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# Effect of oxygen on gas emitted from polymer irradiated using Swift Heavy Ion beams

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## Abstract

At the end of their life, polymers used in the nuclear industry are placed in Intermediate Level - Long Lived Waste packages. For safety purposes, the amount of gas emitted by these organic materials has to be estimated.  $\gamma$  irradiations are commonly used to simulate  $\beta$  and  $\gamma$ -emitters;  $\alpha$ -emitters simulation are more problematic because of experimental difficulties. It is proposed in France to use particle accelerators with ions providing stopping power values in polymers equivalent to the one of  $\alpha$ -emitters. This approach has been validated under inert atmosphere; the question now arises of the effect of the presence of oxygen. We showed that the hydrogen release is slightly affected by atmosphere of irradiation and increases with LET. The evolution with LET of CO<sub>2</sub> release is dependent on the polymer: it increases for polymers with low G(CO<sub>2</sub>) at low LET and decreases for polymers presenting relatively high G(CO<sub>2</sub>) at low LET.

## Keywords

Polymers;  $\alpha$ -emitters simulation; Gas radiation chemical yields; Oxygen presence effect; Heterogeneous energy deposition

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## Highlights

- $\alpha$ -emitters simulation by using particle accelerators
- Effect of oxygen on the irradiation of polymers by Swift Heavy Ion beams
- Hydrogen and carbon dioxide release evolution analysis

## 1. Introduction

Many polymers are used in the nuclear industry and are thus in contact with radionuclides. At the end of their utilization, these materials cannot be disposed *via* conventional waste disposal facilities and are therefore placed in Intermediate Level - Long Lived Waste (IL-LLW) packages. Within these packages, the polymers are in contact with radionuclides and are therefore degraded. Different gases are emitted and safety analyses require to quantify their production.

To model the contact of organic materials with radionuclides, irradiations of simulation have to be carried out. It allows a better understanding of the degradation mechanisms of polymers as a function of the emitter (thus the type of irradiation), the atmosphere during irradiation, the dose and the dose rate [1-7].

Irradiations using  $\gamma$ -rays are used to simulate  $\gamma$  and  $\beta$  emitters, because it is considered that the stopping power of these two types of radiation is equivalent. A huge literature has dealt with polymers irradiated using  $\gamma$ -rays, leading to the publication of many very important books or book sections [8-13], one of the most known being “The Radiation Chemistry of Macromolecules” of Dole [14] which remains a reference even half a century after its edition. A little less articles can be found on gas emission using  $\gamma$ -rays under oxidative atmosphere. However, we can cite, without being exhaustive the articles of Arakawa, Seguchi, Hayakawa and Machi [15], of Izumi, Nishi, Seguchi, Ema and Yamamoto [16] and the very interesting book of Reichmanis, Franck and O’Donnell [17]. These different works brought to light the effect of low LET rays on different kinds of polymers.

The simulation of  $\alpha$  emitters is more problematic. In fact, to obtain exploitable and reproducible results, radiation chemical yields have to be measured under well-defined conditions for which the stopping power, or Linear Energy Transfer (LET), presents a weak variation during the course of the particle in the target material. The use of  $\alpha$ -

emitters to measure the radiochemical yields of materials, even obviously possible [18], has been ruled out for different reasons. The first one is that data collection under active environment is complex to be carried out and complex to implement on a large number of materials. The second difficulty comes from the short penetration of the  $\alpha$ -emitters, which would imply either extremely thin samples to keep the LET roughly constant or the analysis of data obtained with a non-negligible variation of the stopping power. The last but not least drawback is the self-absorption process observed in case of such  $\alpha$ -emitter sources which complicates the interpretation of the obtained results. For all these reasons, the use of particle accelerators has therefore been favoured.

The chosen ions have to fulfil two conditions: *i*) they have to present a stopping power close to the maximum one of the  $\alpha$ -particles emitted by radionuclides and *ii*) they are chosen in a way that stopping power is relatively constant throughout the thickness of the sample. For example in the case of polyethylene (PE) irradiated at a LET equivalent to the maximum stopping power of  $\alpha$ -emitters (approximately equal to  $2.7 \text{ MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^2$ ), SRIM based on the TRIM code [19] estimates that the material is homogeneously irradiated over a thickness of about  $10 \text{ }\mu\text{m}$  for  $4.2 \text{ MeV}$  He ion beam,  $60 \text{ }\mu\text{m}$  for  $5.4 \text{ MeV}\cdot\text{A}^{-1}$  C ion beam and  $3000 \text{ }\mu\text{m}$  for  $88 \text{ MeV}\cdot\text{A}^{-1}$  Ar ion beam. Hence, one of the particle accelerators advantages is to use, for each irradiation, a more important quantity of each polymer, hence decreasing the uncertainty on the obtained data while remaining at a LET equivalent to the maximum stopping power of  $\alpha$ -emitter sources.

Under inert atmosphere, the representativeness of irradiations with heavy ions to simulate  $\alpha$ -emitter irradiations is based on the results obtained by Gervais and Bouffard [20]. The numerical simulations obtained by these authors show that the ionization densities along the trace of a  $\text{He}^{2+}$  ion of  $5 \text{ MeV}$  or of an  $\text{Ar}^{18+}$  ion of  $95 \text{ MeV}\cdot\text{A}^{-1}$  in polyethylene are very close. The main difference lies in the fact that the argon ion has higher energy and ejects more energetic secondary electrons than the helium ion, the secondary electrons (the so-called  $\delta$ -rays) giving up their energy at a greater distance from the ion track. However, the probability of these events is relatively low and corresponds to a small fraction of the energy deposited by the incident particle in the target, so they can be neglected in the nuclear waste packages safety conditions. This approach has later been experimentally validated, using  $\alpha$ -particles from plutonium oxide [18]. Oxygen is known to be highly reactive and to modify the different reaction paths when present during the irradiation. It is thus necessary to question the validity,

in the presence of oxygen, of the hypothesis underlying the work of Gervais and Bouffard [20], that is to say that the size of the ion track, and therefore the heterogeneity of the dose deposition, has no - or weak - influence on the phenomena induced in polymers by radio-oxidation.

To the best of our knowledge, there are only two articles that deal with the irradiation, under oxidative atmosphere, of polymers by  $\alpha$ -emitters [21, 22]. These preliminary works are very interesting because authors quantified hydrogen release and oxygen consumption in the waste packages conditions. However, data obtained are very operational ones and the dose deposited in the polymers was not properly quantified, which prevents a precise quantification of the different radiation chemical yields, and thus a proper comparison with ion beam irradiation. To overcome this drawback and to get as close as possible of the behaviour of the different polymers in IL-LLW packages, we decided to perform irradiations with He ions of 6 MeV.

This article presents the work carried out on this subject in recent years. Three types of polymers (polyethylenes, polyurethanes and polystyrene) have been studied using different irradiation facilities, *i.e.* using different ions at different LET; results have been compared. These polymers are very interesting because either they are found in waste packages (cases of polyethylenes and polyurethanes [4-6, 23, 24]) or they are representative of materials present in the nuclear waste packages (case of polystyrene which is representative of ion exchange resins [25]). Materials were first irradiated under inert atmosphere to validate our experimental procedure by comparing our results to published data from the literature, and more specifically to those of Chang and LaVerne [26] and of Venault *et al.* [18]. Then, the oxygen presence effect on gas radiation chemical yields emitted from polymer irradiated using Swift Heavy Ion beams at different stopping powers is presented.

## **2. Experimental Section**

### **2.1 Materials**

Three types of polymers were chosen for this study – all polymers being used without any further purification: two pure polyethylenes, two polyurethanes (one resin and one industrial material), one pure polystyrene. As just introduced, these polymers were

chosen because they are representative of polymers in IL-LLW packages and because they present very different behaviours as a function of LET. In fact contrary to aromatic materials which are very sensitive to the stopping power, aliphatic materials present a weak evolution with this parameter; PUR materials behaviour being in-between [3, 4, 26].

### **2.1.1 Polyethylenes (PE)**

Two different pure high density polyethylenes (HDPE) were used in this study.

The first one was supplied by Sigma-Aldrich (reference 181900) under the form of pellets. Its weight average molar mass  $M_w$  is given at  $125\,000\text{ g}\cdot\text{mol}^{-1}$  and its density is  $0.95\text{ g}\cdot\text{cm}^{-3}$ . Its crystallinity and its melting temperature were determined using DSC (differential scanning calorimetry) and are respectively  $\chi \simeq 65\%$  and  $T_m \simeq 130^\circ\text{C}$ . An analysis of the sample by Fourier transform infrared spectroscopy (FTIR) has evidenced a low concentration of vinyl bonds in the polymer backbone [7].

The second polyethylene was supplied by Goodfellow (reference ET321010) under the form of films  $10\ \mu\text{m}$  thin. Its density is given at  $0.95\text{ g}\cdot\text{cm}^{-3}$ . Its crystallinity and its melting temperature were also determined using DSC and are respectively  $\chi \simeq 60\%$  and  $T_m \simeq 134^\circ\text{C}$ . Some additives were identified in the polymer using Atmospheric Solids Analysis Probe – Mass Spectrometry (ASAP-MS): palmitic and stearic acids which are known to be used as lubricant and antiadhesive, Irgafos 168 and Irganox 1076 known to be used as antioxidant. An analysis of the sample by FTIR has not evidenced any defect at the molecular level [7].

### **2.1.2 Polyurethanes (PUR)**

Two polyurethanes were used in this study, both composed of 4,4'-methylene diphenyl diisocyanate (MDI) as hard segment, 1,4-butanediol (BDO) as extender and poly(1,4-butylene adipate) (PBA) as soft segment.

The first PUR is an industrial polymer, supplied by Mapa. It is used for making gloves of nuclear glove-boxes (reference AdvanTech 565), shaped like a film of  $0.5\text{ mm}$  thick. Its molecular formula is  $(\text{MDI})_{0.20}(\text{PBA})_{0.57}(\text{BDO})_{0.23}$ , its density is  $1.0\text{ g}\cdot\text{cm}^{-3}$  and its  $M_w$  was determined in the laboratory as  $200\,000\text{ g}\cdot\text{mol}^{-1}$  in equivalent polystyrene with a

polydispersity index of 2.8 (10% of uncertainty). Its glass transition temperature  $T_g$  is equal to  $-32 \pm 5^\circ\text{C}$  and is fully amorphous. Mapa indicates 8.9%<sub>wt</sub> of inorganic additives, 1.8%<sub>wt</sub> of crosslinking agents and 0.4%<sub>wt</sub> of white and green pigments, the remaining total amount being the polymer. Additives were determined by Gas Chromatography – Mass Spectrometry (GC-MS) and Electrospray Ionization – Mass Spectrometry (ESI-MS): palmitic and stearic acids used as lubricant and antiadhesive, 2,6-di-*tert*-butyl-4-ethyphenol as antioxidant, tri(ethylene glycol) dimethacrylate as crosslinking agent, diethyl phthalate and dimethyl adipate as plasticizer. Some synthesis residues were also evidenced in the polymer matrix [6].

The second PUR is the corresponding pure resin, supplied by Lubrizol (reference Estane® 5703). Its molecular formula is  $(\text{MDI})_{0.17} (\text{PBA})_{0.63} (\text{BDO})_{0.20}$ , its density is  $1.19 \text{ g}\cdot\text{cm}^{-3}$  and its  $M_w$  was determined in the laboratory as  $140\,000 \text{ g}\cdot\text{mol}^{-1}$  in equivalent polystyrene with a polydispersity index of 2.5 (10% of uncertainty). Its glass transition temperature  $T_g$  is equal to  $-33 \pm 1^\circ\text{C}$  and is fully amorphous [6].

### ***2.1.3 Polystyrene (PS)***

One pure atactic polystyrene, supplied by Sigma-Aldrich (reference 182435) under the form of pellets, was used in this study. Its weight average molar mass  $M_w$  is given at  $290\,000 \text{ g}\cdot\text{mol}^{-1}$  whereas its number average molar mass  $M_n$  is given at  $130\,000 \text{ g}\cdot\text{mol}^{-1}$ , leading to a polydispersity index of 2.2. As polystyrene is chosen amorphous, the crystallinity is null.

## **2.2 Irradiation conditions**

### ***2.2.1 Samples processing***

Whatever the irradiation nature and/or facility, polymer films are sufficiently thin to ensure that the irradiations are homogeneously performed, from the oxidation and/or from the LET variation points of view.

Oxidation critical thicknesses were estimated for each material using the well-known equation of Gillen & Clough [27]. In the Swift Heavy Ions (SHI) beam cases, the energy

loss was calculated with SRIM [19], and samples thickness were chosen so as to limit the LET variation to less than 25% between the entrance and exit polymer surfaces.

If necessary, thin films were prepared by high pressure moulding using a laboratory press. Polymers were moulded to obtain films between 50 and 100  $\mu\text{m}$  thick for gamma irradiations and between 10 and 25  $\mu\text{m}$  for ion beams.

### **2.2.2 Gamma irradiations**

In this work,  $\gamma$ -irradiations are considered to represent the low LET domain, *i.e.* between 0.001 and 0.002  $\text{MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^{-2}$  [28].

Before irradiation, polymers are put in glass sealed ampoules under around 700 mbar of pure helium for irradiations under inert conditions or of reconstituted air (20.0 %  $\text{O}_2$ , 77.99 %  $\text{N}_2$ , 2.01 %  $\text{Kr}$ ) in case of irradiations under oxidative conditions. In this latter case, krypton was used as a tracer and enabled to determine the final pressure. Sample masses were estimated to obtain, at the end of the irradiation, a final  $\text{H}_2$  content of about 1%vol.

Irradiations were performed at IONISOS (Dagneux, France), at GAMMATEC (Marcoule, France) or at LABRA (Saclay, France). These three irradiation facilities are equipped with  $^{60}\text{Co}$  sources. No electronic correction was made to take into account the electronic density difference between water and the polymers. Uncertainties on given doses are less than 6% and irradiation conditions and facilities are gathered in Table 1.

Table 1.  $\gamma$ -irradiation conditions.

Polymer	Irradiation facility	Atmosphere	Mean dose rate (kGy·h <sup>-1</sup> )	Doses (kGy)
PE Sigma-Aldrich	LABRA	Air	1.04	50
		Helium	1.04	50
			1.04	100
PE Goodfellow	IONISOS	Air	0.7	49
			0.6	101
	LABRA	Helium	1.04	50
			1.04	100
PUR Estane	GAMMATEC	Air	0.7	49
			0.7	100
		Helium	0.7	49
			0.7	100
PUR Mapa	GAMMATEC	Air	0.7	49
			0.7	100
		Helium	0.7	49
			0.7	100
PS Sigma-Aldrich	LABRA	Air	1.04	50
			1.04	100
		Helium	1.04	50
			1.04	100

### 2.2.3 Argon ion experiments

The GANIL (Grand Accélérateur National d'Ions Lourds, Caen, France) irradiation experiments were performed using the high energy beamline of the cyclotron accelerator facility. The beam is a <sup>36</sup>Ar beam of 95 MeV.A<sup>-1</sup> specific energy, the remaining energy at the polymer film entrance being of 88 MeV.A<sup>-1</sup>. As in the case of  $\gamma$ -irradiations, samples are conditioned in glass containers, ampoules under around 700 mbar of pure helium in case of irradiations under inert conditions or of reconstituted air (20.0 % O<sub>2</sub>, 77.99 % N<sub>2</sub>, 2.01 % Kr) in case of irradiations under oxidative conditions. This high ion energy used at GANIL is thus necessary to go through the ampoule glass walls without

reducing drastically the energy of the beam reaching the samples placed in these ampoules.

The irradiation is activating the glass ampoules containing the polymers, and in the conditions we used, the radioactive decay lasts at least one month. Irradiations under inert atmosphere are performed in sealed glass ampoules. When irradiations are performed under oxidative atmosphere and in order to avoid the post-irradiation effect in the irradiated polymers, a sample of the gas is collected just at the end of the irradiation; glass containers with valves are mandatory in these cases.

Homogeneous irradiation was ensured by a x,y-scanned beam. Irradiation conditions are gathered in Table 2. Statistical errors for a given sample and for a single beam are low, at most a few percent. The systematic errors are higher but less than 10%; they are mainly caused by sample thickness' estimation uncertainty.

Table 2. Irradiation conditions using the high-energy beamline of GANIL (Caen, France). All irradiations were performed using  $^{36}\text{Ar}$  ion beam, with an initial particle energy of  $95 \text{ MeV}\cdot\text{A}^{-1}$  and an energy at the polymer entrance of  $88 \text{ MeV}\cdot\text{A}^{-1}$ .

Polymer	Atmosphere	Thickness ( $\mu\text{m}$ )	Mean LET ( $\text{MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^2$ )	Flux ( $10^8 \text{ cm}^{-2}\cdot\text{s}^{-1}$ )	Mean dose rate ( $\text{kGy}\cdot\text{h}^{-1}$ )	Fluence ( $10^{11} \text{ cm}^{-2}$ )	Doses ( $\text{kGy}$ )
PE Sigma- Aldrich	Air	130	2.5	3.5	480	13.0	520
		200		3.5	520	26.0	1040
	Helium	55	2.5	3.3	480	6.7	270
		110		3.5	510	12.5	500
PE Goodfellow	Air	110	2.5	3.6	520	6.2	250
		120		3.5	510	12.5	500
	Helium	64	2.5	3.8	550	6.2	250
		91		3.7	530	12.5	500
PUR Estane	Air	140	2.3	3.6	480	6.2	230
		190		3.3	130	12.5	460
	Helium	600	2.3	3.8	510	6.2	230
		580		3.3	440	12.5	470
PUR Mapa	Air	500	2.3	3.5	470	6.2	230
		460		3.5	470	6.2	230
		460		3.3	430	12.5	460
		430		3.6	480	13.4	490
	Helium	700	2.3	3.5	470	6.7	250
		480		3.5	460	12.5	450
		680		3.4	450	13.4	500
		690		3.4	450	13.4	500
PS Sigma- Aldrich	Air	650	2.3	3.3	440	12.6	470
		710		3.6	480	25.1	940
	Helium	620	2.3	3.3	450	12.6	470
		620		3.6	480	25.1	940
		190		3.8	510	6.2	230
		290		3.3	430	12.5	470

#### 2.2.4 Carbon ion experiments

The GSI (Helmholtz Centre for Heavy Ion Research, Darmstadt, Germany) irradiation experiments were performed using the M3-beamline of the UNILAC accelerator facility. The beam is a  $^{12}\text{C}$  beam of  $5.9 \text{ MeV}\cdot\text{A}^{-1}$  specific energy, the remaining energy at the polymer film entrance being of  $5.4 \text{ MeV}\cdot\text{A}^{-1}$ . Contrary to the experiments performed at

GANIL, the energy beam employed in these experiments is not sufficient to pass through a glass wall. The remaining energy would be insufficient to allow for a homogeneous irradiation through the polymers thickness. A specific device developed by CIMAP (Caen, France) was employed (CHIMERE, Figure 1). The irradiation chamber volume is of 77 cm<sup>3</sup>, the samples diameter being of 16 mm. Two valves allow the gas sampling after irradiation and the chamber flushing, the surrounding atmosphere inside the cell being separated from the beamline high vacuum by a window in Havar® (Co<sub>43</sub>Cr<sub>20</sub>Ni<sub>13</sub>) of 4.45 μm. A motion system is available but was not used in this work: sample holder is positioned as close as possible from the window of the set-up.

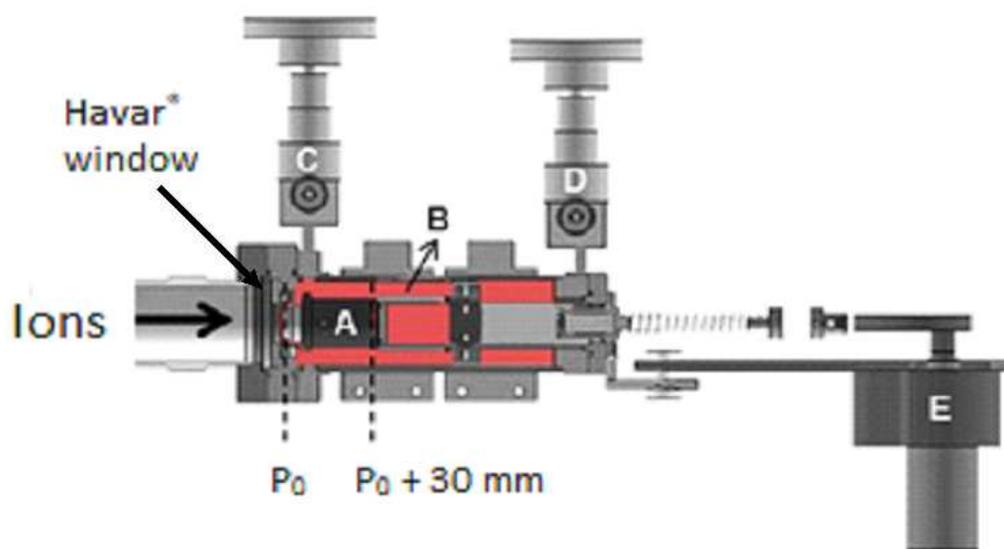


Figure 1: CHIMERE chamber for ion irradiation. The different parts correspond to (A) the sample holder, (B) the irradiation chamber volume, (C and D) the two valves for the gas conditioning of the chamber and the gas sampling after irradiation, (E) the motion system that allows sample displacement during irradiation (not used in this work).

Homogeneous irradiation was ensured by defocusing and beam shaping. Irradiation conditions are gathered in Table 3. As in the case of GANIL experiments, statistical errors for a given sample and for a single beam are at most a few percent, the systematic errors being estimated to be less than 10% - also mainly caused by sample thickness' estimation uncertainty.

Table 3. Irradiation conditions using the M-Branch line of GSI (Darmstadt, Germany). All irradiations were performed using  $^{12}\text{C}$  ions beam, with an initial particle energy of  $5.9 \text{ MeV}\cdot\text{A}^{-1}$  and an energy at the polymer entrance of  $5.4 \text{ MeV}\cdot\text{A}^{-1}$ . The choice of the surrounding gas employed to perform irradiations under inert atmosphere is defined by the analytical tool used to quantify gas released (see section 2.3).

Polymer	Atmosphere	Thickness ( $\mu\text{m}$ )	Mean LET ( $\text{MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^2$ )	Flux ( $10^8 \text{ cm}^{-2}\cdot\text{s}^{-1}$ )	Mean dose rate ( $\text{kGy}\cdot\text{h}^{-1}$ )	Fluence ( $10^{11} \text{ cm}^{-2}$ )	Doses ( $\text{kGy}$ )
PE Sigma-Aldrich	Oxygen	38	3.1	5.4	1520	20.5	1600
PE Goodfellow	Oxygen	43	3.1	7.7	1390	16.7	830
		47	3.1	7.0	1260	20.5	1030
		41	3.1	5.7	1030	41.0	2040
	Helium	44	3.1	12.7	2270	20.5	1020
PUR Mapa	Oxygen	64	2.9	19.6	3260	10.0	460
		64	2.9	21.2	3510	30.0	1380
	Nitrogen	68	2.9	24.3	4050	10.0	460
		68	2.9	22.0	3670	30.0	1390
PS Sigma-Aldrich	Oxygen	54	2.9	21.2	3670	40.0	1870
	Nitrogen	52	2.9	12.4	2080	40.0	1860

### 2.2.5 Helium ion experiments

The JANNuS-Saclay (Jumelage d'Accélérateurs pour les Nanosciences, le Nucléaire et la Simulation, Saclay, France) irradiation experiments were performed using the Épiméthée accelerator [29]. The beam is a  $^4\text{He}$  beam of 6.0 MeV energy, the remaining energy at the polymer film entrance being of 4.2 MeV. Similarly to the irradiations performed at GSI, experiments performed at JANNuS-Saclay were realized using the CHIMERE set-up (Figure 1).

Homogeneous irradiation was ensured by a x,y-scanned beam. Irradiation conditions are gathered in Table 4. Statistical errors for a given sample and for a single beam are higher in the case of the JANNuS-Saclay experiments than in the case of the other irradiation beamlines, because the helium-ion current necessary for the experiments is at the lowest use limit of the Épiméthée accelerator. To obtain reliable and reproducible data, current calibration was done at least once a day. Systematic errors is estimated to about 10% in these conditions – caused by the conditions of use of the accelerator and by the sample thickness' estimation uncertainty.

Table 4. Irradiation conditions using the Épipiméthée accelerator of JANNuS (Saclay, France). All irradiations were performed using  $^4\text{He}$  ion beam, with an initial particle energy of 6.0 MeV and an energy at the polymer entrance of 4.2 MeV.

Polymer	Atmosphere	Thickness ( $\mu\text{m}$ )	Mean LET ( $\text{MeV}\cdot\text{mg}^{-1}\cdot\text{cm}^2$ )	Flux ( $10^8 \text{ cm}^{-2}\cdot\text{s}^{-1}$ )	Mean dose rate ( $\text{kGy}\cdot\text{h}^{-1}$ )	Fluence ( $10^{11} \text{ cm}^{-2}$ )	Doses (kGy)
PE Sigma-Aldrich	Oxygen	10	1.3	15.2	1140	49.6	1030
PE Goodfellow	Oxygen	10	1.3	34.0	2520	14.7	300
		10	1.3	53.6	3870	10.4	210
	Nitrogen	10	1.3	56.6	4090	20.9	420
		9	1.3	11.1	1220	5.20	160
		8	1.3	9.90	1080	10.4	310
		8	1.3	5.15	560	13.0	390
PUR Estane	Oxygen	10	1.1	16.5	1630	17.3	480
		10	1.1	16.9	1670	34.7	950
	Nitrogen	10	1.1	17.9	1770	10.9	300
		10	1.1	18.0	1780	34.6	950
PUR Mapa	Oxygen	10	1.1	16.8	2550	26.2	690
	Nitrogen	10	1.1	22.9	2190	51.9	1370
PS Sigma-Aldrich	Oxygen	9	1.1	36.8	3630	18.3	500
		9	1.1	37.2	3670	36.7	1000
		10	1.2	24.6	2470	46.2	1290
		11	1.2	37.9	3820	52.1	1460
		11	1.2	40.4	4070	71.1	1990
	Helium	12	1.2	92.1	6080	114	2100

### 2.3 Gas analyses

After irradiation, gas contained in the glass ampoules were analysed using a Thermo Fischer Scientific MAT-271 spectrometer, equipped with different detectors (Faraday cups but also electron multiplier). When using this analytical tool, the surrounding gas used to simulate inert atmosphere during irradiation is helium; using helium instead of nitrogen allows avoiding interferences with carbon oxide fragments at  $m/z$  28. This technique has already been presented in details in a former article [1].

When the CHIMERE set-up was used, gas analyses were performed using a AGILENT 490  $\mu$ -gas chromatograph. This apparatus is equipped with four columns, whose

characteristics are given Table 5. The carrier gas of three columns of the  $\mu$ -GC being helium, the surrounding gas used to simulate inert atmosphere during irradiation is nitrogen when using this analytical tool.

Table 5.  $\mu$ -GC columns characteristics.

	<b>Length (m)</b>	<b>Type</b>	<b>Carrier gas</b>	<b>Quantified compounds</b>
Column 1	20	Molsieve 5A	Ar	O <sub>2</sub> , H <sub>2</sub> , He
Column 2	20	Molsieve 5A	He	Kr, CH <sub>4</sub>
Column 3	10	Pora Plot U	He	CO <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub>
Column 4	10	Molsieve 5A	He	N <sub>2</sub> , CO

Whatever the gas analysis technique, radiation chemical yield  $G(X)$  of gas  $X$  was determined using its partial pressure in the closed container and the following equation:

$$G(X) = \frac{P_f \cdot \%_{vol} \cdot V_{free}}{R \cdot T \cdot D \cdot m}$$

with  $G$  in mol.J<sup>-1</sup>,  $P_f$  the total pressure in the glass ampoule at the end of the irradiation in Pa,  $\%_{vol}$  the gas volume fraction,  $V_{free}$  the free volume in the glass ampoule in m<sup>3</sup>,  $R$  the gas constant,  $T$  the sample's temperature under irradiation in K,  $D$  the dose deposited during the irradiation in Gy, and  $m$  the mass of the irradiated sample in kg.

Standard deviation is always inferior to 10% in the hydrogen emission case; it is slightly higher than 10% in case of carbon oxides. The error bars on Figure 2 to Figure 4 correspond to the standard deviation between the different radiation chemical yield values obtained in the same conditions.

### 3. Results and discussion

In a first part of this work, the radiation chemical yields of hydrogen have been measured for all polymers and all irradiation types under an inert atmosphere. These yields were compared to the literature values, and more specifically to those obtained by Chang and LaVerne [26] and those from Venault *et al.* [18]. Figure 2 shows the hydrogen radiation chemical yields as a function of LET for different particle irradiations and compares the experimental measurements with the corresponding literature data.

Chang and LaVerne [26] evaluated, using different ions beams, the hydrogen radiation chemical yields from two polyolefins (PE and PP), one polymethyl methacrylate (PMMA) and one polystyrene (PS). Venault *et al.* [18] investigated also the hydrogen release, but from a PP irradiated under inert atmosphere using a stack of polymer films and thin plutonium dioxide pellets. In such irradiation conditions the LET of the  $\alpha$ -particles varies in the material, which explains why the data is plotted as a rectangle instead of a point. The rectangle width indicates the LET variation of the  $\alpha$ -particles. Figure 2 shows that, for PE and PS, the results obtained in this work are in good agreement with those of the literature, which validates our experimental protocol both with glass containers and with the CHIMERE experimental set-up.

Polyolefins are not very sensitive to the stopping power, contrarily to aromatic polymers which are very sensitive. PMMA and polyurethanes present a similar and intermediate behaviour. This is explained by the presence of carbonyl bonds in their structure which are well known to be very efficient as regard to the energy transfer\*, under photolysis [30], under low LET irradiation [1] as under high LET irradiation [7]. Hydrogen release decrease is correlated to the presence of these C=O bonds which are present in an aliphatic chain; corollary being this carbonyl bond degradation. In the case of the PUR type polymers, the protective group is the urethane bond which lead to CO<sub>2</sub> release. Nonetheless, the higher the LET the lower the energy transfer efficiency [7], leading to G(H<sub>2</sub>) increase and G(CO<sub>2</sub>) decrease when LET increase. This is explained radicals recombinations in the track core which decrease the amount of transferable energy.

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\* Energy transfer in this article includes the mass or reactive species transport (including radicals and ions), lone charge transfers (electrons and holes), and electronic excitation transfers.

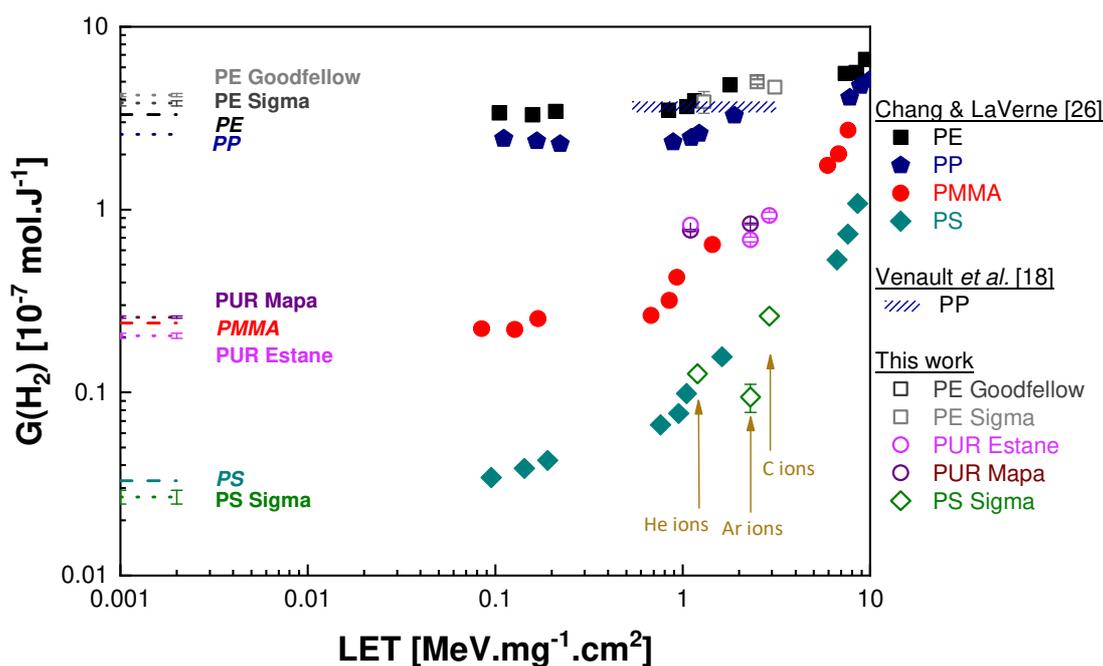


Figure 2. Hydrogen radiation chemical yields as a function of LET for polymers irradiated under inert atmosphere. Lines represent  $\gamma$ -rays. Symbols are for ion irradiation with results obtained in this work (open symbols) and those redrawn from the work of Chang and LaVerne [26] (solid symbols). The blue striped rectangle corresponds to the hydrogen radiation chemical yield obtained by Venault *et al.* [18] from a PP irradiated under inert atmosphere using a stack of polymer films and thin plutonium dioxide pellets.

Figure 2 shows also that at very high LET, radiation chemical yields of hydrogen tends to a common value. Chang and LaVerne [26] explained this tendency by an increased efficiency of the secondary reactions as compared to the scavenging reactions. Picq, Ramillon and Balanzat [31] showed that at low LET, emitted gas are characteristic of the polymer structure: hydrogen is mainly released from polyethylene, hydrogen and methane from polypropylene and so on. For LET higher than 20 MeV.mg<sup>-1</sup>.cm<sup>2</sup>, the initial chemical structure signature of the polymer begins to be lost, leading to the release of acetylene as the main gas evolved from different polymers. This is due to a fragmentation of the chains and the beginning of the regime of tracks formations. These two conclusions are in agreement with each other and show that under inert atmosphere, some groups (esters or aromatic rings) offer an efficient radiation protection at low LET but this protection is progressively lost when stopping power is increasing. Nevertheless, this is much lesser the case in the LET range of the  $\alpha$ -emitters, where the structure of the polymer remains important.

Figure 3 presents the results obtained under inert atmosphere (same data as in Figure 2) along with the hydrogen radiation chemical yields obtained for the same polymers but under oxidative atmosphere.

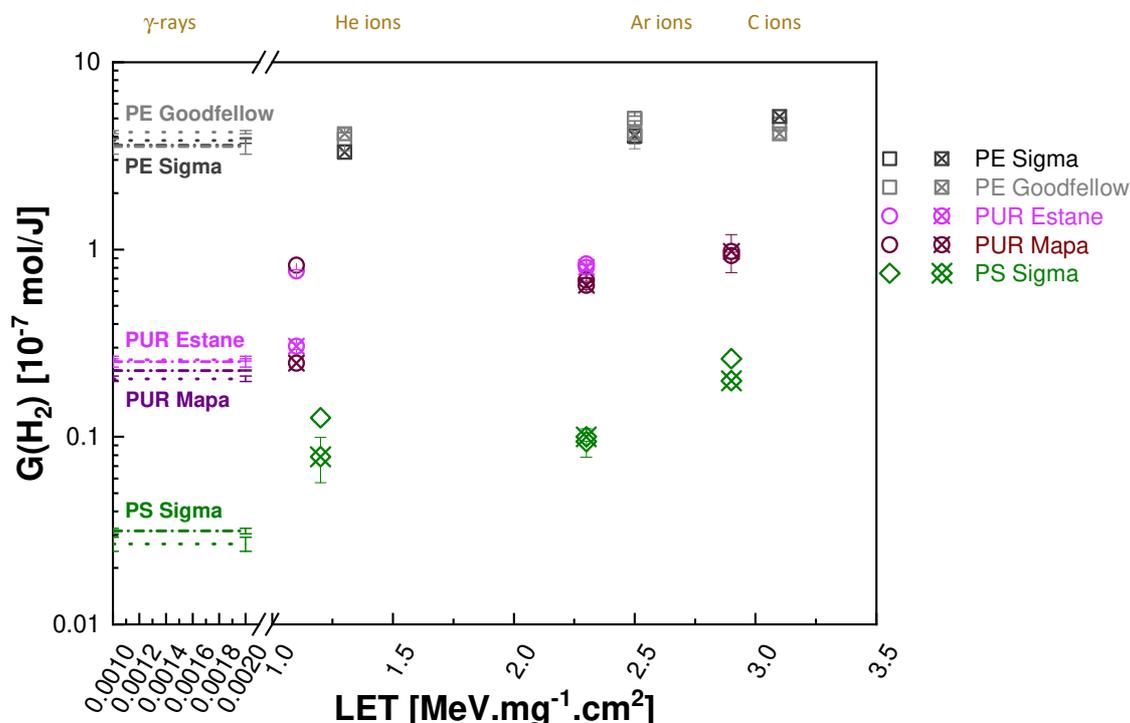


Figure 3. Hydrogen radiation chemical yields as a function of LET for polymers irradiated under inert atmosphere (dotted lines for  $\gamma$ -rays and open symbols for ion irradiations) and under oxidative atmosphere (dashed lines for  $\gamma$ -rays and crossed symbols for ion irradiations).

Figure 3 evidences that hydrogen formation is not influenced by the presence of oxygen, at least for polymers irradiated with beams of Ar  $88 \text{ MeV}\cdot\text{A}^{-1}$  and C  $5.4 \text{ MeV}\cdot\text{A}^{-1}$ . This result, already observed in the case of polyethylene [1], implies that hydrogen formation is faster than oxygen involved degradation reactions.

This conclusion has to be tempered in the case of helium irradiations for PUR and maybe for PS. Due to the low energy of the particles -  $4.2 \text{ MeV}$  - the thicknesses of the samples have to be very small, which implies a low quantity of evolved gas and hence a more pronounced uncertainty on the obtained values. Moreover, the ion current levels used are at the lowest detection limit of the accelerator as compared to those of the two other irradiation type conditions, which will also increase these uncertainties.

From an industrial point of view and in the nuclear waste safety context, it is important to choose conditions which are restrictive but not highly penalizing. In case of the choice

of the hydrogen emission radiation chemical yield, Figure 3 shows that these conditions are met in the case of irradiations carried out with C ions and Ar ions. In fact, the higher the LET, the higher the  $G(\text{H}_2)$ . As SHI irradiations present LET slightly higher than the one of  $\alpha$ -emitter, then hydrogen emission radiation chemical yields are also slightly higher than those of the  $\alpha$ -emitters. These conditions are thus representative of those encountered in the nuclear installations while remaining envelope. He ion irradiations are supposed to be the closest to the  $\alpha$ -emitters irradiations, but this study shows that with C ions and Ar ions irradiations, conditions are conservative and a larger amount of polymer can be irradiated in homogeneous conditions, resulting in more precise results. To validate the procedure of using ion irradiations to simulate  $\alpha$ -emitter under oxidized conditions, the evaluation of an oxidized gas emission is obviously mandatory. The oxygen consumption would have been of definite interest in the context of this study, but the quantity of material irradiated is too small to allow an accurate quantification under our experimental conditions - more specifically in the case of the CHIMERE set-up use. The analysis of the carbon dioxide emission has instead been chosen. Figure 4 shows the carbon dioxide radiation chemical yields as a function of the stopping power for the polymers under study. Note that the dose rate between  $\gamma$ -rays irradiations and ions irradiations is different by at least an order of magnitude, which, as indicated by Decker and Mayo [32], can induce differences in the oxidation of the polymers and thus in the  $\text{CO}_2$  emission radiation chemical yield. We believe for instance that the lower  $\text{CO}_2$  radiation chemical yields obtained from PUR and PS irradiated using He ion irradiation as compared to those obtained under  $\gamma$ -rays is due to this dose rate difference. Hence, only evolutions are here compared.

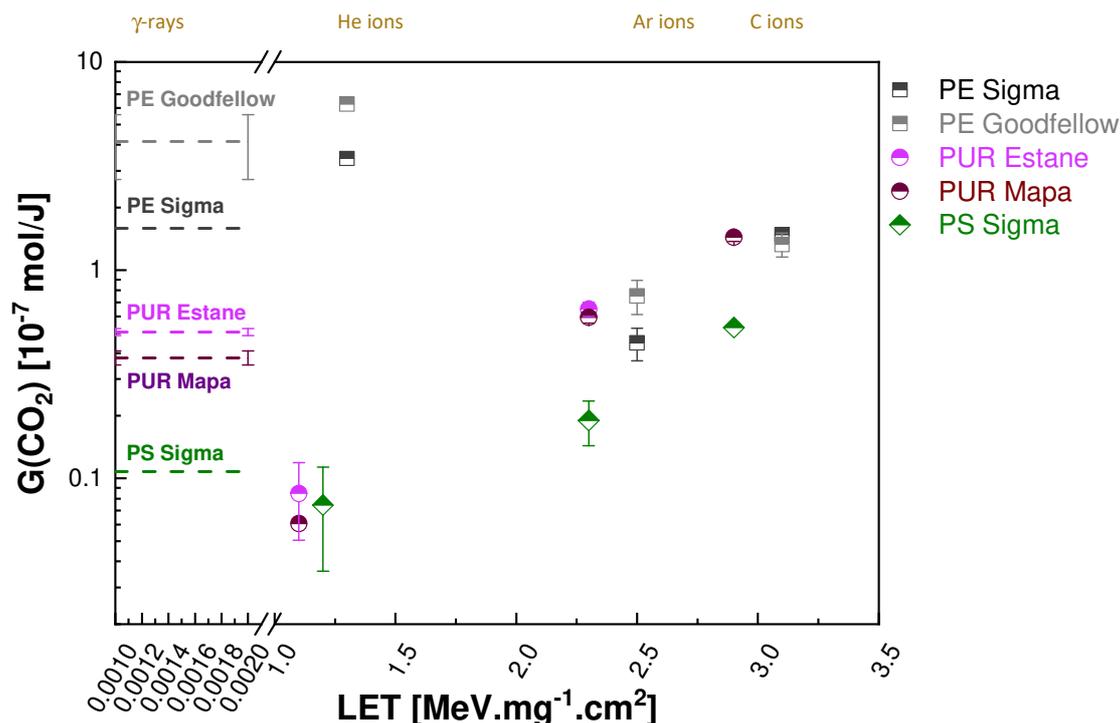


Figure 4. Radiation chemical yields of carbon dioxide release as a function of LET for polymers irradiated under oxidative atmosphere (dashed lines for  $\gamma$ -rays and symbols for ion irradiations).

Figure 4 shows that in case of polyolefins, carbon dioxide radiation chemical yield decreases when the stopping power increases. Dély, Ngonon-Ravache, Ramillon and Balanzat [33] have shown on an EPDM that oxidation is effective at high stopping power, but that the rate of oxygen uptake decreases when LET increases. Authors have attributed this phenomenon to the radicals formed in the ion track which will tend to recombine with each other rather than react with the embedded oxygen. It is likely that the decrease in  $\text{CO}_2$  formation when stopping power increases, observed in Figure 4 for polyethylene, is linked to this so-called ion track effect.

Polystyrene and both polyurethanes (Estane and Mapa) show an increase in radiation chemical yields of carbon dioxide release with the stopping power. In this case, it is believed that two phenomena are in competition. The first one is the ion track effect, which leads to a global  $\text{CO}_2$  decrease when LET increases. The second phenomenon is global increase of  $\text{CO}_2$  release due the loss of radiation protection effect when the stopping power increases. In fact, PUR polymers present ester groups in their soft segments and aromatic rings in their hard segments; PS presents aromatic rings as

pendant groups. These two kinds of groups are very well known to be effective energy scavengers [1, 3, 34, 35] and they will lower the radiation induced polymers degradation. Nevertheless, their protective efficiency decreases when stopping power increases [3]: the formation yield of radicals will thus increase with LET, leading at equivalent stopping power to a more important concentration of radicals, themselves reacting with oxygen. Hence, when LET increases, the evolution of the radiation chemical yield of carbon dioxide observed for PUR and PS in Figure 4 tends to show that the loss of protective efficiency is more important than the decrease in reactivity of the radicals with oxygen (due to their reaction directly in the ion track), inducing an overall increase in carbon dioxide emission.

As already introduced in the hydrogen result analysis section, from an industrial application point of view and in the nuclear waste safety context, the objective is to choose conditions which are restrictive but not highly penalizing. In such conditions and because of the different evolutions of the carbon dioxide emission radiation chemical yields as a function of LET, the solution is here to choose results from LET as close as possible to the  $\alpha$ -emitters.

Finally, these results are very interesting as far as, to the best of our knowledge, it is the first time that CO<sub>2</sub> radiation chemical yields obtained from polymers irradiated under oxidized atmosphere and at LET equivalent to the one of  $\alpha$ -emitters are presented. This article presents first reliable results that can be used in nuclear waste safety management.

#### **4. Conclusion**

The object of this article was to give a first insight into the effect of oxygen in the atmosphere when polymers are irradiated at high stopping power. The first objective was to validate the protocols and set-ups that were developed specifically for this kind of study, *i.e.* to evaluate the possibility to use ion beams instead of the  $\alpha$ -emitters. We have evidenced under helium atmosphere that our data on hydrogen release fit very well with literature.

For all investigated polymers, results on hydrogen radiation chemical yields tend to show little effect of the irradiation atmosphere. Only small effects are obtained with high

energy Ar and C ion irradiations. The slightly more important effect in case of He ion irradiations is probably due to experimental uncertainties accumulation; we do not believe that there is a special effect concerning He ion irradiation.

Complementary to the hydrogen, carbon dioxide radiation chemical yields have also been analysed to understand the impact of the presence of oxygen during the irradiation at high LET. It appears that as the stopping power increases, the quantity of carbon dioxide decreases in the case of polyethylene and increases in the case of both PUR and PS. We believe that the CO<sub>2</sub> radiation chemical yield decrease in case of polyolefins is due to a P°/P° intra-track recombination increase with LET, the so-called ion track effect. In case of PUR and of PS, this mechanism is competing with a loss of radiation protection effect when the stopping power increases. As G(CO<sub>2</sub>) increases with LET for these two polymers, it seems that the loss of protective efficiency is more important than the decrease in reactivity of the radicals with oxygen due to their reaction directly in the ion track.

The hypotheses proposed in this article have to be confirmed with experiments using ions with higher LET, and with other kinds of polymers. Moreover, to complete and ascertain the evolution of the carbon dioxide radiation chemical yields as a function of LET, other experiments with LET comprised between 1 and 3 MeV.mg<sup>-1</sup>.cm<sup>2</sup> should be performed. Finally, it has been concluded that to fulfil nuclear safety requirements - restrictive but not highly penalizing conditions - the use of ions of slightly higher stopping power than α-emitters have to be chosen in case of hydrogen emission simulation, whereas ions with LET as close as possible to the α-emitters have to be chosen for examining the effect of oxygen in the surrounding atmosphere.

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