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Chemical modifications induced by ionizing radiations on polymers: the specificity of Swift Heavy Ions (SHI)

M. Ferry¹, S. Esnouf¹, Y. Ngono-Ravache², E. Balanzat²

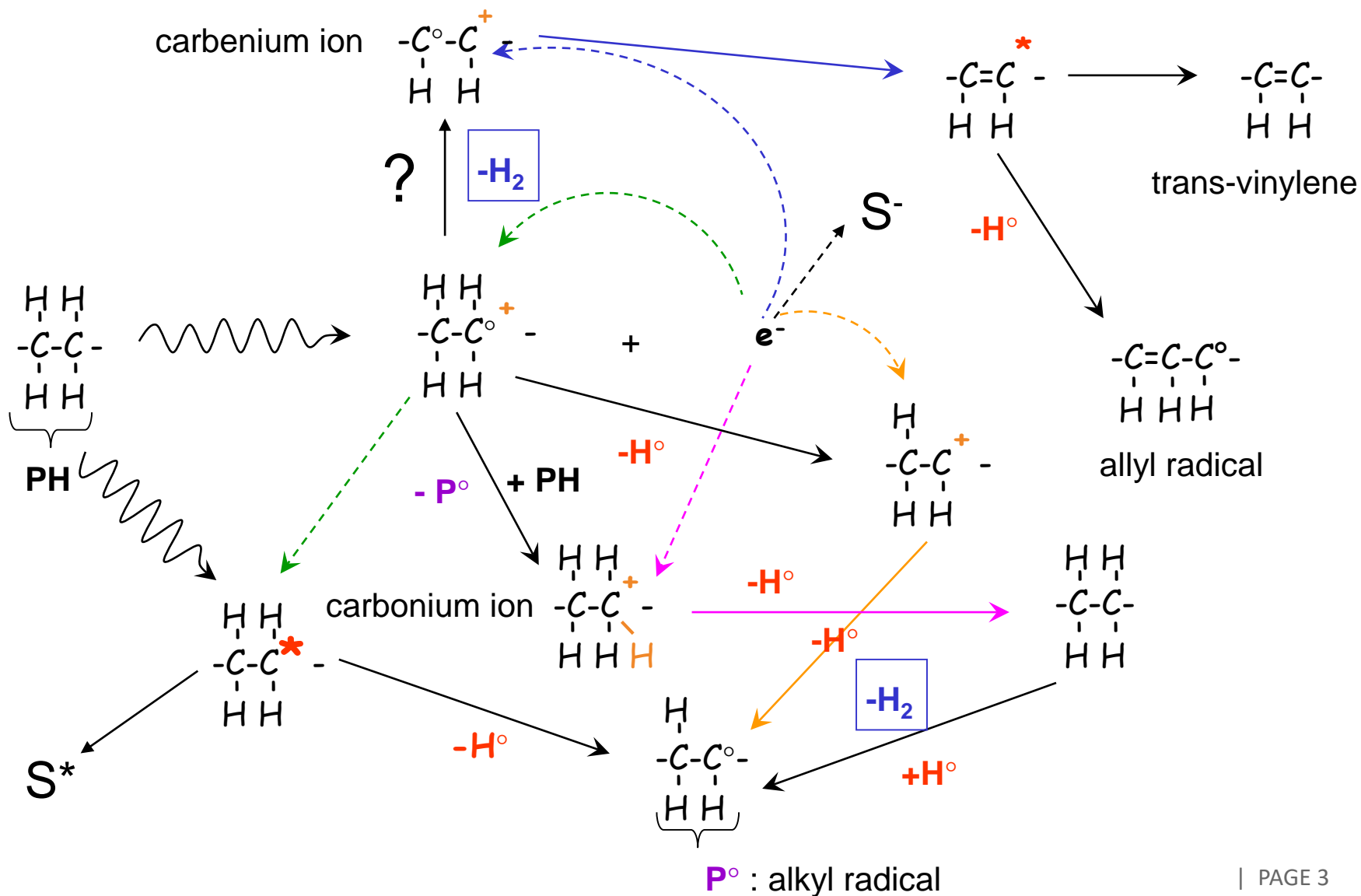
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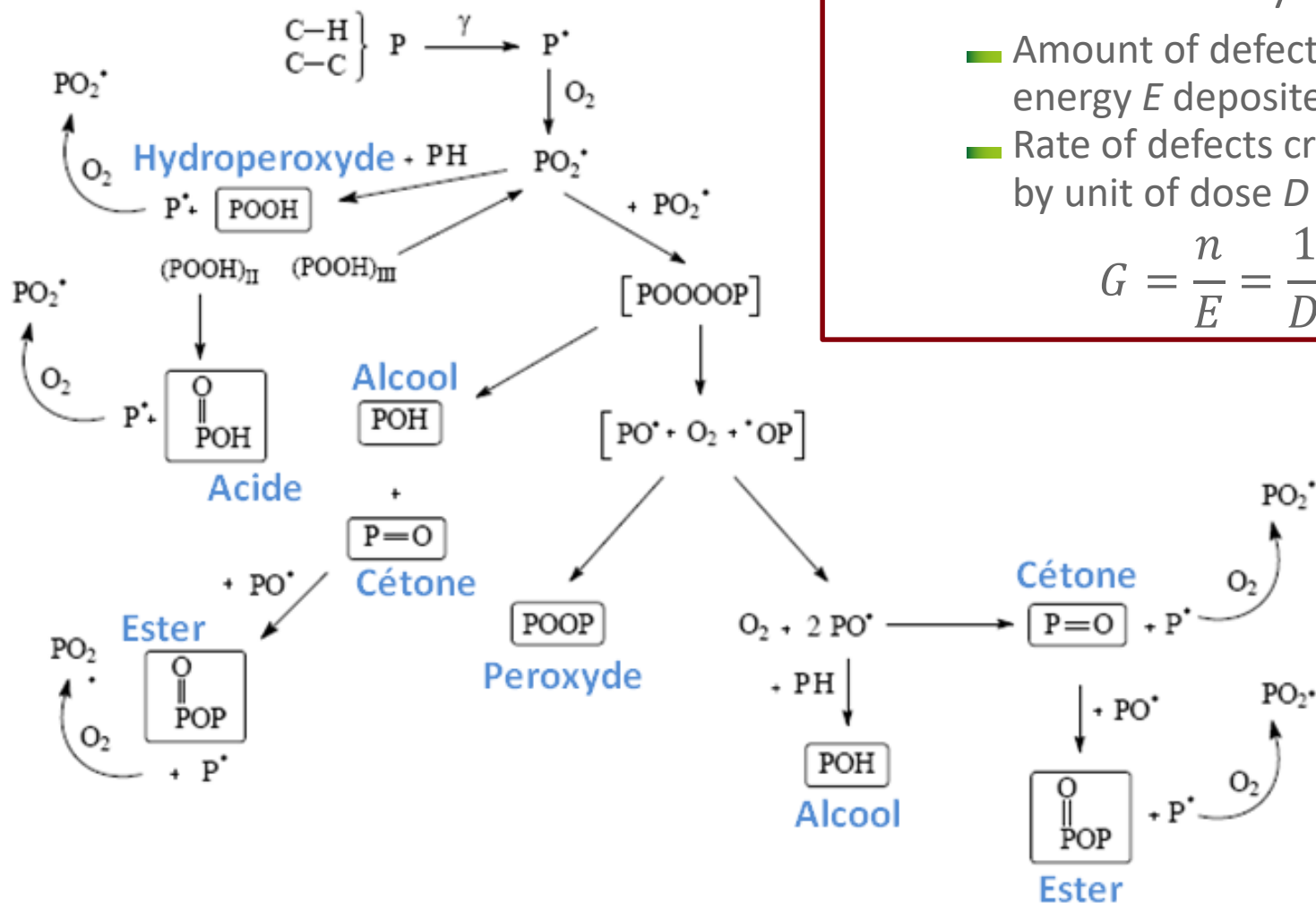
Ionizing radiations effects on polymers

General items

Radiation - organic matter interaction: primary processes (PE example)



Radiation - organic matter interaction: secondary processes in presence of oxygen



■ Radiation chemical yield G (10^{-7} mol/J) :

- Amount of defects n created by unit of energy E deposited into the material
- Rate of defects creation dn/dt created by unit of dose D deposited

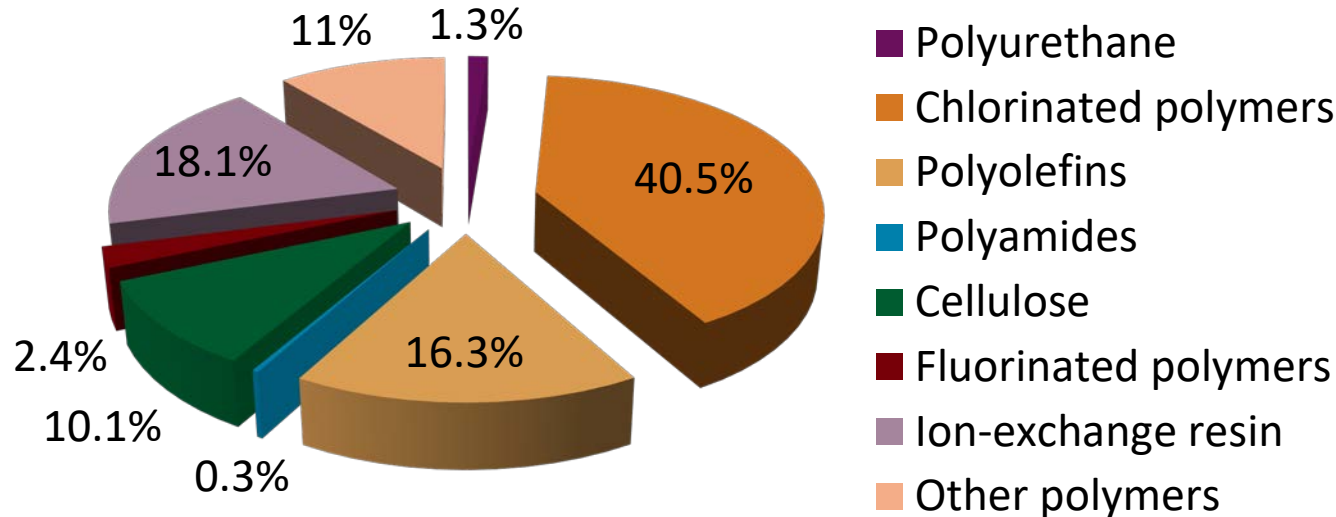
$$G = \frac{n}{E} = \frac{1}{D} \cdot \frac{dn}{dt}$$

- Molecular changes observed in a polymer due to ionizing rays
 - Emission of volatile compounds (H_2 , CO, CO_2 , CH_4 ...),
 - Creation of unsaturations and other molecular bonds and of low molecular weight molecules (alcohols, carboxylic acids...),
 - Crosslinking and chain scissions.

- All these molecular changes are dependent of the structure of the polymer and of the irradiation conditions
 - Polymer structure parameters
 - Repetition unit (side-chain groups)
 - Crystallinity
 - ...
 - Irradiation conditions
 - Dose and dose rate
 - Surrounding atmosphere (inert or oxidative)
 - Irradiation temperature
 - **Linear Energy Transfer (γ -rays, electrons vs SHI)**
 - ...

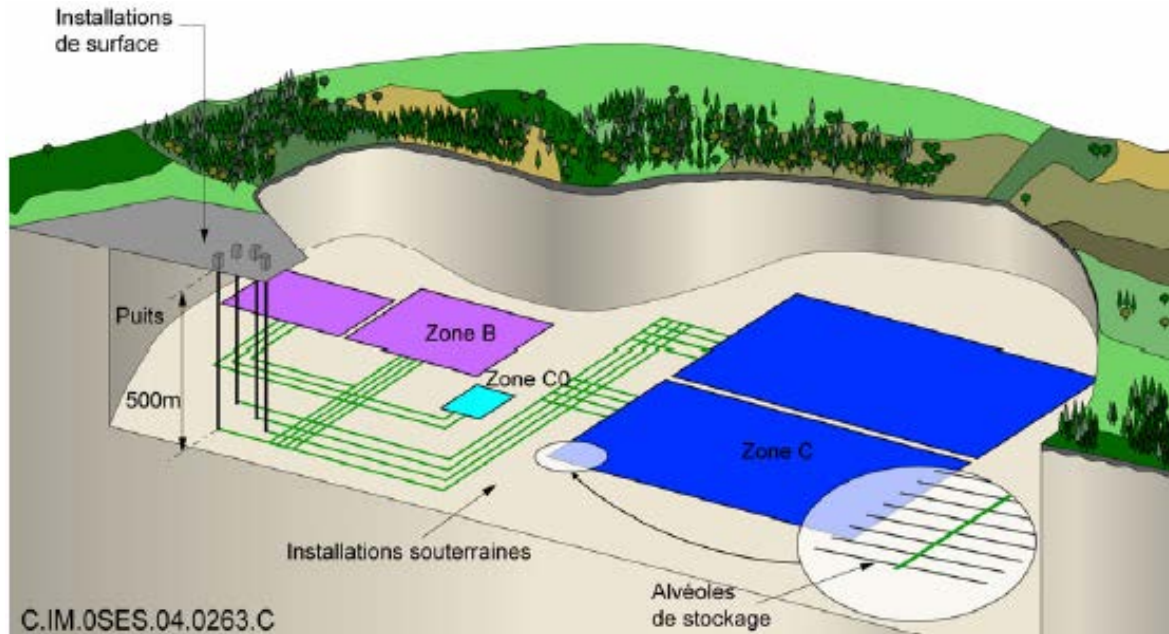
What about the SHI in the nuclear industry context ?

Polymers widely used in nuclear industry



- Intermediate Level Long Lived Waste packages (IL-LLW) : various organic materials, including polymers, in presence of radionuclides
 - Dose received ≈ 10 MGy or even higher when in contact with PuO_2 pellet
- Objective: find a solution for the packages disposal
 - France: projected of a deep underground geological repository

Deep underground geological repository



■ 500-meter deep and around 300 years of use to fill the cells before the supposed closing of the repository

■ Different phases risks

■ During the opened filling period

- Risks issued from gas emission (inflammation, corrosion, carbonation...)

■ After closure

- Irradiated polymers leaching and radionuclides (RN) complexation risk

Organic material and radionuclides (RN) in the ILLW packages : α and β/γ emitters

Understanding of the becoming of organic materials in the nuclear waste containers over several hundreds of years (\approx tens / hundreds of MGy)

Emitters simulation

- β/γ emitters : γ irradiations using ^{60}Co and ^{137}Cs sources (0.3 to 0.7 kGy.h^{-1})

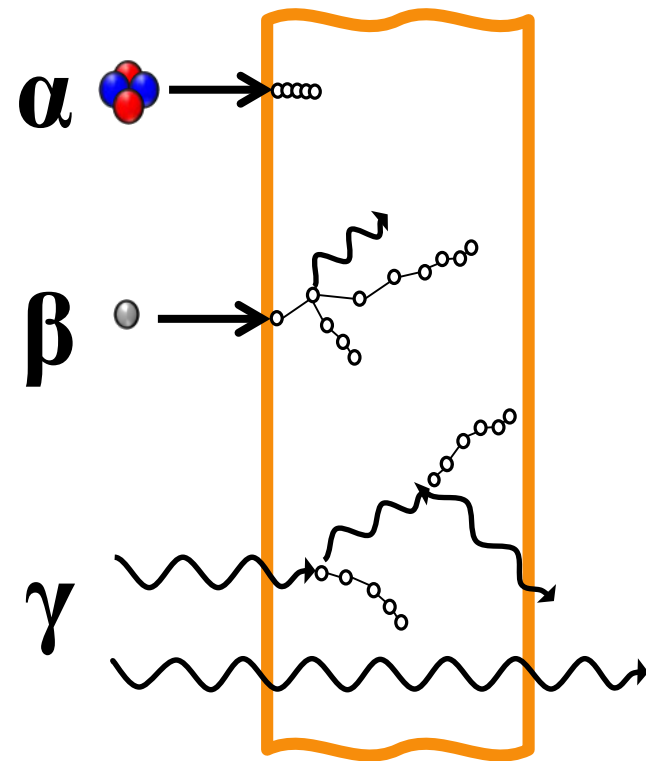
- α emitters :

- Irradiations of simulation, using C and Ar ions ($\approx 500 \text{ kGy.h}^{-1}$, at GANIL, Caen, France)

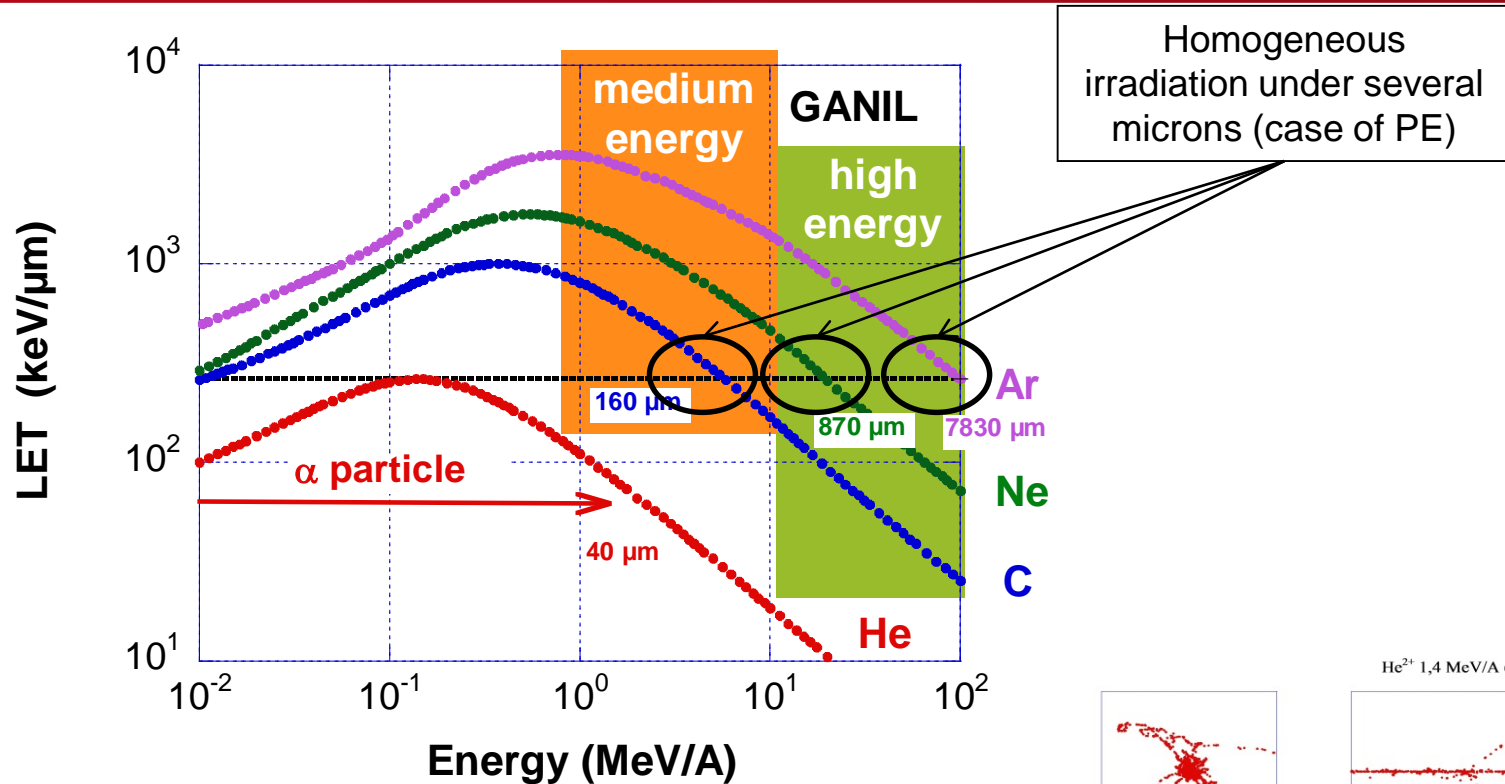
Estimation of the H_2 (and other gases) evolution as a function of the

- Irradiation type

- Dose



Ion beams to simulate α irradiations ?

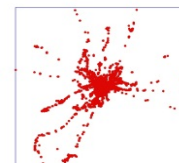
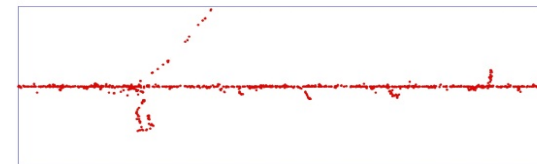


Why SHI instead of α ?

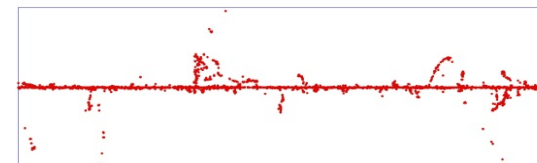
- LET equivalent to radionuclides-emitted α
- Higher penetration range



He²⁺ 1,4 MeV/A (5,6 MeV)



Ar¹⁸⁺ 95 MeV/A (3,4 GeV)



Ionizing radiations effects on polymers

The Swift Heavy Ions (SHI) specificity

What about the SHI specificity ?

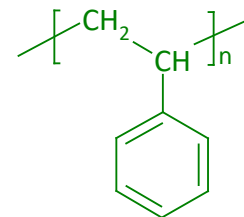
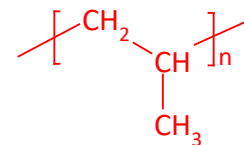
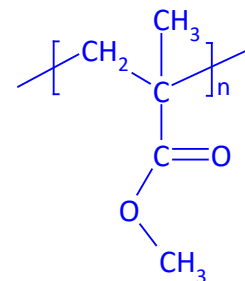
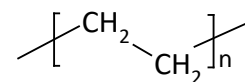
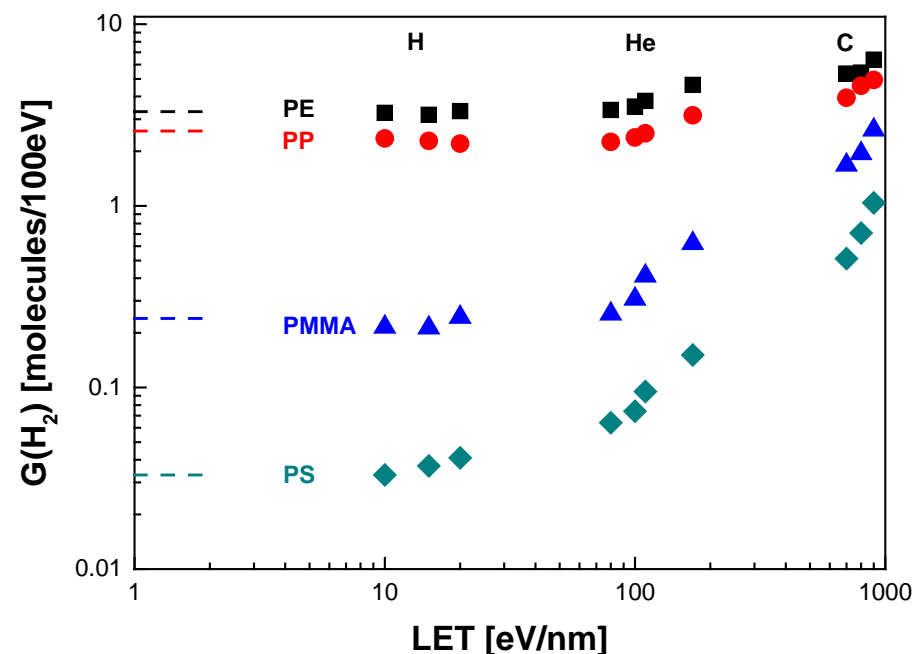
Hydrogen emission

H₂ emission as a function of the LET of the particles and of the polymer structure

- Almost independent of the LET in aliphatic polymers
- LET threshold observed in case of polystyrene
 - More radiation resistant, under low-ionizing rays, than polyethylene
 - Radiation-resistance lost above the LET threshold, due to ring opening

At the highest LET, H₂ emission from PE and PS equivalent

- Radiation-resistance conferred by the aromatic ring lost

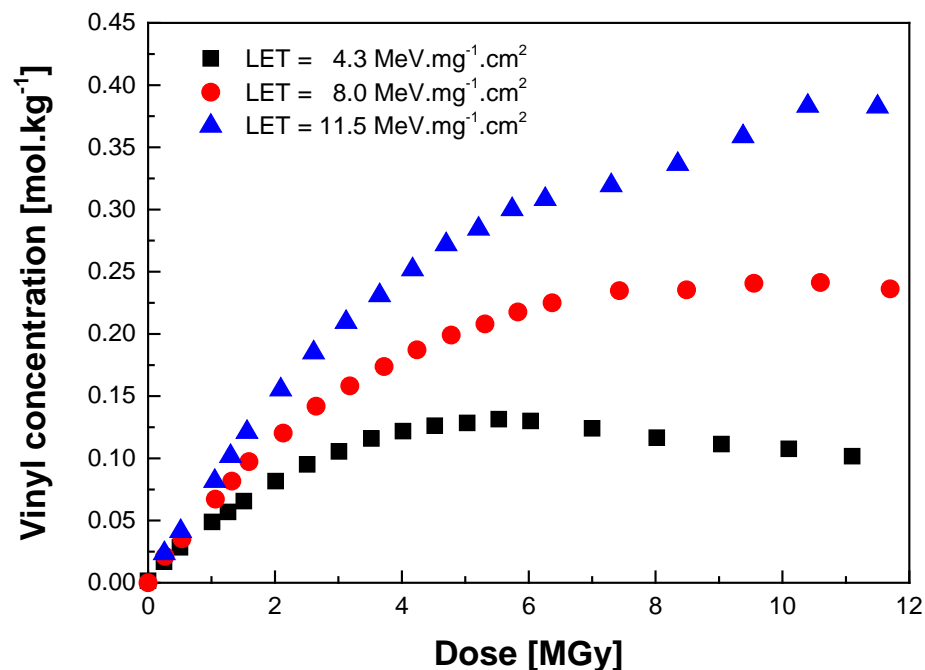
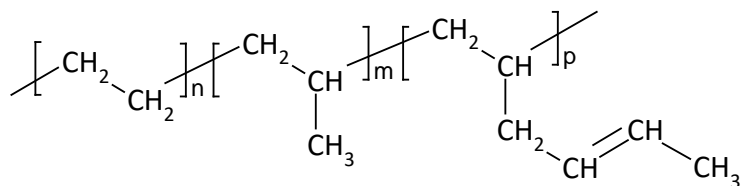


What about the SHI specificity ?

Unsaturated bonds formation

■ Unsaturated bonds creation

- Almost no effect on *trans*-vinylene, vinylidene and *trans-trans*-diene formation from polyethylene
- Specificity of the vinyl bonds
 - Signature of the main chain scission
 - => necessity of high ionizations/excitations density
 - Vinyl concentration increases from low-ionizing radiation to SHI and with LET



What about the SHI specificity ?

New bonds specific to SHI formation

■ New bonds specific to SHI => LET threshold

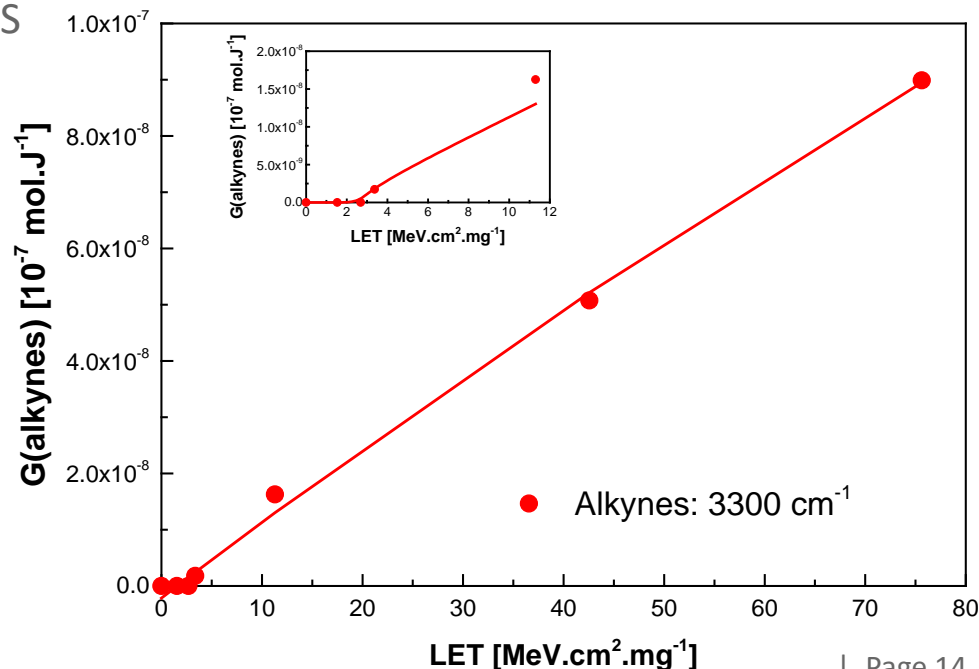
- Triple bonds: alkynes, cyanates...
- Cumulated double bonds: allenes, isocyanates...

■ LET threshold value depends on the polymer and on the new bond

- Threshold in case of alkyne creation
 - LET > 6.6 MeV·mg⁻¹·cm² for PE, PP, PB
 - LET ≈ 2/3 MeV·mg⁻¹·cm² for PS

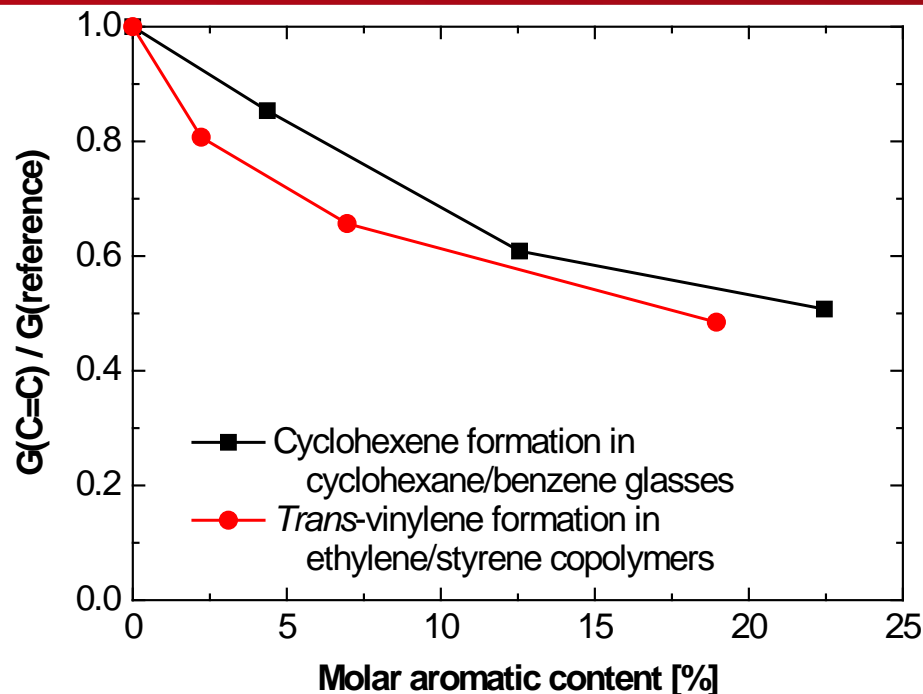
■ If LET < LET_{threshold}

- New bond created above a dose threshold



Energy transfers towards defects evidences

Small molecules as models



Ferry et al., J. Phys. Chem. B 117 (2013), 14497

■ Double bonds formation in cyclohexane/benzene organic glasses and in ethylene/styrene copolymers irradiated using ion beam at 11 K under vacuum

■ Radiation chemical yields equivalent in both systems

- Intrachain and/or interchain (intermolecular) transfers efficient at low temperature
- Transfers nature equally effective

■ Cyclohexane/benzene mixtures never studied at RT using ions irradiation under inert atmosphere

- H₂, cyclohexene quantification but also benzene destruction
- Comparison with results obtained at 11 K

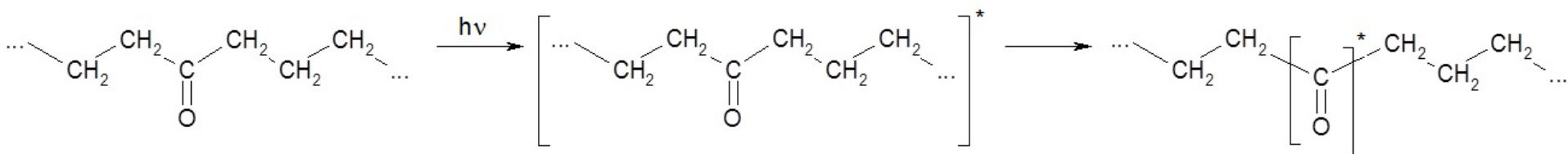
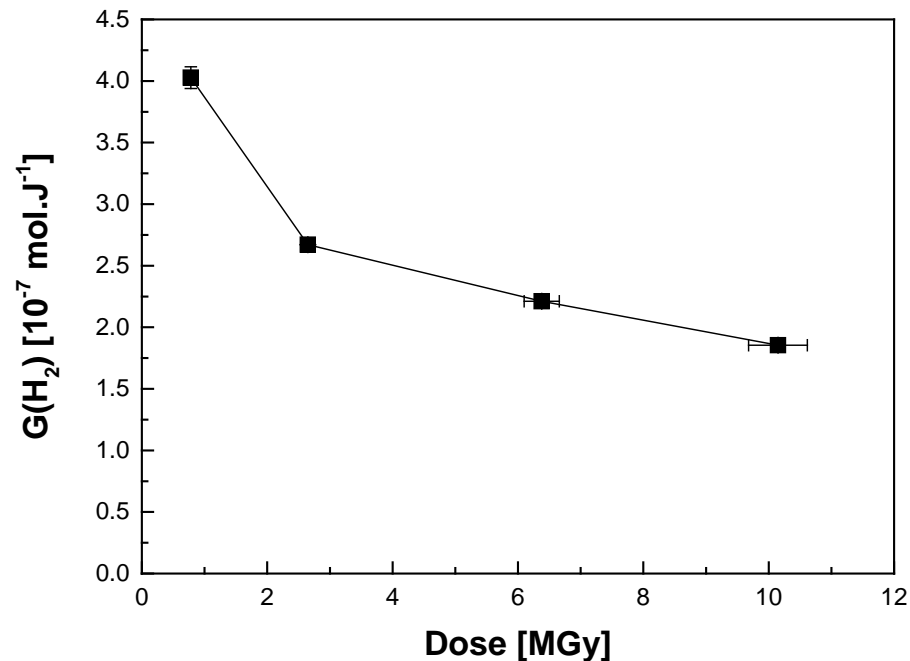
Energy transfers towards defects evidences

Hydrogen emission as a function of dose

Irradiation under oxidative atmosphere

H₂ instantaneous emission rate \searrow when dose \nearrow

- Previously observed by Seguchi
 - Under vacuum and γ -rays up to 2 MGy
 - Assigned to energy transfers towards radiation-induced C=C double bonds
- In this work, first evidence of radiation protection
 - Under oxidative atmosphere and ion beam up to doses as high as 10 MGy
 - Assigned to energy transfers towards oxidized defects



Energy transfers towards defects evidences

Hydrogen emission as a function of PE

Irradiation under oxidative atmosphere

Study of several polyethylenes (PE) with different defects

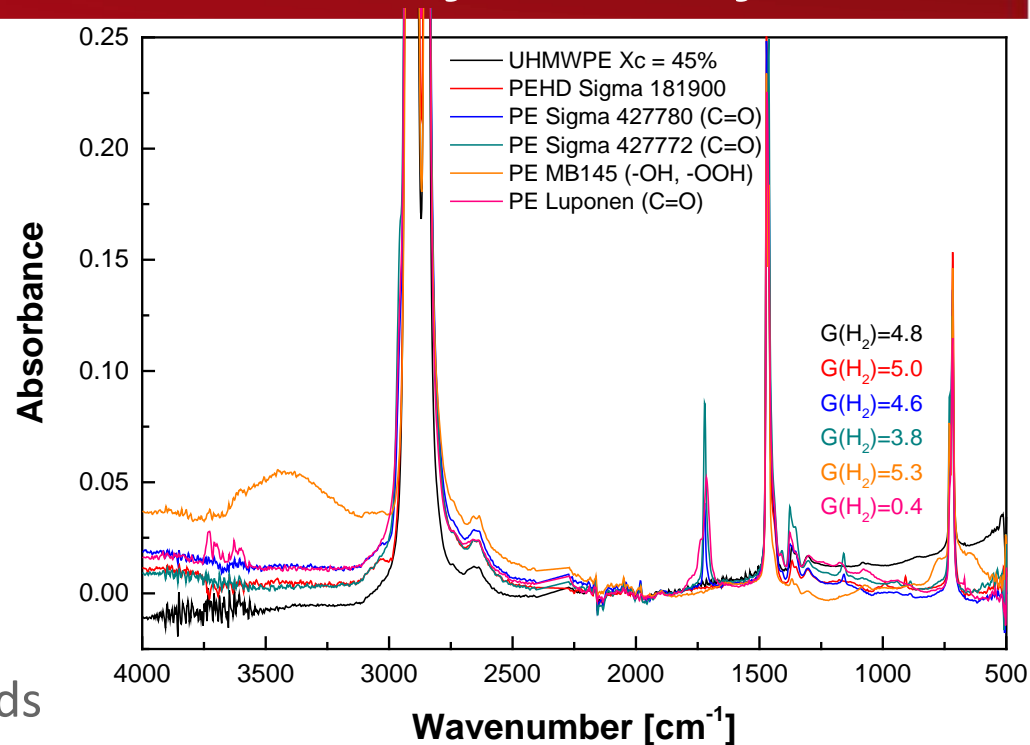
Evolution of $G(H_2)$ as a function of the material irradiated

$G(H_2) \searrow$ with the ketones bonds content

- Ketones act as energy and/or radicals scavenger
- Already observed by Slivinskas & Guillet under γ -rays

No effect of $-OH/-OOH$ bonds

- Simple bonds less effective than double bonds



Conclusion

- In the deep underground repository context
 - Protocol developed to quantify gases even at high doses
 - Use of SHI to simulate irradiations due to α emitters
 - Allows the modeling of the gases evolved from real ILLW packages, even after thousands of years

- From a fundamental point of view
 - Dose effect study
 - Energy and/or radicals transfers evaluation
 - Effect of oxidation under irradiation
 - On the gaseous radiation chemical yields
 - On the in-film defects

Better understanding of the irradiation effects, using SHI, on polymeric materials

**Thank you for your
attention**