UNIVERSITÉ DE STRASBOURG

Polyhydroxybutyrate: PHB

PHB is a highly crystalline biodegradable and biocompatible polymer (Tg = 5 °C, Tm = 153°C)

	PLA Dow–Cargill (NatureWorks)	PHBV Monsanto (Biopol D400G – HV = 7 mol%)
Density	1.25	1.25
Melting point (°C)[a]	152	153
Glass transition (°C)[a]	58	5
Crystallinity[b] (in %)	0–1	51
Modulus (MPa) (NFT 51-035)	2050	900
Elongation at break (%) (NFT 51-035)	9	15
Tensile stress at break or max. (MPa) (NFT 51-035)	–	–
Biodegradation[c] (mineralization in %)	100	100
Water permeability WVTR at 25 °C ($g/m^2/day$)	172	21
Surface tension (γ) (mN/m)	50	–
γ_d (dispersive component)	37	–
γ_p (polar component)	13	–

UNIVERSITÉ DE STRASBOURG

Interest of PHBs

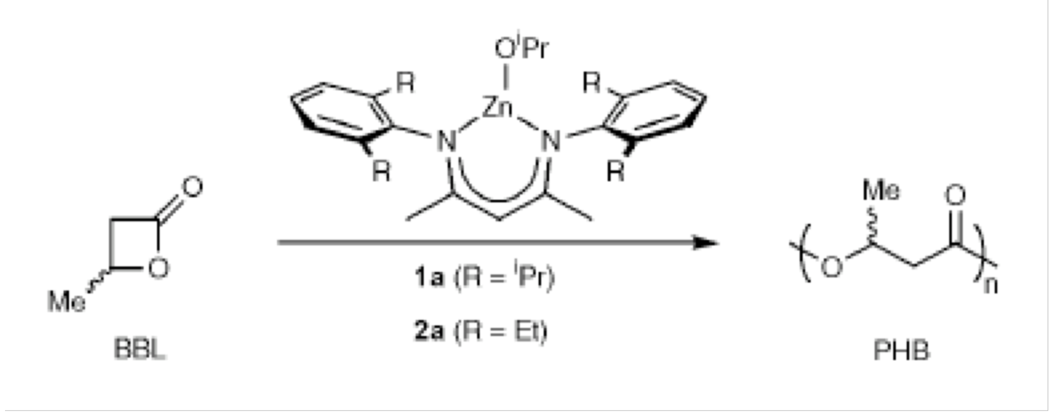
The production of PHBs is intended to replace synthetic non-biodegradable polymers for a wide range of applications:

- Packaging
- Agriculture
- Medicine

Target price: 2 euros/kg

Synthetic PHBs

Synthetic PHBs: obtained via ring-opening polymerization of β-butyrolactone and γ-valerolactone (early examples on that matter used Sn(II)-based initiators.

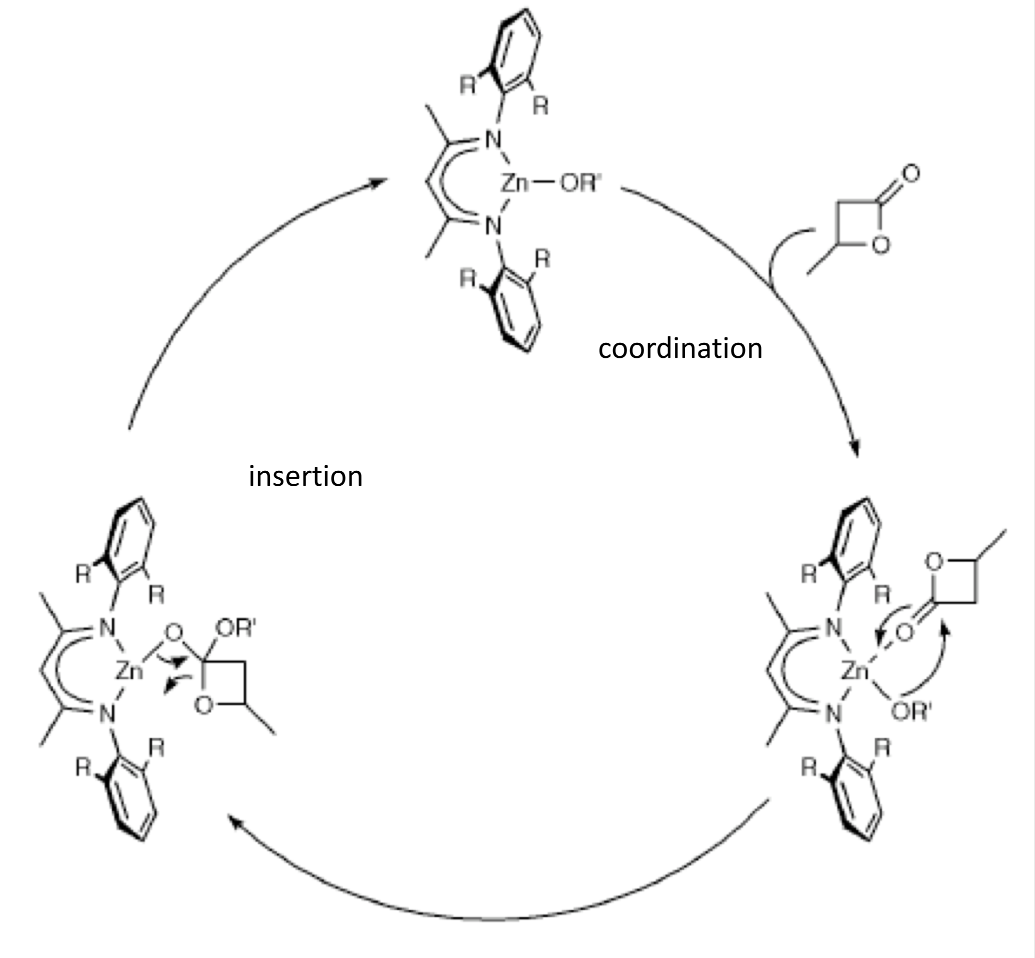


➡ Very active Zn catalysts but obtention atactic PHB

Coates et al. JACS 2002

Mechanism

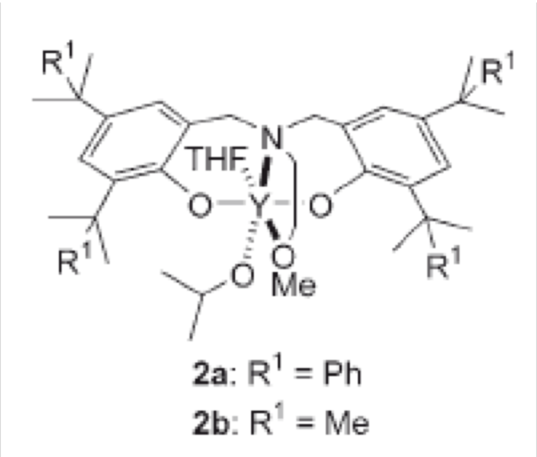
Similar to that observed in the ring-opening polymerization (ROP) of lactide (*vide supra*)

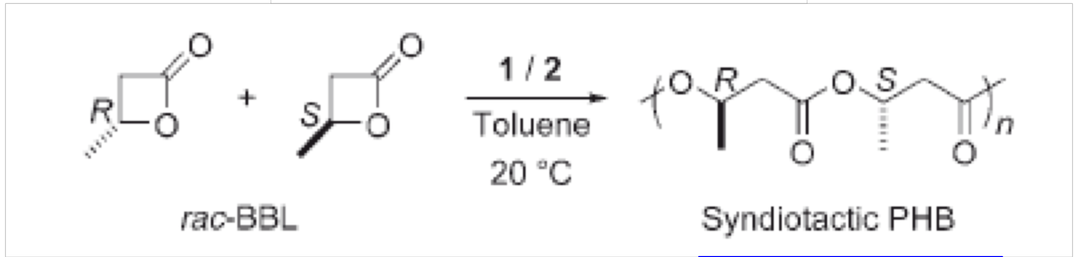


Access to syndiotactic PHBs

Stereoselective ROP of *rac*-BBL by a well-defined yttrium complex

Catalyst:





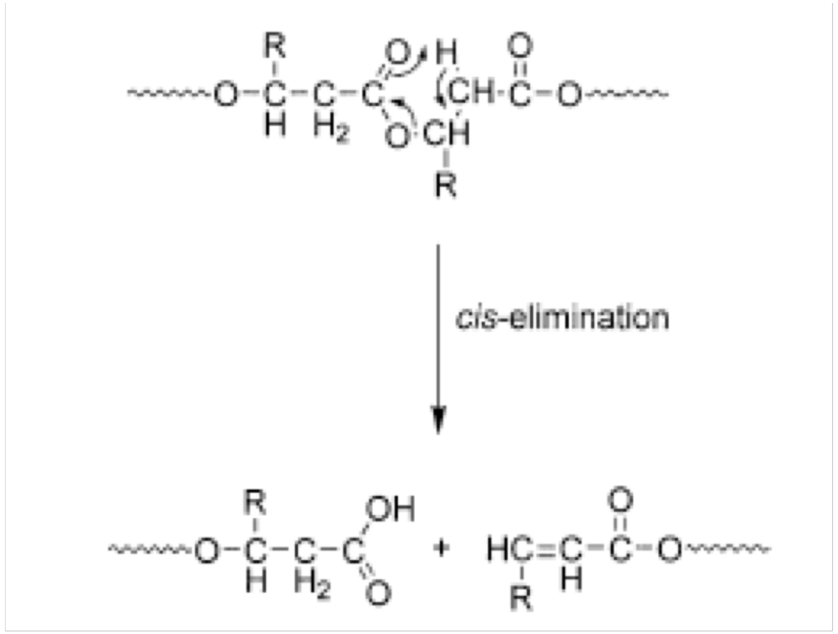
New material

Drawback: the catalyst is highly air-sensitive and Yttrium is a non-biocompatible metal

Carpentier et al. *Angew. Chem. Int. Ed.* **2006**, *45*, 2782–2784

Biodegradation of PHAs

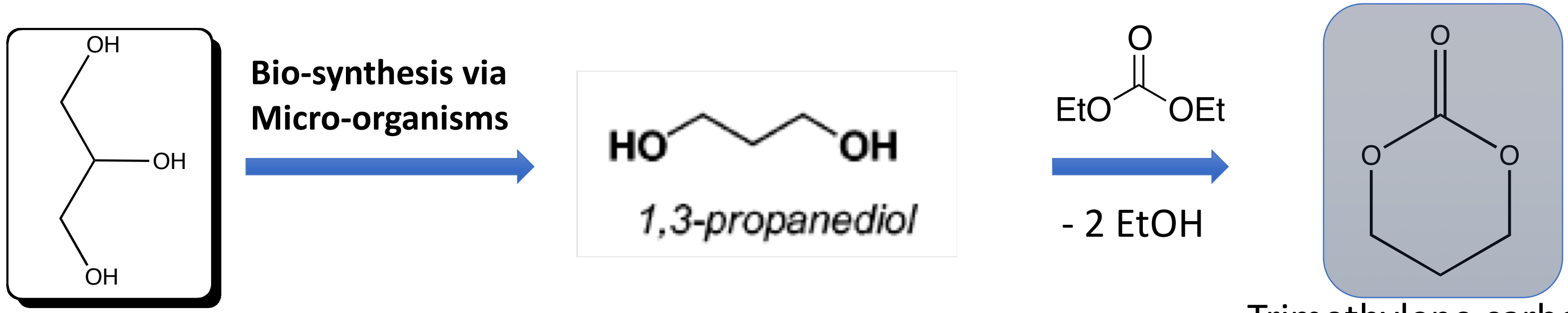
First step: thermal degradation (170 °C)



Second step: Bioassimilation by micro-organisms (obtention of CO_2, CH_4 and other biomass products)

UNIVERSITÉ DE STRASBOURG

1,3 propanediol: a key component for the synthesis of trimethylene carbonate



Glycerol

Sous-produit de la synthèse des biodiesels

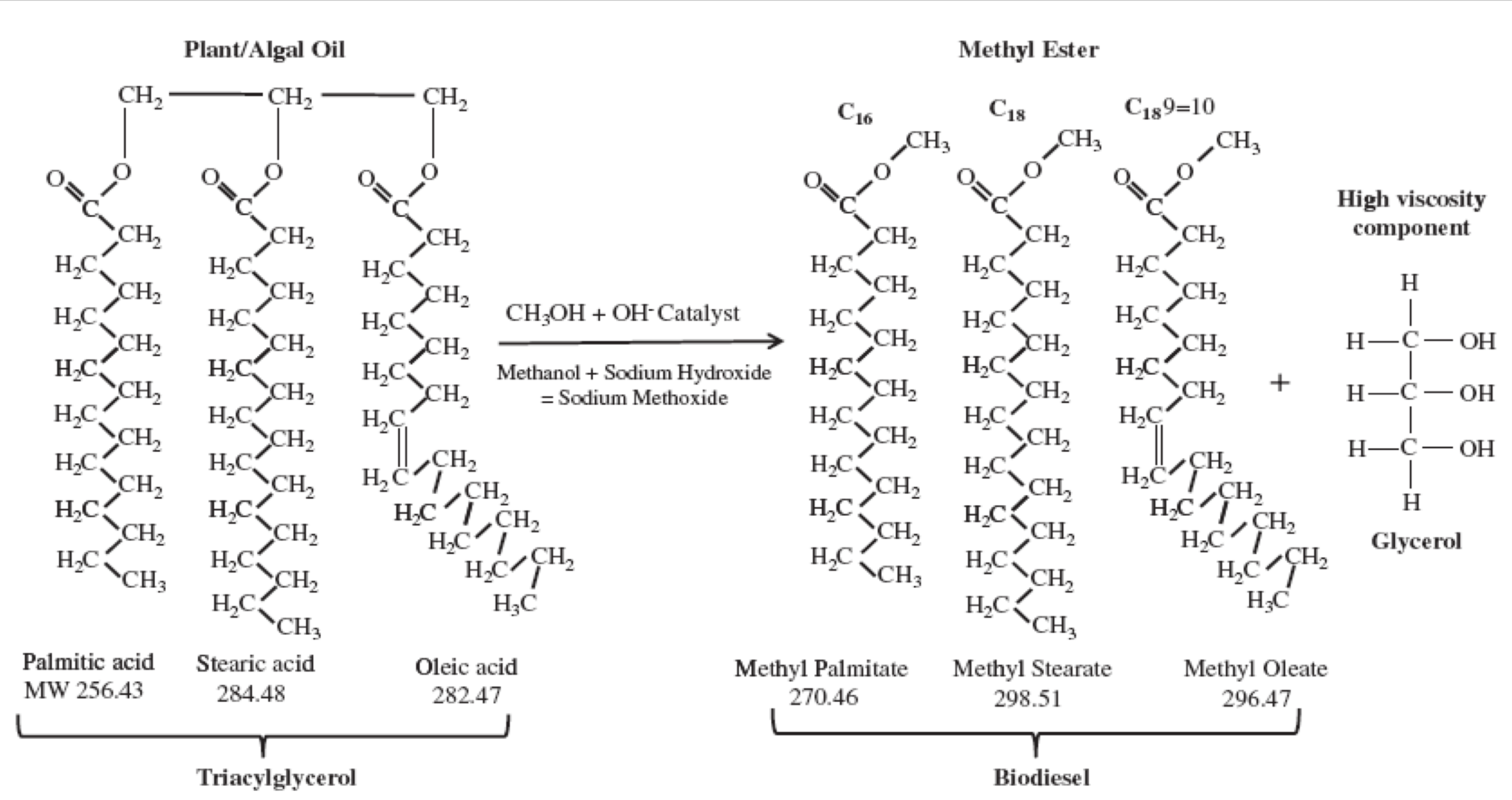
Trimethylene carbonate
- important monomer for the synthesis of polycarbonates
- Interesting properties

General properties of cyclic carbonates:

- Low toxicity
- High boiling point
- biodegradability

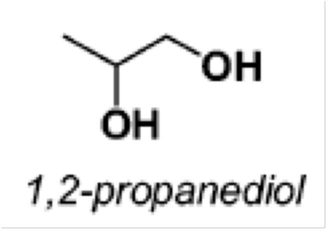
-Applications as inert solvents
-Diluants for polyurethanes
-Hydraulic fluids

Synthesis of Biodiesel

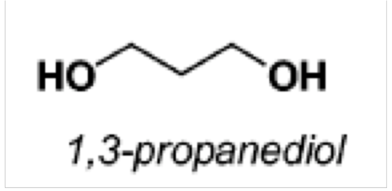


Hydrogenolysis of glycerol

Interest: Access via chemical derivatization of glycerol to small molecules with high added value such as:

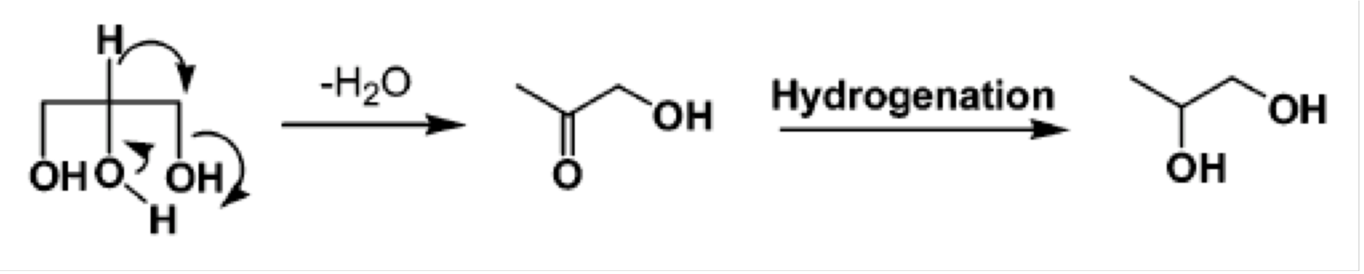


Much less toxic than ethylene glycol (for use in cooling systems)



Important industrial chemical intermediate

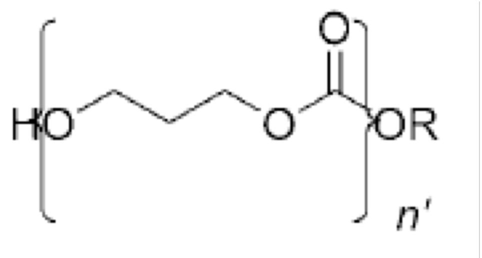
Example: access to 1,2- PPD from glycerol



-A multiple metal catalyst is required as well as high T and P.
- Biocatalysis (enzyme catalysis) is also an option

The case of trimethylene carbonate (TMC)

- TMC: monomer precursor of PTMC



PTMC: poly(trimethylene) carbonate

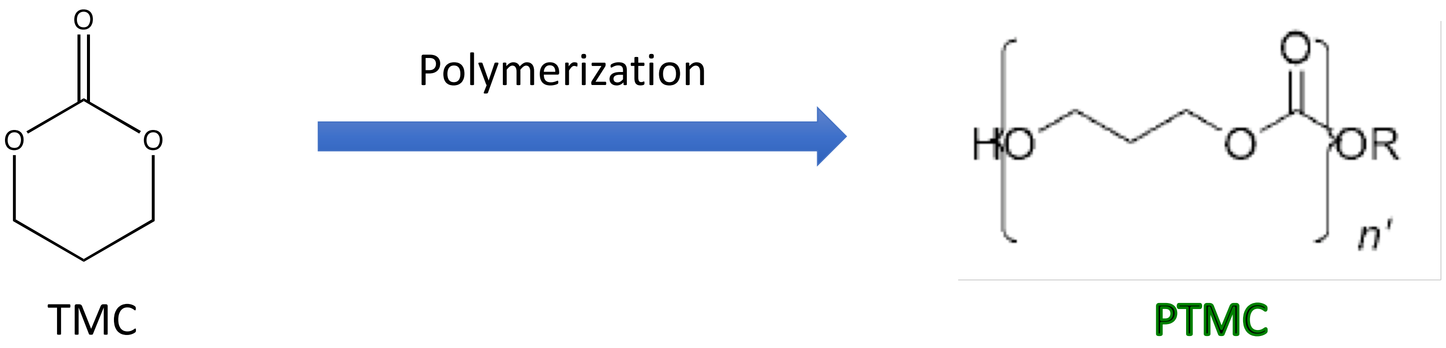
-Interest of PTMC:

-More resistant to acid-hydrolysis than polyesters (such as polylactic acid)
-Useful as diols for incorporation in polyurethanes

Incorporation of poly(carbonate diols) into polyurethanes results in
an increased hydrolytic and thermal stability ⟶ **Outdoor stability**

Applications: resins in coating, medical devices and implants

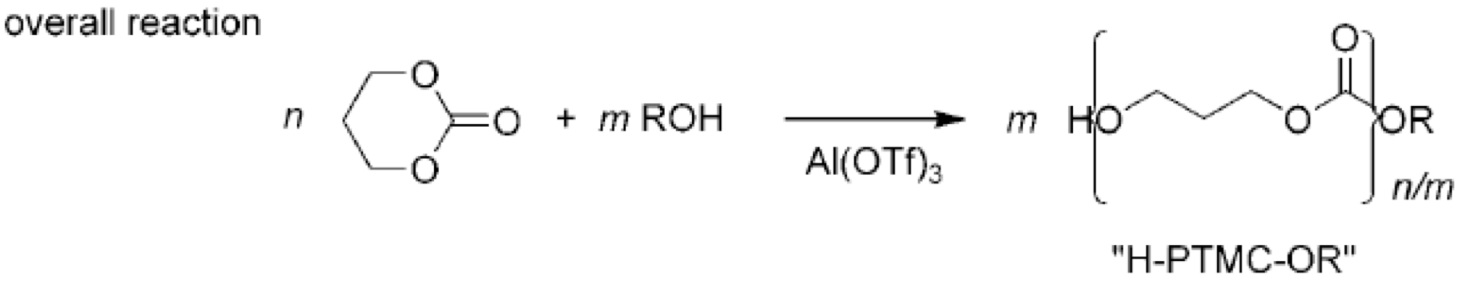
Polymerization of carbonates:
The case of trimethylene carbonate



Preferred route to access PTMC: ring-opening polymerization of TMC

- High polymerization activity
- Controlled polymerization

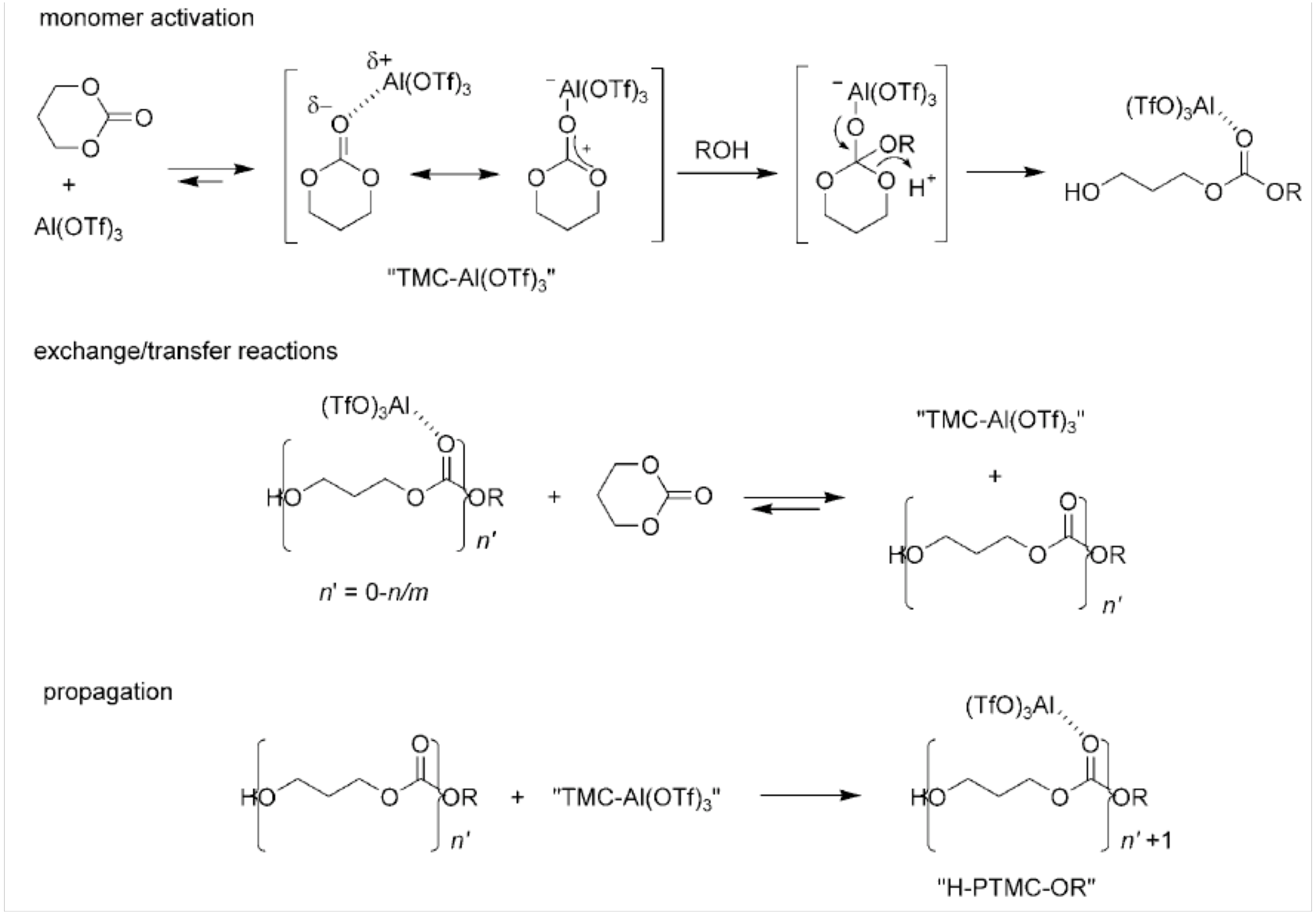
$Al(OTf)_3$- catalyzed Polymerization of TMC



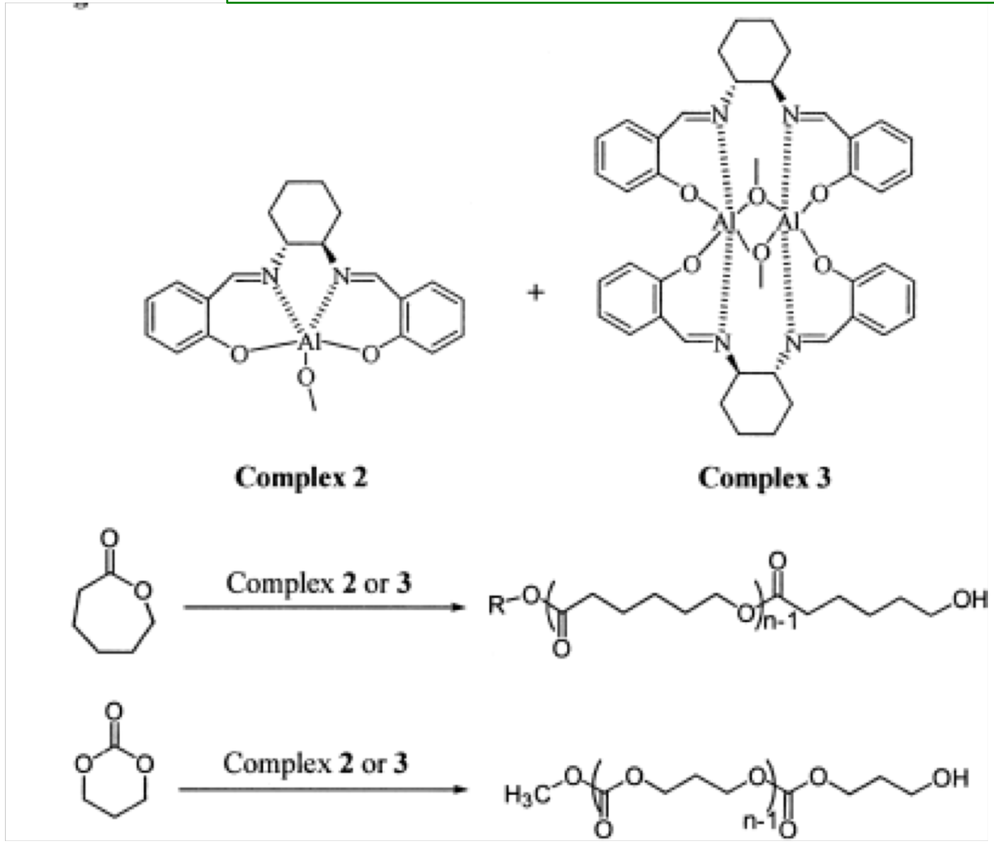
« Immortal » Living ring-opening polymerization of TMC

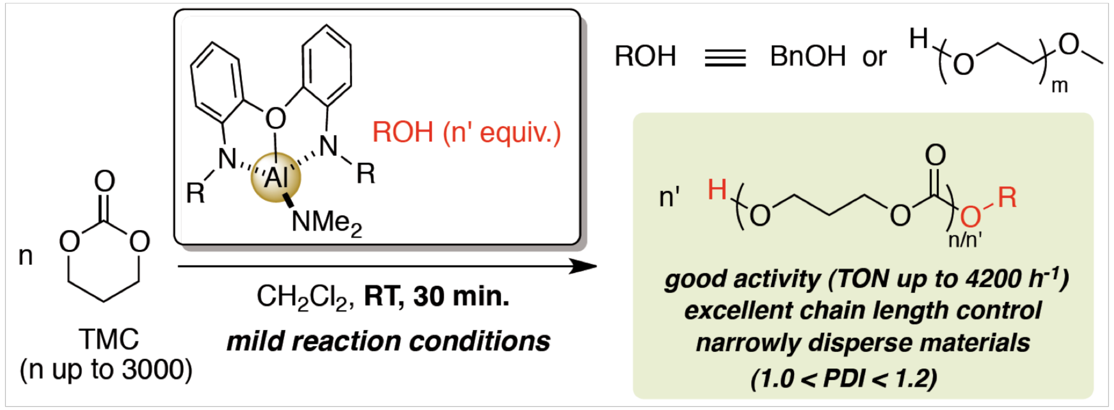
Obtention of PTMC with controlled properties
Via a controllable chain length

Mechanism


monomer activation
δ+
Al(OTf)3
δ−
Al(OTf)3
ROH
Al(OTf)3
OR
H+
(TfO)3Al
HO
OR
Al(OTf)3
"TMC-Al(OTf)3"
exchange/transfer reactions
(TfO)3Al
HO
OR
n'
n' = 0-n/m
"TMC-Al(OTf)3"
HO
OR
n'
propagation
HO
OR
n'
"TMC-Al(OTf)3"
(TfO)3Al
HO
OR
n' +1
"H-PTMC-OR"

Ring-opening Polymerization of TMC by well-defined metal complexes

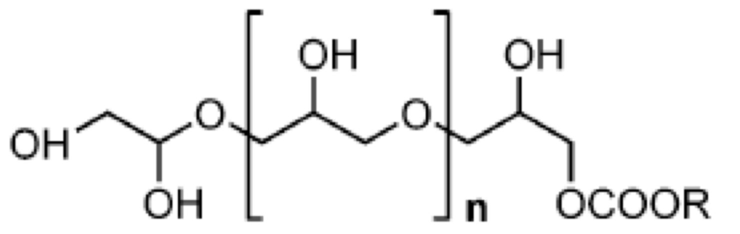


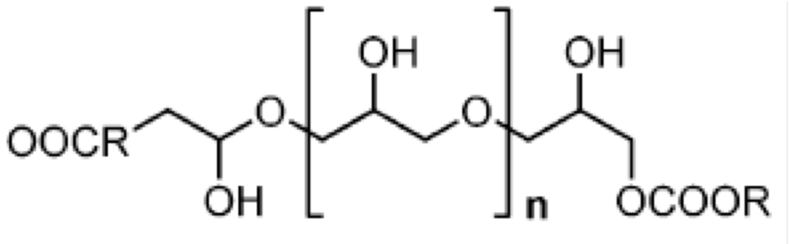


Polyglycerol Fatty Acids Esters (PEG)

Chemically formed by esterification of fatty acids with
One or several hydroxyl groups of polyglycerol

Examples of PEG





Important nonanionic surfactants

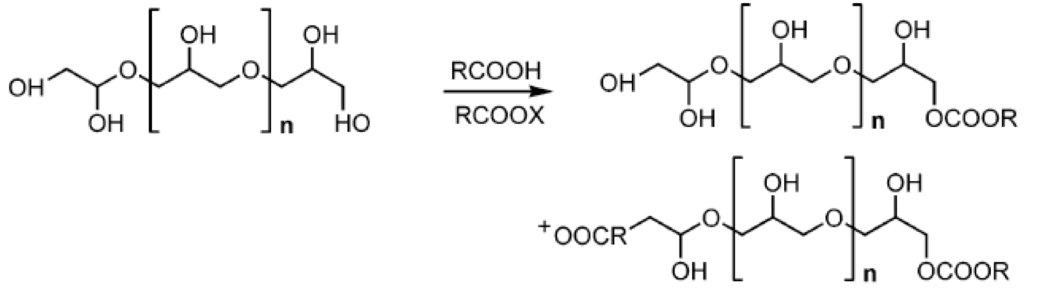
- Important moities with important and various applications:

- **Cosmetics**
- **Food**
- **Pharmaceuticals**

UNIVERSITÉ DE STRASBOURG

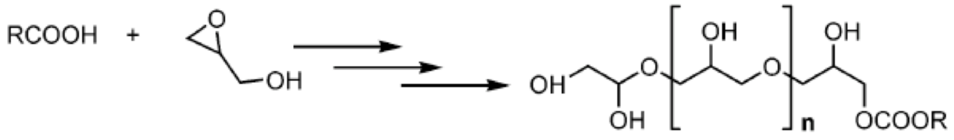
Possible Routes to access Linear PEG

(1) Direct esterification



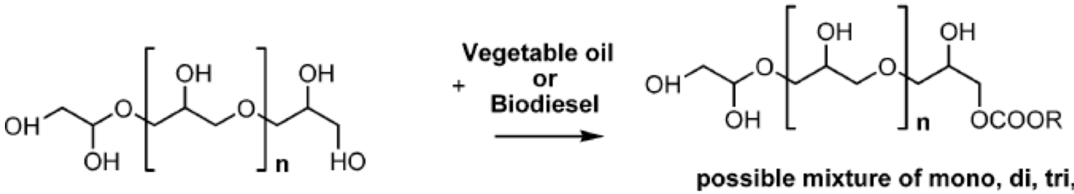
possible mixture of mono, di, tri, tetraesters etc.

(2) Polycondensation of RCOOH with glycidol



possible mixture of mono, di, tri, tetraesters etc.

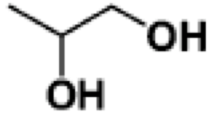
(3) Transesterification



possible mixture of mono, di, tri, tetraesters etc.

Hydrogenolysis of glycerol

Interest: Access via chemical derivatization of glycerol to small molecules with high added value such as:



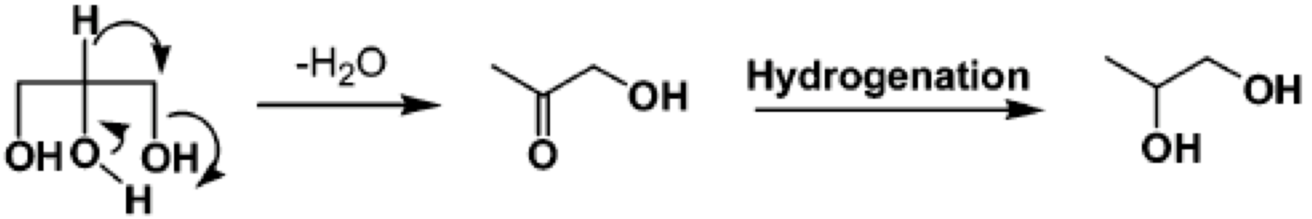
1,2-propanediol

Much less toxic than ethylene glycol (for use in cooling systems)

1,3-propanediol

Important industrial chemical intermediate

Example: access to 1,2- PPD from glycerol



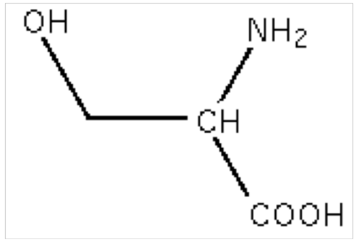
-A multiple metal catalyst is required as well as high T and P.
- Biocatalysis (enzyme catalysis) is also an option

Oxidation of Glycerol

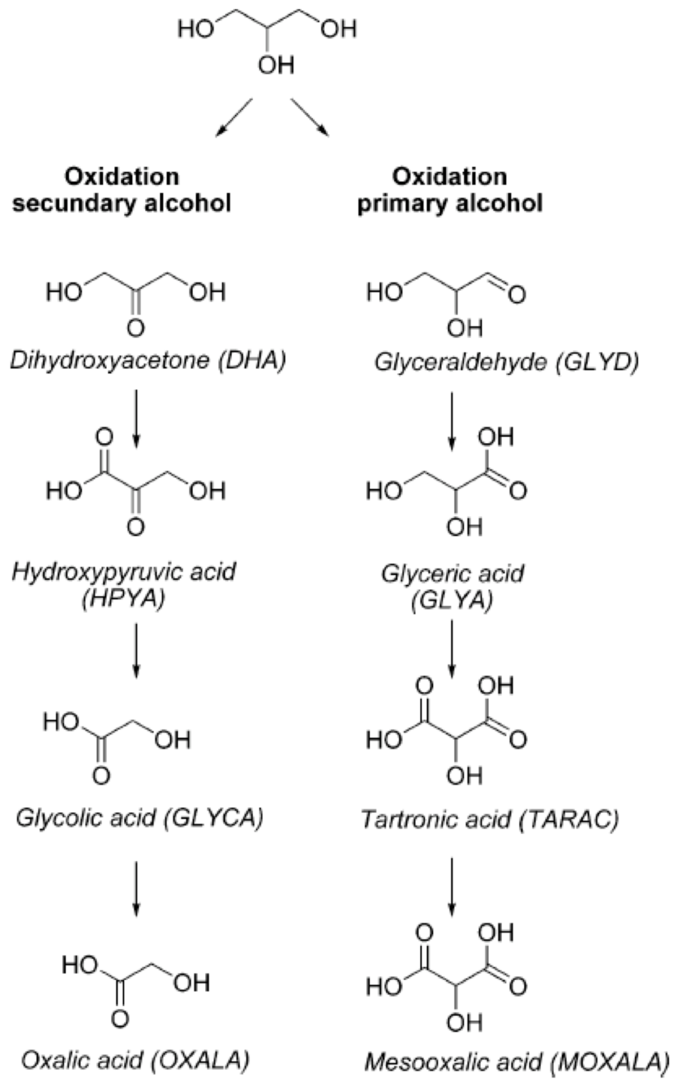
Glyceric acid (GLYA):
- Metabolite in the glycolysis cycle

DHA: used in the manufacture
Of tanning products

HPYA: used as a precursor to serine

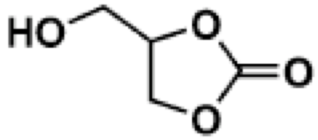


Serine



Problems to be addressed: low yield and selectivity

Glyceryl carbonate

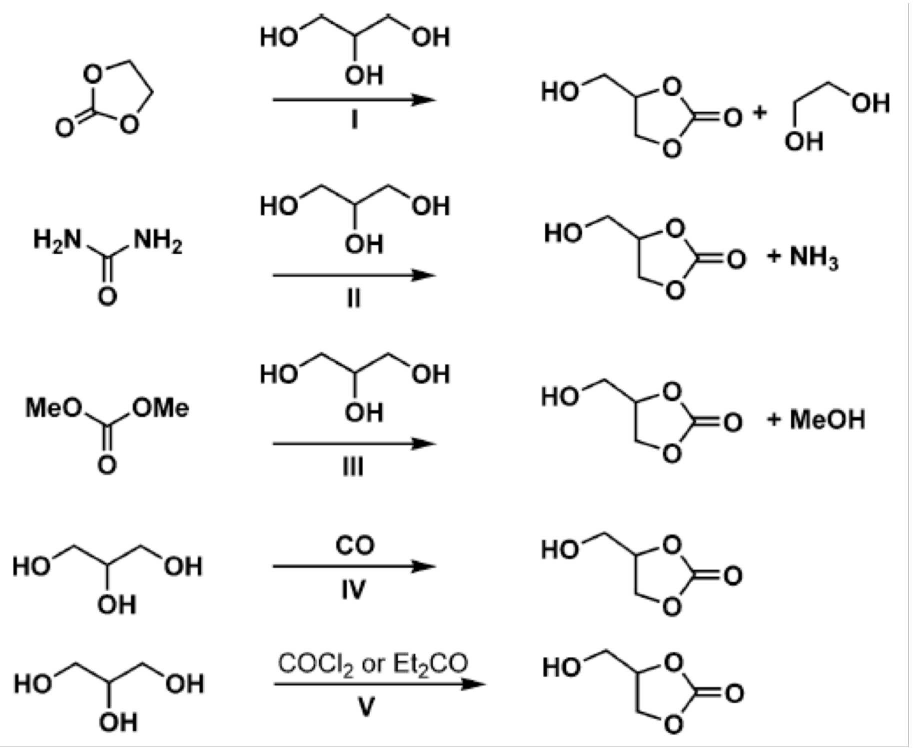


Glyceryl carbonate (GC)

Key low toxic compound employed as:

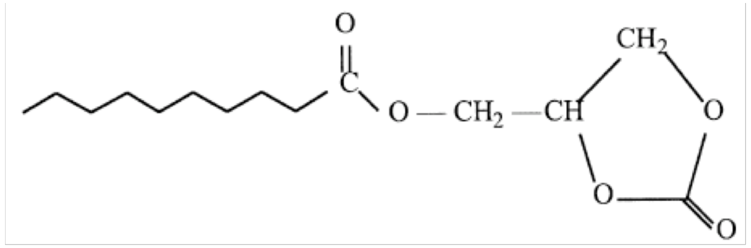
- solvent, additive, monomer, chemical intermediate
- Moisterizing agent in cosmetics
- Solvant carrier in medecine

Possible synthetic routes for the synthesis of GC



Glyceryl Carbonate Fatty Acid Esters

Example

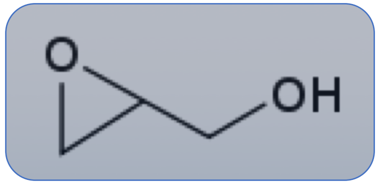


Interesting physical and photophysical properties:

- Good thermal and oxidation stability
- Surfactant characteristics
- Good lubricity and biodegradability

Possible candidates as lubricant oleochemical esters

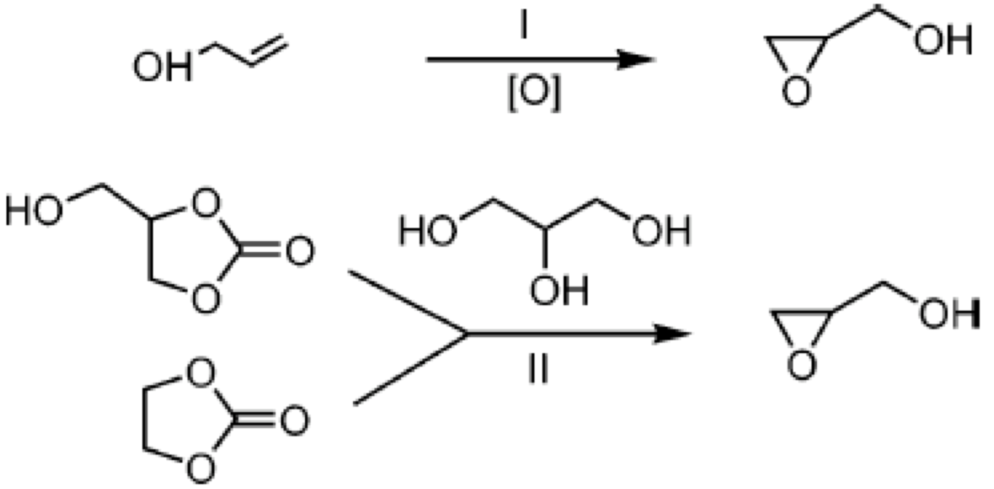
Glycidol



Glycidol

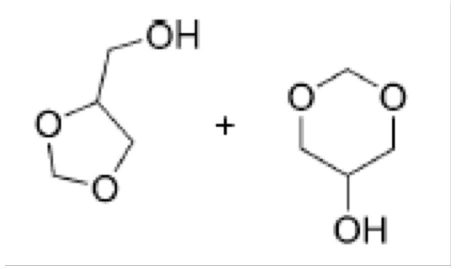
- Used as a stabilizer for natural oils and vinyl polymers
- Applications in chemical synthesis and pharmaceuticals

Classical synthesis



UNIVERSITÉ DE STRASBOURG

Glycerol Formal



dioxolane dioxane

Mixture 40 / 60

-Large number of applications as a low-toxic solvent
(solvent for paints, insecticide delivery)