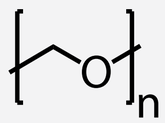
3.3
The Crystalline State

Conformations in the Crystalline State

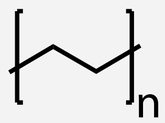
Which Polymers Crystallize?



polyoxymethylene

T_g = -65 ° C

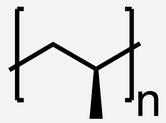
T_m = 175 °C



polyethylene

T_g = -100 ° C

T_m = 130 °C



isotactic polypropylene

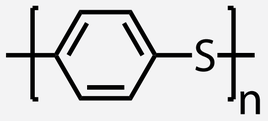
T_g = -10 ° C

T_m = 160 °C

polytetrafluoroethylene

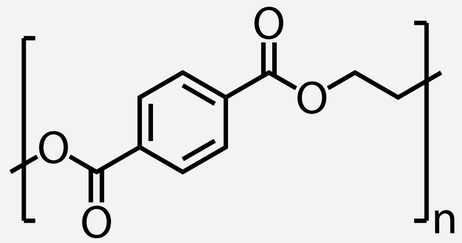
T_g = 115 ° C

T_m = 327 °C



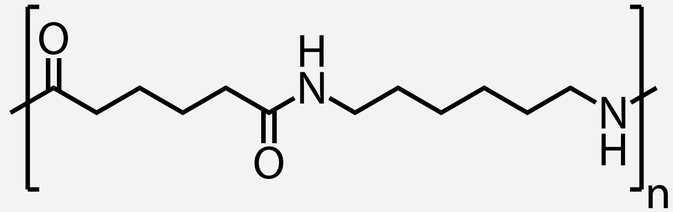
polyphenylenesulfide T_g = 90 ° C

T_m = 285 °C



PET T_g = 70 ° C

T_m = 260 °C



Nylon 6,6 T_g = 50 ° C

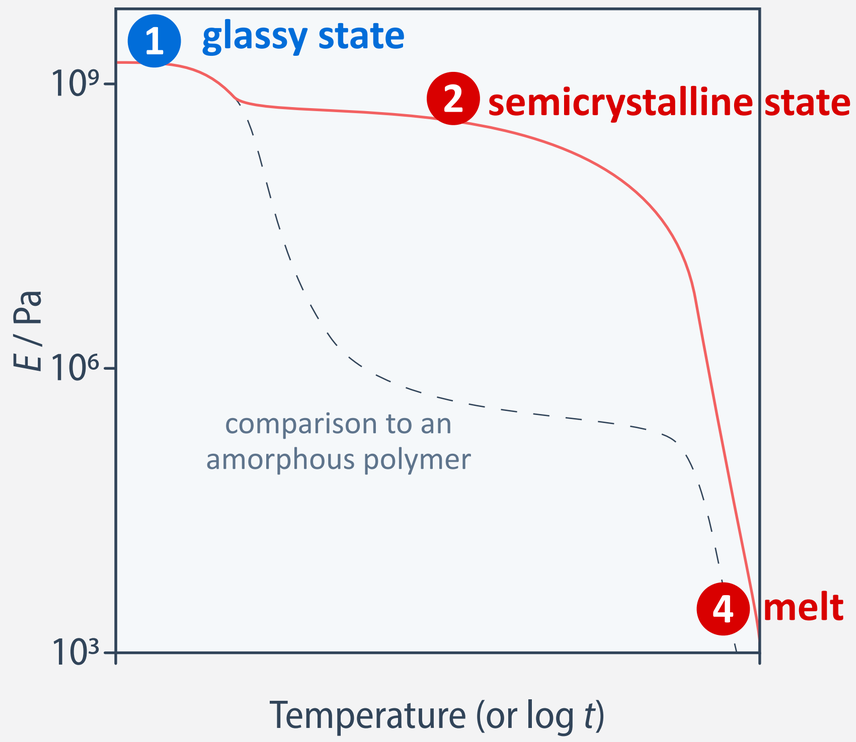
T_m = 265 °C

- regular chemical structures facilitate polymer crystallization
- crystallization/melting only well above the glass transition temperature

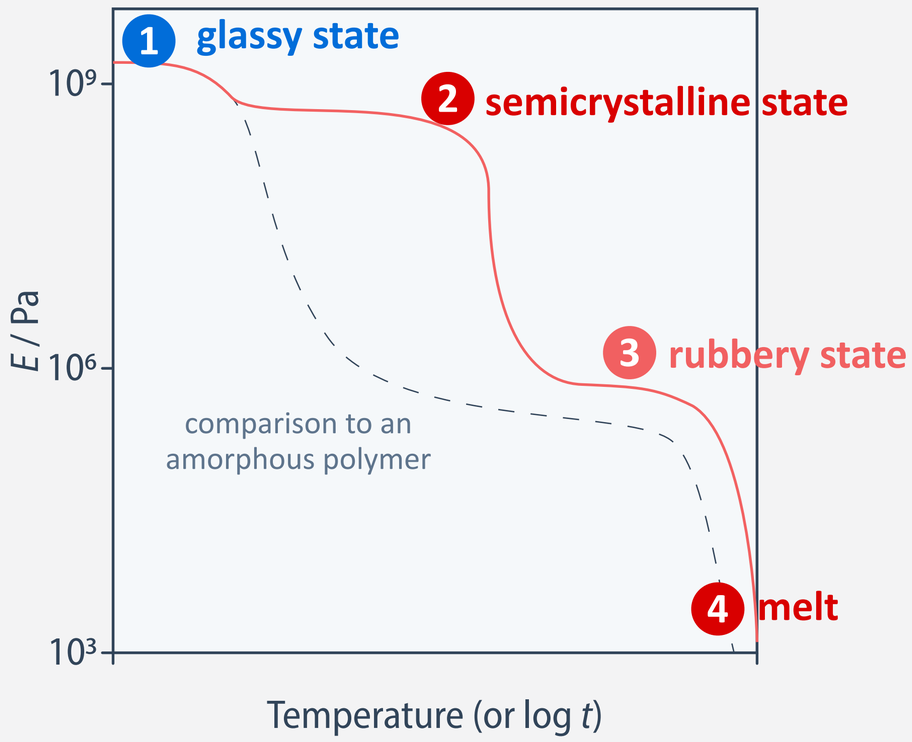
Mechanical Properties of Semicrystalline Polymers

- **stiffness (Young's modulus) comparable to glassy polymers**

high T_m



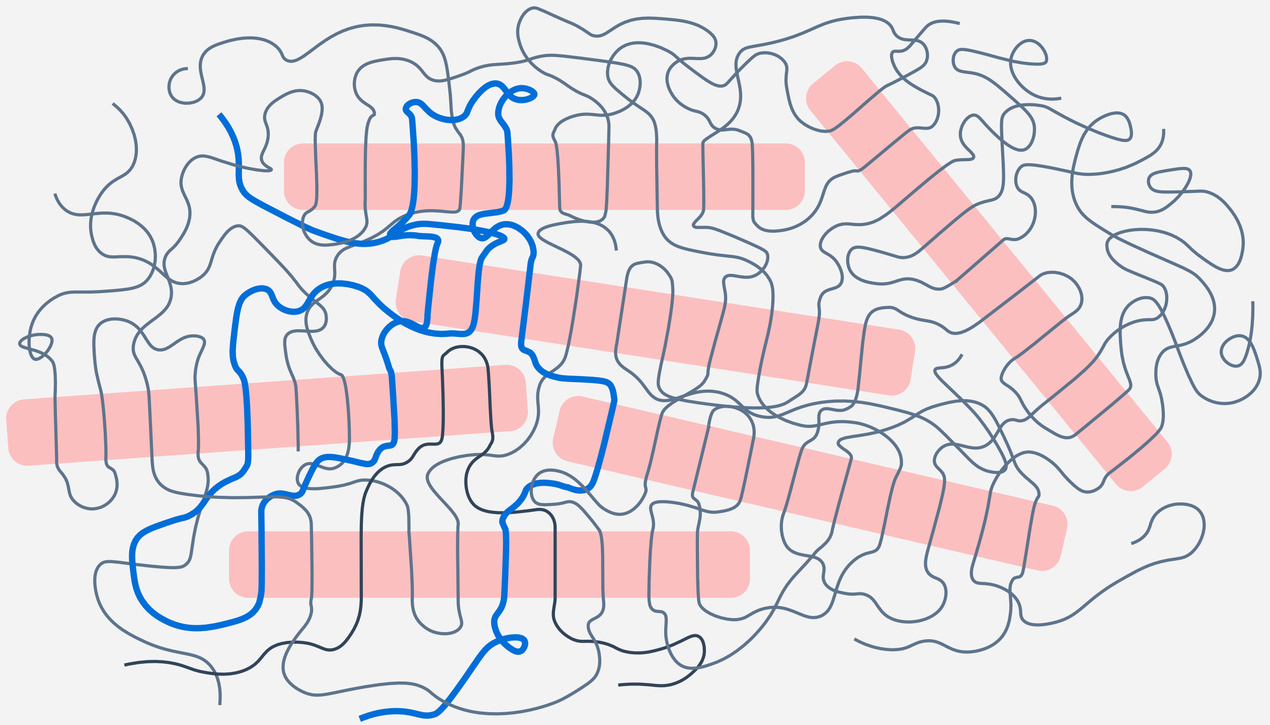
T_m close to T_g
(or sufficiently high molar mass)



- **however, the value of *E* in the crystalline state depends on the degree of crystallinity**

Semi-Crystalline Nature of Polymers

- the same chain can belong to different lamellae
- regions between lamellae usually constitute the amorphous state

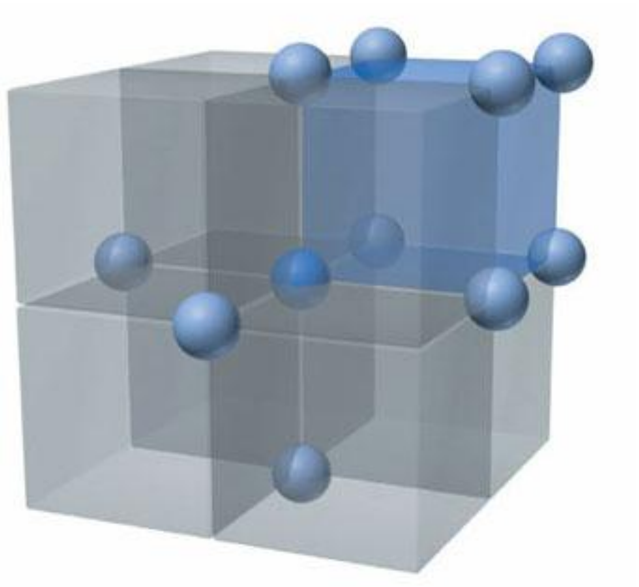


- **polymers are never 100% crystalline under normal processing conditions!**

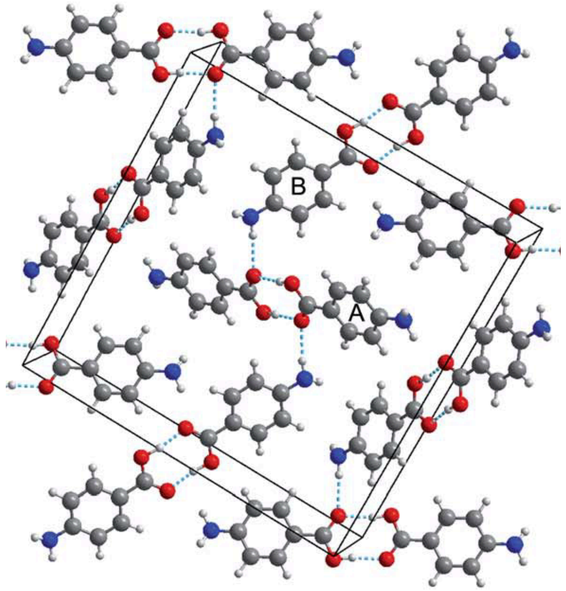
100% Crystalline Entities

- periodic structures with identical repeats of the unit cell in a 3D lattice

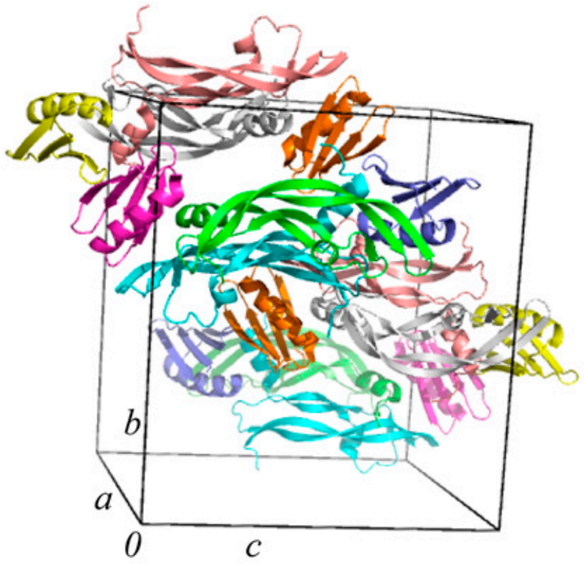
metallic crystals



molecular crystals



protein crystals



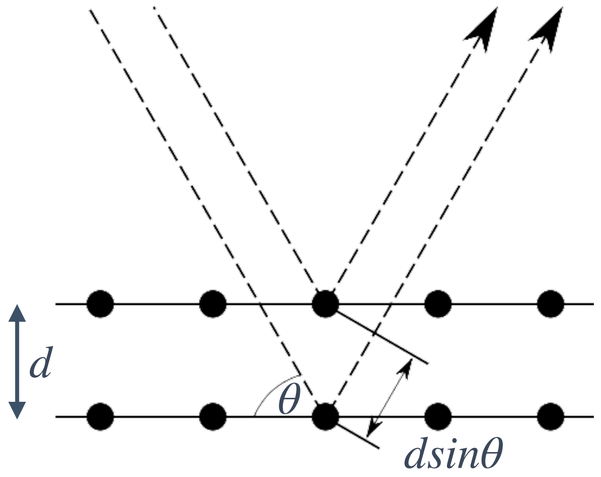
- **100% crystallinity (few defects) for resolving crystal structures with atomic resolution**

Bragg's Law

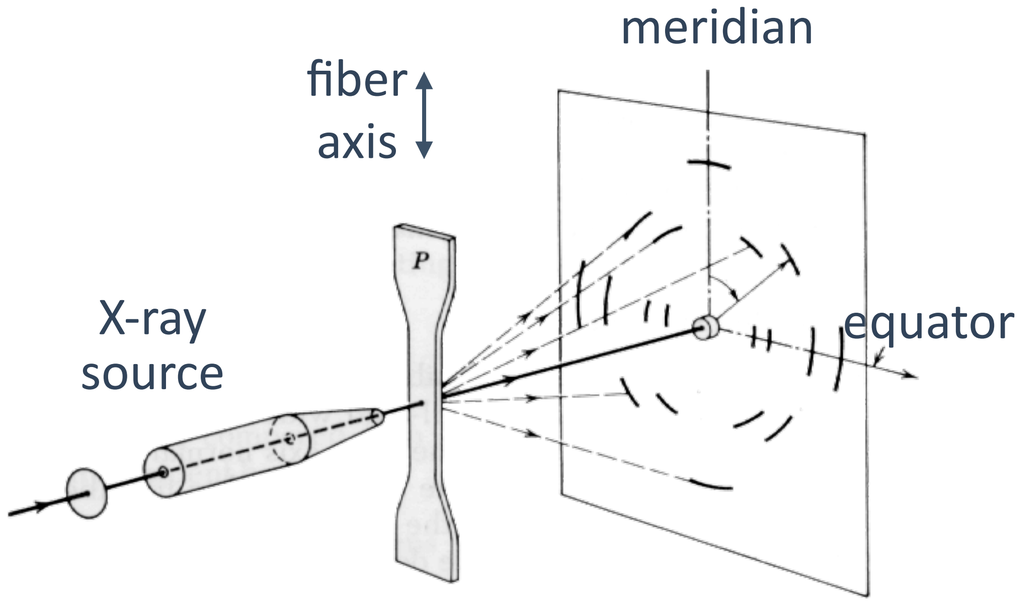
- **diffraction as a result of coherent interference of incident light given by Bragg's law:**

$$2dsin\theta = n\lambda$$

diffraction
(at ordered structures)



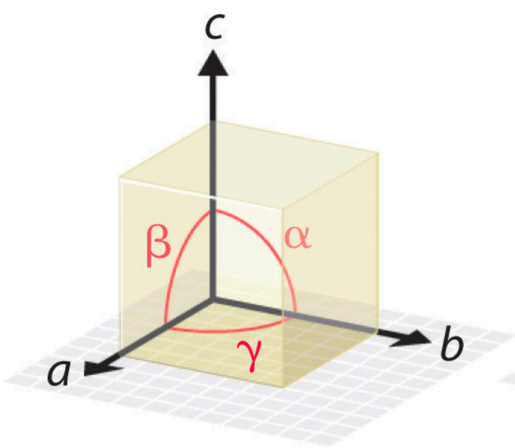
diffractogram
(oriented specimen)

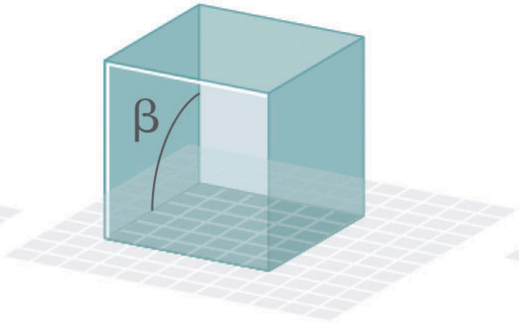


compare with **Slide 123**

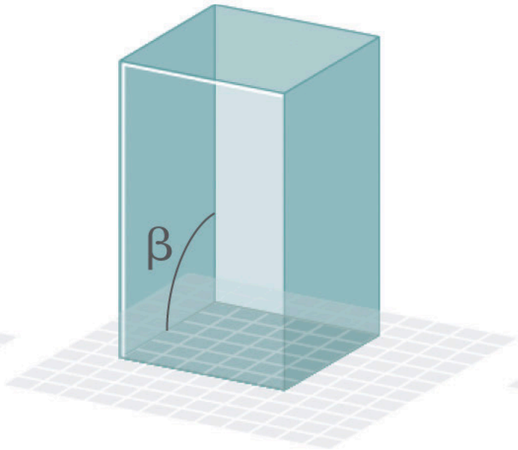
- **polymer specimens should preferably be of sufficient anisotropic nature**

7 Crystal Systems

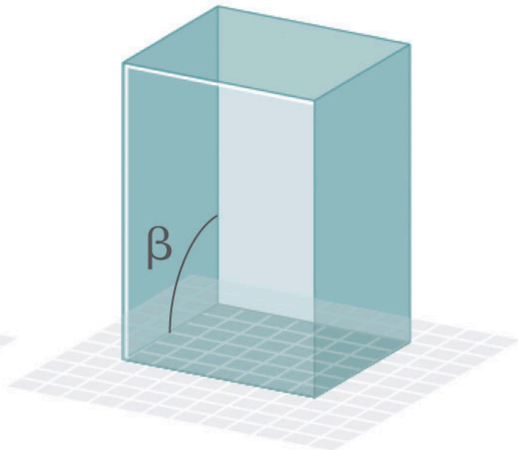




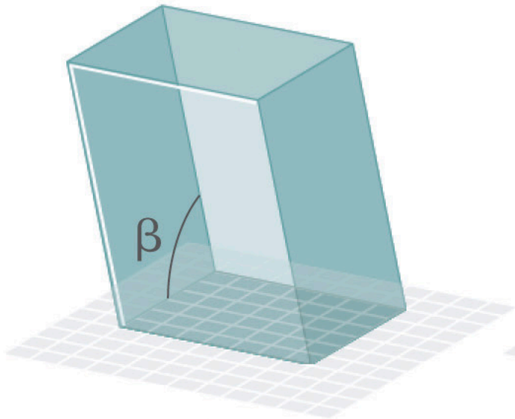
cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$



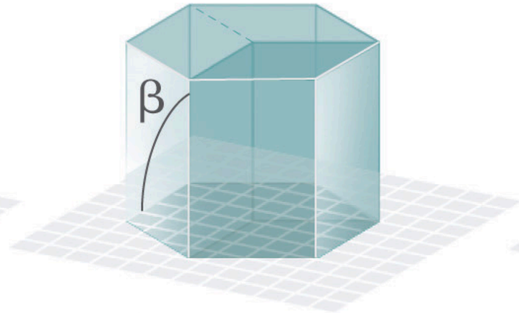
tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



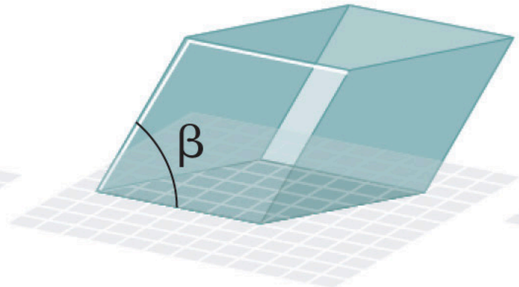
orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



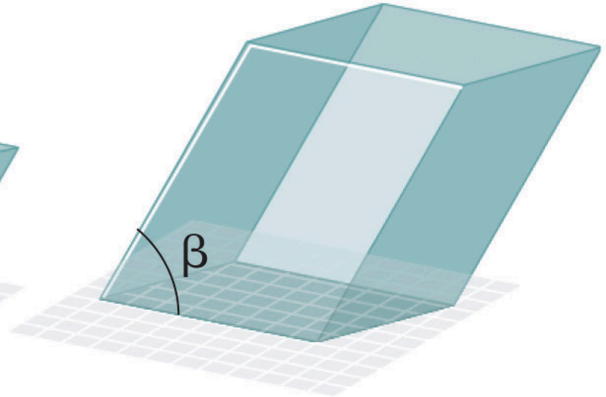
monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90^\circ \neq \beta$



hexagonal
$a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$



trigonal
$a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$

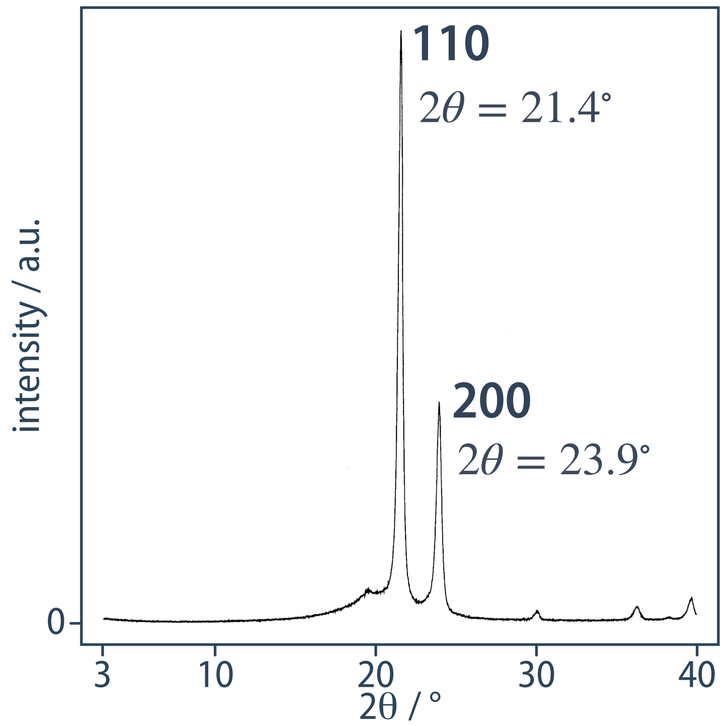


triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

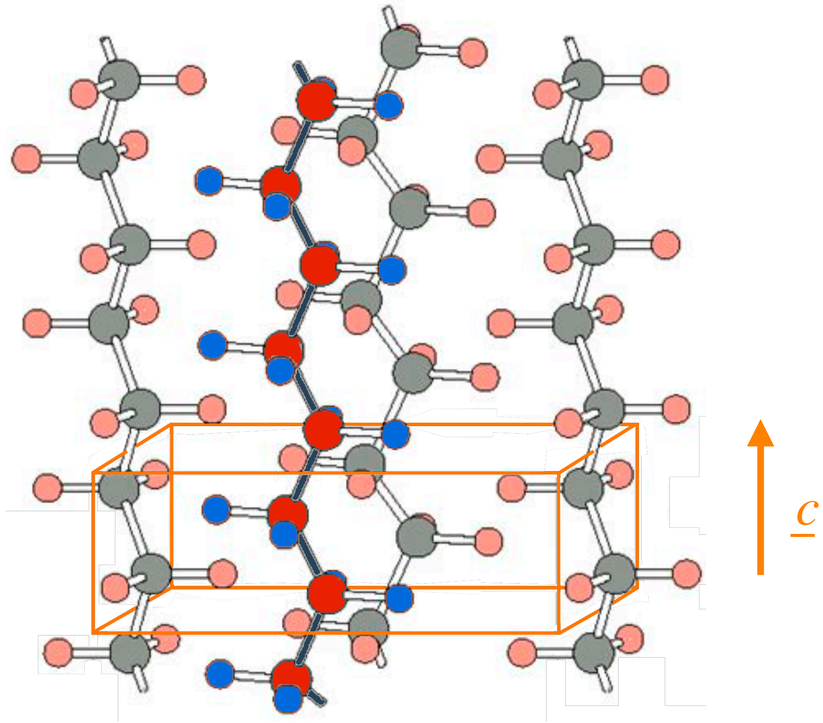
PE Crystal Structure

- by convention, the c-axis of the unit cell is parallel to that of the chains

diffractogram (PE)



orthorhombic unit cell $(a \neq b \neq c)$

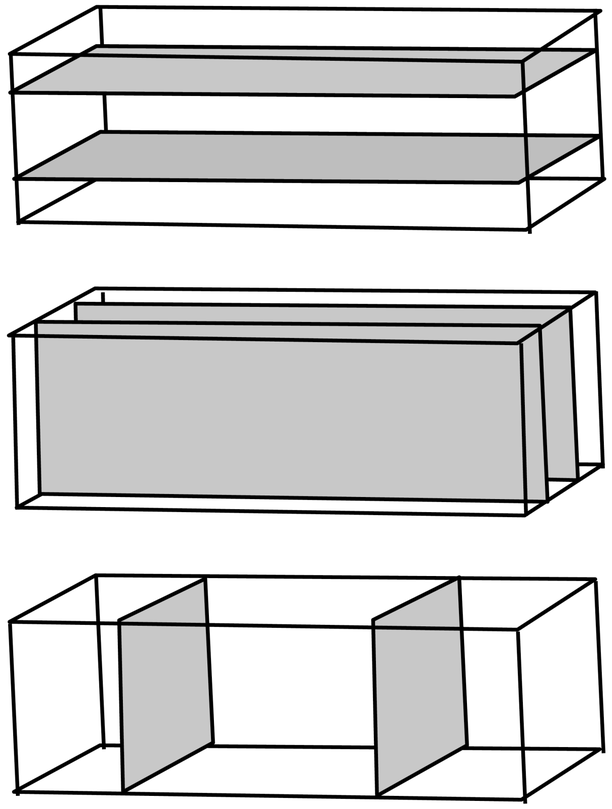


- **the unit cell of polymers does not consist of a single chain (exception: proteins, DNA, …)**

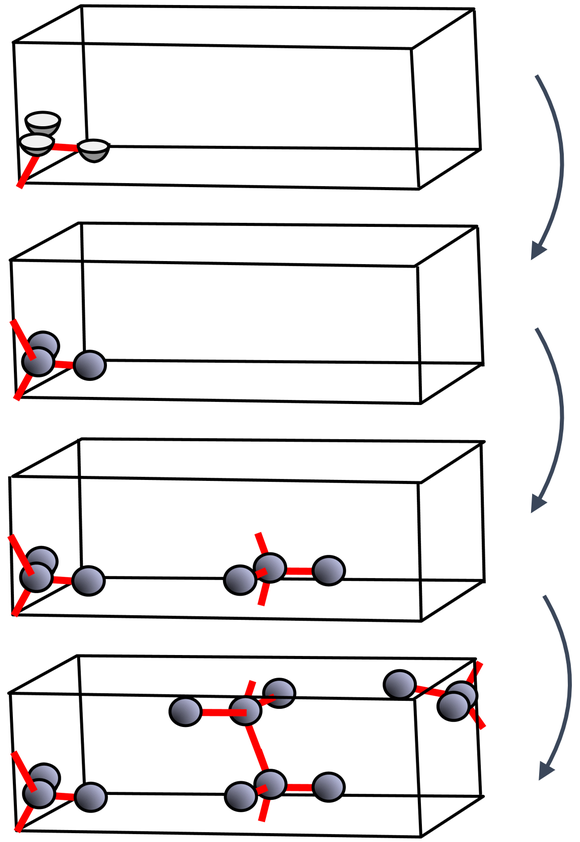
Space Group

- **example: refinement of the orthorhombic PE structure in the space group Pnam**
  (there are 59 orthorhombic space groups)

Pnam symmetrie plans



space group operations



reflexion $\perp \underline{c}$

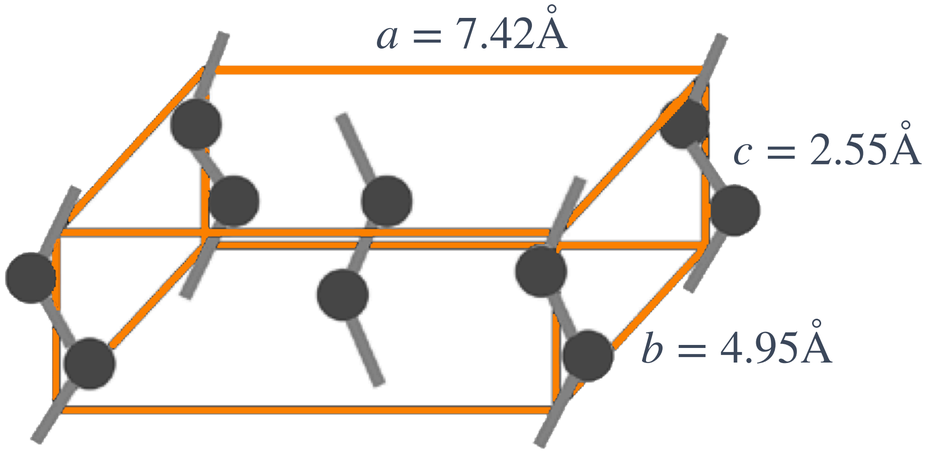
reflexion &
translation $\underline{a}/2$

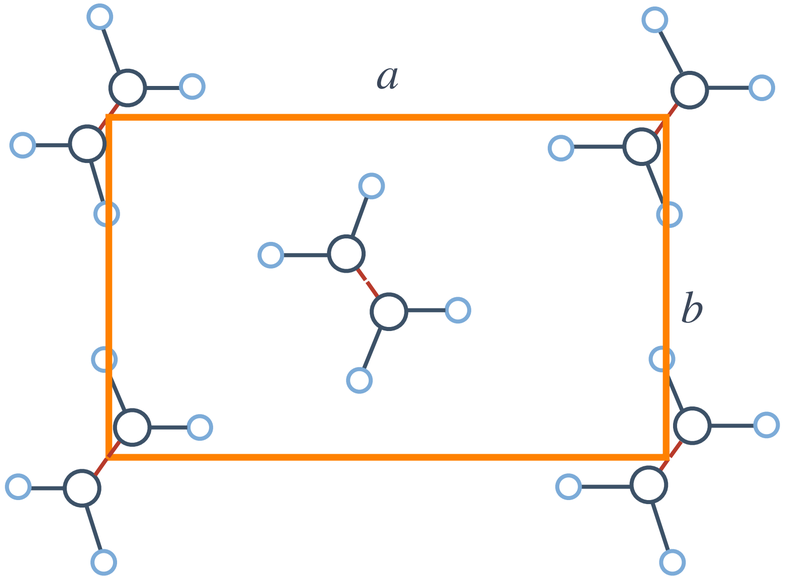
reflexion & translation
$\underline{b}/2$ & $\underline{c}/2$
slip $\perp \underline{c}$

PE Unit Cell

- **PE chains in the crystal structure adopt a linear zig-zag conformation**
- such a conformation can be approximated as a columnar cylinder (viewed along the backbone)

orthorhombic unit cell



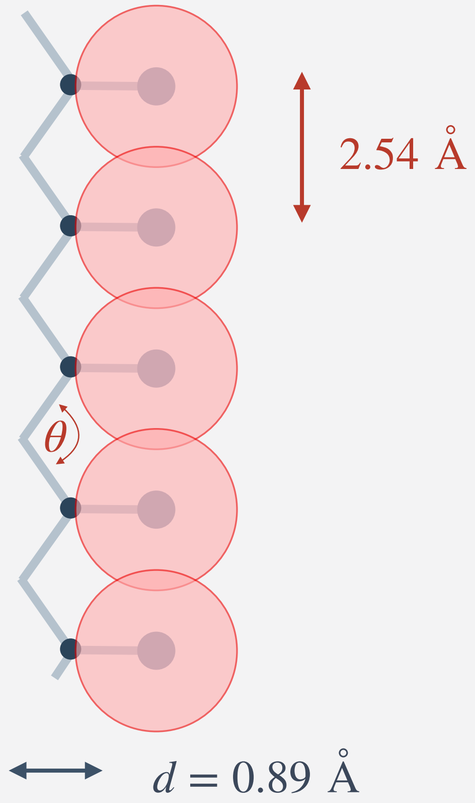


- **cylinders prefer to pack into hexagonal or pseudo-hexagonal (orthorhombic) arrangements**

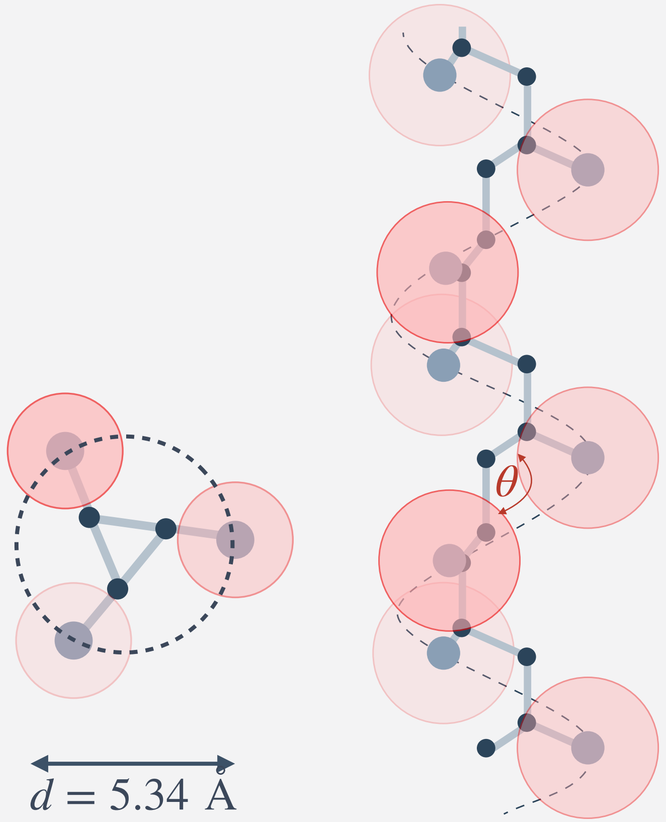
Regular Chain Conformations

- **isotactic and syndiotactic polymers can crystallise via a regular chain conformation**

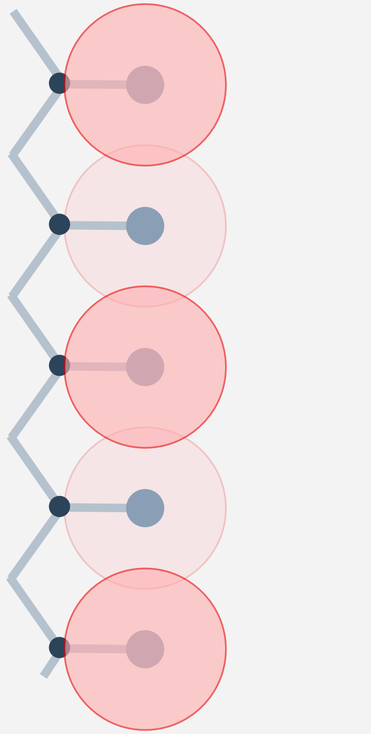
isotactic (i.e. PE)



isotactic (i.e. PP, PS)



syndiotactic

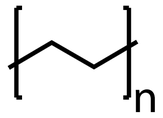


- **often helical conformations, when a zig-zag conformation is not possible for steric reasons**

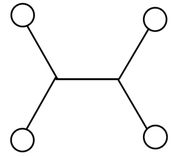
Comparison of PE and PTFE

- **regular “compact” chain conformations for close packing and maximised** E_{coh}

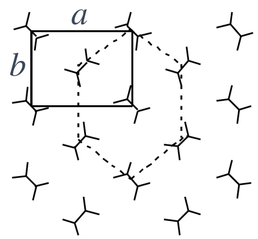
PE:



all-trans conformation

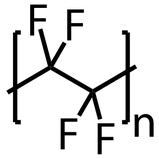


less “cylindrical”

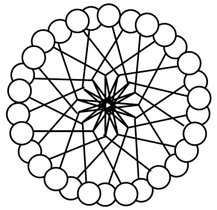


pseudo-hexagonal

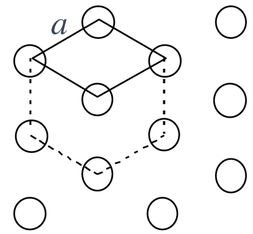
Teflon:



helical conformation



perfect cylinder



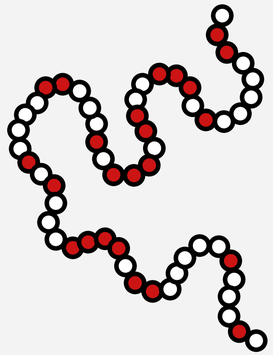
hexagonal

- **PTFE chains pack as perfect columnar cylinders due to steric demand of the F atoms** (vdW radius 1.47 Å)

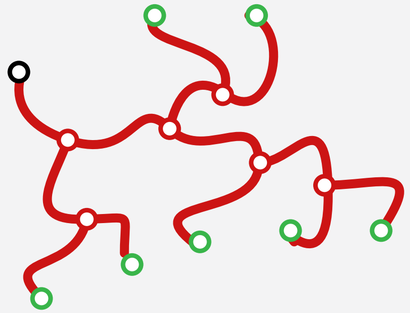
Which Polymers Do Not Crystallize?

- **polymers with an irregular structure are difficult or impossible to crystallise!**

random copolymers



highly branched polymers



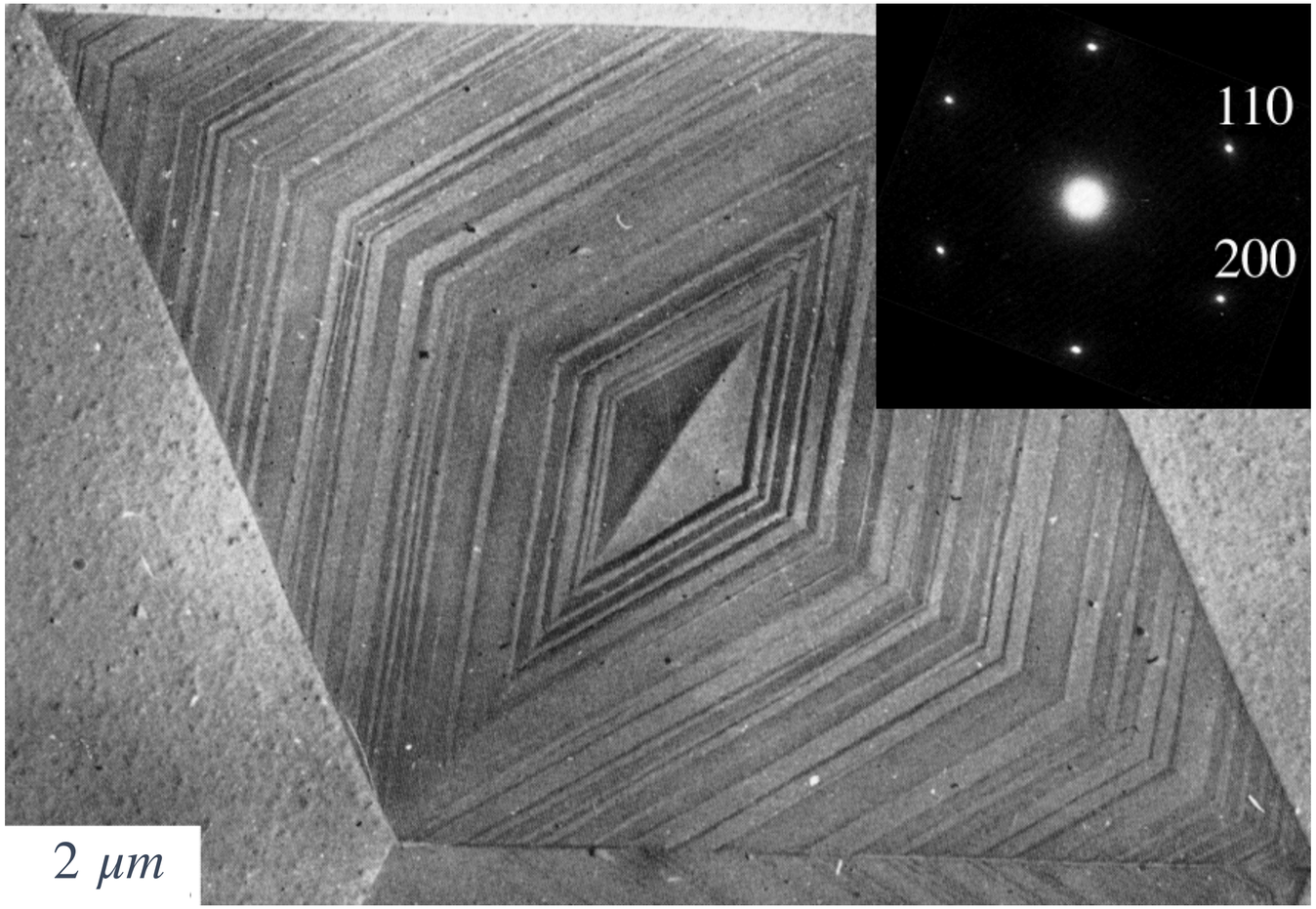
highly cross-linked polymers

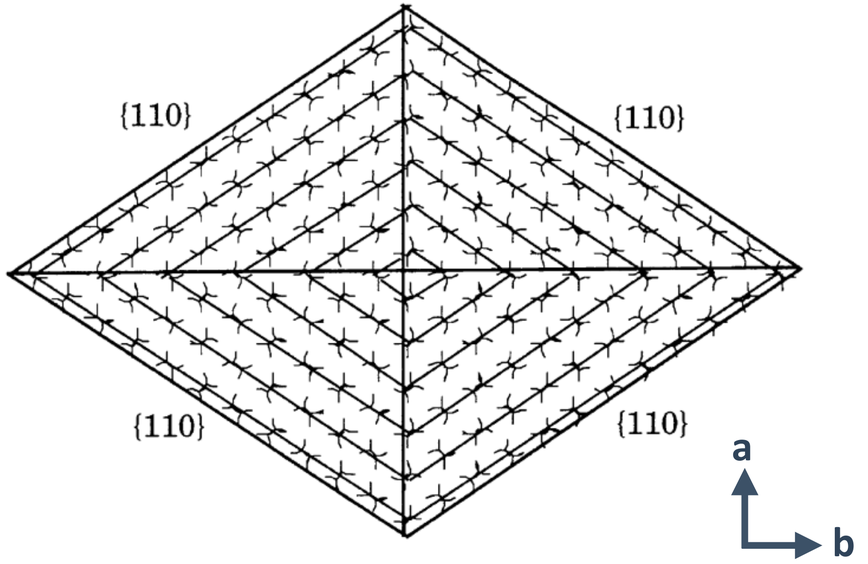
- **polymers do not crystallise below or too close to their T_g**
- **most atactic polymers cannot crystallize (exception: poly(vinyl alcohol))**

The Melting Temperature

Polymeric Single Crystals (Lamellae)

- lamellae can be obtained by isothermal crystallization from extremely dilute solution



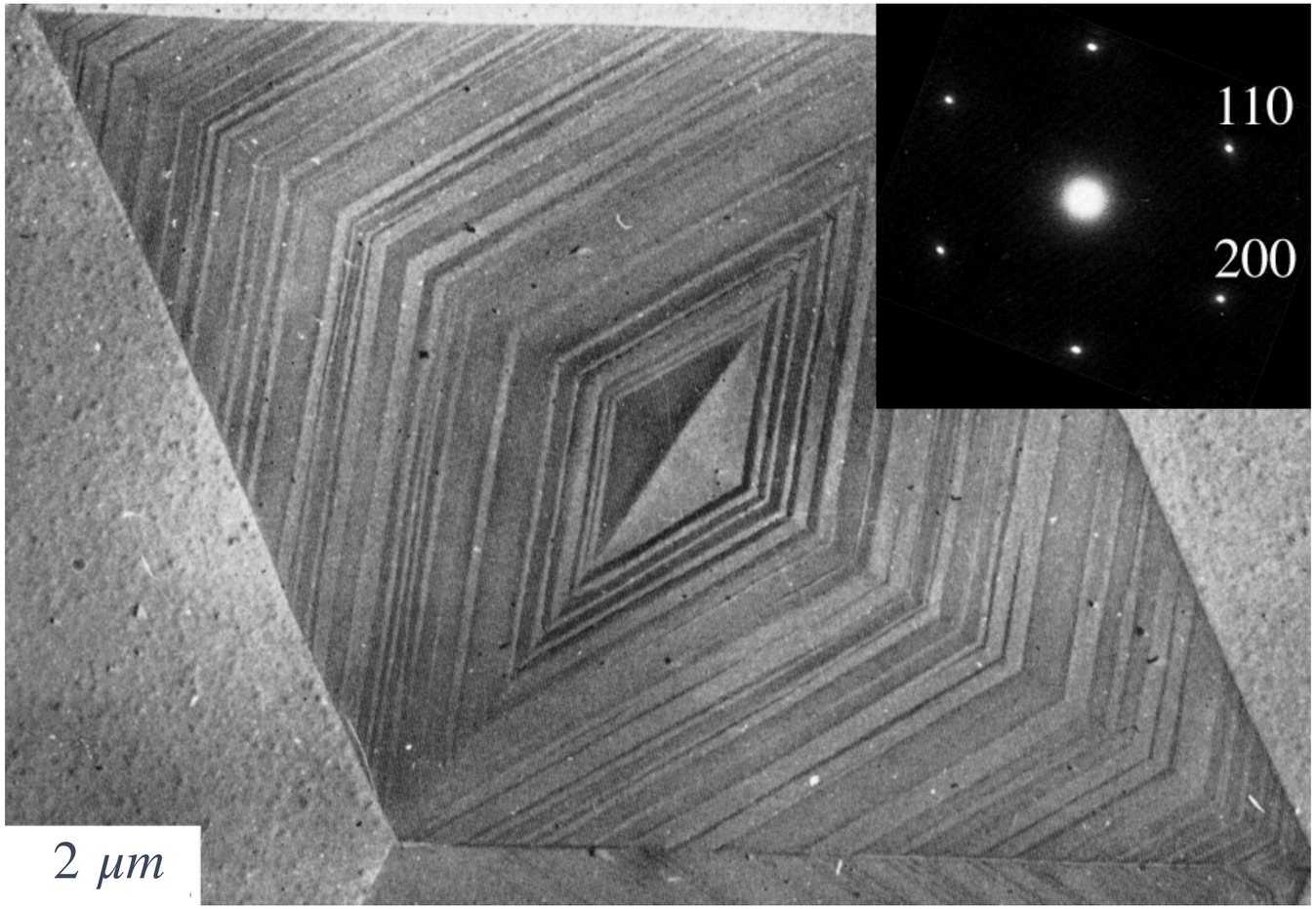


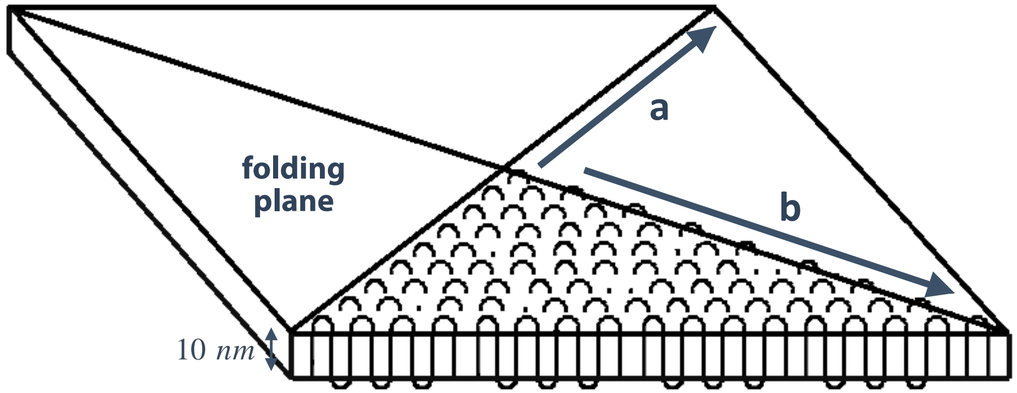
PE chain folded crystals that have grown on top of each other; obtained from xylene

- polymer chain axes are perpendicular to the plane of the crystal as evidenced by TEM

Polymeric Single Crystals (Lamellae)

- the length of a stretched chain (1’000 - 10’000 nm) well exceeds the lamellar thickness of 10 nm

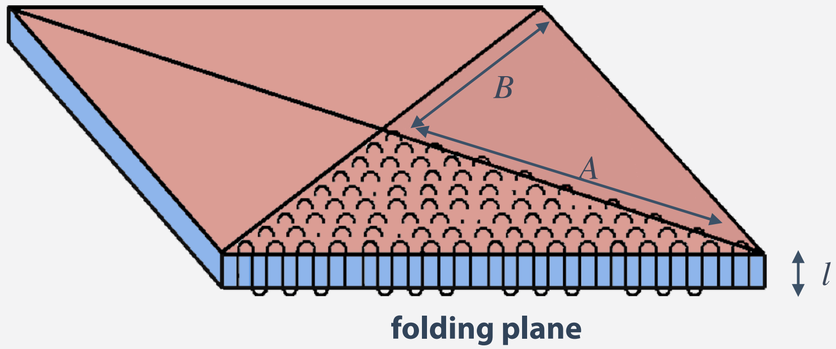




- **the chains fold up during crystallization** (source of disorder: even single crystals are not 100% crystalline!)

Melting Point of a Lamella

- **chain folding is energetically unfavourable, especially if the chain is rigid**



$$\Delta G_{lamella} = 2ABl\Delta H - 4\sqrt{A^2 + B^2}l\sigma - 4AB\sigma_e - 2ABlT\Delta S$$

$$2ABl\Delta H - 4\sqrt{A^2 + B^2}l\sigma - 4AB\sigma_e - 2ABlT_m\Delta S = 0$$

$$T_m = \frac{2ABl\Delta H - 4\sqrt{A^2 + B^2}l\sigma - 4AB\sigma_e}{2ABl\Delta S}$$

$$\sim \frac{\Delta H}{\Delta S}(1 - \frac{2\sigma_e}{l\Delta H}) = T_{m0}(1 - \frac{2\sigma_e}{l\Delta H})$$

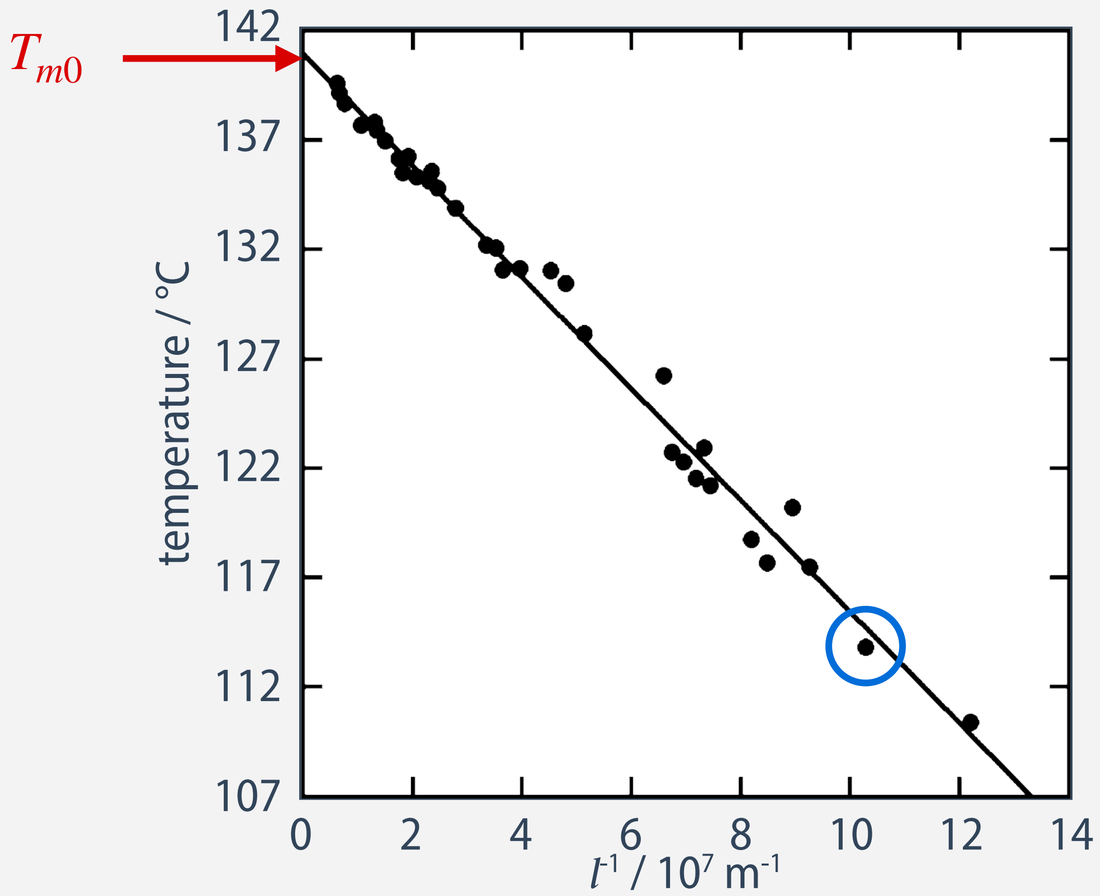
energy penalties:

surface energy associated with folds, σ_e

lateral surface energy, σ

- **the apparent melting temperature, T_m, is less than the thermodynamic T_{m0}**
- **T_m decreases if l decreases due to an increased surface-to-volume ratio of the lamella**
  (and the high surface energy associated with chain folding)

Melting Point of a Lamella



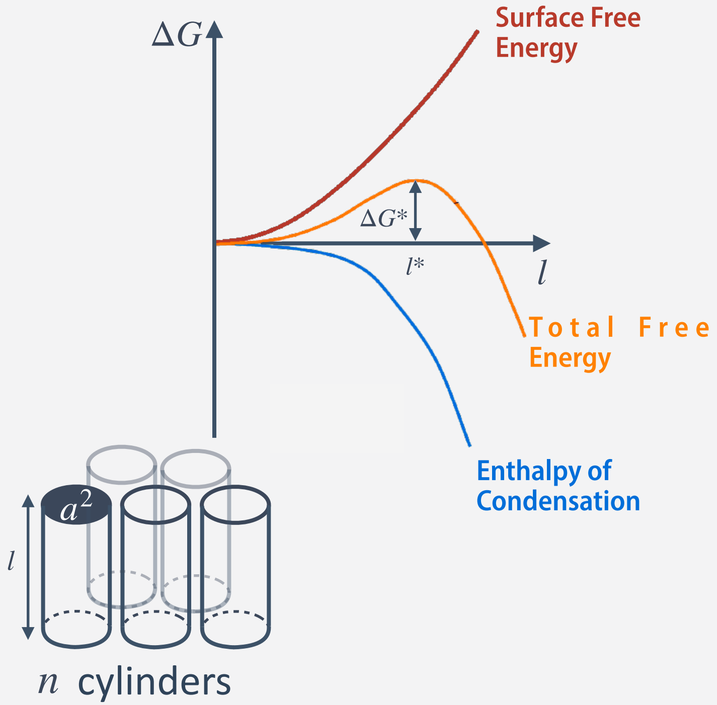
Thomson-Gibbs equation:

$$T_m \sim T_{m0}(1 - \frac{2\sigma_e}{l\Delta H})$$

- T_{m0} refers to an infinite lamellar thickness (see Exercise)
- for a typical lamellar thickness of 10 nm, the T_m can be 40 °C less than T_{m0}

Nucleation as a Limiting Factor of Lamellar Thickness

- **nucleation depends on supercooling and the formation of a nucleus of critical size**



$$\Delta G_{nucleus} \approx 2na^2\sigma_e + 4\sqrt{n}la\sigma - nla^2\Delta G(T)$$

$$\Delta G(T) = \Delta H - T\Delta S = \Delta H(1 - \frac{T}{T_{m0}}) = \frac{\Delta H \Delta T}{T_{m0}}$$

$$\Delta G_{nucleus} \approx 2na^2\sigma_e + 4\sqrt{n}la\sigma - nla^2\frac{\Delta H \Delta T}{T_{m0}}$$

$$\frac{\delta \Delta G_{nucleus}}{\delta n}|_l = \frac{\delta \Delta G_{nucleus}}{\delta l}|_n = 0$$

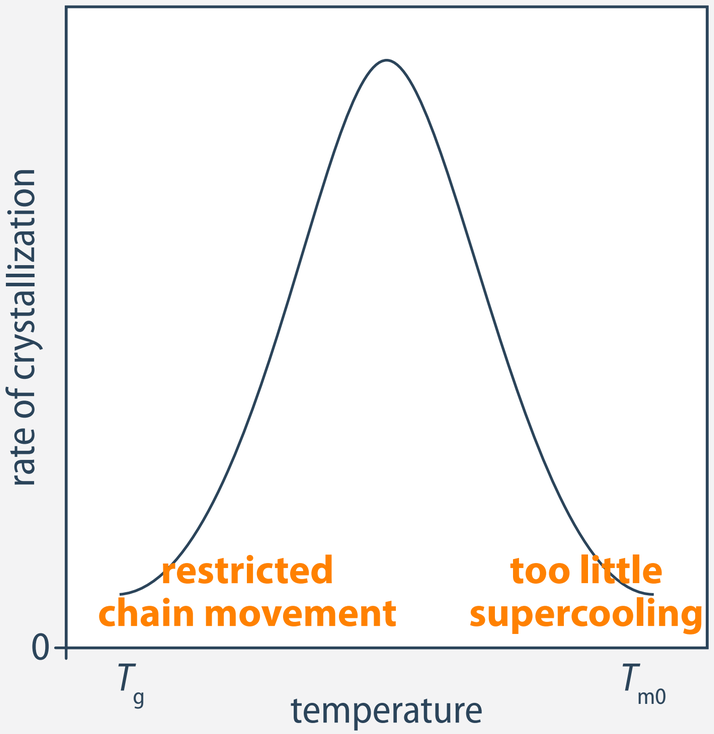
$$l^* = \frac{4\sigma_e T_{m0}}{\Delta H \Delta T}$$

$$\Delta G^* = 32\sigma^2\sigma_e(\frac{T_{m0}}{\Delta H \Delta T})^2$$

- **lamellar thicknesses are determined by crystallization kinetics** (the smaller, the faster)
- **the lamellar thickness (assumed to be l^*) decreases with the degree of supercooling**

Kinetics of Nucleation

- nucleation kinetically limits the lamellar thickness
- in the molten state: constraints on polymer chain mobility (glass transition, entanglement)



$$N = N_0 e^{-\frac{A}{T - T_0}} e^{-\frac{\Delta G^*}{kT}}$$

viscosity term **kinetic term**

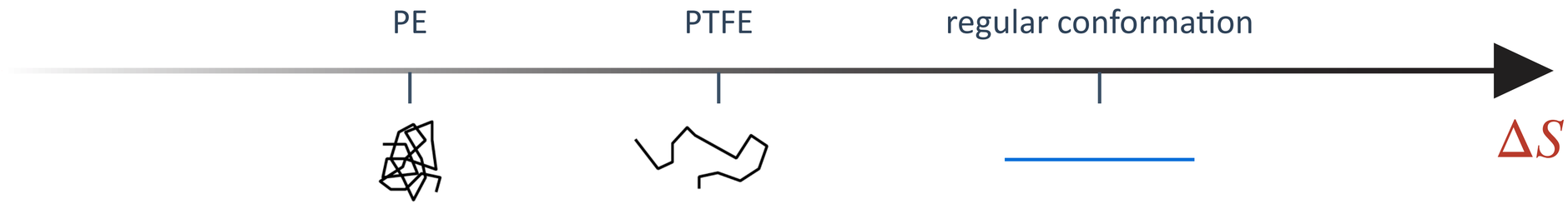
- **practically useful crystallization conditions translate into supercooling of several tens of °C, so that lamellar thicknesses are on the order of 10 nm (i.e. in injection molding)**

Factors Influencing the Melting Temperature

Influence of Chain Ridigity on the Melting Temperature

- crystallization at equilibrium given by Gibbs-Helmholtz equation: $\Delta G = \Delta H - T_{m0}\Delta S = 0$

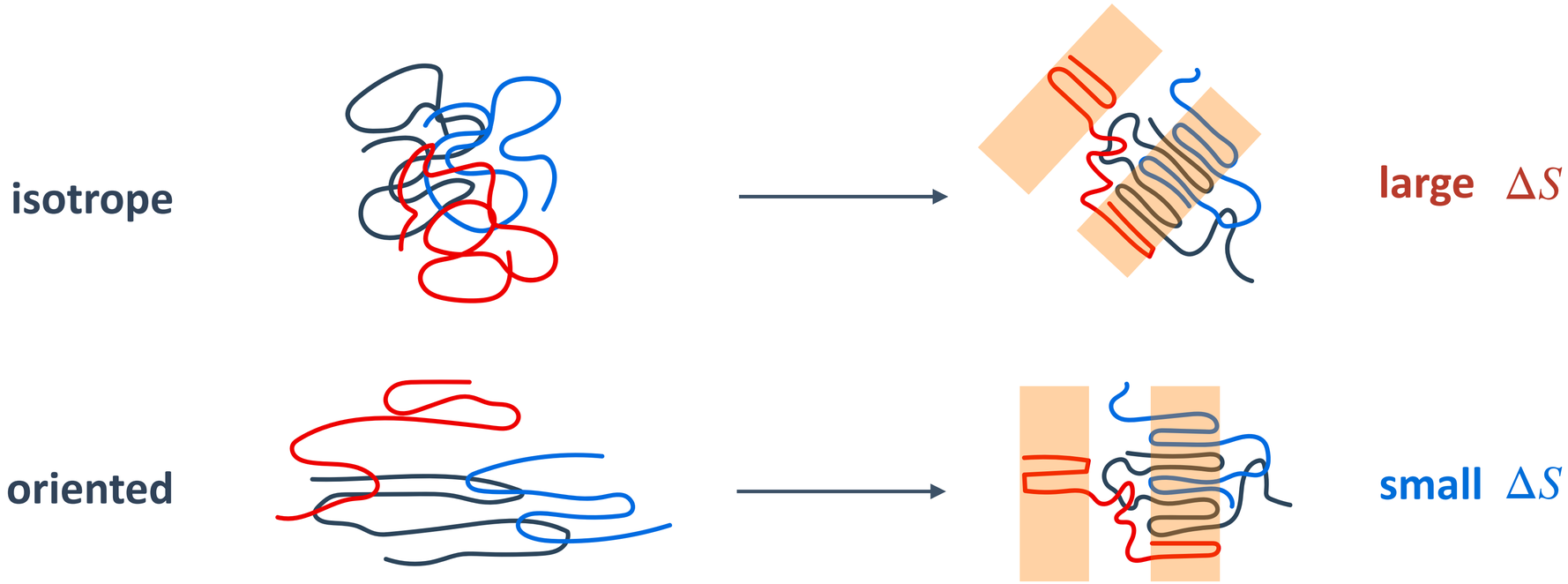
polymer	C_∞	T_m (°C)	ΔH_u (J mol^{-1})	ΔS_u (J K^{-1}
PE	6.7	137	3.970	9.70
Teflon	10-15	372	2.860	4.76



- rotation around CF_2-CF_2 is energetically hindered compared to that of CH_2-CH_2
- **lower entropy loss during crystallization for rigid chains, hence higher T_{m0}**

Orientation

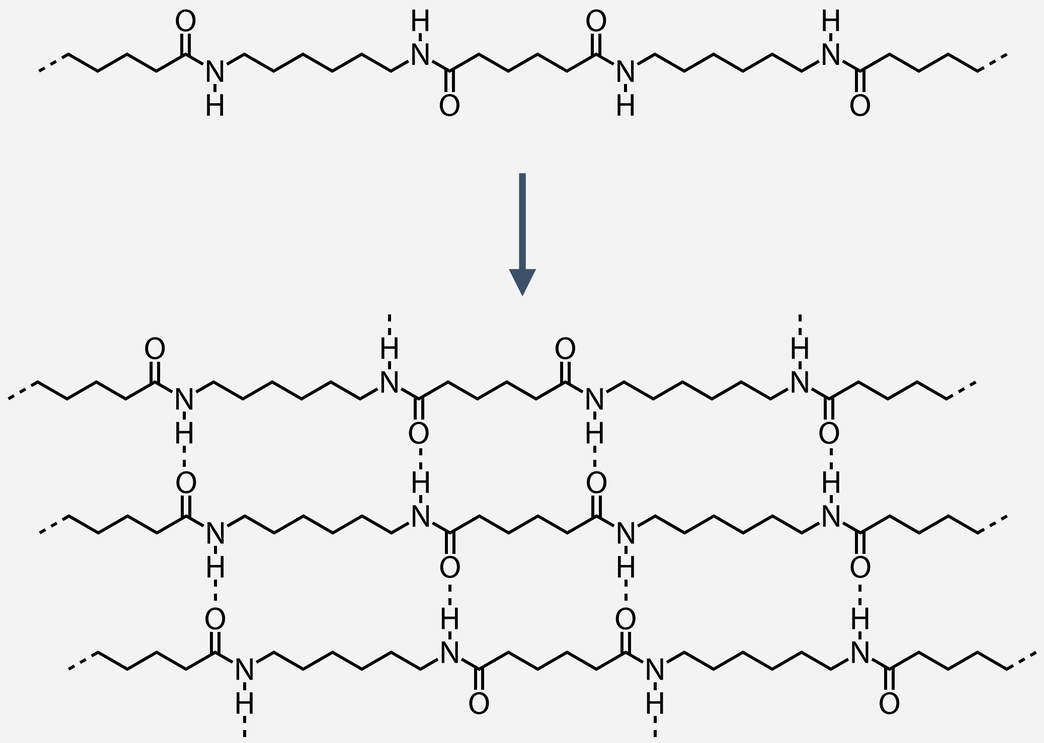
- **favored crystallization for oriented polymer chains (induced by flow or deformation)**



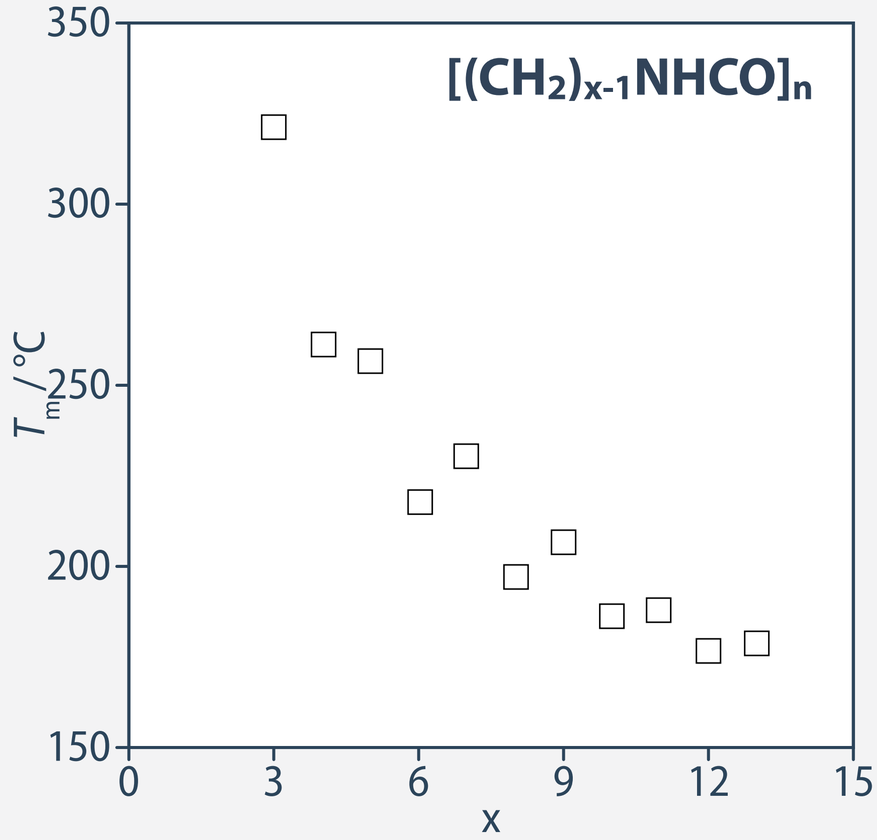
- **lamellae are typically oriented perpendicular to the orientation direction**
- technological relevance: injection molding, crystallization of elastomers (**Chapter 4.1**), fibers

Specific Intermolecular Interactions

- substantial enthalpy gain upon hydrogen-bond formation

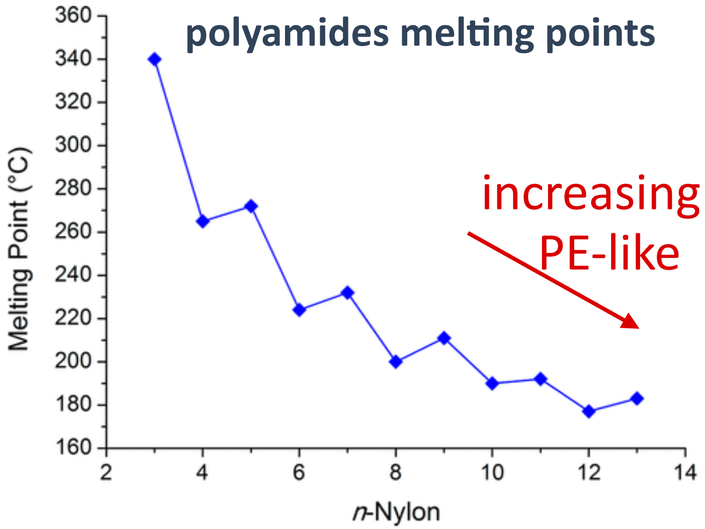


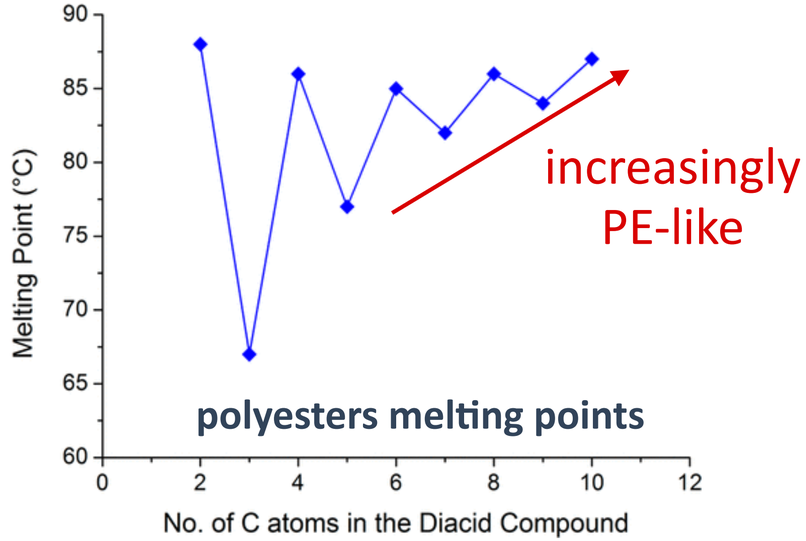
Nylon 6,6: T_m = 265 °C T_g = 50 ° C

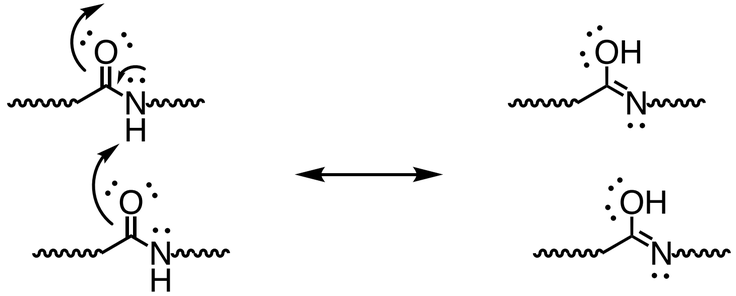


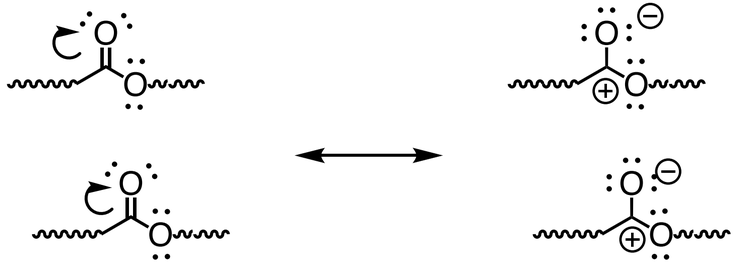
- the stronger the intermolecular interactions, the greater the crystallization enthalpy change, ΔH

Melting Points of Aliphatic Polyamides and Polyesters





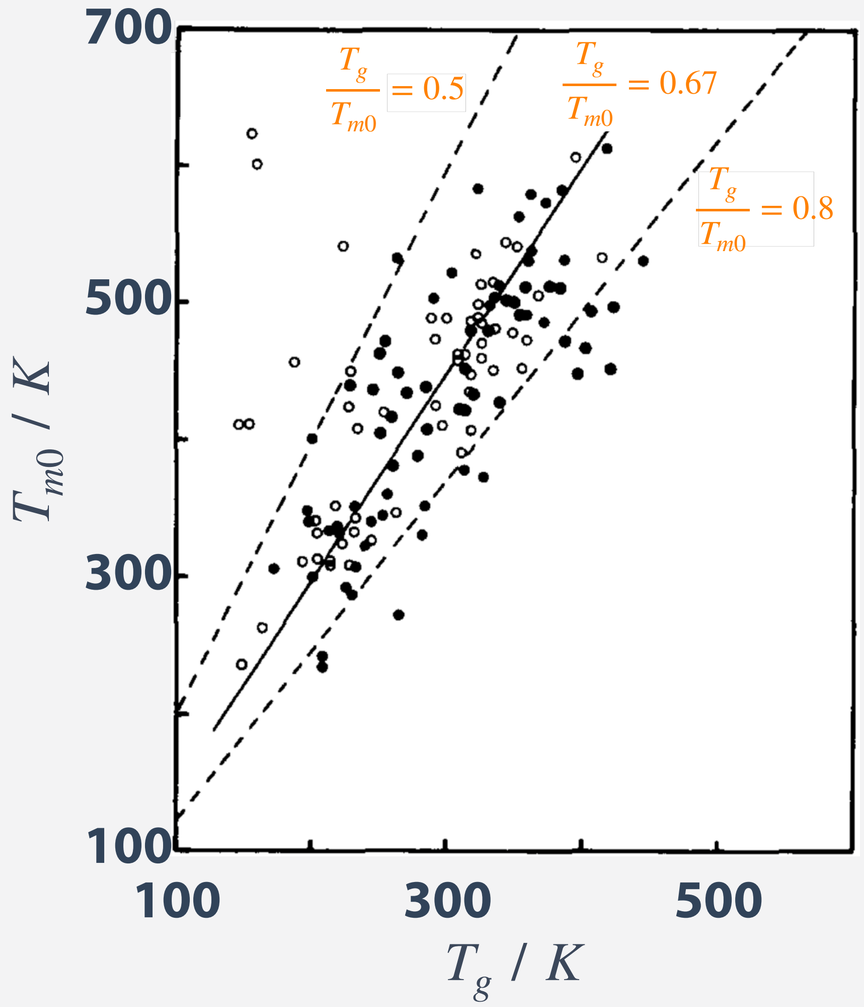




- hydrogen bonds are the origin of high melting points of polyamides as well as the odd-even effect

Correlation with T_g

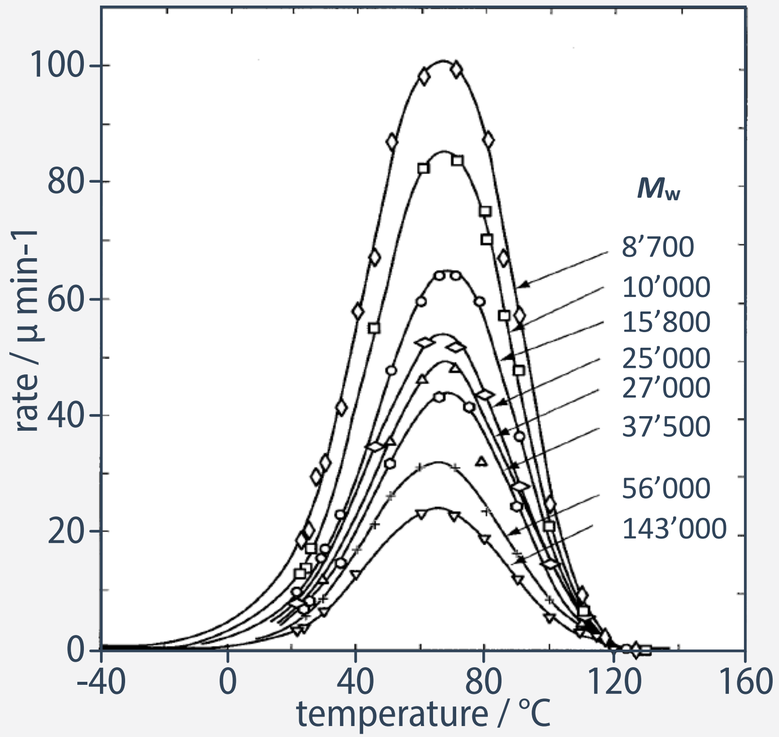
- symmetric repeating units
- unsymmetric repeating units

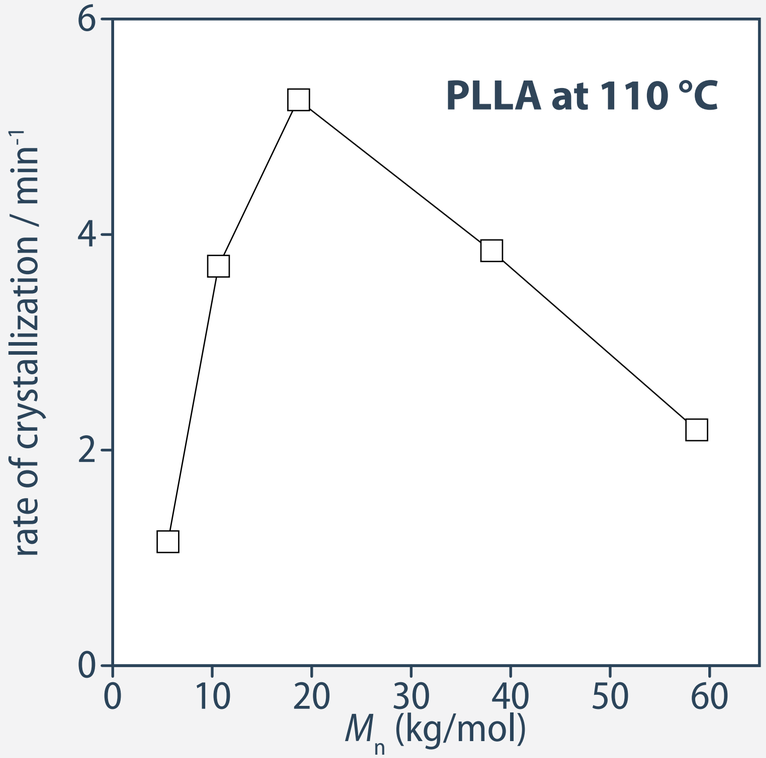


- **T_g and T_m are influenced by similar factors, i.e. chain rigidity and intermolecular interactions**

Molecular Weight Dependence

- increasing molecular weights lead to increases in viscosity (reduced chain mobility)

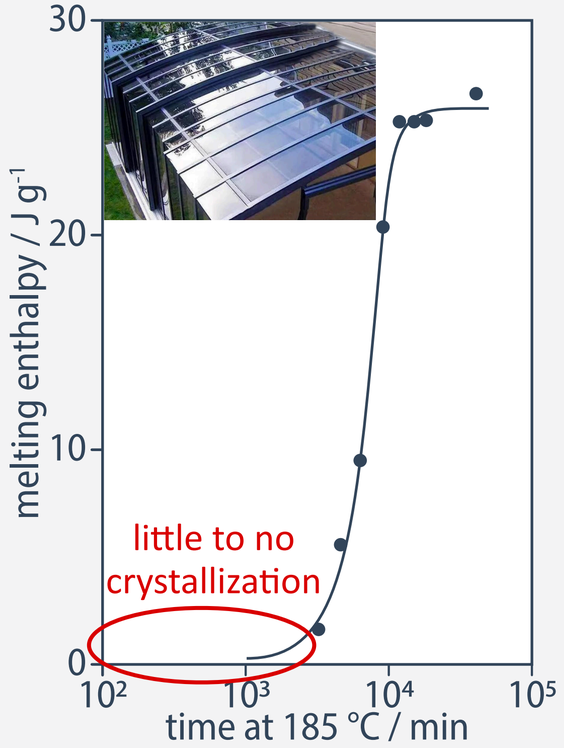




- **practically useful crystallization conditions translate into supercooling of several tens of °C, so that lamellar thicknesses are on the order of 10 nm (i.e. in injection molding).**

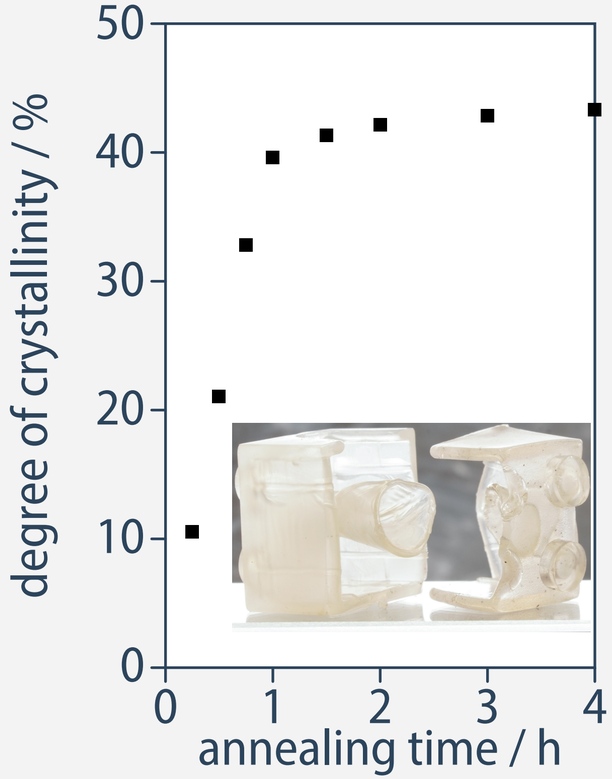
Time as a Limiting Factor

polycarbonate
($T_g \approx 150$ °C, $T_m \approx 300$ °C)



PET
($T_g \approx 70$ °C, $T_m \approx 260$ °C)

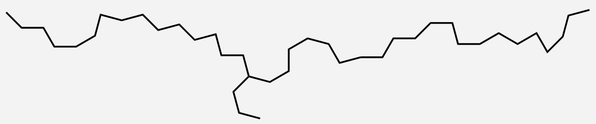
aliphatic polyesters
(T_g(PLLA) ≈ 60 °C, T_m(PLLA)≈ 160 °C)



- **for some products or processes, suppressed polymer crystallization is an actual feature**
- PC is often close to 0% crystalline, PET bottles (ca. 30% crystalline) are made from an amorphous preform

Branching

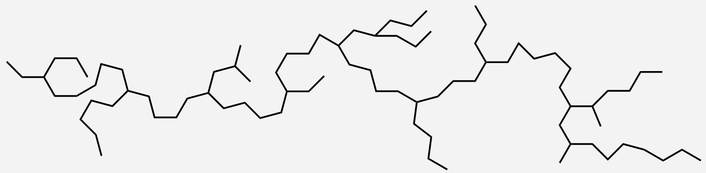
HDPE



high-density polyethylene (HDPE)

structurally “regular” with few branching points (7/1000 carbons)
packs efficiently, high crystallinity, high density

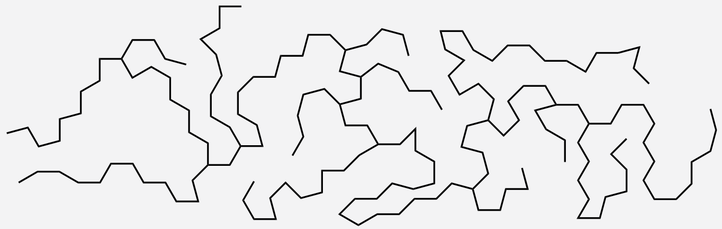
LLDPE



linear low-density polyethylene (LLDPE)

“controlled” number of short-chain branches; properties in between HDPE and LDPE; tuneable to desired property window

LDPE



low-density polyethylene (LDPE)

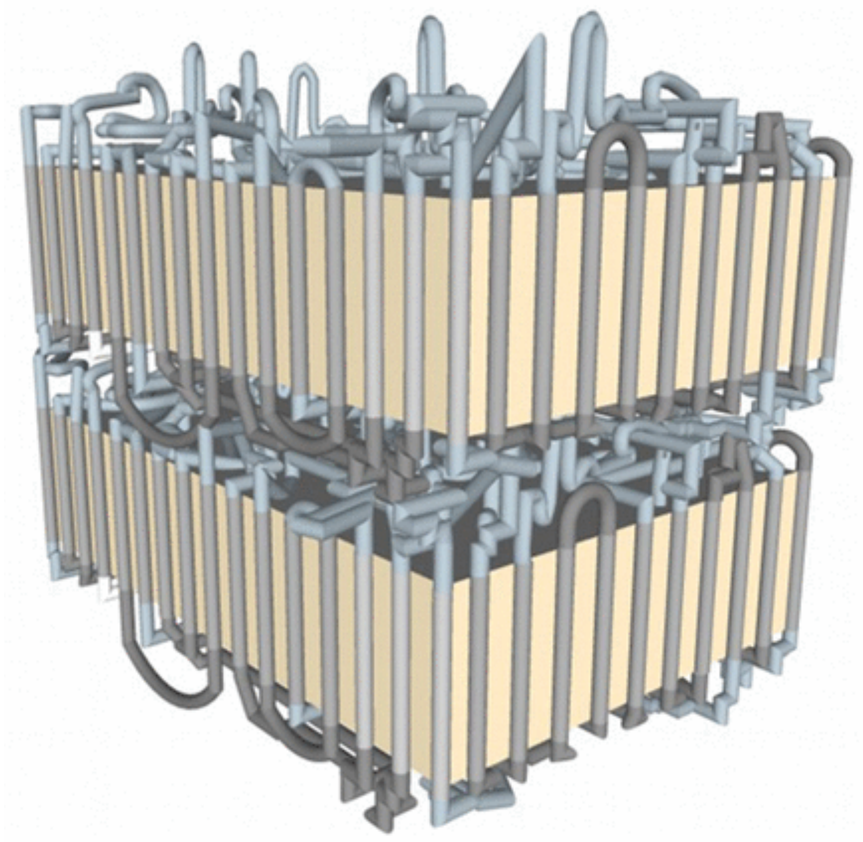
highly branched with many branching points (60/1000 carbons)
low crystallinity, low density, film forming

Property	HDPE	LLDPE	LDPE
melting point (°C)	130	120-130	110
degree of crystallinity (%)	80-90	60-70	30-50
density (g/mL)	0.94-0.97	0.92-0.94	0.92
tensile strength (MPa)	32	25	21

- **HDPE and LDPE display vastly different physical properties; separable based on their density!**

Morphology of Semi-Crystalline Polymers

Semi-Crystalline Nature of Polymers



crystalline lamella

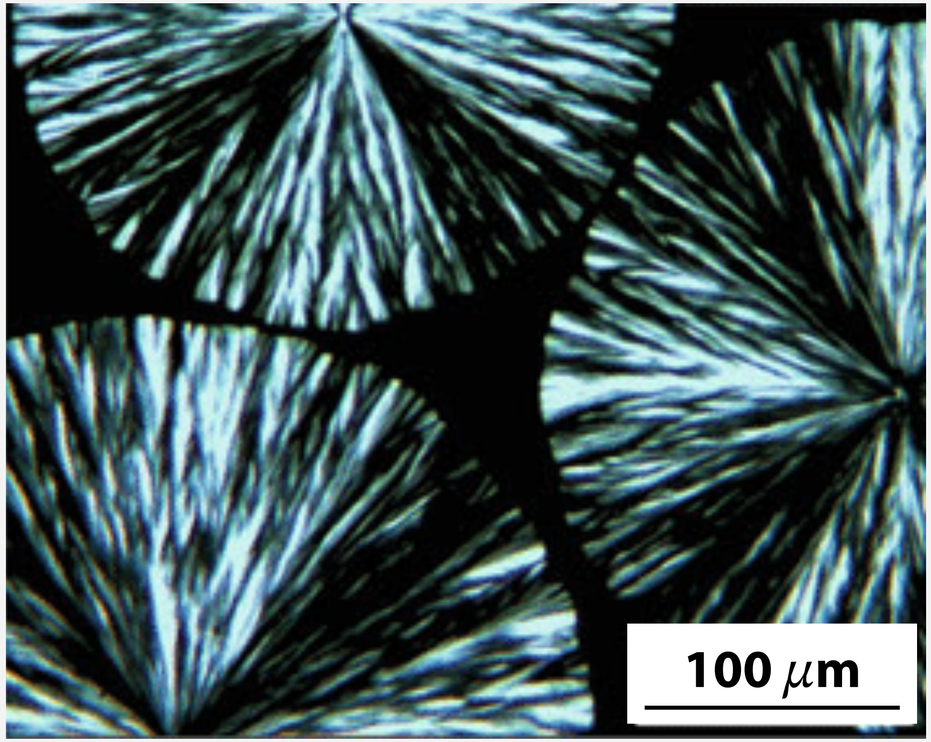
amorphous matrix

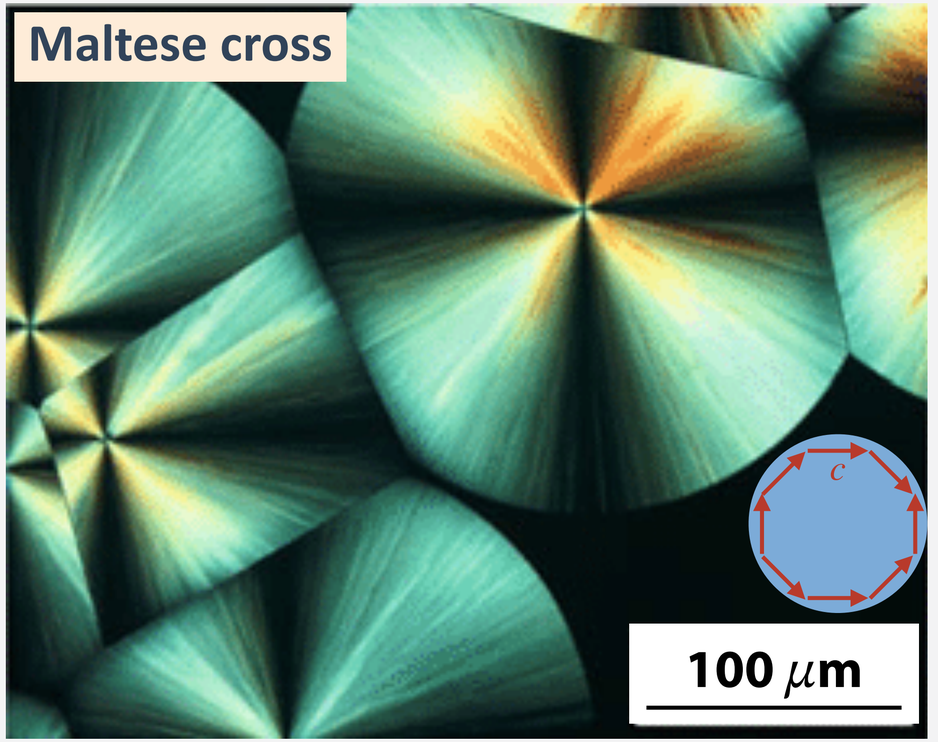
crystalline lamella

- **typical crystallinity: 30-60%. Remaining part is constituted from the amorphous matrix**
- amorphous matrix can be glassy, rubbery, or fluid depending on T_g and the measurement temperature

Spherulites

- the microstructure of a semicrystalline polymer is typically composed of spherulites, a result of the rather spherical organisation of both amorphous and crystalline matter

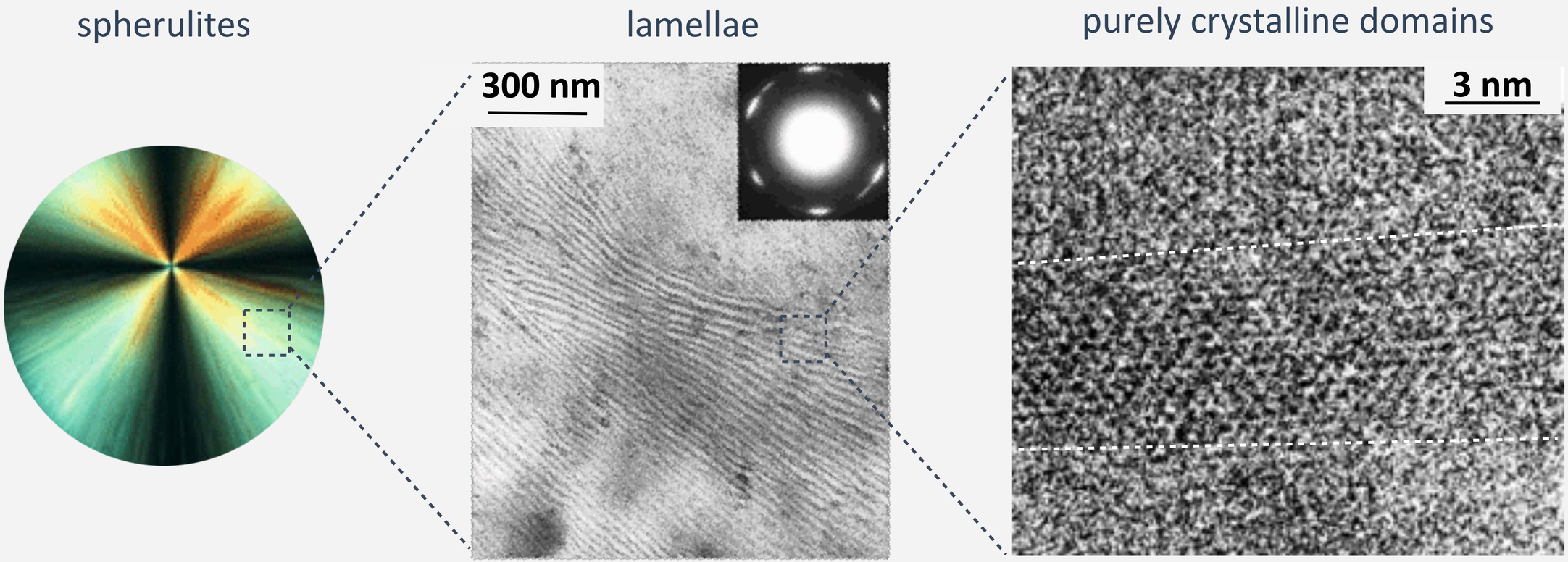




- **birefringence reveals the tangentially oriented crystalline c-axis (polymer chain axis)**
- **generally opaque, but not always (a transparent PET bottle is approximately 30% crystalline)**

Spherulite Structure

- **TEM measurements reveal similar to identical diffraction patterns as for polymeric single crystals**

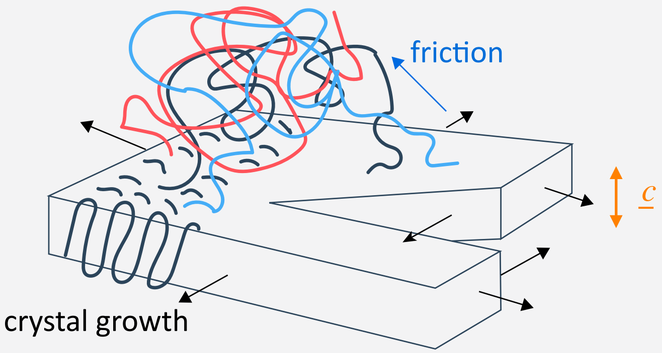


- **lamellae of about 10 nm thickness separated by amorphous layers of similar thickness**
  (depending on the degree of crystallinity)
- **stack of lamellae along the radius of the spherulite**

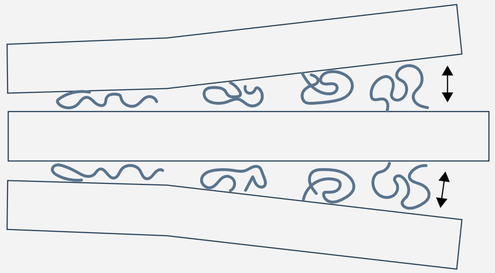
Origin of Spherulites

- friction between growing lamella (low flexural rigidity due to low thickness) and entangled polymer chains of the melt lead to crack and screw dislocation

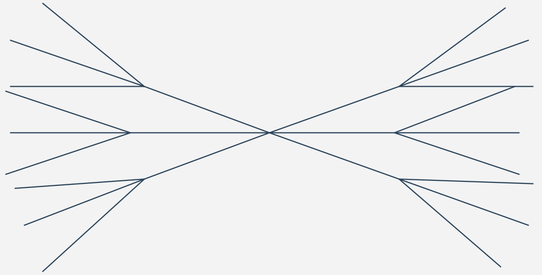
new growth direction

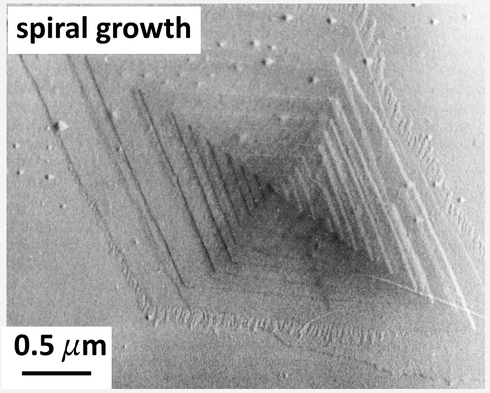


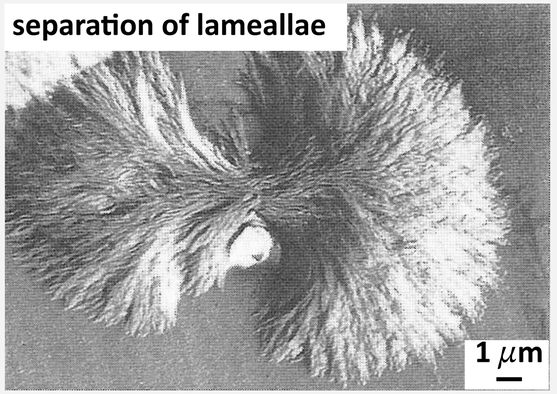
new growth direction

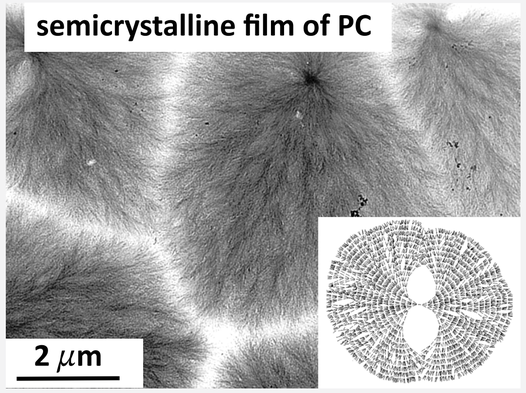


multiple dislocations





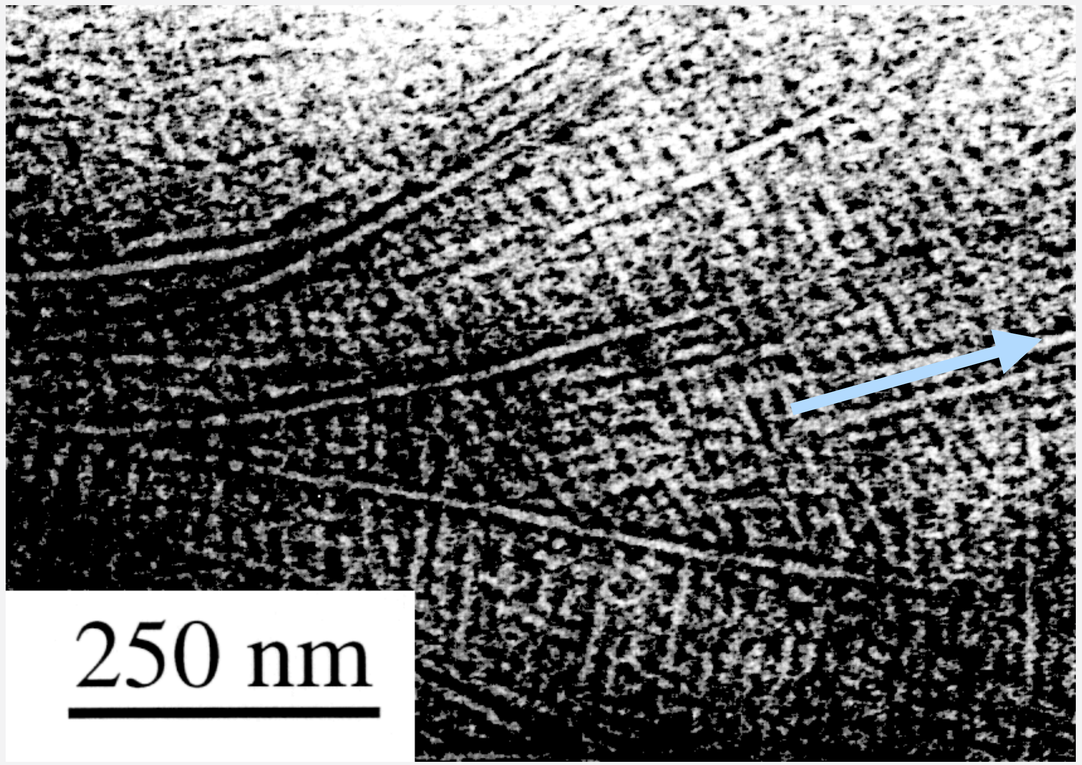




- **lamellae are separated by amorphous layers and are oriented radially**

Twinning

- an unusual but commonly observed spherulitic structure in commercial iPP grades

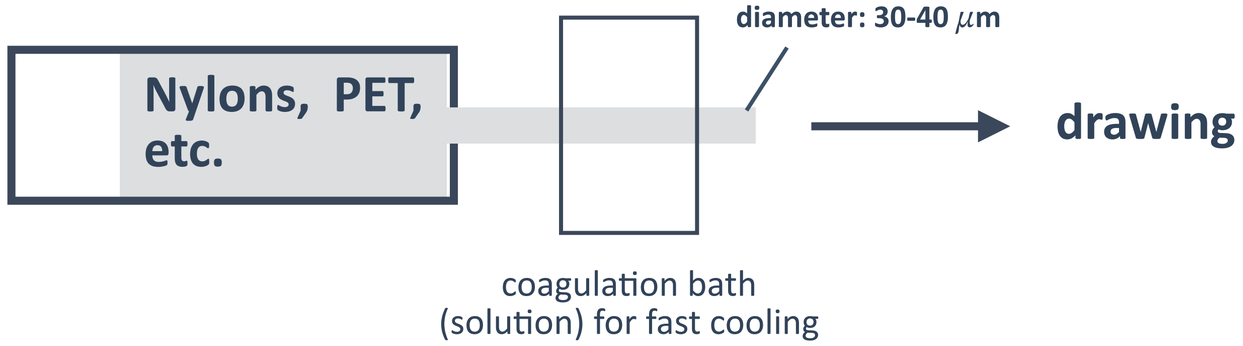


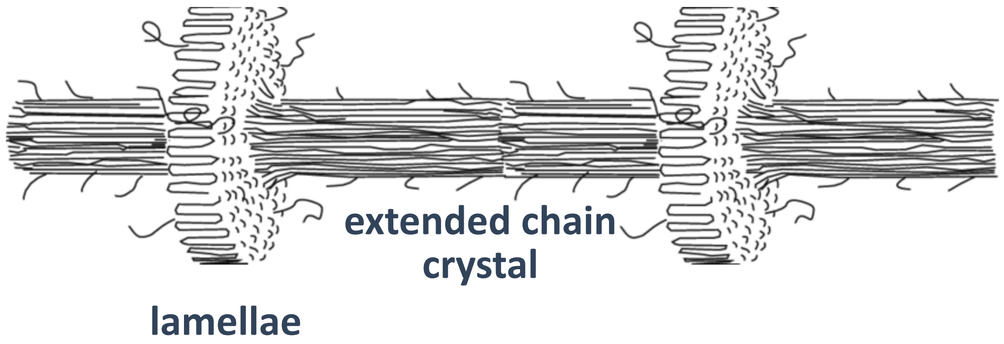
direction of the spherulitic radius

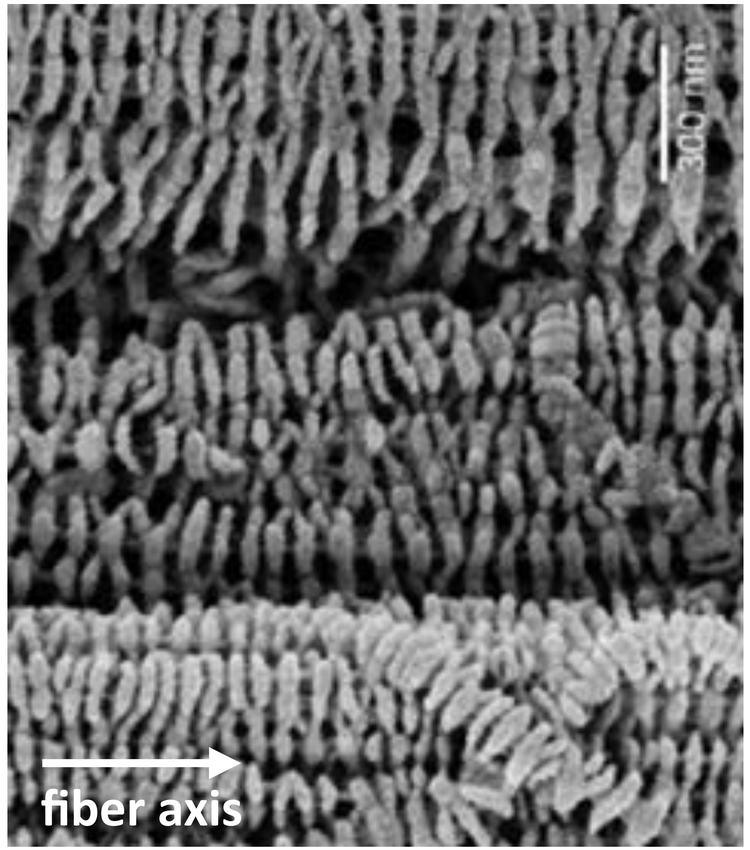
- **multiplication of lamellae by twinning at almost 90° compared to primary lamellae**
- **origin are most likely defects in the regularity of the isotactic sequences**

Shish-Kebab Structures

- conventional fibres exhibit a **“shish-kebab” struture** as a result of high shear forces during processing



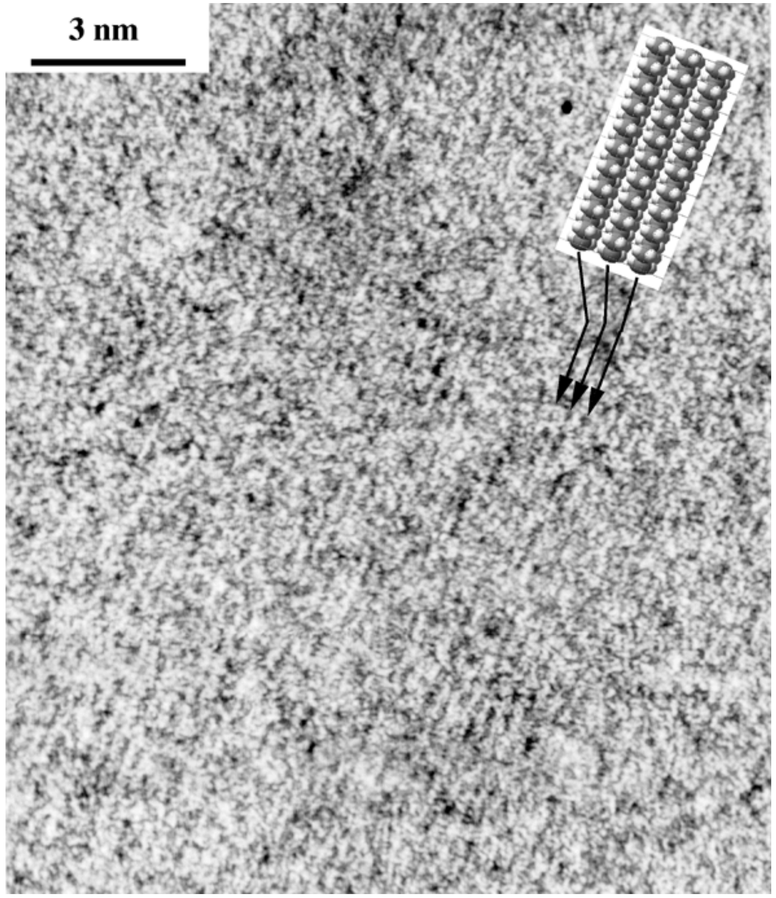




- **during fibre extrusion, lamellae nucleate and grow from an extended chain crystal**

Ultrahigh Molecular Weight PE (UHMWPE)

- fibers formed from linear PE (3’000’000 g/mol) processed from a very dilute gel display extremely high orientation and degree of crystallinity

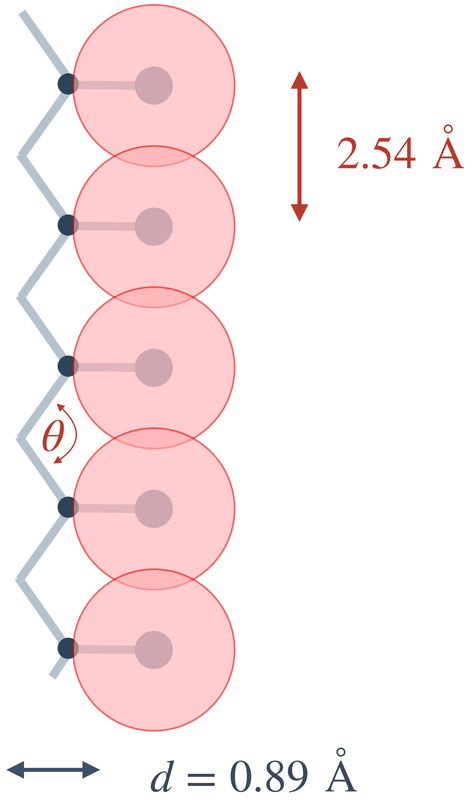


applications

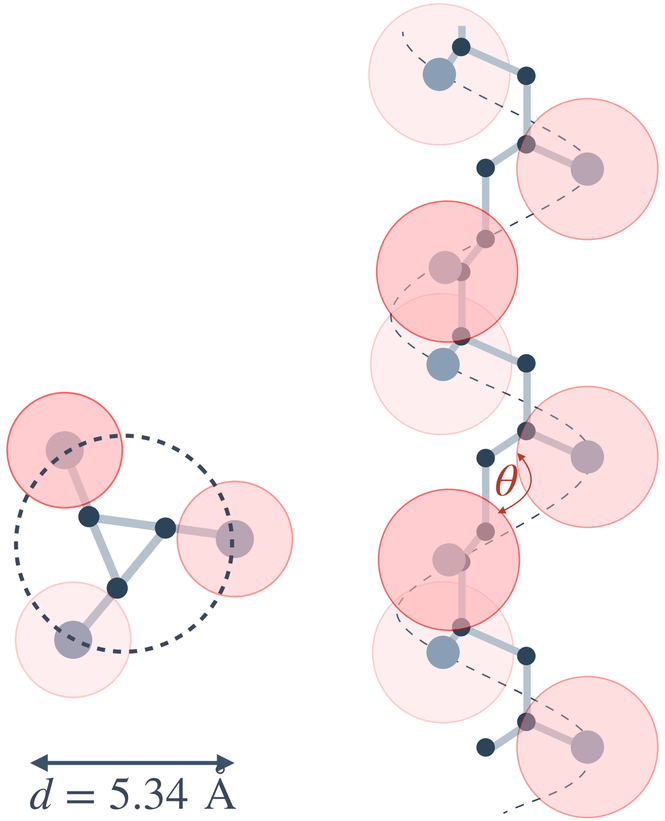
- **mechanical properties comparable to those of inorganic fibers (*E* = 200 GPa, tensile strength: 7 GPa)**

What about Ultrahigh Molecular Weight PP???

isotactic (i.e. PE)



isotactic (i.e. PP, PS)



Learning Outcome

- many polymers are able to crystallize, particularly periodic, linear chains, and those capable of forming linear conformations

- in single crystals, the chains fold to yield monocrystals or “lamellae”. The fold surface energy leads to substantial reduction in melting point.

- the crystallisation rate depends on supercooling and usually exhibits a maximum at some *T* significantly lower than the thermodynamic melting temperature due to competition in nucleation rate and viscosity.

- polymers crystallised from the melt are semicrystalline (often around 50%) and predominantly form spherulites, whereas specific processing ways lead to stacked lamellae (fibers) or extended chain structures (UHMWPE).