# Phosphorus-Containing Sulfonated Polyimides for Proton Exchange Membranes

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Synthesis and characterization of the novel sulfonated BAPPO monomer and its use in the synthesis of a new phosphine oxide-based sulfonated polyimide are described. BTDA, 6FDA, and DDS were used as monomers in the polyimide synthesis. Sulfonated polyimide membranes were obtained by a solution thermal imidization method. The thermal behavior of the polymers was investigated by DSC and TGA. The morphological structure of the membranes was investigated by tapping-mode AFM. The proton conductivities of the sulfonated polyimide increased regularly as a function of sulfonated diamine content. The conductivities are good compared to typical proton exchange membranes.
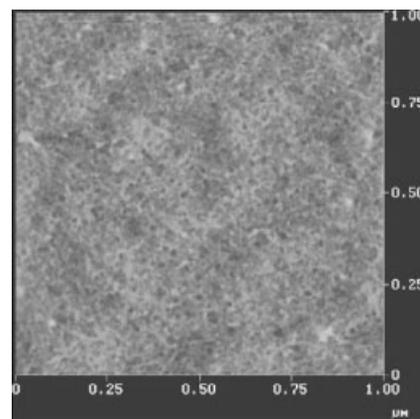
Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are considered to be the most promising alternative energy supplies for automotive and portable applications.[1–3] The proton exchange membrane (PEM) is a key component in the system, which functions as an electrolyte for transferring protons from the anode to the cathode as well as providing a barrier to the passage of electrons and gas cross-leaks between the electrodes. Perfluorosulfonated ionomer (Nafion) membranes have been used for this purpose because of their efficient proton conduction (10^{-1} S $\cdot$ cm^{-1} in the fully hydrated protonic form) and long service life.[4] However, Nafion displays several deficiencies, such as high methanol permeability, low operating temperature, and high cost, which have limited their applicability.[5] The drawbacks of the Nafion membranes have encouraged many efforts for the development of alternative PEMs.

Among many polymer materials, it is thought that sulfonated polyimide membranes are one of the potential

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candidates, because they have excellent thermal stability and mechanical durability, low methanol permeability as well as excellent film-forming ability. They are also reported to display a high proton conductivity, comparable to Nafion.[6]

The first sulfonated polyimides, which are called phthalic polyimides, were synthesized from 4,4′-diamino-biphenyl 2,2′-disulfonic acid, 4,4′-oxydianiline, and oxy-diphthalic dianhydride.[7,8] Unfortunately, the studies showed that these polymers were not very stable under fuel cell working conditions. As a second generation, sulfonated polyimides derived from bis(naphthalenic dianhydride) demonstrated improved performance as a proton exchange membrane. However, they also have some disadvantages such as poor solubility and low processability in commercially available solvents. Therefore, much effort has been spent on synthesizing processable, tractable polyimides without compromising desired properties.

It has been proven that the phenylphosphine oxide moiety provides a strong interacting site for imparting miscibility with several systems.[9–11] Phosphine oxide-containing polymers display excellent adhesion properties.[12] Recently, the synthesis of a phosphine oxide-bearing amine-end capped arylene ether oligomer has been reported as a precursor for polyimides.[13] High-molecular-weight sulfonated polyimide was prepared and thermal characterization demonstrated that the material is thermally stable up to 480 °C. It was also reported that polyimides prepared from novel diamine-containing fluorine and phosphine oxide exhibit excellent solubility and good thermal stability.[14] This paper describes the synthesis and characterization of a new sulfonated bis(*m*-amino phenyl) phenyl phosphine oxide monomer and its utilization in the preparation of homo- and co-polyimides. Their physical properties, water uptake, ion exchange capacity, and proton conductivity are also investigated.

Experimental Part

Materials

The dianhydride monomers, benzophenone tetracarboxylic dianhydride (BTDA) and 4,4′-hexafluoro isopropylidene bis (phthalic anhydride) (6FDA), were obtained from Aldrich. 3,3′-Diaminodiphenyl sulfone (DDS) was also obtained from Aldrich and purified by recrystallization from ethanol. Celite was purchased from Fluka. Triphenyl phosphine oxide (TPPO) was prepared by oxidation of triphenyl phosphine according to the literature.[15] Fuming sulfuric acid (27%), nitric acid (70%), sulfuric acid (98%), hydrogen peroxide (30%), palladium on activated carbon (10% Pd/C), xylene, and *N*-methyl-2-pyrrolidinone (NMP) were obtained from Merck. NMP was dried over P_2O_5 and freshly distilled under vacuum before used. Some common solvents, such as chloroform, ethanol, isopropyl alcohol, and methyl ethyl ketone (MEK) were used as obtained.

Characterization Methods

FT-IR spectra were recorded on a Shimadzu 8303 FT-IR spectrometer in order to confirm the distinct functional groups within the monomers and the polymers. ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry were also used to obtain further structural information for evaluation of the monomer synthesized. NMR spectra were recorded using a Varian Model T-60 NMR spectrometer operated at 200 MHz. GC-MS analyses were obtained using a Thermo Finnigan Trace GC Ultra and Thermo DSQ.

Thermogravimetric analyses (TGA) of polymers were performed using a TA Instruments Q50 model TGA. Samples were run from 30 to 800 °C at a heating rate 10 °C · min^{-1} under nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses of the polymer were performed using a Perkin Elmer DSC Pyris Diamond model. Samples were run under a nitrogen atmosphere from 50 to 220 °C with a heating rate of 10 °C · min^{-1}.

Atomic force microscopy (AFM) images were taken in tapping mode using a Veeko Metrology Group, Nanoscope IIIa Multimode instrument.

The ion-exchange capacity (IEC) was determined by a classical titration method. The swelling experiment in water was carried out by measuring the uptake of water at room temperature. Previously dried and weighed samples were kept in water for at least 24 h until equilibrium was attained. From the weight differences between the dry and wet films, water absorption values were calculated. Intrinsic viscosities of the polymers were measured in NMP (0.1–0.05 g · mL^{-1}) at 30 °C using an Ubbelohde viscometer.

A Parstad 2263 Potentiotate impedance analyzer was used to measure the resistance of each acidified membrane over a frequency range of 100 Hz to 1 MHz under fully hydrated conditions. The ionic conductivity was measured at 24 °C. The electrochemical cell used in this experiment is represented in Figure 1.

Monomers Synthesis

Synthesis of Bis(3-nitrophenyl)phenylphosphine Oxide (BNPPO)

Bis(3-nitrophenyl)phenylphosphine oxide (BNPPO) was synthesized according to the procedure described by McGrath et al.[16] To a three necked round bottom flask equipped with a reflux
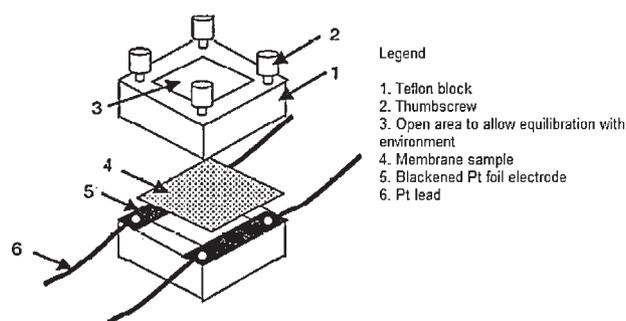

Legend
1. Teflon block
2. Thumbscrew
3. Open area to allow equilibration with environment
4. Membrane sample
5. Blackened Pt foil electrode
6. Pt lead

■ *Figure 1.* Proton conductivity cell with labeled components.

condenser, a nitrogen gas inlet, an overhead mechanical stirrer, and a dropping funnel were charged 150 g (0.539 mol) of triphenylphosphine oxide, and the flask was placed in an ice bath. Concentrated (98%) sulfuric acid (350 mL) was then carefully added to the contents of the flask. The mixture was stirred until all starting materials were dissolved. Separately, a mixture of nitric acid (70%, 97.03 g, 1.078 mol) and sulfuric acid (195 mL) was prepared. After cooling to 0–5 °C, the acid mixture was added dropwise to the triphenylphosphine oxide solution over five hours. The resulting mixture was then stirred for a further 8 h and then precipitated by slowly pouring the flask contents on crashed ice. The precipitated material was dissolved in dichloromethane and washed with dilute Na_2CO_3 solution until neutral (pH $\approx$ 7). After the dichloromethane was removed, the resulting product was crystallized from ethanol three times. A light-yellow product was obtained. Yield: 71%, mp: 133 °C.

FT-IR (KBr): 3 078 (aromatic C−H str.), 1 610–1 573 (aromatic C=C str.), 1 350–1 525 (asym. and sym. −N=O str.), 1 191 cm^{-1} (−P=O str.)

^{1}H NMR: $\delta = 8.50$–8.55 (4H), 8.05–8.10 (4H), 7.60–7.90 (non-substituted aromatic ring, 5H).

Synthesis of Sulfonated Bis(3-nitrophenyl)phenylphosphine Oxide S-(BNPPO)

In a three necked flask, equipped with a reflux condenser, a nitrogen gas inlet, and a thermometer, BNPPO (104 g, 0.282 mol) and fuming sulfuric acid (20%, 242 mL) were added and the reaction mixture was stirred on a magnetic stirrer for about 3 h at room temperature. The reaction mixture was then heated to 90 °C for 6 h. The dark yellow solution was cooled to room temperature and slowly poured into ice water. The precipitated product was dissolved in deionized water and saturated with NaCl. Subsequently, an off-white precipitate was obtained.[17] The crude product (S-BNPPO) was crystallized from isopropyl alcohol/water (2: 1) three times and a white powder was acquired (Yield 63%).

FT-IR (KBr): 1 189 (P=O str.), 1 525–1 350 (asym. and sym. N=O str.) 1 047–1 096 cm^{-1} (asym. and sym. S-O str.)

^{1}H NMR: $\delta = 8.48$–8.58 (4H), 8.12–8.20 (2H), 8.07 (2H), 7.8–7.9 (3H), 7.7–7.8 (1H).

Synthesis of Sulfonated Bis(3-aminophenyl)phenylphosphine oxide S-(BAPPO)

Sulfonated bis(3-aminophenyl)phenylphosphine oxide was obtained by hydrogenation of S-(BNPPO) in a high pressure reactor (Parr Instrument Co., USA). S-BNPPO (20 g, 0.0425 mol), methanol (500 mL), and Pd/C catalyst (0.5 g) were charged into the flame dried pressure reactor. First, the reactor was purged with nitrogen gas for several minutes and then pressured with hydrogen gas to 100 psi. The reaction mixture was heated at 50 °C and allowed to react for 48 h. Next, the reaction mixture was filtered over Celite in a Büchner funnel under vacuum. The methanol was removed by rotary evaporation and a product with bright light yellow crystals was obtained. This material was not purified any further.

FT-IR (KBr): 3 437 and 3 350 (N−H str.), 1 595 (N−H bend), 1 437 (aromatic C−P str.), 1 199 (P=O str.), 1 040–1 098 cm^{-1} (asym. and sym. S−O str.).

^{1}H NMR (CD$_3$OD): $\delta = 8.02$–8.13 (2H), 7.75–7.82 (2H), 7.58–7.64 (2H), 7.18–7.25 (2H), 6.83–6.95 (4H), 4.8–5.0 (amino group, 4H).

Polymer Synthesis

The sulfonated aromatic polyimides were synthesized by a thermal solution imidization method. The diamine monomer, dry NMP, and xylene as an azeotropic agent were charged into a three necked flask equipped with a nitrogen inlet, a Dean-Stark trap, and a condenser. The dianhydride monomers were incrementally added to the contents of the flask. The solid concentration was calculated as 20 wt.-%. The reaction mixture was stirred overnight at room temperature to obtain poly(amic acid)s. The poly(amic acid) solution was then heated at 140 °C for 24 h and at 160 °C for 3 h in order that the desired polyimides were performed. The polyimide solution was cooled to room temperature and became viscous. The viscous solution was precipitated into acetone. The polyimide was filtered off and dried under vacuum at 120 °C.

In this study, both BTDA and 6FDA-based sulfonated polyimides were synthesized. To study the effect of the content of sulfonate group-containing monomer, five additional copolyimides were prepared using (6FDA) or BTDA/DDS/S-(BAPPO) monomers where the sulfonated diamine content in the copolyimide compositions were increased to 20, 30, 40, 50, 75, and 100 mol-%, respectively.

Film Preparation

Sulfonated polyimide membranes were prepared by solution casting on to glass plate from NMP solution of the polymer. Initially, the films were slowly dried on a hot plate that was placed in a box made of Plexiglas under N_2 current. They were then dried under vacuum at 120 °C for 48 h. In order to remove the film from the glass plate, the polymer films were immersed in a beaker that contained hot water

Results and Discussion

Synthesis and Characterization of S-BAPPO

The synthesis route for the novel sulfonated diamine monomer, S-BAPPO, is illustrated in Scheme 1. It was
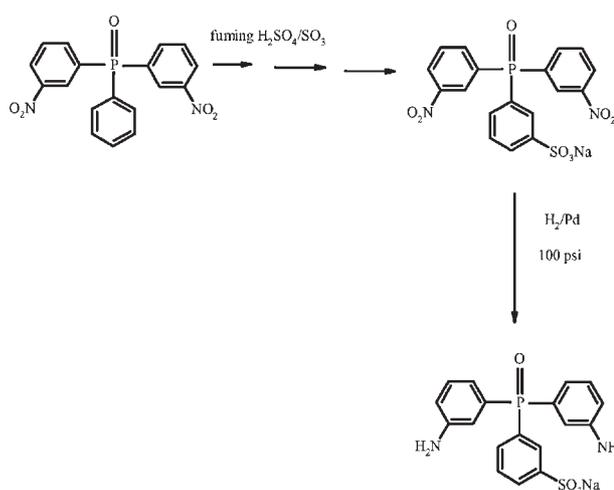
Scheme 1. The synthesis route to sulfonated bis(3-aminophenyl)-phenylphosphine oxide monomer, S-(BAPPO).

synthesized by direct sulfonation of the corresponding dinitro compound (BNPPO) using fuming sulfuric acid, followed by hydrogenation. BNPPO was prepared by nitration of triphenyl phosphine oxide similar to the literature method.[17] After purification the yield was 71% for BNPPO. In the sulfonation process, because of the strongly deactivating phosphine oxide group, sulfonation occurred solely on the unsubstituted phenyl ring. Both,

a)

b)

c)

Figure 2. The FT-IR spectrum of a) BNPPO b) S-BNPPO, and c) S-BAPPO.

FT-IR and ^{1}H NMR spectra (Figure 2 and 3) confirmed that the sulfonic acid groups were attached to the meta-position of the unsubstituted phenyl ring. Finally S-BAPPO was obtained by hydrogenation of S-BNPPO in a high-pressure reactor to result in a yield of 95%.

The chemical structures of BNPPO, S-BNPPO, and S-BAPPO were identified by FT-IR and ^{1}H NMR spectroscopy, while S-BAPPO was further characterized by ^{31}P NMR spectroscopy and mass spectrometry. In the IR spectrum of BNPPO, a peak that appears at $1\,191$ cm^{-1} indicates the existence of a P=O group. Other peaks at $1\,525$–$1\,350$ cm^{-1} for asymmetric and symmetric stretching, respectively, confirm the formation of a dinitro compound. On the other hand, for S-BNPPO the peaks identified in the spectrum at $1\,047$–$1\,096$ cm^{-1} are attributable to the asymmetric and symmetric stretching of sulfone groups. In addition, S-BAPPO shows typical N–H stretching absorptions at $3\,437$ and $3\,350$ cm^{-1}, and N–H bending at $1\,595$ cm^{-1} as a result of amine groups.

In the ^{1}H NMR spectrum (Figure 3a) of BNPPO, the proton peaks arising from the nitro phenyl moieties are observed down field because of the deshielding effect of the electron-withdrawing nitro groups: i.e., at 8.50–8.55 ppm (multiplet, 4H) as opposed to 8.05–8.10 ppm (multiplet, 4H). Upon sulfonation, the signal at 8.12–8.20 ppm represents the protons on the phenyl ring next to the sulfonated group (Figure 3b). Upon hydrogenation of S-BNPPO, nine groups of peaks were observed from S-BAPPO. As can be seen in Figure 3c, protons in the amino groups appear at 4.9 ppm as a sharp singlet. In addition the other proton peaks are shifted up-field compared to dinitro compound, owing to the shielding effect of electron-donating amino groups.[14] As shown in Figure 4, the ^{31}P NMR analysis provides a sharp single peak at 33 ppm for S-BAPPO. Moreover, the molecular weight of S-BAPPO found by mass spectrometry analysis is 387 g · mol^{-1}, which is in very good agreement with theoretical calculation (Figure 5).

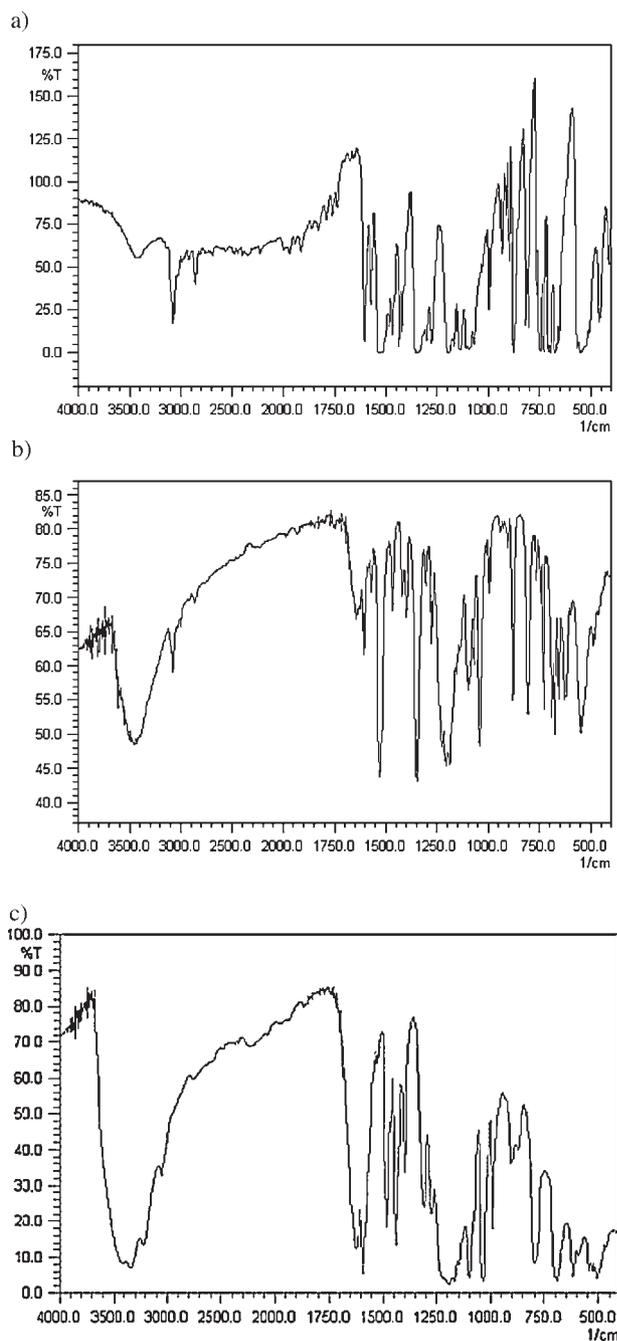### Synthesis and Characterization of Polyimides

The procedure used in the preparation of polyimides is shown in Scheme 2. In this study, BTDA and 6FDA were used as anhydride precursors in the synthesis. Thermal solution imidization of the amic acid was performed in a co-solvent system based on NMP and xylene at 140 °C for 24 h and 160 °C for 3 h. To study the effect of sulfonic acid content five different copolyimides were prepared from each dianhydride where the sulfonated diamine content was increased gradually from 20 to 100 mol-%. The composition of the sulfonated polyimides is shown in Table 1. Figure 6a and 6b show the FT-IR spectra for the BTDA and 6FDA-based sulfonated polyimides, respectively.

a)

b)

c)
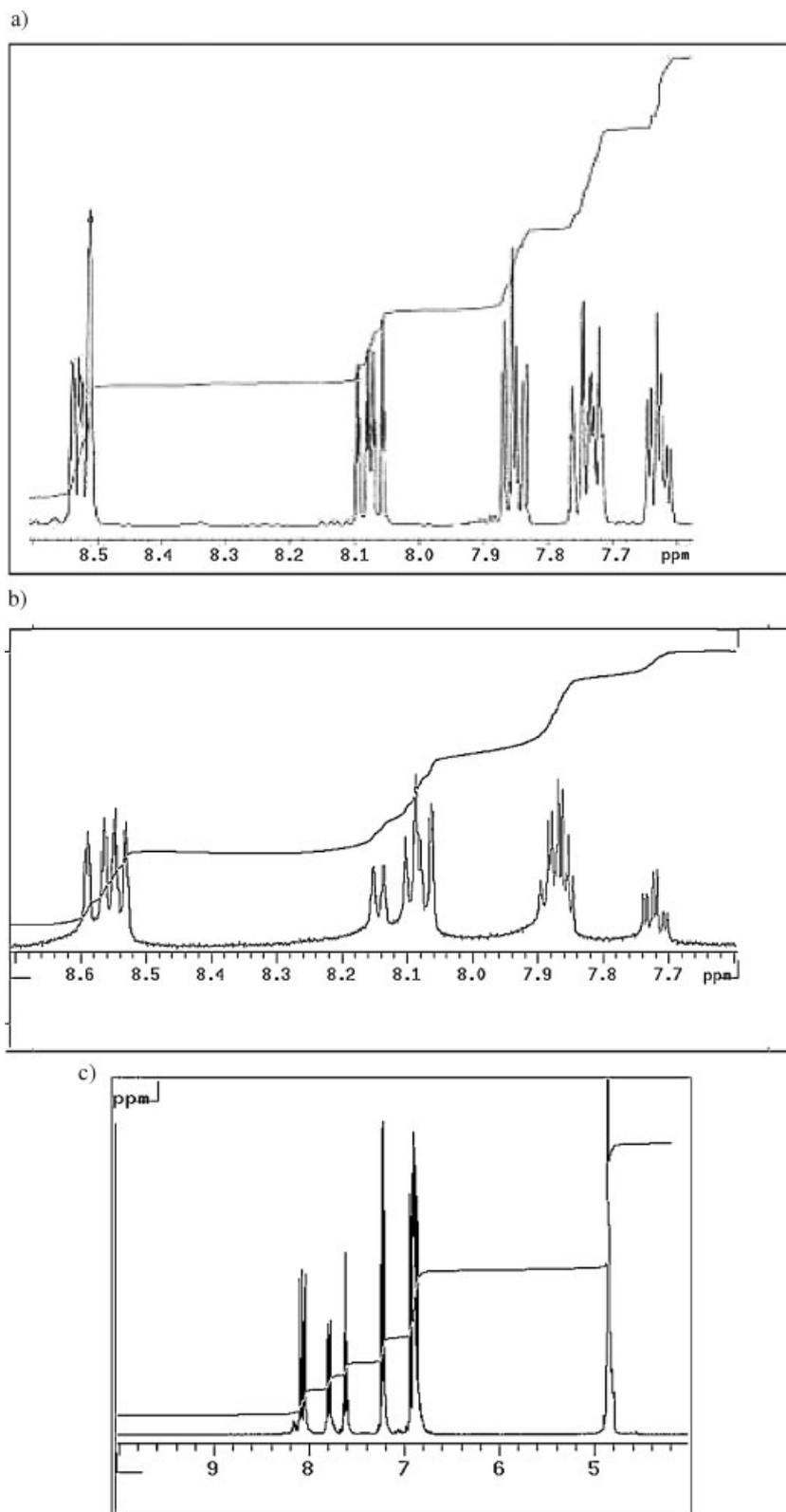
■ *Figure 3.* ¹H NMR spectrum of a) BNPPO, b) S-BNPPO, and c) S-BAPPO.
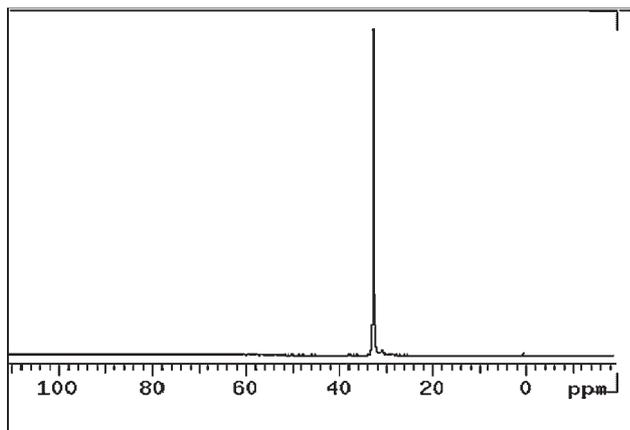
Figure 4. ^{31}P NMR spectrum of S-BAPPO.

Complete imidization was confirmed by observation of an appearance of characteristic imide carbonyl absorption bands in the range of $1\,776$–$1\,786$ cm^{-1}(asym. imide I), $1\,723$–$1\,735$ cm^{-1} (sym. imide I) and disappearance of the amide carbonyl band at $1\,540$ cm^{-1}. Strong bands in the range of $1\,365$–$1\,380$ cm^{-1} (imide II), $1\,300$ cm^{-1} (imide III), and 710 cm^{-1} (imide IV) are observed in the spectrum of both polyimides. Along with these absorption, others arising from P=O at $1\,190$ cm^{-1} and P–phenyl at $1\,425$ cm^{-1} are also observed. The spectra also display the symmetrical and asymmetrical stretching peaks of the sulfonic acid bands at $1\,033$ and $1\,097$ cm^{-1}, respectively.

The main goal of this research is to prepare novel sulfonated polyimide membranes to be used as PEMs in fuel cell applications. Although all the polymers are soluble in polar aprotic solvents like DMAc and DMSO, NMP was chosen for film preparation because of its almost non-toxic nature. Polyimides containing 20–50 mol-% sulfonated monomer gave very good films. However, the polymeric membranes that have more than 50 mol-% S-BAPPO in the polymer composition give brittle films. Creasability tests showed that there is a strong relation with the S-BAPPO monomer content. Incorporation of higher S-BAPPO monomer content causes an increase on the brittleness, as disclosed by Udea et al.[17]

The intrinsic viscosities of the polymers were measured in NMP at 30 °C using an Ubbelohde viscometer and are listed in Table 1. The intrinsic viscosities of the BTDA and 6FDA-based polyimides range from 0.38–0.74 dL·g^{-1}, which indicates that reasonably high molecular weight polymers are obtained for preparing good films. The intrinsic viscosities increased with an increase in sulfonated monomer content. The increased viscosity is accounted for by the association of ionic sulfonate groups. The glass transition temperatures (T_gs) of BTDA and 6FDA-based sulfonated polyimides are given in Table 2. These values are very important for determination of optimum processing and service temperatures at which the polymer preserves its desirable properties. As it is seen in Table 2, polyimides derived from DDS/BTDA-based polyimides had a T_g around 220 °C. However, 6-FDA-based polyimides show higher T_gs than BTDA-based analogues. This could be attributed to the bulky hexafluoropropylidiene group because of the strained CF$_3$ groups. On the other hand, incorporation of S-BAPPO lowers the T_g values of both polyimides. The T_gs of the sulfonated BTDA-based polyimides range from 164–143 °C depending on the sulfonated monomer content. The decrease in T_g is probably a result of the incorporation of the phosphine oxide structure into the polymer backbone.

The thermal stability of the non-sulfonated and sulfonated polyimides has been investigated by TGA. All the sulfonated samples were preheated at 150 °C for 30 min under a nitrogen stream in the TGA furnace to remove absorbed or trapped moisture or solvent. All TGA experiments were run from 100 to 800 °C at a heating rate of 10 °C·min^{-1} under nitrogen. As can be seen in Table 2,
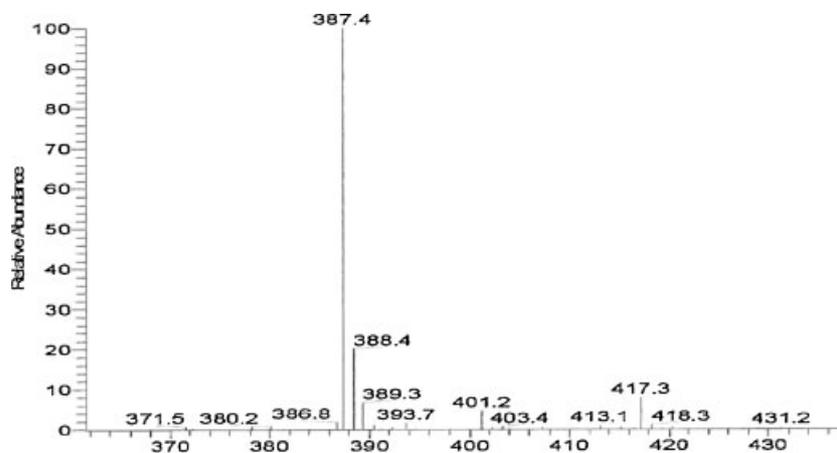
Figure 5. Mass spectrum of S-BAPPO.
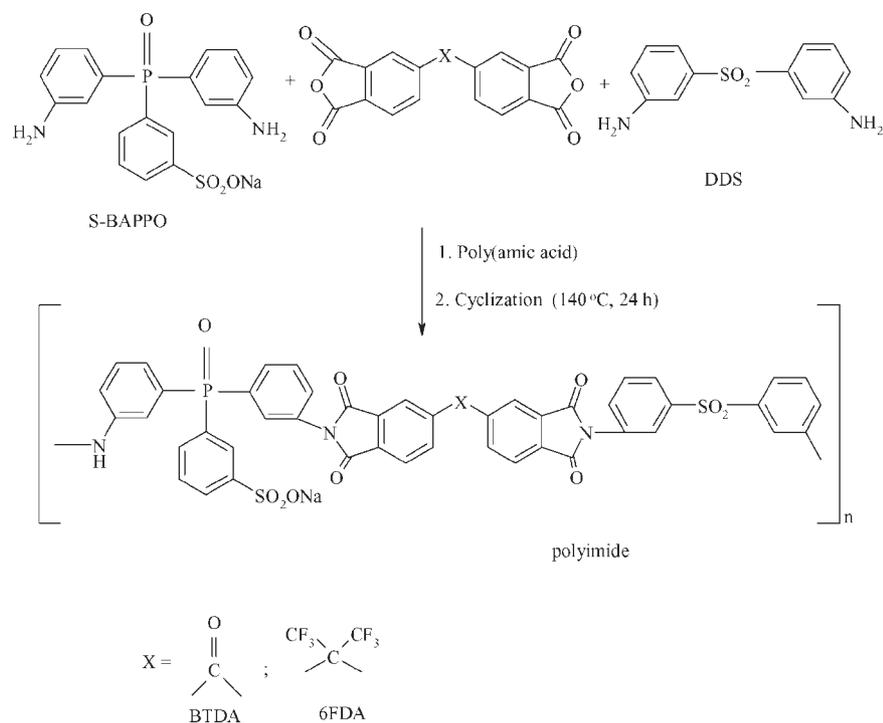
■ *Scheme 2.* The synthesis of the polyimides.

unsulfonated polyimides show an excellent resistance to thermal degradation and 5% weight loss occurs above 480 °C. However, all the sulfonated polyimide films exhibit a two-step degradation pattern. The first step of degrada-

tion is attributed to the decomposition of sulfonic acid groups at approximately 295 °C. The second step indicates the decomposition of the polymer backbone above approximately 535 °C. It has previously been reported that the decomposition temperatures in the range of 250–350 °C is sufficiently high for fuel cell applications.[18,19] Variation in degradation temperature with change in dianhydrides was observed. The relatively less thermal stability of 6FDA-based polyimides could be explained by the poor thermal stability of the hexafluoro-isopropylidene groups on 6FDA.[14] The TGA analysis also demonstrated that P=O containing polyimides posses higher char yield.

Table 1. Compositions and some characteristic properties of sulfonated polyimides.

Sample name	$[\eta]^{a)}$	IEC (calc)	IEC (exp)
	$dL \cdot g^{-1}$	$meq \cdot g^{-1}$	$meq \cdot g^{-1}$
BTDA/DDS	0.38	ND[b]	ND[b]
BTDA/S-BAPPO-20/DDS-80	0.37	0.353	0.335
BTDA/S-BAPPO-30/DDS-70	0.40	0.515	0.505
BTDA/S-BAPPO-40/DDS-60	0.42	0.667	0.622
BTDA/S-BAPPO-50/DDS-50	0.43	0.813	0.701
BTDA/S-BAPPO-75/DDS-25	0.74	1.14	0.997
BTDA/S-BAPPO	0.67	1.40	ND[b]
6FDA/DDS	0.55	ND[b]	ND[b]
6FDA/S-BAPPO-20/DDS-80	ND[b]	0.290	0.186
6FDA/S-BAPPO-30/DDS-70	0.61	0,411	0.401
6FDA/S-BAPPO-40/DDS-60	0.72	0.554	0.513
6FDA/S-BAPPO-50/DDS-50	ND[b]	0.678	0.623
6FDA/S-BAPPO-75/DDS-25	0.73	0.964	0.897
6FDA/S-BAPPO	0.74	1.20	ND[b]

a)At 30 °C in NMP; b)Not determined.

Water Uptake and Morphology

It is very important to characterize the behavior of proton-conducting ionomers in contact with water, since the presence of water in the membrane is a prerequisite for reaching a high proton conductivity. The water absorption of the protonated membranes was measured by drying the membranes at 80 °C, the membranes were then immersed in distilled water at room temperature and equilibrated for 1 d. The weight difference of the swollen membranes was carefully determined. The water absorption values (%) were calculated by dividing the weight of the wet membrane by the dried membrane. As can be seen in Figure 7, the incorporation of ionic sulfonic acid groups
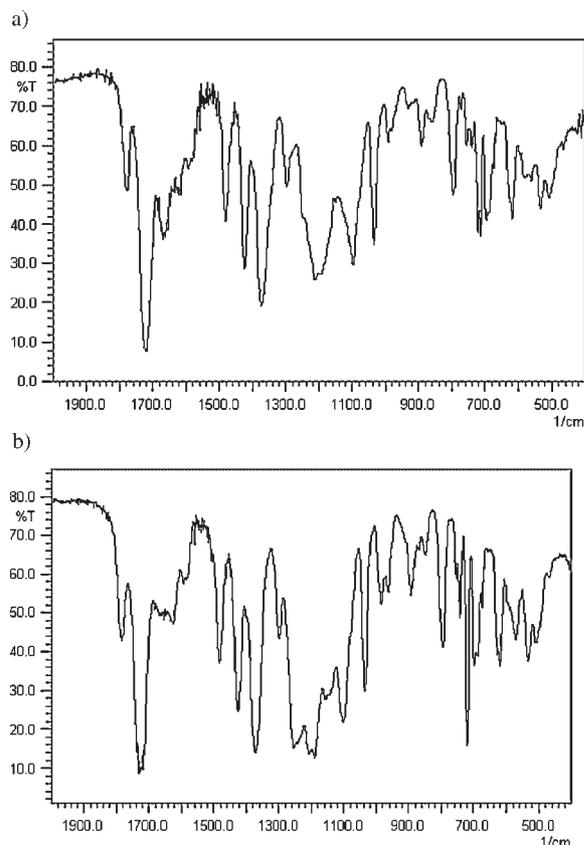
a)

b)

Figure 6. The FT-IR spectrum of a) the BTDA/S-BAPPO homo polyimide, and b) the 6FDA/S-BAPPO homo polyimide.
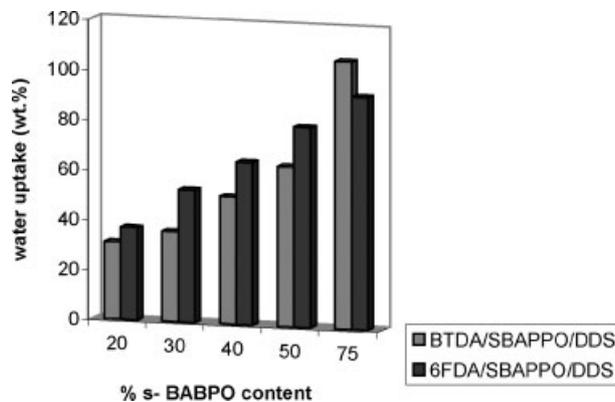

Figure 7. The water uptake of the sulfonated co-polyimides.

enhances the hydrophilicity and in turn the water uptake of the membranes. The water uptake of the sulfonated polyimide membrane gradually increases with an increase in the S-BAPPO content. It is assumed that the increase in water absorption facilitates the proton transfer and thereby increases the proton conductivity in fuel cells. From the water uptake measurements one can also evaluate the stability of the membranes towards water. A practical test for the judgment of the loss of mechanical properties is that the membrane is broken slightly and bends.[20] In this study sulfonated polyimide membranes with up to 50 mol-% S-BAPPO content, have good water stability. However, above 50 mol-% sulfonated monomer
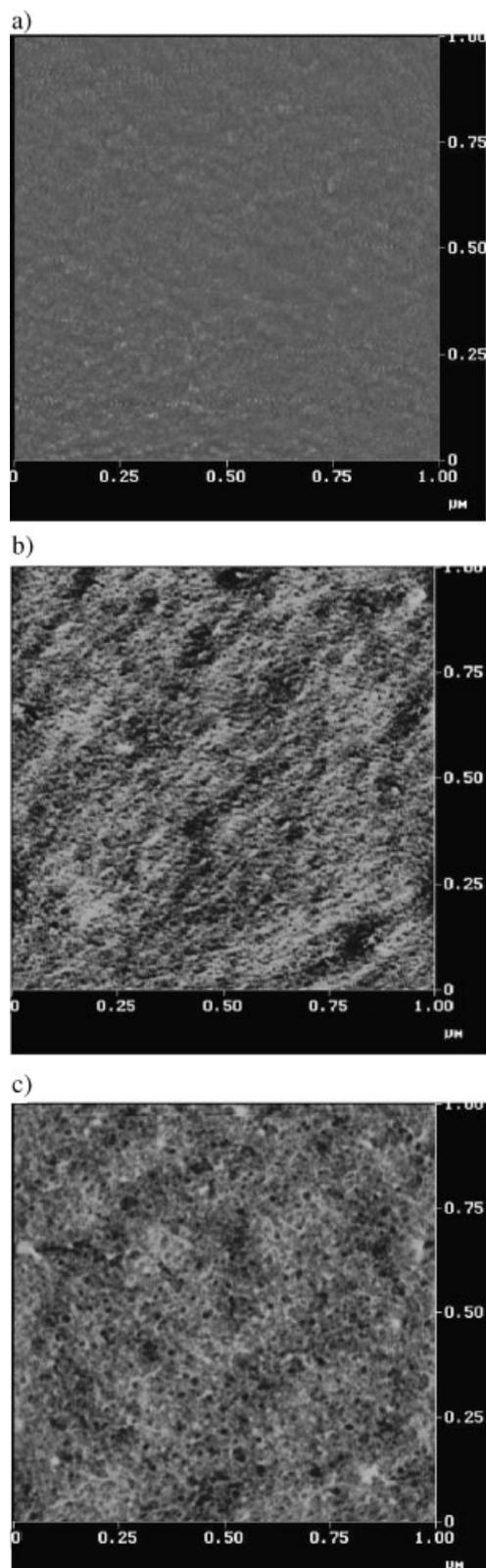
Table 2. Thermal properties of polyimides.

Sample	T_g (DSC)[a]	T_d (1st)[b]	T_d (2nd)[c]	Residue weight[d]
	°C	°C	°C	%
BTDA/DDS	220	480	575	48
BTDA/S-BAPPO-20/DDS-80	165	275	535	51
BTDA/S-BAPPO-30/DDS-70	165	250	549	52
BTDA/S-BAPPO-40/DDS-60	ND[e]	292	550	53
BTDA/S-BAPPO-50/DDS-50	160	295	530	53
BTDA/S-BAPPO-75/DDS-25	150	325	550	55
BTDA-100/S-BAPPO-100	143	225	545	56
6FDA/DDS	247	490	570	44
6FDA/S-BAPPO-20/DDS-80	185	295	537	52
6FDA/S-BAPPO-30/DDS-70	185	290	535	51
6FDA/S-BAPPO-40/DDS-60	ND[e]	285	535	48
6FDA/S-BAPPO-50/DDS-50	180	285	525	50
6FDA/S-BAPPO-75/DDS-25	170	275	525	51
6FDA/S-BAPPO	140	200	520	69

[a]Second heating scan at 10 °C · min^{-1} under N_2; [b]First weight loss temperature determined by TGA under N_2; [c]Second weight loss temperature; [d]By TGA at 800 °C; [e]Not dermined.

Figure 8. Tapping mode, phase image of an a) dry 40% sulfonated BTDA/S-BAPPO/DDS and b) a wet 40% sulfonated BTDA/S-BAPPO/DDS. c) Tapping mode, height image of a wet 40% sulfonated BTDA/S-BAPPO/DDS.

content, the films begin to loose their mechanical strength in the swollen state. The observed poor water stability is a result of its hydrophilicity, which results from the lack of synthesis of combustion polymerization grade S-BAPPO.

The morphology of a BTDA-based sulfonated polyimide membrane with 40 mol-% of sulfonated monomer content was investigated with AFM in the tapping mode. The sulfonated polyimide membrane was dehydrated in a vacuum oven at 115 °C for at least 12 h and was imaged as dry. The membrane was then swollen with deionized water for 24 h and imaged again as wet. Figure 8a and 8b show the phase images of the membrane in a dry and wet state, respectively. Figure 8c shows the height image of the same sample in the wet form. As it is seen from the images, the morphologies are different in both states. The phase image contrast increases with water uptake. The dark region in the image depicts softer hydrophilic regions that contain water, while the light regions correspond to harder hydrophobic regions.[19] It is clear that the hydrophilic ionic domains are continuous and form large channels approximately 5–20 nm wide. In Figure 8c, the hydrophilic dark sites are more easily distinguished from the hydrophobic sites. Based on the phase and height images of polyimide membrane, it may be concluded that the system reaches a percolation limit at 40 mol-% of sulfonated monomer. Previously the percolation threshold has been explained as a sudden increase of water uptake based on the degree of sulfonation of the polymer and it was demonstrated by the transformation of a hydrophobic domain morphology from a segregated to a continuous structure.[21]

IEC of Sulfonated Polyimides

Many important properties of the sulfonated polyimide membranes, such as water uptake, water stability, and proton conductivity, depend on the IEC of the polymer. It is known that IEC values directly relate to the content of the sulfonyl groups present in the polymer.[22,23] High IECs are necessary for good proton conduction because of the high charge density of the membrane. The IEC values for sulfonated polyimides are given in Table 1. The theoretical IEC was calculated from the composition of the polyimides. It is clearly seen that the IECs determined by titration are less than the theoretical values. This result indicates that loss of sulfonated groups is occurring during purification procedures.[24] As expected, the IEC values increase with an increase in sulfonated monomer content.
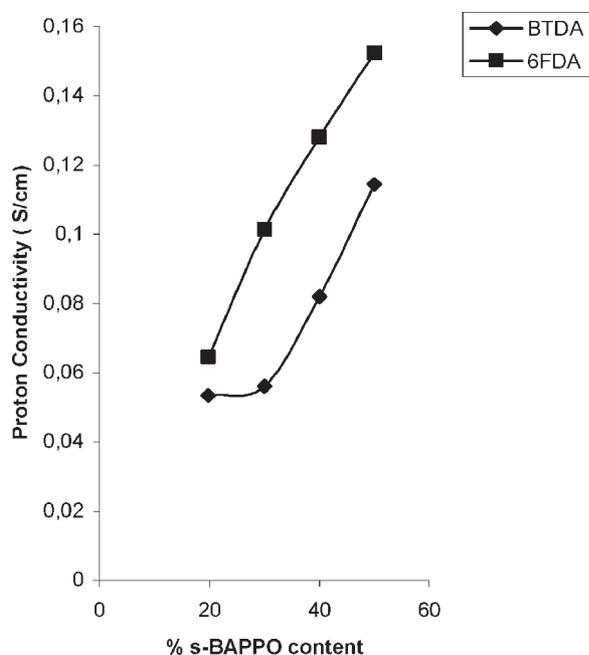
Proton Conductivity

The proton conductivity of the membranes at 24 °C was calculated from a four-point probe electrochemical

impedance spectroscopy measurement. Figure 9 shows the proton conductivities of the fully hydrated sulfonated polyimide membranes as a function of the mole percentage of sulfonated diamine. The 6FDA-based sulfonated polyimides display higher proton conductivity than the BTDA-based polyimides. This is probably because of the higher water uptake capacity of 6FDA-based sulfonated polyimides. As discussed earlier, hydrophilic ion-rich channels facilitate proton transport. The proton conductivities of 6FDA-based sulfonated polyimides increase linearly from 0.06 to 0.15 $S \cdot cm^{-1}$ as a function of sulfonated diamine content. All the membranes possess proton conductivity higher than $10^{-2} \, S \cdot cm^{-1}$, which is the basic required value of practical interest for use as PEMs in fuel cells. The conductivity values of sulfonated polyimides are very good compared to typical proton exchange membranes (Nafion 1135: 0.12 $S \cdot cm^{-1}$)

Conclusion

In this study, a novel sulfonated bis(3-aminophenyl)phenylphosphine oxide monomer (S-BAPPO) is synthesized successfully, and a series of sulfonated phosphine oxide-containing polyimides have been prepared.

An increase in the amount of sulfonated monomer intensifies the brown coloration of the dry films. The polyimide membranes that have more than 50 mol-% S-BAPPO diamine monomer in their composition show brittle film characteristics. Incorporation of S-BAPPO

monomer into both BTDA and 6FDA-based polyimides decreased the T_g. The first weight loss can be attributed to the decomposition of sulfone groups, and the second weight loss between 535–575 °C is a result of the degradation of the polymer chain. This result indicates that the polyimide membranes will be stable enough within the conceivable temperature range of polymer electrolyte fuel cell applications. The char yield increased with the incorporation of phosphine oxide-containing sulfonated diamine monomer into the polyimide backbone. It is possible that the incorporation of ionic sulfonic acid groups enhances the hydrophilicity of the polyimide, so the increase in water absorption facilitates proton transfer and thereby increases the proton conductivity in fuel cells. AFM studies also show that the increase in phase image contrast demonstrates the water uptake of the membrane. The conductivity values of sulfonated polyimides are good compared to the promising proton exchange membranes. For example the 6FDA/S-BAPPO/DADPS-50 sample has a conductivity of 0.15 $S \cdot cm^{-1}$ at 24 °C.

Figure 9. Proton conductivity of the sulfonated polyimides.

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