Investigation of the Vapor-Phase Grafting of Styrene onto PFA

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ABSTRACT: Poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether), PFA, was grafted with styrene from the vapor phase using a simultaneous radiation grafting method. The graft yields were measured as a function of the dose and dose rate and were found to be initially linearly dependent on the dose and independent of the dose rate up to dose rates of ∼3 kGy/h. However, at a dose rate of 6.2 kGy/h, the slope of the yield-grafting time plot decreased. Raman depth profiles of the grafts showed that the polystyrene concentrations were greatest near the surface of the grafted samples and decreased with depth. The maximum penetration depth of the graft depended on the radiation dose for a fixed dose rate. Fmoc-Rink loading tests showed that the grafts displayed superior loading compared to grafts prepared from bulk styrene or from styrene solutions other than methanol.

Introduction

Pioneering work on radiation-induced grafting to poly(tetrafluoroethylene), PTFE, was reported by Chapiro in the late 1950s and early 1960s.[1,2] Examining the process of simultaneous radiation-induced grafting of styrene and methyl methacrylate to PTFE, Chapiro found that at low dose rates the rate of polymerization was slow and grafting was diffusion-controlled. Conversely, at higher dose rates the higher rate of polymerization exceeded the rate of diffusion, and grafting was limited to the surface. When the irradiation temperature was raised, the dose rate required for the rate of polymerization to exceed the rate of diffusion also increased. Because PTFE swells only slightly in styrene, Chapiro concluded that the monomer diffused not into the PTFE but into the partially grafted layers.

Much of the recent interest in grafted fluoropolymers has stemmed from the need to develop membranes for fuel cells. Fluoropolymers are thought to be a good substrate for this application because of their excellent chemical and thermal stability and reasonable mechanical properties.[3] To prepare a conducting fuel-cell membrane from a fluoropolymer, the graft must penetrate the entire substrate. Much of the literature on this subject has been dedicated to studying the effects of dose, dose rate, temperature, chemical structure of the fluoropolymer, additives, graft monomer, and, to a lesser extent, solvents, with the aim of obtaining a homogeneous graft throughout the substrate.[4−16]

Nasef et al. recently reported the effect of solvents on the grafting of styrene to poly(tetrafluoroethylene-*co*-perfluoropropyl vinyl ether), PFA.[12] Later, Nasef reported similar work examining the effects of solvents when grafting to PFA, poly(tetrafluoroethylene-*co*-perfluoropropylene), FEP, and PTFE.[13] The solvents that Nasef and co-workers employed were dichloromethane, benzene, and methanol. They found that by grafting styrene to thin films of PFA the graft yield was strongly dependent on the solvent used and the concentration employed. Like Chapiro,[1,2] Nasef and co-workers found that at low dose rates the diffusion of the monomer was enhanced, leading to high graft yields; at high dose rates, the rate of termination was fast, leading to lower graft yields compared with that for lower dose rates and the same total dose.

Although there have been several other recent studies of the grafting of styrene[17−19] and other monomers, there have been no previous studies of grafting from the vapor phase onto PFA. For the grafting of styrene to polyethylene, the grafting rates are approximately 70% higher in the liquid phase than in the vapor phase.[20] This has been accounted for by the high diffusion resistance at the polymer−vapor interface.

Solid-phase organic chemistry, SPOC, involves the synthesis of molecules that are attached to a solid support. This procedure was first applied to the synthesis of peptides, but more recently the applications have expanded and now include the synthesis of a wide range of organic compounds,[17−19,21] for example, compounds that may display particular biological activity. The traditional solid-phase supports that have been utilized in SPOC have included cross-linked polystyrene, styrene-grafted polypropylene, and polydimethylacrylamide,[21] but the range of temperatures over which these supports can be practically utilized is limited to temperatures below approximately 373 K. Because higher temperatures are desirable for certain synthetic procedures, there is growing interest in investigating other supports that have the potential for use at temperatures above 373 K.

Herein we report an investigation of the vapor-phase grafting of styrene onto PFA as part of an assessment of the potential of these matrices as supports for so-called high-temperature SPOC. Vapor-phase grafting has advantages over liquid- or solution-phase grafting in that no solvent is required and it is a very efficient use of monomer because there is low parasitic loss of monomer by homopolymerization.

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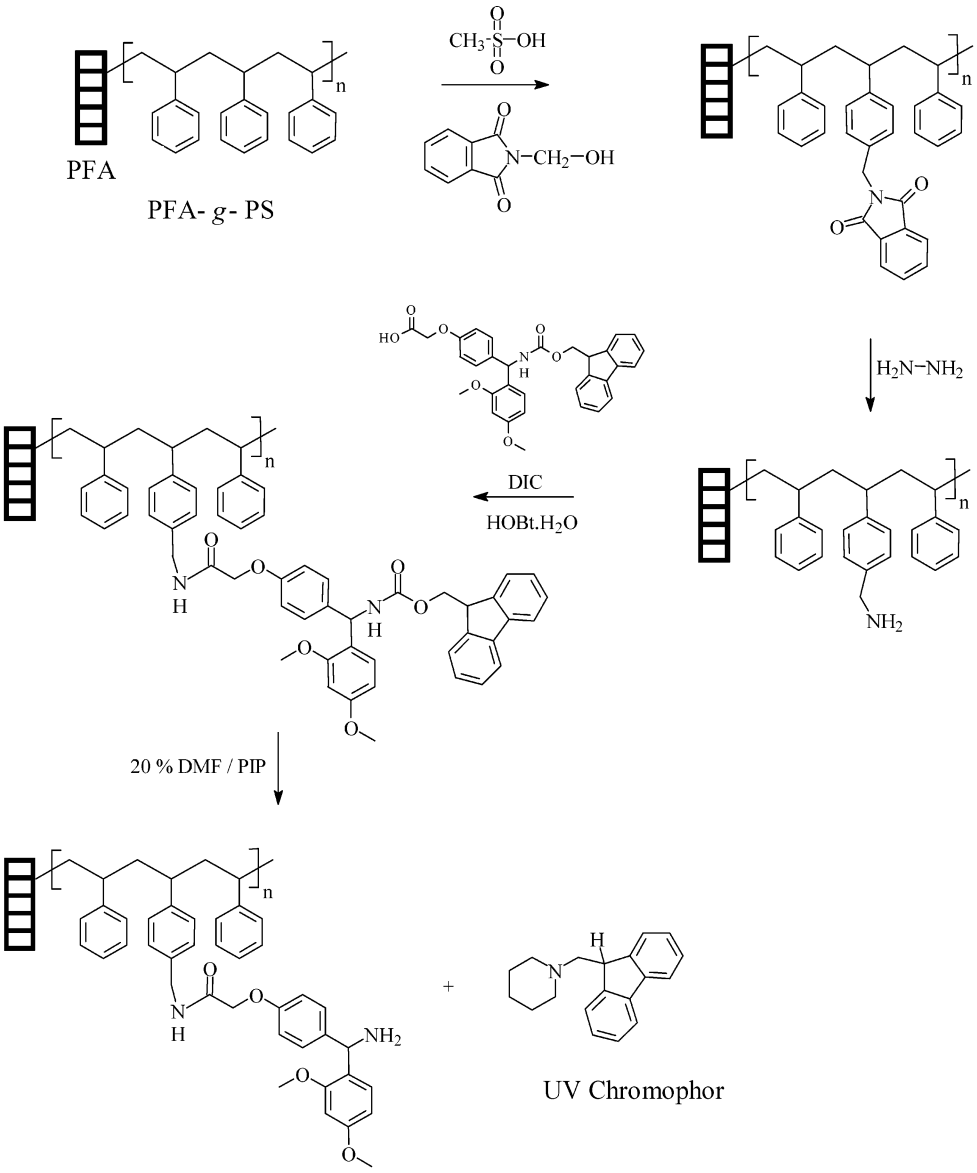
Scheme 1. Loading Test Reaction Procedure



Experimental Section

All substrates were prepared from PFA pellets (DuPont, code TE 7132). Vapor-phase grafting was performed on PFA films pressed from the pellets and cut into 1.9 × 0.8 × 0.05 cm rectangles. The films were washed in acetone overnight in a Soxhlet extractor, dried under vacuum, and weighed before use. Styrene (Fluka, purity 99%) was purified immediately before use by passing through a column of aluminum oxide to remove the 4-*tert*-butylcatechol inhibitor and then distilled under reduced pressure. All other solvents used were of AR or HPLC purity.

Vapor-Phase Grafting. PFA films were placed into the bottom of a long tube designed to fit into the hole passing through the top of a 220 Nordian Gammacell. Styrene feed monomer was put into a reservoir at the top of the tube that could be located outside of the Gammacell. Prior to inserting the tube into the Gammacell, the styrene monomer was degassed by three freeze−pump−thaw cycles. The tube was then sealed at a pressure of approximately 1×10^{-2} Pa. and placed into the Gammacell at 303 K. Lead attenuators placed into the chamber of the Gammacell were used to vary the incident radiation dose rate. After irradiation, the tube was removed from the Gammacell and opened so that the grafted film could be removed and washed for 2 days with dichloromethane in a Soxhlet extractor. The washing procedure guaranteed the removal any ungrafted styrene homopolymer. The grafted PFA was then dried to constant weight under vacuum. The graft yield was calculated as a function of the surface area of the films from the equation

$$\text{graft yield} = \frac{W_f - W_i}{\text{SA}}$$

where W_i is the initial weight of the ungrafted film, W_f is the weight of the film after grafting, and SA is the surface area of the film.

Microprobe Raman Spectroscopy. Microprobe Raman spectroscopy was performed using a Renishaw System 1000 Raman spectrometer (Renishaw plc, Wotton-under-Edge, U.K.) equipped with a Renishaw laser diode emitting at 785 nm. An Olympus MD Plan microscope with a 50× objective lens was used to focus the laser to a spot size of approximately 1 μm. Each spectrum was collected in static mode for 20 s in the range of 700−1200 cm^{-1}. Graft copolymer samples to be analyzed were mounted on a microscope slide and held in place with a generic putty. Maps were made by acquiring spectra over the sample using an automated movable stage.

SPOC Loading Test. The performance of the styrene-grafted PFA as a matrix for SPOC was assessed using the

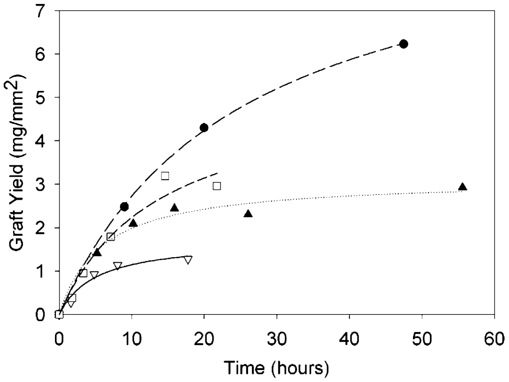


Figure 1. Graft yield as a function of time for the grafting of styrene vapor to PFA films using the simultaneous grafting method. (●) 0.56 kGy/h; (▲) 1.9 kGy/h; (□) 2.8 kGy/h; (▽) 6.2 kGy/h.

standard loading test procedure described by Maeji et al.[21] This loading test provides a measure of the efficiency with which the grafted polystyrene, PS, can be coupled via a linker with another molecule for use in organic synthesis. Under the test procedure (Scheme 1), the styrene graft on the PFA support was first subjected to aminomethylation, and then the aminomethyl groups were modified using 1-hydroxybenzotriazole hydrate, the so-called Fmoc-Rink reagent. Then, to assess the extent of the coupling of the Fmoc-Rink groups to the graft, they were cleaved, and the liberated Fmoc-Rink groups in the surrounding solution were quantified by measuring the UV absorbance of the reaction solution at 301 nm in a 1-cm cell. The loading for the grafted PFA sample (expressed in micromoles) can be calculated from the absorbance of the solution using the procedure for calculating the loading reported by Maeji et al.[21]

Results and Discussion

Vapor-phase grafting is the simplest of all grafting procedures because no solvents are involved and there is no significant homopolymer formation. Previous workers have shown that when monomer vapor is used to graft to polyolefins the diffusion of the monomer at the polymer–vapor interface is hindered, resulting in predominately surface grafting.[17,22–25]

To introduce styrene vapor, experiments were performed using long tubes designed so that the monomer feed solution was outside the radiation source and the PFA film was inside the source, surrounded by the styrene vapor. The location of the monomer liquid outside the radiation source did not completely prevent homopolymerization at high doses because of radiation leakage through the top of the Gammacell.

Graft yields when PFA films were grafted using four different dose rates are shown in Figure 1. Because films were used, the graft yield has been expressed as mass per unit surface area rather than mass increase as a percentage of the original mass. The reason for this was that each film had a slightly different thickness. Because the graft did not penetrate the entire film, the thickness would not affect the graft yield, so this was considered to be a reasonable measure of the graft yield. Figure 1 shows that the graft yield is independent of the dose rate at times less than approximately 10 h. The exception was for the highest dose rate examined, 6.2 kGy/h, which deviated slightly from this trend.

The initial independence of the graft yield on the dose rate suggested that in the early stages of the reaction the grafting was diffusion-controlled. The same observation has been made when grafting to PTFE using bulk monomer solutions,[1,2,4] although in other cases the rate of grafting has been observed to depend on the dose rate. This has been attributed to radiation-induced crystallization of the substrate and increased homopolymer formation at high dose rates.[12,26,27]

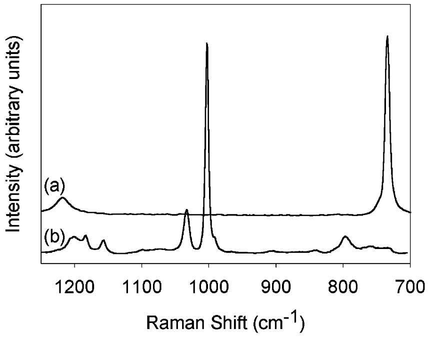


Figure 2. Raman spectra of (a) untreated PFA and (b) pure PS in the region of 1250–700 cm^{-1}.

At higher grafting times and doses, the plots deviate from being diffusion-dependent and begin to plateau. For example, after 20 h, the graft yield was highest at the lowest dose rate studied and lowest for the highest dose rate. Although the results for the two intermediate dose rates fall between these two extremes, they do not conform to this overall trend at the grafting time of 20 h. These observations in Figure 1 could be attributed to one or more of several possible causes. (i) At low dose rates, the grafted chains have higher molecular weights because the rate of termination is slow compared with that at high dose rates. (ii) Radical yield plots based on ESR measurements[28] have shown that the yield of stable radicals reaches a plateau at a high total dose as combination reactions become important because of a high radical density. This could lead to a plateau in the graft yield at high doses. (iii) High dose rates result in higher radiation-induced crystallization, which may lead to lower graft yields because styrene monomer cannot penetrate the crystallites.

Raman Microprobe Mapping of Grafted Surfaces. The distribution of the graft into the substrate is important not only in examining the mechanism of the grafting process but also in determining the applicability of the graft copolymer for use in SPOC. To investigate the penetration depth, we used microprobe Raman spectroscopy.

Raman microspectroscopic mapping of grafted polymer surfaces is a powerful tool in measuring the distribution of polystyrene in a poly(propylene-*g*-styrene) copolymer.[29,30] For this method to be useful, the Raman spectra of the graft and substrate polymers should be easily distinguishable from one another. Fortunately, PFA has a rather simple Raman spectrum (Figure 2), identical to that of PTFE. The major Raman peaks in the range of 1300–700 cm^{-1} include the asymmetric CF_2 stretching vibration (1217 cm^{-1}) and the C–C stretching vibration (734 cm^{-1}).[30,31] No peaks were identified in the Raman spectra that could be used to distinguish between chains in the amorphous and crystalline regions.

The Raman spectrum of PS in the 1250–700 cm^{-1} region is dominated by a peak at 999 cm^{-1}. A comparison of the Raman spectra of PFA and PS over this range is shown in Figure 2. The peak in the spectrum of PS at 999 cm^{-1} has no overlap with peaks in the PFA spectrum and was used as a measure of the PS content

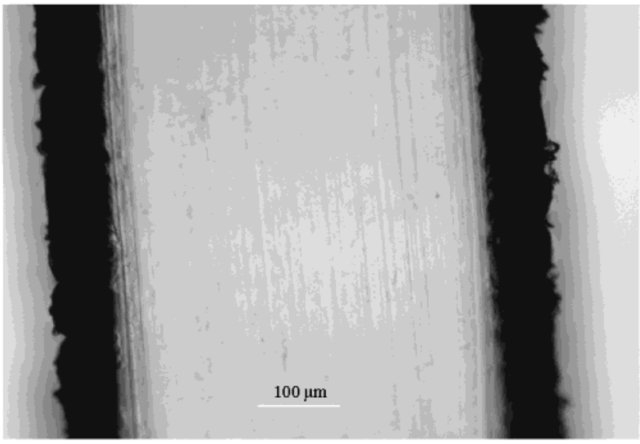


Figure 3. Microscope photograph of a cross section of a PFA film grafted using styrene vapor.

in the Raman maps. Likewise, the characteristic PFA peak at 734 cm^{-1} was used as a measure of the PFA content.

Microprobe Raman spectroscopy was used to map the penetration depth of the graft into PFA after grafting with styrene vapor at different dose rates. To do this, cross sections of the graft copolymer were exposed by physically cutting the grafted films. A microphotograph of one of these cross sections is shown in Figure 3. The dark regions are due to the graft, and the lighter internal region is due to the PFA substrate. From this photograph, it would appear that there is a layer of PS on the PFA substrate and that there is a reasonably sharp boundary between the graft and the substrate. To investigate this further, we used microprobe Raman spectroscopy to construct a radial line map across the grafted region of the cross section. Spectra were recorded at 2-μm intervals over the cross section with the aid of an automated stage controller. An example of a stack plot constructed from the Raman spectra of a vapor-phase grafted PFA film is shown in Figure 4.

In Figure 4, the first three spectra at the front of the stack plot are weak because of the map being started at the very edge of the cross section. For these spectra, the illumination spot was only partially incident with the sample. The next several spectra from the edge of the cross sections show the preponderance of PS from the intensity of the peak at 999 cm^{-1}. The spectra at the rear of the plots were recorded from the interior of the cross section and were composed of mostly PFA (734 cm^{-1}). In the region of the graft, the observed spectra are of a mixture of PS and PFA rather than just PS. The boundary between the graft and the substrate was not sharp but was graded.

To quantify these results further, a method used Keen et al. was adopted.[30] The mole fraction of PS was calculated from the areas under the peaks at 999 and 734 cm^{-1} and then expressed as a fraction of the two signals using the equation

$$\text{mole fraction PS} = \frac{A_{\mathrm{PS(999\ cm^{-1})}}/\sigma_{\mathrm{PS(999\ cm^{-1})}}}{(A_{\mathrm{PS(999\ cm^{-1})}}/\sigma_{\mathrm{PS(999\ cm^{-1})}}) + (A_{\mathrm{PFA(999\ cm^{-1})}}/\sigma_{\mathrm{PFA(999\ cm^{-1})}})}$$

where $A_{\mathrm{PS(999\ cm^{-1})}}$ is the area under the peak at 999 cm^{-1}, $A_{\mathrm{PFA\ (734\ cm^{-1})}}$ is the area under the peak at 734 cm^{-1}, and $\sigma_{\mathrm{PS(999\ cm^{-1})}}$ and $\sigma_{\mathrm{PFA(734\ cm^{-1})}}$ are the relative Raman scattering cross sections. Cross sections $\sigma_{\mathrm{PS(999\ cm^{-1})}}$ and $\sigma_{\mathrm{PFA(734\ cm^{-1})}}$ were measured by acquiring spectra of pure PS and PFA, respectively.

Figure 5 shows the calculated mole fraction of PS as a function of the distance from the edge of the cross sections for PFA films for various total doses over a range of dose rates. The edges of the samples were not perfectly smooth, and this introduced an error in the depth profile estimated to be on the order of ±10 μm. The depth of the grafted layers was between 10 and 70 μm, and they were all a mixture of PFA and PS. The highest proportion of PS was observed when a dose rate of 0.56 kGy/h was used for a total dose of 11.1 kGy, where the mole fraction of PS reached 0.95. The profiles are indicative of a grafting process that begins at the surface and progresses into the substrate, increasing in mole fraction of PS with increasing penetration depth, regardless of the dose rate. What is curious is that in every profile the mole fraction of PS is lower at the surface than just below the surface. This effect may be partially due to the large error in identifying the first few spectra near the edge of the cross section, where the spectra were very weak and focusing was a problem because of surface roughness. However, the trend appears to be very real in samples such as the one irradiated to 11.1 kGy at 0.56 kGy/h where the proportion of PS reached a maximum approximately 20 μm from the surface.

Surface restructuring due to the migration of the graft below the surface has been postulated on the basis of

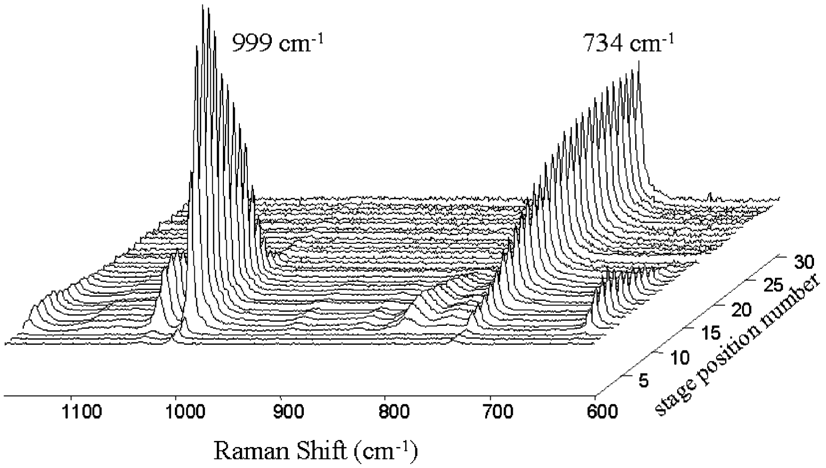


Figure 4. Stack plot of vapor-phase-grafted PFA. The total dose was 19.6 kGy at a dose rate of 1.9 kGy/h. The depth separation between two spectra is 2 μm.

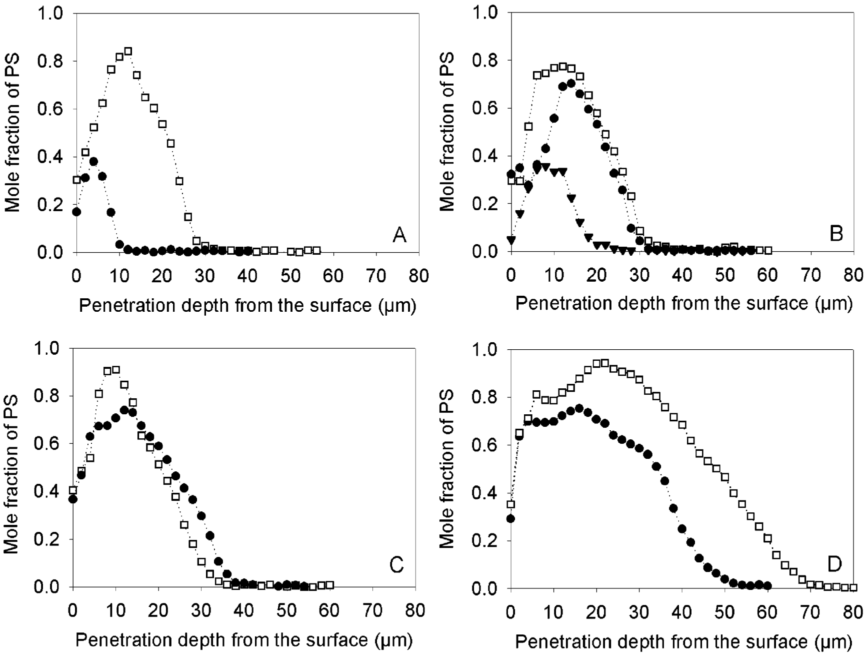


Figure 5. Depth penetration profiles of the mole fraction of PS for films grafted with styrene vapor at different dose rates. A. 6.2 kGy/h: (●) 10.2 kGy, (□) 30.0 kGy. B. 2.8 kGy/h: (▼) 5.0 kGy, (●) 9.4 kGy (□) 20.0 kGy. C. 1.9 kGy/h: (●) 10.0 kGy, (□) 19.6 kGy. D. 0.56 kGy/h (●) 5.0 kGy, (□) 11.1 kGy.

XPS,[31] but this occurs on a nanometer scale, not on the micrometer scale observed here. A more likely explanation for the increase in the proportion of PS below the surface is that it may be due to crystallinity heterogeneity throughout the sample. It was shown using Raman mapping that Mimotopes lanterns made from a blend of poly(propylene), poly(ethylene), and ethylene−propylene rubber have high crystallinity at the surface that was in contact with the mold.[30] The thickness of this highly crystalline layer was approximately 10−20 μm. Although the samples used for the vapor-phase grafting were in the form of films and not lanterns, it is possible that a similar crystallinity profile was present. Because grafting occurs predominately in the amorphous regions of fluoropolymers that are more accessible to monomer,[32] any areas with high levels of crystallinity would have low grafting.

To test the validity of the microprobe Raman mapping as a quantitative method, the area under each penetration profile was plotted as a function of the graft yield and is shown in Figure 6. Although there is a certain amount of scatter, it is evident that the graft yield is directly proportional to the area under the penetration profile, suggesting that the microprobe Raman mapping and calculation of the mole fraction of PS does have merit as a quantitative method.

Results of the Loading Tests. The loading results presented in Table 1 are expressed in terms of the graft yield so that direct comparisons can be made with other samples prepared under different grafting conditions. The loading tests show that, for samples grafted to similar graft yields, the samples grafted in styrene vapor had higher loading than samples grafted in bulk styrene or in solvents other than methanol.[33] Although a direct comparison was not made on the various samples using Raman mapping, it can be assumed that the higher surface grafting characteristic of vapor-phase grafting was responsible for the better loading performance.

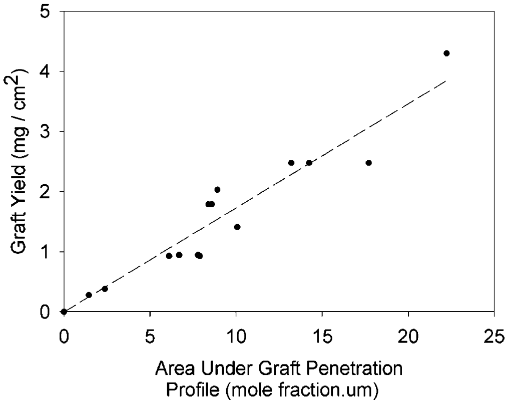


Figure 6. Correlation between the yield for the polystyrene graft and the relative yield for polystyrene calculated from the area under the peaks in the Raman spectra for the vapor-phase grafting of styrene onto PFA.

Table 1. Results of Fmoc-Rink Loading Tests

solvent	% styrene (v/v)	total dose (kGy)	styrene graft yield (mg/cm^2)	loading (μmol/ sample)	loading (μmol/mg of graft)
styrene (bulk)[a]	100	12	13	27	2.0
styrene (vapor)	na	15	16	65	4.0
methanol[a]	30	30	5	27	5.5
methanol[a]	50	15	8	46	5.7
methanol[a]	70	12	12	57	4.8
toluene[a]	50	15	12	11	1.0
dichloromethane[a]	50	15	13	3	0.2

[a] Taken from ref 33.

Conclusions

Grafted solid supports, which may be used in high-temperature SPOC applications, have been prepared. The graft copolymers were characterized in terms of their graft yield and the penetration of the graft into the substrate using microprobe Raman spectroscopy. The vapor-phase grafting was found to be diffusion-controlled at low grafting times and at dose rates of 2.8

kGy/h or below. At higher grafting times, the factors influencing the grafting such as changes in crystallinity and radical−radical recombination reactions led to a deviation from independence on the dose rate. However, the lowering of the styrene vapor pressure due to the formation of some homopolymer in the styrene monomer at longer grafting times, due to a small amount of radiation leakage through the top of the Gammacell, cannot be unequivocally dismissed as having no role in the grafting process.

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