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Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes

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Abstract

Novel biphenol-based wholly aromatic poly(arylene ether sulfone)s containing up to two pendant sulfonate groups per repeat unit were prepared by potassium carbonate mediated direct aromatic nucleophilic substitution polycondensation of disodium 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS), 4,4′-dichlorodiphenylsulfone (DCDPS) and 4,4′-biphenol. Copolymerization proceeded quantitatively to high molecular weight in *N*-methyl-2-pyrrolidinone at 190 °C. Tough membranes with a SDCDPS/DCDPS mole ratio up to 60:40 were successfully cast using *N*,*N*-dimethylactamide. An increase of sulfonate groups in the copolymer resulted in increased glass transition temperature, enhanced membrane hydrophilicity, and intrinsic viscosity; the 100% SDCDPS homopolymer was water soluble. The acid form membranes were successfully obtained by treating the sodium form of the membranes with dilute sulfuric acid solution. Thermogravimetric analysis shows that the sodium form materials have enhanced thermal stability relative to the acid form, as expected. Atomic force microscopy (AFM) phase images of the acid form membranes clearly show the hydrophilic domains, with sizes increasing from 10 to 25 nm as a function of the degree of sulfonation. A phase inversion could be observed for the 60% SCSDPS copolymer, which was consistent with a rapid increase in water absorption. Short-term aging (30 min) indicates that the desired acid form membranes are stable to 220 °C in air and conductivity values at 30 °C of 0.11 S/cm (SDCDPS/DCDPS = 0.4) and 0.17 S/cm (SDCDPS/DCDPS = 0.6) were measured, which are comparable to or higher than the state-of-the-art fluorinated copolymer Nafion 1135 control (0.12 S/cm). The conductivity is greatly influenced by ion exchange capacity, temperature, and water activity. The new copolymers, which contain ion conductivity sites on the deactivated positions of the aryl backbone rings, are candidates as new polymeric electrolyte materials for proton exchange membrane (PEM) fuel cells. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymerization; Proton exchange membrane; Nafion 1135

1. Introduction

Poly(arylene ether sulfone)s (structure **1**) are important, well-known engineering thermoplastics (particularly when devoid of aliphatic units) that display excellent thermal and mechanical properties, as well

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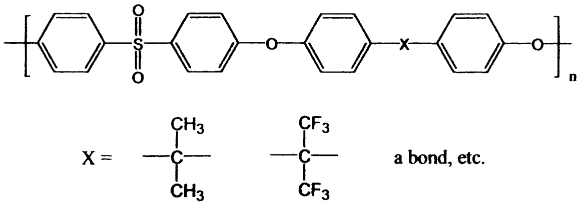
as resistance to oxidation and acid catalyzed hydrolysis [1–4].



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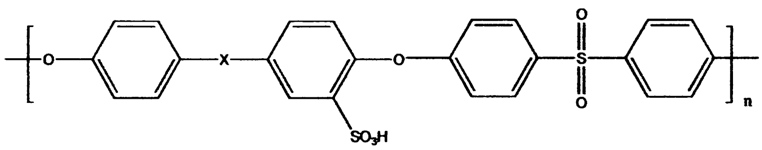
Additionally, chemical modifications of this polymer are of great interest. One objective is to prepare advanced molecules for fuel cells by modifying poly(arylene ether sulfone)s without sacrificing their excellent physical and other properties. Sulfonated poly(arylene ether sulfone)s synthesized by attaching sulfonic acid groups in polymer modification reactions (post-sulfonation route) have been investigated intensively since the pioneering work of Noshay and Robeson, who developed a mild sulfonation procedure for the commercially available bisphenol-A-based poly(ether sulfone) [5]. This approach found considerable interest in the area of desalinization membranes for reverse osmosis and related water purification applications [6–8]. Different sulfonation agents have been employed for this polymer modification such as chlorosulfonic acid and a sulfur trioxide–triethyl phosphate complex. In these post-sulfonation reactions, the sulfonic acid group is usually restricted to the activated position *ortho* to the aromatic ether bond, as indicated in structure **2**, although precise control over the location of sulfonation can be difficult. For the case of the bisphenol-A-based systems, no more than one sulfonic acid group per repeat unit could be achieved. Recently, Kerres et al. reported an alternative sulfonation process of commercial polysulfone based on a series of steps including metalation–sulfination–oxidation reactions [9].

It was of interest to investigate the effect of sulfonation on the deactivated sites of the repeat unit (structure **3**), since one might expect enhanced stability and, perhaps, modestly higher acidity due to strong electron-withdrawing by the sulfone group. Indeed, the first report of the required sulfonated monomer was from Robeson and Matzner [10], who obtained a composition of matter patent, which primarily was of interest for its flame retarding additive properties. More recently, Ueda et al. [11] reported the sulfonation of 4,4′-dichlorodiphenylsulfone and provided general procedures for its purification and characterization—although details were somewhat limited and no reference to potential applications was indicated. We have modified this procedure somewhat, as described in this paper, and have utilized the material to produce wholly aromatic, film forming, highly sulfonated poly(arylene ether sulfone) copolymers via direct polymerization. A preliminary account of the work has been reported in a conference proceeding [12–16].



Activated Ring

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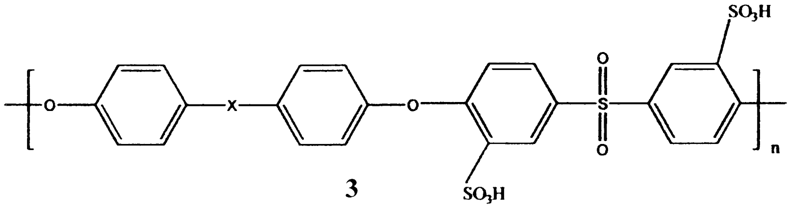

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Deactivated Ring

Our current interest is in the potential of such materials to provide improved and economical proton exchange membranes (PEM) for fuel cell applications [12–16]. Much effort has gone into the development of PEMs via polymer modification method [17]. The potential for fuel cells based on proton exchange membranes is very substantial, and transport mechanisms have been successfully modeled [18–21]. Although, the currently important material for PEMs are the statistical copolymers of tetrafluoroethylene and a fluorinated vinyl sulfonic acid, they are known to have some significant technical limitations. These include low modulus and conductivity at temperatures greater than 80 °C, as well as high methanol permeability, which render sub-optimal the application of these membrane materials in direct methanol fuel cells. The fluoropolymers are also rather expensive, which is considered to be a limiting factor as well. This paper describes the synthesis and characterization of a sulfonated high molecular weight poly(arylene ether sulfone) of controlled hydrophilicity.

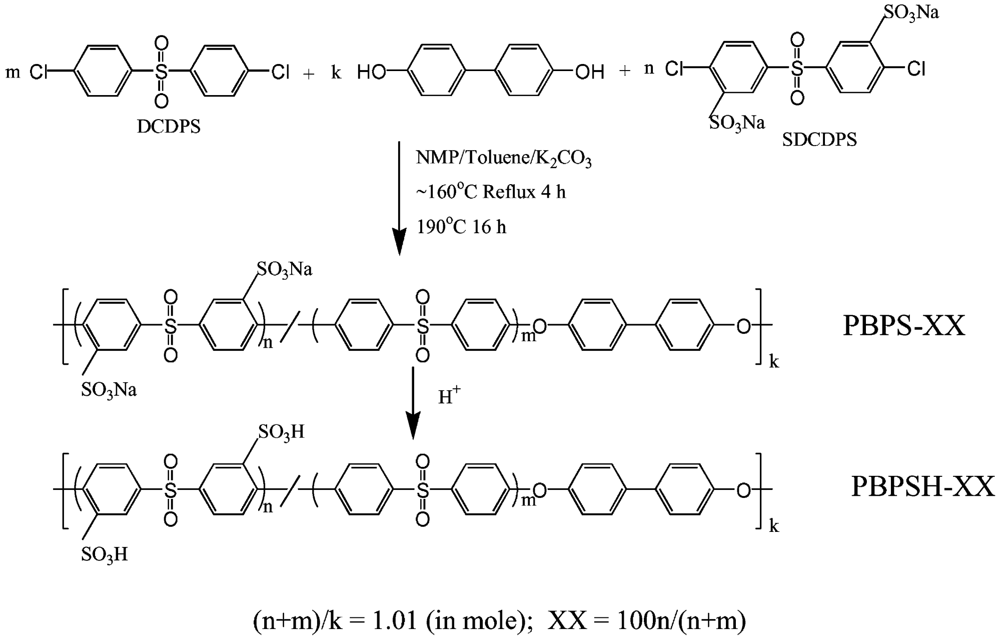
2. Experimental

2.1. Materials

The polymers used for this work were synthesized from commercially available 4,4′-dichlorodiphenylsulfone (DCDPS) and 4,4′-biphenol obtained from BP Amoco and Eastman Chemical, respectively. The sulfonated comonomer, 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS) was synthesized in-house from DCDPS according to a modified literature method [10,11]. Basing the polymers on readily available and inexpensive materials is an important consideration for the cost of the membranes if they are to become commercially important membranes. A general synthesis of the copolymers is shown in Scheme 1, while references [22–25] provide background on general synthesis of poly(arylene ether)s.

2.2. Membrane preparation

Membranes were prepared by redissolving the sodium-neutralized copolymer in DMAC and casting



Scheme 1. Synthesis of random sulfonated poly(arylene ether sulfone)s.

directly onto clean glass substrates. The films were carefully dried by infrared heat at gradually increasing temperatures under a nitrogen atmosphere then vacuum-dried at 120 °C for 24 h and 150 °C for 24 h. The drying procedure was optimized to produce flat, transparent membranes while quantitatively removing the casting solvent. Too rapid a drying rate produced rough, brittle membranes with bubbles. Because, the sulfonated membranes absorb a significant amount of water, the sodium form membranes could be converted into the acid form by addition to 2N H_2SO_4 for 24 h, followed by washing with deionized water for 24 h and vacuum drying at 100 °C for 24 h. Conversion of the sodium neutralized membranes to the acid form membranes was confirmed with X-ray fluorescence. X-ray photoelectron spectroscopy ensured removal of excess H_2SO_4 by washing with deionized water.

3. Characterization methods

3.1. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectroscopy was used to confirm the pendant functional groups on the copolymers. Measurements were recorded using a Nicolet Impact 400 FT-IR spectrometer with thin, homogeneous cast films.

3.2. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

The glass transition temperatures (T_g) were obtained on a Perkin-Elmer DSC-7 differential scanning calorimeter. Scans were conducted under nitrogen at a heating rate of 10 °C/min. Second heat T_g values are reported as the midpoint of the change in the slope of the baseline. Dynamic TGA was employed to assess the thermal stability (weight loss) of the copolymers with a Perkin-Elmer TGA-7 thermogravimetric analyzer. All the samples were first vacuum dried and kept in the TGA furnace at 150 °C in a nitrogen atmosphere for 30 min to remove water before TGA characterization. The typical heating rate was 10 °C/min in nitrogen.

3.3. Solubility and intrinsic viscosities

Sulfonated copolymer solubility was determined at concentration of 10% (w/v) in a number of solvents, including NMP, DMAC, dimethylsulfoxide, chloroform and water. Intrinsic viscosities were determined in NMP at 25 °C using an Ubbelohde viscometer.

3.4. Water uptake of membranes

The 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 quickly weighed again. The water uptake of membranes are reported in weight percent as follows:

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. While seemingly simple, this method has proven accurate and has been established in [26].

3.5. Non-aqueous potentiometric titrations

Non-aqueous potentiometric titrations were conducted using an MCI Automatic Titrator Model GT-05. The acid form membrane solutions in DMAC were titrated by a standard tetramethyl ammonium hydroxide solution. Titration was used to quantitatively determine sulfonic acid concentration in the copolymer, i.e. ion exchange capacity (IEC, meq/g).

3.6. Atomic force microscopy (AFM)

Tapping mode AFM was performed with a Digital Instruments Dimension 3000, using micro-fabricated cantilevers with a force constant of approximately 40 N/m. The ratio of amplitudes used in feedback control was adjusted to 0.6 of the free air amplitude for all the reported images. All samples were dried at 80 °C for 24 h under vacuum conditions. The samples were then imaged immediately in relative humidity of about 35%.

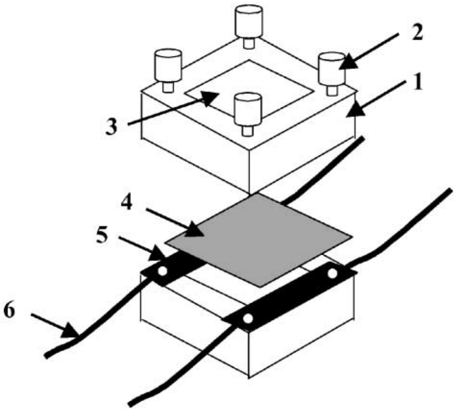


Fig. 1. Conductivity cell: 1, Teflon block; 2, thumbscrew; 3, open area to allow equilibration with environment; 4, membrane sample; 5, blackened Pt foil electrode; 6, Pt lead.

3.7. Conductivity

Conductivity measurements were performed on the acid form of the membranes using the cell shown in Fig. 1. This cell geometry was chosen to ensure that the membrane resistance dominated the response of the system. An impedance spectrum was recorded from 10 MHz to 10 Hz using a Solatron 1260 Impedance/Gain-Phase Analyzer. The resistance of the film was taken at the frequency that produced the minimum imaginary response. All impedance measurements were performed at 30 °C in water.

4. Results and discussion

4.1. Fourier transform infrared (FT-IR) spectroscopy

FT-IR has been used to analyze characteristic bands corresponding to the sulfonate groups in different polymers, e.g. sulfonated poly(arylene ether ketone)s [27–29], polystyrene [30], polyester [31] and poly(phenylene sulfide) [32]. The successful introduction of the sodium sulfonate groups was confirmed by FT-IR spectra (Fig. 2), where strong characteristic peaks at 1030 and 1098 cm^{-1} assigned to symmetric and asymmetric stretchings of the sodium sulfonate groups were observed for all sulfonated copolymers from PBPS-10 to PBPS-60, and the densities of these two characteristic peaks increased with higher SDCDPS content. Tran provided detailed infrared assignments of sulfonated poly(arylene ether sulfone)s [33]. The symmetric stretching of sulfonate groups at 1030 cm^{-1} can be compared to internal standards, such as the in-chain diphenyl ether absorption. Quantitative studies of FT-IR spectra are provided in Fig. 3. A linear relationship exists between the degree of sulfonation and the density ratio of sulfonate stretching (1030 cm^{-1}) to diphenyl ether bands (1006 cm^{-1}). The result proves that the sulfonate groups were indeed quantitatively introduced to the copolymers as expected.

4.2. Thermal analysis

The introduction of sulfonate groups has two effects on glass transition temperature: firstly, to produce increased intermolecular interaction by pendant ions, i.e. ionomer effect; and secondly, to increase molecular bulkiness. Both effects hinder internal rotation, leading to increased glass transition temperatures for sulfonated polymers. Fig. 4 shows the DSC thermograms of the PBPSH system as a function of the degree of sulfonation. This DSC data showed a linear increase of T_g in the range from 0 to 40% acid sulfonate group, followed by more significant and broader base line shift at higher concentrations of sulfonate group. The first derivative DSC traces shown in the small box of Fig. 4 clearly exhibits that only one T_g appeared in 40% sulfonated sample while the 50 and 60% sulfonated samples may have two T_g’s. The lower and upper T_g’s for those two samples are attributed to the glass transitions of the matrix and the ionic cluster, respectively. The detection of two T_g’s by DSC for other sulfonated poly(arylene ether)s has not been easy because phase dimension problems (i.e. sizes of the separated phase) tend to interfere [6,34]; it is believed that this T_g behavior for the sulfonated poly(arylene ether sulfone)s may reflect a significant change of microstructure of the copolymer. The micro-phase change will be discussed in the following section. Table 1 summarizes the glass transition temperatures (T_g’s) determined by DSC.

The thermal stability of the control and sulfonated poly(arylene sulfone) copolymers (sodium form) were investigated by TGA. All the sulfonated samples were pre-heated at 150 °C for 30 min in the TGA furnace to remove moisture. Then, the dynamic TGA

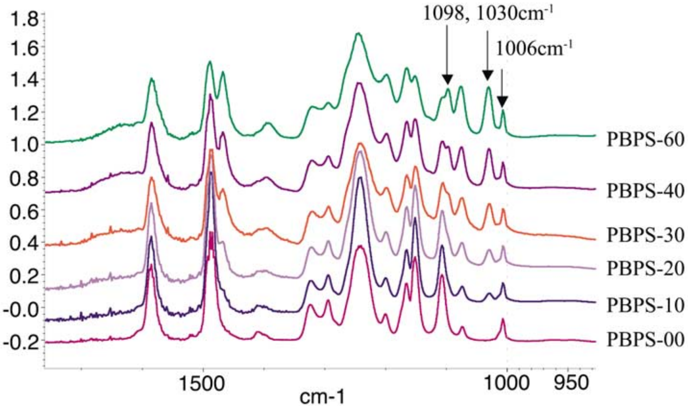


Fig. 2. Influence of the degree of sulfonation on the FT-IR of sulfonated poly(arylene ether sulfone) copolymers.

experiments were run from 50 to 700 °C, at a heating rate of 10 °C/min under nitrogen. The influence of the degree of sulfonation on both 5% weight loss temperature and the residual char yield at 700 °C are summarized in Table 1. PBPS-00 is well known to be a thermally stable polymer and shows a 5% weight loss at 456 °C. The 5% weight loss temperature for the sodium form sulfonated polymers from PBPS-10 to PBPS-60 decreased only slightly with the increase of sodium sulfonate concentration. However, the char yield at 700 °C showed a reverse trend, confirming the objective of Robeson and Matzner that SCDPS was a flame retarding additive [10]. The thermal stability

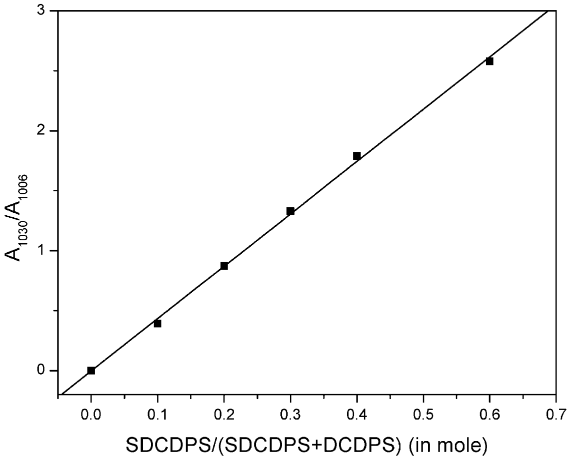


Fig. 3. FT-IR correlation of sulfonate groups and internal standard in polymer chain.

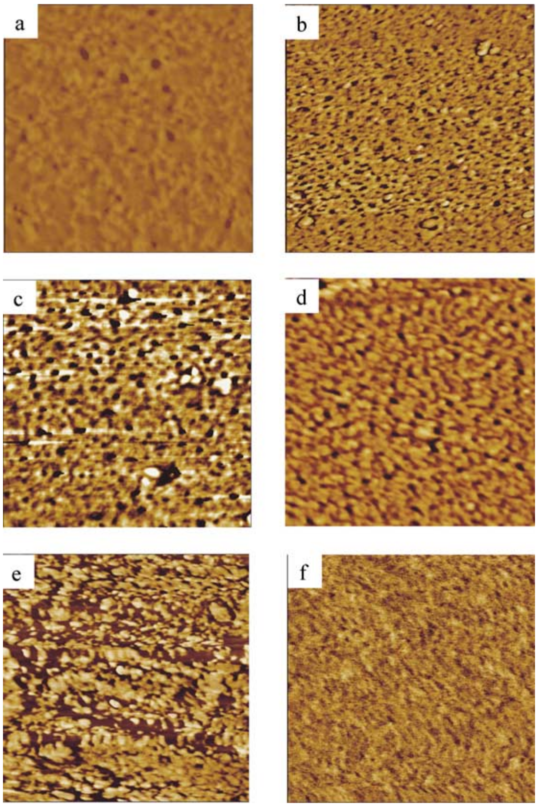


Fig. 6. AFM tapping phase image for sulfonated poly(arylene ether sulfone) copolymers and Nafion 117: (a) PBPS-00; (b) PBPSH-20; (c) PBPSH-40; (d) PBPSH-50; (e) PBPSH-60; (f) Nafion 117 (acid form). Scan boxes are 700 nm × 700 nm, and phase scales are 0–30° for (a)–(d). Scan boxes are 350 nm × 350 nm, and phase scales are 0–10° for (f).

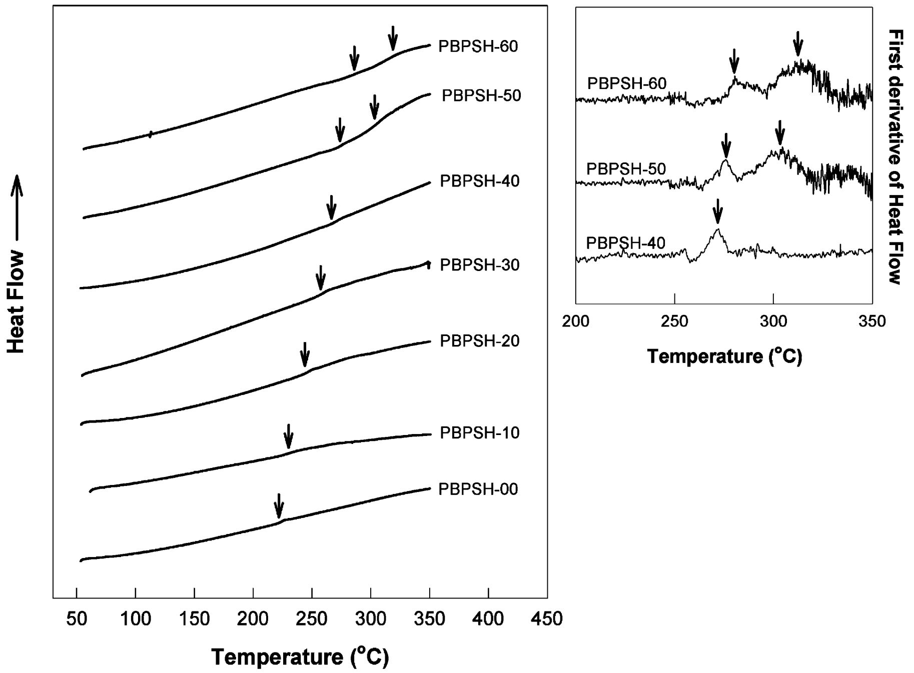


Fig. 4. Influence of the degree of sulfonation on the glass transition temperature of sulfonated poly(arylene ether sulfone) copolymers.

of acid and sodium form membranes (TGA curves for PBPS-60 and PBPSH-60) are compared in Fig. 5. There is only one weight loss step for the salt form of PBPS-60 at around 500 °C, which was assigned to the degradation of the polymer chain. PBPSH-60 shows an initial weight loss of about 17% between 300 and 480 °C, which was assigned to the loss of $–SO_3H$ groups. The second thermal degradation above 500 °C was assigned to the degradation of the main polymer chain. The theoretical weight percent of $–SO_3H$ groups in PBPSH-60 is 19%, assuming that the elimination of a sulfonic acid group would release one SO_3 molecule, which is in close agreement to the first weight loss step in the TGA data for PBPSH-60. This indicates that the degradation of acid form polymers start from the desulfonation of sulfonic groups and, clearly, the sodium form material has a better thermal stability than corresponding acid form. Further studies to compare directly copolymerized copolymers with post-sulfonated materials are in progress. However, preliminary observations are that the post-reacted groups on the activated phenyl rings appear to be less stable.

Table 1
Thermal characterization by differential scanning calorimetry and thermal gravimetric analysis

Polymers	T_g (°C)[a]	$T_{5\%}$ (°C)[b]		Char yield (%) at 700 °C (N_2)
		Sodium	Acid	
PBPS-00	221	516	516	43
PBPS-10	232	507	452	62
PBPS-20	246	506	395	63
PBPS-30	260	506	372	65
PBPS-40	271	501	361	66
PBPS-50	277, 303	498	356	67
PBPS-60	283, 314	495	351	70

[a] Performed on control and acid form membrane.

[b] The 5% weight loss temperatures by dynamic TGA at 10 °C/min under N_2 for acid and sodium form membranes.

4.3. Water uptake and morphology

Water uptake in weight percent and as the molar ratio of water molecules to sulfonic acid moiety are presented in Table 2. Water sorption increased with sulfonate content due to the strong hydrophilicity of

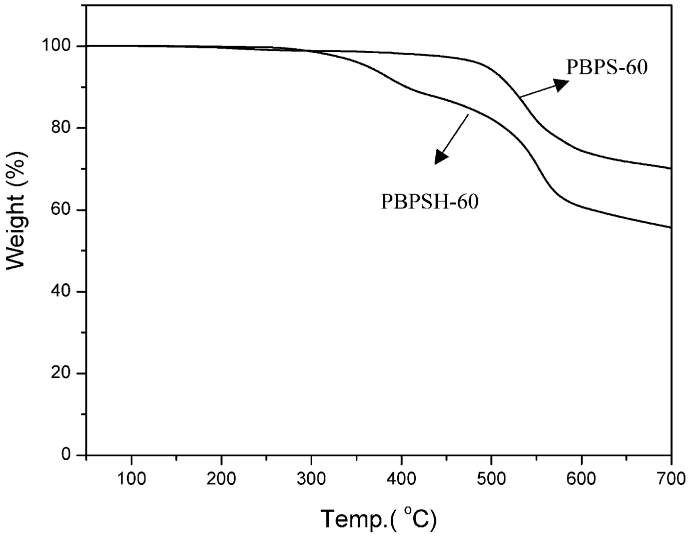


Fig. 5. TGA curves of PBPS-60 and PBPSH-60 (this figure compares the stability of salt and acid form membranes: PBPS-60 (salt form); PBPSH-60 (acid form)).

the sulfonate groups. The acid form of the membranes has a modestly higher water uptake than the corresponding sodium form membranes. The water uptake increased almost linearly from 4.4% for PBPSH-10 to 39% for PBPSH-40 and thereafter increased rapidly to 148% for PBPSH-60. Previous small-angle X-ray studies indicated that the microstructure of Nafion consists of two regions: ionic domains, where the ions are not evenly dispersed but aggregate together to form hydrophilic ion clusters; and a matrix, where the perfluorocarbon polymer backbone forms non-ionic hydrophobic regions [35]. The hydrophilic ion clusters are principally responsible for the water uptake of the polymer. Nonlinear water uptake behavior was also observed with the related sulfonated poly(arylene ether ketone) system [36,37].

Tapping mode phase images of the PBPSH system was recorded under ambient conditions on a 700 nm × 700 nm size scale in order to investigate ionic clusters for sulfonated poly(arylene ether sulfone)s (Fig. 6). For unsubstituted control homopolymers, i.e. PBPS-00, featureless phase morphology was observed. On the other hand, for the sulfonated poly(arylene ether sulfone)s, dark, cluster-like structures with a diameter of 10–25 nm were clearly visible in the phase image. The dark structures were assigned

Table 2
Influence of sulfonate or sulfonic acid groups on water uptake

DCDPS/SDCDPS (molar ratio)	Water uptake (wt.%)[a]		IEC (meq/g)	
	Na^+	H^+	Calculated	Experimental
9/1	4.5	4.4	0.48	0.41
8/2	9.8	12	0.92	0.88
7/3	18	24	1.3	1.2
6/4	28	39	1.7	1.5
5/5	41	56	2.0	1.8
4/6	67	148	2.4	2.2
0/10	Water soluble		3.6	–

[a] Conducted at 23 °C for 24 h.

to a softer region, which represents the hydrophilic sulfonic acid groups containing small amounts of water. The domain size and connectivity vary depending on the degree of sulfonation. For PBPSH-20, an isolated ionic cluster region was formed with a diameter of 10–15 nm, For PBPSH-40, the phase contrast of the hydrophilic ionic domains increased and became more easily distinguished from the non-ionic matrix, but the domains were still segregated with approximately 25 nm diameters. However, for PBPSH-60 sample, the phase image undergoes a significant change, wherein, the hydrophilic ionic domains become continuous to form large channels of an ionic rich phase. Similar continuous ionic channel structure was also observed in the ambient humidity conditioned Nafion 117 ionomer, although the domain size of the Nafion was about 4–10 nm (Fig. 6f). Based on the phase images of PBPSH-50, it was concluded that the PBPSH system reaches a percolation limit at about 50 mol% of the disulfonated monomer. This percolation limit can explain not only the sudden increase of water uptake (Fig. 7), but also earlier discussed T_g behaviors. In other words, the failure to detect the second, higher glass transition at low sulfonic acid concentration is probably due to the small, isolated ionic domain structure. On the other hand, the appearance of the cluster T_g may be associated with percolation of the ionic domain structure at around 50 mol% sulfonation.

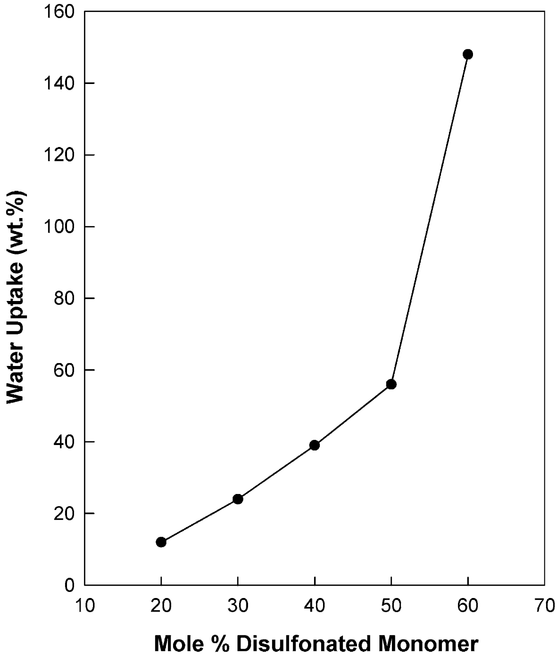


Fig. 7. Influence of the degree of sulfonation on the water uptake of sulfonated poly(arylene ether sulfone) copolymers.

4.4. Ion exchange capacity

Non-aqueous potentiometric titration was used to quantitatively determine the IECs of the polymers. The PBPSH solutions in DMAC were titrated by standard tetramethyl ammonium hydroxide solution (∼0.05N, in *iso*-propanol). One sharp end titration point was observed, confirming the strong acid (–SO_3H) base reaction. All the experimental IEC values are listed in Table 2, and are in good agreement with the calculated IECs, assuming that all of the sulfonated monomers was incorporated into the copolymer. The above results prove again that SO_3Na and proton conductive groups, –SO_3H, could be introduced into polymer via a sulfonated monomer without any side reactions, which are often observed in post-sulfonation methods. In addition to the above TGA measurements on the sulfonic groups, the stability of –SO_3H groups was investigated by combination of non-aqueous potentiometric titration and intrinsic viscosity measurements. The free acid form of the membranes, PBPSH-40 and PBPSH-60, showed significantly more stability than might have been expected from small model molecule experiments. The molecular structure was stable for 0.5 h up to 220 °C at air, as proven by continued solubility, stable IEC, and intrinsic viscosity values (Table 3). This is likely related to the fact that the ionic conductor was located on a deactivated phenyl ring, which should provide enhanced stability to desulfonation, since the anticipated intermediate carbocation required for desulfonation is more difficult to stabilize on such a sulfone deactivated ring.

4.5. Conductivity

The protonic conductivities of the membranes were measured in the cell shown in Fig. 1 at 30 °C in water. The conductivity of membranes over a range of sulfonation is shown in Fig. 8. The acid form membranes had proton conductivities of 0.08 and 0.17 S/cm for the PBSH-40 (IEC 1.72 meq/g) and PBSH-60 (IEC 2.42 meq/g), respectively, while the conductivity of

Table 3
Influence of copolymer sulfonic acid compositions (PBPSH-40 and PBPSH-60) on short-term thermal stability as indicated by intrinsic viscosity and IEC retention at 25 °C[a]

Aging (T, °C)	PBPSH-40		PBPSH-60	
	IV[b] (dl/g)	IEC (meq/g)	IV[b] (dl/g)	IEC (meq/g)
25	2.3	1.5	3.3	2.2
100	2.1	1.6	3.1	2.3
140	2.4	1.6	3.2	2.3
180	2.4	1.6	3.2	2.1
220	2.1	1.6	3.5	2.2
260	2.2	1.5	PS[c]	–

[a] The PBPSH membranes were treated at each temperature for 30 min in air before IEC determination at 25 °C.

[b] Intrinsic viscosities were determined in NMP at 25 °C.

[c] Partially soluble, indicating the thermal onset of branching.

Nafion 1135 (IEC 0.91 meq/g) was 0.12 S/cm under the same conditions. Limited fuel cell testing with methanol and hydrogen has been conducted. The conductivity of the BPSH-40 membrane is sufficient to pass current for both fuels, while the BPSH-30 material is not sufficient for current flow.

Greater ion exchange capacities are needed with sulfonated poly(arylene ethers) to achieve similar conductivities to perfluorosulfonic acid Nafion polymers, which is attributed to the strength of the acid group in each system. The acidity of the pendant perfluorosulfonic acid is much stronger than the aryl sulfonic acid, therefore, more acid moieties are needed in sulfonated poly(arylene ethers) to achieve the desired conductivity.

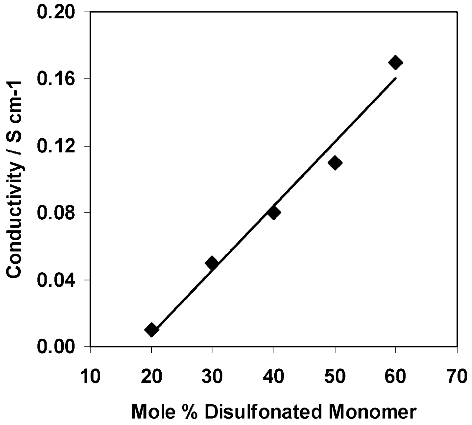


Fig. 8. Conductivity of membranes in water as a function of degree of sulfonation.

5. Conclusions

Poly(arylene ether sulfone)s containing sulfonate groups were successfully prepared by direct polymerization of the sulfonated activated halide using otherwise fairly similar "polysulfone" nucleophilic substitution condensation polymerization conditions. Tough acid form films with up to 1.2 sulfonic acid groups per repeating unit showed high water uptake and good stability when cast from solution. The T_g of the acid form polymers increased with degree of sulfonation, and it is suggested that two T_g's develop when the mol% of sulfonation reached 50%. AFM phase images showed that the diameter of the hydrophilic ionic domains increased from 10 to about 25 nm and became connected to produce a co-continuous morphology as the degree of sulfonation increased. This percolation limit of the PBPSH system was found at about 50 mol% of the disulfonated monomer and was consistent with the subsequent drastic increase in water uptake and the T_g behavior.

The highly sulfonated copolymers (PBPSH-40, PBPSH-50, and PBPSH-60) showed proton conductivity above 0.08 S/cm, which is in the range needed for high-performance fuel cell proton exchange membranes. The conductivity and water swelling of the membranes was greatly influenced by the mole percent sulfonation. The fuel cell performance of these materials is of intense interest and optimization and testing of these membranes in a fuel cell is ongoing. Further research on high temperature conductivity, comparing behavior to post-sulfonated systems, and blending with high conductive inorganic materials are in progress and will be reported in the near future.

Acknowledgements

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