# Synthesis and Properties of Novel Proton-Conducting Aromatic Poly(ether sulfone)s That Contain Triazine Groups

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ABSTRACT: A series of novel fully aromatic poly(arylene ether sulfone)s that contain 1,3,5-*s*-triazine groups were synthesized by the reaction of triazine-containing bisphenols with bis(4-fluorophenylsulfone) to study the effects of branching groups on solubility as well as thermal and mechanical properties. Polymers had inherent viscosities from 0.43 to 1.10 dL/g, thermal stabilities >500 °C in air, glass transition temperatures from 136 to 289 °C, and good film forming abilities. The polymer with pendant diphenylamine groups on the triazine ring were further investigated for use in proton exchange membranes based on solubility, thermo-oxidative stability, and ease of monomer synthesis. A series of copolymers made from 4,6-bis(4-hydroxyphenyl)-*N,N*-diphenyl-1,3,5-triazin-2-amine and 4,4′-biphenol were sulfonated with chlorosulfonic acid to achieve ion exchange capacities up to 2.62 mmol/g. The homopolymer was sulfonated exclusively on the diphenylamine branch and had the highest proton conductivity (0.11 S/cm at 95 °C and 100% relative humidity), even though it had the lowest water uptake and ion exchange capacity. Unsulfonated polymers and sulfonated copolymers showed little uptake of phosphoric acid. However, the sulfonated homopolymer with pendant diphenylamine groups had a 200−250 wt % uptake when soaked in 85% $H_3PO_4$ at 90 °C, but the proton conductivity of this polymer was lower than the hydrated polymer without $H_3PO_4$ added.

## Introduction

Proton exchange membrane (PEM) fuel cells that operate at high temperatures (>150 °C) are desirable for a number of reasons, such as higher tolerance of the anode to CO poisoning, increased catalyst efficiency, and easier thermal management.[1] Fuel cells that operate at lower temperatures generally require water for proton transport. However, at higher temperatures, a polymer must be designed that strongly binds to water or has a different medium of proton transport. Polybenzimidazole (PBI) doped with $H_3PO_4$ has been established as a good polymer system for use in proton exchange membrane (PEM) fuel cells at high operation temperature and low humidity conditions.[2,3] The only true requirement of the polymer in this system is to have a heteroatom that is capable of hydrogen bonding to $H_3PO_4$, which allows for a high uptake.[4] $H_3PO_4$ then becomes the conductive medium in the membrane. PBI offers several other desirable properties as well, such as high thermo-oxidative stability and a rigid structure at high operating temperatures ($T_g = 425$ °C).[4] However, PBI also has several disadvantages. PBI is made from 3,3′,4,4′-tetraaminobiphenyl, which has poor oxidative stability. In addition, PBI cannot be melt processed and has limited solubility in common organic solvents.[5,6] The synthesis of PBI is designed to limit the molecular weight in order to increase solubility, which has an adverse effect on the mechanical properties. Wainright and co-workers have reported heating a 10% solution in DMAc at 94 °C leaves 69% of the polymer undissolved.[4] However, the lower molecular weight material must be extracted to produce a polymer film with sufficient mechanical properties for fuel cell operation.

Other research groups have synthesized aromatic polymers capable of a high uptake of phosphoric acid, but with improved processability. Benicewicz and co-workers have reported the synthesis of PBI in poly(phosphoric acid), followed by casting of the membrane directly from the reaction vessel.[7–9] Phosphoric acid is then produced by the hydrolysis of poly(phosphoric acid). This method of imbibing produces strong PBI films with much higher phosphoric acid uptake than the conventional soaking method. Gourdoupi and co-workers have synthesized poly(arylene ether)s that contain pyridine and phenylphosphine oxide groups.[10] These polymers exhibit good solubility in common organic solvents, high thermal stability, and $H_3PO_4$ uptakes of >300 wt %. However, replacement of the phenylphosphine oxide group with a more commercially viable sulfone group resulted in polymers with low solubility. This groups' novel bisphenol could be copolymerized with other bisphenols to give high molecular weight polymers, but $H_3PO_4$ uptakes decreased.[11,12]

Our laboratory has recently attempted to synthesize a heterocycle-containing polymer that maintains the thermal, mechanical, and $H_3PO_4$ binding properties of PBI, but with increased solubility. Heterocyclic polymers, in general, have limited solubility in common organic solvents. One way to improve solubility is to add flexible ether linkages to the polymer chain. A number of poly(arylene ether)s have been synthesized that contain heterocyclic units.[13] The heterocycles include benzimidazole,[14–16] benzoxazole,[17] quinoxaline,[18] 1,3,4-oxadiazole,[19] and 1,2,4-triazole.[19] These polymers are most commonly made by the reaction of a bisphenol with an activated aromatic dihalide in the presence of base via nucleophilic aromatic substitution.[20,21] Even with the incorporation of the ether groups, solubility is quite often limited. Because of premature crystallization, many of these polymers must be made in solvents like diphenylsulfone at temperatures over 200 °C. In addition, films are usually cast from undesirable solvents like *m*-cresol.

Aromatic 1,3,5-*s*-triazines can be made by the reaction of cyanuric chloride with amines,[22] alcohols,[23] and Grignard reagents.[24,25] Using cyanuric chloride as a building block offers the advantage of having three centers with different reactivities. The first aromatic chlorine group is typically reactive at 0 °C,

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the second at room temperature, and the third at elevated temperatures.[26] This allows for tailoring of the monomers to obtain different polymer properties, such as solubility, thermo-oxidative stability, and tensile strength. A branching aromatic group also offers the advantage of polymer sulfonation exclusively on the branching site. Miyatake and co-workers report the synthesis of poly(arylene ether)s containing fluorenyl groups that are sulfonated exclusively on the branching group.[27–29] They suggest sulfonation on the branching group improves hydrolytic stability because it keeps the main polymer chain in a hydrophobic environment. They also report that these polymers have better conductivity than Nafion at elevated temperatures due to the polymer's high water-holding capability. They suggest that the high water-holding capability is directly related to the structural stiffness of the polymer.[30] Our laboratory has designed a highly rigid polymer system that is capable of binding to $H_3PO_4$ through the triazine ring, can be synthesized and cast into films from a common organic solvent (NMP), has good thermal and mechanical properties, and can be sulfonated exclusively on branching groups. This paper studies the effects of monomer composition on the solubility, thermal properties, $H_3PO_4$ uptake, and proton conductivity of poly(arylene ethers) that contain 1,3,5-*s*-triazine groups.

## Experimental Section

**Materials.** 4-Bromoanisole, magnesium, cyanuric chloride, bis(4-fluorophenyl)sulfone, boron tribromide, diphenylamine, 4-(bromophenyl) ether, and dihexylamine were purchased from Aldrich Chemical Co. and used as received. 1-Methyl-2-pyrrolidinone and THF were purchased from Aldrich as anhydrous grade and used as received. 2,4-Bis(4-methoxyphenyl)-6-(4-phenoxyphenyl)-1,3,5-triazine was synthesized according to a literature procedure.[22]

**Instrumentation.** Differential scanning calorimetry (DSC) was measured on a Series Q1000 modulated DSC with an autosampler at a heating rate of 5 °C/min. A TA thermogravimetric analysis (TGA) was used. Measurements were conducted under air with samples loaded onto a platinum pan. The TGA heats at a rate of 10 °C/min from room temperature to 750 °C. The analysis was completed using Universal Analysis software. Tensile testing was performed on an Instron with ASTM D-638 type V dog-bone-shaped samples. The samples were cut from polymer films using an in-house made punch. DMA's were measured in thin films with a 2980 dynamic mechanical analyzer from TA Instruments.

*2-Chloro-4,6-bis(4-methoxyphenyl)-1,3,5-triazine (Cl-Triaz-OMe).* 12.03 g (495 mmol) of magnesium turnings was heated to 60 °C in 20 mL of THF for 30 min. 94.05 g (503 mmol) of 4-bromoanisole in 100 mL of THF was added dropwise through an addition funnel over 40 min. The reaction was then heated to an oil bath temperature of 100 °C for 2 h and cooled. The Grignard solution was then added dropwise over 2 h to 31.2 g (169 mmol) of cyanuric chloride in 90 mL of THF at 0 °C in a three-neck flask equipped with an overhead stirrer. The reaction was stirred overnight at room temperature and then overnight at 45 °C. The reaction was then cooled in an ice bath, and 150 mL of toluene was added, followed by 150 mL of 12% HCl. The resulting slurry was stirred for 20 min, and a light orange solid was collected by vacuum filtration. The filter cake was washed thoroughly with water and petroleum ether. The product was dried in a vacuum oven at 100 °C to give 52.2 g (94.1%) of product in high purity. $^1$H NMR ($CDCl_3$): 3.90 (s, 6H), 7.00 (d, 4H), 8.54 ppm (d, 4H). $^{13}$C NMR ($CDCl_3$): 55.52, 114.16, 127.14, 131.42, 164.11, 171.71, 172.63 ppm.

*2,4-Bis(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.* 14.1 g (43.0 mmol) of 2-chloro-4,6-bis(4-methoxyphenyl)-1,3,5-triazine was added to 15.4 g (85 mmol) of phenylmagnesium bromide in 75 mL of THF. The reaction was heated to reflux overnight. THF was removed by rotary evaporation, and the product was dissolved in 400 mL of $CHCl_3$. This solution was washed with 5% HCl (2×) and water. The solution was then filtered through silica to remove highly polar impurities and rotavaped to give a tan powder that was dried under vacuum overnight at 100 °C. Yield = 11.2 g (70.4%). $^1$H NMR ($CDCl_3$): 3.93 (s, 6H), 7.06 (d, 4H), 7.5−7.6 (m, 3H), 8.7−8.8 ppm (6H). $^{13}$C NMR ($CDCl_3$): 55.43, 113.93, 128.51, 128.85, 129.06, 130.79, 132.15, 136.67, 163.27, 171.01, 171.21 ppm.

*4,6-Bis(4-methoxyphenyl)-N,N-diphenyl-1,3,5-triazin-2-amine.* 29.8 g (90.9 mmol) of 2-chloro-4,6-bis(4-methoxyphenyl)-1,3,5-triazine and 31.2 g (185 mmol) of diphenylamine were heated to 100 °C for 1 h and 120 °C for 30 min under a nitrogen atmosphere. The reaction was then heated to 180 °C overnight. While still hot, the contents of the reaction were poured into ice water to give a gummy red-orange solid. The product was stirred twice in boiling water and three times in boiling hexane to give an orange powder. The product was collected by vacuum filtration after each wash and dried at 120 °C overnight under vacuum to give 35.2 g (83.8%) of a combination of the correct product, along with partial conversion of the methoxy group to a phenol. $^1$H NMR ($CDCl_3$): 3.86 (s, 6H), 6.92 (d, 4H), 7.28 (m, 2H), 7.42 (m, 8H), 8.34 ppm(d, 4H). $^{13}$C NMR ($CDCl_3$): 55.35, 113.67, 125.88, 127.86, 128.76, 129.38, 130.55, 143.75, 162.84, 166.36, 170.71 ppm.

*N,N-Dihexyl-4,6-bis(4-methoxyphenyl)-1,3,5-triazin-2-amine.* 5.2 g (16 mmol) of 2-chloro-4,6-bis(4-methoxyphenyl)-1,3,5-triazine, 3.5 g (19 mmol) of dihexylamine, 100 mL of dioxane, and 5 mL of triethylamine were heated to 100 °C overnight. The reaction was cooled and filtered to remove protonated triethylamine. Solvent was removed by rotary evaporation to give a brown oil. The oil was dissolved in chloroform and washed with water (3×). Solvent was again removed by rotary evaporation, and the product was dried at 120 °C under vacuum for 2 days to give a brown oil that solidified into a crystalline solid when cooled. Yield = 7.5 g (99%) $^1$H NMR ($CDCl_3$): 0.91 (t, 6H), 1.37 (m, 12H), 1.70 (m, 4H), 3.71 (t, 4H), 3.88 (s, 6H), 6.98 (d, 4H), 8.54 ppm (d, 4H). $^{13}$C NMR ($CDCl_3$): 14.04, 22.65, 26.76, 27.76, 31.70, 47.33, 55.35, 113.54, 130.23, 162.46, 165.03, 169.97 ppm.

**General Procedure for Phenol Deprotection with $BBr_3$.** 17.4 g (37.6 mmol) of 4,6-bis(4-methoxyphenyl)-*N,N*-diphenyl-1,3,5-triazin-2-amine was stirred in 300 mL of $CHCl_3$ in an ice bath. 12 mL of $BBr_3$ was added to the reaction in one go by syringe. The reaction was stirred overnight at room temperature. Roughly 50% of the solvent was removed by rotary evaporation. The contents of the reaction were then poured into 500 mL of ice water containing 30 g of $Na_2CO_3$. After 30 min of stirring, a tan powder was collected by vacuum filtration. The product was then stirred three times in water and collected by vacuum filtration. The filter cake was washed with water and petroleum ether, followed by drying at 100 °C under vacuum overnight to give 13.9 g (85.3%) of 4,6-bis(4-hydroxyphenyl)-*N,N*-diphenyl-1,3,5-triazin-2-amine that was pure enough for polymerization. If the product is slightly impure, it can be recrystallized from THF/heptane to give needlelike crystals. $^1$H NMR (DMSO-$d_6$): 6.83 (d, 4H), 7.32 (m, 2H), 7.44 (m, 8H), 8.12 (d, 4H), 10.13 ppm (br s, 2H). $^{13}$C NMR (DMSO-$d_6$): 115.27, 126.15, 126.82, 127.86, 128.80, 130.17, 143.39, 161.32, 165.82, 169.86 ppm.

*2,4-Bis(4-hydroxyphenyl)-6-phenyl-1,3,5-triazine (Ph-OH).* This reaction was run in refluxing 1,2-dichloroethane to dissolve all starting material. No further purification was needed. Yield = 81%. $^1$H NMR (DMSO-$d_6$): 6.98 (d, 4H), 7.5−7.6 (m, 3H), 8.6−8.7 ppm (m, 6H). $^{13}$C NMR (DMSO-$d_6$): 115.61, 126.41, 127.72, 127.78, 131.13, 131.60, 137.82, 161.87, 170.12, 171.46 ppm.

*2,4-Bis(4-hydroxyphenyl)-6-(4-phenoxyphenyl)-1,3,5-triazine (PhOPh-OH).* A yellow powder was obtained by column chromatography of the crude product on silica with 3:1 hexane:ethyl acetate. Yield = 51%. $^1$H NMR (DMSO-$d_6$): 6.98 (d, 4H), 7.11 (t, 4H), 7.21 (t, 1H), 7.43 (t, 2H), 8.54 (d, 4H), 8.62 ppm (d, 2H). $^{13}$C NMR (DMSO-$d_6$): 116.10, 118.25, 120.00, 124.79, 126.95, 130.66, 131.09, 131.17, 156.02, 161.18, 162.40, 170.15, 170.78 ppm.

*N,N-Dihexyl-4,6-bis(4-hydroxyphenyl)-1,3,5-triazin-2-amine (DHA-OH).* A white powder was obtained by Soxhlet extraction of the crude product with heptane for 3 days. Yield = 24%. $^1$H NMR ($CDCl_3$): 0.90 (t, 6H), 1.37 (m, 12H), 1.70 (m, 4H), 3.71 (t, 4H), 5.07 (s, 2H), 6.92 (d, 4H), 8.48 ppm (d, 4H). $^{13}$C NMR ($CDCl_3$):

14.01, 22.62, 26.72, 27.72, 31.67, 47.33, 115.08, 130.31, 130.54, 158.55, 164.95, 169.82 ppm.

**Polymer Synthesis of DPA-PS.** 5.032 g (11.61 mmol) of **DPA-OH**, 2.952 g (11.61 mmol) of bis(4-fluorophenyl)sulfone, 3.42 g (24.7 mmol) of $K_2CO_3$, 36 mL of NMP (~18 wt %), and 18 mL of toluene were charged into a three-neck flask equipped with a nitrogen inlet, overhead stirrer, condenser, and Dean−Stark trap. The reaction was heated to an oil bath temperature of 150 °C for 4 h as water was removed as an azeotrope with toluene. Toluene was removed from the system with a strong nitrogen purge for 1 h, followed by stirring overnight at 155 °C. At this point, no viscosity increase was observed. The reaction was then heated to 200 °C for 3.5 h. During this time, the reaction had become so viscous it began to wrap around the stirrer shaft. The reaction was diluted with 100 mL of NMP, stirred at room temperature for 2 h, and precipitated into water in a blender. The off-white powder was collected by vacuum filtration, followed by stirring in boiling $H_2O$ (3×) and boiling methanol. The washed polymer was dried under vacuum overnight at 100 °C.

**Polymer Sulfonation.** Procedure 1: From separate addition funnels, 2 g of polymer in 100 mL of $CH_2Cl_2$ and 4.8 mL of $ClSO_3H$ in 50 mL of $CH_2Cl_2$ were added to a flask being cooled in an ice bath over 30 min. The reaction was stirred for 2 h at 0 °C and overnight at room temperature. The solution was decanted from the yellow precipitate, followed by washing with more $CH_2Cl_2$. The solid was then stirred with water in a blender and collected by vacuum filtration. The last step was repeated until the filtrate was neutral to pH paper. Procedure 2: Identical to procedure 1, except 2.4 mL of $ClSO_3H$ was used and the reaction was terminated after 2 h at 0 °C.

*Film casting*: Nonsulfonated polymer solutions (10−20 wt % in NMP) were centrifuged and doctored onto glass plates. These solutions were dried at 100 °C overnight under forced air and for 2 h at 200 °C to give transparent, creasible films. Films could also be dried at room temperature but were opaque. Sulfonated polymer solutions (10−20 wt % in DMAc) were centrifuged and doctored onto glass plates. These solutions were air-dried at room temperature until tack-free, followed by heating to 120 °C overnight to give transparent, creasible films.

*Water uptake*: Sulfonated polymer films were dried overnight at 100 °C under vacuum and immediately weighed. Films were then soaked in water overnight, blotted with a paper towel, and weighed again.

*Ion exchange capacity measurements*: 50 mg of polymer powder was soaked overnight in 0.1 M NaCl solution and titrated with 0.01 M NaOH with a phenolphthalein indicator. The titration was considered finished when the solution remained pink for >1 min. An average of three titrations were taken for each polymer.

*Conductivity measurements*: A four-probe method of measuring conductivity was used.[31] In preparation for measurements, membranes are boiled in water for 3−5 h and then cooled to room temperature while remaining in liquid water. Samples of 3−4 mm wide by 4−5 cm long were cut, and wet thickness was measured (fully hydrated used in conductivity calculations). A sample was then held in place on a flat Teflon support. Four electrodes were attached to the sample/Teflon support, with the outer two for current application and the inner two for potential drop measurement. This cell was placed inside a stainless steel vessel which can be sealed airtight, and the vessel was placed inside an oven (a thermocouple was placed inside the vessel near the sample for temperature measurement). For 100% humidity, excess water was placed inside the vessel, and a valve was opened so as to maintain atmospheric pressure upon raising the temperature. For the low RH measurements, the membranes were equilibrated with the vapor above a LiCl solution of appropriate concentration at room temperature.

Sample resistance measurements were done by measuring the potential drop between the two inner elecrodes while applying a small current sine wave across the two outer electrode contacts from 20 000 to 2 Hz. The measured impedance was that of a resistor with a varying but small phase angle between −10° and +10°. The conductivity was calculated by the expression

$$\sigma = \frac{1}{R}\left(\frac{1}{wh}\right)$$

where $R$ is the measured impedance at nearly zero phase angle, $l$ is the distance between the two inner electrodes, $w$ is the sample width, and $h$ is the measured thickness of the fully hydrated sample. The error in the conductivity measurement is estimated to be on the order of 0.01 S/cm.

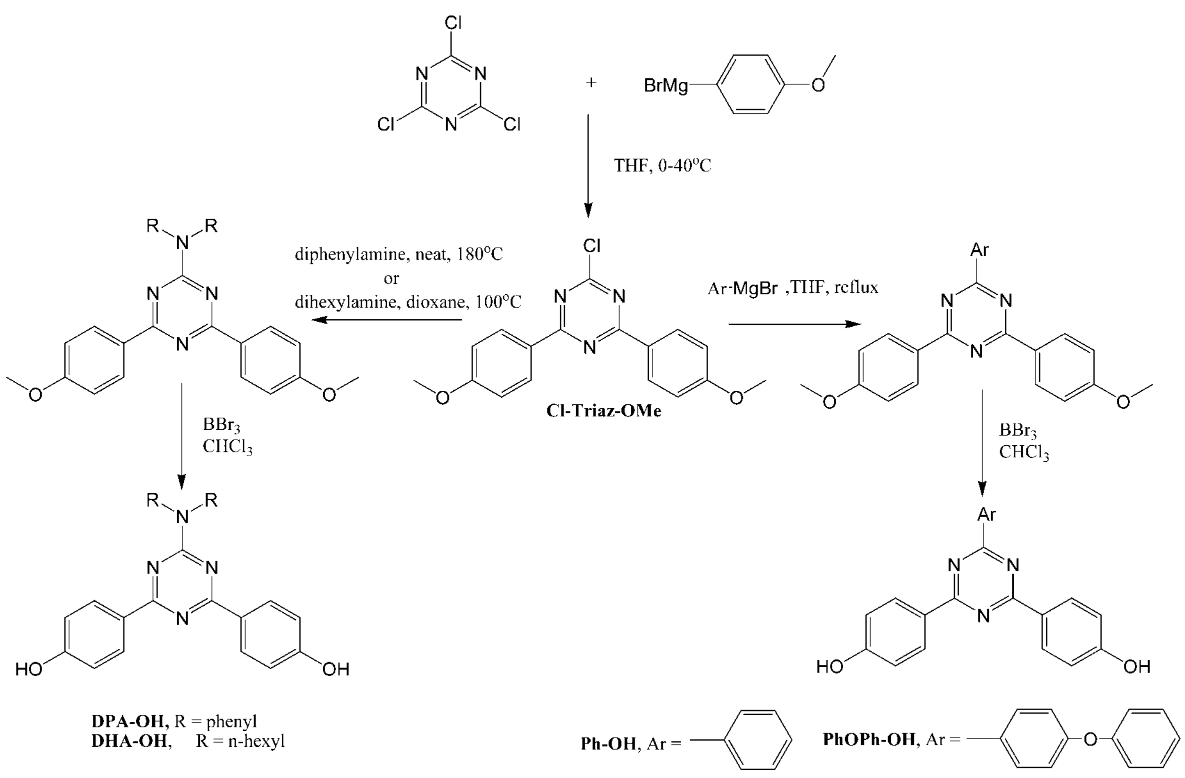
## Results and Discussion

**Monomer Synthesis.** Scheme 1 shows the synthesis of several poly(ether triazine) monomers. 2-Chloro-4,6-bis(4-methoxyphenyl)-1,3,5-triazine (**Cl-Triaz-OMe**) was synthesized by a modification of the procedure by Henneberger and Wagner[32] and used as the intermediate to all the final monomers. The remaining chlorine group was then replaced by a secondary amine or phenyl Grignard reagent by nucleophilic aromatic substitution. Of the fully substituted triazine rings, the reaction with secondary amines proved to be the most convenient. In the case of diphenylamine, the only purification needed was to remove excess diphenylamine with boiling water and heptane. The reaction of **Cl-Triaz-OMe** with diphenylamine also resulted in partial conversion of the methoxyphenyl group to phenol. A similar reaction has been observed in other triazine systems that contain methoxy groups in the presence of *N*-methylaniline at elevated temperatures.[23] Reaction or **Cl-Triaz-OMe** with dihexylamine gave a crystalline solid upon removal of solvent. Reaction of **Cl-Triaz-OMe** with Grignard reagents proved to be more difficult because the reactions would not go to completion even after several days at refluxing temperatures in the presence of excess Grignard reagent. Conversion of the methoxyphenyl groups to phenols was accomplished by reaction with $BBr_3$ at room temperature. The monomer with a diphenylamine branching group (**DPA-OH**) was usually obtained in high purity by precipitation in water, followed by thorough washing to remove inorganic materials. The monomer with a dihexylamine branch (**DHA-OH**) was obtained in high purity by Soxhlet extraction with heptane. Monomers with aromatic branching groups exhibited a side reaction that appears be the formation of a phenylboronic acid derivative and had to be purified by column chromatography.

**Polymer Synthesis.** The synthesis of poly(ether sulfone)s containing triazine rings is shown in Scheme 2. NMP was chosen as the reaction solvent because it provided adequate reaction temperatures to obtain high molecular weight polymers. Reactions were stirred overnight at 155 °C to afford solutions with varying degrees of viscosity. Further heating to 200 °C for 1−8 h was usually needed to obtain very high molecular weights. **Ph-PS**, with a branching phenyl group proved to be too rigid, normally forming a gel in the early stages of the reaction. Polymers with more bulky branching groups improved solubility, allowing formation of high MW polymers. Polymers made from a **DPA-OH** had very high MW (IV > 1.0 dL/g, Table 1) and good solubility (>20 wt %) in $CHCl_3$, NMP, and DMAc. The solubilities of these polymers were higher than poly(ether triazine)s reported by Fink and co-workers, who report solubilities on the order of 0.5 wt %.[33] This is most likely due to lower interchain interactions due to the bulky diphenylamine group. Polymers made from **PhOPh-OH** produced medium MW polymers, but with formation of some gelled material as well.

A polymer was made in which a dihexylamine group is attached to the triazine ring (**DHA-PS**). Anano and co-workers report direct attachment of aliphatic groups to the imide nitrogen of polyimides greatly improves hydrolytic stability.[34,35] The attachment of a dihexylamine group may show similar donating effects to the electron-deficient triazine ring. A proton NMR of

**Scheme 1. Monomer Synthesis**



**Scheme 2. Polymer Synthesis**

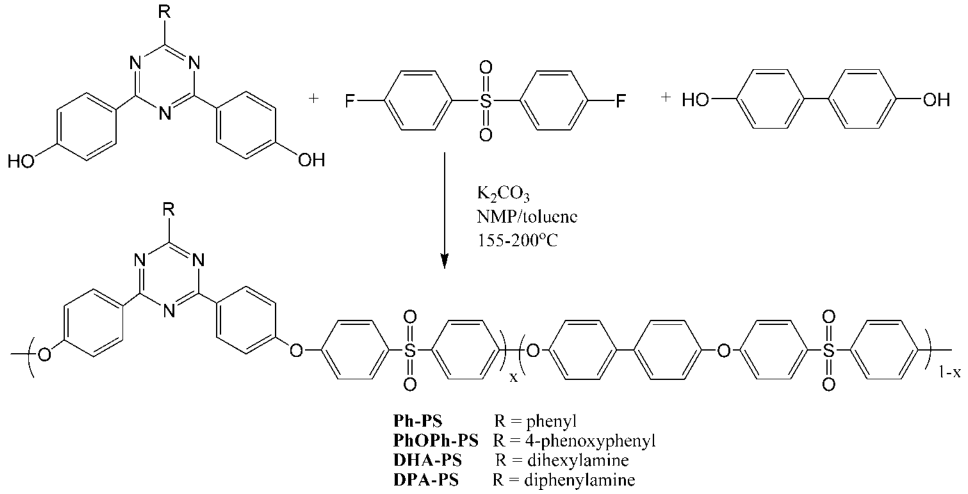


**Table 1. Polymer Characterization**

| polymer | diphenol | IV (dL/g) 25 °C, DMAc 0.5 g/dL | $T_g$ (DMA) (°C) | 5 wt % loss in $N_2$ (10%) | 5 wt % loss in air (10%) | char yield in air[c] | solubilities (20 wt %) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | DMAc | $CF_3CO_2H$ |
| BP-PS | BP[a] | 0.97 | 244 | 486 (514) | 486 (514) | 0 | yes | no |
| Ph-PS | Ph-OH | *b* | NA | 460 (553) | 433 (505) | 8 | no | yes |
| DPA(100)-PS | DPA-OH | 1.01 | 289 | 500 (528) | 537 (556) | 21 | yes | yes |
| DPA(75)-PS | 3:1 DPA-OH:BP | 0.49 | 242 | 535 (564) | 538 (566) | 28 | yes | yes |
| DPA(50)-PS | 1:1 DPA-OH:BP | 1.10 | 281 | 480 (507) | 505 (536) | 13 | yes | yes |
| DPA(25)-PS | 1:3 DPA-OH:BP | 1.03 | 263 | 494 (520) | 500 (524) | 0 | yes | no |
| PhOPh-PS | PhOPh-OH | 0.43 | 269 | 460 (516) | 447 (510) | 0 | yes | yes |
| DHA-PS | DHA-OH | 0.55 | 136 | 466 (485) | 332 (374) | 13 | yes | yes |

[a] BP = 4,4′-biphenol. [b] Solubility is too low to dissolve required amount of polymer in DMAc. [c] Char yield measured at 750 °C.

this polymer shows high purity (Figure 1). The formation of a high MW polymer is also apparent from the lack of phenol or 4-fluorophenyl end groups that should be seen around 6.8 and 7.5 ppm, respectively.

Copolymers were also synthesized by polymerizing 4,4′-biphenol (**BP**) along with **DPA-OH**. **BP** is expected to be much more reactive than **DPA-OH** due to the electron-withdrawing nature of the triazine rings. Copolymers made from various

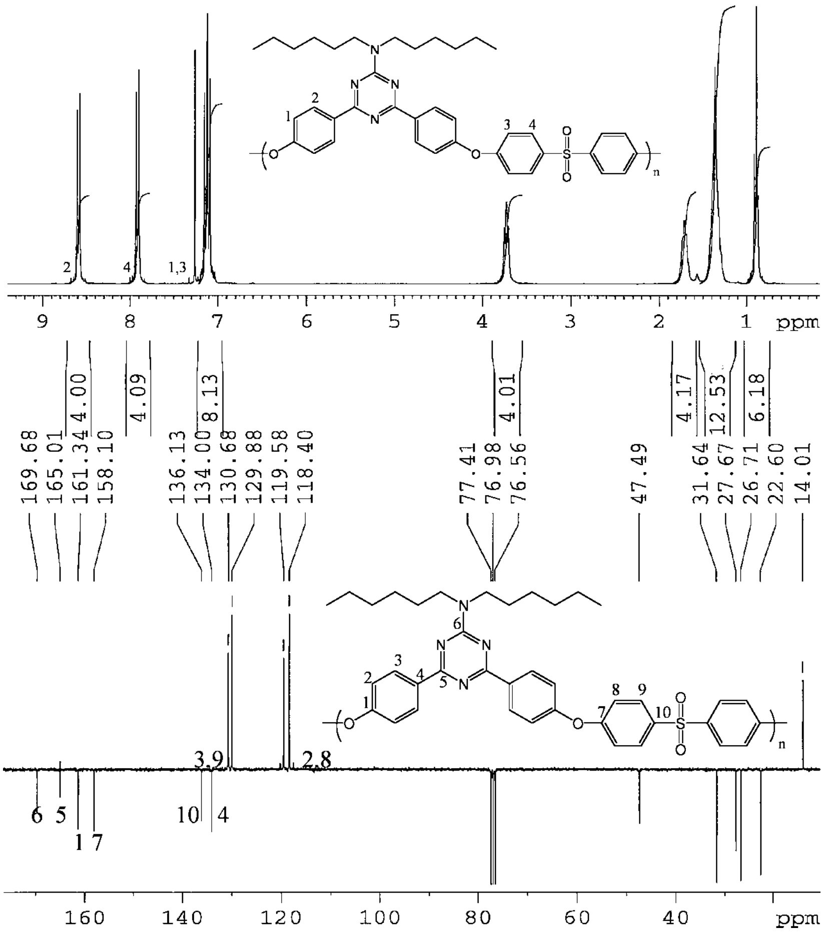


**Figure 1.** $^1$H and $^{13}$C APT NMR of **DHA-PS** in CDCl$_3$.

compositions of the two diols are referred to as **DPA(*x*)-PS**, with *x* referring to the mole fraction of **DPA-OH** used. For the sake of clarity, **DPA-PS** will be referred to as **DPA(100)-PS**. A poly(ether sulfone) containing only **BP** was also made for comparison. The amount of triazine ring within the polymer played a significant role in the solubility in CF$_3$CO$_2$H (TFA). From Table 1, **BP-PS** is insoluble in TFA. All triazine-containing homopolymers are highly soluble in TFA and change color from white to yellow on contact. Copolymers ranged from swollen (**DPA(25)-PS**) to soluble (**DPA(50)-PS**), depending upon the ratio of triazine to biphenol in the polymer chain used. High molecular weight polymers were obtained for **DPA(50)-PS** and **DPA(25)-PS**, but not **DPA(75)-PS**. In the synthesis of all copolymers, a white precipitate formed at the beginning of polymerization. This material, which is believed to be a low MW phenolate salt,[20] redissolved at in all cases except with **DPA(75)-PS**. Films could be cast from NMP or TFA that were yellow, strong, and creasible. Films cast from NMP and dried at 100 °C were transparent, while films dried at room temperature were opaque due to precipitation of a white powder before the solvent completely evaporates.

**Thermal and Mechanical Properties.** Polymer glass transition temperatures were obtained on thin films by dynamic mechanical analysis (DMA) and are shown in Table 1. **PhOPh-PS** exhibited a $T_g$ 25 °C higher than **BP-PS**, while **DPA(100)-PS** exhibited a $T_g$ 45 °C higher than **BP-PS**. When a more flexible dihexylamine group is added, the $T_g$ decreases by over 100 °C.

Thermogravimetric analysis (TGA) showed that polymers exhibited 5% weight loss ~500 °C, as seen in Figure 2. All polymers exhibited similar decomposition temperatures in air and nitrogen (Figure 3), with the exception of **DHA-PS**. This polymer begins to decompose around 500 °C in nitrogen, but around 300 °C in air. Schaefer and co-workers have suggested potential alkyl group migration within amino-*s*-triazine derivatives from the amine group to a neighboring aromatic nitrogen atom.[36] A similar rearrangement may happen in **DHA-PS**, followed by air oxidation to a less stable cyclic urea derivative. Polymers that were made from **DPA-OH** had an unusually high char yield in air, which could lead to investigation of the polymer as a flame-retardant material.[37]

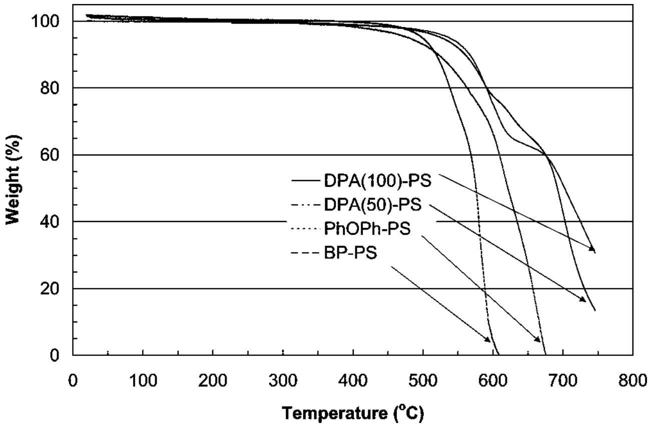


**Figure 2.** TGA in air of triazine-containing poly(ether sulfone)s.

Mechanical properties of some polymers are compared to **BP-PS** in Table 2. Both tensile strength and modulus are much lower than reported for the commercially available material. This may be due to differences in processing and instrumentation. Some general trends can still be extrapolated from the data. All

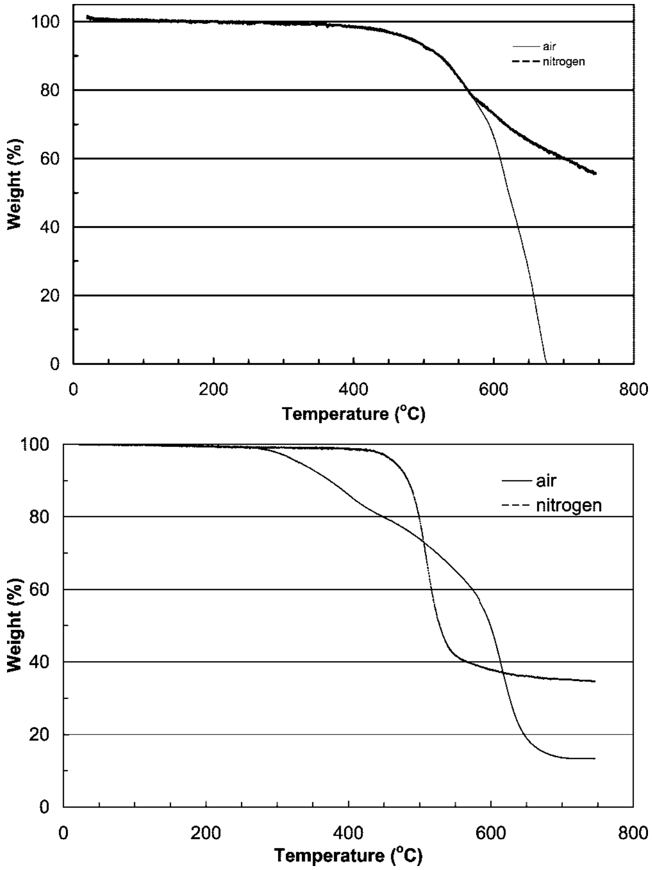


**Figure 3.** TGA of **PhOPh-PS** (top) and **DHA-PS** (bottom) in air and nitrogen.

**Table 2. Room Temperature Tensile Properties of Various Films**

| polymer | tensile strength (MPa) | tensile modulus (GPa) | % elongation at yield | % elongation at break |
|---|---|---|---|---|
| BP-PS | 44.2 | 1.0 | 7.9 | 38.9 |
| BP-PS[a] | 70 | 2.3 | 7.2 | 60−120 |
| DPA-PS | 64.5 | 1.0 | 11.1 | 11.1 |
| DPA(50)-PS | 59.2 | 0.80 | 11.1 | 14.4 |
| DHA-PS | 39.9 | 0.69 | 10.4 | 13.0 |

[a] Reported for commercial polymer (Radel R-5000) according to ASTM D638.

polymers that contained triazine groups broke at or near their yield points, compared to **BP-PS**, which stretched significantly after the yield point before breaking. The polymer containing a dihexylamine branch had both the lowest strength and modulus. **DPA(100)-PS** had a higher tensile strength than **BP-PS** but a similar modulus.

**Polymer Sulfonation.** Polymers were sulfonated by chlorosulfonic acid in dichloromethane.[28] Two different sulfonation methods were used. The reaction was either stirred for 2 h in an ice bath or overnight at room temperature with double the amount of chlorosulfonic acid. Although the polymer precipitated on contact, stirring overnight at room temperature increased the level of sulfonation, with the exception of with **DPA(25)-PS**. Table 3 shows data on these sulfonated polymers. Inherent viscosities increased to varying degrees for all sulfonated polymers. This is believed to be due to increased intermolecular interactions between polymer chains in the sulfonated polymers compared to the unsulfonated polymers.[38] The biphenol group is more reactive toward chlorosulfonic acid than the branching diphenylamine group, evidenced by the ion exchange capacity values. Under the same reaction conditions, **DPA(100)-PS** has an IEC of only 0.34 mmol/g, while **BP-PS** has an IEC of 3.66 mmol/g. Sulfonated polymers were no longer soluble in chloroform or dichloromethane but remained soluble in NMP and DMAc, with the exception of **DPA(25)-PS** when sulfonated by procedure 1 or **BP-PS** when sulfonated by either procedure. Transparent freestanding films of the sulfonated polymers were obtained when cast from DMAc and air-dried at room temperature.

When the diphenylamine branch is sulfonated, it appears to be sulfonated exclusively at the para position. Figure 4 shows the $^1$H NMR spectra of **DPA(100)-PS** and **BP-PS** before sulfonation and all sulfonated copolymers. The ortho and meta protons of the branching DPA group correspond to an eight proton peak at 7.5 ppm, while the para protons are observed at 7.2 ppm. NMR of the sulfonated homopolymer shows a decrease in these two peaks, along with the appearance of a new doublet peak at 7.9 ppm. The new peak corresponds to the protons adjacent to sulfonation at the para position. Moreover, integration of the sulfonated polymer NMR shows sulfonation occurs exclusively on the branching group. Under sulfonation procedure 1, 74% of the branching aromatic groups are sulfonated in the homopolymer, corresponding to an ion exchange capacity of 1.05 mmol/g. This value is less than the value obtained by titration (1.64 mmol/g). Sulfonated polymers are the same yellow color as unsulfonated polymer when they initially come in contact with $CF_3CO_2H$, so it is possible that some $H_2SO_4$ (formed by hydrolysis of $ClSO_3H$) remains coordinated with the triazine nitrogens, even after several wash cycles. The doublet at 7.9 ppm decreases in the spectra of **DPA(75)-PS** and **DPA(50)-PS** but is not seen at all for **DPA(25)-PS**. Conversely, the spectra of all copolymers show a new peak at 8.35 ppm, which increases with higher mole fractions of **BP-OH**. This new peak most likely corresponds to the protons adjacent to sulfonation at position A on the biphenol group. Sulfonation at the less reactive position C has also been reported to show a signal at 8.3 ppm.[39] However, if sulfonation took place at this position, this peak should also be seen in the spectrum of **DPA(100)-PS**, which is not the case.

As shown in Table 3, water uptake decreases when the triazine:BP ratio increases, with the exception of **DPA(75)-PS**. This trend was expected since water uptake is expected to increase with increasing ion exchange capacities. In addition, adding more rigid functional groups, such as **DPA-OH**, is expected to decrease water uptake.[40] **DPA(100)-PS**, **DPA(50)-PS**, and **DPA(25)-PS** also exhibited water uptakes of 91%, 123%, and 174%, respectively, when boiled in water for 1 h. Swelling of these membranes in boiling water also result in an increase in thickness of **DPA(100)-PS**, **DPA(50)-PS**, **DPA(25)-PS**, and Nafion 117 of 28%, 56%, 63%, and 40%, respectively. All soluble sulfonated polymers could by cast into strong, creasible films, with the exception of **DPA(100)-PS**. The film of this polymer becomes brittle due to the increased rigidity from sulfonation. This film remains flexible if plasticized by residual DMAc or $H_2O$ or imbibed by $H_3PO_4$.

**Phosphoric Acid Uptake.** Imbibing of sulfonated and unsulfonated polymers with phosphoric acid was attempted by three different methods. The conventional method for PBI was used, which involves swelling in boiling water, followed by soaking in 11 M $H_3PO_4$ (method A).[4] Films were also soaked in 85% $H_3PO_4$ at 90 °C (method B). A final method was used for unsulfonated polymer films, in which films were soaked in a 6:2:1 mixture of THF, MeOH, and $H_3PO_4$. However, films became so swollen in this solution that it became difficult to remove them in one piece. The nature of the polymer determined whether method A or B was better for imbibing $H_3PO_4$. Method A proved slightly more effective with all sulfonated copolymers. However, results were dramatically different for **DPA(100)-PS**. Using method A, the sulfonated polymer showed no uptake of $H_3PO_4$ after several days

**Table 3. Properties of Sulfonated Polymers**

| | | | | | $H_3PO_4$ uptake[c] | | |
|---|---|---|---|---|---|---|---|
| polymer | sulfonation procedure | IV (dL/g) 25 °C, DMAc 0.5 g/dL | $H_2O$ uptake (wt %) | IEC (mequiv/g) | A | B | C |
| BP-PS | 2 | *a* | *b* | 3.66 | *b* | *b* | |
| DPA-PS | none | 1.01 | | | | 3.0 | 39 |
| | 1 | 2.09 | 128 | 1.64 | 0 | 194 | |
| | 2 | 1.14 | | 0.34 | 0 | 265 | |
| DPA(75)-PS | none | 0.49 | | | | 0 | |
| | 1 | 1.72 | 32 | 1.71 | 70 | 56 | |
| | 2 | 1.16 | | 0.96 | 68 | 2 | |
| DPA(50)-PS | none | 1.10 | | | | 1.8 | 41 |
| | 1 | 3.58 | 213 | 2.11 | 68 | 27 | |
| | 2 | 3.71 | | 1.82 | 41 | 46 | |
| DPA(25)-PS | none | 1.04 | | | | 5.1 | 21 |
| | 1 | *a* | *b* | 2.44 | *b* | *b* | |
| | 2 | 3.62 | 226 | 2.62 | 70 | 58 | |
| DHA-PS | none | 0.55 | | | | 157 | 31 |

[a] Solubility is too low to dissolve required amount of polymer in DMAc. [b] Solubility is too low in to cast film. [c] Methods of $H_3PO_4$ uptake: A: soak in 11 M $H_3PO_4$ at room temperature; B: soak in 85% $H_3PO_4$ at 90 °C; C: soak in 6:2:1 THF:MeOH:$H_3PO_4$ at room temperature.

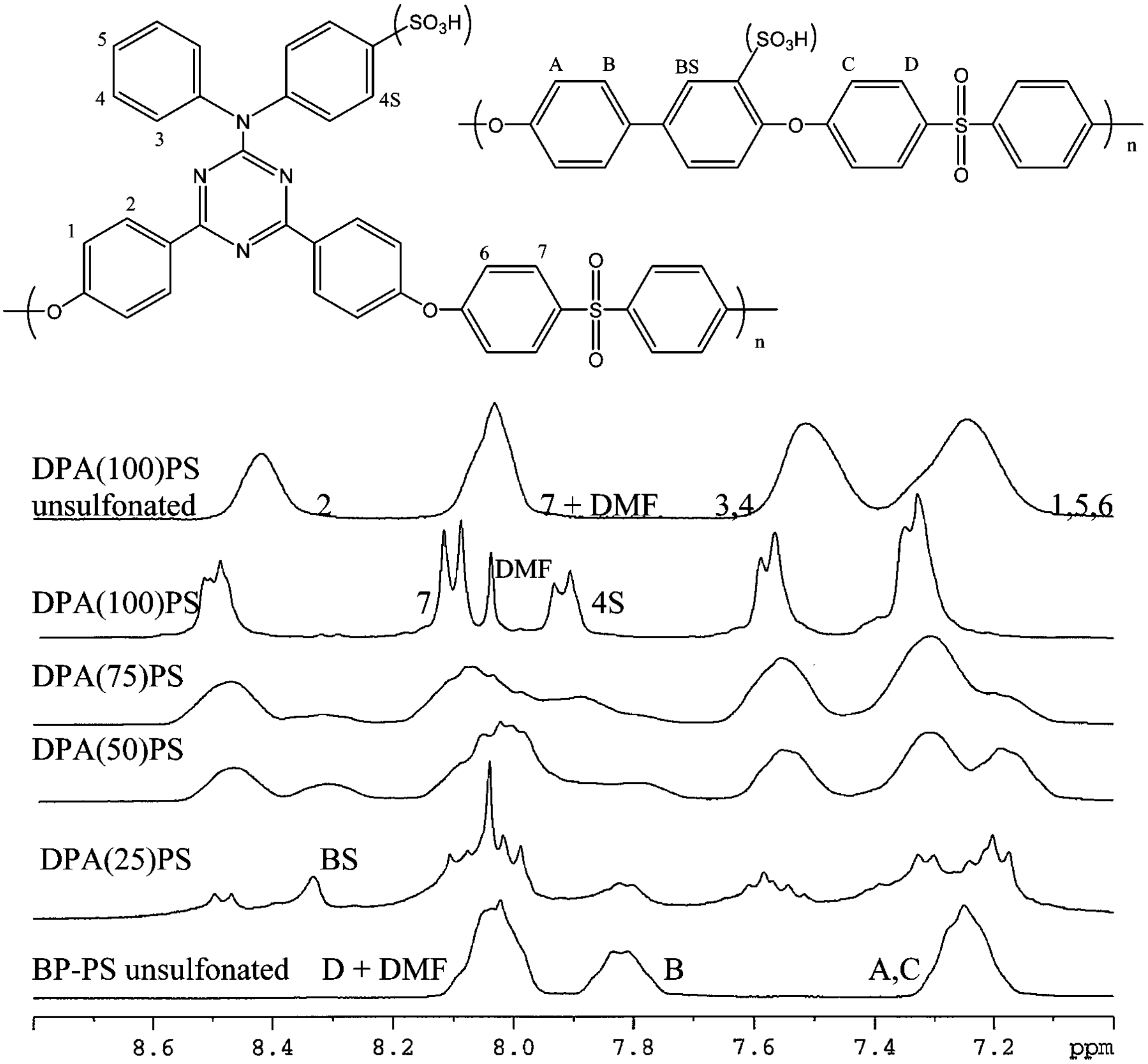


**Figure 4.** $^1H$ NMR spectra of sulfonated polymers in deuterated DMF.

of soaking in 11 M $H_3PO_4$. If this polymer is instead soaked in 85% $H_3PO_4$ at 90 °C, uptake increases to >200 wt %. Under the same conditions, the unsulfonated polymer only has an $H_3PO_4$ uptake of 3%. Even a small degree of sulfonation dramatically increases the polymer's affinity for $H_3PO_4$. We have also observed high uptake in unsulfonated homopolymer films that contain fumed silica or when the sulfone group is replaced by a phosphine oxide group. Kallitsis and co-workers have also reported much higher phosphoric acid uptake in pyridine-containing poly(arylene ether)s that contain phosphine oxide groups compared to sulfone groups.[10–12]

**Conductivity.** Proton conductivities of **DPA(100)-PS**, **DPA(50)-PS**, and **DPA(25)-PS** are shown in Figure 5. Surprisingly, conductivities increased in the order of decreasing water uptake and ion exchange capacity (Figure 6). This trend is opposite to

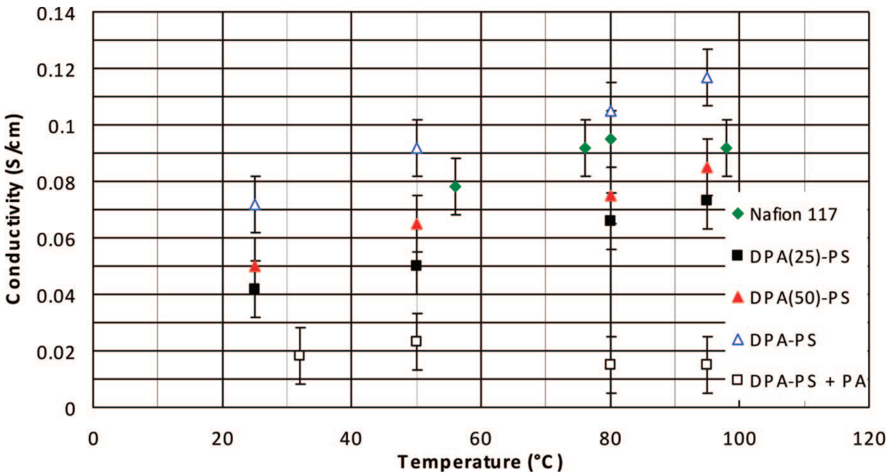


**Figure 5.** Proton conductivity of sulfonated **DPA(100)-PS** (IEC = 1.64 mmol/g, water uptake = 128%), **DPA(50)-PS** (2.11, 213%), **DPA(25)-PS** (2.44, 244%), and Nafion 117 at 100% relative humidity as a function of temperature. Also shown: sulfonated DPA-PS imbibed with 194 wt % $H_3PO_4$.

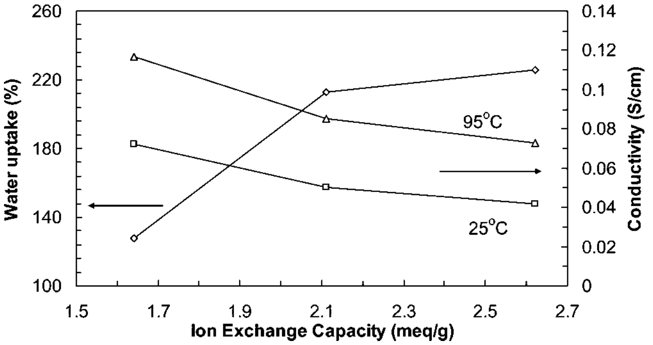


**Figure 6.** Water uptake and proton conductivity at 25 and 95 °C as a function of ion exchange capacity of **DPA(100)-PS** (IEC = 1.64 mmol/g, water uptake = 128%), **DPA(50)-PS** (2.11, 213%), and **DPA(25)-PS** (2.44, 244%).

what has been reported in other sulfonated poly(arylene ether)s.[28,29,38,41] IEC values may be misleading in this case due to the higher molecular weight of the **DPA-OH** (repeat unit weight = 649 g/mol) repeat unit compared to biphenol (repeat unit weight = 401 g/mol). When IEC values are converted to acidic groups per repeat unit, similar values of 1.06, 1.11, and 1.13 are obtained for **DPA(100)-PS**, **DPA(50)-PS**, and **DPA(25)-PS**, respectively. If the degree of sulfonation is considered equal, then conductivity may be dictated by the acidity of the sulfonic acid groups. Sulfonation predominately occurs ortho to the biphenol ether group and at the para position of the DPA group. The latter group is expected to be more acidic due to the electron-withdrawing nature of the triazine ring. The most conductive sample (**DPA(100)-PS**) had a maximum conductivity of 0.11 S/cm at 95 °C and 100% relative humidity. This film is more conductive than Nafion 117 over the temperature range 25−95 °C. In addition, the conductivity of all three sulfonated poly(arylene ether) films continued to increase at elevated temperatures, while the conductivity of Nafion 117 decreased above 80 °C. The conductivities of Nafion and **DPA(100)-PS** were 0.021 and 0.019 S/cm, respectively, at 25 °C and 15% RH. The conductivities of these samples were based on wet thickness. Samples under these low humidity conditions are more like a dry sample, so the true conductivities will be greater. The least conductive film was sulfonated **DPA(100)-PS** imbibed with 194% $H_3PO_4$. Unlike the other samples, this film was not hydrated prior to conductivity measurements. The initial conductivity of this film is similar to that reported by Gourdoupi and co-workers for pyridine-containing poly(arylene ethers) imbibed with 240 wt % $H_3PO_4$.[10] Conductivity decreases at increasing temperatures, possibly due to leaching of $H_3PO_4$ out of the film.

## Conclusions

A series of novel fully aromatic poly(ether sulfone triazine)s have been successfully synthesized at moderate to high molecular weights. The polymers are very rigid ($T_g$ up to 290 °C) but maintain solubility in common organic solvents. The polymers with pendant diphenylamine groups were found to have the best combination of properties, based on ease of monomer and polymer synthesis, thermal and mechanical properties, and unusually high char yields in air. Polymers made from the **DPA-OH** repeat unit were investigated further in copolymers containing the 4,4′-biphenol group. Initial attempts were made to convert polymer films to proton conductive membranes by imbibing the films with phosphoric acid, which was expected to protonate/hydrogen bond with the triazine nitrogens. However, phosphoric acid uptake was low, unless the polymer was sulfonated. Sulfonated **DPA-PS** had a $H_3PO_4$ uptake of up to 265 wt % when soaked in 85% $H_3PO_4$ at 90 °C. Polymers that were sulfonated with chlorosulfonic acid had ion exchange capacities up to 2.62 mmol/g. Proton conductivities of sulfonated **DPA-PS**, **DPA(50)-PS**, and **DPA(25)-PS** increased in order of decreasing water uptake and ion exchange capacity. This is believed to be due to the increased acidity of placing the sulfonic acid group on the diphenylamine group that is attached to the triazine ring. Sulfonated **DPA-PS** exhibited higher proton conductivity than Nafion 117 over the temperature range of 25−95 °C at 100% relative humidity.

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## References and Notes

(1) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896.
(2) Wainright, J. S.; Wang, J. T.; Weng, D.; Savinell, R. F.; Litt, M. *J. Electrochem. Soc.* **1995**, *142*, L121.
(3) Wang, J. T.; Savinell, R. F.; Wainright, J.; Litt, M.; Yu, H. *Electrochim. Acta* **1996**, *41*, 193.
(4) Wainright, J. S.; Litt, M.; Savinell, R. F. In *Handbook of Fuel Cells—Fundamentals, Technology, and Applications*; Vjelstich, W., Gasteiger, H. A., Lamm, A., Eds.; John Wiley and Sons: New York, 2003; Vol. 3.

(5) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511.
(6) Foster, R. T.; Marvel, C. S. *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 417.
(7) Xiao, L.; Zhang, H.; Jana, T.; Scanlon, E.; Chen, R.; Choe, E.-W.; Ramanathan, L. S.; Yu, S.; Benicewicz, B. C. *Fuel Cells* **2005**, *5*, 287.
(8) Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, L. S.; Choe, E.-W.; Rogers, D.; Apple, T.; Benicewicz, B. C. *Chem. Mater.* **2005**, *17*, 5328.
(9) Yu, S.; Xiao, L.; Benicewicz, B. C. *Fuel Cells* **2008**, *8*, 165.
(10) Gourdoupi, N.; Andreopoulou, A. K.; Deimede, V.; Kallitsis, J. K. *Chem. Mater.* **2003**, *15*, 5044.
(11) Daletou, M. K.; Gourdoupi, N.; Kallitsis, J. K. *J. Membr. Sci.* **2005**, *252*, 115.
(12) Pefkianakis, E. K.; Deimede, V.; Daletou, M. K.; Gourdoupi, N.; Kallitsis, J. K. *Macromol. Rapid Commun.* **2005**, *26*, 1724.
(13) Hergenrother, P. M. *High Perform. Polym.* **2003**, *15*, 3.
(14) Hergenrother, P. M.; Smith, J.; Connell, J. W. *Polymer* **1993**, *34*, 856.
(15) Harris, F. W.; Ahn, B. H.; Cheng, S. Z. D. *Polymer* **1993**, *34*, 3083.
(16) Twieg, R.; Matray, T.; Hedrick, J. L. *Macromolecules* **1996**, *29*, 7335.
(17) Smith, J.; Connell, J. W.; Hergenrother, P. M. *Polymer* **1992**, *33*, 1742.
(18) Connell, J. W.; Hergenrother, P. M. *Polymer* **1992**, *33*, 3739.
(19) Connell, J. W.; Hergenrother, P. M.; Wolf, P. *Polymer* **1992**, *33*, 3507.
(20) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A* **1967**, *5*, 2375.
(21) Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827.
(22) Thurston, J. T.; Dudley, J. R.; Kaiser, D. W.; Hechenbleinkner, I.; Schaefer, F. C.; Holm-Hansen, D. *J. Am. Chem. Soc.* **1951**, *73*, 2981.
(23) Thurston, J. T.; Schaefer, F. C.; Dudley, J. R.; Holm-Hansen, D. *J. Am. Chem. Soc.* **1951**, *73*, 2992.
(24) Chang, Y.; Kim, Y. N.; Noh, I.; Kim, C. *Macromol. Chem. Phys.* **2000**, *201*, 1808.
(25) Cho, S. Y.; Chang, Y.; Kim, J. S.; Lee, S. C.; Kim, C. *Macromol. Chem. Phys.* **2001**, *202*, 263.
(26) Steffensen, M. B.; Simanek, E. E. *Org. Lett.* **2003**, *5*, 2359.
(27) Miyatake, K.; Chikashige, Y.; Watanabe, M. *Macromolecules* **2003**, *36*, 9691.
(28) Chikashige, Y.; Chikyu, Y.; Miyatake, K.; Watanabe, M. *Macromolecules* **2005**, *38*, 7121.
(29) Miyatake, K.; Chikashige, Y.; Higuchi, E.; Watanabe, M. *J. Am. Chem. Soc.* **2007**, *129*, 3879.
(30) Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem. Commun.* **2003**, 368.
(31) Cahan, B. D.; Wainright, J. S. *J. Electrochem. Soc.* **1993**, *140*, L185.
(32) Henneberger, H.; Wagner, M. US Patent 5,438,138, **1995**.
(33) Fink, R.; Frenz, C.; Thelakkat, M.; Schmidt, H.-W. *Macromolecules* **1997**, *30*, 8177.
(34) Asano, N.; Miyatake, K.; Watanabe, M. *Chem. Mater.* **2004**, *16*, 2841.
(35) Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J. Am. Chem. Soc.* **2006**, *128*, 1762.
(36) Schaefer, F. C.; Dudley, J. R.; Thurston, J. T. *J. Am. Chem. Soc.* **1951**, *73*, 2996.
(37) Riley, D. J.; Gungor, A.; Srinivasan, S. A.; Sankarapandian, M.; Tchatchoua, C.; Muggli, M. W.; Ward, T. C.; McGrath, J. E. *Polym. Eng. Sci.* **1997**, *37*, 1501.
(38) Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mecham, J.; Zawodzinski, T. A.; McGrath, J. E. *Macromol. Symp.* **2001**, *175*, 387.
(39) Nolte, R.; Ledjeff, K.; Bauer, M.; Mülhaupt, R. *J. Membr. Sci.* **1993**, *83*, 211.
(40) Harrison, W. L.; Wang, F.; Mecham, J. B.; Bhanu, V. A.; Hill, M.; Kim, Y. S.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2264.
(41) Zaidi, S. M. J.; Mikhailenko, S. D.; Robertson, G. P.; Guiver, M. D.; Kaliaguine, S. *J. Membr. Sci.* **2000**, *173*, 17.

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