

Preparation and Characterization of a Proton-Exchange Membrane by the Radiation Grafting of Styrene onto Polytetrafluoroethylene Films

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ABSTRACT: Radiation-induced simultaneous grafting of styrene onto polytetrafluoroethylene (PTFE) films and the subsequent sulfonation in the chlorosulfonic acid/dichloroethane were investigated. The effects of the main radiation grafting conditions, such as the type of solvents, irradiation dose, dose rate, the styrene concentrations, *etc.*, on the degree of grafting (DOG) were studied. To elucidate the influence of both the grafting and sulfonation conditions on the properties of the PTFE-g-polystyrene-sulfonic acid (PSSA) membranes, the sulfonation conditions, including the sulfonation temperature and the concentration of the ClSO_3H with respect to the DOG, were systematically evaluated. The

grafted and sulfonated membranes were characterized by FTIR-ATR spectra, ion-exchange capacity (IEC), water uptake, thickness measurement, *etc.* The as-prepared PTFE-g-PSSA membranes in this work showed a good combination of a high IEC (0.85–2.75 meq g^{-1}), acceptable water uptake (8.86–56.9 wt %), low thickness, and volume expansion and/or contraction. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1415–1428, 2006

Key words: graft copolymers; polytetrafluoroethylene; radiation; membranes; irradiation

INTRODUCTION

The proton-exchange membrane fuel cells (PEMFCs) have been suggested as one of the environment-friendly and clean power sources. Water is the only waste by-product, if hydrogen is used as the fuel. Besides, the all-solid components, relatively mild operational conditions, and high energy efficiencies as well as the high power density, make it quite attractive for many applications.^{1–3} In particular, as transportable power sources are used in zero-emission vehicles instead of the serious polluting petrol-fueled internal combustion engines, PEMFCs have exhibited very promising prospects.

A proton-exchange membrane (PEM) is the vital component of the PEMFCs. The necessary criteria of these membranes for the PEMFC applications are as follows: (i) high proton conductivity (of the magnitude of 10^{-2} S cm^{-1}); (ii) mechanical strength; (iii) high thermal and chemical stability; and (iv) long lifetimes and a low cost ($< \$200 \text{ m}^{-2}$). The most widely used and successful membranes for research and pro-

type fuel cells have been Nafion[®] (DuPont de Nemours Ltd.), Aciplex[®] (Asahi Chemical Co.), and Dow[®] (Dow Chemical Co. Ltd.).⁴ These membranes consist of perfluorinated copolymers with sulfonic acid functionalized side chains. Unfortunately, the synthetic procedures of these membranes are complicated, and hence, these membranes are very expensive, which hampers their large-scale application. Because of this, the development of cheaper and better PEMs has been pursued for the last few years. Several new types of fluorinated and nonfluorinated membranes have been developed using chemical doping methods.^{5–9}

Preparation of PEMs by radiation-induced graft copolymerization of different monomers into polymeric films is an attractive way because of the applicability of this method to most of the polymer–monomer systems. By careful variation of the reaction conditions and the radiation parameters, it is possible to control easily the degree of grafting (DOG), and hence, the membrane properties. Moreover, radiation grafting can be achieved in the film form of a polymer, which overcomes the complicated problem of shaping the graft copolymer into thin foil.

There are a few reported papers on the radiation-induced grafting of styrene onto polytetrafluoroethylene (PTFE). However, up till now, no systematic research has been reported on both the grafting and

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sulfonation conditions and their influence on the properties of the PTFE-g-polystyrene-sulfonic acid (PSSA) membranes, to which the following contributions have been made in this work.

EXPERIMENTAL

Materials

The PTFE films provided by Hanmi Rubber and Plastics Co. (Seoul, Korea) were used as a polymer substrate. Thicknesses of PTFE films used in this work were 80 μm . Prior to use, the PTFE films were cut into $5.0 \times 3.0 \text{ cm}^2$ strips, and washed twice with methanol, and finally dried in a vacuum oven at 60°C for 24 h to a constant weight. The pretreated PTFE films were stored in a desiccator before irradiation.

Styrene ($\geq 99\%$ purity; from Showa, Tokyo, Japan) stabilized with 3 ppm 4-*tert*-butyl catechol was used as a grafting monomer without any further purification. 0.1M HCl standard solution was also provided by Showa. Chlorosulfonic acid (reagent grade) was purchased from Merck. Other reagents such as methanol, dichloromethane, benzene, acetone, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) were of reagent grade and used as-received.

Graft polymerization

The grafting reactions were carried out in an ampoule bottle. A given concentration of styrene in a certain dilute solvent was first prepared in the ampoule bottle, and then, the pretreated PTFE pieces ($5.0 \times 3.0 \text{ cm}^2$) were immersed into the grafting mixture. The ampoule was irradiated using γ -rays from a cobalt-60 source, to a total dose of 60 kGy at a dose rate of 1.25 and 0.85 kGy h^{-1} . After irradiation, the grafted films were taken out from the ampoules and extracted by refluxing benzene in a Soxhlet overnight to remove any unreacted monomer and homopolymer left in the films. The washed films were then dried in a vacuum oven at 80°C to a constant weight. The DOG in percentage was gravimetrically determined using the following equation:

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

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

Sulfonation

Initially, the grafted films were washed with dichloroethane and soaked therein for 30 min. The grafted films were sulfonated in a given concentration of chloro-

sulfonic acid in a dichloroethane at a specific temperature. After completion of the reaction, the sulfonated membranes were removed from the reactor, washed several times with dichloromethane and deionized water in sequence to remove the excesses of the chlorosulfonic acid, and then dried in a vacuum oven at 80°C overnight.

FTIR-ATR analysis

The grafting was verified and confirmed by FTIR spectroscopy, using an FTIR spectrometer Tensor 37 (Bruker, Germany) in a transmittance mode in the frequency range of 500–4000 cm^{-1} .

Water uptake

The dry weight of all the samples was determined after drying the samples in the vacuum oven to constant weight. To measure the water uptake, samples were boiled in water for 1 h and then left to equilibrate at room temperature. After the excess water was removed by blotting the surface, the samples were immediately weighed and the ratio of the weight of the absorbed water to the weight of the dry sample was calculated.

Ion-exchange capacity

Ion-exchange capacity (IEC) of the membranes was determined by acid–base titration. The membrane samples in an acid form were immersed into a known volume of NaOH and then titrating of the excess NaOH using a standard solution of HCl was initiated. Membrane samples were regenerated again into an acid form by boiling with 3.5M HCl for 3 h, and were dried in vacuum oven to a constant weight. Then, the weight of the dry membranes was determined. From the volume of NaOH solution consumed in the titration, IEC of the dry membrane per unit of mass (meq g^{-1}) was calculated.

The success of the sulfonation reaction was evaluated from the IEC. A degree of sulfonation (DOS) of 100% is defined as an IEC equivalent to one $-\text{SO}_3\text{H}$ group per aromatic ring.

$$\text{DOS (\%)} = \frac{\text{IEC}_{\text{exp}}}{\text{IEC}_{\text{theor}}} \times 100 \quad (2)$$

where, $\text{IEC}_{\text{theor}}$ is the IEC calculated from the DOG.

RESULTS AND DISCUSSION

Grafting conditions

The influence of solvents used on the DOG of styrene onto PTFE films at different doses is shown in Table I

TABLE I
Effect of Solvent on the Degree of Grafting of Styrene onto PTFE Films at Different Doses

Solvent	Degree of grafting (%) at different doses		Remarks
	30 kGy	60 kGy	
Acetone	5.35	8.52	
Benzene	19.95	28.62	Some crack
Dichloromethane	35.89	68.12	No homopolymer
DMF	3.09	6.88	
DMSO	2.8	5.32	Too much homopolymer
Methanol	10.25	15.16	Much homopolymer
THF	6.98	10.88	

and Figure 1. The composition of the various styrene/solvent mixtures was 50% (v/v). It was shown that the samples grafted in a styrene mixture diluted by dichloromethane had a dramatically higher DOG than the others, with no homopolymer being formed. Dilution of styrene with solvents such as DMF, DMSO, acetone, *etc.*, caused a quite low DOG. These results can be attributed to a lot of aspects, of which the nature of the solvents and the solubility of the poly-

styrene (PS) homopolymer in the various grafting mixtures may be the main factors.

The process of radiation-induced grafting is a radical chain growth reaction, in which the growing chain of styrene is terminated by the active radical transfer to the solvent. Owing to its electron acceptor nature and low chain transfer constant of dichloromethane (0.15),¹⁰ the termination of the PS growing chains can be greatly delayed, and so, the grafting yield is considerably enhanced.

Dilution with dichloromethane results in a better swelling of the base polymer PTFE, and hence, enhances the diffusion of the monomer into the internal layers of the polymer substrate, *i.e.*, the monomer accessibility to the grafting sites. Therefore, the interactions between the internal active sites and the monomer molecules increases, leading to higher DOGs and homogeneous grafting. Using other solvents, however, results in a poor swelling of the substrate PTFE. Consequently, it is most likely to lead to surface grafting because of the reduction in the monomer diffusibility, and eventually, low DOGs are obtained.

Because the solubility parameter of dichloromethane (20.3) is very close to that of the PS homopolymer

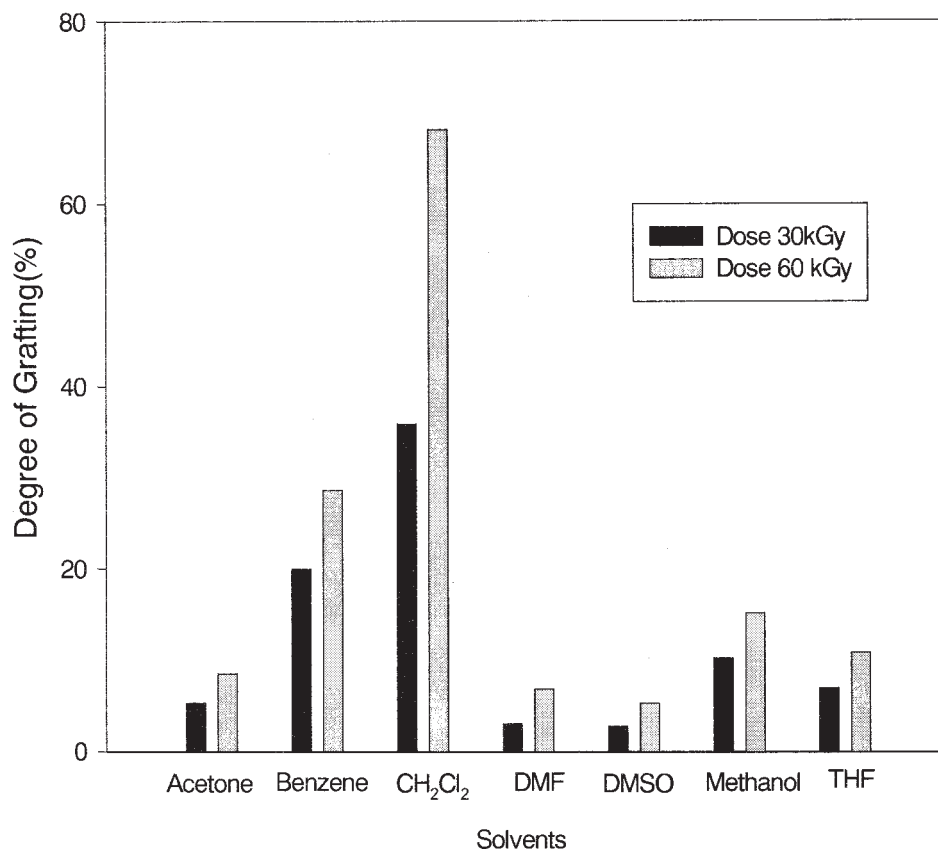


Figure 1 Effect of the type of solvent used to dilute the styrene monomer on the degree of grafting of PTFE. Grafting conditions were dose rate, 1.25 kGy h⁻¹; film thickness, 80 μm; ambient temperature; and absorbed doses, 30 kGy and 60 kGy.

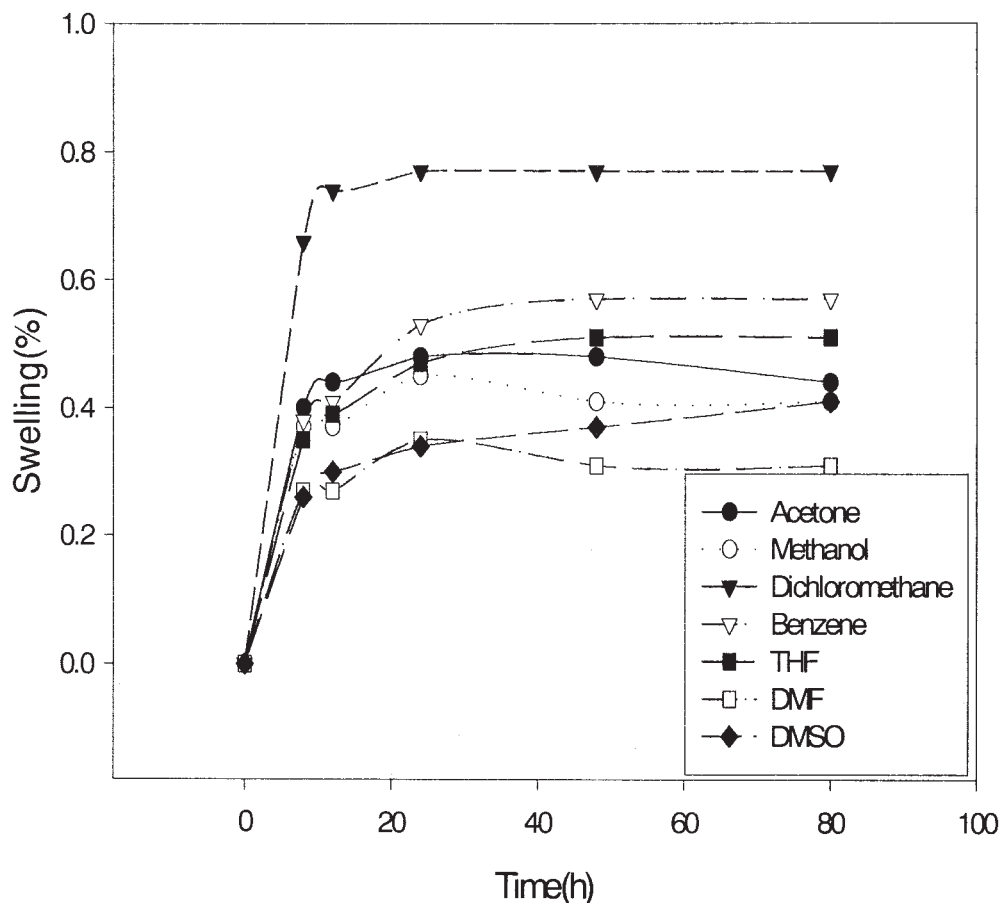


Figure 2 Variation of sorbed liquid amount of 80-mm PTFE films in 40% styrene mixtures diluted by different solvents with the immersing time.

(22.4) that might be formed, homopolymer is not accumulated on the PTFE film surface or in the grafting mixture, during the grafting. As a result, the viscosity of the solution is kept and the swelling of the grafted layers and the diffusion of styrene as well as the concentration of the styrene are enhanced. Therefore, a high DOG is obtained. However, in the cases of methanol and DMSO, much homopolymer is formed during the grafting process and it deposits onto and covers the surface of the PTFE film, which leads to a remarkable increase in the viscosity of the grafting mixture, and therefore, the styrene diffusion is hindered, leading to only surface grafting and a low DOG.

Benzene is a quite good solvent for styrene and PS homopolymers; therefore, dilution with benzene can also give a reasonable DOG, but it is still far lower than that of dichloromethane, and some cracks appear in the grafted film. This is probably due to the presence of a resonance stabilization effect in the benzene ring, which acts as an energy transfer agent. This means that benzene would consume the irradiation energy, and hence, reduce the reactivity of the radicals. As a result, a relatively low DOG is obtained.

Figure 2 shows the swelling properties of the PTFE film in 40% styrene mixtures diluted by different solvents. It can be seen that the swelling rate and the equilibrium absorbed solvent amount depends on the solvent type. The styrene diluted with a dichloromethane mixture was found to produce the greatest weight increase in the PTFE films, followed by the styrene-benzene and styrene-THF. Styrene-DMF mixture resulted in the lowest weight increase. These results indicate that dichloromethane is able to swell the PTFE substrate better than the other solvents, and helps the monomer diffuse to the grafting sites and enhances the growing of a long PS chain, leading to a high DOG.

It has been proved that the amount of solvent sorption is closely related to the difference in the solubility between the polymer and the solvent. The smaller the difference, the larger the film swelling. Therefore, it can be concluded that styrene/dichloromethane and styrene/benzene mixtures have a solubility closer to PTFE than other solvent-diluted styrene mixtures. Accordingly, PS is expected to be more soluble in dichloromethane and benzene than in the other solvents.

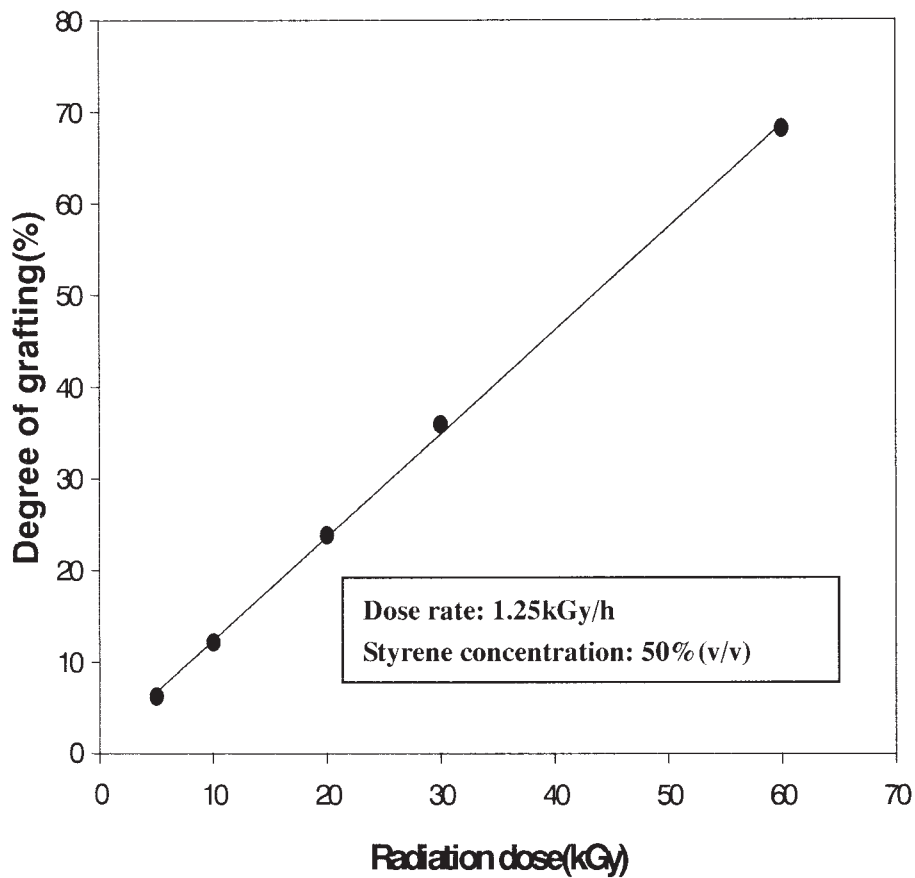


Figure 3 Effect of irradiation dose on the degree of grafting of styrene onto 80- μ m PTFE. Grafting conditions were dose rate, 1.25 kGy h⁻¹; styrene concentration, 50% (v/v); and solvent, dichloromethane.

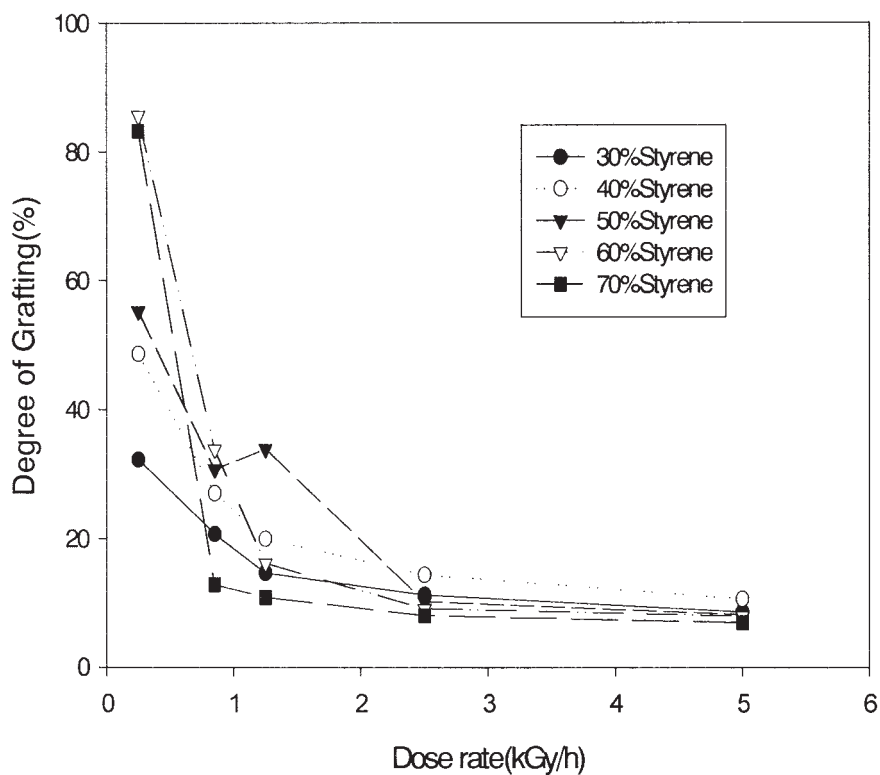


Figure 4 Effect of dose rate on the degree of grafting of styrene onto 80- μ m PTFE in different concentrations of styrene/dichloromethane mixtures with total irradiation dose of 25 kGy.

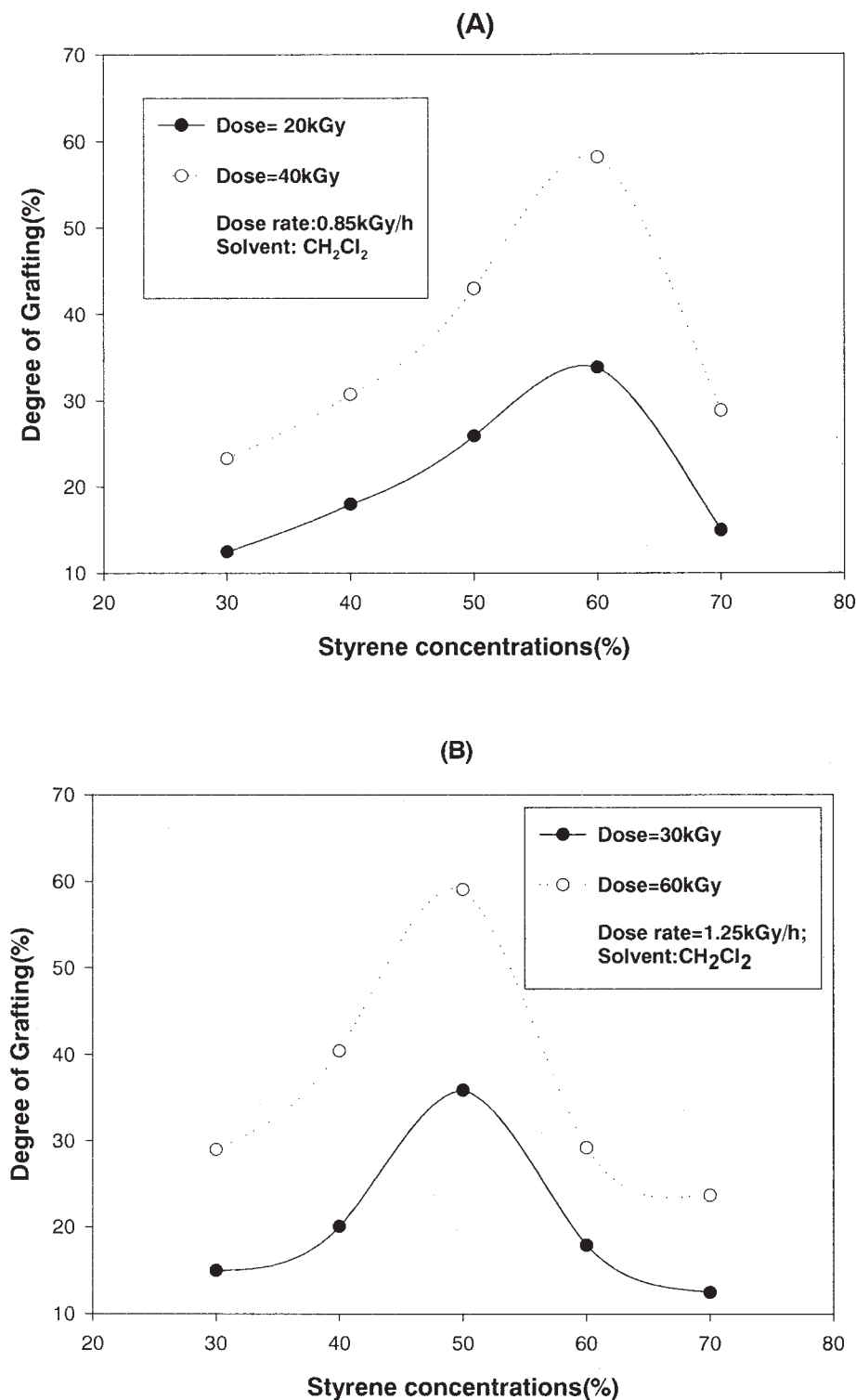


Figure 5 Effect of styrene concentration in dichloromethane on the degree of grafting of styrene onto 80- μm PTFE films. Grafting conditions were as follows: (a) dose rate, 0.85 kGy h⁻¹; doses, 20 kGy and 40 kGy. (b) dose rate, 1.25 kGy h⁻¹; doses, 30 kGy and 60 kGy.

Figure 3 shows the effect of irradiation dose on the DOG of the styrene onto 80- μm PTFE at a dose rate of 1.25 kGy h⁻¹ and an initial styrene concentration of 50% (v/v) in dichloromethane. As can be seen, almost

a linear relationship exists between the DOG and the irradiation dose. The DOG increased gradually with an increase in the irradiation dose within the limits of the studied values from 5 to 60 kGy. With the increase

TABLE II
Approaches to Sulfonation of Styrene-Grafted Fluoropolymers

Polymer matrix	Ref	Sulfonation conditions	Reported degree of sulfonation (%)	Determination method
Teflon-FEP	11	30% ClSO ₃ H, 95°C, 5 h	100	Not given
PTFE	16	10% ClSO ₃ H was added dropwise at 10°C, 3 h at 20°C	100	Mass increase during sulfonation
PVDF	17	98% H ₂ SO ₄ was refluxed under N ₂ , 95°C, 3 h	Not given. ^a	Titration
PFA	18	30% ClSO ₃ H, 90°C, 4 h, N ₂	92–100	Not given
PVDF	19	0.5M ClSO ₃ H, room temperature, 24 h	95	Mass increase

^a IEC = 1.7 meq g⁻¹ for DOG = 30.

of irradiation dose, more and more radicals are formed in the grafting system; therefore, the number of "efficient" active radicals that directly take part in the grafting reaction increases correspondingly. Especially, the number of radicals on the PTFE matrix is also increased. Consequently, more radicals are available for the grafting reaction. As a result, the DOG increases.

On the other hand, the DOG is controlled by the diffusion of the monomer to some extent. At the same dose rate, the increase in radiation dose means a longer reaction time, which enables bulk monomer to diffuse to the reaction sites, and hence, leads to an increasing DOG. These results are in a good agreement with the results obtained by Rouilly *et al.*¹¹ and Gupta *et al.*¹² upon the grafting of styrene onto FEP by simultaneous and preirradiation methods, respectively. They also observed that the DOG increases with the increase in the irradiation dose. However, in simultaneous techniques, relatively lower doses are required to achieve the specific grafting yield comparable to preirradiation.

The effect of dose rates ranging from 0.25 to 5.0 kGy h⁻¹ on the DOG under different styrene concentrations in dichloromethane are shown in Figure 4. On the whole, it was shown that the DOG decreased with the increase in the dose rate. In the case of a high dose rate, the formed radicals tend to decay by recombination, resulting in a high chance for homopolymer formation leading to a considerable increase in the viscosity of the grafting mixture, and as a result, the diffusion of the styrene monomer through the grafted layers to the internal grafting layers is hampered to a remarkable extent. Furthermore, PS growing chains are subjected to a fast termination or degradation whereas the termination by a combination of two growing grafted chains is hindered somewhat. Consequently, short side-chain grafts are formed, and hence, the DOG is decreased.

In contrast, irradiation at a low dose rate gives an adequate time for radicals to survive and react with the monomer molecules and reduces the chance for homopolymer formation, and as a result, the diffusibility of the monomer to the internal layers is en-

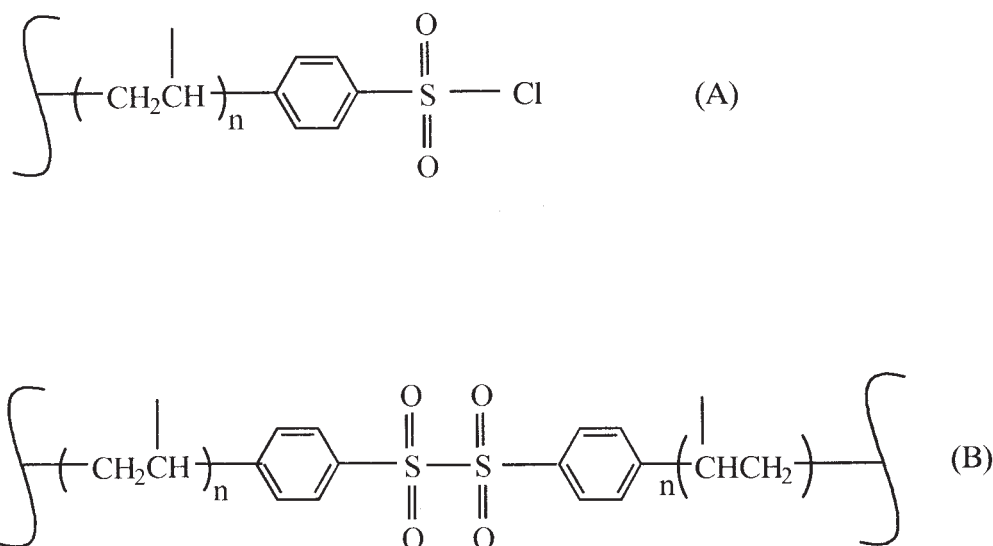


Figure 6 Schematic structure of the most probable by-products of sulfonation. (a) sulfonyl chlorides and (b) crosslinking by sulfone formation.

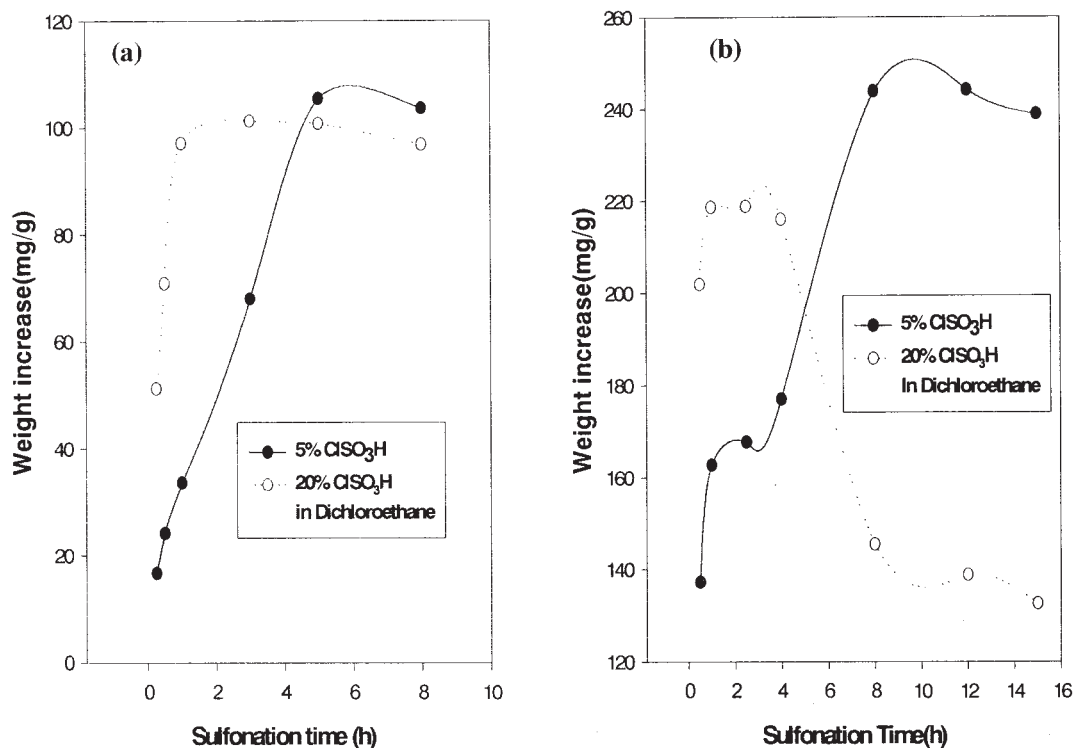


Figure 7 Relationship between the weight increase and the sulfonation time. Sulfonation was conducted in different concentrations of chlorosulfonic acid diluted by dichloroethane at ambient temperature; the degree of grafting of the films tested are 10.76% (a) and 47.38% (b), respectively.

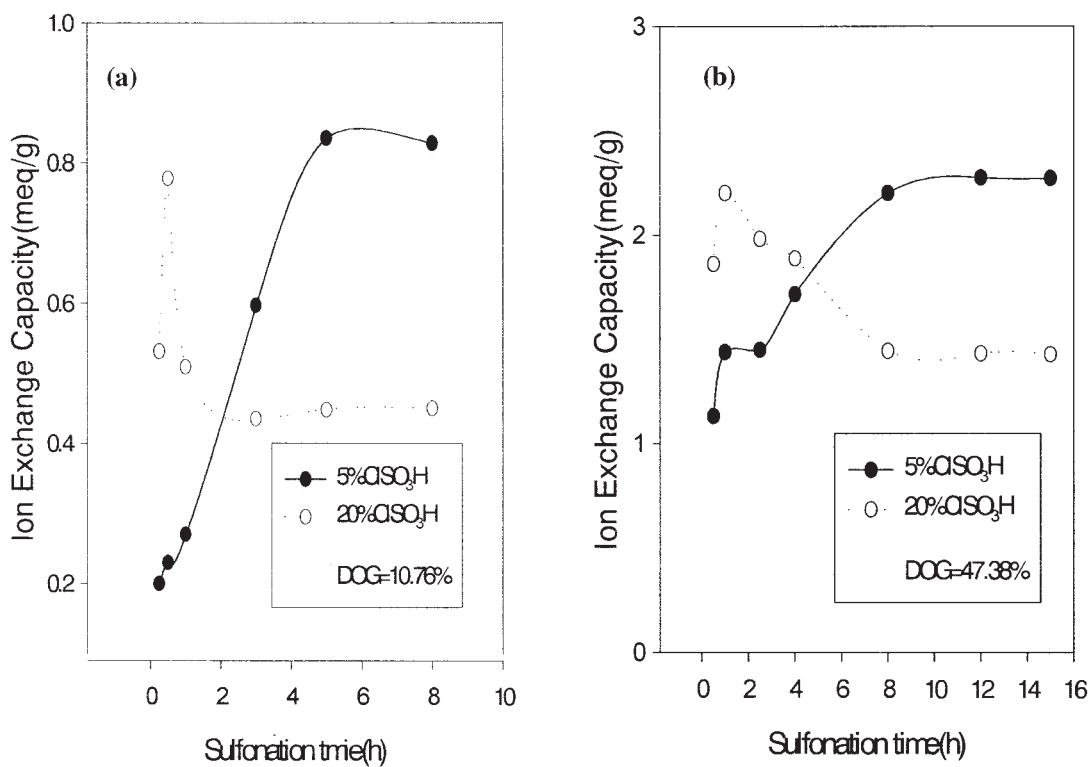


Figure 8 Relationship between the IEC and the sulfonation time. Sulfonation conditions were the same as in Figure 7.

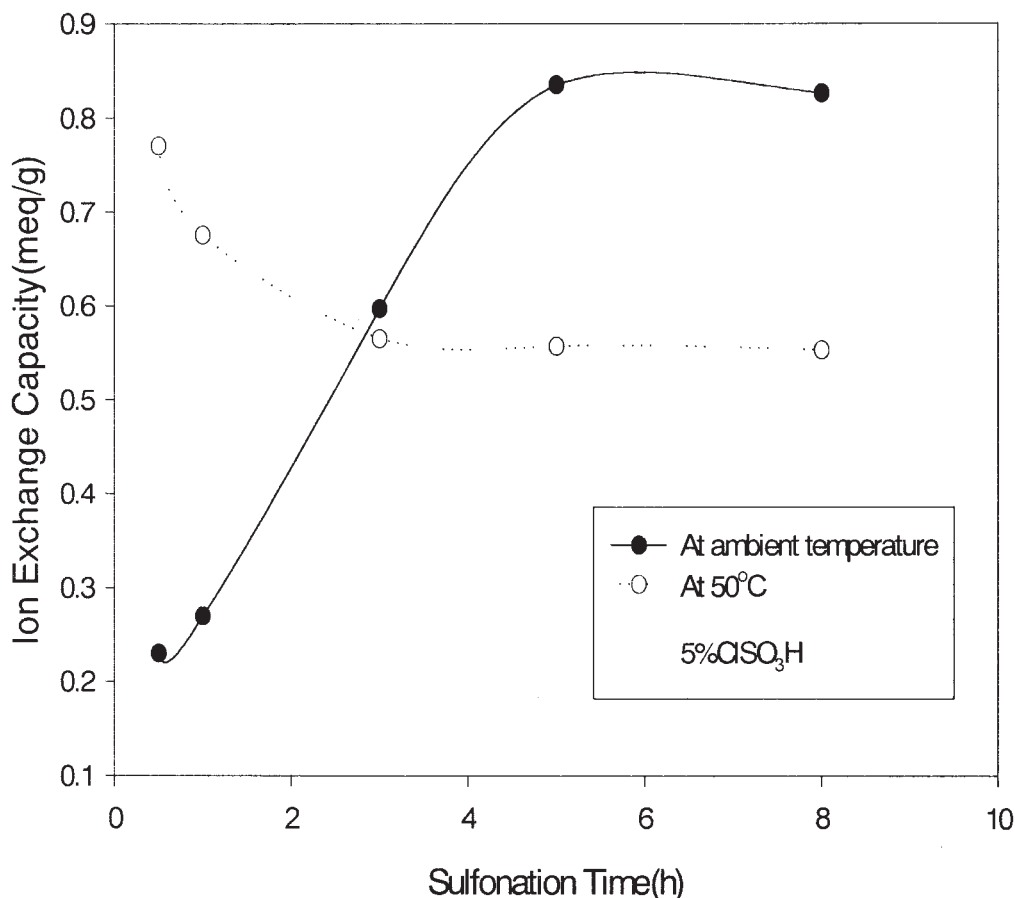


Figure 9 Effect of temperature on sulfonation of PTFE-g-PS films. Sulfonation agent, 5% ClSO_3H in dichloroethane; degree of grafting of PTFE-g-PS, 10.76%; and sulfonation temperatures, ambient and 50°C.

hanced. Hence, an increase in PS growing chains and a high DOG would be obtained. The above results suggest that low dose rates are favorable in the irradiation of polymer films, particularly in simultaneous irradiation where homopolymer formation is most likely to be encountered.

It is worthy to note that, although the DOG is generally decreased with the increase of dose rate, the decreasing rate is quite different between various styrene concentrations. The DOG decreased faster in high styrene concentration than in low ones, as dose rate increases. For instance, at the dose rate of 0.25 kGy h^{-1} , DOG in 70% styrene in dichloromethane was nearly the highest one; however, at the dose rate of 0.85 kGy h^{-1} and above, it became the lowest one. This result suggests that the dose rate has some influence on the optimum styrene concentration.

Figure 5 shows the effect of the styrene concentration on the DOG of the styrene onto 80- μm PTFE films at different dose rates and various absorbed doses. In all the cases, the DOG increased with the styrene concentration at first, till a certain concentration. After that, the DOG reached the highest value, and thereafter, the DOG decreased with the increase of the sty-

rene concentration. This grafting behavior in the present systems can reasonably be attributed to the increase in the styrene diffusion and its concentration in the grafting layers. As the styrene concentration in the grafting mixtures further increases, homopolymer formation is enhanced and diffusion of the styrene is hindered. As a result, the final DOG falls down sharply.

This result demonstrates that the grafting process of styrene onto PTFE is controlled to a great extent by diffusion, which suggests that grafting proceeds by a front mechanism. Grafting starts at the surface of the film and proceeds internally toward the middle of the film by a continuous diffusion of the styrene through the already grafted layers, till equilibrium swelling is reached at a certain monomer concentration.

It is very important to note that the optimum styrene concentration is not fixed, but different at different dose rates. For example, a 60% styrene/dichloromethane mixture gave the highest DOG at the dose rate of 0.85 kGy h^{-1} (Fig. 5(a)), whereas the optimum styrene concentration changed to 50% (v/v) at a dose rate of 1.25 kGy h^{-1} (Fig. 5(b)). At a low dose rate, the formed radical is able to survive for enough time to

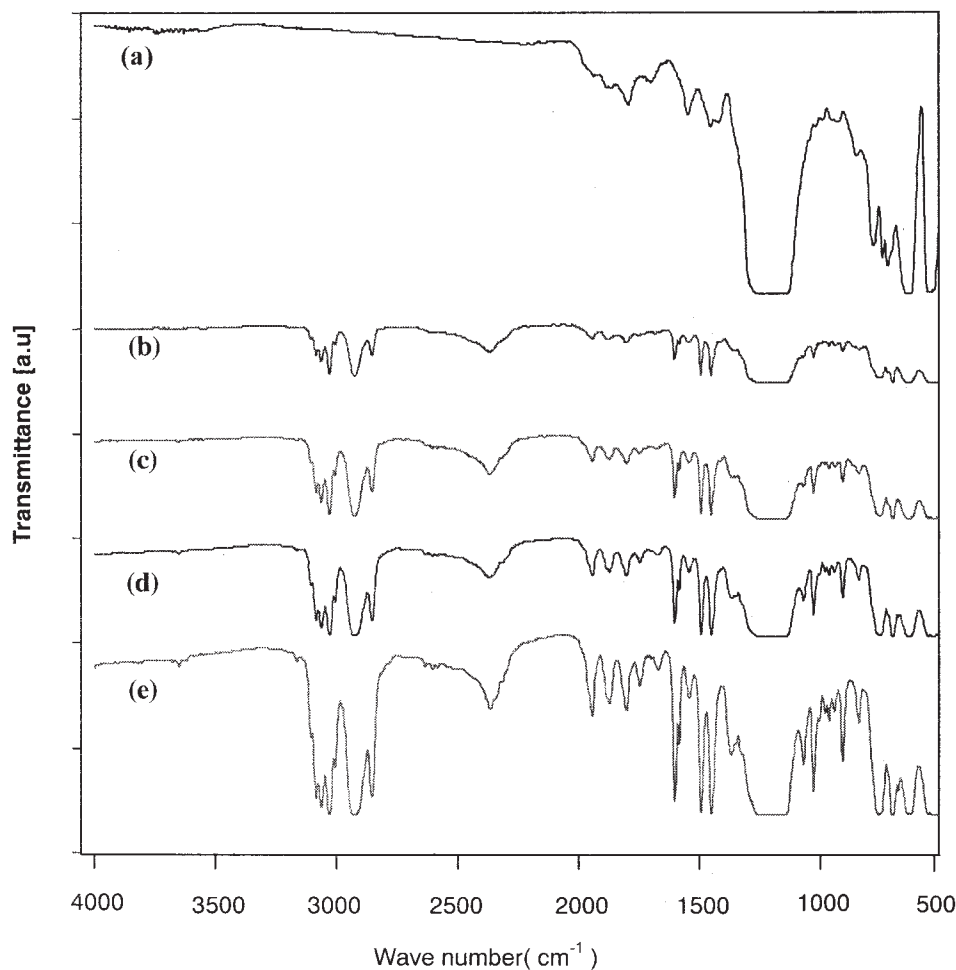


Figure 10 FTIR-ATR spectra of virgin PTFE (a) and grafted PTFE-g-PS films having various degrees of grafting: (b) 12.27%, (c) 21.89%, (d) 38.92%, and (e) 59.06%.

react with the monomer molecules, and the homo polymer formation is hindered. Therefore, the diffusibility of the monomer to the internal layers is smooth. Hence, an increase in PS is favorable. At elevated dose rates, however, the chance of homo polymer formation increased a lot due to the larger concentration of the formed radicals. Therefore, a higher concentration of styrene would give a greater possibility of homopolymer, and hence, result in the increase in viscosity of the grafting solutions and block the styrene diffusion. Therefore, the optimum styrene concentration changes from 60% to 50% (v/v), as the dose rate increases from 0.85 to 1.25 kGy h⁻¹. Thus, it can be concluded that the optimum styrene concentration varies with the dose rate, which is quite different from the results of other researchers.¹³⁻¹⁵

Sulfonation

The sulfonation of PS is a common procedure in the manufacture of exchange materials, membranes, and plasticizers, for which chlorosulfonic acid is a very

common and effective sulfonating agent. In addition, oleum, sulfur trioxide, and acetyl sulfate are used for mild sulfonation. The —SO₃H is added to the aromatic ring by electrophilic substitution.

Most researchers tend to state that full sulfonation, *i.e.*, one sulfonic acid group per aromatic ring, is achieved. But the extent of sulfonation can vary considerably with the conditions of the sulfonation reaction. Some examples of different approaches^{11,16-19} are listed in Table II. The influence of the experimental parameters for sulfonation of PTFE-g-PS has not been investigated in detail. To determine the influence of the reaction conditions on the properties of the membrane, the effects of the reaction time, temperature, and chlorosulfonic acid concentration as well as the DOG were investigated in chlorosulfonic acid/dichloroethane solutions, in this experiment. The key properties monitored were the IEC, the water uptake, and the conductivity.

Several side reactions can occur, notably the formation of sulfonyl chlorides and crosslinking by sulfone formation, as shown in Figure 6. The reaction mecha-

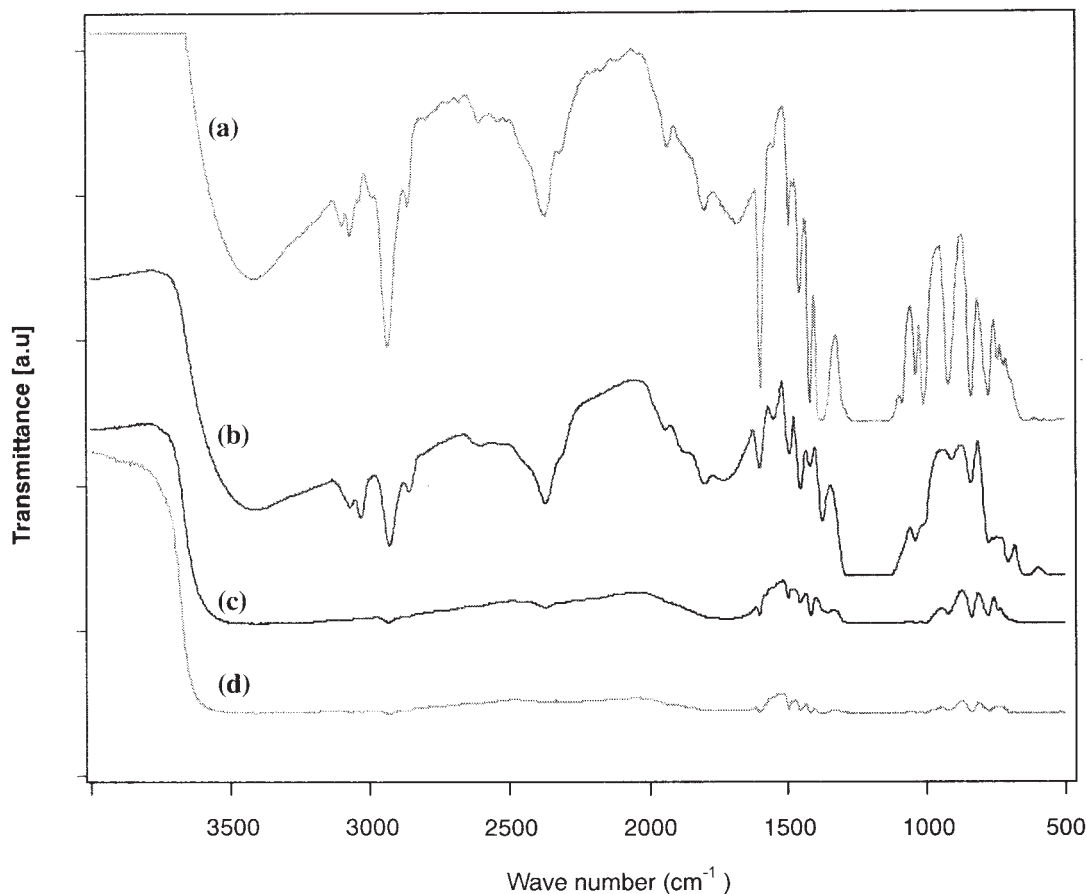


Figure 11 Typical FTIR-ATR spectra of PTFE-g-PSSA films having various degrees of grafting: (a) 19.88%, (b) 30.29%, (c) 58.04%, and (d) 75.32%.

nisms are assumed to be similar to those reported for the sulfonation of PS and nonpolymeric aromatic compounds.

As mentioned earlier, many research groups reported their sulfonation results according to the weight increase. Therefore, at first, we also investigated the weight increase tendency during the sulfonation. Figure 7 shows the relationship between the weight increase and the sulfonation time in different concentrations of chlorosulfonic acid. The DOG of the films tested are (a) 10.76% and (b) 47.38%, respectively. The weight increase caused by the substitution of hydrogen onto the benzene ring for the sulfonic acid group was accelerated at the first stage of sulfonation, because the sulfonation reaction proceeds by a reaction front mechanism, with grafts on the surface sulfonating first and gradually extending to the inner part of the PTFE-g-PS membrane. The maximum weight was reached after most of the styrene aromatic ring was sulfonated, and almost kept this value later on. This is true for membranes of a relatively low DOG (Fig. 7(a), 10.67% for example), where sulfone formation is relatively small. However, for a high DOG of the membrane, as shown in Figure 7(b), sulfonation in

5% chlorosulfonic acid gave the same trend as expected. However, the sulfonated weight in 20% chlorosulfonic acid dropped down quickly after the maximum weight increase was reached. This phenomenon can be explained by considering the side reactions such as the degradation of the graft chains and the sulfone formation caused by the crosslinking of the two moieties of sulfonated PTFE-g-PS, as demonstrated in Figure 6(b).

Obviously, the use of the high concentrations of chlorosulfonic acid shortens the time necessary for full sulfonation. However, at high concentrations, the maximum weight by sulfonation (Fig. 7), IEC (Fig. 8), and water uptake decrease with the concentration. The samples also become more fragile.

IEC is a very important parameter for a membrane in a fuel cell. As can be seen from Figure 7(b), when some side reactions happen, a certain amount of the functional group cannot make any contribution to the IEC. In this case, to estimate the DOS by measuring the weight increase after the sulfonation reaction is apparently improper. We investigated the influence of the sulfonation conditions on the IEC of PTFE-g-PS films. Figure 8 shows the relationship between the IEC and

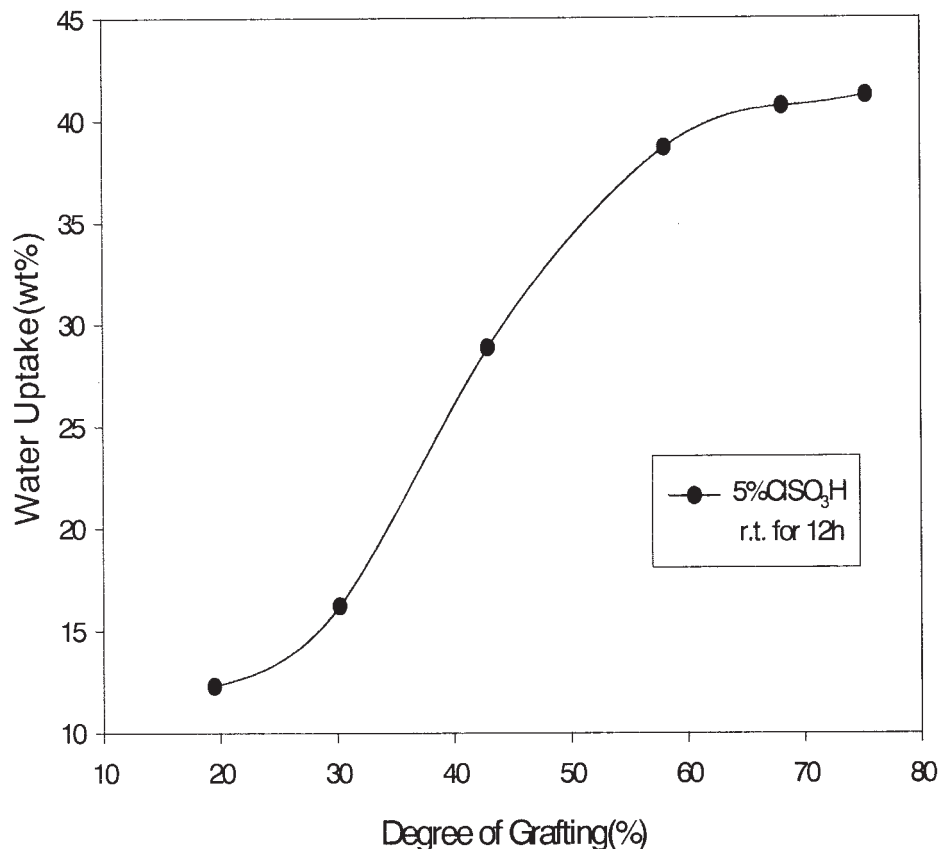


Figure 12 Water uptake at room temperature for PTFE-g-PSSA membranes sulfonated in 5% ClSO_3H /dichloroethane for 12 h, as a function of their degree of grafting.

the sulfonation time in different concentrations of chlorosulfonic acid; the other conditions are similar to Figure 7. When the sulfonation was conducted in 5% chlorosulfonic acid, the highest IEC was obtained at about 10 h, which is 92–100% of the theoretical IEC calculated from the DOG. However, when the sulfonation was conducted in 20% chlorosulfonic acid, the IEC reached its maximum value within 2 h and then dropped down quickly, and only ~50% of its theoretical IEC was obtained. Moreover, the maximum IEC was about 15% smaller than those of the samples of sulfonated in 5% chlorosulfonic acid, although the high concentration of ClSO_3H enhanced greatly the rate of sulfonation reaction.

Figure 9 shows the influence of temperature on the sulfonation of the PTFE-g-PS films with a DOG of 10.76% in 5% ClSO_3H /dichloroethane. Obviously, an elevated temperature drastically increased the sulfonation reaction speed, and in a quite short time, the maximum IEC could be obtained. Unfortunately, a high temperature also induced the side reaction, leading to a low IEC. Especially, for samples with a higher DOG, the obtained IECs were far less than their theoretical values.

On the basis of the above discussion, it could be concluded that 5% chlorosulfonic acid in dichloroeth-

ane and at an ambient temperature were probably the most suitable conditions for the sulfonation of PTFE-g-PS membranes.

Characterizations

FTIR-ATR spectra of the virgin and grafted PTFE films with various DOGs from about 10% to 60% are shown in Figure 10. The characteristic bands at $1150\text{--}1250\text{ cm}^{-1}$ are assigned to the stretching vibration of the —CF_2 groups present in the original PTFE film. The presence of the benzene rings of the PS grafts is confirmed by the =C—H stretching vibration at 3050 cm^{-1} and the skeletal C=C in-plane and stretching vibrations at 1500 and 1600 cm^{-1} , respectively. The absorption bands at $2800\text{--}2900$ and $2900\text{--}3000\text{ cm}^{-1}$ are assigned to the symmetric and asymmetric stretching of the aliphatic groups (—CH_2), respectively. The monosubstitution of the benzene ring is confirmed by the aromatic out-of-plane C—H deformation band at 860 cm^{-1} , C—H out-of-plane bending vibration and the combination band patterns in the $1660\text{--}2000\text{ cm}^{-1}$ region. It is clear that the features of the spectra of the grafted films confirm the successful grafting of the styrene onto the PTFE backbone. The variation in the intensity of PS characteristic bands reflects the differ-

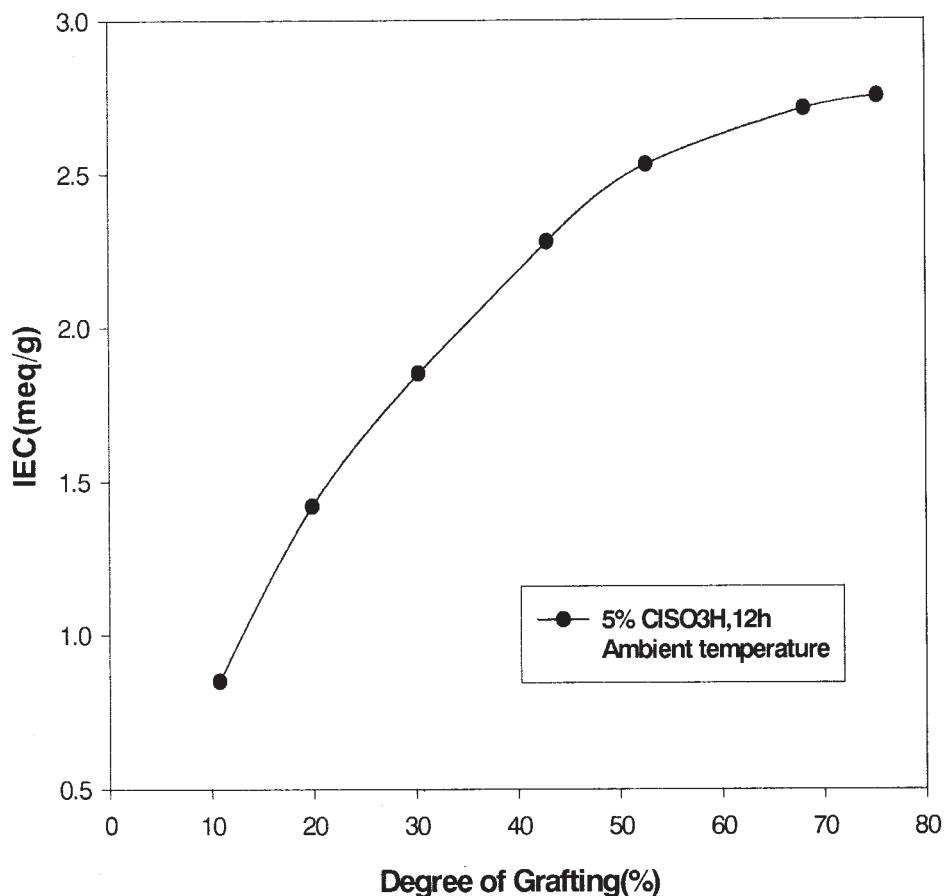


Figure 13 IECs of PTFE-g-PSSA membranes sulfonated in 5% ClSO_3H /dichloroethane.

ence in the DOGs, and all the IR absorption peaks correspondingly become strong with the increase of the DOG.

Figure 11 shows the typical FTIR-ATR spectra of PTFE-g-PSSA films having various DOGs. Compared with Figure 10, the newly appeared broad absorption bands at $3400\text{--}3500\text{ cm}^{-1}$ are attributed to the stretching vibration of the hydroxyl —OH group that comes from the sulfonic acid group $\text{—SO}_3\text{H}$, which verifies the sulfonation. Furthermore, the vibration band at 860 cm^{-1} , which is characteristic of the monosubstitution of the benzene ring has disappeared.

In Figure 12, the water uptake of the PTFE-g-PSSA membranes is presented as a function of the DOG. The water uptake in terms of weight was found to increase steeply with the increase in the DOG. The absorbed water content increased from 8.86% to 56.9%, as the DOG of the membrane increased from 10.76% to 75.32%. This is attributable to the increase in the hydrophilicity of the membranes that results from the incorporation of more sulfonic acid groups with the increase of the DOG. The increase in the content of the sulfonated PS side-chain grafts leads to a decrease in the fluorinated domain (PTFE) in the membranes, and as a result, the hydrophobicity of the membrane decreases.

The water uptake pattern was consistent with successive steps in the hydration of the membrane described by Davis *et al.*,²⁰ in the dry state. The counter ions are tightly bound to the sulfonate groups. Water first solvates the fixed ionic groups and counter ions. When more water is absorbed, the polymer swells, and the hydrophilic zones start to resemble an aqueous electrolyte.

Figure 13 shows the relationship between the IEC and the DOG of the membranes at room temperature. The results show that the IEC increases as the DOG increases. This is due to the increase in the amount of sulfonic acid groups followed by the increase in the water uptake. This can be explained by taking into account the amount of sulfonic acid groups responsible for the ion exchange and the water uptake in the sulfonated membrane. As the DOG increased, more and more PS is introduced to the PTFE film and the equivalent sulfonic acid accordingly is incorporated. However, due to some repulsion forces existing between the condensed sulfonic acid groups at a high DOG, the water uptake tends to reach a saturated content. As a result, the IEC tends to level off.

It can be seen that, with a DOG being only 10.76%, the IEC of the PTFE-g-PSSA reaches 0.85 meq g^{-1} , which is nearly the same as 0.89 meq g^{-1} of Nafion 117. Almost all the samples investigated with a DOG from 10.76% to

TABLE III
Properties of Prepared PTFE-*g*-PSSA Membranes

DOG (%)	Thickness (μm)		Water uptake (%)	IEC (meq g^{-1})	DOS (%)
	Dry	Wet			
10.76	95	99	8.86	0.85	96.07
19.88	100	103	13.3	1.42	100
21.70	101	105	14.6	1.56	100
30.29	111	115	22.69	1.85	97.08
42.91	120	145	28.82	2.28	97.30
52.65	125	155	39.68	2.53	96.72
68.12	128	158	48.80	2.71	91.04
75.32	130	160	56.90	2.75	88.18
Nafion 117 ^a	180	210	37.00	0.89	—

^a Reference polymer.

75.32% had a higher IEC than Nafion 117. As high as 2.75 meq g^{-1} IEC was obtained in this work.

The properties of the as-prepared PTFE-*g*-PSSA membrane are summarized in Table III. The corresponding values of the Nafion 117 membranes from the references are also listed in Table III for comparison. As can be seen, the PTFE-*g*-PSSA membranes prepared in this work show a good combination of a high IEC (0.85–2.75 meq g^{-1}), acceptable water uptake (8.86–56.9 wt %), low thickness, and volume expansion and/or contraction.

CONCLUSIONS

PS-grafted and sulfonated membranes prepared by radiation-induced grafting of styrene onto PTFE films and the subsequent sulfonation in chlorosulfonic acid/dichloroethane were investigated. The properties of the PTFE-*g*-PSSA membranes were affected by not only the radiation grafting conditions but also the sulfonation conditions.

In the radiation grafting process, all the factors, such as the type of solvent, irradiation dose, dose rate as well as the styrene concentration, *etc.* affected the DOG. Of the investigated solvents, dichloromethane was the best one. The DOG linearly increased with irradiation dose, but decreased sharply with the dose rate. Systematic studies of the sulfonation of PTFE-*g*-PS films conducted by our group demonstrated that 5% ClSO_3H in dichloroethane at an ambient temperature for 12 h was the optimum conditions and it was valid for all the DOGs of the PTFE-*g*-PS films. Although the increase in the concentration of ClSO_3H and the reaction temperature promoted the sulfonation markedly, they also induced the side reactions, which could deteriorate the properties of the sulfonated membranes.

The water uptake of the PTFE-*g*-PSSA membranes was found to increase with an increase in the DOG. The absorbed water content increased from 8.86% to 56.9% as the DOG of the membrane increased from 10.76% to 75.32%, due to the increase in the hydrophi-

licity of the membranes. The IECs of the PTFE-*g*-PSSA membranes increased from 0.85 to 2.75 meq g^{-1} as the DOG increased from 10.76% to 75.32%. Initially, the IEC showed a sharp increase, and at a certain DOG, it tended to level off. Almost all the samples with a DOG from 10.76% to 75.32% had higher IECs than Nafion 117. As high as 2.75 meq g^{-1} IEC was obtained in this work.

The prepared PTFE-*g*-PSSA membranes in this work showed a good combination of a high IEC (0.85–2.75 meq g^{-1}), acceptable water uptake (8.86–56.9 wt %), low thickness, and volume expansion and/or contraction. PTFE-*g*-PSSA membranes prepared in this work had quite good properties, which could make them promising candidates of a PEM for a fuel cell.

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