Radiation processing of polymers: basics, applications and perspectives

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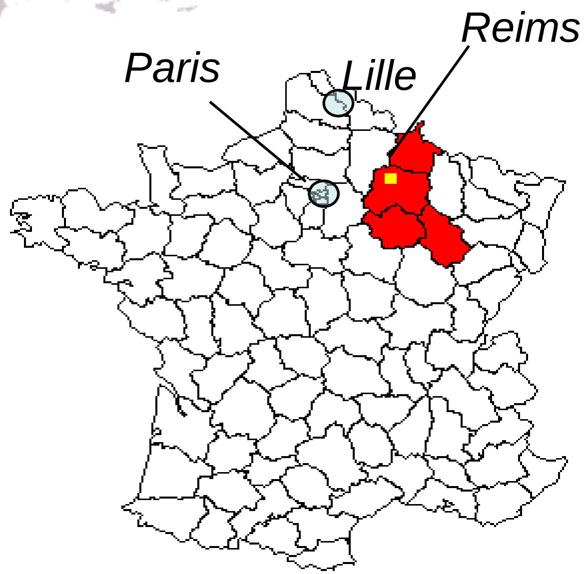
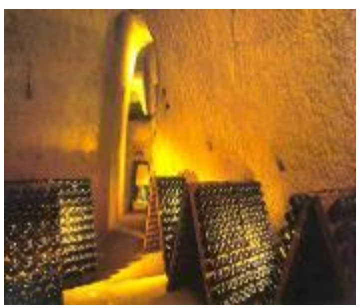
Reims, capital City of Champagne



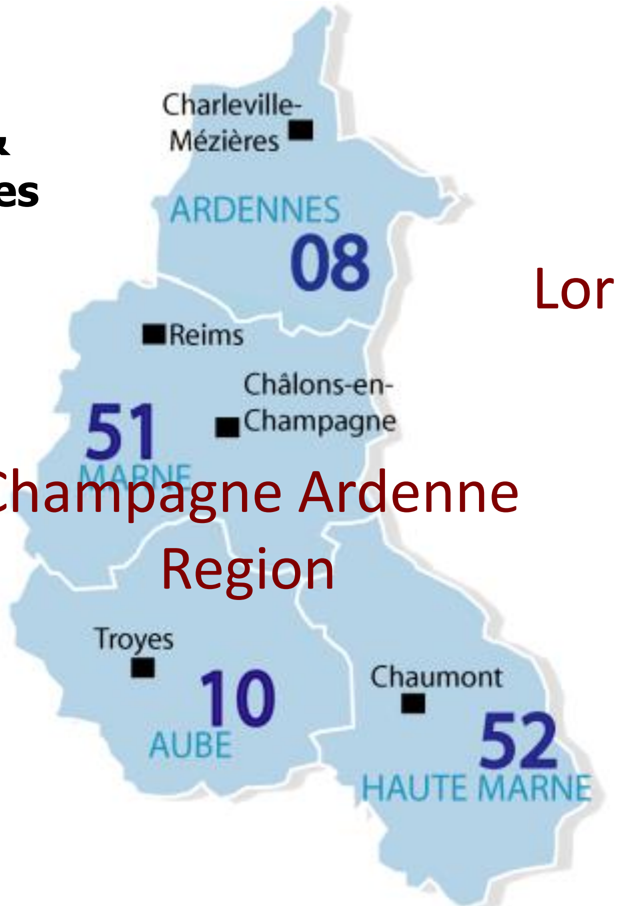


Interactions with Competitiveness Clusters

Industries & agroressources

Picardy Region

Lorraine Region



Champagne Ardenne Region

Developping the biorefinery

Materials for future

Université de Reims Champagne-Ardenne

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- Organization with 5 research groups
  - Methodology in organic synthesis
  - Biomolecules: synthesis and mechanisms of action
  - Coordination chemistry
  - Isolation techniques and structural analysis
  - <u>Functional polymers and networks</u>

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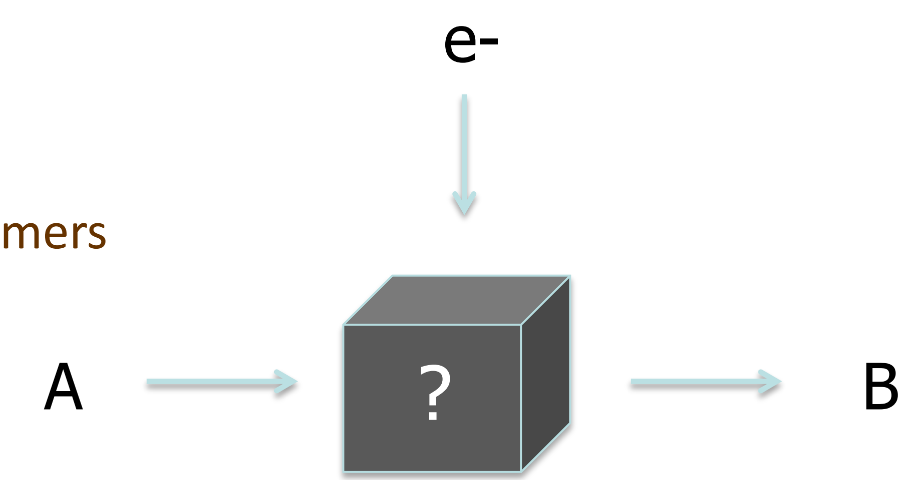
Outline

1. Some basics
   - Energy deposition
   - Early events
   - Domains of application for polymers

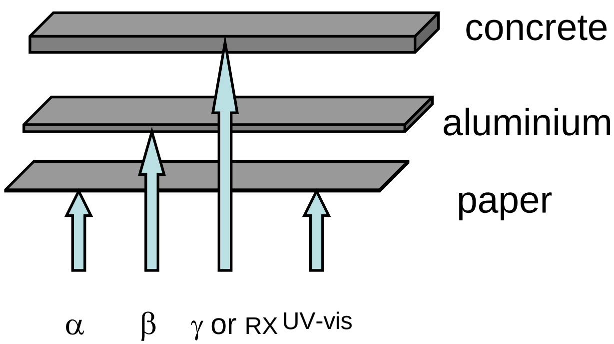


1. Cross-linking
2. Grafting
3. Biomass processing
4. Polymerization

5. Conclusions and opportunities for new developments

Comparing the main features and efficiency of various radiations

- Selectivity of energy deposition (selection rules or random interaction)
- Penetration depth   Chemical effects

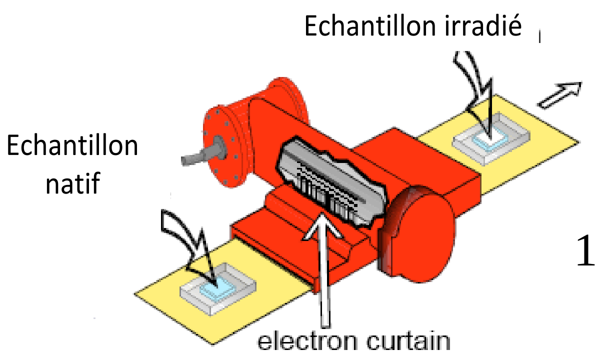


	UV-vis	EB	γ
Type	photons	particles	photons
Origin	electrical power		radioactivity
Energy (**eV**)	2-6	25k - 10 M	1,17M ,1,33M (^{60}Co)
Efficiency R°(**$cm^{-3}.s^{-1}$**)	10^{21}	10^{20}	10^{12}
Applications	**sterilization** **molecular chemistry** **polymerization** **chain scission** **cross-linking** **oxidation** **grafting**		

High energy radiation effects

E (MeV)	d_{50} RX or g	70 % d_0 b or e^-
0.1	4 cm	110 µm
1	10 cm	3.2 mm
3	18 cm	1.1 cm

Lab accelerator 80-150 kV

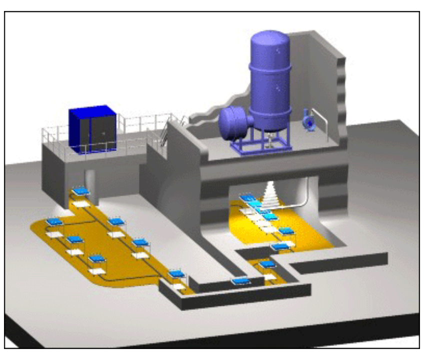


Penetration – Dose - Dose rate

$$1 \quad Gy = 1 \quad J.kg^{-1}$$

Radiation	Dose rate
^{60}Co g	1-100 kGy.h^{-1}
EB	1-1000 kGy.s^{-1}

Industrial facility 10 Me



elastomer vulcanization

thermoplastics cross-linking

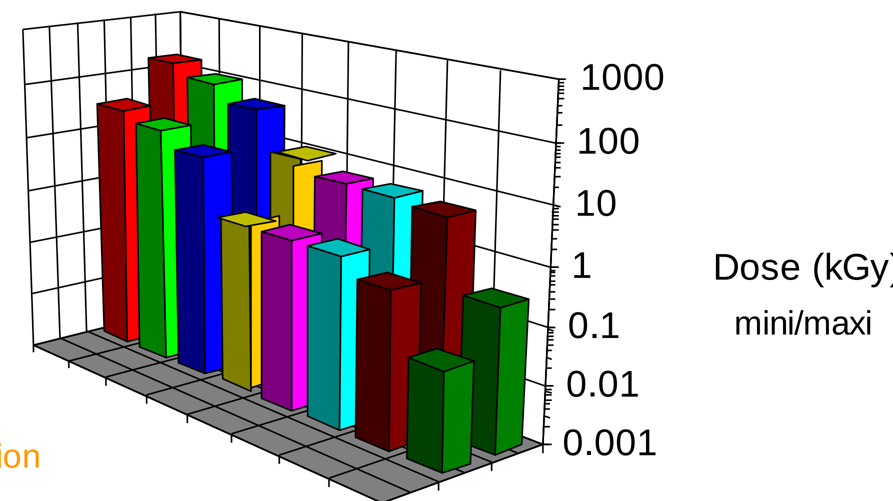
curing of coatings

grafting

food sterilization, preservation

treatment of effluents

surface grafting and modification



desinfection

sprout prevention

Conversion of energy into primary events and chemical effects

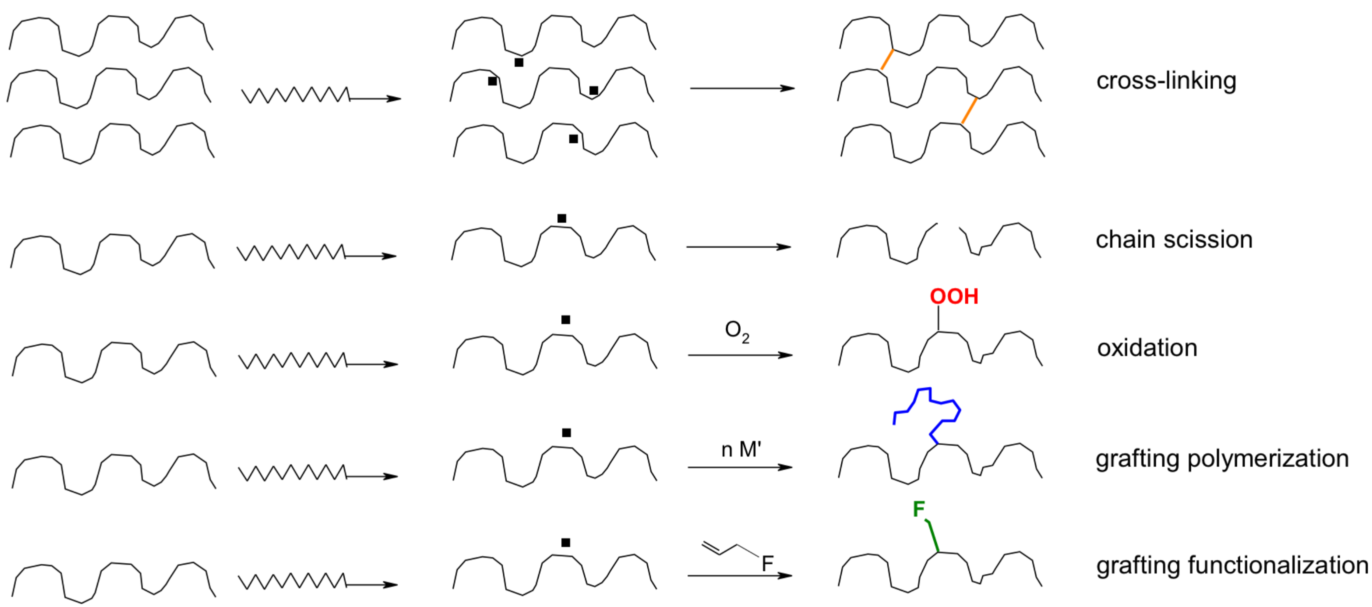
Energy transfer to molecules

Reaction ($A{-}B$ hit by an electron, $\vec{e^-}$)	Process
$A{-}B \rightarrow A{-}B^*$	excitation
$A{-}B \rightarrow A{-}B^{+\bullet} + e^-$	ionization
$A{-}B \rightarrow A^\bullet + B^+ + e^-$	dissociative ionization

Primary effects

e^-	$\longrightarrow$	e^-_{th}	electron thermalization
$A{-}B + e^-_{th}$	$\longrightarrow$	$A{-}B^{-\bullet}$	electron attachment (reduction)
$A{-}B^{+\bullet} + e^-_{th}$	$\longrightarrow$	$A{-}B^*$	neutralization
$A{-}B^{+\bullet} + C{-}D^{-\bullet}$	$\longrightarrow$	$A{-}B^* + C{-}D^*$	charge transfer neutralization
$A{-}B^*$	$\longrightarrow$	$A^\bullet + B^\bullet$	homolytic dissociation

Global chemical transformation induced by high energy radiation applied to polymers



Chain polymerization induced by exposing monomers to high energy radiation

$$M \xrightarrow{\overrightarrow{e^-}} M^{\bullet} \quad \text{radical formation}$$

$$M^{\bullet} + M \longrightarrow M_2^{\bullet} \quad \text{initiation}$$

$$M_2^{\bullet} + M \longrightarrow M_3^{\bullet}$$

- propagation

$$M_{x-1}^{\bullet} + M \longrightarrow M_x^{\bullet}$$

$$M_x^{\bullet} + M_y^{\bullet} \longrightarrow M_{x+y} \quad \text{termination}$$


polymer latex (emulsions)
radiation cured inks, paints, composites, adhesives
patterned devices for microelectronics
polymerization
micro- or nano-lithographic patterns
micro- and nano-porous membranes
surface treatment of fibers for composites
thermoplastics with improved processing properties
degradation, oxidation
monomers
polymers
grafting
curing, cross-linking
hydrophobic or hydrophilic textiles
biocompatible coatings
functionalized membranes
objects with new surface properties: bactericidal, wear resistant, wettable, ...
expandable foams
curable adhesives
vulcanizable elastomers
food packages
electric cables
shrinkable tubing
pressure resistant pipes
self-regulated ...
electrically heating plastics

Tuning of the reactivity of acrylate copolymers exposed to electron beam by compositional effects

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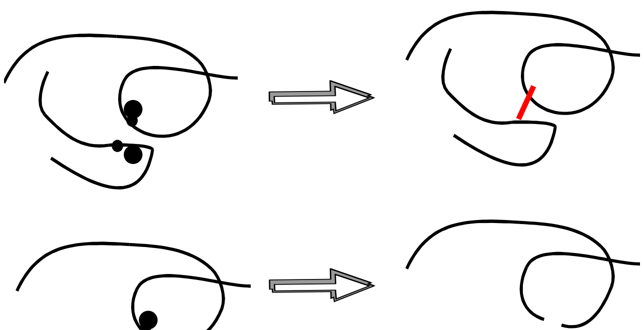
High energy irradiation of common homopolymers

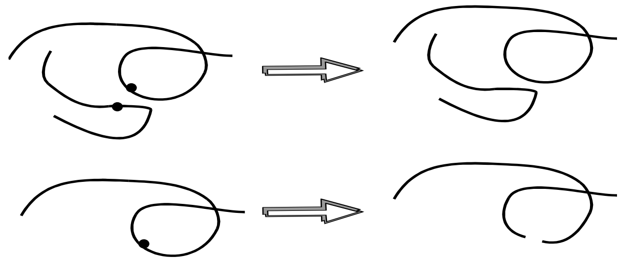


Polymer[a)]	G(X) 100 eV	G(S) 100 eV
PE [b)]	3.0	0.9
PP [b)]	2.5	1.1
Polybutadiene	3.8	
PMA	0.55	0.18
PnBuA	0.63	0.18
PtBuA	0.16	0.18
PMMA		1.2 - 3.5
PVC[c)]	0.33	0.23
PS	0.05	<0.02
PET	0.03 - 0.2	0.07 - 0.2

a) Ionization @ 25°C under exclusion of oxygen
b) Depending on tacticity and of cristallinity
c) Non plasticized

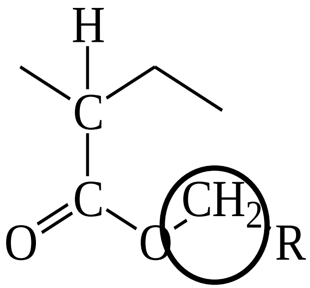
- random energy absorption
- free radical nature of active species

Reactivity of acrylate copolymers

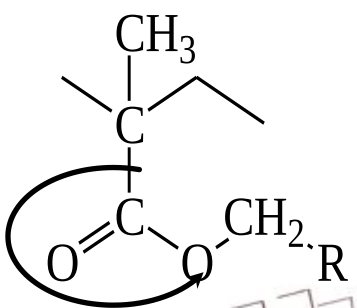


Crosslinking vs. degradation

- homopolyacrylates: X-linking
  - CH_2 on side-chain
  - can degrade if no H present on –(C=O)-O-**C**-C



- homopolymethacrylates: degrade easily
  - ester scission (70%)
  - can undergo cross-linking if R is a long-chained alkyl group



Objectives - Approach

- Guidelines for the synthesis of fast-curing systems

- Composition - reactivity relationship
  - nature of main chain
  - « sensitizing » side groups
- Systems of progressive complexity
  - MMA and butyl acrylate homo- and copolymers
  - functionalized BuA copolymers
  - validation on acrylate-based lateces

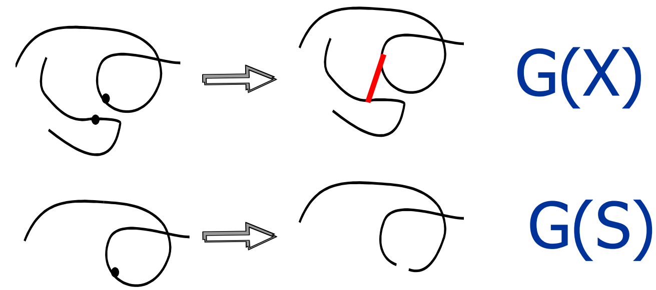
Theoretical models

- Statistical treatment
  - basic hypotheses :

    limited number of random events,

    proportionality to dose,

    Gaussian MWD



$$\frac{1}{\overline{M}_n} = \frac{1}{\overline{M}_n^0} + kD\left(G(s) - G(x)\right)$$

- Changes in molecular weights

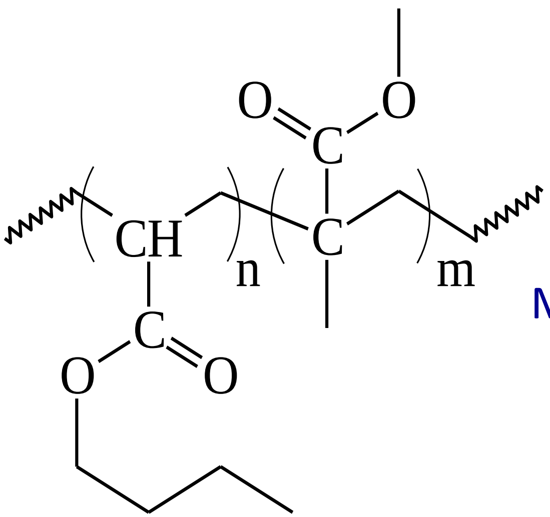
$$\frac{1}{\overline{M}_w} = \frac{1}{\overline{M}_w^0} + kD\left(\frac{G(s)}{2} - 2G(x)\right)$$

- Gel fractions
  - Charlesby-Pinner method

$$s + \sqrt{s} = \frac{G(s)}{2G(x)} + \frac{1}{D}\frac{k'}{G(x)\overline{M}_w}$$

MMA-BuA copolymers

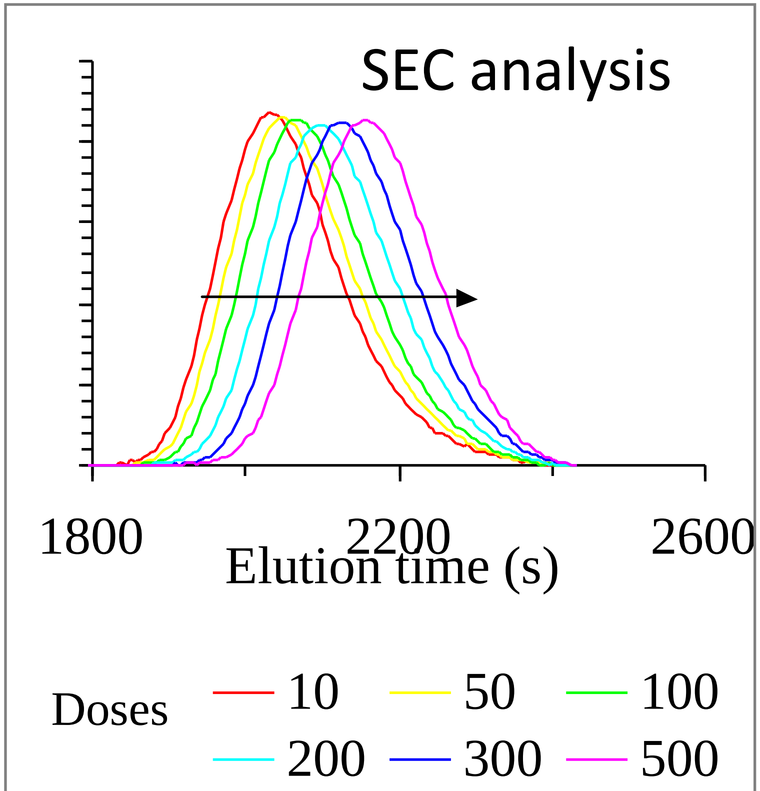
- Free radical copolymerization
- Various compositions
- Molecular weight control
- Microstructural analysis by NMR

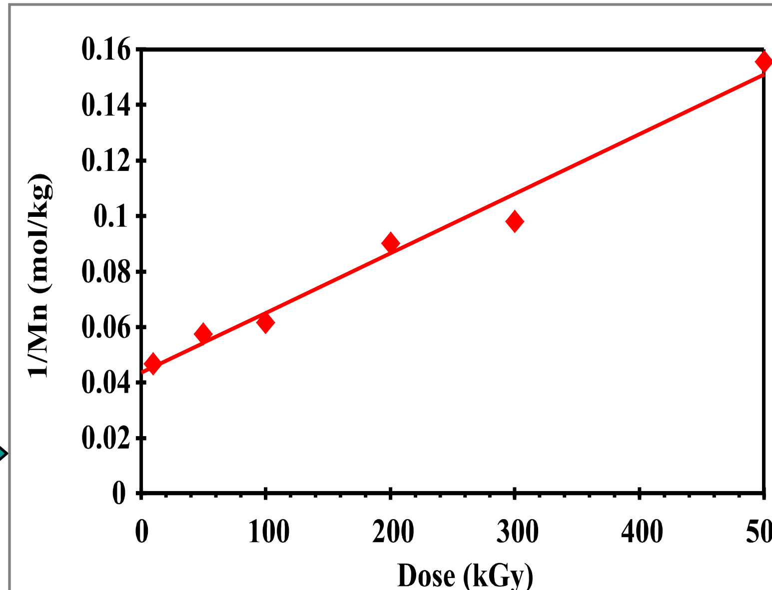


MMA

BuA

Homopolymers: PMMA



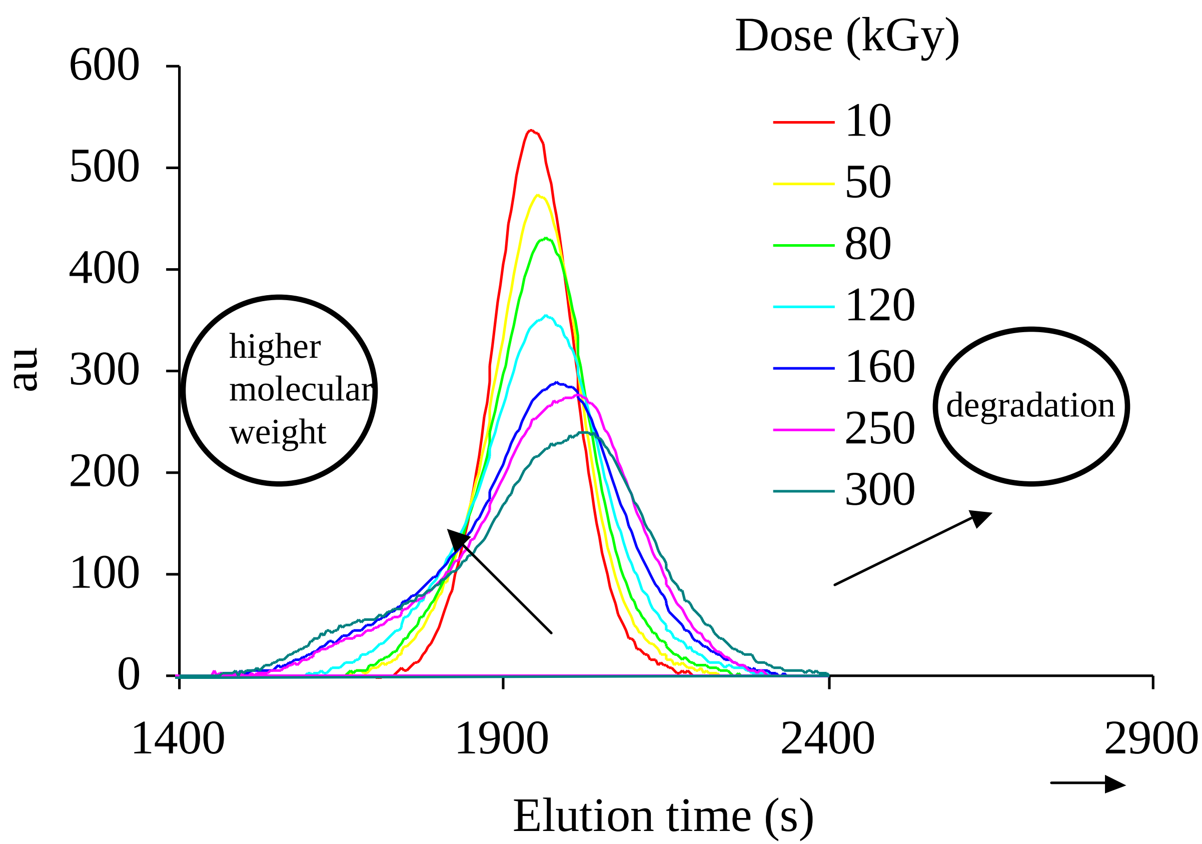


Mn^{-1} varies linearly with Dose (kGy)

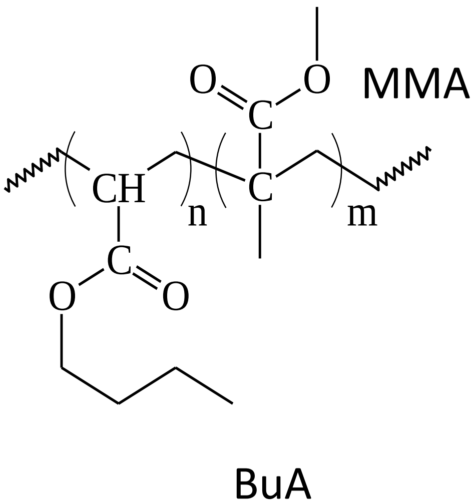
G(s) = 2.1 ± 0.2

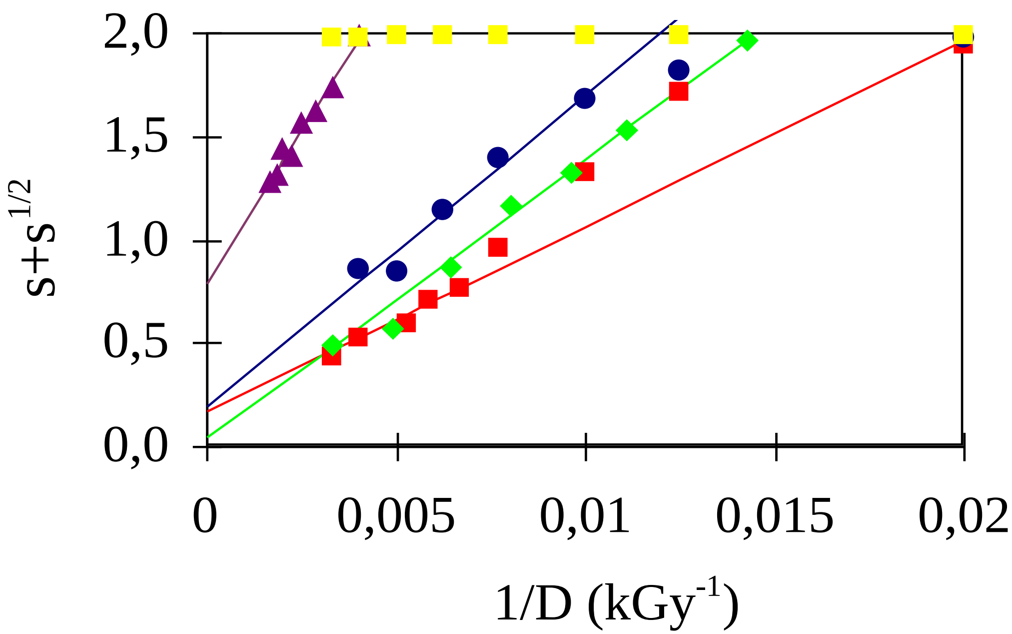
MMA-BuA Copolymers

SEC analysis of (CP21-77k)



MMA-BuA Copolymers





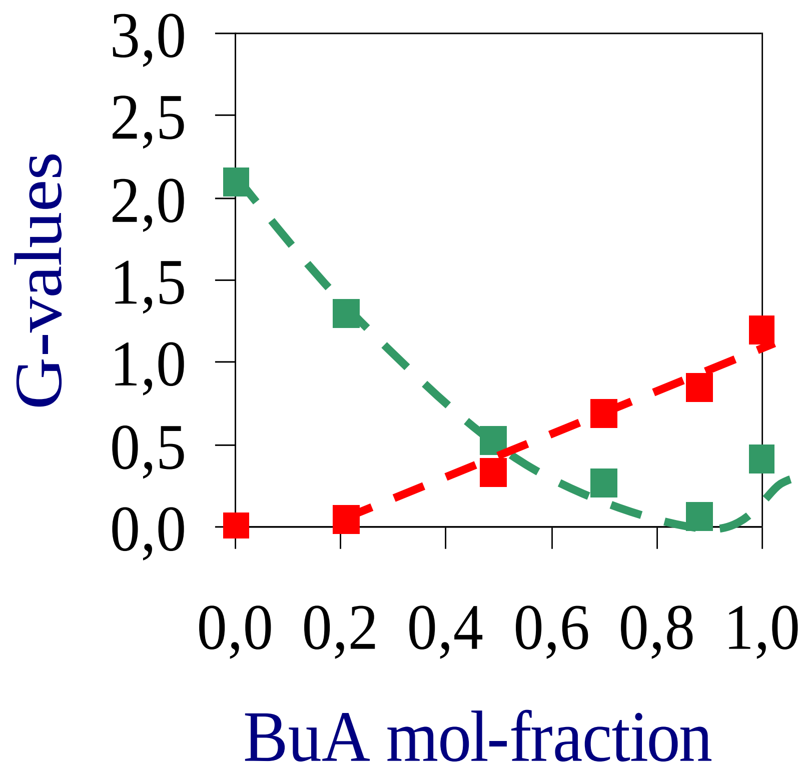
Polymer	poly(BuA)	copo88	copo70	copo49	copo21
BuA mol fraction	1.00	0.88	0.70	0.49	0.21
G(s)	0.41 ± 0.04	0.06 ± 0.01	0.27 ± 0.04	0.52 ± 0.01	≈ 1 (?)
G(x)	1.20 ± 0.05	0.72 ± 0.02	0.69 ± 0.04	0.33 ± 0.01	<0.2 (?)
G(s)/G(x)	0.34	0.08	0.39	1.58	>4

MMA-BuA Copolymers

Dependence of G-values on composition

- G(X)
  monotonous increase
  with the BuA content

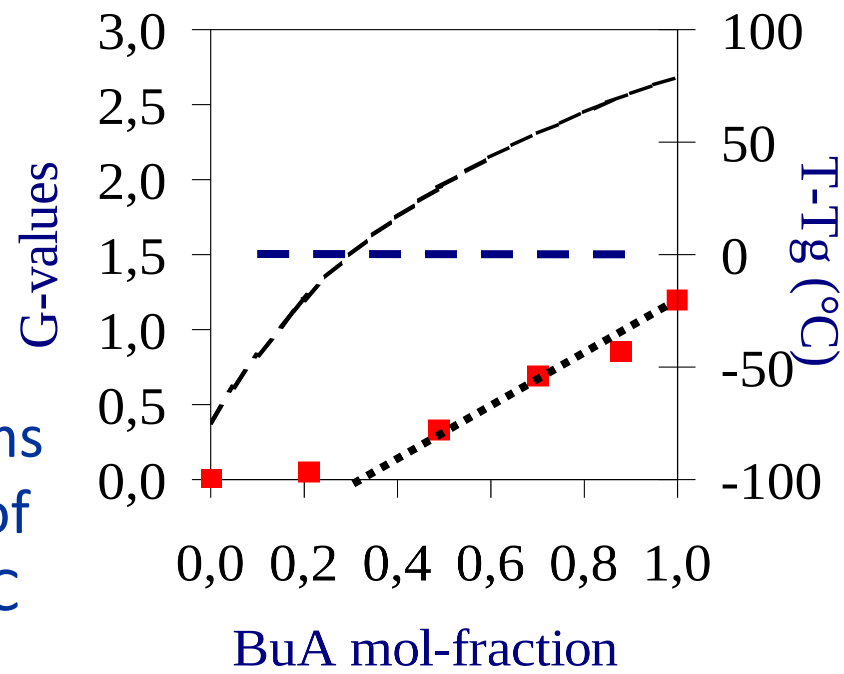
- G(S)
  occurrence of a minimum
  for $f_{MMA} \approx 0.1$



MMA-BuA Copolymers

monotonous dependence of G(X) with f_{BuA}

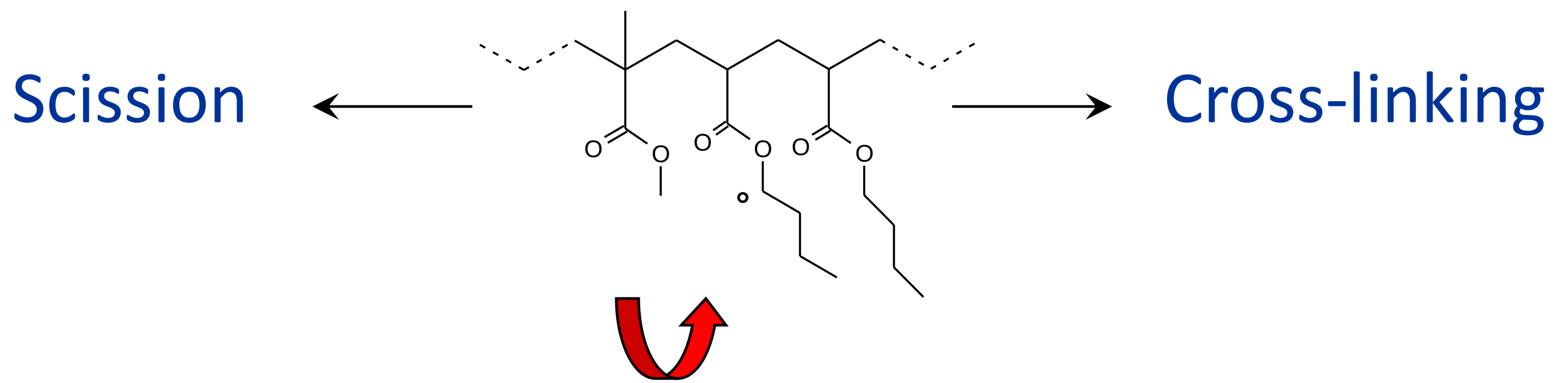
- intrinsic group reactivity is approximately additive
- G(X)≈0 : interpretated in terms of loss mobility with change of composition giving T_g @ 20°C



Reactivity of MMA-BuA copolymers

Minimum for G(S)

- reactivity dependent on the nature of neighbors
- scission event occurring from activated BuA units is inhibited at some stage by MMA neighbors



Competing transfer reaction by MMA unit ?

Functionalized copolymers

Acrylate comonomer	Comonomer Wt-%.	content mol-%	Gel-D (kGy)	G(S)	G(X)	G(S)/G(X)	T_g (°C)
-	0.0	0.0	34.6	0.42	1.18	0.36	-54
allyl	7.0	8.0	24.3	0.84	1.74	0.48	-53
allyl	10.4	11.7	19.2	0.98	2.18	0.45	-51
DCPOE	10.7	5.8	29.4	0.26	1.31	0.20	-46
DCPOE	39.8	25.4	20.4	0.51	1.94	0.27	-22
2-ethylhexyl	6.0	4.25	66.7	0.26	0.62	0.41	-54
2-ethylhexyl	9.0	6.4	62.5	0.23	0.65	0.35	-54
2-ethylhexyl	20.0	14.8	58.8	0.36	0.73	0.49	-53
2-methylthioethyl	2.2	2.0	28.6	0.59	1.45	0.41	-54
2-chloroethyl	7.0	6.7	21.6	0.33	1.80	0.11	-52

Functionalized copolymers

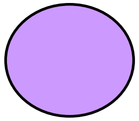
- Intrinsic change of reactivity due to comonomer

$$\Gamma\ (\mathrm{i}) = \left(\frac{\partial \mathrm{G(i)}}{\partial \mathrm{C}}\right)_{C=0}$$

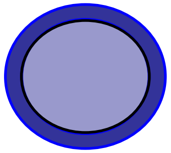
Functional acrylate	Γ (X)	Γ (S)	Γ (X)/[G(X)]	Γ (S)/[G(S)]
allyl	7.0	5.2	5.9	12.4
DCPOE	2.2	-2.8	1.9	-6.7
2-chloroethyl	9.3	-1.4	7.9	-3.3
2-methylthioethyl	13.5	8.5	11.4	20.2
2-ethylhexyl	-13.2	-3.8	-11.2	-9.0

Transposition to acrylic lateces

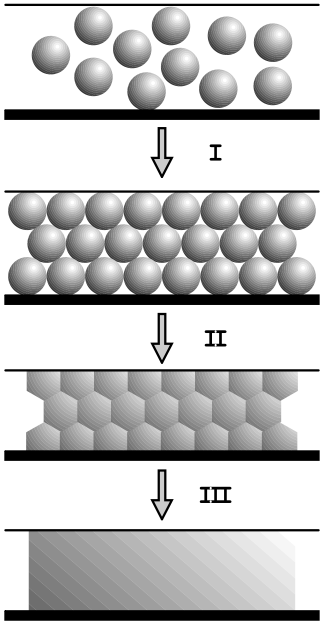
- Emulsion polymerization
- Particle of uniform composition



  particle with a core-shell structure

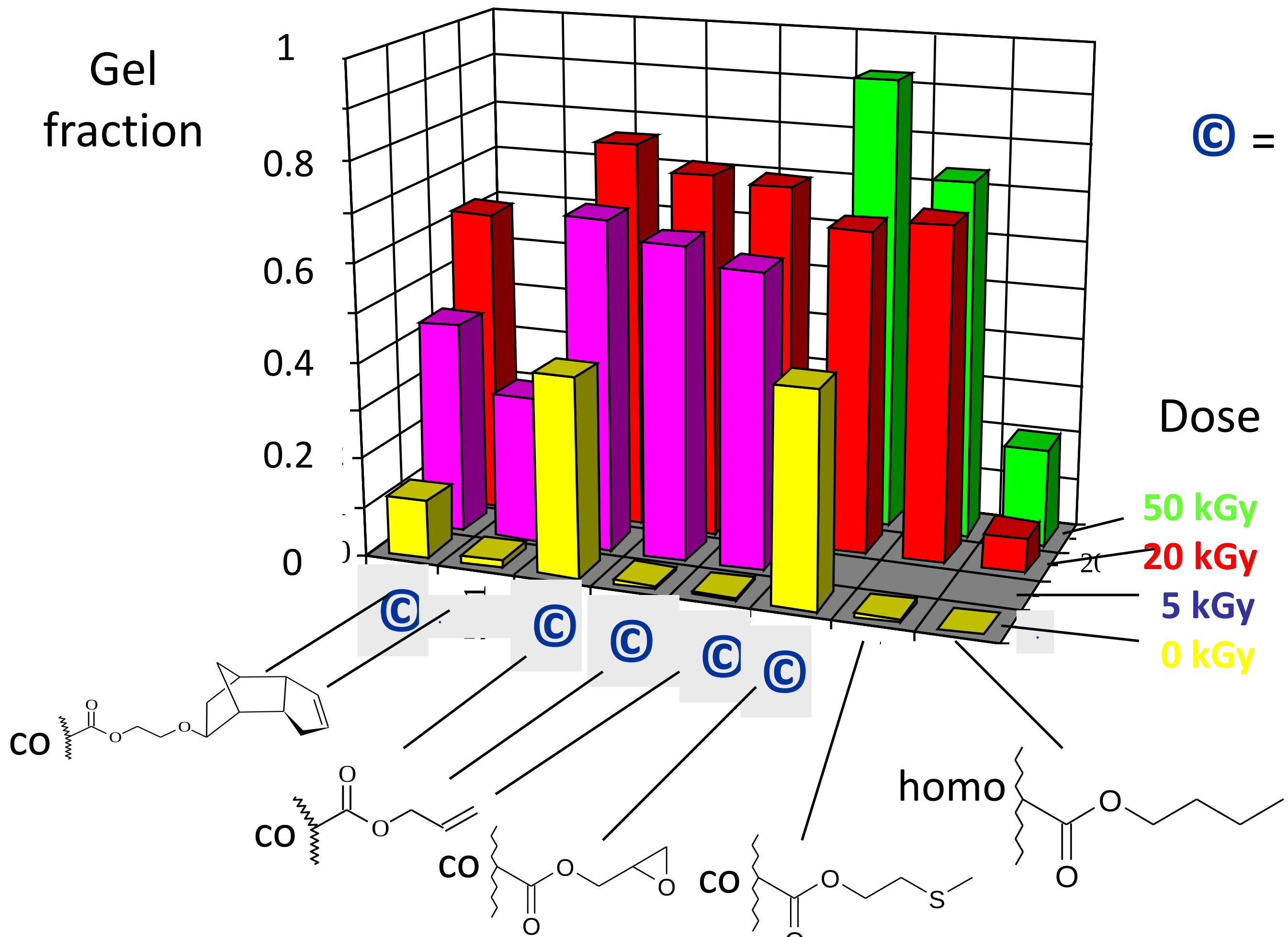


- Filmification (low T_g)



- Casting
- Drying
- EB-irradiation

EB-curing of films from acrylic lateces



Conclusions

- Statistical treatment of competing X and S processes
  - useful information for tuning the reactivity of copolymers
  - pertinent selection of reactive materials
  - control of processing parameters

- Study of temperature effects

- Study of the reactivity of monomer sequences by using models

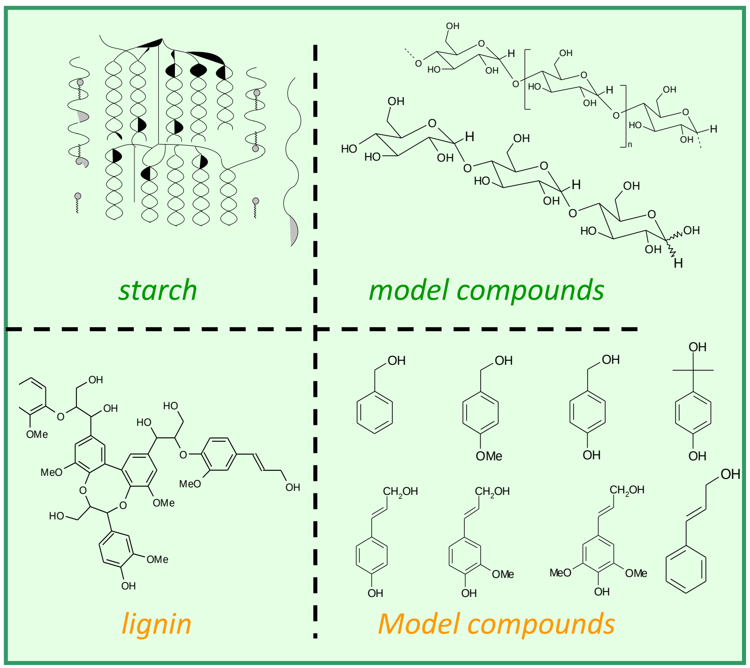
- Application to radiation curable coatings and adhesives

Lignostarch

Electron-beam modification of starch with lignins: a study of radiation grafting

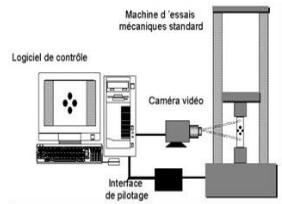
LignoStarch project

Understand and master the structural modifications and the changes of properties by means of a multidisciplinary and multi-scale approach

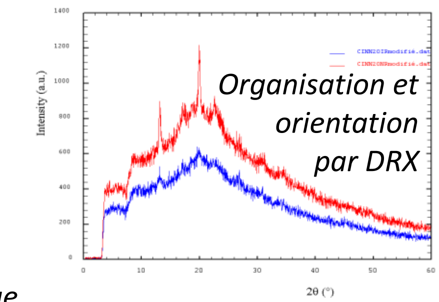


1) Destructuriztion + blending

2) Irradiation (electrons) and / or orientation by stretching

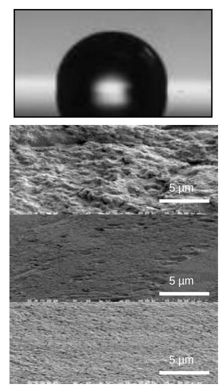


Essais mécaniques et vidéotraction

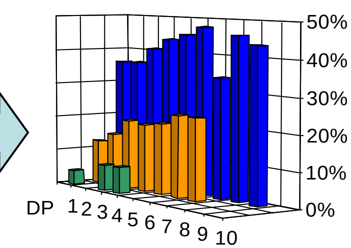


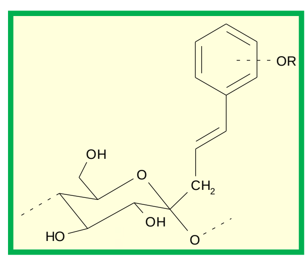
Organisation et orientation par DRX

Mouillage, propriétés superficielles

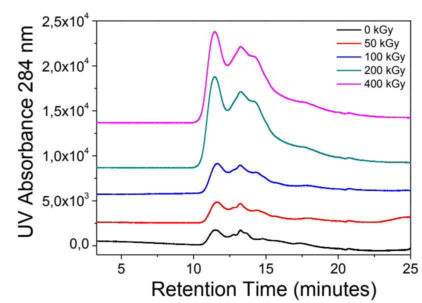


Quantification des adduits (modèles) par SM Maldi-Tof



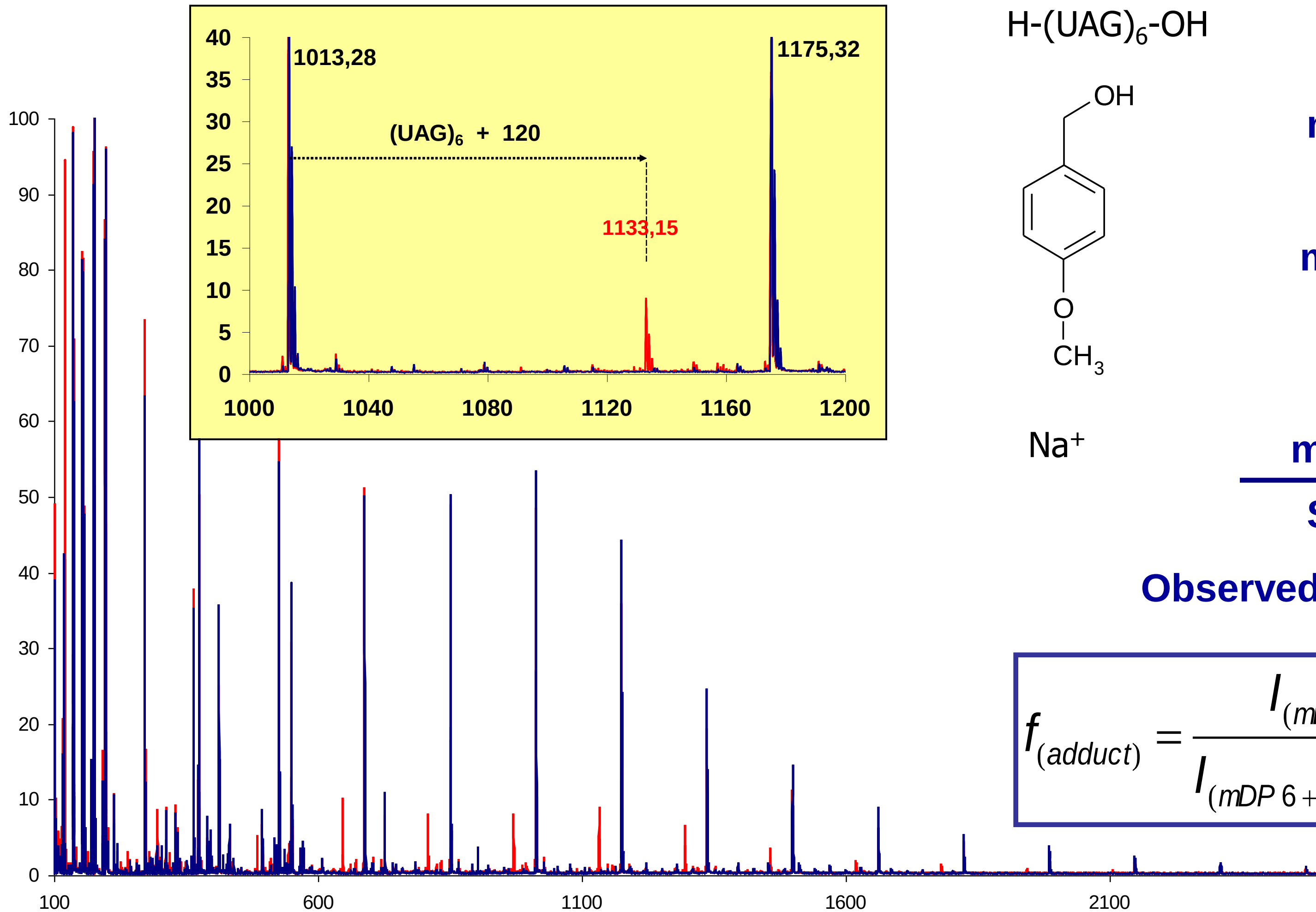


Description moléculaire



Quantification par analyse CES

Reactivity of p-methoxybenzyl alcohol with maltodextrine



H-$(UAG)_6$-OH

Na^+

$m_{hexamer}$ = 1013 Da

$m_{alcohol}$ = 138 Da

m_{Na^+} = 23 Da

Sum = 1154 Da

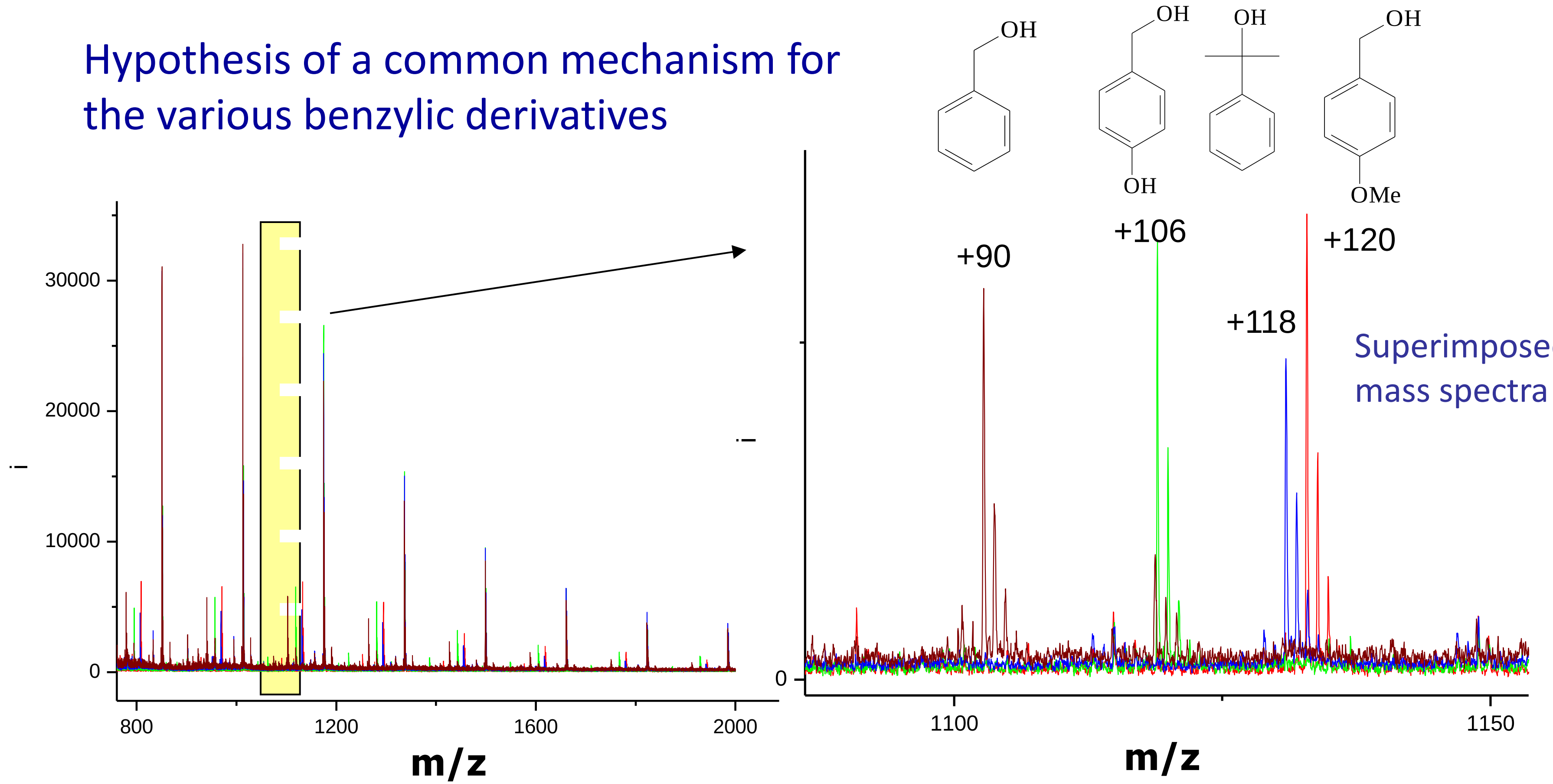
Observed adduct = 1133 Da

$$f_{(adduct)} = \frac{I_{(mDP\,6\,+120)}}{I_{(mDP\,6+120)} + I_{(mDP\,6)}} = 0.16$$

-Ardenne

Reactivity of various benzyl alcohols with maltodextrine

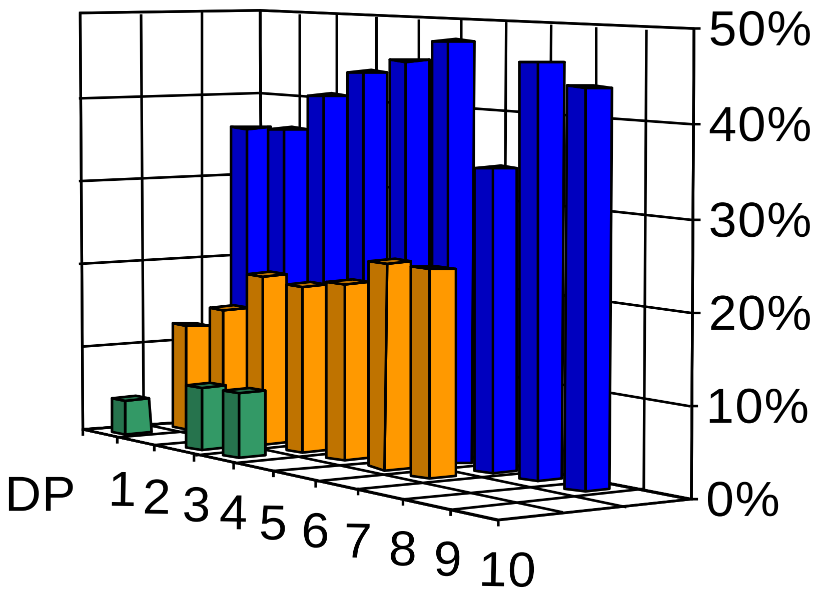
Hypothesis of a common mechanism for the various benzylic derivatives



The benzyl alcohol function seems to be involved in the condensation process

Formation of multiple adducts between glucides and aromatic model compounds

- Maltodextrine G19 + p-methoxybenzyl alcohol - 400 kGy

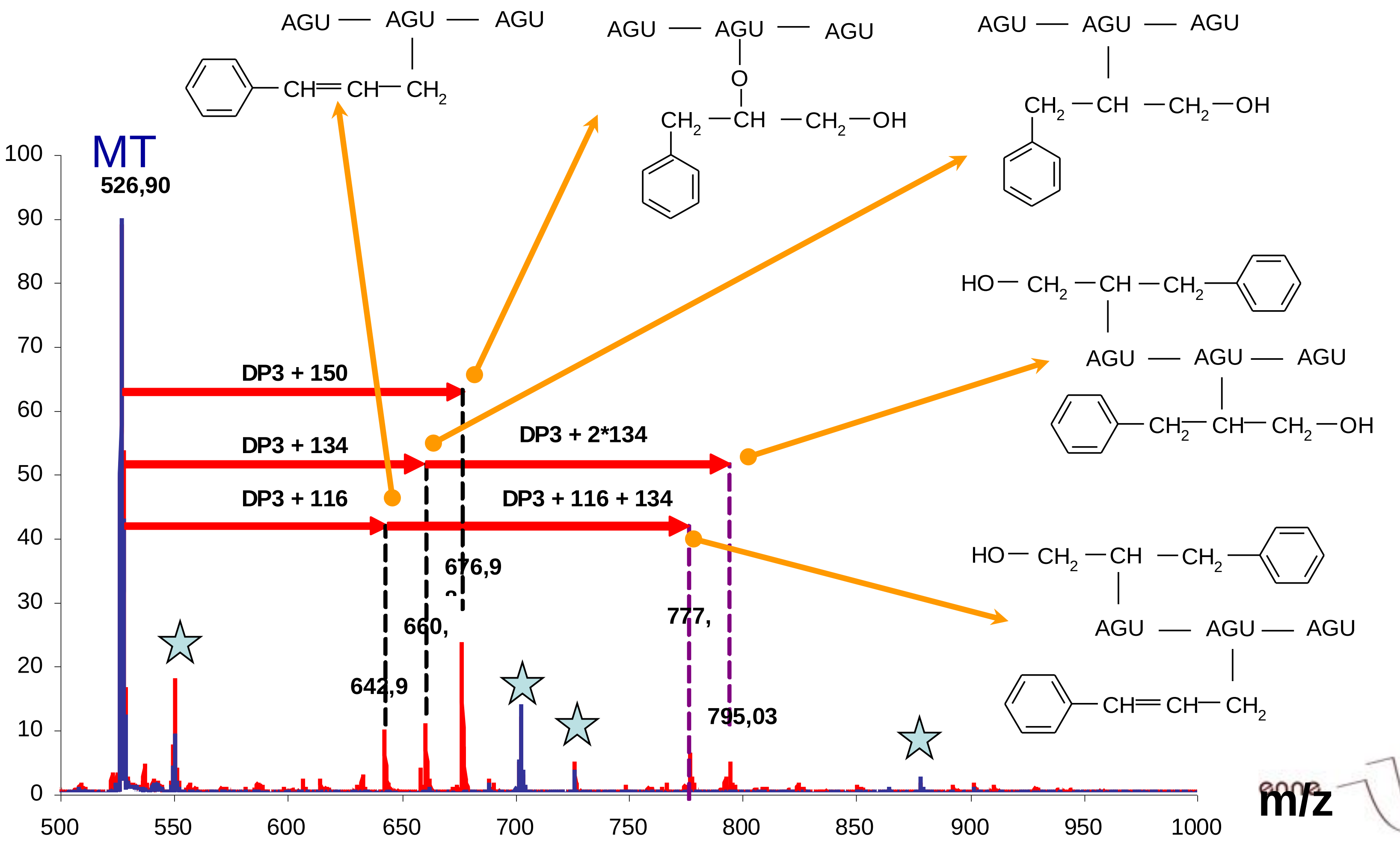


Peak intensity in MALDI TOF mass spectra relative to parent oligomer of DP=x

1 addition   (+120 Da)
2 additions (+240 Da)
3 additions (+360 Da)

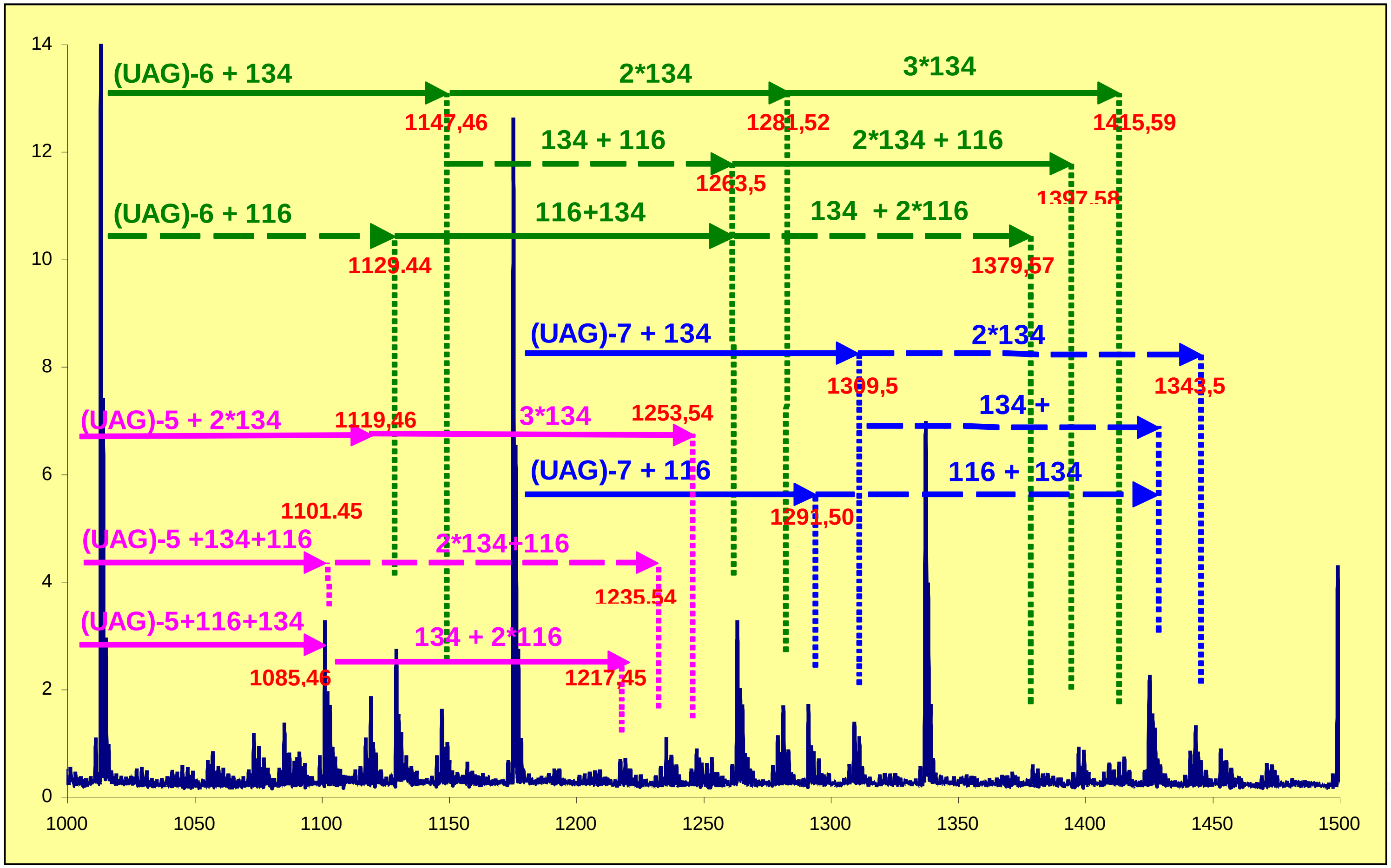
- High grafting yield, and multiple grafting
- Confirmation of free radical mechanism for grafting since there is only a single site for acetalization per molecule

Grafting of Cinnamyl alcohol onto maltotriose (200 kGy dose)



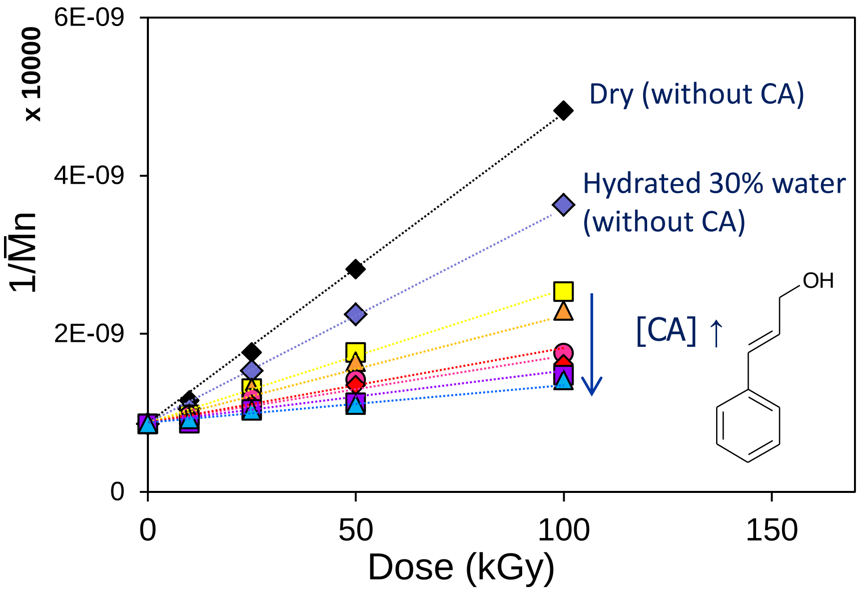
Grafting of cinnamyl alcohol onto maltodextrine Glucidex 19 (400 kGy dose)

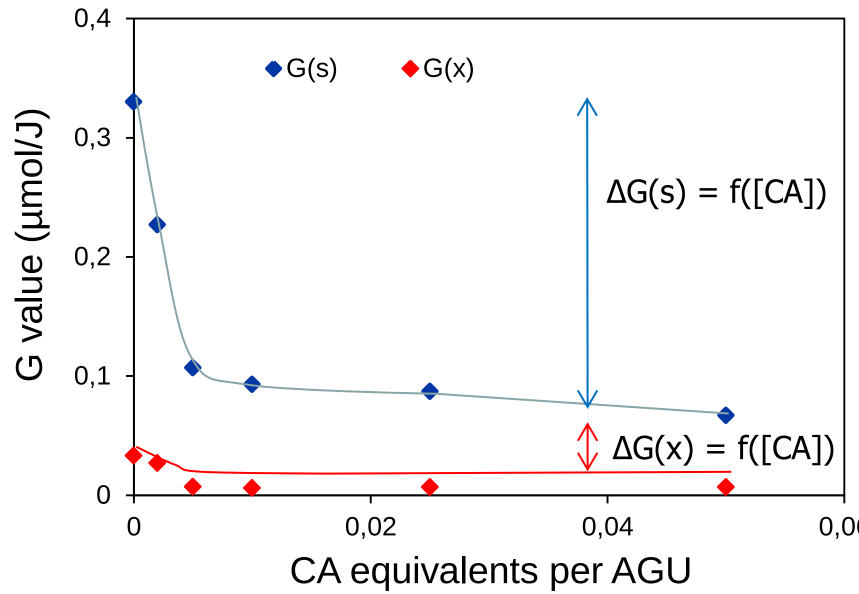
Composition : Glucidex 19 63%, H_2O 16%, CML 5%, MeOH 16% - 400 kGy



Pullulan:
Model of Starch for quantifying G(s), G(x)

Radiolytic yields for scission and crosslinking ($mol.J^{-1}$)



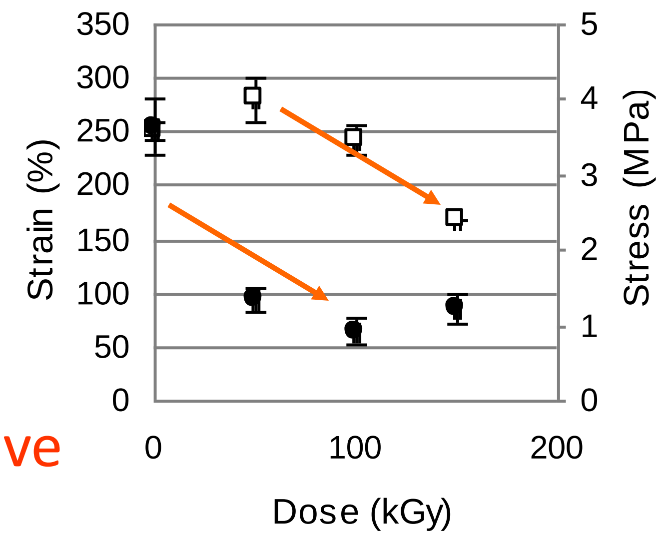


- G(s) and G(x) ↓ in presence of CA
- Marked decrease in G(s)
- G(s) ≠ 0 and G(s) > G(x)
- G(s) and G(x) constant [CA] > 0.01 eqv

Khandal et al. Radiat. Phys. Chem 2013

Combined effects of blending and irradiation on tensile properties

Tensile strain (◘, in %)
and stress (●, MPa) at break

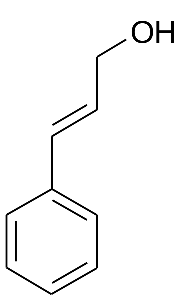


Starch : Glycerol : 80 : 20 wt-parts

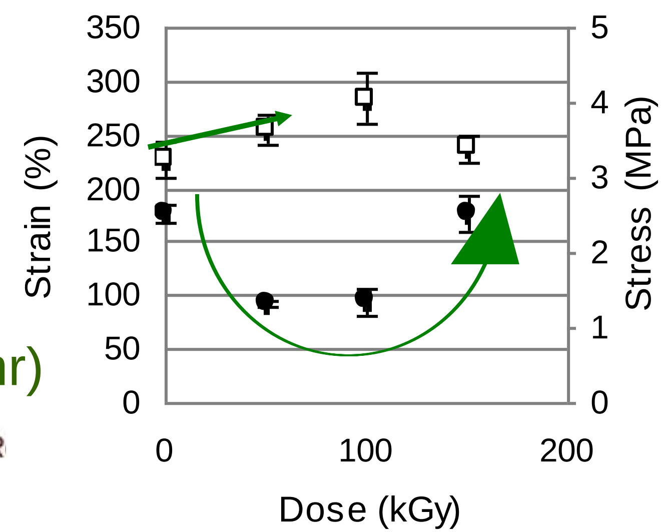
no additive

Starch : Glycerol : 80 : 20 wt-parts
+ 2 phr cinnamyl alcohol

Samples conditioned at 50 % RH before irradiation



with cinnamyl alcohol (2 phr)



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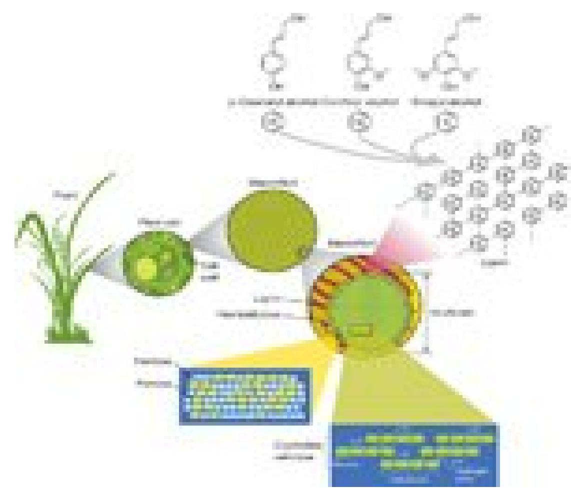
Khandal et al. Radiat. Phys. Chem 2012

Biomass deconstruction and pretreatment


Courtesy of www.sechilienne-sidec.com/



IAEA

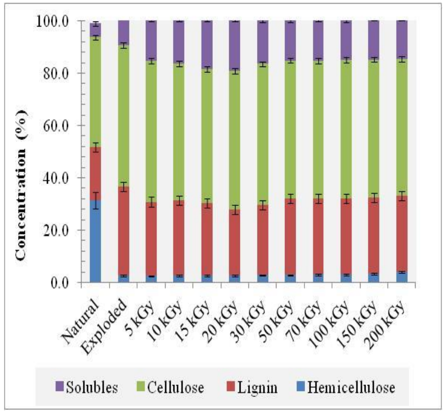
CRP F22046

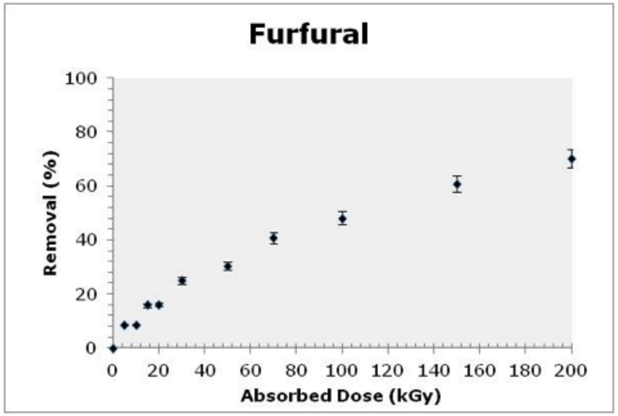
« Development of radiation processed products from natural polymers »

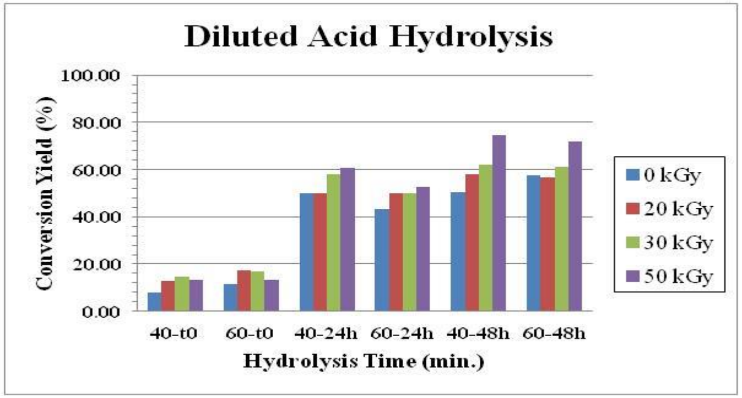
Université de Reims Champagne-Ardenne

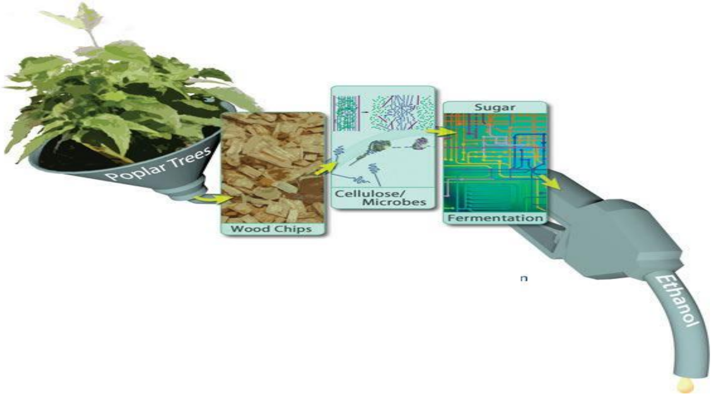
Deconstruction and pretreatment of biomass

- Fermentation of sugars extracted from bagasse (lignocellulosic part)
- ISPEN, Brazil, Dr. Celina Duarte
- EB pretreatment









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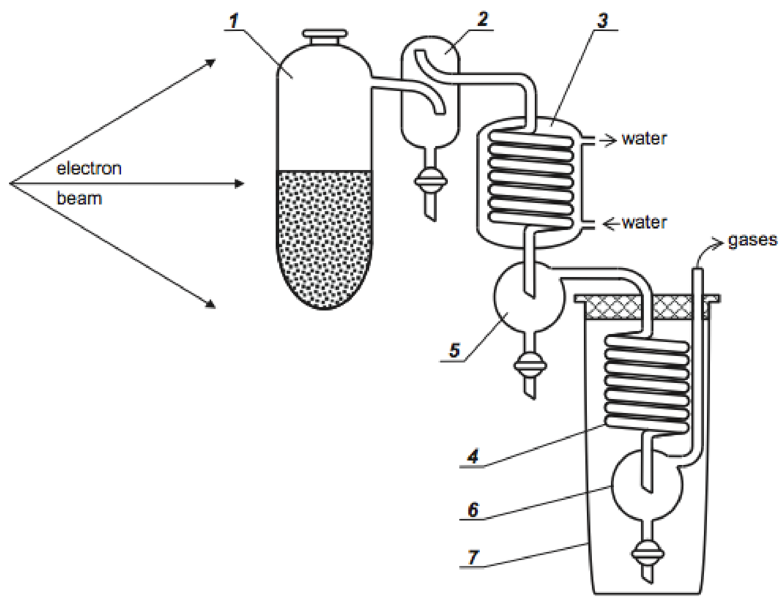
Depolymerization / deconstruction



Deconstruction and pretreatment of biomass

- Depolymerization by combining radiation and thermal processing:
  - aromatics from lignocellulosic by-products
  - heterocycles extracted from cellulose or chitin
- RAS, Russia, Dr A. V. Ponomarev

Contents lists available at ScienceDirect

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Phase distribution of products of radiation and post-radiation distillation of biopolymers: Cellulose, lignin and chitin

A.V. Ponomarev*, E.M. Kholodkova, A.K. Metreveli, P.K. Metreveli, V.S. Erasov, A.V. Bludenko, V.N. Chulkov

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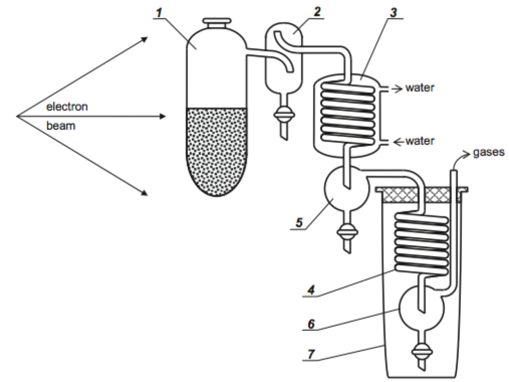
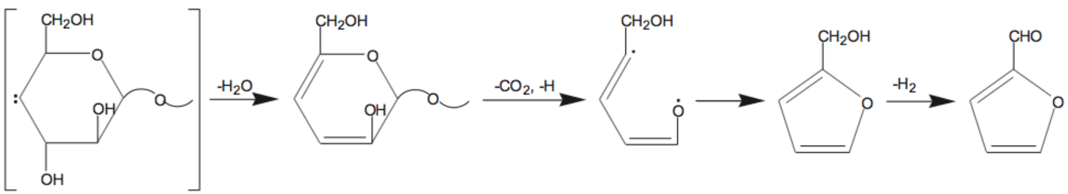
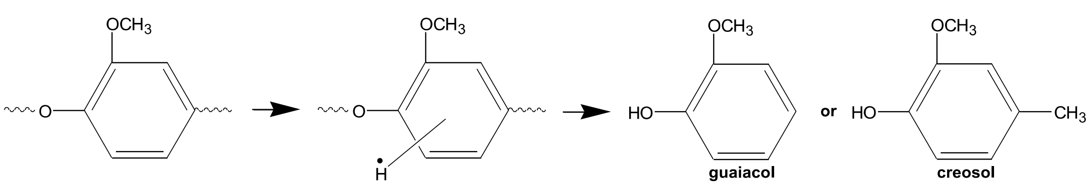
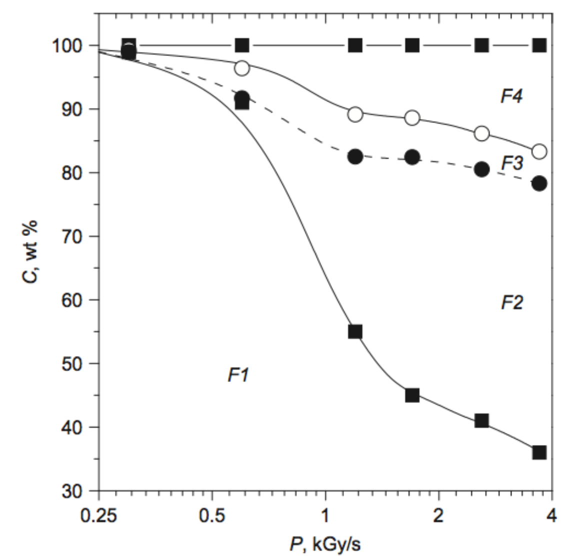
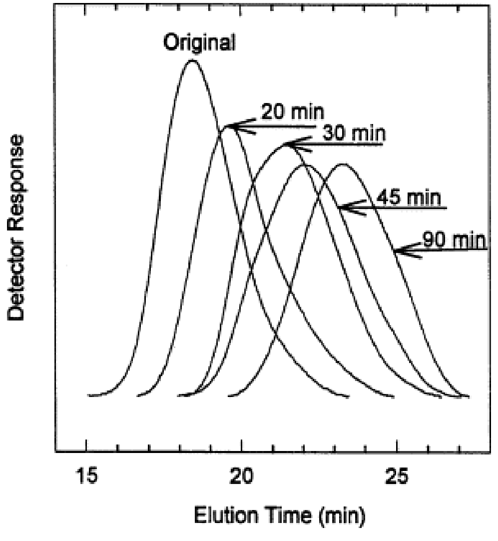








Depolymerization

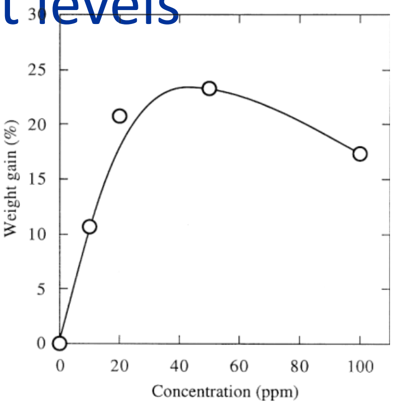


Plant-growth promoters

- Effets variés du chitosane
  - Rice, tea, tomato, lettuce …
  - Control
  - Study of mechanisms
  - Programmes IAEA - FAO
- Treatments conducted at different levels
  - Seed encasulation
  - Field spraying
- Other polysaccharides
  - Alginates
  - Carrageenan

- Paddy

- Peanuts



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Vietnam Atomic Energy Institute, Ho Chi Minh City
Malaysian Nuclear Agency, Bangi, 43000 Kajang.

Summary and perspectives

- Increasing knowledge
  - Monitoring of transformation at various dimension scales
  - Study of complex systems
  - Structure – properties relations (basic and applied aspects)
  - Influence of temperature
  - Modeling

- Technological improvements

- Need to valorize the environmental value of EB (low energy consumption of radiation, « greener » chemicals)

- Emerging domains of application
  - Composites, biomass, improved thermoplastics, lithography

Acknowledgements

ANR CP2D

LignoStarch Project

CRP F22046 IAEA

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Programme PlAneT