NRC Publications Archive
Archives des publications du CNRC

Poly(arylene ether sulfone) proton exchange membranes with flexible acid side chains

Wang, Chenyi; Shin, Dong Won; Lee, So Young; Kang, Na Rae; Lee, Young Moo; Guiver, Michael D.

This publication could be one of several versions: author’s original, accepted manuscript or the publisher’s version. / La version de cette publication peut être l’une des suivantes : la version prépublication de l’auteur, la version acceptée du manuscrit ou la version de l’éditeur.
For the publisher’s version, please access the DOI link below./ Pour consulter la version de l’éditeur, utilisez le lien DOI ci-dessous.

Publisher’s version / Version de l'éditeur:
https://doi.org/10.1016/j.memsci.2012.02.045

Journal of Membrane Science, 405-406, pp. 68-78, 2012-03-02

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=f477fc47-775a-47f0-833d-85026b9f0c22
https://publications-cnrc.canada.ca/fra/voir/objet/?id=f477fc47-775a-47f0-833d-85026b9f0c22

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L’accès à ce site Web et l’utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D’UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n’arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada
Conseil national de recherches Canada

53062

Poly(arylene ether sulfone) proton exchange membranes with flexible acid side chains

Chenyi Wang[1, 2], Dong Won Shin[3], So Young Lee[3], Na Rae Kang [1],
Young Moo Lee [1, 3] *, and Michael D. Guiver [1, 4] *

[1] *WCU Department of Energy Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea*

[2] *School of Materials Science and Engineering, Changzhou University, Changzhou, 213164, China*

[3] *School of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Republic of Korea*

[4] *Institute for Chemical Process and Environmental Technology, National Research Council Canada, Ottawa, Ont. K1A 0R6, Canada*

*** Corresponding authors. E-mail: ymlee@hanyang.ac.kr ; michael.guiver@nrc-cnrc.gc.ca**

ABSTRACT:

New monomers containing two or four pendent methoxyphenyl groups were synthesized by bromination of bis(4-fluorophenyl)sulfone, followed by Suzuki coupling with 4-methoxybenzeneboronic acid. Copoly(arylene ether sulfone)s containing methoxyphenyl groups (2-MPAES-xx and 4-MPAES-xx) based on the corresponding monomers were prepared by aromatic nucleophilic substitution (SNAr) polycondensation. After demethylation of the methoxy group to the reactive hydroxyl group, the respective side chain-type sulfonated copolymers (2-SPAES-xx and 4-SPAES-xx) were obtained by sulfobutylation. Flexible and tough membranes having good mechanical strength were obtained by solution casting of all copolymers. The sulfonated copolymers with two or four pendent sulfobutoxyphenyl groups had high proton conductivities in the range of 0.108 - 0.258 S/cm for 2-SPAES-*xx* and 0.135 - 0.194 S/cm for 4-SPAES-*xx* at 80 °C, respectively. The methanol permeabilities of these membranes were in the range of 1.59×10^{-7} - 4.69×10^{-7} cm^2/s, which is much lower than Nafion® (15.5×10^{-7} cm^2/s). 2-SPAES-xx and 4-SPAES-xx display comparatively better balance between proton conductivity and water swelling than the analogous poly(arylene ether sulfone)s containing pendent sulfophenyl groups. A combination of high proton conductivities, low water uptake, and low methanol permeabilities for some of the obtained copolymers indicated that they have some of the requisite properties for proton exchange membranes in fuel cell applications.

Keywords: Sulfonated poly(arylene ether sulfone); Polymer electrolyte membranes; Proton conductivity; Dimensional stability

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely investigated for automotive, stationary, and portable power devices because of their high efficiency, high power density, quiet operation and low emissions levels [1-4]. As one of the key components of PEMFCs, the proton exchange membrane (PEM) acts as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport. Currently, perfluorosulfonic acid (PFSA) polymers, such as Nafion® (DuPont), are commercialized PEMs normally utilized in PEMFC and direct methanol fuel cells (DMFC) because of their excellent chemical stability and high proton conductivity. However, their well-recognized drawbacks, such as a limited operating temperature range up to 80 °C due to dehydration, high methanol/fuel gas diffusion, environmental recyclability, and high cost, has led to intensive research efforts in developing hydrocarbon-based proton conducting polymers as alternative materials having high conductivity, higher operating temperature, and lower cost [5-7]. The most widely reported aromatic PEMs include sulfonated derivatives of poly(arylene ether ketone)s [8-10], poly(arylene ether sulfone)s [11,12], poly(arylene sulfide sulfone)s [13,14], poly(arylene ether)s [15,16], and polyimides [17,18]. Generally, the randomly distributed sulfonic acid groups in these polymers are located on the main chain, and the rigid polyaromatic backbone prevents continuous ionic domain clustering from occurring to form distinct phase-separated structures [19]. As a result, these sulfonated polymers only attain suitable conductivities comparable with Nafion, at much higher ion exchange capacities (IEC) and high water contents, which consequently lead to large dimensional variations and poor mechanical properties. The balance between dimensional stability and proton conductivity of aromatic PEMs are crucial issues that require improvement through careful structural design.

As is well-known, Nafion exhibits high proton conductivity at low IEC values due to ion-rich channels that formed by phase separation between the hydrophilic sulfonic acid groups, which are strongly acidic and the highly hydrophobic domains [20,21]. Inspired by the chemical structure of Nafion® bearing flexible pendant hydrophilic sulfonic acid groups attached to the hydrophobic perfluorinated backbone, aromatic PEMs tailored with pendant sulfoalkyl groups have been developed, which generally exhibited a comparatively better balance between proton conductivity and water dimensional swelling than PEMs with sulfonic acid groups attached directly onto the aromatic chain [22–34]. These side-chain-type PEMs have been prepared by the direct copolymerization method or by chemical grafting the pendants onto polymers. Compared to the direct copolymerization method, the chemical grafting method avoids the need to prepare sulfonated monomers and offers an easier route to introduce locally and densely populated sulfonated structures into the aromatic polymer backbone. Jannasch and coworkers [22], Hvilsted and coworkers [25], Na and coworkers [26,27], and Zhang and coworkers [28,29] reported sulfonated aromatic PEMs containing one or two pendant sulfoalkyl groups in each hydrophilic unit by the chemical grafting method. The highest conductivity of 0.179 S/cm was obtained for these copolymers (IEC= 1.82 mequiv/g) under a hydrated state at 80 °C, which is higher than that of Nafion117 (0.146 S/cm) [26]. In our previous work, we reported fluorene-based poly(arylene ether sulfone)s containing locally and densely populated flexible butylsulfonic acid pendant units [35]. The results indicated that these side-chain-type sulfonated polymers displayed advantageous proton conductivities with relatively low water contents.

In this article, we present a study of poly(arylene ether sulfone) copolymers containing two or four pendent butylsulfonic groups prepared by chemical the grafting method. Poly(arylene ether sulfone) copolymers containing methoxy groups were first prepared based on two novel bis(fluorophenyl) sulfone monomers, and then the methoxy groups were converted to reactive hydroxyl groups, which reacted with 1,4-butanesultone resulting in sulfonated copolymers bearing sulfobutoxyphenyl side chains. The copolymers are characterized in detail, and the membrane properties of this new series of polymer electrolytes with flexible side chains are investigated and compared with previously reported analogous poly(arylene ether sulfone)s containing the inflexible pendant sulfophenyl groups. In addition, the effects of the amount of pendent groups on the properties of these PEMs are discussed.

2. Experimental Section

2.1. Materials.

4,4'-Difluorodiphenyl sulfone (DFDPS), N-bromosuccinimide (NBS), 4-methoxybenzeneboronic acid and tetrakis(triphenylphosphine) palladium (0), and 1,4-butanesultone were purchased from Sigma-Aldrich Ltd. 4,4'-(Hexafluoroisopropylidene) diphenol (6F-BPA) was purchased from Alfa aesar and recrystallized with toluene. All other solvents and reagents (obtained from Sigma-Aldrich) were reagent grade and were used as received.

2.2. 3,3'-Dibromo-4,4'-difluorodiphenyl sulfone (DBDFDPS) and 3,3',5,5'-Tetrabromo-4,4'-difluorodiphenyl sulfone (TBDFDPS)

3,3'-Dibromo-4,4'-difluorodiphenyl sulfone (mp: 158-160 °C) and 3,3',5,5'-Tetrabromo-4,4'-difluorodiphenyl sulfone (mp: 180-182 °C) were synthesized according to the method reported in our preceding studies [36].

2.3. 3,3'-Di(4"-methoxyphenyl)-4,4'-difluorodiphenyl sulfone (DMDFDPS)

To a 1 L three-necked round-bottom flask, equipped with a reflux condenser, mechanical stirrer, and nitrogen inlet, 41.20 g (0.1 mol) of DBDFDPS, 31.91 g (0.21 mol) of 4-methoxybenzeneboronic acid, and 300 mL of toluene were charged. The solid was completely dissolved at 50 ^{o}C with stirring. 300 mL of 10 wt % aqueous sodium carbonate solution and 2.00 g (0.0017 mol) of tetrakis(triphenylphosphine) palladium(0) were carefully added into the solution. The reaction mixture was heated at 110 ^{o}C for 10 h, and then the solvent was evaporated to obtain a solid. Crude product was recrystallized from toluene/dimethylformamide (DMF) (2:1) twice to afford 39.65 g of pure white crystalline 3,3'-di(4"-methoxyphenyl)-4,4'-difluorodiphenyl sulfone. Yield: 85 %, mp: 174–176 °C. ^{1}H NMR (300 MHz, DMSO-d_6; ppm): 8.13 (d, *J*=7.2, 2H, H-4), 8.07 (m, 2H, H-3), 7.52-7.58 (m, 6H, H-2, H-5), 7.08 (d, *J*=8.8, 4H, H-1), 3.81 (s, 6H, –OCH_3).

2.4. 3,3',5,5'-Tetra(4"-methoxyphenyl)-4,4'-difluorodiphenyl sulfone (TMDFDPS).

Using similar methodology to the di(4-methoxy)phenyl analogue above, the monomer with four pendent 4-methoxyphenyl groups, 3,3',5,5'-tetra(4"-methoxyphenyl)-4,4'-difluorodiphenyl sulfone was prepared from 3,3',5,5'-tetrabromo-4,4'-difluorodiphenyl sulfone (TBDFDPS) by reaction with 4.4 mol equiv. 4-methoxybenzeneboronic acid at 115 °C for 24 h. The purified product was obtained by recrystallization from DMF twice. Yield: 71 %, mp: 280-282 °C. ^{1}H NMR (300 MHz, $CDCl_3$; ppm): 7.93 (m, 4H, H-3), 7.47-7.51 (m, 8H, H-2), 6.98-7.02 (m, 8H, H-1), 3.87 (s, 12H, $-OCH_3$).

2.5. Synthesis of poly(arylene ether sulfone)s containing methoxy groups

A typical synthetic procedure, illustrated by the preparation of 2-MPAES-60 copolymer (xx=60: DMDFDPS/DFDPS=60/40), is described as follows. 2.799 g (6 mmol) DMDFDPS, 1.017 g (4 mmol) DFDPS, 3.362 g (10 mmol) 6F-BPA, 1.656 g (12 mmol) K_2CO_3, 20 mL N-methylpyrrolidone (NMP) and 10 mL toluene were added into a 100 mL round-bottomed flask which was equipped with a Dean-Stark trap, condenser, a mechanical stirrer, and gas adapter. The reaction mixture was refluxed at 140 °C for 4 h to remove water. After removal of toluene and water, the reaction temperature was raised to 155 °C. After 5-8 h, 8 mL of NMP was added to the mixture to reduce the solution viscosity. The solution was poured into 500 mL deionized water with vigorous stirring. The resulting fibrous copolymer was washed several times with deionized water and dried at 100 °C under vacuum for 10 h.

2.6. Conversion of methoxy (MPAES-xx) to hydroxyl group (HPAES-xx)

The methoxy-containing copolymers were converted into hydroxyl functionalities according to the method reported in the preceding studies [32,35]. Typically, 4.0 g 2-MPAES-60 was dissolved into 100 mL CH_3Cl in a 100 mL three-neck flask equipped with a mechanical stirrer and a nitrogen inlet. After complete dissolution, the temperature was cooled down to °C (ice bath) and an excess (3 mL) BBr_3 dissolved in 25 mL CH_3Cl was added dropwise. The reaction mixture was stirred at room temperature for an additional 6 h under nitrogen. Then, the resulting copolymer (2-HPAES-60) was filtered, washed with boiling water, recovered and then dried under vacuum at 100 °C for 24 h.

2.7. Preparation of sulfonated copolymer (SPAES-xx)

A typical synthetic procedure, illustrated by the preparation of 2-SPAES-60 copolymer, is described as follows. 2.0 g 2-HPAES-60 and 40 mL of dimethyl sulfoxide (DMSO) were added into a nitrogen-flushed reactor equipped with a mechanical stirrer. After complete dissolution, 1.5 mL 1,4-butanesultone was added to the solution and the reaction mixture was stirred for 10 min at room temperature; then either 0.50 g NaOH or 0.30 g NaH was added. The reaction mixture was allowed to proceed for another 6 h at 100 °C (NaOH) or another 4 h at 30 °C (NaH) before precipitation of the polymer in isopropanol. The copolymer was separated by filtration and dried in a vacuum oven at 100 °C for 10 h.

2.8. Membrane preparation

The dried sulfonated copolymers in the sodium salt form were readily dissolved as 10–15 wt % solutions in DMSO at 60 °C. The solutions were filtered, cast onto glass plates with a doctor blade, dried at 60 °C for 12 h, and then treated in vacuum at 100 °C for 10 h. The as-cast membranes were immersed into 2.0 M H_2SO_4 solution for 24 h at room temperature and then thoroughly washed with deionized water.

Tough, ductile ionomer membranes were prepared with controlled thickness in the range of of 50–70 μm, depending on the casting solution concentration.

2.9. Characterization

2.9.1. Copolymer analysis and measurements

^{1}H NMR spectra were measured on a 300 MHz Bruker AV 300 spectrometer using DMSO-d_6 or $CDCl_3$ as solvent. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. The gel permeation chromatographic (GPC) analysis was carried out with Tosoh HLC-8320 instrument (NMP as eluent and polystyrene as standard).

2.9.2. Proton conductivity

The proton conductivity (σ, S/cm) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s W_s R$ (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 over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough, Hampshire, UK). 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 1.0 cm. Conductivity measurements under fully hydrated conditions were carried out in a thermo-controlled chamber with the cell immersed in liquid water.

2.9.3. Methanol permeability

The methanol permeability was determined by using a cell consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 M) was placed on one side of the diffusion cell, and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure solution uniformity. The concentration of the methanol was measured by using a Shimadzu GC-1020A series gas chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{A}{V_B} \cdot \frac{DK}{L} \cdot C_A \cdot (t - t_0) \qquad (1)$$

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

2.9.4. Density, water uptake, dimensional change and ion-exchange capacity (IEC)

The membrane density was measured from a known membrane dimension and weight after drying at 100 °C for 24 h. Water uptake was measured after drying the membrane in acid form at 100 °C under vacuum overnight. The dried membrane was immersed in water at 30 °C and 80 °C, and periodically weighed on an analytical balance until a constant water uptake weight was obtained. Then, the volume-based water uptake (WU) was obtained. A volume-based IEC (IEC_v) was obtained by multiplying the membrane density by the IEC_w values which were estimated from the copolymer structure. This calculation resulted in IEC_v (dry) based on the dry membrane density. An IEC_v (wet) was then calculated based on membrane water uptake [36,37].

The dimensional changes of the membranes were measured in the thickness and in-plane direction, which were calculated by $\Delta T= (T_{wet}-T_{dry})/T_{dry}$, $\Delta L= (L_{wet}-L_{dry})/L_{dry}$, where T_{dry}, T_{wet}, L_{dry}, and L_{wet} are the thickness and length of dry and wet samples, respectively.

Ion exchange capacities (IEC) of the membranes were determined by titration. A sample membrane in proton form was immersed in 2M NaCl aqueous solution for 48 h to exchange the H^+ ions with Na^+ ion. Released protons were titrated by 0.01 M NaOH solution using phenolphthalein as an indicator.

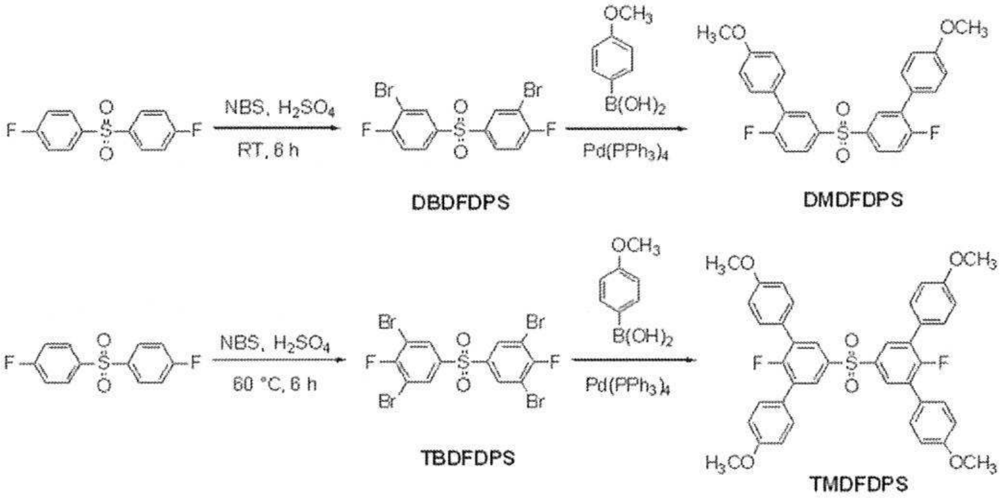
2.9.5. Transmission electron microscopy

For transmission electron microscopy (TEM) observations, the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution. After ion exchange, the membranes were rinsed several times with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 70 nm thickness with a RMCMTX Ultra microtome, and placed on copper grids. Electron micrographs were taken with a Carl Zeiss LIBRA 120 energy-filtering transmission electron microscope using an accelerating voltage of 120 kV.

3. Results and Discussion

3.1. Synthesis and Characterization of the Monomers and Polymers

Two new difluorodiphenyl sulfone monomers having two or four pendent 4-methoxyphenyl groups were synthesized by a two-step reaction as shown in Scheme 1.



Scheme 1. Synthesis of the monomers DMDFDPS and TMDFDPS.

First, the precursors DBDFDPS and TBDFDPS were synthesized by bromination of 4,4'-difluorodiphenyl sulfone using NBS. The reactions were conducted in concentrated sulfuric acid as solvent and catalyst and at different temperatures, as reported in our preceding studies [34]. The degree of bromination was readily controlled by adjusting the temperature and the amount of NBS. Following this, Suzuki coupling reactions of DBDFDPS or TBDFDPS with

4-methoxybenzeneboronic acid produced 3,3'-di(4''-methoxyphenyl)-4,4'-difluorodiphenyl sulfone (DPDFDPS) or 3,3',5,5'-tetra(4''-methoxyphenyl)-4,4'-difluorodiphenyl sulfone (TPDFDPS) respectively, both in high yields (> 70 %). The structures were confirmed by ^{1}H NMR analysis, as shown in Fig. 1. The signals at about 3.81 and 3.87 ppm were assigned to the pendent methoxy groups of DMDFDPS and TMDFDPS, respectively.

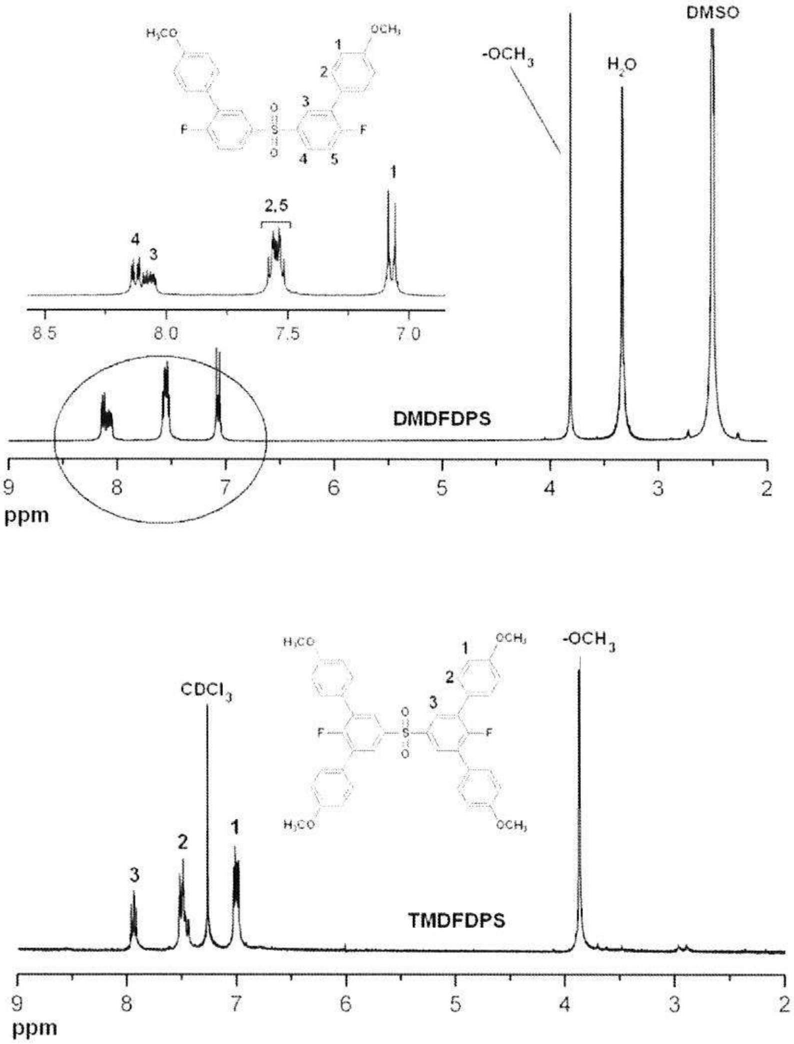


Fig. 1. ^{1}H NMR spectra of DMDFDPS and TMDFDPS.

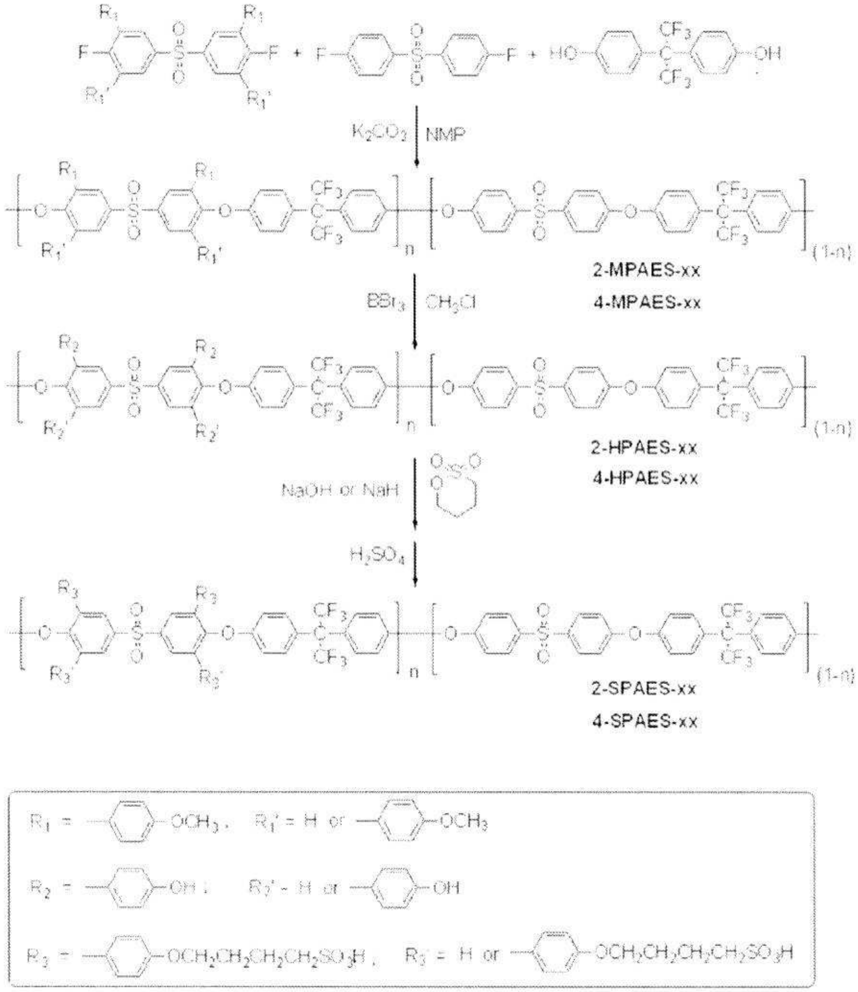
A series of poly(arylene ether sulfone) copolymers containing methoxy groups (2-MPAES-xx and 4-MPAES-xx, xx: mole ratio (%) of DMDFDPS or TMDFDPS) were prepared via a standard K_2CO_3-catalyzed aromatic nucleophilic substitution polycondensation using various feed ratios of DMDFDPS/DFDPS or TMDFDPS/DFDPS, so that polymers with different molar percentage of pendant methoxy groups were obtained. The polymerization reactions proceeded smoothly to high molecular weight, and no cross-linking was evident when the temperature was controlled by an oil bath (less than 165 °C) and the reaction time was less than 10 h. GPC results (Table 1) showed that high molecular weight polymers (M_n > 50,000 g/mol) were obtained, and molecular weight distribution (PDI) ranged from 2.12 to 2.60, which is consistent with the results of typical polycondensation reactions. 2-MPAES-xx had higher molecular weight compared to 4-MPAES-xx due to the higher reactivity of monomer DMDFDPS.

Table 1. Molecular Weights of 2-MPAES-xx and 4-MPAES-xx Copolymers.

Copolymers	M_n[a] ($\times 10^4$ g/mol)	M_w ($\times 10^4$ g/mol)	PDI
2-MPAES-50	9.86	20.93	2.12
2-MPAES-60	8.87	19.68	2.22
2-MPAES-70	8.60	19.17	2.23
2-MPAES-80	6.74	15.25	2.26
4-MPAES-25	6.32	15.20	2.40
4-MPAES-35	5.25	13.63	2.60

[a] Measured at 30 °C using NMP as solvent and polystyrene standards.

The demethylation of 2-MPAES-xx and 4-MPAES-xx to the reactive hydroxyl-containing 2-HPAES-xx and 4-HPAES-xx for grafting was conducted using BBr_3 in chloroform (Scheme 2). Due to the polar nature of the –OH group, 2-HPAES-xx and 4-HPAES-xx copolymer resulted in precipitation from chloroform.



Scheme 2. Synthesis of copolymers MPAES-xx, HPAES-xx and SPAES-xx.

Representative ^1H NMR spectra of 2-MPAES-60 (–OCH_3) and 2-HPAES-60 copolymers (–OH) confirmed complete demethylation occurred. The hydroxyl proton signals appeared at around 9.66 ppm, with the concurrent disappearance of the signal at around 3.66 ppm, corresponding to the $-OCH_3$ protons, as shown in Fig. 2.

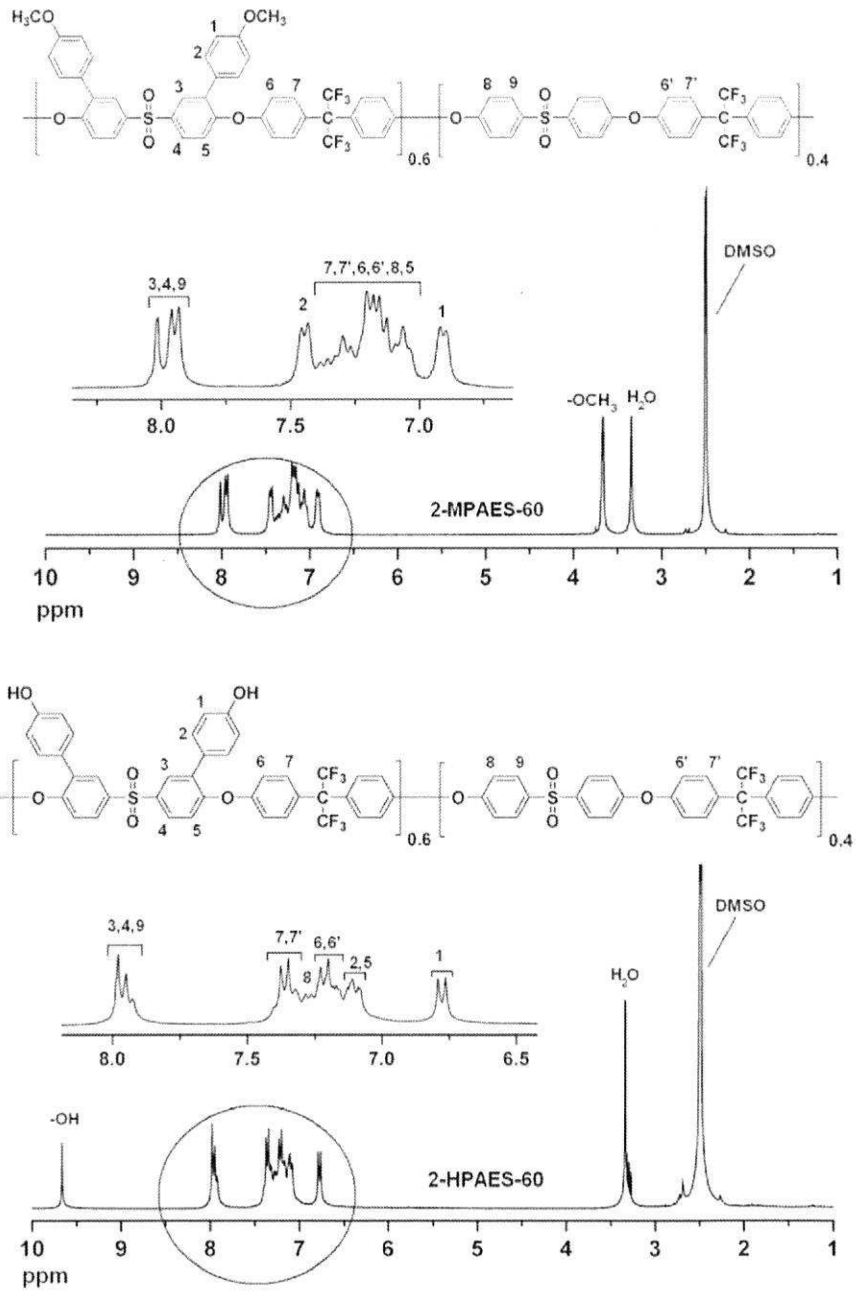


Fig. 2. Comparative ^{1}H NMR spectra of the 2-MPAES-60 ($-OCH_3$) and 2-HPAES-60 ($-OH$) copolymers.

Hvilsted and coworkers and Na and coworkers recently demonstrated that the parent polymers containing hydroxyl groups at the aromatic ring could be sulfopropylated or sulfobutylated through a nucleophilic ring-opening reaction with 1,3-propanesultone or 1,4-butanesultone using NaOH as a base [25,26]. Zhang and coworkers also prepared side-chain-type PEMs by the grafting reaction with the hydroxy polymer and 1,3-propanesultone using NaH as a base [28]. Here, we applied similar methodology. Scheme 2 shows the grafting reaction of sulfobutyl groups onto 2-HPAES-xx and 4-HPAES-xx by nucleophilic ring opening reaction with 1,4-butanesultone. A series of polymers with different sulfobutyl content were obtained by adjusting the –OH content in 2-HPAES-xx and 4-HPAES-xx copolymers, followed by reaction with an excess of 1,4-butanesultone. Both NaOH and NaH are all effective as a base for this grafting reaction. The entire series of the resulting sulfonated polymers (SPAES-xx) in the sodium salt form showed good solubility in DMSO, and afforded flexible and transparent films by solution casting. Fig. 3 shows a representative ^{1}H NMR spectrum of 2-SPAES-60 having signal assignments consistent with the designed molecular structure, which is appreciably different from the spectrum of the non-sulfonated precursor polymer 2-HPAES-60 shown in Fig. 2. The –OH protons at 9.66 ppm disappeared completely, while new signals appear at 3.96 ppm, 2.48 ppm and 1.73 ppm, corresponding to the sulfobutyl protons, which confirms that all of the hydroxyl groups reacted with 1,4-butanesultone.

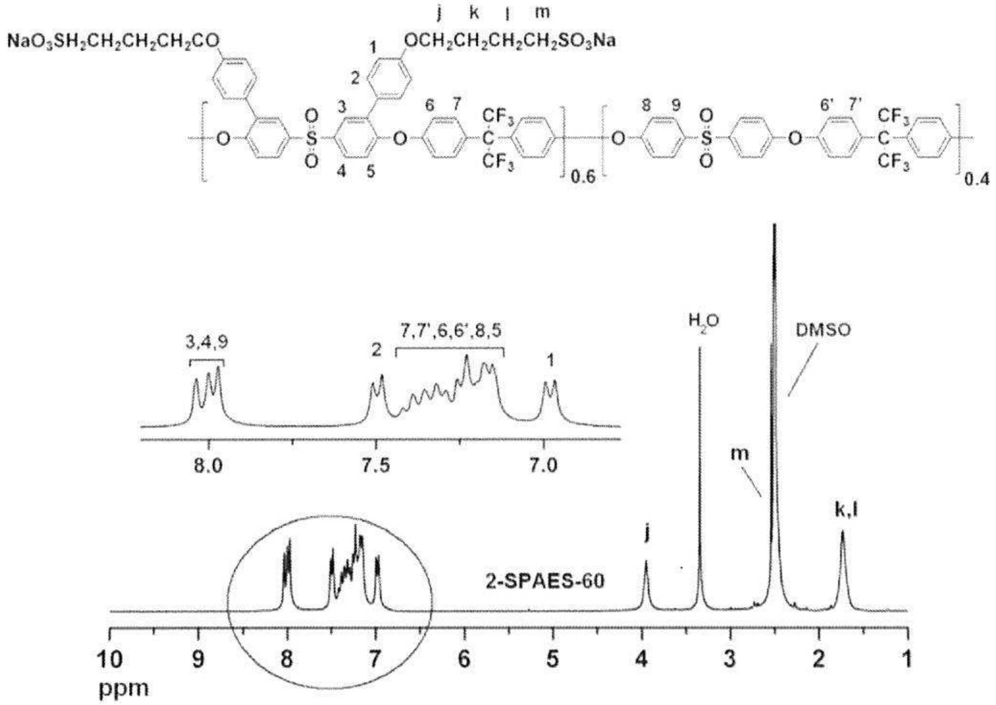


Fig. 3. ^{1}H NMR spectrum of 2-SPAES-60 (salt form).

3.2. IEC, water uptake, and dimensional swelling

Table 2 compares the ion exchange capacity (IEC), density and water uptake of the sulfonated polymer (2-SPAES-*xx*, 4-SPAES-*xx*) and Nafion 117. Water uptake (weight and volume based) of PEMs is an important parameter for IEC, proton conductivity, dimensional stability, mechanical strength, and membrane-electrode compatibility. The water uptake directly affects the ion exchange capacity within the polymer matrix under hydrated conditions, which can be gauged by comparing wet volume based IEC_v (wet) values with IEC_w values.

Table 2. IEC, Density, and Water uptake of the 2-SPAES-xx, 4-SPAES-xx and Nafion membranes.

Copolymers	IEC_w [a] (mequiv/g)	Density (g/cm^3)	IEC_v [b] ($mequiv/cm^3$)		Water Uptake			
					wt % [c]		vol % [d]	
			dry	wet	30 °C	80 °C	30 °C	80 °C
2-SPAES-50	1.24	1.38	1.71	1.60	5.1	12.8	7.0	17.7
2-SPAES-60	1.40	1.42	1.99	1.80	7.4	16.1	10.5	22.9
2-SPAES-70	1.60	1.43	2.29	1.97	11.4	20.1	16.3	28.7
2-SPAES-80	1.73	1.45	2.51	1.94	20.1	32.3	29.1	46.8
4-SPAES-25	1.24	1.40	1.74	1.63	4.7	10.4	6.6	14.6
4-SPAES-35	1.59	1.44	2.29	1.99	10.3	17.5	14.8	25.2
Nafion 117	0.90	1.98	1.78	1.30	18.5	30.6	36.6	60.6

[a] Determined by acid-base titration.

[b] Based on volume of dry and/or wet membranes ($IEC_v(wet)=IEC_v(dry)/(1 + 0.01WU)$).

[c] WU (wt %) $=(W_{wet} - W_{dry})/W_{dry} \times 100$.

[d] WU (vol %) $=((W_{wet} - W_{dry})/\delta_w)/(W_{dry}/\delta_m) \times 100$. ($W_{wet}$ and W_{dry} are the weights of the wet and dry membranes, respectively; δ_w is the density of water (1 g/cm^3), and δ_m is the membrane density in the dry state.)

Fig. 4 shows a clear trend of increasing water uptake with IEC_w and IEC_v (dry). The volume-based data in Figure 4b showed the same trends as the weight based data in Fig. 4a. The water uptake of 2-SPAES-*xx* series increased linearly up to 2-SPAES-70 (IEC_w=1.60 mequiv/g, IEC_v(dry)=2.29 mequiv/cm^3) and then dramatically increased at 2-SPAES-80, similar to that reported for other systems in the literature and related to a percolation threshold [36,38]. However, the IEC_v (wet) of S-2PAES-80 was lower than that of 2-SPAES-70 in Fig. 4c. For 2-SPAES-*xx* and 4-SPAES-*xx* polymers, the increased sulfonic acid group concentration in the dry polymer was retained after equilibration with water, while hydration of 2-SPAES-80 resulted in excessive swelling and dilution of the ion concentration after equilibration with water.

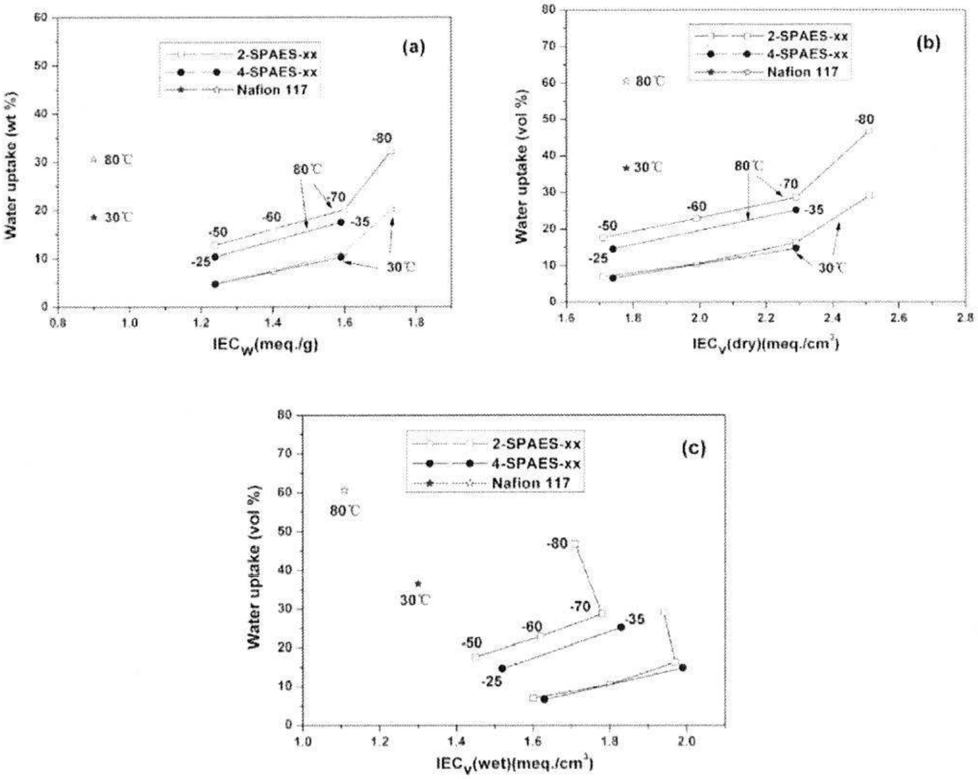


Fig. 4. The water uptake dependence of IEC (IEC$_W$), IEC$_V$ (dry), and IEC$_V$ (wet) values of 2-SPAES-xx and 4-SPAES-xx membranes.

This is observed in Fig. 4c whereby the slope of the curves assumes a reverse direction due to high water uptake (vol %) and reduced IEC$_V$ (wet). Moreover, the 4-SPAES-*xx* membranes showed a slightly lower water uptake trend than the 2-SPAES-*xx* membranes of the same IEC value. This is attributed to the higher local concentrations of hydrophilic sulfonic acid groups in the 4-SPAES-*xx* membranes. A similar effect was observed for another side-chain type PEM containing two or four sulfophenyl groups [36].

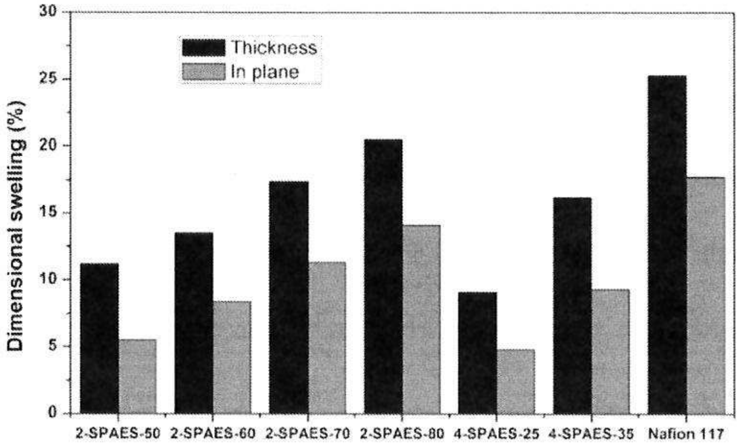


Fig. 5. Dimensional swelling of 2-SPAES-xx, 4-SPAES-xx and Nafion 117 at 80 °C.

The dimensional swelling of 2-SPAES-xx, 4-SPAES-xx and Nafion in the through-plane and in-plane direction are shown in Fig. 5. Due to their low water uptake, all of the PEMs exhibited lower dimensional swelling than that of Nafion at 80 °C. The present side-chain-type sulfonated PEMs also showed generally lower swelling than many main-chain-type sulfonated poly(arylene ether)s with similar IEC values [8,9,11,28]. The side-chain-type SPAES having sulfonic acid units on flexible side chains may be more effective in separating hydrophilic sulfonic acid groups from the hydrophobic polymer main chain. Thus, water molecules can be restricted to hydrophilic domains in the membranes and separated from hydrophobic domains, leading to a suppression of the water swelling. In addition, these PEMs displayed mildly anisotropic membrane swelling, in which the dimensional change was larger in the thickness direction than in the planar direction.

3.3. Proton conductivity

Proton conductivity is a key property for PEMs, and high conductivity is necessary for their effective utilization in fuel cell devices. The proton conductivities of 2-SPAES-xx and 4-SPAES-xx PEMs were compared with Nafion 117, measured under the same conditions. All the PEMs in the series had conductivities higher than 10^{-2} S/cm, which is a requirement for their utilization in fuel cells (Fig. 6 and Table 3).

Table 3. Proton conductivity and methanol permeability of the 2-SPAES-xx and 4-SPAES-xx membranes.

Copolymers	Proton Conductivity (S/cm)		P_M ($\times 10^{-7}$ cm^{2}s^{-1})	Relative Selectivity
	30°C	80°C		
2-SPAES-50	0.024	0.108	1.96	2.46
2-SPAES-60	0.066	0.152	2.86	4.65
2-SPAES-70	0.080	0.183	3.57	4.51
2-SPAES-80	0.111	0.258	4.69	4.76
4-SPAES-25	0.026	0.135	1.59	3.29
4-SPAES-35	0.089	0.194	3.22	5.56
Nafion117	0.077	0.165	15.5	1.00

The highest value of 0.111 S/cm was obtained from 2-SPAES-80, comparable with that of Nafion 117 (0.077 S/cm) at 30 °C. With increasing IEC_w values for 4-SPAES-xx from 1.24 to 1.59 mequiv/g, proton conductivities increased from 0.026 to 0.089 S/cm at 30 °C and from 0.135 to 0.194 mS/cm at 80 °C.

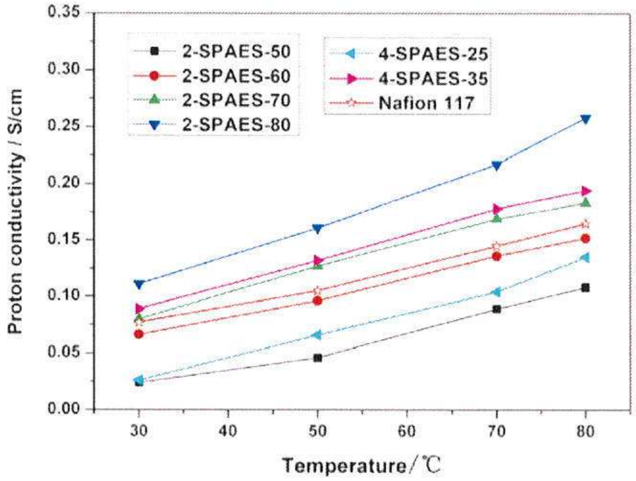


Fig. 6. Proton conductivities of 2-SPAES-xx and 4-SPAES-xx membranes and Nafion 117 at different temperatures under fully hydrated conditions.

The proton conductivities of 4-SPAES-xx are slightly higher than the corresponding copolymer 2-SPAES-xx with similar IEC value, which indicates that the more densely sulfoalkyl segments in the polymer chain are more effective in proton conduction. Therefore, the 4-SPAES-xx membranes exhibit higher relative proton conductivity and lower relative water uptake (vol %) than the 2-SPAES-xx membranes, as shown in Fig. 7. A comparison of the properties of the present PEMs with some other related side-chain-type poly(arylene ether sulfone)s (S2-PAES-60 and S4-PAES-30) containing inflexible pendant sulfophenyl groups [36] is also shown in Fig. 7. 2-SPAES-70 and 4-SPAES-35 with similar IEC exhibited higher relative proton conductivity and much lower relative water uptake. This provides a further indication that the present approach of introducing flexible sulfoalkyl groups as side-chain is effective in promoting proton-conducting domains that improve the properties of PEMs.

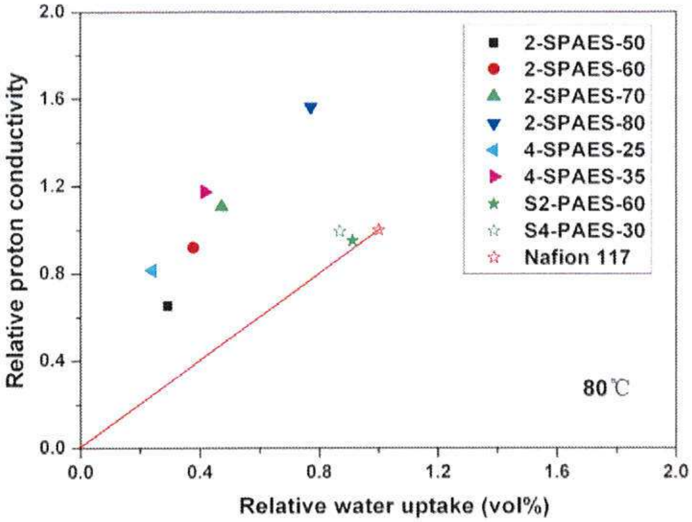


Fig. 7. Comparison of water uptake as a function of proton conductivity, relative to Nafion 117 and analogous sulfophenyl S2-PAES-60 and S4-PAES-30 [36].

PEMs with randomly sulfonated aromatic rings generally require comparatively higher IEC values to attain high proton conductivity because of lower acidity and side-chain flexibility of the sulfonic acid groups, and lesser delineation between the hydrophilic and hydrophobic units compared to Nafion. For 2-SPAES-xx and 4-SPAES-xx copolymers, the incorporation of flexible side-chain sulfonic acid groups could be beneficial to aggregate the ionic clusters, which would lead to more obvious hydrophilic/hydrophobic separation and improve proton conductivity. The typical microstructure of 2-SPAES-70 and 4-SPAES-35 membranes studied by TEM is shown in Fig. 8. The dark lead-stained regions represent localized ionic domains and the light regions referred to the domain formed by hydrophobic polymer backbones. The TEM image suggests that the sulfonic acid groups aggregate into small hydrophilic clusters (~1-3 nm), which could provide proton transport pathways or ionic transport channels. A similar nanophase separation morphology also observed in the microstructure of some aromatic PEMs with flexible pendant sulfoalkyl groups [28,35].

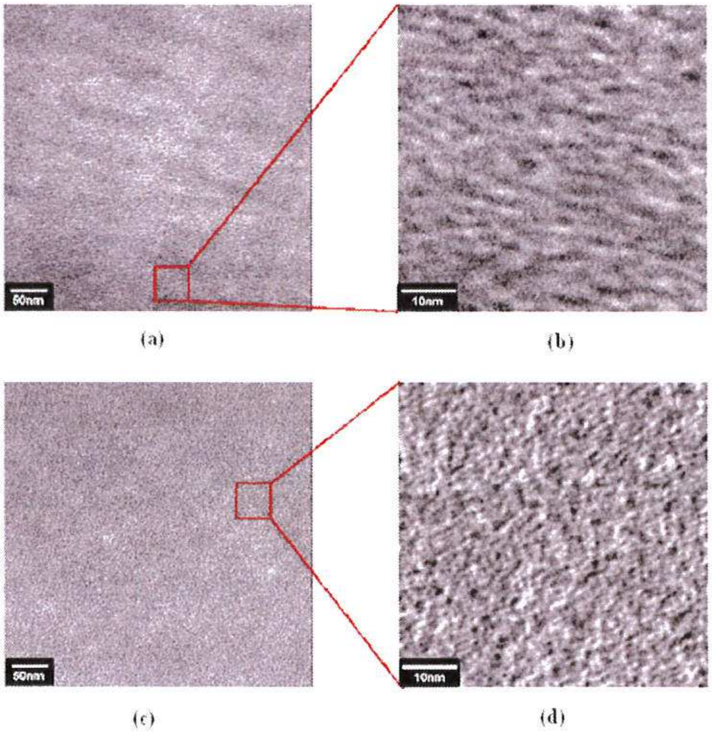


Fig. 8. TEM photographs of (a) and (b) 2-SPAES-70 membrane and (c) and (d) 4-SPAES-35 membrane.

3.4. Methanol permeability

Membranes intended for direct methanol fuel cells (DMFCs) should have not only high proton conductivity but also effective barriers in preventing methanol crossover. One significant drawback for Nafion in DMFC application is its high methanol crossover. This limitation is associated with the microstructure of Nafion, whereby interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion. As shown in Table 3, the present membranes exhibited low methanol permeability, with values for

10% methanol concentration at room temperature in the range of 1.59×10^{-7}-4.69×10^{-7} cm^2/s, which is much lower than the value for Nafion of 15.5×10^{-7} cm^2/s. Selectivity, which is the ratio of proton conductivity to methanol permeability, is a useful predictor of the potential performance of DMFC membranes, providing the membranes have sufficiently high proton conductivity. The relative selectivity (to Nafion) of 2-SPAES-xx and 4-SPAES-xx are all higher than that of Nafion as listed in Table 3. A convenient way to evaluate the membranes is illustrated by a performance trade-off plot containing both relative methanol permeability and relative proton conductivity [30,33]. Target membranes suitable for DMFC are ideally located in the upper left-hand corner, as shown by the dotted circle, i.e., high conductivity and low methanol permeability. As shown in Fig. 9, all the data is situated in the upper left-hand corner of the plot. The membranes having a combination of high proton conductivity and low methanol crossover are being pursued for DMFC system.

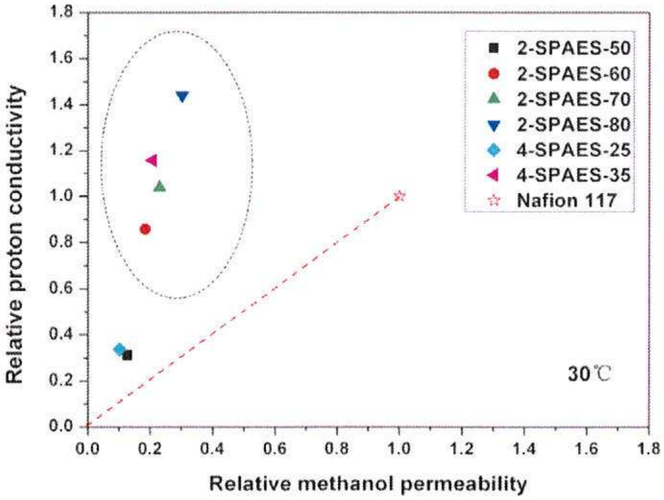


Fig. 9. Trade-off plot of proton conductivity as a function of methanol permeability, relative to Nafion 117.

3.5. Thermal and mechanical properties

The thermal stabilities as measured by TGA 5% weight loss temperatures are listed in Table 4.

Table 4. Thermal and Mechanical Properties.

Copolymers	$T_{d5\%}$ (°C)[a]	Tensile Strength at Break (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
2-SPAES-50	245	60.1[b]	1.67	15.3
2-SPAES-60	231	55.2	1.47	10.2
2-SPAES-70	227	51.1	1.32	8.1
2-SPAES-80	226	53.0	1.28	9.7
4-SPAES-25	253	55.5	1.68	8.6
4-SPAES-35	226	44.9	1.38	7.6

[a] 5% weight loss temperature in N_2 gas (acid form membrane).

[b] Dry samples.

The TGA curves of 2-SPAES-xx and 4-SPAES-xx in the sulfonic acid form shown in Fig. 10 have two distinct degradation steps. The first weight loss stage at around 220-320 °C is associated with the thermal degradation of the side chain. The second steps starting at about 450 °C mainly correspond to the main chain decomposition.

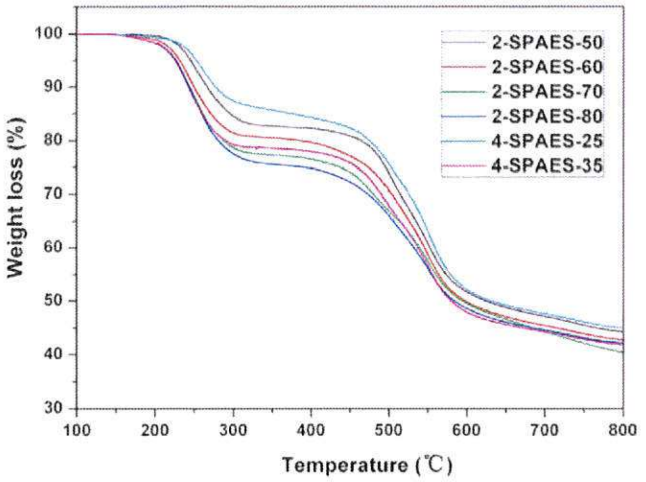


Fig. 10. TGA curves of 2-SPAES-xx and 4-SPAES-xx (acid form) membranes from measurements run at 10 °C/min in N_2.

Good mechanical properties of the membranes are one of the necessary requirements for their effective use in DMFC or PEMFC applications. Films in the dry state had tensile moduli in the range of 1.28-1.68 GPa, tensile stress at maximum load of 44.9-60.1 MPa and elongation at break of 7.6-15.3%, as shown in Table 1. The mechanical properties indicate that the copolymer films were strong and flexible, suitable for potential use as PEMs materials in a fuel cell.

Conclusions

Novel difluorodiphenyl sulfone monomers containing two or four pendent methoxyphenyl groups have been successfully synthesized in high yields by sequential bromination and Suzuki coupling. Sulfonated poly(arylene ether sulfone)s with two or four pendant sulfobutoxyphenyl chains were obtained by sequential polycondensation, demethylation and sulfobutylation. The polymer electrolyte membranes showed good thermal stability and mechanical properties. The flexible nature of the hydrophilic sulfobutyl side-chain in the polymer electrolyte membranes had a positive effect on the proton transport and other properties. The membranes exhibited high proton conductivities, very low water uptake and dimensional change even at elevated temperature (80 ^oC), and small nanophase separated proton-conducting domains of 1-3 nm. 2-SPAES-70 and 4-SPAES-35 had proton conductivity of 0.183 and 0.194 S/cm, and water uptake of 20.1% and 17.5% at 80 °C, respectively. In comparison with the analogous poly(arylene ether sulfone)s containing inflexible pendant sulfophenyl groups, 2-SPAES-70 and 4-SPAES-35 displayed higher relative proton conductivity and much lower relative water uptake. Meanwhile, the methanol permeability values of 2-SPAES-70 and 4-SPAES-35 were 3.57×10^{-7} and 3.22×10^{-7} cm^2/s, respectively, which are several times lower than Nafion. The combination of good thermal stability, excellent balance between proton conductivity and water swelling or methanol transport makes 2-SPAES-70 and 4-SPAES-35 attractive as PEM materials for fuel cells applications.

Acknowledgement.

Funding for the project by the WCU program, National Research Foundation (NRF) of the Korean Ministry of Science and Technology (No. R31-2008-000-10092-0) is gratefully acknowledged.

References and Notes

[1] L. Carrette, K.A. Friedrich, U. Stimming, Fuel cells fundamentals and applications, Fuel Cells 1 (2001) 5–39.

[2] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), Chem. Rev. 104 (2004) 4587–4611.

[3] M.Z. Jacobson, W.G. Colella, D.M. Golden, Cleaning the air and improving health with hydrogen fuel-cell vehicles, Science 308 (2005) 1901– 1905.

[4] N. Li, C.Y. Wang, S.Y. Lee, C.H. Park, Y.M. Lee, M.D. Guiver, Enhancement of proton transport by nanochannels in comb-shaped copoly(arylene ether sulfone)s, Angew. Chem. Int. Ed. 50 (2011) 9158 –9161.

[5] T.J. Peckham, S. Holdcroft, Structure-morphology-property relationships of non-perfluorinated proton-conducting membranes, Adv. Mater. 22 (2010) 4667–4690.

[6] T. Higashihara, K. Matsumoto, M. Ueda, Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells, Polymer 50 (2009) 5341–5357.

[7] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Lee, Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs), Prog. Polym. Sci. 36 (2011) 1443-1496.

[8] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, Sulfonated poly(aryl ether ketone)s containing the hexafluoroisopropylidene

diphenyl moiety prepared by direct copolymerization, as proton exchange membranes for fuel cell application, Macromolecules 37 (2004) 7960-7967.

[9] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, Synthesis of poly(arylene ether ether ketone ketone) copolymers containing pendant sulfonic acid groups bonded to naphthalene as proton exchange membrane materials, Macromolecules 37 (2004) 6748-6754.

[10] X.Y. Shang, S.H. Tian, L.H. Kong, Y.Z. Meng, Synthesis and characterization of sulfonated fluorene-containing poly(arylene ether ketone) for proton exchange membrane, J. Membr. Sci. 266 (2005) 94–101.

[11] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes, J. Membr. Sci. 197 (2002) 231–242.

[12] Y. Chikashige, Y. Chikyu, K Miyatake, M. Watanabe, Poly(arylene ether) ionomers containing sulfofluorenyl groups for fuel cell applications, Macromolecules 38 (2005) 7121–7126.

[13] M. Schuster, K.D. Kreuer, H.T. Andersen, J. Maier, Sulfonated poly(phenylene sulfone) polymers as hydrolytically and thermooxidatively stable proton conducting ionomers, Macromolecules 40 (2007) 598–607.

[14] D.S. Phu, C.H. Lee, C.H. Park, S.Y. Lee, Y.M. Lee, Synthesis of crosslinked sulfonated poly(phenylene sulfide sulfone nitrile) for direct methanol fuel cell applications, Macromol. Rapid Commun. 30 (2009) 64–68.

[15] Y. Gao, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, X. Li, S. Kaliaguine, Synthesis of copoly(aryl ether ether nitrile)s containing sulfonic acid groups for PEM application, Macromolecules 38 (2005) 3237–3245.

[16] Z.H. Zhang, L. Wu, T.W. Xu, Synthesis and properties of side-chain-type sulfonated poly(phenylene oxide) for proton exchange membranes, J. Membr. Sci. 373 (2011) 160–166.

[17] K. Miyatake, H. Zhou, T. Matsuo, H. Uchida, M. Watanabe, Proton conductive polyimide electrolytes containing trifluoromethyl groups: synthesis, properties, and DMFC performance, Macromolecules 37 (2004) 4961–4966.

[18] Y. Yin, Y. Suto, T. Sakabe, S. Chen, S. Hayashi, T. Mishima, O. Yamada, K. Kita, H. Tanaka, K.I. Okamoto, Water stability of sulfonated polyimide membranes, Macromolecules 39 (2006) 1189–1198.

[19] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, J. Membr. Sci. 185 (2001) 29–39.

[20] J. Won, H.H. Park, Fixation of nanosized proton transport channels in membranes, Macromolecules 36 (2003), 3228–3234.

[21] S.H. Tian, Y.Z. Meng, A.S. Hay, Membranes from poly(aryl ether)-based ionomers containing randomly distributed nanoclusters of 6 or 12 sulfonic acid groups, Macromolecules 42 (2009), 1153-1160

[22] L.E. Karlsson, P. Jannsch, Polysulfone ionomers for proton-conducting fuel cell membranes: sulfoalkylated polysulfone, J. Membr. Sci. 230 (2004) 61–70.

[23] J.H. Pang, H.B. Zhang, X.F. Li, D.F. Ren, Z.H. Jiang, Low water swelling and

high proton conducting sulfonated poly(arylene ether) with pendant sulfoalkyl groups for proton exchange membranes, Macromol. Rapid Commun. 28 (2007) 2332–2338.

[24] J.H. Pang, H.B. Zhang, X.F. Li, B.J. Liu, Z.H. Jiang, Synthesis and characterization of sulfonated poly(arylene ether)s with sulfoalkyl pendant groups for proton exchange membranes, J. Membr. Sci. 318 (2008) 271–279.

[25] I. Dimitrov, K. Jankova, S. Hvilsted, Controlled synthesis of fluorinated copolymers with pendant sulfonates, J. Polym. Sci., Part A: Polym. Chem. 46 (2008) 7827–7834.

[26] K. Shao, J. Zhu, G.J. Zhao, X.F. Li, Z.M. Cui, Y. Zhang, H.T. Li, D. Xu, G. Zhang, T.Z. Fu, J. Wu, H. Na, W. Xing, Naphthalene-based poly(arylene ether ketone) copolymers containing sulfobutyl pendant groups for proton exchange membranes, J. Polym. Sci., Part A: Polym. Chem. 47 (2009) 5772–5783.

[27] Y. Zhang, G. Zhang, Y. Wan, C.J. Zhao, K. Shao, H.T. Li,; M.M. Han, J. Zhu, S. Xu, Z.G. Liu, H. Na, Synthesis and characterization of poly(arylene ether ketone)s bearing pendant sulfonic acid groups for proton exchange membrane materials, J. Polym. Sci., Part A: Polym. Chem. 48 (2010) 5824–57832.

[28] Q. Zhang, F.X. Gong, S.B. Zhang, S.H. Li, Novel side-chain-type cardo poly(aryl ether sulfone) bearing pendant sulfoalkyl groups for proton exchange membranes, J. Membr. Sci. 367 (2011) 166–173.

[29] L. Gao, F. Zhang, S.B. Zhang, J. Liu, Novel cardo poly(arylene ether sulfone)s with pendant sulfonated aliphatic side chains for proton exchange membranes, J.

Membr. Sci. 372 (2011) 49–56.

[30] Y. Yin, O. Yamada, Y. Suto, T. Mishima, K. Tanaka, H. Kita, K. Okamoto, Synthesis and characterization of proton-conducting copolyimides bearing pendant sulfonic acid groups, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 1545–1553.

[31] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, Aliphatic/aromatic polyimide ionomers as a proton conductive membrane for fuel cell applications, J. Am. Chem. Soc. 128 (2006) 1762–1769.

[32] T. Nakagawa, K. Nakabayashi, T. Higashihara, M. Ueda, Polymer electrolyte membrane based on poly(ether sulfone) containing binaphthyl units with pendant perfluoroalkyl sulfonic acids, J. Polym. Sci., Part A: Polym. Chem. 49 (2011) 2997–3003.

[33] K. Xu, H. Oh, M.A. Hickner, Q. Wang, Highly conductive aromatic ionomers with perfluorosulfonic acid side chains for elevated temperature fuel cells, Macromolecules 44 (2011) 4605–4609.

[34] H. Ghassemi, D.A. Schiraldi, T.A. Zawodzinski, S. Hamrock, Poly(arylene ether)s with pendant perfluoroalkyl sulfonic acid groups as proton-exchange membrane materials, Macromol. Chem. Phys. 212 (2011) 673–678.

[35] C.Y. Wang, N. Li, D.W. Shin, S.Y. Lee, N.R. Kang, Y.M. Lee, M.D. Guiver, Fluorene-based poly(arylene ether sulfone)s containing clustered flexible pendant sulfonic acids as proton exchange membranes, Macromolecules 44 (2011) 7296–7306.

[36] N. Li, D.W. Shin, D.S. Hwang, Y.M. Lee, M.D. Guiver, Polymer electrolyte membranes derived from new sulfone monomers with pendent sulfonic acid groups, Macromolecules 43 (2010) 9810–9820.

[37] Y.S. Kim, B. Einsla, M. Sankir, W. Harrison, B.S. Pivovar, Structure–property–performance relationships of sulfonated poly(arylene ether sulfone)s as a polymer electrolyte for fuel cell application, Polymer 47 (2006) 4026–4035.

[38] D.S. Kim, G.P. Robertson, M.D. Guiver, Comb-shaped poly(arylene ether sulfone)s as proton exchange membranes, Macromolecules 41 (2008) 2126-2134.