Sulfonated Poly(ether imide) and Poly(ether sulfone) Blends for Direct Methanol Fuel Cells. I. Sulfonation of PEI and Characterization of the Products

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ABSTRACT: This investigation examines characteristics of sulfonated polyether imides (SPEI) with various ion exchange capacity values (IEC) and completes previous work to enable its blends to be adopted as polyelectrolyte in direct methanol fuel cells (DMFC). Polyether imides (PEI) were sulfonated by using chlorosulfonic acid as the sulfonating agent and chloroform as the solvent. The structure of SPEI was observed by FTIR and ^{1}H NMR. The sulfonate or sulfonic acid content of the polymers, expressed as a number per repeat unit of the polymer, was accurately determined by elemental analysis and conductometric titration. Physical properties such as solubility, intrinsic viscosities, thermal stability, and glass transi-

tion temperature (T_g) were studied for both PEI and SPEI. TGA-FTIR verified that sulfonic groups, attached to the aromatic ring in the PEI backbone, are split at 230–350°C, but the main-chain splitting temperature of SPEI is similar to that of pure polymer. The sulfonated samples exhibited good solubilities and increased glass transition temperatures (T_g values) as degree of sulfonation (DS) increased; two T_g values were detected when IEC was sufficiently high. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2963–2969, 2008

Key words: sulfonated poly(ether imide); poly(ether sulfone); polymer blends; electrolyte membrane; fuel cells

INTRODUCTION

Aromatic polyimides are known for their excellent thermal stability, chemical and solvent resistance, and stability when illuminated. Their outstanding characteristics have resulted in their being extensively employed as industrial films, coatings, adhesives, and moldings at high temperatures.[1] Polyether imide (PEI) is an important member in this class. It is a versatile and well-known specific engineering polymer that consists of repeated phenyl groups, imide groups, ether linkages, and angular bonds between aromatic rings. The aromatic imide units of PEI are responsible for high-performance characteristics such as high mechanical strength, thermal stability, and chemical resistance, while the flexible ether linkages provide good processability.[2,3] Among numerous aromatic polymers with high glass transition temperatures (T_g), PEI exhibits impressively high selectivities for all important gas pairs and has been used commonly in the preparation of asymmetric membranes for gas separation and pervaporation.[3–6] Barbari et al.[7] reported that the selectivities

of PEI dense membranes for He/N_2, CO_2/N_2, and N_2/O_2 gas pairs are 264, 37.4, and 7.6 at 35°C, respectively. Reportedly, PEI can be applied in the vapor permeation of water/1-propanol[8] and the field of ultrafiltration.[9,10]

In general, a kind of material does not posses all the excellent properties required for membranes. As for PEI, its application is sometimes limited by hydrophobicity. Therefore, polymers may need some modification to improve their performance for specific applications.[11,12] Sulfonation is a frequently used means for polymer modification to increase hydrophilicity and other membrane properties such as higher water flux, improved permeability.[13,14] Furthermore, sulfonation is also a commonly adopted approach for enhancing the ion conductivity of polymers.[15,16] Many engineering polymers, such as polyether ether ketone,[17,18] polyether sulfone (PES),[19] polyphenylene oxide (PPO)[20–22] and others, can be used as polyelectrolytes in fuel cells following sulfonation.

The sulfonation reaction is an electrophilic substitution affected by both the electrophilicity of the sulfonating agent and the electron-donating characteristic of the polymer.[23] Concentrated sulfuric acid, SO_3 or SO_3 complexes and chlorosulfonic acid are generally employed as sulfonating agents. Every technique

for the sulfonation of PEI has advantages and disadvantages. For example, PEI sulfonated by concentrated sulfuric acid must need a reaction of a long period of time at high temperature. Therefore, the sulfonating reaction is commonly out of control and generally accompanied by side reactions. SO_3 or SO_3 complexes require special handling and/or preparation. Using chlorosulfuric acid readily causes a secondary reaction because the Cl—S bond is weak.[11] However, sulfonation by chlorosulfonic acid is simple and adaptable. The side reactions can be substantially inhibited if the main reaction is performed under controlled conditions of reaction temperature, time, and others.

The purpose of this investigation is to evaluate the physico-chemical characteristics of SPEI and complete previous work to make SPEI/PES blends applicable in DMFC. In this investigation, a series of sulfonated PEI (SPEI) with various IEC values were prepared by using chlorosulfonic acid as the sulfonating agent and chloroform as the solvent. SPEI samples were characterized in terms of its structure (FTIR and ^{1}H-NMR), IEC, intrinsic viscosities, thermal stability, T_g, and solubility in some common solvents.

EXPERIMENTAL

Materials

PEI (Ultem[®] 1000) in pellet form was purchased from General Electric Corporation and dried for 8 h at 100°C before used. Chloroform was distilled under reduced pressure and stored in 4 Å molecular sieves until used. Chlorosulfonic acid (Practical grade, 99% purity), and other chemicals were of analytical reagent grade and used without further purification.

Sulfonation of PEI

Sulfonation of PEI was carried out in a chloroform solvent using chlorosulfonic acid as the sulfonating agent referred to the PPO sulfonation procedure described by Huang and Kim.[24] The DS was controlled by the adding content of the chlorosulfonic acid.

FTIR

FTIR spectra were obtained by using a Nicolet 380 Fourier transform spectrometer with a resolution of 2 cm^{-1}. Samples for FTIR analysis were obtained by casting the PEI or SPEI dilute solution on the pure KBr pellets, and then by drying them under an infra-red lamp.

^{1}H-NMR

Proton spectra were obtained by using a Varian Unity Inova 600 NMR spectrometer. Tetramethylsilane was used as the internal-standard chemical-shift reference. The ^{1}H-NMR spectrum of PEI was obtained at 20°C in deuterated chloroform (CDCl$_3$). Deuterated dimethyl sulfoxide (DMSO-d_6) was the selective solvent for dissolving SPEI.

Determining the DS of SPEI

The degrees of sulfonation (DS) were determined by both conductometric titration and elemental analysis.

The conductometric titration was performed on a DDSJ-308 Conductivitimeter (Shanghai Leici Instrument CO.). SPEI(0.1–0.2 g) was dissolved in DMAc and the solution was then titrated with $0.1M$ NaOH standard solution. The DS can be obtained from the titration curve.

DS can also be calculated from the sulfur content determined by elemental analysis on Vario EL III using CHNS mode.

Intrinsic viscosities

The viscosities were measured by using an automated Ubbelohde viscometer whose temperature was maintained at 30°C by using a thermostat. The polymer concentration was 0.1 g/25 mL in NMP.

TGA-FTIR

The thermogravimetric spectra were obtained by using TGA (TA SDT-Q600) in a nitrogen environment at a heating rate of 10°C/min over the range 25–850°C. The TGA outlet was coupled on-line with a Nicolet 380 FTIR spectrometer through a gas cell, which was warmed up to 180°C and stabilized for 2 h before the running of TGA.

DSC

The glass transition temperatures were obtained by using a Perkin-Elmer DSC-7 differential scanning calorimeter. Scans were conducted under nitrogen by heating to 220°C, annealing at 220°C for 10 min to eliminate the prior thermal and solvent histories, and then quenching quickly to room temperature. A DSC heating experiment was performed at 10°C/min to measure T_g. The T_g values are reported as midpoints of the changes in the slope of the baseline.

Dynamic mechanical thermal analysis (DMTA)

DMTA measurements were carried out on a Rheometric Scientific MKIII dynamic mechanical analyzer (Rheometrics, Piscataway, NJ). The frequency was
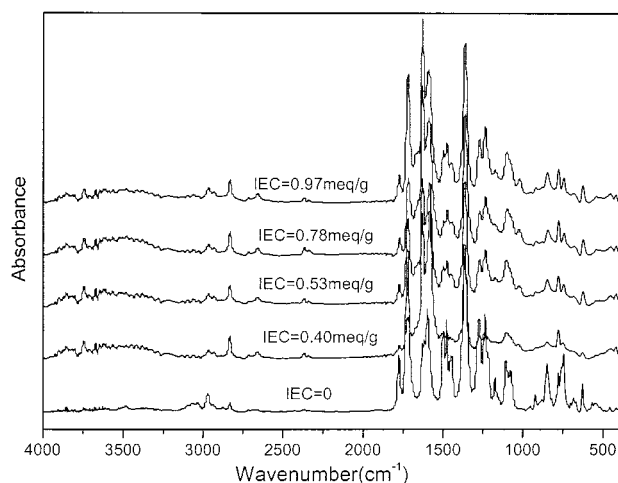
Figure 1 FTIR spectra of pure PEI and sulfonated PEI.

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 350°C at a heating rate of 3°C/min.

Determination of Solubility

In a sealed polymer-solvent system, the mass ratio of solute/solvent was 5%. After 24 h, the solution may be in one of three forms-dissolved (when all of the polymer samples were dissolved and formed a limpid solution), insoluble (when the solutes were insoluble, the shape of the samples did not vary visibly), and swelling (when the shape of the solutes was evidently changed, but no limpid solution was formed).

RESULTS AND DISCUSSION

FTIR

FTIR has been employed to analyze the characteristic bands of the sulfonation groups in different polymers, such as sulfonated poly(arylene ether ketone)s,[19] polystyrene,[25] and etc.

In Figure 1, with different IEC values the FTIR spectra of the PEI and SPEI samples are compared. The double peaks in the spectrum of PEI at 1724 and 1777.9 cm^{-1} are the characteristic absorption bands of $\nu_{C=O}$ in the imide ring. The peaks at 1362, 1237, and 1275 cm^{-1} are attributable to the aromatic ether ν_{C-O-C}. The stretching vibrations of the aromatic ring bone are in the 1446–1630 cm^{-1} wave band.

The characteristic peaks at 1022 cm^{-1} in the SPEI spectra, assigned to symmetric stretching of O=S=O stretching vibrations, were observed for all of the SPEI samples, and the intensity of these characteristic peaks increased with the rise of IEC values. Another —SO$_3^-$ band at 1200 cm^{-1} overlapped the

aromatic ether band ν_{C-O-C}. The decline of intensity of the peak at 3040 cm^{-1} (δ_{C-H} in aromatic ring) indicates that the substitution number of aromatic nuclei is increasing. Additionally, the broad absorption band in SPEI samples at 3600 cm^{-1} was assigned to O—H vibration associated with the interaction between sulfonic acid groups and molecular water. The results demonstrated that the sulfonate groups were indeed introduced to the polymer backbone.

^{1}H-NMR

Figure 2 presents the ^{1}H-NMR spectrum and characteristic protons in the aromatic ring in the PEI repeat unit. The peaks at 1.66–1.75 ppm are associated with the 6H of the methyl groups in the PEI unit. The low-field δ7.029–7.890 is associated with the peaks of the aromatic protons. In this area, the doublet at ∼ 7.03 ppm is the chemical shift of the bH in the aromatic ring because of p-π conjugation. The signals at ∼ 7.89 ppm arose from the dH because the neighboring carboxyl group attracts electrons. The other are signals as follows: iH (7.26 ppm), aH (7.32–7.34 ppm), hH (7.42 ppm), cH (∼ 7.5 ppm), fH and gH (7.59–7.62 ppm), and eH (7.64 ppm).

Sulfonation is an electrophilic substitution reaction, and the active site for substitution is governed mainly by the electron density of the site.[11] Substitution occurs preferentially in one of the b sites of the aromatic ring. The repeat unit and ^{1}H-NMR spectrum of SPEI are given in Figure 3. The introduction of —SO$_3$H results in a significant downfield shift from ∼ 7.32 to ∼ 7.76 ppm of the hydrogen A compared with aH in the PEI units. Meanwhile, the chemical shifts of the other aromatic protons also move to the low field to some extent because of the strong induction of sulfonated groups. These signals are attributed to the following protons: ∼ 7.13 ppm (i′H and b″H), 7.26–7.46 ppm (a′H, a″H, b′H and h′H), ∼ 7.52 ppm (f′H and g′H), ∼ 7.66 ppm (c′H), 7.76 ppm (AH), 7.79 ppm (e′H), and 7.88–8.01 ppm (d′H). As for the methyl groups, the signals split to two peaks (1.71 and 2.50 ppm), which are associated
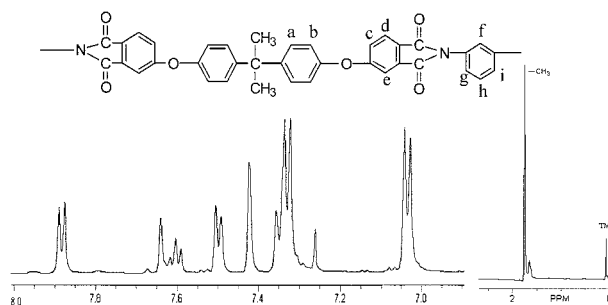

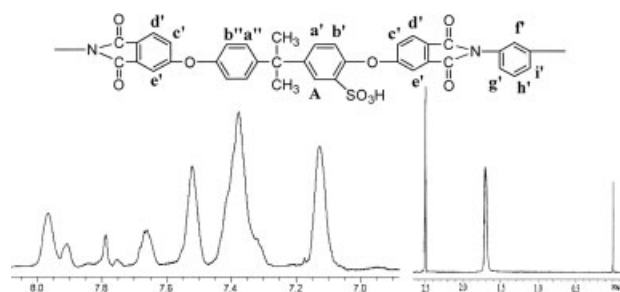**Figure 2** ^{1}H NMR spectrum of PEI.

Figure 3 ^{1}H NMR spectrum of SPEI.

with the protons of —CH$_3$ in the unsulfonated and sulfonated units, respectively.

Determination of IEC values

SPEI is a copolymer that has a PEI-SO$_3$H unit and a PEI unit. The DS can thus be defined as,[11]

$$DS = \frac{A}{A + B} \qquad (1)$$

where A and B are the molar numbers of the PEI-SO$_3$H unit and the PEI unit, respectively.

Under the titration conditions, the SPEI/DMAc solutions were titrated by using standard NaOH solution. The titration curve revealed a sharp end titration point, showing a strong acid (—SO$_3$H) and base reaction. The PEI batches were sulfonated to various degrees of sulfonation from 25.08% to 64.42%.

The elemental analysis yielded the following relationship between DS and sulfur content:

$$DS = \frac{598 \times 100 \cdot S}{32 \times 100 - 80 \cdot S} \qquad (2)$$

where S is the sulfur content (wt %) in the polymer, and 598, 32, and 80 are the molecular weights of the PEI unit, sulfur and the sulfonic group, respectively.

IEC indicates the number of milligram equivalents of ions in 1 g of the dry polymer.[16] The relationship between the DS and IEC values was calculated with the following equation:

$$DS = \frac{598IEC}{(1000 - 80IEC)} \times 100\% \qquad (3)$$

The targeted IEC values are compared in Table I with the values determined experimentally by acid base titration and ^{1}H-NMR. It can be noticed that, in general, the experimental IEC values were close to the anticipated values. Furthermore, the DS determined by elemental analysis was close to the values determined by titration. However, interestingly, the DS values determined by titration exceeded those determined by elemental analysis for all SPEI samples, perhaps because some residual acid, such as hydrogen chloride, was present in the SPEI samples in which chlorosulfonic acid reacted with a trace of water in the solvents. Hence, sodium hydroxide can react not only with the proton on the sulfonic group, but also with that on the hydrogen chloride.

Viscosity analysis

Intrinsic viscosities were measured to detect possible chain scission during electrophilic substitution.[23] As presented in Table I, the inherent viscosities of the SPES samples with IEC values of below 0.67 mequiv/g are slightly lower, indicating that the polymer chain is slightly degraded during sulfonation. However, the inherent viscosities of SPES increased with IEC values, because of the increase in the sulfonated group content, which is undoubtedly related to the increase in the number of intermolecular hydrogen bonds in the sulfonated polymer chain.[19]

TGA-FTIR

The thermal stabilities of SPEI with various IEC values were compared with those of pure PEI. Figure 4 displays the TGA weight loss and DTG thermograms of samples obtained in a nitrogen atmosphere. Figures 5 and 6 present the stacked IR spectra of gas that escapes from TGA at various temperatures.

In Figure 4, PEI was thermally stable up to $\sim 475°C$ and its maximum temperature was at 535°C.

TABLE I
Comparison of the Aimed and Actual IEC Values of SPEI

Sample	Target IEC (mequiv/g)	Titration		elemental analysis		$[\eta]_{inh}$ (dL/g)
		DS (%)	IEC (mequiv/g)	DS (%)	IEC (mequiv/g)	
1	0	0	0	0	0	0.450
2	0.50	25.08	0.41	24.94	0.40	0.433
3	0.60	33.56	0.54	32.97	0.53	0.428
4	0.70	43.55	0.69	42.55	0.67	0.419
5	0.80	50.49	0.79	49.63	0.78	0.435
6	0.90	57.00	0.89	55.18	0.86	0.442
7	1.0	64.42	0.99	62.60	0.97	0.464
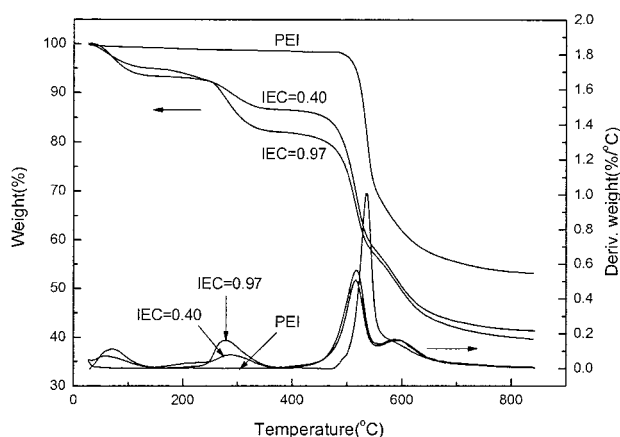
Figure 4 Thermogravimetric and DTG for pure PEI and SPEI.

Figure 6 FTIR spectra of gas escaping from SPEI of IEC equal to 0.97 mequiv/g at different temperature.

On the basis of Figure 5, this weight loss is assigned to the degradation of the PEI main chain. The spectra of the evolved volatile components, which are the product of PEI heated at 507–642°C, exhibits clear features that correspond to the matrix. The sharp peak at 2358 cm^{-1} is related to the adsorption peak of CO_2 and CO, which is split from the carbonyl groups in the main chain. Peaks associated with sp^2 carbon hydrogen and sp^3 carbon hydrogen stretching, above and below 3000 cm^{-1}, respectively, as well as peaks associated with phenyl ring stretching and skeletal vibration at 1497 and 1602 cm^{-1}, are observed.

Figure 4 indicates three stages of weight loss for SPEI with IEC values equal to 0.97 mequiv/g and 0.40 mequiv/g, unlike unsulfonated PEI. In the first step, the weight loss begins below 100°C and continues up to ~ 160°C. This step is followed in that order by two other degradation steps at ~ 230 and 450°C. The initial weight loss (about 10% weight loss) is caused by the removal of water from the hy-
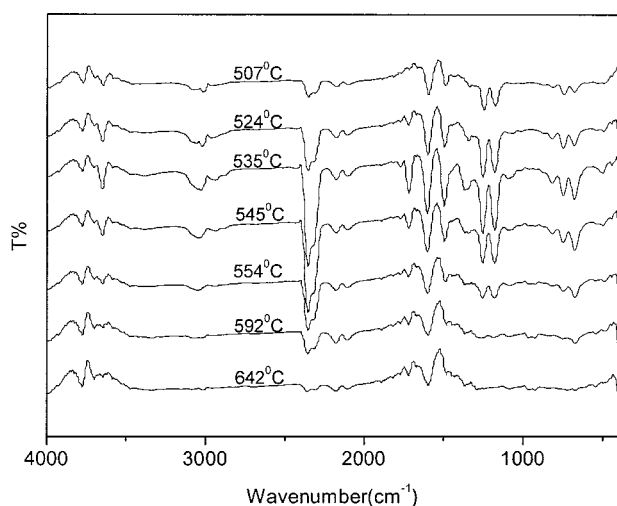
groscopic samples. The continuous water loss up to 160°C is caused by the strong hydrogen bonding between the water molecules and the sulfonic acid groups in the samples. This fact was verified by the FTIR spectrum of the degradation gas products of SPEI at 120°C, displayed in Figure 6. The absorption of bands at 3630–3885 cm^{-1} is due to the O—H stretching vibrations of water absorbed in the sample. The absorption band at ~ 3270 cm^{-1} is characteristic of hydrogen bonding of O—H groups. Additionally, some other sulfonated polymers[26] and commercial perfluoro-sulfonic acid membranes, such as Nafion 117,[27] exhibited similar behavior.

The second weight loss, starting from 227°C, which has not been observed in a TG spectrum of PEI, is believed to be associated primarily with the loss of sulfonic groups. This fact was evidenced by the FTIR spectra of the gaseous products of SPEI at 247–330°C, presented in Figure 6. S=O stretching vibrations at 1365 cm^{-1} are evidence of the evolution of sulfonic acid group fragments. Furthermore, the adsorption peak of CO_2/CO at ~ 2358 cm^{-1} began to increase with temperature above ~ 300°C. This behavior demonstrated that the presence of sulfonic acid groups slightly splits the carbonyl groups in the main chain.

The third stage occurring at about 450°C, close to the PEI decomposition temperature, is related to the splitting of the main chain. The sulfonated samples have lower decomposition temperatures than PEI because of the increase in the asymmetry of the SPEI structure associated with the introduction of —SO$_3$H groups that render it less regular and hence less stable.

Figure 5 FTIR spectra of gas escaping from PEI at different temperature.

Glass-transition behavior of SPPO

The introduction of sulfonate groups has two effects on the glass transition temperature (T_g)[16,28]: firstly, it
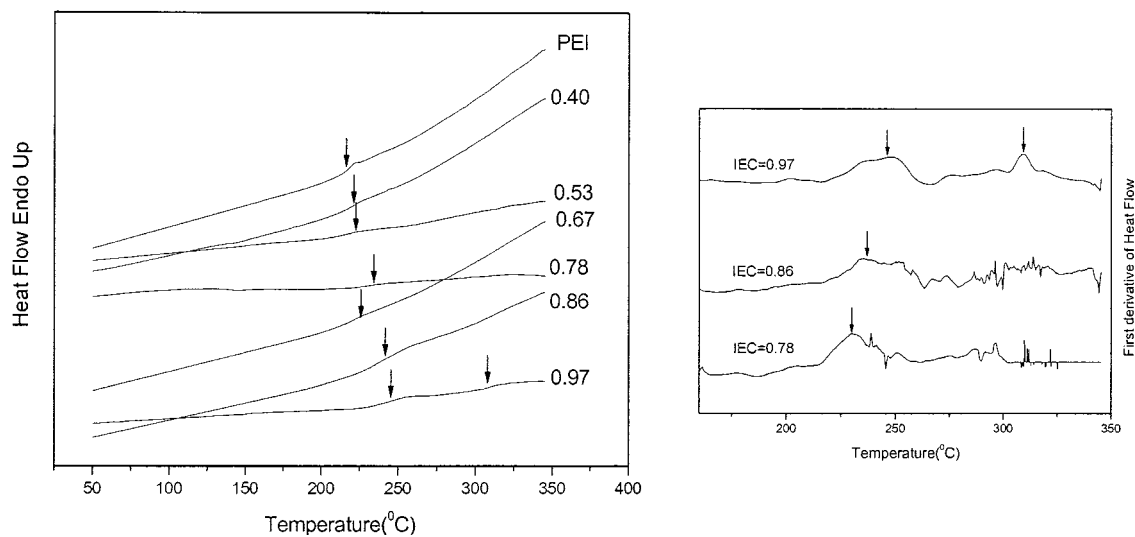
Figure 7 DSC spectra of PEI and SPEI.

increases the intermolecular interaction of pendant ions, i.e. the ionomer effect. The —SO_3H groups on adjacent chains easily form H bonds between macromolecular chains, where they strengthen the interaction; secondly, it increases molecular bulkiness. The substitution of PEI with a relatively rigid and bulky side group —SO_3H may directly suppress torsional motion in the polymer by interfering with it, the phenomenon which increases the stiffness of the chain. Both effects inhibit internal rotation, increasing the T_g value of sulfonated polymers.

The T_g values of PEI and SPEI were determined in two ways: from the temperature of the DMTA tan δ peak measured at 1 Hz and by DSC at a heating rate of 10°C/min. Figures 7 and 8 shows the DSC and DMTA spectra of PEI and SPEI systems. Table II summarizes the glass transition temperatures (T_g values). The T_g values determined by DSC and DMTA were in substantial agreement. These T_g data exhibit a slight increase for IEC increasing from 0 to 0.67 mequiv/g. For example, T_g increased from 217°C for unmodified PEI to 223°C for SPEI with IEC equal to 0.67 mequiv/g. Nevertheless, the T_g values of the 0.86 mequiv/g and 0.97 mequiv/g sulfonated samples increased dramatically, perhaps because the sulfonate groups were isolated in the polymer matrix when IEC was low but began to aggregate at higher concentrations of —SO_3H groups. The DMTA spectra and the first derivative of DSC presented in the small box on the right of Figure 7 clearly revealed that the 0.78 mequiv/g and 0.86 mequiv/g sulfonated samples had only one T_g while the 0.97 mequiv/g sulfonated sample had two T_g values. The two T_g values of the sample with the highest IEC value are attributed to spontaneous phase separation in the hydrated SPEI polymer: the hydrophilic phase formed by sulfonation is segregated into ion cluster phases that are dispersed in a hydrophobic PEI matrix.
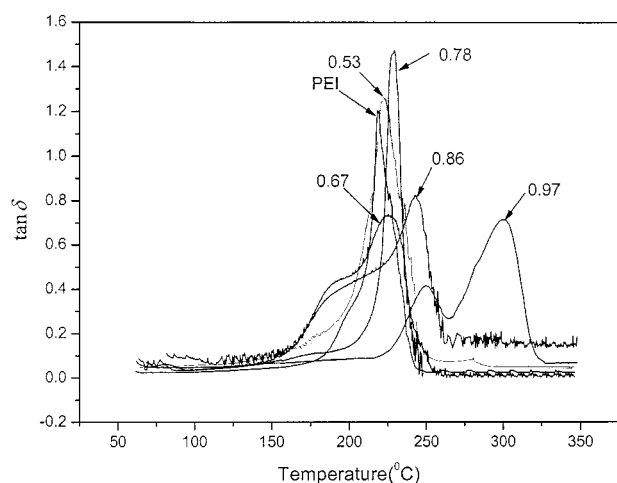

Figure 8 DMTA spectra of PEI and SPEI.

TABLE II
Thermal Characterization of DSC, DMTA, and TG

| Samples | T_g (°C) | | T_1 (°C)[a] | T_2 (°C)[b] |
	DSC	DMTA		
PEI	217	218		472
SPEI-0.40	220		237	436
SPEI-0.53	221	221	237	435
SPEI-0.67	223	225	238	435
SPEI-0.78	228	228	237	434
SPEI-0.86	240	242	234	433
SPEI-0.97	247,307	249,300	230	433

[a] The initial loss temperature of the second stage.
[b] The initial loss temperature of the third stage.

TABLE III
Solubilities of PEI and SPEI

Solvent	PEI	SD 24.94%	SD 42.55%	SD 62.60%
n-Hexane	−	−	−	−
Toluene	−	−	−	−
Acetone	−	−	−	Δ
Dichloroethane	+	Δ	−	−
Chloroform	+	+	Δ	−
Tetrahydro furan	Slightly swell	Δ	Δ	Δ
DMSO	Slightly swell	Δ	+	+
DMAc	±	+	+	+
DMF	±	+	+	+
NMP	±	+	+	+
Ethanol	−	Δ	Δ	Δ
Methanol	−	Δ	Δ	Δ
water	−	Δ	Δ	Δ

Solubility: (+) soluble at room temperature, (−) insoluble, (±) soluble at high temperature, (Δ) swollen.

Solubility behavior

Table III presents the measured solubilities of PEI and SPEI. PEI is a hydrophobic material and exhibits weak solubility at room temperature in almost all of the tested solvents, except for some of the chlorinated solvents, such as dichloroethane and chloroform. Sulfonation is a feasible approach for improving the solubility of PEI in widely adopted conventional dipolar solvents. The samples show good solubility in dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMAc), N,N-dimethyl formamide (DMF), and N-methyl-2-pyrrolidone (NMP) following sulfonation. Even when the DS is sufficiently high, it can be dissolved in water, methanol and ethanol at high temperature. Introducing —SO$_3$H groups into PEI increases the solubility in high-polarity solvents and reduces the solubility in chlorinated solvents.

CONCLUSIONS

In this investigation, a series of SPEI with different IEC values ranging from 0.41 mequiv/g to 0.99 mequiv/g were successfully prepared by using chlorosulfonic acid as a sulfonating agent and chloroform as a solvent. Under the conditions of moderate reaction, polymers could be obtained without evident chain scission. The structure of SPEI was verified by FTIR and NMR spectroscopy. TG-FTIR verified that the SPEI samples were thermally stable up to ∼ 230°C in an atmosphere of N$_2$. As the IEC values of SPEI increased, T_g and the solubility in highly polar solvents increased. The first derivative of DSC traces clearly revealed that the SPEI samples

had only one T_g when IEC was below 0.99 mequiv/g. However, when IEC value was equal to 0.99 mequiv/g, two T_g values were detected, which was attributed to the spontaneous phase separation in the hydrated SPEI polymer and would lead to form the unique transport characteristics. The unique transport characteristics of SPEI can provide the high proton conductivity which is needed for fuel cells. Therefore, SPEI is considered to be an attractive candidate material for proton exchange membranes in fuel cells.

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