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

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

DE LA RECHERCHE À L'INDUSTRIE

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# Polymers under ionizing radiations:

## *Evidence of energy transfers towards radiation-induced defects*

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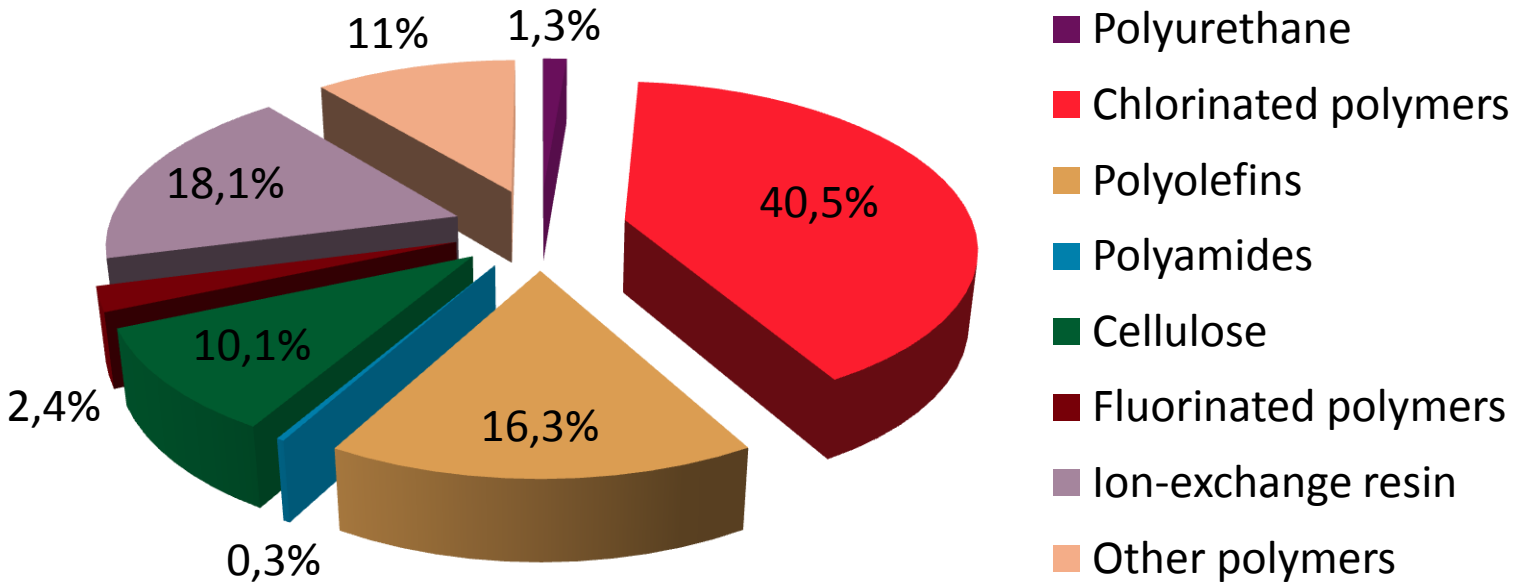
# Introduction & context

*From the industrial needs to fundamental research*

# Polymers used in the electronuclear industry

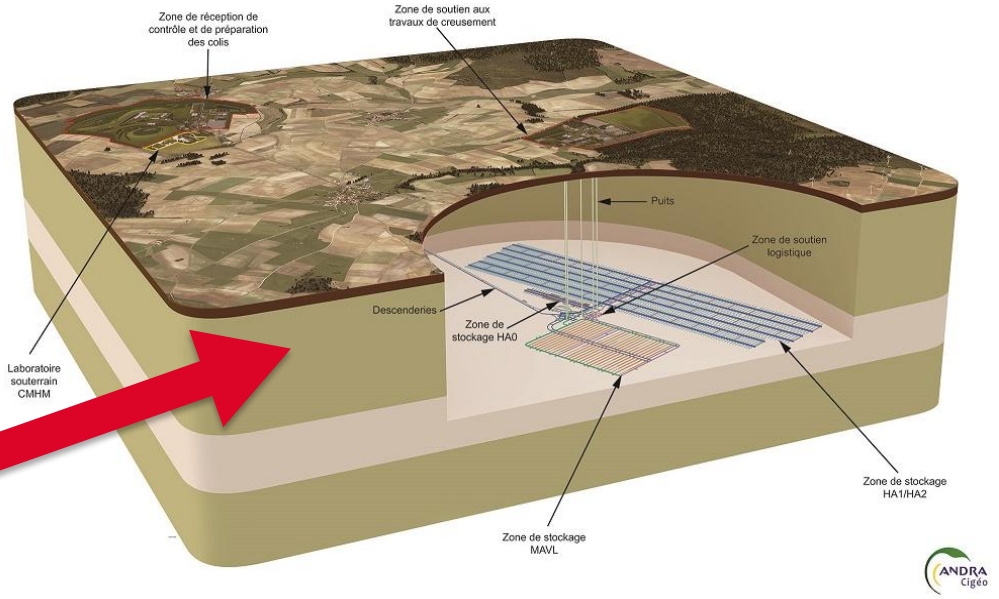
| Nitrile rubber | Fluoro elastomer | Chlorinated polymer | EPDM | Epoxy | Polyurethane | Acrylic |
|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |
| Seals | Seals | Hot cell sleeve<br>Protection sheet | Seals<br>Insulation | Coating<br>Paints | Gloves<br>Cables sheath<br>Insulation | Scotch |



# A deep geological disposal


ILW-LL package

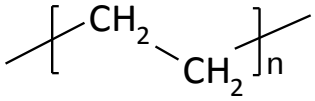
The French disposal project: Cigeo




- 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)

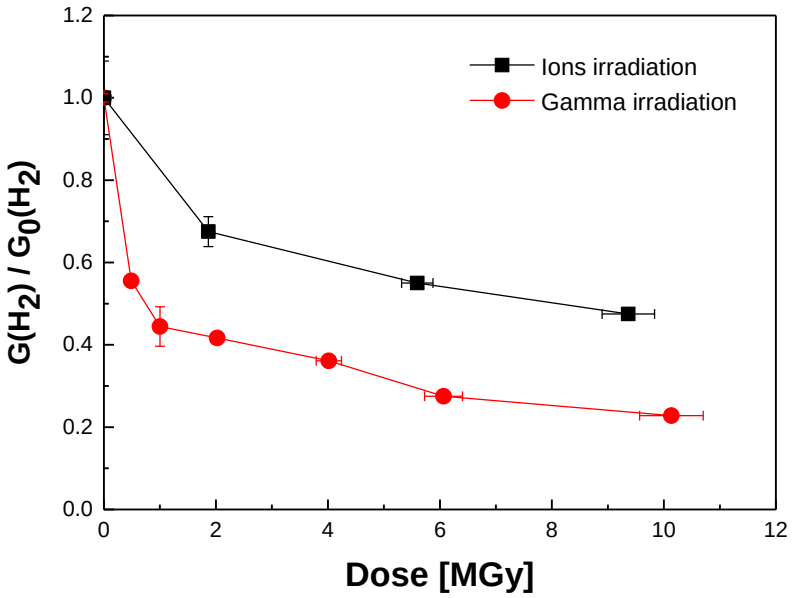
# To understand hydrogen emission mechanisms
## *Study of polyethylene as model polymer*

- "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



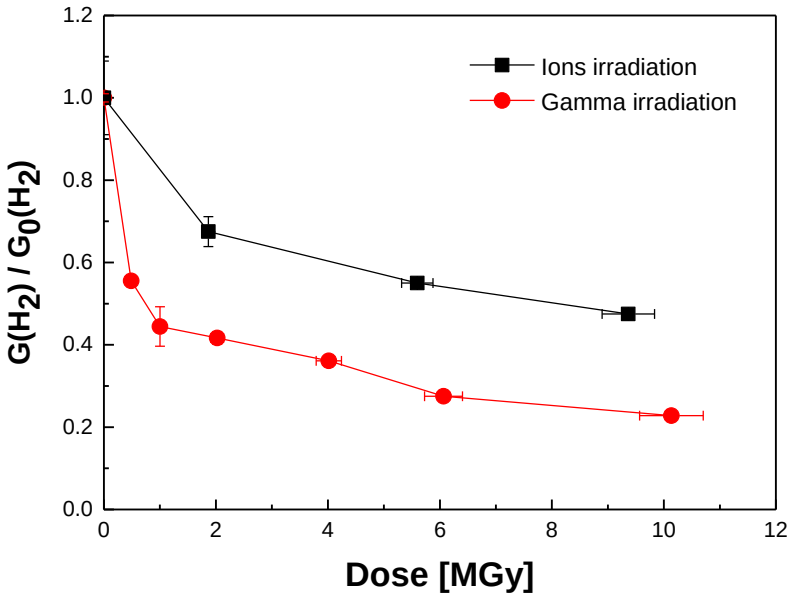

- Polyethylene irradiated under conditions representative of storage
- Important ↘ of the hydrogen release yield when D ↗

***=> 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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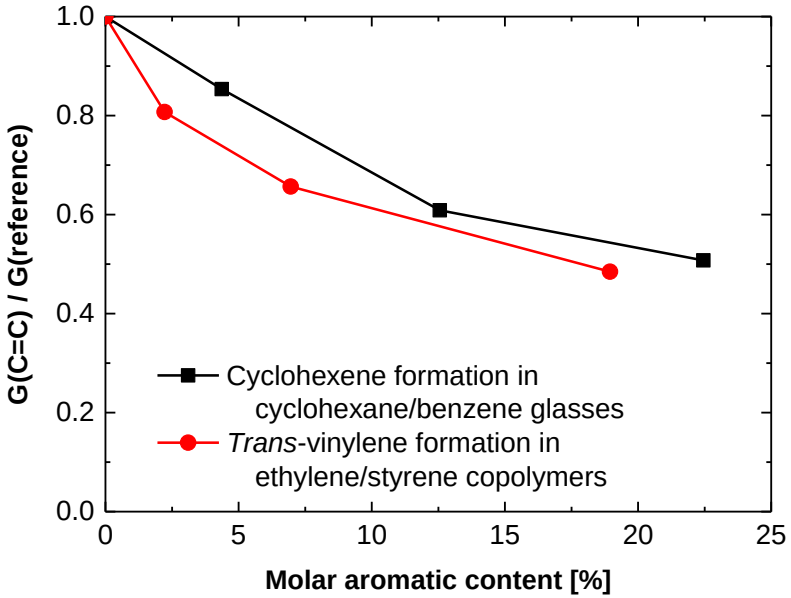
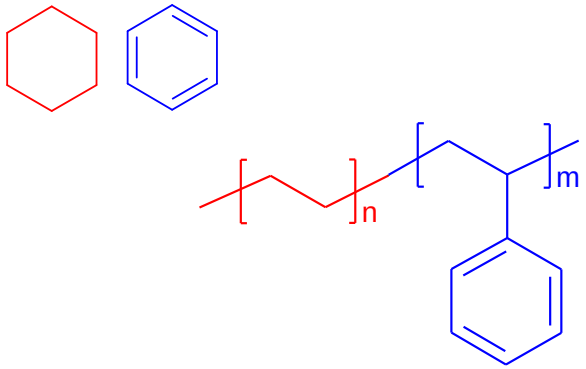
# Evidences of energy transfers in copolymers

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

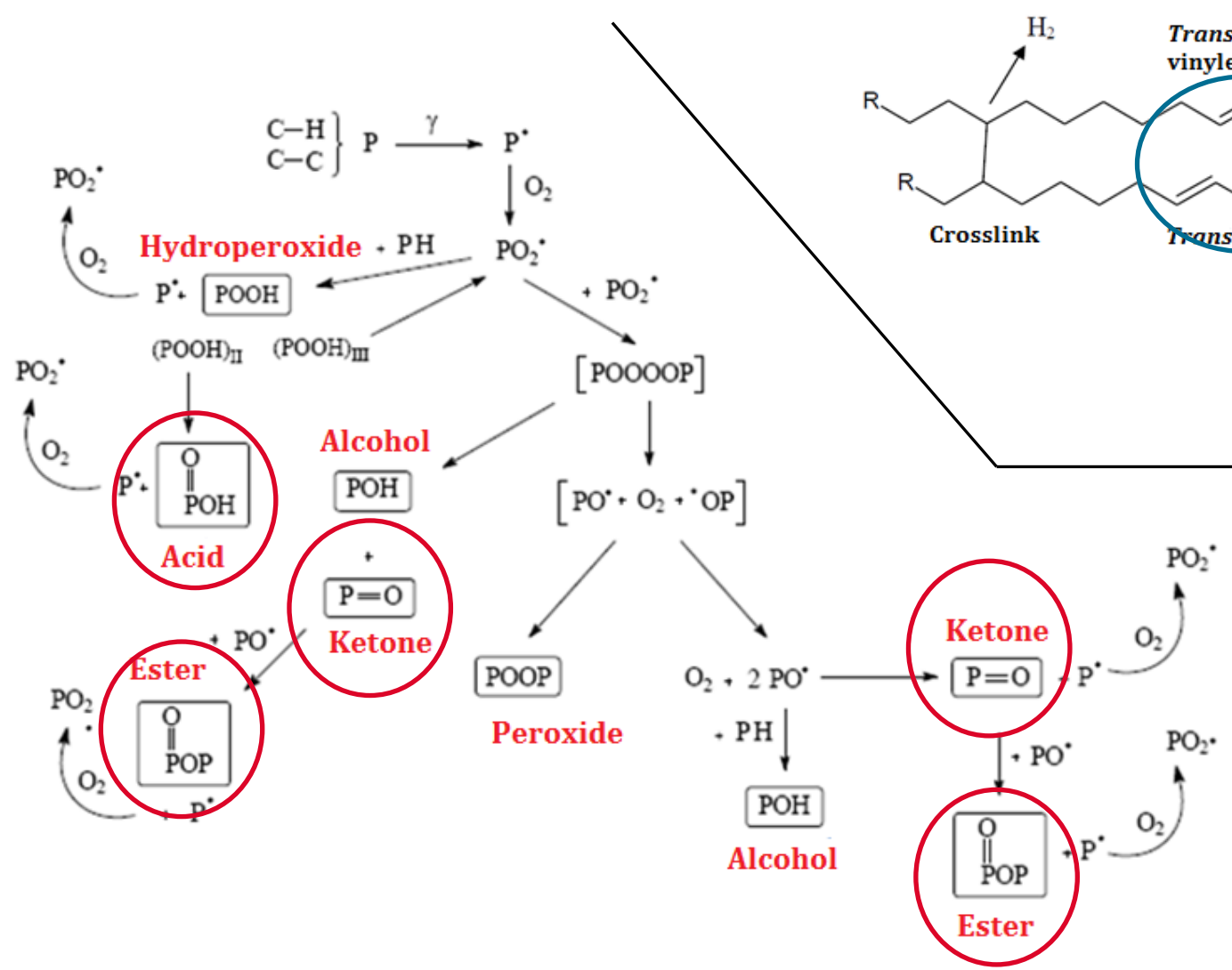


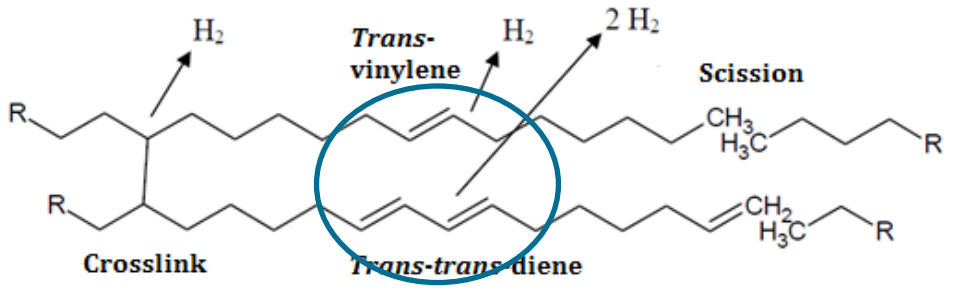




- Non conjugated bonds (C=C and C=O) also efficient


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)



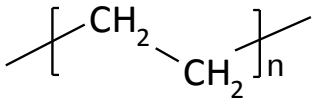
Rivation, Cambon & Gardette, *Nucl. Instrum. Methods Phys. Res., Sect. B* 227 (2005), 357

## Methodology developed

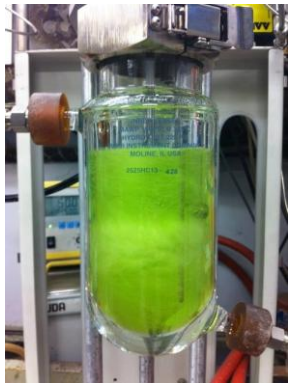
*To assess energy transfers towards radiation-induced defects*

# 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

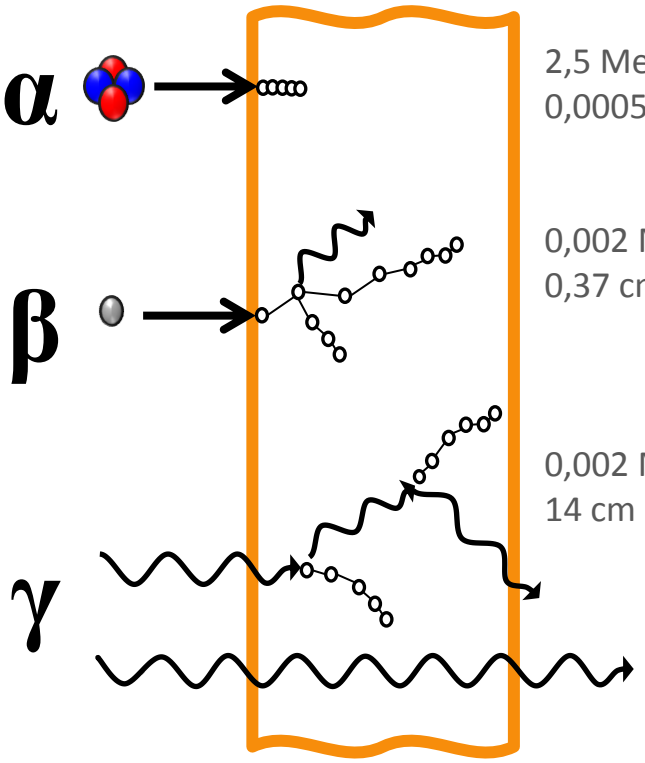
# Irradiations under conditions representative of those in nuclear waste containers

- Organic material and radionuclides (RN) in the ILLW packages : $\alpha$ and $\beta/\gamma$ emitters

- Emitters simulation
  - $\beta/\gamma$ emitters : $\gamma$ irradiations using $^{60}Co$ and $^{137}Cs$ sources (0.3 to 0.7 kGy.h$^{-1}$)
  - $\alpha$ emitters :
    - Irradiations of simulation, using C and Ar ions (≈ 500 kGy.h$^{-1}$, at GANIL, Caen, France or at GSI, Darmstadt, Germany)

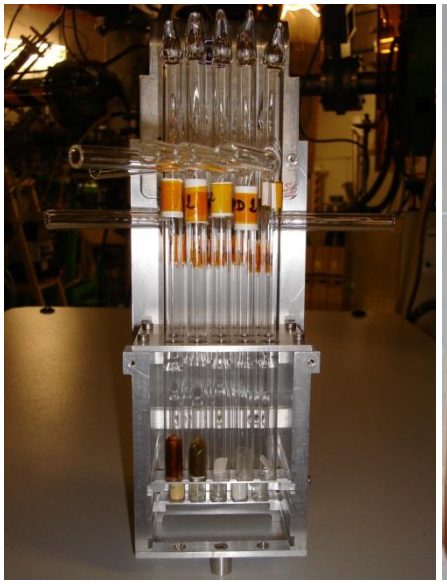
- Underlying mechanisms to be better understood
  - Which parameters allow a decrease in the gas emission?

**$E_i$ ≈ 1 MeV (PE)**

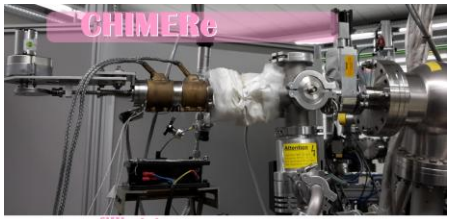


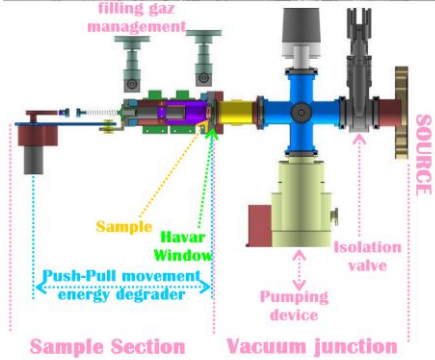
# Irradiation and tracked-changes

- 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



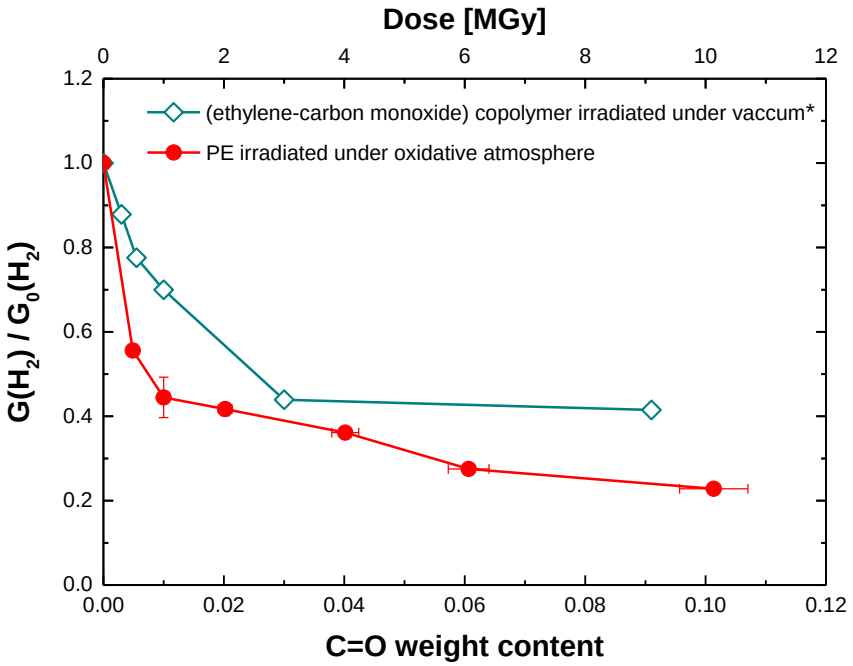
- Modifications induced by irradiation followed by
  - High resolution gas mass spectrometry
  - FTIR

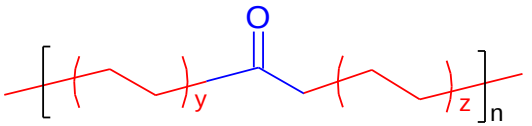


# Main results

# Energy transfers on ketone (>C=O) bonds
## *Main defect under oxidative atmosphere*



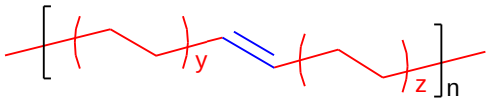




- Conversion dose <=> [C=O]
  - G(C=O) ~ $4.10^{-7}$ mol.$J^{-1}$

- $G(H_2)$ ↘ 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…)

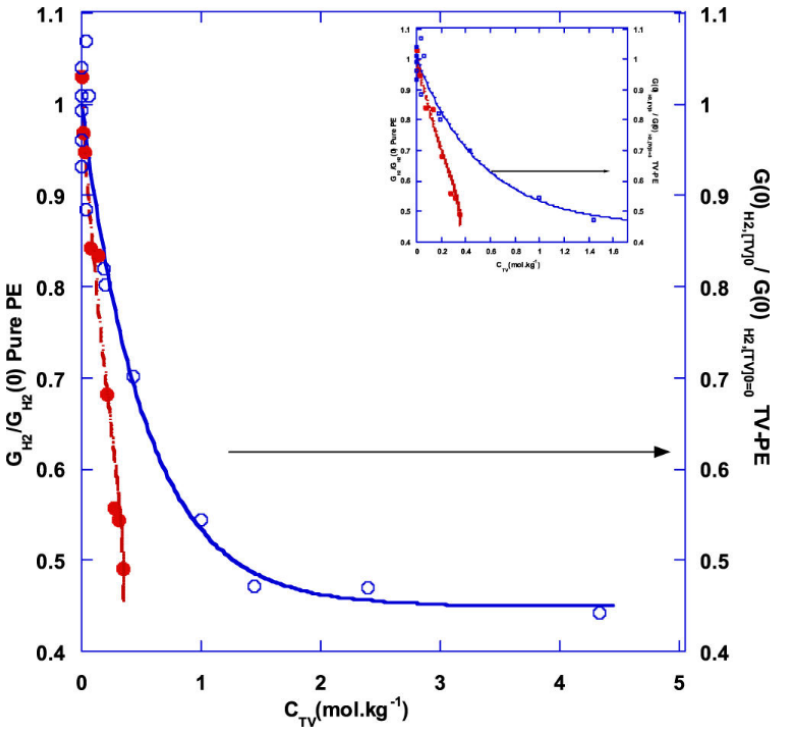

Slivinskas & Guillet, *J. Polym. Sci.: Polym. Chem. Ed.* 12 (1974), 1469
Lacoste & Carlsson, *J. Polym. Sci. Part A: Polym. Chem.* 30 (1992), 493

# 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



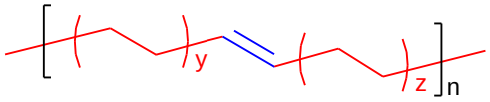

Perfect PE irradiated at high dose

PE containing C=C bonds

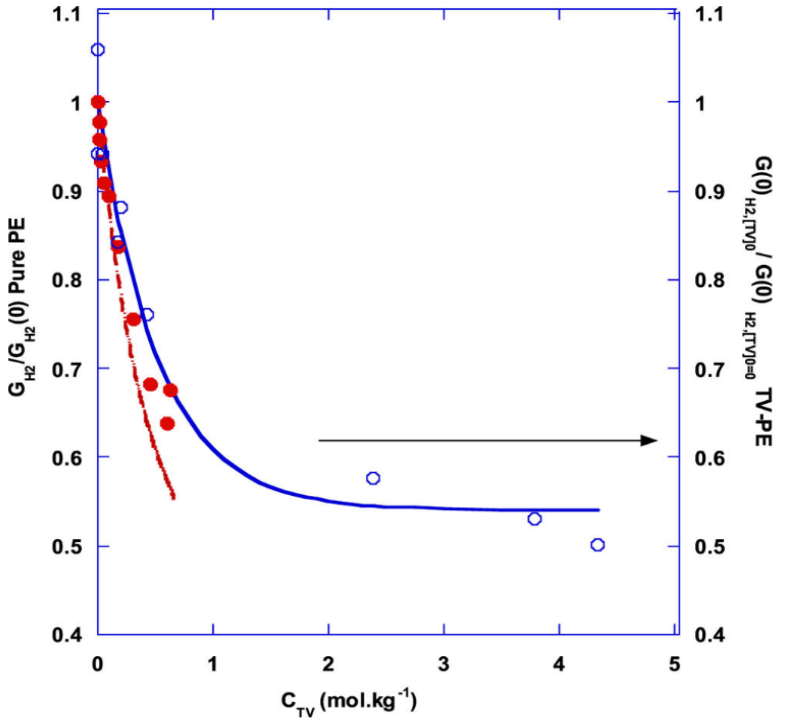
Inert atmosphere at low LET

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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Inert atmosphere using SHI

Ventura *et al.*, *J. Phys. Chem. B* 120 (2016), 10367
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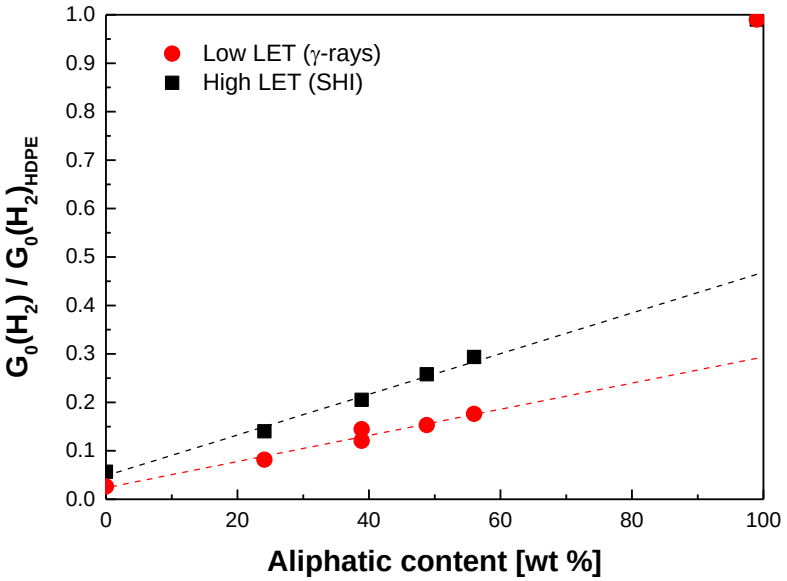
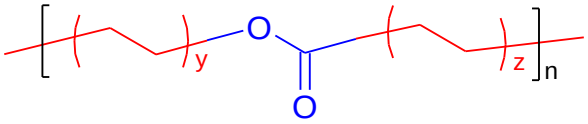
# LET effect

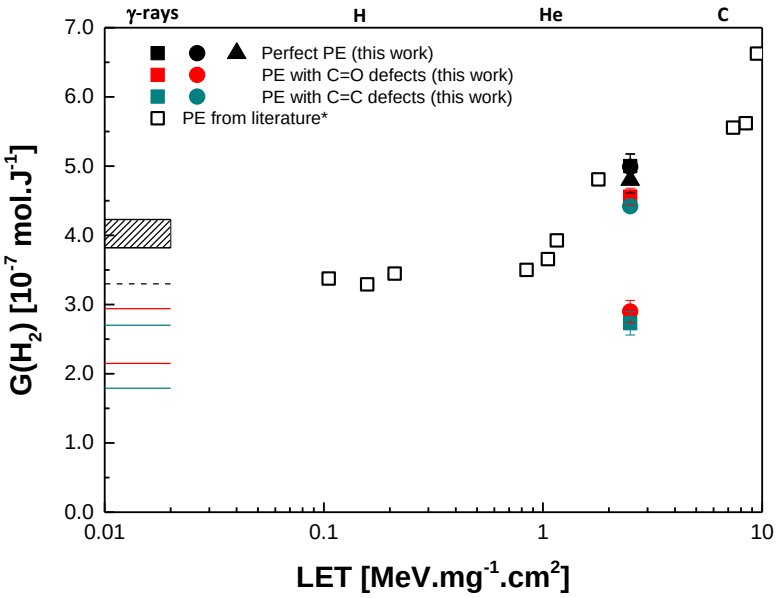



Esters in the backbone




- 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

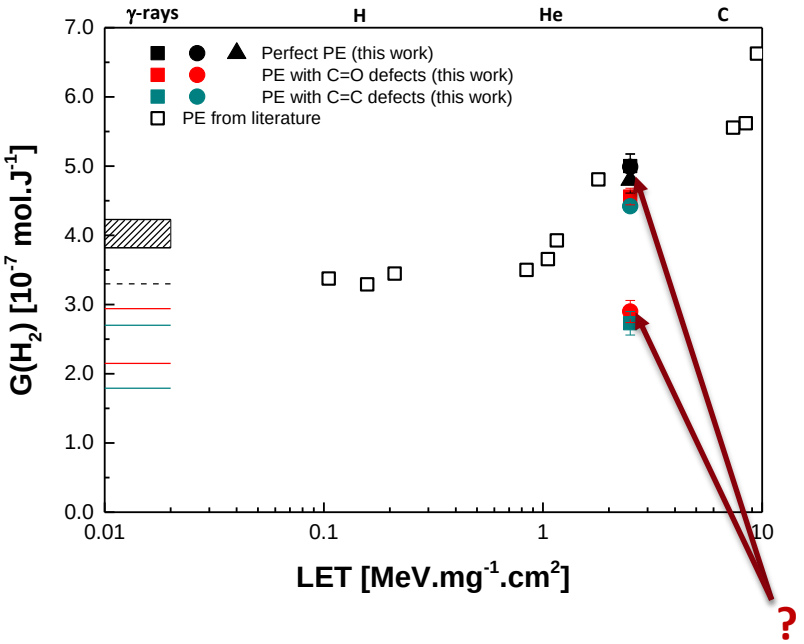



- $G(H_2)$ ↘ with C=O and C=C bonds
  - Energy transfers effective whatever the double bond type
- Radiation protection effect more effective at low LET than at high LET
  - In-track radicals recombination



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

# LET and defects position effects

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

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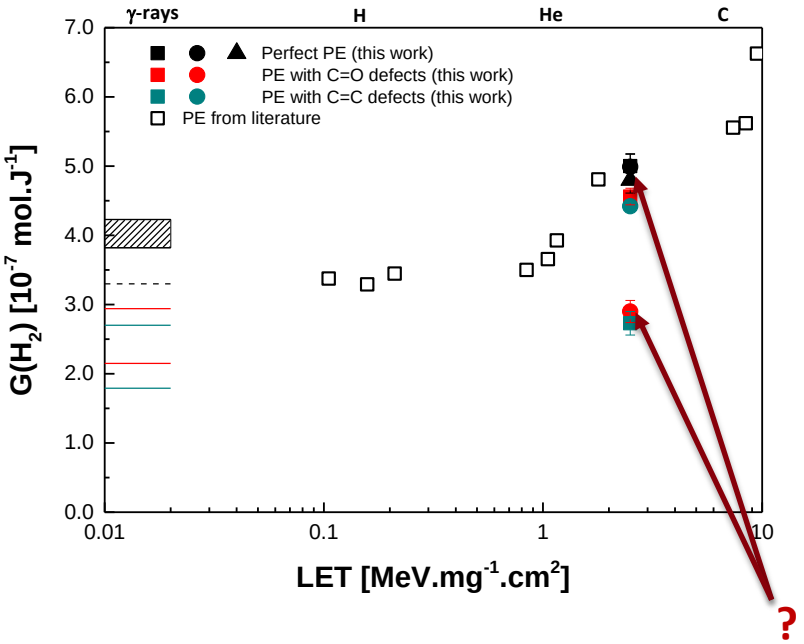


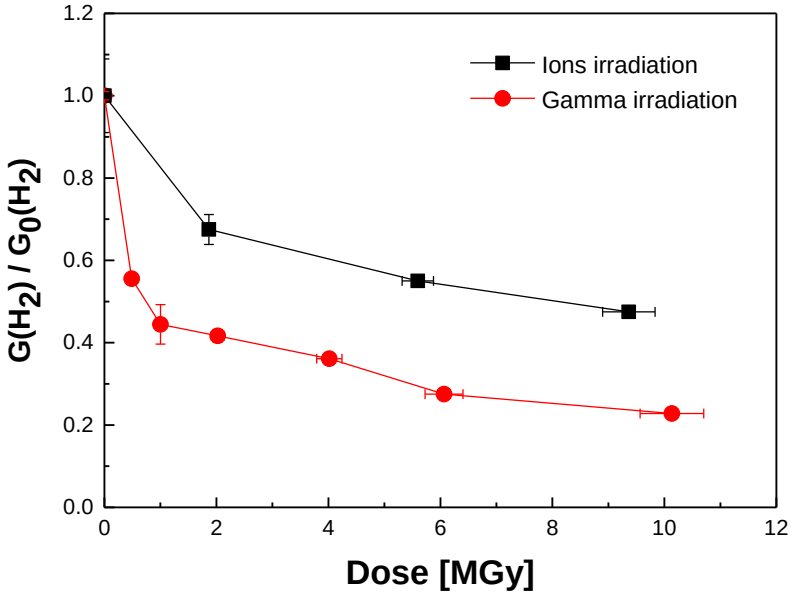

- $G(H_2)$ ↘ with C=O and C=C bonds
  - Energy transfers effective whatever the double bond type
- Radiation protection effect more effective at low LET than at high LET
  - In-track radicals recombination
- Differences in PE with defects due to defects position
  - Case for PE with C=C defects : defects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



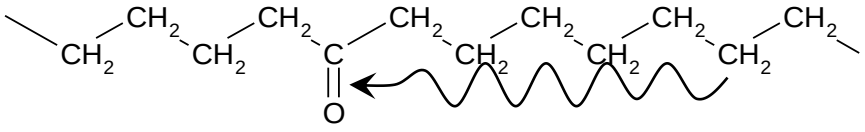
Chang & LaVerne, J. Polym. Sci.: Part A: Polym. Chem. 38 (2000),1656

# 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

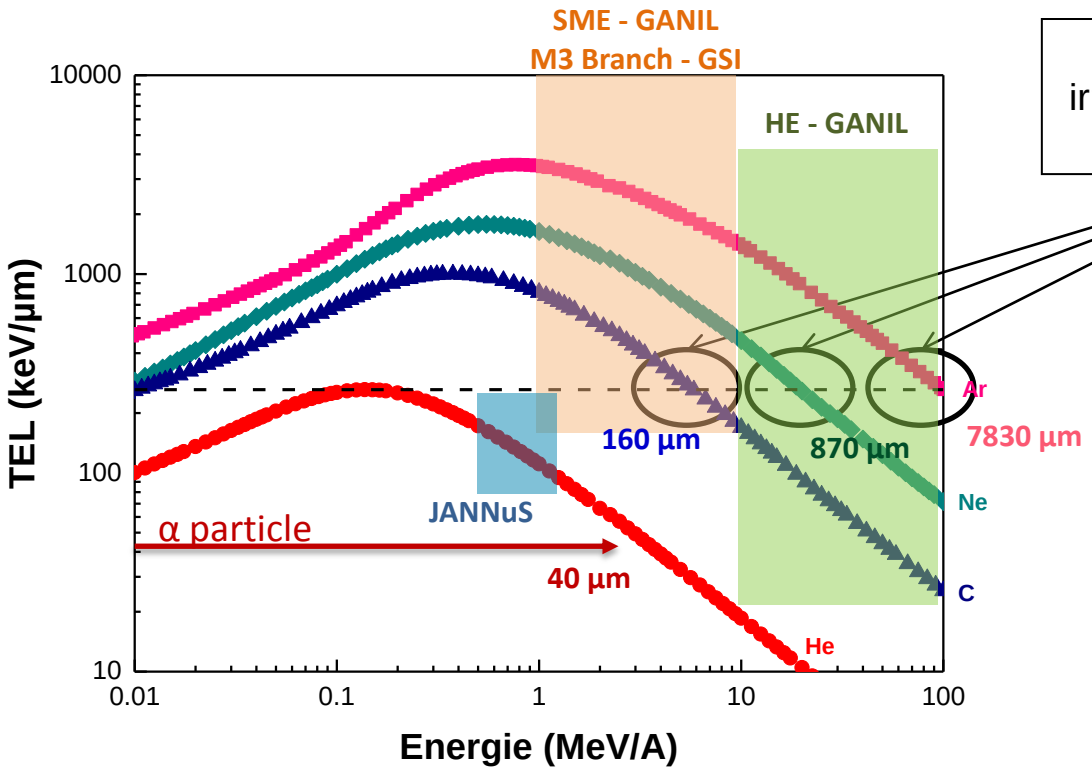
# Conclusion

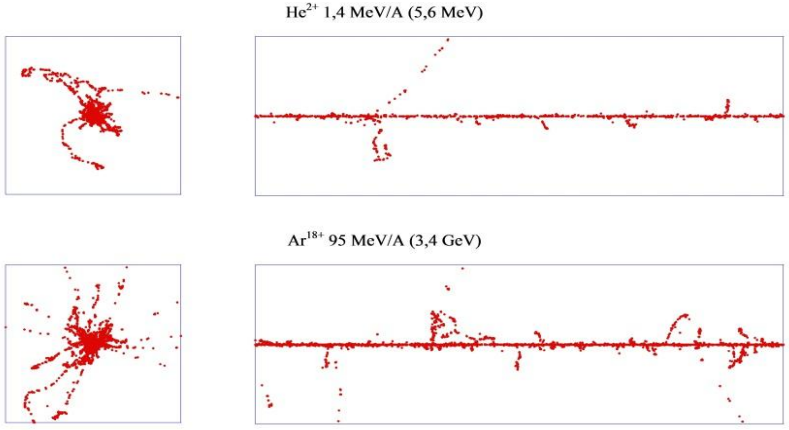
- In the deep underground repository context
  - Energy transfers decrease the hydrogen release
  - Positive effects on safety purpose
    - Up to now, $G_0(H_2) \sim 4.10^{-7}$ mol.J$^{-1}$ used in the nuclear safety cases
      *=> Very conservative value*
  - Update possible with detailed explanations

- 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

# Ion beams to simulate α irradiations ?

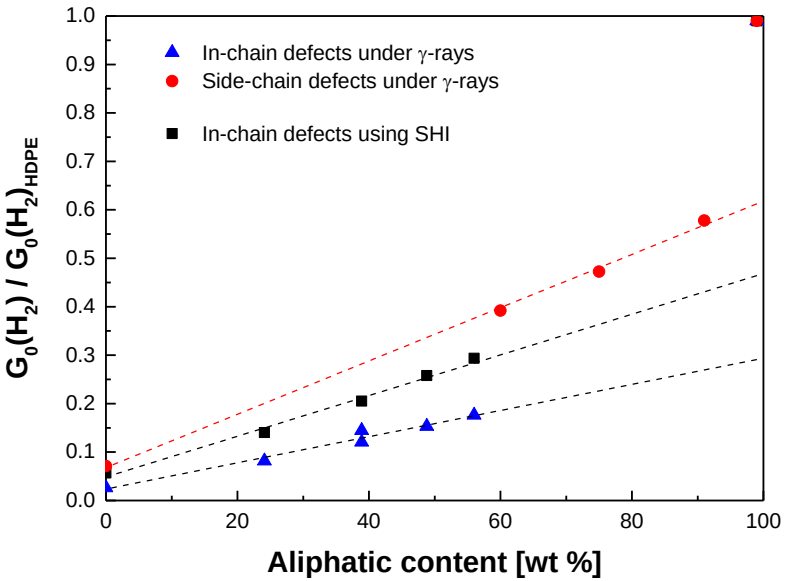


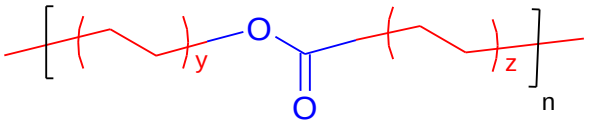

- Why SHI instead of α ?
  - LET equivalent to radionuclides-emitted α
  - Higher penetration range

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

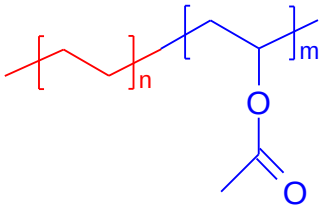
# Combined effects of position and LET




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