Mécanique des matériaux biosourcés
De l'extraction au recyclage, conséquences sur les propriétés effectives
MECAMAT
AMAC
Colloque National, du 20 au 24 janvier 2014, Aussois.

Synthesis of new biobased building blocks for Polymer Synthesis

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ICG Montpellier IAM
INSTITUT CARNOT CED2

Contexte: enjeux des polymères biosourcés

Limitations de ressources fossiles

- *Anticipation de pénurie / débit*
- *Pas de Naphta dans le gaz de schiste*
- *Prix / pénurie de ressources fossiles bon marché*

Règlementation

- *Règlementation accrue: substitution de composés dangereux*
- *Réduction d'impacts / ACV*
- *Objectifs chimie biosourcée*

Pression des marchés

- *Demande de produits plus "verts", écoconçus*
- *Concurrence*
- *Labels*

LA DOUBLE SUBSTITUTION

Biosourcés et moins dangereux

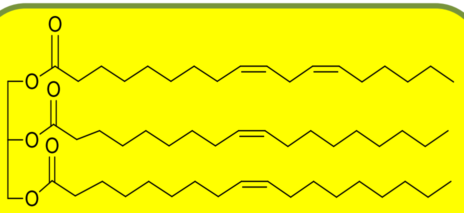
Positionnement Polymères Bisourcés

- **DOUBLE SUBSTITUTION : De nouveaux *building blocks* biosourcés et moins dangereux pour la synthèse de polymères**
- **APPROCHE PLATE-FORME : de la synthèse des molécules jusqu'aux matériaux**

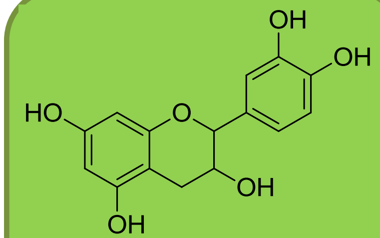
From MOLECULES…

…BUILDING BLOCKS…

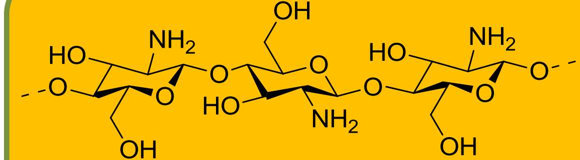
…TO MATERIALS



Vegetable oils



Natural phenols



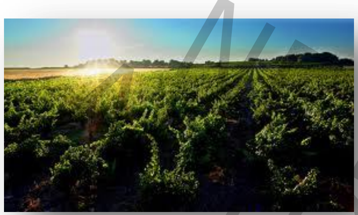
Polysaccharides

PUs, Epoxy, Phénoliques, Vinyl Esters …

ICG Montpellier IAM

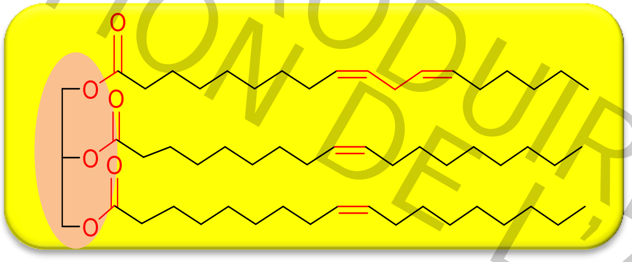
Approche Plate-Forme pour la Synthèse de Building Blocks

Synthèse de building blocks / approche plate-forme sur les huiles végétales

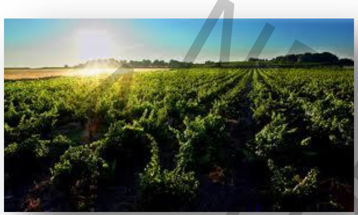

Grapeseed oil


Soybean oil


Rapeseed oil



Synthèse de building blocks / approche plate-forme sur les huiles végétales



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Soybean oil

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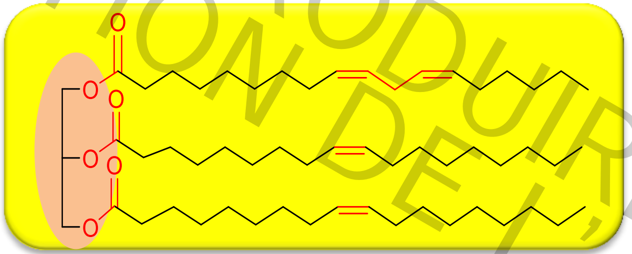
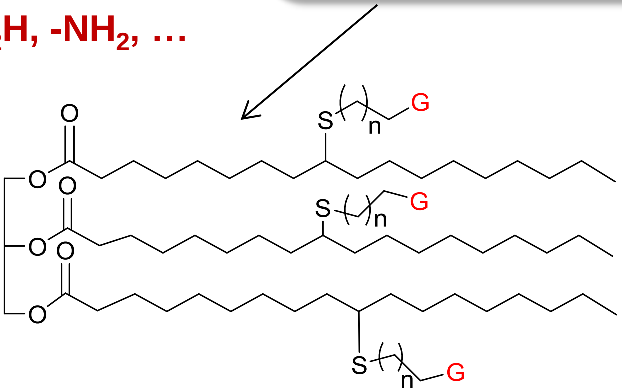


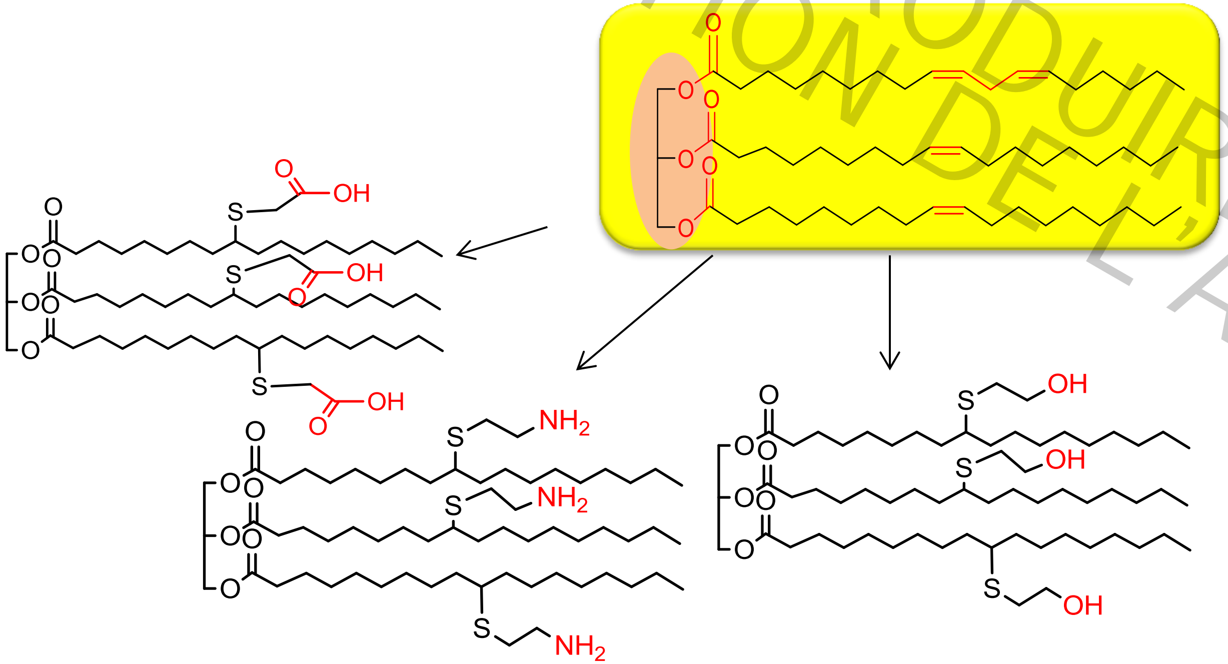
J. Pol. Sci. Part A: Pol. Chem., 2011, 49, 2434–2444,
Macromolecules, 2011, 44, 2489–2500
Brevets FR 2962131, 2010 - WO2012001315, 2012

G = -OH, -CO_2H, -NH_2, …



CROSSLINKED POLYMERS

Synthèse de building blocks / approche plate-forme sur les huiles végétales

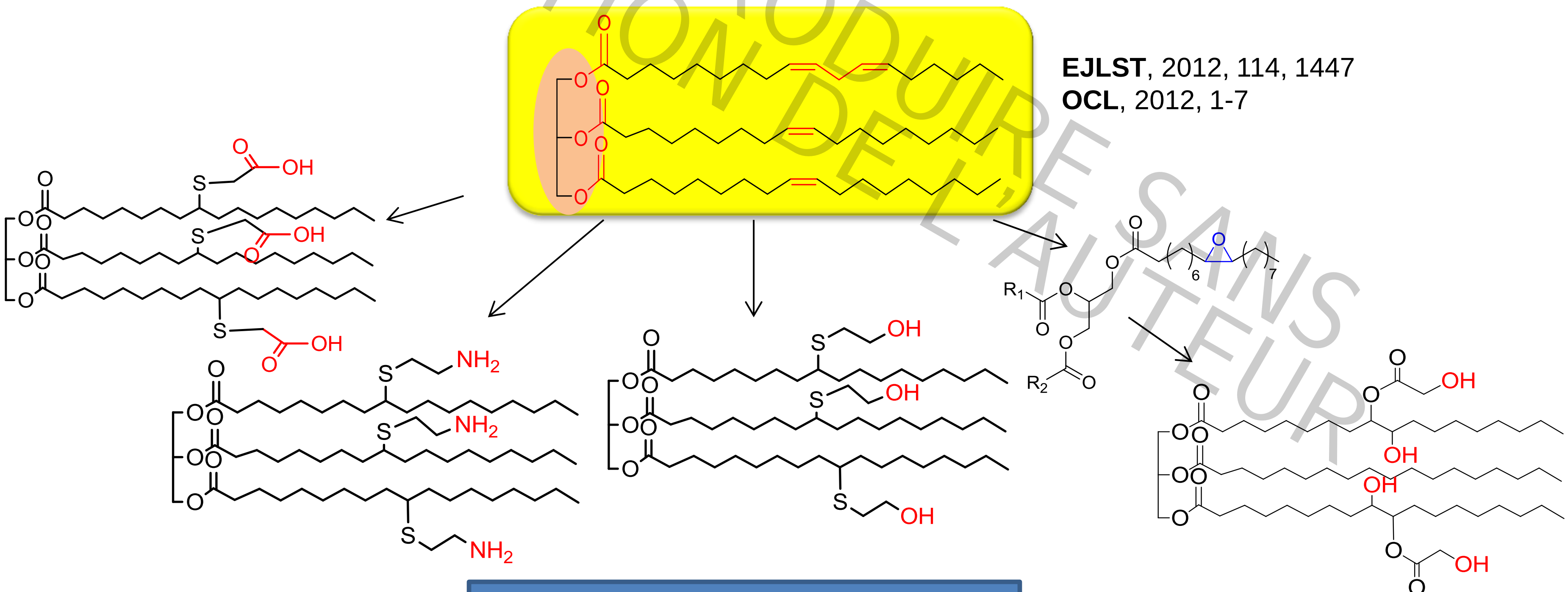


J. Pol. Sci. Part A: Pol. Chem., 2011, 49, 2434–2444,
Brevets FR 2962131, 2010 - WO2012001315, 2012

CROSSLINKED POLYMERS

Synthèse de building blocks / approche plate-forme sur les huiles végétales

EJLST, 2012, 114, 1447
OCL, 2012, 1-7



CROSSLINKED POLYMERS

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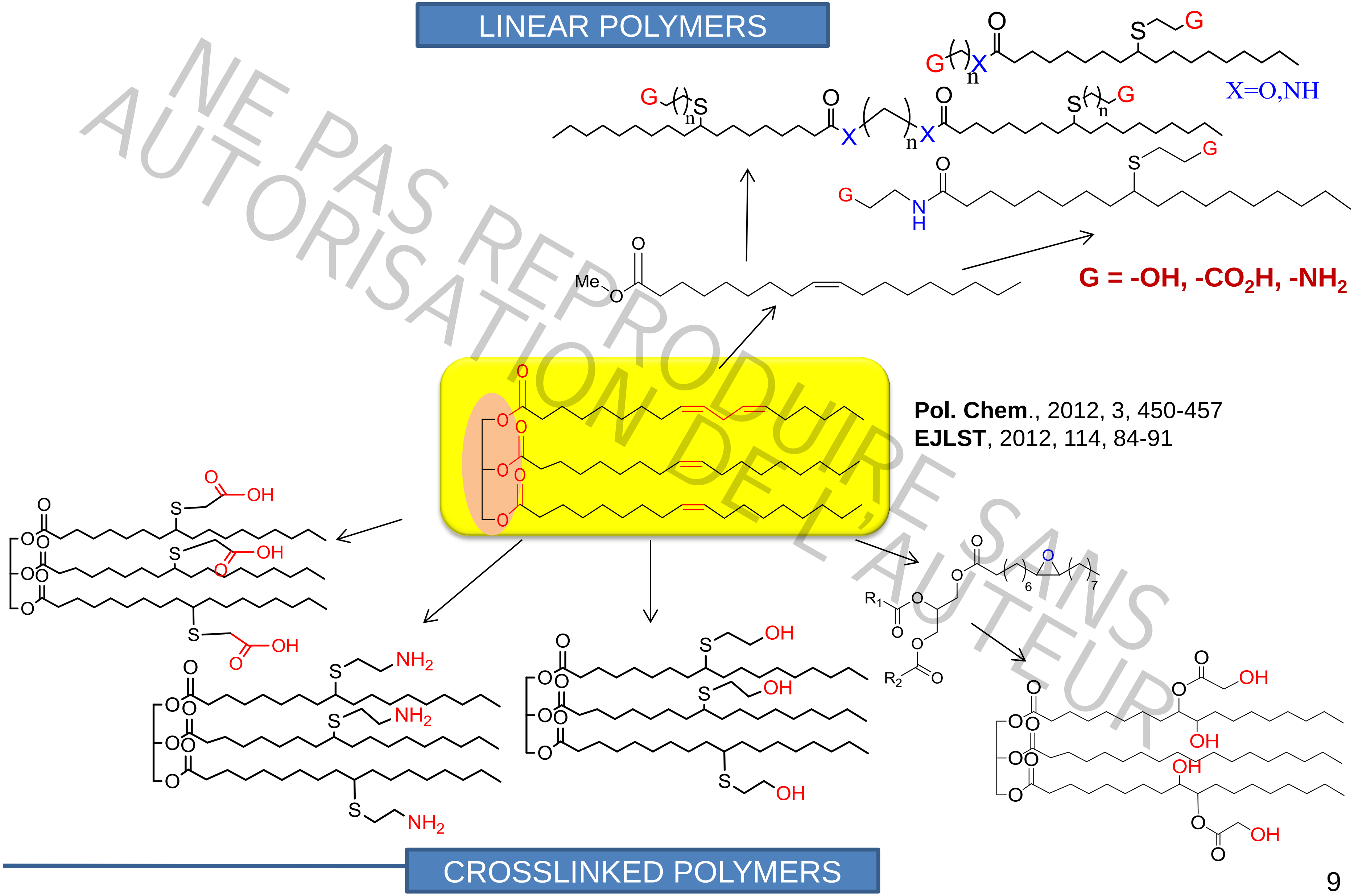
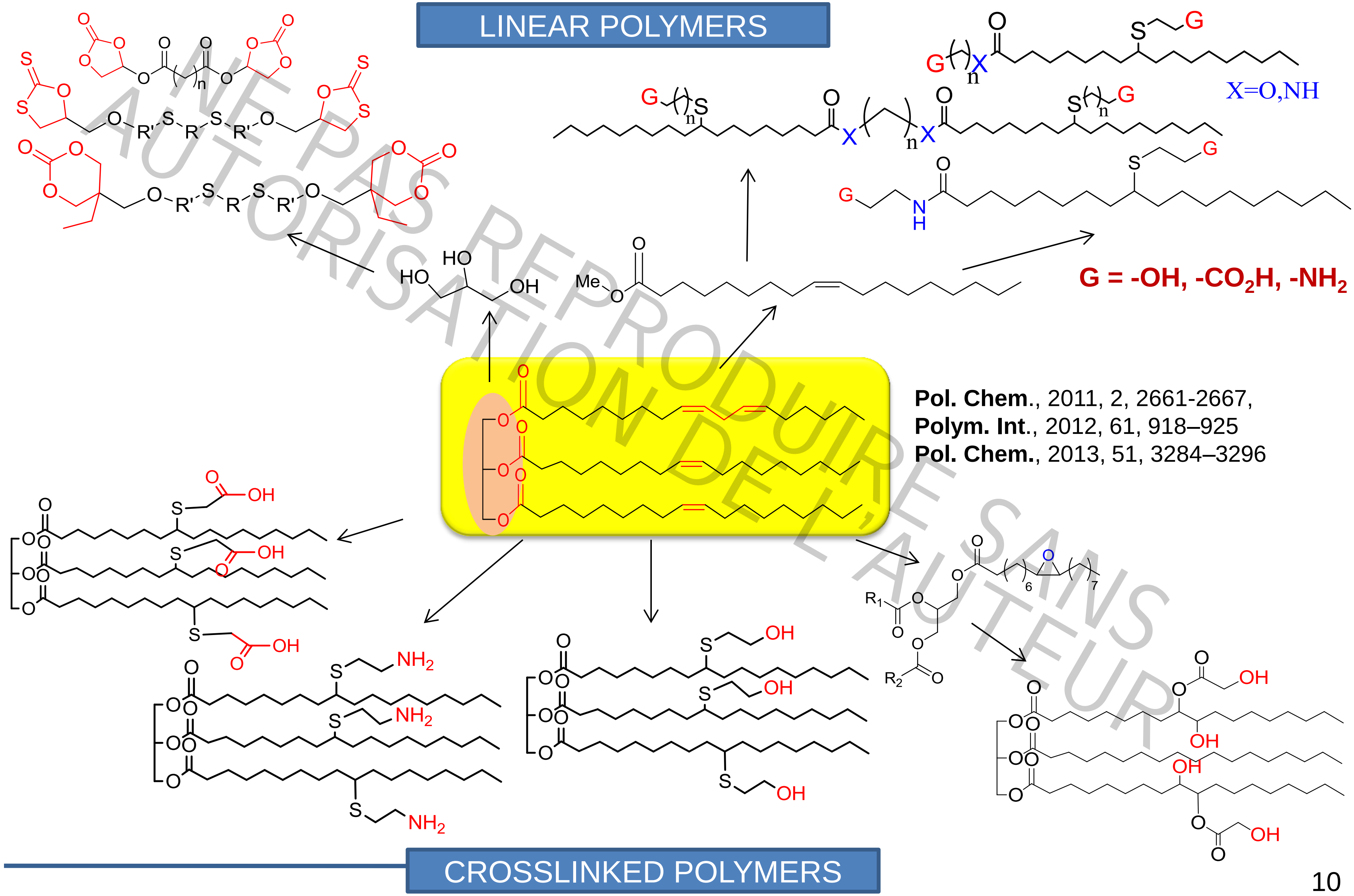
Synthèse de building blocks / approche plate-forme sur les huiles végétales



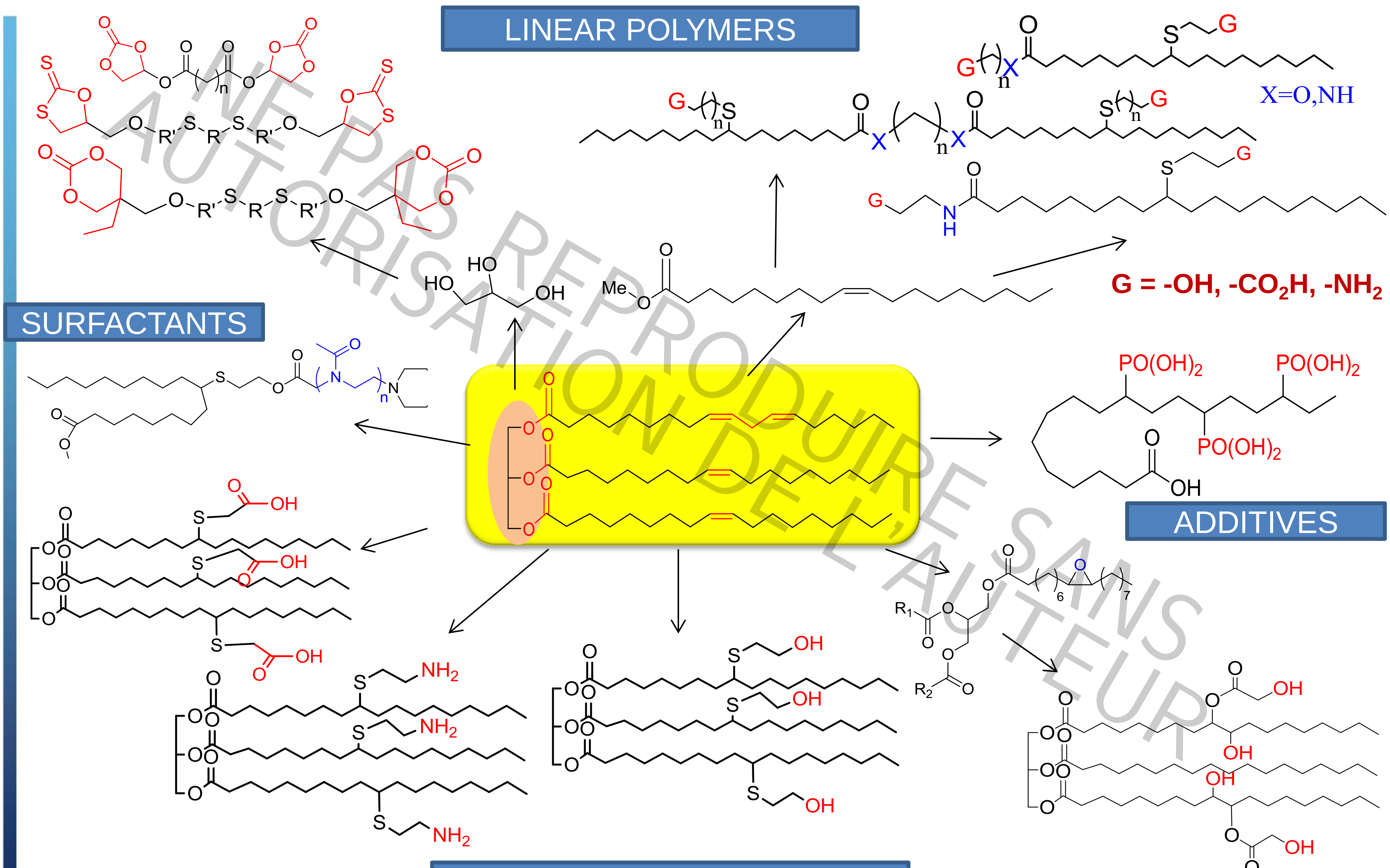
Pol. Chem., 2012, 3, 450-457
EJLST, 2012, 114, 84-91

Synthèse de building blocks / approche plate-forme sur les huiles végétales



Pol. Chem., 2011, 2, 2661-2667,
Polym. Int., 2012, 61, 918–925
Pol. Chem., 2013, 51, 3284–3296

Synthèse de building blocks / approche plate-forme sur les huiles végétales

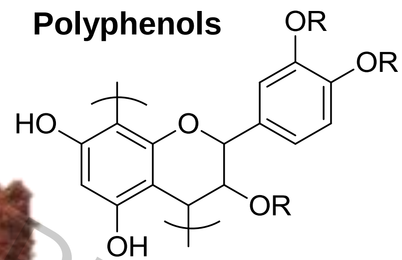


Synthèse de building blocks aromatiques / approche plate-forme sur les phénols naturels

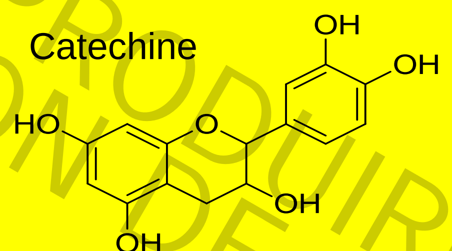
Tanins

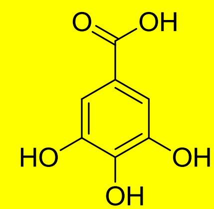
200kt/an

Polyphenols

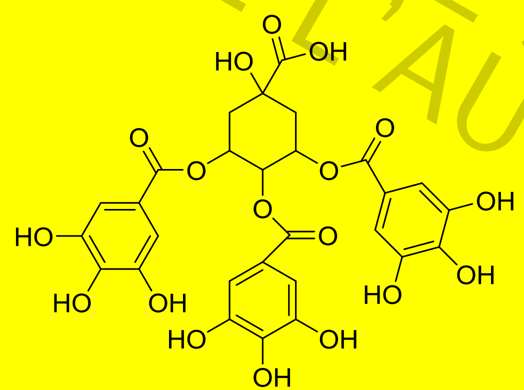


Catechine

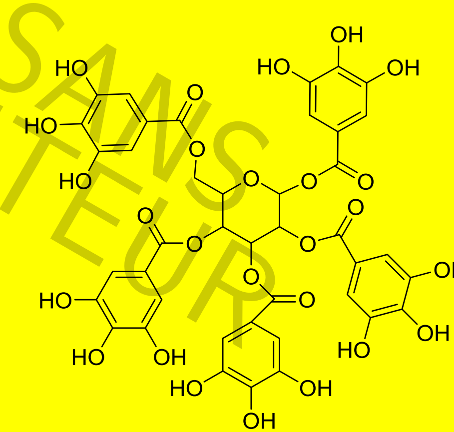




Acide Gallique



Tara tanins

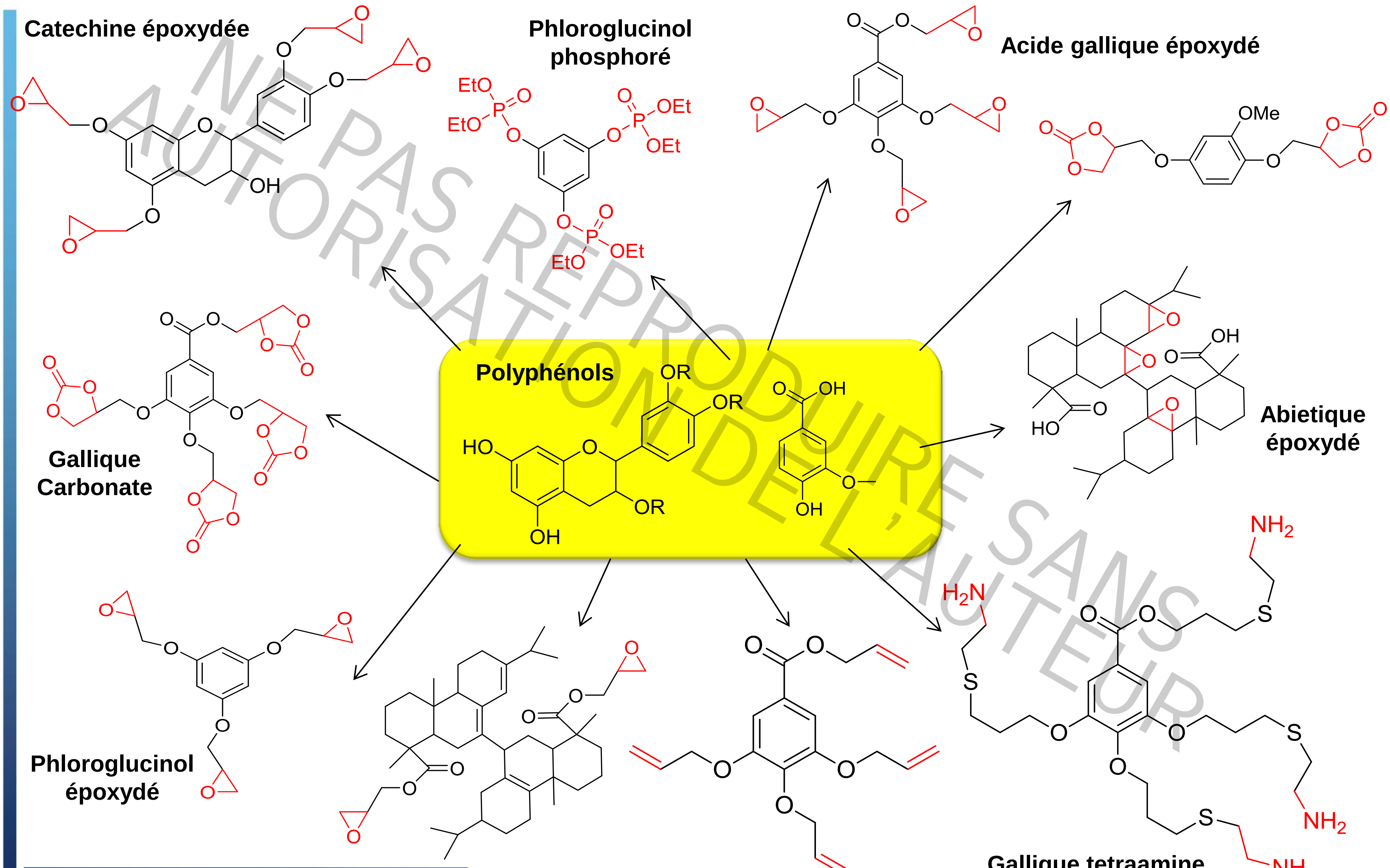


Tanins hydrolysables

Europ. Pol. J., 2013, 49, 1185–1195
Tetrahedron, 2013, 69, 1345-1353
Ind. Crops Prod., 2014, accepted
J. Pol. Sci. Part A: Pol. Chem., 2011, 49, 2261–2270

Chem. Rev. , 2014, accepted

Synthèse de building blocks aromatiques / approche plate-forme sur les phénols naturels



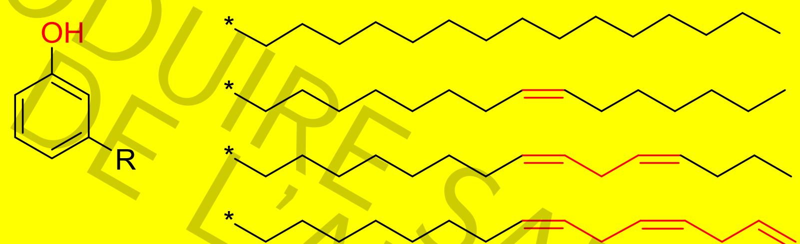
Green Chem., 2013, 15, 3091-3098

Platform molecule for new biobased building blocks: Example of cardanol

Cashew Nut

CNSL
900kt/an

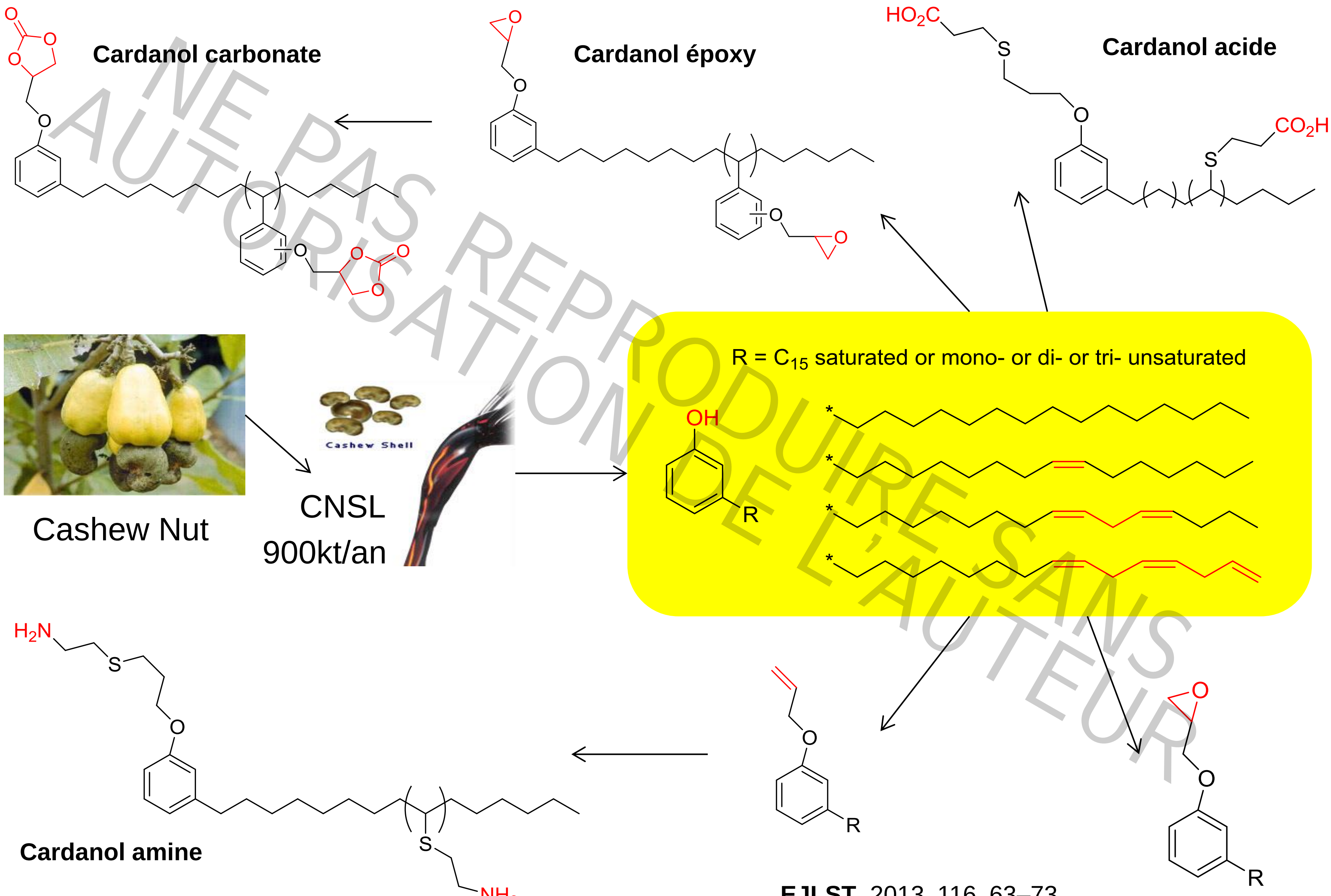
R = C_{15} saturated or mono- or di- or tri- unsaturated



Collaboration with P. P. Wadgaonkar et col.

EJLST, 2013, 116, 63–73
Pol. Chem., 2013, accepted

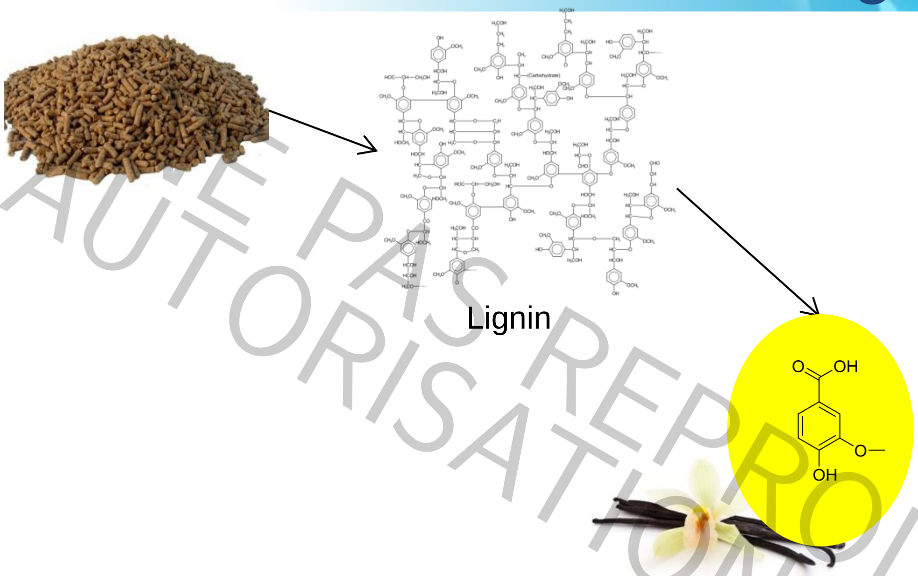
Platform molecule for new biobased building blocks: Example of cardanol



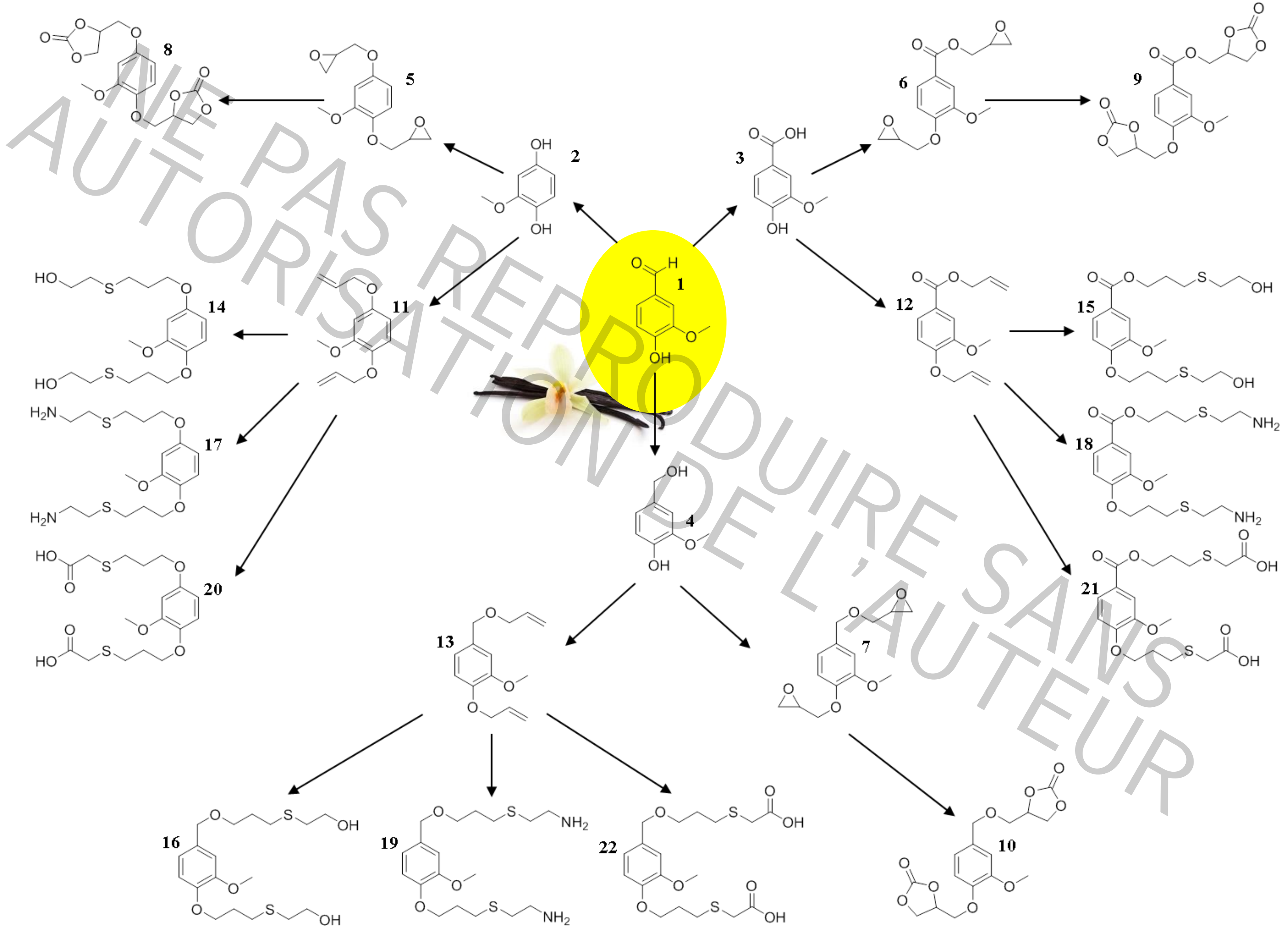
Collaboration with P. P. Wadgaonkar et col.

EJLST, 2013, 116, 63–73
Pol. Chem., 2013, accepted

Platform molecule for new biobased building blocks: Example of vanillin

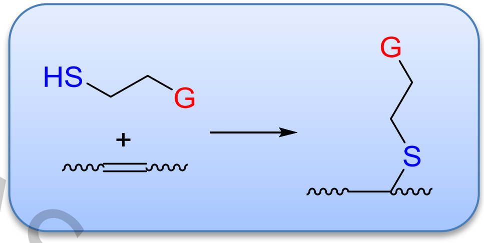


Platform molecule for new biobased building blocks: Example of vanillin



Fonctionnalisation des Huiles Végétales : Couplage Thiol-Ene (TEC)

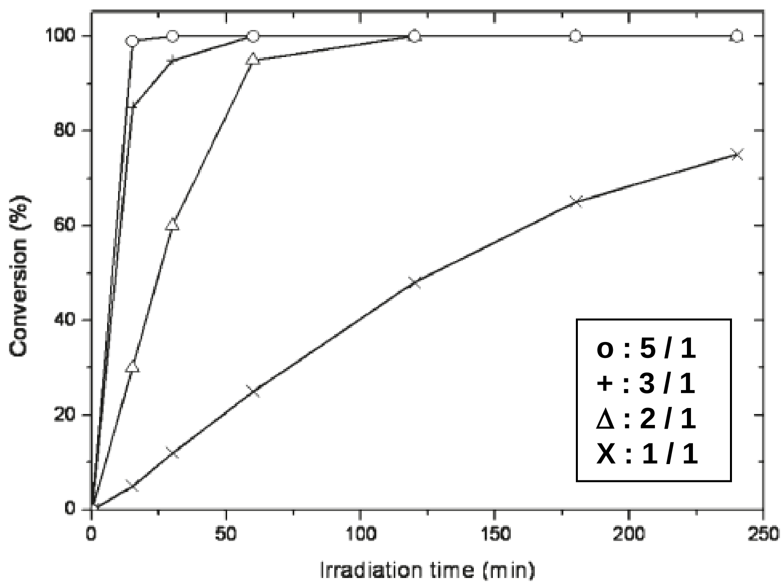
Couplage Thiol-ène



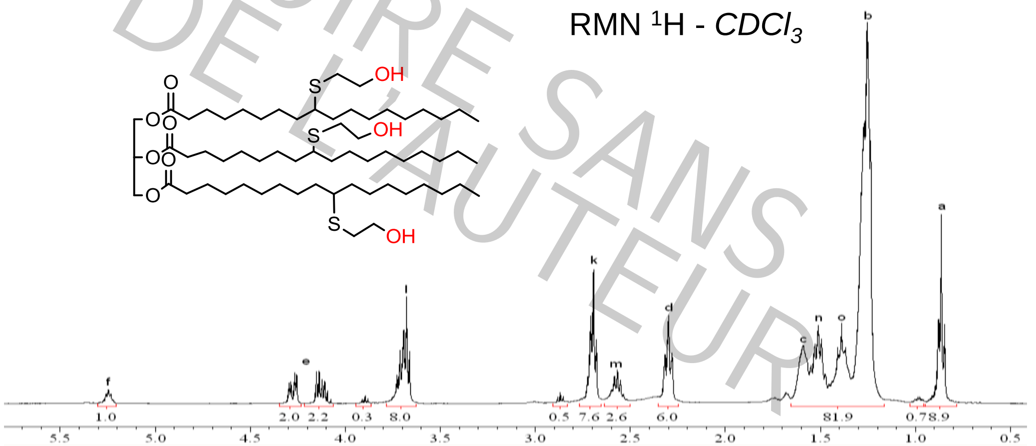
Photoinitiation / UV
with / without photoinitiator

Thermal initiation
AIBN

Etude réactivité, sélectivité TEC



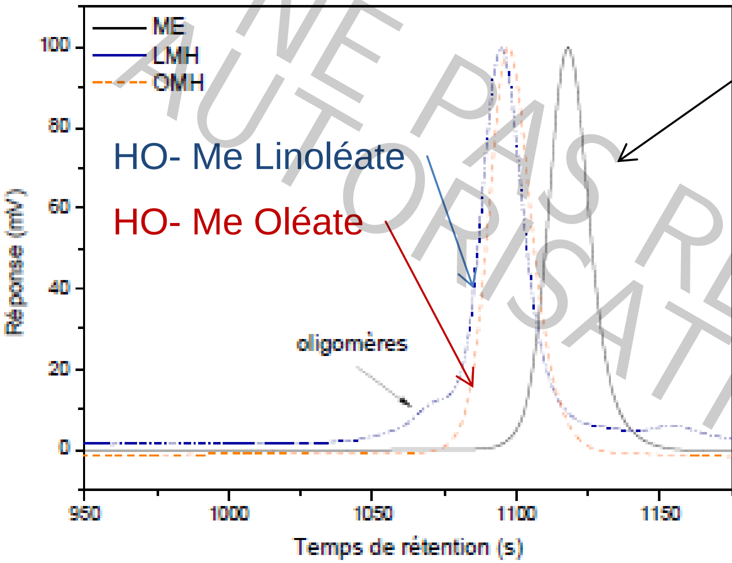
RMN ^{1}H - $CDCl_3$



Macromolecules, 2011, 44, 2489–2500

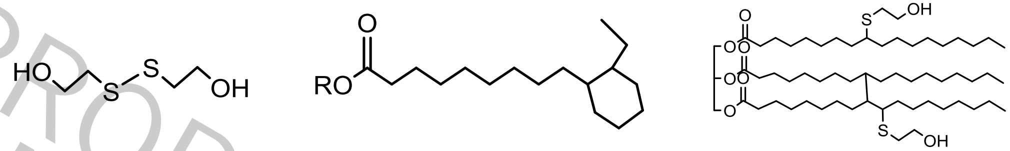
Fonctionnalisation des Huiles Végétales : Couplage Thiol-Ene

Etude réactions secondaires TEC

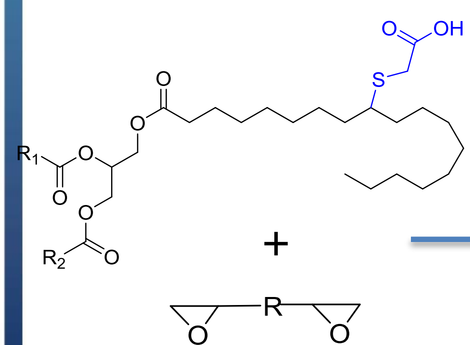


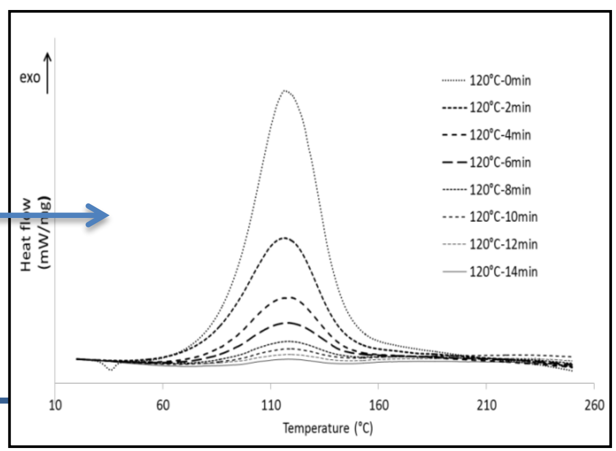
Me Oléate C=C
Me Linoléate 3 C=C

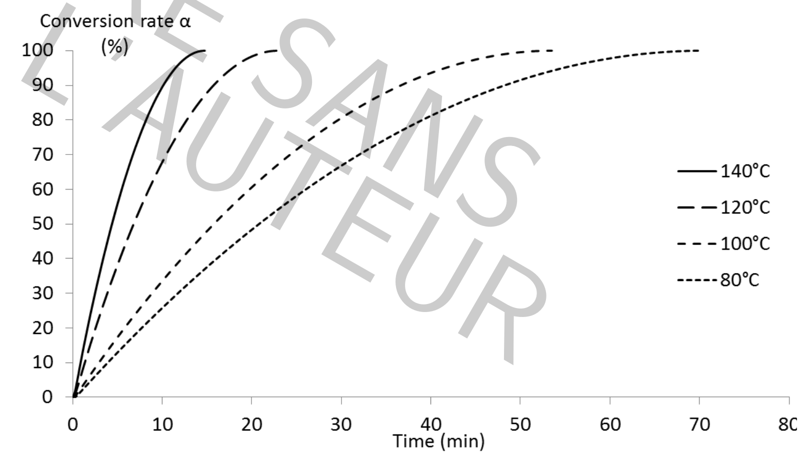
Sous-produits de réactions intra- et inter-moléculaires; disulfures; thioesters; non fonctionnalisés



Etude réactivité des building blocks



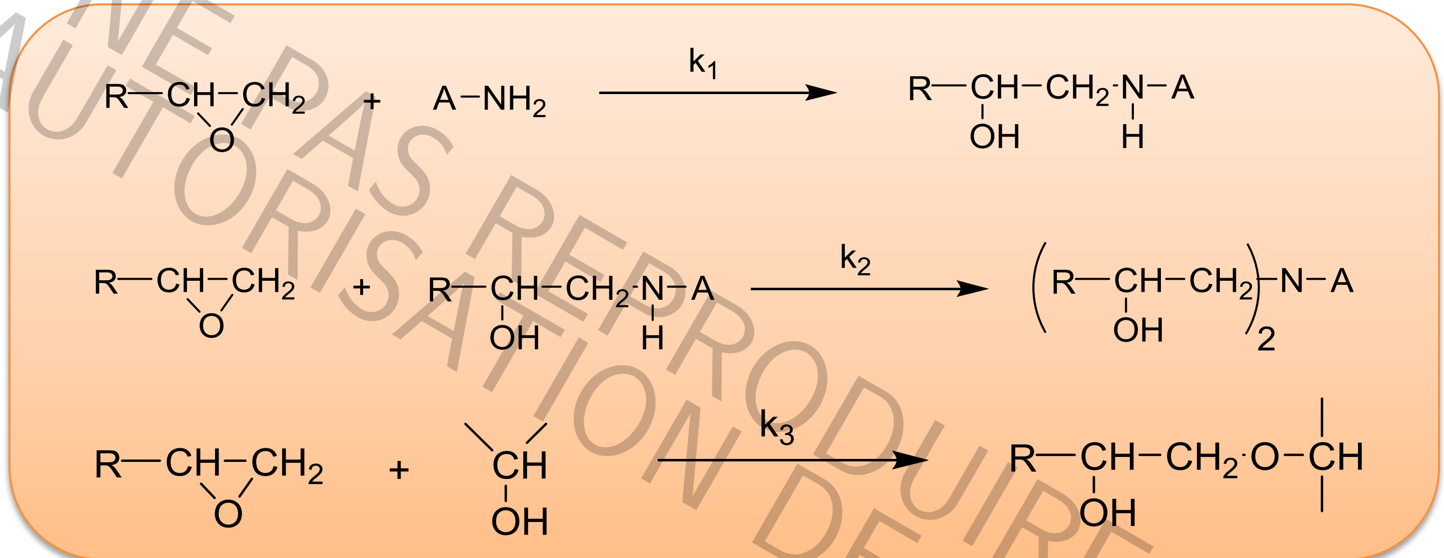




EJLST, 2013, 115, 698-708

Epoxy Resins

Epoxy resins : 2Mt/y - various applications



⇨ Issues

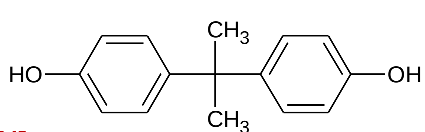
- **Fossil resources** reactants
- **Harmful** reactants
  - Epoxy and Amines
- **Lower reactivtiy** of acids

⇨ Targets

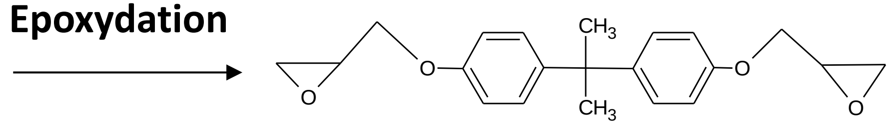
- Use of **vegetable oils**
- **Biobased reactants**
- **Reactive hardeners**

Bisphenol A (BPA)

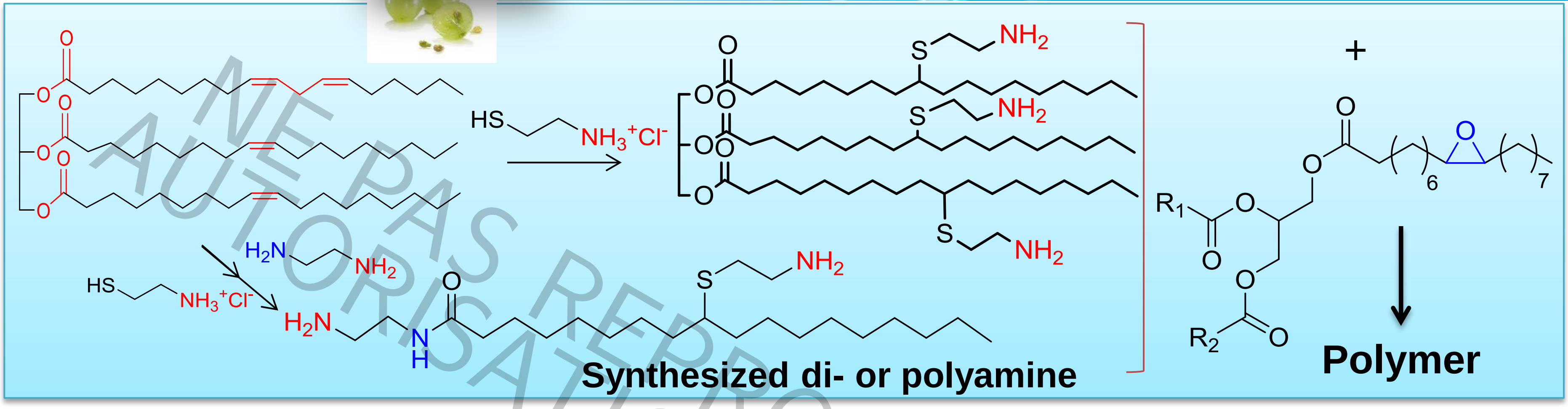
- CMR Repr. Cat. 2
- Perturbateur endocrinien



Epoxydation



Biobased amines for biobased resins

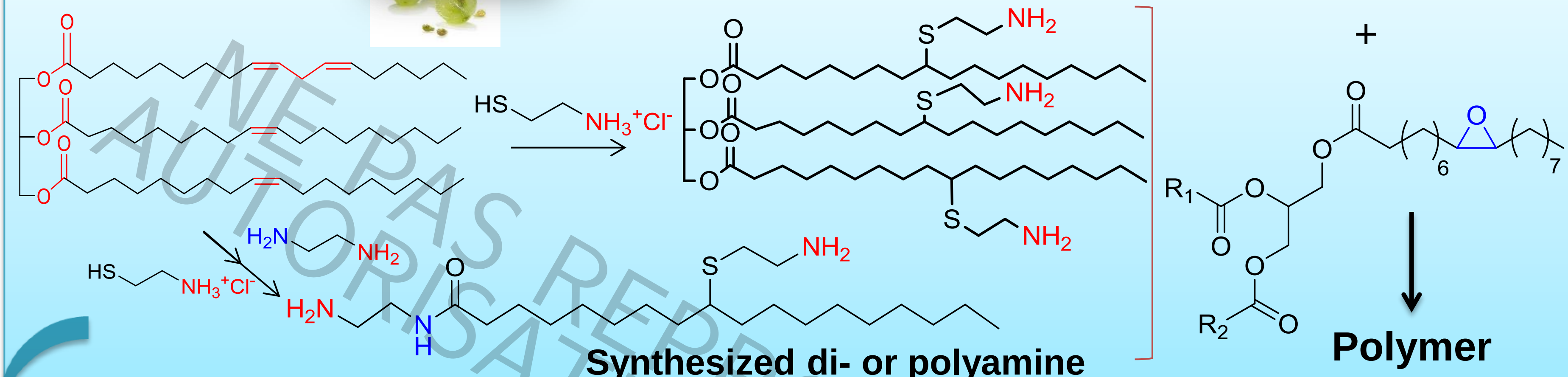


TEC : UV with DMPA 0.1 eq

DMPA : 2,2-dimethoxy-2-phenylacetophenone

M. Stemmelen et al., J Pol Sci Part A: Pol Chem, 2011, 49, 2434–2444

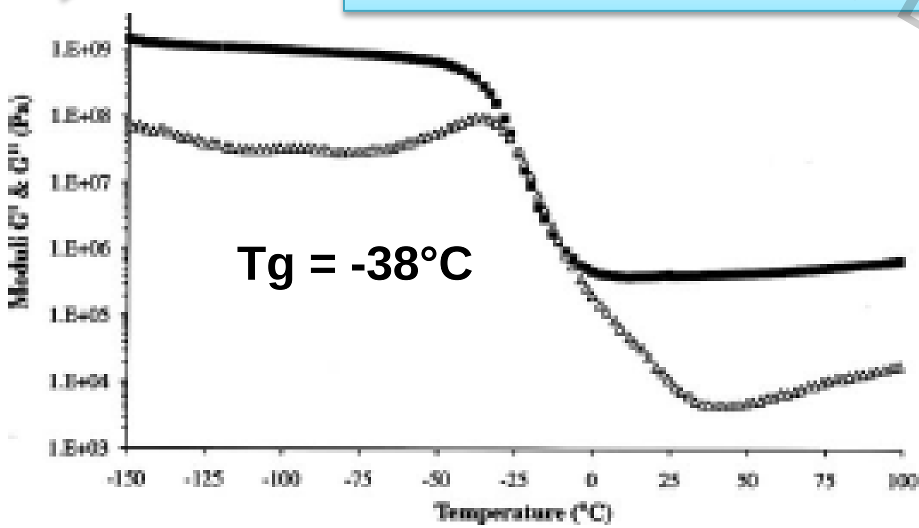
Biobased amines for biobased resins

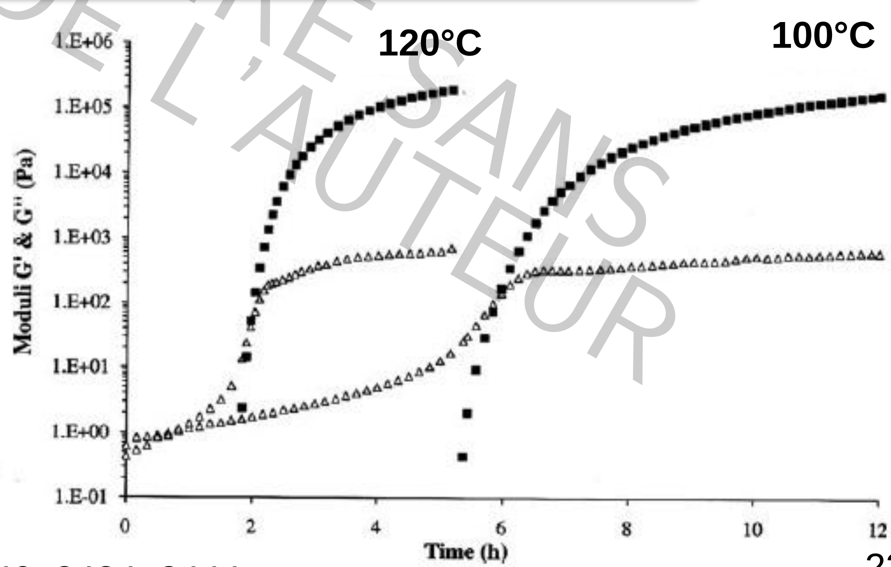


TEC : UV with DMPA 0.1 eq

DMPA : 2,2-dimethoxy-2-phenylacetophenone

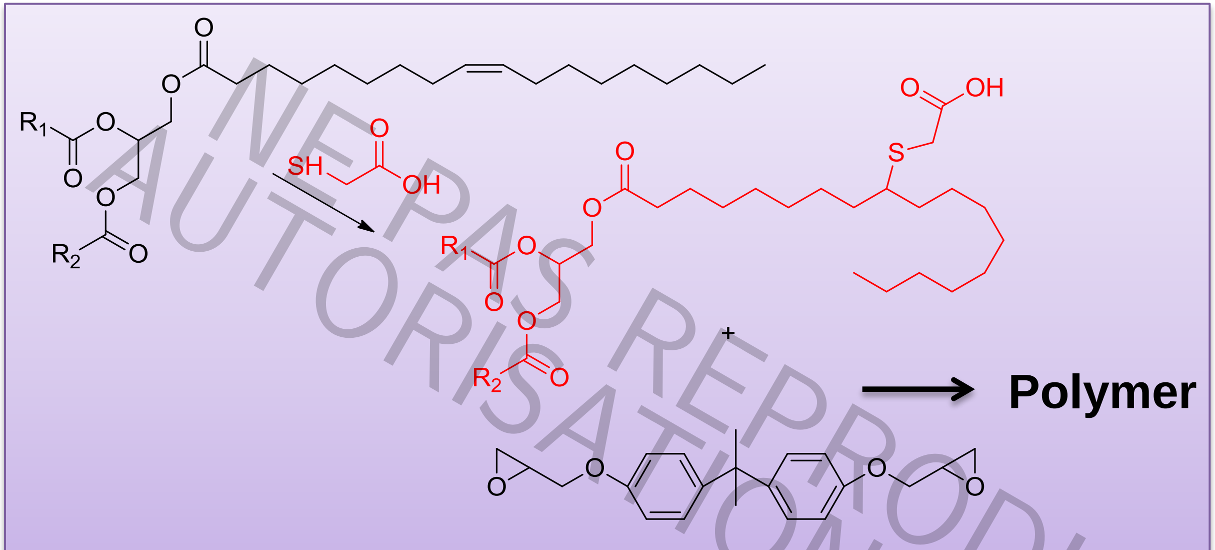
Thermomechanical analyses of mixture with G' (■) and G'' (Δ)





M. Stemmelen et al., J Pol Sci Part A: Pol Chem, 2011, 49, 2434–2444

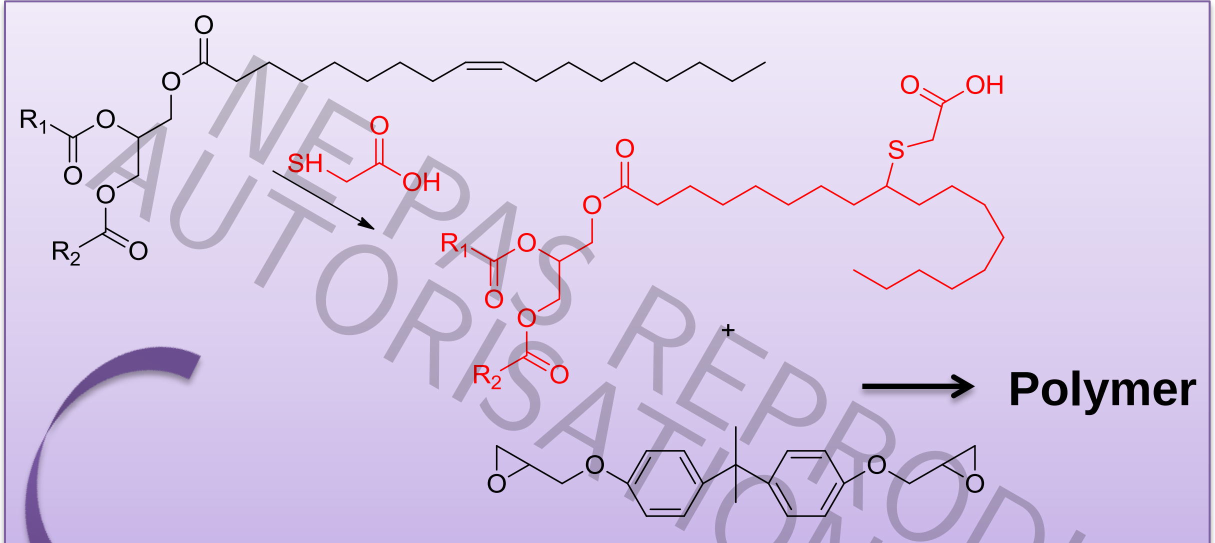
Biobased polyacids/TEC from vegetable oils



Soybean Oil

F. Jaillet et al., EJLST, 2013, 115, 698-708

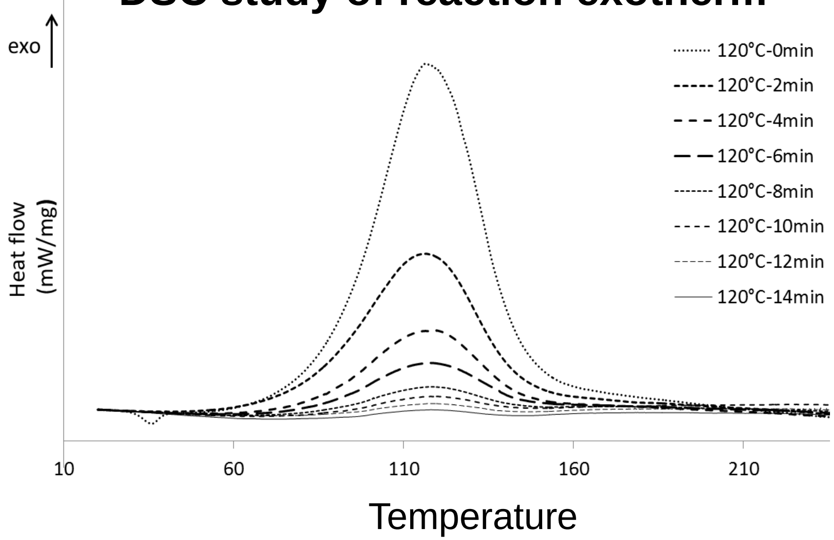
Biobased polyacids/TEC from vegetable oils



Soybean Oil

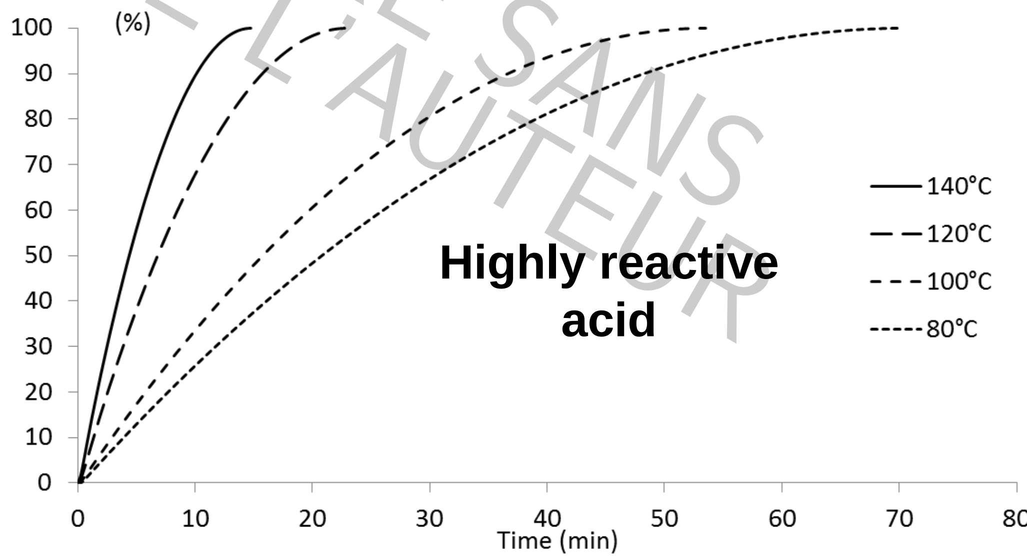
Tg (°C)	Td (°C) under N_2/air	
-12	348	340

DSC study of reaction exotherm



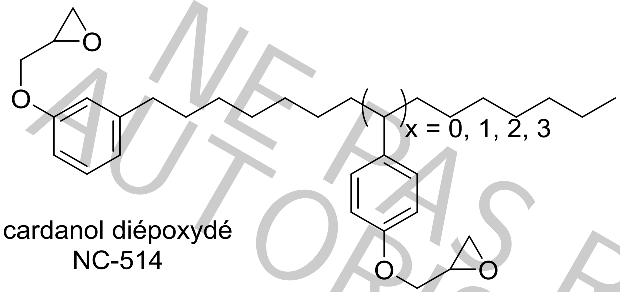
Determination of crosslinking conditions

Conversion



F. Jaillet et al., EJLST, 2013, 115, 698-708

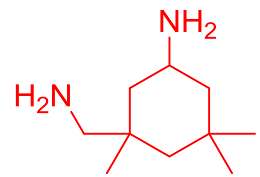
From cardanol to epoxy resins and vinyl esters



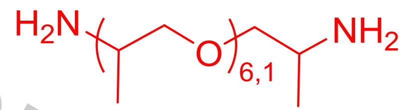
cardanol diépoxydé
NC-514

Epoxidized Cardanol prepolymer
(from Cardolite) – fonct° = 1.3

+

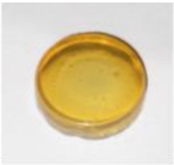


IsoPhorone DiAmine (IPDA)



Jeffamine D400

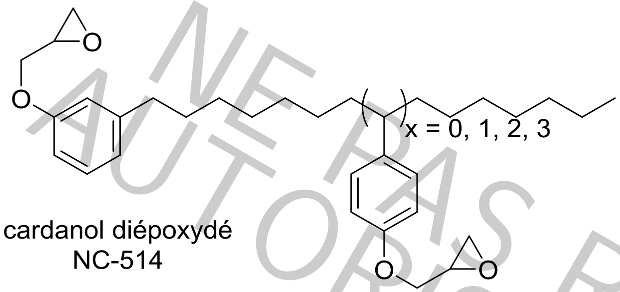
120°C → **Epoxy resin**



Epoxided Cardanol	Td (°C)	Tα (°C)	E' (MPa)	
			20°C	Tα+60°C
Card-IPDA	366	59	1218	3,2
DGEBA-IPDA	378	158	1480	2,6

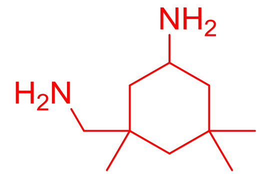
F. Jaillet et al., EJLST, 2013, accepted

From cardanol to epoxy resins and vinyl esters

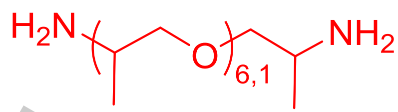


Epoxidized Cardanol prepolymer
(from Cardolite) – fonct° = 1.3

+



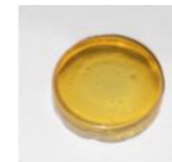
IsoPhorone DiAmine (IPDA)



Jeffamine D400

120°C →

Epoxy resin



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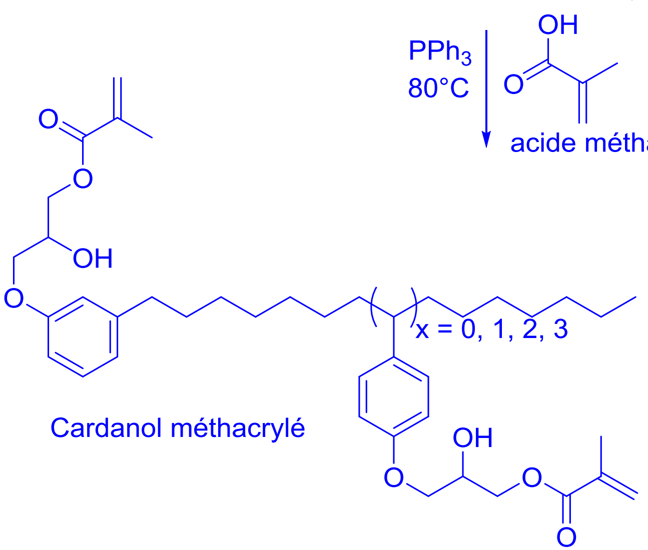
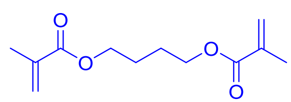
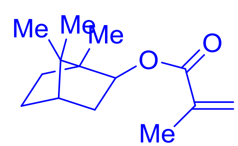


Cardanol méthacrylé

+



BDDMA



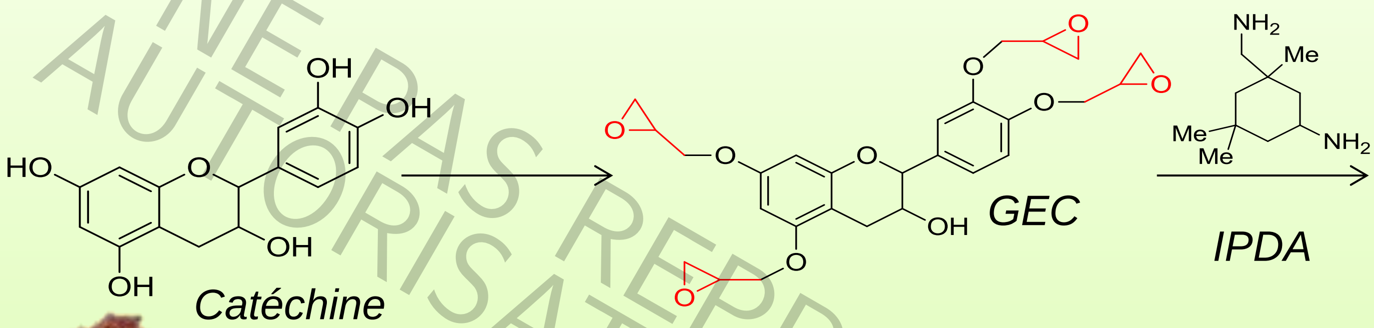
IsoBOrnylMethAcrylate

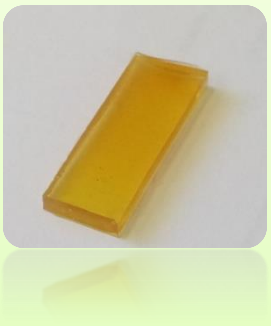
→ **Vinyl ester**

F. Jaillet et al., EJLST, 2013, accepted

Epoxidation of natural phenol : catechin

- **Substitution of Bisphenol A in aromatic epoxy resins**

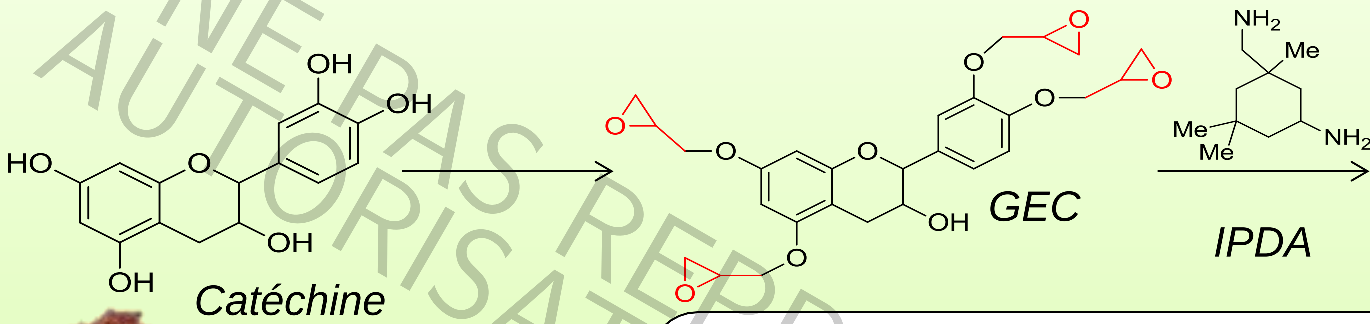


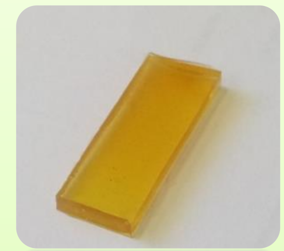


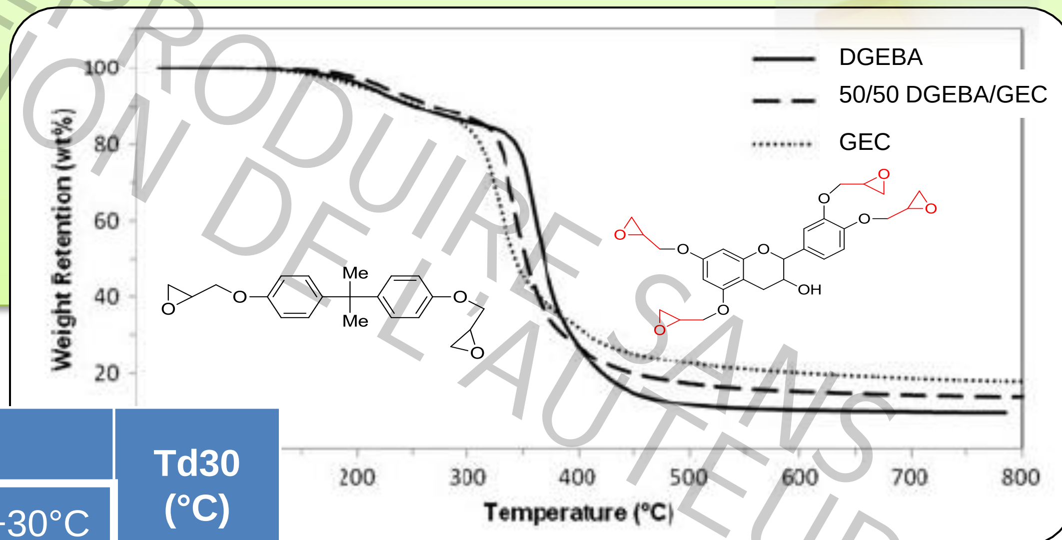
H. Nouailhas et al., J. Pol. Sci. Part A: Polym. Chem., 2011, 49, 2261–2270
Patent FR 0905594, WO 2010136725

Epoxidation of natural phenol : catechin

- **Substitution of Bisphenol A in aromatic epoxy resins**







System	Tα (°C)	E' (MPa)		Td30 (°C)
		30°C	Tg+30°C	
GEC-IPD	179	1.50 10^3	36.4	334
DGEBA-IPD	140	1.29 10^3	13.6	353

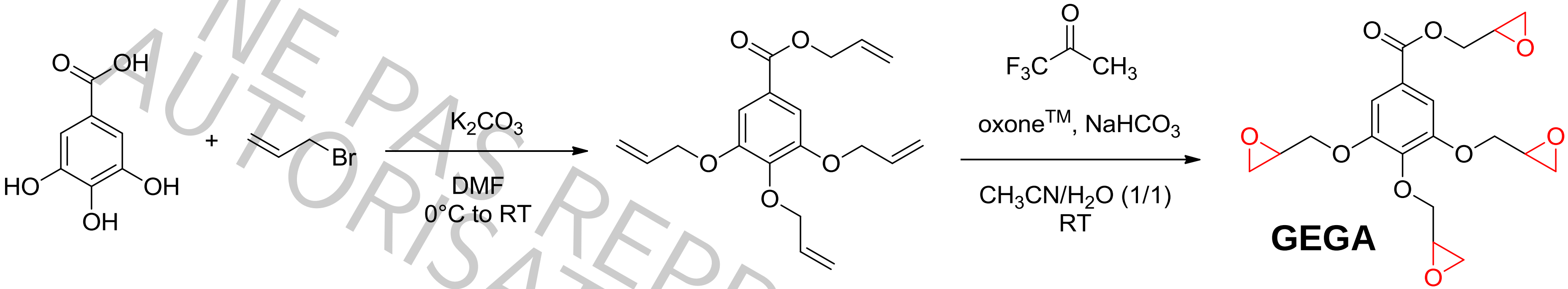
H. Nouailhas et al., J. Pol. Sci. Part A: Polym. Chem., 2011, 49, 2261–2270

Patent FR 0905594, WO 2010136725

Epoxidation of natural phenol : gallic acid

Dioxirane synthétisé *in situ* avec
trifluoroacetone et potassium peroxysulfate

- Epoxidation of Gallic acid

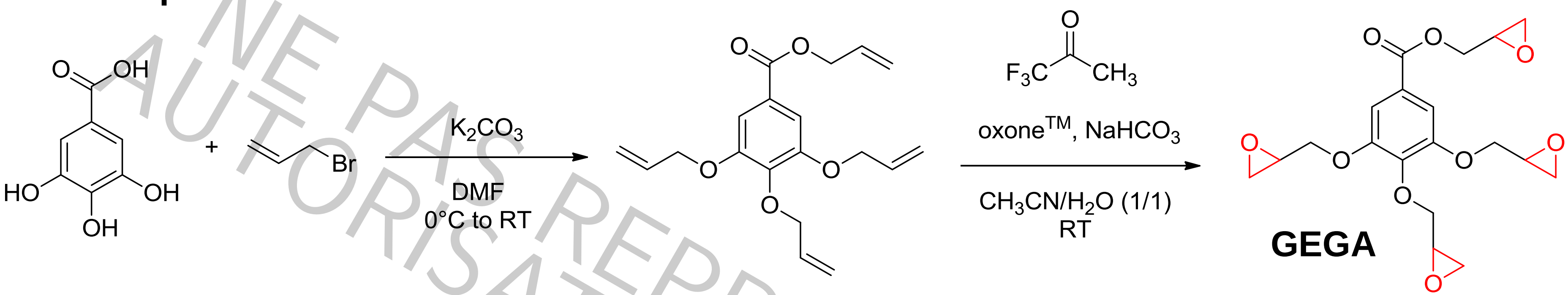


C. Aouf et al., Europ Polym J., 2013, 49, 1185–1195

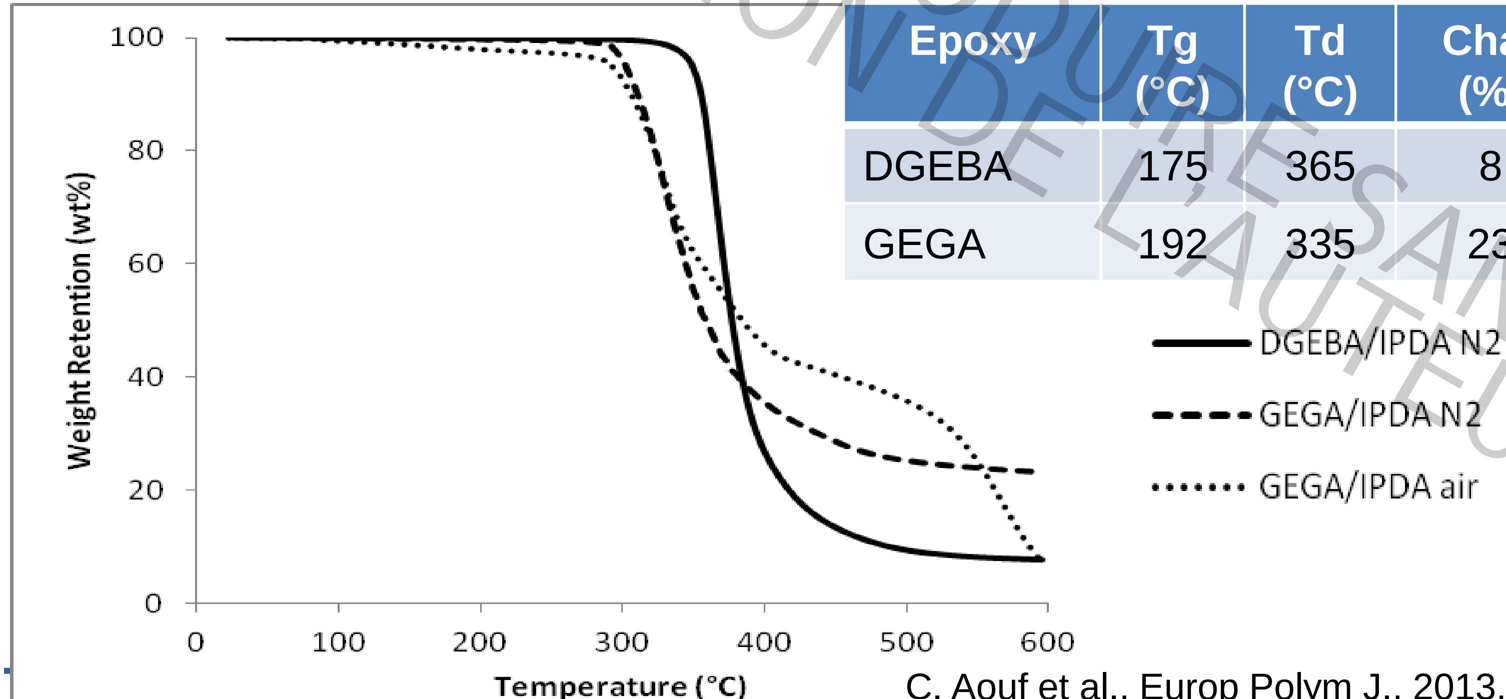
Epoxidation of natural phenol : gallic acid

Dioxirane synthétisé *in situ* avec
trifluoroacetone et potassium peroxysulfate

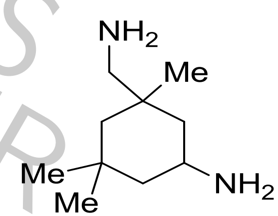
- Epoxidation of Gallic acid



- Comparison of epoxy resins of DGEBA and epoxided gallic acid with iPDA



Epoxy	Tg (°C)	Td (°C)	Char (%)	Solubles (%)
DGEBA	175	365	8	1
GEGA	192	335	23	1

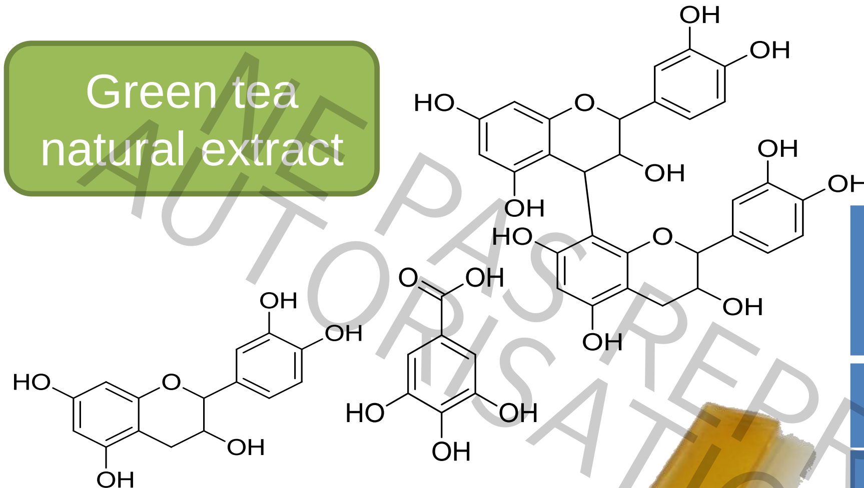


iPDA

C. Aouf et al., Europ Polym J., 2013, 49, 1185–1195

Synthesis of epoxy resins from tannins extracts

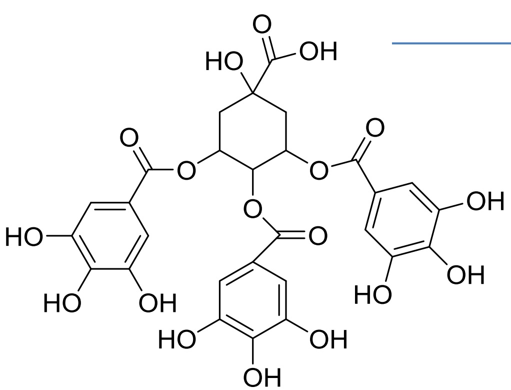
Green tea natural extract



Epoxydation $\xrightarrow{\text{iPDA}}$ **Résines époxy**

System	Tα (°C)	E' (MPa)		Td30 (°C)
		30°C	Tg+30°C	
Tea-IPD	142	2.34 10^3	59.3	299
DGEBA-IPD	140	1.29 10^3	13.6	353

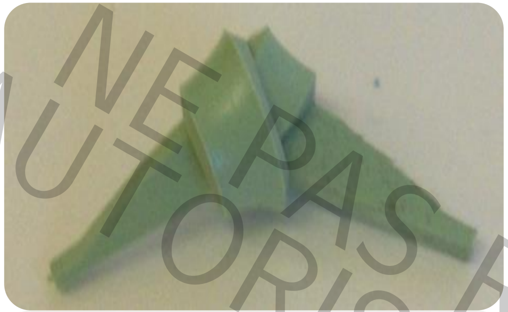
Tara natural extract



Epoxydation $\xrightarrow{\text{iPDA}}$ **Résines époxy**

System	Tα (°C)	E' (MPa)		Td30 (°C)
		30°C	Tg+30°C	
Tara-IPD	139	5.28 10^3	116.0	294
DGEBA-IPD	140	1.29 10^3	13.6	353

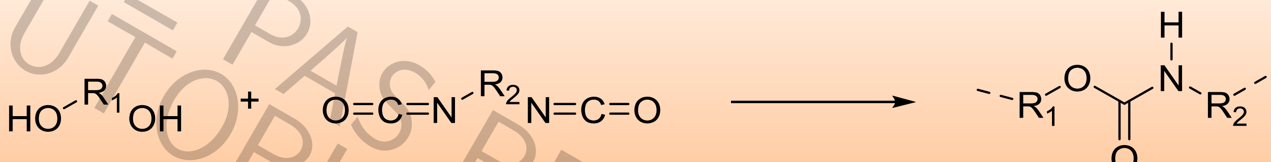
C. Aouf et al., Ind. Crops and Products, accepted



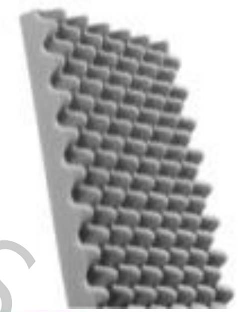
Polyurethanes

Context: Polyurethanes

Polyurethanes: 6th polymer in the world - 14Mt/y various applications

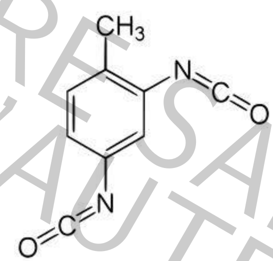


diols | diisocyanates | **Polyurethanes**



⇒ Issues

- **Fossil resources** reactants
- **Harmful** reactants
- Isocyanates - TDI and MDI : **CMR**
- Regulations
  - REACH: **MDI** in annex XVII

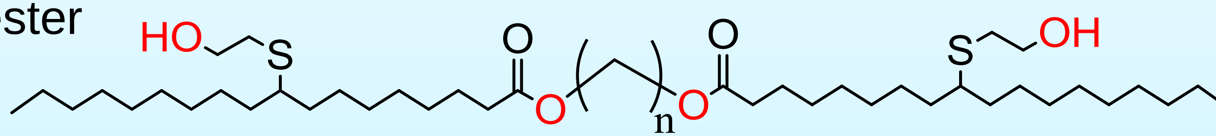


⇒ Targets

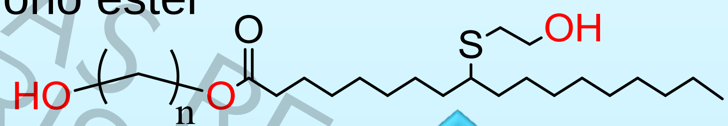
- Use of **vegetable oils** # 20Mt used in chemistry
- Synthesize **biobased polyols** (70% w/w PU)
- **PU without isocyanates: Non Isocyanate PU**

Part 1: New biobased polyols from vegetable oils by TEC

Dimer ester



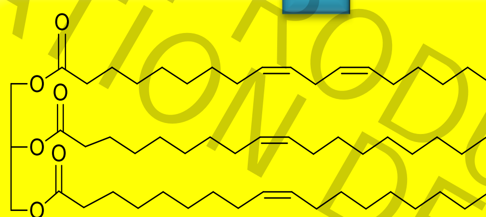
Mono ester



n= 2, 4, 6

Photoinitiation without photoinitiator

6h - UV, thiol/ene 3/1



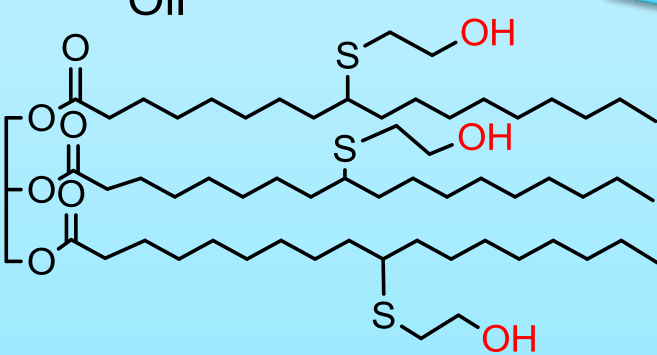
Rapeseed oil

Thermal

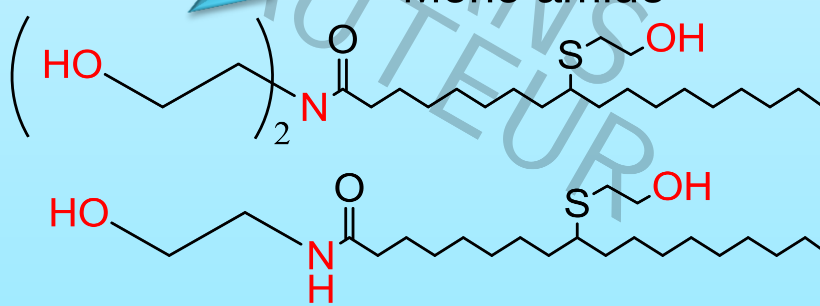
AIBN

80°C, 8h, thiol/ene 3/1

Oil



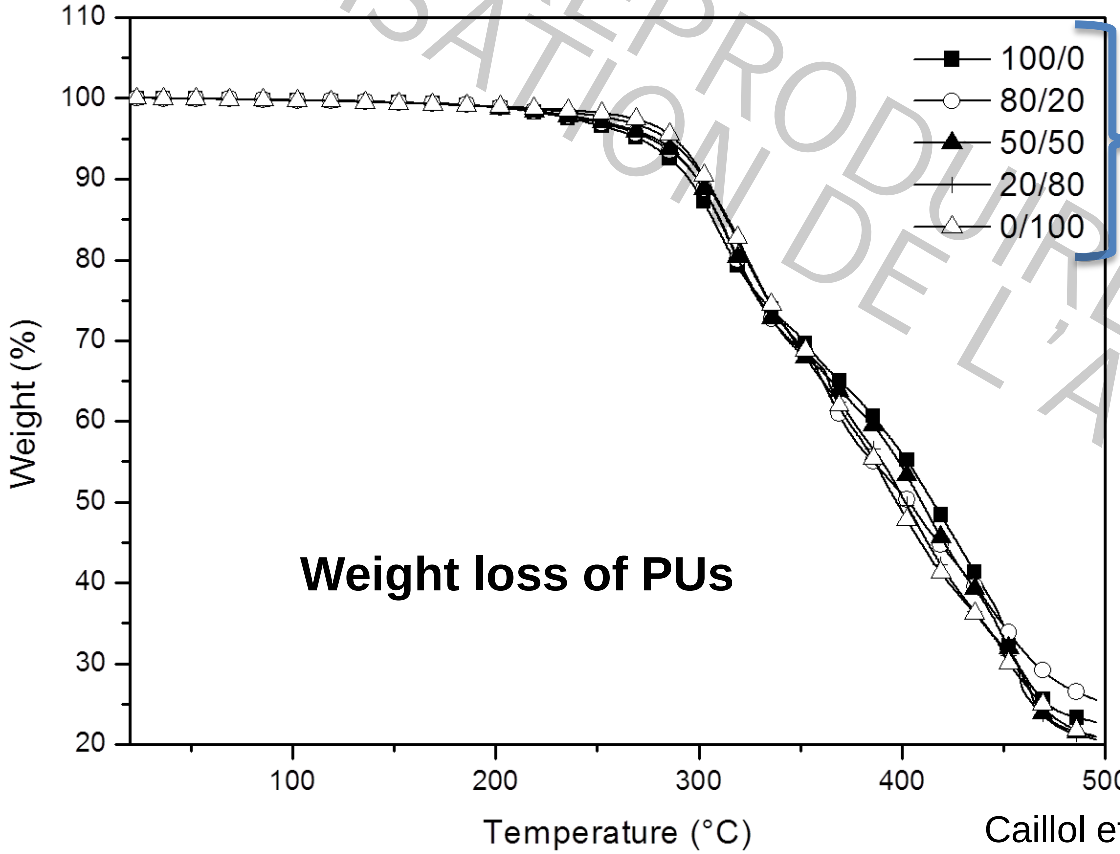
Mono amide



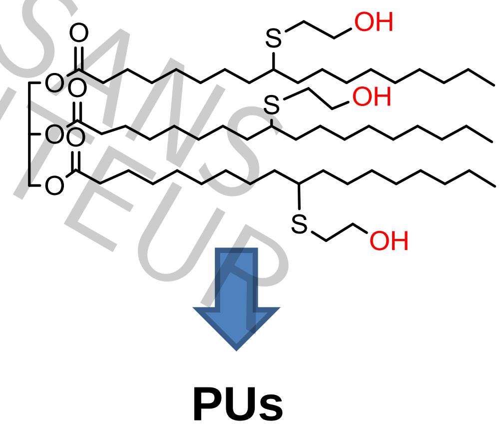
M. Desroches et al. Macromolecules, 2011, 44 (8), pp 2489–2500
Patent CNRS, FR 1002738, 2010

Thermal stability of PUs/MDI

Polyol	Viscosity η_{polyol} (Pa.s)	Eq.wt. (g/eq)	I_{OH} (mg KOH/g)	% OH (%)
Desmophen 1150	0.999	362	165	4.7
Polyol TEC/vegetable Oil	0.999	382	223	4.4

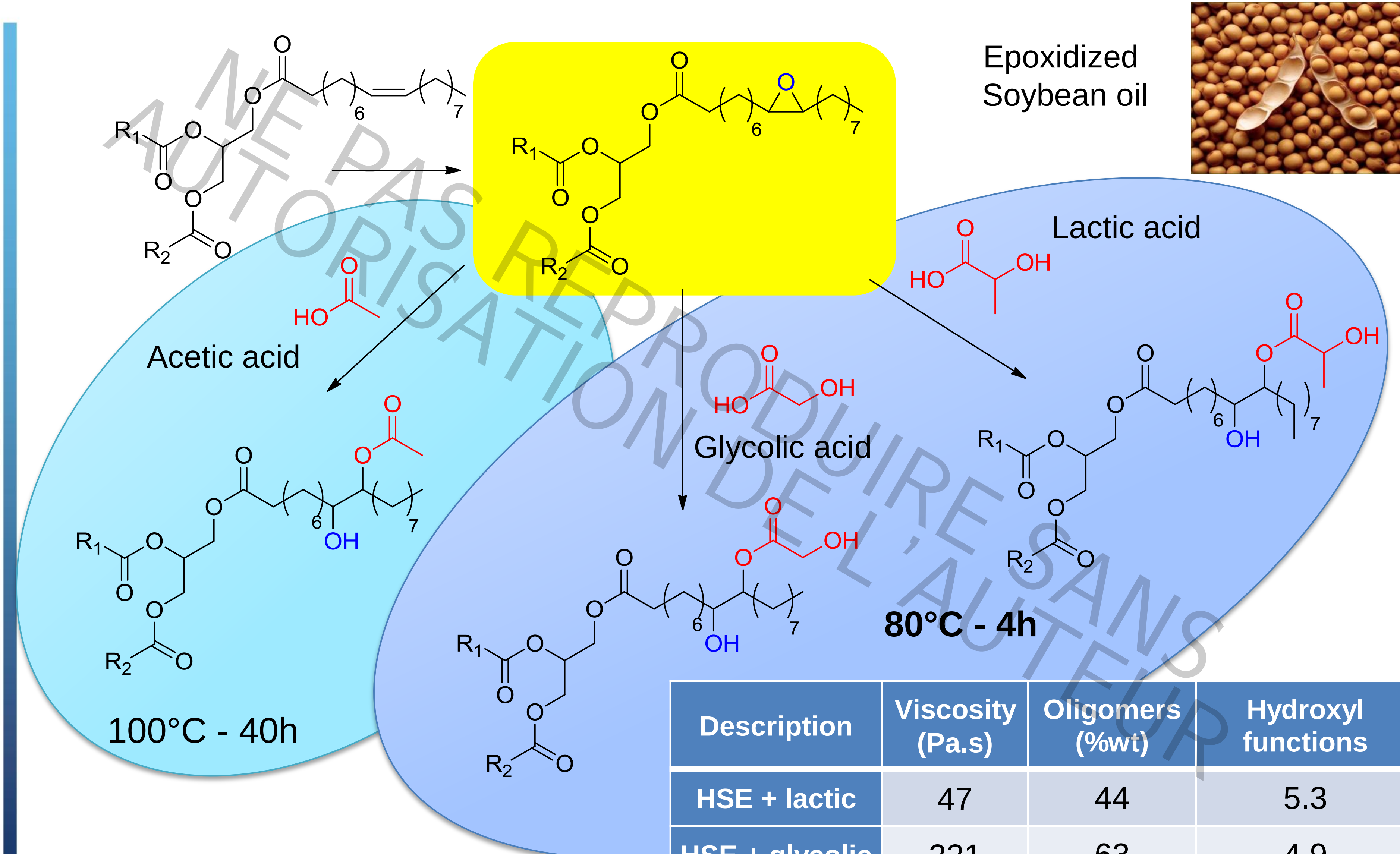


Similar thermal properties of PU / MDI Polyol TEC / Desmophen (PPG)



Caillol et al., Green Materials, 2013, 1, 16-26

Polyols Part 2: New biobased polyols from epoxidized vegetable oils



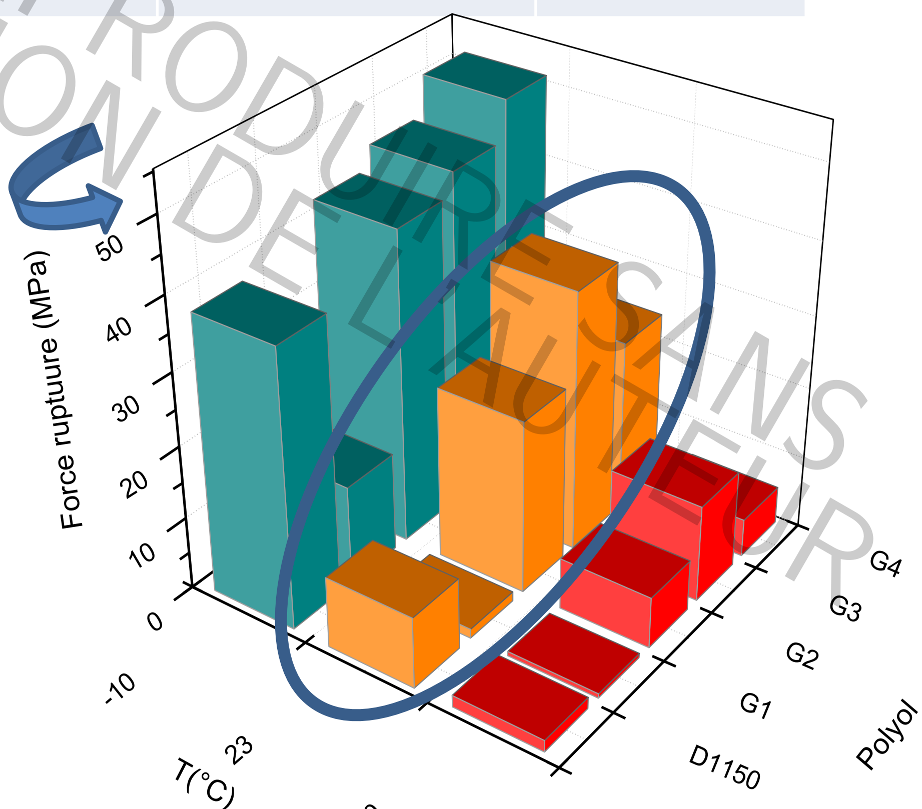
Description	Viscosity (Pa.s)	Oligomers (%wt)	Hydroxyl functions
HSE + lactic	47	44	5.3
HSE + glycolic	221	63	4.9
HSE + acetic	55	57	4.3

M. Desroches et al., EJLST, 2012, 114, 1447–1459

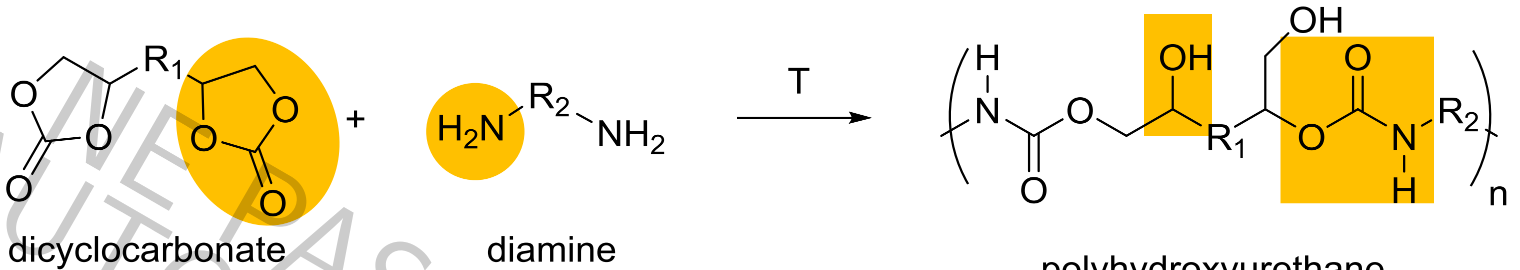
Biobased polyols for higher properties

PU @ T=23°C / MDI	Tensile strenght at break (MPa)	Young Modulus N/mm2	Shore Hardness
Desmophen 1150	*10*	*64*	*A76*
Polyol-lactate G2	24	954	D56
Polyol-glycolate **G3**	**36**	**1284**	**D70**
Polyol-acetate **G4**	**24**	**977**	**D65**

Improved mechanical properties for biobased PUs



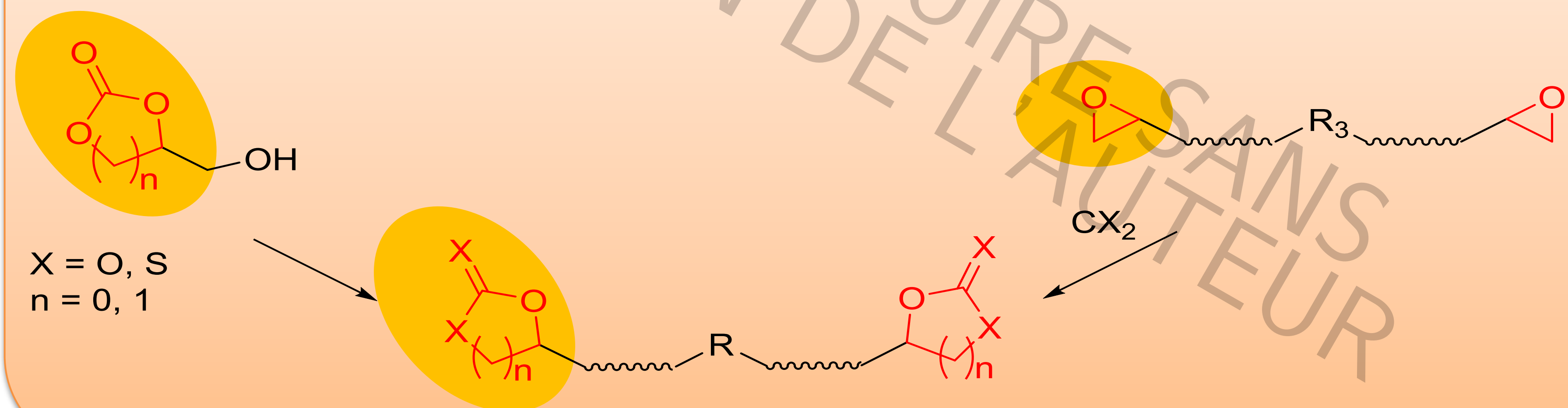
Part 3: Non Isocyanate Polyurethanes (NIPUs)



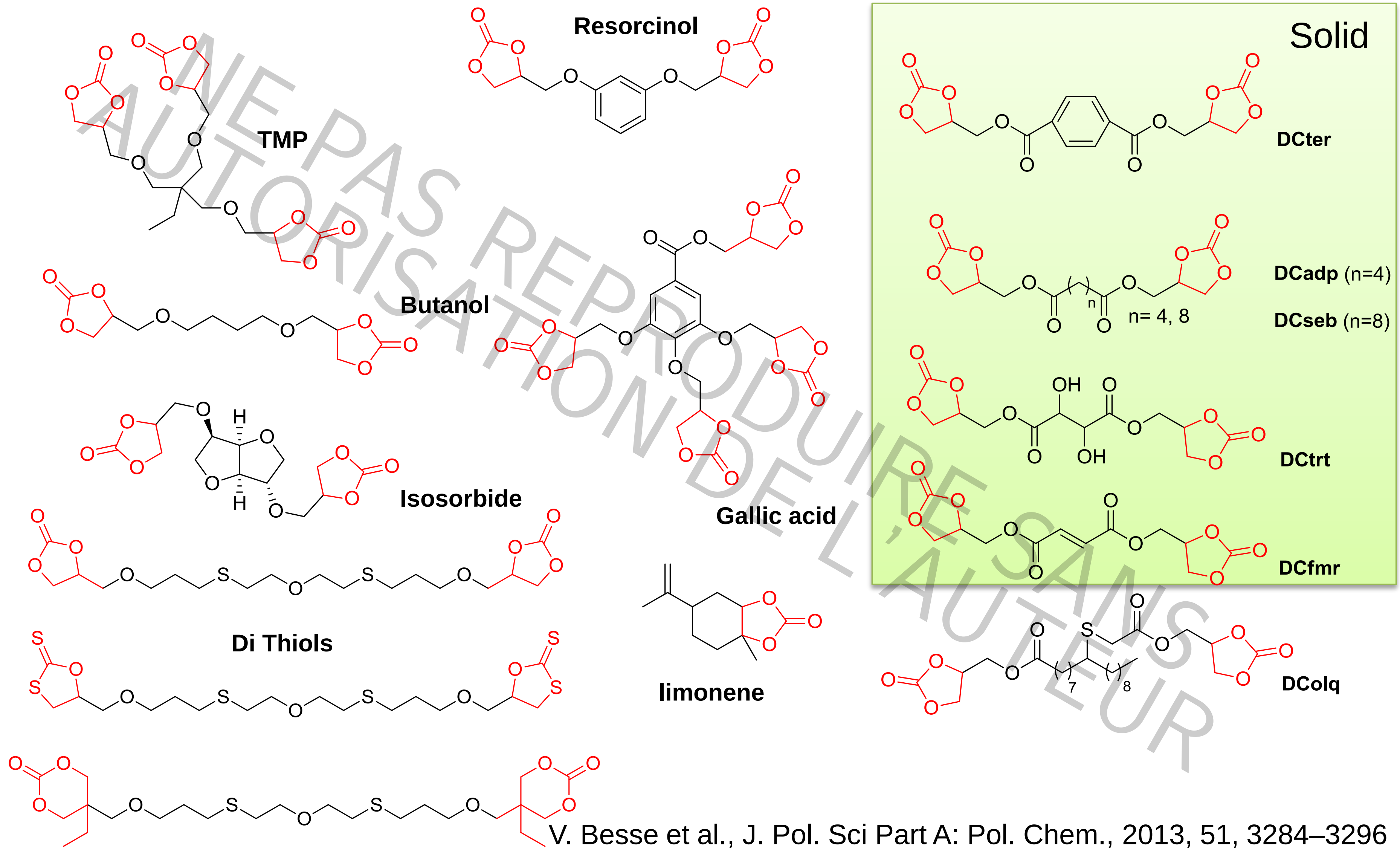
Reaction extensively studied by T. Endo et al.

Main issue : REACTIVITY OF CYCLIC CARBONATE WITH AMINE

Synthèse de C5, C6 et thio- dicyclocarbonates

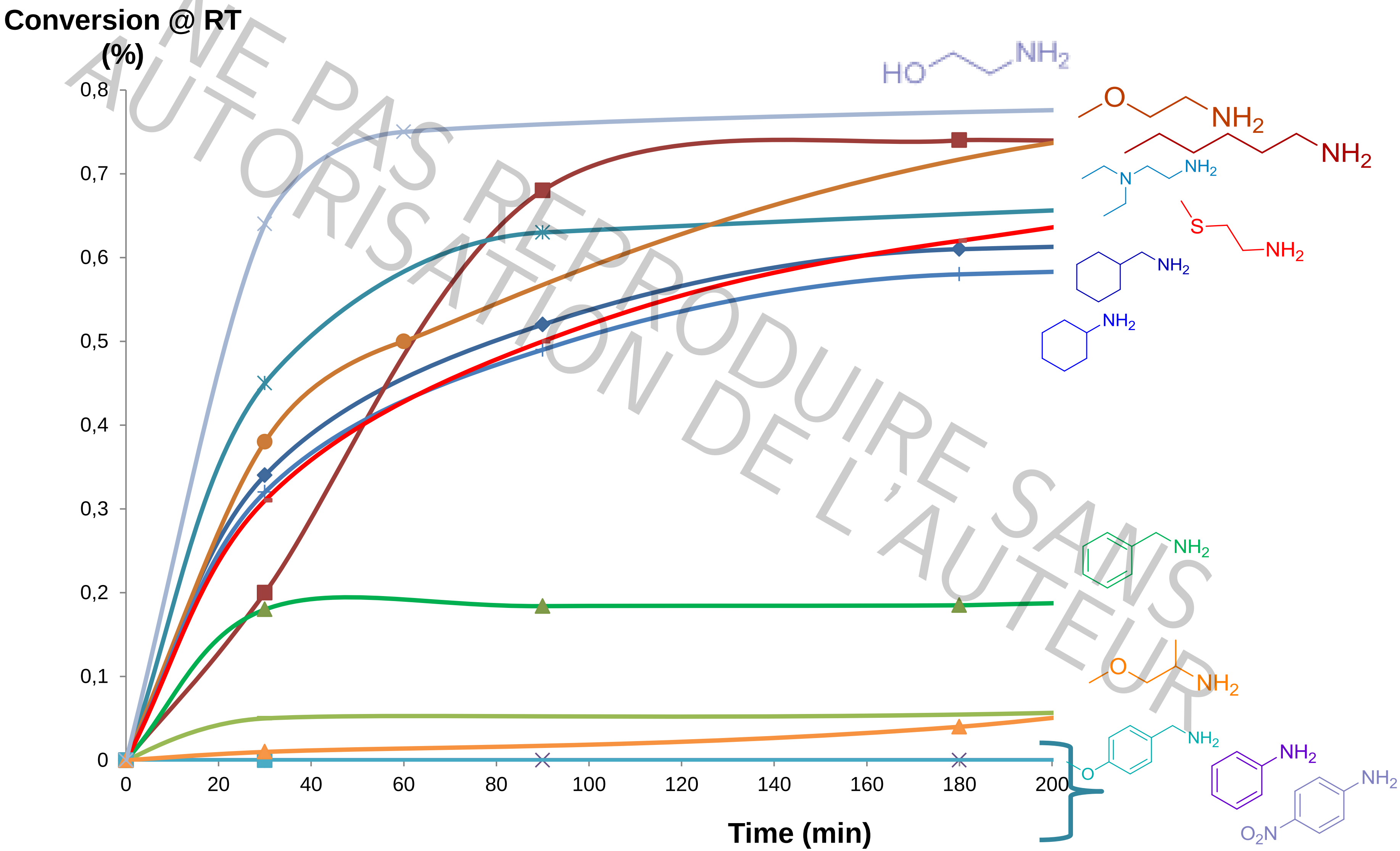


Examples of various biobased C5 di-cyclic carbonates for NIPUs



V. Besse et al., J. Pol. Sci Part A: Pol. Chem., 2013, 51, 3284–3296
S. Benyahya et al., Polymer International, 2012, 61, 1666-1674
V. Besse et al., Reactive and Functional Polymers, 2012, 3, 588-594

Nature of amine plays important role on reactivity with cyclic carbonates

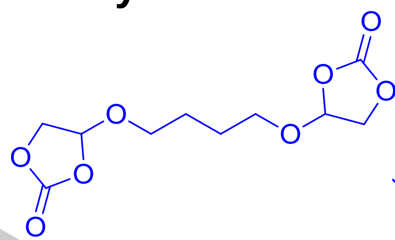


F. Camara et al., unpublished work

ICG Montpellier IAM

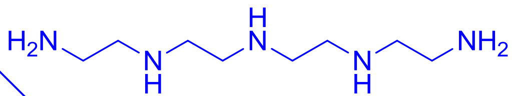
NIPUs Synthesis: Influence of amines II

Literature was not clear on reactivity of secondary amines



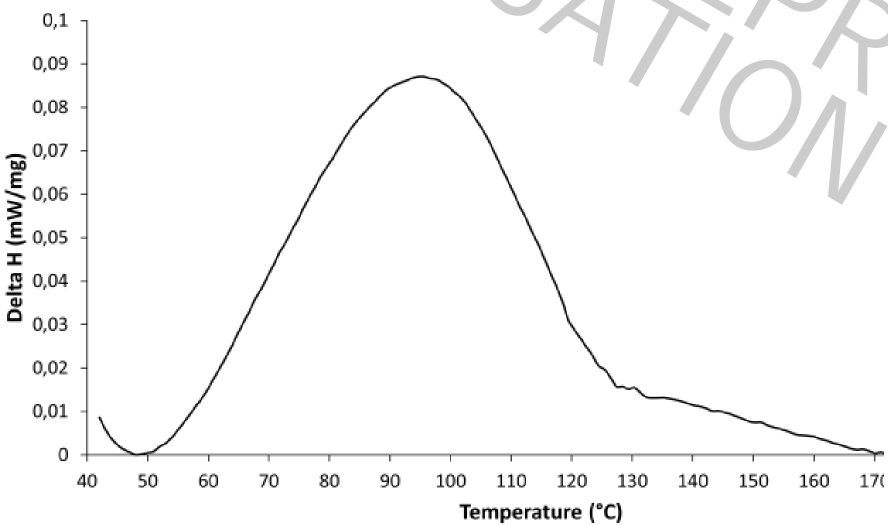
butanediol bis carbonate

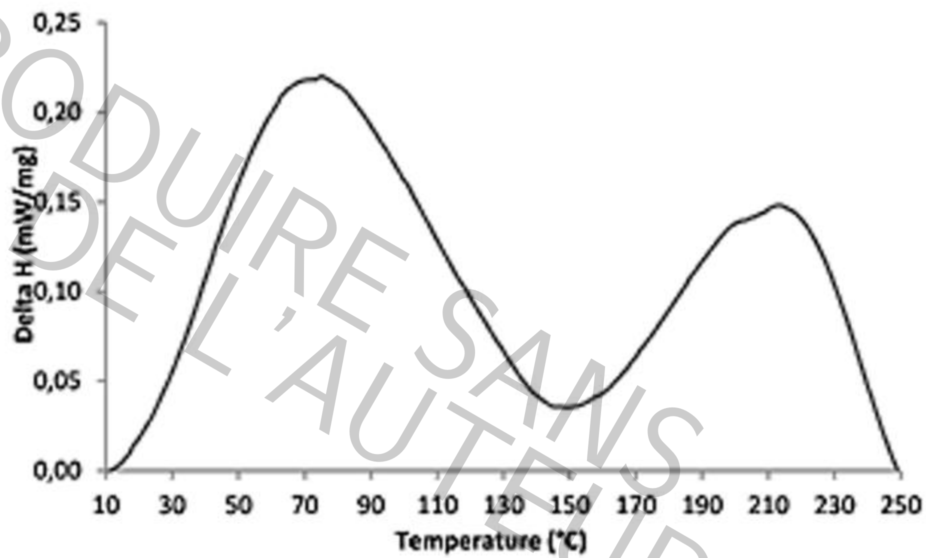
N,N′-Dimethyl-1,6-hexanediamine



TEPA

differential scanning calorimetry





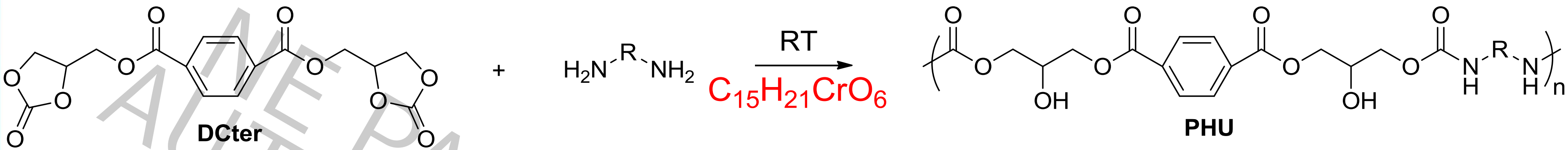
- Secondary amine is also reactive with cyclic carbonate but at higher temperature

- Cross linked polymer

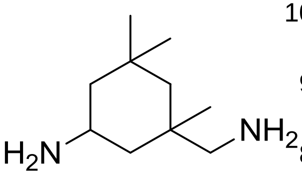
Polymer in THF	Swelling (%)	Soluble Part (%)
BBC-TEPA	1.2	1.7

V. Besse et al., Europ Pol J., submitted

NIPUs Synthesis: Influence of catalysts

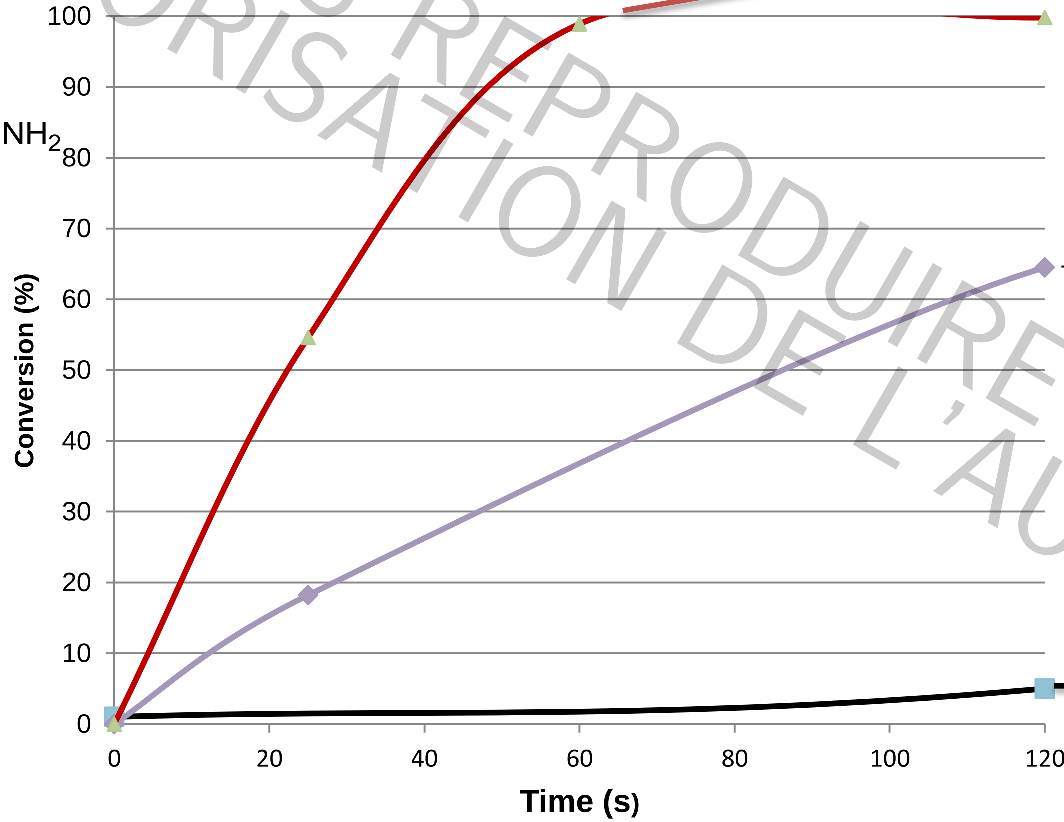


Conversion @ RT



chromium(III) acetyl acetonate / Et_3N 0,2%

Full conversion in few mn



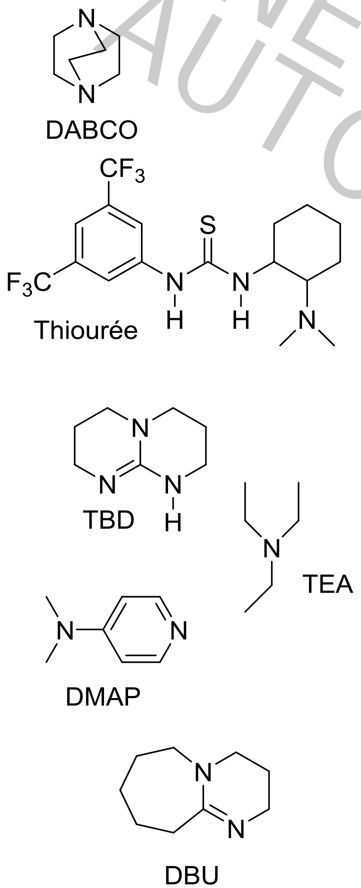
Et_3N

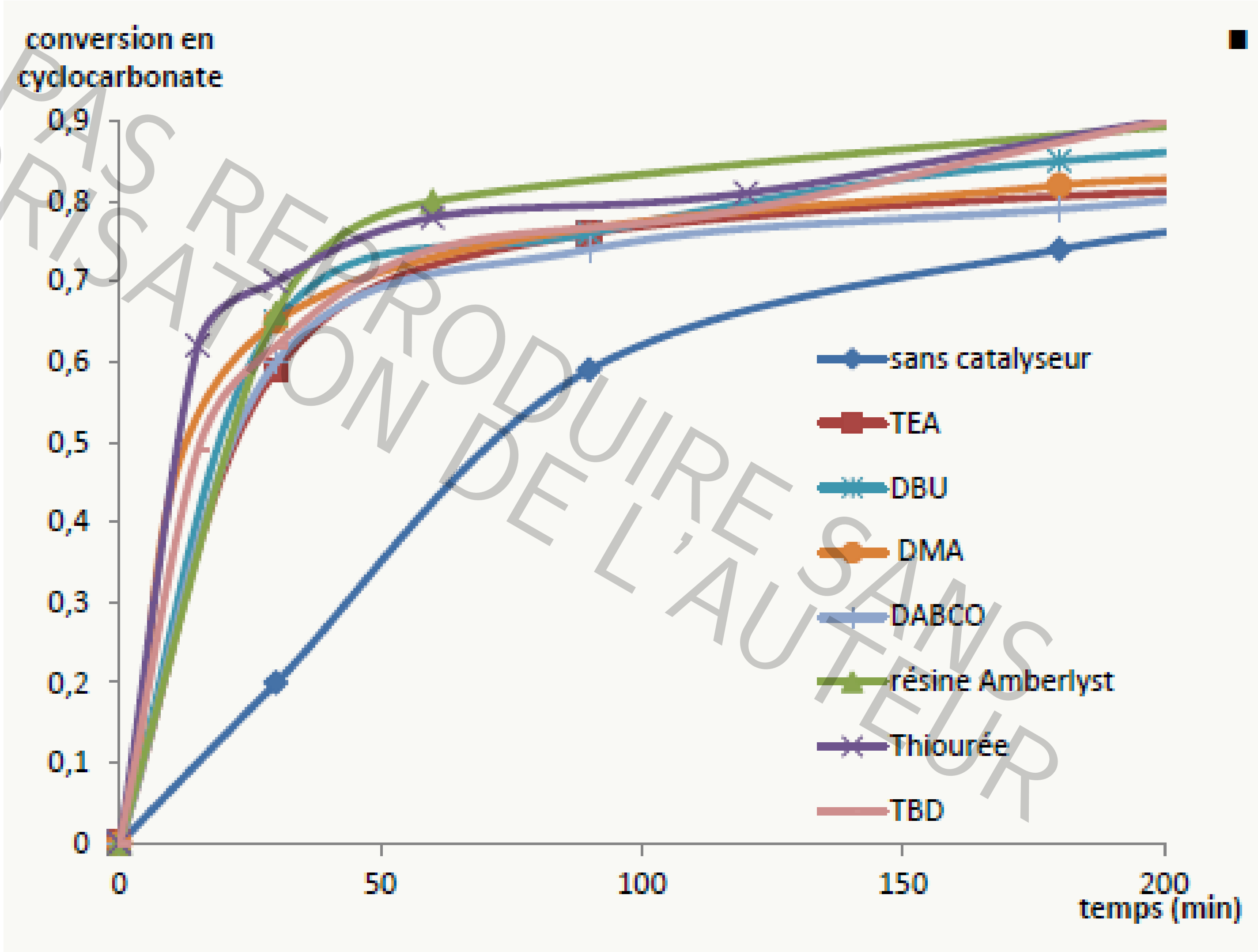
Without any catalyst

Patent SEG, CNRS FR1159818, 2011

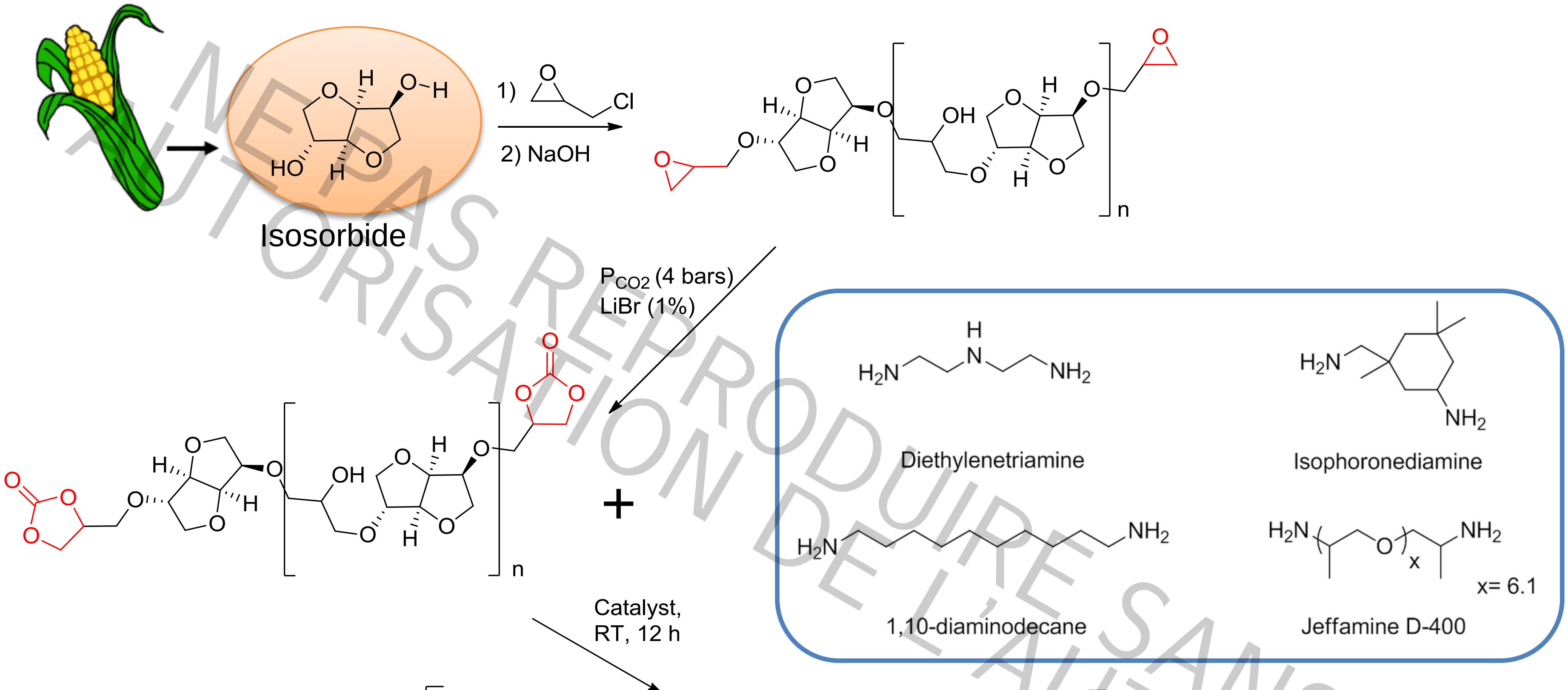
Etude des NIPUs

Etude de la catalyse de la réaction

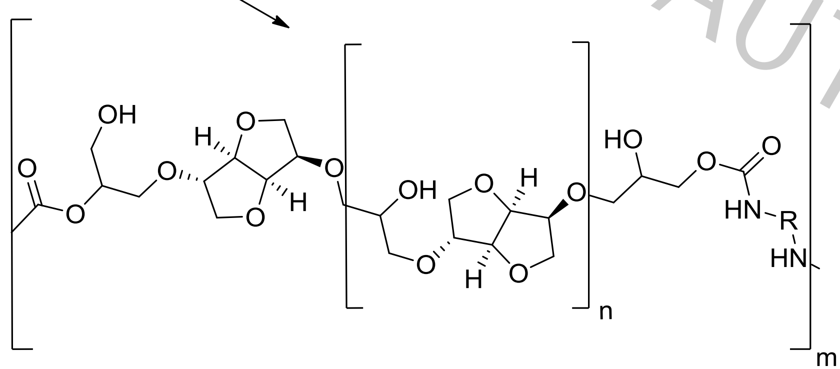




Biobased NIPUS from isosorbide



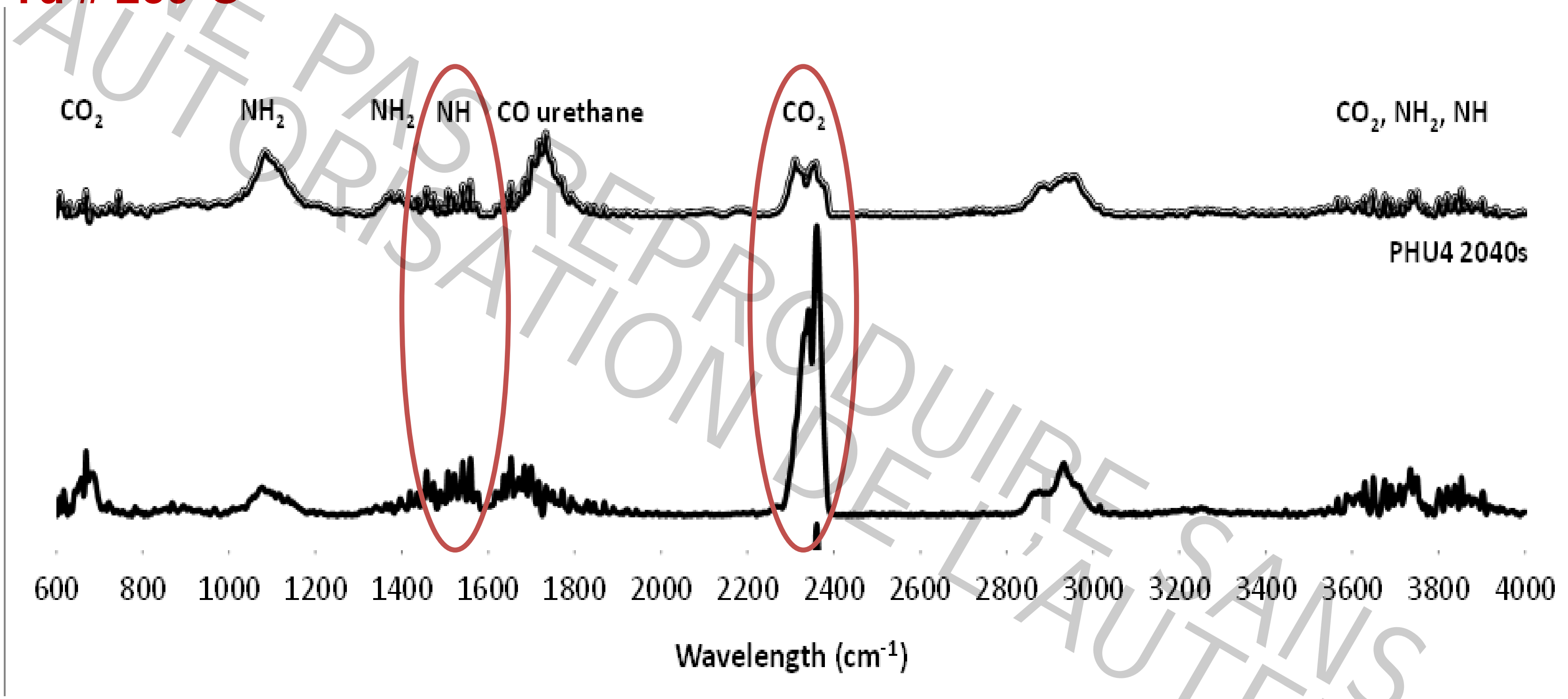
NIPUs :
Tg from -8 to 60°C
Td # 250°C



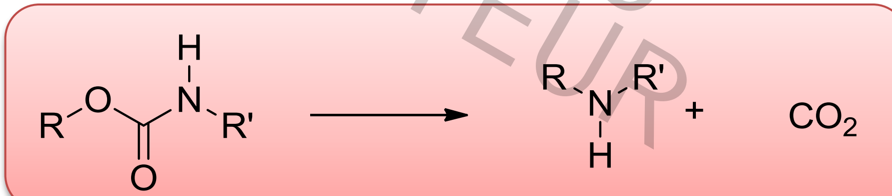
V. Besse et al., Reactive and Functional Polymers, 2012, 3, 588-594

Thermal degradation

Thermal degradation monitored by ATG/IR : no formation of NCO bonds
Td # 260°C



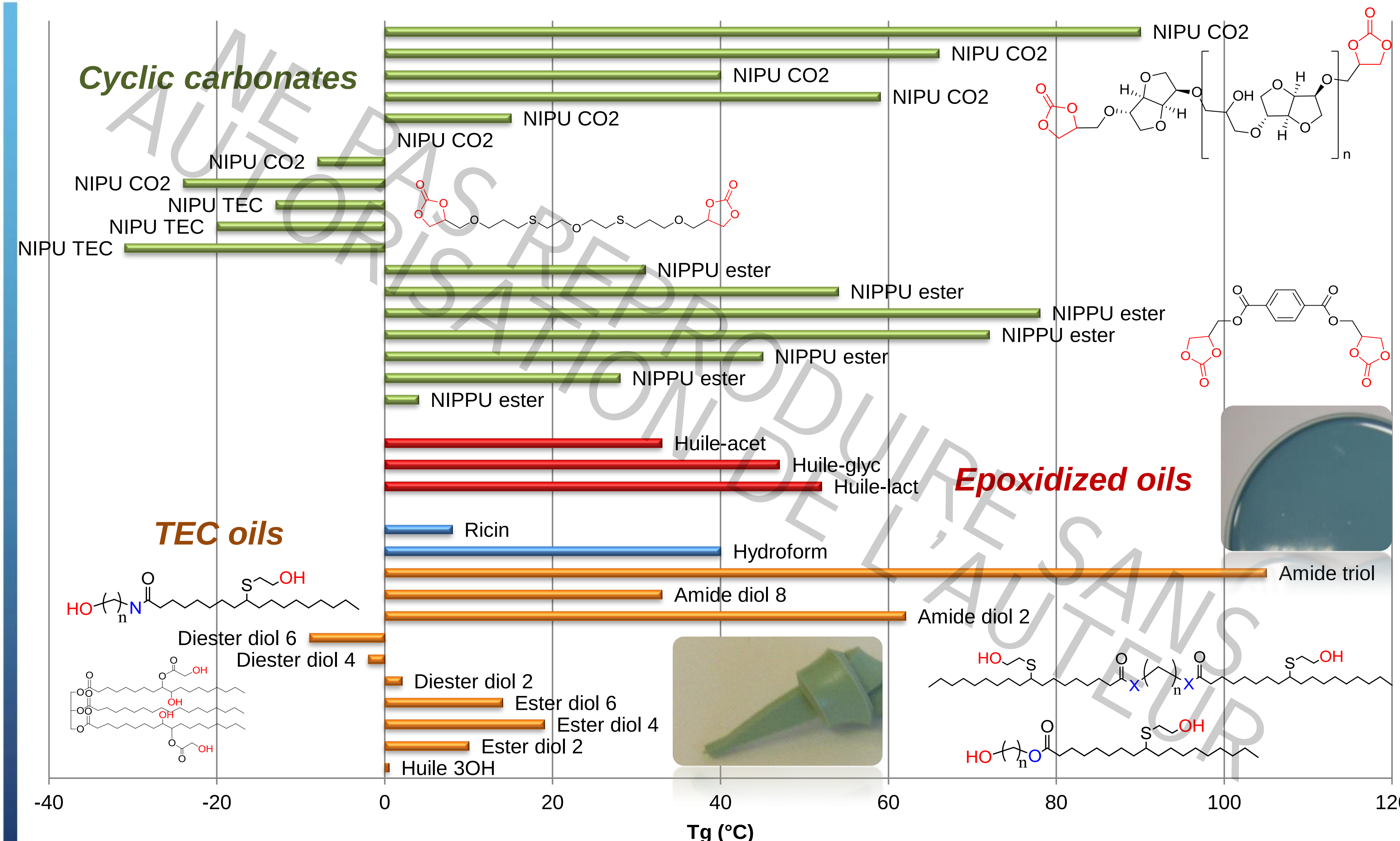
Degradation mechanism :



NIPUs not only synthesized without isocyanates
but don't yield isocyanates by thermal degradation

V. Besse et al., Reactive and Functional Polymers, 2012, 3, 588-594

Polyurethanes materials polyol/MDI or cyclocarbonate/amine

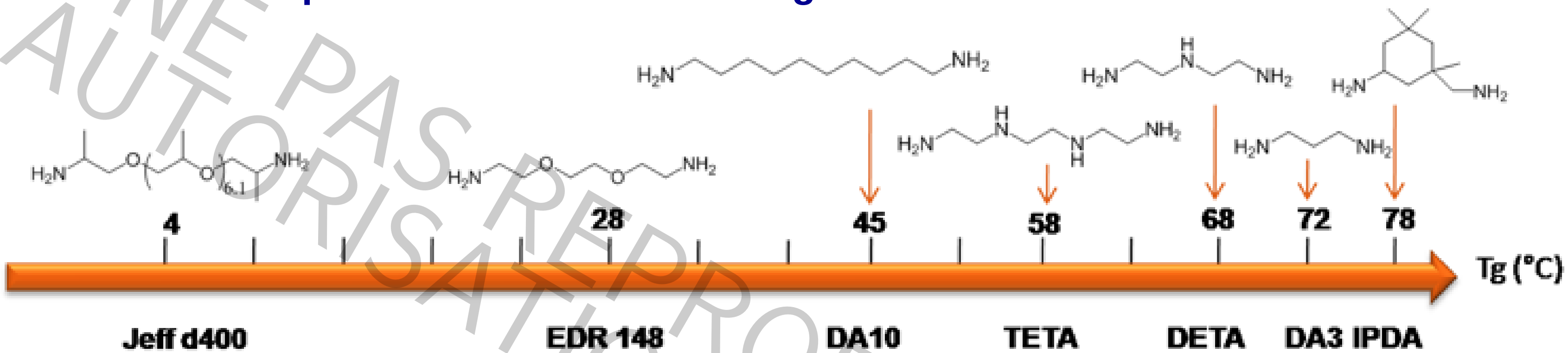


MDI : diphénylméthylène 4,4'-diisocyanate

M. Desroches et al., Polymer Reviews, 2012, 52(1), 38-79
V. Besse et al., Polymer Chemistry, 2013, 4, 4545-4561

Une contribution au développement des polyhydroxyuréthanes

Valorisation des liants époxy/amine et NIPUs à partir d'huiles végétales pour l'élaboration de composites avec des fibres végétales.



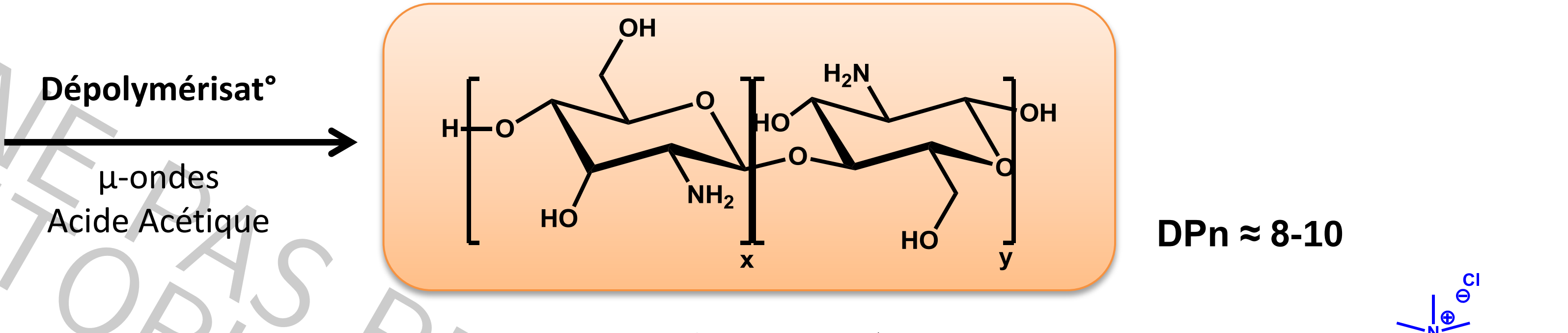
Web of vegetable wool fibres of which the mechanical cohesion is ensured by a thermoplastic polymer binder - WO2013093346 (2013)

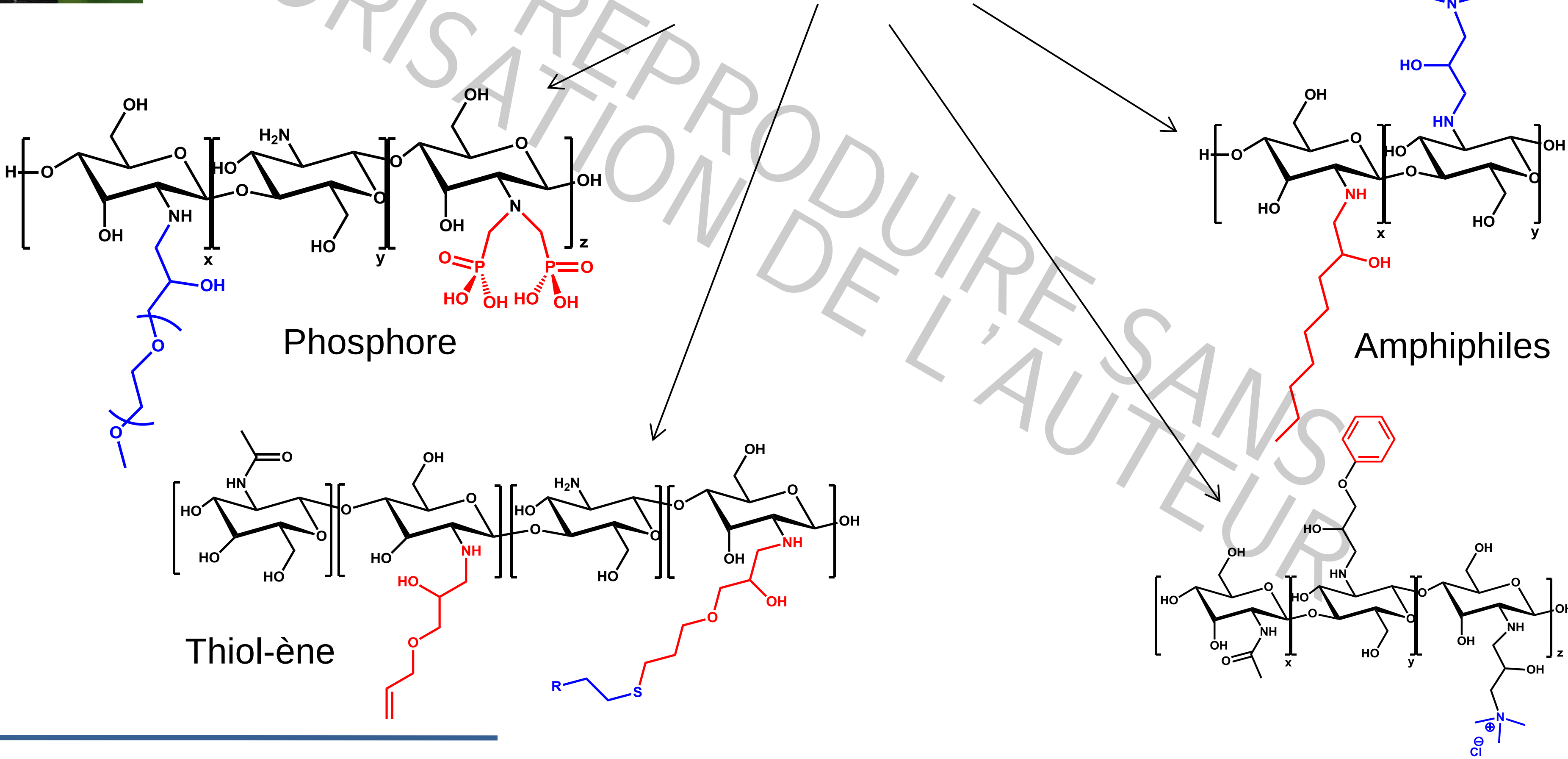
Valorisation du Chitosane

ICG Montpellier IAM

Synthèse de building blocks à base d'oligomères de chitosane

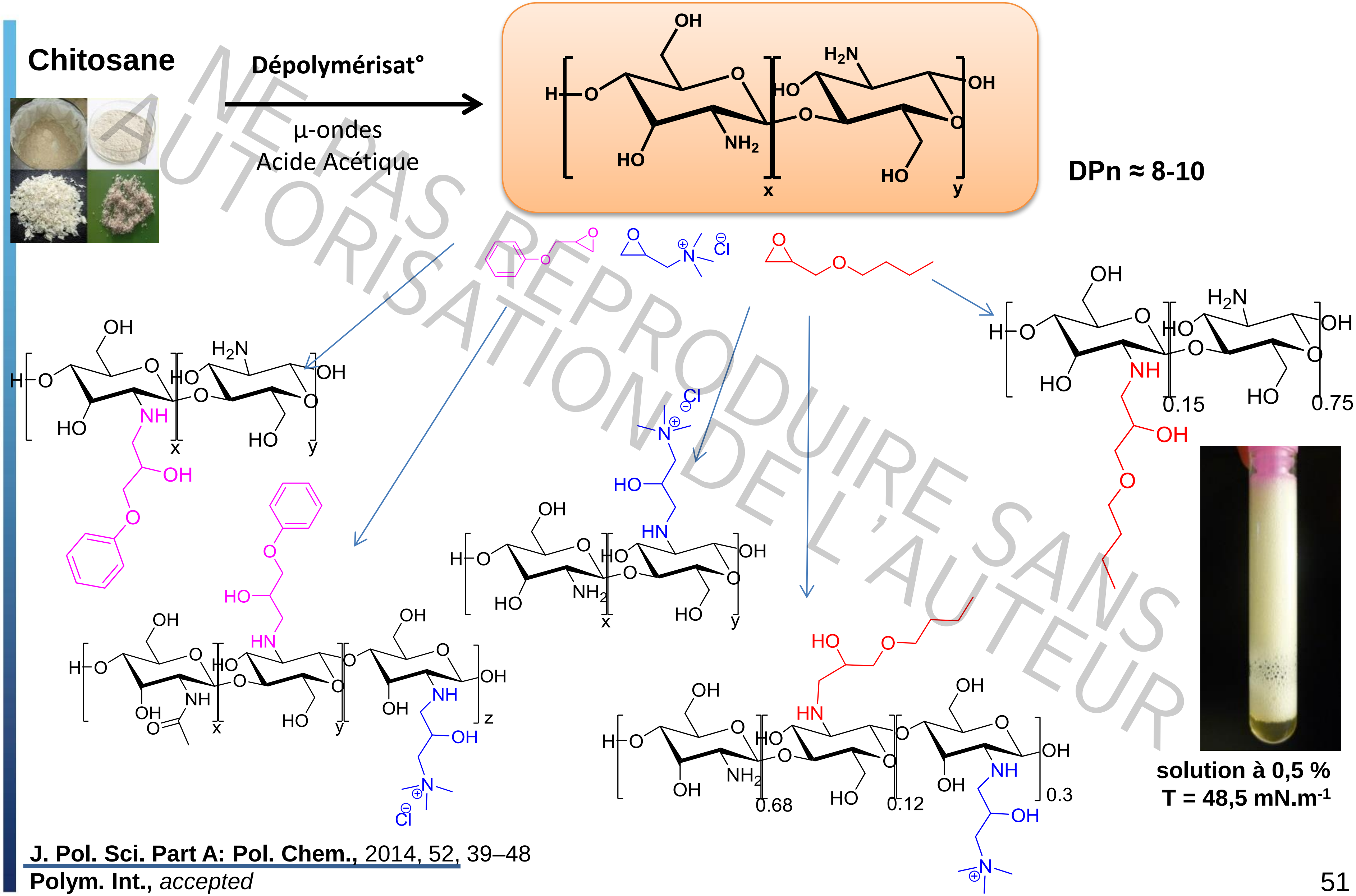
Chitosane





Synthèse de tensio-actifs à base d'oligomères de chitosane

Chitosane



solution à 0,5 %
T = 48,5 mN.m-1

J. Pol. Sci. Part A: Pol. Chem., 2014, 52, 39–48
Polym. Int., *accepted*

Traduction en enjeux scientifiques

Avantages

- Origine **renouvelable**
- Présence de **centres chiraux**
- Présence de **fonctions**

Inconvénients

- Trop **d'OH** – souvent besoin de protection
- Trop de **centres chiraux**
- Trop peu de fonctions **réactives** C=O, C=C

L'utilisation de la biomasse entraîne :

- ***Une chimie de la réduction*** *– biomasse oxygénée*
- ***Le développement de la dépolymérisation*** *– polymères naturels sont souvent de masses molaires élevées*
- ***Le recours à la polycondensation*** *au détriment de la polymérisation en chaine*
- ***Le choix de voies d'accès robustes*** *– biomasse très variable*

ACV de produits biosourcés

- **Voies pétrochimiques *vs* biosourcées :**

Pétrole → Raffinage → Intermédiaire chimique

Pétrole → Industrie chimique → Intrants agricoles → Agriculture → Biomasse → Bio-raffinage → Intermédiaire chimique

- **Premier critère** : culture ou non (huiles/forêt)
- De nombreuses **émissions** au **champ** difficiles à quantifier
- Un **transfert de pollution** est souvent observé
  - Réduction des catégories de dommages *Climate change* et *Resources*
  - Augmentation des catégories de dommages *Human health* et *Ecosystem quality*
- Nécessité de **hiérarchiser** les impacts
  - Réchauffement climatique ?
  - Consommations de ressources non renouvelables ?
  - Santé humaine ?
  - **Biodiversité ?**
- **Eau non prise en compte**

➔ Recycler
➔ Réduire la tox/écotox
➔ Utiliser les co-produits
pour allonger le cycle de vie
et réduire les impacts

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Dr Vincent Lapinte
Dr Claire Negrell
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