Preparation and Properties of Bisphenol A-Based Sulfonated Poly(arylene ether sulfone) Proton Exchange Membranes for Direct Methanol Fuel Cell

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ABSTRACT: Novel bisphenol A-based sulfonated poly(arylene ether sulfone) (bi A-SPAES) copolymers were successfully synthesized via direct copolymerization of disodium 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone, 4,4′-dichlorodiphenylsulfone, and bisphenol A. The copolymer structure was confirmed by Fourier transform infrared spectra and ^{1}H NMR analysis. The series of sulfonated copolymers based membranes were prepared and evaluated for proton exchange membranes (PEM). The membranes showed good thermal stability and mechanical property. Transmission electron microscopy was used to obtain the microstructures of the synthesized polymers. The membranes exhibit increased water uptake from 8% to 66%, ion exchange capacities from 0.41 to 2.18 meq/g and proton conductivities (25°C) from 0.012 to 0.102 S/cm with the degree of sulfonation increasing. The proton conductivities of bi A-SPAES-6 membrane (0.10–0.15 S/cm) with high-sulfonated degree are higher than that of Nafion 117 membrane (0.095–0.117 S/cm) at all temperatures (20–100°C). Especially, the methanol diffusion coefficients of membranes (1.7×10^{-8} cm^2/s–8.5×10^{-7} cm^2/s) are much lower than that of Nafion 117 membrane (2.1×10^{-6} cm^2/s). The new synthesized copolymer was therefore proposed as a candidate of material for PEM in direct methanol fuel cell. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 304–312, 2009

Key words: copolymerization; high performance polymers; bisphenol A-based sulfonated poly(arylene ether sulfone); proton exchange membrane; direct methanol fuel cell

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) have been identified as environmentally attractive energy sources for application both in stationary power and automobiles because of their low emissions and high conversion efficiency.[1,2] As one of the most important components of PEMFC, proton exchange membrane (PEM) transfers protons from anode to cathode as well as providing a barrier to fuel gas cross-leaks between the electrodes. Currently, the most commonly used membrane materials are perfluorinated polymers such as Dupont Nafion. Although, they exhibit good mechanical properties and long-time stability, their high cost and loss of proton conductivity at temperatures above 80°C as well as high methanol permeability have limited their widespread commercial application in PEMFC and DMFC.[3–6] Therefore, numerous efforts have been dedicated to develop new PEM materials.

An applicable PEM in PEMFC and DMFC should possess high proton conductivity, low methanol permeability, and adequate mechanical strength, etc.[7] Recently, among developed alternative PEM materials, sulfonated derivates of high performance polymers, such as polyketone,[8–10] polysulfone,[11–13] polyimides,[14,15] and polybenzimidazole[16,17] have attracted much attention because of their good properties related to PEM. Generally, they are prepared either by postsulfonation with sulfonating agents, such as concentrated sulfuric acid or sulfur trioxide, or by direct copolymerization of sulfonated monomers.

With respect to the method of postsulfonation, only one sulfonic acid group is introduced to the polymer repeat unit, and the degree of sulfonation (Ds) is hard to control and too high Ds value can result in the loss of membrane stability when immersing in hot water.[18] In addition, the partial degradation and the side reaction might occur in postsulfonation reaction process. However, the direct copolymerization of sulfonated monomer easily introduced two sulfonic acid groups in per repeat unit on the deactivated ring positions, which might provide the resulting polymer structure with the
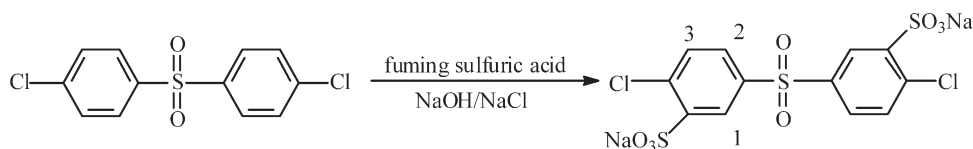
Scheme 1 Synthesis of sulfonated monomer.

increase of sulfonated acid groups, resulting in more facile proton transport channels. Therefore, the method of direct copolymerization of sulfonated monomer has become a promising way to prepare high-performance PEM.

Sulfonated poly(arylene ether sulfone)s (SPAES)s have been examined systematically as alternative PEM materials.[19–21] Bisphenol A based poly(arylene ether sulfone) (bi A-PAES) is a novel environment-friendly material and a high-performance engineering thermoplastics with excellent mechanical property, high thermal stability as well as the resistance to oxidation and stability under acidic conditions. However, there are no reports aiming at the systemic study on the properties of bisphenol A-based sulfonated poly(arylene ether sulfone) (bi A-SPAES) prepared by direct copolymerization of sulfonated monomer for PEM.

In this article, a series of bi A-SPAES copolymers with different Ds were prepared by direct polycondensation of sulfonated monomer (SDCDPS), non-sulfonated monomer (DCDPS), and bisphenol A. We systemically investigated the relationship between Ds and some properties such as water uptake, ion exchange capacity (IEC), thermal stability, proton conductivity, and methanol permeability, respectively, and also tested and compared the mechanical properties of the membranes with those of Nafion 117 membrane. The relationship between morphologies and properties of these membranes were discussed by transmission electron microscopy (TEM). Proton conductivity is the foremost criterion for

PEM because a membrane can never be applicable to PEMFC without a sufficient value of proton conductivity; Good methanol resistance performance is a necessary condition for practical use of PEM in DMFC. In this study, we tried to increase the proton conductivity of membranes by adjusting molar fractions of the sulfonic acid groups of the polymers and studied the changing trend of both proton conductivities of bi A-SPAES membranes with temperatures increasing and methanol diffusion coefficients of bi A-SPAES membranes with Ds increasing. The objective of this work is to prepare novel bi A-SPAES membranes with excellent properties to make them become applied candidates of PEM materials in PEMFC and DMFC.

EXPERIMENTAL

Polymer synthesis and characterization

The polymers were synthesized via two ways: (1) synthesis of monomer and (2) preparation of polymers. The sulfonated monomer was synthesized via sulfonation of 4,4′-dichlorodiphenylsulfone (DCDPS) with fuming sulfuric acid (50% SO_3), followed by neutralization with NaOH solution and precipitated with NaCl solution (Scheme 1). The crude product was recrystallized from a mixture of ethanol and deionized water, forming white needle-like crystals. The yield of SDCDPS was above 80%. ^{1}H NMR (400 MHz, DMSO, ppm): δ_{H1} = 8.34 ppm (d, J = 2.34 Hz), δ_{H2} = 7.82–7.86 ppm (dd, J = 2.46, 2.46 Hz), δ_{H3} = 7.66 ppm (d, J = 8.30 Hz).
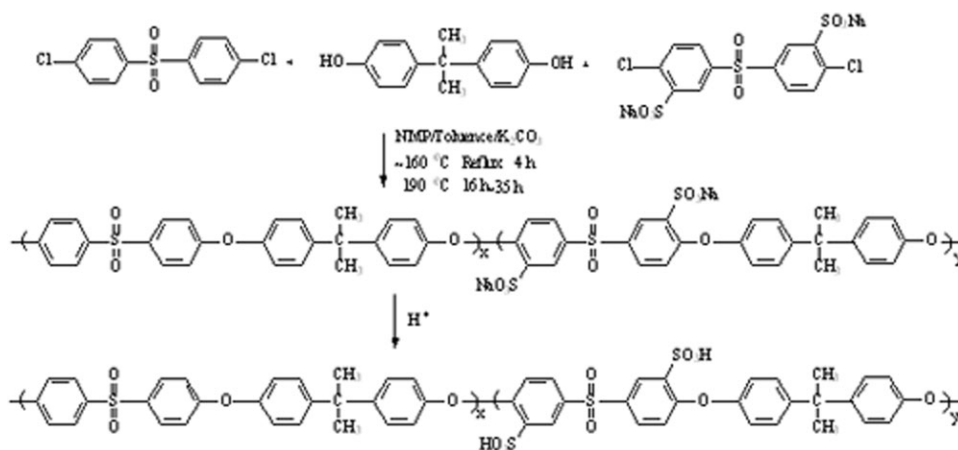
Scheme 2 Synthesis of bi A-SPAES.

TABLE I
Polymerization Results and Analytical Data of Bi A-SPAES Membranes

Sample	Monomer n (mmol)	Monomer m (mmol)	n/m	Yield (%)	η_{sp}/c	Ds^a	Ds^b
1	1	9	1/9	94	0.81	0.22	0.2
2	2	8	2/8	93	1.24	0.43	0.4
3	3	7	3/7	90	1.36	0.56	0.6
4	4	6	4/6	92	1.54	0.75	0.8
5	5	5	5/5	91	1.82	0.96	1.0
6	6	4	6/4	90	1.98	1.14	1.2

[a] Sulfonated degree measured by titration.
[b] Sulfonated degree obtained by calculation.

As shown in Scheme 2, the bi A-SPAES polymers with different degrees of sulfonation were synthesized via direct aromatic nucleophilic substitution condensation of 4,4′-bisphenol A (BPA, monomer k) with different ratios of DCDPS (monomer m) and disodium 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS, monomer n) in a NMP/toluene solvent system. The reaction mixture was heated under reflux at about 160°C for 4 h to dehydrate the system. Next, the temperature was raised to 190°C and kept at this temperature until the solution became very viscous. The reaction product was cooled to room temperature, added into deionized water to remove residual salts, and dried under vacuum at 120°C for 24 h. The degrees of sulfonation (D_S) were controlled by the different amount of the monomers n and m, which are listed in Table I.

Intrinsic viscosities

Intrinsic viscosity was determined in DMAc at 25 ± 0.1°C with a polymer concentration of 5.0 g/L using an Ubbelohde viscometer and calculated as follows:

$$\eta_{sp}/c[dL/g] = (\eta_r - 1)/c = (t/t_0 - 1)/c \qquad (1)$$

Where t and t_0 are the outflow-time of the solution and pure solvent, respectively, and c is the concentration of the solution.

Microstructures of polymers

The powder of bi A-SPAES polymers was first converted into Ag^+ form by immersing in $1M$ $AgNO_3$ solution overnight. Then, the powder was fully rinsed using ethanol and dispersed on the copper grid for transmission electron microscopy (TEM). Hitachi H-7650 was used for TEM.

Membrane preparation and characterization

A solution of the sulfonated copolymer dissolving in DMAc (10 wt %) was prepared and filtered through a 0.45 μm syringe filter. Membrane of sodium-form was obtained by casting the filtered solution directly onto clean glass substrates and dried at gradually increasing temperature under vacuum at 50°C for 24 h and 100°C for 24 h. The films were cooled to room temperature and detached from the glass substrates after they were immersed into water and then converted into the acid form by immersing in $2M$ H_2SO_4 overnight. Finally, the membranes were thoroughly washed with deionized water to remove any excess H_2SO_4 and vacuum-dried at 100°C overnight. All the polymers can be successfully cast into tough membranes and the thickness of all membranes was in the range of 20–50 μm.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

Glass transition temperature (Tg) was obtained on a SETARAM DSC-141 instrument. Scans were conducted under nitrogen at a heating rate of 10°C/min. Dynamic TGA was employed to show the thermal stability (weight loss) of the copolymers with a ZRY-2P synthesis thermogravimetric analyzer. All the samples were first vacuum dried and kept in the TGA furnace at 150°C under nitrogen atmosphere for 30 min to remove water before TGA characterization. The heating rate was 10°C/min in nitrogen.

Water uptake (WU) of membranes

The water uptake of the membranes was determined gravimetrically. The membranes were vacuum dried at 100°C for 24 h, weighed and then immersed in deionized water at room temperature for 48 h. The wet membranes were wiped dry and quickly weighed again. The water uptake of the membranes was calculated according to eq. (2).

$$WU = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\% \qquad (2)$$

Where, M_{wet} and M_{dry} refer to the weight of the wet membrane and the weight of the dry membrane, respectively.

Ion exchange capacity (IEC)

Titration was used to quantitatively determine sulfonic acid concentration in the copolymer. First, the acid form membranes were converted to the sodium form membranes by immersing the membranes in $2M$ NaCl solution for 48 h to exchange the H^+ ions with Na^+ ions. Then, the solutions were titrated with a $0.1M$ NaOH solution. IEC was calculated by eq. (3):

$$IEC \ [meq/g] = \frac{C \times V}{M_{dry}} \times 1000 \qquad (3)$$

Where C is the concentration of NaOH solution, V is the volume of NaOH solution, and M_{dry} is the weight of the dried membranes.

The theoretical IEC values, which were calculated from theoretical Ds, were obtained from eq. (4):

$$IEC = \frac{1000Ds}{442 + 80Ds} \qquad (4)$$

Where, Ds is calculated from the molar fractions of the monomer SDCDPS as shown in Table I.

Proton conductivity

The impedance of each acidified film was performed in a frequency range of 10 mHz to 0.1 MHz under fully hydrated conditions using a electrochemistry synthesis analyzer (Potentiostat/Galvanostat Model 263A). The resistance of the film was recorded when the imaginary resistance was at a minimum. The detailed procedure has been reported previously.[19]

The proton conductivity was calculated by eq. (5).

$$\sigma = \frac{L}{RS} \qquad (5)$$

Where σ is the proton conductivity (S/cm), L is the length between electrodes (cm), R is the membrane resistance (ohms) and S is the cross-sectional area of film (cm^2).

Methanol diffusion coefficient

Diffusion coefficients were determined by using the cell as shown in Figure 1. Methanol was placed on one side of the cell and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. Methanol analysis was performed by using a SHTMADU GC-4890 chromatograph. Peak areas were converted to methanol concentration by using a calibration curve. The methanol diffusion coefficient was calculated and obtained according to the eq. (6):[22]

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_A (t - t_0) \qquad (6)$$
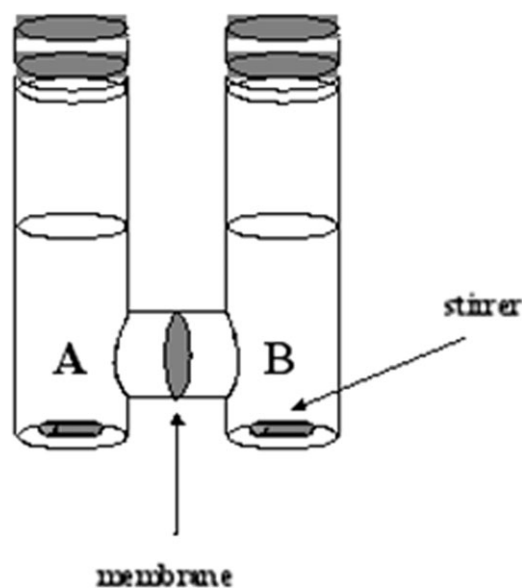
Figure 1 Schematic representation of the methanol diffusion cell.

Where, C_B and C_A are the methanol concentration of permeated and feed side through the membrane, respectively. A, L, and V_B are the effective area of membrane, the thickness of membrane and the volume of permeated compartment, respectively. $(t - t_0)$ is the time during the whole penetration. DK is the methanol diffusion coefficient.

Mechanical property

Mechanical tensile tests were performed using an INSTRON 1121 Universal Testing Machine at room temperature with a crosshead displacement speed of 2 mm/min. For each testing reported, at least three specimens were taken and average value was calculated.

RESULTS AND DISCUSSION

Polymer synthesis and characterization

The chemical structure of the copolymers was confirmed by a Perkin Elmer spectrum One B FT-IR spectrometer. Figure 2 shows the IR spectrums of bi A-PAES and bi A-SPAES. The absorption bands at 1029 cm^{-1} and 1098 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of the sodium sulfonate groups, respectively. While in none sulfonated copolymer, there are no related stretching vibrations of SO$_3$Na. The absence of aromatic-sulfone group vibrations in the range of 1140–1110 cm^{-1} indicates that no crosslinking occurred during the process of copolymerization. The chemical structure of sulfonated copolymer was also confirmed by ^{1}H NMR spectra (Fig. 3).
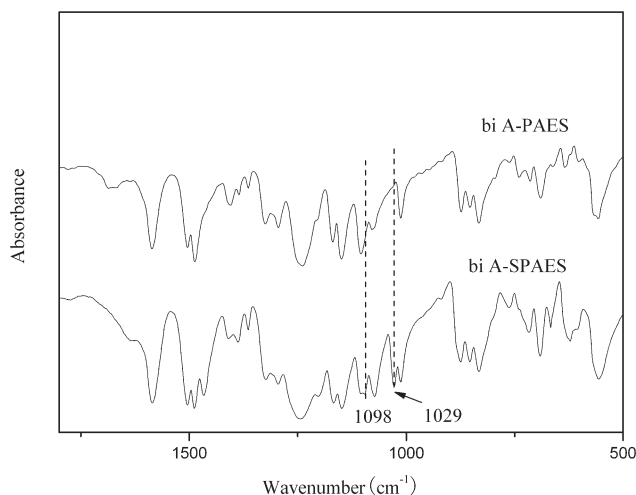
Figure 2 The FT-IR of bi A-PAES and bi A-SPAES.

Thermal stability

The onset temperatures for decomposition steps are given in Table II, and the thermograms are given in Figure 4. From the TG results of copolymers (Fig. 4),

the copolymers were all stable at about 400°C, which represents the good thermal stability of copolymers. Two weight loss steps are observed in Figure 4. The first weight loss step was about from 375 to 470°C, which was assigned to the loss of sulfonic acid groups of bi A-SPAES.[13,23] The second weight loss step was at 500°C, which corresponds to the decomposition of main polymer chain. The 5% and 10% weight loss temperatures of bi A-SPAES-1 to bi A-SPAES-6 were about in the ranges of 320 to 460°C and 400 to 480°C, respectively, and presented a slight decreasing tendency with the increase of Ds. This may be explained by the relatively lower degrade temperatures of sulfonated groups than those of polymer backbone. The Tgs of the SPAES copolymers in their salt form were observed in Table II. The Tgs of bi A-SPAES-1 to bi A-SPAES-6 show an increase tendency (175–260°C) with the increase of the mole fraction of disulfonation, which may be attributed to the increase of intermolecular interactions and thereby the reduction of mobility in the sulfonated groups of polymers with increasing Ds. From these results, it is concluded that, the bi
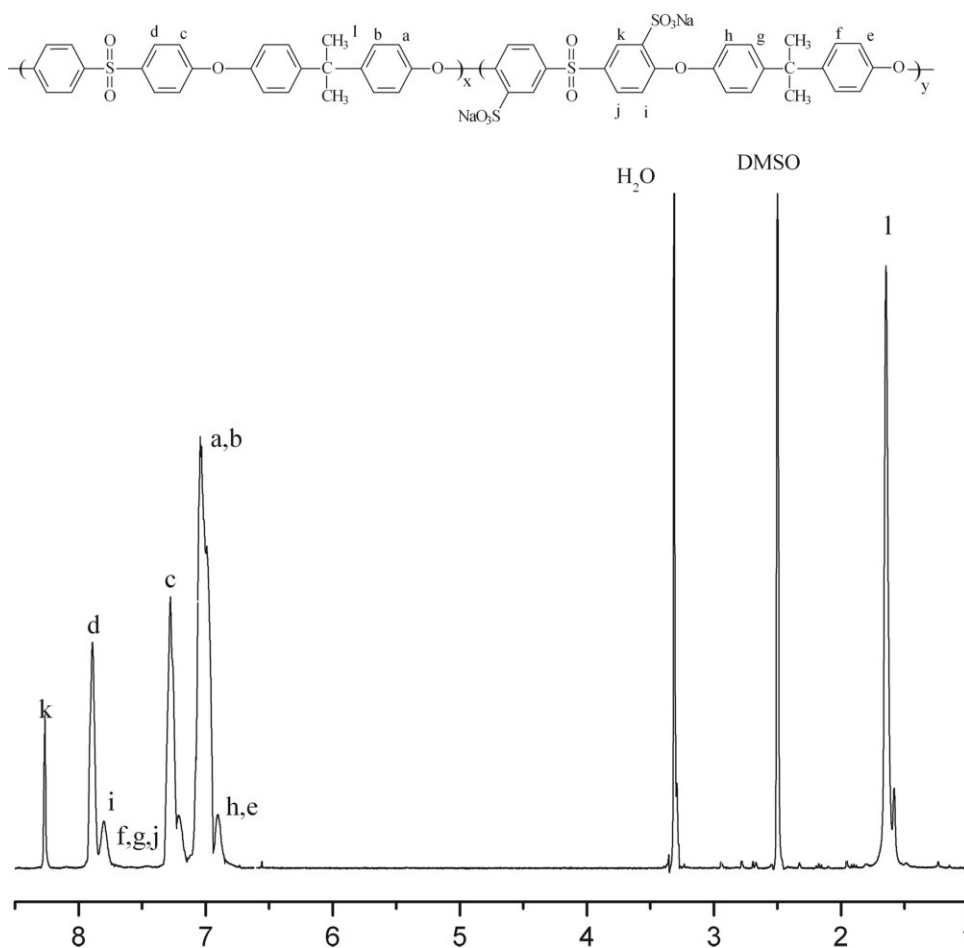
Figure 3 ^{1}H NMR spectrum of bi A-SPAES- 4.

TABLE II
TGA and DSC Results of i A-SPAES Copolymers

Polymer	$Td_{5\%}$ (°C)[a]	$Td_{10\%}$ (°C)[b]	Tgs (°C)[c]
1	454	478	175
2	436	462	197
3	431	458	212
4	423	446	231
5	362	418	245
6	324	408	260

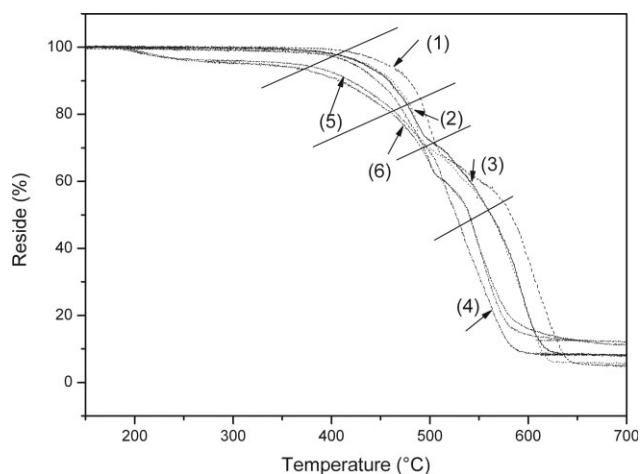[a] Temperature of 5% weight loss.
[b] Temperature of 10% weight loss.
[c] Glass transition temperature of copolymers.

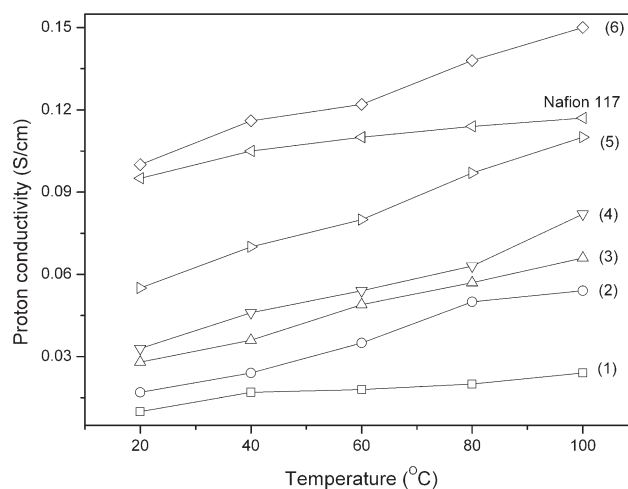A-SPAES membranes are thermally stable within the temperature range for PEMFC applications.

Water uptake of membranes

Water uptake plays a very important role in PEM. Proton transport in PEM is largely influenced by the water content of membranes. The proton exchange requires a significant amount of water to coordinate with proton as it moves through the membrane. That is the reason why the proton conductivity of bi A-SPAES membranes increases with the increase of water uptake (Ds, Fig. 5). As shown in Table III, the bi A-SPAES membranes from 1 to 6, which, respectively, have degrees of sulfonation of 0.2 to 1.2, exhibit an increasing water uptake of 8% to 66% because of the strong hydrophilicity of the sulfonic acid groups. As expected, the results are comparable to that of Nafion 117 membrane (38%). However, the excessively high level of water uptake can result in membrane swelling and decrease the mechanic properties of the membranes. Therefore, selecting membranes with appropriate levels of water uptake

Figure 5 The proton conductivities of bi A-SPAESs with different temperatures where (1) bi A-SPAES-1, (2) bi A-SPAES-2, (3) biA-SPAES-3, (4) bi A-SPAES-4, (5) bi A-SPAES-5, (6) bi A-SPAES-6.

is very important for creating new membrane materials for fuel cell.

Ion exchange capacity

Ion exchange capacity, which was obtained by titration and calculation, is listed in Table III. These bi A-SPAES membranes show increased IEC (from 0.41 to 2.18 meq/g) with the increase of Ds (from 0.2 to 1.2), which are comparable to that of Nafion 117 membrane. Moreover, the experimental IEC values are in good agreement with the calculated IEC values, which is consistent with the hypothesis that all of the sulfonated monomers can be incorporated into the polymer by direct synthesis of sulfonated monomer copolymerization without any side reactions.

Proton conductivity

The proton conductivities of the membranes with different Ds were estimated by AC impedance spectroscopy. The conductivity data are listed in Table III and plotted in Figure 5 as a function of temperature. From an application point-of-view, good proton conductivity is clearly one of the most important properties of PEM. As expected, the proton conductivities of bi A-SPAES membranes increase with increasing Ds because of the strength of the acid group in each system. For example, the acid form membranes with Ds of 0.2 to 1.2 exhibit proton conductivities of 0.012 to 0.102 S/cm at 25°C, respectively. In common with the results found in many other studies, the proton conductivities of SPAES membranes increased with the increase of Ds.[19,21] All the membranes show a proton

Figure 4 The TG curves of (1) bi A-SPAES-1, (2) bi A-SPAES-2, (3) biA-SPAES-3, (4) bi A-SPAES-4, (5) bi A-SPAES-5, (6) bi A-SPAES-6.

TABLE III
The Analytic Data of i A-SPAES Membranes

Properties	1	2	3	4	5	6	Nafion 117
Ds	0.2	0.4	0.6	0.8	1.0	1.2	1.0
IEC_{cal} (meq/g)[a]	0.44	0.84	1.22	1.58	1.92	2.23	–
IEC_m (meq/g)[b]	0.41	0.81	1.15	1.51	1.87	2.18	0.91
WU (%)	8	10	24	31	42	66	38
Conductivity (S/cm) at 25°C	0.012	0.019	0.031	0.036	0.060	0.102	0.096
Conductivity (S/cm) at 80°C	0.020	0.050	0.057	0.063	0.097	0.138	0.114
MeOH diffusion coefficient (cm²/s) at 25°C	1.7×10^{-8}	4.2×10^{-8}	3.1×10^{-7}	5.2×10^{-7}	7.3×10^{-7}	8.5×10^{-7}	2.1×10^{-6}

[a] IEC calculated from degree of sulfonation.
[b] IEC obtained by titration.

conductivity that is higher than 0.01 S/cm, which is the lowest value of PEM in fuel cell from a practical point of view. Moreover, similar to Nafion 117 membrane, the proton conductivities of membranes increased with the increase of temperature. It is also noted that the proton conductivities of these membranes showed more marked increment with the increase of temperature than that of Nafion 117 membrane. Especially, the proton conductivity of bi A-SPAES-6 membrane (0.10–0.15 S/cm) is much higher than that of Nafion 117 membrane (0.095–0.117 S/cm) at all temperatures (20–100°C). These comparisons suggest the feasibility of using directly synthesized bi A-SPAES copolymers as candidates of material for PEM.

Methanol diffusion coefficient

One of the major drawbacks of the commercial Nafion membranes used as PEMs in DMFC systems is their high methanol permeability. As shown in Table III, the methanol diffusion coefficient increases with the increase of proton conductivity, which can be explained by the different morphologies of membranes. Both proton conductivity and methanol permeability were accomplished by interconnected hydrophilic domains in the membranes. These interconnected hydrophilic domains strongly contributed to high proton conductivity, but at the same time they can promote methanol permeability. Moreover, bi A-SPAES membranes exhibit methanol diffusion coefficient at 25°C of 1.7×10^{-8} cm²/s to 8.5×10^{-7} cm²/s, which is about one order of magnitude lower than that of Nafion 117 membrane (2.1×10^{-6} cm²/s) at the same temperature (Table III). The explanation for this may be that the sulfonated groups in the bi A-SPAES membranes dispersed throughout the polymer matrix and are not easily phase separated, while the sulfonated groups in Nafion is easily lead to phase separated.[24] All these characteristics reduce the hydrodynamic solvent transport properties of the membranes. The results show that the new synthesized bi A-SPAES mem-

branes have good methanol resistance than that of Nafion 117 membrane and may reduce the problem associated with water and methanol crossover for DMFC.

Mechanical property

It is essential for PEMs to possess adequate mechanical strength to withstand fabrication of the membrane electrode assembly and operation in fuel cell. Here, the mechanical properties of bi A-SPAES membranes are shown in Table IV. All the membranes show tensile strength in the range from 46.31 MPa to 34.17 MPa, which are higher than that of Nafion 117 membrane, therefore, are enough for the usage of PEM. The elongations at break of these membranes are much lower than that of Nafion 117 membrane because of rigid benzene ring of bi A-SPAES polymers and soft fluorocarbon structure of Nafion 117 membrane. While the initial Young's modulus for all the membranes of bi A-SPAES (1.02 GPa–2.30 GPa) is much higher than that of Nafion 117 membrane (0.26 GPa). One primary use of fuel cell is dynamical device of vehicle, so the accessories in fuel cell must have high aseismatic property. The membranes with high modulus can be highly airproof and not easy to be distorted at high temperature under the operating condition of fuel cell when being used as PEM. Thus, the bi A-SPAES membranes synthesized in this study can adequately meet the requirement of fuel cell.

TABLE IV
The Mechanical Properties of i A-SPAES Membranes

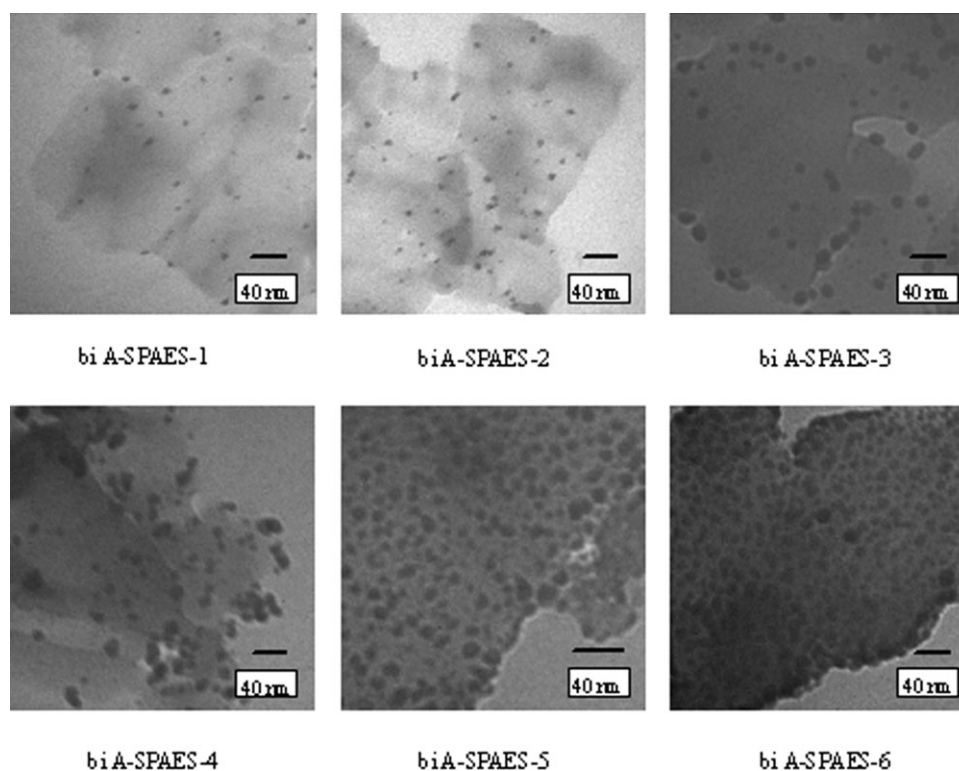| Polymer	Tensile strength (MPa)	Tensile modulus (GPa)	Maximum elongation (%)
1	46.31	1.85	3.28
2	44.35	1.87	7.86
3	41.15	1.72	4.90
4	39.75	2.30	6.17
5	36.88	1.02	2.92
6	34.17	1.54	4.48
Nafion 117	25.65	0.26	197.71

Figure 6 TEM micrographs of bi A-SPAES membranes.

It is noted that the mechanical properties of the membranes do not have the same tendency with Ds increasing. It has been reported in the literature that various factors can influence the mechanical properties of membranes including characteristic of polymers such as molecular weight, the intermolecular dissociation of the sulfonate moieties, etc., and the characteristic of membranes such as the structure, the solvents, the uniformity of membranes, etc.[5] Therefore, the content of sufonated groups has no obvious influence on the mechanical properties of these membranes from the results.

Morphology of membranes

The electrochemical performance of bi A-SPAES membranes should be closely related to their internal structures, especially the spatial distribution of ionic site. Metal ions can chelate with ionic groups, such as Ag^+, Pb^+, which produce the metal clusters with ionic polymers matrix.[25,26] In this study, Ag^+ was used to observe the microstructures of bi A-SPAES copolymers by TEM (Fig. 6). The dark regions represent the hydrophilic Ag^+ clusters ($—SO_3Ag$) and the brighter regions are assigned to the hydrophobic domain (polymer backbone). As clearly seen in the images, silver particles disperse within the bi A-SPAES matrix randomly, which proved that the sulfonated groups were successfully introduced into the copolymers. With the increase of sulfonated groups from bi A-SPAES-1 to bi A-SPAES-6 copolymers, the density of sulfonated groups increases, resulting in the higher density of silver particles in bi A-SPAES matrix. Especially to bi A-SPAES-6 the silver particles distribute with very high density and show relatively large ion domain. Therefore, higher Ds resulted in more ionic groups, more proton transport channels and thus larger proton conductivity values.

CONCLUSION

The bi A-SPAES copolymers with different Ds were prepared by direct copolymerization of sulfonated monomer. All the copolymers were successfully cast into membranes and showed good thermal stability. Bi A-SPAES-6 membrane with higher Ds (1.2) showed much higher water uptake, IEC and proton conductivity than that of Nafion 117 membrane, and especially the marked predominance of proton conductivity at high temperature. Moreover, all the membranes also exhibited good mechanical property, proton conductivity, and methanol resistant. As a result, the new synthesized bi A-SPAES copolymers can be good alternative materials for PEM in DMFC.

References

1. Costamagna, P.; Srinivasan, S. J Power Sources 2001, 102, 253.
2. Mehta, V.; Cooper, J. S. J Power Sources 2003, 114, 32.

3. Tsai, J. C.; Kuo, J. F.; Chen, C. Y. J Power Sources 2007, 174, 103.
4. Kreuer, K. D. Solid State Ionics 1997, 97, 1.
5. Kreuer, K. D. J Membr Sci 2001, 185, 29.
6. Inzelt, G.; Pineri, M.; Schultze, J. W.; Vorotyntsev, M. A. Electrochim Acta 2000, 45, 2403.
7. Gil, M.; Ji, X. L.; Li, X. F.; Na, H. J Membr Sci 2004, 234, 75.
8. Alberti, G.; Casciola, M.; Massinelli, L.; Bauer, B. J Membr Sci 2001, 185, 73.
9. Li, X. F.; Zhang, G. D.; Zhao, C. J.; Na, H. J Power Sources 2007, 165, 701.
10. Li, X. F.; Zhao, C. J.; Lu, H.; Wang, Z.; Na, H. Polymer 2005, 46, 5820.
11. Cho, C. G.; Kim, Y. S.; Yu, X.; Hill, M.; Mcgrath, J. E. J Polym Sci Part A: Polym Chem 2006, 44, 6007.
12. Wang, Z.; Ni, H. Z.; Zhao, C. J.; Li, X. F.; Zhang, G.; Shao, K.; Na, H. J Membr Sci 2006, 285, 239.
13. Wang, Z.; Li, X. F.; Zhao, C. J.; Hong, Z. N.; Na, H. J Appl Polym Sci 2007, 104, 1443.
14. Zhai, F. X.; Guo, X. X.; Fang, J. H.; Xu, H. J. J Membr Sci 2007, 296, 102.
15. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359.
16. Kerres, J. A. J Membr Sci 2001, 185, 3.
17. Jones, D. J.; Roziere, J. J Membr Sci 2001, 185, 41.
18. Zhao, C. J.; Li, X. F.; Lin, H. D.; Ke, S.; Na, H. J Appl Polym Sci 2008, 108, 671.
19. Wang, F.; Hickner, M. A.; Kim, Y. S.; Zawodzinski, T. A.; Mcgrath, J. E. J Membr Sci 2002, 197, 231.
20. Jung, H. Y.; Cho, K. Y.; Sung, K. A.; Kim, W. K.; Kurkuri, M.; Park, J. K. Electrochim Acta 2007, 52, 4916.
21. Kim, Y. S.; Einsla, B.; Sankir, M.; Harrison, W.; Pivovar, B. S. Polymer 2006, 47, 4026.
22. Jung, B.; Kim, B. Y.; Yang, J. M. J Membr Sci 2004, 245, 61.
23. Lee, H. S.; Badami, A. S.; Roy, A.; Mcgrath, J. E. J Appl Polym Sci Part A: Polym Chem 2007, 45, 4879.
24. Karlsson, L. E.; Jannasch, P. J Membr Sci 2004, 230, 61.
25. Yang, Y. S.; Shi, Z. Q.; Holdcroft, S. Macromolecules 2004, 37, 1678.
26. Yin, Y.; Fang, J. H.; Watari, T.; Tanaka, K. J Mater Chem 004, 14.