Direct mass spectrometry analysis for the understanding of polymers degradation

Diane Lebeau

DE LA RECHERCHE À L'INDUSTRIE

cea den

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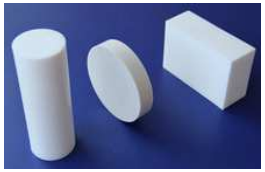
EUROANALYSIS 2017 – STOCKHOLM

INTRODUCTION

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

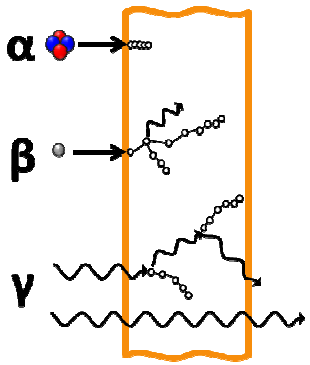
➔ To maintain a safe and cost efficient operation of nuclear power plants, an understanding of the ageing and degradation phenomena of these components is required

INTERACTION OF RADIATION WITH ORGANIC MATTER

- Polymers (organic molecules) + radionuclides (emitters α and β/γ)

➔ Interaction of radiation with organic matter

➔ Irradiation induces chemical reactions in the material



- Mechanism under **oxidative** conditions (radiation, heat or light)
  - Initiation:

    $PH \rightarrow P^{\bullet} + H^{\bullet}$
  - Propagation:

    $P^{\bullet} + O_2 \rightarrow POO^{\bullet}$

    $POO^{\bullet} + P'H \rightarrow POOH + P'^{\bullet}$

    $POOH \rightarrow PO^{\bullet} + HO^{\bullet}$

    $PO^{\bullet} + PH \rightarrow POH + P^{\bullet}$

    $HO^{\bullet} + PH \rightarrow HOH + P^{\bullet}$
  - Termination: recombinaison

    $P^{\bullet} + P'^{\bullet} \rightarrow$ P-P' (crosslinking) or

    PH + >C=C< (dismutation)

    $P^{\bullet} + POO^{\bullet} \rightarrow$ PO-OP or

    POOH +>C=C<

    $POO^{\bullet} + POO^{\bullet} \rightarrow$ Inactive products + O_2

- Crosslinking: ↗ Mw ➔ ↘ solubility to insolubility ➔ hardness

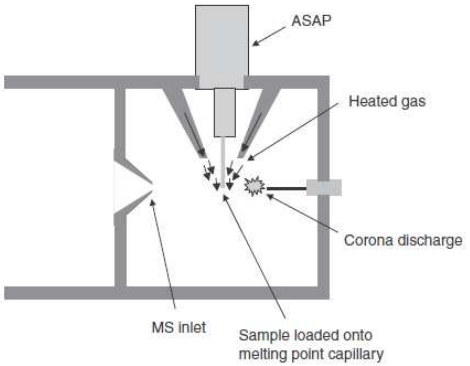
- Scission: ↘ Mw ➔ ↗ solubility ➔ viscous material

2 MGy **10 MGy**

A. Rivaton et al. Polymer Degradation and Stability 91 (2006) 136

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_2 flux
  - Ionization from plasma generated by a corona discharge



- Charge transfer ($M^{+\bullet}$)

$N_2 + e^- \rightarrow N_2^{+\bullet} + 2e^-$

$N_2^{+\bullet} + 2N_2 \rightarrow N_4^{+\bullet} + N_2$

$N_4^{+\bullet}$ (or $N_2^{+\bullet}$) + **M** → **$M^{+\bullet}$** + xN_2

- Proton transfer (MH+)

$N_4^{+\bullet} + H_2O \rightarrow H_2O^{+\bullet} + N_2$

$H_2O^{+\bullet} + H_2O \rightarrow H_3O^+ + HO^\bullet$

$H_3O^+ + n(H_2O) + N_2 \rightarrow H^+(H_2O)_n + N_2$

$H^+(H_2O)_n$ + **M** → **MH^+** + $n(H_2O)$

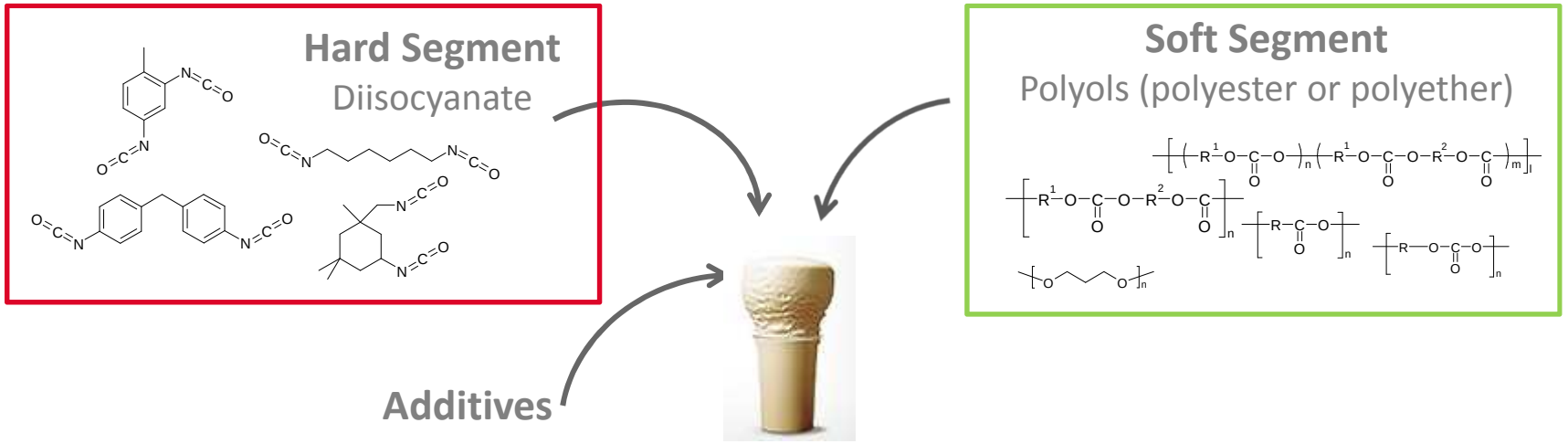
Charles N. McEwen, et al., *Anal. Chem.* 2005, 77, 7826-7831

POLYURETHANE ANALYSIS

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

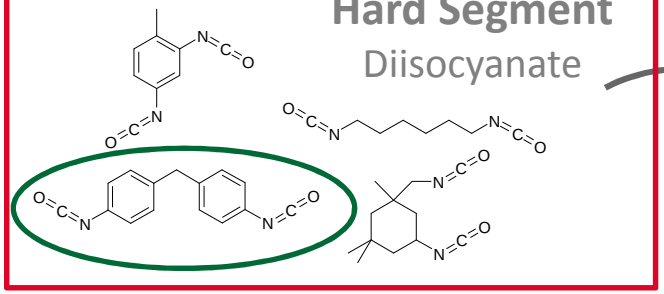
⇒ **Aim: direct analysis of PU by mass spectrometry**

POLYURETHANE ANALYSIS

Polyurethane synthesis

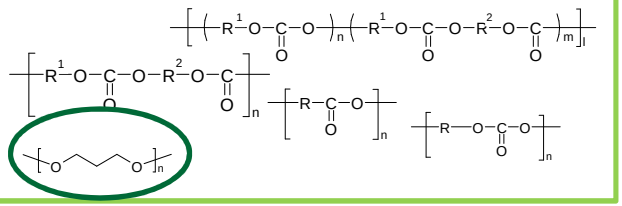
- Polyaddition of a diisocyanate to a polyol in the presence of additives

Hard Segment
Diisocyanate



Methylene diphenyl diisocyanate (MDI)

Soft Segment
Polyols (polyester or polyether)



Poly(tetramethylene ether) glycol (PTMEG)

Additives

Electric cable sheath

Non irradiated

Dose rate: 0.6 à 0.75 kGy/h

Oxidative conditions

2 MGy

10 MGy

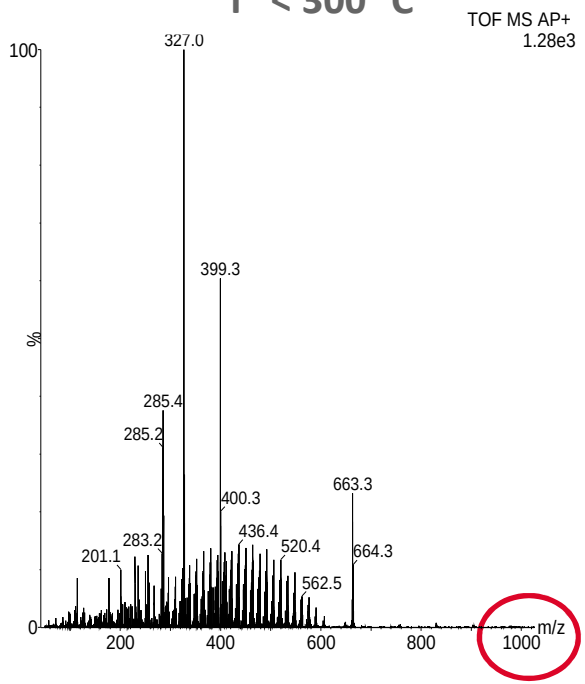
ASAP ANALYSIS: NON IRRADIATED MATERIAL

ASAP: thermal plasma desorption

Non irradiated

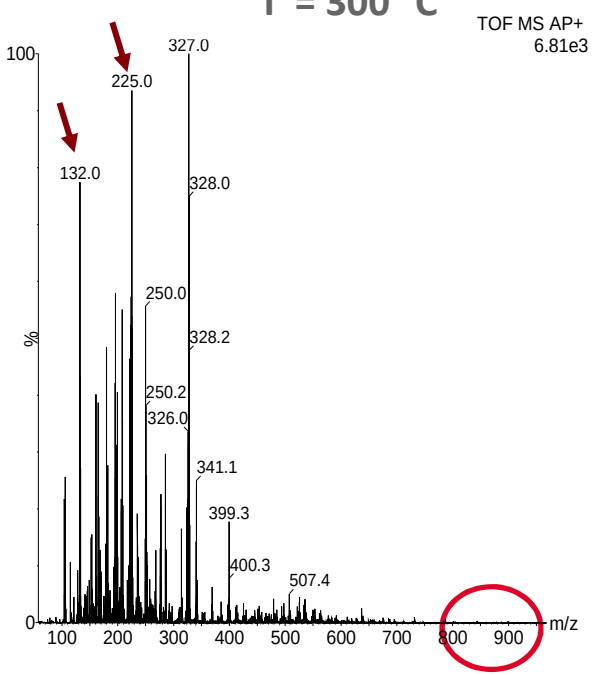
➔ analysis of sample at different temperatures

T° < 300 °C



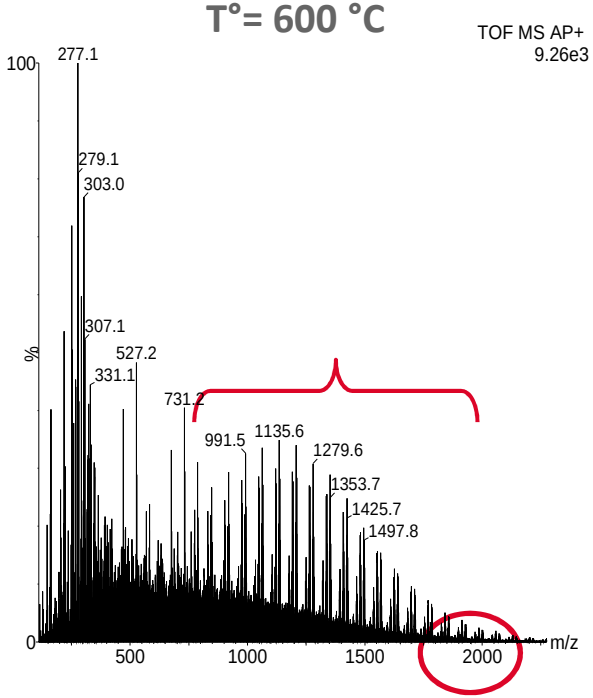
- Low m/z range

T°= 300 °C



- Low m/z range
- Different m/z than < 300 °C

T°= 600 °C



- higher m/z range
- polymeric profile

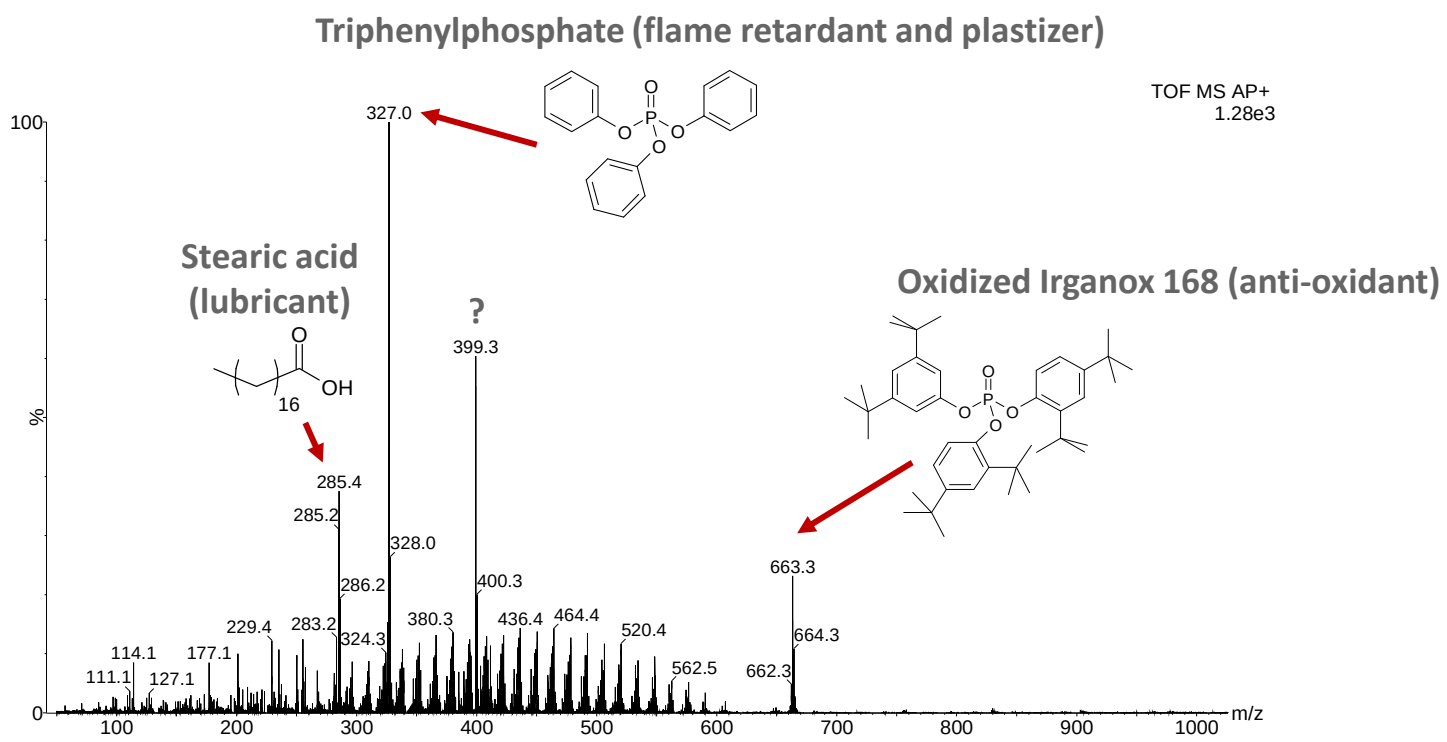
➔ **Desorption of compounds with temperature**

ASAP ANALYSIS OF A CABLE SHEATH (PU)

Analysis at low temperature (T° < 300°C)

Non irradiated

- TOF analyzer → exact mass measurements → additives identification

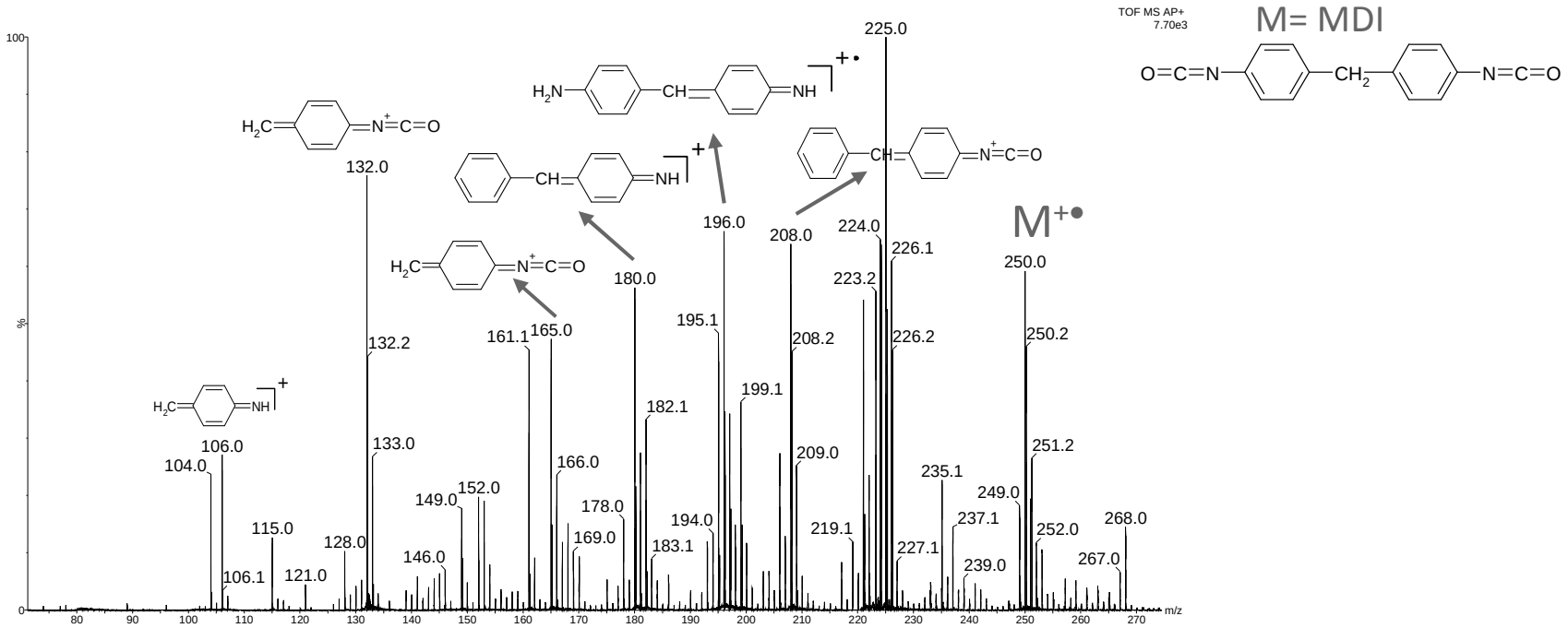


- At low desorption temperature ➔ detection of additives of the polymer

ASAP ANALYSIS OF A CABLE SHEATH (PU)

Analysis at 300°C

Non irradiated



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

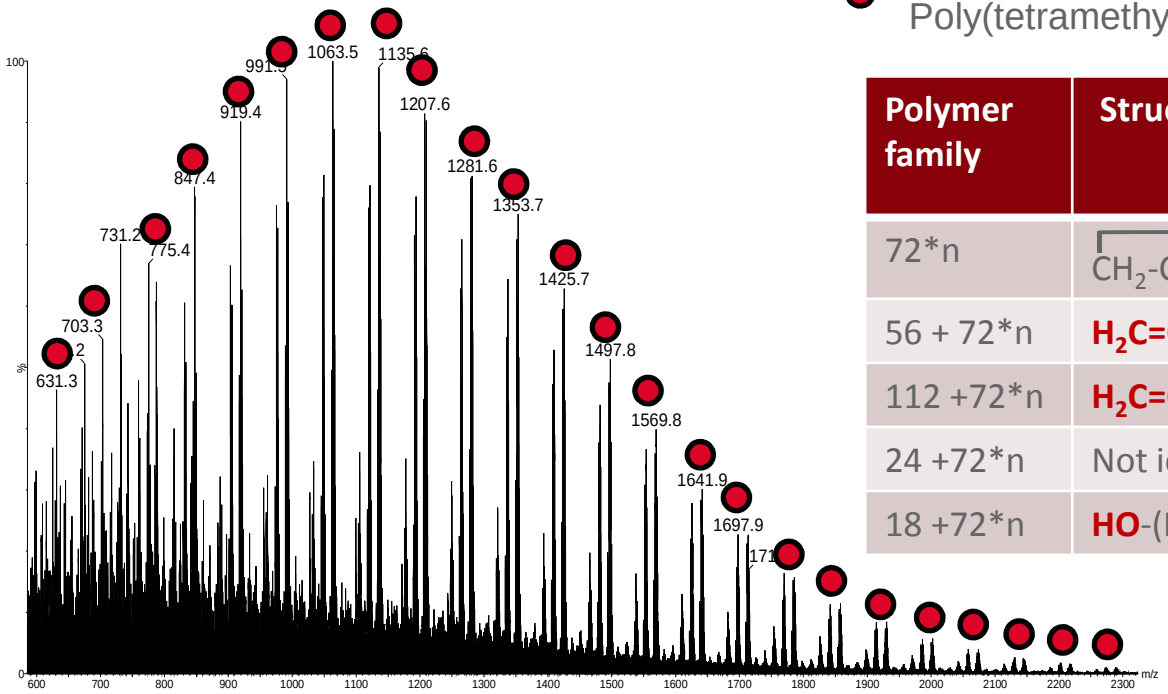
Robert P. Lattimer *et al.*, J Anal Appl Pyrol 17(3):237–249

ASAP ANALYSIS OF A CABLE SHEATH (PU)

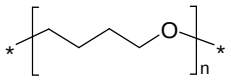
Analysis at high temperature (T°= 600°C)

Non irradiated

- Detection of a characteristic polymeric profile



- Δm = 72 u: PTMEG
  Poly(tetramethyleneglycol)



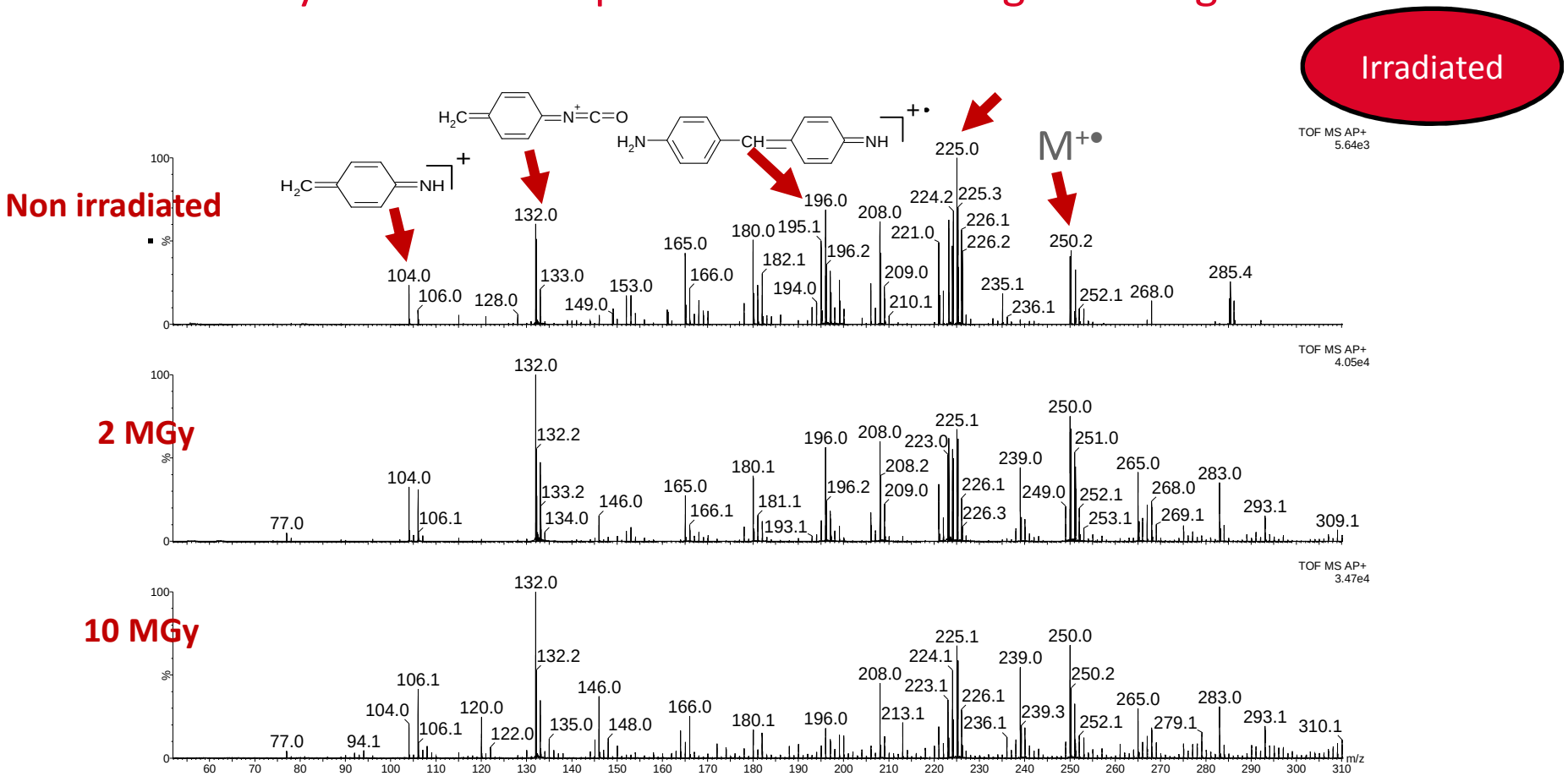
Polymer family	Structures
72*n	CH_2-CH_2-CH_2-CH_2- $(PTMEG)_n$-O
56 + 72*n	**H_2C=CH**-CH_2-CH_2-$(PTMEG)_n$-H
112 +72*n	**H_2C=CH**-CH_2-CH_2-$(PTMEG)_{n-1}$-O-CH_2-**CH=CH_2**
24 +72*n	Not identified
18 +72*n	**HO**-$(PTMEG)_n$-H

- Δm = 72 u: PTMEG → **detection of Soft Segment**
- Thermal degradation products ➔ Structural identification of **Soft Segment** of PU

➔ **Desorption of the copolymer components can be controlled by temperature**

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Analysis at low temperature ➔ **Hard** Segment degradation



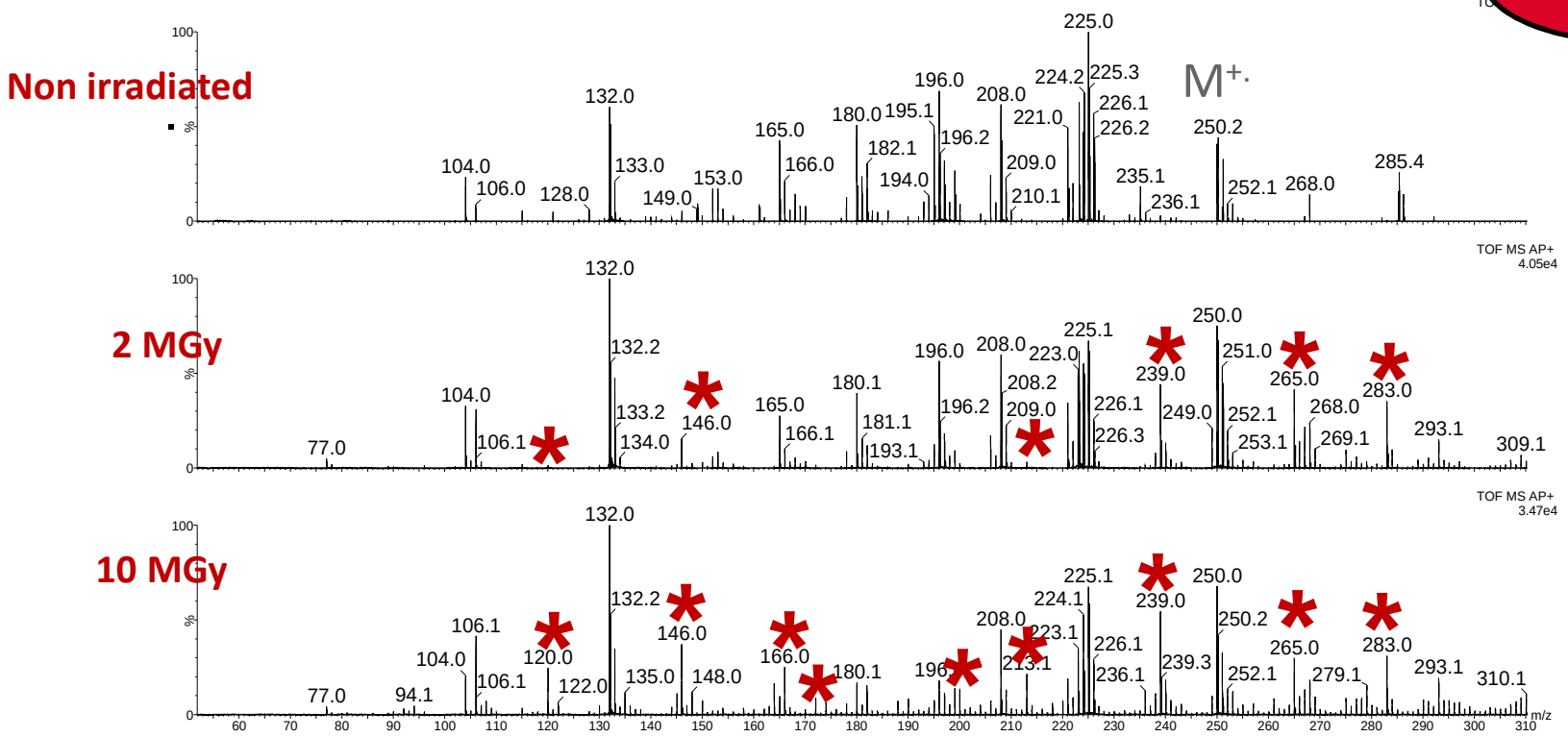
- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI

➔ Impact on Hard Segment seems low

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Analysis at low temperature ➔ **Hard** Segment degradation

Irradiated

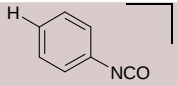
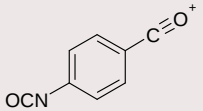
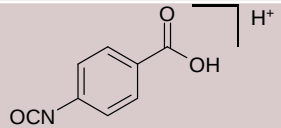
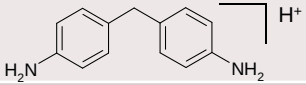
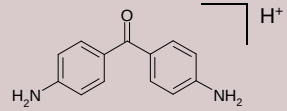
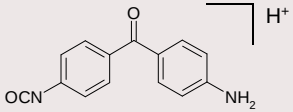
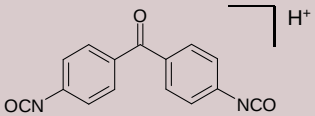
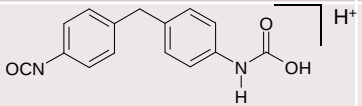


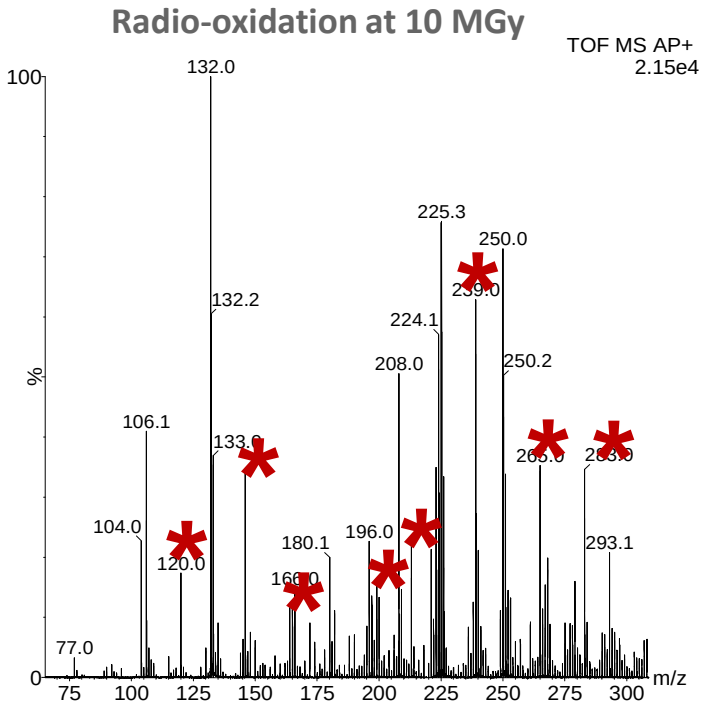
- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI
  ➔ impact of radiolysis on Hard Segment seems low
- * However some new signals are detected

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Identification of **hard** segment degradation molecules

Irradiated

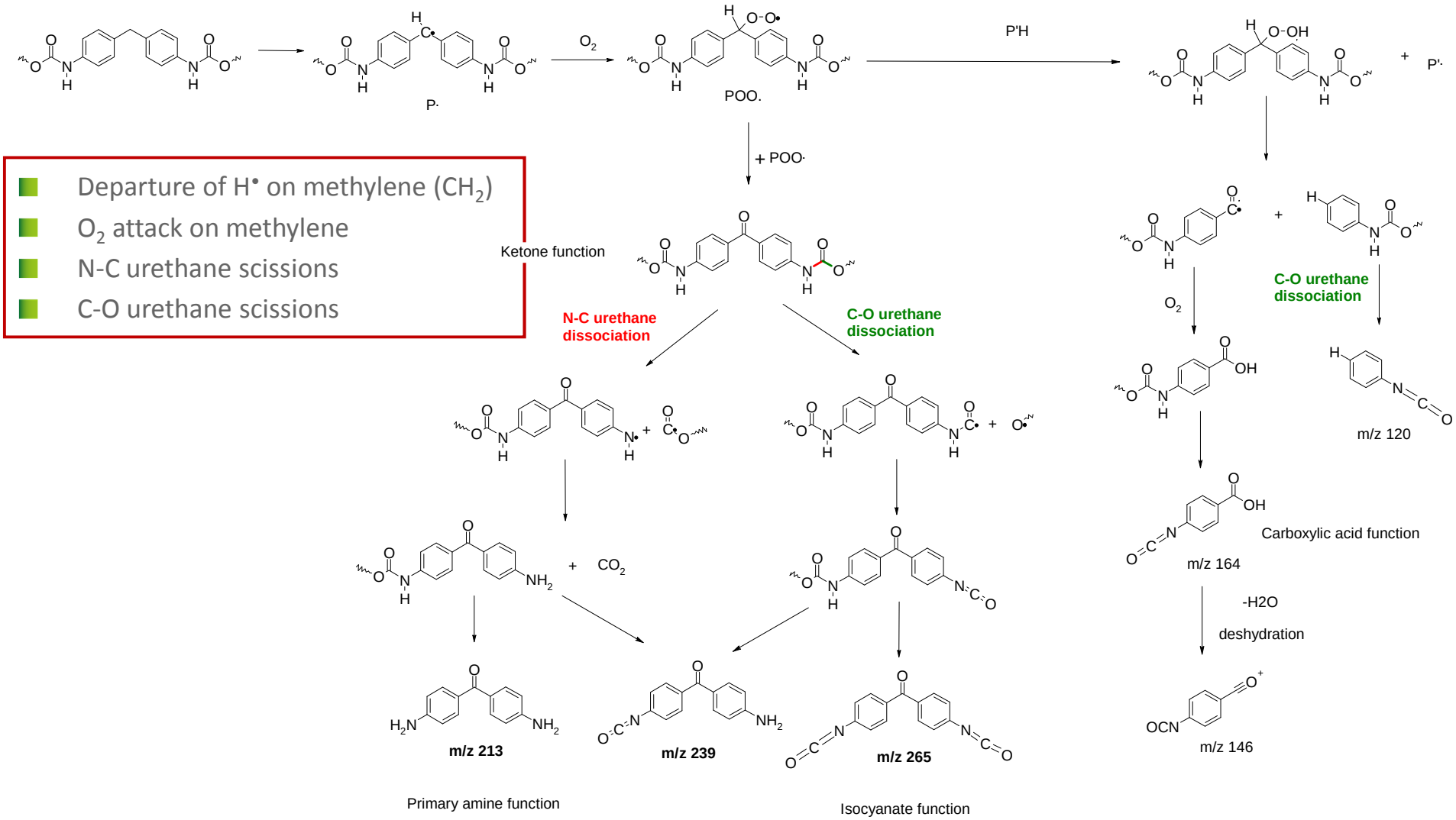
m/z	Fragments structure	2 MGy	10 MGy
120		X	X
146		X	X
164			X
199			X
213		X	X
239		X	X
265		X	X
283		X	X



➔ carbonyl and carboxylic acid functions ➔ oxidation reaction

PROPOSED MECHANISM OF HARD SEGMENT DEGRADATION

- Departure of H• on methylene (CH_2)
- O_2 attack on methylene
- N-C urethane scissions
- C-O urethane scissions

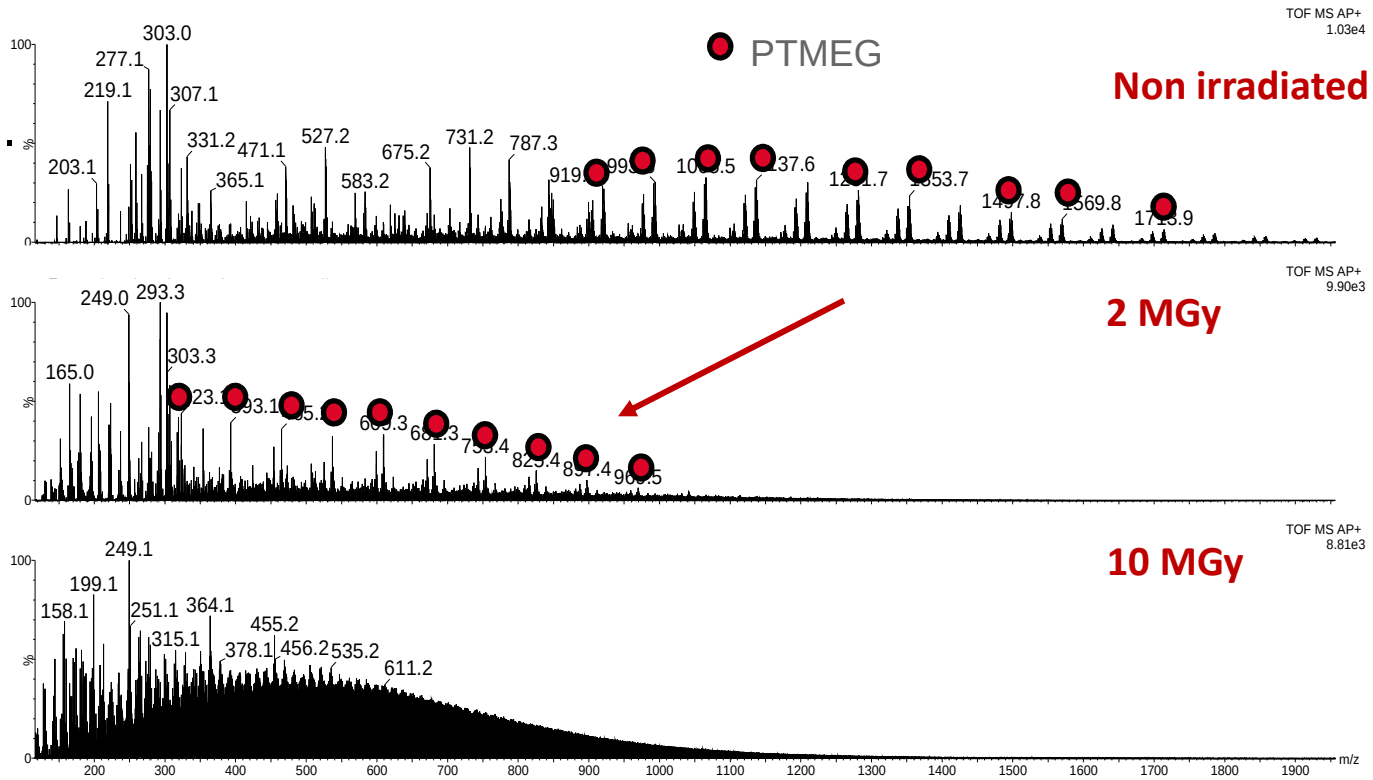


T. Servay, T., *et al.* Polymer 41(14)-5247-5256; Wilhelm C., et al. Polymer, 39(5) (1998), 1223-1232; Dannoux, A., et al. J. Polym. Sci.: Part B. 46 (2008), 861-878

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Analysis at high temperature ➔ **Soft** Segment degradation

Irradiated



- Very different mass spectra with the dose

➔ Important impact on Soft Segment of the irradiation

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

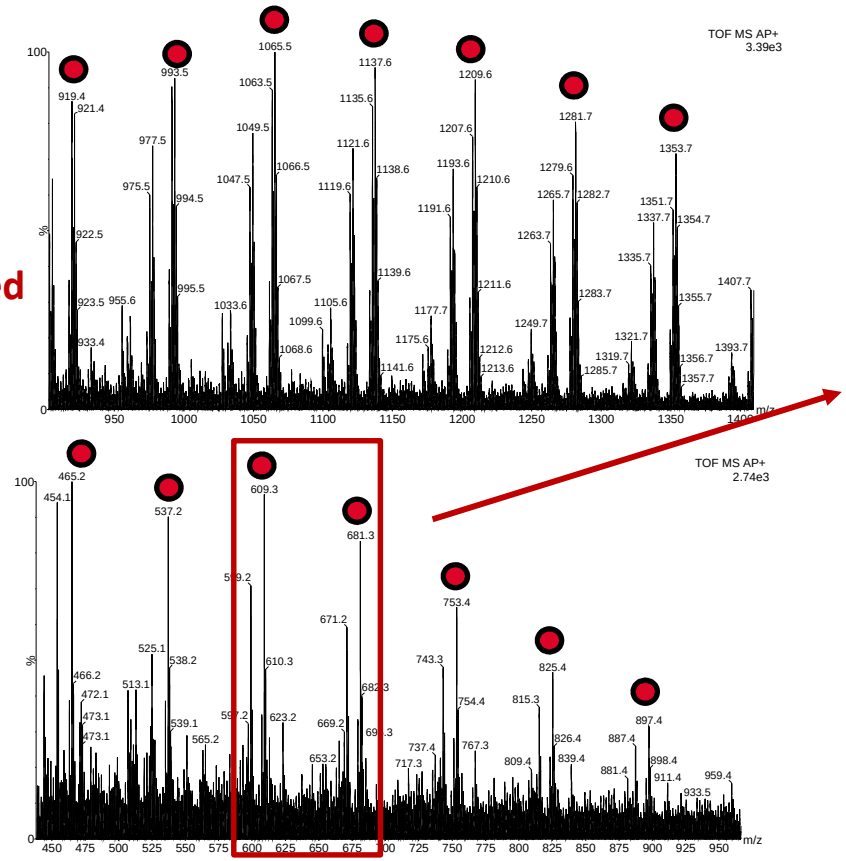
Identification of degraded polymers families after irradiation

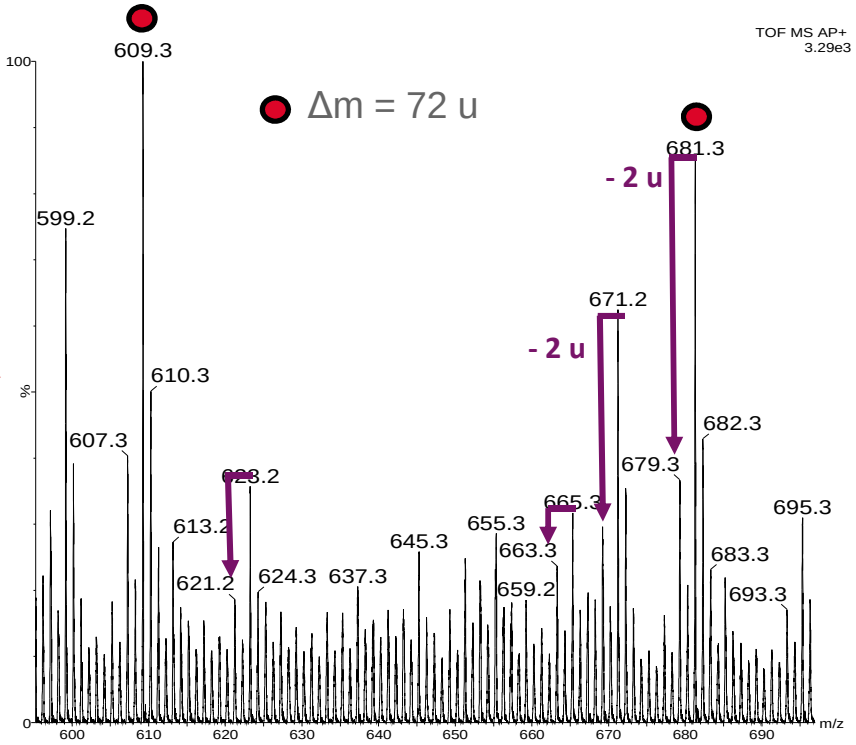
Irradiated

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

Non irradiated

2 MGy





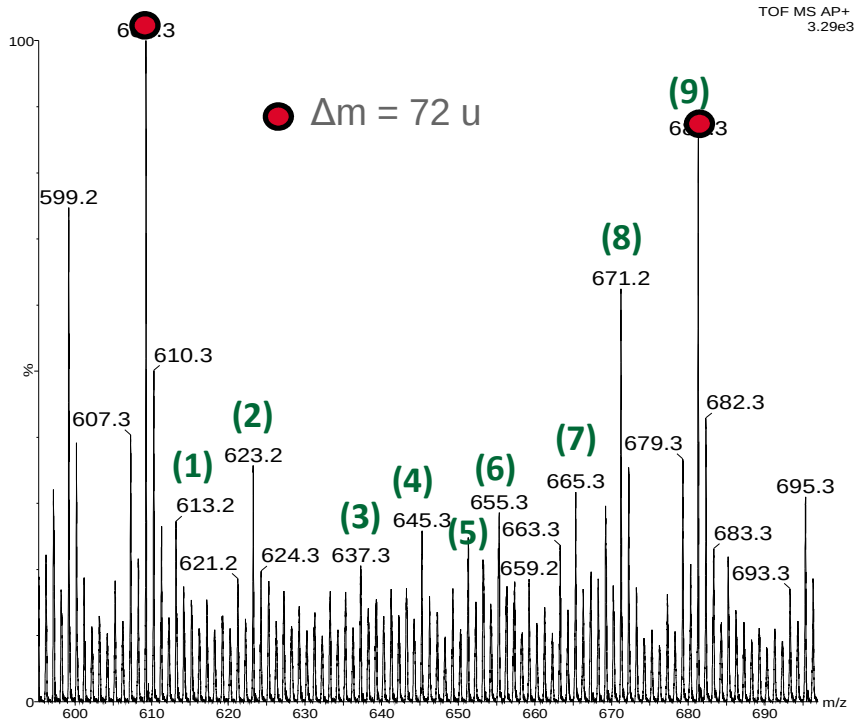
ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

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**

Family	m/z	Structures
(1)	36 + 72*n	Non identified
(2)	46 + 72*n	HO-(PTMEG)$_n$-**CHO**
(3)	60 + 72*n	**HO**-CH$_2$-(PTMEG)$_n$-**CHO**
(4)	68 + 72*n	H$_3$C-**CH=CH$_2$**-(PTMEG)$_n$-**CH=CH$_2$**
(5)	74 + 72*n	H$_3$C-CH$_2$-CH$_2$-CH$_2$-O-(PTMEG)$_n$-H
(6)	78 + 72*n	HO-CH$_2$-**O-CH(OH)**-(PTMEG)$_n$-OH
(7)	88 + 72*n	HO-(CH$_2$)$_3$-**CH(OH)**-(PTMEG)$_n$-H
(8)	94 + 72*n	HO-CH$_2$-**O-CH(OH)**-(PTMEG)$_n$-OH
(9)	104 +72*n	**HOOC**-(CH$_2$)$_3$-(PTMEG)$_n$-**OH**



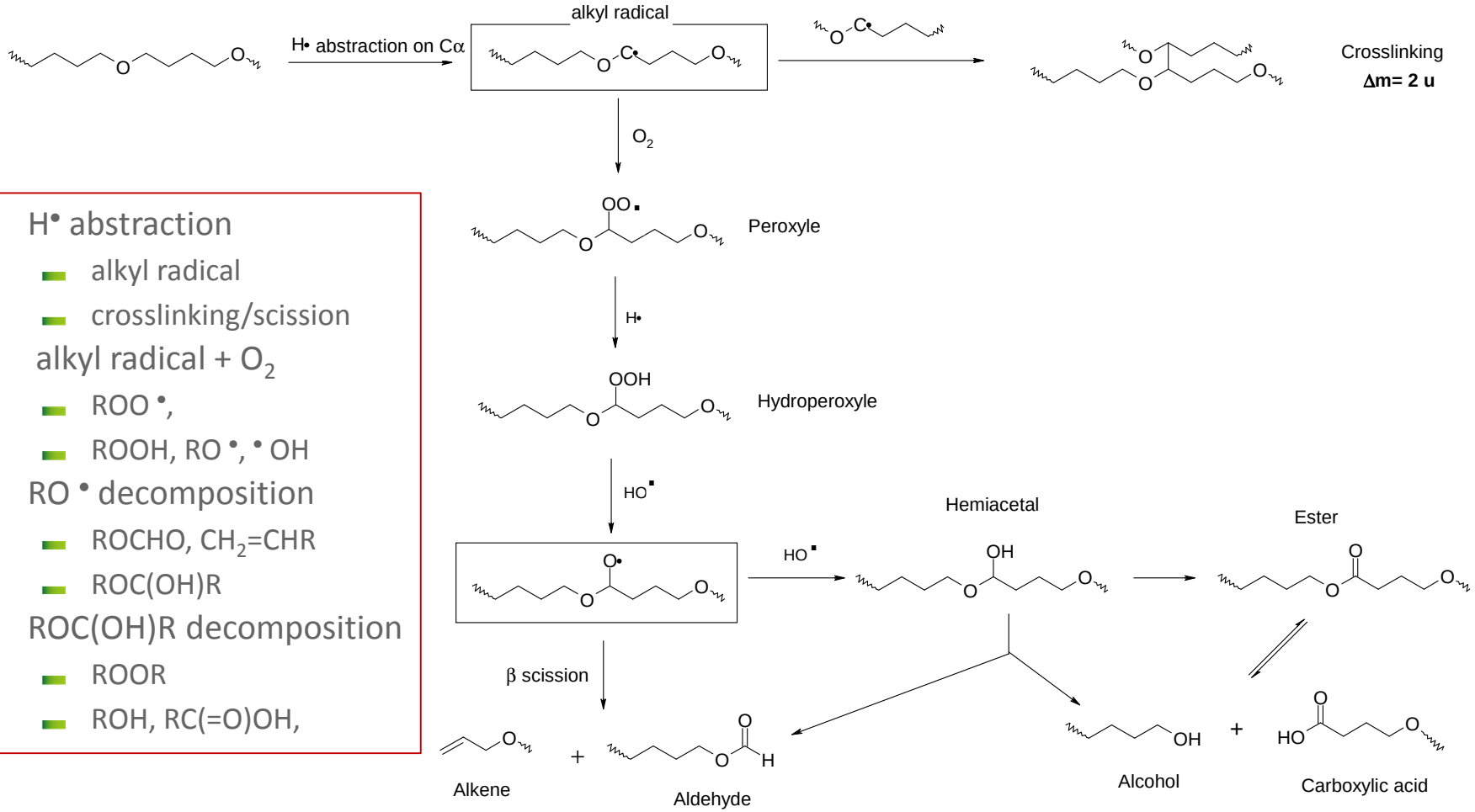
➔ **Oxidized functions: alcohol, hemiacetal, carboxylic acid and aldehyde**

➔ **Unsaturation function: alkenes**

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Proposed mechanism of **Soft** Segment degradation

- H• abstraction
  - alkyl radical
  - crosslinking/scission
- alkyl radical + O_2
  - ROO •,
  - ROOH, RO •, • OH
- RO • decomposition
  - ROCHO, CH_2=CHR
  - ROC(OH)R
- ROC(OH)R decomposition
  - ROOR
  - ROH, RC(=O)OH,

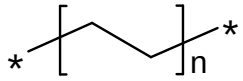


Gardette, J. L., et al. Macromol. Symp. 143 (1999), 95-109
Dannoux, A., et al. J. Polym. Sci.: Part B. 46 (2008), 861-878

POLYETHYLENE ANALYSIS

POLYETHYLENE (PE) ANALYSIS

Structural composition

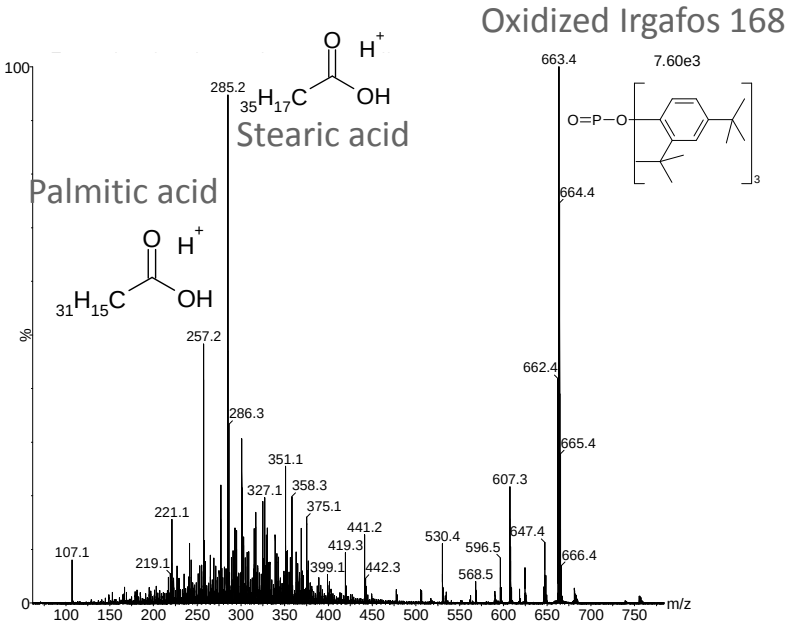


- Saturated, aliphatic hydrocarbons
- Difficulty of mass spectrometry analysis: large saturated polymer without heteroatoms

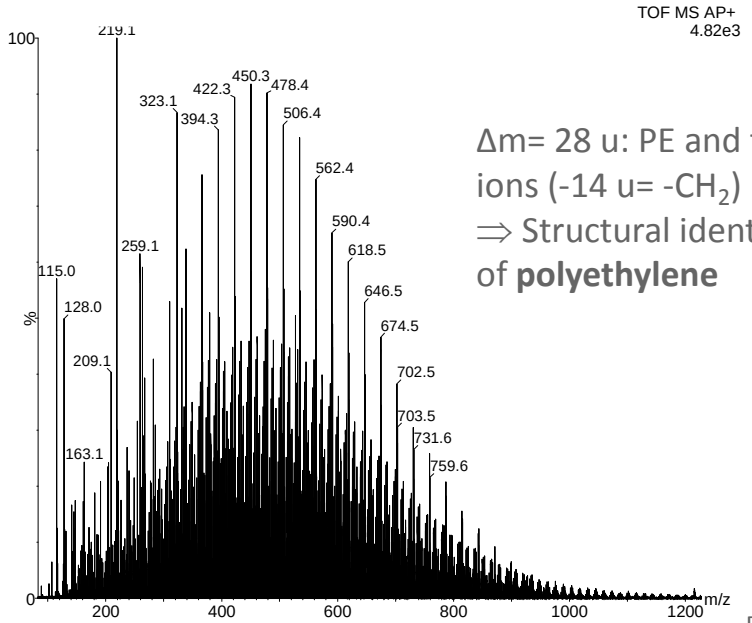
ASAP-MS analysis of non irradiated PE

Non irradiated

T°= 300 °C



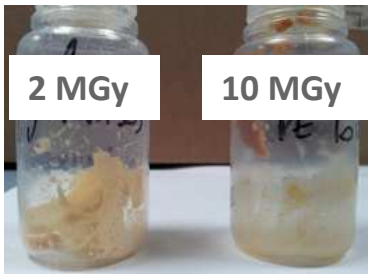
T°= 500 °C

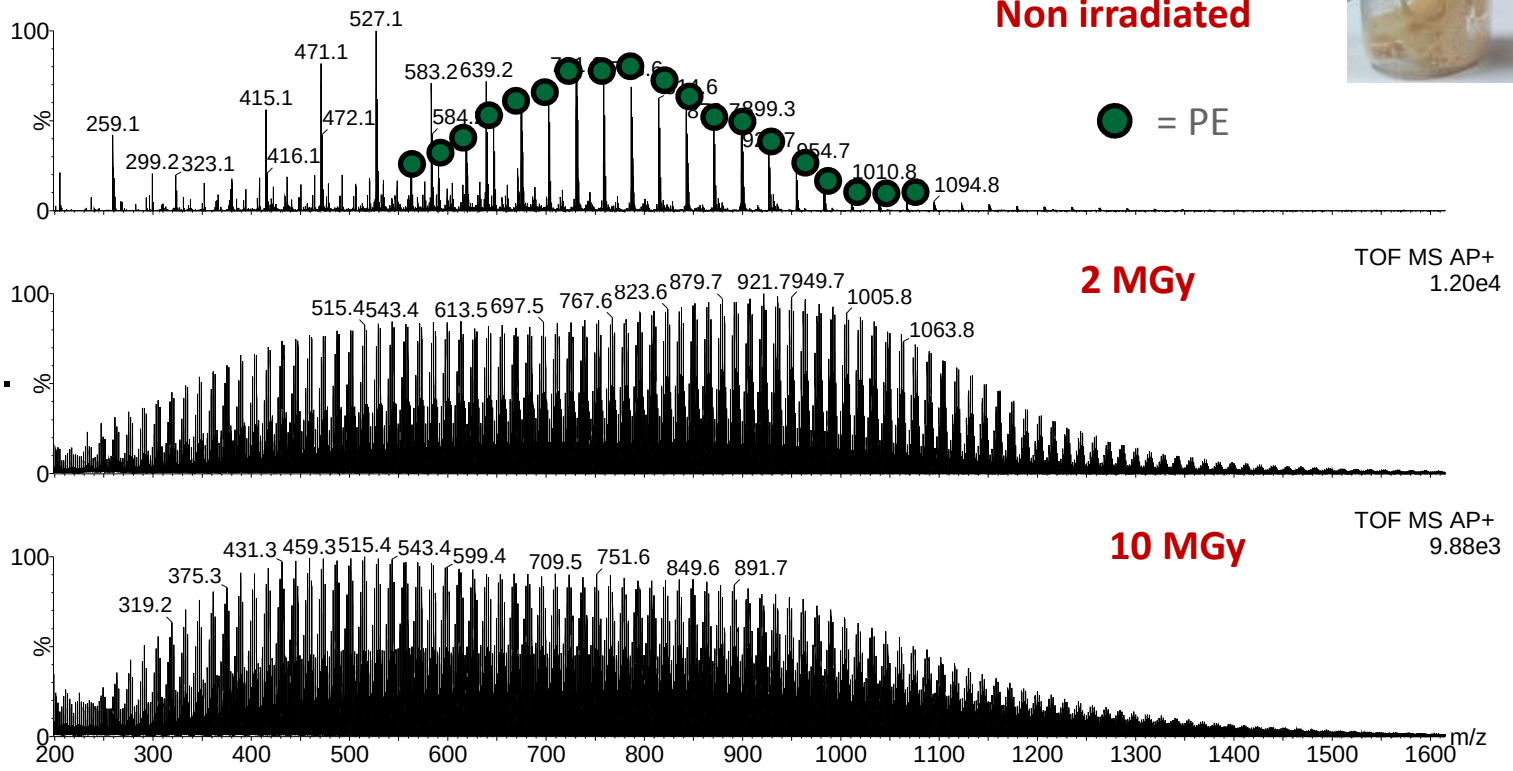


Δm= 28 u: PE and fragments ions (-14 u= -CH_2)
⇒ Structural identification of **polyethylene**

ASAP ANALYSIS OF PE AFTER IRRADIATION

Irradiated PE analyzed at same T°





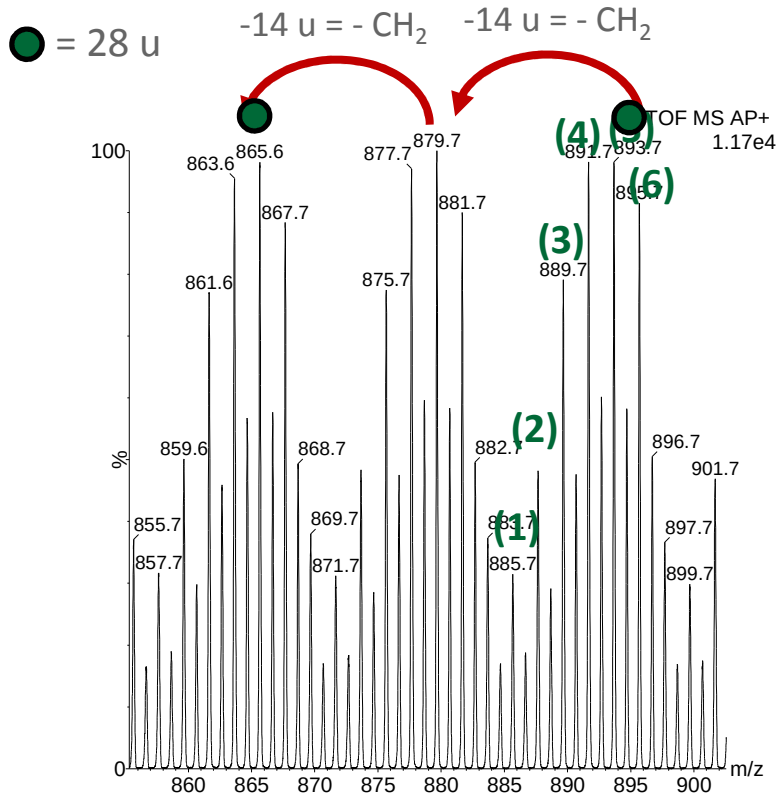
- Very different mass spectra after irradiation at 2 and 10 Mgy ➔ Important impact of radio-oxidation
- Similar mass spectra after irradiation at 2 and 10 MGy

ASAP ANALYSIS OF PE AFTER IRRADIATION

PE after irradiation at 2 MGy

Irradiated

- Mainly Δm= 2 u ➔ **unsaturation and/or crosslinking**



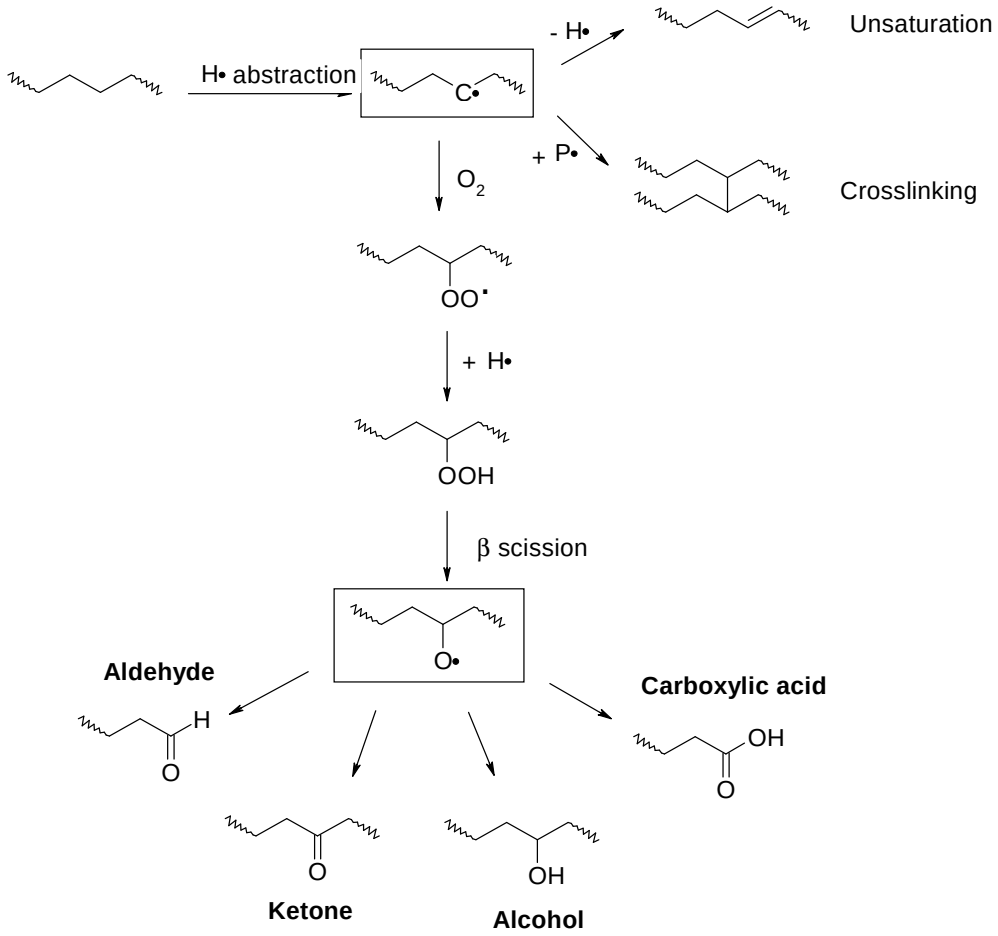
	polymer	Structures
(1)	44 + 28*n	**H_3C-CO**-$(PE)_n$-H
(2)	46 + 28*n	**H_3C-CH(OH)**-$(PE)_n$-H **HOOC**-$(PE)_n$-H
(3)	48 + 28*n	**HO-H_2C**-$(PE)_n$-**OH**
(4)	78 + 28*n	**HO-COO**-$(PE)_n$-**OH**
(5)	52 + 28*n	Non identified
(6)	54 + 28*n	**H_2C=CH**-$(PE)_n$-**CH=CH_2**

➔**Oxidized functions: alcohol, carboxylic acid and aldehyde**

➔**Unsaturation function: alkenes**

ASAP ANALYSIS OF PE AFTER IRRADIATION

Proposed mechanism of PE degradation



Torikai, A., *et al.* Polym Degrad Stabil 16 (1986) 199-212

CONCLUSIONS AND PERSPECTIVES

ASAP-MS for analysis of degradated 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 degradated products with the doses
- Analysis at lower doses to explore impact of additives

Thank you for your attention.

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