

# Synthesis and Properties of Novel Sulfonated Polyimide Membranes for Fuel Cell Application

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**Abstract:** Two sulfonated diamines, 4,4'-bis(4-aminophenoxy)benzophenone-3,3'-disulfonic acid (BAPBPDS) and 4,4'-bis(4-aminophenylthio)benzophenone-3,3'-disulfonic acid (BAPTBPDS), were synthesized via two-step reactions and a series of sulfonated polyimides (SPIs) were prepared from these sulfonated diamines, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and common non-sulfonated diamines via conventional one-step polymerization approach. The resulting SPIs showed good solubility, high thermal stability, high proton conductivity (comparable to that of Nafion 112) and rather low methanol permeability (one fifth to one tenth of that of Nafion 112).

## INTRODUCTION

Aromatic polyimides, known for their excellent thermal stability, high mechanical strength and modulus, superior electric properties, and good chemical strength, have found wide application in industry. Recent researches have demonstrated that six-membered ring sulfonated polyimides (SPIs) are one of the most promising electrolyte membrane materials for fuel cell application. [1-18] The synthesis of sulfonated polyimides was generally performed by polymerization of a typical six-membered ring dianhydride monomer, 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), a sulfonated diamine, and common nonsulfonated diamine monomers. The ion exchange capacity (IEC) of a SPI can be precisely controlled by regulating the molar ratio between the sulfonated diamine and the non-sulfonated one. The structure of sulfonated diamines greatly affects the water stability and other properties of SPIs, i.e., SPIs derived from the sulfonated diamines with high basicity, linear configuration, flexible linkages, and/or pendant sulfonic acid groups (side-chain-type) tends to have high water stability.[3-12] To contribute more understandings of the 'structure-property' relationship of SPIs, in this presentation we report on the synthesis of a series of novel SPIs from NTDA, two sulfonated diamines, 4,4'-bis(4-aminophenoxy)benzophenone-3,3'-disulfonic acid (BAPBPDS) and 4,4'-bis(4-aminophenylthio)benzophenone-3,3'-disulfonic acid (BAPTBPDS), and common non-sulfonated diamines. The proton conductivity, water uptake, water stability and methanol permeability of these SPI membranes are also investigated.

## EXPERIMENTAL

BAPBPDS was synthesized by reaction of 4,4'-Dichlorobenzophenone-3,3'-disulfonic acid disodium salt (DCBPDS) and 4-aminophenol in 1-methylpyrrolidone (NMP) under nitrogen flow in the presence of potassium carbonate at 180 °C for 20 h followed by acidification. Yield: 63%. m.p. (DSC):> 350 °C. <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub> in the presence of a drop of Et<sub>3</sub>N for dissolution of 1): 8.15 (d, *J* = 2.4 Hz, 2H), 7.55 (dd, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 4H), 6.67 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 4H), 5.01 (s, 4H of amino groups). Elementary analysis: Calculated for C<sub>25</sub>H<sub>20</sub>O<sub>9</sub> N<sub>2</sub>S<sub>2</sub>·0.8H<sub>2</sub>O: C, 52.59; H, 3.79; N, 4.91; S, 11.22; found: C,

52.63; H, 3.91; N, 4.93; S, 10.87.

BAPTBPDS was synthesized by following the same procedures for BAPBPDS and using 4-aminothiophenol to replace 4-aminophenol. Yield: 79%, m.p. (DSC): > 350 °C. <sup>1</sup>H NMR spectrum (in DMSO-*d*<sub>6</sub> in the presence of a drop of Et<sub>3</sub>N for dissolution of 1): 8.04 (d, J = 1.6 Hz, 2H), 7.34 (dd, J = 8.4 Hz, 2H), 7.14 (d, J = 8.8 Hz, 4H), 6.65 (m, 6H), 5.56 (s, 4H of amino groups). Elementary analysis: Calculated for C<sub>25</sub>H<sub>20</sub>O<sub>7</sub>N<sub>2</sub>S<sub>4</sub>·0.8H<sub>2</sub>O: C, 49.96; H, 3.56; S, 4.66; N, 21.31; found: C, 49.80; H, 3.60; N, 4.34; S, 21.08.

Various SPIs were prepared by random polymerization of NTDA, sulfonated diamines (BAPBPDS and BAPTBPDS) and non-sulfonated diamines [4,4'-diaminodiphenyl ether (ODA), 4,4'-bis(4-aminophenoxy)biphenyl (BAPB) and 9,9-bis(4-aminophenyl)fluorene (BAPF)] in *m*-cresol in the presence of triethylamine (Et<sub>3</sub>N) and benzoic acid under nitrogen flow at 180 °C for 20 h. Membranes (in triethylammonium salt form) of the resulting SPIs were prepared by casting their DMSO solutions (~5 wt %) onto glass dishes and dried at 80 °C for 10 h. The as-cast films were soaked in methanol at 60 °C for 1 h to remove the residual solvent, and then immersing into 1.0 N hydrochloric acid at room temperature for two days for the proton exchange. The resulting films were thoroughly washed with deionized water till water is neutral and dried in vacuum at 150 °C for 20 h.

Proton conductivity (σ) was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [11]. Methanol permeability (P<sub>M</sub>) was measured using a liquid permeation cell and measuring the methanol concentration in feed and in permeate with permeation time at 30 °C.[13] The initial methanol concentration in feed was 8.6 wt%, while pure water was used in the permeate side.

## RESULTS AND DISCUSSION

Two sulfonated diamine monomers, BAPBPDS and BAPTBPDS, were synthesized by two-step reactions, respectively. Their chemical structures were characterized by IR, <sup>1</sup>HNMR and elemental analysis. Various SPIs were prepared by one-step random polymerization method from NTDA, BAPBPDS, BAPTBPDS, and non-sulfonated diamines (BAPF, BAPB and ODA) in *m*-cresol in the presence of triethylamine (Et<sub>3</sub>N) and benzoic acid at 180 °C (Scheme 1). The molar ratio between the sulfonated diamines and non-sulfonated ones was controlled to be 2:1 or 3:1 to provide reasonably high IECs (~2.0 meq/g) of the SPIs.

The resulting SPIs showed moderate inherent viscosities which are in the range of 0.9-1.7 dL/g in dimethylsulfoxide (DMSO) at a polymer concentration of 0.5 g/dL at 35 °C (Table 1). Membranes with good mechanical strength were fabricated by using the conventional solution cast method. All the SPIs showed good solubility in some organic solvents such as DMSO and NMP. The thermal stability of BAPBPDS and BAPTBPDS-based SPIs were investigated by TGA measurements (Figure 2). For both types of SPIs, the decomposition temperatures of sulfonic acid groups are higher than 250 °C indicating high thermal stability of the SPIs.

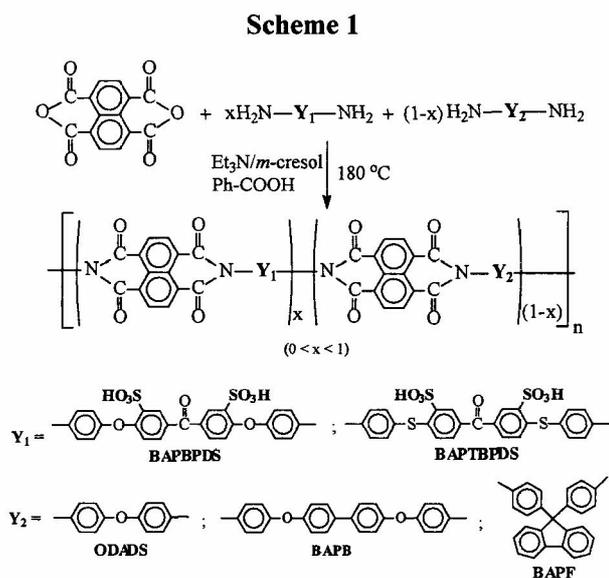


Table 1 shows the IEC, water uptake, proton conductivity in water at 60 °C, water stability (80 °C) and methanol permeability (30 °C) of BAPBPDS and BAPTBPDS-based SPI membranes. The IEC values measured by titration method are somewhat (~10%) lower than the corresponding theoretical ones probably because of incomplete proton exchange and/or incomplete dehydration of the SPI samples for test. Water uptake values of these SPI membranes are in the range of 53-79% depending on the non-sulfonated diamine moiety, i.e., BAPF-based SPI membranes showed lower water uptake than other non-sulfonated diamine-based ones. The proton conductivities of these SPI membranes in water at 60 °C are in the range of 0.11-0.16 S/cm which is comparable to that of Nafion 112.

Table 1 IEC, water uptake (WU), proton conductivity ( $\sigma$ ) in water at 60 °C, water stability at 80 °C and methanol permeability ( $P_M$ ) at 30 °C of various SPI membranes.

Polymer	IEC <sup>b</sup> [meq/g]	WU <sup>c</sup> [wt%]	$\sigma$ [S/cm]	Water Stability [h]	$P_M$ [10 <sup>-7</sup> cm <sup>2</sup> /s]	Ref.
NTDA-BAPBPDS/ODA(2/1)	1.99 (1.75)	79	0.14	390	3.7	d
NTDA-BAPBPDS/BAPB(3/1)	2.02 (1.75)	71	0.11	360	4.5	d
NTDA-BAPBPDS/BAPF(3/1)	2.04 (1.81)	53	0.16	293	2.4	d
NTDA-BAPTBPDS/ODA(2/1)	1.93 (1.76)	75	0.14	>1000	3.2	d
NTDA-BAPTBPDS/BAPB(3/1)	1.96 (1.80)	68	0.15	>1000	4.1	d
NTDA-BAPTBPDS/BAPF(3/1)	1.97 (1.80)	56	0.14	>1000	2.7	d
ODA <sup>a</sup>	1.09-2.14	22-102	0.03-0.12	65-0.5	5.1-6.9	17
Nafion 112	0.91	-	0.10	-	24	13

<sup>a</sup>The SPI was prepared from NTDA, 4,4'-bis(3-aminophenoxy)diphenyl sulfone-3,3'-disulfonic acid and ODA. <sup>b</sup>The values in parenthesis were obtained by titration method. <sup>c</sup>Measured at 80 °C. <sup>d</sup>This study

The water stability test for the SPI membranes was performed by immersing them into deionized water at 80 °C and the stability was characterized by the elapsed time when the hydrated membranes lost mechanical properties. As shown in Table 1, despite the similar IECs, BAPTBPDS-based SPI membranes showed significantly better water stability than BAPBPDS-based ones. The structures of BAPBPDS and BAPTBPDS are quite similar and the only difference is that the former is comprised of ether bond linkage whereas the latter consists of thio-ether bond linkage. The electron-donating effect of thio-ether bond is stronger than that of ether bond, i.e., BAPTBPDS is more basic than BAPBPDS. Previous researches have revealed that SPIs derived from the sulfonated diamines with higher basicity tended to have slower hydrolytic rate and thus better water stability.[7,10,12-17] This is why BAPTBPDS-based SPI membranes displayed better water stability than BAPBPDS-based ones. Moreover, recently McGrath and coworkers have reported a sulfonated diamine, 4,4-bis(3-aminophenoxy)diphenyl sulfone-3,3'-disulfonic acid (*m*BAPPSDS), and various SPIs derived from this monomer.[16,17] The IECs of these SPIs are in the range of 0.88-2.14 meq/g and the water stability at 80 °C is around 0.5-96 h which is much shorter than that of both BAPBPDS and BAPTBPDS-based SPI membranes. This is because BAPBPDS and BAPTBPDS have linear (para-substituted, sulfonate is the pendent group) configuration whereas *m*BAPPSDS is a non-linear molecule.[3]

As shown in Table 1, the methanol permeability of the SPI membranes is in the range of  $2.4 - 4.5 \times 10^{-7} \text{ cm}^2/\text{s}$  at  $30^\circ\text{C}$  (methanol concentration of feed solution: 8.9 wt%) which is mainly determined by the non-sulfonated diamine moieties. For both BAPBPDS and BAPTBPDS-based SPI membranes, the methanol permeability is in the order: BAPF-based SPIs < ODA-based SPIs < BAPB-based SPIs. NTDA-BAPBPDS/BAPF(3/1) displayed the lowest methanol permeability which is one order lower than that of Nafion 112, while the proton conductivity is almost the same, indicating high performance of this membrane. All the SPI membranes showed lower methanol permeability and higher proton conductivity than those reported in the literature.[17]

## CONCLUSIONS

Two kinds of sulfonated diamine monomers, BAPBPDS and BAPTBPDS, and the relevant sulfonated copolyimides were successfully synthesized. The resulting sulfonated copolyimides showed good solubility in some organic solvents, high thermal stability, high proton conductivities (comparable to that of Nafion 112) and rather low methanol permeability (one fifth to one tenth of that of Nafion 112). BAPTBPDS-based copolyimide membranes displayed much better water stability than BAPBPDS-based ones because of the higher basicity of BAPTBPDS moiety resulting from the larger electronic-donating effect of this bond.

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