Fat crystallization seen through the eyes of a polymer scientist

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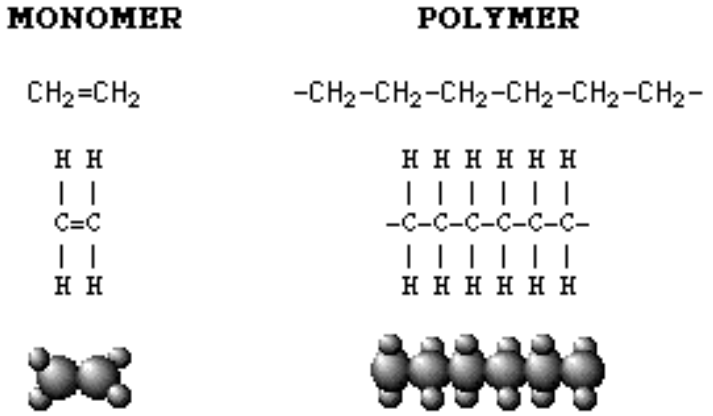
Content

1. Morphology of polymers and fats
2. A view on layered crystals an polymorphism

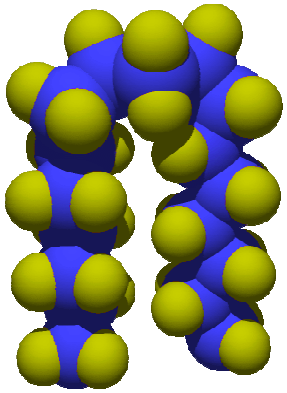
1. Morphology of polymers and fats

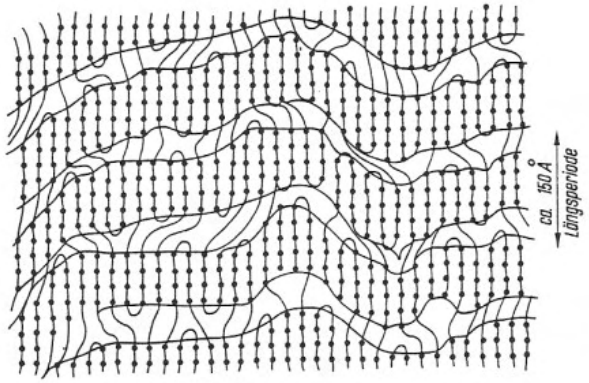


1. Morphology of polymers and fats

Spherulites

Chain folding

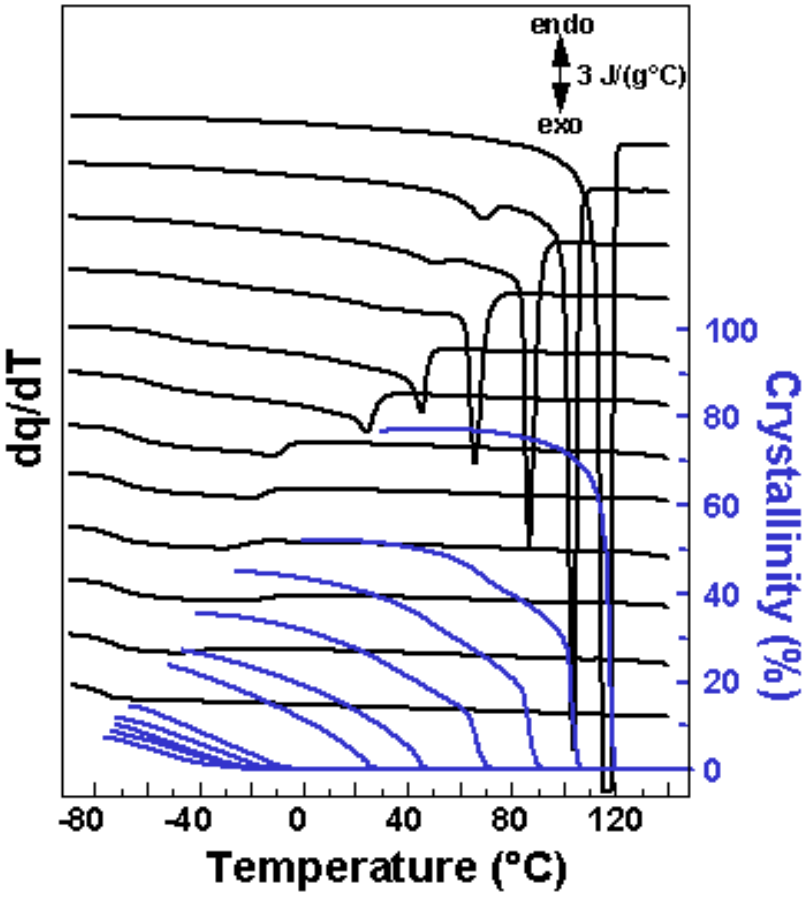




Lamellae

1. Morphology of polymers and fats

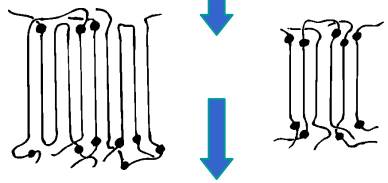
LPE up to 44 mol% 1-octene



COOLING at -10°C/min

Increasing Comonomer Content

Shorter < Ethylene Sequence Length >



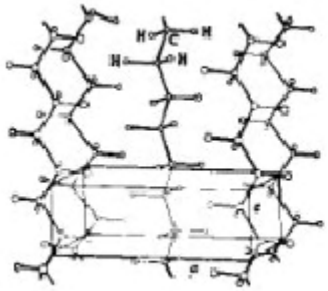
Comonomer Exclusion
Crystal Size Reduction

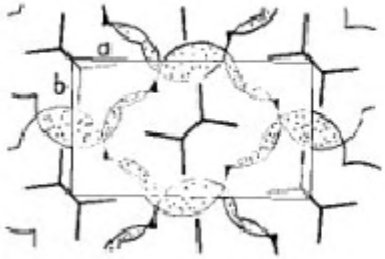
Lowering of Crystallinity and Melting Point and Modulus

1. Morphology of polymers and fats

orthorhombic PE

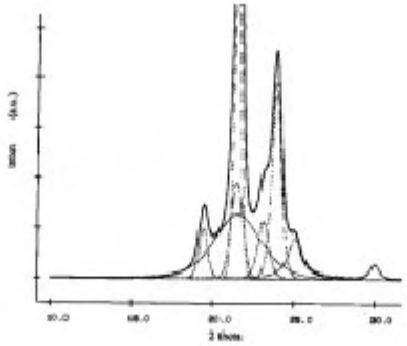
standard
most stable

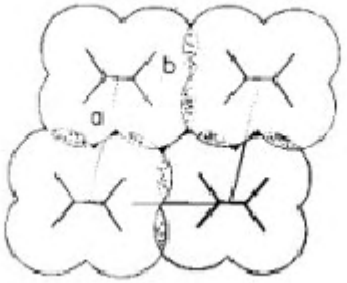




triclinic PE

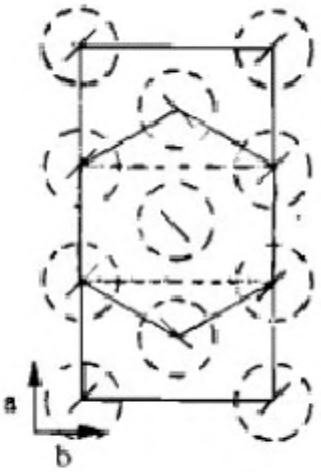
after deformation
exceptional



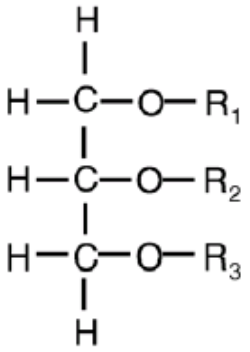


hexagonal PE

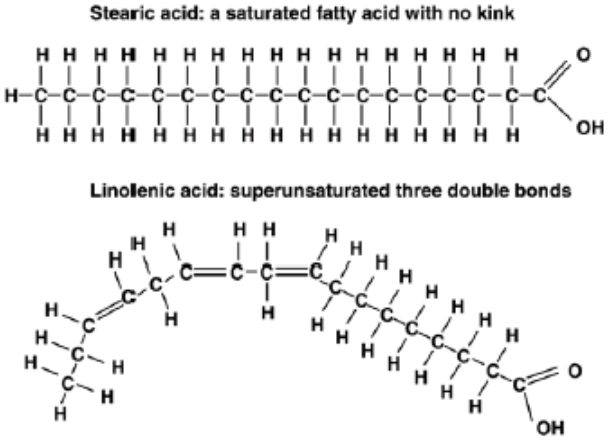
high pressure/temperature



1. Morphology of polymers and fats



(a)



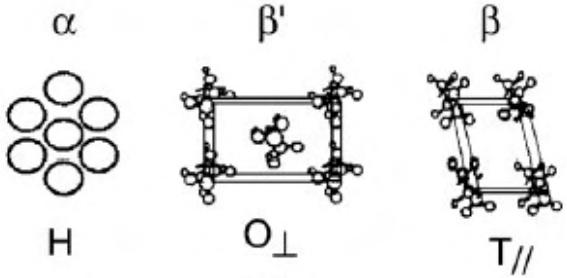
(b)

molecular

~ ethylene sequence length

stacking

(a)

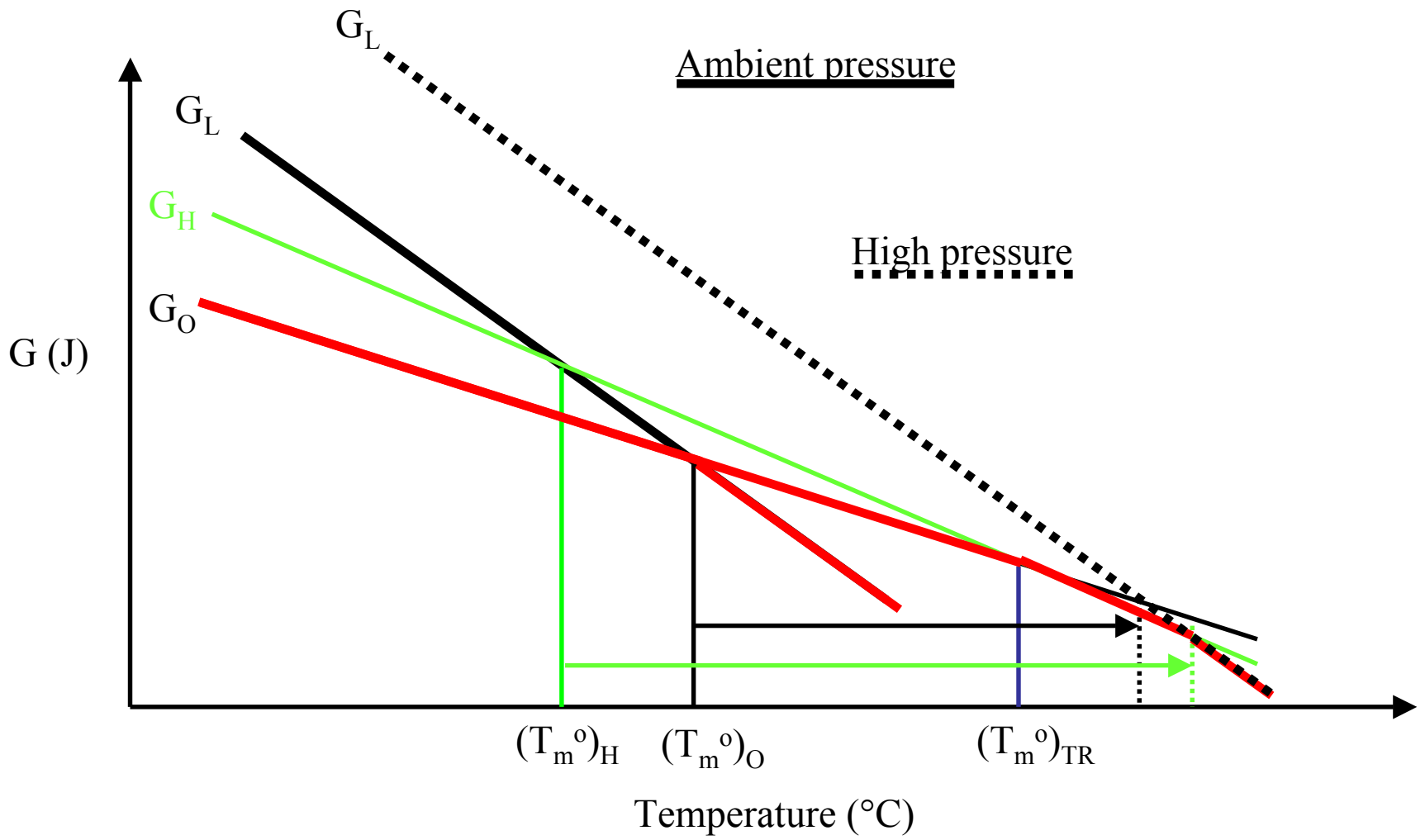


(b)

~ lamellar crystals
~ orthorhomic and hexagonal

2. A view on layered crystals and polymorphism

Thermodynamics



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Thermodynamics

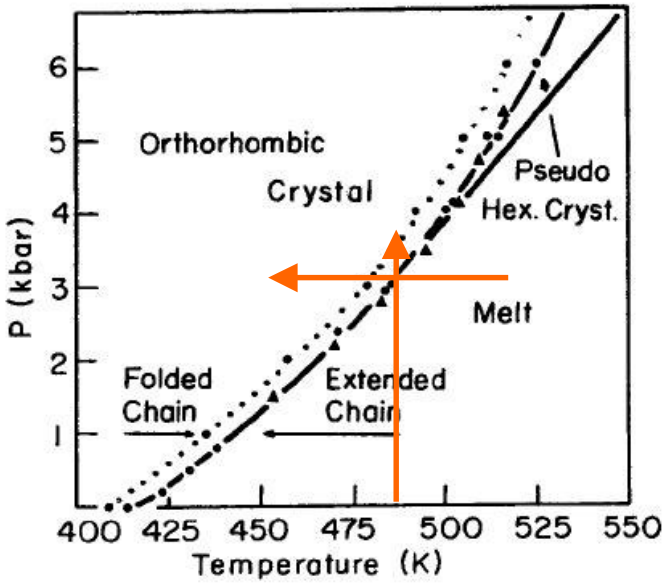


Fig. VIII.25 *Phase Diagram of Polyethylene.*
Data points of extended chain crystal melting temperatures by Davidson and Wunderlich (1969) and Yasuniwa *et al.* (1973) (filled circles); and Bassett and Turner (1974) (filled triangles). All measurements at 0.5–6 K/min so that the points lie somewhat above the equilibrium melting temperature due to some superheating. Typical broad molecular weight polyethylene, $\bar{M}_n$ = 10 – 20 000, $\bar{M}_w$ = 100–200 000. The high pressure phase boundary is drawn according to Bassett and Turner (1972, 1974) and Yasuniwa *et al.* (1976). The melting curve for folded chain crystals (dotted curve) is drawn according to Yasuniwa *et al.* (1973).

no hexagonal phase expected at 3.2 kbar

2. A view on layered crystals and polymorphism

Thermodynamics

the hexagonal phase is also observed ***at 3.2 kbar*** *as a transient phase: size matters!*

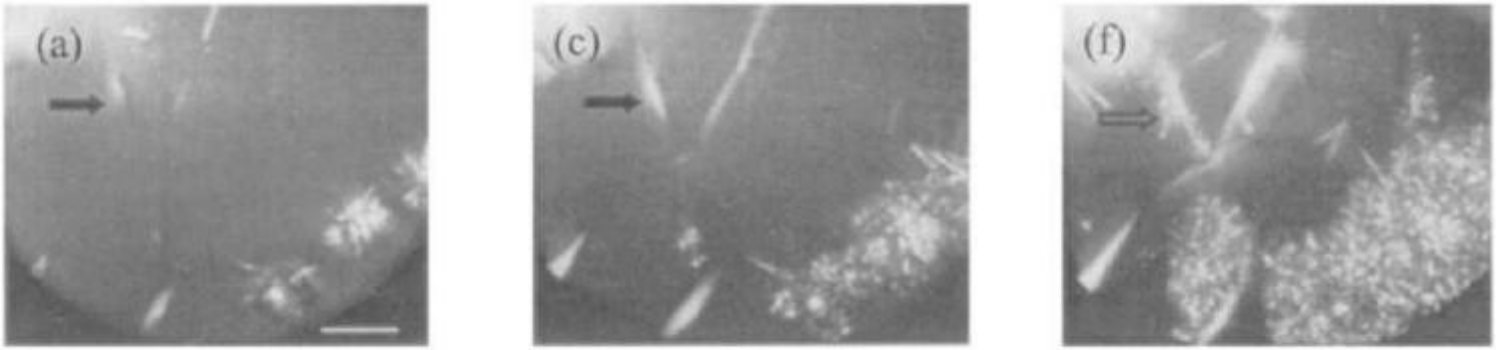
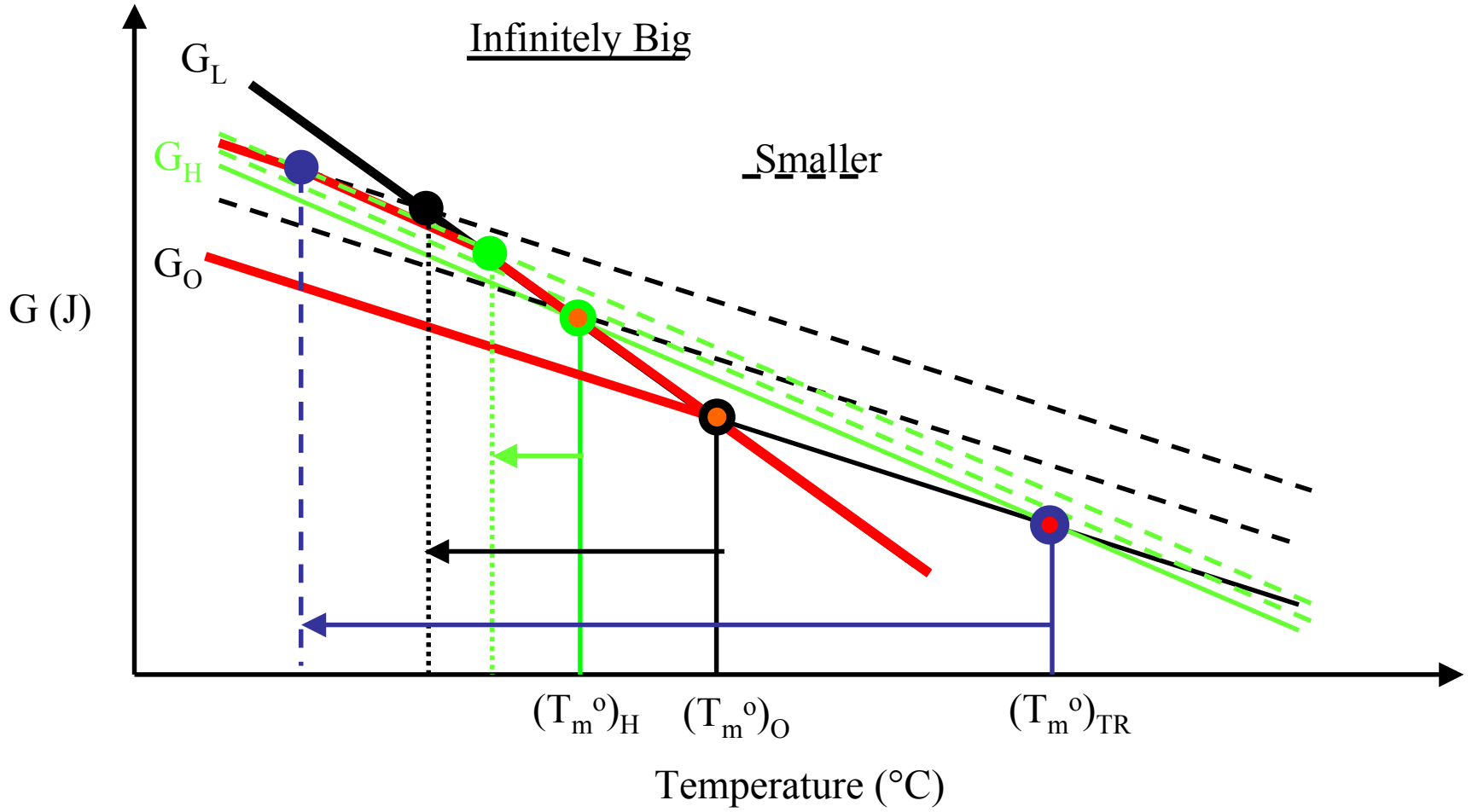


Fig. 51. LPE, M=32.000, isothermal crystallization under an applied pressure of 3.2 kbar observed in a polarizing microscope: Different stages of crystal development. Initiation and growth in the hexagonal phase and transition to the orthorhombic phase which leads to a stop of growth. Transitions are indicated by a change in the appearance of the crystallites (arrowed crystal: transition between (c) and (f)). From Rastogi et al [63].

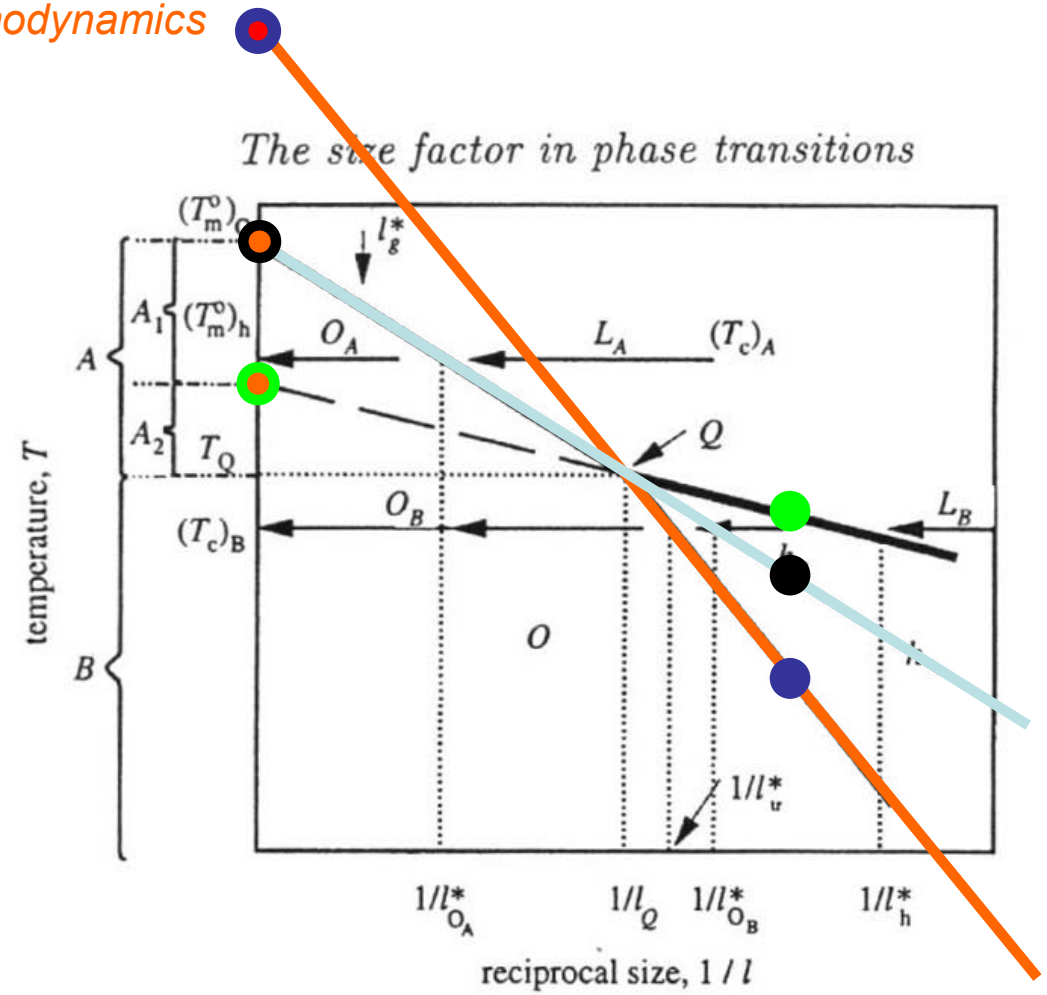
2. A view on layered crystals and polymorphism

Thermodynamics



2. A view on layered crystals and polymorphism

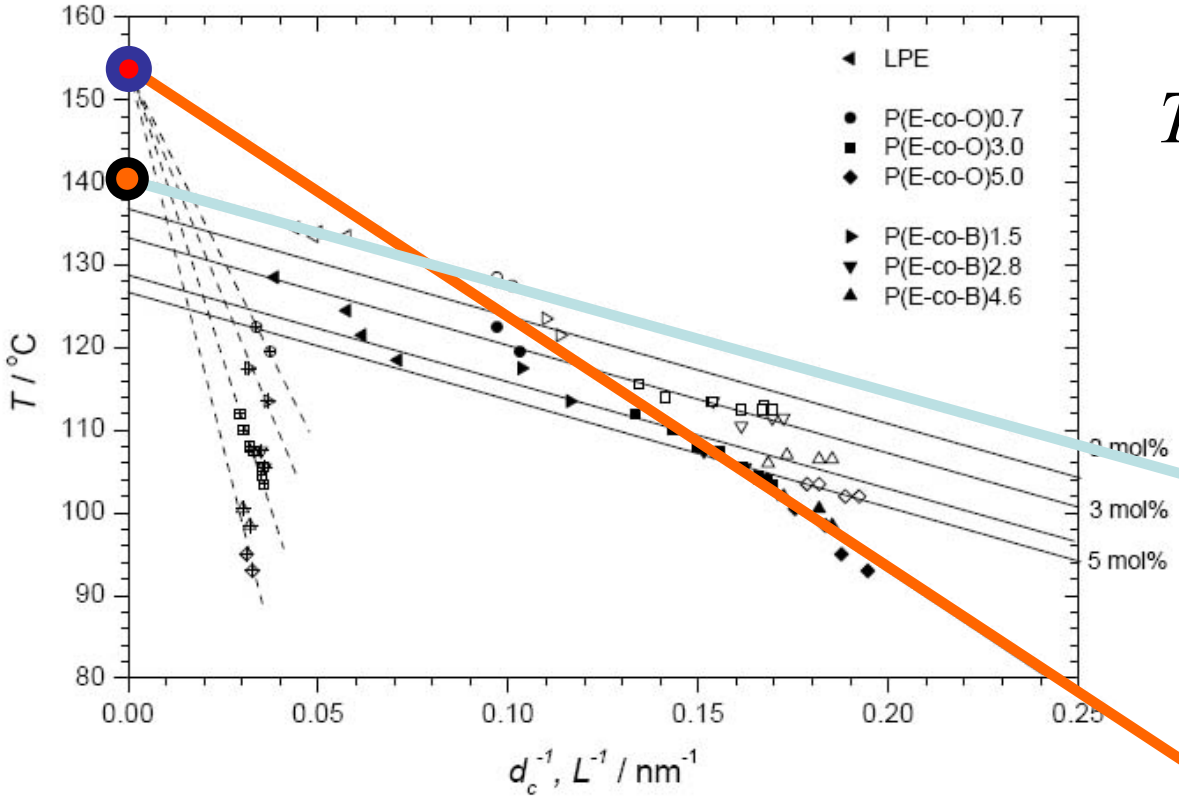
Thermodynamics



A. Keller, M. Hikosaka, S. Rastogi, A. Toda, P.J. Barham, G. Goldbeck-Wood
Phil. Trans. R. Soc. Lond. 348, 3-17 (1994)

2. A view on layered crystals and polymorphism

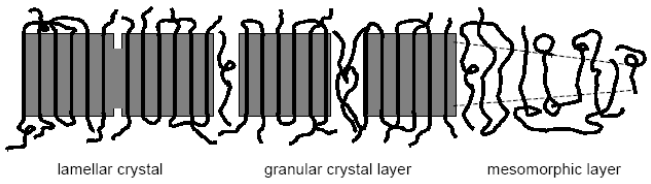
Thermodynamics



$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{d_c \Delta H}\right)$$

Melting Line

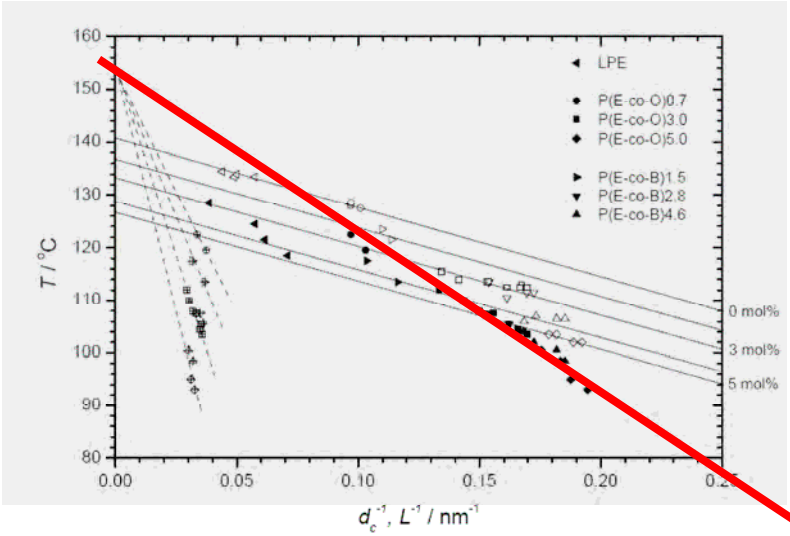
Crystallization Line



G. Strobl

2. A view on layered crystals and polymorphism

Thermodynamics



Problems:

- Melting not via the hexagonal phase
- Crystallization memory effect
- Precisely branched polyethylenes:
  a **mesomorphic phase**

Likely the 'crystallization line' represents the transition from melt to mesomorphic rather than from hexagonal to orthorhombic

End melting HPEO21: 16°C, d_c = 22.7 Å

Melting onset HPEO15: -23 °C, d_c = 17.5 Å

2. A view on layered crystals and polymorphism

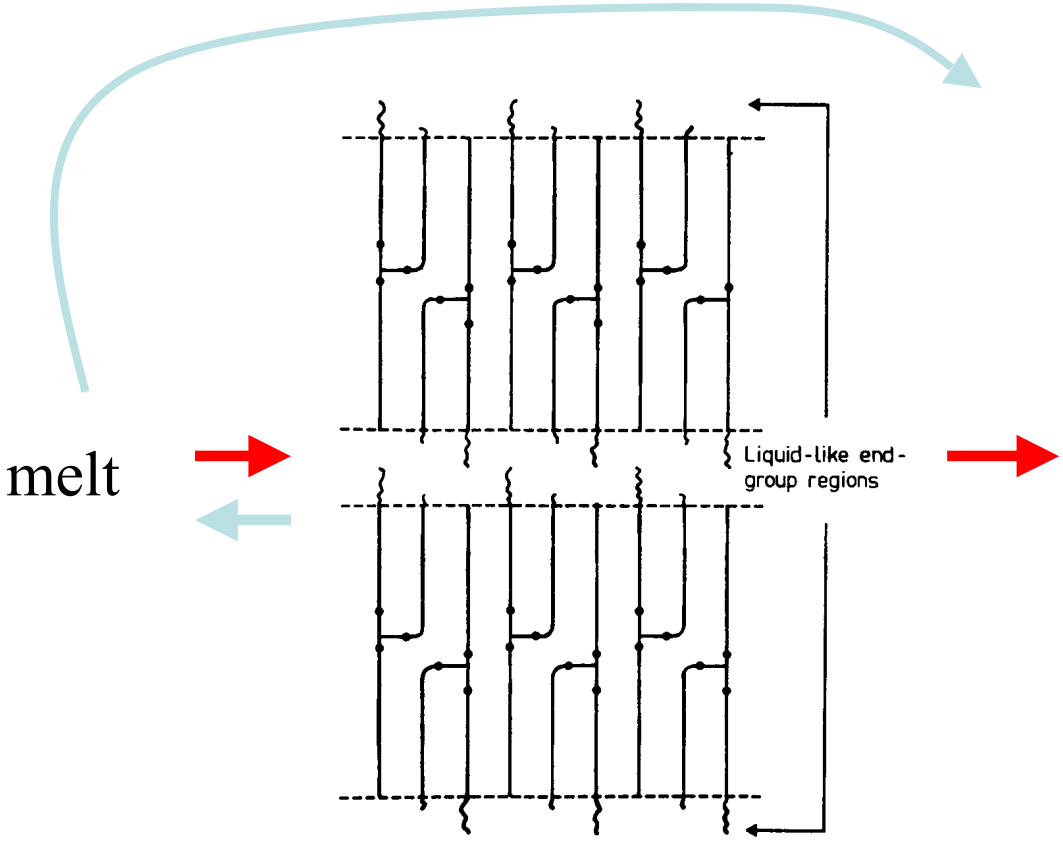


Figure 8.51 Proposed structure in the α-form of triglycerides (Hernqvist and Larsson, 1982).

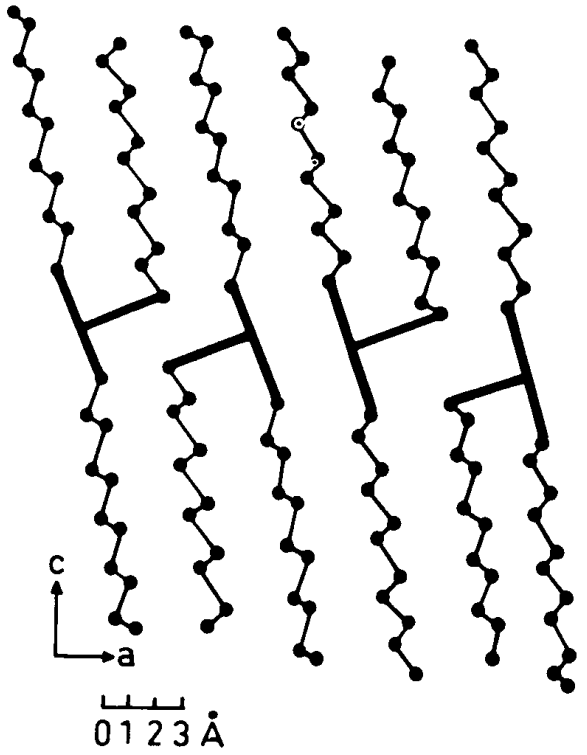
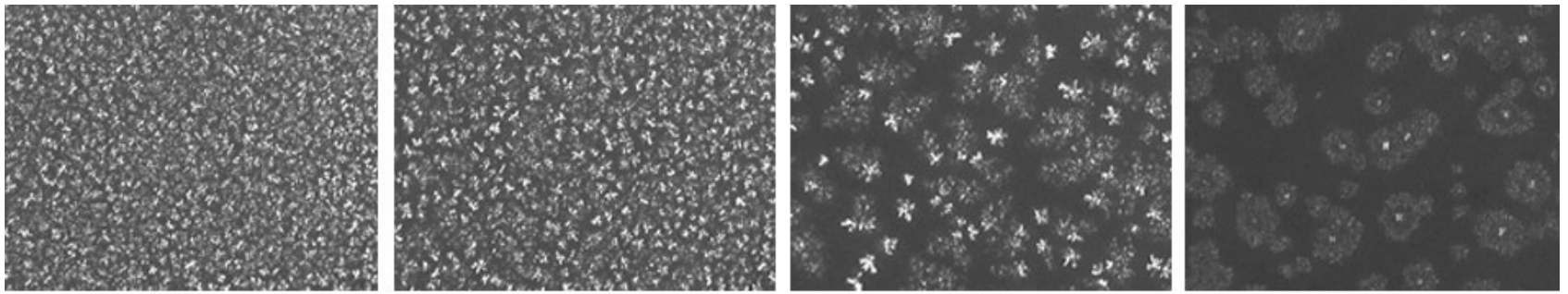


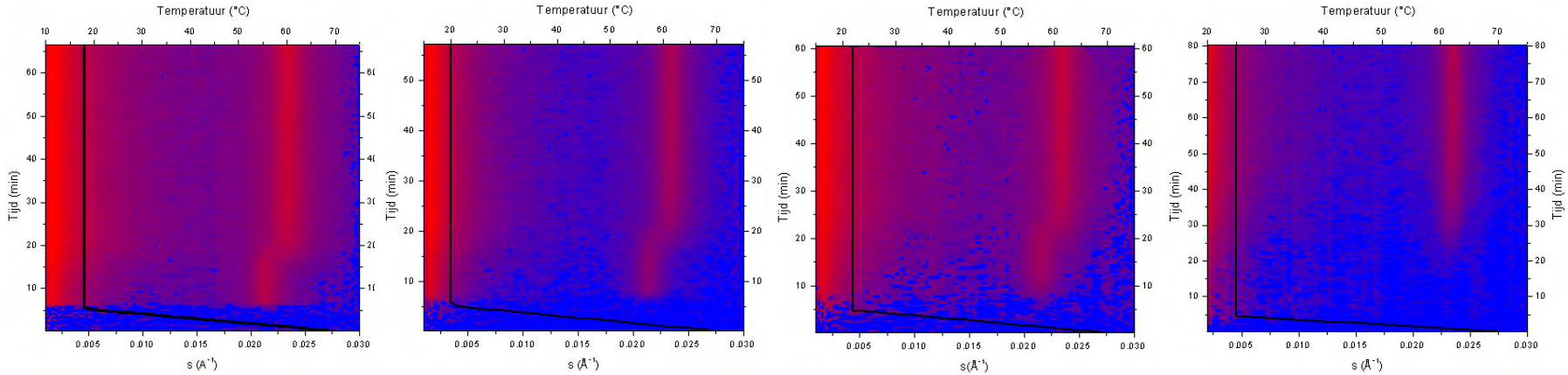
Figure 8.52 Main structural features of the β_1'-form of triundecanoin projected along the shortest unit cell axis (b).

2. A view on layered crystals and polymorphism

TWO STEP ← ONE STEP →

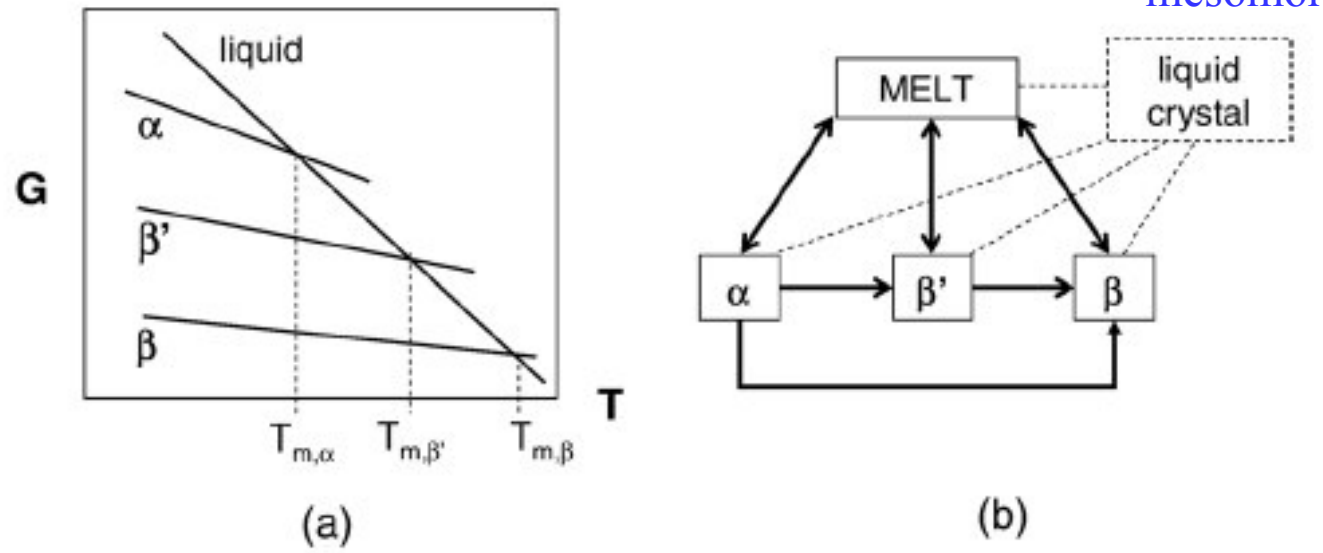


Palm oil crystallization at different crystallization temperatures



2. A view on layered crystals and polymorphism

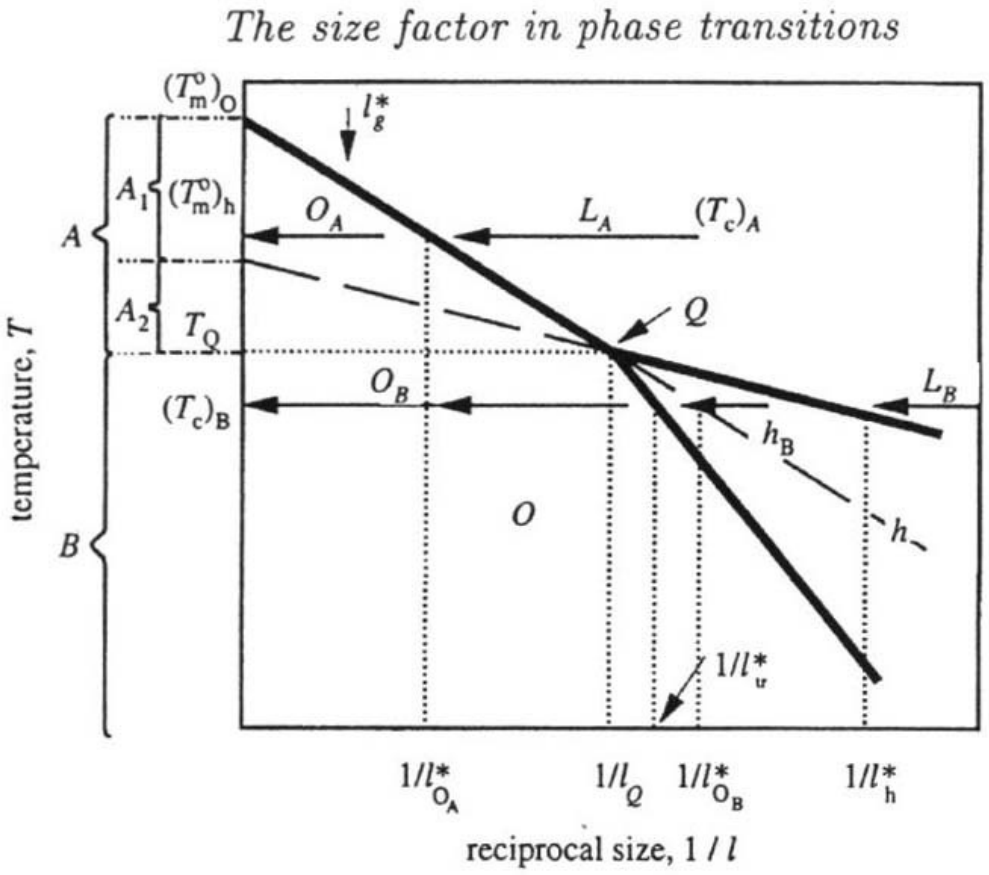
~ mesomorphic phase

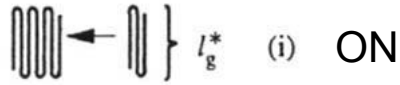


α at low T and β' at high T due to 'nucleation problems'

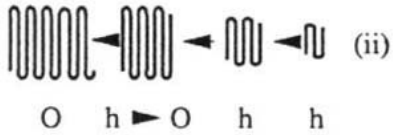
- What is a nucleation problem: size or perfection?
- What triggers the transition between polymorphs?

2. A view on layered crystals and polymorphism





ONE-STEP PROCESS



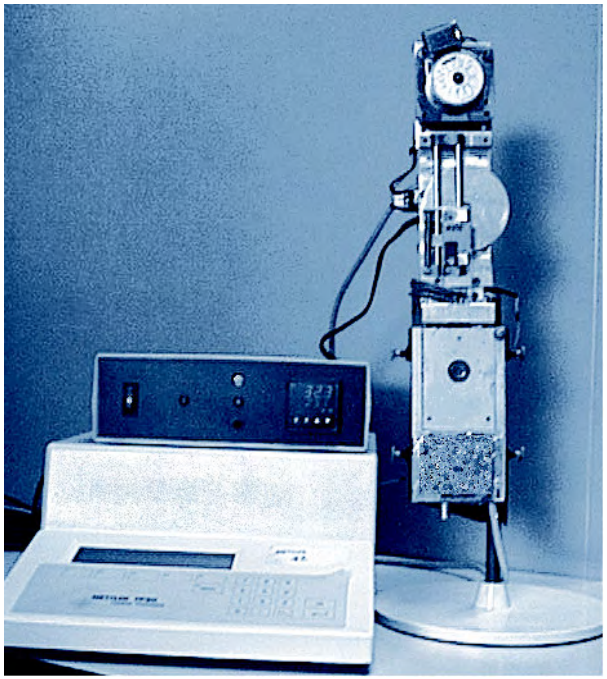
TWO-STEP PROCESS

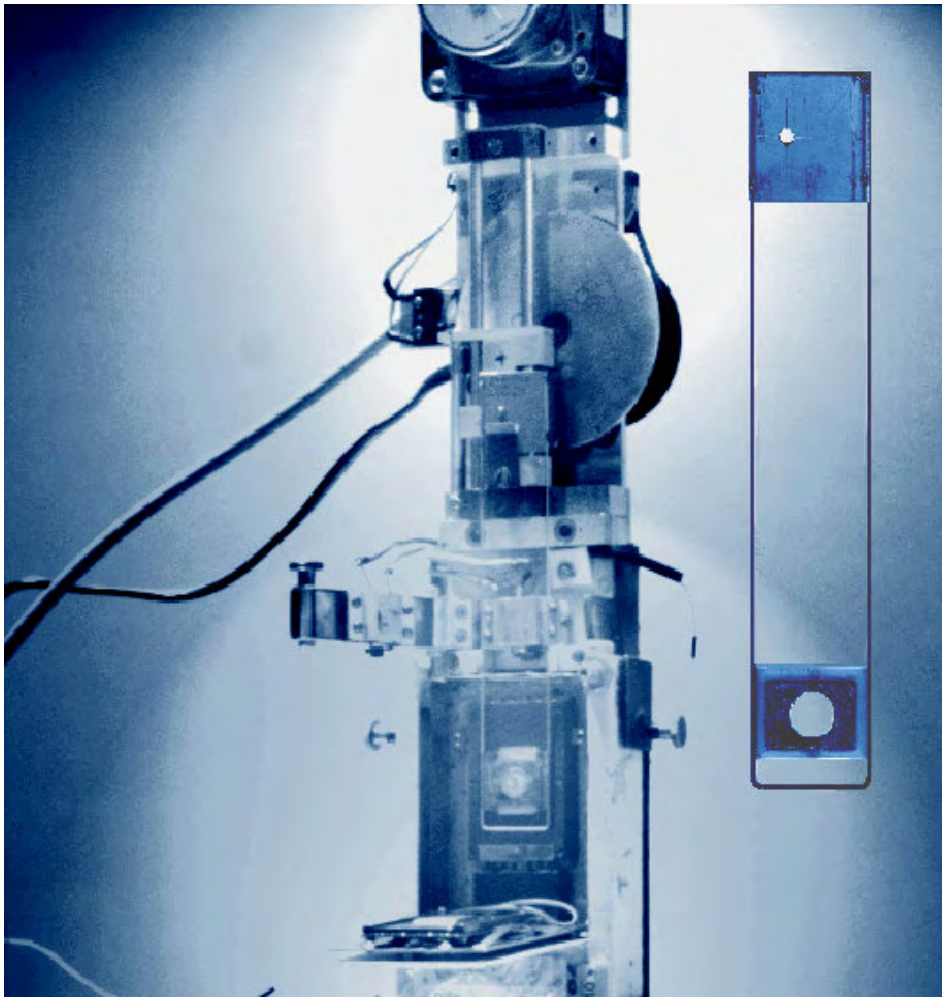
Size or perfection ?

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{d_c \Delta H}\right)$$

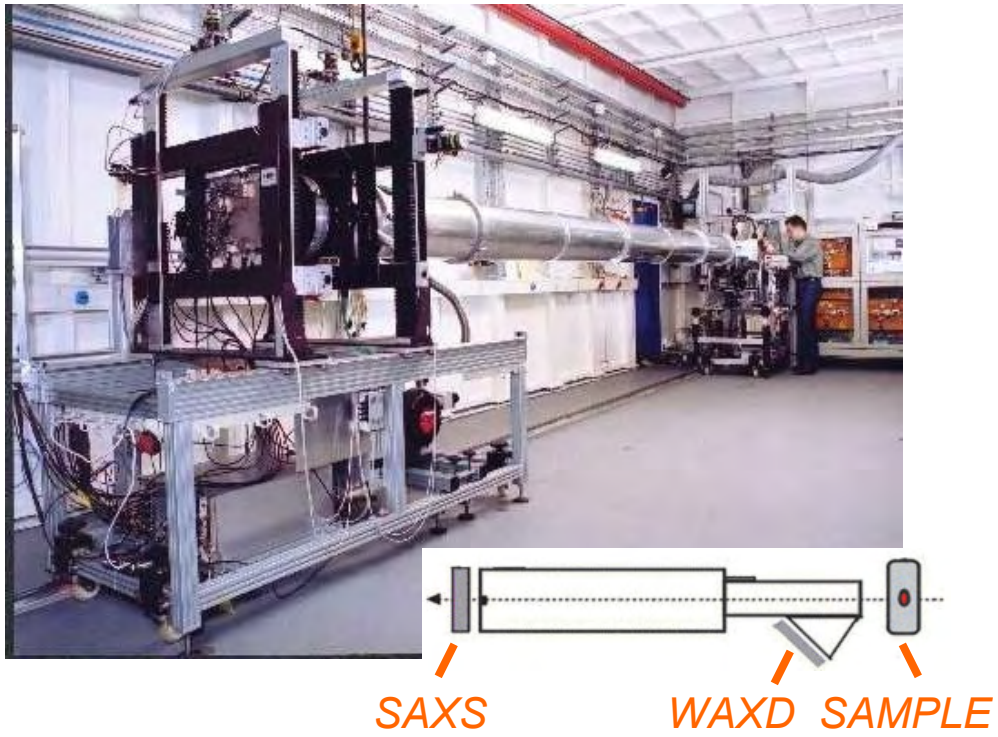
2. A view on layered crystals and polymorphism

COOLING AT 1000 °C/min





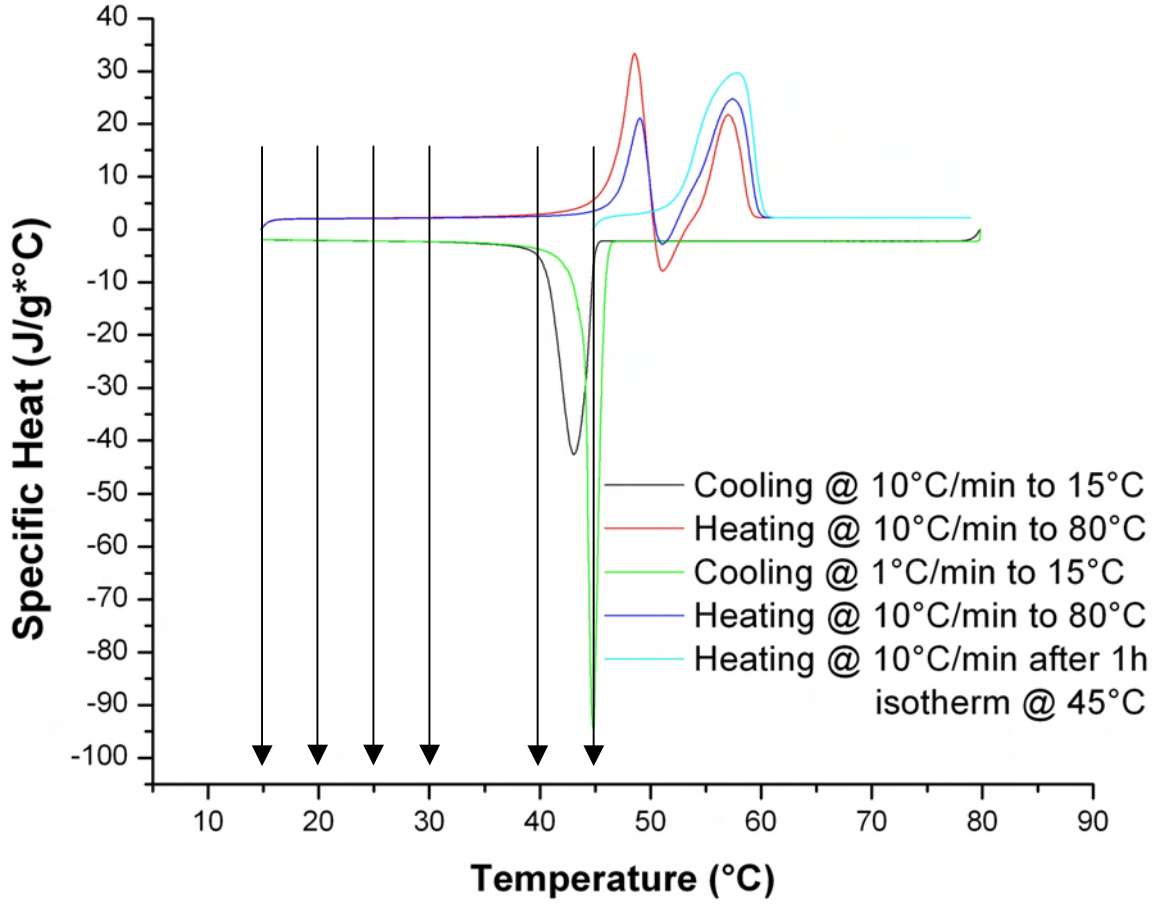
2. A view on layered crystals and polymorphism



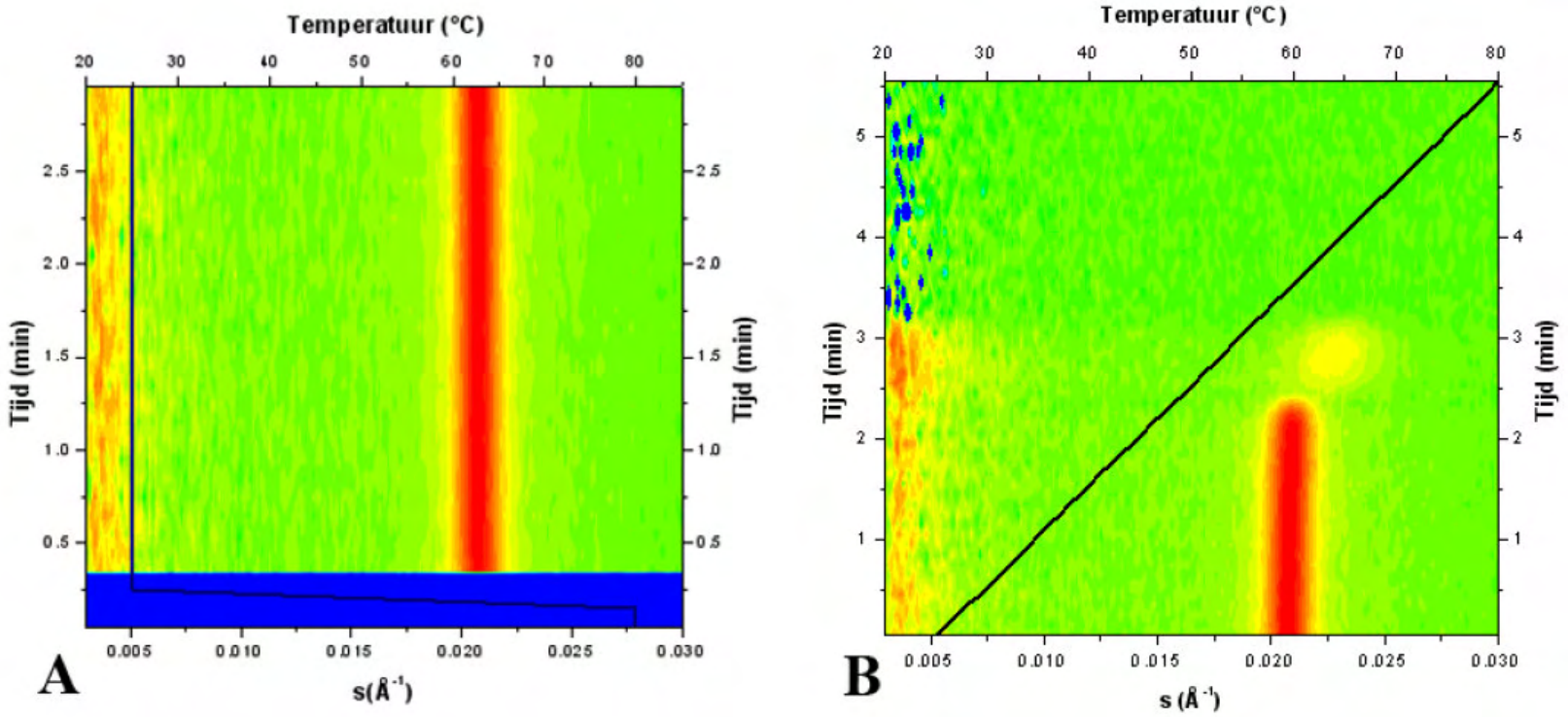
DUBBLE

2. A view on layered crystals and polymorphism

PPP	PPS	PSS	SSS
17.99	47.54	30.26	4.2



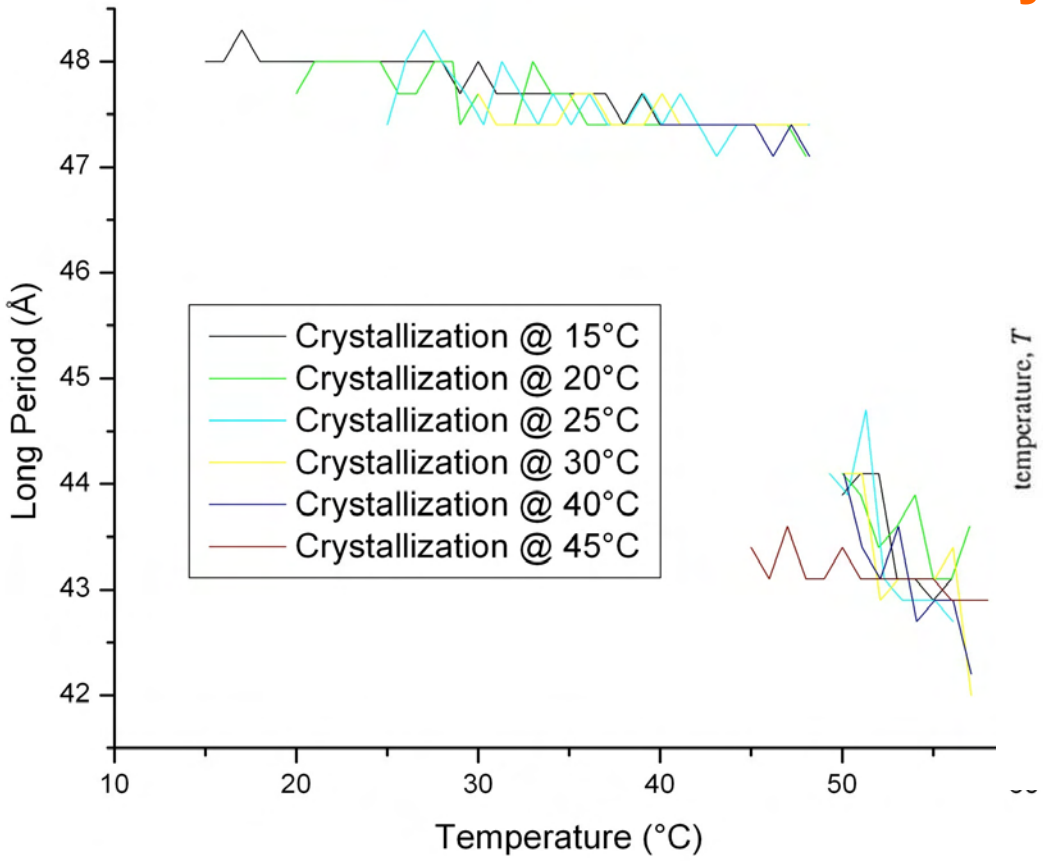
2. A view on layered crystals and polymorphism

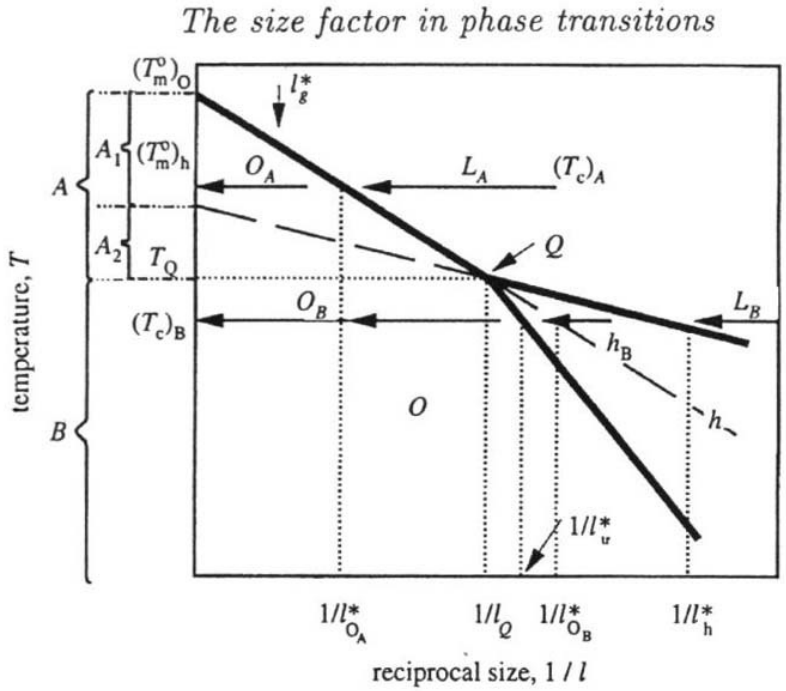


Crystallization at 25 °C followed by heating at 10°C/min

2. A view on layered crystals and polymorphism

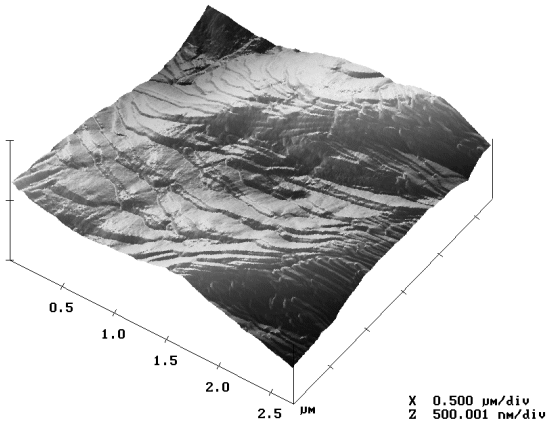
Long period depends on temperature
Not on crystallization temperature !

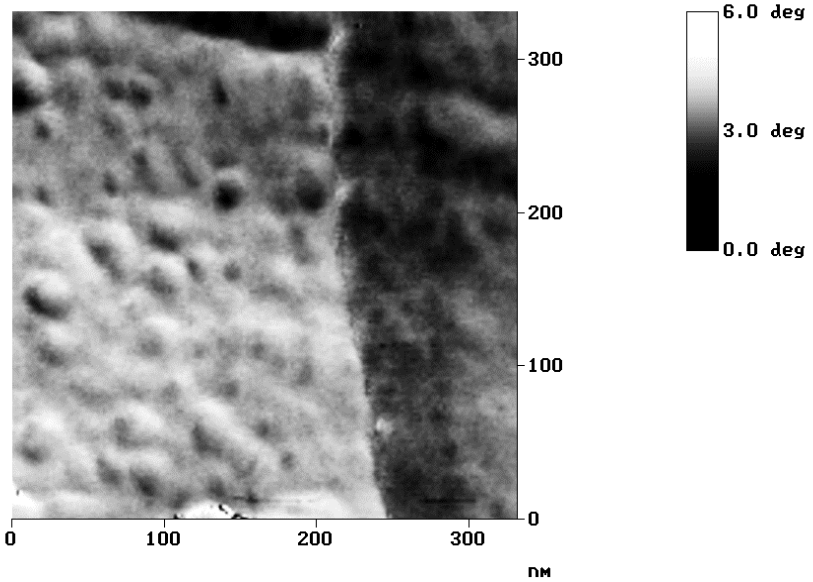




2. A view on layered crystals and polymorphism

layer thickness is not critical: finite molecular dimensions!

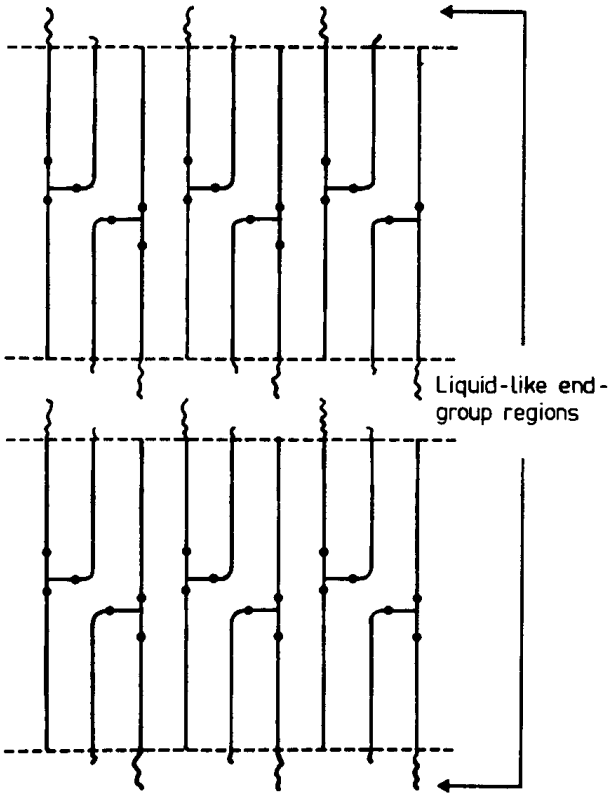




The mosaic structure of polymeric crystals is a trace of a nucleation induced transition

Linear Polyethylene

2. A view on layered crystals and polymorphism



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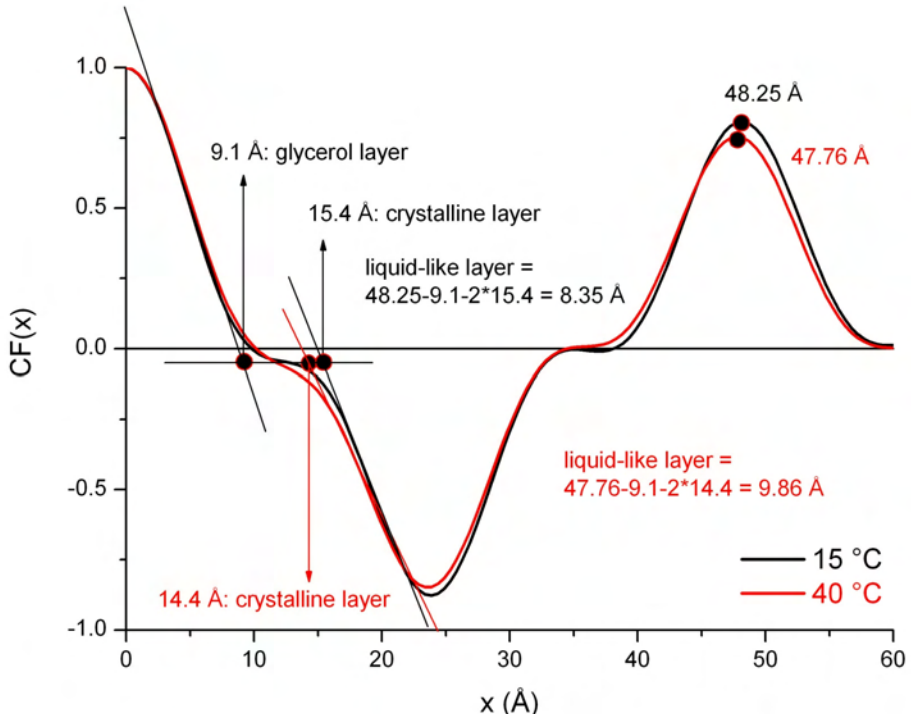
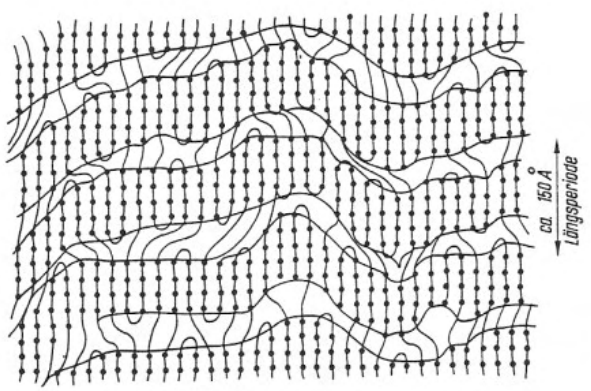
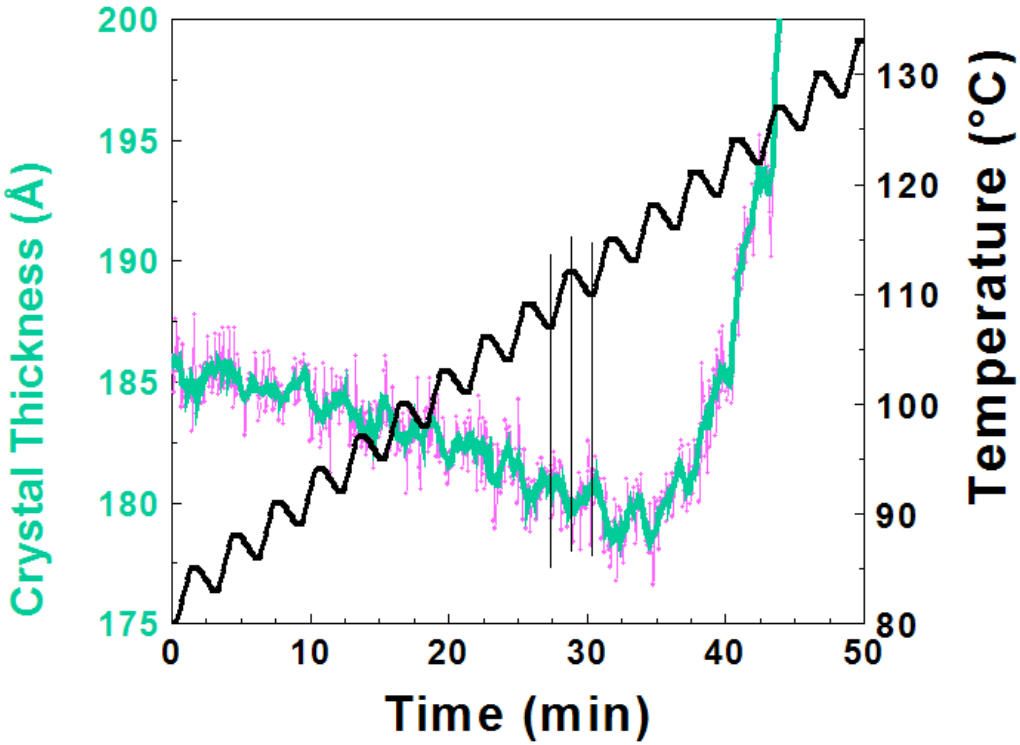


2. A view on layered crystals and polymorphism

Linear polyethylene



Temperature Modulated Heating



Surface Melting = Melting without complete crystal destruction
= Reversible Process !

Conclusions

Fat as model for Polyethylene:

+ Morphological similarity
+ The life time of the different polymorphs is longer
+ The chemical composition can be quite pure
  (no molar mass distribution)
+ Studies of mixtures is possible
- Fats are low molar mass substances
- Normal fats do not exhibit a mesomorphic phase

Polyethylene as model for Fat:

+ (Elaborate) theories are available for testing
+ Experimental tools available, designed for polymers under processing conditions (SAXS, WAXD, SALS)