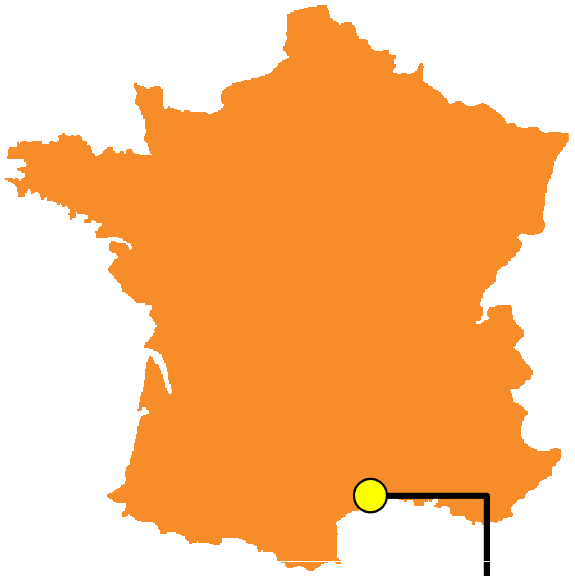
Journées Chevreul
Maison Alfort, France
Juin, 5th 2012

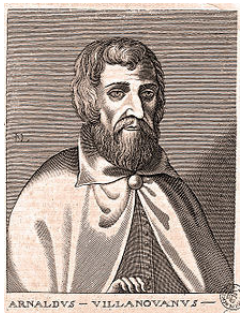
Synthesis of bio-based building blocks from vegetable oils: toward platform chemicals

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

IAM Team : head Pr JJ Robin

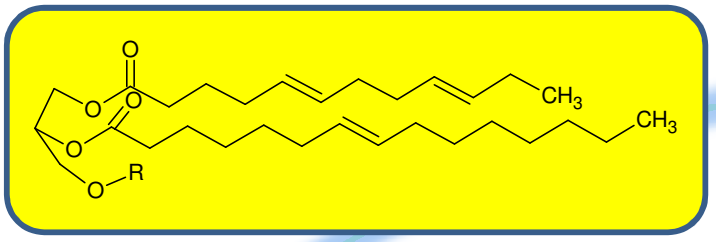
Design and Architecture for Macromolecules

 # 60 pers.

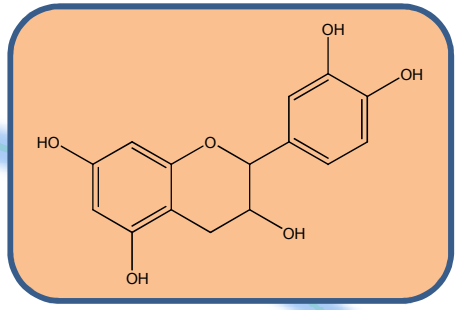
➢ **Polymer team** of the Chemistry Institute **ICGM**

Research topic: Biobased polymers and composites

- **Non harmful biobased intermediates for biobased polymers**

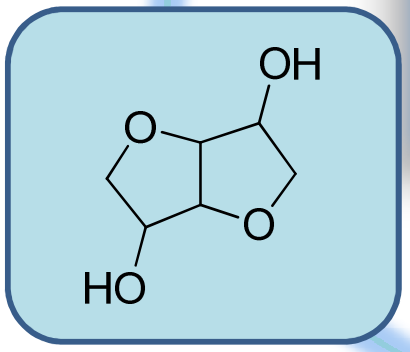


Vegetable oils

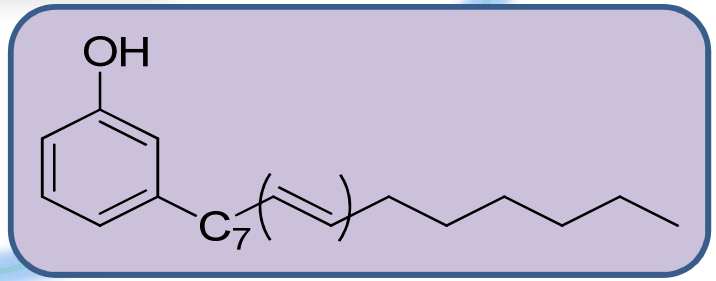


Polyphenols

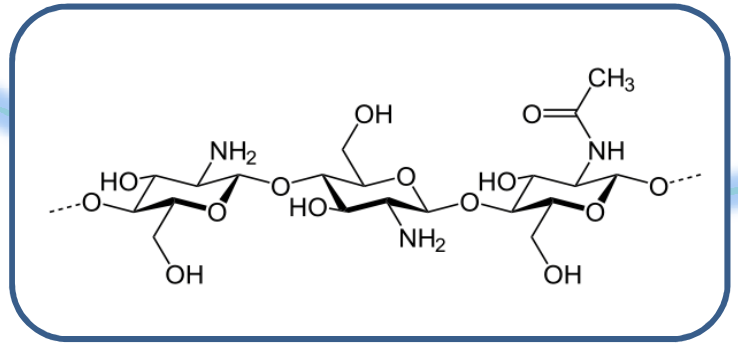
From molecular synthesis to functional materials : PU, epoxy, vinyl esters…



Isosorbide

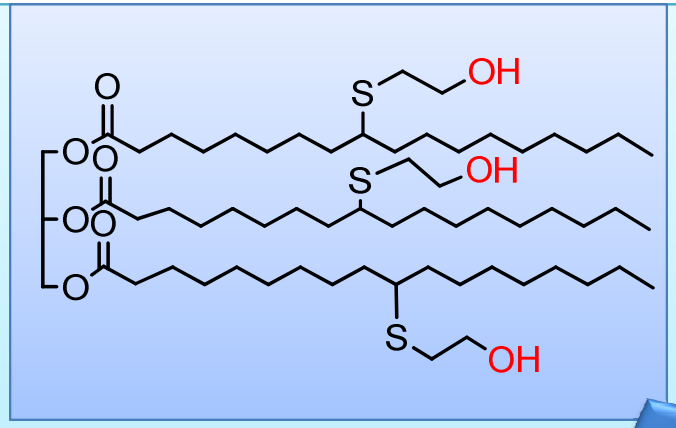


Cardanol

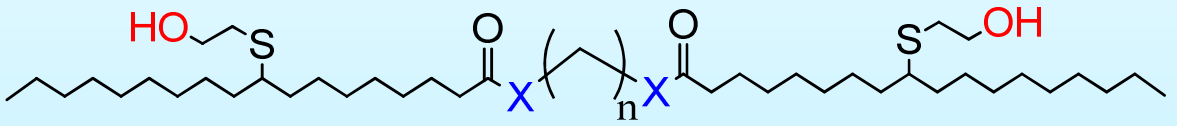


Polysaccharides

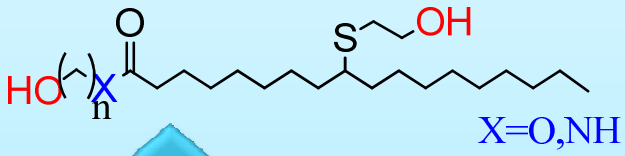
Vegetable oils: a platform molecule for new biobased intermediates

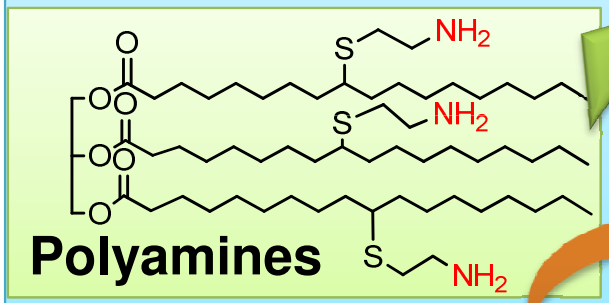


Patent FR1002738 - WO2012001315

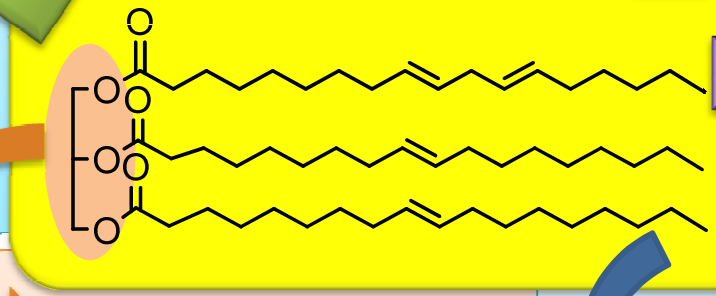


POLYOLS (TEC)
Mass/UV

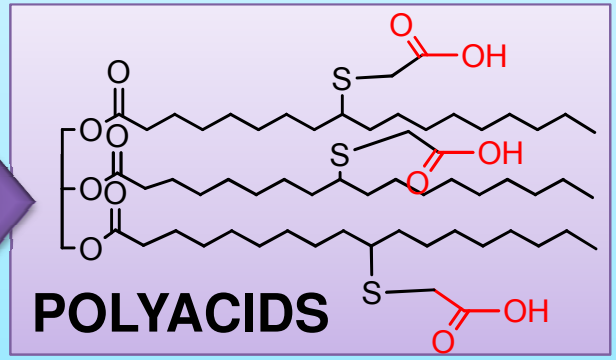




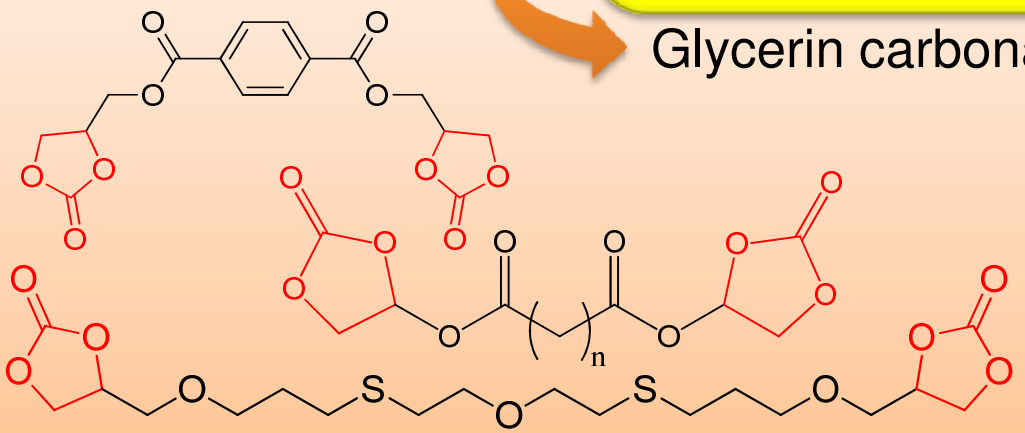
Polyamines



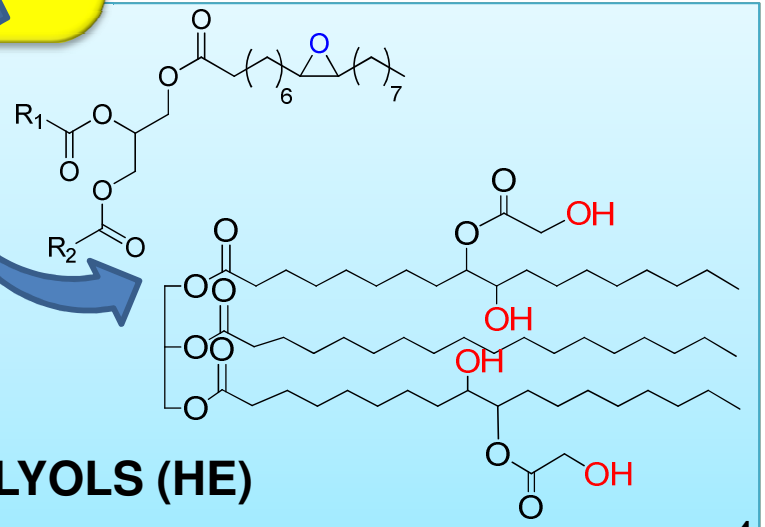
Glycerin carbonate



POLYACIDS



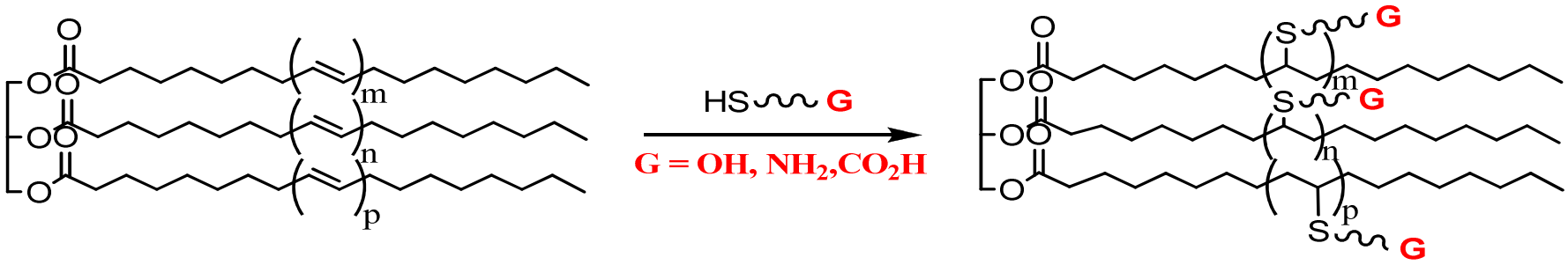
CYCLOCARBONATES FOR NON ISOCYANATE PU

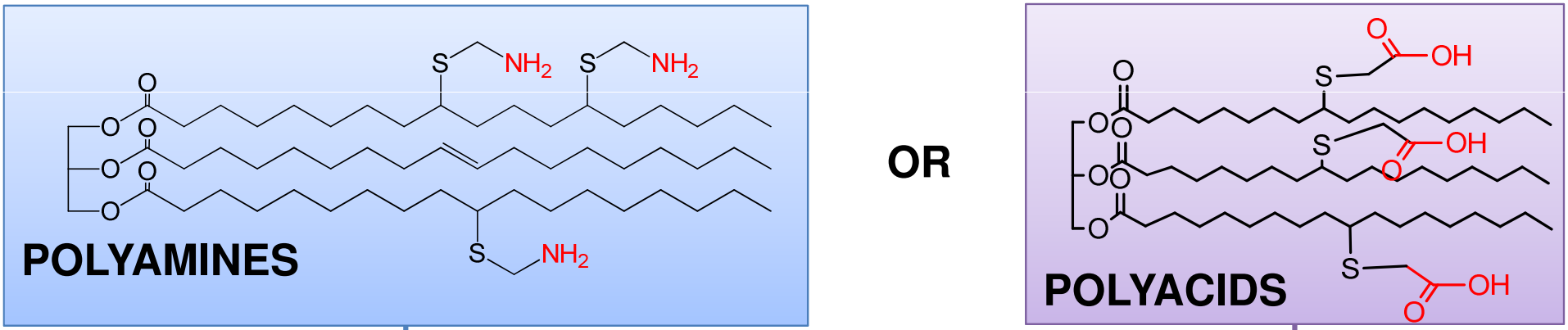


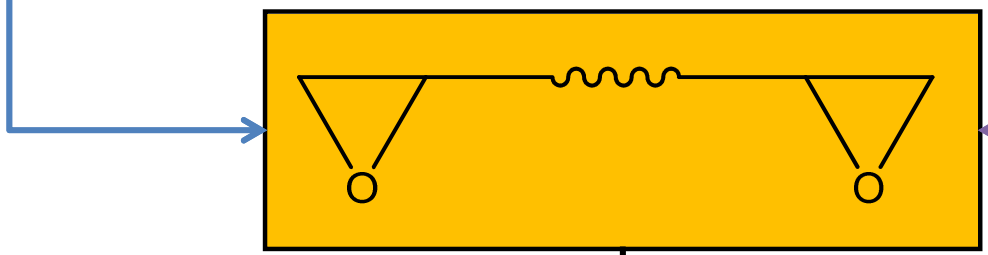
POLYOLS (HE)

Part 1: Thiol-Ene Coupling Strategy

- Polyfonctional reactants from vegetable oil by Thiol-Ene Coupling



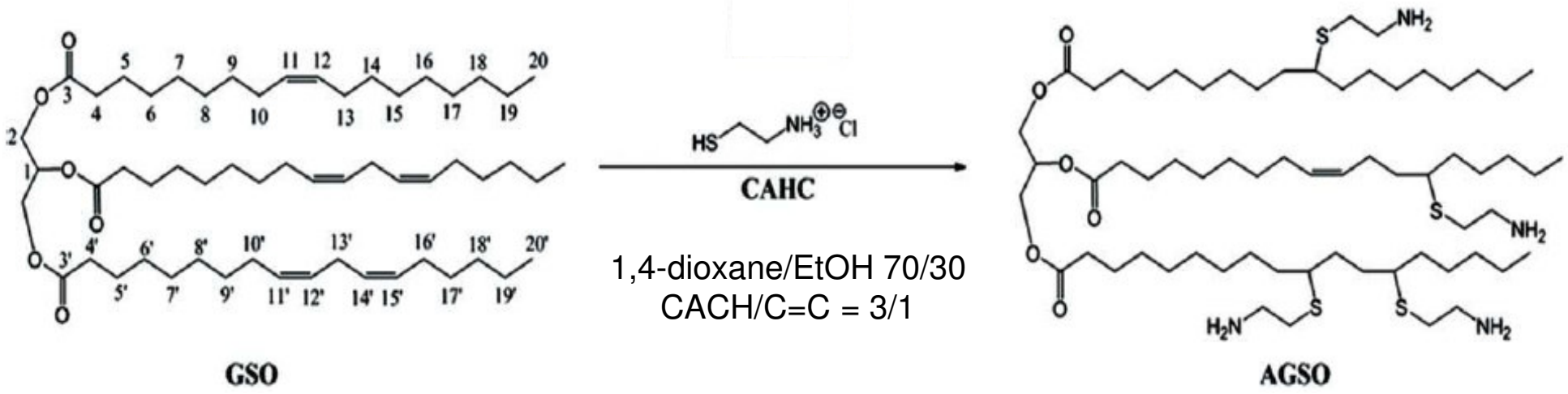




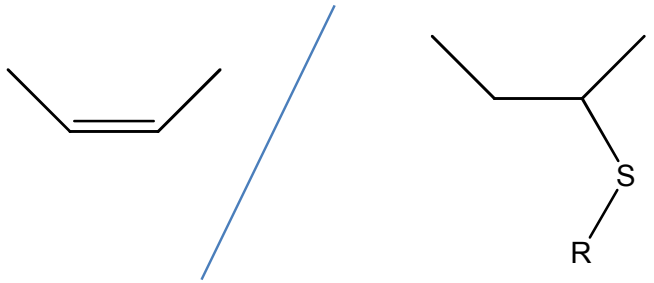
EPOXY RESINS

New biobased polyamines

Grapeseed oil funtionalized with cysteamine by TEC under UV



DMPA (eq)	*t* (h)	ρ (%)[a]/ρ (%)[b]
0.01	8	41/22
0.01	8	17/20
0.1	8	100/87
0.01	24	25/23
–	24	23/22
–	72	62/65
0.1	8	86/66

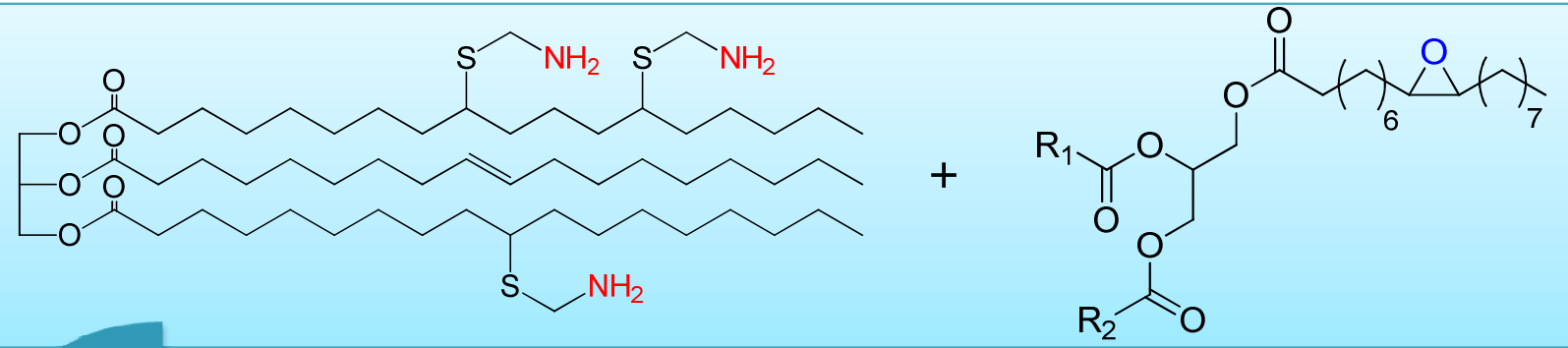


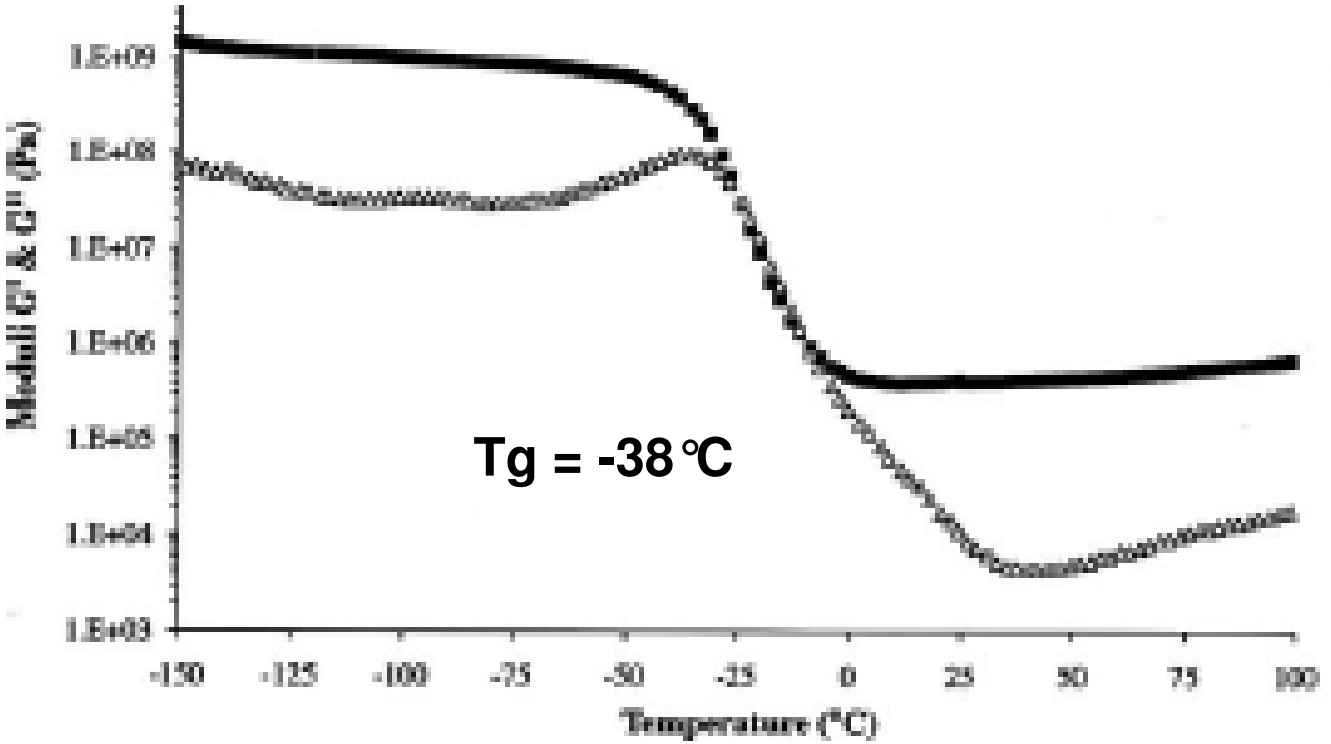
DMPA : 2,2-dimethoxy-2-phenylacetophenone

M. Stemmelen et al., J Pol Sci Part A: Pol Chem, 2011, 49, (11), 2434–2444

Polyamine and epoxidized oil

Polyamine and epoxidized oil - RT 24h

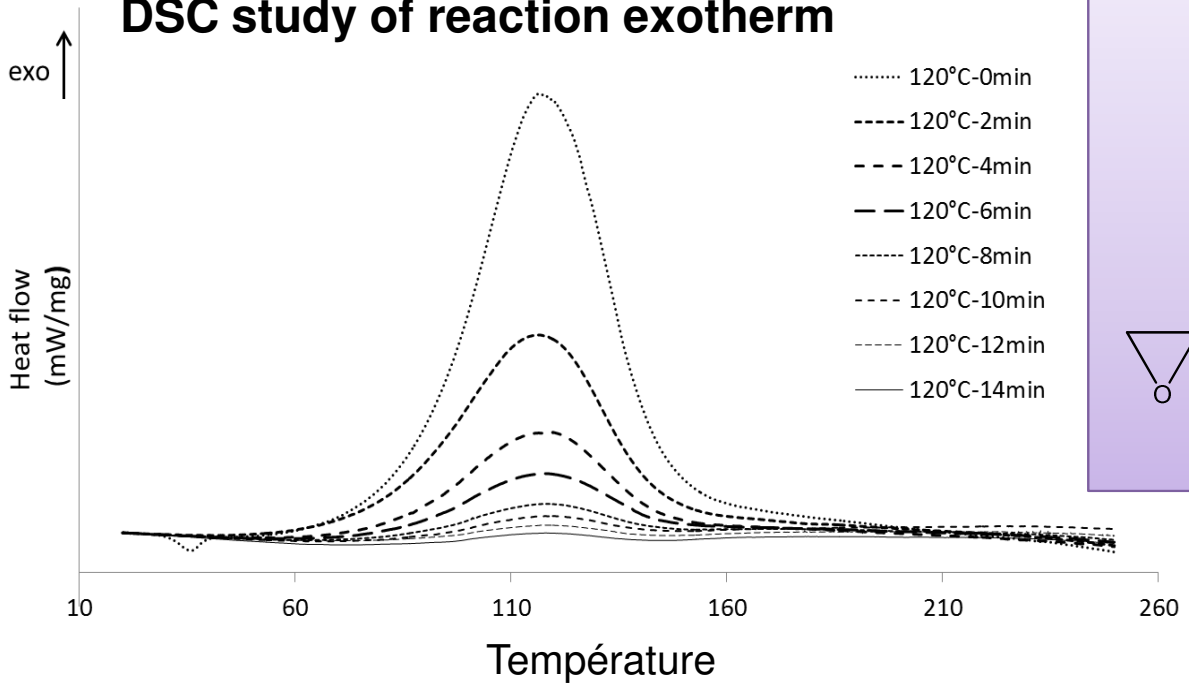


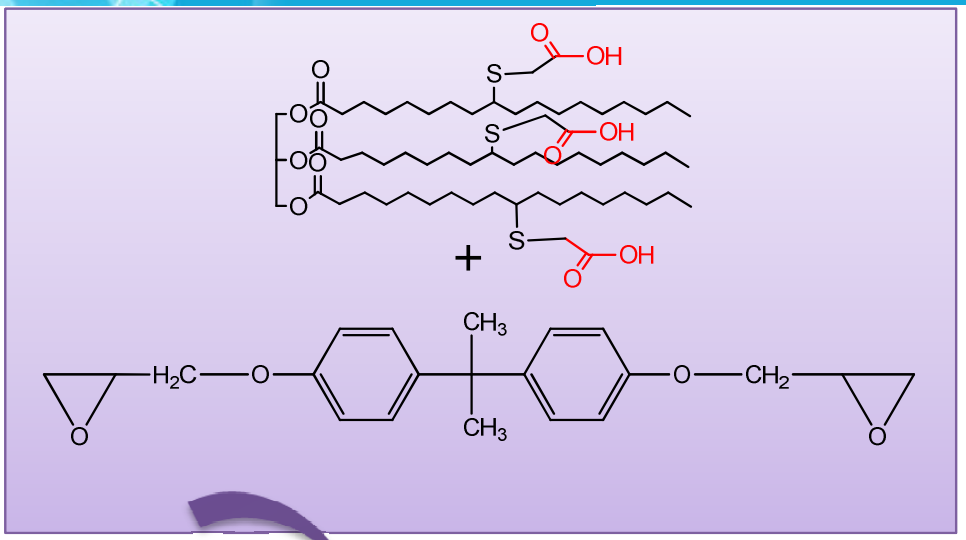


Thermomechanical analysis of cured AGSO-ELO mixture with G' (■) and G'' (Δ)

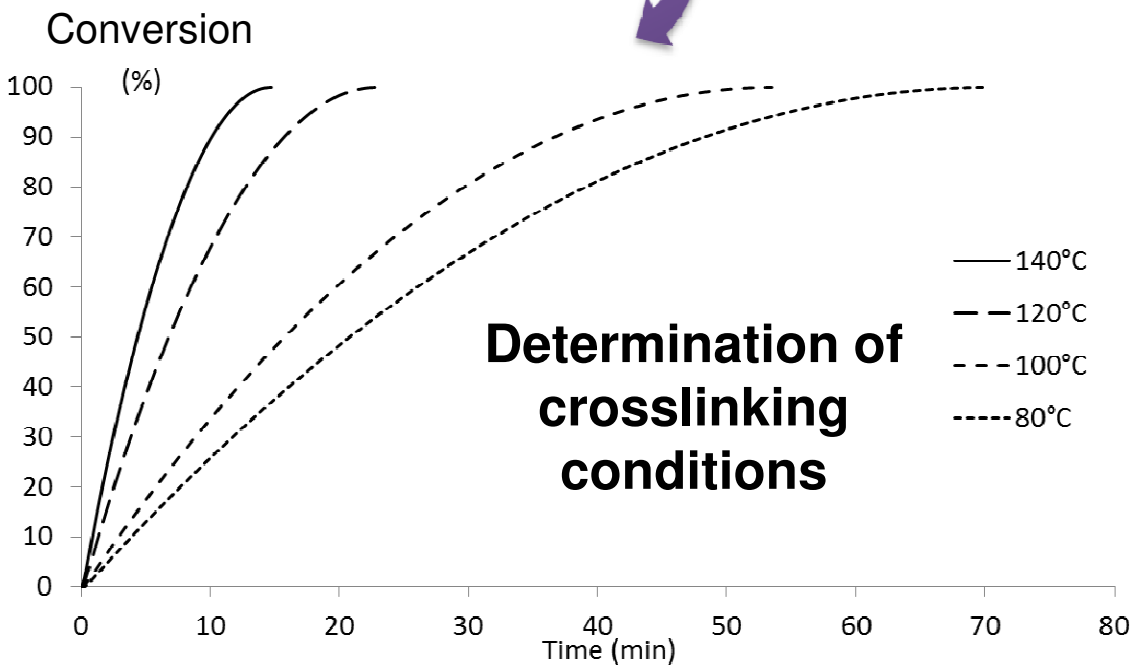
Polyacids and DGEBA

DSC study of reaction exotherm





Tg (°C)	TGA (°C) under N2/air	
-12	348	340



Determination of crosslinking conditions

Context: Polyurethanes

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

⇨ **Issues**

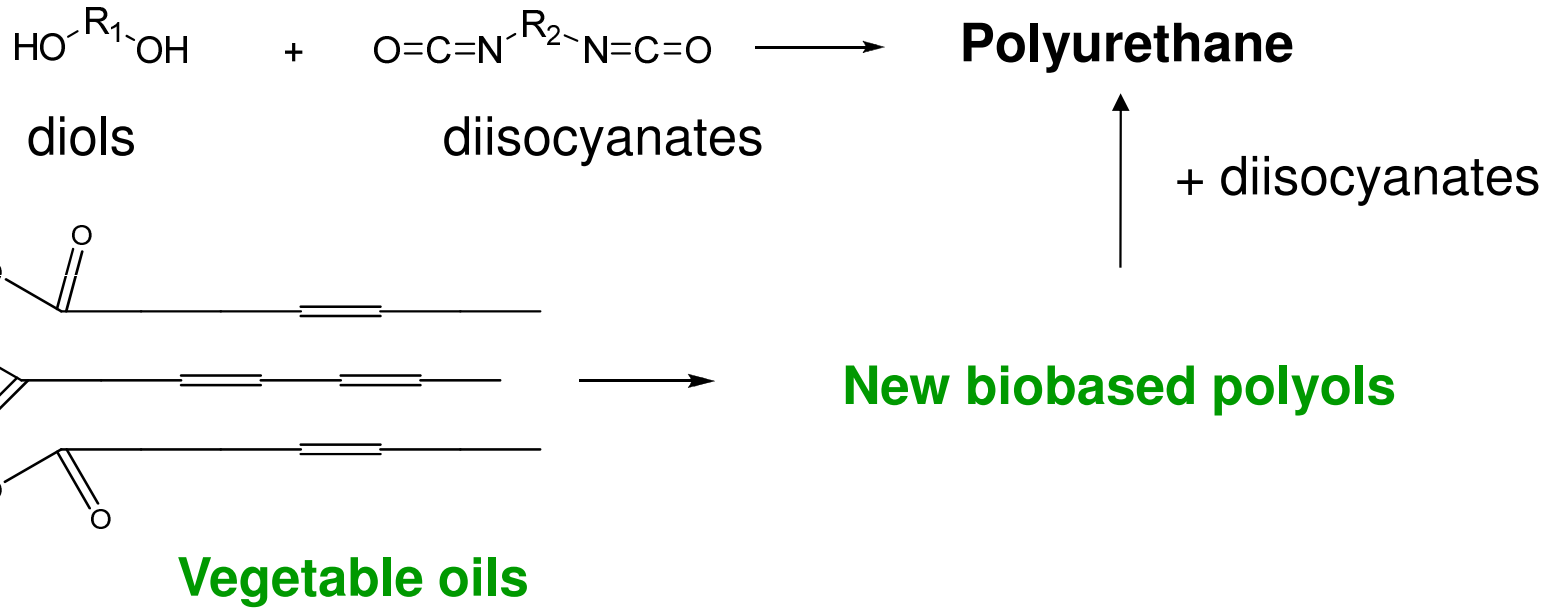
- **Fossil resources** reactants
- **Harmful** reactants
- Isocyanates - TDI and MDI : **CMR**
- Regulations
  - REACH: **MDI** in annex XVII

⇨ **Targets**

- Use of **vegetable oils** # 20Mt used in chemistry
- Synthesize **biobased polyols** (70% w/w PU)
  - **Polyethers** 1st group of polyols for PU
  - **Polyesters** 2nd group of polyols for PU
- **PU without isocyanates: Non Isocyanate PU**

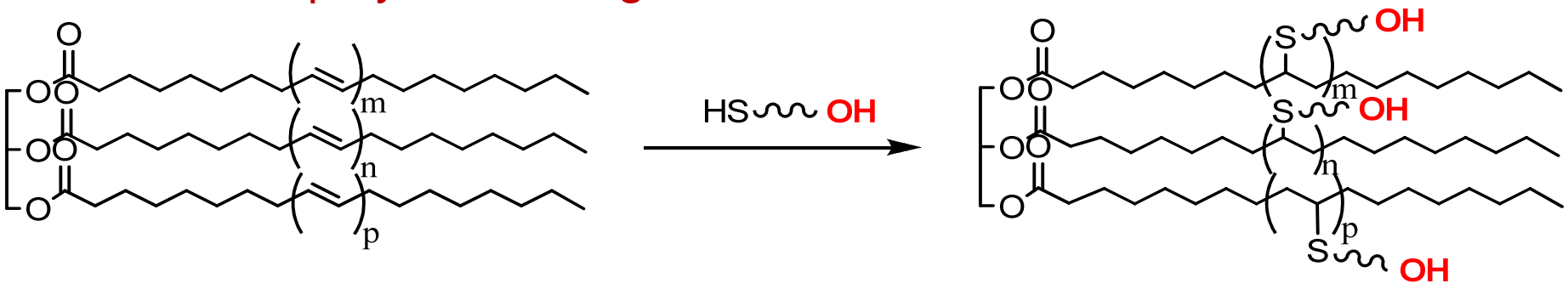
Part 2: New biobased polyols by TEC

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



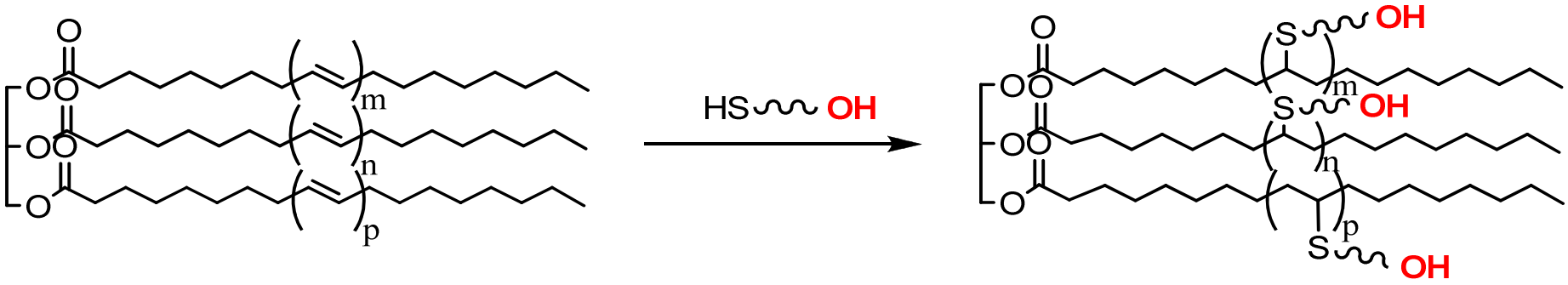
- **Method**
  - Direct hydroxyl functionalization of vegetable oils and derivatives by TEC

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

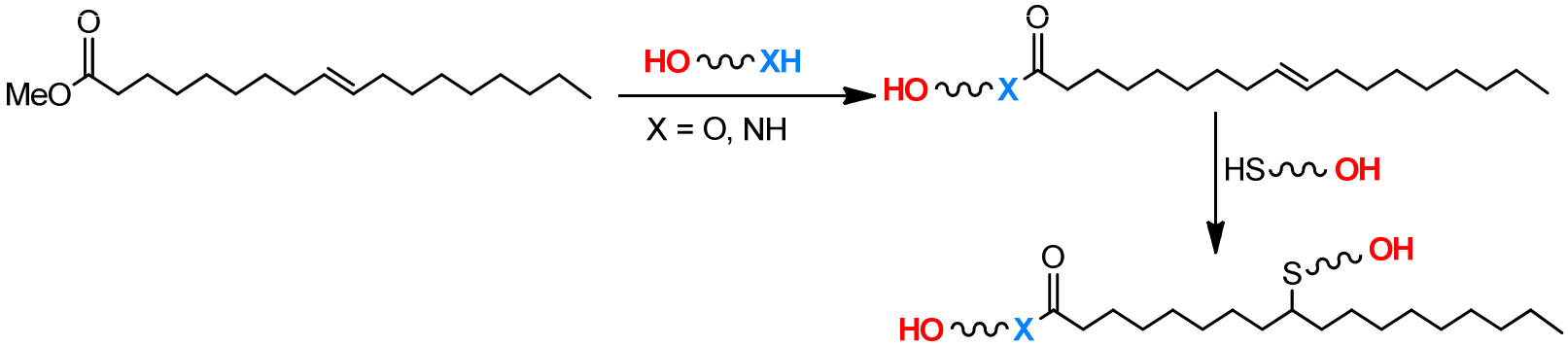


REACTIONS

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

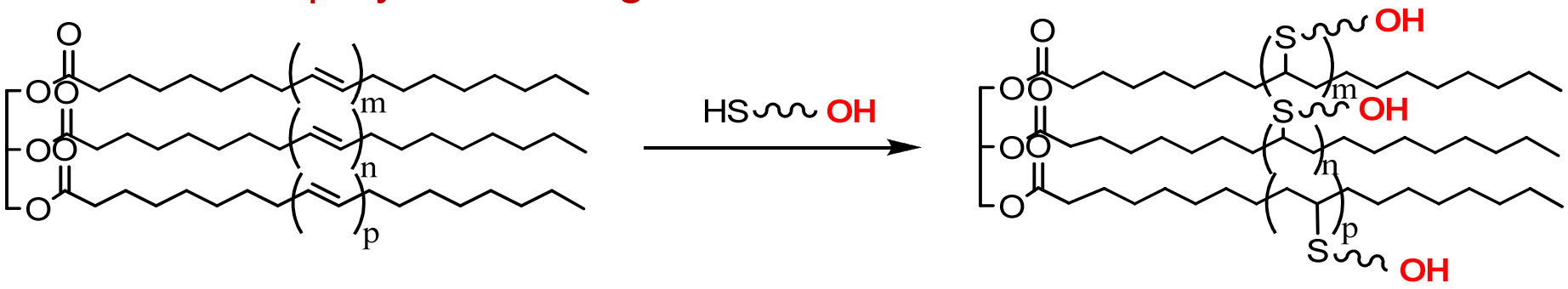


  - *Route 2* : diol from FAME

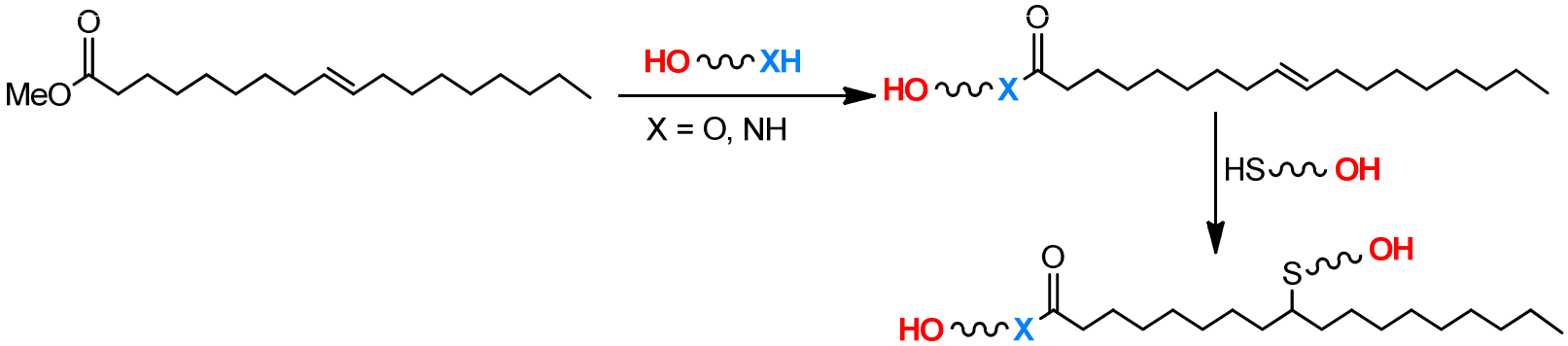


REACTIONS

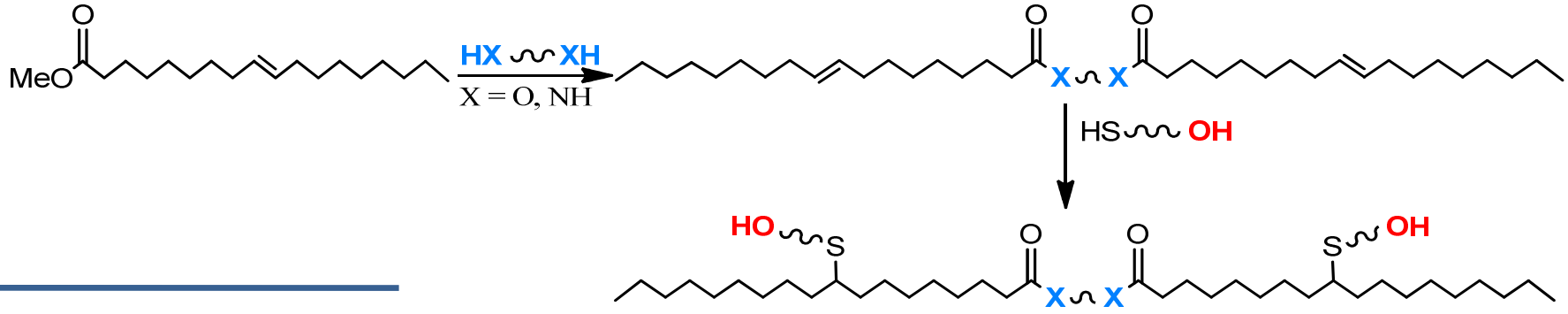
- **Reactants: rapeseed oils and oleic acid or oleic methyl ester**
  - *Route 1* : polyol from vegetable oil



  - *Route 2* : diol from FAME

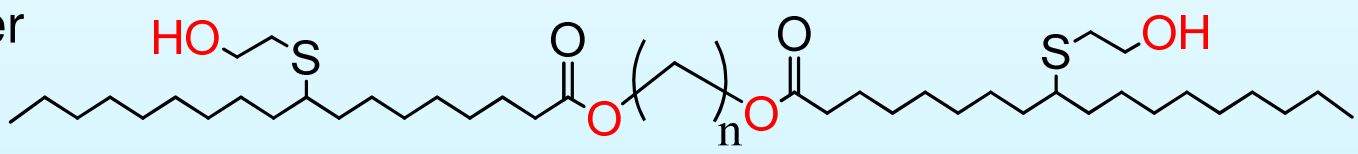


  - *Route 3* : diol dimers from FAME

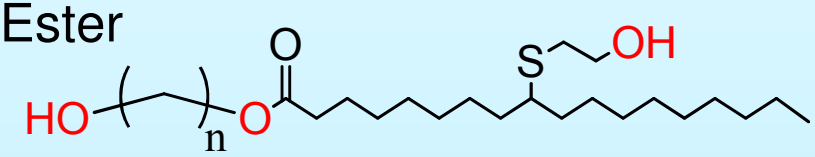


New biobased polyols from vegetable oils by TEC

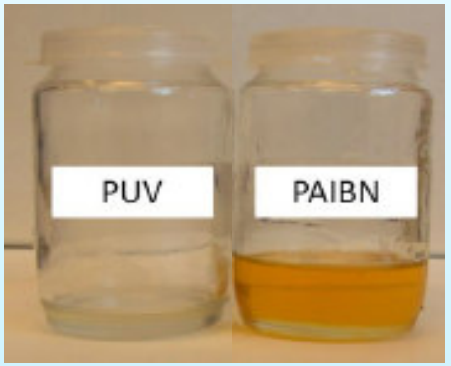
Diester



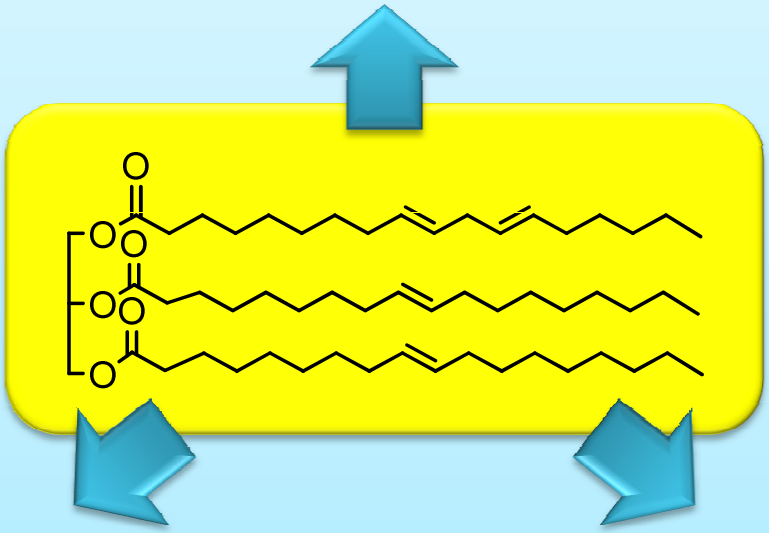
Ester



n= 2, 4, 6

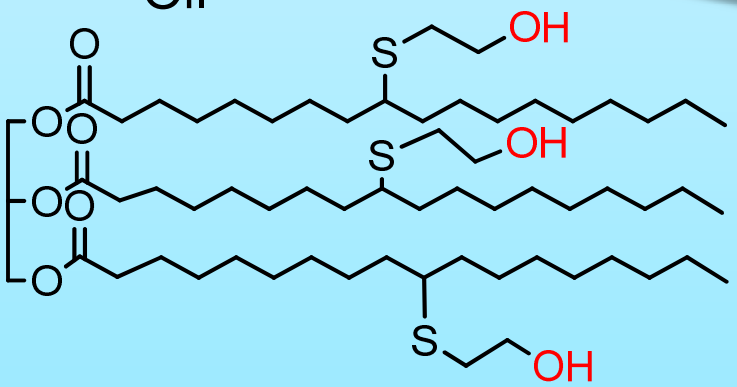


Photoinitiation
without photoinitiator
6h - UV, thiol/ene 3/1

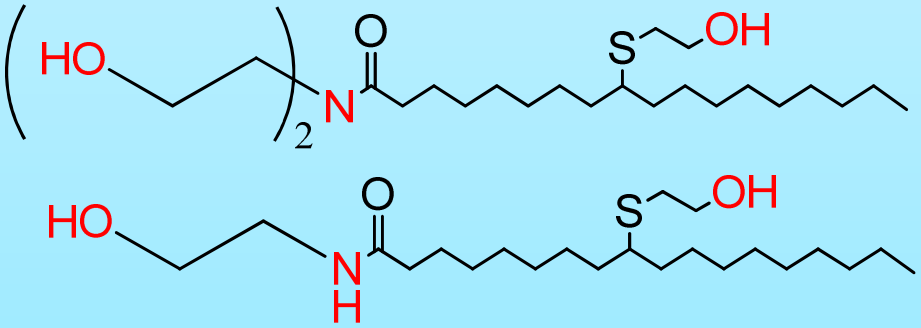


Thermal
AIBN
80°C, 8h, thiol/ene 3/1

Oil



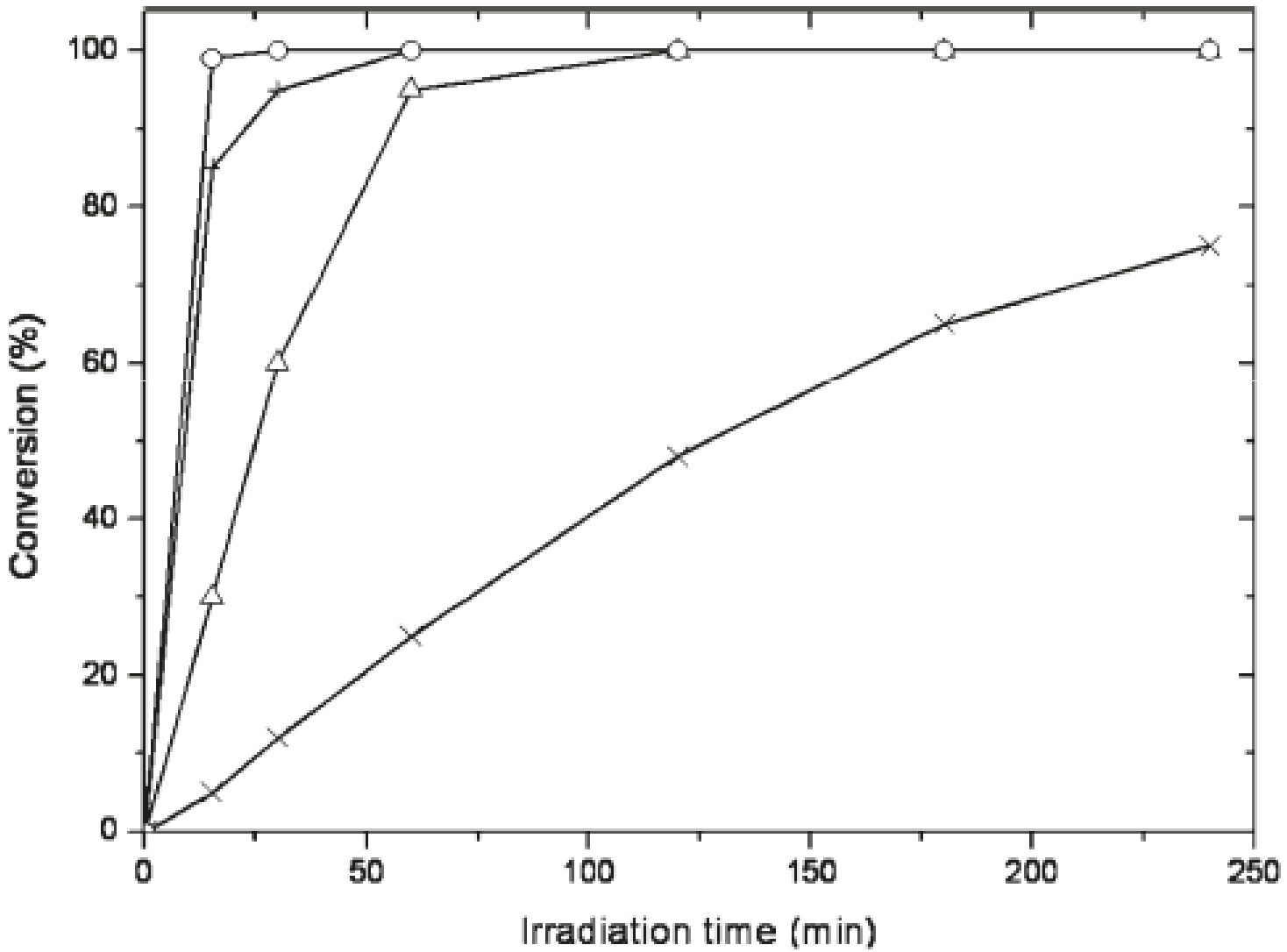
Amide



Patent CNRS, FR 1002738, 2010

Influence of ratio thiol/ene

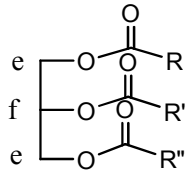
2-mercaptoethanol/oleic acid



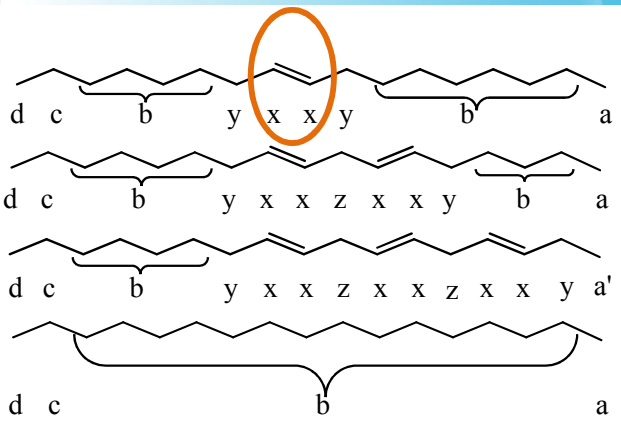
o : 5 / 1
+ : 3 / 1
Δ : 2 / 1
X : 1 / 1

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

Polyols : NMR ^{1}H analysis

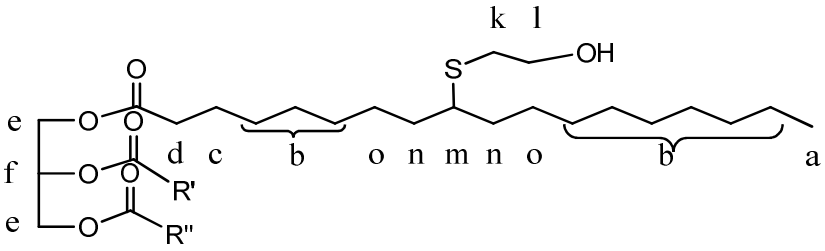


R,R',R"=



$CDCl_3$

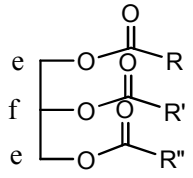
Oil before



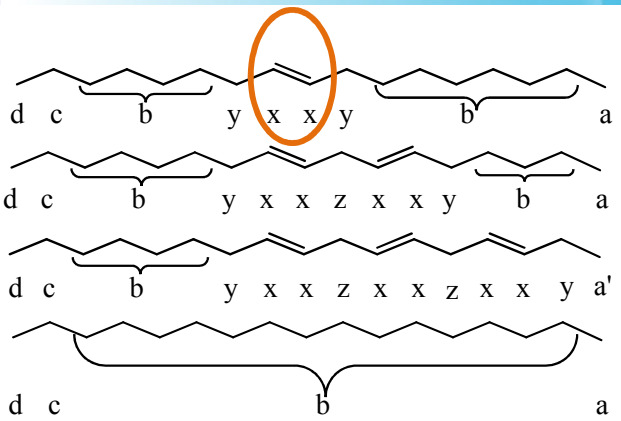
Oil after TEC

Total conversion of C=C

Polyols : NMR ^{1}H analysis

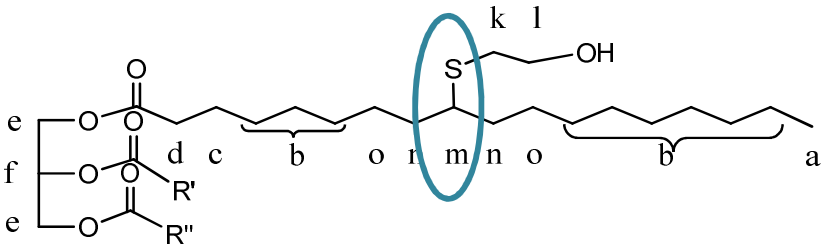


R,R',R"=



$CDCl_3$

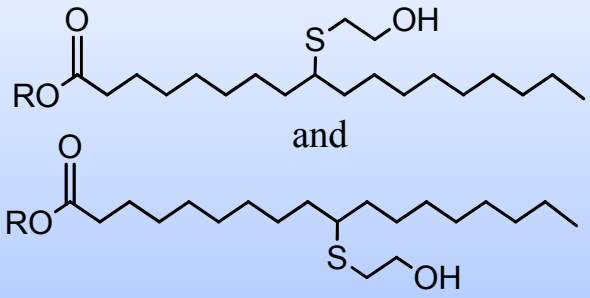
Oil before



Oil after TEC

Total conversion of C=C

Click chemistry !



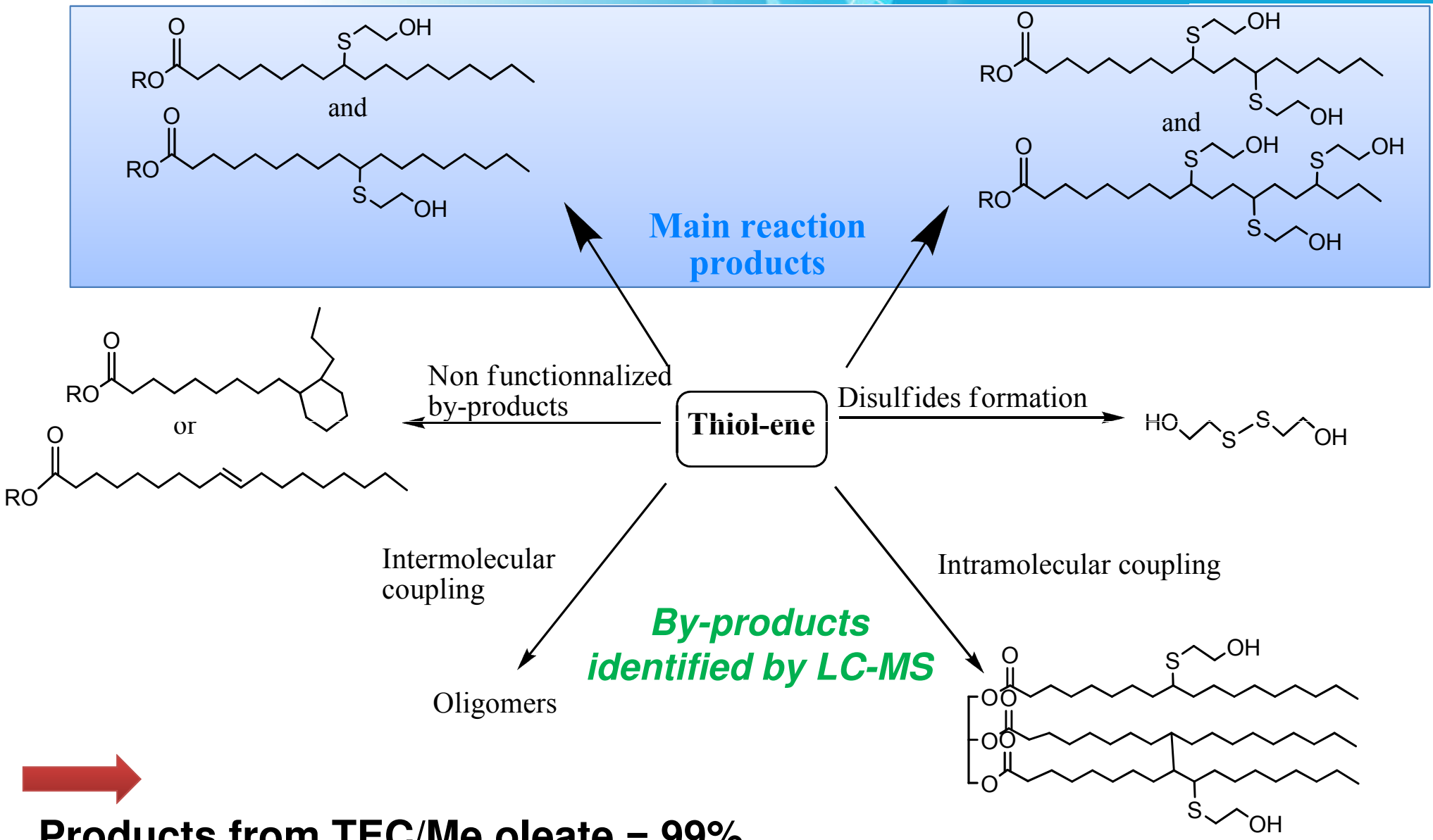
Main reaction products

Thiol-ene

Products from TEC/Me oleate = 99%

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

The limits to the "click" !

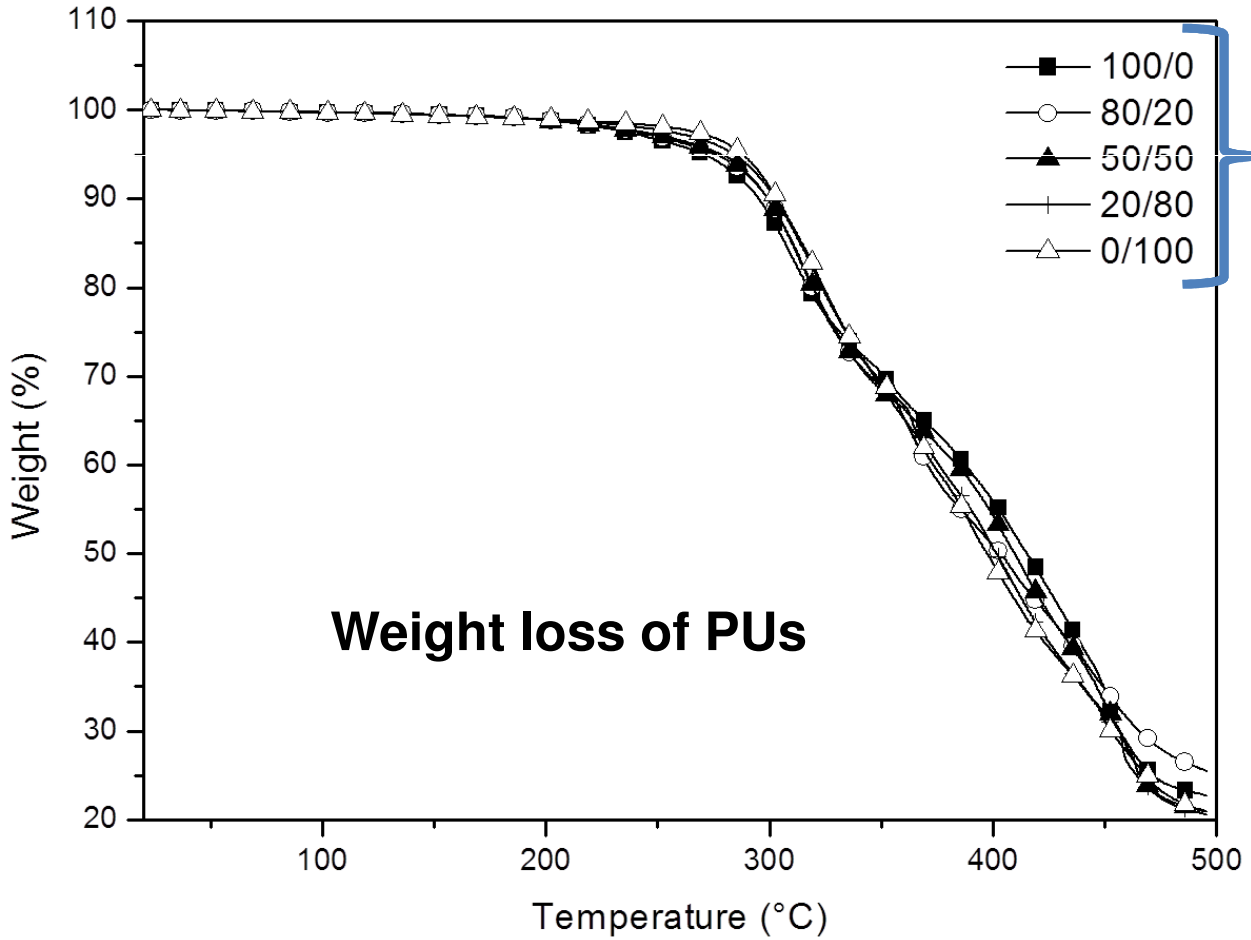


Products from TEC/Me oleate = 99%

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

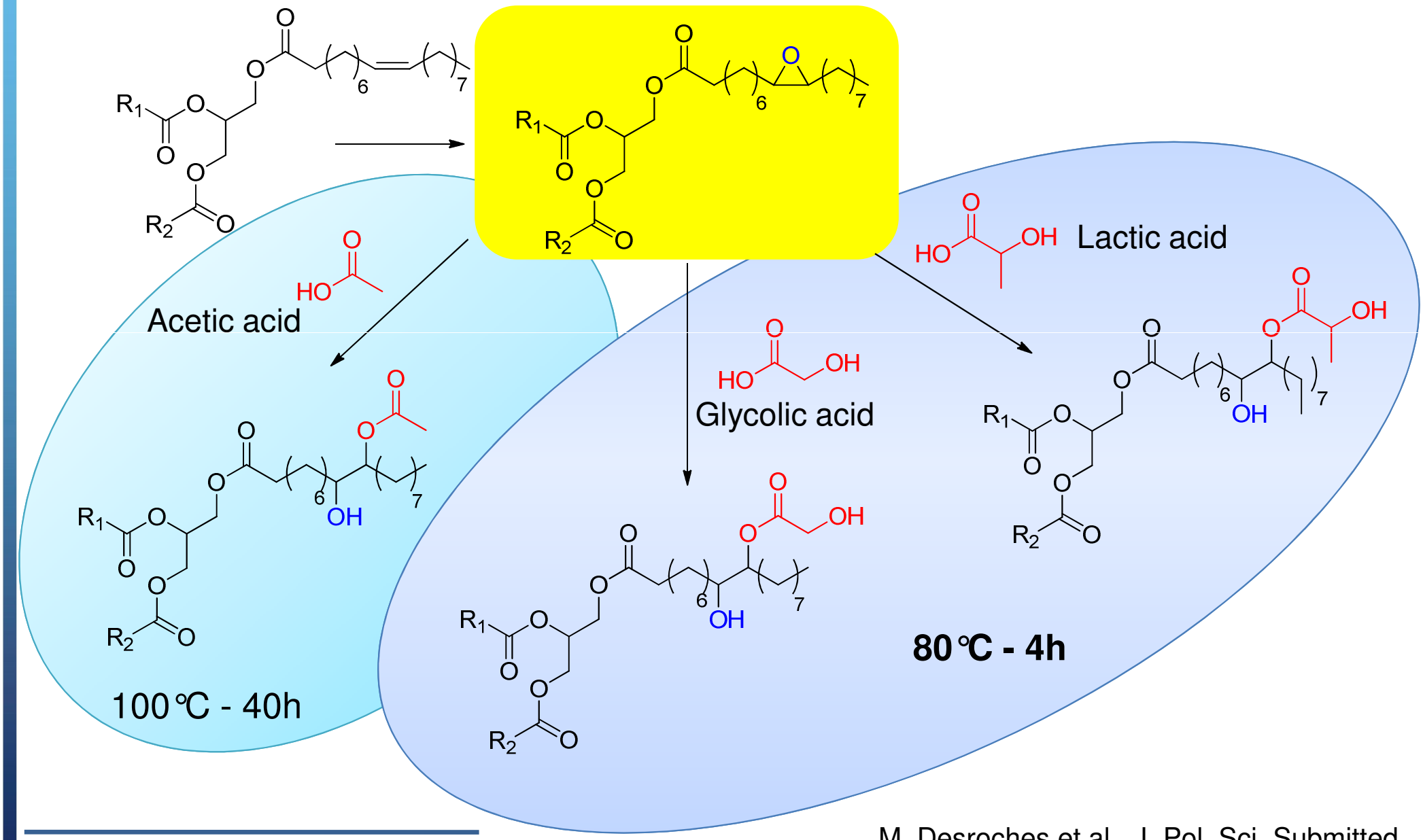
Thermal stability of PUs

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



Desmophen (PPG) / Polyol TEC

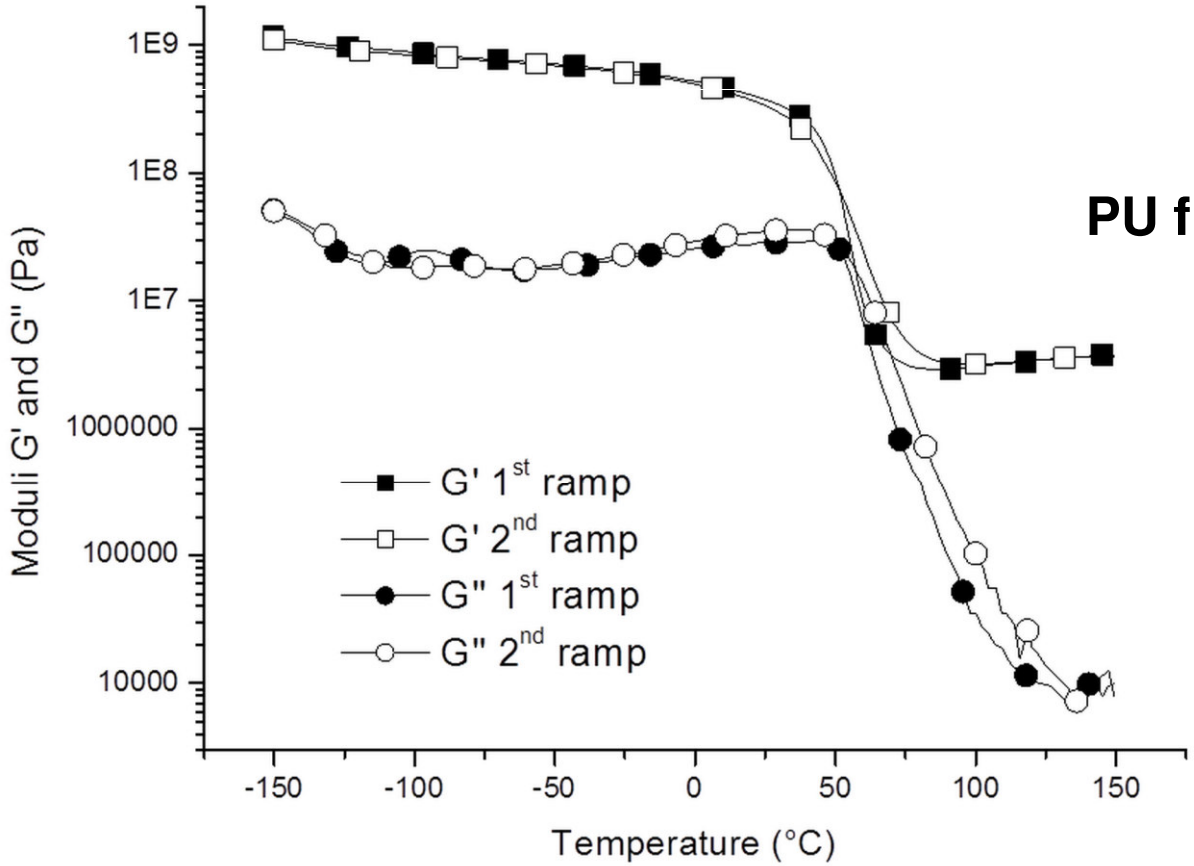
Part 3: New biobased polyols from epoxided vegetable oils



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

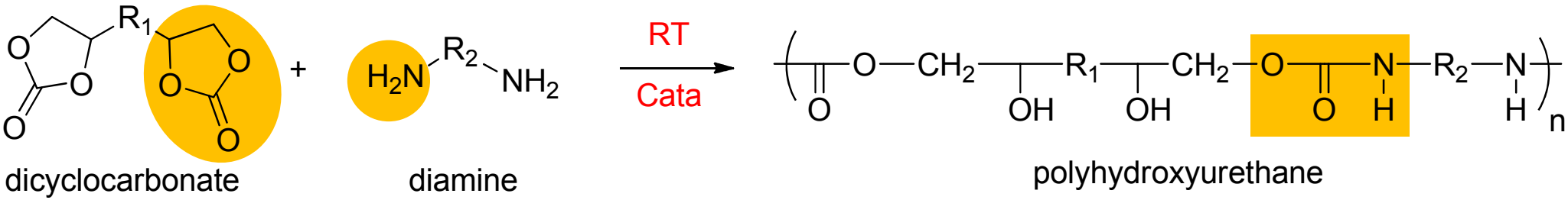
Part 3: New biobased polyols from epoxided vegetable oils

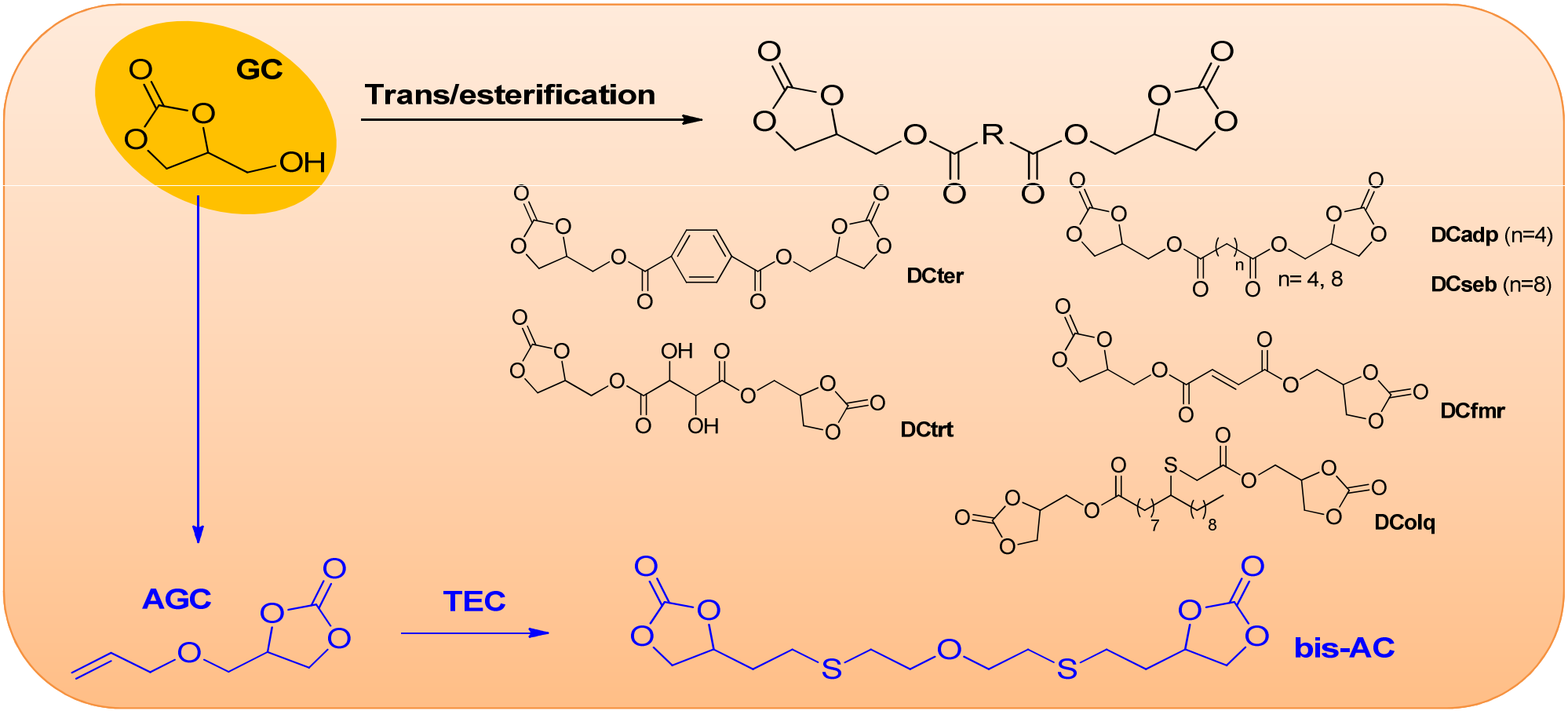
Polyol	F	Viscosity η_{polyol} (Pa.s)	Eq.wt. (g/eq)	Oligomers (%wt)	I_A (mg KOH/g)
Oil+lactic acid	5.3	47	328	44	3.6
Oil+glycolic acid	4.9	221	276	63	2.6
Oil+acetic acid	4.3	55	298	57	1.8



PU from Oil + Lactic Acid

Part 4: Non Isocyanate Polyurethanes





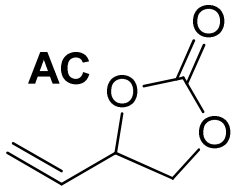
Patent SEG, CNRS FR1159818, 2011

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

Synthesis of dicyclocarbonates by thiol-ene

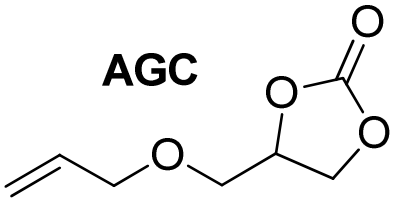
- **Two TEC-cyclocarbonates**

Commercial ⬅ **AC**



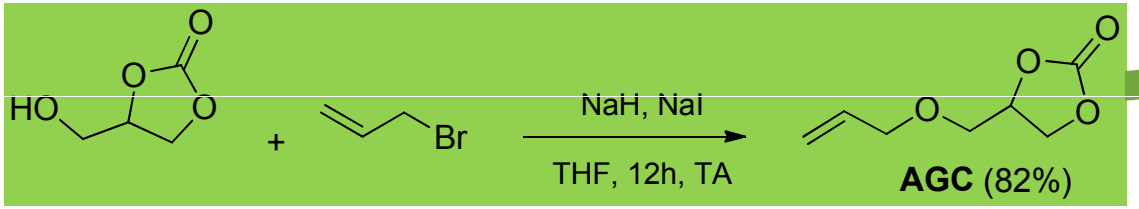
4-vinyl-1,3-dioxolan-2-one

AGC

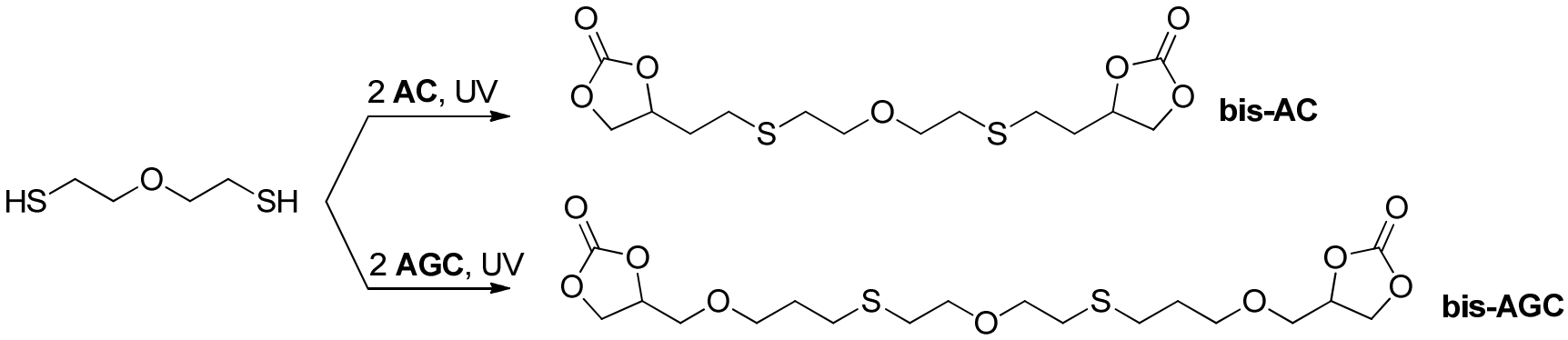


4-((allyloxy)methyl)-1,3-dioxolan-2-one

➡ **Synthesized**

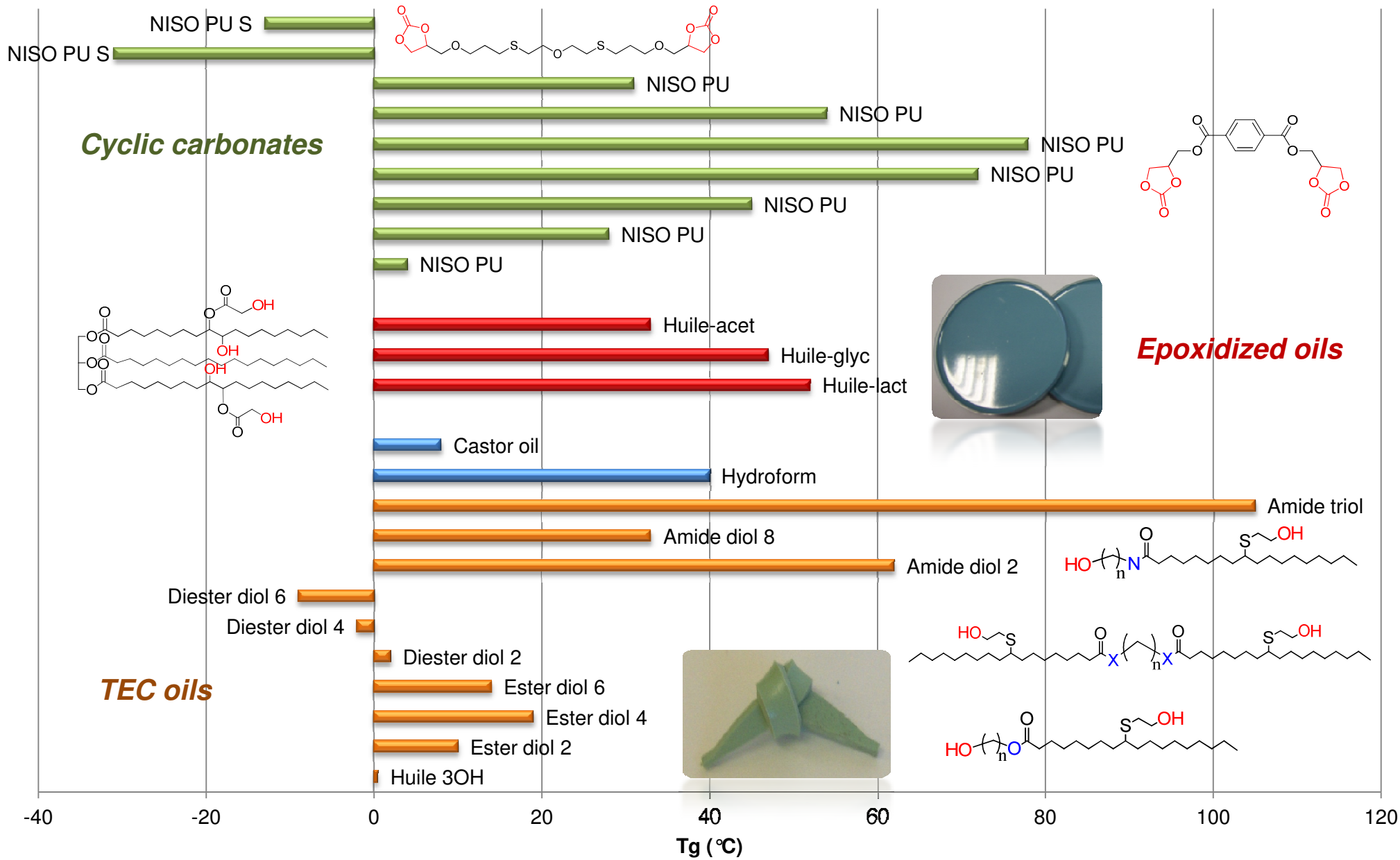


- **Synthesis of cyclic carbonates by thiol-ene coupling / UV**



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

Polyurethanes materials polyol/MDI or cyclocarbonate/amine

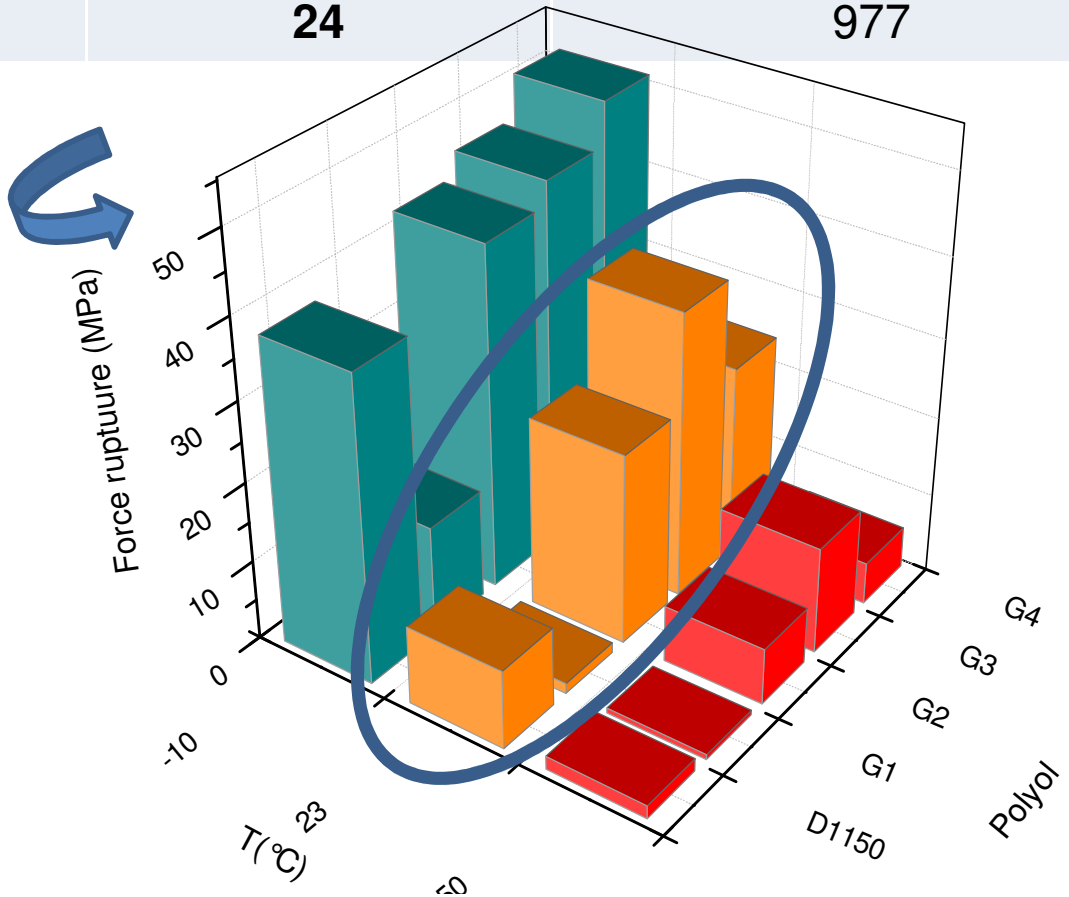


MDI : diphénylméthylène 4,4'-diisocyanate

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

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RÉSIPOLY CHRYSOR

SEG DIÉLECTRIQUES

THANK YOU FOR ATTENTION