LABORATOIRE DE CHIMIE AGRO-INDUSTRIELLE

Superhydrophilic interfaces and short and medium chain solvo-surfactants

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JOURNÉES CHEVREUL

PLANT CHEMISTRY AND LIPOCHEMISTRY

Maisons-Alfort (Ecole Vétérinaire)

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Objectives

Ways of synthesis of short and medium chain Monoglycerides and Glycerol carbonate esters

Physco-chemical properties

- Intrinsic
- At interfaces
- Possiblities of formulations

Applicative properties

- Emulsifying agents
  - Solubilization
  - Encapsulation
- Surface agents
  - Anti-adhesion
  - Anti-corrosion
  - Cross barriers
- Gelation Properties
  - Water retention
  - Thickening agent

Application domains

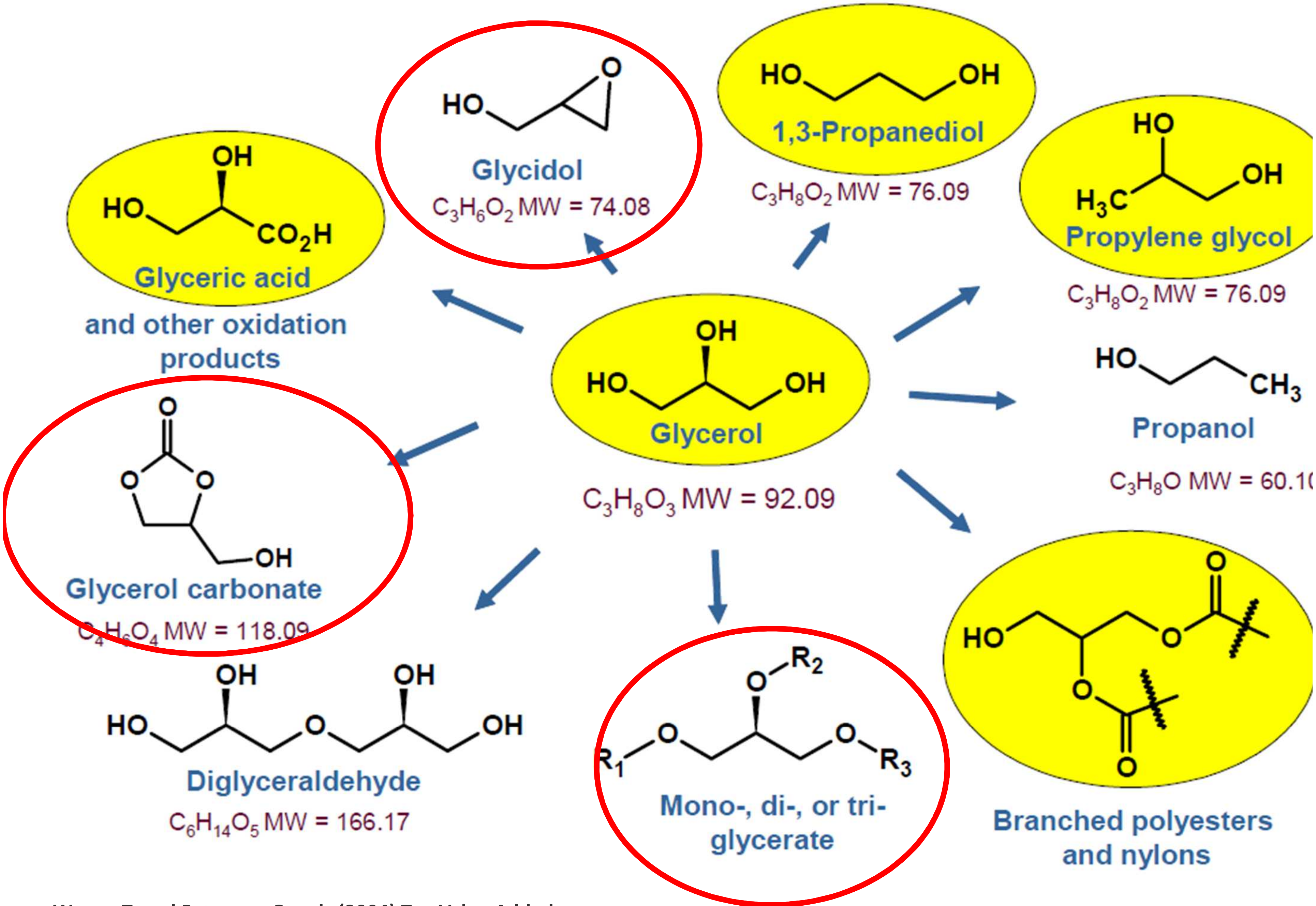
Paints

Foods

Cosmetics

Pharmaceutics

…………………………

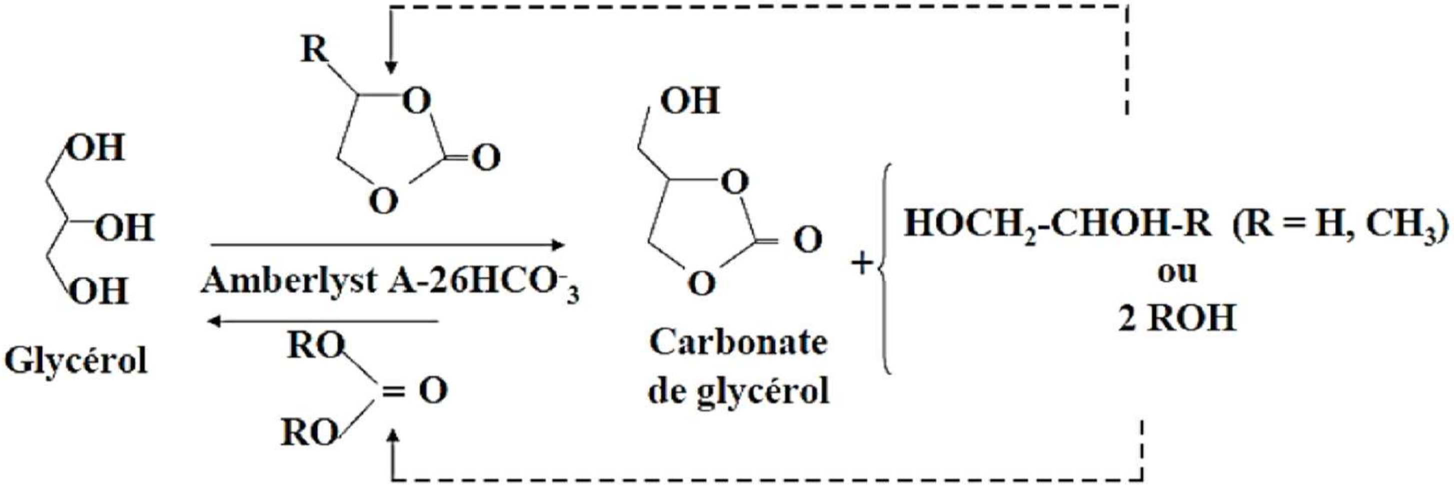


Werpy, T. and Petersen, G., eds (2004) Top Value Added Chemicals From Biomass, US Department of Energy

Derivatives of Glycerol

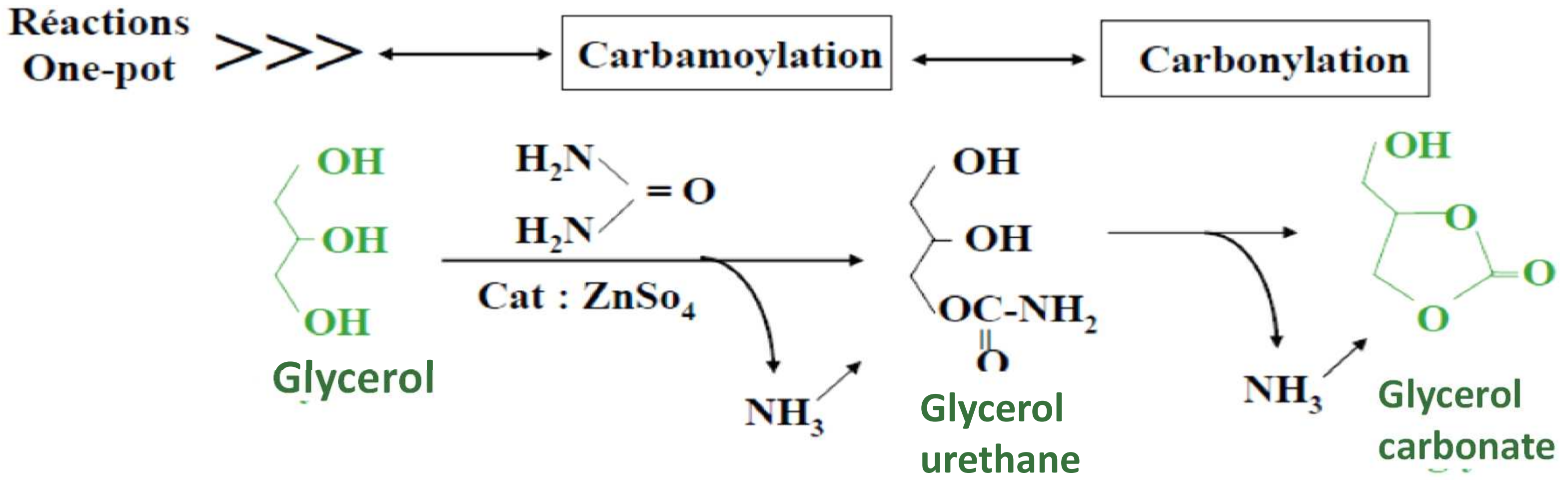
Routes of Glycerol carbonate synthesis

- **Catalytic transcarbonation of glycerol**



ONIDOL/INPT : FR 95 04 961 (24.04.1995) ; EP 0739 888 A1 (30.10.1996)

- **Catalytic carbonylation of glycerol by reaction of urea with glycerol**



ONIDOL/INPT : FR 98 055 47 (30 Avril 1998) ; US Pat 6 025 504 (15 Février 2000)
EP 99 390 009 A1 (27 Mars 2001)

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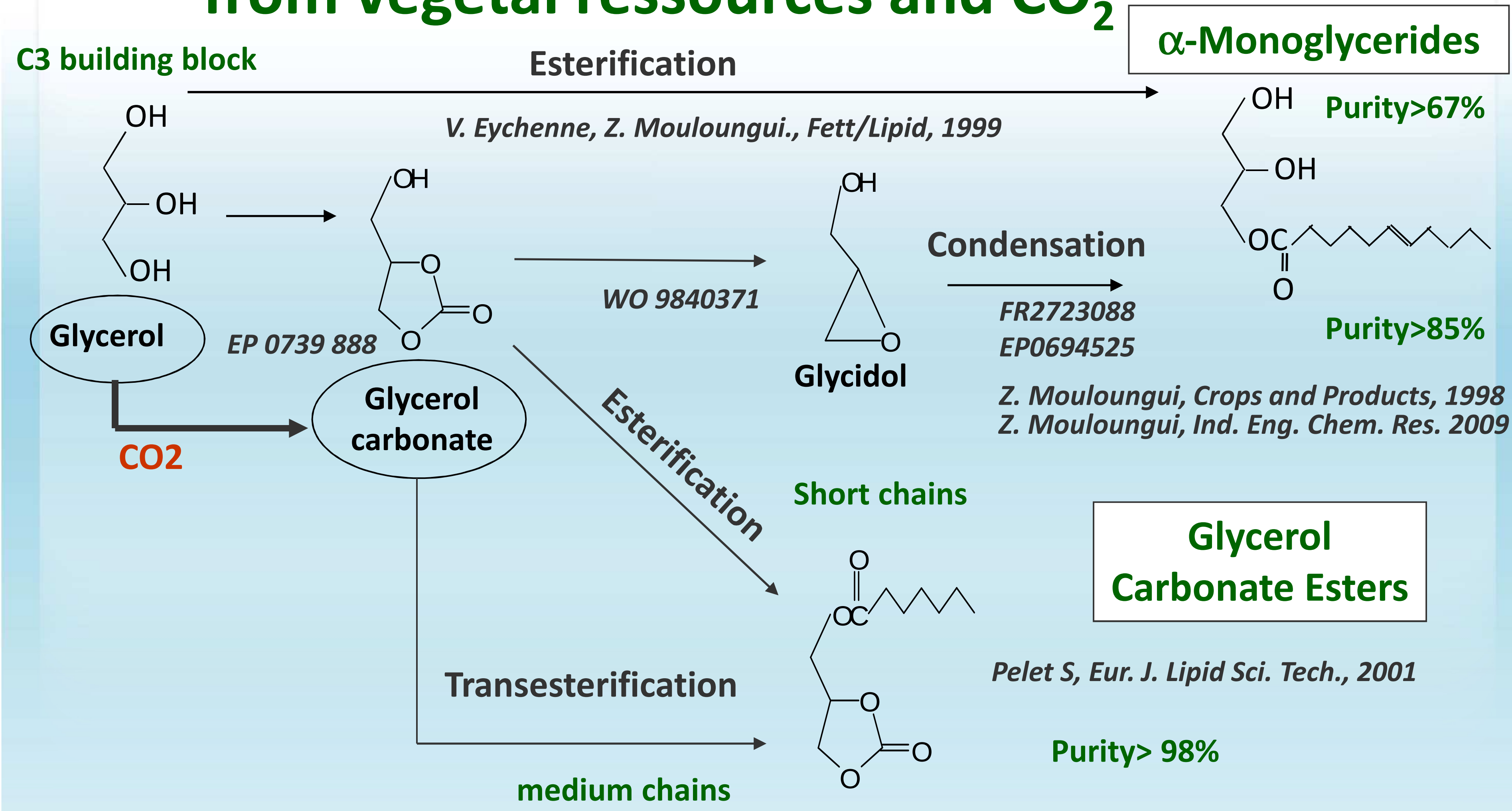
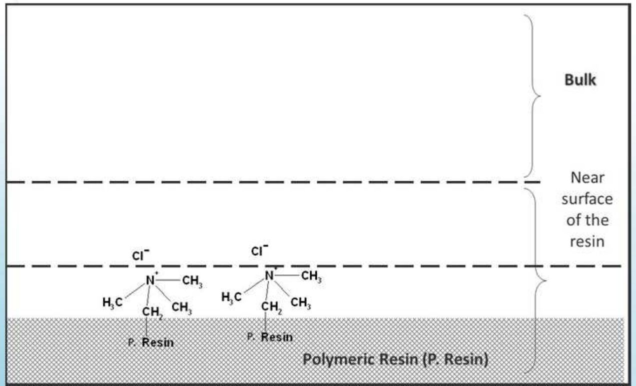
α-Monoglycerides / Glycerol carbonate esters from vegetal ressources and CO_2

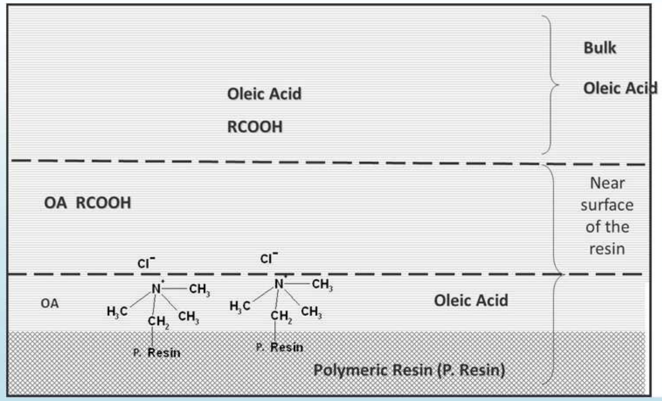


Atom Economy, CO_2 sequestration, No solvent, Direct Use

Synthesis of Glycerol 1-Monooleate by Condensation of Oleic Acid with Glycidol Catalyzed by Anion-Exchange Resin in Aqueous Organic Polymorphic System

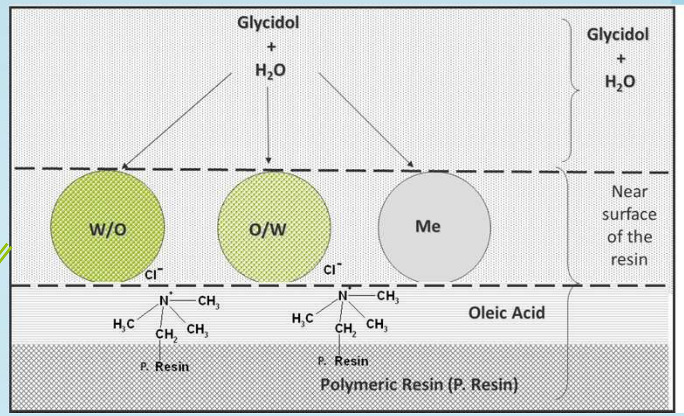


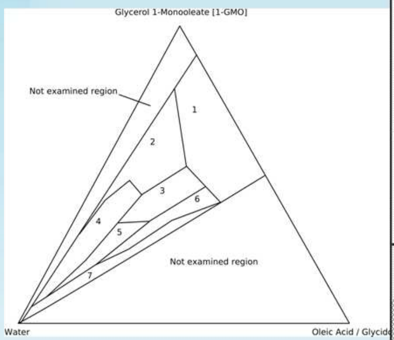
Resin hydrophobation

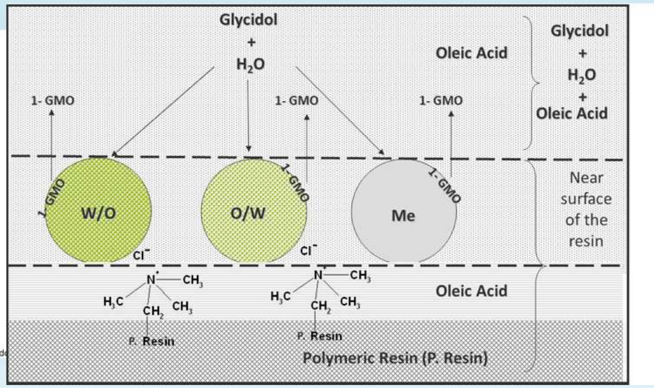


Diffusion of reagents, Adsorption, Surface reactions, diffusion of reaction products, desorption of the reaction products

Emulsion/microemulsion catalytic medium



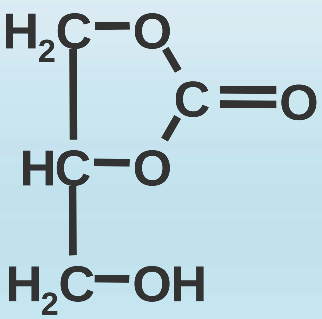




1-MGO Synthesis

Z. Mouloungui et al., Industrial & Engineering Chemistry Research 48(15): 6949-6956.

Synthesis of Glycerol Carbonate Esters



Glycerol carbonate

Acylation by acyl chlorides

OEHLENSCHLÄEGER J., 1979

Acylation by acidic anhydrides

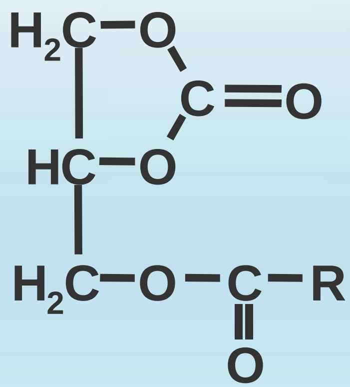
DE 3804820 (1989)
Dainippon Ink and Chemicals

Esterification by carboxylic acids

DE 3937116 (1991)
Dainippon Ink and Chemicals

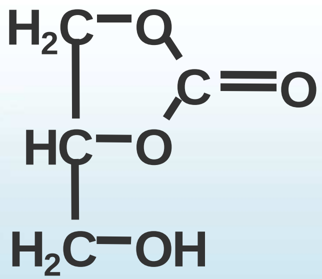
Transesterification by methyl esters

US 2979514 (1961)
Rohm & Haas Company

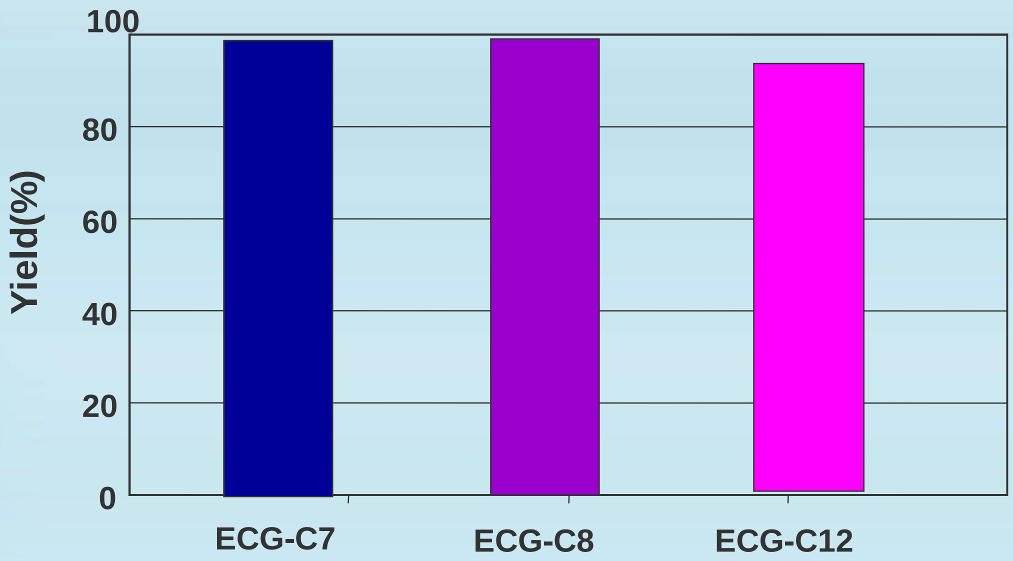


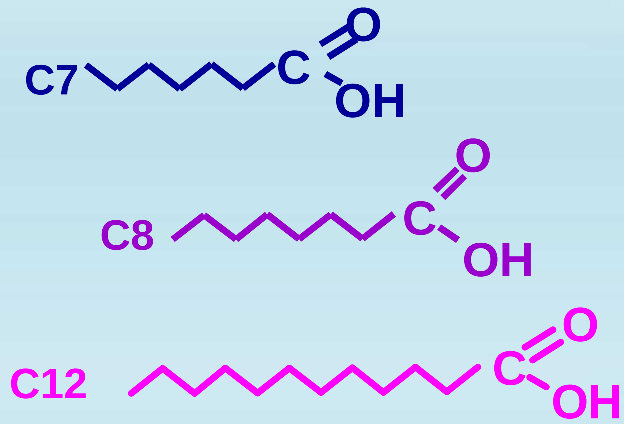
Glycerol carbonate esters

Glycerol carbonate esterification by short chain fatty acids



$+$ **FA** $\rightleftharpoons$ **GCE** $+ H_2O\uparrow$





- M = 2 (Molar ratio FA/GC)
- r = 1 (Catalytic ratio : % molar PTsA/GC)
- T = 110°C
- Reaction duration = 3 h

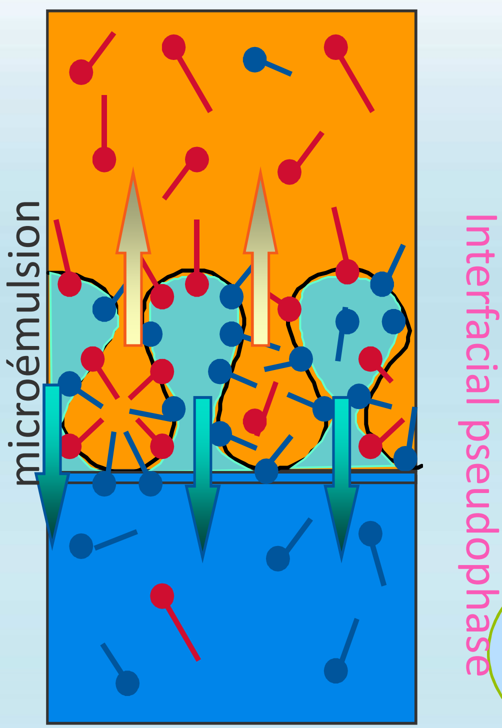
Generic reaction systems/Microorganized systems

Heterogeneous self-organized liquid system

Adsorption/désorption
Diffusion, Reaction,
Dynamical microréactor

Direct usable molecules
No purification

Lipophilic phase



Hydrophilic phase

Polyphasic systems

Continous reactors

Batch reactors

Hydrophobic catalytic bed microreactor

Kintetic Models

- Diffusivity – Material *Transfert*

- Temperature – Energy *Transfert*

Molecules ready to use

Solvent economy

Formulated systems

From Laboratory scale 250 mL

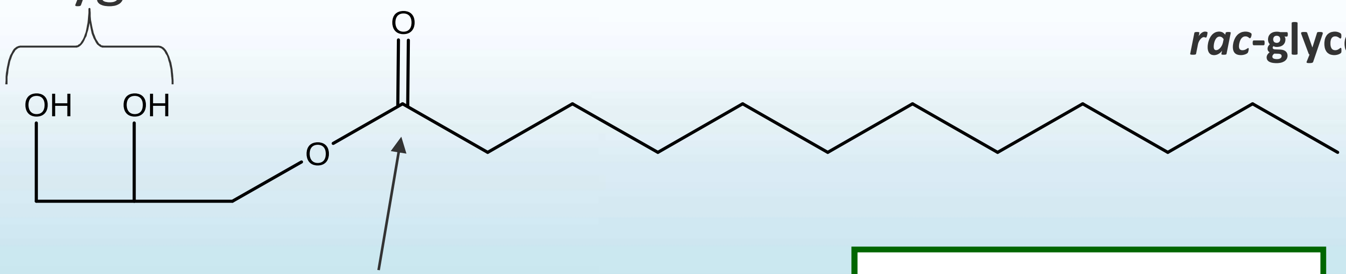
Continuous reactor (30-100 g/h)

Batch reactor

To pre-pilote scale 25 L

Chemical structures of fatty bifunctional molecules

2 free Oxygens



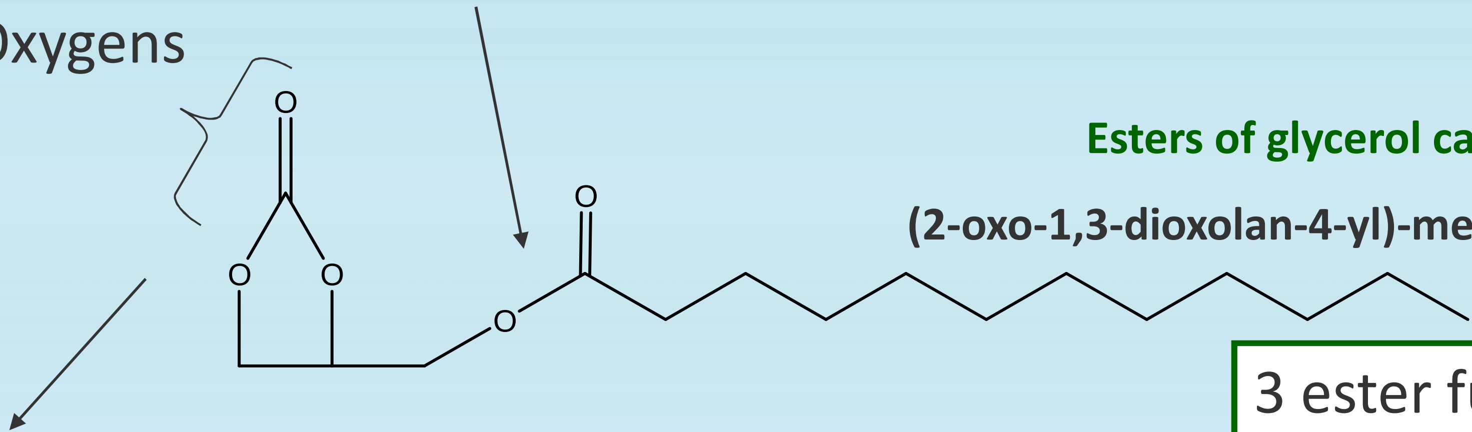
Esters of glycerol

***rac*-glycerol 1 alcanoate**

Exocyclic ester function

1 ester function

2 blocked Oxygens



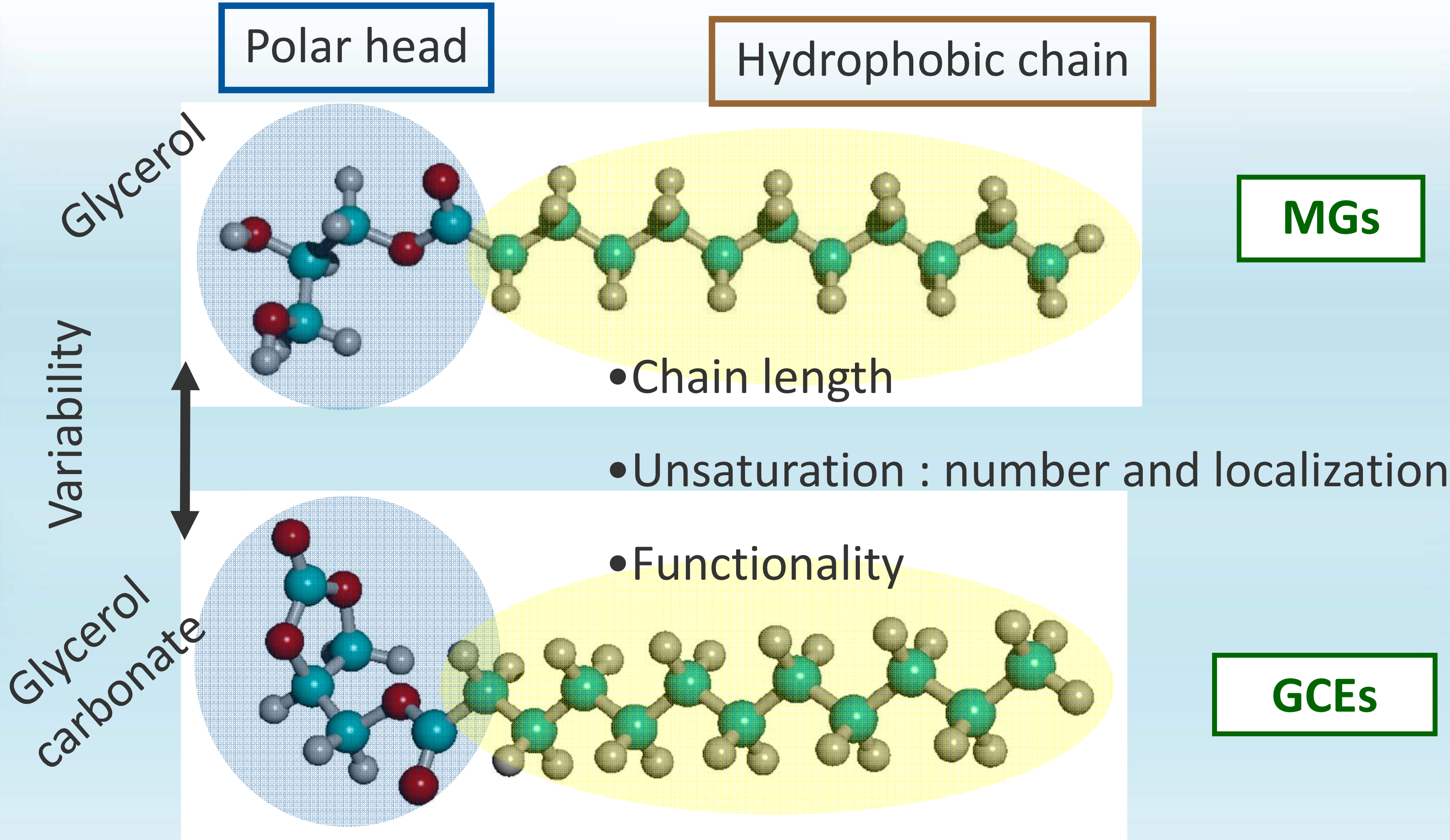
Esters of glycerol carbonate

(2-oxo-1,3-dioxolan-4-yl)-methyl alcanoate

3 ester functions

Five-membered cyclic carbonate function, endocyclic ester function

Amphiphilic structures of fatty bifunctional molecules

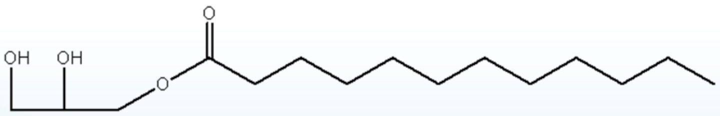


- Chain length
- Unsaturation : number and localization
- Functionality

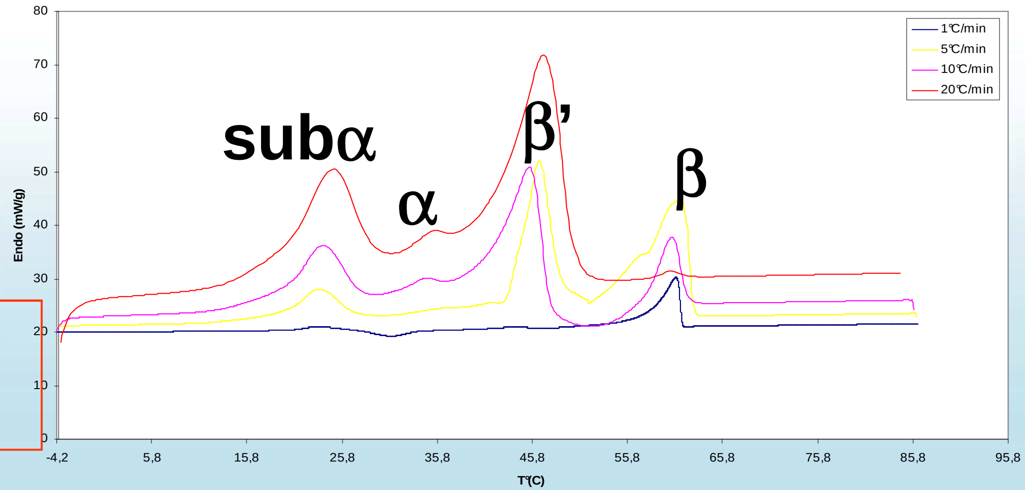
Polymorphism of pure molecules

DSC experiments

Glycerol monolaurate

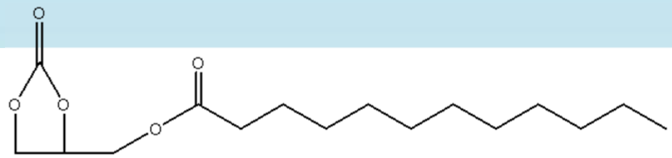


According with littérature (***T. Malkin, M.R.E. Shurbagy, J. Chem. Soc., 1936***)



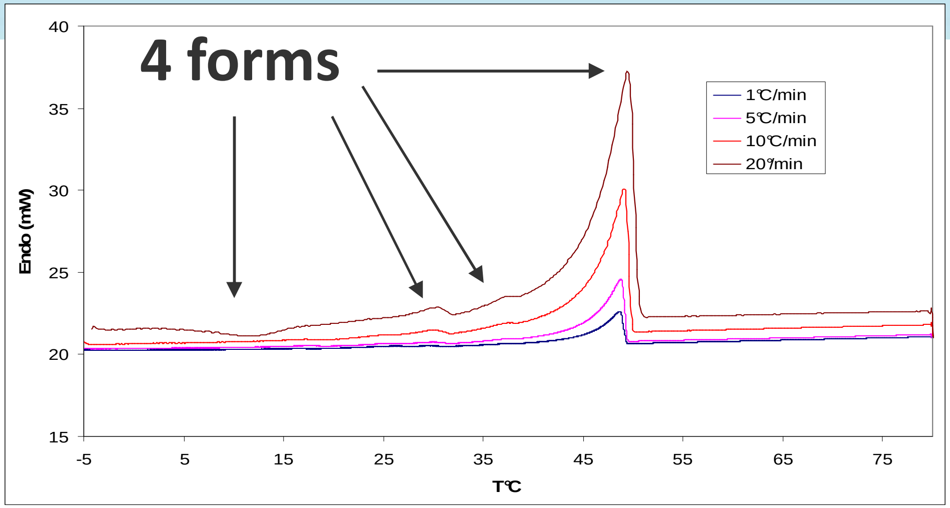
Different identified forms with different thermal stabilty

Glycerol carbonate laurate



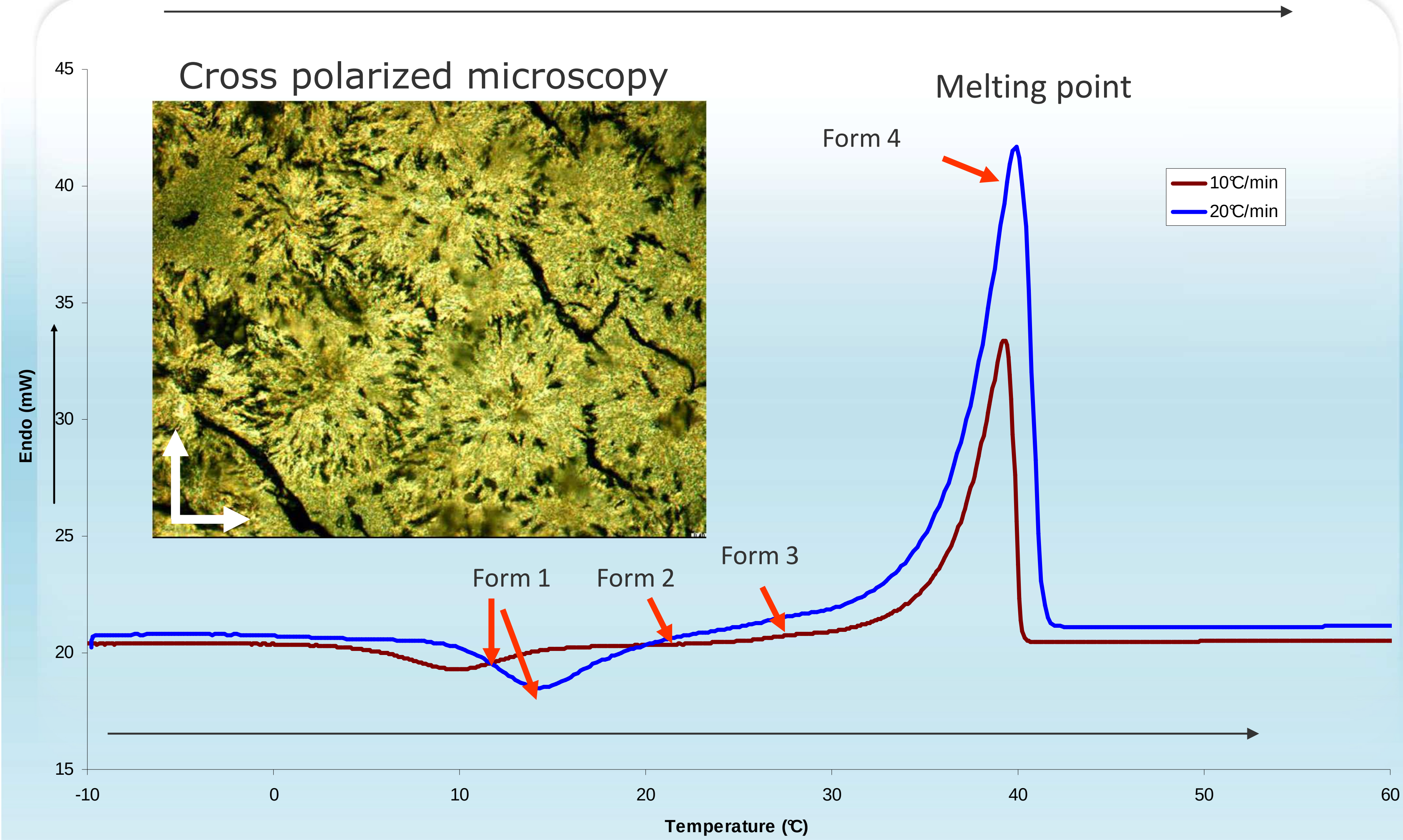
Carbon number	Melting T°	Other transition
8	18	9
9	31	19
10	39	-
12	52	37.5

New phenomena



- **Effect of polar head on polymorphic behavior: GCEs are less sensitive to the cooling rate**

GCE-C10 Heating



GCE-C12 Heating

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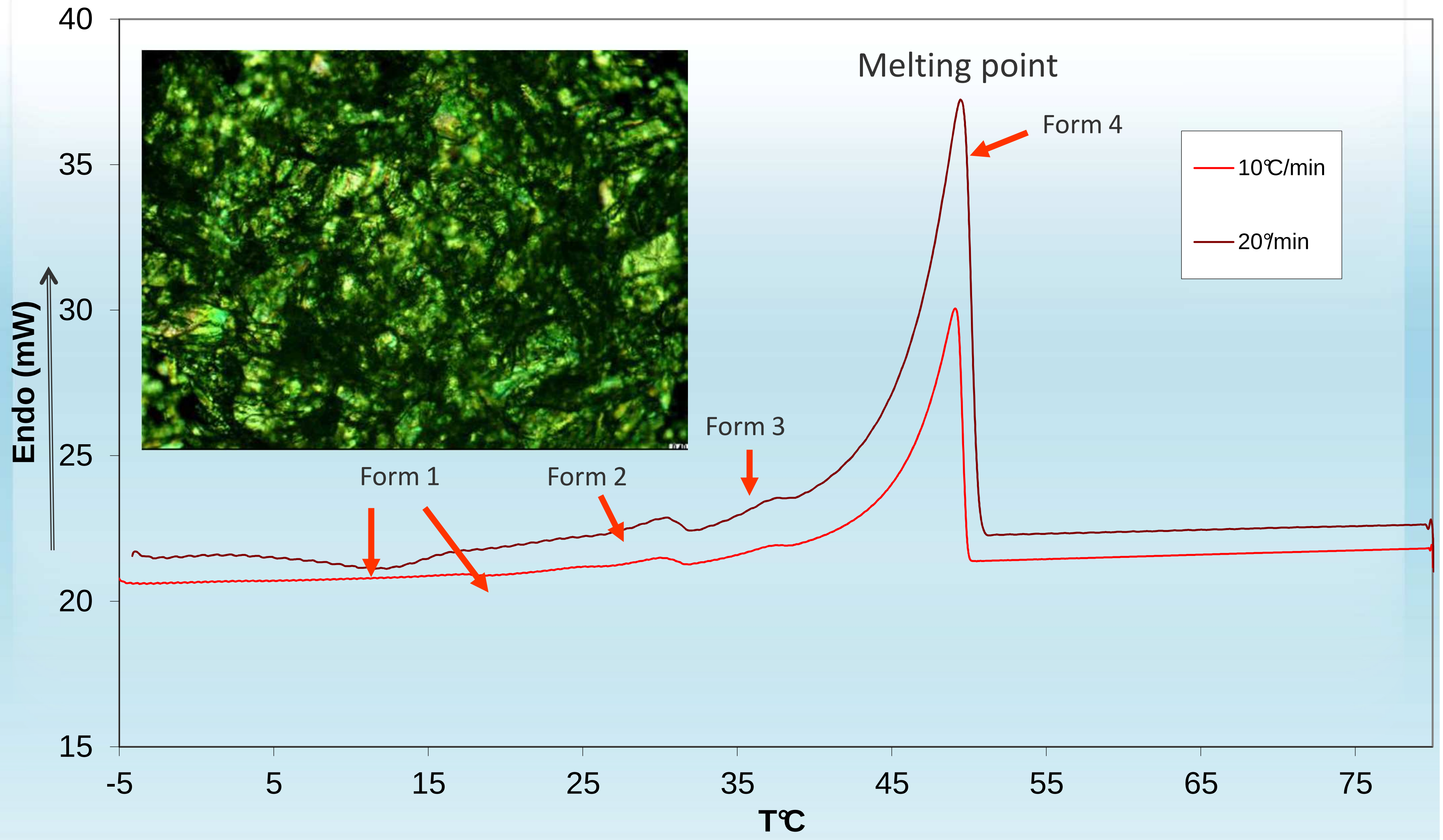

GCE-C10 COOLING

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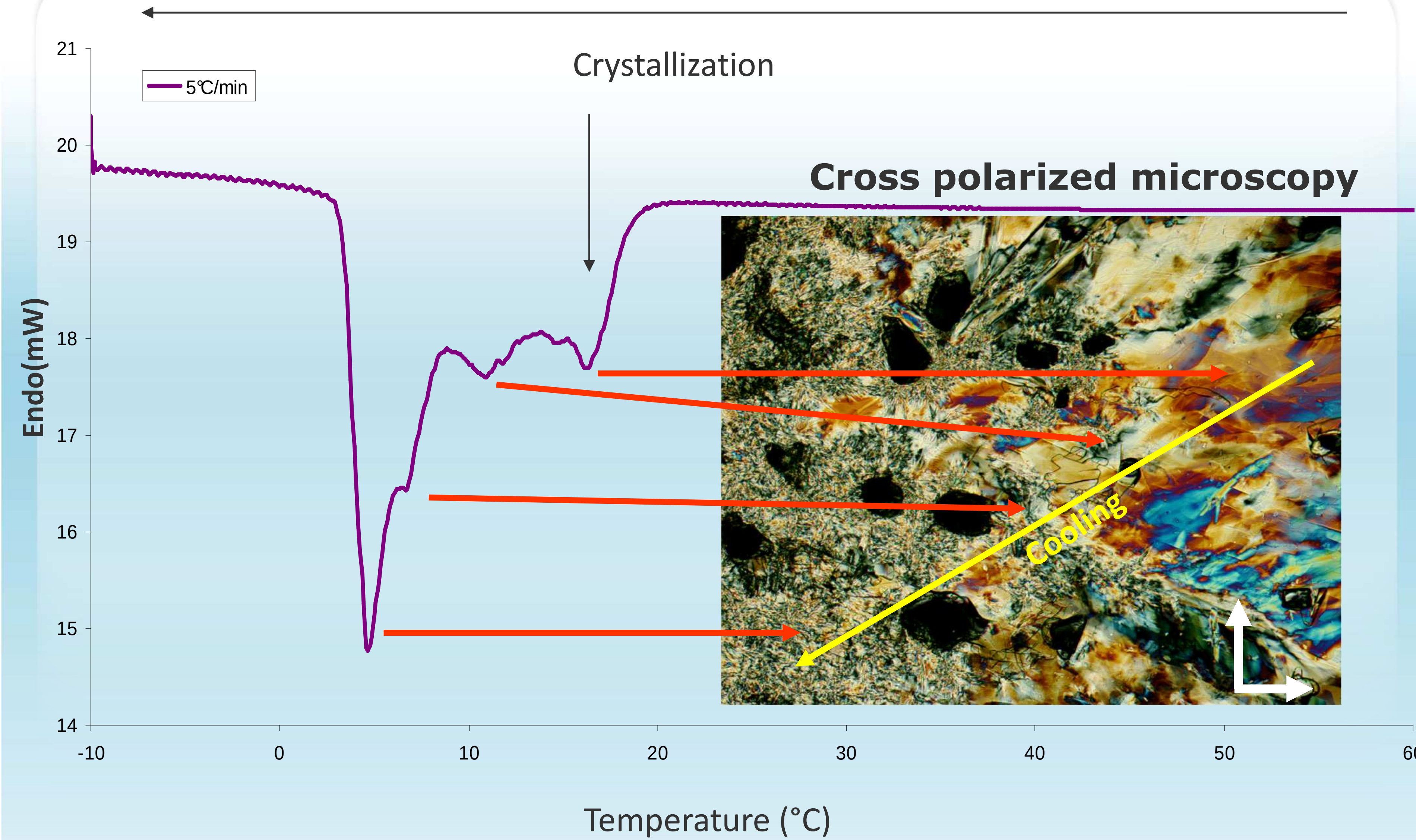
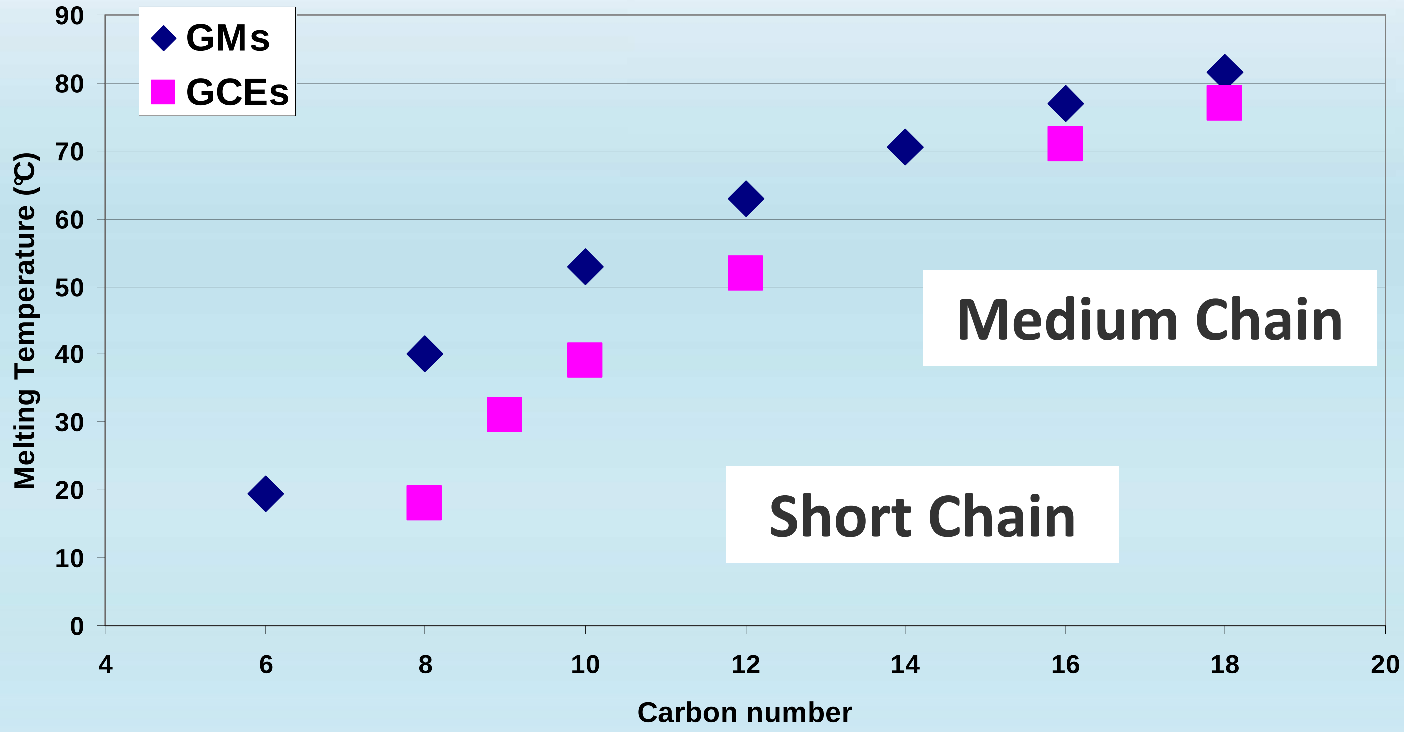


Melting points

- Taken on the higher stable form from DSC experiments



MP of the β form MGs is higher than the more stable form observed with GCEs

Blocked oxygens on GC lead to the decrease of MP.

Structuration of surfaces

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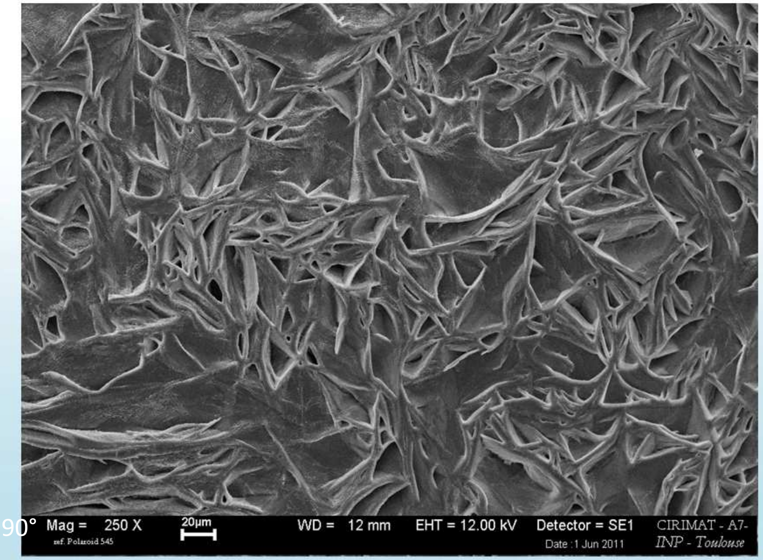
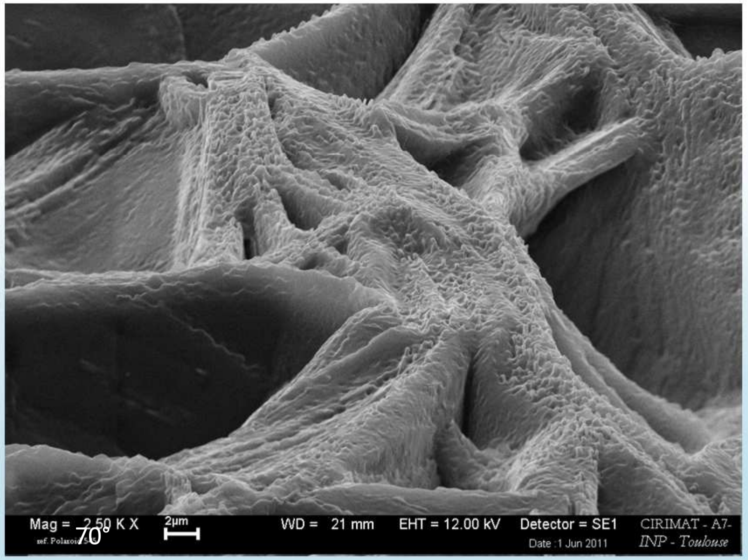
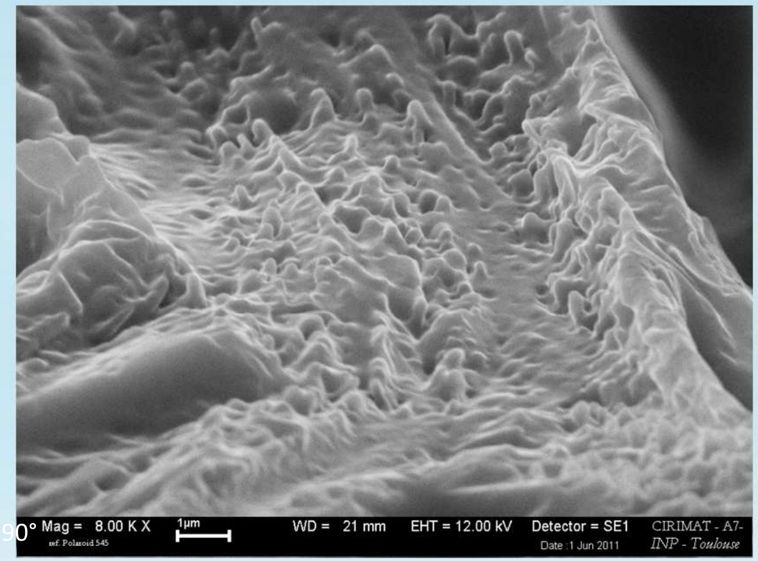
Glycerol monolaurate crystallization







The surfaces can by texturated by crystallization of molecules of high melting point

The roughness is of nanometer scale

→ **domain of the capillarity**

R. Valentin, et al. (2012). Journal of Colloid and Interface Science **365(1): 280-288.**

Super-Water-Repellent Fractal Surfaces

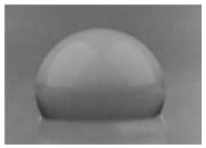
T. Onda,*,† S. Shibuichi,† N. Satoh,‡ and K. Tsujii†

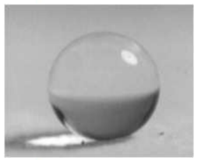
Langmuir, Vol. 12, No. 9, 1996

$$\cos\theta^* = r\cos\theta$$

$$r = \frac{area}{apparent\ area} \geq 1$$

Superhydrophilicity





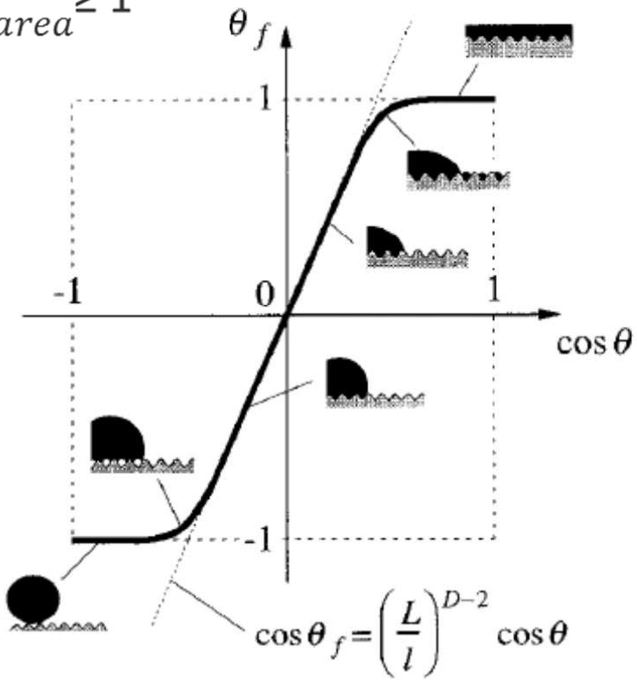


Figure 1. Schematic illustration for $\cos\theta_f$ vs $\cos\theta$ theoretically predicted.

Superhydrophobicity

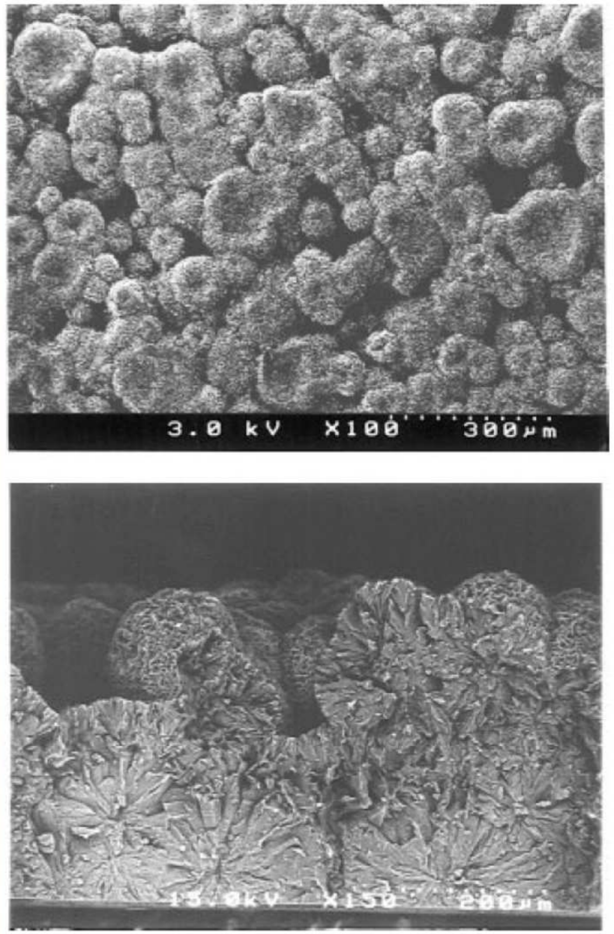


Figure 2. SEM images of the fractal AKD surface: (a, top) top view, (b, bottom) cross section.

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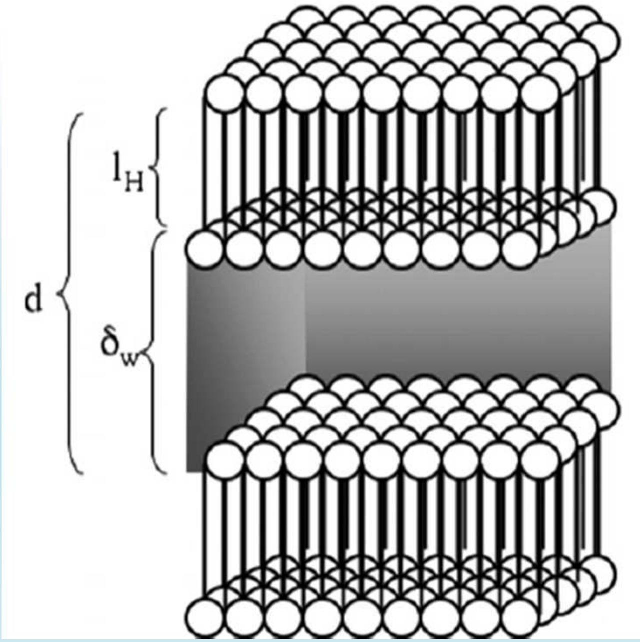
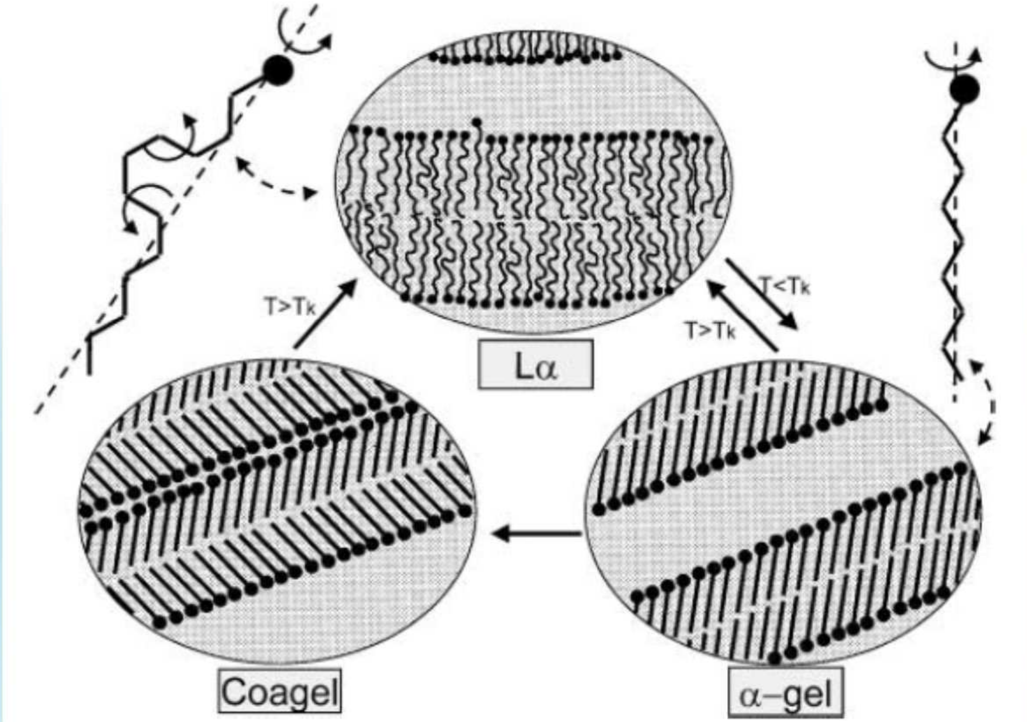
Hydratation properties of GCEs

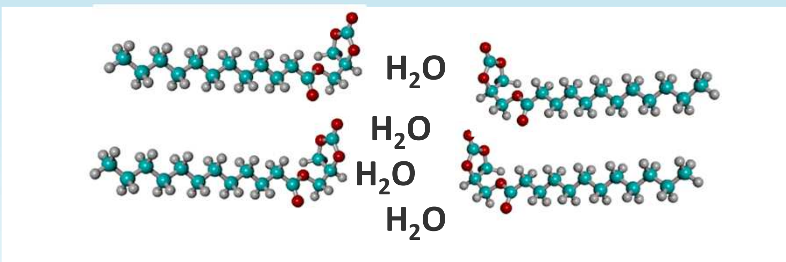


M. Ambrosi, Phys. Chem. Chem . Phys., 2004



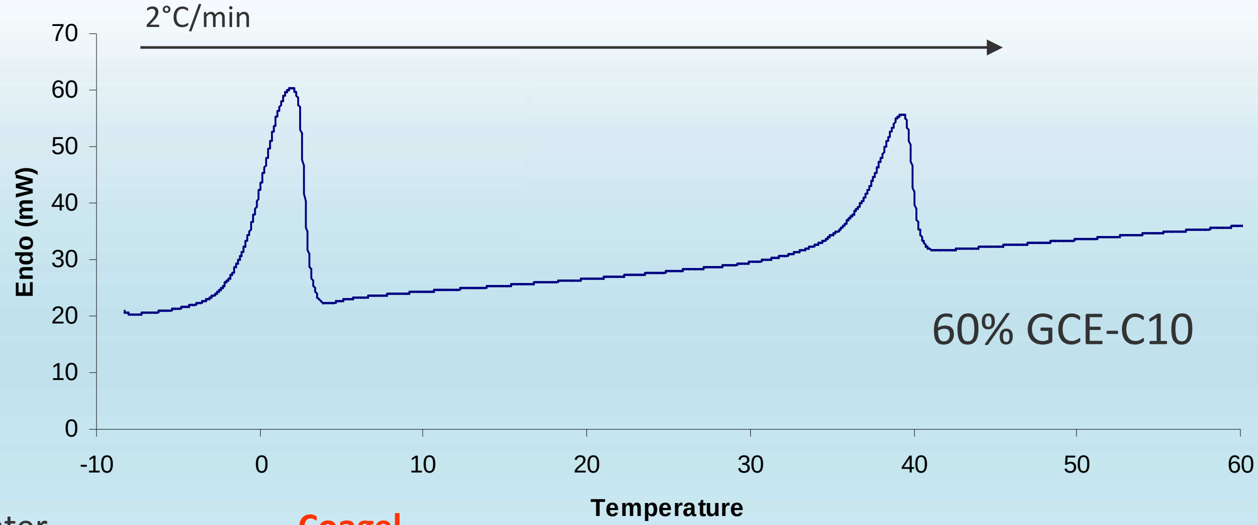
A. Sein et al., J.Coll. Interf. Sci. 2002

How many water interact with polar head of GCEs?



Hydratation properties of GCEs

Detection of the amount of non-melting water by DSC analysis



Pure water

Coagel

$$W_b(\%) = \frac{333.79 - \Delta H_{exp}}{333.79}(100 - P)$$

$$N = \frac{M_n W_b}{M_w P}$$

Amount of water hardly bounded to the glycerol carbonate fatty acid esters

M. Ambrosi, Phys. Chem. Chem . Phys., 2004

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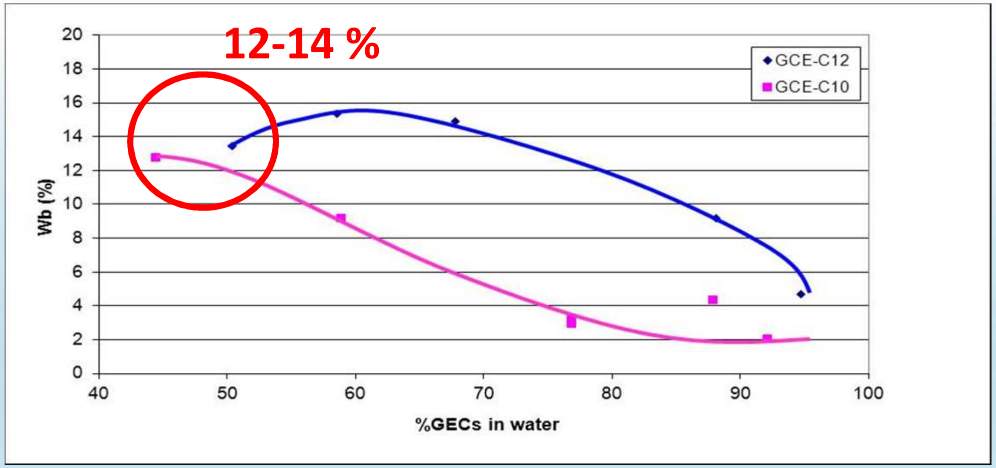
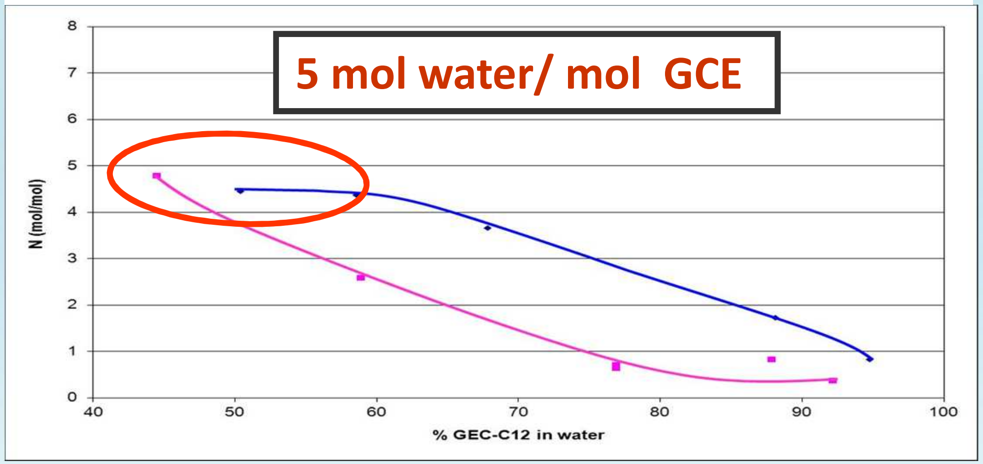
Hydratation properties in GCEs coagels

% of strongly bounded water



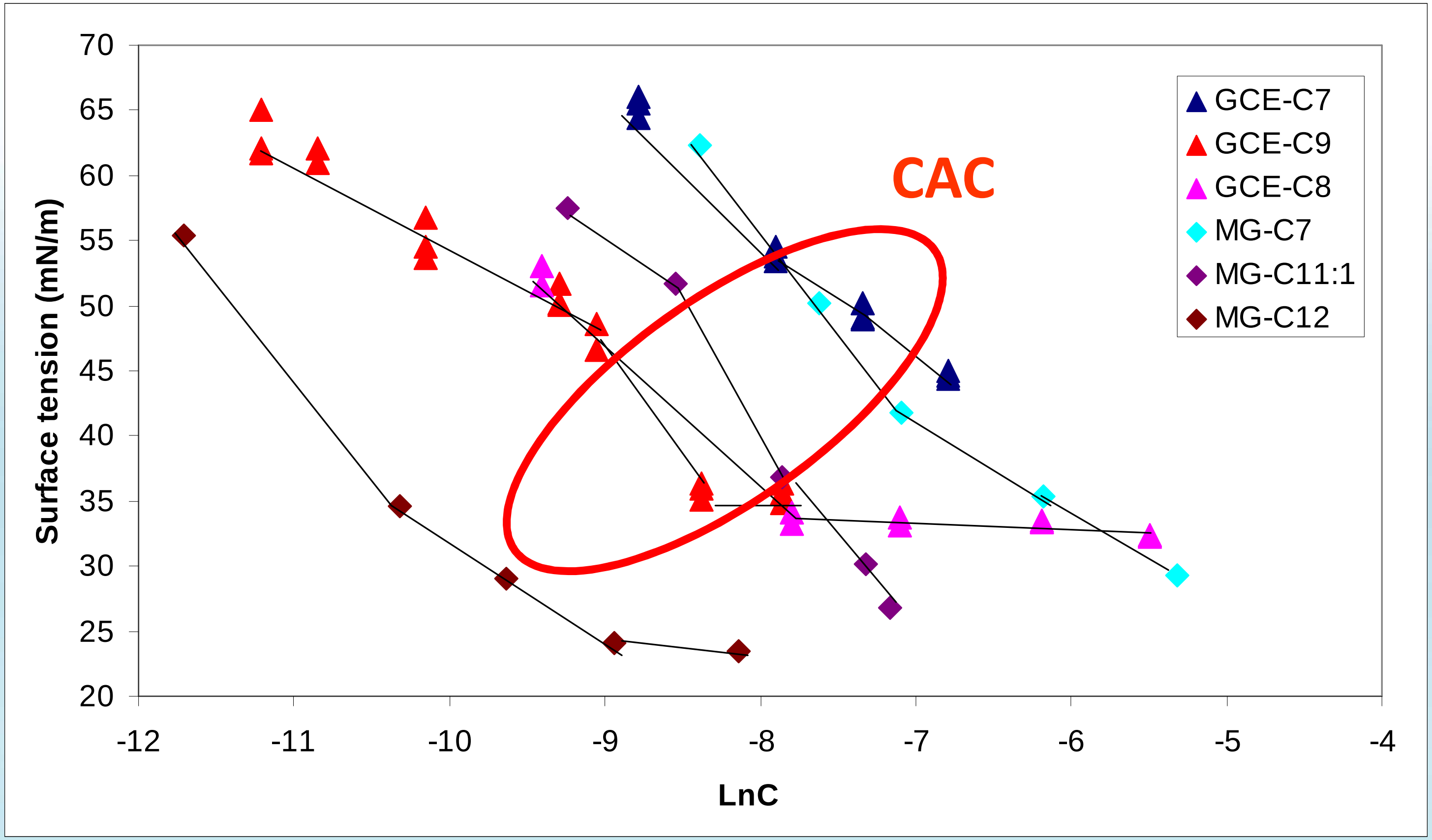
High **influence** of the the **chain length** on the hydratation of **glycerol carbonate esters coagel**

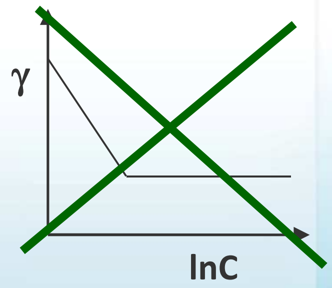
Mol of bounded water/GCE polar head



« freezed » water increase with chain length

Surface properties CMC/CAC



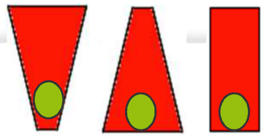


Progressive fall in γ → Aggregation rather than micellization

These molecules are hydrotrope → **Solvo-surfactants**

K. Lunkenheimer, S. Schroedle and W. Kunz, Prog. Colloid Polym. Sci., 2004
C. Neuberg, J. Chem. Soc., Trans., 1916, 110, II, 555.

Interfacial Parameters



	CMC/CAC mmol/L	CMC/CAC mg/L	A Area/molecule (A^2)	γ cmc mN/m	CPP
MG-C7	1	204	25.6	35.3	0.8
MG-C11:1	0.38	89.04	23	36.9	0.9
MG-C12	0.29	79.46	31.1	24.1	0.7
GCE-C7	1.13	259.9	38.7	44.4	0.5
GCE-C8	0.41	100.04	34	33.3	0.6
GCE-C9	0.25	64.5	60	35.5	0.3
C_9COE_3	0.9	273.6	45	27.3	0.47
C_9COE_4	0.8	278.4	50	28.5	0.42

$$CPP = \frac{V}{A \times Lc}$$

$V = 27.4 + 26.9\, n_c$

$Lc = 1.5 + 1.265\, n_c$

SPHERIC >0.33

ROD-LIKE 0.33<P<0.5

DISC-LIKE >0.5

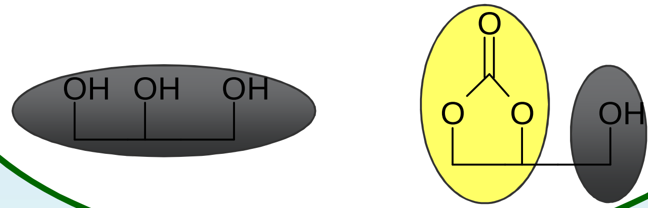
Y. Zhu et *al.* J.Colloid Interface. Sci. **2007,** 312, (2), 397-404.

- Esters of glycerol carbonate are surface active molecules
- Self-assembling in water

- GCEs objects more rod-like

- MGs objects more disk-like

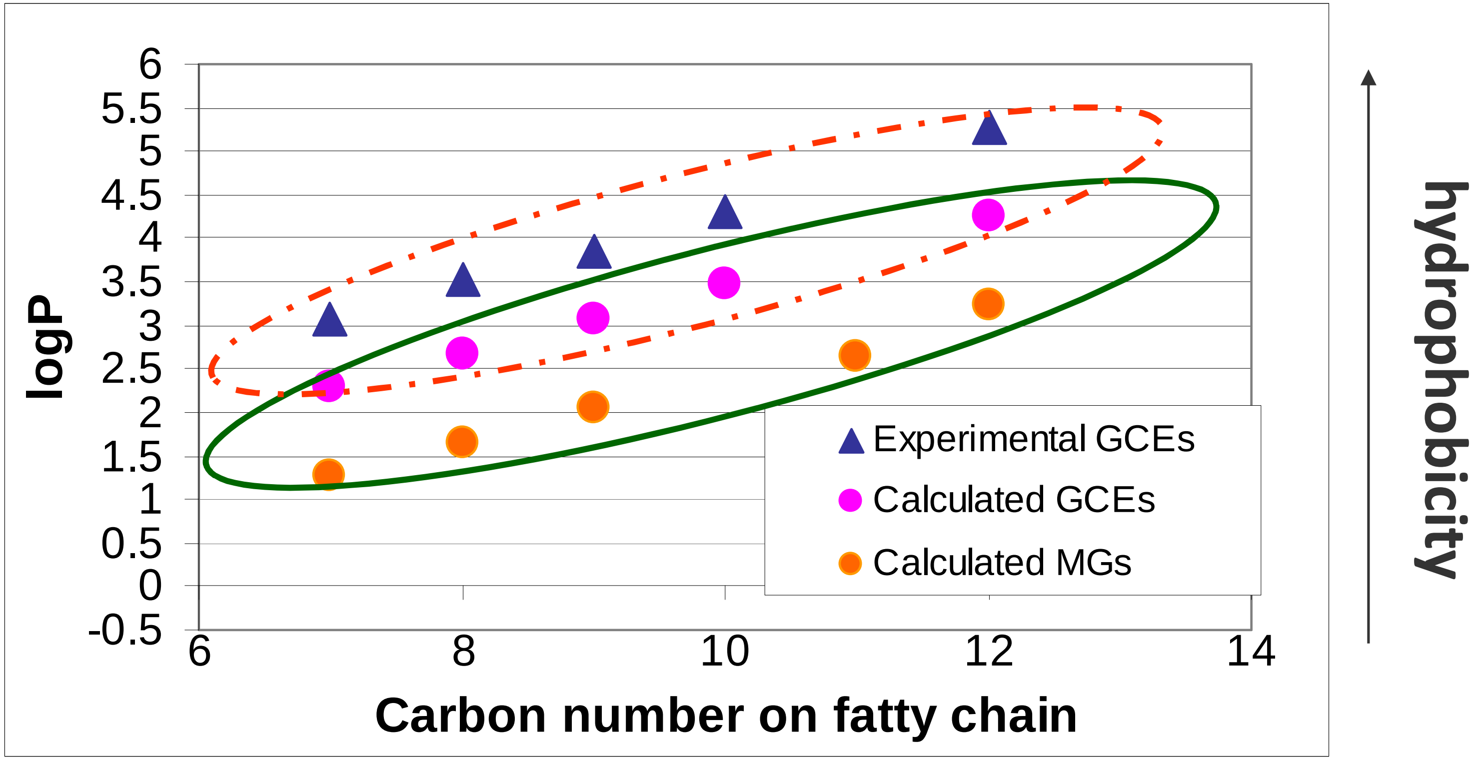
Polar head influence



Water/octanol partition Coefficient

Polarity parameter determined by HPLC on C18 column

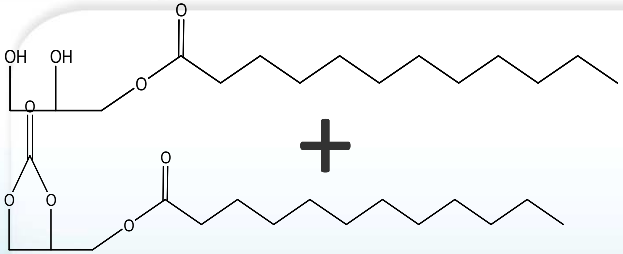
Polarity parameter calculated by Quantitative Structure Activity Relatioship



- Linearity of values with the number of carbon on the fatty chain → **Influence of the fatty chain**
- GCEs more hydrophobic than MGs

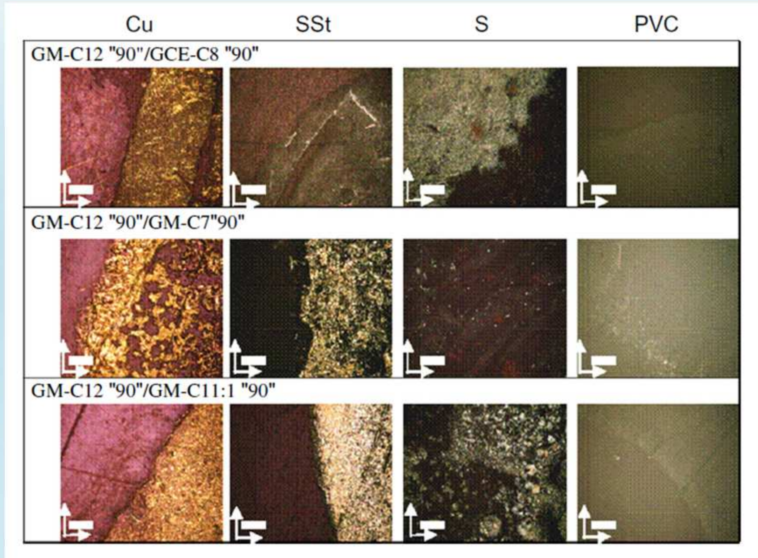
→ **Effect of the polar Head**

Surface Formulations



Self assembling on surfaces : Cu, S, SSt, PVC

Fatty acid esters	Surfaces undiluted coating	just coated	washed
		θ (°)	θ (°)
GM-C12"90"/GM-C7"90" 50/50 (w/w)	Cu	12.5	26.9
	S	9.1	11.7
	SSt	9.6	28.3
	PVC	6.0	29.4
GM-C12"90"/GM-C11:1"90" 50/50 (w/w)	Cu	7.4	8.5
	S	6.0	18.9
	SSt	6.8	9.6
	PVC	7.4	28.3
GM-C12"90"/GCE-C8"90" 50/50 (w/w)	Cu	24.7	36.1
	S	24.3	29.1
	SSt	26.4	37.3
	PVC	32.2	39.1

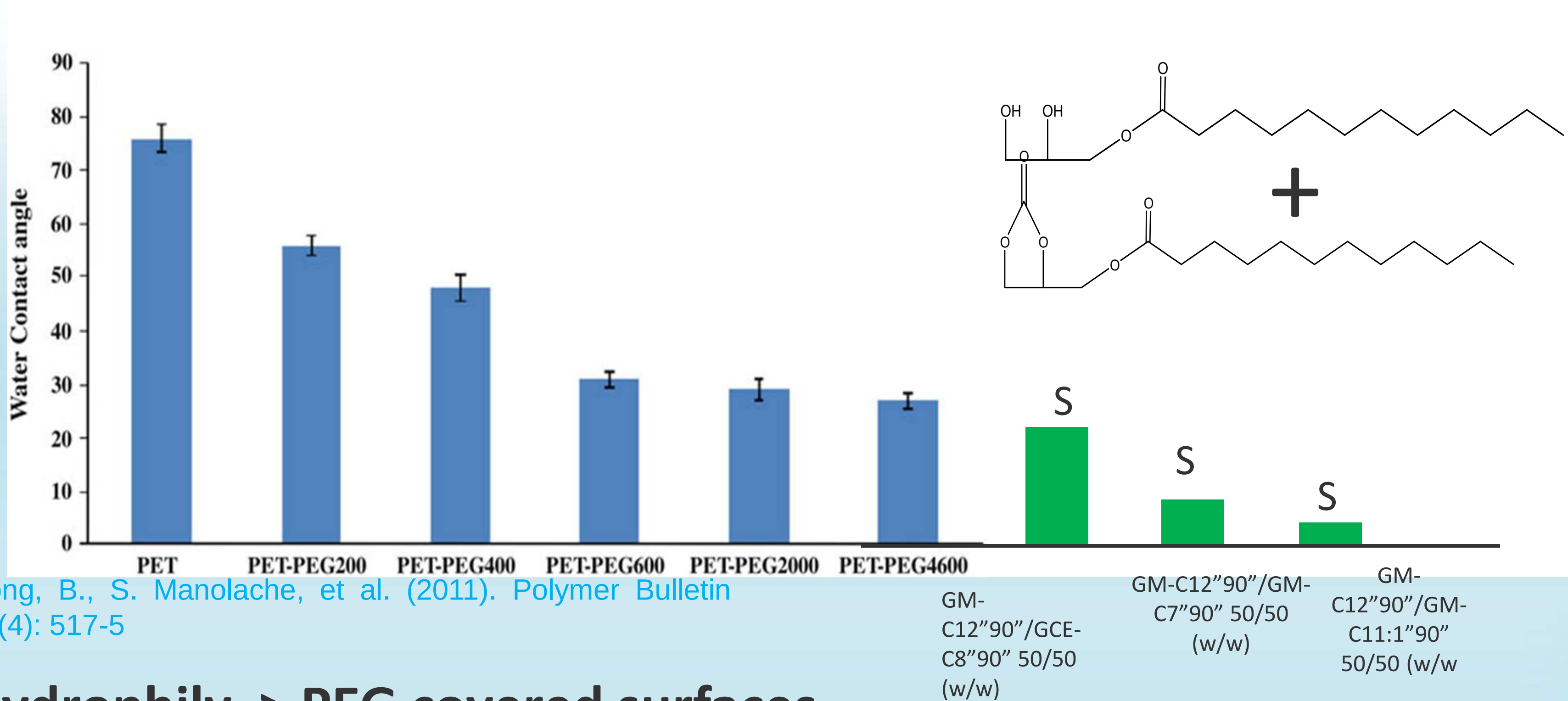


R. Valentin, et al. (2012). Journal of Colloid and Interface Science **365(1): 280-288**

Water contact angle < 10°

Superhydrophilic surfaces

Superhydrophilicity of Surfaces



Dong, B., S. Manolache, et al. (2011). Polymer Bulletin 66(4): 517-5

R. Valentin, et al. (2012). Journal of Colloid and Interface Science 365(1): 280-288

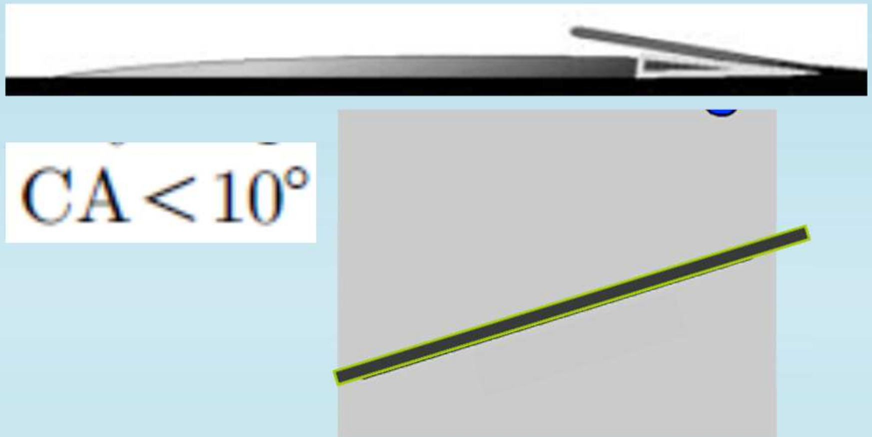
Hydrophily > PEG covered surfaces

Hydrogel-like systems on surfaces = water-repellency induced by superhydrophilicity

Biomimetism

Synergy between the melting properties and solvo-surfactant properties to obtain superhydrophilic surfaces

Structuration + texturation + surfactant activity + CA <10° **= Superhydrophilicity**



« The glands secrete hydrophilic substances that, in combination with the surface roughness, lead to superhydrophilicity. » (*Ruellia devosiana*)

K. Koch; W. Barthlott, Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **2009,** 367, (1893), 1487-1509.

Conclusion

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- **GCEs are new polymorphic molecules different from MGs**
- **Carbonation decreases melting points : 2 OH functions are blocked on GCEs versus MGs where 2 OH are involved in intra and intermolecular hydrogen bonds**
- **Carbonation deacreases the hydrophilic character of the polar head of surface-active GCEs**
- **Short chain and medium chain MGs and GCEs are solvo-surfactants molecules**
- **Formulations of Monoglycerides and Glycerol carbonate esters on surfaces induce superhydrophilicity by biomimetism**

Perspectives

- Better understanding of polymorphic behavior of MGs and GCEs with short and medium chain : crystallographic studies
- New uses for theses self-assembled biomolecules
- Protecting / stabilization / vehiculation
- Water and protic molecules transport

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Thank you for your attention !

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