Hydrocarbon and partially fluorinated sulfonated copolymer blends as functional membranes for proton exchange membrane fuel cells

Natalie Y. Arnett [a], William L. Harrison [b], Anand S. Badami [a], Abhishek Roy [a],
Ozma Lane [a], Frank Cromer [a], Limin Dong, James E. McGrath [a,*]

[a] *Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*
[b] *NanoSonic, Inc., 1485 South Main Street, Blacksburg, VA 24060, USA*

Abstract

Polymer blending is recognized as a valuable technique used to modify and improve the mechanical, thermal, and surface properties of two different polymers or copolymers. This paper investigated the solution properties and membrane properties of a biphenol-based disulfonated poly (arylene ether sulfone) random copolymer (BPS-35) with hexafluoroisopropylidene bisphenol based sulfonated poly (arylene ether sulfone) copolymers (6FSH) and an unsulfonated biphenol-based poly (arylene ether sulfone)s. The development of blended membranes with desirable surface characteristics, reduced water swelling and similar proton conductivity is presented.

Polymer blends were prepared both in the sodium salt and acid forms from dimethylacetamide (DMAc). Water uptake, specific conductivity, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and contact angles were used to characterize the blended films. Surface enrichment of the fluorinated component is illustrated by an significant increase in the water–surface contact angle was observed when 10 wt.% 6FBPA-00 (106°) was added to BPS 35 (80°). Water weight gain was reduced by a factor of 2.
© 2007 Published by Elsevier B.V.

Keywords: Poly(arylene ether sulfone) (PAES); Copolymer blends; Radel®; Nafion®; Proton exchange membrane fuel cell (PEMFC)

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are being investigated worldwide as alternative energy devices for applications in stationary, automotive, and portable power [1–3]. PEMFCs convert chemical energy directly into electrical energy using a series of electrochemical redox reactions.

To date perfluorinated sulfonic acid copolymers, such as Nafion® produced by DuPont, have been the most widely studied proton exchange membranes (PEMs) in fuel cells. Drawbacks of many perfluorinated membranes include high cost [4], limited operation temperature (<100 °C) [5]. In addition, high methanol permeability limits usage in direct methanol fuel cells (DMFCs) [6]. Therefore, many alternative nonfluorinated and partially fluorinated membranes that exhibit comparable performance to perfluorinated polymers have been investigated. These materials are potentially less expensive, have higher operation temperatures, and lower methanol permeabilities [7,8].

Poly(arylene ether sulfone)s represent a promising group of alternative PEMs for direct methanol and hydrogen/air fuel cells. A series of sulfonated poly(arylene ether sulfone) copolymers have been reported by McGrath et al. [9,10]. The high molecular weight sulfonated copolymers exhibit excellent film forming behavior, high glass transition temperatures, and proton conductivities greater than $0.1\,S\,cm^{-1}$. Previous research [11] has shown that aromatic membranes displayed fuel cell performance comparable to Nafion. However, the adhesion of these polymers to DMFC Nafion electrodes was inferior. This produces undesirable high frequency resistance (HFR) and decreased cell longevity due to delamination between the hydrocarbon based PEM membrane and the Nafion electrode [12].

Polymer blends are recognized as a valuable means to combine the properties of two different polymers [13,14]. Polymer blending has been shown to improve many characteristics including impact strength, thermal behavior, and surface character [15]. Advantages of polymer blending may include reduction

---

* Corresponding author. Tel.: +1 540 2315976; fax: +1 540 2318517.
E-mail address: jmcgrath@vt.edu (J.E. McGrath).

of cost since synthesis of new polymers is not required to obtain novel materials, improved processability of high temperature thermoplastics, and improved mechanical properties [16]. Furthermore, due to the different possible microstructures within the blend, the surface composition can be significantly different from the bulk. This possibility can be desirable as in the case of blends of fluorinated polymers due to their hydrophobic surface properties [17].

Blends of sulfonated poly(arylene ether) with polyethersulfone (PES), polysulfone (PSf), or polybenzimidazoles (PBI) have been investigated as potential candidates for applications in PEMFCs [18]. Typically, many of these studies utilized unsulfonated copolymers to reduce the aqueous swelling of the sulfonated polymer blends [19]. However, it has been well documented that the majority of polymer pairs are thermodynamically immiscible [20]. Therefore, many polymer-blend pairs macrophase separate yielding poor adhesion at the interphase of the two polymers.

Manea and Mulder investigated blends of polyethersulfone (PES) with sulfonated polysulfone (SPAU) or sulfonated poly(ether ether ketone) (SPEEK) [6]. Phase separation between the hydrophobic PES with the hydrophilic polymers lead to undesirable inhomogeneous blends.

Bowen et al. [21] reported that miscible PES/SPEEK blends were achieved at polymer weight ratios of 0.02–40 wt.% of SPEEK. The solution, containing 20 wt.% total polymer in NMP, remained homogenous at room temperature for at least 2 months. Lower miscibility was observed for blend solutions of PSU/SPEEK which became turbid after only 2 weeks when the weight ratio was increased to 0.25 wt.%.

Blends based on sulfonated poly(ether ketone ketone) SPEKK/polyetherimide (PEI) and SPEKK/PES (85/15 wt.%) and have been prepared by Swier et al. [22]. SPEKK/ polyetherimide (PEI) blends displayed limited solubility due to increased IEC (>0.8 mequiv. g^{-1}) and higher degrees of sul-

fonation typically resulted in heterogeneous morphologies. On the other hand, SPEKK/PES blends which initially proved to be interfacially inhomogeneous, exhibited increased miscibility between the two polymers in DMAc. The absence of strong specific interactions (hydrogen bonding or acid–base interaction) between the polymers was responsible for the polymers' incompatibility in the solid state.

Improvements to copolymer–copolymer miscibility can be achieved by promoting intermolecular interactions such as hydrogen bonding, dipole–dipole interaction, acid–base interactions, and covalent crosslinking [23]. Kerres et al. [24] have conducted comprehensive studies on these interactions and their effects in various blends of sulfonated poly(arylene ether sulfone)s (SPAES)or sulfonated poly(ether ether ketones)s (SPEEK). These researchers determined that increasing the bond strength of each interaction between the blend components led to increased copolymer–copolymer miscibility.

This paper reports the development of fluorinated and nonfluorinated directly copolymerized poly(arylene ether sulfone) random copolymers blended membranes with desirable surface characteristics and reduced water swelling (Fig. 1).

2. Experimental

2.1. Materials

4,4′-Hexafluoroisopropylidenediphenol (6F BPA), received from Ciba, was purified by sublimation and dried under vacuum. Eastman Chemical provided high purity 4,4′-biphenol (BP), which was dried at 50 °C under vacuum before each use. Solvay Advanced Polymers supplied highly purified 4,4′-dichlorodiphenylsulfone (DCDPS) and polyphenylene sulfone (Radel®). 4,4′-Dichlorodiphenylsulfone was dried at 60 °C under vacuum before each use. *N*-Methyl-2-pyrrolidinone (NMP) (Aldrich) was vacuum distilled from calcium hydride
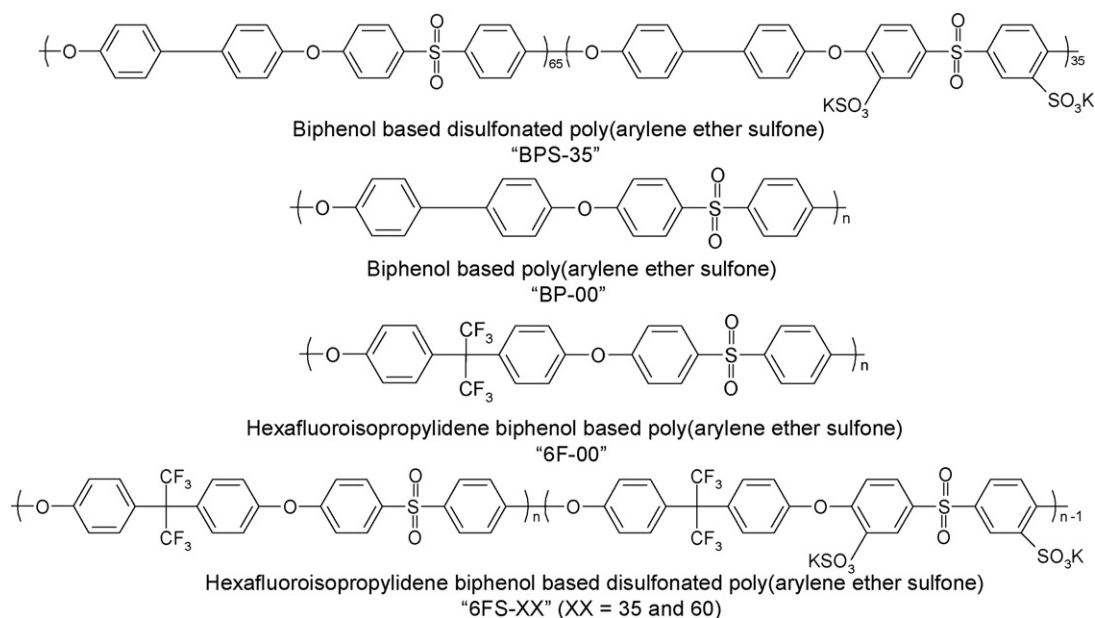

Fig. 1. Chemical structures of the directly copolymerized poly(arylene ether sulfone) disulfonated random copolymers utilized. [9,25].

onto molecular sieves, then stored under nitrogen. *N,N*-Dimethylacetamide (DMAc) (Aldrich) was distilled under vacuum from phosphorous pentoxide and stored over molecular sieves under nitrogen. Potassium carbonate was vacuum-dried at 150 °C prior to polymerization. Toluene obtained from Aldrich was used as received. The detailed synthesis of 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone monomer (SDCDPS) has been reported [9].

2.2. Copolymer synthesis by direct copolymerization

Similar copolymerization procedures were used to synthesize BP or 6F BPA copolymers. A typical copolymerization for the sulfonated copolymers is described using the 6FS-60 system. First, 6F-BPA (1.8494 g, 5.5 mmol), DCDPS (0.6318 g, 2.2 mmol), and SDCDPS (1.6211 g, 3.3 mmol) were added to a three-neck flask equipped with an overhead mechanical stirrer, nitrogen inlet and a Dean-Stark trap. Potassium carbonate (0.8707 g, 6.3 mmol), and DMAc (18 mL) were introduced to afford a 20% (w/v) solids concentration. Toluene (usually DMAc/Toluene = 2/1, v/v) was used as an azeotroping agent. The reaction mixture was refluxed at 150 °C for 4 h to dehydrate the system. The temperature was raised slowly to 190 °C by controlled removal of the toluene. The reaction was allowed to proceed for 30 h or until a viscous solution was observed. The solution was cooled to room temperature and the copolymer was isolated by coagulation in stirring deionized water. The precipitate was stirred overnight at 60 °C to remove most of the salts. The copolymer was then collected by vacuum filtration and dried in a vacuum oven at 120 °C for 24 h. Similar procedures with appropriate monomers and comonomer ratios were used to prepare the BPS-35, 6FS-35 and the 6F-00 copolymers and have been previously reported [26,27].

2.3. Polymer blending and membrane acidification

Separate solutions of the copolymers at different weight ratios with a total combined solution concentration of 5% (w/v) were prepared in DMAc. The 6F copolymer solutions were added to BPS-35 solutions and stirred at 80 °C for 1 h. Solutions were hot filtered through a 0.45 μm PTFE filter onto clean glass substrates. The membranes were dried gradually via a heating lamp with increasing intensity for 24 h and then under vacuum at 100 °C for 24 h. The copolymer blend membranes in the potassium salt form were converted to the acid form by first boiling in 0.5 M H_2SO_4 for 2 h and immediately followed by extraction in boiling deionized water for 2 h as described earlier [28].

2.4. Characterization

2.4.1. ¹H NMR
¹H NMR analysis was conducted on a Varian Unity 400 spectrometer to determine monomer purity and degree of sulfonation in the copolymers. All spectra were obtained from a 10% solution (w/v) in a DMSO-d_6 solution at room temperature.

2.4.2. Intrinsic viscosity
The intrinsic viscosities were determined in NMP with 0.05 M lithium bromide (LiBr) at 25 °C with an Ubbelohde viscometer (0.05 M). LiBr was used to control ionic aggregates associated with the sulfonated copolymers and minimize the ionic effect.

2.4.3. Fourier transform infrared (FTIR) spectroscopy
FTIR spectra were recorded on a Brunker Tensor 27 FTIR Spectrometer using thin polymer films in the acid form. The samples were dried at 100–110 °C for up to 48 h before collecting the spectra. All spectra were measured at a resolution of 2 cm^{-1} and represent the average of 32 scans.

2.4.4. Turbidity measurements
The clarity of the blended membranes was obtained from qualitative visual observations. The blended membranes were characterized in both the salt and acid forms to understand the effect of hydrothermal treatment (Method 2 acidification).

2.4.5. Aqueous potentiometric titrations
Aqueous potentiometric titrations were carried out on a Schott Instruments TA20 plus titration unit for ion-exchange capacities measurements of the blended membranes. The acidified membrane was placed in a concentrated 1 M solution of sodium sulphate and stirred for 24 h. The solution was then titrated with a standard sodium hydroxide solution at 0.02 mL s^{-1} and potential stretches from simple endpoint titrations were recorded.

2.4.6. Water uptake
The water uptake of the blended membranes was performed by immersing the membranes in deionized water at room temperature for 24 h. The wet membranes were then blotted to remove surface water droplets and quickly weighed. These membranes were then vacuum dried at 90 °C for 24 h and weighed again. The water uptake (%) of the membranes was calculated by:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{drt}}}{W_{\text{dry}}} \times 100\% \qquad (1)$$

where W_{wet} is the weight of the wet membrane and W_{dry} represents the weight of the dry membrane.

2.4.7. Proton conductivity
A Solartron (1287 + 1252) impedance/gain phase was used to measure the proton conductivity of each film in the acid form over a frequency range of 10 Hz–1 MHz under fully hydrated conditions. The resistance of each film was measured at ∼25 °C using the conductivity cell [8a].

2.4.8. Thermogravimetric analysis (TGA)
The thermooxidative stabilities of the membranes (10–15 mg) were determined using a TA Instruments TGA Q 500. Both the salt and acid form blended membranes were vacuum dried at 100 °C for 12 h prior to analysis. Before TGA characterization the membranes were placed in the TGA furnace at 150 °C in a nitrogen atmosphere for 30 min. The
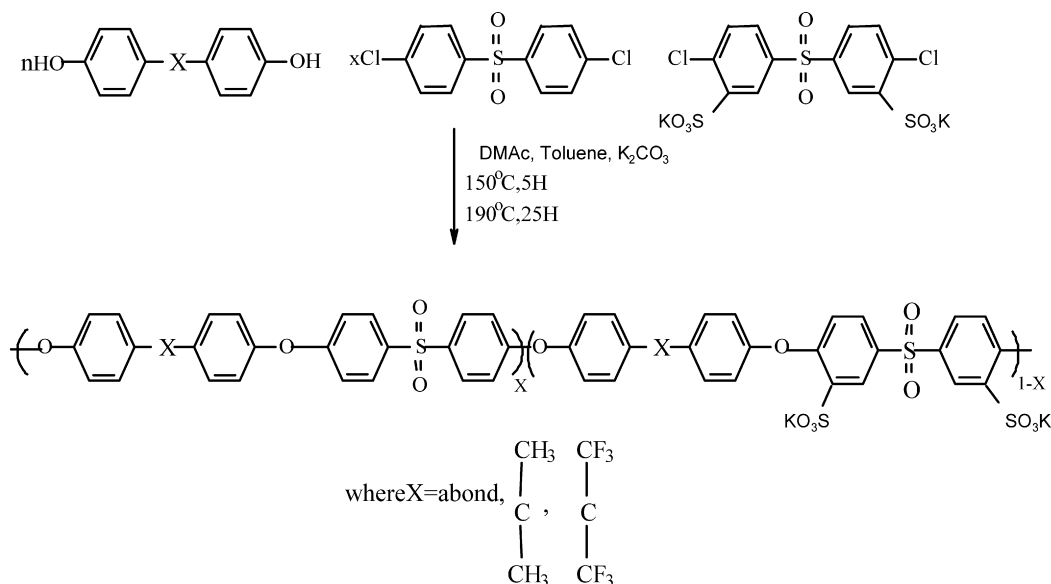
Fig. 2. Sample synthesis of disulfonated poly(arylene ether sulfone) copolymers via direct copolymerization.

samples were evaluated over the range of 30–700 °C at a heating rate of 10 °C min^{-1} in air.

2.4.9. Differential scanning calorimetry (DSC)

The glass transition temperatures (T_g) of the films were obtained on a TA Instrument DSC Q 1000. Scans were conducted under nitrogen at a heating rate of 10 °C min^{-1}. Second heat T_g values are reported as the midpoints of the changes in the slopes of the baselines.

2.4.10. Dynamic mechanical analysis (DMA)

Membranes were cut into dogbones with length of 20 mm, width of 4 mm, and thickness ranging between 0.05 and 0.1 mm and analyzed on a DMA 2980 instrument. The dogbone samples were placed in vacuum oven for 24 h at 120 °C to extract excess water. The dogbones were then placed in thin film tension clamps tested between 100 and 300 °C at 1 Hz.

2.4.11. Contact angles

The "instantaneous" (1–5 s) contact angle measurements were obtained on a Ten Angstroms (FTA 32) instrument that utilized the sessile-drop method. Contact angle was a quantitative method used to determine the hydrophobicity or hydrophilicity of the film surface.

2.4.12. Tapping mode atomic force microscopy (TP-AFM)

Tapping mode atomic force microscopy (TP-AFM) images of the blends were obtained using a Digital Instruments MultiMode scanning probe microscope with a NanoScope IVa controller. A silicon probe (Veeco) with an end radius of <10 nm and a force constant of 5 N m^{-1} was used to image samples. Samples were dried under vacuum at 100 °C for 12 h and then equilibrated at 50% relative humidity for at least 12 h before being imaged immediately at room temperature in a relative humidity of approximately, 15–20%.

3. Results and discussion

Two series of copolymers have been synthesized via nucleophilic aromatic step or polycondensation reactions. Biphenol and 6F BPA were, respectively, reacted with DCDPS and SDCDPS in NMP in the presence on potassium carbonate. The copolymer compositions and degrees of sulfonation were controlled by varying the molar stoichiometries of the DCDPS and SDCDPS. An example of preparation of poly(arylene ether sulfone) polymer and copolymers is described below (Fig. 2). The unsulfonated and sulfonated copolymers produced ductile transparent films from DMAc on glass plates.

NMR and FTIR were essential tools to investigate the sulfonated poly(arylene ether sulfone) copolymers structural compositions and functional groups. Proton NMR integration was utilized to confirm successful incorporation of the 60 or 35 mol.% SDCDPS comonomer into the copolymers. The sulfonation values for the copolymers used and their intrinsic viscosities are recorded in Table 1. All degrees of disulfonation determined by ^{1}H NMR were in good agreement with the molar feed ratios of SDCDPS, which verifies incorporation of the sulfonated comonomer into the copolymers.

Tough, ductile polymer blend membranes were obtained from DMAc solutions. BPS-35 was blended with various weight percentages of the unsulfonated partially fluorinated polymer

Table 1
Summary of general characteristics of polymers and copolymers used to prepare blends

Copolymer composition	IV	Degree of sulfonation
Radel	0.6	0
BPS-35	1.1	35
6F-00	0.6	0
6FS-35	0.57	35
6FS-60	0.45	60

(6F-00), or the partially fluorinated copolymers, 6FS-35 or 6FS-60, containing 35 or 60 mol.% of SDCDPS, respectively. Higher weight fractions (>10 wt.%) of these polymers into BPS-35 initially resulted in microphase separation which was determined by DSC. Visible macrophase separation was seen above 20 wt.%. Therefore, low weight percentages (0–10 wt.%) of the blends were investigated to eliminate the possibility of phase separation. Blends of commercially available polyphenylene sulfone (Radel® with BPS-35 were also prepared to evaluate the effect of the unsulfonated polymer on the water uptake of membranes. The films were analyzed in both the salt and acidified form.

3.1. Turbidity and optical clarity

The optical clarity of the membranes was inspected visually as a preliminary means of identifying compatibility between the polymers. Observation of clarity and miscibility of salt and acid form membranes are listed in Table 2. Low weight percentages (0–5 wt.%) of the 6F moiety in BPS-35 resulted in transparent films. As the amounts of 6F polymers or copolymers were increased to 10 wt.%, some hazing on the outer edges of the membranes in the salt form was observed. The addition of 5–10 wt.% of Radel into the blends yielded cloudy membranes. Higher ratios (>10 wt.%) of 6F moieties and Radel into the blends resulted in opaque films with large regions of *macrophase* separation.

Table 2
The effect of blend compositions on the optical clarity and appearance of blended membranes in the salt and acid forms

Composition (wt.%)	Optical clarity (salt)[a]	Optical clarity (acid)[b]
BPS-35	T	T
BPS-35/6F-00		
98/2	T	T
95/5	T	T
90/10	H	C
0/100	T	T
BPS-35/6FS-35		
98/2	T	T
95/5	T	H
90/10	C	C
0/100	T	T
BPS-35/6FS-60		
98/2	T	T
95/5	T	H
90/10	H	H
0/100	T	T
BPS-35/Radel		
98/2	T	T
95/5	C	T
90/10	C	T
0/100	T	T

The abbreviations for each membrane indicate the level of optical clarity observed where T = transparent; H = white discoloration on membrane outer edges; C = cloudy; O = opaque.

[a] The appearance of membrane upon direct release from glass substrate.
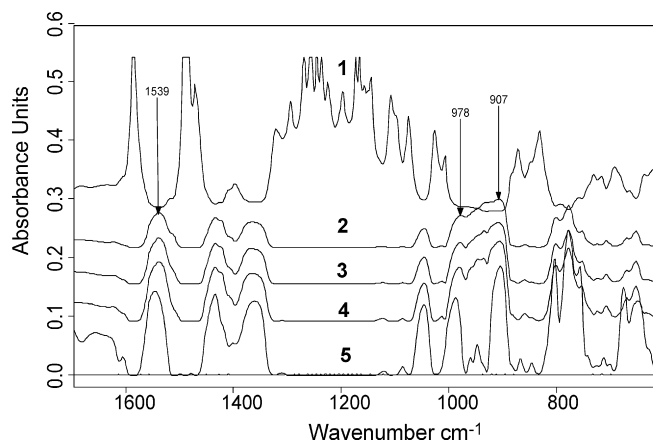[b] The appearance of membrane after undergoing Method 2 acidification.

Fig. 3. FTIR spectra of selected BPS-35/6FS-35 blend compositions: (1) BPS35; (2) 98 wt.% BPS35/2 wt.% 6FS-35; (3) 95 wt.% BPS35/5 wt.% 6F00; (4) 90 wt.% BPS35/10 wt.% 6F00; (5) 6FS-35.

The clarity of the blended membrane after hydrothermal treatment (Method 2 acidification) was also investigated. Previous research has shown that Method 2 acidification of disulfonated PAES membranes lead to the formation of larger hydrophilic domains with more phase continuity [28]. In the polymer blends comprised of 5 wt.% of 6F-00 and 6FS-60 in BPS-35, no obvious differences in membrane clarity were observed after being subjected to Method 2 acidification process. The incorporation of 10 wt.% of these copolymers in BPS-35 caused the membranes to become cloudy. This cloudiness was also apparent at lower weight percents (5 wt.%) of 6FS-35 in the blends. However, blended membranes containing even 5–10 wt.% of Radel became transparent after undergoing Method 2 acidification.

FTIR was used to probe and elucidate information on the surface of the copolymer blends. Chen and Gardella reported the use of ATR-FTIR to quantitatively surface analysis polystyrene/polystyrene-co-poly(dimethylsiloxane) blends [29]. As shown in Fig. 3, a definite trend was observed with increasing concentrations of 6FS-35 into the blends. The appearance of between 900 and 970 cm^{-1} and also at 1539 cm^{-1} which may be associated with the symmetrical and asymmetrical stretches of the hexafluoroisipropylidene group peaks clearly indicate practical compatibility of 6FS-35 into BPS-35. The continual increase in the intensity of these peaks was also seen as a function of 6FS-35 weight fraction and could possible corroborate with the surface enrichment from the partially fluorine containing copolymer.

3.2. Water uptake

The presence of water in PEMs is vitally important to transport and the overall PEMFC performance and dependent on several parameters such as degree of sulfonation, temperature, and relative humidity [25]. A decrease in the water uptake was observed in all the blends membranes except those containing 6FS-60 where the reverse effects (i.e., increased water uptake values) occurred (see Table 3). These changes were a function of weight percents. Additionally, the 6F-00 and Radel series were more effective in reducing the sorption of water in the mem-

Table 3
Summary of the water uptake and specific conductivity of selected poly(arylene ether sulfone) copolymer blend

Composition (wt.%)	IEC (mequiv. g^{-1})	Water uptake (wt.%)	Conductivity[a] (S cm^{-1})
BPS-35	1.33	39	0.08
BPS35/6F00			
98/2	1.30	33	0.06
95/5	1.29	27	0.06
90/10	1.20	18	0.06
0/100	0	0	0
BPS35/6FS-35			
98/2	1.37	33	0.06
95/5	1.34	28	0.06
90/10	1.32	24	0.06
0/100	0.85	20	0.05
BPS35/6FS-60			
98/2	1.40	48	0.12
95/5	1.51	57	0.13
90/10	1.76	90	0.14
0/100	2.19	400	0.15
BPS35/Radel			
98/2	1.32	35	0.07
95/5	1.30	31	0.07
90/10	1.23	21	0.07
0/100	0	0	0

[a] The error bar is within ±10%.

brane. From the table, a 15% greater reduction in water uptake values compared to BPS-35/6FS-35 can be seen with the addition of 2–10 wt.% 6F-00 into the blends. This was expected due to the absence of conducting sulfonic acid groups on these polymers that increased membrane hydrophobicity and decreased IEC [30].

The decrease in the water uptake and IEC with increasing concentration of these polymers can be seen morphologically with TM-AFM. An example of this change is shown in the phase images of BPS-35/6FS-35 series (Fig. 4) where the dark phases represent the soft hydrophilic ionic domains and the lighter phases the hard hydrophilic domains. As seen, the addition of larger concentration of 6FS-35 the domains sizes of the hydrophilic regions become smaller. The decrease in hydrophilic domain sizes directly correlates with a reduction in water uptakes from 33 to 24 wt.% when 2–10% of 6FS-35 was added.

In the 6FS-60 series the reverse effects (i.e., increased water uptake values) in water uptake were observed. The increase in the

water uptakes is due to the highly hydrophilic nature of 6FSH-60, which may be further amplified by the introduction of hydrogen bonding with water. Consequently, increasing the weight fraction of 6FS-60 in the blends resulted in membranes with higher degrees of swelling and extremely poor membrane integrity in the wet state.

3.3. Proton conductivity

The proton conductivities of the BPSH-35/6F00, BPSH-35/6FS-35 and BPSH-35/6FS-60 all followed similar trends as observed for the water uptakes (Table 3). However, these differences in proton conductivity were found to be a function of weight fractions only in the BPSH-35/6FSH-60 series. A reduction in conductivities from 0.08 S cm^{-1} for BPSH-35–0.06 S cm^{-1} occurred with increasing weight percentages 6F-00 and 6FS-35. A decrease in proton conductivity from 0.08 for BPSH-35 to 0.07 and 0.06 S cm^{-1} with increasing weight percentages 6F-00 and 6FS-35 or BP-00, respectively was also observed. Lower proton conductivities with incorporation of the 6F moieties were expected due to the hexafluoroisopropylidene connecting units that increase the hydrophobicity along the backbone segments [9]. In an effort to reduce water uptake without adversely affecting the proton conductivity and minimize the possibility of phase separation only small weight fractions of these polymers were introduced into the blends. Additionally, a reduction in IEC values (see Table 3) with the introduction of a nonconductive material in an ionic polymer should cause a decline in the proton conductivity of the membrane. This trend was seen in blends of sulfonated poly(ether ketone ketone) (SPEKK) with poly(ether imide) (PEI) [31] or polyvinylidene fluoride (PVDF) [32]. Interestingly, however, the conductivities of these samples, which should have closely followed those of the water uptake and IEC, remained unchanged as the concentration of unsulfonated polymer was increased from 2 to 10 wt.%. Further investigations using are underway to determine the reasoning behind this trend.

Higher proton conductivities from 0.12 to 0.14 S cm^{-1} exhibited by BPSH-35/6FSH-60 membranes were directly related to the higher IEC and water uptake values of the acidified 6FSH-60 compared to BPSH-35. Although these values are comparable or better than to commercial Nafion, higher water sorption values associated with these membranes cause excessive swelling. Therefore, the utilization of BPSH35/6FSH-60 membranes as successful PEMs is virtually impossible since
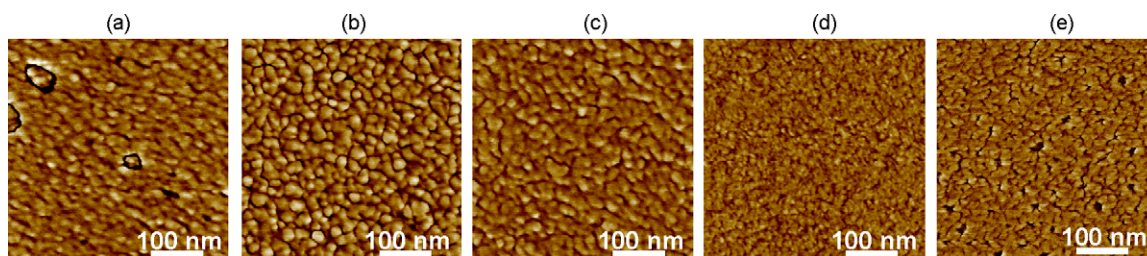

Fig. 4. The effect of 6FS-35 incorporation on the TM-AFM phase images of selected BPS-35/Radel blended membranes in the acid form: (a) BPS35; (b) 98 wt.% BPS-35/2 wt.% 6FS-35; (c) 95 wt.% BPS35/5 wt.% 6FS-35; (d) 90 wt.% BPS35/10 wt.% 6FS-35; (e) Radel.
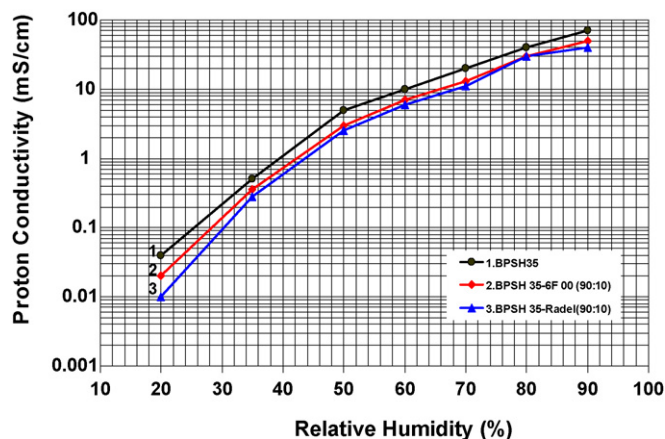
Fig. 5. Influence of temperature and chemical structure on proton conductivity at 100% relative humidity of blended membranes with 10 wt.% of unsulfonated homopolymers.

Fig. 6. Effect of chemical composition on the decomposition temperatures on 90/10 blended membranes.

the swelling properties of these membranes far exceed those required for practical PEMFC applications. For these reasons we have primarily focused the attention in this study to blends comprised of BPS-35 with 0–10 wt.% of 6F-00, 6FS-35, and Radel.

3.4. Proton conduction under partially hydrated conditions

The hydrated properties of disulfonated PAESs can be dramatically increase by both temperature and water content [33]. Fig. 5 illustrates the effect of hydration level and chemical structure on proton conductivity at 80 °C between 30 and 90% relative humidity (RH). BPSH-35 was used as a control. As seen, the addition of 10 wt.% unsulfonated 6F-00 and Radel resulted in a small but constant decrease in proton conductivity. Furthermore, the incorporation of 6F-00 into the blend yielded higher proton conductivities as a function of relative humidity even though these membranes exhibited lower water uptake and proton conductivity values. This phenomenon, which has been reported [34], is caused by the increased hydrophobicity of the 6F backbone resulting in shorter conduction pathway and increased "free water" content. As with many disulfonated copolymers that have been previously investigated, low proton conductivities (0.01 S cm^{-1}) at low relative humidities ($\sim$20%) were observed. This could possibly be overcome by preparing blocks copolymers between PAESs with high levels of disulfonation (>60%) and unsulfonated homopolymers. The clearly defined hydrophilic/hydrophobic microstuctures of these block copolymers may facilitated proton conduction even at low relative humidities.

3.5. TGA

The influence of blend composition of the acidified membranes on the thermo-oxidative stability from 50 to 700 °C was explored. In the salt form, the same high thermal stabilities up to 500 °C were observed for all the blended membranes. The acidified membranes, which were clearly influenced by the copolymer composition and the weight percent, blend composi-
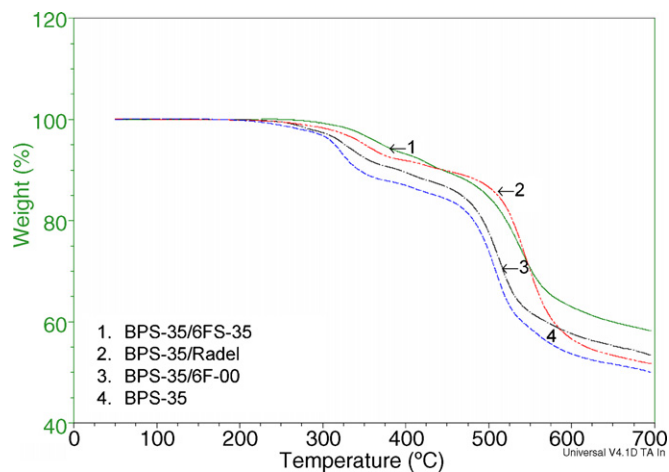
tions. From Fig. 6, it can be seen that the addition of 10 wt.% of 6FS-35 lead a higher decomposition temperature (371 °C) compared to the other blends of the same weight fractions. From the graph, all the copolymers in the acid form exhibited a two-step degradation profile with the first weight loss being assigned to desulfonation process and the second weight loss peak to main chain polymer degradation [35,36].

A summary of the thermal properties of the blended membranes are listed in Table 4. As seen, the thermo-oxidative stability of the all blends increased as a function of weight fractions with the highest thermal stabilities being displayed by BPS-35/6FS-35 series. This was unexpected since the presence of higher concentrations of sulfonic acid groups might have been expected at lower degradation temperatures. The enhanced thermal stability of these membranes may be due to crosslinking of the sulfonic acid group by crosslinking. Unpublished DMA data from this group illustrates this possible crosslinking occurring in both the disulfonated copolymers and blended membranes due to shifts in the glass transition to higher temperatures after several experimental runs. Kerres et al. [37] observed good thermal stabilities in crosslinked sulfonated blend membranes of poly(ethersulfone) PSU Udel^{TM} with pendant sulfinic (PSU-SO$_2$H) and sulfonic (PSU-SO$_3$H) acid groups. The improved

Table 4
Summary of the thermal properties by TGA and DSC of blended membranes in acid form

Composition (wt.%)	TGA (T_d, °C, 5% wt. loss)	DSC (T_g, °C)
BPS-35	265	264
BPS35/6F00		
98/2	295	262
95/5	307	261
90/10	321	260
0/100	485	194
BPS35/Radel		
98/2	289	263
95/5	313	263
90/10	346	261
0/100	500	220
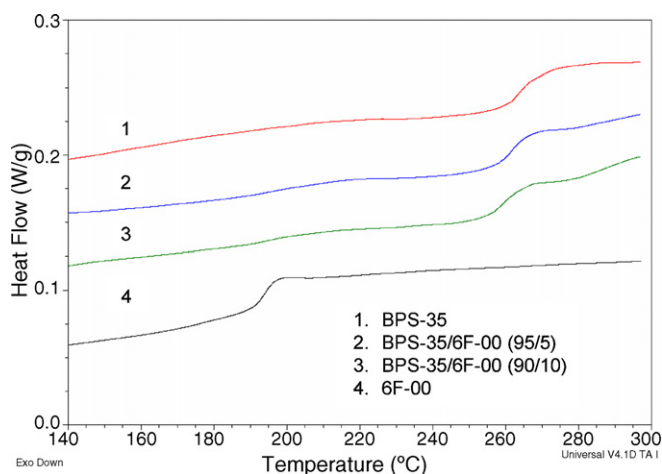
Fig. 7. Influence of weight fractions on thermal transition on acid form BPS-35/6F-00 membranes.

Table 5
Summary of the thermal properties of BPS-35/6FS-35 blends

Composition (wt.%)	TGA (T_d, °C, 5% wt. loss)	DMA (storage modulus T_g, °C)
BPS-35	265	279
BPS35/6FS-35		
98/2	355	276
95/5	367	271
90/10	371	263
0/100	350	235

thermal stability could be observed using TGA where a 5% weight loss for the PSU-SO$_2$H/PSU-SO$_3$H (70:30) crosslinked membranes resulted in a 60 °C increase compared membranes that only had 30% PSU-SO$_2$H. A similar trend of unexpectedly high desulfonation temperatures (>350 °C) for 6F poly(arylene ether sulfones) copolymers containing less than 40% degree of disulfonated has been previously reported [9]. By monitoring of the sulfonic acid peak at 1030 cm^{-1} with FTIR these researchers showed that a decrease in peak intensity when the film is exposed to 260 °C for 30 min could be observed.

3.6. DSC

The thermal properties (T_g) of the blends as a function of composition were investigated using DSC. DSC analyzes were conducted on the membranes in the acid form. Fig. 7 shows selected DSC thermoscans (2nd heat) of BPS-35/6F-00 as a function of wt.%. As shown, larger amounts of 6F-00 in the blends lead to small but subtle shifts in the T_gs to lower temperatures. The decrease in T_g was expected since the introduction of a unsulfonated copolymers into the blends would decrease molecular bulkiness and diminishes intermolecular interaction by hydrogen bonding of SO$_3$H groups (ionomer effect) [38]. The thermoscan suggested some miscibility between the copolymers was obtained because only a single T_g was observed for each blend. Although the same type of shifts in the DSC spectra were also observed for blends containing Radel, higher glass transition temperature were observed. Higher weight fractions of unsulfonated copolymers or 6FS-35 into BPS-35 first resulted in microphase separation above 20 wt.%, ultimately progressing into clearly defined macrophase separation at about 50 wt.%. This can be observed by the appearance of two T_g peaks in DSC scans.

Furthermore, it is well known that ion containing copolymers display complex thermal transition due to the presence of aggregates by the sulfonic acid (of varying sizes) and the influence to the 'normal' polymer transitions [39,40]. As previously stated crosslink can possibly be formed in these membranes at temperatures above 230 °C. The presence of crosslinks in these

membranes can hinder the internal rotations within the polymers making it more difficult to determine the glass transition temperatures of these membranes in the acid form using DSC. DMA, which is a more sensitive technique than DSC, was used to detect the glass transition (T_g) in the acidified BPS-35/6FS-35 membranes. As shown in Table 5 the blends of BPS35/6FS-35 exhibited the same decrease in glass transition temperatures as higher concentrations of 6FS-35 were introduced. Notably, these T_g temperatures were higher than the aforementioned membranes. The reason for this was that these blends were analyzed in the salt instead of the acid form, which resulted in shifts of the glass transition temperatures to higher temperatures after several runs.

3.7. Surface properties of blended membranes

Contact angle experiments were conducted on the various copolymer blend systems to explore the surface properties, including hydrophobicity, of the cast membranes. The data may provide information on the nature of the surface and confirm the surface enrichment of the fluorine atoms in the membranes. Linemann et al. used fluoropolymers as a means to reduce surface energy in latex blends of fluorinated acrylates with poly(n-butyl methacrylate) for water, oil, and soil repellence [41]. In blends of BPS-35 with 6F-00 and 6FS-35, higher contact angles were observed as the ratio of the partially fluorinated in the blend was increased. Fig. 8 illustrates the effect of increasing 6F-00-concentration on the instantaneous contact angle. As the weight fraction of 6F-00 in the blends was increased (from 0 to 10 wt.%) the contact angle changed by 21° on the air side of the membranes. The contact angle for the blends with 6F polymers are listed in table. From the table, the air and glass side of the membranes refer to the air/membrane and glass/membrane interfaces, respectively. The higher contact angles associated with increasing 6F-00 concentration may be attributed to increased amounts of the fluorine moieties on the membrane surfaces leading to enhanced hydrophobicity. Compared to the air/solid interface, lower contact angles on the glass/solid interface can be attributed to an increase in the surface energy. Furthermore, lower contact angle values in the BPS-35/6FS-35 blends were also seen due to the presence of higher concentration of sulfonic acid groups that increased surface hydrophilicity.

The calculated amounts of fluorine atoms present on the surface of these films were confirmed by XPS and are recorded in Table 6. Although no general trend occurred as a function
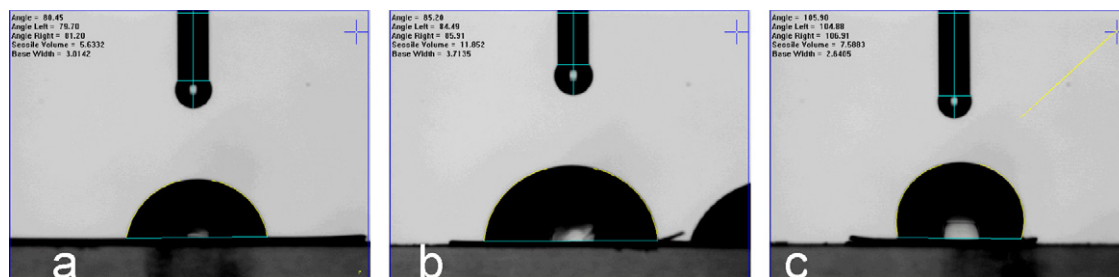
Fig. 8. The effect of 6F00 incorporation on the water contact angles of selected BPS35:6F00 blend membranes: (a) BPS35 (80°); (b) 98 wt.% BPS35/2 wt.% 6F00 (85°); (c) 90 wt.% BPS35/10 wt.% 6F00 (106°).

Table 6
Summary of the surface properties of fluorinated blended membranes by contact angles and XPS

Composition (wt.%)	Contact angle		XPS	
	Air side	Glass side	Air side	Glass side
BPS35/6F00				
100/0	80	64	0.08	0.0
98/2	85	70	8.4	0.0
95/5	87	77	0.2	0.3
90/10	106	78	10.9	0.0
0/100	109	89	10.2	9.9
BPS35/6FS35				
98/2	83	69	10.4	0.4
95/5	87	73	–	–
90/10	91	77	6.5	2.2
0/100	93	87	7.4	1.3

of weight fraction, a difference in the fluorine content on the air and glass surfaces of the membranes was observed. The changes in the quantitative amounts of fluorine on each surface directly correspond with angular changes observed by contact angle. This affirms that an enrichment of fluorine atoms on the surface of the membranes occurred leading to reduced surface energy and an increase in contact angle. As with the contact angles, the fluorine content on the air/membrane interface was notable higher than those on the glass/membrane interface in all the blend compositions.

4. Summary

A series of random copolymer blends composed of varying weight percent BPS-35 with 6F polyether sulfone, 6FS-35, and 6FS-60 has been made. The partially miscibility between the 6F containing copolymers and BPS-35 was observed by the appearance and increase of the appearance of hexafluoroisipropylidene group symmetrical and asymmetrical peaks between 900 and $970\,cm^{-1}$ and also at $1539\,cm^{-1}$. In the salt form, low weight percentages (0–5 wt.%) of the 6F moiety in BPS-35 resulted in transparent films, whereas, the addition of 5–10 wt.% of Radel into the blends yielded cloudy membranes. No changes in the optical clarity of membranes with 6F-00 and 6FS-60 were seen after being subjected to Method 2 acidification.

A decrease in the water uptake was observed in all the blends membranes except those containing 6FS-60 and were directly correlated to morphological and IECs changes as function of

weight fraction. Introduction of 6F-00, 6FS-35 and Radel into the blends initially lead to reduction in proton conductivities although these conductivities remained constant as the concentration of unsulfonated polymer was increased from 2 to 10 wt.%. Compared to BPSH-35 a small but constant decrease in proton conductivity with 10 wt.% of 6F-00 and Radel was also seen at 80 °C under relative humidity conditions. However, an increased in conductivity occurred as relative humidity was raised from 30 to 90%.

The thermo-oxidative stability and thermal properties (T_g) of the all blends were found to be a function of weight fractions. The self-enrichment of the fluorine atoms on the both the air and glass surface of the membranes was confirmed using contact angle and XPS measurements.

References

[1] M. Zalbowitz, S. Thomas, Fuel Cells: Green Power, Department of Energy, 1999, LA-UR-99-3231.
[2] K.S. Dhathathreyan, P. Sridhr, G. Sasikumar, K.K. Ghosh, G. Velayuthan, N. Rajalakshmi, C.K. Subramaniam, M. Raja, K. Ramya, Int. J. Hydrogen Energy 24 (1999) 1107–1115.
[3] K. Korgesch, G. Simader, Fuel Cells and their Applications, Wiley-VCH, Weinheim, 1996.
[4] G. Pourcelly, C. Gavach, in: P. Colomban (Ed.), Proton Conductors, Cambridge University Press, London, 1992, p. 295.
[5] M.K. Daletou, N. Gourdoupi, J.K. Kallitsis, J. Membr. Sci. 252 (2005) 115.
[6] C. Manea, M. Mulder, J. Membr. Sci. 206 (2002) 443–453.
[7] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4612.
[8] (a) A. Roy, M.A. Hickner, X. Yu, Y. Li, T.E. Glass, J.E. McGrath, J. Polym. Sci. B: Polym. Phys. 44 (2006) 2226–2239;
(b) O. Olabisi, L.M. Robeson, M.T. Shaw, Polymer–Polymer Miscibility, Academic Press, New York, 1979.
[9] W.L. Harrison, F. Wang, J.B. Mecham, V.A. Bhanu, M. Hill, Y.S. Kim, J.E. McGrath, J. Polym. Sci. A: Polym. Chem. 41 (2003) 2264–2276.
[10] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, J. Membr. Sci. 197 (2002) 231–242.
[11] J. Kerres, W. Zhang, A. Ullrich, C.M. Tang, M. Hein, V. Gogel, T. Frey, L. Jörissen, Desalination 147 (2002) 173–178.
[12] M.S. Wilson, Membrane catalyst layer for fuel cells, US Patent 5211984, 1993.

[13] D.R. Paul, C.B. Bucknall (Eds.), Polymer Blends, John Wiley & Sons Ltd., New York, 2000, p. 1217.

[14] For example, see;
(a) J.E. Yoo, C.K. Kim, Polym. Int. 53 (2004) 1950–1956;
(b) M.-S. Kang, J. Hak Kim, J. Won, S.-H. Moon, Y. Soo Kang, J. Membr. Sci. 247 (2005) 127–135.

[15] A. Noshay, J.E. McGrath, Block Copolymers: Overview and Critical Survey, Academic Press, New York, 1977.

[16] A. Rudin, Elements of Polymer Science and Engineering, 2nd ed., Academic Press, New York, 1999.

[17] P. Charoensirisomboon, T. Inoue, S.I. Solomko, G.M. Sigalov, M. Weber, Polymer 41 (2000) 7033–7042.

[18] (a) S. Swier, V. Ramani, J.M. Fenton, H.R. Kunz, M.T. Shaw, R.A. Weiss, J. Membr. Sci. 256 (2005) 122–133;
(b) W. Cui, J. Kerres, G. Eigenberger, Sep. Purif. Technol. 14 (1998) 145–154.

[19] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.

[20] D. Gan, W. Cao, Z. Wang, J. Fluor. Chem. 116 (2002) 59–63.

[21] R.W. Bowen, T.A. Doneva, H.B. Yin, J. Membr. Sci. 181 (2001) 253–263.

[22] (a) S. Swier, M.T. Shaw, R.A. Weiss, J. Membr. Sci. 270 (2006) 22–31;
(b) S. Swier, V. Ramani, J.M. Fenton, H.R. Kunz, M.T. Shaw, R.A. Weiss, J. Membr. Sci 256 (2005) 122–133.

[23] R.T. Tucker, C.C. Han, A.V. Dobrynin, R.A. Weiss, Macromolecules 36 (2003) 4404–4410.

[24] (a) W. Zhang, C.-M. Tang, J. Kerres, Sep. Purif. Technol. 209 (2001) 22–23;
(b) M. Walker, K.-M. Baumgärtner, M. Kaise, J. Kerres, A. Ullrich, E. Räuchle, J. Appl. Polym. Chem. 74 (1999) 67–73;
(c) J.A. Kerres, J. Membr. Sci. 185 (2001) 3–27.

[25] W.L. Harrison, M. Hickner, Y.S. Kim, J.E. McGrath, Fuel Cells 5 (2005) 201–212.

[26] F. Wang, M. Hickner, Q. Ji, W. Harrison, J. Mecham, T.A. Zawodzinski, J.E. McGrath, Macromol. Symp. 175 (2001) 387.

[27] Y.S. Kim, F. Wang, Mcv. Hickner, T.A. Zawodzinski, J.E. McGrath, J. Membr. Sci. 212 (2003) 263–282.

[28] Y.S. Kim, F. Wang, M. Hickner, S. McCartney, W.L. Harrison, Y.T. Hong, T.A. Zawodzinski, J.E. McGrath, J. Polym. Sci., B: Polym. Phys. 41 (2003) 2816–2828.

[29] J. Chen, J.A. Gardella, Appl. Spectro. 52 (3) (1998) 361.

[30] Y.S. Kim, M.A. Hickner, L. Dong, B.S. Pivovar, J.E. McGrath, J. Membr. Sci. 243 (2004) 317–326.

[31] J.V. Gasa, R.A. Weiss, M.T. Shaw, J. Polym. Sci., B: Polym. Phys. 44 (2006) 2253–2266.

[32] S. Ren, G. Sun, C. Li, Z. Wu, W. Jin, W. Chen, Q. Xin, X. Yang, Mater. Lett. 60 (2006) 44–47.

[33] R.W. Kopitzke, C.A. Linkous, H.R. Anderson, G.L. Nelson, J. Electrochem. Soc. 147 (2000) 1677–1681.

[34] Y. Seung Kim, B. Einsla, M. Sankir, W. Harrison, B.S. Pivovar, Polymer 47 (2006) 4026–4035.

[35] J.P. Quentin, Sulfonated polyarylether sulfones, U.S. 3,709,841, Rhone-Poulenc, January 9, 1973.

[36] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhaupt, J. Membr. Sci. 83 (1993) 211.

[37] J. Kerres, W. Cui, R. Disson, W. Neubrand, J. Membr. Sci. 139 (1998) 211–225.

[38] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 173 (2000) 17–34.

[39] M. Ehramann, R. Muller, J.C. Galin, C.G. Bazuin, Macromolecules 26 (1993) 1918–4910.

[40] A. Eisenberg, J. Kim, Introduction to Ionomers, Wiley-Interscience Publ., 1998;
(b) G.L. Wilkes, M.R. Tant, K.A. Mauritz (Eds.), Ionomers: Synthesis, Structure, Properties and Applications, Blackie Academic and Professional, New York, 1997.

[41] R.F. Linemann, T.E. Malner, R. Brandsch, G. Bar, W. Ritter, R. Mulhupt, Macromolecules 32 (6) (1999) 1715–1721.