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

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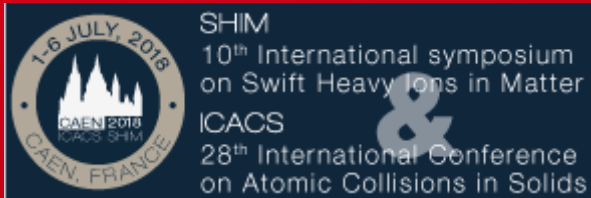
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Polymers under ionizing radiations: *Evidence of energy transfers towards radiation-induced defects*







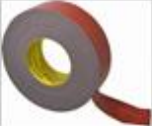
M. Ferry¹, A. Ventura², S. Esnouf¹, E. Balanzat², Y. Ngonon-Ravache²

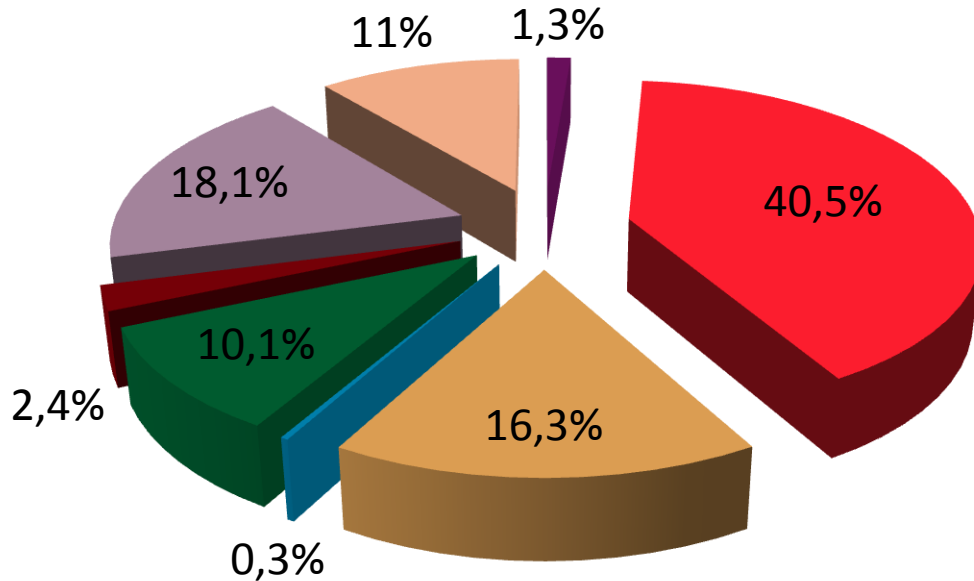
¹ Den-Service d'Étude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France.

² CIMAP (CEA/CNRS/ENSICAen/UNICAen), CIMAP site GANIL, Caen, France.

Introduction & context

*From the industrial needs to
fundamental research*

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

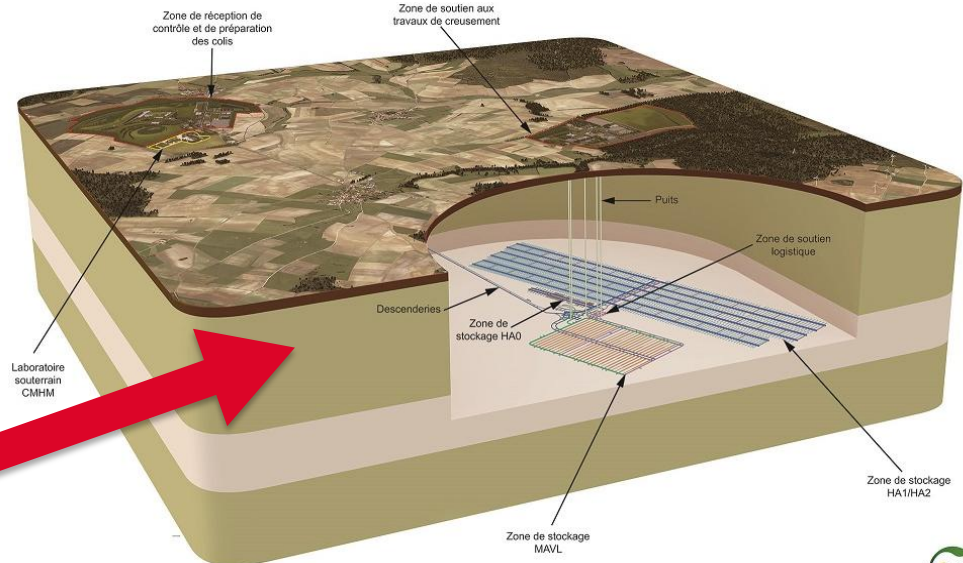


- Polyurethane
- Chlorinated polymers
- Polyolefins
- Polyamides
- Cellulose
- Fluorinated polymers
- Ion-exchange resin
- Other polymers

The French disposal project: Cigeo



ILW-LL package

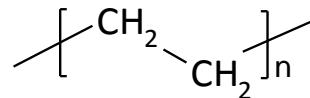


- Polymers in contact with radionuclides in the Intermediate Level Long Lived Waste (IL-LLW) packages
- Main risk associated with storage : gas emission (inflammation, corrosion...)
- Estimate gas emission over at least 100 years (reversibility period)
 - Function of the irradiation conditions
 - Function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

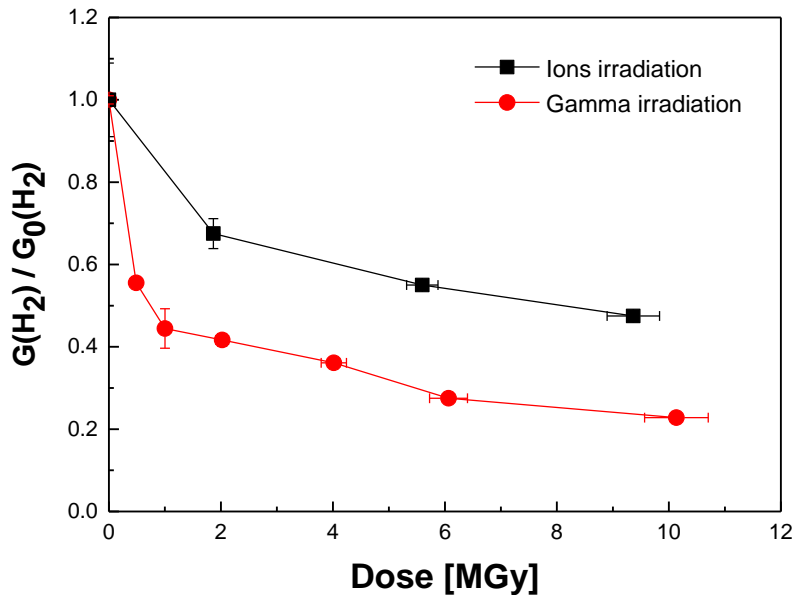
To understand hydrogen emission mechanisms

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 H₂/PE couple
 - Need to understand H₂ emission mechanisms



PE chemical structure



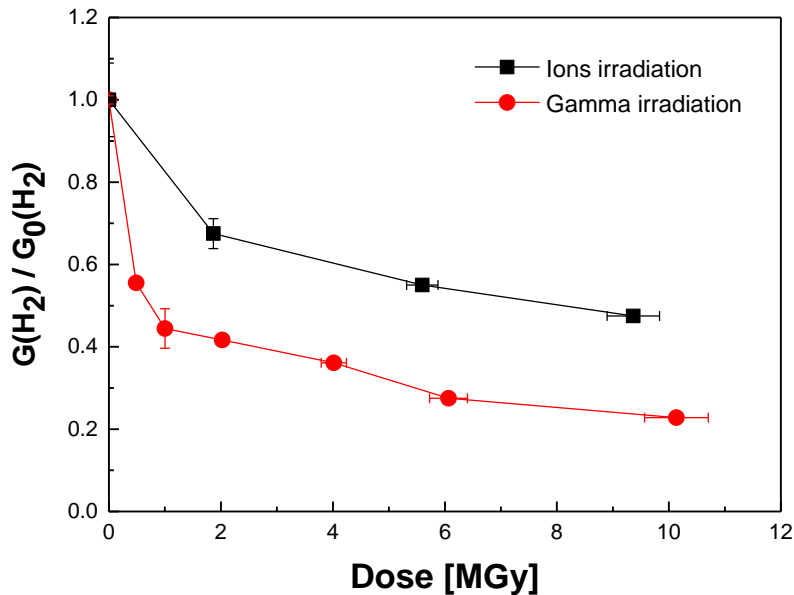
■ Polyethylene irradiated under conditions representative of storage

■ Important \searrow of the hydrogen release yield when $D \nearrow$

=> Why?

■ Hypotheses to explain this decrease

1. Mass loss
2. \searrow hydrogen reservoir in the polymer
3. Energy transfers on the radiation-induced defects
 -> *Transfers of excitation, charges and radicals*



■ Polyethylene irradiated under conditions representative of storage

■ Important \searrow of the hydrogen release yield when $D \nearrow$

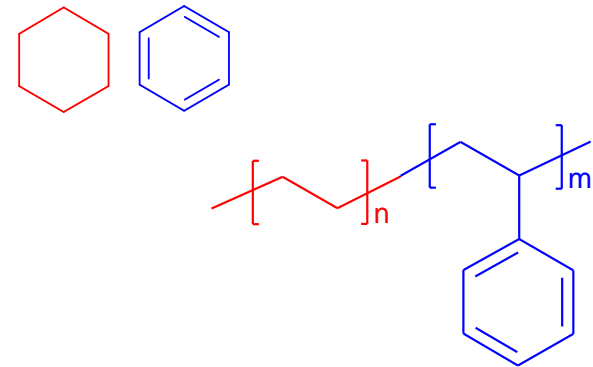
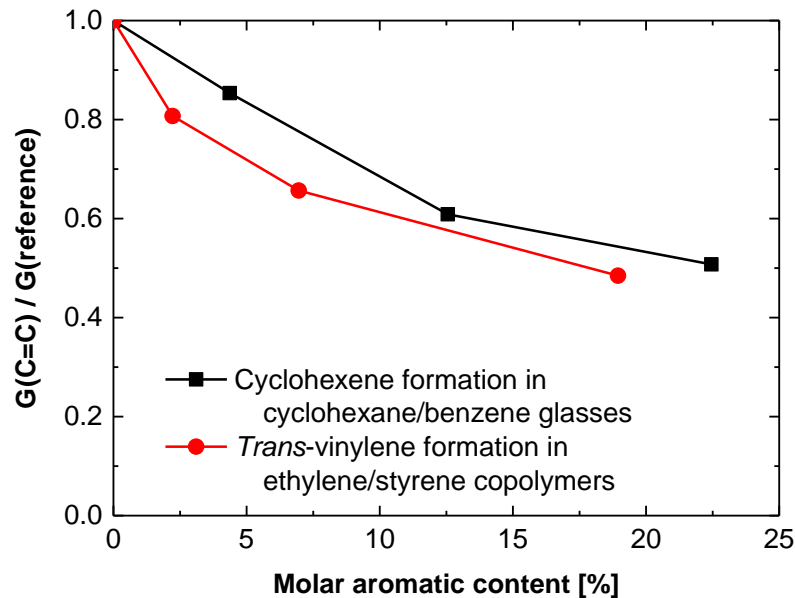
=> Why?

■ Hypotheses to explain this decrease

1. ~~Mass loss~~
2. ~~\searrow hydrogen reservoir in the polymer~~
3. Energy transfers on the radiation-induced defects
-> *Transfers of excitation, charges and radicals*

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

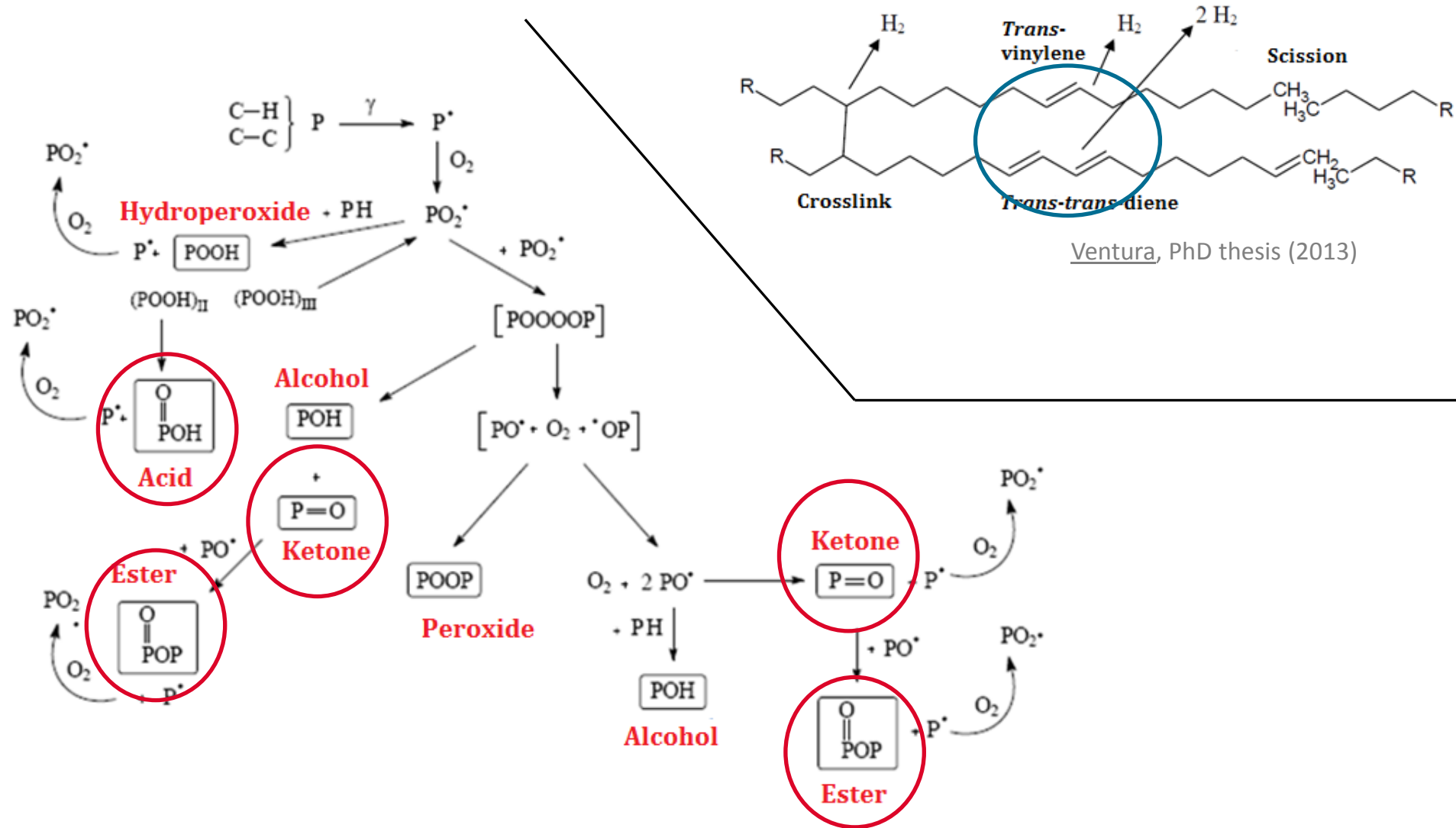
Basheer & Dole, *J. Polym. Sci.: Polym. Phys. Ed.* 22 (1984), 1313

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



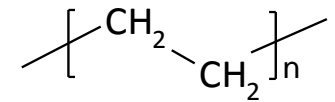
Ventura, PhD thesis (2013)

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

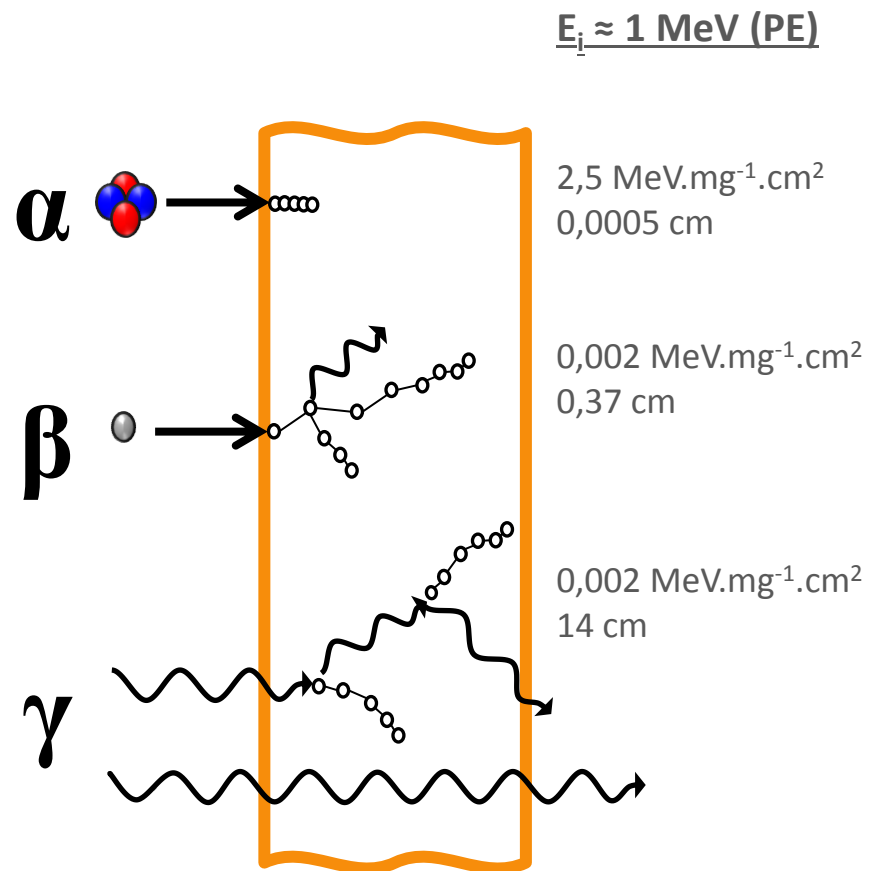
Organic material and radionuclides (RN) in the ILLW packages : α and β/γ emitters

Emitters simulation

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

Underlying mechanisms to be better understood

- Which parameters allow a decrease in the gas emission?

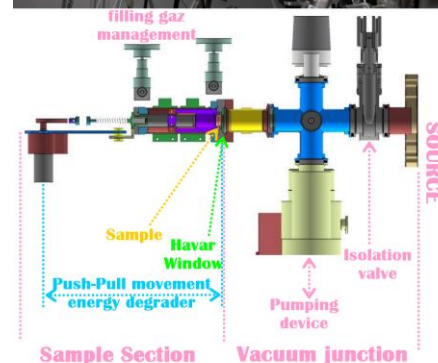
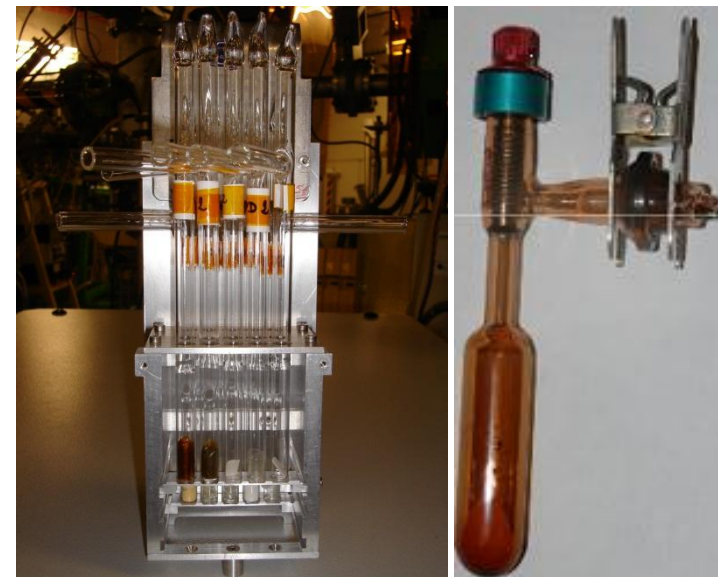


Set-ups depending on the irradiation conditions

- Closed ampoules
 - Gamma and High Energy GANIL line
- Specific devices
 - Medium Energy GANIL line
 - M-Branch GSI line

Modifications induced by irradiation followed by

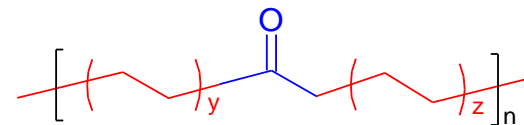
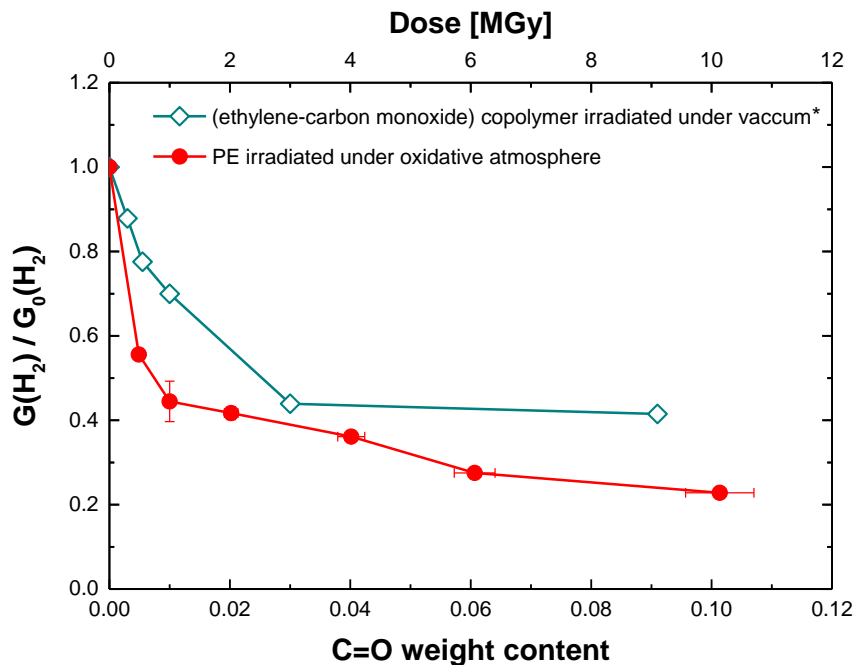
- High resolution gas mass spectrometry
- FTIR



Main results

Energy transfers on ketone ($>C=O$) bonds

Main defect under oxidative atmosphere



- Conversion dose $\Leftrightarrow [C=O]$
- $G(C=O) \sim 4 \cdot 10^{-7} \text{ mol} \cdot \text{J}^{-1}$

- $G(H_2) \searrow$ 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...)

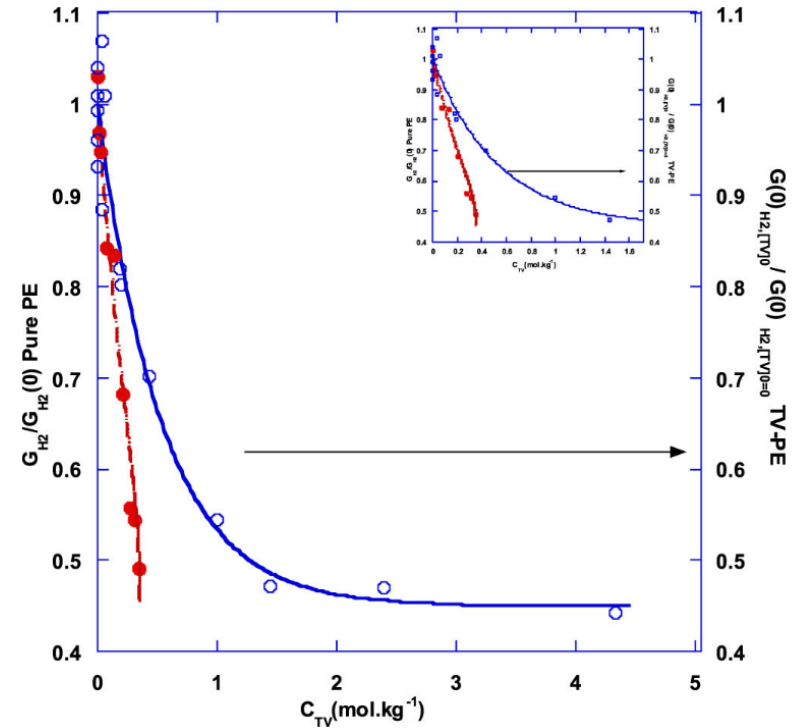
Energy transfers on vinylene (C=C) bonds

Main defect under inert atmosphere



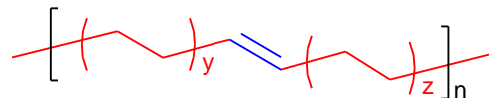
- PE containing C=C bonds
 - Saturation effect at high concentrations
 - Activity per protective bond \searrow
 - Dilution effect

- \searrow of $G(\text{H}_2)$ in both cases
 - Equivalent up to $[\text{C}=\text{C}] \approx 0.2 \text{ mol.kg}^{-1}$ in PE, *i.e.* $\approx 2 \text{ MGy}$
 - 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

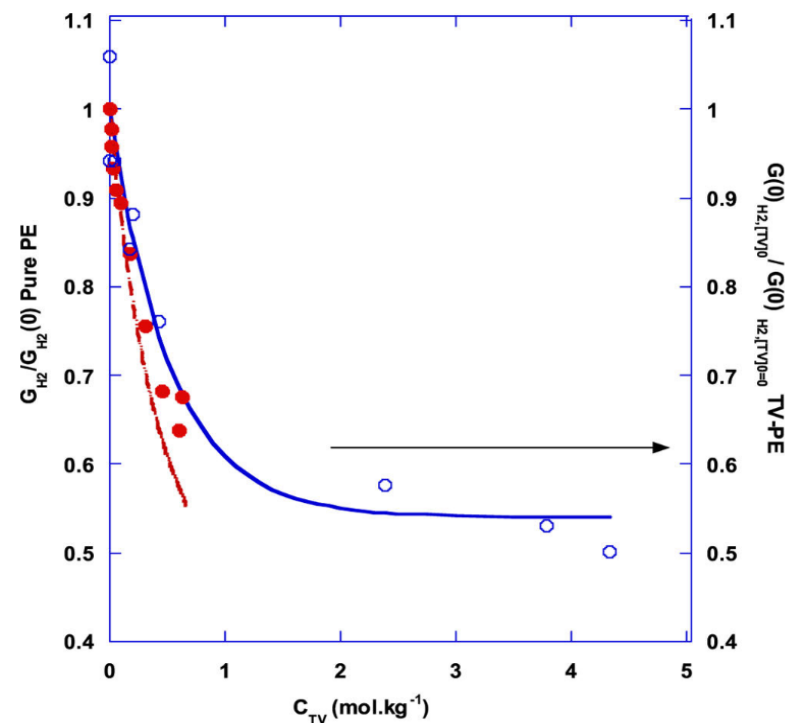


■ AT high LET using SHI

- *Trans*-vinylenes are the predominant protective bond up to $[C=C] \approx 0.6 \text{ mol.kg}^{-1}$ in PE, *i.e.* $\approx 10 \text{ MGy}$

■ Protection less effective using SHI than γ -rays

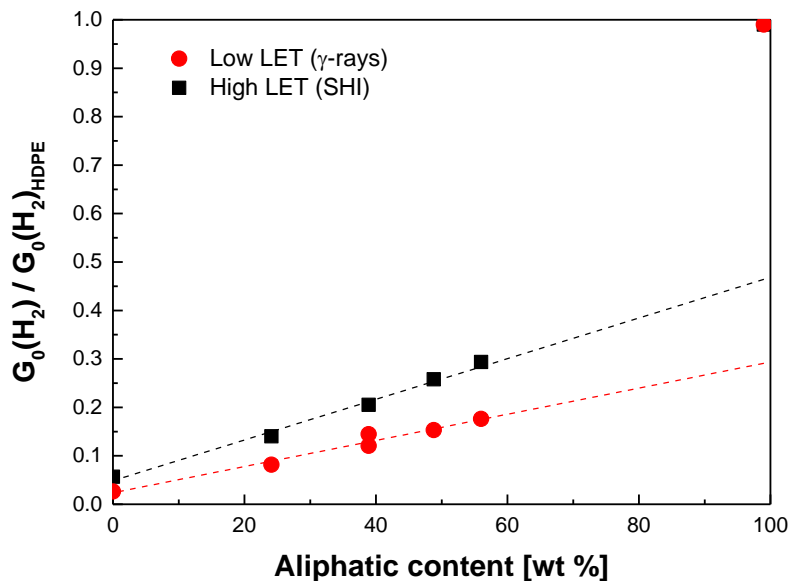
- In track recombination before migration
- Non-homogeneous radiation-induced C=C bonds repartition using SHI



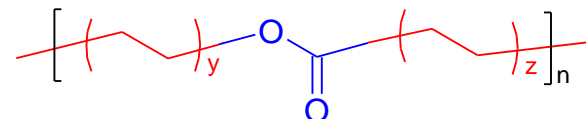
Perfect PE irradiated at high dose

PE containing C=C bonds

Inert atmosphere using SHI



Esters in the backbone



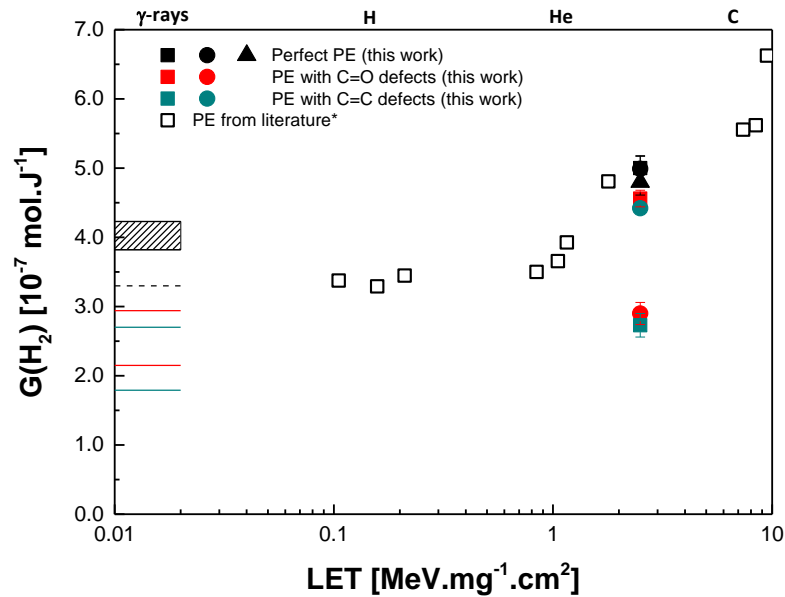
Confirmation of LET effect on in-chain ester polymers

- \searrow 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 $\approx 2/3$ for γ -rays \Leftrightarrow about $\approx 1/2$ for SHI

LET and defects position effects



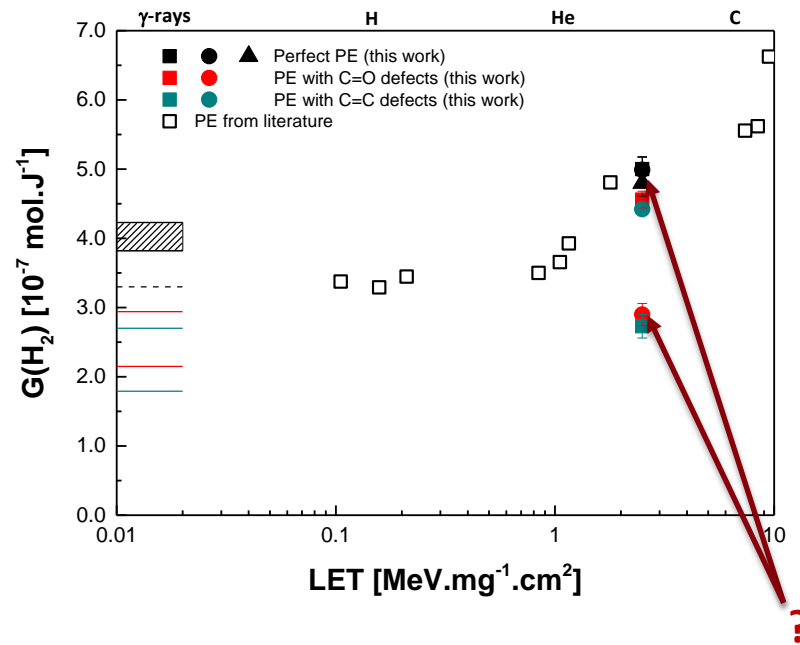
■ $G(H_2) \searrow$ with C=O and C=C bonds

■ Energy transfers effective whatever the double bond type

■ Radiation protection effect more effective at low LET than at high LET

■ In-track radicals recombination

LET and defects position effects



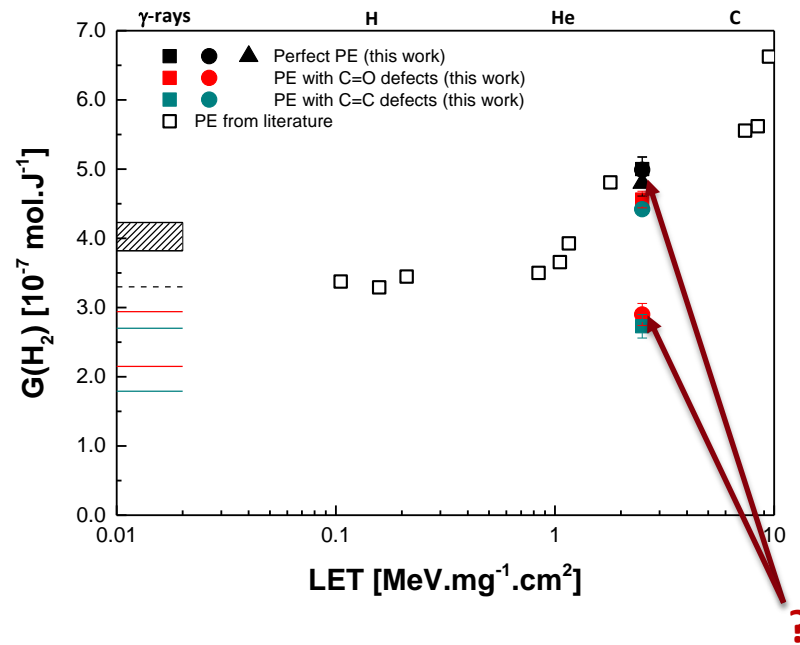
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LET and defects position effects



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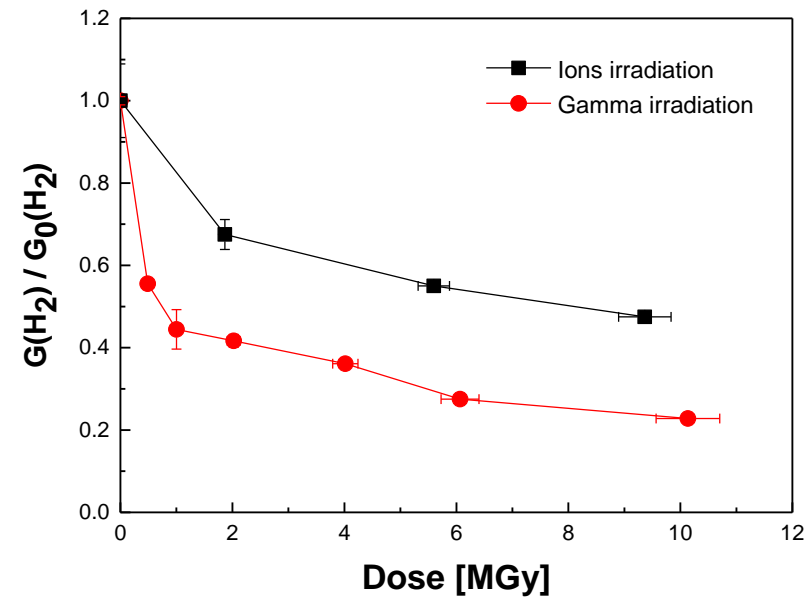
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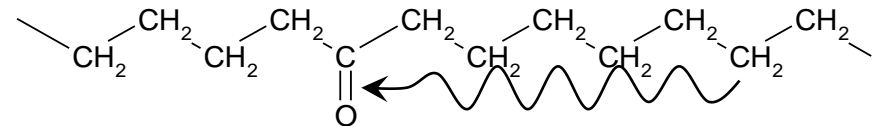
■ Differences in PE with defects due to defects position

■ Case for PE with C=C defects : defects in the backbone with lower $G(\text{H}_2)$

- 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

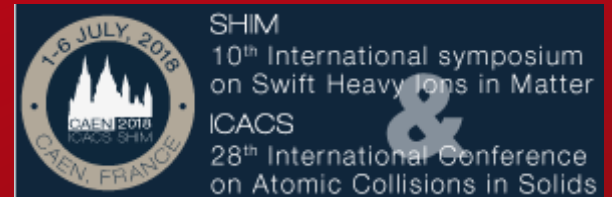


Conclusion

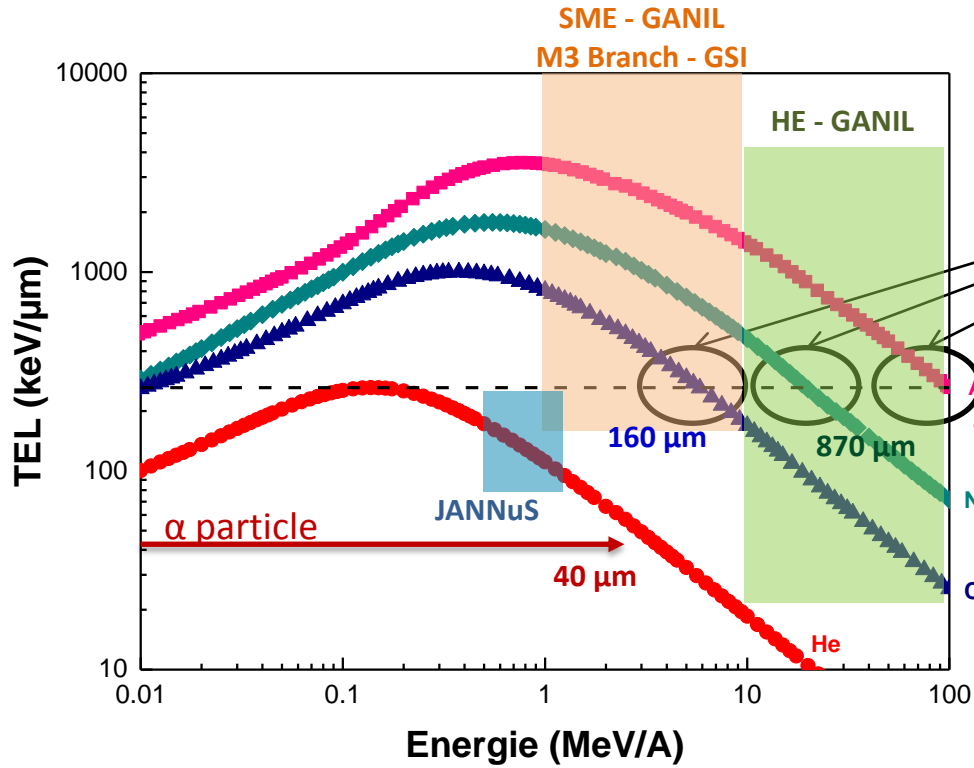
- In the deep underground repository context
 - Energy transfers decrease the hydrogen release
 - Positive effects on safety purpose
 - Up to now, $G_0(\text{H}_2) \sim 4.10^{-7} \text{ mol.J}^{-1}$ used in the nuclear safety cases
 - => *Very conservative value*
 - Update possible with detailed explanations

- 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

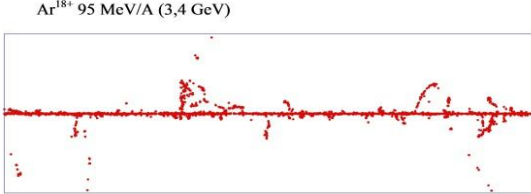
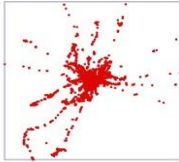
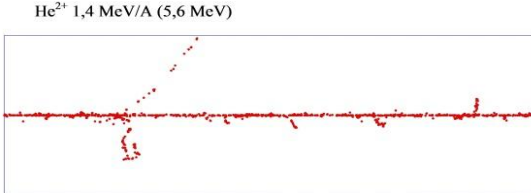
Thank you for your attention



Ion beams to simulate α irradiations ?



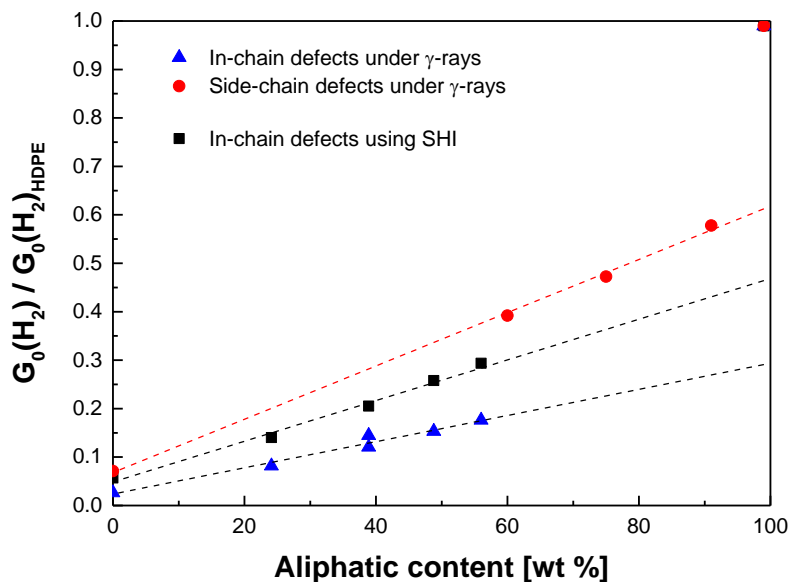
Homogeneous irradiation under several microns (case of PE)



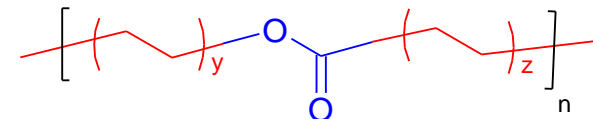
Why SHI instead of α ?

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

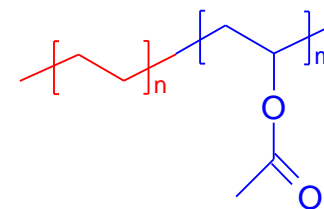
Combined effects of position and LET



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 \searrow when LET \nearrow

- But part of energy migrates out of the ions tracks

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

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