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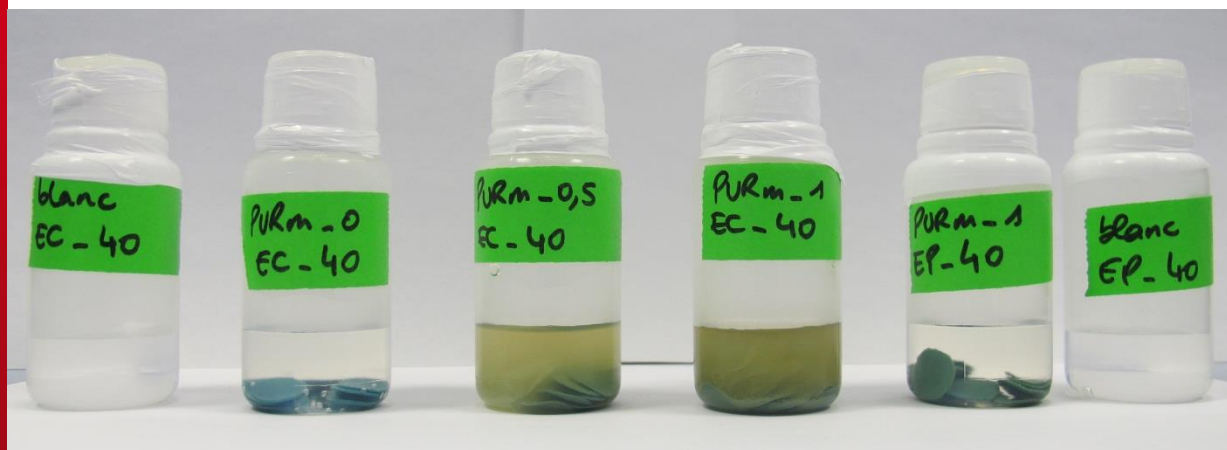
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Leaching of radio-oxidized poly(ester urethane): water-soluble molecules characterization



E. Fromentin^{1*}, M.Pielawski¹, D.Lebeau¹, S. Esnouf¹, M.Ferry¹,
F.Cochin², N.Caron³ and S. Legand¹

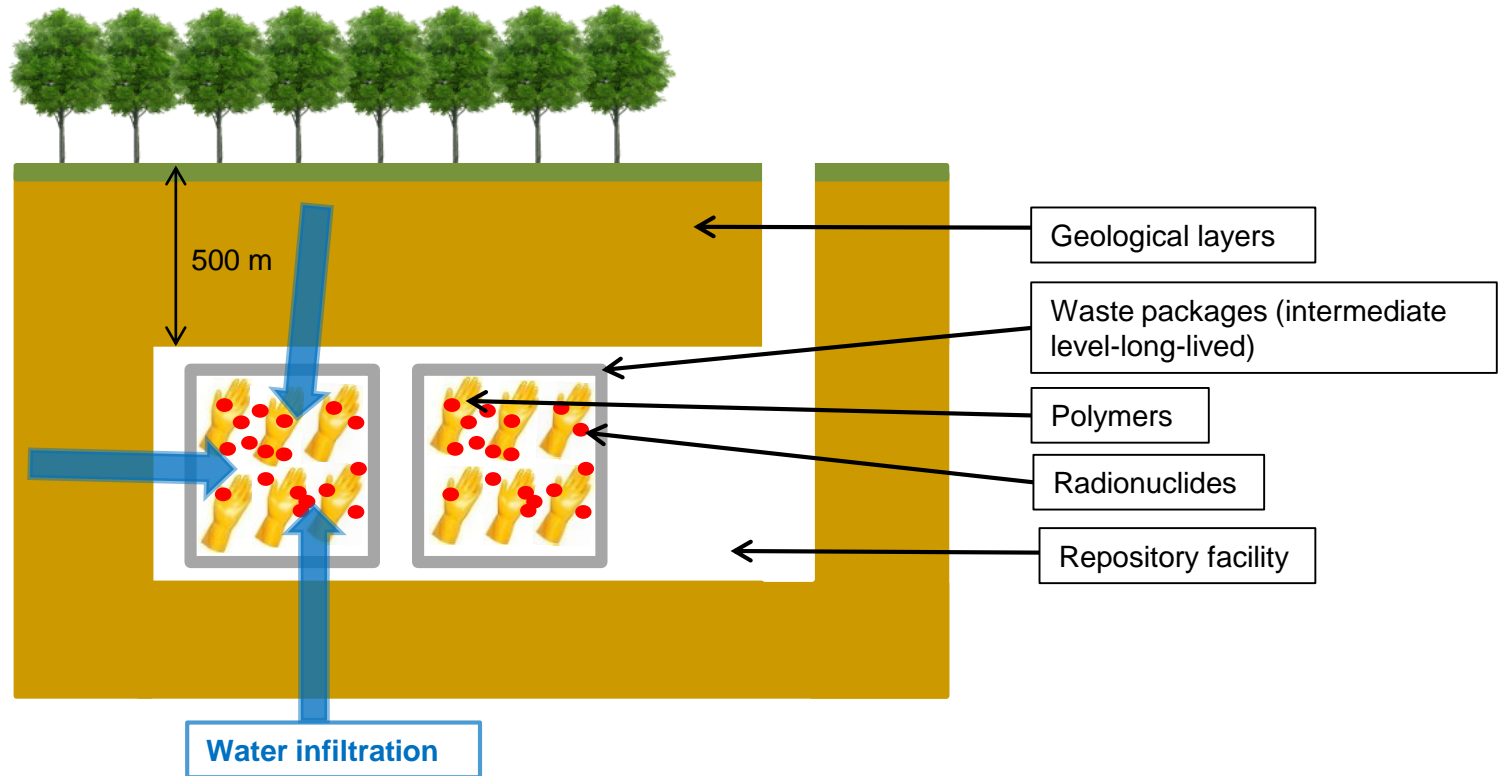
¹ CEA, DEN, DPC, SECR, LRMO, F-91191 Gif-sur-Yvette, France.

² AREVA NC DOR/RDP, 1 place Jean Millier, F-92084 La Défense Cedex, France.

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13th Tihany Symposium on Radiation Chemistry
29th August-3rd September 2015

A repository disposal diagram:



- **Long-term degradation ($\approx 1,000$ years): radiolysis *and* alkaline hydrolysis**
- Question: what is the effect of water-soluble products on the radionuclides mobility?

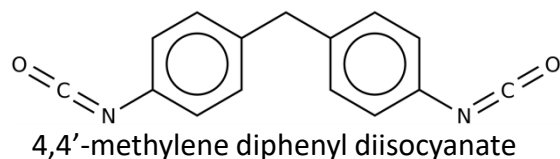
Considered polymer

- Poly(ester urethane) (PUR)
- Used as glove for glove boxes



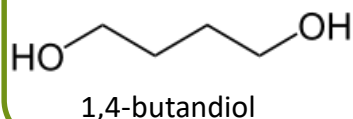
- Composed of 3 segments issued from these molecules

hard segment

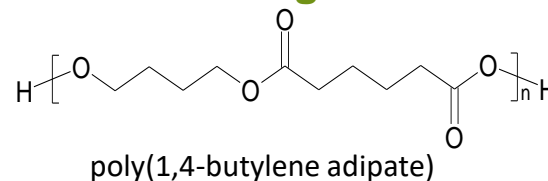


↓
25.5%_w

extender



soft segment



↓
63.4%_w

+ 8.9% inorganic fillers
+ 1.8% cross linking agents
+ 0.4% pigments

Objectives

- Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non-irradiated and irradiated PUR at different doses

- Understanding the degradation mechanisms
 - PUR under radiolysis
 - Irradiated PUR under hydrolysis

- Identifying the products than can complex with the radionuclides

- Being able to model the complexant release kinetics

Objectives



Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non-irradiated and irradiated PUR at different doses



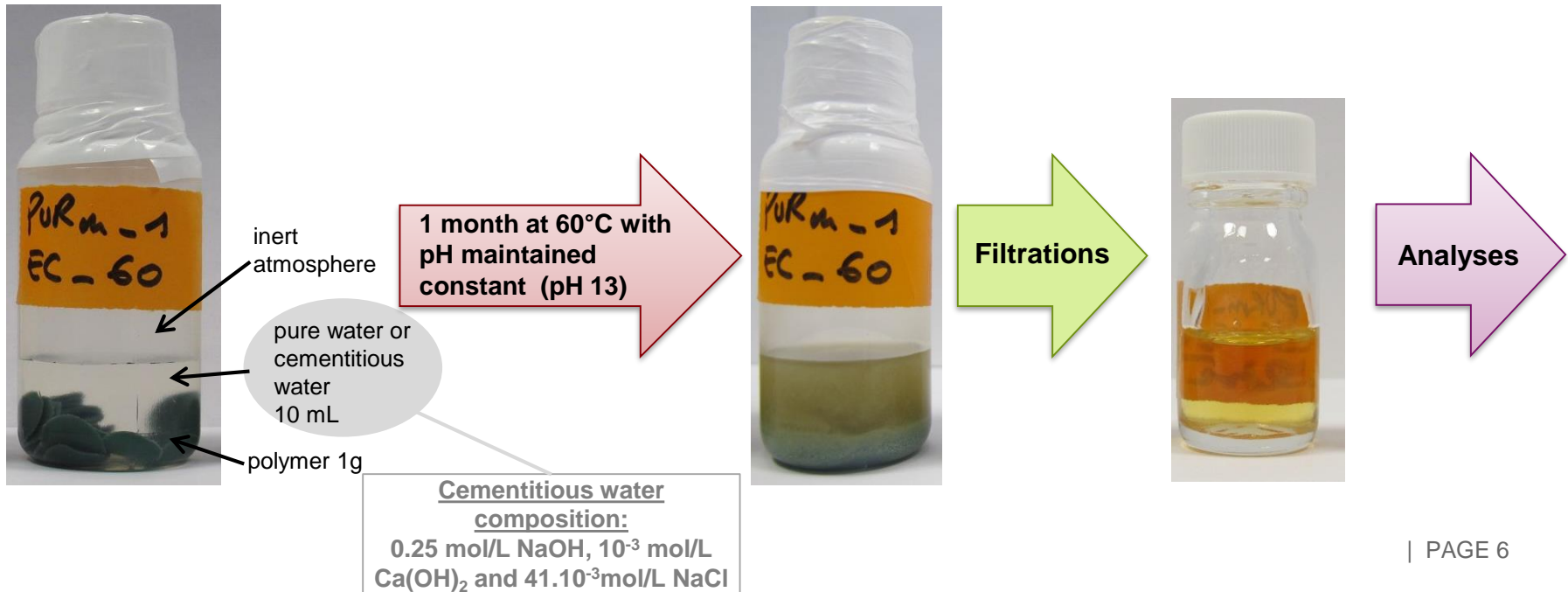
Understanding the degradation mechanisms

- **PUR under radiolysis**
- **Irradiated PUR under hydrolysis**

- Identifying the products than can complex with the radionuclides
- Being able to model the complexant release kinetics

A two-step preparation

- **1st step:** PUR is irradiated under air using γ rays by IONISOS (^{60}Co source), dose rate: $\sim 0.7 \text{ kGy.h}^{-1}$, doses: 4 MGy (~ 8 months irradiation) and 10 MGy (~ 20 months irradiation)
- **2nd step:** non-irradiated and irradiated PUR is then hydrolyzed and the pH is maintained constant = **leaching**



RESULTS AND DISCUSSION

Analytical approach



Leachate

Total Organic
Carbon analysis
TOC analyzer



Targeted analyses
of **low** molecular
weight molecules
($< 2\,000$ Da)

Targeted analyses
of **high** molecular
weight molecules

Organic acids
IC

Volatile and semi-
volatile organic
molecules
GC-MS

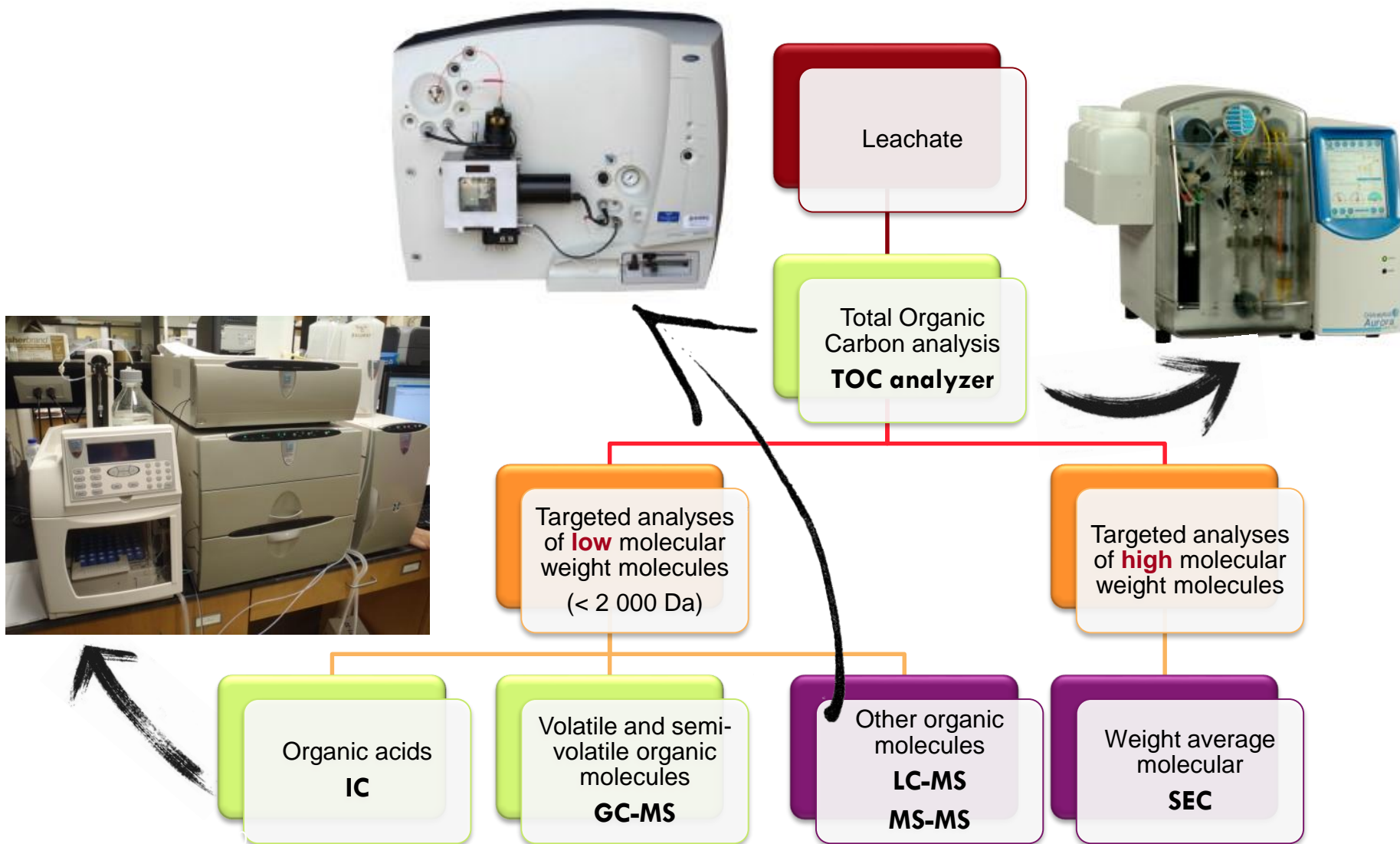
Other organic
molecules
LC-MS
MS-MS

Weight average
molecular
SEC



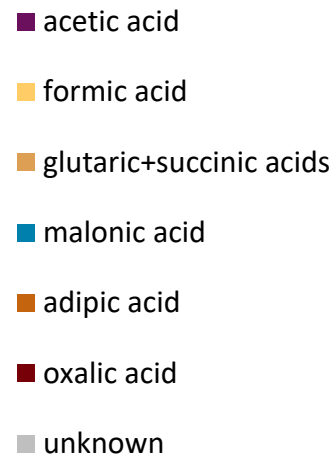
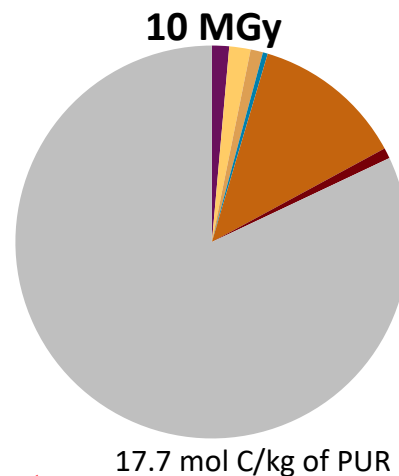
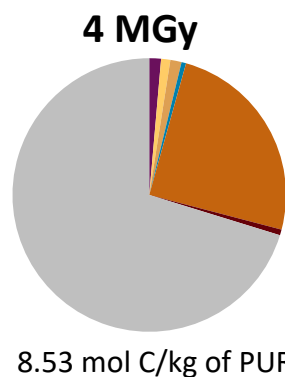
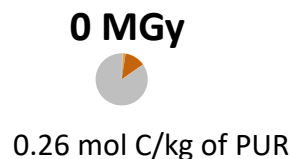
RESULTS AND DISCUSSION

Analytical approach

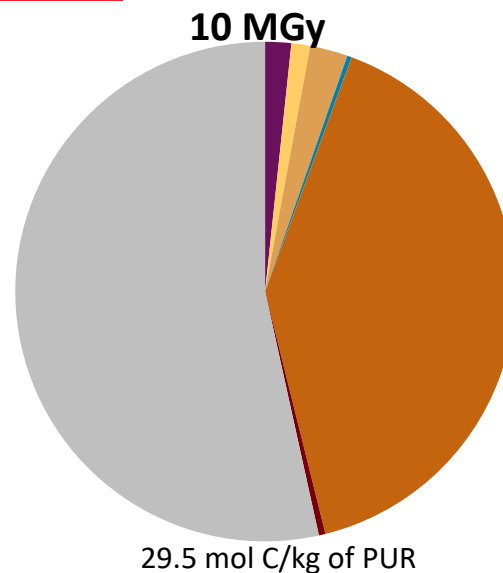
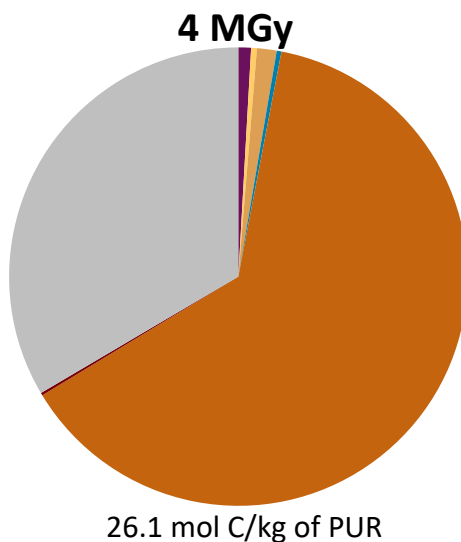
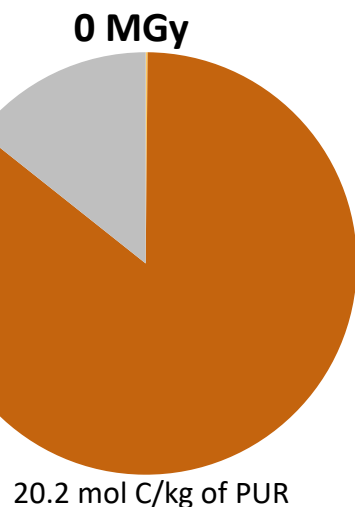


■ **Total Organic Carbon = TOC, ionic chromatography → carboxylic acids quantification**

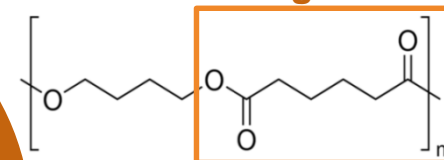
Material balances obtained for leachates in **pure water**:



Material balances obtained for leachates in **cementitious water**:



**Origin of adipic acid :
PUR soft segment**



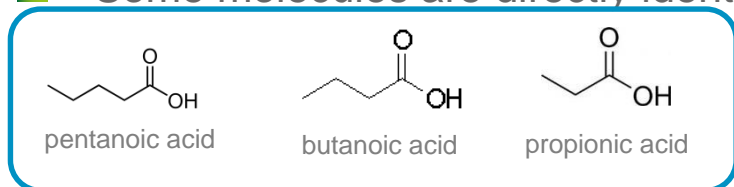
There is a need to investigate the leachates by other analytical techniques.

RESULTS AND DISCUSSION

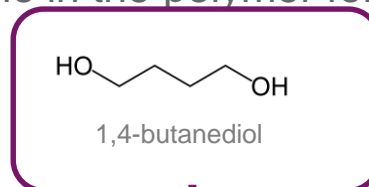
Gas chromatography-mass spectrometry

Molecules detected in the **10 MGy irradiated PUR leachate in pure water**

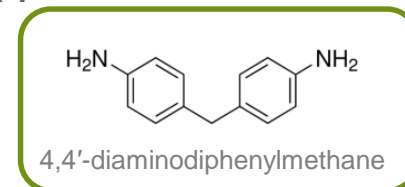
■ Some molecules are directly identifiable in the polymer formula :



↓
soft segment

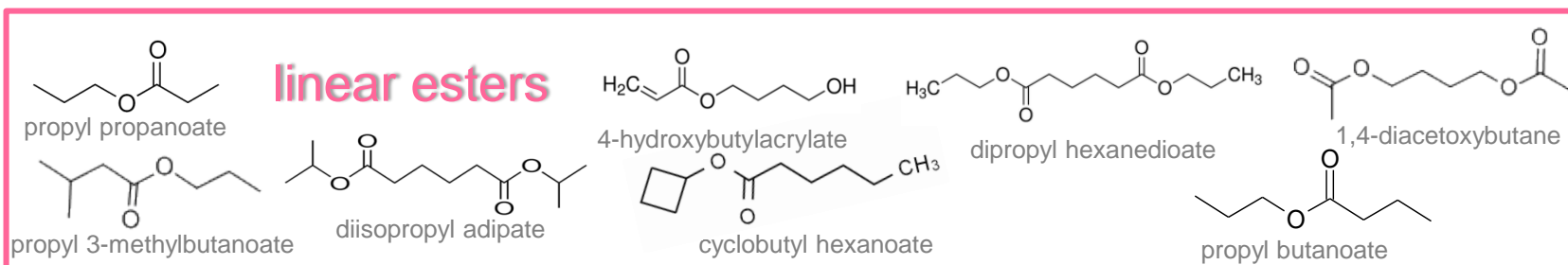
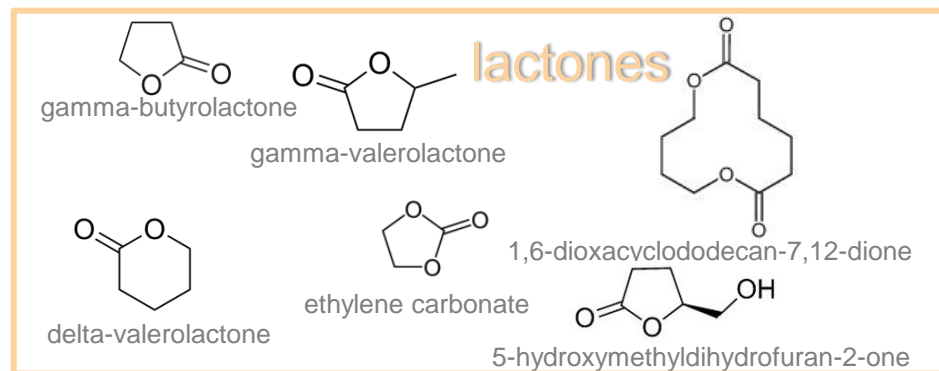
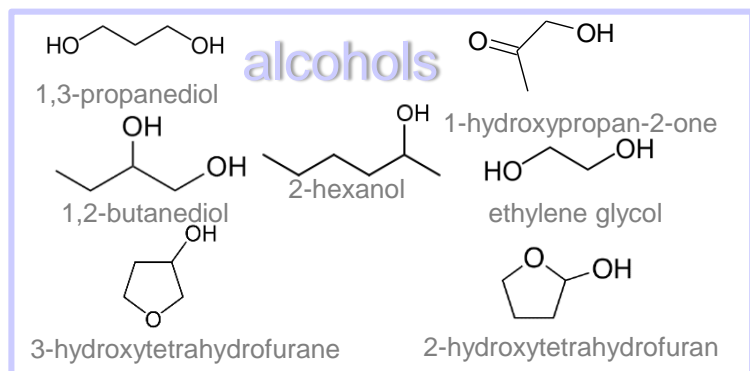


↓
extender



↓
hard segment

■ Other molecules are due to chain scission or chain ends radio-oxidation, or due to ester groups hydrolysis and rearrangements.

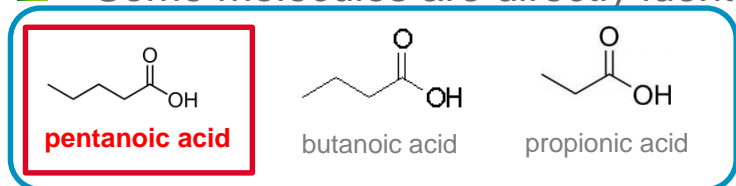


RESULTS AND DISCUSSION

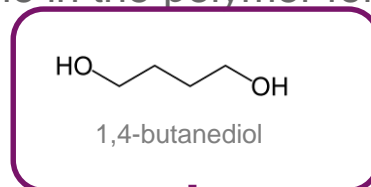
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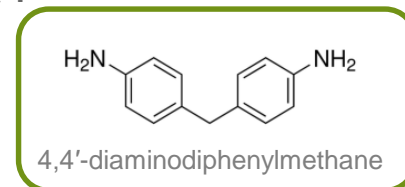
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soft segment

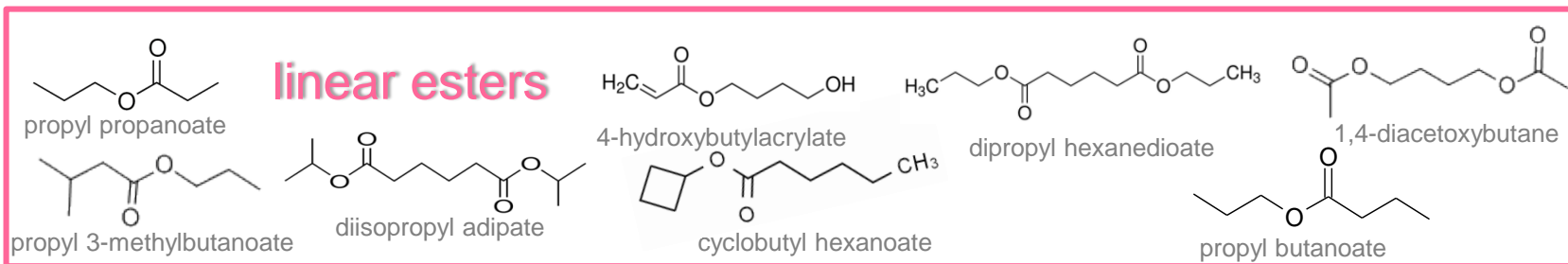
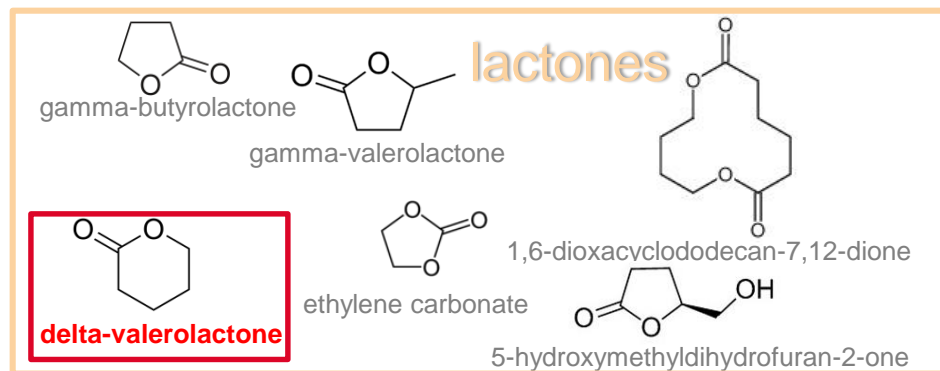
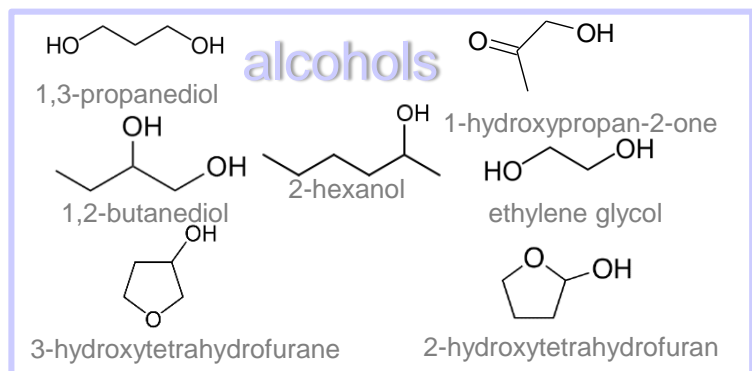


extender

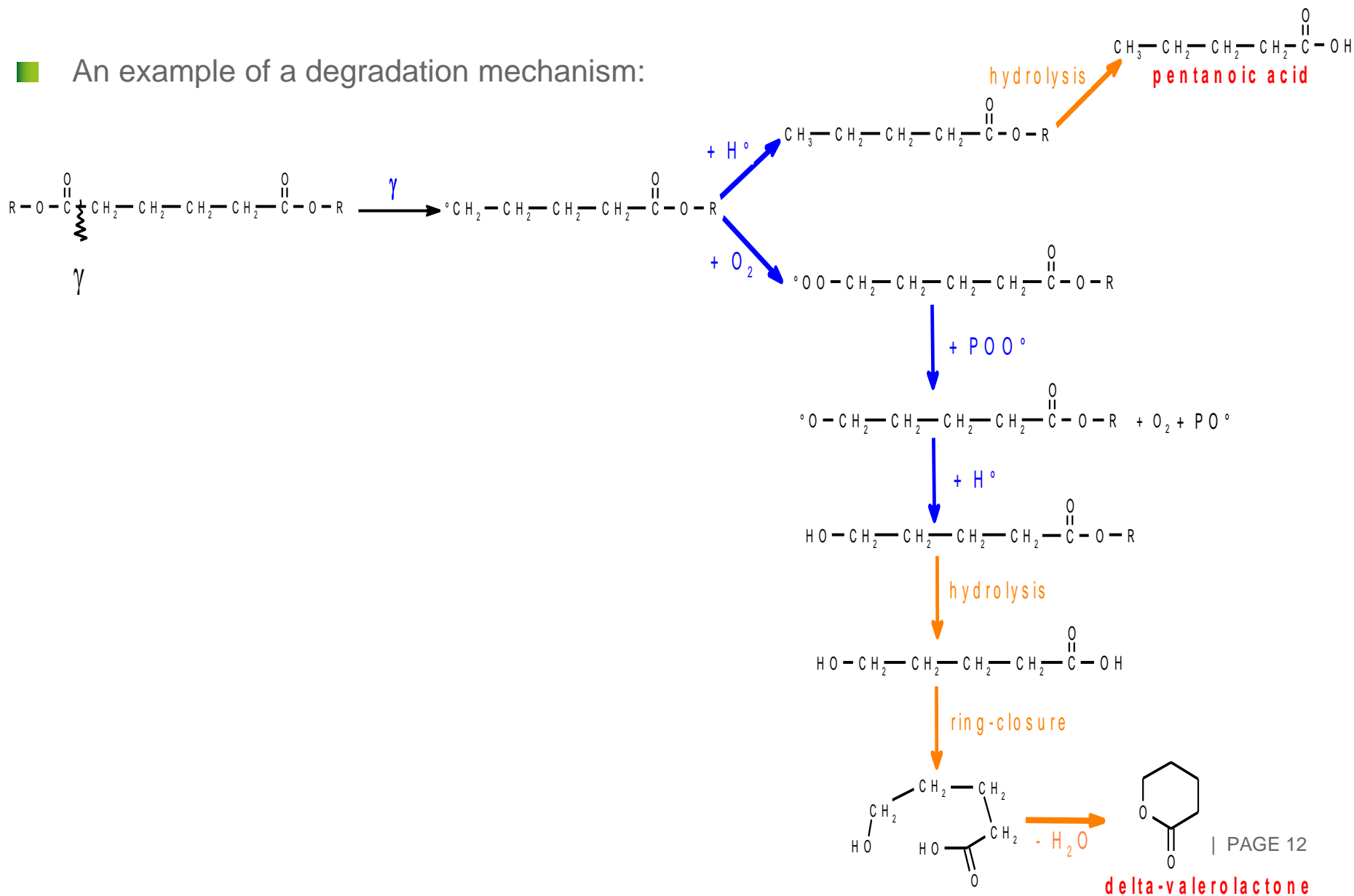


hard segment

■ Other molecules are due to chain scission or chain ends radio-oxidation, or due to ester groups hydrolysis and rearrangements.



■ An example of a degradation mechanism:



■ Goals of the study:

- Characterizing and quantifying water-soluble molecules created by the alkaline hydrolysis of the non irradiated and irradiated PUR
- Understanding the degradation mechanisms
 - PUR under radiolysis
 - Irradiated PUR under hydrolysis

- Ionic chromatography + TOC analyzer = material balance, **but** the material balances are not complete. **Solution** → developing other analytical techniques such as:
 - Gas chromatography coupled with mass spectrometry

■ Results:

- New molecules detected: the knowledge of released molecules is improved
- Identification of the molecules origin
 - Fragments of the polymer formula
 - Compounds obtained by chain scission, chain ends oxidation, ester groups hydrolysis or/and rearrangements

=> Better understanding of the mechanisms of irradiation and of leaching

■ Perspectives:

- Quantifying the molecules detected by GC-MS
- Identifying the molecules than can complex with the radionuclides
- Following the complexant release kinetics

=> Irradiated PURm hydrolysis mechanisms to be proposed

**Do you have
any questions?**



Thank you for your attention.

ACKNOWLEDGMENT

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