23</sup>

To realize the properties of PFSA ionomers, it appears hydrocarbon analogues must emulate the morphology of PFSAs, i.e., an appropriate proportion of hydrophilic and hydrophobic segments are required to form nanophase-separated

proton channels.<sup>24,25</sup> Recent research has found that localizing, or densifying, ionic rich regions on a random copolymer architecture by way of incorporating highly sulfonated moieties can be a means to achieve high proton conductivity and enhanced oxidative/hydrolytic stability.<sup>11,12,15,20,23</sup> For example, Li et al. report fully aromatic triblock copolymers based on sulfonated poly(2,6-diphenyl-1,4-phenylene oxide)s and poly(arylene ether sulfone)s that form well-connected hydrophilic nanochannels. The hydrophilic segments consist of highly localized sulfonic acid groups.<sup>9</sup> Matsumoto et al. report novel random copolymers of poly(ether sulfone) bearing pendent phenyl groups with a high density of sulfonic acid groups to facilitate proton transport.<sup>11,12</sup> Chen et al. investigated the introduction of bulky, hydrophilic domains and long hydrophobic chains to facilitate phase separation and the formation of proton conductive channels,<sup>15</sup> while Seo et al. describe copolymers containing sulfonated poly(tetraphenyl ether ketone sulfone)s as the hydrophilic domain, demonstrating good proton conductivity and fuel cell performance.<sup>21</sup> Weiber et al. developed two distinct sulfonated poly(arylene ether sulfone)s, and poly(arylene sulfone)s-

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SCHEME 1 Synthesis of monomer 1.

varying the positions and number density of the sulfonic acid functionality.<sup>26,27</sup> The tetra-sulfonated copolymers provided densely located sulfonic acid groups and provided high proton conductivity due to distinct phase separation of the ionic domains.

The above work provides an impetus to further examine polymers bearing densely sulfonated/localized functionality. The present work is further motivated by the observation that in order to achieve a contiguous network of ion channels in a polymer membrane (without resorting to very high ion exchange capacities) the constituent polymer must contain highly localized regions sulfonic acids to facilitate selfaggregation both of ion clusters and hydrophobic segments, thus enhancing mechanical strength and restricting excessive swelling. In the present work, we explore this concept by designing bulky, rigid architectures of sulfonated poly(arvlene ethers) distinctly characterized by their bearing multiple phenyl groups and multiple sulfonic acid functionality per repeat unit. A novel monomer, 2",3",5",6"-tetraphenyl-[1, 1':4',1":4",1"':4"',1"''- quinquephenyl]-4,4""-diol (1), is herein reported and copolymerized with 4,4'-difluorobenzophenone and bisphenol A. The inter-relationship between structure, conductivity, and morphology of densely-sulfonated, sterically encumbered, rigid poly(arylene ether)s is investigated.

# **EXPERIMENTAL**

#### Materials

4,4"-Dibromo-2',3'-5'-6'-tetraphenyl-[1,1';4',1"]-terphenyl was synthesized as described previously.<sup>28,29</sup> Reagents and solvents were purchased from Aldrich Chemical Co., Merck, Lancaster, Fluoko, or Fisher. *N*,*N*'-Dimethylacetamide (DMAc), dimethyl sulfoxide, toluene, CH<sub>2</sub>Cl<sub>2</sub>, methanol, ClSO<sub>3</sub>H, HCl, NaOH, Boron tribromide, anhydrous K<sub>2</sub>CO<sub>3</sub>, and aqueous H<sub>2</sub>O<sub>2</sub> (30%) were obtained from commercial sources. Toluene was dried over CaH, distilled under argon atmosphere, and deoxygenated by purging with argon for 30 min in preparation for the monomer synthesis. Bisphenol A, 4,4'-difluorobenzophenone, 4-methoxyphenyl boronic acid and Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Aldrich Chemical Co. and used without further purification. Polymerizations were conducted using standard vacuum-line techniques. In order to remove the water produced, a slow stream of argon was passed through the reaction vessel during the polymerization process.

# 2",3"',5",6"-Tetraphenyl-[1,1':4',1":4",1"':4"',1"''quinquephenyl]-4,4""-diol (1)

The monomer was synthesized according to Scheme 1. A mixture of 4,4"-dibromo-2',3'-5'-6'-tetraphenyl-[1,1';4',1"]-terphenyl (5 g, 7.22 mmol), 4-methoxyphenyl boronic acid (3.3 g, 21 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 g, 0.432 mmol), K<sub>2</sub>CO<sub>3</sub> (4 g, 28.9 mmol), H<sub>2</sub>O (13 mL), and toluene (200 mL) was placed in a flame-dried flask and refluxed for 48 h under hydrogen atmosphere. The resultant mixture was passed through a short column packed with silica gel. Evaporation of the solvent yielded a crude product, which was purified by column chromatography to obtain a white solid product, 4,4''''-dimethoxy-2'',3'',5'',6''tetraphenyl-1,1':4',1'':4'', 1''':4''',1''''-quinquephenyl (90%). A three-necked flask equipped with a magnetic stirrer was charged with 3 g (4.01 mmol) of the dimethoxy groups monomer in dichloromethane (40 mL), to which was added to BBr<sub>3</sub> (1.14 mL, 12.0 mmol) in dichloromethane (10 mL) at -78 °C under a nitrogen atmosphere. The solution was allowed to warm at room temperature and then stirred overnight. The solution was cooled in an ice bath and quenched with water. The guenched reaction was extracted twice using ethyl acetate and (1M) NaOH. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated at a yield of 92.1%: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$  = ppm): 4.68 (s, 2H, OH), 6.79-7.33 (m, 36H, ArH).

#### **Polymer Synthesis**

The polymers were synthesized according to Scheme 2. Condensation polymerization followed our previously reported procedure.<sup>30</sup> Polymerizations were carried out in a 50 mL three-necked round-bottom flask equipped with a stir bar, a Dean–Stark apparatus fitted with a condenser, and a nitrogen inlet. The flask was charged with **1** (2 g, 2.78 mmol), 4,4'difluorobenzophenone (1.21 g, 5.56 mmol), bisphenol A (0.635 g, 2.78 mmol), potassium carbonate (0.84 g, 6.12 mmol), DMAc (20 mL), and toluene (15 mL). The solution mixture was stirred at 130 to 150 °C for several hours.



SCHEME 2 Synthesis of SP1-X. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

During the reaction, a slow stream of nitrogen was passed through the reaction vessel to remove the water produced by the reaction and then azeotroped with toluene. After complete removal of the water, the reaction solution was stirred under reflux (160 °C) for 24 h. The resultant polymer solution was diluted with 10 to 15 mL of THF and poured with stirring into methanol (250 mL). A fibrous polymer, **P1**, was collected by filtration, washed, and vacuum-dried for 24 h at 120 °C.

To a solution of **P1** (0.4 g) in dichloromethane (30 mL) at room temperature, 0.748 M of chlorosulfonic acid solution in dichloromethane (30 mL, containing 1.5 mL [22.4 mmol] chlorosulfonic acid) was added dropwise. The reaction mixture was stirred for 24 h and poured into water. The precipitate formed was filtered, washed thoroughly with deionized water until pH neutral, and dried under vacuum at room temperature overnight to yield sulfonated polymer, **SP1**. **P1** was sulfonated to different extents according to the above procedure by adding 4 mL (59.9 mmol), 5 mL (74.8 mmol), and 5.5 mL (82.3 mmol) of chlorosulfonic acid, respectively.

# Measurements

The chemical structure of the monomer and polymers was identified by 500 MHz <sup>1</sup>H NMR spectroscopy (Varian UNITY INOVA-500) using DMSO-d<sub>6</sub> and CDCl<sub>3</sub> as solvents. The molecular weights of the polymer were measured by GPC (Viscotek) with a refractive index detector (Viscotek 270). THF was used as the eluent (flow rate, 1 mL/min), and the molecular weights of the polymers were calibrated using polystyrene standards. FT-IR spectroscopy of the dry membrane samples was recorded by using a BRUKER Vector 70

spectrometer at a resolution of 4  $\text{cm}^{-1} \text{min}^{-1}$  from 4000 to 400  $\text{cm}^{-1}$ .

Membranes of **SP1** were obtained by filtering and casting DMAc solutions of the polymer onto a flat glass plate, drying at 80 °C for 12 h, and then under reduced pressure for another 12 h. The ion exchange capacity (IEC) of the membranes was determined by acid-base titration. Dried membranes were weighed and immersed in 1.0 M HCl solution for 24 h to protonate the sulfonic acid groups. The membranes were washed thoroughly with deionized water until pH neutral. The membranes were immersed in 1.0 M NaCl for 24 h and the proton released titrated with 0.01 M NaOH to a phenolphthalein end point. IEC (mmol/g) was calculated as follows eq 1:

$$IEC(mmol/g) = \frac{V_{NaOH} \times M_{NaOH}}{W_{dry}}$$
(1)

where  $V_{\text{NaOH}}$  and  $M_{\text{NaOH}}$  are the volume and concentration of the NaOH solution, respectively, and  $W_{\text{dry}}$  is the weight of the dried membrane.

Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Pyris 1 over a temperature range of 100 to 600 °C using a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. Prior to analysis, the membranes were dried and kept in the TGA furnace at 150 °C under air for 20 min to remove residual water. Thermomechanical analysis (TMA) was performed on specimens with controlled size (length, 10 mm; width, 2 mm; thickness, 30 um) using a Seiko Pyris Diamond TMA at 25 °C.



Oxidative stability was evaluated by immersing membranes into Fenton's reagent (aq. 3% H<sub>2</sub>O<sub>2</sub>, containing 2 ppm FeSO<sub>4</sub>) at 80 °C. Water uptakes were determined according to their increased mass after soaking in deionized water at rt for 24 h. Water uptake was calculated using eq 2:

water uptake = 
$$\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$
 (2)

The temperature was increased from 20 °C to 80 °C to investigate temperature dependence. The hydration number,  $\lambda$  (water molecules per sulfonic acid group), was calculated by combining the water uptake data and the IEC value as follows eq 3:

$$\lambda = \frac{1000 \times (W_{\text{wet}} - W_{\text{dry}})}{IEC \times W_{\text{dry}} \times 18}$$
(3)

where  $W_{dry}$  and  $W_{wet}$  are the weights of the dried and wet samples, respectively. The dimensional swelling ratio was calculated from the change in film dimensions as follows eqs 4 and 5:

$$\Delta L = \frac{L_{\text{wet}} - L_{\text{day}}}{L_{\text{day}}} \times 100\%$$
<sup>(4)</sup>

$$\Delta T = \frac{T_{\text{wet}} - T_{\text{day}}}{T_{\text{day}}} \times 100\%$$
(5)

where  $T_{dry}$ ,  $T_{wet}$ ,  $L_{dry}$ , and  $L_{wet}$  are the thickness and length of dry and wet samples, respectively.

In-plane proton conductivity was measured by ac impedance spectroscopy, using a Solartron 1260 frequency response analyzer (FRA) that employed a two-electrode configuration, according to a procedure described elsewhere.<sup>31</sup> The membrane (10 × 5 mm) was placed between the two Pt electrodes of a conductivity cell, and a 100 mV sinusoidal ac voltage over a frequency range of 10 MHz-100 Hz was applied. The resulting Nyquist plots were fitted to a standard Randles-equivalent circuit to determine the membrane resistance. Proton conductivity ( $\sigma$ ) was calculated using eq 6:

$$\sigma = \frac{L}{RA} \tag{6}$$

where L (cm) is the distance between electrodes, R ( $\Omega$ ) is the membrane resistance, and A (cm<sup>2</sup>) is the cross-sectional area of the membrane. An ESPEC SH-241 temperature/ humidity chamber was used to measure membrane conductivity under conditions of variable temperature and humidity. The membranes were equilibrated overnight in the chamber at a predetermined temperature and relative humidity.

For TEM analysis, membranes were stained with sliver ions by immersion overnight in 1 M  $AgNO_3$ , rinsing with water and drying under vacuum for 24 h. The stained membranes

were embedded in epoxy resin and sectioned 70 nm thick. TEM images were taken on a JEOL, JEM-2100 (HR) TEM using an accelerating voltage of 200 kV.

# **RESULTS AND DISCUSSION**

#### Synthesis and Chemical Characterization of SP1

A novel bisphenol monomer, **1**, possessing six possible sulfonation sites, was synthesized as described, and characterized by <sup>1</sup>H NMR spectroscopy. A NMR spectrum of **1** is shown in Figure 1. It consists of a singlet peak at 4.68 ppm and a multiplet of peaks at 6.8 to 7.5 ppm, assigned to the OH group and aromatic protons, respectively, as indicated. **P1** was synthesized by a one-pot polymerization of monomer **1** in the presence of 4,4'-difluorobenzophenone and bisphenol A in 87% yield. The weight-average and number-average molecular weights of **P1** were 879 kDa and 437 kDa, respectively, as determined by a single peak in the GPC analysis. Polymers were also synthesized from other molar ratios of *bis*(4-fluorophenyl) sulfone, 4,4'-(hexafluoroisopropylidene)diphenol, and **1**, but multi-modal molecular weights were produced (as observed by GPC traces) and were not analyzed further.

The <sup>1</sup>H NMR spectrum of the **P1** is shown in Figure 2(a). Peaks located at 7.78 ppm are assigned to the protons of 4'difluorobenzophenone labeled i and n. The two peaks at 6.9 ppm and 7.05 ppm are assigned to the bisphenol A protons (labeled j and k). The multiplet at 6.8 to 7.5 ppm is assigned to aromatic protons of monomer **1**, but the single peak at 4.68 ppm position (OH group of monomer **1**) disappeared upon polymerization. The <sup>1</sup>H NMR analysis is in complete agreement with the target structures of the copolymer composition (monomer 1: 4,4'-(hexafluoroisopropylide-ne)diphenol : *bis*(4-fluorophenyl) sulfone, feed ratio 0.5:0.5:1), as shown in Figure 2(a).

**P1** was sulfonated to various extents using chlorosulfonic acid. Generally, the introduction of sulfonic acid groups by chlorosulfonic acid preferentially occurs on electron-rich aromatic rings. The structures of the SP1-X copolymers (where X indicates IEC) was confirmed by <sup>1</sup>H NMR spectroscopy, as shown in Figure 2(b). The signals at 6.7–7.2 ppm become broad after sulfonation and new signals appear at 7.6 ppm and 7.75 ppm [labeled 1- and 7 in Fig. 2(b)], due to the presence of the sulfonic acid group.

Baseline-corrected FTIR spectra of **P1** and **SP1** are shown in Supporting Information Figure S1, off-set for clarity. The absorption band at 1023 cm<sup>-1</sup> corresponds to Ph-O-Ph symmetric stretching, and the bands at 1330 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> correspond to Ph-O-Ph asymmetric stretching of the poly(arylene ether). All polymers exhibit absorption bands at 1606 and 1651 cm<sup>-1</sup> due to C=C and C=O stretching. Characteristic bands at 1035 cm<sup>-1</sup> and 1110 cm<sup>-1</sup> are assigned to symmetric and asymmetric stretching of the O=S=O group. The intensity of this peak increased with increasing degree of sulfonation (IEC), again confirming introduction of the sulfonic acid groups. Further support of sulfonation is provided by IEC analysis, determined by



titration, which are listed in Table 1 and ranged from 1.88–2.67 mmol/g. The degree of sulfonation of SP1-X increased upon increasing the IEC values and ranged from 57 to 81%.

# **Characterization of Membranes**

TGA curves of **P1** and **SP1** are shown in Supporting Information Figure S2 and the data extracted are listed in Table 1. **P1** exhibits excellent thermal stability, with 5 wt % loss occurring at 490 °C (T<sub>d</sub>5%). **SP1** polymers are less thermally stable, exhibiting several distinct degradation steps, with a major processes occurring at ~250 °C, attributed to loss of sulfonic acid groups. Further degradation occurs at ~530 °C, presumable due to fragmentation of the SP1-X main chain.  $T_d5\%$  for **SP1** membranes decreased (from 291 to 258 °C) upon increasing the IEC (from 1.88 to 2.67 mmol/g), supporting the assertion that degradation of the sulfonate group is responsible for their overall degradation within this temperature region. The corresponding thickness of SP1-X membranes are listed in Table 1 and ranged from 28 to 40  $\mu$ m. The water uptake of SP1 increased with increasing IEC, as shown in Figure 3, and were much higher than Nafion 117. The Figure 4, shown as hydration number increased with temperature with the exception of SP1-1.88, which remained relatively constant. The in-plane and through-plane dimensional length changes of SP1 membranes (listed in Table 1) were evaluated by comparing their hydrated state and dry states. Generally, dimensional changes increased with increasing IEC and water content. SP1-2.22 and SP1-2.44 membranes exhibited good dimensional stability yet high water uptake. Their swelling ratio varied by 5 and 18% at 80 °C, respectively, similar to that of Nafion 117. Comparisons with Nafion 117, indicate that the higher rigidity of the aromatic chain of SP1 confers a distinct improvement over other flexible chain analogues. Despite the much larger water sorption capacities, the dimensional swelling of the SP1 is relatively low. We attribute this to a high free volume resulting from bulkiness of the tetra-phenylated structure, leading to water sorption without excessive dimensional swelling.

The hydrolytic stability of the membranes was examined by immersing them in water at 140 °C for 24 h (see Table 2). Of the four types of SP1 membranes examined, **SP1-1.88, SP1-2.22**, and **SP1-2.44** lost 2, 9, and 10 wt %, respectively, by dissolution, but retained their flexibility and transparency. **SP1-2.67** completely dissolved. Oxidative stability was evaluated using Fenton's reagent (3% aq.H<sub>2</sub>O<sub>2</sub>, 3 ppm FeSO<sub>4</sub>) at 80 °C for 1 h. **SP1-1.88** remained unaltered after 1h immersion, while **SP1-2.22** and **SP1-2.44** lost 2 and 4 wt %, respectively. **SP1-2.67** dissolved. **SP1-2.22** and **SP1-2.44** membranes had good oxidative stabilities, as compared to the findings of previous work in which a sulfonated poly(arylene ether sulfone ketone) possessing IECs of 2.12 and 2.43 mmol/g are reported to completely dissolve/degrade.<sup>32</sup>



FIGURE 2 <sup>1</sup>H NMR spectrum of the (a)P1, (b)SP1–2.67. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sample Name	IEC <sup>a</sup> (titr.)	Degree of Sulfonation (%) <sup>b</sup>	<i>T</i> d5%(°C) <sup>c</sup>	Water Uptake <sup>d</sup>	λ	$\Delta I(\%)^{e}$	$\Delta T(\%)^{e}$	Thickness (µm)
SP1-1.88	1.88	57	291	34	10	5	3	30
SP1–2.22	2.22	67	267	87	21	15	15	28
SP1–2.44	2.44	74	262	98	22	18	20	40
SP1–2.67	2.67	81	258	_f	_	-	-	35
Nafion117	0.091		-	30	19	18	7.7	175

**TABLE 1** Thermal Properties, Water Uptake,  $\lambda$ , and Dimensional Stability of SP1 Membranes

<sup>a</sup> IEC determined by acid-base titration.

<sup>b</sup> The degree of sulfonation was calculated by assuming six sulfonic acid groups per monomer unit. The theoretical highest IEC values of SP1-X is 3.3 mmol/g.(degree of sulfonation: 100%).

<sup>c</sup> 5% weight loss temperature (acid form).

Proton conductivities of SP1 are observed to increase with RH (at 80 °C), as shown in Figure 5. SP1 membranes exhibited lower conductivities than Nafion 117, with the highest conductivity being 4.51 mS/cm (SP1-2.67) at 40% RH, and 16.39 mS/cm at 60% RH, compared to 10 and 20 mS/cm for Nafion 117. However, the proton conductivity of SP1 membranes showed a greater temperature dependence (measured under 95% RH), as shown in Figure 6 and listed in Table 2, and the conductivity increased to a greater extent with increasing IEC. For example, the proton conductivity of the SP1-2.67 increased from 0.05 to 0.169 S/cm between 30 °C and 80 °C, i.e., much greater than Nafion 117, while the conductivities of SP1-2.44 were similar to Nafion 117. SP1-1.88 showed very little variation in proton conductivity with increasing temperature, similar to that observed for water uptake.

TEM images of **SP1** under two magnifications are shown in Figure 7. Nanoscale phase separation is observed: dark

 $^{\rm d}$  In the hydrated state (80  $^\circ\text{C}$  and 100% RH).

 $^{\rm e}$  Change in film length ( $\Delta$ /) and thickness ( $\Delta$ 7) in hydrated state (80  $^{\circ}{\rm C}$  and 100% RH).

<sup>f</sup> Dissolved in water.

regions represents domains of ionic clusters; bright areas represent hydrophobic regions. The TEM images of **SP1-2.22, SP1-2.44**, and **SP1-2.67** reveal ionic cluster sizes of 6 to 12, 14 to 16, and 17 to 20 nm, respectively indicating that the ion domains increase with increasing IEC. In comparison, Nafion membrane exhibits ionic domains 4 to 5 nm in diameter.<sup>32</sup>

Stress-strain curves, determined at room temperature, are shown in Figure 8 and Table 3. **SP1-1.88** exhibits a tensile strength 70.2MPa with elongation at break of 230.7%, similar to the parent polymer, **P1**, but the tensile strength decreases with IEC. SP1-X membranes exhibit tensile strengths ranging from 35.3 to 70.2 MPa, much higher than Nafion 117 (21.8 MPa). Elongation at break ranged from 62% to 230%, respectively, generally lower than those of the Nafion 117 (>243%). The Young's moduli were between 0.20 and 1.17 GPa, which is much higher than that of Nafion 117 (at 0.05 GPa). In general, the **SP1** membranes tolerated much larger deformations and larger stresses without



**FIGURE 3** Water uptake as a function of temperature for SP1-X copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 4** Hydration number as a function of temperature for SP1-X. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

# TABLE 2 Proton Conductivity, Hydrolytic and Oxidative Stability of SP1 Membranes

		Proton Conductivity (mS/cm), 80 °C		Proton Conductivity (mS/cm), 95%RH		Oxidative Stability <sup>a</sup>	Hydrolytic Stability <sup>b</sup>	
Sample Name	IEC (mmol/g)	40%RH	60%RH	30 °C	80 °C	Residual Weight (%)	Residual Weight (%)	
SP1-1.88	1.88	0.1	0.24	1.07	3	100	98	
SP1–2.22	2.22	0.5	2.61	14.73	15	98	91	
SP1–2.44	2.44	1.81	8.44	43.1	102	94	90	
SP1–2.67	2.67	4.51	16.39	52.66	169	_c	_c	
Nafion117	0.091	10	20	64	100	-	-	

<sup>b</sup> After 24 h at 140 °C.

<sup>c</sup> Dissolved in water.

 $^a$  The polymer was heated in Fenton's reagent (FeSO\_4 (2 ppm) in 3%  $H_2O_2)$  at 80  $^\circ C$  for 1 h.



**FIGURE 5** Proton conductivity of SP1-X membranes as a function of RH at 80 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 6** Proton conductivity of SP1-X membranes as a function of temperature at 95% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 7 TEM images of stained membranes: (a) SP1-2.22 (b) SP1-2.44, (c) SP1-2.67, membranes. Scale bar 100 nm. Inset scale bar is 20 nm.



FIGURE 8 Stress-strain curves of SP1-X membranes.

breaking compared to Nafion 117, demonstrating their excellent mechanical properties, again attributed to the rigidity and free volume of the multiphenylated structure.

# CONCLUSIONS

A series of sulfonated, multiphenylated poly(arylene ether)s copolymers were synthesized for examination as proton conducting membranes. The membranes exhibited exceptionally high mechanical strength and tolerance to deformation, even with high IEC. In a highly humidified environment (100% RH) at 80 °C, water uptakes were relatively low (34% to 98%). However the higher IEC membranes dissolved, or showed evidence of dissolution in liquid water at elevated temperatures. In a simple Fenton's reagent test, all but the lowest IEC, showed evidence of degradation to free radicals. The proton conductivity of the highest IEC membrane under 60% RH reached 16 mS/cm at 80  $^\circ\text{C}$  and 167 mS/cm at 80 °C. The high conductivity was achieved despite TEM analysis indicating the existence of discrete ionic clusters embedded in a hydrophobic matrix. Noting that TEM analysis is performed under vacuum on dehydrated polymers it is presumed that a hydrophilic network is formed upon hydration. Network formation is either caused by coalescence of the

TABLE 3 Mechanical Properties of SP1 Membranes

	Young's Modulus (GPa)	Tensile Strength/MPa	Elongation at Break (%)
P1	0.68	68.4	118
SP1-1.88	0.47	70.2	231
SP1–2.22	0.34	35.3	104
SP1-2.44	1.17	45.0	62
SP1–2.67	0.20	52.6	124
Nafion 117	0.05	21.8	244

Measured at room temperature and 50%RH. Sample length, 10 mm; width, 2 mm; thickness, 30–40  $\mu m.$ 

ionic aggregates or absorption of water in the free volume of the polymer—the latter being supported by the lower degree of dimensional swelling with respect to water uptake.

This work demonstrates that the multiphenylated polymer backbone confers high rigidity and induces free volume in membranes that facilitate water sorption for proton conductivity, while retaining high mechanical strength. Current research is directed to examining these materials in fuel cells, both as the proton exchange membrane and the ionomer for the catalyst layer.

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