

RADIATION GRAFTED POLY(VINYLDENE FLUORIDE)-GRAFT-POLYSTYRENE SULFONIC ACID MEMBRANES FOR FUEL CELLS: STRUCTURE-PROPERTY RELATIONSHIPS

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Abstract Structure-property relationships for poly(vinylidene fluoride)-graft-polystyrene sulfonic acid (PVDF-g-PSSA) fuel cell membranes prepared by a single step method involving radiation-induced grafting of sodium styrene sulfonate (SSS) onto electron beam (EB) irradiated poly(vinylidene fluoride) (PVDF) films were established. The physico-chemical properties of the membranes such as ion exchange capacity, water swelling and proton conductivity were correlated with the degree of grafting (G , %) and the structural changes taking place in the membrane matrix during the preparation procedure. The variation in the crystallinity and the thermal stability of membranes was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The membranes were found to undergo substantial structural changes in forms of ionic sites increase, hydrophilicity enhancement, hydrophobicity reduction and crystallinity decrease with the variation in G (%) and the preparation method. The structural and thermal properties of the obtained membranes were also compared with their counterparts prepared by a conventional two-steps method *i.e.* radiation induced grafting of styrene onto EB irradiated PVDF films followed by sulfonation. The PVDF-g-PSSA membranes obtained by a single-step method were found to have superior properties compared to those obtained by the conventional two-steps method.

Keywords: PVDF films; Sodium styrene sulfonate; Radiation-induced grafting; Proton exchange membranes.

INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs) are receiving an increasing attention because of their high efficiency and power density, and potential application in automobiles as well as portable electrical devices^[1]. However, the cost of some key components including polymer electrolyte membrane has to be reduced to prompt commercialization^[2]. This situation has raised an ever-increasing demand to develop new alternative materials to substitute the inherently expensive commercial perfluorinated electrolyte membranes (Nafion, Aciplex and Dow) utilizing fluorine chemistry.

Radiation grafted membranes bearing sulfonic acid groups have been proposed as alternative cost effective proton conducting materials for PEMFC and subjected to intensive investigation for the past 2 decades. These membranes are conventionally prepared in two steps: radiation induced grafting of styrene or its substituents with or without crosslinking agents (*e.g.* divinyl benzene, triallyl cyanurate, *etc.*) onto fluorinated polymer films having high chemical, thermal and mechanical stability and subsequent sulfonation to introduce proton conducting sites to the grafted benzene rings. The latest developments in these membranes have been recently

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reviewed in few chapters and articles^[3–8].

Alternatively, radiation induced grafting of sodium styrene sulfonate (SSS), a vinyl monomer with sulfonate groups known for its poor kinetics arising from the incompatibility between highly ionized sulfonic acid groups with their hydration spheres and hydrophobic polymer backbone to be grafted, has been recently proposed for preparation of proton conducting membranes through using specific diluent systems to prompt grafting reaction with or without addition of acid solution^[9, 10]. The advantage of this single route method stems mainly from elimination of the hazardous sulfonation reaction, cost reduction and setting basis for membrane continuous large scale production. Grafting of SSS onto various polymer forms was also reported apparently for separation purposes by co-grafting acrylic acid prior- or with SSS^[11–18].

In a previous communication, we briefly reported the preparation of proton exchange membrane (PVDF-g-PSSA) by radiation induced grafting of SSS onto poly(vinylidene fluoride) PVDF films without adding acrylic acid monomer for the first time^[10]. The role of acid in accelerating the grafting reaction was also reported^[19]. The membrane physico-chemical properties such as ion exchange capacity (IEC), swelling behavior and ionic conductivity were found to be strongly dependant on the degree of grafting. However, variation of the degree of grafting induces changes in the structure of the membranes matrix, which is presumably responsible for the variation in the physico-chemical properties. Correlating such structural changes with the physico-chemical properties is very essential to understand the membrane transport mechanism and to elucidate the merits of PVDF-g-PSSA membranes obtained by the newly reported single-step method compared to similar membranes prepared by conventional radiation grafting method *i.e.* radiation grafting of styrene onto PVDF films followed by sulfonation. The objective of the present study is to establish the correlations between the properties of PVDF-g-PSSA membranes obtained by two different radiation grafting methods with the structural changes taking place during the preparation procedures.

EXPERIMENTAL

Materials

PVDF films with thickness of 50 μm and density of 1.76 g/cm^3 were obtained from commercial source. Sodium styrene sulfonate (SSS) was obtained from Aldrich. Styrene of purity $\geq 99\%$ (Fluka) was used without any further purification. Chlorosulfonic acid (purum) was purchased from Fluka. Solvents such as methanol, ethanol, toluene, chloromethane and dimethylformamide (DMF) were obtained from J.T. Bakers in research grade and used as received. Deionized water (E-pure, 18 $\text{M}\Omega$) was used to dilute sulfuric acid (98%, J.T. Bakers).

Irradiation of PVDF Films

PVDF films were washed with ethanol and vacuum dried. The films were irradiated by an electron beam (EB) accelerator (Curetron, EBC-200-AA2, Nisshin High Voltage Kabushiki Kaisha, Japan) operating at 300 kV to a total dose of 100 kGy at 10 kGy per pass under N_2 atmosphere. The irradiated PVDF films were quickly sealed in an evacuated thin polyethylene bag and kept in a low temperature freezer at -60°C for 1 day.

Preparation of Membranes Using Single-step Grafting Method

The preparation of the membrane in this method started by placing the irradiated PVDF film in a glass ampoule tightly sealed and evacuated to remove air. A nitrogen-bubbled monomer solution of SSS/DMF/ H_2SO_4 (aqueous) with specific concentrations and volumes was introduced to the film-containing ampoule through a special connection and the reaction was allowed for 24 h at a temperature of 60°C . More details on grafting apparatus and procedure can be found in a previous communication^[10]. The grafted film was removed and extracted in a hot water-containing vessel placed in an ultrasonic machine for several hours to remove the un-reacted monomer. The obtained membrane was dried under vacuum and the degree of grafting (G , %) was calculated as follows:

$$G(\%) = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

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

Preparation of Membranes Using Conventional Two-steps Grafting Method

The preparation of membranes with conventional method involved grafting of styrene and subsequent sulfonation. Grafting was carried out by diluting styrene with desired solvent to a prescribed concentration and placing it with EB irradiated PVDF film in a glass ampoule bubbled with nitrogen and tightly sealed. To obtain degrees of grafting similar to those resulted from a single-step method, two solvents (methanol and toluene) were used to dilute styrene with specific concentrations according to the data presented in Table 1. The selection of such particular styrene concentrations and solvent types was based on manipulation of various styrene/solvent combinations (data are not given here). The grafting reaction of styrene onto PVDF films was carried out on samples irradiated at a total dose of 100 kGy in a tightly sealed glass ampoule for a period of 4 h at a temperature of 60°C under N_2 atmosphere. The grafted film was removed and extracted in a warm toluene for several hours to remove the un-reacted monomer and homopolymer. The obtained membranes were dried under vacuum, and the degree of grafting (G , %) was calculated according to Eq. (1).

Table 1. Grafting conditions used to obtain specific degrees of grafting for styrene onto PVDF film

G (%)	Styrene conc. (vol%)	Solvent
5	41	Toluene
12	80	Toluene
29	25	Methanol
44	31	Methanol
53	35	Methanol

The grafted films were sulfonated using 0.5 mol/L chlorosulfonic acid in dichloromethane at room temperature for 16 h in a glass reactor under nitrogen atmosphere. After sulfonation, the samples were washed several times with dichloromethane to remove the excess of chlorosulfonic acid and then dried in vacuum oven overnight. The sulfonated membranes were then treated with aqueous KOH (0.5 mol/L) for 16 h at room temperature. The membranes were finally regenerated into acid form by boiling with aqueous HCl (1 mol/L) for 4 h and washed acid free with deionized water few times then dried in vacuum oven and kept over fresh silica gel in an evacuated dissicator. The degree of sulfonation was estimated by taking the ratio between experimental IEC and theoretical IEC into consideration.

Ion Exchange Capacity

Ion exchange capacity (IEC) was measured on membrane samples converted to H^+ -form by treating with 1 mol/L HCl solution. The membranes were removed and washed acid free with deionized water several times. The samples were subsequently immersed in a 0.1 mol/L NaCl aqueous solution at room temperature for 16 h under continuous stirring conditions. The H^+ released in the solution was titrated against a standardized 0.5 NaOH solution using an automatic titrator (Metrohom, Switzerland) until pH 7 was reached. IEC per unit mass of the dry membrane (mmol/g) was calculated by taking the concentration and the volume of NaOH solution consumed in titration into account.

Water Swelling

The water uptake of the membranes was determined by soaking the membrane samples in deionized water until a swelling equilibrium was achieved. Samples were removed and the excess water adhered to their surfaces was quickly blotted by tissue papers and then weighed. The water uptake was determined as the weight gain of the membrane in the wet state compared to the dry one. The hydration number ($n(H_2O)/SO_3H$) or the number of sorbed water molecules per sulfonic acid group was also calculated by dividing the obtained water uptake values onto water molecular weight and IEC.

Ionic Conductivity

The ionic conductivity of the membranes in H^+ form was measured by an *ac* impedance technique using a PGSTAT30 frequency response analyzer manufactured by Eco Chemie B.V. Impedance spectra were recorded

in a frequency range of 0.1 Hz–1 MHz. Samples were equilibrated in a deionized water for 24 h prior to test performance. A two-probe conductivity cell having two stainless steel electrodes with round-end discs of 2 cm diameter was used to host the samples. The resistance was taken at the high-frequency intercept of the electrode impedance semi-circle with the real axis. The conductivity was calculated from the resistance by taking the electrode area and membrane thickness into account.

Determination of Degree of Crystallinity in the Membranes

Differential scanning calorimetry (DSC) measurements were recorded on a Perkin Elmer Pyris-1 calorimeter under N_2 atmosphere. The temperature was varied in the range of 50–200°C at a heating rate of 20 K/min. The degree of crystallinity of the samples was obtained from the melting exotherms after correcting the recorded heat of melting by dividing over the weight fraction of PVDF in the investigated grafted films and sulfonated membranes as reported elsewhere^[20].

Sulfur Distribution across the Membranes

The sulfur distribution in transverse plane of the membranes was determined by a scanning transmission electron microscope (STEM, SEI Quanta 400 microanalyzer) coupled with an energy dispersive X-ray analyzer (EDX). To view the cross section of the membrane, the sample was sliced with a microtome, mounted on a sample holder by double sided tape and gold sputtered.

RESULTS AND DISCUSSION

PVDF-g-PSSA membranes with degrees of grafting in the range of 5%–65% were obtained by variation of SSS concentration in the range 0.2–1.0 mol/L in grafting solutions diluted with DMF/ H_2SO_4 ^[10]. Similar PVDF-g-PSSA membranes prepared by conventional two-steps grafting method with grafting parameters carefully chosen to adjust G in a range of 5%–65% according to the data present in Table 1. A schematic representation of the single-step preparation procedure compared to conventional two-step of PVDF-g-PSSA membranes is presented in Fig. 1.

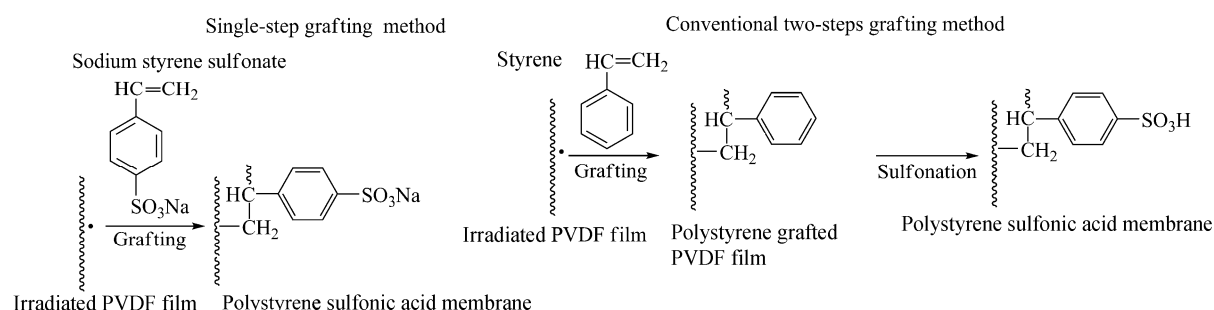


Fig. 1 A schematic representation of the single-step preparation procedure compared to the conventional two-step one of PVDF-g-PSSA membranes

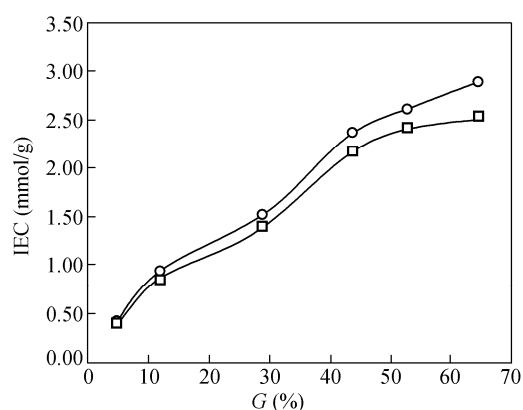
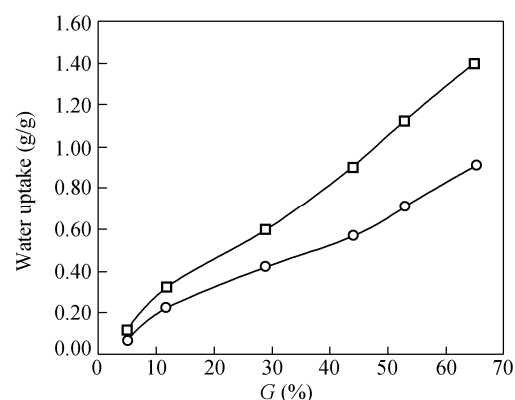
Figure 2 shows the variation of the ion exchange capacity (IEC) of both types of membranes versus the degree of grafting. The IEC was found to increase with the increase in G (%) in both membranes. This is due to the increase in the number of incorporated aromatic rings available for sulfonation in the membranes prepared by conventional method and the incorporation of more sulfonic acid groups originated from the grafted SSS in the membranes prepared by the single-step method. The difference in IEC between both membranes despite their similarity in G (%) *i.e.* polystyrene content is attributed to the deviation from achieving 100% sulfonation in conventionally-prepared membranes as depicted by data presented in Table 2. These results confirm that the composition of such membranes can be controlled by varying the degree of grafting *via* manipulation of the grafting parameters. Moreover, the single step method is advantageous in achieving degrees of sulfonation of 100% regardless of G (%).

Table 2. Degree of sulfonation and ion exchange capacity of PVDF-g-PSSA membranes obtained by conventional radiation grafting method and having various degrees of grafting

G (%)	Degree of sulfonation (%)	IEC (mmol/g)
5	90	0.39
12	92	0.86
29	91	1.38
44	92	2.17
53	92	2.40
65	90	2.52

Since, benzene rings introduced by grafting of pre-sulfonated monomer in the single-step method and post-sulfonation in conventional method are the host for sulfonic acid groups providing functionality in both membranes, the physico-chemical properties of the membranes are compared on the basis of the similarity in the degree of grafting.

Figure 3 shows the variation of the water uptake with the degree of grafting in the membranes prepared by the two different methods. As can be seen, the water uptake increases steeply with the increase in G (%) in both membranes with membranes obtained by conventional method showing considerably higher water uptake. The rising trend of water uptake in both membranes can be attributed to the increase in the hydrophilicity imparted by incorporation of more ionic moiety of PSSA in the membranes. However, the fairly higher water uptake in membranes obtained by conventional method compared to those prepared by the single-step method suggests a possible higher reduction in the degree of crystallinity and hydrophobicity in the former than the latter.

**Fig. 2** Variation of the ion exchange capacity (IEC) versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes**Fig. 3** Variation of the water uptake versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes

To elucidate the differences of swelling behavior in both membranes, the hydration number ($n(\text{H}_2\text{O})/\text{SO}_3\text{H}$) is correlated with the degree of grafting as shown in Fig. 4. It can be clearly seen that there is an increasing trend in the hydration number of both membranes with the increase in G (%) with an evidence of higher hydration number in membranes obtained by conventional method than the corresponding ones prepared by the single-step method. This trend is caused by the increase in the content of sulfonic acid groups and their associated water molecules forming ionic water clusters, which have larger size in membranes obtained by conventional method than the corresponding ones prepared by the single-step method. The hydration number of membranes prepared by conventional method ($n(\text{H}_2\text{O})/\text{SO}_3\text{H} = 14\text{--}33$ for $G = 5\%\text{--}65\%$) appears to have close values with that of similar membranes reported in literature^[20–22] while that of membranes prepared by a single-step method ($n(\text{H}_2\text{O})/\text{SO}_3\text{H} = 9\text{--}18$ for $G = 5\%\text{--}65\%$) is comparable with that of Nafion 112 and 117 commercial membranes^[23]. Since water uptake is not only depending on availability of sulfonic acid groups imparted by

ionic moiety but also on structural changes taking place in the membranes during preparation procedure^[24, 25], it can be suggested that structural changes in the membranes during grafting and sulfonation in conventional method are mostly in form of reduction in the inherent crystallinity of PVDF film and the accompanied diminishing of hydrophobicity which are the main causes behind the considerable increase in water absorption of both membranes with the increase in G (%). However, such changes are profound in case of the membranes prepared by conventional method indicating more drastic structural changes than in membranes prepared by the single-step method.

Figure 5 shows lg-lg plot of the variation of the ionic conductivity with the degree of grafting in the membranes prepared by two different methods. In both membranes, the ionic conductivity showed an initial small increase followed by percolation threshold up to 44% beyond which the conductivity in both membranes tend to level off. Generally, the increase in conductivity can be substantially attributed to the increase in IEC, water uptake and hydration number accompanying the increase in G (%). The early slow increase is caused by proton transfer limitation caused by internal resistance of the un-grafted layers remaining in the core of the membranes. Further increase in G (%) imparts more hydrophilic ionic sites to the membrane core facilitating proton mobility, which become more pronounced at $G = 53\%$ where a homogenous graft distribution is most likely achieved. These findings are supported by the results of sulfur distribution probed by EDX shown in Figs. 6 and 7, respectively together with cross-sectional view STEM images of both types of membranes. At low G (12%), the sulfur concentration profile was found confined to the surfaces in both membranes leaving the core part un-grafted. At higher G (53%) beyond threshold percolation, the sulfur distribution invaded the middle parts in both membranes with the concentration of sulfur apparently higher than that on their surfaces *i.e.* a definite homogenous sulfur distribution was achieved in both membranes at such degree of grafting.

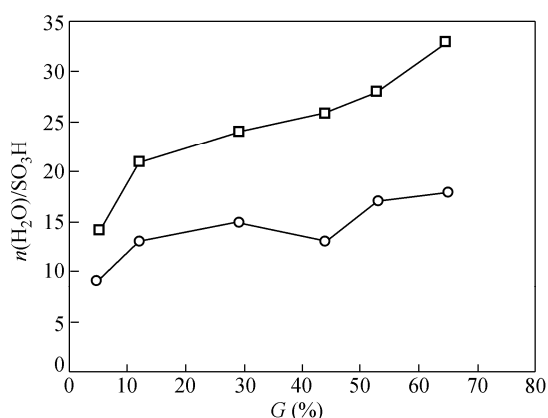


Fig. 4 Variation of hydration number versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes

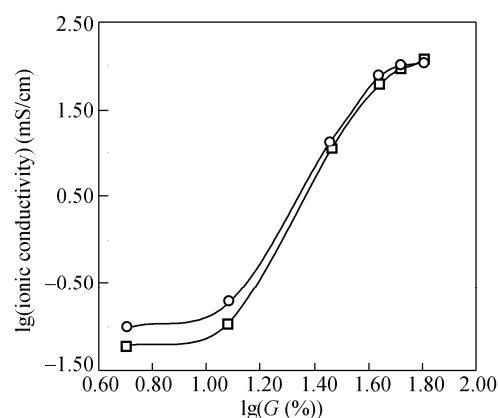


Fig. 5 lg-lg plot for variation of the ionic conductivity versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes

Interestingly, the proton conductivity of conventionally-prepared membranes was found to be slightly higher than that of the corresponding single-step prepared membranes despite the later higher IEC trend recorded earlier. Considering proton transport takes place in aqueous phase of the membrane, this trend is consistent with the earlier findings showing conventionally-prepared membranes exerted higher water uptake and hydration number than single-step-prepared membranes. Radiation grafted membranes of similar kind obtained by grafting of styrene and subsequent sulfonation is well known to undergo structural changes in forms of dilution the crystalline structure and partial disruption of crystallinities^[24, 25]. Thus, it can be suggested that structural changes induced in conventionally-prepared membranes are greater than those in single-step-prepared ones.

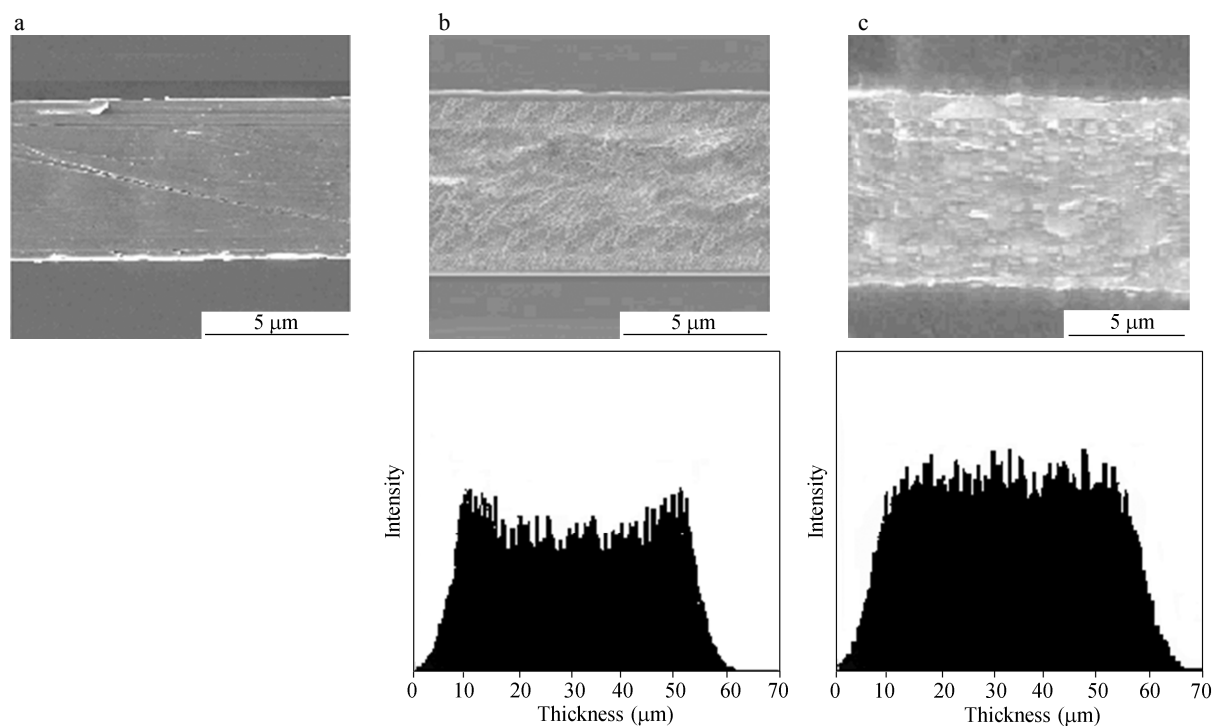


Fig. 6 STEM images of cross-sections of (a) original PVDF film, membranes prepared by conventional two-steps method: (b) $G = 12\%$ and (c) $G = 53\%$ together with their sulfur distribution profile

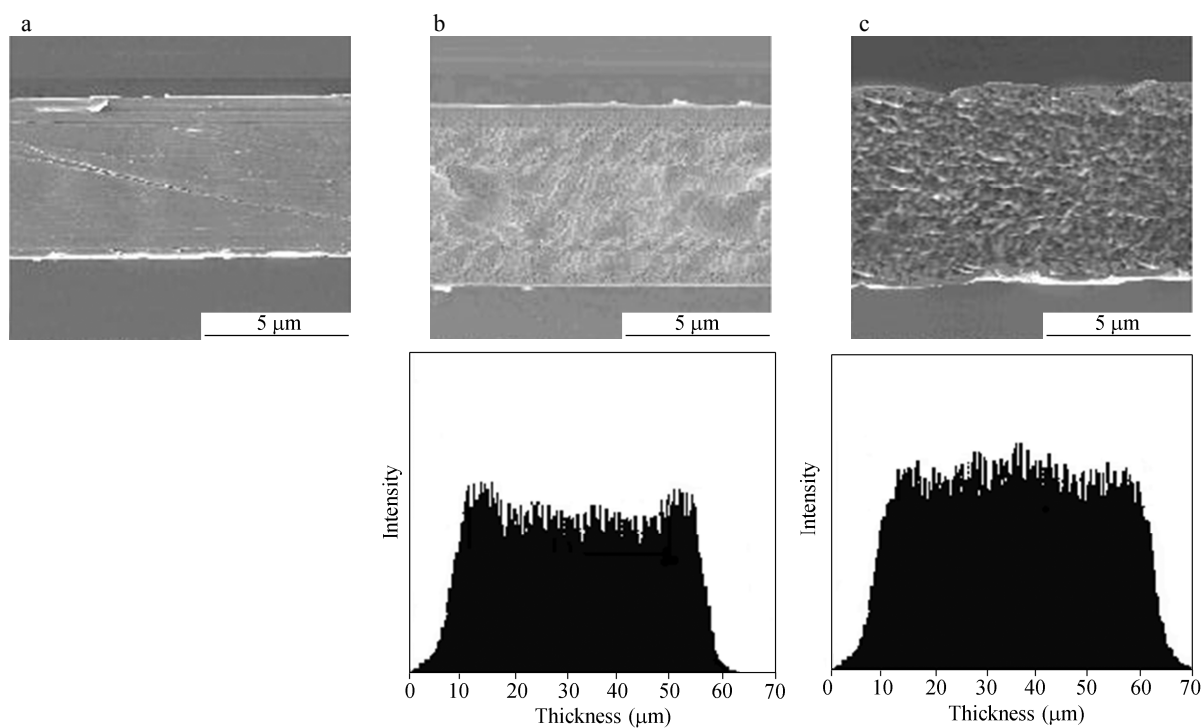


Fig. 7 STEM images of cross-sections of (a) original PVDF film, membranes prepared by single-step method: (b) $G = 12\%$ and (c) $G = 53\%$ together with their sulfur distribution profile

To confirm such remark, the degree of crystallinity (X_c) of the membranes prepared by two different methods was investigated and the obtained data were plotted against the degree of grafting as depicted in Fig. 8. X_c values were obtained from areas under melting peak of the endothermic thermograms of both membranes (not shown here) as reported elsewhere^[20, 25]. X_c in both membranes was found to decrease with the increase in G (%). The reduction in X_c , however, was found to be higher in conventionally-prepared membranes than those prepared by a single-step method. This is most likely due to the difference in the magnitude of the structural changes caused by the incorporated grafted moieties *i.e.* pre-sulfonated polystyrene in the single step method and post-sulfonated polystyrene in the conventional two-steps method.

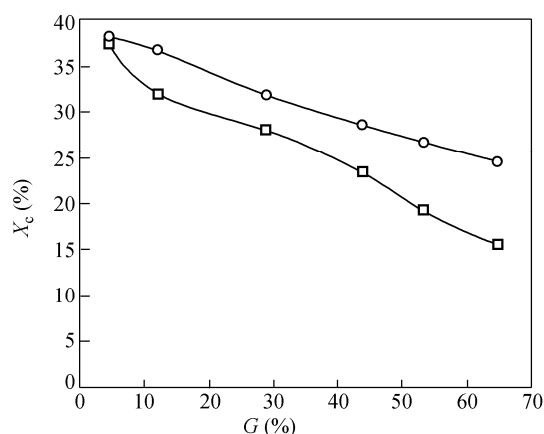


Fig. 8 Variation of the degree of crystallinity (X_c) versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes

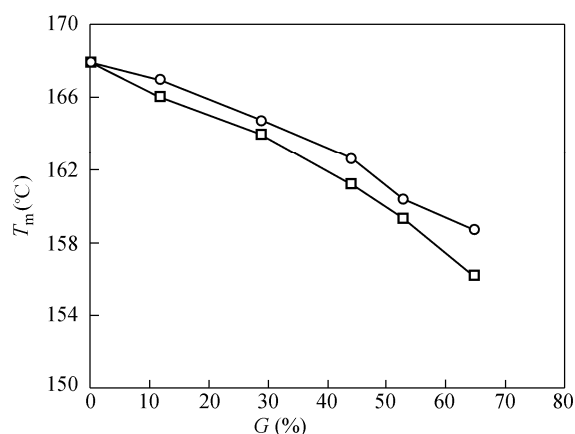


Fig. 9 Variation of the melting temperature (T_m) versus the degree of grafting of (○) single-step prepared and (□) conventionally prepared membranes

To further elucidate the effect of preparation procedures *i.e.* styrene grafting and subsequent sulfonation and single-step grafting of SSS, the melting temperatures (T_m) were recorded, and the obtained data are plotted in Fig. 9. The data clearly show that there is a shift in T_m of both membranes to lower values and such lowering effect is higher in membranes prepared by conventional method. A closer look on the downward variation trends of both T_m and X_c in both types of membranes clearly indicate the existence of not only a dilution effect stemmed from incorporation of amorphous polystyrene but also a partial disruption in the inherent crystallites of the PVDF matrix in conventionally-prepared membranes unlike those prepared by single-step in which incorporation of SSS seems to exert only a dilution effect on the crystalline structure. These results are also going very well with the variation of water uptake, hydration number and ionic conductivity which were found to have relatively higher values in conventionally-prepared membranes than in single-step prepared membranes.

Earlier investigation showed that grafting of polystyrene onto PVDF film takes place in the amorphous phase leading to no disorder in the crystalline structure. Instead, polystyrene exerted a dilution effect caused by the increase in the amorphous content^[24, 25]. Moreover, sulfonation was found to introduce additional structural change in a form of partial disruption in the crystallinities that further downshifted T_m and X_c to lower values. The partial disruption was attributed to the penetration of the crystallites by some polystyrene grafts under the influence of the aggressiveness of sulfonation reaction and the hydrophilic/hydrophobic stress at grafts-lamellae interface in the swollen membranes. The latter is a result of the strongly hydrophilic nature of sulfonic acid groups, which are prompted at the surface of the lamellae causing scission in some of polystyrene grafts. Similar trend in the structural changes was reported for PVDF based membranes prepared by simultaneous radiation grafting method^[26] and preirradiation methods^[27].

Figure 10 shows TGA thermograms of the two membranes with degree of grafting of 44% prepared by two different methods. As expected, both membranes show three-step degradation patterns owing to dehydration,

desulfonation, depolymerization and decomposition of PVDF. The initial weight loss up to 150°C is attributed to the loss of water strongly bound to sulfonic acid groups by hydrogen bonding. The weight loss in the second step (200°C in both membranes) is due to the elimination of sulfonic acid groups (desulfonation). This is followed by the decomposition of polystyrene (depolymerization), which took place at 383 and 392°C in conventionally-prepared and single-step prepared membranes, respectively. The final transition is due to the decomposition of PVDF by random chain scissions, took place at 503°C in conventionally-prepared membrane and at 519°C in single-step prepared membrane, both of which are lower than that of pristine PVDF film (thermogram is not shown), which has the value of 530°C. Both membranes do not undergo complete degradation and some residues of carbon-sulfur complex are left behind at the end of the heating runs. These results suggest that membranes prepared by the single-step method have higher tendency to resist heat treatment in terms of grafted moiety and polymer backbone despite the fact that no difference was observed in desulfonation temperature in both membrane. In other words, grafting sulfonated monomer has improved the stability of grafted moiety and polymer backbone. Similar multistage thermal degradation trend was reported for membranes obtained by grafting of styrene onto PVDF films followed by sulfonation^[28, 29].

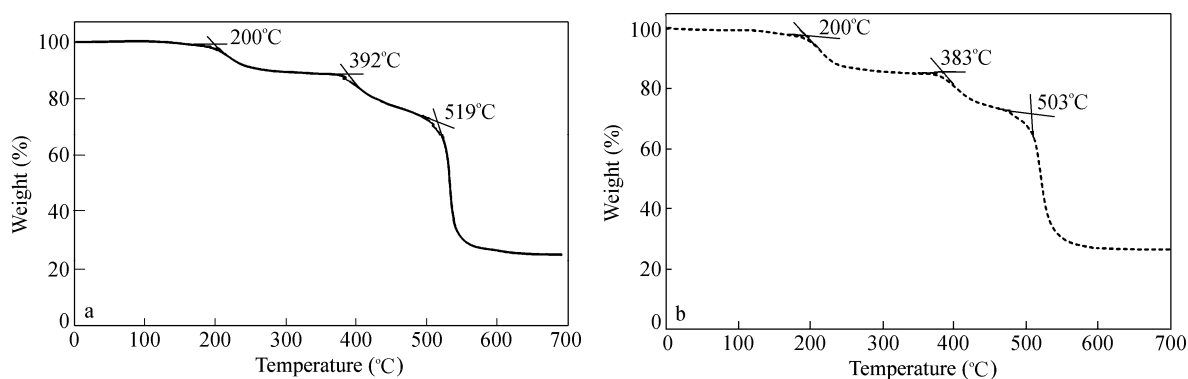


Fig. 10 TGA thermograms of two membranes with degree of grafting of 44% prepared by (a) single-step method and (b) conventional method

CONCLUSIONS

Structure-property relationships for two PVDF-g-PSSA proton exchange membranes obtained by two different radiation-induced grafting comprising a single-step procedure involving grafting of SSS onto EB irradiated PVDF films and conventional two-steps method involving grafting of styrene onto EB irradiated PVDF films followed by sulfonation reaction have been established. The physico-chemical properties in both membranes were found to be strongly dependent upon degree of grafting and preparation method. Membranes prepared by the single-step method showed higher ion exchange capacity, lower water uptake, hydration numbers and slightly lower proton conductivity compared to those obtained by conventional two-step method. This is due to the variation in the level of structural changes taking place in forms of reduction in the degree of crystallinity and melting characteristics. The introduction of PSSA in single-step prepared membranes exerted a dilution effect on the crystalline structure caused by amorphous polystyrene whereas introducing PSSA by the conventional two-step method caused a combination of dilution and partial disruption in the inherent crystallinities of PVDF films. The structure-property changes in forms of ionic sites increase, hydrophilicity enhancement, hydrophobicity reduction and crystallinity decrease with the increase in degree of grafting found to have a collective effect, and their relative contribution depends on the degree of grafting. Both membranes showed multi-step thermal degradation pattern with their functionality remained up to 200°C, however, single-step prepared membranes showed higher depolymerization and backbone thermal stability than those of the conventionally-prepared membranes. Finally, it can be stated that the membranes obtained by the single-step method have superior properties (despite their slightly lower ion conductivity) compared to those obtained by

conventional two-step method upon taking fuel cell requirements into consideration.

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