

Proton Exchange Membranes Prepared by Simultaneous Radiation Grafting of Styrene onto Poly(tetrafluoroethylene-co-hexafluoropropylene) Films. I. Effect of Grafting Conditions

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ABSTRACT: The simultaneous radiation grafting of styrene onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films was studied at room temperature. The effects of grafting conditions (type of solvent, irradiation dose, dose rate, and monomer concentration) were investigated. The degree of grafting was found to be dependent on the investigated grafting conditions. The dependence of the initial rate of grafting on the dose rate and the monomer concentration was found to be of 0.5 and 1.3 orders, respectively. The results suggest that grafting proceeds by the so-called front mechanism in which the grafting front starts at the surface of the film and moves internally toward the middle of the film by successive diffusion of styrene through the grafted layers. Some selected properties of the grafted films were evaluated in correlation with the degree of grafting. We found that the grafted FEP films possess good mechanical stability, which encourages their use for the preparation of proton exchange membranes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 220–227, 2000

Key words: radiation grafting; styrene; poly(tetrafluoroethylene-co-hexafluoropropylene) films

INTRODUCTION

Radiation grafting of polymers is a well-known technique for modification of the physical and chemical properties of polymers.^{1–3} Irradiation of polymers by means of ionizing radiation such as γ -rays induces the formation of radicals on the polymer main chain from which polymerization of another monomer can be initiated. Therefore, this technique makes it possible to bring together two highly incompatible polymers in one material

having combined properties. In recent years the amount of efforts devoted to use this technique for the preparation of various types of membranes significantly increased because it provides the ability to closely control the membrane compositions and properties by proper selection of the degree of grafting. Moreover, it overcomes the membrane shaping problem where grafting can be started with a film already in a membrane form. Fluorinated polymers are commonly used as base polymers to enhance the chemical stability of the membranes.^{4,5} Of the fluorinated polymers, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) is advantageous in terms of high radiation resistance, which provides the possibility for applying a wide range of irradiation doses.^{6,7} A number of studies were published on

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grafting of weak acids such acrylic acid onto FEP films.⁸⁻¹² Two groups studied the preparation of a proton exchange membrane by preirradiation grafting of styrene onto FEP followed by a sulfonation reaction.^{13,14} The content of the polystyrene contained in the membrane was found to be strongly dependent upon the grafting conditions. These membranes were also prepared by simultaneous irradiation grafting.¹⁵⁻¹⁷ However, details of the effects of the grafting conditions on the degree of grafting and the properties of the grafted FEP films were not revealed. In this work the effects of various grafting conditions on the degree of grafting of styrene onto FEP films by simultaneous irradiation were studied. Some selected properties of the grafted FEP films were investigated in correlation with the degree of grafting.

EXPERIMENTAL

Materials

A 120- μm thickness FEP film (Porghof) was used as a base polymer. Styrene of purity more than 99% (Fluka) was used as a grafting monomer without any further purification. Other chemicals were reagent grades and were used as received.

Grafting Procedure

The FEP film was cut into pieces ($5 \times 5 \text{ cm}^2$), washed with acetone, and then dried in a vacuum oven (10 mbar) at 60°C. The dried film was immersed into a styrene solution of known concentration placed in a glass ampoule. The grafting solution was bubbled with nitrogen for 8 min to create an inert atmosphere, then the ampoule was sealed. The ampoule was irradiated at ambient temperature using γ -rays from a Co 60 source at dose rates in the range of 1.32–15.00 kGy/h for the required period of time. The grafted film was removed, washed with methyl benzene, and soaked therein overnight to remove the residual monomer and homopolymer adhered to the film surface. The grafted film was dried in the vacuum oven at 80°C until a constant weight was obtained. The degree of grafting was gravimetrically determined as a percentage of the weight increase of FEP 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 the grafted and original FEP films, respectively.

Characterization of Grafted Films

The spectra of the original and grafted FEP films were measured by a Mattson 6020-Galaxy Series FTIR spectrophotometer at ambient conditions in transmittance mode. The spectra were detected by an attenuated total reflectance (ATR) accessory equipped with a KRS5 crystal having a crystal face angle of 45° and refractive index of 2.38.

The structural changes induced by styrene grafting were investigated by a Philips PW 1830 X-ray diffractometer. The diffractograms were measured at ambient temperature and 2θ in the range of 5–60° by means Cu-K α radiation ($\lambda = 1.54$) monochromated by means of a nickel filter.

The mechanical properties of the grafted films with respect to the tensile strength and the elongation percent at break were measured by an Instron model 4301. Dumbbell-shaped specimens of 50-mm length with a neck of 28- and 4-mm width (ASTM D882) were tested at ambient temperature and a crosshead speed of 50 mm/min. A minimum of five specimens were tested for each sample.

RESULTS AND DISCUSSION

Effect of Grafting Conditions

The degree of grafting–time curves for styrene diluted with methanol, benzene, and dichloromethane solvents is shown in Figure 1. It can be clearly seen that the degree of grafting obtained upon using dichloromethane as a solvent is much higher than those obtained upon using methanol and benzene. The behavior of the three solvents is quite similar to that obtained upon grafting of styrene onto PFA films.¹⁸ These results can be explained by taking the nature of the three solvents and the solubility of the polystyrene homopolymer in styrene/methanol, styrene/benzene, and styrene/dichloromethane grafting solutions into consideration.

Dilution of styrene by dichloromethane, which has a low chain transfer constant¹⁹ (0.15) and is an electron acceptor in nature, slows down the termination of the polystyrene growing chains. This is accompanied by complete solubility of the polystyrene homopolymer, which might be formed

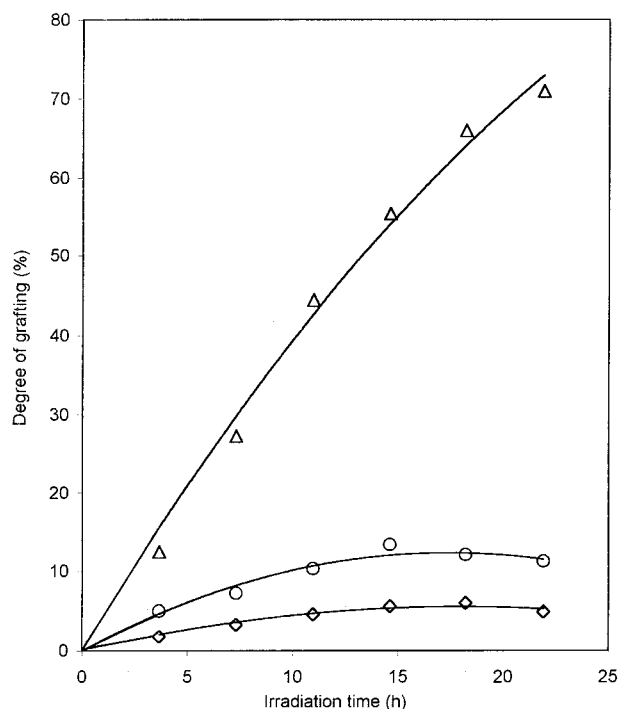


Figure 1 The degree of grafting–time curves for styrene diluted with various types of solvents: (◇) Methanol, (○) benzene, and (△) dichloromethane. The grafting conditions are 60 vol % styrene concentration, 20 kGy dose, 0.37 Gy/s dose rate, ambient temperature, nitrogen atmosphere.

in the grafting mixture. Therefore, swelling of the grafted layers and the styrene diffusion is enhanced and as a result longer polystyrene grafted branches are obtained. However, dilution of styrene with methanol, which has a high chain transfer constant and is an electron donor¹⁹ (0.296), causes quick termination in the growing chains enhanced by the reduction in the monomer diffusion. This reduction is due to the increase in the viscosity of the grafting mixture enhanced by the insolubility of the polystyrene homopolymer in the grafting solution. Thus, low levels of grafting are obtained. 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. These results encourage the use of dichloromethane as a cheap, inert, and noncarcinogenic solvent for monomer dilution in such grafting systems.

Figure 2 shows the variation of the degree of grafting of styrene onto FEP films with the irradiation dose at a styrene concentration of 60 vol % in dichloromethane. The dose was varied in the

range of 5–30 kGy at a dose rate of 0.37 Gy/s. As can be seen the degree of grafting increases gradually with the increase in the irradiation dose. This behavior can be ascribed to the increase in the number of radicals formed in the grafting system with the increase of the irradiation dose. These results are in a good agreement with those obtained by Gupta et al.¹⁴ upon grafting of styrene onto an FEP film by the preirradiation method. However, the doses applied in their work to achieve degrees of grafting comparable to those obtained by simultaneous irradiation employed in this study were considerably higher (25–100 kGy). Similar behavior was also obtained upon grafting of other monomers such as acrylic acid and onto FEP films.^{8–10}

The variation of the degree of grafting with the dose rate is shown in Figure 3. The degree of grafting decreases with the increase in the dose rate. The increase in dose rates causes two major effects on the grafting reaction. The first effect is the enhancement of the tendency of the formed radicals to decay by recombination and the second one is the fast termination and/or degradation of the polystyrene growing chains. Together these two effects lead to a decrease in styrene diffusion

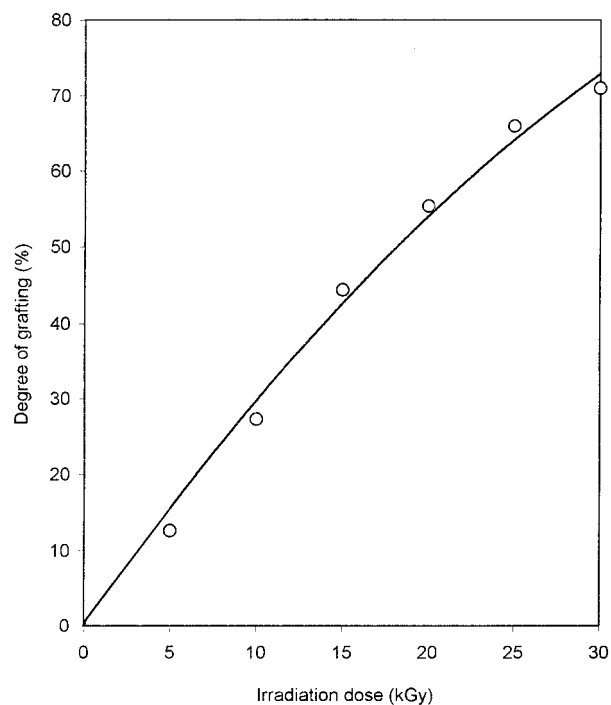


Figure 2 The variation of the degree of grafting with the irradiation dose. The grafting conditions are 60 vol % styrene concentration, dichloromethane solvent, and the rest are similar to those in Figure 1.

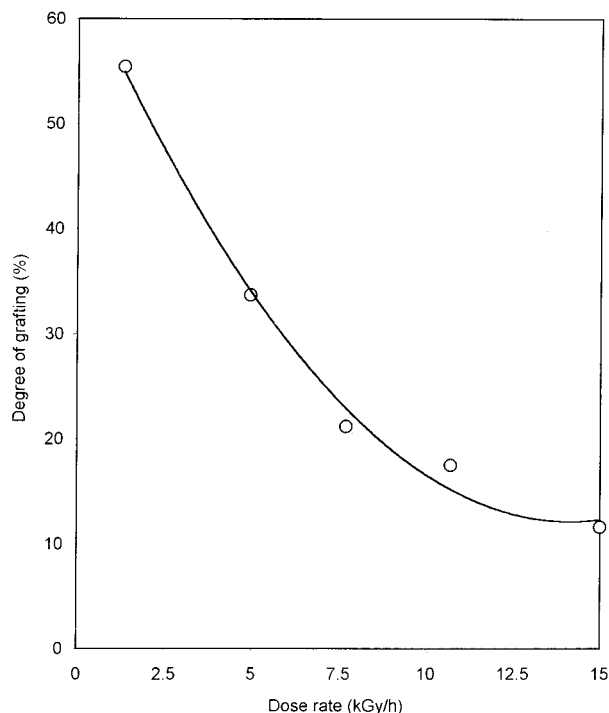


Figure 3 The variation the degree of grafting with dose rate. The grafting conditions are 60 vol % styrene concentration, dichloromethane solvent, and the rest are similar to those in Figure 1.

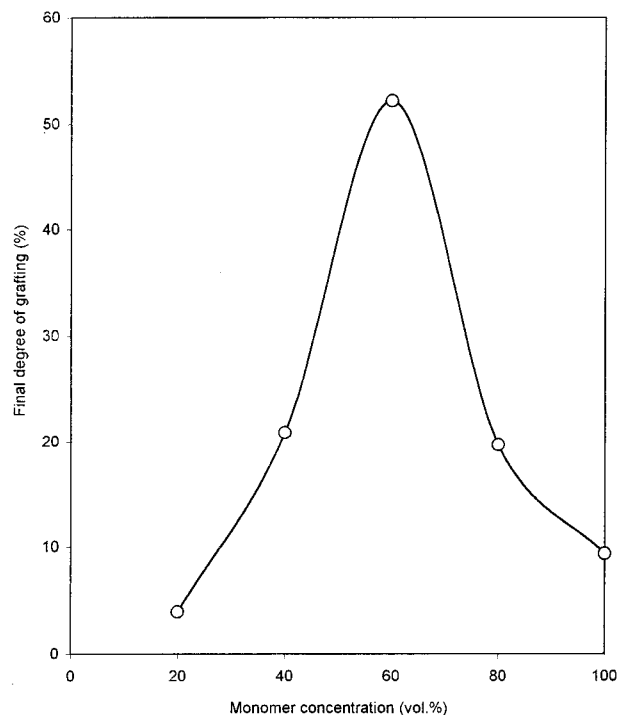


Figure 4 The relationship between the degree of grafting and monomer concentration. The grafting conditions are 20 kGy dose, dichloromethane solvent, and the rest are similar to those in Figure 1.

and its concentration in the internal grafting layers.

Figure 4 shows the relationship between the final degree of grafting and the monomer concentration. The degree of grafting increases drastically as the monomer concentration increases up to 60 vol % and falls sharply at higher concentrations. This behavior is most likely attributed to the increase in the styrene diffusion and its concentration in the grafting layers, which reach maximum values at a concentration of 60 vol %. A further increase in the monomer concentration is accompanied by a homopolymer formation and as a result the diffusion of styrene is hindered and its concentration is decreased. However, the grafting is not completely controlled by the styrene diffusion through the FEP matrix. These results suggest that the degree of grafting of styrene onto FEP films not only depends on the amount of radicals but also on the diffusibility of styrene through the polymer matrix and its concentration in the grafting layers as well. Similar trends were obtained upon grafting of styrene onto FEP films by preirradiation.¹⁴

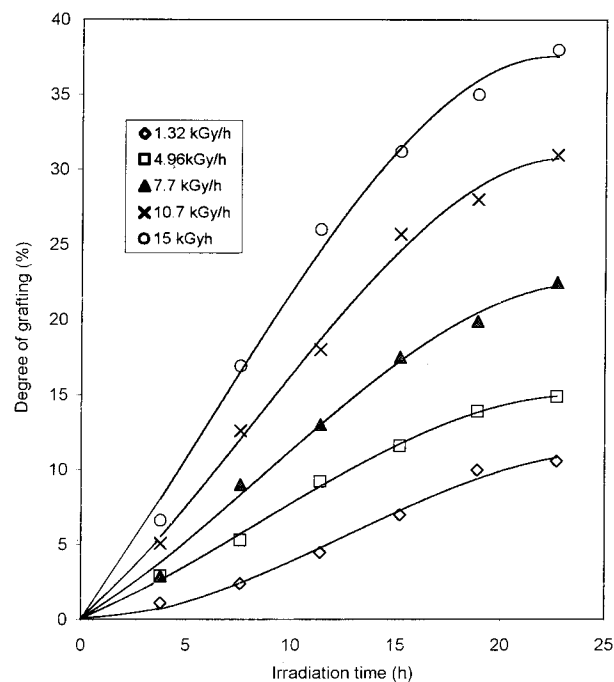


Figure 5 The degree of grafting and irradiation time curves at various dose rates. The grafting conditions are 20 vol % styrene concentration, dichloromethane solvent, and the rest are similar to those in Figure 1.

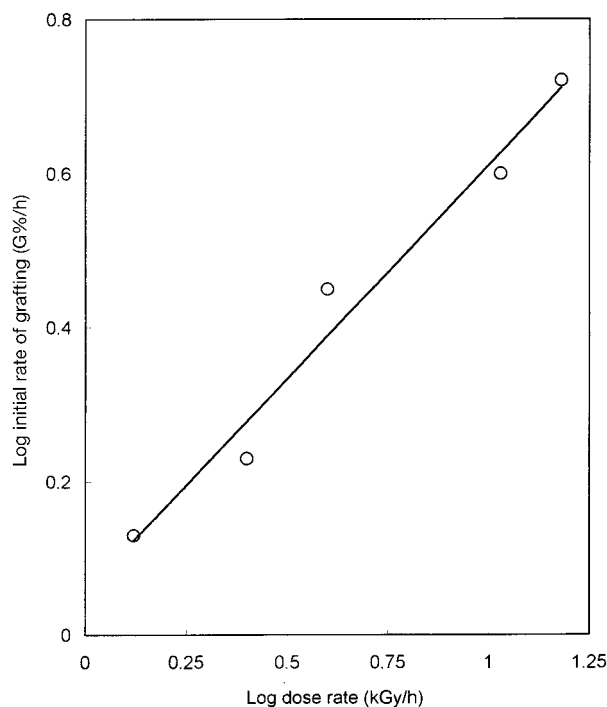


Figure 6 Log-log plots of the initial rate of grafting versus the dose rate. The grafting conditions are 20 vol % styrene concentration, dichloromethane solvent, and the rest are similar to those in Figure 1.

Kinetics of Grafting

Figure 5 shows the degree of grafting and irradiation time curves at various dose rates and at a styrene concentration of 20 vol % in dichloromethane. The degree of grafting increases with the increase in the irradiation time and tends to level off at higher irradiation times. The initial rate of grafting (R_g) is graphically determined from Figure 5.

The log-log plot of the initial rate of grafting versus the dose rate is shown in Figure 6. The dependence of the initial rate of grafting on the dose rate is found to be of 0.5 order.

Figure 7 shows the degree of grafting versus irradiation time curves at various styrene concentrations (20–100 vol %). As can be seen the degree of grafting increases with the increase in the irradiation time and tends to level off at higher irradiation times. The log-log plot of the initial rate of grafting versus the monomer concentration is shown in Figure 8. The initial rate of grafting increases with styrene concentration up to 60 vol % and drops sharply at higher styrene concentrations. The dependence of the initial rate of grafting on the styrene concentration is found to

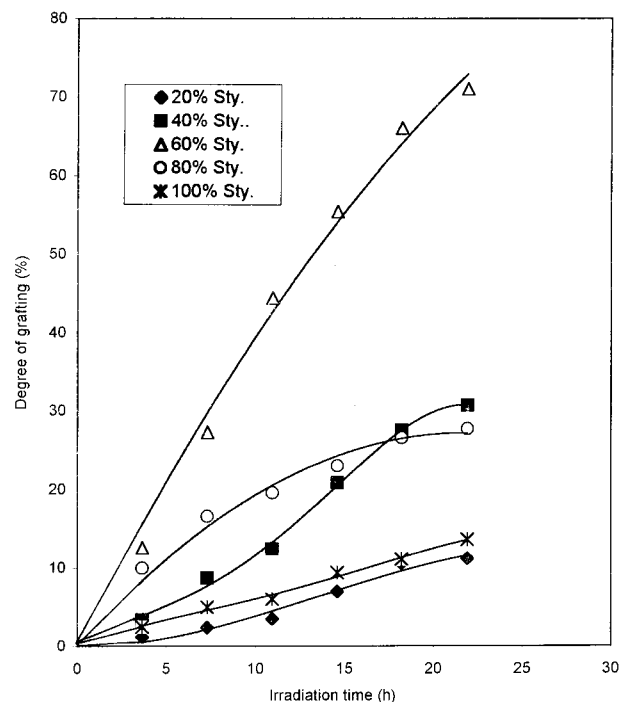


Figure 7 The degree of grafting versus irradiation time curves at various styrene concentrations (20–100 vol %). The grafting conditions are dichloromethane solvent and the rest are similar to those in Figure 1.

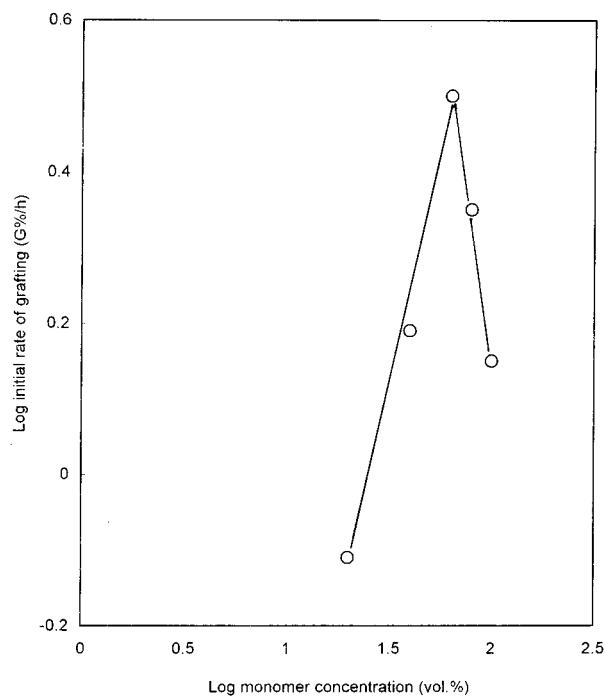


Figure 8 Log-log plots of the initial rate of grafting versus monomer concentration. The grafting conditions are 20 kGy dose, dichloromethane solvent, and the rest are similar to those in Figure 1.

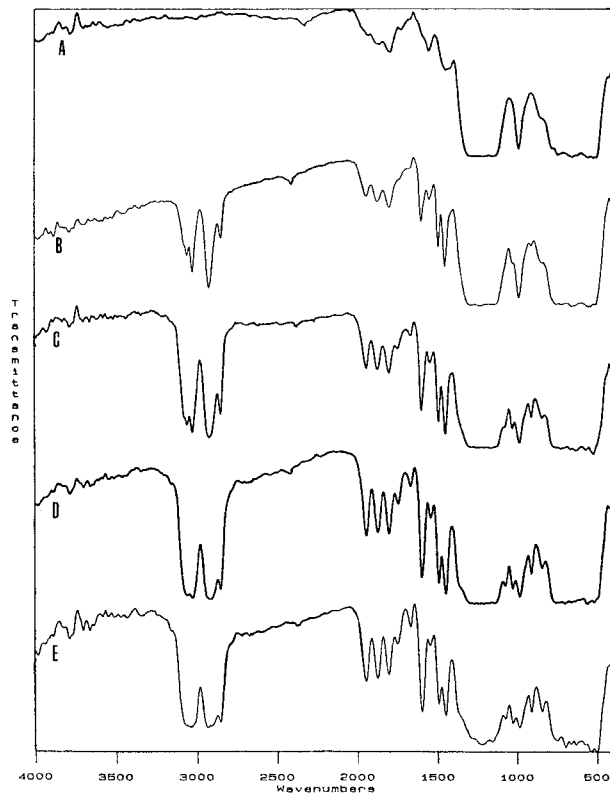


Figure 9 The typical FTIR spectra of original FEP (spectrum A) and polystyrene grafted FEP films with degrees of grafting of 6, 21, 41, and 52% for spectra B–E, respectively.

be of 1.3 order. An order of dependence of 1.9 for the preirradiation grafting of styrene onto FEP was obtained by Gupta et al.¹⁵ Because FEP film hardly swells in the grafting solution, the grafting is suggested to proceed by the front mechanism. The grafting front starts at the surface of the film and moves internally toward the middle of the film by successive diffusion of the monomer until swelling equilibrium is reached at a concentration of 60 vol %.

Based on the previous results the kinetic equation of grafting in the present system can be expressed by the following correlation:

$$R_g \propto [D]^{0.5} [M]^{1.3}$$

It can be concluded that the rate of grafting and the final degree of grafting in the present system are not only dependent on the efficiency of formed radicals but also on the continuous abundance of monomer molecules in the grafting layers.

Characteristics of Grafted Films

The FTIR-ATR spectra of the original and grafted FEP films are shown in Figure 9. Spec-

trum A shows a sharp peak at 980 cm^{-1} due to the C—F stretching vibration of the CF_3 group and a broad band at $1150\text{--}1250\text{ cm}^{-1}$ due to the stretching vibration of the CF_2 groups present in the original FEP film. Compared to the original film spectrum, spectra B–E are characterized by the appearance of the new bands at 3050 and $1500\text{--}1600\text{ cm}^{-1}$ due to the stretching vibration of $=\text{C—H}$ and the skeletal $\text{C}=\text{C}$ of the benzene ring. The aromatic out of plane C—H deformation band at 860 cm^{-1} and C—H out of plane bending overtone and combination band patterns in the region of $1660\text{--}2000\text{ cm}^{-1}$ confirms the monosubstitution of the benzene ring. The absorption bands at $2800\text{--}2900$ and $2900\text{--}3000\text{ cm}^{-1}$ that are due to symmetric and asymmetric stretching are characteristics for aliphatic CH_2 groups. These absorption bands increase with the increase in the degree of grafting. These features prove that styrene is grafted onto FEP films.

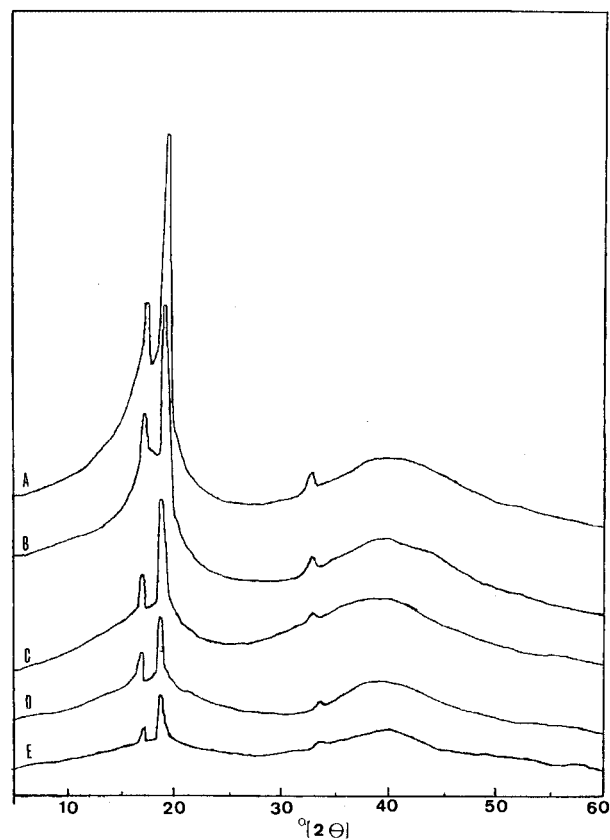


Figure 10 Diffractograms of original FEP (spectrum A) and polystyrene grafted FEP films with degrees of grafting of 6, 21, 41, and 52% for spectra B–E, respectively.

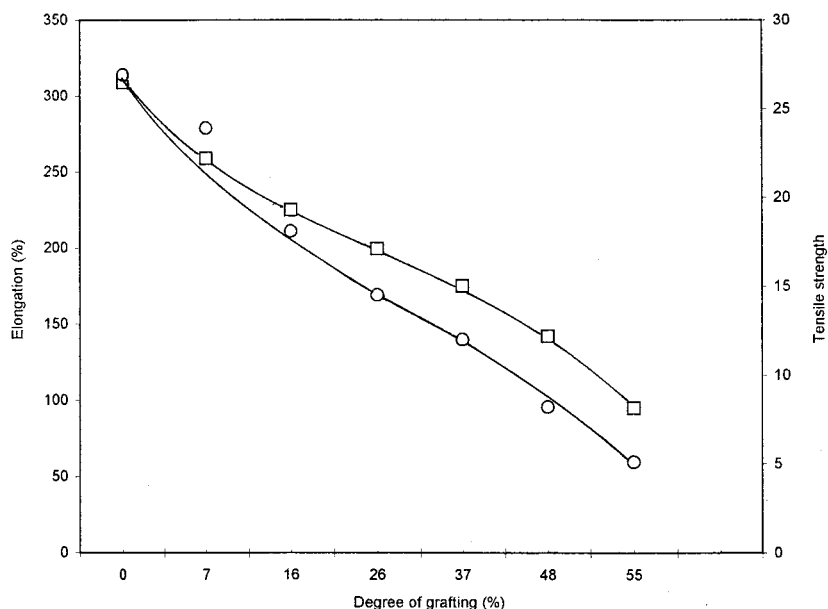


Figure 11 (□) Tensile strength and (○) elongation percent at break of the grafted FEP films versus the degree of grafting.

Figure 10 shows the diffractograms of the original and grafted FEP films having various degrees of grafting. It can be seen that the crystallinity peaks for the original and all grafted films occur at the same angle (2θ), giving an indication that the original and the grafted films have a similar chemical structure. However, the results obviously show a remarkable decrease in the degree of crystallinity of the grafted films compared to the original one. Moreover, the degree of crystallinity decreases with the increase in the degree of grafting within the grafted film as illustrated by the inverse relationship between the peak intensity and the degree of grafting. The decrease in the crystallinity is assumed 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 the FEP films. This behavior is similar to that obtained during the investigation of the structural changes induced by grafting styrene onto PFA films.¹⁸

The changes in tensile strength and elongation percent at break for the FEP-*g*-polystyrene films were studied as a function of the degree of grafting as shown in Figure 11. Note that the tensile strength and the elongation percent both decrease with the increase in the degree of grafting. However, the grafted films still retain reasonable mechanical stability up to a degree of grafting as high as 50%. The reduction in these mechanical

properties is attributed to the structural changes taking place in the FEP film upon the introduction of the amorphous polystyrene grafts that lead to the decrease in the crystallinity content with the increase in the degree of grafting. These results suggest that FEP films have the potential to be used as base polymers for preparation of proton exchange membranes.

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