



Ionomers based on multisulfonated perylene dianhydride: Synthesis and properties of water resistant sulfonated polyimides

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ABSTRACT

A novel locally and densely sulfonated dianhydride with four sulfonic acid groups, 1,6,7,12-tetra[4-(sulfonic acid)phenoxy]perylene-3,4,9,10-tetracarboxylic dianhydride (SPTDA), was successfully synthesized by direct sulfonation of the parent dianhydride, 1,6,7,12-tetraphenoxypylene-3,4,9,10-tetracarboxylic dianhydride (PTDA). Sulfonated copolyimides were prepared from SPTDA, nonsulfonated dianhydride 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride, 4,4'-diaminodiphenyl ether (a) or dodecane-1,12-diamine (b). The synthesized copolymers, with the $-SO_3H$ group on the polymer side chain, possess high molecular weights and high viscosities, and they form tough, flexible membranes. The copolymer membrane with an ion exchange capacity of 2.69 mequiv. g^{-1} had a proton conductivity of 0.126 $S\ cm^{-1}$ at 20 °C and 0.292 $S\ cm^{-1}$ at 100 °C; the latter is much higher than that of Nafion[®] 117 under the same conditions. The mechanical properties of the copolymer membranes were almost unchanged after accelerated water stability testing at 140 °C for 100 h; this indicates excellent hydrolytic stability of the synthesized copolyimides.

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1. Introduction

Due to their pollution-free operation, high power density, and significant energy-conversion efficiency, proton exchange membrane fuel cells (PEMFCs) have attracted considerable attention as candidates for alternative power sources [1–4]. The function of PEMFCs is critically related to thin electrolyte membranes that act as key components for the transfer of protons from the anode to the cathode; these membranes also provide a barrier to fuel gas cross-leaks between electrodes. To successfully fulfill these tasks in the harsh conditions of a fuel cell system, membrane materials should possess such excellent properties as high chemical and thermal stabilities, robust mechanical properties, low fuel permeability, and high ionic conductivity. Unfortunately, up to now, commercial membranes, such as Nafion[®] 117, cannot satisfy all these requirements [5,6]. This has stimulated numerous efforts toward developing alternative nonfluorinated materials. For example, aromatic hydrocarbon polymers bearing acid functions have been developed that are thermally stable, inexpensive, and easy to modify chemically [7–10]. Among these, sulfonated polyimides (SPIs) with six-membered imide rings have been identified as one of the most promising membrane materials for PEMFC applications.

Generally, aromatic ionomers for PEM fuel cells rely on absorbed water and its interaction with acid groups to produce proton conductivity. To ensure high proton conductivity, polymers with significant ion exchange capacities (IECs) have been utilized, but these materials swell excessively in water (thereby losing their mechanical properties) and are brittle when dry. It is widely recognized that the lower proton conductivity of sulfonated aromatic polymers can be attributed to the lack of ion channels and low acidity of $Ar-SO_3H$ [11–13]. In addition, aromatic polyimides tend to hydrolyze under conditions of high-moisture content and high temperature; these conditions degrade the main polymer chain and cause a dramatic drop in mechanical strength [10].

To achieve high water stability, several SPIs based on novel sulfonated diamines have been designed using knowledge acquired about structure–property relationships. It has been reported that polyimides from flexible and highly basic diamines tend to have good water stability [14–17]. However, there are few reports on the synthesis of new dianhydrides and the effects of dianhydride structure on electrolyte properties [18]. In this paper, we report the synthesis of a novel sulfonated dianhydride, 1,6,7,12-tetra[4-(sulfonic acid)phenoxy]perylene-3,4,9,10-tetracarboxylic dianhydride (SPTDA), which bears four sulfophenoxy groups on the pendant chain. The introduction of electron-donating phenoxy groups into dianhydride units should decrease the positive charge density of imide rings, thereby helping to depress hydrolysis of the imide rings.

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Random copolymers with locally and densely sulfonated units are also attracting attention because of their high contrast in polarity between hydrophilic and hydrophobic units; this promotes the formation of hydrophilic–hydrophobic phase-separated structures. For example, Ueda and coworkers reported the synthesis of locally sulfonated poly(ether sulfone)s with highly sulfonate units. The proton conductivity of the sulfonated polymer had an ion exchange capacity of 2.38 mequiv. g⁻¹, which is comparable to that of Nafion® 117 even at 30% relative humidity [19]. Hay et al. [20] prepared sulfonated poly(aryl ether) containing randomly distributed nanoclusters of six or 12 sulfonic acid groups. They found the morphological structure of the copolymers to be comparable to that of Nafion® 117, which explains their high proton conductivity. Similarly, we expect that sulfonated polyimides from SPTDA with four sulfonated phenoxy groups will display high proton conductivity and water stability.

2. Materials and methods

2.1. Materials

Phenol, 1,6,7,12-tetrachlorine-3,4,9,10-tetracarboxylic dianhydride, *n*-butylamine, concentrated sulfonic acid (98%), and triethylamine (NEt₃) were used as received from Beijing Multi-Technology Co., Ltd. Quantities of 1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic dianhydride were prepared according to a previously reported method [21]. Dodecane-1,12-diamine (DDA) and 4,4'-diaminodiphenyl ether (ODA) were purchased from Aldrich and used as received. Synthesis of 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BTDA) was performed according to a previously described procedure [18]. All other reagents were obtained from commercial sources and used as received.

2.2. Synthesis of 1,6,7,12-tetra[4-(sulfonic acid)phenoxy]perylene-3,4,9,10-tetracarboxylic dianhydride (SPTDA)

The synthesis began by adding 1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic dianhydride (2 g) to concentrated sulfonic acid (5 mL). The flask was sealed, and the mixture was stirred at room temperature for 24 h. Water (10 mL) was slowly added to the flask to form a precipitate, which was removed by filtration under suction. The red precipitate was then added to a 100-mL round-bottom flask equipped with a Dean-Stark distilling trap and a condenser. Toluene (30 mL) was added, then the mixture was heated to 140 °C and stirred for 5 h; during this time water was azeotropically removed. After cooling to room temperature, the red solid was collected by filtration and dried at 100 °C in vacuo. Two grams of red product were obtained (yield: 83.3%). Infrared spectra showed peaks at 1771, 1730, 1058, 1155, 1228 (KBr, cm⁻¹). Spectra from ¹H NMR and ¹³C NMR (DMSO-*d*₆) are shown in Fig. 1.

2.3. General procedure for synthesis of sulfonated copolymers (SPIa-50)

To a 100-mL, completely dried, three-neck flask was successively charged 0.5 mmol of SPTDA, 10 mL of *m*-cresol, 0.68 mL (about 2 mmol) of Et₃N, 0.5 mmol BTDA, and 1 mmol diamine (ODA) monomer under nitrogen flow. After a homogeneous solution formed, 0.2442 g (2 mmol) of benzoic acid was added. The mixture was stirred at room temperature for a few minutes and then heated to 80 °C for 4 h and to 180 °C for 20 h. After cooling to 80 °C, an additional 5 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into 200 mL of acetone. The fiber-like precipitate was filtered off, washed with

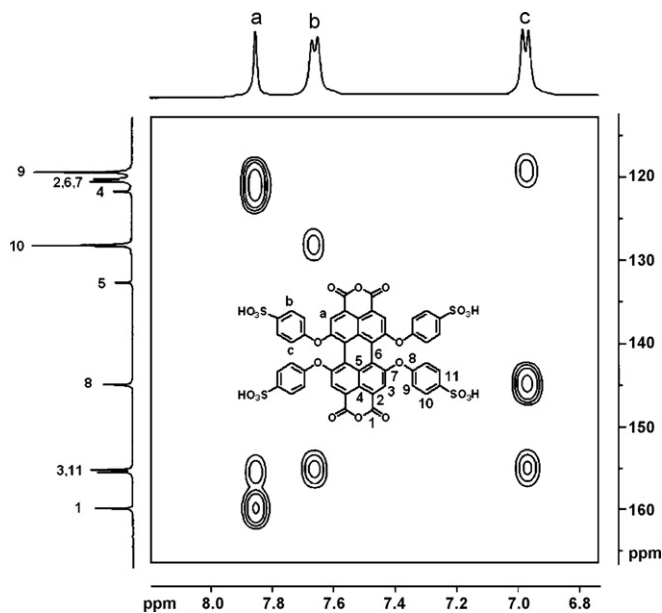


Fig. 1. C-H HMQC spectrum of sulfonated dianhydride monomer.

acetone thoroughly, and dried in a vacuum oven for 12 h at 150 °C; the resulting product had a yield of 97%.

The above procedures were followed for the synthesis of SPIa-*x*, where *x* refers to the mole fraction of the monomer SPTDA in the feed. The only exception was a different molar ratio of BTDA. The same procedure was also used in the synthesis of SPIb-*x* from SPTDA and DDA.

2.4. Membrane preparation

Tough, ductile ionomer membranes with controlled thicknesses of 30–50 μm were prepared. The triethylamine salt form of the polymer was dissolved in *m*-cresol to form an 8–10 wt% solution at 80 °C. This solution was filtered and cast onto glass plates at 120 °C for 12 h, after which the ionomer membrane was dried in a vacuum oven (150 °C for 4 h, 200 °C for 4 h, and 220 °C for 4 h). The as-cast membranes were treated with 1.0N sulfonic acid at room temperature for 4 days for proton exchange. The proton-exchanged membranes were thoroughly washed with deionized water and then dried in vacuum at 100 °C for 10 h.

2.5. Measurements

Spectra from ¹H and ¹³C NMR were obtained at 400 MHz on an AV400 spectrometer. FT-IR spectra were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. Reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL⁻¹ concentrations of polymer in *m*-cresol. Thermogravimetric analysis (TGA) was performed in nitrogen and air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min⁻¹. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min⁻¹. The samples were prepared by placing them in vacuum at 100 °C for 10 h and then equilibrating them at 30% RH (ambient condition) for 24 h prior to the measurements.

2.6. Water uptake and swelling ratio measurements

The membranes (30–40 mg per sheet) were dried at 100 °C under vacuum for 10 h until constant weights were obtained. They were then immersed in deionized water at room temperature for

4 h. After this, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptakes (*WU*) of the membranes were calculated according to

$$WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where W_{dry} and W_{wet} are the weights of the dry and the corresponding water-swollen membranes, respectively.

The swelling ratios of the membranes were determined by immersing the round-shaped samples in water at room temperature for a given time; then swelling ratios (*SR*) were calculated from

$$SR(\%) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \quad (2)$$

here l_{dry} and l_{wet} are the lengths of the dry and wet samples, respectively.

2.7. Oxidative and hydrolytic stability

Small pieces of membrane samples, with thicknesses of approximately 40 μm , were soaked in Fenton's reagent (30 ppm FeSO_4 in 30% H_2O_2) at room temperature. Stability was evaluated by recording the time (τ_1) at which the membranes broke into pieces after being drastically shaken, as well as the time (τ_2) at which they dissolved completely. Hydrolytic stability was evaluated by an accelerated testing in which the membrane samples remained in water at 140 °C for 100 h. Weights of the membranes were measured after this treatment.

2.8. Ion exchange capacity

Ion exchange capacity (IEC) was determined through titration. Membranes in H^+ form were immersed in a 1 M NaCl solution for 24 h to liberate H^+ ions and replace them with Na^+ ions. The H^+ ions in solution were then titrated with 0.01N NaOH using phenolph-

thalein as an indicator; the membranes were kept in the solution during the titration.

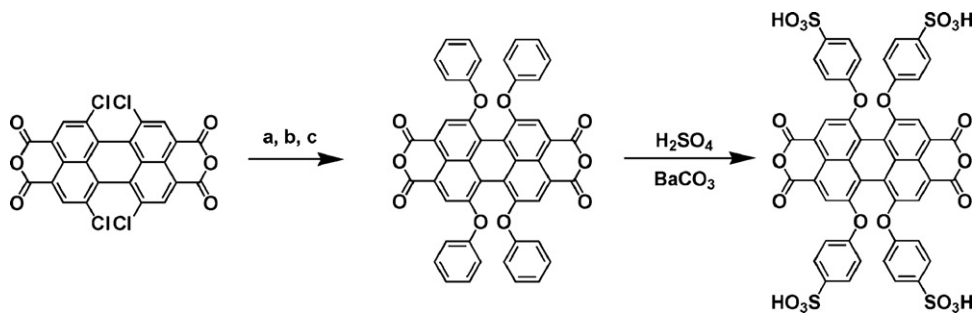
2.9. Proton conductivity

Proton conductivities of the copolymer membranes were evaluated through electrochemical impedance spectroscopy in the temperature range of 20–100 °C by a four-point probe method. The impedance measurements were carried out on a Solartron 1255B Frequency Response Analyzer and a Solartron 1470 Battery Test Unit (Solartron Inc., UK) coupled with a computer. Membrane samples, with 1- cm^2 surface areas, were sandwiched between two Au blocking electrodes. The samples were allowed to equilibrate at the desired temperature for 0.5 h. The impedance spectra were then recorded with the help of ZPlot/ZView software (Scribner Associates Inc.) under an ac perturbation signal of 10 mV in the frequency range of 100 mHz to 100 kHz.

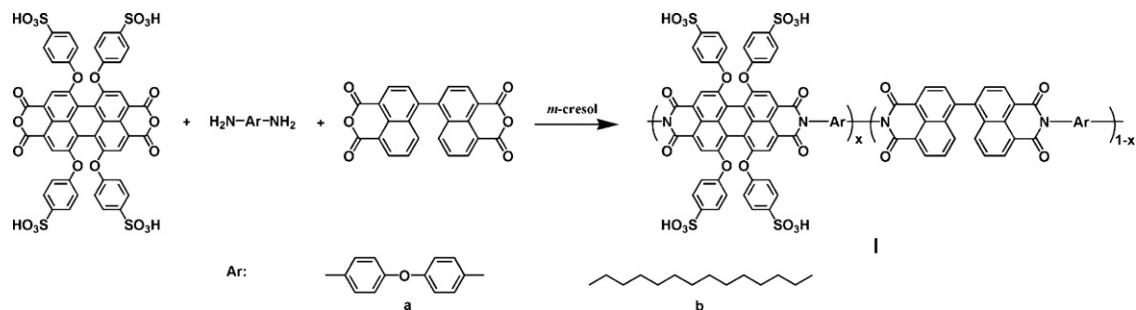
3. Results and discussion

3.1. Synthesis of the sulfonated monomer

SPTDA was synthesized by direct sulfonation of the parent dianhydride, 1,6,7,12-tetraphenoxyperylene-3,4,9,10-tetracarboxylic dianhydride (PTDA), as shown in Scheme 1. PTDA was sulfonated with concentrated sulfuric acid (98%) at room temperature for 24 h. The sulfonation reaction occurred at the four positions of the phenoxy groups because these positions are more reactive than other ones. The crude product was obtained by precipitating in cool water and collected by filtration. It was purified by treating with hot toluene to give the pure product as a red powder with a yield of 83.3%. The structure of the resulting sulfonated dianhydride (SPTDA) was confirmed by IR and NMR spectroscopy. The IR spectrum of SPTDA showed characteristic cyclic anhydride absorption at 1772 and 1730 cm^{-1} , attributed to asymmetrical and symmetrical vibrations of $\text{C}=\text{O}$ of anhydride groups. The 2D C–H HMQC spectrum of the dianhydride monomer is shown in Fig. 1.



Scheme 1. Synthesis of sulfonated perylene dianhydride compounds: (a) *n*-butylamine, propanol/water, 70 °C, 10 h, 85%; (b) ArOH, K_2CO_3 , 1-methyl-2-pyrrolidinone (NMP), argon, 140 °C, 14 h, 84%; (c) KOH, *t*-BuOH, 80 °C, 10 h, 95%.



Scheme 2. Synthesis of the multisulfonated copolyimides SPIa-*x* and SPIb-*x*.

Table 1
Reduced viscosities and solubilities data of SPIs in TEA salt forms and proton forms.

Samples	η_r^a (dL g ⁻¹)	Solvent ^b							
		<i>m</i> -Cresol		DMSO		NMP		DMAc	
		TEA	H ⁺	TEA	H ⁺	TEA	H ⁺	TEA	H ⁺
Ia-30	1.09	++	++	++	--	+–	--	--	--
Ia-50	1.17	++	++	++	--	+–	--	--	--
Ia-70	1.14	++	++	++	--	+–	--	--	--
Ib-50	0.96	++	++	++	--	+–	--	--	--
Ib-70	1.03	++	++	++	--	+–	--	--	--

^a 0.5 g dL⁻¹ in *m*-cresol at 30 °C, in TEA form.

^b (++) Soluble at room temperature, (+–) partially soluble, and (–) insoluble.

The assignments of each carbon and proton are also given in the figure; this spectrum agrees well with the proposed structure.

3.2. Synthesis and characterization of sulfonated polyimides (SPIa-*x* and SPIb-*x*)

Sulfonated copolyimides were obtained by a one-step, high-temperature solution polycondensation, according to Scheme 2. The syntheses were carried out in *m*-cresol in the presence of benzoic acid, which acted as a catalyst and has been employed in the preparation of many other sulfonated polyimides (Scheme 2). In all reactions, a homogeneous, intensely red, clear viscous solution formed. The SPI copolymers were obtained in almost quantitative yields (above 96%) and displayed reduced viscosities of more than 0.96 dL g⁻¹ (Table 1). The resulting copolymers in triethylamine salt form were found to be soluble with a 10% solid content both in *m*-cresol and in DMSO; however, the copolymers in proton form were only soluble in *m*-cresol (Table 1). Films of SPIs cast from the *m*-cresol solution were transparent and flexible.

The SPIa polymers were characterized by FT-IR; an example is Fig. 2, which displays the FT-IR spectra of SPIa-30, SPIa-50, and SPIa-70. The strong absorption bands around 1710 cm⁻¹ ($\nu_{\text{sym}}\text{C=O}$), 1666 cm⁻¹ ($\nu_{\text{asym}}\text{C=O}$), and 1348 cm⁻¹ ($\nu_{\text{C-N}}$ imide) are assigned to naphthalenic imide rings. The bands around 1121 and 1034 cm⁻¹ are assigned to the stretch vibration of sulfonic acid groups; the intensity of these peaks increased with increasing sulfonated monomer ratio.

Typical TGA curves for SPIa-50 and SPIb-50 in nitrogen and air atmosphere are shown in Fig. 3. The figure shows that the polymer films exhibited a typical three-step degradation pattern in nitrogen

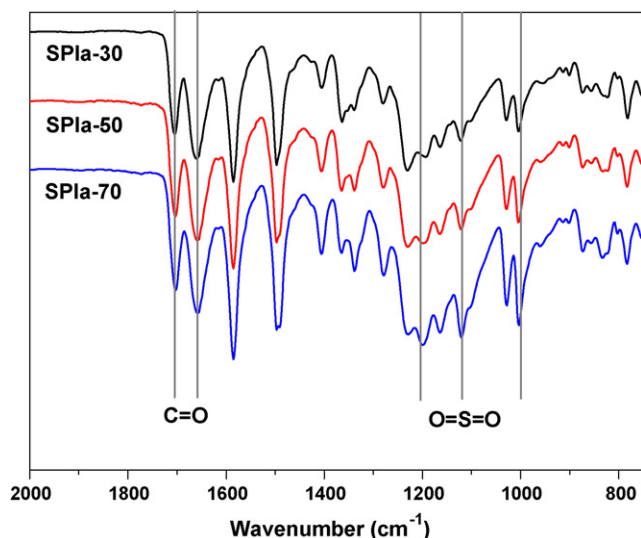


Fig. 2. Typical FT-IR spectra of the SPI membranes.

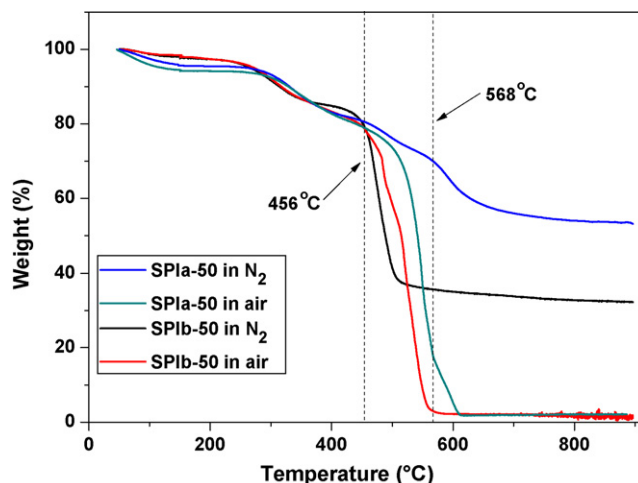


Fig. 3. TGA curves of the SPIa-50 and SPIb-50 membranes in nitrogen and air atmosphere.

atmosphere. The first weight loss, at up to ca. 200 °C, is ascribed to loss of water molecules, absorbed by the highly hygroscopic –SO₃H groups. The second weight loss near 260 °C is due to decomposition of sulfonic acid groups by desulfonation. The third weight loss, around 560 °C for SPIa-50, is assigned to decomposition of the main polymer chain. For the aliphatic diamine polymer SPIb-50, decomposition of the main polymer chain occurred around 460 °C, which is lower than that of the aromatic polyimide SPIa-50. Furthermore, their TGA curves showed on-set weight losses of polymer chain more than 400 °C in air atmosphere, which indicated that the SPI membranes are thermal oxidative stable.

Mechanical properties of the polymers and Nafion[®] 117 are summarized in Table 2. For the sulfonated polymers in the dry state, the membranes had tensile stresses of 41.2–112.1 MPa, Young's moduli of 0.46–1.10 GPa, and elongation-at-break values of 30.1–43.4%. In the wet state, the SPI membranes showed tensile stresses of 26.9–72.2 MPa, Young's moduli of 0.28–0.69 GPa, and elongation-at-break values of 32.6–56.2%. Note that in both the dry and wet states, SPIa membranes displayed superior mechanical properties compared to SPIb membranes, due to the relatively flexible aliphatic diamine of SPIb membranes. Compared to Nafion[®] 117 membranes, the synthesized sulfonated polyimide membranes showed higher tensile stresses and Young's moduli but the lower elongation rate than Nafion[®] 117. These results indicate that SPI membranes are, at high degrees of sulfonation, strong and tough enough for fuel cell applications.

3.3. Water uptake, proton conductivity, and methanol permeability

Proton exchange membranes are typically poor proton conductors unless water is present. The level of hydration of the membrane has a profound effect on conductivity and mechanical properties. Water uptake is typically a function of the degree of sulfonation or the ion exchange capacity (IEC), which is a measure of exchangeable protons in the material. As listed in Table 3, at room temperature, water uptake increased from 28.0% for SPIa-30 with an IEC of 1.53 mequiv. g⁻¹ to 60.5% for SPIa-70 with an IEC of 2.61 mequiv. g⁻¹. In general, SPI membranes based on locally and densely sulfonated dianhydride (SPTDA) showed lower water uptakes than our previously reported sulfonated polyimides (SBTDA/ODA) based on conventional sulfonated dianhydride (SBTDA) [22]. For example, with the same IEC of 2.61 mequiv. g⁻¹, SPIa-70 shows a smaller WU (60.5%) than SBTDA/ODA (WU = 89.2%). The lower WU of SPIa-70 would

Table 2
Mechanical properties of sulfonated copolyimide and Nafion® 117 membranes in dry and wet states.

Samples	IEC (mequiv. g ⁻¹)	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
		Dry ^a	Wet ^b	Dry	Wet	Dry	Wet
SPIa-30	1.57	112.1	72.2	1.10	0.69	39.2	50.2
SPIa-50	2.22	100.4	54.2	1.09	0.54	35.3	43.8
SPIa-70	2.69	94.8	37.6	0.98	0.41	32.3	32.6
SPIb-50	2.22	50.5	31.8	0.58	0.32	30.1	48.9
SPIb-70	2.69	41.2	26.9	0.46	0.28	43.4	56.2
Nafion® 117 ^c	0.90	34.2	24.1	0.14	0.11	235.6	278.1

^a Samples were dried at ambient conditions for 1 day and tested at 30 °C, 50% RH.

^b Samples were soaked in deionized water for 12 h at room temperature and tested in fully hydrated state at 30 °C.

^c Data measured in our lab.

Table 3
The IEC, water uptake, swelling ratio of the SPI membranes.

Samples	IEC (mequiv. g ⁻¹)		Water uptake ^c (w/w%) 20 °C	λ	Swelling ratio (%)		Ref.
	Calculated ^a	Measured ^b			Δl	Δt	
SPIa-30	1.57	1.53	28.0	9.9	4.5	12.8	This
SPIa-50	2.22	2.16	46.1	11.5	6.7	26.0	This
SPIa-70	2.69	2.61	60.5	12.5	9.5	35.2	This
SPIb-50	2.22	2.17	21.7	5.4	1.4	4.2	This
SPIb-70	2.69	2.59	37.5	7.7	5.4	18.2	This
SBTDA/ODA	2.78	2.69	89.2	18.4	15	25	[22]
Nafion® 117	0.90	–	19.6	12.1	11.4	–	This

^a IEC as calculated from DS.

^b IEC as measured with titration.

^c Samples were measured at 20 °C, in water.

Table 4
Proton conductivity and methanol permeability of SPI membranes.

Samples	IEC (mequiv. g ⁻¹) ^a	Water uptake (w/w%)	P_M (cm ² S ⁻¹) 10 ⁶	ϕ (S cm ⁻¹ s cm ²) 10 ⁻⁴	σ (mS cm ⁻¹)	
					20 °C	100 °C
Ia-30	1.57	28.0	0.05	70	35	124
Ia-50	2.22	46.1	0.11	77	85	239
Ia-70	2.69	60.5	0.20	63	126	292
Ib-50	2.22	21.7	0.06	68	41	158
Ib-70	2.69	37.5	0.13	60	78	225
Nafion® 117	0.90	19.6	2.4	3.8	90	178

^a IEC as calculated from DS.

be caused by its longer hydrophobic segments compared to SBTDA/ODA. Accordingly, with the same IEC values, SPIb-50 with wholly aliphatic diamine units exhibits much lower water uptake than SPIa-50, due to their hydrophobic and long aliphatic chains. Fig. 4 shows the temperature dependence of water uptake and dimensional change in the lengthwise direction for the SPI membranes. SPI membranes with low IEC values show slight increases in water uptake with temperature. A sharp increase of water uptake at 100 °C was observed for Nafion® 117 and SPIa-70. This suggests

that the IEC value of 2.69 mequiv. g⁻¹ is a critical value for SPIa membranes.

The dimensional changes of the SPI membranes were evaluated by comparing their hydrated states with their dry states (Table 3). As a trend, dimensional changes in both length and thickness increase with increasing IEC values. However, all membranes exhibit anisotropic swelling in water; that is, much more swelling occurs in membrane thickness than in the plane direction. This anisotropic swelling is considered to be due to in-plane polymer

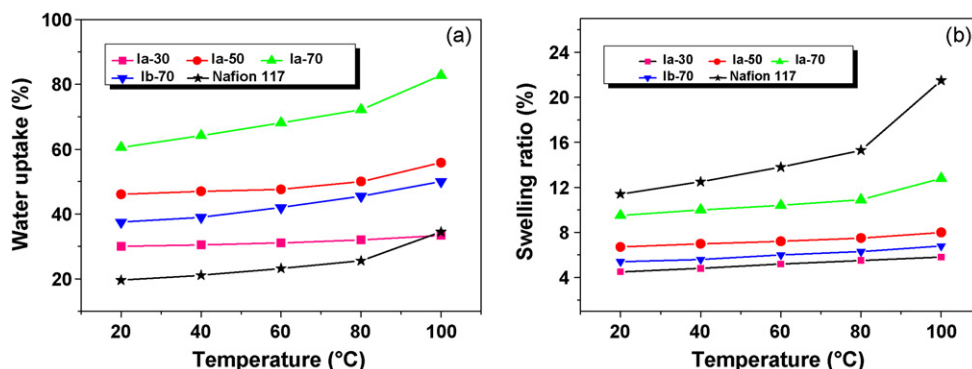


Fig. 4. Temperature dependence of WU (a) and SR (b) of SPI membranes and Nafion® 117.

Table 5
Hydrolytic stability and oxidative stability of SPI and Nafion® 117 membranes.

Samples	IEC (mequiv. g ⁻¹)	Hydrolytic stability		Oxidative stability ^a (h)	
		Loss in weight (%)		τ_1^b (h)	τ_2^c (h)
Ia-30	1.57	6		32	48
Ia-50	2.22	11		28	37
Ia-70	2.69	13		24	32
Ib-50	1.57	3		58	102
Ib-70	2.69	5		46	86
Nafion® 117	0.90	1		>80	–

^a 30 °C in 30% H₂O₂ containing 30 ppm FeSO₄.

^b The time when the membrane broke into pieces after vigorous shaking.

^c The time when the membrane dissolved completely.

chain alignment. A similar tendency has been found in other rigid sulfonated polyimide membranes [18,23,24].

The proton conductivities of the SPI membranes, along with that of Nafion® 117, were measured in water in the temperature range of 20–100 °C; the results are listed in Table 4. The SPI membranes exhibited proton conductivities in the range of 0.035–0.126 S cm⁻¹ at 20 °C. In general, proton conductivity depended on IEC, hydration state, and temperature. With the same IEC values, the SPIb membranes with wholly aliphatic diamine exhibit much lower proton conductivity than SPIa membranes, due to their lower water uptake. Fig. 5 shows proton conductivities at different temperatures measured under immersed conditions. All SPI membranes exhibit an Arrhenius-like behavior and similar activation energies were found. In particular, conductivities well above Nafion® 117 were obtained for membranes SPIa-50, SPIa-70, and SPIb-70 at high temperature. In addition, membranes based on SPIa-30 having an IEC of 1.57 mequiv. g⁻¹ reached the level of conductivity of Nafion® 117 at high temperature. At 100 °C, the SPIa-70 membranes with high IECs of 2.69 mequiv. g⁻¹ showed the highest proton conductivity, i.e., 0.292 S cm⁻¹. This value is much higher than that of Nafion® 117 (0.178 S cm⁻¹).

Table 4 lists the methanol permeability of the membranes at room temperature (20 °C). The SPI membranes showed much lower values than that containing Nafion® 117. For example, the SPIa-50 exhibited a methanol permeability of 1.1(10⁻⁷) cm² s⁻¹ as opposed to 2.4(10⁻⁶) cm² s⁻¹ for Nafion® 117. For a fully hydrated membrane, methanol transport across a proton exchange membrane should strongly depend on water uptake, due to methanol permeating through the membranes in such complex forms as CH₃OH₂⁺ and H₃O⁺. The membranes presented higher water uptake values,

and thus methanol permeabilities increased with IEC values of SPI membranes.

To understand the performance tradeoff between permeability and conductivity, an investigation was carried out using selectivity to represent the transport characteristics of both protons and methanol (σ/P) in SPI and Nafion® 117 membranes. The results are shown in Table 4. The composite membrane was approximately 20 times more selective than that of Nafion® 117. These results indicate that multisulfonated molecular structures favored proton transport but block methanol permeability.

3.4. Hydrolytic and oxidative stability of the SPI membranes

The stability of sulfonated polyimide membranes in water has been the subject of much research because it is one of the important factors affecting membrane performance [10]. The structural feature common to SPIa and SPIb is that the sulfonic acid groups are attached to the electron-donating phenyl ring on the side chain of the copolymers. It has been reported that the attachment of sulfonic acid groups to the pendent chain enhances proton conductivity and improves water stability. In addition, the introduction of four electron-donating phenoxy groups into the imide rings should decrease the positive charge density of the imide rings, thus enhancing their hydrolytic stability. Hydrolytic stability of SPI membranes was evaluated by an accelerated testing in which a membrane sample was treated with water at 140 °C for 1 h. For all samples, no weight loss was observed, and their film properties, such as flexibility and transparency, were unaffected by the test. However, most polyimide ionomers based on the conventional 1,4,5,8-naphthalenetetracarboxylic dianhydride did not endure the test [15,17]. For example, some aromatic polyimide ionomers broke into pieces after testing, indicating significant hydrolysis. Weight losses after longer test times of 100 h for the SPI membranes are listed in Table 5, large weight losses occurred in membranes with high IEC values.

Oxidative stabilities of the SPI membranes were evaluated in Fenton's reagent (30 ppm FeSO₄ in 30% H₂O₂) at 25 °C, the results are presented in Table 5. The time for the SPI membranes to start to break into pieces was more than 24 h, and more than 32 h were required for the pieces to completely dissolve. The oxidative stability of the membranes decreased with an increasing degree of sulfonation. This was a result of oxidative attack by radical species (HO• and HOO•) occurring mainly in or near water-containing hydrophilic domains. In the oxidative stability tests, the aromatic diamine-based SPIa membranes started to break into pieces before their aliphatic diamine-based SPIb counterparts, demonstrating the outstanding oxidative stability of SPIb membranes over SPIa membranes; this is consistent with the observed hydrophilic stabilities. Therefore, we assume that the hydrophobic main chain and lower water uptake of SPIb prevents radical species from attacking the polymer chains.

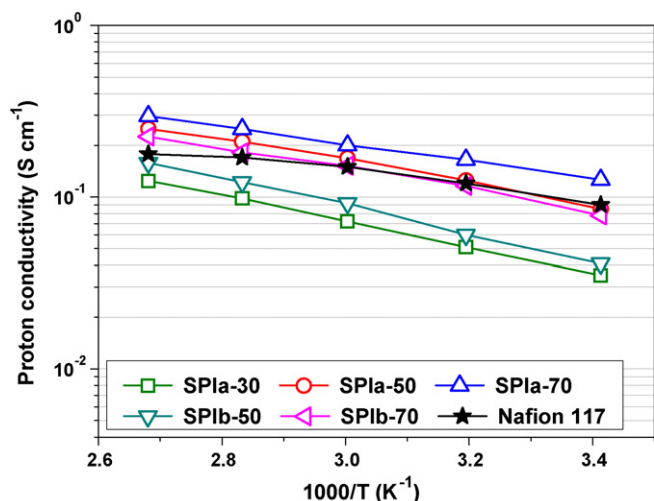


Fig. 5. Temperature dependence of the proton conductivity of the SPI membranes and Nafion® 117.

4. Conclusions

A novel locally and densely sulfonated dianhydride (SPTDA) was easily synthesized. Two copolyimides, SPIa and SPIb, were prepared from SPTDA, nonsulfonated dianhydride, and common diamines, ODA and DDA. These as-prepared polymers gave flexible and tough membranes from a solution casting method. Membranes of SPIa-30 having IECs of 1.57 mequiv. g⁻¹ reached a level of conductivity comparable to Nafion[®] 117 at 100 °C, while membranes of SPIa-70 with IECs of 2.69 mequiv. g⁻¹ displayed 0.292 S cm⁻¹ which was larger than that of Nafion[®] 117 (0.178 S cm⁻¹) at high temperature. The locally and densely sulfonated copolymers tended to generate long hydrophobic segments, leading to moderate water uptakes and modest dimensional changes. The SPI membranes also exhibited excellent hydrolytic stability due to the introduction of pendant sulfophenoxy groups in the imide rings. SPIb membranes with aliphatic diamine units exhibited lower water uptake and better water stability than aromatic diamine-based SPIa membranes.

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