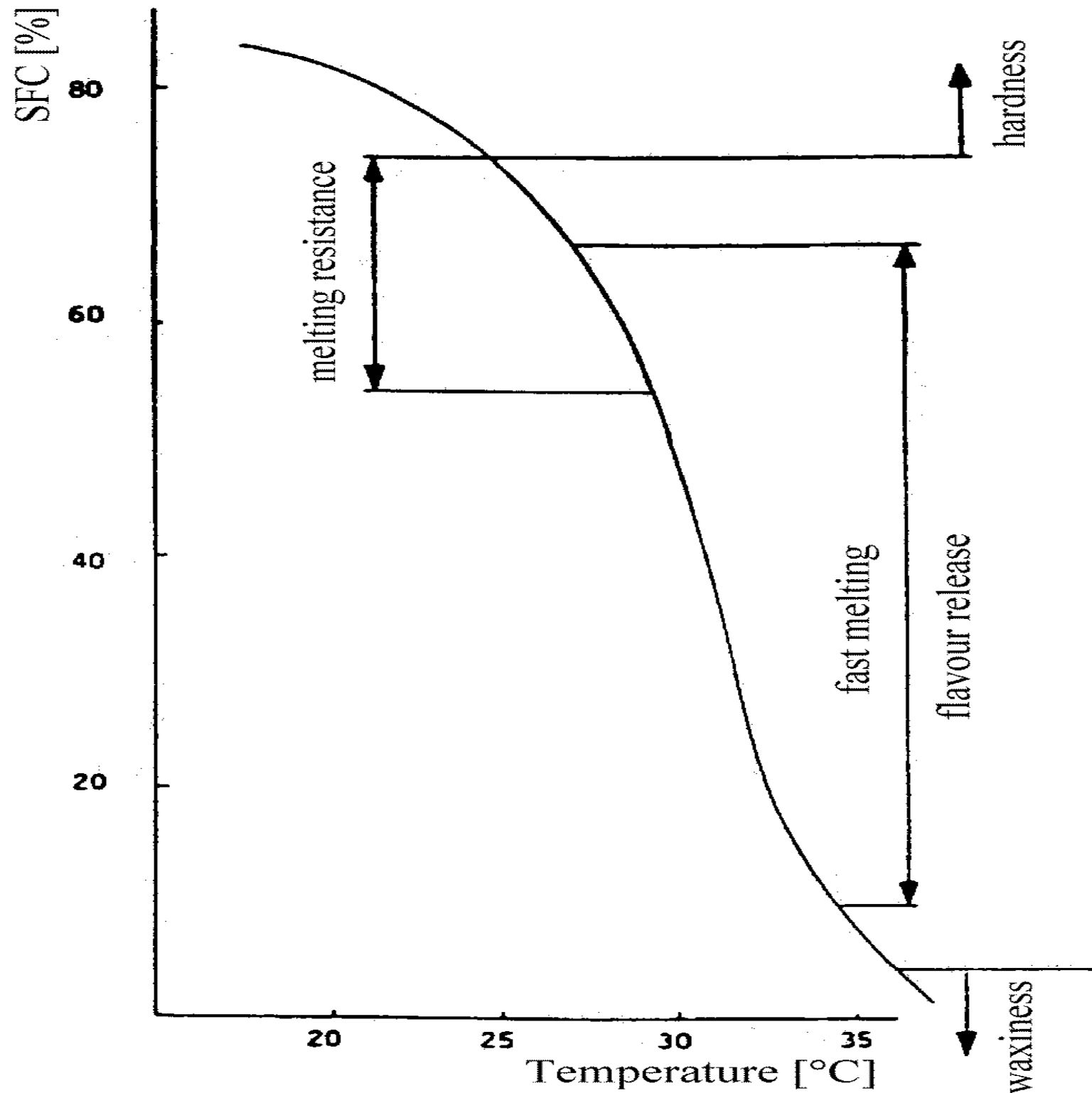


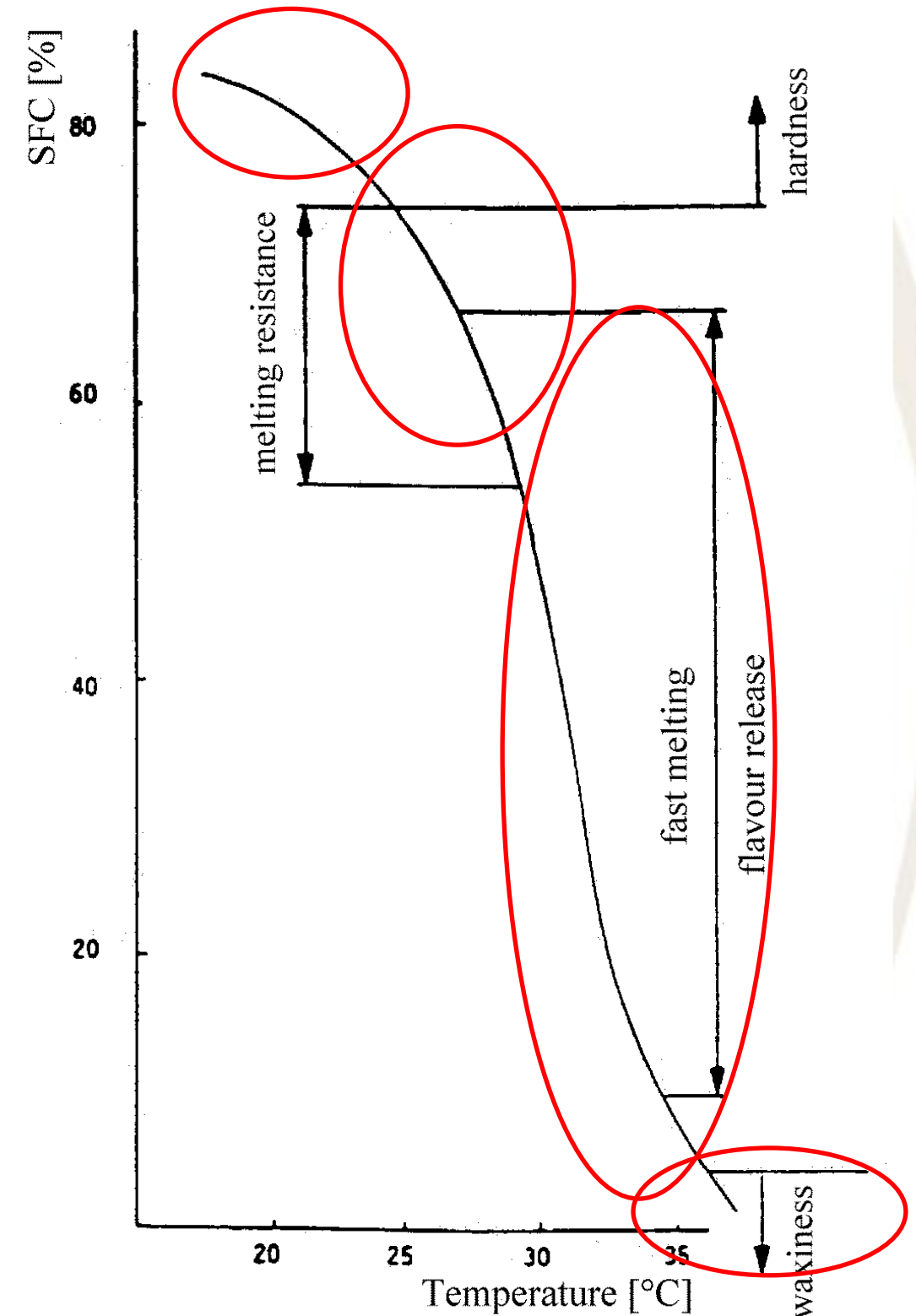
# Crystallization of fat and oils

Dr. ir. Nathalie De Clercq  
9<sup>th</sup> of September

# Crystallization → Melting behaviour = demands for a good chocolate



- ❖ Enough solid fat at 20°C :
  - **good 'snap' upon fracture**
- ❖ Enough solid fat between 20-25°C:
  - **preventing stickiness at consumption**
- ❖ Sharp melting profile between 25-30°C:
  - **mouthfeel, flavour release and cold sensation**
- ❖ Melted at body temperature:
  - **preventing 'waxy feeling'**

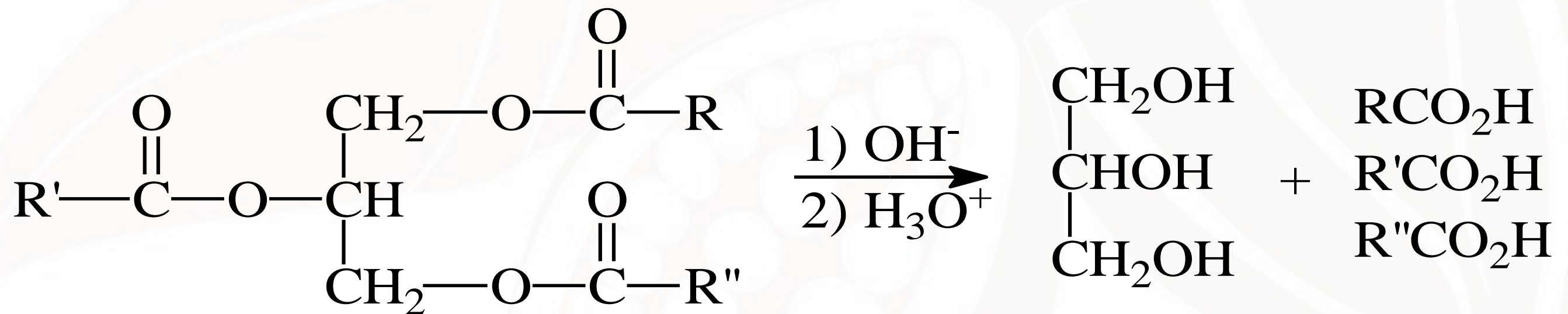




- Fats and oil: chemistry
- Importance of fat crystallization
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- How to measure?
- Case study cocoa butter

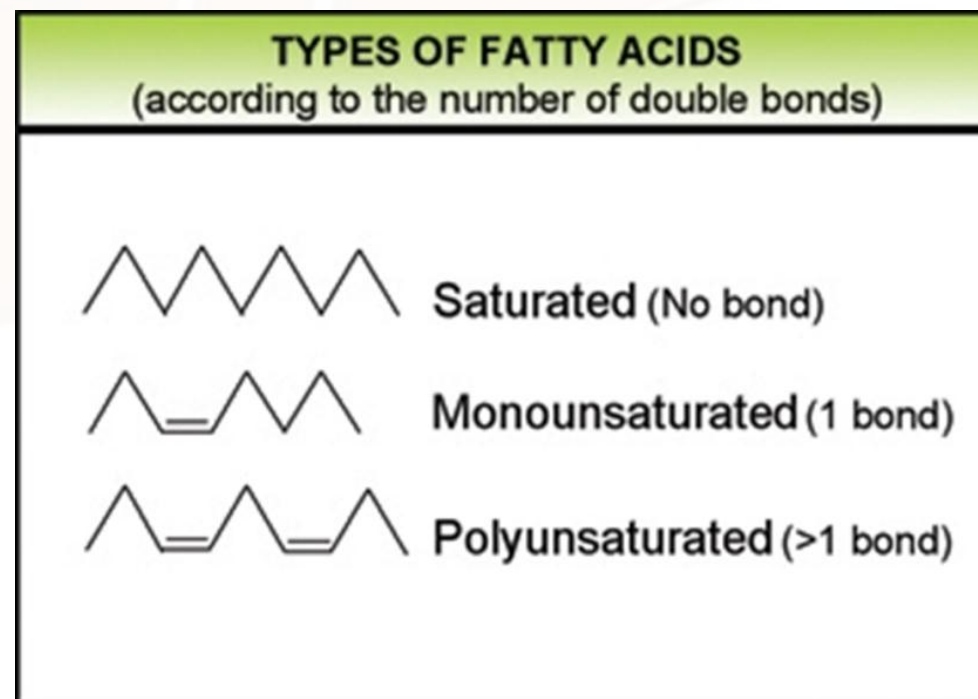
- **Fats and oil: chemistry**
- Importance of fat crystallization
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- How to measure?
- Case study cocoa butter

- Oil/fat = mixture of triacylglycerols
- Animal or vegetable origin
- Triacylglycerols





- Aliphatic carboxylic acids with 4 or more carbon atoms
- Even number of carbon atoms
- 3 different types of fatty acids



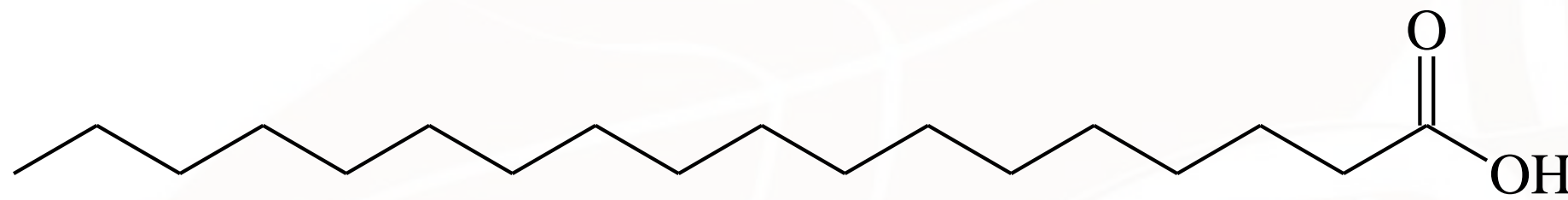
- Short (4 - 6 C-atoms), medium (8 - 14 C-atoms) and long chain ( $\geq 16$  C-atoms) fatty acids

- Systematic and trivial names of frequently occurring saturated and unsaturated fatty acids

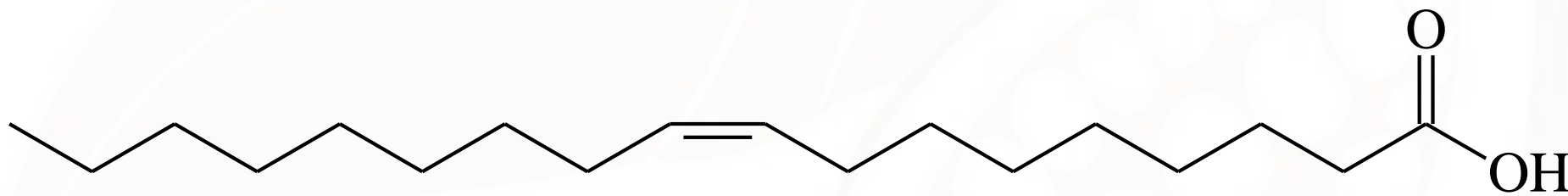
Systematic name (acid)	Trivial name	Chain Length ( $\omega$ -notation)	m.p. ( $^{\circ}\text{C}$ )
Decanoic	Capric	10:0	31.6
Dodecanoic	Lauric	12:0	44.4
Tetradecanoic	Myristic	14:0	54.3
Hexadecanoic	Palmitic	16:0	62.9
Octadecanoic	Stearic	18:0	70.0
9-Octadecanoic	Oleic	18:1 $\omega$ 9	13.0
9- <i>trans</i> -Octadecanoic	Elaidic	18:1 $\omega$ 9	36.0
13-Docosenoic	Erucic	22:1 $\omega$ 9	33.5
9,12-Octadecadienoic	Linoleic	18:2 $\omega$ 6	-3.0
9,12,15-Octadecatrienoic	$\alpha$ -Linolenic	18:3 $\omega$ 3	-11.9
5,8,11,14-Eicosatetraenoic	Arachidonic	20:4 $\omega$ 6	
5,8,11,14,17-eicosapentanoic	EPA	20:5 $\omega$ 3	-11.9
4,7,10,13,16,19-Docosahexaenoic	DHA	22:6 $\omega$ 3	



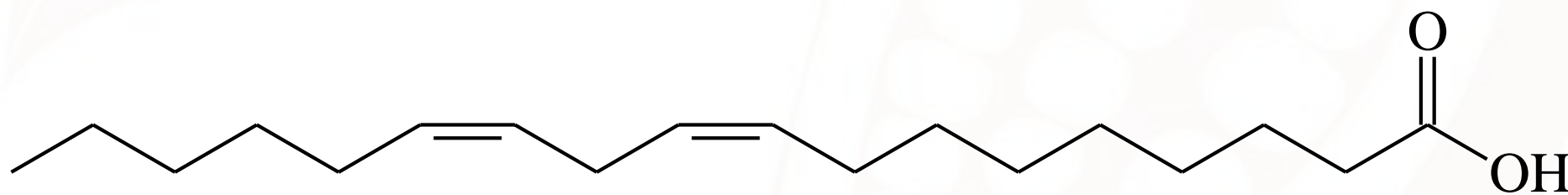
- *cis* isomer predominates in unsaturated fatty acids
- more unsaturation  $\Rightarrow$  lower melting point



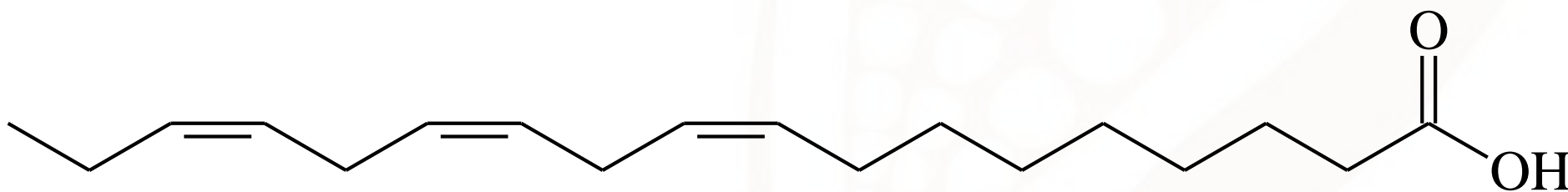
stearic acid (18:0)  
m.p. 70°C



oleic acid (9-18:1)  
an  $\omega$ -9 fatty acid  
m.p. 16°C

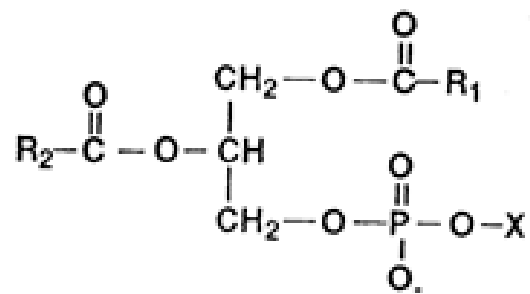


linoleic acid (9,12-18:2)  
an  $\omega$ -6 fatty acid  
m.p. -5°C



linolenic acid (9,12,15-18:3)  
an  $\omega$ -3 fatty acid  
m.p. -11°C

- Minor components:
  - free fatty acids, monoacylglycerols, diacylglycerols
  - phospholipids
  - unsaponifiable matter: sterols, tocopherols, wax esters, hydrocarbons, fat soluble vitamins



$R_1, R_2$ : fatty acids

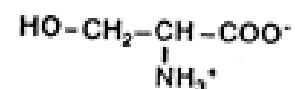
X: choline



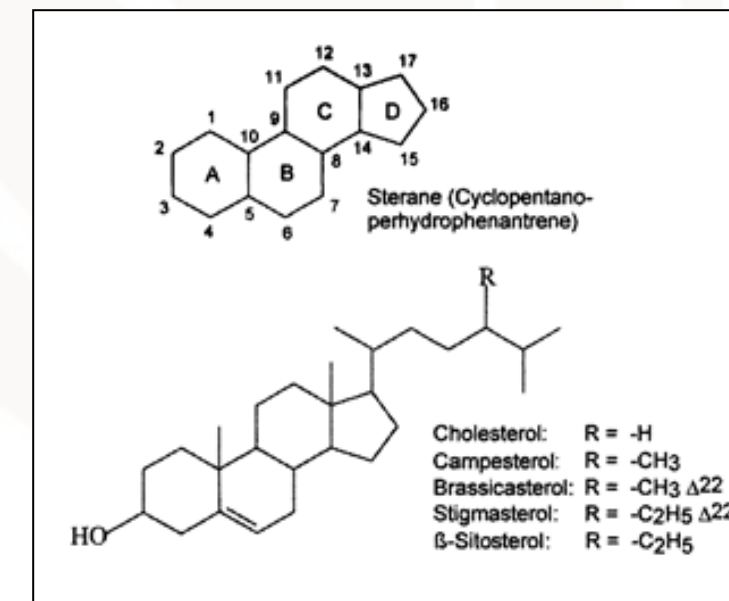
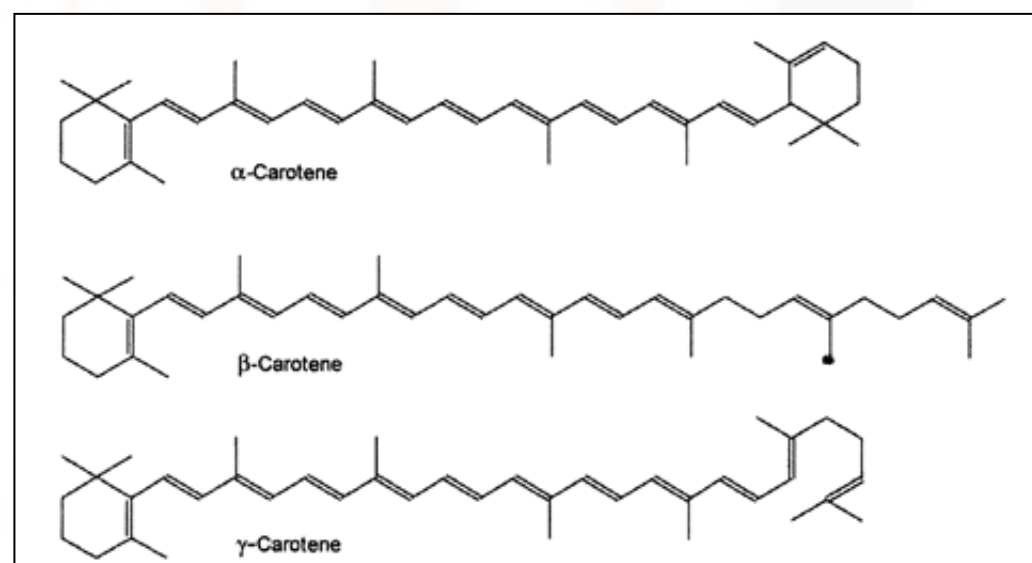
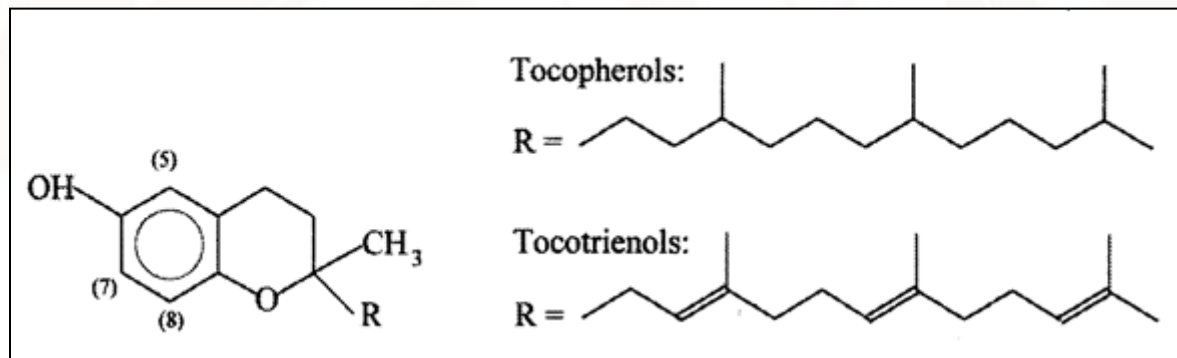
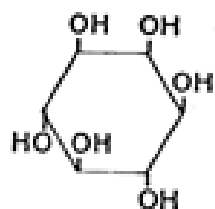
ethanolamine



serine



inositol



## Cocoa butter

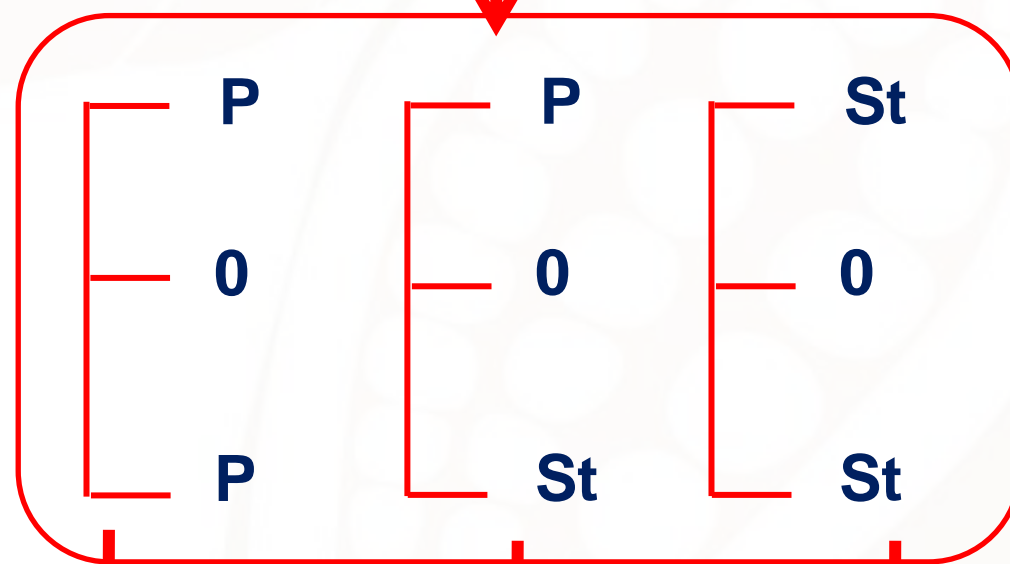
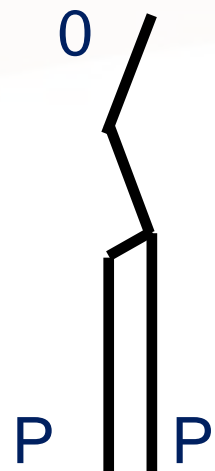
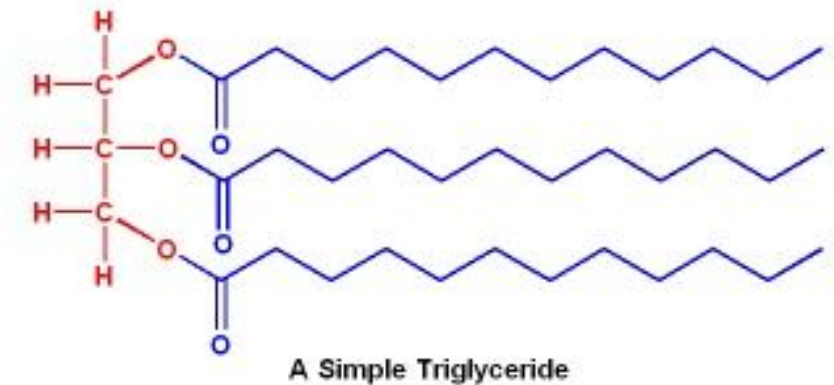
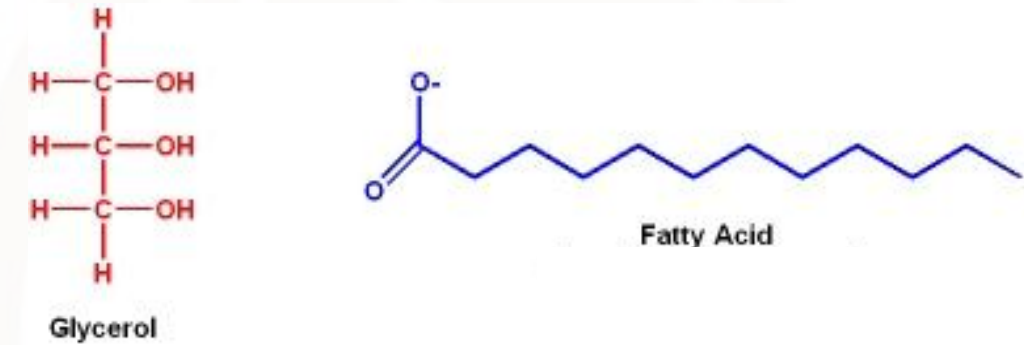
Fatty acid (1)

Fatty acid (2)

Fatty acid (3)

(1) & (3) = Palmitic acid (P)  
(± 26%) and/or Stearic Acid (St) (± 36%)

(2) = Oleic acid (O) (± 33%)



16,5%-19%

38,5%-40%

23%-26%

Typical chemical composition = **Unique physical properties**

→ Depending on the origin



- Fats and oil: chemistry
- **Importance of fat crystallization**
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- How to measure?
- Case study cocoa butter

## ■ Importance of fat crystallization

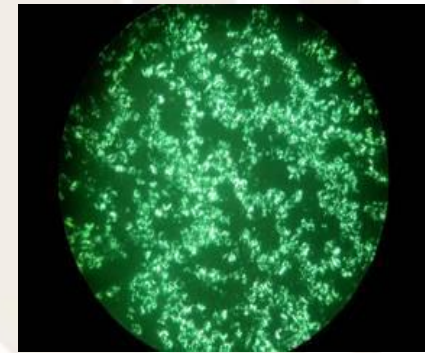
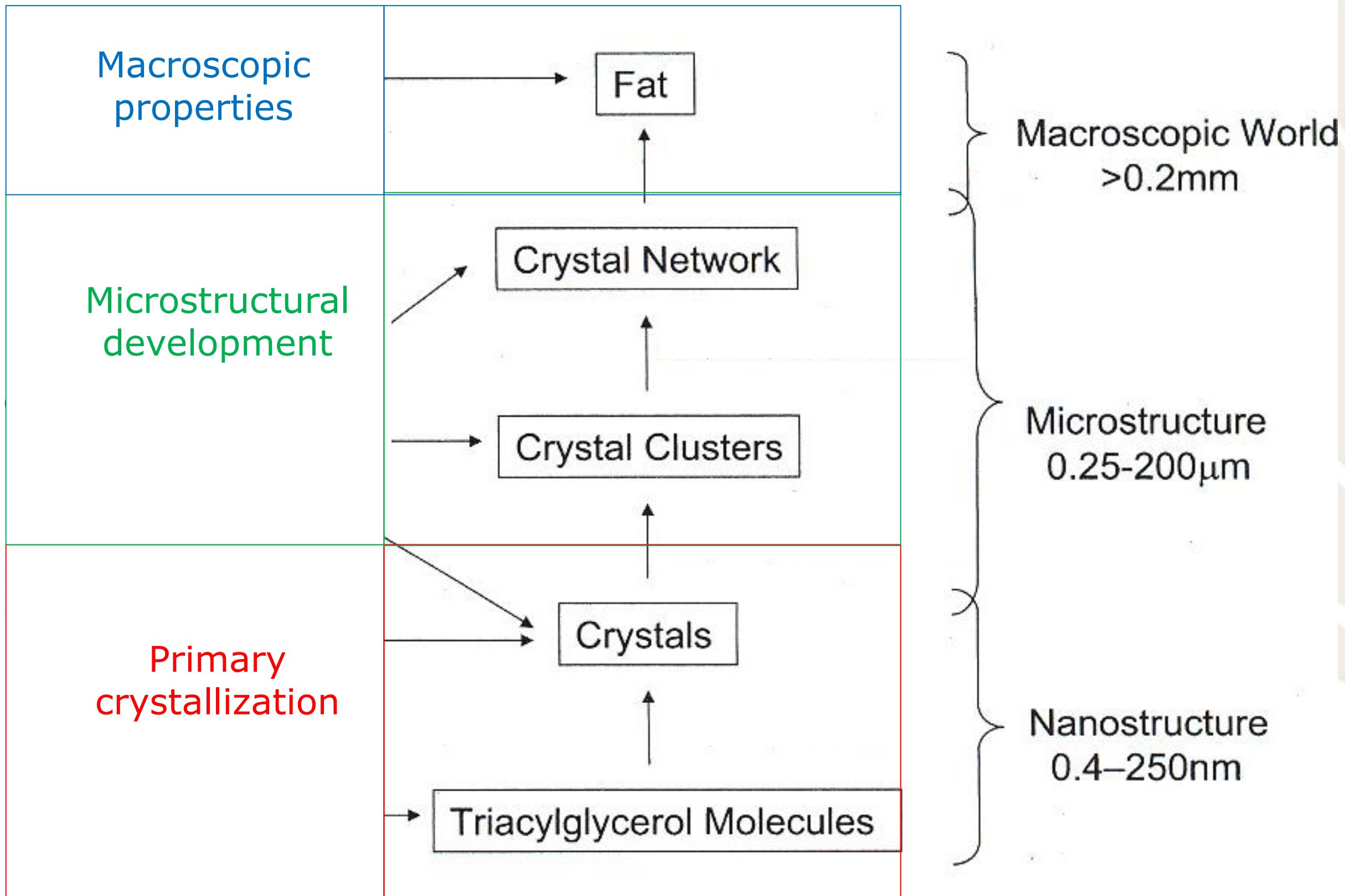
Many fat-rich products with a substantial amount present in the crystallized form

- Affects product structure and texture
- Determines product quality



- Fats and oil: chemistry
- Importance of fat crystallization
- **Structural levels in fat crystallization**
  - **Primary crystallization**
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - **Microstructural development**
  - **Macroscopic properties**
- How to measure?
- Case study cocoa butter





- Driving force  
= difference in chemical potential  $\Delta\mu$  between liquid and solid

## 1. Crystallization from solution

Supersaturation needed

- = concentration  $C$  ( $\text{m}^{-3}$ ) > concentration at saturation  $C_s$  ( $\text{m}^{-3}$ )

$$\Delta\mu = R_g \times T_k \times \ln\left(\frac{C}{C_s}\right)$$

$R_g$  = universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T_k$  = absolute temperature (K)

$(C/C_s)$  : supersaturation ratio =  $\sigma$  (-)



## 2. Crystallization from the melt:

### Supercooling needed

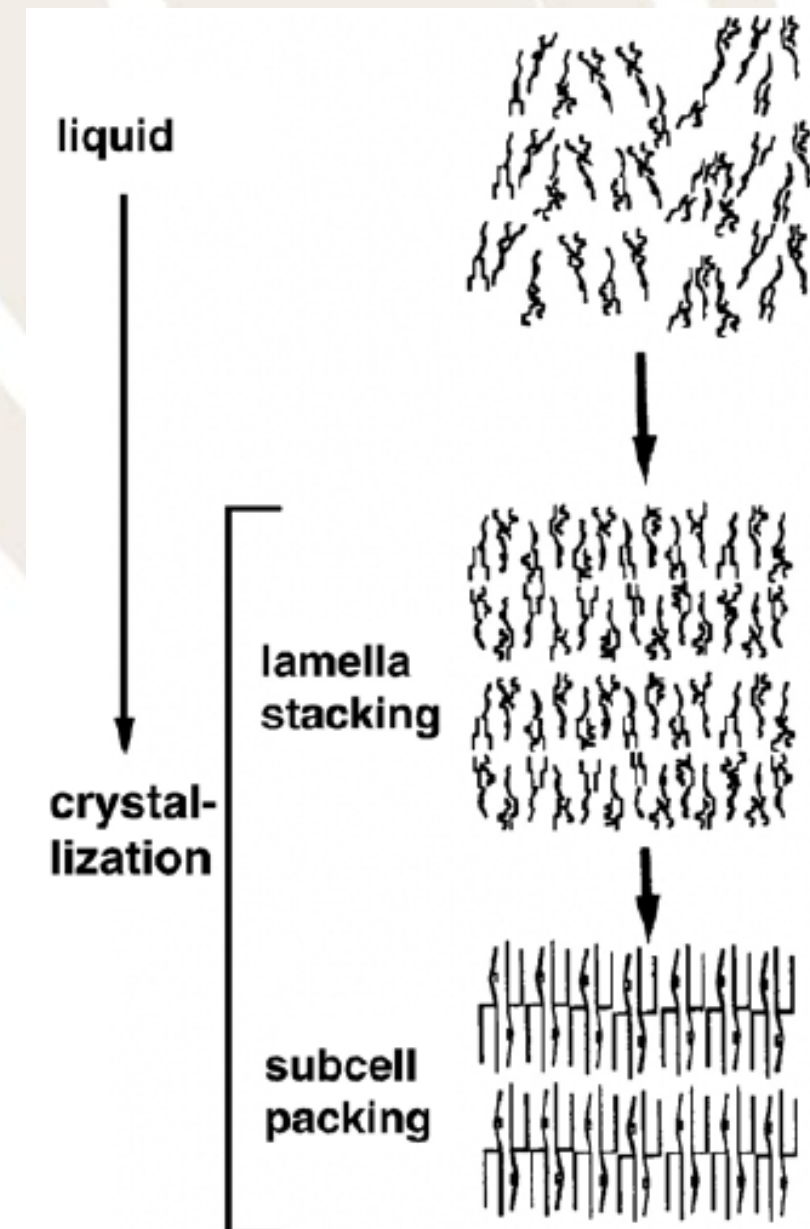
- = temperature ( $T_K$ ) (K) < melting temperature ( $T_{Km}$ ) (K)

$$\Delta\mu = \Delta H_m \times \frac{T_{km} - T}{T_{km}} = \Delta H_m \times \frac{\Delta T}{T_{km}}$$

$T_{km} - T_K = \Delta T =$  supercooling (K)

$\Delta H_m$ : molar melting heat (J/mol)

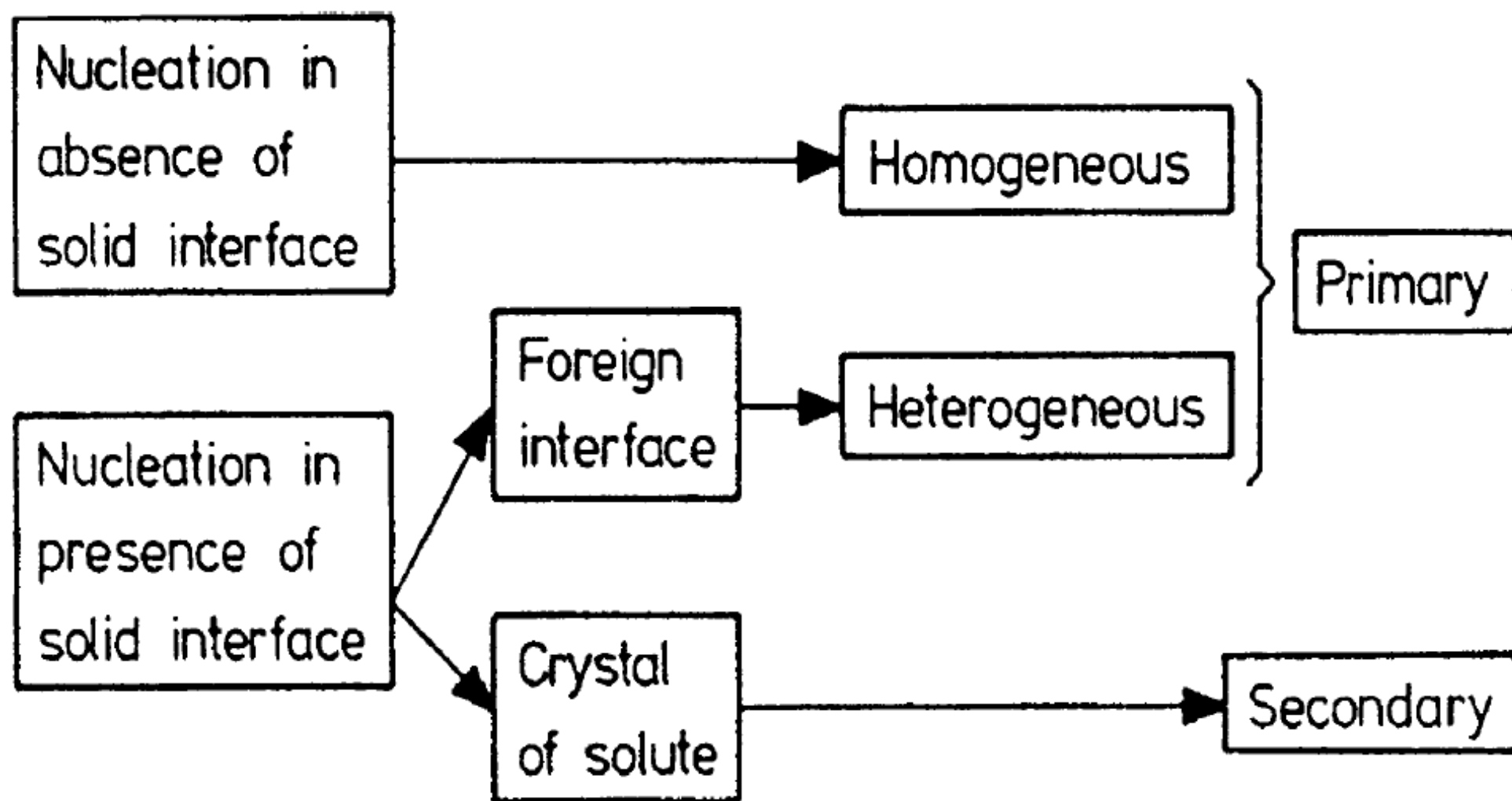
$(\Delta T / T_{km}) = \sigma_r (-)$ : relative supercooling





Nucleation = generation of a crystal nucleus by assembling growth units

⇒ critical activation-energy needed!!!





# Primary crystallization: nucleation



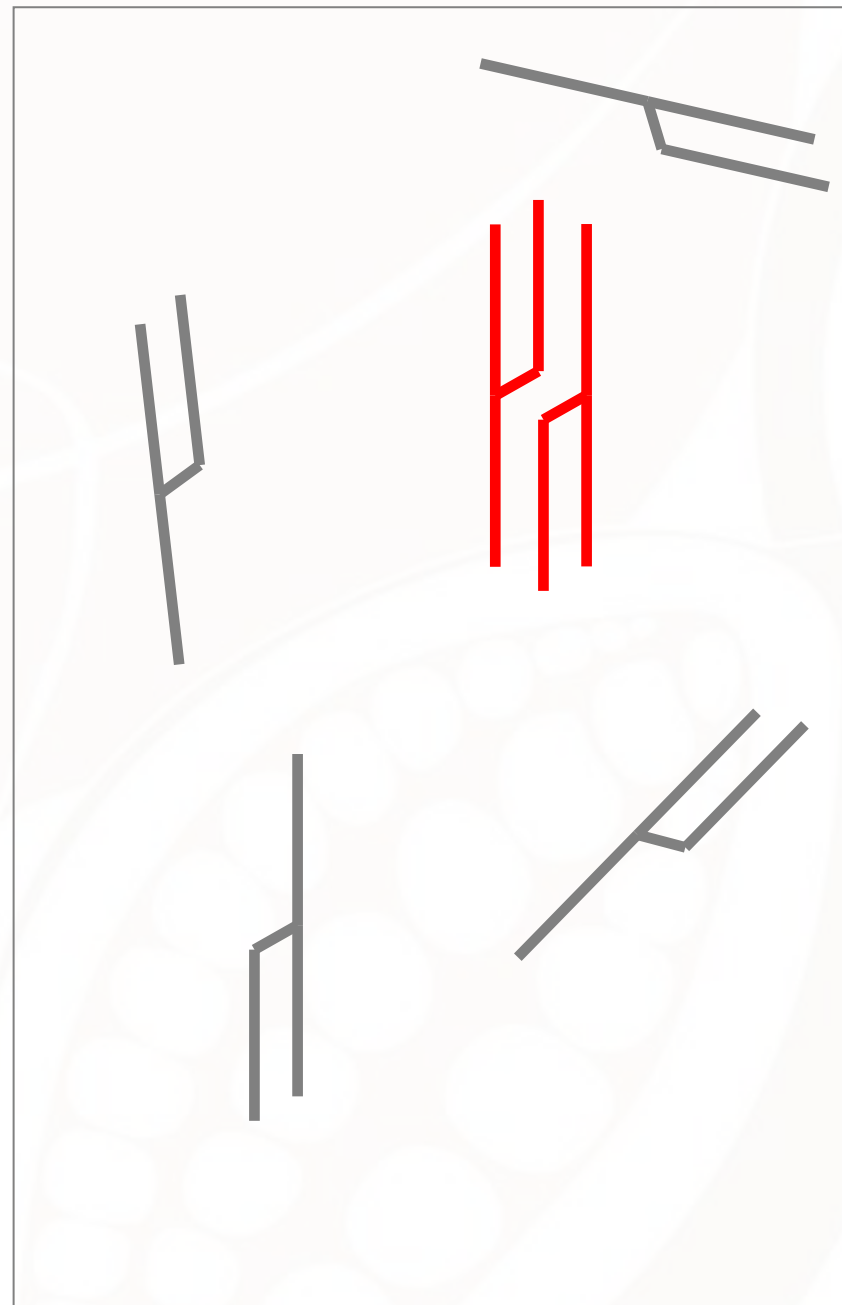
## 1. Primary homogeneous nucleation

- = not catalyzed by foreign surfaces or existing fat crystals
- Up to 30K supercooling needed



$T > T_{\text{melt}}$

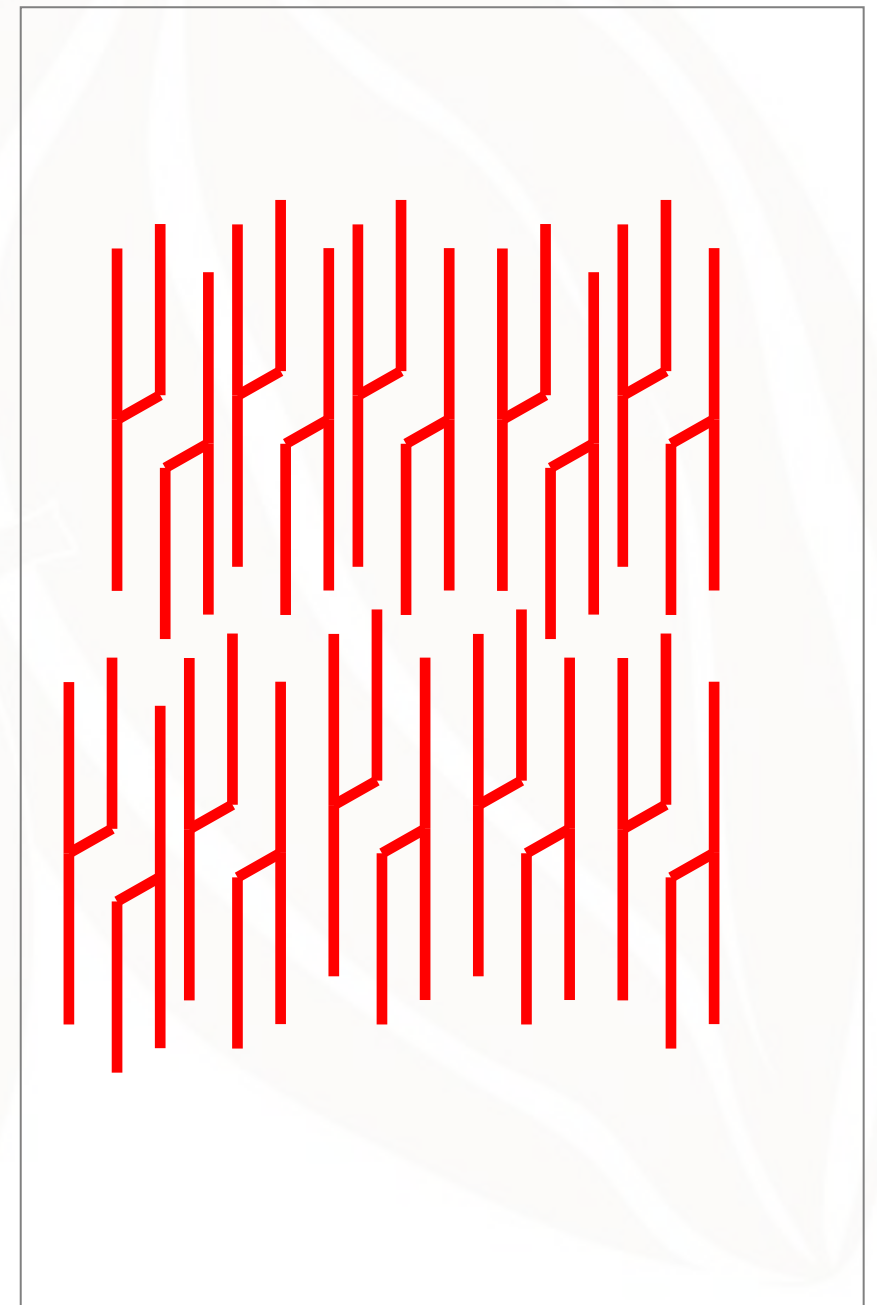
True melt



$T = T_{\text{melt}}$

Crystal embryos

—————→ supercooling  $T \ll T_{\text{melt}}$



Crystal lattice



## 1. Primary homogeneous nucleation

- = not catalyzed by foreign surfaces or existing fat crystals
- Up to 30K supercooling needed

## 2. Primary heterogeneous nucleation

- = catalyzed by foreign surfaces (e.g. impurities, impeller blades etc.)
- Most frequent in natural fats and oils, enough impurities present



$T > T_{\text{melt}}$

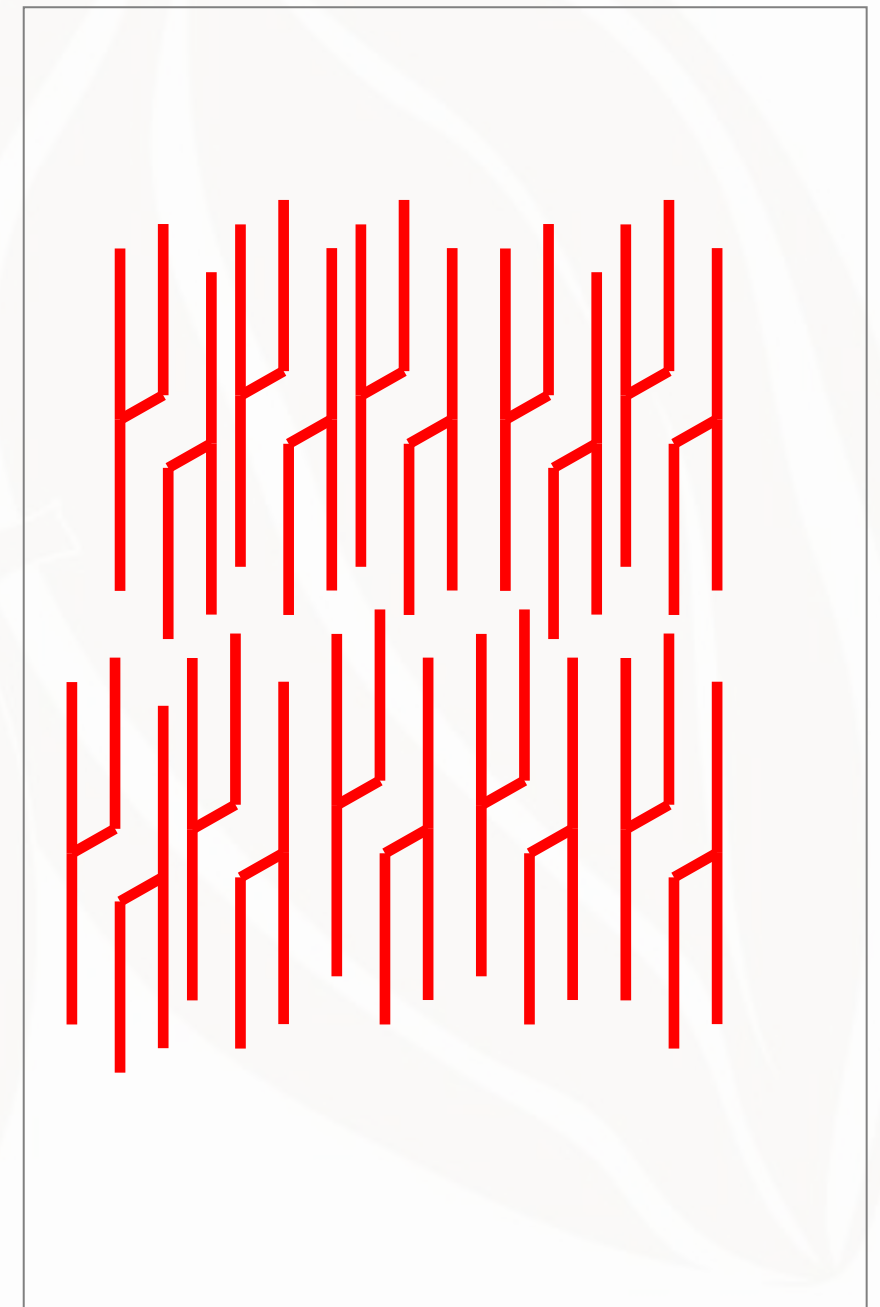
True melt



$T = T_{\text{melt}}$

Nucleation

less supercooling



$T < T_{\text{melt}}$

Crystal lattice

## 1. Primary homogeneous nucleation

- = not catalyzed by foreign surfaces or existing fat crystals
- Up to 30K supercooling needed

## 2. Primary heterogeneous nucleation

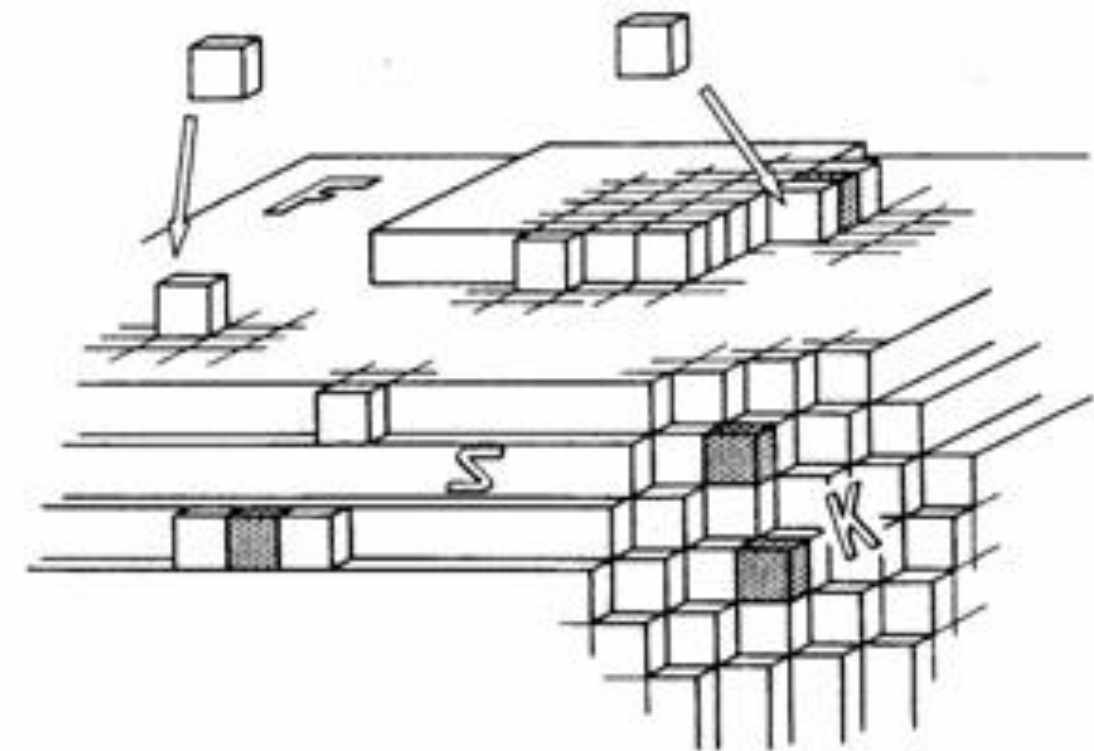
- = catalyzed by foreign surfaces (e.g. impurities, impeller blades etc.)
- Most frequent in natural fats and oils, enough impurities present

## 3. Secondary nucleation

- = catalyzed by crystals of the crystallizing material ⇒ secondary nuclei
- Very frequent in crystallization from solution and in industrial crystallizers



- Depends on
  - **external factors:**
    - Supersaturation, supercooling, solvent, temperature, presence of impurities, ...
  - **internal factors:**
    - Structure, bonds, crystal defects, ...
- **Mechanism** of crystal growth depends on the type of interface:
  - flat (F), kinked (K), stepped (S)



Schematic representation of three types of growth sites. Each cube depicts a growth unit

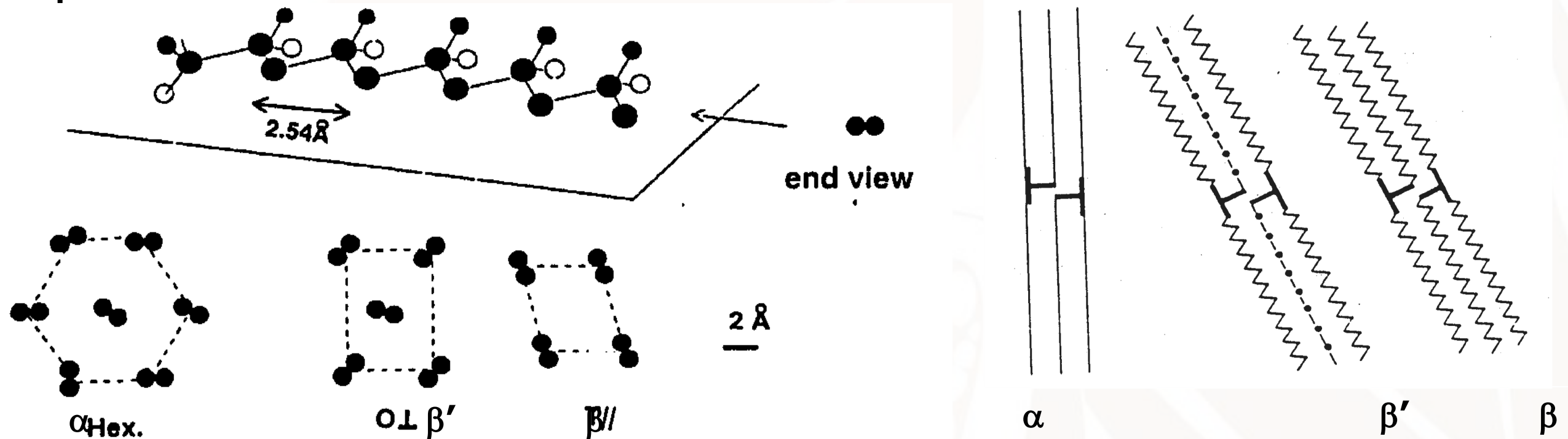


- Palm stearin crystallizing at 30°C after cooling down from 80°C at 10°C/min
- Real time duration of the movie: 5min, 2.5 min to volume filling

- Polymorphism  
= the existence of several crystalline phases with the same chemical composition that have a different structure, but yield identical liquid phases upon melting.
  
- Polymorphic transition
  - ⇒ less stable to more stable polymorphs
  - ⇒ 'solid-state', 'melt-mediated' or 'solvent mediated'
  
- Importance: obtaining and maintaining (during storage) of specific macroscopic properties
  - E.g. sandiness in margarine and fat bloom on chocolate are caused by a polymorphic transition

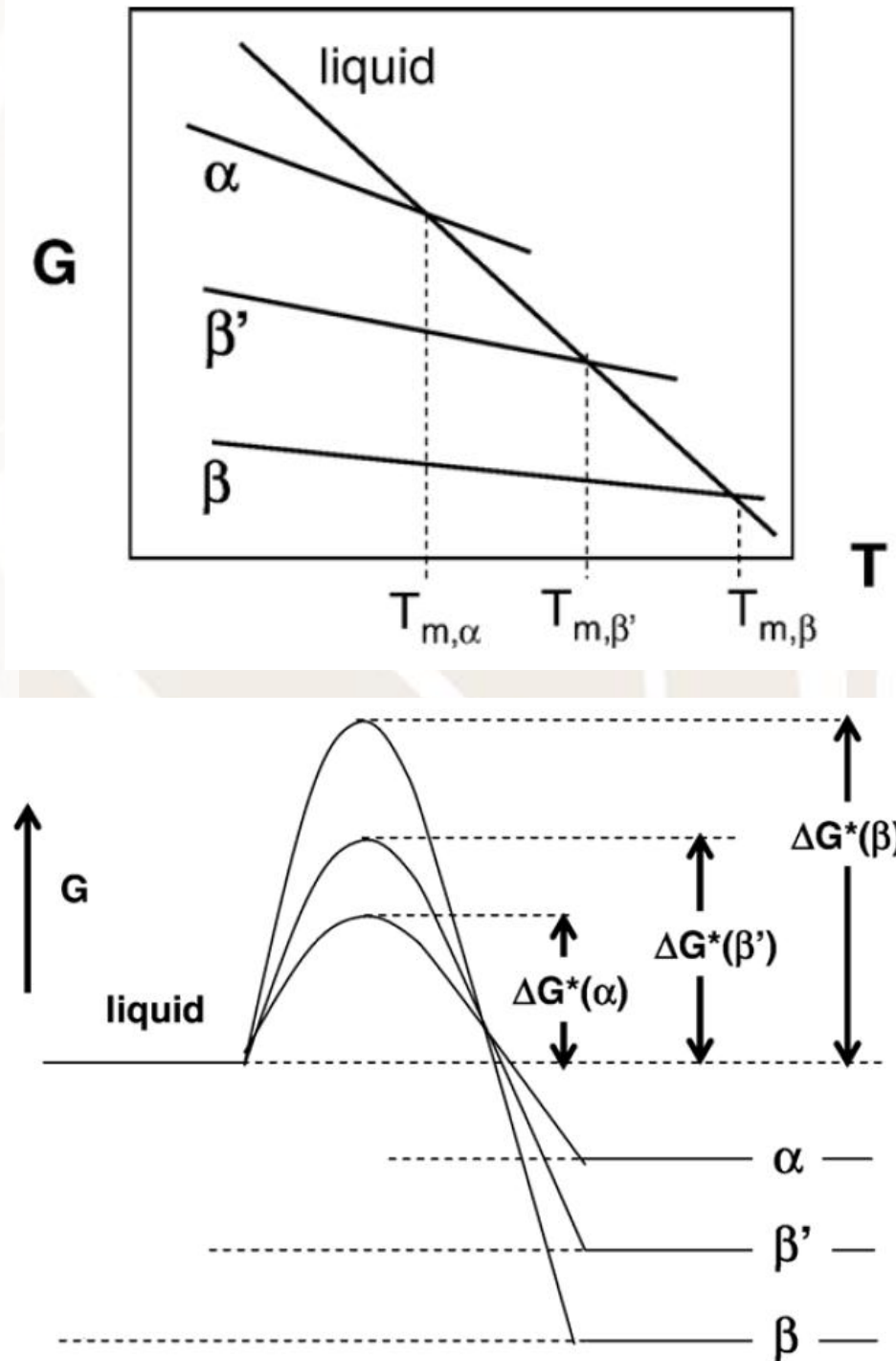


- 3 basic polymorphs ( $\alpha$ ,  $\beta'$ ,  $\beta$ ), each with their specific properties

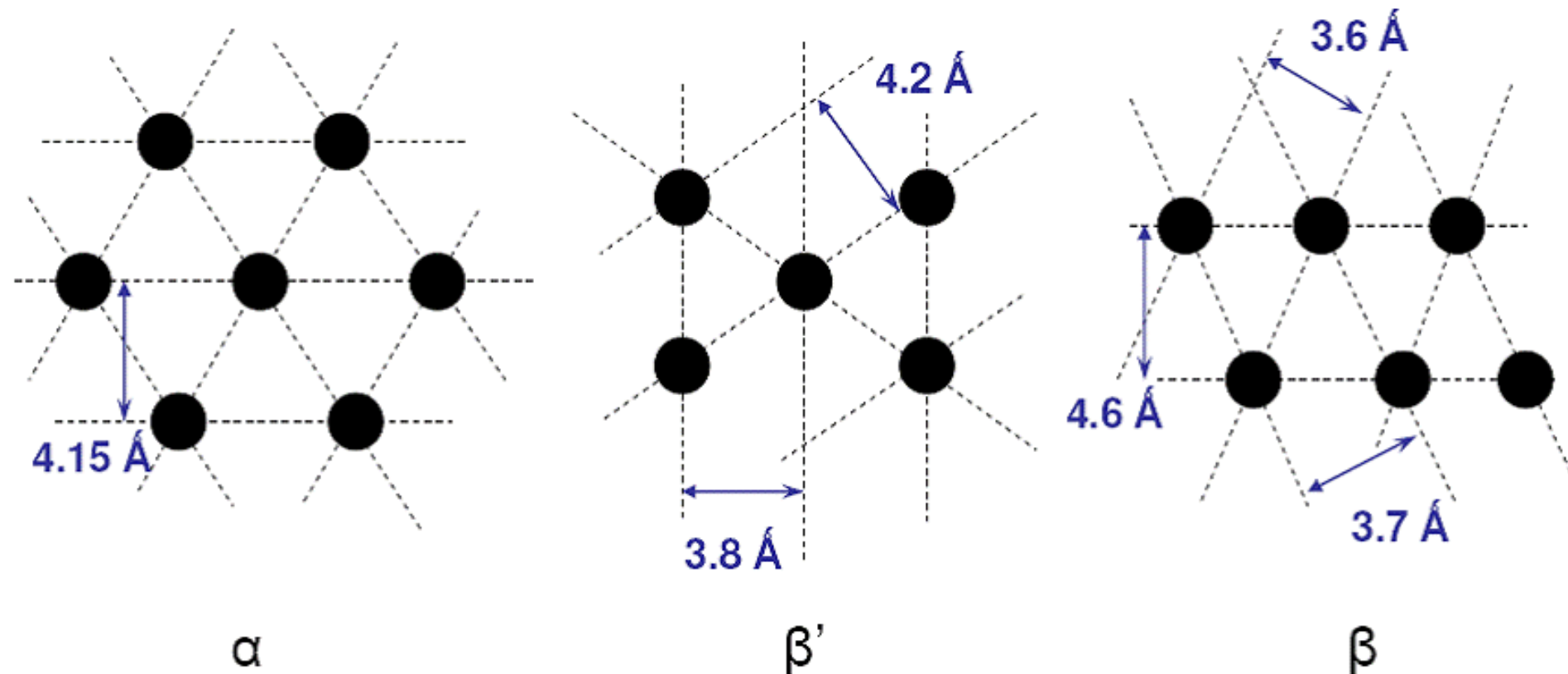


- Subcell packing of the hydrocarbon chains (cross section of the aliphatic chains): hexagonal ( $\alpha$ ), orthorhombic ( $\beta'$ ), triclinic ( $\beta$ )
- Different angle with respect to the end methyl group for the different polymorphs
- Zigzag form of one of the 3 chains perpendicular to the other 2 for the  $\beta'$  form
- Zigzag structures of 3 fatty acid chains in the same plane for the  $\beta$  form

- 3 basic polymorphs ( $\alpha$ ,  $\beta'$ ,  $\beta$ ), each with their specific properties
  - Melting range, melting heat:  $\alpha < \beta' < \beta$
  - Density :  $\alpha < \beta' < \beta$
  - Stability:  $\alpha < \beta' < \beta$
  - Activation-energy for nucleation:  $\alpha < \beta' < \beta$
  - ➔ onset of spontaneous nucleation:  $\alpha > \beta' > \beta$
  - ➔ the least stable polymorph crystallizes first and will transform to a more stable polymorph as a function of time
- Different submodifications possible depending on the TAG composition
- At low temperatures:  $\gamma$  polymorph = sub  $\alpha$  polymorph

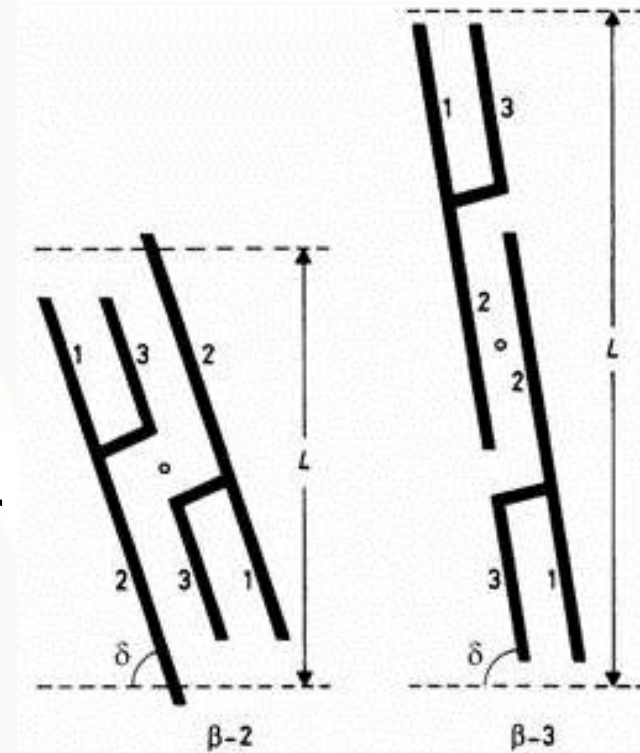


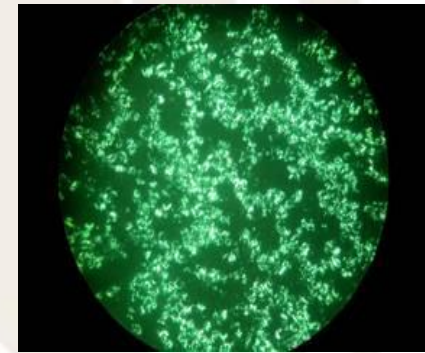
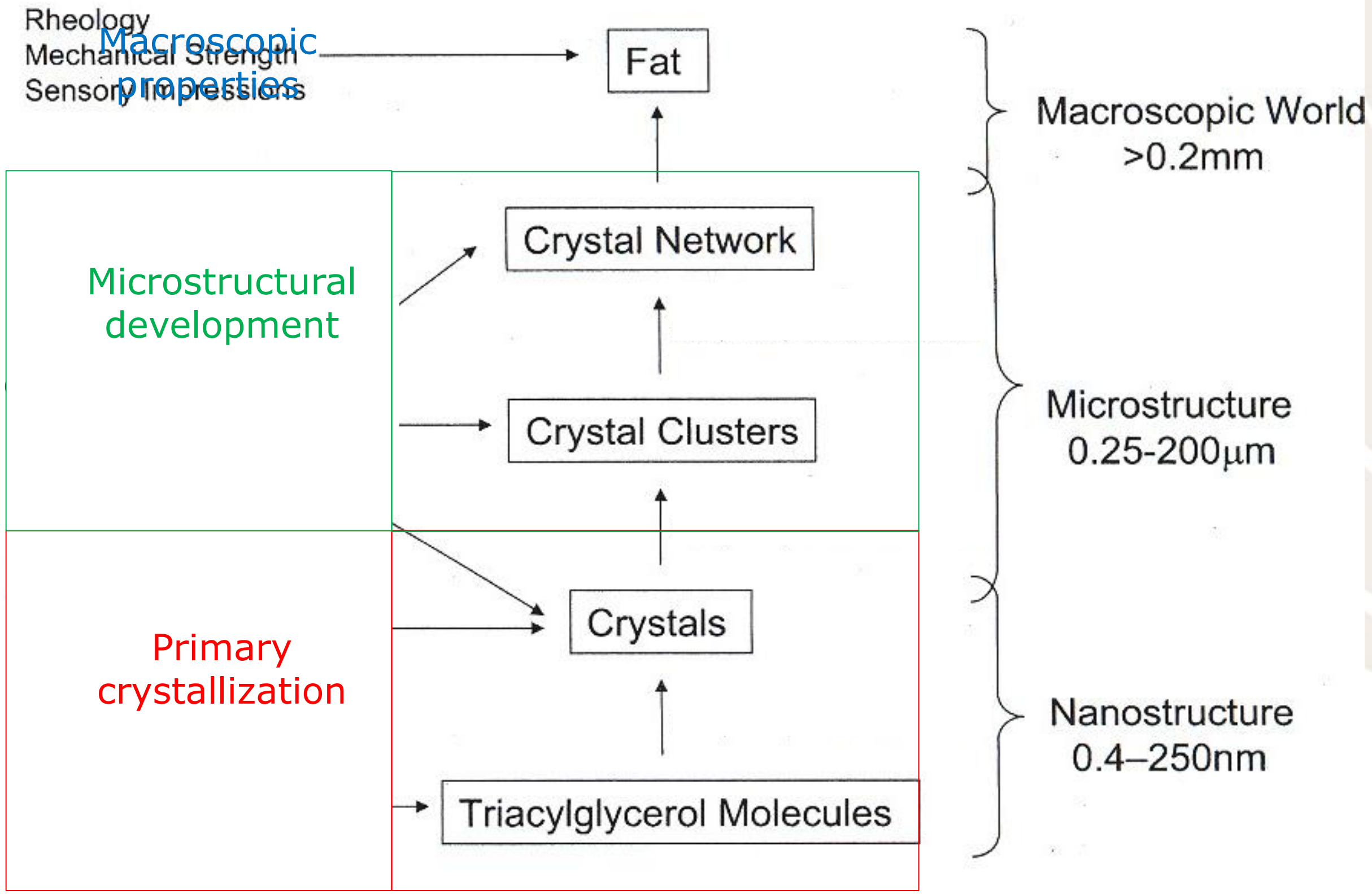
- Identification of the different polymorphs
  - ⇒ XRD diffraction lines: WAXD (wide angle X-ray diffraction) → short spacings





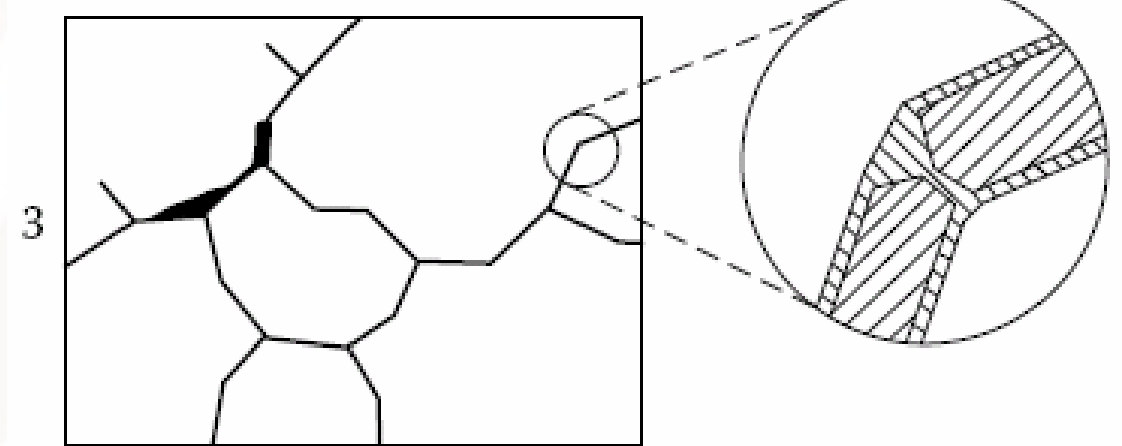
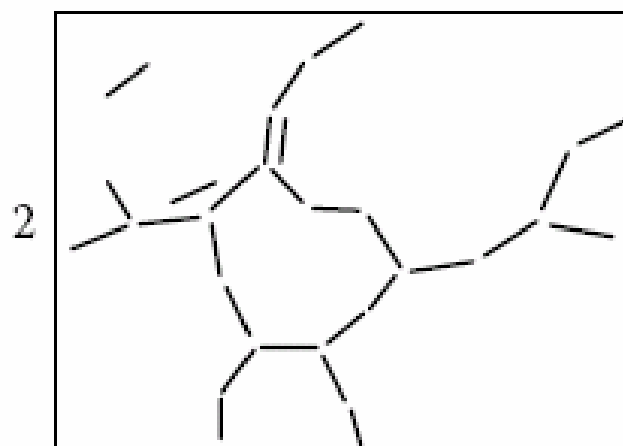
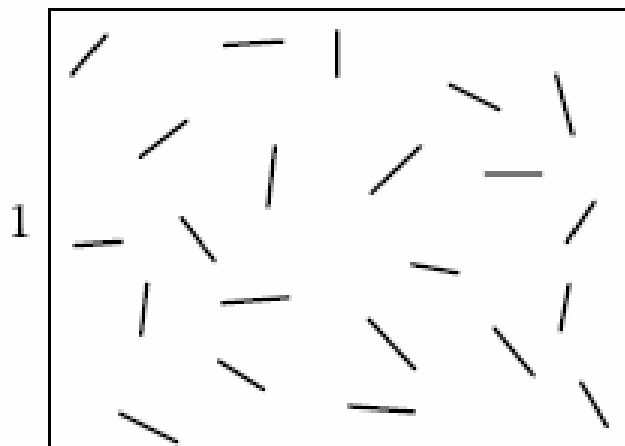
- The TAG molecules form layers in a specific stacking
- Layer thickness  $\sim$ 
  - Chain length
  - Tilt of the end methyl group
  - Type of packing
- Two types of longitudinal packing, resulting in pairs of 2 or 3 fatty acid chains long, 2L and 3L resp.
- Longitudinal packing  $\sim$  TAG composition
  - Many mono-unsaturated TAGs (unsaturation on 2-position)
    - preferentially 3L
    - fatty acids separated in saturated and unsaturated zone
- Determination by XRD diffraction pattern: SAXS (small angle X-ray scattering) → long spacings





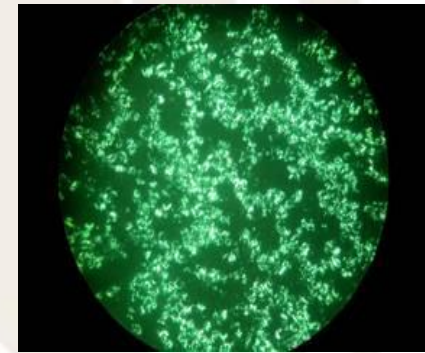
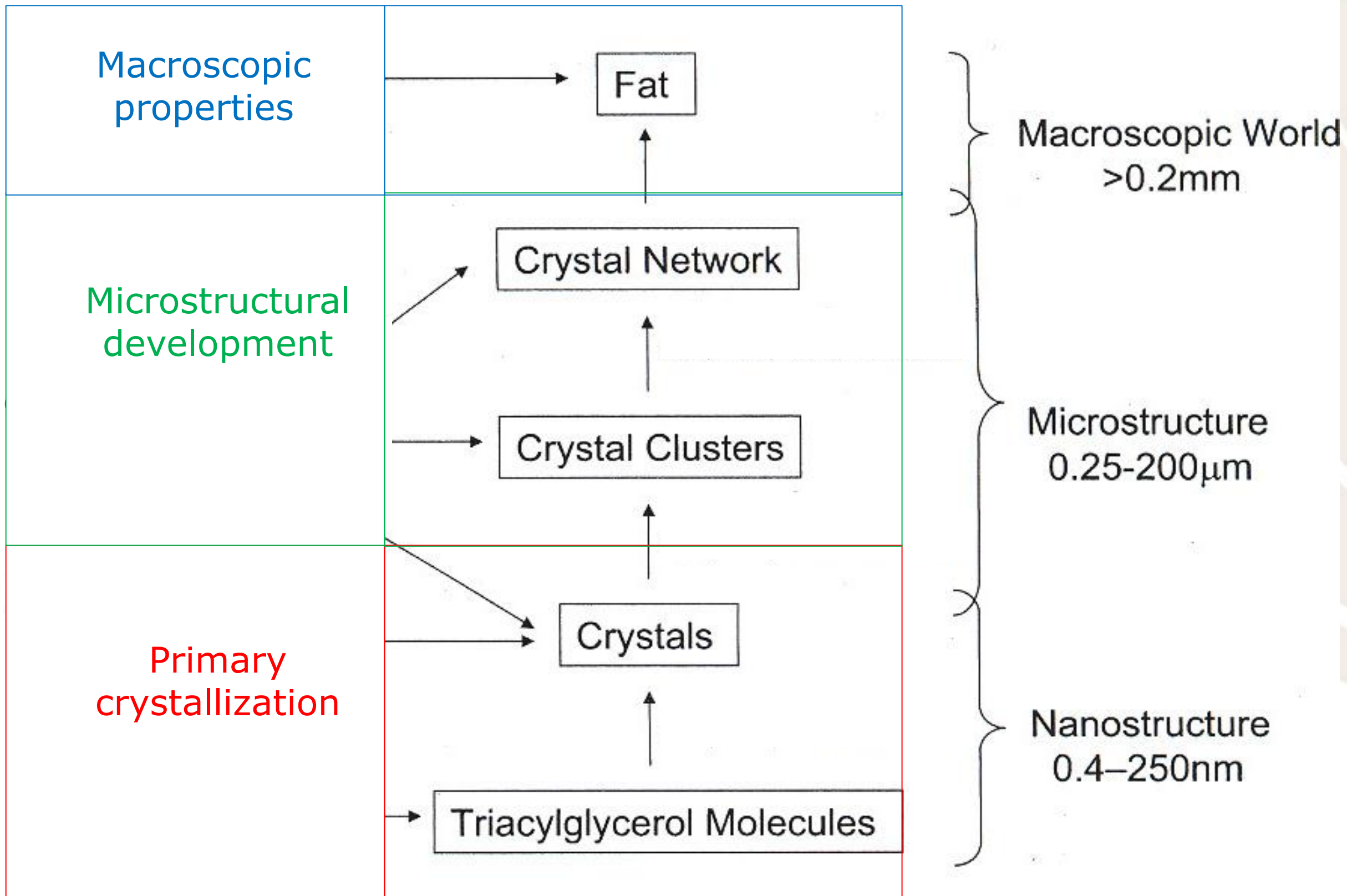


- Schematic presentation of the microstructural development:
  1. aggregation of crystals
  2. network formation
    - Continuous 3D network
    - Liquid fat trapped within the network
  3. sintering





- Network properties depend on:
  - Number and size of the crystals
  - Interactions between the crystals
  - Presence of other components
- Influencing factors
  - Crystallization temperature
  - Cooling rate
  - Agitation
  - Storage time



- How does the consumer experience the product?
  - Smell
  - Taste
  - Appearance e.g. Fat bloom
  - Mouth feel (cool sensation, no waxy taste)
  - Melting in the hand, sticking to fingers
  - Snap
  - ...



- Fats and oil: chemistry
- Importance of fat crystallization
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- **How to measure?**
- Case study cocoa butter



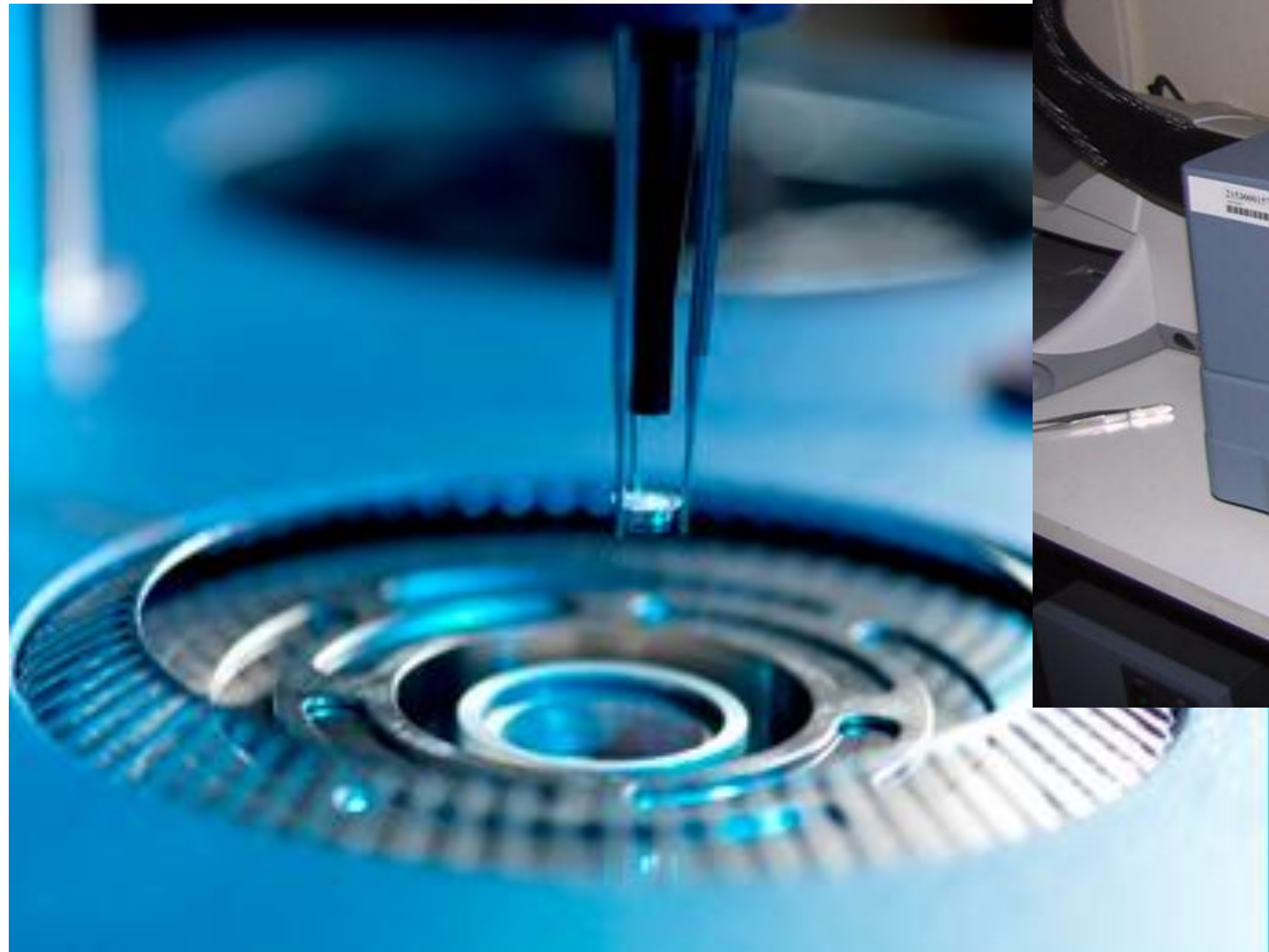
# How to measure?



- DSC (Differential Scanning Calorimetry)
- pNMR (pulsed Nuclear Magnetic Resonance)
- XRD (X-ray Diffraction)
- Microscopy
- Rheology
- Texture analysis
- Sensorial analysis



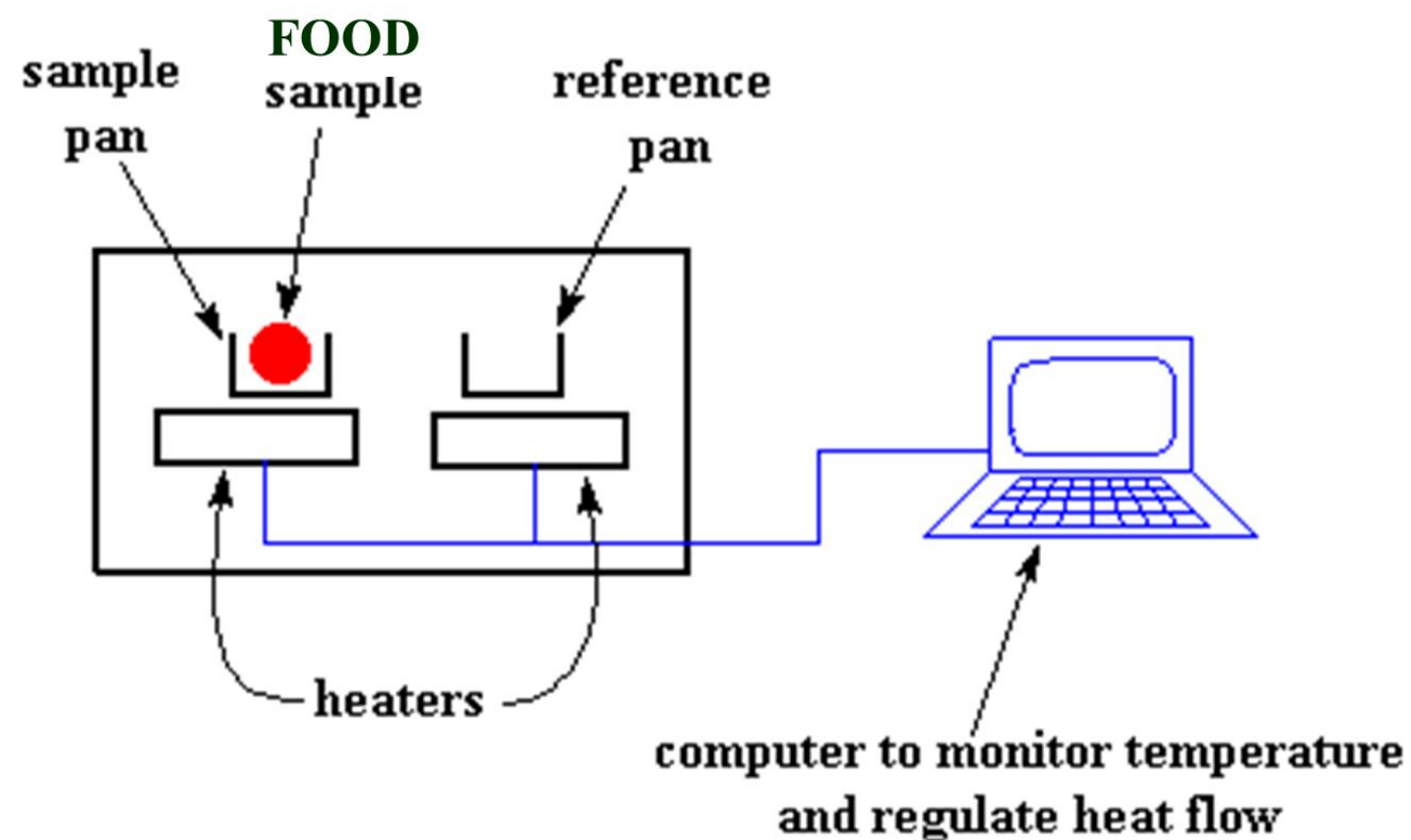
## ■ DSC





## ■ DSC (Differential Scanning Calorimetry)

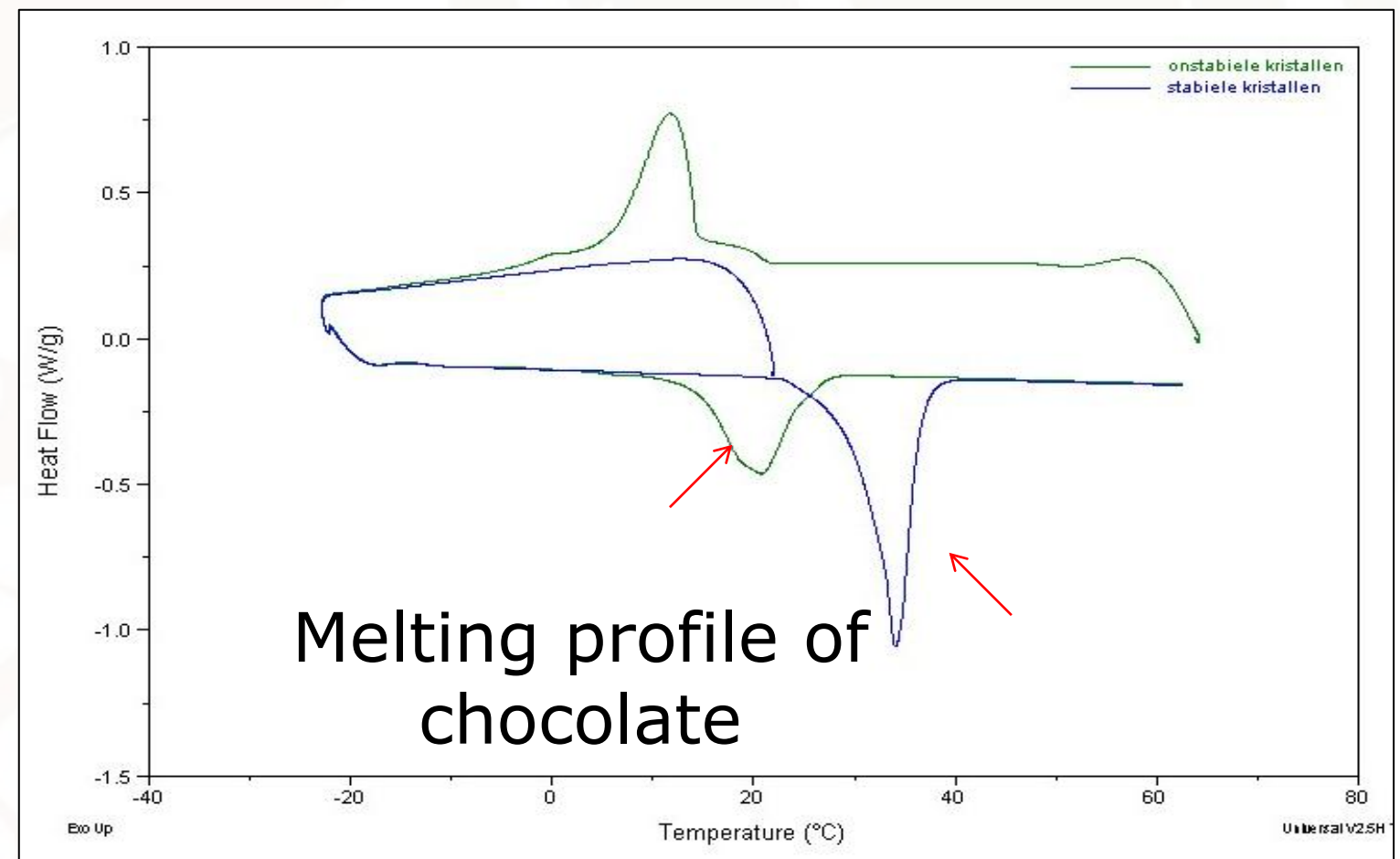
- Measures the difference in heat flow between the sample (=fat) and the reference (=air) while both are subjected to the same temperature-time protocol



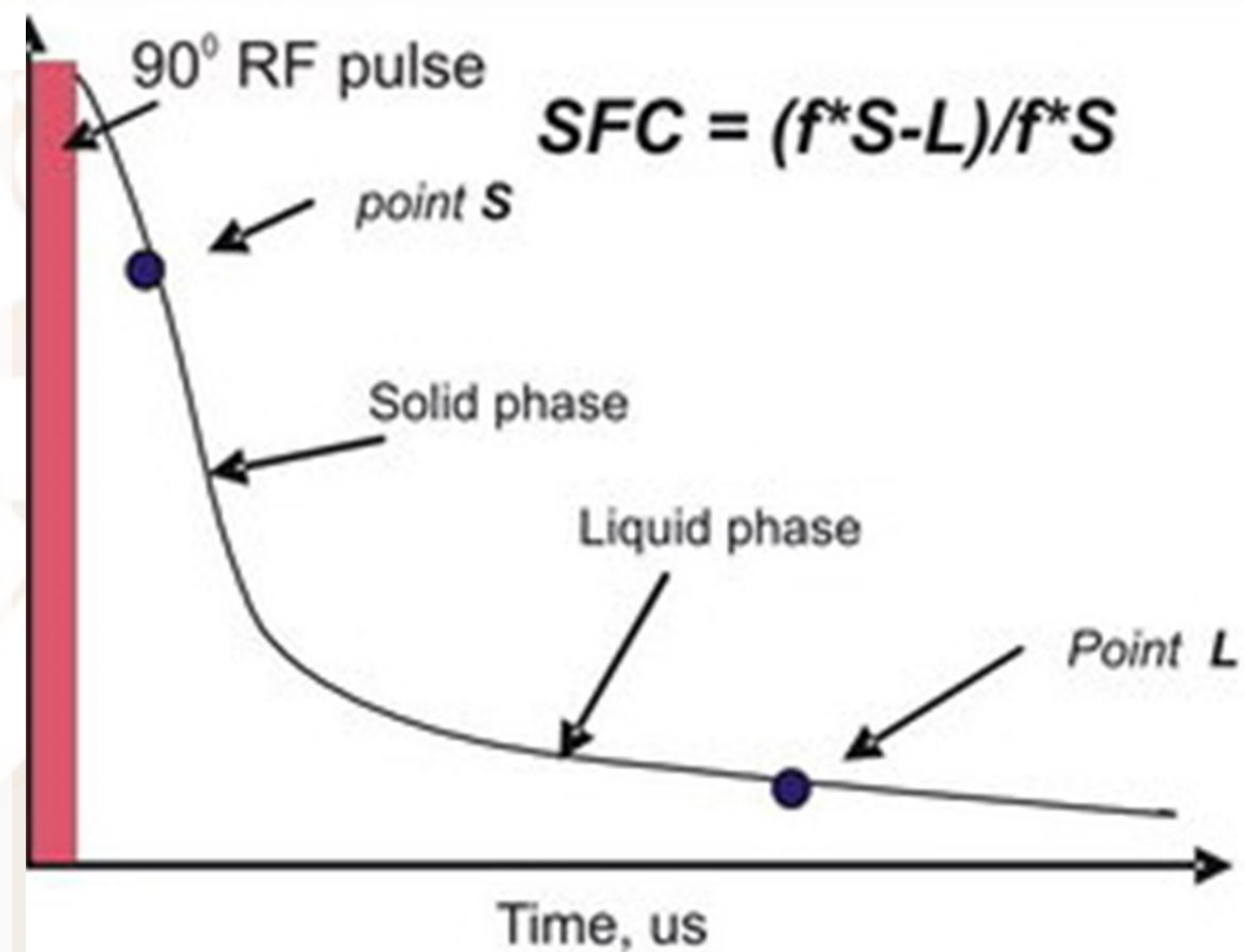
- **DSC (Differential Scanning Calorimetry)**
  - Provides information on processes that involve heat release (exothermic processes, e.g. crystallization) or heat absorption (endothermic processes, e.g. melting)

## – Applications

- Monitoring kinetics of crystallization
- Recording melting profile → melting point provides an indication of polymorphism



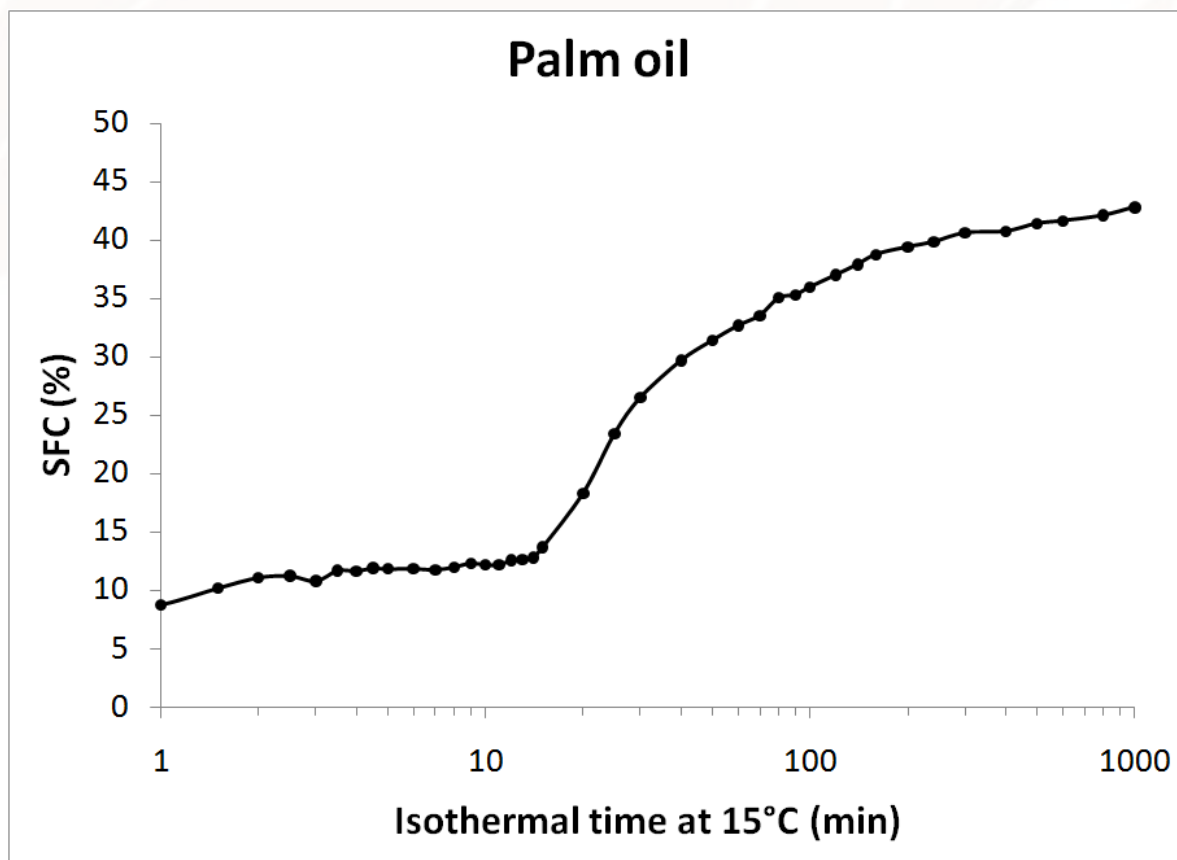
- pNMR (pulsed Nuclear Magnetic Resonance)
  - Electromagnetic pulse absorbed by  $^1\text{H}$ -protons
  - Disturbance of the spin of the protons
  - Relaxation to the equilibrium
  - Fast for "solid" protons (crystals)
  - Slow for "liquid" protons



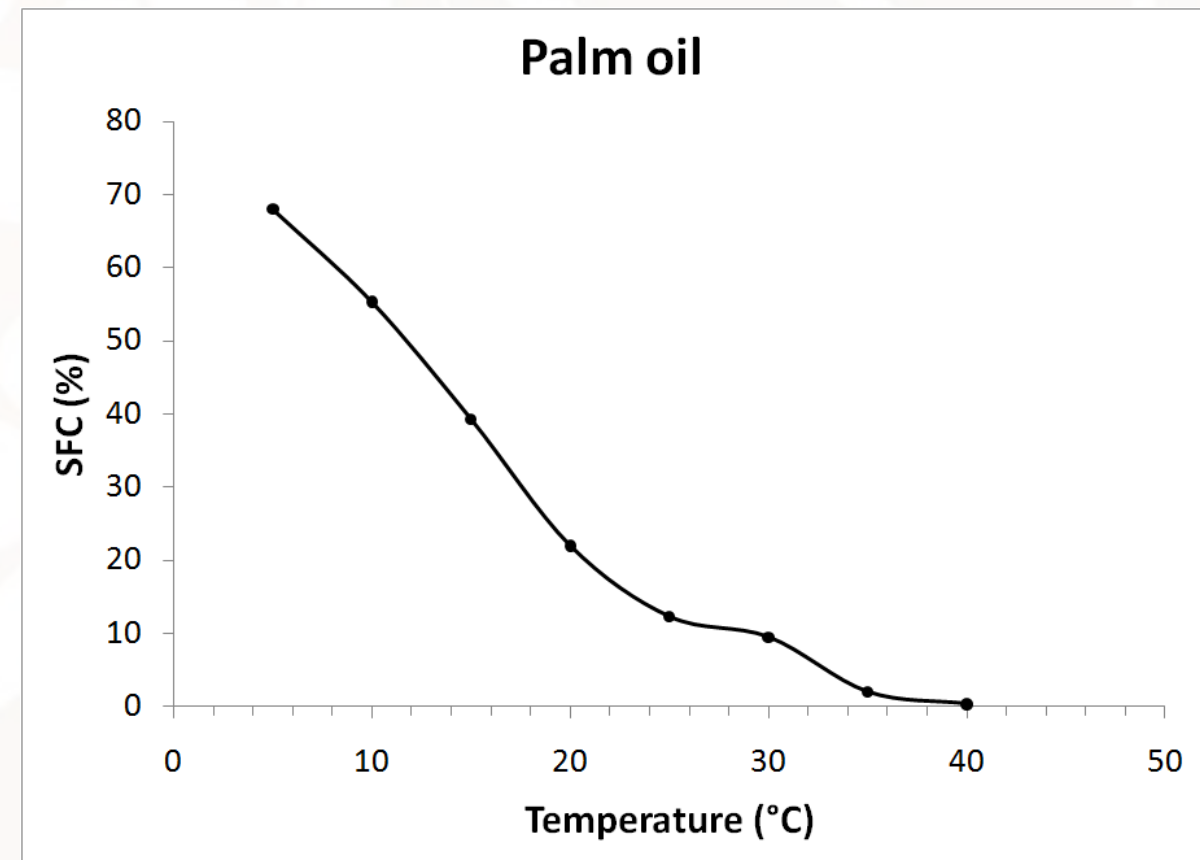


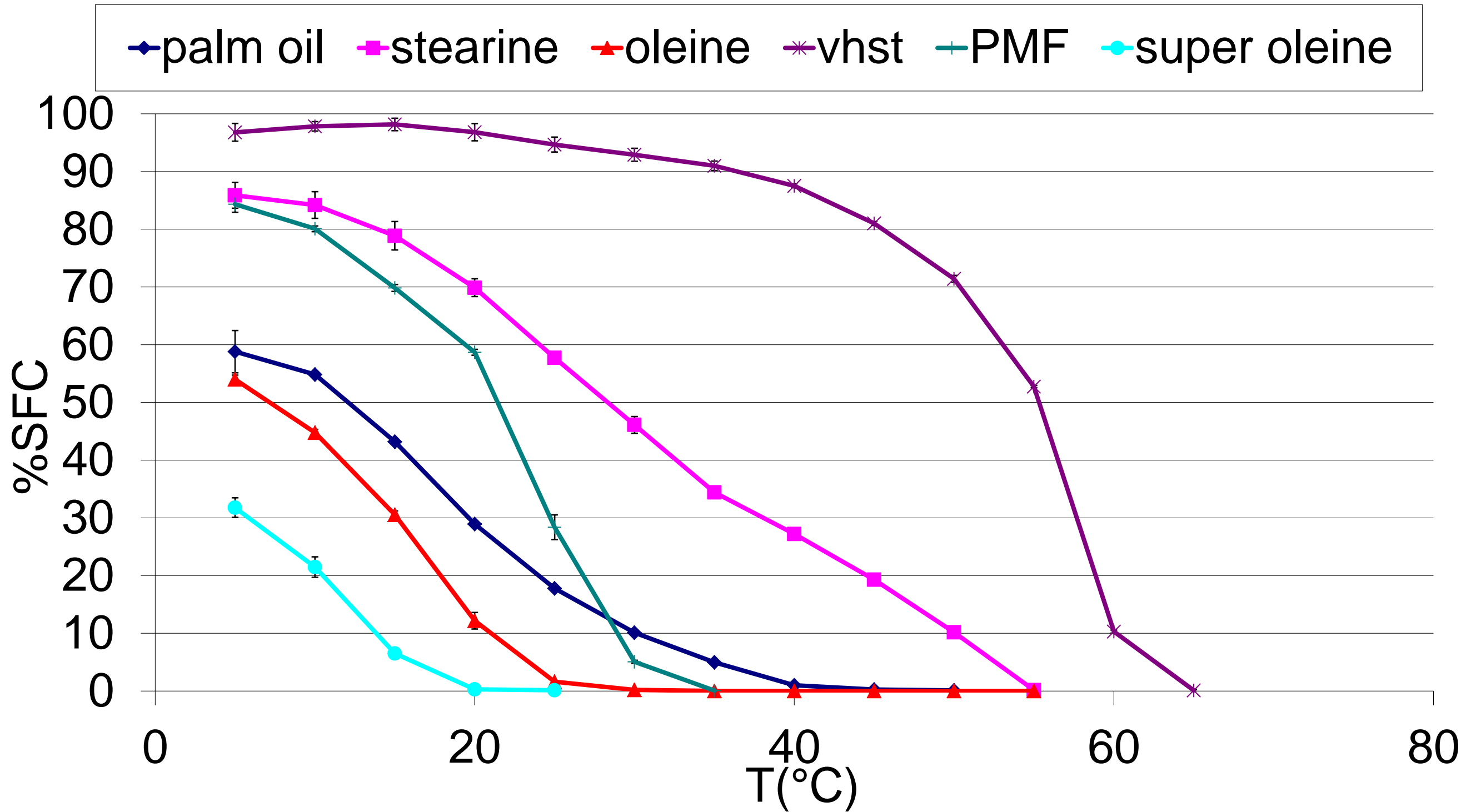
- pNMR (pulsed Nuclear Magnetic Resonance)
  - Solid fat content as a function of time (isothermal) or temperature (non-isothermal)
  - SFC as a function of temperature:
    - Equilibrium situation at each T, no information on kinetics

**Isothermal at 15°C**

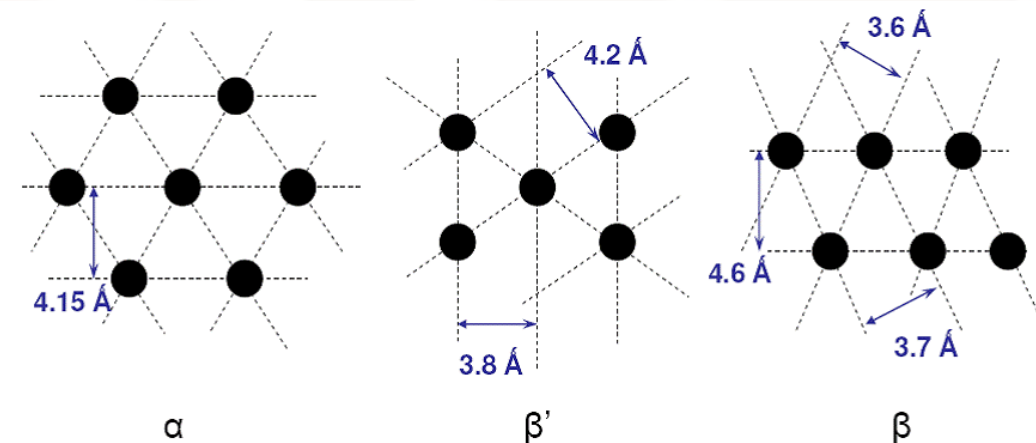


**Non-isothermal**



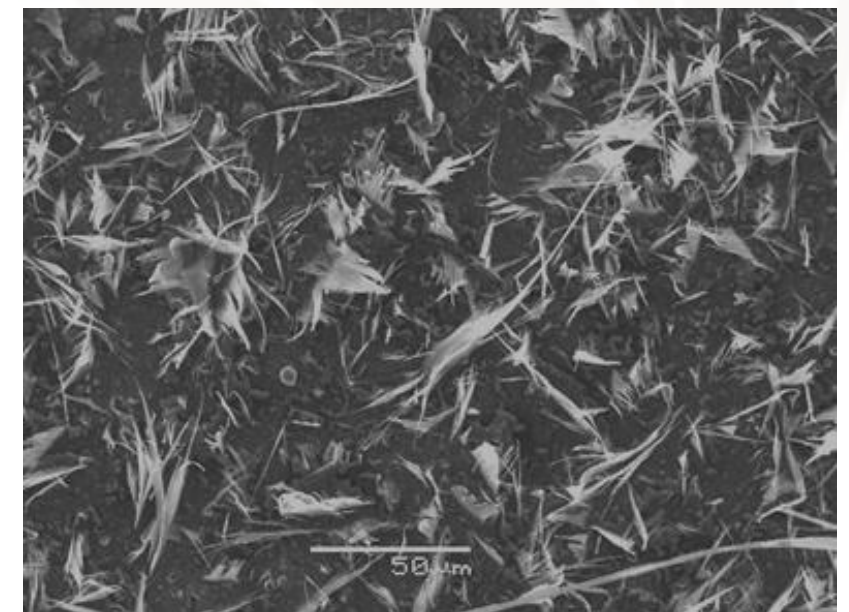
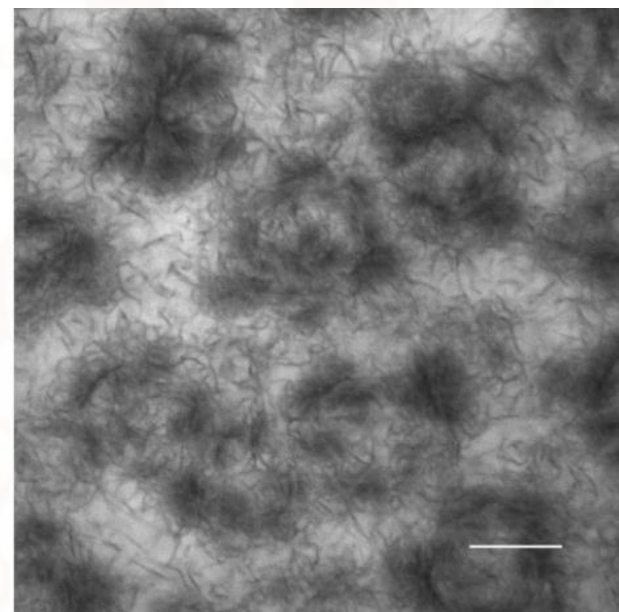
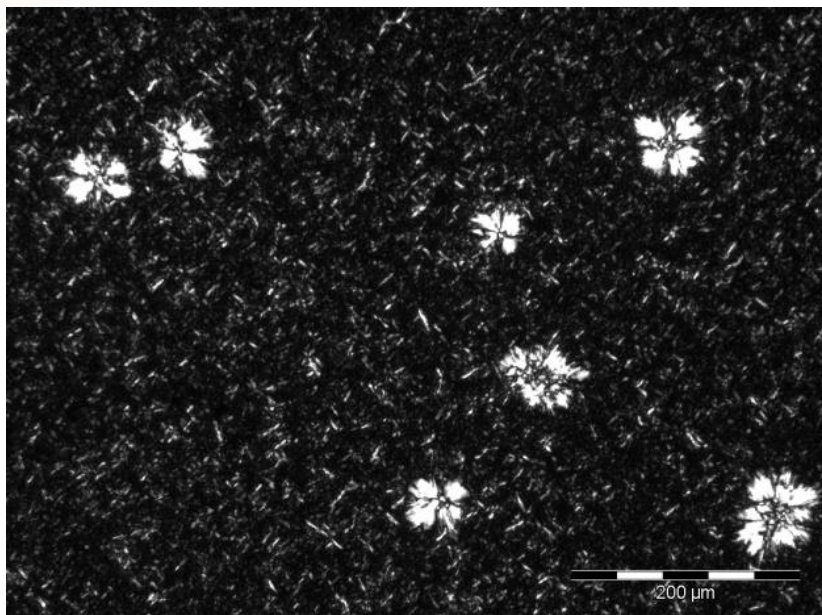


- XRD (X-ray Diffraction)
  - 100% certainty on the polymorphic form
- Synchrotron radiation (ESRF (European Synchrotron Radiation Facility) in Grenoble)
  - More intense X-rays → recording time is limited to a few seconds





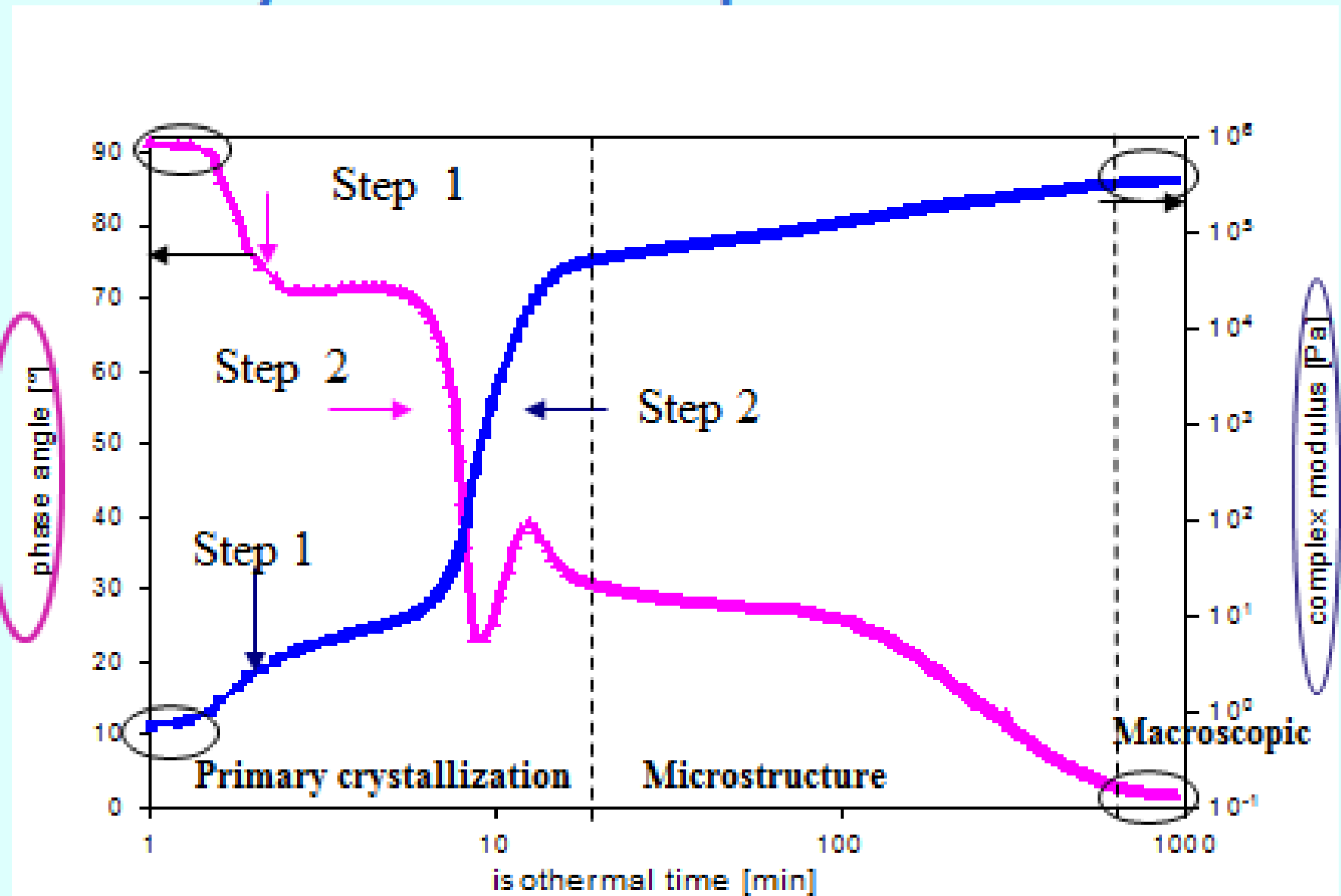
- Microscopy
  - Visual representation
    - Morphology, size, number of crystals
    - Aggregation and network formation
  - Several techniques
    - Polarized light microscopy
    - Confocal scanning laser microscopy
    - (Cryo-) Scanning electron microscopy



## ■ Rheology

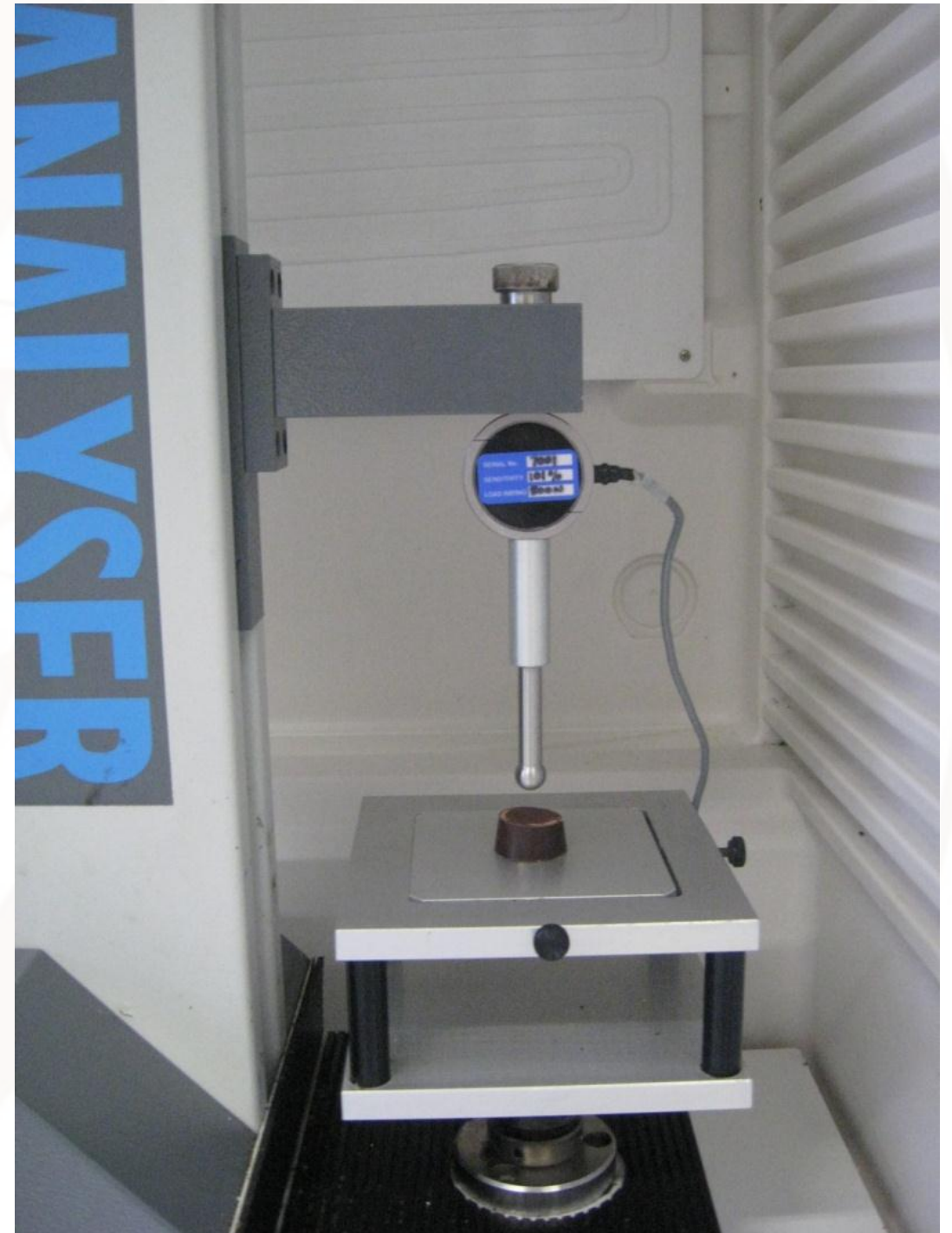


### Crystallization of palm oil at 18°C





- Texture analysis
  - Puncture test
  - Breaking test
  - Texture profile analysis test
- Sensorial analysis
  - Taste panel



SENS  LAB

FUTURE IS NOW!



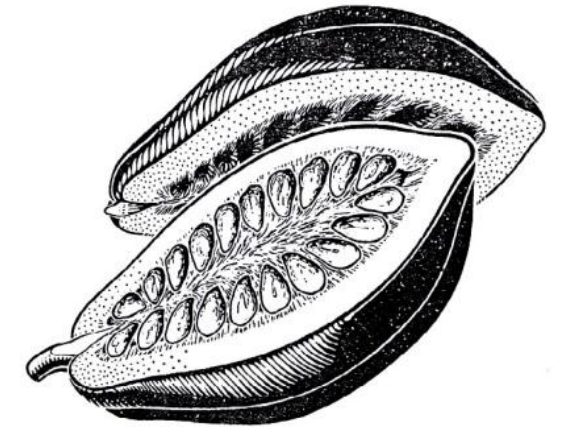
Food sensory research





- Fats and oil: chemistry
- Importance of fat crystallization
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- How to measure?
- **Case study cocoa butter**

- *Theobroma cacao* :
  - Up to 6 m tall
  - Cocoa fruit: 20 cm
  - Contains 30-40 seeds (65% moisture)
  - Originally from tropical Amazon forest
  - Cultivated by
    - Mayas from Yucatan, Guatemala
    - Aztecs from Mexico

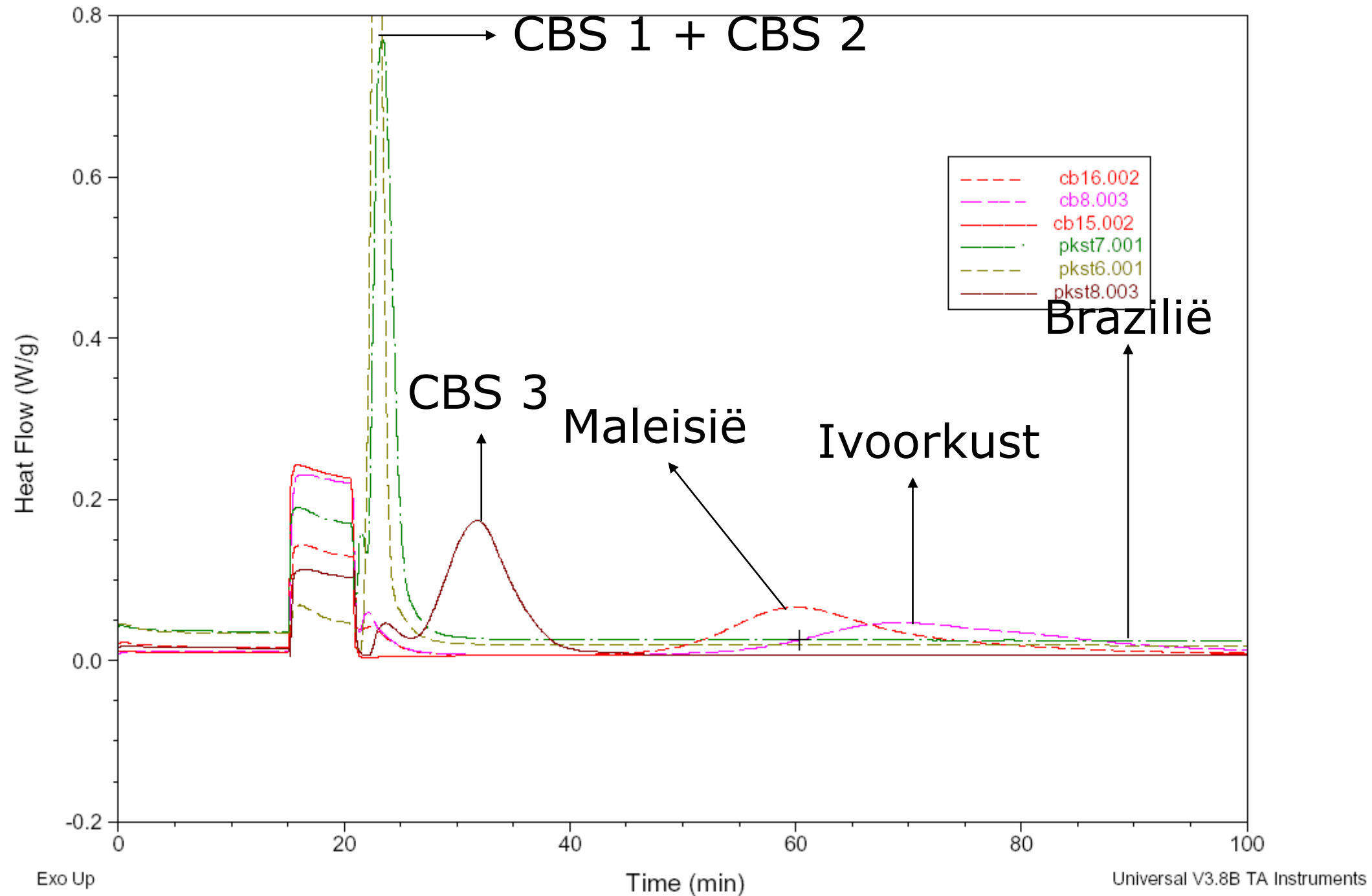




- Narrow triacylglycerol composition:
  - Mainly POP, POS & SOS
  - But also PLP, POO, PLS, SOO, SLS & SOA
- Variation in triacylglycerol composition depending on geographical origin

Land	#stalen	PLP	POO	PLS	POP	SOO	SLS	POS	SOS	SOA
Bolivië	1	1.1	3.3	3.5	22.6	4.0	2.1	40.4	22.8	0.5
Brazilië	6	0.9	3.9	3.7	17.9	6.7	3.2	37.1	26.0	0.4
Ecuador	3	1.2	3.0	3.2	19.2	5.4	2.3	38.4	26.9	0.4
Dom. rep.	4	1.1	3.3	3.2	18.4	6.1	2.7	38.2	26.5	0.6
Ivoorkust	9	1.0	1.9	3.0	19.0	3.9	2.5	39.6	28.5	0.6
Ghana	3	1.2	2.2	3.4	17.8	4.9	2.2	39.0	27.5	0.4
Indonesië	2	1.1	1.6	3.0	19.9	3.6	1.7	40.6	28.1	0.5
Maleisië	20	0.7	1.2	2.8	18.4	2.9	2.2	40.0	31.1	0.8



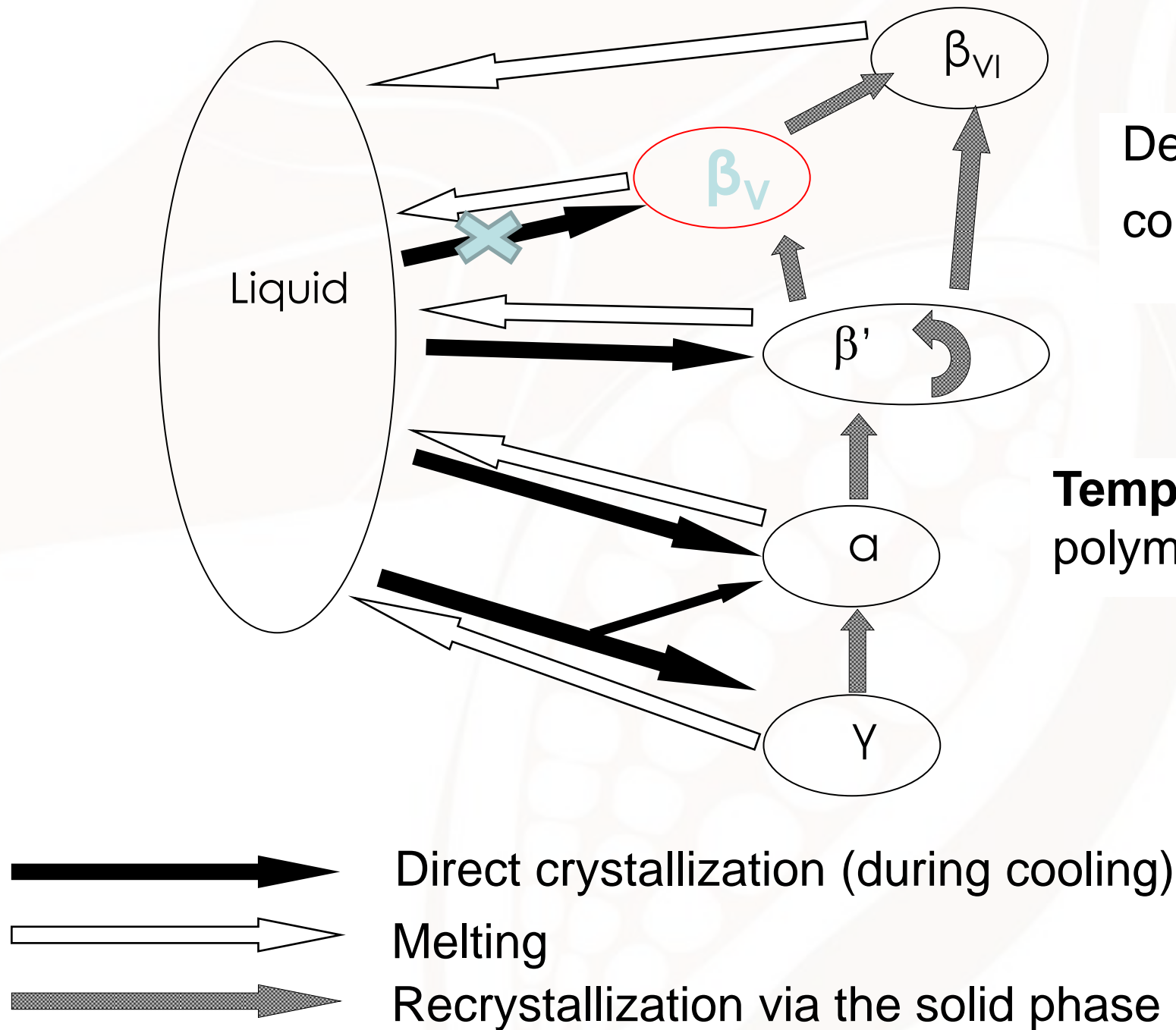


Isothermal crystallization (20°C) of cocoa butters of various origins and CBS monitored by DSC

- Narrow triacylglycerol composition  
 → complex crystallization behavior/ polymorphism
- 3 basic polymorphs + # sub polymorphs
- 4 to 6 polymorphs recognized and named depending on the author

Author	Polymorphic form					
Vaeck (1961)	$\gamma$	$\alpha$		$\beta'$	$\beta$	
Larsson (1966)	$\beta'_2$	$\alpha$	*	$\beta'$	$\beta_2$	$\beta_1$
Wille & Lutton (1966)	I	II	III	IV	V	VI
Van Malssen et al. (1999)	$\gamma$	$\alpha$		$\beta'$	$\beta^V$	$\beta^{VI}$
Systematic nomenclature	$\beta'_3$ (sub- $\alpha$ )	$\alpha-2$	$\beta'_2-2$	$\beta'_1-2$	$\beta_2-3$	$\beta_1-3$

Possible phase transitions in cocoa butter (Van Malssen et al., 1999)



Desired polymorphic form:  
contraction, gloss, snap



**Tempering** of chocolate to the desired polymorphic form





# Importance of crystallization in chocolate production

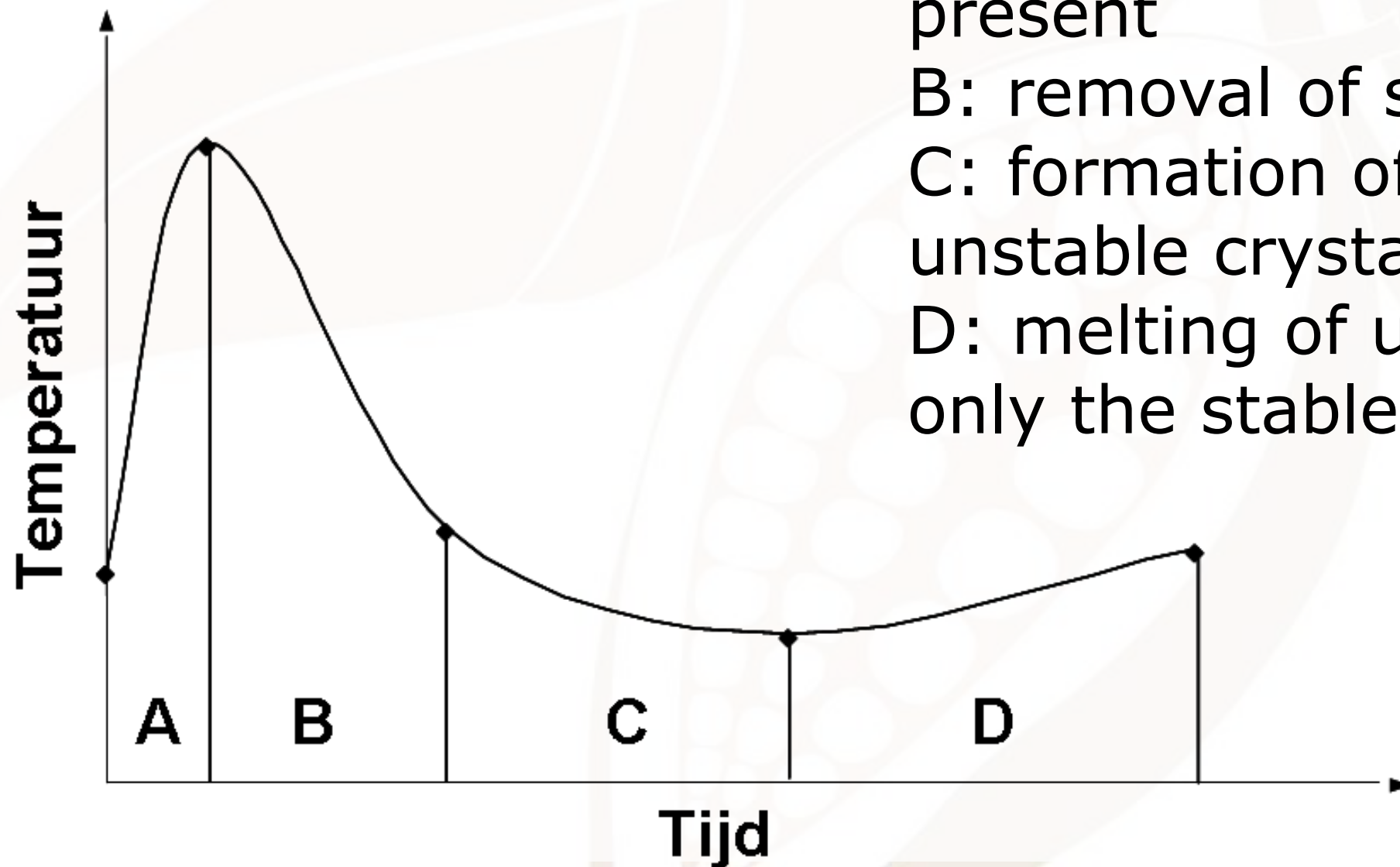


## ■ TEMPERING

- = step in the production process during which seed crystals are formed in the molten chocolate
- Important to obtain crystals in polymorph V as this results in the desired properties such as gloss, color, hardness, snap and shelflife
- The seed crystals in polymorph V created during tempering will ensure that the rest of the chocolate also crystallizes in polymorph V

## ■ TEMPERING

- Several steps can be identified (see figure)



A: melting all the crystals present

B: removal of sensitive heat

C: formation of stable and unstable crystals

D: melting of unstable crystals , only the stable crystals remain



# Importance of crystallization in chocolate production



## ■ COOLING

- Further crystallization based on seeds formed during tempering
- Proper time-temperature program in cooling tunnel is important: gloss, sufficient hardening at the end of the cooling

## ■ STORAGE

- Ongoing crystallization (depending on the cooling): crystallization heat can get trapped in the wrapping
- Amongst others, polymorphic transition to form VI  
→ Fat bloom





# Tempering



- VIDEO !

# Case study: Influence of refining on the cocoa butter properties

## Conventional Cocoa Butter Refining

### ■ Good quality refined cocoa butter

- < 1.75% free fatty acids
- Free from foreign material
- Molds
- Rancidity

**Crude Cocoa Butter**

**Polish Filtration**

**Deodorization  
Steam stripping**

Batch/Continuous  
Long/Short time

**Refined Cocoa Butter**



- High demand → more poor quality crude cocoa butter
  - High FFA, high (non-hydratable) phosphatides, Fe
  - High alkalinity, dark colour (difficult to bleach)
- Increasing demand for different types of cocoa butter
  - Colour ranges
  - Degree of neutral flavours
- Removal of alkaloids: theobromine and caffeine
  - Deposit on the surface of vapour scrubbers → reduce the performance
- Steam refining should preserve unique crystallisation properties of cocoa butter

→ ***Improved refining process required***

## Conventional Cocoa Butter Refining

## Improved Cocoa Butter Refining

**Crude Cocoa Butter**



**Polish Filtration**



**Deodorization  
Steam stripping**



**Refined Cocoa Butter**

Acid and/or silica - 80°C/atm.  
pressure

Bleaching earth (and activated carbon)  
90°C/50 mbar

Packed column stripping or tray  
deodorization  
short time/low pressure, adjustable temp.

**Crude Cocoa Butter**



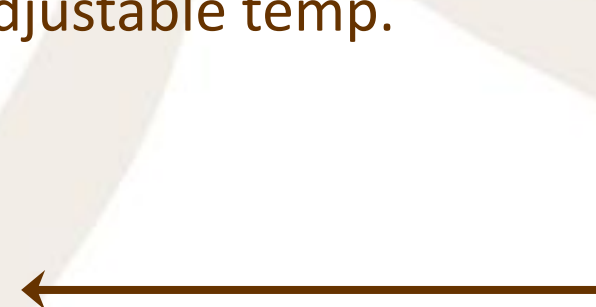
**Silica Pretreatment**



**Bleaching**



**Deodorization  
Steam stripping**

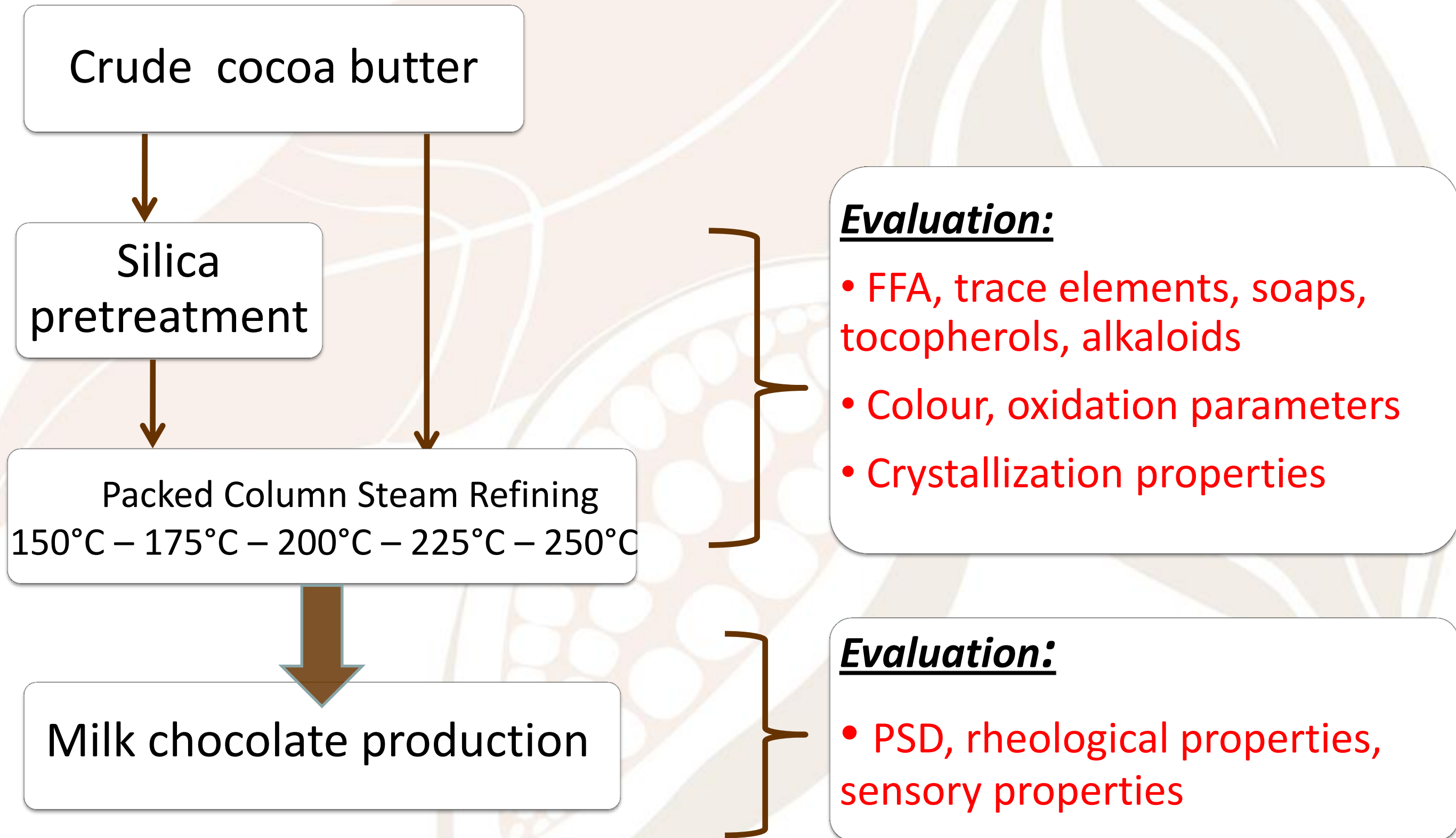


Cocoa butter refining conditions



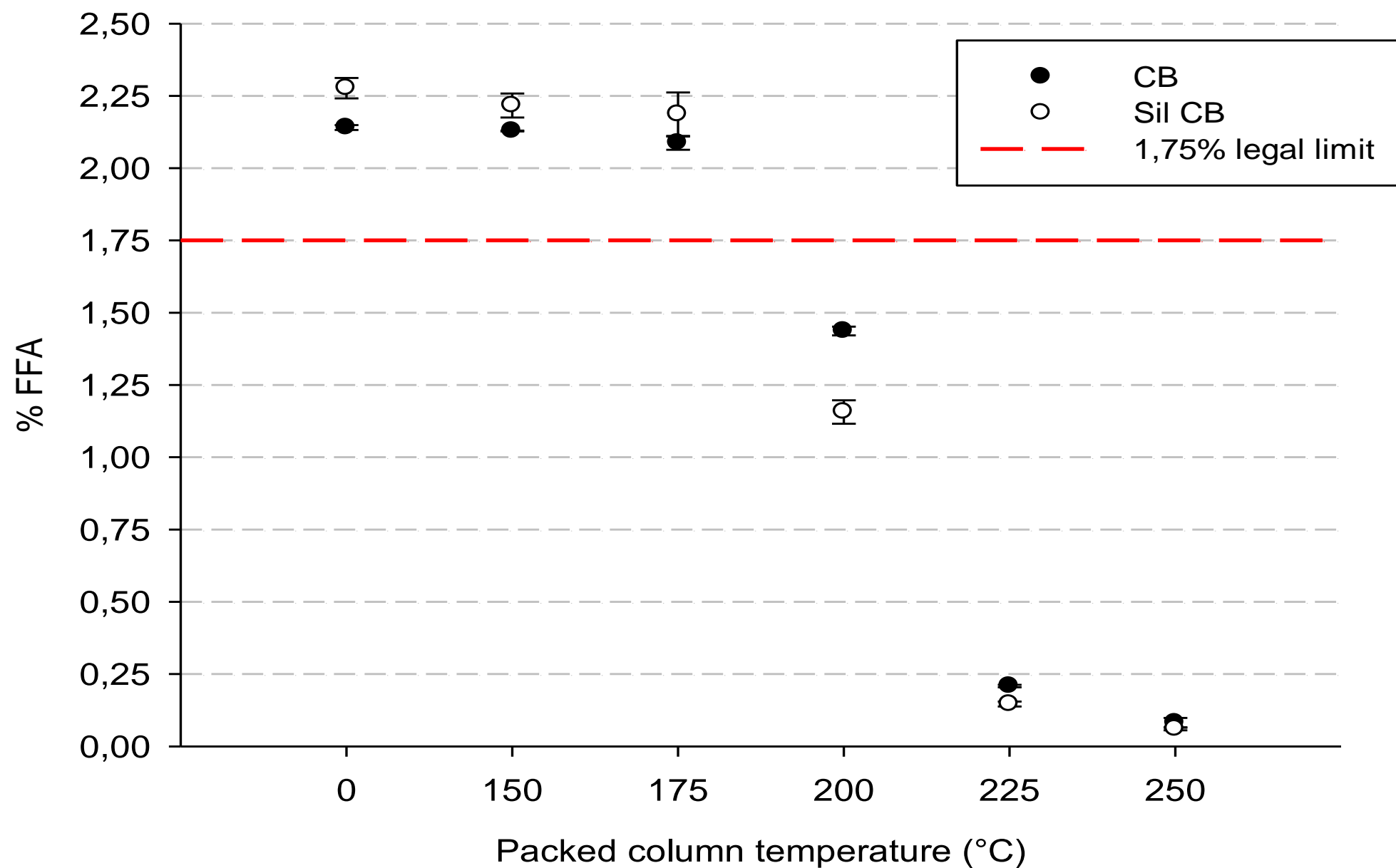
Milk chocolate quality





	Crude CB	Silica pretreatment	Observation
FFA (%)	2.14	2.28	≈
Trace elements			
P (ppm)	63.52	8.66	~90% ↘ <b>Degumming</b>
Fe (ppm)	3.20	0.24	~90% ↘
Tocopherols	264.64	246.55	≈
Alkaloids			
Theobromin	75.71	35.17	~54% ↘
Caffeine	437.96	331.36	~25% ↘
Soaps (ppm sodium oleate)	392	N.D.	<b>Complete removal</b>
Colour	$L^* 37a^*3.8b^*59.2$	$L^* 73a^*-4.83b^*100.5$	$L^* ↗$ <b>Bleaching effect</b> $b^* ↗$ <b>more yellow</b>
OSI (hours)	32.43	61.30	~50% ↗

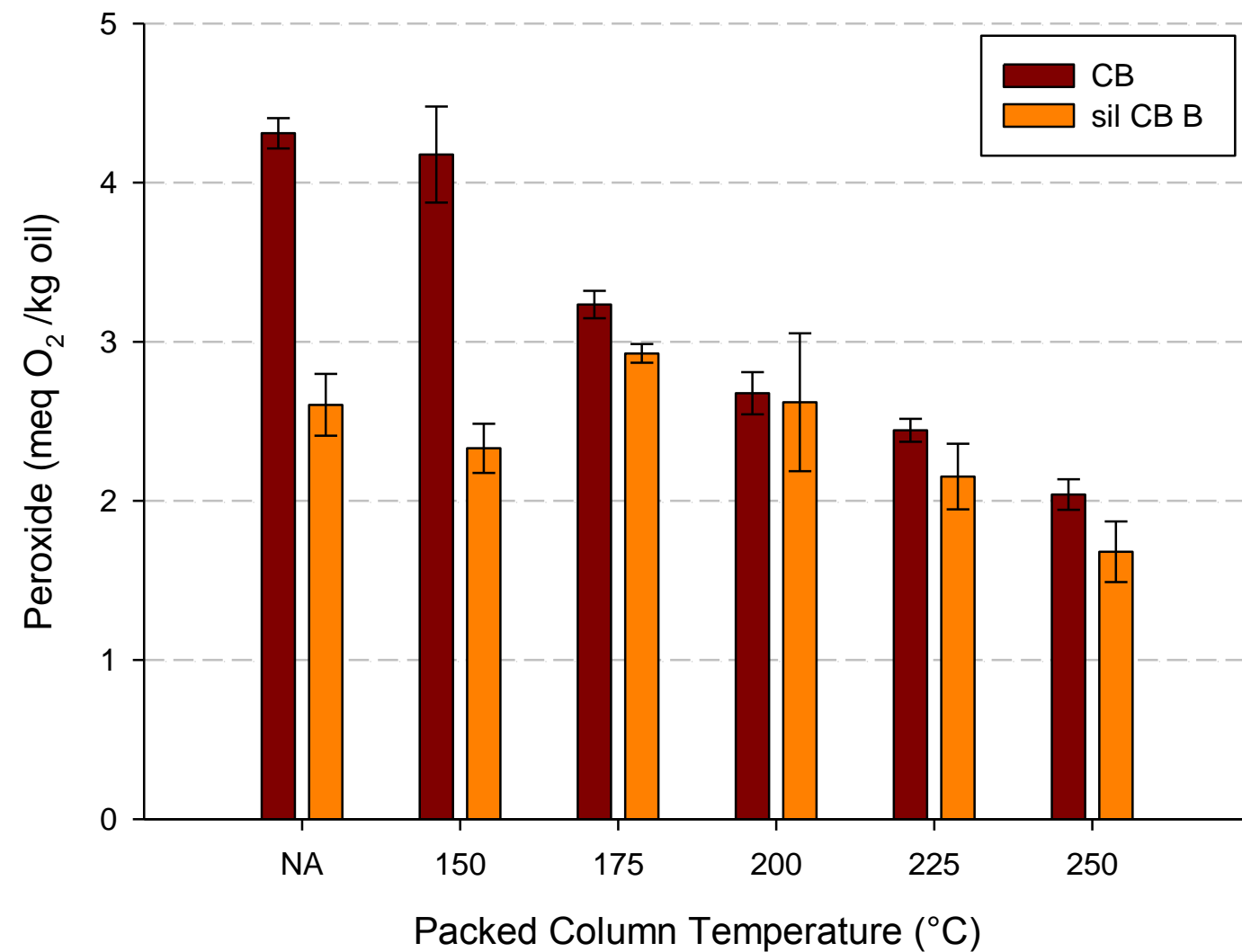
## FFA removal as function of refining temperature: sigmoid decrease



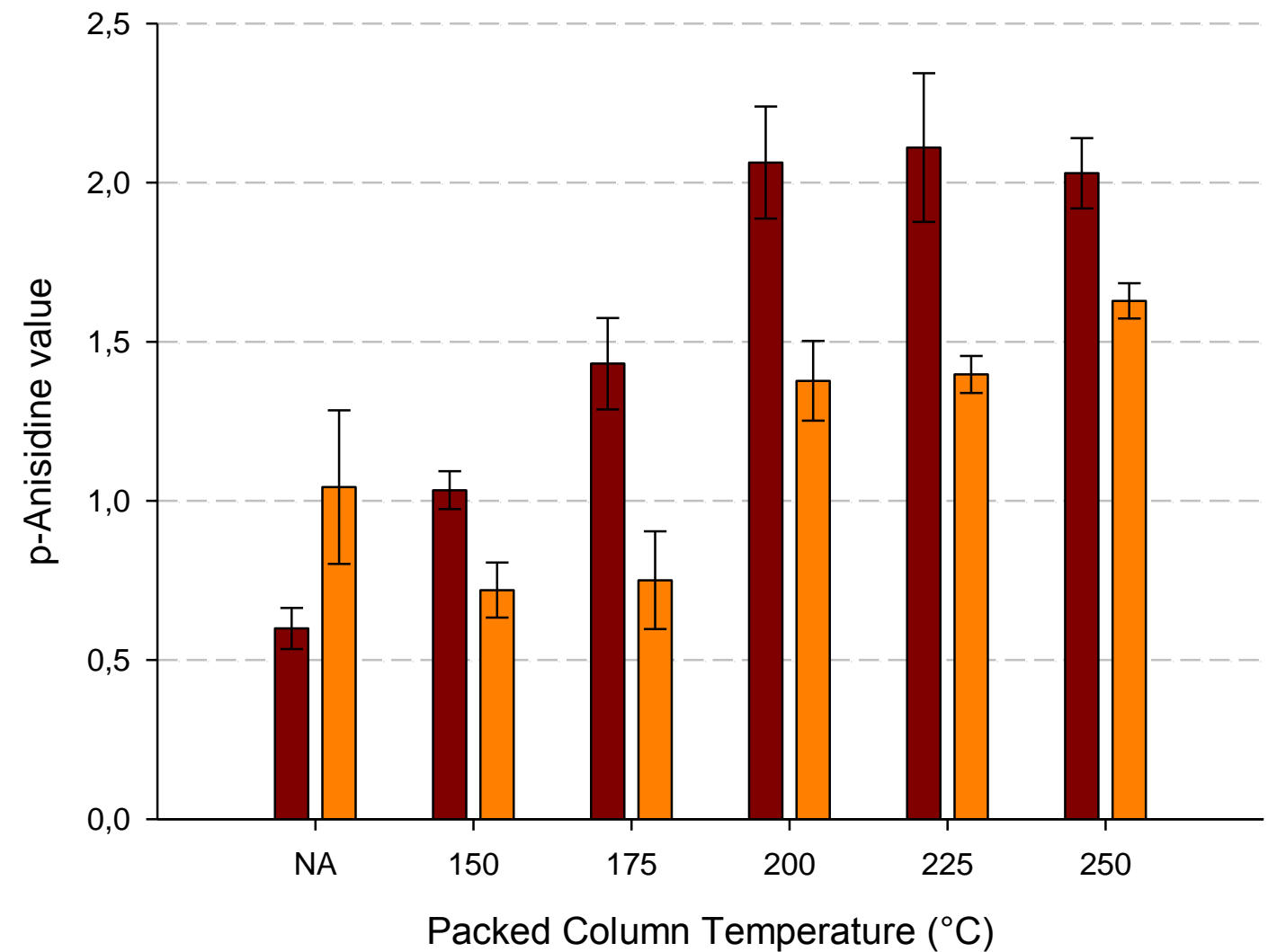


- Temperature during packed column steam refining
  - No influence
    - ✓ P and Fe
    - ✓ Acylglycerol composition
  - Limited influence
    - ✓  $T > 175^{\circ}\text{C}$ : 30% reduction soaps
    - ✓  $T > 175^{\circ}\text{C}$ : limited reduction tocopherols
  - Complete removal theobromine and caffeine at  $T \geq 200^{\circ}\text{C}$
  - Exponential decrease of  $b^*$  as function of temperature: less yellow

Oxidative properties:  $T \nearrow$  primary oxidation products transform to secondary oxidation products



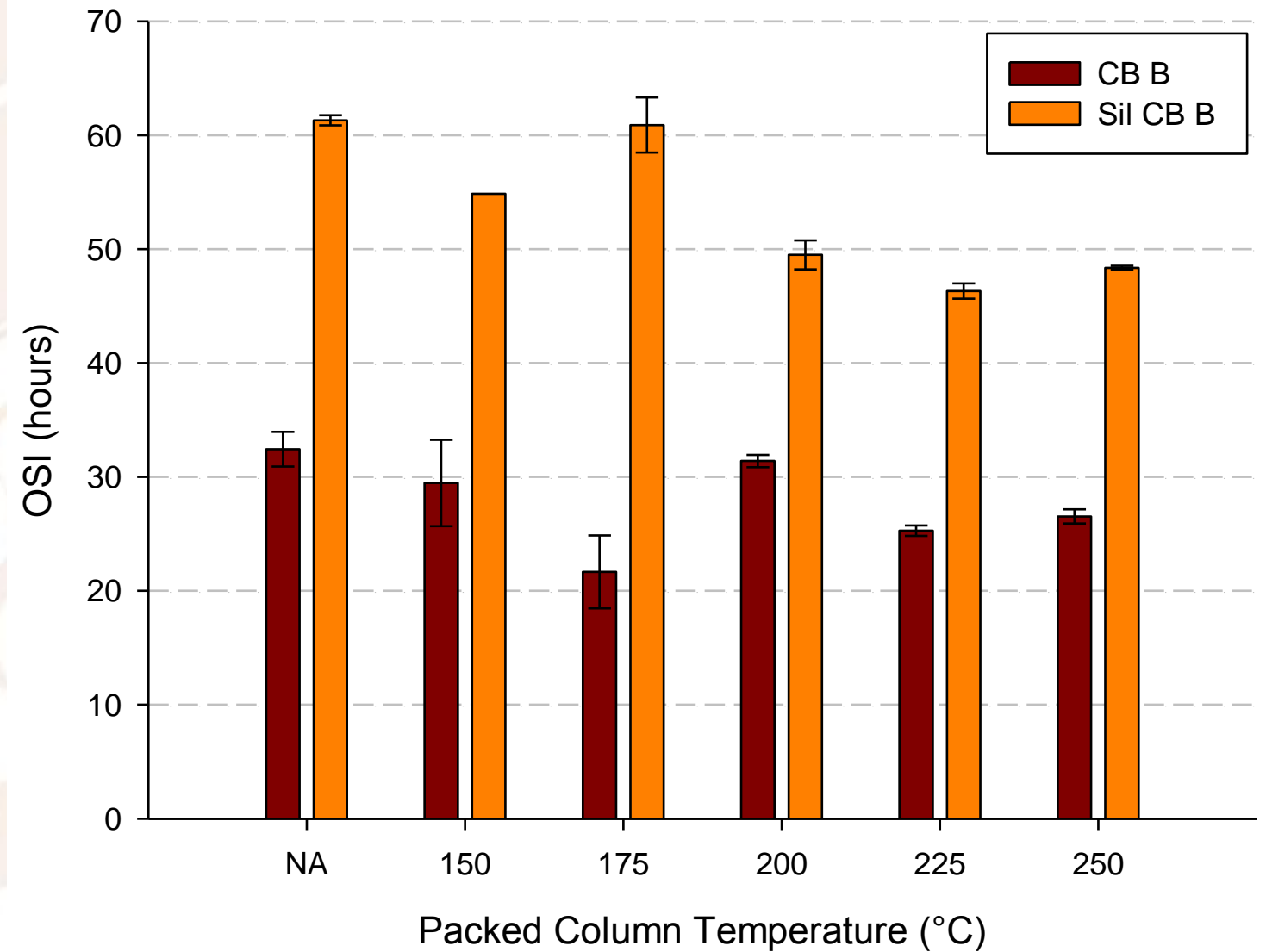
**Peroxide**



**p-Anisidine**

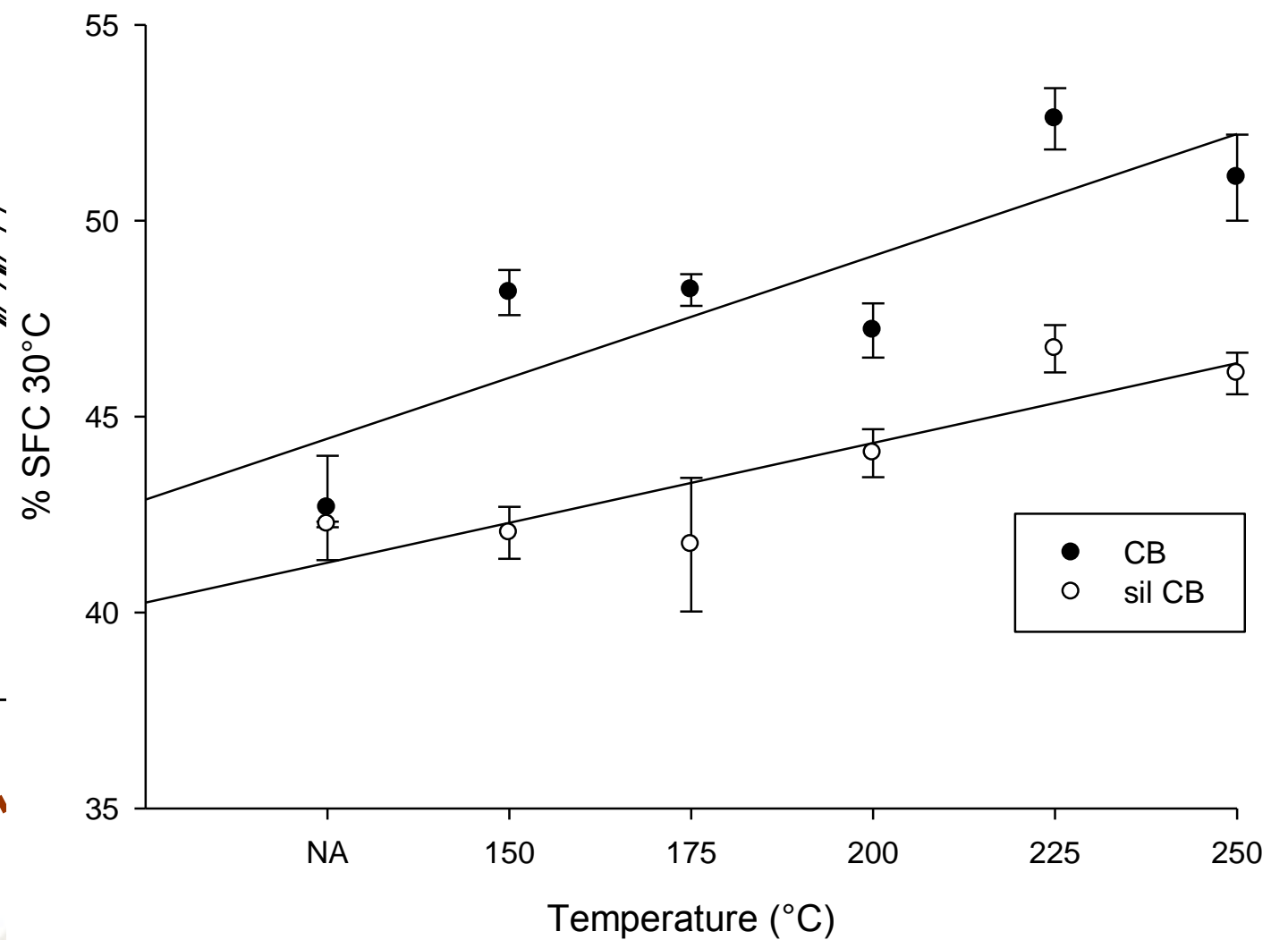
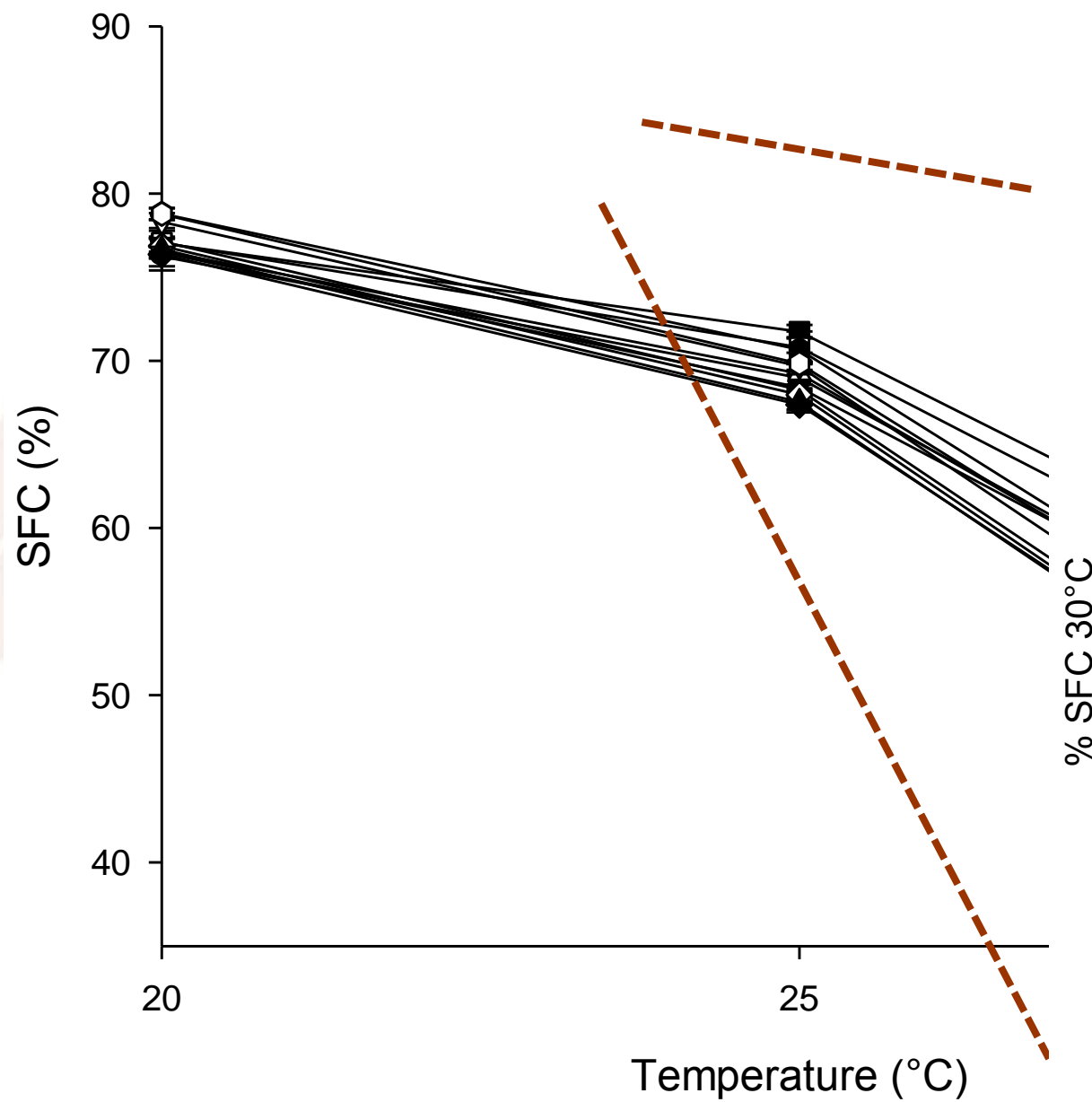
## Oil stability index (OSI):

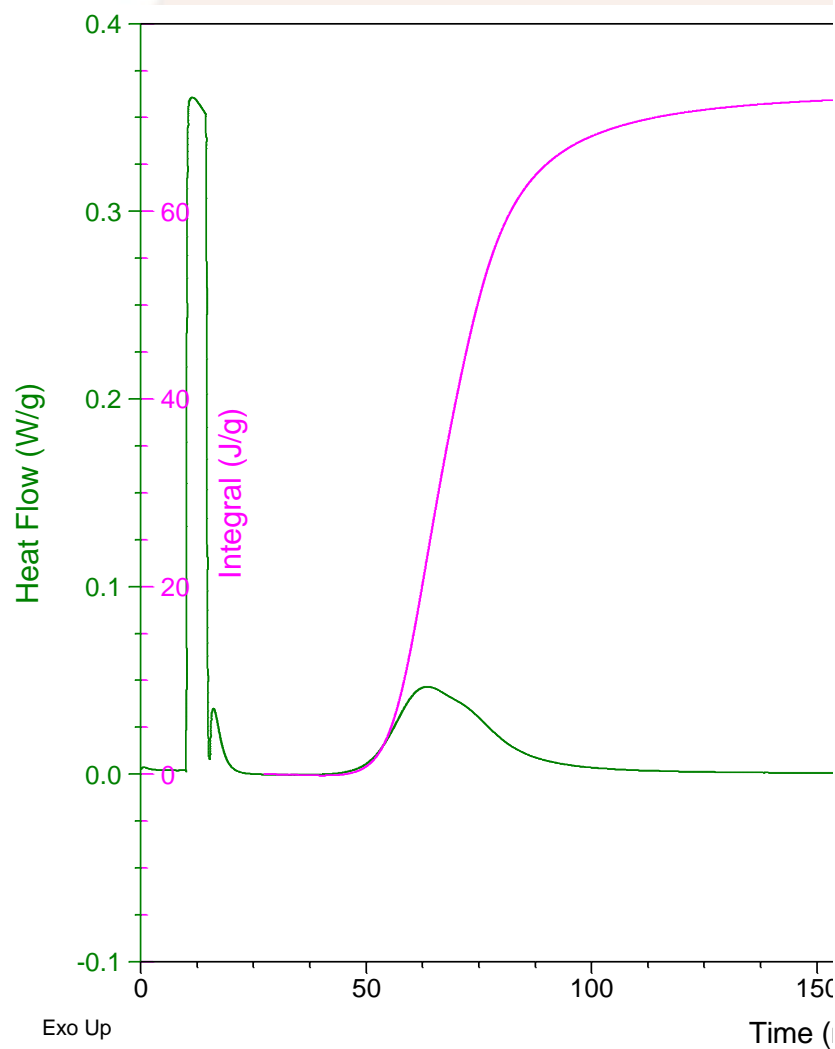
- Limited influence of temperature
- Si-pretreatment: less prone to oxidation  
→ Removal of Fe





SFC content in temperature range 20°C to 30°C (tempered IUPAC procedure: 40 hours at 26°C)





- Isothermal crystallization at 20°C for 240 min
- Start with formation of  $\alpha$ , followed by transition to the  $\beta'$ -polymorph
- Kinetics of the  $\beta'$  crystallization: Foubert Model parameters

- $t_{ind}$ : time needed to achieve 1% crystallization: decrease as function of column temperature
- $K$ : rate constant: increase as function of column temperature
- $a$ : no clear effect

→ sooner and faster crystallization as  $T$  increases, so as function of FFA removal



# Influence of refining on CB properties



## ■ Read more

- Ayala et al. 2007, *JAOCs*, 84, 1069-1077
- Calliauw et al. 2008, *Journal of Food Engineering*, 89, 274-284
- De Clercq et al., 2012, *Journal of Food Engineering*, 111, 412-419



# Case study: Influence of DAG on the crystallization of CB

(crude) cocoa butter

MODIFICATION

chocolate

## ■ Innovation

= Creation of new products, high added value

- Nutritionally, taste, appearance, functionality
- BUT with same quality level as the standard product

→ Modification of cocoa butter

○ Cocoa butter based diacylglycerols

○ DAG

- Distinct physicochemical properties compared to TAG
- More hydrophilic and water soluble
- Nutritional benefits (mainly 1,3-DAG)
  - Different metabolic pathway
  - Lower body weight gain and body fat accumulation



**CB**

**Production**

***CB Diacylglycerols***

**Characterization**

**Phase behaviour  
0 – 100 % CB – DAG**

**Isothermal crystallization  
CB + max. 10% DAG**

**Dark chocolate  
Migration fat bloom**

**Fundamental**

**Applied**

**CB**

**Production**

***CB Diacylglycerols***

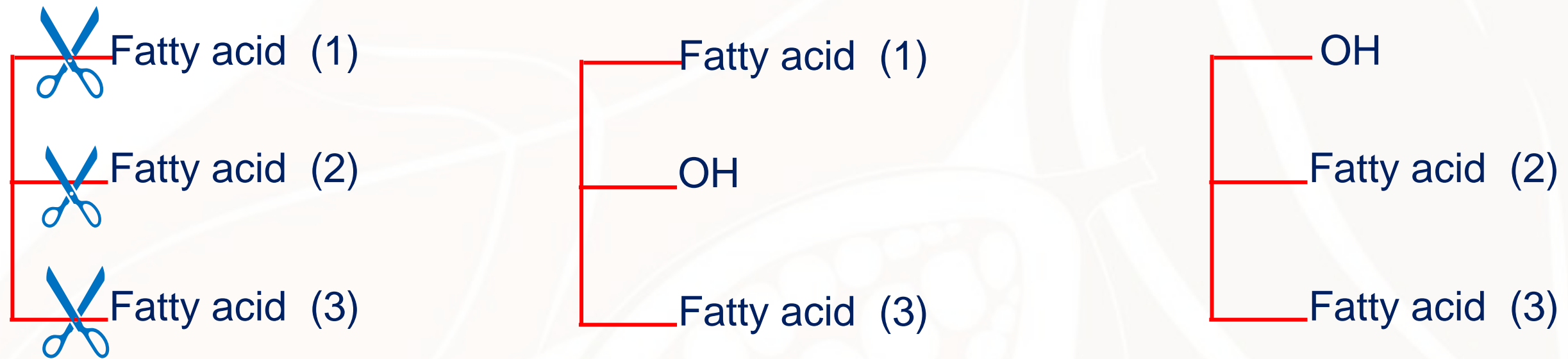
**Characterization**

**Phase behaviour  
0 – 100 % CB – DAG**

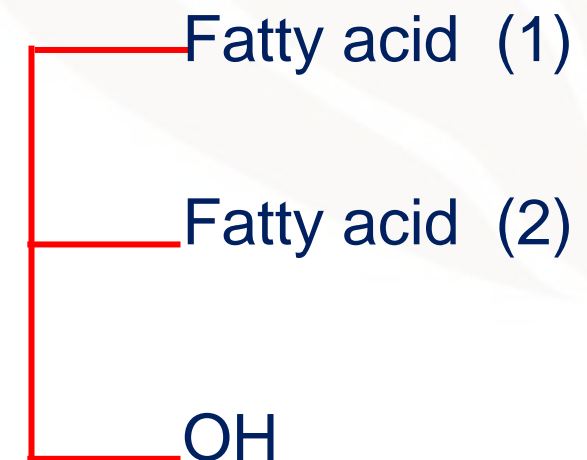
**Isothermal crystallization  
CB + max. 10% DAG**

**Dark chocolate  
Migration fat bloom**

- Diacylglycerol= DAG= 2 fatty acids + glycerol

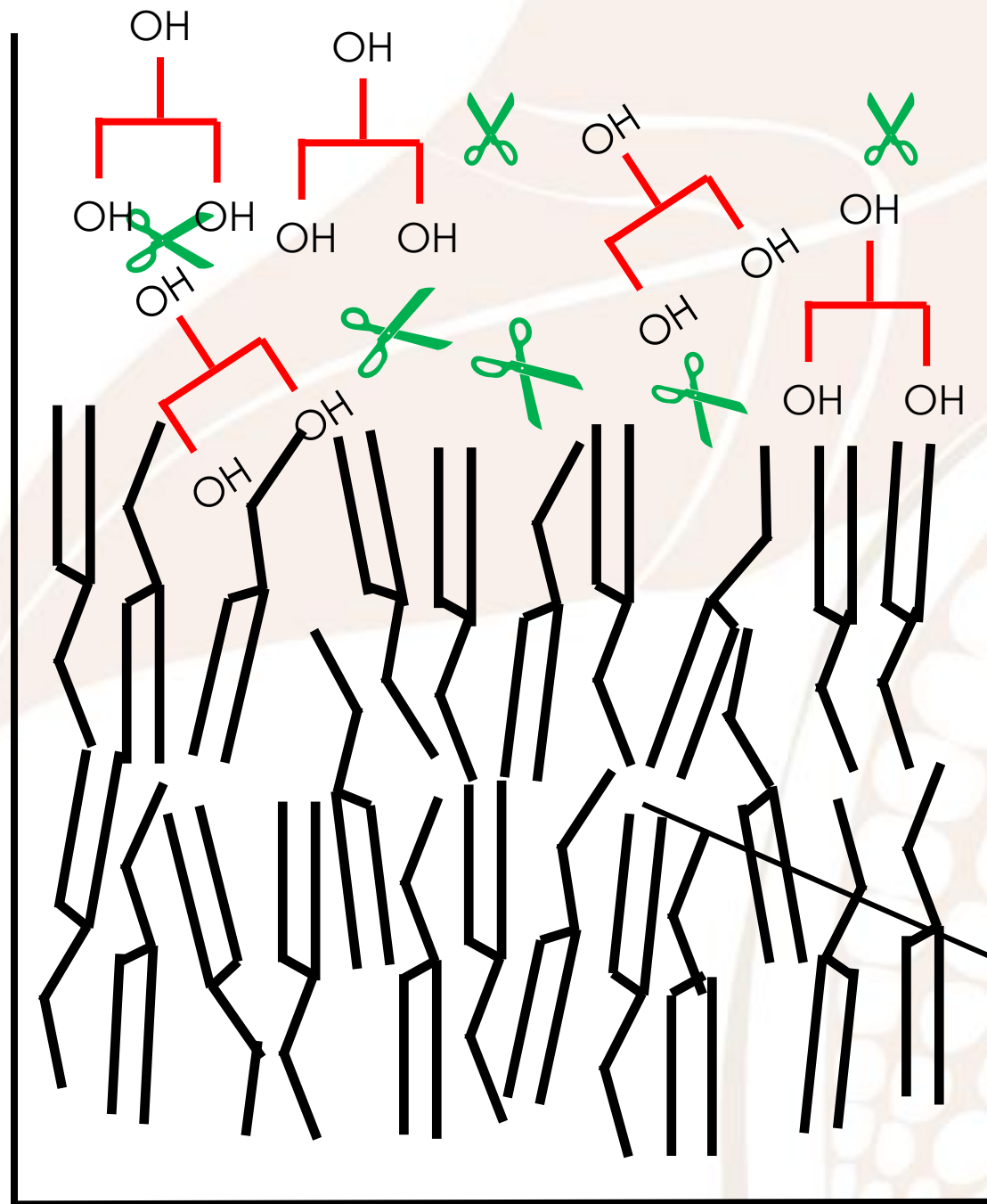



- 1,3-DAG
- 2,3-DAG  
= 1,2-DAG





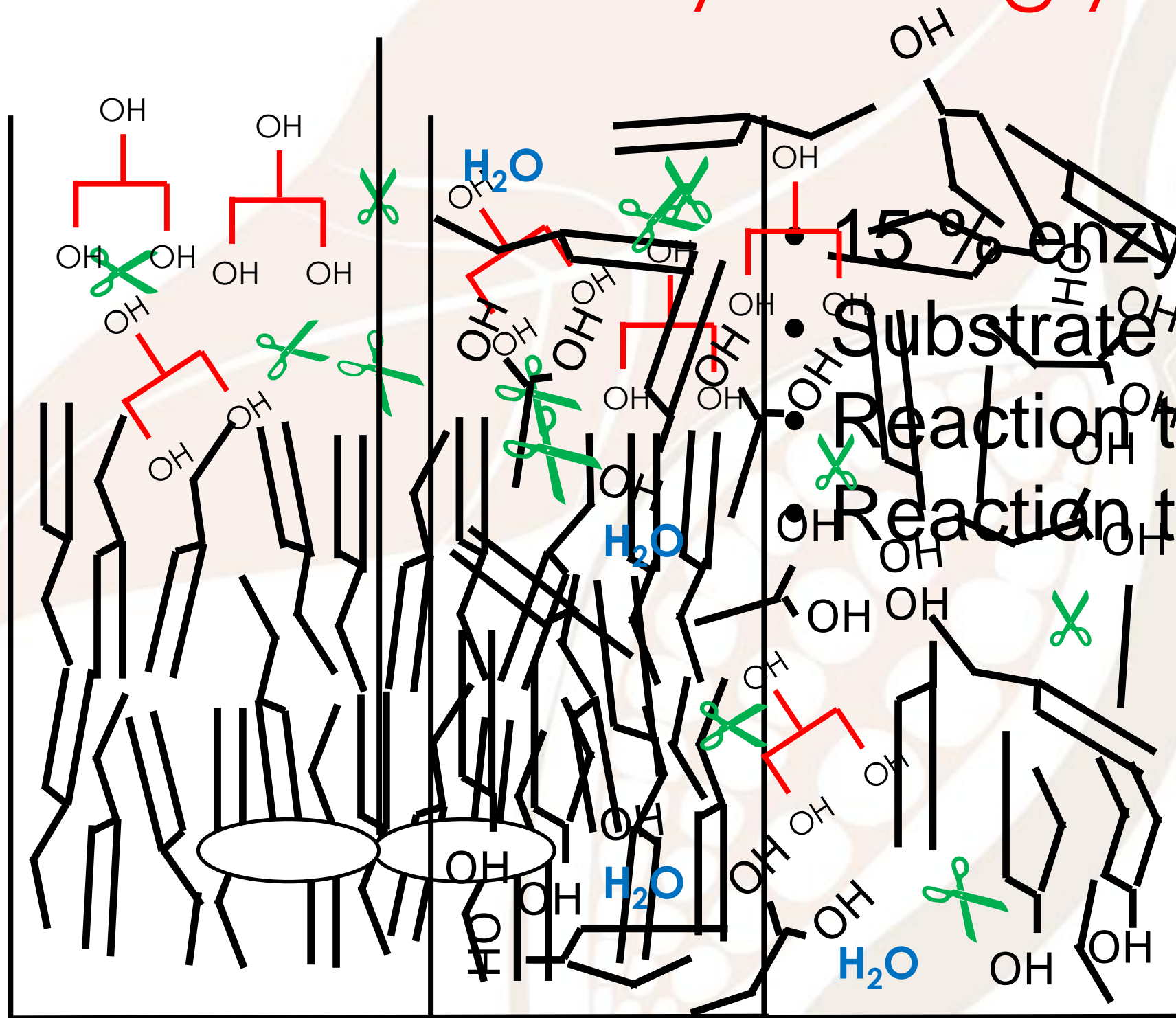
## enzymatic glycerolysis



- 15 % enzyme 
- Substrate molar ratio: 1.12
- Reaction temperature: 70°C
- Reaction time: 6 hours

→ **Cocoa butter TAG**

## enzymatic glycerolysis



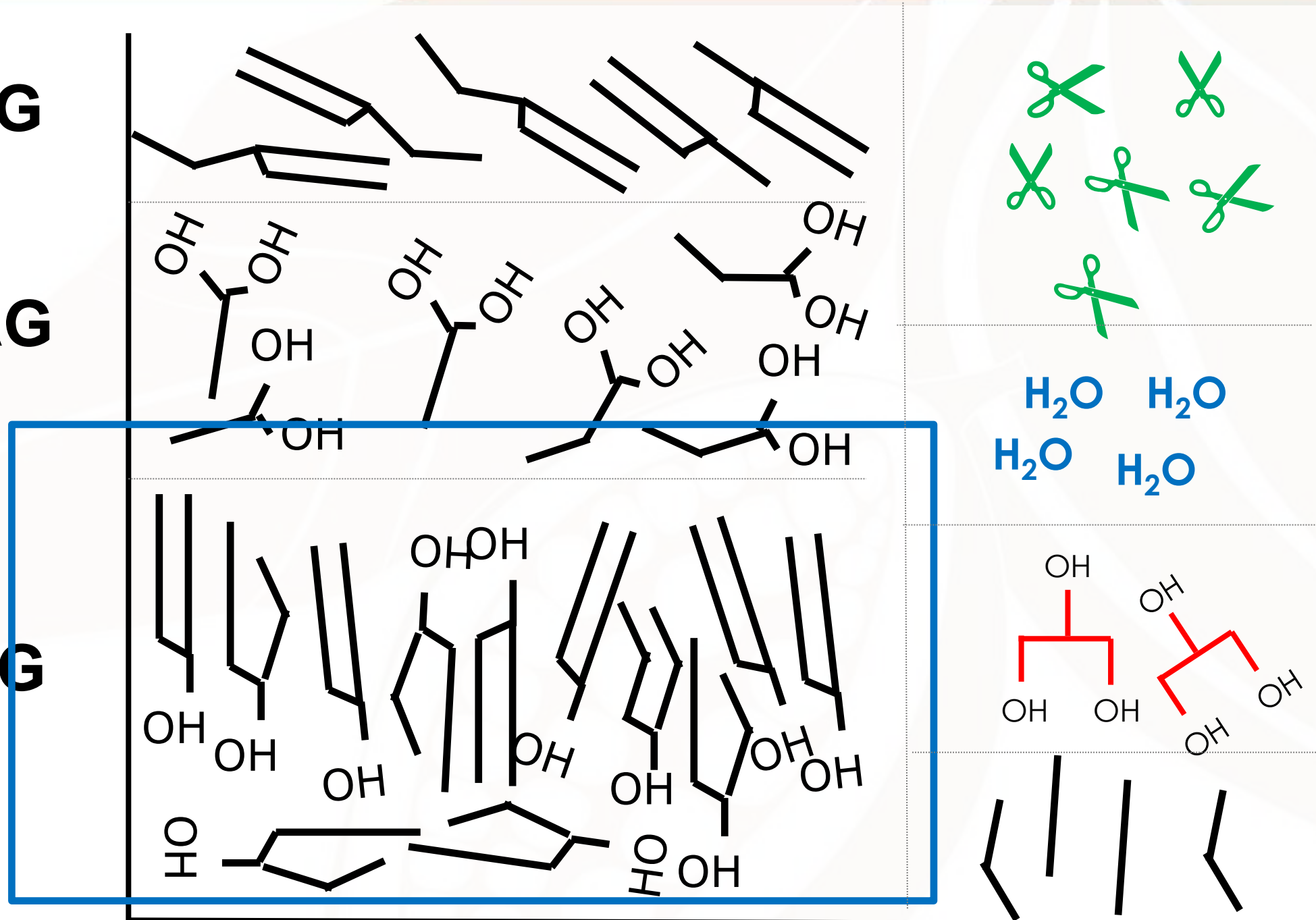
15% enzyme

- Substrate molar ratio: 1.12
- Reaction time: 6 hours
- Reaction temperature: 70°C

**20% TAG**

**30% MAG**

**50% DAG**



**Enzyme**

**Water**

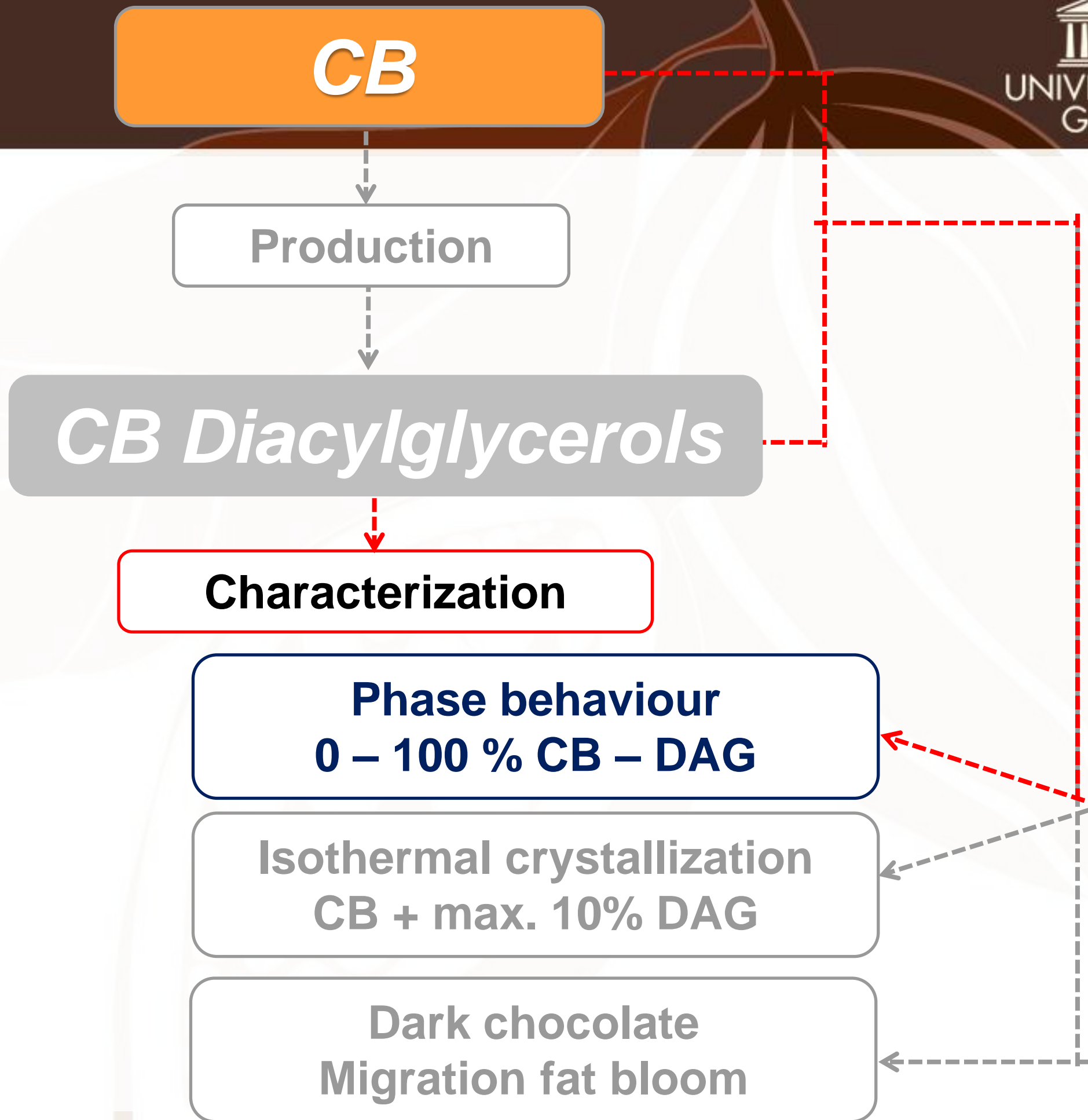
**Glycerol**

**FFA**

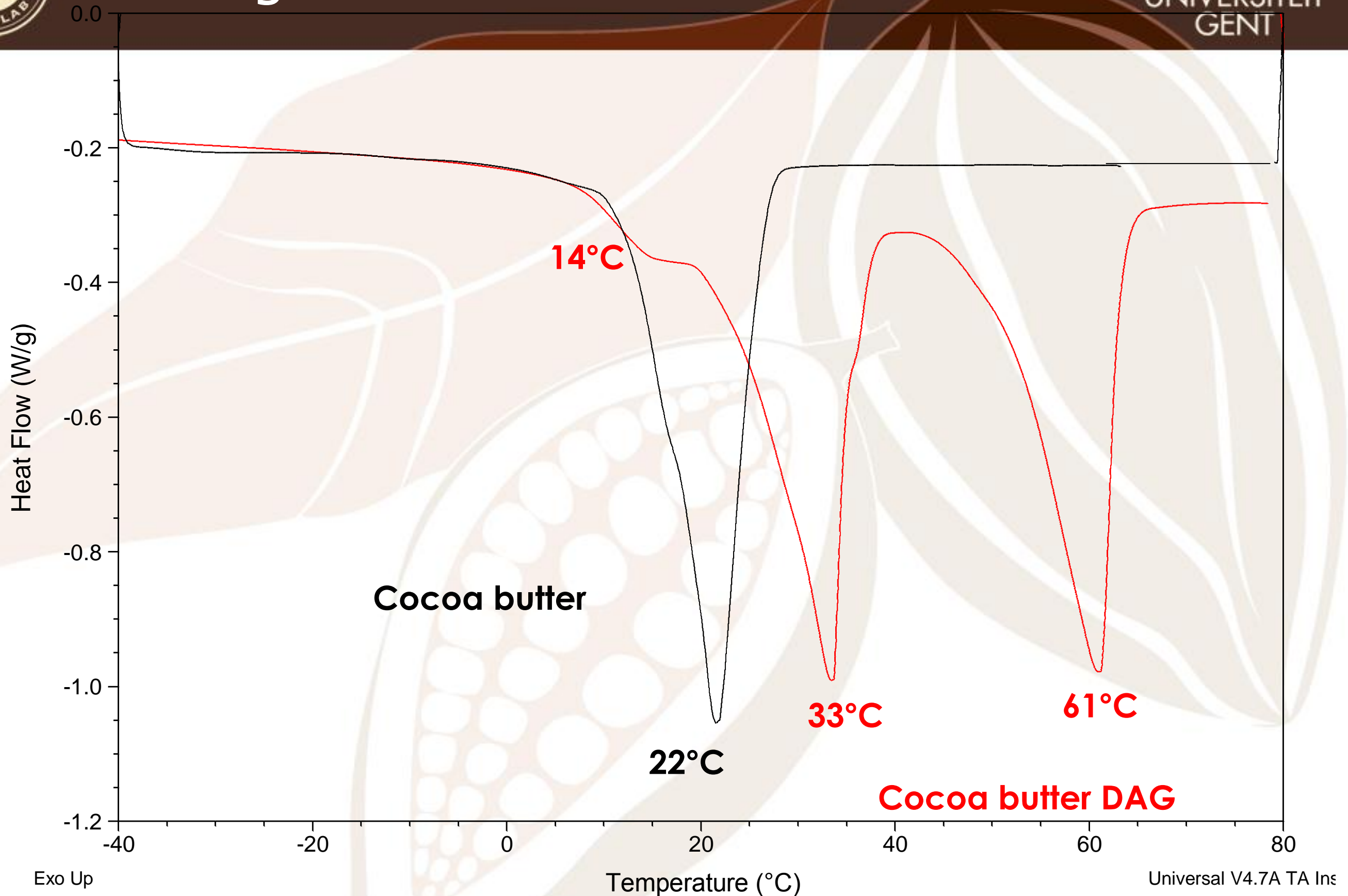
## Short path distillation:

4 steps, combination temperature and reduced pressure

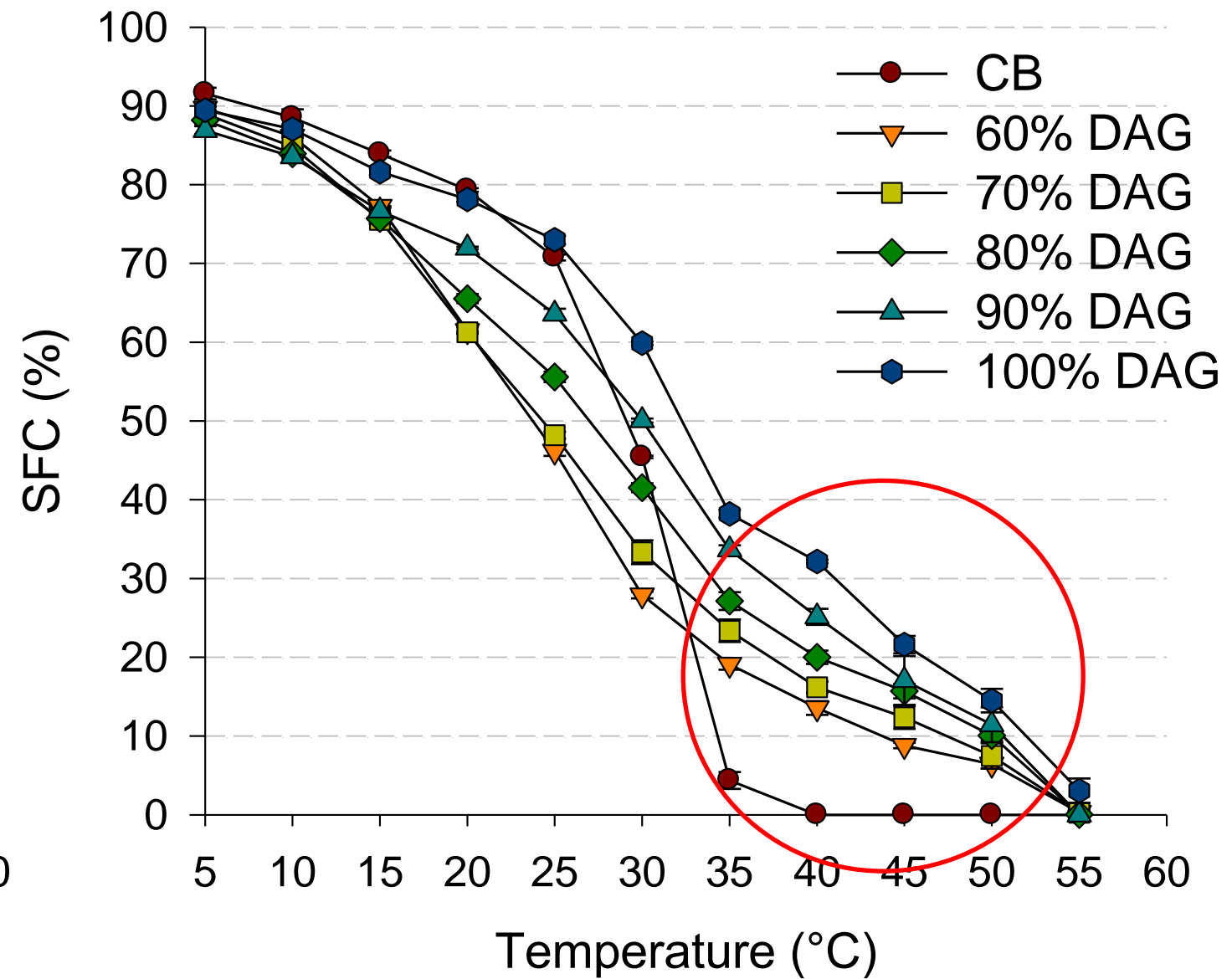
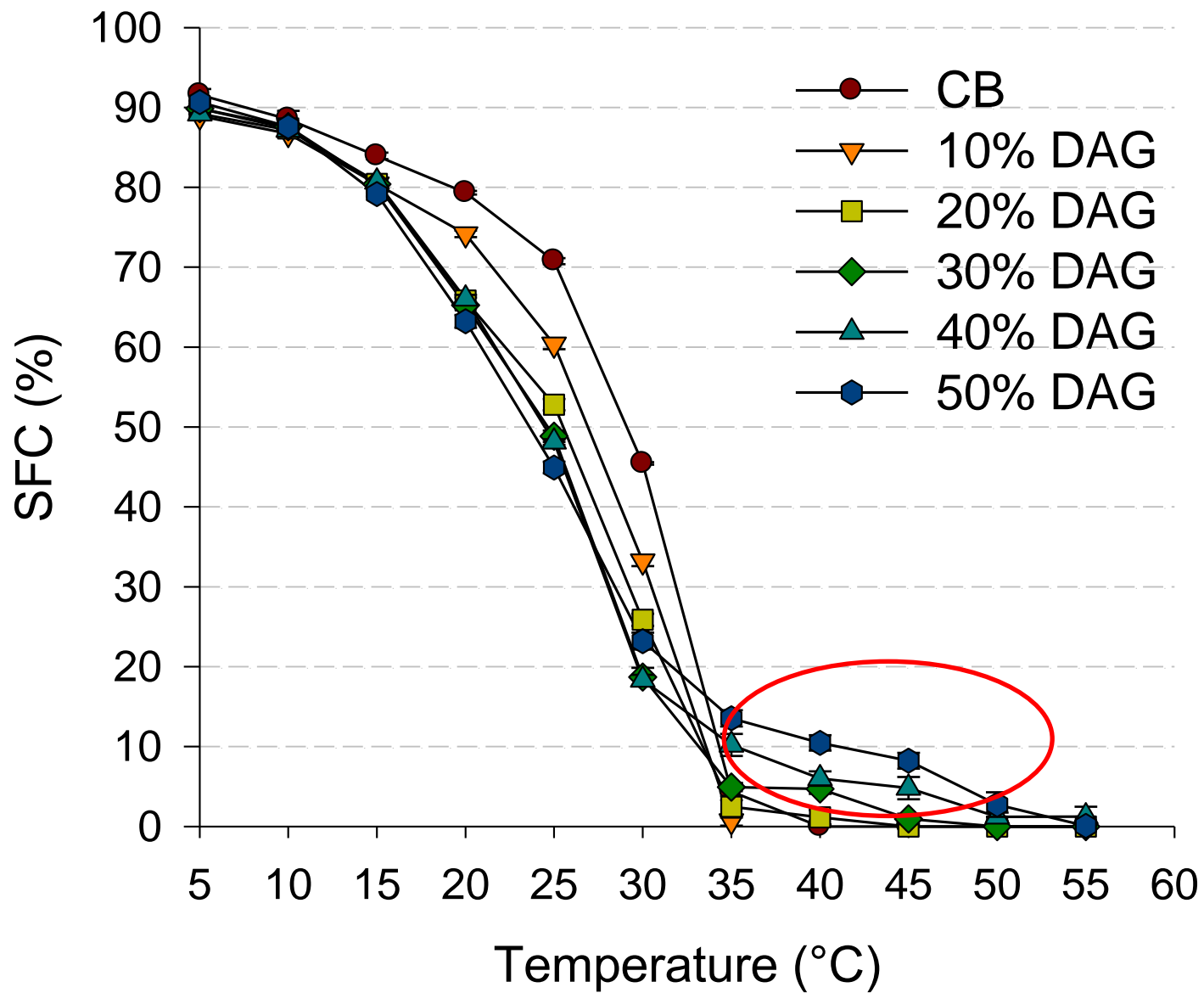




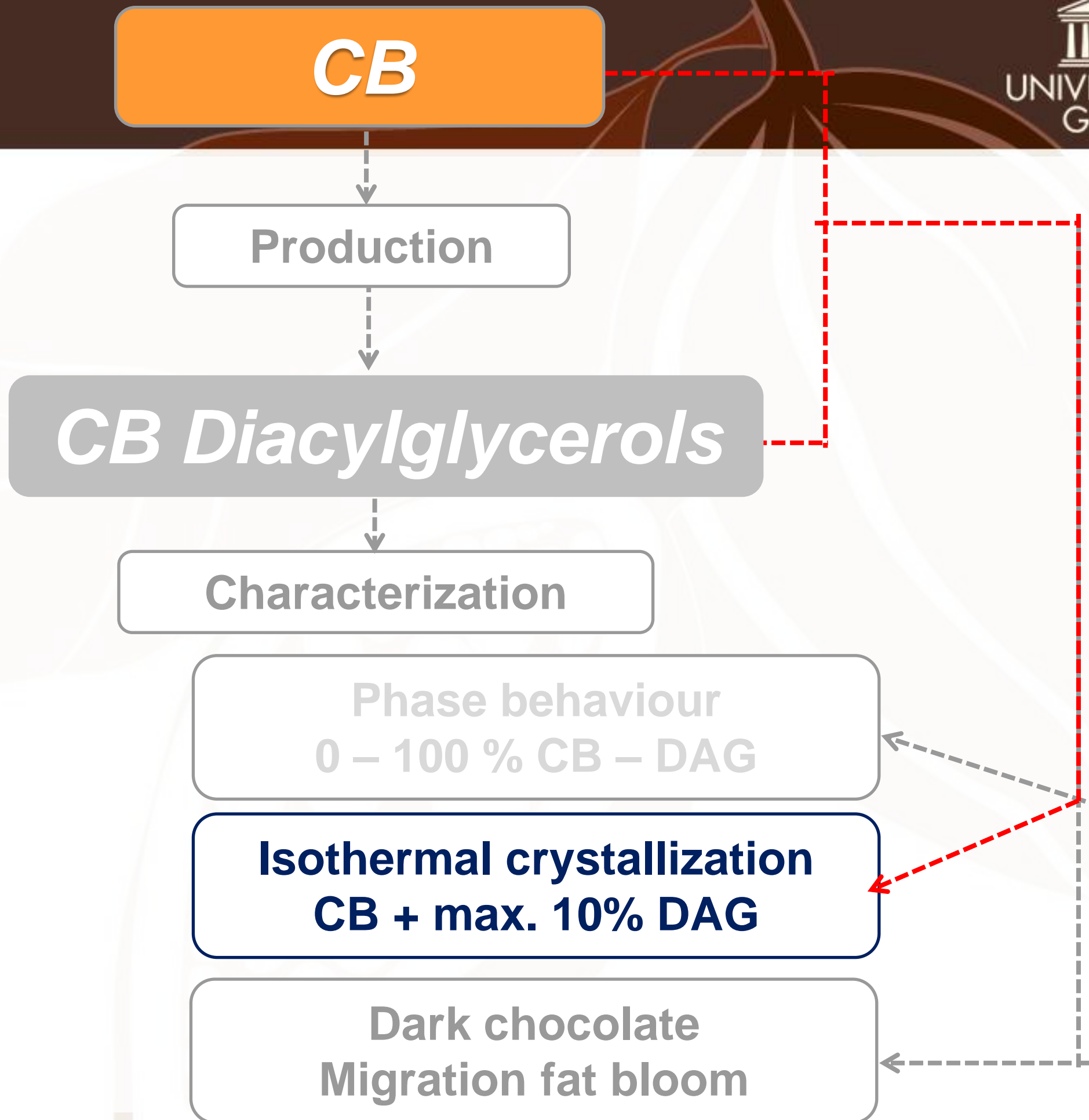
# Melting behaviour of CB vs CB DAG



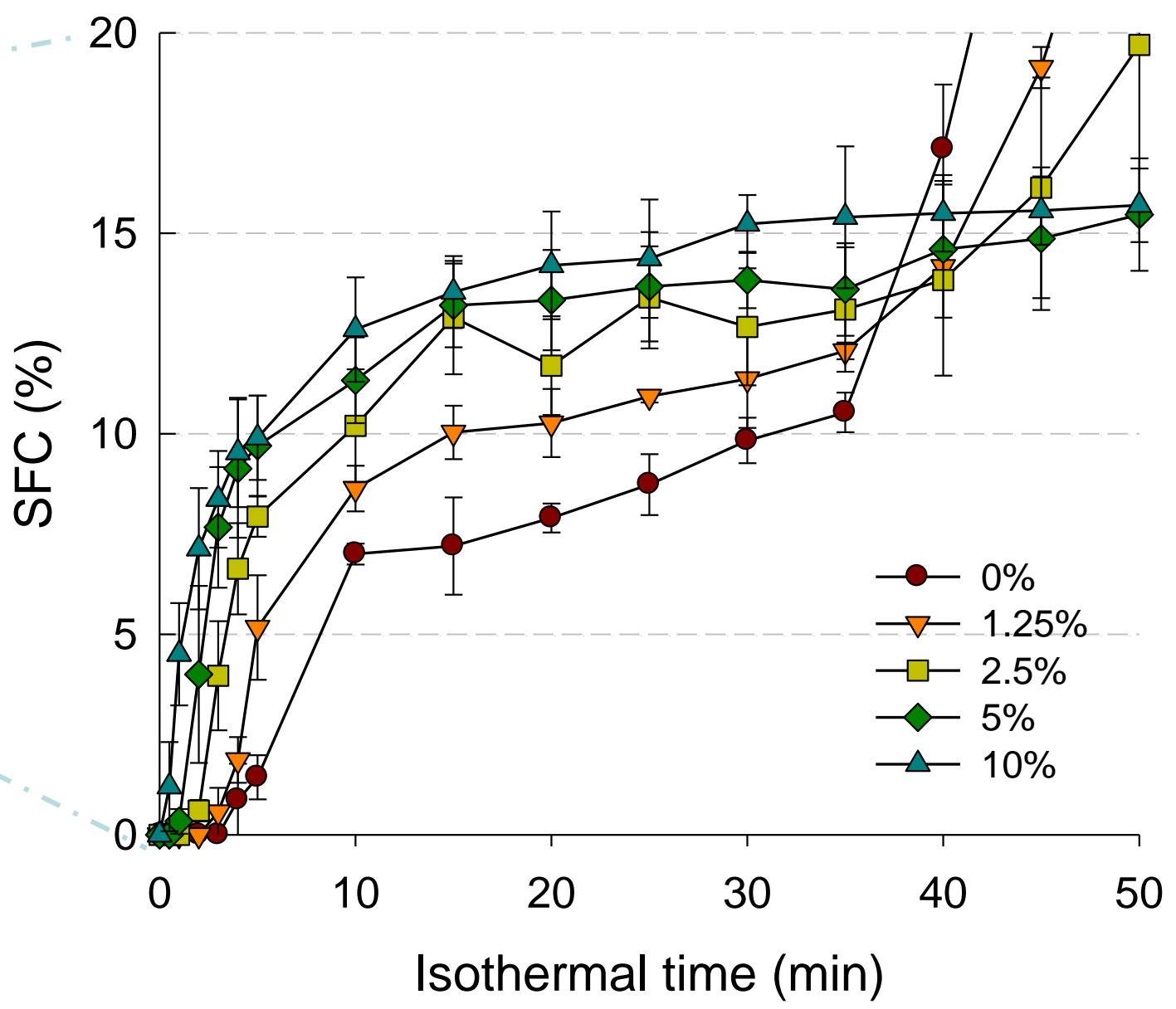
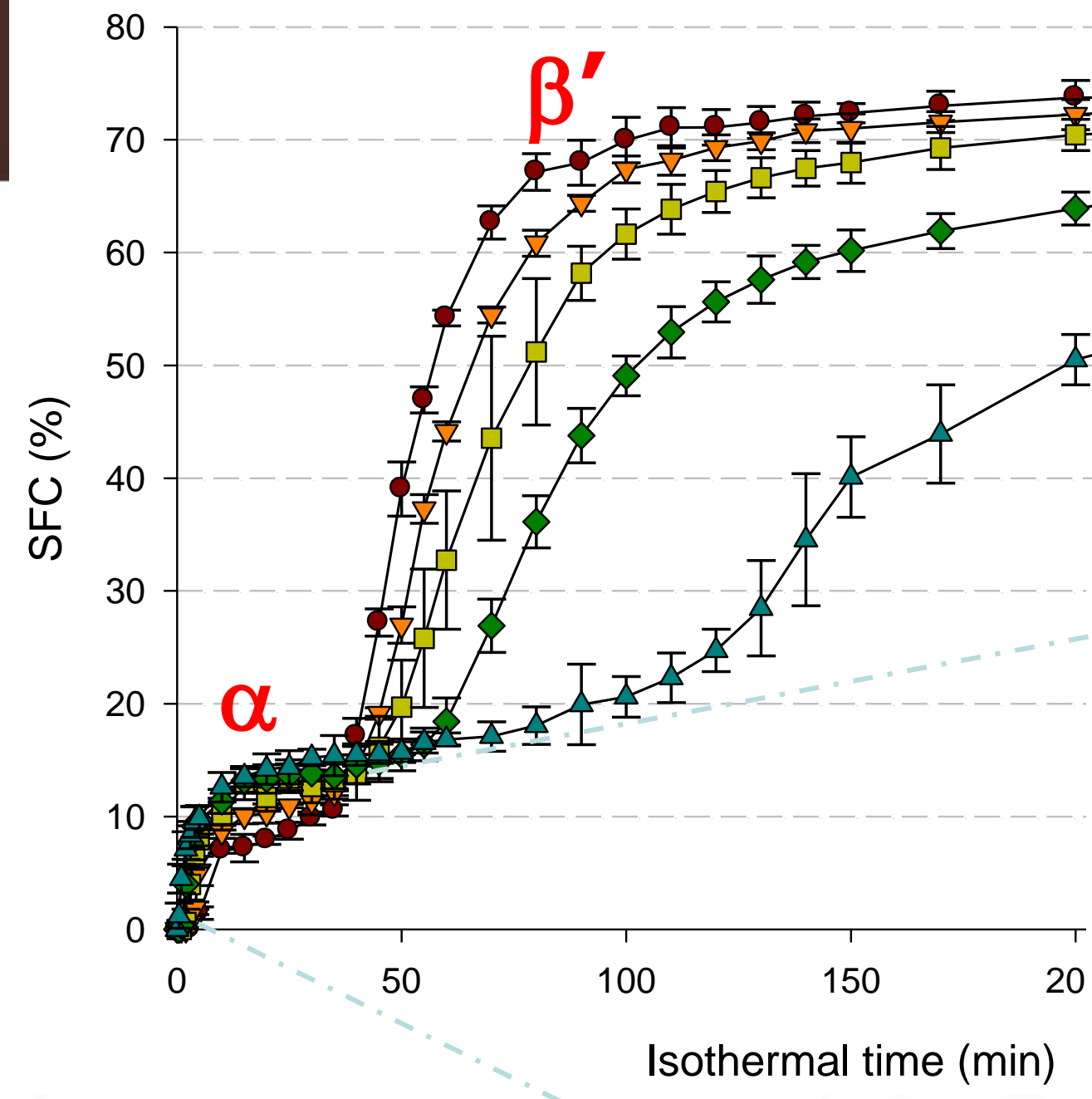
# Cocoa butter /diacylglycerol: 100/0; 90/10 ... 10/90; 0/100







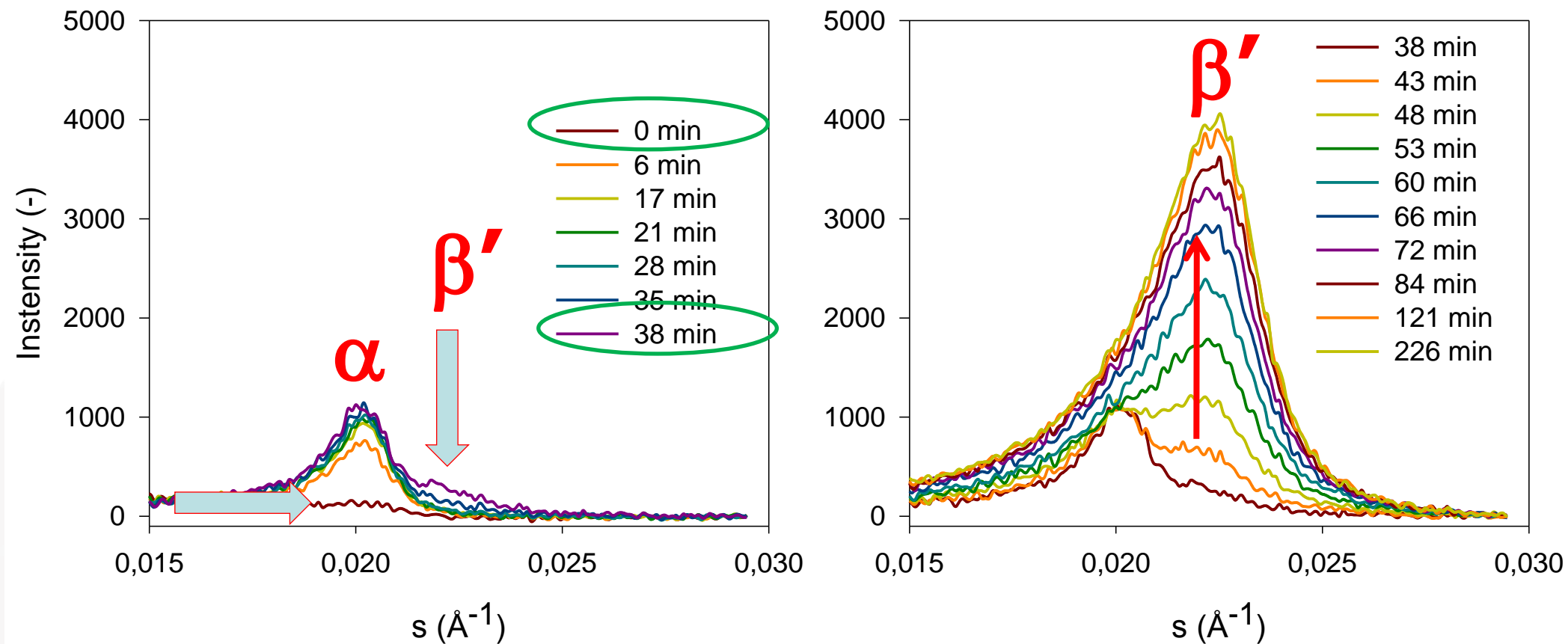
- Isothermal crystallization behaviour
  - Heating to melt all the crystals
  - Cooling at 10°C/min
  - Isothermal at 20°C for a defined time
- Different experimental techniques
- At 20°C: two step crystallization process:  $\alpha$  to  $\beta'$



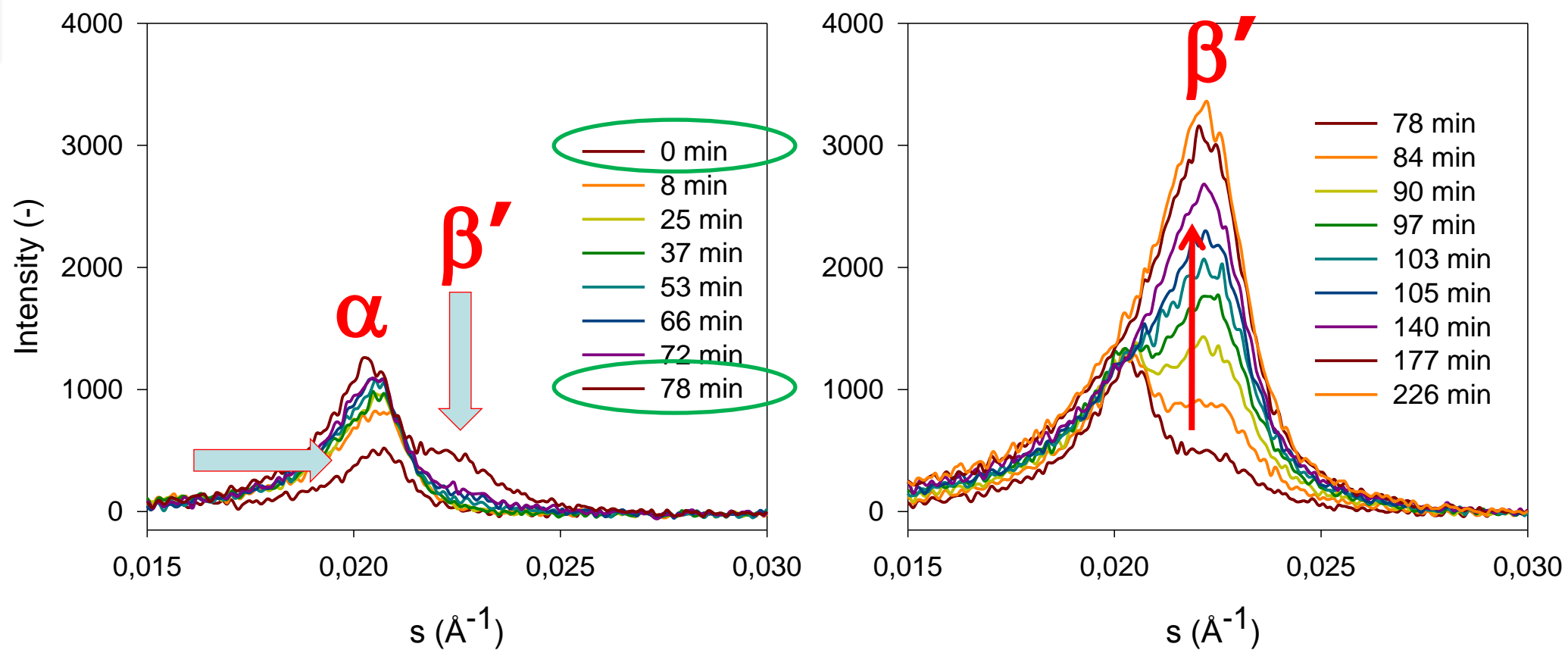


# SAXS diffraction patterns

## Cocoa butter



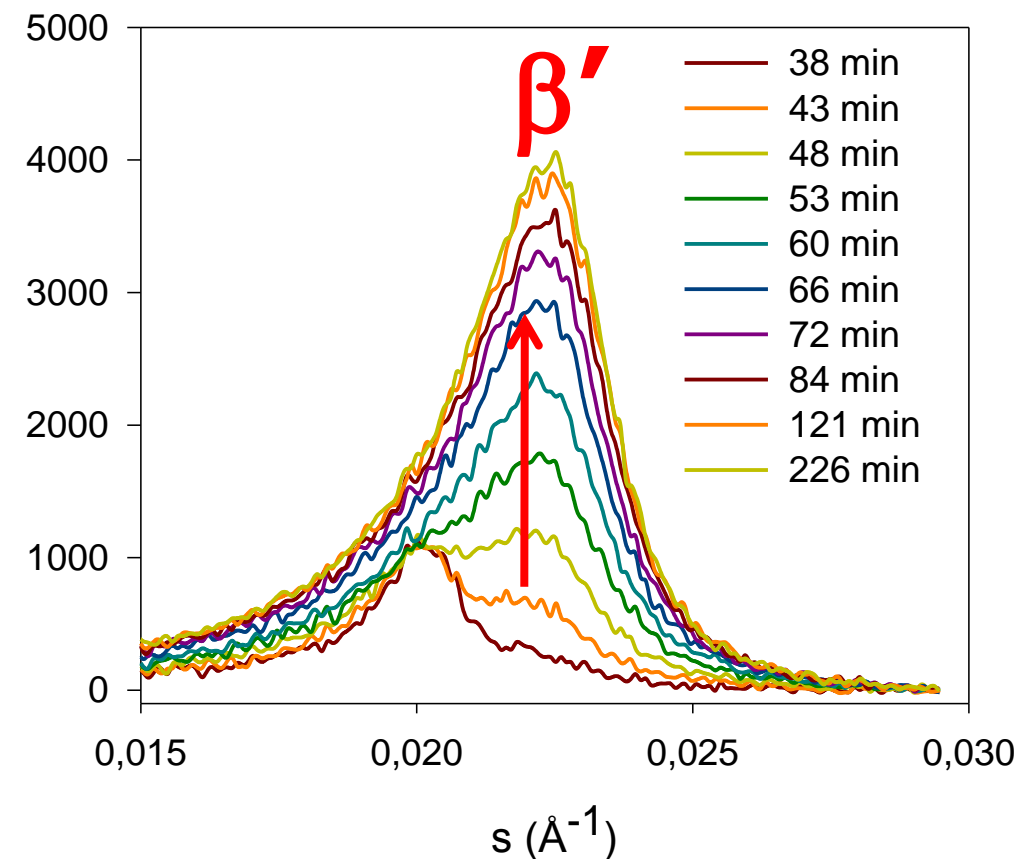
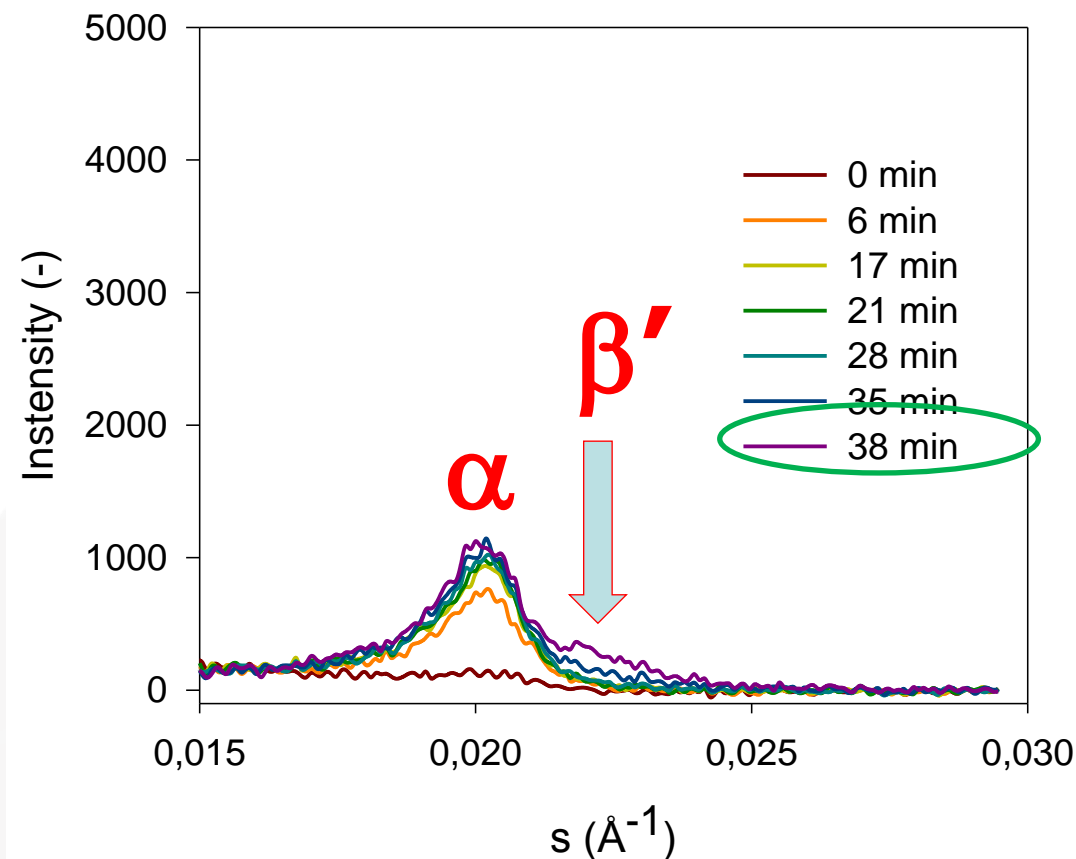
## 2.5% DAG



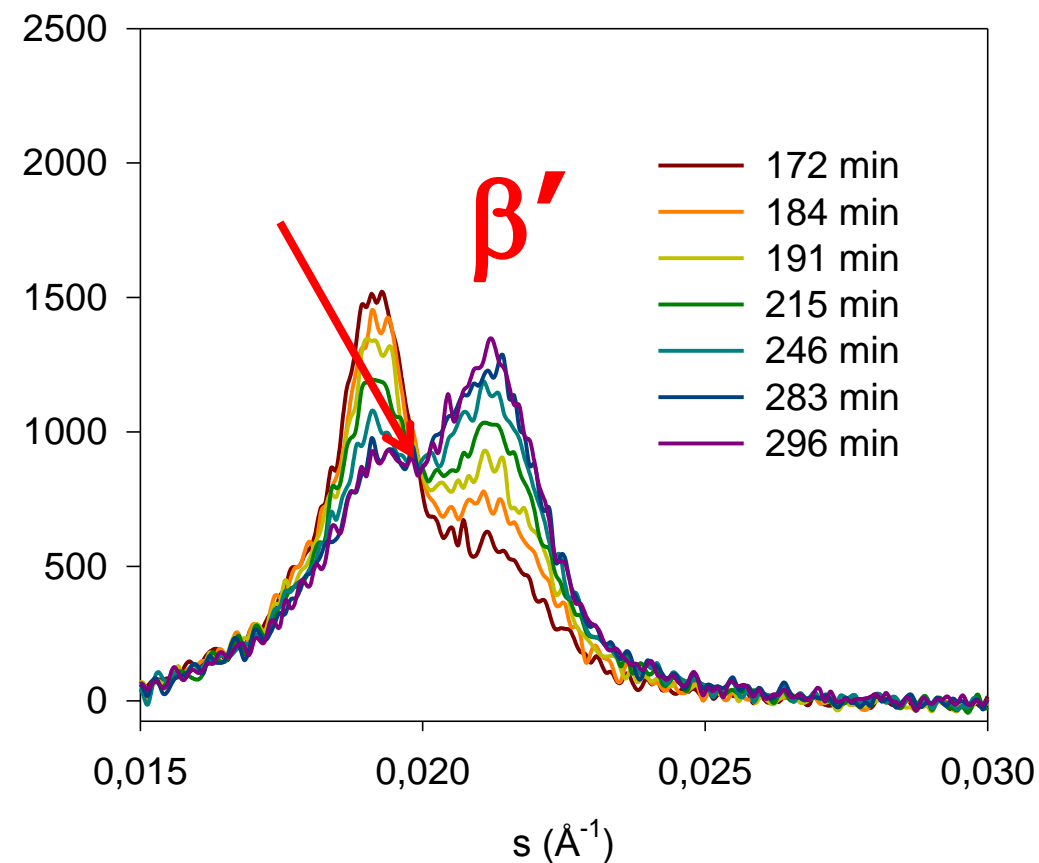
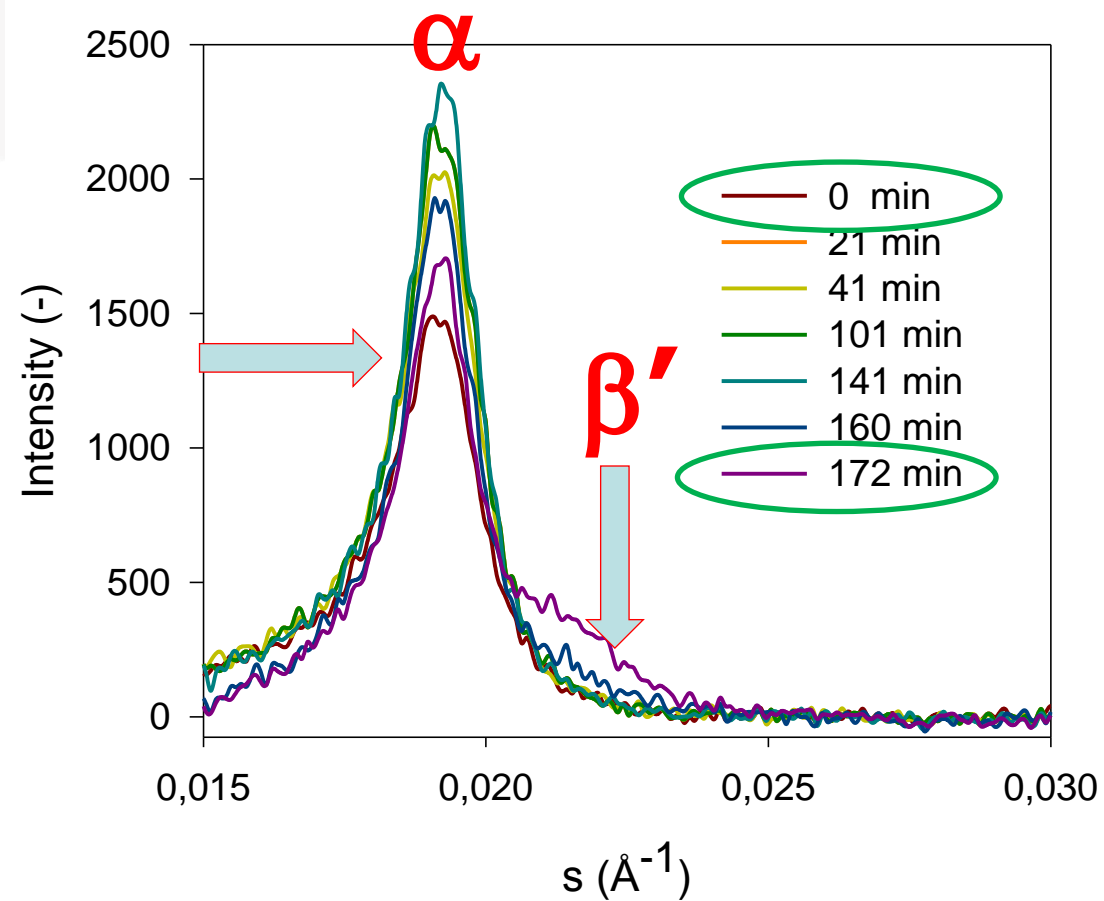
processing

# SAXS diffraction patterns

## Cocoa butter

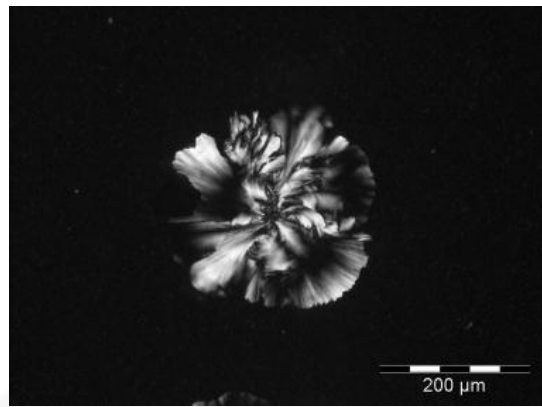


## 10% DAG

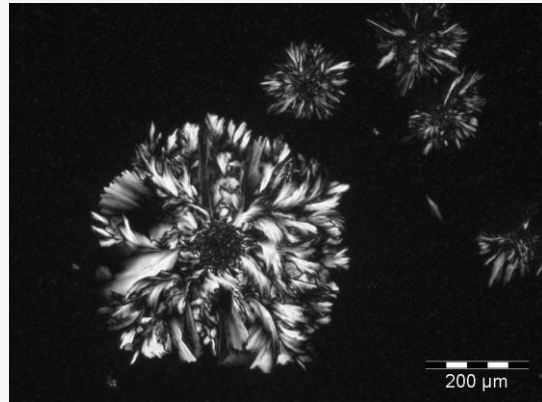


# WEEK 1

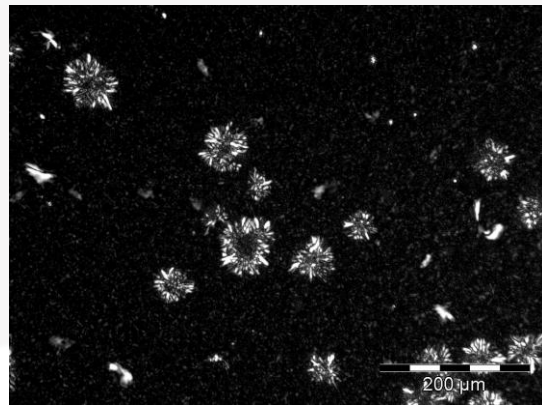
Cocoa butter



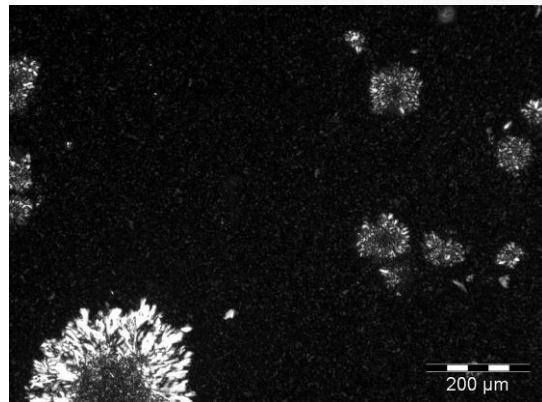
1.25% DAG



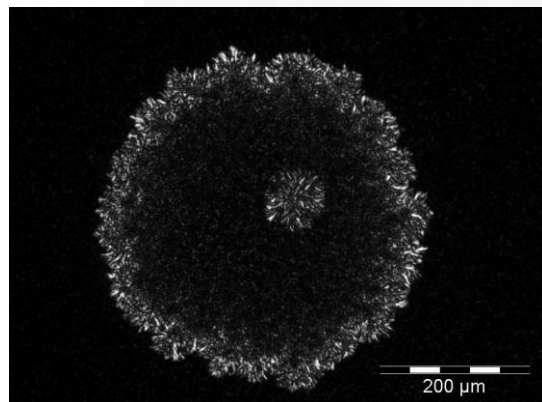
2.5% DAG



5% DAG



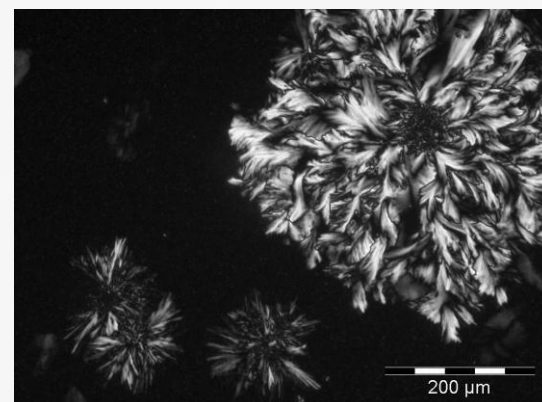
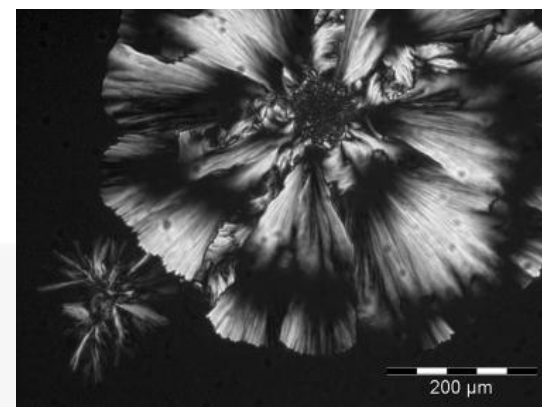
10% DAG



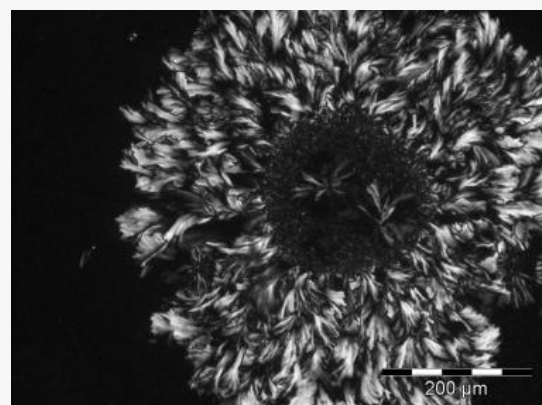
# WEEK 3

Cocoa butter

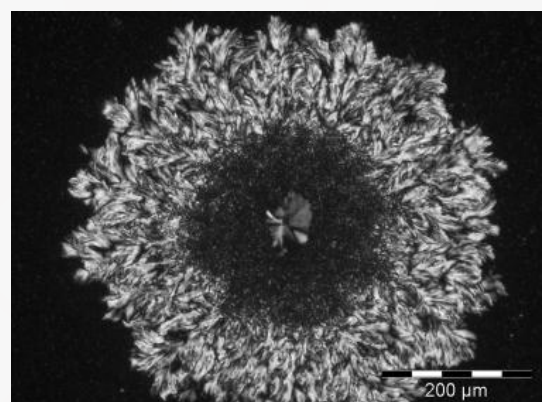
1.25% DAG



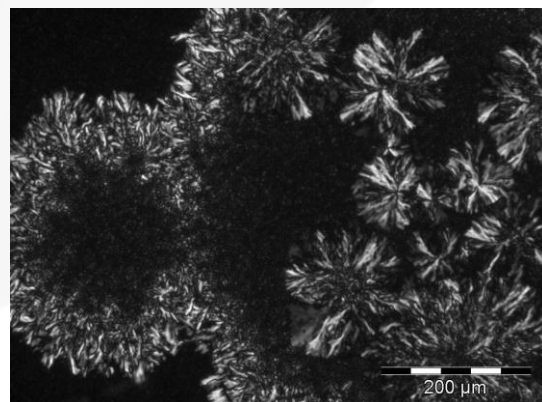
2.5% DAG



5% DAG



10% DAG







## Conclusion

- Crystallization mechanism is changed !
- Microstructure  $\neq$   $\rightarrow$  Macrostructure  $\neq$

# Crystallization of fat and oils

Dr. ir. Nathalie De Clercq  
9<sup>th</sup> of September