Acid-Synergized Grafting of Sodium Styrene Sulfonate onto Electron Beam Irradiated-Poly(vinylidene fluoride) Films for Preparation of Fuel Cell Membrane

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ABSTRACT: The role of acid addition in synergizing radiation induced grafting of sodium styrene sulfonate (SSS) onto electron beam-irradiated poly(vinylidene fluoride) (PVDF) films as a single-step route for preparation of proton exchange membranes containing sulfonic acid groups was systematically investigated. The grafting reaction, known for its poor kinetics, was studied using SSS diluted in various solvents and solvent/acid solutions of different concentrations and volumes. The addition of acid solution was found to marvelously synergize the grafting reaction from very low values (e.g., 0.5%) to achieve high degrees (e.g., 65%) of grafting and such synergetic effect depends on the type, concentration and volume of the added acid. The degree of grafting was also found to be function of the monomer concentration and the irradiation dose at constant acid concentration and volume. The obtained membranes were investigated with Fourier transform infrared spectroscopy (FTIR), scanning transmission electron microscopy (STEM), and X-ray diffractometry (XRD). The results of present study reveal that grafting of SSS to levels suitable for fuel cell application onto PVDF film is only possible by adding aqueous acids solution. Moreover, the addition of acid makes this shorter single-step method more economical route for preparation of proton exchange membranes for fuel cells. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2801–2809, 2010

Key words: radiation induced grafting; sodium styrene sulfonate; PVDF; acid addition; proton exchange membranes

INTRODUCTION

Radiation grafted sulfonic acid membranes have recently received an increasing attention after their potential for use as proton conducting materials in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) has been explored.[1–5] The method used in preparing these membranes i.e., radiation induced grafting, utilizes high energy radiation (e.g., γ-rays, electron beam and ion beam) to initiate radicals or active sites in a polymer substrate which induces graft copolymerization when brought in contact with monomer units during or after irradiation step forming macroradicals that propagate leading to formation of side chain grafts upon termination. The use of this method in preparation of these membranes offers various advantageous including setting a simplified preparation route through which the membrane properties and shape can be tailored by respectively controlling the reaction parameters and starting the reaction on a film of desired thickness in addition to low cost. The latest development in radiation grafted membranes and their applications including PEMFC have been recently reviewed in several occasions.[6–10]

Radiation grafted proton conducting membranes are commonly prepared by radiation induced grafting of styrene, styrene/crosslinker mixtures, or substituted styrene monomers onto fluorinated polymer films followed by sulfonation reaction to confer the ionic character.[6–10] Sulfonation is commonly performed using a strong sulfonating agent such as chlorosulfonic acid diluted with sulfonation resisting solvent (e.g., 1,2-dichloromethane) under controlled parameters. However, sulfonation is a hazardous aggressive reaction that has to be carefully controlled to obtain a 100% degree of sulfonation (every benzene ring should contain one pendant sulfonic acid group) without compromising the physical strength of the obtained membranes. Therefore, developing a method to directly introduce sulfonic

TABLE I
Summary of Previous Studies on Radiation Grafting of Sodium Styrene Sulfonate onto Various Polymers

Monomer	Acid addition	Substrate	Radiation source	Grafting method	References
AA followed by SSS	N/A	PE	Co 60	Preirradiation	15
AAA and SSS	N/A	PE hollow-fibers, polypropylene (PP) tube, PE and PP nonwoven fabric and polytetrafluoroethylene (PTFE) film.	EB	Preirradiation	14
AA and SSS	HCl	HDPE	Co 60	Direct irradiation and Preirradiation	12
AA and SSS		HDPE	EB	Preirradiation	11, 13
AA and SSS		PE	Co 60	Direct irradiation	12
SSS and AA		FEP	Co 60	Preirradiation	22
AA and SSS		PP	EB	Preirrdiation	20, 21
AA and SSS		PVDF	EB	Preirrdiation	18
SSS/DMSO	N/A	Nylon-MXD6	Co 60	Preirradiation	19
SSSS/DMF	H_2SO_4	PVDF	EB	Preirradiation	17

acid groups to a fluorinated films is highly sought to shorten the preparation stages and eventually improve the economy of the obtained membranes.

Recently, few research groups have turn their attention to develop a single-step radiation induced grafting route for preparation of sulfonic acid containing polymers to substitute the conventional route (grafting and sulfonation) by radiation grafting of sodium styrene sulfonate (SSS) onto few polymer substrates such as high density polyethylene (HDPE), polypropylene (PP) and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) apparently for separation and purification applications.[11–22] A summary of previous studies of radiation induced grafting of SSS is presented in Table I. Because of its poor kinetics, SSS showed a low tendency for graft copolymerization with polymer substrates caused by the incompatibility between the highly ionized hydrophilic sulfonic acid groups and the hydrophobic polymer backbone. However, grafting of SSS was only performed by introducing acrylic acid, a highly polymerizable monomer in aqueous solution,

as comonomer prior- or with SSS grafting reaction. Grafting of SSS onto aromatic polyamides (nylon MXD6) without acrylic acid was also reported by Li et al.[19]

In a previous communication, we briefly reported radiation induced grafting of SSS onto poly(vinylidene fluoride) PVDF films without adding acrylic acid to prepare proton exchange membrane for possible use in fuel cells.[17] A schematic representation of this single-step method is shown in Figure 1. Interestingly, the addition of acid solution was found to overwhelmingly boost the degree of grafting from 0.4 to 65% unlike grafting of vinyl and acrylic acid monomers onto polyolefins in which the addition of acid solution enhanced grafting already taking place at considerable level.[23–26] As grafting of SSS offers shorter, less hazardous and more economical single-step grafting method suitable for line production, such synergizing effect in the present grafting system is quite interesting and worth further investigation to optimize acid addition and understand its role.
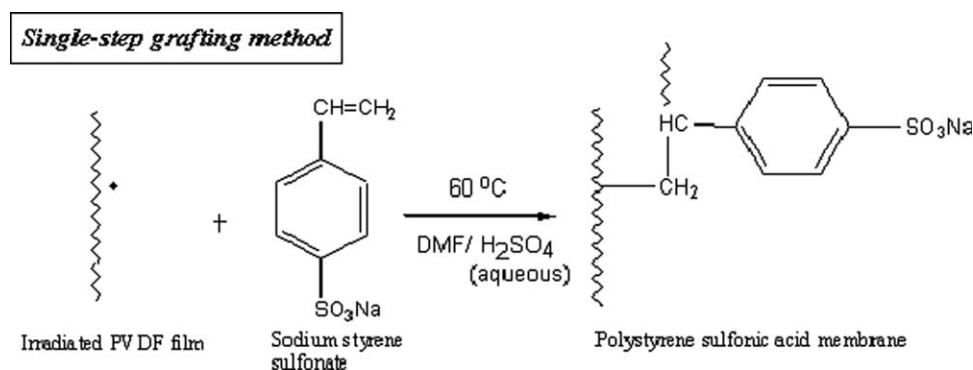

Figure 1 Schematic representation of preparation of proton exchange membrane in a single-step reaction.

TABLE II
Parameters of Electron Beam during Irradiation of PVDF Films

Voltage	200 keV
Beam Current	2 mA
Dose per pass	10 kGy
Conveyor speed	2.25 m/min
Atmosphere	Nitrogen
Temperature	Ambient

The objective of this communication is to systematically investigate the effect of acid addition in terms of type, concentration and volume on radiation induced grafting of SSS monomer onto electron beam-irradiated (PVDF) films. The effects of other grafting parameters such as monomer concentration and irradiation dose were also investigated. The chemical composition and structure of the obtained grafted membranes is investigated using various materials characterization techniques.

EXPERIMENTAL

Materials

PVDF films (50 μm thickness and density of 1.76 g/cm^3) were obtained from commercial source. Sodium styrene sulfonate (SSS) was obtained from Aldrich and used without any further purification. Solvents such as methanol, ethanol, isopropanol and dimethylformamide (DMF) were research grade and used as received. Deionized water (E-pure, 18 MΩ) was used to dilute sulfuric acid (98%, J.T. Bakers).

Irradiation of PVDF films

PVDF films were washed with ethanol and vacuum dried. PVDF films were irradiated by an electron beam (EB) accelerator (Curetron, EBC-200-AA2, Nisshin High Voltage Kabushiki Kaisha, Japan) to a total dose of 100 kGy at 10 kGy per pass under N$_2$ atmosphere. Summary of the operational parameters of EB during the irradiation is presented in Table II. The irradiated films were quickly sealed in an evacuated thin polyethylene bag and kept in a low temperature freezer at −60°C.

Graft polymerization

Graft copolymerization of SSS onto PVDF film was performed by placing the irradiated PVDF film in a glass ampoule, which was tightly sealed and evacuated to remove air. A nitrogen- bubbled monomer solution composes of SSS/DMF/H$_2$SO$_4$(aqueous) with specific concentrations was introduced to the ampoule through a special connection and the reaction was carried out for 24 h at a temperature of 60°C. 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 membranes were dried under vacuum and the degree of grafting (G%) was calculated as follows:

$$G\% = \frac{W_g - W_o}{W_o} \times 100$$

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

Characterization of the grafted membranes

Fourier Transform Infrared (FTIR) spectra of the membranes were recorded on a Digilab-FTS7000 spectrophotometer in transmittance mode over a range of 4000–500 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were detected and analyzed using commercial software of WIN-IR Pro^{TM} (DIGILAB$^®$).

Scanning transmission electron microscope (STEM) measurements were conducted using SEI Quanta 400 microanalyzer coupled with energy dispersive X-ray (EDX) analyzer to determine the sulfur distribution across the membrane. To view the cross-section, 100 μm samples were sliced with a rotary microtome, perpendicularly mounted on a sample holder by double sided tape and gold sputtered.

X-ray diffraction (XRD) measurements were performed using a Philips, PW 1840, X-ray diffractometer. The diffractograms were collected at ambient temperature in scanning range of 2θ 5–50° by means Cu Kα radiation (λ = 1.54) and monochromated by means of Nickel filter.

RESULTS AND DISCUSSION

Screening of dilutents

Various solvents such as water, methanol, isopropanol, and DMF were used to dilute SSS during its grafting onto PVDF films to determine the best diluent to be used in the present work. Table III shows the effect of various diluting solvents on the degree

TABLE III
The Effect of Various Solvents on the Degree of Grafting of SSS onto Preirradiated PVDF Film

Solvents	G (%)
Water	0.0
Methanol	0.2
DMF	0.4
Isopropanol	0.5

Reaction conditions: Irradiation dose, 100 kGy; monomer concentration, 1 mol/L; reaction time, 24 h; temperature, 60°C.
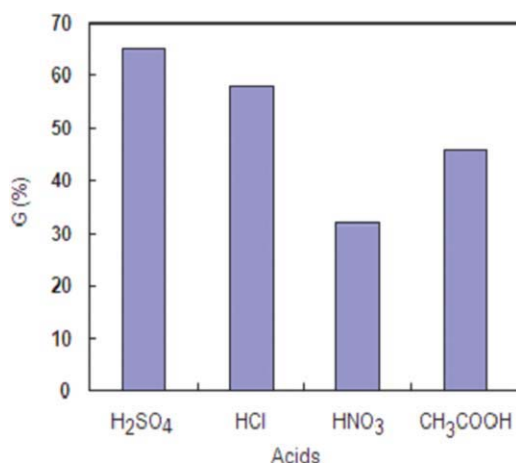
Figure 2 Variation of the degree of grafting of SSS onto PVDF films with the addition of different acids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com].

of grafting of SSS onto preirradiated PVDF films. Dilution of SSS with not only solublizing solvents such as water, methanol and DMF but also nonsolublizing solvents such as isopropanol was found to have no or little effect on the degree of grafting ($G = 0.0$–0.5%). Thus, it can be suggested that none of the investigated solvents can be used independently to dilute SSS during its grafting onto PVDF films. These results agree very well with literature which pointed out the poor kinetics of SSS caused by its strongly hydrophilic nature.[15]

Screening of acid additives

To enhance grafting of SSS onto PVDF films that was proved to be very low, the authors decided to add acid to achieve degrees of grafting in the obtained membranes suitable for PEMFC and DMFC applications. Various acids (minerals and organic) solutions were used as additives (at the same concentration and volume) to SSS diluted with DMF during its grafting onto PVDF films. Figure 2 shows variation of the degree of grafting with the type of added acid. As can be seen, acid addition drastically increases $G\%$ and such effect is profound with H_2SO_4, which has two replaceable hydrogens that can form hydrogen sulfate and sulfate ionic species in its aqueous solutions. The acid order in increasing $G\%$ is $H_2SO_4 > HCl > CH_3COOH > HNO_3$. To explain such behavior a brief review of the role of acid addition in previous studies has to be furnished.

Addition of acid has been reported to play a significant role in radiation included grafting of vinyl monomers onto polymer substrates using simultaneous and preirradiation methods.[7,27] The addition of mineral acids such as sulfuric acid has been found

to enhance grafting of vinyl monomers onto polyethylene, polypropylene, and cellulose upon using simultaneous grafting method where the three components of the grafting system (polymer, monomer, and solvent) are exposed to the high energy radiation and yield radical products. This behavior was interpreted on the radiolysis basis where irradiation of the solvent gives an increase to the hydrogen atom yield, which facilitates the hydrogen abstraction from the polymer matrix forming additional sites for initiating grafting.[28,29] Subsequent research work by Garnett et al. proposed another explanation for the acid enhancement of grafting on the basis of partitioning effect. The acid was suggested to modify the partition coefficient of the styrene between the polymer film (solid phase) and the external liquid phase leading to an increase in swelling equilibrium giving rise to the local styrene concentration around the graft growing chains i.e., the concentration of the absorbed styrene becomes higher than its corresponding one in the bulk solution leading to grafting enhancement.[30–32]

Investigation of the effects of addition of acids on grafting of vinyl monomers onto fluoropolymers, however, has received relatively little attention in the literature with mixed findings obtained. Dworjanyn et al. reported a slight but definite increase in the degree of grafting of a mixture of styrene and 2-hydroxyethyl methacrylate in methanol onto polytetrafluoroethylene (PTFE) using the simultaneous method upon addition of an unspecified acid.[33] In contrast, Nasef found no acid effects on the degree of grafting upon addition of specific amount of diluted mineral and organic acids during grafting of styrene diluted in methanol, benzene or dichloromethane onto PTFE, FEP, and poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) using the simultaneous method.[34]

Acid acceleration effect on grafting was also reported when preirradiation method was used for grafting of acrylic monomers onto polyolefines despite the absence of any change in the yield of hydrogen radicals, as the solvent was not irradiated. For example, Gupta et al. reported that sulfuric acid enhances the grafting yield upon grafting of acrylic acid into preirradiated PE film.[23] These authors noted in their report that acid effect is in part related to the enhancement of redox initiation. The enhancing acid effect was also assumed to be more related to partitioning phenomenon of the acrylic acid into polymer than the enhancement of redox initiation in this experiment because the grafting reaction formed by the decomposition of the peroxide was very small under the investigated grafting conditions. Addition of sulfuric acid was also found to enhance grafting of acrylonitrile, acrylonitrile/acrylic acid, acrylonitrile/methacrylic acid, and acrylonitrile/

TABLE IV
Summary of Studies Reported on the Effect of Acid Addition on the Degree of Grafting

| Monomer	Substrate	Solvent	Acid	Grafting method	Effect on grafting	References
Styrene	PE, PP, Cellulose	Methanol	Sulfuric acid	Simultaneous	Increase	24
Styrene	PE	Toluene, benzene, dichloromethane	Sulfuric, hydrochloric, nitric, acetic, oxalic, formic	Simultaneous	Increase	33
Styrene and 2-hydroxyethyl methacrylate	PE	Methanol	–	Simultaneous	Slight increase	34
Styrene	PE	Dichloromethane	Sulfuric acid	Simultaneous	Increase	32
Styrene	PTFE, FEP, PFA	Dichloromethane	Sulfuric, hydrochloric, nitric and acetic acid	Simultaneous	No effect	35
Acrylic acid	PE	Water	Sulfuric acid	Preirradiation	Increase	23
Acrylonitrile, Acrylonitrile/acrylic acid, Acrylonitrile/ methacrylic acid and Acrylonitrile/ glycidylmethacrylate	PE fabrics	Dioxane No solvent No solvent No solvent	Sulfuric acid	Preirradiation	Increase	36
Acrylonitrile	PP fibers	DMF	Sulfuric	Preirradiation	Increase	37
SSS/acrylic acid	HDPE		Hydrochloric		Increase	13

glycidylmethacrylate onto polyethylene fabrics.[35] Similar acid accelerating trend was reported for grafting of acrylonitrile onto polypropylene (PP) fibers.[36]

Recently Zu et al. reported that addition of HCl solution also increases the degree of grafting of AA combined with SSS onto preirradiated HDPE films and such increase is a function of pH. The highest grafting level was obtained at pH of 2.8. These authors attributed such trend to the increase in the viscosity in the grafting zone, which leads to an inhibition in the movement of grafting chains having great molecular weight hindering the termination by combination with other growing chains, but does not appreciably disturb the diffusion of monomers. The authors further argued that the rate of the chain propagation is faster than chain termination, leading to an obvious increase in the grafting yield. In the absence of HCl, the viscosity of system was so high that diffusion rate of monomers into the matrix decreased distinctly. Under such conditions, the rate of monomer reaction with the growing chain may be considerably lowered, so grafting yield decreases without addition of HCl.[13] A summary of studies reported on the effect of acid addition on the degree of grafting is given in Table IV.

The acid synergetic effect observed in the present study seems to be complex and can be part attributed to the partitioning effect proposed by Garnett et al. and several other workers according to the earlier discussion. Such effect in the present system is related to the swelling behavior of PVDF film in the grafting solution and subsequent availability of the monomer into the grafting sites. The presence of DMF (a good solvent for SSS) in the grafting mixture brings about swelling enhancement of PVDF film in the grafting solution. The presence of acid solution increases swelling equilibrium allowing monomer diffusion through the swollen layers to the grafting sites and as a result more monomer supply was provided to the propagating chains in the polymer substrate. The presence of acid may also have increased the pH of grafting solution affecting the viscosity in the grafting zone in a way that reduces the motion of long graft growing chains and termination by recombination without compromising the monomer diffusion.

In addition, it is highly possible that ion exchange reaction as the one shown below:
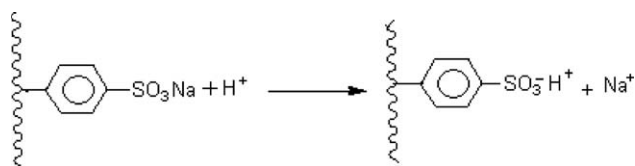
took place where Na^+ available in SSS grafting monomer is replaced with H^+ in the aqueous acid solution leading to formation ionizable salt of the corresponding acid (e.g., $NaHSO_4$ or Na_2SO_4) that might suppress the homopolymer formation since swollen PVDF form a viscous barrier hindering the diffusion of Na^+ cations to the graft growing chains.
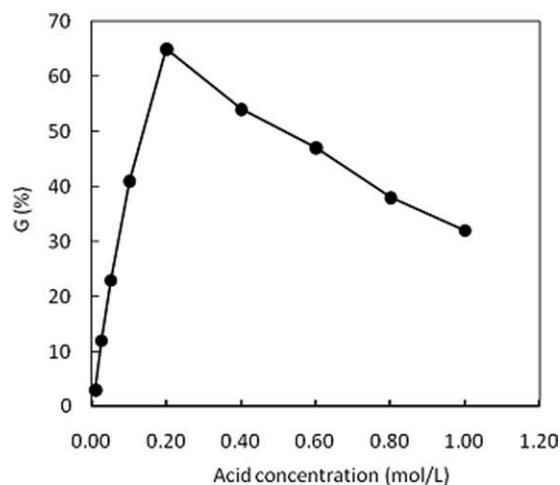
Figure 3 Variation of the degree of grafting of SSS onto PVDF film with the acid concentration at constant volume of 10 vol % of total grafting solution volume.

Therefore, aqueous H_2SO_4 solution was added to DMF and SSS during grafting reaction in the rest of the experiments. Earlier investigations on the effect of acid on grafting of vinyl (styrene) and acrylic monomer showed that aqueous H_2SO_4 solution provides higher grafting levels than other mineral acids.[23,30] Knowing the accelerating effect of H_2SO_4 on grafting reaction, it is of concern to optimize, the concentration and the volume of H_2SO_4 solution to be added to achieve desired degrees of grafting. It is noteworthy to point out that the role of acid in the present system is essential for the grafting to embark from negligible levels unlike grafting system reported in earlier studies where grafting took place to appreciable levels without the acid addition and was enhanced by introducing the acid solution.

Effect of acid concentration

Figure 3 show the effect of variation of sulfuric acid concentration on the degree of grafting of SSS diluted with DMF onto PVDF film. The H_2SO_4 acid concentration in the aqueous solution was varied in the range of 0.01–1.0 mol/L. $G\%$ was found to increase dramatically with increasing acid concentration until it achieved a maxima at a 0.2 mol/L beyond which it was sharply dropped with more acid content. This trend is presumably due to the increase in acid reactivity readily synergizes the monomer grafting to certain concentration extent (0.2 mol/L) beyond which grafting becomes lesser under the influence of rising viscosity of grafting solution that lowers monomer diffusion and consequently propagating chains partly terminates by recombination. Therefore, a 0.2 mol/L of H_2SO_4 was added to SSS diluted with DMF during grafting reaction in the rest of the experiments. Zu et al. suggested that the increase in the grafting of AA combined with SSS onto preirradiated HDPE is due to pH effect.[13]

Effect of acid solution volume

Figure 4 show the effect of variation of volume of the acid additive having a concentration of 0.2 ml/L on the degree of grafting of SSS diluted with DMF onto PVDF film. The volume of H_2SO_4 solution was varied in the range 5–25 vol % of the total volume of SSS/DMF mixture. The increase in acid solution volume was at the expense of that of volume of SSS solution in DMF since the total grafting solution volume was kept constant in all experiments. $G\%$ was found to increase with increase in the volume from 5 to 10 vol % where it achieves a maxima beyond, which it abruptly dropped and continued to decrease with the increase in volume of H_2SO_4. The pH of grafting system decreases with the addition of more aqueous solution of H_2SO_4 until it reaches a critical value beyond which the viscosity of the grafting zone rises in a way leading to a reduction in the monomer diffusion prompting an early termination of graft growing chains by mutual recombination. These results suggest that pH of grafting solution play a role in optimizing the required grafting level. Similar findings were reported for grafting of SSS combined with AA (comonomer) onto preirradaited PE and FEP films.[13,22]

Effect of monomer concentration

The effect of variation of the monomer concentration on the degree of grafting of SSS onto PVDF film is shown in Figure 5. The variation of SSS
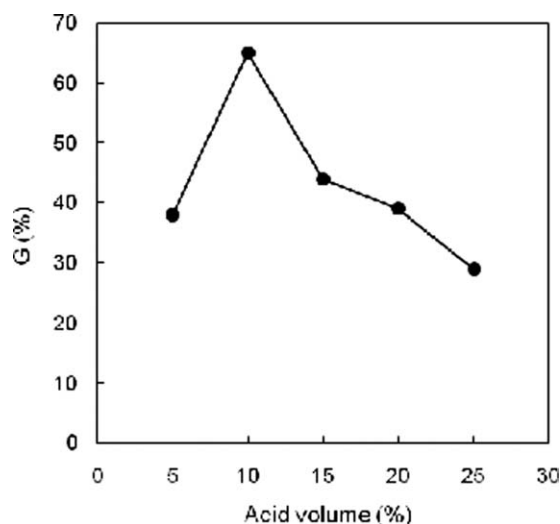

Figure 4 Variation of the degree of grafting with the volume of added acid at constant acid concentration of 0.2 mol/L.
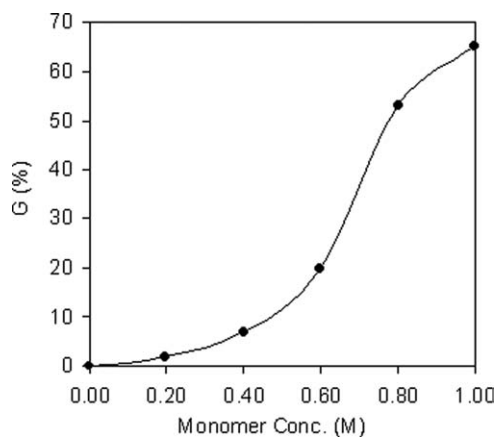
Figure 5 The effect of monomer concentration on the degree of grafting. Reaction conditions: irradiation dose, 100 kGy; solvent, DMF; acid concentration, 0.2 mol/L at constant volume of 10 vol % of total grafting solution volume; reaction time, 24 h and temperature, 60°C.

concentration in the range of 0.2–1.0 mol/L at a constant H_2SO_4 concentration led to an increase in G% of the obtained grafted film in the range of 5–65%. The increase in G% with the increase in SSS concentration is most likely caused by the increase in the diffusion of SSS through the swollen layers of PVDF films and its subsequent increased availability in the grafting sites caused by the presence of acid.

Effect of irradiation dose

Figure 6 shows the variation of the degree of grafting with the irradiation dose. G% was found to increase linearly with the increase in irradiation dose. This trend reflects a typical free radical polymerization reaction. The grafting increase at higher doses can be attributed the formation of more efficient trapped radicals in the polymer films which
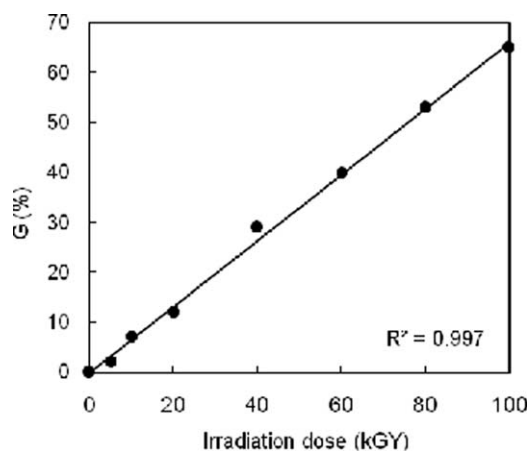

Figure 6 Effect of irradiation dose on the degree of grafting. Monomer concentration is 1.0 mol/L and the rest of reaction conditions are as in Figure 5.

increasingly take part in the copolymerization reaction leading to an increase in G%.

From the results of the effects of the monomer concentration and the dose on the degree of grafting, it can be concluded that grafting in the present system is not only a dependent on the monomer availability in the grafting sites but also on the amount of efficient radicals formed in the polymer substrate.

Characterization of grafted membranes

Figure 7 shows typical FTIR spectra of original PVDF film and grafted poly(styrene sulfonic acid) membranes having various degrees of grafting. Compared to original PVDF film, the grafted membranes displayed features confirming the presence of aromatic ring features established by the presence of skeletal C=C in plane-stretching vibrations at 1603 and 1495 cm^{-1} together with C—H aromatic stretching vibrations at 3024 cm^{-1} and in-plane CH notable band of bending vibration of the substituted benzene ring at 695 cm^{-1}. The band at 1034 cm^{-1} is due to the in-plane CH bending vibration of the disubstituted benzene ring. The bands at 1453, 1128, 1062, and 1000 cm^{-1} are due to the presence of —SO$_3$H groups. The broad peak at 3460 cm^{-1} is assigned for —OH of water molecules involved in hydrogen bonding with SO$_3$H groups. The intensity of the characteristics bands vary with the variation of the degree of grafting. From FTIR results, it can be confirmed that SSS was grafted onto PVDF films and sulfonic acid membranes were obtained.

The grafting of poly(styrene sulfonic acid) was further confirmed by investigating the distribution of the sulfur in microstructure of the membranes using STEM. The STEM image of cross-sectional
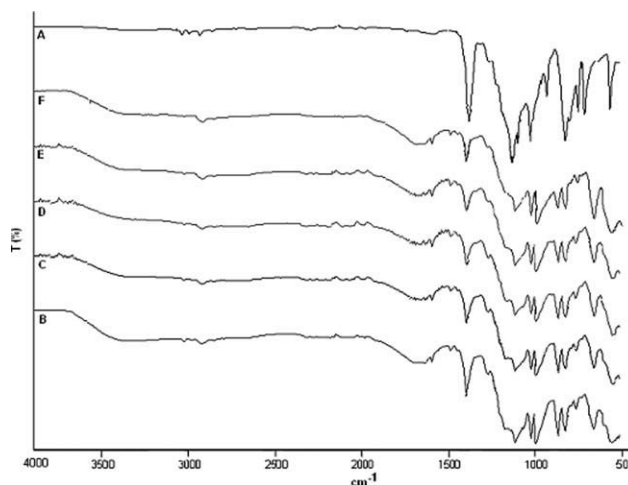

Figure 7 FTIR spectra of: (A) original PVDF film and poly(styrene sulfonic acid) grafted PVDF membranes with various degrees of grafting, (B) 12%; (C) 29%; (D) 44%; (E) 53%, and (F) 65%.

view of the membrane ($G = 53\%$) displays a morphology reflecting a homogenous graft distribution of polystyrene sulfonic acid groups across the membrane i.e., radiation induced grafting of SSS occurred not only on the surfaces but also within in the bulk membrane when compared with that of original PVDF film as depicted in Figure 8. The figure also shows the variation in the membrane thickness associated with the incorporation of the grafted moiety.

The structural changes caused by grafting of SSS onto PVDF films at various levels were investigated by XRD analysis and the obtained curves are presented in Figure 9. Original PVDF film displays a typical diffraction curve that reflects the semicrystalline nature of the polymer which have two crystal sizes. When grafted with SSS, the overall crystalline peaks area decreased and such decrease is a function of $G\%$. Coincidently, there is no obvious shift in crystalline peak position appeared at Bragg angles of $2\Theta = 19$ and 21, respectively. These observations suggest a reduction in the inherent crystallinity of PVDF film is most likely caused by the dilution effect stemmed from the incorporation of amorphous poly(styrene sulfonic acid), which increases with the rise in $G\%$. It can be assumed that the semicrystalline nature of PVDF is still preserved and grafting occurs in amorphous region of polymer matrix without causing disruption in crystalline structure. These results go along with crystallinity investigation conducted on these membranes with differential scanning calorimeter.[17] Similar observations have been made in earlier studies on similar membranes obtained by grafting of styrene onto PVDF films followed by sulfonation.[37,38]

CONCLUSIONS

Grafting of SSS onto electron beam-irradiated PVDF film for preparation of proton exchange membrane for fuel cells was synergized by addition of aqueous acid solution to the grafting mixture. Unlike previous studies, the acid addition was very essential for
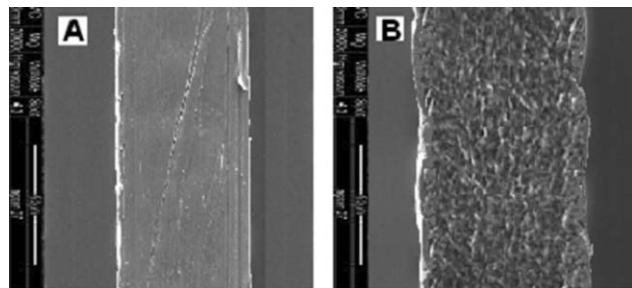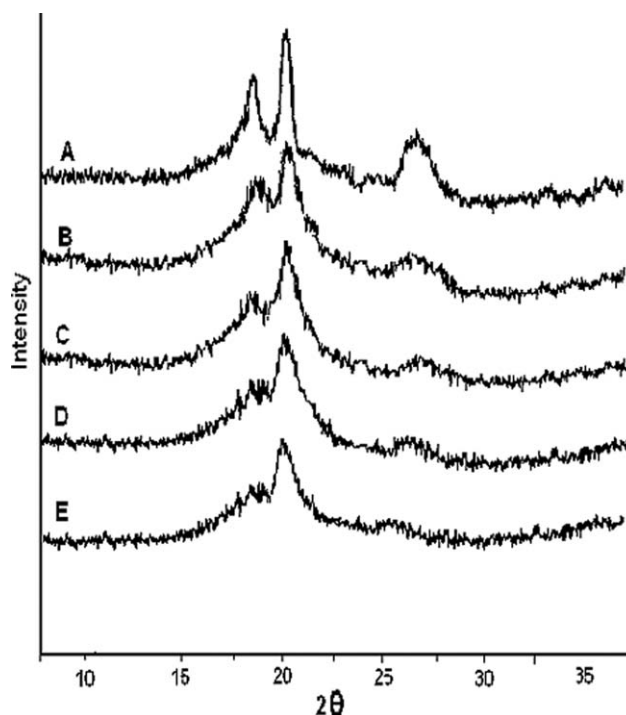

Figure 9 XRD diffraction curves of: (A) original PVDF film and poly(styrene sulfonic acid)-grafted PVDF membranes with various degrees of grafting, (B) 12%; (C) 29%; (D) 44%; and (E) 53%.

the grafting to embark from negligible levels to values suitable for fuel cell application. The role of acid in boosting the degree of grafting followed the sequence: $H_2SO_4 > HCl > CH_3COOH > HNO_3$. The acid concentration and volume were found to heavily affect $G\%$. The highest G (65%) was achieved with an aqueous solution of sulfuric acid having concentration of 0.2 mol/L at 10 vol % of the total volume of SSS diluted with DMF. The synergetic acid effect was attributed to increase in monomer supply to graft growing chains under the influence of portioning effect, the inhibition of termination by recombination in the graft propagating chains and suppression of homopolyme by Na-salt formed in the grafting solution. $G\%$ was also found to be function of monomer concentration and irradiation dose under constant values of acid concentration and volume. The incorporation of poly(styrene sulfonic acid) in PVDF films was evident from FTIR spectra, STEM images and XRD diffractograms. The method reported in this work seems to be more attractive than conventional two-step method (grafting and sulfonation) for preparation of proton exchange membranes. The elimination of sulfonation offers shorter and cost-effective preparation route.

Figure 8 Cross-sectional STEM images of: (A) original PVDF film and (B) poly(styrene sulfonic acid)-grafted PVDF membrane with degree of grafting of 53%.

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