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Aliphatic/Aromatic Polyimide Ionomers as a Proton Conductive Membrane for Fuel Cell Applications

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Abstract: To produce a proton conductive and durable polymer electrolyte membrane for fuel cell applications, a series of sulfonated polyimide ionomers containing aliphatic groups both in the main and in the side chains have been synthesized. The title polyimide ionomers **1** with the ion exchange capacity of 1.78−2.33 mequiv/g were obtained by a typical polycondensation reaction as transparent, ductile, and flexible membranes. The proton conductivity of **1** was slightly lower than that of the perfluorinated ionomer (Nafion) below 100 °C, but comparable at higher temperature and 100% RH. The highest conductivity of 0.18 S cm^{-1} was obtained for **1** at 140 °C. Ionomer **1** with high IEC and branched chemical structure exhibited improved proton conducting behavior without sacrificing membrane stability. Microscopic analyses revealed that smaller (<5 nm) and well-dispersed hydrophilic domains contribute to better proton conducting properties. Hydrogen and oxygen permeability of **1** was 1−2 orders of magnitude lower than that of Nafion under both dry and wet conditions. Fuel cell was fabricated with **1** membrane and operated at 80 °C and 0.2 A/cm^2 supplying H_2 and air both at 60% or 90% RH. Ionomer **1** membrane showed comparable performance to Nafion and was durable for 5000 h without distinct degradation.

Introduction

Fuel cells are efficient devices that generate electric power via chemical reaction of fuels and oxygen and therefore have been attracting more and more attention as a clean energy system.[1] Polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) using proton conductive ionomer membrane have been extensively studied for the applications to electric vehicles, residential power sources, and portable devices.[2] One of the important challenges in the current fuel cell research is to develop an alternative membrane to the perfluorinated ionomers, for example, Nafion (du Pont). The perfluorinated ionomer membranes are highly proton conductive and chemically and physically stable at moderate temperatures; however, these preferable properties are deteriorated above their glass transition temperature (T_g = ca. 110 °C).[3] High gas permeability, high cost, and environmental inadaptability of the fluorinated materials are also serious drawbacks for the practical fuel cell applications.

In the past decade, a variety of proton conductive materials have been proposed as an alternative membrane.[4] Nonfluorinated hydrocarbon ionomers,[5] acid-doped polymers,[6] inorganic/organic nanohybrids,[7] solid acids with superprotonic phase transition,[8] and acid/base ionic liquids[9] fall into this category. Although each material has its own advantages, most of them have failed to meet the requirements of high conductivity and durability under fuel cell operating conditions. The perfluorinated ionomers still stand as the state-of-the-art membrane.

Through the extensive research works on the nonfluorinated hydrocarbon ionomers, we have developed a series of sulfonated polyimide ionomers with high proton conductivity and substantial stability.[10] One of our most important findings is that

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(1) (a) Appleby, A. J.; Foulkes, F. R. *Fuel Cell Handbook*; Van Nostrand Reinhold: New York, 1989. (b) Carratte, L.; Friedlich, K. A.; Stimming, U. *Fuel Cells* **2001**, *1*, 5. (c) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.

(2) (a) Lemmons, R. J. *J. Power Sources* **1990**, *29*, 251. (b) Strasser, K. *J. Power Sources* **1992**, *37*, 209. (c) Kordesch, K.; Simander, G. *Fuel Cells and Their Applications*; Wiley-VCH: Weinheim, 1996.

(3) (a) Eisenberg, A.; Yeager, H. L. *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982. (b) Tant, M. R.; Kauritz, K. A.; Wilkes, G. L. *Ionomers*; Chapman & Hall: UK, 1997.

(4) (a) Kreuer, K.-D. *Chem. Mater.* **1996**, *8*, 610. (b) Savadogo, O. *J. New Mater. Electrochem. Syst.* **1998**, *1*, 47. (c) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Chem. Mater.* **2003**, *15*, 4896. (d) Miyatake, K.; Watanabe, M. *Electrochemistry* **2005**, *73*, 12.

(5) (a) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463. (b) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem. Rev.* **2004**, *104*, 4587.

(6) (a) Wainright, J. S.; Wang, J.-T.; Weng, D.; Savinell, R. F.; Litt, M. H. *J. Electrochem. Soc.* **1995**, *142*, L121. (b) Jones, D. J.; Rozière, J. *J. Membr. Sci.* **2001**, *185*, 41.

(7) Honma, I.; Takeda, Y.; Bae, J. M. *Solid State Ionics* **1999**, *120*, 255.

(8) (a) Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. *Nature* **2001**, *410*, 910. (b) Boysen, D. A.; Uda, T.; Chisholm, C. R. I.; Haile, S. M. *Science* **2004**, *303*, 68.

(9) (a) Susan, M. A. B. H.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* **2003**, 938. (b) Yoshizawa, M.; Ohno, H. *Chem. Commun.* **2004**, 1828.

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introducing aliphatic segments both in the main and in the side chains could significantly reduce the chances of nucleophilic attack by water onto the imide linkage resulting in the extreme hydrolytic stability of polyimide ionomers.[10e] It has been supported by the semiempirical MO calculations using model compounds, which revealed that imide nitrogen atom attached to an aliphatic group possesses higher electron density than that attached to an aromatic group. In this Article, we report a detailed investigation on the properties of these aliphatic/aromatic polyimide ionomers. Their proton conductivity, microphase structure, gas permeability, thermal, hydrolytic, oxidative, and mechanical stability are described as compared to those of the Nafion membrane. We have further demonstrated 5000 h of stable fuel cell operation with the polyimide ionomer membrane. While there have been a few recent reports on long-term fuel cell experiments (>3000 h) using acid-doped polybenzimidazole[11] or sulfonated polyimide membrane,[12] this is one of the longest successful fuel cell operations for a nonfluorinated ionomer membrane.

Experimental Section

Materials. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (TCND) (Aldrich), 1,6-hexamethylenediamine (HMDA) (98%, Kanto Chemicals), and 1,10-decamethylenediamine (DMDA) (97%, TCI) were used as received. Tris(2-aminoethyl) amine (96%, ACROS) was purified by distillation under reduced pressure. 3,3′-Bis(sulfopropoxy)-4,4′-diaminobiphenyl (BSPA) and 3,3′-bis(sufobutoxy)-4,4′-diaminobiphenyl (BSBA) were synthesized from 3,3′-dihydroxy benzidine (98%, TCI) and 1,3-propanesultone (Kanto Chemicals) or 1,4-butanesultone (Merck) according to the literature.[13] These monomers were characterized by IR and ^{1}H NMR spectra and stored under nitrogen in the dark. Triethylamine and benzoic acid (both Kanto Chemicals) were used as received. *m*-Cresol was dried over molecular sieves 3A prior to use. Other chemicals are of commercial grade and used as received unless otherwise mentioned.

Polymerization. A typical procedure for the copolymerization is as follows. BSBA (1.0 mmol), DMDA (1.0 mmol), triethylamine (4.3 mmol), and 7 mL of *m*-cresol were placed in a four-neck round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet. The mixture was stirred at 70 °C for 30 min. After clear solution was obtained, TCND (2 mmol), benzoic acid (4 mmol), and 6 mL of *m*-cresol were added into the mixture. The mixture was then cooled to room temperature and stirred for 24 h under a stream of nitrogen. The mixture was heated at 175 °C for 15 h and at 195 °C for 3 h. After the reaction, the mixture was poured dropwise into a large excess of acetone. A yellow powder of the precipitate was filtered, washed with acetone, and dried at 60 °C for 12 h to obtain **1d(50)**.

Membrane Preparation. The ionomer **1** (0.5 g) was dissolved in 15 mL of dimethyl sulfoxide (DMSO) and cast onto a flat glass plate. After drying at 80 °C under reduced pressure, crude membrane in salt form was immersed in ethanol containing 1 N HNO_3 for 12 h. The acidification procedure was repeated three times followed by washing with pure ethanol. The ionomer membrane **1** in acid form was obtained with a thickness of 50 μm.

Measurements. Infrared spectra were obtained as KBr pellets on a Jasco FT/IR-500 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400S spectrometer with DMSO-d_6 as a solvent and tetramethylsilane as an internal reference.

Proton Conductivity. A four-point-probe conductivity cell with two gold plate outer current-carrying electrodes and two platinum wire inner potential detecting electrodes was fabricated. Membrane samples were cut into strips of 0.5 cm wide and 4.5 cm long, and 50 μm thick prior to mounting in the cell. The cell was placed in a stainless steel chamber where the temperature and the humidity were controlled by flowing humidified nitrogen. For the measurement above 100 °C at 100% RH, a pressure-resistant (up to 7 bar) closed chamber was used. Impedance measurements were made using a Solartron SI1280 electrochemical impedance analyzer. The instrument was used in galvanostatistic mode with an ac current amplitude of 0.005 mA over a frequency range from 10 to 20 000 Hz.

STEM Observation. Membranes were stained with silver by ion exchange of sulfonic acid groups by immersing them overnight in 0.5 M $AgNO_3$ aqueous solution, rinsed with water, and dried at room temperature for 12 h. The stained membranes were embedded in epoxy resin and sectioned to yield 90 nm thick using a Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi HD-2300C scanning transmission electron microscope using an accelerating voltage of 200 kV.

Gas Permeability. Hydrogen and oxygen permeability through the ionomer membrane was measured with a GTR-Tech 20XFYC gas permeation measurement apparatus equipped with a Yanaco G2700T gas chromatography. The gas chromatography contained a Porapak-Q column and a TCD detector. Argon and helium were used as a carrier gas for the measurement of hydrogen and oxygen, respectively. A membrane sample ($\varphi = 30$ mm, thickness = ca. 50 μm) was set in a cell that has a gas inlet and outlet on both sides of the membrane. The cell temperature was controlled by placing it in an oven. On one side of the membrane, dry or humidified test gas (hydrogen or oxygen) was supplied at a flow rate of 30 mL/min, while on the other side of the membrane, the same gas as the carrier used in the gas chromatograph (flow gas) was supplied at a flow rate of 30 mL/min. The flow gas was humidified under the same conditions as the test gas so as to keep the membrane's wetting uniform. Before each measurement was done, the membrane was equilibrated with the gases at the given temperature and humidity for at least 3 h. Next, 3.7 mL of flow gas was sampled and subjected to the gas chromatography to quantify the test gas permeated through the membrane. The gas permeation rate, r (cm^3 (STD) cm^{-2} s^{-1}), and the gas permeation coefficient, Q (cm^3 (STD) cm cm^{-2} s^{-1} cmHg^{-1}), were calculated according to the following equations:

$$r = \frac{273}{T} \times \frac{1}{A} \times B \frac{1}{t}$$

$$Q = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t} \times l \times \frac{1}{76 - P_{H_2O}}$$

where T (K) is the absolute temperature of the cell, A (cm^2) is the permeation area, B (cm^3) is the volume of test gas permeated through the membrane, t (s) is the sampling time, l (cm) is the thickness of the membrane, and P_{H_2O} (cmHg) is the water vapor pressure.

Stability Testing. Thermal analyses were performed via TG/DTA-MS with a Mac Science TG-DTA 2000 equipped with a Bruker MS 9600 mass spectrometer at a heating rate of 20 °C/min under argon. Hydrolytic stability was evaluated by treating the membrane samples in water at 140 °C as an accelerated testing. Gravimetric analyses were done after the treatment. Oxidative stability was examined by immersing the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C for 1 h. Mechanical tensile testing was performed with a Shimadzu universal testing instrument Autograph

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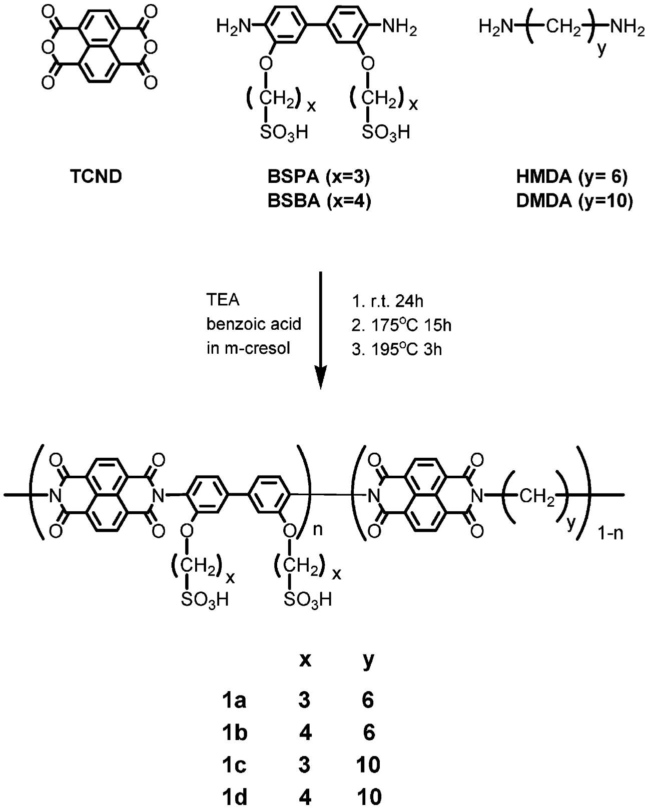
(10) (a) Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem. Commun.* **2003**, 368. (b) Miyatake, K.; Asano, N.; Watanabe, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3901. (c) Miyatake, K.; Zhou, H.; Watanabe, M. *Macromolecules* **2004**, *37*, 13, 4956. (d) Miyatake, K.; Zhou, H.; Matsuo, T.; Uchida, H.; Watanabe, M. *Macromolecules* **2004**, *37*, 4961. (e) Asano, N.; Miyatake, K.; Watanabe, M. *Chem. Mater*. **2004**, *16*, 2841.

(11) Li, Q.; He, R.; Jensen, J. O.; Bjerrum, N. J. *Fuel Cells* **2004**, *4*, 147.

(12) (a) Besse, S.; Capron, O.; Diat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Pineri, M.; Marestin, C.; Mercier, R. *J. New Mater. Electrochem. Syst.* **2002**, *5*, 109. (b) Rozière, J.; Jones, D. J. *Annu. Rev. Mater. Res.* **2003**, *33*, 503.

(13) (a) Jönsson, N. A.; Merenyi, F.; Svahn, C. M.; Gullander, J. *Acta Chem. Scand.* **1978**, *B32*, 317. (b) Jönsson, N. A.; Merenyi, F.; Lars-Erik, W. U.S. Patent 3859341, 1971.

Scheme 1. Synthesis of Aliphatic/Aromatic Polyimide Ionomers **1**



AGS-J500N equipped with a chamber in which the temperature and the humidity were controlled by flowing humidified air with a Toshin Kogyo temperature control unit Bethel-3A. Stress versus strain curves were obtained at a speed of 10 mm/min for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)).

Fuel Cell Operation. Gas diffusion electrodes were prepared as previously reported.[14] The loading amount of Pt catalyst on the electrode was 0.5 mg/cm^2. Membrane electrode assembly (MEA) was fabricated by sandwiching **1c(50)** or Nafion 112 membrane (both 50 μm thick) with two gas diffusion electrodes (25 cm^2 of geometric area). The MEA was mounted in a single cell holder composed of two carbon plates with ribbed channels for supplying gases. The cells were operated at a constant current density of 0.2 A/cm^2 at 80 °C for 5000 h. Hydrogen and oxygen utilization were 15% and 10%, respectively. Two cells were operated for each membrane, the one with reactant gases humidified at 68 °C (60% RH, low humidification conditions) and the other humidified at 77 °C (90% RH, high humidification conditions).

Results and Discussion

Synthesis and Characterization of Ionomers. The copolymerization of BSPA or BSBA, HMDA or DMDA, and TCND proceeds quantitatively in *m*-cresol to give the title ionomers **1** (Scheme 1). A series of polyimide ionomers **1a**−**d** with different main chain (y = 6, 10) and side chain (x = 3, 4) length were synthesized. The copolymer composition was set at 50/50 or 70/30 by moles to obtain the ionomers **1** with the ion exchange capacity (IEC) ranging from 1.78 to 2.31 mequiv/g (Table 1). The resulting ionomers are abbreviated as **1a**−**d**(**50 or 70**). A chemically branched ionomer **b-1c**(**70-2**) (Figure 1, IEC = 2.33 mequiv/g) containing 70 mol % of sulfonated component was also synthesized by applying 2 mol % of trifunctional monomer (tris(2-aminoethyl)amine) in the polymerization. The ionomers **1** are soluble in polar aprotic solvents such as DMSO, DMAc, and NMP. Molecular weight measurements, however, were not available due to insufficient solubility of **1** in DMF, which is as an eluent in our size exclusion chromatography (SEC) system. Casting from DMSO solution of the ionomers gave a tough and ductile brown membrane with a thickness of 50 μm. Because of the aliphatic groups both in the main and in the side chains, these membranes are more flexible than the wholly aromatic analogues.[10a−d] Ionomers **1** were characterized by IR and ^{1}H NMR spectroscopies (Supporting Information, Figures S1, S2). The IEC values obtained from the integration of the peaks in the ^{1}H NMR spectra were in good agreement with the ones expected from the copolymer composition (Table 1).

Table 1. Ion Exchange Capacity and Water Uptake of **1**

ionomer	x	y	IEC[a] (mequiv/g)	IEC[b] (mequiv/g)	water uptake (wt %)	λ[c]
1a(50)	3	6	1.92	1.99	22	6.1
1b(50)	4	6	1.87	1.89	19	5.6
1c(50)	3	10	1.82	1.84	18	5.4
1d(50)	4	10	1.78	1.85	18	5.4
1c(70)	3	10	2.31	2.31	21	5.1
b-1c(70-2)	3	10	2.33	2.32	18	4.3

[a] Calculated from the feed monomer ratio. [b] Obtained from the ^{1}H NMR spectra. [c] $\lambda = H_2O/SO_3H$.

As a polymer electrolyte, the ionomers **1** show considerable hydrophilicity. The water uptake data are summarized in Table 1. Ionomers **1** absorb ca. 20 wt % of water at 80 °C and 75% RH. These values correspond to 5.1−6.1 water molecules per sulfonic acid group (λ). The branched ionomer **b-1c**(**70-2**) showed lower water uptake (18 wt %, $\lambda = 4.3$) than that of the linear ionomers because the branching should suppress the swelling by absorbing water. The water uptake of $\lambda = 4-6$ is generally assumed to bring about the smooth transportation of protons via vehicle mechanism (migration of hydronium ions).[15]

Proton Conductivity. The proton conductivity of the ionomer membranes **1a**−**d**(**50**) at 100% RH is plotted as a function of temperature (Figure 2). The proton conductivity was $(2-9) \times 10^{-2}$ S cm^{-1} at 40 °C and increased with the temperature to the order of 10^{-1} S cm^{-1} above 80 °C. The highest proton conductivity of 0.21 S cm^{-1} was obtained for **1a**(**50**) at 120 °C. Ionomer **1c**(**50**) showed the most preferable proton conducting behavior with the conductivity increasing up to 140 °C. The advantage of **1** over Nafion membrane is that the high proton conductivity is durable for more than several hundred hours while Nafion lost its mechanical stability to exhibit stable conductivity at high temperature and high humidity (140 °C, 100% RH). The slope in Figure 2 is almost identical for **1** and Nafion 112 to give an E_a value of ca. 20 kJ/mol, suggesting that both share the same proton conduction mechanism involving the migration of hydronium ions.

The humidity dependence of the proton conductivity was investigated at 80, 100, and 120 °C (Figure 3). The ionomers **1a**−**d**(**50**) showed conductivity comparable to that of Nafion 112 at high humidity (>80% RH) at 80 and 100 °C. At lower humidity (<50% RH), however, the proton conductivity of **1a**−**d**(**50**) decreased down to the order of 10^{-4} S cm^{-1} at any temperature examined. This is the behavior often observed for

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(14) Song, J. M.; Uchida, H.; Watanabe, M. *Electrochemistry* **2005**, *73*, 189.

(15) Kreuer, K. D. *Solid State Ionics* **1997**, *97*, 1.

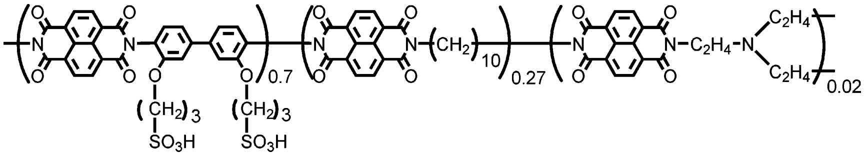

Figure 1. Chemical structure of branched **b-1c(70-2)**.

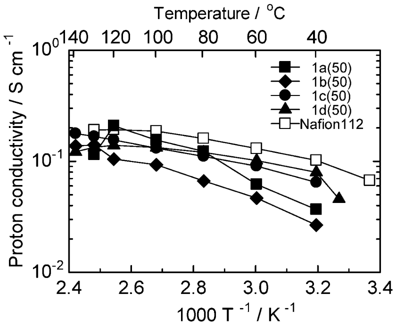

Figure 2. Temperature dependence of the proton conductivity of **1** membranes and Nafion 112 at 100% RH. The system was pressurized above 100 °C (e.g., 3.5 bar at 140 °C).

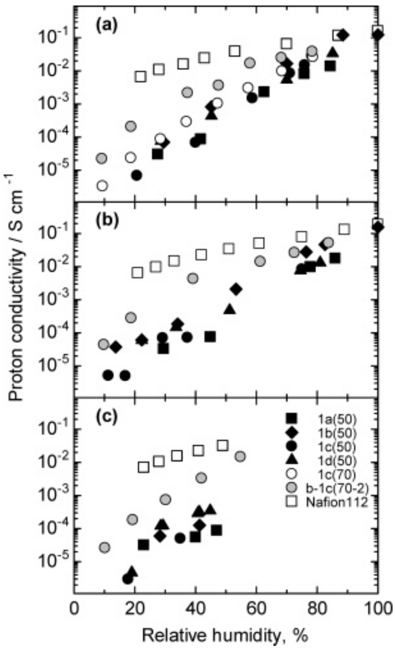

Figure 3. Humidity dependence of the proton conductivity of **1** membranes and Nafion 112 at (a) 80, (b) 100, and (c) 120 °C.

hydrocarbon-based ionomers, due to the lack of the formation of properly ordered microphase separation for the proton conduction as compared to the perfluorinated ionomers.[16] The lower acidity of Ar−SO_3H than that of $-CF_2-SO_3H$ should also be responsible. The proton conductivity of **1** at low humidity is independent of the temperature. It is assumed that the carrier (hydronium ions) concentration rather than the mobility and/or the diffusivity would be more crucial for the proton conduction when membranes are not fully hydrated.

The ionomer **1c**(**70**) with higher IEC than **1a**−**d**(**50**) showed slightly higher proton conductivity. It should be noted that the branched ionomer **b-1c**(**70-2**) showed considerably higher conductivity than **1c**(**70**), although both have the same IEC values; the proton conductivity of **b-1c**(**70-2**) is about 1 order of magnitude higher than that of **1c**(**70**) at <40% RH. As evidenced in the humidity dependence of water uptake (Figure 4), the three ionomers **1c**(**50**), **1c**(**70**), and **b-1c**(**70-2**) absorb the same amount of water, and the higher proton conductivity of **b-1c**(**70-2**) could not be attributed to the differences in the number of carrier ions but their diffusivity. It is discussed below together with their microscopic analyses.

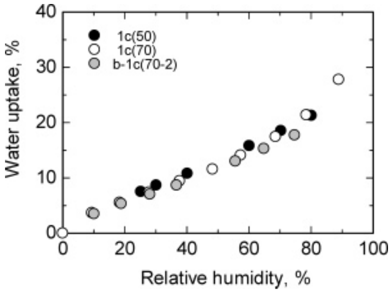

Figure 4. Humidity dependence of the water uptake of **1c** membrane at 80 °C.

Microscopic Observation. To investigate hydrophilic/hydrophobic microphase separation and the proton transport pathway in the ionomer membranes, we first carried out small-angle X-ray scattering (SAXS) experiments for water-swollen samples (Supporting Information, Figure S3). A clear maximum is observed for Nafion 112 at $q = 1.1$ nm^{-1}, which corresponds to a Bragg spacing of 5.3 nm and coincides with the value in the literature.[17] No distinct maximum was observed for **1c**(**50**) and **b-1c**(**70-2**). The results imply that a uniform size hydrophilic domain (or clusters) does not form in the hydrated polyimide ionomers. Instead, water molecules would distribute throughout the membranes.

We then performed scanning transmission electron microscopy (STEM) for the membranes stained with silver ions. In the STEM images, therefore, the dark areas represent the hydrophilic (ionic) domain and the brighter areas represent the hydrophobic domain. As is clearly seen in Figure 5a, **1c**(**50**) exhibited spherical ionic clusters with relatively uniform size (ca. 5−8 nm). The similar microstructure has been reported for the other series of polyimide ionomers.[18] In the STEM image of **1c**(**70**) (Figure 5b), a large number of smaller ionic clusters (3−5 nm) and a certain amount of bigger ionic clusters (∼12 nm) were observed together with the medium size clusters similar to those of **1c**(**50**) (see Supporting Information, Figure S4 for cluster size distribution). The higher IEC causes the formation of such smaller and bigger ionic clusters than those of **1c**(**50**) and, therefore, the better connection of proton transport pathway. In the image of **b-1c**(**70-2**) (Figure 5c), even smaller ionic clusters (<5 nm) were observed as the minority despite

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(16) Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.

(17) (a) Gebel, G.; Lambard, J. *Macromolecules* **1997**, *30*, 7914. (b) Gebel, G.; Moore, R. B. *Macromolecules* **2000**, *33*, 4850.

(18) (a) Yin, Y.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *J. Mater. Chem.* **2004**, *14*, 1062. (b) Okamoto, K.; Yin, Y.; Yamada, O.; Islam, M. N.; Honda, Y.; Mishima, T.; Suto, Y.; Tanaka, K.; Kita, H. *J. Membr. Sci.* **2005**, *258*, 115.

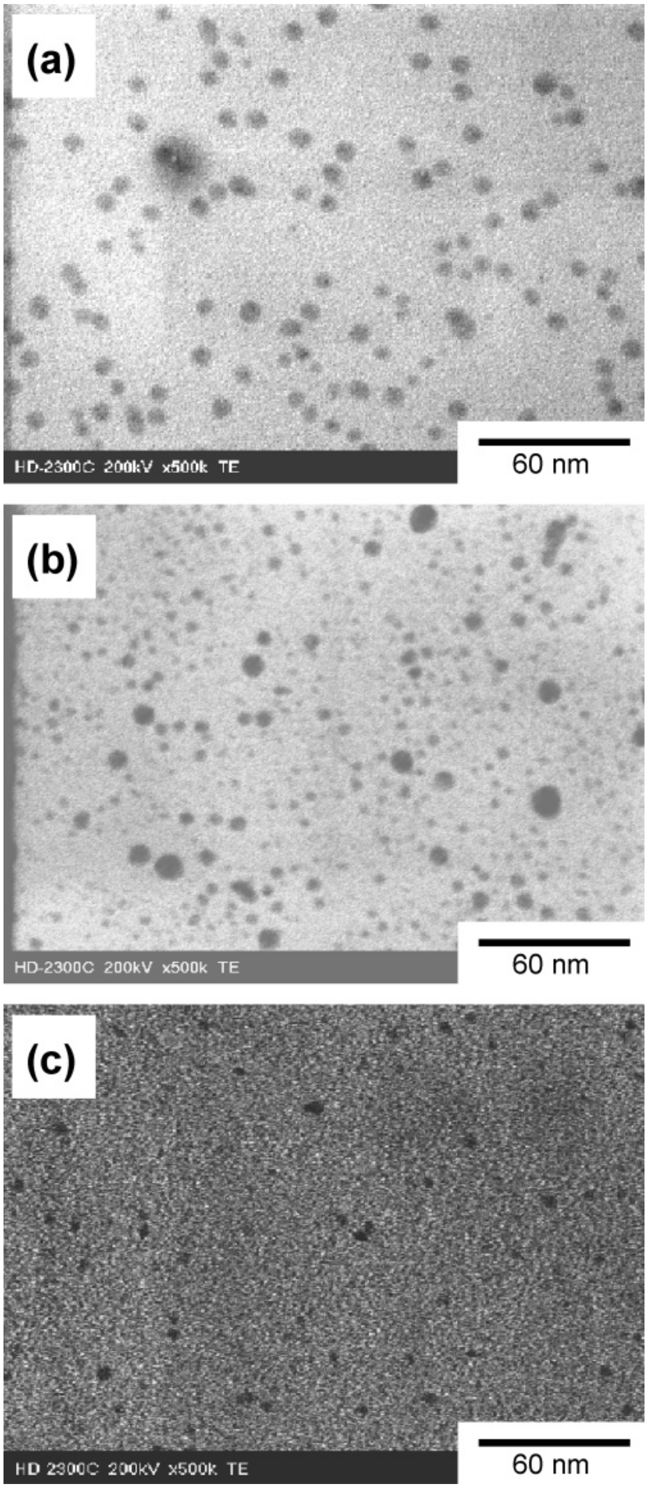

Figure 5. STEM images of (a) **1c(50)**, (b) **1c(70)**, and (c) **b-1c(70-2)**.

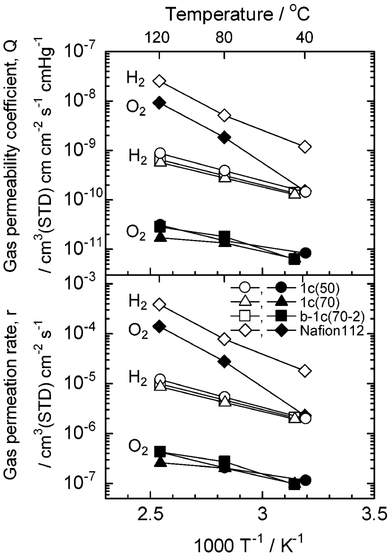

Figure 6. Temperature dependence of dry hydrogen and oxygen permeability for **1c** and Nafion 112.

having the same IEC value as **1c**(**70**). Instead, back areas were darker and spread uniformly throughout the sight. By EDX analyses, these areas were found to contain silver, while only negligible silver was detected in the back areas of **1c**(**50**) and **1c**(**70**). The chemical branching in **b-1c**(**70-2**) should presumably prevent the ionic groups from aggregating to build up microphase separation. These images were not topical but observed at many spots in the membranes as confirmed in the images with the lower magnification (Supporting Information, Figure S5). By combining the microscopic observation and proton conducting behavior (Figure 3), it is concluded that smaller ionic clusters and dispersed and well-distributed water molecules are likely to promote proton transport properties in the polyimide ionomer membranes.

Gas Permeation Properties. Gas permeation through ionomer membranes is another important factor that affects fuel cell performance, because the permeated hydrogen or oxygen from one electrode to the other causes direct chemical reaction combustion resulting in lower utilization of fuels and higher overpotential, particularly at the cathode reaction. It has been pointed out that hydrogen and oxygen cross-leaked to the electrodes enhance the degradation of ionomer membranes.[19] Therefore, we have investigated hydrogen and oxygen permeability for **1c**(**50**), **1c**(**70**), **b-1c**(**70-2**), and Nafion 112 membranes under both dry and wet conditions. The gas permeation rate (r) and the gas permeability coefficient (Q) under dry conditions are summarized in Figure 6 as a function of temperature. The hydrogen and oxygen permeability is much lower for **1c**(**50**), **1c**(**70**), and **b-1c**(**70-2**) membranes than for Nafion 112. At 40 °C, hydrogen and oxygen permeation rates of **1** membranes are more than 1 order of magnitude lower than those of Nafion 112. The tendency of lower gas permeation of **1** membranes is much more pronounced at 120 °C. The apparent activation energy of the gas permeation is $E_a(H_2) = 23$ and $E_a(O_2) = 17$ kJ/mol for **1c**(**50**), $E_a(H_2) = 21$ and $E_a(O_2) = 14$ kJ/mol for **1c**(**70**), $E_a(H_2) = 22$ and $E_a(O_2) = 21$ kJ/ mol for **b-1c**(**70-2**), and much lower than that for Nafion 112 ($E_a(H_2) = 39$ and $E_a(O_2) = 53$ kJ/mol).

The gas permeation properties under humidified conditions are depicted in Figures 7 and 8. It should be emphasized that **1** membranes are much less permeable to both hydrogen and oxygen than Nafion 112 under any given conditions (80 and 120 °C, 0−90% RH). Among them, **b-1c**(**70-2**) showed the lowest permeability, 1−2 orders of magnitude lower than Nafion

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(19) (a) LaConti, A. B.; Hanndan, M.; McDonald, R. C. *Handbook of Fuel Cells*; John Wiley and Sons Ltd.: Chichester, England, 2003; Vol. 3, pp 647. (b) Endo, E.; Terazono, S.; Widjaja, H.; Takimoto, Y. *Electrochem. Solid-State Lett.* **2004**, *7*, A209. (c) Healy, J.; Hayden, C.; Xie, T.; Olson, K.; Waldo, R.; Brundage, M.; Gasteiger, H.; Abbott, J. *Fuel Cells* **2005**, *5*, 302. (d) Aoki, M.; Uchida, H.; Watanabe, M. *Electrochem. Commun.* **2005**, *7*, 1434.

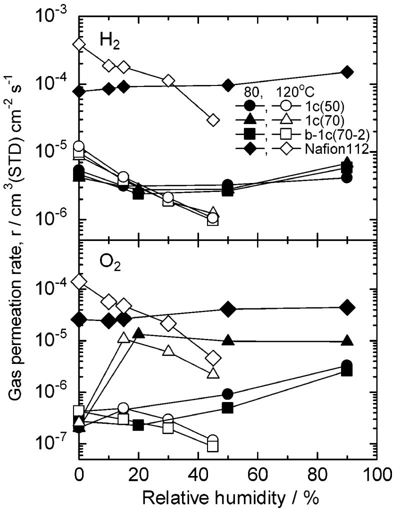

Figure 7. Humidity dependence of hydrogen (top) and oxygen (bottom) permeation rates for **1** and Nafion 112 at 80 and 120 °C.

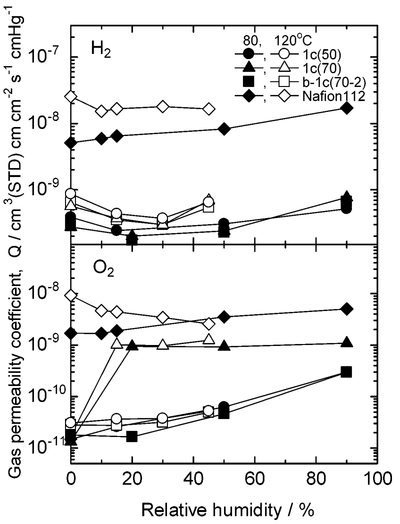

Figure 8. Humidity dependence of hydrogen (top) and oxygen (botom) permeability coefficient for **1** and Nafion 112 at 80 and 120 °C.

112 because of the better molecular packing and suppressed swelling by branching. The three polyimide ionomers **1** and Nafion 112 showed an almost constant hydrogen permeation rate ($r(H_2)$) at 0−80% RH and 80 °C. The permeation coefficient ($Q(H_2)$) showed a slight increase with increase of the humidity. It is generally recognized that the gases permeate mainly through the hydrophobic domain of a polymer electrolyte membrane.[20] The slight increase of $Q(H_2)$ with the humidity arises from the increased contribution of the hydrophilic domain due to the swelling. Although $r(H_2)$ decreased for all of the membranes at 120 °C, $Q(H_2)$ showed trends similar to those at 80 °C. It is not clear at the present why the linear **1c**(**70**) with higher IEC showed a rapid increase in oxygen permeability from 0% to 15% RH, of which the behavior is distinct from the others. A possible explanation would be some specific interaction between oxygen molecules and the hydrophilic domain in **1c**(**70**), probably relating to the large ionic clusters as seen in Figure 5b and Figure S4 distinctive from **1c**(**50**) and **b-1c**(**70-2**).

Stability. The thermal stability of **1** was investigated under dry conditions via TG/DTA-MS (Supporting Information, Figure S6). In the TG curve, two-step weight loss was observed from room temperature to 150 °C and above 200 °C. By combining with the mass chromatograms, the first weight loss was assigned to the evaporation of hydrated water, and the second one was due to the thermal decomposition of the ionomer. The major fragment ions observed in the second weight loss were 48 (SO), 64 (SO_2), 58 (C_3H_6O), and 122 ($C_3H_6SO_3$) m/z, indicating that the thermal decomposition was due to the degradation of sulfoalkoxy side chains. All of the polyimide showed similar TG/DTA-MS curves with only minor differences in the amount of absorbed water. In the DTA curves, no clear T_g has been detected for the ionomers **1** up to 200 °C. Incorporation of the flexible aliphatic segments does not practically lower the T_g of the sulfonated polyimides below their decomposition temperature. These thermal properties are comparable to those of wholly aromatic polyimide ionomers or perfluorinated ionomers.[10a−d]

Table 2. Hydrolytic and Oxidative Stability of **1** and Nafion 112

ionomer	residue after hydrolytic testing (wt %)	residue after oxidative testing (wt %)
1a(50)	90	94
1b(50)	74	96
1c(50)	92	98
1d(50)	96	96
1c(70)	0	62
b-1c(70-2)	81	85
Nafion 112	99	98

As an accelerated hydrolytic stability testing, the polyimide ionomers were treated at 140 °C in water for 24 h, and the results are listed in Table 2. In our previous experiments, no polyimide ionomers have endured the testing. For example, wholly aromatic polyimide ionomers have broken into pieces after the testing, indicative of serious hydrolysis. The instability could not be well improved by either changing the hydrophobic component or its composition. The polyimide ionomers having pendant aliphatic groups exhibited somewhat better hydrolytic stability.[21] The new series of polyimide ionomers **1** have shown much improved hydrolytic stability without any changes in appearance, flexibility, and toughness after the testing. Although the molecular weight measurement was not available due to their insolubility, these observations imply no significant degradation occurred. The ^{1}H NMR analyses suggested that the **1c**(**50**) membrane showed only a minor change in the IEC (from 1.87 to 1.76 mequiv/g) after the testing, which further supports the outstanding hydrolytic stability of **1**. Gravimetric measurements revealed that **1a**−**d**(**50**) membranes retained more than 74% of their original weight. As we have discussed in the preceding communication,[10e] the imide nitrogen attached to an aliphatic group possesses higher electron density than that attached to a phenyl group, and therefore is less susceptible to the nucleophilic attack by water molecules. The higher IEC causes dissolution of the ionomer **1c**(**70**); however, it can be avoided in **b-1c**(**70-2**) by incorporating 2 mol % of branched structure.

The oxidative stability of **1** tested in Fenton's reagent at 80 °C is also included in Table 2. Ionomers **1a**−**d**(**50**) exhibited highly oxidative stability. All of the **1**(**50**) membranes retained more than 94% of their original weight after the testing. Because the oxidative attack by radical species (HO• and HOO•) should

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(20) Piroux, F.; Espuche, E.; Mercier, R. *J. Membr. Sci.* **2004**, *232*, 115.

(21) (a) Yin, Y.; Fang, J.; Kita, H.; Okamoto, K. *Chem. Lett.* **2003**, *4*, 328. (b) Yin, Y.; Fang, J.; Cui, Y.; Tanaka, K.; Kita, H.; Okamoto, K. *Polymer* **2003**, *44*, 4509. (c) Zhou, H.; Miyatake, K.; Watanabe, M. *Fuel Cells* **2005**, *5*, 296.

Table 3. Mechanical Properties of **1**

	maximum stress (MPa)		Young's modulus (GPa)		elongation at break (%)	
ionomer	85 °C	120 °C	85 °C	120 °C	85 °C	120 °C
1a(50)	33	26	0.7	0.8	34	9
1b(50)	28	31	1.0	1.2	4	3
1c(50)	34	29	1.0	1.0	9	10
1c(50)	30	31	0.8	0.9	14	20
1c(70)	16	12	0.36	0.20	17	6
b-1c(70-2)	40	22	0.36	0.48	76	25
Nafion 112	24	18	0.007	0.004	334	460

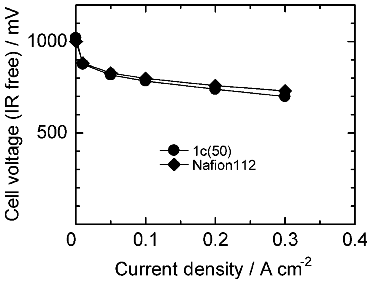

Figure 9. IV curves of PEFCs with **1c(50)** and Nafion 112 membranes at low humidity (60% RH).

mainly occur in or in the proximity of water-containing hydrophilic domains, the main chain degradation is significantly suppressed in **1**. By comparing **1c**(**70**) and **b-1c**(**70-2**), we have concluded that a small amount of branching is very effective to amend both oxidative and hydrolytic stability. As an ionomer membrane with hydrocarbon structure, **1**(**50**) membranes showed high hydrolytic and oxidative stability nearly comparable to that of Nafion 112.

The mechanical properties of **1** membranes were measured at 85 and 120 °C, 93% RH. The stress–strain data are shown in Figure S7 (Supporting Information) and summarized in Table 3 together with those of Nafion 117. Nafion 117 showed 24 MPa of maximum stress at break and 334% of elongation at break at 85 °C. Increasing temperature deteriorates these mechanical properties. The maximum stress decreased to 18 MPa, and the elongation reached 460% at 120 °C. Ionomer **1c**(**50**) membrane exhibited much higher maximum stress (34 MPa) at break at 85 °C, and elongation at break was as low as 9%. **1c**(**50**) membrane showed little changes in the mechanical properties at 120 °C. Young's modulus estimated from the slopes was as high as 1 GPa at both 85 and 120 °C, which is much higher than that of Nafion 117 (7 MPa at 85 °C and 4 MPa at 120 °C). These mechanical properties of ionomers **1c**(**50**) membrane are comparable to those of the wholly aromatic polyimide ionomers we have reported previously,[10a−d] indicating that the flexible aliphatic groups do not deteriorate the mechanical stability of polyimide ionomers at least up to the composition of 50 mol %. All four ionomers **1a**−**d**(**50**) showed similar mechanical properties, which were superior to those of Nafion under the given conditions. **1c**(**70**) showed lower mechanical strength; however, the disadvantage of higher IEC membrane has been overcome in **b-1c**(**70-2**) to the almost comparable level of **1c**(**50**).

Fuel Cell Operation. The initial fuel cell performance (I−V curve) with the reactant gases humidified at 68 °C (60% RH) is shown in Figure 9 for **1c**(**50**) and Nafion 112 membranes. The IR free cell voltages (cell voltages excluding the internal cell resistance (IR)) were almost identical for both **1c**(**50**) and Nafion 112 cells at the current density from 0 to 300 mA/cm^2, indicative that the same electrode performance was obtained. We then proceeded to the durability testing for both membranes.

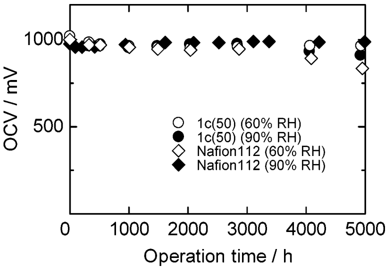

Figure 10. Time course of OCV of PEFCs with **1c(50)** and Nafion 112 membranes.

Two sets of fuel cells were fabricated with each **1c**(**50**) and Nafion 112 membrane; one cell was operated at 80 °C under high humidification conditions (90% RH) and the other at 80 °C and low humidification conditions (60% RH). All of the four cells could successfully operate at a constant current density of 0.2 A/cm^2 for 5000 h. Open circuit voltage (OCV), which is a good measure of the reactant permeation through membrane, was taken as a function of the operation time (Figure 10). The fuel cells using **1c**(**50**) exhibited constant OCVs during 5000 h operation both at 60% and at 90% RH as well as the ones using Nafion 112. This is a clear evidence of no noticeable degradation of newly developed ionomer **1c**(**50**) membrane for such a long time operation. To the best of our knowledge, this is one of the longest successful fuel cell operations reported for a nonfluorinated ionomer membrane. Detailed analyses are under investigation and will be reported elsewhere. In any cases, we have been able to prove that the polyimide ionomer **1** membranes are available and durable in a practical fuel cell operation.

Conclusions

Proton conductive aliphatic/aromatic polyimide ionomers **1** were synthesized. The aliphatic segments introduced both in the main and in the side chains could effectively improve the hydrolytic stability of polyimide ionomers without sacrificing other preferable properties (proton conductivity, oxidative and mechanical stability). Both electronic and steric effects are crucial for the hydrolytic and oxidative stability. Ionomers **1** were stable under harsh hydrolytic conditions at 140 °C and 100% RH. The mechanical properties of **1** membranes were comparable to those of the wholly aromatic polyimide ionomers and much better than the Nafion membrane. Under humidified conditions, **1** membranes are highly proton conductive with 0.18 S cm^{-1} of the conductivity at 140 °C. A significant decrease in the conductivity at low humidity observed for the linear ionomers was improved to the level nearly required for the practical fuel cell applications by increasing the IEC and introducing branching structure (**b-1c**(**70-2**)). STEM images have revealed that aggregation of ionic groups was suppressed by the branching and therefore small (<5 nm) and well-dispersed hydrophilic domains distributed throughout the membrane. The morphology is distinctive from that of the perfluorinated ionomers (in which 5−10 nm sized hydrophilic clusters are observed) and is likely to contribute better proton conducting properties. Hydrogen and oxygen permeability of **1** membranes was more than 1 order of magnitude lower than that of Nafion under a wide range of conditions (40−120 °C and 0−90% RH). High performance fuel cells have been achieved with the polyimide ionomer membrane. As evidenced in little changes in open circuit voltage (OCV) during the operation, **1** membrane was durable for 5000 h, which is the longest fuel cell operation reported for an alternative electrolyte membrane.

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Supporting Information Available: Spectroscopic and other detailed data. This material is available free of charge via the Internet at http://pubs.acs.org.

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