

Cation Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene onto PFA Copolymer Films. I. Preparation and Characterization of the Graft Copolymer

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ABSTRACT: PFA-*g*-polystyrene graft copolymers were prepared by simultaneous radiation-induced graft copolymerization of styrene onto poly(tetrafluoroethylene-*co*-perfluorovinyl ether) (PFA) films. The effects of grafting conditions such as monomer concentration, dose, and dose rate were investigated. Three solvents, i.e., methanol, benzene, and dichloromethane, were used as diluents in this grafting system. Of the three solvents employed, dichloromethane was found to greatly enhance the grafting process, and the degree of grafting increased with the increase of monomer concentration until it reached its highest value at a styrene concentration of 60 (vol %). The dependence of the initial rate of grafting on the monomer concentration was found to be of the order of 1.2. The degree of grafting was found to increase with the increase in irradiation dose, while it considerably decreased with the increase in dose rate. The formation of graft copolymers was confirmed by FTIR analysis. The structural investigation by X-ray diffraction (XRD) shows that the degree of crystallinity content of such graft copolymers decreases with the increase in grafting, and consequently, the mechanical properties of the graft copolymers were influenced to some extent. Both tensile strength and elongation percent decreased with the increase in the degree of grafting. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 73: 2095–2102, 1999

Key words: radiation-induced graft copolymerization; styrene; PFA copolymer films; cation exchange membranes

INTRODUCTION

Much effort has been devoted to develop cation exchange membranes by radiation-induced graft copolymerization techniques.^{1–6,8–23} The attractiveness of these techniques arises from the abil-

ity to introduce desirable properties to a preexisting polymer without altering its bulk properties.¹ Moreover, they offer the ability to closely control the graft copolymer compositions and properties by the selection of suitable grafting conditions.²

Cation exchange membranes can be prepared by graft copolymerization of different hydrophilic monomers onto hydrophobic base polymers.³ The grafting monomers fall into two categories; functionalized monomers such as acrylic acid, and nonfunctionalized monomers such as styrene. The

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grafting of acrylic monomers directly confers a weakly acidic character to the polymer backbone, while grafting of vinyl monomers leads to graft copolymers that have to be functionalized in a subsequent step. Sulfonation is the most common process to confer the graft copolymer strongly acidic character. The base polymer may be hydrocarbon polymers such as polyethylene (PE) or fluorine-containing polymers such as polytetrafluoroethylene (PTFE).^{4,5} However, fluorine-containing polymers have drawn much attention and are extensively used as base polymers for the preparation of cation exchange membranes owing to their excellent thermal, chemical, and mechanical properties compared to hydrocarbon polymers.⁷ To date, many studies have been published on the development of cation exchange membranes by radiation grafting of styrene and its derivatives such as α,β,β -trifluorostyrene and α -methylstyrene onto fluorinated polymers such as polytetrafluoroethylene (PTFE),^{5,6} copolymer of tetrafluoroethylene-hexafluoropropylene (FEP),⁸⁻¹¹ polyvinylidene fluoride (PVF),^{12,13} and copolymer of ethylene-tetrafluoroethylene (ETFE).¹⁴⁻¹⁶ However, to our knowledge, no detail studies on radiation grafting of styrene onto PFA have been made. Therefore, in the present study we report the simultaneous radiation-induced graft copolymerization of styrene onto PFA copolymer films under various grafting conditions.

EXPERIMENTAL

Materials

A PFA film of 120 μm thickness (Porchorf, USA) was used as a base polymer. Styrene of purity more than 99% (Fluka) was used without any further purification. Other chemicals were reagent grades and used as received.

Graft Copolymerization

The PFA film was cut into pieces ($5 \times 5 \text{ cm}^2$), washed with acetone, and then dried in a vacuum oven at 60°C to constant weight. The dried film was immersed into a known volume of monomer solution in a glass ampoule. The solution was flashed with nitrogen for 8 min to remove the air, then the ampoule was sealed. The ampoule was subjected to γ -rays from a ^{60}Co (Bhabha Atomic Research Center, Bombay, India) at dose rates ranging from 0.37 to 4.17 Gy/s. After irradiation,

the film was washed with methyl benzene and soaked therein over night to remove the residual monomer and homopolymer occluded in the film. The grafted film was dried in the vacuum oven at 60°C until a constant weight was obtained. The degree of grafting was gravimetrically determined as the percentage of weight increase of the PFA film using the following equation:

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

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

FTIR-ATR Measurements

FTIR-ATR measurements of original and grafted PFA films were carried out with an FTIR Spectrometer (Mattson, 6020-Galaxy Series) at ambient conditions in the transmittance mode. The spectra of the films were detected by an ATR accessory equipped with a KRS5 crystal that has a crystal face angle of 45° and refractive index of 2.38.

X-ray Diffraction Measurements

X-ray diffraction (XRD) measurements were made using an X-ray diffractometer (Philips, PW 1830). The diffractograms were measured at 2θ , 5 – 50° using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54$) monochromated by means of a Nickel filter.

Mechanical Properties Measurements

Dumbbell-shaped specimens of 50 mm long with a neck of 28 and 4 mm wide (ASTM D882) were used. The measurements of tensile strength and elongation percent at break point were recorded on an Instron (model 4301, UK) at room temperature. The crosshead speed was fixed at 50 mm/min. A minimum of five specimens was tested for each sample.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

Figure 1 shows the relationship between the degree of grafting and irradiation time at various styrene concentrations in nitrogen atmosphere. As can be seen, the degree of grafting increases with the irradiation time for all styrene concen-

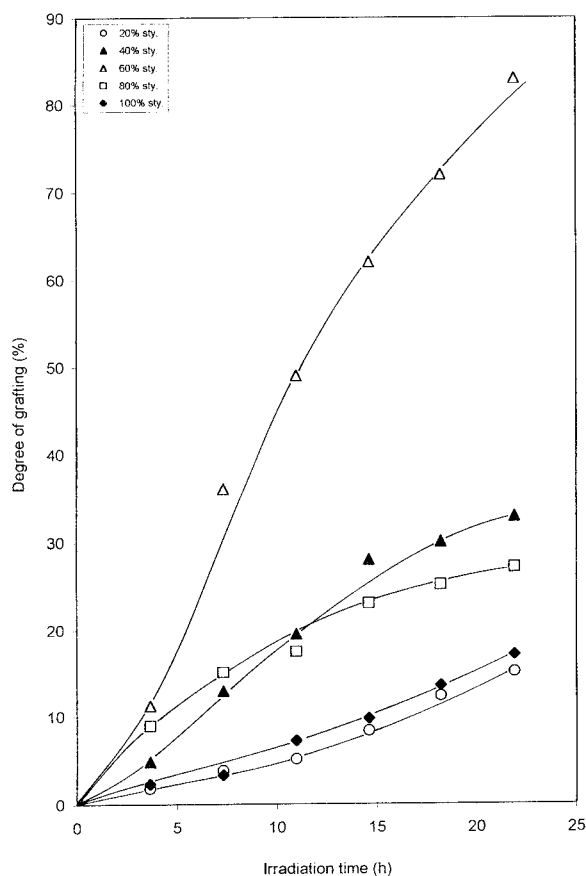


Figure 1 The degree of grafting–time curves at various styrene concentrations (20–100 vol %), in dichloromethane as a diluent, in nitrogen atmosphere, at room temperature, and at a total irradiation dose of 20 kGy.

trations, and tends to level off at longer irradiation time. Moreover, the degree of grafting increases as styrene concentration increases from 20 up to 60 vol %. However, above 60 vol % the degree of grafting falls sharply. This phenomenon is most likely attributed to the increase in the viscosity of the grafting mixture due to homopolymerization, then followed by a reduction in the diffusibility of styrene and its concentration in the grafting layers. The relationship between the initial rate of grafting as well as the final degree of grafting and styrene concentration is shown in Figure 2. Both the initial rate of grafting and final degree of grafting increase with styrene concentration up to 60 vol %, and sharply drop at higher styrene concentration. The dependence of the initial rate of grafting on the styrene concentration (20–60 vol %) was obtained from the slope, and found to be of the order of 1.2.

These results suggest that the degree of grafting of styrene onto PFA films not only depends on the amount of trapped radicals but also on the diffusibility of styrene through the polymer matrix and its concentration in the grafting layers as well. The results also suggest that the grafting process starts at the surface of the film and proceeds internally by successive diffusion of the styrene until equilibrium swelling is reached at 60 vol % monomer concentration. The same trend was also obtained upon grafting of different monomers such as acrylic acid, methacrylic acid, and vinyl acetate onto PFA.^{17–19}

Effect of Irradiation Dose

Figure 3 shows the relationship between the degree of grafting and irradiation dose for the grafting of styrene (60 vol %) onto PFA films in dichloromethane at a dose rate of 0.37 Gy/s. Generally the degree of grafting increases with the increase in irradiation dose. This behavior could be explained on the basis of the fact that higher irra-

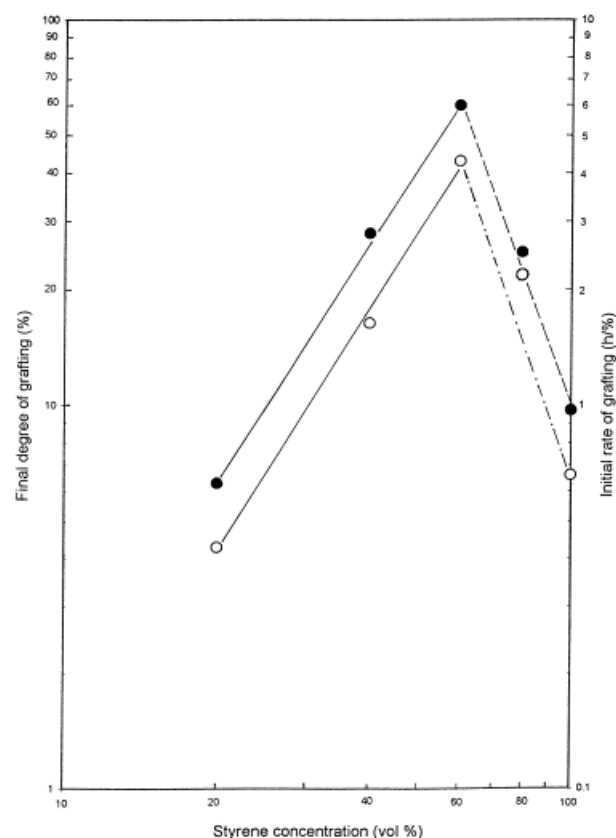


Figure 2 Logarithmic plot of the initial rate of grafting (○) and the final degree of grafting (●) vs. styrene concentration (vol %); the same conditions as in Figure 1.

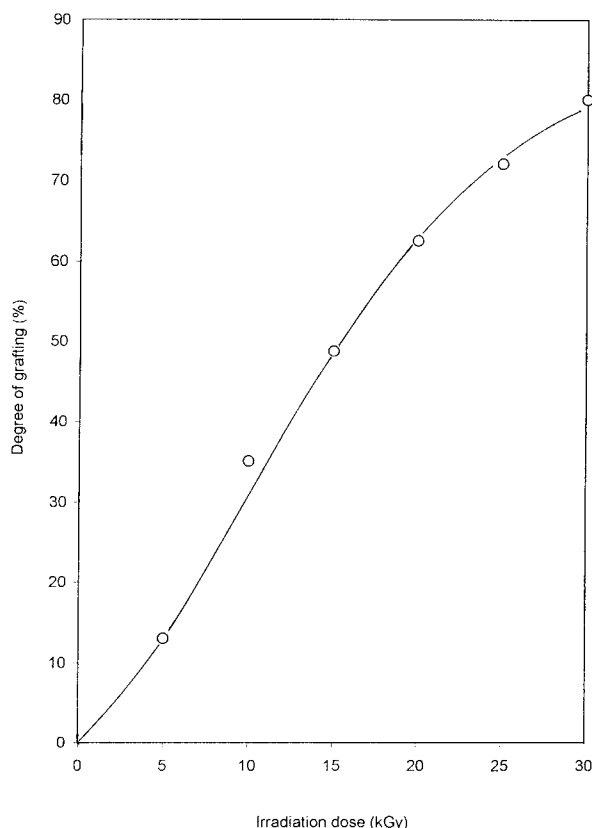


Figure 3 The degree of grafting (%) of styrene onto PFA vs. irradiation dose (kGy) at a dose rate of 0.37 G/s.

diation doses lead to more free radical formation in the grafting system; consequently, more radicals are available for the grafting reaction. Those results are in a good agreement with the results obtained by Rouilly et al.⁹ and Gupta et al.²⁰ upon grafting of styrene onto FEP by simultaneous and preirradiation methods, respectively.^{9,20} They also observed that the degree of grafting increases with the increase in the irradiation dose. However, in simultaneous techniques relatively lower doses are required to achieve the degree of grafting comparable to preirradiation.

Effect of Dose Rate

The effect of dose rates ranging from 0.37 to 4.17 Gy/s on the degree of grafting is shown in Figure 4. It can obviously be seen that the degree of grafting decreases with the increase in the dose rate, and vice versa. At 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. This is followed by significant decrease in styrene diffusibility to the internal grafting layers. Furthermore, polystyrene growing chains are subjected to fast termination and/or degradation; consequently, the degree of grafting is decreased. In contrast, irradiation at a low dose rate gives an adequate time for radicals to survive and react with monomer molecules, reduces the chance for homopolymer formation, and as a result, the diffusibility of the monomer to the internal layers is enhanced. Hence, an increase in polystyrene growing chains and in the overall degree of grafting takes place. The above results suggest that low radiation dose rates are favorable in the irradiation of polymer films, particularly in simultaneous irradiation where homopolymer formation is most likely encountered. Such an effect was properly discussed by Chapiro,²¹ with particular reference to grafting onto PTFE where this effect is severe, and by El-Assy,²³ with particular reference to enhance-

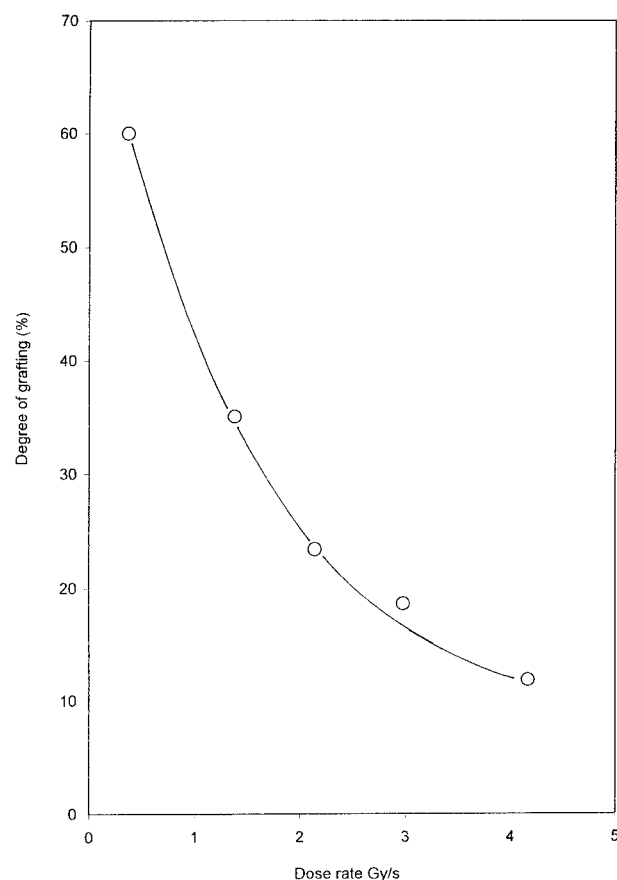


Figure 4 The degree of grafting (%) of styrene onto PFA vs. dose rate (G/s) at a total irradiation dose of 20 kGy.

Table I Effect of Various Diluents on the Degree of Grafting (%) of Styrene (60 vol %) onto PFA Films at an Irradiation Dose of 20 kGy

Diluent	Chain Transfer Constant (60°C) ²⁵	Degree of Grafting (%)	Remarks
Methanol	0.296	7.2	Much homopolymer formed
Benzene	0.2	11.8	Little homopolymer formed
Dichloromethane	0.15	60	No homopolymer formed

ment of grafting of styrene onto PE by acid addition.^{22,23}

Effect of Diluent Type

Diluent is basically used in radiation-induced graft copolymerization processes to bring about swelling of the base polymer, and hence enhance the degree of monomer accessibility to grafting sites. Therefore, the correct choice of diluent is one of the essential elements towards the success of the radiation-induced grafting process. The effect of three different diluents, i.e., methanol, benzene, and dichloromethane, on the graft copolymerization of styrene (60 vol %) onto PFA films in nitrogen atmosphere is shown in Table I. It can be clearly seen that the dilution of styrene with dichloromethane greatly enhances the degree of grafting compared to the dilution with methanol and benzene. This can be explained by taking into consideration the nature of the three solvents used to dilute the monomer as well as the solubility of polystyrene homopolymer in their grafting mixtures.^{1,24} The use of dichloromethane, which has a low chain transfer constant (0.15)²⁵ and electron acceptor in nature, caused a slow down in the termination of the polystyrene growing chains, and as a result, grafting yield was enhanced. A high chain transfer constant of an electron donor, methanol (0.296),²⁵ caused quick termination in growing chains, and consequently led to low level of grafting. The presence of a resonance stabilization effect of the benzene ring, which acts as an energy transfer agent, resulted in a low degree of grafting due to the consumption of energy of irradiation. A similar observation was reported by Al-Assy²³ upon using both benzene and toluene as diluents in the grafting of styrene onto PE films.

FTIR Measurements

Figure 5 shows FTIR spectra of the original and grafted PFA films. The original PFA film is char-

acterized by broad band at 1000–1400 cm⁻¹, which represents the stretching vibration of C—F, and a narrow sharp band at 1000–1150 cm⁻¹, which represents the stretching vibration of the C—O group of the alkoxy vinyl ether. The presence of a benzene ring of styrene in grafted PFA films is established by the =C—H stretching vibration at 3050 cm⁻¹ and the skeletal C=C in-plane stretching vibrations at 1500 and 1600 cm⁻¹. The monosubstitution of a benzene ring is confirmed by an aromatic out-of-plane C—H deformation band at 860 cm⁻¹ and by a C—H out-of-plane bending overtone and combination band

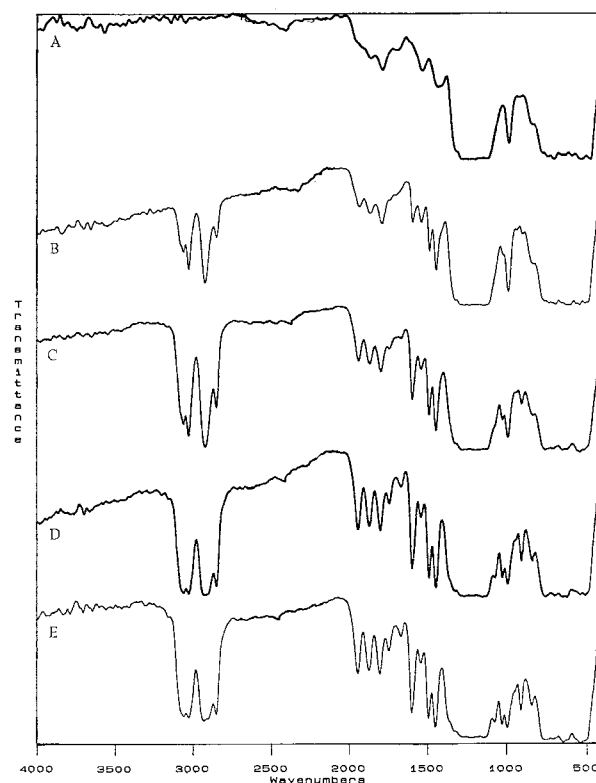


Figure 5 FTIR-spectra of original PFA (A) and polystyrene-grafted PFA films having various degrees of grafting: (B) 5%, (C) 16%, (D) 35%, and (E) 49%.

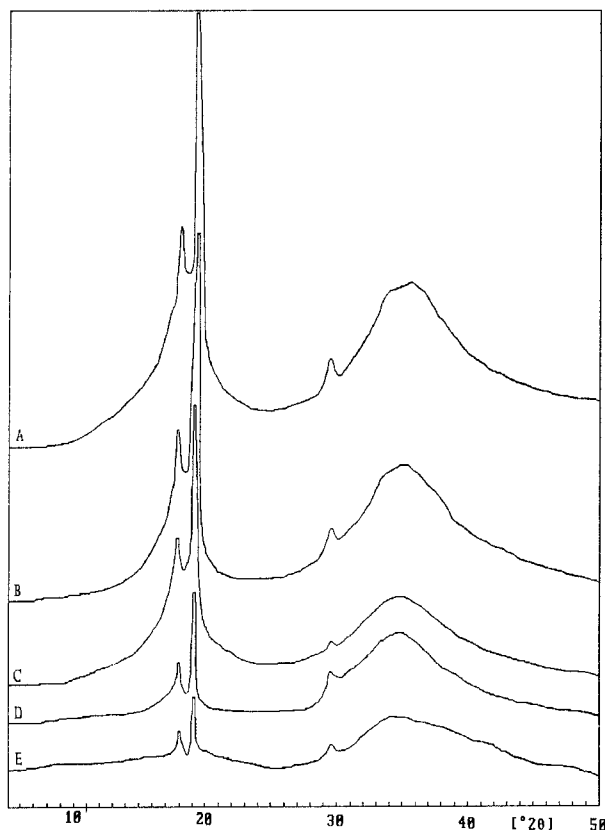


Figure 6 Diffraction patterns of original PFA (A) and polystyrene-grafted PFA films having various degrees of grafting: (B) 5%, (C) 16%, (D) 35%, and (E) 49%.

patterns in the region of $1660\text{--}2000\text{ cm}^{-1}$. The absorption bands at $2800\text{--}2900\text{ cm}^{-1}$ and $2900\text{--}3000\text{ cm}^{-1}$ are assigned to symmetric and asymmetric stretching of the CH_2 group, respectively. The spectra clearly indicate that all the bands arising from the presence of polystyrene increase with the increase in the degree of grafting. This means that polystyrene is successfully grafted to the PFA backbone.

X-ray Diffraction Measurements

The grafting of styrene onto FEP has been found to bring about considerable changes in the crystallinity of the graft copolymer.²⁴ The crystallinity was found to decrease with the increase in the degree of grafting. The decrease in crystallinity was found to be in the form of dilution of the inherent crystallinity by incorporation of amorphous polystyrene grafts and partial destruction of the inherent crystallinity in FEP film.^{26,27} X-ray diffraction measurements were carried out in this study to investigate the structural changes owing to the introduction of polystyrene grafts to the PFA film. Diffraction patterns of the original and grafted PFA films are shown in Figure 6. It was found that the crystallinity peak for the original and all grafted films occurs at the same angle (2θ), meaning that there is no change in the structure. However, the peak intensities of all grafted films are lower, and decrease with the increase in the degree of grafting. This means that the crys-

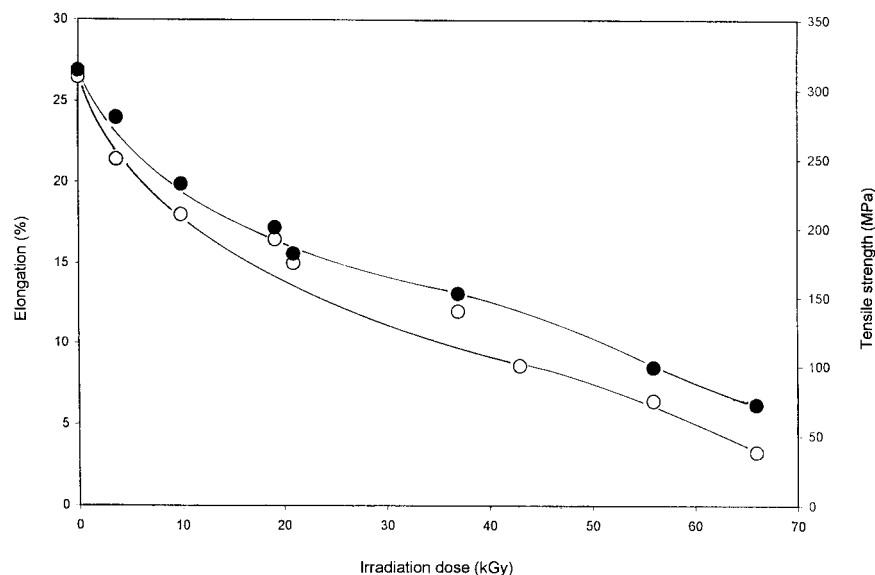


Figure 7 Tensile strength (○) and elongation percent at break (●) vs. irradiation dose for irradiated PFA films at a dose rate of 0.37 G/s.

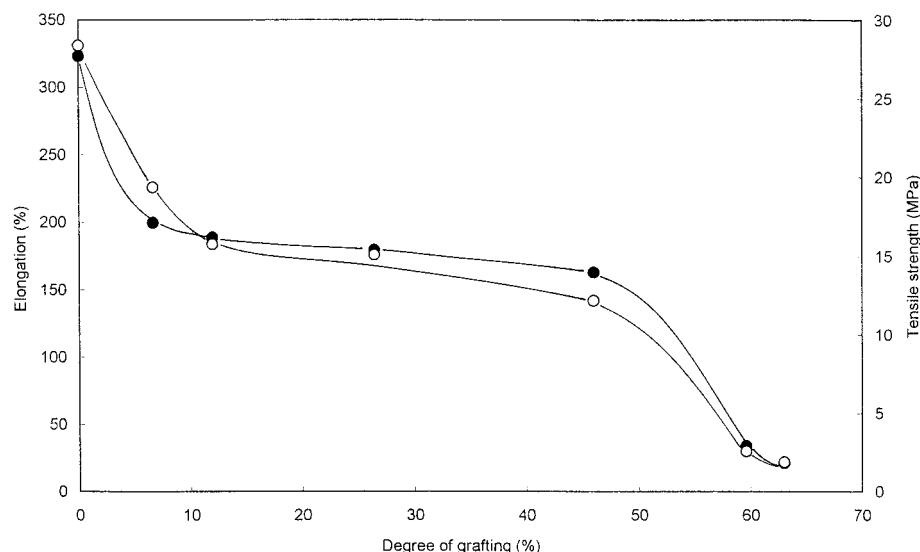


Figure 8 Tensile strength (○) and elongation percent at break (●) vs. degree of grafting (%) of PFA-g-polystyrene films.

tallinity content decreases with the increase in the degree of grafting. It can be noticed that these results are similar to those obtained upon grafting of styrene onto FEP,^{26,27} and hence, this behavior can also be explained on the bases of dilution and partial destruction of the inherent crystallinity.

Mechanical Properties

One of the requirements for grafted membranes is to exhibit mechanical properties accepted for practical use. Accordingly, the mechanical properties of the original and grafted PFA films were investigated. The influence of irradiation dose on the tensile strength and elongation percent at break for the PFA film is given in Figure 7. It was found that both tensile strength and elongation percent gradually decreases with the increase in the irradiation dose. The film shows good mechanical properties at low irradiation doses (less than 25 kGy), while it undergoes considerable degradation at higher irradiation doses. This may be due to the oxidative degradation of the film upon irradiation in air. These results suggest that PFA films are not recommended for the grafting processes that employ preirradiation in air where high irradiation doses are required. The changes in tensile strength and elongation percent at break for the PFA-g-polystyrene films were studied as a function of degree of grafting as shown in Figure 8. It can be noticed that the tensile

strength as well as the elongation percent also decreases with the increase in the degree of grafting. Such results were expected from the structural changes of the PFA film upon the introduction of the amorphous polystyrene grafts leading to the reduction in the crystallinity content of the grafted film with the increase in the degree of grafting. However, the grafted films show reasonable mechanical properties at degrees of grafting up to 40%. The results strongly suggests that PFA film is a potential base polymer to be used in the preparation of cation exchange membranes.

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