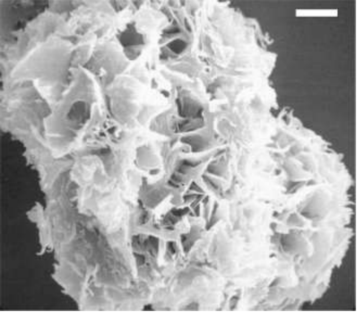

Influence of Minor Components on Fat Crystallisation

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Importance of Crystallisation

- Fats used in food and personal care products
- Physical state often critical for product quality and functionality
- Not simply due to SFC and polymorphism
- Crystal number, size, morphology and interaction highly significant factors
- Greatly dictated by crystallisation processes
  - During production
  - Post production

Background

- Two good reviews on crystallization
  - Himawan C, Starov VM, Stapley AGF, *Thermodynamic and kinetic aspects of fat crystallization*. Adv Colloid Interface Sci (2006) 122:3-33
  - Sato K, *Crystallization behavior of fats and lipids: a review*. Chem Eng Sci (2001) 56:2255-2265

- Minor components, indigenous or added, can play a big role in:
  - Crystallisation
  - Surface gloss
  - Temperature stability
  - Rheology
  - Polymorphic stability
  - etc.

What is a Minor Component

- No firm definition!
- In practice, depends on amount of the ‘major’ components
  - 10% might be considered minor
  - Usually less than about 2-3%
    - Often <1%
    - Or even <0.1%

Indigenous Minor Components

- FFA, MAG and phospholipids (lecithin)
  - Mainly reduced/removed during refining
- DAG
  - Usually survive refining, thus desire low level in the raw oil
- Waxes
  - Often removed by winterisation
- Specific TAG in a given fat

Added Minor Components

- Any indigenous components
  - May be removed and added back (to other oils)
  - May be synthesised
    - MAG (e.g. glycerol monostearate)
    - TAG (e.g. 1,3,-dibehenoyl-2-oleoyl glycerol, BOB)

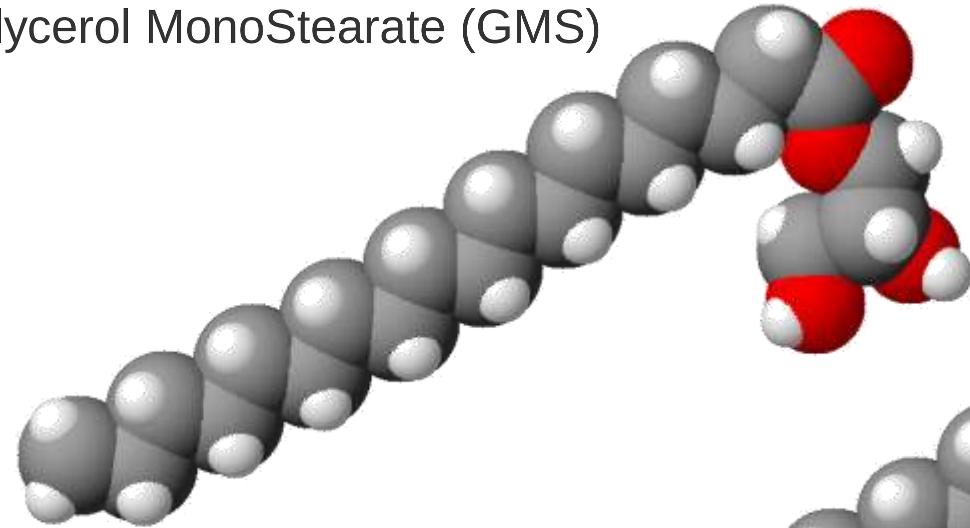
- Frequently derivatives of fatty acids
  - Citric acid
  - Propylene glycol
  - Sugars
    - E.g. Sorbitan, Sucrose
  - etc.

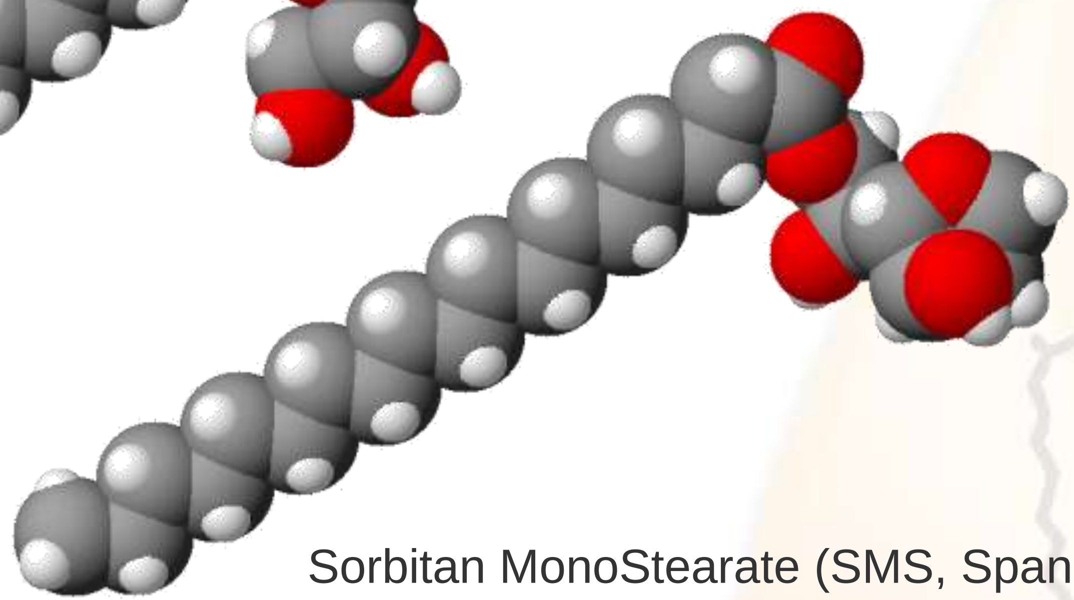
Examples of Common Additives

Abbreviation / trade name	Description
3G1S®	Triglycerol monostearate
Acidan®, CAE	Citric acid ester
DATA esters, DATE(M)	Diacetyl tartaric acid esters (of monoglycerides)
GLP	Lactic acid esters / Glycerol lacto palmitate
GMO	Glycerol monooleate
GMS	Glycerol monostearate
P-170, S-170	Sucrose esters
PGE	Polyglycerol esters
PGMS	Propylene glycol monostearate
SAE	Succinic acid esters
Span 20, 40, 60 / SMS	Sorbitan monolaurate, monopalmitate, monostearate
Span 65 / STS / Crill 36 / Durtan	Sorbitan tristearate
Span 80, 85	Sorbitan monooleate, trioleate
Tween 20, 40, etc.	Ethoxylated sorbitan esters

Differing sizes & Polarities

Glycerol MonoStearate (GMS)





Sorbitan MonoStearate (SMS, Span 60)

Overview of Studies

	Cocoa butter	Milk fat	Lauric fats	Palm oil	Sunflower oil	Fatty acids	Pure TAG	Other
FFA	✓		✓	✓			✓	
MAG	✓	✓	✓	✓	✓		✓	✓
DAG	✓	✓	✓	✓			✓	✓
TAG	✓	✓		✓			✓	✓
Phospholipids	✓	✓	✓	✓	✓		✓	✓
STS & other Span	✓		✓	✓			✓	✓
SMS/Span 60	✓			✓		✓	✓	✓
Tween	✓	✓				✓	✓	✓
Sucrose Esters		✓	✓	✓			✓	✓
Other	✓	✓	✓	✓	✓	✓	✓	✓

Difficulties in this Area

- Additives often referred to by trade names
  - Some variation over batches and time
- Generally, not pure
  - Other components present, dependent on production route
    - E.g. Sorbitan tristearate contains, perhaps,1-3% of the named compound (FFA, mono-, di-, tri-, tetra- palmitoyl & stearoyl esters of sorbitan and sorbitol are present)
  - Composition varies by producer
  - Different components may have different influences
- Comprehensive composition rarely supplied
- Difficult to compare effects across different studies

Further Words of Caution

- Effect of a minor component may be influenced by other components present
  - E.g. Solid particles, other additives
- Same minor component may have different effects at different concentrations
- Different effects may be seen in the presence and absence of agitation

Different Effect with Level and Agitation

	Induction Time (min)	Maximum Crystn. Rate (% solid/min)
Coconut oil	8.0	3.4
+5% OO(OH)	8.0	4.6
+10% OO(OH)	8.0	2.5

Gordon & Rahman, JAOCS (1991), 68: 577-579

	Mode	Polymorph
fhCS	Static	β
fhCS	Stirred	β (less structured)
fhCS+PGPR	Static	β
fhCS+PGPR	Stirred	α, β' & β

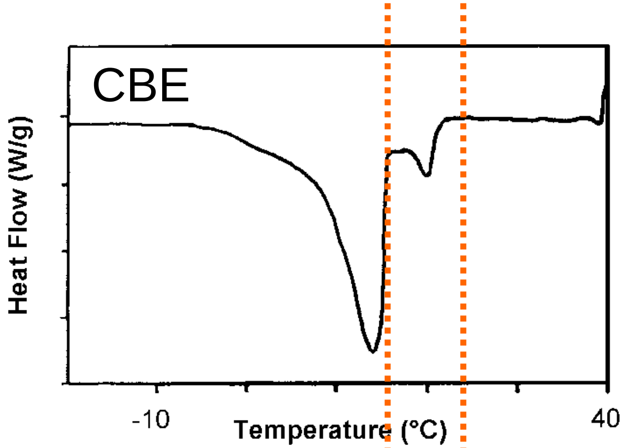
Rousseau *et al.* JAOCS (2005) 82: 7-12

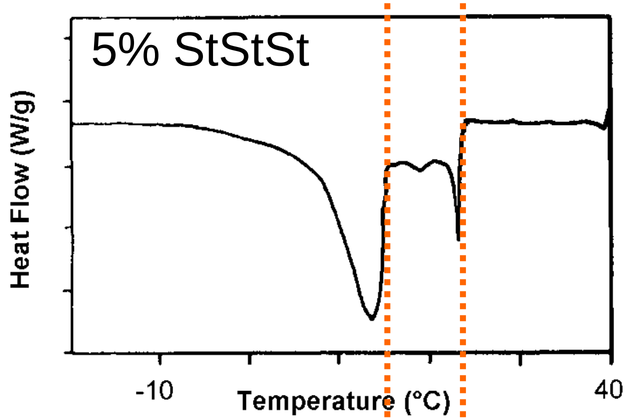
Effect on Nucleation

- Inhibition
  - Removal of phospholipids from coconut oil reduces induction time (46 min down to 7.5 min @ 15°C) - Gordon & Rahman, JACOS (1991) 68:577-579
  - Addition of milkfat DAG to milkfat delays onset of crystallisation – Wright et al., JAOCS (2000) 77:463-475
  - Lauric acid delays crystallisation of coconut oil (more than does palmitic acid) - Gordon & Rahman, JACOS (1991) 68:577-579
  - PGE increases the nucleation rate of high melting fraction of milkfat – Cerdeira *et al.*, (2005) 107:877-885

- Promotion
  - E.g. Saturated MAG promote nucleation in palm oil (attributed to initial crystallisation of MAG) – Fredrick *et al.*, Cryst Growth Des (2008) 8:1833-1839
  - Trisaturated TAG promote crystallisation onset in CBE – Cebula & Smith, JAOCS (1992) 69:992-998

Effect on Nucleation





- Tristearin added to CBE induces earlier crystallisation
  - Only of initial small peak
    - Which is principally trisaturated TAG
  - Little effect on main crystallisation

Caution: Nucleation Studies

- Analysis of early ‘seed’ crystals to determine components that influence nucleation can lead to wrong conclusions
  - Initial crystals of cocoa butter are rich in trisaturated TAG
  - Addition of trisaturated TAG to cocoa butter does not accelerate main crystallisation

Effect on Crystal Growth

- Growth of trilaurin accelerated by FFA, but slowed by DAG (1,3 more than 1,2) – Smith *et al.*, JAOCS (1994) 71:1367-1372; Smith & Povey, JAOCS (1997) 74:169-171

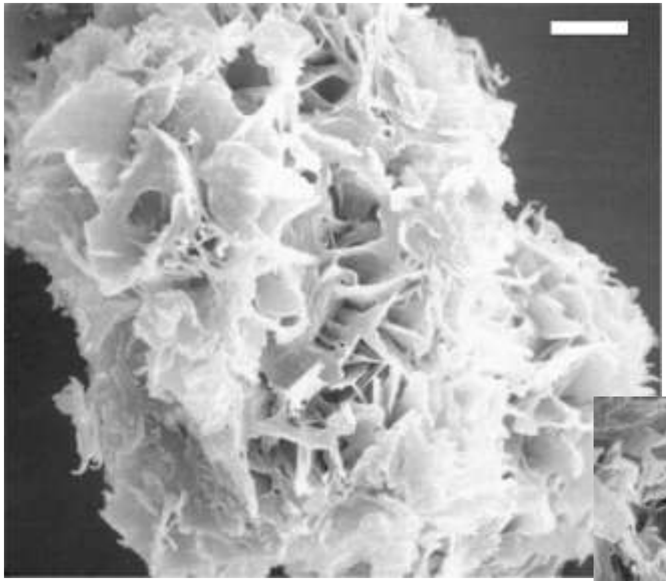
- DAG reduce the crystallisation rate of cocoa butter – Loisel *et al.*, J Food Sci (1998) 63:73-79

- Phospholipids alter crystal morphology of trilaurin – Smith, EJLST (2000) 102:122-127
  - Phosphatidyl ethanolamine reduces the growth rate of the fastest growing faces
  - Yields larger, denser palm oil spherulites

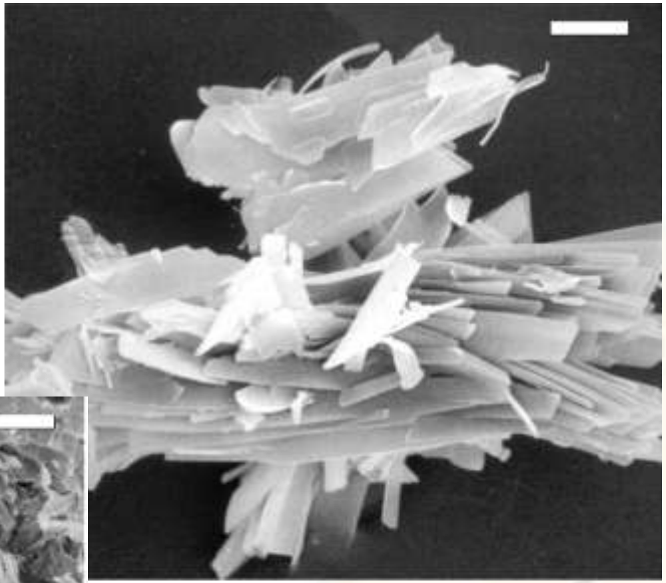
- Often an optimum level
  - Milkfat with more, <u>or less</u>, minor components crystallises more slowly and leads to faster bloom when blended with cocoa butter – Tietz & Hartel, JACOS (2000) 77:763-771

Effect on Crystal Morphology

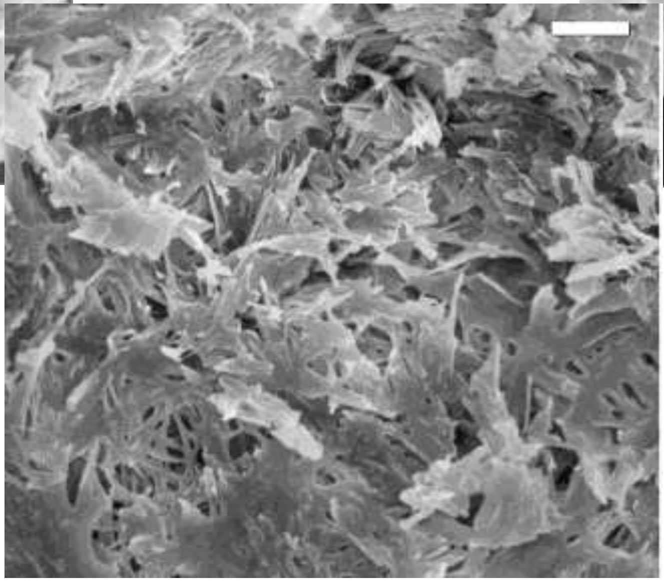
white bar = 20μm



POP



PPP



POP + 2% PPP

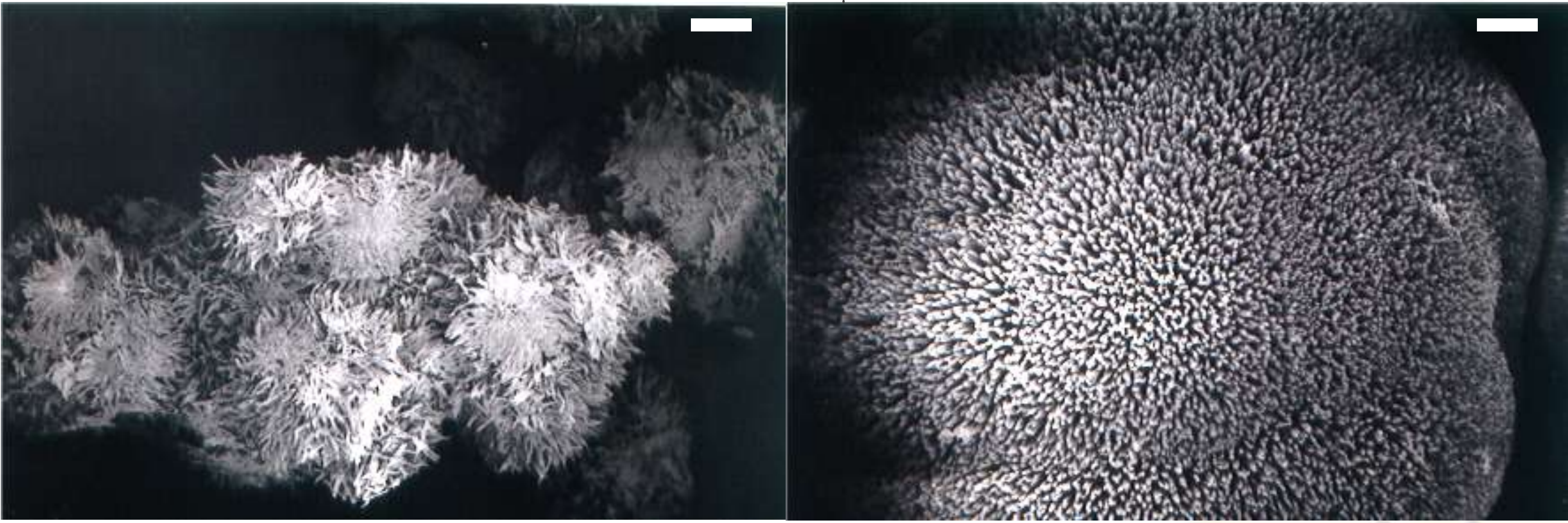
Crystallised from acetone

Smith *et al.*, EJLST (2005) 107:583-593

Additive Effect on Morphology

Palm Oil + 0.2% Phosphatidyl Ethanolamine

white bar = 20µm



Without

With

Smith, EJLST (2000) 102:122-127

Effect on Polymorphism

- Span 65 (STS) reduces melting point and broadens melting range of cocoa butter β_V – Aronhime *et al.*, Food Struct (1990) 9:337-352
  - Slows β_V to β_{VI} transition
  - Promotes β'_{III} and β'_{IV} to β_V transition

- Blend of Span 60 (SMS) and Tween 60 improves bloom resistance of chocolate – Garti *et al.*, JAOCS (1986) 63:230-236

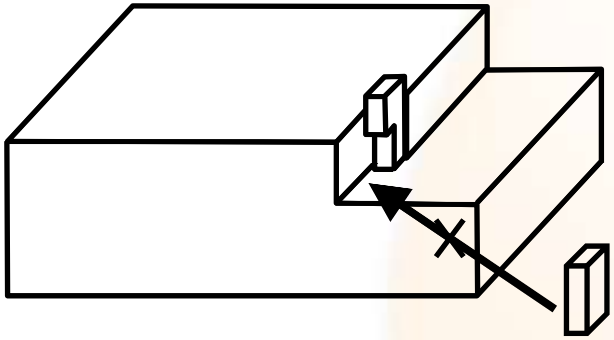
Mechanisms: Nucleation

- Inhibition
  - Coating, or shielding, of heterogeneous nuclei
  - Poisoning of growth sites on nuclei
- Promotion
  - Crystallise first and provide suitable ‘heterogeneous’ nuclei
  - By incorporation, cause weak points in crystal structure – breakage yielding secondary nuclei
- Caution: many techniques to measure nucleation do so indirectly
  - After some degree of crystallisation yields detectable particles

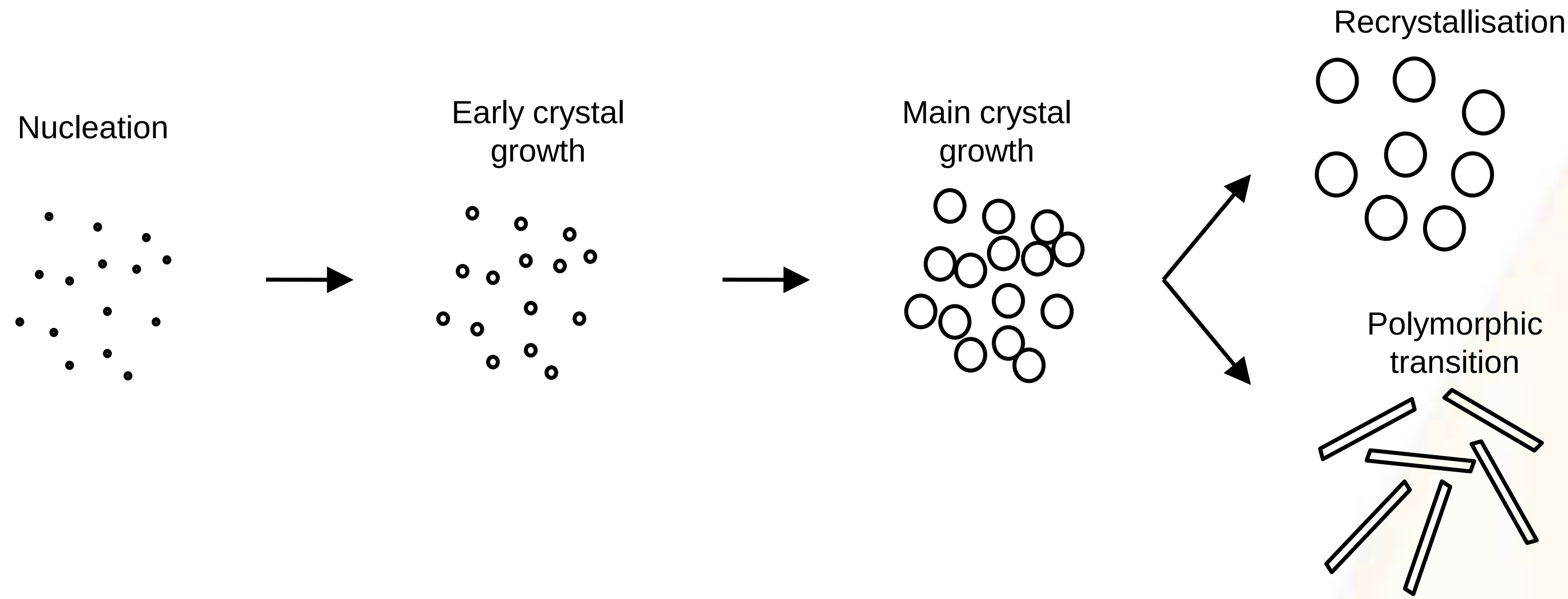
Mechanisms: Crystal Growth

- TAG crystallisation from solution or melt appears to occur by a screw dislocation mechanism on the larger faces – Hollander, 2001, PhD Thesis, University of Nijmegen
  - Acceleration by forming additional growth sites

- SMS (Span 60), for example, shows the same mechanism but slows the rate – Beckmann & Boistelle, J Cryst Growth (1985) 72:621-630
  - Adsorption at kink (growth) sites
  - Poisoning of crystal



Overview of Additive Effects



Nucleation
- coat heterogeneous nuclei, preventing their use as such
- form nuclei by crystallizing first

Early crystal growth
- crystallize first to form seeds
- slow crystal growth

Main crystal growth
- accelerate growth by forming additional growth sites
- slow crystal growth

Recrystallisation / Polymorphic transition
- stabilize unstable polymorph
- destabilize stable polymorph
- increase energy barrier for transformation
- slow recrystallization

- by blocking growth sites
- may also alter crystal morphology by blocking specific faces

General Rules for Additives

- Maximum influence when acyl groups are similar to crystallising TAGs
- To influence crystallisation, they must be similar enough to join at growth site
  - Amount depends on inclusion or blocking
    - Small amounts needed if additive blocks growth site, more needed if included into crystal structure
  - Blocking of specific faces leads to change in morphology
- To influence polymorphic transition
  - Needs to be part of crystal (or modify habit) to affect solid-solid transitions
  - Needs to be in the liquid phase with similar melting point to solid fat to affect melt mediated transition
- Greatest influence often seen at lower undercooling
  - Hence, can have small effect on initial crystallisation while still affecting recrystallisation or post-crystallisation

Summary

- Much has been published on minor components and additives
  - Majority is empirical and descriptive
  - Few propose underlying mechanisms
- Influence strongly dependent on similarity between additive and bulk fats
  - Especially acyl chain (length, unsaturation)
- Degree of undercooling influences impact of additive
- Effective concentration of additive depends on mode of action
  - Poisoning, blocking crystal growth, changing morphology: <0.1%
  - Providing heterogeneous nuclei, inclusion in crystal: >>0.1%
- General guidelines provide starting point for additive rational design.

For more information: **Smith KW, Bhaggan K, Talbot G, Van Malssen KF, *Crystallization of fats: Influence of minor components and additives*, JAOCS (2011) 88:1085-1101**

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Thank You!

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