Functionalization of vegetable oils and their derivatives for new bio-based polyurethane coatings

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- **Supervisors**
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- **Financial support**
  ANR Greencoat
- **Collaboration**
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  SEG Dielectriques

INTRODUCTION

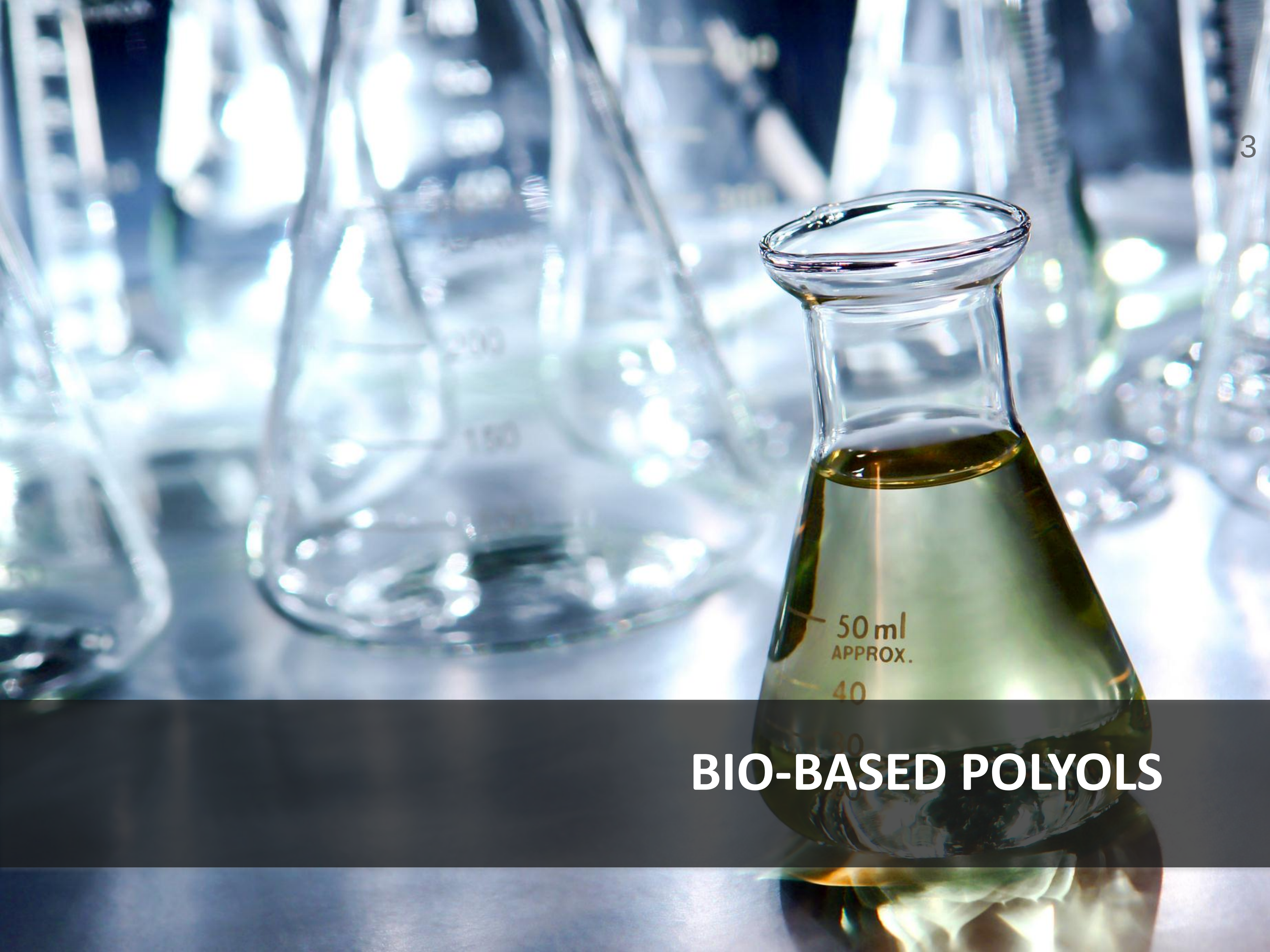
Strategies

Precursors From oils

Partially bio-based PU

Isocyanate free PU

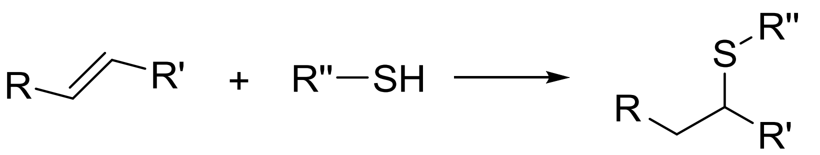
- **Raw material**
  Vegetable oils
  Glycerin carbonate
- **PU from biobased polyols**
  polyol + isocyanate
- **PU from cyclocarbonates**
  cyclocarbonate + amine



BIO-BASED POLYOLS

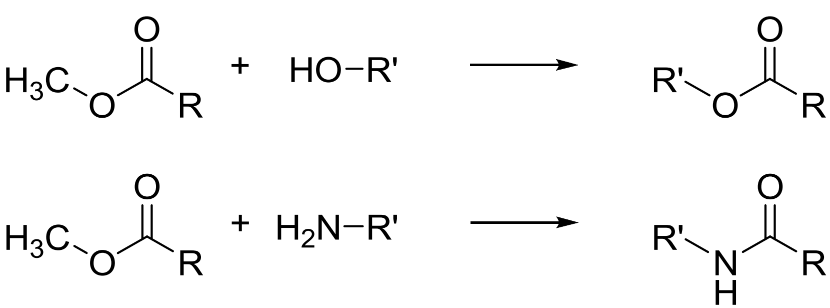
TOOL BOX

Vegetable oils hydroxylation



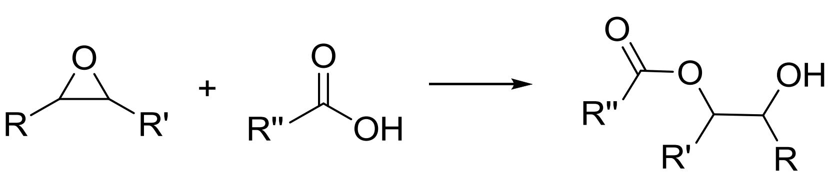
Thiol-ene

« Click chemistry »
Primary alcohol in one step



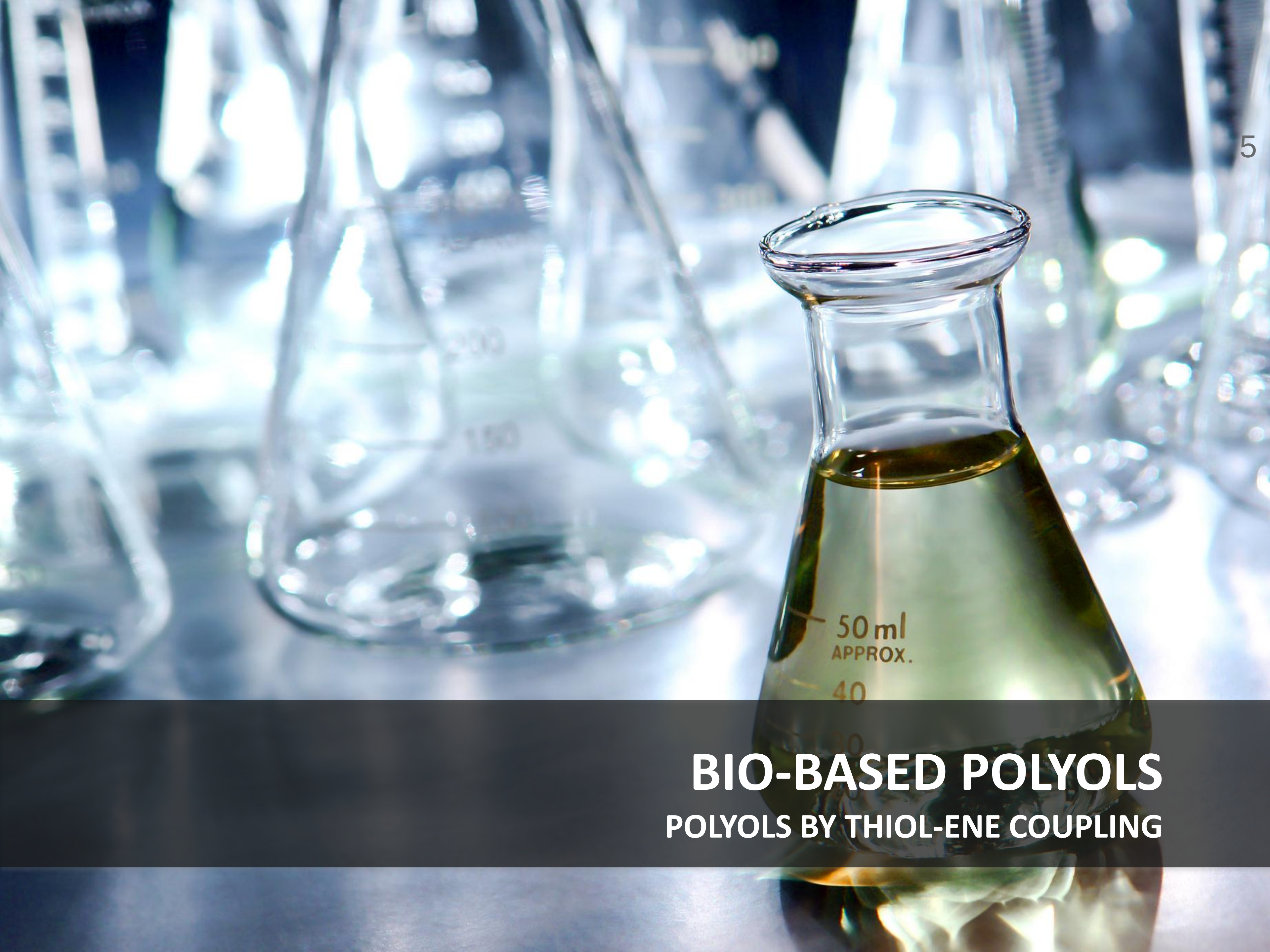
Trans-esterification / Amidification

Range of precursors
Good yields



Epoxy ring opening

No thiol
Bio-based reagents



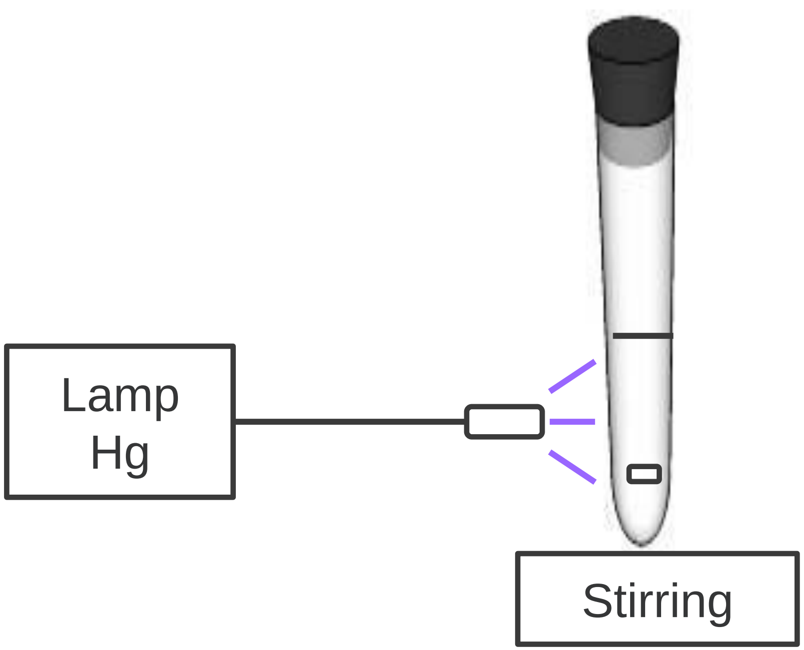
BIO-BASED POLYOLS

POLYOLS BY THIOL-ENE COUPLING

POLYOL IN ONE STEP

Protocole

Vegetable oil
+ $HS(CH_2)_2OH$



Photochemical synthesis

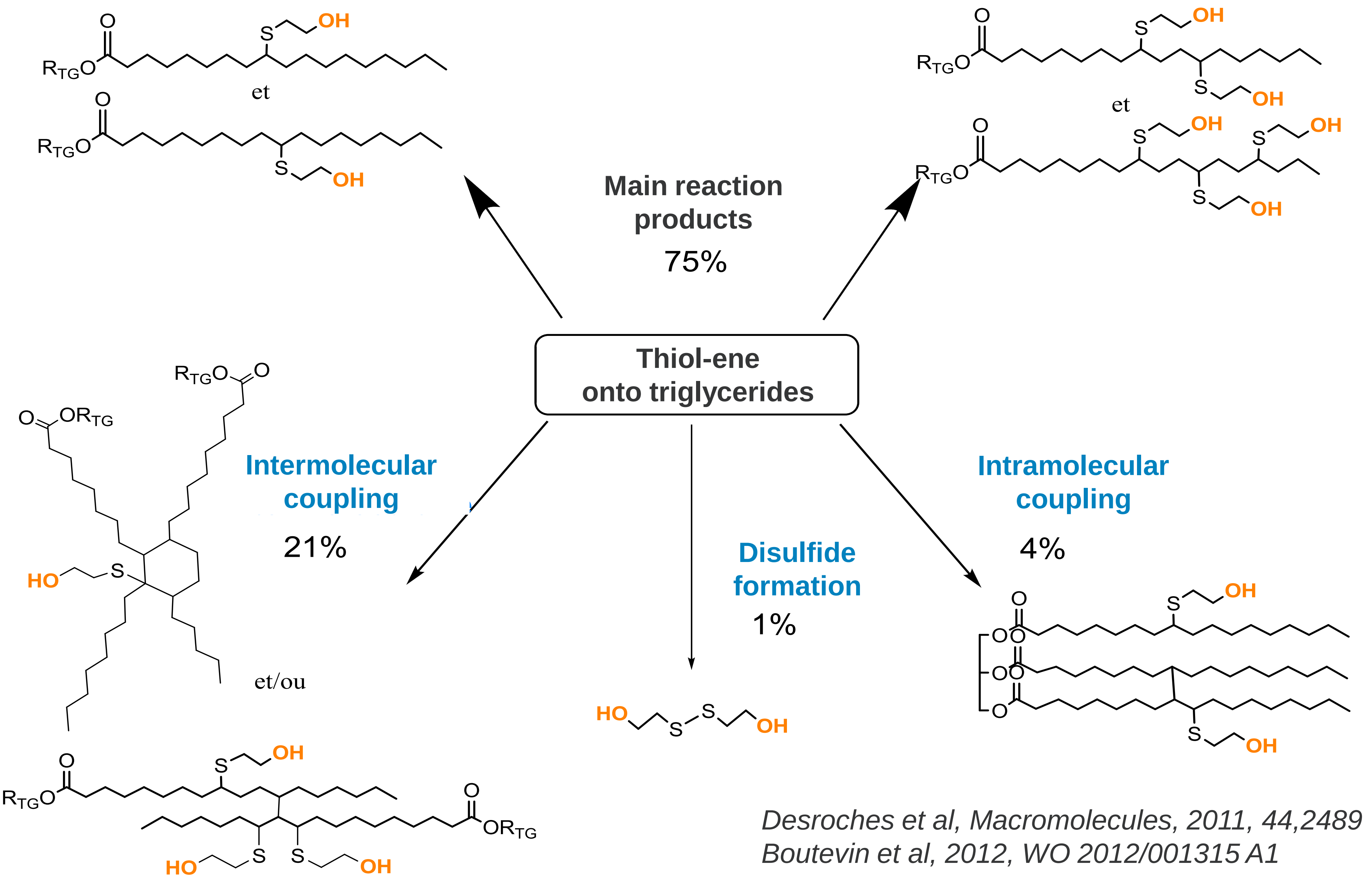
UV intensity 15W/cm^2
Initiator free
Solvent free
Thiol excess
Purification

Thermal synthesis

Radical initiator
Mild temperature 60ºC
Solvent free
Thiol excess
Purification

POLYOL IN ONE STEP

"Click chemistry" but...



Desroches et al, Macromolecules, 2011, 44,2489
Boutevin et al, 2012, WO 2012/001315 A1

POLYOL IN ONE STEP

To Pilot scale

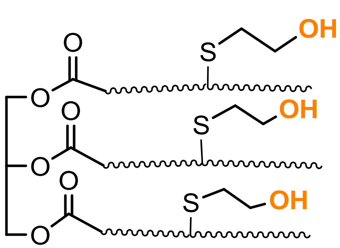
Thermal synthesis 2 kg

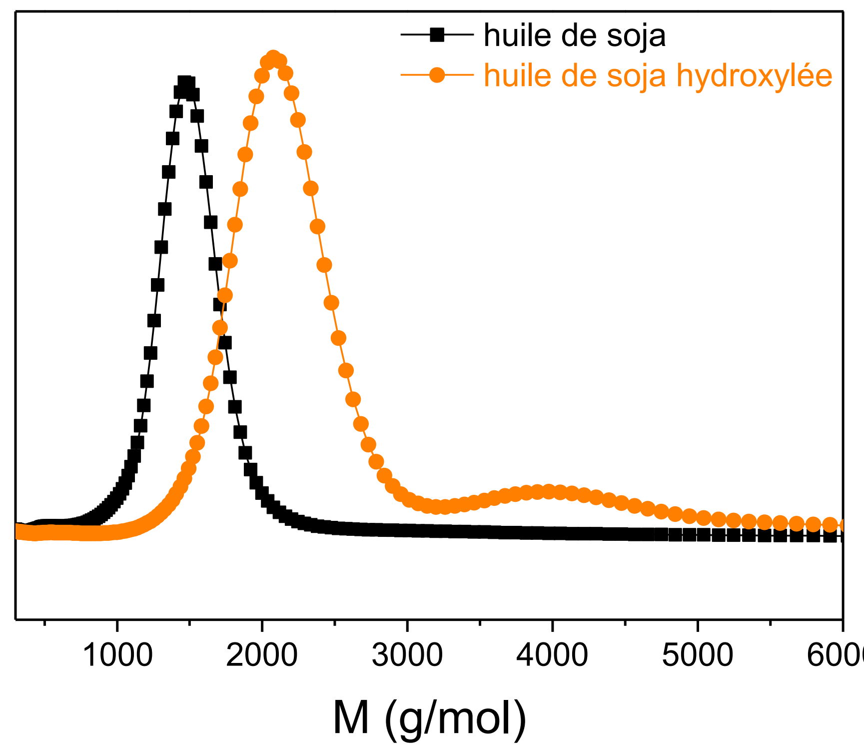
initiator : AIBN
75ºC
Thiol / double bonds ratio : 2/1
Liquid-liquid extraction

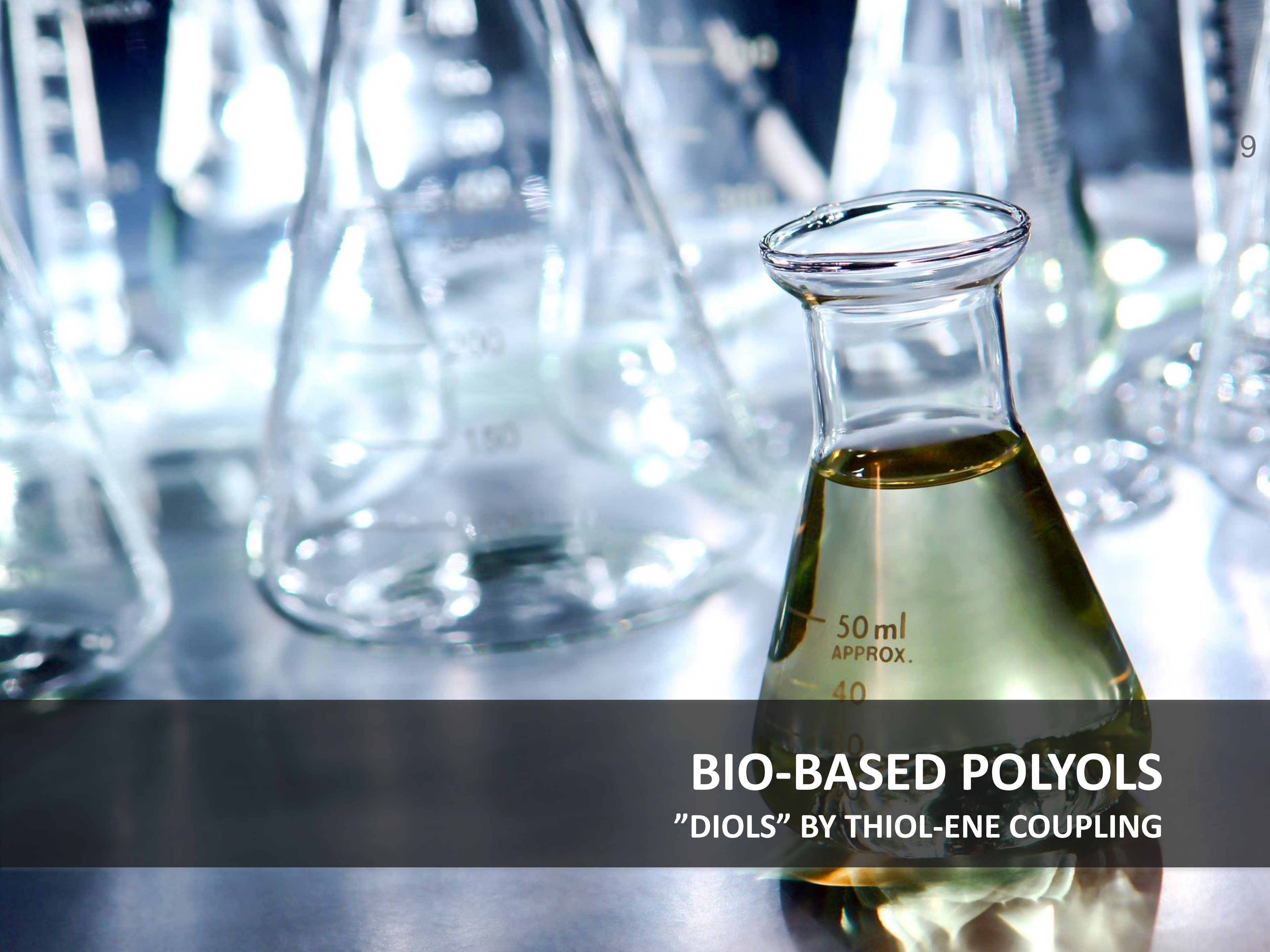
SPECIFIC POLYMERS

TEP properties:

f_m	3
Viscosity	3 Pa.s
Oligomers	21 %wt. (GPC THF)







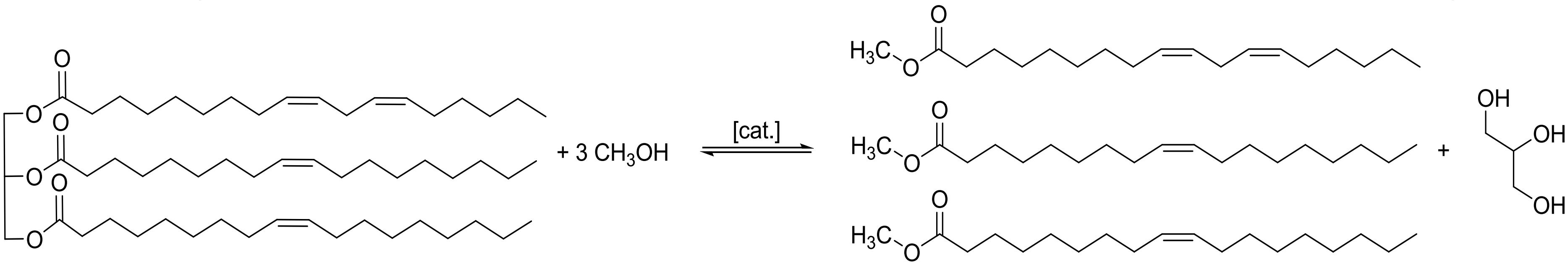
BIO-BASED POLYOLS

”DIOLS” BY THIOL-ENE COUPLING

"DIOLS" SYNTHESIS

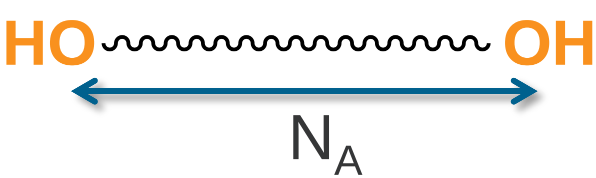
Methyl esters

Vegetable oils | Esters | Glycerin



Diol synthesis based on the ester mixture

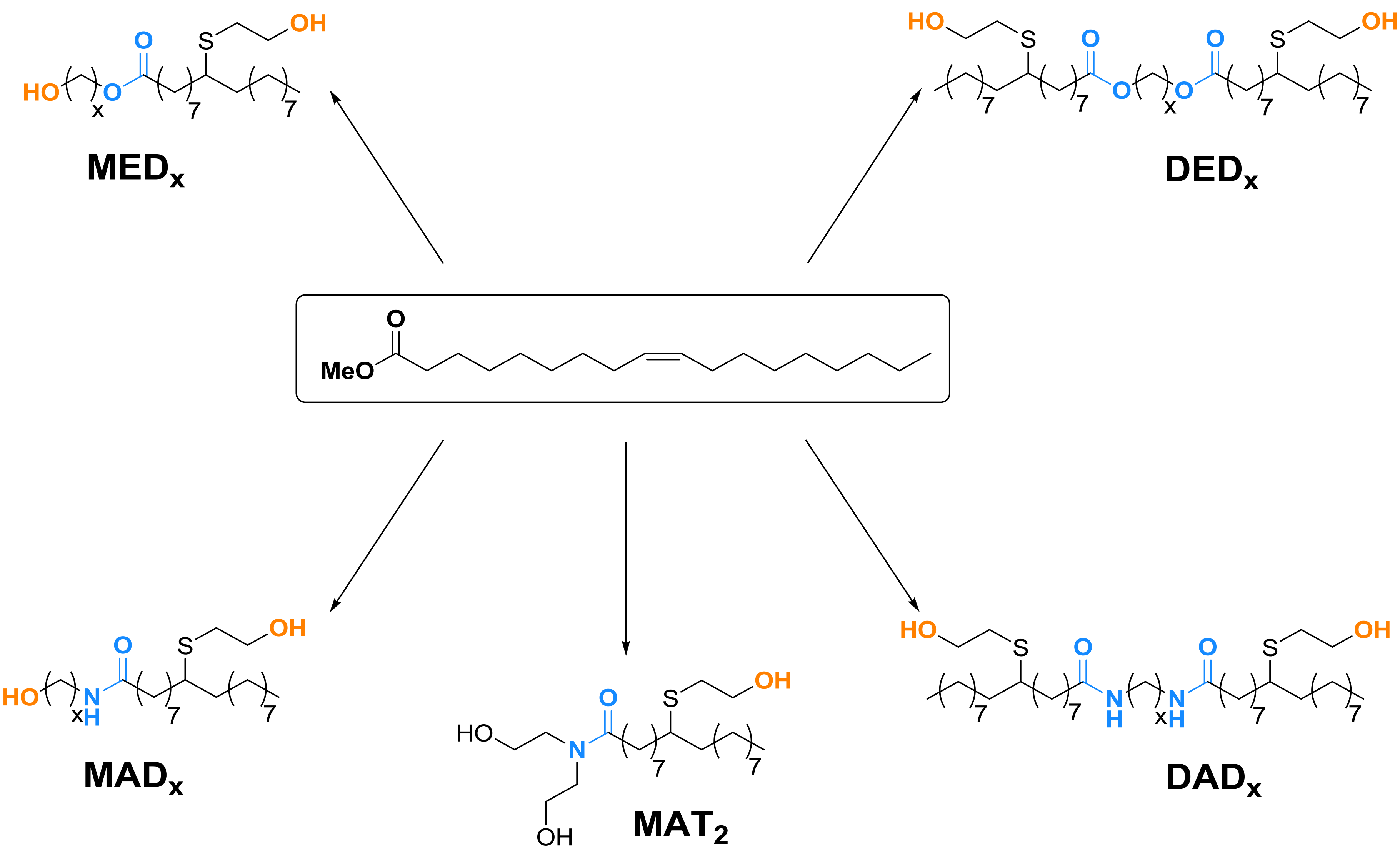
- ester/amide functions
- different number of atoms between the OH functions



« Biodiesel »

"DIOLS" SYNTHESIS

Several precursors



Desroches et al, EJLST, 2012,114, 1, 84

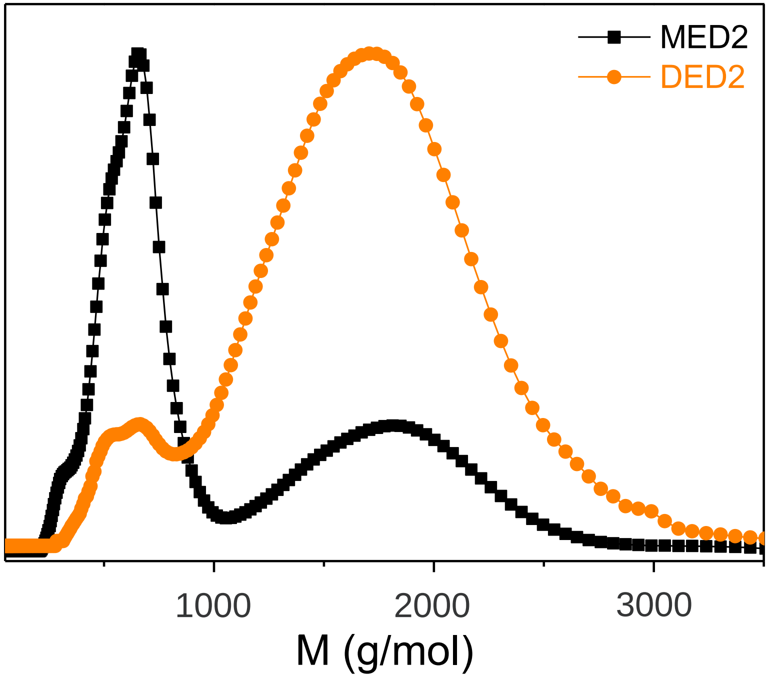
"DIOLS" SYNTHESIS

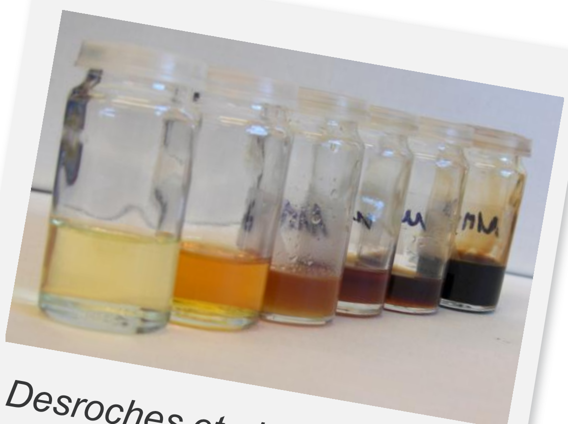
Protocole

Esterification 100 °C, cat. APTS, 7h
yield > 95%mol

Amidification 100 °C, 48h
yield > 98%mol

Thiol-ene coupling 60 °C, AIBN, 8d
yield > 98%mol

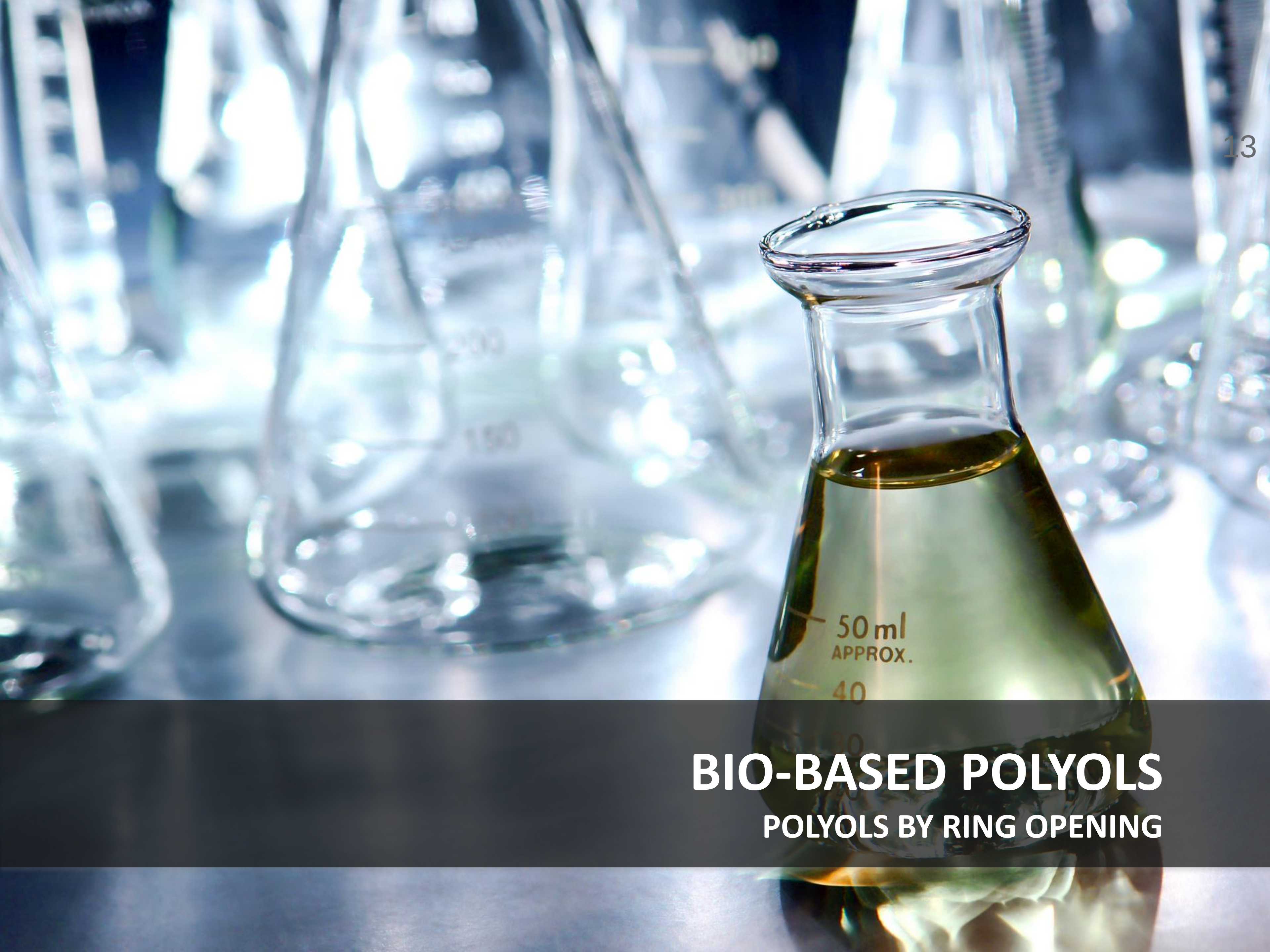




Desroches et al, Polym Chem, 2012, 3, 450

By produts

Monoesters/diesters = 20 %wt
Amides = n.d.
Oligomers due to thiol-ene coupling ≈ 5 %wt

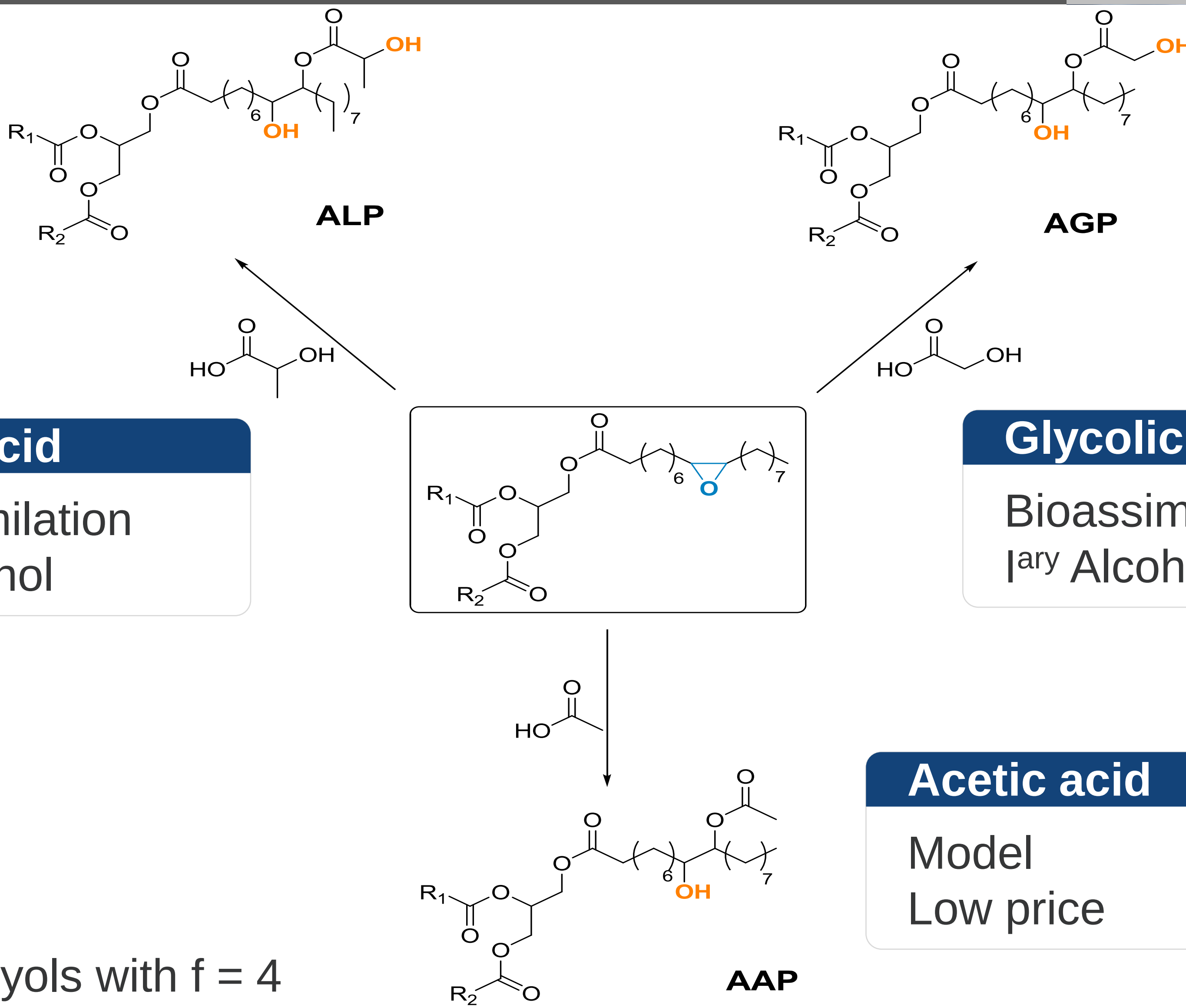


BIO-BASED POLYOLS

POLYOLS BY RING OPENING

EPOXYDIZED OILS

Bio-based carboxylic acids



Lactic acid

Bioassimilation

II^{ary} Alcohol

Glycolic acid

Bioassimilation

I^{ary} Alcohol

Acetic acid

Model

Low price

→ Polyols with f = 4

EPOXYDIZED OILS

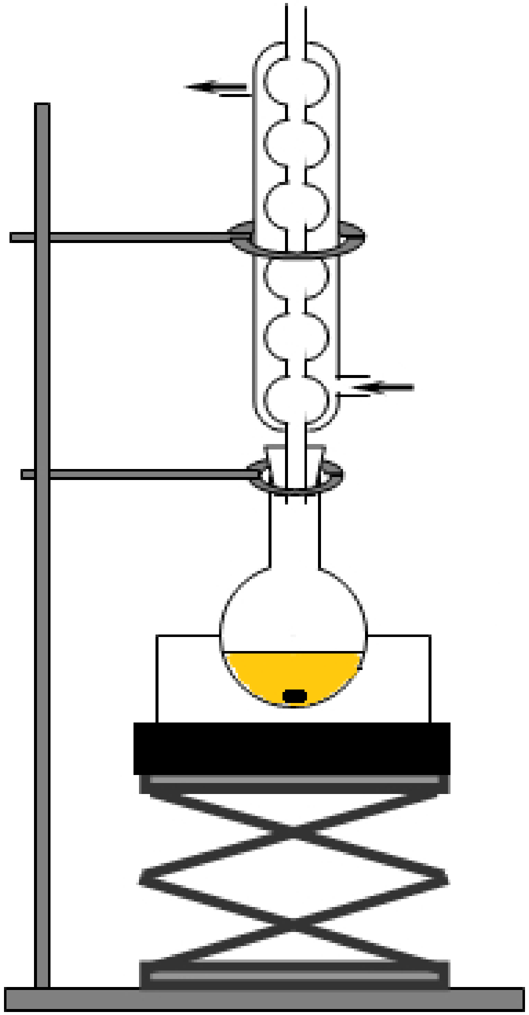
Protocole

Lactic & glycolic acids

Acid/epoxy ratio = 2/4
80 °C, 4h
Solvent free
Initiator free
Extraction

Acetic acid

Acid/epoxy ratio = 5/4
100 °C, 40h
Solvent free
Initiator free
Extraction



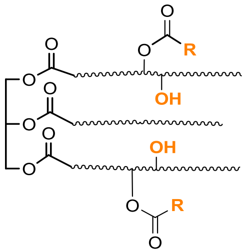
→ Extrapolation 1 kg

Specific Polymers

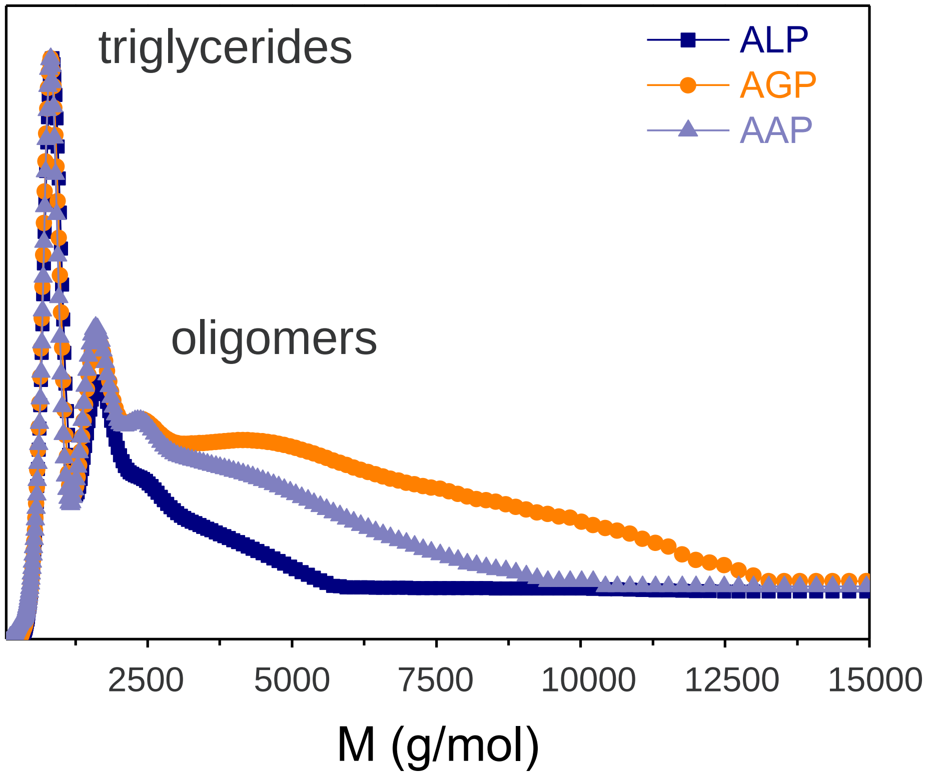
EPOXYDIZED OILS

Side reactions

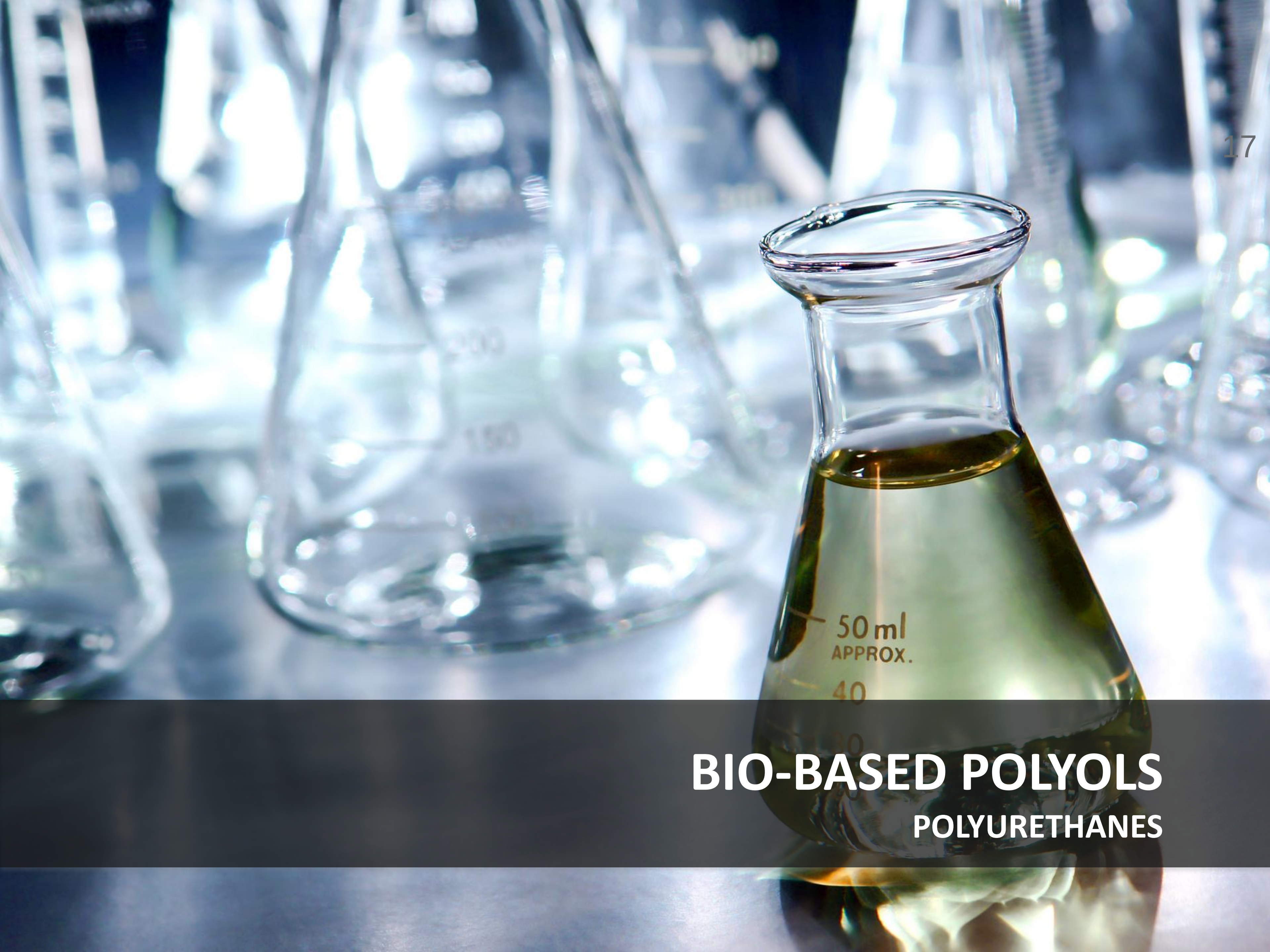
Polyol	ALP	AGP	AAP
f_m	5,3	4,9	4,3



Conclusion : $f > f_{théo}$ due to oligomers (GPC THF – RI detection)



Desroches et al, J Pol Sci, submitted



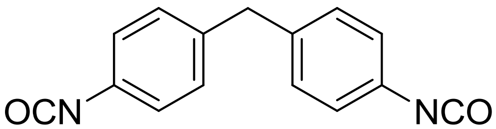
BIO-BASED POLYOLS

POLYURETHANES

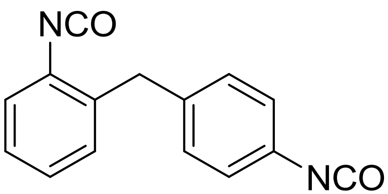
PU SYNTHESIS

Protocole

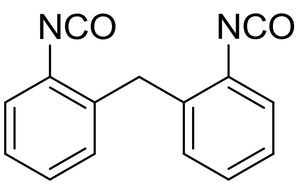
Hardener Voramer 2093 : MDI prepolymer, mixture



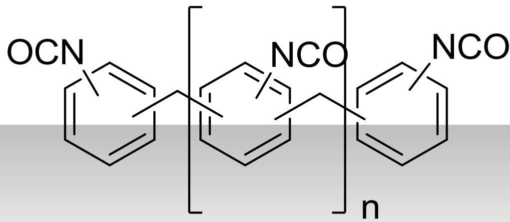
4,4'-MDI



2,4'-MDI

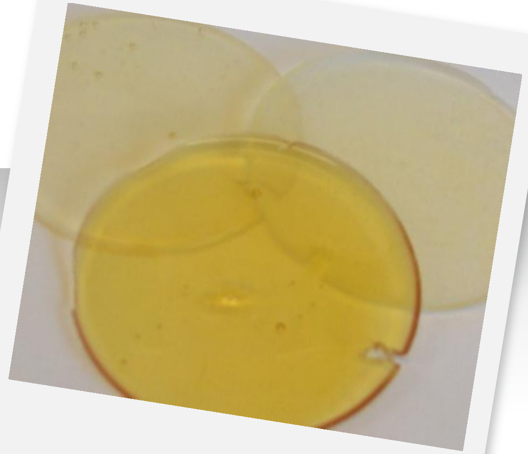


2,2'-MDI



oligoisocyanates

n = 1,2,3...



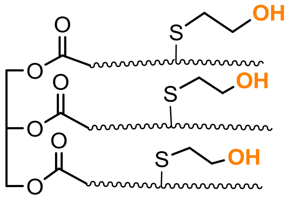
PU samples

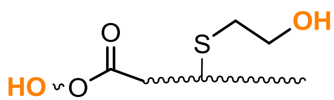
NCO/OH ratio ≈ 1,05

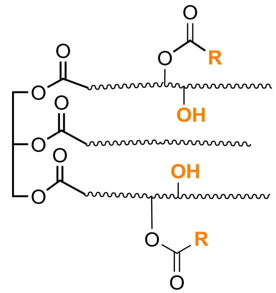
Cross-linking Room temperature
Catalyst free

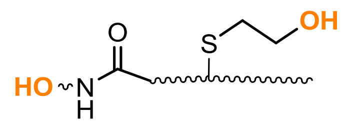
PU SYNTHESIS

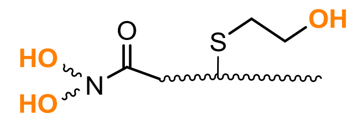
Tg determination - DSC











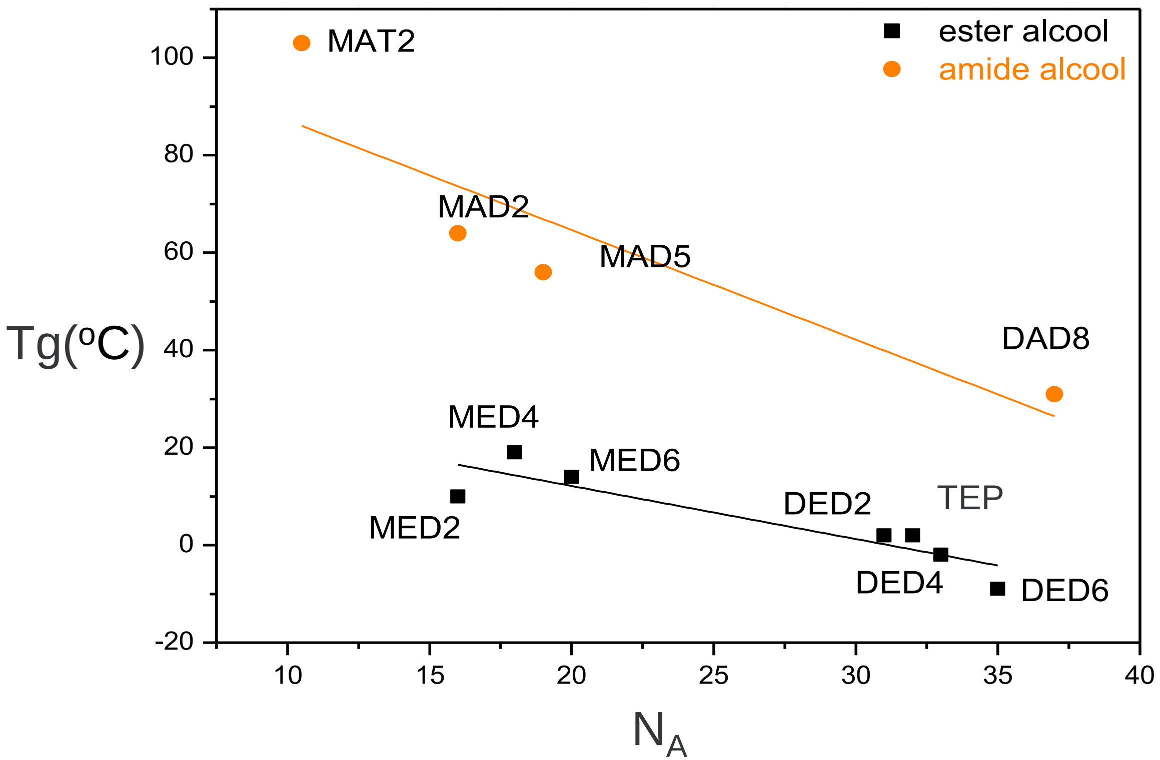
	PU-DED$_x$ PU-TEP	PU-MED$_x$	PU-ALP PU-AGP PU-AAP	PU-MAD$_x$	PU-MAT$_2$
Tg	0 ºC	20 ºC	45 ºC	60 ºC	100 ºC

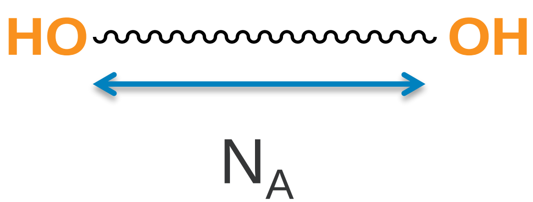
Glass transition temperature parameters

Amide function

Cross-linking density

Tg determination - DSC





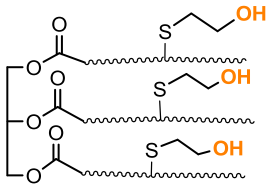
Glass transition temperature parameters

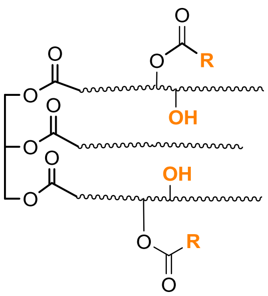
Amide function
Cross-linking density
Distance between alcohol functions

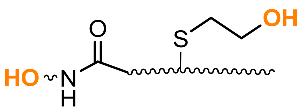
PU SYNTHESIS

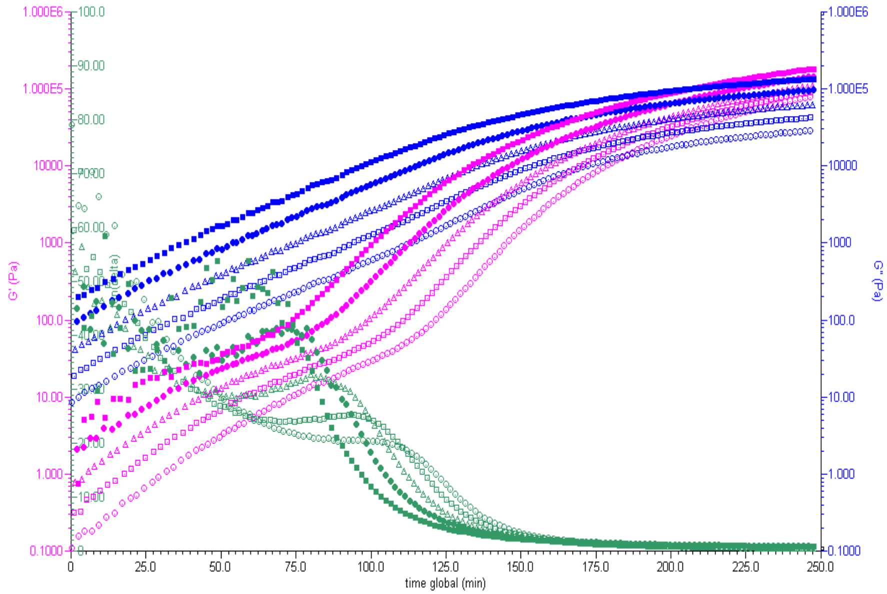
Rheology – gel time

Polymer	Gel time 20°C (min)
PU-TEP	170
PU-ALP	490
PU-AGP	370
PU-AAP	690
PU-MAD2	45









→ Fast and exothermic cross-linking of TEP/AP
Catalysis of alcohol/isocyanate reaction by amide*

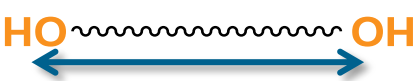
**Arnold et al, Chem Rev, 1957, 57, 47*
Sato et al, JACS, 1960, 82, 3893

PU SYNTHESIS

Summary

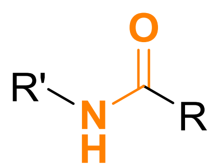
1 Distance OH

Tg ↘
Hardness Shore ↘
Swelling rate ↗



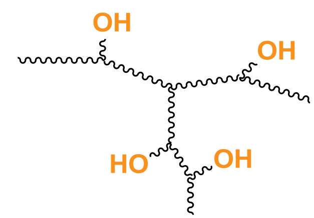
2 Amide function

Tg ↗
Reaction time ↘



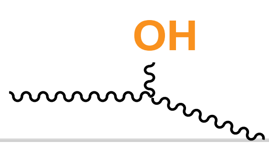
3 Functionality

Tg ↗
Swelling rate ↘



4 OH type

Reaction time ↘
Exothermic ↗



5 Functionalisation

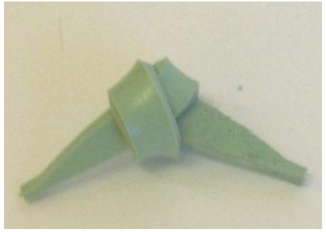
Thiol-ene : soft PU

Epoxy/acid : hard PU

FORMULATIONS

From soft to hard PU

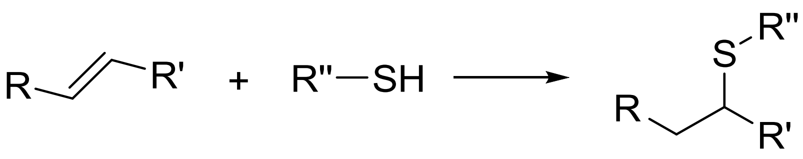
PU	M-TEP	M-ALP
Tg (°C)	**2**	**45**
Hardness Shore	59 (A)	80 (D)
$T_{d5\,\%}$ air (°C)	240	290
Char 500 °C air (%)	35	48
ε_R 23 °C (%)	**70**	2
σ_R 23 °C (MPa)	2	660
E 23 °C (Pa)	5	**2450**
F_{PU}(%wt)	11	40



ISOCYANATE FREE POLYURETHANES

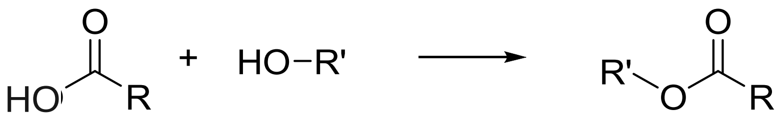
TOOL BOX

Cyclocarbonate dimers



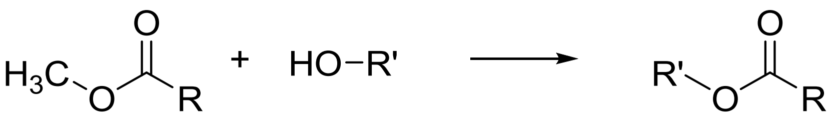
Thiol-ene coupling

« Click chemistry »
Formation of thioethers/ethers



Esterification

No thiol
Range of monomers



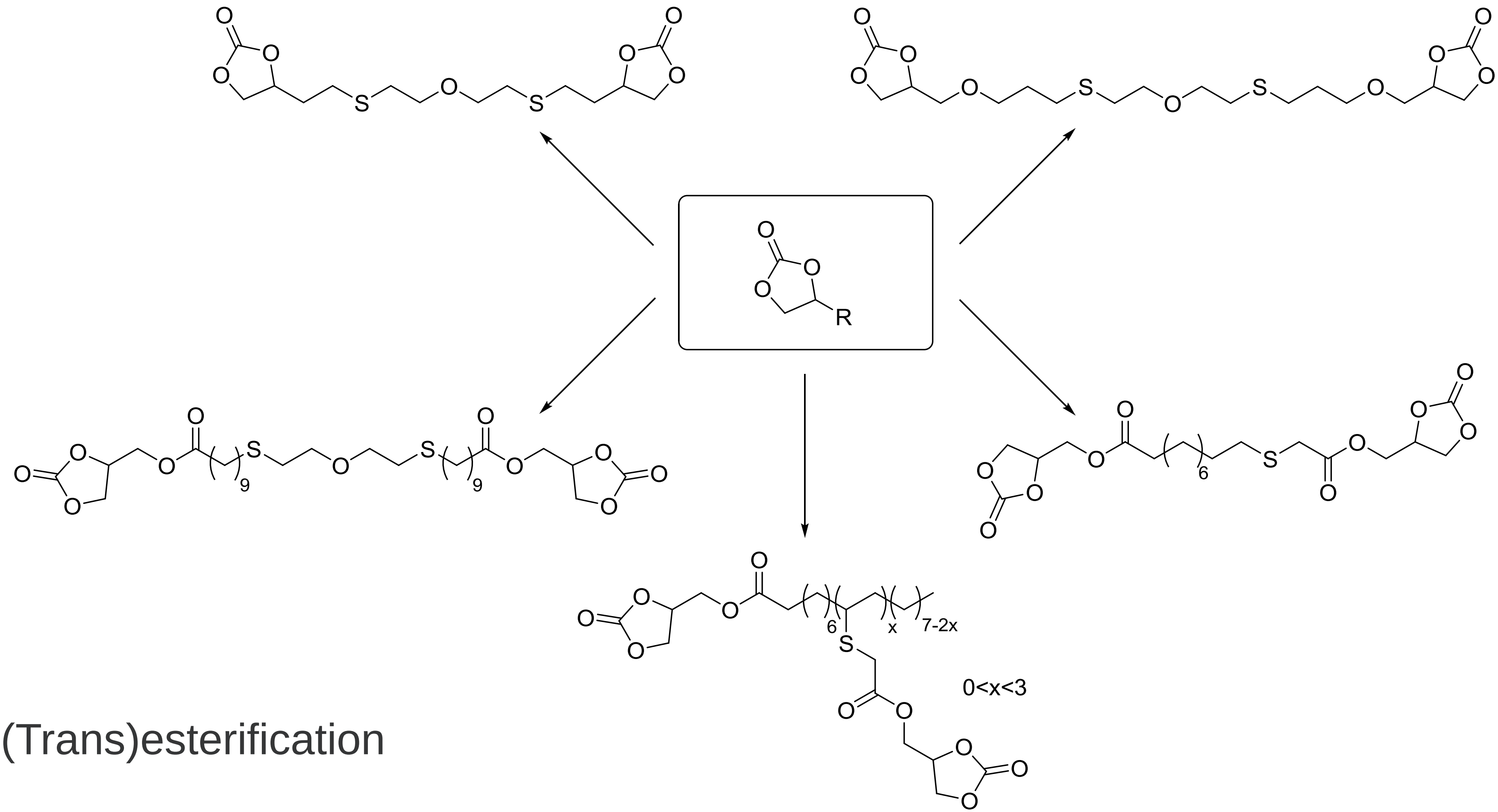
Trans-esterification

No thiol
Mild conditions

DICYCLOCARBONATES

Different precursors

Thiol-ene coupling

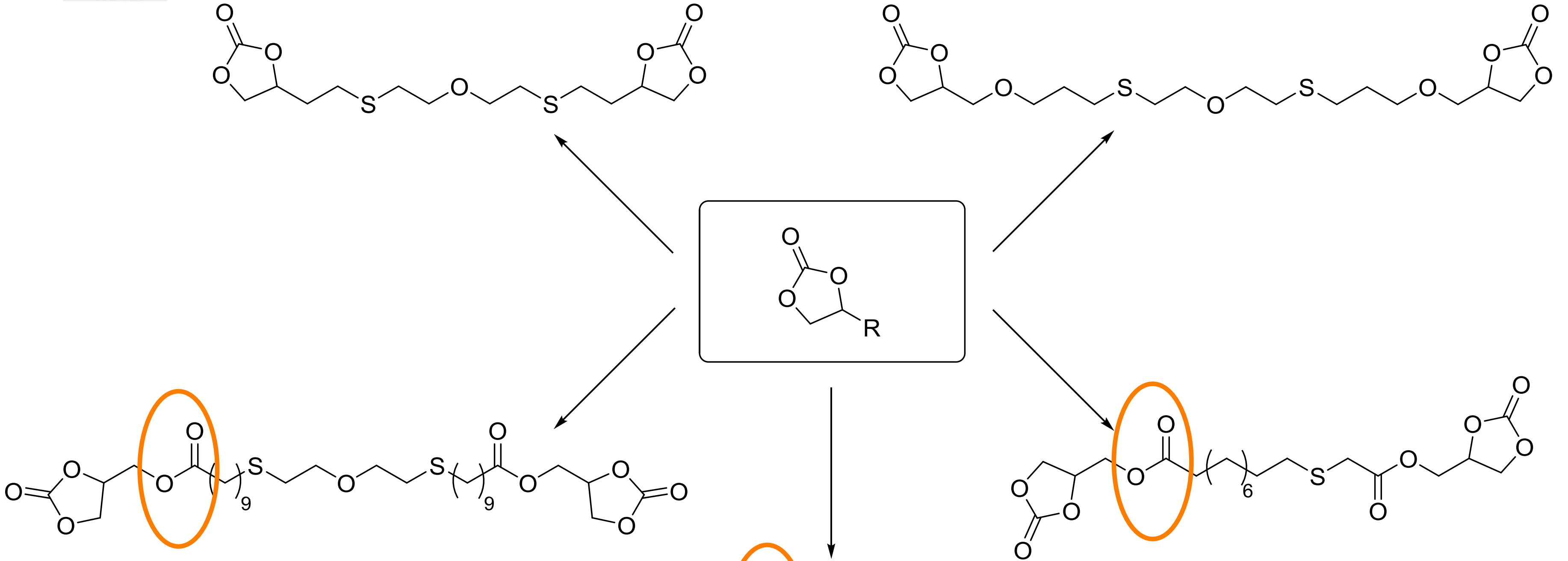


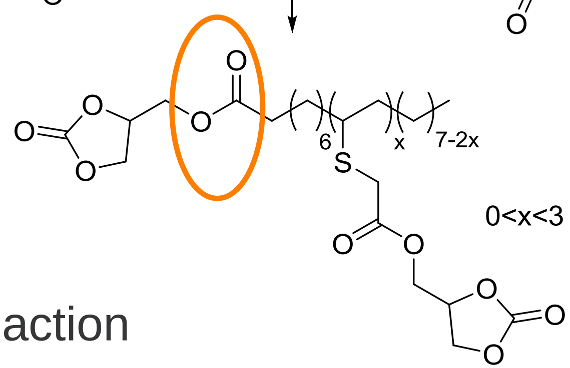
(Trans)esterification

DICYCLOCARBONATES

Thiol-ene coupling benefits

Liquid
Thioether/ether functions





Solid
Ester/amine side reaction

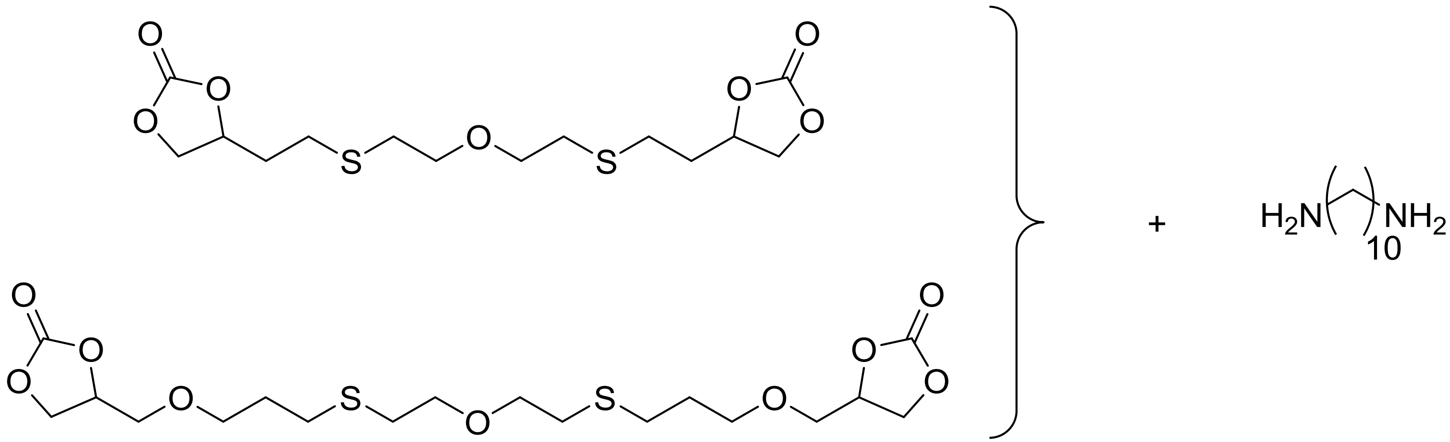
MATERIALS

Polyhydroxyurethane synthesis

Dicyclocarbonates by thiol grafting

DCA

DCG



PHU	Tg (°C)	$T_{d5\%}$ (°C)	Mn (g/mol)	Ip
PHU-DCA	-14	230	7000	1,5
PHU-DCG	-31	250	9000	3,2

Benyahya et al, Polym Chem, 2011, 2,2661

CONCLUSIONS

CONCLUSIONS

Results - polyols for PU

Building blocks

15 polyols from vegetable oils (f, distance between OH, properties…)
4 polyols at larger scale (>1 kg)
6 dicyclocarbonates from allyl carbonate or bio-based polyacids

Polyurethanes

Partially « green » PU (isocyanate chemistry) = 70% C_{green}
Wide range of PU (Tg from 0ºC to 100 ºC)
Totally « green » PU (carbonate chemistry) in progress

Materials

2 formulations : various applications
soft PU - thiol-ene coupling
hard PU - epoxy/nucleophile
Test at pilot scale considered (100 m^2)

Thank you for your attention