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Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 2. Synthesis and Proton Conductivity of Polyimides from 9,9-Bis(4-aminophenyl)fluorene-2,7-disulfonic Acid

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ABSTRACT: A new sulfonated diamine monomer, 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS), was synthesized by direct sulfonation of the parent diamine, 9,9-bis(4-aminophenyl)fluorene (BAPF), using fuming sulfuric acid as the sulfonating reagent. A series of sulfonated polyimides with different sulfonation degrees were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), BAPFDS, and common nonsulfonated diamines. The resulting sulfonated polyimides generally showed good solubility in *m*-cresol and DMSO. Proton conductivities of these polyimide membranes were measured as the functions of relative humidity and temperature. The resulting homopolyimide, NTDA-BAPFDS, displayed proton conductivities quite similar to those of Nafion 117 in the whole humidity range (RH < 100%). At 100% relative humidity, all the BAPFDS-based polyimide membranes showed proton conductivities similar to or higher than those of Nafion 117. In addition, BAPFDS-based polyimide membranes exhibited much better water stability than those derived from a widely used sulfonated diamine, 2,2′-benzidinedisulfonic acid (BDSA), with similar IEC. This is probably because of the higher basicity of BAPFDS, which is favorable for maintaining the stability of imido rings.

Introduction

Proton-conducting polymers have attracted much attention in the past few decades due to their important application in fuel cell systems. The well studied and practically used proton-conducting polymers are sulfonated perfluoropolymers such as DuPont's Nafion membrane and Dow's membrane because of their high performance including high proton conductivity, high mechanical strength, and good thermal and chemical stability. However, some drawbacks such as high cost, low conductivity at high temperature, and high methanol permeability limit their further application.[1] Therefore, many efforts have gone into the development of low-cost and high performance nonfluorinated hydrocarbon membrane materials. The major approach has been the attachment of sulfonic acid groups onto highly stable aromatic polymers, such as poly(ether ether ketone) (PEEK),[2] polysulfone (PSF),[3] and poly(phenylene sulfide).[4] The introduction of sulfonic acid groups is achieved either by direct sulfonation of the parent polymers or by polymerization of sulfonated monomers. Recently, sulfonated polyimides have been successfully developed in several laboratories. Mercier and coworkers first synthesized various sulfonated copolyimides from naphthalene-1,4,5,8-tetracaboxylic dianhydride (NTDA), 2,2′-bendizine sulfonic acid (BDSA, a kind of commercially available sulfonated diamine), and common nonsulfonated diamine monomers.[5] These sulfonated copolyimide membranes were practically tested in a fuel cell system and showed fairly good performance. However, the proton conductivity of these membranes is rather low ($<10^{-2}$ S cm^{-1}, at 100% relative humidity) due to the low ion exchange capacity (IEC) which is essential for maintaining hydrolysis stability of the membranes. The fairly short lifetime (maximum: 3000 h) comparing with that of the fuel cells using Nafion membrane is another problem. Litt's group has also used BDSA as the sulfonated diamine monomer for preparation of various random and sequenced copolyimides.[6] They reported that some copolyimide membranes containing bulky and/or angled comonomers produced higher conductivities at all humidities than Nafion.[6] However, the poor hydrolysis stability of their membranes is still a problem. McGrath et al. prepared a series of sulfonated polyimides from both BDSA and another kind of commercially available sulfonated diamine, 2,5-diaminobenzenesulfonic acid (DABSA),[7a,b] but no information in proton conductivity and membrane stability can be found. They also reported on a new sulfonated diamine, 3-sulfo-4′,4”-bis(3-aminophenoxy)triphenyl phosphine oxide sodium salt (SBAPPO), and the related polyimides,[7c] but similarly, no data for proton conductivity and membrane stability were demonstrated.

To develop high performance membranes with both high proton conductivity and good stability, the “structure−property” relationship of the sulfonated polyimides should be systematically studied. Although, as mentioned before, much work has been done on BDSA-based copolyimides (polymer structure was modified by only changing the *non*-sulfonated diamine moieties), few studies on different sulfonated diamines-based (co)polyimides can be found in the literature, which are obviously very important for identifying the “structure−property” relationship. As there are only three kinds of commercially available sulfonated diamines, BDSA, DABSA, and 5,5′-dimethylbenzidine-2,2′-disulfonic acid (DMBDSA), syntheses of various new sulfonated diamine monomers are greatly desired. Recently we have synthesized a sulfonated diamine, 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), and found that

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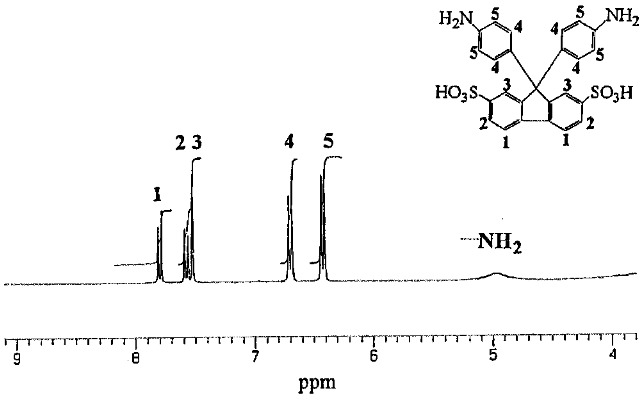


Figure 1. ^{1}H NMR spectrum of BAPFDS in DMSO-d_6 in the presence of trace amount of triethylamine.

ODADS-based polyimide membranes displayed similar proton conductivity but much better hydrolysis stability than BDSA-based ones with similar IEC.[8] In this article, a new kind of sulfonated diamine, 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS), and a series of BAPFDS-based polyimides with controlled sulfonation degrees were synthesized. Proton conductivity and water stability of these polyimide membranes were also investigated and compared with those of BDSA- and ODADS-based ones in order to make a contribution on the understanding of the "structure−property" relationship of sulfonated polyimides.

Experimental Section

Materials. NTDA, ODA, 4,4′-bis(4-aminophenoxy)biphenyl (BAPB), 9,9-bis(4-aminophenyl)fluorene (BAPF), and bis[4-(3-aminophenoxy)phenyl] sulfone (BAPPS) were purchased from Tokyo Kasei Co. NTDA and ODA were purified by vacuum sublimation before use. BAPB and BAPF were used as received. BAPPS was recrystallized from ethanol prior to use. Concentrated sulfuric acid (95%), fuming sulfuric acid (SO_3, 60%), *m*-cresol, ethyl acetate, and benzoic acid were purchased from Wako Co. and were used as received. Triethylamine (Et_3N) was dried with molecular sieve 4A prior to use.

Synthesis of 9,9-Bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS). To a 100 mL of three-neck flask equipped with a mechanical stirring device was charged 1.74 g (5.0 mmol) of 9,9-bis(4-aminophenyl)fluorene (BAPF). The flask was cooled on an ice bath, and then 2 mL of concentrated (95%) sulfuric acid was slowly added with stirring. The mixture was slowly heated to 55 °C and kept at this temperature until the BAPF was completely dissolved. The solution mixture was recooled to 0 °C on an ice bath, and 1.0 mL of fuming (SO_3 60%) sulfuric acid was added dropwise. The reaction mixture was stirred at 0 °C for 0.5 h and then slowly reheated to 60 °C for 2 h. After cooling to room temperature, the mixture was carefully poured into crushed ice. The resulting white precipitate was filtered off and then dissolved in sodium hydroxide solution. The solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The resulting precipitate was filtered off, washed with water and methanol successively, and dried at 80 °C in vacuo. Thus, 2.1 g of reddish product was obtained. Yield: 83%. Mp (DSC): 271 °C. IR spectrum (KBr, cm^{-1}): 3441, 2910, 2608, 1631, 1506, 1458, 1395, 1325, 1178, 1098, 1028, 1006, 823, 797, 740, 709, 620. The ^{1}H NMR spectrum (see Figure 1) was measured in DMSO-d_6 in the presence of a drop of Et_3N for dissolution of BAPFDS.

Synthesis of NTDA-BAPFDS Homopolyimide. To a 100 mL of completely dried 4-neck flask were added 0.762 g (1.5 mmol) of BAPFDS, 5 mL of *m*-cresol, and 0.51 mL of triethylamine successively under nitrogen flow. After the BAPFDS was completely dissolved, 0.402 g (1.5 mmol) of NTDA and 0.26 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 the reaction mixture was cooled to 80 °C, an additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into ethyl acetate. The fiberlike precipitate was filtered off, washed with acetone thoroughly, and dried in vacuo at 60 °C for 15 h.

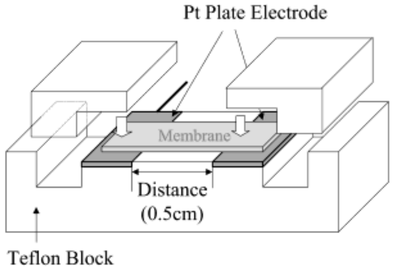


Figure 2. Schematic diagram of proton conductivity measurement cell.

Synthesis of Random Copolyimides. The above procedures were followed except that a nonsulfonated diamine (ODA, BAPB, or BAPPS) was used as a comonomer. The molar ratios between BAPFDS and the nonsulfonated diamines were in the range from 4:1 to 1:1.

Synthesis of Sequenced Copolyimides. A literature method[5] was used for preparation of sequenced copolyimides from NTDA, BAPFDS, and ODA or BAPPS. A typical experimental procedure is described as follow, using NTDA-BAPFDS/ODA(2/1)-s ($r_1 = n_{NTDA}/n_{BAPFDS} = 5/6$, and $r_2 = n_{BAPFDS}/n_{ODA} = 2/1$) sequenced polyimide as an example.

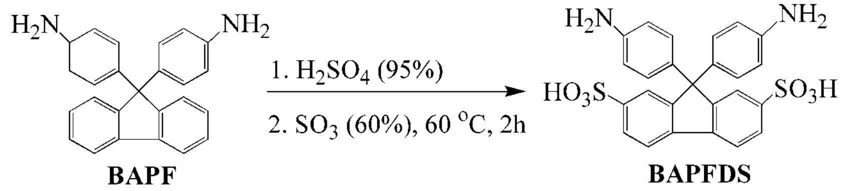
To a 100 mL of completely dried 4-neck flask were added 0.6096 g (1.2 mmol) of BAPFDS, 6 mL of *m*-cresol, and 0.41 mL of triethylamine successively under nitrogen flow. After the BAPFDS was dissolved completely, 0.268 g (1.0 mmol) of NTDA and 0.173 g of benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 16 h. After cooling to room temperature, 0.120 g (0.6 mmol) of ODA and 1 mL of *m*-cresol were added. The mixture was slightly heated with stirring. Then 0.2144 g (0.8 mmol) of NTDA and 0.138 g of benzoic acid were added. The reaction mixture was then reheated to 80 °C for 4 h and 180 °C for 20 h. Before cooling, an additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into ethyl acetate. The precipitated polyimide was collected by filtration, washed with acetone, and dried in vacuo at 60 °C for 15 h.

Film Formation and Proton Exchange. The (co)polyimides (in triethylammonium salt form) were dissolved in DMSO, and the solution was cast onto glass dishes 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 5−10 h successively. The proton-exchanged films were thoroughly washed with deionized water and then dried in vacuo at 150 °C for 20 h.

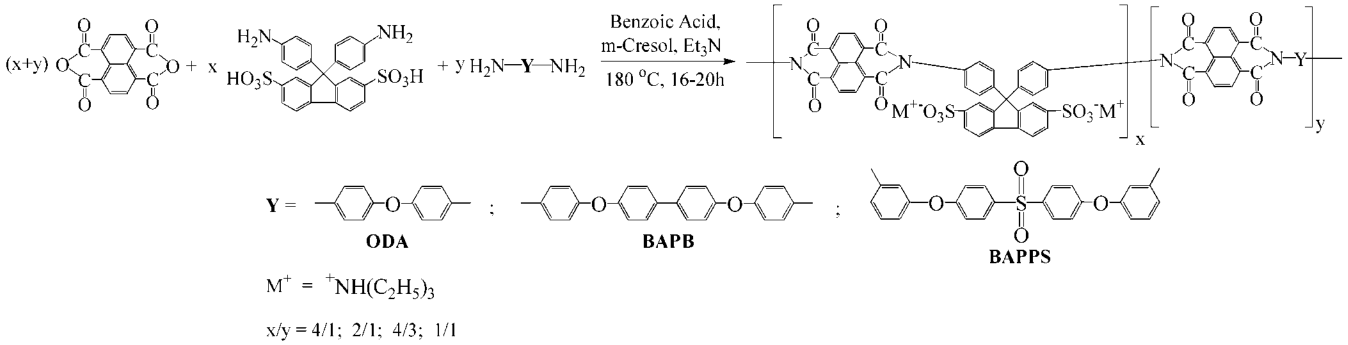
Measurements. Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Differential scanning calorimetry (DSC) was performed with a Seiko DSC-5200 at a heating rate of 10 °C/min. Thermogravimetry-mass spectroscopy (TG-MS) was measured with a JEOL MS-TG/DTA220 in helium (flow rate: 100 cm^3/min) at a heating rate of 5 °C/min. Gel permeation chromatography (GPC) was performed with a HLC-8020 apparatus (column: Shodex KD-80 M). NMP was used as the eluant at a flow rate of 1.0 mL/min. Polymer solutions containing 0.05 M of LiCl and 0.05 M of phosphoric acid were filtered through a 0.5 μm PTFE filter prior to injecting into the column. Molecular weights were calculated against poly(ethylene oxide) standards.

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). The schematic view of the cell is illustrated in Figure 2. A sheet of

Scheme 1



Scheme 2



membrane (1.0 × 0.5 cm^2) and two blackened platinum plate electrodes were set in a Teflon cell. The distance between two electrodes was 0.5 cm. The cell was placed in either a thermocontrolled humidic chamber to measure the temperature and humidity dependence of proton conductivity (from measurement at relative humidity lower than 100%) or distilled deionized water (for measurement at 100% relative humidity). The resistance value associated with the membrane conductance was determined from a high-frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = D/(LBR) \tag{1}$$

where *D* is the distance between the two electrodes, *L* and *B* are the thickness and width, 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 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

$$S = (W_s - W_d)/W_d \times 100\ (\%) \tag{2}$$

where W_d and W_s are the weights 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.

Results and Discussion

Synthesis and Characterization of the Monomer and Polyimides. BAPFDS was synthesized by direct sulfonation of the parent diamine BAPF as shown in Scheme 1. BAPF was primarily dissolved in concentrated sulfuric acid and consequently sulfonated with fuming sulfuric acid (60% SO_3) at 60 °C. The sulfonation reaction occurred in the 2,7-positions of the fluorenylidene ring because these two positions are more reactive than other ones. The two phenyl-rings to which two amino groups are attached are less reactive due to the strong electron withdrawing effect of the protonized amino groups. ^1H NMR (Figure 1) and IR spectra confirmed the chemical structure of the product.

As shown in Scheme 2, the preparation of BAPFDS-based homopolyimide and random copolyimides were carried out by a one-step method in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid (catalyst), which has been employed for preparation of many other sulfonated polyimides in the literature.[5] Sequenced copolyimides were also prepared according to a literature method,[5] and the polymerization was performed via two stages in one pot (Scheme 3). At first, an excess of BAPFDS was used to polymerize with NTDA to give an amine end-capped sulfonated polyimide oligomer which was then further polymerized with a nonsulfonated diamine (ODA or BAPPS) and NTDA. The molar ratio between BAPFDS and NTDA in the first step was controlled to be 6:5. To distinguish the resulting copolyimides, the letter r or s was added in the end of a copolyimide's name (r and s refer to random and sequenced, respectively).

The resulting polyimides (in triethylammonium form) generally showed fairly good solubility in both *m*-cresol and DMSO (Table 1), and the random copolyimides were more readily soluble than the sequenced ones. NTDA-BAPFDS/BAPPS(2/1)-s had better solubility than NTDA-BAPFDS/ODA(2/1)-s despite of the lower IEC of the former. In addition, it should be noted that although NTDA-BAPFDS/ODA(2/1)-s and NTDA-BAPFDS/BAPB-(4/3)-r could be dissolved in *m*-cresol and DMSO, the solutions were not very clear and the cast films were not so transparent. Nevertheless, the cast films showed good mechanical strength.

Proton exchange of the polyimide membranes was performed with 1.0 N hydrochloric acid, and the completion of proton exchange was confirmed by ^1H NMR measurement judging from the disappearance of the peaks corresponding to triethylamine.

All the prepared polyimides displayed fairly high molecular weights. NTDA-BAPFDS and NTDA-BAPFDS/ODA(2/1)-r (in proton form), for example, had weight-averaged molecular weights of 32 000 and 37 000, respectively. In addition, for all the polyimides no glass transition temperature (T_g) was observed from the DSC curves. TG−MS measurement revealed that BAPFDS-based polyimides had fairly good thermal stability. The sulfonic acid groups of NTDA-BAPFDS homopolyimide started to decompose around 270 °C judging from the

Scheme 3

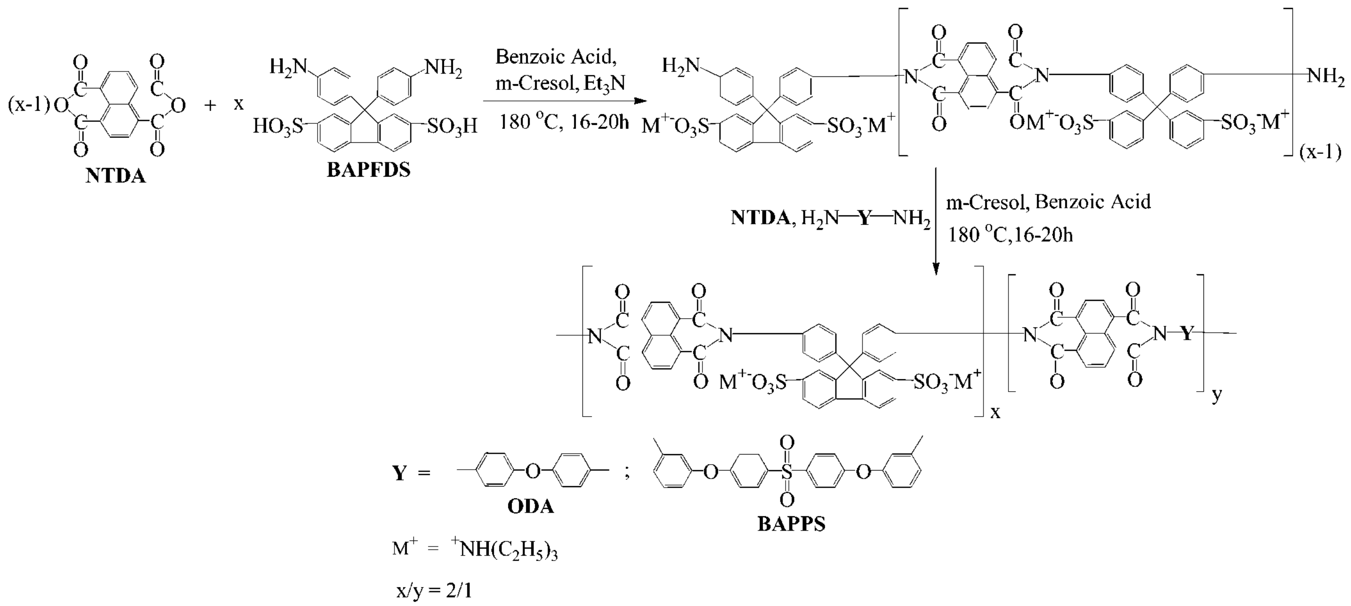


Table 1. Solubility Behaviors of Various Sulfonated Polyimides in Triethylammonium Salt Form

polyimide	*m*-cresol	DMSO	NMP	DMAc
NTDA-BAPFDS	+[b]	+	−	−
NTDA-BAPFDS/ODA(4/1)-r	+	+	−	−
NTDA-BAPFDS/ODA(2/1)-r	+	+	−	−
NTDA-BAPFDS/ODA(1/1)-r	+	+	−	−
NTDA-BAPFDS/BAPB(4/3)-r	+	+	−	−
NTDA-BAPFDS/BAPPS(2/1)-r	+	+	−	−
NTDA-BDSA/BAPB(1/1)-r[a]	+ −	−	−	−
NTDA-BAPFDS/ODA(2/1)-s	+	+	−	−
NTDA-BAPFDS/BAPPS(2/1)-s	+	+	−	−

[a] Ref 8. [b] Key: "+", soluble; "+ −", partially soluble; "−", insoluble.

evolution of sulfur monoxide and sulfur dioxide, which was at the same level as that of NTDA-ODADS.

Proton Conductivity. The proton conductivities of BAPFDS-based polyimide membranes were measured at 50 °C as a function of relative humidity (see Figure 3). For comparison purpose, the data of another type of polyimide membrane, NTDA-ODADS/ODA(3/1)-r, as well as Nafion 117[9] are also shown in this figure. It can be seen that for all the polyimide membranes the proton conductivities increased sigmoidally with increasing the relative humidity, which is a typical behavior as has been observed for Nafion 117 and many other sulfonated polymer membranes. The homopolyimide membrane, NTDA-BAPFDS, displayed the highest proton conductivity among the polyimide membranes due to the highest IEC (see Table 2). Decreasing the sulfonation degree led to a decrease in proton conductivity. However, it should be noted that although NTDA-BAPFDS and NTDA-ODADS/ODA(3/1)-r had the same IEC, the former showed much higher proton conductivities than the latter especially at low humidities. This might be related to their different structures and the detailed studies on the mechanism are in progress.

From Figure 3, it can also be seen that the proton conductivity is also affected by the morphology of polyimide membranes. NTDA-BAPFDS/ODA(2/1)-s showed about 50% larger conductivity than NTDA-BAPFDS/ODA(2/1)-r at the same relative humidity.

It is interesting to compare the proton conductivities of the polyimide membranes with that of Nafion 117.

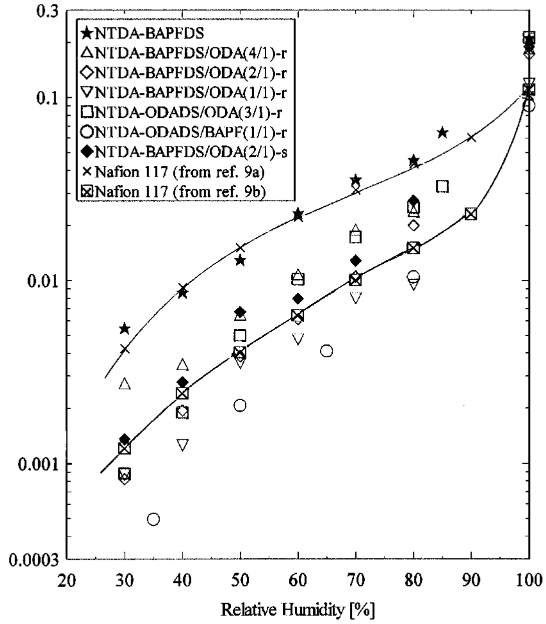


Figure 3. Variation of the proton conductivities of sulfonated polymer membranes as a function of relative humidity at 50 °C.

The proton conductivity of Nafion 117 membrane as a function of relative humidity has been investigated in several laboratories. However the data are quite different from each other. As shown in Figure 3, the upper line was depicted according to the data reported by Miyatake with the membrane being pretreated via a complicated process and finally dried at 110 °C.[9a] The lower line was obtained from the data reported by Sone,[9b] and the membrane was also pretreated in a roughly similar way to that described in ref 9a but the final drying temperature was 80 °C. The upper line was reproduced in our laboratory by treating the membrane using the literature method, and therefore, it is used for comparison. It can be seen that NTDA-BAPFDS showed quite similar proton conductivities to Nafion 117 at the relative humidity below 100%. Other polyimide membranes displayed significantly poorer proton-con-

Table 2. Thickness, IEC, Water Uptake, Proton Conductivity at 50 °C, and Water Stability of Various Sulfonated Polyimide Membranes

				σ (S cm^{-1})		membrane stability[e]			
membrane	thickness (μm)	IEC (mequiv g^{-1})	water uptake[b] (% w/w)	RH = 50%	RH = 100%	T (°C)	t (h)	stability	ref
NTDA-BAPFDS	40	2.70	122	0.013	0.21	50 80	50 5	○ dissolved	g
NTDA-BAPFDS/ODA(4/1)-r	15	2.36	100	0.0065	0.20	80	6	×	g
NTDA-BAPFDS/ODA(2/1)-r	28	2.09	76	0.0038	0.17	80	20	○	g
NTDA-BAPFDS/ODA(1/1)-r	30	1.71	57	0.0035	0.12	80	26	○	g
NTDA-BAPFDS/BAPB(4/3)-r	30	1.68	56	NM[c]	0.10	80	27	○	g
NTDA-BAPFDS/BAPPS(2/1)-r	25	1.87	69	NM[c]	0.11	80	20	○	g
NTDA-BAPFDS/ODA(2/1)-s	23	2.09	102	0.0067	0.19	80	7	×	g
NTDA-BAPFDS/BAPPS(2/1)-s	25	1.87	77	NM[c]	0.14	80	14	×	g
NTDA-BDSA/ODA(1/1)-r	34	1.98	79	0.0030	0.11	80	5	×	8
NTDA-BDSA/mAPFI(60/40)-s[a]	~20	1.86	46.5	–[c]	0.0083[d]	80	~200[f]	×	5d
NTDA-ODADS/ODA(3/1)-r	44	2.70	113	0.0050	0.21	80	15	dissolved	g
NTDA-ODADS/ODA(1/1)-r	34	1.95	87	0.0032	0.12	80	25	○	8
NTDA-ODADS/BAPF(1/1)-r	37	1.71	69	0.0021	0.090	80	13	×	8
NTDA-ODADS/BAPB(1/1)-r	36	1.68	57	0.0025	0.10	80	200	○	8

[a] mAPFI refers to bis[3-aminophenoxy)-4-phenyl]hexafluoroisopropylidene. [b] Measured at 80 °C except for NTDA-BAPFDS and NTDA-ODADS/ODA(3/1) at 50 °C and NTDA-BDSA/mAPFI(60/40)-s at room temperature. [c] NM: not measured. –: not given in the literature. [d] At room temperature. [e] T: temperature. t: time. ○: mechanical strength was maintained. ×: membrane was broken when being lightly bent. [f] No description of the criterion for judgment of loss of mechanical properties of the membrane is given in the literature. [g] This study.

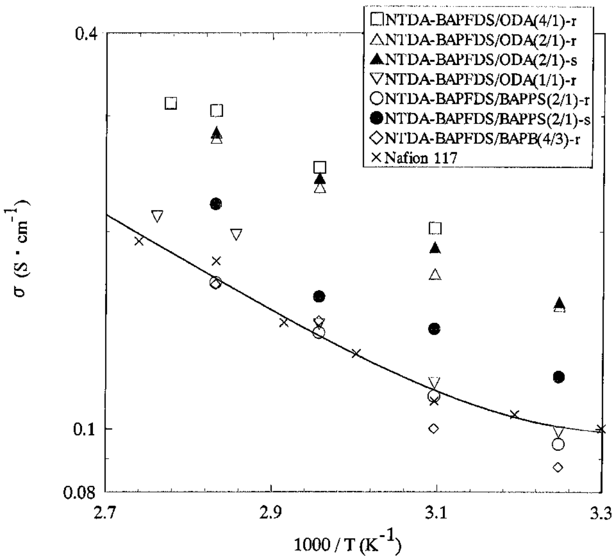


Figure 4. Temperature dependence of the proton conductivities of sulfonated polymer membranes at 100% relative humidity.

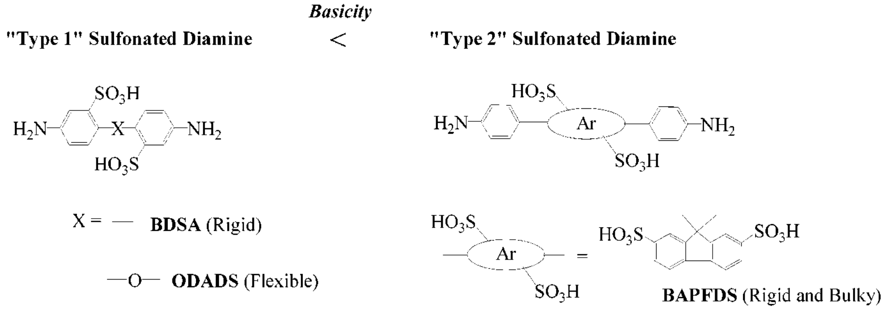
ducting performance than Nafion 117 (the upper line) despite of their much larger IEC values. This is probably because the sulfonated polyimide membranes had homogeneous structure (no significant microphase separation), whereas Nafion had the unique ion-rich channels (clusters) which were favorable for proton transport. Nevertheless, it should be noted that the proton conductivities of all the present polyimide membranes are much larger (over 1 order of magnitude) than those reported in the literature.[5]

Figure 4 shows the temperature dependence of proton conductivity of the polyimide membranes at 100% relative humidity. The conductivity of Nafion 117 shown in this figure was determined in our laboratory. For all the membranes, the proton conductivity increased as temperature increased. In addition, unlike the case of the humidity dependence shown in Figure 3, at 100% relative humidity all the polyimide membranes displayed similar or higher proton conductivities than Nafion 117, indicating good proton-conducting performance of these membranes. This is probably because at 100% relative humidity the polyimide membranes are in fully hydrated state and the transport of protons becomes quite easy, making the effect of channels (for facilitation of proton transport) less important. The morphology had a rather weak effect on proton conductivity of the membranes in the fully hydrated state. The sequenced polyimide membranes displayed similar or only a little higher proton conductivities than the corresponding random ones.

Water Uptake and Membrane Stability. Table 2 lists water uptake and water stability of the polyimide membranes at 80 or 50 °C. Membranes with higher IEC values tended to have larger water uptake. The sequenced copolyimide membranes showed higher water uptake than the corresponding random ones.

The stability toward water of the polyimide membranes was examined by soaking the membranes into distilled water at a given temperature (50 or 80 °C) and was characterized by the expended time until the hydrated membranes lost mechanical properties. The criterion for the judgment of the loss of mechanical properties is that the membrane is broken when being lightly bent. As shown in Table 2, the homopolyimide membrane, NTDA-BAPFDS, was relatively stable only at low temperature (50 °C), and it could be completely dissolved in water at 80 °C due to the high IEC. Decreasing the sulfonation degree by incorporation of nonsulfonated diamines to the polyimide structure led to a significant improvement in water stability of the membranes. All the copolyimide membranes were insoluble at elevated temperature (e.g., 80 °C) and could keep their forms even after being soaked in water at 80 °C for more than 200 h. However, there is still large difference in stability between these copolyimide membranes. According to the foregoing criterion for the judgment of the loss of mechanical properties of membranes, NTDA-BAPFDS/ODA(4/1)-r became somewhat

Scheme 4



brittle after being soaked at 80 °C for 6 h. The stability of the membranes was improved by decreasing the IEC. NTDA-BAPFDS/ODA(1/1), for example, could maintain mechanical strength after being soaked at 80 °C for 26 h. In addition, the morphology of the polyimide membranes also had great effect on water stability. The random copolyimides showed much better stability than the corresponding sequenced ones.

It is interesting to compare the stability of BAPFDS-based polyimide membranes with that of BDSA- and ODADS-based ones. Although NTDA-BAPFDS/ODA(2/1)-r had even a little larger IEC than NTDA-BDSA/ODA(1/1)-r, the stability was much better for the former than for the latter. On the other hand, the difference in water stability between NTDA-BAPFDS/ODA(2/1)-r and NTDA-ODADS/ODA(1/1)-r was less significant. In a previous paper,[8] we have reported that the flexibility of polymer chains and the IEC had great effects on water stability of the polyimide membranes. Flexible structure and lower IEC result in better water stability and vice versa. ODADS-based polyimide membranes had fairly flexible structure due to the flexible linkage of ether bond in ODADS moiety, whereas BDSA-based ones had rather rigid structure. Therefore, ODADS-based polyimide membranes displayed much better water stability than the corresponding BDSA-based ones with similar IEC. In the present case, although BAPFDS is a kind of rigid and bulky diamine monomer, the stability of BAPFDS-based copolyimide membranes is not so poor as expected. In fact, BAPFDS-based random copolyimide membranes displayed much better water stability than BDSA-based ones with the same nonsulfonated diamine moiety (ODA) and similar IEC. NTDA-BAPFDS/ODA(1/1)-r and NTDA-ODADS/BAPF-(1/1)-r had the same IEC and chain flexibility, and the difference in structure between the two kinds of copolyimides is only that the sulfonic acid groups are attached in different diamine moieties. However, NTDA-BAPFDS/ODA(1/1)-r displayed much better water stability than NTDA-ODADS/BAPF(1/1)-r. This clearly indicates the stability of polyimide membranes depends not only on the flexibility of polymer chains and the IEC but also on other factor(s). A common structural feature between ODADS and BDSA is that the sulfonic acid groups are directly attached to the phenyl rings to which the amino groups are attached, and here they are noted as "type 1" sulfonated diamines. Unlike the case of ODADS and BDSA, the sulfonic acid groups of BAPFDS are attached to the bridged phenyl rings, and it is noted as "type 2" sulfonated diamine (Scheme 4). Because the sulfonic acid group is a strong electron-withdrawing group, the electron density of the phenyl rings to which the amino groups are attached should be larger for BAPFDS than for ODADS or BDSA; i.e., BAPFDS is more basic than ODADS or BDSA. It is well-known that aromatic diamines with higher basicity are generally more reactive with dianhydrides than those with lower basicity.[10] Since hydrolysis is the reverse reaction of polymerization, polyimides derived from more basic diamines should have higher hydrolysis stability. As a result, the high basicity of BAPFDS is favorable for maintaining the stability of the imido rings, which offsets the unfavorable effect on water stability due to the rigid structure, and this might be the reason that BAPFDS-based polyimide membranes had much better water stability than BDSA-based ones with similar IEC. Further studies on the structural effects on the stability of the polyimides derived from "type 2" diamines are in progress.

It should be noted that, although Mercier et al. declared that the stability of their membrane, NTDA-BDSA/mAPFI(60/40)-s, was around 200 h at 80 °C,[5d] it cannot be simply used to compare with that of our membranes because they did not give any description how they judged the loss of mechanical properties of their membranes. Using our criterion for judgment of loss of mechanical strength, the stability of NTDA-BDSA/mAPFI(60/40)-s might be at the same level as that of NTDA-BDSA/ODA(1/1)-r because of their roughly similar IEC values and rigidities of polymer chains.

Although the present BAPFDS-based polyimide membranes showed much better water stability than the corresponding BDSA-based ones, these membranes might be good candidates only for the application in low-temperature (<80 °C) fuel cell systems. For high temperature (>100 °C) use, the stability of these membranes might not be sufficiently good enough yet.

The stability of the polyimides to oxidation was also investigated by immersing the membranes (the size of each sheet: 0.5×1.0 cm^2) into Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2; see ref 11) at room temperature. The oxidative stability of the membranes was characterized by the expended time that the membranes started to become a little brittle (the membranes were broken when being lightly bent) or started to dissolve in the solution. As shown in Table 3, BAPFDS-based random copolyimide membranes generally showed fairly good oxidative stability which was comparable to that of ODADS-based ones, whereas the sequenced ones displayed rather poor oxidative stability.

Conclusions

1. A novel sulfonated diamine monomer, BAPFDS, was successfully synthesized by direct sulfonation of the parent diamine, BAPF. A series of sulfonated polyimides were prepared from NTDA, BAPFDS, and common nonsulfonated diamines.

Table 3. Results of Fenton's Reagent Test of Various Sulfonated Polyimide Membranes at Room Temperature

membrane	thickness (μm)	τ_1[a] (h)	τ_2[a] (h)	ref
NTDA-BAPFDS/ODA(4/1)-r	58	17	21	*b*
NTDA-BAPFDS/ODA(1/1)-r	23	18	22	*b*
NTDA-BAPFDS/BAPB(4/3)-r	31	22	26	*b*
NTDA-BAPFDS/BAPPS(2/1)-r	26	21	26	*b*
NTDA-BAPFDS/ODA(2/1)-s	30	12	16	*b*
NTDA-BAPFDS/BAPPS(2/1)-s	21	7	10	*b*
NTDA-BDSA/ODA(1/1)-r	21	13	20	8
NTDA-ODADS/BAPF(1/1)-r	40	29	32	8

[a] τ_1 and τ_2 refer to the expended time that the membranes became a little brittle and started to dissolve in the solution, respectively. [b] This study.

2. Although NTDA-BAPFDS and NTDA-ODADS/ODA(3/1)-r polyimide membranes had the same IEC, the proton conductivity was much larger for the former than for the latter at relative humidity below 100%. At 100% relative humidity, all the BAPFDS-based polyimide membranes displayed similar or higher proton conductivities than Nafion 117, indicating good proton-conducting performance.

3. Besides the flexibility and the IEC, the basicity of the sulfonated diamine moieties also had great effect on water stability of the polyimide membranes. BAPFDS-based polyimide membranes displayed much better water stability than the corresponding BDSA-based ones with similar IEC because for the former the unfavorable effect due to the rigid structure was offset by the favorable effect due to the high basicity of BAPFDS.

4. The sequenced polyimide membranes displayed similar or only a little higher proton conductivities but much poorer water stability and oxidative stability than the corresponding random ones, indicating relatively poor performance of the former.

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