European Polymer Journal 44 (2008) 4054–4062

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Poly(arylene ether) ionomers containing sulfofluorenyl groups: Effect of electron-withdrawing groups on the properties

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ARTICLE INFO

Article history:
Received 2 May 2008
Received in revised form 1 August 2008
Accepted 17 September 2008
Available online 25 September 2008

Keywords:
Ionomers
Fuel cells
Poly(arylene ether)s
Proton conduction
Electron-withdrawing groups

ABSTRACT

For polymer electrolyte membrane fuel cell (PEMFC) applications, the effect of electron-withdrawing groups on the properties of sulfonated poly(arylene ether) (SPE) ionomer membranes was investigated. A series of poly(arylene ether)s containing fluorenyl groups and electron-withdrawing groups (sulfone, nitrile, or fluorine) was synthesized, which were sulfonated with chlorosulfonic acid using a flow reactor to obtain the title ionomers. The ionomers had high molecular weight ($M_n > 77$ kDa, $M_w > 238$ kDa) and gave tough, ductile membranes by solution casting. The ion exchange capacity (IEC) of the membranes ranged from 1.6 to 3.5 mequiv/g as determined by titration. The electron-withdrawing groups did not appear to affect the thermal properties (decomposition temperature higher than 200 °C). The presence of nitrile groups, especially at positions *meta* to the ether linkages, improved the oxidative stability of the SPE membranes, while it led to a deterioration of the hydrolytic stability. The perfluorinated biphenylene groups were effective in providing high mechanical strength with reasonable dimensional change, probably due to a somewhat decreased water absorbability. The SPE membrane containing sulfone groups showed the highest proton conductivity (10^{-3}–10^{-1} S/cm) at 20–93% RH (relative humidity) and 80 °C. The nitrile-containing SPE membrane showed smaller apparent activation energies for oxygen and hydrogen permeability and is thus considered to be a possible candidate for applications in PEMFCs.

1. Introduction

Ionomer membranes are of interest for a variety of applications, such as sensors, actuators, batteries, and fuel cells [1]. In particular, recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton-conductive ionomer membranes. Perfluorinated ionomers [2,3], e.g., Nafion (DuPont), are the state-of-the-art in fuel cell membranes; however, there is a great demand for alternative, non-fluorinated ionomers, which are considered to be promising in terms of providing improved high temperature stability, decreased gas permeability, and greater environmental friendliness (or recyclability), as well as lowered production costs [4–13].

A reasonable approach for this purpose is the acid functionalization of hydrocarbon polymers [14]. For example, aromatic polymers are attractive candidates as base frameworks due to their excellent thermal and chemical stability and high susceptibility to electrophilic sulfonation reactions. A number of aromatic polymers such as poly(ether ether ketone)s [15], poly(arylene ether)s [16], polyimides [17–19], polyphosphazenes [20,21], polybenzimidazoles [22,23], polyphenylenes [15], and others have been sulfonated or doped with mineral acids. Some of the resulting ionomer membranes are claimed to show high proton conductivity at high temperature. We have recently reported that the sulfonated poly(arylene ether sulfone)s containing fluorenylidene biphenylene groups showed high performance in fuel cell operation and survived for as long as

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doi:10.1016/j.eurpolymj.2008.09.017

5000 h without significant degradation [24–26]. The properties of the polyether ionomer membranes have been improved by detailed molecular consideration (number and position of methyl group substitution and/or copolymerization) [27]. However, proton conductivity and durability are still issues and need to be further improved. There have been a number of recent research relevant to this topic [28–31].

As part of an overall program in which we are seeking to develop new, high-stability, high-conductivity fuel cell ionomers, we examine herein the effects of modifying the hydrophobic component on the properties of the sulfonated polyether membranes. We hypothesize that electron-withdrawing groups should effectively lower the electron density of the attaching aromatic rings, resulting in decreased susceptibility to oxidative attack by radical species. A series of poly(arylene ether)s containing sulfofluorenyl groups as the hydrophilic component and electron-withdrawing groups (sulfone, nitrile, or fluorine) on the hydrophobic main chain was synthesized, and the thermal, oxidative, hydrolytic, and mechanical stability, water uptake, proton conduction, and gas permeability were investigated. The substitution position of the nitrile groups was also examined.

2. Experimental

2.1. Measurements

^{1}H (400 MHz) NMR experiments were performed on a Bruker AVANCE 400S spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. Molecular weight measurements were performed via gel permeation chromatography (Jasco 880-PU) on an instrument equipped with two Shodex KF-805 columns and a Jasco 875 UV detector set at 300 nm. *N*,*N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL/min. M_w and M_n were calibrated with standard polystyrene samples. TG/DTA was carried out with a Mac Science TG/DTA 2000, equipped with a Bruker MS 9600 mass spectrometer, at a heating rate of 5 °C/min under dry argon atmosphere.

2.2. Materials

2,6-Difluorobenzonitrile (2,6-DFB) (97%, TCI Co., Inc.), 3,5-difluorobenzonitrile (3,5-DFB) (99%, TCI Co., Inc.), decafluorobiphenyl (DFBP) (98% TCI Co., Inc.), 9,9-bis(4-hydroxyphenyl)fluorene (BHF) (98%, TCI Co., Inc.), potassium carbonate (99.5%, Kanto Chemical Co., Inc.), toluene (99.5%, Kanto Chemical Co., Inc.), chlorosulfonic acid (99%, Kanto Chemical Co., Inc.), and dichloromethane (99.5%, dehydrated, Kanto Chemical Co., Inc.) were used as received. 4-Fluorophenyl sulfone (FPS) (99%, Acros Organics) was purified by crystallization from ethanol. *N*,*N*-Dimethyl acetamide (DMAc) (99%, Kanto Chemical Co., Inc.) was dried over 3 A molecular sieves prior to use. Other chemicals were of commercially available grade and used as received.

2.3. Synthesis of homopolymers (PE-1a, -1b, -1c, and -1e)

The polymerization procedure for PE-1a has been reported in the literature [25]. The other homopolymers were synthesized in the same manner. A typical procedure is as follows. A 200-mL three-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BHF (5.0 mmol, 1.75 g), 2,6-DFB (5.0 mmol, 0.70 g), potassium carbonate (12.5 mmol, 1.73 g), toluene (3.0 mL), and DMAc (10 mL). The mixture was stirred at room temperature for a few minutes and heated at 140 °C for 3 h and at 165 °C for 3 h under N_2 atmosphere. Then, 60 mL of DMAc was added to the mixture to lower the viscosity. The mixture was poured dropwise into 1 L of deionized water to precipitate a white, flaky product. The crude product was washed with hot deionized water and methanol several times and purified by reprecipitation from chloroform/acetone. The resulting fibrous product was dried under vacuum at 60 °C for 15 h to give PE-1b in 65% yield. Using 3,5-DFB or DFBP instead of 2,6-DFB gave PE-1c in 70% yield or PE-1e in 40% yield, respectively.

2.4. Synthesis of copolymers (PE-1d)

Polymerization conditions for the copolymer were similar to those for the homopolymers. The molar ratio of 2,6-DFB to 3,5-DFB was set at 1:1. A white, flaky copolymer PE-1d was obtained in 65% yield.

2.5. Sulfonation

The sulfonation of fluorenyl-containing poly(arylene ether)s (PE-1) using a flow reactor was previously reported [32]. In order to achieve efficient mixing of polymer and chlorosulfonic acid solutions, a flow reactor was used in which both solutions were supplied through a narrow passage (1 mm) in the reactor via a microfeeder at a constant rate, so that the sulfonation reaction occurred rapidly before the sulfonated product precipitated out of the mixture. A typical procedure is as follows: a 200-mL syringe was charged with 100 mL of 0.01 M PE solution in dichloromethane, and a 100-mL syringe was charged with 30 mL of 0.1 M chlorosulfonic acid in dichloromethane. Both syringes were connected to the reactor via a Teflon tube. Each solution was supplied to the reactor simultaneously using the microfeeder. The flow rates of the polymer solution and the chlorosulfonic acid solution were set at 10 and 2–6 mL/min, respectively. The reaction was done at room temperature. The mixture obtained was poured dropwise into 500 mL of hexane. The resulting product was washed with hexane and water several times and dried under vacuum at 60 °C for 15 h to obtain a yellow powder of the sulfonated polymers (SPE-1).

2.6. Membrane preparation

SPE (0.35 g) solution in 10 mL of DMAc were cast onto a clean flat glass plate (9 cm × 6 cm). Drying the solution at 60 °C under atmospheric pressure for 15 h gave colorless and transparent membranes (50 μm thick). The membranes were immersed in 1 N HNO_3 for 12 h. The acidification process was repeated three times. The membranes were then washed with deionized water several times and dried under vacuum at 60 °C for 15 h.

2.7. Ion exchange capacity (IEC)

The IEC of the SPE-1 membranes was determined by ^1H NMR spectra and titration. In the ^1H NMR technique, changes in the integration ratio for the aromatic protons were taken. In the titration method, a piece of SPE membranes (1 × 2 cm, 50 μm thick) was equilibrated in 50 mL of 0.1 M NaCl aq for 15 h. The amount of HCl released from the membrane samples was determined by titration with 0.01 N NaOH aq using phenolphthalein as an indicator.

2.8. Oxidative stability

A small piece of membrane sample (1 cm× 2 cm) was soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h. The stability was evaluated by monitoring changes in molecular weight, IEC, and weight of the test samples. The values were averaged from two experiments (errors were within 10%).

2.9. Hydrolytic stability

A small piece of membrane sample (1 cm× 2 cm) was treated at 140 °C and 100% RH in a closed, pressurized vial for 24 h. The stability was again evaluated by monitoring changes in molecular weight, IEC, and weight of the test samples.

2.10. Mechanical strength

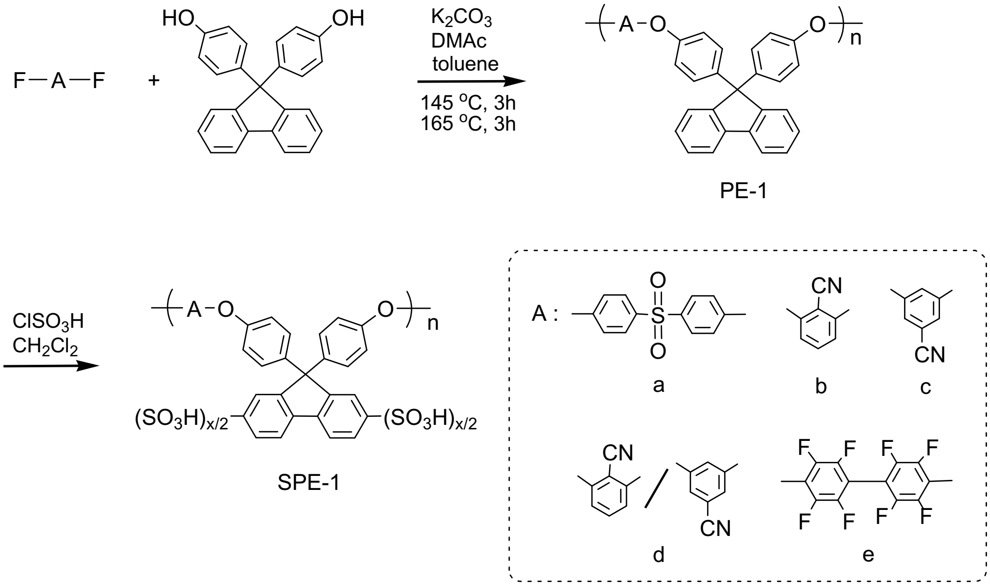
Tensile testing was performed with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a chamber in which the temperature and the humidity were controlled by flowing humidified air with a Toshin Kogyo temperature control unit Bethel-3A. Stress–strain curves were obtained at a speed 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)).

2.11. Water uptake and proton conductivity

Water uptake and proton conductivity of the SPE-1 membranes were measured with a Bel Japan solid electrolyte analyzer system MSB-AD-V-FC equipped with a chamber, a magnetic suspension balance, and a four-point probe conductivity cell. For water uptake measurements, membrane samples (50–70 mg, ca. 1 × 5 cm) were placed in a chamber and dried at 80 °C under vacuum for 3 h until constant weight as a dry material was obtained. The membranes were then equilibrated with N_2 gas at the given temperature and humidity for at least 1 h before the gravimetry was carried out. For the proton conductivity measurements, membrane samples (1.0 cm wide and 3.0 cm long) were placed in the same chamber. The samples were contacted with two gold wire outer current-carrying electrodes and two gold wire inner potential-detecting electrodes. Impedance measurements were carried out using a Solartron 1255B frequency response analyzer and Solartron SI 1287 potentiostat. The instrument was used in the potentiostatic mode with an AC amplitude of 300 mV and a frequency range from 1 to 100,000 Hz.

2.12. Gas permeability

Hydrogen and oxygen permeabilities of the SPE-1 membranes were measured with a GTR Tech 20XFYC gas permeation measurement apparatus equipped with a Yanaco G2700T gas chromatograph. The latter utilized a Porapak-Q column and a TCD detector. Argon and helium were used



Scheme 1. Synthesis of sulfonated poly(arylene ether) ionomers.

as the carrier gases for the hydrogen and oxygen measurements, respectively. A membrane sample (30 mm in diameter, 50 μm thick) was placed in a cell which has both 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, a dry 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. Before each measurement was carried out, the membrane was equilibrated with the gases at the given temperature for at least 3 h. The flow gas (3.7 mL) was sampled and subjected to gas chromatography to quantify the test gas permeating through the membrane. The gas permeation coefficient, Q (cm^3 (STD) cm cm^{-2} s^{-1} cm Hg^{-1}), was calculated according to the following equation:

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

where T (K) is the absolute temperature, 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, and l (cm) is the thickness of the membrane.

3. Results and discussion

3.1. Synthesis and characterization of polymers

A series of fluorenyl-containing poly(arylene ether)s, PE-1a–1e, with electron-withdrawing sulfone, nitrile, or fluorine groups was synthesized via nucleophilic substitution polycondensation reactions. PE-1a, -1b, -1c, and -1e were homopolymers, while PE-1d was a 1:1 copolymer of b and c (Scheme 1). The polymers were obtained as fibers with high molecular weights (M_n > 70 kDa, M_w > 200 kDa) (Table 1). Due to its very high reactivity, decafluorobiphenyl gave the highest molecular weight polymer PE-1e (M_n = 280 kDa, M_w = 667 kDa). The polymers were soluble in dichloromethane, chloroform and DMF and gave tough, flexible, transparent films by solution casting. NMR analyses confirmed the chemical structure of the polymers. In Fig. 1 is shown the ^{1}H NMR spectrum of PE-1c as a typical example, in which all of the aromatic protons have been well assigned to the proposed polymer structure. The integration ratios of the peaks were in fair agreement with the theoretical values.

Polymers PE-1a–1e were sulfonated with chlorosulfonic acid in dichloromethane solution, as described in Section 2. The sulfonated polymers SPE-1 showed solubilities that were different from those of the parent PE-1; they were insoluble in less polar solvents (dichloromethane and chloroform) but soluble in polar solvents (DMF and DMAc). The SPE-1 polymers were also able to be formed into transparent films with toughness and flexibility by solution casting. The ion exchange capacity (IEC) values and degree of sulfonation (×) of the SPE-1 membranes, as determined by titration, ranged from 1.6 to 3.5 mequiv/g (from 1.0 to 2.2 for ×). The sulfonation reaction was rather controllable, as indicated by the roughly linear relationship between [chlorosulfonic acid]/[polymer repeating unit] molar ratio and × (Fig. 2). The GPC analyses showed that the sulfonated polymers had higher apparent molecular weights

Table 1
Molecular weight and ion exchange capacity (IEC) of the polymers

Polymer	M_n (kDa)	M_w (kDa)	M_w/M_n	IEC[a] (mequiv/g)	×[b]
PE-1a	97	260	2.7	–	–
SPE-1a	216	657	3.0	1.6	1.0
SPE-1a	419	1494	3.6	2.5	1.8
PE-1b	120	340	2.8	–	–
SPE-1b	103	823	8.0	2.1	1.2
SPE-1b	365	1187	3.3	3.0	1.9
PE-1c	70	204	2.9	–	–
SPE-1c	77	384	5.0	2.1	1.3
SPE-1c	186	535	2.9	2.7	1.6
PE-1d	90	238	2.6	–	–
SPE-1d	132	419	3.2	2.0	1.1
SPE-1d	190	610	3.2	3.5	2.2
PE-1e	280	667	2.4	–	–
SPE-1e	170	305	1.8	1.6	1.2
SPE-1e	360	1073	3.0	2.7	2.2

[a] Determined by titration.
[b] Degree of sulfonation (see Scheme 1).

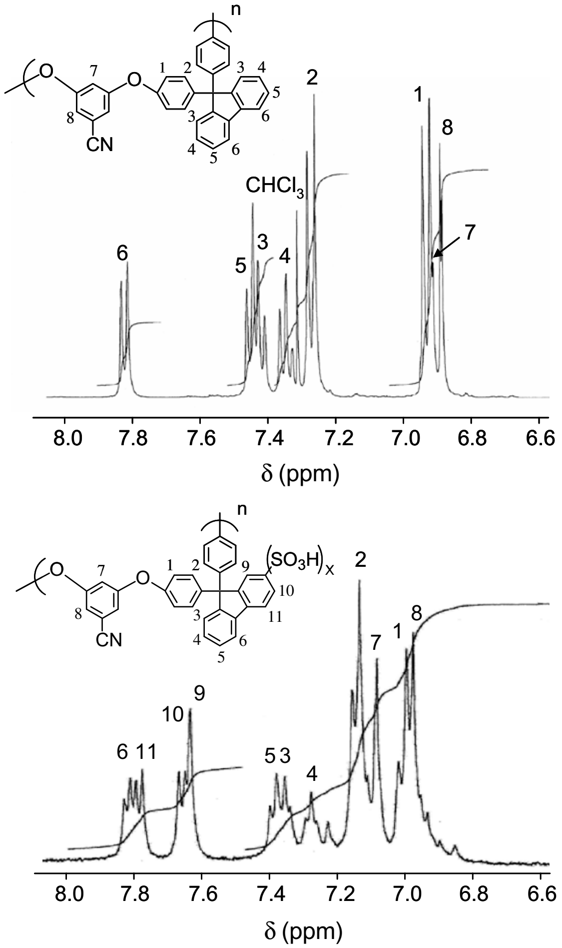


Fig. 1. ^{1}H NMR spectra of PE-1c (top) in CDCl$_3$ and SPE-1c (bottom) in DMSO-d_6.

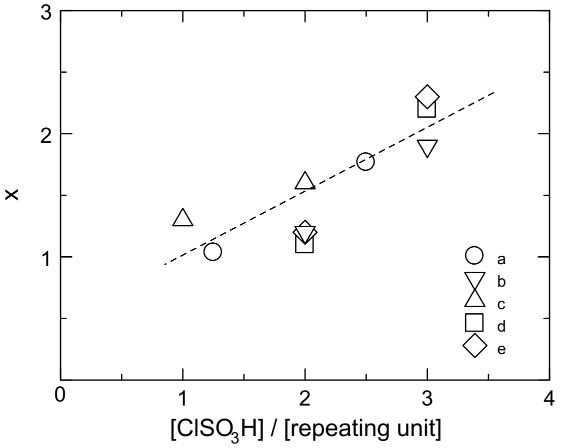


Fig. 2. Degree of sulfonation (×) as a function of molar stoichiometry of the sulfonation reaction.

than those of the corresponding parent polymers in most cases. The increase was greater than the mass of the substituted sulfonic acid groups. This is most likely because the sulfonated polymers have larger radii of gyration due to electrostatic repulsion between the sulfonic acid groups and thus exhibit larger volumes. This tendency was, as expected, more pronounced for the more highly sulfonated polymers.

The SPE-1 polymers were characterized by ^{1}H NMR analyses. Fig. 1 compares the ^{1}H NMR spectra of PE-1c and SPE-1c. While some chemical shifts were confirmed for protons 1, 2, 7 and 8 on the unsulfonated aromatic rings, more significant changes were observed for protons 3–6 on the fluorenyl rings. In the spectrum of SPE-1c, peaks 3–6 were smaller, and new peaks 9–11 appeared at 7.6–7.8 ppm. These new peaks were assignable to the protons of the sulfonated fluorenyl rings. The integration ratio of the peaks enabled us to estimate IEC as 2.2 mequiv/g. This value was in fair agreement with that obtained by titration (2.1 mequiv/g), indicating that the sulfonic acid groups were selectively substituted on the fluorenyl groups (at position 4). There were no evidences for the possible cross-linking via sulfone groups.

3.2. Thermal, oxidative, hydrolytic and mechanical stability of SPE ionomers

The thermal stability of the SPE ionomers was evaluated by TG/DTA-MS analyses under dry air. As a typical example, the TG/DTA-MS curve for SPE-1c (IEC = 2.1 mequiv/g) is shown in Fig. 3. It turned out that the SPE-1c decomposed from ca. 200 °C with the loss of sulfonic acid groups. The severer decomposition was observed from 350 °C due to the thermal oxidation of polymer structure as confirmed by the evolution of carbon dioxide. The TG/DTA-MS measurements were also done under dry Ar and the results are shown in Fig. 4. Three weight loss steps were observed. The first step was a minor weight loss from room temperature to ca. 200 °C and was assigned to the evaporation of hydrated water (H_2O = 18 *m*/*z*). The second one was a ma-

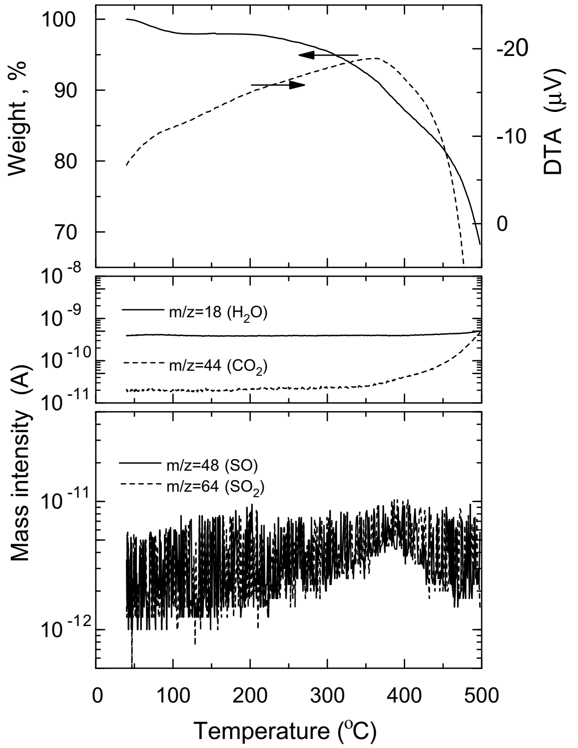


Fig. 3. TG/DTA-MS curves of SPI-1c (IEC = 2.1 mequiv/g) under dry air.

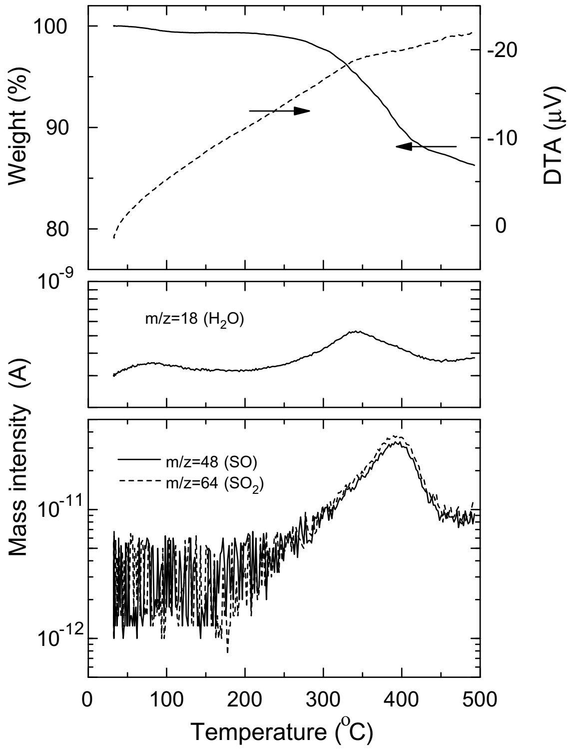


Fig. 4. TG/DTA-MS curves of SPI-1c (IEC = 2.1 mequiv/g) under dry argon.

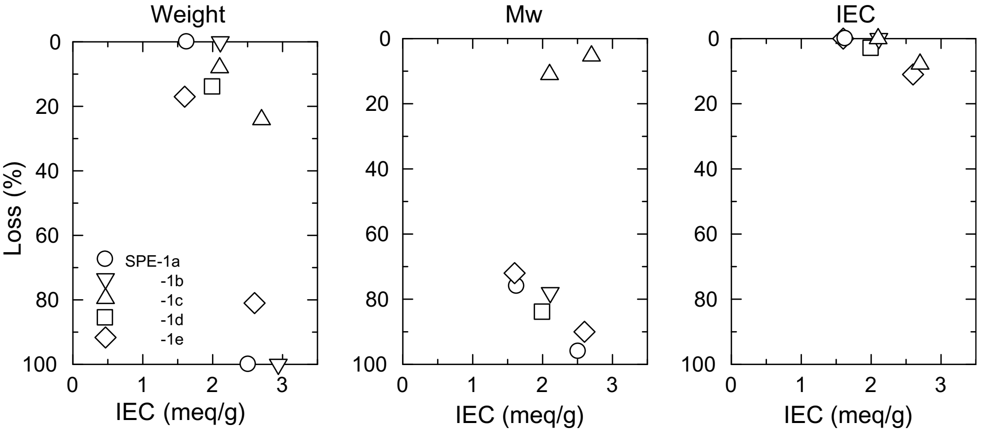


Fig. 5. Oxidative stability of SPI ionomer membranes; losses in weight, M_w and IEC.

jor weight loss from 200 to 400 °C and was assigned to the loss of sulfonic acid groups (SO = 48, $SO_2 = 64$ m/z). The third step was above 400 °C and was due to the degradation of the polymer structure. SPE-1c did not show an obvious glass transition behavior in the DTA curve. These thermal properties of SPE-1c were similar to those of SPE-1a [32] and thus, the nature of the electron-withdrawing groups in the ionomer main chain did not appear to affect the thermal properties of the ionomers.

Taking fuel cell applications into account, stability, both oxidative and hydrolytic, is a critical issue for proton-conductive ionomer membranes. We have investigated the oxidative and hydrolytic stability of SPE ionomer membranes under accelerated conditions. In the oxidative stability test, we used Fenton's reagent with which polymer main chains degrade as a result of attack by radical species ($HO^{\cdot}$ and $HOO^{\cdot}$). The losses in weight, molecular weight (M_w) and IEC resulting from the oxidative stability test are plotted as a function of IEC in Fig. 5. A general trend is that higher IEC membranes are less oxidatively stable due to the increased hydrophilicity. The SPE-1a, -1b and -1e membranes, with IEC values greater than 2.5 mequiv/g, have mostly dissolved in the hot Fenton's reagent. In contrast, the SPE-1c membrane, with an IEC of 2.7 mequiv/g, was much more oxidatively stable, with a weight loss of 24%. The better stability of the SPE-1c membrane was also supported by a lower loss in M_w compared to those of the other SPE ionomer membranes. It is probably because there are no displaceable hydrogen atoms *meta* to the nitrile groups in SPE-1c. The perfluorinated biphenylene groups in SPE-1e were not effective in improving the oxidative stability. The SPE ionomer membranes showed only minor losses in IEC, suggesting that the sulfonic acid groups are rather robust with respect to the harsh oxidative conditions.

In Fig. 6, the losses in weight, M_w and IEC resulting from the hydrolytic stability test are shown as a function of IEC. Although the weight losses were relatively low and relatively less dependent on IEC, losses in M_w and IEC were significant. SPE-1b and -1c showed particularly large M_w losses. Since nucleophilic attack by water should be the major mechanism for hydrolytic degradation of SPE ionomers, the nitrile groups, with their strong electron-withdrawing nature, have an opposite (i.e., deleterious) effect

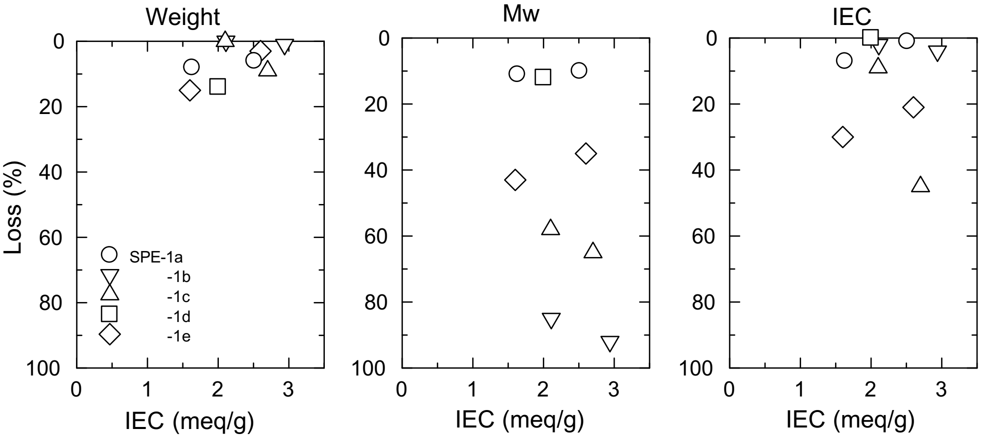


Fig. 6. Hydrolytic stability of SPI ionomer membranes; losses in weight, M_w and IEC.

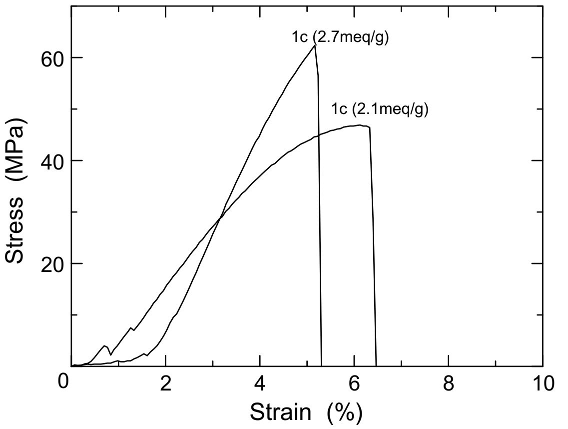


Fig. 7. Stress versus strain curves of SPE-1c membranes at 85 °C and 0% RH with IEC (mequiv/g) in parentheses.

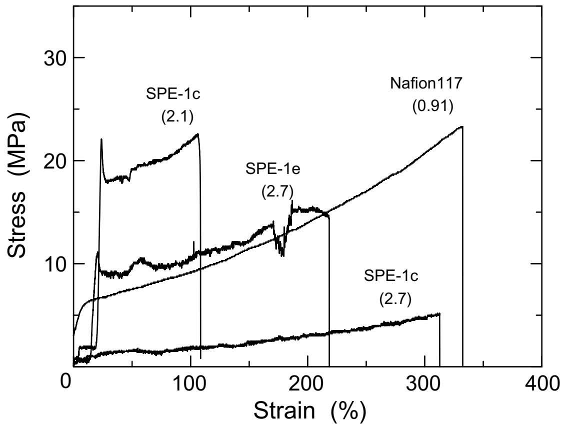


Fig. 8. Stress versus strain curves of SPE-1c and -1e, and Nafion 117 membranes at 85 °C and 93% RH with IEC (mequiv/g) in parentheses.

on the hydrolytic stability compared to the oxidative stability. This is reasonable, since oxidation involves an electrophilic attack by hydroxyl radicals, and hydrolysis involves nucleophilic attack by water. It may be noted that IEC decreased to some extent for the SPE-1c and -1e membranes, that is, both main chain degradation and loss of sulfonic acid groups are involved. SPE-1a, containing biphenylene sulfone groups, was most hydrolytically stable. The SPE-1a membrane with an IEC of 2.5 mequiv/g showed 6% (weight), 10% (M_w) and 1% (IEC) losses, respectively, and retained its flexibility and ductility after the testing.

Stress–strain curves were measured for SPE-1c (IEC = 2.1, 2.7 mequiv/g) membranes at 85 °C under dry conditions and the results are shown in Fig. 7. Both membranes were tough with maximum stress higher than 40 MPa and strain lower than 7%. The higher mechanical strength for the SPE-1c with IEC = 2.7 mequiv/g probably implies more hydrogen bondings involved in the higher IEC membranes. The stress–strain curves were also measured for SPE-1c (IEC = 2.1, 2.7 mequiv/g) and -1e (IEC = 2.7 mequiv/g) membranes at 85 °C and 93% RH (relative humidity) and are compared to that of the perfluorinated ionomer (Nafion 117) membrane in Fig. 8. The SPE-1c (IEC = 2.1 mequiv/g) membrane showed high maximum stress (24 MPa) comparable to that of Nafion 117, with much lower strain (108%) than that of Nafion 117 (332%). Despite its higher IEC, the SPE-1c membrane was dimensionally more stable than Nafion 117, due to the rigid aromatic main chain structure. Increasing the IEC significantly lowered the mechanical strength of the SPE-1c membrane; the maximum stress was 5 MPa and the strain at break was 313% for SPE-1c with IEC = 2.7 mequiv/g. Since higher IEC membranes absorb more water under humidified conditions, as discussed below, intermolecular interactions would be weakened, leading to lower mechanical strength. The SPE-1e membrane (IEC = 2.7 mequiv/g) showed higher maximum stress (15 MPa) and lower strain at break (218%) than those for the SPE-1c membrane with the same IEC. Clearly, the introduction of perfluorinated biphenylene groups as linear and rigid moieties improved the mechanical properties. The perfluorinated biphenylene groups contribute to the hydrophobicity of the membranes, as confirmed by the lower water uptake, in spite of its high IEC value (see below).

3.3. Water uptake, proton conductivity and gas permeability of SPE ionomers

Water uptake and proton conductivity for the SPE ionomer membranes were measured as a function of humidity (20–93% RH) at 80 °C and compared to those for the Nafion 112 membrane in Fig. 9. The electron-withdrawing hydrophobic substituents greatly affected the water uptake behavior. The water uptake did not track the IEC. Taking the IEC value into account, SPE-1c showed the highest water uptake among the SPE ionomer membranes (hydration number per sulfonic acid (λ) was 2.7 at 20% RH and 9.7 at 93% RH, respectively.). It is thought that the nitrile groups *meta* to the ether linkages contribute to producing greater free volume in the membrane and increasing ability to absorb water. This effect was not obvious for SPE-1b, with nitrile groups at positions *ortho* to the ether groups, or for the copolymer SPE-1d, with nitrile groups at *ortho*/*meta* (=50/50) positions. SPE-1e showed water uptake less dependent on IEC compared to SPE-1a. Strong hydrophobicity and bulkiness of the perfluorinated biphenylene groups may have counteracted the water absorbability of SPE-1e.

The proton conductivities of the SPE membranes approximately followed the order of the IEC, and the effect of the electron-withdrawing substituents was smaller than that on the water uptake. However, the perfluorinated biphenylene groups appeared to have a negative effect on the proton conductivity. The SPE-1e (IEC = 2.7 mequiv/g) membrane showed a much lower proton conductivity (4.3×10^{-5} to 2.9×10^{-2}) than that of SPI-1a (IEC = 2.5 mequiv/g) (1.2×10^{-4} to 0.1) at all humidity conditions (20–93% RH) examined, despite the former's higher IEC. It is rather surprising that the lower IEC SPE-1e membrane (1.6 mequiv/g) also showed higher water uptake but lower

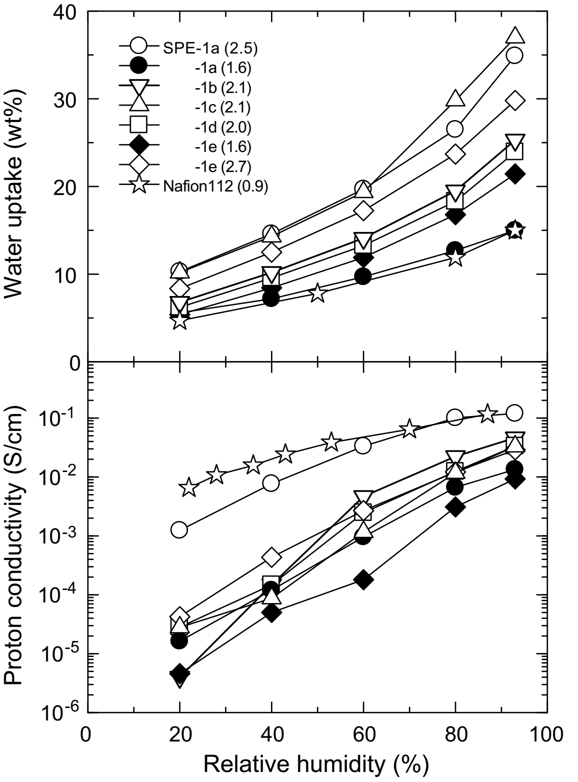


Fig. 9. Humidity dependence of water uptake and proton conductivity of SPE and Nafion 112 membranes at 80 °C with IEC (mequiv/g) in parentheses.

proton conductivity than those of the SPE-1a membrane with the same IEC value. The results indicate that much of the absorbed water did not contribute to the proton conduction in the SPE-1e membrane. On the other hand, comparison of the proton conductivities among the SPE-1b, -1c and -1d membranes revealed that the substitution position of the nitrile groups was less likely to affect the proton conductivity; the humidity dependence of the proton conductivities of the three membranes was very similar. Among these, the SPE-1d membrane with the proton conductivity ranging from 2.8×10^{-5} (20% RH) to 3.3×10^{-2} (93% RH) S/cm is the most preferable in terms of its relatively low water uptake (i.e., smaller swellability).

The hydrogen and oxygen permeabilities of SPE-1a (IEC = 1.6 mequiv/g), SPE-1c (IEC = 2.1 mequiv/g) and Nafion112, measured by gas chromatography under dry conditions, resulted in the temperature dependences of the gas permeability coefficient shown in Fig. 10. Both the SPE-1a and SPE-1c membranes showed slightly higher gas permeabilities at 40 °C. Since the apparent activation energies for the gas permeability coefficients for the SPE membranes were much lower than those for the Nafion 112 membrane, the gas permeability coefficients for the SPE membranes became smaller at high temperatures (80 and 120 °C); $E_a(H_2) = 15$ (SPE-1a), 11 (SPE-1c), 39 (Nafion 112) and $E_a(O_2) = 17$ (SPE-1a), 7 (SPE-1c), 53 (Nafion 112) kJ/mol. This tendency was more pronounced for oxygen than hydrogen, probably because of the high affinity of the perfluorinated polymers for oxygen. Accordingly, the oxygen permeability coefficients for the SPE membranes were more than an order of magnitude lower than that for the Nafion 112 membrane, which is a definite advantage for fuel cell membranes. The slightly lower gas permeability for SPE-1c than that for SPE-1a probably reflects the former's high IEC value, since gases are considered to permeate mainly through the nonionic hydrophobic domains of ionomer membranes.

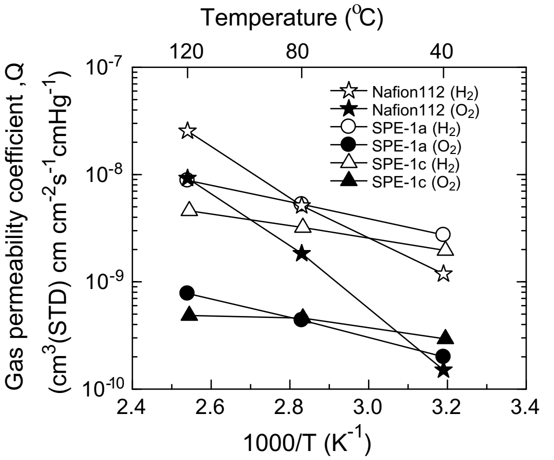


Fig. 10. Temperature dependence of gas permeability coefficient of SPE-1a (IEC = 1.6 mequiv/g), -1c (IEC = 2.1 mequiv/g), and Nafion 112 membranes.

4. Conclusions

High molecular weight poly(arylene ether)s containing fluorenyl groups and electron-withdrawing groups were synthesized via aromatic nucleophilic substitution polymerization. The sulfonation reaction of the polymers with chlorosulfonic acid proceeded quantitatively using a flow reactor to give the title ionomers, with the sulfonic acid groups attached at pre-specified positions on the fluorenyl groups. The resulting ionomer membranes were transparent, tough and flexible. The electron-withdrawing groups did not significantly affect the thermal decomposition behavior of the membranes (which was shown to correspond to the desulfonation reaction), since they were attached to the polymer main chain and were electronically and sterically separate from the sulfonic acid groups. In contrast, the nitrile groups improved the resistance to oxidative attack (presumably due to electrophilic substitution by hydroxyl radicals) and degraded the resistance to hydrolytic attack (presumably due to nucleophilic substitution by water molecules). Both oxidative and hydrolytic degradation involved main chain scission, while desulfonation occurred in the hydrolysis. The perfluorinated biphenylene groups were apparently effective in improving the mechanical strength. The water uptake and proton conductivity behavior were somewhat more complex and could not be simply explained in terms of the nature of the electron-withdrawing groups. The sulfone-containing SPE-1a membrane with high IEC showed high proton conductivity due to its high water absorbability. The apparent activation energies for hydrogen and oxygen permeability for the SPE membranes were much lower than those for the Nafion membrane, with the lowest values for the nitrile-containing SPE-1c membrane.

Acknowledgements

This work was partly supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan through a grant-in-aid for Scientific Research (20350086) and by the New Energy and Industrial Technology Development Organization (NEDO) through HiPer-FC project.

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