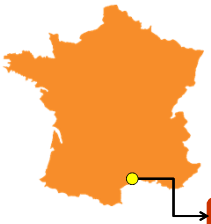
BiPoCo 2012
Lake Balaton, Hungary
May, 28th 2012

Synthesis of bio-based building blocks from vegetable oils: toward platform chemicals

Dr Sylvain Caillol
Pr Bernard Boutevin, Dr Rémi Auvergne

CHEMISTRY IN MONTPELLIER, FRANCE



- Arnaud De Villeneuve, 13th century Alchemist – acids and distillations…
- 1st Chemistry Institute created in 1889
- 2012 : 700 chemists and 1700 students
- Sustainable Chemistry Chair

ChemSuD Montpellier http://www.chemsud.fr

MONTPELLIER

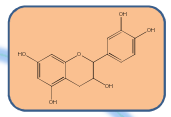
IAM Team : head Pr JJ Robin
Design and Architecture for Macromolecules
 # 60 pers.

➢ **Polymer team** of the Chemistry Institute **ICGM**

Research topic: Biobased polymers and composites

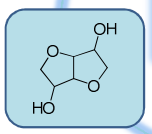
➢ **Non harmful biobased intermediates for biobased polymers**

Vegetable oils

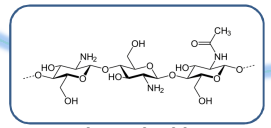


Polyphenols

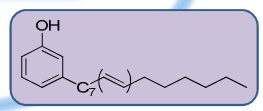
From molecular synthesis to functional materials : PU, epoxy, vinyl esters…



Isosorbide



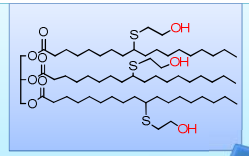
Polysaccharides



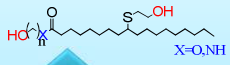
Cardanol

Vegetable oils: a platform molecule for new biobased intermediates

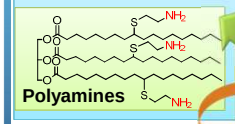
Patent FR1002738 - WO2012001315



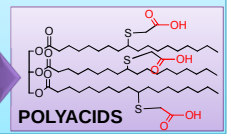
POLYOLS (TEC) Mass/UV



X=O,NH

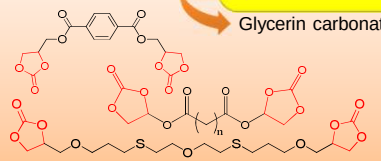


Polyamines

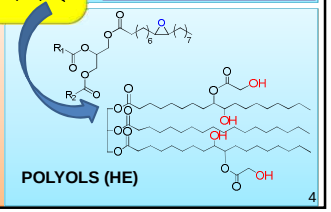


POLYACIDS

Glycerin carbonate



CYCLOCARBONATES FOR NON ISOCYANATE PU



POLYOLS (HE)

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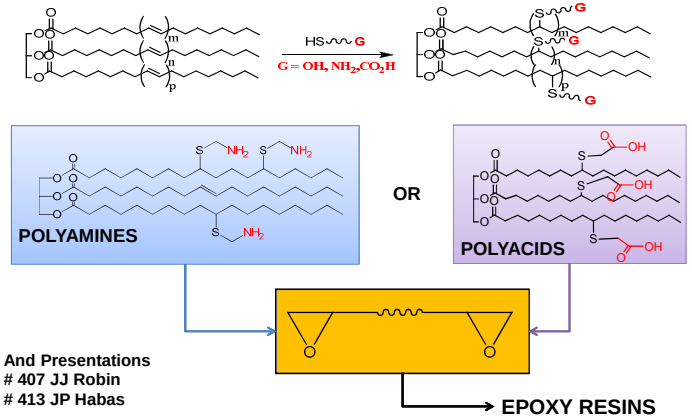
Part 1: Thiol-Ene Coupling Strategy

- Polyfonctinnal reactants from vegetable oil by Thiol-Ene Coupling



And Presentations
 # 407 JJ Robin
 # 413 JP Habas

Context: Polyurethanes

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

⇨ **Issues**

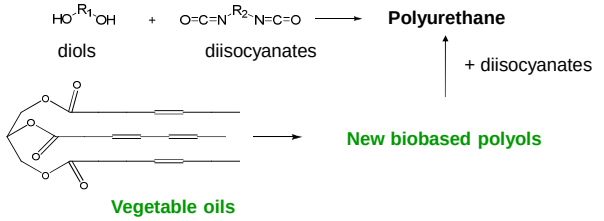
- **Fossil resources** reactants
- **Harmful** reactants
- Isocyanates - TDI and MDI : **CMR**
- Regulations
  - REACH: **MDI** in annex XVII

⇨ **Targets**

- Use of **biobased polyols** (70% w/w PU)
- Use of **vegetable oils** # 20Mt used in chemistry
- **Polyesters** 2nd group of polyols for PU
- **PU without isocyanates: Non Isocyanate PU**

Part 2: New biobased polyols by TEC

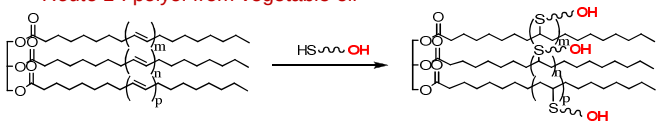
- **Objective**
  - Synthesis of biobased polyurethanes materials from vegetable oils



- **Method**
  - Direct hydroxyl functionalization of vegetable oils and derivatives by TEC

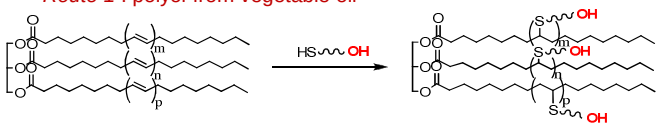
REACTIONS

- **Reactants: rapeseed oils and derivatives**
  - *Route 1* : polyol from vegetable oil

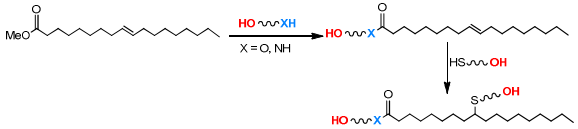


REACTIONS

- **Reactants: rapeseed oils and derivatives**
  - *Route 1* : polyol from vegetable oil

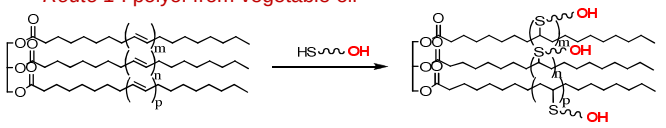


  - *Route 2* : diol from FAME

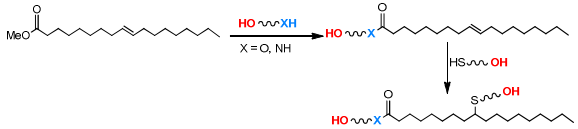


REACTIONS

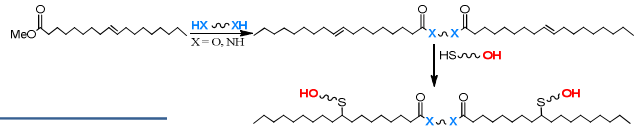
- **Reactants: rapeseed oils and oleic acid or oleic methyl ester**
  - *Route 1* : polyol from vegetable oil



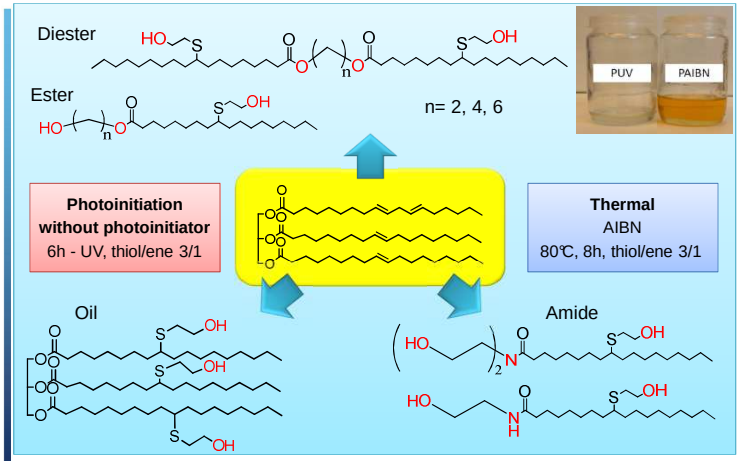
  - *Route 2* : diol from FAME



  - *Route 3* : diol dimers from FAME



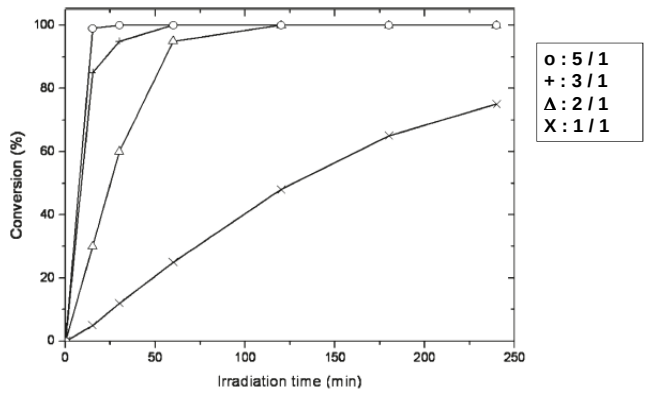
New biobased polyols from vegetable oils by TEC



Patent CNRS, FR 1002738, 2010

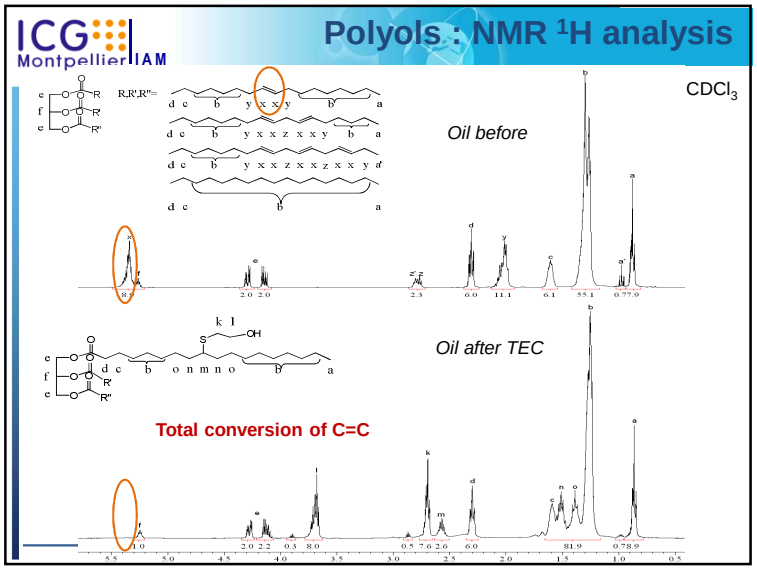
Influence of ratio thiol/ene

2-mercaptoethanol/oleic acid

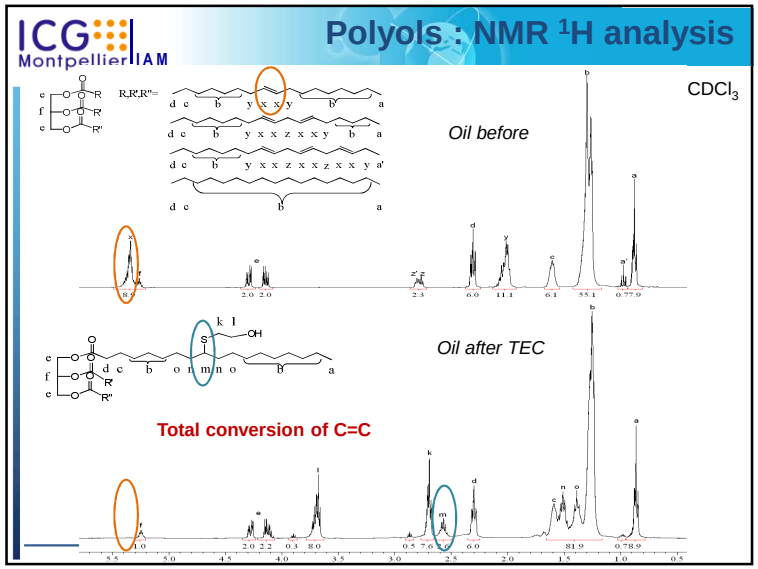


M. Desroches et al. Macromolecules, 2011, 44 (8), pp 2489–2500
M. Desroches et al, Polymer Chemistry, *accepted*

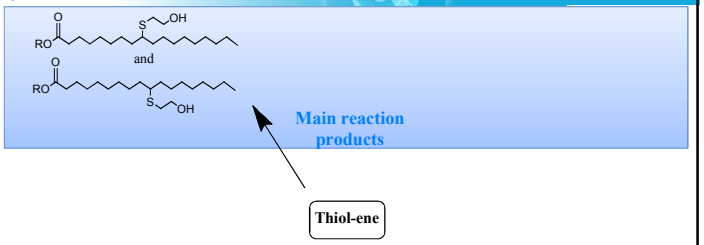
Polyols : NMR ^{1}H analysis



Polyols : NMR ^{1}H analysis



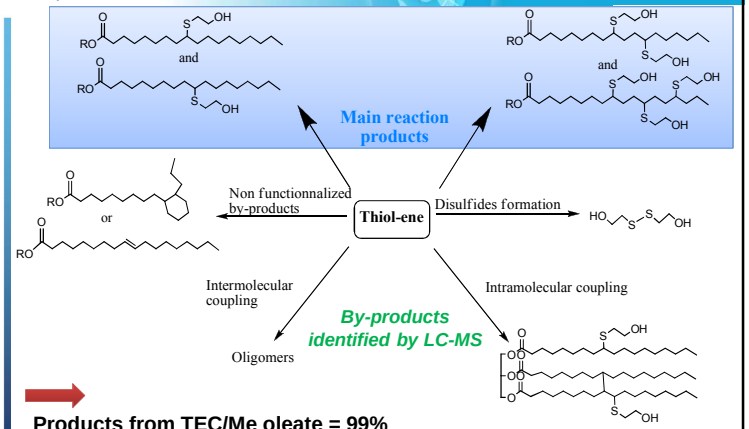
Click chemistry !



Products from TEC/Me oleate = 99%

M. Desroches et al. Eur J of Lip Sci Tech, 2011, asap

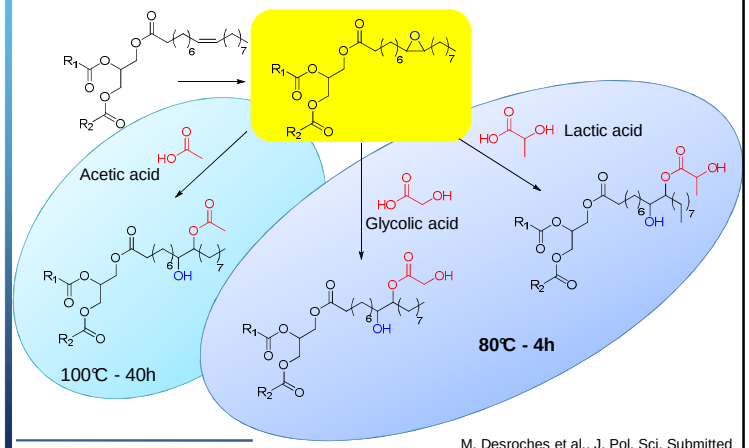
The limits to the "click" !



Products from TEC/Me oleate = 99%

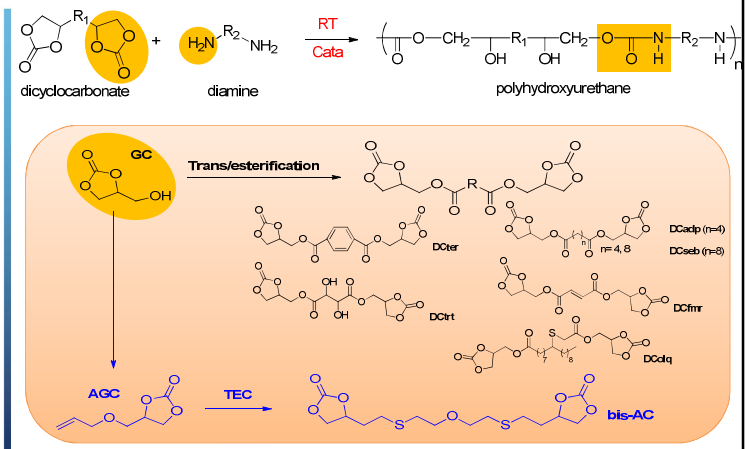
Products from TEC/oil = 65% but functionalized products > 95%

Part 3: New biobased polyols from epoxided vegetable oils



M. Desroches et al., J. Pol. Sci, Submitted

Part 4: Non Isocyanate Polyurethanes

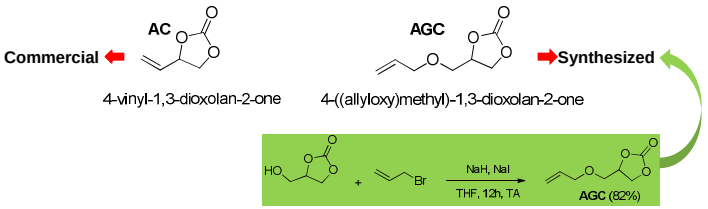


Patent SEG, CNRS FR1159818, 2011

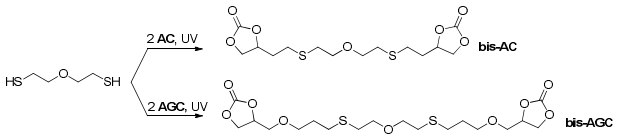
S. Benyahya et al., Polymer Chemistry, 2011, 2, 2661-2667
Polymer International, 2012, *Accepted*

Synthesis of dicyclocarbonates by thiol-ene

- **Two TEC-cyclocarbonates**

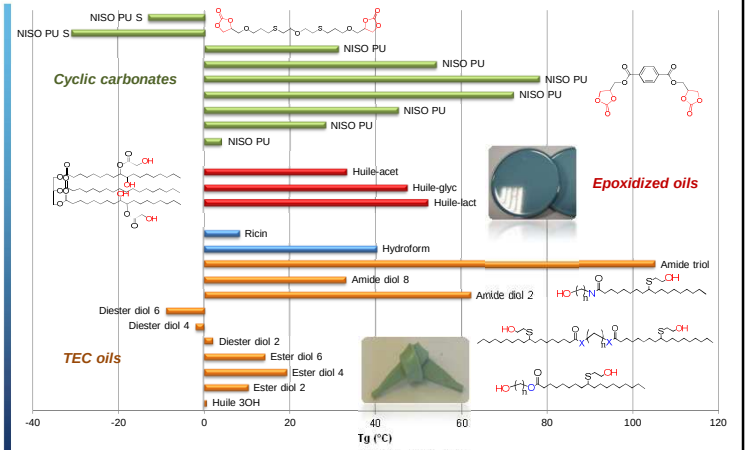


- **Synthesis of cyclic carbonates by thiol-ene coupling / UV**



S. Benyahya et al., Polymer Chemistry, 2011, 2, 2661-2667

Polyurethanes materials polyol/MDI or cyclocarbonate/amine

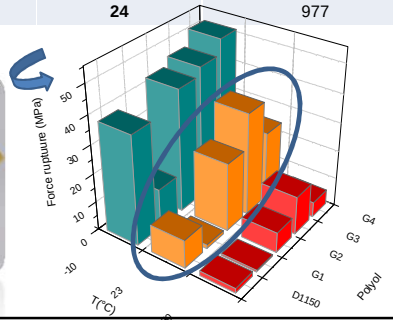


MDI : diphénylméthylène 4,4'-diisocyanate

S. Benyahya et al., Polymer Chemistry, 2011, 2, 2661-2667
M. Desroches et al., Polymer Chemistry, 2012, 3, 450-457

Mechanical tests

T=23°C	Max elongation (%)	Tensile strenght at break (MPa)	Young Modulus N/mm2
TEC Oil-polyol G1	20	**1**	7
Polyol-lactate G2	6	**24**	954
Polyol-glycolate G3	5	**36**	1284
Polyol-acetate G4	7	**24**	977



Conclusions

- **Polyol synthesis**
  - New diols and polyols synthesized easily from vegetable oils and FAME
  - Thiol-ene coupling : very efficient reaction, “green” : no solvent, UV without photoinitiator - by-products of TEC used in material synthesis
  - New biobased polyols from epoxidized oils – primary or secondary alcohols
- **Cyclocarbonates**
  - New dicyclocarbonates from gycerin carbonates or by TEC
- **Polyurethanes**
  - **Biobased** : # 70% of renewable carbon
  - Polyols without purification
  - **Without isocyanates**, from dicyclocarbonates and amines
  - Properties comparable to those from commercial polyols
- **In progress**
  - « Pilot » scale production of polyols and dicyclocarbonates for PU synthesis by industrial companies partners of project

ACKNOWLEDGEMENT

PROJECT GREENCOAT funded by ANR MatEtPro

The Polymer team IAM

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CHRYSO RÉSIPOLY — RÉSIPOLY CHRYSOR

SEG — SEG DIÉLECTRIQUES

THANK YOU FOR ATTENTION