

Development and Characterization of Homogeneous Membranes Prepared from Sulfonated Poly(phenylene oxide)

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ABSTRACT: This article investigates the comprehensive properties of sulfonated poly(phenylene oxide) (SPPO) membranes with different sulfonation degrees and presents the completion of previous work necessary for the application of SPPO membranes to proton-exchange membrane fuel cells. The sulfonation level has been accurately determined by conductometric titration and $^1\text{H-NMR}$, and the glass-transition temperature has been obtained with both differential scanning calorimetry and dynamic mechanical thermal analysis. Sulfonic groups attached to the aromatic ring in the poly(phenylene oxide) backbone split at 220–340°C, but the main-chain splitting temperature of SPPO is similar to that of the pure polymer. In addition, the effects of sul-

fonic groups and water on the tensile strength of these membranes have been studied. An increase in the sulfonate groups in the polymer results in an increase in the water uptake. Atomic force microscopy phase images of the acid-form membranes clearly show the hydrophilic domains, and the ionic regions of the membranes with a low sulfonation degree are isolated and become connected to produce a cocontinuous morphology as the degree of sulfonation increases. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1244–1250, 2005

Key words: ionomers; membranes; poly(phenylene oxide)

INTRODUCTION

Nowadays, there is much interest in thin polymer films based on sulfonated poly(phenylene oxide) (SPPO) because of their importance in science and technology.¹ Most earlier works on the application of SPPO membranes have been directed to gas separations to reverse osmosis.^{2–5} Poly(phenylene oxide) (PPO) is a high glass-transition temperature (T_g) amorphous polymer that has already been proven to be a highly permeable membrane material with excellent mechanical properties and resistance to a number of chemical agents.⁵ However, its selectivity for gases is relatively low. Sulfonation has been found to be an effective method for improving gas selectivity. Kruczek and Matsuura² reported that an increase in the ion-exchange capacity (IEC) of SPPO resulted in O_2/N_2 and CO_2/CH_4 selectivity and a decrease in O_2 and CO_2 permeabilities. For the membranes prepared from the polymer of the highest IEC value (equal to 1.80 mequiv/g), they observed that the O_2/N_2 and CO_2/CH_4 permeability ratios were 6.69 and 43.38, respectively, and the O_2 permeability was 2.11 barrer.

It is generally accepted that proton-exchange membrane (PEM) fuel cells present an attractive alternative to traditional power sources,^{6–8} but the cost of the cell components precludes their immediate implementation for most stationary and vehicular applications. A primary contributor to the high cost of PEM fuel cells is the perfluorosulfonated ionomer membrane.⁸ Therefore, the development of novel PEM materials is very necessary. SPPO membranes are considered new polymeric electrolyte materials for PEM fuel cells.^{9–12} SPPO possesses extraordinary electrochemical and mechanical properties. Its unique transport characteristics are closely associated with a spontaneous phase separation that occurs in the hydrated SPPO polymer: the conductive aqueous phase due to sulfonation segregates into ion cluster phases containing functional groups that are dispersed in an insulating PPO matrix. Xu et al.¹³ employed both percolation theory and the three-phase model to study the ionic transport behavior in SPPO membranes. They reported that the conductivity with a degree of sulfonation equal to 28.7% was 0.015 s/cm.

Although there has been much research on SPPO membranes in the last decade,^{14–16} few studies have been reported on the whole-property investigation of sulfonated PPO membranes. The aim of this work was to investigate the comprehensive characterization of SPPO membranes and finish the previous studies for SPPO membrane applications in PEM fuel cells. In this

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research, PPO sulfonation was explored. The sulfonation level was accurately determined by conductometric titration and $^1\text{H-NMR}$. The physicochemical properties of the membranes reported here include the thermal stability, T_g , water uptake at different temperatures, and tensile strength in both dry and wet states. The surface morphology of polymer films was obtained with atomic force microscopy (AFM).

EXPERIMENTAL

Materials

All the following materials were used as received, without further purification. PPO with an intrinsic viscosity of 0.4 dL/g in chloroform at 25°C was purchased from General Electric Co. Chlorosulfonic acid (practical-grade, 99% pure; Shanghai Tingxin Chemical Agent Co., Shanghai, China) and other chemicals were analytical-reagent-grade.

Sulfonation of PPO

PPO was dissolved in chloroform under the ambient conditions to form a 5–8 wt % solution. Chlorosulfonic acid in chloroform (6 wt %) was first kept in an ice bath and then slowly added to the PPO chloroform solution at 25°C with vigorous mechanical stirring. If there were precipitated materials in the flask, the precipitated polymer was separated, and the liquid was discarded. If not, the reaction solution was stirred at 25°C for another 3–4 h; then, the reaction was stopped, and the mixture liquid was precipitated into deionized water. The precipitated sulfonated product was washed with deionized water many times until the precipitated polymer was neutral, and then the precipitated SPPO was dried.

Preparation of the membranes

The membranes were prepared by solvent-casting techniques. The sulfonated polymer was dissolved in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), or *N*-methylpyrrolidone (NMP) to form a 10–15 wt % casting solution, and then the solution was poured onto a leveled glass plate with a casting knife. The membranes were air-dried in a dust-free box at room temperature for 1 day, and this was followed by air drying at 40°C for 8 h and at 60°C for 10 h and then drying *in vacuo* at 80°C for 1 day.

Determination of IEC of SPPO

IEC indicates the number of milligram equivalents of ions in 1 g of the dry polymer.¹⁷ The degree of substitution (DS) was the average number of sulfonic groups present in the sulfonated polymer. The rela-

tionship between the DS and IEC values was calculated with the following equation:²

$$\text{DS} = 120\text{IEC}/(1000 + 120\text{IEC} - 200\text{IEC}) \quad (1)$$

The sulfonation degree of SPPO was determined by conductometric titration with a DDSJ-308 conductivity meter (Shanghai Leici Instrument Co., Shanghai, China). SPPO (0.1–0.2 g) was dissolved in THF or DMF, and then the solution was titrated with a 0.1N NaOH standard solution. According to the obtained titration curve, we could calculate the sulfonation degree and obtain the IEC value.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were recorded with a PerkinElmer spectrometer (PerkinElmer, Wellesley, MA) directly from polymer film samples.

$^1\text{H-NMR}$

Proton spectra were obtained on a Varian Unity Inova 600 NMR spectrometer (Varian, San Francisco, CA). Tetramethylsilane was used as the internal-standard chemical-shift reference. The $^1\text{H-NMR}$ spectrum of PPO was acquired at 20°C in deuterated chloroform (CDCl_3). Deuterated acetone (CD_3COCD_3) or methanol (CD_3OD) was the NMR solvent of choice for SPPO. The presaturation of the large water peak always present in SPPO around 4 ppm improved the spectra by increasing the signal-to-noise ratio and by removing interference signals from the large water absorption.

Thermogravimetric analysis (TGA)

The thermal stability of the membranes was examined with a PerkinElmer TGA7 analyzer running from 25 to 600°C at heating rate of 20°C/min and in an atmosphere of N_2 . The samples were subjected to TGA both before and after sulfonation to determine the decomposition temperatures.

Differential scanning calorimetry (DSC)

DSC measurements were carried out on a PerkinElmer DSC-7 at a scanning rate of 20°C/min under a nitrogen atmosphere. To delete the heat history during the preparation of the membranes, the second heating scan was carried out at the same scanning rate and taken as the DSC analysis results.

Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out on a Rheometric Scientific MKIII dynamic mechanical analyzer

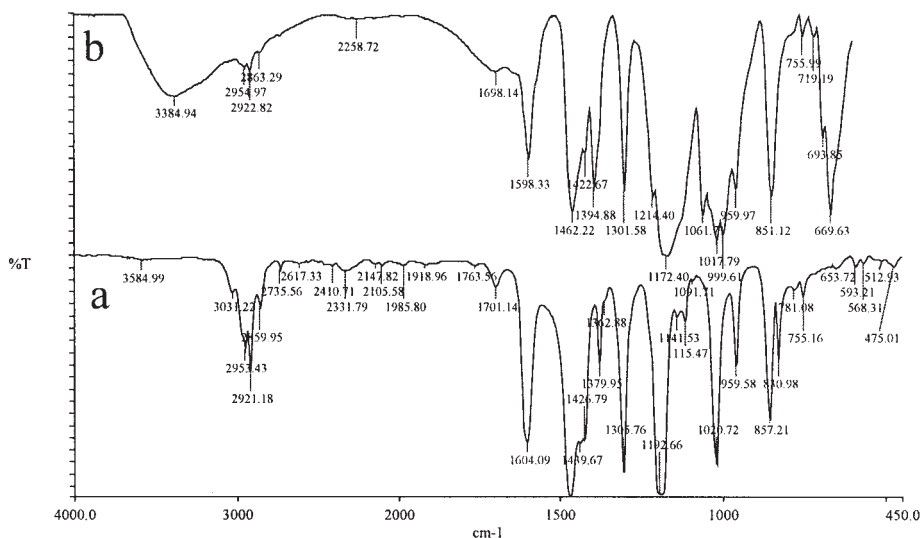


Figure 1 FTIR spectra of (a) pure PPO and (b) sulfonated PPO.

(Rheometrics, Piscataway, NJ). The samples for DMTA analysis were about 0.5 mm thick. The frequency was 1 Hz, and the strain level was 1; that is, the average strain was 1.141%. The torque was 40 cN/m. The experiments were run from 60 to 280°C at a heating rate of 3°C/min.

Water uptake

The studies of the water uptake were performed as follows. All membrane samples were dried at 80°C *in vacuo*, and the dry weight (W_1) was taken. The samples were then immersed in deionized water at room temperature. After 24 h of equilibration, we removed the excess liquid on the surface of the membranes and quickly weighed them (W_2). The water content (ΔW) was calculated as follows:⁸

$$\Delta W = (W_2 - W_1) / W_1 \times 100\% \quad (2)$$

Mechanical properties

All membrane samples were dried in a vacuum oven at 80°C for 24 h before the measurements. Wet samples (membranes swollen by water) were immersed in deionized water for 1 day at room temperature. The tensile strength was measured with a Shimadzu Autograph AG-10kNA tension tester (Shimadzu, Kyoto, Japan) at room temperature. The tensile conditions were based on Chinese Standard GB-1040-92 (type V), and the samples were measured with a programmed elongation rate of 5 mm/min. More than five specimens were tested for each composition.

Morphology

The surface morphology of the polymer films was investigated with a Nanoscope IIIa atomic force mi-

croscope (Veeco, Woodbury, NY) operating in the tapping mode. Silicon probes (Nanoprobes, Digital Instruments) with 125- μm cantilevers were used at their fundamental resonance frequencies, which varied from 270 to 350 Hz. The measurements were made under the ambient conditions with a vibration isolation-floating table. The films were prepared from a 1 wt % polymer solution that was filtered through a 0.1- μm -pore-size Teflon filter in advance.

RESULTS AND DISCUSSION

FTIR analysis

FTIR has been used to analyze characteristic bands corresponding to the sulfonation groups in different polymers, such as sulfonated poly(arylene ether ketone)s,^{18,19} polystyrene,²⁰ and polyester.²¹ The successful introduction of the $-\text{SO}_3\text{H}$ groups was confirmed by FTIR spectra (Fig. 1). The spectra were directly obtained from sulfonated and unsulfonated polymer membrane samples having a thickness of about 30 μm . As shown in Figure 1, the sharp peak at 1192 cm^{-1} is the characteristic absorption band of the aromatic ether $\text{V}_{\text{C}-\text{O}-\text{C}}$. In the SPPO spectra, some peaks at the wave numbers of 1061 and 669 cm^{-1} appeared after sulfonation. These bands were assigned to symmetric stretching of $-\text{SO}_3^-$ groups and C—S stretching vibrations, respectively. Another $-\text{SO}_3^-$ band at 1200 cm^{-1} overlapped with the aromatic ether band. The intensity of the peak at 3030 cm^{-1} ($\delta\text{C}-\text{H}$ in aromatic ring) decreased. This suggests that the substitution number of aromatic nuclei increased. These bands observed here were almost identical to the bands reported by Huang and Kim.⁴ The results prove that the sulfonate groups were indeed introduced into the polymer backbone.

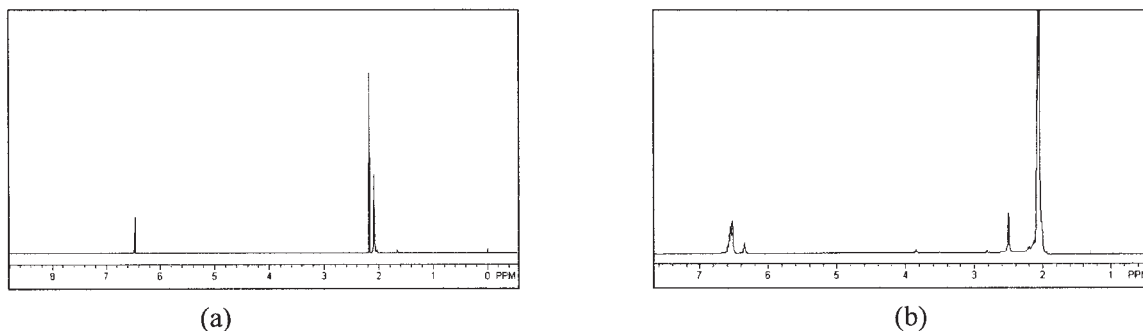


Figure 2 $^1\text{H-NMR}$ spectra of (a) PPO in CDCl_3 and (b) SPPO in CD_3COCD_3 .

Determination of IEC of SPPO

The DS value was determined by conductometric titration and $^1\text{H-NMR}$. Under the condition of titration, the dried SPPO solutions in THF or DMF were titrated by standard NaOH solutions. In the obtained titration curve, a sharp end titration point could be observed, indicating a strong acid ($-\text{SO}_3\text{H}$) and base reaction. The PPO batches were sulfonated to various degrees of sulfonation ranging from 9.8 to 40.1%, and the corresponding IEC values ranged from 0.77 to 2.63 mequiv/g.

The $^1\text{H-NMR}$ spectra of PPO and SPPO are shown in Figure 2. Figure 2(a) presents the NMR spectrum of PPO. The low-field peak ($\delta = 6.4$) is the peak of the aromatic proton, and the upfield signals (2.08–2.18 ppm) arose from the 6H of the methyl groups on the aromatic ring. After sulfonation, the sulfonic group in the PPO repeat units resulted in the shifting of the signal from protons attached to the methyl group in the ortho position to the sulfonic group and that from the aromatic proton of the substituted unit. In Figure 2(b), the two low-field peaks ($\delta = 6.52$ and $\delta = 6.35$) belong to the proton of the $-\text{SO}_3\text{H}$ and unsubstituted aromatic proton separately. The upfield peak ($\delta = 2.49$) is due to the hydrogen of the methyl group in the ortho position to the sulfonic group, and the signals (2.01–2.08 ppm) belong to $-\text{CH}_3$ in the para position to the sulfonic group. The chemical shift of the aromatic proton moved to the low field because of

TABLE I
Comparison of the IEC Values of SPPO from Titration and $^1\text{H-NMR}$

Sample	Titration		$^1\text{H-NMR}$	
	DS (%)	IEC (mequiv/g)	DS (%)	IEC (mequiv/g)
1	9.8	0.77	—	—
2	17.2	1.28	18.6	1.38
3	25.9	1.84	26.7	1.89
4	36.7	2.46	37.0	2.47
5	40.1	2.63	43.2	2.79

the strong induction of $-\text{SO}_3\text{H}$. Therefore, the NMR spectrum of SPPO shows two extra signals in addition to those of PPO. The degree of sulfonation was calculated from the intensities of the additional signals. The IEC values from both titration and $^1\text{H-NMR}$ are presented in Table I. The values obtained by $^1\text{H-NMR}$ are a little higher than those by titration. The IEC value determined by $^1\text{H-NMR}$ indicates the total degree of polymer substitution, including both sulfonic and chlorine groups because shifts caused by these two groups could not be distinguished by the resolution of the $^1\text{H-NMR}$ equipment.

TGA

Figure 3 presents TGA spectra of PPO and SPPO. PPO is a thermally stable polymer. The initial decomposition temperature is about 450°C at a heating rate of $20^\circ\text{C}/\text{min}$. Three weight-loss stages can be observed in the TGA curve of SPPO. The first stage at $25\text{--}100^\circ\text{C}$ can be attributed to the loss of moisture absorbed from the air. The second one at $220\text{--}340^\circ\text{C}$, which cannot be observed in the TGA spectra of PPO, can be taken as the splitting of $-\text{SO}_3\text{H}$. The location of the weight-

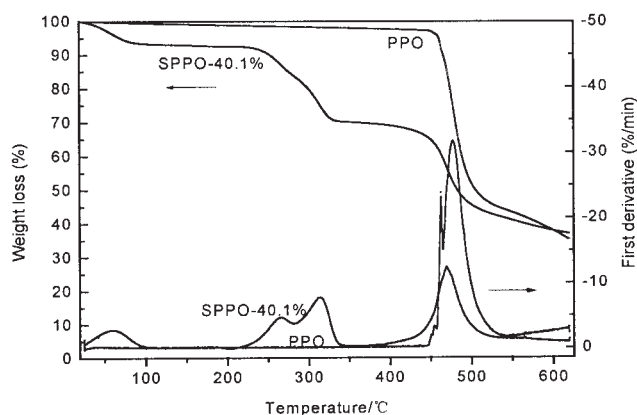


Figure 3 Thermogravimetric and first derivative curves for pure PPO and an SPPO membrane cast from an NMP solution.

TABLE II
 T_g Values from DSC and DMTA

DS (%)	Solvent	T_g (°C)	
		DSC	DMTA
0	CHCl ₃	214	217
9.8	THF	220	222
17.2	DMF	226	225
25.9	NMP	229	224
36.7	NMP	232	230
40.1	NMP	233	230

loss stages observed here is almost identical to that reported by Gilbert.²² In addition, from the DTG curve of SPPO, there are two peaks in the second stage. This indicates that the second stage could also be related to the evaporation of residual NMP. The boiling point of NMP at atmospheric pressure is about 205°C, which is much less than the temperatures in the second stage. In a 220–340°C temperature interval, SPPO is already in a rubbery state.^{2,5} An increase in the free volume in the rubbery state and increasing sliding of polymer chains with an increase in the temperature would enhance the evaporation of the residual solvent entrapped in the polymer in the glass state.² Therefore, the first slope in the second stage is a result of evaporation of residual NMP. However, such NMP would represent the solvent strongly bound to the polymer, which could only be removed well above its boiling point when the polymer is in a rubbery state. Unfortunately, the residual solvent cannot be removed from SPPO films by heat treatment completely because of the decomposition of sulfonic groups below T_g . The third one is close to the decomposition temperature of PPO and is related to the splitting of the main chain. As previously shown, the initial decomposition temperature of SPPO is lower than that of PPO because of the side-group splitting. The main-chain splitting temperature is also slightly lower than that of PPO. Therefore, the thermal stability of PPO decreased after sulfonation.

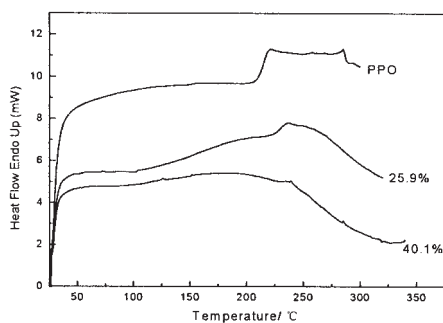


Figure 4 DSC spectra of PPO and SPPO.

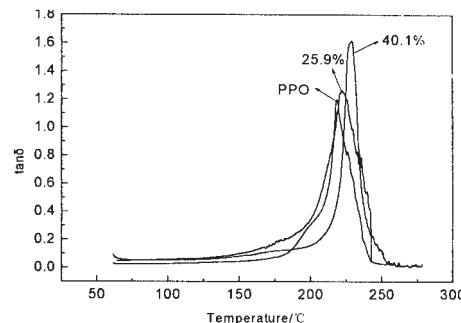


Figure 5 DMTA spectra of PPO and SPPO.

Glass-transition behavior of SPPO

The introduction of sulfonate groups has two effects on T_g .²³ First, it produces increased intermolecular interactions by pendant ions (i.e., an ionomer effect). The $-\text{SO}_3\text{H}$ groups on adjacent chains may easily form H bonds between macromolecular chains, and this leads to increasing interactions between macromolecular chains. Second, the introduction of sulfonate groups increases molecular bulkiness. The substitution of PPO with a relatively rigid and bulky side group ($-\text{SO}_3\text{H}$) may directly suppress torsional motions in the polymer by interference, leading to increasing chain stiffness. Both effects hinder internal rotation, leading to increased T_g for sulfonated polymers. The T_g values of PPO and SPPO were determined in two ways: from the temperature of the DMTA $\tan \delta$ peak measured at 1 Hz and by DSC at a heating rate of 20°C/min. These measurements were in substantial agreement, and a general trend toward an increase in T_g with an increasing sulfonic group concentration was clearly perceptible. The results obtained with DSC and DMTA are presented in Table II and Figures 4 and 5. From the DSC spectra, it can be seen that T_g increased from 214°C for unmodified PPO to 233°C for SPPO with a sulfonation degree of 40.1%. As for the DMTA spectra, the T_g value of PPO was about 217°C. After sulfonation, the T_g value of SPPO with a sulfonation degree of 40.1% increased to 230°C. In both cases, the observed dependence of T_g on the sulfonation level was nonlinear. The nonlinearity agreed with observations for other ionomeric systems.^{24,25} The unneutralized acid forms ($-\text{SO}_3\text{H}$) of all the sulfonated polymers used in the study displayed a significantly higher T_g value than the unsulfonated polymer.

Water uptake

Figure 6 shows the percentage of the saturated (24-h equilibration) sorption of water in the normal and sulfonated polymers with the temperature. The water uptake increased with an increase in the sulfonation

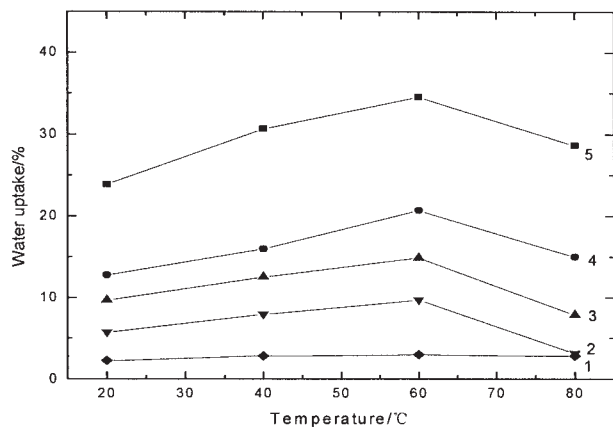


Figure 6 Temperature and DS dependence of the water uptake of the SPPO membranes: (1) SPPO-9.8%, (2) SPPO-17.2%, (3) SPPO-25.9%, (4) SPPO-36.7%, and (5) SPPO-40.1%.

degree and temperature. The water sorption depended on the extent of sulfonation; therefore, higher DS was, the greater the water uptake was. Unmodified hydrophobic polymer PPO hardly had water uptake. Smitha et al.²⁶ reported that the water uptake of PPO was only 0.27%. After sulfonation, the obtained values were quite high and were in the range of 2.25–23.8% at 20°C for a sulfonation degree of 9.8–40.1%. This indicated the presence of hydrophilic sites within the hydrophobic matrix. Figure 6 shows that the water uptake also increased with the temperature, but the water uptake of all the membranes slightly decreased at 80°C in comparison with 60°C; that is, for the SPPO membrane with DS equal to 40.1%, the values of water sorption at 20, 60, and 80°C were 23.8, 34.5, and 28.5%, respectively.

Mechanical strength of the membranes

The mechanical strength of membranes affects manufacturing conditions in practice. Table III shows the tensile strength of dry and wet PPO and SPPO membranes. There was a decrease in the tensile strength after sulfonation, and the higher DS was, the lower the tensile strength was. This reduction may be attributed to the degree of sulfonation. The introduction of strong polar $-\text{SO}_3\text{H}$ in the polymer chain could damage the ordering of the aggregative state. The higher the degree of sulfonation was, the lower the degree of order was. Under wet conditions, all membranes had lower mechanical strength than those under dry conditions. It was supposed that water in the membranes functioned as a plasticizer. The results show that even though the SPPO membranes were wet, they still possessed high mechanical strength, and this indicates that the membranes could be used in high-humidity conditions.

Morphology

Tapping-mode phase images of the PPO and SPPO membranes were recorded under ambient conditions on a $1\ \mu\text{m} \times 1\ \mu\text{m}$ size scale to investigate ionic clusters for SPPO (Fig. 7). For the unsubstituted polymer, a featureless phase morphology was observed. On the other hand, for SPPO with a sulfonation degree of 9.8–40.1%, there was unevenness in the surface. We can obviously find two phases in the phase image, especially for SPPO with a sulfonation degree of 40.1%. The dark structures were assigned to a softer region, which represents the hydrophilic sulfonic acid groups containing small amounts of water. For SPPO-25.9%, the cluster regions increased in comparison with Figure 7(b,c) and became more easily distinguished from the nonionic matrix. However, for the SPPO-40.1% sample, the phase image changed significantly: the dark regions became continuous to form the bands of an ion-rich phase. A similar continuous ionic structure for Nafion 117 was also observed under ambient-humidity conditions reported by James et al. This indicates that an SPPO membranes with a high sulfonation degree may possess high proton conductivity.

Further research on the protonic conductivities of the membranes will be carried out in the near future.

CONCLUSIONS

A series of SPPOs with different DS values ranging from 9.8 to 40.1% were prepared. The structure of SPPO was confirmed by FTIR, and the DS values of SPPO were determined by conductometric titration and $^1\text{H-NMR}$. Sulfonic groups attached to the aromatic ring in the PPO backbone decomposed at the stage of 220–340°C, but the main-chain splitting temperature of SPPO was similar to that of the pure polymer. As DS of SPPO increased, T_g increased. The water uptake of SPPO increased with an increase in the sulfonation and temperature. There was a decrease in the tensile strength after sulfonation, and the higher DS was, the lower the tensile strength was. Even

TABLE III
Mechanical Properties of the PPO, SPPO, and Nafion 112 Membranes

Membrane sample	DS (%)	Tensile strength (MPa)	
		Dry	Wet
1	0	62.68	61.74
2	9.8	48.25	40.51
3	17.2	41.56	27.53
4	25.9	36.62	34.55
5	36.7	37.39	31.99
6	40.1	30.96	24.43
7	Nafion 112	26.13	20.90

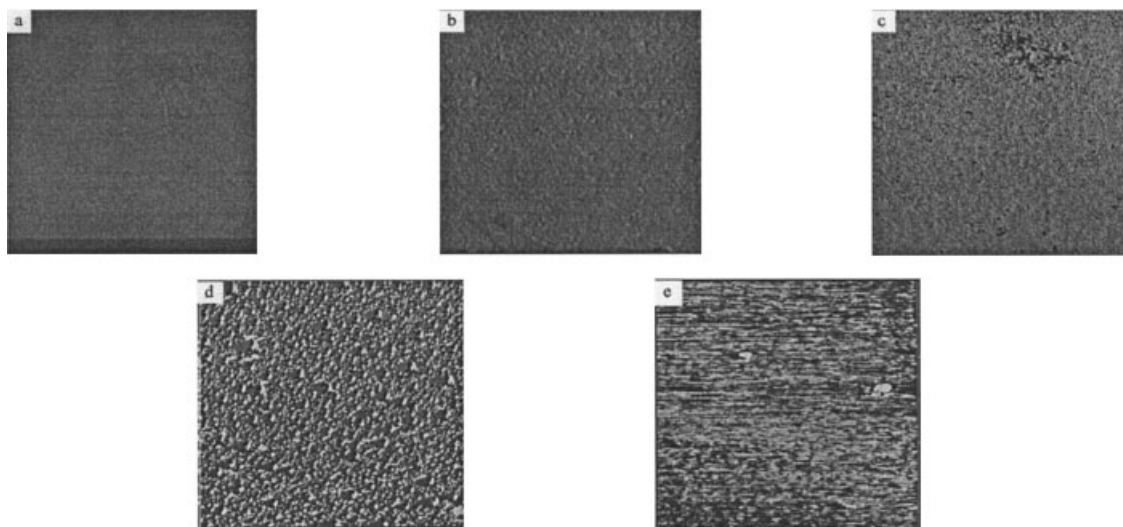


Figure 7 AFM tapping phase images of PPO and SPPO: (a) PPO, (b) SPPO-9.8%, (c) SPPO-17.2%, (d) SPPO-25.9%, and (e) SPPO-40.1%. The scan size was $1 \mu \times 1 \mu\text{m}$.

though the SPPO membranes were wet, they still possessed high mechanical strength, and this indicated that the membranes could be used under high-humidity conditions. AFM phase images showed that the ionic regions of the membranes with a low sulfonation degree were isolated and became connected to produce a cocontinuous morphology as the degree of sulfonation increased.

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