Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 47 (2006) 2660–2669

polymer

www.elsevier.com/locate/polymer

Synthesis and properties of novel side-chain-sulfonated polyimides from bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone

Shouwen Chen [a], Yan Yin [b], Kazuhiro Tanaka [a], Hidetoshi Kita [a], Ken-ichi Okamoto [a,*]

[a] *Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611, Japan*
[b] *Venture Business Laboratory, Yamaguchi University, Yamaguchi, Japan*

Received 7 December 2005; received in revised form 11 February 2006; accepted 15 February 2006

Abstract

A novel side-chain-sulfonated aromatic diamine of bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS) was synthesized. Sulfonated copolyimides were synthesized by random and sequenced block copolymerization of 1,4,5,8-naphthalene tetracarboxylic dianhydride, BAPSBPS and nonsulfonated diamine. They displayed good solubility in common aprotic solvents and high desulfonation temperature of 350 °C, suggesting the high stability of sulfonic acid groups. The reduced viscosity was in the range of 0.4–1.8 dl/g at 0.5 g/dl and 35 °C. Flexible and tough membranes with reasonably high mechanical strength were prepared. They showed anisotropic membrane swelling with larger swelling in thickness than in plane. They displayed reasonably high proton conductivity (σ), taking their lower ion exchanging capacity (IEC) into account. For example, the membrane with IEC of 1.54 mequiv/g showed σ values of 81 and 11 mS/cm in water and 70% RH, respectively, at 60 °C.

Keywords: Sulfonated polyimide; Polymer electrolyte membrane; Proton conductivity

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been developed as promising alternative energy supplies for mobile and stationary applications. The most important part of fuel cell is polymer electrolyte membrane (PEM) [1–4]. Up to date, the commercially available PEMs for PEFCs are perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, which have high proton conductivity and excellent chemical stability. However, high cost, high methanol permeability and lower operating temperature below 80 °C limit their industrial applications. This stimulated many efforts in the development of alternative PEMs.

In recent years, many kinds of sulfonated aromatic polymers have been developed. Sulfonated polyimides (SPIs) with six-membered imide rings have been studied as one of the promising candidates for fuel cell applications because of their low methanol permeability, excellent thermal and chemical stabilities [1,4–20]. Some SPIs showed both relatively high proton conductivity and relatively high water stability. One example is main-chain-type SPIs derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), 4,4′-bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) and nonsulfonated diamine such as 4,4′-bis(4-aminophenoxy)biphenyl (BAPB) [9,10,13]. The relatively high water stability of the BAPBDS-based SPI membranes was attributed to the flexible structure and the higher basicity of BAPBDS due to the absence of electron-withdrawing substitution on amino phenyl groups [9]. Another example is side-chain-type SPIs derived from NTDA, 2,2′- or 3,3′-bis(3-sulfopropoxy)benzidine (2,2′- or 3,3′-BSPB), and nonsulfonated diamine [11–13,16]. The relatively high water stability of the BSPB-based SPIs was attributed to the higher basicity of BSPB and the microphase-separated structure composed of hydrophilic side chain domains and hydrophobic polyimide main chain domains. These suggest that a sulfonated diamine with high basicity of diamine, high flexibility and sulfonated pendant groups lead to favorable SPIs for fuel cell applications.

Based on this consideration, in this study, a novel sulfonated aromatic diamine of bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS) has been developed. BAPSBPS has flexible structure due to the sulfone and ether linkages and sulfonic acid groups bonded to the aromatic side chain. This paper reports on synthesis and characterization of BAPSBPS and BAPBDS-based SPIs together with the

---

* Corresponding author. Tel.: +81 836 85 9660; fax: +81 836 85 9601.
E-mail address: okamotok@yamaguchi-u.ac.jp (K.- Okamoto).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.02.045

preliminary results about membrane properties such as proton conductivity.

2. Experimental

2.1. Materials

4,4′-Dichlorodiphenyl sulfone (DCDPS) and aluminum chloride were purchased from Aldrich and used as received. Butyllithium (1.6 M in hexane) and thionyl chloride were purchased from Wako and used as received. NTDA (Aldrich) and *p*-aminophenol (*p*-AP, Wako) were purified by vacuum sublimation before use. Benzene and tetrahydrofuran (THF) were purchased from Wako and were distilled over anhydrous P_2O_5 and sodium, respectively. Triethylamine (TEA), sulfuric acid (95%), fuming sulfuric acid (60%), *m*-cresol, dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl acetamide (DMAc), *N*,*N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone (NMP) were purchased from Wako and used as received. BAPB, 1,3-bis(4-aminophenoxy)benzene (1,3-BAPBz) and 1,4-bis(4-aminophenoxy) benzene (1,4-BAPBz) were purchased from Wako and recrystallized from ethanol before use. Ultra-pure water was obtained from a Millipore Mill-Q purification system.

2.2. Monomer synthesis

2.2.1. 2,2′-Dicarboxy-4,4′-dichlorodiphenyl sulfone (*I*)

To a fully dried 500 ml 4-neck flask, which was equipped with a pressure-equilibrium drop funnel, a magnetic stirrer, a N_2 inlet/outlet and a thermometer, 11.5 g (40 mmol) of DCDPS and 200 ml of THF were charged under N_2 flow. After the solution was cooled to −60 °C by ethanol-dry ice bath, 53 ml (84 mmol) of BuLi solution was added at a rate to keep the inner temperature below −55 °C. After the addition, the reaction mixture was maintained at this temperature for 2 h. Then, the reaction solution was cooled to −70 °C and dry CO_2 gas was bubbled through a pipe at the rate to keep the inner temperature below −50 °C. When CO_2 gas escaped, the inflow rate was turned down and kept for about 3 h. Then, 80 ml of 10% NaOH solution was added and two phases appeared, which were separated. The organic layer was extracted twice with 40 ml of 10% NaOH solution. The aqueous solutions were collected and acidified with 20% HCl solution. White precipitate appeared and was filtrated and dried to get 12.8 g of compound **I**. After being washed with 100 ml of chloroform, 10.7 g of pure product **I** was obtained (yield: 71%). FT-IR (KBr; cm^{-1}): 1722 (C=O, carboxylic acid), 1329 (S=O, asymmetric, sulfone), 1156 (S=O, symmetric, sulfone). ^{1}H NMR (270 MHz; DMSO-*d6*; ppm): 8.06 (d, 2H), 7.80–7.86 (m, 4H).

2.2.2. 2,2′-Dichlorocarbonyl-4,4′-dichlorodiphenyl sulfone (*II*)

To a fully dried 100 ml flask, 15.0 g (40 mmol) of compound **I** and 60 ml of SO_2Cl were charged. The mixture was heated to reflux for 8 h. After the exceed SO_2Cl was distilled, the residue was recrystallized from 1,2-dichloroethane. 14.0 g of product **II** was obtained (yield: 85%). FT-IR (KBr; cm^{-1}): 1788 (C=O), 1334 (S=O, asymmetric, sulfone), 1160 (S=O, symmetric, sulfone). ^{1}H NMR (270 MHz; $CDCl_3$; ppm): 8.18 (d, 2H), 7.85 (d, 2H), 7.75 (dd, 2H).

2.2.3. 2,2′-Dibenzoyl-4,4′-dichlorodiphenyl sulfone (*III*)

To a fully dried 300 ml 3-necked flask, 10.3 g (25 mmol) of compound **II** and 225 ml of benzene were charged. The temperature was raised to 35 °C until the solid was dissolved completely, and then, 7.34 g (55 mmol) of $AlCl_3$ was added part by part. After the addition, the reaction mixture was kept at 35 °C for 20 h, and then poured into a large amount of ice water containing 10 ml of 10% HCl solution. The resulting solid was filtrated to get about a half of the product. The filtrate was separated to two phases, and the organic phase was evaporated to get another half of the product. The two parts of product were combined and recrystallized from acetonitrile, 10.5 g of **III** was obtained (yield: 85%). FT-IR (KBr; cm^{-1}): 1676 (C=O, aromatic ketone), 1332 (S=O, asymmetric, sulfone), 1158 (S=O, symmetric, sulfone). ^{1}H NMR (270 MHz; $CDCl_3$; ppm): 8.05 (d, 2H), 7.78 (m, 4H), 7.55–7.65 (m, 4H), 7.42–7.50 (m, 4H), 7.25 (d, 2H).

2.2.4. Bis[4-dichloro-2-(3-sulfobenzoyl)] phenyl sulfone, disodium salt (*IV*)

9.75 g (19.8 mmol) of compound **III** was added to a 100 ml flask. At room temperature, 9.8 ml of concentrated sulfuric acid was added slowly. After the solid was dissolved, 9.8 ml of fuming sulfuric acid was added. Then, the mixture was slowly heated to 75 °C and kept at this temperature for 12 h. Cooled to room temperature, the mixture was poured into 450 ml of ice water, and 120 g of NaCl was added into the solution to produce precipitate of the product. The solid was filtrated and redissolved in 450 ml of water and neutralized to the pH of 6–7 with 10% NaOH solution. 100 g of NaCl was added to salt out the product **IV**. The precipitate was filtrated and dried, and then added into 100 ml of DMSO. After the undissolved part was filtrated off, the filtrate was distilled under vacuum, and the residue was washed by acetone, and dried at 60 °C under vacuum for 8 h to get 13.7 g of product **IV** (yield: 99%). FT-IR (KBr; cm^{-1}): 1677 (C=O, aromatic ketone), 1330 (S=O, asymmetric, sulfone), 1164 (S=O, symmetric, sulfone), 1198 (S=O, sulfonate), 1037 (S=O, sulfonate). ^{1}H NMR (270 MHz; DMSO-*d6*; ppm): 8.07 (s, 2H), 7.90–8.04 (m, 6H), 7.85 (d, 2H), 7.73 (d, 2H), 7.62 (t, 2H).

2.2.5. Bis[4-(4-aminophenoxy)-2-(3-sulfobenzoyl)]phenyl sulfone (BAPSBPS, *V*)

To a 200 ml 4-neck flask, which was equipped with a magnetic stirrer, a Dean–Stark trap mounted a condenser and a N_2 inlet/outlet, 2.36 g (21.6 mmol) of *p*-AP, 2.99 g (21.6 mmol) of K_2CO_3, 5.60 g (9 mmol) of compound **IV**, 70 ml of NMP and 35 ml of toluene were added under N_2 flow. While the solution was refluxed for 4 h at 140 °C, the produced water was removed with toluene as azeotrope. Then, the reaction temperature was raised to 170 °C for 20 h. After cooled to ambient temperature, the mixture was poured into 500 ml of cold water. The pH value of the solution was adjusted to below 1 by addition of 10% HCl solution. The solid was filtrated and washed by 1% HCl solution four times (about 30 ml each time), dried at 60 °C for 8 h under vacuum to give 5.90 g of crude product. Under nitrogen flow, the crude product was dissolved in 30 ml of *m*-cresol with 2.5 ml of TEA. Then the solution was slowly added to 300 ml of 2% HCl solution, and the resulting white precipitate was filtrated and washed first by 1% HCl solution then by isopropanol, and dried at 60 °C under vacuum for 8 h. 5.34 g of BAPSBPS was obtained. Finally, the product was recrystallized from the mixture of DMSO and water, and 4.27 g of *V* was obtained (yield: 59%). ^{1}H NMR (270 MHz; DMSO-*d*6; a drop of TEA was added to free the amine groups; ppm): 7.96 (s, 2H), 7.88 (d, 2*H*), 7.77 (d, 2H), 7.63 (d, 2H), 7.52 (t, 2H), 7.13 (dd, 2*H*), 6.85 (m, 6*H*), 6.60 (d, 4*H*), 5.1 (NH_2). FT-IR (KBr; cm^{-1}): 1675 (C=O, aromatic ketone), 1323 (S=O, asymmetric, sulfone), 1164 (S=O, symmetric, sulfone), 1202 (S=O, sulfonic acid), 1035 cm^{-1} (S=O, sulfonic acid).

2.3. Polymer synthesis and membrane preparation

2.3.1. Synthesis of NTDA–BAPSBPS homopolymer

To a completely dried 100 ml 3-neck flask, which was equipped with a mechanical stirrer, a N_2 inlet and a condenser, 3.844 g (4.8 mmol) of BAPSBPS, 28 ml of *m*-cresol, and 1.9 ml of TEA were added with stirring under nitrogen flow. After BAPSBPS was dissolved completely, 1.278 g (4.8 mmol) of NTDA and 0.821 g of benzoic acid were added successively. The mixture was heated to 80 °C for 4 h and 180 °C for 20 h, respectively. After cooling to room temperature, the reaction mixture was poured into 150 ml of acetone, the resulting fiber-like precipitate was collected by filtration, and dried in vacuum at 100 °C for 10 h (yield: >98%).

The practical nomenclature for the NTDA-based SPIs in this article is as follows. BAPSBPS/X(*a*/*b*)-r (or s), where X refers to the nonsulfonated diamine, *a*/*b* is the molar ratio of BAPSBPS to X, r and s refer to random and sequenced copolymerization, respectively.

2.3.2. Synthesis of random copolyimides

As an example, synthesis of BAPSBPS/1,3-BAPBz(3/1)-r is described below. To a 100 ml completely dried 3-neck flask, 2.402 g (3.0 mmol) of BAPSBPS, 20 ml of *m*-cresol, and 1.2 ml of TEA were added under nitrogen flow. After BAPSBPS was completely dissolved, 0.292 g (1.0 mmol) of nonsulfonated diamine 1,3-BAPBz, 1.073 g (4.0 mmol) of NTDA and 0.684 g of benzoic acid were added to the flask. The mixture was stirred at room temperature for about half an hour and then heated to 80 °C for 4 h and then 180 °C for 20 h. After cooling to 80 °C, an additional 15 ml of *m*-cresol was added to dilute the highly viscous solution, and the solution was poured into 200 ml of acetone. The resulting fiber-like precipitate was collected by filtration, washed with acetone, and dried at 100 °C for 10 h in vacuum (yield: >98%).

2.3.3. Synthesis of sequenced copolyimides

As an example, synthesis of BAPSBPS/1,3-BAPBz (3/1)-s is described below. To a 100 ml completely dried 3-neck flask, 4.805 g (6.0 mmol) of BAPSBPS, 40 ml of *m*-cresol, and 2.4 ml of TEA were added under nitrogen flow. After BAPSBPS was completely dissolved, 2.145 g (8.0 mmol) of NTDA and 1.37 g of benzoic acid were added. The reaction mixture was kept at 80 °C for 4 h and then 180 °C for 5 h. After the mixture was cooled to room temperature, 4 ml of *m*-cresol and 0.585 g (2.0 mmol) of 1,3-BAPBz were added to the solution successively. The mixture was stirred at room temperature for a few minutes and then heated to 80 °C for 4 h and then 180 °C for 20 h, followed by the similar treatment to get the polymer solid (yield: >98%).

2.3.4. Membrane preparation

A 5–7 wt% *m*-cresol solution of SPI (in TEA salt form) was filtrated and then cast onto glass substrates (glass plate or dish). The cast membranes were dried at 80 °C for 1 h, 100 °C for 1 h, and 120 °C for 10 h, respectively. They were soaked in methanol at 40 °C for 48 h to remove the residue solvent, and then the proton exchange treatment was performed by immersing the membranes into 1.0 M sulfonic acid solution at 40 °C for 72 h. The proton-exchanged membranes were thoroughly washed with water (immersed in water for 48 h at 40 °C) and then dried in vacuum at 150 °C for 1 h and then 180 °C for 1 h.

2.4. Polymer characterization

2.4.1. Measurements

^{1}H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument in DMSO-*d*6 (except for compound **II** and **III** in $CDCl_3$). FT-IR spectra were recorded on a Horiba FT-200 Spectrometer as KBr pellets for monomers, and IR spectra of polymer membranes were recorded by ATR (attenuated total reflection) on the same machine. Thermogravimetry analysis (TGA) was performed on Rigaku TG-8120 in helium (flow rate: 100 cm^3/min) at a heating rate of 10 °C/min. Mechanical tensile tests were performed on a universal testing machine (Orientic, TENSILON RTC-1150A) at 25 °C and around 60% RH. The reduced viscosity η_r was measured with an Ostwald viscometer at 35 °C using 0.5 g/dl solutions in *m*-cresol or in DMSO solution containing 1% LiCl (Fig. 1).

Ion exchange capacity (IEC) of SPIs was calculated from the molar ratio of sulfonated diamine to nonsulfonated diamine in feed, and also evaluated by means of ^{1}H NMR and titration. In ^{1}H NMR method, proton exchanged SPI sample was dissolved in DMSO-*d*6 at a concentration of about 2 wt%. The typical ^{1}H NMR spectrum of **M3** is shown in Fig. 2(b). The IEC value was evaluated from the ratio of peak integration values of $H_{a,k}$ and H_h. In titration method, a sample membrane in proton form was soaked in 15 wt% NaCl solution for 24 h at 30 °C to exchange H^+ ion with Na^+ ion. Then, H^+ ion released into the solution was titrated with a 0.05 N NaOH solution using phenolphthalein as the indicator.

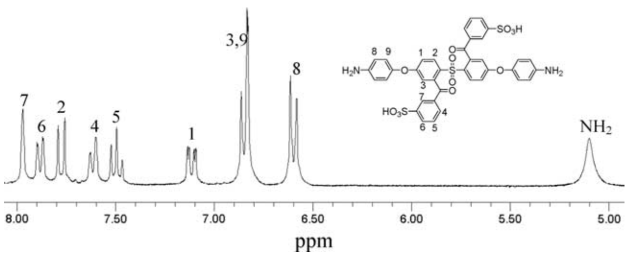


Fig. 1. ^{1}H NMR spectra of SPIs (a) In TEA salt form; (b) in proton form.

2.4.2. Water uptake and dimensional change

The water vapor sorption isotherms, water uptake (WU), dimensional change in membrane thickness (Δt_c) and in plane (Δl_c) were measured according to the method described elsewhere [9,11].

Water vapor sorption at different water vapor activities ($a_w < 0.95$) was measured at 60 °C using a sorption apparatus (BEL-18SP) by means of a volumetric method. The weight of sample membrane was about 100 mg.

Water uptake was measured by immersing a SPI sample sheet into water at room temperature for 5 h, then, the membrane was taken out, wiped with tissue paper very quickly, and weighed on a microbalance to get the wet weight W_s. Then the sample was dried at 120 °C for 3 h under vacuum to get the dry weight W_d. Water uptake value was calculated from:

$$\mathrm{WU} = \frac{W_s - W_d}{W_d} \times 100\ [\mathrm{wt\%}] \quad (1)$$

Dimensional change of membrane was investigated by immersing circle sample sheets into water at 25 °C for 5 h, the dimensional change in thickness and in plane were calculated from

$$\Delta t_c = \frac{t - t_s}{t_s}$$

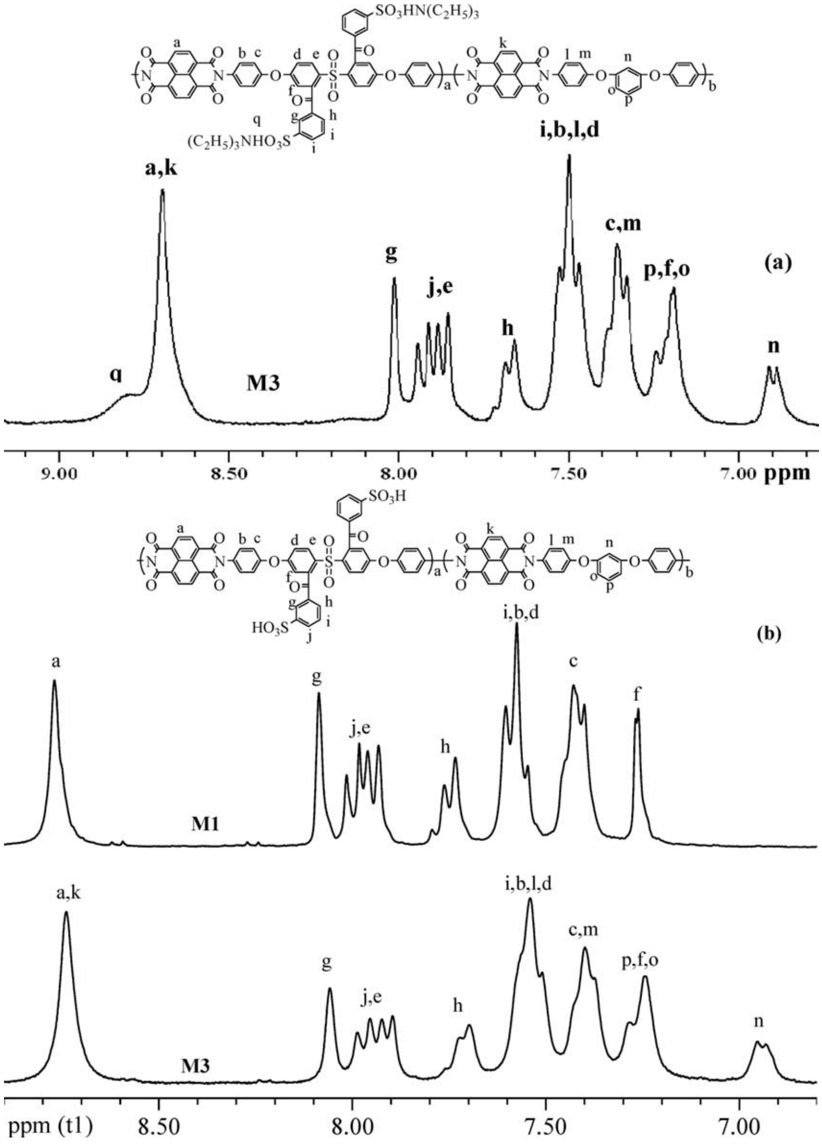


Fig. 2. ^{1}H NMR spectrum of BAPSBPS.

$$\Delta l_c = \frac{l - l_s}{l_s} \qquad (2)$$

where t_s and l_s are the thickness and diameter of membrane equilibrated at 70% relative humidity (RH), respectively; t and l refer to those of the membrane in water.

2.4.3. Proton conductivity

Proton conductivity in plane direction of membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 10 Hz to 100 KHz (Hioki 3532-80). A single cell with two blackened platinum plate electrodes was mounted on a Teflon plate at 0.5 cm distance. The proton conductivity as a function of RH and temperature was measured by a humidity- and thermo-controlled cell module device (SHINYEI SRI-01, Japan). Proton conductivity, σ, was calculated from:

$$\sigma = \frac{d}{L_s w_s R} \qquad (3)$$

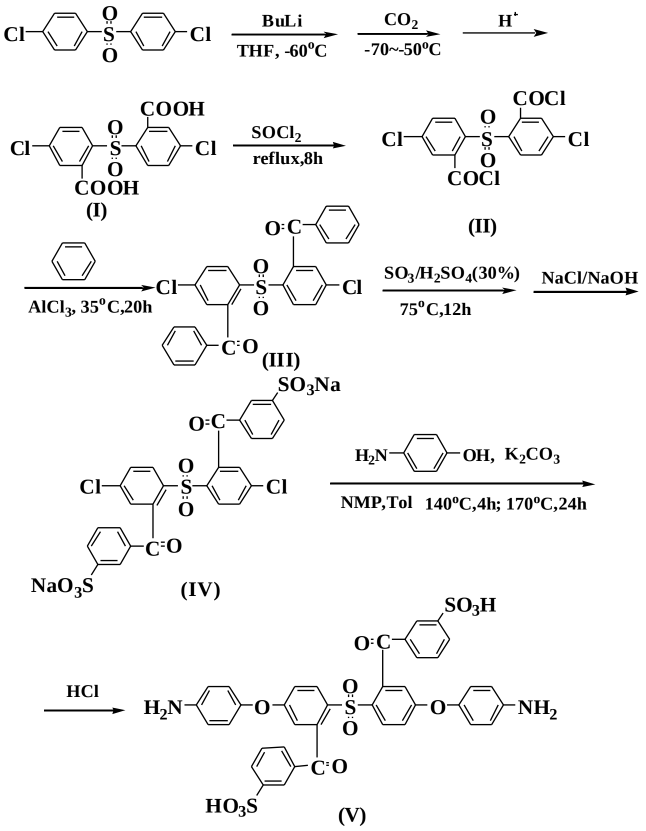
where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane at a standard condition of 70% RH, respectively, and R is the measured resistance value. For the measurements in liquid water, the swollen membrane thickness was used in the calculation of σ.

3. Results and discussion

3.1. Monomers synthesis

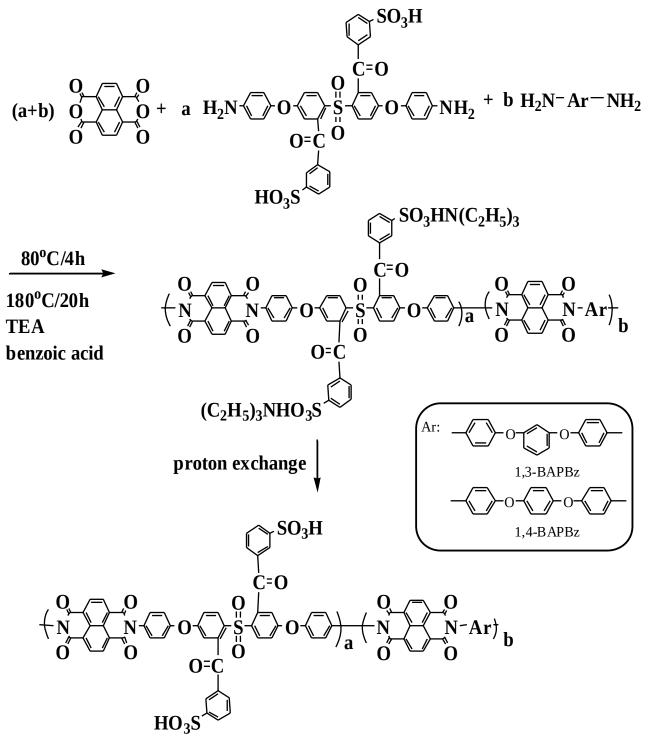
The synthesis of BAPSBPS is shown in Scheme 1. The first three steps were in one pot. The lithiation of DCDPS was performed by BuLi at the low temperature, then reacted with CO_2 and acidified to introduce carboxyl groups onto DCDPS. This was similar to the method previously reported by Brinon et al. [21]. Lithiation and consequently carbonation took place at ortho position to the sulfone group due to the electron withdrawing effect. During the lithiation reaction and carbonate groups substitution, it was very important to keep the reaction mixture at the low temperature. If the resultant organolithium mixture was allowed to warm to 20 °C, the cyclization reaction would occur, leading to a mixture of 2,8-dichlorodibenzothiophene, 2,8-dichlorodibenzothiophene-5,5-dioxide and substantial amount of unchanged substrate. In this study, although the reaction was carried out at −60 °C, some of yellow oily substance appeared after acidification. This was probably because some places in the solution reached higher temperatures and the above-mentioned mixtures were formed. However, the yellow oily substance dissolved in chloroform but compound **I** could not. So, it was easy to purify the product by washing with chloroform.

Compounds **II** and **III** were synthesized according to common methods [22]. The sulfonation of **III** was performed by fuming sulfuric acid at 75 °C for 12 h. The electrophilic substitution reaction occurred on a meta position to the carbonyl group due to its electron withdrawing nature. It was necessary to keep the high temperature and the long reaction time to reach fully two substituted product.



Scheme 1. Synthesis of BAPSBPS.

Hawakami et al. previously described the preparation of a sulfone ether diamine by nucleophilic aromatic substitution [23]. The sulfone ether diamine in high purity was prepared by the reaction of DCDPS with the sodium salt of *m*-aminophenol (*m*-AP) in DMSO solution. In the similar fashion, McGrath et al. demonstrated the synthesis of 3,3′-disulfonic acid-bis[4-(3-aminophenoxy)-phenyl] sulfone (SA-DADPS) [17]. In this study, BAPSBPS was synthesized in the similar fashion. After the reaction, the mixture was acidified by HCl solution, and BAPSBPS was precipitated as the inner salt. The crude BAPSBPS was purified by reprecipitation from the TEA salt form of *m*-cresol solution to inner salt form in acid solution and then was recrystallized from mixture of DMSO and water. Fig. 1 shows the ^{1}H NMR spectrum of BAPSBPS, indicating no impurity in the product. Elemental analysis was also performed. The calculated value: C, 56.99%; H, 3.52%; N, 3.50%. The found value: C, 52.76%; H, 4.03%; N, 2.91%. The errors should be mainly caused by the sorbed water. The TGA result of BAPSBPS showed about 7% weight loss below 200 °C. If the sample contains 7.4% water, the calculated values are C, 52.77%; H, 4.08% and N, 3.24%, which are close to the found values.



Scheme 2. Synthesis of BAPSBPS-based homopolymer and random copolyimides.

3.2. Polymers synthesis and characterization

As shown in Scheme 2, the preparation of BAPSBPS-based homopolymer and random copolymers were carried out by a one-step method in *m*-cresol in the presence of TEA and benzoic acid as the catalyst. The synthesis of six-membered ring polyimide has been reported in literatures [6,17,24]. By varying the molar ratio of BAPSBPS to nonsulfonated diamine, a series of copolymers with different IEC values were obtained.

As shown in Scheme 3, sequenced copolyimides were prepared via a two-step method [4,6,12]. The anhydride-terminated SPI oligomer was first prepared before the nonsulfonated diamine monomer was introduced. The molar ratio, r, of NTDA to BAPSBPS in the first step was controlled to a certain value, and the sequence length, l, was calculated according to the following equation

$$l = \frac{r+l}{r-l} \tag{4}$$

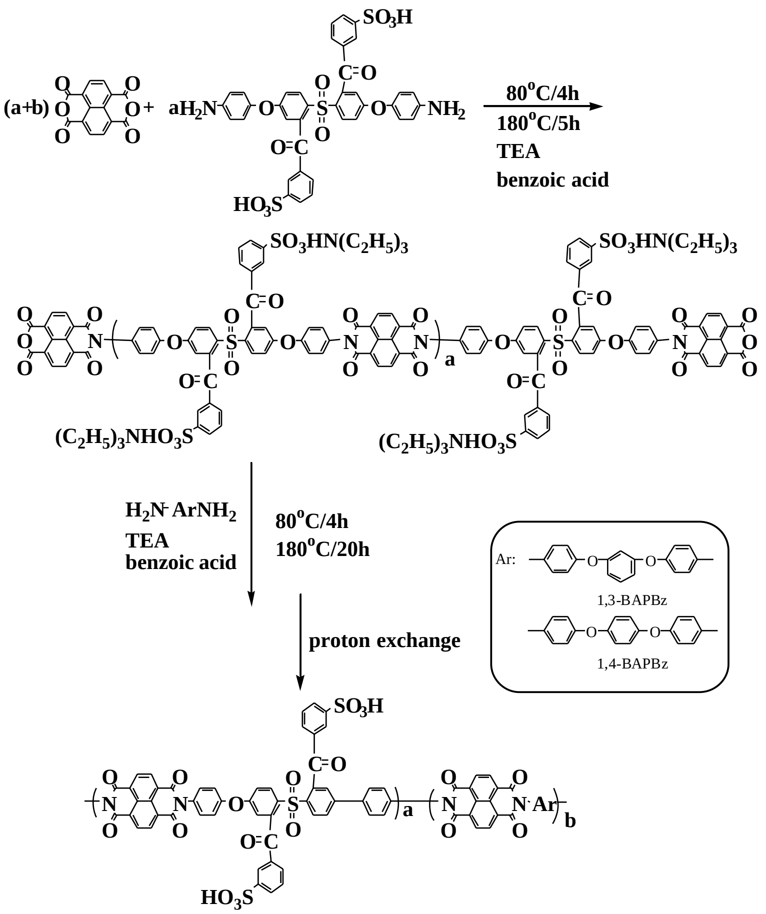
In this study, all of the sulfonated diamine and NTDA were added in the first step, the l values were 7, 5 and 4 for a/b of 3/1, 2/1 and 3/2, respectively.

^{1}H NMR spectra of SPIs in TEA salt form and FT-IR spectra of SPI membranes in proton form were used to confirm the structure of the polymers. The ^{1}H NMR spectra of SPIs in TEA salt form and in proton form are shown in Fig. 2(a) and (b), respectively. The singlet peak at 8.75 ppm indicates the formation of naphthalimide, of which two protons are equivalent irrespective of the sulfonated and nonsulfonated diamine moieties. In other cases, the doublet peak should appear, as reported in literatures [5,17]. The peak around 8.85 ppm in Fig. 2(a), which corresponds to the proton in the triethylamonium sulfonate [$-SO_3NH(C_2H_5)_3$], disappears in Fig. 2(b), indicating completion of proton exchange. Fig. 3 shows the IR spectra of SPIs. The spectra displayed the naphthalimide absorption bands at 1712 (C=O, symmetric), 1666 (C=O, asymmetric) and 1349 cm^{-1} (C–N, asymmetric; overlapped with sulfone). The characteristic peak of polyamic acid at 1784 cm^{-1} was not found, indicating the complete imidization. The O=S=O bond of sulfonic acid group appeared at 1030 and 1200 cm^{-1}, respectively. The 1155 cm^{-1} peak was corresponded to the vibration of O=S=O bond of sulfone group in the backbone.

Table 1 shows the properties of SPIs. The BAPSBPS-based SPIs except for NTDA-BAPSBPS/1,3-BAPBz(2/1)-s (**M4**) showed rather low reduced viscosity of 0.4–1.0 dl/g. However, optimized polymerization conditions could achieve polymers with higher viscosities. For example, using a little excess of diamine to dianhydride, the η_r of **M4** increased up to 1.8 dl/g. Therefore, further investigation to achieve the higher molecular weight is in progress.

In Table 1, the IEC values evaluated from ^{1}H NMR spectra were in good agreement with the calculated values, indicating that the polymerization was quantitatively performed. The IEC values by the titration method were as large as 83–97% of the corresponding calculated values.

The present SPIs gave flexible and tough membranes with reasonably high mechanical strength, although their η_r values



Scheme 3. Synthesis of BAPSBPS-based sequenced copolyimides.

were not very large. Fig. 4 shows the tensile stress–strain curves of membranes. **M3** displayed a Young's modulus of 1.4 GPa, a maximum stress of 58 MPa and an elongation degree at break point of 110%, whereas the corresponding values for BAPBDS/BAPB(2/1)-r (**M8**) with η_r of 2.7 dl/g were 1.7 GPa, 128 MPa and 128%, respectively. Maximum stress of **M3** was about half of **M8**, probably because of the lower molecular weight. **M3** and **M8** displayed much stronger tensile stress than that of Nafion 112. The SPI membranes are expected to have higher mechanical stability compared with Nafion 112.

The solubility of the SPIs was tested in common aprotic solvents such as DMSO, NMP and DMAc. As shown in Table 2, all of the SPIs in TEA salt form displayed good solubility in aprotic solvents. However, in proton form, the solubility was generally poor. In the proton form, with an increase in the content of sulfonated diamine moiety, the solubility decreased. For example, in proton form, homopolymer of **M1** did not dissolve in DMAc, copolymers of BAPSBPS/1,3-BAPBz(3/1)-r (**M2**) and **M3** partially dissolved in DMAc, **M4** and BAPSBPS/1,3-BAPBz(3/2)-s (**M5**) dissolved in DMAc.

Thermal stability of the SPIs was investigated by TGA. The TGA result is shown in Fig. 5. For comparison, NTDA-BAPBDS and 3,3′-BSPB/BAPB(2/1)-r (**M7**) were cited in the figure. Above 150 °C, a two-step degradation profile was observed for all of the SPIs. The weight loss below 400–450 °C was attributed to desulfonation, whereas the weight loss above 470 °C was attributed to the decomposition of polymer backbone. The temperature of desulfonation (T_{dl}) is listed in Table 1. The BAPSBPS-based SPIs showed higher T_{dl} of 344–

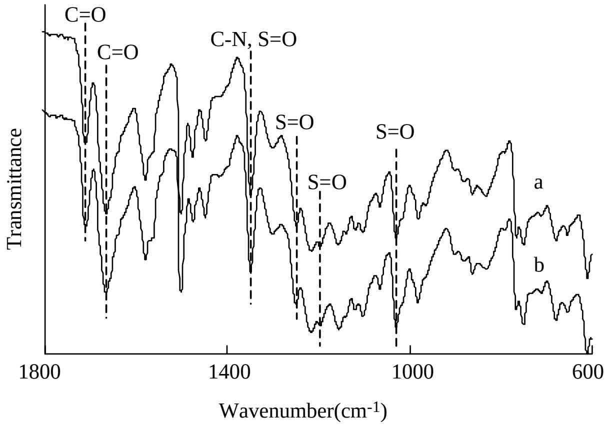


Fig. 3. IR spectra of BAPSBPS-based SPIs membranes (proton form). (a) **M5**; (b) **M2**.

Table 1
Properties of NTDA-based SPIs

Code	NTDA-based SPI	IEC (mequiv/g)			η_r[a] (dl/g)	WU (wt%)	λ	T_{d1} (°C)	Δt_c	Δl_c	σ[b] (mS/cm)	
		Cal.	NMR	Titr.							70%	In water
M1	BAPSBPS	1.94		1.75	0.43	57	16	344	0.18	0.10	20	135
M2	BAPSBPS/1,3-BAPBz(3/1)-r	1.66	1.63	1.45	0.60	47	16	346	0.17	0.05	7.7	78
M3	BAPSBPS/1,3-BAPBz(2/1)-r	1.54	1.49	1.50	0.80	33	12	349	0.10	0.04	11	81
M4	BAPSBPS/1,3-BAPBz(2/1)-s	1.54	1.53	1.29	1.80	37	14	NM[c]	0.13	0.05	NM	NM
M5	BAPSBPS/1,3-BAPBz(3/2)-s	1.45	1.45	1.20	0.94	37	15	350	0.09	0.03	5.8	69
M6	BAPSBPS/1,4-BAPBz(3/1)-r	1.66	1.64	1.54	1.04	43	14	NM	0.11	0.07	NM	NM
M7	3,3′-BSPB/BAPB(2/1)-r	2.02		1.72	5.70	62	17	252	0.39	0.03	16	135
M8	BAPBDS/BAPB(2/1)-r	1.89		1.86	2.70	51	15	300	0.20	0.04	29	127
Nafion112		0.91		0.89[d]		39	24		0.13	0.12	59	141

[a] In *m*-cresol solution, except for M1, M2 and M5 (in 1% LiCl-DMSO solution).
[b] Measured at 60 °C.
[c] NM, not measured.
[d] From product information of DuPont.

350 °C than the BAPBDS- and BSPB-based SPIs by 50 and 100 °C, respectively. This was attributed to the lower electron density of the sulfonated phenyl ring due to the electron withdrawing carbonyl group.

3.3. Water uptake and proton conductivity

The WU in water was larger for SPI with the higher IEC. However, the number of water molecules sorbed per sulfonic acid group, λ, for BAPSBPS-based SPIs was similar in the range of 12–16 and also similar to that of **M7** and **M8**, as listed in Table 1. The BAPSBPS-based SPIs showed the anisotropic membrane swelling, where the dimensional change was 1.6–3 times larger in thickness direction than in plane direction. This anisotropy degree was similar to that for **M8** but was not so strong as for **M7**.

Water vapor sorption isotherms of BAPSBPS-based SPI membranes at 60 °C are shown in WU$-a_w$ and $\lambda-a_w$ forms in

Table 2
Solubility of BAPSBPS-based SPIs

Polymer	DMSO	DMAc	NMP
Et_3N^+ form			
M1	+	+	+
M2	+	+	+
M3	+	+	+
M4	+	+	+
M5	+	+	+
H^+ form			
M1	+	−	+−
M2	+	+−	+−
M3	+	+−	+−
M4	+	+	+−
M5	+	+	+

+, soluble; +−, partially soluble; −, insoluble.

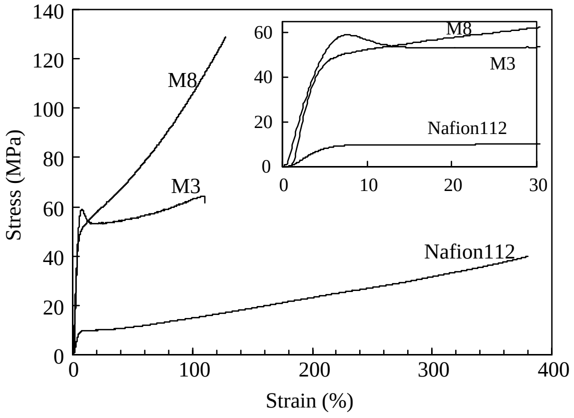


Fig. 4. Tensile stress–strain curves of membranes.

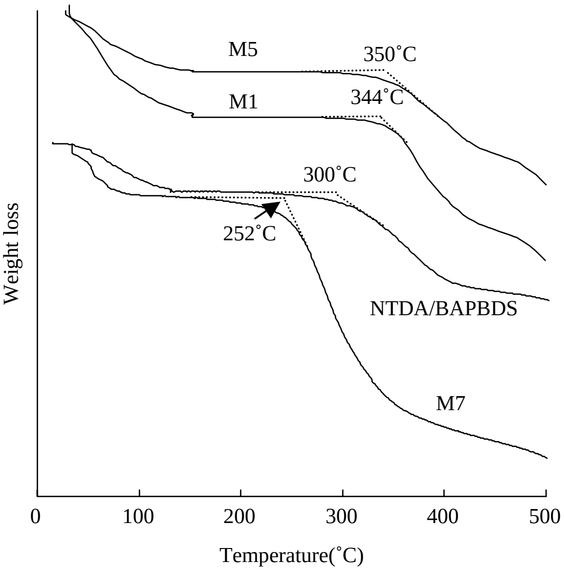


Fig. 5. TGA of SPIs in proton form.

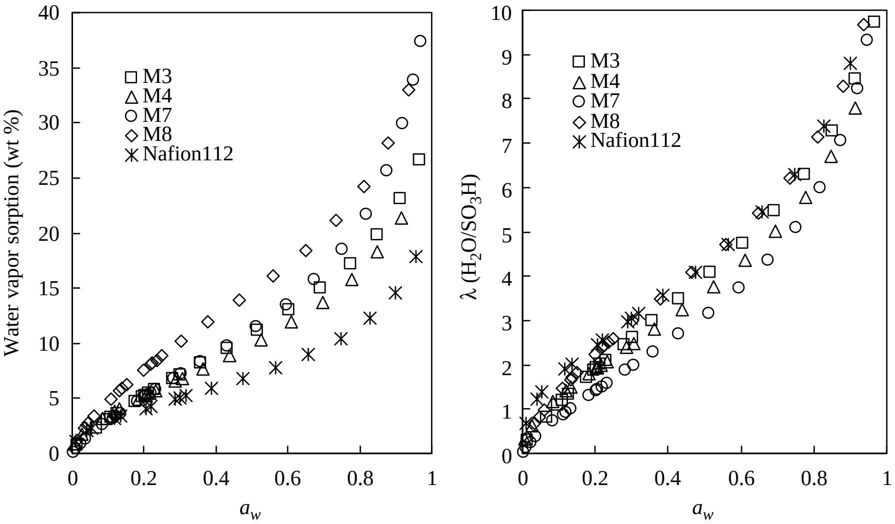


Fig. 6. Water vapor sorption isotherms of sulfonated polyimides at 60 °C.

Fig. 6(a) and (b), respectively. With an increase in a_w, the water vapor sorption increased sigmoidally. The sigmoidal sorption isotherms have been explained by means of a superposition of dual-mode sorption and plasticization effect of sorbed water [25,26]. At low a_w (<0.2), the sulfonic acid groups interact strongly with water molecules and act as water sorption sites, resulting in a Langmuir-type isotherm. With an increase in a_w, Henry-type sorption becomes larger. At high a_w (>0.8), the sorbed water substantially causes the molecular relaxation of polymer chains and a further increase in WU. In the range of a_w below 0.7, the BAPSBPS-based SPIs displayed larger λ values than the BSPB-based SPIs, but smaller than the BAPBDS-based SPIs and Nafion 112. This seems due to a difference in contribution of Langmuir-type sorption.

Nafion 112 showed larger λ value in water of 24 than SPI membranes in spite of the similar λ values at $a_\mathrm{w} < 0.9$. In Nafion membrane, the extremely high hydrophobicity of perfluorinated backbone and the extremely high hydrophilicity of the sulfonic acid groups give rise to some hydrophobic/hydrophilic nano-separation in the presence of water [27]. The wide channels performed in Nafion membrane let it display larger capacity in water uptake and dimensional change.

The proton conductivity values at 70% RH and in water are listed in Table 1. The RH dependence of proton conductivity is shown in Fig. 7. Compared with Nafion 112, all of the SPI membranes displayed the larger humidity dependence. The SPI membranes displayed much lower σ values at lower RHs than Nafion 112, whereas they showed similar or slightly lower σ values in water. NTDA-BAPSBPS with a high IEC of 1.94 mequiv/g displayed high σ values of 135 and 20 mS/cm in water and 70% RH, respectively, which were comparable to those for the BSPB- and BAPBDS-based SPIs, **M7** and **M8**. The BAPSBPS-based co-SPIs also displayed reasonably high σ values, taking their lower IECs into account. They showed the similar RH dependence of σ to that for the BAPBDS-based co-SPIs and did not show significant decreases in σ at lower RHs less than 70% RH. This was different from the case of the BSPB-based co-SPIs, which was probably due to the difference in the water vapor sorption isotherms.

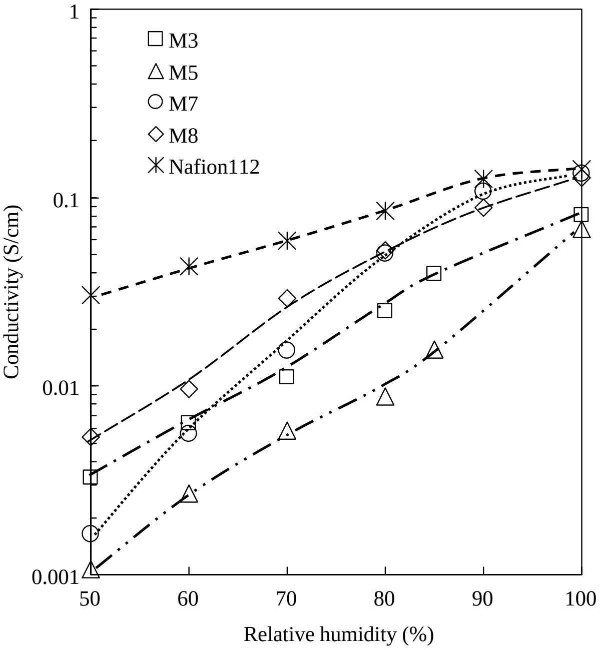


Fig. 7. Proton conductivity of SPI membranes as a function of relative humidity at 60 °C.

4. Conclusion

A novel sulfonated side-chain aromatic diamine of BAPSBPS was synthesized successfully. BAPSBPS-based SPIs displayed good solubility in common aprotic solvents and the high desulfonation temperature of 350 °C, suggesting the high stability of sulfonic acid groups. Flexible and tough membranes with reasonably high mechanical strength were prepared. They showed anisotropic membrane swelling with larger swelling in thickness than in plane. They displayed reasonably high σ values, taking their lower IECs into account.

Acknowledgements

This work was financially supported by NEDO (New Energy and Industrial Technology Development): Fuel cell and hydrogen technology development department, 'Research and development of polymer electrolyte fuel cells', and by the Venture Business Laboratory of Yamaguchi University, Japan, and by a Grant-in-aid for Developmental Science Research (17750205) from the Ministry of Education, Science, and Culture of Japan.

References

[1] Savadogo O. J New Mater Electrochem Syst 1998;1:47.
[2] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463.
[3] Roziere J, Jones DJ. Annu Rev Mater Res 2003;33:503.
[4] Hinkner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104:4587.
[5] Cornet N, Diat O, Gebel G, Jousse F, Marsacq D, Mercier R, et al. J New Mater Electrochem Syst 2000;3:33.
[6] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.
[7] Besse S, Capron P, Diat O, Gebel G, Jousse F, Marsacq D, et al. J New Mater Electrochem Syst 2002;5:109.
[8] Fang J, Guo X, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35(9022):6707.
[9] Watari T, Fang J, Tanaka K, Kita H, Okamoto K. J Membr Sci 2004;230:111.
[10] Yamada O, Yin Y, Tanaka K, Kita H, Okamoto K. Electrochim Acta 2005;50:2655.
[11] Yin Y, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. J Mater Chem 2004;14:1062.
[12] Yin Y, Yamada O, Suto Y, Mishima T, Tanaka K, Kita H, et al. J Polym Sci, Part A: Polym Chem 2005;43:1545.
[13] Yin Y, Yamada O, Kita H, Okamoto K. Macromol Rapid Commun 2005;26:696.
[14] Miyatake K, Zhou H, Matsuo T, Uchida H, Watanabe M. Macromolecules 2004;37:4961.
[15] Miyatake K, Zhou H, Watanabe M. Macromolecules 2004;37:4956.
[16] Asano N, Miyatake K, Watanabe M. Chem Mater 2004;16:2841.
[17] Einsla BR, Hong Y-T, Kim YS, Wang F, Gunduz N, McGrath JE. J Polym Sci, Part A: Polym Chem 2004;42:862.
[18] Einsla BR, Hong Y-T, Kim YS, Wang F, Gunduz N, McGrath JE. J Membr Sci 2005;255:141.
[19] Lee C, Sundar S, Kwon J, Han H. J Polym Sci, Part A: Polym Chem 2004;42:3621.
[20] Yin Y, Suto Y, Sakabe T, Chen S, Hayashi S, Mishima T, et al. Macromolecules 2006;39:1189.
[21] Brinon MC, de Bertorello MM, Bertorello HE. An Asoc Quim Argent 1986;74(2):189.
[22] Calloway NO. Chem Rev 1935;17:327.
[23] Hawakami JH, Kwiatkowki GT, Brode GL, Bedwin AW. J Polym Sci, Polym Chem Ed 1974;12:565.
[24] Sek D, Wanic A, Schab-Balcerzak E. Polymer 1993;34:2440.
[25] Watari T, Wang H, Kuwahara K, Tanaka K, Kita H, Okamoto K. J Membr Sci 2003;219:137.
[26] Guo X, Fang J, Tanaka K, Kita H, Okamoto K. J Polym Sci, Part A: Polym Chem 2004;42:1432.
[27] Kreuer KD. J Membr Sci 2001;185:29.