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

M. Ferry, S. Esnouf, Y. Ngono, E. Balanzat

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

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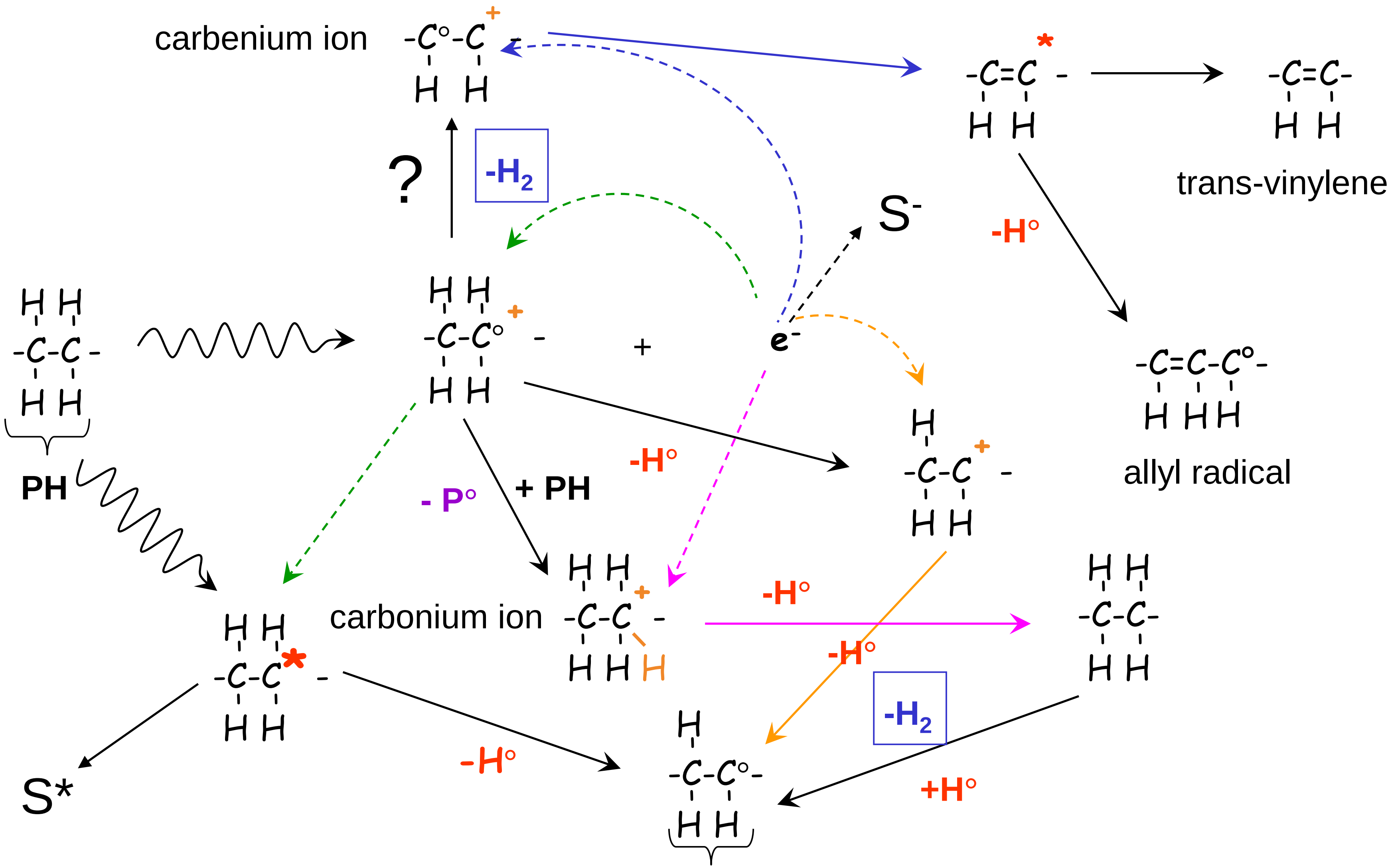
Ionizing radiations effects on polymers

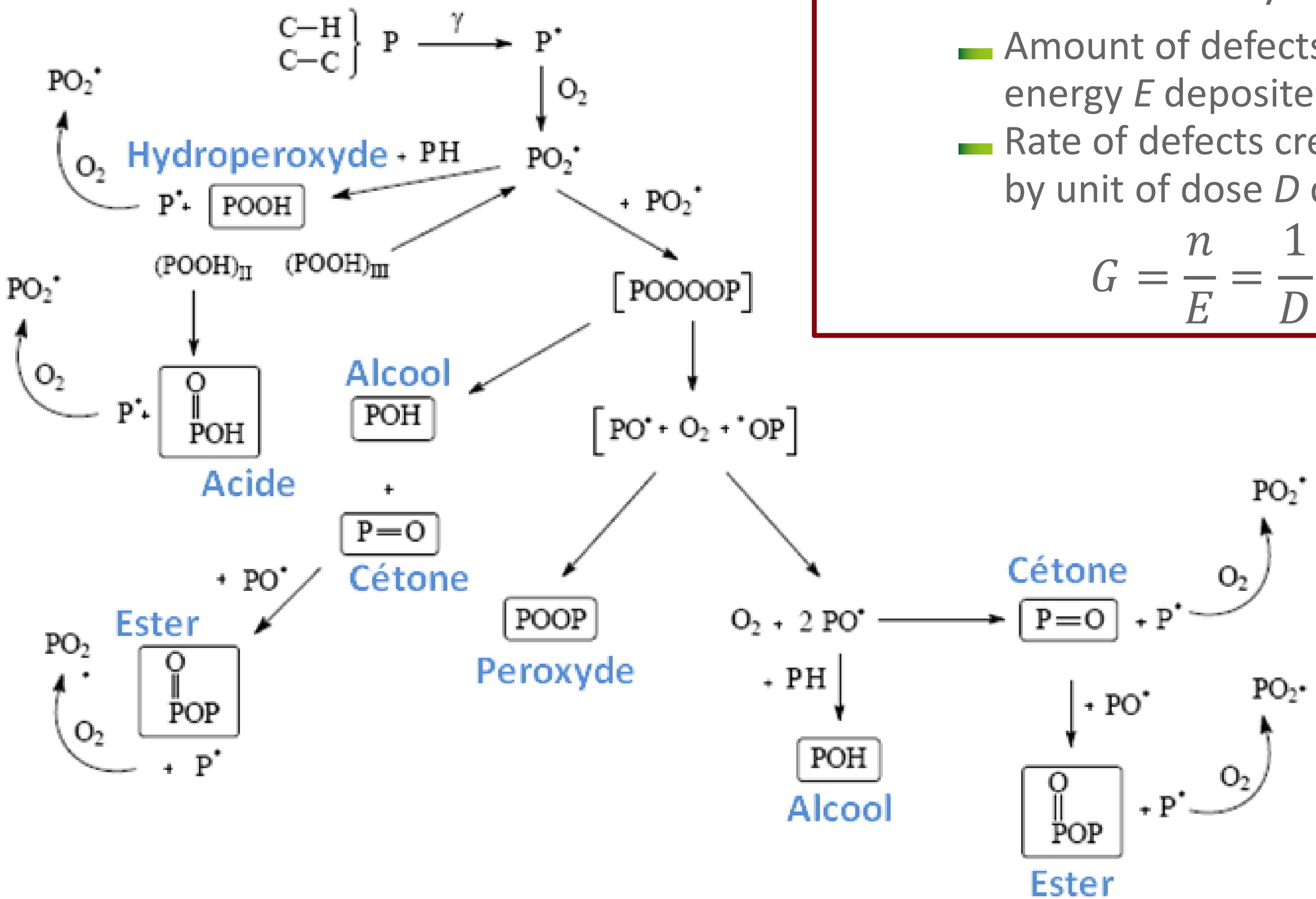
General items

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



P° : alkyl radical

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

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

Rivation, Cambon & Gardette, Nucl. Instrum. Methods Phys. Res., Sect. B 227 (2005), 357

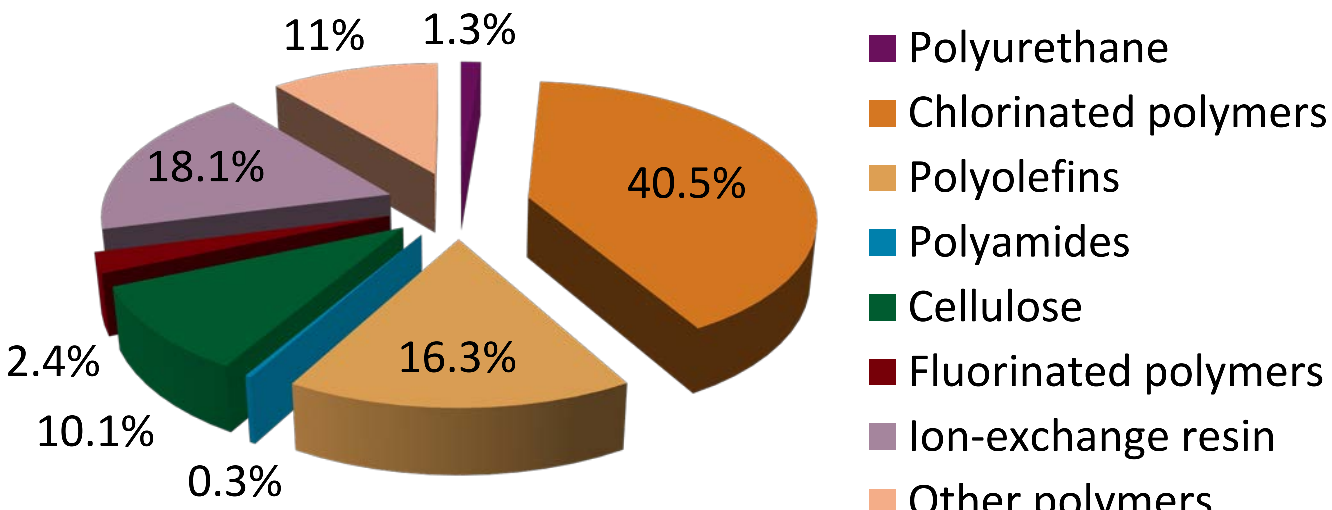
Induced modifications in polymers

- 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)**
    - …

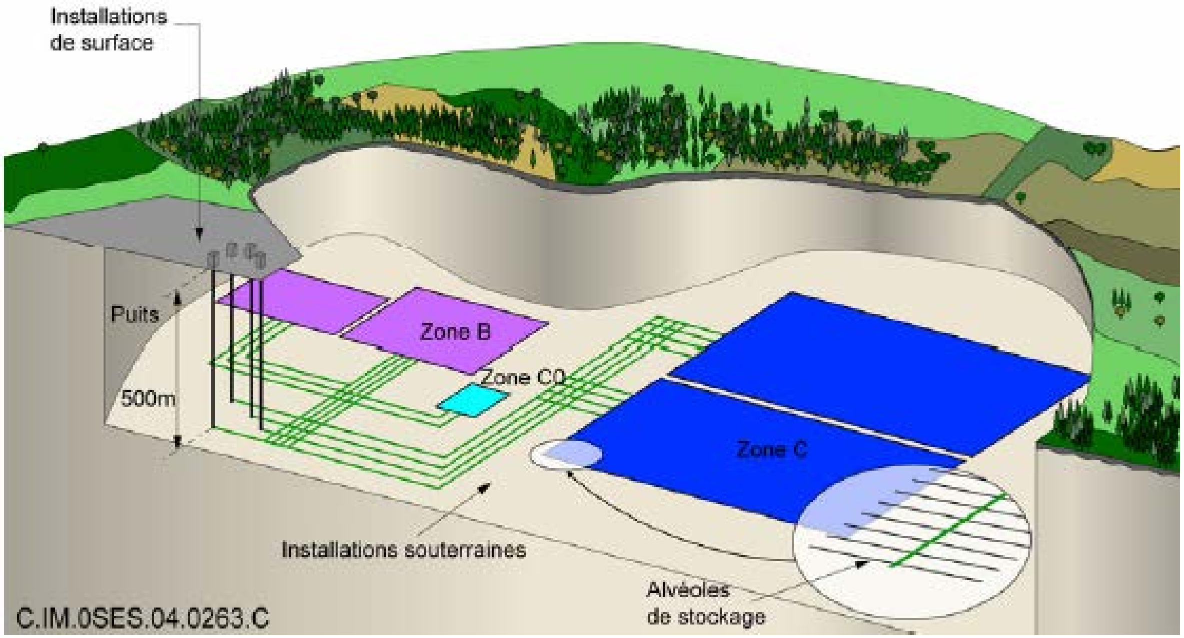
What about the SHI in the nuclear industry context ?

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

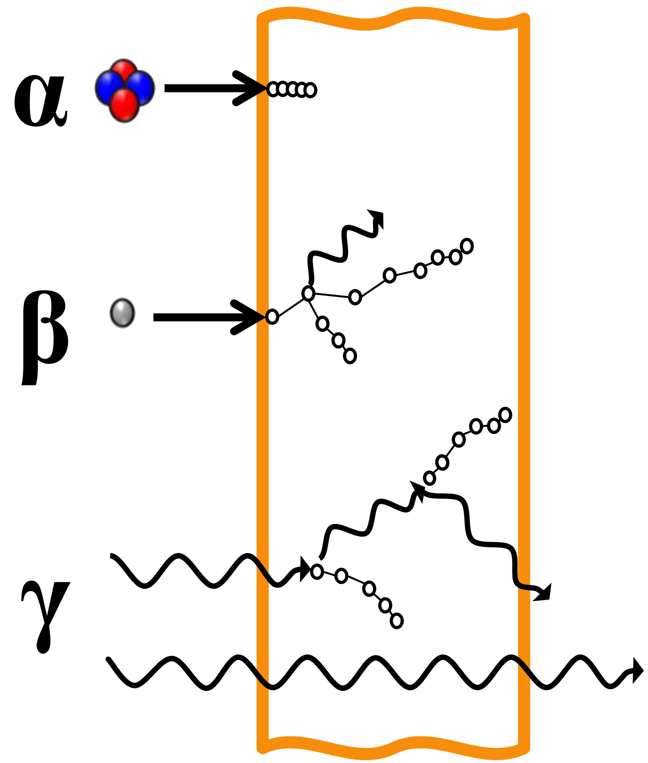


- 500-meter deep and around 300 years of use to fill the cells before the supposed closing of the repository

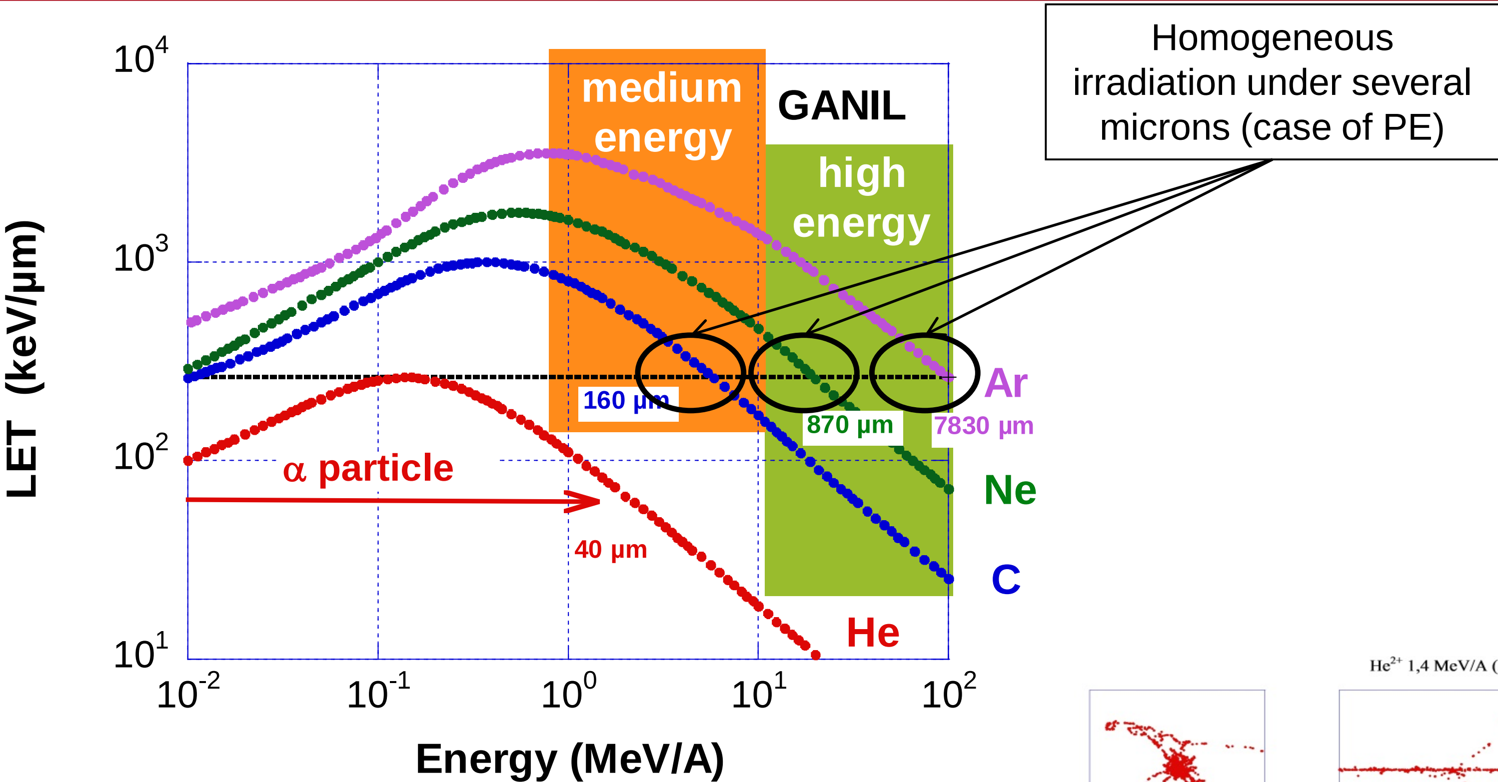
- Different phases risks
  - During the opened filling period
    - Risks issued from gas emission (inflammation, corrosion, carbonation…)
  - After closure
    - Irradiated polymers leaching and radionuclides (RN) complexation risk

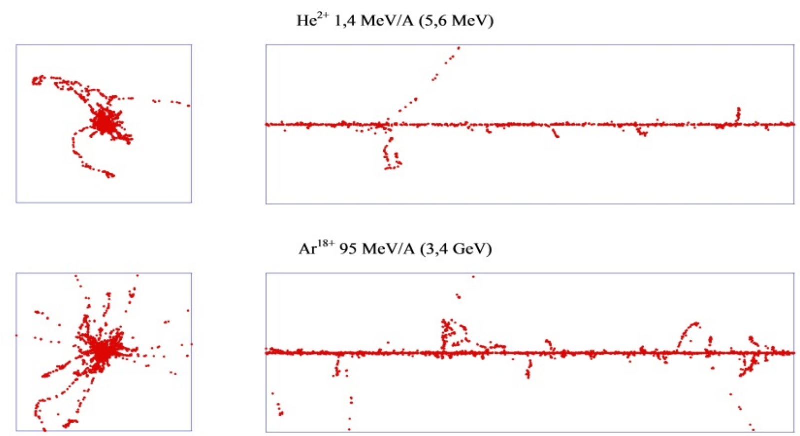
Nuclear waste containers

- 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 (≈ 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 (≈ 500 $kGy.h^{-1}$, 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

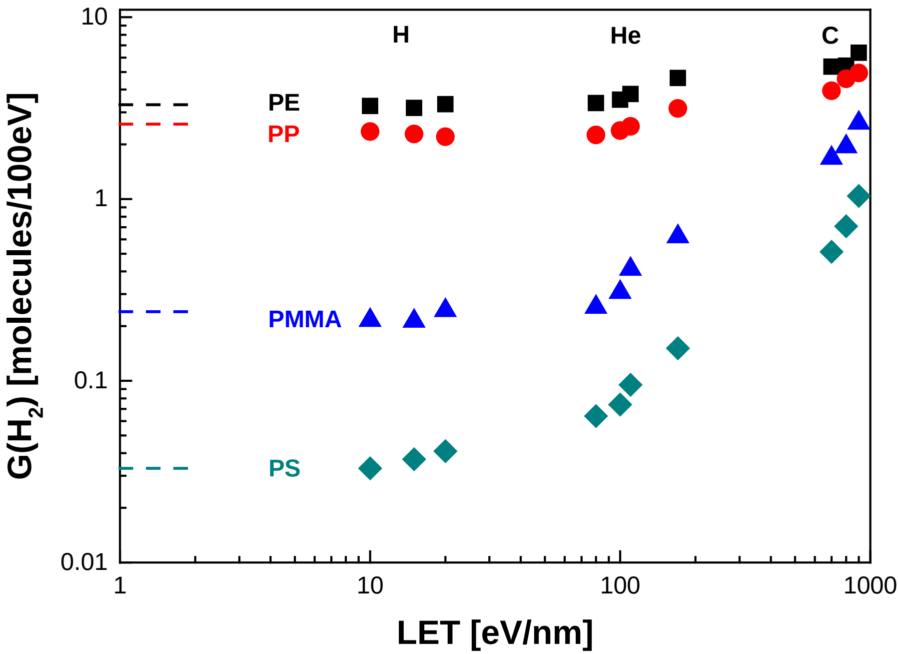
Gervais & Bouffard, Nucl. Instrum. Methods Phys. Res., Sect. B 88 (1994), 355

Ionizing radiations effects on polymers

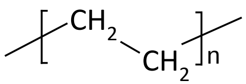
The Swift Heavy Ions (SHI) specificity

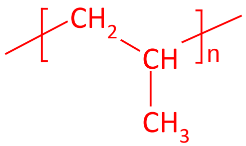
What about the SHI specificity ?
Hydrogen emission

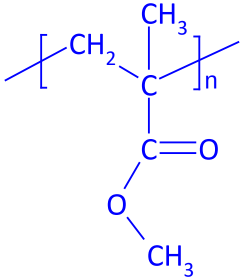
- H_2 emission as a function of the LET of the particles and of the polymer structure
  - Almost independent of the LET in aliphatic polymers
  - LET threshold observed in case of polystyrene
    - More radiation resistant, under low-ionizing rays, than polyethylene
    - Radiation-resistance lost above the LET threshold, due to ring opening

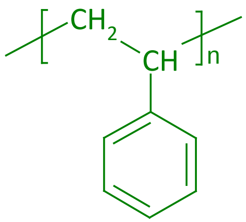


- At the highest LET, H_2 emission from PE and PS equivalent
  - Radiation-resistance conferred by the aromatic ring lost





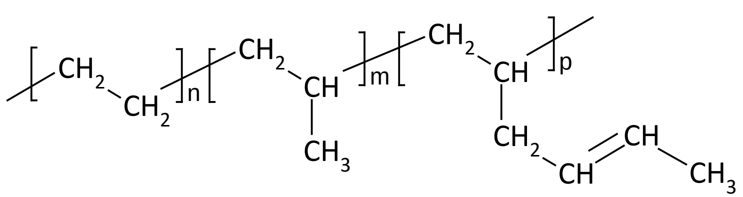


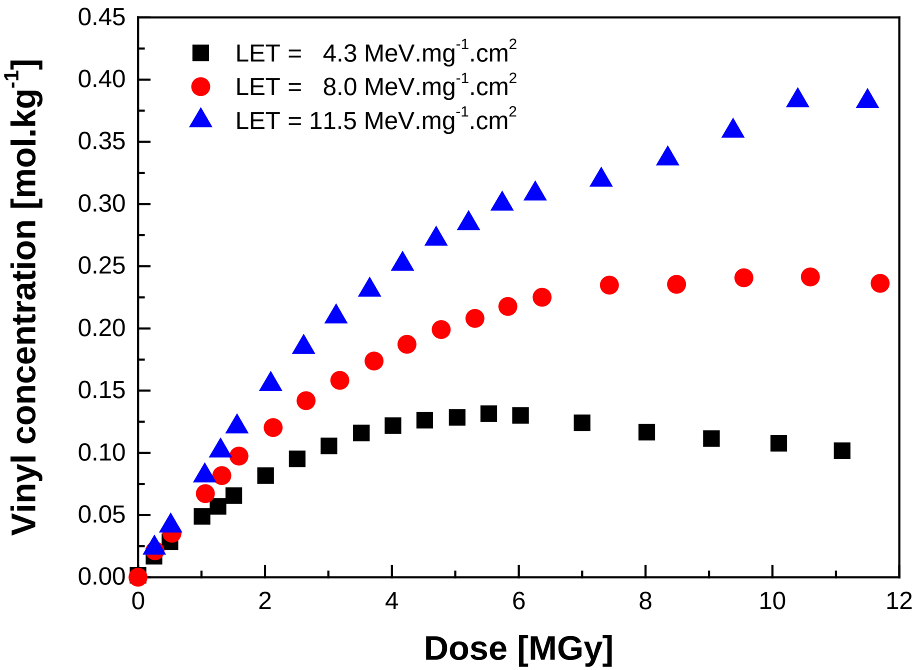


Chang & LaVerne, J. Polym. Sci.: Part A: Polym. Chem. 38 (2000),1656

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





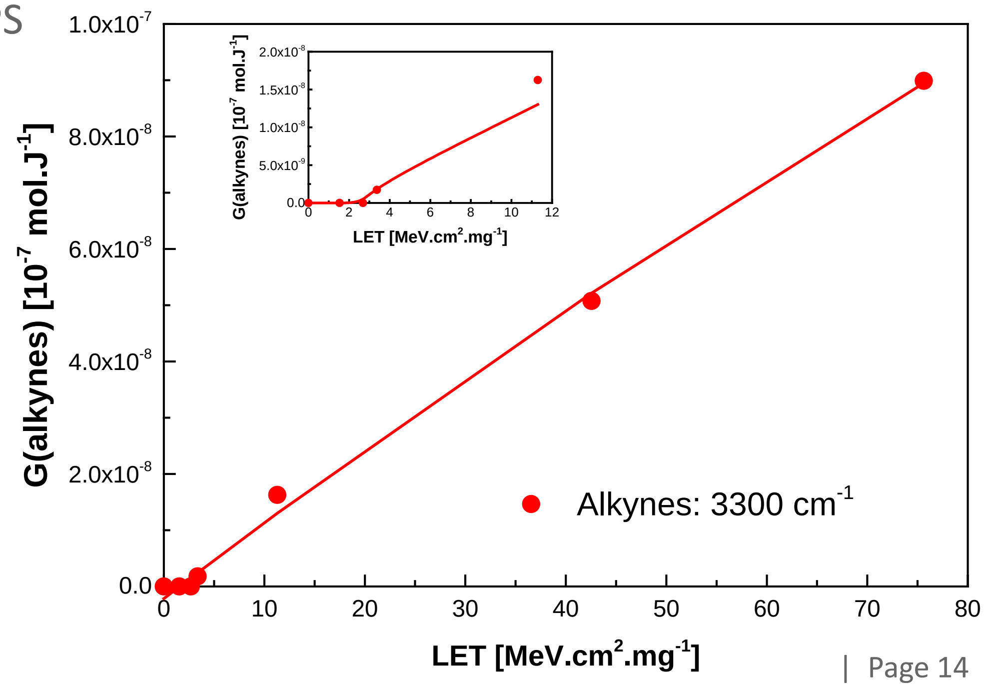
Ngono-Ravache et al., Polym. Deg. Stab. 111 (2015), 89

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…

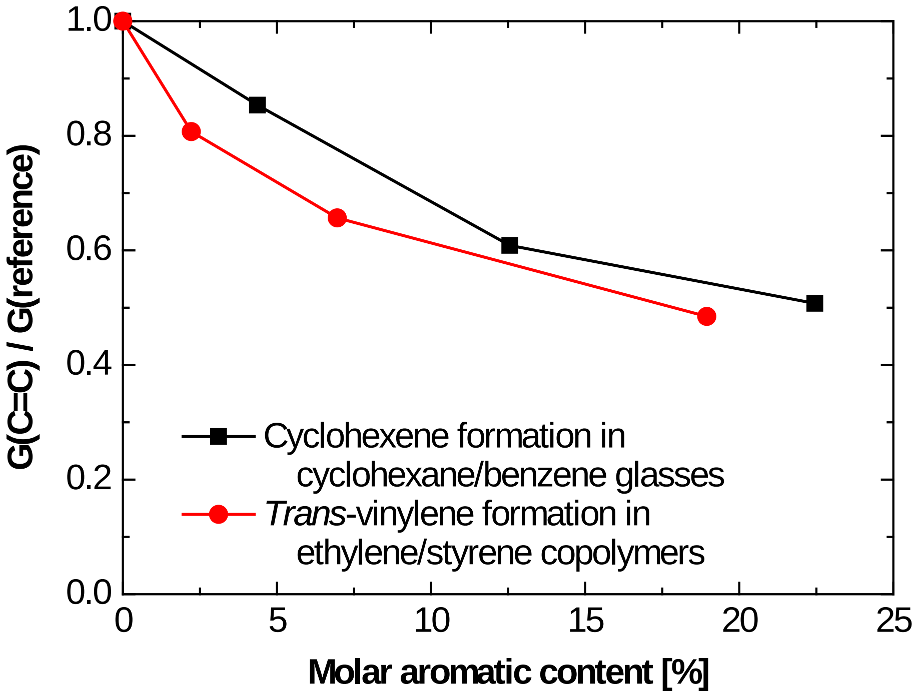
- LET threshold value depends on the polymer and on the new bond
  - Threshold in case of alkyne creation
    - LET > 6.6 $MeV \cdot mg^{-1} \cdot cm^2$ for PE, PP, PB
    - LET ≈ 2/3 $MeV \cdot mg^{-1} \cdot cm^2$ for PS

- If $LET < LET_{threshold}$
  - New bond created above a dose threshold



Ferry et al, J. Phys. Chem. B 112 (2008), 10879

Energy transfers towards defects evidences
Small molecules as models

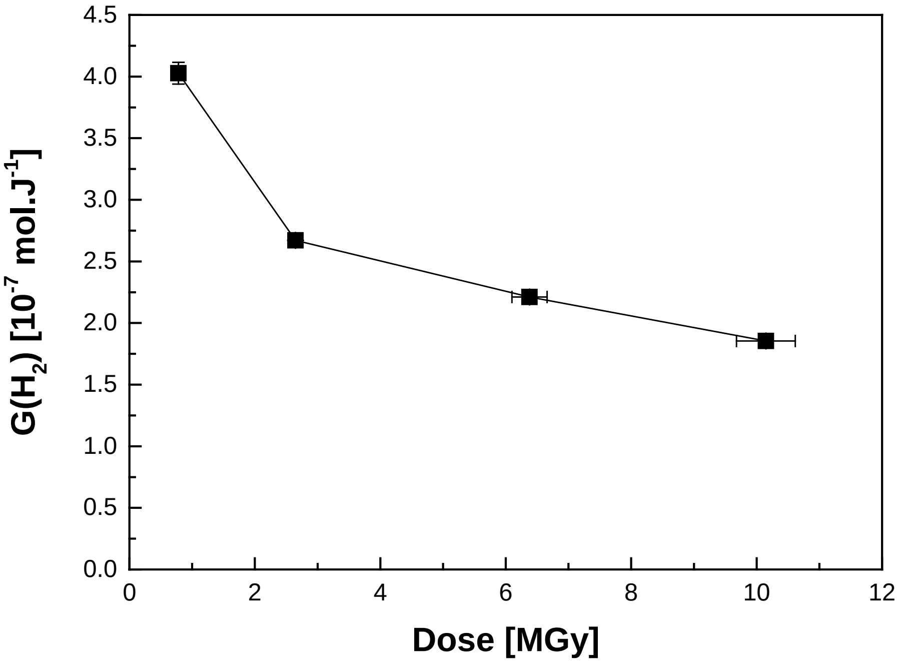


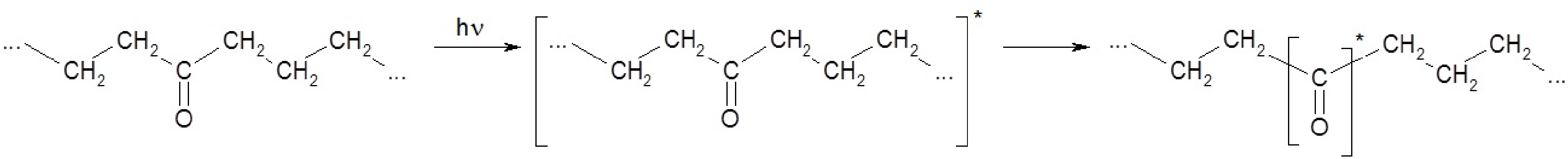
Ferry et al., J. Phys. Chem. B 117 (2013), 14497

- 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
  - H_2, cyclohexene formation quantification but also benzene destruction
    - Comparison with results obtained at 11 K

Energy transfers towards defects evidences
Hydrogen emission as a function of dose

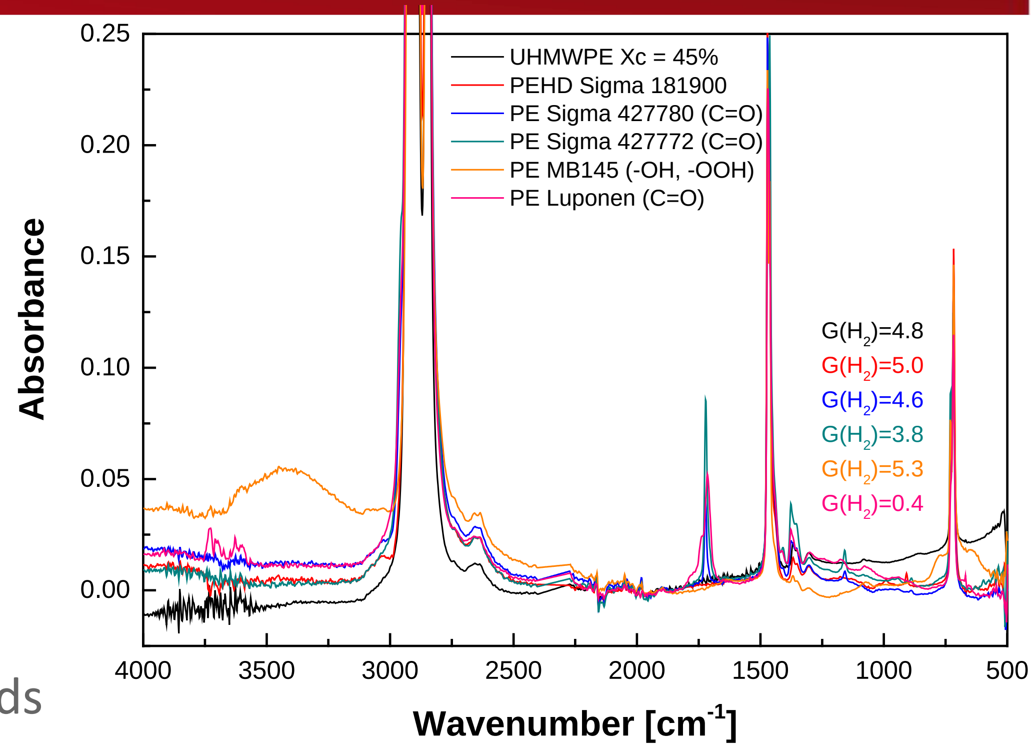
- Irradiation under oxidative atmosphere
- H_2 instantaneous emission rate ↘ when dose ↗
  - Previously observed by Seguchi
    - Under vacuum and γ-rays up to 2 MGy
    - Assigned to energy transfers towards radiation-induced C=C double bonds
  - In this work, first evidence of radiation protection
    - Under oxidative atmosphere and ion beam up to doses as high as 10 MGy
    - Assigned to energy transfers towards oxidized defects





Slivinskas & Guillet, J. Polym. Sci. : Polym. Chem. Ed. 12 (1974), 1469

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
  - $G(H_2)$ ↘ 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

Slivinskas & Guillet, J. Polym. Sci. : Polym. Chem. Ed. 12 (1974), 1469

Conclusion

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