Spectroscopic study of chemical modifications induced by swift heavy ions on polymers: the contribution of the CIRIL Platform and the CIMAP Laboratory

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Abstract. This paper gathers results obtained on the chemical ageing of polymers, at the CIRIL platform, using Swift heavy ions (SHI) from the GANIL accelerator. Swift heavy ions induce high values of electronic stopping power or LET (Linear Energy Transfer) and deposit their energy in the polymer through electronic processes, in a few nanometer size cylinder centered on the ion path. This results in huge local doses and dose rates. Both defects created in the polymer chain and gas release were quantified using spectroscopic methods (FTIR and Residual gas analysis (RGA)). Defects created in polymers submitted to SHI can be separated in two main series: defects common to all ionizing radiations and defects specific to SHI. A common trend of the evolution of these defects, under inert environment, is the following: 1) for the first group of defects, in most of the polyolefins, there is a limited (if inexistent) effect of LET on the radiation chemical yield of creation at low doses. Among defects of this first series, the behavior of vinyl groups is particular, 2) LET effect on SHI specific defects (triple bonds and cumulenes) is tremendous. Triple bonds (alkynes, alkyl or aryl cyanates) are created after a LET threshold value, depending on the polymer chemical structure. The dose effect on macromolecular defects, under inert environment, is also presented. The study of the LET effect on gas release, in various polyolefines, gives an insight on the mechanism of bond cleavage in presence of high ionization and excitation densities. Finally, few results on radiation-induced oxidation are presented. Compared to low-ionizing radiations, oxidation is reduced and unsaturated bonds are created under SHI.

1. Introduction
Since the industrial development of organic synthetic polymers in the mid 20th century, the question of their behavior, first under weathering (UV irradiation) and then under ionizing radiation has been considered.

The effect of ionizing radiations on polymers can be either beneficial or detrimental. Low-ionizing radiations such as electron-beam (e-beam) or \( \gamma \)-rays can be used to increase some of the mechanical properties of the polymer, through controlled cross-linking. As an example heat shrinkable...
polyethylene (PE) for goods wrapping are obtained by low dose e-beam irradiation. In the same way, wooden art craft or antiquity can be rehabilitated through $\gamma$-curing of polyester resins. Besides, some of polymer-based medical disposal are sterilized using either $\gamma$-rays or e-beam at low doses. Unfortunately there are situations were irradiation is detrimental for the polymers; that is the case for insulation sheath of electrical cables in nuclear plants or for polymers composing glove boxes used during nuclear fuel handling and analyses processes. In the latter case, polymers are submitted concomitantly to $\alpha$, $\beta$ and $\gamma$ rays.

First studies on polymer ageing under ionizing radiation were performed using $\gamma$-rays and e-beam. Ion beam irradiation of polymers was belated. This started with the study of the behavior of photoresists used during semiconductor doping. The great development of ion beam irradiation of polymers is related first to the research of particle detectors for monitoring low fluences, and second for either commercial manufacture of filters or polymer micro- and nano-structuration.

Ionizing radiations interact with the polymers through electronic processes, resulting in the creation of excitation and ionization. These initial species lead, after a time scale of around $10^{-12}$ s, to the formation of chemical modifications (called hereafter defects) in the polymer and the subsequent mechanical and optical modifications.

Organic synthetic polymers are defined as the repetition of a chemical unit, of small mass, through covalent bonds. They are composed of a backbone and, in some cases, have pendant groups or side chains. Polymers are very sensitive to ionizing radiations, as compared to other materials such as ceramics or steel. Ionizing radiations induce bonds scissions leading to chemical defects. These defects can be created either in the polymer chain in the form of new chemical groups (macromolecular defects) or as small molecules leaving the polymer in the form of gas (gas release). Both macromolecular defects and gas release are function of the polymer chemical structure and the irradiation conditions (projectile nature, environment, dose, dose rate, temperature…).

Gamma-rays and e-beams deposit their energy in the material rather homogeneously. On the contrary, swift heavy ions (SHI) deposit their energy through electronic processes occurring close to the ion path: the latent track. Most of the primary excitations and ionizations occur in a track core of a few nanometers. High energy electrons, emitted during ion/polymer interactions, induce ionization/excitations at larger distances from the ion trajectory, in the so-called track halo. This halo is defined by the range of secondary electrons, which increases with the projectile velocity [1]. The huge amount of energy locally deposited by SHI within the track can induce specific damage processes, which involve complex molecular rearrangements and collective atoms motion.

The LET induced by SHI in polymers are very high and lead to high ionizing and excitation densities. The comprehension of processes triggered by these high ionization/excitation densities was one of the motivation of the research, on SHI/polymer interactions, performed at CIRIL, using the GANIL beam lines, during the last 30 years. Basic research, aiming to the comprehension of the mechanisms leading to defects formation, as well as more applied research was considered. For the latter, the LET domain of interest is that of actinide-emitted $\alpha$ particles. In terms of LET, actinide-emitted $\alpha$ particles are simulated by 11 to 13 MeV/A energy C-Ne ion beams. Both macromolecular defects and gas emission were studied and their evolutions as a function of, the polymer chemical structure, the irradiation conditions (projectile nature, environment, dose, dose rate, temperature…).

2. Experimental

One of the advantages of polymer irradiation studies performed at CIRIL is the use of on-line analyses. The analytical approaches are essentially Residual gas analysis (RGA), Fourier transformed infrared and UV-visible spectroscopies. Specific equipments enable to irradiate and analyze the material without removing it from the set-up. There are two main advantages for this procedure. The first advantage is to probe the same point of the sample, thus avoiding possible heterogeneity in the sample thickness. The second advantage is first to prevent the post-irradiation oxidation prior the analysis (as polymers are known to be sensitive to radiation-induced oxidation), and second to avoid annealing, prior to analysis, after low temperature irradiations.

A large range of ions and energies was used for the actual studies. Most of them from the medium energy line of GANIL.
Various polymers were used. The chemical structures of the repeating units of most of them are presented in figure 1.

![Chemical structures of polymers](image)

**Figure 1.** Chemical structures of the repeating units of some of the polymers presented in this paper.

Results can be discussed either as a function of the ion fluence or as a function of the dose deposited. Fluence (Φ in ion.cm⁻²) and dose (D in Gy) are related through the LET (MeV.mg⁻¹.cm²) according to the following equation: \( D = 1.6 \times 10^{-7} \cdot \Phi \cdot \text{LET} \).

Defects creation (or group destruction) is generally quantified using the radiation chemical yield of creation (or destruction), G. It represents the number of moles of defect created (or group destroyed) per unit dose and is expressed in mol.J⁻¹.

### 3. Results

In this section, for comprehension purposes, and since processes involved are quite different, results obtained during irradiation under vacuum will be separated from those concerning irradiations under oxidative environment.

#### 3.1. SHI effect under vacuum or inert atmosphere

Under anoxic conditions (vacuum or He atmosphere), both macromolecular defects and gas release were monitored.

When a polymer is submitted to ionizing radiations, its FTIR spectra present two main features: 1) the decrease of some of the bands present in the spectrum of the virgin polymer and 2) the appearance and subsequent increase of new absorption bands. The first group of bands gives indications on the overall destruction of the initial polymer and the second group of bands is related to the creation of new defects in the polymer chain. Both features are shown in figure 2, which presents the evolution of the spectrum of a polyethylene (PE) film irradiated with a 6.6 MeV/A Sn ion beam [2].
Macromolecular defects created in the polymer chains irradiated under anoxic conditions are:

- **Double bonds.** They can be either isolated or conjugated alkenes. Isolated alkenes such as \( \text{trans-vinylene} \), vinyl, and vinylidene are formed in almost all polymers under SHI. \( \text{trans-trans} \)-diienes are also created but in a lesser extent. In polymers containing heteroatoms in the main chains, specific groups are created. As an example, in bisphenol A polycarbonate (BA-PC), carboxylic acids (along with phenols) are created after the carbonate group scission [3].

- **Triple bonds and cumulated double bonds.** In certain conditions, alkyne triple bonds are formed in polymers irradiated with swift heavy ions [4-7]. In Polyimide (PI), triple bonds formed are not only alkynes but also alkyl or aryl cyanates [8, 9]. Concerning cumulated double bonds, allenes and isocyanates are formed in polyolefines [7] and polyimide, respectively.

- **Cross-linking or chain scissions.** In this document, “chain scissions” stands for bond cleavages in the main chain (also called the backbone). The ratio between cross-linking and chain scissions depends on the chemical structure of the polymer. A tentative general trend to distinguish between polymers with prominent scissions or prominent cross-linking is the following. Chain scissions prevail in presence of a quaternary carbon atom, a carbonate or an ester group in the polymer backbone: as in BA-PC [3], in poly(allyl diglycol carbonate) [10] (PADC or CR-39) or in Poly(ethylene terephtalate) (PET) [8, 9, 11]. Defining cross-linking polymers is more difficult. In polymers containing at least one H atom on the carbon adjacent to a \( \text{CH}_2 \) group or in polymers containing alkenes, cross-linking is favored: as in polyethylene (PE) or in polystyrene (PS) [12]. The situation is rather complicated for polypropylene (PP).

Following the behavior of the absorption bands related to groups present in the virgin polymer, as a function of the irradiation conditions, gives information on the evolution of the crystalline ratio, the setting of chain scissions or the implication of these groups on the polymer ageing under irradiation. All these features are called hereafter polymer “overall destruction”. For example, the destruction of ester or carbonate groups, when these are located in the backbone, is a good template for chain scissions since it leads to backbone length shortening. In polymer containing halogen atoms, chlorine or fluorine [13], the carbon-halogen bond is the weakest link.

For a thorough description of ion beam irradiations, the atomic number, the velocity and the fluence should be specified [1]. However, for quantification purposes, these parameters can suitably be reduced into two main parameters: the LET and the ion fluence or the dose deposited.
3.1.1. LET effect. Macromolecular defects created in polymer submitted to SHI can be classified into two series. The first series concerns defects created both under low-ionizing radiations and SHI. The second series concerns defects created solely under SHI or defects, such as vinyl groups in most of the polymers, which creation is highly increased with increasing LET.

3.1.1.1 Defects common to low and high ionizing radiations

In-chain unsaturated bonds. Under vacuum or inert environments, among macromolecular defects of the first series are C=C unsaturations, such as trans-vinylene, trans-trans-diene or vinylidene. In alkenes created in polymers containing halogen atoms, such as PVDF [2, 14], some of the olefinic hydrogen atoms can be substituted by halogen atoms. In simple polyolefins, LET effect on the alkenes of this series, at low doses, is reduced if not inexistent. In polymers containing a benzene ring, as PS, an influence of LET does exist and an increase in trans-vinylene and vinylidene radiation chemical yield at initial dose, \( G_0 \), is observed with increasing LET [5].

Along with cross-linking, trans-vinyles are one of the major defects created in PE. In this polymer, values of the trans-vinylene creation yield at initial dose, \( G_0(\text{tv}) \), in a large domain of LET (0.44 keV/nm to 18.2 keV/nm) appear to be rather constant [2, 5, 7, 14]. A quite reduced variation in \( G_0(\text{tv}) \) values was observed, when going from a 2.5 MeV e-beam to a \( ^{13}\text{C} \) 11 MeV/A ion beam [2]. In polymers containing native trans-vinyles, the fate of these groups depends on the value of the initial concentration compared to the value at saturation, \( C_{\text{sat}} \) (see section 3.1.2.1). At a given LET. If the initial concentration is lower than \( C_{\text{sat}} \) then the group is further created. At the reverse, if the initial concentration is higher than \( C_{\text{sat}} \), the group is destroyed. In PE, \( C_{\text{sat}} \), at a given LET, is observed with increasing LET [15].

At room temperature, in an ethylene-propylene diene monomer with 2.2% 1,4 hexadiene molar content (EPDMh₂), the trans-vinylene group is destroyed both under a 1 MeV e-beam and a 11 MeV/A \( ^{13}\text{C} \) ion beam [16]. At higher LET, when the dose increases, there is first destruction, followed by further creation. The dose at which the destruction is overwhelmed by the creation decreases with increasing LET [17].

Vinylidenes are created in polyolefins and their creation yield depends on the polymer chemical structure. In simple polyolefins and at low doses, their creation yields can be classified as followed: PP≥PB>PE. PB is the poly(butene-1). No tangible effect of the LET is observed for this defect in PP irradiated with ion beams starting from C to Kr.

Trans-trans-diienes are conjugated structures made of C=C bonds. Their radiation chemical yield of creation is low compared to that of simple alkenes. The same trend, as for trans-vinylene, is observed in the evolution of trans-trans-diene as a function of the LET, in PE, PP, and PB [6].

For all of the alkenes of this first series, there is almost no LET effect on the radiation chemical yields at low doses, in most of aliphatic polyolefins. To the contrary, values of the concentration at saturation clearly increase when going from low-ionizing radiations to ion beams. Moreover, the saturation occurs at a lower dose for e-beam irradiations than for SHI. In PE, trans-vinylene concentration at saturation is multiplied by a factor of 2 when going from a 1 MeV e-beam (1.84 \( 10^4 \) eV/nm) to a 4.84 MeV/A \( ^{16}\text{O} \) beam (0.51 eV/nm); at the same dose rate. The same evolution is observed in poly(vinylidene fluoride), PVDF [2]. For both polymers, when increasing the LET, under SHI, from 0.51 to 8.52 eV/nm, the trans-vinylene concentration at saturation is almost constant. Since the saturation corresponds to a balance between creation and destruction, and since there is no LET effect on creation yields of at low doses, then the highest concentrations at saturation at high LET are assigned to reduced destruction efficiency.

Chain scissions and cross-linking. Direct analysis of both cross-linking and chain scissions by FTIR spectroscopy is difficult. Nevertheless, an indication of chain scissions can be obtained through the monitoring of the creation of vinyl groups (in polyolefins with no side chains) and triple bonds, the destruction of the carbonate or ester groups when present in the backbone (such as in BA-PC for example), or gas release. Since all of these features increases with increasing LET (sections 3.1.1.2 and 3.1.1.3), one can conclude on an increase in chain scissions with increasing LET.

The LET effect on cross-linking was studied in polystyrene irradiated either with a 2.5 MeV/A proton beam or a 9.8 MeV/A carbon beam, under vacuum and at low doses, leading to LET values of 0.02 and 0.18 keV/nm, respectively. This study showed first, that the partial yields for multiple cross-
links increase with the LET increase and second, that a gel fraction can be created directly in the C ion track [12].

**Polymer overall degradation.** Following the evolution of groups present in the virgin polymer gives information on the polymer “overall degradation” and on the presence of weak groups or bonds in the polymer chain. For instance, in BA-PC irradiated with various ion beams, giving different LET values, the carbonate group is shown to be the most fragile group [3]. In PET, the ester group is the most fragile. In both polymers, the cleavage of these fragile groups leads to the creation of carboxylic acids, carbonyls other than acids or esters, alcohols or alkenes. In BA-PC, the effect of LET on the polymer “overall destruction” is huge: the destruction yield of carbonate groups increases with increasing LET. The most striking effect, which has also been shown in PS and in ethylene/styrene copolymers, is the loss of the benzene ring stability [3, 4, 5] at high LET. This reduced stability is due to an increase in the benzene ring opening with increasing LET; as shown by acetylene emission or the decrease of the FTIR bands of the benzene ring. This huge destruction of benzene ring corresponds to a progressive change in the radiolysis mechanism. As a consequence, because of their huge destruction yield, benzene rings can no longer be used to stabilize efficiently aliphatic polymers at very high LET.

In semi-crystalline polymers, the crystalline ratio decreases: amorphization occurs in the polymer. This amorphization was shown to be poorly sensitive to LET, in PE and PVDF [2, 14].

3.1.1.2 **Defects specific to high ionizing radiations or related.** In polymers devoid of native vinyl groups, these defects are created under e-beam or γ-rays but in very low concentrations. Under SHI, in polyolefins with no side chains, both their radiation chemical yield at low doses and their concentration at saturation increase sharply [18]. The vinyl group creation yield, in olefins homopolymers or copolymers such as PE, PP, or EPDMh, increases drastically first when going from e-beam to C ion beam, and second when increasing the LET from C to Pb ion beam [2, 14, 19]. In most of the polymers in which the formation of a vinyl group comes along with main chain bonds cleavage, an increase in the creation of vinyl groups with increasing LET gives an indirect evidence of the increase in chain scissions with increasing LET.

Most of alkynes studied are monosubstituted acetylenes. In PE submitted to a 1 MeV e-beam, at doses as high as 105 MGy, independently of the dose rate, alkynes are not created [14]. In the same polymer, submitted to 36S 11 MeV/A ion beam, alkynes are created at doses as low as 1 MGy. Therefore, for alkyn to be created, a huge energy deposition in a limited time scale (~10^{-15} s) is mandatory. In most polymers, the simultaneous breakage of multiple bonds and the subsequent reorganization are required for alkyn to be created. In polymers containing benzene rings in their structure, alkyn creation originates from the ring destruction [5].

Under SHI, alkyn creation, since low doses, is only effective after a LET threshold [8, 9, 11], which depends on the polymer chemical structure. The LET threshold value is higher than 6.6 MeV.mg^{-1}.cm^{2}, in PE, PP or PB [7]. In these polymers, above the LET threshold, the radiation chemical yield of creation of monosubstituted acetylene is function of the side chain length: it decreases when going from PE to PB. This behavior is LET dependant [7]. The present behavior can be only understood if one considers, at high LET, the increase of highly unsaturated hydrocarbon gases created from the side chain departure [20, 21]. Below the LET threshold, alkynes are created after a threshold of dose of around 10 MGy, independently of the side group length [7]. This threshold of dose was shown to decrease with increasing LET in α-PVDF [22].

LET effect on cumulene is similar to the one observed on alkynes: a LET Threshold is needed for them to be created and, above the threshold, their creation yield increases with the LET.

In polyimide, triple bonds and cumulenes created include a nitrogen atom to form respectively cyanates and isocyanates [8].

Both the LET threshold for alkyne creation and the threshold of dose, when the ion LET is below the LET threshold of creation, can be modified by modifying the polymer chemical structure. Inserting double bonds in the polymer reduces the LET threshold. This phenomenon is assigned to the increase in the electronic density in the environment of unsaturated bonds and the set-up of important energy transfers from the saturated moiety to the C=C bond [7].
3.1.1.3 Gas release. In simple polyolefins with no heteroatom, one of the most important gases emitted is hydrogen (H\textsubscript{2}). This gas is formed from H°, resulting from C-H homolytic scissions, which reacts within the polymer. Apart from H\textsubscript{2}, hydrocarbon gases are created in polyolefins under SHI. Probing hydrocarbon gases is an indirect way to access to chain scissions. In polymers with no side chains or pendant groups, the emission of hydrocarbons is related to bond cleavage in the polymer backbone. At low LET, hydrocarbon gases are fingerprints of the polymer chemical structure. In polyolefins with side chains, the complementary gases are representative of the chemical structure of the side chain (CH\textsubscript{4} for PP, C\textsubscript{2}H\textsubscript{x} for PB…).

Based on this behavior, one can infer that bond scissions occur at the side chain, on the tertiary carbon. When the LET is increased, the degree of unsaturation of hydrocarbon gases increases. At very high LET, the chemical structure signature is lost and acetylene becomes the preponderant gas among hydrocarbons [20] (table 1).

Another effect of the LET on gas emission is the increase of the radiation chemical yield of creation of hydrocarbon gases in all the polymers studied (PE, PP, PB, PS and EPDMh), with increasing LET. At LET as high as 20 MeV.mg\textsuperscript{-1}.cm\textsuperscript{2}, the radiation chemical yields of hydrocarbon gas emission in PS and PE are almost equal; indicating the lost in stability of styrene groups [5, 20, 21, 23].

Table 1. Evolution of hydrocarbon gaseous molecules release in PE, PP and PB irradiated at different LET, at a dose of 2 MGy, under vacuum and at room temperature (from reference [20]).

| Polymer | \(^{13}\text{C}\) | \(^{14}\text{N}\) | \(^{58}\text{Ni}\) |
|---------|----------------|----------------|------------------|
| PE      | 1.8            | 6.8            | 39.7             |
| PP      | 0.16           | 0.5            | 1.4              |
| PB      | 0.4            | 0.2            | 1.7              |

| Total gas G value (10\textsuperscript{-7} mol/J) |
| PE | PP | PB |
| 0.03 | 0.16 | 0.4 |

| Number of C atoms in the molecule (%) |
|---|---|---|
| 1  | 10.8 | 87.4 | 9.0 |
| 2  | 42  | 8   | 73  |
| 3  | 7.7 | 4.4 | 4   |
| 4  | 39.8| 0   | 13.7|

| Percentage of alkanes, alkenes and alkynes |
|---|---|---|---|---|
| Alkanes | PE | PP | PB | PE | PP | PB |
| 72 | 87 | 57 | 15 | 49 | 28 | 13 | 34 | 24 |
| Alkenes | PE | PP | PB | PE | PP | PB |
| 11 | 6 | 29 | 18 | 15 | 29 | 19 | 21 | 21 |
| Alkynes | PE | PP | PB | PE | PP | PB |
| 17 | 7 | 13 | 67 | 37 | 43 | 68 | 45 | 55 |

In polymers containing ester groups (PET) or carbonate groups (BA-PC, CR-39), carbon oxides are among the most important gases emitted. These gases are created through the scission of the backbone on the ester or the carbonate site, depending on the polymer structure. Since the destruction of these groups was shown to increase with increasing LET [3], one can assume that the resulting gases would increase as the LET increases. In an aromatic polyimide irradiated at cryogenic temperatures [24], the major gaseous product is CO. Besides this molecule, CO\textsubscript{2} and hydrocarbon molecules (C\textsubscript{2}H\textsubscript{x}) are emitted. All of these gaseous products are indications of chain scissions.

In polymers containing benzene rings such as PI, PS, PET or BA-PC, benzene derivatives are present in the radiation-induced emitted gases at low LET. At higher LET, their ratio in the gas mixture is reduced at the benefit of acetylene coming from benzene ring opening [5, 23].

3.1.2. Dose effect

3.1.2.1 Macromolecular defects. Under SHI, the influence of the dose varies with 1) the defect considered, 2) the irradiation temperature and 3) the polymer chemical structure. Under inert atmosphere and at room temperature, for most of the macromolecular defects created in polymers,
there is a tendency towards saturation: the concentration increases with increasing dose then levels off, at the saturation concentration (C\textsubscript{sat}) [2-5, 13, 16, 18]. This means their radiation chemical yield of creation, or destruction, decreases with increasing dose. Under ionizing radiations, creation and destruction happen simultaneously. Therefore, at saturation, destruction is strictly compensated by creation. This saturation can be ascribed to track overlapping at high doses. An example of this evolution is shown on figure 3, for alkyne creation.

At a given LET and in a given polymer, at room temperature, when a chemical group that can also be created under irradiation is present in the pristine polymer, its evolution as a function of dose is more complex. When the concentration of this group in the pristine polymer is higher than its concentration at saturation, when radiation-induced, then it is destroyed under irradiation. To the contrary, when its concentration in the pristine polymer is lower than the concentration at saturation, when radiation-induced, it is created under irradiation. This was particularly studied in PE containing chemically inserted C=C of the trans-vinyylene type [15].

![Figure 3](image_url)  
**Figure 3.** Normalized absorbance of alkyne band (\(v_{CH}\) stretching vibration in RC≡CH, 3295 cm\(^{-1}\)) and related creation radii, in various polymers irradiated with Kr ions (720 MeV) under vacuum (from reference [9]). Creation radii values are extracted from an exponential fit, as assumed from the saturated track model.

One of the initial defect precursors in polyolefins is the C-H bond homolytic scission. This leads to the emission of H\(_2\) along with the creation of unsaturated bonds of the alkene type. In polymers containing chemical functions such as esters and carbonates, or carbon-halogen bonds, the unsaturated bonds are created from the cleavage of these specific features. At limited doses, the prevalence of a given defect type is function of the polymer chemical structure. But, if one increases the irradiation dose up to very high values, all the polymers tend to merge into a carbon like structure made of aromatic structures containing aliphatic moieties [25].This structure is obtained by the progressive change in the polymeric structure with increasing dose, through the increase in the number of conjugated unsaturated bonds, as demonstrated by Infrared spectroscopy [2].

In semi-crystalline polymers, the crystalline ratio decreases with increasing dose and can almost disappear at very high doses.

The radius, R, in which a given defect is formed, can be calculated assuming a saturated track model. According to this model, defects are located exclusively in the latent track, which is continuous. The leveling off of the defects concentration, with the fluence, results from overlapping of latent tracks. From this, the evolution of the concentration (C) with the fluence (\(\Phi\)) can be fitted by an exponential law following C=\(C_{sat}(1-\exp(-\pi R^2\Phi))\). Based on this model, spatial distribution of defects within the track was calculated in PVDF [22] (figure 4) as well as in PE [6].
The value of the creation radius, R, is as high as the defect creation is easy. For Both PVDF and PE, whatever the defect considered, the creation radius increases with increasing LET [22, 6].

3.1.2.2 **Gas release.** As mentioned previously, the hydrogen molecule is the major gaseous molecule emitted from olefin homopolymers or their copolymers, in the absence of heteroatoms. In these polymers, the radiation chemical yield of creation of H\(_2\) decreases with increasing dose and then levels off. This decrease has been studied more precisely for PE and EPDMh. It has been shown, experimentally, to be due to the set-up of energy transfers from the non-modified part of the polymer to defects previously created in the polymer chain [15].

In PE and PP, the emission yields of hydrocarbon gases increase with increasing dose. The total creation yield of hydrocarbon gases is multiplied by a factor of 1.5 in PE and 2 in PP, when increasing the irradiation dose from 2 MGy to 22 MGy, under \(^{17}\text{O} (4.6 \text{ MeV}.\text{mg}^{-1}.\text{cm}^{-2})\) beam. In the course of the increase of the creation yield of hydrocarbon gases, the ratio of unsaturated gases (alkenes and alkynes) over alkanes is increased. Consequently, chain scissions increase with increasing dose and this is accompanied by further dehydrogenation [23].

3.1.3 **Influence of the irradiation temperature.** The mechanisms underlying defect creation under SHI were studied using irradiation at very low temperatures (8 K-15 K), on different polymers or organic compounds. Despite their relatively simple chemical structures, it is difficult to evaluate mechanisms involved in polymers ageing, due to their chain length. Therefore, studying the effect of irradiation temperatures on polymer ageing can give valuable information on defect creation mechanisms. Studying polymers behavior at different irradiation temperatures or under annealing after irradiation at low temperatures has permitted to assess one of the most important questions concerning the formation of stable groups from radicals [19].

In PE, both **trans-vinylene** and **cross-linking** are formed from alkyl radicals. It was shown that, at temperatures where chains are frozen (8 K), only **trans-vinylene** groups are created. When the temperature rises close to the glass transition temperature, cross-linkings are formed in majority and part of the alkyl radicals leads to allyl radicals and to a lesser extent to **trans-trans**-diene [19]. In the same study, comparing radiation chemical yields at initial dose at 8 K and at room temperature showed that, half of the **trans-vinylene** is formed in the cage (immediate vicinity of the alkyl radical creation site) and half outside the cage. Therefore, only half of the **trans-vinylene** created at room temperature is diffusion-dependent [16, 18].

A similar phenomenon is proposed to explain the evolution of the **trans-vinylene** concentration in EPDMh\(_{22}\) containing native **trans-vinylene**. In this polymer, the temperature effect on the C=C behavior is tremendous at low LET. At low temperatures (8 K) **trans-vinylene** concentration increases, with increasing dose, then saturates. To the contrary, at room temperature, **trans-vinylene** groups are consumed down to a saturation concentration. This consumption is assigned to C=C attack by migrating radicals [16].

**Trans-trans-dienes** are not created in PE irradiated at low temperature (8 K). Thus, these defects are not created in the cage. As a consequence, migration of reactive species is mandatory for **trans-trans**-diene to be created. In the same way, species migration was shown to be of great importance for **allyl radical** creation in PE. In the presence of native unsaturated bonds in the pristine polymer, the temperature effect on both **trans-trans**-diene and allyl radicals creation is very low [16].

**Figure 4.** Spatial distribution of defects within the latent track in \(\alpha\)-PVDF irradiated with a 10.6 MeV/A Ar beam, at room temperature (from reference [22]).
Concerning vinyls and alkynes of the monosubstituted acetylene type, the influence of the irradiation temperature is clearly visible, in PE. When lowering the irradiation temperature from room temperature to 8 K, the alkyne creation yield, \( G(\text{alkynes}) \), increases. The ratio of \( G(\text{alkynes}) \) in PE when going from RT to 8 K is 2.6. Consequently, although rapid, alkynes formation time scale is low enough to allow initial species migration. Thus, the creation time scale is higher than the diffusion time scale allowing the most mobile radicals, \( H^0 \), to escape from their creation site.

Studying the behavior of simple molecule blends, at very low temperatures (11 K), enabled the comprehension of mechanisms in action during polymer irradiation with SHI. As stated above, aromatic molecules or benzene rings have been used since decades to stabilize aliphatic polymers under low-ionization irradiations, via energy transfers. Excitations and reactive species created in the aliphatic parts are transferred to the aromatic moiety. This stabilization effect still exists under SHI at low LET. Thus, despite the huge ionization/excitation densities induced by SHI, transfers exist and are efficient. However, the stabilization is lost at LET values higher than 7 MeV.mg\(^{-1}\).cm\(^2\); thanks to benzene ring opening. Furthermore, against the general knowledge, it has been shown (figure 5), using ethylene/styrene copolymers or amorphous solids of organic molecules, that the aliphatic moiety is protected at the expense of the aromatic moiety that is destroyed [26-28].

Transfers in polymers can happen either along a given chain (intrachain processes) or between two chains (interchain processes). In order to assess the importance of each of these processes, the behavior of cyclohexane/benzene amorphous solid mixtures, under SHI, was considered. It appears from this study that, contrary to what was considered in the past, excitations and charge transfers can also happen through the interchain route; and not solely through the intrachain route [26-28]. Besides, in ethylene/styrene copolymers with various styrene molar contents, increasing the irradiation temperature from 8 K to 298 K only showed a limited variation in the radiation chemical yields of defect creation. Therefore, the influence of reactive species, such as radicals, in the stabilization mechanism of aliphatic moiety by the aromatic one, under SHI, is reduced.

![Figure 5](image)

**Figure 5.** Evolution of the styrene moiety destruction \((A-A_0)/A_0\) as a function of the dose in different Ethylene/Styrene copolymers irradiated with \(^{13}\text{C}\) ions (LET = 1.7 MeV.mg\(^{-1}\).cm\(^2\)), under vacuum and at RT (from reference [28]). \(A_0\) and A correspond to the absorbance before irradiation and at a given dose, respectively.

3.2. Influence of the irradiation environment: the radiation-induced oxidation

Studies on the combined effect of oxygen and SHI are less numerous and detailed than those concerning irradiations under anoxic conditions. In the following, EPDMh\(_{2.2}\) is an ethylene-propylene-diene terpolymer based on 1,4 hexadiene (2.2% molar).
Under low-ionizing radiations, when oxygen is present in the irradiation environment, radicals created from C-H (or C-C) homolytic scissions, readily react with oxygen molecules giving peroxy radicals. According to the generally accepted chain reaction, involving alkyl and peroxy radicals, inactive products are created. These products are made of both oxidized and non-oxidized groups. Detailed studies on the radiation-induced oxidation of EPDMh$_{2.2}$, irradiated with various ion beams were handled [17, 29-31]. It appears from these studies that: first the oxidative ageing is effective under SHI and second, the oxygen uptake is lower under SHI. Oxygen uptake is multiplied by five when going from a 13 MeV/A $^{13}$C beam irradiation to a 1 MeV e-beam irradiation.

In EPDMh$_{2.2}$ irradiated with a 13 MeV/A $^{13}$C beam, oxidation occurs since very low oxygen pressures in the irradiation cell. The radiation chemical yield of oxygen uptake is function of the oxygen relative pressure in the irradiation vessel: it increases up to 10 mbar and then levels off [29].

Oxidized defects created under SHI are of the same type as those created under low ionizing radiations. However, their radiation chemical yields of creation are lower under SHI, as is the oxygen uptake [29,30]. This reduced oxidation effect can be due to 1) the huge energy deposit, corresponding to very high local dose rates, induced by SHI or 2) the use of higher macroscopic dose rates during irradiations with SHI or 3) the combination of both effects. The first hypothesis seems by far the most credible.

Possible oxidised defects are carbonyl groups (ketones, carboxylic acids, esters, peresters or peracids), ethers, alcohols or hydroperoxides. No LET effect was observed on total carbonyl concentration, in EPDMh$_{2.2}$ irradiated under Ne beams at LET ranging from 4.8 to 11.5 MeV.mg$^{-1}$.cm$^{-2}$. Among carbonyl containing functions, thanks to curve fitting, ketones were shown to accumulate more than carboxylic acids; even if the ratio of ketones to carboxylic acids decreases with increasing dose [17].

Contrary to what is observed under low ionizing radiations, unsaturated groups are created under SHI in presence of oxygen. Creation of unsaturated groups under SHI can be accounted for the very high ionizing densities created along the ion track and the resulting enhanced alkyl radical recombinations, prior to reaction with oxygen molecule. Alkenes, created are of the same type as those created under inert environments. In EPDMh$_{2.2}$, irradiated at LET varying from 4.8 to 11.5 MeV.mg$^{-1}$.cm$^{-2}$, in presence of oxygen, vinyl creation increases with increasing LET. Moreover, this LET effect is dose dependent [17]. In PVDF irradiated with a 5.3 MeV/A Kr beam, the creation of conjugated double bonds is enhanced under oxygen atmosphere [13]. Alkynes are created under oxidative environment, above a LET threshold and no effect of the irradiation environment was observed in their creation in PVDF films [13] or in EPDMh$_{2.2}$ films [17].

As a consequence of the oxygen uptake and the subsequent defects created, most of the polymers are degraded under oxidation. For those that are degrading under vacuum, the degradation rate is increased [8].

Under low-ionizing radiations, the oxygen uptake radiation chemical yield, G(-O$_2$), in polymers evolves linearly with the reverse of the square root of the dose rate (I) following: G(-O$_2$)=a+b/$\sqrt{I}$. Under a 11 MeV/A $^{13}$C beam, whatever the oxygen relative pressure, no dose rate effect was observed in the G(-O$_2$) values in the EPDMh$_{2.2}$ at dose rates varying from 100 kGy/h to 1000 kGy/h [30]. The situation is different for some of the oxidized macromolecular defects [31]. Indeed, studies on the same EPDM hexadiene, irradiated with e-beam and $^{13}$C 11 MeV/A beam under 200 mbar oxygen, showed that, for carbonyls or hydroxyls groups 1) the radiation chemical yields of creation are related to the dose rate square root by the linear relation presented upper, 2) the values of a and b are lower under $^{13}$C beam irradiations as compared to e-beam. These lower values can be understood if one considers the higher local dose rate induced by SHI along the ion path.

4. Conclusion
An important effort was made to understand the behavior of polymers under SHI. Most of the studies were performed with, olefins homopolymers or their copolymers, PVDF, BA-PC, PS and Ethylene/styrene copolymers; under inert atmosphere. Studying the emission of radiation-induced hydrocarbon gases and their evolution as a function of the LET gives an insight on mechanisms involved on polymers ageing and their dependence with the density of excitations and ionizations.
Besides, varying the irradiation temperature is of great interest for the comprehension of mechanisms underlying the creation of stable defects.

Despite the huge energy deposition and the subsequent high ionization and excitation density induced by SHI, phenomena such as electronic excitation or reactive species transfers do exist. Besides, it has been shown that the aliphatic moiety stabilization occurs at the expense of the aromatic moiety.

The increase in the hydrocarbon gas emission as well as the increase in vinyl groups (in most of the polymers) and in alkyne groups creation with increasing LET gives a clear indication on the increase of chain scissions with increasing LET. The stability of polymers containing benzene rings, known and used under low-ionizing radiations, still exist under SHI at moderate LET. At the highest LET, this stability is lost due to the ring opening. Consequently, the radiation stabilization of aliphatic polymers by benzene ring insertion is no longer efficient at LET higher than $7 \text{ MeV.mg}^{-1}\text{cm}^2$.

Few results were obtained under oxidative environment. Therefore great efforts should be oriented towards the comprehension of the influence of high LET on radiation-induced oxidation, especially the fate of non oxidized defects and hydrocarbon gas emission and their evolution either with irradiation dose, LET or dose rate.

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