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Copolymers Obtained by the Radiation-Induced Grafting of Styrene onto Poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) Substrates. 1. Preparation and Structural Investigation

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ABSTRACT: A study has been made to investigate the radiation grafting of styrene onto poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA) substrates, using the simultaneous irradiation method. Two PFA polymers of different comonomer perfluoropropyl vinyl ether (PPVE) content and degree of crystallinity were used. Effects of grafting conditions such as monomer concentrations, type of solvent, dose rate, and irradiation dose on the grafting yield were investigated. Of the six different solvents used, the most efficient in terms of increasing grafting yield were dichloromethane, benzene, and methanol. The degree of grafting increased with increasing radiation dose up to 500 kGy, stabilizing above this dose. However, the grafting yield decreased with an increase in the dose rate. The grafting of styrene onto the PFA substrates was confirmed by FTIR-ATR and micro-Raman spectroscopy. The increase in the overall grafting yield was accompanied by a proportional increase in the penetration depth of the grafts into the substrate.

Introduction

Fluoropolymers have drawn much attention in the past and gained wide practical use because of their excellent chemical and thermal stability and their outstanding mechanical properties.[1,2] Graft copolymerization is an attractive mean for modifying base polymers because grafting frequently results in the superposition of properties related to backbone and grafted chains. Radiation-induced grafting is the cleanest and most versatile method of grafting available because ionizing radiation can create active sites, such as free radicals, excited molecules, and ionic species on the polymer substrate, from which the grafting of a monomer can be initiated.[3−6] Also, the degree of grafting can be controlled by proper selection of grafting conditions.[3,6,7] Grafting vinyl monomers into fluoropolymer substrates has been used to produce membranes for various purposes, including separation processes and electrochemical applications.[6−12]

In the past significant research work has been done on the radiation grafting of styrene onto fluoropolymers such as poly(tetrafluoroethylene) (PTFE),[7,13−15] poly(vinylidene fluoride) (PVDF),[16−22] poly(ethylene-*alt*-tetrafluoroethylene) (ETFE),[4,12,23,24] and poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP).[9,11,12,15,22,25−29] However, only few studies of the radiation-induced grafting of styrene onto poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA) substrate, of unknown comonomer (PPVE) content, have been previously reported.[15,30,31] Also surprising is the lack of research interest in the study of the penetration depth of the grafted polystyrene onto the different fluorinated substrates, in the published studies. In the present work we report the characterization of the copolymers obtained by the simultaneous radiation-induced grafting of styrene onto PFA substrates (PFA-*g*-PSTY), with different degrees of crystallinity (%) and different comonomer (PPVE) content, under various grafting conditions. A detailed analysis of the penetration depth of the grafted PSTY under different experimental conditions is provided.

Experimental Section

Materials. Two different poly(tetrafluoroethylene-*co*-perfluoropropylvinyl ether) (PFA) substrates (crowns) were supplied by Mimotopes Pty Ltd. (Melbourne, Australia). The crowns are of cylindrical shape 5 mm diameter by 10 mm length and 0.5 mm thickness. The degree of crystallinity (%) and the molar content of perfluoropropylvinyl ether (PPVE) in the two PFA substrates have been established.[32] The first sample (PFA-A) has a molar content of PPVE equal to 3.9% and a degree of crystallinity of 31.0%, whereas the second PFA substrate (PFA-B) has a 2.0% molar content of PPVE and a degree of crystallinity of 40%. Styrene monomer, which was purchased from AJAX Laboratory Chemicals (stabilized with 10−15 mg/L of *tert*-butyl catechol), was utilized without any further purification in the grafting. Polystyrene (PSTY) pellets ($M_w = 4.0 \times 10^5$), acquired from Aldrich, were used together with PTFE films of 90 μm thickness (Porghof) as reference materials in the spectroscopic analysis. The solvents used for the solutions were HPLC grades and were used as received.

Graft Copolymerization. The PFA substrates were washed with acetone, dried in a vacuum oven at 60 °C, weighed, and

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then immersed in solutions of styrene with different volume concentrations (vol %) of the solvents in glass tubes. Six different solvents were used: dichloromethane, benzene, methanol, 1,2-dichlorobenzene, 1,1,1-trichloroethane, and cyclohexane. The volume of the styrene solutions in the tubes was 10 mL in all cases. The tubes (15 mL) were flushed for 15 min with nitrogen gas before being sealed and irradiated using γ-rays from a ^{60}Co source located in a 220 Gamma-Cell (MDS Nordion, Canada). The samples were irradiated at dose rates in the range of 0.9−6.5 kGy/h for the different total doses applied (in kGy).

The degree of grafting (%) was obtained gravimetricaly by measuring the weight of the substrate (PFA) before and after the radiation-induced grafting, using the following equation:

$$\text{degree of grafting (\%)} = [(W_g - W_o)/W_o] \times 100 \qquad (1)$$

where W_g and W_o are the weights of the grafted and original PFA substrates, respectively.

The grafted samples were removed and washed thoroughly overnight with dichloromethane in a Soxhlet extractor to remove any residual monomer and homopolymer adhered to the substrate surfaces. The grafted samples were then washed free of dichloromethane in methanol and dried in a vacuum oven at 70 °C to constant weight. All the values reported in this work as the degree of grafting (%) at different experimental conditions correspond to the average value given by five samples for each case.

Infrared Spectroscopy. FTIR-ATR measurements were carried out using a Nicolet NEXUS 870 spectrophotometer in transmittance mode at a frequency range of 4000−700 cm^{-1}, equipped with a continuum microscope and a germanium ATR objective. The size of the scan is 100 μm × 100 μm, with a mirror velocity of 1.89 cm s^{-1} and resolution equal to 8.0 cm^{-1}. The penetration depth of the evanescent wave is about 3 μm at 600 cm^{-1}.

Micro-Raman Spectroscopy (Renishaw Raman). Measurements were made under a Renishaw Raman microscope in a frequency range of 4000−500 cm^{-1}. The excitation source was an argon ion laser, and the spectra were collected using the 633 nm radiation at 8 mW power and CCD detector. The spectrometer slits widths were 700 μm giving a typical spectral width of 5.0 cm^{-1}.

NIR−Raman. NIR−Raman spectra were recorded using a Perkin-Elmer 2000 NIR FT-Raman instrument. This system use a diode-pumped Nd:YAG (yttrium aluminum garnet crystal doped with triply ionized neodymium) laser. The wavelength of the laser is 1064 nm. The resolution used was 8.0 cm^{-1}, and the laser power was 400 mW.

XPS Measurements. XPS analyses were performed using a PHI model 560 XPS/SAM/SIMSI multitechnique surface analysis system at the Brisbane Surface Analysis Facility (BASF). The system incorporates a PHI model 25-270AR CMA electron energy analyzer and a dual Mg/Al X-ray source. Spectra were generated using Mg K$\alpha_{1,2}$ (1253.6 eV) radiation, 400 W, and 15 keV. XPS survey wide scans were taken in the range of 1000−0 eV and at a pass energy of 100 eV, with a step size of 0.5 eV and dwell time of 0.015 s. The acquisition time was 3 min in all cases. The multiplex (narrow) scans at higher resolution of the selected elements (C 1s, F 1s, and O 1s regions) were taken at a pass energy of 25 eV, with a step size of 0.1 eV and dwell time of 0.015 s. The acquisition time was 15 min in all cases. The atomic concentrations were calculated from peak areas divided by "in-house" determined experimental sensitivity factors.[33] Samples were mounted on double-sided adhesive tape. The pressure during analysis was kept at 5 × 10^{-8} Torr. Corrections of charging of the scanned elements for all samples were carried out by referencing to the position of the fluorine (F 1s) peak at 689.67 eV[34] (charging effect of the ungrafted PFA film = 2.3 eV). Areas of the peaks were measured after subtraction of the satellite peaks (arising from the Mg K$\alpha_{3,4}$ transition) using the XPS software. Therefore, all the XPS spectra in this work are presented after corrections of the charging effect and subtraction of the X-rays satellite peaks.

Micrographs. Micrographs of the cross section of the grafted copolymers were taken using a Panasonic color CCTV camera (model WV-CP410/G) attached to an Olympus microscope (model SZ-CTV). The images were processed using Flash Point software.

Results and Discussion

Grafting Mechanism. Before discussing the influence of the grafting conditions such as radiation dose, dose rate, monomer concentration, radiation atmosphere, and solvent on the degree of grafting and the properties of the grafted copolymers (PFA-*g*-PSTY), it is important to illustrate the mechanism of grafting onto the PFA substrates. The overall graft copolymerization process involves three kinetic steps, which may be represented as follows:[15,35]

$$\mathrm{P} \xrightarrow{\gamma\text{-irradiation}} \mathrm{P}^{\bullet}\ \text{(substrate radicals)} \qquad (2)$$

$$\text{initiation:}\quad \mathrm{P}^{\bullet} + \mathrm{M} \rightarrow \mathrm{PM}^{\bullet} \qquad (3)$$

$$\text{propagation:}\quad \mathrm{PM}^{\bullet} + \mathrm{M} \rightarrow \mathrm{PM}^{\bullet}_{n+1} \qquad (4)$$

termination:

$$\mathrm{PM}^{\bullet}_{n} + \mathrm{PM}^{\bullet}_{m} \rightarrow \mathrm{PM}_{n+m}\ \text{(grafted polymer)} \qquad (5)$$

where P is the polymer substrate, P$^{\bullet}$ is the primary radical site formed on the substrate, PM$^{\bullet}$ is the initiated graft chain, M is the monomer unit, and PM$^{\bullet}_{n}$ and PM$^{\bullet}_{m}$ are the grafted growing chains. Changes in the grafting conditions may affect one or more of these three kinetic steps (eqs 3−5), leading to changes in the rate and overall degree of grafting.

The deactivation of the primary radicals formed on the polymer substrate (eq 1) might take place by mutual recombination and represented as follows:

$$\mathrm{P}^{\bullet} + \mathrm{P}^{\bullet} \rightarrow \mathrm{PP} \qquad (6)$$

The growing chain of the graft might be quickly terminated by a high chain transfer to the solvent (S) leading to low graft levels[3,35]

$$\mathrm{PM}^{\bullet}_{n} + \mathrm{S}_{x} \rightarrow \mathrm{PM}_{nx} + \mathrm{S}^{\bullet} \qquad (7)$$

Since the monomer (M) is also being irradiated, significant homopolymer formation takes place in the grafting medium, which reduces the grafting yield to a large extent. This process can be represented as follows:

$$\mathrm{M} \xrightarrow{\gamma\text{-irradiation}} \mathrm{M}^{\bullet} \qquad (8)$$

$$\mathrm{M}^{\bullet} + n\mathrm{M} \rightarrow \mathrm{M}^{\bullet}_{n}\ \text{(growing chains)} \qquad (9)$$

$$\mathrm{M}^{\bullet}_{n} + \mathrm{M}^{\bullet}_{m} \rightarrow M_{nm}\ \text{(homopolymer)} \qquad (10)$$

where M$^{\bullet}_{n}$ and M$^{\bullet}_{m}$ represent the homopolymer growing chains.

The growing grafted polymer and the homopolymer chains might also be terminated via chain transfer to the solvent (S), which can be represented as

$$\mathrm{M}^{\bullet}_{n} + \mathrm{S}_{x} \rightarrow \mathrm{MS}_{nx} + \mathrm{S}^{\bullet} \qquad (11)$$

This study of the grafting of styrene into PFA substrates, and previous studies on the grafting of vinyl

Table 1. Effect of Solvent on Radiation-Induced Grafting of Styrene onto PFA Substrates

dose (kGy)	degree of grafting (%)					
	dichloromethane/ styrene		benzene/styrene		methanol/ styrene	
	PFA-A[a]	PFA-B[b,c]	PFA-A	PFA-B[c]	PFA-A	PFA-B[c]
25	5 ± 0.2	4	9 ± 0.5	8	7 ± 0.8	6
50	15 ± 0.7	13	14 ± 1.0	12	8 ± 1.0	7
100	29 ± 1.2	28	26 ± 2.0	20	14 ± 1.5	12
150	46 ± 1.7	44	44 ± 2.5	37	17 ± 1.5	15
200	64 ± 3.0	62	60 ± 3.0	52	19 ± 2.0	17
250	70 ± 3.0	68	71 ± 3.0	77	21 ± 2.0	18
300	79 ± 3.0	73	78 ± 4.0	90	22 ± 2.3	20
400	86 ± 3.5	82	91 ± 4.5	128	24 ± 2.3	22
500	91 ± 4.0	85	115 ± 5.0	145	25 ± 2.5	22

[a] PFA-A (crystallinity = 31%). [b] PFA-B (crystallinity = 40%). [c] The standard deviations for the grafting onto PFA-B were of the same magnitude to PFA-A substrates.

monomers into fluoropolymers, revealed that the grafting can be described by the Chapiro's *Grafting Front Mechanism*.[3,35−39] This mechanism for the grafting greatly depends on the diffusivity of the monomer solution into the polymer matrix. However, fluorine-containing polymers such as PFA scarcely swell in any solvent or monomer solutions; therefore, initially the grafting takes place at the substrate surface only. This initial grafted layer swells in the grafting medium (dichloromethane or any other solvent used together with styrene), giving place to further grafting into the substrate by the progressive diffusion of monomer through the swollen grafted layers. The grafting into the bulk increases with time until the "*grafting front*" reaches the middle of the PFA substrate, i.e., completely invading the substrate from one edge to the other. Since the degree of grafting with increasing dose depends also on other grafting conditions in a given system, the distribution and penetration of the grafting will also vary with each particular set of conditions.

Effect of Solvent. The relationship between the degree of grafting and the irradiation dose is shown in Table 1 for two PFA substrates, irradiated in the presence of styrene monomer diluted in dichloromethane, benzene, and methanol solvents (50 vol %). The simultaneous radiation method was undertaken under nitrogen atmosphere with a dose rate of 6.5 kGy/h. In addition to the solvents dichloromethane, benzene, and methanol shown in Table 1, we also used solutions of styrene in 1,2-dichlorobenzene, cyclohexane, and 1,1,1-trichloroethane. These last three solvents gave a much lower degree of grafting for styrene than with methanol at all irradiation doses. Because of this, we concentrated our study and analysis of the effect of solvents on the grafting of styrene on the solutions prepared using the three solvents given in Table 1. It has been established that the viscosity of the grafted layers controls the diffusion of the monomer to the grafting sites and that the solvent is basically used in grafting processes to induce swelling of the grafted layers, enhancing the degree of monomer accessibility to grafting sites.[15,31,35] Therefore, the choice of solvent is one of the main factors in the radiation-induced grafting processes. Despite the characteristic small swelling of fluorinated polymers in monomers and all types of organic solvents, the swelling of PFA films has been found to be different in the three grafting mixtures investigated.[15] The swelling of PFA in methanol/styrene mixture (40:60 v/v) was found to be 0.17 (wt %), whereas in benzene/styrene and dichloromethane/styrene were 0.22 and 0.40, respectively. Therefore, we might expect a higher diffusibility of styrene into the PFA substrates when the monomer is in solutions with dichloromethane than with benzene or methanol.

The results in Table 1 show that at low doses (up to 250 kGy) the degree of grafting using dichloromethane as the solvent is higher than that when benzene or methanol were used. Nasef et al.[7,11,15,31] observed a similar behavior of the three solvents upon grafting styrene onto PTFE,[7,15] FEP,[11,15] and PFA[15,31] substrates. These results can be explained by taking into consideration the nature of the three solvents and the solubility of polystyrene homopolymer in the respective grafting solution. The higher degree of grafting obtained by using dichloromethane as the styrene solvent has been explained by the lower chain transfer constant of dichloromethane (0.15)[41] in comparison to benzene (0.2)[42] and methanol (0.296).[41] Chapiro[42] demonstrated that if the solvent has a high chain transfer constant (C_S), the growing chain will be quickly terminated, leading to low grafting yields (see eq 7). Therefore, the use of dichloromethane, which has a low chain transfer constant and is an electron acceptor in nature, slows down the termination of the grafted polystyrene growing chains, and as a result of this the grafting yield increased. Methanol, which is an electron donor and which has a higher chain transfer constant than dichloromethane, caused faster termination of the graft growing polystyrene chains, leading to lower degree of grafting. Methanol also induces a reduction in the monomer diffusion during irradiation due to the increase in the viscosity of the grafting solution enhanced by the insolubility of the polystyrene homopolymer in methanol. The higher transfer constant of benzene, in comparison with dichloromethane and the resonance stabilization effect of the benzene ring, which induces an energy transfer during radiation,[31] caused a lower degree of grafting at low radiation doses. However, at high radiation dose (>250 kGy) the use of benzene gave a higher degree of grafting than for dichloromethane or methanol (see Table 1). This can be explained by the higher proximity of the solubility parameter of the benzene/styrene solution (9.3)[15] to the value of polystyrene (9.2)[15] than dichloromethane/styrene (9.5)[15] and methanol/styrene (11.4)[15] mixtures. The solubility parameter (also known as the Hildebrand parameter) governs the process of dissolving an amorphous polymer such as the grafted polystyrene chains in a solvent. The closer the values of the solubility parameters of the solvent and the polymer the more the polymer swells in the solvent. It appears that both dichloromethane/styrene and benzene/styrene mixtures are good solvents for polystyrene. However, the better dissolution of the grafted polystyrene chains in the benzene/styrene solution enhances the diffusion of the monomer through the grafted polystyrene and, as a result, leads to an increase in the grafting yield. Because of the large amount of grafted polystyrene obtained on the surface of the substrates, this effect of the solubility parameter of the grafting mixture on the grafting yield appears to be significant at high radiation doses. The more these grafted polystyrene chains swell in the grafting mixture, the higher the further diffusion of monomer into the substrate. The low degree of grafting of styrene in methanol can also be accounted for by the fact that methanol is a nonsolvent for the polystyrene homopoly-

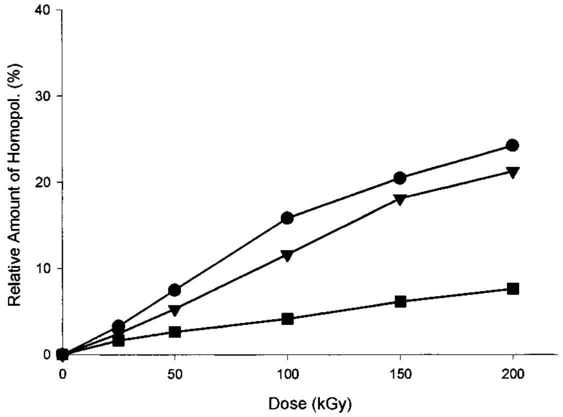

Figure 1. Plot of the relative amount of homopolymer formed (%) vs the applied dose. Solutions of styrene (50 vol %) in dichloromethane (●), in benzene (▼), and in methane (■) solvents. The irradiation was undertaken in nitrogen gas and dose rate equal to 6.5 kGy/h.

Table 2. Effect of Dose and Solvent on Radiation Grafting Efficiency of Styrene onto PFA-B Substrates[a]

	radiation grafting efficiency (%)		
dose (kGy)	methanol/styrene	DCM/styrene	benzene/styrene
50	10.4	16.7	12.8
100	11.3	18.1	14.6
150	11.1	17.4	15.3
200	11.5	18.5	14.8

[a] Dose rate equal to 6.5 kGy/h and irradiated in nitrogen gas.

mer (whereas dichloromethane and benzene are good solvents). Therefore, the formed polystyrene homopolymer in the methanol solution precipitates over the substrate, restricting the further diffusion of styrene monomer onto the internal layers, with a subsequent decrease in the grafting yield.

The degree of grafting is also affected by the free radical yield ($G(\mathrm{R}^\bullet)$) of the different solvent/monomer mixtures. In a study of the radiation of styrene and α-methylstyrene monomers in solution in organic solvents,[43] it was established that the radical yields of irradiated styrene solutions in methanol, cyclohexane, benzene, and carbon tetrachloride increases as methanol < cyclohexane < benzene < carbon tetrachloride. The $G(\mathrm{R}^\bullet)$ of styrene chain radicals in methanol appears to be lower than that of the styrene chain radicals in the other solvents, and as a result, a lower degree of grafting is correspondingly obtained, as shown in Table 1. Also, the relative amount of polystyrene homopolymer formed (given as the ratio of the mass of homopolymer to the initial mass of monomer in the grafting solution) is lower in methanol solutions in comparison to the solutions of styrene in dichloromethane or benzene, as shown in Figure 1. The grafting efficiency (given as the ratio of the mass of grafted polystyrene to the sum of the graft and homopolymer) is also lower in the solutions with methanol (see Table 2).

Effect of Irradiation Dose. As shown in Table 1, the degree of grafting increases with the increase in the irradiation dose within the limits of this study (25–500 kGy). This is due to the higher formation of free radicals with dose in the grafting system, which subsequently leads to a higher amount of grafting.

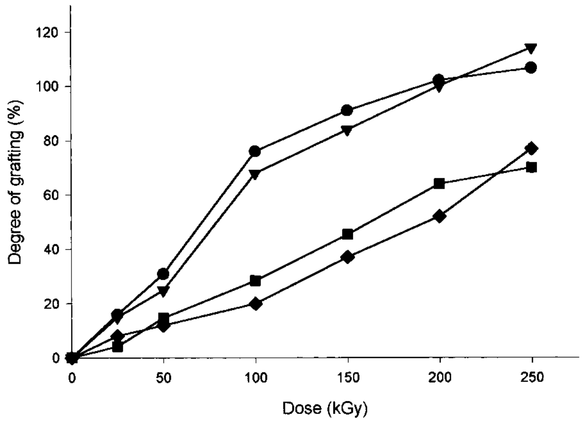

Figure 2. Variation of the degree of grafting (%) of styrene onto PFA-B substrates with irradiation dose at two different dose rates (kGy/h): Solutions of styrene (50 vol %) in dichloromethane, 3.2 kGy/h (●) and 6.5 kGy/h (■), and in benzene, 3.2 kGy/h (▼) and 6.5 kGy/h (◆).

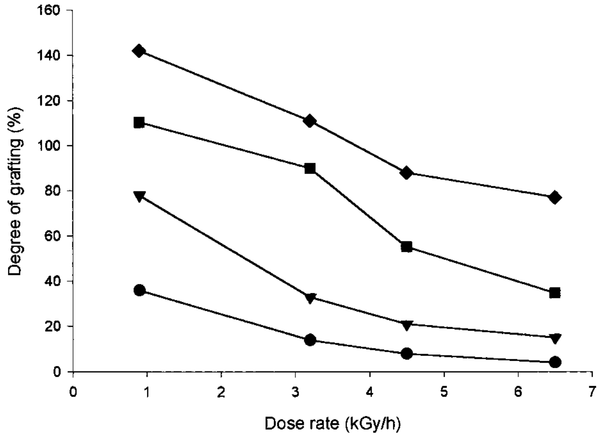

Figure 3. Variation of the degree of grafting of styrene onto PFA-B with dose rate (kGy/h) at various irradiation doses (kGy): 50 (●), 100 (▼), 150 (■), and 300 kGy (◆). Solutions of styrene were prepared in dichloromethane solvent (50 vol %).

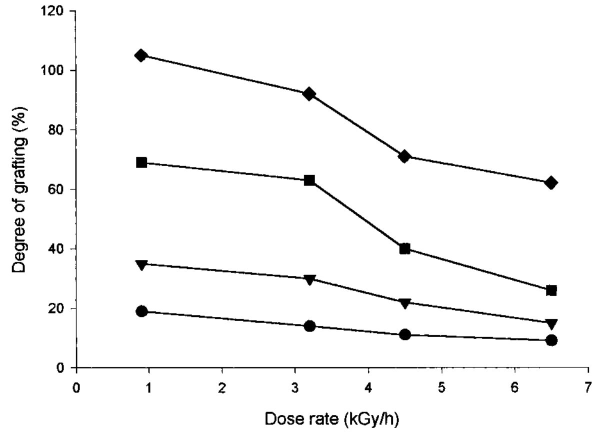

Figure 4. Variation of the degree of grafting of styrene onto PFA-B with dose rate (kGy/h) at various irradiation doses (kGy): 50 (●), 100 (▼), 150 (■), and 300 kGy (◆). Solutions of styrene were prepared in benzene solvent (50 vol %).

Effect of Dose Rate. Figure 2 shows the degree of grafting of styrene onto PFA-B substrates vs the applied dose at two different dose rates, 6.5 and 3.2 kGy/h. The concentration of styrene in the initial grafting mixture was 50% v/v in dichloromethane and benzene solvents. The degree of grafting increased with dose for the two different dose rates. However, the increase in the dose rate during irradiation resulted in a decrease in the degree of grafting, as shown in Figures 3 and 4 for a set of samples irradiated in monomer solutions with dichloromethane and benzene solvents (50 vol %),

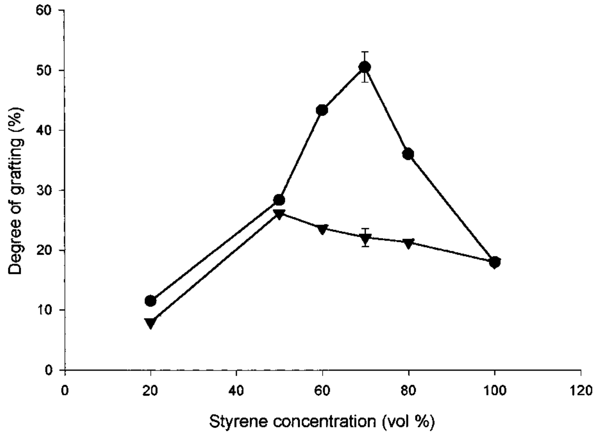

Figure 5. Plot of the degree of grafting vs styrene concentration (vol %) in dichloromethane (●) and benzene (▼) solvents. Irradiation dose is 100 kGy in a nitrogen atmosphere.

respectively. At a high dose rate, the radicals formed in the PFA substrate tend to decay by recombination faster than at lower dose rate. This subsequently results in a lower availability of radical sites in the substrate for grafting reactions. Also at higher dose rate, the grafted polystyrene chains are subjected to faster termination and/or degradation, and consequently the degree of grafting decreased. Similar observation have been reported by other workers who have investigated styrene grafting onto fluoropolymers.[31,44]

Effect of Styrene Concentration. The effect of the monomer concentration in the initial grafting mixture in two different solvents (dichloromethane and benzene) on the degree of grafting of styrene onto PFA-B substrates is shown in Figure 5. It can be seen that the degree of grafting increases as styrene concentration increases up to 70 vol % with dichloromethane and up to 50 vol % for PFA samples with benzene solvent. However, above these concentrations the degree of grafting decreased. The maxima observed with the two solvents have been attributed to the Thrommsdoff effect, as explained for the grafting of styrene in methanol onto polypropylene substrates.[45−47] At low monomer concentrations, the rates of propagation and chain initiation increase with increasing monomer concentration. The termination rate of the radicals formed in the solution is low due to their low concentration. As the monomer concentration increases, the propagation and termination rates increase due to a higher radical concentration, whereas at high monomer concentration the rate of the propagation reaction is overcome by the greatly increased termination rate of the monomer radicals reacting between them and between the growing polymer chains grafted to the substrate. However, the Thrommsdoff effect is not the only factor affecting the efficiency of the grafting with increasing monomer concentration. The grafting of styrene onto PTFE, FEP, and PFA films by the simultaneous radiation method has been found to obey a diffusion-controlled process.[7,11,31] Therefore, the degree of grafting of styrene onto PFA substrates depends also on the diffusibility of the monomer through the grafting growing chains. The diffusibility of the monomer into the polymer matrix may be hindered by the increases in the viscosity of the grafting medium due to homopolymerization. The amount of polystyrene homopolymer during the grafting process increases with the monomer concentration in the initial grafting mixture. A similar result was obtained for the styrene/PFA grafting system by Nasef et al.[31] and by Hegazy et al. upon grafting of different monomers such as methacrylic acid,[36] acrylic acid,[48] and vinyl acetate[49] onto PFA films.

Effect of Crystallinity. Table 1 shows that the degree of grafting in PFA-A (31% crystallinity) is higher than in PFA-B (40% crystallinity) at all irradiation doses, when the grafting was undertaken in solutions of styrene (50 vol %) in dichloromethane and methanol solvents. The data in this table indicate that for the same grafting dose the grafting amount increases with decreasing crystallinity. Also, these results suggest that the styrene grafting proceeds more efficiently in the amorphous region of PFA than in the crystal region. A similar observation was made for the grafting of PMMA onto PTFE films of different crystallinity content.[50] Studies of the crystal structure of PFA copolymers have suggested the exclusion of the PPVE groups from the crystals, which are exclusive conformed by PTFE chains.[51,52] The crystal structure of PTFE below 292 K has been reported to has an ordered repeating pattern of a left- and right-handed pair of molecules in a unit cell having the following projected parameters: a' (along one axis), b' (along the other axis), and γ' (the angle between the two axis) of 9.6 Å, 5.5 Å, and 91.4°, respectively.[53] The diameter of a cross section of the PTFE chain is ca. 3.3 Å. Thus, the dimensions of the voids among the PTFE chains in the a' and b' axis directions are ca. 6.3 and 2.3 Å, respectively. The void dimension is smaller in the b' axis than the molecular size of styrene (ca. 4.5 Å). Therefore, styrene molecules cannot readily diffuse into the crystalline region. The XPS analysis of the grafted PFA-*g*-PSTY copolymers presented below showed that the **C**−H/**C**−F ratio in the grafted PFA-A is higher than in grafted PFA-B (see Figure 8A). This result further suggests that styrene monomer can more efficiently diffuse and be grafted into the PFA substrates with higher amorphous region content, yielding a higher amount of grafted PSTY copolymer. However, the degree of grafting at high irradiation doses (above 250 kGy) is higher in PFA-B than in PFA-A when benzene was used as the solvent (see Table 1). This might be due to the relative higher decrease in crystallinity in the PFA-B substrates in comparison to PFA-A during the radiation-induced grafting process.[32] This effect, which is associated with the better dissolution of the grafted polystyrene chains in the benzene/styrene solution, might explain the observed higher degree of grafting in PFA-B at high applied doses. However, further work is required to completely clarify this aspect.

Spectroscopic Analysis. A. XPS Analysis. Figures 6 shows the survey wide scan (A) and the C 1s spectrum of the ungrafted PFA substrate (B). The different components of the C 1s peaks after radiation grafting at 25 kGy are also presented (C) and the C 1s (D) and F 1s (E) spectra of PFA substrates before and after radiation grafting using different doses. The C 1s spectrum of the ungrafted PFA consists of a main peak with a BE of 292.5 eV (after correction for the charging effect) attributable to the **C**F_2 species and two minor components (<5% of the main component area) at 294.4 and 290.9 eV attributable to **C**F_3 and **C**F, respectively.[54,55] With grafting, new peaks appear in the C 1s spectrum as shown in Figure 6C, with the main new peak being a hydrocarbon peak (**C**−C and **C**−H), associated with the grafted polystyrene, at 286.3 and 285.0 eV, respectively. The peak at 285.0 eV is formed by the aliphatic part of the grafted polystyrene (−CH_2−

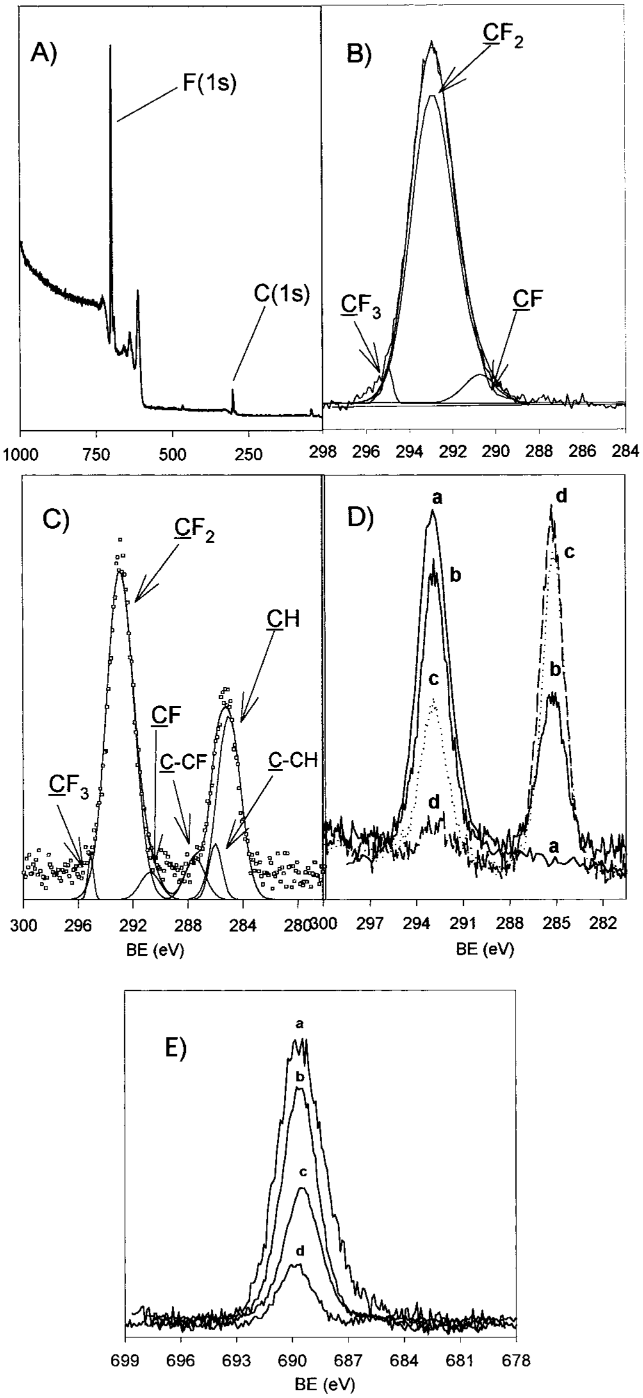

Figure 6. XPS spectra of the initial and the grafted PFA-B substrates. Wide scan of unirradiated PFA (A), C 1s spectrum and its components of ungrafted PFA (B), C 1s spectrum and its components of PFA after grafting to a dose of 10 kGy (C), C 1s spectra of PFA after grafting at different doses (D): ungrafted (a), 10 kGy (b), 25 kGy (c), and 50 kGy (d). The irradiation was undertaken in nitrogen gas, with styrene solutions in dichloromethane solvent (50 vol %) and dose rate equal to 6.5 kGy/h. (E). Survey scans of F 1s spectra of PFA-*g*-PSTY copolymers after grafting at different doses: ungrafted (a), 10 kGy (b), 25 kGy (c), and 50 kGy (d). The irradiation was undertaken in nitrogen gas, with styrene solutions in dichloromethane solvent (50 vol %) and dose rate equal to 6.5 kGy/h.

CH=) (285.0 eV) and the aromatic component $-(C_6H_5)$ (284.67 eV).[34] The changes in the relative concentration (%) of the different C 1s and F 1s species are shown in Figure 7, for samples grafted onto PFA-B under nitrogen gas and styrene in solution (dichloromethane 50 vol %).

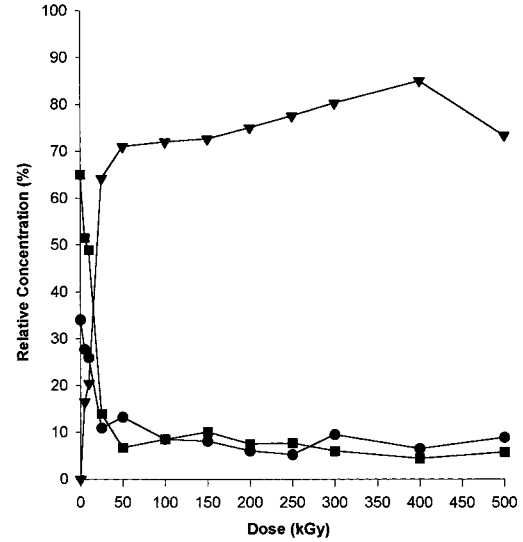

Figure 7. Changes in the relative concentration (%) of C 1s and F 1s atomic species in the XPS spectra of grafted PFA-B with irradiation dose. **C**−H (▼), **C**F$_2$ (●), and F 1s (■). Grafting conditions are the same as in Figure 6.

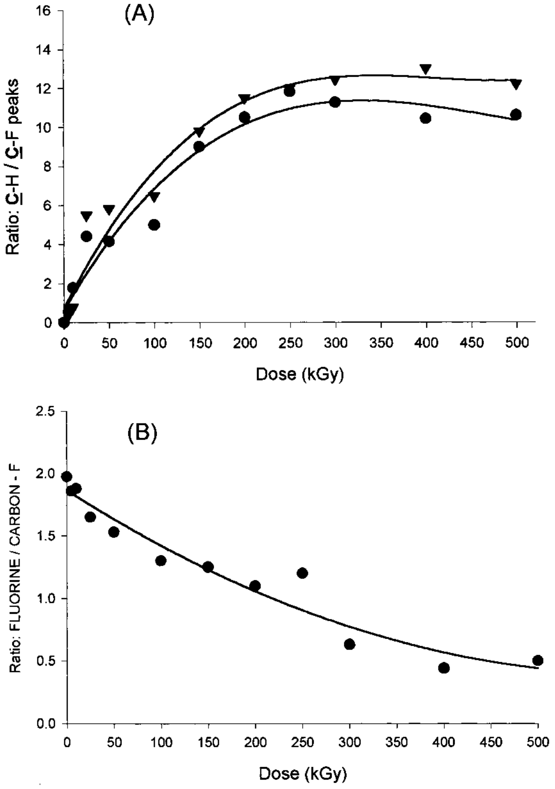

Figure 8. Plots of the hydrogenated carbons (**C**−H) to fluorinated carbons (**C**−F) atomic ratio (A) and fluorine (F 1s) to fluorinated carbons (**C**−F) ratio (B) as a function of applied grafting dose. PFA-A (▼) and PFA-B (●). Grafting conditions are the same as in Figure 6.

Clearly, there is an initial strong increase in the relative amount of hydrocarbon species with irradiation, reaching a plateau at about 50 kGy. At the same time, in the radiation range between 0 and 50 kGy, the relative amounts of F 1s and fluorinated carbons (centered at 292.5 eV) strongly decrease, eventually forming a plateau corresponding to that observed for the hydrocarbon groups. These strong changes in the relative concentrations of carbon and fluorine elements during the initial stage of radiation are due to the grafting taking place preferentially on the surface of the substrates, as proposed in the *Grafting Front Mechanism*. Once the surface has been "saturated" with grafted PSTY, it has been shown that further irradiation ($>$50 kGy) causes the grafted polystyrene chains to grow, giving place to an increase in the molecular weight (M_w),[56] and simultaneously to form grafted chains deeper into the substrates, by diffusion of the monomer through the grafted polystyrene surface layers.

XPS measurements performed on all of the grafted samples reveal the evolution of the **F**/**C**−F (**C**−F includes CF$_2$, CF$_3$, and CF components) and **C**−H/**C**−F (**C**−H including all forms of hydrogenated and C−C carbons) atomic ratios, as a function of the radiation dose (see Figure 8A,B). The increased grafting of PSTY with dose is indicated by the rapid increase of the **C**−H/**C**−F atomic ratio up to about 200 kGy, followed by a constant value for higher doses, whereas the **F**/**C**−F ratio decreased progressively with dose from an initial value of almost 2 (2 fluorine atoms per each carbon present), reaching values below 1.0 at high radiation doses ($>$250 kGy). A similar observation was reported in a study of the surface modification of PTFE[57] after exposure to NH$_3$ plasma radiation to high doses, but no reason as to why the **F**/**C**−F atomic ratio decreased to a value below 1.0 was offered. The decrease from an initial value close to 2 is due to the defluorination process during the simultaneous radiation-induced grafting of PSTY. However, this **F**/**C**−F ratio in the XPS spectra should not be lower than 1.0 because, even in the unlikely case of substitution of both fluorine atoms of the same carbon (**C**F$_2$), the BE of the **C**−C to which both fluorine have been removed is 285.8 eV,[34] and therefore, this carbon will become a component of the **C**−C peak instead of the **C**−F (291.4 eV) peak (see Figure 6C). Clearly, the **F**/**C**−F atomic ratio in irradiated PTFE and PFA samples should only change value between 2.0 and 1.0. A possible explanation for this ratio reaching values below 1.0 lies in the sampling depth of the XPS scans (defined as the depth from which 95% of the signal arises);[58] 63% of the signal comes from a "mean free path" (λ) equal to 1 ($\sim$20 Å). From a path of 3λ (60 Å) 95% of the XPS signal is obtained. Therefore, if the grafted PSTY is located on the outermost surface, the XPS will detect it preferentially, due to the fact that $\sim$63% of the XPS signal arises from 1λ. In addition, the presence of grafted PSTY on the outer surface will result in a lower measured F 1s content, due to the increased attenuation of the much lower KE of F 1s in comparison to the C 1s electrons.

B. NIR−Raman. Figure 9A shows the Raman spectra of PS, PTFE, PFA-A, and PFA-B. The spectra showed no significant luminescence signal, which indicates that the samples were fairly pure. The assignments of the spectra can be found elsewhere in the literature.[59−61] As Figure 9A shows, the spectra of the PFA substrates are very similar to the one of PTFE. The most significant difference is the presence of a small peak at 805 cm^{-1} in PFA, associated with the perfluoropropylvinyl ether group.[60]

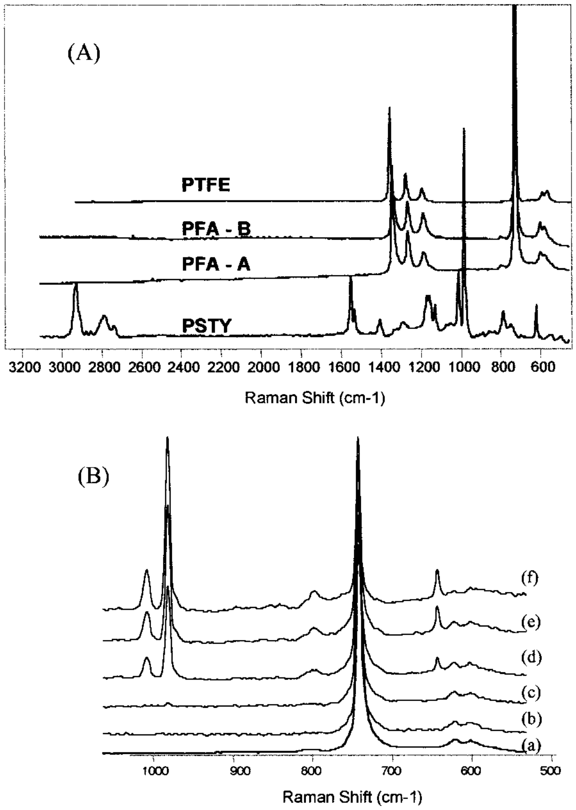

Figure 9. Raman spectra of the ungrafted PFA substrates, PTFE and PSTY (A) and that of PFA-B after radiation grafting using different irradiation doses (B): 0 (a), 5 kGy (b), 10 kGy (c), 25 kGy (d), 50 kGy (e), and 100 kGy (f). The rest of grafting conditions as in Figure 6.

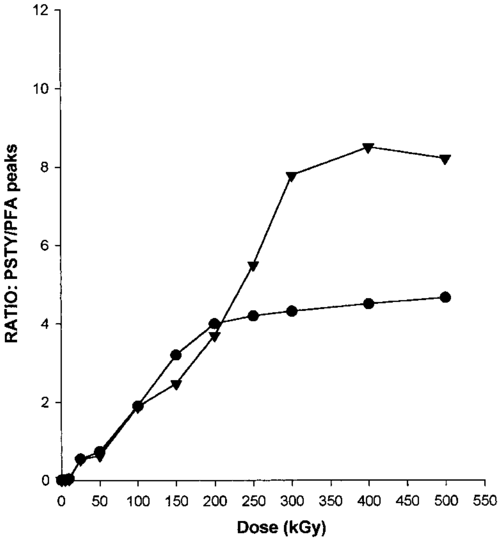

Figure 10. Changes in the ratio of the areas of the Raman peaks due to polystyrene (996 cm^{-1}) and PFA (734 cm^{-1}), with irradiation dose. Samples irradiated in solutions of styrene (50 vol %) in benzene (▼) and in dichloromethane (●) solvents.

The grafting of styrene onto the surface of PFA substrates gives rise to a proportional increase with dose of a strong Raman band at 996 cm^{-1}, which is characteristic of polystyrene (C− C ring "breathing" vibration),[61] as shown in Figure 9B. The grafting also results in a decrease of the 734 cm^{-1} band (C−F stretching of CF$_2$ groups),[59] indicating the defluorination of the PFA substrate during the grafting. The change in the grafting of styrene with dose and with different solvents for the monomer (dichloromethane and methanol, 50 vol %) was followed by taking the ratio of PSTY$_{(996\ \mathrm{cm}^{-1})}$/PFA$_{(734\ \mathrm{cm}^{-1})}$ peaks, with the results shown in Figure 10. The increase in dose results in a subsequent increase of the PS/PFA ratio up to about 400 kGy, where a plateau is reached. Figure 10 confirms that the amount of grafted polystyrene onto the substrates increases with

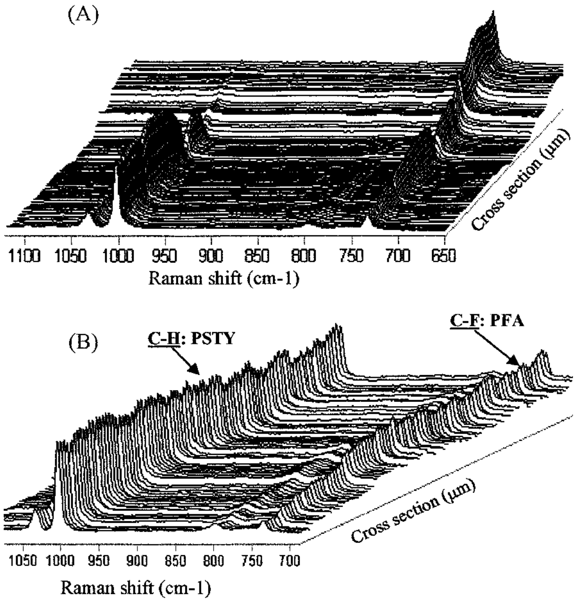

Figure 11. 3D Raman spectra (Renishaw) of the cross section of grafted PFA-*g*-PSTY using irradiation doses of 50 kGy (A) and 300 kGy (B). Grafting conditions are the same as in Figure 6.

dose and that this process can be monitored by the use of FT-Raman spectroscopy. It is also evident that the grafting in dichloromethane was characterized by higher ratio values of the Raman peaks at low irradiation doses (<200 kGy), in a comparison with benzene, in a fashion similar to that observed for the overall grafting of styrene measured gravimetrically (see Table 1).

Depth Profile Analysis of Grafted PFA Substrates. A. Micro-Raman (Renishaw) Spectroscopy. The depth profile analysis of PFA-*g*-PSTY copolymers was investigated by Micro-Raman spectroscopy. Scans of 1.0 μm size were taken (exposure time = 20 s) every 1.0 μm from one edge to the other of the cross section of PFA-*g*-PSTY substrates. Parts A and B of Figure 11 show the 3D spectra of grafted PFA-*g*-PSTY obtained at total dose of 50 and 250 kGy, respectively. The peaks of interest are the strongest in the PFA and PSTY, i.e., 735 cm^{-1} in PFA and 996 cm^{-1} in PSTY. As the scans move into the graft from the surface, the intensity of the PFA peak at 735 cm^{-1} becomes stronger while the PSTY peak at 996 cm^{-1} decreases (see Figure 11A). The depth profile of the grafting is given by the ratio of the PSTY/PFA peaks, as shown in Figure 12, for copolymers grafted at different doses (50, 200, and 400 kGy) and with different solvents (dichloromethane and methanol). As mentioned above, the higher degree of grafting (%) is obtained using dichloromethane as the solvent. This is further confirmed in the depth profile of the grafting where at low dose (50 kGy) the penetration depth of the grafted PSTY in dichloromethane is approximately 100 μm (Figure 12A, curve 2), whereas with methanol, which gives a lower degree of grafting at all irradiation doses (see Figure 1), it is ~40 μm (see Figure 12A, curve 1). With the increase in the irradiation dose, the amount of PSTY grafts and their penetration depth increase so that a homogeneous graft distribution is achieved in the samples irradiated at 200 and 400 kGy (Figure 12B), respectively. Also, Figure 12B shows that in the middle of the cross section the amount of grafted PSTY increased with increasing grafting dose.

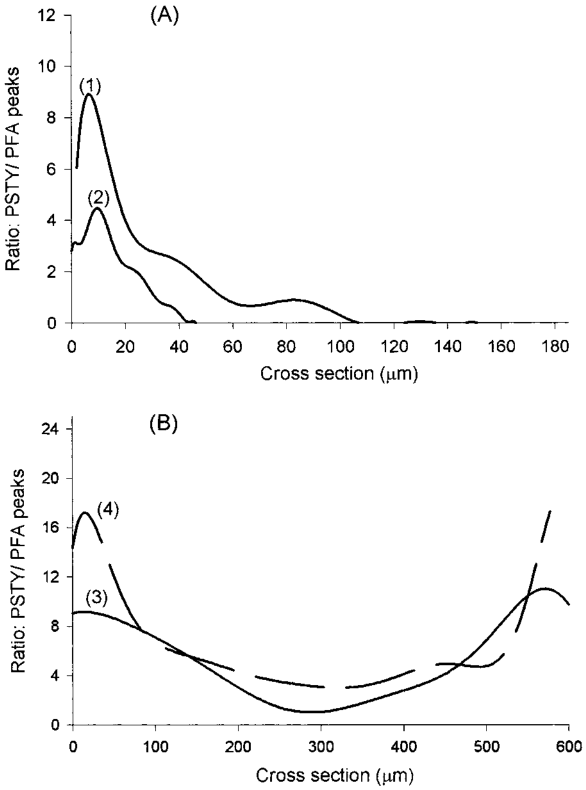

Figure 12. Plots of the (PSTY$_{996\ cm^{-1}}$/PFA$_{734\ cm^{-1}}$) ratios, taken from the Raman peaks, vs the cross section of the grafted substrates. Grafted using a dose of 50 kGy (A) in dichloromethane (1) and in methanol (2). Grafted in dichloromethane (B) to 200 kGy (3) and 400 kGy (4). The styrene concentration on the solutions was 50 vol %, and the dose rate was equal to 6.5 kGh/h.

The presence of a small fraction of PFA on the surface of PFA-*g*-PSTY copolymers even after high grafting doses such as 500 kGy has been detected in the Raman spectra. It has been established that *G*(R$^{\bullet}$) values (the number of free radicals formed per 100 eV of absorbed energy) are usually greater in amorphous than crystalline regions in most polymers.[62] Therefore, the radiation grafting is preferentially taking place in the amorphous region rather than in the crystalline. This explains the presence of ungrafted PFA in the Raman spectra, which is the PFA of the crystalline component of the copolymers. In a study of the thermal properties of the PFA-*g*-PSTY copolymers[32] it was found that the degree of crystallinity (%) of the PFA component shows a relatively small changes at all radiation doses, decreasing after a dose of 500 kGy by only 20% for 85% grafted PFA-A and 30.5% for 91% grafted PFA-B. This confirms that the grafting of PSTY takes place mostly in the amorphous region rather than in the crystalline region of the PFA substrates.

B. FTIR-ATR Measurements. The FTIR spectra of the surface of PTFE and the ungrafted and the grafted PFA substrates are shown in Figure 13. The assignments of the absorption peaks are given in the literature.[31,59,63] The main difference between the spectra of PFA and PTFE is the peak at 994 cm^{-1}. This peak contains a satellite peak at about 985 cm^{-1}, causing a shoulder on the lower wavenumber side of the peak. The 994 cm^{-1} peak is assigned to C–O–C vibrations of the perfluoropropylvinyl ether, whereas the 985 cm^{-1} peak is related to the perfluoropropyl end group CF_3.[63] The grafted polystyrene shows the characteristic absorption peaks of the benzene ring at 3050 cm^{-1} (=C–H stretching vibration) and the skeletal (C=C) in-plane stretching

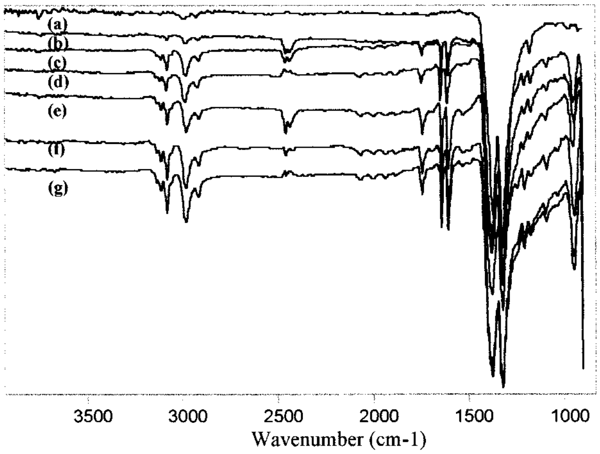

Figure 13. FTIR-ATR spectra of PFA-B substrates before and after radiation-induced grafting at different doses: 0 (a), 25 kGy (b), 50 kGy (c), 100 kGy (d), 200 kGy (e), 300 kGy (f), and 400 kGy (g). Grafting conditions are the same as in Figure 6.

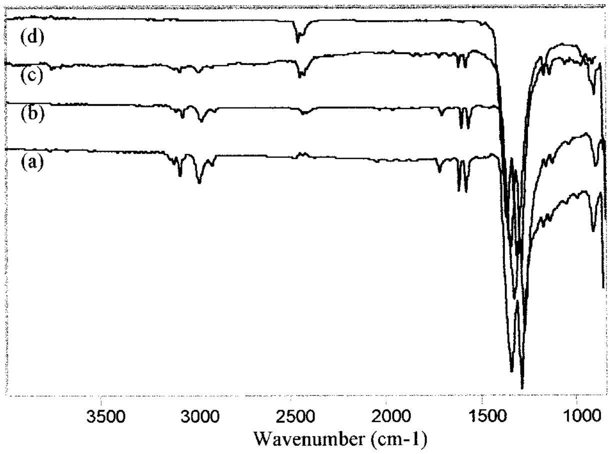

Figure 14. FTIR-ATR spectra of the cross section of PFA-*g*-PSTY, grafted to a total dose of 150 kGy: at the surface (a), 100 μm from the surface (b), 200 μm (c), and 300 μm (d). Grafting conditions are the same as in Figure 6.

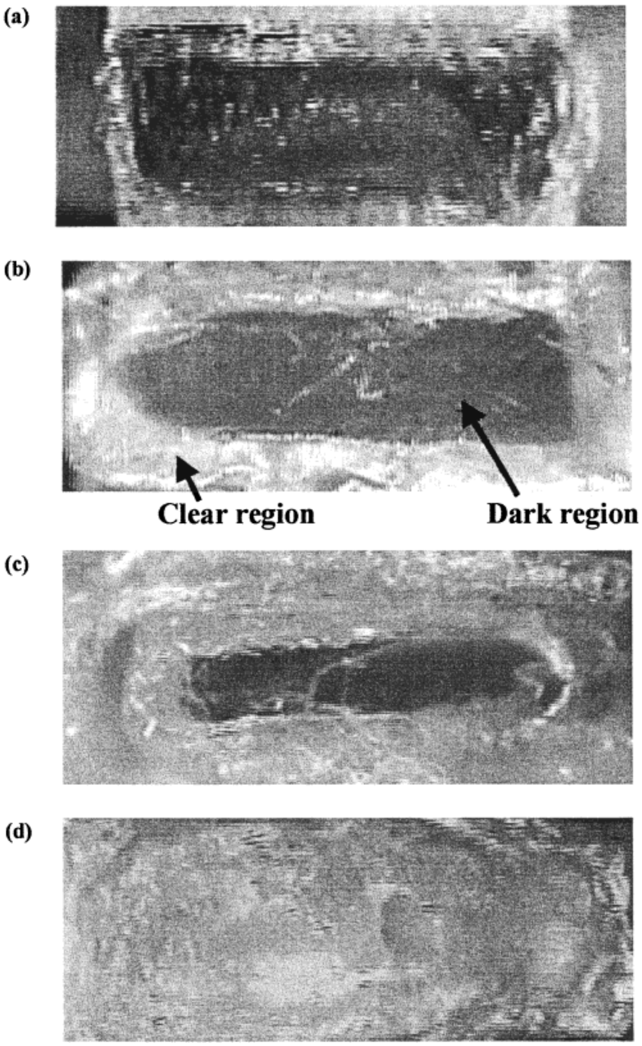

Figure 15. Micrographs of the cross section of PFA g-PSTY, obtained by grafting at different doses: 25 kGy (a), 50 kGy (b), 150 kGy (c) and 300 kGy (d). Grafting conditions are the same as in Figure 6.

vibrations at 1500 and 1600 cm^{-1}. The bands at 2800−2900 and 2900−3000 cm^{-1} are assigned to symmetric and asymmetric stretching of the CH_2 group, respectively. There is also an aromatic out-of-plane C−H deformation band at 860 cm^{-1} and C−H out-of-plane bending overtone and combination bands in the 1600−2000 cm^{-1} region. The spectra show that the absorption bands associated with the grafted PSTY increase with an increase in the grafting dose. This confirms the increase in the degree of grafting with irradiation dose.

Figure 14 shows the FTIR spectra of different regions in the cross section of a PFA-*g*-PSTY copolymer after a grafting dose of 150 kGy in dichloromethane irradiated under nitrogen gas. The spectra clearly indicate that the amount of grafted polystyrene decreases with the increase in the penetration depth into the PFA substrate, which are in a complete agreement with the results obtained by micro-Raman spectroscopy.

C. Micrographs. Figure 15 shows a set of micrographs of the crossection of PFA-*g*-PSTY copolymers, grafted at different irradiation doses. In the cross section two regions can be differentiated: a clear region on the edge and a dark region toward the center of the cross section. The spectroscopic analysis of the cross section (micro-Raman and FTIR-ATR) revealed that the clear region corresponded to the area of the substrate where grafted polystyrene is present, whereas the dark region (middle of the cross sections) corresponds to PFA without any grafted polystyrene. The clear region of the cross sections increase in size with increasing grafting dose, and at the same time the dark regions decrease until they completely disappear at doses above 200−250 kGy. This observation is in good agreement with the spectroscopic analysis presented previously, which indicates that, at 200 kGy radiation dose and above, the grafted polystyrene is present through out the cross section of PFA-*g*-PSTY copolymers.

Conclusions

The simultaneous irradiation grafting of styrene onto PFA substrates with different degrees of crystallinity and PPVE comonomer content has been studied. The dependence of the degree of grafting on irradiation dose, dose rate, monomer concentration, and type of solvent used was established. The final degree of grafting was found to increase with dose up to a plateau at high doses and also increased with decreasing dose rate. It was observed that with increased monomer concentration the degree of grafting reached a maximum for all PFA samples and with grafting solutions having different solvents, until the degree of grafting decreased at larger monomer concentrations. It was confirmed by spectroscopic analysis that the grafting takes place not only on the surface but also in the bulk of the substrates, with the penetration depth increasing proportionally with dose from both surfaces of the substrates, in accordance with the grafting front mechanism. The increase in the overall degree of grafting was accompanied by a proportional increase in the amount and penetration depth of polystyrene grafts into the substrates. However, it was also apparent that the grafting takes place preferentially in the amorphous regions of PFA, with little effect on the initial crystallinity of the substrates even after high doses and degrees of grafting.

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