Polymers under ionizing radiations:
Evidence of energy transfers towards radiation – induced defects

M. Ferry, A. Ventura, S. Esnouf, E. Balanzat, Y. Ravache

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Polymers under ionizing radiations: *Evidence of energy transfers towards radiation-induced defects*

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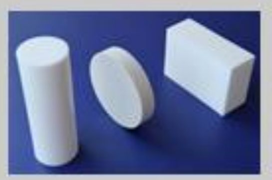
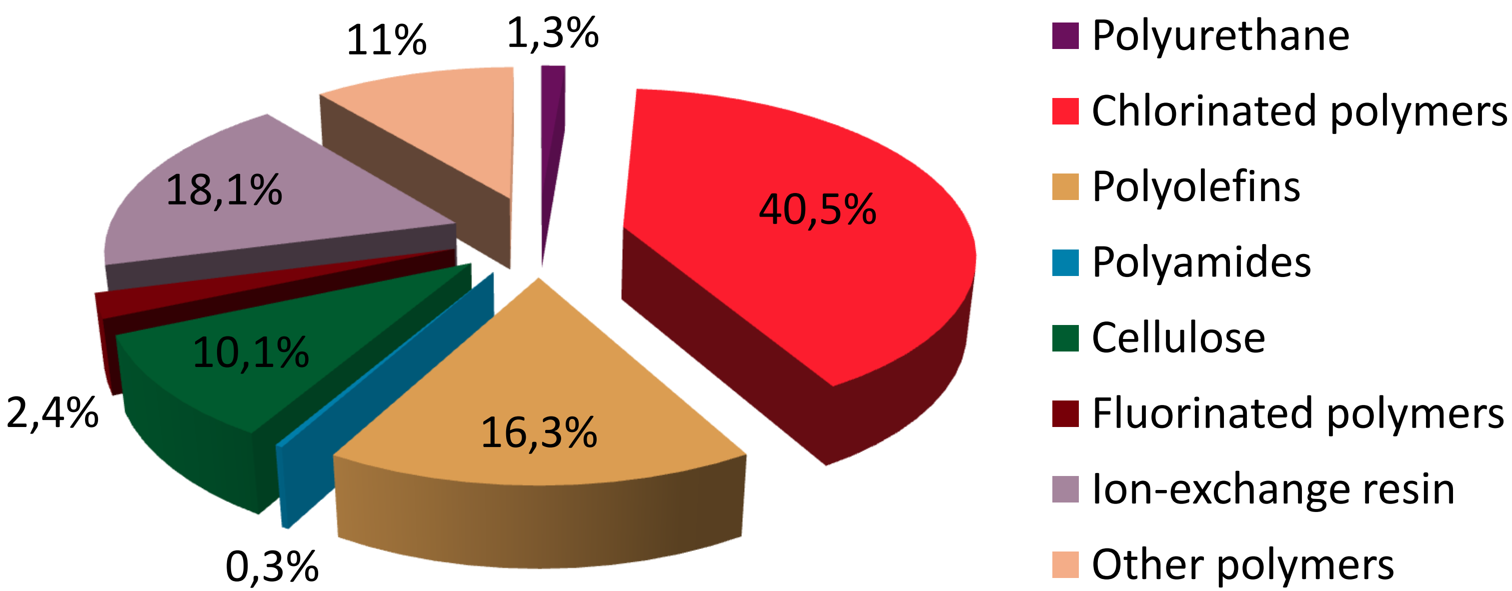
Introduction & context

From the industrial needs to fundamental research

Polymers used in the electronuclear industry

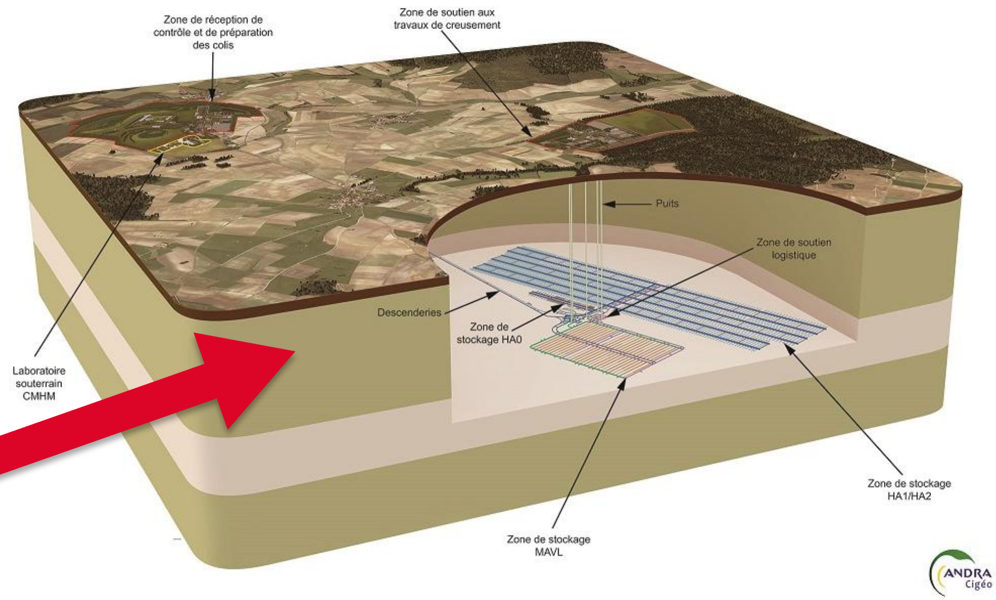
Nitrile rubber	Fluoro elastomer	Chlorinated polymer	EPDM	Epoxy	Polyurethane	Acrylic
						
Seals	Seals	Hot cell sleeve Protection sheet	Seals Insulation	Coating Paints	Gloves Cables sheath Insulation	Scotch



A deep geological disposal

ILW-LL package

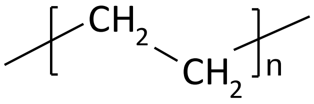
The French disposal project: Cigeo



- Polymers in contact with radionuclides in the Intermediate Level Long Lived Waste (IL-LLW) packages
- Main risk associated with storage : gas emission (inflammation, corrosion…)
- Estimate gas emission over at least 100 years (reversibility period)
  - Function of the irradiation conditions
  - Function of the polymer chemical structure (evolution with time & dose)

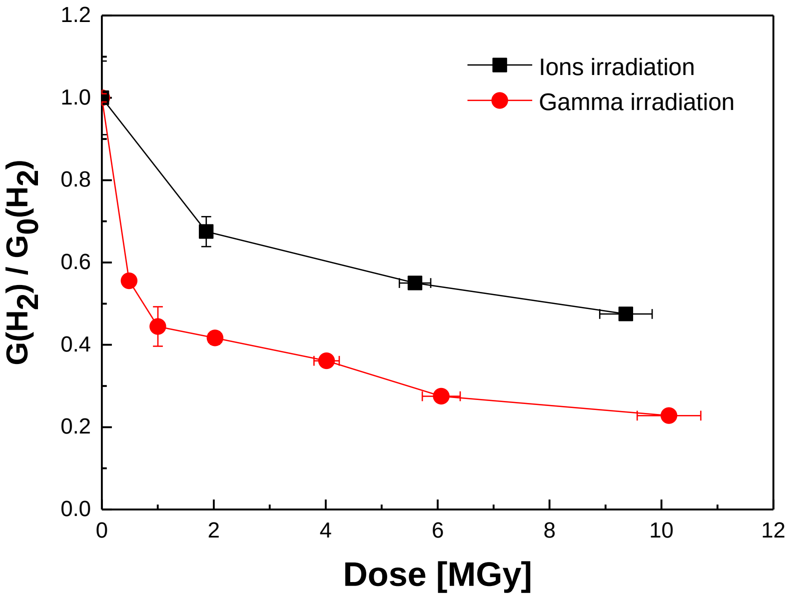
To understand hydrogen emission mechanisms
Study of polyethylene as model polymer

- "Simplest" polymer chemical structure before irradiation
- Representative of polymers in IL-LLW packages
- Presents the highest hydrogen radiation chemical yield
  - Whatever the irradiation conditions
- Hydrogen is explosive/inflammable at high concentrations
  - Safety studies focused on H_2/PE couple
  - Need to understand H_2 emission mechanisms



PE chemical structure

Effect of high doses on hydrogen release from PE



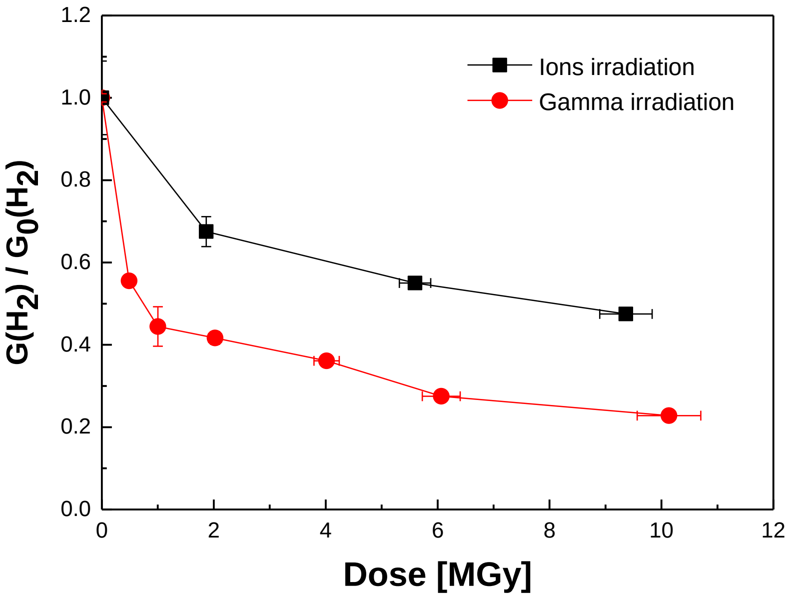
- Polyethylene irradiated under conditions representative of storage
- Important ↘ of the hydrogen release yield when D ↗

=> Why?

- Hypotheses to explain this decrease
  1. Mass loss
  2. ↘ hydrogen reservoir in the polymer
  3. Energy transfers on the radiation-induced defects

     -> Transfers of excitation, charges and radicals

Effect of high doses on hydrogen release from PE



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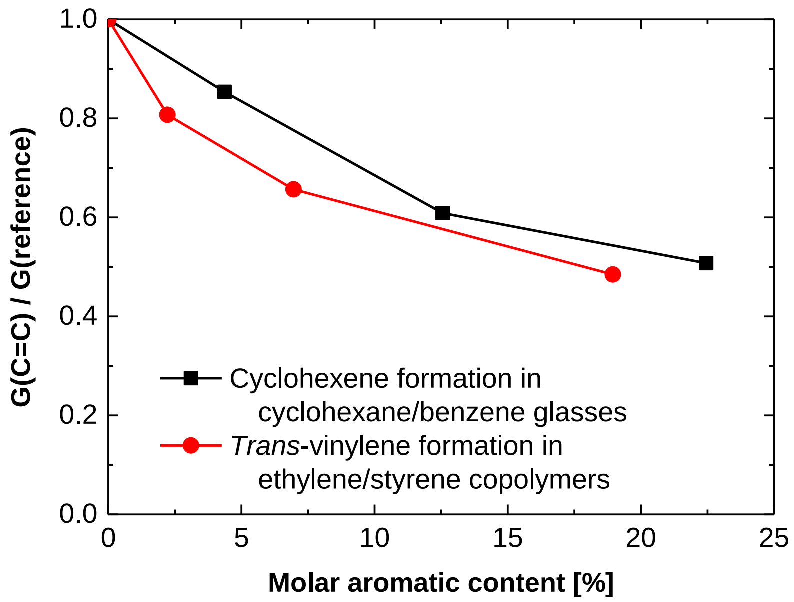
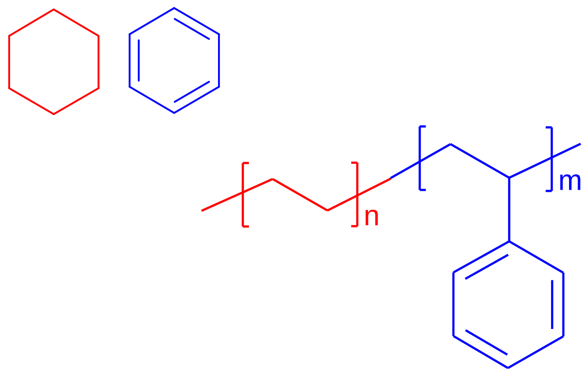
Evidences of energy transfers in copolymers

- Materials containing benzene rings shown in literature to be very stable under low LET ionizing radiation
- Efficient at high LET too

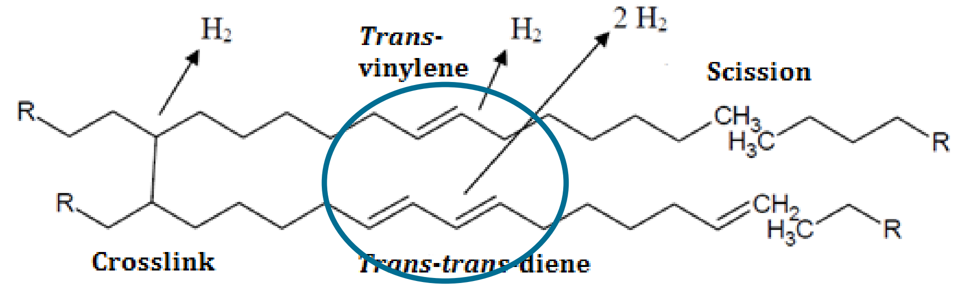




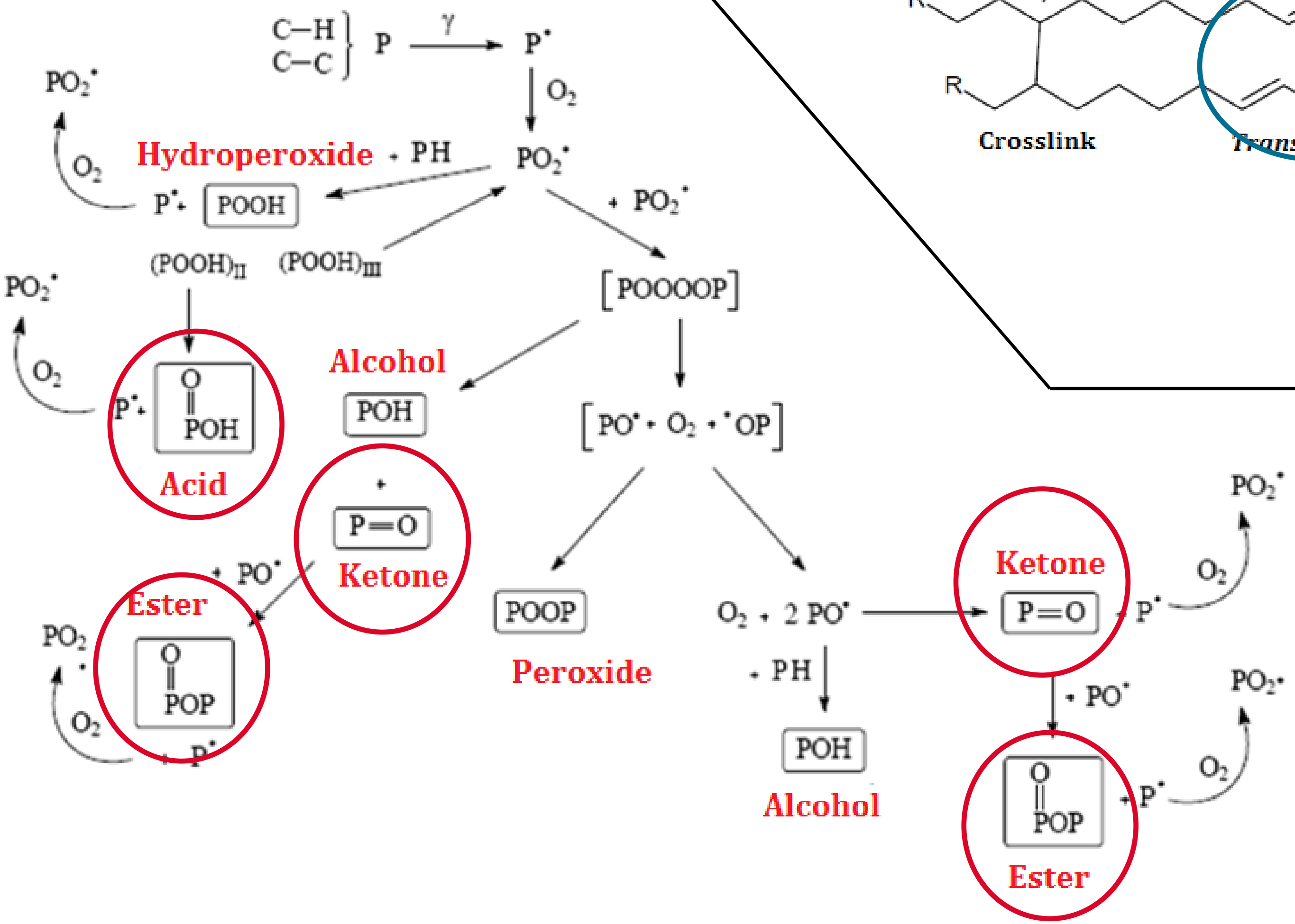
- Non conjugated bonds (C=C and C=O) also efficient

Schoepfle & Fellows, *Ind. Eng. Chem.* 23 (1931), 1396
Alexander & Charlesby, *Proc. R. Soc. London, Ser. A* 230 (1955), 136
Basheer & Dole, *J. Polym. Sci.: Polym. Phys. Ed.* 22 (1984), 1313
Partridge, *J. Chem. Phys.* 52 (1970), 2485
Slivinskas & Guillet, *J. Polym. Sci.: Polym. Chem. Ed.* 12 (1974), 1469
Ferry *et al.*, *J. Phys. Chem. B* 117 (2013), 14497

Defects formed during irradiation of polyethylene



Ventura, PhD thesis (2013)



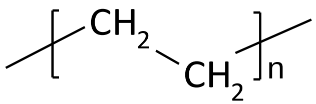
Rivation, Cambon & Gardette, *Nucl. Instrum. Methods Phys. Res., Sect. B* 227 (2005), 357

Methodology developed

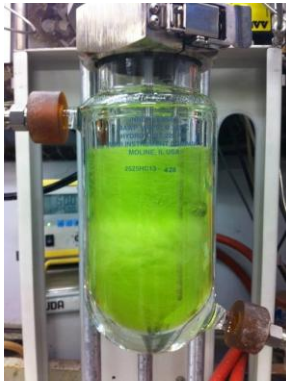
To assess energy transfers towards radiation-induced defects

Polyethylene(s) with controlled « defects »

- Study of very well controlled polyethylene(s)
  - Addition of specific groups with controlled:
    - Concentrations
    - Position of insertion (backbone or on side-chains)
- Polyethylenes commercially found
- Polyethylenes syntheses



PE perfect chemical structure



UCCS/CIMAP collaboration

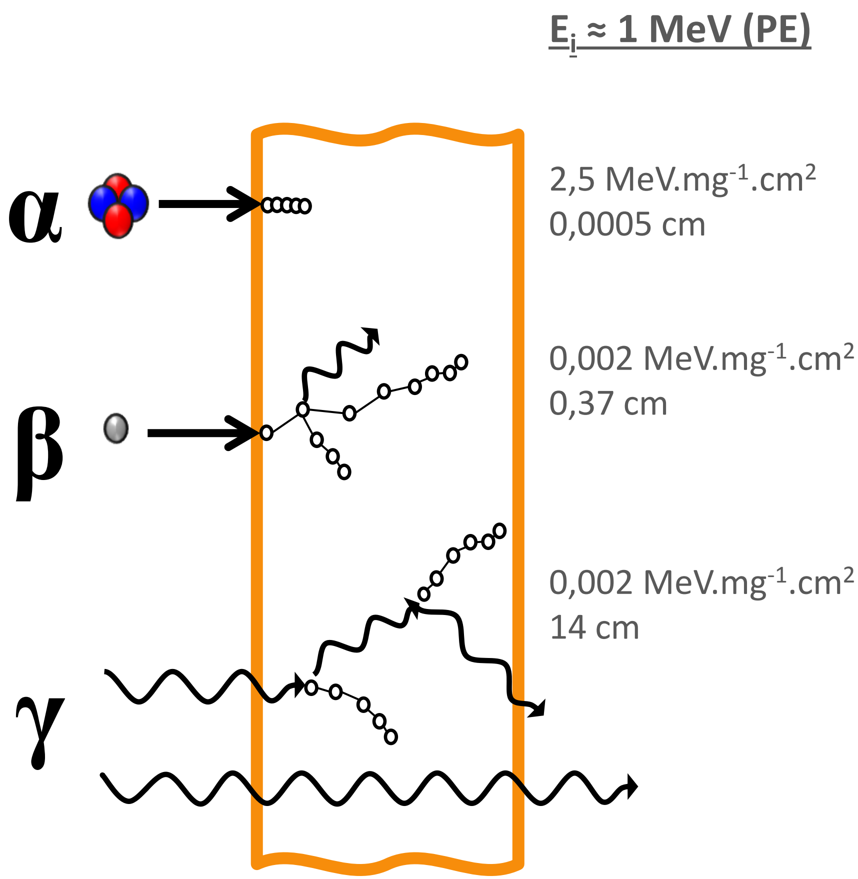
ICS/CIMAP collaboration

Irradiations under conditions representative of those in nuclear waste containers

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

- 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 or at GSI, Darmstadt, Germany)

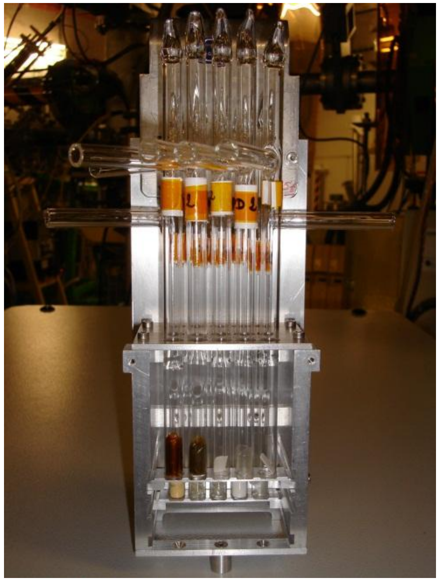
- Underlying mechanisms to be better understood
  - Which parameters allow a decrease in the gas emission?

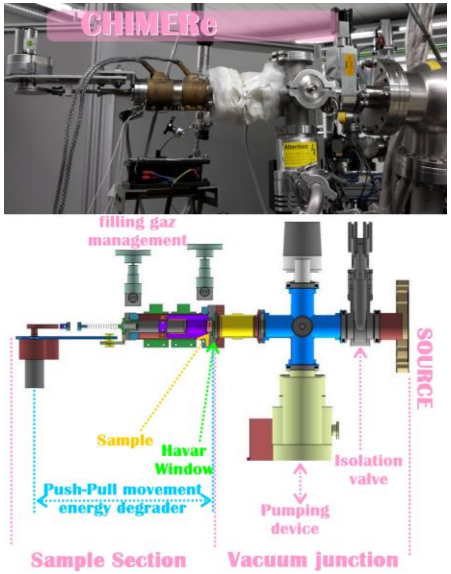


Irradiation and tracked-changes

- Set-ups depending on the irradiation conditions
  - Closed ampoules
    - Gamma and High Energy GANIL line
  - Specific devices
    - Medium Energy GANIL line
    - M-Branch GSI line

- Modifications induced by irradiation followed by
  - High resolution gas mass spectrometry
  - FTIR

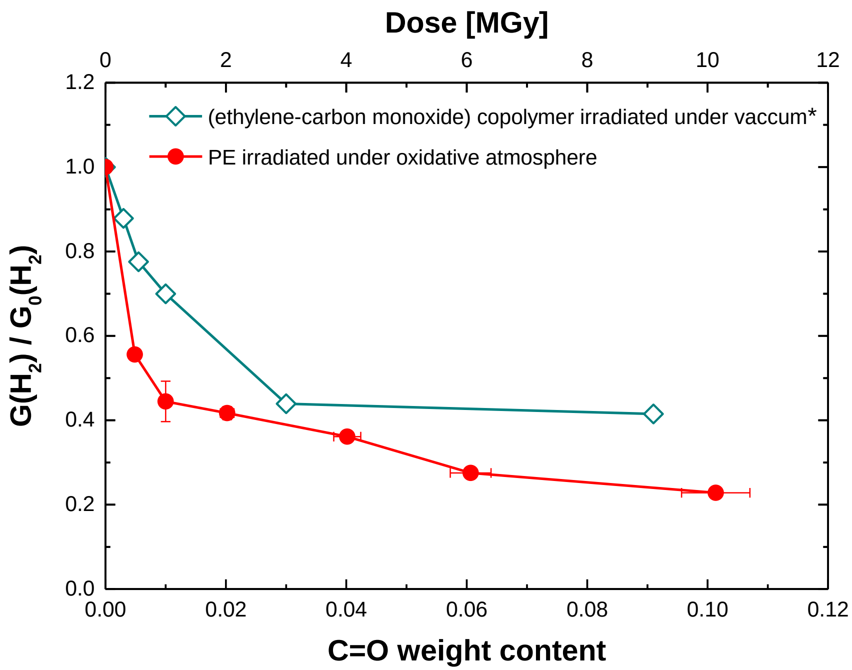


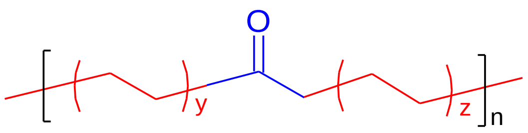


Main results

Energy transfers on ketone (>C=O) bonds

Main defect under oxidative atmosphere





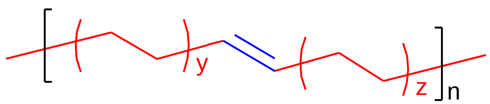
- Conversion dose <=> [C=O]
  - G(C=O) ~ 4.10^{-7} mol.J^{-1}

- $G(H_2)$ ↘ more effective in PE under radio-oxidation than in copolymers with C=O defects chemically inserted in the backbone
  - Indication of the contribution of the secondary defects (carboxylic acids…)

Slivinskas & Guillet, *J. Polym. Sci.: Polym. Chem. Ed.* 12 (1974), 1469
Lacoste & Carlsson, *J. Polym. Sci. Part A: Polym. Chem.* 30 (1992), 493

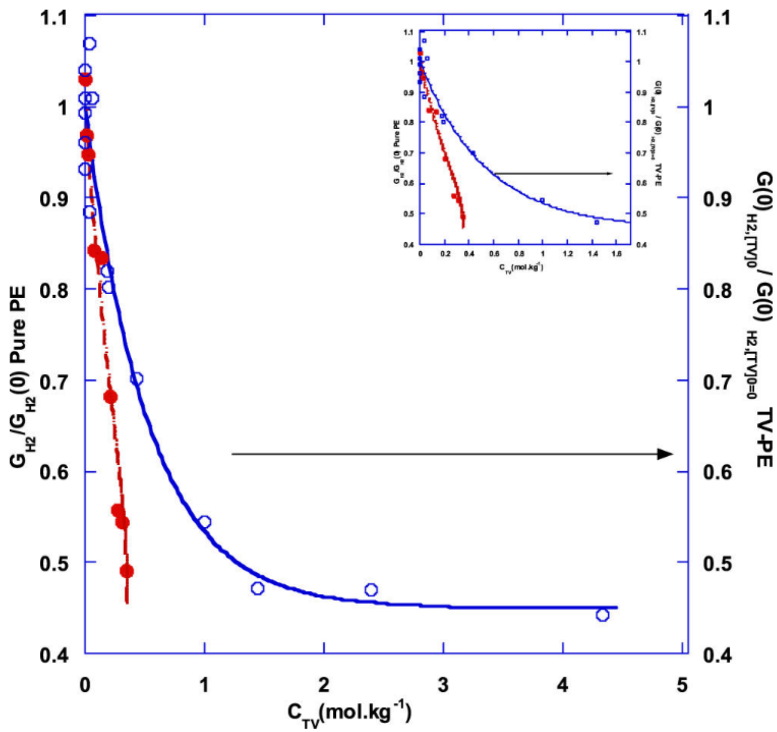
Energy transfers on vinylene (C=C) bonds

Main defect under inert atmosphere



- PE containing C=C bonds
  - Saturation effect at high concentrations
  - Activity per protective bond ↘ - Dilution effect

- ↘ of $G(H_2)$ in both cases
  - Equivalent up to [C=C] ≈ 0.2 $mol.kg^{-1}$ in PE, *i.e.* ≈ 2 MGy
  - At higher doses, other defects have to be taken into account



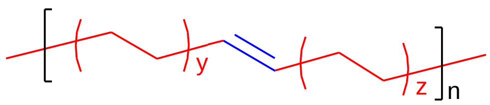
Perfect PE irradiated at high dose

PE containing C=C bonds

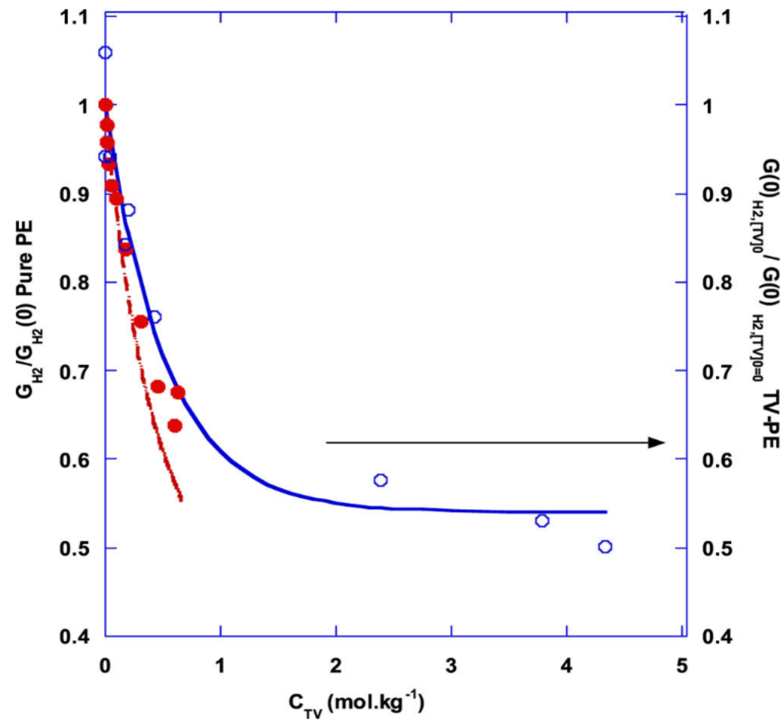
Inert atmosphere at low LET

Ventura *et al.*, *J. Phys. Chem. B* 120 (2016), 10367
Ventura, PhD thesis (2013)

Energy transfers on vinylene (C=C) bonds
Main defect under inert atmosphere: LET



- AT high LET using SHI
  - *Trans*-vinylenes are the predominant protective bond up to [C=C] ≈ 0.6 $mol.kg^{-1}$ in PE, *i.e.* ≈ 10 MGy
- Protection less effective using SHI than γ-rays
  - In track recombination before migration
  - Non-homogeneous radiation-induced C=C bonds repartition using SHI



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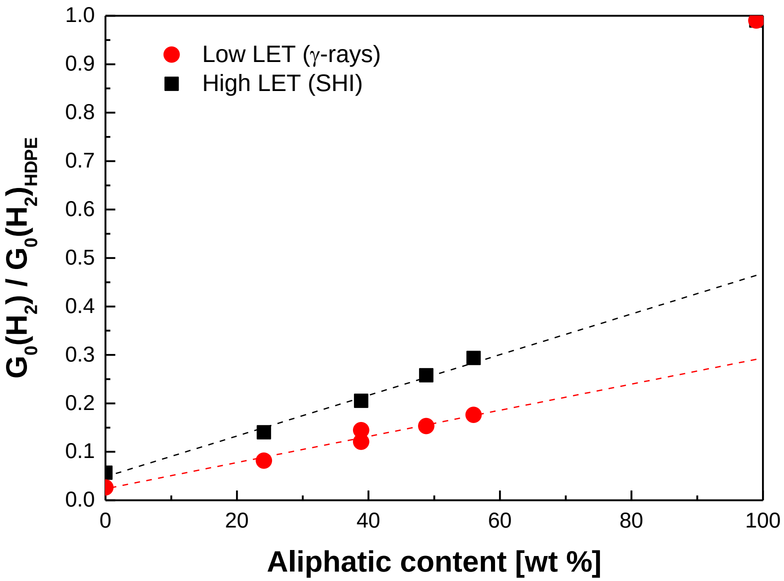
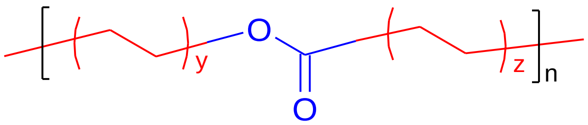
LET effect



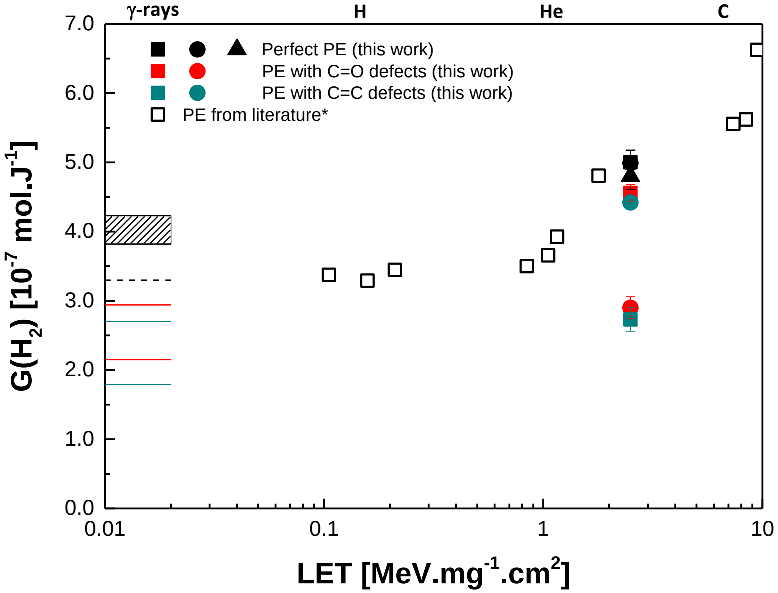
Esters in the backbone



- Confirmation of LET effect on in-chain ester polymers
  - ↘ of $G(H_2)$ more important per ester unit using low LET irradiation
  - At high LET, non-scavengeable energy trapped in ion tracks
    - Excited and ionized molecules concentration too high to allow migration
    - In-track recombinations

- Scavengeable energy fraction
  - About ≈ 2/3 for γ-rays <=> about ≈ 1/2 for SHI

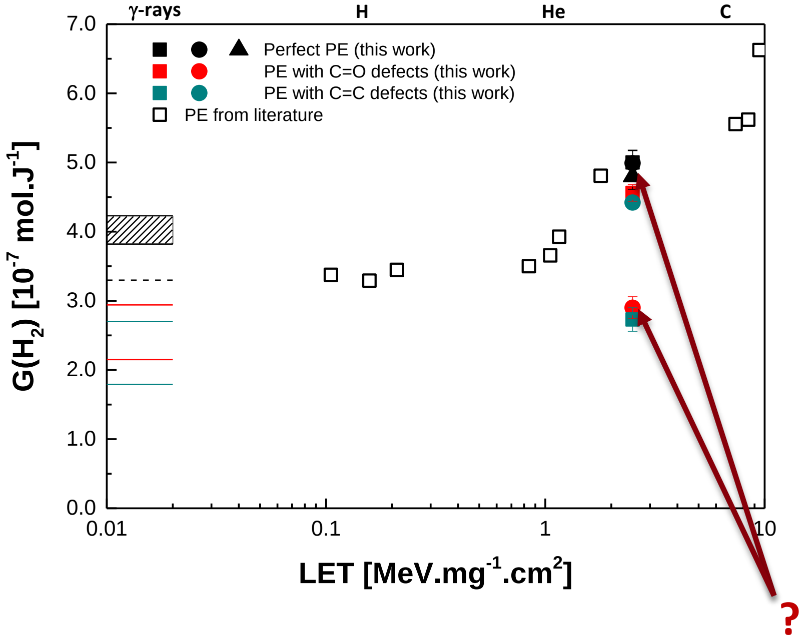
LET and defects position effects



- $G(H_2)$ ↘ with C=O and C=C bonds
  - Energy transfers effective whatever the double bond type
- Radiation protection effect more effective at low LET than at high LET
  - In-track radicals recombination

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

LET and defects position effects



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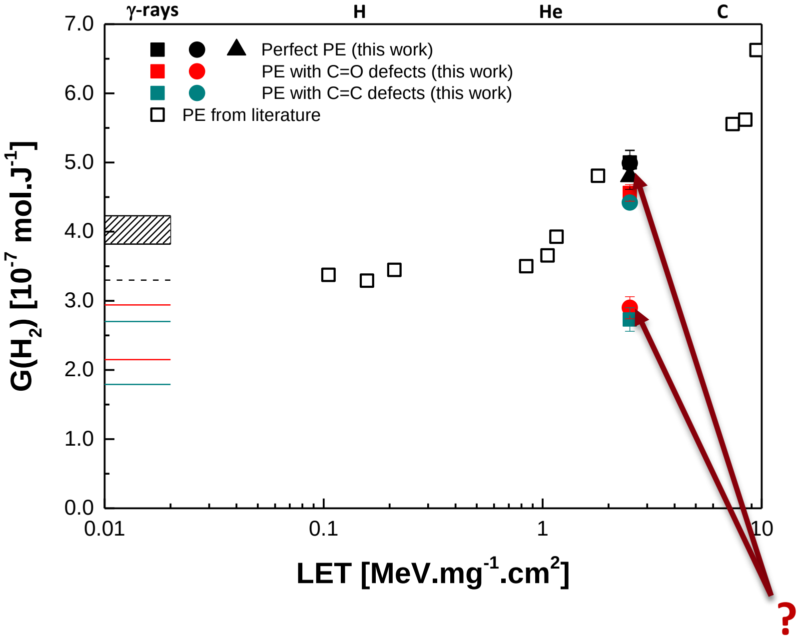
LET and defects position effects



- $G(H_2)$ ↘ with C=O and C=C bonds
  - Energy transfers effective whatever the double bond type
- Radiation protection effect more effective at low LET than at high LET
  - In-track radicals recombination
- Differences in PE with defects due to defects position
  - Case for PE with C=C defects : defects in the backbone with lower $G(H_2)$

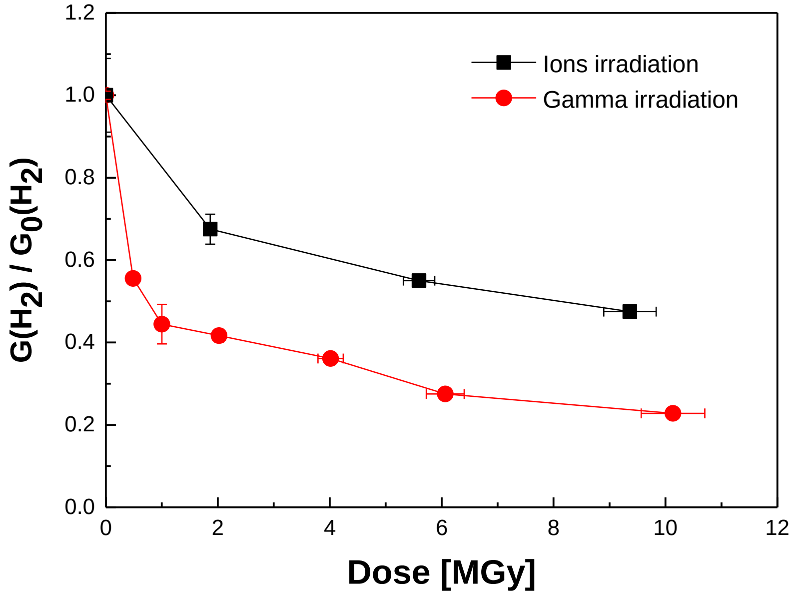
Chang & LaVerne, J. Polym. Sci.: Part A: Polym. Chem. 38 (2000),1656

Application for the industrial cases

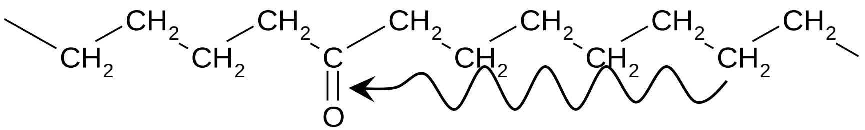
- Radiation protection effective and due to energy transfers

- Better radiation protection at low LET than under SHI
  - Whatever the defect studied

- Two phenomena
  - Ion-track density effect
  - Non-homogeneous repartition of the defects



PE irradiated under SHI and γ-rays under oxidative atmosphere



Conclusion

Conclusion

- In the deep underground repository context
  - Energy transfers decrease the hydrogen release
  - Positive effects on safety purpose
    - Up to now, $G_0(H_2)$ ~ 4.10^{-7} $mol.J^{-1}$ used in the nuclear safety cases

      => *Very conservative value*
  - Update possible with detailed explanations

- From a fundamental point of view
  - Efficiency depends on the protective group of the material
    - Its nature
    - Its concentration
    - Its position (backbone or on side-chain)
  - LET effect
    - Energy transfers probably less effective in the track core
    - Effect of the density and repartition of the protective bonds

Thank you for your attention

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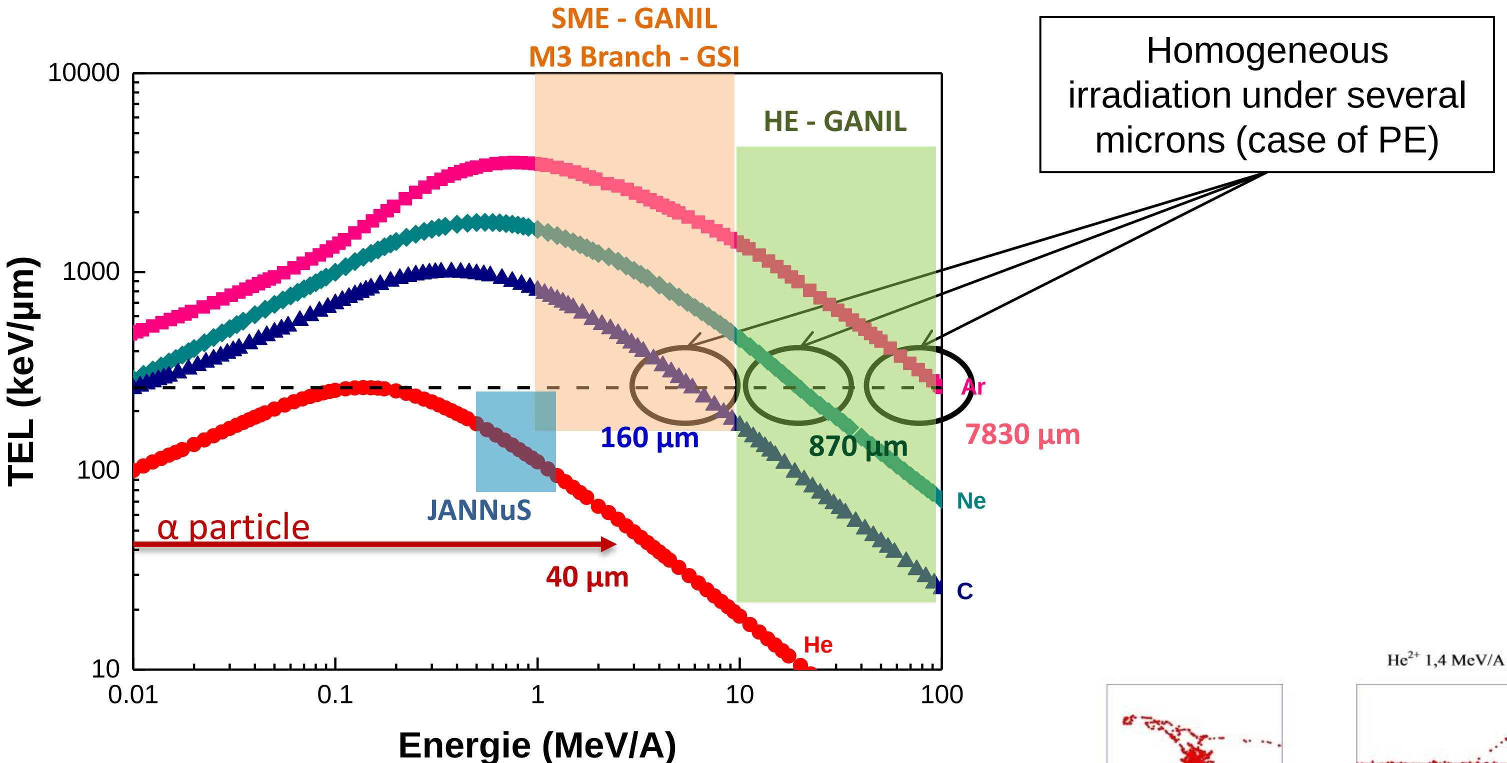
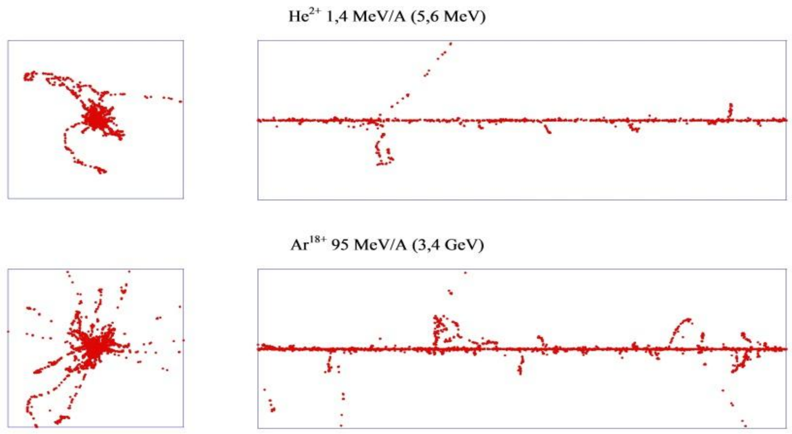
Ion beams to simulate α irradiations ?

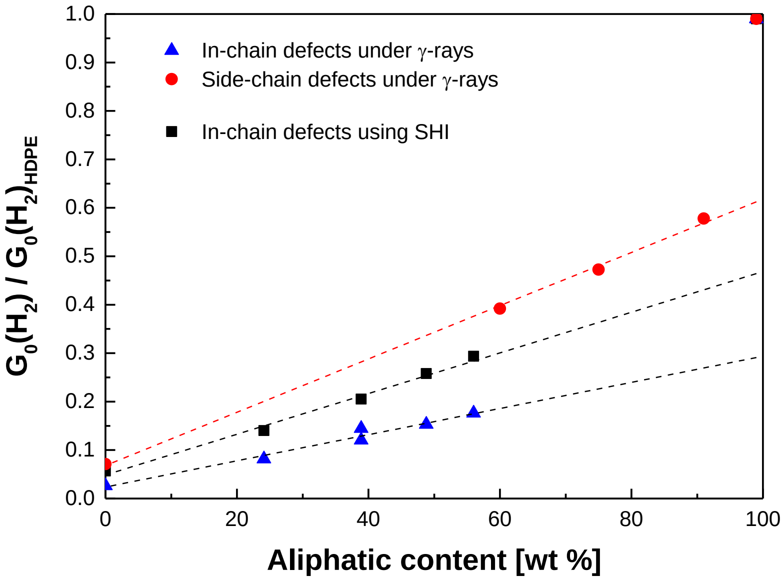




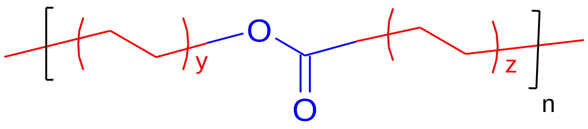
- Why SHI instead of α ?
  - LET equivalent to radionuclides-emitted α
  - Higher penetration range

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

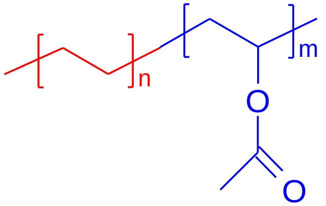
Combined effects of position and LET



Esters in the backbone



Side-chain ester



- In-chain defects more effective than side-chain ester
  - 1/3 energy scavenged by *side-chain* esters
  - 2/3 energy scavenged by esters *in the backbone*

    => Same repartition than C-C transfers (2/3) and C-H transfers (1/3) in PE*

    => 1/3 of non scavengeable energy

- In-chain defects
  - Energy scavenged by in-chain effect ↘ when LET ↗
  - But part of energy migrates out of the ions tracks

    - Better ↘ with in-chain defects at high LET than with side-chain protection

*Partridge, *J. Chem. Phys.* 52 (1970), 2485