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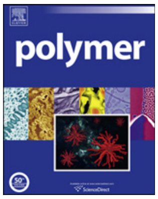

Synthesis and characterization of fully disulfonated poly(arylenethioethersulfone)s containing hexafluoroisopropylidene moiety

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ABSTRACT

High molecular weight sulfonated poly(arylenethioethersulfone) homopolymer containing hexafluoroisopropylidene moiety (6F-SPTES-100) was synthesized from the monomers 3, 3′-disulfonated-4, 4′-difluorodiphenylsulfone and 4, 4′-(hexafluoroisopropylidene) diphenylthiol, using 4-fluorobenzophenone as the end-capping agent in polar aprotic solvents at temperatures up to 180 °C to provide the desired polymeric composition for utilization as proton exchange membrane (PEM) in fuel cells applications. Tough, ductile freestanding membranes were fabricated from *N*, *N*-dimethylacetamide (DMAc) by solvent-casting. The end-capped 6F-SPTES-100 polymer was fully characterized and the membrane was found to have proton conductivity as high as 180 mS/cm which was measured at 85 °C and 65% relative humidity. The proton conductivity of 6F-SPTES-100 was approximately two and half times higher than that of Nafion-117 under comparable conditions. The swelling and solubility characteristics of the 6F-SPTES-100 polymer in water are directly related to the high degree of sulfonation of the polymer backbone.

1. Introduction

In the proton exchange membrane fuel cells (PEMFCs), the proton exchange membrane (PEM) is, undoubtedly, the most critical component. Till recently, the perfluorinated ionomer Nafion has been the only commercially available, state-of-the-art proton exchange membrane successfully utilized in PEMFCs. Besides the high costs, the major drawbacks of Nafion membranes for large scale commercial fuel cell applications mainly arise from their low proton conductivities at higher temperatures (>80 °C) due to their loss of hydration and their inability to perform under relatively low humidity conditions [1,2]. With the energy crisis looming recognizably large in the late 20th/early 21st centuries, there has been an explosion of research activity related to the synthesis and fabrication of new proton exchange membranes (PEMs) that might serve as viable alternatives to Nafion in fuel cell operations. Several reviews have appeared recently, describing a range of PEMs from aromatic hydrocarbon-based/non-fluorinated polymeric structures to poly(aromatic heterocycles) such as polybenzimidazoles with proton conducting groups chemically grafted on to the main chain or as acid–base complexes [3–5].

There are essentially two strategies employed to synthesize sulfonated aromatic hydrocarbon polymers. The first one is the post-sulfonation of the polymer backbone utilizing one of the following sulfonating reagents: concentrated sulfuric acid, oleum, trimethyl chlorosulfonate and sulfur trioxide–triethylphosphate complex. Post-sulfonation is relatively facile in the case of polymer structures with electron-rich aromatic moieties such as aryl ethers and is thus restrictive in its scope. The sulfonic acid groups can also be eliminated from activated aromatic rings via desulfonation under acidic conditions at high temperatures. Moreover, the degree of sulfonation is difficult to control and post-sulfonation might also cause partial chemical degradation when strong sulfonation agents such as chlorosulfonic acid are employed. Recently, direct polymerization routes involving the use of monomers with the sulfonic acids attached to the deactivated aromatic ring positions have been increasingly employed [6,7]. This has a two-fold advantage; one is the ability to control the degree of sulfonation in copolymer structures and the second consideration is based on the chemical stability of sulfonic acid groups attached to electron-deficient aromatic rings. Sulfonated copolymer versions of both arylethersulfones and arylthioethersulfones have been prepared and evaluated as proton exchange membranes. Poly(arylenethioethersulfone)s copolymer with lower degrees of sulfonation (20–50 mol% of incorporated disulfonate moiety in the polymer backbone) by direct polymerization have been reported by McGrath et al [8], while we have recently reported the synthesis and characterization of end-capped

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poly(arylenethioethersulfone) homopolymer (SPTES-100, 100 mol% incorporation of the disulfonated monomer unit) prepared from 4, 4′-thiobenzenethiol and disodium 3, 3′-disulfonate-4, 4′-difluorodiphenylsulfone as well as those of the copolymers with high degrees of sulfonation (50–80 mol% incorporation of the disulfonated monomer unit) [9,10]. Proton conductivities in the range of 100–300 mS/cm were measured for these highly/fully sulfonated membranes at 65 °C and 85% relative humidity.

In this paper, we exclusively report on the synthesis, characterization and proton conductivity of a fully sulfonated arylthioethersulfone homopolymer containing hexafluoroisopropylidene moiety (6F-SPTES-100) derived from the polycondensation of disodium 3, 3′-disulfonate-4, 4′-difluorodiphenylsulfone with 4, 4′-(hexafluoroisopropylidene)bisbenzenethiol. This is also the first known report of a successfully synthesized sulfonated poly(arylenethioethersulfone) homopolymer with hexafluoroisopropylidene groups in the backbone. The rationale of this research has been based on our curiosity to examine the proton conductivity characteristics of these fully sulfonated polymers since the measured membrane proton conductivities would represent the limiting values that can be obtained for these classes of polymers as a function of the extent of sulfonation of the polymer backbone. While it is well-known that highly sulfonated polymers would dissolve or excessively swell in water due to their high levels of hydration thus rendering them unsuitable for utilization as proton exchange membranes, our efforts were focused, by the replacement of the central thioether group [9] with the hexafluoroisopropylidene (6F) group, on potentially balancing the homopolymer hydrophilicity due to the sulfonic acid pendants with the hydrophobicity of the polymer backbone. The synthesis of the sulfonated homopolymer with end-caps, detailed polymer characterization and proton conductivities of the membrane at different temperatures and relative humidities, are discussed in detail.

2. Experimental

2.1. Materials

4, 4′-Diflourodiphenylsulfone (4-Fluorophenylsulfone, 99%, Sigma–Aldrich Co.), 4, 4-(Hexafluoroisopropylidene) diphenol (Bisphenol AF, 6F-BPA, 97%, TCI America), 4-fluorobenzophenone (99%, Sigma–Aldrich Co.), *N*, *N*-dimethylthiocarbamyl chloride (97%, Sigma–Aldrich Co.), Potassium carbonate (K_2CO_3, 99%, ACS reagent, Sigma–Aldrich Co.), Potassium hydroxide (97%, Sigma–Aldrich Co.), Sulfuric acid (Fuming, 30%SO_3, Sigma–Aldrich Co.), were used without further purification. Tetramethylene sulfone (Sulfolane, 99%, Sigma–Aldrich Co.), *N*, *N*-dimethylacetamide (DMAc, anhydrous, 99.8%, Sigma–Aldrich Co.), *N*, *N*-dimethylformamide (DMF, anhydrous, 99%, Sigma–Aldrich Co.), *N*-methyl-2-pyrrolidone (NMP, anhydrous, 99%, Sigma–Aldrich Co.), Benzene (98%, Sigma–Aldrich Co.), were used as received. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

Sulfonated monomer, 3, 3′-disulfonate-4, 4′-difluorodiphenylsulfone, was prepared as reported before [6], by the sulfonation of 4-fluorophenylsulfone with fuming sulfuric acid followed by neutralization with sodium chloride and sodium hydroxide.

Unsulfonated poly(arylenethioethersulfone) with the hexafluoroisopropylidene moiety (6F-PTES) was synthesized from a standard K_2CO_3/NMP/toluene route and was utilized in this study for comparison with the sulfonated polymer.

2.2. Monomer synthesis

The 6F-dithiol monomer, 4, 4-(hexafluoroisopropylidene) bisbenezenethiol, was prepared with slight modifications from the corresponding 4, 4-(hexafluoroisopropylidene)diphenol (6F-BPA) by the conversion of the latter to its O,O-bisthiocarbamate derivative followed by Newmann-Kwart thermal rearrangement to S,S-bisthiocarbamate, which is a masked dithiol, and its subsequent hydrolysis to the aromatic dithiol monomer [11]. The preparing procedure as follows (see Fig. 1 for reaction scheme).

Bisphenol AF (15.1 g, 0.045 mol), benzene (70 ml), and potassium hydroxide (6.17 g, 0.11 mol) were added into a 250 ml three-neck, round-bottom flask, equipped with a mechanical stirrer, Dean–Stark trap and condenser, nitrogen in-outlet. The resulting solution was refluxed with a trap to remove water; then, the benzene was removed at reduced pressure to obtain **(1)**. DMF (70 ml) was added to **(1)**, cooled down to 0 °C, and added *N*, *N*-dimethylthiocarbamyl chloride (13.6 g, 0.11 mol), then heated to room temperature and 60 °C, and maintained at 60 °C for 1 h. The mixture was diluted with 1 L of water and extracted twice with an 80:20 benzene/hexane solution. The organic phase was evaporated the under reduced pressure and recrystallized from a 5:1 methanol/benezene solution, to obtain 15.2 g of **(2)** (mp: 209–211 °C, yield: 80%). 15.2 g (0.036 mol) of **(2)** was placed in a reaction vessel (100 ml), and heated it at 250 °C under argon for 1 h. After cooling the product to room temperature, the glassy residue was recrystallized from 60 ml of methanol, and 11 g of **(3)** (mp: 141–144 °C, yield: 75%) was obtained. 7.5 g (0.018 mol) of **(3)** was then placed in 40 ml of methanol, and added a solution of potassium hydroxide (4.0 g, 0.071 mol) in 20 ml of water. The mixture was refluxed for 1 h, cooled and diluted with 500 ml of water to obtain **(4)**. A solution of 16.5 ml of concentrated HCl in 100 ml of water was added and a precipitate was obtained which was recrystallized from a 3:1 methanol/water mixture to yield 5.0 g of **(5)** (mp: 112 °C–113 °C, yield: 90%).

2.3. Synthesis of fully sulfonated homopolymer (6F-SPTES-100)

The synthesis of fully sulfonated poly(arylenethioethersulfone) containing hexafluoroisopropylidene moiety (6F-SPTES-100) is exemplified by the following polycondensation procedure (see Fig. 2 for reaction scheme). 3, 3′-disulfonate-4, 4′-difluorodiphenylsulfone (1.3521 g, 2.95 mmol), 4, 4-hexafluoroisopropylidenebisbenzenethiol (1.1051 g, 3 mmol) and potassium carbonate (1.3821 g, 10 mmol) were taken up in a 100 ml round-bottomed flask equipped with a mechanical stirrer, a condenser and a dry nitrogen inlet-outlet adapter. 20 ml sulfolane and 15 ml chlorobenzene were added to the flask and the solution temperature was raised to 120 °C with stirring and maintained at that temperature overnight. After azeotroping off chlorobenzene from the reaction mixture, 4-fluorobenzophenone (0.02 g, 0.1 mmol) was added as the end-capping agent. The reaction mixture was heated at 180 °C for 6 h, and after cooling, was quenched with acetic acid followed by precipitation in acetone. The filtered polymer was air-dried, dissolved in boiling deionized, distilled water and reprecipitated in acetone. The white polymer was again filtered, soxhlet-extracted with methanol for 48 h, and dried in vacuum overnight at 80 °C resulting in a 90% yield for the recovered polymer.

2.4. Fully sulfonated homopolymer membrane preparation

The salt form of 6F-SPTES-100 polymer was dissolved in the DMAc to form ∼10 wt% clear solution, and filtered at room temperature. The membranes were directly cast onto a flat dish and dried at 80 °C in vacuum for 24 h. The membranes (in salt form) were converted to the corresponding sulfonic acids in the presence of diluted sulfuric acid (4.0 M) at room temperature for 48 h (See Fig. 2 for reaction scheme). The acid form membranes were washed by immersion in deionized water and dried at room temperature, and then at 100 °C in vacuum for 24 h. This procedure yielded tough, clear, flexible membranes of 6F-SPTES-100 polymer. The thickness of all membrane samples was in the range of 75–100 μm.

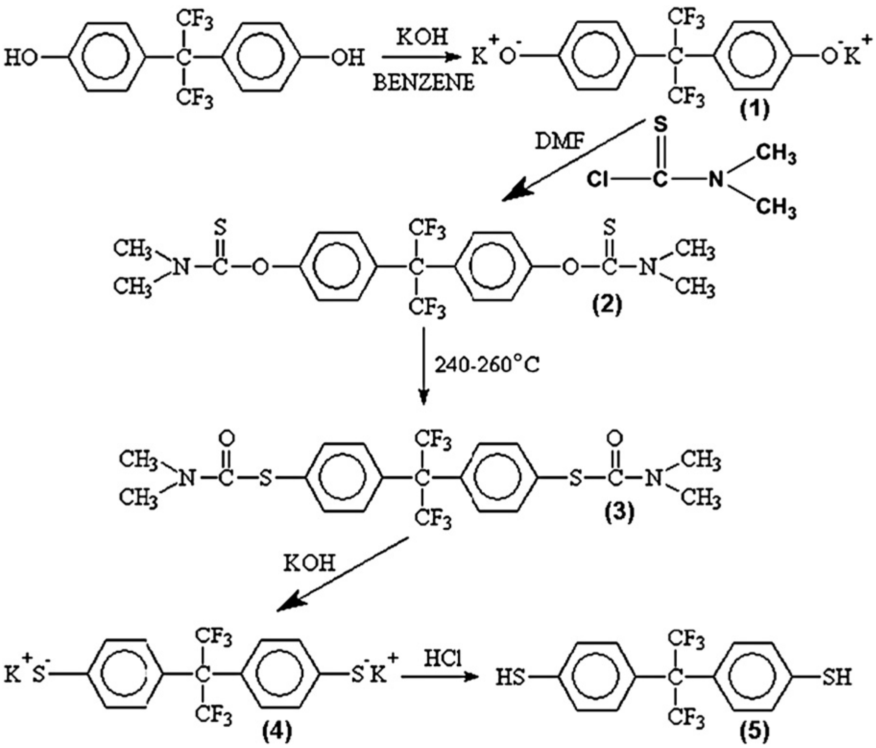

Fig. 1. The synthetic scheme of 4, 4′-(hexafluoroisopropylidene)-diphenylthiol (Hexafluorobisphenylthiol A).

2.5. Polymer characterization

Gel Permeation Chromatography (GPC), performed on the polymer solution in 0.5% LiBr/NMP at 70 °C using TriSEC Version 3.00, provided molecular weights and molecular weight distributions. Intrinsic viscosity was measured by dilute solution viscometry of the polymer solution in NMP containing 0.5% LiBr at 30 °C.

Nuclear magnetic resonance (^{1}H NMR) analyses were conducted using a Bruker Avance 400 NMR spectrometer operating at a resonance frequency of 399.95 MHz for ^{1}H. All spectra were obtained from a 10% solution (w/v) in deuterated dimethylsulfoxide (DMSO-d_6) at room temperature. The chemical shift of tetramethylsilane (TMS) was used as the internal reference.

The ion exchange capacity (IEC) is defined as the millie-quivalents of ions in 1 g of the dry polymer (mequiv/g). Titration was used to quantitatively determine the sulfonic acid concentration (degree of sulfonation, DS) in the polymer. The dried 6F-SPTES-100 polymer membrane was weighed and then immersed in a 2.0 M solution of

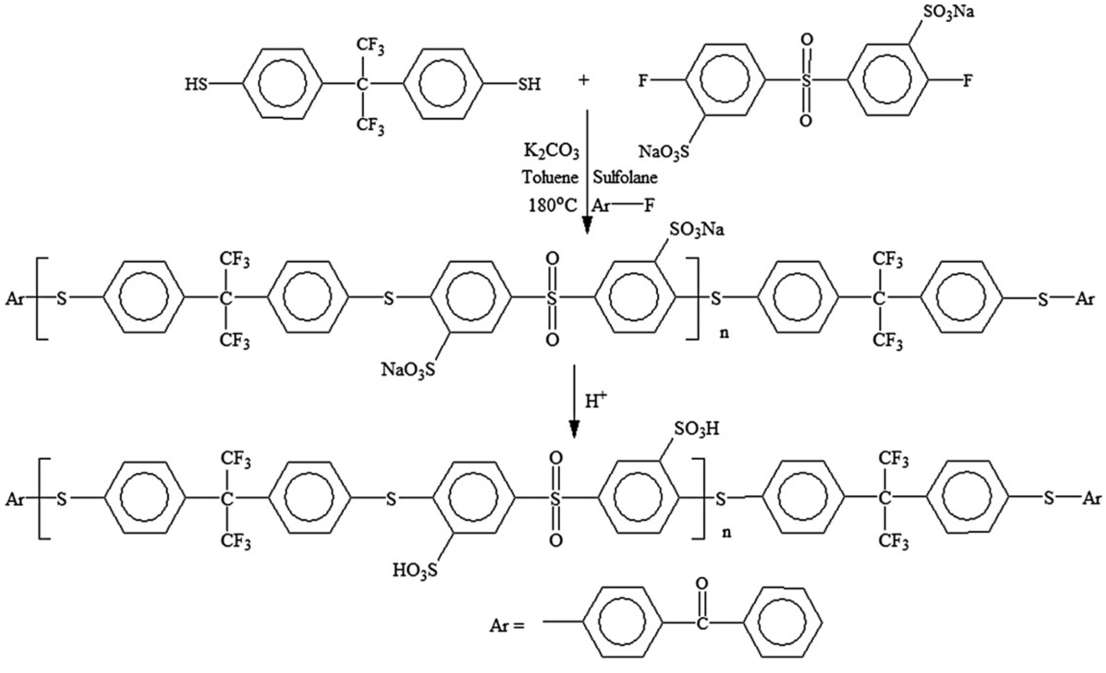

Fig. 2. Synthesis of the end-capped, fully sulfonated poly(arylenethioethersulfone) (6F-SPTES-100) described in this study.

Table 1
Properties of end-capped 6F-SPTES-100 in comparison to the end-capped SPTES-100 [9] and Nafion-117.

Polymers	Intrinsic Viscosity[a] (dL/g)	Mw/Mn (GPC)	Solubility[b] in Water	Solubility[b] in DMAc & NMP	Membrane Behavior
End-capped 6F-SPTES-100	1.41	160 K/53 K	SW/S	S	Clear, ductile, tough
End-capped SPTES-100	1.69	93 K/41 K	SW/S	S	Clear, ductile, tough
Nafion 117[c]	N/A	N/A	N	N	Ductile, tough

[a] Solution viscosity was measured at 30 °C, in 0.5% LiBr/NMP.
[b] S = Soluble, N = Insoluble, SW = Swollen.
[c] Evaluated for comparative purposes.

NaCl for 4–5 h to exchange 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 number of moles of the proton is equal to the number of moles of the sulfonic acid group and the IEC was calculated from the titration data.

Thermogravimetry (TGA) was conducted at a heating rate of 10 °C/min using an Auto TGA 2950HR V5.4A instrument in air and in helium to study the thermal stability of 6F-SPTES polymer samples. The samples were preheated under air from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to 90 °C, and then reheated to 900 °C at 10 °C/min.

The proton conductivity of the homopolymer film was measured using AC Impedance Spectroscopy and utilized a standard 4-electrode measurement setup to eliminate electrode and interfacial effects. The proton conductivity was calculated by using equation as follows:

$$\sigma = \frac{l}{R \times (d \times w)}$$

where l is the distance between the electrodes, d and w are the thickness and the width of the membranes respectively and R is the resistivity that was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the axis of the abscissa. Membrane samples were cut into strips that were approximately 1.0 cm width, 5 cm length, and 0.01 cm thickness prior to mounting in the cell.

3. Results and discussion

3.1. Sulfonated homopolymer synthesis

The sulfonated polymer syntheses, especially with the sulfonated poly(arylenethioethersulfone) (SPTES) polymer system, have been previously reported [6–8] with a relatively lower sulfonic acid content, up to 50 mol% of the disulfonated arylenethioethersulfone in the polymer backbone. These condensations typically employed NMP as the solvent in a base-mediated nucleophilic displacement of activated aromatic fluoro groups by the aromatic thiolate anions. However, we found the procedure employing NMP as the solvent especially unrewarding and ineffective, particularly in the preparation of fully disulfonated poly(arylenethioethersulfone)s such as SPTES-100 and 6F-SPTES-100. We attribute this to the limited solubility in NMP of the polyionic species generated in the reaction owing to the high proportions of the sulfonate monomer employed in the reaction. Premature precipitation of darkly colored products occurred in the polymerization reaction which also indicated that side-reactions could also be occurring at the high temperatures (~180 °C) of the reaction. We resorted to the use of sulfolane as the polar aprotic solvent for the polymerization reaction. We could successfully isolate high molecular weight homopolymers from homogeneous solutions of the reaction mixture; in both cases, the homopolymers obtained were white and very fibrous. The synthetic scheme for the preparation of the homopolymers is shown in Fig. 2. The end-capped homopolymers, generated in the salt form, were converted to their free acid form by the acidification procedure described earlier in the Experimental section.

3.2. Structure and properties of sulfonated homopolymer

Table 1 lists the solution properties of the homopolymer, 6F-SPTES-100 after the conversion of its salt form to the free sulfonic acid form by acidification. The properties of SPTES-100 [9] are also listed for comparison. The high molecular weights of the homopolymers are evidenced by the intrinsic viscosity values as well as by the molecular weight determination using GPC. This was also corroborated by the fabrication of tough, ductile, clear and flexible film membranes (~100 μm thick) from DMAc solutions of both homopolymers.

From Table 1, it is evident that the SPTES-100 and 6F-SPTES-100 have similar solution properties and membrane behavior. At least qualitatively, this indicates that there is no profound influence of -6F substitution on membrane properties relative to the thioether group in the polymer structure. This was further corroborated by a comparison of the water uptake tests of the two membranes; both exhibited equally high water uptake (>300%), indicating that the -6F group did not significantly alter the hydrophobicity of the polymer backbone relative to the thioether group in the SPTES polymer.

^{1}H NMR spectrum of 6F-SPTES-100 is shown in Fig. 3. The downfield resonance in the spectrum at 8.25 ppm is assigned to the

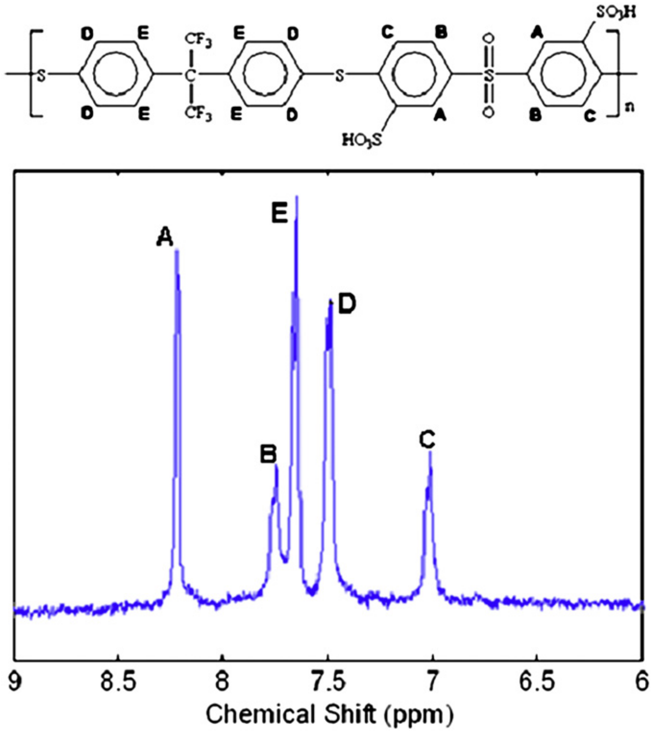

Fig. 3. The 400 MHz proton NMR spectrum of 6F-SPTES-100 in DMSO-d_6.

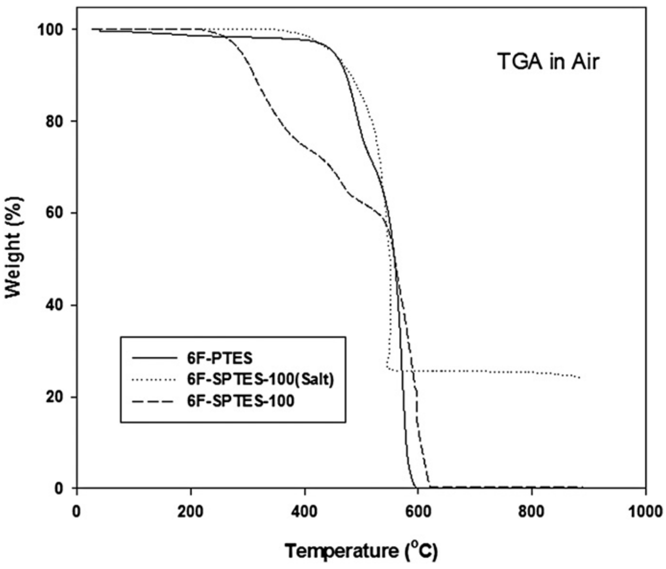

Fig. 4. Thermal stability profiles (TGA) of 6F-SPTES-100 in salt and acid forms.

protons ortho- to the sulfonic acid group in the 6F-SPTES-100 homopolymer; it is well-separated from the other aromatic proton resonances occurring in the 7.0–7.75 ppm range in the spectrum. In general, these show good agreement with the ^{1}H NMR spectra of the respective monomers from which the 6F-SPTES monomer is derived. We also found that the protons in the aromatic ring adjacent to the trifluoromethyl groups exhibits a downfield resonance of 7.45 ppm, compared to an upfield resonance of 7.0 ppm for the aromatic protons adjacent to the central thioether group [9] due to a change in the substitution of the central sulfide linkage by the carbon attached to electron-withdrawing trifluoromethyl groups.

3.3. Thermal properties of sulfonated homopolymer

An overlay plot of the TGA analyses, in air, of the 6F-SPTES-100 polymer in both their salt and acid forms as well as that of the unsulfonated poly(arylenethioethersulfone) (6F-PTES), for comparison, is depicted in Fig. 4. The salt form of the 6F-SPTES-100 polymer exhibited a nearly single stage thermal decomposition profile in air, somewhat similar to the thermal decomposition of unsulfonated poly(arylenethioethersulfone), with the onset of the sulfonate salt pendant degradation occurring in the 400–425 °C range. On the other hand, a distinct two-stage thermal degradation profile is evident for the free acid form of 6F-SPTES-100. The first stage weight loss in the broad 260–375 °C region for the 6F-SPTES-100 polymer corresponds to the degradation of the pendant sulfonic acid groups. Unlike the case of the salt form, complete thermo-oxidative degradation is observed in air, leaving no inorganic residue. This provides evidence of complete conversion of the salt into its free acid form.

Table 2
Properties of 6F-SPTES polymer membrane and comparison with SPTES polymer and Nafion-117.

Polymers	Cal. IEC (meq./g)	Exp. IEC (meq./g)	DS[a,b] (IEC/^{1}H NMR)	Proton Conductivity[c] (mS/cm)
End-capped 6F-SPTES-100	2.69	2.49	93/99	180
End-capped SPTES-100	3.20	2.89	91/98	210
Nafion 117[d]	0.91	N/A	N/A	72

[a] DS: Degree of Sulfonation.
[b] Based on resonance assignment and integration of the various aromatic protons.
[c] Of the membrane, measured at 85 °C, 65% relative humidity.
[d] Evaluated for comparative purposes.

3.4. Proton conductivities of sulfonated homopolymer membranes

The proton conductivity of the cast membrane of end-capped 6F-SPTES-100 at 85 °C and at 65% relative humidity was measured to be 180 mS/cm and in comparison, the end-capped SPTES-100 exhibited a membrane proton conductivity of 210 mS/cm (see Table 2). These high proton conductivities can be considered to be the limiting values for proton conductivity, under the measurement conditions, in these fully sulfonated poly(arylenethioethersulfone) membranes. These values represent nearly three times the proton conductivity measured for Nafion-117 (72 mS/cm) under the same conditions of temperature and relative humidity. It is also pertinent to mention that the high proton conductivities of the two fully sulfonated poly(arylenethioethersulfone) systems have been measured under controlled humidity conditions. This represents a significant departure from previous reports on the copolymer compositions[8] incorporating 20–50 mol% of the disulfonated monomer in the SPTES system wherein proton conductivities were measured under fully hydrated conditions (immersion in water) and at room temperature.

The dependence of 6F-SPTES-100 membrane proton conductivity on both temperature and relative humidity is also clearly indicated in Fig. 5. The trends are shown for measured proton conductivities as a function of temperature at relative humidity that was varied from 45% to 65%. The increase in proton conductivity with increase in relative humidity is consistent with higher proton conductivity requiring a larger degree of hydration of the membrane. At the even higher relative humidity of 75% at 85 °C, a higher proton conductivity of ∼275 mS/cm was measured for 6F-SPTES-100; however, no more than a single measurement could be made, presumably due to the excessive swelling and loss of mechanical integrity of the membrane at the higher relative humidity.

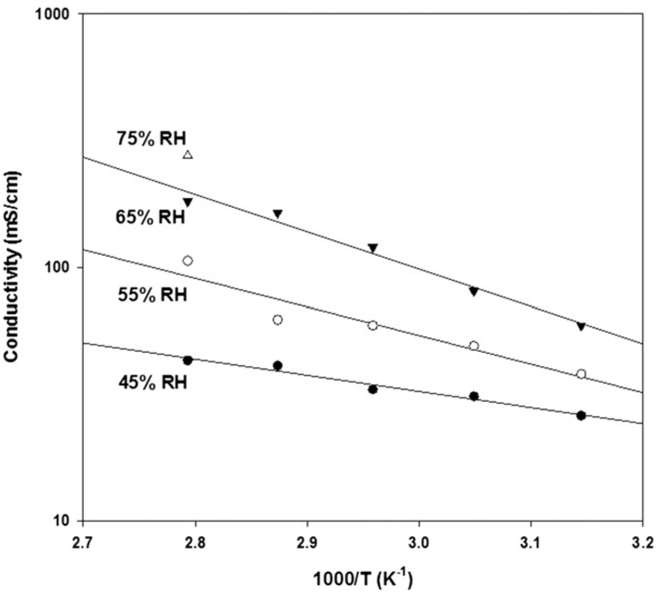

Fig. 5. Proton conductivity dependence of 6F-SPTES-100 membrane on temperature and relative humidity.

4. Conclusions

A fully sulfonated poly(arylenethioethersulfone) homopolymer with a central hexafluoroisopropylidene group, was successfully synthesized in high molecular weight by polycondensation. The polymer was fabricated into tough, ductile, transparent membranes; proton conductivity as high as 180 mS/cm was measured for the membrane at 85 °C and 65% relative humidity. This represents the limiting proton conductivity value, that can be measured for the wholly disulfonated polymer electrolyte membrane under the experimental conditions. This can be attributed to the high sulfonic acid content and the high water uptake associated with these hydrophilic acid groups. As in the case of SPTES-100 reported before, the proton conductivity of 6F-SPTES-100 was measured to be approximately two and half times higher than that of Nafion-117 under comparable conditions. The TGA analysis of the polymer indicated that the onset of weight loss due to the degradation of sulfonic acid pendant to the polymer backbone does not begin to occur till around 260 °C, indicating that this class of polymer membranes could be potentially utilized in higher temperature fuel cells operation. A comparison of the properties of 6F-SPTES-100 and SPTES-100 membranes in terms of their solubility, and measured membrane proton conductivity shows qualitatively similar trends, indicating that the backbone hydrophobicity may not be influenced to any measurable extent by the substitution of the central thioether group by the hexafluoroisopropylidene structural unit.

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References

[1] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463–502.
[2] Kerres JA. J Membr Sci 2001;185:3–27.
[3] Roziere J, Jones DJ. Ann Rev Mater Res 2003;33:503–55.
[4] Jannasch P. Fuel Cells 2005;5:248–60.
[5] Smitha B, Sridhar S, Khan AA. J Membr Sci 2005;259:10–26.
[6] Ueda M, Toyota H, Teramoto T. J Polym Sci (Part A Polym Chem) 1993;31: 853–8.
[7] Wang F, Chen TL, Xu JP. Macromol Chem Phys 1998;99:1421–6.
[8] Wiles KB, Wang F, McGrath JE. J Polym Sci (Polym Chem Ed) 2005;43:2964–76.
[9] Bai Z, Dang TD. Macromol Rapid Commun 2006;27:1271–7.
[10] Bai Z, Dang TD, Durstock FM. J Membr Sci 2006;281:508–16.
[11] Giants TW, Dougherty TK. US Pat. 4,720,590; 1988.