



HAL
open science

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

D. Lebeau

► **To cite this version:**

D. Lebeau. ASAP and DART mass spectrometry analysis for the understanding of polymers degradation mechanisms.. Nuclear Chemistry 2016, Dec 2016, San Antonio, United States. hal-02442252

HAL Id: hal-02442252

<https://cea.hal.science/hal-02442252>

Submitted on 16 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DE LA RECHERCHE À L'INDUSTRIE

cea den

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




Diane Lebeau

CEA, DEN, DANS, DPC, SECR, LRMO, F-91191 Gif-sur-Yvette, France.

NUCLEAR CHEMISTRY 2016 – SAN ANTONIO

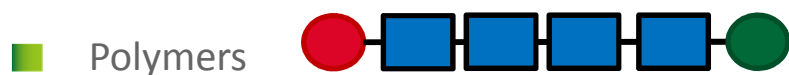
Polymers in nuclear industry

- 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

Polymers



- Repeating units
- Ends groups
- Average mass

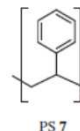
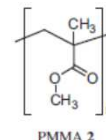
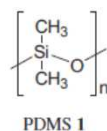


- Heteroatoms (PEG, PMMA...)
- Unsaturated (PB)
- Aromatics (PS)
- Saturated (PE, PP...)

$$M_n = (\sum niMi) / \sum ni$$

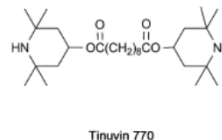
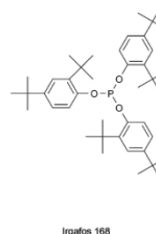
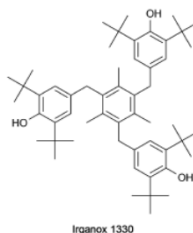
$$M_w = (\sum ni Mi^2) / (\sum ni Mi)$$

→ Polydispersity
Pd = Mw/Mn

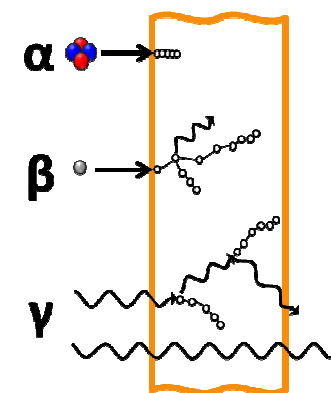


Additives

- Anti-UV
- Antioxidants
- Photostabilizants
- ...



- Polymers (organic molecules) + radionuclides (emitters α and β/γ)
- Interaction of radiation with organic matter
- Irradiation induces chemical reactions in the material

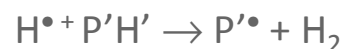


■ Mechanism under **inert** conditions

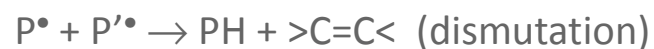
■ Initiation:



■ Propagation:



■ Termination

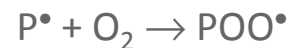


■ Mechanism under **oxidative** conditions

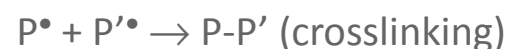
■ Initiation:



■ Propagation:



■ Termination: recombinaison



Consequences of irradiation → changes in physical structure and properties

- Crosslinking: \nearrow Mw \rightarrow \searrow solubility to insolubility \rightarrow hardness
- Scission: \searrow Mw \rightarrow \nearrow solubility \rightarrow viscous material

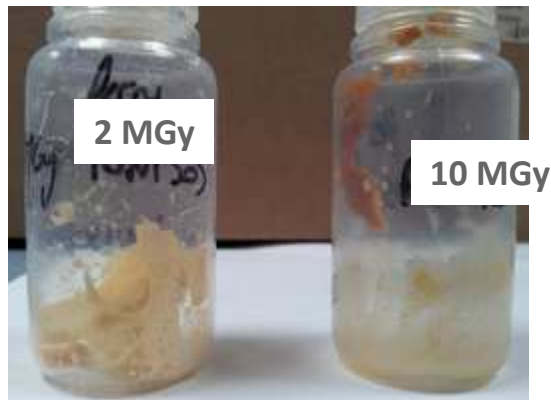
Polyurethane



1, 2 and 5 MGy

10, 15 and 20 MGy

Polyethylene



2 MGy

10 MGy

Ethylene-vinyl acetate (EVA)



2 MGy

10 MGy

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



Gas

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



Liquid

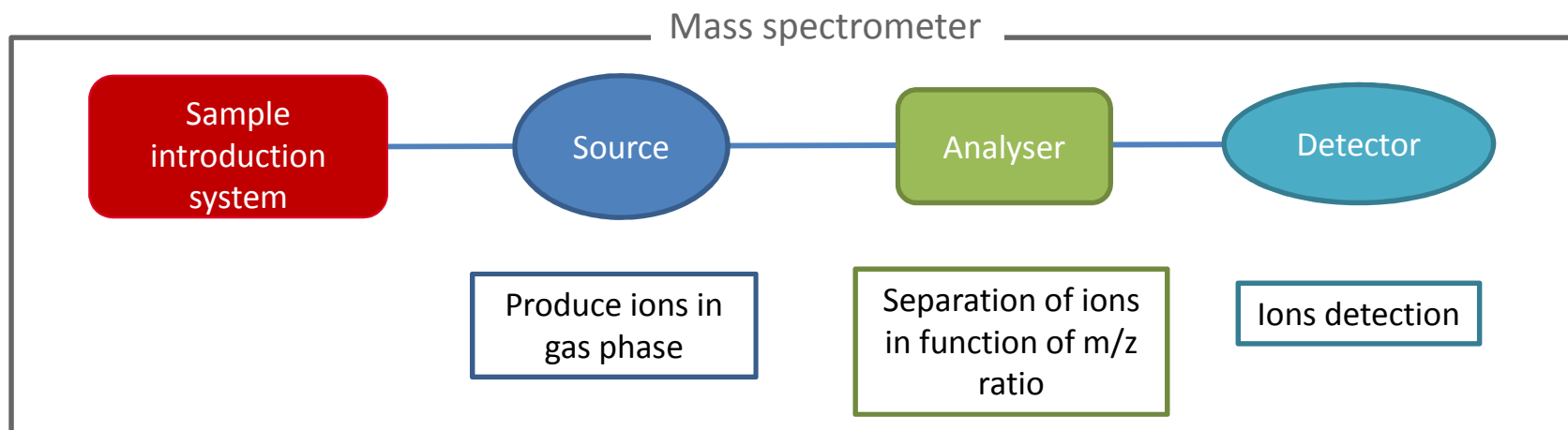
- Size exclusion chromatography
- **Mass spectrometry** (ESI, MALDI)
- UV-spectroscopy



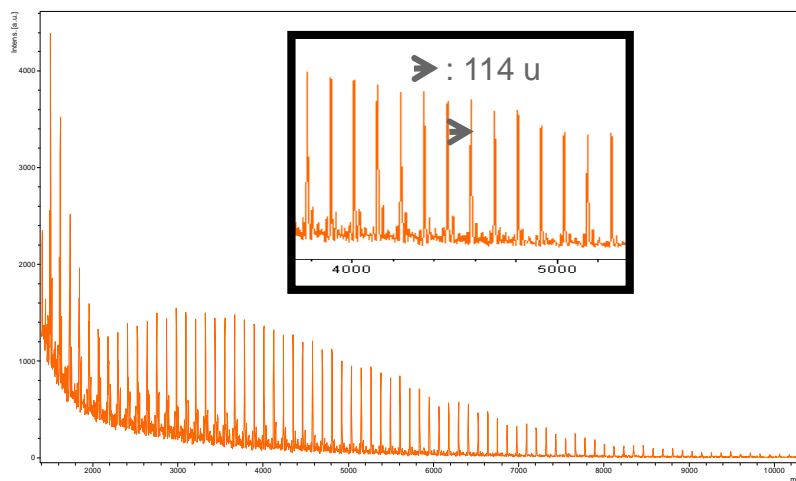
Solid

- Fourier transform infrared spectroscopy (FTIR)
- Electron paramagnetic resonance (radical analysis)
- X-ray diffraction
- **Mass spectrometry**





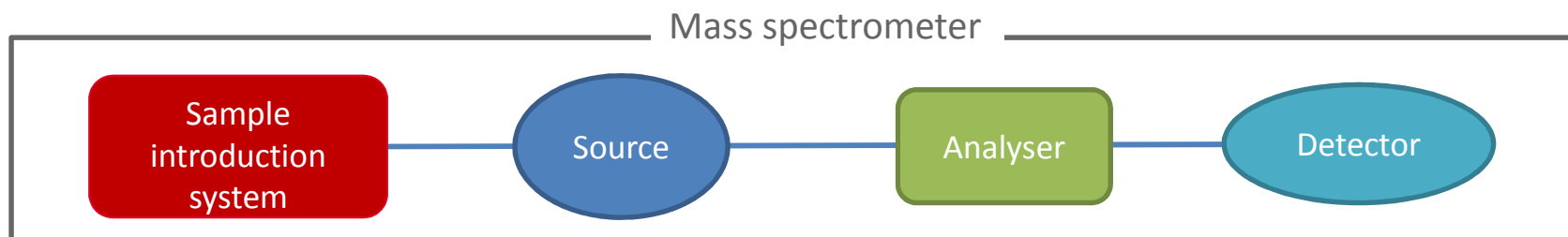
■ In case of polymers analysis: determination of characteristic parameters of polymer



- 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 $Pd = M_w/M_n$

$$\left(\text{with } M_n = \frac{\sum n_i M_i}{\sum n_i} \text{ and } M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}\right)$$



■ Choice of mass spectrometry techniques

Sample introduction	Source	Analyser
<ul style="list-style-type: none"> • Solubility • Volatility • Thermal stability 	<ul style="list-style-type: none"> • Polarity • Thermal stability • Molecular mass • Solubility 	<ul style="list-style-type: none"> Mass range Mass resolution Scan speed Limit of detection Dynamic range

■ After irradiation:

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

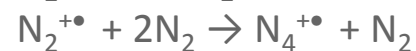
→ an analytical method **without any sample pretreatment** is required

Atmospheric Solids Analysis Probe (ASAP)

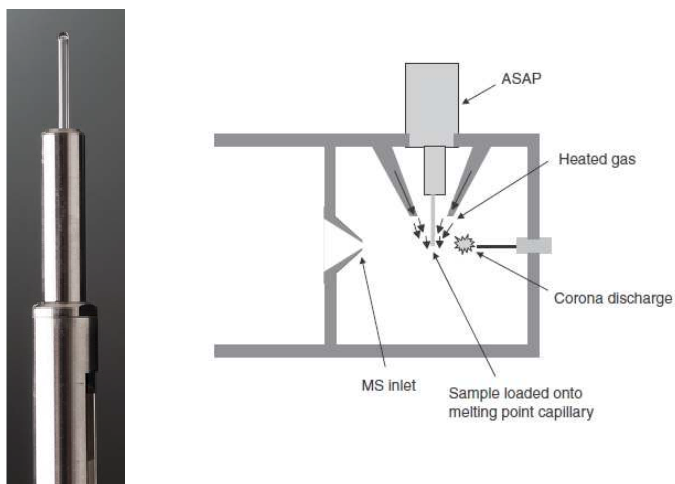
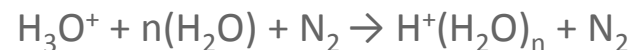
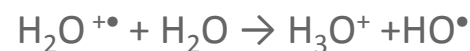
- Chemical and structural Identification of unknown component analytes comprising a complex mixture → **Direct solid analysis**

- Sample deposited onto glass tube
 - Use of pure sample
 - No solvent required
- Desorption using a hot N₂ flux
- Ionization from plasma generated by a corona discharge

- Charge transfer (M^{+•})

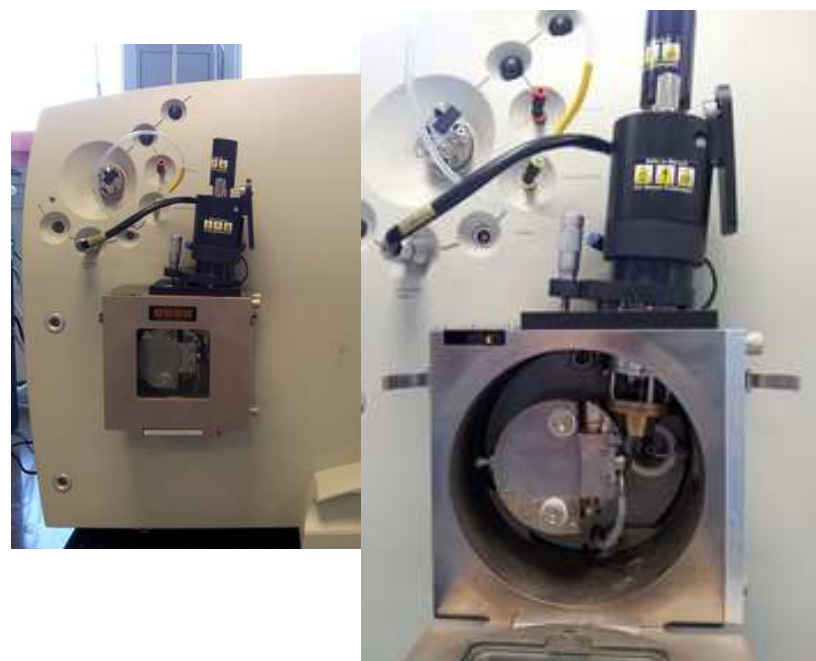
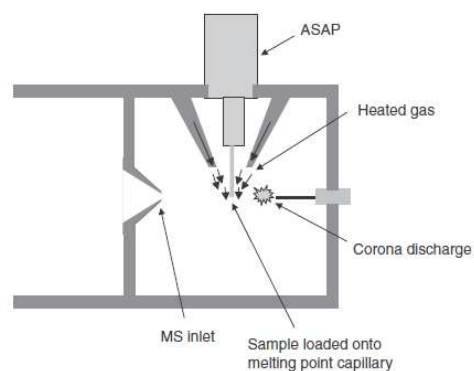


- Proton transfer (MH⁺)



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 N₂ flux
 - Ionization from plasma generated by a corona discharge

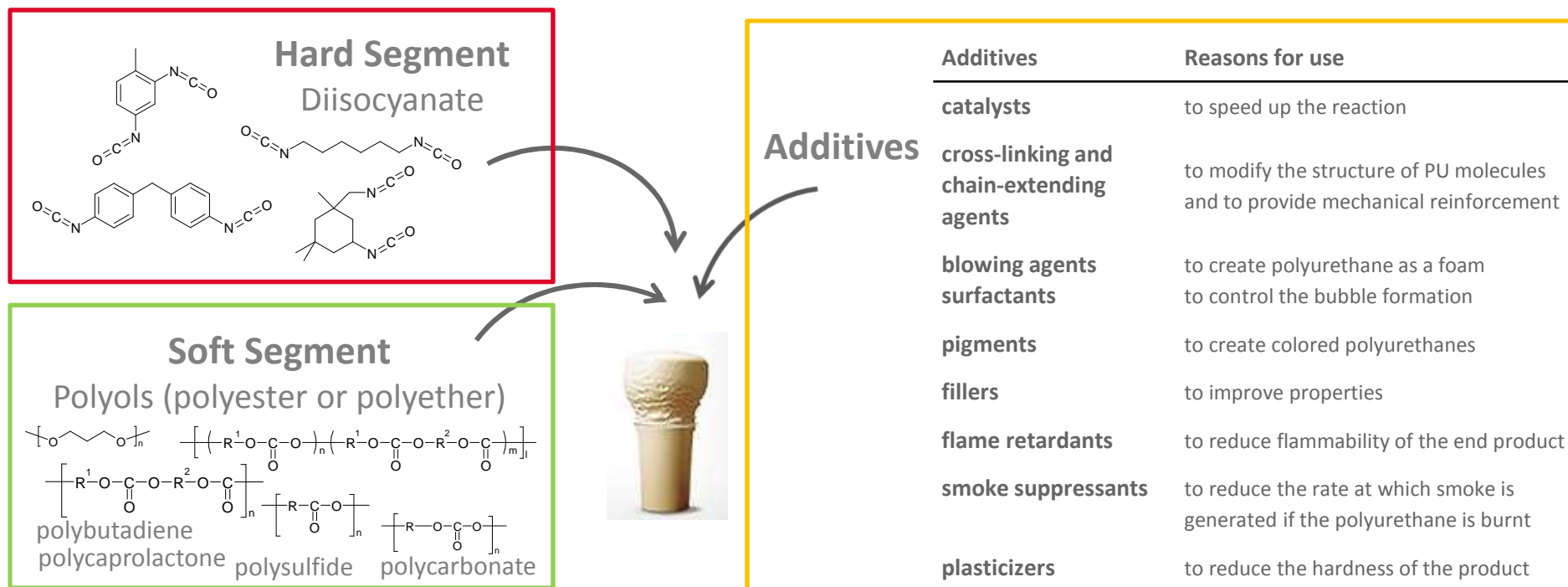


Analysis on LCT-XE Premier (Waters) with a single TOF analyzer

**CASE I: CO - POLYMER
POLYURETHANE (PU)**

Polyurethane synthesis

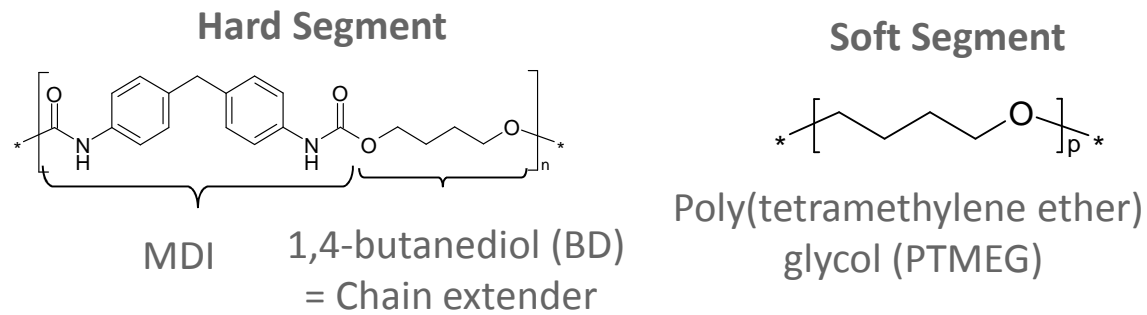
- Polyaddition of a diisocyanate to a polyol in the presence of additives



- 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**

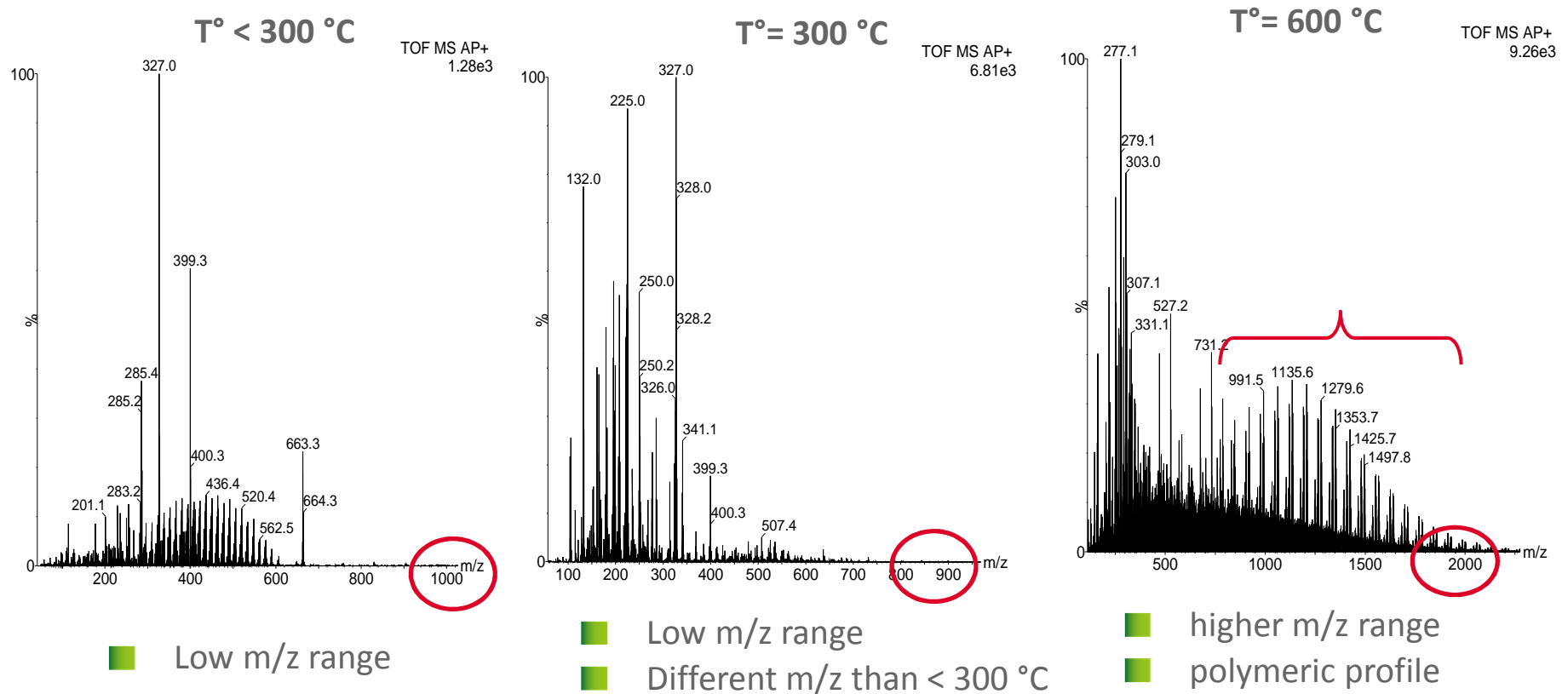
Polyether polyurethane: electric cable sheath



Non irradiated

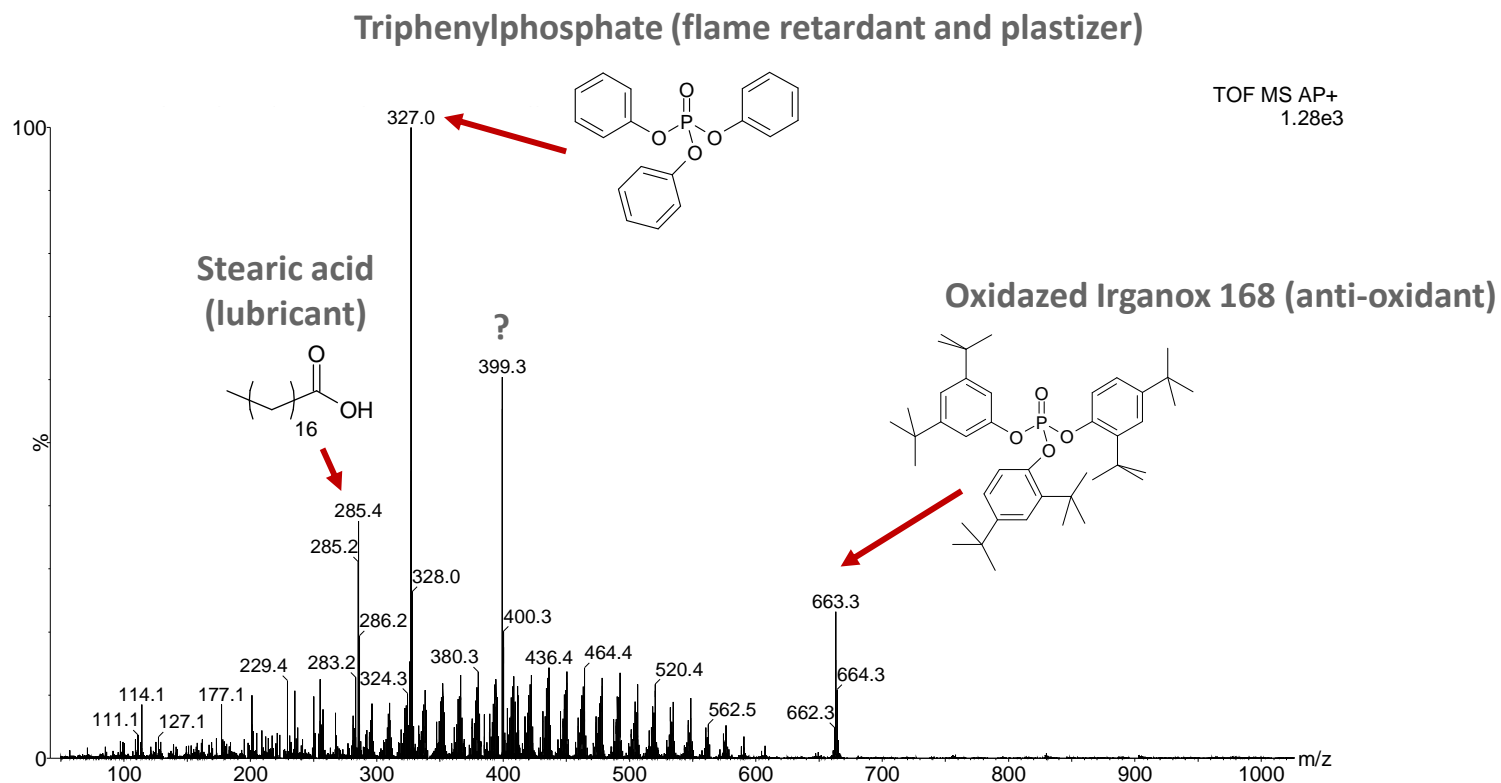


ASAP: thermal plasma desorption → analysis of sample at different temperatures



→ Desorption of compounds with temperature

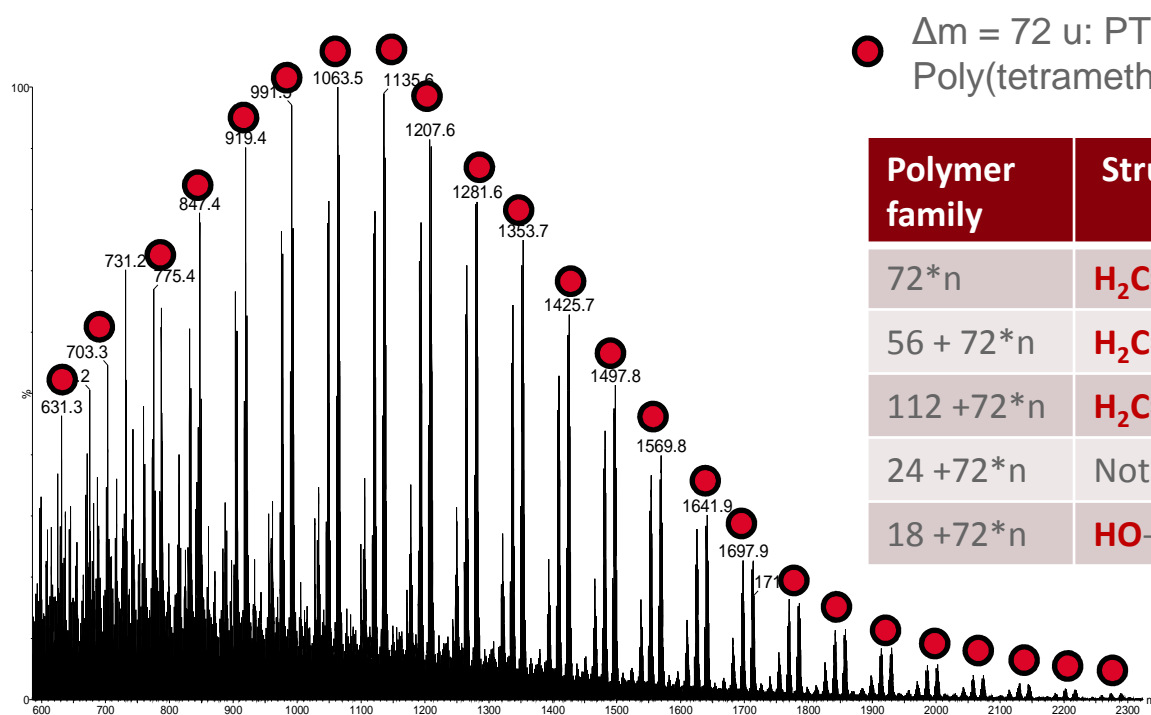
Analysis at low temperature ($T^\circ < 300^\circ\text{C}$)



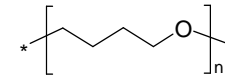
- Detection of additives of the polymer
- TOF analyzer → exact mass measurements → additives identification

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

■ Detection of a characteristic polymeric profile



● $\Delta m = 72 \text{ u}$: PTMEG
Poly(tetramethyleneglycol)



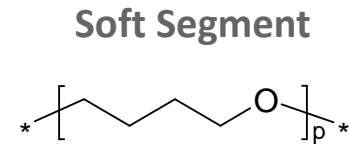
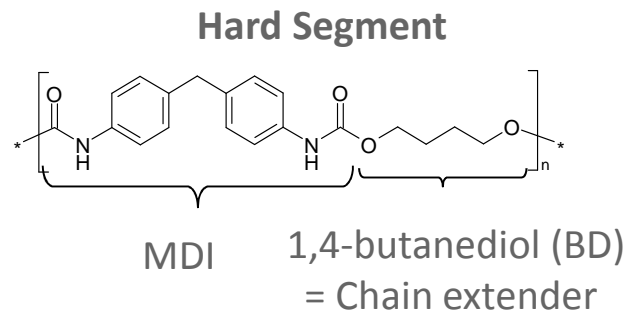
Polymer family	Structures
$72*n$	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{O}-(\text{PTMEG})_n-\text{H}$
$56 + 72*n$	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-(\text{PTMEG})_n-\text{H}$
$112 + 72*n$	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-(\text{PTMEG})_{n-1}-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2$
$24 + 72*n$	Not identified
$18 + 72*n$	$\text{HO}-(\text{PTMEG})_n-\text{H}$

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

■ Fragments ions → Structural identification of Soft Segment of PU

➔ Desorption of the copolymer components can be controlled by temperature

Polyether polyurethane



Poly(tetramethylene ether) glycol (PTMEG)

Non irradiated



Dose rate: 0.6 à 0.75 kGy/h
 $\xrightarrow{\hspace{2cm}}$
 Oxidative conditions

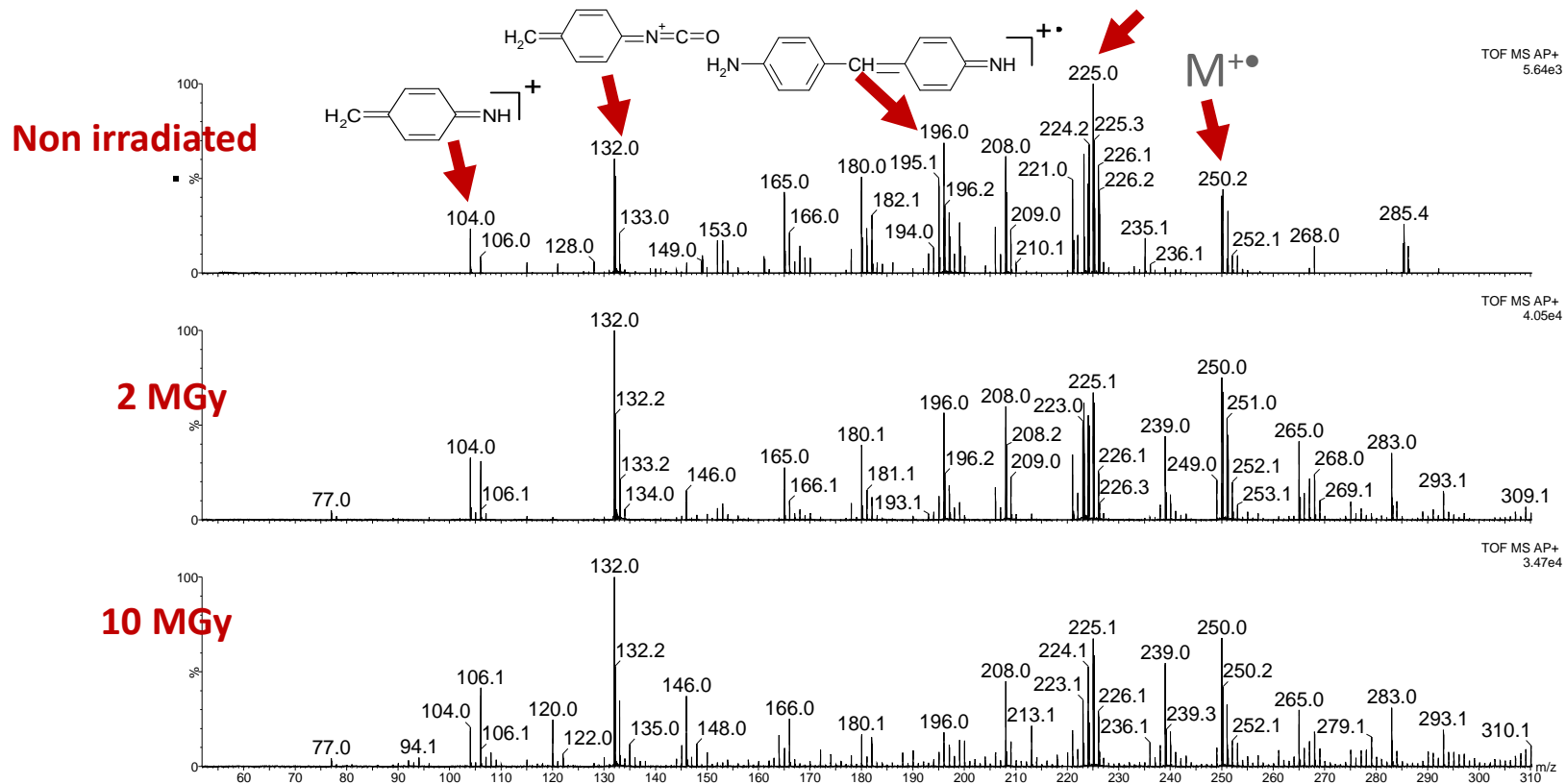
2 MGy



10 MGy

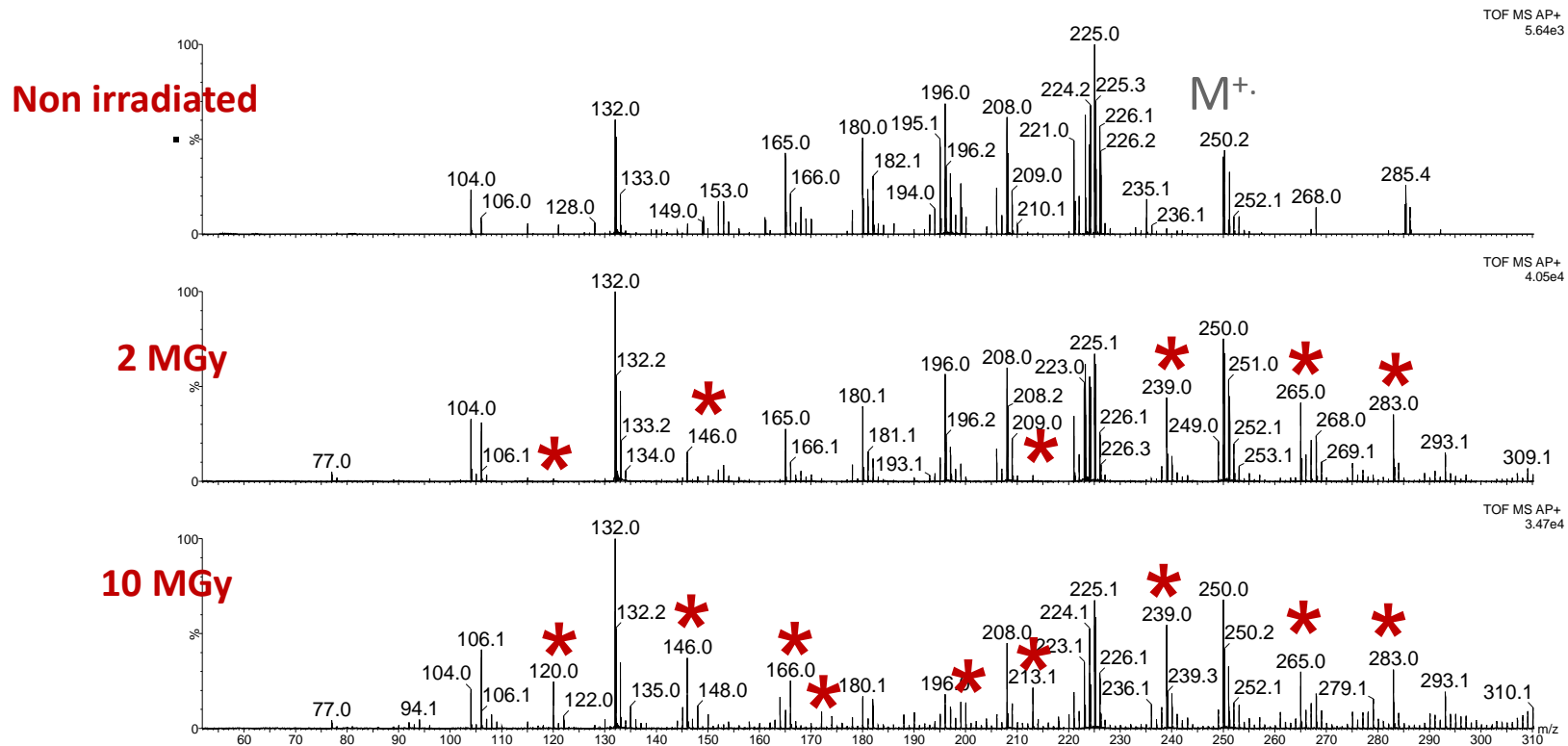


Analysis at 300 °C → Hard Segment degradation



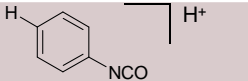
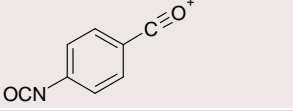
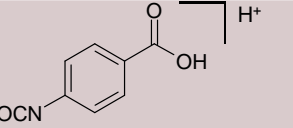
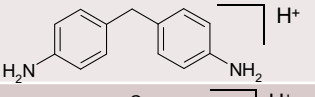
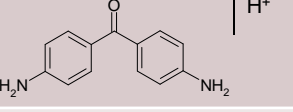
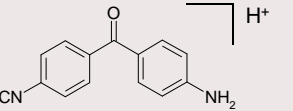
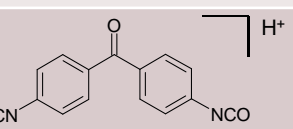
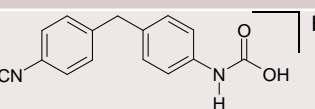
- Very similar mass spectra with the dose: detection of characteristic ions fragments of MDI
- Impact on Hard Segment seems low

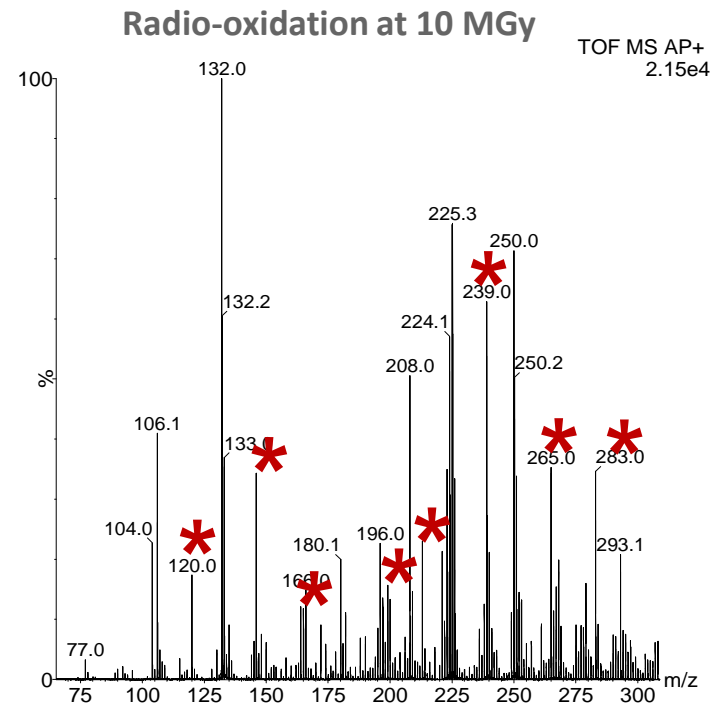
Analysis at low temperature → Hard Segment degradation



- 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

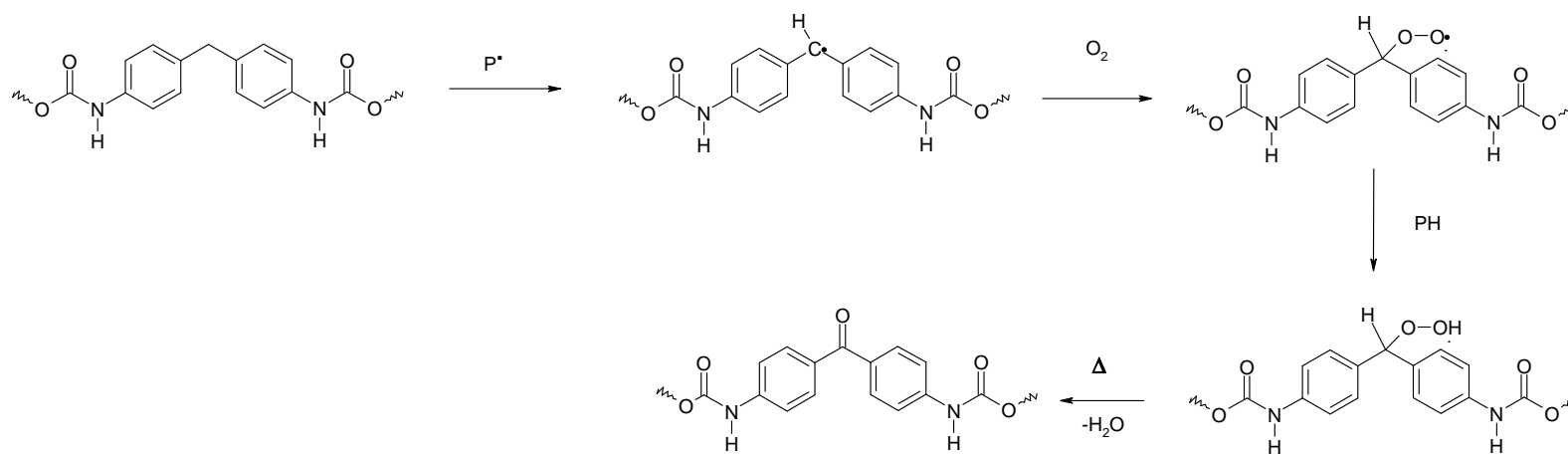
Identification of degradation molecules

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

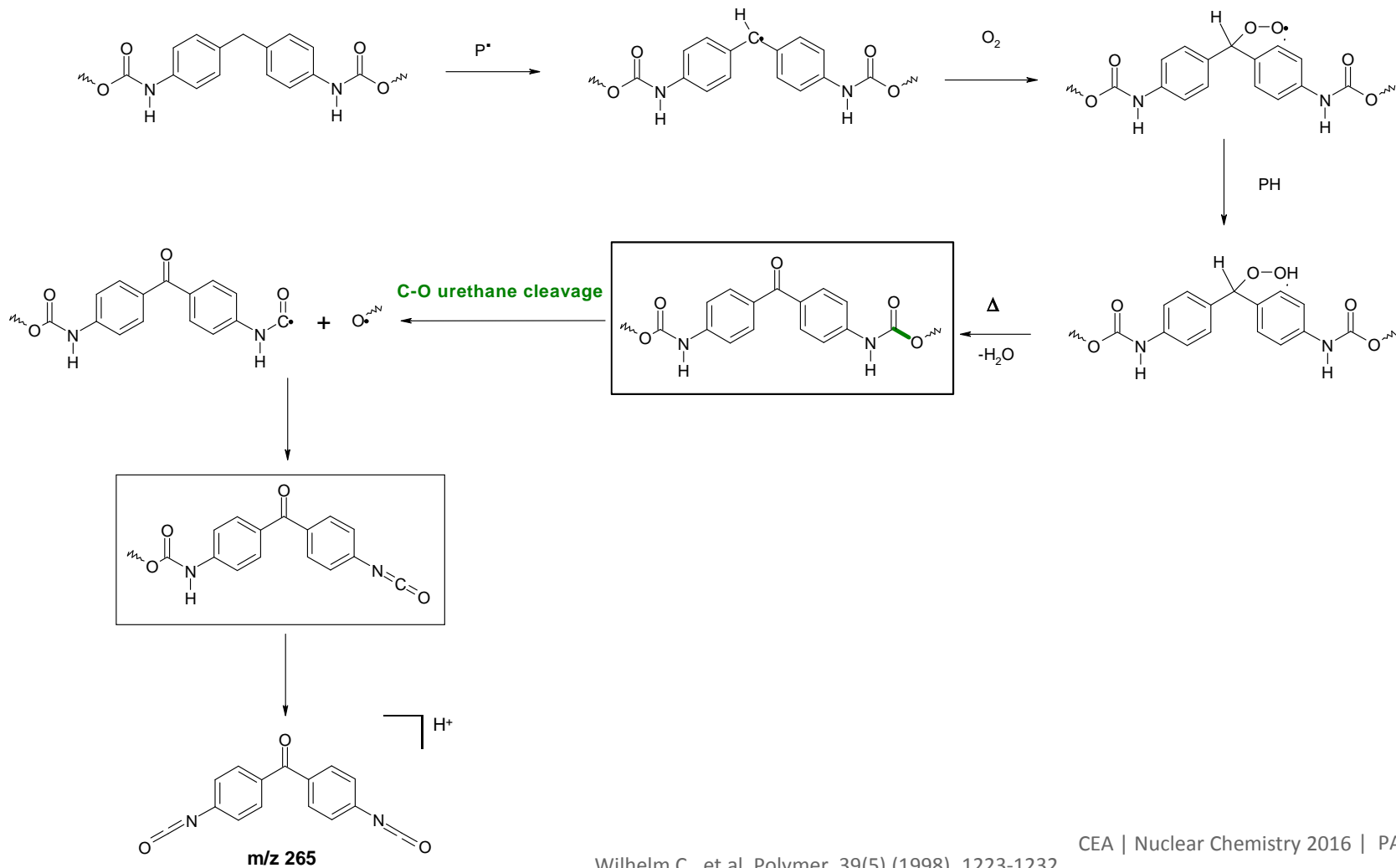


→ carbonyl and carboxylic acid functions → oxidation reaction

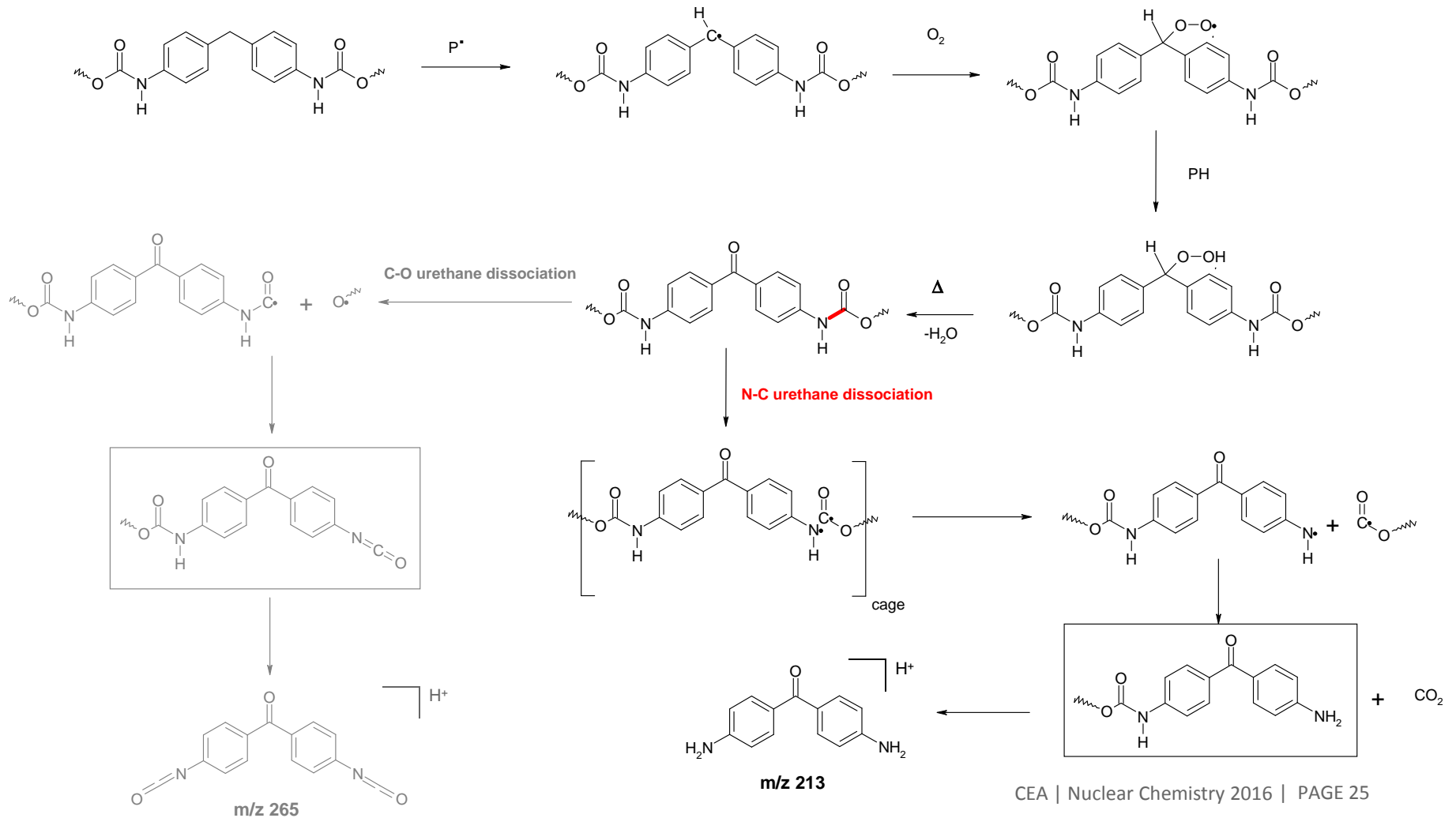
Proposed mechanism of Hard Segment degradation



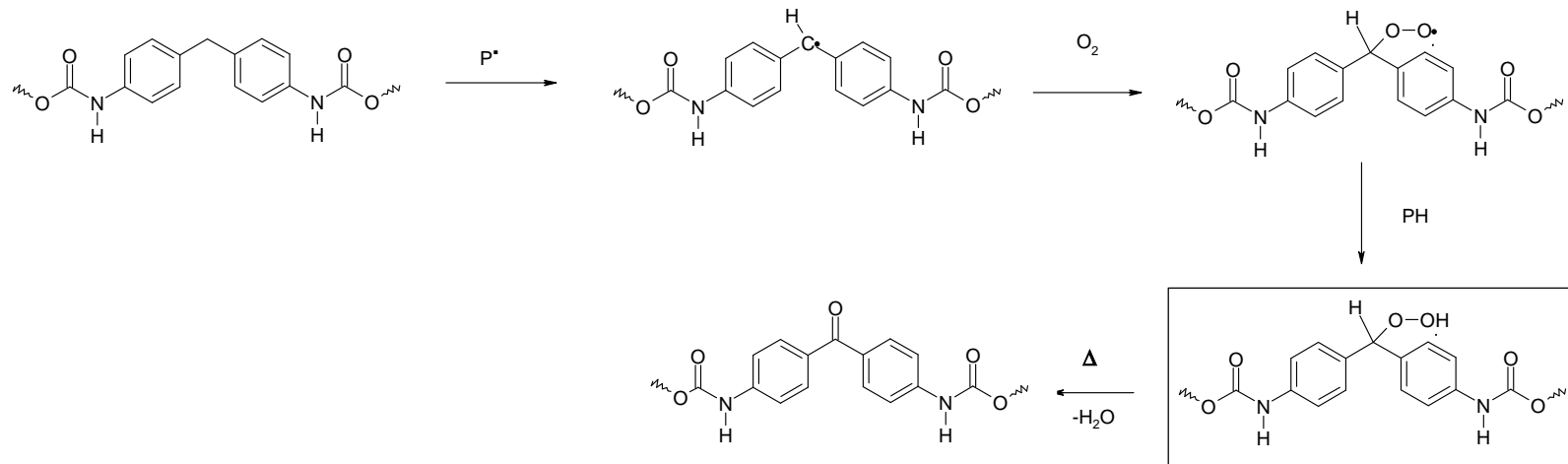
Proposed mechanism of HS degradation: Radio-oxidation degradation



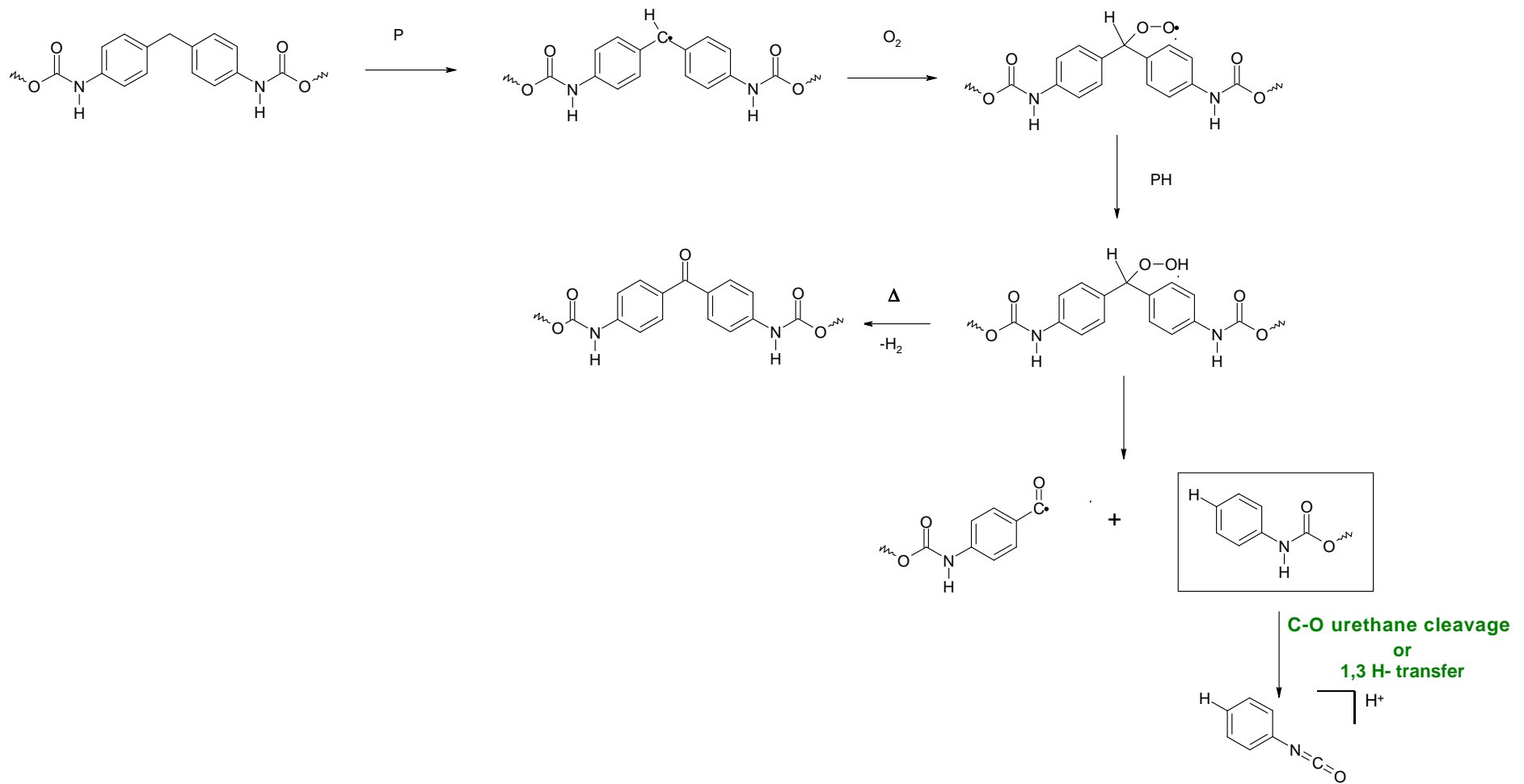
Proposed mechanism of HS degradation: Radio-oxidation degradation



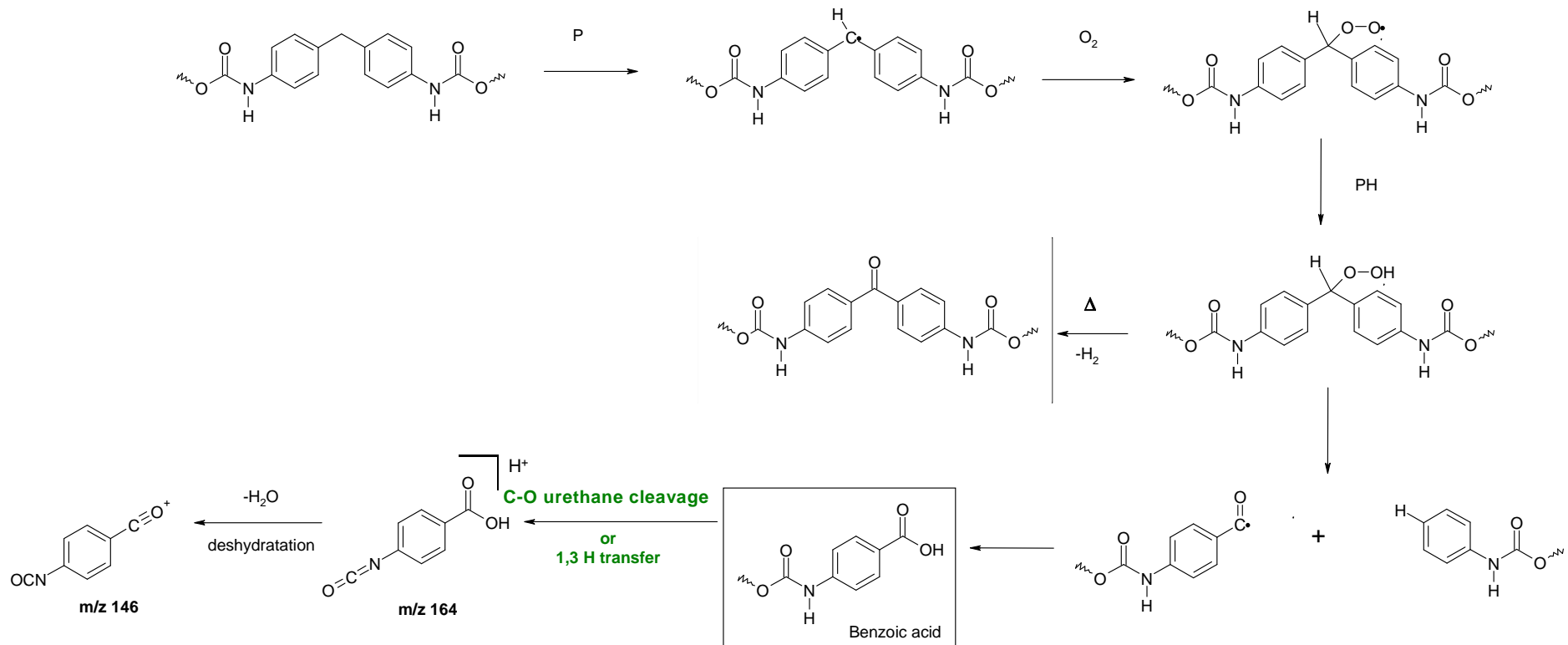
Proposed mechanism of HS degradation: **Radio-oxidation degradation**



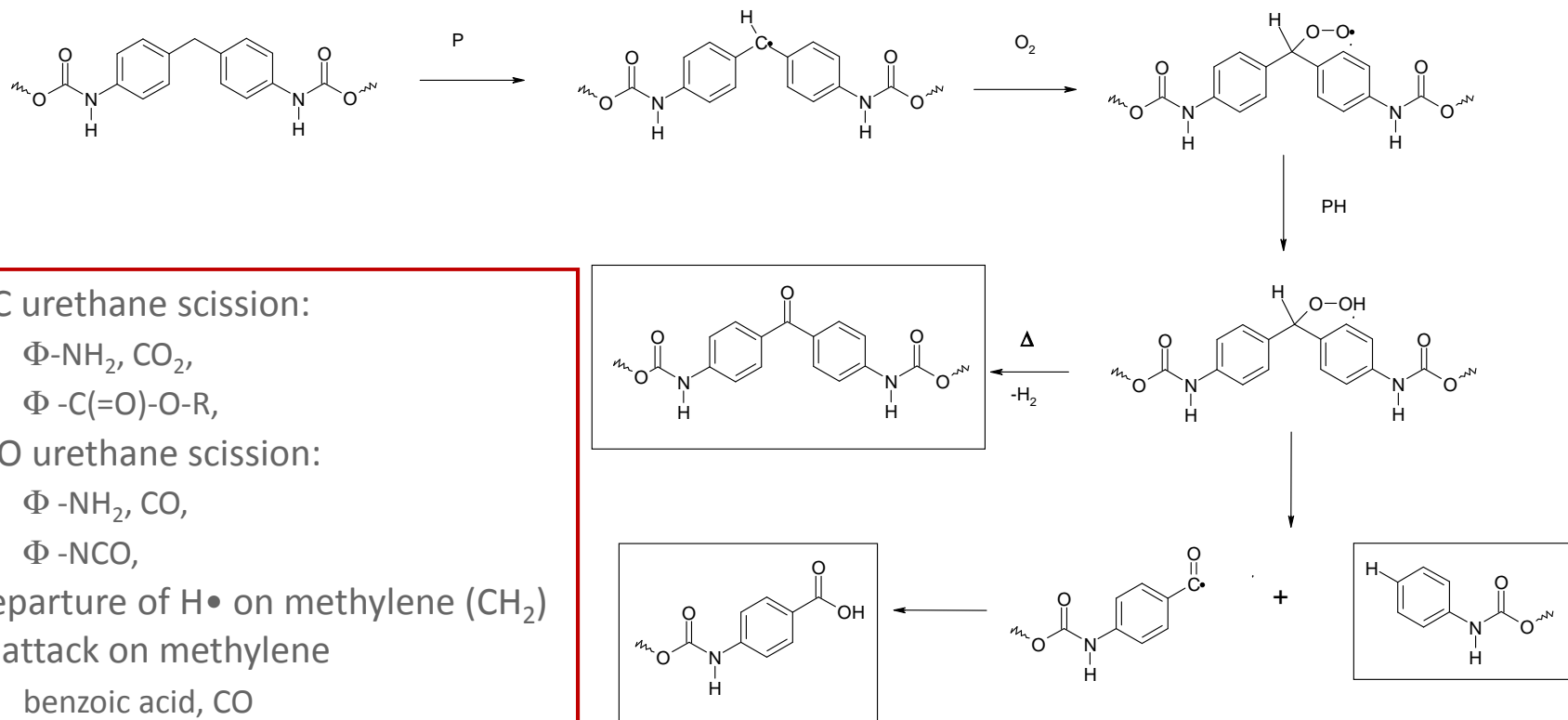
Proposed mechanism of HS degradation: Radio-oxidation degradation



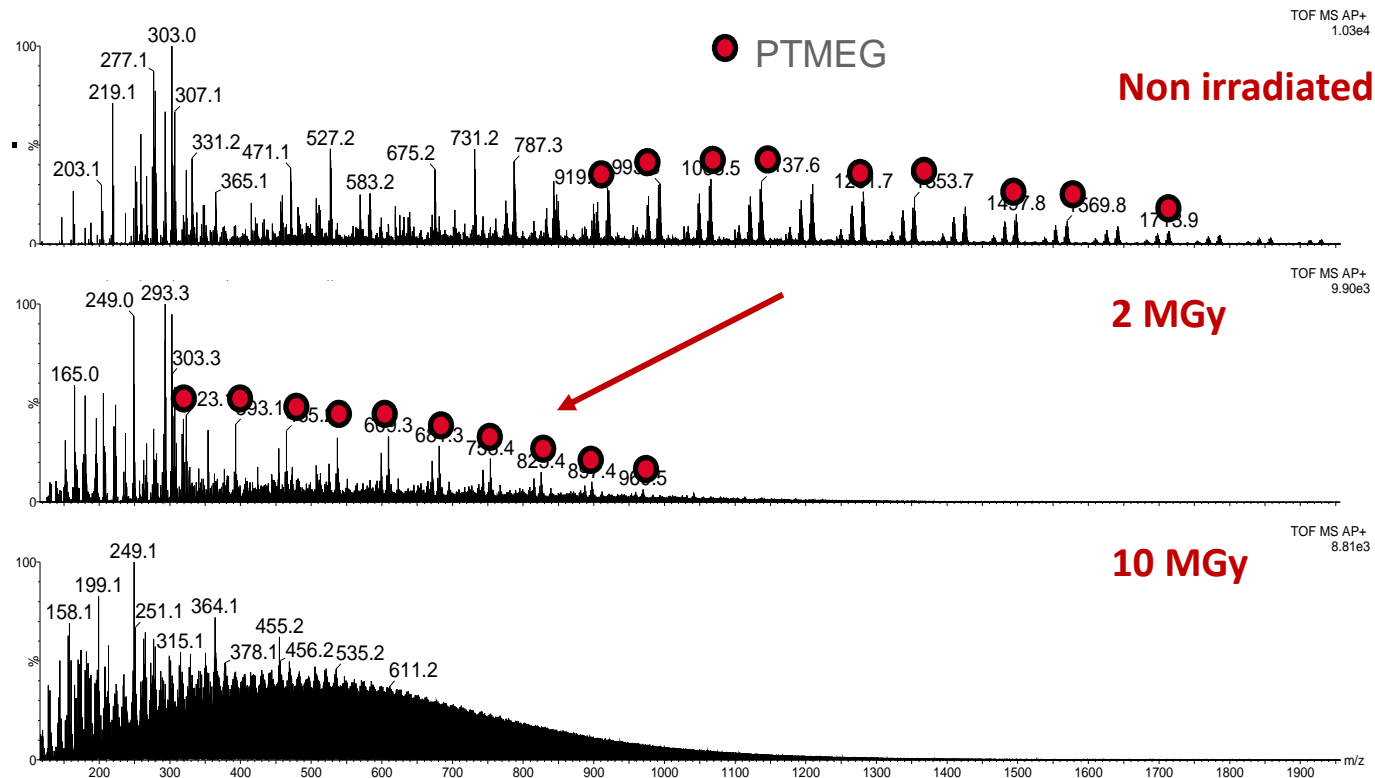
Proposed mechanism of HS degradation: Radio-oxidation degradation



Hard Segment dissociation



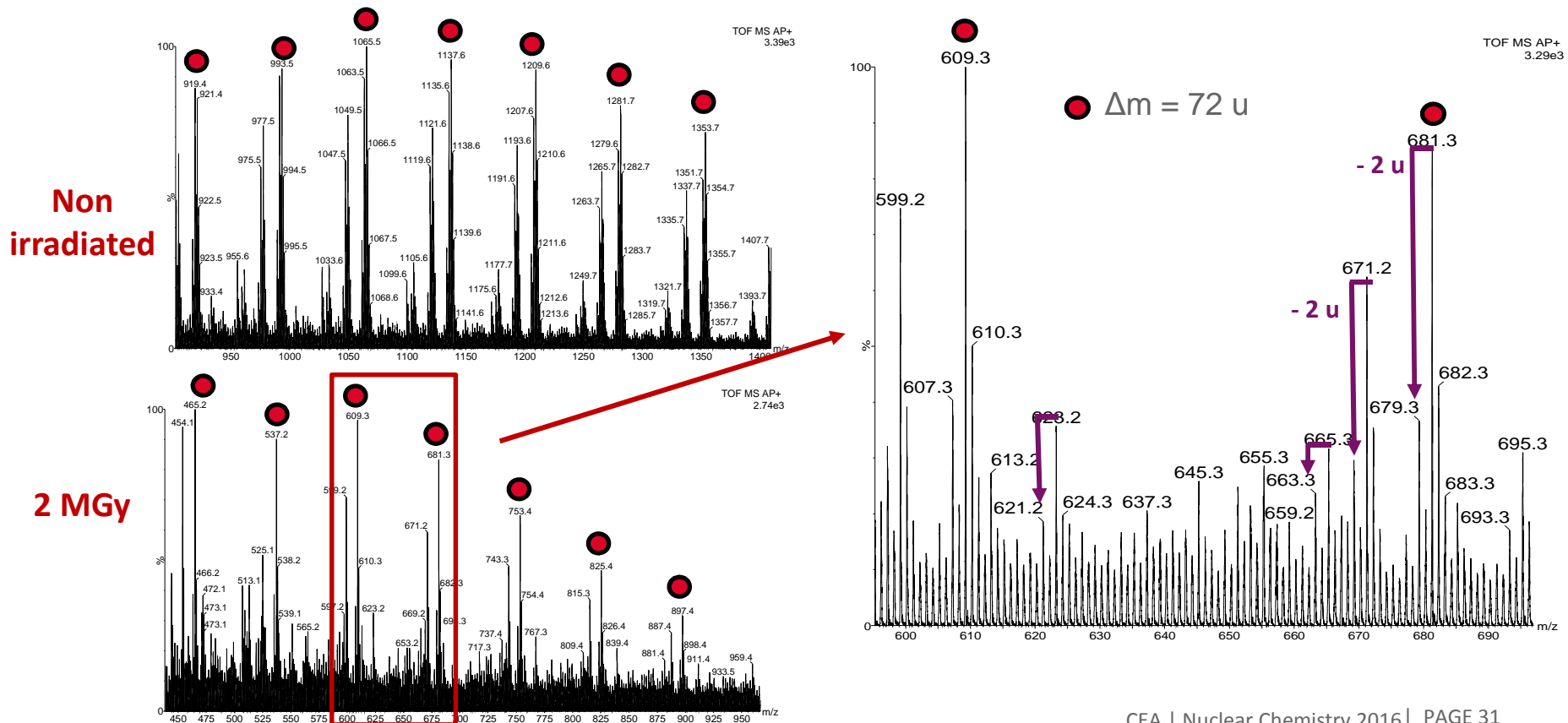
Analysis at high temperature → Soft Segment degradation



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

Identification of degraded polymers families after irradiation at 2 MGy

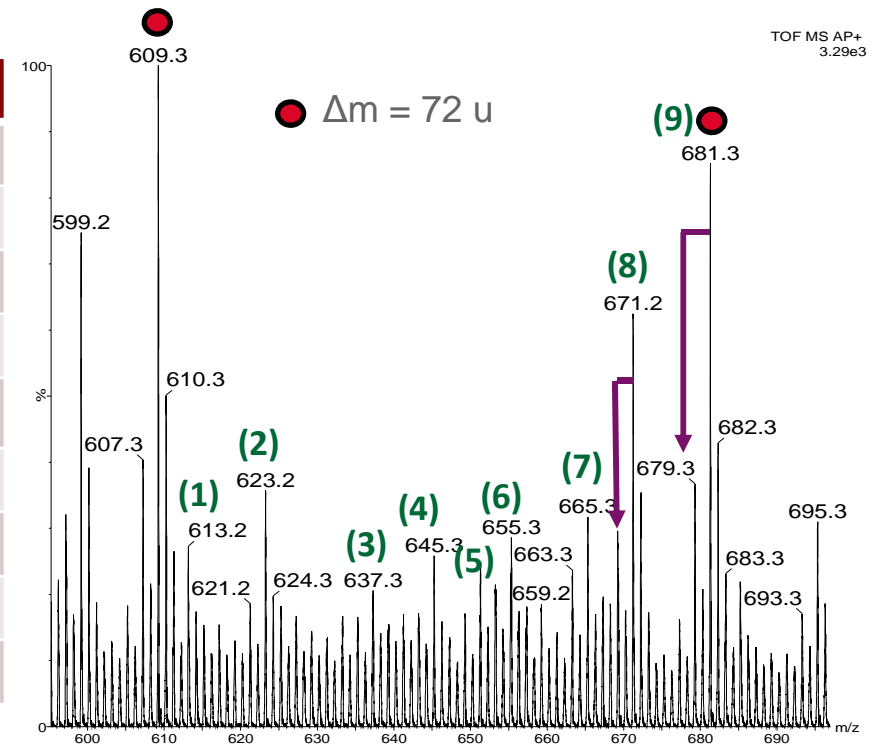
- ▀ ↗ of the number of peaks between repeating units after irradiation
- ▀ Several peaks separated of 2 u → characteristic of presence of **unsaturation or crosslinking**



Identification of degraded polymers families after irradiation at 2 MGy

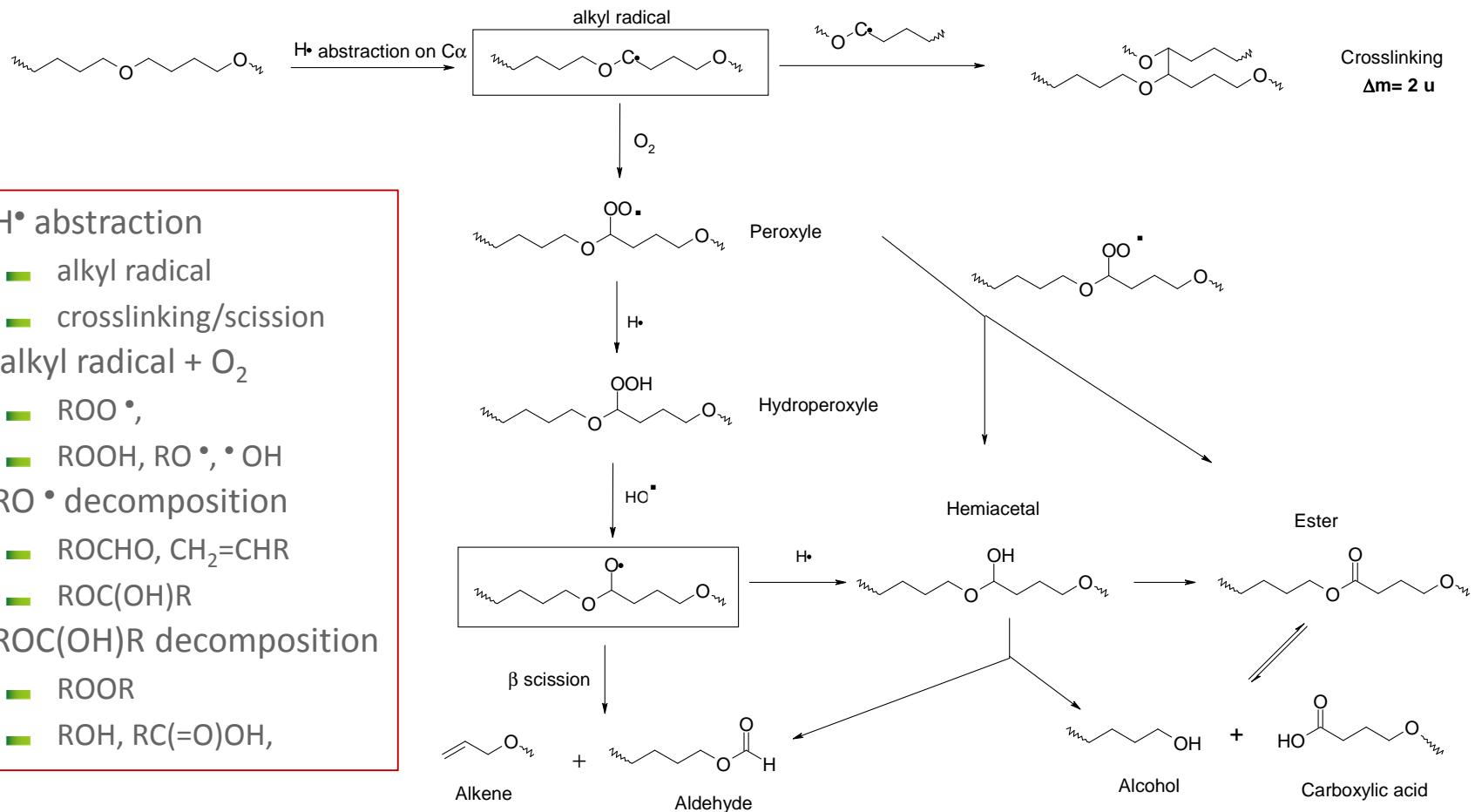
- ▀ ↗ of number of peaks between repeating units after irradiation
- ▀ Several peaks separated of 2 u → characteristic of presence of **unsaturation or crosslinking**

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

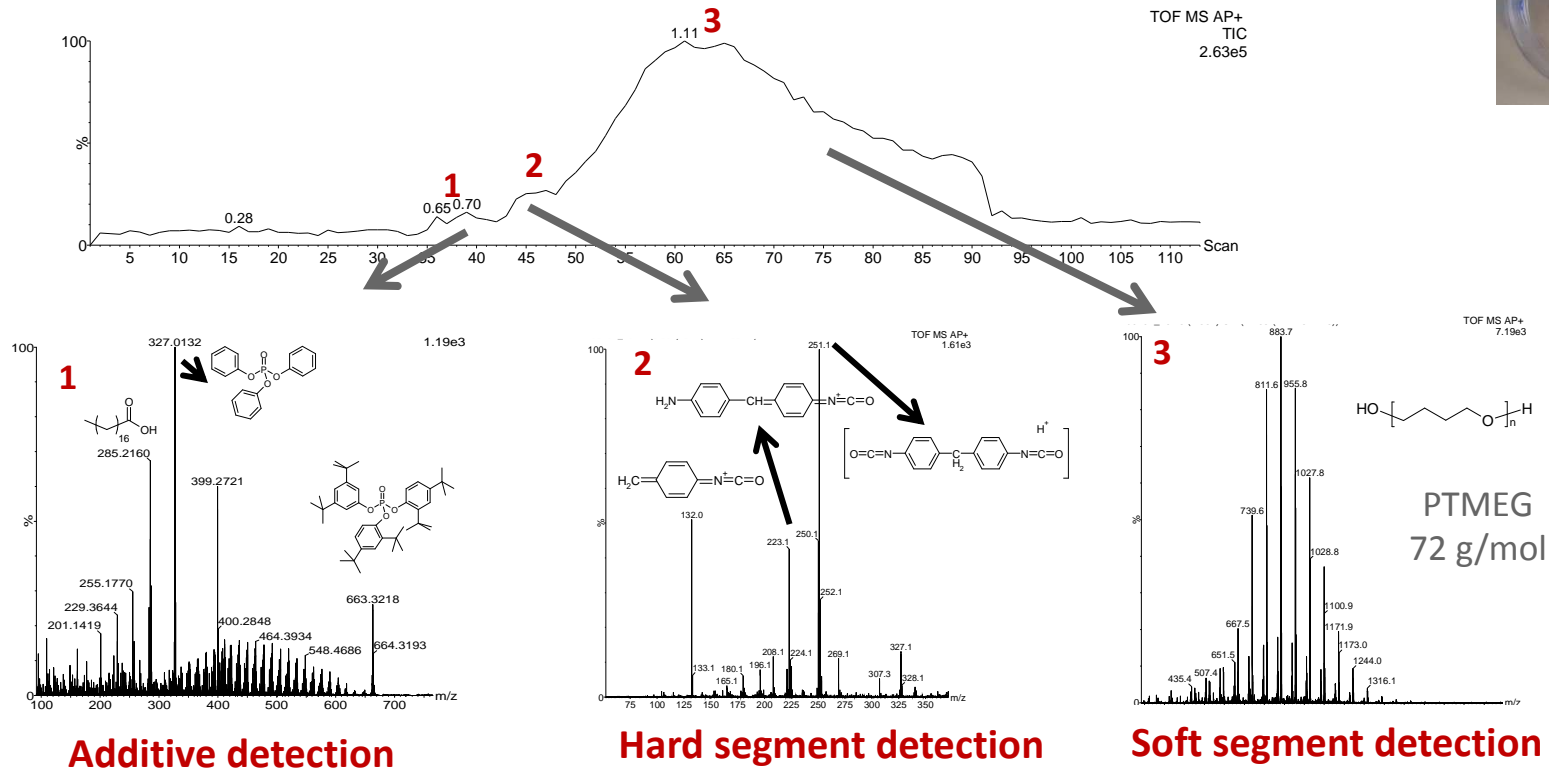


- ➔ Oxidized functions: alcohol, hemiacetal, carboxylic acid and aldehyde
- ➔ Unsaturation function: alkenes

Proposed mechanism of **Soft** Segment degradation



ASAP Analysis: desorption with temperature

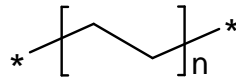


- Desorption of the components controlled by the temperature
 - Hard Segment is thermally degraded at lower temperature than Soft Segment (confirmed by TGA)
 - But Hard Segment more resistant to irradiation than Soft Segment
- ➔ Mechanisms of both segments degradation under radio-oxidation is proposed using only one analytical method

**CASE II: ALIPHATIC POLYMER (APOLAR)
POLYETHYLENE**

Structural composition

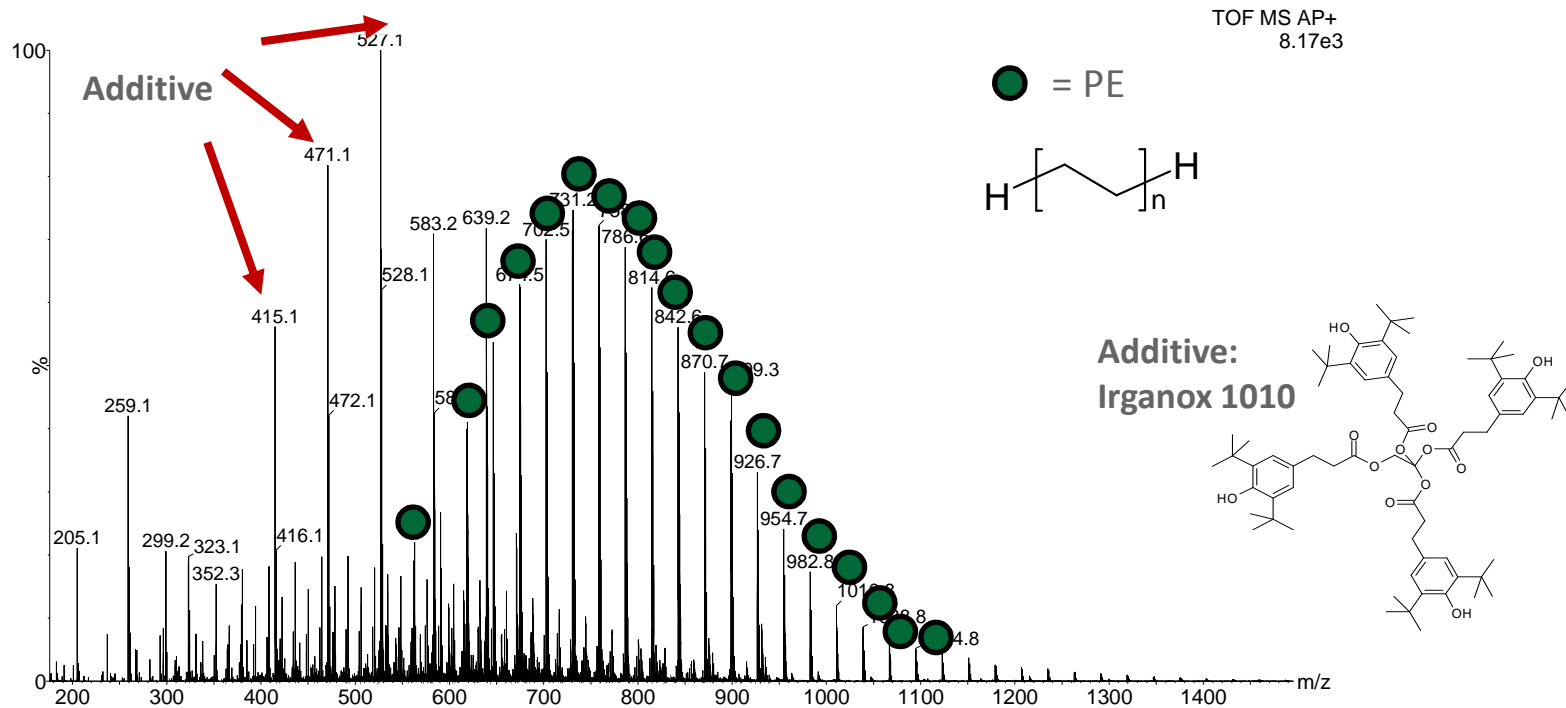
- Unsaturated, aliphatic hydrocarbons



- 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

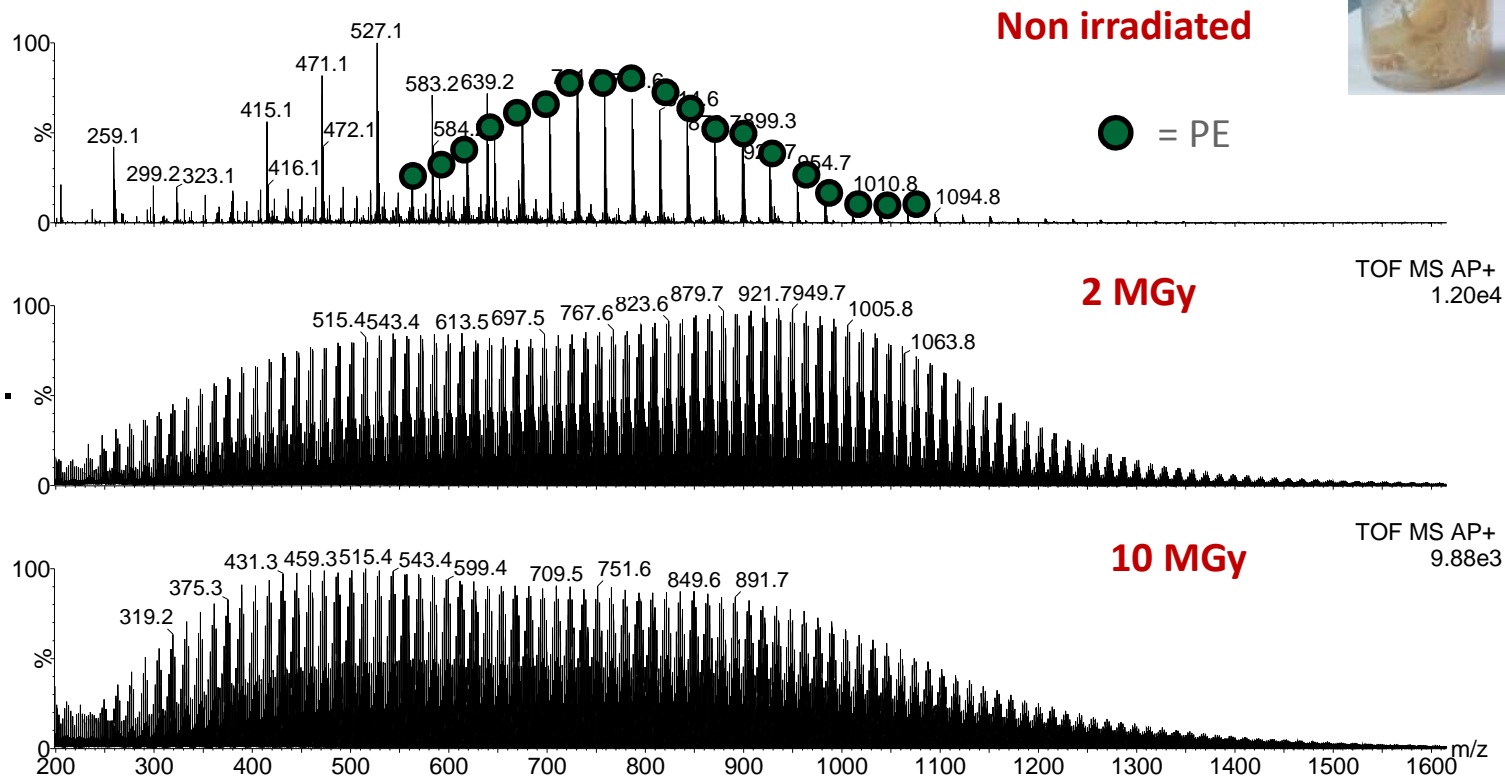
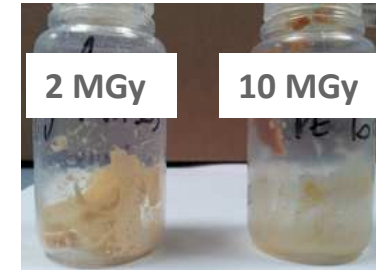
Non irradiated polymer

- Detection of a characteristic polymeric profile



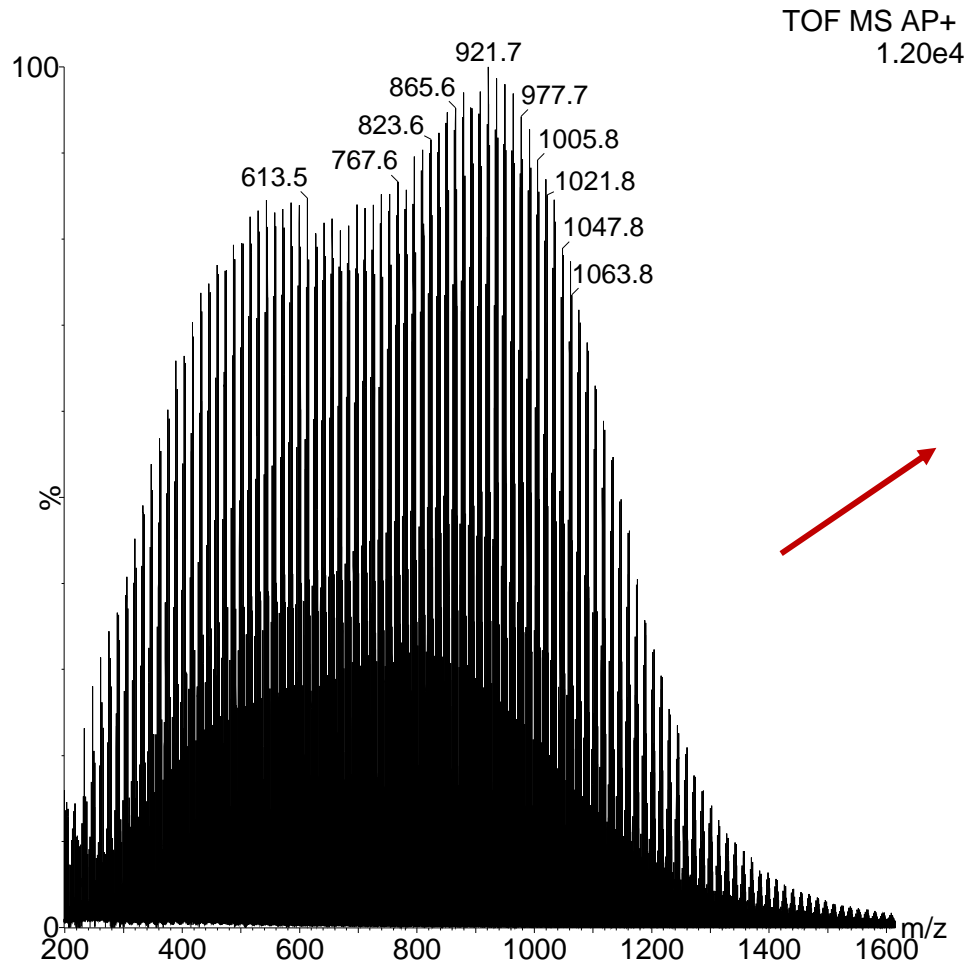
- Detection of additive
- $\Delta m = 28$ u: PE and Fragments ions (-14 u = $-\text{CH}_2$)
- ⇒ Structural identification of **polyethylene**

Irradiated PE

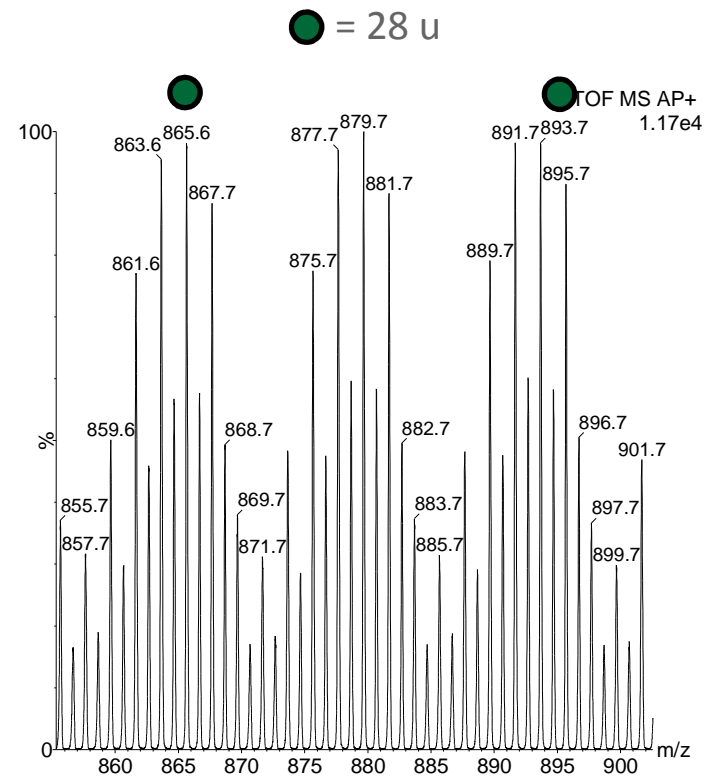


- Very different mass spectra after irradiation at 2 and 10 MGy
- ➔ Important impact of radio-oxidation
- Similar mass spectra after irradiation at 2 and 10 MGy

PE after irradiation at 2 MGy



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

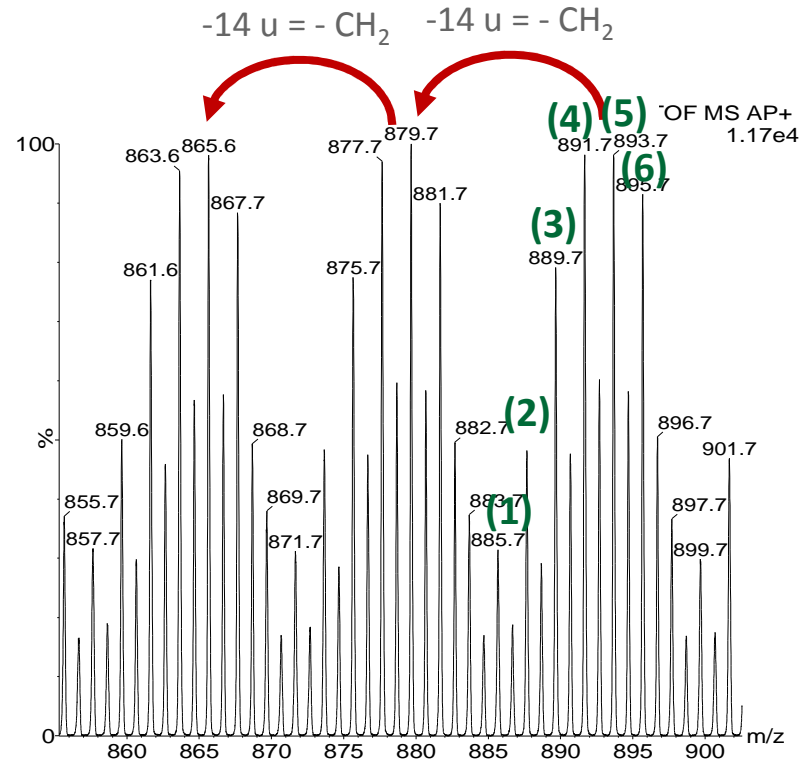


PE after irradiation at 2 MGy

■ Mainly $\Delta m = 2$ u

➔ **unsaturation and/or crosslinking**

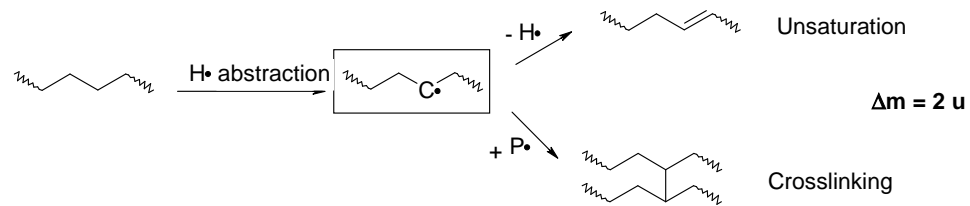
	polymer	Structures
(1)	$44 + 28 \cdot n$	$\text{H}_3\text{C-CO-(PE)}_n\text{-H}$
(2)	$46 + 28 \cdot n$	$\text{H}_3\text{C-CH(OH)-(PE)}_n\text{-H}$ $\text{HOOC-(PE)}_n\text{-H}$
(3)	$48 + 28 \cdot n$	$\text{HO-H}_2\text{C-(PE)}_n\text{-OH}$
(4)	$78 + 28 \cdot n$	$\text{HO-COO-(PE)}_n\text{-OH}$
(5)	$52 + 28 \cdot n$	Non identified
(6)	$54 + 28 \cdot n$	$\text{H}_2\text{C=CH-(PE)}_n\text{-CH=CH}_2$



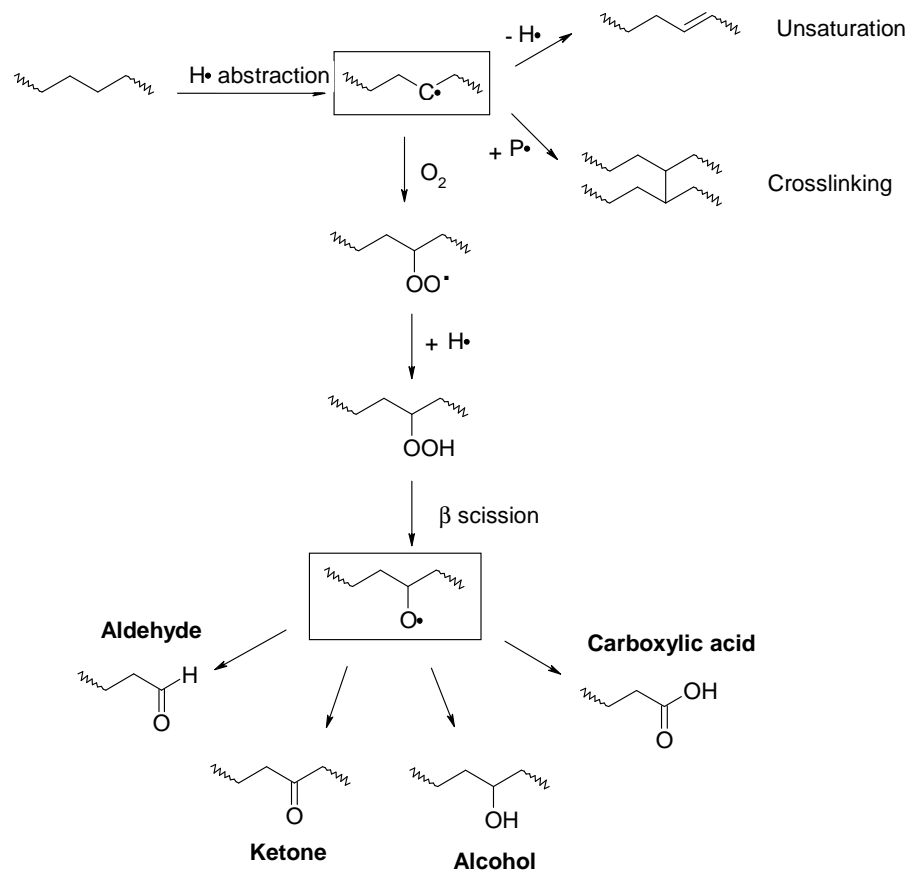
➔ **Oxidized functions: alcohol, carboxylic acid and aldehyde**

➔ **unsaturation function: alkenes**

Proposed mechanism of PE degradation



Proposed mechanism of PE degradation



Analysis of degraded 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)

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

Thank you for your attention.

ACKNOWLEDGMENTS

Radiolysis group from LRMO:

Muriel Ferry

Vincent Dauvois

Delphine Durand

Stéphane Esnouf

Solène Legand

Jean Luc Roujou

Manon Cornaton

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
Secrétariat : T. +33 (0)1 69 08 32 50 | F. +33 (0)1 69 08 52 54

Etablissement public à caractère industriel et commercial | RCS Paris B 775 685 019

Direction de l'énergie nucléaire
Direction déléguée aux activités nucléaires de Saclay
Département de physico-chimie
Service d'étude du comportement des radionucléides