Physical and Electrochemical Behaviors of Directly Polymerized Sulfonated Poly(arylene ether ketone sulfone)s Proton Exchange Membranes with Different Backbone Structures

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ABSTRACT: Sulfonated poly(ether ether ketone sulfone) (SPEEKS) and sulfonated poly(ether ether ketone ketone sulfone) (SPEEKKS) copolymers with different degree of sulfonation (DS) were synthesized by aromatic nucleophilic polycondensation of disodium 3,3′-disulfonate-4,4′-dichloro-diphenylsulfone (SDCDPS), tertbutylhydroquione, and 4,4′-difluorobenzophenone or 1,4′-bi(4-fluorobenzoyl) benzene. Prepared sulfonated copolymers were characterized by Fourier transform infrared spectra, thermogravimetric analysis, and differential scanning calorimetry. The transmission electron microscope was used to investigate the microstructure of membranes. The different distance between two adjacent sulfonic groups in two series of membranes resulted in different physical and electrochemical properties between two kinds of membranes with the same DS. The proton conductivity, ionic exchange capacity and water uptake of SPEEKS membranes were higher than those of SPEEKKS membranes while the mechanical strength of SPEEKS membranes was lower than that of SPEEKKS membranes at the same DS. Moreover, the SPEEKKS membranes with DS equals to 0.8 showed a good combination of a high proton conductivity (0.046 S/cm at 25°C, 0.061 S/cm at 80°C), acceptable water uptake (33–65 wt %), excellent mechanical strength (tensile strength reached 49.7 MPa), and good thermal properties (T_g above 250°C, $T_{d5\%}$ above 300°C). It suggested that this could be a promising membrane for proton exchange membrane fuel cell application. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 858–866, 2009

Key words: sulfonated; proton exchange membrane fuel cell; SPEEKS; SPEEKKS

INTRODUCTION

Proton exchange membranes fuel cell (PEMFC) is one of the most promising efficient and environmental friendly power generation systems because of its low noise, low pollution, and high working efficiency.[1,2] The key component of a PEMFC is proton exchange membrane (PEM), which acts as a separator to prevent the mixing of the fuel and the oxidant, as well as an electrolyte to transfer protons from the anode to the cathode. Nowadays, Nafion® perfluorosulfonated polymers have been extensively used because of their high conductivity and chemical stability. However, there are some drawbacks, such as high price, high methanol permeability, and relatively low proton conductivity at high temperature under low humidity, which limited their further application.[3] Therefore, several different kinds of sulfonated hydrocarbon polymers have been synthesized to overcome the drawbacks of the perfluorosulfonated polymers. New PEMs mainly focus on sulfonated poly(ether ether ketone)s (SPEEKs),[4–7] sulfonated poly(arylene ether sulfone)s (SPAESs),[8–10] sulfonated polyimides (SPIs),[11–13] sulfonated polybenzimidazoles (SPBIs),[14] composite membranes,[15–17] etc.

Series of SPEEK and sulfonated poly(arylene ether ketone sulfones) (SPAEKS) copolymers were synthesized by direct polycondensation,[4–7,9] and the influence of the hydroquinone with different pendent groups on physical and electrochemical behaviors of sulfonated poly(ether ether sulfones) (SPEES) membranes had been investigated in our previous work.[10] The difference in physical and electrochemical behaviors of membranes at the same degree of sulfonation (DS) was ascribed to the chemical structure of flouorobenzophenone, which affected the distribution of sulfonic acid groups in SPAEKS copolymer. Furthermore, the distance between two adjacent sulfonic acid groups of SPEEKS copolymer is shorter than that of SPEEKKS copolymer, which improves the speed of proton transporting from one
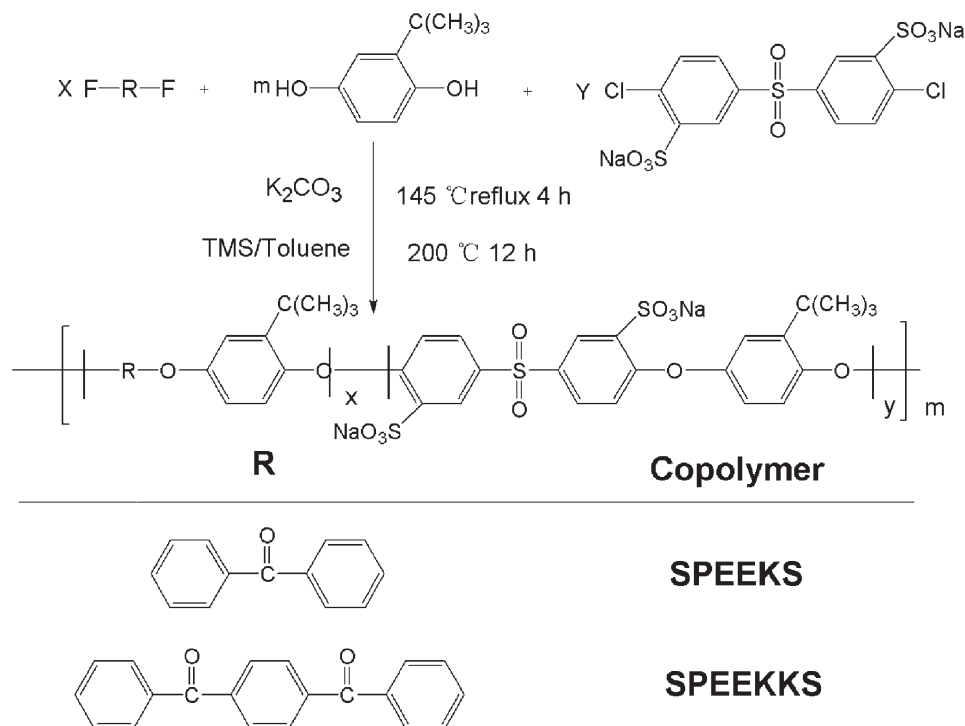
Scheme 1 Synthesis of SPEEKS and SPEEKKS copolymers.

sulfonic acid group to another one. Therefore, the proton conductivity of SPEEKS membranes is higher than that of SPEEKKS membranes at the same DS. However, the length of nonsulfonated segments for SPEEKKS copolymers is longer than that of SPEEKS copolymers, which results in the better mechanical strength than the former one.

In this article, the tertbutylhydroquione (TBHQ) was chosen as a bisphenol monomer, SDCDPS as a sulfonated monomer, and 4,4′-diflouorobenzophenone or 1,4′-bi(4-fluorobenzoyl) benzene as the nonsulfonated monomer. Two series of SPAEKS copolymers with different DS were synthesized by aromatic nucleophilic polycondensation. The structure-properties relationship was established as well as the influence of SPAEKS with different backbone structures on physical and electrochemical behaviors was discussed in detail.

EXPERIMENT

Materials

4,4′-difluorobenzophenone and 1,4′-bi(4-fluorobenzoyl) benzene were purchased from Yanbian Longjing Chemical Factory, China. TBHQ was received from Jiangshu Yancheng Chemical Factory, China. Disodium 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS) was prepared according to the procedures described in our previous work.[18] All the organic solvents were obtained from Beijing Chemi-

cal Company and K_2CO_3 was dried at 120°C for 48 h before use.

Synthesis of SPEEKS and SPEEKKS copolymers

SPEEKS and SPEEKKS copolymers with different DS were synthesized by the aromatic nucleophilic substitution polycondensation. The schematic reaction was shown in Scheme 1. Monomers 4,4′-difluorobenzophenone or 1,4′-bi(4-fluorobenzoyl) benzene, disodium 3,3′-disulfonate-4,4′-dichlorodiphenyl-sulfone, and potassium carbonate were added into a 500-mL three-neck round-bottom flask with an atmosphere of nitrogen inlet, a mechanical stirrer, and a Dean-Stark trap with a reflux condenser. Tetramethylene sulfone (TMS) was used as a solvent and toluene was used as an azeotroping agent. The reaction mixture was refluxed at 145°C for 4 h until water was fully removed from the reaction system by azeotropic distillation, and then the excess toluene was distilled out. The reaction temperature was then slowly raised to 200°C and kept at this temperature for another12 h. After the reaction mixture became highly viscous, TMS was added to dilute the solution, and then the solution was cooled to room temperature. The cooled copolymers with low DS solutions were directly poured into deionized water. While the copolymers with high DS solutions were poured into acetone. The precipitated copolymers

were washed by boiling deionized water several times and dried at 80°C for 48 h.

Preparation of membrane

"The SPEEKS and SPEEKKS membranes in sodium salt form were prepared by casting 10% polymer DMF solutions directly onto a glass plate, followed by vacuum evaporating at 80°C until most of the solvent was removed," in the original manuscript it has been replaced by the sentence "the SPEEKS and SPEEKKS membranes in sodium salt form were prepared by casting 10% polymer DMF solutions directly onto a glass plate, followed by vacuum evaporating at 80°C for 24 h and then were vacuum dried overnight at 120°C until most of the solvent was removed." The transformation from sodium salt form into their acid form was realized by immersing the membranes in deionized water overnight and then soaking in a 2M HCl solutions for 24 h. The resulting membrane in acid form was washed by using deionized water until pH values reached 6–7. The wettest membranes in acid form were vacuum dried at 120°C until the constant weight was obtained, which proved to gain the dry membrane.

Characterization of copolymer

Fourier transform infrared (FTIR) spectroscopy of copolymer were recorded by a Nicolet Impact 410 FTIR spectrometer. Intrinsic viscosities of the samples were measured in DMF solutions with the polymer concentration of 0.5 g/dL at 25°C using an Ubbelohde viscometer. Thermogravimetric analysis (TGA) measurements were performed on a Pyris TGA (Perkin–Elmer). Approximately 5 mg copolymer film samples were preheated at 150°C for 20 min to remove residual water and solvent under the protection of pure N_2. The samples were cooled to 80°C and then reheated to 700°C in air. The heating rate is 10°C/min. Differential scanning calorimetry (DSC) (Mettler Toledo DSC821^e) was used to determine the glass transition temperature (T_g) of copolymer in acid form. The samples were preheated under nitrogen (flow rate, 200 mL/min) from room temperature to 150°C at a heating rate of 20°C/min to remove moisture and eliminate the effects of the thermal history, cooled to 50°C and then reheated from 50 to 300°C at a heating rate of 10°C/min in N_2 atmosphere. The solubility of sulfonated copolymer was determined with the concentration of 10% (w/v) in 20 mL solvents, such as DMF, NMP, DMAC, acetone, methanol, and H_2O.

Mechanical property of membrane

The mechanical strength of the membrane was determined by SHIMADU AG-I 1KN at a tensile speed of 2 mm/min under ambient conditions, the size of samples is 15 mm × 4 mm. Three samples of each membrane were analyzed and average value was obtained.

Water uptake of membrane

The membranes in acid form were vacuum dried at 120°C and weighed as W_{dry}, and then the dry membrane was soaked into deionized water until the constant weight was obtained, which was recorded as W_{wet}. For each sample, at least three measurements were carried out until it reached to a constant value. The water uptake of membrane was calculated using the following eq. (1):

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

Ion-exchange capacity of membrane

Ion-exchange capacity (IEC) value of membranes in acid form was measured by conventional titration method. Membrane was soaked in 1M NaCl solutions for 24 h so that H^+ ions were thoroughly replaced by Na^+ ions. The free H^+ ions were titrated by 0.1M NaOH solutions using phenolphthalein as an indicator. This procedure was repeated at least three times to obtain a satisfactory data reproducibility. The following equation allowed for the calculation of IEC of the membranes:

$$\text{IEC [meq/g]} = \frac{\text{consumed NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}}$$
$$(2)$$

The theoretical IEC values of membranes were calculated using the following formula (3):

$$\text{IEC} = \frac{\text{DS} \times 1000}{M + 80\text{DS}} \qquad (3)$$

where M refers to the molecular weight of nonsulfonated section in each repeat unit.

Microstructure of membrane

The sulfonated copolymer in acid form was immersed in 1M $AgNO_3$ solutions for 24 h to make sure that copolymer in H^+ form was converted completely into Ag^+ form. The copolymer was washed with deionized water and vacuum dried, and then dispersed on copper grid with the concentration of

Polymer	X^a (mmol)	Y^a (mmol)	X/Y	DS (cal)[b]	DS (mea)[c]	Yield (%)	η_{sp} (dL/g)[d]
SPEEKS-1	4	36	1 : 9	0.2	0.18	94	0.76
SPEEKS-2	8	32	2 : 8	0.4	0.37	96	1.0
SPEEKS-3	12	28	3 : 7	0.6	0.53	94	1.64
SPEEKS-4	16	24	4 : 6	0.8	0.75	95	1.75
SPEEKS-5	20	20	5 : 5	1.0	0.93	94	1.68
SPEEKKS-2	8	32	2 : 8	0.4	0.38	95	1.13
SPEEKKS-3	12	28	3 : 7	0.6	0.54	96	1.75
SPEEKKS-4	16	24	4 : 6	0.8	0.75	93	1.98
SPEEKKS-5	20	20	5 : 5	1.0	0.91	92	1.81

[a] The content of sulfonated monomer and nonsulfonated monomer in the reaction.
[b] Degree of sulfonation obtained by calculation.
[c] Degree of sulfonation obtained by titration.
[d] The intrinsic viscosity in DMF at 25°C.

5% DMF solutions for transmission electron microscope (TEM) (JEM-2000EX) analysis.

Proton conductivity of membrane

The proton conductivity (σ) of membrane was determined by AC impedance spectroscopy over a frequency range of 10 Hz–1 MHz using Philips 1260 impedance analyzer. The membrane in acid form was immersed in deionized water overnight to make membrane fully hydrated before measurement. The proton conductivity of hydrated membrane was determined at desired temperature (from 20 to 80°C) under water saturated environment.[19] The proton conductivity was calculated from the measured resistance based on the following eq. (4):

$$\sigma = \frac{l}{RS} \tag{4}$$

where l is the distance between the two electrodes, R is the membrane resistance, and S is the cross-sectional area of membrane.

RESULTS AND DISCUSSION

Synthesis and characterization of copolymers

Two series of sulfonated copolymers with different DS were prepared by nucleophilic polycondensation of TBHQ (monomer Z) with different ratios of sulfonated monomers SDCDPS (monomer X) to nonsulfonated monomers 4,4′-difluorobenzophenone or 1,4′-bi(4-fluorobenzoyl) benzene (monomer Y) in a TMS/toluene system (Scheme 1). The detailed synthesis procedure was reported in our previous work.[10] The polymerization results and data were listed in Table I. It can be seen that all sulfonated copolymers are high intrinsic viscosities corresponding to high molecular weight and can be cast into tough membrane. However, 4,4′-difluorobenzophenone or 1,4′-bi(4-fluorobenzoyl) benzene as nonsulfonated monomer is

more reactive than SDCDPS monomer in TMS system. So, the formation of a slight block like structure of SPAEKS copolymers was not avoided during the random copolymers preparation.[20]

The successful introduction of sodium sulfonate groups to the copolymer chains was confirmed by FTIR spectroscopy, as shown in Figure 1. The characteristic absorption peaks at 1079 and 1023 cm^{-1} correspond to asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups, respectively. The S=O stretching band of sodium sulfonate groups was observed at 1233 cm^{-1}. These results confirmed that the sodium sulfonate groups were surely incorporated into the copolymers as expected.

Thermal property and solubility of copolymers

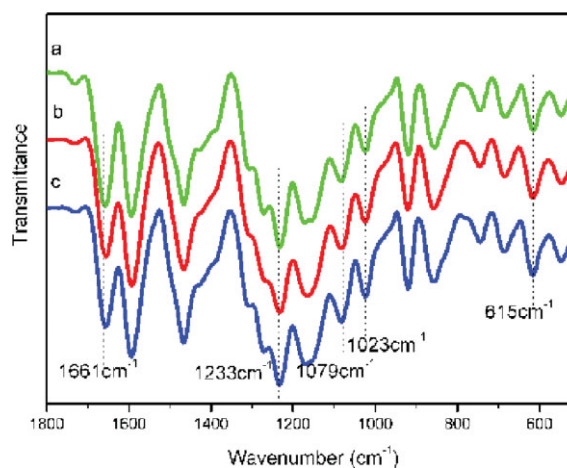The thermal property of copolymer was analyzed by TGA and DSC instruments. The TGA and DSC

Figure 1 FTIR spectra of SPEEKS-2 (line a), SPEEKS-3 (line b), and SPEEKKS-3 (line c) copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
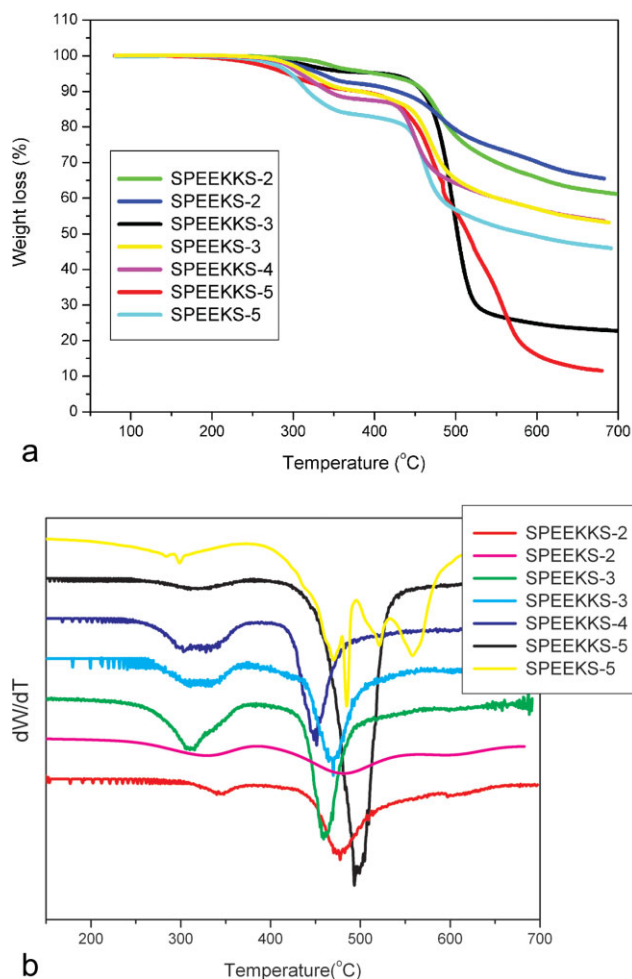
Figure 2 The TGA curves (a) and derivative curves (b) of SPEEKS and SPEEKKS copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

curves of copolymers in acid form were shown in Figures 2 and 3, respectively. Figure 2(a) shows that the degradation of all copolymers in acid form has two steps. The first weigh loss was observed around 220°C, which was assigned to the separation of sulfonic groups. The second weigh loss at around 420°C was attributed to the decomposition of copolymer backbone. Figure 2(b) shows that the onset weight loss temperatures (T_{onset}) of all copolymers in acid forms are observed between 278 and 340°C. The temperature of the onset weight loss gradually decreased with increasing DS. Most importantly, all temperatures of weight loss are higher than 250°C, which meet thermal request of PEMFC. The T_gs of copolymers in acid form were detected by DSC. The measurements were conducted from 50 to 300°C at a heating rate of 10°C/min and the results were listed in Figure 3. It can be seen that from Figure 3 that there is only one single T_g on each curve. It proved that all sulfonated copolymers were amorphous. The T_g of all samples in acid form was above 150°C and

the T_g increased with the DS increasing. It is because that the sulfonic group is a larger pendant group, which can hinder molecular internal rotation and also enhance intermolecular interaction. Whereas the T_g was not observed on DSC curves of SPEEKS-5 and SPEEKKS-5. This may be due to the fact that the T_g is higher than 300°C or the temperature of sulfonic group degradation is lower than T_g of copolymers.

All sulfonated copolymers exhibited good solubility in polar aprotic solvents with higher donor number such as NMP, DMF, and DMAC due to the larger pendant groups of TBHQ, which facilitates the solvent molecules entering into copolymers. Also, all copolymers do not dissolve in polar solvents with higher acceptor number such as water, methanol, and acetone. The solubility of sulfonated copolymers in polar solvent with higher donor number decreased with the increasing DS because of the strong affinity between sodium sulfonate groups in the same series. In a word, the solubility of SPEEKS copolymers is identical with that of SPEEKKS copolymers at the same DS.

Morphology of membrane

The physical and electrochemical property of membranes depends on their microstructure. For random sulfonated hydrocarbon copolymers, sulfonic groups aggregate into hydrophilic ionic domains contributing to transport proton and the nonsulfonated copolymers backbone form hydrophobic domains relating to their mechanical strength. To study the morphology of the membranes, some researchers have used AFM, TEM, SAXS,[21–23] etc. In this article, the microstructure of the membranes was analyzed by TEM. The ionic group sites in membrane were
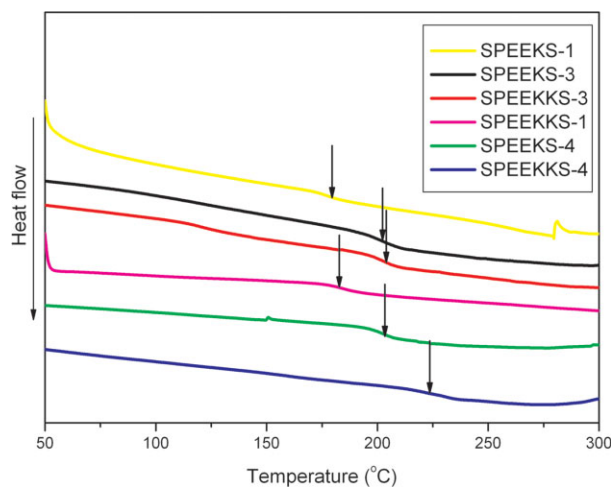

Figure 3 The DSC curves of SPEEKS and SPEEKKS copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
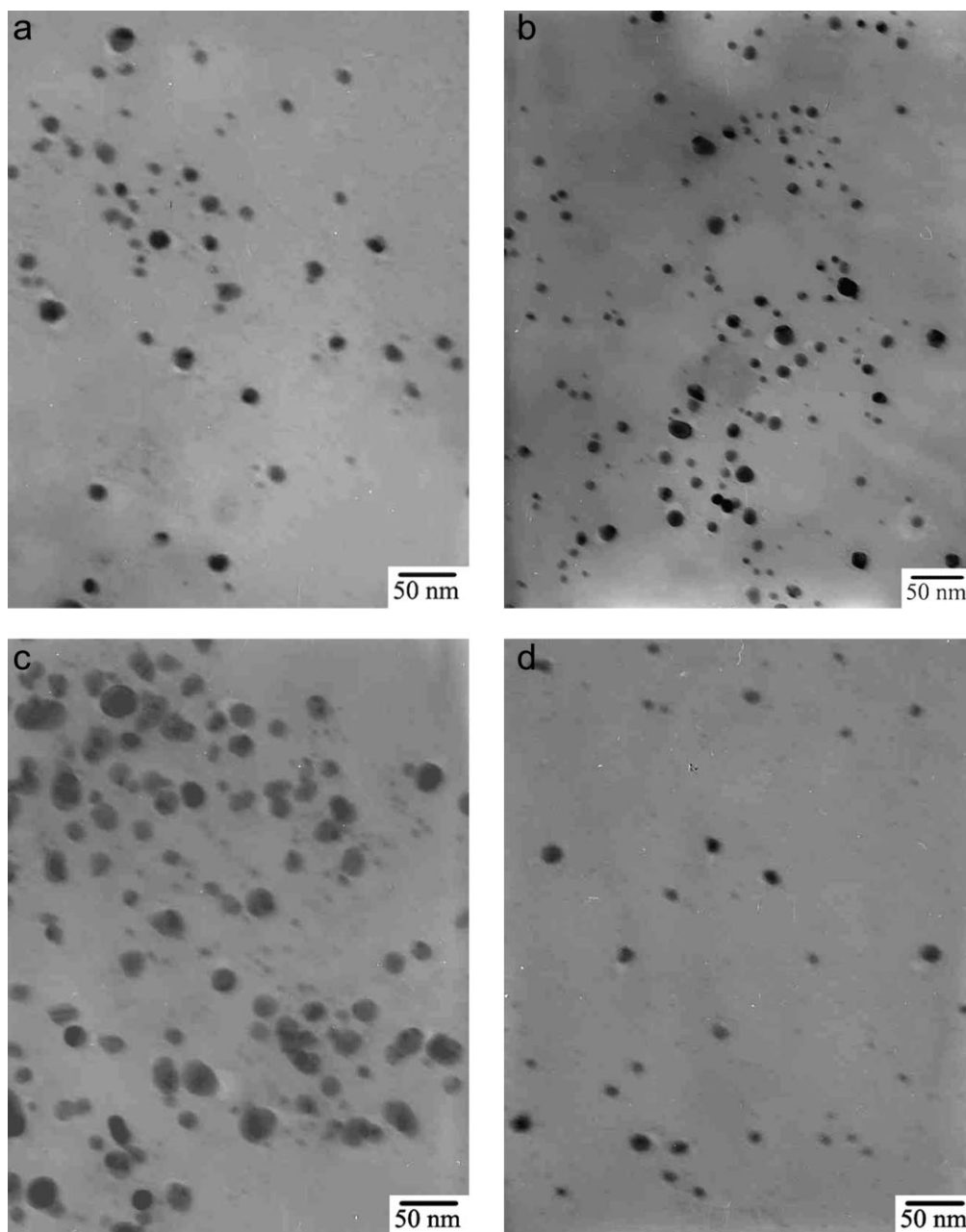
Figure 4 TEM micrographs of SPEEKS and SPEEKKS membranes: (a) SPEEKS-3; (b) SPEEKS-4; (c) SPEEKS-5; (d) SPEEKKS-3.

observed using Ag^+ to chelate with sulfonic groups because Ag^+ gives a good contrast to the micrograph. The TEM pictures of membranes were shown in Figure 4 and the dark domains refer to hydrophilic sulfonic groups, while the light domains represent hydrophobic copolymer backbone. It can also be seen that the sulfonic groups randomly distribute in copolymer matrix. With increasing DS, the density and the size of the sulfonic group become larger. This indicated that copolymers with high DS have more and larger ionic domains. Moreover, the density of sulfonic group in SPEEKS membranes was higher than that of SPEEKKS membranes at the

same DS because the distance between adjacent sulfonic groups in SPEEKS membrane was closer than that of SPEEKKS membrane. This also explained why the water uptake and proton conductivity of membrane increased with increasing DS in the same series while the water uptake and proton conductivity of SPEEKS membrane were higher than those of SPEEKKS membrane at the same DS.

The mechanical property of membrane

The mechanical strength of self-synthesized membranes and Nafion® 117 were measured by tensile

TABLE II
The Mechanical Property of SPEEKS and SPEEKKS Membranes

Polymer	Tensile strength (MPa)	Maximum elongation (%)	Tensile modulus (GPa)
SPEEKS-1	54.9 ± 1.02	9.01 ± 0.74	1.93 ± 0.042
SPEEKS-2	49.3 ± 0.83	10.56 ± 1.15	1.74 ± 0.051
SPEEKS-3	48.2 ± 0.76	8.29 ± 0.56	1.55 ± 0.062
SPEEKS-4	47.0 ± 1.24	7.18 ± 0.78	1.39 ± 0.055
SPEEKS-5	45.0 ± 0.96	7.01 ± 0.47	1.23 ± 0.037
SPEEKKS-2	58.7 ± 0.53	9.06 ± 1.06	1.83 ± 0.097
SPEEKKS-3	52.3 ± 1.11	7.94 ± 0.97	1.72 ± 0.120
SPEEKKS-4	49.7 ± 1.05	6.85 ± 0.48	1.53 ± 0.083
SPEEKKS-5	46.6 ± 0.66	5.52 ± 0.28	1.33 ± 0.072

tests at ambient conditions with relative humidity 45% and the results were listed in Table II. It can be seen that the SPEEKS and SPEEKKS membranes exhibit good mechanical properties. It indicates that they are tough enough to be performed as a functional membrane material. The tensile strength and tensile modulus of all prepared membranes were much better than those of Nafion® 117. However, their elongation was lower than that of Nafion® 117 because of the rigid backbone of SPAEKS membrane. The mechanical performance of SPEEKKS membrane was better than that of SPEEKS membrane at the same DS because of the longer length hydrophobic nonsulfonated backbone segments in SPEEKKS membranes.

Water uptake and ionic exchange capacity of membrane

Water management plays a critical role in mechanical performance and proton conductivity of membrane. Low water management of Nafion® at high temperature resulting in low proton conductivity was one of the drawbacks, which limited their further commercial application. Therefore, polymer electrolyte membrane with low water uptake together with high proton conductivity is desirable for PEMFC application. The water uptake of membrane was measured from 25 to 80°C and the results were displayed in Figure 5. The water uptake of membrane increased with increasing DS and temperature. But the excessive swelling of SPEEKS-5 membrane at high temperature (water uptake is 108% at 80°C) lost its mechanical performance and retarded its application. We also found that the water uptake of SPEEKS membrane was higher than that of SPEEKKS membrane at the same DS because the distance between two adjacent sulfonic groups in SPEEKS membrane is relatively shorter in each repeat unit, which facilities water molecules transporting in membrane.

IEC is usually defined as the mole of fixed SO_3 sites per gram copolymer. The IEC values of membrane were determined by titration and calculation. The results were shown in Table III. It was observed that SPEEKS and SPEEKKS membranes had relatively high theoretical and experimental IEC values because of the simple chemical structure of TBHQ monomer. We also found that experimental IEC values were consistent with the calculated IEC ones, which indicated all sulfonated monomers were incorporated into the copolymers via direct polycondensation method.

Proton conductivity of membrane

The proton conductivity of electrolyte membrane is particularly important for PEMFC since the aim of polyelectrolyte membrane is transporting proton. Different results will be obtained using different measured methods and instruments. In this work, Nafion® 117 was selected as a reference to compare the proton conductivity with the synthesized
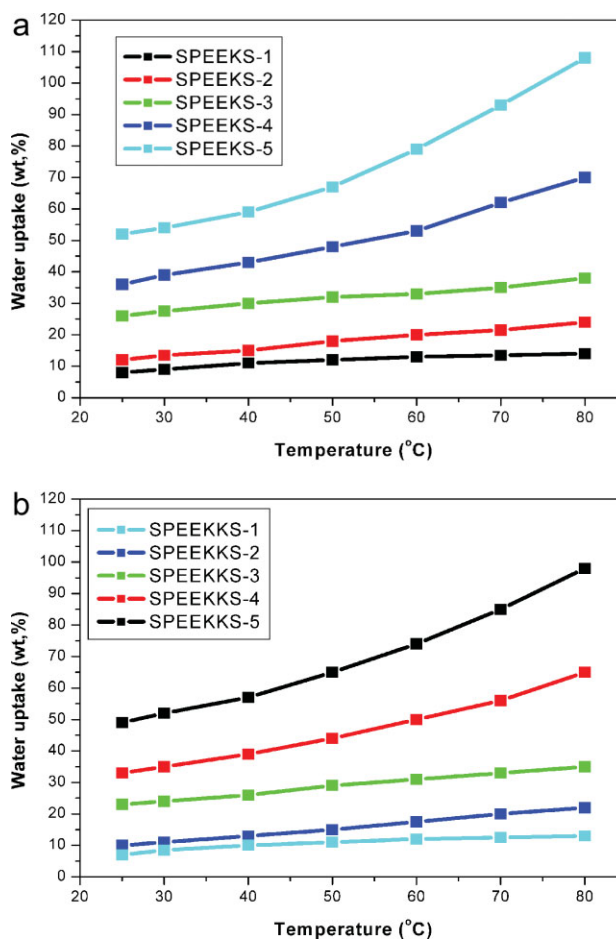

Figure 5 The water uptakes of SPEEKS (a) and SPEEKKS (b) membranes from 25 to 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
The Properties of SPEEKS and SPEEKKS Membranes

Polymer	d^a (μm)	IEC (mmol/g)		Water uptake (%)	
		Calculated[b]	Measured[c]	25°C	80°C
SPEEKS-1	85	0.55	0.48 ± 0.01	8 ± 0.53	14 ± 0.98
SPEEKS-2	90	1.04	0.93 ± 0.01	12 ± 0.76	24 ± 1.14
SPEEKS-3	88	1.49	1.31 ± 0.02	26 ± 0.98	38 ± 1.25
SPEEKS-4	92	1.89	1.74 ± 0.04	36 ± 1.06	70 ± 1.37
SPEEKS-5	85	2.26	2.03 ± 0.08	52 ± 1.08	108 ± 2.06
SPEEKKS-2	85	0.86	0.80 ± 0.03	10 ± 0.87	22 ± 0.92
SPEEKKS-3	88	1.26	1.17 ± 0.04	23 ± 0.96	35 ± 0.78
SPEEKKS-4	90	1.65	1.50 ± 0.06	33 ± 0.76	65 ± 1.34
SPEEKKS-5	85	2.02	1.82 ± 0.06	49 ± 1.23	98 ± 1.65

[a] Thickness of membranes.
[b] IEC obtained by calculation from DS.
[c] IEC obtained by titration.

membranes. The proton conductivities of fully hydrated membranes were calculated from AC impedance spectroscopy measurement in the temperature range of 25–80°C and the results were illuminated in Figure 6. As we can see, most of the proton conductivities of SPEEKS and SPEEKKS membranes were lower than that of Nafion® 117 at the same testing temperatures. However, all the proton conductivities of synthesized membranes were still higher than 0.01 S/cm, which meet the least requirement for PEMFC.[19,24] Moreover, the proton conductivity of membrane increased with increasing DS and temperature. The proton conductivity of SPEEKS-5 membrane was greater than that of Nafion® 117 at 80°C. This might be attributed to the increasing of size and density of ion domains when DS increases, which can be concluded from TEM micrograph. Also, the speed of H⁺ transmitting in membrane was fastened with increasing temperature, which greatly improved the proton conductivity. The proton conductivity of SPEEKS-5 membrane reached 0.083 S/cm at 80°C, but excessive swelling seriously destroyed its mechanical strength, which limited its application as PEMFC membrane. Therefore, polyelectrolyte membranes have not only high proton conductivity but also good mechanical strength. It was noticeable that the proton conductivity of SPEEKS membrane was higher than that of SPEEKKS membrane at the same DS. This might be interpreted by two reasons. Firstly, the sulfonic groups on SPEEKS membrane were relatively concentrated than SPEEKKS membrane, which may easily aggregate into proton transporting channel. Secondly, the IEC values of SPEEKS membrane were higher than those of SPEEKKS membrane at the same DS. The proton conductivity of SPEEKKS-4 membrane with good mechanical strength reaches 0.046 S/cm at 25°C and 0.061 S/cm at 80°C as well as it is inexpensive and promising in practical
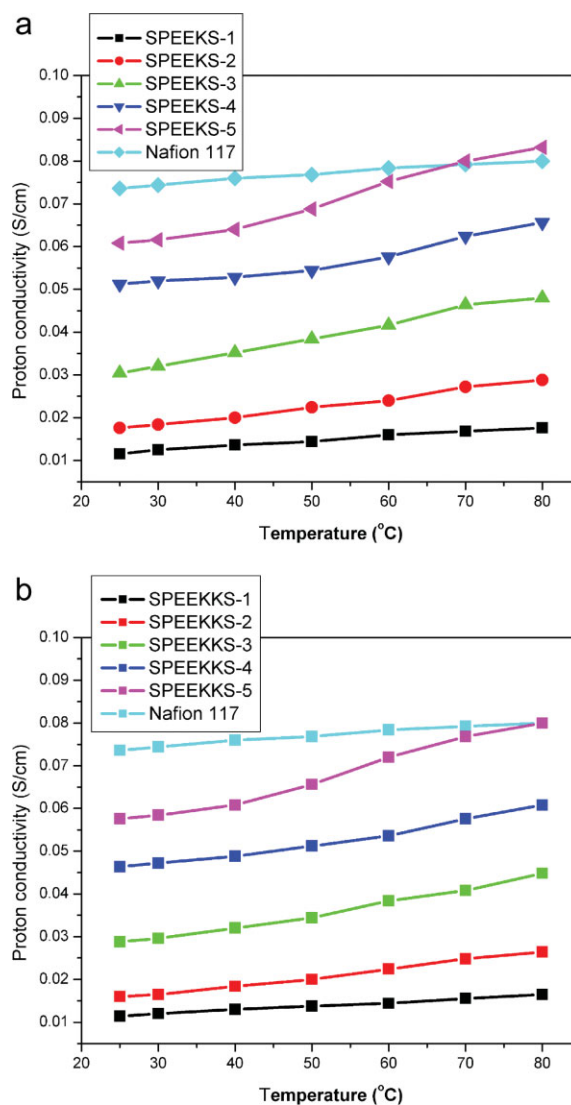

Figure 6 The proton conductivities of SPEEKS (a) and SPEEKKS (b) membranes from 25 to 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

application. It was concluded that the prospects of application of SPEEKKS-4 membrane in PEMFC.

CONCLUSIONS

Two series of SPEEKS and SPEEKKS copolymers with different DS were successfully prepared by direct polycondensation methods. The difference of physical and electrochemical properties between SPEEKS and SPEEKKS membrane was fully investigated. The water uptake, IEC, and proton conductivity of SPEEKS membranes were higher than those of SPEEKKS membranes, while the mechanical strength of SPEEKKS membrane was better than that of SPEEKS membrane at the same DS. The relationship between the performance and the microstructure was established. The SPEEKKS-4 membrane with conductivity of 0.061 S/cm at 80°C has good mechanical strength. These studies display the possibility of synthesized low-cost PEM for fuel cell applications.

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