

Sulfonated Poly(ether ether sulfone) Copolymers for Proton Exchange Membrane Fuel Cells

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ABSTRACT: Novel aromatic sulfonated poly(ether ether sulfone)s (SPEESs) with *tert*-butyl groups were synthesized by aromatic nucleophilic polycondensation of disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS), 4,4'-dichlorodiphenylsulfone (DCDPS), and *tert*-butylhydroquinone (TBHQ). The resulting copolymers showed very good thermal stability and could be cast into tough membranes. The morphology of the membranes was investigated with atomic force microscopy. The proton conductivity of SPEES-40

membranes increased from 0.062 S/cm at 25°C to 0.083 S/cm at 80°C, which was higher than the 0.077 S/cm of Nafion 117 under the same testing conditions. These copolymers are good candidates to be new polymeric electrolyte materials for proton exchange membrane fuel cells. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1443–1450, 2007

Key words: sulfonated poly(ether ether sulfone)s; membranes; proton conductivity; fuel cell

INTRODUCTION

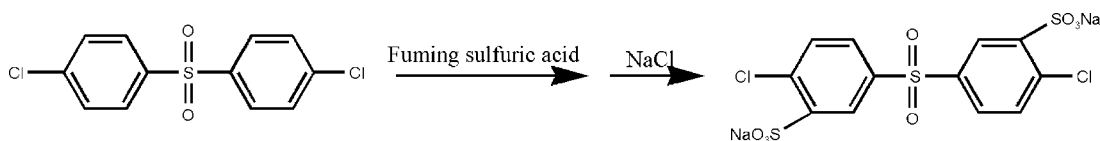
A proton exchange membrane fuel cell (PEMFC) is an attractive energy conversion device for portable power applications. As one of the key elements in a PEMFC system, a proton exchange membrane (PEM) is sandwiched between two platinum-porous catalytic electrodes (namely, an anode and a cathode) and functions as an electrolyte for transferring protons from the anode to the cathode as well as providing a barrier to the passage of electrons and to cross leakage of gas between the electrodes.^{1,2} Currently, typically used membrane materials for PEMFC are perfluorinated copolymers (such as Nafion[®]) because of their excellent mechanical properties and chemical stability. However, very high cost, poor water management capability, and loss of proton conductivity at temperatures above 80°C as well as high methanol permeability limit their commercial development.^{3,4}

However, sulfonated derivatives of aromatic polymers, such as polybenzimidazole (PBI), poly(ether ether ketone) (PEEK), and poly(arylene ether sulfone) (PAES) have been widely investigated as PEM materials because they have excellent chemical stability and good mechanical properties and are lower in cost.^{5–12} Poly(ether ether sulfone) (PEES), one type of thermal plastic, is well known for having excellent thermal and mechanical properties as well as being

resistance to oxidation and having stability under acidic conditions. SPEES membranes may be used as proton exchange membranes. Sulfonated copolymers may be obtained either by postsulfonation of the polymers or by polycondensation of sulfonated monomers with other nonsulfonated aromatic monomers. The latter method has been proved to be more advantageous than postsulfonation. Some of the advantages are: (1) position and content of sulfonated groups can easily be controlled and (2) crosslinking and other side reactions can be avoided.^{13–15} Therefore, in our work, a series of SPEES copolymers with different degrees of sulfonation (DS) were prepared by direct polycondensation of sulfonated monomers (SDCDPS) with nonsulfonated monomers (DCDPS) and *tert*-butylhydroquinone (TBHQ).

Proton conductivity is the foremost criterion for proton exchange membranes. Without sufficient proton conductivity, a membrane can never be applicable to PEMFC. This article describes our efforts to increase the proton conductivity of membranes by incorporating *tert*-butyl groups in the SPEES copolymers. *Tert*-butyl groups force chains farther apart in copolymers, generate unoccupied volume in the form of pores lined with sulfonic acid groups, and form proton transport pathways, which should absorb water very strongly and keep conductivity relatively high even at low humidity and temperature. We also investigated the influence of *tert*-butyl groups on the water uptake and proton conductivity of membranes at different temperatures. The relationship between morphology and property was established by atomic force microscopy (AFM).

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Scheme 1 Synthesis of disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS).

EXPERIMENTAL

Materials

4,4'-Dichlorodiphenylsulfone (DCDPS; supplied by Longjing Chemical Plants, Jilin, China) and *tert*-butylhydroquinone (TBHQ; Yancheng Chemical Plant, Jiangsu, China) were used as received. Potassium carbonate was dried at 180°C for 10 h before use. Fuming sulfuric acid (30% SO₃) and other organic solvents were obtained commercially and used without further purification.

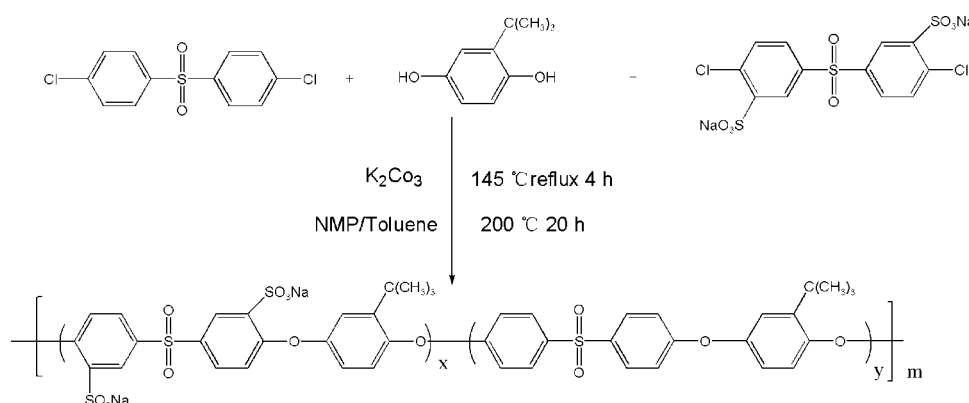
Preparation of sulfonated monomers and copolymers

Synthesis of disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) monomers. Sulfonation is an aromatic electrophilic reaction. A powered sulfonating agent [fuming sulfuric acid (30% SO₃)] and elevated temperature (110°C) are required for the sulfonation reaction because DCDPS has two electron-withdrawing groups in each phenyl ring. Therefore, DCDPS (114 g, 0.4 mol) was dissolved in fuming sulfuric acid containing 30 wt % SO₃ (160 mL), reacted for 6 h at 110°C, and cooled to room temperature. The reacted acidic solution was slowly added to ice water. To neutralize the excess fuming sulfuric acid, 260 g of NaOH solids was added. The mixture was cooled to room temperature again, and the subsequent addition of 130 g of NaCl resulted in a white precipitate, which was filtered and dried. The recovered monomers were recrystallized from an ethanol/water (4 : 1) mixture, filtered and dried in a vacuum oven at 100°C for 24 h, and then stored at room temperature.

The yield of the white needle-shaped product was 75%. This process is shown in Scheme 1.

Synthesis of SPEES copolymers. SPEES copolymers with different degrees of sulfonation were synthesized via an aromatic nucleophilic polycondensation reaction with SDCDPS (monomer X), DCDPS (monomer Y), and TBHQ (monomer Z) in the presence of potassium carbonate in *N*-methyl-2-pyrrolidone (NMP) with toluene as an azeotroping agent (Scheme 2). Polymerization was carried out in a 500-mL, three-necked, round-bottomed flask fitted with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap with a reflux condenser. The mixture was refluxed for 4 h at 140°C until water was removed from the reaction mixture by azeotropic distillation; then the excess toluene was distilled out, and the temperature of the reaction mixture was slowly raised to 190°C, at which it was maintained for 20 h. After the solution became highly viscous, NMP was added to dilute the reaction, it was cooled to room temperature, and the copolymers were poured into deionized water. The recovered copolymers were dried at room temperature for 2 days and in a vacuum oven at 80°C for an additional day.

Membrane preparation. Approximately 2 g of the dried copolymers in sodium salt form was dissolved in 20 mL of NMP solvents. The solution was cast directly onto a glass plate, which was then heated at 80°C for 2 days until most of the solvent was removed. The SPEES membranes were torn off the glass plate to obtain membranes in sodium form. Membranes in acidic form were obtained by immersing the membranes in sodium form in a 2 M HCl solution for 24 h, followed



Scheme 2 Synthesis of SPEES copolymers.

by washing with deionized water until the pH reached 6–7. The thickness of all membranes was in the range of 80–100 μm .

Characterization

FTIR spectroscopy

FTIR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer, using either a membrane sample or KBr pellets composed of 50 mg of IR spectroscopic-grade KBr and a 1-mg sample of copolymer.

Intrinsic viscosity

To determine intrinsic viscosity, 25-mg samples of SPEES copolymers were dissolved in 50 mL of DMF and filtered. The intrinsic viscosity of the samples was measured in DMF at 25°C using an Ubbelohde viscometer.

Thermal properties of SPEES copolymers

Thermogravimetric analysis. A Pyris 1 thermogravimetric analyzer (TGA; Perkin Elmer) was used to study the thermal stability behavior of the SPEES copolymers. First 5- to 10-mg samples of the copolymers were heated to 150°C and kept at that temperature for 20 min in order to remove any residual water or solvent remaining in the copolymers in N_2 . The samples were cooled to 80°C and then reheated to 700°C at a rate of 10°C/min, and the temperature at which 5% weight loss occurred for each material was recorded, from which onset of first weight loss was extrapolated.

Differential scanning calorimetry. A METTLER 821^e model differential scanning calorimeter (DSC) was employed to determine the glass-transition temperatures (T_g) of the SPEES samples. The samples were preheated under nitrogen at 200 cc/min from room temperature to 150°C at a rate of 20°C/min in order to remove moisture and to avoid the effects of the thermal history, cooled to 50°C, and then reheated to 300°C at a rate of 10°C/min.

Atomic force microscopy

An understanding of the morphology of the hydrophilic and hydrophobic phases of the SPEES copolymers was gained through an investigation using tapping mode atomic force microscopy (TM-AFM), with a SPA300HV/SPI3800N Probe Microscope (Seiko Instruments Inc., Japan) in tapping mode. A silicon microcantilever (spring constant 2 N/m, resonance frequency 70 kHz; Olympus Co., Japan) with an etched conical tip (radius of curvature 40 nm as characterized by scanning over a very sharp needle array, NT-MDT;

Russia) was used for the scan. The scan rate ranged from 1.0 to 2.0 Hz in order to optimize the image quality. Each scan line contained 256 pixels, and an entire image was composed of 256 scan lines. The membranes were obtained by spin-coating a copolymer solution in 0.05 g/mL DMF onto a freshly cleaned silicon wafer at 3000 rpm for 50 s at room temperature. All samples were dried at 80°C for 24 h under vacuum conditions and were allowed to equilibrate by exposure to 35% relative humidity at room temperature for 2 h before testing. The samples were then imaged immediately in a relative humidity of about 35%.

Ion-exchange capacity

Measurement of ion-exchange capacity (IEC, meq of $\text{SO}_3\text{H/g}$) was performed according to the following procedures. Membranes in acidic form were immersed into 50 mL of 1M NaCl solution for 1 day to allow H^+ to exchange with Na^+ . The released H^+ was titrated with a 0.1M NaOH solution. From the consumed NaOH, the ion-exchange capacity of a membrane was calculated according to eq. (1).¹⁶

$$\text{IEC} = \frac{\text{Consumed NaOH} \times \text{molarity NaOH}}{\text{Weight dried membrane}} \text{ [meq/g]} \quad (1)$$

The theoretical IEC values calculated from the degrees of sulfonation were obtained from eq. (2):

$$\text{IEC} = \frac{\text{DS} \times 1000}{380 + 80 \text{ DS}} \quad (2)$$

Water uptake

After membranes were acidified, the membranes were vacuum dried overnight at 120°C, the drying membranes were repeatedly weighed (W_{dry}) until constant. The membranes were then immersed in deionized water for 2 days before being removed. Surface-attached water was quickly removed with tissue paper, and the weight of the wet membranes (W_{wet}) was determined. Water uptake by the membranes was calculated with eq. (3).¹⁷

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (3)$$

Proton conductivity

The proton conductivity of the membranes was determined by Ac impedance spectroscopy using a Princeton Applied Research Model 273A potentiostat with a Model 5210 Frequency Response Detector (EG&G PARC, Princeton, NJ) from 100 mHz to 100 KHz. All membranes were initially hydrated by immersion in deionized water for 24 h at room temper-

TABLE I
Data on SPEES Copolymers

Copolymer	X (mmol) ^a	Y (mmol) ^a	X/Y	DS (cal) ^b	DS (mea) ^c	Yield (%)	η_{sp}/c^d
PEES	0	40	0 : 10	0	0	96	0.64
SPEES-10	4	36	1 : 9	0.2	0.17	95	0.84
SPEES-20	8	32	2 : 8	0.4	0.39	93	1.07
SPEES-30	12	28	3 : 7	0.6	0.55	94	1.37
SPEES-40	16	24	4 : 6	0.8	0.73	92	1.52

^a X and Y are the molar numbers of the sulfonated monomer SDCDPS and the nonsulfonated monomer DCDPS in the reaction.

^b Degree of sulfonation obtained by calculation.

^c Degree of sulfonation obtained by titration.

^d Intrinsic viscosity in DMF at 25°C.

ature. Measurement of the conductivity of fully hydrated membranes was performed with the cell immersed in water.¹² All impedance measurements were performed at temperatures from 25°C to 80°C in deionized water. Proton conductivity (σ) of membranes in the acidic form was calculated from the resistance according to eq. (4):

$$\sigma = \frac{d}{RS} \quad (4)$$

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

RESULTS AND DISCUSSION

Synthesis and characterization of SPEES copolymers

A series of samples was prepared by aromatic nucleophilic polycondensation of monomers TBHQ (monomer Z) with differing ratios of the sulfonated monomer SDCDPS (monomer X) to the nonsulfonated monomer DCDPS (monomer Y) in an NMP/toluene solvent system. The polymerization results and analytical data are given in Table I. The intrinsic viscosity of the copolymers, which indicated that they were high in molecular weight, increased as the sodium sulfonate group content increased. This was because (1) the electron-withdrawing sodium sulfonate group increased the positive charge density of the carbon atom connected to the chlorine atom and thus enhanced the electrophilic reactive activity and (2) the steric hindrance of the sodium sulfonate group decreased the reactive activity, with the former factor probably the dominant influence on this reaction. Therefore, the intrinsic viscosity of the copolymers increased with increasing DS. Moreover, it can be seen from Table I that the DS measured by titration accorded with the calculated DS, indicating DS could be readily controlled by varying the feed ratio of sulfonated monomers to nonsulfonated monomers. This has the advantage over the postsulfonated reaction of introducing sulfonic groups into the copolymers

without a sulfonation degradation reaction on the polymer chain by direct copolymerization.

The successful introduction of the sodium sulfonate groups into SPEES copolymers was confirmed by Fourier transform infrared (FTIR) spectroscopy (Fig. 1). Strong characteristic peaks at 1102 and 1027 cm^{-1} could be assigned to asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups. The S—O stretching of sodium sulfonate groups and the asymmetric sulfonated arylene ring peak were observed at 688 and 1235 cm^{-1} , respectively. As expected, the results confirmed that the sulfonate groups were indeed incorporated into the copolymers.

Thermal properties of SPEES copolymers

The thermal stability of the SPEES copolymers in sodium and acidic forms was investigated by TGA analysis. TGA measurements were conducted from 80°C to 700°C at a heating rate of 10°C/min. The results, given in Table II, show that the temperature of 5% weight loss ($T_{d5\%}$) and the temperature of extrapolated onset for first weight loss (T_d) of the SPEES

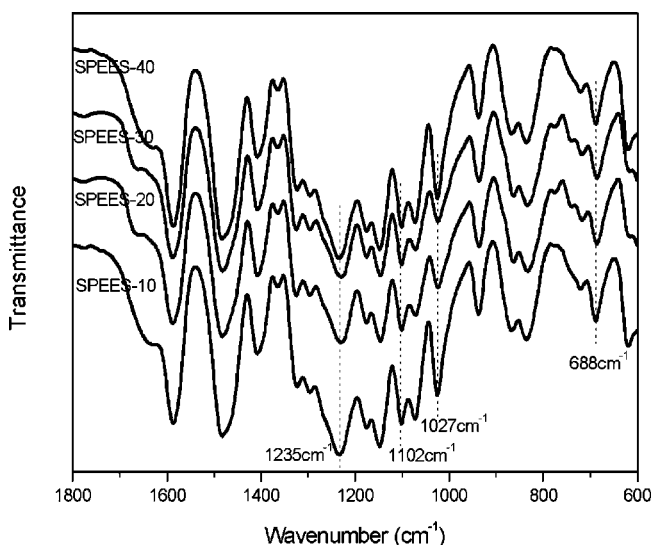


Figure 1 FTIR of SPEES copolymers.

TABLE II
Thermal Properties of SPEES Copolymers

Copolymer	T_g (°C)		$T_{d5\%}$ (°C) ^b		T_d (°C) ^c	
	Sodium form	Acidic form	Sodium form	Acidic form	Sodium form	Acidic form
SPEES-0	172	172	470	470	496	496
SPEES-10	181	175	463	408	479	318
SPEES-20	198	189	454	342	473	309
SPEES-30	220	210	425	311	461	306
SPEES-40	— ^a	— ^a	292	300	454	303

^a Not detected from 50°C to 300°C.

^b Temperature of 5% weight loss.

^c Temperature of extrapolated onset for first weight loss.

copolymers in sodium form were observed from 463°C to 292°C and from 479°C to 454°C, respectively. The copolymers were observed to have lower $T_{d5\%}$ and T_d values in acidic form than in sodium form, in the range of 408°C–300°C and 477°C–450°C, respectively. The TGA curves of copolymers in sodium and acidic forms are displayed in Figures 2 and 3. Copolymers in sodium form exhibited only one weight-loss step in their TGA curves, attributed mainly to the decomposition of the copolymer backbone. Compared with copolymers in sodium form, copolymers in acidic form exhibited much earlier decomposition before the copolymer backbone decomposed, which was assigned to the decomposition of sulfonic groups. Moreover, the TGA results indicate the $T_{d5\%}$ of copolymers in both sodium and acidic forms gradually decreased with increasing DS. For SPEES-20 copolymer in sodium form, the first weight loss began around 454°C, whereas for the SPEES-20 copolymer in acidic form the first weight loss began around 242°C because of decomposition of sulfonic groups. It can be seen from these results that

SPEES copolymers in sodium form had much higher thermal stability than the corresponding SPEES copolymers in acidic form. But the thermal stability of SPEES in acidic form was satisfied with requests of PEM.

The glass-transition temperatures (T_g s) of the SPEES copolymers were measured using DSC. Figure 4 shows that all samples were amorphous, and only a single T_g was discernible on each curve. The obtained T_g s are listed in Table II. All the SPEES copolymers had a T_g between 181°C and 220°C in sodium form and a T_g between 175°C and 209°C in acidic form. It was observed that the T_g of copolymers in both sodium and acidic forms showed an increase from SPEES-10 to SPEES-30 and was higher than that of pure PEES copolymer. The introduction of sodium sulfonate groups had two effects on the glass-transition temperature: first, intermolecular interaction was increased by pendant ions, that is, the ionomer effect; and second, molecular bulkiness was enhanced. Both effects hindered internal rotation and increased the glass-transition temperatures of sulfonated copolymers, especially of the SPEES-40

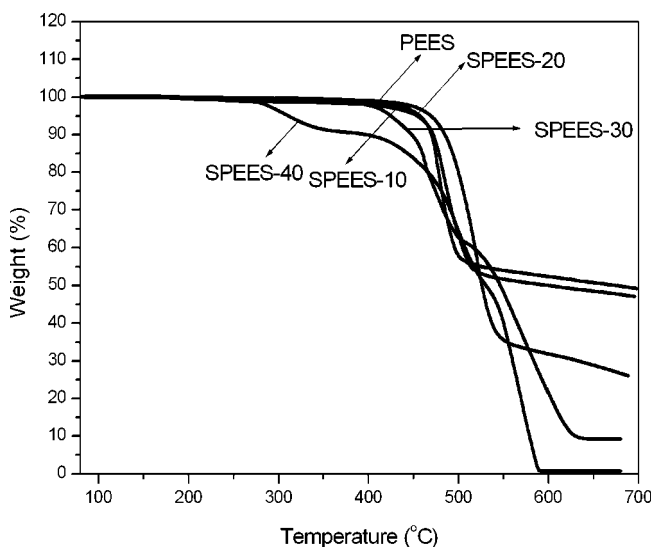


Figure 2 TGA curves of PEES copolymer and SPEES copolymers in sodium form.

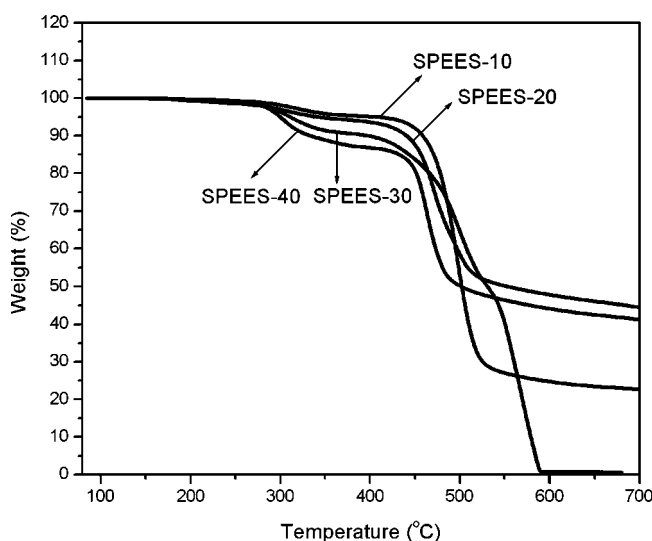


Figure 3 TGA curves of all SPEES copolymers in acidic form.

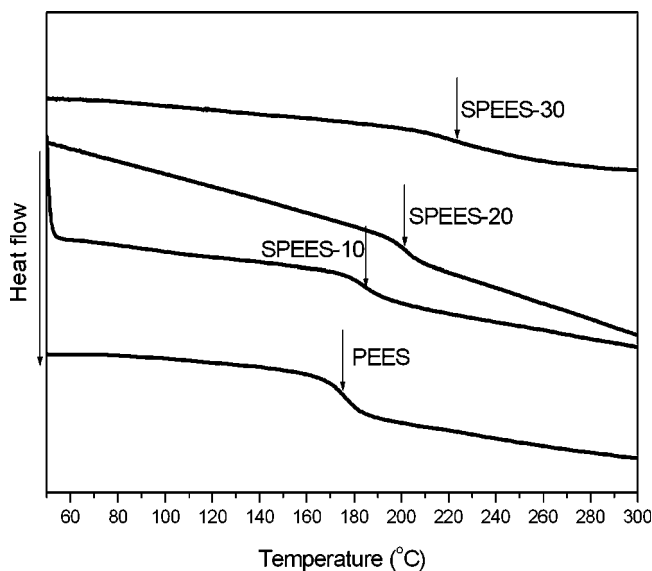


Figure 4 Glass-transition temperatures of PEES copolymer and SPEES copolymers.

copolymer, for which no glass-transition temperature was observed in the range of 50°C–300°C. This indicated that the strong intermolecular interaction led to a stiffer polymer segment and the glass transition should have occurred above 300°C.

Ion exchange capacities of SPEES membranes

The ion exchange capacities (IEC) of the SPEES membranes are shown in Table III. It can be seen that SPEES membranes possessed relatively high theoretical ion exchange capacity and that the IEC increased with increasing DS. The experimental IEC values were in good agreement with the IEC values from eq. (2), assuming that almost all the sulfonated monomers were incorporated into the copolymers by polycondensation of sulfonated monomers with non sulfonated monomers without any side reactions, which often was observed with the postsulfonation method.

Morphology, water uptake, and conductivity of SPEES membranes

Previous studies have used small-angle X-ray scattering, AFM, transmission electron microscopy, and other methods to extensively investigate the relationship between the morphology and properties of membranes.^{6,7,18} In the present study, tapping-mode phase images of the SPEES membranes were recorded under ambient conditions on a 2 × 2 dm²-size scale.

Water uptake by membranes is known to have an important effect on their conductivity and mechanical properties.¹⁸ The proton-exchanging reaction requires enough water to coordinate with protons as it moves through the membrane. Water uptake of all membranes

in acidic form was measured at room temperature, and the results are given in Table III, which shows that water uptake of all SPEES membranes increased with increasing DS because of the strong hydrophilicity of the sulfonic groups. The water uptake of the SPEES membranes increased from 11% for SPEES-10 to 28% for SPEES-30 and increased rapidly to 52% for SPEES-40. The related sulfonated poly(arylene ether sulfone) (SPAES) membrane system was not observed to have any linear water uptake behavior.¹⁹ These aspects were well explained by the morphologies of membranes.

The tapping mode, phase-image atomic force micrographs shown in Figure 5 indicate that all the samples had hydrophilic/hydrophobic domain morphologies, represented by dark and light regions, respectively. In these tapping-mode images, the darker regions were the hydrophilic phases, which absorbed a small amount of water and were lower in modulus than the non-water-absorbing hydrophobic phases, which appeared as lighter regions.^{20,21} This shows how the corresponding morphology changed with the DS of the SPEES membranes. The domain size and connectivity of ionic clusters increased with the increasing degree of sulfonation. It could be clearly seen that the hydrophilic ionic domains were segregated in an essentially spherical form in the nonionic hydrophobic matrix from SPEES-10 to SPEES-30. However, for SPEES-40, the ionic domains appeared to connect with each other, which may have provided more or larger transport channels. The domain structure significantly increased the water uptake capacity of the membrane. The other reason for the faster absorption and higher water uptake of the SPEES membranes was that these membranes had a more open structure than the other membranes because the *tert*-butyl groups were incorporated into the membranes.

Proton conductivity might differ with different measurement approaches and instruments. In this study, we selected Nafion 117 as a reference in order to compare the conductivities of membranes. The proton conductivity of the membranes was measured in the temperature range of 25°C–80°C. It can be seen from Figure 6 that all proton conductivity values of SPEES membranes were higher than 0.01 S/cm and increased from 0.01 S/cm for SPEES-10 membranes to 0.062 S/cm for SPEES-40 membranes at 25°C and from 0.018 S/cm

TABLE III
Properties of Membranes in Acidic Form

Copolymer	SPEES-10	SPEES-20	SPEES-30	SPEES-40
Water uptake (%)	11	15	28	52
IEC _(c) (meq/g) ^a	0.50	0.97	1.40	1.80
IEC _(m) (meq/g) ^b	0.43	0.94	1.29	1.66

^a IEC calculated from degree of sulfonation.

^b IEC obtained by titration.

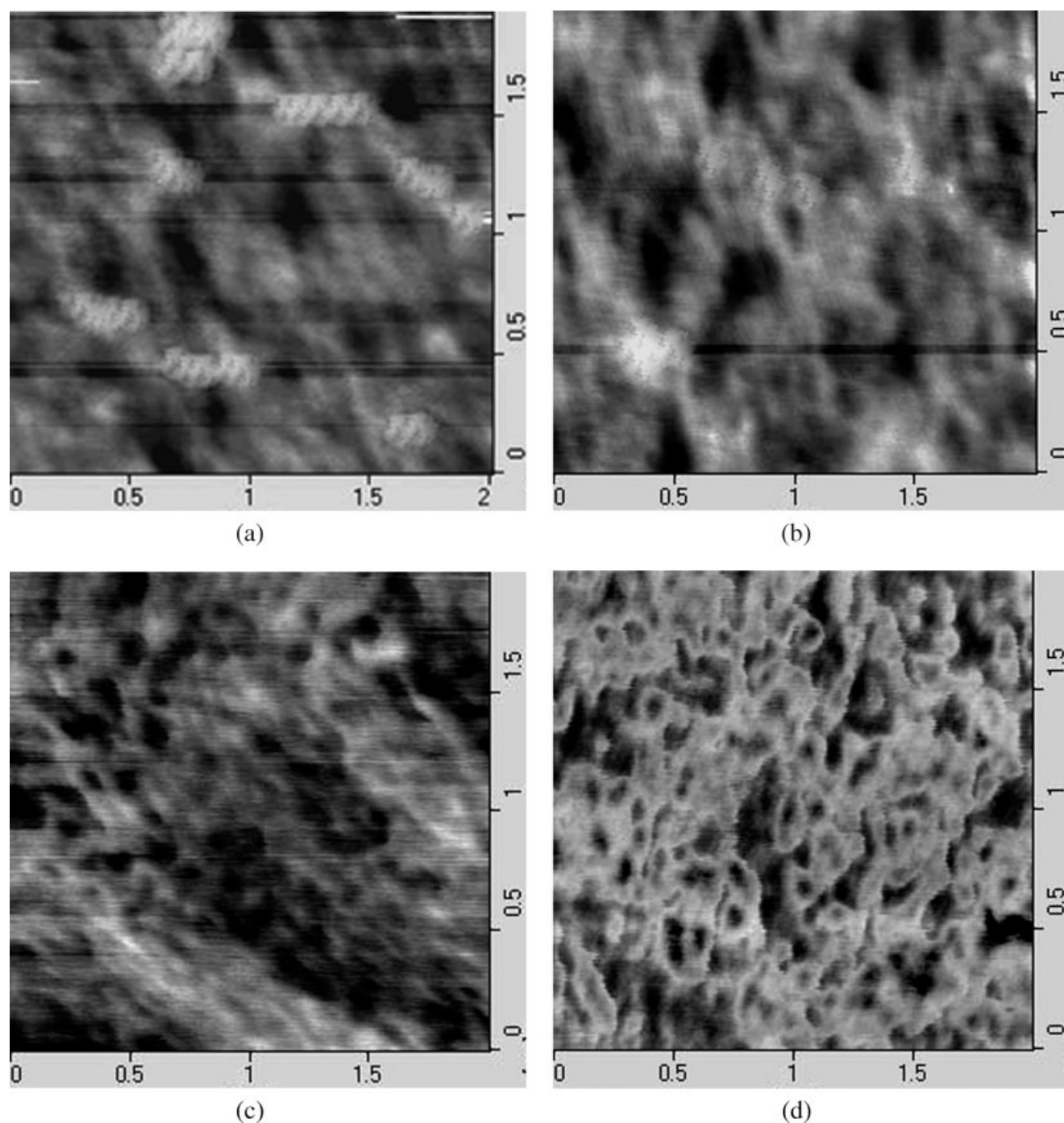


Figure 5 AFM phase images of SPEES membranes.

for SPEES-10 membranes to 0.083 S/cm for SPEES-40 membranes at 80°C. It is obvious that proton conductivity increased with increasing DS and temperature, which was in accord with the water uptake by the membranes. This might have been a result of the increasing size of clusters in membranes or large ion transport channels, which was concluded from the morphologies of the membranes. Moreover, the proton conductivity of SPEES-40 membranes reached 0.077 S/cm, which was higher than the 0.074 S/cm of

Nafion 117 at 60°C. This may have been because SPEES-40 had a relatively high IEC compared with Nafion 117, and a *tert*-butyl group, a large pendent group, was attributed to forming an ionic transport pathway, which resulted in proton conductivity apparently increasing.²² Phase imaging of SPEES-40 showed that hydrophilic and hydrophobic images formed connectivity with each other's morphology. A transport channel with more and larger protons resulted in increased proton conductivity.

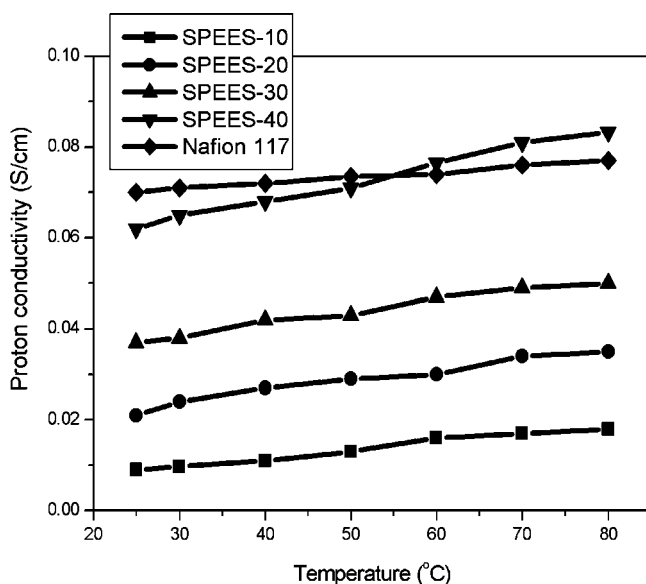


Figure 6 Proton conductivity of the SPEES membranes and Nafion 117 as a function of temperature.

CONCLUSIONS

A series of sulfonated SPEES copolymers containing *tert*-butyl groups was successfully prepared by direct aromatic nucleophilic polycondensation of disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone, 4,4'-dichlorodiphenylsulfone, and *tert*-butylhydroquinone in various ratios. DSC showed the T_g of the copolymers increased with increasing DS. The thermal stability of the copolymers was studied by TGA, which showed that SPEES copolymers in sodium form were thermally stable up to 450°C, whereas SPEES copolymers in acidic form were thermally stable up to 260°C. The temperature of 5% weight loss decreased as DS increased. Although the copolymers in sodium form had better thermal stability than the corresponding copolymers in acidic form, the thermal stability of SPEES in acidic form met the requirement of PEM. Phase images of SPEES membranes showed that the diameter of the hydrophilic ionic domains increased with increasing DS. Domains became connected to produce a cocontinuous morphology when the DS of the copoly-

mer reached 0.8, leading to SPEES-40 membrane conductivity reaching 0.083 S/cm and exceed that of Nafion 117 at 80°C. This study has demonstrated the possibility of synthesizing low-cost proton exchange membranes with high conductivity at relatively low DS for fuel cell applications.

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