Novel Proton Conducting Polyimides from Sulfonated Sulfonyl-Containing Diamine Monomer

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ABSTRACT: A novel sulfonated diamine monomer, 4,4'-bis(4-aminophenoxy)diphenyl sulfone-3,3'-disulfonic acid (BAPPSDS), was synthesized via two-step reactions. A series of sulfonated (co)polyimides with controlled sulfonation degrees were prepared from NTDA, BAPPSDS, and common nonsulfonated diamines. The homopolyimide NTDA-BAPPSDS was insoluble in common organic solvents, whereas the copolyimides could be dissolved in m-cresol and dimethylsulfoxide (DMSO) when a proper nonsulfonated diamine was used. Water uptakes, proton conductivities, water stability and methanol permeability of these copolyimide membranes were investigated and compared with those of other sulfonated diamine-based ones. Polyimide membranes with good proton conductivity as well as good water stability were developed.
Key words: sulfonated diamine, sulfonated polyimide, polymer electrolyte membrane, water stability, proton conductivity

1. INTRODUCTION

Recently six-membered ring sulfonated polyimides have been identified as promising electrolyte membrane materials for fuel cell application [1-3]. 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 use of NTDA is based on the fact that six-membered ring polyimides are much more stable toward water than common five-membered ring ones which are usually hydrolyzed rapidly especially under acid condition [1d, 4, 6]. Sulfonated diamines are used for the introduction of sulfonic acid groups, while nonsulfonated diamines are used as comonomers to control the sulfonation degree. 2,2'-Benzidinedisulfonic acid (BDSA) is a widely used and commercially available monomer. A BDSA-based copolyimide membrane has been reported to have high performance when settled in a fuel cell system which is comparable to that of Nafion [1b]. The major problem associated with the BDSA-based polyimides is the rather poor water stability, and we have ascribed it to the highly rigid structure of polymer backbone as well as the low basicity of BDSA moiety [3]. Recently we have systematically studied the "structure-property" relationship of sulfonated polyimides by synthesizing various novel sulfonated diamine monomers, and successfully developed sulfonated polyimide membranes with extremely high water stability as well as high proton conductivity [3c]. However, so far, the stability of the sulfonic acid groups has not been explored yet, and this problem might not be neglected when the fuel cells work at relatively high temperature (> 120 °C). Theoretically, the sulfonic acid groups are more stable toward hydrolysis when the phenyl rings to which the sulfonic acid groups are bonded have lower electron density. In this paper, a novel sulfonated diamine monomer, 4,4'-bis(4-aminophenoxy)diphenyl sulfone-3,3'- disulfonic acid (BAPPSDS), was synthesized, and the related polyimides were prepared.

The central sulfonyl group of BAPPSDS is a strong electron withdrawing group, and therefore, the sulfonic acid groups of BAPPDS are expected to be stable toward hydrolysis. The proton conductivity, water uptake, membrane stability toward water and methanol permeability of BAPPSDS-based polyimide membranes are also described.

2. EXPERIMENTAL

2.1 Materials

Bis[4-(4-aminophenoxy)phenyl]sulfone (BAPPS), bis[4-(3-aminophenoxy)-phenyl]sulfone (mBAPPS), 3,3'-dimethylbenzidine (DMBz), 2,2-bis[4-(4-amino phenoxy)phenyl]propane(BAPP), 4,4'-dichlorodiphenyl sulfone, 4-aminophenol, and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) were purchased from Tokyo Kasei Co.. Benzoic acid, m-cresol, triethylamine (Et₃N), dimethylsulfoxide (DMSO), N-methyl-pyrrolidinone (NMP), N,N-dimethyl acetamide (DMAc), N,N-dimethylfomamide (DMF), concentrated sulfuric acid (95 %), fuming sulfuric acid (SO₃, 60 %), concentrated hydrochloric acid (35-37%) were purchased from Wako Co.. BAPPS, mBAPPS, and NTDA were purified by vacuum sublimation prior to use. DMSO, NMP, DMAc, and DMF were distilled under reduced pressure and dried with molecular sieve 4 A prior to use. Et₃N was distilled under constant pressure and also dried with molecular sieve 4 A. Other compounds were used as received.

2. 2 Synthesis of 4,4'-dichlorodiphenyl sulfone-3,3'-disulfonic acid disodium salt (2)

2 was synthesized according to a literature method [7] by direct sulfonation of 4,4'-dichloro diphenyl sulfone (1) using fuming sulfuric acid as the sulfonating reagent.

2.3 Synthesis of bis[4-(4-aminophenoxy)phenyl]sulfone 3,3'-disulfonic acid (BAPPSDS) (4).

To a 100 mL of 4-neck flask were added 4.91 g (10.0 mmol) of 2, 10 mL of anhydrous NMP, and 4.0 g

of K_2CO_3 successively under nitrogen flow. After stirred for 0.5 h, 10 mL of toluene was added, and the mixture was heated to 150 °C for 3 h. Water and toluene were evaporated as azeotrope and collected in a Dean-Starktrap. Then the mixture was heated to 175 °C for 18 h. After cooling to room temperature, 100 mL of actone was added with magnetic stirring. The mixture was filtered, and the white precipitate was dissolved in water, and then acidified with hydrochloric acid. The resulting precipitate was filtered off, washed with water, and dried in vacuo. 5.16 g of product 4 was obtained. Yield: 87%.^{1}H NMR (in DMSO-d_6), δ (ppm): 8.21 (2H, ArH), 7.74 (2H, ArH), 6.76 (2H, ArH), 6.73 (4H, ArH), 6.61 (4H, ArH), 5.07 (4H, -NH$_2$).
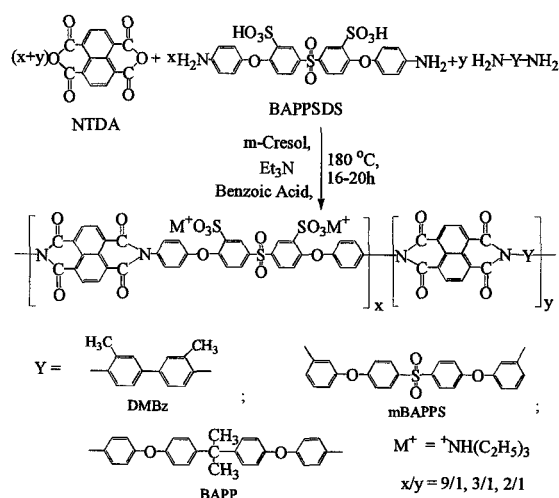
Scheme 1
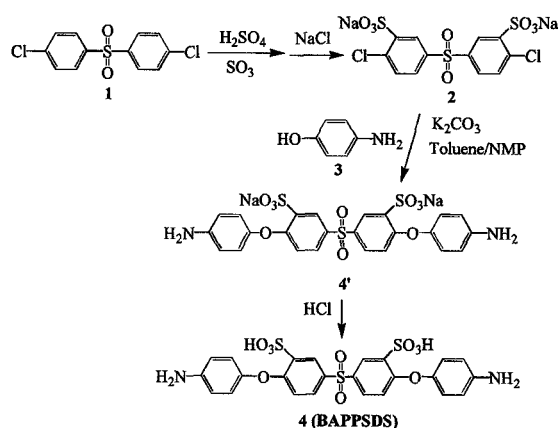
2.4 Synthesis of sulfonated polyimides.

A literature method was used for preparation of the sulfonated polyimides[1d]. A typical procedure is described below using NTDA-BAPPSDS/TMBz(2/1) sulfonated copolyimide as an example.

Scheme 2

To a 100 mL completely dried 4-neck flask were added 0.710 g (1.2 mmol) of BAPPSDS, 6 mL of m-cresol, and 0.41 mL of triethylamine successively under nitrogen flow. After the BAPPSDS was completely dissolved, 0.127 g (0.6 mmol) of DMBz,

0.482 g (1.8 mmol) of NTDA, and 0.31 g of benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, additional 5 mL of m-cresol was added to dilute the highly viscous solution, and then the solution was poured into acetone. The fiber-like precipitate was filtered off, washed with acetone thoroughly, and dried in vacuo at 60 °C for 20 h.

2.5 Film Formation and Proton-exchange.

The resulting sulfonated copolyimides (in triethylammonium salt form) were dissolved in DMSO, and the solution was cast onto glass plates at 80 °C for 10 h. The as-cast films were soaked in methanol at 60 °C for 1 h and in 1.0 N hydrochloric acid at room temperature for 10-15 h successively. The proton-exchanged films were thoroughly washed with de-ionized water and then dried in vacuo at 150 °C for 20 h.

2.6 Measurements

^{1}H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Inherent viscosity was measured in DMSO at a polymer concentration of 0.5 g/dL at 35 °C using a viscometer.

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [3a]. The resistance value associated with the membrane conductance was determined from high frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = D/(LBR) \qquad (1)$$

where D is the distance between the two electrodes, L and B are the thickness and width of the membrane in "dry state" (stored in a desiccator), respectively, and R is the resistance value measured.

Water sorption was measured by immersing three sheets of films (20-30 mg per sheet) of each polyimide into water at 80 °C or 100 °C for 3-5 h. Then the films were taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake of the films, S, was calculated from

$$S = (W_s - W_d)/W_d \times 100 \ (\%) \qquad (2)$$

where W_d and W_s are the weight of dry and corresponding water-swollen film sheets, respectively. Water uptake of a polyimide was estimated from the average value of S of each sheet.

Methanol permeability (P_M) was measured using a liquid permeation cell and measuring the methanol concentration in feed and in permeate with permeation time [8].

3. RESULTS AND DISCUSSION
3.1 Monomer synthesis and polymerization.

As shown in Scheme 1, the new sulfonated diamine monomer, BAPPSDS, was synthesized by two step reactions in a high yield. At first, 4,4'-dichlorodiphenyl sulfone (1) was sulfonated by using fuming sulfuric acid as the sulfonating reagent to give 4,4'-dichlorodiphenyl sulfone-3,3'-disulfonic acid disodium salt (2). The intermediate product 2 was then reacted with

4-aminophenol under basic condition to give bis[4-(4-aminophenoxy)phenyl] sulfone-3,3'-disulfonic acid disodium salt (4'). The resulting intermediate product 4' was treated with hydrochloric acid to give BAPPSDS (4).

On the other hand, recently we have successfully synthesized a series of novel sulfonated diamine monomers by direct sulfonation of the parent nonsulfonated diamines using fuming sulfuric acid as the sulfonating reagent [3a, b]. However, the direct sulfonation of BAPPS failed to give the sulfonated diamine BAPPSDS. This is because the strong electron withdrawing effect of the sulfonyl group of BAPPS deactivated the two central phenyl rings, making it difficult for the sulfonation reaction to selectively occur in the two central phenyl rings of BAPPS.

A series of novel sulfonated (co)polyimides were synthesized by (co)polymerization of NTDA, BAPPSDS, and common nonsulfonated diamines in the presence of triethylamine and benzoic acid (Scheme 2). This is a literature method which has been used for preparation of various six-membered ring polyimides [1, 5]. The resulting copolyimides showed fairly high inherent viscosity (Table I). For all the copolyimides, tough films were obtained by solution cast method. The solubility behaviors of the resulting sulfonated (co)polyimides were investigated. The homopolyimide, NTDA-BAPPSDS, was insoluble in common organic solvents, indicating very poor solubility. The solubility was significantly improved by incorporation of proper nonsulfonated diamine moieties. All the copolyimides are well soluble in both m-cresol and DMSO.

3.2 Water stability.

Table I lists the thickness, IEC, water uptake, and water stability of BAPPSDS-based copolyimides and NTDA-BAPBDS membranes. The stability test toward water of the polyimide membranes was performed by immersing the membranes into distilled water at 80 °C

or 100 °C and characterized by the time elapsed when the membranes became brittle in water. As shown in Table I, the water stability of BAPPSDS-based copolyimide membranes showed strong temperature dependence. NTDA-BAPPSDS/*m*BAPPS(3/1), for example, did not break into pieces after being soaked in deionized water at 80 °C for 600 h indicating fairly good water stability. However, at 100 °C the membrane dissolved in deionized water within 5 h. The water stability was significantly improved by reducing the IEC level. NTDA-BAPPSDS/*m*BAPPS(2/1) had slightly lower IEC than NTDA-BAPPSDS/*m*BAPPS(3/1), but the water stability is much better for the former. It could maintain film form after being soaked in deionized water at 100 °C for more than 200 h. The water stability is also affected by the nonsulfonated diamine moieties. NTDA-BAPPSDS/*m*BAPPS(2/1) and NTDA-BAPPSDS/DMBz(2/1) had the same chemical composition except the nonsulfonated diamine moieties. However, their water stability is extremely different. NTDA-BAPPSDS/*m*BAPPS(2/1) showed much better water stability than NTDA-BAPPSDS/DMBz(2/1). The structural difference between *m*BAPPS and DMBz is that the former is relatively flexible, whereas the latter is rather rigid. We have previously investigated that sulfonated polyimide membranes with flexible structure tended to have better water stability than those with rigid structure [3b]. The present water stability result is just consistent with our previous investigation. It should be noted that the water stability of BAPPSDS-based copolyimides is still poorer than that of NTDA-BAPBDS which has been reported to have excellent water stability despite the high IEC. This is probably because the basicity of BAPPSDS moiety is somewhat lower than BAPBDS due to the electron withdrawing effect of the sulfonyl group of the former. The reason is not clear at present.

Table I Thickness, IEC, water uptake, inherent viscosity and water stability of various sulfonated polyimide membranes.

Membrane	Thickness [μm]	IEC [meq g⁻¹]	Water Uptake[a] [%w/w]	η_inh [dL/g]	Membrane Stability[b] T [°C]	Membrane Stability[b] t [h]	Ref.
NTDA-BAPPSDS/BAPP(3/1)	58	1.93	150[a1]	3.74	100	12	c
NTDA-BAPPSDS/*m*BAPPS(9/1)	40	2.22	NM	2.30	100	Soluble	c
NTDA-BAPPSDS/*m*BAPPS(3/1)	41	1.91	NM	3.82	80	600	c
					100	5	c
NTDA-BAPPSDS/*m*BAPPS(2/1)	61	1.73	98[a1]	2.87	100	>200	c
NTDA-BAPPSDS/DMBz(2/1)	28	1.91	72	NM	80	80	c
NTDA-BAPBDS	23	2.63	142	NM	80	>1000	3c
					100	1000	3c

[a]Measured at 80 °C in water; [a1] Measured at 100 °C in deionized water for 5 h. [b]T: temperature; t: The time elapsed when the membranes became brittle in water; [c]This study. NM: not measured; >: Stability test is going on.

Table II Proton conductivity, methanol permeability and their ratios of sulfonated polymer membranes

Membranes	IEC [meq g⁻¹]	σ (S/cm)[a] 90%RH	σ (S/cm)[a] In water	P_M(10⁻⁶cm²/s)[b] 30°C	P_M(10⁻⁶cm²/s)[b] 50°C	$\phi = \sigma/P_M$(10⁴ S.cm⁻³ s)(30°C)	Ref.
NTDA-BAPPSDS/*m*BAPPS(2/1)	1.73	0.071	0.07	0.84[b]	1.64[b]	8.3	c
NTDA-BAPBDS	2.63	0.031	0.19	1.14	-	18	8
NTDA-2,2'-BSPB	2.89	0.11	0.18	1.05	2.06	13	8
Nafion 117	0.91	0.085	0.12	2.21	3.32	4.8	8

[a]Measured at 50 °C; [b] Methanol concentration in feed: 8.6wt%, [b1] 10wt%; [c]This study.

3.3 Proton conductivity.

The proton conductivities (σ) of a series of sulfonated polymer membranes at different relative humidities are shown in Fig. 1. It can be seen that for all the membranes σ increased significantly with an increase in relative humidity (RH). BAPPSDS-based polyimides displayed much lower σ at low RH, and similar or higher σ at high RH (>70%) or in water.
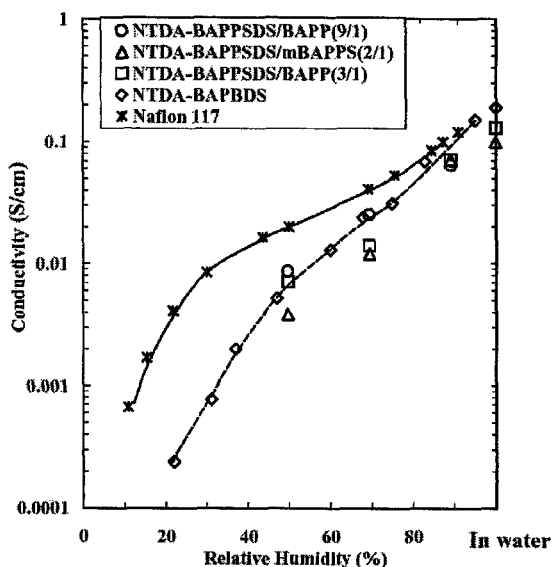

Fig. 1 Relative humidity dependence of proton conductivity for sulfonated polymer membranes at 50 °C.

Fig. 2 shows the variation of σ of the sulfonated polymer membranes as a function of temperature. All the membranes displayed increased σ with increasing temperature, and BAPPSDS-based copolyimdes displayed similar or a little higher σ to Nafion 117.
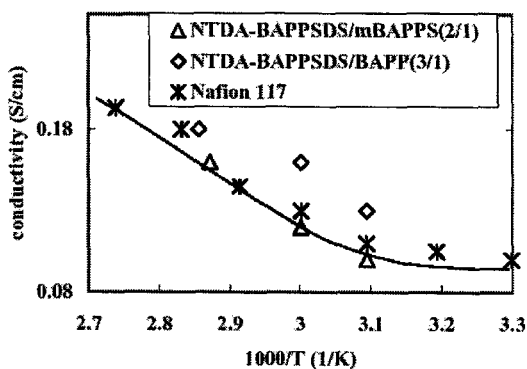

Fig.2 Temperature dependence of proton conductivity for sulfonated polymer membranes in water.

3.4 Methanol permeability

Table II lists the proton conductivity and methanol permeability and their ratio ϕ (= σ/P_M) of a series of sulfonated polyimides and Nafion 117. The P_M values of NTDA-BAPPSDS/mBAPPS(2/1) were much smaller than those of other sulfonated polyimides and Nafion 117 membrane at 30 °C and 50 °C. As a result, the BAPPSDS-based membrane displayed much larger ϕ

value than Nafion 117, but lower than other sulfonated polyimide membranes because of the lower proton conductivity. Thus, the BAPPSDS-based membrane had reasonable proton conductivity and low methanol permeability and might be potential polyelectrolytes for direct methanol fuel cell applications.

4. Conclusions

1. A novel sulfonated diamine monomer BAPPSDS was successfully synthesized by two step reactions and the related copolyimides were prepared.

2. NTDA-BAPPSDS/mBAPPS(2/1) membrane showed fairly good water stability in hot water but poorer than that of NTDA-BAPBDS despite the higher IEC of the latter.

3. The BAPPSDS-based copolyimides displayed similar or slightly higher proton conductivity at high relative humidity (>70%) or in water than that of Nafion 117.

4. NTDA-BAPPSDS/mBAPPS(2/1) membrane displayed lower methanol permeability and higher ϕ than that of Nafion 117.

5. References

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