Synthesis of sulfonated poly(arylene-*co*-naphthalimide)s as novel polymers for proton exchange membranes

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ARTICLE INFO

ABSTRACT

A series of novel sulfonated poly(arylene-*co*-binaphthalimide)s (SPPIs) were successfully synthesized via Ni(0) catalytic coupling of sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate and bis(chloronaphthalimide)s. Bis(chloronaphthalimide)s were conveniently prepared from 5-chloro-1,8-naphthalic anhydride and various diamines. Tough and transparent SPPI membranes were prepared and the electrolyte properties of the copolymers were intensively investigated as were the effects of different diamine structures on the copolymer characterisitics. The copolymer membrane **Ia-80**, with an ion exchange capacity (IEC) of 2.50 meq g^{-1}, displayed a higher proton conductivity, i.e. 0.135 S cm^{-1} at 20 °C, as compared to Nafion 117 (0.09 S cm^{-1}, 20 °C). The copolymer membrane **Id-70**, containing 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA) units, exhibited excellent stability toward water and oxidation due to the introduction of hydrophobic methyl groups on the *ortho*-position of the imido bond in the copolymer. The mechanical property of **Id-70** remained virtually unchanged after immersing membrane in pressured water at 140 °C for 24 h. Furthermore, the introduction of aliphatic segment a hexane-1,6-diamine (HDA) in copolymer led to a significant increase in proton conductivity and water uptake with increasing temperature; the proton conductivity of the **Ic-70** membrane reached 0.212 S cm^{-1} at 80 °C, which was higher than Nafion 117 as well as of the membranes based on aromatic diamines at equivalent IEC values. Consequently, these materials proved to be promising as proton exchange membranes.

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1. Introduction

A growing attention has been focused on proton exchange membrane fuel cells (PEMFCs) for transport, as well as stationary and portable applications, due to their low emissions and high conversion efficiency [1–3]. As key component in PEMFC fabrication, polymer electrolyte membranes (PEMs) should satisfy certain essential requirements in order for the fuel cell application to be successful. Perfluorinated sulfonic acid ionomers such as Nafion, developed by DuPont, are state-of-the-art PEMs in commercial systems due to their high proton conductivity and excellent stability. However, some specific limitations for Nafion, including high cost and considerable gas permeability, as well as the loss of the preferable properties at high temperature, have stimulated the development of new alternatives for PEM material [4–6].

In recent years, many kinds of sulfonated aromatic polymers have been widely investigated as candidates for PEM materials [7–20]. Particularly, sulfonated aromatic polyimides have been largely developed by several groups due to their superior chemical

resistance, excellent thermal and mechanical stabilities, and good film forming ability, which properties comply with those required for PEMs [21–34]. The "structure–property" relationships of the sulfonated polyimides have been systematically studied. Okamoto et al. has reported that the water stability of the SPIs could be improved by utilizing high basic and more flexible sulfonated and nonsulfonated diamines [26]. It was also revealed that sulfonated polyimides bearing pendant sulfonic acid groups are favorable for forming continuous ionic channel as well as for water keeping and proton transport [30].

The most common method used for preparing SPIs is the polycondensation of 1,4,5,8-naphthalenetetracarboxylic dianhydride, nonsulfonated diamine with sulfonated diamine. Since bis(naphthalene anhydride)s display a reduced electrophilic reactivity, its polycondensation reaction has been shown to require a high reaction temperature (>180 °C) and the use of an organic acid or base as catalyst. The Ni(0) catalytic coupling of bis(aryl halide)s is one of the most recent approaches for developing high performance materials. Aromatic dichlorides containing phthalimide moieties can be readily prepared from 4-chlorophthalic anhydride and diamines. In a previous paper, we reported on the successful synthesis of asymmetrical sulfonated poly(arylene-*co*-naphthalimide)s bearing a CF$_3$ group at the *ortho*-position of the imido

groups. The synthesized material exhibited a high proton conductivity and an improved water stability by Ni(0) catalytic copolymerization, thus showing potential as a polymer for proton exchange membranes [29]. As a continuation of this study, symmetrical sulfonated poly(arylene-*co*-binaphthalimide)s, prepared from bis(chloronaphthalimide)s and sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate were introduced as new polyelectrolytes for PEMFC applications. Bis(chloronaphthalimide)s were obtained from a simple reaction between 5-chloro-1,8-naphthalic anhydride and diamines, and thus the structure of the copolymer could be easily tuned by introducing various diamines to binaphthalimide dichlorides.

In the study reported in the present paper, the properties that are related to the initial fuel cell performance of these membranes has been intensively investigated, and the effects of the diamines structures on the properties of the copolymers were evaluated based on their electrolyte properties (IEC, water uptake, thermal stability, water stability, oxidative stability, mechanical properties and proton conductivity). The results should be instructional in the design of superior membranes for an improved fuel cell performance.

2. Experimental section

2.1. Materials

Reagent-grade anhydrous $NiBr_2$ was dried at 220 °C under vacuum. Triphenylphosphine (PPh_3) was recrystallized from hexane. Zinc dust was stirred with acetic acid, filtrated, washed thoroughly with ethyl ether, and dried under vacuum. Isoquinoline (99%) and 5-chloro-1,8-naphthalic anhydride were used as-received from Shanghai Kuilin Chemical Co., Ltd. and Beijing Multi. Technology Co., Ltd., respectively. 4,4′-Methylenedianiline (MDA) (diaminodiphenylmethane), 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA), hexane-1,6-diamine (HDA), 4,4′-diaminodiphenylether (ODA) were purchased from Aldrich and used without further treatment. Sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate was prepared according to a previously described procedure [20]. *N,N*-Dimethylacetamide(DMAc) was dried over CaH_2, distilled under reduced pressure and stored over 4 Å molecular sieves.

2.2. Monomer and polymer syntheses

2.2.1. Synthesis of 4,4′-bis(5-chloro-1,8-naphthalimido)-diphenylether (1a)

In a 500 mL round-bottomed flask, 23.3 g (0.10 mol) of 5-chloro-1,8-naphthalic anhydride, 10.01 g (0.05 mol) of 4,4′-diaminodiphenylether (ODA), 7.2 mmol of isoquinoline and 300 mL of acetic acid were added, and this solution was refluxed for 48 h. The precipitate was filtrated and recrystallized by acetic acid, washed with ethanol, and dried in vacuum. A yellow product (denoted 1a) was obtained at a yield of 72%. ^{1}H NMR (DMSO-d_6): δ 8.64–8.67 (2H, d), 8.60–8.63 (2H, d), 8.44–8.47 (2H, d), 8.03–8.09 (4H, m), 7.44–7.47 (2H, d), 7.22–7.25 (2H, d). IR (KBr): 1709 and 1665 cm^{-1} (C=O of imide).

2.2.2. Synthesis of 4,4′-bis(5-chloro-1,8-naphthalimido)-diphenylmethane (1b)

This compound (denoted 1b) was synthesized from 5-chloro-1,8-naphthalic anhydride and 4,4′-methylenedianiline (MDA) following a similar procedure to that described above. The yield of 1b was 84%. ^{1}H NMR (DMSO-d_6): δ 8.67–8.70 (2H, d), 8.59–8.62 (2H, d), 8.44–8.47 (2H, d), 8.03–8.10 (4H, m), 7.44–7.47 (2H, d), 7.33–7.36 (2H, d). IR (KBr): 1708 and 1664 cm^{-1} (C=O of imide).

2.2.3. Synthesis of 1,6-bis(5-chloro-1,8-naphthalimido)hexane (1c)

This compound (denoted 1c) was synthesized from 5-chloro-1,8-naphthalic anhydride and hexane-1,6-diamine (HDA) according to a procedure similar to that described above. The yield of 1c was 74%. ^{1}H NMR (DMSO-d_6): δ 8.60–8.62 (2H, d), 8.55–8.58 (2H, d), 8.40–8.43 (2H, d), 7.99–8.06 (4H, m), 4.06(4H, NCH_2), 1.40–1.66 (8H, 4CH_2). IR (KBr): 1700 and 1658 cm^{-1} (C=O of imide).

2.2.4. Synthesis of 3,3′-dimethyl-4,4′-bis(5-chloro-1,8-naphthalimido)diphenylmethane (1d)

This compound (denoted 1d) was synthesized from 5-chloro-1,8-naphthalic anhydride and 3,3′-dimethyl-4,4′-methylenedianiline (DMMDA) in a similar manner as that described above. The yield of 1d was 78%. ^{1}H NMR (DMSO-d_6): δ 8.65–8.68 (2H, d), 8.60–8.63 (2H, d), 8.45–8.48 (2H, d), 8.02–8.09 (4H, m), 7.35 (2H, s), 7.24–7.30 (4H, d), 4.07 (2H, s), 2.07 (6H, s). IR (KBr): 1711 and 1664 cm^{-1} (C=O of imide).

2.2.5. General procedure for synthesis of the copolymers

The synthesis of **Ia-70** is here given as an example: $NiBr_2$ (0.16 g, 0.71 mmol), PPh_3 (1.30 g, 4.96 mmol) and zinc (2.60 g, 40.00 mmol) were charged to a 100 mL three-necked round-bottomed flask. The flask was evacuated and filled with nitrogen for three times. Dry DMAc (20 mL) was added via a syringe and the mixture became reddish brown over a time period of 20 min. The **1a** monomer (1.88 g, 3 mmol) and sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate (monomer **2**) (2.46 g, 7 mmol) were added, and the reaction mixture was stirred at 90 °C for 4 h. The resulting viscous mixture was diluted with 10 mL of DMAc, filtered, and then poured into 200 mL of 25% HCl/water. The copolymer was collected by filtration, washed with water, and then dried in vacuum at 200 °C for 24 h. The copolymer yield was 97%.

2.3. Membrane preparation and characterization

2.3.1. Membrane preparation

The copolymers were dissolved in NMP in order to form a 5–8 wt% solution at 80 °C, after which the solution was filtered and cast on a glass sheet. The solvent was then evaporated by heating at 120 °C for 12 h. The as-cast membranes were soaked in methanol for 24 h to remove the residual solvent, and then treated with 1.0 mol L^{-1} sulfuric acid at room temperature for 72 h for proton exchange. The proton exchange membranes were thoroughly washed with water and subsequently dried in vacuum at 100 °C for 12 h.

2.3.2. Measurements

Nuclear magnetic resonance (NMR) spectra were measured at 300 MHz on a Bruker AV400 spectrometer (Germany). FT-IR spectra of the copolymers were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer (Cambridge, MA). The inherent viscosities were determined on solutions of polymer (at a concentration of 0.5 g dL^{-1}) *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. Molecular weight measurement was performed via gel permeation chromatography/light scattering (GPC/LS) at 30 °C using an HPLC 515 pump equipped with Wyatt Optilab DSP and Wyatt DAWN EOS light scattering detectors. The separations were achieved in HMW 6E columns with 0.1 M LiBr in DMF as eluent at a flow rate of 1.0 mL min^{-1}. M_n and M_w were calibrated with a polystyrene standard. Thermogravimetric analyses (TGA) were carried out in nitrogen on a Perkin–Elemer TGA-2 thermogravimetric analyzer (Inspiratech 2000 Ltd, UK) at a heating rate of 10 °C min^{-1}. Tensile measurement was performed on a mechanical tester Instron-1211 instrument (Instron Co., USA) at a speed of 2 mm min^{-1} at ambient humidity ($\sim$50% relative humidity). The proton conductivity (σ, S cm^{-1}) of each membrane coupon (size: 1 cm × 4 cm) was obtained according to $\sigma = d/L_s W_s R$ (where d is the distance between the reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, the

ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK) [35]. The membranes were sandwiched between two pairs of gold-plate electrodes, and this sandwich structure was placed in a Teflon cell. The distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water so as to carry out conductivity measurements under fully hydrated conditions out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements, and at any given temperature, the samples were re-equilibrated for at least 30 min prior to the measurements. Repeated measurements were then performed at each temperature with 10 min intervals, until the conductivity became constant.

2.3.3. Water uptake and dimensional change

The membrane sample (30–40 mg per sheet) was dried at 80 °C under vacuum for 10 h until it reached a constant weight. It was then immersed in deionized water at given temperature for 4 h, after which it was quickly taken out, wiped with tissue paper, and quickly weighted on a microbalance. The water uptake (WU) was calculated according to Eq. (1):

$$WU = (W_s - W_d)/W_d \tag{1}$$

where W_s and W_d are the weights of the dry and corresponding water-swollen membranes, respectively.

The dimensional changes of the membranes with respect to their thickness and diameter were characterized by Eqs. (2a) and (2b):

$$\Delta T_c = (T - T_s)/T_s \tag{2a}$$

$$\Delta L_c = (L - L_s)/L_s \tag{2b}$$

Here T_s and L_s represent, respectively, the thickness and diameter of the membrane equilibrated at 70% relative humidity (RH), and T and L refer to the corresponding values in a membrane equilibrated in liquid water for 5 h.

The number of water molecules per ionic group (λ) can be determined from water uptake and the IEC of the membrane according to Eq. (3):

$$\lambda = n(H_2O)/n(SO_3) = (\text{water uptake})/(18\text{IEC}) \tag{3}$$

where $n(H_2O)$ is the H_2O mole number, $n(SO_3^-)$ the SO_3^- group mole number, and 18 corresponds to the molecular weight of water (18 g mol^{-1}).

2.3.4. Oxidative stability and water stability

A small membrane sample (30–40 mg) with a thickness of approx. 40 μm was soaked in Fenton's reagent (30% H_2O_2 containing 30 ppm $FeSO_4$) at room temperature. The stability was evaluated by recording the time at which the membranes began to break into pieces and completely dissolve.

The water stability test was carried out by immersing a sample into deionized water at 140 °C (to represent accelerated conditions) and was evaluated as the time it took for the sample to lose its mechanical strength.

2.3.5. Ion exchange capacity

The ion exchange capacity (IEC) was calculated from the molar ratio of sulfonated monomer **2** to monomer **1** in the feed, and was also determined by titration. The membranes in the H$^+$ form were immersed in an 1 M NaCl solution for 24 h to liberate the H$^+$ ions (which were replaced by Na$^+$), and the H$^+$ ions in solution were then titrated with 0.01 mol L^{-1} NaOH.

3. Results and discussion

3.1. Synthesis and characterization of monomers and polymers

The synthetic route of the monomers is outlined in Scheme 1. Monomers (**1a**–**1d**) were synthesized from of 5-chloro-1,8-naphthalic anhydride and either of four diamines (**a**–**d**) in acetic acid in the presence of isoquinoline. The reactions proceeded for relatively long periods of time (approx. 48 h) in order to obtain completely converted products. The products were then purified by recrystallizing from acetic acid.

The molecular structures of binaphthalimide dichloride monomers were confirmed by FT-IR and NMR spectroscopies. In FT-IR spectra, these dichloride monomers displayed characteristic bands associated with the six-membered naphthalimide ring. The ^{1}H NMR data were also consistent with the assigned structures of these aromatic dichlorides. Fig. 1 shows a representative ^{1}H NMR spectrum of dichloride **1a**. Monomer (**2**), i.e. sodium 3-(2,5-dichlorobenzoyl)benzenesulfonate was prepared according to a previously described procedure [36], and used to introduce the sulfonic acid groups along the copolymer backbone.

The synthetic route and general chemical structure of the sulfonated poly(arylene-*co*-naphthalimide)s (SPPIs) are shown in Scheme 2. In a previous investigation, sulfonated fluorinated poly-(arylene-*co*-naphthalimide)s (F-SPPIs) were prepared according to Scheme 2(b). The hydrophobic segments consisted of an asymmetric fluorinated naphthalimide dichloride. In the present study, the hydrophobic monomers were extended to the symmetrical bis(chloronaphthalimide)s derived from various aromatic
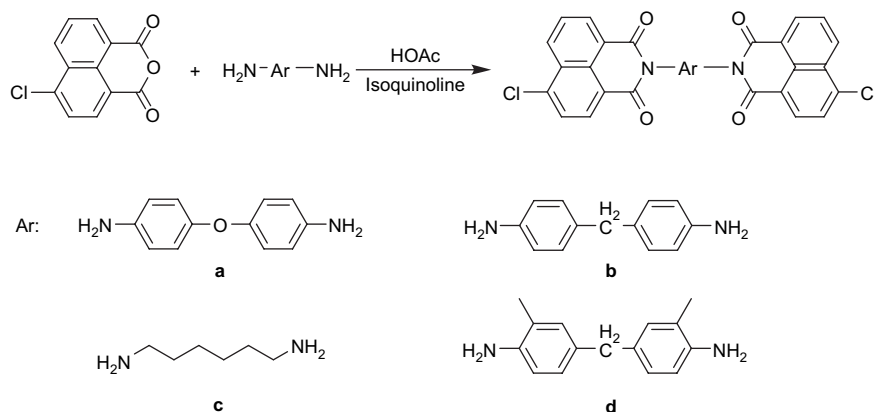
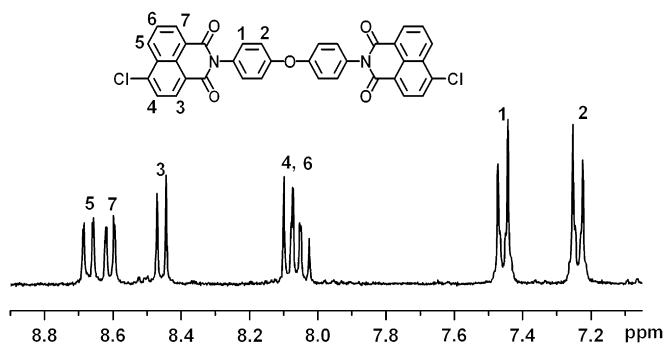**Scheme 1.** Synthesis of bis(chloronaphthalimide) monomers **1a**–**1d**.

Fig. 1. An ^{1}H NMR spectrum of monomer **1a** in DMSO-d_6.

Table 1
Inherent viscosities, molecular weights and solubility data of SPPIs in salt form

Samples	η_r^a (dL g^{-1})	M_n^b ($\times 10^5$)	M_w^b ($\times 10^5$)	M_w/M_n	NMP^c	DMAc^c	MeOH^c
Ia-60	1.24	0.97	2.09	2.15	++	+−	−
Ia-70	1.70	0.92	1.95	2.12	++	++	−
Ia-80	0.88	0.87	2.04	2.34	++	++	−
Ib-70	1.72	0.89	2.17	2.42	++	++	−
Ic-70	0.80	0.97	2.45	2.52	++	++	−
Id-70	1.22	1.09	2.48	2.27	++	++	−

^{a} In DMAc with 0.5 g dL^{-1} at 30 °C.
^{b} Measured at 30 °C using DMF as solvent and polystyrene as standard.
^{c} (++) Soluble at room temperature; (+−) partially soluble; (−) insoluble.

diamines. The SPPIs' preparation was carried out through a Ni(0)-catalyzed coupling polymerization of monomer binaphthalimide dichloride **1a**–**1d** with **2** under reaction conditions described elsewhere [29]. The degree of sulfonation (DS) of the copolymers was readily controlled through the monomer feed ratios of **1** to **2**. The copolymers were donated **I-*x***, where ***x*** corresponding to the mole fraction of the monomer **2** in the feed. The successful introduction of sulfonic acid groups in the copolymers was confirmed by FT-IR. The strong absorption bands around 1705 cm^{-1} (ν_{sym}C=O), 1659 cm^{-1} (ν_{asym}C=O) and 1368 cm^{-1} (ν_{C-N} imide) were assigned to the naphthalimide rings. The bands around 1197 and 1034 cm^{-1} were attributed to asymmetric and symmetric S=O stretching vibrations of the sulfonic acid groups. All the SPPIs in salt form displayed good solubility in common aprotic solvents such as NMP, DMSO, DMAc except **Ia-60** which was partly soluble in DMAc.

The as-prepared SPPIs were not soluble in MeOH, EtOH, etc. The present SPPIs gave flexible and tough films by solution casting. The inherent viscosity values of these copolymers are listed in Table 1. As confirmed by GPC analyses, the SPPIs were of high molecular weight ($M_w > 1.9 \times 10^5$, $M_n > 8.0 \times 10^4$), the polydispersity indices (M_w/M_n) were in range 2.12–2.52 (Table 1). The thermal stability of the SPPI membranes was investigated by TGA and the respective spectra are shown in Fig. 2. All polymers exhibited a typical three-step degradation pattern. The first weight loss at ca. 200 °C was ascribed to the loss of water molecules, absorbed by the highly hygroscopic –SO$_3$H groups. The second weight loss at around 300 °C was due to the decomposition of sulfonic acid groups by the desulfonation. The third stage weight loss at approx. 560 °C was attributed to the main chain of the aromatic diamine-based polymer. For the aliphatic diamine polymer **Ic**, the decomposition temperature of the polymer main chain was at around 470 °C which is lower than that of the aromatic polymers.
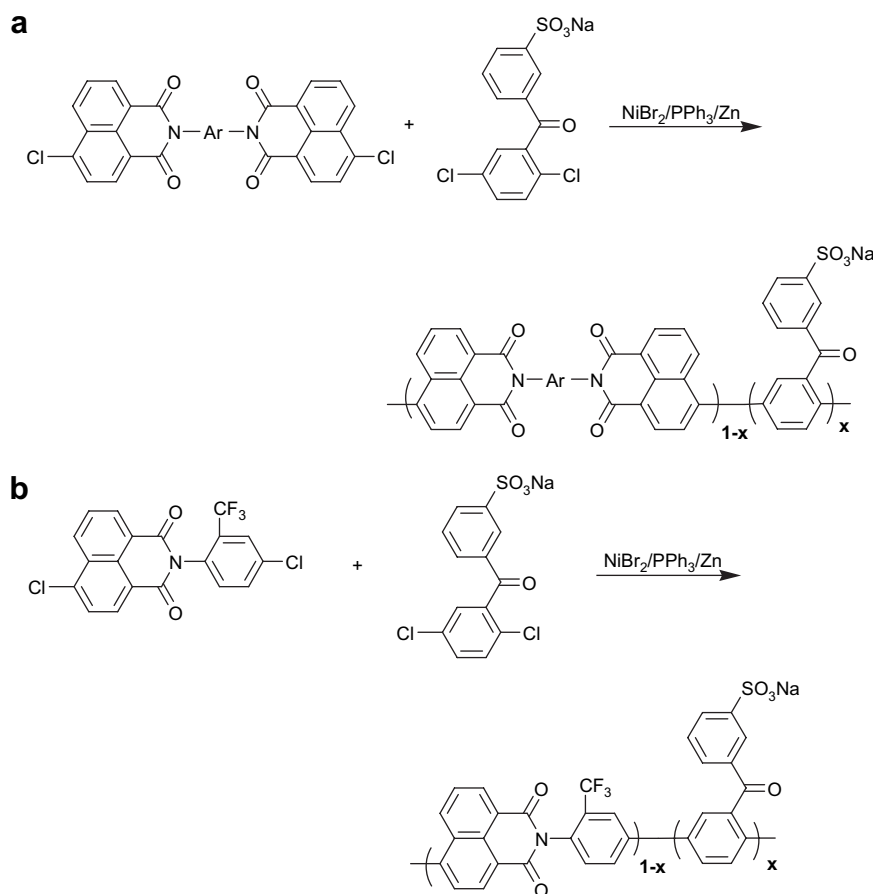
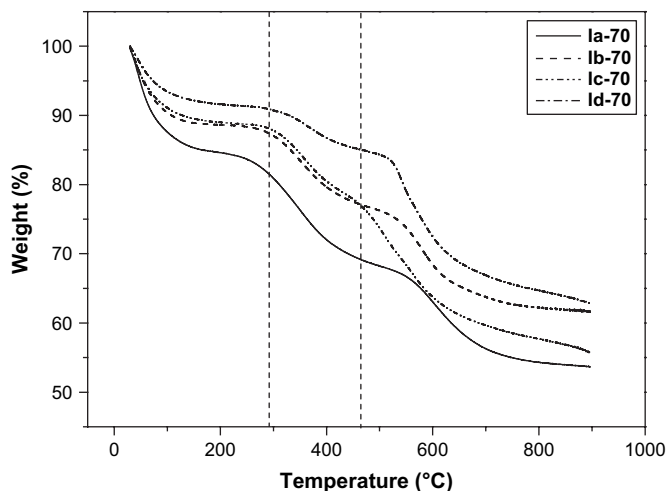**Scheme 2.** The synthetic route for sulfonated poly(arylene-co-naphthalimide)s.

Fig. 2. TGA curves of the **Ia–Id** copolymer membranes.

Table 3
Mechanical properties and water stability of SPPI copolymers[a]

Samples	IEC[c] (meq g^{-1})	Time (h)	Tensile strength[d] (MPa)	Young's modulus (GPa)	Elongation at break (%)	Reference
Ia-70	2.00	0	80.6	1.22	14.8	This
		24	39.2	0.84	6.6	
Ib-70	1.99	0	70.1	1.17	10.4	This
		24	37.4	0.78	5.9	
Ic-70	2.15	0	43.8	0.69	31.2	This
		24	37.5	0.52	9.5	
Id-70	1.96	0	78.5	1.01	18.0	This
		24	72.8	0.97	15.5	
F-SPPI-50(I)	1.67	0	60	1.28	9	[29]
		24	–	–	–	
F-SPPI-50(II)[b]	1.13	0	65	1.80	7	[29]
		23	–	–	–	

[a] Measured after soaking in water at 140 °C.
[b] Measured after soaking in water at 100 °C.
[c] IEC as calculated from DS.
[d] The samples were dried at ambient conditions for one day and tested at 30 °C, 50% RH.

3.2. Water uptake and dimensional changes

The level of hydration of the membrane has a profound effect on the conductivity and mechanical properties. The water uptake (WU) was thus measured from the ratio of the weight of water absorbed by the membrane when immersed in water (or at 70% RH), with respect to the dry membrane weight. The data are shown in Table 2. As expected, the membranes with high IEC values absorbed the most water. For example, the water uptake of **Ia-x** (that had IECs in the range 1.53–2.41) was 32–58%, thus, corresponding to an absorption of 11.3–12.9 water molecules per –SO$_3$H group. Accordingly, the swelling degree of the copolymer membranes was consistent with their water uptake values. As shown in Table 2, the aliphatic copolyimide (**Ic-70**) displayed isotropic membrane swelling in water, whereas the other SPPIs demonstrated an anisotropic membrane swelling. In other words, the swelling for the other SPPIs was much larger in the membrane thickness direction than in the plane direction. It was assumed that the flexibility of aliphatic hexane-1,6-diamine segment gave rise to a rather random orientation of the polymer chains. On the other hand, the orientation was favorable in the plane direction for SPPIs from aromatic diamine due to the relatively rigid planar structure of polymer chain.

3.3. Mechanical properties and water stability

The mechanical properties of the SPPI membranes were measured at room temperature, 50% RH, and are listed in Table 3. The tensile strength, Young's modulus, and elongation at break of the

copolymer membranes ranged between 43.8–80.6 MPa, 0.69–1.22 GPa, and 10.4–31.2%, respectively, which indicated that these membranes were strong and tough enough for fuel cell application. The **Ic** membrane, which was composed entirely of aliphatic diamine, showed a lower maximum stress (43.8 MPa) and a higher elongation at break (31.2%) than other aromatic diamine-based SPPIs. This was a result of the flexible and long aliphatic diamine structures. In general, these SPPI membranes demonstrated higher values of elongation at break than those of previously reported fluorinated poly(arylene-co-imide)s. This was attributed to the increased flexibility of the copolymer main chain as opposed to that of the latter.

The **Ia-70**, **Ib-70**, **Ic-70**, and **Id-70** membranes (of equivalent sulfonation degree) were subjected to the water stability tests performed under accelerated conditions by immersing the samples in deionized water at 140 °C. The mechanical properties of the membranes were measured after soaking in the water and the results are summarized in Table 3. Since the degradation of the copolymer membrane containing naphthalimide moieties mainly arose from the hydrolysis of the imide rings, the water stability of the sulfonated poly(arylene-co-imide)s was related to the structure of the naphthalimide units in the backbone of the copolymers. Most sulfonated polyimides (SPIs) synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride have four carbonyl groups in the naphthalimide rings, whereas, the synthesized sulfonated poly(arylene-co-imide)s (SPPIs) in the present study had only two carbonyl groups in the naphthalimide rings. Due to the electron-withdrawing characteristics of carbonyl groups, the SPPIs should possess decreased positive charge densities in the imide rings

Table 2
IEC, water uptake and dimensional changes of SPPI-x membranes

Samples	IEC (meq g^{-1})		λ	Water uptake (%W/W)		Dimensional changes		Reference
	Caculated[a]	Measured[b]		RH 70%[c]	In water	Δt	Δl	
Ia-60	1.58	1.53	11.6	14	32	0.08	0.03	This
Ia-70	2.00	1.92	12.4	18	43	0.09	0.05	This
Ia-80	2.50	2.41	13.4	29	58	0.11	0.06	This
Ib-70	1.99	1.92	11.6	20	40	0.07	0.05	This
Ic-70	2.15	2.08	11.0	21	41	0.05	0.04	This
Id-70	1.96	1.88	11.5	18	39	0.06	0.04	This
F-SPPI-50(I)	1.67	1.65	20.5	35	61	0.19	0.03	[29]
F-SPPI-50(II)	1.13	1.11	10.0	10	20	0.12	0.01	[29]

[a] IEC as calculated from DS.
[b] IEC as measured with titration.
[c] Samples were measured at 25 °C, 70% RH.

Table 4
Oxidative stability of SPPI copolymers

Samples	IEC (meq g^{-1})	Oxidative stability[a]	
		τ_1[b] (h)	τ_2[c] (h)
Ia-70	2.00	12	36
Ib-70	1.99	16	36
Ic-70	2.15	12	24
Id-70	1.96	41	262

[a] In 30% H_2O_2 containing 30 ppm $FeSO_4$ at 30 °C.
[b] The time when the membrane broke into pieces after vigorous shaking.
[c] The time when the membrane dissolved completely.

Table 5
Proton conductivity of SPPI-x membranes

Samples	IEC[a] (meq g^{-1})	Water uptake (%W/W) in water	σ (S cm^{-1})		Reference
			20 °C	80 °C	
Ia-60	1.58	32	0.035	0.078	This
Ia-70	2.00	43	0.075	0.164	This
Ia-80	2.50	58	0.135	0.234	This
Ib-70	1.99	40	0.064	0.131	This
Ic-70	2.15	41	0.086	0.212	This
Id-70	1.96	39	0.053	0.106	This
F-SPPI-50(I)	1.67	61	0.050	0.260	[29]
F-SPPI-50(II)	1.13	20	0.011	0.025	[29]
Nafion 117	0.9	19	0.090	0.175	This

[a] IEC as calculated from DS.

compared to SPIs, and should thus demonstrate an improved water stability. Moreover, the structure of the diamines the main chain had a dramatic influence on the water stability. The **Ia-70**, **Ib-70**, **Ic-70** and **Id-70** membranes displayed quite different water stabilities, even though they possessed the similar IEC values. Among the investigated SPPIs, **Id** exhibited the best water stability. After the soaking treatment in pressurized water at 140 °C for 24 h, the **Id-70** membrane displayed a Young's modulus of 0.97 GPa, a tensile strength of 72.8 MPa, and an elongation at break of 15.5%, corresponding to, respectively, 96, 91, and 86% of the values obtained for the non-treated membrane. The high stability of **Id** was a result of a stronger basicity of DMMDA due to the electron-donating effect of its methyl groups in DMMDA. In addition, introducing hydrophobic methyl groups at the *ortho*-position of the imido bond in the copolymer protected the polymer chain from being attacked by water molecules. Although the **Ic-70** membrane contained a strong basic hexane-1,6-diamine, it showed a lower stability than **Id**. This was because the aliphatic copolyimide possessed a lower solvent resistance, and thus also a lower solubility stability than the aromatic copolyimide. The F-SPPI-x could not endure the rigorous test and lost mechanical properties after the treatment. This is attributed to the higher swelling ratio of the F-SPPI-x at high temperature in water.

3.4. Oxidative stability

The stability of the membranes toward oxidation was examined by observing their dissolution behavior in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at 25 °C. This is one of the standard tests for oxidative stability. The oxidative stability of the samples was characterized by the elapsed time after which the membranes started to dissolve (τ_1) and had dissolved completely (τ_2) in the solution. As shown in Table 4, the **Id-70** membrane exhibited a much better oxidation stability as compared to the other three membranes. In a previous paper, we reported that the fluorinated sulfonated poly(arylene-*co*-imide)s displayed a superior oxidation stability as compared to that of other polyimides reported in the literature. The observed enhancement in oxidation stability was attributed to the introduction of the hydrophobic CF_3 groups at the *ortho*-position of the imido bond in the copolymers, thus leading to a protection of the polymer main chains from being attached by water molecules containing highly oxidative radical species. In this case, **Id-70** exhibited a comparable stability ($\tau_2 = 262$ h) to that of the fluorinated sulfonated poly(arylene-*co*-imide)s ($\tau_2 = 263$ h), thus implying that the methyl groups on the *ortho*-position of the imido bond in copolymers played a similar role to that of the tri-fluoromethyl groups.

3.5. Proton conductivity

The proton conductivities of the SPPI membranes along with that of Nafion 117 were measured in water in the temperature range of 20–80 °C, and the results are listed in Table 5. The proton conductivity of the SPPI membranes strongly depended on IEC, the hydration state, and the temperature. For example, the proton conductivity increased from 0.078 S cm^{-1} for **Ia-60** to 0.234 S cm^{-1} for **Ia-80** along as the IEC increased from 1.58 to 2.50 meq g^{-1}. The **Ia-80** (with an IEC of 2.50 meq g^{-1}) showed a higher conductivity than that of Nafion 117. For the SPPI membranes with IEC of 1.96–2.00 meq g^{-1}, i.e. **Ia-70**, **Ib-70**, and **Id-70**, the conductivities in water were slightly smaller than that of Nafion 117. For **Ic-70,** a somewhat higher IEC and a greater water uptake value resulted in a slightly larger proton conductivity. The temperature dependence of the proton conductivities and water uptake of **Ia-70**, **Ib-70**, **Ic-70**, **Id-70** as well as Nafion 117, measured in liquid water are shown in Fig. 3. The proton conductivity of these copolymer membranes showed a linear dependence on the temperature, and the same was observed
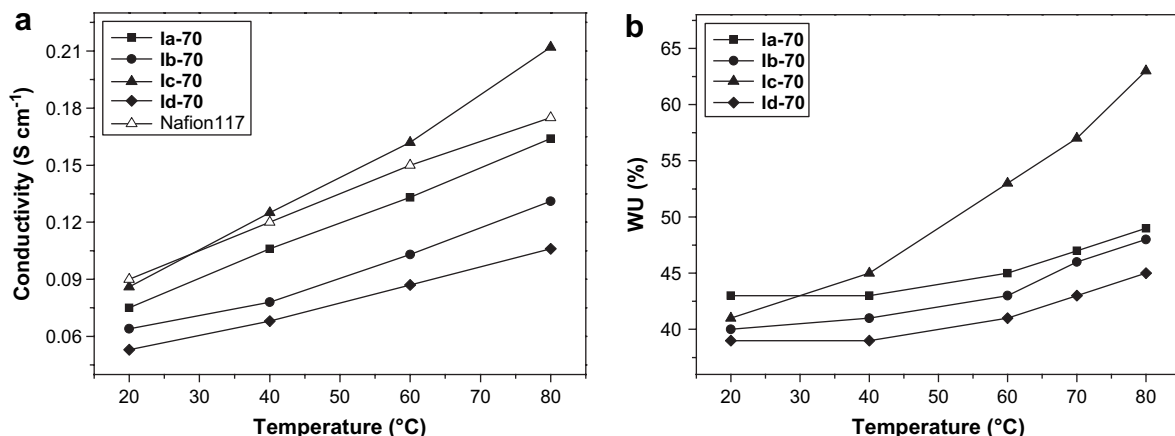

Fig. 3. The temperature dependence of (a) the proton conductivity and (b) the water uptake of the **Ia**–**Id** copolymers and Nafion 117.
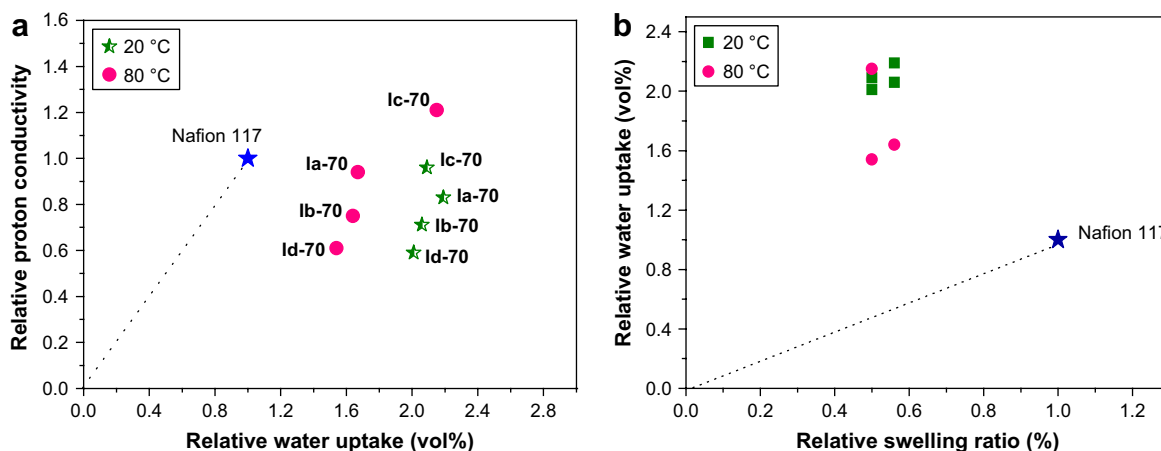
Fig. 4. (a) Relative water uptake as a function of relative proton conductivity and (b) relative water uptake versus relative swelling ratios of **Ia**–**Id** and Nafion 117.

for the water uptakes (Fig. 3a). As shown in Fig. 3b, the HAD-based membrane exhibited a sharp increase in water uptake with increasing temperature as a result of molecular mobility increasing with temperature. Hence, the water molecules could easily penetrate through the polymer backbone and hydrate a maximum number of SO$_3$H groups, which was ultimately responsible for the proton conductivity behavior at high temperature. The relative conductivity to Nafion 117 versus relative water uptake at 20 and 80 °C are shown in Fig. 4a. At the comparable conductivity value, SPPI membranes exhibited higher water uptake than Nafion 117 while they showed better swelling stability than Nafion 117 (Fig. 4b).

4. Conclusions

Novel sulfonated poly(arylene-*co*-imide)s were synthesized by a Ni(0) catalytic copolymerization from bis(chloronaphthalimide)s based on various diamines. Hydrophilic sodium 3-(2,5-dichloro-benzoyl)benzenesulfonate was used to provide sulfonated sites along the copolymer backbone. The effect of the structures of the diamines on the properties of the copolymers was evaluated by studying their electrolyte properties. The **Ia-80** copolymer membrane (with an IEC of 2.50 meq g^{-1}) displayed a higher proton conductivity (i.e. 0.135 S cm^{-1} at 20 °C) than that of Nafion 117 (0.09 S cm^{-1}, 20 °C). The **Id** copolymer membrane exhibited excellent water and oxidative stabilities due to the introduction of the hydrophobic methyl groups at the *ortho*-position of the imido groups, thus protecting them from being attacked by water molecules containing highly oxidizing radical species. Flexible aliphatic segment in the copolymers was favorable to water uptake and proton transport at high temperature, and the proton conductivity of the hexane-1,6-diamine (HDA)-based **Ic-70** membrane was found to reach 0.212 S cm^{-1} at 80 °C. This was higher than for Nafion 117 and other aromatic diamine-based membranes. Consequently, the synthesized materials proved to be promising as proton exchange membranes.

References

[1] Tant MR, Mauritz KA, Wilkes GL. Ionomers. New York: Chapman & Hall; 1997.
[2] Carrette L, Friedrich KA, Stimming U. Fuel Cells 2001;1:5–39.
[3] Costamagna P, Srinivasan S. J Power Sources 2001;102:253–69.
[4] Hickner MA, Ghassem H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104: 4587–612.
[5] Li QF, He RH, Jensen JO, Bjerrum N. J Chem Mater 2003;15:4896–915.
[6] Miyatake K, Watanabe M. Electrochemistry 2005;73:12–9.
[7] Gao Y, Robertson GP, Guiver MD, Mikhailenko SD, Kaliaguine S. Macromolecules 2004;37:6748–54.
[8] Xing P, Robertson GD, Guiver MD, Mikhailenko SD, Kaliaguine S. Macromolecules 2004;37:7960–7.
[9] Chen YL, Meng YZ, Hay AS. Macromolecules 2005;38:3564–6.
[10] Liu BJ, Robertson GP, Kim DS, Guiver MD, Hu W, Jiang ZH. Macromolecules 2007;40:1934–44.
[11] Wang F, Hickner M, Kim YS, Zawodzinski TA, McGrath JE. J Membr Sci 2002; 197:231–42.
[12] Willes KB, Wang F, McGrath JE. J Polym Sci Part A Polym Chem 2005;43: 2964–76.
[13] Schuster M, Kreuer KD, Andersen HT, Maier J. Macromolecules 2007;40: 598–607.
[14] Miyatake K, Chikashige Y, Higuchi E, Watanabe M. J Am Chem Soc 2007;129: 3879–87.
[15] Gourdoupi N, Andreopoulou AK, Deimede V, Kallitsis JK. Chem Mater 2003;15: 5044–50.
[16] Miyatake K, Hay AS. J Polym Sci Part A Polym Chem 2001;39:3211–7.
[17] Wang L, Meng YZ, Wang SJ, Hay AS. J Polym Sci Part A Polym Chem 2004;42: 1779–88.
[18] Miyatake K, Chikashige Y, Watanabe M. Macromolecules 2003;36:9691–3.
[19] Jouanneau J, Mercier R, Gonon L, Gebel G. Macromolecules 2007;40:983–90.
[20] Wu SQ, Qiu ZM, Zhang SB. Polymer 2006;47:6993–7000.
[21] Ghosh MK, Mittal KL. Polyimides: fundamentals and applications. New York; 1996. p. 7.
[22] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42: 359–73.
[23] Zhang Y, Litt MH, Savinell RF, Wainright JS. Polym Prepr 2000;41:1561–2.
[24] Guo XX, Fang JH, Watari T, Tanaka K, Kita H, Okamoto KI. Macromolecules 2002;35:6707–13.
[25] Miyatake K, Zhou H, Uchida H, Watanabe M. Chem Commun 2003:368–9.
[26] Yin Y, Fang J, Watari T, Tanaka K, Kita H, Okamoto KI. J Mater Chem 2004;14: 1062–70.
[27] Einsla BR, Kim YS, Hickner MA, Hong YT, Hill ML, Pivovar BS, et al. J Membr Sci 2005;255:141–8.
[28] Yasuda T, Miyatake K, Hirai M, Nanasawa M, Watanabe M. J Polym Sci Part A Polym Chem 2005;43:4439–45.
[29] Qiu ZM, Wu SQ, Zhang SB. Macromolecules 2006;39:6425–32.
[30] Yin Y, Yamada O, Suto Y, Mishima T, Tanaka K, Kita H, et al. J Polym Sci Part A Polym Chem 2005;43:1545–53.
[31] Chen S, Yin Y, Tanaka K, Okamoto KI. Polymer 2006;47:2660–9.
[32] Li NW, Cui ZM, Zhang SB, Xing W. J Membr Sci 2007;295:148–58.
[33] Yin Y, Suto Y, Sakabe T, Chen S, Hayashi S, Mishima T, et al. Macromolecules 2006;39:1189–98.
[34] Yin Y, Yamada O, Tanaka K, Okamoto KI. Polym J 2006;38:197–216.
[35] Sone Y, Ekdunge P, Simonsson D. J Electrochem Soc 1996;143:1254–8.
[36] Wu SQ, Li WM, Zhang SB. Polymer 2005;46:8396–402.