Synthesis, Characterization, and Copolymerization of a Series of Novel Acid Monomers Based on Sulfonimides for Proton Conducting Membranes

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ABSTRACT: The synthesis and characterization of a series of novel acid monomers based on sulfonimides with different acidities are described. Copolymerization of the acid monomers with acrylonitrile was carried out, and the proton exchange membranes were cast from solutions of the resulting copolymers. Flexible, mechanically strong, and transparent membranes with different equivalent weights could be prepared. The membranes with lower equivalent weights and higher acidities exhibited higher proton conductivity under humidifying conditions compared to those with higher equivalent weights and lower acidities. The membrane electrode assembly was fabricated using a synthesized sulfonimide copolymer. The H_2/O_2 fuel cell performance was tested in a single cell, which revealed potential applicability of the sulfonimide membranes to polymer electrolyte fuel cells.

Introduction

New proton exchange membranes for fuel cells are required for a wide range of demanding applications, such as portable electronic devices and vehicles as well as stationary power generation.[1−3] Until now, numerous membrane materials have been claimed to be promising for fuel cell applications. Among them, perfluorosulfonic acid membranes, typically Nafion, have been chosen as a standard membrane because of their high performance, including high proton conductivity, high mechanical strength, and excellent thermal and chemical stability.[1−3] However, a few drawbacks, such as the high cost and evaporation of water at elevated temperatures, limit its wide-scale commercialization.[1−3]

Extensive efforts have been devoted to innovation of the cost and performance, including the studies on nonfluorinated and partially fluorinated membrane materials.[2,3] Sulfonimide membranes are of particular interest because of their strongest gas-phase superacidity, excellent thermal stability, capacity to promote oxygen reduction kinetics at cathode, and weak adsorption on platinum catalyst. Thus, sulfonimide membranes have proved to be potential candidates for fuel cell applications.[4−10] Sumner and co-workers have developed a new class of ionically conducting polymers based on a bis[(perfluoroalkyl)sulfon]imide.[8] This polymer is structurally similar to Nafion, but the sulfonic acid group is substituted by a sulfonimide group. Similarly to Nafion, the conductivity of the sulfonimide membrane is found to be strongly dependent on the level of hydration and temperature. The conductivity of this membrane is reported to be 2 times higher than that of Nafion 117, measured under the same conditions. They also reported that the water uptake of this membrane was high due to the internal pore and/or channel structure of sulfonimide acid groups. This also allows the membrane to maintain a more hydrated state at above 80 °C, giving this membrane a distinct advantage over Nafion, whose conductivity drops sharply due to dehydration. Des-Marteau and co-workers described that the thermal cyclopolymerization of various trifluorovinyl aromatic ether monomers, bearing both pendant sulfonimide groups and sulfonimide groups incorporated into the monomer main chain to yield perfluorocyclobutane aromatic polyethers, were quite interesting materials for fuel cell membranes.[11−13] A series of novel polystyrenes with pendant lithium perfluoroalkylsulfonate or sulfonimide groups have been synthesized by Feiring and co-workers and identified as potential electrolytes for lithium batteries. They proposed that the ionomers of this variety might also be used as fuel cell electrolytes.[9] Hofmann et al. have reported that the sulfonimide-functionalized phosphazene membrane is an excellent proton conductor.[10] The membrane and a blended membrane of the sulfonimide-functionalized phosphazene polymer with poly(vinylidene fluoride) appear to be promising candidates for use as proton-conducting membranes in fuel cell applications.[10]

In addition to the sulfonimide membranes, Guo and co-workers synthesized a series of novel sulfonated polyimides with different sulfonation degrees from 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid, 1,4,5,8-naphthalenetetracarboxylic dianhydride, and common nonsulfonated diamines and found that the polyimide membranes showed proton conductivities similar to or higher than those of Nafion 117 at 100% relative humidity.[14] They also reported that the polyimide membranes were good for low operating temperature fuel cell systems due to the low hydrolysis stability. Quite recently, it has been reported that the sulfonated and phosphonated poly[(aryloxy)phosphazene] membranes are good proton conductors with low methanol permeation, as compared with Nafion.[15]

Although numerous studies on the synthesis and proton conductive behavior have been conducted on

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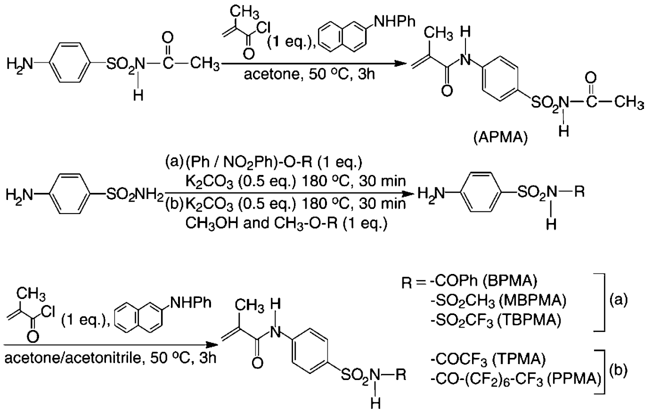
Scheme 1. Synthesis of Novel Acid Monomers



these sulfonimide and sulfonated membranes, at present there is little available fuel cell performance data in the literature on these materials. In the present research, we synthesized a series of novel acid monomers based on sulfonimides (Scheme 1) and copolymerized them with a vinyl monomer to realize proton exchange membranes with high proton conductivity by changing the acidity, water uptake, and equivalent weight of the membranes.[16−19] Thermal properties of the dry membranes as well as the hydrated membranes were investigated to know the state of water in the membranes.[20] The hydrated membranes showed lower glass transition temperatures than the dry membranes. The proton conductivity and water uptake with different equivalent weights were investigated. Finally, a sulfonimide-based membrane electrode assembly was fabricated and tested in an H_2/O_2 fuel cell.

Experimental Section

Materials. Sulfacetamide (Lancaster), methyl trifluoroacetate (Wako), sulfanilamide (Cica), phenyl trifluoroacetate (Wako), phenyl methanesulfonate (Aldrich), 4-nitrophenyl trifluoromethanesulfonate (Aldrich), methyl pentadecafluorooctanoate (Aldrich), pottasium carbonate (Wako), phenyl benzoate (Cica), methacryloyl chloride (Wako), *N*-phenyl-2-naphthylamine (TCI), 2,2′-azobis(2-methylpropionitrile) AIBN (JUNSEI), dimethyl-d_6 sulfoxide (Aldrich), carbon paper (Toray), and Pt/C (46.7 wt %) (Tanaka Kikinzoku Kogyo) were used as purchased. Acrylonitrile (Wako) was used after distillation. All reagents used were of reagent grade.

Synthesis of *N*-(4-Acetylimidesulfonyl)phenyl-2-methylacrylamide (APMA). Sulfacetamide (10.0 g, 46 mmol) was dissolved in acetone (50 mL), to which a small amount of *N*-phenyl-2-naphthylamine was added, and cooled to 10 °C. Methacryloyl chloride (4.87 g, 46 mmol) was added dropwise to the mixture at 10 °C, and the solution was heated for 3 h under reflux condition with constant stirring. To the reaction mixture, 30 wt % $NaHCO_3$ aqueous solution was added, and the precipitated solid was collected by filtration. The solid product was recrystallized from ethanol and dried under vacuum to obtain 7.50 g of a white crystalline powder. The yield was 57%. ^{1}H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 11.96 (s, 1H), 10.18 (s, 1H), 7.88 (m, 4H), 5.86 (s, 1H), 5.58 (s, 1H), 1.96 (s, 3H), 1.91 (s, 3H). Electron impact ionization (EI) mass spectrum: Calculated for $C_{12}H_{14}N_2O_4S$: *m*/*e* 282.31. Found: *m*/*e* 282. Elemental analysis (%): Calculated for $C_{12}H_{14}N_2O_4S$: C, 51.05; N, 9.92; S, 11.35. Found: C, 50.48; N, 9.86; S, 11.35.

Synthesis of *N*-(4-Benzoylimidesulfonyl)phenylamine (BPA). Sulfanilamide (10.33 g, 60 mmol), K_2CO_3 (4.15 g, 30 mmol), and phenyl benzoate (11.89 g, 60 mmol) were completely mixed and put into a round-bottom flask. This mixture was heated at 180 °C in an oil bath for 20 min with a condenser. The flask was removed from the oil bath and was cooled to room temperature. Then 100 mL of 5 wt % Na_2CO_3 aqueous solution was added to dissolve the resulting solid. After filtration of the solution, the filtrate was extracted three times with benzene (50 mL) to remove phenol. In a 500 mL round-bottom flask concentrated HCl (17 mL) with water (180 mL) was taken, and the filtrate was added dropwise under stirring. The resulting mixture was filtered off to discard the filtrate and washed with ether. The solid white compound was collected, recrystallized from ethanol, and dried under vacuum for several hours to obtain 8.20 g of the solid compound. The yield was 49%.

Synthesis of *N*-(4-Benzoylimidesulfonyl)phenyl-2-methylacrylamide (BPMA). BPMA was synthesized from BPA and methacryloyl chloride in a similar way to APMA. The crude product was recrystallized from ethanol and dried under vacuum for several hours to obtain a solid compound. The yield was 41%. ^{1}H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 12.43 (s, 1H), 10.20 (s, 1H), 7.90 (m, 6H), 7.55 (m, 3H), 5.84 (s, 1H), 5.58 (s, 1H), 1.94 (s, 3H). EI mass spectrum: Calculated for $C_{17}H_{16}N_2O_4S$: *m*/*e* 344.38. Found: *m*/*e* 344. Elemental analysis (%): Calculated for $C_{17}H_{16}N_2O_4S$: C, 59.28; N, 8.13; S, 9.30. Found: C, 59.12; N, 8.25; S, 9.09.

Synthesis of *N*-[4-Methylbis(sulfonyl)imide]phenylamine (MBPA). MBPA was synthesized in a similar way to BPA. The crude product was purified on a silica gel column using ethanol/benzene (1/2 by volume) as the eluent. The solvent was evaporated, and the solid product was recrystallized from ethanol to obtain a white solid of MBPA (yield: 26%).

Synthesis of *N*-[4-Methyl-bis(sulfonyl)imide]phenyl-2-methylacrylamide (MBPMA). MBPMA was synthesized in a similar way to APMA. The monomer was recrystallized from ethanol and dried under vacuum to obtain a white crystalline powder. The yield was 45%. ^{1}H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 9.99 (s, 1H), 7.72 (m, 4H), 5.84 (s, 1H), 5.54 (s, 1H), 2.87 (s, 3H), 1.94 (s, 3H). EI mass spectrum: Calculated for $C_{11}H_{14}N_2O_5S_2$: *m*/*e* 318.36. Found: *m*/*e* 318. Elemental analysis (%): Calculated for $C_{11}H_{14}N_2O_5S_2$: C, 41.50; N, 8.79; S, 20.14. Found: C, 41.46; N, 8.76; S, 19.76.

Synthesis of *N*-[4-Trifluoromethylbis(sulfonyl)imide]-phenylamine (TBPA). Sulfanilamide (17.22 g, 100 mmol), K_2CO_3 (6.91 g, 50 mmol), and 4-nitrophenyl trifluoromethanesulfonate (27.11 g, 100 mmol) were completely mixed and put into a round-bottom flask. Then, TBPA was synthesized in a similar way to BPA. The crude product was purified by silica gel column chromatography eluted with ethanol/benzene (1:2). The solvent was removed with a rotary evaporator, and the product was recrystallized from ethyl acetate to obtain TBPA (yield 15%) as a white powder.

Synthesis of *N*-[4-Trifluoromethylbis(sulfonyl)imide]-phenyl-2-methylacrylamide (TBPMA). The synthesis of TBPMA followed the same procedure as APMA. The monomer was recrystallized from ethyl acetate and dried under vacuum to obtain a slightly yellowish powder. The yield was 10%. ^{1}H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 10.01 (s, 1H), 7.72 (m, 4H), 5.84 (s, 1H), 5.54 (s, 1H), 1.94 (s, 3H). Electron impact ionization (EI) mass spectrum: Calculated for $C_{11}H_{11}F_3N_2O_5S_2$: *m*/*e* 372.33. Found: *m*/*e* 372. Elemental analysis (%): Calculated for $C_{11}H_{11}F_3N_2O_5S_2$: C, 35.48; N, 7.52; S, 17.22. Found: C, 35.11; N, 7.48; S, 16.90.

Synthesis of *N*-(4-Trifluoroacetylimidesulfonyl)phenylamine (TPA). Sulfanilamide (10.33 g, 60 mmol) and K_2CO_3 (4.14 g, 30 mmol) were mixed, put into a round-bottom flask, and heated at 180 °C in an oil bath for 20 min under moisture-free conditions. The flask was removed from the oil bath and cooled to room temperature. Methanol was added to dissolve the resulting product, to which methyl trifluoroacetate (7.68 g, 60 mmol) or phenyl trifluoroacetate (11.4 g, 60 mmol) was added dropwise, and the mixture was stirred at room temperature for 3 h. The resulting solution was filtered off, and the solution was evaporated. The solid was dissolved in 100 mL of 5 wt % Na_2CO_3 aqueous solution. Then concentrated HCl with water was added to the solution for the neutralization. The solution was filtered off, and water was evaporated. The crude product was dried under vacuum for 12 h. The product

Table 1. Conversions, Molecular Weights, Molecular Weight Distributions, Equivalent Weight, and Water Uptake at 25 °C of the Membranes

polymer	conversion (wt %)	M_n ($\times 10^5$)	M_w/M_n	EW in feed (g/mol H^+)	EW of copolymers[a] (g/mol H^+)	water uptake (wt %) RH = 30%	water uptake (wt %) RH = 98%
P(AN/APMA)	50	4.08	3.06	1100	680	1.66	9.33
P(AN/BPMA)	54	4.85	2.53	1139	594	1.83	10.82
P(AN/MBPMA)	47	2.09	2.39	1166	655	1.25	16.21
P(AN/TBPMA)	46			1590	1353	1.41	10.13
P(AN/TBPMA)	43	4.08	2.25	1319	764	1.16	8.60
P(AN/TPMA)	36	3.85	3.66	1343	666	0.64	4.59
P(AN/PPMA)	45	1.64	2.16	1535	1214	0.60	2.05

[a] Equivalent weight was estimated from the relative peaks of phenylene protons of the acidic site to the α-proton of the nitrile group in the copolymers in ^1H NMR spectra.

was then purified by silica gel column chromatography eluted with ethanol/benzene (1:2), and the solvent was evaporated. The final product was recrystallized from acetone/ethanol (7:3) and dried under vacuum to obtain TPA (6.60 g, 41% yield) as a white powder.

Synthesis of *N*-(4-(Trifluoroacetylimidesulfonyl)phenyl-2-methylacrylamide (TPMA). The TPA (6.0 g, 22 mmol) was dissolved in acetonitrile and reacted with methacryloyl chloride, following the same procedure as APMA. The monomer was recrystallized from acetonitrile and dried under vacuum to obtain 3.10 g of a white crystalline powder. The yield was 41%. ^1H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 9.99 (s, 1H), 7.74 (m, 4H), 5.82 (s, 1H), 5.54 (s, 1H), 1.94 (s, 3H). EI mass spectrum: Calculated for $C_{12}H_{11}F_3N_2O_4S$: *m*/*e* 336.28. Found: *m*/*e* 336. Elemental analysis (%): Calculated for $C_{12}H_{11}F_3N_2O_4S$: C, 42.86; N, 8.32; S, 9.53. Found: C, 41.16; N, 8.20; S, 9.44.

Synthesis of *N*-(4-Pentadecafluoroheptylimidesulfonyl)phenylamine (PPA). The synthesis of PPA followed a similar procedure to that of TPA. The crude product was purified by silica gel column chromatography eluted with ethanol/benzene (1:2), and the solvent was evaporated to obtain PPA (yield 37%) as a white powder.

Synthesis of *N*-(4-Pentadecafluoroheptylimidesulfonyl)phenyl-2-methylacrylamide (PPMA). PPMA was synthesized in a similar way to TPMA. The monomer was recrystallized from acetone/acetonitrile (1:1) and dried under vacuum to obtain a white crystalline powder. The yield was 28%. ^1H NMR (270 MHz, DMSO-d_6) δ (TMS, ppm): 9.95 (s, 1H), 7.69 (m, 4H), 5.82 (s, 1H), 5.52 (s, 1H), 1.94 (s, 3H). EI mass spectrum: Calculated for $C_{18}H_{11}F_{15}N_2O_4S$: *m*/*e* 636.33. Found: *m*/*e* 636. Elemental analysis (%): Calculated for $C_{18}H_{11}F_{15}N_2O_4S$: C, 33.97; N, 4.40; S, 5.03. Found: C, 33.61; N, 4.49; S, 4.85.

Acid Dissociation Constant (p*K*$_a$) of Monomers. The acid dissociation constant (pK_a) for an aqueous solution of APMA was determined by the pH titration method. Since BPMA was insoluble in water even in the salt form, the pK_a value for BPMA was estimated from the comparison of the chemical shift of the peak corresponding to the acidic proton of BPMA with that of APMA in the ^1H NMR spectra. The pK_a values for MBPMA, TBPMA, and TPMA were calculated from H^+ activities of aqueous solutions of the monomers (1 mM) determined by a pH meter. The pK_a value of PPMA, which was insoluble in water and also did not show NMR peaks in ^1H NMR spectra using common deuterated solvents, was approximated to be close to that of the structurally similar acid monomer, TPMA.

Preparation of Copolymers. Prior to polymerization, acrylonitrile (AN) was deoxygenated with bubbling N_2 gas for 20 min. The acid monomers and AN were dissolved in *N*,*N*-dimethylformamide (DMF), and 0.1 mol % AIBN was added to the solution as a radical initiator. N_2 gas was then bubbled for 5 min to the mixture to ensure an inert atmosphere. The copolymerization was carried out at 60 °C with continuous shaking for 10 h in the case of P(AN/APMA), P(AN/BPMA), P(AN/MBPMA), P(AN/TBPMA), and P(AN/TPMA) and for 30 h for P(AN/PPMA). The resulting copolymers were diluted with DMF, precipitated in excess methanol, and filtered. The copolymers were then washed with hot methanol to remove impurities, especially unreacted acid monomers. The final products were dried under vacuum at 80 °C for 24 h. A typical experimental condition is as follows.

TBPMA (0.465 g, 1.25 mmol) and AN (1.521 g, 28.6 mmol) were dissolved in DMF (1.5 g), and 0.1 mol % of AIBN was added to this solution. After purging oxygen from the solution, the copolymerization was conduced for 10 h at 60 °C under shaking. The copolymer was isolated by precipitation with methanol, washed with hot methanol, and dried to yield P(AN/TBPMA) (0.93 g, conversion 46%).

The conversions for all the prepared copolymers are presented in Table 1. The copolymers were characterized by ^1H NMR spectra. The EWs of the copolymers were estimated from the relative peak areas of phenylene protons of the acidic monomer to the α-proton of acrylonitrile.

Gel Permeation Chromatography (GPC). The dried copolymer was dissolved in a DMF/LiBr (2000 mL/1.737 g) solution at a concentration of 2.5 mg/mL. The solution was filtered through a syringe filter. GPC analyses were carried out using Shodex GPC KD-806M columns (two columns connected in series). A Shimadzu SPD-10AV UV detector, operated at 254 nm, was used for detection. The DMF/LiBr solution was used as the eluent at a flow rate of 1 mL/min driven by a Shimadzu LC-10AD pump. The injection volume was 100 μL. Narrow distribution polystyrene standards (Showa Denko) with molecular weights ranging from 580 to 3.16×10^6 were used for calibration. Since P(AN/TBPMA) (EW = 1353 g/mol H^+) was insoluble in the same solvent, the comparable GPC result could not be obtained.

Preparation of Membranes. The membranes were cast from copolymer solutions (10 wt %) in DMF.[16] The solvent was evaporated under atmospheric pressure at 50 °C for 12 h, followed by heating at 100 °C under vacuum for 24 h. The obtained membranes were stored in a desiccator over P_2O_5.[9] The membranes were mechanically strong, flexible, and transparent. The membrane, P(AN/PPMA), was a little brittle.

Water Uptake Measurements. Properly weighed dry membranes were placed inside an oven to reach equilibrium at various relative humidities. The membranes were then weighed on a microbalance immediately after wiping off the surface water, and the water uptake was calculated.[16]

Proton Conductivity Measurements. Proton conductivity measurements were conducted using the two-probe technique.[16] Prior to measurements, the cells with the membranes were placed inside the humidifying chamber for at least 5 h to reach equilibrium water uptake. The proton conductivity was determined using the complex impedance method over the frequency range from 5 Hz to 13 MHz.

Thermal Analysis. Differential scanning calorimetry (DSC) measurements were performed for dry and hydrated membranes on a Seiko Instruments differential scanning calorimeter (DSC 220C). To hydrate the membranes, 10−12 mg of the previously dried sample was placed in deionized water for about 6 h, followed by blotting to remove surface water. The samples were immediately transferred to aluminum pans and tightly sealed. The thermograms were recorded during cooling (+30 to −120 °C) and the following heating (−120 to +300 °C) scans at a cooling or heating rate of 10 °C min^{-1}. High-temperature stabilities for the samples were measured on a Seiko Instruments thermogravimetry/differential thermal analyzer 6200 (TG/DTA) from 30 to 550 °C at a heating rate of 10 °C $\min^{-1}$ under a N_2 atmosphere with open aluminum pans.

Membrane Electrode Assembly (MEA) Preparation. Carbon paper was cut into a square shape (2 × 2 cm^2). The catalyst slurry was prepared by mixing Pt/C and a sulfonimide polymer solution (5 wt %) in DMSO. The resulting solution was sonicated for 30 min and mixed using a high-speed homogenizer for 5 min. Then the catalyst slurry was pasted on the carbon paper. The electrodes were heated under an atmospheric pressure at 50 °C, followed by heating under vacuum at 80 °C for 24 h to evaporate the solvent. The catalyst loading on the electrodes was ca. 1 mg cm^{-2}. The membrane electrode assembly was fabricated by sandwiching a copolymer membrane between the two catalyst-loaded carbon papers, followed by hot-pressing the assembly at 50 °C and 6 MPa for 1 min.

Fuel Cell Evaluation. The MEA was placed in a 4 cm^2 single cell test fixture. The gas pressure, flow rate, humidification, and temperature were controlled using an Eiwa MET-S fuel cell humidification system. Pure H_2 and O_2 were provided at the anode and cathode, respectively. During the fuel cell operation, the test cell was operated at a constant temperature, and fully humidified H_2 and O_2 were supplied to the anode and cathode, respectively, at a rate of 200 mL $\min^{-1}$. The cell was maintained under open-circuit conditions until reaching a constant value. The current−voltage characteristics were then monitored with waiting time of 1 min for each measuring point.

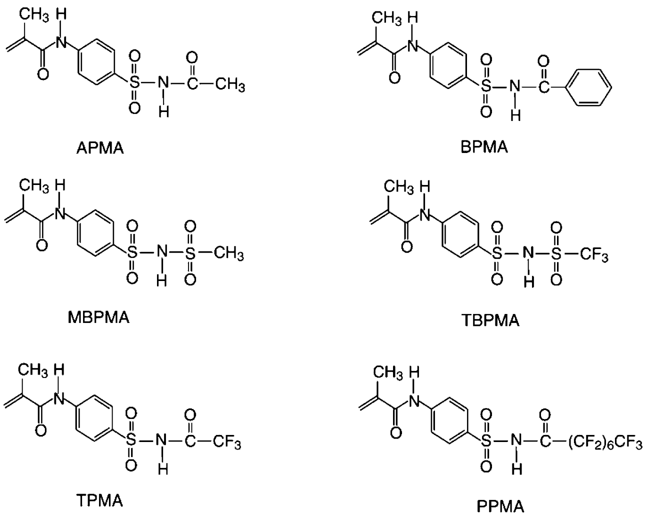
Results and Discussion

Synthesis and Characterization of the Monomers and Copolymers. The general synthetic route of the monomers is outlined in Scheme 1. The sulfanilamide has two amino groups in its structure. The nucleophilicity of the two groups is higher for the group directly attached to the phenylene group and lower for that attached to the sulfonyl group. To perform selective nucleophilic substitution to the lower reactive group, the reaction was carried out in the molten state at a higher temperature than the melting point of sulfanilamide (165 °C) in the presence of K_2CO_3, which dissolved in the molten sulfanilamide. The base, K_2CO_3, reacts with more acidic sulfonamide to yield the imide anion ($-SO_2N^-H$), which can be confirmed by evolution of CO_2. The nucleophilicity, now, becomes higher than that of the amino group directly attached to the phenylene group, which makes the selective nucleophilic substitution toward the esters and sulfonates. By changing R of the esters and sulfonates (Scheme 1), six different aniline derivatives could be obtained, and the successive reaction with methacryloyl chloride yielded the six different acid monomers.

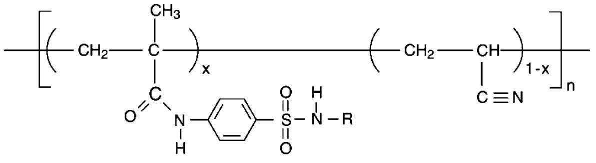
It is interesting to note that acidities of the sulfonimide monomers (Scheme 2) can be controlled by changing the substituted groups on the sulfonimides. The sulfonimide monomers show different acidities with a wide difference in the pK_a values, depending on the electron-withdrawing nature of the substituted groups.[16,17,21] The monomers APMA (pK_a = 4.95) and BPMA (pK_a < 4.95) are weak acids in nature. The acidic proton of water-insoluble BPMA showed a downfield chemical shift compared to that of the acidic proton of APMA in the NMR spectra, which is indicative of the relatively higher acidity of BPMA compared to that of APMA. Although the determination of pK_a values for strong acids is experimentally very difficult, and the estimation in this study is simply based on pH measurements of the 1 mM solutions, MBPMA, TBPMA, TPMA, and PPMA are found to be strong or superstrong acids (pK_a < 1).[16] The bis(sulfonyl) links in the imide group make the acidic proton of MBPMA and TBPMA highly dissociable in aqueous solutions, resulting in strong acidities of the monomers.[22] TBPMA seems to have the highest acidity (lowest pK_a) among the six different monomers.

Scheme 2. Structures of Acid Monomers and Copolymers

(a) Acid monomers



(b) Copolymers



R = $-COCH_3$, $-COPh$, $-SO_2CH_3$, $-SO_2CF_3$, $-COCF_3$, $-CO(CF_2)_6CF_3$

The acid monomers were copolymerized with AN monomer (Scheme 2) and characterized by ^{1}H NMR spectra. The ^{1}H NMR spectra correspond to the expected molecular structures of the copolymers. The monomer compositions in the feed for the copolymerization and the copolymer compositions are shown in Table 1 as EW in the feed and EW of the copolymers, respectively. It can be noticed that the acid monomer compositions in the copolymers become higher than those in the feed for all the copolymers, depending on monomer reactivity ratio of the monomers, though the precise determination has not been conducted. Table 1 also lists the molecular weights and molecular weight distributions of the prepared copolymers determined by GPC. The number-average molecular weights (M_n) of the copolymers are high, indicating high radical copolymerization reactivity of the acid monomers.

Thermal Behavior of the Membranes. Thermal properties for the dry membranes and hydrated membranes are tabulated in Table 2. All the membranes have reasonable thermal stability up to 250 °C. However, below the degradation temperature (T_d), all the copolymers show an exothermic peak (T_c) in the DSC thermograms, ranging from 179 to 195 °C. This corresponds to the temperature for the commencement of cyclization for the acrylonitrile moiety in the copolymers.[16] The membranes are amorphous and do not show any melting temperature in the DSC thermograms. Instead, the dry membranes form homogeneous glasses with a single T_g, ranging from 54 to 124 °C, depending

Table 2. Thermal Properties and Proton Conductivity of the Membranes

polymer	EW[a] (g/mol H^+)	T_g (°C)[b]		T_c (°C)[c]	T_d (°C)[d]	σ at RH = 98% (S cm^{-1})	
		dry	hydrated			40 °C	80 °C
P(AN/APMA)	680	92	66	179	271	1.2×10^{-4}	1.2×10^{-4}
P(AN/BPMA)	594	96	83	182	279	1.7×10^{-3}	2.1×10^{-4}
P(AN/MBPMA)	655	54	*e*	184	297	4.2×10^{-3}	2.9×10^{-2}
P(AN/TBPMA)	1353	71	35	187	267	1.3×10^{-3}	2.3×10^{-3}
P(AN/TBPMA)	764	71	54	187	316	2.3×10^{-2}	4.0×10^{-2}
P(AN/TPMA)	666	85	68	195	287	8.7×10^{-3}	3.7×10^{-3}
P(AN/PPMA)	1214	124	96	185	318	8.4×10^{-4}	2.1×10^{-5}

[a] Equivalent weight was estimated from the relative peaks of phenylene protons of the acidic site to the α-proton of the nitrile group in the copolymers in ^1H NMR spectra. [b] Onset temperatures of a heat capacity change of dry membrane and hydrated membrane, respectively (glass transition temperature, T_g). [c] An exothermic peak (cyclization temperature, T_c). [d] Temperature of 10% weight loss during heating scans from room temperature by using thermogravimetry. [e] No T_g was observed.

on the structures. With hydration of the membranes, the T_g is lowered compared with that of the dry membranes, ranging from 35 to 96 °C (Table 2). However, no melting endotherm of water is observed in the thermograms, indicating that water molecules in the membranes are highly hydrated to the acidic groups. The hydrated membrane, P(AN/MBPMA), does not show any T_g but showed an endothermic peak at ca. 0 °C, corresponding to melting of the free water.[20] This seems to be due to the largest water uptake among the membranes (vide infra). The fraction of the free water to the total adsorbed water is found to be 45 wt % from the DSC result.

Water Uptake of the Membranes. The results of the adsorption isotherm for water uptake for all of the membranes at 25 °C are presented in Table 1. The water uptake by all the synthesized membranes is relatively low compared with the membranes bearing the same acid functional groups but different backbone.[8,10] This is possibly due to the hydrophobicity of the acid monomers. The water uptake was increased for all the membranes with increasing relative humidity (Table 1). Water uptake by the nonfluorinated acid membranes, P(AN/APMA), P(AN/BPMA), and P(AN/MBPMA), becomes higher compared with those with higher equivalent weights.[16,23] The results suggest that hydrophilicity of the membrane increases with increasing the acid monomer compositions. On the contrary, the fluorinated membranes, P(AN/TBPMA), P(AN/TPMA) and P(AN/PPMA), adsorbed a lower amount of water compared with those with higher equivalent weights.[16] The lower water uptake may be due to the increase in the hydrophobicity. The replacement of the nonfluorinated substituted groups by the highly electron-withdrawing fluorinated substituted groups causes an increase in the acidity, while it simultaneously causes significant increase in the hydrophobicity. The water uptake seems to be determined by the change in the amphiphilicity with the composition of the acid monomers. The lowest water uptake is observed in the membrane, P(AN/PPMA), due to its long fluorinated side chain. The highest water uptake of 16 wt % is observed for the P(AN/MBPMA) membrane at 98% relative humidity.

Proton Conductivity of the Membranes. Proton conductivities of the hydrated membranes were measured in the temperature range of 40−95 °C. The conductivity data are tabulated in Table 2. All the membranes exhibit reasonable proton conductivity under the humidifying conditions, while the conductivity for dry membranes was 10^{-9}−10^{-8} S cm^{-1}.[16] The proton conductivity is influenced not only by acidity of the acid monomers but also by the water uptake. If a comparison of the conductivities is made between the weak acid membranes, P(AN/APMA) and P(AN/BPMA), and the strongly acidic but hydrophobic membranes, P(AN/TPMA) and P(AN/PPMA), one can recognize that the conductivities are comparable. The meager water uptake of the latter membranes cannot afford high conductivity, even if the acidity is high. Furthermore, the conductivities of the latter membranes decrease, whereas those of the former increase, with an increase in the temperature from 40 to 80 °C. The high proton conductivity is achieved by the membranes, P(AN/MBPMA) and P(AN/TBPMA), with high acidities of the acid monomers as well as the high water uptake. The conductivities of the membranes become higher than 10^{-2} S cm^{-1} at 80 °C.

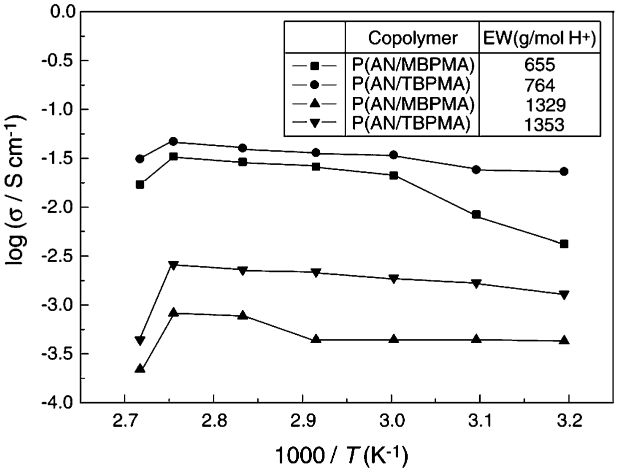


Figure 1. Temperature dependence of proton conductivities for the membranes, P(AN/MBPMA) and P(AN/TBPMA), with different equivalent weights (EW) at 98% relative humidity.

Figure 1 shows the temperature dependence of the proton conductivity for P(AN/MBPMA) and P(AN/TBPMA), having different EWs. Both of the membranes show higher proton conductivities, when the membrane has a lower EW. This comparison suggests that the conductivity correlates with the composition of the acid monomers in the copolymers. In addition, at a similar EW, P(AN/TBPMA) exhibits a higher conductivity than that of P(AN/MBPMA), being attributable to the stronger acidity of TBPMA. The proton conductivity for these membranes is high, though their water uptake is low, compared with the membranes having the same acid group but different backbone, which might be due to relatively strong interactions with the acid groups or an internal pore and/or a channel structure that is more favorable for proton conduction.[2,8] Although the temperature dependences of proton conductivity are shown only for the P(AN/MBPMA) and P(AN/TBPMA) membranes (Figure 1), the proton conductivity of the all of

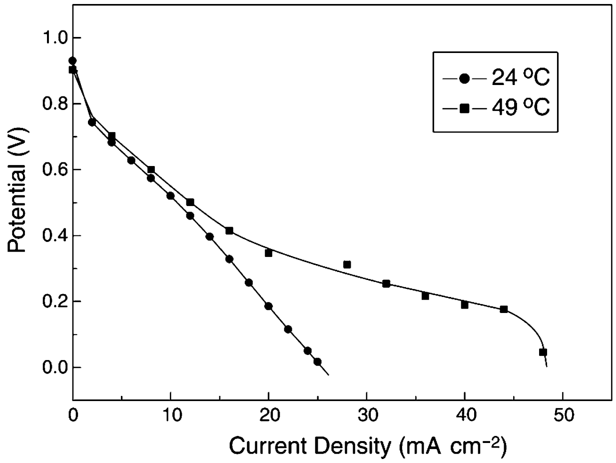


Figure 2. Potential–current polarization curves of an H_2/O_2 fuel cell using a P(AN/TBPMA) membrane at 24 and 49 °C.

membranes in this study greatly decreases at above 60–90 °C. The weak acid membranes tend to decrease the conductivity at lower temperatures. This decrease seems to be related to the adsorbed water property rather than T_g of the hydrated membranes.

Fuel Cell Performance. Preliminary experiments to explore the applicability of the present copolymer membranes to fuel cells were conducted. Figure 2 shows the current vs potential curve of an H_2/O_2 fuel cell using a P(AN/TBPMA) membrane with EW = 1353 g/mol H^+ and 90 μm thickness at 24 and 49 °C. Although this is just a preliminary experiment, we can confirm that electric power generation by the fuel cell using the present copolymer membrane is possible. At 80 °C, a stable polarization curve for the fuel cell could not be obtained. This may be due to weak hydrolysis stability of the membrane. The hydrolysis problem became more serious for a P(AN/TBPMA) membrane with the highest conductivity (a lower EW = 764 g/mol H^+), and it was impossible to obtain stable polarization curves, especially at higher temperatures. As evidence, we obtained the ^{1}H NMR spectrum of the membrane after the fuel cell test and observed some additional peaks which did not correspond to the ^{1}H NMR spectrum of the original structure. It is clarified by a hydrolysis stability test for the monomers by using ^{1}H NMR in water that the $-SO_2-NH-SO_2-$ group has much higher hydrolysis stability than the $-SO_2-NH-CO-$. However, even for the monomers having the $-SO_2-NH-SO_2-$ groups (MBPMA, TBPMA), the hydrolysis at the amide group, $-CONH-$, occurs at a high temperature. The hydrolysis stability of the monomers should be increased in our future study.

Conclusion

A series of novel acid monomers with different acid groups based on sulfonimides were successfully synthesized and characterized. The acid monomers were copolymerized with acrylonitrile monomer. The membranes were prepared from the resulting copolymers. The proton conductivity was measured for the hydrated membranes with a variation of EWs. The lower EW membranes show higher proton conductivity than the higher EW membranes. The MEA fabrication and fuel cell test were performed using a P(AN/TBPMA) membrane. In a single cell test, electric power generation was possible at 24 and 49 °C, indicating the possible applicability to fuel cell electrolyte membranes.

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References and Notes

(1) Pourcelly, G.; Gavach, C. In *Proton Conductors, Solids, Membranes and Gels–Materials and Devices*; Colomban, P., Ed.; Cambridge University Press: Cambridge, 1992.
(2) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.
(3) Savadogo, O. *J. New Mater. Electrochem. Syst.* **1998**, *1*, 47.
(4) Koppel, I. A.; Taft, R. W.; Anvia, F.; Zhu, S.-Z.; Hu, L.-Q.; Sung, K.-S.; DesMarteau, D. D.; Yagupolskii, L. M.; Yagupolskii, Y. L.; Ignat'ev, N. V.; Kondratenko, N. V.; Volkonskii, A. Y.; Slasov, V. M.; Notario, R.; Maria, P.-C. *J. Am. Chem. Soc.* **1994**, *116*, 3047.
(5) Razaq, M.; Razaq, A.; Yeager, E.; DesMarteau, D. D.; Singh, S. *J. Appl. Electrochem.* **1987**, *17*, 1057.
(6) Razaq, M.; Razaq, A.; Yeager, E.; DesMarteau, D. D.; Singh, S. *J. Electrochem. Soc.* **1989**, *136*, 385.
(7) Appleby, A. J.; Velev, O. A.; LeHelloco, J.-G.; Parthasarthy, A.; Srinivasan, S.; DesMarteau, D. D.; Gillette, M. S.; Ghosh, J. K. *J. Electrochem. Soc.* **1993**, *140*, 109.
(8) Sumner, J. J.; Creager, S. E.; Ma, J. J.; DesMarteau, D. D. *J. Electrochem. Soc.* **1998**, *145*, 107.
(9) Feiring, A. E.; Choi, S. K.; Doyle, M.; Wonchoba, E. R. *Macromolecules* **2000**, *33*, 9262.
(10) Hofmann, M. A.; Ambler, C. M.; Maher, A. E.; Chalkova, E.; Zhou, X. Y.; Lvov, S. N.; Allcock, H. R. *Macromolecules* **2002**, *35*, 6490.
(11) DesMarteau, D. D.; Martin, C. W.; Ford, L. A.; Xie, Y. Sulfonated Perfluorovinyl Functional Monomers, US Patent 6, 268, 532 B1, 2001.
(12) Ford, L. A.; Smith, D. W.; DesMarteau, D. D. *Abstr. Pap. Am. Chem. Soc.* **2000**, *220*, 7.
(13) Ford, L. A.; Smith, D. W.; DesMarteau, D. D. *Abstr. Pap. Am. Chem. Soc.* **2000**, *220*, 208.
(14) Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* **2002**, *35*, 6707.
(15) Zhou, X.; Weston, J.; Chalkova, E.; Hofmann, M. A.; Ambler, C. M.; Allcock, H. R.; Lvov, S. N. *Electrochim. Acta* **2003**, *48*, 2173.
(16) Rahman, M. K.; Aiba, G.; Susan, M. A. B. H.; Watanabe, M. *Electrochim. Acta* **2004**, in press.
(17) Park, S. Y.; Bae, Y. H. *Macromol. Rapid Commun.* **1999**, *20*, 269.
(18) Solan, A. D. B. *J. Appl. Chem. Biotechnol.* **1973**, *23*, 251.
(19) Yoda, N.; Marvel, C. S. *J. Polym. Sci., Part A* **1965**, *3*, 2229.
(20) Kim, Y. S.; Dong, L.; Hickner, M. A.; Glass, T. E.; Webb, V.; McGrath, J. E. *Macromolecules* **2003**, *36*, 6281.
(21) Bell, P. H.; Roblin, R. O., Jr. *J. Am. Chem. Soc.* **1942**, *64*, 2905.
(22) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.
(23) Bae, J.-M.; Honma, I.; Murata, M.; Yamamoto, T.; Rikukawa, M.; Ogata, N. *Solid State Ionics* **2002**, *147*, 189.

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