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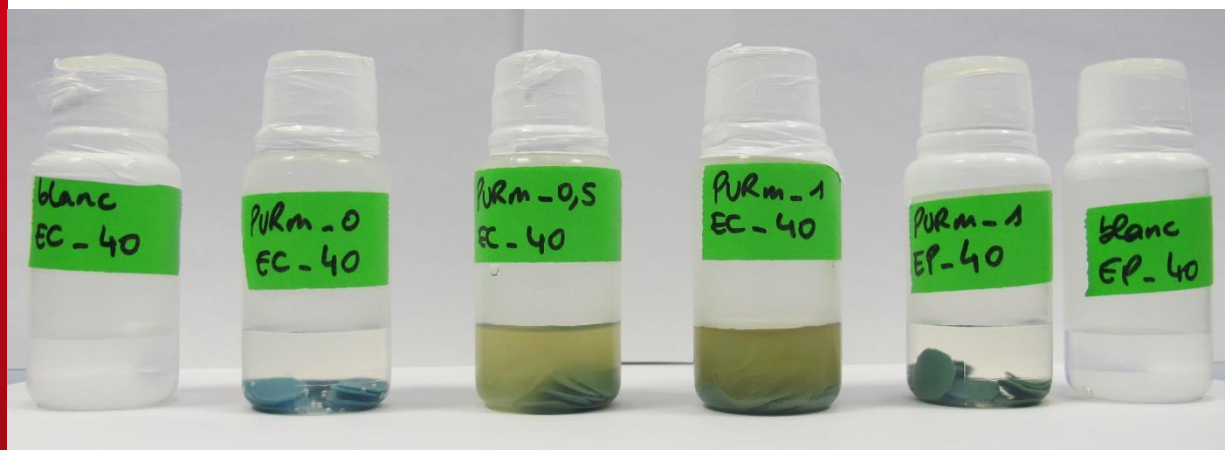
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Leaching of radio-oxidized poly(ester urethane): water-soluble molecules characterization

DE LA RECHERCHE À L'INDUSTRIE

cea den



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

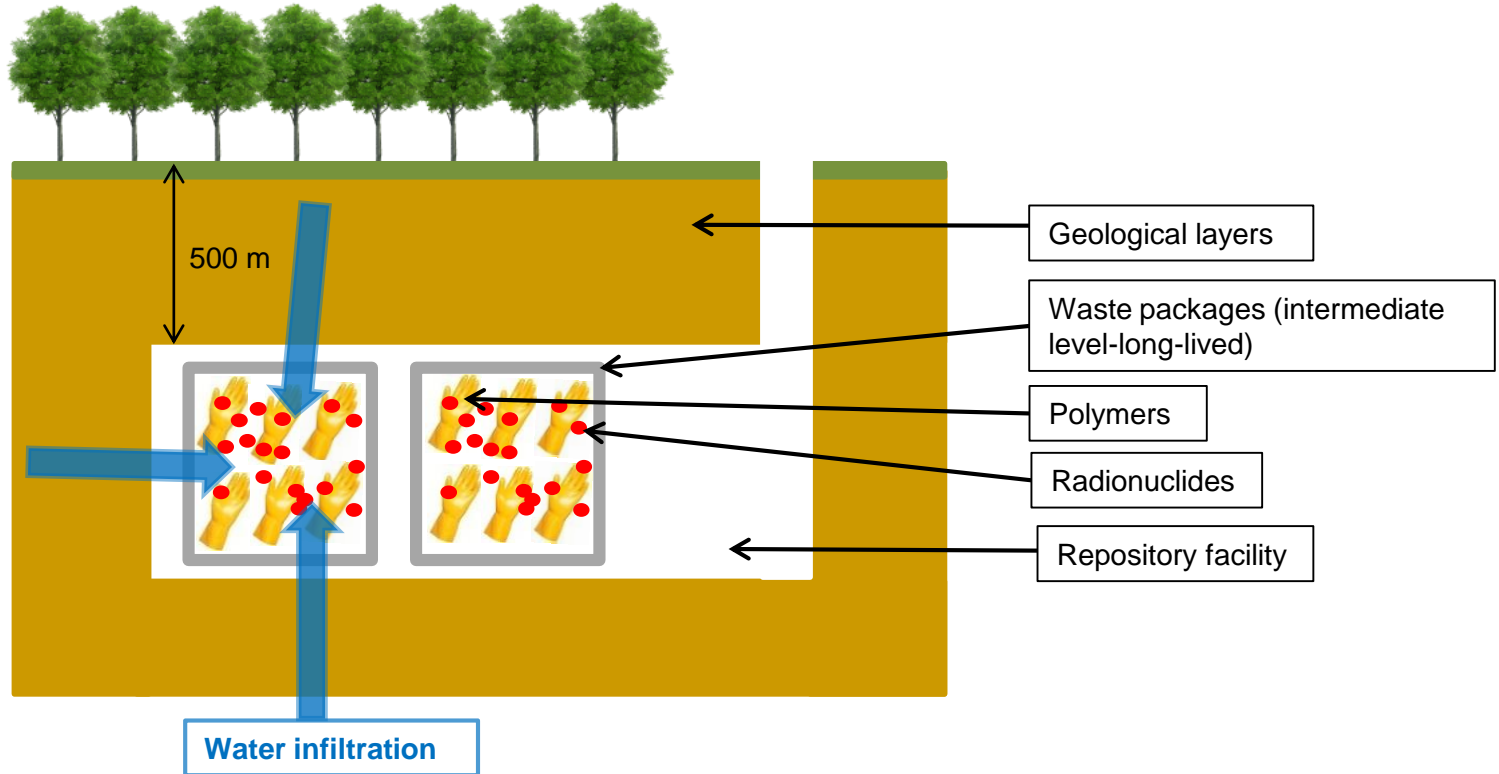
¹ CEA, DEN, DPC, SECR, LRMO, F-91191 Gif-sur-Yvette, France.

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

³ CEA, DEN, DPC, F-91191 Gif-sur-Yvette, France.

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

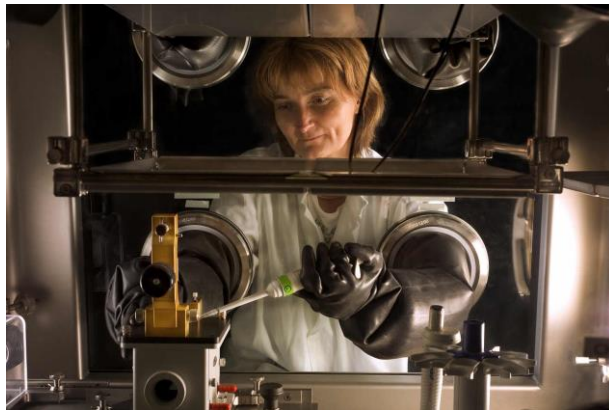
A repository disposal diagram:



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

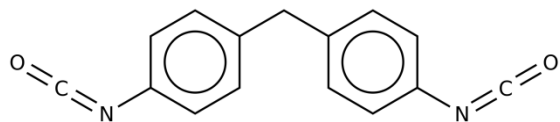
Considered polymer

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



- Composed of 3 segments issued from these molecules

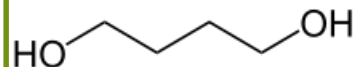
hard segment



4,4'-methylene diphenyl diisocyanate

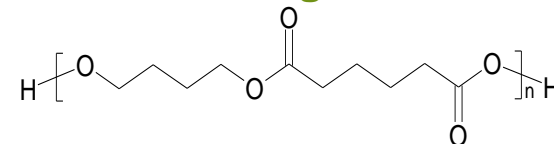
25.5%_w

extender



1,4-butandiol

soft segment



poly(1,4-butylene adipate)

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**

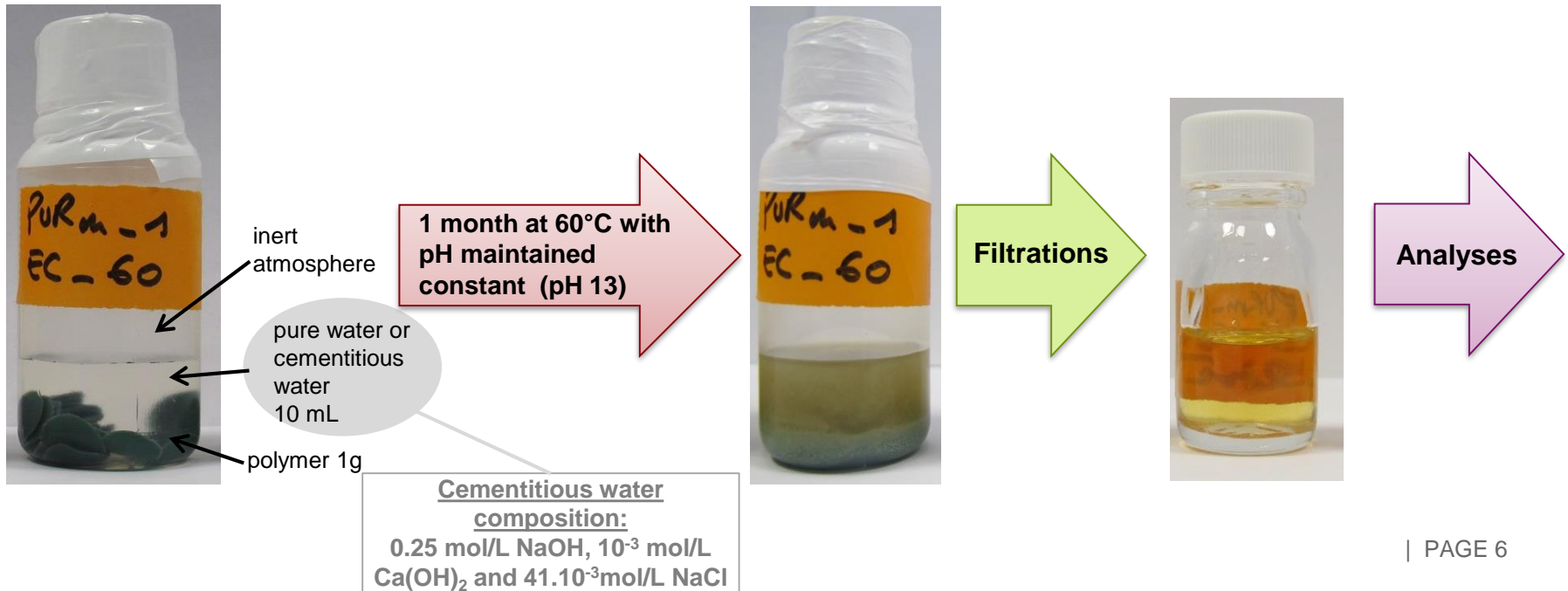
-  **Understanding the degradation mechanisms**
 -  **PUR under radiolysis**
 -  **Irradiated PUR under hydrolysis**

-  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: $\sim 0.7 \text{ kGy}\cdot\text{h}^{-1}$, 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



Leachate



Total Organic Carbon analysis
TOC analyzer

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

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Organic acids
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Volatile and semi-volatile organic molecules
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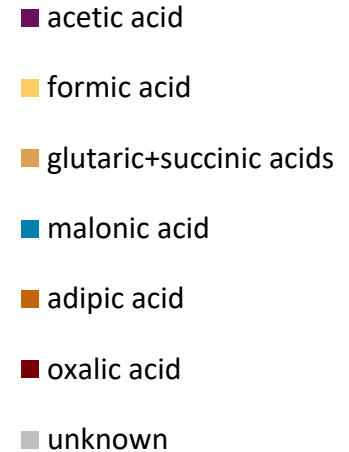
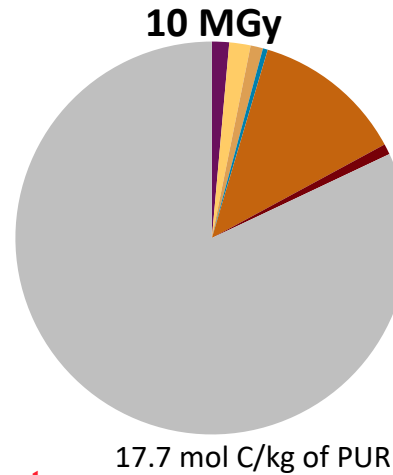
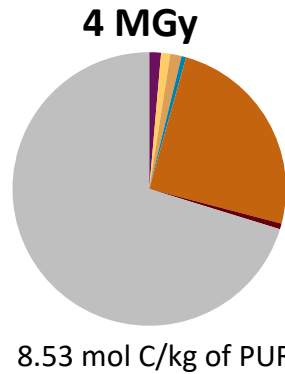
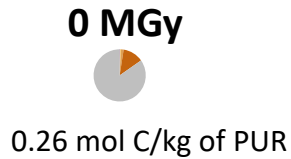
Other organic molecules
LC-MS
MS-MS

Weight average molecular
SEC

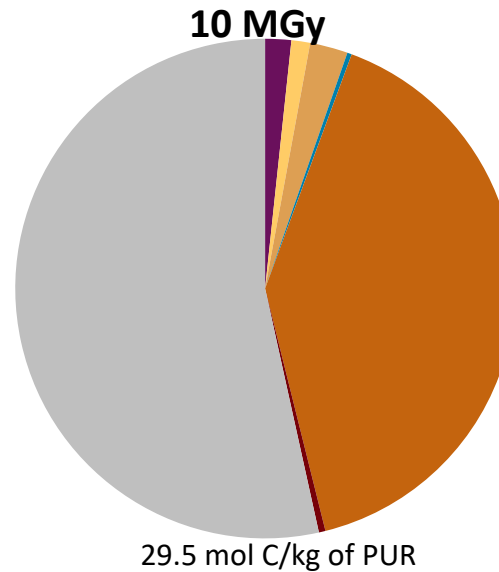
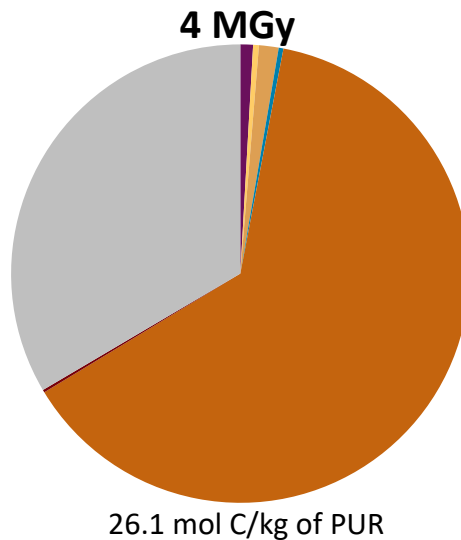
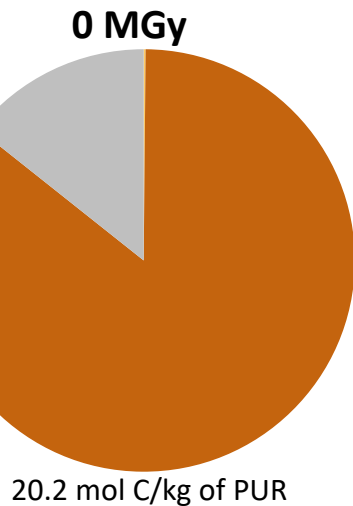


■ **Total Organic Carbon = TOC, ionic chromatography → carboxylic acids quantification**

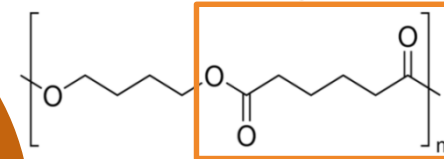
Material balances obtained for leachates in **pure water**:



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



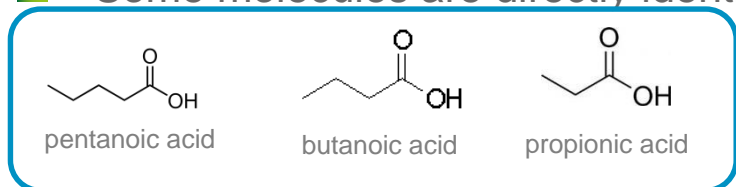
**Origin of adipic acid :
PUR soft segment**



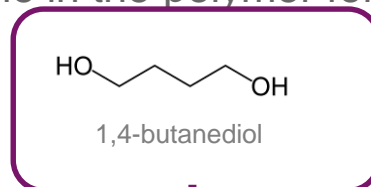
There is a need to investigate the leachates by other analytical techniques.

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

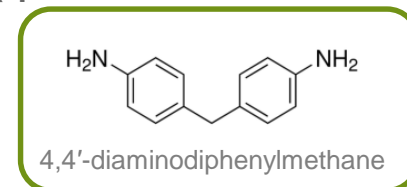
Some molecules are directly identifiable in the polymer formula :



soft segment

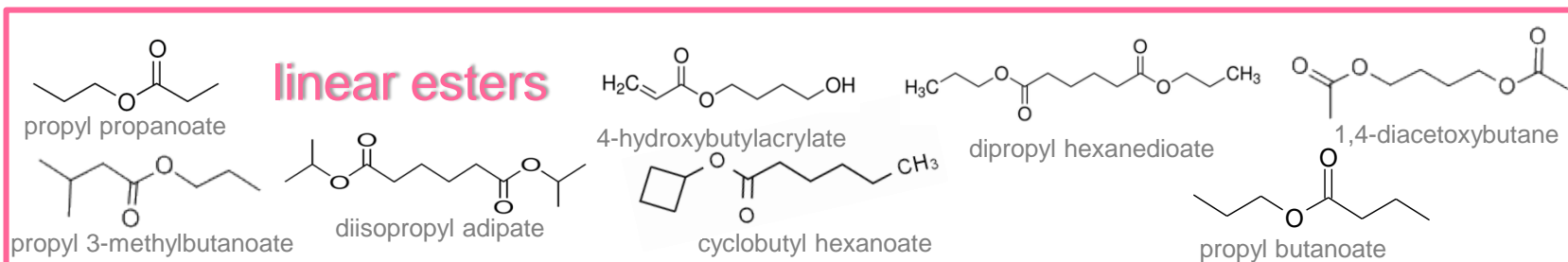
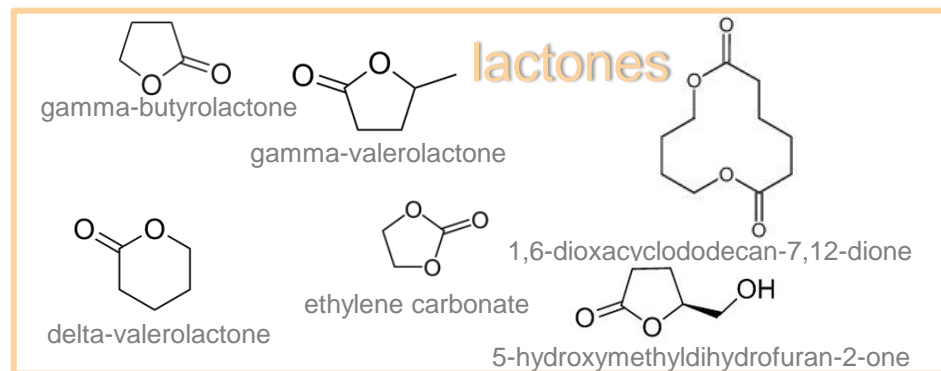
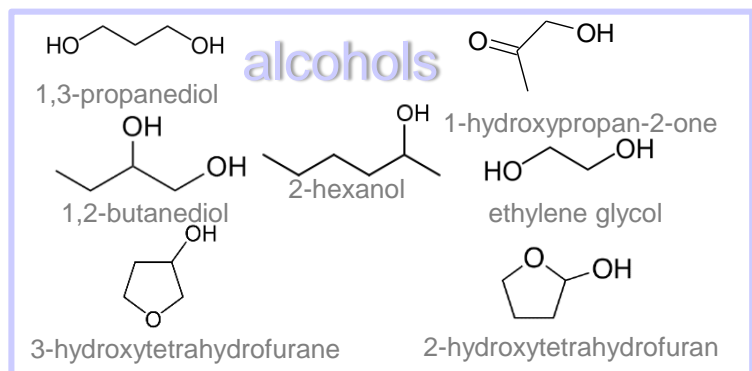


extender



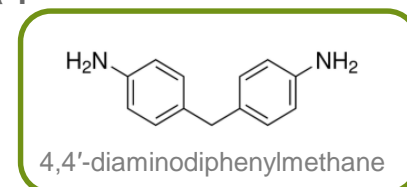
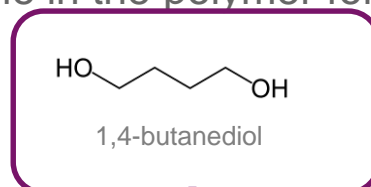
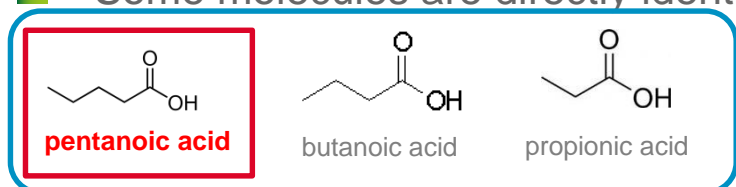
hard segment

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



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

■ Some molecules are directly identifiable in the polymer formula :

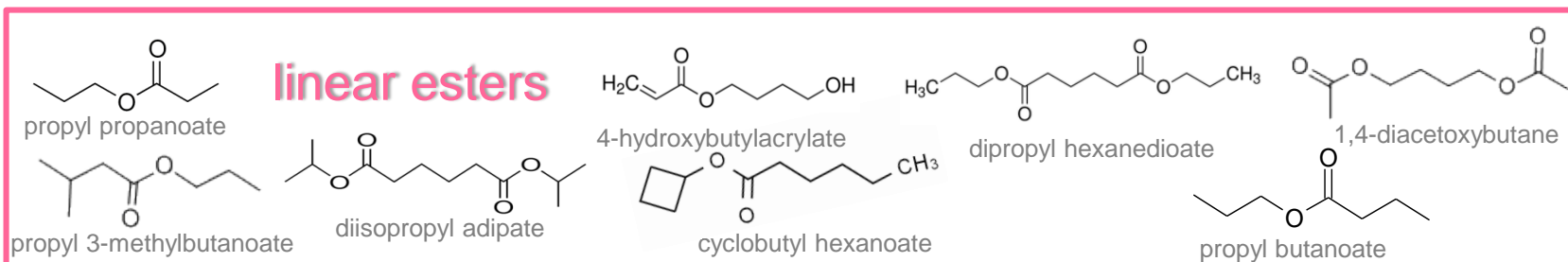
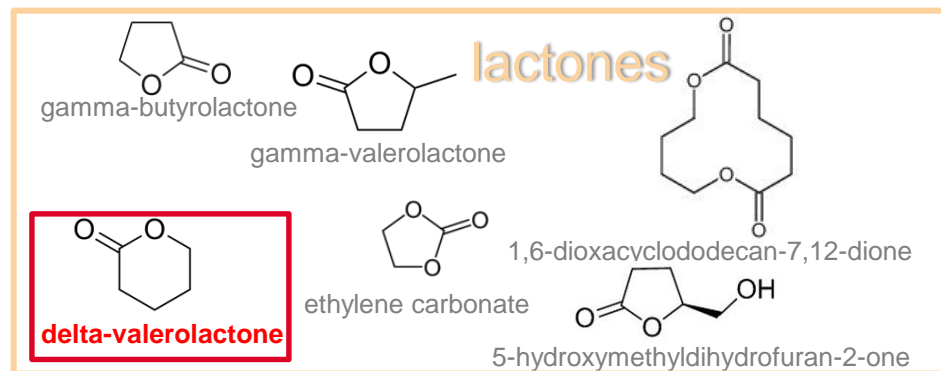
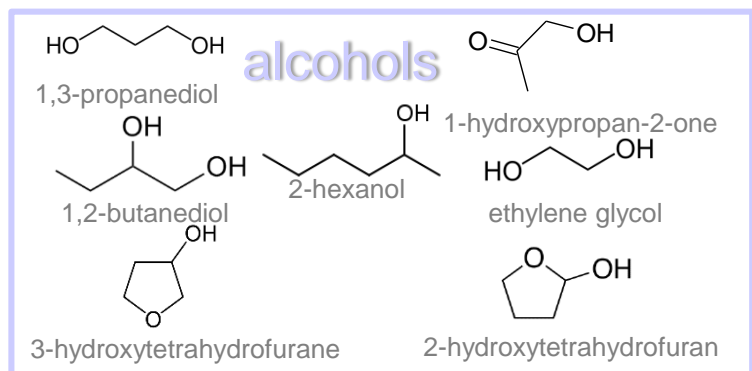


soft segment

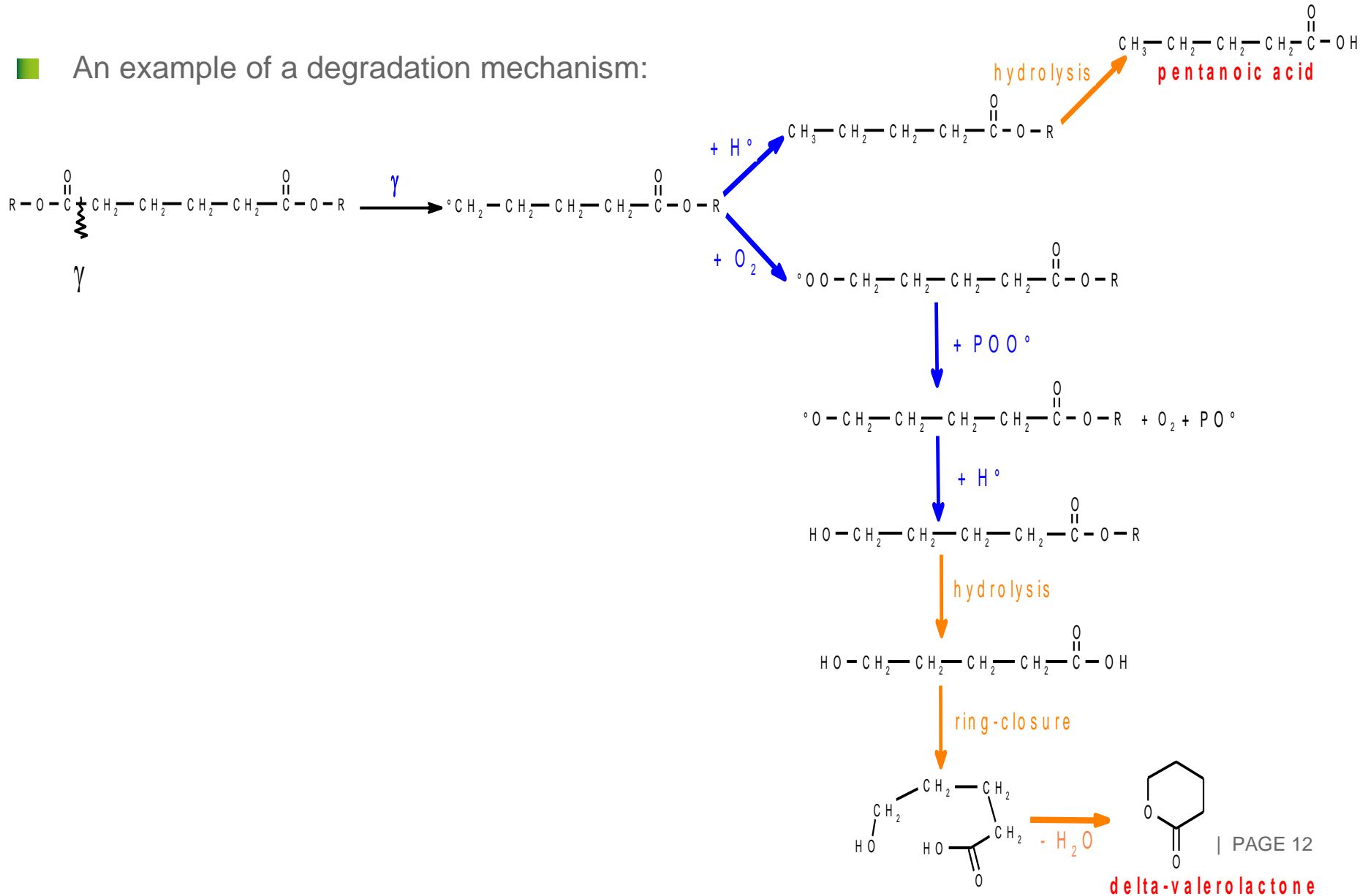
extender

hard segment

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



■ 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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French Alternative Energies and Atomic Energy Commission (CEA)
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 1 69 08 27 62 | elodie.fromentin@cea.fr

Nuclear Energy Division
Departement of Physical Chemistry
Laboratory of Radiolysis and Organic
Matter

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