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# Direct mass spectrometry analysis for the understanding of polymers degradation

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# Direct mass spectrometry analysis for the understanding of polymers degradation

Diane Lebeau

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EUROANALYSIS 2017 – STOCKHOLM

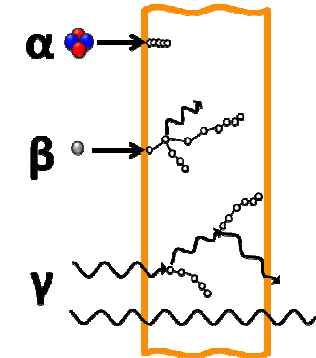
## Polymers in nuclear industry

- A wide variety of polymers
- Even if used amounts are smaller than others engineering materials (concrete, steel, zirconium, etc...), they play a crucial role as

Nitrile rubber	Fluoro elastomer	Silicone rubber	EPDM	Epoxy	Polyurethane	Acrylic
						
Seals	Seals	Hot cell sleeve Protection sheet	Seals Insulation	Paints Coating	Cable sheath Insulation Gloves	Adhesive tape

➔ To maintain a safe and cost efficient operation of nuclear power plants, an understanding of the ageing and degradation phenomena of these components is required

- Polymers (organic molecules) + radionuclides (emitters  $\alpha$  and  $\beta/\gamma$ )
- ➔ Interaction of radiation with organic matter
- ➔ Irradiation induces chemical reactions in the material

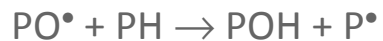
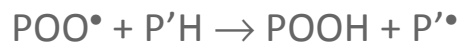
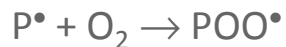


■ Mechanism under **oxidative** conditions (radiation, heat or light)

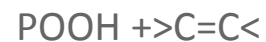
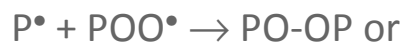
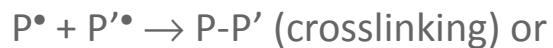
■ Initiation:



■ Propagation:



■ Termination: recombinaison



- Crosslinking:  $\nearrow$  Mw  $\rightarrow$   $\searrow$  solubility  $\rightarrow$  hardness



- Scission:  $\searrow$  Mw  $\rightarrow$   $\nearrow$  solubility  $\rightarrow$  viscous material

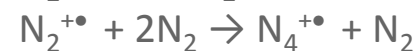


## Atmospheric Solids Analysis Probe (ASAP)

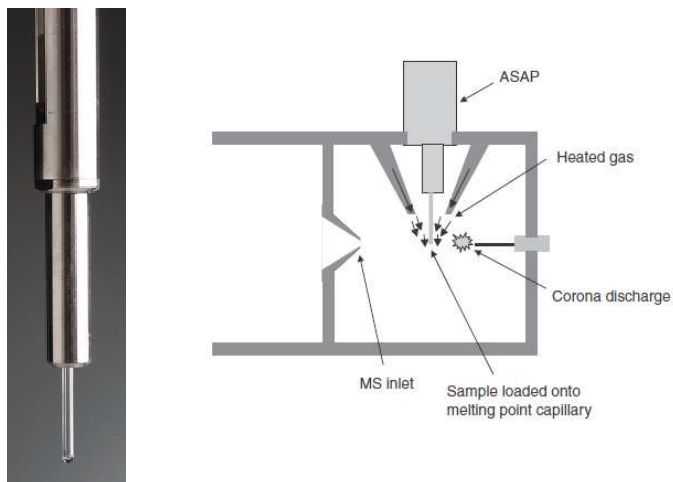
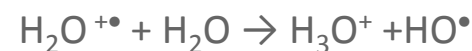
- Chemical and structural identification of unknown component analytes comprising a complex mixture → **Direct solid analysis**

- Sample deposited onto glass tube
  - Direct use of the sample
  - No solvent required
- Desorption using a hot N<sub>2</sub> flux
- Ionization from plasma generated by a corona discharge

- Charge transfer (M<sup>+•</sup>)



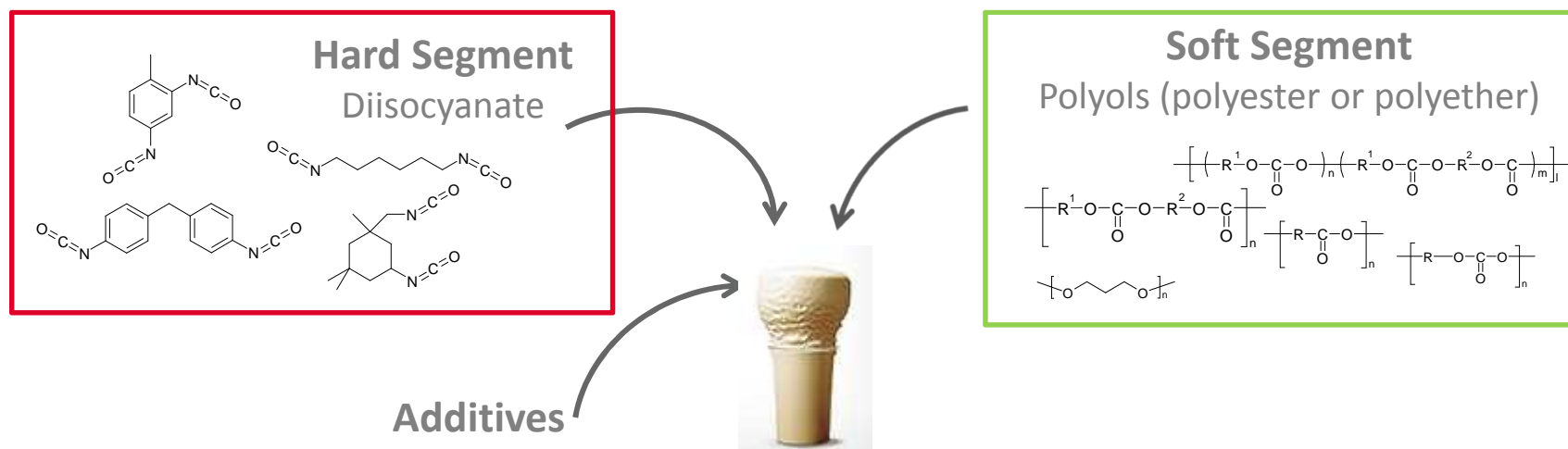
- Proton transfer (MH<sup>+</sup>)



# **POLYURETHANE ANALYSIS**

## Polyurethane synthesis

- Polyaddition of a diisocyanate to a polyol in the presence of additives

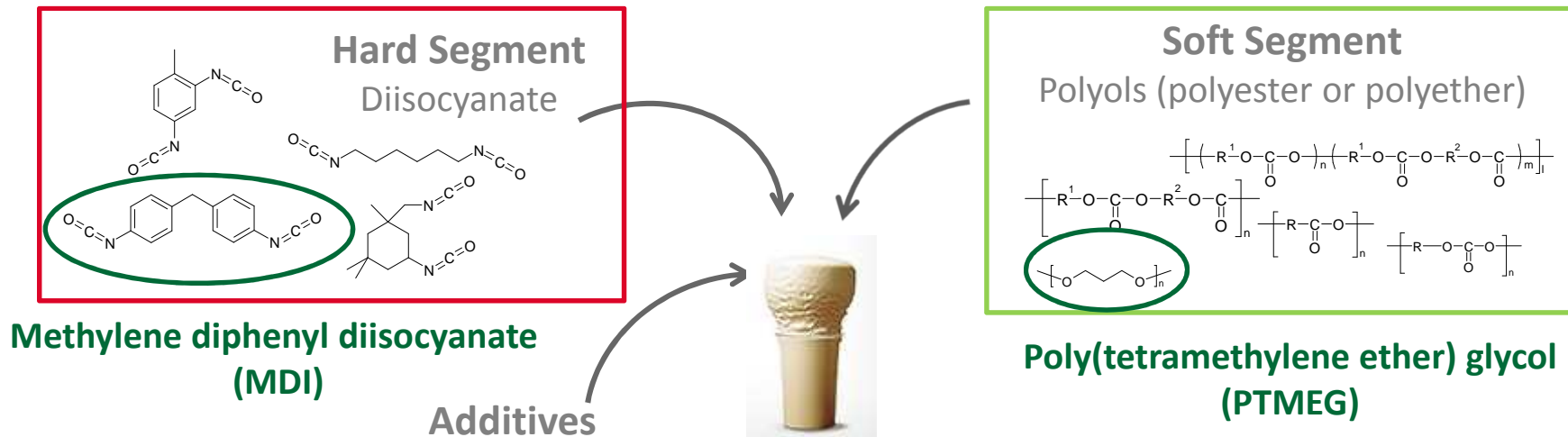


- Complex composition and different structures
- Copolymer → difficult to characterize directly by MS without sample treatment:
  - preliminary dissociation of each segment from the copolymer (e.g. pyrolysis or chemical dissociation)
  - Py-GC/MS and/or MALDI/MS

⇒ **Aim: direct analysis of PU by mass spectrometry**

## Polyurethane synthesis

- Polyaddition of a diisocyanate to a polyol in the presence of additives



**Electric cable  
sheath**

**Non irradiated**



Dose rate: 0.6 à 0.75 kGy/h  
 →  
 Oxidative conditions

**2 MGy**



**10 MGy**

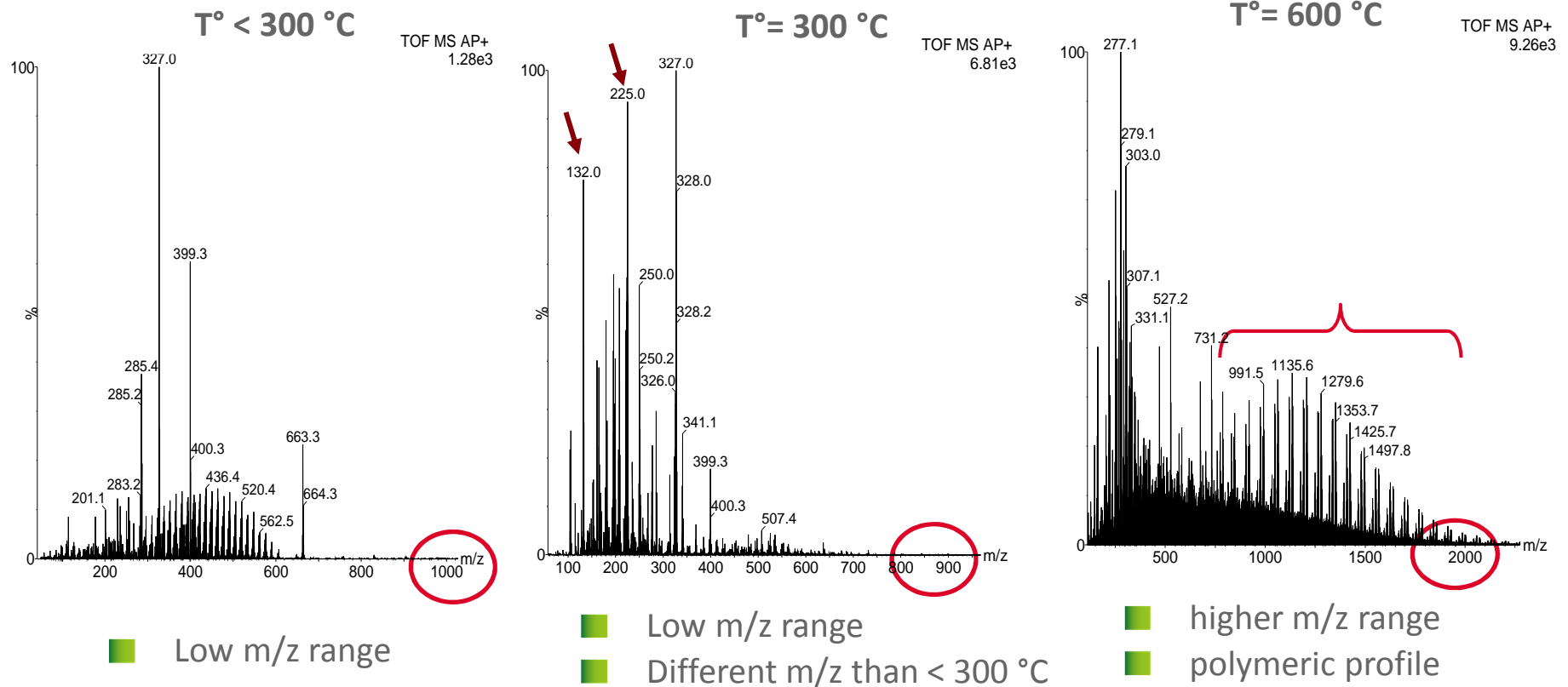




Non irradiated

## ASAP: thermal plasma desorption

→ analysis of sample at different temperatures

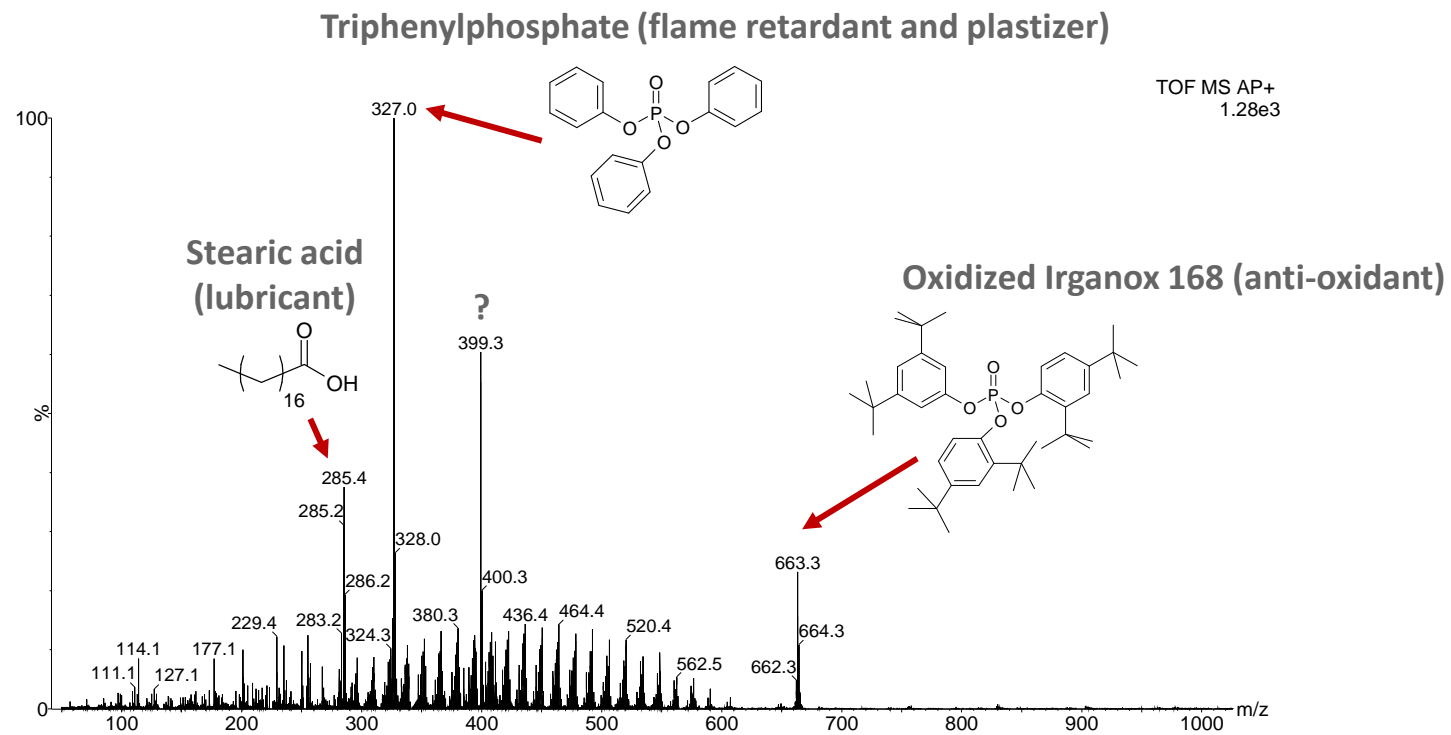


→ Desorption of compounds with temperature

Analysis at low temperature ( $T^\circ < 300^\circ\text{C}$ )

Non irradiated

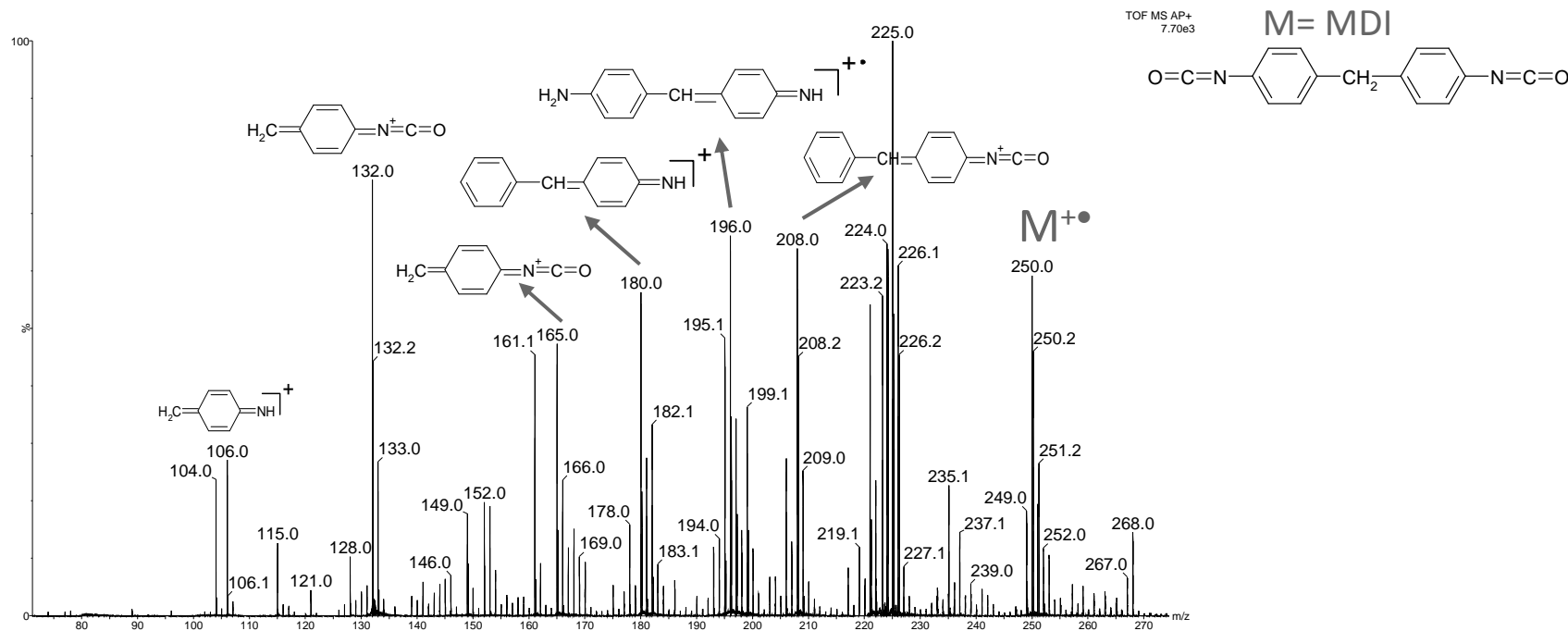
■ TOF analyzer → exact mass measurements → additives identification



■ At low desorption temperature → detection of additives of the polymer

Analysis at 300°C

Non irradiated

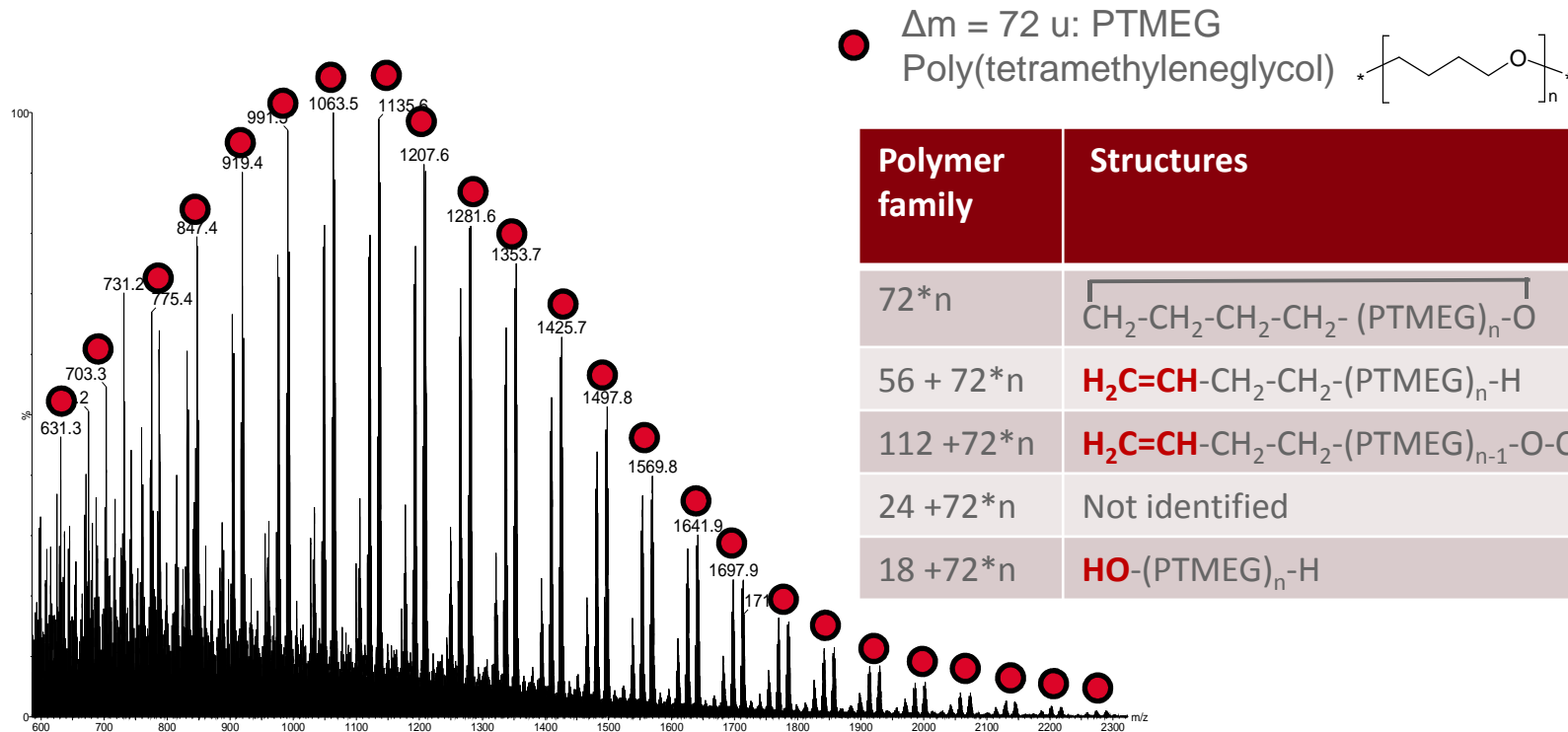


- Detection of molecular ion  $M^{+\bullet}$  for MDI
- Detection of characteristic thermal degradation products of MDI  $\Rightarrow$  Structural identification of the PU **Hard Segment**

Analysis at high temperature ( $T^\circ = 600^\circ\text{C}$ )

Non irradiated

Detection of a characteristic polymeric profile

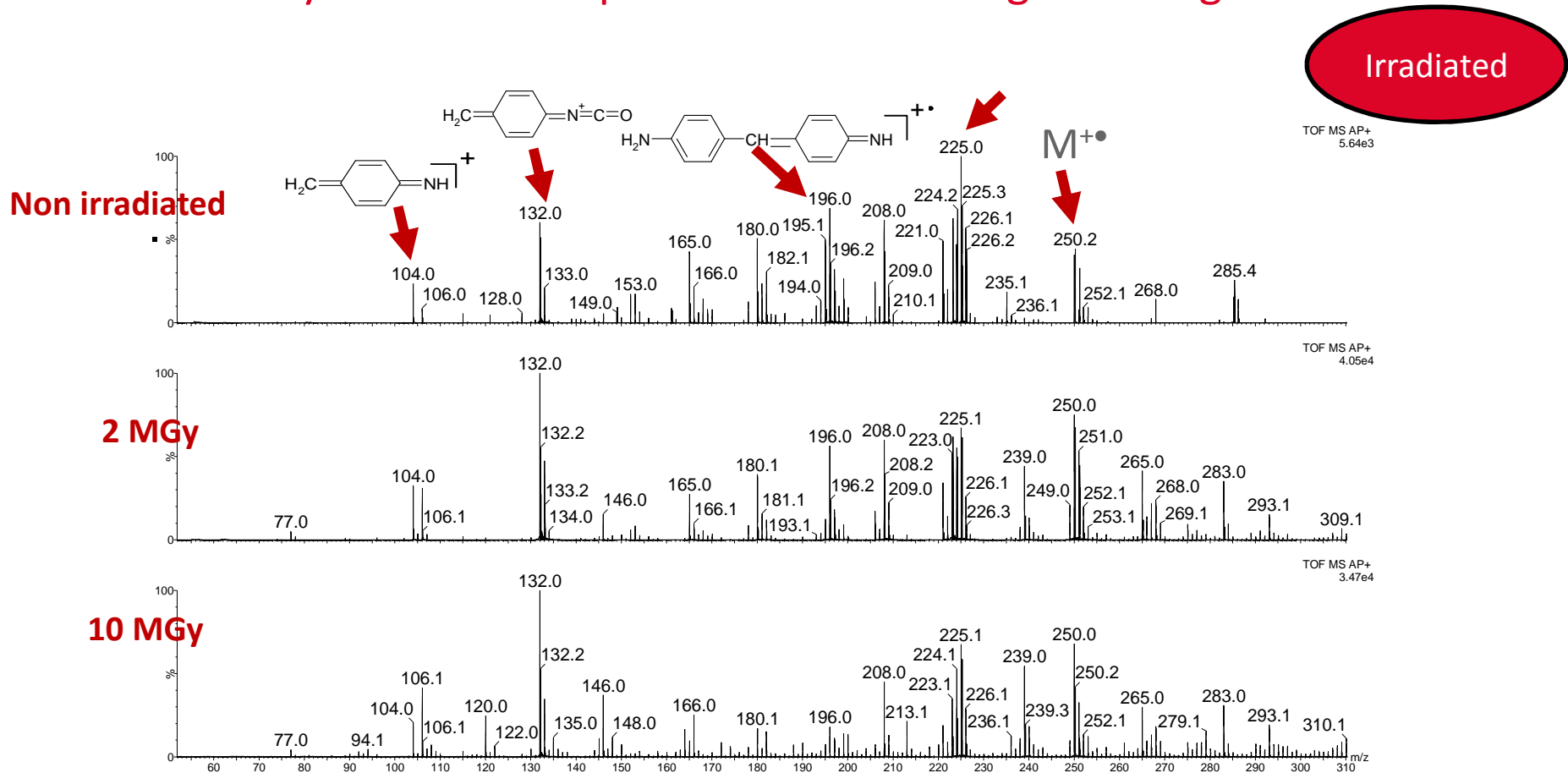


$\Delta m = 72 \text{ u}$ : PTMEG  $\rightarrow$  detection of Soft Segment

Thermal degradation products  $\rightarrow$  Structural identification of Soft Segment of PU

$\rightarrow$  Desorption of the copolymer components can be controlled by temperature

Analysis at low temperature → Hard Segment degradation

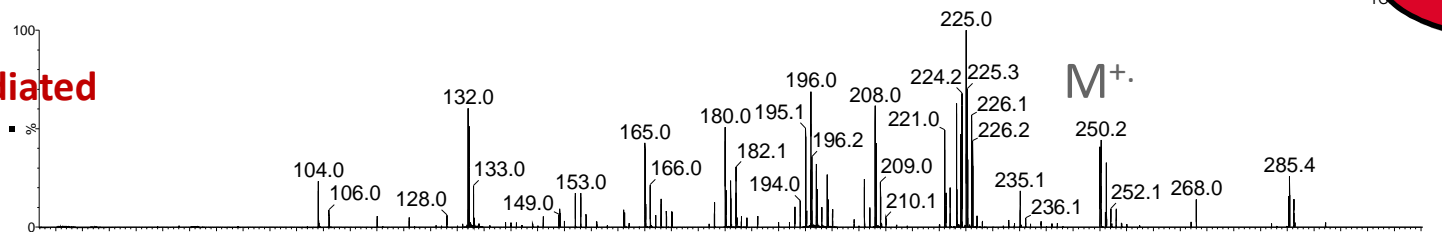


- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI
- Impact on Hard Segment seems low

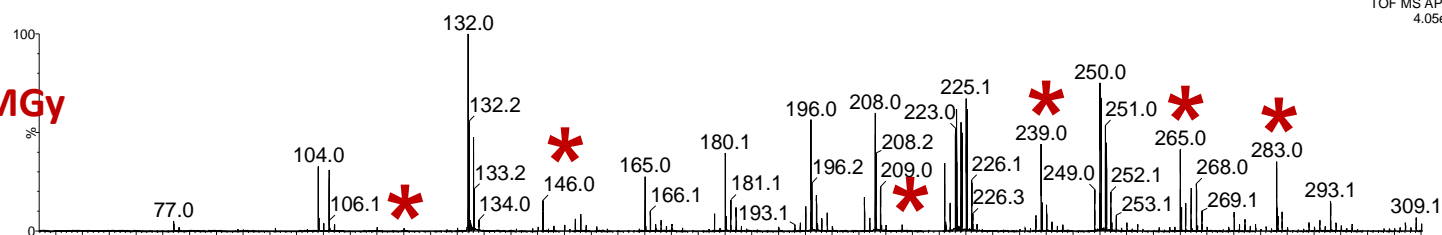
Analysis at low temperature → Hard Segment degradation

Irradiated

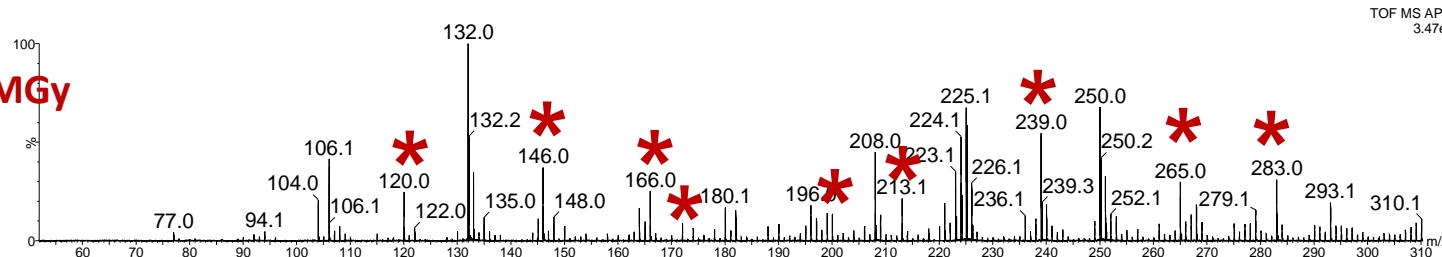
Non irradiated



2 MGy



10 MGy



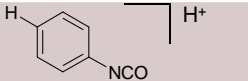
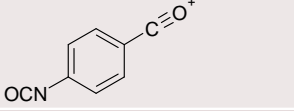
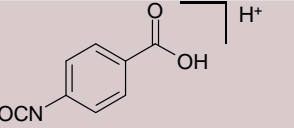
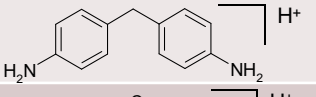
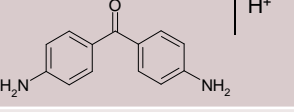
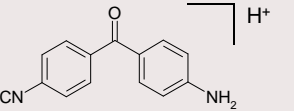
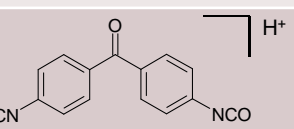
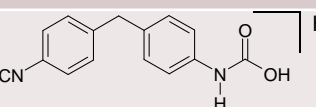
Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI

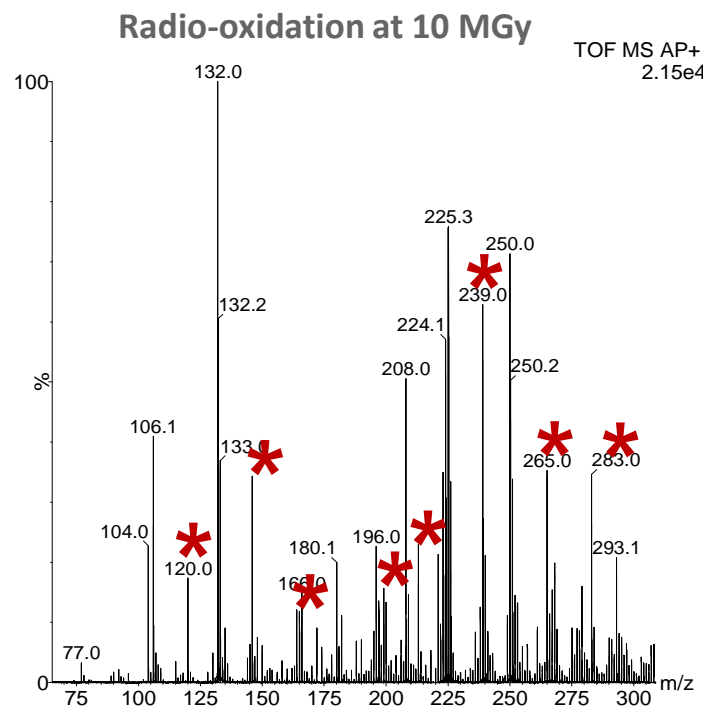
→ impact of radiolysis on Hard Segment seems low

\* However some new signals are detected

## Identification of **hard** segment degradation molecules

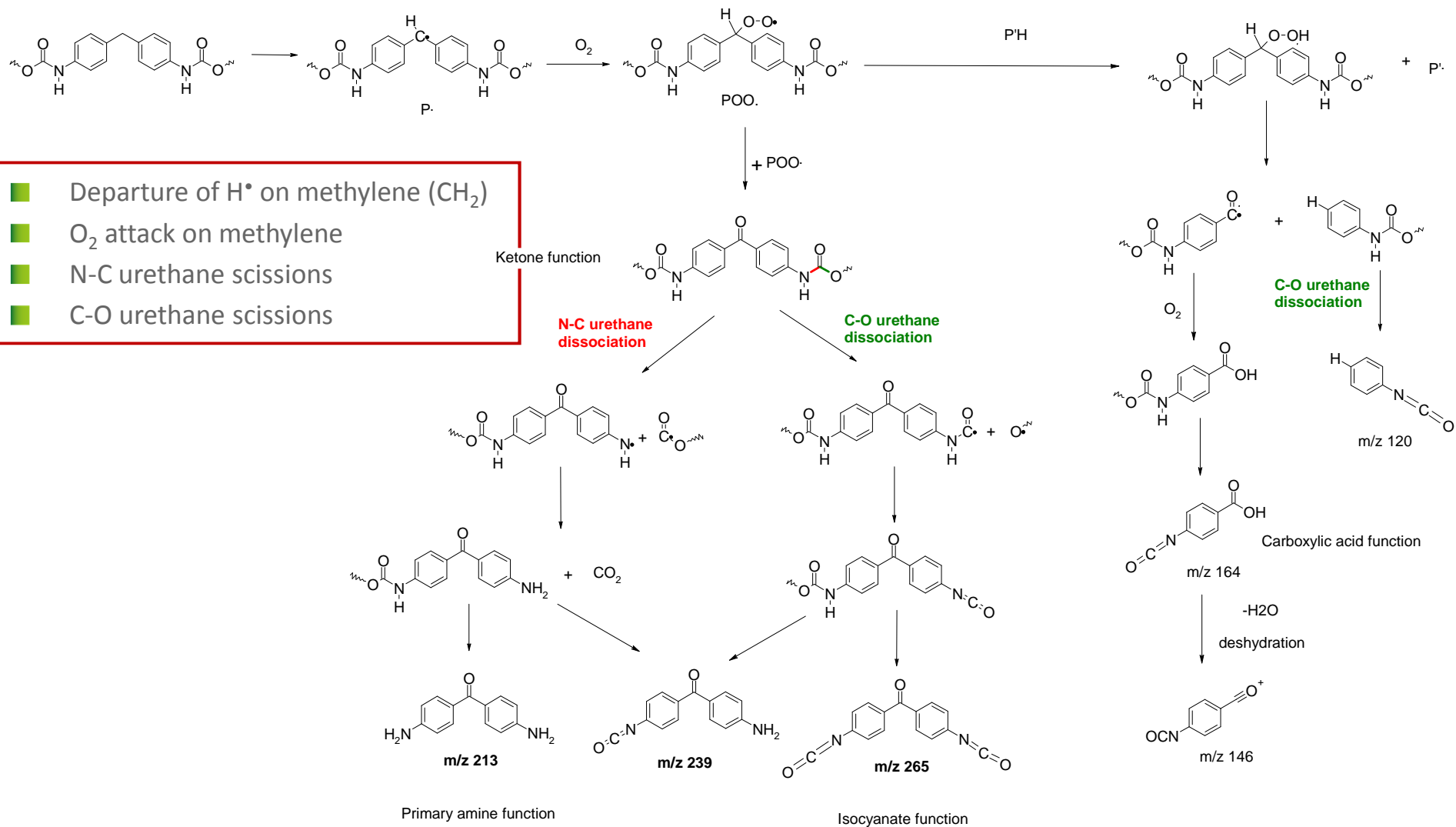
Irradiated

m/z	Fragments structure	2 MGy	10 MGy
120		X	X
146		X	X
164			X
199			X
213		X	X
239		X	X
265		X	X
283		X	X



→ carbonyl and carboxylic acid  
functions → oxidation reaction

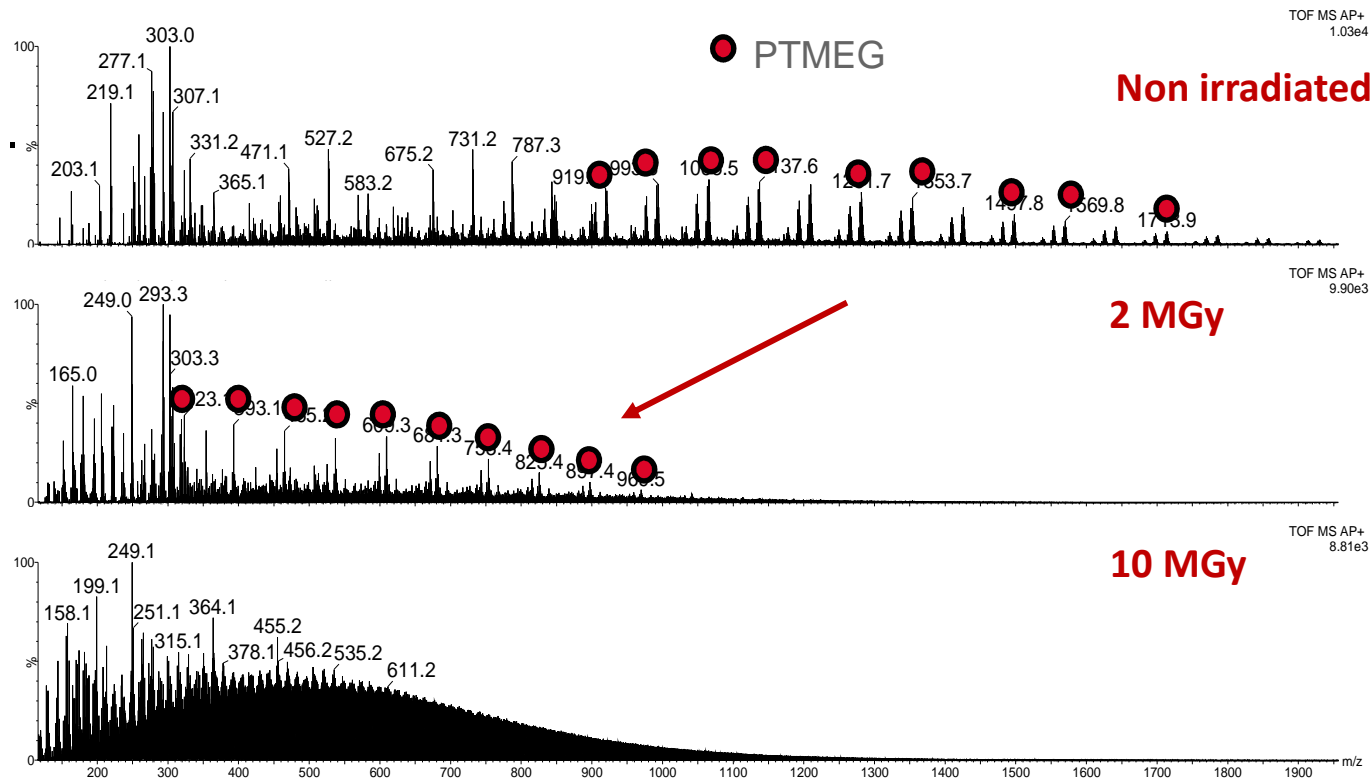
# PROPOSED MECHANISM OF HARD SEGMENT DEGRADATION





Analysis at high temperature → Soft Segment degradation

Irradiated

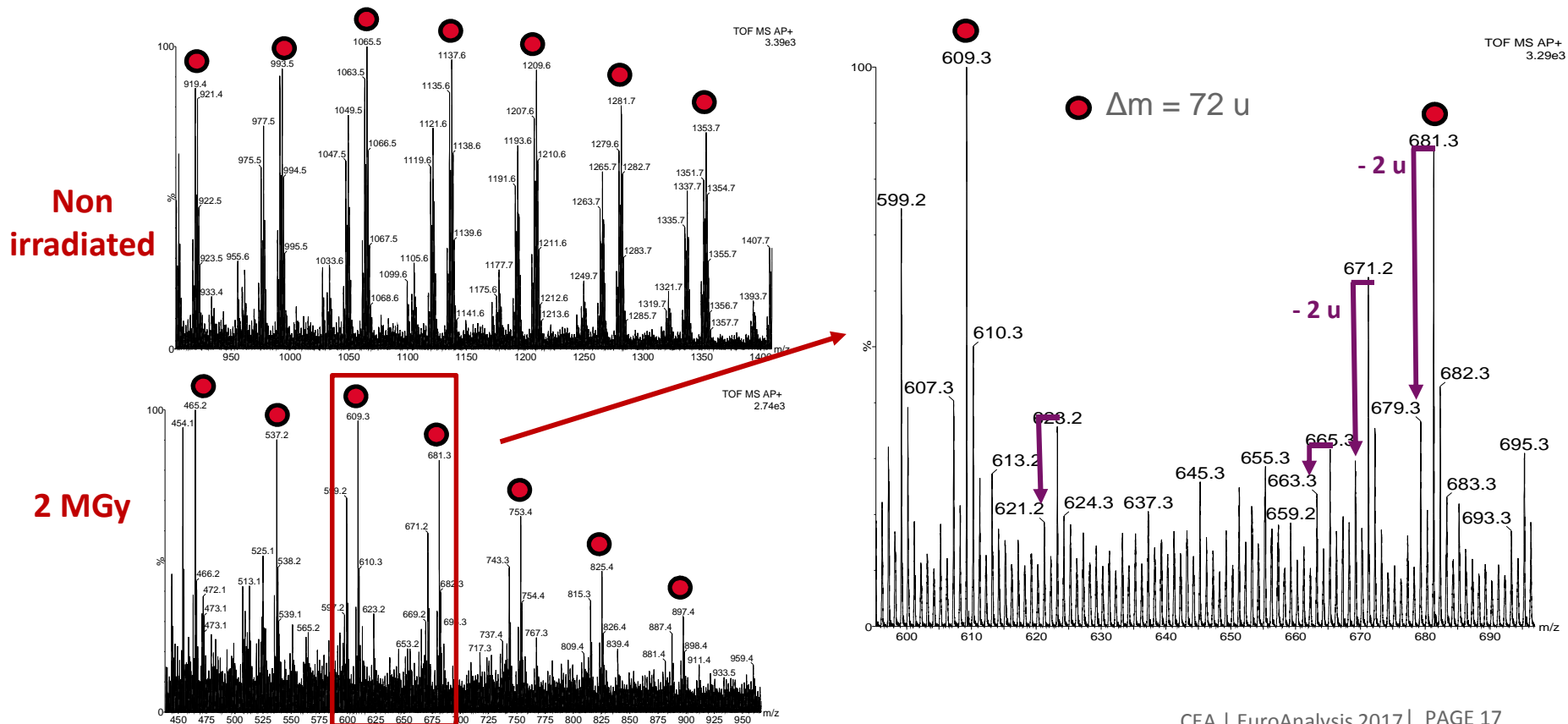


- Very different mass spectra with the dose
- Important impact on Soft Segment of the irradiation

## Identification of degraded polymers families after irradiation

Irradiated

- █ ↗ of the number of signals between repeating units after irradiation
- █ Several signals separated of 2 u → characteristic of presence of **unsaturation or crosslinking**

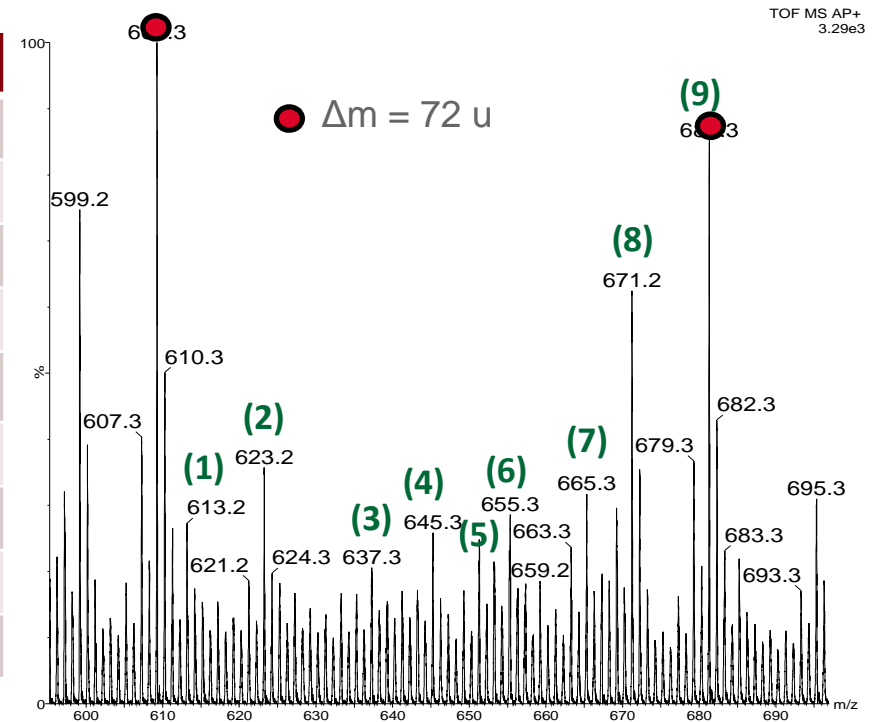


## Identification of degraded polymers families after irradiation

Irradiated

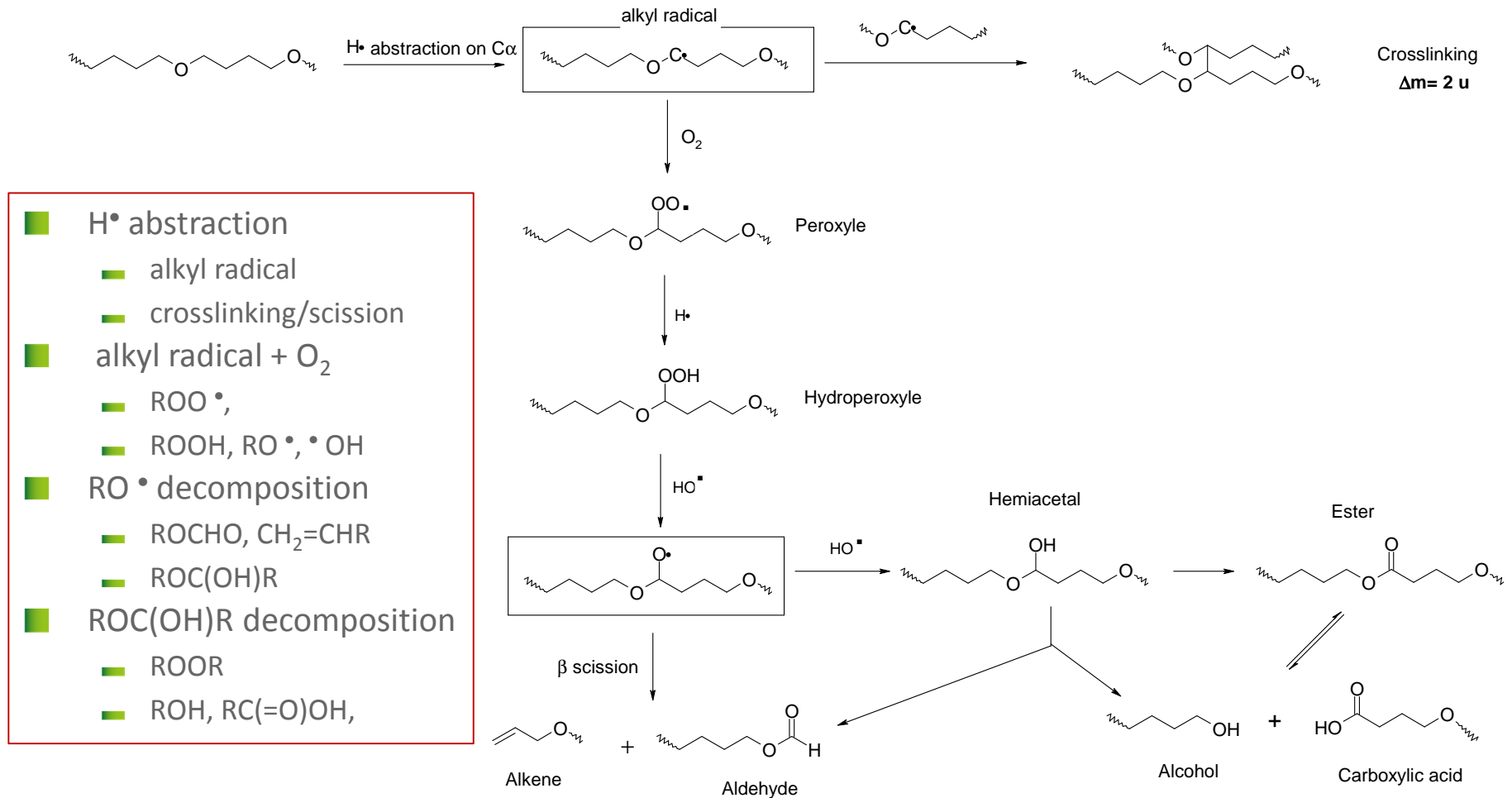
- ↗ of the number of signals between repeating units after irradiation
- Several signals separated of 2 u → characteristic of presence of **unsaturation or crosslinking**

Family	m/z	Structures
(1)	36 + 72*n	Non identified
(2)	46 + 72*n	HO-(PTMEG) <sub>n</sub> -CHO
(3)	60 + 72*n	HO-CH <sub>2</sub> -(PTMEG) <sub>n</sub> -CHO
(4)	68 + 72*n	H <sub>3</sub> C-CH=CH <sub>2</sub> -(PTMEG) <sub>n</sub> -CH=CH <sub>2</sub>
(5)	74 + 72*n	H <sub>3</sub> C-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -O-(PTMEG) <sub>n</sub> -H
(6)	78 + 72*n	HO-CH <sub>2</sub> -O-CH(OH)-(PTMEG) <sub>n</sub> -OH
(7)	88 + 72*n	HO-(CH <sub>2</sub> ) <sub>3</sub> -CH(OH)-(PTMEG) <sub>n</sub> -H
(8)	94 + 72*n	HO-CH <sub>2</sub> -O-CH(OH)-(PTMEG) <sub>n</sub> -OH
(9)	104 + 72*n	HOOC-(CH <sub>2</sub> ) <sub>3</sub> -(PTMEG) <sub>n</sub> -OH



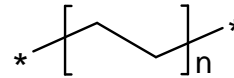
- Oxidized functions: alcohol, hemiacetal, carboxylic acid and aldehyde
- Unsaturation function: alkenes

## Proposed mechanism of **Soft** Segment degradation



# **POLYETHYLENE ANALYSIS**

## Structural composition



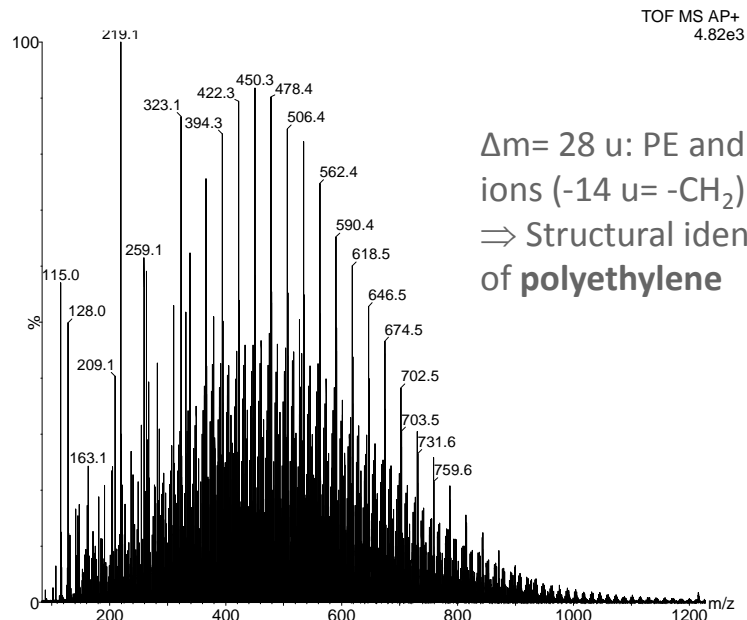
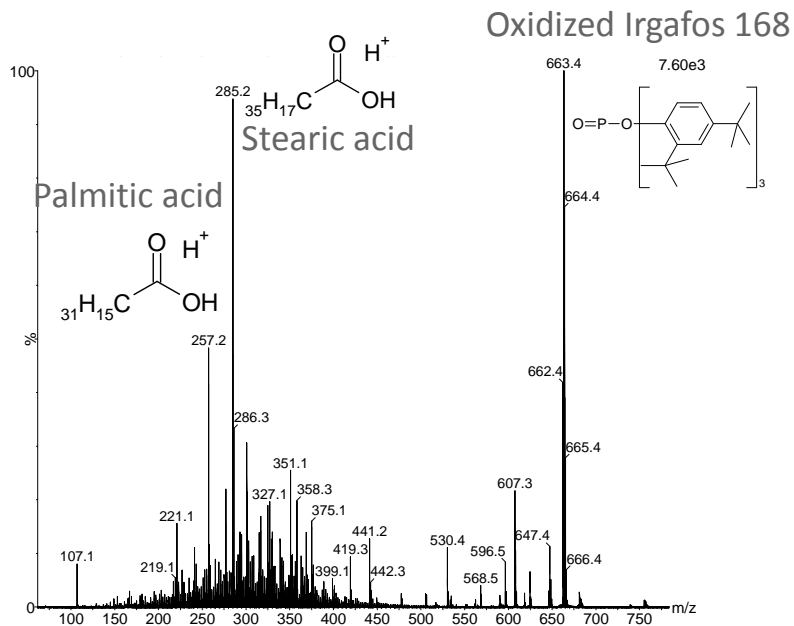
- Saturated, aliphatic hydrocarbons
- Difficulty of mass spectrometry analysis: large saturated polymer without heteroatoms

## ASAP-MS analysis of non irradiated PE

Non irradiated

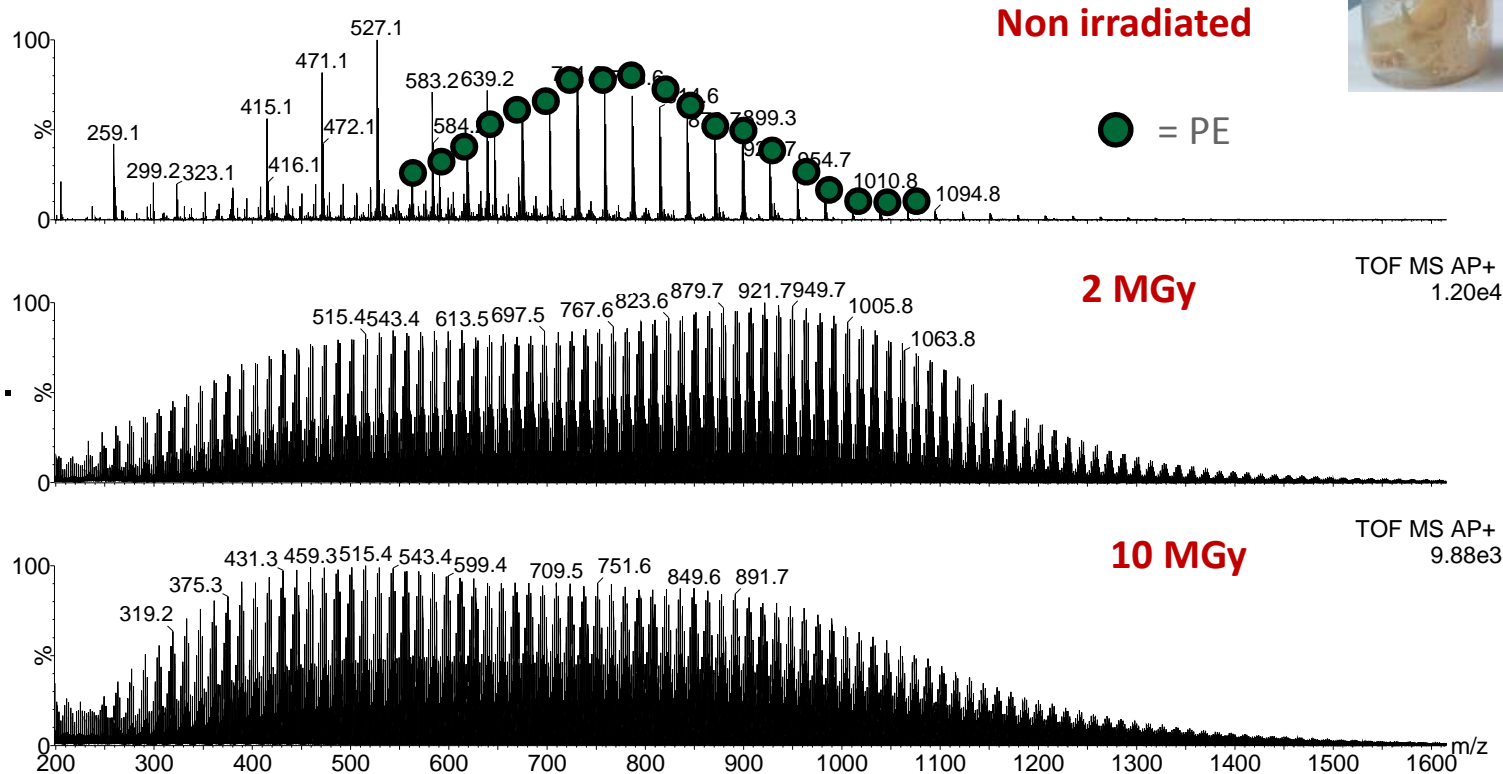
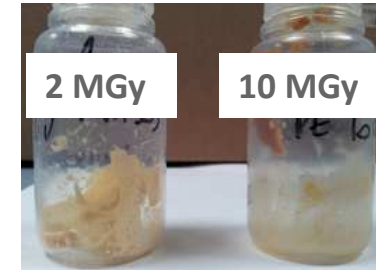
T°= 300 °C

T°= 500 °C



$\Delta m = 28 \text{ u}$ : PE and fragments ions (-14 u = -CH<sub>2</sub>)  
 ⇒ Structural identification of polyethylene

Irradiated PE analyzed at same T°

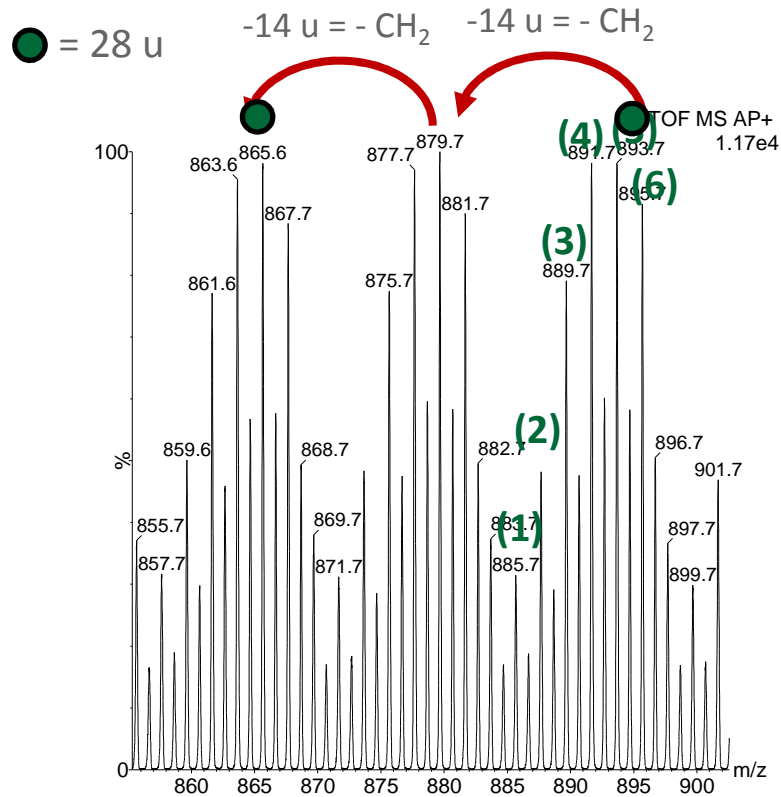


- Very different mass spectra after irradiation at 2 and 10 Mgy → Important impact of radio-oxidation
- Similar mass spectra after irradiation at 2 and 10 MGy

## PE after irradiation at 2 MGy

Irradiated

■ Mainly  $\Delta m = 2$  u → unsaturation and/or crosslinking



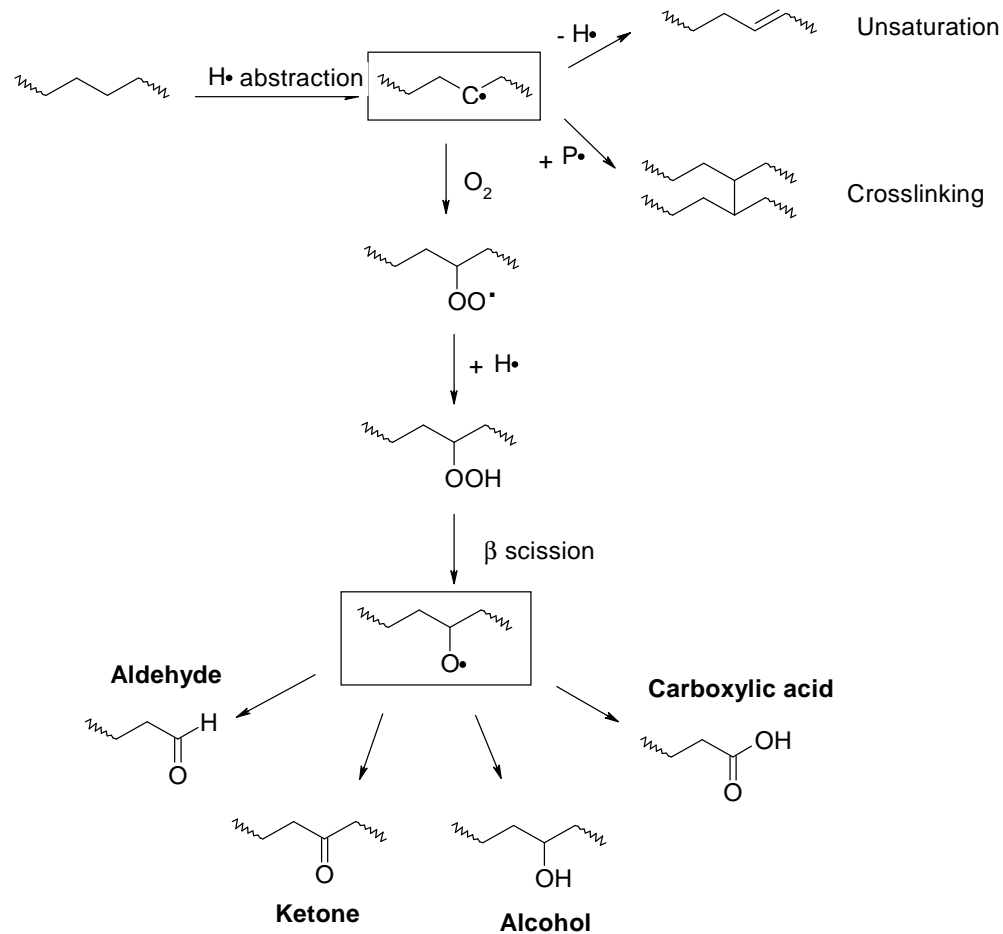
	polymer	Structures
(1)	44 + 28*n	<b>H<sub>3</sub>C-CO-(PE)<sub>n</sub>-H</b>
(2)	46 + 28*n	<b>H<sub>3</sub>C-CH(OH)-(PE)<sub>n</sub>-H</b> <b>HOOC-(PE)<sub>n</sub>-H</b>
(3)	48 + 28*n	<b>HO-H<sub>2</sub>C-(PE)<sub>n</sub>-OH</b>
(4)	78 + 28*n	<b>HO-COO-(PE)<sub>n</sub>-OH</b>
(5)	52 + 28*n	Non identified
(6)	54 + 28*n	<b>H<sub>2</sub>C=CH-(PE)<sub>n</sub>-CH=CH<sub>2</sub></b>

→ Oxidized functions: alcohol, carboxylic acid and aldehyde

→ Unsaturation function: alkenes



## Proposed mechanism of PE degradation



### ASAP-MS for analysis of degraded polymers

- Fast analysis (< 1 min)
- No sample preparation
- Complete characterization of polymer and copolymer
  - Detection of additives
  - Temporal separation of molecules in function of their volatilization and/or degradation temperature
  - Identification of degraded products after irradiation
    - Sensibility of different segment to irradiation
    - Mechanisms of degradation could be proposed
    - In one analysis: same results observed as those obtained with several techniques (FTIR, MS, UV, TGA, etc...)

### Perspectives

- Semi-quantification of degraded products with the doses
- Analysis at lower doses to explore impact of additives

# Thank you for your attention.

## ACKNOWLEDGMENTS

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**Jean Luc Roujou**

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