# Irradiation of Ethylene/Styrene Copolymers: Evidence of Sensitization of the Aromatic Moiety As Counterpart of the Radiation Protection Effect

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ABSTRACT: Molecules containing aromatics systems are more stable in the presence of ionizing radiations than alkanes. In the same way, introducing aromatic rings into aliphatic compounds increases their stability. The protective effect is nonlocal and likely results from the transfer of energy and species from the aliphatic moiety to the aromatic one. For years, it was commonly assumed that the aromatic moiety, which is very radiation resistant, accommodates the extra energy remaining unaffected. The use of Fourier transform infrared spectroscopy, online with high energy ion beam irradiation of ethylene/styrene random copolymers, allows us to bring experimental evidence that the benzene rings are sensitized by transfer reactions and consequently that this effect is more important in polymers with low benzene ring molar content.
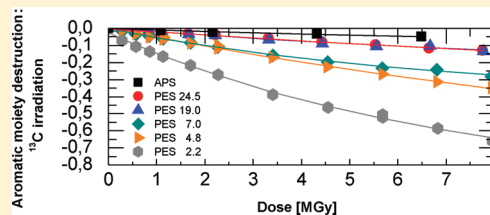
INTRODUCTION

Under anoxic conditions, organic molecules reveal very different behaviors under ionizing radiations. In particular, aromatic compounds present an exceptional radiation resistance, at least under low ionizing irradiation conditions (low Linear Energy Transfer (LET) irradiations).[1,2] This is the case for very different organic systems from small molecules (generally liquids) to polymers. As an example, polystyrene is approximately 2 orders of magnitude more resistant under ionizing radiations than polyethylene. A parallel behavior exists between benzene and cyclohexane. It is also well-known that the introduction of aromatic molecules in aliphatic compounds induces an important increase in their radiation resistance. The overall radiation yield of a given defect is not the weighted average of its yield in the pure compounds: a small amount of aromatic molecules induces a strong decrease of the aliphatic radiation product yields.[3−5] Because of that, aromatic additives are sometimes referred as "antirads".[6]

This effect was discovered at the very beginning of the radiation chemistry history. Already in 1931, C. S. Schoepfle and C. H. Fellows[7] noticed that the quantity of H_2 formed in benzene and cyclohexane (noted hereafter C_6H_6 and c-C_6H_{12}, respectively) mixtures submitted to X-rays did not follow the law of averages. In the fifties, in a thorough study on the radiation protection effect in liquid hydrocarbon mixtures irradiated with 1.5 MeV electron beams, J. P. Manion and M. Burton[3] showed that the strongest radiation protection effect is observed with aromatic molecules and that alkenes also ensure a radiation protection to alkanes. This radiation protection effect has often been considered as one of the most striking results in radiation chemistry.[5] There are few doubts that radiation protection is due to energy (or eventually reactive species) transfers from the aliphatic moiety toward the aromatic molecules acting as energy traps.

The first work realized in this field on polymers was done by J. B. Gardner and B. G. Harper in 1965.[8] In their study, they performed irradiations of either polyethylene (PE)/polystyrene (PS) mixtures or polyethylene grafted polystyrene (poly-(ethylene-g-styrene)) with 1.05 MeV electrons. After this pioneering work, a series of studies were published.[9−13] The role of the aromatic unit distribution within the polymer was debated; considering the relative efficiencies of intrachain and interchain energy transfers, as well as the spatial distribution of the aromatic units.

In this article, we focus on the behavior of the aromatic moiety under ionizing radiation during the stabilization process of the aliphatic moiety. The excess of energy on the aromatic molecules, resulting from energy transfers, is assumed to be dissipated by heat and light emission without any chemical modification on the aromatic molecule. Because of that, it is often stated that aromatic molecules act as "energy sponges".[3,14,15] Surprisingly, little interest was devoted to the fate of aromatic molecules in aliphatic/aromatic systems. To our best knowledge, the veracity of the integrity of the aromatic molecules after irradiation was never seriously tested. This lack can be explained by the fact that most studies were confined to the quantification of gaseous products (H_2 in most of the cases), involving the entire system, with no specification of the moiety associated to. And, as the aliphatic moiety is largely the most sensitive, the overall damage was assumed to be ruled by the aliphatic moiety. However, a few studies, using experimental protocols that distinguish the damage in each moiety, were reported in the literature. Combining gas and liquid chromatography to analyze irradiated C_6H_6/c-C_6H_{12} and

C_6D_6/c-C_6H_{12} mixtures, J. A. Stone and P. J. Dyne[5] got information either on changes in the benzene content or on the creation of products involving both molecules (HD, C_6D_5H, and phenylcyclohexane). They did not conclude on a detectable sensitization of benzene. Electron spin resonance (ESR) was also used to characterize irradiated C_6H_6/c-C_6H_{12}, in the liquid[16] and in the solid state,[17] as well as in ethylene/styrene random copolymers.[18] In the latter, Fourier transform infrared spectroscopy (FTIR) was also used, but the authors did not give any result on the modification of the styrene moiety.

Interestingly, analyzing the acetylene released from electron beam irradiated liquid C_6H_6/c-C_6H_{12}, at room temperature, J. P. Manion and M. Burton[3] have envisaged that, in the process of cyclohexane protection, benzene is "itself sacrificed to a relatively small extent". Despite the fact that the experimental data were not, by far, accurate enough to be conclusive, the eventuality of a radiation sensitization of benzene was not excluded. The aim of this article is to try to determine, at the molecular level, the fate of benzene rings in their stabilization process of aliphatic compounds.

This article presents the results we obtained, using FTIR, on the radiation induced modification on the aromatic moiety in ethylene/styrene random copolymers, as a function of the styrene molar content. The aim is to address the issue of the radiation stability of aromatic molecules surrounded by aliphatic ones under ionizing radiations.

■ EXPERIMENTAL SECTION

Polyethylene and polystyrene are poorly miscible. To avoid any spurious interference coming from the spatial arrangement of the aromatic units, we discarded physical blends as well as block or grafted copolymers. We selected ethylene/styrene random copolymers (poly(ethylene-s-styrene), called hereafter PES). As these materials were not commercially available, we specifically synthesized them at the Institut Charles Sadron (ICS) of Strasbourg, France. The PES were obtained during coordination copolymerization of ethylene and styrene using the titanium based catalyst (I), in presence of methylaluminoxane (II) as cocatalyst (see Figure 1). This polymerization was made
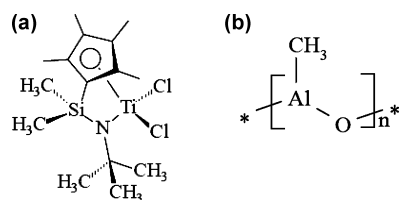
Figure 1. (a) CGC catalyst (I). (b) Methylaluminoxane (II) cocatalyst.

following the protocol proposed by D.-H. Lee,[19] according to the generally accepted mechanism, proposed by P. Cossee[20] and E. J. Arlman.[21] The materials synthesis is intensively presented elsewhere.[22]

Polymers were irradiated with ion beams in the form of films, at room temperature and under vacuum, using the medium energy line (SME) at the GANIL accelerator (Caen, France). A scanned (x,y) beam was used to ensure a homogeneous irradiation field over the sample surface (typically 0.75 cm²). The target temperature was not monitored during irradiation. However, the flux was chosen to limit the power deposited on the sample to 0.5 mW·cm⁻², thus avoiding any significant sample heating. The code used for energy loss calculation is based on SRIM.[23] Whatever the sample, the projectile range remains always much larger than the sample thickness. Furthermore, the beam energy was high enough to ensure a relatively constant LET through the sample thickness. In all cases, the relative decrease of the projectile energy in the sample was lower than 10%. Besides, in the aliphatic moiety, the mass stopping power is only about 9% higher than the corresponding one in the aromatic moiety. Hence, the KERMA (Kinetic Energy Released in MAtter) is higher in the aliphatic moiety by the same small amount. Concerning the absorbed dose, the materials studied are random copolymers of ethylene and styrene. Meanwhile, there is an intimate mixture of both monomer moieties. Moreover, as ion beams used in this study are of high energy (>10 MeV·A⁻¹), secondary electron ranges are larger than either of the monomers units. Considering different absorbed doses in both moieties makes no sense. Consequently, for calculating the absorbed dose, the LET used here is a mean stopping power, taking into account the copolymer as a whole.

Sample characteristics as well as irradiation conditions are gathered in Table 1. The aromatic content, which corresponds

Table 1. Sample Characteristics and Irradiation Conditions[a]

name	aromatic content (molar %)	irradiation ion (LET in MeV·mg⁻¹·cm²)	sample thickness (mg·cm⁻²)
PES 2.2	2.2	¹³C (1.7)/²⁰Ne (3.9)	4.8/4.8
PES 4.8	4.8	¹³C (1.7)	3.7
PES 7.0	7.0	¹³C (1.7)/²⁰Ne (3.9)	6.5/6.0
PES 19.0	19.0	¹³C (1.7)/²⁰Ne (3.8)	6.7/6.2
PES 24.5	24.5	¹³C (1.6)	5.7
APS	100	¹³C (1.5)/¹⁸O (3.4)	1.2/1.8

[a]The energies at the entrance of the films are 143 MeV, 272 MeV, and 149 MeV for ¹³C, ²⁰Ne, and ¹⁸O, respectively.

to the molar content in a styrene moiety ($CH_2CHC_6H_5$), was determined by liquid ¹H NMR. In addition to PES samples, we irradiated atactic and hence amorphous PS (noted APS) samples. The APS sample sets the reference value for the radiation resistance of a fully aromatic polymer. The PES films were irradiated with ¹³C and ²⁰Ne, in the hundreds of MeV energy range, inducing moderate LET values. For technical reasons, the APS sample was irradiated with ¹⁸O beam with an energy chosen to induce almost the same LET as the ²⁰Ne beam.

Radiation induced modifications were monitored using infrared spectroscopy. IRTF spectra were recorded in the transmission mode with a resolution of 2 cm⁻¹, at room temperature. Interference fringes were avoided by recording the spectra with a polarized beam at the Brewster angle (55 degrees). Spectra were recorded in situ, after each absorbed dose step. A specific device allowed us to perform irradiations and record the FTIR spectra without removing the sample from the cell.[24] Hence, the contact between the sample and the air was avoided and post-irradiation oxidation was discarded. Besides, as irradiation is performed by dose steps, using the same sample to explore the entire range of dose greatly increases the accuracy: as exactly the same spot on the sample is analyzed, no further thickness normalization is required.

Samples were analyzed using IRTF spectroscopy. According to the Beer−Lambert Law, the absorbance A of a given band is

linked to the molar concentration C (in mol·L^{-1}) of the absorber following the formula $A = \varepsilon C l$, where ε (in mol^{-1}·cm^{-1}) is the molar extinction coefficient and l (in cm) is the sample thickness. The radiation chemical yield of destruction, specific to styrene monomer, can be expressed by the following: $G = (\Delta A/A_0)(1/\Delta D)(1/M)$, with A_0 being the absorbance of the considered band at zero dose, D (in Gy) the absorbed dose, and M (in g·mol^{-1}) the molar mass of the chemical group considered. Since we are dealing with the destruction of bands specific to the benzene ring, we have chosen to express the related radiation chemical yields in mole of "destroyed" groups per unit of energy deposited in the component in which these defects are created, i.e., in the aromatic moiety. As mentioned before, the absorbed dose has to be considered uniform in the polymer. Consequently, the amount of energy initially deposited by the ion beam in each component is proportional to its mass fraction. In the limit of low doses, G equals G_0, the radiation chemical yield at initial dose.

As a matter of fact, the decrease of the chemical groups, as a function of the absorbed dose, follows an exponential law expected from the Poisson law. The relationship between the $\Delta A/A_0$ and the absorbed dose is expressed by the following equation: $y = P_1 + P_2(e^{(-P_3 D)} - 1)$, where P_1, P_2, and P_3 are constants used to fit the experimental points. The use of P_1 enables an additional degree of freedom to C_0 values during curve fitting. In the limit of very low doses, the above equation reduces to $y = P_1 - P_2 P_3 D$.

The aromatic moiety destruction yield at the initial dose is then $G(\text{destruction}) = P_2 P_3/M$ with M being the molar mass of the styrene monomer ($M = 0.104$ kg·mol^{-1}).

■ RESULTS AND DISCUSSION

As a general rule, the radiation-induced modifications appear in the FTIR spectra in two different ways: (i) the emergence of new bands indicating the creation of new chemical groups and (ii) the decrease in the intensities of bands related to the pristine sample, with eventually tenuous changes in the width and the position. This decrease in bands intensity is due to the gradual transformation of the initial chemical groups to new ones. We call this effect "the overall or global destruction".

Several absorption bands related to the benzene ring vibrations were analyzed to follow the aromatic moiety behavior, but in this article, we focus on the absorption band at 3083 cm^{-1} related to ν(C–H) vibrations in the benzene ring. The same results are obtained with the other styrene absorption bands, similarly to what we observed in PS.[2] Indeed, in this polymer, all bands decreased in a similar way under ion beam irradiations.

Figure 2 shows the evolution of the infrared spectra of PES 7.0 in the area 3120−2980 cm^{-1}, at three absorbed doses.

This Figure clearly shows the decrease of all the ν(C–H) benzene ring absorption bands when the absorbed dose increases.

Except for the APS, the polymers were irradiated up to doses of 6 MGy and 8 MGy with ^{20}Ne and ^{13}C ion beams, respectively. Figure 3a,b represents the evolution of the aromatic moiety destruction as a function of the absorbed dose, for either the PES copolymers or the reference APS. Results in Figure 3a were obtained with a ^{20}Ne ion beam, at LET $\approx$ 3.8 MeV·mg^{-1}·cm^2, whereas those represented in Figure 3b were obtained with ^{13}C ion beam at LET $\approx$ 1.7 MeV·mg^{-1}·cm^2.
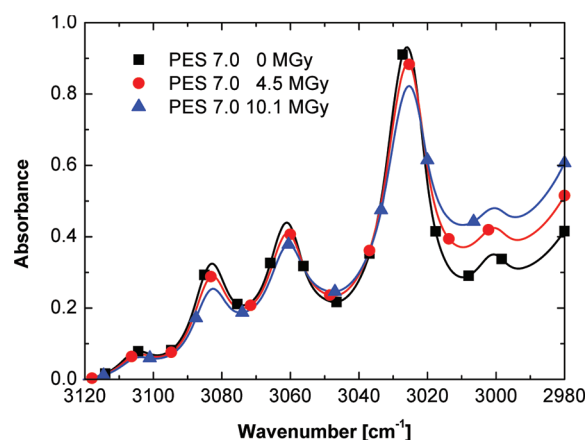
Figure 2. Infrared spectra of ethylene/styrene random copolymer 7.0% molar styrene percentage in the area 3120−2980 cm^{-1} at three different absorbed doses. Irradiations performed with ^{20}Ne ions at LET = 3.9 MeV·mg^{-1}·cm^2.
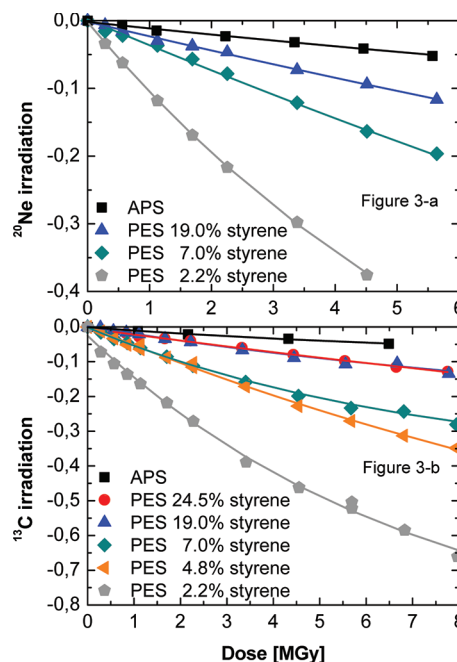

Figure 3. (a) Evolution of the aromatic moiety destruction (expressed in $(A - A_0)/A_0$) in PES as a function of dose (in MGy) for irradiations performed with ^{20}Ne ions at room temperature (LET = 3.8 MeV·mg^{-1}·cm^2). (b) Same evolution of the aromatic moiety destruction in PES as a function of dose (in MGy) for irradiations performed with ^{13}C ions at room temperature (LET = 1.7 MeV·mg^{-1}·cm^2).

Whatever the dose and the LET, the aromatic moiety destruction increases markedly when the styrene molar fraction in PES decreases, that is when the ethylene content increases. The benzene ring is highly sensitized in the presence of aliphatic groups: the stabilization of the ethylene moiety by the styrene one occurs at the sacrifices of the benzene ring.

Figure 4 represents the evolution of the styrene-specific destruction radiation chemical yield as a function of the styrene molar content, for irradiations performed at both LET values. The use of a specific radiation chemical yield instead of a global radiation chemical yield (calculated considering the energy deposited in the entire copolymer) is to focus on the
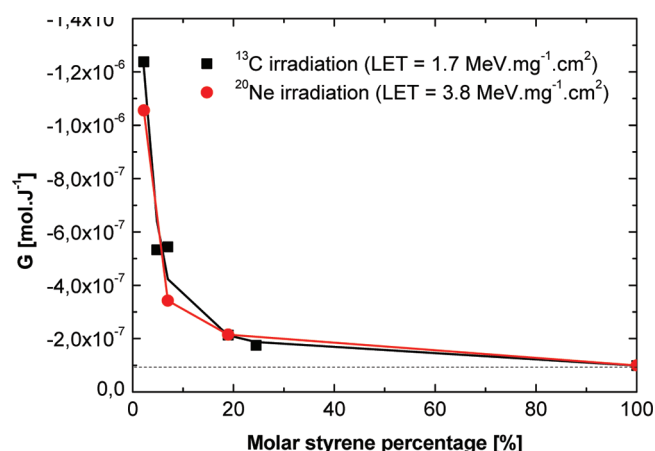
Figure 4. Evolution of the specific radiation chemical yields of the benzene ring destruction as a function of the styrene molar percentage in PES random copolymers irradiated with ^{20}Ne ions (LET = 3.8 MeV·mg^{-1}·cm^2) and ^{13}C ions (LET = 1.7 MeV·mg^{-1}·cm^2). The dashed line represents the evolution of the specific radiation chemical yield of the styrene moiety destruction in the absence of interaction between aliphatic and aromatic moieties.

component in which the considered effect occurs. Therefore, in the absence of interactions between the aliphatic and the aromatic components, the specific radiation chemical yield is constant, independent of the styrene molar content (as shown by the dashed line in Figure 4).

It can be seen from Figure 4 that the sensitization of the styrene moiety by the ethylene one is highly marked at the two LET values under study, for low molar styrene contents.

The stabilization of aliphatic systems in the presence of aromatic molecules is likely due to the set up of energy and species transfer from the energized aliphatic moiety (the donor) to the aromatic molecules (the acceptor). In the PES copolymers under study here, the decrease in styrene content results in the decrease of the number of acceptors and inversely results in the increase of the number of donors. This happens as if there were a high excitation/ionization density in the styrene moiety environment. Locally, it would be for the styrene moiety as if the LET was higher and thus leading to a higher destruction ratio of benzene rings. Indeed, during our previous study,[2] we have shown that the polystyrene behavior under ionizing radiations strongly depends on the stopping power: the high radiation resistance observed at low LET is drastically lowered at high LET. This behavior, as a function of the LET, can tentatively be explained as follows. Energized benzene rings are known to be stable enough to permit the dissipation of extra energy without totally being decomposed. Thus, because of this stability, in the presence of a high excitation density, an already energized benzene ring can be re-excited or re-ionized, leading to a less stable molecule promoted to decomposition.

At this stage of the study, the relative influence of excitation energy transfers and species transfer can hardly be discriminated. Irradiations were performed at room temperature, and at this temperature, all mechanisms can occur. However, we have recently performed irradiation at temperatures as low as 11 K, well below the glass transition temperatures of the copolymers under study, following the procedure describe in previous papers.[25,26] At such low temperatures, species diffusion should be drastically reduced and only excitation energy transfers as well as species reactions implying tunneling effect should be allowed. This study is still in progress.

CONCLUSIONS

It has been known for decades that, in aliphatic/aromatic systems irradiated at room temperature, a radiation protection phenomenon of the aliphatic moiety by the aromatic one exists. It has always been supposed, in the presence of low LET irradiations (gamma or electrons), that the aromatic moiety protects the aliphatic one without being affected, following a "sponge-type" mechanism. However, very few studies related to the fate of aromatic molecules after this protection effect were actually done. Therefore, the aim of this study was to experimentally determine, at the molecular level, the fate of the styrene moiety in ethylene/styrene copolymers irradiated under swift heavy ions. Indeed, because of different LET, the present irradiation conditions are slightly different from those presented in the literature. Nevertheless, we demonstrate here that the benzene ring is highly sensitized, under swift light ion irradiation by the presence of the aliphatic moiety and that this sensitization is as high as the benzene ring content is low.

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1776

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