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Grafting of Polystyrene in Poly(vinylidene fluoride) Films by Means of Energetic Heavy Ions

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ABSTRACT: Thin poly(vinylidene fluoride) foils were irradiated in the presence of oxygen with very energetic heavy ions (Xe, E = 44 MeV/amu) in the electronic stopping power energy range to produce peroxides along the ion paths. They were then grafted with styrene monomer. Grafting yields were similar to those obtained with γ or electron irradiation. Structural analyses (XPS, FTIR) were carried out on the material prepared. The new copolymer formed by means of energetic heavy-ion irradiation has a complex structure which is directly related to the anisotropy of the energetic ion/polymer interaction.

Introduction

In the past 3 decades, irradiation with ionizing particles, such as γ and X photons or electrons, has been extensively used to induce grafting on polymeric substrates.[1,2] These irradiations, especially γ-rays, were developed to modify polymers by grafting functional groups or monomers which could change the physicochemical properties of the initial material.[3] Due to the interaction of these particles with the polymer, the final compound is a homogeneous graft copolymer.

Energetic ions induce a continuous trail of ionizations and excitations along their wake, giving rise to a latent track in the solid.[4] It was of interest to attempt to exploit the anisotropy of the energetic ion/polymer damage to graft some monomers or reactive species into these ion paths. Inhomogeneous modifications of the polymer volume could be used to bring about new properties not accessible with conventional chemical, radiochemical, or physical means.

To the best of our knowledge, the first published work concerning grafting in polymeric films by means of energetic ions is by Monnin and Blanford.[5] It concerned the optical detection of charged particles. Consequently, extremely low irradiation fluences were used. The use of fast heavy ions for creation, by grafting, of new composite materials has not been explored. We have recently presented some preliminary results,[6] and this paper reports more systematic studies of fast heavy-ion grafting. Grafting of styrene monomer was initiated in poly(vinylidene fluoride) (PVDF) films by means of energetic xenon ions (E = 44 MeV/amu).

This system (PVDF film grafted with styrene) has not been thoroughly investigated, as shown by the small number of publications, but it is nevertheless highly interesting. PVDF is chemically resistant, is thermally and physically stable (like other fluorinated polymers), can be cast (unlike most fluorinated polymers), and, if crystallized in its β form, exhibits piezoelectric and pyroelectric properties. The polymerization of styrene can be initiated by radicals and the phenyl group can then be chemically modified to induce changes in chemical or physical properties.[3] Radiation-induced grafting for this system has always been performed with γ-rays,[3,7] like most of the work done in this field.[1,2]

Fast Heavy-Ion Irradiation

An energetic ion which penetrates a solid loses its energy via two nearly independent processes: ion–atomic nucleus interactions and ion–electron interactions. The first mode of energy loss (nuclear stopping power) must be considered only at very low energies, roughly below 100 keV/amu. At higher energies, electron interaction (electronic stopping power $(\mathrm{d}E/\mathrm{d}X)_e$) predominates. If starting at rest, increasing the energy of the ion leads to a maximum value for $(\mathrm{d}E/\mathrm{d}X)_e$, the Bragg peak, located around 1 MeV/amu for a heavy ion. Any further increase in the ion energy causes a decrease of $(\mathrm{d}E/\mathrm{d}X)_e$. In the energy range used here, tenths of MeV/amu, the ion trajectories are straight lines, and since the total range in matter is much greater than the sample thickness, the energy in the sample remains virtually constant. The values of the electronic stopping power reached are extremely high, around 5 keV/nm, which is a factor of 2 higher than $(\mathrm{d}E/\mathrm{d}X)_e$ for a 1-MeV electron irradiation (2.5 keV/nm).

The energy lost is spread along the ion path by the ejected electrons, and a radial dose profile exists. The local dose decreases with increasing radius (r) from the ion path, varying approximately with r^{-2}. More accurate estimates were made based on Monte Carlo calculations.[8] These indicate that half of the total deposited dose is lost in a radius of 6.6 nm for a 44-MeV/amu Xe irradiation. The mean local dose in this cylinder is close to 1.75 MGy. Energy deposition in the wake of the ion is very fast (10^{-15} s) and leads to a huge, probably meaningless, local dose rate. Since, at a scale of tenths of nm, energy deposition is very inhomogeneous, at least two parameters are needed to characterize the irradiation: $(\mathrm{d}E/\mathrm{d}X)_e$ and the fluence F_t (number of ions per cm^2). In any case, for comparison with the case of electron or γ irradiation, the mean dose based on the sample averages to very high dose values near the ion path and low dose values elsewhere.

The high density of excitations and ionizations, typical of fast heavy-ion irradiation, may induce a cylindrical damage zone called the latent track[4] even in materials

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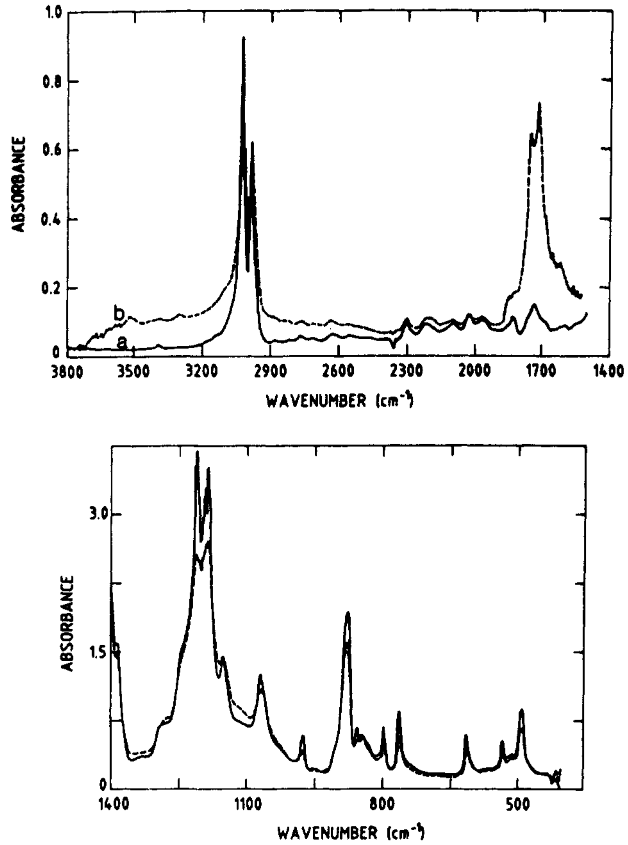

Figure 1. Infrared spectra. 3800–1400-cm^{-1} zone: sample 50 μm thick. 1400–400-cm^{-1} zone: sample 10 μm thick. (a) Nonirradiated PVDF, (b) irradiated PVDF, xenon ions, E = 27 MeV/amu. 3800–1400-cm^{-1} zone: D = 3.43 MGy. 1400–400-cm^{-1} zone: D = 3.89 MGy.

unaffected by electron or γ irradiation. A rather complete description of latent track formation has been given[9] for some inorganic materials. The case of polymers appears to be more complex. Small-angle X-ray and neutron scattering in poly(ethylene terephthalate)[10,11] exhibited cylindrical damage zones along the ion path characterized by an atomic density decrease of 5% in a radius of 4 nm. ESR experiments detected[9] several radicals: radicals induced by backbone scissions and C–H bond breakings and the corresponding peroxidic radicals. Figure 1 shows the infrared spectra of a nonirradiated PVDF sample and an energetic Xe-irradiated sample at 3 × 10^{11} ions/cm^2. The spectrum of the irradiated sample shows the emergence of a new structure located at 1750–1718 cm^{-1} due to chain breaking ($-C{=}CF_2$, $-CH{=}CF_2$, $-CF{=}CH_2$), dehydrofluorination ($-CH{=}CF-$), and oxidation ($-COF$, $>CFCOCF<$).[13,14] In addition, the intensity of the other bands decreased by ca. 30%. It may be concluded that 70% of the polymer bulk is unchanged. Assuming a track[15] model in which all the damage is concentrated in a cylinder of radius r, the undamaged fraction f is given by $f = \exp(-\pi r^2 F_t)$, where F_t is the fluence in ions/cm^2; a track radius of 6 nm is found. In addition, heavy-ion tracks are more permeable to various atoms and molecules.[16] They are very efficiently etched;[17] the core etch rate may be a thousand times greater than the bulk rate, so that a thin cylindrical pore is created for each ion impact.

Experimental Section

PVDF 25 and 10 μm thick was provided by Atochem. All the films were extracted with toluene for 24 h in a Soxhlet apparatus and dried to constant weight prior to use.

All irradiations were carried out in the presence of oxygen. Heavy-ion irradiations were carried out at the GANIL national laboratory, Caen, France, with xenon ions (E = 44 MeV/amu). The experimental irradiation conditions are listed in Table I. γ-ray irradiations were carried out at the CESTA, Bordeaux, France, using a cobalt-60 source, with a dose rate of 5 kGy/h. Electron irradiations (1 MeV) were carried out at the SESI, Palaiseau, France, using a Van de Graaff accelerator.

Table I
Experimental Data for the Heavy-Ion Xenon Irradiation

fluence, ions/cm^2	9.0 × 10^{10}	2.3 × 10^{10}	6.7 × 10^9	4.9 × 10^8
irradiation time, s	866.4	162.4	52.2	148.8
flux, ions/cm^2·s	2.1 × 10^9	2.6 × 10^9	2.4 × 10^9	6.1 × 10^7
mean dose, kGy	488	125	38	3
mean distance,[a] nm	33	66	122	452

[a] Representing the mean distance between two nuclear tracks and calculated by $1/(F_t)^{1/2}$.

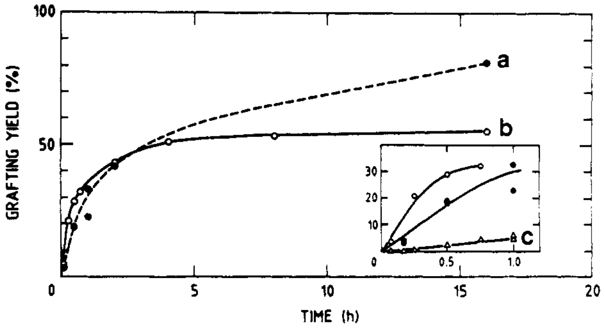

Figure 2. Influence of temperature on grafting kinetics; Xe irradiation, D = 38 kGy: (a) T = 61 °C; (b) T = 75 °C; (c) T = 42 °C.

Styrene monomer produced by Janssen was grafted "as received". Irradiated polymeric films were placed in test tubes, to which was added the liquid styrene monomer, and deoxygenated by alternate freeze–thaw cycles under vacuum. The tubes were then vacuum sealed and immersed in a controlled-temperature bath at the selected temperature and time. The degree of grafting (Y), or grafting yield, was determined after extraction of the grafted polymer films with toluene in a Soxhlet apparatus for 30 h and drying of the films in a vacuum oven at 50 °C to constant weight. The grafting yield is given by

$$Y = (W_f - W_i)/W_i\ (\%) \qquad (1)$$

where W_i and W_f are the weights of the samples before and after grafting.

X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab MK2 spectrometer fitted with a monochromatized X-ray Al source (1486.6 eV). A flood gun was used to cancel the charging-up effect. The analysis chamber pressure was maintained near 2 × 10^{-8} Pa.

Infrared transmission measurements were carried out on a Bruker FT-IR IFS 66 (4000–400 cm^{-1}) equipped with a DTGS detector. The resolution was 2 cm^{-1}.

UV measurements were taken on a Perkin-Elmer Lambda 6 spectrometer (the 400–190-nm zone was explored). The resolution was 4 nm. These measurements allow the determination of grafting yields lower than 10% as the absorbance measured at 269 nm was linearly related to the grafting yield.

Results

Grafting Yields. We first studied the effect of temperature. Samples were irradiated with 44 MeV/amu Xe ions with a fluence of 6.7 × 10^9 ions/cm^2, corresponding to a dose of 38 kGy (see Table I). As peroxides formed by irradiation in oxygen must be thermally decomposed, three grafting temperatures were tested (42, 61, and 75 °C). The grafting kinetics (grafting yield versus grafting time) are shown in Figure 2. The initial grafting rate increases with temperature (0.06, 0.34, and 1.36 h^{-1} for 42, 61, and 75 °C, respectively). The corresponding overall activation energy is around 90 kJ/mol. Grafting yields

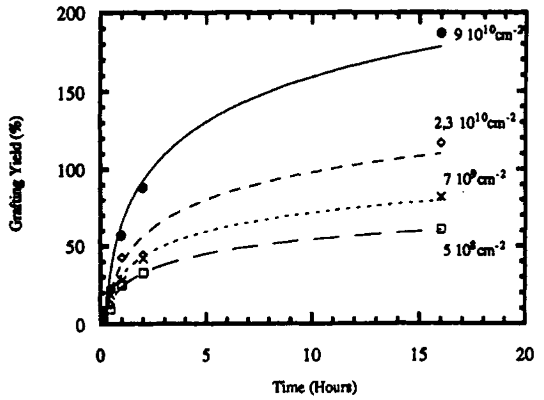

Figure 3. Influence of the fluence on grafting kinetics; Xe irradiation, grafting temperature = 61 °C: (●) $F_t = 9.0 \times 10^{10}$ ions/cm^2, D = 488 kGy; (◇) $F_t = 2.3 \times 10^{10}$ ions/cm^2, D = 125 kGy; (×) $F_t = 6.7 \times 10^9$ ions/cm^2, D = 38 kGy; (□) $F_t = 4.9 \times 10^8$ ions/cm^2, D = 3 kGy.

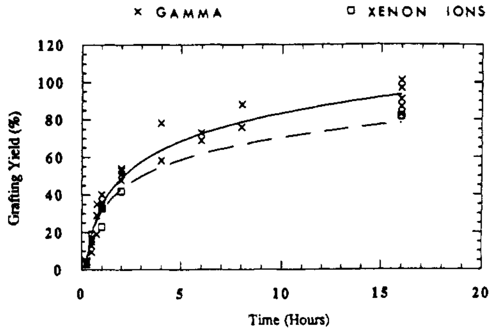

Figure 4. Influence of type of irradiation; grafting temperature = 61 °C: (×) γ irradiation, D = 30 kGy; (□) heavy-ion Xe irradiation, D = 38 kGy.

obtained after 16 h of grafting time decreased with temperature. This could be related to an increasing mobility of radicals with temperature, leading to an increase of termination.

Figure 3 shows the grafting kinetics for four doses, 488, 125, 38, and 3 kGy, corresponding to fluences of 9.0×10^{10}, 2.3×10^{10}, 6.7×10^9, and 4.9×10^8 ions/cm^2, respectively. The grafting temperature was 61 °C. The grafting yield increased with the grafting time and appeared to reach a saturation level at about 16 h (saturation grafting yield). The initial grafting rate and the saturation grafting yield increased with increasing fluence (hence, mean dose). Note that, whatever the grafting time, grafting yield ratios are always different from fluence ratios; this point will be examined further in the Discussion.

A comparison of grafting kinetics between xenon irradiation and γ irradiation at similar doses (38 and 30 kGy, respectively) and identical grafting temperatures (61 °C) revealed no significant differences: the initial grafting rate is the same and grafting yields increase in the same way with increasing grafting time to reach similar grafting yields at 16 h (see Figure 4).

Figure 5 shows grafting yields obtained at 61 °C after 16 h of grafting time plotted against the dose. Three different types of ionizing radiation were used to initiate grafting on PVDF films: γ-rays, electron beam, and xenon ions. The grafting yields are closely comparable. At low doses, between 0 and 10 kGy, the grafting yield rises rapidly. When the dose exceeds 10 kGy, an increase of grafting yield with increasing dose is observed. The points corresponding to films grafted after γ or electron irradiation fit on the curve exactly as if there was no difference in the type of irradiation.

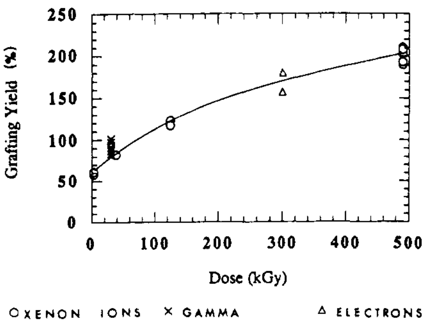

Figure 5. Influence of dose on grafting yield; grafting temperature = 61 °C; grafting time = 16 h.

Swelling Results. Grafted samples have larger dimensions than the initial PVDF film. Hence, macroscopically, grafting can be seen as a swelling process. Let us consider a PVDF film defined by its surface area S_i and its thickness t_i. If such a film is grafted with styrene, swelling is observed in thickness and in surface, which means that swelling takes place in a three-dimensional space, i.e., in the bulk. The surface and thickness grafting yields can be written as

$$Y_S = (S_f - S_i)/S_i \tag{2}$$

$$Y_t = (t_f - t_i)/t_i \tag{3}$$

where S_f and t_f are the dimensions of the film after grafting. Hence, bulk swelling $Y_B = (V_f - V_i)/V_i$ (where V_i and V_f are the initial and final sample volumes) can be expressed:

$$Y_B = Y_S + Y_t + Y_S Y_t \tag{4}$$

Surface changes are easily measurable, but the same is not true for thickness. The film thickness is 10 or 25 μm, and the changes to be measured are a few microns. This leads to considerable error in the thickness yield. If we assume that the densities of PVDF (ρ_{PVDF}) and PS (ρ_{PS}) are not modified in the final copolymer, we can calculate the thickness yield more accurately from Y_S and Y (see Appendix A) by

$$Y_t = [Y(\rho_{PVDF}/\rho_{PS}) - Y_S]/[1 + Y_S] \tag{5}$$

Isotropic swelling means that all the initial dimensions (t_i and $S_i = l_i L_i$, where l_i and L_i are, respectively, the initial width and length) are increased by the same factor k; we can write $t_f = t_i(1 + k)$, $l_f = l_i(1 + k)$, and $L_f = L_i(1 + k)$, l_f and L_f being the final width and length. These equations can be combined into a single one:

$$1 + k = (1 + Y_B)^{1/3} = (1 + Y_S)^{1/2} = 1 + Y_t \tag{6}$$

A graft sample displaying isotropic swelling must obey (6). Figure 6 shows $(1 + Y_S)^{1/2}$ versus $(1 + Y_t)$, where Y_S and Y_t are calculated with (2) and (5), respectively. All the samples that exhibit isotropic swelling must be placed on a straight line of slope 1. To present a clear diagram, neither the ionizing radiation used to induce grafting nor the grafting time has been specified but all samples have the same thickness (25 μm). This figure shows clearly a significant deviation from isotropic behavior: the thickness yield increases faster than the surface yield. This behavior is observed whatever the radiation source (electrons, γ-rays, or heavy ions).

XPS Results. The polystyrene (PS) reference (see Figure 7a) was obtained by polymerization of styrene monomer on a copper plate under UV light at room tem-

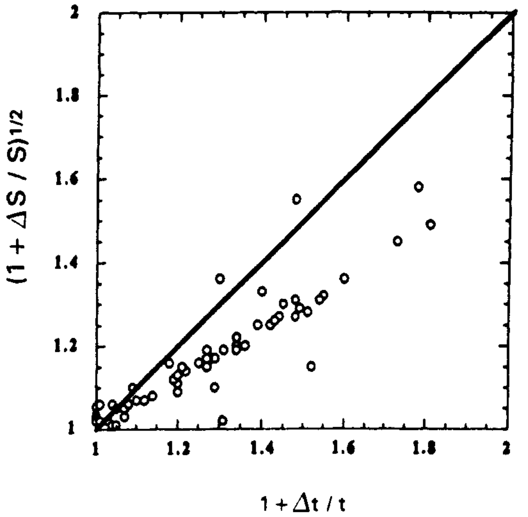

Figure 6. Swelling results; grafting temperature = 61 °C. $\Delta t/t$ is the thickness yield, and $\Delta S/S$ is the surface yield.

perature and in air. The main C1s structure is seen at 284.3 eV and is assigned to a CH_2 group. A high-energy satellite arising from a $\pi^* \leftarrow \pi$ shake-up transition, which is characteristic of the π electronic structure of the pendant phenyl group, is clearly seen at 0.7 eV from the photoionization peak. A small O1s photoionization peak exists, which is assigned to oxidation groups due to polymerization in air. These structures cause little broadening of the C1s photoionization peak.

The unmodified PVDF has a clean surface where no oxygen is found. The PVDF's C1s photoionization structure exhibits two main peaks located at 286.3 and 290.8 eV (binding energy scale) corresponding to CH_2 and CF_2, respectively,[18] and the CH_2 peak is broadened on its low-energy side by carbon contamination. The F1s peak is wide (fwhm of 1.8 eV), is symmetrical, and is located at 689.6 eV.

The PVDF surface appears unaffected by xenon irradiation (see Figure 7a). The F1s peak remains unchanged (same fwhm and same binding energy, 1.8 and 689.6 eV, respectively). An O1s peak appears when the irradiation dose exceeds 38 kGy. The C1s structure is slightly broadened under energetic heavy-ion irradiation because of the creation of new bonds (>C=C<, >C=C=C<, >C=O, etc.) near the CH_2 structure and possible cross-linking or degradation near the CF_2 peak.

We studied the variation in surface composition with grafting yield for a Xe irradiation dose of 488 kGy (see Figure 7b) and for γ irradiation with a 30-kGy absorbed dose (see Figure 7c). Samples grafted by means of xenon ions and samples grafted by means of γ-rays exhibit exactly the same behavior: at low grafting yield (respectively 8 and 3%) the C1s structure is composed of both graft PS and PVDF. The C1s structure in this case shows three peaks located at 290.8, 286.3, and 285 eV, corresponding respectively to CF_2 and CH_2 of PVDF and CH_2 of PS; note that the CF_2 peak is broadened at its base by the shake-up satellite structure. At 22 and 13%, respectively, the C1s feature looks like a C1s PS structure, i.e., a CH_2 photoionization peak at 285 eV and shake-up structure at 7.2 eV on its high binding energy side.

As the grafting yield increases, the C1s structure is always identical to that of a PS sample, whatever the type of radiation and the deposited dose. Samples grafted up to 58% by means of xenon ions with two different irradiation doses (488 and 3 kGy) only reveal a C1s PS structure. At the same irradiation dose (38 kGy for xenon ions and 30 kGy for γ-rays) and similar grafting yield (18.6 and 13%, respectively), the C1s structure observed is also identical to the PS C1s structure.

When PVDF samples are irradiated with the same kind of radiation, very energetic Xe ions, and grafted at identical grafting yields but with a different irradiation dose (488 and 3 kGy), the same behavior (coexistence of PVDF and PS at low grafting yields and pure PS surface at high grafting yields) is observed.

Infrared Results. At the doses used here to initiate grafting, no particular changes in PVDF structure by heavy-ion irradiation can be detected by IR. IR bands typical of the α form[19] (532, 976, and 1150 cm^{-1}) are not specially affected. For doses increasing from 3 to 488 kGy, a constant decrease of the intensity is observed on IR spectra (around 20% for 488 kGy).

Styrene is grafted in its polymerized form: this is clearly seen in Figure 8a. Bands characteristic of PS are located at 2923, 2849, 1601, and 1583 cm^{-1}. The 2923- and 2849-cm^{-1} bands are attributed, respectively, to the antisymmetric and symmetric $-CH_2-$ stretching vibrations, while the 1601- and 1583-cm^{-1} bands are due to the -C=C- stretching vibrations in a six-carbon aromatic ring that is not conjugated. In addition, bands characteristic of styrene monomer do not exist on the spectra, especially the -C=C- stretching vibration conjugated to a benzene ring (1630 cm^{-1}) and the -C=C- stretching vibration of benzenoid carbons that are conjugated with an external -C=C- double bond (1576 cm^{-1}). A study of the 4000–1500-cm^{-1} zone indicates an increase in film thickness upon grafting: from 10.6 or 9.0 μm (nonirradiated and irradiated film thickness) to 16.0 μm for a 61% grafted film (thicknesses are measured with the help of interference undulations[20] shown in Figure 8a).

Figure 8b represents the 1500–400-cm^{-1} zone and shows that grafting seriously affects the $-CF_2-$ stretching vibration bands located around 1200 cm^{-1} as well as the others (which are not pure stretching vibrations bands[19]) which are all decreased uniformly. Many PS vibration bands exist in the 1500–1100-cm^{-1} region (see Table II), and they could be responsible for the deformation of the PVDF bands located in the same zone. Below 1100 cm^{-1}, PS exhibits several vibration bands, but all of weak intensity, apart from the 700 cm^{-1} that corresponds to the vibrations of a monosubstituted benzenoid ring.[14,21] This band is clearly visible in Figure 8b as no PVDF bands occur around 700 cm^{-1}. This decrease in all PVDF bands (especially clear in Figure 8b) indicates that swelling of PVDF by PS occurs in the bulk of the film. If a "sandwich"-like structure (PS–PVDF–PS) were conceivable, the intensity of PVDF bands would be unaffected by grafting. The IR beam would see the same quantity of PVDF vibrators per square centimeter as seen before grafting if PS chains were growing on the PVDF film surface.

Besides these considerations, Table II shows that no significant frequency shift occurs upon grafting.

Discussion

Grafting can be initiated in a solid substrate with the radicals created by ionizing radiations such as γ-rays and electron beams. Our results show that radiation grafting is also possible with very energetic heavy ions. At the same absorbed dose, the grafting yields obtained with xenon ions are similar to those reached with γ or electron irradiation, which is quite surprising as the radiation/matter interaction mechanisms and the microscopic dose distribution are different. Grafting yields increase with absorbed dose. We found that heavy ions can lead to

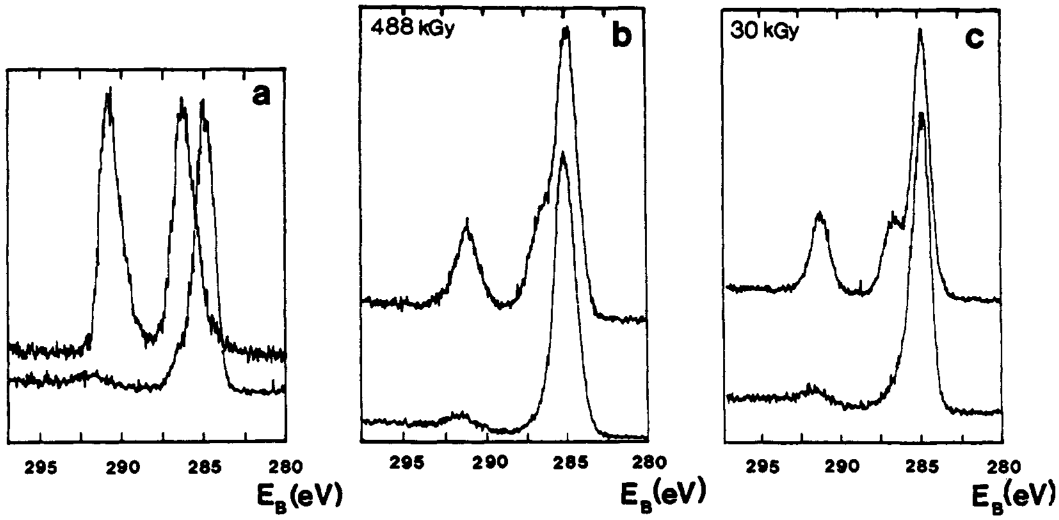

Figure 7. XPS spectra. Two ionizing radiations were used to initiate grafting, xenon irradiation ($D = 488$ kGy, $F_t = 9.0 \times 10^{10}$ ions/cm^2) and γ irradiation ($D = 30$ kGy). (a) Reference samples: Xe-irradiated PVDF (upper spectrum) and PS (lower spectrum). (b) Grafting by means of heavy ions: 8% (upper spectrum) and 22% (lower spectrum). (c) Grafting by means of γ-rays: 3% (upper spectrum) and 13% (lower spectrum).

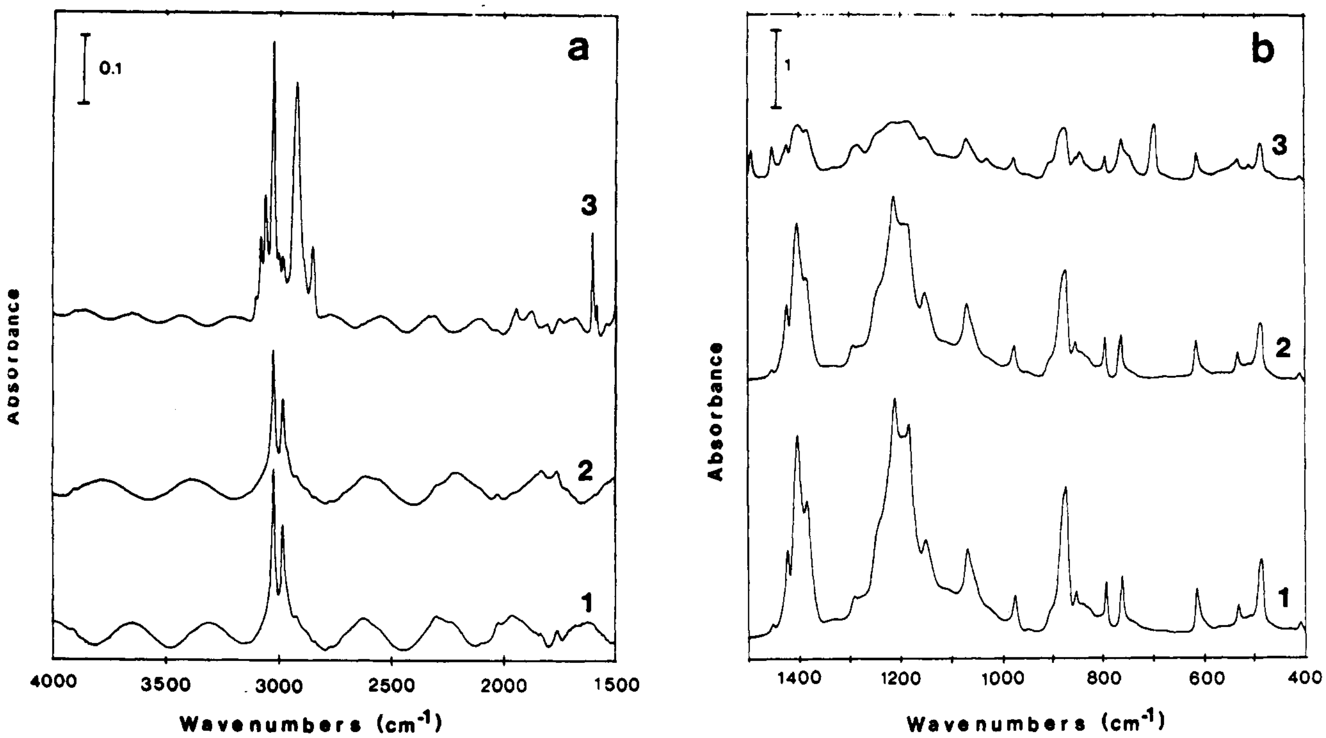

Figure 8. Infrared spectra: (1) PVDF sample (10 μm thick); (2) Xe-irradiated PVDF (10 μm thick), $F_t = 4.9 \times 10^8$ ions/cm^2; (3) PS graft PVDF (10 μm thick; irradiation conditions are the same as sample 2; $Y = 61\%$).

considerable grafting yields. Heavy-ion beams suitable for use have intensities of 10^{11}–10^{12} ions/s, and for the absorbed doses required we only need about 10^8 ions/cm^2, which means that large surfaces can be irradiated with very short exposure times (see Table I).

Grafting by means of energetic xenon ions occurs in the bulk, as seen on IR spectra. The measurement of surface and thickness yields reveals the existence of a thickness gradient. The thickness yield is greater than the surface yield. This is consistent with our XPS results. The surface structure of grafted films does not depend on the type of irradiation (heavy ions or γ-rays) or the absorbed dose but appears to be controlled exclusively by the grafting yield: when the grafting yield exceeds about 20%, we find that PS covers the entire sample surface.

The grafting kinetics (Figure 3) shows that the grafting yield can be controlled by the fluence, hence, the dose (yield rises with increasing dose), and by grafting time (yield rises with increasing time). It also reveals that ratios between fluences cannot be related simply to grafting yield ratios (see Table III). This means that grafting does not occur independently in each nuclear track; there must be overlapping either between nuclear tracks during irradiation or between the grafted tracks as they grow during styrene polymerization. In a first approach, we decided to test the second hypothesis with the use of a crude model describing graft nuclear tracks as polystyrene cylinders embedded in a PVDF matrix. In this case, grafted tracks start to overlap each other significantly above a grafting yield of 10% (see Appendix B) which means that grafted tracks can be considered independent only for very small grafting yields. The grafting temperature therefore was lowered to provide grafting yields of less than 10% without the need of very short, and consequently inaccurate,

Table II
FTIR Absorption Bands

PVDF	irradiated PVDF[a]	graft PVDF[b]	PS[c]
		3102	3102
		3082	3082
		3060	3060
3025	3025	3025	3025
		3001	3002
2986	2986	2985	
		2924	2923
		2850	2849
		1943	1944
		1871	1872
1833	1833		
		1803	1804
1761	1761		
		1750	1747
		1601	1601
		1583	1583
		1540	1542
		1493	1493
1453	1453	1452	1452
1424	1424	1424	
1403	1403	1401	
1385	1385	1384	
1292	1292		
1211	1213	1213	
1183	1193	1183	
1151	1151	1151	
1069	1070	1069	1069
976	976	976	
874	874	877	
855	854	854	
796	796	796	
		698	700
615	615	614	
532	532	533	539
487	487	488	

[a] Xe ions, $F_t = 4.9 \times 10^8$ ions/cm^2. [b] Same irradiation conditions as in footnote *a*, $Y = 61\%$. [c] Homemade PS.

Table III
Comparison of Fluence and Grafting Yield Ratios

	grafting yield ratio		
fluence ratio	1 h, 61 °C	16 h, 61 °C	1 h, 42 °C
$9.0 \times 10^{10}/2.3 \times 10^{10} = 3.9$	1.3	1.7	1.3
$9.0 \times 10^{10}/4.9 \times 10^8 = 184$	2.3	3.3	2.3

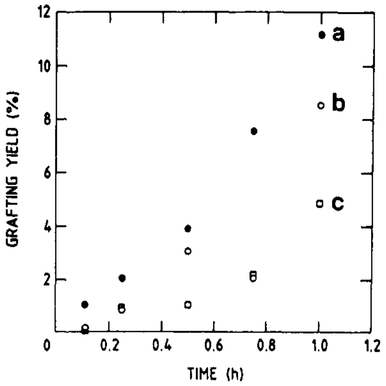

Figure 9. Study of grafting yields lower than 10%; grafting temperature = 42 °C: (a) 9.0×10^{10} ions/cm^2; (b) 2.3×10^{10} ions/cm^2; (c) 4.9×10^8 ions/cm^2.

grafting times. Grafting kinetics were determined between 0 and 1 h, at 42 °C, with three fluences (see Figure 9). Grafting yields were estimated by measuring the UV absorption at 269 nm. They still cannot be linearly related to fluences. Based on a fluence of 9.0×10^{10} ions/cm^2, decreasing the fluence by factors of 3.9 and 184 only results in a decrease of the initial grafting rate by factors of 1.3 and 2.3, respectively. It is therefore hard to consider that copolymerization is initiated only very close to the ion path. Due to the radial extension of the deposited dose, some grafting seems to be initiated far from the ion path, smoothing the ideal structure formed by isolated and cylindrical grafted tracks embedded in a PVDF matrix.

Conclusion

Using a commercial PVDF in its α-form, we grafted styrene monomer using energetic heavy ions which create highly reactive nuclear tracks on their way through the solid polymer. The grafting yields obtained by this method are similar to those reached with γ-ray or electron irradiation. Copolymerization takes place in the bulk, a fact that is clearly evident as the polymer surface expands markedly, as shown by dimensional measurements and infrared spectroscopy. However, for high grafting yields, a thickness gradient exists for the grafting yield.

No significant differences were observed in the behavior of the surface, or in the recorded infrared spectra, when, at fixed grafting yield, the irradiation conditions were changed, for example, the ion fluence.

Even at low grafting yields (less than 10%), where crude calculations predict that isolated grafted tracks may exist, the grafting rate is not proportional to the fluence, indicating that interactions between tracks prevail. Small-angle neutron scattering and transmission electron microscopy experiments are under way, as they can provide radial dimensions of the grafted tracks and the degree of anisotropy of the modified films, offering a more complete description of the original anisotropic graft structure obtained by heavy-ion irradiation.

Appendix A

The grafting yield *Y*, defined by (1), can also be written as $Y = W_g/W_i$ where W_g is the weight of the PS graft and W_i the weight of the PVDF sample. The densities of PVDF (ρ_{PVDF}) and PS (ρ_{PS}) can be used to express the grafting yield: $Y = V_g\rho_{PS}/V_i\rho_{PVDF} = (V_f - V_i)\rho_{PS}/V_i\rho_{PVDF}$ where V_g is the volume of PS graft (all other parameters are defined in the section Swelling Results). *Y* can accordingly be expressed as a function of bulk swelling: $Y = Y_B\rho_{PS}/\rho_{PVDF}$. When *Y* and Y_B can be measured precisely (grafting yields > 10%), this expression is always verified. Using the expression of Y_B given by (4), we can write the thickness yield Y_t as

$$Y_t = [Y(\rho_{PVDF}/\rho_{PS}) - Y_S]/[1 + Y_S]$$

Appendix B

If we describe the graft film as parallel graft PS cylinders, perpendicular to the surface and embedded in a PVDF matrix, we can define a grafted area fraction A_n as the ratio of the sum of all individual track grafted areas S_g to total surface area *S*: $A_n = S_g/S$.

S is the surface area after grafting S_f (which is larger than the initial surface area S_i due to swelling). S_g is given by $S_g = \pi r^2 F_t S_i$.

F_t is the fluence, i.e., the number of ions per cm^2 reaching the initial surface S_i. πr^2 is the cylinder surface area that appears on the film surface and *r* is the graft track radius (see Appendix C). A_n can then be expressed as $A_n = F_t S_i \pi r^2/S_f$. If we now use the graft track radius expression, the grafted area fraction becomes

$$A_n = S_i t_i Y \rho_i / S_f t_f \rho_g$$

where *Y* is the grafting yield, and ρ_i and ρ_g are the PVDF and the PS densities, respectively. If we now assume that the densities are not modified in the final copolymer, the

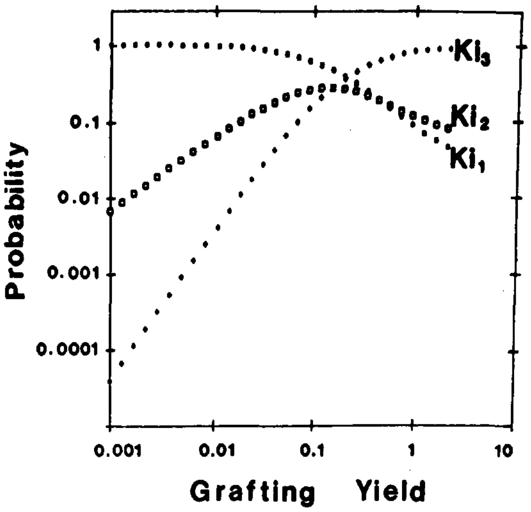

Figure 10. Overlapping probabilities as a function of grafting yield.

surface and thickness ratios can be expressed as a function of the grafting yield (see eqs 2, 3, and 5) and the grafted area fraction can be written as

$$A_n = Y\rho_i/[\rho_g(1 + Y\rho_i/\rho_g)]$$

It now becomes clear that the grafted area fraction depends exclusively on the grafting yield and not at all on the fluence. The arrival of heavy ions on a surface is a random phenomenon that can be described by Poisson statistics. The probability of having a single grafted track without any interaction is[22]

$$Ki_1 = \exp(-4A_n)$$

The probability of having encounters between only two grafted tracks is

$$Ki_2 = 4A_n[1 - (3/2)A_n + (11/9)A_n^2] \exp(-4A_n)$$

The probability of having encounters between three grafted tracks or more is

$$Ki_3 = 1 - [1 + 4A_n - 6A_n^2 + (44/9)A_n^3] \exp(-4A_n)$$

Figure 10 shows these probabilities as a function of grafting yield.

Appendix C: Expression of Graft Track Radius

We assume here that the structure of the grafted film can be described as cylinders of grafted PS, normal to the surface, in an unmodified PVDF matrix. The weight of the grafted cylinder is $W_c = \rho_g\pi r^2 t_f$, where $\rho_g = \rho_{PS}$ is the graft density, r the cylinder radius, and t_f the cylinder length (i.e., the final film thickness). The number of graft cylinders N_c is the same as the number of tracks and can be expressed as the product of the fluence [F_t in ions/cm^2] multiplied by the initial film surface area [S_i in cm^2].

On the other hand, the grafting yield is defined by $Y = W_g/W_i$, where W_g and W_i are, respectively, the weight of the graft and the weight of the film before grafting. Hence we can write

$$Y = W_g/W_i = W_cN_c/(\rho_i t_i S_i) = (\rho_g \pi r^2 t_f S_i F_t)/(\rho_i t_i S_i)$$

and the graft track radius r can now be written as

$$r = [Y\rho_i t_i/\rho_g t_f F_t \pi]^{1/2}$$

References and Notes

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