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Ionomeric Poly(phenylene) Prepared by Diels−Alder Polymerization: Synthesis and Physical Properties of a Novel Polyelectrolyte

Cy H. Fujimoto,[†] Michael A. Hickner,[†] Christopher J. Cornelius,*[,†] and Douglas A. Loy*[,‡]

Chem & Bio Technologies, Org. 6245, Sandia National Laboratories,
Albuquerque, New Mexico 87185-0888, and Polymers and Coatings Group, MS E549,
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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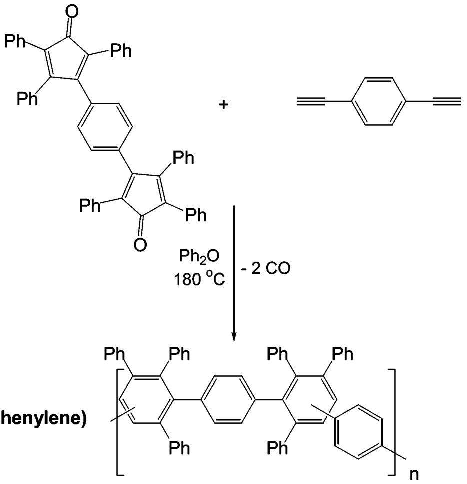
ABSTRACT: A series of poly(phenylene)-based polyelectrolytes were synthesized from 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene and 1,4-diethynylbenzene by Diels−Alder polymerization. Postsulfonation of this high molecular weight and thermochemically stable poly(phenylene) with chlorosulfonic acid resulted in homogeneous polyelectrolytes with controllable ion content (IEC = 0.98−2.2 mequiv/g). Fuel cell relevant properties such as high proton conductivity (123 mS/cm), chemical/thermal stability, and film toughness suggest that this polyelectrolyte material shows promise as a potential candidate for polymer electrolyte membrane fuel cells. Physical properties of this material, such as water uptake, thermal stability, and proton conductivity, are reported with respect to ion exchange capacity and compared to Nafion and a series of sulfonated poly(ether sulfone)s.

Introduction

The cost and performance limitations of current perfluorinated polymer electrolyte membranes (PEM) such as Nafion have hindered large-scale commercialization and market penetration of polymer electrolyte membrane fuel cells (PEMFC) in mobile and stationary systems. This has sparked worldwide research efforts to design alternative polymer electrolyte membrane (PEM) materials with high ionic conductivity, thermal stability to allow operation over 100 °C, chemical stability to a strong acid proton conductor and oxidation, good processability, and excellent barrier properties to fuels (e.g., methanol, oxygen, etc.).[1,2] One common approach has been to sulfonate existing thermoplastics such as polystyrene,[3,4] poly(ether ketone)s,[5,6] and poly(ether sulfone)s.[7,8] This has generated mostly PEM's with lower costs and improved thermal stability, but generally lower ionic conductivities at comparable ion exchange capacities than Nafion,[9] and many of these thermoplastics-based PEMs are more susceptible to oxidative or acid-catalyzed degradation than Nafion.[10]

Utilizing a purely aromatic polymer, such as poly(phenylene)s, provides a route to potentially improve the thermochemical stability of PEMs due to their inherent thermochemical stability. High molecular weights are necessary for these aromatic polymers to ensure polymer chain entanglements that are responsible for producing physically robust PEM films. A physically robust film is one necessary characteristic of a membrane electrode assembly in order to survive with a PEMFC environment. An example of a sulfonated substituted poly(phenylene) is poly(4-phenoxybenzoyl-1,4-phenylene) which has shown relatively high proton conductivities (10^{-2} S/cm) and good PEM characteristics.[11] However, achieving high molecular weights based upon this class of polymer is dependent on the pendent group of the aryl halide monomer,[12] which limits sulfonation and broad functionalization.

Scheme 1. Diels−Alder Polymerization of 1,4-Bis(2,4,5-triphenylcyclopentadienone)benzene and Di(ethynyl)benzene



The subject of this paper is the synthesis and physical properties of a sulfonated, highly phenylated poly(phenylene) that provides a very promising solution to achieving PEMs with high molecular weights and overcomes the limitations of sulfonation and broad functionalization (Scheme 1). Here we report the first fully aromatic polymer electrolyte that is designed to be processable and thermally and chemically robust, with ionic conductivities rivaling those of Nafion. The backbone polymer, prepared by the Diels−Alder polymerization of 1,4-bis(2,4,5-triphenylcyclopentadienone)benzene with diethynylbenzene, (Scheme 1),[13] can be prepared with a wide range of functionalities and configurations that provide an almost unprecedented opportunity to optimize the chemical and physical properties desirable for PEM's. A minimum-energy molecular model (Figure 1) of the polymer repeat unit shows a noncoplanar phenylene backbone and indicates a rigid-rod structure. By themselves, the polymers are insulating and thermally stable to 500 °C, a fact that has made them one of the more important spin-on

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[†] Sandia National Laboratories.
[‡] Los Alamos National Laboratory.
* Corresponding author. E-mail cjcorne@sanda.gov.

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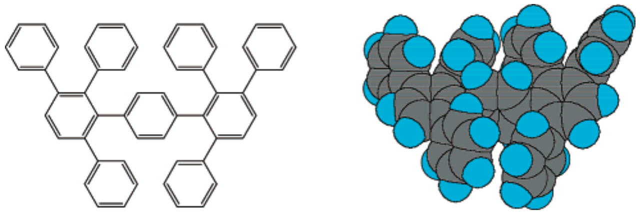


Figure 1. Minimum-energy molecular model of repeat unit.

dielectric materials.[14] Six pendant phenyl groups per repeat unit and the mix of meta and para configurations imparted by the regiochemistry of the Diels−Alder polymerization make these materials readily soluble in organic solvents and easily processed into thin films. The large number of pendant phenyl groups provides for the facile introduction of up to six sulfonic acid groups per repeat unit, a fact that we use to study the influence of the degree of sulfonation on ionic conductivity, water uptake, and thermal stability.

Experimental Section

Materials. 1,4-Bis(2,4,5-triphenylcyclopentadienone)benzene, or bis(tetracyclone), was prepared as described elsewhere.[15] 1,4-Diethynylbenzene was purchased from GFS and sublimed at room temperature before use. Diphenyl ether, chlorosulfonic acid, dimethylacetamide (DMAc), and anhydrous methylene chloride were used as received from Aldrich.

Synthesis of DA Poly(phenylene) [SDAPP0]. Polymerizations were performed using a slight modification of the method described in the literature.[16] To bis(tetracyclone) (50.0 g, 72.4 mmol) and 1,4-diethynylbenzene (9.13 g, 72.4 mmol) in a 500 mL Schlenk flask, diphenyl ether (250 mL) was added, and the resulting mixture was frozen in an ice bath. The mixture was freeze−thaw degassed (3 times) before heating under argon (1 atm) at 180 °C for 24 h. Periodically, carbon monoxide was vented to avoid over-pressurization of the reaction flask. Subsequently, additional diethynylbenzene (0.10 g, 0.8 mmol) was added to the viscous slurry, and the mixture was stirred for an additional 12 h at 180 °C. The reaction vessel was then cooled to room temperature, and its contents were diluted with toluene (300 mL). The polymer was precipitated by dropwise addition of the solution to 1000 mL of acetone. This dilution in toluene and precipitation in acetone was repeated, and the resultant white solid was dried in a vacuum oven for 12 h at 80 °C, 48 h at 230 °C, and 24 h at room temperature. A 96% yield (52 g collected) of a tough, yellow solid was obtained.

Sulfonation of DA Poly(phenylene). In a typical sulfonation, SDAPP0 (7.02 g) was added to a flame-dried, 500 mL three-neck, round-bottom flask under argon and dissolved in methylene chloride (6% solution by weight). The solution was cooled to −50 °C (dry ice/acetonitrile), and chlorosulfonic acid (4.30 g, 36.9 mmol) diluted in chloroform (20 mL) was added dropwise though an addition funnel over 15 min while being vigorously stirred with a mechanical stirrer under an argon atmosphere. This amount of chlorosulfonic acid gave a 4:1 ratio of acid to polymer repeat unit. Other ratios of sulfonating agent to polymer repeat unit were prepared to attain polymers with various ion exchange capacities, as discussed in the Results and Discussion section. The mixture darkened from bright yellow to black during chlorosulfonic acid addition. After 30 min the reaction was warmed to room temperature, at which point a dark solid precipitated. The organic solvent was decanted, and to the remaining solid was added 300 mL of a 0.5 M solution of NaOH that was allowed to react at room temperature for 12 h. The slurry was then heated for 4 h at 80 °C to ensure sulfonyl chloride conversion. The off-white solid was Soxhlet extracted with deionized water for 48 h and dried in a vacuum oven at 100 °C for 48 h to obtain light yellow solid (9.52 g). ^{1}H NMR (d-DMSO): δ (ppm) = broad signal 6.35−7.22 (peaks at 7.19, 7.09, 6.95, 6.88, 6.64, 6.54). ^{13}C NMR (DMSO-d_6): δ (ppm) = broad signal 138−141 (peak at 139) broad signal 131−126 (peaks at 126.9, 128.7, 129.5, 131.0).

Formation of Films. The sodium salt of the sulfonated polymer was dissolved in DMAc (10 wt % solution) and filtered though a 2 μm syringe filter (glass microfiber filter). The solution was cast onto a clean glass plate in an oven at 90 °C under N_2. After 20 h, the film was removed from the glass plate and immersed in deionized water (1 L, 18 MΩ) for 1 h at 100 °C to extract any residual DMAc. The resultant film was then converted into the acid (proton) form by immersion in 2.0 M H_2SO_4 at 100 °C for 1 h. The film was then rinsed thoroughly with deionized water and then soaked in deionized water (18 MΩ) at 100 °C for another hour to remove any residual acid. The film was stored in deionized water until used. A nominal film thickness of 3.0 mil (76.2 μm) was used for all experiments, and film thickness was controlled by the amount of solution used and casting area.

Characterization. FTIR spectra of polymer powders/KBr pellets were collected using a Perkin-Elmer System 2000 spectrometer. Thermogravimetric analysis (TGA) under nitrogen was carried out on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min. All samples were heated in the TGA furnace at 110 °C under dry nitrogen for 30 min to remove water before the full scan from 50 to 950 °C was performed. Differential scanning calorimetery (DSC) was performed on a TA Instruments 2010 with a heating rate of 10 °C/min.

The ion exchange capacity (IEC) of the samples was determined by titration of acidified films. Films (approximately 5 cm × 2 cm) were soaked in 50 mL of 1.0 M Na_2SO_4 for 24 h. The solutions were then titrated to an end point of pH 7 with 0.01 M NaOH. The IEC of the film was computed by

$$\mathrm{IEC} = \frac{v_{\mathrm{base}}[\mathrm{NaOH}]}{m_{\mathrm{dry}} \times 0.001} \tag{1}$$

where v_{base} is the volume of base required to reach the end point, [NaOH] is the concentration of the base, and m_{dry} is the mass of the dry polymer. All IEC values reported in this work are the average of three titrations.

To reduce ion aggregation for in-situ characterization (viscosity and GPC) in NMP, LiBr was added at a concentration level of 0.05 M. Intrinsic viscosities of the sulfonated polymers were determined at 25 °C using a Ubbelohde viscometer. Gel permeation chromatography was used to determine molecular weights with respect with polystyrene standards. GPC was conducted with a Waters GPC/ALC 150C instrument equipped with a differential refractometer detector.

Films after conversion to the acid form were stored in deionized water for at least 24 h. The films were removed from the water, blotted dry to remove surface water, and quickly weighed to determine the wet mass of the film (W_{wet}). The films were then dried under P_2O_5 and full vacuum at room temperature for 24 h and weighed again to determine the dry mass of the film (W_{dry}). Water uptake was calculated by the following equation:

$$\mathrm{uptake} = \left[\frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}}\right] \times 100\% \tag{2}$$

The proton conductivity of films samples was measured by four-probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 frequency response analyzer and a Solartron 1287 potentiostat. A schematic diagram of the membrane conductivity cell is shown in Figure 2. The outer electrodes are connected to the working and counter electrodes on the 1287 potentiostat, and the two inner electrodes are connected to the reference electrodes.

EIS was performed by imposing a small sinusoidal (ac signal) voltage, 10 mV, across the membrane sample at frequencies between 100 kHz and 100 Hz (scanning from high to low frequencies) and measuring the resultant current response. From the amplitude and phase lag of the current response, a complex number was computed which is called the

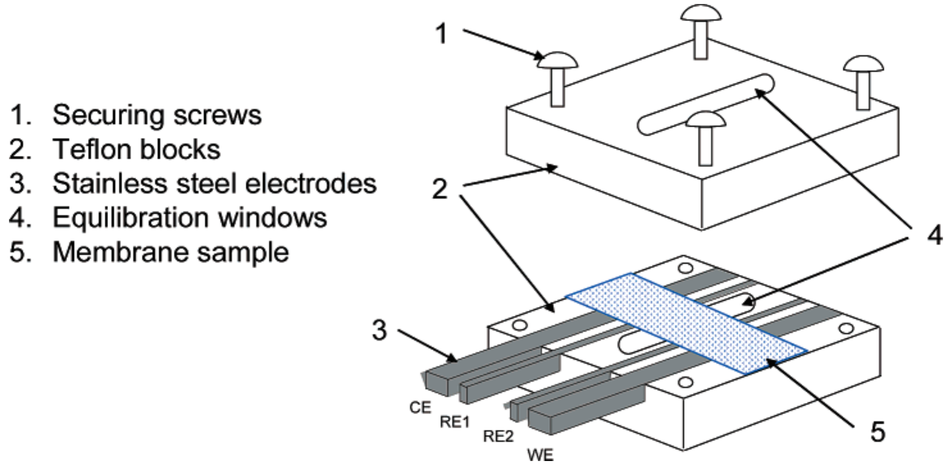


Figure 2. Schematic of four-point membrane proton conductivity cell.

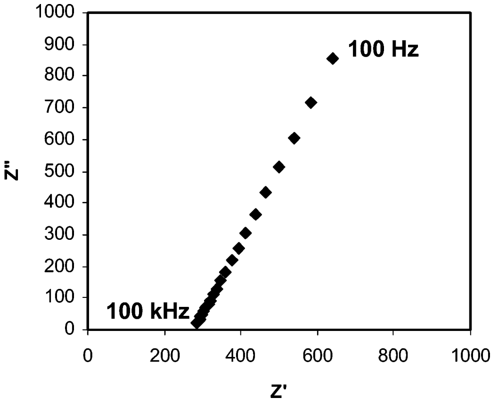


Figure 3. Impedance response of a typical proton conducting membrane between 100 kHz and 100 Hz.

impedance composed of a real component, Z', and an imaginary component, Z''. An example of the raw data is shown in Figure 3. To compute the membrane proton conductivity from the complex impedance response, the impedance line is extrapolated to the x-axis. The extrapolated value of the real impedance where the imaginary response is zero (Z' at $Z'' = 0$) is then taken as the resistance of the membrane, and eq 3 is used to compute the membrane proton conductivity

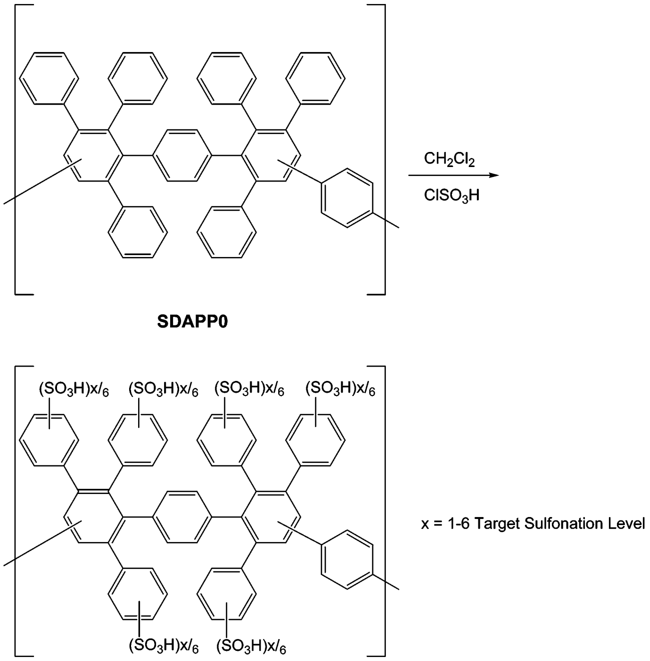
$$\kappa = \frac{L}{Z'A} \tag{3}$$

where L is the length between the sense electrodes, Z' is the real part of the impedance response (extrapolated to $Z'' = 0$), and A is the area available for proton conduction (width × thickness). All proton conductivities reported here were measured with the film immersed in liquid water at 30 °C during the measurement time.

The tensile stress−strain properties of the SDAPP3 membranes were compared with Nafion 117 in order to evaluate the mechanical strength of a typical sulfonated poly(phenylene) vs the state-of-the-art membrane. The samples were tested using a Com-Ten Industries 95T series load frame equipped with a 200 lbf load cell and computerized data acquisition software. Samples of 9 mm width were deformed at a crosshead speed of 5 mm/min with gauge length of 30 mm. Reported stress−strain measurements are the average of at least three tests.

Results and Discussion

Scheme 2. Sulfonation of Diels−Alder Poly(phenylene)



Synthesis and Characterization. Preparation of Diels−Alder poly(phenylene)s has been described elsewhere[16] and briefly described above (vide supra). Sulfonation of SDAPP0 has not been reported, but substituted 1,4-poly(phenylene) has been sulfonated with concentrated sulfuric acid with levels of sulfonation controlled by varying the reaction time.[11] Our approach to sulfonating SDAPP0 was the creation of a 6 wt % polymer solution of SDAPP0 in methylene chloride that was subsequently homogeneously sulfonated in situ with chlorosulfonic acid.

The repeat unit of SDAPP0 with its six pendent phenyl groups (Scheme 2) provides a number of possible sites for sulfonation. However, sulfonation is thought to occur predominantly at the para positions of the pendant phenyl groups due to their positioning[17] about the sterically congested, concoplanar, rigid-rod backbone (Figure 1). Therefore, the limits of sulfonation are projected to be between 0 and 6 sulfonic acid groups per repeat unit. By varying the ratio of moles of chlorosulfonic acid to moles of polymer repeat unit charged to the sulfonation reaction, 0.8−2.1 sulfonic acid groups per repeat unit were achieved as measured by titration (see below).

Introduction of increasing numbers of sulfonic acid groups onto polymers improves their ionic conductivity

Table 1. Solubility of Sulfonated Diels−Alder Poly(phenylene) Samples (SDAPP) in the Sodium Salt Form[a]

sample	IEC	methylene chloride	DMAC	NMP	water
SDAPP0	0	+	−	−	−
SDAPP1	0.98	−	+	+	−
SDAPP2	1.4	−	+	+	−
SDAPP3	1.8	−	+	+	−
SDAPP4	2.2	−	+	+	−

[a] Key: "+", soluble; "− +", swell; "−", insoluble.

but also makes the polymers more hydrophilic. To have a suitable membrane for PEMFC's, there must be sufficient sulfonic acid groups (mequiv/g) to provide suitable proton conduction but few enough to ensure that the polymeric film does not lose its mechanical integrity. Table 1 displays the solubility characteristics of the sulfonated samples in a variety of common solvents with respect to the sample's IEC. At every level of sulfonation, the polymer was insoluble in methylene chloride, in contrast to unsulfonated parent polymer. Between IECs of 0.98 and 2.2 mequiv/g, the samples were soluble in polar aprotic solvents, while remaining insoluble in both nonpolar organic solvents and water. This IEC range is very similar to IEC values studied in other sulfonated aromatic polymers such as sulfonated poly(ether ether ketone) (SPEEK).[9] However, when the IEC was increased over 2.2 mequiv/g, the polymer formed a hydrogel in water, eliminating the feasibility of forming a film from these highly sulfonated samples.

Table 2 summarizes the ratio of moles of sulfonating agent to polymer repeat unit charged in the reaction (sulfonation stoichiometry), experimentally determined IEC, actual sulfonic acid per repeat unit (actual sulfonation), and the ratio of actual sulfonation to sulfonation stoichiometry (sulfonation efficiency). As expected, the actual sulfonation steadily increased with increasing stoichiometry of chlorosulfonic acid. At low sulfonation levels the sulfonation efficiency was relatively high (80%) but decreased to 60−66% with increasing concentration of chlorosulfonic acid.

Spectroscopic evidence of sulfonation of the base polymer was provided with the presence of infrared absorptions characteristic of arylsulfonic acids. In Figure 4, the IR spectra of SDAPP0 through SDAPP4 are plotted. The infrared spectra of *p*-poly(phenylene)s contain two single bands, 770−730 and 710−690 cm^{-1}, which correspond to the out-of-plane vibrations of the five adjacent aromatic hydrogen−carbon bonds of the pendant phenyl groups.[18] In the unsulfonated polymer, these strong absorptions occur at 758 and 696 cm^{-1}, respectively. The intensities of these peaks in SDAPP are diminished (Figure 4), which suggests that sulfonation is occurring predominately on the pendent phenyl groups due to the conversion of monosubstituted phenyl rings to disubstituted. The asymmetric and symmetric sulfonate stretching frequencies adsorptions, 1126 and 1036 cm^{-1}, respectively, increased in intensity with sulfonation level. The aromatic in-plane skeletal deformation[19] at 1494 cm^{-1}, present in both unsulfonated and sulfonated polyphenylene, was used as an internal standard to quantify the amount of sulfonic acid groups in each sample. The ratio of the intensity of the absorption peaks at 1036 and 1494 cm^{-1} were plotted vs IEC resulting in a linear correlation (Figure 5), providing additional evidence of sulfonation and incorporation of sulfonic acid units on the polymer backbone in addition to IEC.

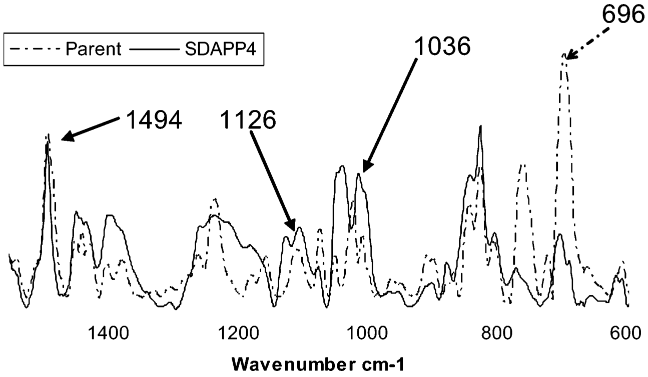


Figure 4. FT-IR spectra of SDAPP0 and SDAPP.

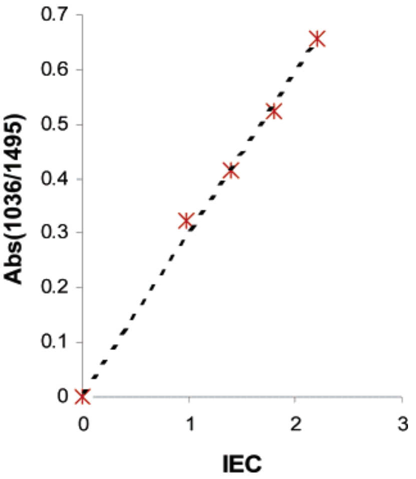


Figure 5. Correlation of ratio of FT-IR peak intensities of sulfonate groups (1036 cm^{-1}) and internal standard in polymer chain (1495 cm^{-1}) to membrane ion exchange capacity.

Furthermore, the sulfonic acid attachment was confirmed by elemental analysis. Elemental analysis for sulfur was performed on cast membranes after they had been converted to the acid form and thoroughly dried. In Table 3, the experimental values obtained for sulfur content on a weight percent basis are compared to the theoretical values computed from the experimentally measured ion exchange capacities found in Table 2. As can be seen in Table 3, the experimentally measured

Table 2. Targeted Sulfonation (Sulfonation Stoichiometry) and Experimentally Determined Ion Exchange Capacity of SDAPP

sample	sulfonation stoichiometry[a]	actual sulfonation[b]	sulfonation efficiency[c]	IEC (experimental)	IEC (elemental analysis)
SDAPP1	1	0.8	80	0.98	1.18
SDAPP2	2	1.2	60	1.4	1.55
SDAPP3	3	1.6	53	1.8	2.14
SDAPP4	4	2.0	50	2.2	2.64

[a] Moles of chlorosulfonic acid added per moles of polymer repeat unit in reaction. [b] Calculated average number of sulfonic acid groups per repeat unit from IEC. [c] {[Actual sulfonation] ÷ [sulfonation stoichiometry]} × 100.

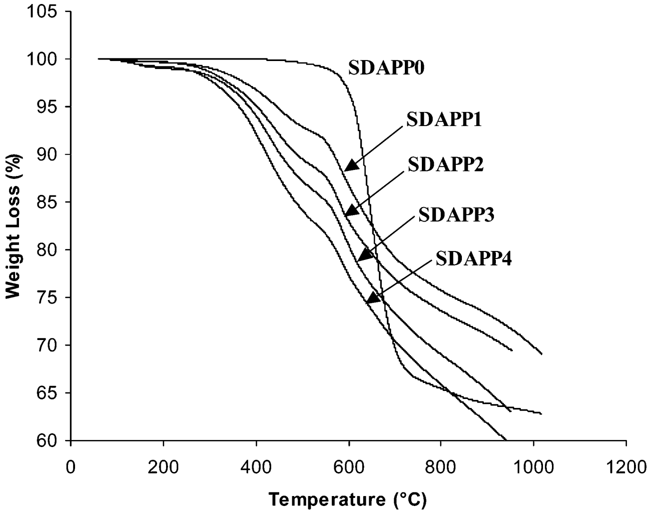


Figure 6. TGA curves for **1** and SDAPP samples.

Table 3. Comparison of Theoretical and Experimental Sulfur Content

	sulfur content (wt %)	
sample	theoretical	experimental
SDAPP0	0	<0.5
SDAPP1	3.1	3.7
SDAPP2	4.5	5.0
SDAPP3	5.8	6.7
SDAPP4	7.3	8.3

Table 4. Molecular Weight and Intrinsic Viscosity of SDAPP 1−4

sample	M_n	M_w	PD	IV
SDAPP1	55 720	120 683	2.2	1.3
SDAPP2	55 093	121 491	2.2	1.5
SDAPP3	82 920	171 603	2.1	1.9
SDAPP4	67 978	156 349	2.3	2.2

values for sulfur content compared well with the theoretical calculations, confirming that the sulfonic acid groups were indeed attached to the polymer as the IEC values indicated.

Molecular weight and intrinsic viscosity of SDAPP 1−4 are compiled in Table 4. The weight-average molecular weights of SDAPP 1−4 ranged from 120,683 to 171,603. An average polydispersity of 2 was observed that is typical for condensation polymerizations. The intrinsic viscosity of SDAPP 1−4 increased with IEC; however, this increase may not be due to an increase of molecular weight but rather higher ion concentration.[20]

Thermal and Mechanical Properties. Thermal gravimetric analysis of SDAPP0 under nitrogen revealed a 5% weight loss occurring at 660 °C. SDAPP in the acid form displayed a three-stage weight loss pattern (Figure 6). Although the sulfonated polymers were dried at 110 °C for 30 min immediately prior to the analyses, the samples showed an initial weight loss between 0.5 and 1.0% due to the loss of water. As the sulfonation level increased from 0.98 to 2.2 mequiv/g, the second decomposition temperature (at 5% weight loss) decreased from 442 to 363 °C. SDAPP2 lost 13.6% of its mass (after absorbed water loss), which is close to the theoretical value of 11.2% after SO_3 cleavage. These results suggest the second weight loss (after water loss) in SDAPP is attributed to the loss of sulfonic acid groups, which typically range from 285 to 426 °C in highly phenylated arylene−sulfonic polymers, while the third transition was associated with backbone degradation.[21] Overall, the high thermal stability of these sulfonated poly(phenylene)s is an attractive PEM trait.

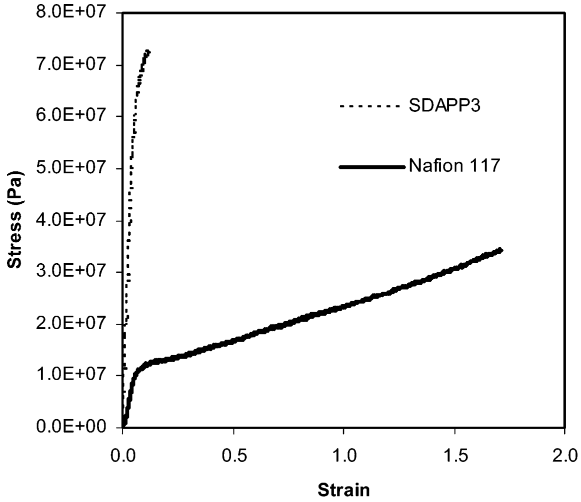


Figure 7. Tensile stress−strain properties of SDAPP3 and Nafion 117 dry films.

Differential scanning calorimetry was used to determine the glass transitions temperature (T_g) of SDAPP0 and the sulfonated SDAPP samples. High-T_g PEM materials are desirable in high-temperature fuel cell applications since maintaining good mechanical properties requires the glass transitional temperature to be higher than the operating temperature. In addition, hydrated ionomeric membranes have reduced T_g's since water acts as a plasticizer,[22] further reducing the operational fuel cell temperature range of the membrane. The unsulfonated polymer SDAPP0 had a high T_g occurring at 388 °C, indicating a very stiff backbone due to the large pendent groups (aryl) and rigid-rod backbone. Although the high T_g of the material was desirable, the structure−property relationship between high degree of chain stiffness as it relates to proton conductivity and water uptake was of interest.

Since sulfonic acid groups increase the steric congestion of a polymer backbone and can interact via hydrogen bonding, the T_gs of sulfonated polymers are greater than their nonsulfonated analogues.[21] Unfortunately, the thermal decomposition of the sulfonic acid group occurred below the T_g of all sulfonated SDAPP0 polyelectrolytes, which prohibited the measurement of the T_gs of these samples by by DSC or dynamic mechanical analysis (DMA).

Dry sample tensile stress−strain curves are shown in Figure 7. The Young's modulus of Nafion 117 was found to be 2.0×10^8 Pa as compared to 1.2×10^9 Pa for SDAPP3. Nafion, being a rubbery material, has a large elongation to break of about 170% whereas SDAPP3 behaves more like an engineering thermoplastic with an elongation to break of 12%. The high modulus and modest elongation properties of SDAPP3 afford flexible, creaseable films that are not brittle. The tensile properties of wet films (soaked in water then immediately tested) were also examined. It was found that the wet membranes had Young's moduli and elongations to break of 5.2×10^7 Pa and 160% for Nafion 117, respectively, and 2.8×10^8 and 6% for SDAPP3. The higher modulus, especially for wet membranes, of SDAPP3 is a distinct advantage of this material over Nafion for high-temperature fuel cell applications.

Water Uptake and Proton Conductivity. Recently, it has been suggested that the temperature

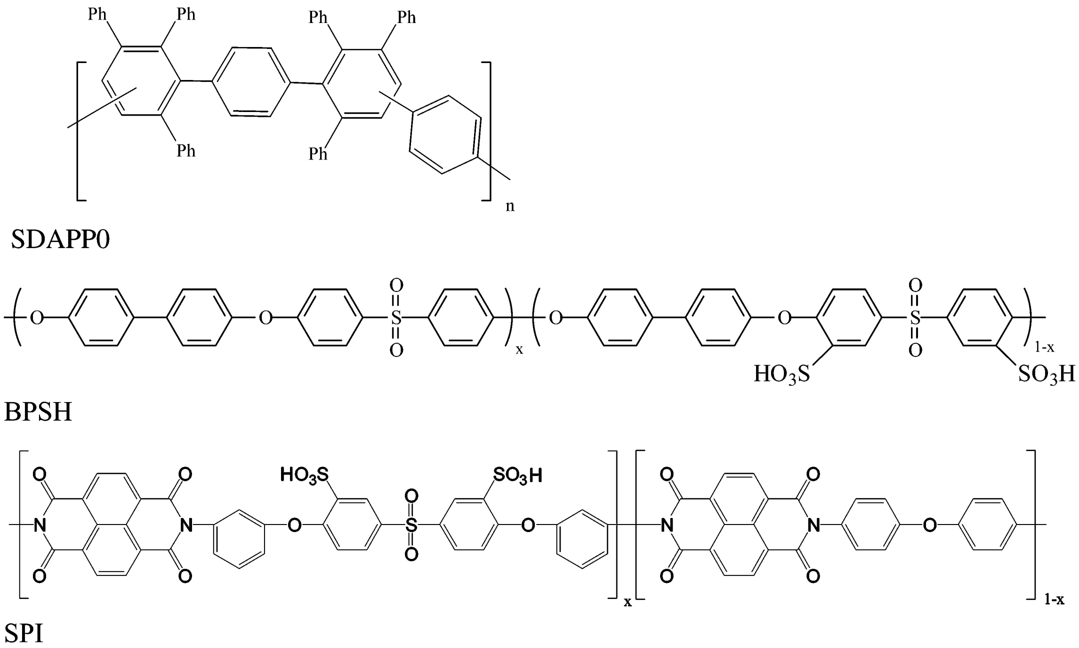


Figure 8. Chemical structures of SDAPP, BPSH, and SPI.

Table 5. Decomposition Temperatures at 5% Weight Loss under Nitrogen for Acid Form SDAPP Samples

sample	$T_{5\%}$ (°C)	wt loss % through loss of SO_3 (theoretical)	wt loss % (actual)
SDAPP0	660		
SDAPP1	442	8.32	9.9
SDAPP2	401	11.2	13.6
SDAPP3	383	17.1	15.7
SDAPP4	363	22.0	19.5

Table 6. Influence of Ion Exchange Capacity for SDAPP Samples on Water Uptake and Proton Conductivity

sample	IEC (mequiv/g)	water uptake (wt %)	λ (H_2O/SO_3H)	conductivity (mS/cm)
SDAPP1	0.98	21	12	13
SDAPP2	1.4	36	14	49
SDAPP3	1.8	75	19	87
SDAPP4	2.2	137	30	123

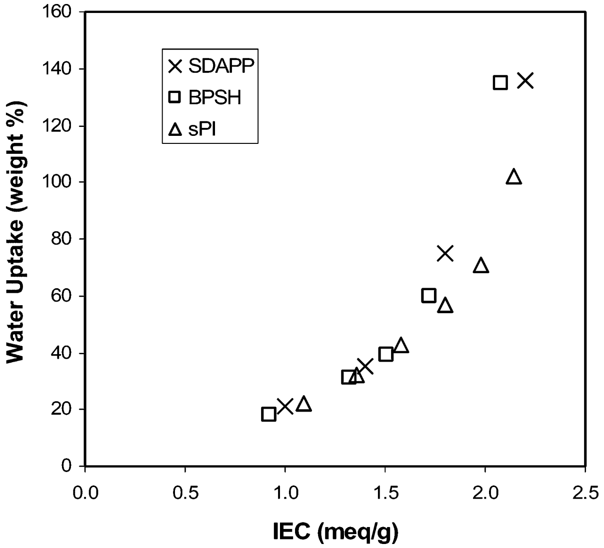


Figure 9. Water uptake vs IEC for SDAPP, BSPH, and SPI.

(either room temperature or 100 °C) used in acid pretreating films influences the ionic domain microstructure of sulfonated polymers.[23] Sulfonated poly(arylene ether sulfone) copolymer membranes acidified at elevated temperatures were found to imbibe more water and have higher proton conductivities than membranes acidified at room temperature. Since fuel cells typically operate above room temperature all films in this work were pretreated at 100 °C.

Table 6 shows the water uptake and proton conductivity of the SDAPP samples. To ascertain structure–property relationships, the SDAPP polymers were compared to other aromatic sulfonated polymers such as BPSH[24] and sulfonated polyimide (SPI),[25] whose structures are presented in Figure 8. A plot comparing water uptake vs IEC of SDAPP, BPSH,[26] and SPI[25] is displayed in Figure 9. BPSH was used as a reference experimental proton exchange membrane because it has been widely studied, while SPI represented an example of a rigid-rod-type backbone, similar to SDAPP. The SDAPP water uptake increased linearly from 21% to 75% as the IEC increased from 0.98 to 1.8 mequiv/g, respectively. As the IEC was further increased to 2.2 mequiv/g, water uptake increased markedly to 136%, indicating that the sulfonic acid domains may have begun to form a cocontinuous morphology between IECs of 1.8 to 2.2 mequiv/g. Wang et al. using tapping mode AFM provided evidence of this cocontinuous morphology of the sulfonic acid containing domains in the BPSH series of polymers.[8] We believe that this same phenomenon may be occurring in the SDAPP series of polymers, and attempts are underway to image the domain structure of these polymers.

In Figure 10, proton conductivity of SDAPP when fully immersed in liquid water at 30 °C increased with IEC from 13 mS/cm (1 mequiv/g) to 123 mS/cm (2.2 mequiv/g). The proton conductivity of BPSH and the sulfonated polyimide polymer increased in a linear fashion with IEC. At similar IEC, the BPSH and SPI polymer showed slightly higher proton conductivities than the SDAPP. This may be due to the nature of the polymer backbone, the concentration density of ionic groups within the polymer, and how the water is bound within its microstructure. Hickner[26] proposed that polymers with stiffer backbones will have lower conductivities due to the inability for the ionic groups to

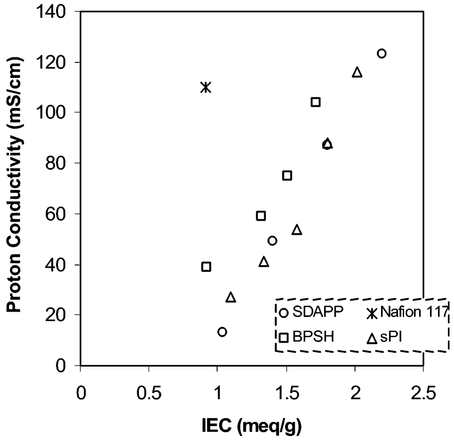


Figure 10. Proton conductivity vs IEC for SDAPP, BSPH, and SPI.

fully phase separate and form concentrated ionic domains, thus causing the absorbed water to be more bound in the polymer microstructure. The similar responses of changing proton conductivity and water uptake with IEC for these series polymers appear to conform to hypothesis of stiff polymer backbone.

Interestingly, even though the SDAPP polymers have very stiff backbone which result in high-T_g materials, the membrane properties of this class of polymer are comparable to the water uptake and proton conductivity of other types of sulfonated aromatic polymers such as BPSH. BPSH reaches its percolation limit at a lower IEC and has higher proton conductivity than SDAPP at comparable IECs. This could be attributed to the concentration density of ionic groups within the polymer and the stiffness of the backbone. Other factors for these differences may stem from a variety of reasons such as sulfonation (post vs monomer), position of sulfonic acid (pendent group vs backbone),[27] and repeat group (phenylene vs either sulfone). This class of polymer affords attractive proton conductivities with relatively low water uptakes.

Conclusions

In conclusion, the poly(phenylene)s synthesized via Diels−Alder condensation resulted in polyelectrolytes that could be postsulfonated in a controllable manner with chrolosulfonic acid. The aryl backbone resulted in a tough rigid-rod material, indicated by its high T_g and inherently high thermochemical stability. This type of high glass transitional temperature material possesses physical properties that are attractive in high-temperature fuel cell applications. In addition, the backbone stiffness does not negatively affect membrane properties such as water uptake (21−137%) and proton conductivity (13−123 mS/cm) with IEC that are typically employed with sulfonated aromatic polymers (0.98−2.2 mequiv/g). The resultant polymers could be solution cast into robust, creaseable films and displayed properties that suggested this class of sulfonated polymer is a potential candidate for hydrogen and methanol fuel cell applications. Strategies to enhance their conductivity especially under partially dry conditions are being explored.

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