

Cation Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene onto PFA Copolymer Films. II. Characterization of Sulfonated Graft Copolymer Membranes

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ABSTRACT: PFA-g-polystyrene sulfonic acid membranes were prepared by simultaneous radiation-induced graft copolymerization of styrene onto poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) film followed by sulfonation. The membrane physico-chemical properties such as swelling behavior, ion exchange capacity, hydration number, and ionic conductivity were studied as a function of the degree of grafting. Thermal as well as chemical stability of the membranes was also investigated. The membrane properties were found to be mainly dependent upon the degree of grafting. The water uptake, ion exchange capacity, hydration number, and ionic conductivity of the membranes were increased, whereas the chemical stability decreased as the degree of grafting increased. The membranes showed reasonable physico-chemical properties compared to Nafion 117 membranes. However, their chemical stability has to be further improved to make them acceptable for practical use in electrochemical applications.
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Key words: cation exchange membrane; radiation-induced graft copolymerization; PFA; styrene; properties

INTRODUCTION

Cation exchange membranes have been proposed for the use as a solid polymer electrolyte in various electrochemical applications, including chlor-alkali industry, water electrolysis, and fuel cells.^{1–3} Among various electrochemical cells, proton exchange membrane (PEM) fuel cells have received increasing attention due to their high efficiency, which stimulated their development for various applications.^{4,5} Currently, the standard commercial

material for such application is Nafion (duPont de Nemours) membranes. This is due to their excellent chemical stability and high conductivity as well as low resistivity.^{6,7} However, the high price of Nafion (approximately U\$1,000/m²) and similar perfluorinated materials such as Dow developmental membranes (Dow Chemicals Co.) and Aciplex (Asahi Chemical Industry Co. Ltd) has limited their use in large-scale applications.^{8,9} This situation has stimulated research to find more economical ways to produce other good membranes. Several new fluorinated and nonfluorinated membranes have been recently developed at experimental as well as commercial scales using various conventional polymerization methods, and have demonstrated good performances in fuel cells.^{10–16}

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In development of new membranes, radiation-induced graft copolymerization offers an attractive method for the preparation of cation exchange membranes, particularly in terms of cost and membrane shaping.^{17,18} This method utilizes a base polymer already having the physical shape of a membrane. Many studies have reported the development of various types of cation exchange membranes by radiation grafting of styrene onto PTFE,^{19–21} FEP,^{22–25} PVDF,^{26,27} and ETFE²⁸ using both simultaneous and preirradiation techniques. Similar radiation grafted and crosslinked membranes are commercially available, and have exhibited a stability up to 1000 h in polymer electrolyte fuel cells.^{29,30}

Poly(tetrafluoroethylene-*co*-perfluorovinyl ether), PFA, is one of the common fluorinated polymers that has high thermal, mechanical, and chemical stability. However, PFA films have not yet been reported to have been used as polymer matrices for the preparation of cation exchange membranes bearing strong chemical functionality such as sulfonic acid by radiation-induced graft copolymerization. One can expect PFA-based membranes to show a combination of high conductivity and good chemical stability. Therefore, it was the intention of the authors to study the development of cation exchange membranes by radiation-induced graft copolymerization of styrene onto PFA films and subsequent sulfonation.

Previously, we reported the radiation-induced graft copolymerization of styrene onto PFA films by a simultaneous technique to produce graft copolymers having the ability to host strong chemical functionality such as sulfonic acid groups.³¹ The effect of grafting conditions on the degree of grafting was investigated, and the mechanical properties as well as the structural changes that take place in the graft copolymers were evaluated.

In the present study we report the functionalization of PFA-*g*-polystyrene films by a sulfonation process to introduce sulfonic acid groups to the grafted polystyrene side chains. The physicochemical properties of the PFA-*g*-polystyrene sulfonic acid membranes such as water uptake, ion exchange capacity, hydration number, and ionic conductivity were investigated in correlation with the degree of grafting. Moreover, the thermal as well as chemical stability of the membranes was also evaluated. Comparison of the measured membrane properties with those of Nafion 117 membranes was also reported.

EXPERIMENTAL

Graft Copolymerization

PFA-*g*-polystyrene films were prepared by radiation-induced graft copolymerization of styrene (Fluka 85960, >99%, used without further purification) onto PFA film (Porghof, USA), having a thickness of 120 μm using a simultaneous irradiation technique.³¹ A glass ampoule containing PFA film of known weight and size immersed in styrene (20–50 vol %) diluted with dichloromethane (J.T. Baker, A.S.C reagent) was irradiated using γ -rays from a ⁶⁰Co source to a total dose of 20 kGy at a dose rate of 0.37 G/s under nitrogen atmosphere. The grafted film (PFA-*g*-polystyrene) was washed with methyl benzene and soaked therein over night to remove the residual styrene and its homopolymer occluded in the film and subsequently dried in the vacuum oven at 60°C overnight. The degree of grafting was gravimetrically estimated as the percentage of weight increase of PFA film after grafting reaction as follows:

$$\text{Degree of Grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where, W_g and W_0 are the weights of grafted and original films, respectively.

Sulfonation

The grafted films were sulfonated using a mixture of chlorosulfonic acid/tetrachloroethane. Initially, the grafted films were washed with dichloromethane and soaked therein for 30 min. The grafted films were then removed and dried in a vacuum oven for 1 h. The dried films were placed in a glass reactor, which was then filled with the sulfonation mixture that was composed of 30 parts chlorosulfonic acid (Fluka, purum) in 70 parts of 1,1,2,2-tetrachloroethane (Fluka, purum) (v/v). The reactor temperature was maintained at 90°C using an oil bath, and the reaction was allowed to continue for 4 h. After completion of the reaction, the sulfonated membranes were removed from the reactor, washed several times with 1,1,2,2-tetrachloroethane and dichloromethane to remove the excess of chlorosulfonic acid, and then dried in vacuum oven at 60°C overnight. The sulfonated membranes were treated with 0.5 M KOH solution for 2 days at room temperature. The membranes were finally regenerated into acid

form by boiling with 1 *M* HCl for 4 h. The samples were then washed free of excess HCl with deionized water (E-pure, 18 *M* cm) several times and kept therein.

Ion Exchange Capacity

Ion exchange capacity (IEC) of the membranes was determined by acid-base titration. The membrane samples (2×2 cm²) in acid form were immersed into 50 mL of 0.5 *M* KCl solution overnight at room temperature, with frequent stirring. The protons (H⁺) released in the solution were titrated with standardized 0.05 *M* KOH solution by automatic titrator (Metrohm, Switzerland) until pH 7 was reached. Membrane samples were regenerated into acid form again by boiling with 3.5 *M* HCl for 3 h, and were dried in vacuum oven (1 Torr, 80°C, 24 h). The samples were kept dry under an evacuated desiccator having fresh silica gel for 30 min and the weight of the dry membranes was determined. From the volume of KOH solution consumed in titration, IEC of the dry membrane per unit mass (meq/g) and per unit volume (meq/cm³) were calculated by taking the volume changes during swelling into account, whereas the degree of sulfonation was calculated by taking the total number of grafted styrene molecules in the PFA film obtained from the degree of grafting into account.²⁴

Swelling Behavior

Swelling measurements of the membranes were carried out using initialized and vacuum-dried (1 Torr, 80°C, 24 h) samples. The samples were immersed in deionized water and boiled under reflux for 4 h to achieve swelling equilibrium. The samples were removed, the excess of water adhering to the surface was quickly blotted by absorbent paper, and then weighed. The membrane water uptake was calculated as per the following equation:

$$\text{Water uptake (wt \%)} = \frac{W_w - W_d}{W_d} \times 100$$

where, W_w and W_d are the weights of wet and dry membranes, respectively. The weight of the dry samples was determined as mentioned in the previous section.

Ionic Conductivity

Ionic conductivity of the membranes, in acid form, was measured at room temperature by AC imped-

ance spectroscopy. Measurements were carried out using frequency response analyzer (Solartron, 1250) in combination with electrochemical interface (EG & G Princeton Applied Research) at 0.01–100 kHz frequency range. The swollen samples of circular shape were clamped between two blocked stainless steel electrodes having disc ends of 20-mm diameter and located in a specially designed conductivity cell made of Teflon. Fresh electrodes were used for each experiment to maintain electrode sensitivity, which might be affected by the presence of highly corrosive sulfonic acid groups in the wet membrane samples. The resistance was obtained from the intercept of the impedance curve with real axis at high frequency end. The resistance values were corrected by deduction of the resistance of conductivity cell without samples. The ionic conductivity (σ) was calculated according to the following equation:

$$\sigma = (1/R)(L/A)\Omega^{-1} \text{ cm}^{-1}$$

where L is the thickness of the membrane sample (cm), A or (πr^2) is the sample surface area (cm²) and R is the resistance (Ω).

Thermal Stability

Determination of thermal stability of the membranes was carried by thermogravimetric analysis (TGA). Membrane samples were dried under vacuum at 50°C for 24 h and were stored in a dessicator prior to TGA runs. TGA runs were carried out using Perkin-Elmer TGA-7, in a temperature range of 50–700°C, under nitrogen atmosphere, and with a constant heating rate of 20°C/min. in all the experiments. Original and grafted films were included as references.

Chemical Stability

Chemical stability test was performed on initialized and vacuum dried (1 Torr, 80°C, 24 h) membrane samples having known weights and various degrees of grafting. The test was carried out by immersing the samples in 3% H₂O₂ (diluted from 30% H₂O₂, J.T. Baker, CMOS electronic grade) solution containing 4 ppm ferrous ions obtained from FeSO₄ · 7H₂O (BDH, “AnalaR”) for 5 h at different temperatures ranging from 40 to 70°C under reflux. After each test, the samples were dried in vacuum oven (1 Torr, 80°C, 24 h), then weighed, and the weight loss of the dry membrane was subsequently calculated.

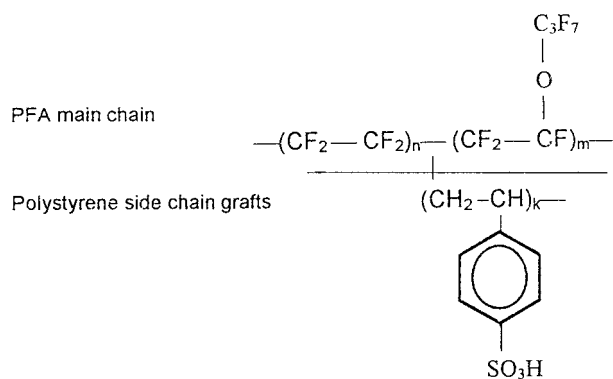


Figure 1 An idealized structure of PFA-g-polystyrene sulfonic acid membrane; (a) PFA main chain, (b) sulfonated polystyrene side chain.

Commercial Nafion 117 (Du Pont) membranes were used as a reference material. They were converted to proton form by boiling in HNO_3 (33%) for 2 h and then washed free of acid with deionized boiling water several times.

RESULTS AND DISCUSSION

The idealized molecular structure of PFA-g-polystyrene sulfonic acid membranes is given in Figure 1. The degree of sulfonation of the membranes vs. the degree of grafting is shown in Table I. It can be clearly seen that all membranes have a degree of sulfonation close to 100%, i.e., the ratio of sulfonic acid groups to polystyrene content is ~ 1 . Therefore, all the membrane properties investigated in this work are related only to the degree of grafting.

Ion Exchange Capacity

Figure 2 shows the relationship between ion exchange capacity (IEC) of PFA-g-polystyrene sulfonic acid membranes and the degree of grafting. It can be observed that IEC depends strongly on the degree of grafting. As the degree of grafting increases, the IEC of the membranes per unit mass (meq/g) as well as per unit volume (meq/

cm^3) increases. This behavior can be reasonably attributed to the increase in the number of sulfonic acid groups incorporated in the membrane with the increase in the degree of grafting. Because IEC is well known to control the membrane properties to a large extent, its variation via controlling the degree of grafting in the present grafting system provides a real opportunity to obtain cation exchange membranes having desirable properties. The IEC for the dry Nafion 117 membranes is found to be 0.9 meq/g as well as 1.9 meq/ cm^3 .

Swelling Behavior

The variation of the membrane water uptake with the degree of grafting of the membranes is shown in Figure 3. The water uptake in terms of weight is found to increase steeply and linearly with the increase in the degree of grafting. This is owing to the increase in the hydrophilicity of the membranes that resulted from the incorporation of more sulfonic acid groups with the increase of the degree of grafting. The increase in the content of sulfonated polystyrene side-chain grafts leads to a decrease in fluorinated domain (PFA) in the membranes, and as a result, the hydrophobicity of the membrane decreases. The water uptake by weight of Nafion 117 membranes under the same conditions is 39%.

The relationship between the hydration number and the degree of grafting is shown Figure 4. The increase in the degree of grafting causes an increase in the hydration number ($\text{H}_2\text{O}/\text{SO}_3\text{H}$). The hydration number increases from 4 to 16 as the degree of grafting increases from 6.3 to 48.7%. It can be concluded that the hydration number of PFA-g-polystyrene sulfonic acid membranes is strongly dependent upon the degree of grafting and the ability of the membrane to retain water increases with the increase in the degree of grafting. This effect can also be ascribed to two main factors: the increase in the hydrophilicity due to the incorporation of more ionic sites, and the decrease in the hydrophobicity of the membrane with the increase in the degree of grafting. The

Table I Degree of Sulfonation and Equivalent Weights of PFA-g-polystyrene Sulfonic Acid Membranes with Various Degrees of Grafting

Degree of grafting (wt %)	6.3	16.4	26.0	38.0	48.7
Degree of sulfonation (mol %)	100	96	95	93	92

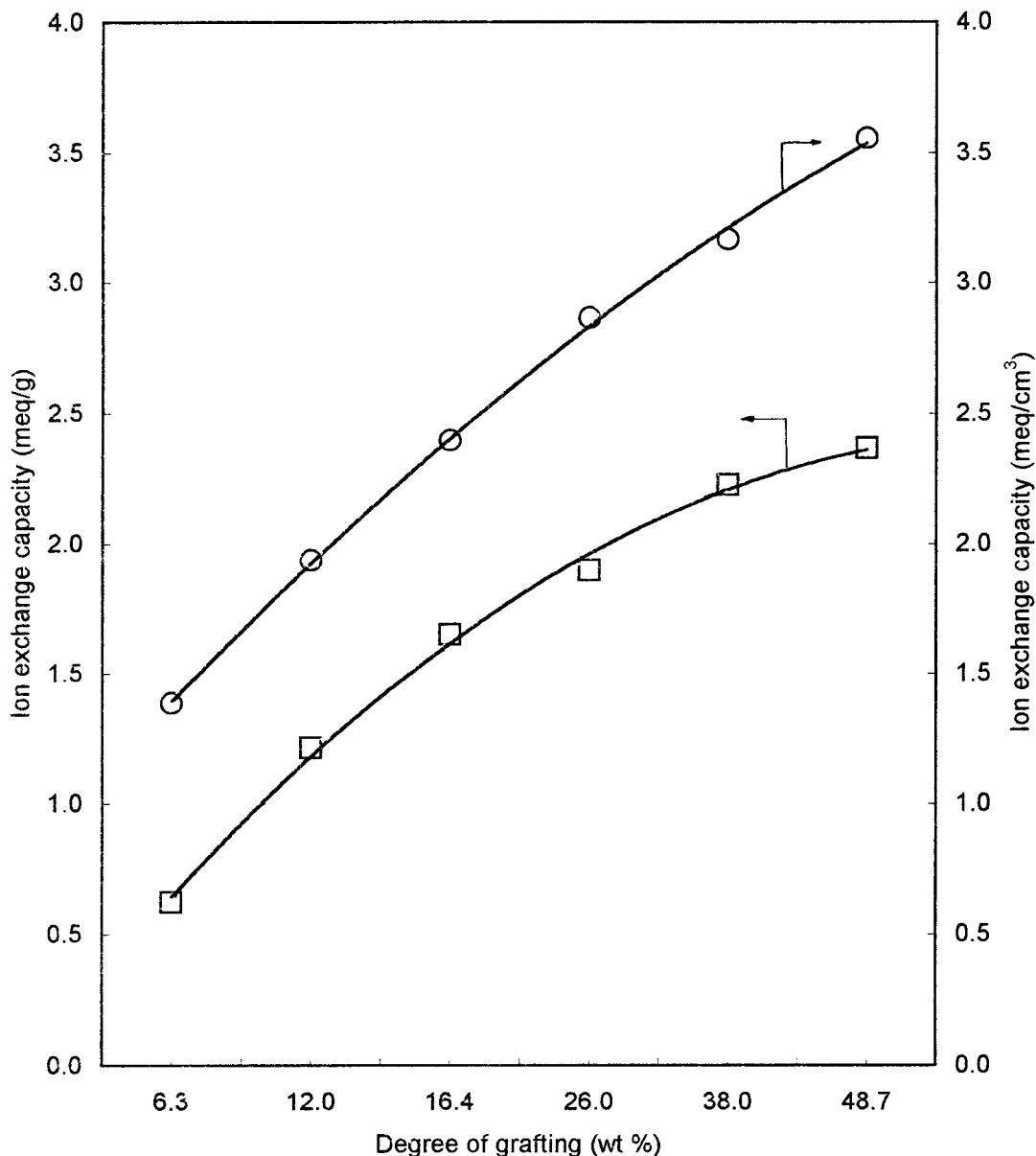


Figure 2 The relationship between ion the exchange capacity of PFA-g-polystyrene sulfonic acid membranes and the degree of grafting.

hydration number of Nafion 117 membranes under the same conditions is found to be 23.

Ionic Conductivity

Figure 5 shows the relationship between proton conductivity and the degree of grafting of the membranes at room temperature. The results show that the proton conductivity increases as the degree of grafting increases. This is due to the increase in the amount of sulfonic acid groups followed by the increase in the water uptake and

hydration number. These results are evident from the variation of proton conductivity of membranes having various degrees of grafting (6.3–48.7%) with ion exchange capacity and hydration number presented in Table II. The initial conductivity shows a sharp increase, and at a certain degree of grafting it tends to level off. This can be explained by taking the distribution of sulfonated polystyrene grafts in the membrane into consideration. It was reported that the grafting of styrene onto PFA film starts at the surface of the film and continues to the middle by progressive diffusion of

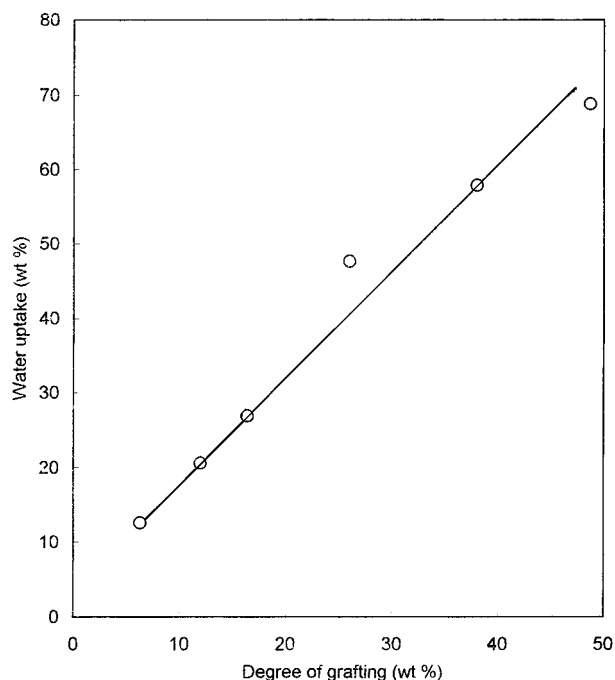


Figure 3 Variation of the membrane water uptake with the degree of grafting of the membranes.

the monomer through the grafted layers.³¹ Therefore, at low degrees of grafting the grafting is located near to the surface of the film, while its

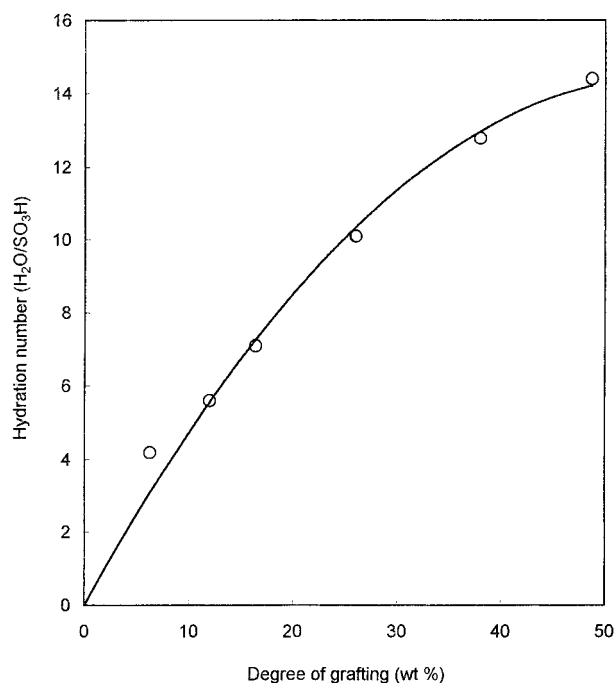


Figure 4 The relationship between the hydration number ($\text{H}_2\text{O}/\text{SO}_3\text{H}$) and the degree of grafting of the membranes.

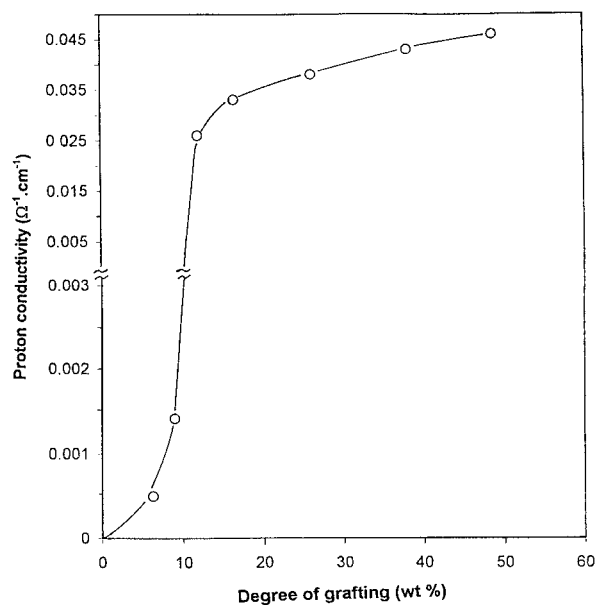


Figure 5 The relationship between the proton conductivity and the degree of grafting of membranes at room temperature.

middle remains ungrafted and subsequently exerts simultaneous higher local resistance and low ionic conductivity. As the grafted layers move internally and reach the middle of the film beyond 12%, the local resistance vanished and, consequently, the ionic conductivity increased. Further increase in the degree of grafting does not bring considerable changes to the proton conductivity due to the achievement of homogenous distribution of sulfonated polystyrene grafts in the membrane.

A summary of the physico-chemical properties of PFA-g-polystyrene sulfonic acid membranes compared to those of Nafion 117 membranes is shown in Table III. As can be seen, the four PFA-g-polystyrene sulfonic acid membranes prepared in this work show a good combination of high ion exchange capacity (1.2–2.3 meq/g and 1.9–3.2 meq/cm³), acceptable water uptake (21–58 wt %), low equivalent weight (826–450 g/eq⁻¹), and ionic conductivity in the order of magnitude of $10^{-2}\Omega^{-1}\text{cm}^{-1}$. These results suggest that PFA-g-polystyrene sulfonic acid membranes prepared in this study have acceptable electrochemical capabilities to be used as cation exchange membranes.

Thermal Stability

Thermal stability measurements of radiation-grafted PFA-g-polystyrene sulfonic acid mem-

Table II Variation of Ionic Conductivity of PFA-*g*-polystyrene Sulfonic Acid Membranes with the Ion Exchange Capacity and Hydration Number

Degree of Grafting (wt %)	Hydration Number (H ₂ O/SO ₃ H)	IEC (meq/g)	Proton Conductivity (Ω ⁻¹ cm ⁻¹) × 10 ⁻²
6.3	4.2	0.625	0.05
12.0	7.1	1.210	2.60
16.4	10.1	1.650	3.30
26.0	12.8	1.895	3.80
38.0	14.4	2.224	4.30
48.7	15.5	2.347	4.60

branes is carried out by thermal gravimetric analysis (TGA) in a temperature range of 50–700°C under nitrogen atmosphere. The samples tested include original, grafted, and sulfonated films to investigate the effect of the two-step preparation method, i.e., radiation grafting of styrene onto a PFA film and subsequent sulfonation on the stability of membranes. Figure 6 shows TGA thermograms of original PFA and PFA-*g*-polystyrene films as well as PFA-*g*-polystyrene sulfonic acid membranes. Both the grafted film and the sulfonated membrane have 38% degrees of grafting. As can be seen from thermogram “A,” the original PFA film undergoes one-step degradation where it sustains temperature up to 530°C. Grafting of styrene onto PFA film results in PFA-*g*-polystyrene film having a two-step degradation pattern under the heat treatment. According to thermogram “B,” the incorporated polystyrene grafts and the PFA matrix undergo two distinct degradation temperature starting at 420 and 530°C, respectively. It is found that the incorporation of polystyrene grafts in the PFA film does not bring any changes to the inherent decomposition temperature of the PFA matrix. These results suggest that polystyrene grafts are incompatible with PFA matrix and form phase-separated microdomains in the grafted PFA film. Similar observations were reported by Gupta et al.³² and Hietala et al.³³ upon studying the thermal decomposition of styrene-grafted FEP and styrene-grafted polyvinylidene fluoride (PVDF) films, respectively.

The sulfonation of the grafted films introduces a three-step degradation pattern as depicted from the three decomposition regions shown in thermogram “C.” The weight loss, starting at a temperature below 100°C and continues to 200°C, is due to the removal of water bound to the hydrophilic sulfonic acid groups present in the membrane during the initial heating. The remaining of some

water up to temperatures higher than 100°C is due to the strong hydrogen bonding between some water molecules and sulfonic acid groups. Similar behavior was reported for FEP-*g*-polystyrene sulfonic acid,³² PVDF-*g*-polystyrene sulfonic acid,³³ and commercial membranes such as Nafion 117 membranes.³⁴

The initial and massive degradation of the sulfonated membrane starts at 320°C, where the sulfonic acid groups degradation begins. The final degradation pattern at 530°C is due the decomposition of PFA matrix. It can be observed that the degradation region represented by the continuous weight loss in the range of 320–520°C does not show clear discrimination between desulfonation and decomposition of polystyrene grafts. These observations suggest that the sulfonation of polystyrene grafted PFA films makes the membrane more susceptible to thermal decomposition than only grafted ones. However, a residue of 20% or more of the mass of the sulfonated membrane is found to remain at the end of thermogram, indicating that the membrane does not undergo complete decomposition, unlike the original and the grafted films. Such observation indicates that the presence of sulfonic acid groups enhances the stability of the PFA matrix by stimulating the tendency of ash formation. This is probably due to depolymerization of the PFA matrix and volatilization of the polystyrene grafts in the presence of SO₂ and other components originated from sulfonic acid groups as proposed by Gupta et al.³⁵ and Hietala et al.³³ for FEP and PVDF-grafted polystyrene sulfonic acid membranes. Based on the aforementioned results, it may be stated that the membranes are thermally stable up to ~320°C under the present experimental conditions. Details of the thermal stability investigations and thermal degradation behavior of PFA-

Table III Physico-chemical Properties of PFA-g-polystyrene Sulfonic Acid Membranes Compared to Those of Nafion 117

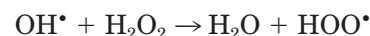
Membrane Type	Degree of Grafting (wt %)	Water Uptake (wt %)	Hydration No. (H ₂ O/SO ₃ H)	IEC (meq/g)	IEC (meq/cm ³)	Ionic Conductivity (Ω ⁻¹ cm ⁻¹) × 10 ⁻²	Equivalent Weight (g eq ⁻¹)	Thickness (μm)
PFA-g-PSSA ^a	12.0	21	7	1.2	1.9	2.6	826	150
PFA-g-PSSA ^a	16.4	27	10	1.7	2.4	3.3	606	160
PFA-g-PSSA ^a	26.0	48	13	1.9	2.9	3.8	527	165
PFA-g-PSSA ^a	38.0	58	15	2.2	3.2	4.3	450	170
Nafion 117 (Du Pont)	—	39	19	0.9	1.8	7.6	1115	180

^a PSSA = Polystyrene sulfonic acid.

g-polystyrene sulfonic acid membranes were discussed elsewhere.³⁶

Chemical Stability

Chemical stability tests were carried out in ferrous ion catalyzed H₂O₂ solution to investigate the chemical resistance of the membranes in vigorous conditions most likely to be encountered in electrochemical applications such as PEM fuel cells. During the operation of these cells, some O₂ diffuse across the membrane from the cathode to the anode, and recombine with H₂ leading to the formation of H₂O₂. The presence of Pt at electrode interface catalyzes H₂O₂ to hydroperoxy radicals (HOO•), which attacks the membrane and causes its decomposition.^{37,38} To simulate a similar situation, ferrous ion-catalyzed H₂O₂ solution was proposed by Hodgdon.³⁷ The presence of the ferrous ions in the H₂O₂ solution leads to the formation of (HOO•) according to the following reactions:³⁹



Membrane samples having various degrees of grafting (6.3–38%) were immersed in 3% H₂O₂ solution in the presence of 4 ppm Fe⁺⁺ at a temperature ranging from 40–70°C for 5 h. The weight loss of the dry membrane is used as an indicator for the oxidative degradation. Figure 7 shows the variation of the weight loss (%) of the dry membranes with the degree of grafting at various temperatures ranging from 40–70°C. It can be seen that all the membranes record no loss in the weight, and remain stable at a temperature of 40°C. However, as the temperature rises to 50°C and above, all membranes start to suffer oxidative degradation, and the recorded weight loss is found to increase with the increase in the degree of grafting. Moreover, the weight loss is also found to increase as the temperature of ferrous ion catalyzed H₂O₂ solution increases (up to 70°C). These results indicate that degradation of the membrane is not only dependent on the degree of grafting of the membrane, but also on the temperature of ferrous ion-catalyzed H₂O₂.

The stability exerted by the membranes at a temperature of 40°C is attributed to the effect of the presence of a degradation-resistant fluorinated domain (PFA) that adheres them to a high

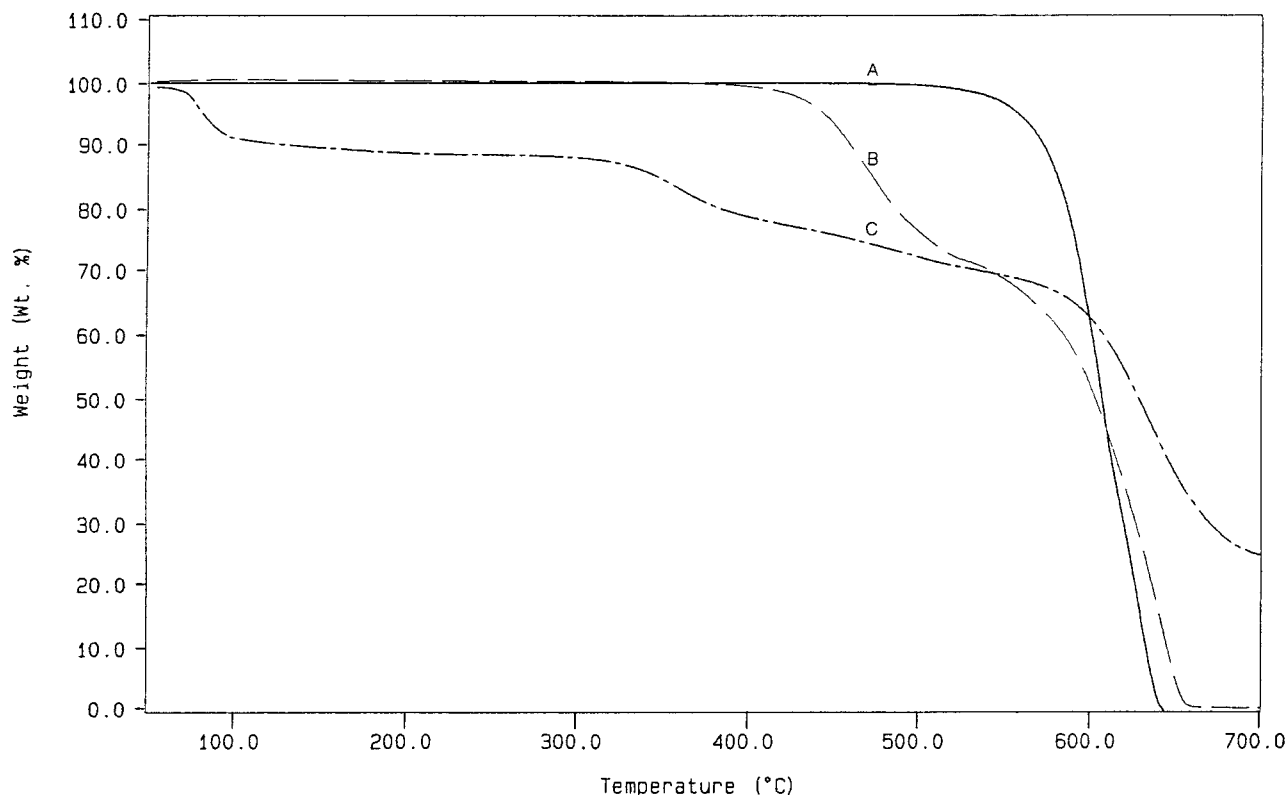


Figure 6 TGA thermograms of (A) original PFA film, (B) 38% polystyrene-grafted PFA film, and (C) 38% polystyrene-grafted and sulfonated PFA membranes.

chemical resistance towards oxidative degradation. The increase in the degradation effect with the increase in the temperature is most probably due to generation of more oxidative radicals in the ferrous ion-catalyzed H_2O_2 solution. These radicals most probably attack the tertiary hydrogen at the α -carbon of the sulfonated polystyrene side chains causing membrane degradation.^{37,40} On the other hand, the increase in the degradation with the increase in the degree of grafting at constant temperature is attributed to the increase in the oxidizing agent uptake with the increase in the content of grafted and sulfonated hydrocarbon polystyrene. However, at a temperature of 70°C , all the membranes showed substantial degradation where the weight loss was found to be higher than the degree of grafting. Such results indicate that not only the grafted polystyrene and sulfonic acid groups were degraded, but also the PFA matrix. The reasons behind such behavior and the mechanism of degradation need to be explored by postmortam analysis in future studies.

The weight loss of grafted membrane having a 12% degree of grafting and IEC of 1.2 meq/g at 70°C is found to be 15.2% of the dry weight,

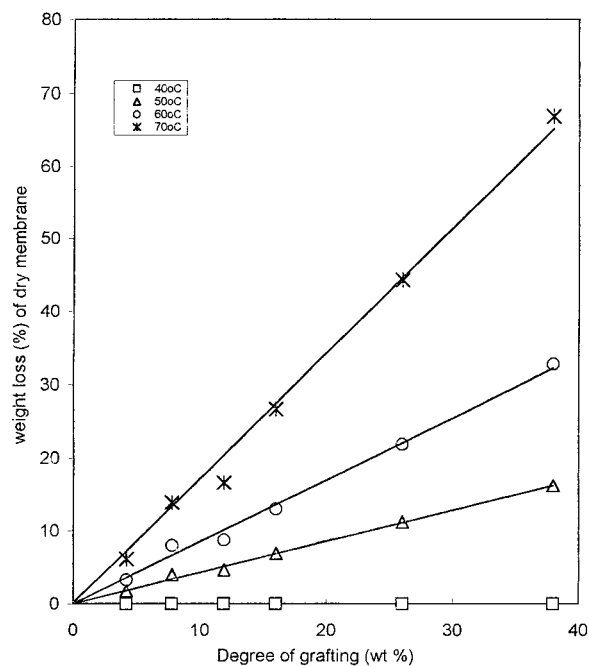


Figure 7 Variation of weight loss (%) of the dry membranes with the degree of grafting at temperatures ranging from 40 to 70°C .

whereas the weight loss of the Nafion 117 membrane (IEC of 0.9 meq/g) is less than 1%, which is much lower than that of radiation-grafted membrane prepared in this study under the same severe conditions. These results suggest that radiation-grafted membranes prepared in this work are liable to substantial degradation compared to Nafion 117 membranes. Therefore, further improvements in the chemical stability of grafted membranes are required to promote their use in the applications having a highly oxidative environment. One way to achieve this goal is to use styrene-substituted monomers such as α -methylstyrene⁴¹ and α,β,β -trifluorostyrene,⁴² and to incorporate a suitable crosslinking agent.³⁸

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