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Sulfonated polyimides bearing benzimidazole groups for proton exchange membranes

Nanwen Li [a,b], Zhiming Cui [b,c], Suobo Zhang [a,*], Wei Xing [c]

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*
[b] *Graduate School of Chinese Academy of Sciences, China*
[c] *State Key Laboratory of Electroanalytical Chemistry, China*

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Abstract

A series of sulfonated polyimides containing benzimidazole groups were synthesized using 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA), 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) as the sulfonated diamine, and 2-(3′,5′-diaminophenyl)benzimidazole (**a**) or 6,4′-diamino-2-phenylbenzimidazole (**b**) as the nonsulfonated diamine. The electrolyte properties of the synthesized polyimides (**Ia** − *x*, **Ib** − *x*, *x* refers to molar percentage of the sulfonated diamine) were investigated and compared with those of polyimides (**Ic** − *x*) from BTDA, ODADS, and *m*-phenylenediamine (**c**). All synthesized polyimides possessed high molecular weights revealed by their high viscosity, and formation of tough and flexible membranes. Polyimides with benzimidazole groups exhibited much better swelling capacity than those without benzimidazole groups. This was attributed to the strong interchain interaction through basic benzimidazole functions and sulfonic acid groups. The sulfonated polyimides that are incorporated with 1,1′,8,8′-binaphthalimide exhibited better hydrolytic stability than that with 1,4,5,8-naphthalimide. Polyimide membranes with good water stability as well as high proton conductivity were developed. Polyimide membrane (**Ia** − 90), for example, did not lose mechanical properties after being soaked in boiling water for 1000 h, while its proton conductivity was still at a high level (compared to that of Nafion 117).
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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention as alternative sources of electricity due to their low emissions and high conversion efficiency [1,2]. Improvement in performance of the polymer electrolyte membrane (PEM) has been the focus in the development of PEMFCs because the PEM is one of the key components for successful PEMFC fabrications [3]. Nafion (Dupont), a perfluorosulfonic acid polymer, is a currently used PEM in commercial systems. Nafion is highly proton conductive and chemically and physically stable at moderate temperatures. However, these preferable properties are deteriorated above their glass transition temperature (T_g = ca. 110 °C) [4,5]. High gas permeability, high cost, high methanol crossover, and environmental inadaptability of the fluorinated materials are also serious drawbacks for the practical fuel cell applications. These limitations have stimulated many efforts in the development of alternative non-fluorinated materials with low cost and high performance [6–8]. So far, many kinds of sulfonated aromatic polymers, such as poly(ether ether ketone) [9–14], poly(ether sulfone)s [15–22], polysulfone [23], polyimide [24–31], and poly(*p*-phenylene)s [32–35] have been widely investigated as candidates for PEM materials. Among those sulfonated aromatic polymers, sulfonated aromatic polyimides (SPIs) are considered as promising alternative

* Corresponding author. +86 431 5605139.
E-mail address: sbzhang@ciac.jl.cn (S. Zhang).

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materials for fuel cell applications due to their high thermal stability, excellent mechanical strength, superior chemical resistance, and good film forming ability. However, water stability of sulfonated polyimides has been an issue to be addressed. The aromatic imide linkage tends to hydrolyze under high moisture conditions and at high temperatures, and this results in the degradation of the polymer main chain and a dramatic drop in the mechanical strength for SPI membranes. To investigate the relationship between water stability and chemical structure of SPIs and to achieve the high water stability, many types of SPIs based on novel sulfonated diamines have been developed. Okamoto and co-workers have reported on the water stability of sulfonated polyimides from different sulfonated diamines. They revealed the factors controlling the water stability of sulfonated polyimide membranes, of which the most important factor is the basicity of the sulfonated diamine [36,37]. Moreover, they have found that the sulfonated and nonsulfonated diamines having flexible linkages could improve water stability of the polyimide based on six-membered ring dianhydride [38,39]. Watanabe et al. had shown that NTDA-based SPIs with bulky fluorenyl groups having unique water uptake behavior produced higher conductivities than Nafion [40]. They also reported that polyimides bearing aliphatic sulfonic acid groups had enhanced water stability [41,42].

Acid–base blend membranes synthesized by a combination of polymeric nitrogen-containing bases (N-bases) with polymeric sulfonic acids are new class of interesting materials that exhibit improved thermal stability and good resistance to swelling. For example, Han and co-workers reported the synthesis of the base polyimide using diaminoacrydine hemisulfate and 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), and its blending with a polyimide having sulfonic acid group in the main chain [43]. The formation and properties of the blend membranes are based on the interaction between the sulfonic acid groups and the N-bases. The formed polysalt between the acid polymer and base polymer acts as ionic cross-linking point and it also resists the polymer swelling. In the similar manner, the polymers bearing both sulfonic acid groups and N-bases should possess the improved water stability. In view of this consideration, efforts have been made to develop membrane materials based on sulfonated polyimides containing benzimidazole groups. In this article, we report the synthesis of sulfonated polyimides by copolymerization of 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA), 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), and 2-(3′,5′-diaminophenyl)benzimidazole (**a**) or 6,4′-diamino-2–phenylbenzimidazole (**b**). The introduction of basic benzimidazole groups was expected to increase interchain interaction of the SPIs, thus to improve the water swelling capacity of the SPIs. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) was used due to its unique structure. BTDA dianhydride has two anhydride groups which are located on the two twist noncoplanar naphthalene rings. As a result, the polyimides from BTDA should possess a decreased positive charge density of carbonyl groups in the naphthalimide moieties compared with that from NTDA. This is favorable to depress the hydrolysis of the imide rings. For comparison study, the polyimides (**IIc** – *x*) from BTDA, ODADS, and *m*-phenylenediamine were also synthesized. The effects of both the dianhydride and the diamine structures on the properties of the copolymers were evaluated through the study of their electrolyte properties.

2. Experimental

2.1. Materials

3,5-Dinitrobenzoyl chloride, *o*-phenylenediamine, *m*-phenylenediamine (MPDA), and 4,4′-diaminodiphenyl ether (ODA) were purchased from Aldrich and used without further purification. 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 diethyl ether, and dried under vacuum. Polyphosphoric acid, 5-chloro-1,8-naphthalic anhydride and 1,4,5,8-naphthalenetetracarboxylic dianhydride were used as received from Beijing Multi. Technology Co., Ltd. 4,4′-Diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) was prepared according to a previously described procedure [38]. All other reactants and solvents were obtained from commercial sources and used as received.

2.2. Monomer and polymer syntheses

2.2.1. Synthesis of dimethyl-4-chloro-1,8-naphthalenedicarboxylate

A mixture of 100 g (0.43 mol) of 4-chloro-1,8-naphthalic anhydride (**1**), 128 g (0.62 mol) of phosphorus pentachloride and 180 mL of phosphorus oxychloride was refluxed for 24 h and the solvent then removed by distillation. The residual solid was added slowly into 500 mL methanol while cooling in an ice-bath and stirring vigorously. The resulting mixture was allowed to stand for 0.5 h at room temperature and diluted with water to 1500 mL. The solid was filtered off and washed with water and recrystallized from about 400 mL of methanol which gave 100.6 g (84.0%) of white crystals, m.p. 80–81 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 3.92 (s, 6H, $-CH_3$), 7.64–7.72 (t, 2H, Ar-H), 7.91–7.94 (d, 1H, Ar-H), 8.06–8.08 (d, 1H, Ar-H), 8.51–8.53 (d, 1H, Ar-H).

2.2.2. Synthesis of 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA)

To a 100 mL three-necked round-bottomed flask equipped with a serum cap, nitrogen inlet and outlet was added anhydrous $NiBr_2$ (0.087 g, 0.4 mmol), PPh_3 (0.786 g, 3 mmol), zinc dust (1.56 g, 24 mmol), and dry DMAc (5 mL). The flask was evacuated and filled with nitrogen three times and then placed in an oil bath heated at 85–90 °C. After the red-brown color was formed, a nitrogen purged solution of dimethyl-4-chloro-1,8-naphthalenedicarboxylate (1.67 g, 6 mmol) in 15 mL dry DMAc was added via a syringe. The mixture was stirred at 85 °C for another 2–4 h until the red color resumed. The resulting mixture was poured into 300 mL 10% HCl/

water. The solid was collected by filtration and washed with ethanol. The tetra-ester was treated with potassium hydroxide (1.5 g) in ethylene glycol (20 mL) at 150 °C for 18 h. After cooling to room temperature, the solid was filtered off and washed with acetone. It was dissolved in water and the solution was acidified with concentrated hydrochloric acid to yield the tetra-acid. The solid was washed with water thoroughly and dehydrated at 200 °C under vacuum for 12 h to afford pure dianhydride BTDA 1.02 g (89%). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 7.70–7.73 (d, 1H), 7.77–7.82 (t, 1H), 7.97–7.99 (d, 1H), 8.57–8.59 (d, 1H), 8.68–8.71 (d, 1H). Anal. Calcd for $C_{24}H_{10}O_6$ (394.05): C, 73.10; H, 2.56; Found: C, 73.00; H, 2.67. IR (KBr, $\nu_{c=o}$, cm^{-1}): 1773, 1732.

2.2.3. Synthesis of sulfonated copolyimide (**Ia** – 50)

To a 100 mL completely dried 3-necked flask were added 0.3604 g (1 mmol) of ODADS, 10 mL of *m*-cresol, and 0.68 mL (about 2 mmol) of Et_3N successively under nitrogen flow. After the sulfonated diamine was completely dissolved, 0.7886 g (2 mmol) of BTDA, 0.2243 g (1 mmol) of nonsulfonated diamine (DAPBI) and 0.4884 g (4 mmol) benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, additional 20 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into acetone. The fibre-like precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C to give product with 97% yield. FT-IR: 1705 cm^{-1} (ν_{sym}C=O), 1659 cm^{-1} (ν_{asym}C=O) and 1368 cm^{-1} (ν_{C-N} imide).

The above procedures were followed for the synthesis of polyimides **Ib** – *x*, **Ic** – *x* expecting that the molar ratios of nonsulfonated diamine (DAPBI, BIA or MPDA) were different. The polyimide **IIc** – 60 was synthesized from NTDA, ODADS and *m*-phenylenediamine (1/0.6/0.4) following the same procedure as above.

2.3. Membrane preparation and proton exchange

A series of tough, ductile copolymer membranes were prepared with a controlled thickness of 30–50 μm. The triethylammonium salts of the copolymers were redissolved in *m*-cresol to form a 4–5% solution at 80 °C. The solutions was filtered and cast onto glass plates at 120 °C for 12 h. The as-cast membranes were soaked in ethanol for 24 h to remove the residual solvent, and then treated with 1.0 N 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 150 °C for 10 h.

2.4. Polymer characterization

2.4.1. Measurements

^{1}H NMR spectra were measured at 300 MHz on an AV600 spectrometer. FT-IR spectra were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. The inherent viscosities were determined on 0.5 g/dL concentration of polymer in *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were carried out in nitrogen with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. Tensile measurements were performed with a mechanical tester Instron-1211 instrument at a speed of 1 mm/min. The relative humidity was 50% RH.

2.4.2. Water uptake and dimensional changes

The membrane (30–40 mg per sheet) was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was immersed into deionized water at room temperature for 4 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake of the membranes was calculated from:

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

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

Dimensional changes of the copolymer membranes was investigated by immersing the round shaped samples into water at room temperature for a given time, the changes of thickness and diameter were calculated from:

$$\Delta T_c = (T - T_s)/T_s; \quad \Delta L_c = (L - L_s)/L_s \tag{2}$$

where T_s and L_s are the thickness and diameter of the membrane equilibrated at 70% RH, respectively; T and L refer to those of the membrane immersed in liquid water for 5 h.

2.4.3. Oxidative stability

A small piece of membrane sample with a thickness of about 40 μm was soaked in Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at room temperature. The stability was evaluated by recording the time when membranes began to dissolve and dissolved completely.

2.4.4. Ion exchange capacity

Ion exchange capacity (IEC) was determined through titration. The membranes in the H^+ form were immersed in a 1 N NaCl solution for 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions in solution were then titrated with 0.01 N NaOH using phenolphthalein as an indicatior, and the membrane was kept in the solution for the titration.

2.4.5. Methanol permeability

Methanol diffusion coefficients were determined using an H's test cell with a solution containing 2 N methanol in water on one side and pure water on the other side. Magnetic stirrers were used in each compartment to ensure uniformity. Methanol concentration within the water cell was monitored by SHIMADZU GC-1020A series gas chromatograph. The methanol diffusion coefficients were calculated by the following equation:

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \quad (3)$$

Where C_A and C_B are the methanol concentration of feed side and that permeated through the membrane, respectively. A, L and V_B are the effective area, the thickness of membrane and the volume of permeated compartment, respectively. DK is defined as the methanol permeability and t_0 is the time lag.

2.4.6. Proton conductivity

The proton conductivity (σ, S/cm) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_sW_sR$ (d: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (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) [44]. The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in conductivity was observed.

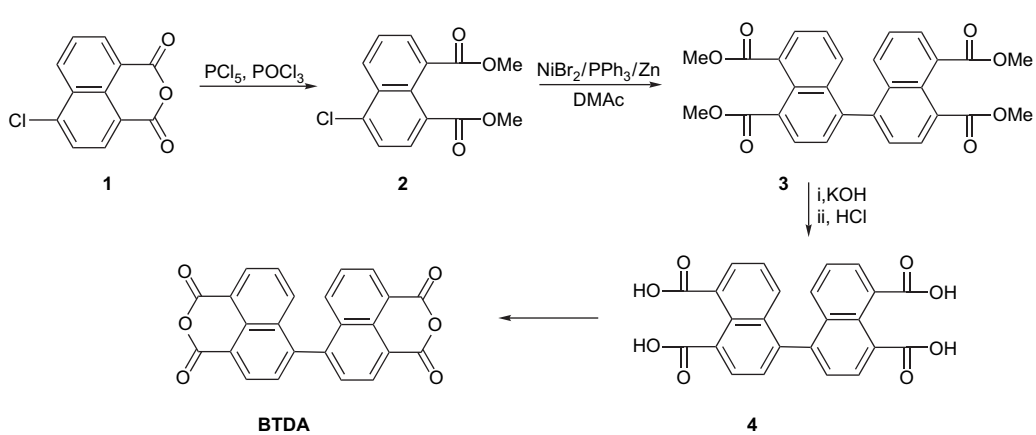
3. Results and discussion

3.1. Monomer synthesis

The synthetic route of 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) is outlined in Scheme 1. Dimethyl-4-chloro-1,8-naphthalenedicarboxylate (**2**) was synthesized with 84% yield by the reaction of 4-chloro-1,8-naphthalic anhydride (**1**) with phosphorus pentachloride and subsequent esterification with methanol. The Ni(0) catalytic coupling of **2** afforded tetra-ester **3** in almost quantitative yield. Hydrolysis of the tetra-ester **3** with potassium hydroxide in ethylene glycol and subsequent acidification with hydrochloric acid give tetra-acid **4**, which was cyclodehydrate at 200 °C under vacuum for 12 h to generate a 89% yield of 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA). The chemical structure of the dianhydride (BTDA) was confirmed by FT-IR, ^{1}H NMR (Fig. 1). Wang has independently prepared this monomer utilizing the Ni(0) catalytic coupling of di-*n*-butyl-4-chloro-1,8-naphthalenedicarboxylate [45]. There was no report on the NMR data of BTDA in their paper. 2-(3′,5′-Diaminophenyl)benzimidazole (DAPBI) and 6,4′-diamino-2-phenylbenzimidazole (BIA) were synthesized according to the reported procedures [46,47]. These monomers were pure enough for polymerization as confirmed by ^{1}H NMR spectra and elemental analyses.

3.2. Polymer syntheses

As shown in Scheme 2, the preparation of BTDA based SPIs were carried out by a one-step method in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid (catalyst), which has been employed for preparation of many other sulfonated polyimides in the literature [38]. ODADS was used to provide sulfonated sites along the copolymer backbone. The nonsulfonated diamines used in this study were DAPBI (**a**), BIA (**b**), and MPDA (**c**). The copolymers were denoted as **Ia** – x, **Ib** – x, and **Ic** – x, where x was the mole fraction of the monomer ODADS in the feed. For comparison purpose, NTDA-based SPI (**IIc** – 60) was also prepared. All copolyimides (in triethylammonium salt form) were completely soluble in *m*-cresol and DMSO, and form a flexible and tough film membrane by casting from the *m*-cresol solution. The obtained membranes were treated with 1.0 M sulfuric acid at room temperature for 4 days and washed with deionized water at room temperature for another 24 h. The inherent viscosity values of all copolymers were higher than 1.80 dL/g, which indicated successful copolymerization in producing high molecular weight copolymers. Fig. 2 shows the FT-IR spectra of the



Scheme 1. Synthesis of BTDA dianhydride.

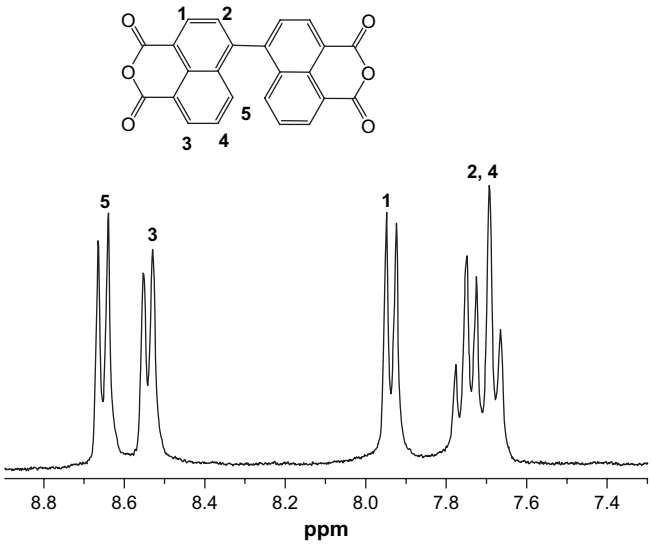


Fig. 1. ^{1}H NMR spectrum of BTDA (**I**) in DMSO-d_6.

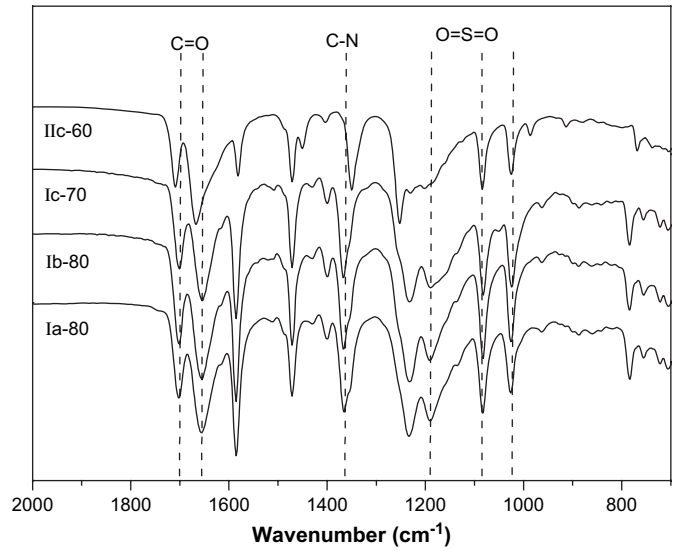
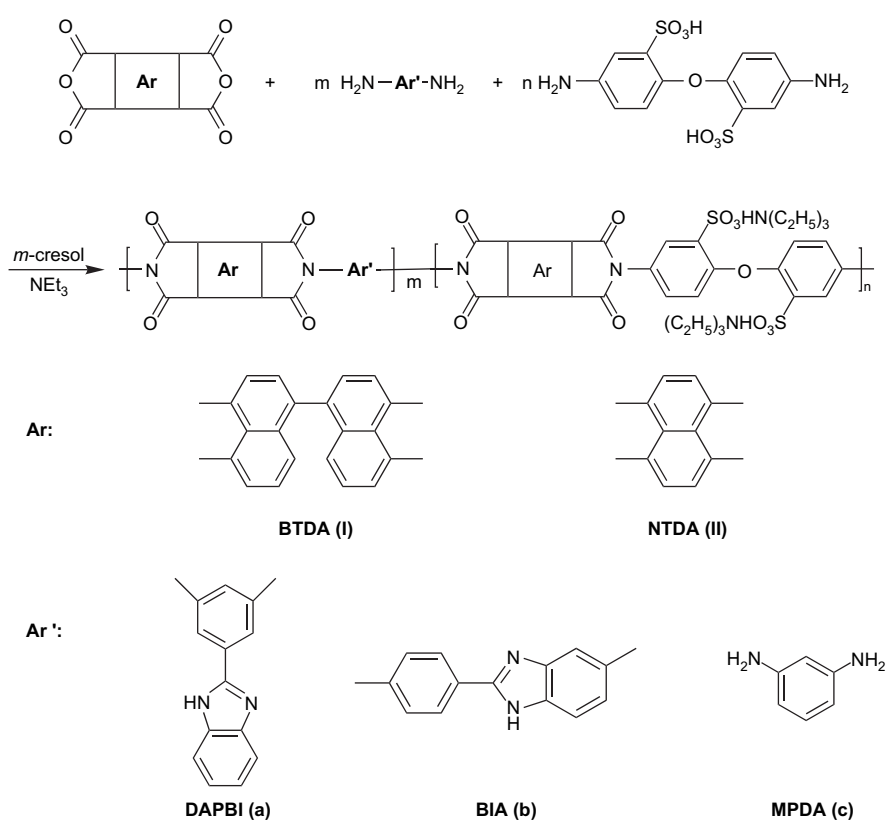


Fig. 2. FT-IR spectra of copolyimide membranes.

SPI membranes. The typical absorption bands for naphthalene imido rings are found around 1705 cm^{-1} (ν_{sym}C=O), 1659 cm^{-1} (ν_{asym}C=O) and 1368 cm^{-1} (ν_{C-N} imide) for **Ia**–c membranes, and 1710 cm^{-1} (ν_{sym}C=O), 1667 cm^{-1} (ν_{asym}C=O) and 1348 cm^{-1} (ν_{C-N} imide) for **IIc** – 60 membrane, respectively. No peaks at 1780 cm^{-1} [corresponding to poly(amic acid)] was observed, and this suggested complete imidization of the SPI membranes. Furthermore, the bands around 1197 cm^{-1}, 1090 cm^{-1} and 1020 cm^{-1} were assigned to the stretching vibration (O=S=O) of sulfonic acid groups.

3.3. IEC, water uptake, and size changes

Ion exchange capacity (IEC) of the copolymers synthesized was calculated from the molar ratio of sulfonated diamine to nonsulfonated diamine in feed, and also evaluated by means of titration. The method commonly used to determine IEC of sulfonated polymers involves the immersion in a 1 N NaCl solution of the membrane in the acid form. The membrane is converted to the sodium form by exchanging its H^+



Scheme 2. Syntheses of sulfonated copolyimides **I** and **II**.

ions with Na^+ from the solution. Then, the membrane is removed from solution, and the H^+ ions within the solution are titrated with 0.01 N NaOH solution using phenolphthalein as the indicator. The experimental IEC values of the membranes **Ic** and **IIc** fit well with the theoretical values. However, the IEC values of the copolymers containing benzimidazole groups, which were determined by the titration method, were much lower than the theoretical values. For example, soaking copolymer **Ia** – 70 membrane in a 1 N NaCl solution, could exchange only 66.9% of the total amount of H^+ in its polymers. This observation implied that the acid protons of the copolymer are more difficult to exchange than for the other kind of sulfonated polyimides, probably because of the formation of an acid–base complex between benzimidazole and the sulfonic acid groups of the copolymer. The same behavior was observed by Rozier and Mercier groups [48,49]. To overcome this uncompleted exchange problem, the membrane was kept in the solution for titration. The IEC values measured from this method were in good agreement with the theoretical values.

The water uptake and swelling ratio of copolymer membranes were determined by measuring the changes in the mass and size, respectively, before and after hydration. The data are reported in Table 1. As expected, the water uptake increases with the increasing IEC. The water uptakes observed for copolymer **Ia** – *x* varied from 24–65% for IEC values varying from 1.26–2.55 meq/g, which were lower than that of **Ic** – *x* with a comparable IEC values. For example, copolymer **Ia** – 80 (IEC = 2.26 meq/g) shows lower water uptake (55%) than **Ic** – 70 (59%) (IEC = 2.15 meq/g), even though the IEC value of **Ia** – 80 is higher than that of **Ic** – 70. The difference of water uptake between **Ia** – 80 and **Ic** – 70 can be attributed to their difference in molecular structure. Both copolymers **Ia** – *x* and **Ic** – *x* have the same sulfonated diamine of ODADS. However, copolymers **Ia** – *x* contain pendant benzimidazole groups. The basic benzimidazole groups in the copolymers preferentially interact with sulfonic acid group and decrease the amount of free sulfonic acid group available to form hydrogen bond with water molecules. This enhanced intermolecular/intramolecular interactions in **Ia** – *x* copolymers consequently improved the dimensional stability of the membrane films. The results indicate that the basic benzimidazole is effective for retaining the dimensional stability in water especially for high IEC membranes.

Table 2
Hydrolytic stability and oxidation stability of copolyimide membranes

Samples	IEC (meq/g)	Water uptake (%)	Hydrolytic stability		Oxidative stability[c] (h)	
			Time[a]	Decrease in weight[b] (%)	τ_1[d]	τ_2[e]
Ia – 40	1.26	24	>1000	0	24	30
Ia – 50	1.54	32	>1000	0	22	27
Ia – 70	2.07	46	>1000	1	18	26
Ia – 80	2.31	55	>1000	1	16	26
Ia – 90	2.55	65	>1000	2	14	23
Ib – 80	2.31	57	>1000	1	16	24
Ib – 90	2.55	65	>1000	2	13	21
Ic – 70	2.18	59	>1000	3	18	23
Ic – 90	2.58	79	>1000	5	17	24
IIc – 60	2.44	78	4	×	16	24

'x' broken into pieces.
[a] Measured at 90 °C.
[b] Measured at 140 °C for 24 h.
[c] Measured at 30 °C in 30% H_2O_2 containing 30 ppm $FeSO_4$.
[d] The time when the membrane broke into pieces after being shaken drastically.
[e] The time when the membrane dissolved completely.

3.4. Membrane stability toward water and oxidation

The stability test of the copolymer membranes toward water was carried out by immersing the membranes into water at 90 °C and is justified by the loss of mechanical strength of the hydrated membranes. The criterion for the judgment of the loss of mechanical strength is that the membrane is broken after being lightly bent at 90 °C in water, or start to be broken into pieces under the test conditions. As shown in Table 2, the copolyimide membranes based on BTDA display much better water stability than those of the copolyimides based on NTDA. The copolyimide membrane (**Ia** – 90), for example, did not lose mechanical properties after being soaked in hot water for 1000 h but the **IIc** – 60 membranes became brittle at 4 h. Both **Ic** – *x* and **IIc** – *x* have the same sulfonated diamine and nonsulfonated diamine moieties but the different dianhydride units. However, **Ic** – *x* shows much better water stability than **IIc** – *x*. From this observation, it can be

Table 1
IEC, water uptake, dimensional change, methanol permeability and proton conductivity of copolyimide membranes

Samples	IEC[a] (meq/g)		λ	Water uptake (%W/W)	P_M	σ (S/cm)		Size change	
	Calculated	Measured			(10^{-6} cm^2/S)	20 °C	80 °C	ΔT	ΔL
Ia – 40	1.26	1.27	10.5	24	0.05	0.012	0.021	0.13	0.03
Ia – 50	1.54	1.53	11.6	32	0.09	0.024	0.045	0.13	0.04
Ia – 70	2.07	2.01	12.7	46	0.15	0.048	0.084	0.15	0.05
Ia – 80	2.31	2.26	13.5	55	0.24	0.093	0.166	0.18	0.06
Ia – 90	2.55	2.47	14.6	65	0.30	0.108	0.182	0.21	0.06
Ib – 80	2.31	2.27	13.9	57	0.25	0.092	0.178	0.16	0.06
Ib – 90	2.55	2.49	14.3	65	0.35	0.121	0.197	0.19	0.06
Ic – 70	2.18	2.15	15.2	59	0.37	0.044	0.073	0.20	0.09
Ic – 90	2.58	2.54	17.3	79	0.48	0.098	0.187	0.22	0.12
IIc – 60	2.44	2.40	18.0	78	0.58	0.105	0.184	0.19	0.15

[a] Calculated, IEC calculated from DS; measured, IEC measured with titration.

concluded that the enhanced hydrolytic stability of **I** series of copolyimides could be contributed to its unique binaphthalimide structure. Copolymer **Ia** – x had two carbonyl groups in the naphthyl groups whereas copolymer **II** – x had four carbonyl groups. Therefore, copolymer **Ia** – x should possess decreased positive charge density in carbonyl groups compared with copolymer **IIc** – 60 because of the electron withdrawing characteristics of carbonyl groups. The quantum-chemical calculations also revealed that 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) has a lower affinity to the electron, i.e., 3.7790 vs 4.0102 eV, than NTDA [50]. In addition, the binaphthalimide groups are more hydrophobic than the naphthalimide groups due to the decreased density of the polar carbonyl groups in the binaphthalimide groups. The highly hydrophobic nature of the binaphthalene backbone resists the approach of water to a great extent and hence prevents the rapid attack of water; hence, increases the overall stability. In an accelerated hydrolytic stability testing, the polyimide ionomers were treated at 140 °C in water for 24 h, and the weight loss of the copolymers were determined. As listed in Table 2, **I** series of polyimide ionomers showed a little weight loss whereas **II** series polyimide completely broke into pieces in the solution after the testing. The result further confirmed the excellent water stability of the copolyimides based on the BTDA dianhydride.

The oxidative stabilities of the SPIs were investigated by measuring the elapsed times, when a membrane began to dissolve (τ_1), and a membrane was dissolved completely (τ_2) after immersion into Fenton's reagent of the 30 wt% H_2O_2 containing 30 ppm $FeSO_4$ solution at room temperature. As listed in Table 2, the SPI membranes with an IEC lower than 2.0 meq/g showed relatively good resistance to oxidation and endured without dissolving for 18 h, while membranes with higher IEC dissolved to some extent. The membranes **Ia** – x and **Ic** – x with the similar IEC values showed the similar oxidative stability. The results indicate that the oxidative degradation of these ionomers may occur on the main chains rather than the pendent benzimidazole groups. It is reasonable to consider that the oxidative attacks by HO• and HOO• radicals are electrophilic and occur more likely on the main chain aromatic rings bound with electron-donating ether groups [51,52].

3.5. Thermal and mechanical properties

The thermal stability of the SPIs was investigated by thermogravimetric analysis (TGA). As shown in Fig. 3, all the copolyimide membranes exhibited three-step degradation pattern. The first weight loss was observed around 100 °C. This weight loss is attributed to the loss of absorbed moisture by the hygroscopic sulfonic groups in the copolyimides. The second weight loss from 200 to 400 °C was closely associated with the thermal degradation of the sulfonic acid groups. The desulfonation temperatures increased with increase in the basic benzimidazole component. The sulfonic groups form polysalt with basic benzimidazole groups and this leads to the stabilization of the aromatic sulfonate groups, which might be the reason for increase in thermal stability in the second step.

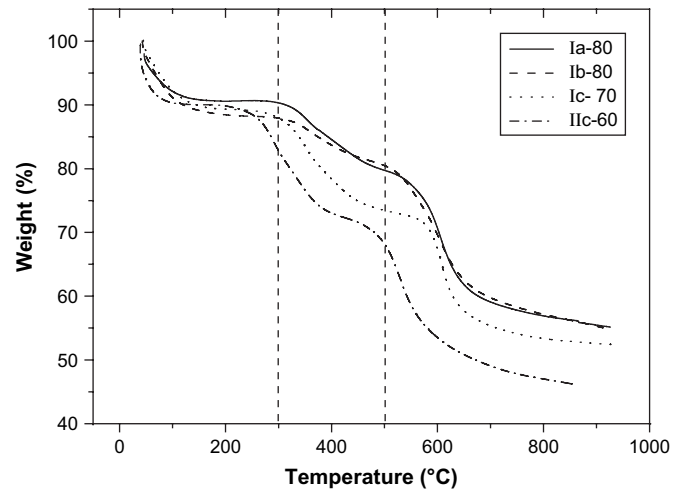


Fig. 3. TGA thermodiagram of the sulfonated copolyimide membranes.

The mechanical properties of the SPI membranes are summarized in Table 3. The stress–strain data are shown in Fig. 4. The **Ia** – x and **Ib** – x membranes in the dry state had tensile stress at maximum load of 123.4–150.4 MPa, Young's moduli of 0.86–1.67 GPa, and elongations at break of 24.7–50.2%. In the wet state, the samples showed excellent mechanical properties with tensile stress of 38.2–80.4 MPa and Young's moduli of 0.34–0.91 GPa. Especially, their elongations at break were up to 35.2–87.8%, which showed that they were very flexible materials. All SPI membranes showed the general trend of lower maximum stress for the higher IEC membranes. Comparison between the **Ic** – 90 and **Ic** – 60 membranes revealed that **Ic** – 90 membrane based on BTDA is mechanically stronger than **IIc** – 60 membrane from NTDA. It is assumed that the unique binaphthyl moieties restrict the molecular motion of the polymer chains resulting in stronger membranes.

Table 3
Mechanical properties of sulfonated copolyimide membranes in dry and wet state

Samples	IEC (meq/g)	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
		Dry[a]	Wet[b]	Dry	Wet	Dry	Wet
Ia – 40	1.26	150.4	80.4	1.67	0.91	24.7	35.2
Ia – 50	1.54	143.3	74.8	1.56	0.86	34.2	40.3
Ia – 70	2.07	138.8	64.6	1.36	0.70	40.7	49.7
Ia – 80	2.31	137.0	58.6	1.21	0.67	45.3	70.8
Ia – 90	2.55	115.7	38.9	0.92	0.34	46.7	75.6
Ib – 80	2.31	134.7	48.7	1.01	0.67	50.2	87.8
Ib – 90	2.55	123.4	38.2	0.86	0.55	43.5	78.9
Ic – 70	2.18	128.5	55.9	1.07	0.76	43.8	79.9
Ic – 90	2.58	96.5	43.9	0.96	0.36	36.8	65.3
IIc – 60	2.44	92.1	25.4	1.04	0.60	23.1	53.0

[a] Samples were dried at ambient conditions for one 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.

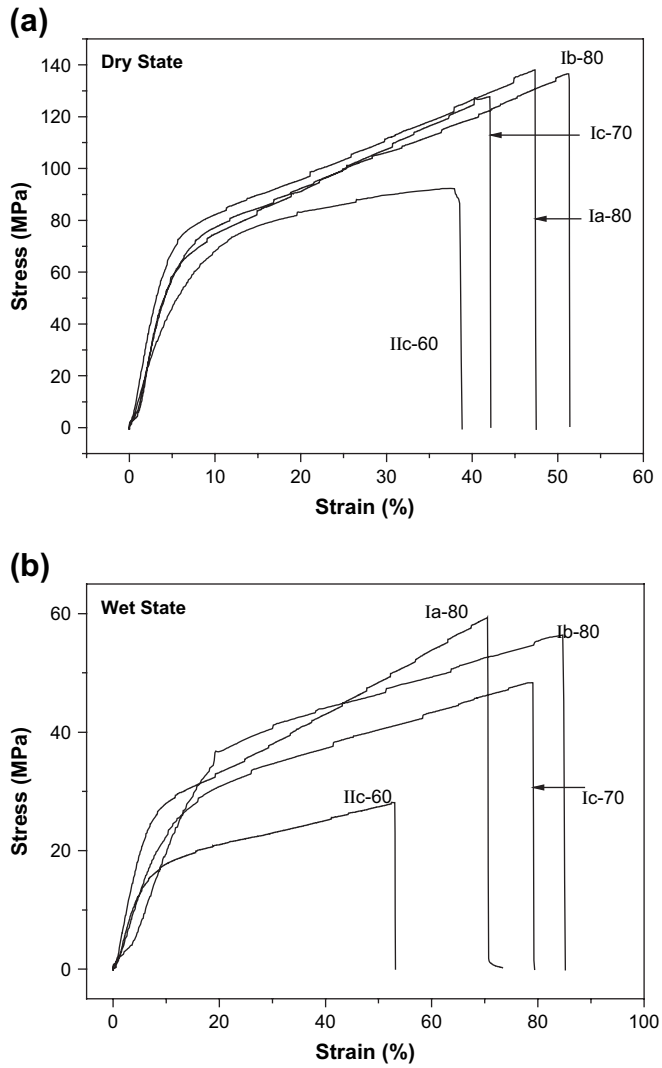


Fig. 4. Stress vs strain curves of copolyimide membranes: (a) dry state (samples were dried at ambient conditions for one day and tested at 30 °C, 50% RH); (b) wet state (samples were soaked in deionized water for 12 h at room temperature and tested in fully hydrated state at 30 °C).

3.6. Proton conductivity and methanol permeation properties

Proton conductivities of the hydrated membranes were measured in the temperature range of 20–80 °C. The conductivity data are tabulated in Table 1. Copolyimide **Ia** – x exhibited comparable proton conductivity with copolyimide **Ib** – x at a similar IEC. The proton conductivities of such benzimidazole based copolyimides were much lower than those of polyimides from NTDA, MPDA and the same sulfonated diamine of ODADS [38]. This can be attributed to the interchain interactions between the sulfonic acid groups and the benzimidazole groups. This kind of interaction decreases the amount of free sulfonic acid group available to release and transport protons. The decreased proton conductivity was also attributed to the low water uptakes of the benzimidazole based copolyimides. When **Ic** – 90 and **IIc** – 60 are compared, which have the same diamine moieties, but different dianhydride components,

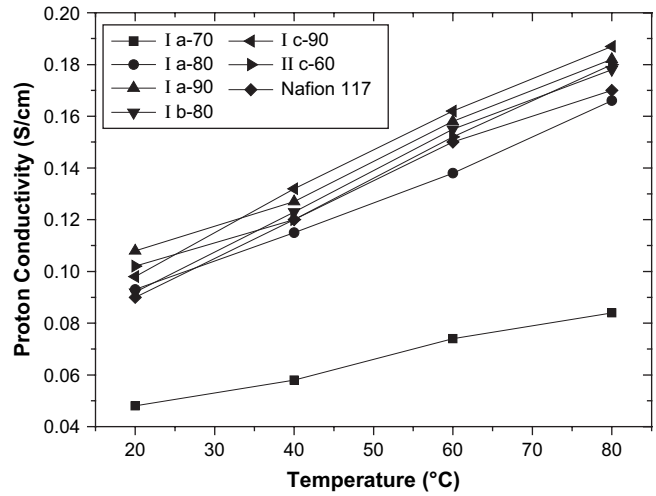


Fig. 5. Proton conductivity of copolyimide membranes at different temperatures under fully hydrated conditions.

copolymer **Ic** – 90 exhibited lower proton conductivity than copolymer **IIc** – 60. The results indicate that the bulky binaphthalimide moieties in the copolymer interferes in the proton conductivity, probably due to its rigid and hydrophobic characters. However, the effect of the dianhydride structure on the conductivity is not pronounced between NTDA and BTDA based benzimidazole polyimides. The other factors such as morphology, interchain interaction may also affect the proton conductivity of the copolymers. Fig. 5 shows the temperature dependence of the proton conductivity. All the membranes displayed increased proton conductivities with increasing temperature. BTDA–ODADS/BAPBI (7/3) and BTDA–ODADS/MPDA (7/3) displayed slightly lower proton conductivities than Nafion 117, whereas other copolyimide membranes showed fairly high proton conductivities, which were roughly comparable to that of Nafion 117.

Table 1 lists the methanol transport behavior of the **Ia** – x and **Ic** – x membranes. The methanol permeability increased with increase in IEC values and water uptake. This indicated that methanol transport across the sulfonated polymer membranes was strongly dependent upon the water uptake content, and the methanol permeates through the membranes in complex forms such as $CH_3OH_2^+$ and H_3O^+ [53]. The methanol permeability of the **Ia** – x membranes decreased with increasing DAPBI content. This can be interpreted by the formation of base–acid complex between the sulfonic acid groups and benzimidazole groups. The formation of base–acid complex reduces vacant space that absorbs free water molecules and induces a much denser structure to act as a methanol barrier. Moreover, the **Ia** – 80 membrane, which has comparable proton conductivity to Nafion 117, shows nearly one order of magnitude lower methanol permeability than Nafion 117.

4. Conclusion

4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) and diamines containing benzimidazole moieties (BAPBI and BIA) were synthesized and used as comonomers to generate

water stable copolymers for proton exchange membranes. The electrolyte properties of the synthesized polyimides were investigated and compared to those of polyimides based on 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). The sulfonated polyimides based on BTDA exhibited much better water stability than those based on NTDA. Such improvement in the stability could be attributed to the low hydrolysis activity of the binaphthalimide moieties. The SPI membranes incorporated with basic benzimidazole groups showed the enhanced thermal and water stabilities at the expanse of some proton conductivity. Furthermore, the low methanol permeation was achieved by the introduction of the benzimidazole into the SPIs backbone.

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References

[1] Carrette L, Friedrich K, Stimming U. Fuel Cells 2001;1:5.
[2] Costamagna P, Srinivasan S. J Power Sources 2001;102:253.
[3] Rikukawa K, Sanui K. Prog Polym Sci 2000;25:1463.
[4] Inzelt G, Pineri M, Schultze J, Vorofyntsev M. Electrochim Acta 2000;45:240.
[5] Savadogo O. J New Mater Electrochem Syst 1998;1:47.
[6] Hickner M, Ghassem H, Kim Y, Einsla B, McGrath J. Chem Rev 2004;104:4587.
[7] Li Q, He R, Jensen J, Bjerrum N. Chem Mater 2003;15:4896.
[8] Kerres J. J Membr Sci 2001;185:3.
[9] Jones D, Rozière J. J Membr Sci 2001;185:41.
[10] Xing P, Robertson G, Guiver M, Mikhailenko S, Wang K, Kaliaguine S. J Membr Sci 2004;229:95.
[11] Gil M, Ji X, Li X, Na H, Hampsey J, Lu Y. J Membr Sci 2004;234:75.
[12] Xing P, Robertson G, Guiver M, Mikhailenko S, Kaliaguine S. Macromolecules 2004;37:7960.
[13] Vetter S, Ruffmann B, Buder I, Nunes S. J Membr Sci 2004;260:181.
[14] Liu B, Robertson G, Kim D, Guiver M, Hu W, Jiang Z. Macromolecules 2007;40:1934.
[15] Nolte R, Ledjeff K, Bauer M, Malhaupt R. J Membr Sci 1993;83:211.
[16] Kerres J, Cui W, Reichle S. J Polym Sci Part A Polym Chem 1996;34:2421.
[17] Wang F, Hickner M, Kim Y, Zawodzinski T, McGrath J. J Membr Sci 2002;197:231.
[18] Karlsson L, Jannasch P. J Membr Sci 2004;230:61.
[19] Willes K, Wang F, McGrath J. J Polym Sci Part A Polym Chem 2005;43:2964.
[20] Miyatake K, Chikashige Y, Watanabe M. Macromolecules 2003;36:9691.
[21] Miyatake K, Oyaizu K, Tsuchida E, Hay A. Macromolecules 2001;34:2065.
[22] Miyatake K, Chikashige Y, Higuchi E, Watanabe M. J Am Chem Soc 2007;129:3879.
[23] Schuster M, Kreuer K, Andersen H, Maier J. Macromolecules 2007;40:598.
[24] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.
[25] Zhang Y, Litt M, Savinell R, Wainright J. Polym Prepr 2000;41:1561.
[26] Guo X, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. Macromolecules 2002;35:6707.
[27] Miyatake K, Zhou H, Uchida H, Watanabe M. Chem Commun 2003:368.
[28] Yin Y, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. J Mater Chem 2004;14:1062.
[29] Einsla B, Kim Y, Hickner M, Hong Y, Hill M, Pivovar B, et al. J Membr Sci 2005;255:141.
[30] Yasuda T, Miyatake K, Hirai M, Nanasawa M, Watanabe M. J Polym Sci Part A Polym Chem 2005;43:4439.
[31] Miyatake K, Watanabe M. J Mater Chem 2006;16:4464.
[32] Kobayashi T, Rikukawa M, Sanui K, Ogata N. Solid State Ionics 1998;106:219.
[33] Ghassemi H, Ndip G, McGrath J. Polymer 2004;45:5855.
[34] Qiu Z, Wu S, Li Z, Zhang S, Xing W, Liu C. Macromolecules 2006;39:6425.
[35] Wu S, Qiu Z, Zhang S, Yang X, Yang F, Li Z. Polymer 2006;47:6993.
[36] Yin Y, Suto Y, Sakabe T, Chen S, Hayashi S, Mishima T, et al. Macromolecules 2006;39:1189.
[37] Yin Y, Yamada O, Tanaka K, Okamoto K. Polym J 2006;38:197.
[38] Fang J, Guo X, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35:9022.
[39] Watari T, Fang J, Tanak K, Kita H, Okamoto K. J Membr Sci 2004;230:111.
[40] Miyatake K, Zhou H, Watanabe M. Macromolecules 2004;37:4956.
[41] Asano N, Miyatake K, Watanabe M. Chem Mater 2004;16:2841.
[42] Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M. J Am Chem Soc 2006;128:1762.
[43] Jang W, Sundar S, Choi S, Shul YG, Han H. J Membr Sci 2006;280:321.
[44] Lee C, Park H, Lee Y, Lee R. Ind Eng Chem Res 2005;44:7617.
[45] Gao J, Wang Z. J Polym Sci Part A Polym Chem 1995;33:1627.
[46] Chung I, Kim S. Polym Bull 1997;38:627.
[47] Prost L. Canadian Patent 950,146; 1974.
[48] Rozière J, Jones D, Marrony M, Glipa X, Mula B. Solid State Ionics 2001;145:61.
[49] Jouanneau J, Mercier R, Gonon L, Gebel G. Macromolecules 2007;40:983.
[50] Rusanov AL. Adv Polym Sci 1994;111:115.
[51] Huiibner G, Roduner E. J Mater Chem 1999;9:409.
[52] Panchenko A. J Membr Sci 2006;278:269.
[53] Won J, Park H, Kim Y, Choi S, Ha H, Oh I, et al. Macromolecules 2003;36:3228.