Novel Sulfonated Polyimides as Polyelectrolytes for Fuel Cell Application. 1. Synthesis, Proton Conductivity, and Water Stability of Polyimides from 4,4′-Diaminodiphenyl Ether-2,2′-disulfonic Acid

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ABSTRACT: A sulfonated diamine monomer, 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), was successfully synthesized by direct sulfonation of a commercially available diamine, 4,4′-diamino-diphenyl ether (ODA), using fuming sulfuric acid as the sulfonating reagent. A series of sulfonated polyimides were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), ODADS, and common nonsulfonated diamines. The resulting sulfonated polyimides displayed much better stability toward water than those derived from the widely used sulfonated diamine 2,2′-benzidinedisulfonic acid (BDSA). This is because ODADS-based polyimide membranes have a more flexible structure than the corresponding BDSA-based ones. Fenton's reagent test revealed that ODADS-based polyimide membranes also had fair good stability to oxidation. Polyimide membranes with good water stability as well as high proton conductivity were developed. NTDA−ODADS/BAPB(1/1) copolyimide membrane (BAPB refers to 4,4′-bis(4-aminophenoxy)biphenyl)), for example, did not lose mechanical properties after being soaked in water at 80 °C for 200 h, while its proton conductivity was still at a high level (comparable to that of Nafion 117).

Introduction

Polymer electrolyte fuel cells (PEFCs) have been identified as promising power sources for vehicular transportation and for other applications requiring cleaning, quiet, and portable power.[1,2] The most important component of a PEFC is polymer electrolyte membrane itself. At present, sulfonated perfluoropolymers such as Nafion have been almost the only advanced membranes that are used in practical systems due to their high proton conductivity, good mechanical strength, and high thermal and chemical stability.[1] Unfortunately, however, there are some demerits which seriously limit their application. These include high cost, low conductivity at low humidity or high temperatures, and high methanol permeability. Thus, the development of alternative materials overcoming these problems is strongly desired. Up to now, a large number of sulfonated polymers such as poly(styrene sulfonic acid) and the analogous polymers,[3] sulfonated polysulfone,[4] sulfonated poly(ether ether ketone),[5] and sulfonated poly-(phenylene sulfide)[6] have been developed, and very recently sulfonated polyimides have been reported to be promising materials for PEFC.[7]

It is well-known that aromatic polyimides have found wide applications in many industrial fields due to their excellent thermal stability, high mechanical strength, good film forming ability, and superior chemical resistance. These merits are just what is required for the polyelectrolyte membrane materials used in fuel cell systems. However, common five-membered ring polyimides are generally unstable toward acid due to the ease of hydrolysis of imido rings, and sulfonated polyimides are expected to be more unstable than the nonsulfonated ones. Six-membered ring polyimides

derived from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) have been found to be fairly stable toward both acid and pure water.[7,8] Faure and his workers might be the first who successfully synthesized a series of sulfonated five-membered and six-membered ring polyimides from oxydiphthalic dianhydride (ODPA) and NTDA, respectively, which were practically tested in fuel cell systems.[9,10] Their results indicated that ODPA-based polyimides were not stable enough in fuel cell conditions, whereas NTDA-based ones were fairly stable as long as the sulfonation degree was controlled to an appropriate level. The introduction of sulfonic group to polymer structure was achieved by using a commercially available sulfonated diamine monomer, 2,2′-benzidinedisulfonic acid (BDSA). Sulfonation degree could be precisely controlled by regulating the molar ratio between BDSA and common nonsulfonated diamines such as 4,4′-diaminodiphenyl ether (ODA) during copolymerization process. It is well-known that the control of sulfonation degree is very important because high sulfonation degree generally leads to high swelling degree or even dissolution in water of the membranes. However, low sulfonation degree generally results in poor proton conductivity, and therefore it seems that improving membrane stability and enhancing proton conductivity are contradictory to each other. Indeed, the proton conductivities of BDSA-based copolyimides reported in the literature[7] are rather poor ($<10^{-2}$ S/cm at fully hydrated state and room temperature) due to the rather low sulfonation degree. On the other hand, so far, little information on the relationship between membrane stability and polyimide structure (diamine moiety) can be found in the literature. To systematically study the "structure−property" relationship of sulfonated polyimides, novel sulfonated polyimides are desired. However, besides BDSA, the only commercially available sulfonated diamines are 2,5-diaminobenzene-

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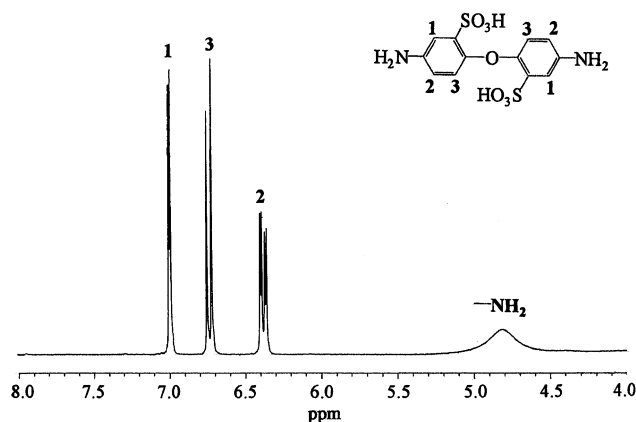* To whom correspondence should be addressed. E-mail: okamotok@po.cc.yamaguchi-u.ac.jp.

Figure 1. ^{1}H NMR spectrum of ODADS.

sulfonic acid (DABS) and 5,5′-dimethylbenzidine-2,2′-disulfonic acid (DMBDS). DABS-based polyimides generally have poor solubility and poor mechanical properties, and therefore, DBSA is seldom used. DMBDS-based polyimides are expected to have similar properties to BDSA-based ones due to their similar structure. Therefore, the development of novel sulfonated diamine monomers is strongly desired. In this paper, a sulfonated diamine monomer, 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), was synthesized, and a series of ODADS-based polyimides were prepared. Physical properties, proton conductivity, and water stability of these polyimides were also investigated.

Experimental Section

Materials. NTDA, 4,4′-diaminodiphenyl ether (ODA), 4,4′-bis(4-aminophenoxy)biphenyl (BAPB), and 9,9-bis(4-aminophenyl)fluorene (BAPF) were purchased from Tokyo Kasei Co., and were purified by vacuo sublimation prior to use. 2,2-bis-(4-aminophenyl)hexafluoropropane (BAPHF) was also purchased from Tokyo Kasei Co., and was used as-received. BDSA, triethylamine (Et₃N), *m*-cresol, concentrated sulfuric acid (95%), and fuming sulfuric acid (SO₃, 60%) were purchased from Wako Chemical Co.. BDSA was soaked in boiling deionized water for several hours, filtered while hot, and washed thoroughly with boiling water followed by drying at 90 °C in vacuo prior to use. Et₃N was distilled and dried with 4 A molecular sieve prior to use. *m*-Cresol was used as received.

Synthesis of 4,4′-Diaminodiphenyl Ether-2,2′-disulfonic Acid (ODADS). To a 100 mL three-neck flask equipped with a mechanical stirring device was charged 2.00 g (10.0 mmol) of 4,4′-diaminodiphenyl ether (ODA). The flask was cooled in an ice bath, and then 1.7 mL of concentrated (95%) sulfuric acid was slowly added with stirring. After ODA was completely dissolved, 3.5 mL of fuming (SO₃ 60%) sulfuric acid was slowly added to the flask. The reaction mixture was stirred at 0 °C for 2 h and then slowly heated to 80 °C and kept at this temperature for additional 2 h. After cooling to room temperature, the slurry solution mixture was carefully poured into 20 g of crushed ice. The resulting white precipitate was filtered off and then redissolved in a sodium hydroxide solution. The basic solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The solid was filtered off, washed with water and methanol successively, and dried at 80 °C in vacuo. Then 3.05 g of white product was obtained (yield: 85%); mp 264.8 °C. IR (KBr, cm⁻¹): 3477, 3092, 1628, 1529, 1476, 1422, 1213, 1146, 1089, 1031, 910, 892, 839, 825, 718, 705, 625. ^{1}H NMR spectrum (DMSO-d_6; Et₃N was added for dissolution in DMSO) is shown in Figure 1.

Synthesis of NTDA–ODADS and NTDA–BDSA Homopolyimides. To a 100 mL completely dried 4-neck flask were added 0.540 g (1.5 mmol) of ODADS or 0.516 g (1.5 mmol) of BDSA, 5.0 mL of *m*-cresol, and 0.36 g (3.6 mmol) of triethylamine successively under nitrogen flow with stirring.

After ODADS or BDSA was completely dissolved, 0.402 g (1.5 mmol) of NTDA and 0.26 g (2.13 mmol) 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 100 °C, an additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, which was then poured into 100 mL of acetone. The fiberlike precipitate was filtered off, washed with acetone, and dried in vacuo.

Synthesis of ODADS and BDSA-Based Copolyimides. To a 100 mL completely dried 4-neck flask were added 0.360 g (1.0 mmol) of ODADS or 0.344 g (1.0 mmol) of BDSA, 6.0 mL of *m*-cresol, and 0.24 g (2.4 mmol) of triethylamine successively under nitrogen flow with stirring. After ODADS or BDSA was completely dissolved, 1.0 mmol of nonsulfonated diamine (ODA, BAPB, BAPHF, or BAPF), 0.536 g (2.0 mmol) of NTDA, and 0.34 g (2.8 mmol) 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 100 °C, an additional 10–15 mL of *m*-cresol was added to dilute the highly viscous solution, which was then poured into 100 mL of acetone. The fiberlike precipitate was filtered off, washed with acetone, and dried in vacuo.

Film Formation and Proton Exchange. Films (in triethylammonium salt form) of the two homopolyimides, NTDA–ODADS and NTDA–BDSA, and the copolyimides derived from BAPF or BAPHF were prepared by casting their DMSO solutions (∼5 wt %) onto glass dishes and dried at 80 °C for 10 h. Other copolyimide films were prepared by casting their *m*-cresol solution at 120 °C. The as-cast films were soaked in methanol at 60 °C for 1 h to remove the residual solvent (DMSO or *m*-cresol), and then the proton exchange treatment was performed by immersing the films in 1.0 N hydrochloric acid at room temperature for 5–10 h. The films in proton form were thoroughly washed with deionized water and then dried in vacuo at 150 °C for 20 h. The thickness of the films was in the range 20–40 μm.

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 cm³/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 by an ac impedance method with two platinum electrodes using a Hioki 3552 Hitester instrument over the frequency range from 100 Hz to 100 kHz. The details of the measurement have been reported in ref 11. The standard deviations of the conductivity values were less than ±5% at relative humidities above 60% and ±8% at a relative humidity of 50%.

Water sorption experiments were carried out by immersing three sheets of films (20–30 mg per sheet) of a polyimide into water at 80 °C for 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

$$S = (W_s - W_d)/W_d \times 100 \ (\%) \tag{1}$$

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.

Tensile measurement was performed with an Intesco model 2005 instrument at 23 °C and 50% relative humidity at a crosshead speed of 1 mm/min. Sulfonated polyimide mem-
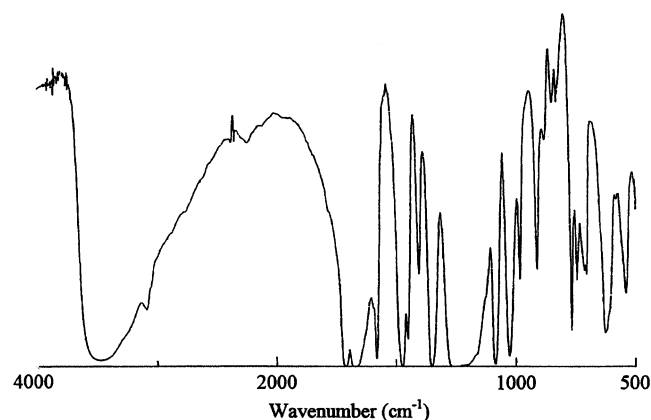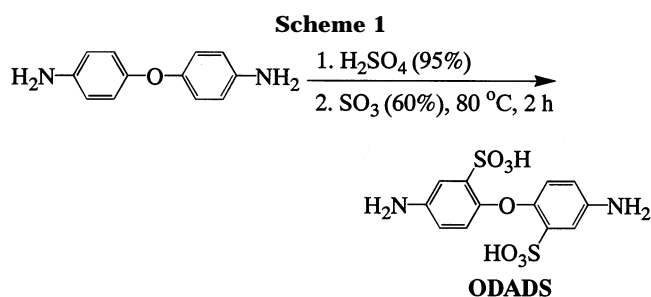
Figure 2. IR spectrum of NTDA–ODADS polyimide (proton form).

Scheme 1

branes were soaked in distilled water for 3 h and subject to tensile measurement as soon as they were taken out.

Results and Discussion

Monomer Synthesis and Polymerization. As shown in Scheme 1, ODADS was prepared by direct sulfonation of the parent diamine, ODA, using fuming sulfuric acid as the sulfonating agent. Primarily, ODA reacted with concentrated sulfuric acid to form the sulfuric acid salt of ODA. SO_3 in fuming sulfuric acid was the real sulfonating agent, which reacted with ODA when the reaction temperature was raised to 80 °C. Since the protonized amino group is a strong electron-withdrawing group, the sulfonation reaction mainly occurred in the meta position of the amino group. The ether bond in the para position of the amino group also supported such a meta-position substitution. The chemical structure of the resulting product was characterized by IR and ^1H NMR spectra.

Polymerization of NTDA and ODADS was carried out by "one-step" method in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid. Et_3N was used to liberate the protonized amino groups for polymerization with NTDA, and benzoic acid functioned as catalyst. This is a literature method which has been employed for preparation of a series of BDSA-based (co)polyimides.[4] Random copolymerization of NTDA, ODADS, and nonsulfonated diamines was also carried out using this method. For comparison purpose, BDSA-based polyimides were also prepared. The as-synthesized polyimides are in the triethylammonium sulfonate form and were converted to the proton form by treating with 1.0 N hydrochloric acid. The completion of proton exchange was confirmed from the disappearance of the peaks corresponding to the protons of triethylamine from the ^1H NMR spectra of the polyimides. Figure 2 shows the IR spectrum of proton-exchanged NTDA–ODADS polyimide. The broad absorption band around

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

polyimide	*m*-cresol	DMSO	NMP	DMAc
NTDA–ODADS	+	+	−	−
NTDA–ODADS/ODA(1/1)	+	−	−	−
NTDA–ODADS/BAPB(1/1)	+	−	−	−
NTDA–ODADS/BAPF(1/1)	+	+	−	−
NTDA–ODADS/BAPHF(1/1)	+	+	−	−
NTDA–BDSA	+	+	−	−
NTDA–BDSA/ODA(1/1)	+	−	−	−
NTDA–BDSA/BAPB(1/1)	+ −	−	−	−
NTDA–BDSA/BAPF(1/1)	+	+	−	−
NTDA–BDSA/BAPHF(1/1)	+	+	−	−

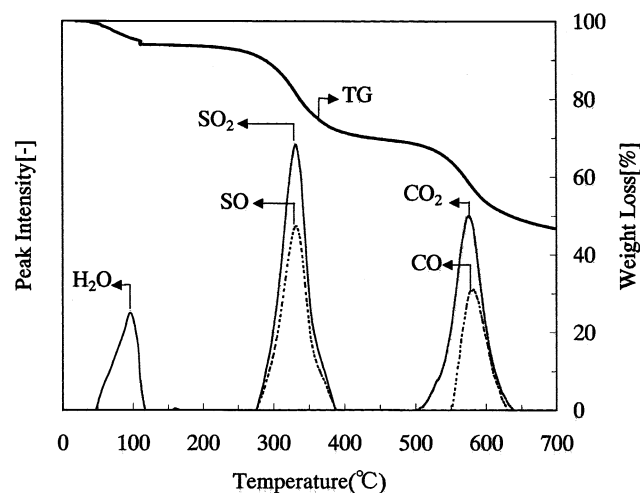[a] Key: "+", soluble; "+ −", partially soluble; "−", insoluble.

Figure 3. Thermogravimetry–mass spectroscopy (TG–MS) of NTDA–ODADS polyimide membrane (proton form).

3500 cm^{-1} is assigned to the absorbed water in the sample (the sulfonic acid groups are highly hydrophilic). The strong absorption bands around 1717 and 1671 cm^{-1} are assigned to the stretch vibration of carbonyl groups of imido rings. The broad band around 1255 cm^{-1} and the band around 1088 cm^{-1} correspond to the stretch vibrations of sulfonic acid groups.

Solubility behaviors of the sulfonated polyimides (in triethylammonium salt form) are shown in Table 1. All the polyimides except NTDA–BDSA/BAPB(1/1) are soluble in *m*-cresol but insoluble in common dipolar aprotic solvents such as NMP and DMAc, which are good solvents for many five-membered ring (nonsulfonated) polyimides. The two homopolyimides NTDA–ODADS and NTDA–BDSA and the copolyimides derived from BAPF or BAPHF are still soluble in DMSO besides in *m*-cresol, indicating a better solubility than the other ones. NTDA–BDSA/BAPB(1/1) is only partially soluble in *m*-cresol by heating. Its solution in *m*-cresol is not clear even at very low concentration (1%), and the cast films are not transparent. In fact, the preparation of this copolyimide is not successful because some precipitate formed during polymerization process. Proton exchange led to significant improvement in solubility for both ODADS and BDSA-based polyimides because most of them became soluble even in NMP by slight heating.

Thermal stability of the sulfonated polyimides was investigated by TG–MS measurement. Figure 3 shows the TG–MS curve of NTDA–ODADS polyimide (proton form). The initial weight loss around 100 °C is due to the absorbed water in the membrane. The secondary weight loss started from 288 °C is due to the decomposi-
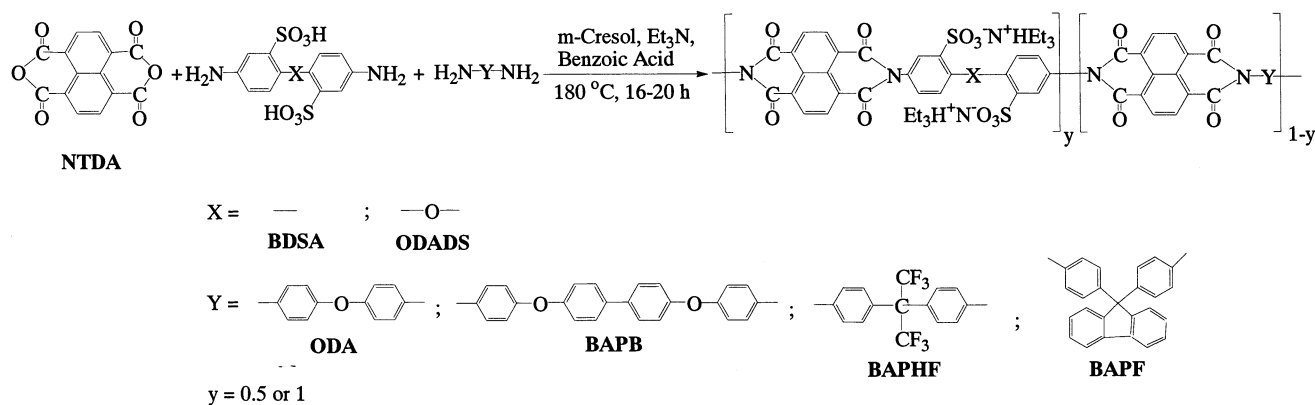
Scheme 2

X = — ; —O—
  BDSA   **ODADS**

Y = ... **ODA** ; ... **BAPB** ; ... **BAPHF** ; ... **BAPF**

y = 0.5 or 1

Table 2. Molecular Weights and Molecular Weight Distributions of Proton Exchanged Polyimides

polyimide	M_n	M_w	M_w/M_n
NTDA−ODADS	18 000	53 000	2.9
NTDA−BDSA	15 000	34 000	2.3
NTDA−ODADS/ODA(1/1)	16 000	72 000	4.5
NTDA−BDSA/ODA(1/1)	14 000	47 000	3.4

tion of sulfonic acid groups judging from the evolution of sulfur monoxide and sulfur dioxide. The TG−MS curve clearly indicates that this polyimide has fairly good thermal stability.

Table 2 lists the molecular weights and molecular weight distributions of some of the prepared polyimides (proton form) determined by GPC. The number-averaged molecular weights (M_n) of these sulfonated polyimides are roughly close to each other. However, the molecular weight distributions are different. The copolyimides showed broader molecular weight distributions than the homopolyimides.

Proton Conductivity. Table 3 lists the ion exchange capacities (IECs) and proton conductivities of the sulfonated polyimide membranes at 50 °C and different humidities. Here the data of IEC refer to the theoretical values because the completion of proton exchange was confirmed by ^{1}H NMR spectra for every polyimide membrane. Since the difference in molecular weights between BDSA and ODADS is not large, these two types of polyimides with similar chemical composition (e.g., NTDA−ODADS/ODA(1/1) and NTDA−BDSA/ODA(1/1)) displayed similar IEC values. Proton conductivities of these polyimide membranes are strongly dependent on their IEC values and the relative humidities, i.e., membranes with higher IEC tend to have higher proton conductivity, and for the same polyimide membrane the proton conductivity increases with increasing the relative humidity. The homopolyimide NTDA−ODADS had the highest IEC value and therefore the highest proton conductivity. Another kind of homopolyimide, NTDA−BDSA, had very poor membrane stability, and therefore the proton conductivity was not measured. Among the copolyimides, NTDA−ODADS/ODA(1/1) and NTDA−BDSA/ODA(1/1) had a little larger IEC values; however, their proton conductivities were similar to those of the other ones. In addition, although all the copolyimide membranes had much larger IEC values than Nafion 117, their proton conductivities were roughly in the same level as that of Nafion 117. This is probably because Nafion had unique ion-rich channels (clusters) which were favorable for proton transport, whereas the present copolyimide membranes might have a rather
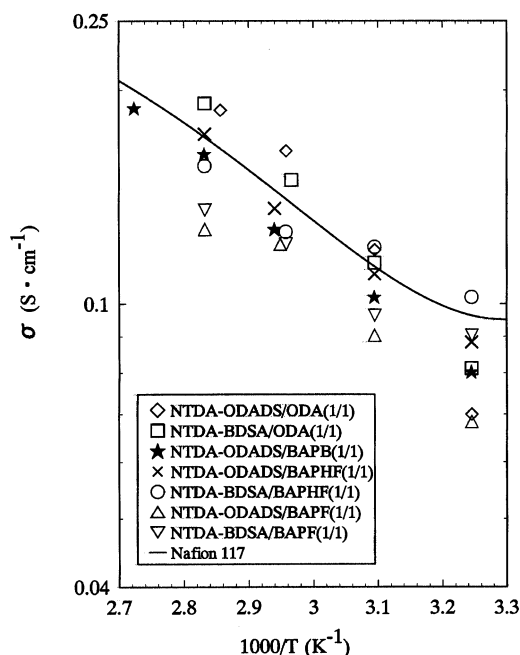

Figure 4. Variation of proton conductivities of sulfonated polymer membranes as a function of temperature at a relative humidity of 100%.

homogeneous structure. The small-angle X-ray scattering spectra of ODADS-based copolyimides in ambient atmosphere were measured, but no clear peak corresponding to the ionic domains separated from the hydrophobic polymer matrix was observed, suggesting that these copolyimides might have rather homogeneous structure. Nevertheless, the proton conductivities of these copolyimide membranes are much larger than those reported in the literature.[7b] For example, as shown in Table 3, the two sequenced copolyimides CH₃ 5 50/50 and CF₃ 5 50/50 reported in the literature displayed more than one order lower proton conductivities than the present copolyimide membranes. Figure 4 shows the variation of proton conductivity of the copolyimide membranes at 100% relative humidity as a function of temperature. All the membranes displayed increased proton conductivities with increasing temperature, and ODADS-based copolyimide membranes displayed similar proton conductivities to the corresponding BDSA-based ones. In addition, NTDA−BDSA/BAPF(1/1) and NTDA−ODADS/BAPF(1/1) displayed slightly lower proton conductivities than Nafion 117, whereas other copolyimide membranes showed fairly high proton conductivities, which were roughly comparable to that of Nafion 117.

Table 3. IEC and Proton Conductivity of the Prepared Polyimide Membranes at 50 °C and Different Humidities

		σ (S cm^{-1})			
polyimide	IEC (mequiv g^{-1})	RH = 50%	RH = 80%	RH = 100%	ref
NTDA−ODADS	3.37	0.0090	0.043	0.30[a]	b
NTDA−ODADS/ODA(1/1)	1.95	0.0032	0.017	0.12	b
NTDA−ODADS/BAPB(1/1)	1.68	0.0025	0.011	0.10	b
NTDA−ODADS/BAPHF(1/1)	1.73	0.0018	0.012	0.11	b
NTDA−ODADS/BAPF(1/1)	1.71	0.0021	0.011	0.090	b
NTDA−BDSA	3.46	NM	NM	NM	b
NTDA−BDSA/ODA(1/1)	1.98	0.0030	0.013	0.11	b
NTDA−BDSA/BAPHF(1/1)	1.75	0.0028	0.012	0.12	b
NTDA−BDSA/BAPF(1/1)	1.73	0.0036	0.010	0.096	b
CH$_3$ 5 50/50[c]	1.64	−	−	0.0059[c]	7b
CF$_3$ 5 50/50[c]	1.51	−	−	0.0071[c]	7b
Nafion 117	0.91	0.0040[d]	0.015[d]	0.1[d]	12

[a] Transient datum. [b] This study. [c] CH$_3$ 5 50/50 and CF$_3$ 5 50/50 refer to sequenced copolyimides derived from NTDA, BDSA, and bis[4-(aminophenoxy)4-phenyl]isopropylidene (pAPI) and from NTDA, BDSA, and bis[4-(aminophenoxy)4-phenyl]hexafluoroisopropylidene (pAPFI), respectively. Each copolyimide has a block length of five, and the molar ratio between BDSA and pAPI or pAPFI is 1:1. The proton conductivities were measured at room temperature. [d] Data obtained at 45 °C. NM: not measurable. (−): cannot find in the literature.

Table 4. Thickness, Water Uptake, and Water Stability of Various Sulfonated Polyimide Membranes

membrane	thickness (μm)	IEC (mequiv g^{-1})	water uptake[b] (% w/w)	temp (°C)	time	membrane stability[a]
NTDA−ODADS	22	3.37	NM	50	10 min	○
				50	2 h	dissolved
NTDA−BDSA	20	3.47	NM	50	a few seconds	dissolved
NTDA−ODADS/ODA(1/1)	34	1.95	87	80	25 h	○
NTDA−BDSA/ODA(1/1)	34	1.98	79	80	5.5 h	×
NTDA−ODADS/BAPB(1/1)	36	1.68	57	80	200 h	○
NTDA−ODADS/BAPHF(1/1)	31	1.73	72	80	11 h	×
NTDA−BDSA/BAPHF(1/1)	28	1.75	61	80	6 h	×
NTDA−ODADS/BAPF(1/1)	37	1.71	69	80	13 h	×
NTDA−BDSA/BAPF(1/1)	27	1.73	63	80	6 h	×

[a] Key: (○) mechanical strength was maintained; (×) somewhat brittle. [b] NM: not measured.

Membrane Stability. The stability test toward water of the polyimide membranes was performed by immersing the membranes into distilled water at a given temperature (50 or 80 °C) and characterized by the loss of mechanical properties of the hydrated membranes. The criterion for the judgment of the loss of mechanical properties is that the membrane is broken when lightly bent. Table 4 lists the thickness, water uptake, and the stability of the polyimide membranes. NTDA−BDSA homopolyimide membrane displayed the poorest stability among the prepared membranes. It was completely dissolved in water at 50 °C within a few seconds. NTDA−ODADS, however, could maintain mechanical strength after being soaked in water for 10 min at the same temperature, and it took more than 2 h to completely dissolve in water. This indicates NTDA−ODADS is much more stable toward water than NTDA−BDSA despite of their similar IEC values (Table 3).

All the copolyimides are insoluble in hot water due to the greatly reduced IEC. However, there is still large difference in water stability between ODADS and BDSA-based copolyimide membranes. NTDA−BDSA/ODA(1/1), for example, became somewhat brittle (the membrane was broken when lightly bent) after being soaked into water at 80 °C for 5.5 h, whereas the NTDA−ODADS/ODA(1/1) membrane remained very tough. It did not become brittle even after it was soaked in water at the same temperature for 25 h. Tensile measurement demonstrated that NTDA−ODADS/ODA-(1/1) membrane had a stress at break of 100 MPa at ambient atmosphere before soaking in water and 32 MPa in a hydrated state after being soaked in water at 100 °C for 3 h, whereas for NTDA−BDSA/ODA(1/1) the tensile measurement could not be performed because

the membrane was broken after being soaked in water at 100 °C for even only 10 min. This clearly indicates that ODADS-based copolyimide membranes are much more stable than the corresponding BDSA-based ones despite their similar IEC values. Usually water stability of polymer membranes is strongly dependent on the water uptake which is mainly determined by the IEC. Membranes with lower water uptake should have better water stability. However, in the present case, the difference in water stability between NTDA−ODADS/ODA(1/1) and NTDA−BDSA/ODA(1/1) is not because of the difference in water uptake because the former displayed even a little larger water uptake than the latter. A comparison of the chemical structures revealed that these two kinds of copolyimides had quite different chain flexibility. BDSA moiety is highly rigid because the two phenyl rings cannot rotate along the axis due to the steric effect of the two sulfonic groups. In contrast, ODADS is fairly flexible due to the existence of a flexible linkage, ether bond (Figure 5), and therefore, the backbone of NTDA−ODADS/ODA(1/1) should be much more flexible than that of NTDA−BDSA/ODA(1/1). A flexible chain can undergo relaxation more easily than the rigid one, and this is likely the main reason that NTDA−ODADS/ODA(1/1) displayed much better water stability than NTDA−BDSA/ODA(1/1). To make more clear understanding on the effects of polymer chain flexibility on water stability of the membranes, two rigid nonsulfonated diamines, BAPF and BAPHF, were used to replace the flexible one, ODA, for preparation of the copolyimides. The resulting copolyimides, NTDA−ODADS/BAPF(1/1) and NTDA−ODADS/BAPHF (1/1), have even lower IEC values and lower water uptake than NTDA−ODADS/ODA(1/1); however, their water
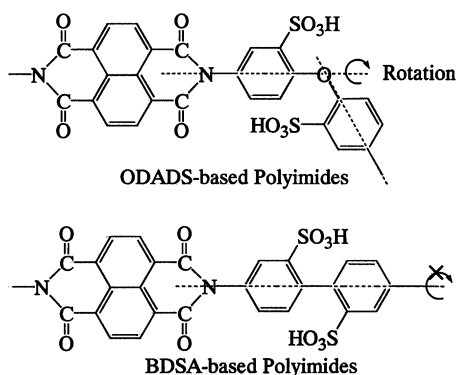
Figure 5. Schematic diagram for the different intrasegmental mobility between ODADS and BDSA-based polyimides.

stability is much poorer than that of the latter. This clearly indicates that water stability of the membranes not only depends on the flexibility of the sulfonated diamine moiety but also is affected by the flexibility of the nonsulfonated diamine moiety; i.e., water stability is determined by the flexibility of the whole polymer chain. NTDA−BDSA/BAPF(1/1) and NTDA−BDSA/BAPHF (1/1) have more rigid structures and therefore even poorer water stabilities than the corresponding ODADS-based ones. However, it should be noted that for BDSA-based copolyimides (i.e., "rigid"-type), the replacement of the nonsulfonated diamine moieties did not cause a large change in water stability of the membranes. NTDA−BDSA/ODA(1/1), for example, displayed water stability quite similar to that of NTDA−BDSA/BAPF(1/1) and NTDA−BDSA/BAPHF (1/1) despite the less rigid structure of the former; i.e., the favorable effect of the less rigid structure of NTDA−BDSA/ODA(1/1) on water stability was offset by the unfavorable effect of the higher water uptake. In contrast, for the "flexible"-type copolyimides, the reduction of the IEC (and therefore the water uptake) by changing the nonsulfonated diamine moiety led to great improvement in water stability of the membranes. NTDA−ODADS/BAPB(1/1) displayed the best water stability among the prepared polyimide membranes because of its highly flexible structure and the lowest IEC.

It should be noted that in the literature[7b,13] the criterion for the judgment of the loss or maintaining mechanical properties of membranes is described by the phrase, "the membranes become highly brittle" or "keep its form", which is not so strict as that proposed in this paper. Using the literature method, the time measured for charactering the stability of the copolyimide membranes should be much longer than those listed in Table 4. The NTDA−ODADS/ODA(1/1) membrane, for example, did not break into pieces (i.e., it kept its form), after being soaked in water at 80 °C for more than 200 h even by vigorously shaking the bottle where the membrane and distilled water were charged.

Membrane stability to oxidation was also investigated. The copolyimide membranes (the size of each sheet: 0.5×1.0 cm^2) were soaked in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at room temperature. Oxidative stability of the membranes was characterized by the elapsed time that the membranes started to become a little brittle (the membranes were broken when lightly bent) or started to dissolve in the solution. As shown in Table 5, all the copolyimide membranes displayed fairly good stability to oxidation, which is

Table 5. Results of Fenton's Reagent Test of Various Sulfonated Polyimide Membranes at Room Temperature

membrane	thickness (μm)	$\tau_1{}^a$ (h)	$\tau_2{}^a$ (h)
NTDA−ODADS/ODA(1/1)	29	20	24
NTDA−ODADS/BAPB(1/1)	37	29	32
NTDA−ODADS/BAPF(1/1)	40	29	32
NTDA−ODADS/BAPHF(1/1)	26	24	29
NTDA−BDSA/ODA(1/1)	21	13	20
NTDA−BDSA/BAPF(1/1)	34	23	26
NTDA−BDSA/BAPHF(1/1)	25	18	20

^{a} τ_1 and τ_2 refer to the elapsed time that the membranes became a little brittle and started to dissolve in the solution, respectively.

much better than that of the sulfonated arylene ether/fluorinated alkane copolymers reported in the literature.[13] In addition, ODADS-based copolyimide membranes generally showed better stability to oxidation than the corresponding BDSA-based ones. NTDA−ODADS/BAPB(1/1) and NTDA−ODADS/BAPF(1/1) copolyimide membranes displayed the best stability to oxidation among the prepared membranes.

Conclusions

1. A sulfonated diamine monomer ODADS was successfully synthesized by direct sulfonation of the parent diamine ODA using fuming sulfuric acid as the sulfonating reagent.

2. A series of polyimides were prepared from NTDA, ODADS, and nonsulfonated diamines. The resulting ODADS-based polyimide membranes displayed similar proton conductivities but much better water stability than the corresponding BDSA-based ones.

3. Water stability of polyimide membranes is greatly affected by the flexibility of polymer chains. Flexible chain structure results in good water stability.

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