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Grafting of pre-irradiated poly(ethylene-*alt*-tetrafluoroethylene) films with styrene: influence of base polymer film properties and processing parameters

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The radiation grafting method is of interest for the preparation of ion-exchange membranes for electrochemical and other applications. Typically styrene is used in this method because the grafted polystyrene can be readily modified to introduce a variety of functionalities. The grafting of poly(ethylene-*alt*-tetrafluoroethylene), or ETFE, films with styrene by the pre-irradiation method has been investigated and compared to that of poly(tetrafluorethylene-*co*-hexafluoropropylene), or FEP, and poly(vinylidene fluoride), or PVDF. The influence of base polymer film properties such as film thickness, extent of orientation, and molar mass on the grafting behavior of ETFE films is reported. Film orientation was found to often have a dominant influence either directly, as in the case of monoaxially oriented films, or indirectly, as a result of the film extrusion process. In addition, the effects of the irradiation type and atmosphere and grafting temperature on the grafting behavior of one ETFE film type were examined in more detail.

Introduction

The modification of polymers by radiation processing has been of interest since the 1950s, and much of the important early work has been carried out or reviewed by Chapiró.[1] Polymer films can be modified by the radiation grafting method[1] in which typically gamma or electron beam irradiation are used to create active sites for grafting.

Radiation grafting can be used[1] to modify either only the surface properties or also the bulk properties. For example, the bulk can be modified[2] to impart ion-exchange or ion-transport properties. The resulting bulk-modified films are used[3,4] as membranes in electrodialysis, electrosynthesis, and pervaporization and as fuel cell membranes[2] and battery separators.[4]

In the *pre-irradiation method*,[1] the film is activated in a pre-irradiation step and then grafted with monomer in a subsequent step. The film may be pre-irradiated in the absence of oxygen or, alternatively, in the *peroxide method*, the base polymers can be irradiated in air.[1]

Some of the advantages of radiation graft copolymerization include:[5] (1) the ready variation of the initiation step, for example, (a) by creating either primarily carbon-based radical active sites or peroxy- or hydroperoxy-based active sites, (b) varying the total irradiation dose or (c) varying the dose rate, (2) initiation under conditions where conventional methods fail (low-temperature, solid-phase polymerization), (3) lack of need for chemical initiators or catalysts, and (4) the materials can be modified in an already prefabricated form.

Monomer transport into the film is often the rate-limiting step in radiation grafting.[1] This is true even in the case of simultaneous radiation grafting of a monomer with some solubility in the base polymer, for example, styrene in polyethylene (PE). Even if the PE base film is pre-swollen in monomer, the grafting process is often diffusion limited.[6]

If the base polymer film does not swell in the grafting monomer solution and the pre-irradiation method is used, radiation grafting occurs by a grafting front mechanism.[1] In this mechanism, grafting initially occurs only at the surface which is in intimate contact with the monomer solution, as shown in Fig. 1a. The grafted surface region swells in monomer and thus the monomer diffuses further into the film interior and reacts (1b). The two grafting fronts continue to move further into the film interior until they meet (1d). For applications in which ions should be conducted from one side of the membrane to the other, as, for example, in electrochemical cells, grafting should proceed to a point at which a homogeneous grafting level is achieved throughout the film thickness (1f).

If radiation grafting is monomer transport limited, as in those cases described by the grafting front mechanism,[1,2] the base polymer film properties would be expected to have a significant effect on monomer transport into the film and thus the grafting process.

In spite of this expected "large-scale" influence of base polymer film properties on radiation grafting, often only the most rudimentary information on the base polymer films, for example, the film thickness and the name of the film manufacturer, have been provided in the literature. This makes it difficult to interpret the often contradictory results on

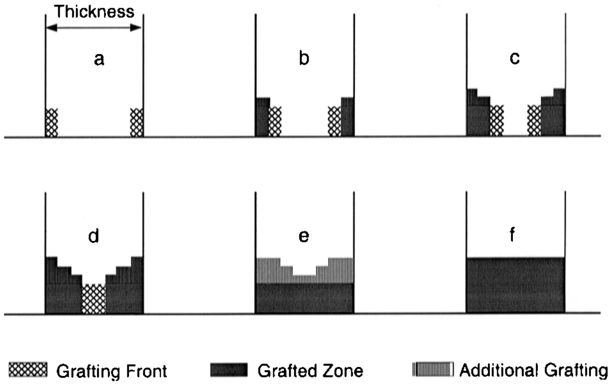

Fig. 1 Simplified qualitative view of the grafting front mechanism.

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the influence of such basic film properties as thickness on the grafting process, even in such widely studied systems as the radiation grafting of styrene onto polyolefin films,[6–8] as pointed out in the review by Chapiró.[1] In one case the initial rate of grafting, R_g, where $R_g = \Delta\text{mass}/\Delta\text{time}$, has been reported to be inversely proportional to the film thickness in the case of 250 to 2410 µm thick PE base films[6], but the rate of grafting was lower than that expected based on the ideal diffusion-limited relationship, $R_g \propto 1/\text{thickness}$, for thinner films. In another investigation the rate of simultaneous radiation grafting, R_g, has been reported[7] to be inversely proportional to the film thickness at low temperatures, but the ordering of the R_g values was random at higher temperatures (above 40 °C).

Ranogajec and co-workers reported that grafting levels[8] increased with film thickness, although the effects were less pronounced at the higher temperatures. In contrast Matsuo and co-workers have reported[9] that the grafting levels of 200 µm or thicker films at constant grafting times was inversely proportional to the film thickness. However, the grafting levels decreased as the PP film thickness decreased further. In one of the above cited investigations, only the film thicknesses were reported,[9] in another two cases the film manufacturer and crystallinity or density were reported in addition,[7,8] in the fourth case the molecular mass was also reported.[6] Film orientation was not characterized in any of these investigations.

Although the radiation grafting of fluoropolymer films has been demonstrated to be a useful method for preparing membranes,[2,4,5] the grafting behavior of these base polymers has not been as widely investigated as that of the polyolefins. However, some information is known. For example, R_g was reported to be inversely proportional to the base polymer thickness in the pre-irradiation grafting of styrene onto poly(tetrafluoroethylene-*co*-hexafluoropropylene), or FEP, base films,[10] the pre-irradiation grafting of acrylic acid onto PTFE films,[11] and the simultaneous radiation grafting of acrylic acid onto poly(ethylene-*alt*-tetrafluoroethylene), or ETFE, base films.[12] The fact that both of these monomers, styrene and acrylic acid, do not swell these fluoropolymer films to any significant extent is likely to be part of the reason for the "ideal" monomer-transport limited grafting behavior ($R_g \propto 1/\text{thickness}$) observed in these three systems.

In contrast, we have reported earlier[2] that thinner FEP and ETFE films require higher irradiation doses than their thicker counterparts in order to achieve the same pseudo-saturation graft level on a mass basis. The saturation grafting level, SGL, is the maximum grafting level achievable at quasi-infinite reaction time (typically reached after several hundreds or thousands of minutes). We postulated that this difference in grafting behavior might be attributable to such differences in the base polymer film properties as molar mass, crystallinity, or orientation. This grafting behavior appears at first to be in contradiction with our earlier reported dependence of the initial rates of grafting on film thickness.[10] It should be noted however that there are several important differences between the two observations. Initial grafting rates were determined in the first investigation,[10] whereas the latter investigation concerns much longer grafting times and higher pseudo-saturation grafting levels. In addition, gamma irradiation in air and styrene without crosslinkers were used in the first investigation, and electron beam irradiation under nitrogen and styrene plus the crosslinking monomers divinylbenzene and triallyl cyanurate were used in the later investigation.

In contrast to our work, both the SGL and R_g were reported by Momose and co-workers[13] to be independent of film thickness in the pre-irradiation grafting of trifluorostyrene (TFS) onto ETFE base polymer films. Based on these results and the observation that their ETFE base films swelled slightly in TFS, Momose and co-workers concluded[13] that R_g and the SGL were controlled by the radical concentration in the films and not by the monomer transport.

Although radiation-grafted membranes based on ETFE base polymers and styrene monomer are commercially available,[14] the overall kinetics of this system, and possible base polymer effects on grafting, have not yet been reported in detail. For example, Elmidaoui and co-workers[15] reported on the grafting rates and yields obtained in the pre-irradiation grafting of ETFE with styrene, but unfortunately much important information was not divulged. For example, the primary source of the ETFE film and even its thickness and other properties, the type of inhibitor used, the source and purity of the styrene and divinylbenzene monomers, and even the chemical structure of one of the aromatic monomers studied were all not revealed.

It is important however to understand how base polymer film and radiation processing properties affect the extent and rate of grafting so that grafted film and membrane preparation can be carried out rapidly and reproducibly. We have reported elsewhere[16] that the performance (current–voltage behavior) of fuel cells containing such membranes compares favorably with those of cells containing commercially available perfluorinated membranes under the same operating conditions. In the present work, the effects of such properties of the base polymer film as thickness, composition, crystallinity, and orientation on the pre-irradiation grafting of ETFE and FEP films with the same monomer, styrene, have been investigated and compared. In addition the influence of such process parameters as the irradiation type and atmosphere and grafting temperature on the grafting reaction have also been investigated for one of the ETFE film types. The kinetics of the grafting of styrene into pre-irradiated FEP films have been reported[10] already and provide a basis for comparison with the present investigations using ETFE base films. The FEP film type studied previously and the two ETFE film types studied in this investigation are widely available, and both the films and the resins from which they are produced have been well characterized by their manufacturers and others.

Experimental

Materials

ETFE films. Nowoflon ET-6235 films with thicknesses of 25, 50, and 100 m and extruded roll widths of 155 cm designated here as N-25, N-50, N-100 were purchased from Nowofol GmbH, Siegsdorf, Germany. The average molar weight, $\bar{M}_w$, of the Dyneon ET 6235 copolymer used[17] to make these films is approximately 400 000 Da. Tefzel® ETFE 100LZ and 200LZ films having thicknesses of 25 and 50 µm and extruded widths of 183 cm designated here as D-25 and D-50 were purchased from DuPont, Circleville, OH, USA. Uniaxially oriented DuPont T^2 90 ZH and 150ZH films of Tefzel® ETFE approximately 23 and 64 µm in thickness, designated here as D-23O and D-64O, were a gift from DuPont, USA. The average molar weight, $\bar{M}_w$, of the Tefzel® 280 copolymers typically used to make the Tefzel® and Tefzel® T^2 films is 1 200 000 Da.[18] These films are uniaxially oriented through a short gap machine direction stretch process.[19]

PVDF film. Nowoflon PVDF homopolymer type 1008 film with a thickness of 25 µm and extruded width of 50 cm was obtained from Nowofol GmbH, Siegsdorf, Germany. The average molar weight, $\bar{M}_w$, of the Solef 1008 homopolymer (Solvay) used[20] to make this film is 110 000 Da.

FEP film. DuPont Teflon-FEP 100A film with a thickness of 25 µm was purchased from DuPont, Circleville, OH, USA. The average molar weight, $\bar{M}_w$, of the FEP 100 copolymer resin used[21] to make these films is 325 000 Da, and its hexafluoropropylene content is 7–10 mol%.[21]

Approximately one fourth of the extruded film roll width was trimmed away from each edge of each film sample and discarded. Unless otherwise stated all samples for film characterization and grafting experiments were taken from within the remaining interior 50% of the extruded film roll width.

Film characterization

Thermal analysis. The melting points (MP) and heats of fusion (ΔH_f) of the fluoropolymer films were determined from single heating (melting) curves measured under N_2 using a heating rate of 20 °C min^{-1}. The heats of fusion were calculated using a linear baseline and constant integration limits of 125–180 °C, 210–295 °C, and 230–285 °C, in the case of the PVDF, FEP, and ETFE film samples, respectively. The heats of fusion of 100% crystalline PVDF, FEP, and ETFE have been reported to be[22,23] 104.6, 87.9, and 113.4 J g^{-1}.

Melt Flow Index (MFI) values were measured according to DIN 53′735 at 230 °C using a mass of 2.16 or 5 kg, at 300 °C using a mass of 1 or 3.8 kg, and at 372 °C using a mass of 1 or 3.8 kg in the case of the PVDF, ETFE, and FEP films, respectively.

Analysis of film orientation. The percent heat shrinkage of strips of the ETFE sample films in the machine (extrusion) direction was measured after they were heated for 5 min at 150 °C.

Dichroic ratios of the films were calculated from their infrared absorption spectra measured in the transmission mode using a polarizer. The dichroic ratios of the absorption bands were calculated[24] by dividing the absorbance of this band measured with the film machine direction oriented parallel to the plane of the light polarization by that measured in the perpendicular orientation ($\mathrm{Abs}_{\parallel}/\mathrm{Abs}_{\perp}$).

Film irradiation

All films were washed with ethanol and dried prior to their irradiation. The total irradiation dose was 20 kGy (1 Gray = 1 J g^{-1} energy absorbed). Gamma irradiation (γ) was carried out using a cavity type Co^{60} source, which emits gamma irradiation at 1.17 and 1.33 MeV and has a dose rate of 5.9 ± 0.1 kGy h^{-1}. Samples were irradiated at approximately room temperature in air.

Some samples that were irradiated using an electron beam source were first evacuated and purged with purified N_2 repeatedly and then packed in heat-sealed barrier film bags. Other samples were packed in polyethylene (PE) bags under air. The samples were cooled with dry ice during electron beam irradiation, and they were irradiated while still packed under either their N_2 or air purging atmospheres. The accelerating voltage was 2.2 MV, the beam current was between 5 and 20 mA, and the dose rate was typically 15.1 ± 1.1 kGy s^{-1}.

Samples were stored at −80 °C after irradiation. The samples that had been irradiated in air (γ/air or e^-/air) were packed and stored in Al foil, and the samples that were irradiated under a N_2 atmosphere were stored in the barrier film bags.

Grafting reactions

The *tert*-butylcatechol inhibitor was removed from the styrene (Fluka purum grade) by means of an aluminium oxide (Scientific Polymer Products) column. Film samples were rapidly removed from storage and reacted with styrene under a N_2 atmosphere. The grafting reaction was initiated by placing the reaction flask in a water bath at the desired temperature. The moment at which the reaction flasks were placed in the water bath was taken to be time zero. The grafting investigations using the different types of base polymer films were all carried out at 60 °C. Grafting investigations of one ETFE film type, N-100, were carried out at several additional temperatures (40, 50, 80, and 90 °C).

After the desired reaction time, the grafted film sample was extracted with toluene in a soxhlet for 5 h. Typically less than 2 mol% of the grafting liquid was consumed by the grafting process (based on the mass uptake of the grafted films).

The extracted samples were dried under vacuum. The graft levels of the ETFE films were determined in the traditional manner[1] based on the percent difference between the mass of the unirradiated sample, M_i, and the mass of the grafted sample, M_g: Graft Level = $(M_g - M_i)/M_i \times 100\%$. This traditional mass-based system was used to compare the grafting behavior of different types of ETFE films, but it is not as useful however in comparing the grafting behavior of fluoropolymers having "mer" units of very different relative molar masses. Therefore, for the comparison between the grafting behavior of different film types, we have calculated the graft level based on the percent difference between the number of moles of monomer units incorporated in the unirradiated sample, N_i, and the number of moles of monomer units incorporated in the grafted sample, N_g: Graft Level = $(N_g - N_i)/N_i \times 100\%$.

Results

Base polymer film characterization

Unirradiated films. The heat shrinkage and dichroic ratios of the base polymer films are reported in Table 1. The heat shrinkages in the machine direction are: (1) greater in the case of the uniaxially oriented films than those of the corresponding non-oriented films, (2) greater at the roll edges than in the middle for the non-oriented films, (3) greater at the roll edges for the thinner N-type films, and (4) fairly low and uniform in the case of the non-oriented 25 and 50 µm D-type films.

The infrared spectra in the C–H stretching frequency region obtained in the case of the uniaxially oriented D-23O film are shown in Fig. 2. The absorption band at 2975 cm^{-1}, assigned[24] to the CH_2 out-of-phase or asymmetric stretching vibration, was determined to be quite sensitive to the film orientation. The intensity of this band was greatest when the machine direction of the film was oriented perpendicular to the plane of the light polarization. The dichroic ratios ($\mathrm{Abs}_{\parallel}/\mathrm{Abs}_{\perp}$) of this band are tabulated in Table 1. The dichroic ratios are: (1) lower at the edge than in the middle of each N-type film, (2) progressively lower at the edges for the thinner N-type films, (3) lower in the monoaxially oriented D-type films than in the non-oriented D-type films, and (4) about the same and close to one for both "non-oriented" D-type films.

Irradiated films. The results of their differential scanning calorimetry (DSC) and MFI characterization are given in Table 2. The melting points (MP) and degrees of crystallinity (as characterized by ΔH_f) of the films remain relatively unchanged by the irradiation. The crystallinities of the monoaxially oriented films (D-23O and D-64O) remain higher than those of their non-oriented counterparts (D-25 and D-50), as was also the case in the unirradiated films (data not shown).

The MFIs of the ETFE, PVDF, and FEP base polymers that were irradiated in air are higher than those of their unirradiated starting materials. Although they are now smaller, the differences between the MFIs of the N-type and D-type films are still present after irradiation. The N-type films of different thickness have all about the same MFI after the γ/air irradiation treatment and they are slightly higher than the D-type films. There does not appear to be any difference between the MFIs of the oriented and unoriented D-type films. The MFIs of the irradiated N-100 ETFE films vary according to how they were irradiated in the following manner: $e^-/N_2 < e^-/\mathrm{air} < \gamma/\mathrm{air}$.

Table 1 Characterization of orientation of ETFE films

ETFE film type	Position on extruded roll	Heat shrinkage in machine direction [%] at 150 °C	Infrared dichroic ratio[a]
N-25	edge	8.2	0.72
	middle	−0.3	0.90
N-50	edge	5.5	0.90
	middle	−0.1	0.96
N-100	edge	4.4	0.94
	middle	0.5	0.99
D-25	edge	1.2	0.97
	middle	0.0	0.96
D-50	edge	1.6	0.98
	middle	0.0	0.98
D-23O	n.a.[b]	16.2	0.41
D-64O	n.a.	14.7	0.48

[a] Determined based on the relative absorbance of the band at 2975 cm^{-1} and using the band at 2880 cm^{-1} as an internal standard. [b] n.a. = not available.

The infrared dichroic ratios of the absorbance band due to the CH_2 asymmetric stretching vibration at 2975 cm^{-1} did not change upon film irradiation.

Grafting reactions

In this section, we present the results of grafting experiments using the pre-irradiated base polymer films whose characteristics were reported in the previous section.

Fluoropolymer type. The graft levels (mol%), obtained as a function of reaction time at 60 °C are compared for the 25 µm ETFE, PVDF, and FEP films in Fig. 3. The graft levels initially increase linearly with time over a period of about 100 min, and then plateau out into another gently sloping fairly linear region extending from about 250 to 2800 min. After 3000 min the graft level remains essentially unchanged and the saturation graft level was taken to be the graft level reached at 3000 min. The grafting rates ($\Delta GL/\Delta t$) in the steeply increasing initial linear region (approximately the first 50 to 80 min) are reported in Table 3. The initial grafting rates of the partially fluorinated ETFE and PVDF films are higher than that of the perfluorinated FEP. The grafting levels of the partially fluorinated films are much higher than that of FEP for all subsequent reaction times. If the grafting rates or levels were calculated on a mass basis instead of a molar basis, these differences would be even greater.

N-type films of different thickness. The curves of the graft levels obtained as a function of reaction time in the grafting experiments using the different thickness N-type films were similar in appearance to those shown in Fig. 3, and the grafting rates in the initial sharply increasing region and the saturation grafting levels (SGL) are given in Table 3. The initial grafting rates, on a mass% basis, are only slightly higher for the thinner films, and they clearly vary in a manner that is less than $R_g \propto 1/$thickness. In addition, the grafting levels at the later reaction times and the SGL are about the same for the thinner N-25 and N-50 films, and they are lower than those of the N-100 film.

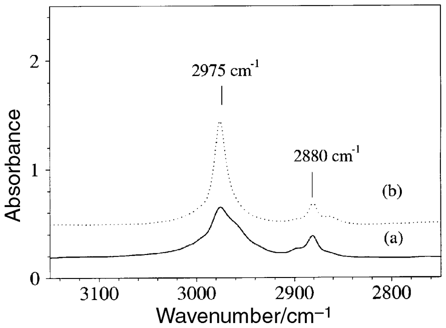

Fig. 2 C–H stretching region of the infrared spectra of the D-23O film measured with the machine direction oriented (—) parallel and (···) perpendicular to the plane of polarization of the infrared radiation.

D-type films: thickness and orientation. The grafting rates of the non-oriented and the monoaxially oriented D-type films are given in Table 3, and their graft levels as a function of time are shown in Fig. 4. The initial grafting rate of the thinner non-oriented film, D-25, is roughly double that of the twice as thick non-oriented film, D-50, but at longer reaction times the grafting levels and SGLs of the two films are about the same, or perhaps even slightly lower in the case of the thinner film, D-25. As shown in Table 3, the grafting rate and graft level as a function of time of the monoaxially oriented D-23O are in general lower than that of the non-oriented D-type film of similar thickness, D-25. The grafting levels of the oriented films remain considerably lower than those of their non-oriented counterparts for reaction times of up to about 1200 min, and only later do they become equal to those of the non-oriented films. It is interesting to note that the N-type films graft faster and to a greater extent than their higher molar mass D-type film counterparts (Table 3).

Position on the extruded film roll width. In an earlier section the N-25 films were shown to have the greatest heat shrinkage and lowest dichroic ratio at the film edge (Table 1) and the greatest difference between these properties at the film edge and roll middle of all of the films studied. To understand the influence of this inhomogeneity on our grafting process, grafting experiments for constant irradiation and grafting conditions were carried out on samples taken at different positions over the full extruded film roll width. Their graft levels are shown as a function of their position on the roll width in the upper part of Fig. 5. For comparison purposes, the heat shrinkage values and infrared dichroic ratios are shown in the lower part of Fig. 5.

The graft levels correlate with the heat shrinkage levels and dichroic ratios in the following manner. In the middle region of the roll width where the heat shrinkage levels are low and the dichroic ratios are highest, the graft levels are at their highest. At and near the film edge, the opposite behavior is observed. There the heat shrinkage levels are high, the dichroic ratios are at their lowest, and the graft levels are at their lowest.

The differences between the heat shrinkage values and the infrared dichroic ratios of the D-25 films at the film edge and in the film middle were smaller than those differences in these properties of the N-25 films. In a similar manner to that described previously for the N-25 films, the heat shrinkage levels, infrared dichroic ratios, and graft levels for constant irradiation and grafting conditions were measured over the roll width of the D-25 films (data not shown). In contrast to what

Table 2 Characterization of irradiated[a] base polymer films

Film sample	Irradiation Type	Differential Scanning Calorimetry		Melt Flow Index at 300 °C (1 kg mass)
		Mp/°C	ΔH_f/J g^{-1}	MFI/g (10 min)$^{-1}$
N-25	γ/air	268.6±1.9	37.0±0.6	4.2±0.2
N-50	γ/air	266.7±0.6	36.1±1.3	4.1±0.1
N-100	γ/air	268.6±2.3	36.0±1.5	3.9±0.1
	e^-/air	269.8±1.1	34.0±1.2	2.3±0.2
	e^-/N_2	268.8±2.0	37.8±1.2	0.9±0.2
D-25	γ/air	264.8±1.0	39.6±1.6	3.6±0.2
D-23O	γ/air	263.1±1.1	44.4±2.4	3.7±0.2
D-50	γ/air	264.7±1.0	39.2±1.8	3.5±0.3
D-64O	γ/air	266.4±2.4	46.9±2.3	3.2±0.2
PVDF-25	γ/air	174.9±1.8	43.9±2.2	6.2±0.2[b]
FEP-25	γ/air	273.4±0.4	15.5±0.7	3.6±0.2[c]

[a]All films irradiated with a dose of 20 kGy. [b]Measured at a temperature of 230 °C. [c]Measured at a temperature of 372 °C.

was found in the case of the N-25 films, the heat shrinkage levels are lower and vary only −0.4 and 0.8%, the dichroic ratios are higher and vary only between 0.9 and 1.0, and the graft levels vary only between 13 to 18 mass% over the roll width of the D-25 roll.

Irradiation method and atmosphere. The graft levels obtained as a function of grafting time using the 20 kGy γ/air, e^-/air, and e^-/N_2 pre-irradiated N-100 films were quite similar (not shown). The initial grafting rates are given in Table 3. The initial grafting rates vary, at most, only slightly according to their pre-irradiation treatment, as γ/air < e^-/air < e^-/N_2. The SGLs of the films irradiated in air using either irradiation method, γ/air or e^-/air, are about the same and somewhat less than that of the samples irradiated under N_2 by the e^-/N_2 method. The grafting behavior of the e^-/N_2 pre-irradiated N-100 films was not measurably different even if all subsequent handling involving the sample transfer was carried out under N_2 (data not shown).

Grafting temperature. The influence of temperature on the grafting levels of the N-100 ETFE films pre-irradiated with a dose of 20 kGy by the γ/air method is shown as a function of grafting time in Fig. 6 and the initial grafting rates and saturation grafting levels (SGL) are given in Table 3. The initial grafting rates, R_g, increase with temperature over the range of 40 to 80 °C and then decrease in the case of the experiment at 90 °C. The grafting rates at the highest temperatures (80 and 90 °C) decrease quite rapidly over the first 100 min and the SGL is approached already during that time. In contrast the grafting rates decrease much more slowly and the SGL is approached only after several hundred minutes in the case of the grafting experiments at the lower temperatures. In addition, the R_g values in Table 3 discussed do not vary in a linear manner when plotted as $\log_{10} R_g$ as a function of T^{-1} (data not shown).

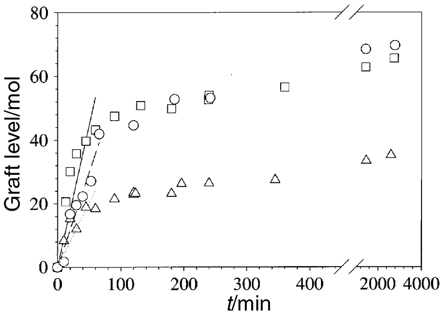

Fig. 3 Grafting levels (mol%) of 25 μm thick (□) ETFE, (○) PVDF, and (△) FEP films as a function of reaction time with styrene at 60 °C. All films were pre-irradiated with 20 kGy γ irradiation in air (γ/air).

Discussion

Base polymer film characterization

Unirradiated films. The unirradiated non-oriented ETFE films are about 30% crystalline, the monoaxially oriented films are about 37% crystalline, and the 25 μm thick FEP and PVDF films are about 17% and 41% crystalline.

The dichroic ratios ($\mathrm{Abs}_{\parallel}/\mathrm{Abs}_{\perp}$) of the asymmetric CH_2 stretching absorption band of ETFE at 2975 cm^{-1} are expected to decrease as the film orientation level increases because the transition moment vector of this vibrational mode is perpendicular[24] to the direction of the polymer backbone. Support for our conclusion comes from Siesler's infrared spectroscopic investigations[25] of uniaxially elongated films of the compositionally related polymer PVDF. His spectra show that the dichroic ratios of the PVDF absorption band due to the asymmetric $-CH_2-$ stretching vibration (at 3022 cm^{-1} in PVDF films) decrease as the films become more oriented.

The results of our characterization of the film heat shrinkage and infrared dichroism in Table 1 indicate that the dichroic ratio of the asymmetric $-CH_2-$ stretching band at 2975 cm^{-1} is a useful measure of the extent of orientation of ETFE films. The dichroic ratios of the monoaxially oriented films are low, and the dichroic ratios are low for other thin films or film regions having high heat shrinkage levels. Taken together, the heat shrinkage values and dichroic ratios indicate that (1) the N-type films are progressively more oriented as they become thinner, especially at the film edges, (2) the D-type films are relatively unoriented, presumably due to a proprietary post-extrusion thermal toughening process,[19] and (3) the monoaxially oriented D-O films are much more highly oriented than any of the other ETFE films.

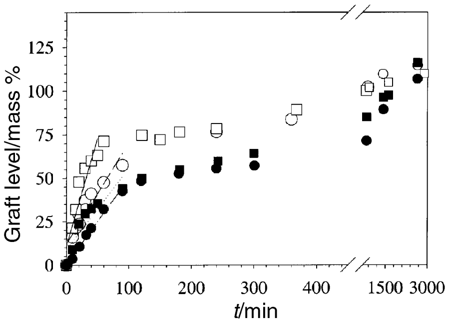

Fig. 4 Grafting levels (mass%) of (□) 25 μm thick "non-oriented" D-25, (○) 50 μm thick "non-oriented" D-50, (■) 25 μm monoaxially oriented D-25O, and (●) 50 μm thick monoaxially oriented D-50O ETFE films as a function of reaction time with styrene at 60 °C. All films were pre-irradiated with 20 kGy γ irradiation in air (γ/air).

Table 3 Grafting rates and Saturation Grafting Levels of ETFE films

			Initial period (approximately 0–75 min)			
ETFE film type	Irradiation type	Temp./°C	Rate/mass% min^{-1}	r^2	Saturation Grafting Level (SGL)/mass%	Comp.[b]
N-25	γ/air	60	1.33	0.92	135	a
N-50	γ/air	60	1.01	0.87	135	a
N100	γ/air	60	0.96	0.95	150	a,c,d
D-25	γ/air	60	1.08	0.88	110	b
D-50	γ/air	60	0.59	0.87	115	b
D-23O	γ/air	60	0.77	0.90	115	b
D-64O	γ/air	60	0.55	0.99	110	b
N-100	e^-/air	60	1.12	0.98	160	c
N-100	e^-/N_2	60	1.20	0.99	185	c
N-100	γ/air	40	5.73×10^{-2}	0.97	170	d
N-100	γ/air	50	5.75×10^{-1}	0.99	215	d
N-100	γ/air	80	1.2[a]	0.94[a]	90	d
N-100	γ/air	90	5.39×10^{-1}[a]	0.99[a]	70	d

[a] Initial grafting rate and r^2 for the time period of approximately 0–30 min. [b] The letters are provided to assist in comparing experiments as a function of (a) N-type film thickness, (b) orientation, (c) irradiation type, and (d) grafting temperature.

Irradiated films. The increase in the MFI values (decrease in molar mass) upon ETFE film irradiation in air is the most dominant change resulting from film irradiation that was observed in the properties characterized in this investigation. Chain scission is a well known consequence of the irradiation of PTFE, FEP, and ETFE in air[1,2,26,27] and will not be discussed in detail here.

Polymer crystallinity is well-known to be affected by radiation processing, and polymer irradiation can result in either increases or decreases in crystallinity.[1] Interestingly, the results of the present investigation indicate that the radiation processing of ETFE, PVDF, and FEP films with a total dose of 20 kGy, typically used[2,28] for the radiation grafting of ETFE films, do not result in significant changes in the film melting points (average crystallite size) or heats of fusion (degrees of crystallinity).

Grafting reaction

In this section the results of our investigations on the effects of base polymer film properties on grafting are discussed.

Fluoropolymer type. The results in Fig. 3 indicate that the grafting behavior of the compositionally related ETFE and PVDF films are fairly similar. Their initial grafting rates are higher than that of the perfluorinated FEP film, and their graft levels as a function of time are similar in magnitude and much greater than those of FEP. It should be noted that grafting rates ($R_g = \Delta GL/\Delta t$, in mass% or mol% per unit time) in the radiation grafting process differ fundamentally from the propagation rate constants ($l\ mol^{-1}\ s^{-1}$) of typical homogeneous solution phase polymerizations. R_g is a rate constant that is averaged over the entire sample volume, in which the available monomer and active radical concentrations may be quite different, as illustrated schematically in Fig. 1. So R_g is likely to be very much a function of monomer transport rates and concentrations in the case of grafting reactions describable by the grafting front mechanism.

One important factor in understanding this difference in grafting behavior between the three different base polymers is that their swelling in aromatic liquids increases as FEP < ETFE < PVDF. For example, the swelling levels of 25 m thick FEP, ETFE, and PVDF films after 4.5 h in toluene at 60 °C are about 0, 2, and 4 mass% or about 0, 1, and 2 mol%. The greater extent of swelling of the partially fluorinated base polymer films, ETFE and PVDF, in styrene is expected to enhance the transport of styrene into the base polymer film during grafting.

Another important factor is that the extent of radical formation per unit irradiation dose is likely to be greater in the case of the partially fluorinated ETFE and PVDF films in comparison to the perfluorinated FEP films. Indeed our EPR investigations of electron beam induced radical formation in these three films[29] indicates that more radicals are formed in the case of the partially fluorinated ETFE and PVDF films than in the case of perfluorinated FEP.

The crystallinities of the base polymers would be expected to have some influence on the extent of grafting because grafting is expected to occur[1,30] primarily in the amorphous or amorphous/crystalline interfacial regions. In contrast to this expectation, the PVDF and ETFE base polymer films graft to a greater extent than the FEP film on both a molar and mass basis even though their degrees of crystallinity are higher than that of the FEP film. This result suggests that some other factor, such as perhaps (1) monomer transport into the film, (2) the extent of radical formation, or (3) compatibility or miscibility of the graft component and the base polymer exerts a controlling influence.

The grafting behavior of γ/air perfluorinated FEP and non-fluorinated PE films with acrylic acid were compared by Gupta and Chapiró.[31] They found that at temperatures below 40 °C

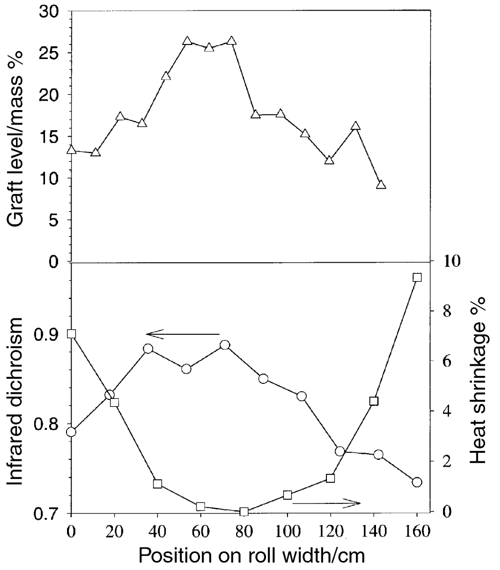

Fig. 5 (□) Heat shrinkage and (○) dichroic ratio of the 2975 cm^{-1} absorption and of the unirradiated N-25 ETFE starting film. (△) Graft level (mass%) as a function of distance from film edge 1 of the same film after 20 kGy γ/air pre-irradiation and subsequent grafting. The extruded film roll width is 155 cm. The pre-irradiated films were grafted by reaction with a 50 : 50 (vol : vol) mixture of styrene and benzene at 60 °C for 2.25 h.

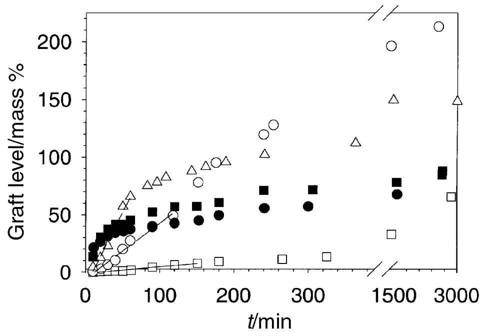

Fig. 6 Grafting levels of 100 μm thick N-100 ETFE films that were pre-irradiated by 20 kGy γ irradiation in air (γ/air) as a function of reaction time with styrene at (□) 40 °C, (○) 50 °C, (△) 60 °C, (■) 80 °C, and (●) 90 °C.

FEP grafted faster and more extensively than PE, but PE grafted faster and more extensively at higher temperatures. Their reported higher grafting rates and saturation grafting levels of the non-fluorinated PE at 60 °C is consistent with the higher grafting rates and saturated grafting levels of the partially fluorinated ETFE and PVDF base polymers in the present investigation.

N-type films of different thickness. The fact that the initial grafting rates in our grafting experiments of the N-type films of different thickness are not inversely proportional to the film thickness indicates that some film property other than film thickness has an important influence on grafting. The mid-infrared spectra of these films do not indicate that there are any chain microstructural or functional differences that would be responsible for differences in the reactivity of the polymer chains in the different thickness films (not shown).

Therefore the difference between the films would seem to lie with a property related to the transport of monomer into the films during the grafting reaction. Molar mass, crystallinity, and orientation are all known to have important influences on diffusion in polymer films. Our results in the previous section, however, did not indicate that any large scale variation occurs in the molar mass, as reflected in the MFI value, or in the DSC-determined crystallinity. Both our heat shrinkage and infrared dichroic ratios do indicate, however, that the N-type films are progressively more oriented as they become thinner. Therefore we propose that the greater extent of orientation in the thinner N-type films inhibits the transport of monomer into the film during grafting relative to their thicker counterparts. This transport inhibition results in grafting rates, R_gs, that vary by less than that expected based on the case of ideal base films differing only in their thickness, *i.e.* $R_g \propto 1/\text{thickness}$.

Alternatively this deviation from the ideal behavior, $R_g \propto 1/\text{thickness}$, for thin films could be interpreted as resulting from an inhomogeneous distribution of reactive sites and thus grafted polystyrene through the film thickness. For example, if the graft level in the near surface region is lower than in the bulk, this would lead to negative deviations from $R_g \propto 1/\text{thickness}$ for thinner films, as we observed. Such inhomogeneities could result from an inhomogeneous radical distribution through the film depth. Another possibility would be the presence of toluene-soluble PS homopolymer or ETFE-*g*-PS molecules having only relatively low ETFE content in the grafted film. These toluene-soluble molecules would be extracted from the near surface region during the subsequent Soxhlet extraction. Neither of these possibilities would explain however our results with the D-type ETFE films or the results of others that the grafting of other fluoropolymers with styrene[10] or other monomers[11–13] do follow the ideal behavior, $R_g \propto 1/\text{thickness}$, over this same thickness range. In addition, the chain transfer constant to styrene monomer at 60 °C is quite low[32] and significant homopolymerization or thermal polymerization is not expected over the course of a few hours at 60 °C. Also, our previous investigations[33] of the related simultaneously radiation-grafted FEP-*graft*-PS system using Attenuated Total Reflectance (ATR) and transmission mode infrared spectroscopic measurements found the grafting levels of the near surface region to be the same or slightly higher than that of the bulk in all cases.

D-type films: thickness and orientation. It appears that because the non-oriented D-25 and D-50 films have similar molar masses and crystallinities *and low orientation* they exhibit grafting behavior more like that expected for ideal films differing only in thickness, namely $R_g \propto 1/\text{thickness}$.

The lower grafting rates and Grafting Levels, GLs, of the D-type films compared to those of their N-type film counterparts may be due to the lower permeability of the D-type films resulting from their higher molecular weight and thus more extensive physical crosslinking. In addition, a greater extent of physical crosslinking may reduce the free volume available for graft component by inhibiting the ability of the ETFE structure to expand during grafting (not only the mass *but also the volume* increases[1] significantly during grafting).

The R_gs of the monoaxially oriented films clearly do not fit the ideal relationship, $R_g \propto 1/\text{thickness}$, and the grafting rate of the monoaxially oriented D-23O film is about 30% lower than that of the comparably thick D-25 film. In addition the grafting levels, GLs, of the monoaxially oriented films are up to about 40% lower than those of the non-oriented D-type films for grafting times of less than 1000 min. These differences in grafting behavior are most likely due to the decrease in monomer permeability due to the film orientation and also the associated higher film crystallinities of the monoaxially oriented films.

Position on extruded film roll width. The observed correlation between the relative rates of grafting and graft levels as a function of time and film orientation is also observed in the grafting investigations of different regions of the same film. Based on a similar reasoning as earlier, this variation in the grafting behavior of the N-25 films over the roll width is attributed to differences in film orientation over the roll width. The D-type films have much less variation in their orientation over the roll width, and thus their grafting behavior is much more homogeneous over the roll width.

Irradiation method and atmosphere. The fact that the initial grafting rates are about the same for the samples irradiated using different irradiation method or atmosphere is likely to be due to the grafting rate depending more on the rates of monomer transport into the film than on differences in radical content and type. The somewhat higher graft levels as a function of longer grafting times in the case of the e-beam irradiated films than those in the case of the γ irradiated films is likely to be due to the higher radical content in the former. The loss of active sites due to radical recombination and combination reactions is expected to occur to a lesser extent in the case of our faster and lower temperature (cooled) e-beam processing. Not too different from the present results, Gupta and Chapiró reported[31] that the grafting yield of γ/air and e^-/air pre-irradiated FEP films with acrylic acid was about the same when reacted under the same grafting conditions.

The highest grafting yields and rate obtained when the e-beam irradiation was carried out under an inert atmosphere is ascribed to the higher content of radical active sites obtained.[29] Less of the highly reactive carbon-based radicals are lost due to reactions with oxygen or through recombination reactions if the pre-irradiation processing conditions exclude oxygen and are rapid, respectively.

Oxygen is not always detrimental to the grafting of non-fluorinated or partially fluorinated base polymers however. Morgan and Corelli reported[34] that the grafting levels of acrylonitrile onto PE films were higher if the electron pre-irradiation was carried out in air rather than under vacuum. They attributed the greater extent of reaction of the samples irradiated in air to additional reactive sites formed under these conditions due to chain peroxidation reactions. In the case of ETFE base polymers, our previous FTIR spectroscopic investigations have shown[2] that hydroperoxides are formed during the γ/air irradiation of ETFE and that they are active in the subsequent grafting process.

Grafting temperature. The increase in the initial grafting rates, R_g, of the N-100 films pre-irradiated with a dose of 20 kGy by the γ/air method as the grafting reaction temperature increases to 60 °C and their increase in Saturation Grafting Levels (SGL) as the grafting temperature increases to 50 °C (Table 3 and Fig. 6) are probably due to an increase in the monomer transport and the initiation and propagation reaction rates at higher temperatures. This latter aspect is particularly important if many of the initiating sites in the pre-irradiated films are peroxides since the half lives of peroxides and hydroperoxides decrease[32] considerably over this temperature range.

The lack of further significant increase in the grafting rate at temperatures above about 60 °C, its decrease between 80 and 90 °C, and the decrease in SGL at temperatures above 50 °C are likely a reflection of an increase in the rate of termination due to radical combination reactions. Increased termination results from the higher macroradical mobility in the temperature range of the glass transition temperatures of the polystyrene graft component and the ETFE base film.

For example, the T_g of polystyrene (PS) is reported[35] to be 80–100 °C, and ETFE is reported[36] to have a transition in the range of 110–135 °C which is associated with the motion of long chain segments in the amorphous domains. We have reported[37] earlier that the onset of the T_g of the PS component in FEP-*graft*-PS films lies between about 80 and 105 °C (decreasing for higher grafting levels), and our DSC measurements on ETFE-*graft*-PS films indicate[38] that the T_g of the PS graft component is about 80–85 °C for an N-100 film having a graft level of 54 mass%. An important additional factor is that the T_g of the PS component during grafting is actually expected to be lower due to the plasticizing effect of the styrene monomer on the PS component during grafting.

Therefore, the change in grafting behavior with temperature appears to be largely influenced by the T_g of the grafted PS domains. Increased monomer transport rates into the film and higher reaction propagation rates at higher temperatures appear to be counterbalanced by an increase in the rate of termination due to higher segmental mobility in the monomer-swollen PS grafted domains, thus leading to a change in grafting behavior.

For example, the grafting rates, R_g, plotted as log R_g as a function of $1/T$ (data not shown) do not exhibit a simple linear dependence (constant apparent activation energy) over this temperature range, and some type of discontinuity or break is observed in the region between about 45 and 70 °C. We attribute this apparent lack of constant activation energy to a loss of reactive radical sites due to termination reactions as the glass transition temperature of the styrene-swollen PS component of ETFE-*graft*-PS is approached.

Similar changes in grafting behavior as a function of temperature have been observed for other systems, although the details and their interpretation can differ significantly for each monomer/base polymer system. For example, Chapiró[1] found a discontinuity or break in the Arrhenius plots at about 110 °C in the grafting of acrylonitrile and methyl methacrylate onto γ/air pre-irradiated high and low density PE films. He interpreted this discontinuity as resulting from hindered monomer diffusion into the crystalline regions below the melting point. In contrast, the Arrhenius plot for his grafting experiments with styrene yielded a single activation energy over the entire measurement range of 0 to 120 °C.

Arrhenius plots and activation energies for the radiation grafting of some fluoropolymers have also been reported. For example, the activation energies were constant and of similar magnitude for the grafting of γ/air pre-irradiated FEP films with styrene[10] over the temperature range of 50 to 80 °C and for the grafting of acrylic acid into e^-/air pre-irradiated ETFE films[39] with acrylic acid over the temperature range of 45 to 75 °C. However the Arrhenius plot for the grafting of e^-/N_2 pre-irradiated ETFE films with α,β,β-trifluorostyrene exhibited[13] a discontinuity at 50 °C and a factor of 6 decrease in the apparent activation energy above this temperature. Momose and co-workers attributed[13] this discontinuity to a decay of the trapped radicals rather than to a glass transition of ETFE. Discontinuities were reported to occur at about 35 to 40 °C in the Arrhenius plots obtained from the grafting experiments of Hegazy and co-workers[11] and Gupta and Chapiró[31] using acrylic acid monomer and γ/vacuum and γ/air pre-irradiated PTFE and γ/air pre-irradiated FEP base polymer films, respectively. Hegazy and co-workers[12] attributed this behavior to an increase in the rate of monomer diffusion into the PTFE matrix; whereas Gupta and Chapiró[31] attributed this behavior to diffusion controlled bimolecular chain termination with a high temperature coefficient. In our case of the styrene monomer and ETFE base film system, the discontinuous region between 45 and 70 °C does correlate qualitatively with the temperature range expected for the glass transition of styrene-swollen ETFE-*graft*-PS.

Conclusions

Such properties of base fluoropolymer films as their extent of fluorination and orientation, both intentional and unintentional, have an important influence on their grafting behavior. The grafting behavior of base polymer films from different manufacturers may differ significantly, and, in some cases, the grafting behavior of the same film material may differ in different regions due to inhomogeneities arising during the extrusion process. Although the radiation grafting method is a valuable synthetic method for the preparation of ion-exchange membranes and other useful materials, such processing parameters as the irradiation type and irradiation atmosphere and grafting temperature have complex influences on grafting behavior, and they must be optimized for each base polymer/monomer system.

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