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Structures and properties of highly sulfonated poly(arylenethioethersulfone)s as proton exchange membranes

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Abstract

A series of sulfonated poly(sulfonium cation) polymers, sulfonated poly(arylenethioethersulfone)s (SPTES)s possess up to two sulfonate groups per repeat unit, and can be easily converted into corresponding acid form of the SPTES polymer to form a tough, ductile, free-standing, pinhole-free membranes with excellent mechanical properties. The SPTES polymers exhibit good water affinity and excellent proton conductivity due to the high water uptake. Proton conductivities between 100 and 300 mS/cm (at 65 °C, 85% relative humidity) were observed for the SPTES polymers with 50 mol% (SPTES-50) to 100 mol% (SPTES-100) of sulfonated monomer. The evaluation by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA) showed that the SPTES polymers have excellent thermal stability, mechanical properties, and dimensional stability, making them excellent candidates for the next generation of proton exchange membranes (PEMs) in fuel cell applications.
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Keywords: Proton exchange membrane (PEM); Thermal stability; Dimensional stability

1. Introduction

A proton exchange membrane fuel cell (PEMFC) is attractive alternative energy device that converts chemical energy directly into electrical energy by a series of platinum-catalyzed reactions [1]. PEMFC consists of two electrodes and a solid polymer membrane, which acts as an electrolyte. The proton exchange membrane (PEM) is sandwiched between two layers of porous platinum electrodes coated with a thin layer of a proton-conducting material, and this assembly is placed between two gas diffusion layers such as carbon cloth or carbon paper, enabling transfer of electrical current and humidified gas [2].

Proton-conducting polymers are usually polymer electrolyte materials with negatively charged groups on the polymer backbone or side chain. The proton conductivity of hydrated polymer electrolyte materials increases dramatically with water content and reaches values as high as 10^{-2} to 10^{-1} S/cm. With good chemical stability and proton conductivity, perfluorinated copolymers, such as Nafion [3], are the current PEM materials of choice. However, commercial use of Nafion is limited by (i) a low modulus and a modest glass-transition temperature; (ii) reduced conductivity at temperatures above 80 °C; and (iii) a relatively high methanol permeability, which limits its use in direct methanol fuel cells, as well as (4) the price of Nafion.

Proton-conducting polymer materials that exhibit fast proton transport at elevated temperatures are needed for PEMFCs and other electrochemical devices operated in higher temperature [2] (100–200 °C) where the devices are most efficient. The operation of a PEMFC at elevated temperatures has several advantages, including the increase of the kinetic rates for the fuel cell reactions, fewer problems with catalyst poisoning by absorbed carbon monoxide in the 150–200 °C

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range, a reduced need for the use of expensive catalysts, and minimization of problems due to electrode flooding. Thus, the thermal stability of the proton-conducting polymer for PEMs is a very important factor for fuel cell applications. Over the last decade, several new proton-conducting polymer materials have been introduced, including poly(styrene sulfonic acid), poly(trifluorostyrene sulfonic acid) [4,5], as well as chemically and thermally stable aromatic polymers such as poly(phenylenesulfide) [6] after sulfonation. The water uptake, mechanical integrity, and proton conductivity of these polymers were promising enough to evaluate them as PEM candidates in fuel cells. More recently, McGrath et al. [7] reported the synthesis and characterization of poly(arylenethioethersulfone) copolymers with lower sulfonated levels (<50 mol%) by direct polymerization using 1-methyl-2-pyrrodinone as solvent. The proton conductivity of the copolymers was measured in the fully hydrated state at 30 °C and was 160 mS/cm for the copolymer with the highest sulfonic acid content.

In this article, the sulfonated poly(arylenethioethersulfone) (SPTES) polymers containing 50–100 mol% of sulfonated monomers are investigated for thermal and dimensional stabilities using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA) to show that the SPTES polymer materials can be used as PEMs in fuel cells at high temperatures. The structures and properties of the SPTES polymers are evaluated by NMR analysis and proton conductivity measurement.

2. Experimental

2.1. Materials

N,*N*-dimethylacetamide (DMAc, anhydrous, 99%, Sigma–Aldrich Co.) was used as received. Other chemicals were of analytical grade and used as received unless otherwise mentioned. Sulfonated poly(arylenethioethersulfone) (SPTES) polymers were prepared by using a procedure developed in our previous works [8,9]. The chemical structure of the SPTES polymers is shown in Fig. 1.

Fig. 1 shows the chemical structure of homopolymer SPTES-100 ($x=1$, $y=0$), and copolymers SPTES-80 ($x=0.8$, $y=0.2$), SPTES-70 ($x=0.7$, $y=0.3$), SPTES-60 ($x=0.6$, $y=0.4$), and SPTES-50 ($x=y=0.5$).

2.2. Preparation of the SPTES polymer membranes

Membranes were prepared by dissolving the SPTES polymer salt in DMAc to form ~10 wt% clear solutions, which, after filtration, were taken up in a clean glass dish for casting. The membranes were vacuum-dried at gradually increasing temperatures of up to 100 °C for 24 h and 120 °C for 2 h. The drying procedure was optimized to produce flat, transparent membranes with the maximum removal of the solvent. We found that rapid drying causes the membranes to form bubbles and be brittle. The polymer salt membranes were converted into the acid form by the immersion for 24 h in 4 M sulfuric acid at room temperature followed by soaking for 2–4 h in deionized water, and washing with deionized water for 2 h prior to vacuum drying at 80 °C for 24 h.

2.3. Water uptake measurement

The SPTES polymer membranes were vacuum-dried at 100 °C for 24 h, weighed and immersed in deionized water at room temperature for 24 h. The wet membranes were wiped dry and then quickly weighed again. The water uptake of the polymer membranes is reported in weight percent in Eq. (1):

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{1}$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. This method provides an accurate measurement of water uptake and has been established in literature [10].

2.4. Ion exchange capacity measurement

The ion exchange capacity (IEC) was measured by the following procedure: the SPTES polymer membrane was immersed in a 2.0 M solution of NaCl for 4–5 h to replace the protons of sulfonic acid groups with sodium ions. The replaced protons were titrated using 0.1 M NaOH solution, with phenolphthalein as indicator. The moles of the proton are equal to the moles of sulfonic group and the IEC was calculated from the titration data.

2.5. Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR analyses were conducted on a Bruker Avance 400 NMR spectrometer. All spectra were obtained from a 10% solution (w/v) in DMSO-d_6 at room temperature.

2.6. Proton conductivity measurement

The proton conductivity of the SPTES polymers was measured by AC Impedance Spectroscopy. The experiment utilized a standard 4-electrode measurement setup to eliminate

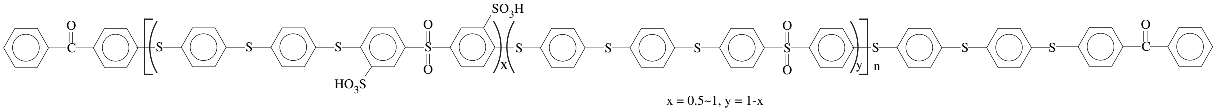

Fig. 1. Chemical structure of the SPTES polymers.

electrode and interfacial effects. The Teflon sample fixture was placed inside a temperature and humidity controlled oven fabricated in such a way to allow the sample to be exposed to the humidified air within the chamber. The two outer electrodes (source and drain) were made of platinum foil. Two inner platinum wire electrodes (spaced 1 cm apart) were then used to measure the voltage drop across a known distance. By measuring the impedance of the film as a function of frequency at a set temperature and humidity, the conductivity of the membrane is obtained using the magnitude of the impedance in a region where the phase angle is effectively zero. Membrane samples were cut into strips that were approximately 1.0 cm width, 5 cm length, and 0.01 cm thickness prior to mounting on the cell.

2.7. Thermal analysis

Differential scanning calorimetry (DSC) was used measurement the T_g's and detect any other thermal transitions. A TA Instrument Model DSC 2910 was used with a heating rate of 5 °C/min for samples weighing 5–15 mg.

The thermooxidative behavior of the SPTES polymers was determined by thermogravimetric analysis (TGA) on an Auto TGA 2950HR V5.4A instrument. Before the analysis, the membranes were dried *in vacuo* for at least 12 h for the removal of absorbed water. The analyses were performed over the range of 30–900 °C at a heating rate of 10 °C/min in air.

2.8. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed to determine the influence of the polymer constitution on tensile modulus and mechanical relaxation behavior. A Perkin–Elmer DMA-7 was run in tensile mode at an oscillation frequency of 1 Hz with a static stress level of 5×10^5 Pa and a superposed oscillatory stress of 4×10^5 Pa. With this stress controlled instrument, the strain and phase difference between stress and strain are the measured outputs. Typically, the resulting strain levels ranged from 0.05 to 0.2% when the sample dimensions were 8 mm × 2 mm × 0.1 mm. A gaseous helium purge and a heating rate of 3 °C/min were employed. The temperature scale was calibrated with indium, and the force and compliance calibrations were performed according to conventional methods.

2.9. Thermomechanical analysis

The in-plane coefficient of thermal expansion (CTE) of the SPTES polymers was measured as a function of temperature via thermomechanical analysis (TMA). The technique utilized a TA Instrument TMA 2940 in tensile film mode with a heating rate of 4 °C/min and typical sample dimensions of 100 mm × 15 mm × 0.25 mm. The CTE was determined from the slope of the resultant expansion temperature plots.

3. Results and discussion

3.1. Structures and properties of the SPTES polymers

The SPTES polymers were synthesized by the polymerization of 3,3′-disulfonated-4,4′-dichlorodiphenylsulfone, 4-chlorophenylsulfone, and 4,4′-thiobisbenzenethiol in tetramethylene sulfone as solvent in the presence of potassium carbonate as shown in our previous work [8,9]. The resulting poly(sulfonium cation), having a thioether sulfone and sulfonated structure, is soluble in DMAc, DMF, and NMP as well as slightly soluble in methanol and water, depending on the sulfonate composition of the SPTES polymers.

The proton conductivities of the SPTES polymer membranes in the longitudinal direction were measured by AC impedance spectroscopy. The SPTES polymer membranes were initially hydrated by immersion in deionized water for at least 24 h at room temperature. The proton conductivities were measured at 65 °C and 85% relative humidity and were 100, 145, 175, 215, and 300 mS/cm for SPTES-50, SPTES-60, SPTES-70, SPTES-80, and SPTES-100; these highly proton-conducting membranes are undoubtedly promising for fuel cell applications. The proton conductivities increase as the sulfonic acid content of the SPTES polymer increases. We note that even the sulfonated polymer with a relatively lower sulfonic acid content, i.e., SPTES-50, has a proton conductivity slightly exceeding that of Nafion-117 under the same conditions.

Previous studies have shown that proton conductivity is temperature dependent. Fig. 2 shows the proton conductivity of the SPTES polymers and Nafion-117 at 85% relative humidity as a function of temperature. In all the cases, we observe an increase in proton conductivity with increasing temperature. All SPTES polymer membranes exhibited higher proton conductivity than Nafion-117 except in the lower temperature region for SPTES-50 where a slight crossover is observed.

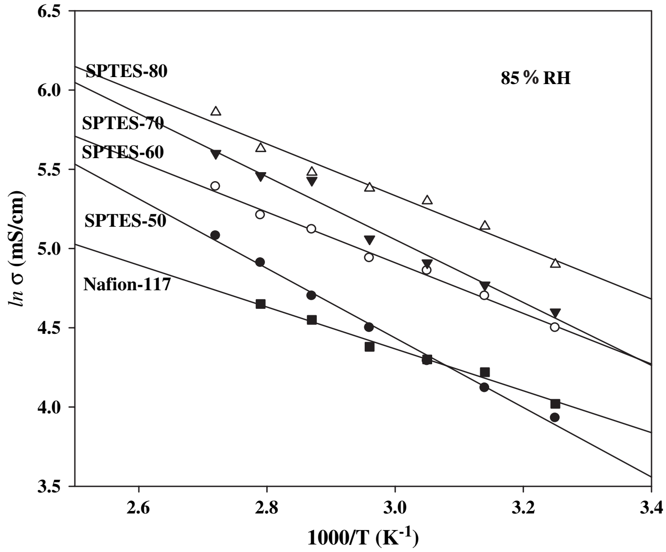

Fig. 2. Temperature dependence of proton conductivity of the SPTES polymers.

From Fig. 2, we found that the proton conductivities of the SPTES polymers have a linear dependence on temperature and show Arrhenius-type temperature dependent behavior. The activation energies (E_a) are calculated from a linear least square fit to the data presented in the Fig. 2 according to Arrhenius equation (2) are given by:

$$\sigma = A\mathrm{e}^{-E_\mathrm{a}/RT} \tag{2}$$

where σ is the proton conductivity (S/cm), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature (K). The activation energies calculated for Nafion-117 and the SPTES polymers are listed in Table 1.

From Table 1, we note that the activation energy we measured for Nafion-117 (9.79 kJ/mol) is comparable with the reported values 9.41 kJ/mol [11] and 9.53 kJ/mol [12]. It is generally accepted that the proton transfer occurs through two main mechanisms in hydrated polymer electrolyte membranes, migration of hydronium ions and the orientational mode assisted proton hoping or structural diffusion [13,14]. The difference in activation energy suggests that the proton-conducting mechanism for SPTES and Nafion-117 is different or the contribution of the two mechanisms is different. The activation energies of the SPTES polymers are in the range of $14.8-18.2$ kJ/mol, and the average activation energy of the SPTES polymers is 16.5 ± 1.7 kJ/mol, indicating that the proton transfer mechanism is similar for SPTES-50, SPTES-60, SPTES-70 and SPTES-80.

The composition of the SPTES polymers was analyzed by ^{1}H NMR in DMSO-d_6 and typical NMR spectra are shown in Fig. 3. The spectra show that the peaks at 7.8 and 7.3 ppm increase in intensity as the amount of non-sulfonated monomer is increased. The composition of sulfonated (A) and non-sulfonated (B) monomers can be evaluated by integrating the aromatic region of NMR spectra. The analysis relies on the observation that the protons adjacent to the sulfonic acid at 8.16 ppm are resolved from all other protons, and the polymer composition can be determined from the ratio of the peak at 8.16 ppm to the remaining aromatic protons. Since there are 12 aromatic protons in addition to the 2 protons at 8.16 ppm in the sulfonated monomer (A) and 16 protons in the non-sulfonated monomer (B), the ratio r is given by Eq. (3):

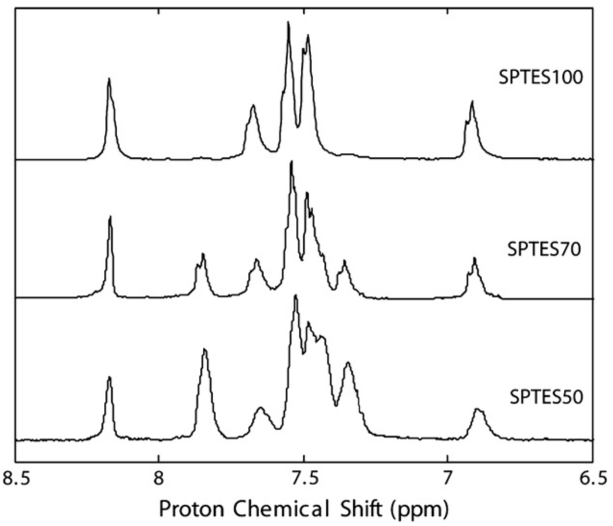

Fig. 3. The aromatic part of NMR spectra for the SPTES polymers.

$$r = \frac{2f_\mathrm{A}}{12f_\mathrm{A} + 16(1 - f_\mathrm{A})} \tag{3}$$

where f_A is the fraction of sulfonated monomer, which is called Sulfonate Content (SC). Conversely, the value of f_A calculated from r is given by Eq. (4):

$$f_\mathrm{A} = \frac{16r}{2 + 4r} \tag{4}$$

The calculated and measured SC of the SPTES polymers from the analysis of the aromatic peak intensities are listed in Table 1. The calculated compositions of the SPTES polymers from NMR results were 98, 69, and 47% of sulfonated monomer for SPTES-100, SPTES-70, and SPTES-50, respectively, which is in close agreement with the monomer feed ratios. This shows that the polymerization was run to completion. We believe that the SC from the NMR experiments is accurate than the titration results, which gave 91, 63, and 45% of sulfonated monomer for SPTES-100, SPTES-70, and SPTES-50, respectively.

3.2. Thermal stability of the SPTES polymers

The thermal properties of the SPTES polymers were examined by TGA under nitrogen and air at a heating rate

Table 1
Characteristics of the SPTES polymer membranes and Nafion-117

Polymers	Cal. IEC[a] (meq./g)	Exp. IEC[a] (meq./g)	EW[c] (mg/meq.)	SC[b] (%mol) (IEC)	SC[b] (%mol) (NMR)	Activation energy (kJ/mol)
SPTES-100	3.20	2.89	346	91	98	N/A
SPTES-80	2.68	2.40	417	72	N/A	14.8
SPTES-70	2.41	2.18	459	63	69	16.5
SPTES-60	2.12	1.94	515	55	N/A	15.5
SPTES-50	1.82	1.64	610	45	47	18.2
Nafion-117	0.91	N/A	1100	N/A	N/A	9.79

[a] The ion exchange capacity (IEC) is defined as the number of milliequivalents of ions in 1 g of the dry polymer (meq./g). Titration was used to quantitatively determine sulfonic acid concentration in the polymer.

[b] SC: sulfonate content. The SC is expressed as the mole percentage of $-SO_3H$ groups per average repeat unit of the synthesized 6F-SPTES copolymers.

[c] EW: equivalent weight; EW = 1/IEC.

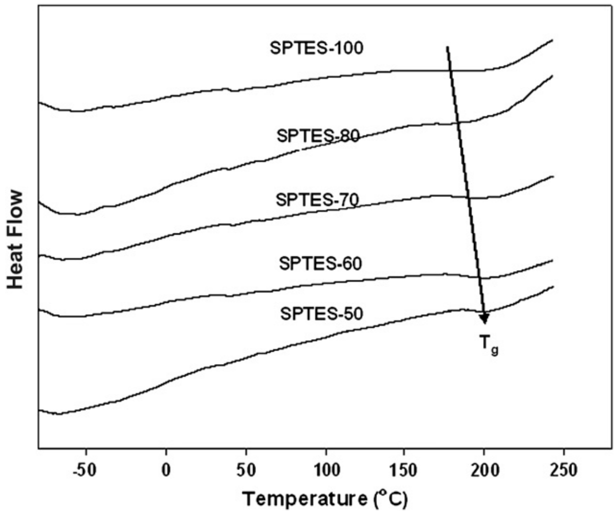

Fig. 4. DSC curves of the SPTES polymers.

of 10 °C/min. The TGA results show that all SPTES polymers have excellent thermal stability, and the polymers are stable at least up to 300 °C (the onset of thermal decomposition). All SPTES polymers exhibited two distinct thermal degradation steps. The first weight loss occurs near 300 °C or higher and is associated with the loss of sulfonic acid groups while the second weight loss step starts near 420 °C and is related to the main chain decomposition.

The DSC (see Fig. 4) shows that T_g increases with decreasing sulfonic acid content in the range of polymer compositions from SPTES-100 to SPTES-50. The T_gs of the SPTES polymers were also determined by DMA, as shown in Fig. 5. The data in Fig. 5 show the tan δ versus temperature at 1 Hz frequency for the SPTES polymers. The maximum damping peaks for SPTES-100 appear at 202 and 238 °C. The presence of two peaks is presumably an indication of two segments in the polymer chain requiring different levels of thermal energy to initiate chain segmental motions. The maximum damping peaks for SPTES-80 appear at 204 and 235 °C, while the ones for the SPTES-70 are at 215 and 235 °C. SPTES-60 shows a shoulder peak at 216 and a high intensity peak at 228 °C, while the T_g of SPTES-50 is a single peak at 223 °C. The lower temperature peak starts to shift toward higher temperatures with decreasing sulfonic acid content. The higher temperature transition shifts toward lower temperatures with a concomitant increase in its intensity.

The trends in T_g from the two methods are in close agreement. The T_gs of the SPTES polymers, determined by DSC are in the range of 180–210 °C, while the T_g values for the SPTES polymers from DMA are in the range of 200–230 °C (see Fig. 6). Increasing the sulfonic acid content of the SPTES polymers dramatically decreases the T_g, as indicated by the low temperature shift of the loss tangent peak with sulfonic acid content, from a value of 223 °C for SPTES-50 polymer to 202 °C for SPTES-100 polymer ($\Delta T_g = 21$ °C, DMA).

The DSC shows a clear decrease as the sulfonation level decreases ($\Delta T_g = 20$ °C, DSC), but we note that the DMA value is slightly higher for the SPTES polymers (17 °C for the SPTES-100 and 18 °C for SPTES-50). This slight discrepancy is reproducible, in particular, the sulfonate composition of polymers is in the ranges from polymer PTES with no sulfonate content to polymer SPTES-100 with 100% content of the sulfonate-bearing repeat unit. The T_g decreases substantially, whereas the negative slope of temperature versus sulfonate content increases. We also observed that the T_g value of the PTES polymer is 229 °C based on the DMA results and 214 °C based on the DSC results. The shift in T_g of two methods is 15 °C, which is smaller than sulfonated SPTES polymers (20 °C).

3.3. Dimensional stability of the SPTES polymer membranes

Dimensional stability of PEM materials is important for the operation of fuel cells at high temperatures and humidities. The temperatures, mechanical properties, and humidities are

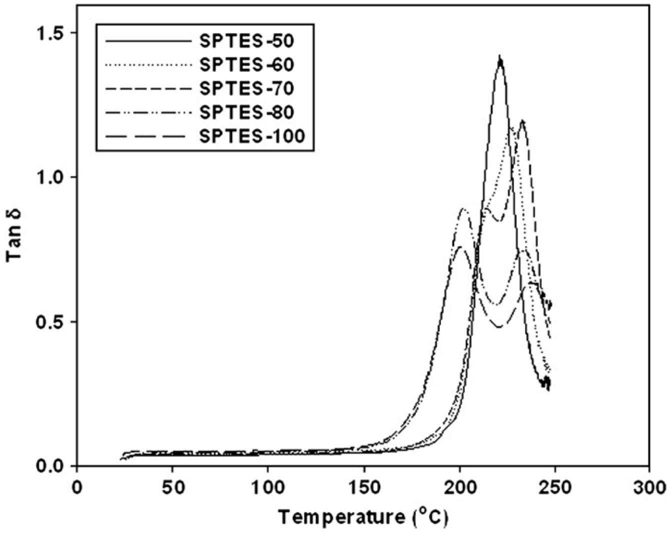

Fig. 5. DMA tensile loss tangents (1 Hz) as a function of temperature for the SPTES polymers.

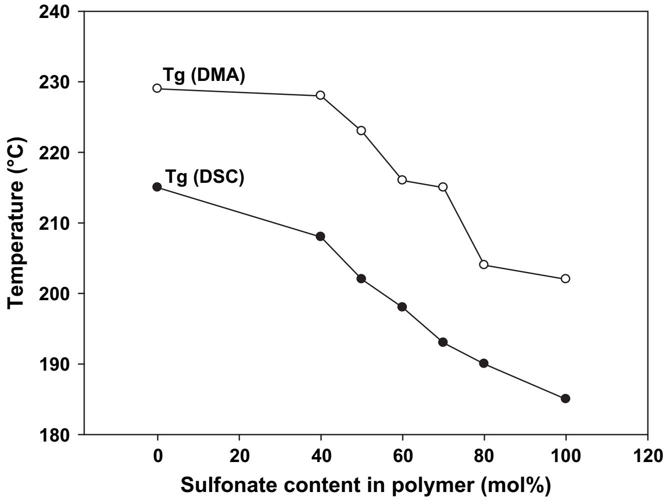

Fig. 6. Trend in the T_g of the SPTES polymers with increasing sulfonated content as measured by DSC and DMA.

known to affect dimensional changes of polymer electrolyte materials. To evaluate the PEMs for high temperature applications, we measured the mechanical properties, dynamic mechanical properties, and water absorption at elevated temperature along with the dimensional changes of the SPTES polymers.

Mechanical properties of the PEM materials affect manufacturing conditions of MEAs and the durability of PEMFC operations. The mechanical properties of the SPTES polymer membranes and Nafion-117 membrane were determined by a tensile tester under ambient conditions [9]. The results showed that the elongation and strength at break decrease as the sulfonic acid content increases. This suggests that the hydration may have interchain H-bonding interactions mediated by bridging water molecules in the sulfonated polymers. However, at high sulfonation levels the higher water levels would plasticize the polymer, resulting in the reduction of mechanical properties.

The results from the DMA experiments are shown in Fig. 7, where the tensile storage modulus (E') for all SPTES polymers is plotted against the temperature. The secondary peak in E' is assigned to a β transition. This comparison shows the influence of the sulfonate content on the mechanical behavior. The tensile moduli are all in the range of 400–700 MPa near room temperature; as the sulfonate content increases, the tensile moduli are going up to 1700 MPa, especially for SPTES-50, while the storage modulus at temperatures near T_g shows the sensitivity to the SPTES polymer composition; as the sulfonate content increases, the storage modulus of the SPTES polymers at temperatures near the T_g decreases, as observed with the T_g results of DSC and DMA shown in Fig. 6.

The thermomechanical behavior of the SPTES polymer membranes was examined by TMA to determine the in-plane coefficient of thermal expansion (CTE). The SPTES polymer membranes were loaded uniaxially with a tensile stress of 0.5 MPa, and the growth in the sample dimension was monitored with increasing temperature. Below T_g, the applied stress is significantly below the yield stress of the polymers. However, above T_g the applied stress yielded a significant creep in the samples, allowing the accurate determination of T_g itself, albeit with an inaccurate measurement of the expansion coefficient above T_g. The results for the SPTES polymers are shown in Fig. 8. At low temperatures, we observed a broad linear regime with small upward curvature (around 50 °C), indicating a nearly constant coefficient of thermal expansion with slight increases along with increasing temperature. At temperatures near T_g, the applied stress can yield a significant creep in the samples. The dimensional change in tensile model shows a large jump in linear expansion for all SPTES polymers.

From a comparison with the DMA data presented previously (see Fig. 7), it appears that the slope change occurs at the same temperature as a secondary mechanical relaxation. At this point, we cannot conclusively identify the origin of a decrease in thermal expansion coinciding with β relaxation. It is possibly suggested that the secondary mechanical relaxations will create enough mobility to allow the release of small amounts of hydrogen-bonded water, leading to a membrane with lower plasticization by water and a smaller coefficient of thermal expansion.

The water absorption was used to quantitatively determine the dimensional changes of the SPTES polymers and to relate the presence of water in the SPTES polymeric membrane to changes in thickness, length, and width of the SPTES polymer membranes. The measurement procedure was as follows: the SPTES polymer membrane samples were vacuum-dried at 100 °C for 24 h, cut into 30 × 30 × 0.25 mm, and immersed in deionized water at room temperature (25 °C) to 85 °C for 4 h. Then the wet membranes were wiped dry and then quickly measured. The dimensional changes (%) were calculated. The results are shown in Fig. 9(A)–(C) for SPTES-50, SPTES-60, and SPTES-70.

Fig. 9 shows the dimensional stability of the SPTES polymers in water with increasing temperature. From Fig. 9(A),

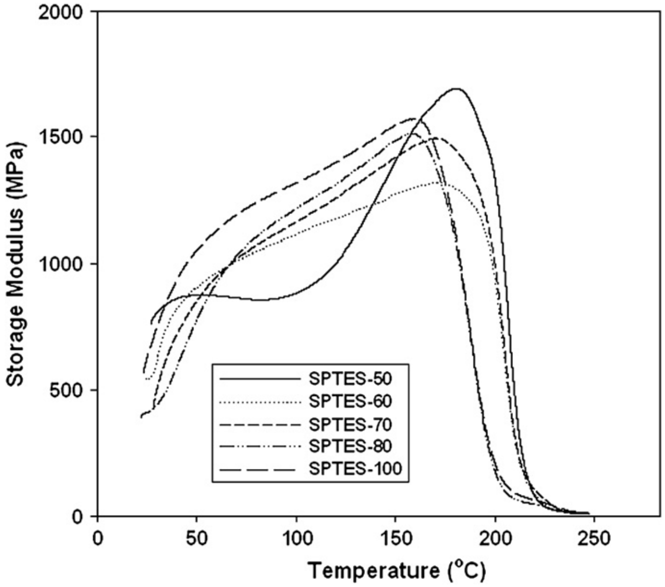

Fig. 7. DMA tensile storage modulus (1 Hz) as a function of temperature for the SPTES polymers.

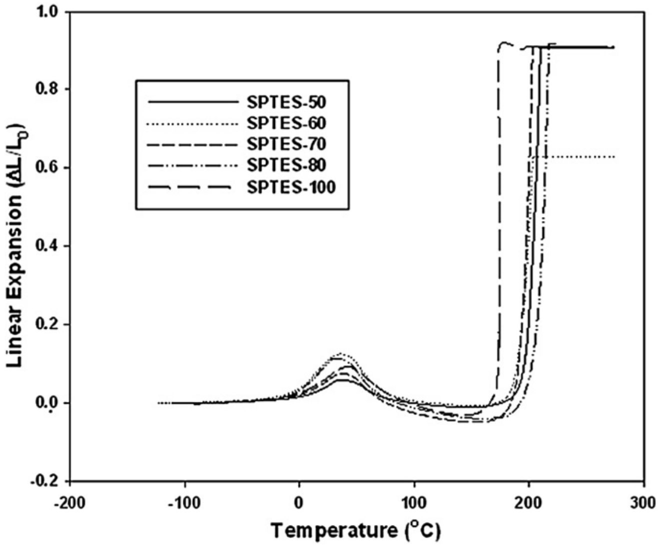

Fig. 8. TMA dimensional changes versus temperature in the tensile mode for the SPTES polymer membranes heated at a rate of 4 °C/min.

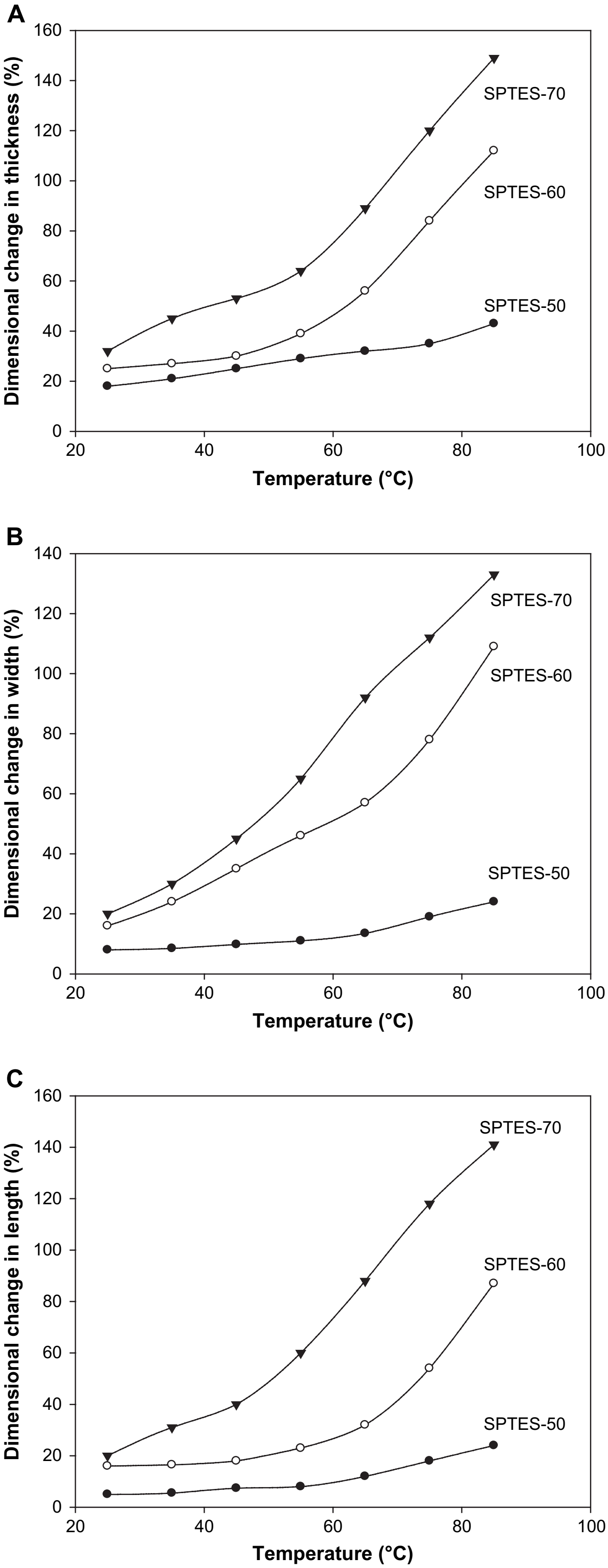

Fig. 9. Dimensional changes of the SPTES polymers in water at different temperatures. (A) SPTES polymers when thickness changes; (B) SPTES polymers when width changes; (C) SPTES polymers when length changes.

we can observe that the thickness changes as the temperature increases for the SPTES polymers. The thickness change (<40%) of SPTES-50 membrane is acceptable over the entire temperature range, while the thickness change for SPTES-60 and SPTES-70 membranes is acceptable only below 55 °C. Fig. 9(B) is the width change as the temperature increased for the SPTES polymers. The width change (<20%) of SPTES-50 membrane is acceptable in the whole range of temperatures, while the width changes of SPTES-60 and SPTES-70 membranes are acceptable only at 25 °C. Fig. 9(C) shows the length change of the SPTES polymers as the temperature increased. The length change (<20%) of SPTES-50 membrane is acceptable over the entire temperature range, while the length change (<20%) of SPTES-60 membrane is acceptable below 55 °C and the length change of SPTES-70 membrane is acceptable one at 25 °C.

4. Conclusions

Sulfonated poly(arylenethioethersulfone) (SPTES) polymers were synthesized via direct polymerization. This method results in the random incorporation of the sulfonated monomer throughout the poly(arylenethioethersulfone) structure. The SPTES polymers can be fabricated into tough, flexible membranes by casting from DMAc. The characterization of the SPTES polymers shows excellent thermooxidative stabilities and the proton conductivities were in the range of 100–300 mS/cm. Evaluation by dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) showed that the SPTES polymers have excellent thermal stability, mechanical properties, and dimensional stability, demonstrating that they are very promising materials for PEM fuel cell applications.

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