Quelques exemples de synthèses de monomères verts

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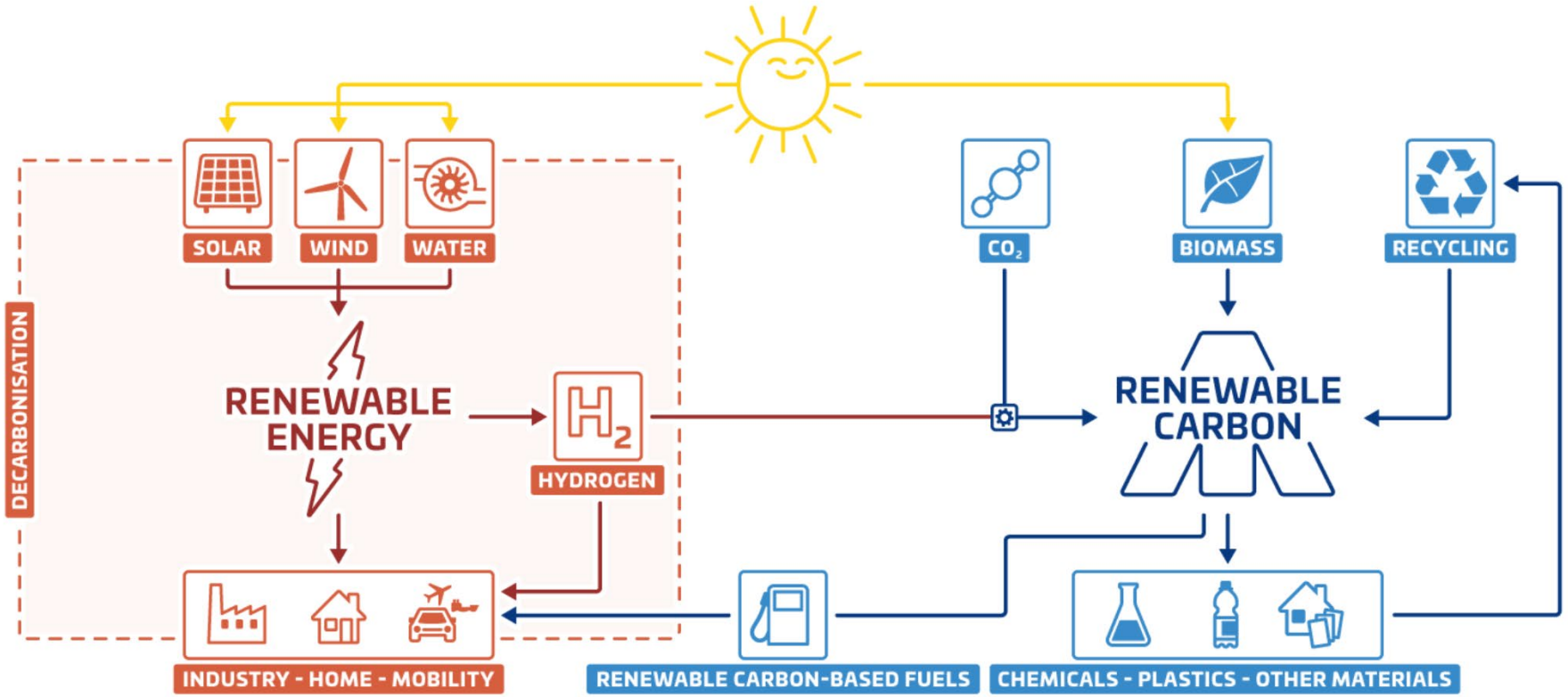
Rendez-vous des écomatériaux
Val-des-Sources, QC.
25-26 octobre 2022

Renewable Energy and Renewable Carbon for a Sustainable Future



Global current plastic production
360 Mt in 2018

Most important plastics:

Polypropylene (PP)	23%
Low density Polyethylene (LDPE)	17%
High density Polyethylene (HDPE)	16%
Polyvinyl chloride (PVC)	16%
Polyurethane (PU)	7%
Polyethylene terephthalate (PET)	7%
Polystyrene (PS)	6%
Others	8%

Source Plastics Europe _ Plastics _ The facts 2019
http://www.plasticseurope.org/application/files/9715/7129/9584

Polymères d'intérêt pour le secteur du bâtiment

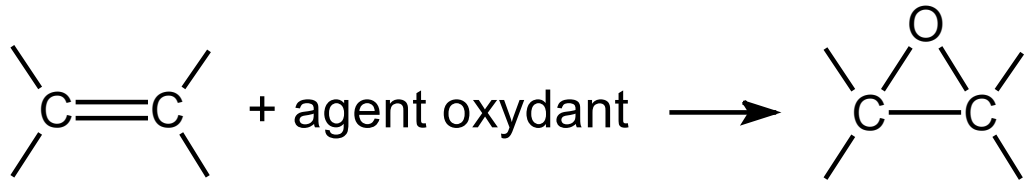
	production mondiale (2018) Mt/an
▪ **Résines époxy** adhésifs, agents scellant, additifs au mortier	3.9
▪ **Polyuréthane** mousses isolantes, colles, laques, agents de recouvrement	7.5
▪ **Polycarbonates** panneaux translucides	5.2

Une estimation grossière de la quantité de CO_2 produite par oxydation de la totalité de ces polymères: 45-50 Mt CO_2/an

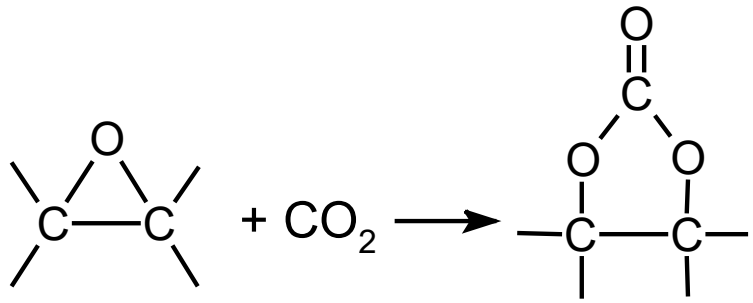
Objectifs:

développer des catalyseurs hétérogènes pour deux types de réactions:

- **Époxydation:**



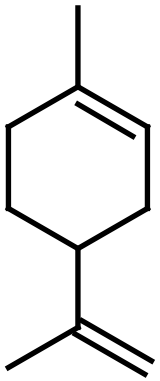
- **Cyclocarbonatation:**



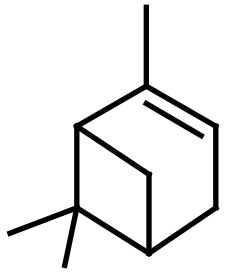
en utilisant des substrats d'origine végétale.

Terpenes

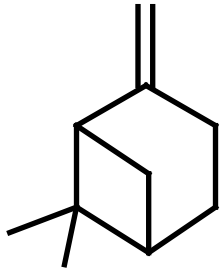
limonene



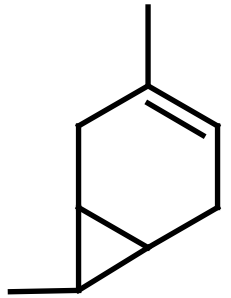
α-pinene



β-pinene



3-carene

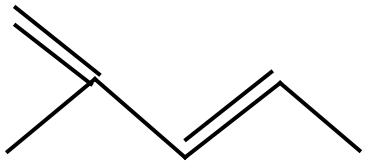


Global production

90,000 t/y

300,000 t/y

Natural dimers of isoprene

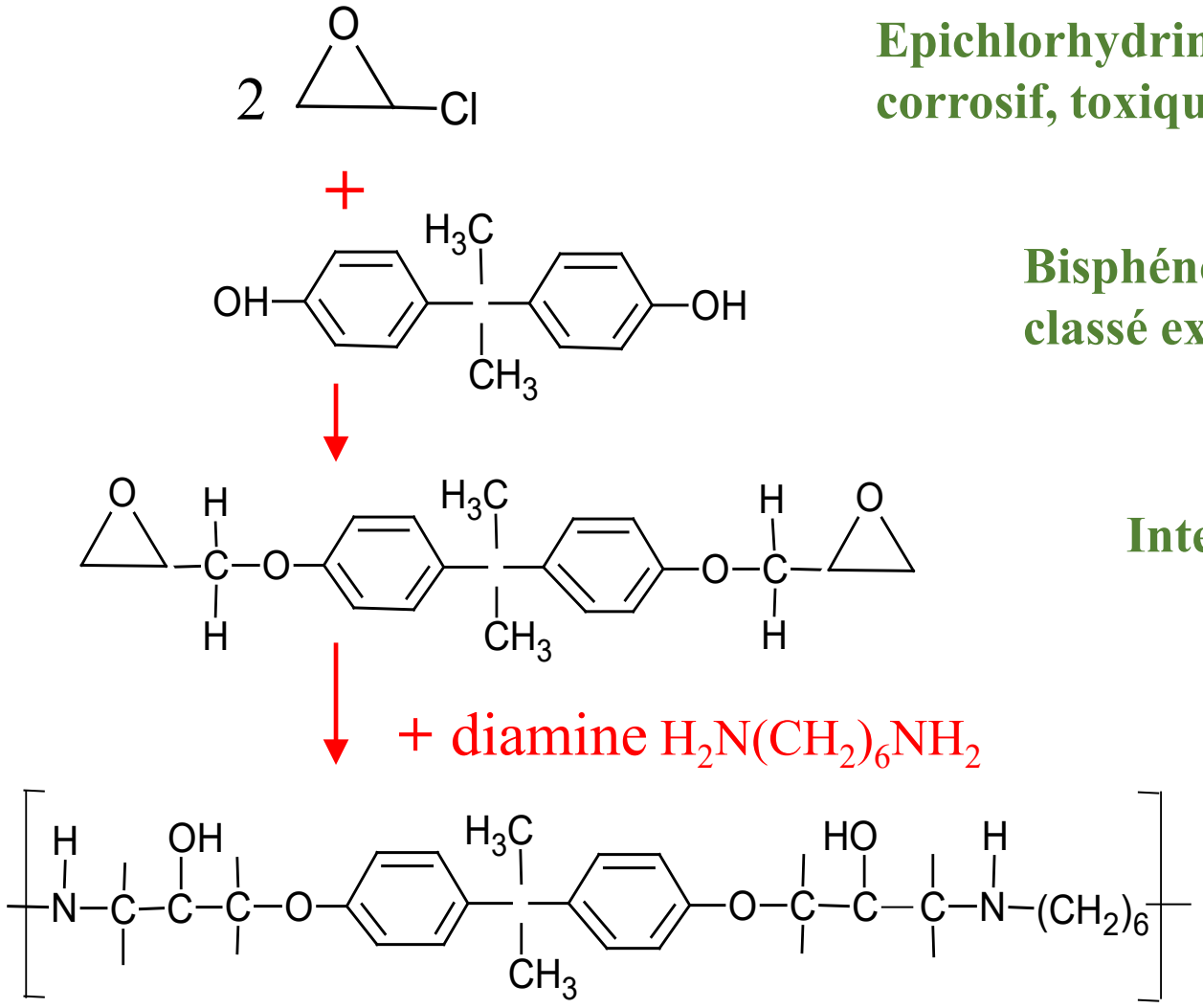


Produced by Genencor (IFF)/Goodyear* by bacteria conversion of various amino acid sources (casein, gelatin, lactalbumin)

* R.R. Fall, J. Kuzma, M. Nemeek-Marshall, US patent 5,849,970.

Les résines époxy

Méthodes actuelles de production



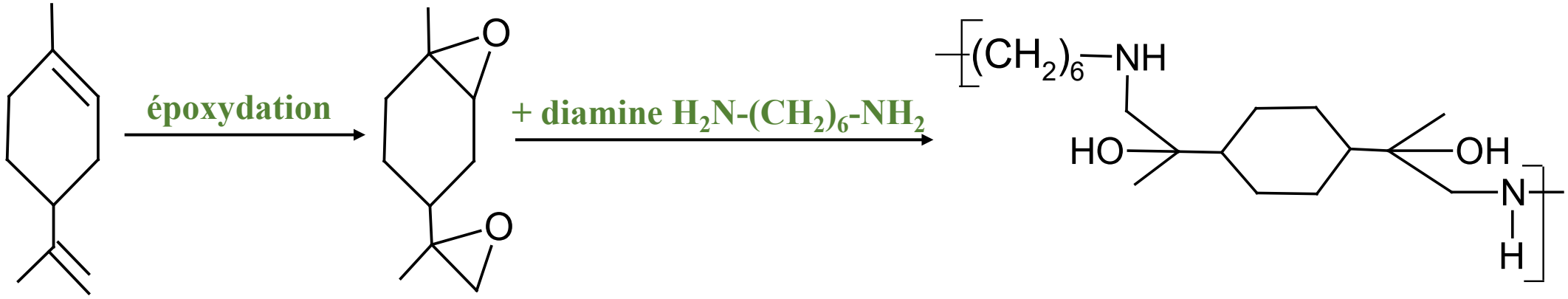
Epichlorhydrine, produit chimique corrosif, toxique et cancérigène

Bisphénol A, (4 Mt/an) classé extrêmement préoccupant

Intermédiaire diépoxy

Les résines époxy

La méthode proposée



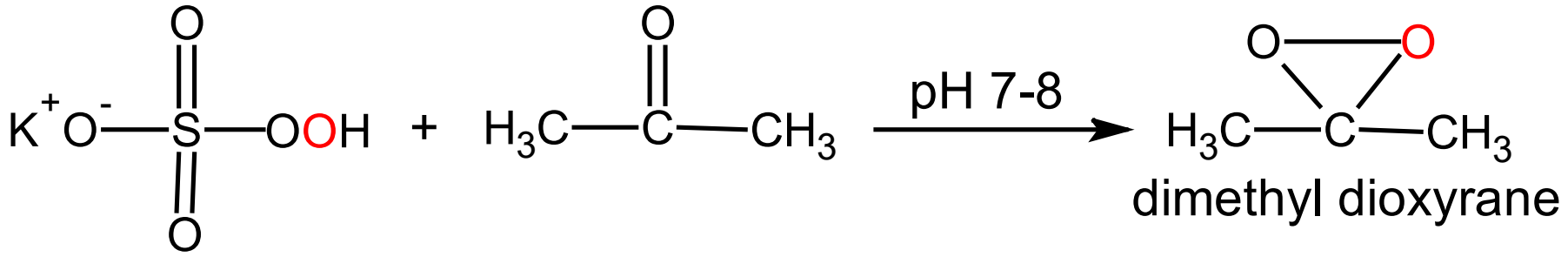
limonène

diépoxy limonène
intermédiaire diépoxy

nouvelle résine verte

Epoxidation of terpenes

1. **Oxone as oxidizing agent**

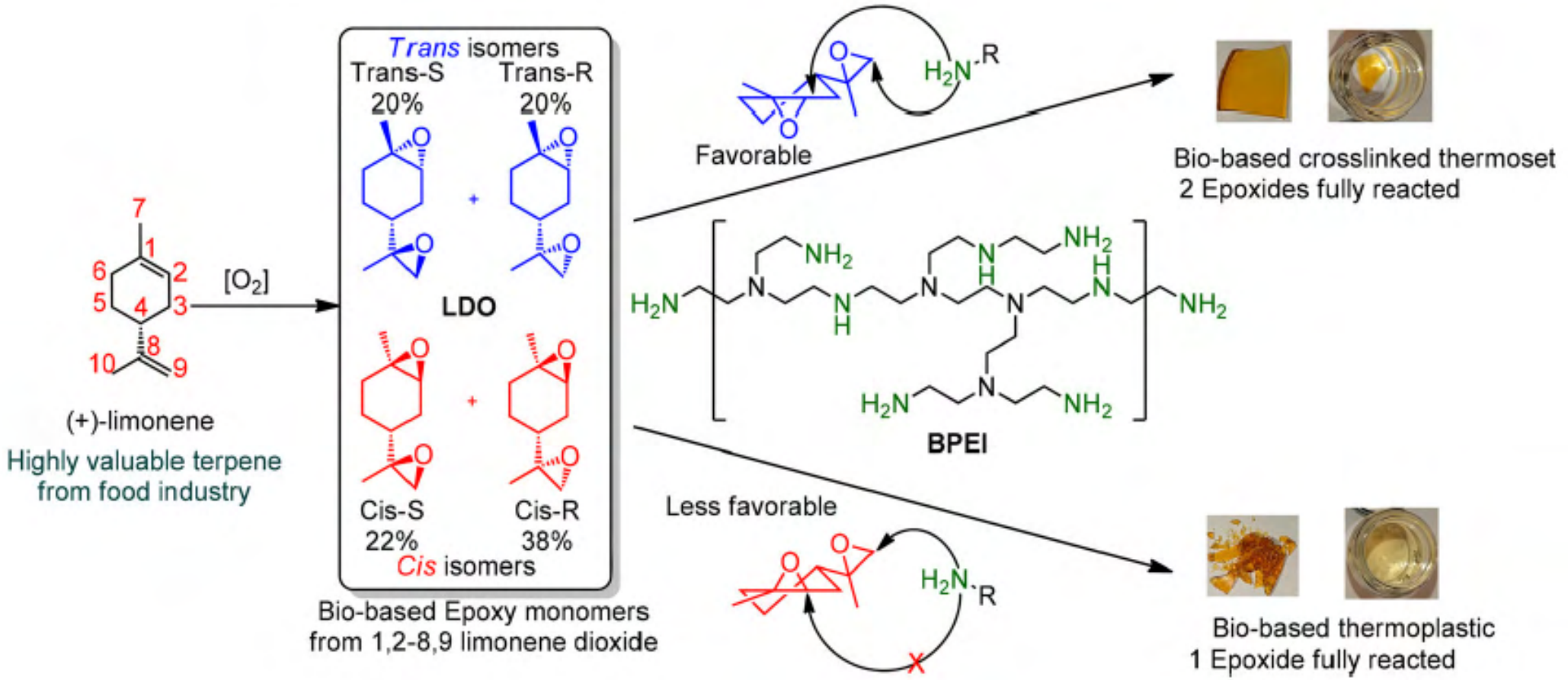


- **Extremely selective: limonene → LDO 100% yield**
- **Using microemulsions → facilitates scale-up**

2. **Aerobic epoxidation**
   - **Ru/AC exceptional catalyst: no solvent, no initiator**
     35% limonene conversion, 60% epoxide selectivity

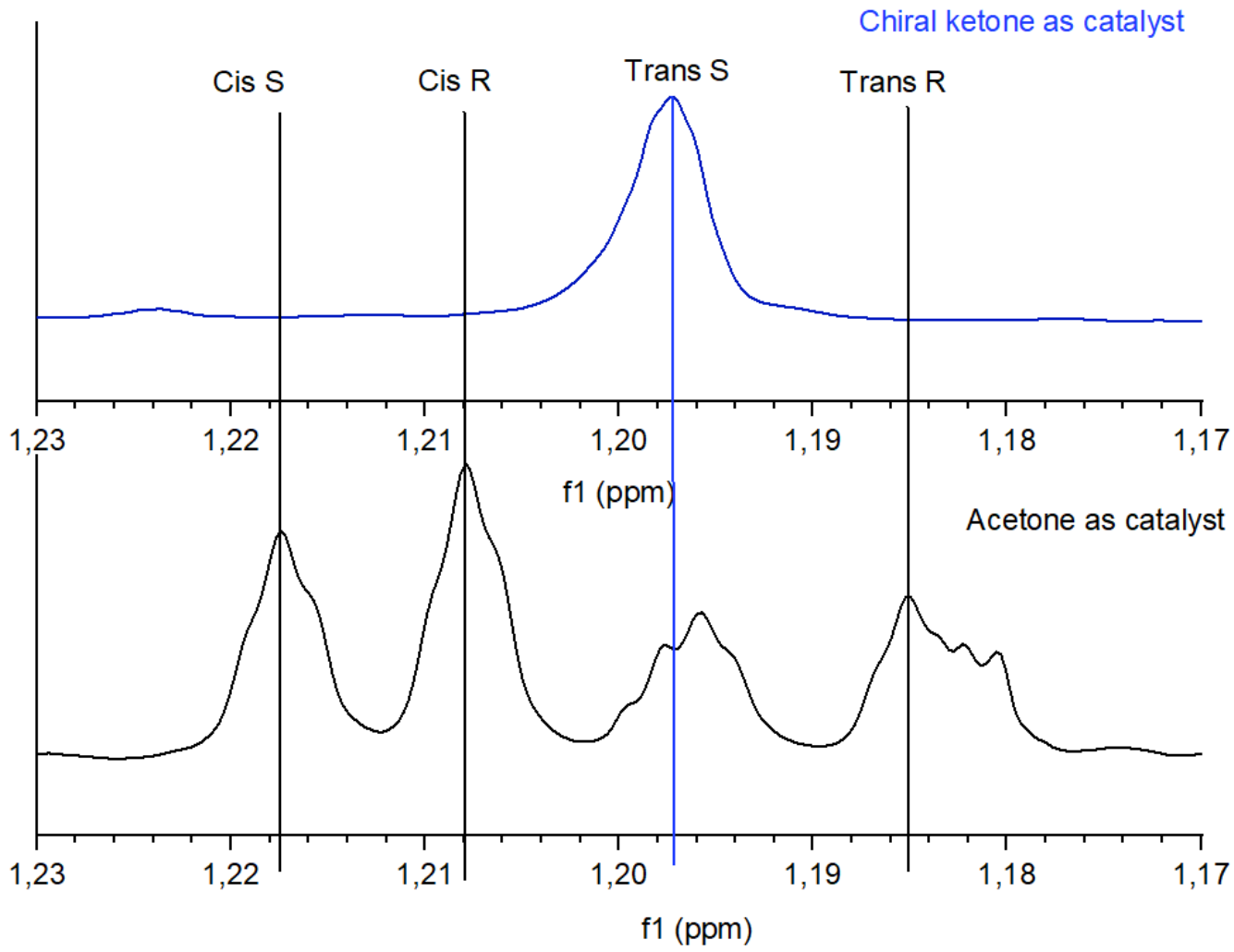
Y. Mahmat Ahmat, S. Madadi, L. Charbonneau, S. Kaliaguine, Epoxidation of terpenes, Catalysts 2021, 11(7), 847.

Epoxy resins from limonene dioxide



L. Schutz, F. Kazemi, E. Mackenzie, J-Y. Bergeron, E. Gagnon, J.P. Claverie, Trans-limonene dioxide, a promising bio-based epoxy monomer, J Polym Sci. 2021;59:321–328.

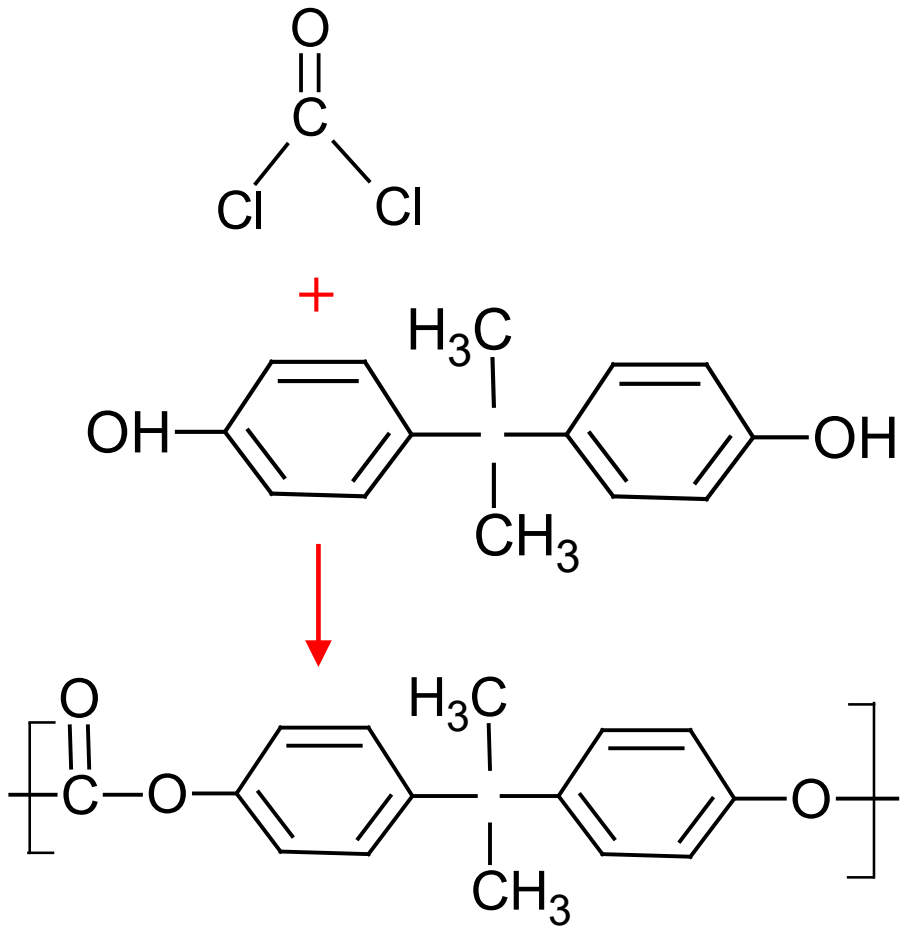
Limonene stereospecific epoxidation



^{1}H NMR assignments: **M. Soto, K. Koschek, Diastereoisomeric diversity dictates reactivity of epoxy groups in limonene dioxide polymerization, eXPRESS Polymer Letters, 12 (2018) 583–589.**

Polycarbonates

Méthodes actuelles de production

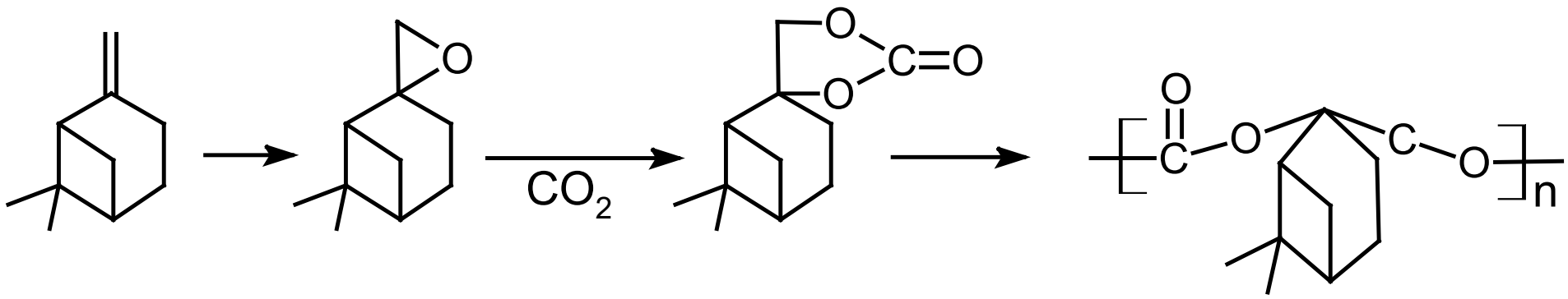


Phosgène (gaz de combat)

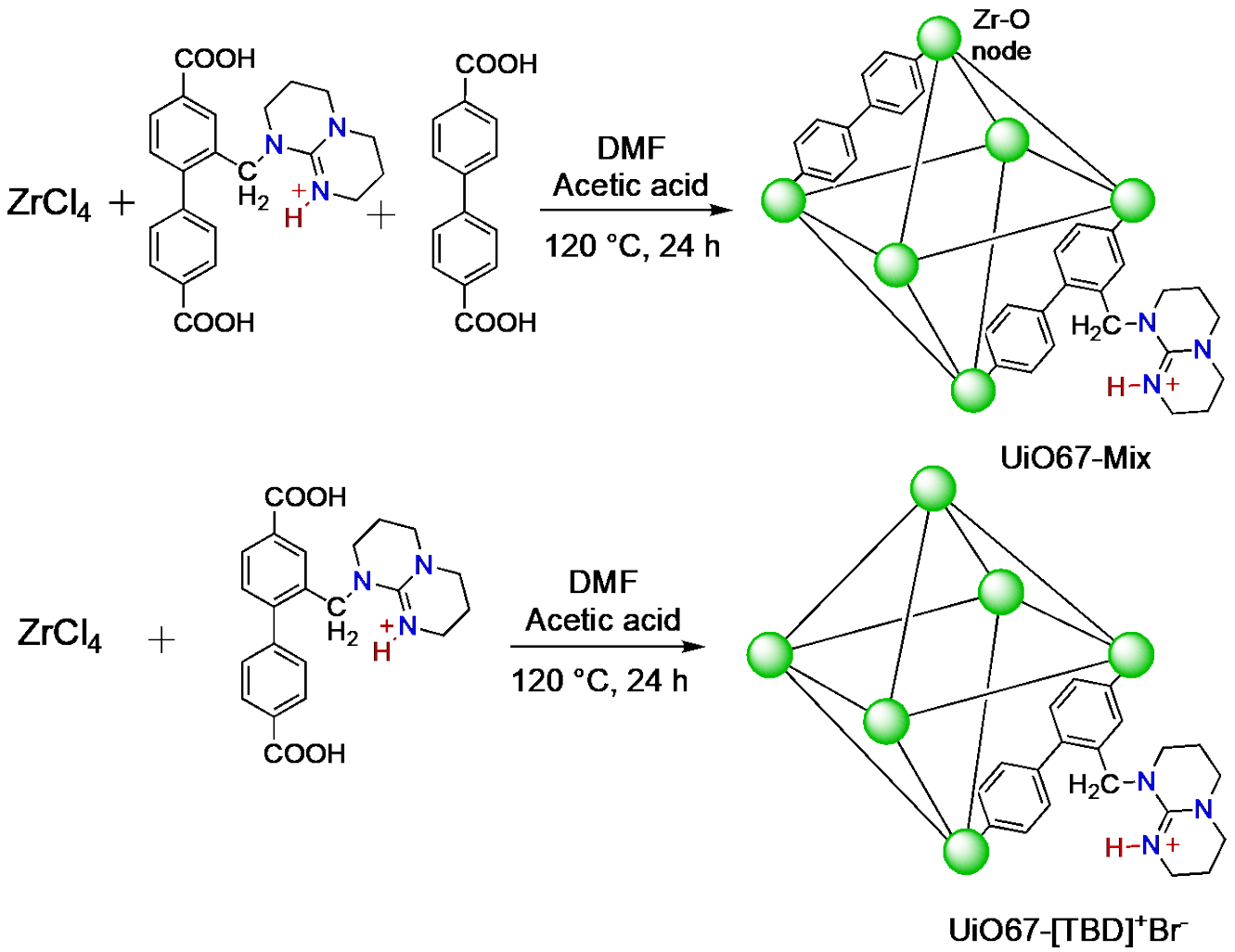
Bisphénol A

Polycarbonates

La méthode proposée



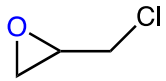
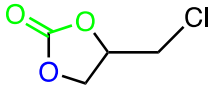
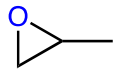
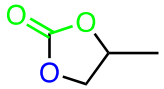
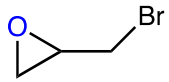
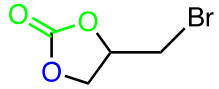
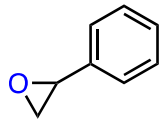
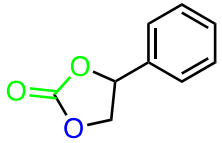
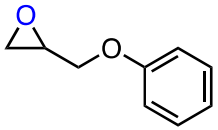
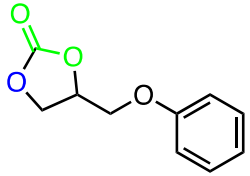
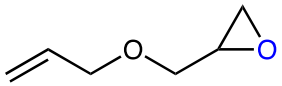
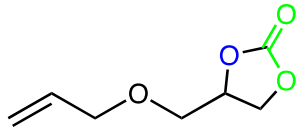
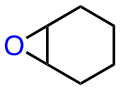
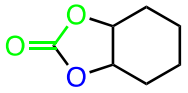
β-pinène epoxyde cyclocarbonate polycarbonate



Catalyseur de cyclocarbonation UiO67-[TBD]$^{+}$Br^{-}

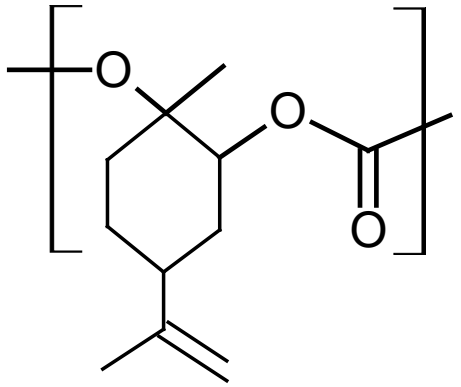
S.M. Masoom Nataj, S. Kaliaguine, F.G. Fontaine, soumis.

Cycloaddition de CO_2 à divers époxydes catalysée par UiO67-$[TBD]^+Br^-$

Entry	Epoxide	product	time (h)	Reaction results	
				Yield[a]	Selectivity
1			6	55	>99
2			18	98	>99
3			6	56	>99
4			18	99	>99
5			6	57	>99
6			18	97	>99
7			6	53	>99
8			18	89	>99
9			9	42	>99
10			18	88	>99
11			9	57	>99
12			18	79	>99
13			18	29	>99
14			24	31	>99

Conditions: temp. 80°C, pression: 0.1MPa CO_2, catalyseur: 0.14 mol%, aucun solvant, aucun co-catalyseur

Inspired by the properties of PLimC



O. Hauenstein et al., Biobased Polycarbonate as a Gas Separation Membrane and "Breathing Glass" for Energy Saving Applications, Adv. Mater. Technol. 2017, 2, 1700026.

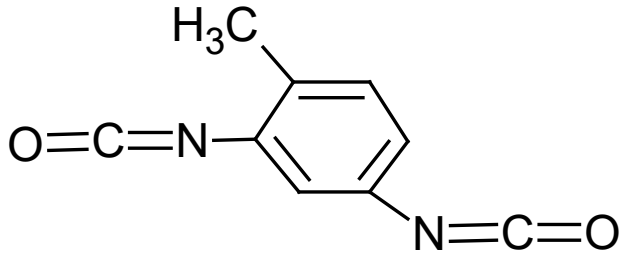
Property	PLimC	BPA-PC	PMMA	Soda-lime glass
Permeability				
CO_2 [barrer]	68	6.8	0.85	-
O_2 [barrer]	12	1.6	0.24	-
H_2O vapor [barrer]	284	114	0.13	-
T_g [°C]	130	150	105	573
Transmittance [%]	92	90	92	90
Refractive index [589 nm, 25 °C]	1.501	1.587	1.491	1.518
Specific gravity [g cm^{-3}]	1.08	1.20	1.19	2.52
Impact resistance [J]	2.00	3.33	0.55	0.33
Hardness	B	8B	4H	10H
Thermal conductivity [W $K^{-1}m^{-1}$]	0.15	0.20	0.19	1.05

O. Hauenstein et al., Biobased Polycarbonate as a Gas Separation Membrane and "Breathing Glass" for Energy Saving Applications, Adv. Mater. Technol. 2017, 2, 1700026.

Les polyuréthanes

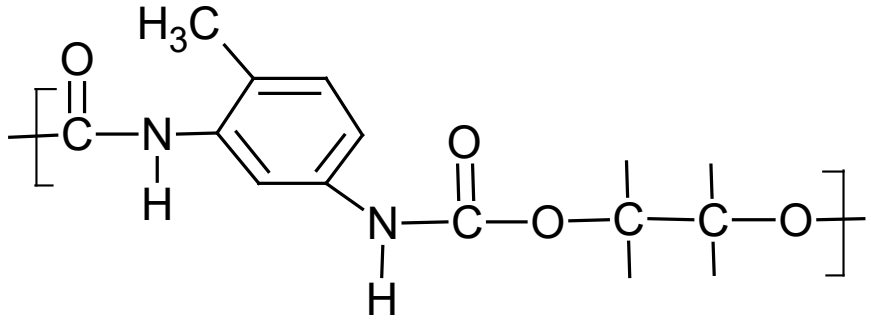
Méthodes actuelles de production

par réaction d'un diisocyanate



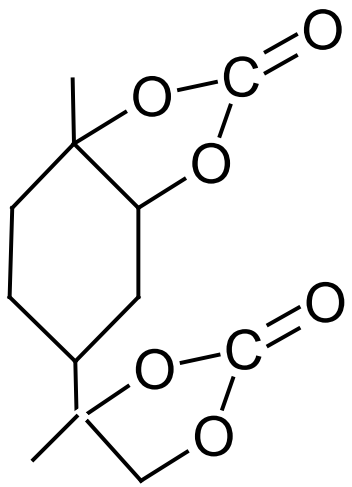
extrêmement toxique

sur un diacide, un dialcool, une diamine et même le bisphénol A
par exemple avec HO-CH_2-CH_2-OH



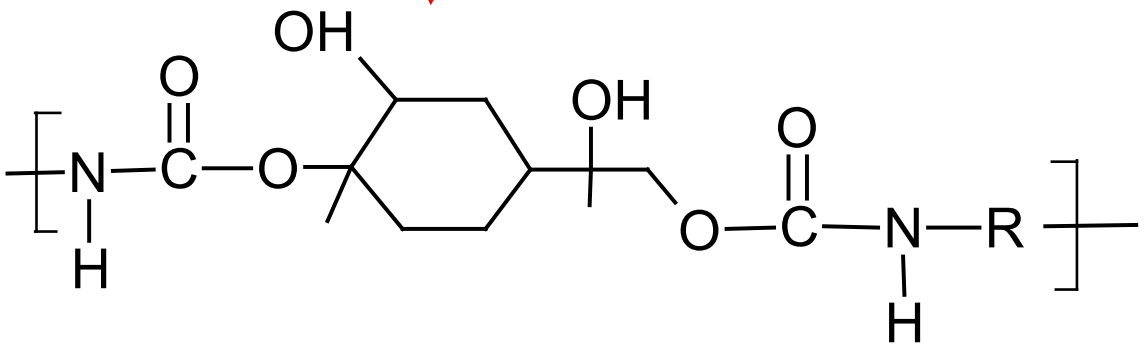
Les polyuréthanes

La méthode proposée



dicarbonate cyclique de limonène

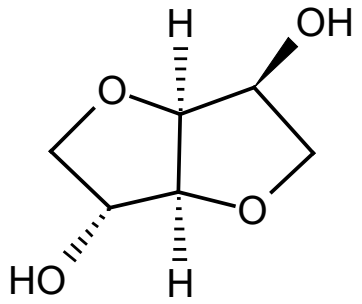
$H_2N\text{-}R\text{-}NH_2$ diamine



Polyhydroxy uréthane

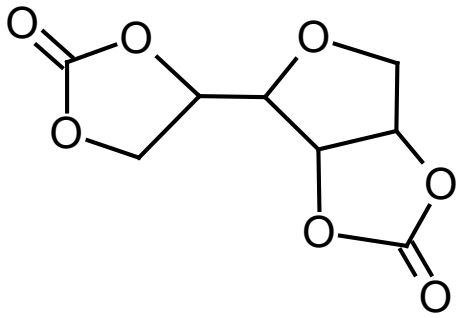
Substrats dérivés des sucres

Isosorbide*

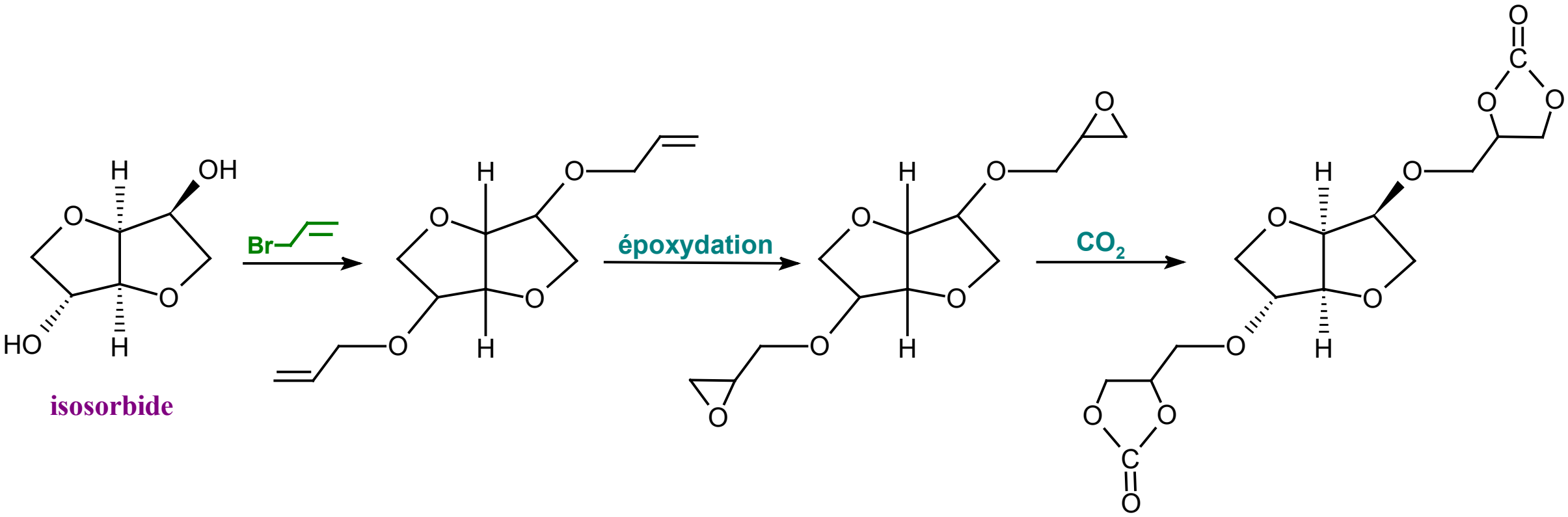


produit commercialement par Roquette (France), environ 20,000 t/an

Sorb-bisCC**

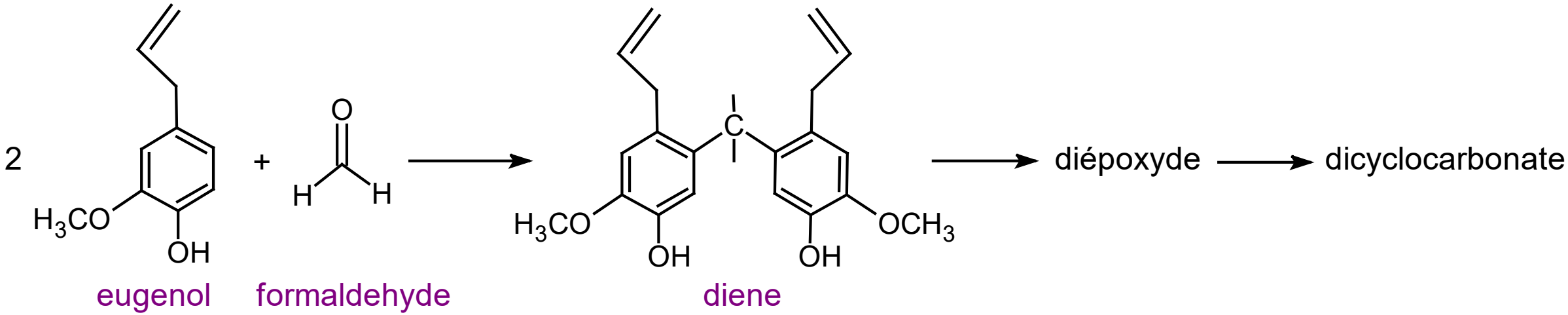


* M.Rose, R. Palkovits, ChemSusChem, 2012, 5, 167-176.
* P. Furtwengler, L. Averous, Nature Scientific Reports, 2048, 8, 9134.



isosorbide

Substrats dérivés de la lignine



Conclusions

- **Vaste champ de possibilités de polymères verts**
- **Valorisation du CO_2**
- **Substrats moins toxiques**
- **Perspective de déboucher sur des matériaux inattendus**
- **Développement de catalyseurs, crucial**

Les monomères utilisés actuellement

1. **Résines époxy**
   - **épichlorhydrine: corrosif, toxique et cancérigène**
   - **bisphénol A: extrêmement toxique, fabrication interdite au Canada**
2. **Polyuréthanes**
   - **diisocyanates: extrêmement toxiques, isocyanate de méthyle → Bhopal**
   - **dialcool, diamine ou bisphénol A**
3. **Polycarbonates**
   - **phosgène: gaz de combat**
   - **bisphénol A**