ASAP and DART mass spectrometry analysis for the understanding of polymers degradation mechanisms.

D. Lebeau

DE LA RECHERCHE À L'INDUSTRIE

cea den

Direct mass spectrometry analysis for the understanding of polymers degradation under radio-oxidation

Diane Lebeau

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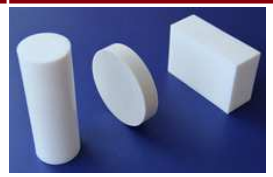
NUCLEAR CHEMISTRY 2016 – SAN ANTONIO

INTRODUCTION

Polymers in nuclear industry

- A wide variety of polymers
- Even if used amounts are smaller than other engineering materials (concrete, steel, zirconium, etc…), they play a crucial role as
  - Polymeric parts in system components (valves, lining to protect tanks and pipes, …)
  - Seals in building structures
  - Electrical cables
- Examples of used polymers

Nitrile rubber	Fluoro elastomer	Silicone rubber	EPDM	Epoxy	Polyurethane	Acrylic
						

➔ 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

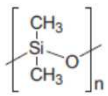
INTERACTION OF RADIATION WITH ORGANIC MATTER

Polymers

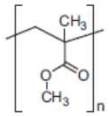
- Polymers

  - Repeating units
  - Ends groups
  - Average mass

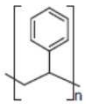
- Heteroatoms (PEG, PMMA…)
- Unsaturated (PB)
- Aromatics (PS)
- Saturated (PE, PP…)



PDMS 1



PMMA 2



PS 7

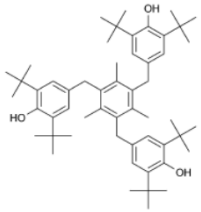
$Mn = (\Sigma niMi)/\Sigma ni$

$Mw = (\Sigma ni\ Mi^{2})/(\Sigma ni\ Mi)$

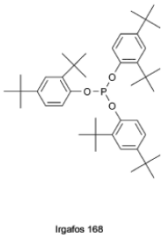
➔ Polydispersity

Pd = Mw/Mn

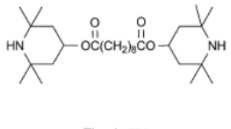
- Additives
  - Anti-UV
  - Antioxidants
  - Photostabilizants
  - …



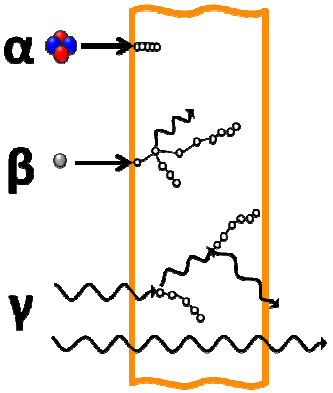
Irganox 1330



Irgafos 168



Tinuvin 770



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

➔ Interaction of radiation with organic matter

➔ Irradiation induces chemical reactions in the material

INTERACTION OF RADIATION WITH ORGANIC MATTER

- Mechanism under **inert** conditions
  - Initiation:

$PH \rightarrow P^{\bullet} + H^{\bullet}$

  - Propagation:

$P^{\bullet} + P'H' \rightarrow PH' + P'^{\bullet}$ (hydrogen transfert)

$H^{\bullet} + P'H' \rightarrow P'^{\bullet} + H_2$

  - Termination

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

$P^{\bullet} + P'^{\bullet} \rightarrow PH + >C=C<$ (dismutation)

- Mechanism under **oxidative** conditions
  - Initiation:

$PH \rightarrow P^{\bullet} + H^{\bullet}$

  - Propagation:

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

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

  - Termination: recombinaison

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

or $PH + >C=C<$ (dismutation)

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

or $POOH + >C=C<$

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

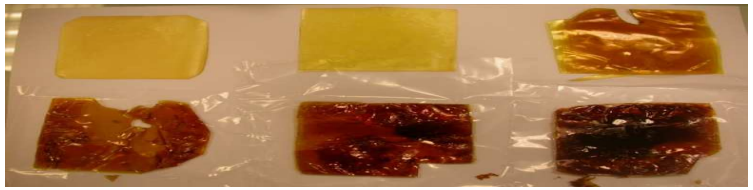
A. Rivaton et al. Polymer Degradation and Stability 91 (2006) 136

INTERACTION OF RADIATION WITH ORGANIC MATTER

Consequences of irradiation ➔ changes in physical structure and properties

- Crosslinking: ↗ Mw ➔ ↘ solubility to insolubility ➔ hardness
- Scission: ↘ Mw ➔ ↗ solubility ➔ viscous material

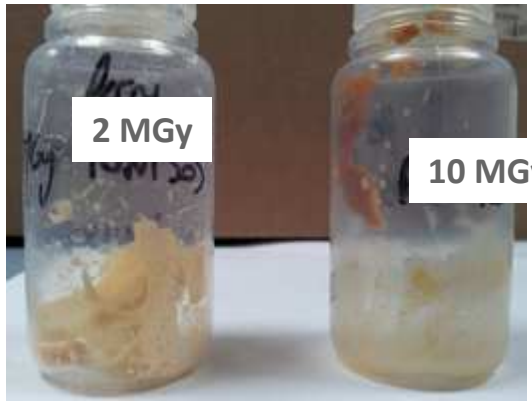
Polyurethane



1, 2 and 5 MGy

10, 15 and 20 MGy

Polyethylene



Ethylene-vinyl acetate (EVA)

ANALYTICAL METHODS FOR POLYMERS ANALYSIS

Gas

- High resolution gas-mass spectrometry with direct introduction
- Gas chromatography coupled with mass spectrometry (GC/MS)

Liquid

- Size exclusion chromatography
- Mass spectrometry (ESI, MALDI)
- UV-spectroscopy

Solid

- Fourier transform infrared spectroscopy (FTIR)
- Electron paramagnetic resonance (radicals analysis)
- X-ray diffraction

ANALYTICAL METHODS FOR POLYMERS ANALYSIS

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Solid

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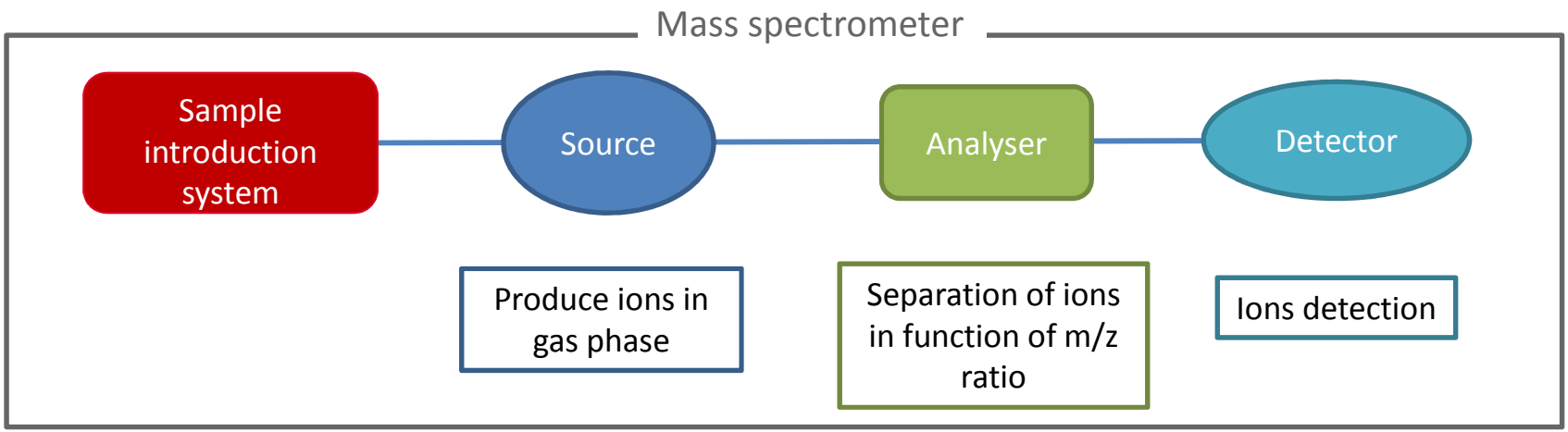
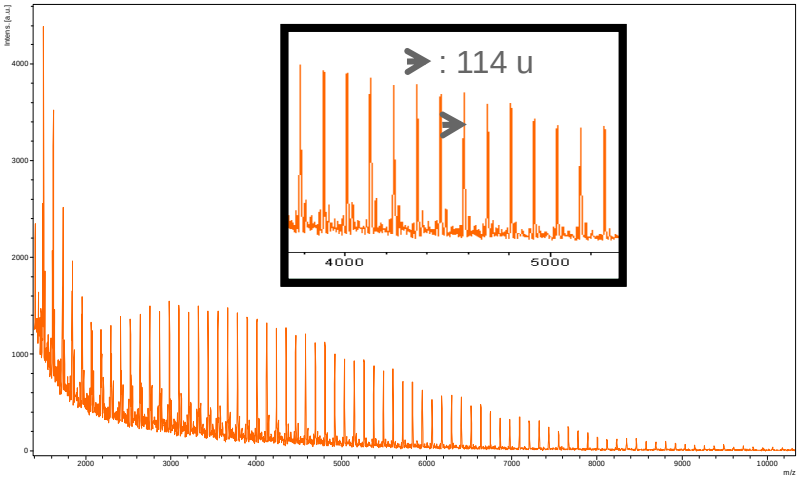
- **Mass spectrometry**

MASS SPECTROMETRY: PRINCIPLE



- In case of polymers analysis: determination of characteristic parameters of polymer

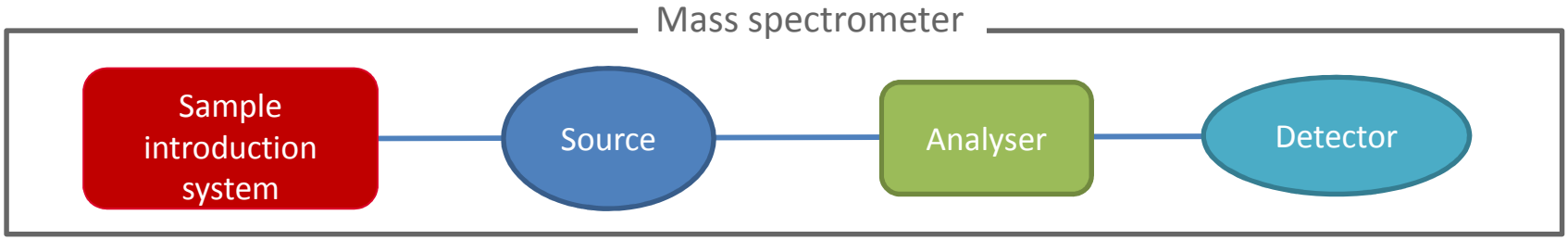


- Identification of the structure of Repeating unit (e.g. 114 u = polycaprolactone)
- Identification of end groups of the polymer
- Properties of the studied polymer:

  Polydispersity Pd = Mw/Mn

  (with $M_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$ and $M_w = \frac{\Sigma n_i {M_i}^2}{\Sigma n_i M_i}$)

MASS SPECTROMETRY



- Choice of mass spectrometry techniques

Sample introduction	Source	Analyser
• Solubility • Volatility • Thermal stability	• **Polarity** • Thermal stability • Molecular mass • **Solubility**	Mass range Mass resolution Scan speed Limit of detection Dynamic range

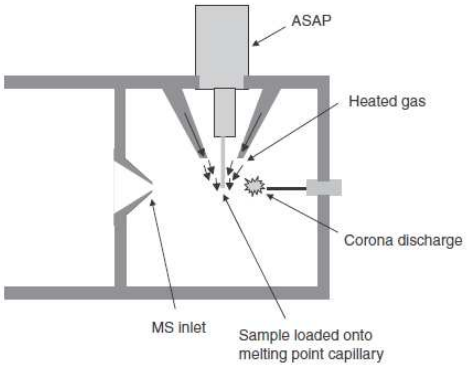
- After irradiation:

➔ because of crosslinking and scission: solubility is modified → insolubility and hardness

➔ an analytical method **without any sample pretreatment** is required

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
    - Use of pure 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

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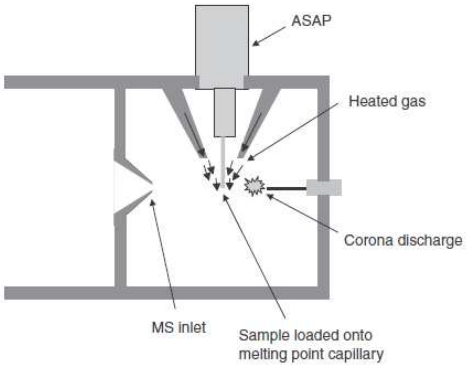
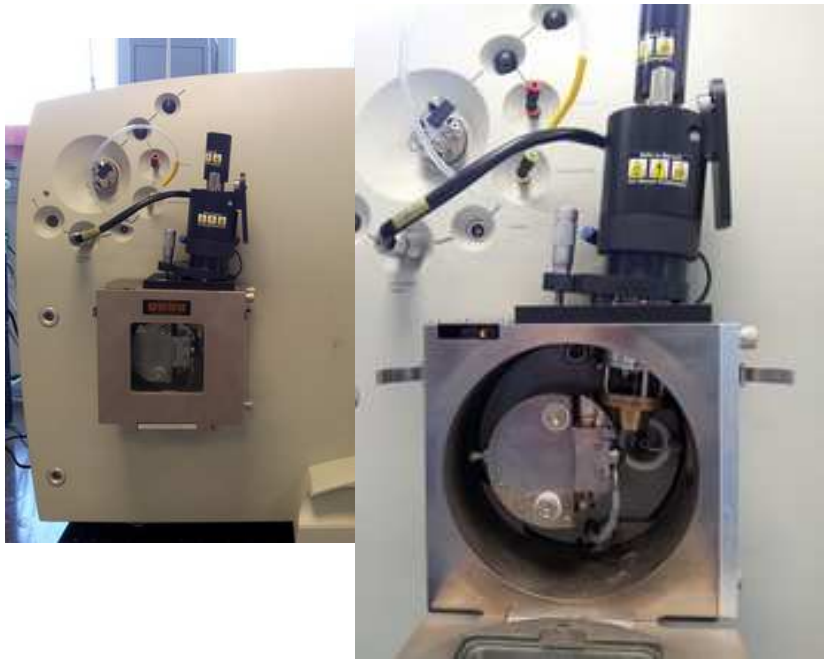




Analysis on LCT-XE Premier (Waters) with a single TOF analyzer

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

CASE I: CO - POLYMER
POLYURETHANE (PU)

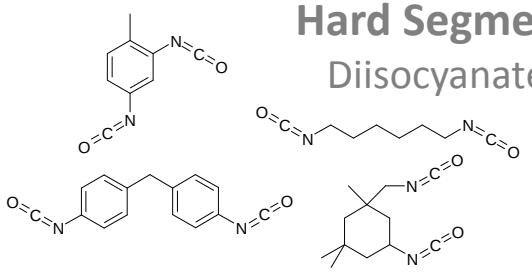
STRUCTURAL COMPOSITION

Polyurethane synthesis

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

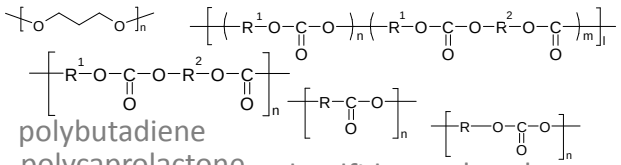
Hard Segment

Diisocyanate



Soft Segment

Polyols (polyester or polyether)



polybutadiene polycaprolactone | polysulfide | polycarbonate

Additives

Additives	Reasons for use
catalysts	to speed up the reaction
cross-linking and chain-extending agents	to modify the structure of PU molecules and to provide mechanical reinforcement
blowing agents **surfactants**	to create polyurethane as a foam to control the bubble formation
pigments	to create colored polyurethanes
fillers	to improve properties
flame retardants	to reduce flammability of the end product
smoke suppressants	to reduce the rate at which smoke is generated if the polyurethane is burnt
plasticizers	to reduce the hardness of the product

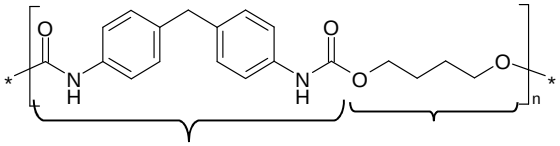
- Complex composition and different structures
- Copolymer → difficult to characterize directly by MS without sample treatment:
  - preliminary dissociation of each segment from the copolymer (e.g. pyrolysis or chemical dissociation)
  - Py-GC/MS and/or MALDI/MS

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

ELECTRIC CABLE SHEATH ANALYZED BY ASAP

Polyether polyurethane: electric cable sheath

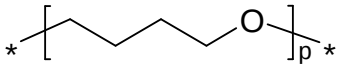
Hard Segment



MDI

1,4-butanediol (BD)
= Chain extender

Soft Segment



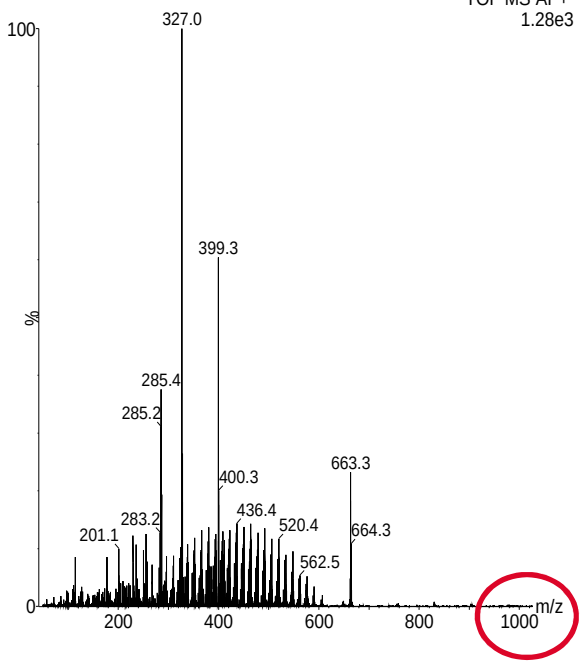
Poly(tetramethylene ether) glycol (PTMEG)

Non irradiated

ASAP ANALYSIS: NON IRRADIATED MATERIAL

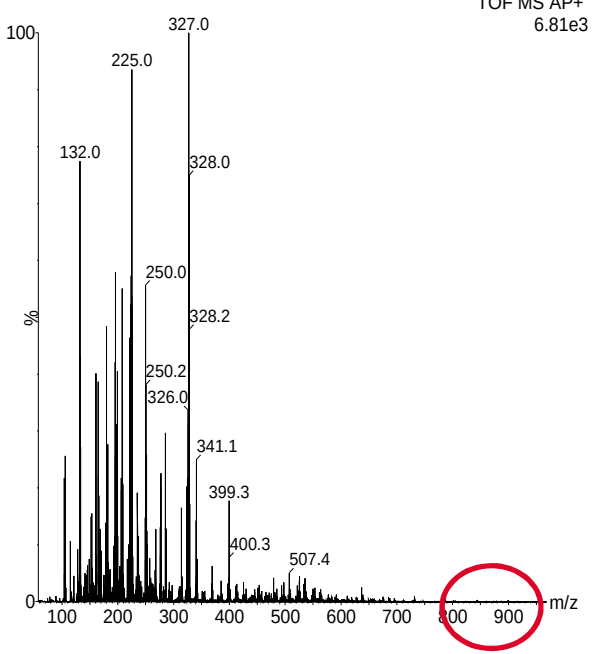
ASAP: thermal plasma desorption ➔ analysis of sample at different temperatures

T° < 300 °C



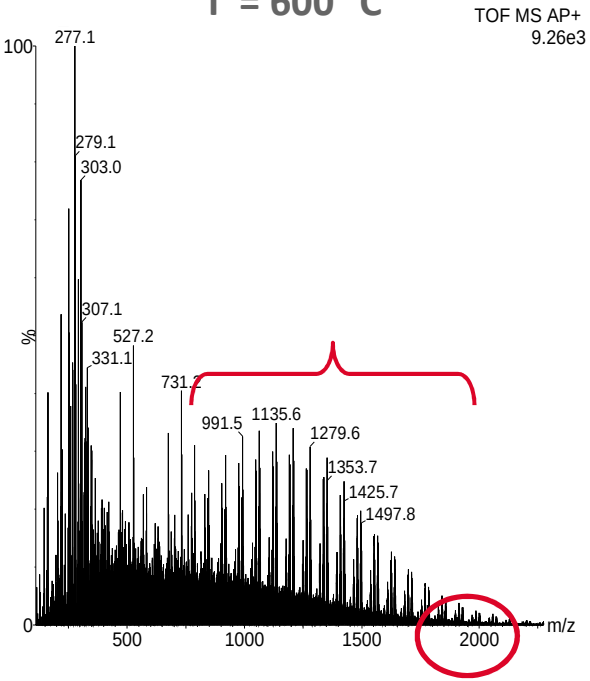
- Low m/z range

T°= 300 °C



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

T°= 600 °C

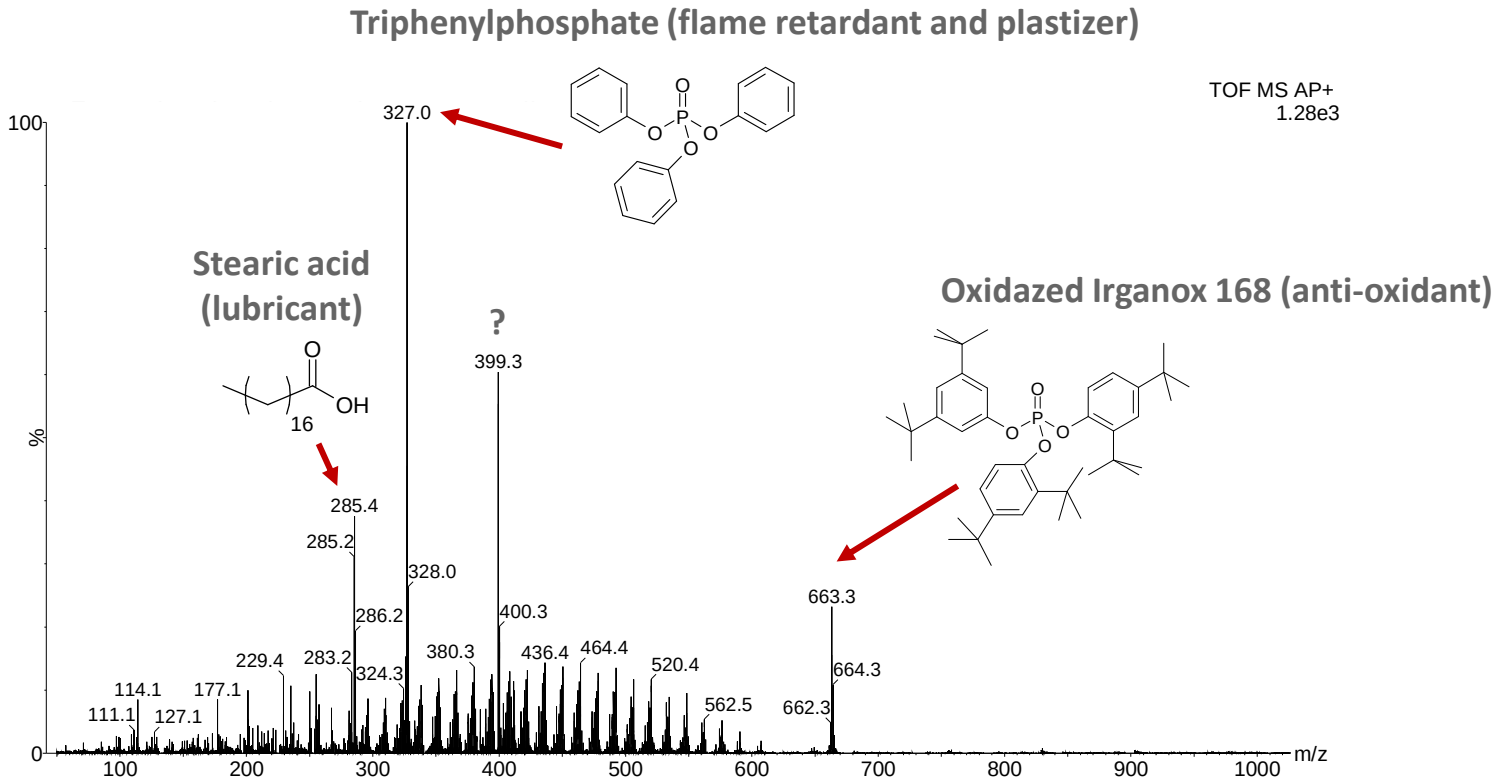


- higher m/z range
- polymeric profile

➔ **Desorption of compounds with temperature**

ASAP ANALYSIS OF A CABLE SHEATH (PU)

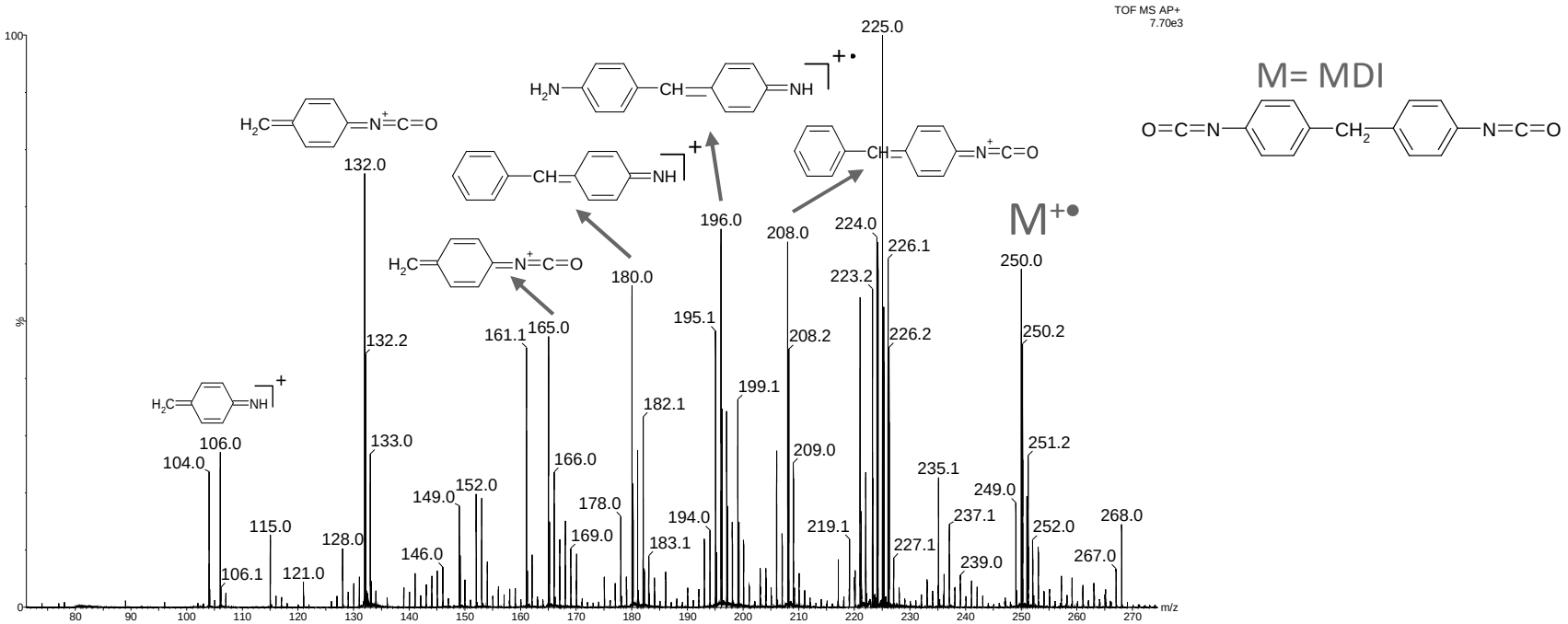
Analysis at low temperature (T° < 300°C)



- Detection of additives of the polymer
- TOF analyzer → exact mass measurements → additives identification

ASAP ANALYSIS OF A CABLE SHEATH (PU)

Analysis at 300°C



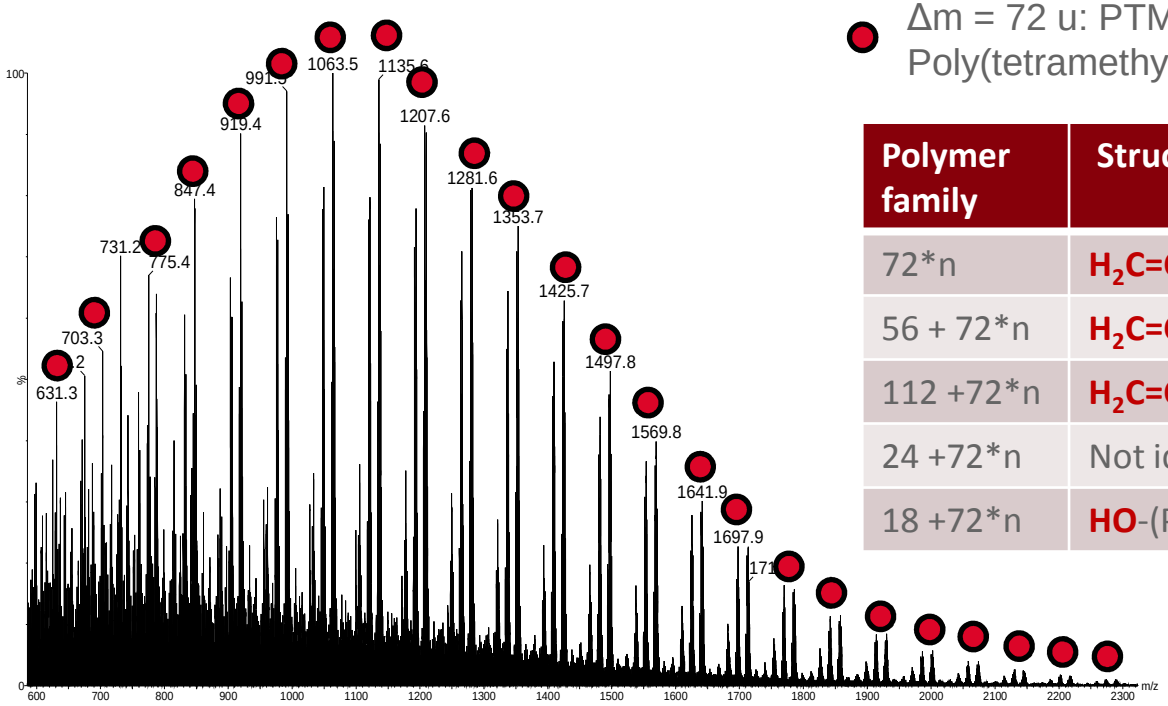
- Detection of molecular ion $M^{+\bullet}$ for MDI
- Detection of characteristic fragments of MDI ⇒ Structural identification of the PU **Hard Segment**

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

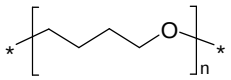
ASAP ANALYSIS OF A CABLE SHEATH (PU)

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

- Detection of a characteristic polymeric profile



- Δm = 72 u: PTMEG
  Poly(tetramethyleneglycol)



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

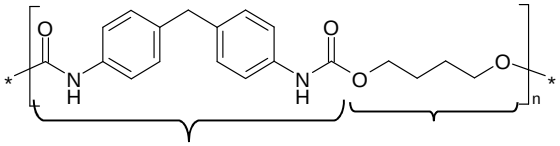
- Δm= 72 u: PTMEG → **detection of Soft Segment**
- Fragments ions ➔ Structural identification of **Soft Segment** of PU

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

ELECTRIC CABLE SHEATH ANALYZED BY ASAP

Polyether polyurethane

Hard Segment



MDI

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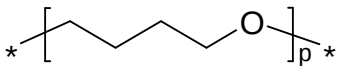


Poly(tetramethylene ether) glycol (PTMEG)

Non irradiated

Dose rate: 0.6 à 0.75 kGy/h

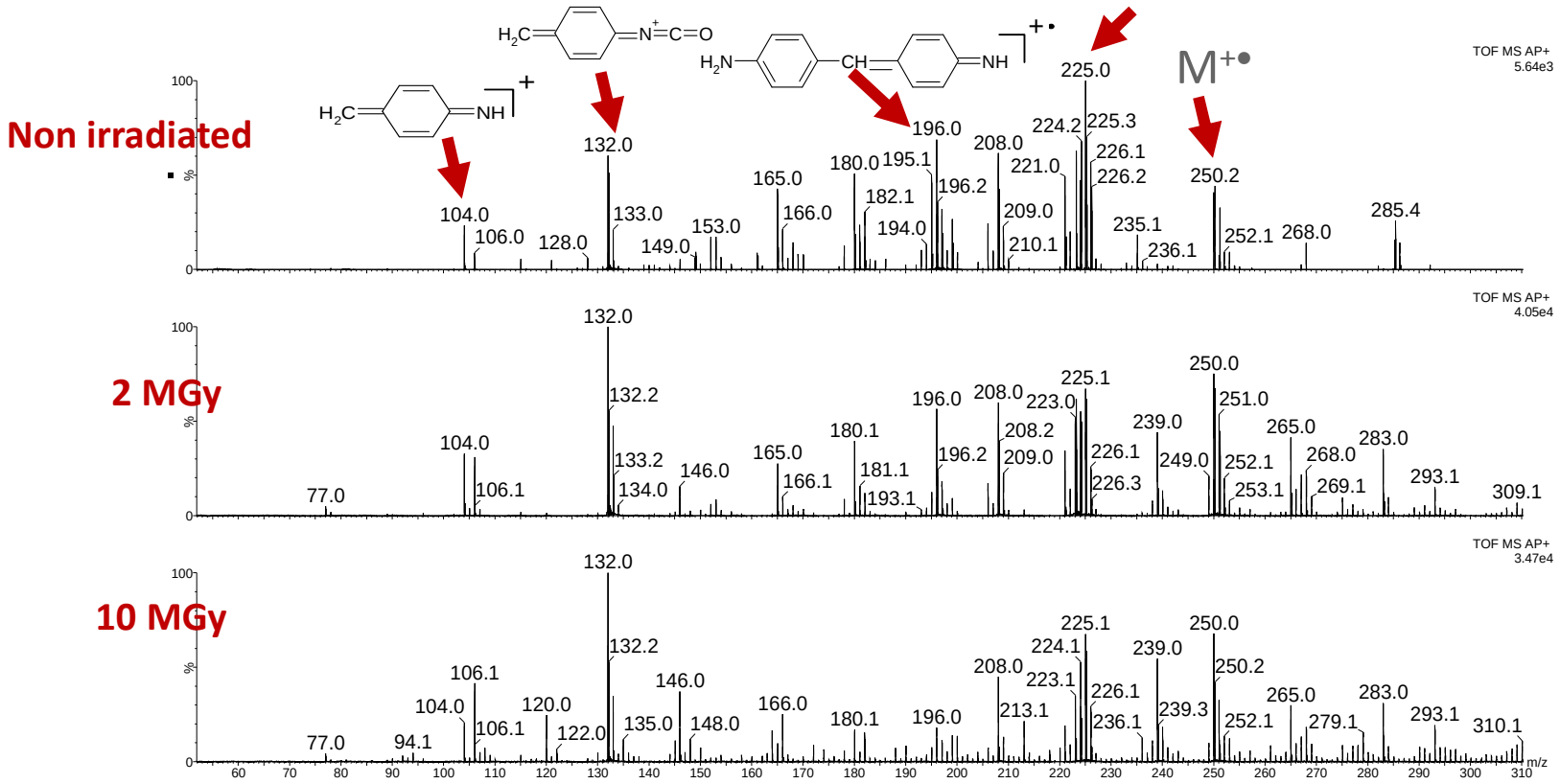
→ Oxidative conditions

2 MGy

10 MGy

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Analysis at 300 °C ➔ Hard Segment degradation

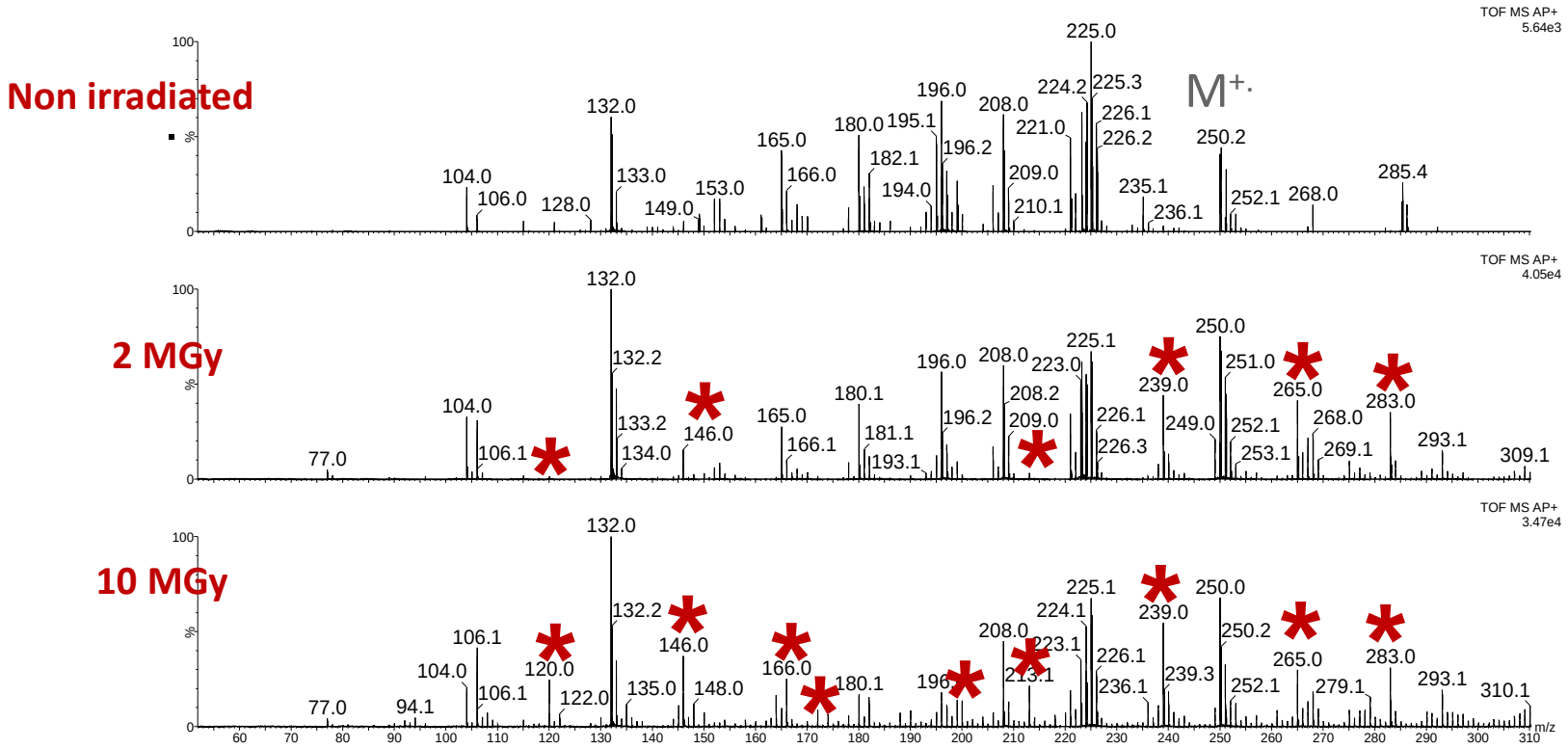


- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI

➔ Impact on Hard Segment seems low

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Analysis at low temperature ➔ Hard Segment degradation



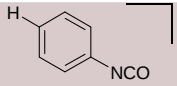
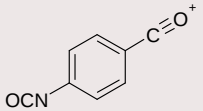
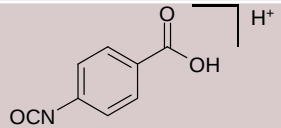
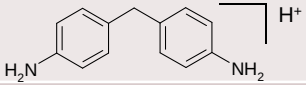
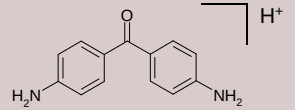
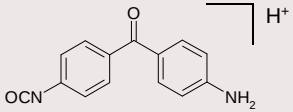
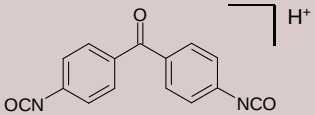
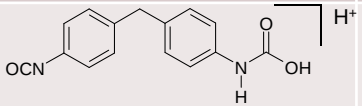
- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI

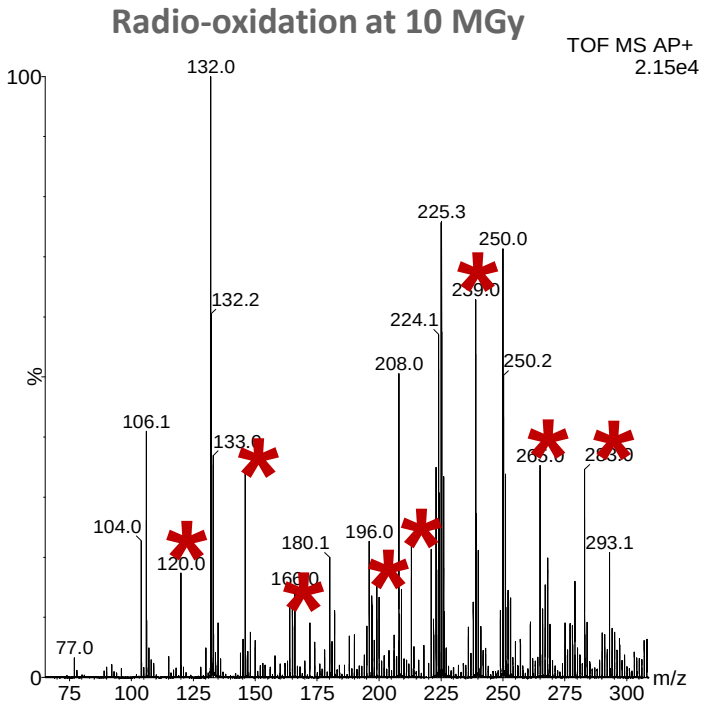
➔ impact of radiolysis on Hard Segment seems low

- However some new peaks are detected

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

Identification of degradation molecules

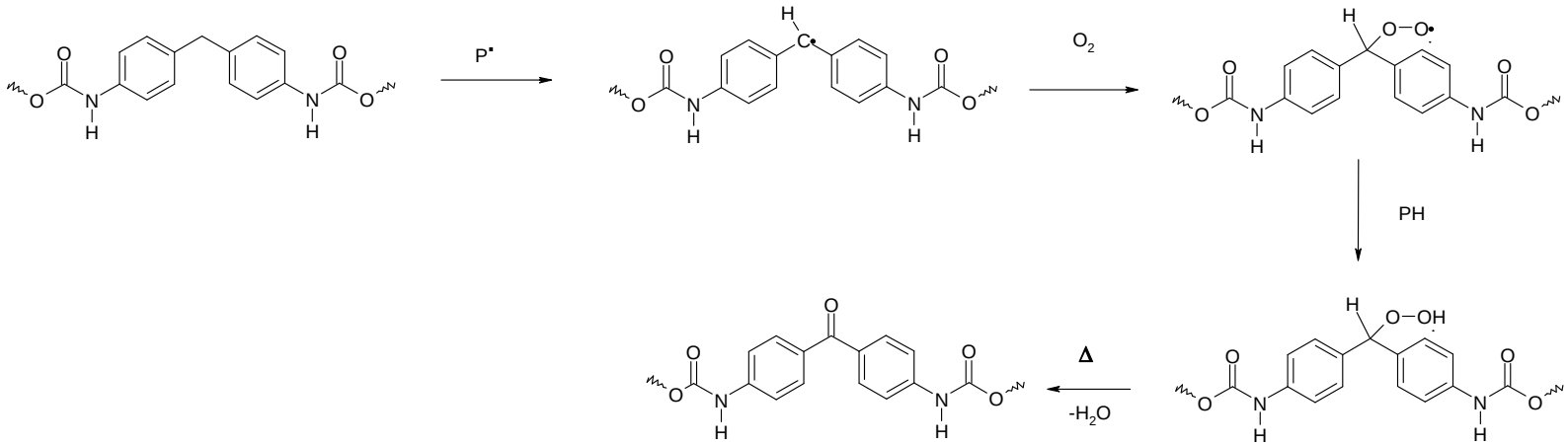
m/z	Fragments structure	2 MGy	10 MGy
120		X	X
146		X	X
164			X
199			X
213		X	X
239		X	X
265		X	X
283		X	X



➔ carbonyl and carboxylic acid functions ➔ oxidation reaction

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

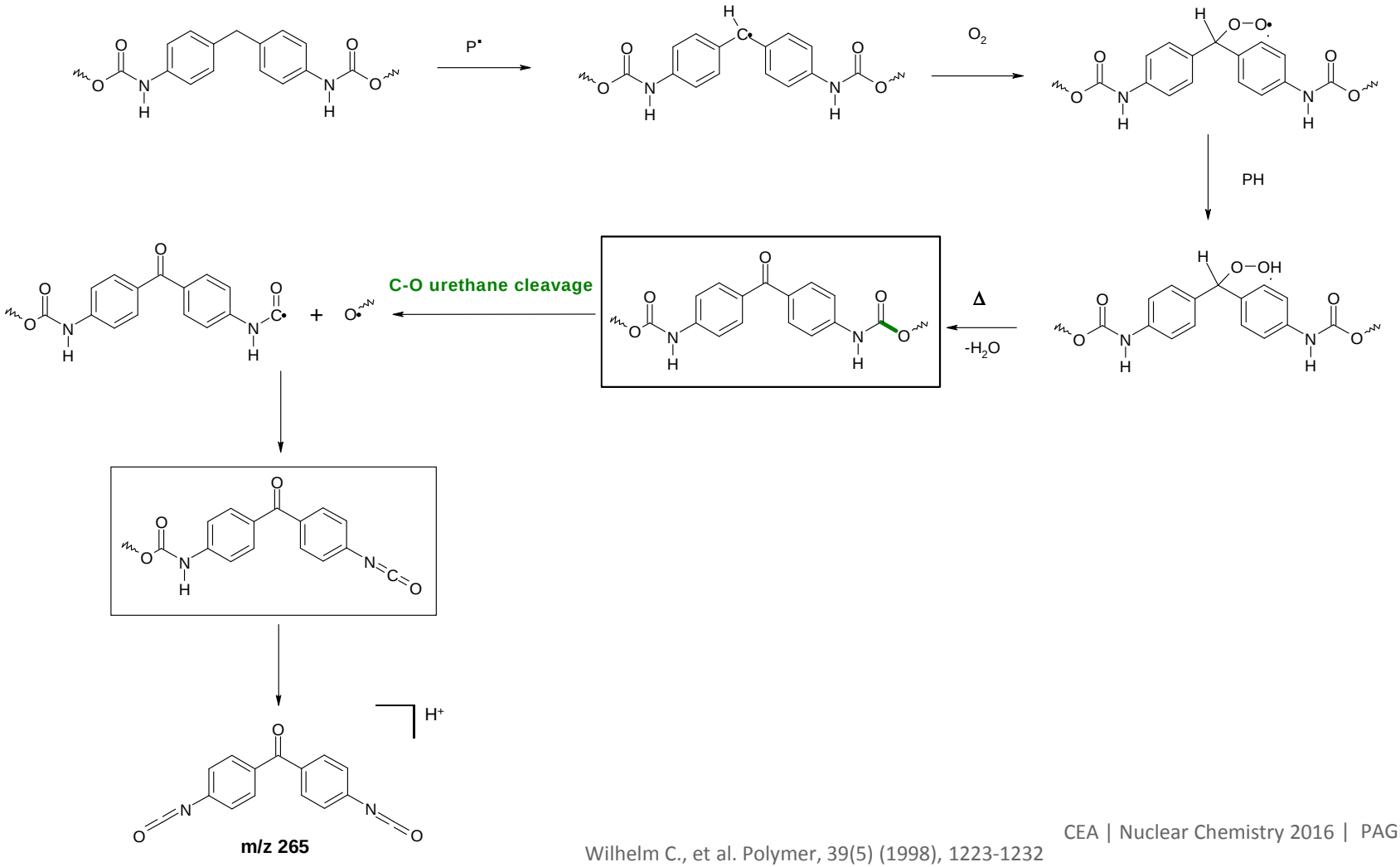
Proposed mechanism of Hard Segment degradation



T. Servay, T., *et al.* Polymer 41(14)-5247-5256

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

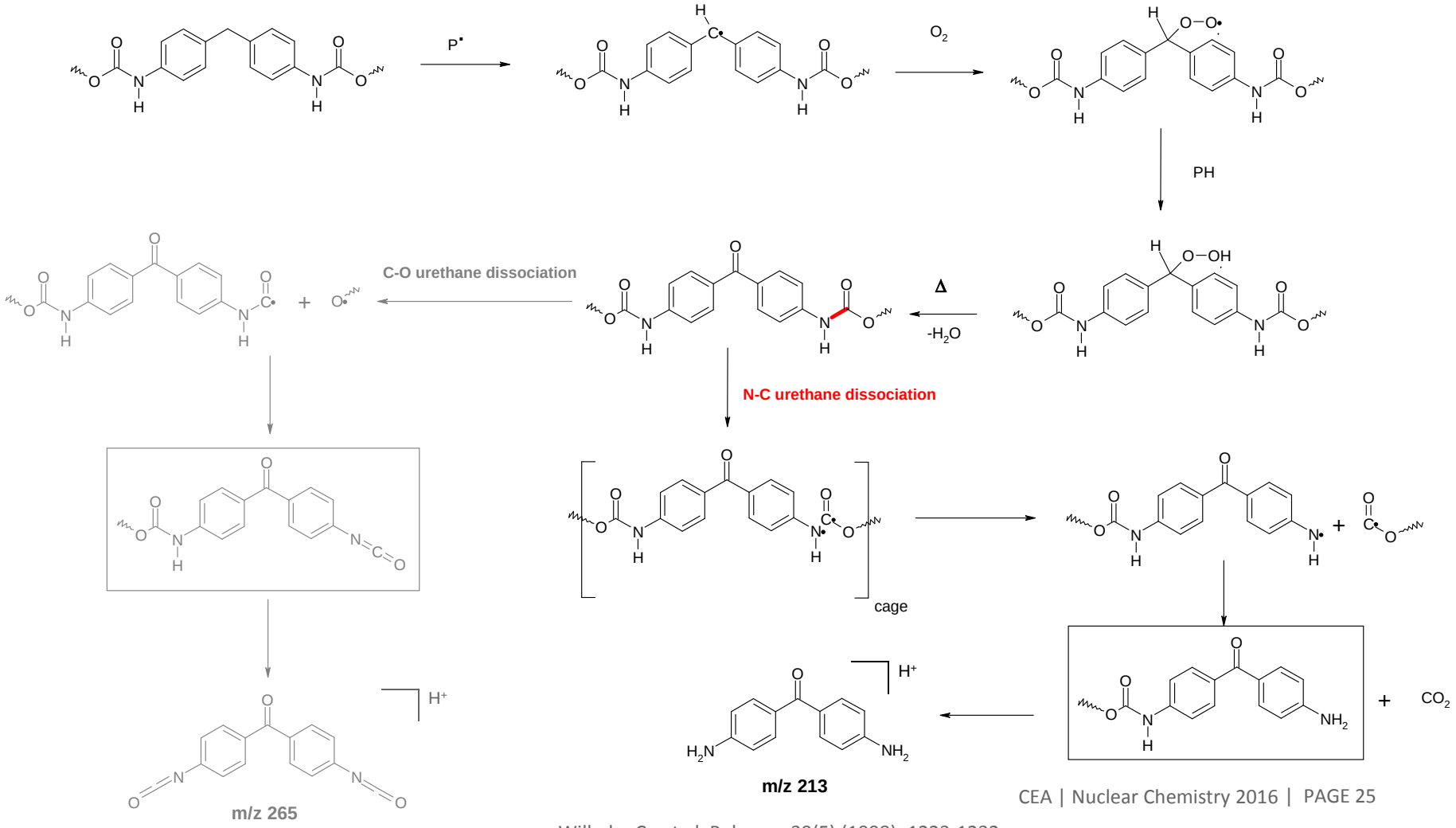
Proposed mechanism of HS degradation: **Radio-oxidation degradation**



Wilhelm C., et al. Polymer, 39(5) (1998), 1223-1232

ASAP ANALYSIS OF A CABLE SHEATH (PU) AFTER IRRADIATION

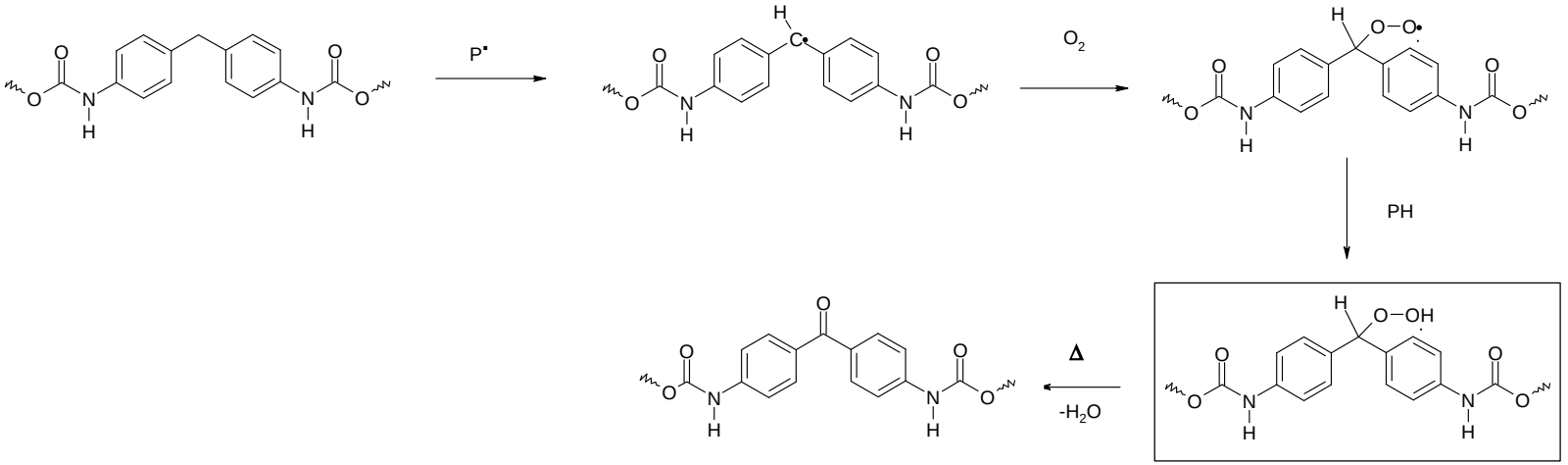
Proposed mechanism of HS degradation: **Radio-oxidation degradation**



Wilhelm C., et al. Polymer, 39(5) (1998), 1223-1232

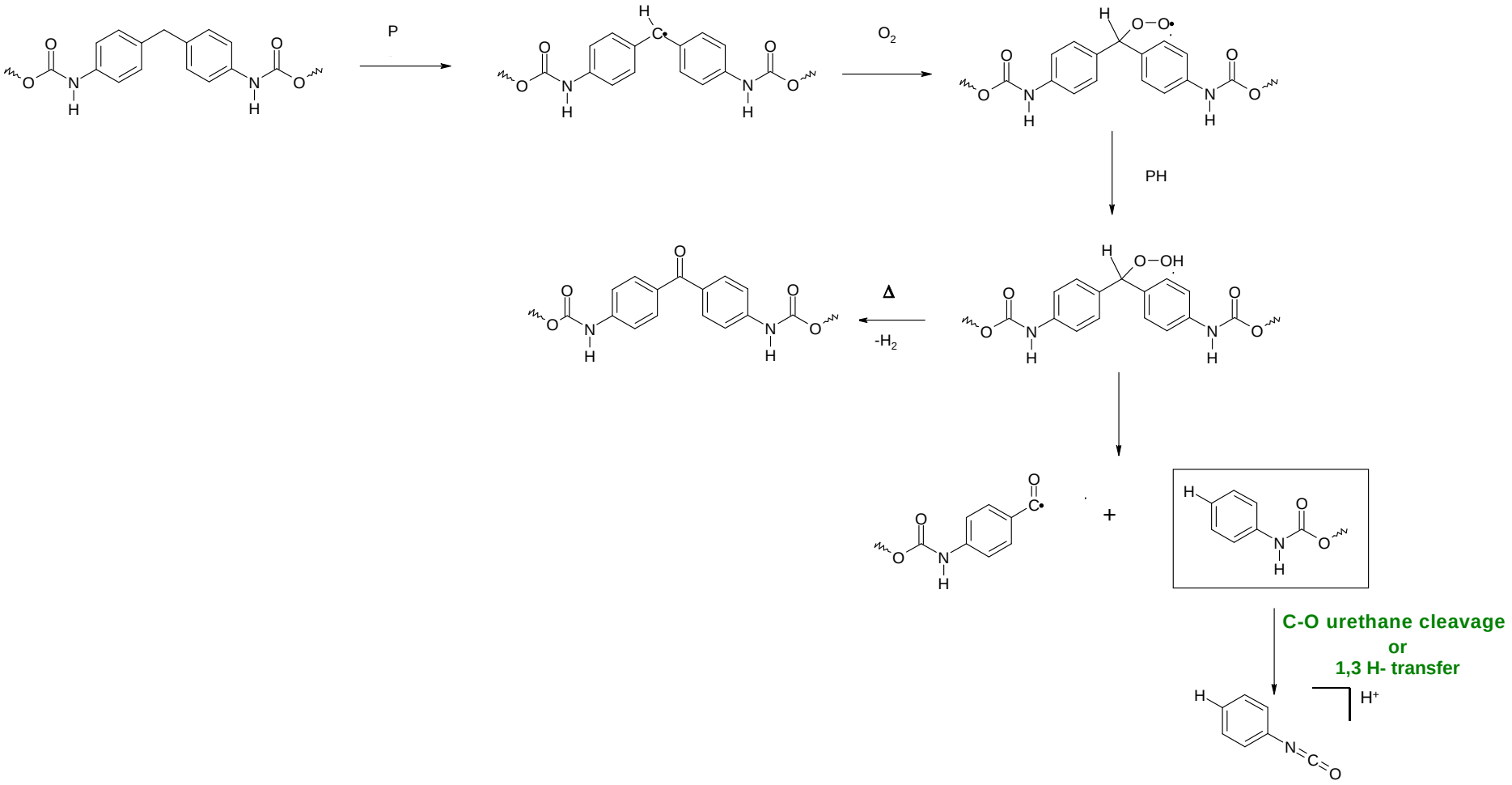
ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Proposed mechanism of HS degradation: **Radio-oxidation degradation**



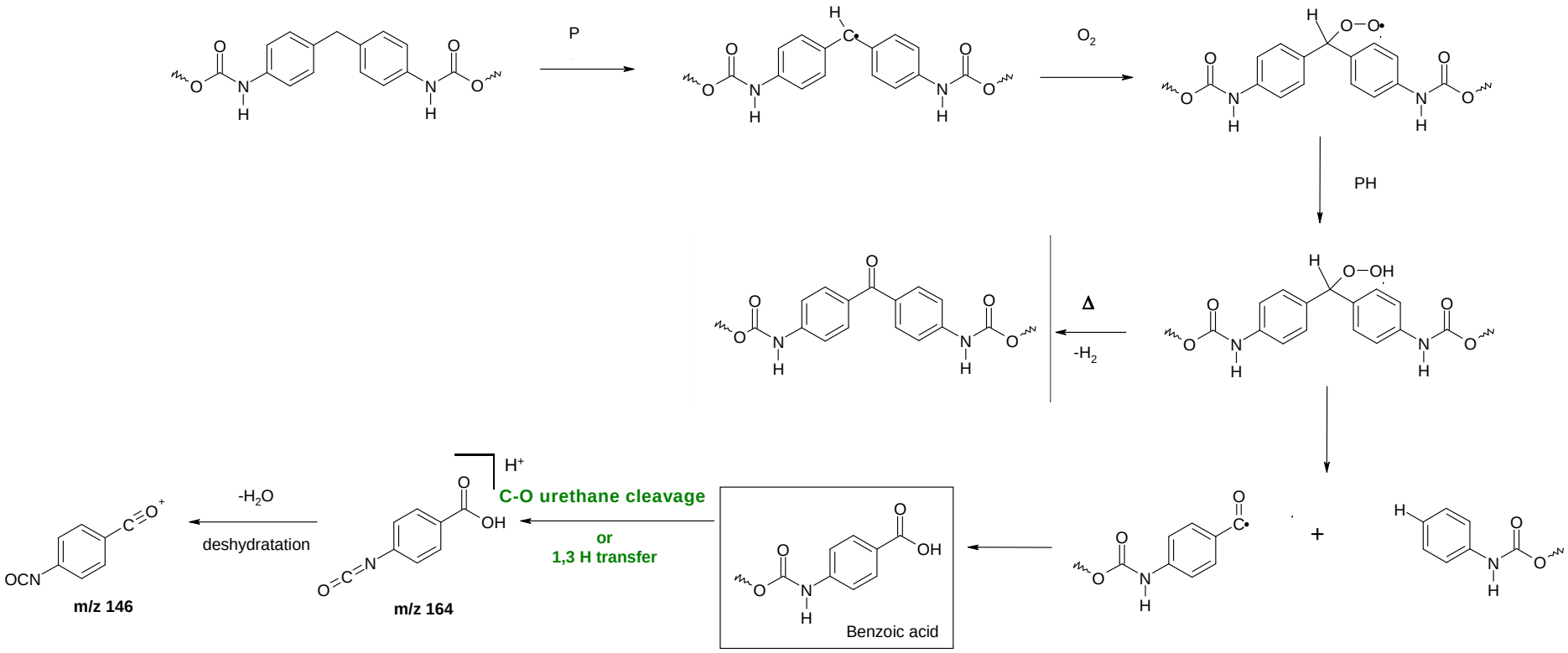
ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Proposed mechanism of HS degradation: **Radio-oxidation degradation**



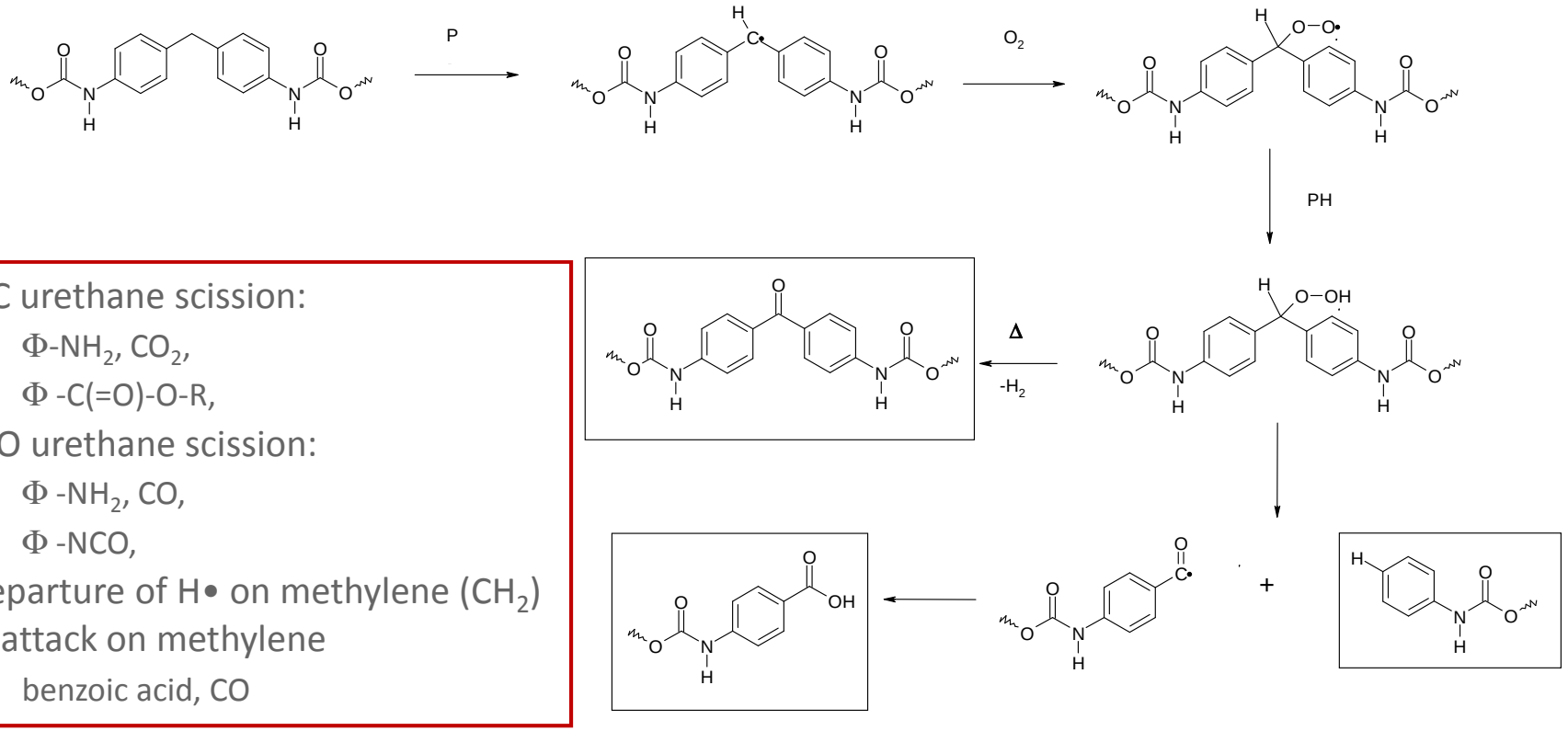
ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Proposed mechanism of HS degradation: **Radio-oxidation degradation**



ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Hard Segment dissociation

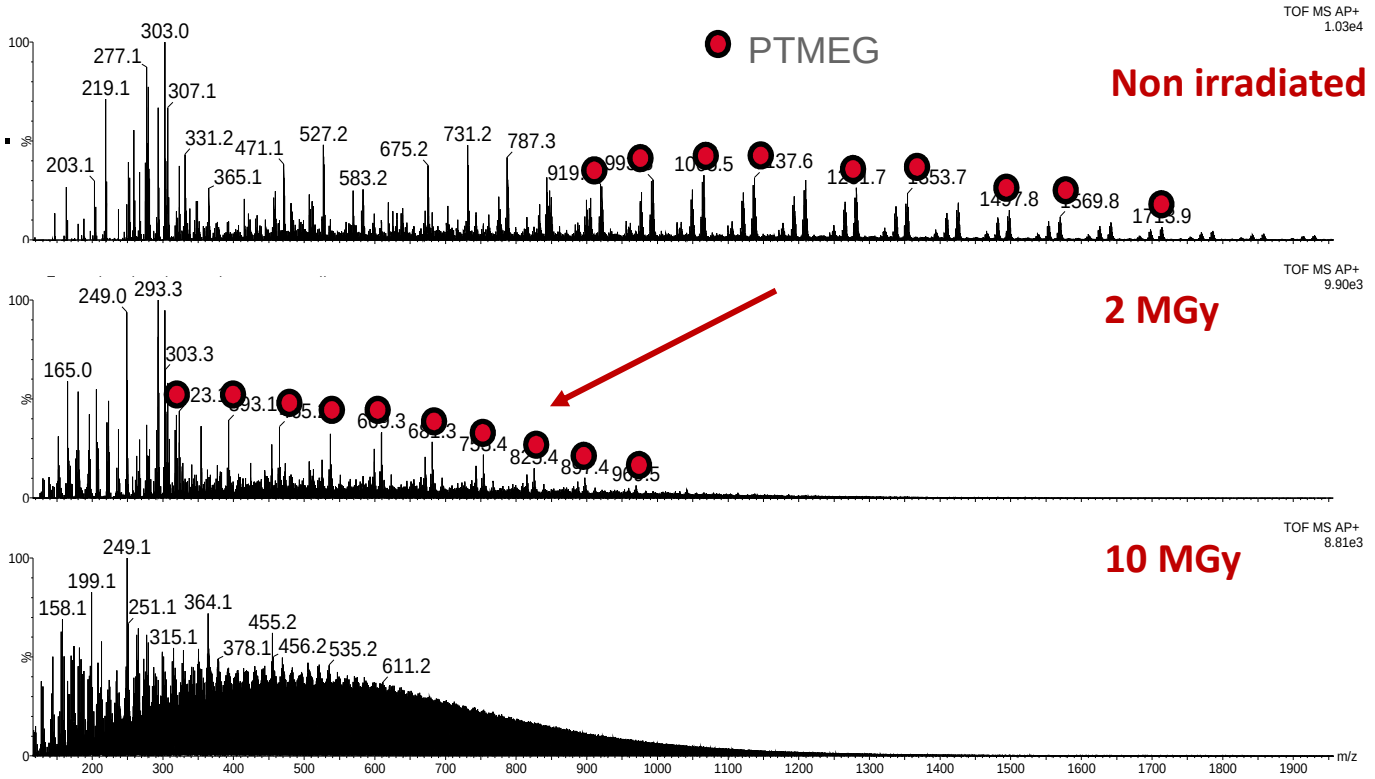


- N-C urethane scission:
  - Φ-NH_2, CO_2,
  - Φ -C(=O)-O-R,
- C-O urethane scission:
  - Φ -NH_2, CO,
  - Φ -NCO,
- Departure of H• on methylene (CH_2)
- O_2 attack on methylene
  - benzoic acid, CO

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



- Very different mass spectra with the dose

➔ Important impact on Soft Segment of the irradiation

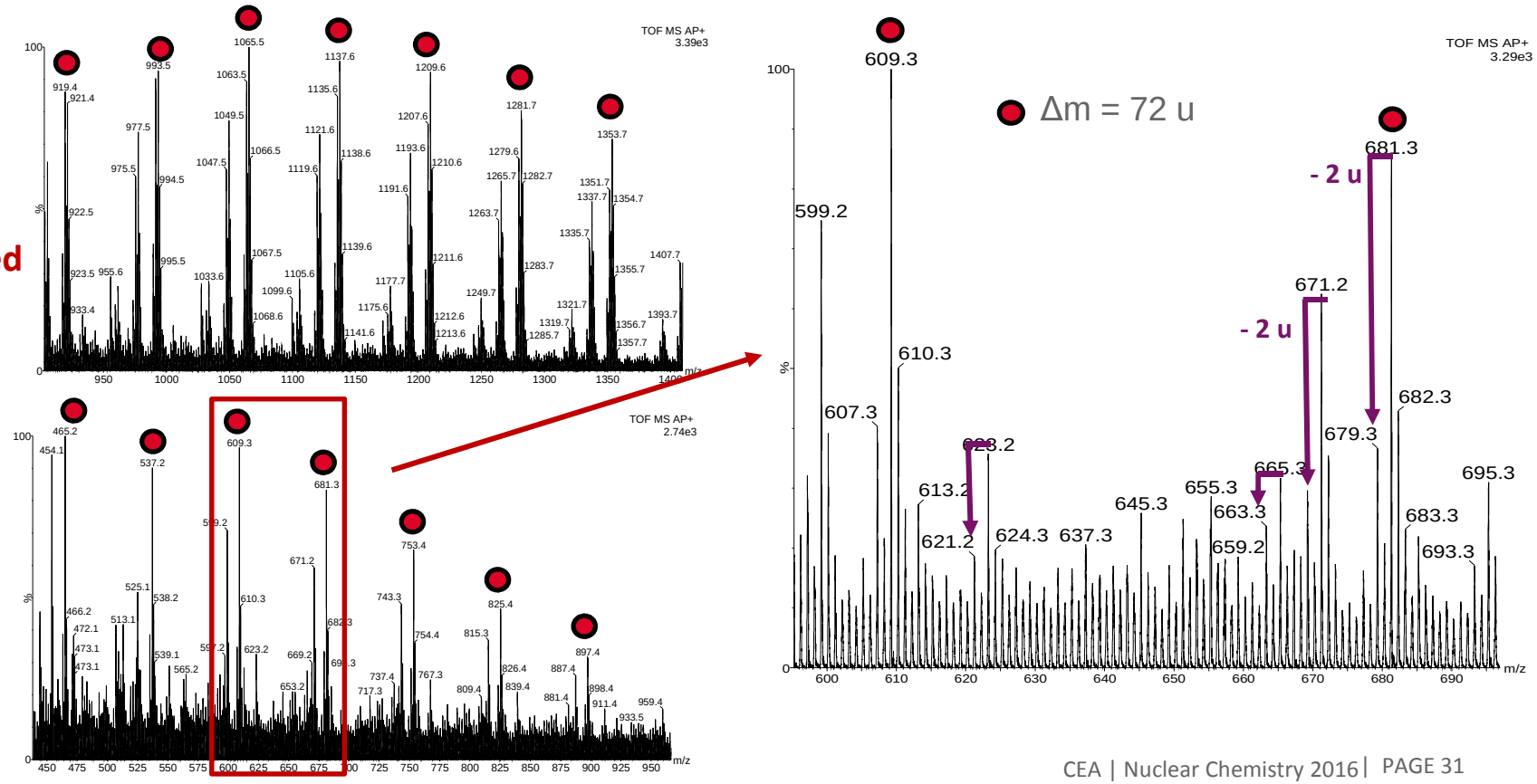
ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Identification of degraded polymers families after irradiation at 2 MGy

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

Non irradiated

2 MGy

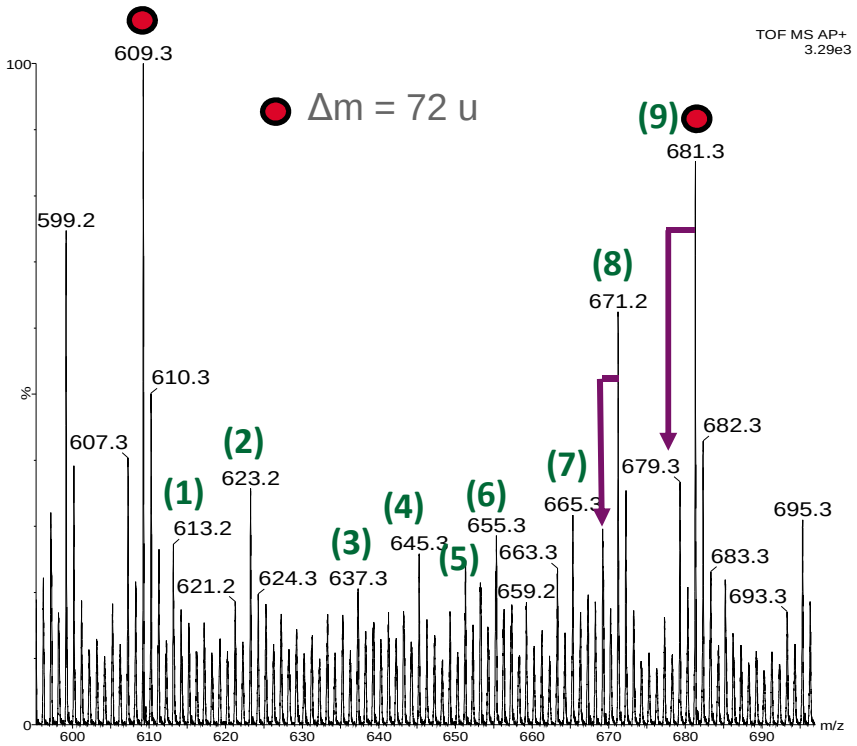


ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Identification of degraded polymers families after irradiation at 2 MGy

- ↗ of number of peaks between repeating units after irradiation
- Several peaks 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$_2$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**



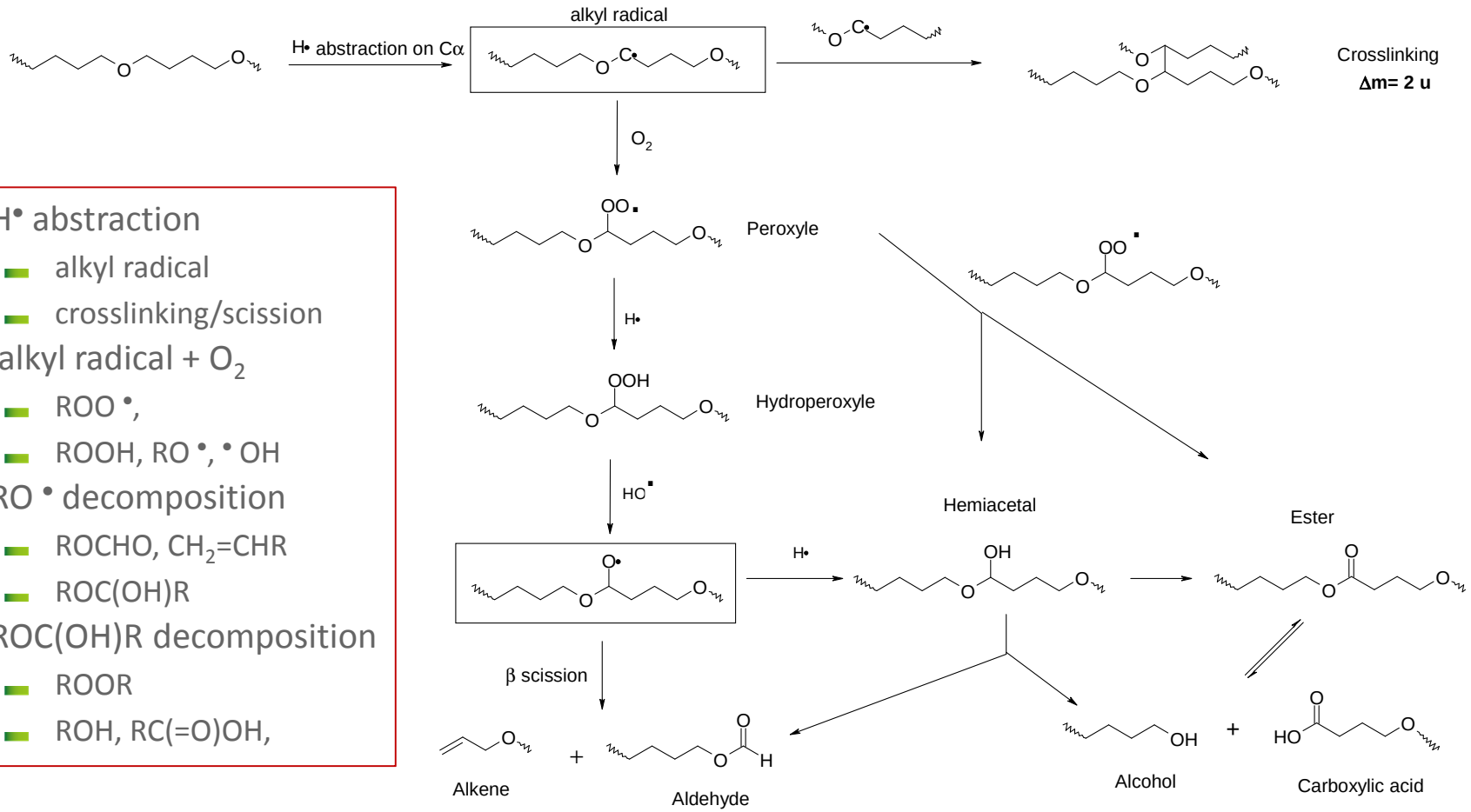
➔ **Oxidized functions: alcohol, hemiacetal, carboxylic acid and aldehyde**

➔ **Unsaturation function: alkenes**

ASAP ANALYSIS OF A CABLE SHEATH (PUR) AFTER IRRADIATION

Proposed mechanism of **Soft** Segment degradation

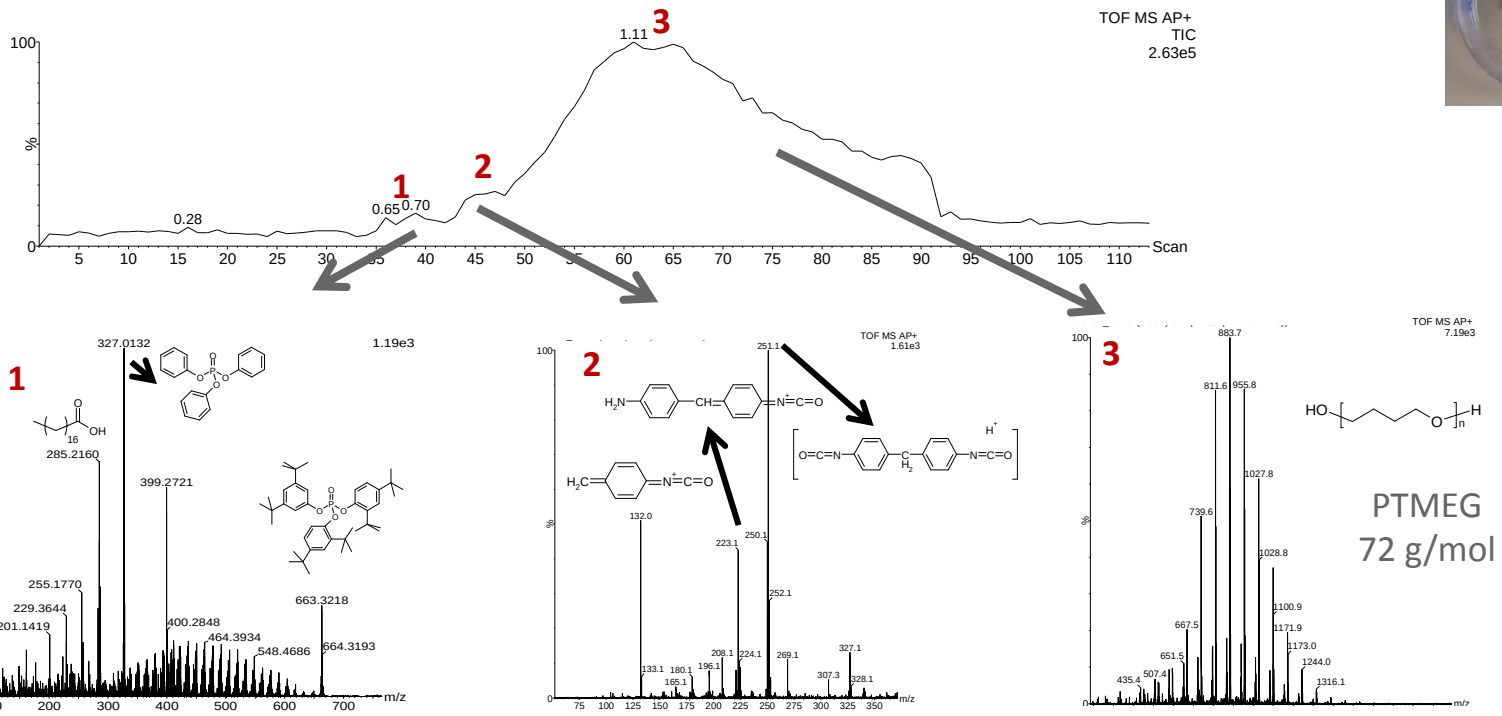
- H• abstraction
  - alkyl radical
  - crosslinking/scission
- alkyl radical + O_2
  - ROO •,
  - ROOH, RO •, • OH
- RO • decomposition
  - ROCHO, CH_2=CHR
  - ROC(OH)R
- ROC(OH)R decomposition
  - ROOR
  - ROH, RC(=O)OH,



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

PU POLYETHER - ELECTRIC CABLE SHEATH

ASAP Analysis: desorption with temperature



Additive detection | **Hard segment detection** | **Soft segment detection**

- Desorption of the components controlled by the temperature
- Hard Segment is thermally degraded at lower temperature than Soft Segment (confirmed by TGA)
- But Hard Segment more resistant to irradiation than Soft Segment

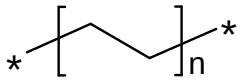
➔ **Mechanisms of both segments degradation under radio-oxidation is proposed using only one analytical method**

CASE II: ALIPHATIC POLYMER (APOLAR) POLYETHYLENE

POLYETHYLENE (PE)

Structural composition

- Unsaturated, aliphatic hydrocarbons



- Produced by cracking higher hydrocarbons of natural gas or petroleum
- Utilized in many important applications
  - Lubricants,
  - Surface coatings,
  - Additives,
  - For improving the flow and molding properties of plastics during processing.

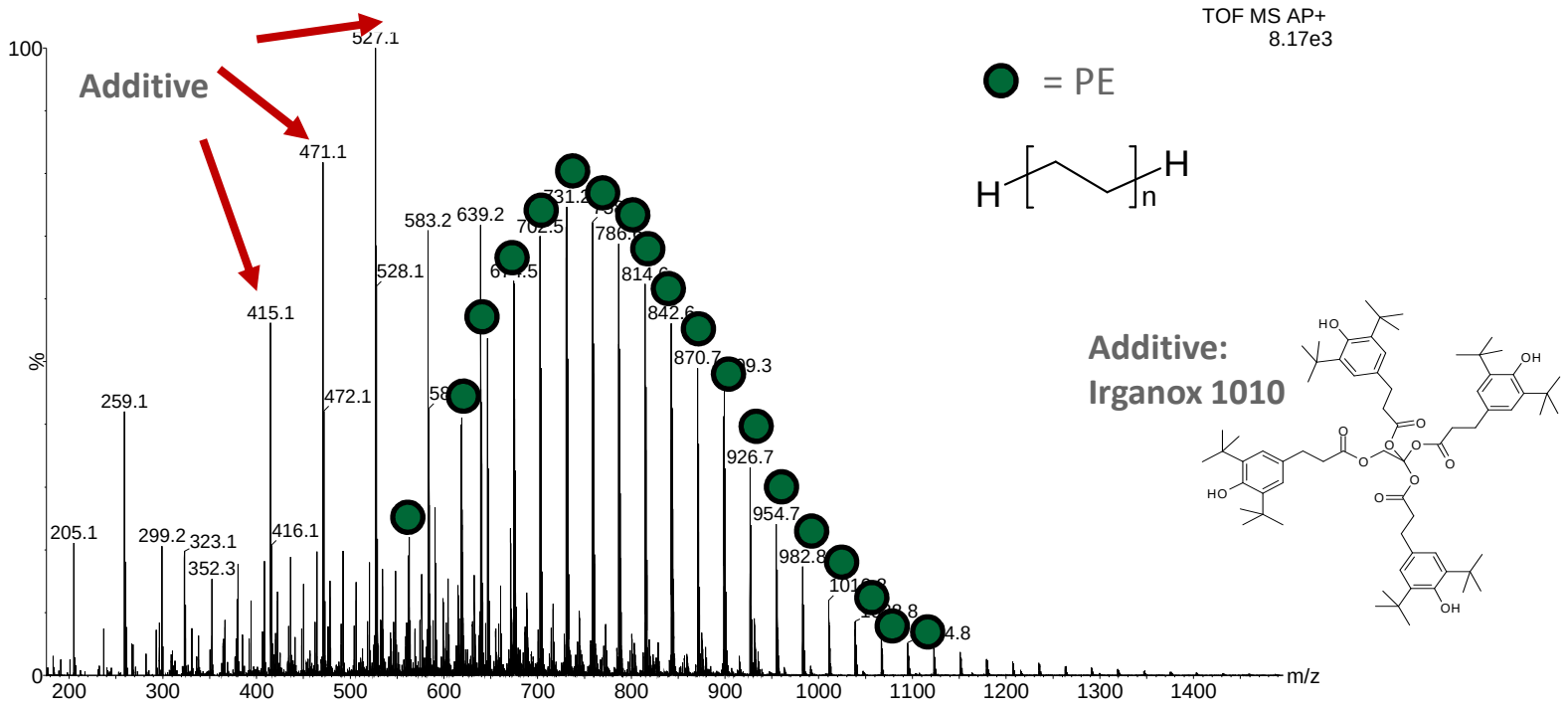
- Difficulty of mass spectrometry analysis: large saturated polymer without heteroatoms

➔ Used of plasma desorption ionization method as ASAP-MS

ASAP ANALYSIS OF PE

Non irradiated polymer

- Detection of a characteristic polymeric profile

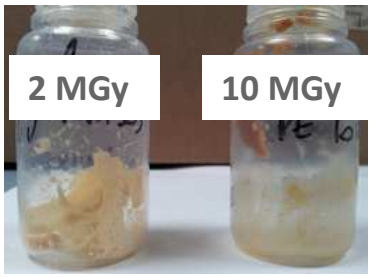


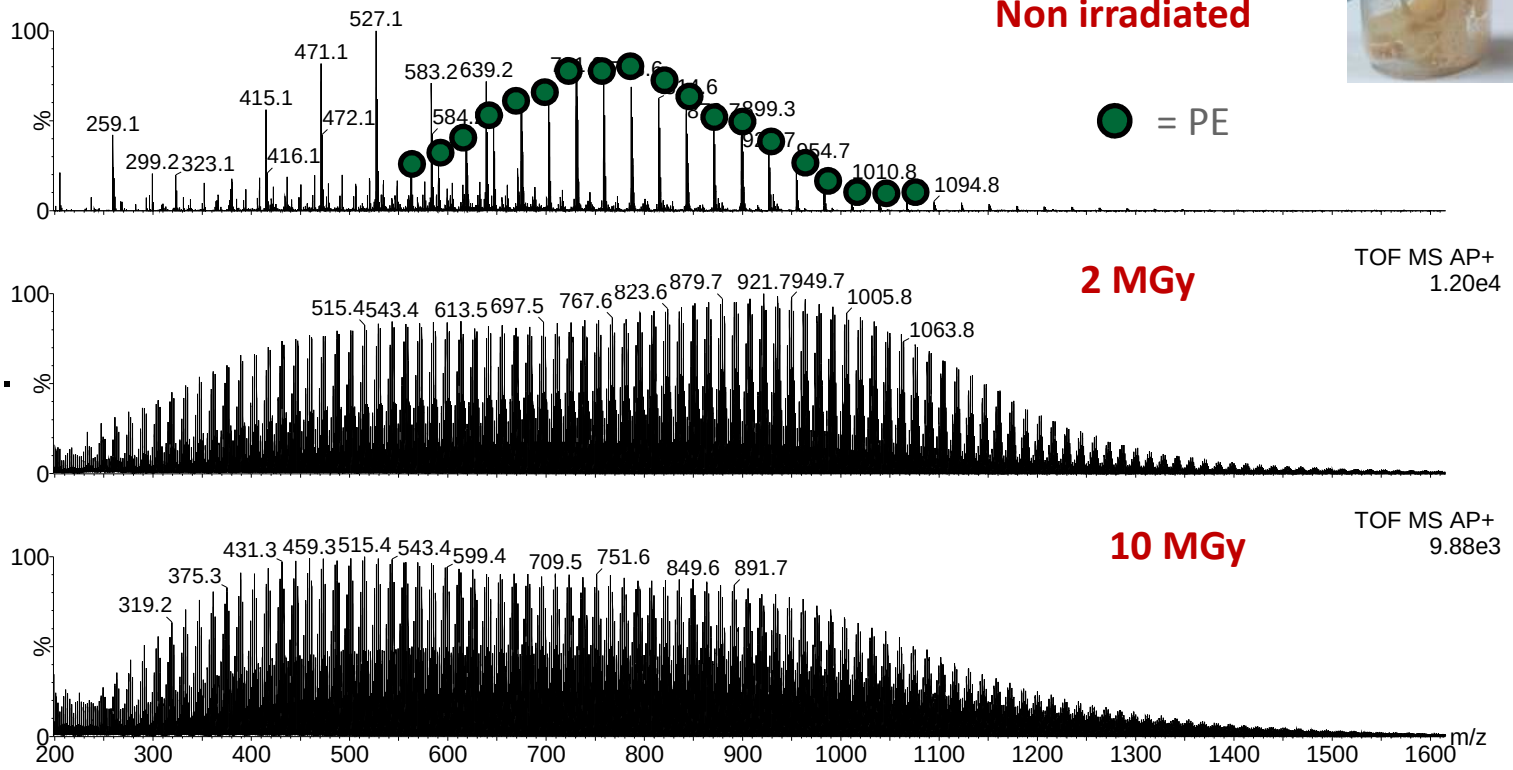
- Detection of additive
- Δm= 28 u: PE and Fragments ions (-14 u= -CH_2)

⇒ Structural identification of **polyethylene**

ASAP ANALYSIS OF PE AFTER IRRADIATION

Irradiated PE





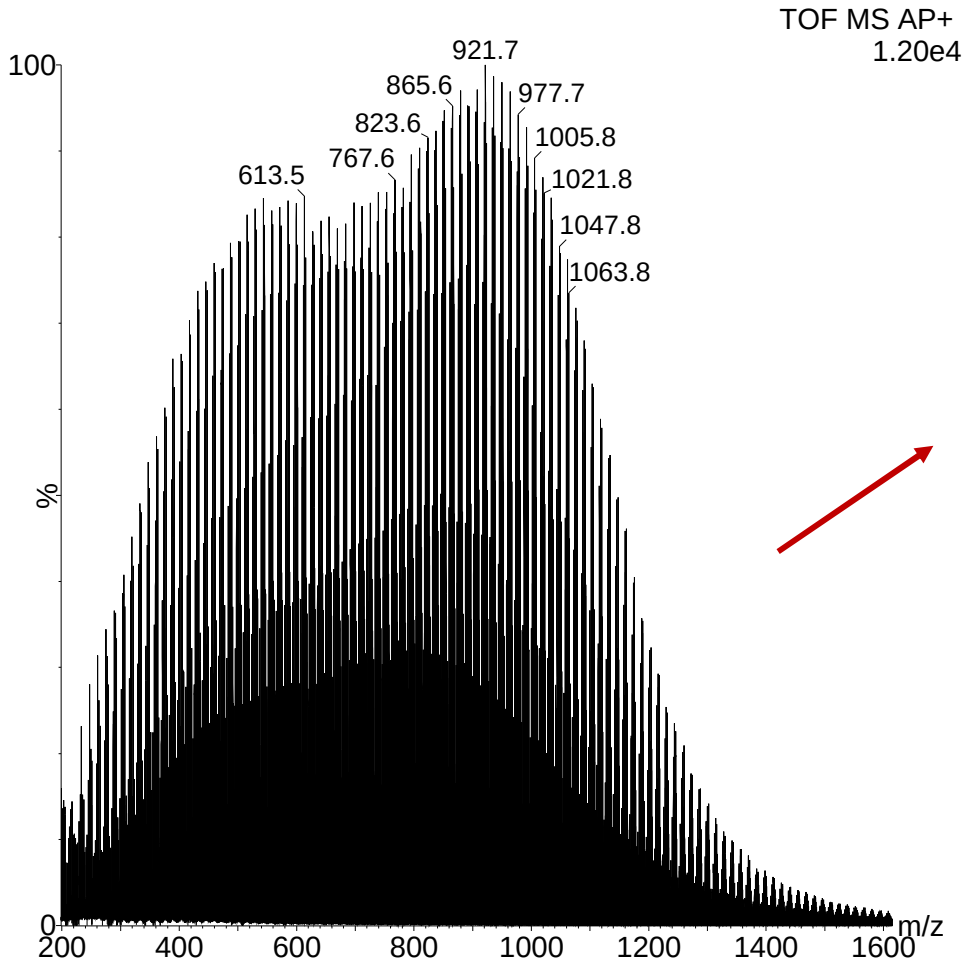
- Very different mass spectra after irradiation at 2 and 10 MGy

➔ Important impact of radio-oxidation

- Similar mass spectra after irradiation at 2 and 10 MGy

ASAP ANALYSIS OF PE AFTER IRRADIATION

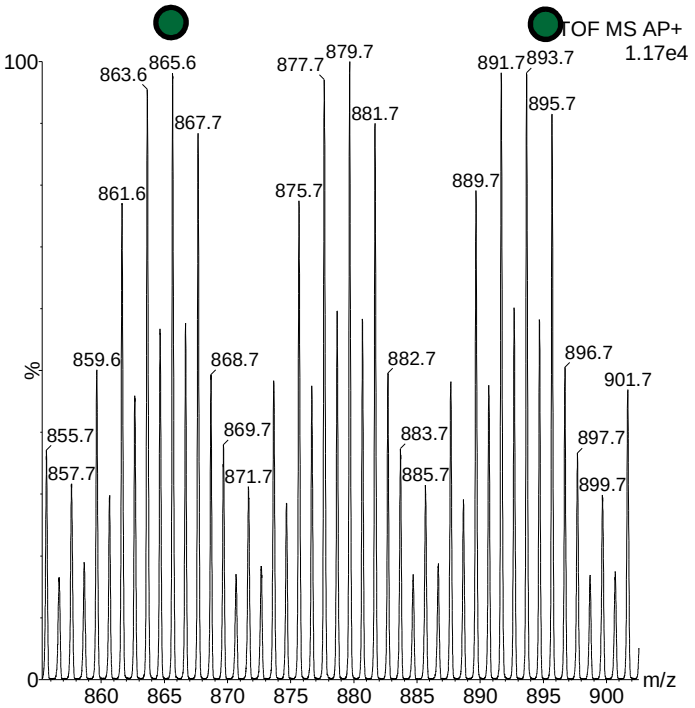
PE after irradiation at 2 MGy



Mainly Δm= 2 u

➔ **unsaturation and/or crosslinking**

= 28 u



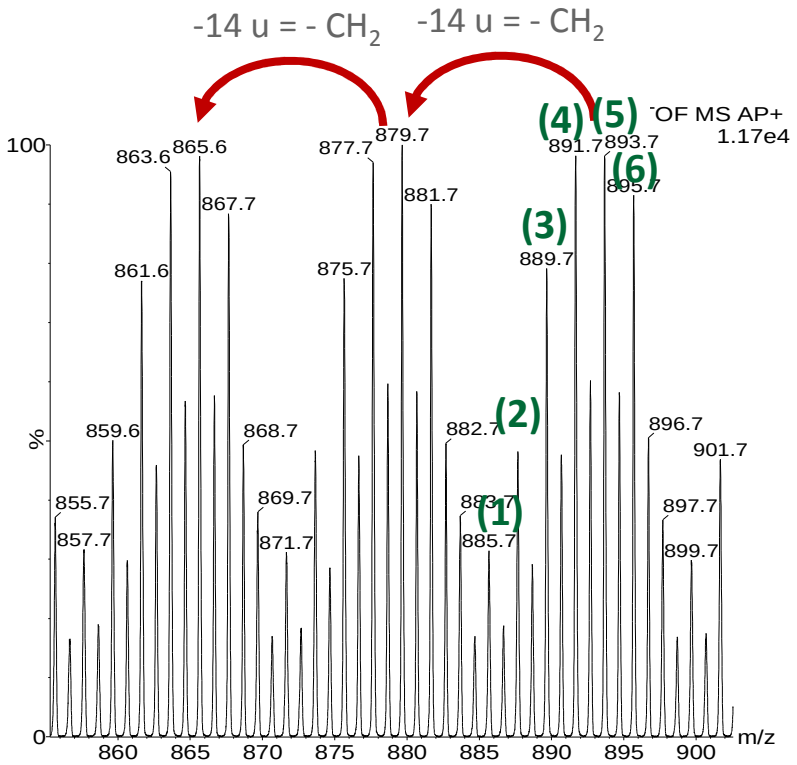
ASAP ANALYSIS OF PE AFTER IRRADIATION

PE after irradiation at 2 MGy

- 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**

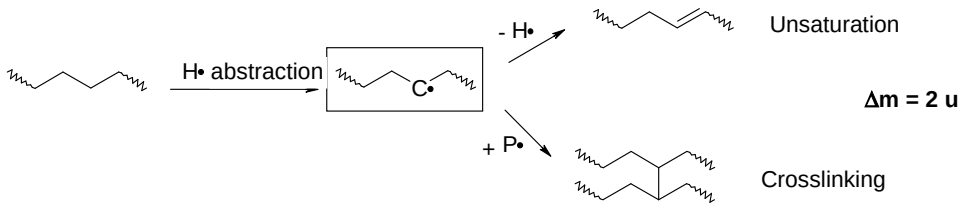


➔ **Oxidized functions: alcohol, carboxylic acid and aldehyde**

➔ **unsaturation function: alkenes**

ASAP ANALYSIS OF PE AFTER IRRADIATION

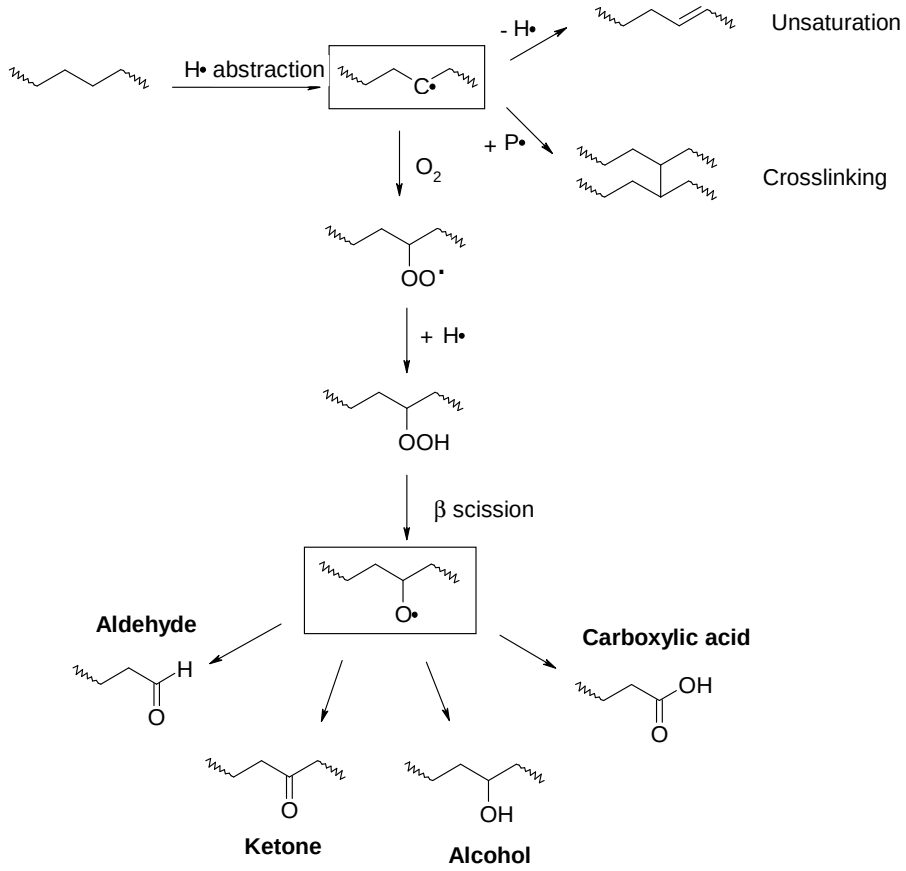
Proposed mechanism of PE degradation



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

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 1/2

Analysis of degradated polymers by ASAP-MS

- Characterization of the PU: a copolymer
  - Detection of additives
  - Hard and Soft Segments separation with a gradient of temperature: temporal separation of molecules in function of their volatilization and/or degradation temperature
  - Identification of degraded products after irradiation:
    - Hard segment: mainly amine, isocyanate and carboxylic acid functions
    - Soft Segment:
      - More sensible to radio-oxidation
      - Mainly oxidized functions (carboxylic acid, alcohol, aldehyde and hemi-acetal)
  - A mechanism of degradation could be proposed

- Characterization of PE: an aliphatic polymer
  - Detection of additives
  - Characterization of polymer before and after radio-oxidation
  - Identification of degraded products:
    - mainly unsaturation and/or crosslinking
    - Oxidized functions (carboxylic acid, alcohol and aldehyde)

CONCLUSIONS AND PERSPECTIVES 2/2

ASAP-MS

- Fast analysis (< 1 min)
- no sample preparation
- Detection of polymer AND additives
- In one analysis: same results observed as those obtained with several techniques (FTIR, MS, UV, TGA, etc…)

➔ Confirmation of degradation mechanisms under oxidation irradiation

Perspectives

- semi-quantification of degradated products with the doses
- Analysis at lower doses to explore impact of additives

Thank you for your attention.

ACKNOLEDGMENTS

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Solène Legand
Jean Luc Roujou
Manon Cornaton

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Service d'étude du comportement des radionucléides