Radiation-induced grafting of styrene onto poly(tetrafluoroethylene) films. Part II. Properties of the grafted and sulfonated membranes

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Abstract: The physical and chemical properties of polystyrene grafted and sulfonated polytetrafluoroethylene (PTFE-*graft*-PSSA) membranes prepared by radiation-induced grafting of styrene onto commercial PTFE films using simultaneous irradiation technique followed by a sulfonation reaction are evaluated. The investigated properties include water uptake, ion exchange capacity, hydration number and ionic conductivity. All properties are correlated with the amount of grafted polystyrene (degree of grafting). The thermal stability of the membrane evaluated by thermal gravimetric analysis (TGA) is compared with that of original and grafted PTFE films. The membrane surface structural properties are analysed by electron spectroscopy for chemical analysis (ESCA). Membranes having degrees of grafting of 18% and above show a good combination of physical and chemical properties that allow them to be proposed for use as proton conducting membranes, provided that they have sufficient chemical and mechanical stability.
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INTRODUCTION

Membranes prepared by radiation-induced grafting are receiving increasing attention in the field of polymer, solid state and separation science and technology. This is due to their potential to substitute similar membranes prepared by conventional polymerization methods in various applications of industrial interest such as pervaporation,[1] dialysis,[2] water electrolysers,[3] sensors[4] and fuel cells.[5] In particular, radiation grafted membranes bearing sulfonic acid groups have been proposed as proton conductors in solid polymer electrolyte (SPE) fuel cells.[6] This is because of the complete dissociation of sufonic acid groups, which results in high current density. Experimental radiation grafted sulfonic acid membranes based on poly(tetrafluoroethylene-*co*-hexafluropropylene) (FEP) films were developed by Scherer and co-workers and found to be stable for 1400h in SPE fuel cells at temperatures up to 80 °C.[7–9] Recent experiments on commercial radiation grafted membranes showed a satisfying performance with an initial lifetime up to 1000h at an operating temperature of 60 °C.[5]

For a membrane to be qualified for use in SPE fuel cells, it must combine high ionic conductivity ($10^{-2} \Omega^{-1} cm^{-1}$), mechanical strength, chemical/thermal stability and controlled swelling behaviour.[10] Commercial perfluoronated sulfonic acid membranes such as Nafion (DuPont de Nemours Ltd), Aciplex (Asahi Chemical Co) and Dow developmental membranes (Dow Chemical Co Ltd) have been found to meet these requirements. However, the high cost of these membranes has prompted the development of cheaper and better proton conducting membranes in the last few years.[11] Several new types of fluorinated and non-fluorinated membranes have been developed using chemical doping methods.[12–16]

Radiation grafting of functional monomers onto polymer films was used as one of the alternative routes to prepare tailored sulfonic acid membranes. This was due to the ability to have better control over the membrane composition and properties by applying appropriate grafting conditions. A number of studies have reported the preparation of radiation grafted and sulfonated membranes using simultaneous and preirradiation techniques.[17–22] Due to the chemical stability needed in these membranes, styrene is commonly grafted onto fluorinated polymers, and

the resulting polystyrene graft copolymers are subsequently sulfonated.[10]

We have used commercial poly(tetrafluoroethylene) (PTFE) film as a polymer matrix despite its radiation sensitivity. PTFE was selected because of its outstanding chemical, thermal and mechanical stability. Styrene was grafted onto PTFE films using a simultaneous irradiation technique under appropriate grafting conditions. Kinetics of the grafting were investigated in correlation with the grafting conditions, ie solvent type, irradiation dose, dose rate and initial monomer concentration. The degree of grafting was found to be a function of the grafting conditions and has a strong influence on the properties of the grafted films.[23]

In the present study, the grafted PTFE films were sulfonated and the physicochemical properties of the obtained polystyrene grafted and sulfonated membranes were determined. The thermal stability was investigated in correlation with the membrane preparation procedure, ie grafting and sulfonation using TGA. Surface analysis of the membranes was also carried out by ESCA.

EXPERIMENTAL
Materials
PTFE film of 90 μm thickness (Porghof) was used as a polymer matrix. Styrene of purity more than 99% (Fluka) was used as the grafting monomer without any further purification. Dichloromethane (JT Baker), chlorosulfonic acid (Fluka) and 1,1,2,2-tetrachloroethane (Fluka) were reagent grade and used as received. Nafion 117 (DuPont) was used as a reference material.

Membrane preparation
The preparation of the membranes was carried out in a two-step procedure. In the first step, styrene was grafted onto the PTFE film using a simultaneous irradiation technique. A glass ampoule containing PTFE film of known weight was immersed in a solution of styrene monomer in dichloromethane at concentrations in the range 20–50 vol%. The ampoule was irradiated using γ-rays from a ^{60}Co source located at the Malaysian Institute for Nuclear Technology Research (MINT) to a total dose of 20 kGy at a dose rate of 0.37 Gy s^{-1} under nitrogen atmosphere at room temperature. The grafted films were washed thoroughly with toluene and soaked therein for 16 h, then dried under vacuum until a constant weight was obtained. More details on the grafting procedure and properties of the grafted PTFE films have been reported elsewhere.[23] The degree of grafting was calculated using the following equation:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_o}{W_o} \times 100$$

where W_g and W_o are the weights of grafted and original PTFE films, respectively.

In the second step, the grafted PTFE films were sulfonated using a sulfonation mixture composed of 30 parts chlorosulfonic acid and 70 parts of 1,1,2,2-tetrachloroethane (v/v). The grafted films were initially washed with dichloromethane where they were soaked therein for 30 min then removed and dried in a vacuum oven for 1 h. The grafted films were sulfonated in a glass reactor at 90 °C and the reaction was allowed to continue for 4 h under N$_2$ atmosphere. The sulfonated membranes were removed, washed several times with 1,1,2,2-tetrachloroethane and dichloromethane to remove the excess of chlorosulfonic acid. The sulfonated membranes were then hydrolysed with 0.5 M KOH solution overnight and regenerated by boiling with 1 M HCl for several hours. The membranes were then washed with deionized water several times to ensure complete removal of acid, and finally stored in the dark under water.

FTIR measurements
FTIR measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with an attenuated total reflector (ATR) (Thunder dome-HATR) having a germanium spherical crystal. The spectra were measured in absorbance mode in the wavenumber range 4000–500 cm^{-1} and analysed using commercial software.

Water uptake
Water uptake was determined by equilibrating vacuum dried membrane samples in acid form in deionized water (18 MΩ cm) for 4 h. The swollen membrane samples were removed and the excess of water adhering to the surface was quickly wiped with absorbent paper and then the samples were weighed. The water uptake was determined as the percentage weight increase in the dry membrane. The dry weight of the samples was determined after drying in a vacuum oven (16 h, 80 °C and 10^{-3} torr) then over silica gel in an evacuated desiccator (1 h) as reported in our previous study.[17] Measurements were also made to determine the dimensional changes caused by swelling in water and compared with the corresponding values for the dry membranes

Ion exchange capacity
The ion exchange capacity (IEC) of dry membranes was determined by measuring the concentration of protons (H$^+$) exchanged by K$^+$ when the membrane samples were equilibrated with KCl solution. The dry membrane samples in acidic form of known weight and volume were immersed in 0.5 M KCl solution overnight at room temperature with occasional stirring. The amount of protons (H$^+$) released in the solution was determined by titration with standardized 0.05 M KOH solution using an automatic titrator (Metrohom, Switzerland) until pH 7 was reached. IEC per unit mass (meq g^{-1}) and also per unit volume (meq cm^{-3}) of the dry membrane was calculated by taking into account the weight and dimensional

changes in the dry membrane during swelling. The degree of sulfonation was calculated from the number of moles of KOH consumed and the total number of styrene units obtained from the degree of grafting as reported by Rouilly *et al.*[24]

Proton conductivity

Proton conductivity of the membranes was measured at room temperature by complex AC impedance spectroscopy. Measurements were carried out on membranes in acidic form using a frequency response analyser (Solartron, 1250) in combination with electrochemical interface (EG&G Princeton Applied Research) at frequencies in the range 0.01–100 kHz. Fully hydrated samples of known dimensions were sandwiched between two stainless steel electrodes and assembled with a sample holder located in the laboratory-made conductivity cell. Fresh electrodes were always used in each experiment to maintain high electrode sensitivity. The resistance of the membranes was obtained from the intercept of the impedance curve with the real axis at the high frequency end. The proton conductivity was calculated from the resistance after taking the surface area and the thickness of the membrane samples into account.

Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) measurements were performed using a Perkin-Elmer TGA-7 analyser. Thermograms were obtained for samples of vacuum dried membranes, original and grafted PTFE films having typical weight of 10–20 mg in the temperature range 50–700 °C. All TGA runs were made at a constant heating rate of $20°\,min^{-1}$ in nitrogen atmosphere.

Surface characterization

Surface investigations were carried out using a Kratos XSAM-HS electron spectrometer having an overall resolution of 1.3 eV. A low X-ray flux of the non-monochromatized $MgK\alpha$ line, normally operated at 10 mA and 12 kV, was used to minimize the charging effect. The chamber pressure was set at a value of not less than 8×10^{-9} torr. Binding energies were calibrated using a gold standard (Au $4f_{1/2}$ at 84 eV). Samples were mounted on the sample holder with double-sided adhesive tape. ESCA spectra were taken for both membrane surfaces.

Commercial Nafion 117 (DuPont) membranes were used as a reference. They were converted to the protonic form by boiling in H_2O_2 (3%) for 1 h, rinsing in boiling water for 1 h and boiling in 0.5 M H_2SO_4. The membranes were finally washed free of acid with boiling deionized water several times.

RESULTS AND DISCUSSION

Grafting of styrene onto PTFE films by a simultaneous irradiation technique resulted in polystyrene grafted PTFE films having various degrees of grafting (5–36%). Figure 1 shows the relationship between the degree of grafting and the monomer concentration in the grafting solution. The degree of grafting in the membranes was found to increase steeply with the increase in the monomer concentration within the concentration range investigated. This behaviour was attributed to the increase in styrene diffusion and its concentration inside the grafting layers despite the fact that PTFE films scarcely swell in most solvents and monomers.[23] Moreover, the grafting reaction in this system was suggested to proceed by a front mechanism, where styrene grafting starts at layers close to the PTFE film surface and moves internally towards the middle of the film by progressive diffusion through successive swollen grafted layers. These results are in a complete agreement with those reported by Chapiro *et al*[25] for grafting styrene onto PTFE films using a simultaneous irradiation technique.

Sulfonation of polystyrene grafted PTFE films having various degrees of grafting resulted in polystyrene grafted and sulfonated membranes that can be simply called PTFE-*graft*-PSSA membranes with various equivalent weights. All membranes achieved degrees of sulfonation in the range of 93–100% and therefore the ratio of sulfonic acid groups to phenyl groups of polystyrene can be considered to equal unity. Consequently, all the membrane properties are discussed only in relation to the degree of grafting in this study.

Typical FTIR spectra of original PTFE film, 36% grafted PTFE film and PTFE-*graft*-PSSA membrane having the same degree of grafting are shown in Fig 2. The strong bands at 1150 and 1205 cm^{-1} are characteristic for the stretching vibrations of CF_2 of the original PTFE film as shown in spectrum A. Grafting
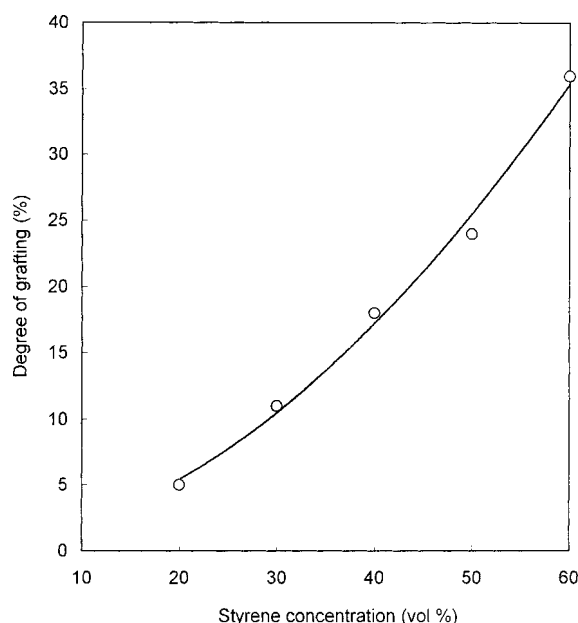

Figure 1. Relationship between degree of grafting and monomer concentration for grafting of styrene onto PTFE films. Grafting conditions are: dose, 20 kGy; dose rate, $0.37\,Gy\,s^{-1}$; diluent, dichloromethane; film thickness, 90 μm; temperature, 28 °C; atmosphere, N_2.
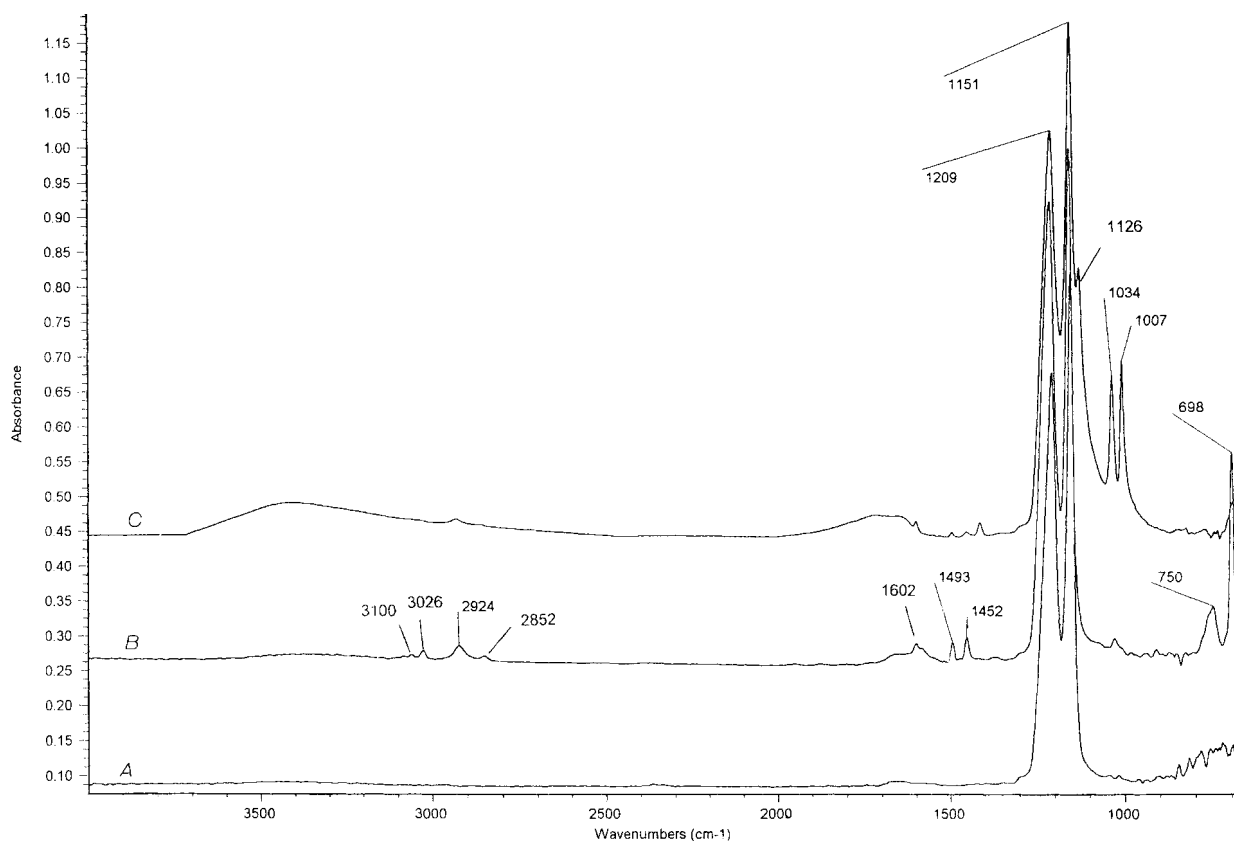
Figure 2. Typical FTIR spectra of (A) original film, (B) 36% grafted PTFE film, and (C) 36% grafted PTFE-*graft*-PSSA membrane.

of styrene was confirmed by the presence of the aromatic ring features such as the skeletal C=C in-plane stretching vibrations at 1493 and 1602 cm^{-1} and C—H aromatic stretching vibrations at 3100–3026 cm^{-1} as depicted in spectrum B. The spectral bands at 698 and 750 cm^{-1} were assigned to the aromatic CH deformation of the disubstituted benzene ring, whereas those at 2924–2852 cm^{-1} were attributed to the aliphatic C—H stretching vibrations. Sulfonation of the grafted film was confirmed through the disappearance of the CH deformation bands and the emergence of sharp bands at 1126, 1034 and 1007 cm^{-1} due to SO$_3^-$ groups, as can be seen in spectrum C. The complete disappearance of the CH deformation bands confirms that the membrane has achieved a degree of sulfonation close to 100%.

Figure 3 shows the relationship between the membrane water uptake and the degree of grafting of PTFE-*graft*-PSSA membranes. The water uptake by weight and by volume was found to increase gradually with increase in the degree of grafting. This can be attributed to the increase in the hydrophilicity imparted to the membranes by the incorporation of more sulfonic acid groups with increasing degree of grafting as previously reported.[8,17,24] The water uptake of Nafion 117 was found to be around 39 wt%.

Figure 4 shows the relationship between ion exchange capacity and the degree of grafting of PTFE-*graft*-PSSA membranes. The ion exchange capacity (IEC) was found to increase with increasing

degree of grafting. The increase in the degree of grafting from 5 to 36% leads to an increase in the IEC from 0.36 to 2.20 meq g^{-1} and from 0.8 to 3.0 meq cm^{-3} of the dry membranes, respectively. The corresponding IEC values of Nafion 117 membrane are equal to 0.9 meq g^{-1} and 1.9 meq cm^{-3},
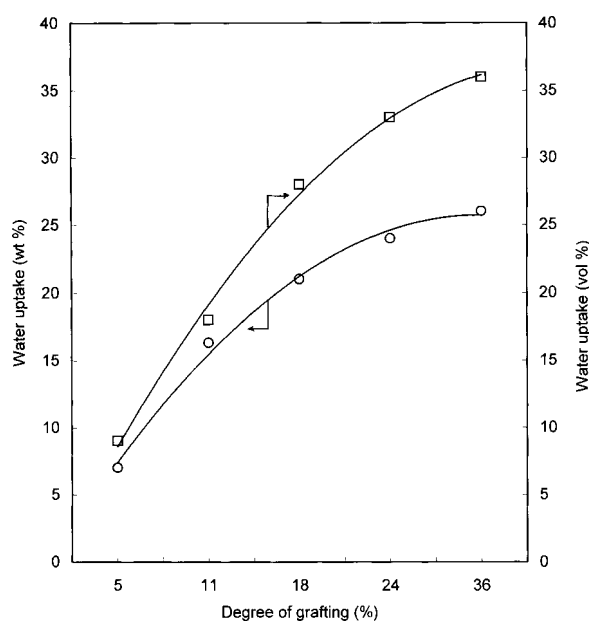

Figure 3. Relationship between water uptake and degree of grafting of PTFE-*graft*-PSSA membranes.
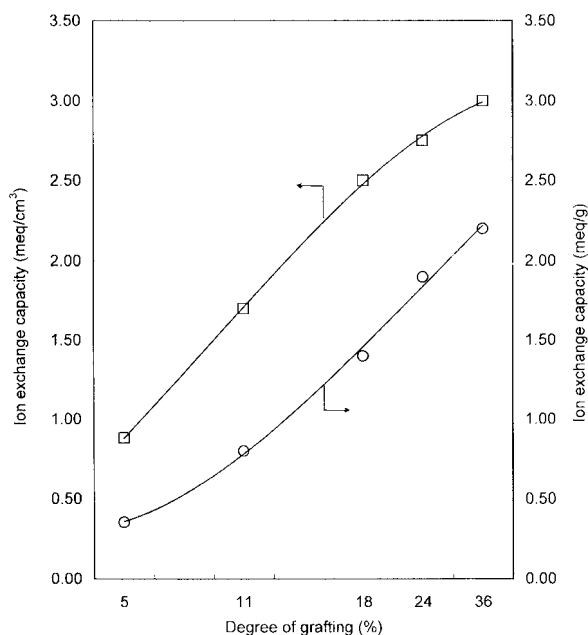
Figure 4. Relationship between ion exchange capacity (IEC) and degree of grafting of PTFE-*graft*-PSSA membranes.
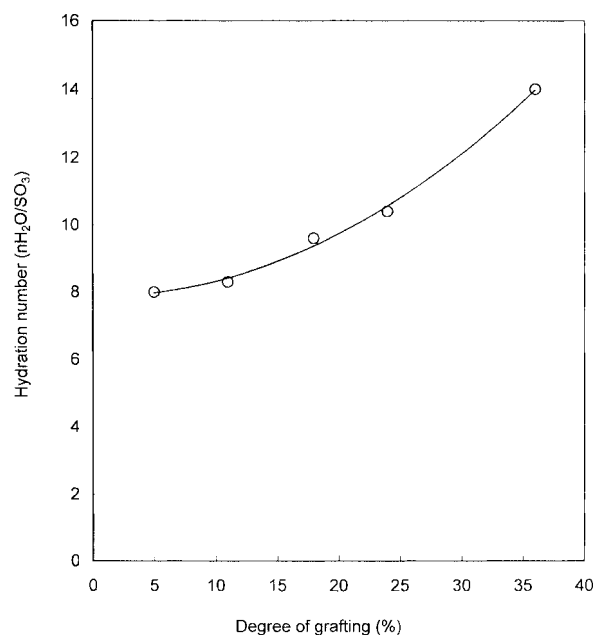

Figure 5. Relationship between hydration number (nH_2O/SO_3H) and degree of grafting of PTFE-*graft*-PSSA membranes.

respectively. This behaviour can be attributed to the increase in the content of polystyrene grafts in the PTFE polymer matrices, which provides more benzene rings to host sulfonic acid groups. Therefore, a desirable number of ionic sites can be achieved by controlling the degree of grafting. This behaviour is similar to that reported for polystyrene grafted and sulfonated membranes based on polytetrafluoroethylene-*co*-hexafluoropropylene) (FEP),[8] polyvinylidene fluoride (PVDF)[26] and poly(tetrafluoroethylene-*co*-perfluorovinylether) (PFA).[17]

Figure 5 shows the relationship between the hydration number of the sulfonic acid groups and the degree of grafting of PTFE-*graft*-PSSA membranes. The hydration number (nH_2O/SO_3H) was found to increase with an increase in the degree of grafting. The increase in the degree of grafting from 5 to 36 % leads to an increase in the hydration number from 8 to 14. This can be reasonably attributed to the cumulative effect of three main factors: an increase in the number of sulfonic acid groups, an increase in hydrophilicity, and a decrease in the degree of crystallinity of the membrane with increasing degree of grafting.[28] The observed hydration numbers for PTFE-*graft*-PSSA membranes in this study were found to be lower than those reported for FEP-*graft*-PSSA (8–18 for a degree of grafting in the range 5–40 %)[27] prepared by grafting of styrene onto FEP films under the same grafting and sulfonation conditions. This is most probably due to the difference in the structural changes taking place in the radiation-sensitive PTFE film as a result of styrene grafting and subsequent sulfonation compared to that in radiation-resistant FEP films. The hydration number of Nafion 117 was found to be around 23. This result is in good agreement with those reported by Zawodzinski *et al*[29] and Halim *et al*.[30]

Figure 6 shows the relationship between the log of proton conductivity and the degree of grafting of PTFE-*graft*-PSSA membranes at room temperature. The proton conductivity increases with an increase in the degree of grafting. This can be understood on the basis that ionic conductivity is a function of ion exchange capacity and water uptake of the membranes, which were found to be strongly dependant upon the degree of grafting. However, the increase in proton conductivity is found to be drastic at the beginning, but tends to level off at a degree of grafting of 18 %. Such behaviour can be explained by taking
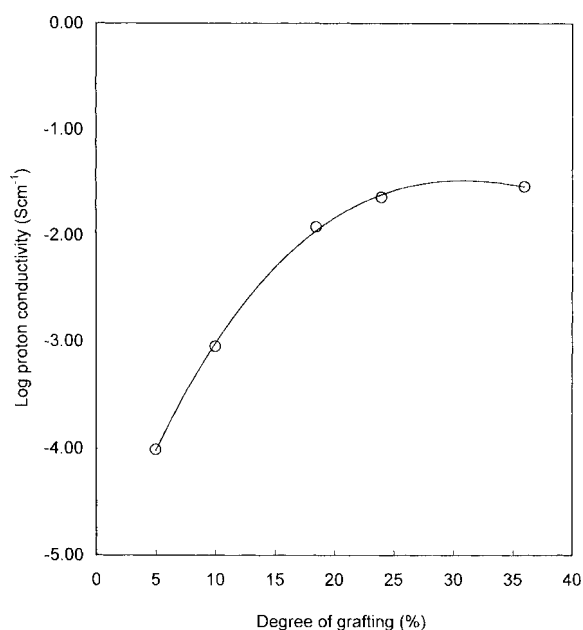

Figure 6. Relationship between proton conductivity and degree of grafting of PTFE-*graft*-PSSA membranes at room temperature.

into consideration the distribution of the sulfonated polystyrene grafts. At low degrees of grafting, the polystyrene grafts are only distributed near the surface of the membranes while their centres remain ungrafted and subsequently exert high local resistance to proton transport. As the degree of grafting increases to 18 % more grafts tend to be formed near the centre of the membranes, resulting in a sharp decrease in the local resistance and drastic increase in the proton conductivity. Further increase in the degree of grafting does not bring much change to the proton conductivity because of the possible effects of homogenous distribution of the sulfonated polystyrene grafts in the membranes. These results show a similar trend to those for PFA and FEP based membranes.[8,23,27] The corresponding proton conductivity of Nafion 117 was found to be equal to $5.3 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at room temperature. This value is in a good agreement with that reported by Zawodzinski *et al*[31] and Rieke and Vanderborgh.[32]

The effect of the membrane two-step preparation procedure, ie grafting and sulfonation, on the thermal stability of the PTFE matrix was studied. Figure 7 shows TGA thermograms of original PTFE film, grafted PTFE film having a degree of grafting of 36 % and PTFE-*graft*-PSSA membrane having a degree of grafting of 36 %. The fluorinated structure of the PTFE matrix was found to exhibit thermal stability up to about 550 °C, followed by one-step degradation as depicted by thermogram A. Grafting of styrene onto PTFE matrix introduces a two-step degradation pattern. Both grafted film components, however, show two distinct degradation temperatures as shown in thermogram B. The polystyrene grafts started to degrade at about 400 °C, and this continued until around 460 °C. This was followed by the degradation of PTFE backbone, which started at about 550 °C. The polystyrene grafts, which have a pure hydrocarbon structure, seem to be incompatible with the fluorocarbon structure of the PTFE matrix. There-

fore, phase separated microdomains were formed in PTFE-*graft*-polystyrene films.

Sulfonation of the grafted films introduces a three-step degradation pattern as shown in thermogram C. In the first step, the weight lost started below 100 °C and continued up to around 200 °C. This was followed by another degradation step that began around 300 °C and continued up to around 390 °C. In the third step, the degradation began at about 550 °C and continued up to around 680 °C. The initial weight loss shown in Fig 7, curve C is ascribed to the loss of water from the membrane, based on the fact that sulfonated membranes have a strong hydrophilic nature. The continuous water loss up to 200 °C is due to the strong interaction between water molecules and sulfonic acid groups in the membranes. Similar behaviour was observed for styrene grafted and sulfonated FEP,[33] PVDF[34] and PFA[35] membranes, respectively. Commercial sulfonic acid membranes such as Nafion 117 were also reported to behave in the same manner.[36] The weight loss in the second step (starting at 300 °C) is attributed to the elimination of sulfonic acid groups, which is mostly accompanied by evolution of SO_2 as reported by Gupta and Scherer,[33] and Hietala *et al.*[34] The weight loss starting at 550 °C is due to the degradation of the PTFE matrix, which takes place in the presence of other fragments of the membrane components. It can be observed that there is a difficulty in discriminating between the temperatures at which elimination of sulfonic acid groups and decomposition of polystyrene grafts take place. Instead, the thermogram shows a continuous weight loss in the 300–530 °C range. Such behaviour is similar to that of styrene grafted and sulfonated FEP[33] and PFA[35] membranes. It may be suggested that sulfonation of polystyrene grafts makes the membrane more susceptible to thermal degradation than non-sulfonated films. However, from thermogram C, it can be concluded that the membranes are thermally stable up to about 300 °C under the present experimental conditions. It can be noted that a residue of 25 % of the original weight of the sulfonated membrane remained after a complete TGA run, in contrast to the original and grafted PTFE films. This indicates that the presence of sulfonic acid groups in the membrane affects the stability of the PTFE matrix and increases its tendency to form ash.

A comprehensive investigation on the thermal stability of PTFE-*graft*-PSSA has been reported elsewhere.[37] Measuring the thermal stability of Nafion 117 membrane under the same heat treatment conditions showed that under nitrogen it exhibits a one-step degradation pattern and remains thermally stable up to around 300 °C.

A summary of the properties of PTFE-*graft*-PSSA membranes compared to similar radiation grafted membranes based on other fluorinated films and commercial Nafion 117 membrane is given in Table 1. Compared to Nafion 117 and other radiation grafted membranes, PTFE-*graft*-PSSA membranes
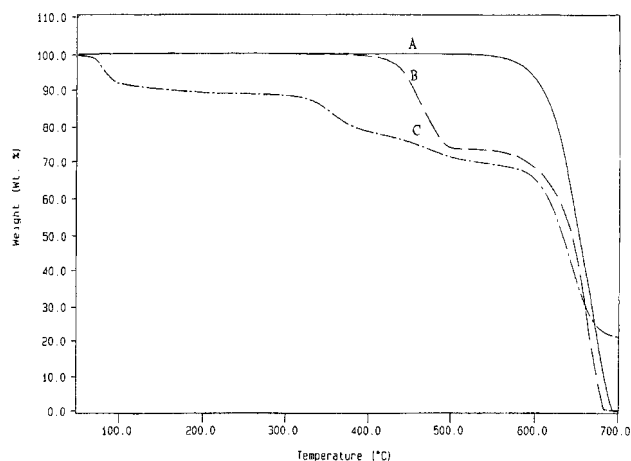

Figure 7. TGA thermograms of: (A) original PTFE film; (B) 36% grafted PTFE film, and (C) 36% grafted PTFE-*graft*-PSSA membrane.

Table 1. Summary of the properties of PTFE-*graft*-PSSA membranes compared to similar radiation grafted membranes based on other fluorinated films and commercial Nafion 117 membrane

Membrane type	Ref	Degree of grafting (%)	Water uptake (wt%)	Ion exchange capacity (meq g^{-1})	Proton conductivity ($\Omega^{-1}cm^{-1}$)× 10^{-2}	Thickness (μm)	Equivalent weight (geq^{-1})	Thermal stability[a] (°C)
PTFE-*graft*-PSSA	This work	18	21	1.23	1.2	120	813	300
PTFE-*graft*-PSSA	This work	24	24	1.90	2.3	130	526	300
PTFE-*graft*-PSSA	This work	36	26	2.20	2.9	140	454	300
FEP-*graft*-PSSA	9	19	68	1.39	Higher than Nafion 117	78	718	300
PVDF-*graft*-PSSA	11	23	52	–	2.5	120	–	200
PFA-*graft*-PSSA	17	16	27	1.70	3.3	160	606	300
Nafion 117	This work	–	39	0.91	5.3	180	1110	300

[a] Measured under nitrogen atmosphere.

show lower water uptake, which may be an advantage because it reduces the dimensional changes in the membrane during drying and swelling. Moreover, the proton conductivity, despite being lower than other membranes, is of the order of magnitude required for SPE fuel cell application ($10^{-2}\Omega^{-1}cm^{-1}$). Furthermore, they have reasonable thickness, ion exchange capacity, and thermal stability as high as 300 °C. Therefore, it can be concluded that the PTFE-*graft*-PSSA membranes prepared in this study have an acceptable combination of physical and chemical properties for SPE fuel cell application. However, these properties alone do not guarantee good fuel cell performance. Determination of other properties such as chemical stability, graft distribution and gas permeation rates is very important to obtain a better insight into the membrane quality, and the final judgement on this membranes will eventually depend upon long-term tests of SPE fuel cells.

Surface investigation of the membranes was carried out to obtain information on the structural properties of their surface. Such information is of special interest because it can be utilized to estimate the stability of PTFE-*graft*-PSSA membranes upon assembly with electrodes in fuel cells. Surface analysis of original PTFE and grafted PTFE films was reported in the first part of this study.[23] Figure 8 shows narrow scan and curve fitting of the C1s line of the spectrum of the 36 % PTFE-*graft*-PSSA membrane. The surface of the membrane was found to be dominated by the C1s peak at 285.9 eV (FWHM 1.4 eV), which belongs to the hydrocarbon component introduced by grafting of styrene. This was accompanied by a very small peak at 293.2 eV (FWHM 1.3 eV) representing the fluorinated domain in the membrane matrix. The separation of the two peaks by 7.3 eV is in complete agreement with the difference in binding energy between CH_2 of polyethylene and CF_2 of polytetrafluoroethylene as reported by Scherer *et al.*[38] Deconvolution of the spectrum results in five peaks at 292.1, 287.5, 286.5, 285.2 and 284.5 eV (corrected), which were assigned to CF_2, C—S, C—CF, —C— and C—, respectively. The emergence of the peak at 287.5 eV is due to the attachment of the sulfonic acid groups to the benzene ring of polystyrene, which led to further decrease in the

F/C ratio from 0.26 in the grafted PTFE film to 0.066. The difficulty in the determination of —C— and C— of aliphatic (—CH_2—CH=) and aromatic —(C_6H_4) groups in the polystyrene incorporated in the grafted film is due to the minor chemical shift differences in these carbon atoms. The main conclusion that can be drawn from these results and those on the original and grafted films is that the PTFE film surface undergoes structural changes in terms of chemical composition as a result of styrene grafting and its subsequent sulfonation. Moreover, the membrane surface seems to be dominated by the pure hydrocarbon fraction, ie sulfonated polystyrene grafts. This feature is expected to has a serious effect on the membrane stability and performance during the fuel cell operation.

ESCA spectra of both membrane surfaces were found to be identical. Therefore, it can be concluded that PTFE-*graft*-PSSA membranes produced by radiation grafting in this study have a symmetrical structure. More details on the surface properties of membranes having various degrees of grafting can be found elsewhere.[35]

Unlike PTFE-*graft*-PSSA membrane, Nafion 117 membrane was found to have only one C1s peak at 290.5 eV (FWHM 1.7 eV) related to its fluorinated structure. Deconvolution of the peak showed three
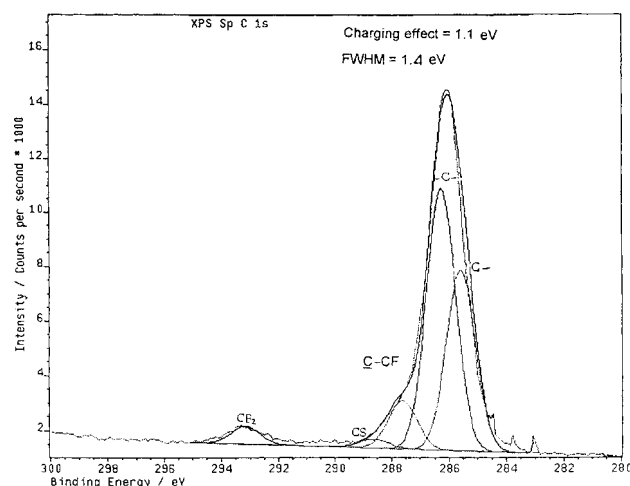

Figure 8. Narrow scan and curve fitting of C1s spectrum of 36 % grafted PTFE-*graft*-PSSA membrane.

main components at 289.4, 290.2 and 292.0 eV (corrected), which can be assigned to CF, CF_2 and CF_3, respectively.

ACKNOWLEDGEMENTS

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