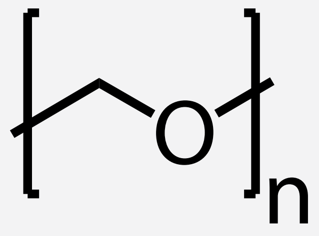
3.3

The Crystalline State

Conformations in the Crystalline State

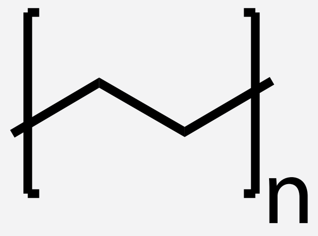
Which Polymers Crystallize?



polyoxymethylene

$T_g = -65\ ^{\circ}C$

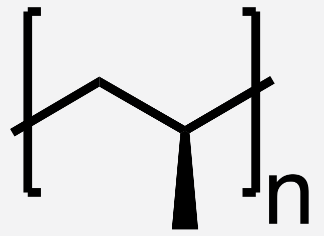
$T_m = 175\ ^{\circ}C$



polyethylene

$T_g = -100\ ^{\circ}C$

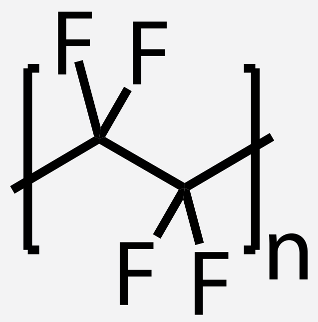
$T_m = 130\ ^{\circ}C$



isotactic polypropylene

$T_g = -10\ ^{\circ}C$

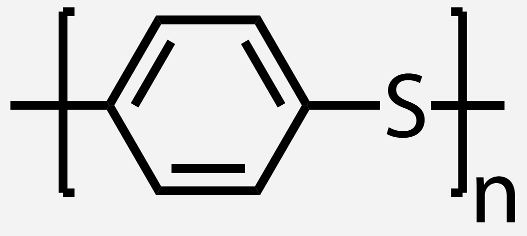
$T_m = 160\ ^{\circ}C$



polytetrafluoroethylene

$T_g = 115\ ^{\circ}C$

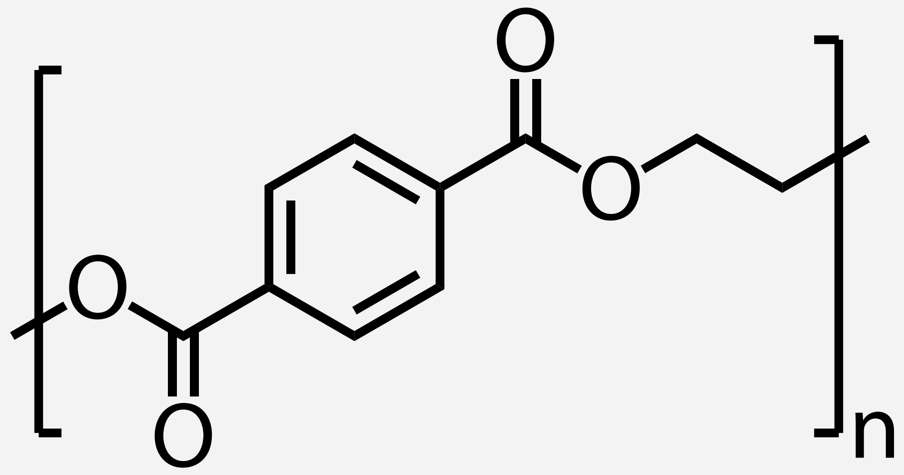
$T_m = 327\ ^{\circ}C$



polyphenylenesulfide

$T_g = 90\ ^{\circ}C$

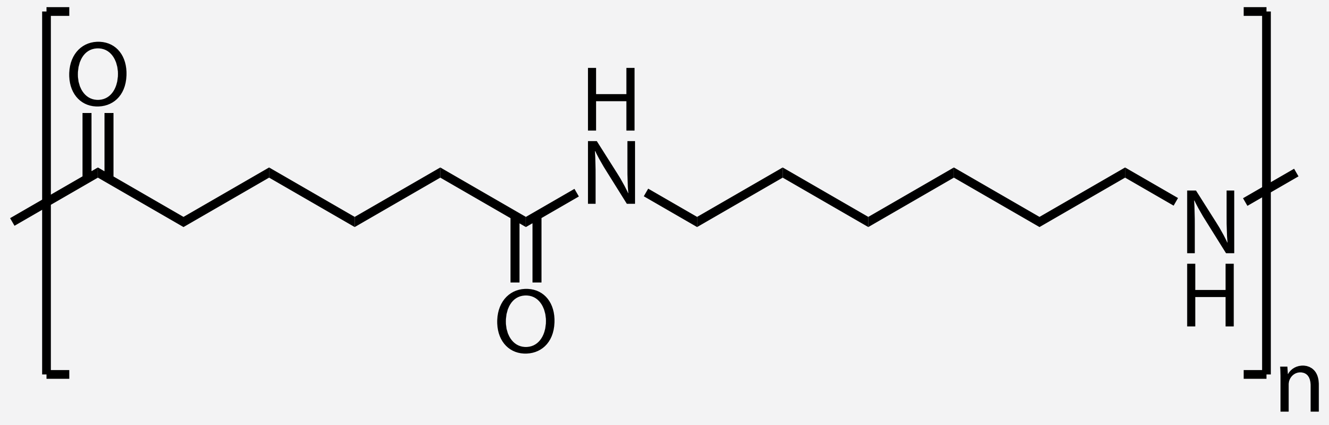
$T_m = 285\ ^{\circ}C$



PET

$T_g = 70\ ^{\circ}C$

$T_m = 260\ ^{\circ}C$



Nylon 6,6

$T_g = 50\ ^{\circ}C$

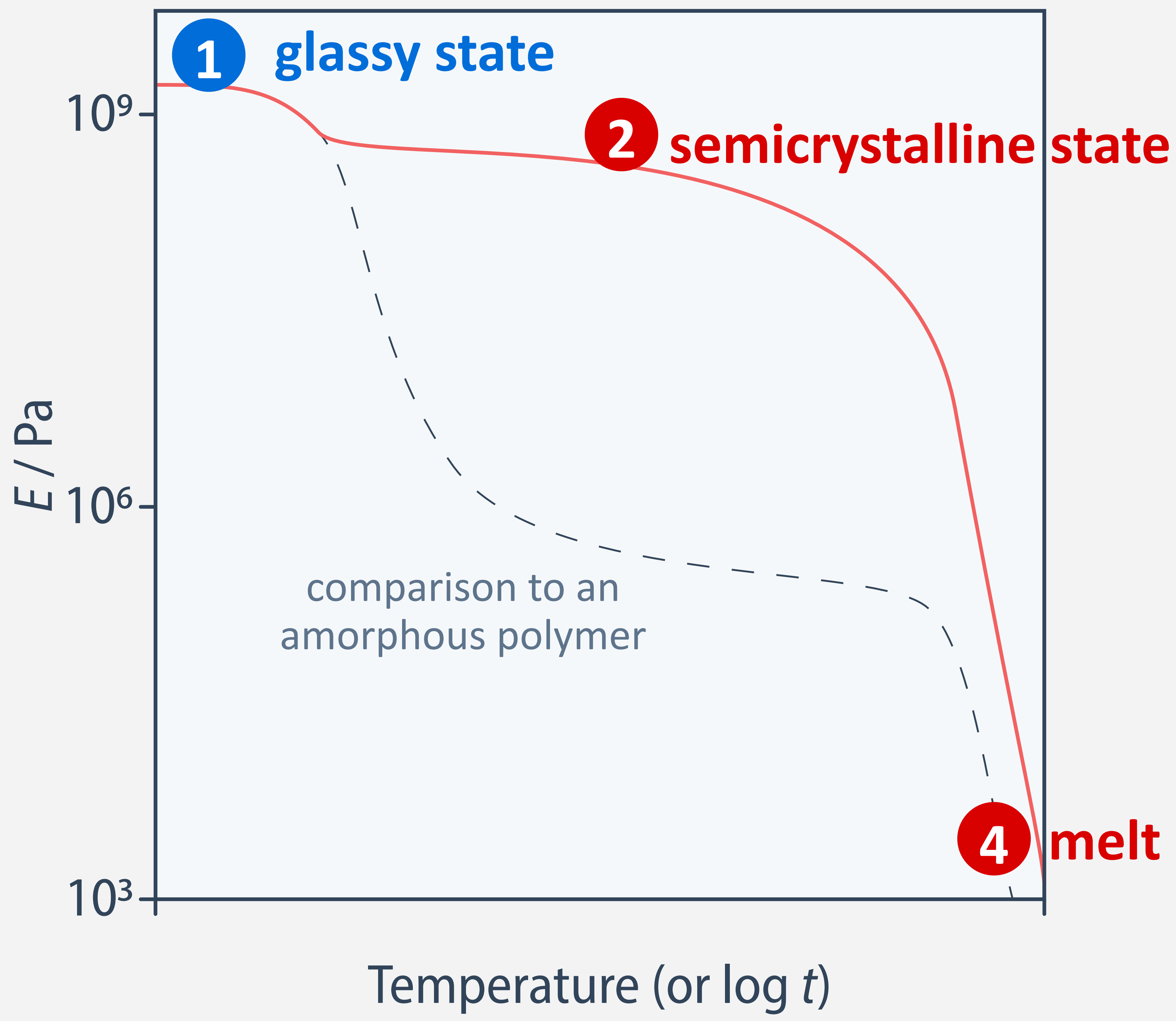
$T_m = 265\ ^{\circ}C$

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

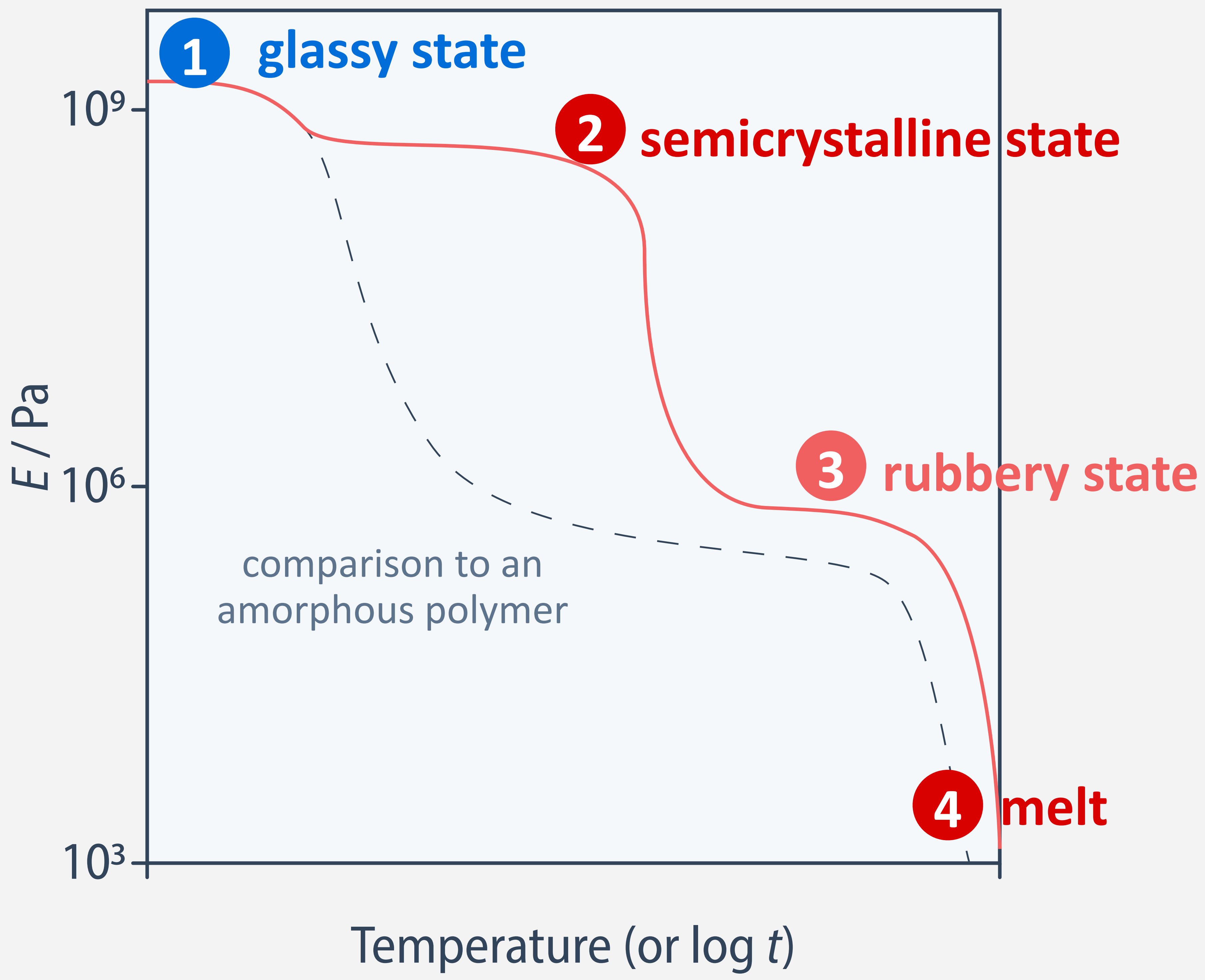
Mechanical Properties of Semicrystalline Polymers

- **semicrystalline polymers show stiffness (Young's modulus) similar to glassy polymers**

high T_m



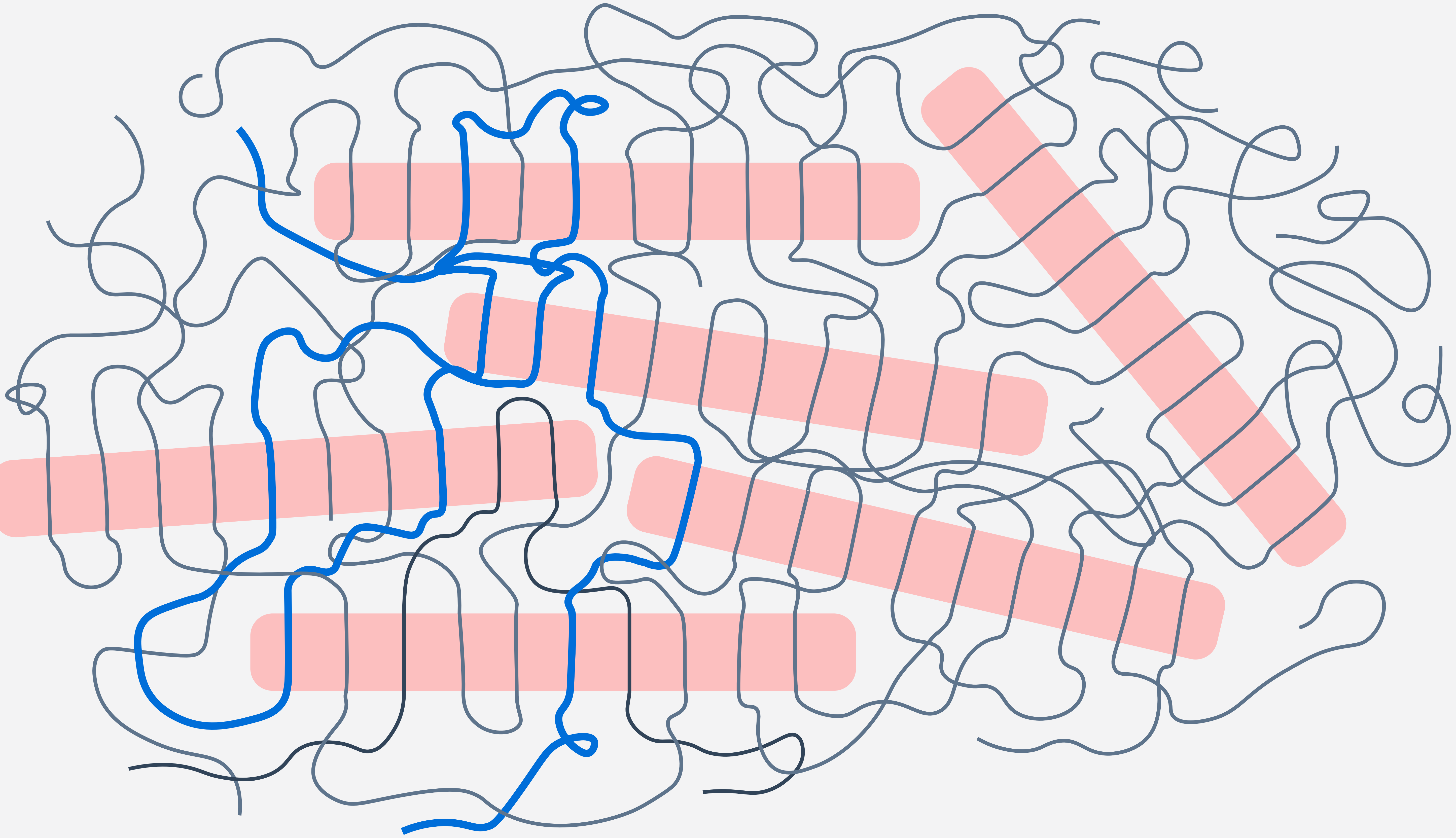
T_m close to T_g
(or sufficiently high molar mass)



- **the absolute value of *E* in the crystalline state increases with degree of crystallinity**

Semicrystalline Nature of Polymers

- one chain can participate in multiple lamellae (chain folding, tie chains)

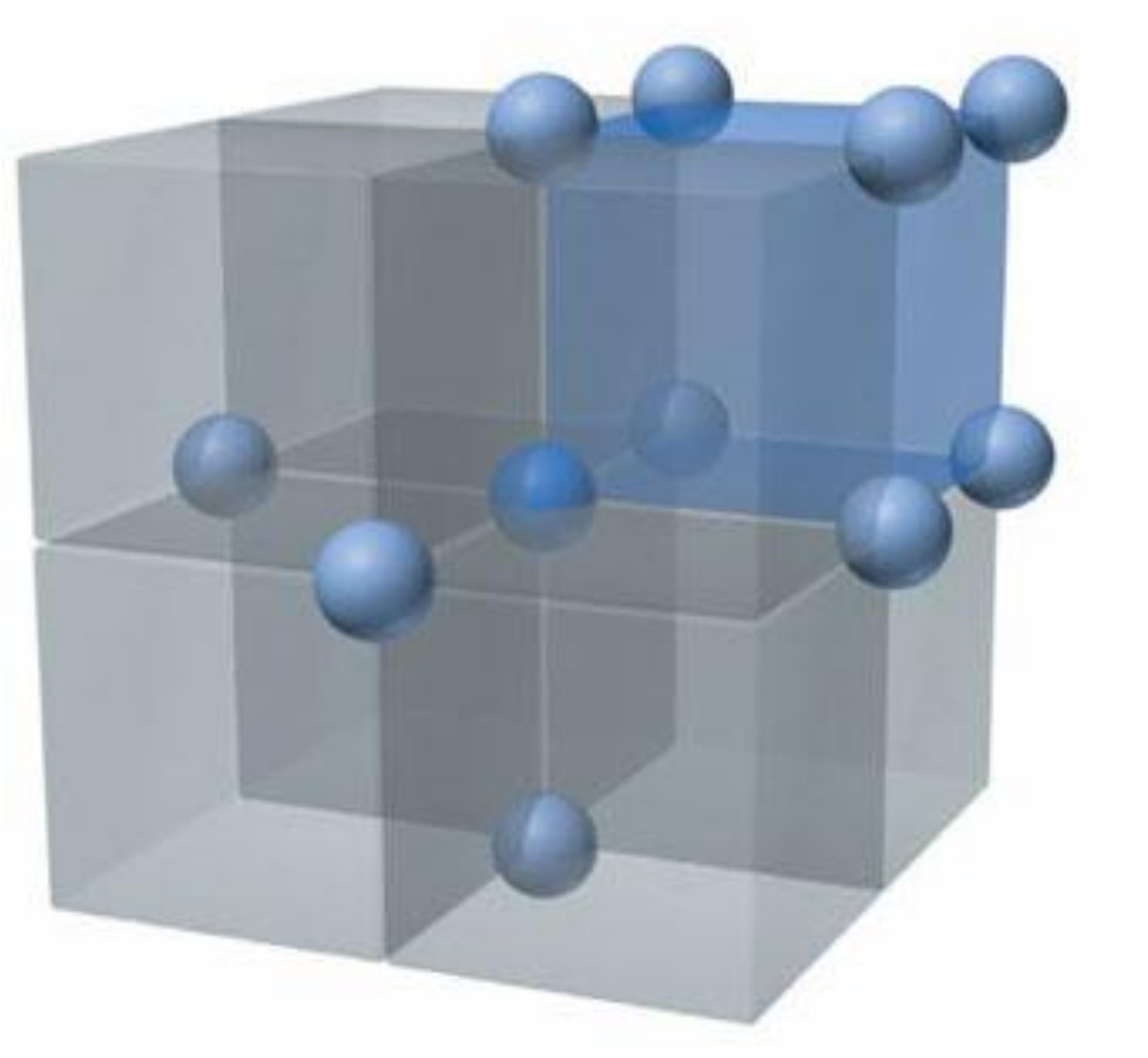


- **interlamellar regions are amorphous: No polymer reaches 100% crystalline under practical conditions!**

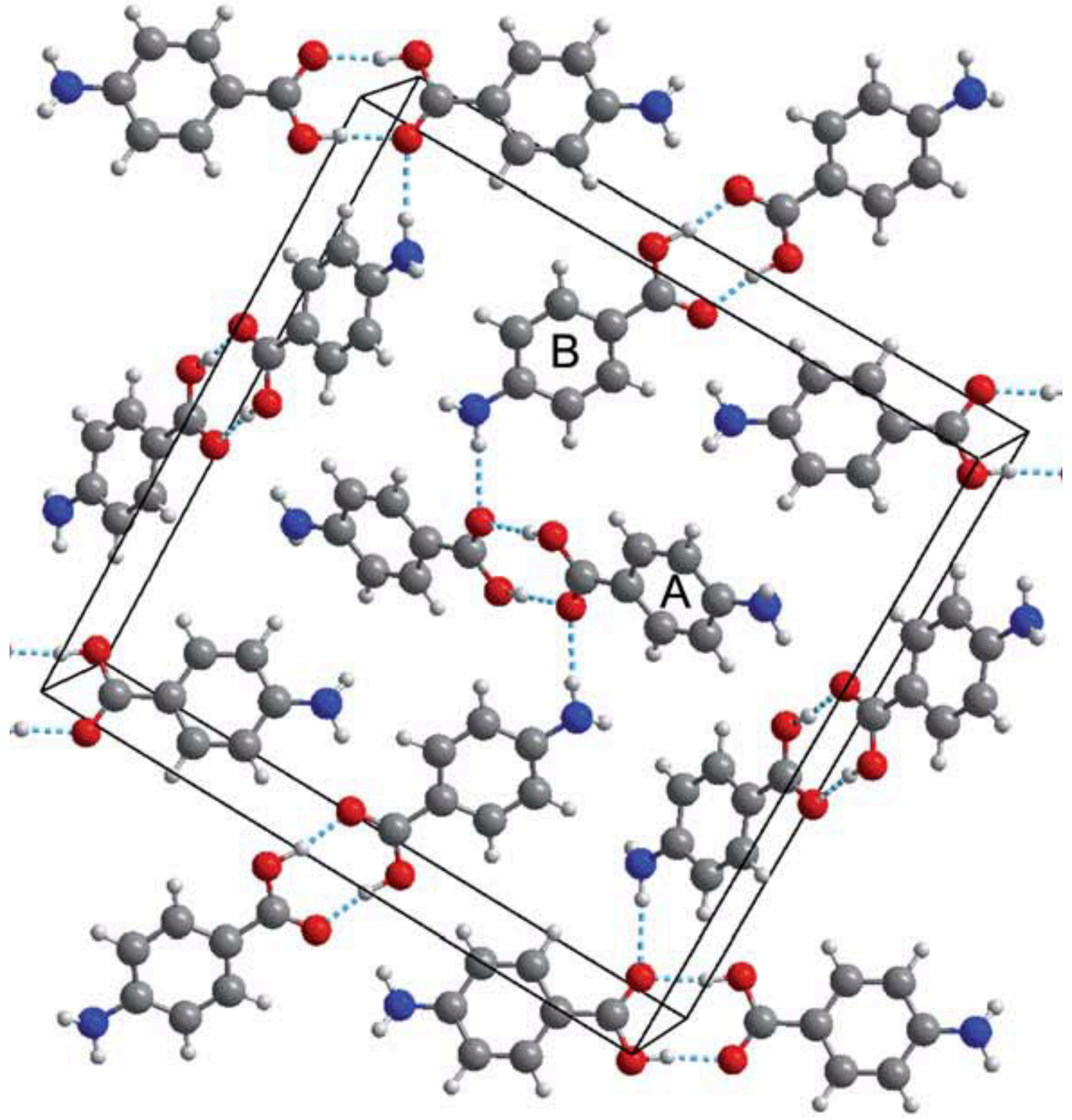
100% Crystalline Entities

- perfect crystals are constituted of a periodic repetition of a unit cell in 3D

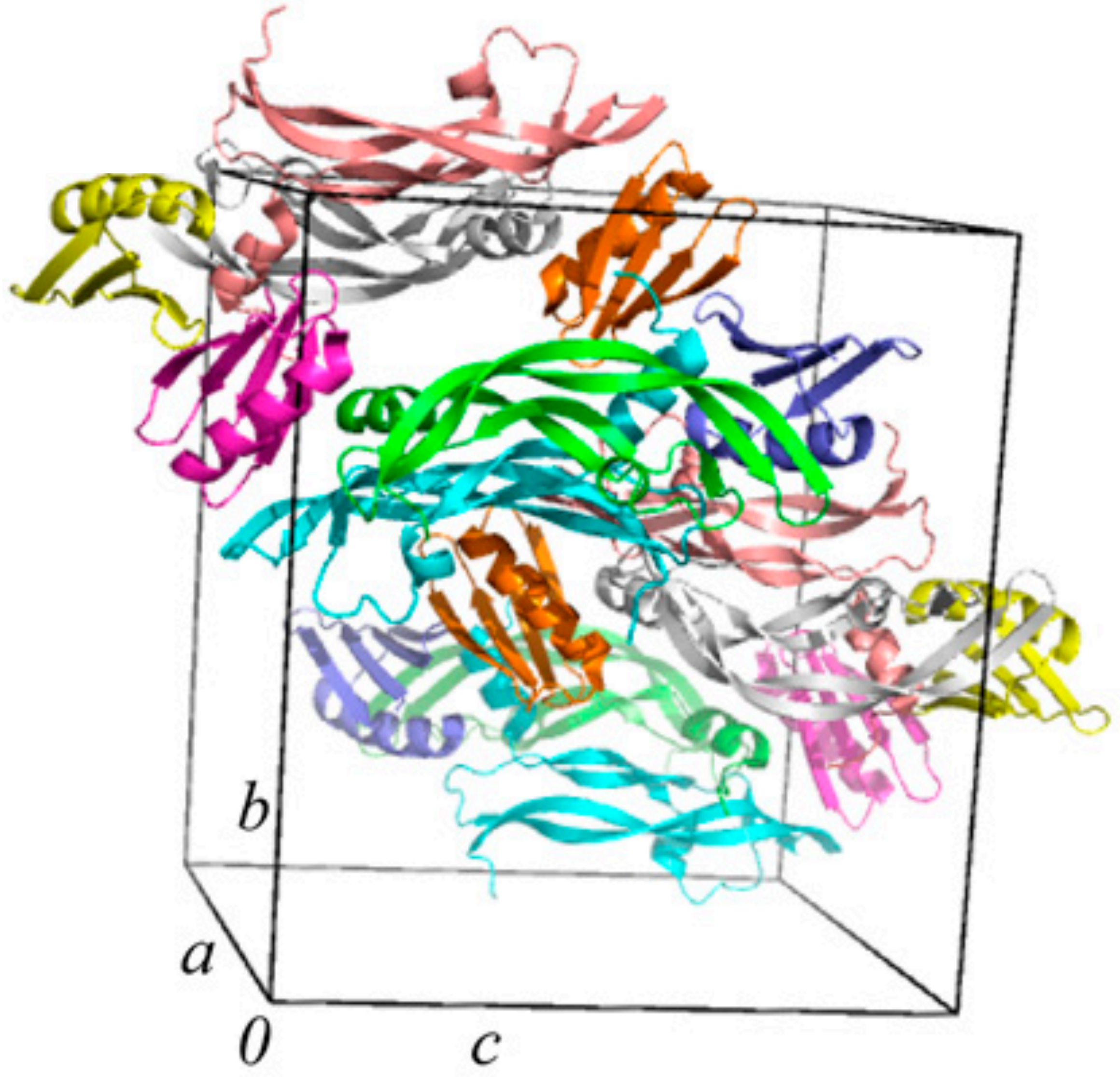
metallic crystals



molecular crystals



protein crystals

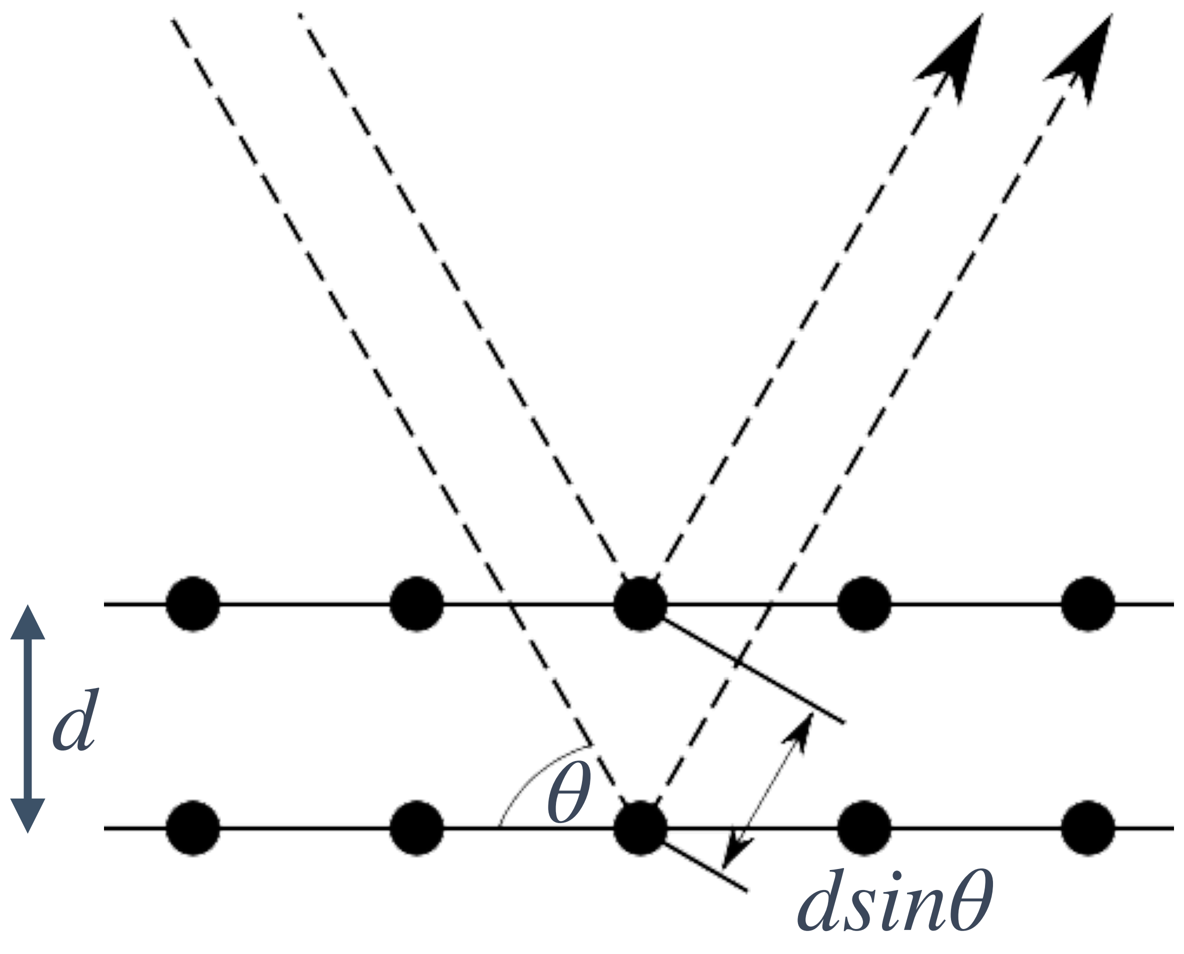


- **such "near 100% crystallinity" (few defects) is needed for crystal structure determination with atomic resolution**

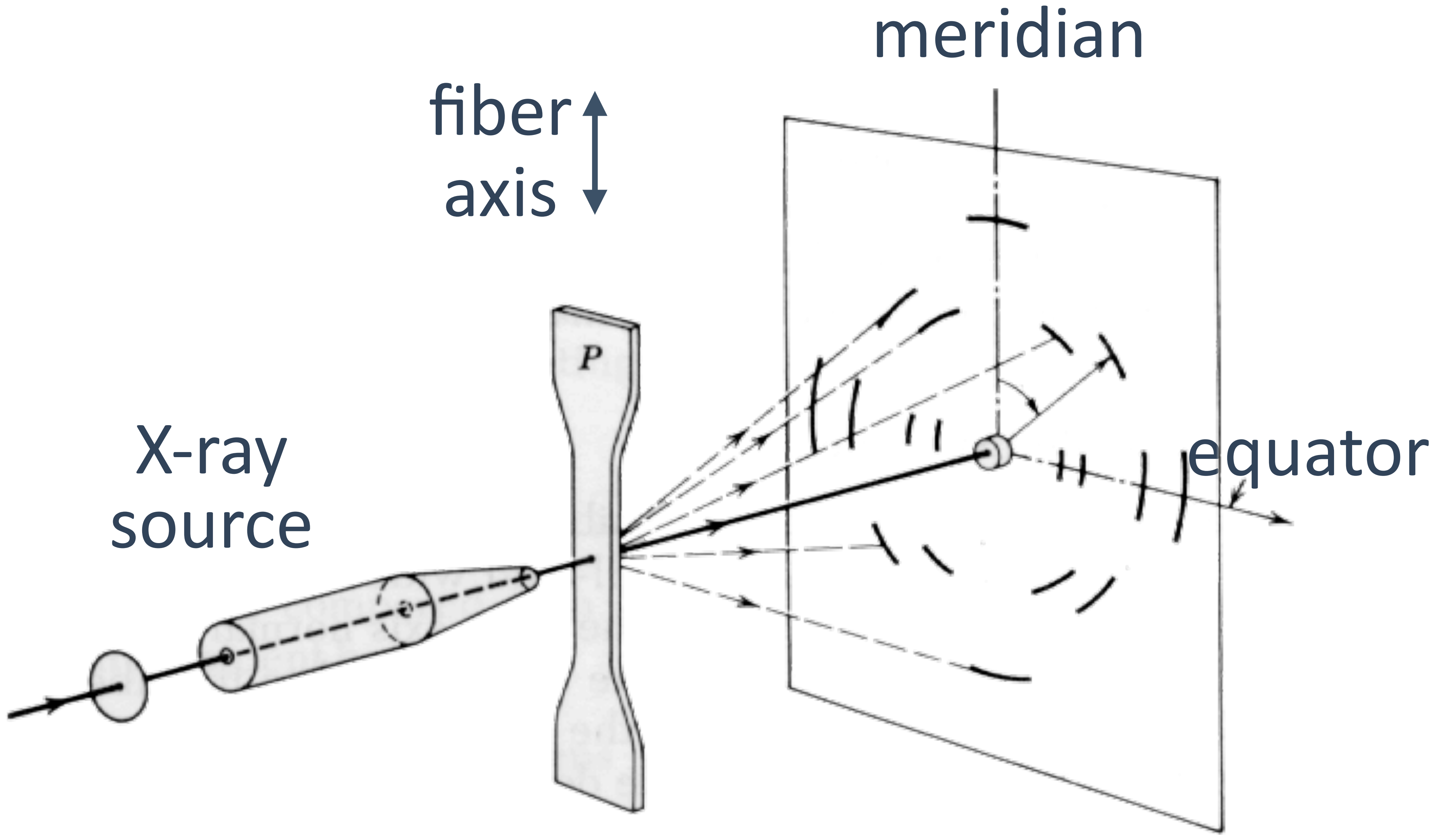
Bragg's Law

- **Constructive interference of X-rays by crystal planes is described by Bragg's law:** $2dsin\theta = n\lambda$

diffraction
(at ordered structures)



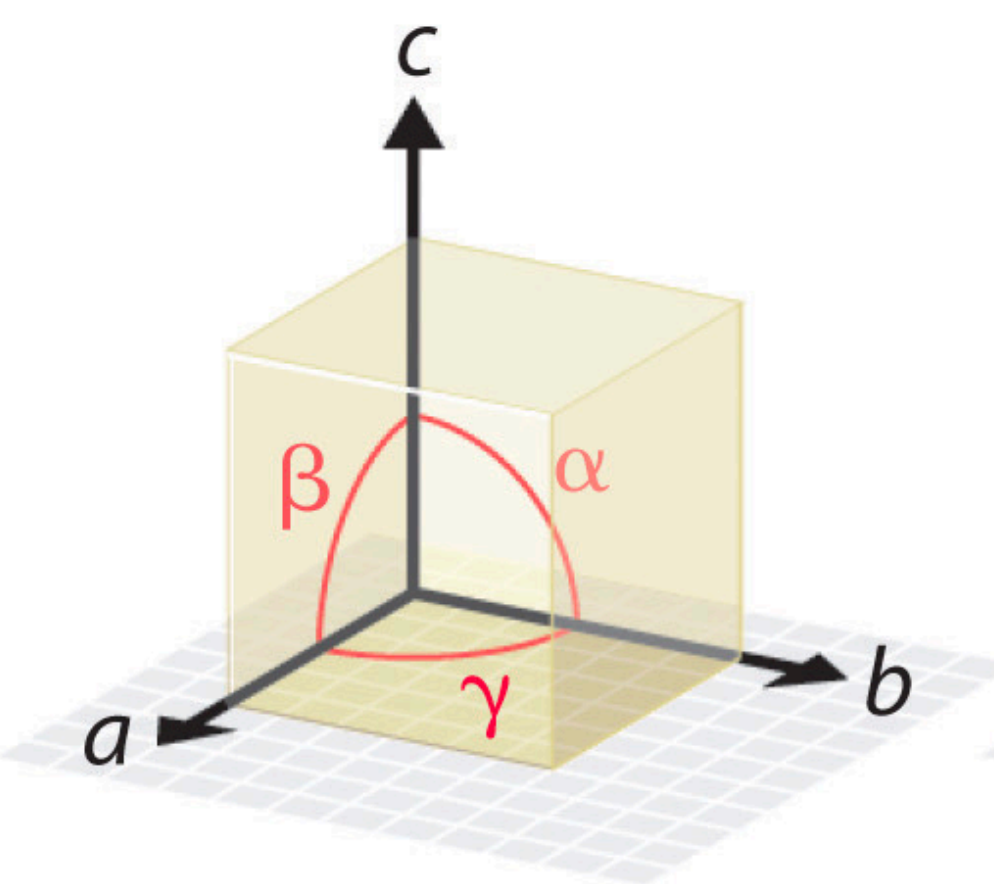
diffractogram
(oriented specimen)

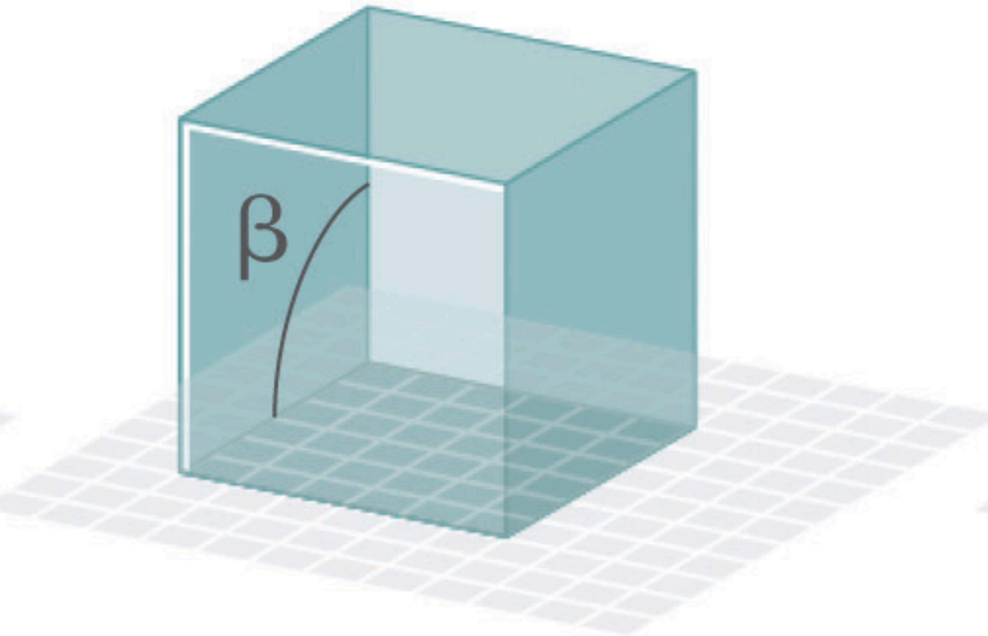


compare with **Slide 138**

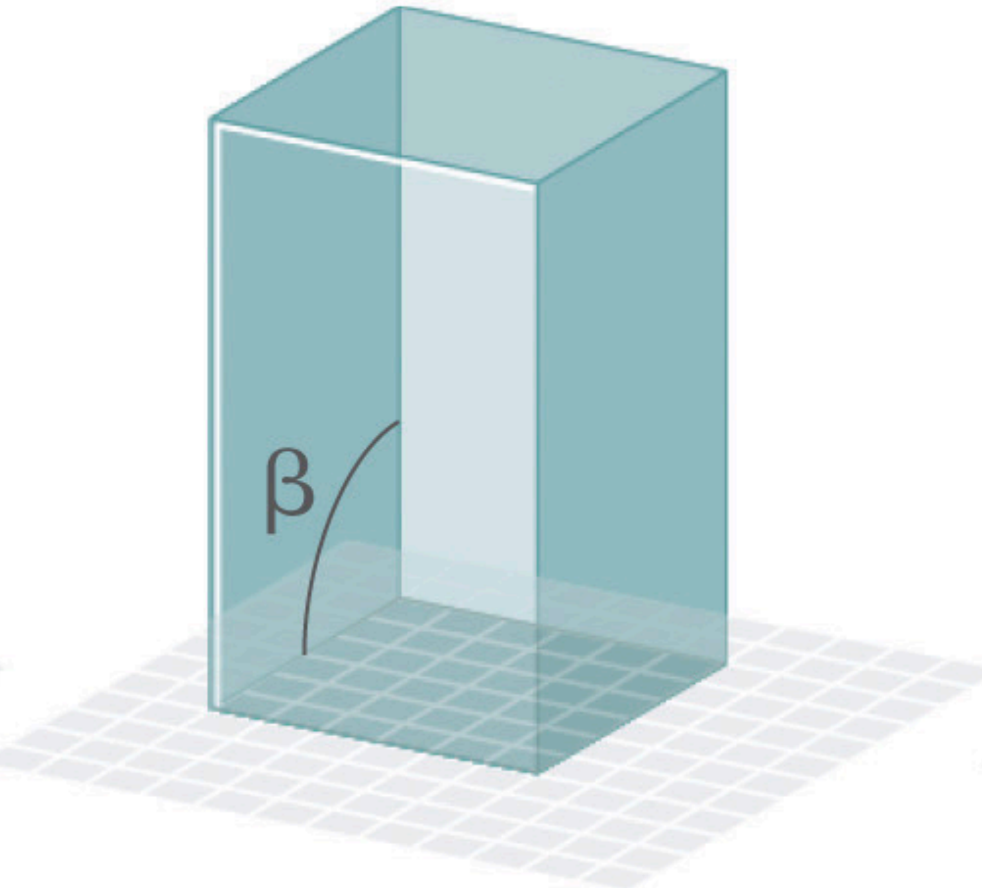
- **polymer diffraction requires oriented (anisotropic) specimens for clear diffraction patterns**

7 Crystal Systems

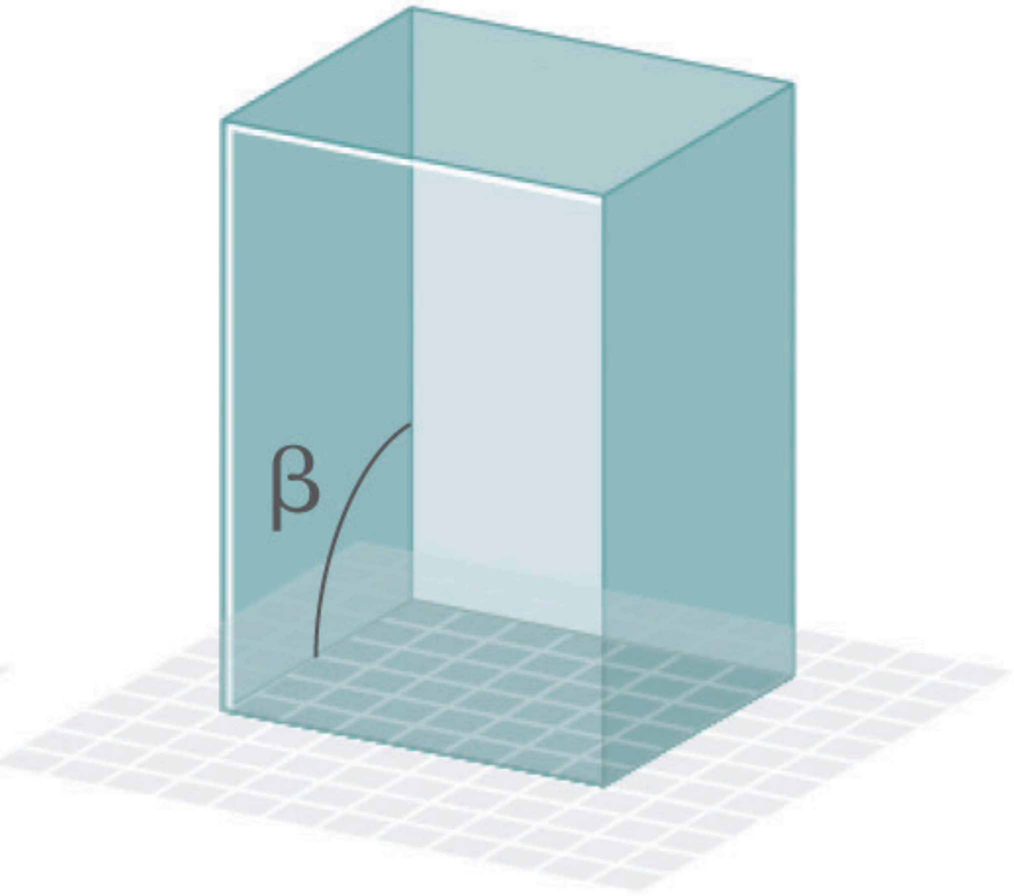




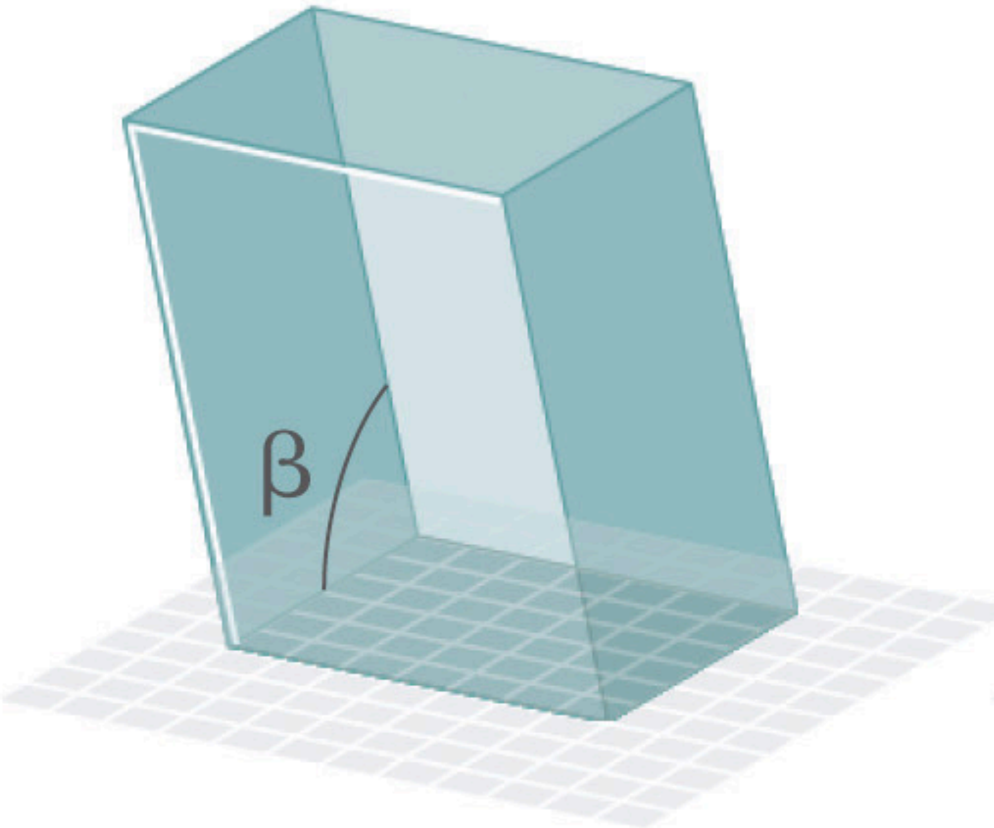
cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$



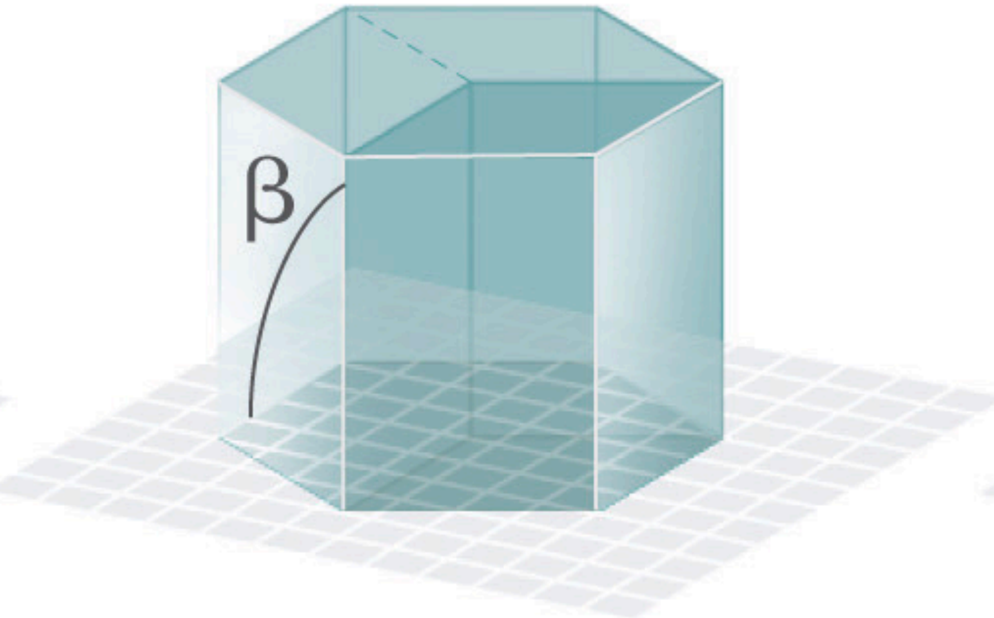
tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



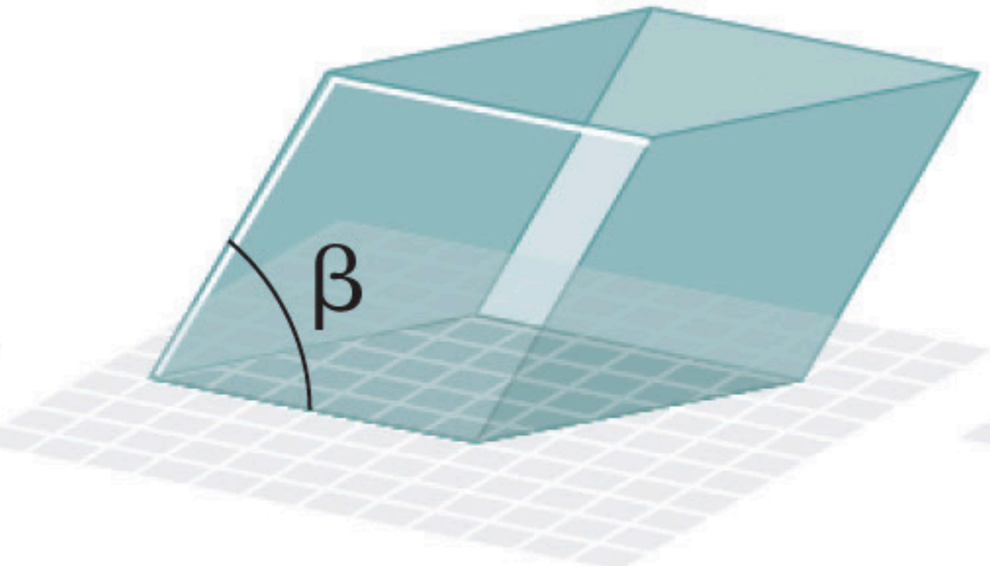
orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



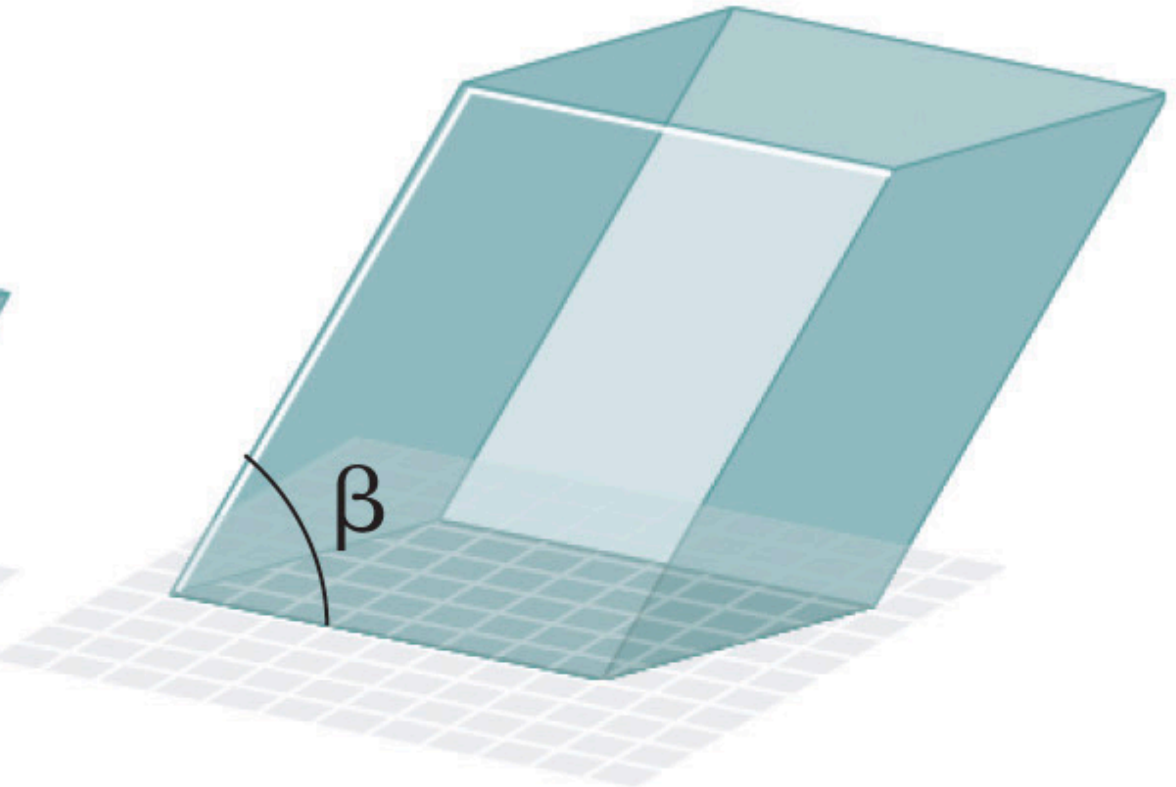
monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90^\circ \neq \beta$



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



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

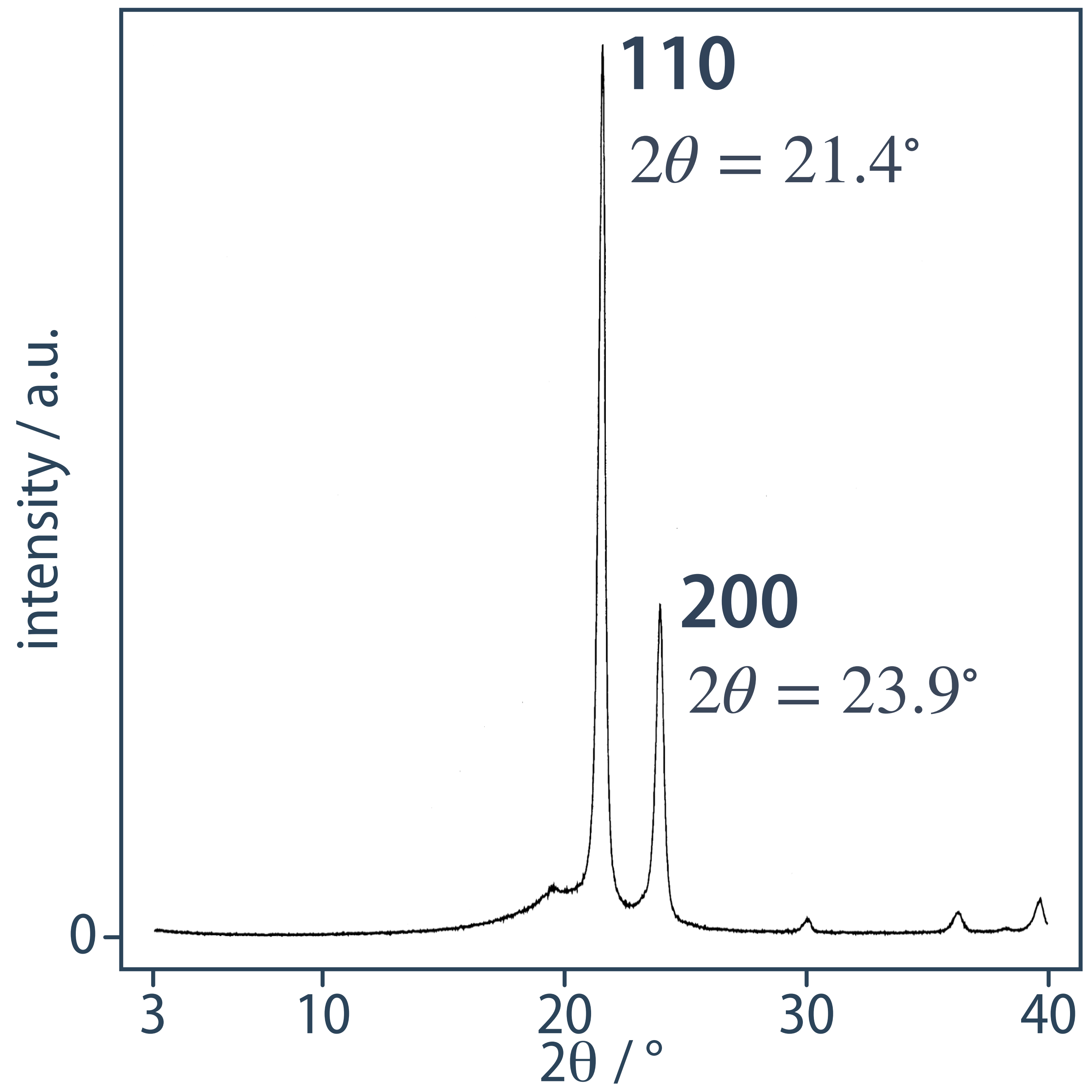


triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$

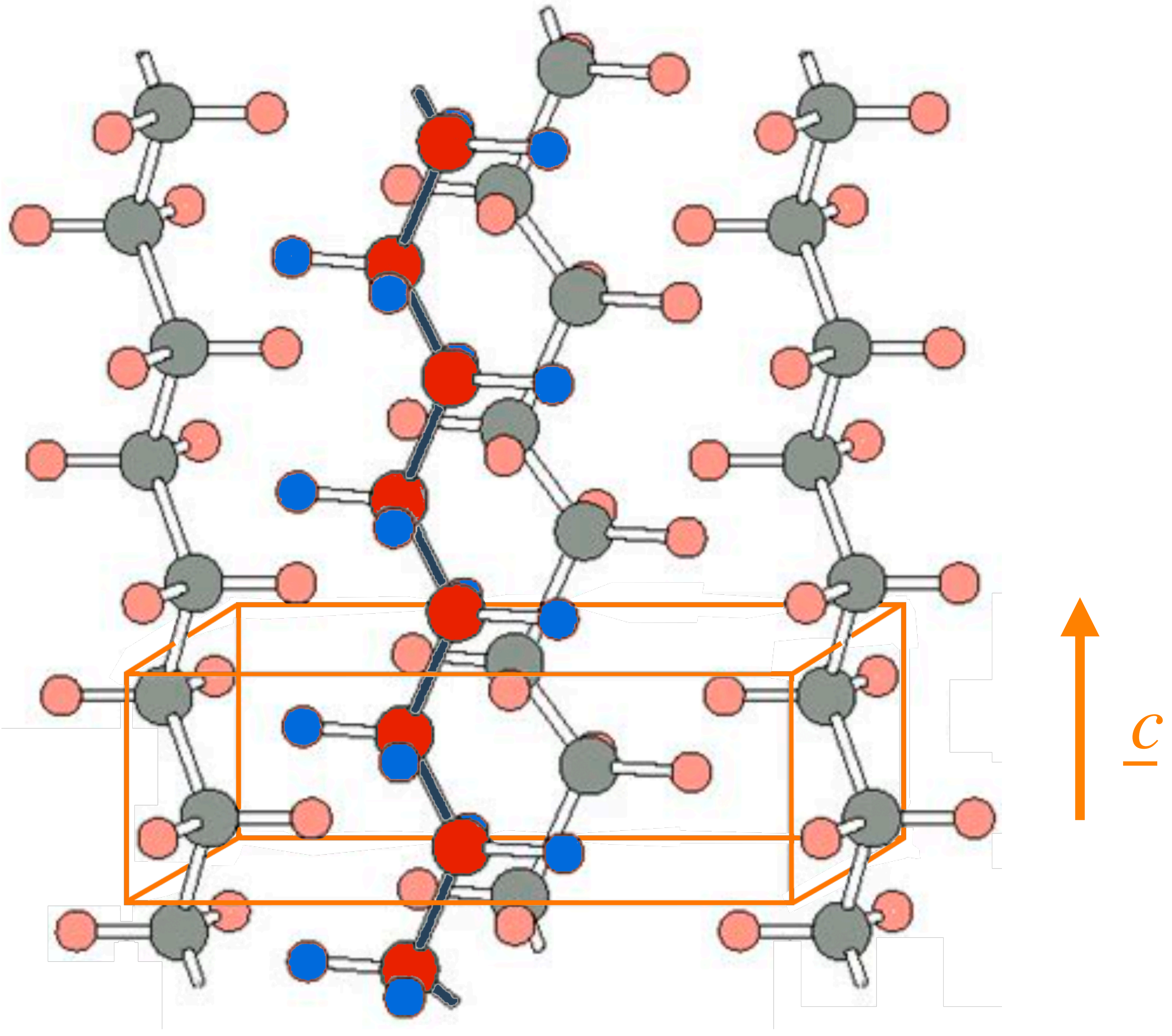
PE Crystal Structure

- by convention, the *c*-axis of the unit cell is aligned with polymer chain axis

diffractogram (PE)



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

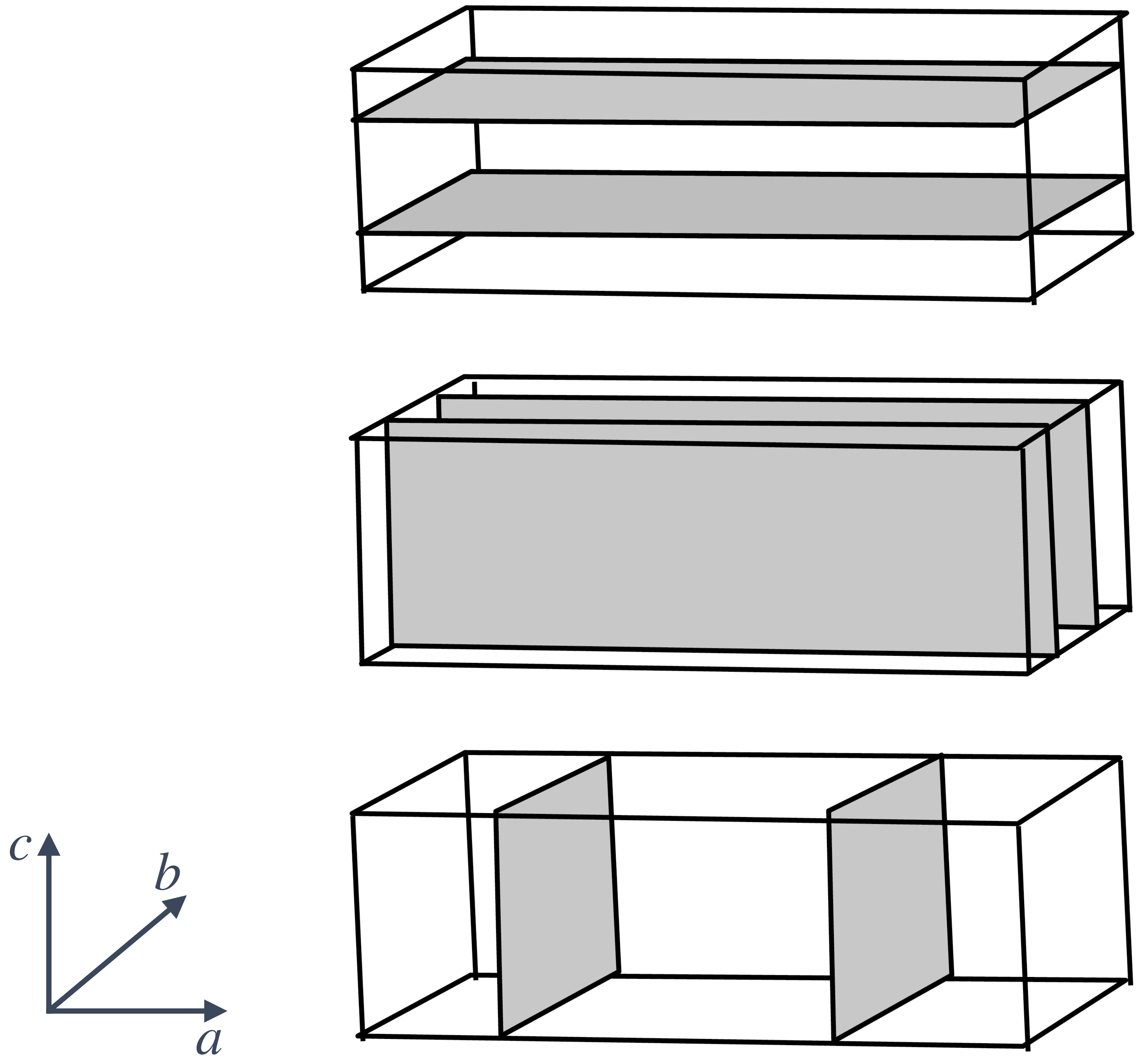


- **a polymer unit cell typically contains several chain segments (exception:biopolymers like proteins)**

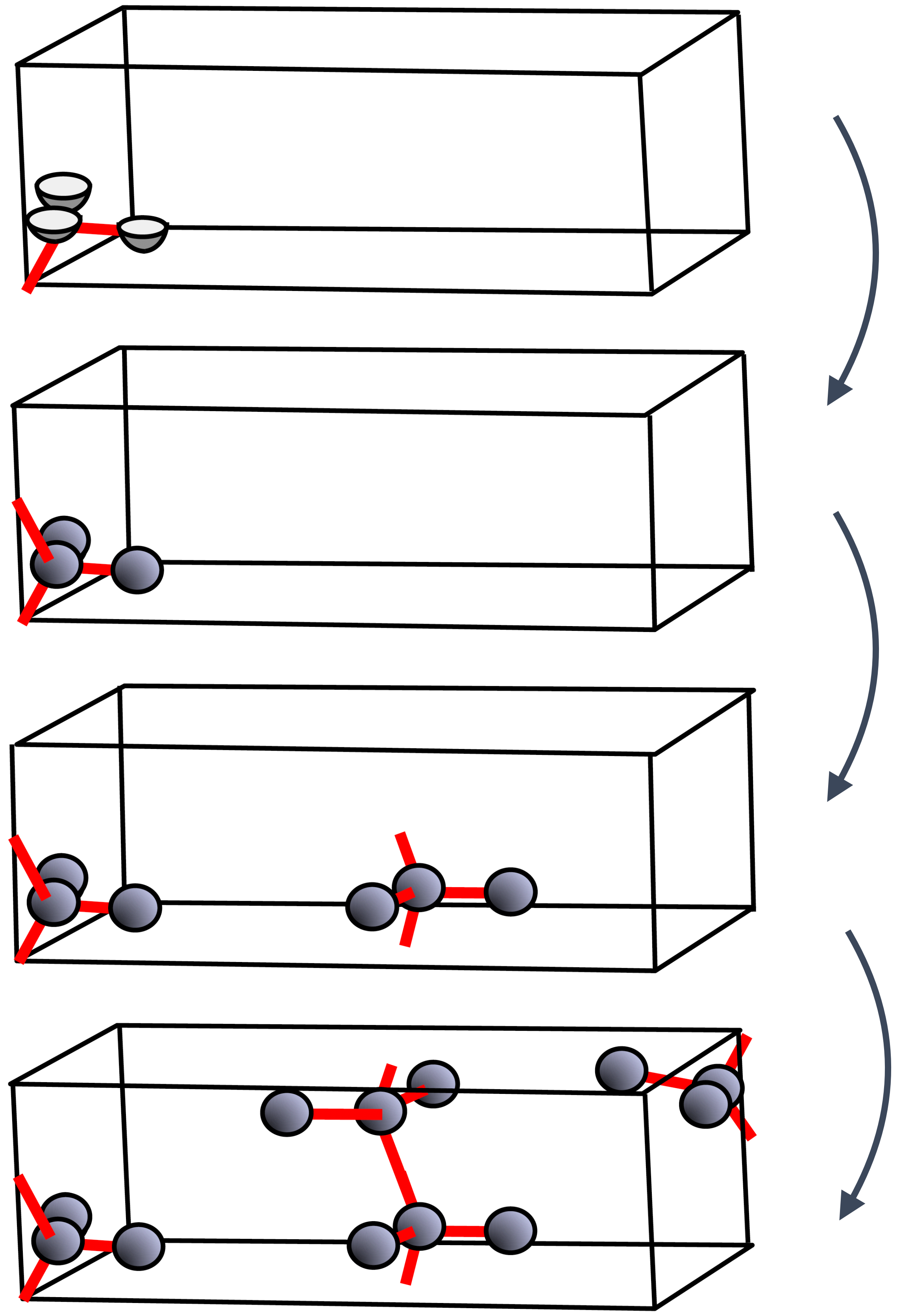
Space Group

- **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 ⊥ $\underline{c}$

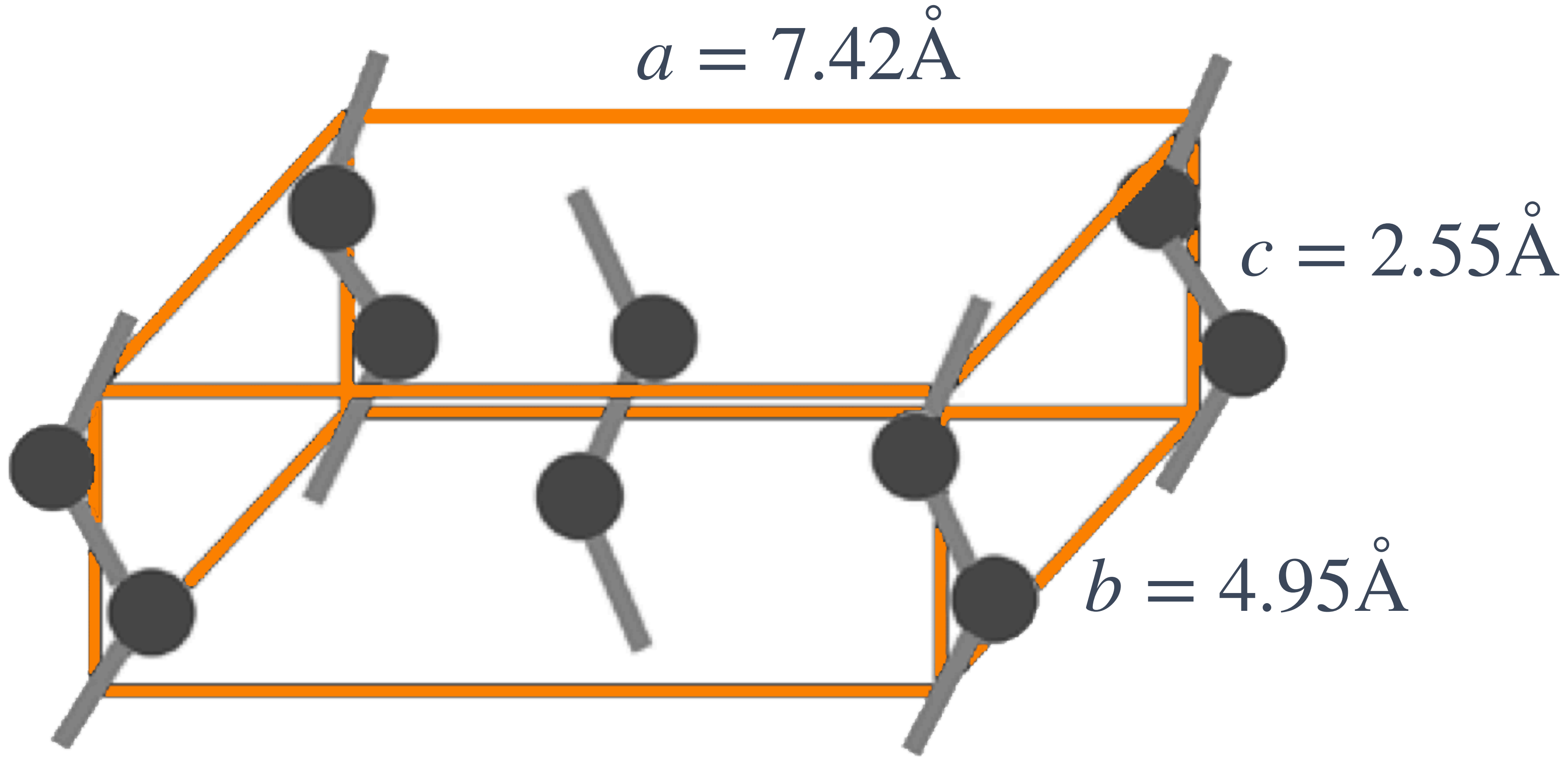
reflexion &
translation $\underline{a}/2$

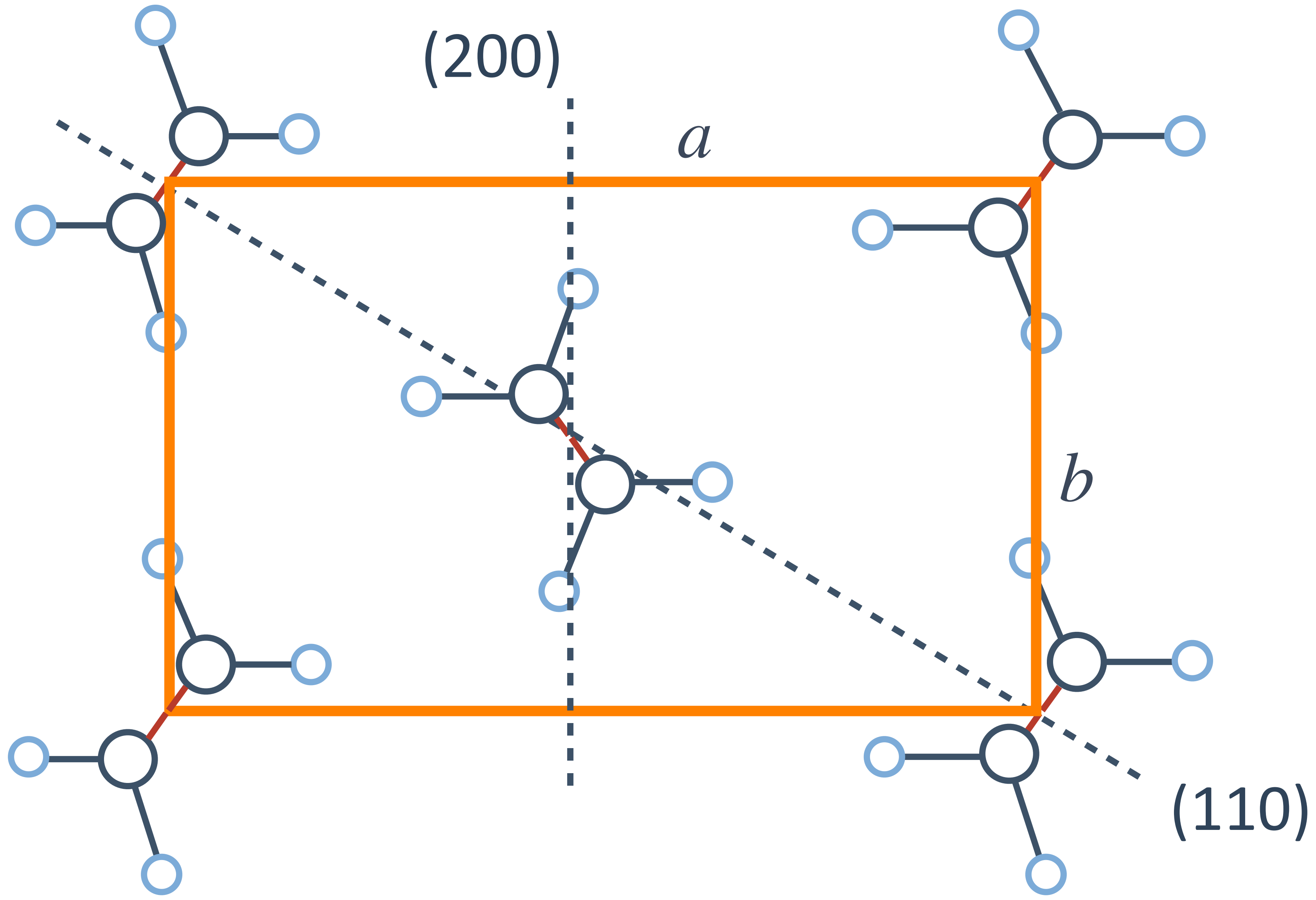
reflexion & translation
$\underline{b}/2$ & $\underline{c}/2$
slip ⊥ $\underline{c}$

PE Unit Cell

- **PE chains adopt a linear zig-zag conformation in the crystal structure**
- viewed along the backbone, such conformations resemble columnar cylinders

orthorhombic unit cell

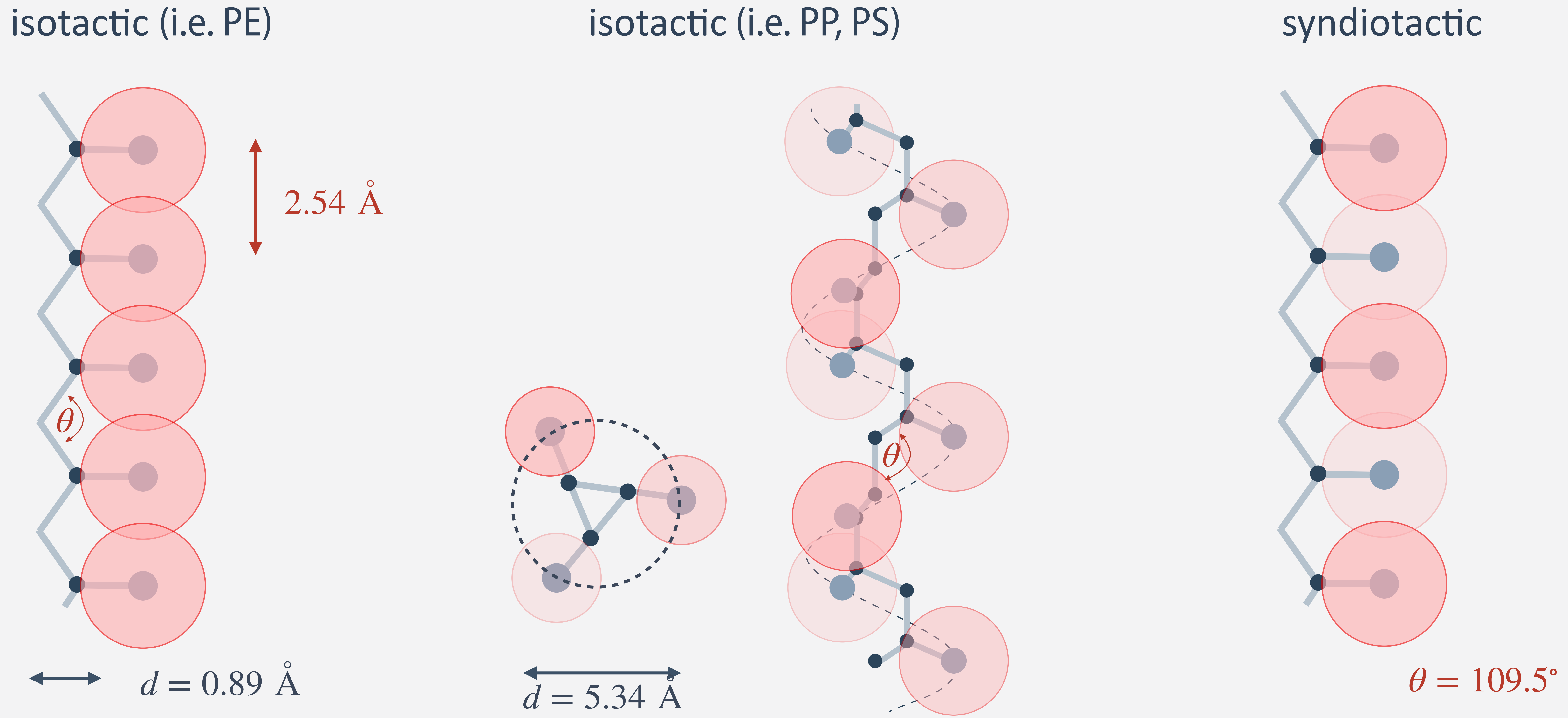




- **cylinders pack in hexagonal or pseudo-hexagonal (orthorhombic) lattices**

Regular Chain Conformations

- **isotactic and syndiotactic polymers crystallise via a regular chain conformations**

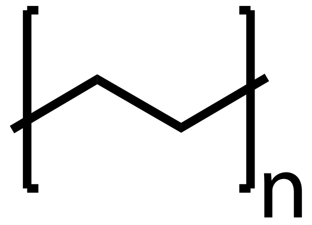


- **helical conformations are obtained when adoption of a zig-zag conformation is sterically hindered**

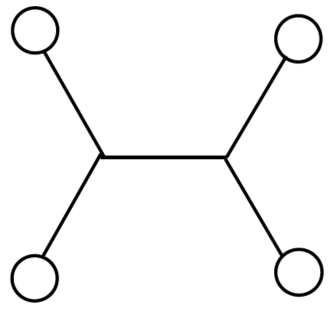
Comparison of PE and PTFE

- **regular “compact” chain conformations pack closely and maximize cohesive energy** E_{coh}

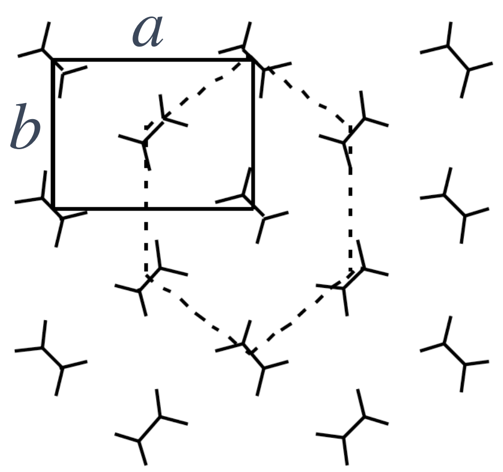
PE:



all-trans conformation

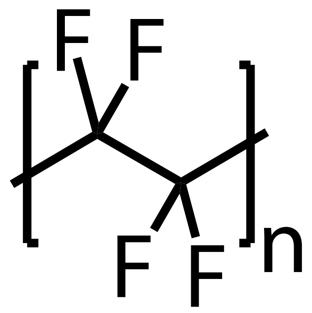


less “cylindrical”

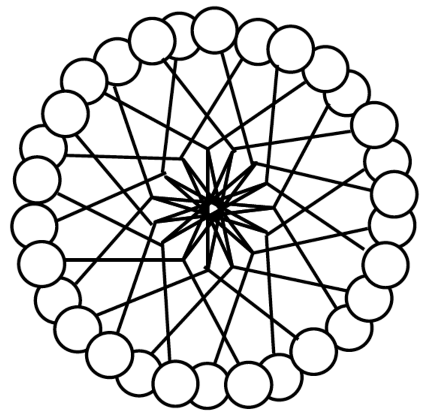


pseudo-hexagonal

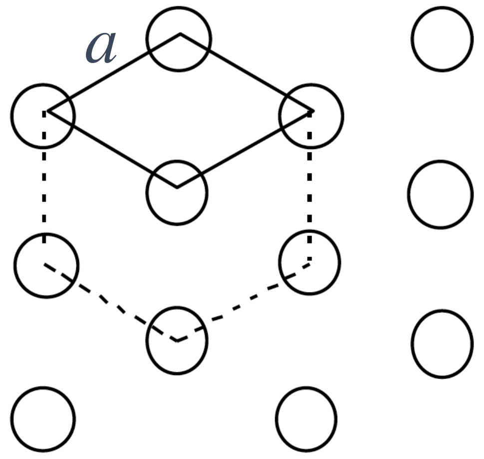
Teflon:



helical conformation



perfect cylinder



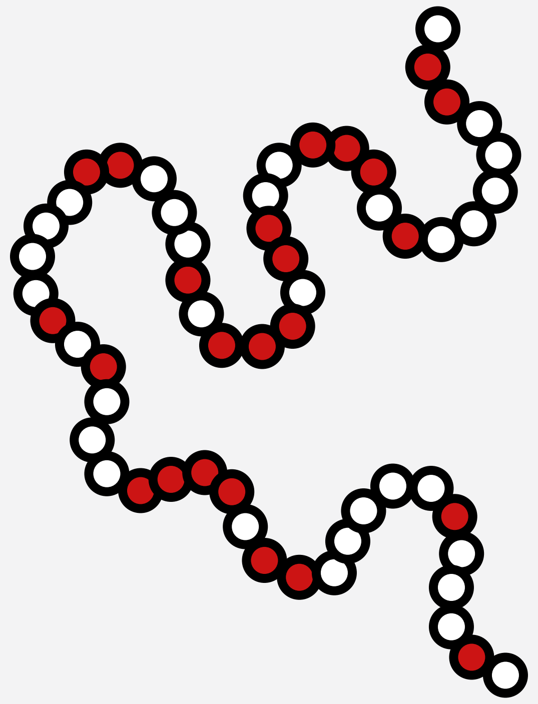
hexagonal

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

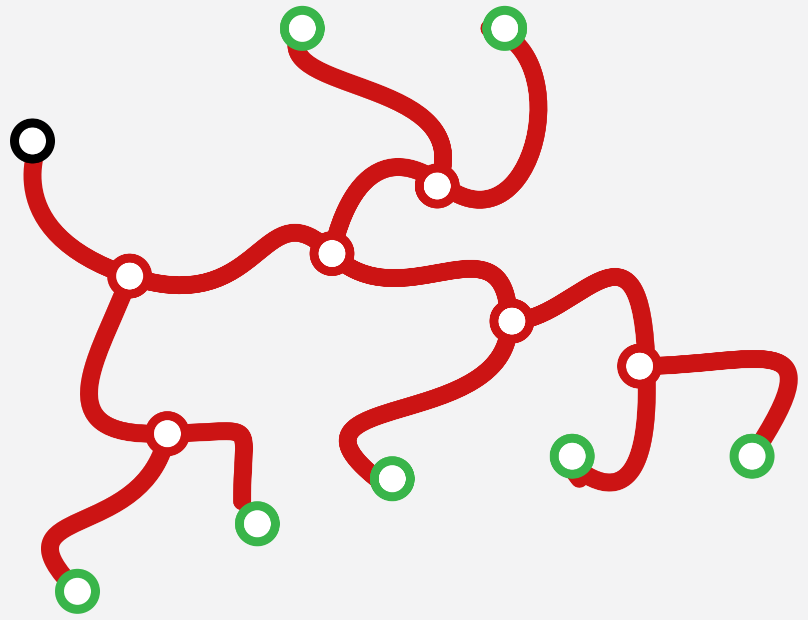
Which Polymers Do Not Crystallize?

- **irregular structures strongly hinder crystallization**

random copolymers



highly branched polymers



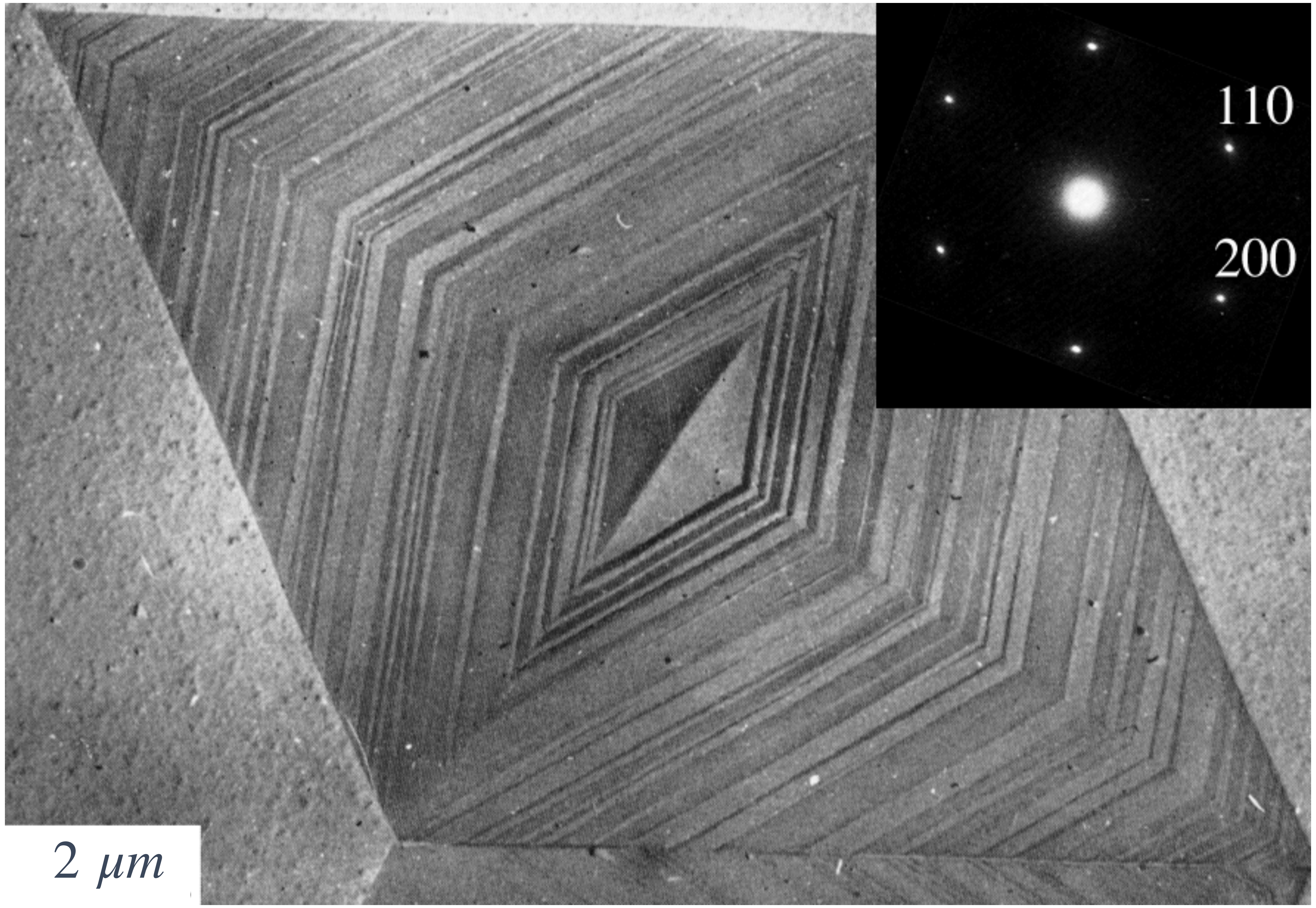
highly cross-linked polymers

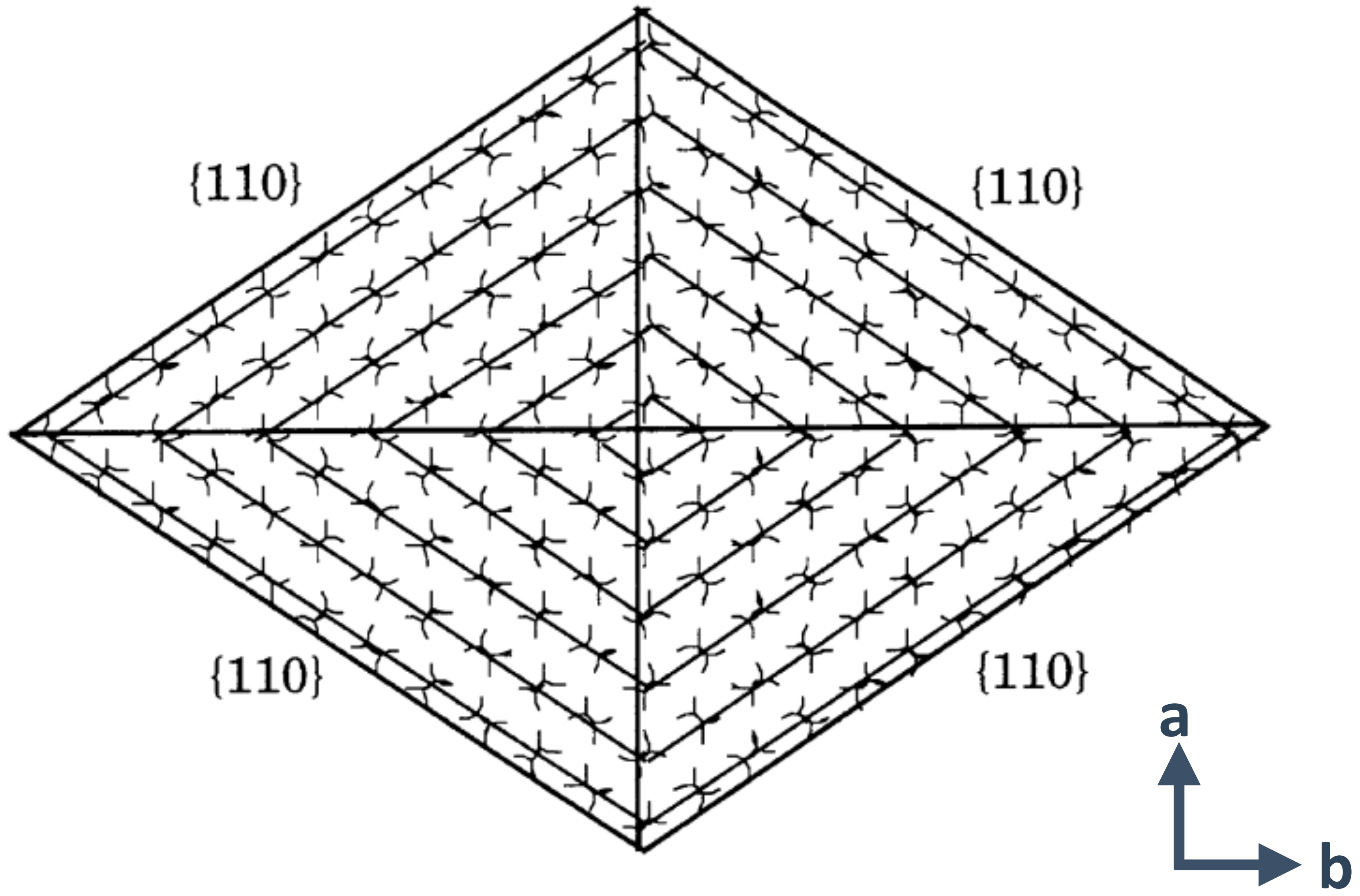
- **no crystallise occurs below (or too close to) T_g**
- **most atactic polymers are amorphous and do not crystallize (exception: poly(vinyl alcohol) (PVA))**

The Melting Temperature

Polymeric Single Crystals (Lamellae)

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



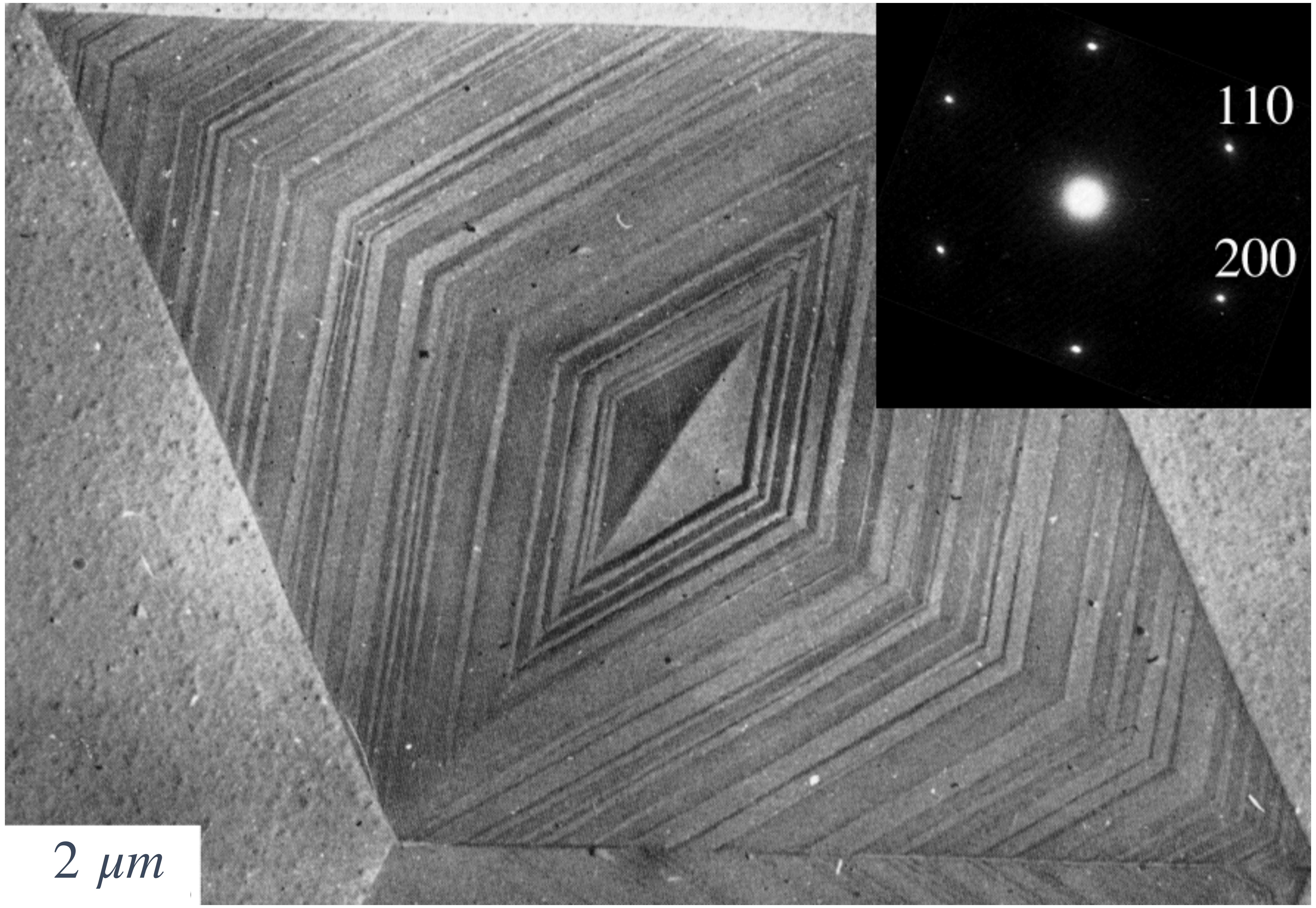


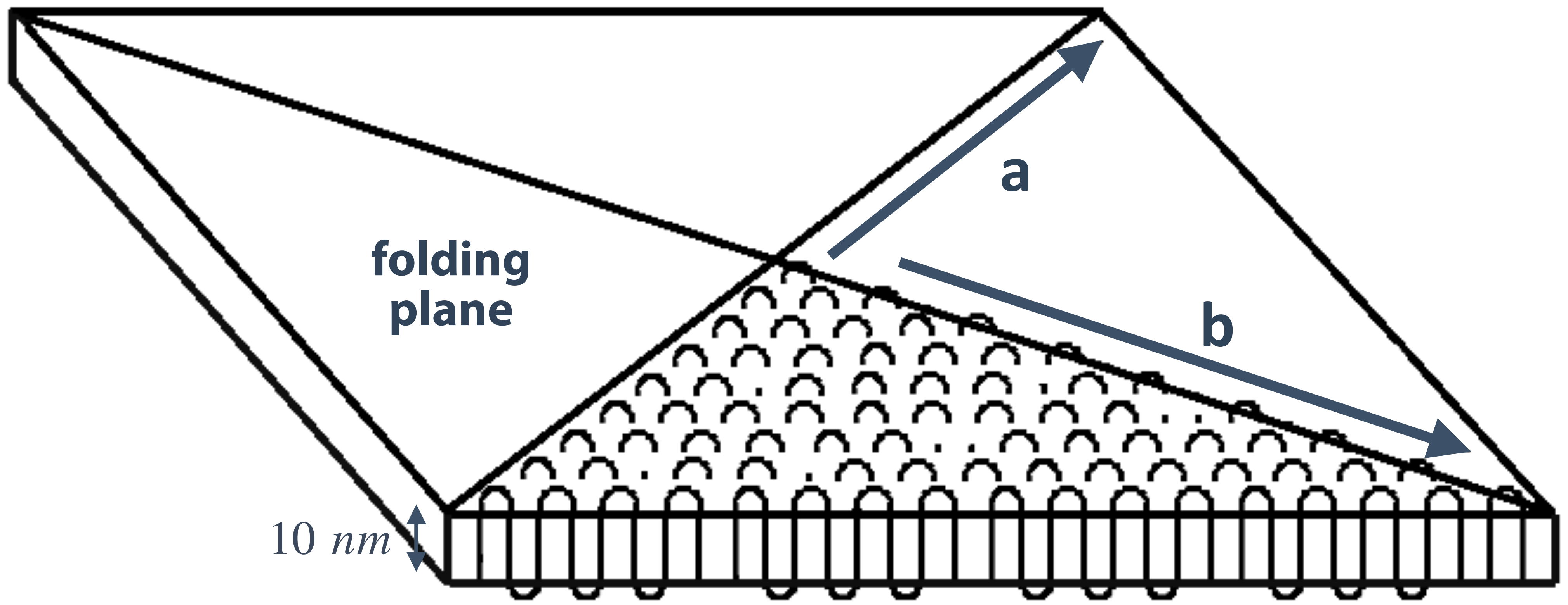
PE chain folded crystals that have grown on top of each other; obtained from xylene

- **polymer chain axes are perpendicular to the lamellar plane as evidenced by TEM**

Chain Folding in Lamellae

- the length of a fully extended chain (1’000 - 10’000 nm) by far exceeds the lamellar thickness (~10 nm)

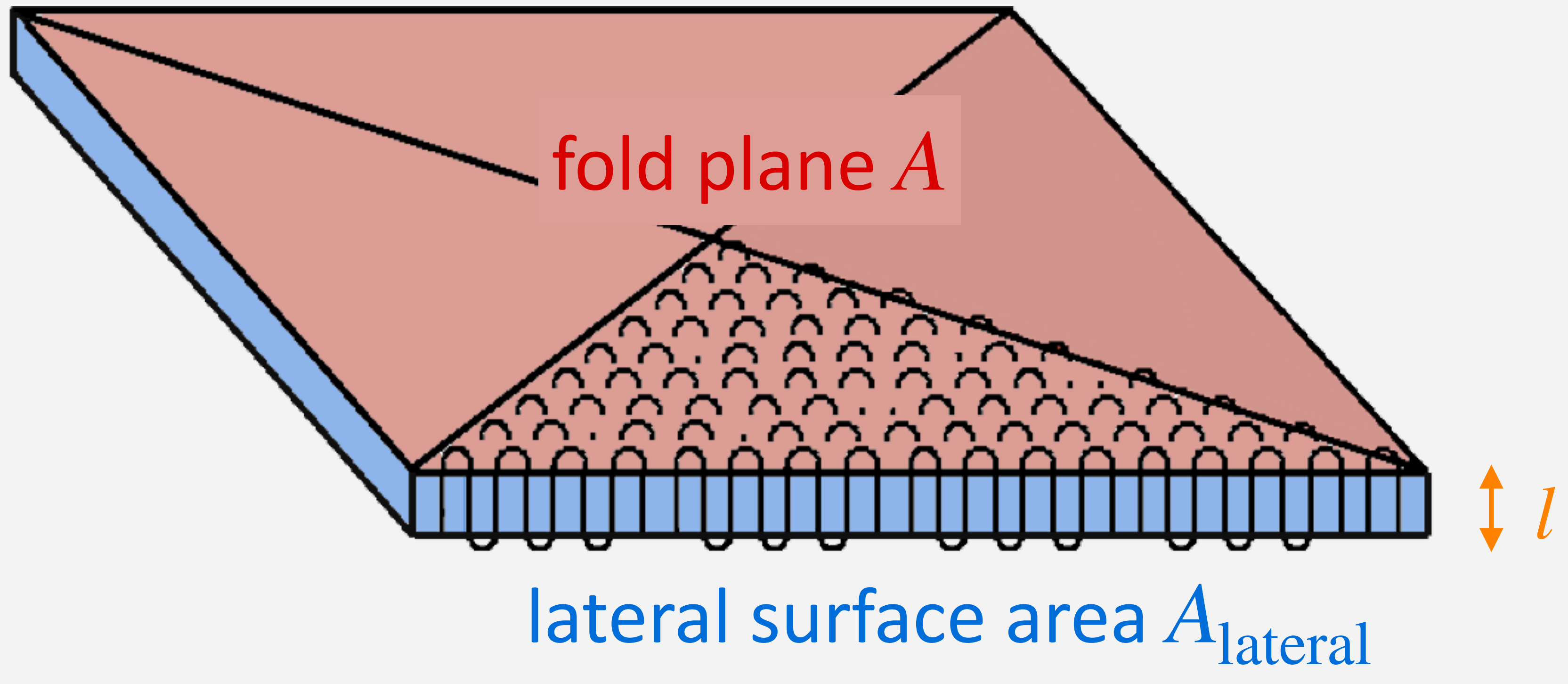




- **chains must fold during crystallization** (source of disorder: even “single crystals” are not 100% crystalline!)

Melting Temperature of a Lamella

- **chain folding is energetically costly, especially for rigid chains**



$$\Delta G_\text{lamella} = -\Delta g_v \cdot Al + 2\sigma_\text{e} \cdot A \cancel{+ \sigma_l \cdot A_\text{lateral}} \approx -\Delta g_v \cdot Al + 2\sigma_\text{e}$$

total free energy change

free energy change per unit volume

$$-(\Delta h_v - T_\text{m}\Delta s_v) \cdot Al + 2\sigma_\text{e} \cdot A = 0$$

enthalpy change per unit volume

entropy change per unit volume

energy penalties:

surface energy associated with folds, σ_e

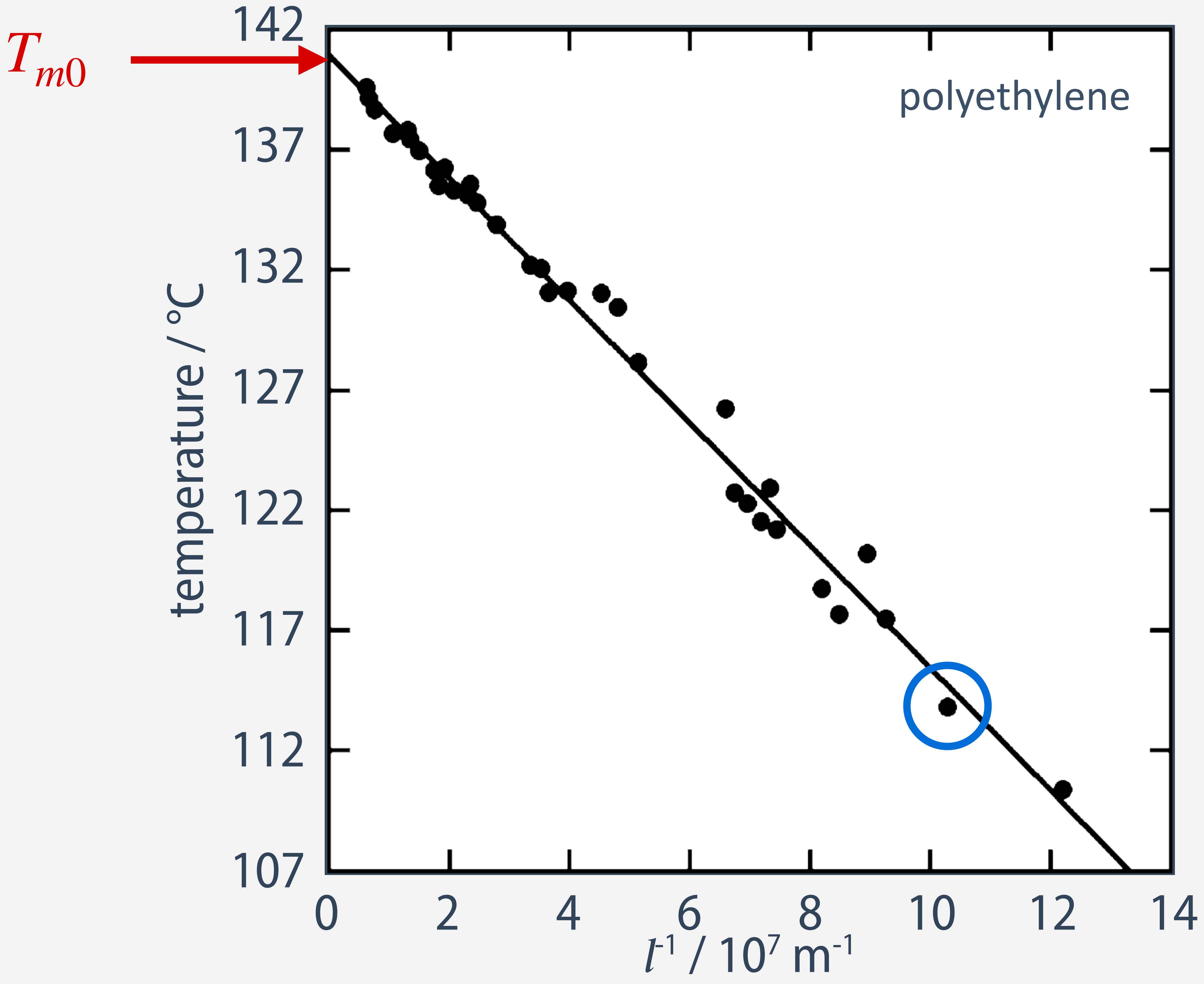
lateral surface energy, σ_l

$$T_\text{m} = \frac{\Delta h_v}{\Delta s_v} - \frac{2\sigma_\text{e}}{\Delta s_v \cdot l} = \frac{\Delta h_v}{\Delta s_v}(1 - \frac{2\sigma_\text{e}}{\Delta h_v \cdot l}) = T_\text{m0}(1 - \frac{2\sigma_\text{e}}{\Delta h_v \cdot l})$$

- **the apparent melting temperature, T_m, is always lower than the thermodynamic T_m0**
- **T_m decreases with decreasing lamellar thickness (surface-to-volume effect, fold surface penalty)**

key concept: see Reader on Melting Temperature

Thomson-Gibbs Equation



Thomson-Gibbs equation:

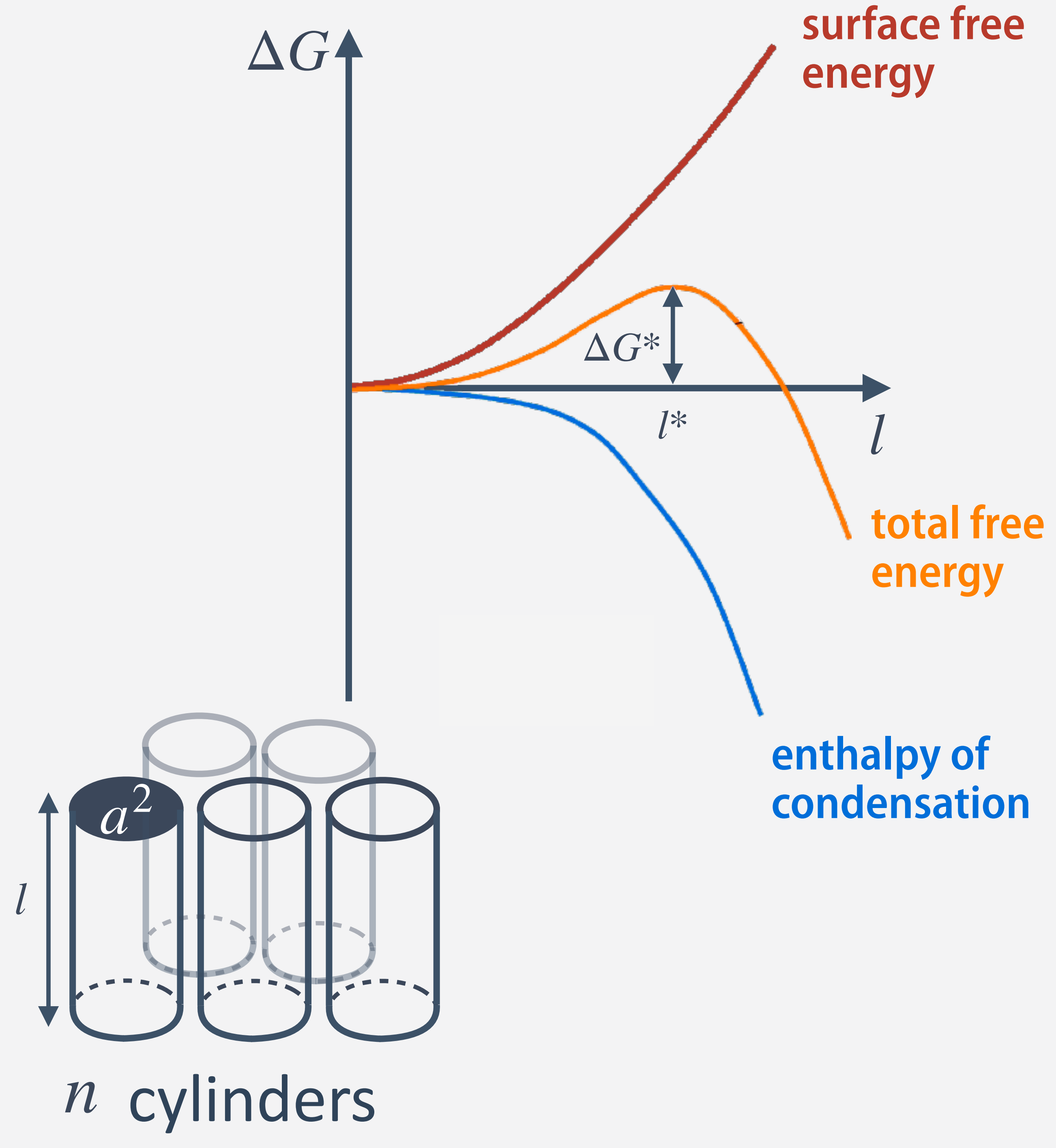
$$T_m \sim T_{m0}\left(1 - \frac{2\sigma_e}{l\Delta H}\right)$$

- ***T_{m0}* refers to infinite lamellar thickness (see Exercise)**
- **for a typical lamella with thickness of 10 nm, *T_m* can be ~40 °C below *T_{m0}***

key concept: see Reader on Melting Temperature

Nucleation as a Limiting Factor of Lamellar Thickness

- **nucleation requires supercooling and formation of a nucleus of critical size**



$$\Delta G_{nucleus} = -na^2 l \Delta g_v + 2na^2\sigma_e + 2\sqrt{\pi}\sqrt{n}al\sigma_l \qquad \text{with } \Delta g_v = \frac{\Delta h_v \Delta T}{T_{\mathrm{m0}}}$$

crystal stability requirement in the large-*n* limit:

$$-na^2 l \Delta g_v + 2na^2\sigma_e = 0$$

$$\boxed{l^* = \frac{2\sigma_e T_{m0}}{\Delta h_v \Delta T}}$$

critical nucleus size:

$$\frac{\partial \Delta G_{nucleus}}{\partial n}\Big|_l = 0 \quad \text{and} \quad \frac{\partial \Delta G_{nucleus}}{\partial l}\Big|_n = 0$$

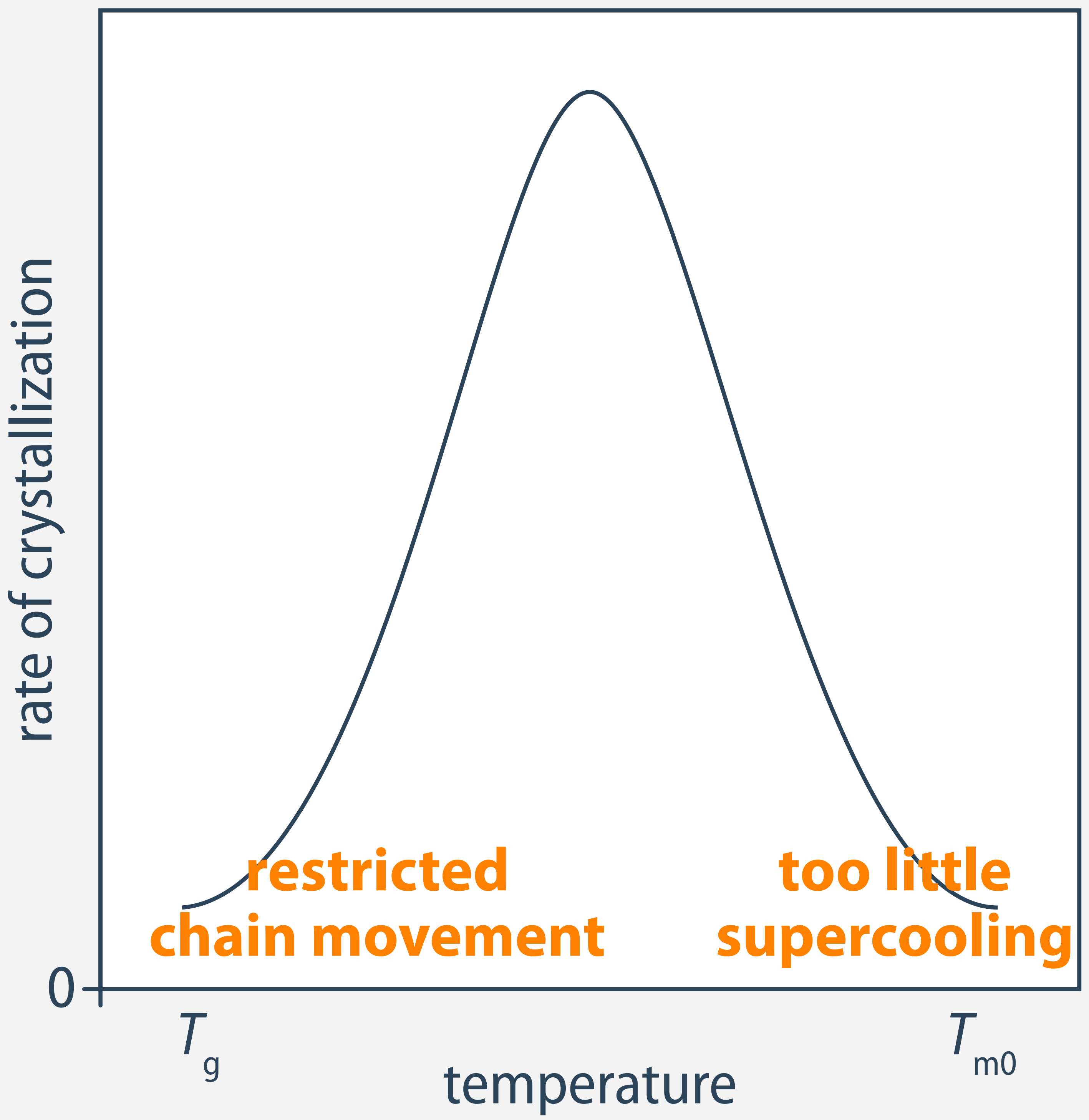
$$\boxed{\Delta G^* \propto \sigma^2 \sigma_e \left(\frac{T_{m0}}{\Delta H \Delta T}\right)^2}$$

- **lamellar thicknesses is kinetically selected** (thinner lamellae nucleate faster)
- **typical observed thicknesses are approximately 2*l**, decreasing with degree of supercooling**

key concept: see Reader on Melting Temperature

Kinetics of Nucleation in Practice

- nucleation kinetics ultimately limit lamellar thickness
- polymer mobility in the melt is constrained (glass transition, entanglement)



$$N = \underbrace{N_0 e^{-\frac{A}{T-T_0}}}_{\text{viscosity term}} \underbrace{e^{-\frac{\Delta G^*}{kT}}}_{\text{kinetic term}}$$

- **practically relevant supercooling (tens of °C) give lamellar thicknesses of 5–20 nm** (e.g. injection molding)

Factors Influencing the Melting Temperature

Influence of Chain Ridigity

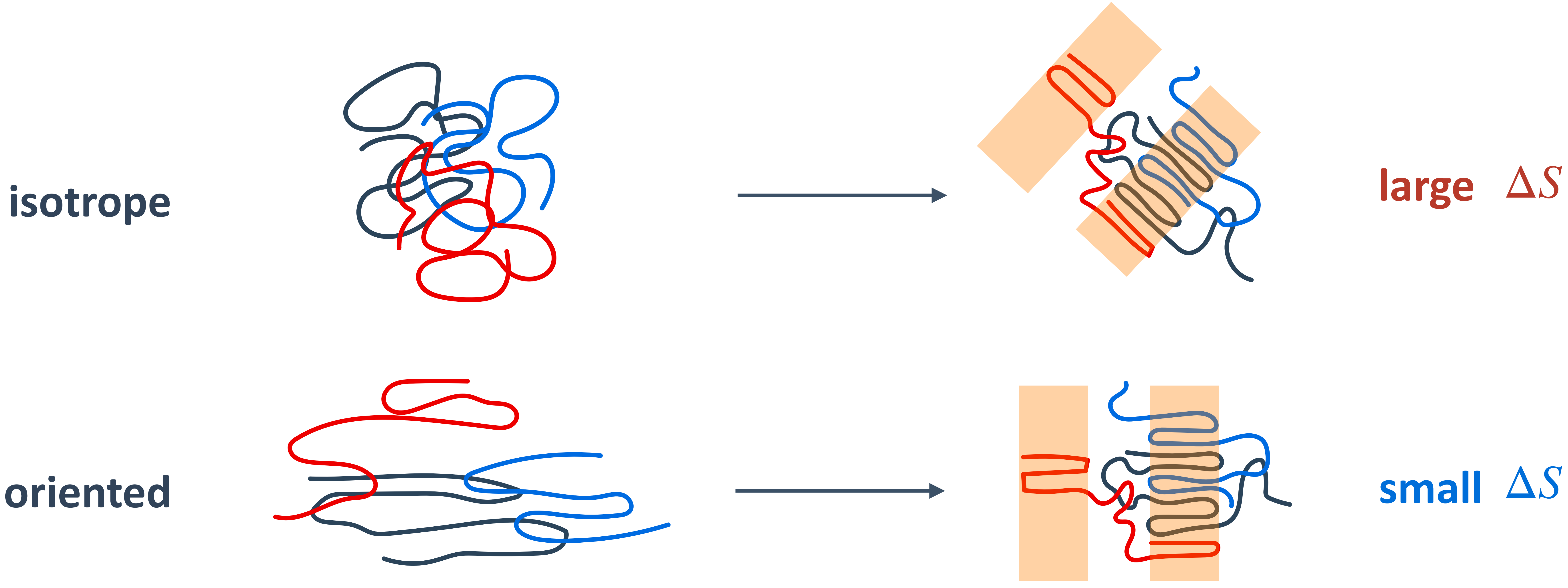
- crystallization at equilibrium given by Gibbs-Helmholtz equation: $\Delta G = \Delta H - T_{m0}\Delta S = 0$

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

- **oriented polymer chains (by flow or deformation) crystallize more easily**



isotrope

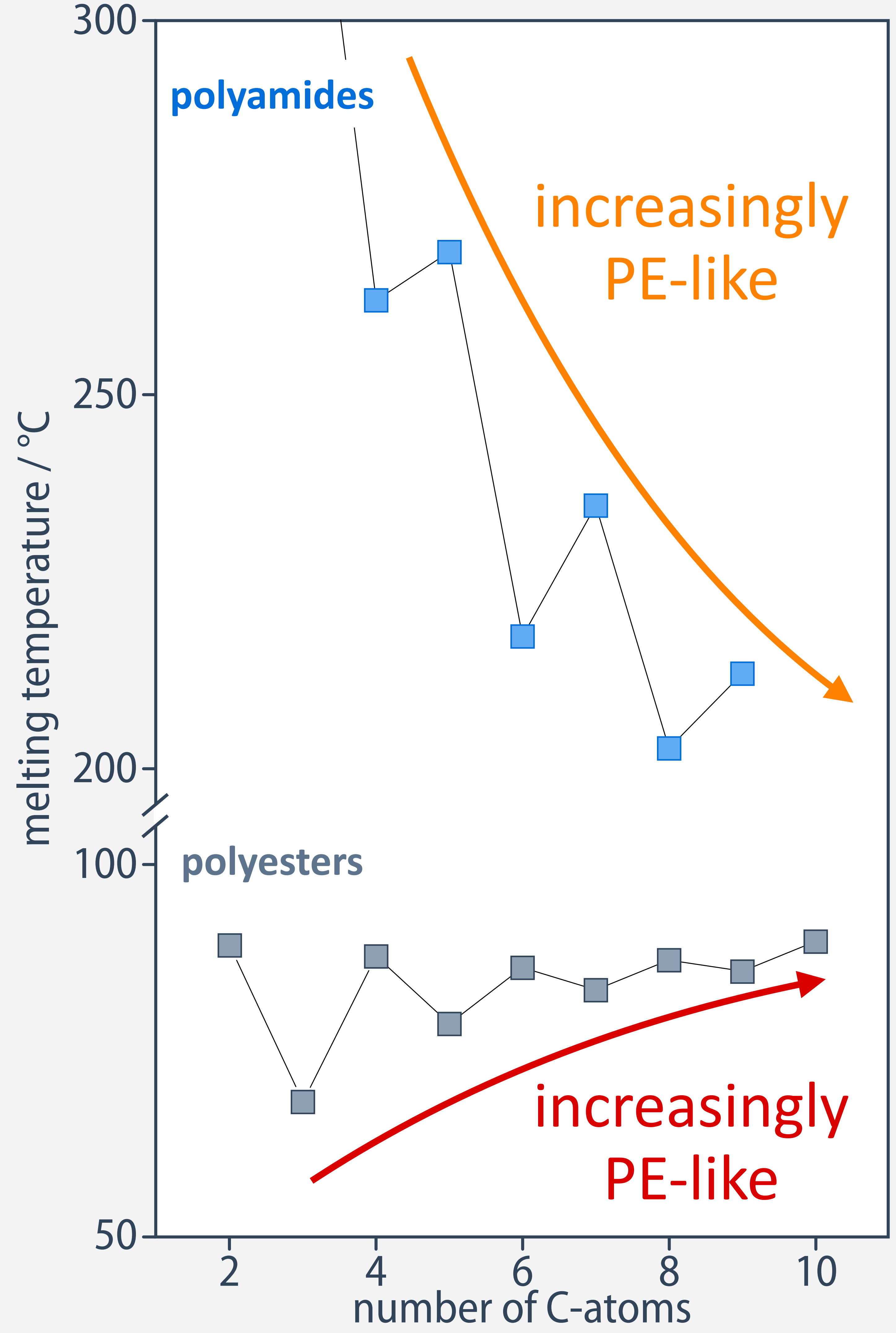
large ΔS

oriented

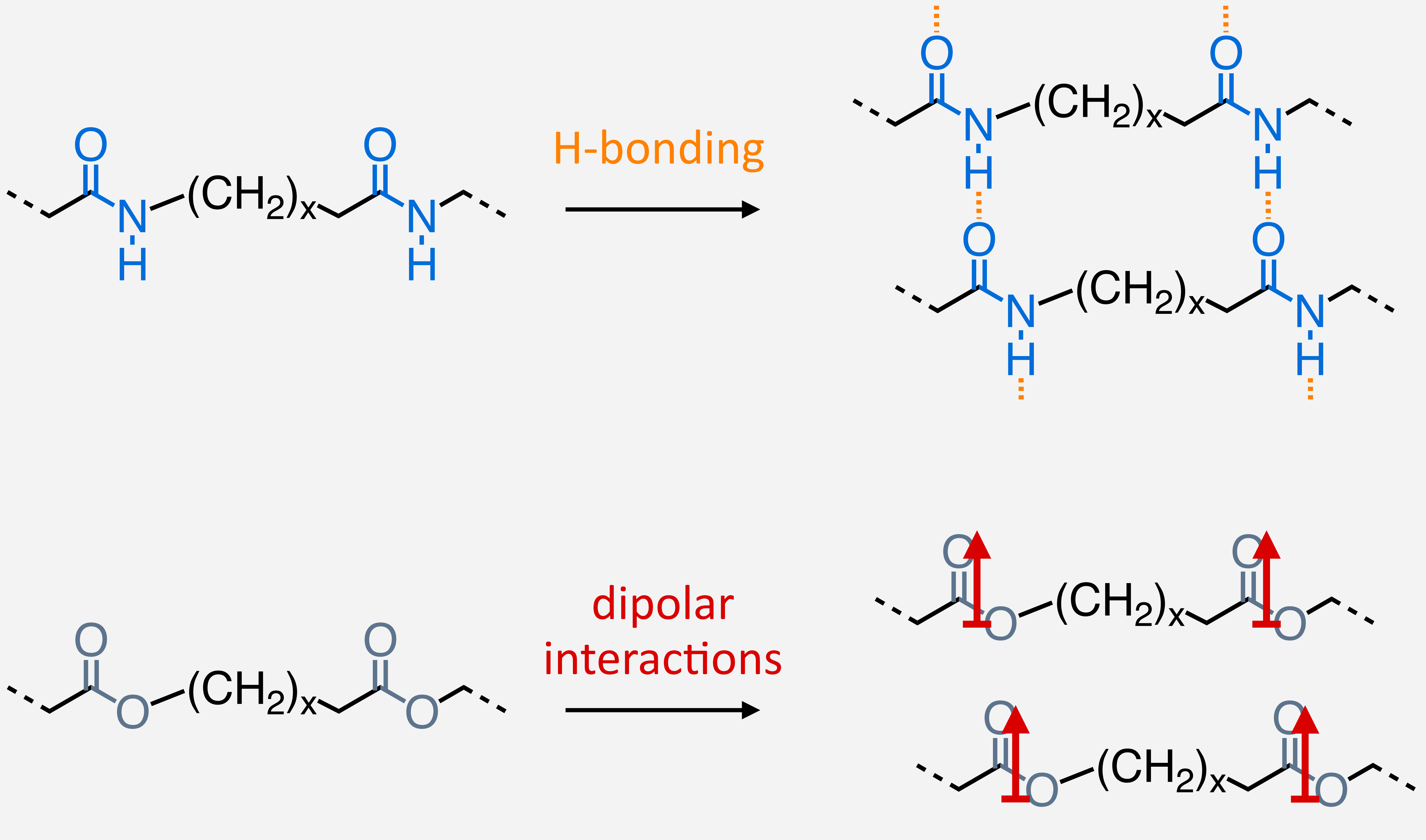
small ΔS

- **lamellae align perpendicular to the orientation direction**
- technological relevance: crystallization of elastomers (**Chapter 4.1**), fibers, injection molding (**Chapter 6**)

Specific Intermolecular Interactions

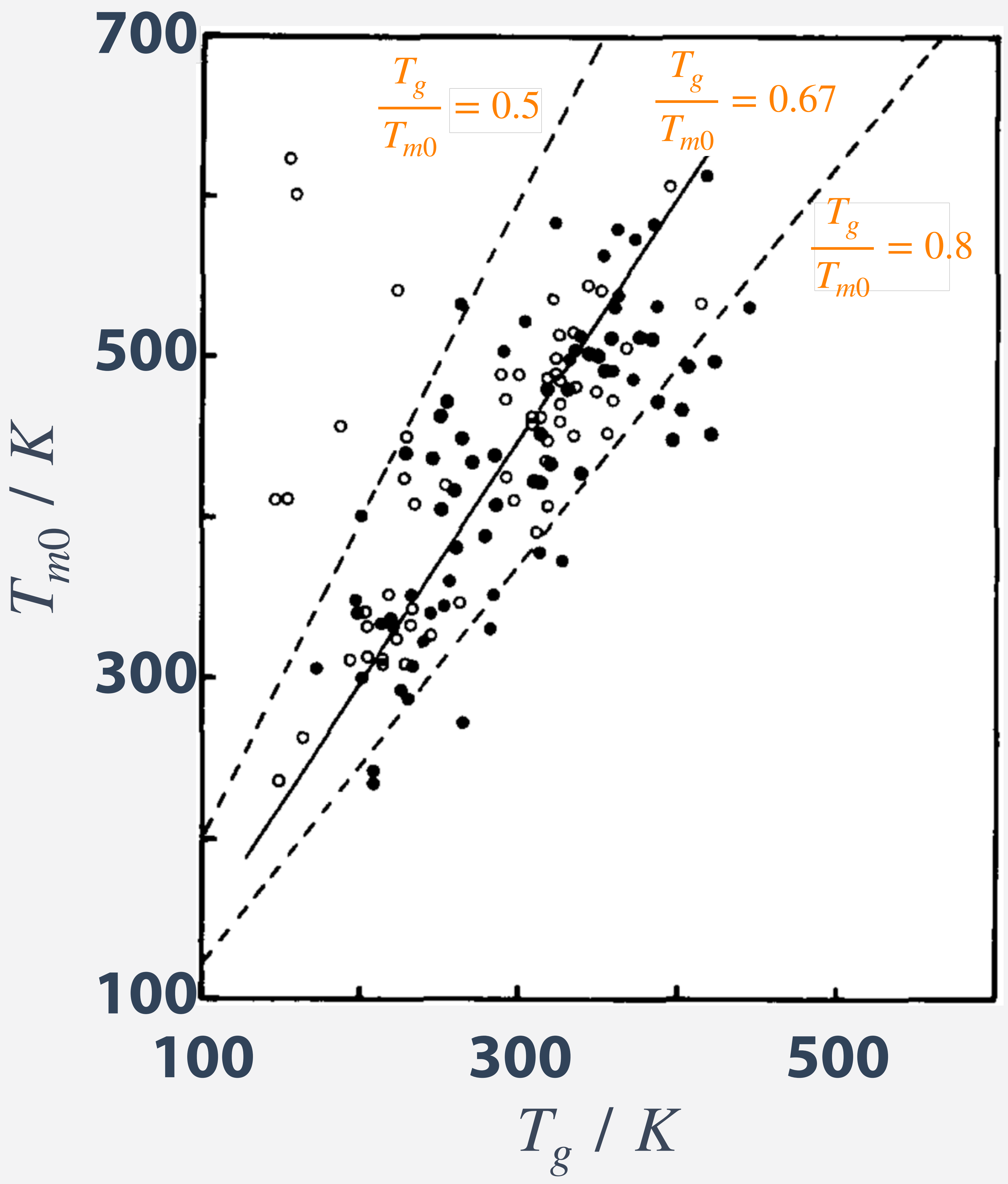


- **H-bonds add large enthalpy gain during crystallization**



- **the stronger the intermolecular interactions, the larger ΔH, the higher T_{m0}**

Correlation with T_g



○ symmetric repeating units

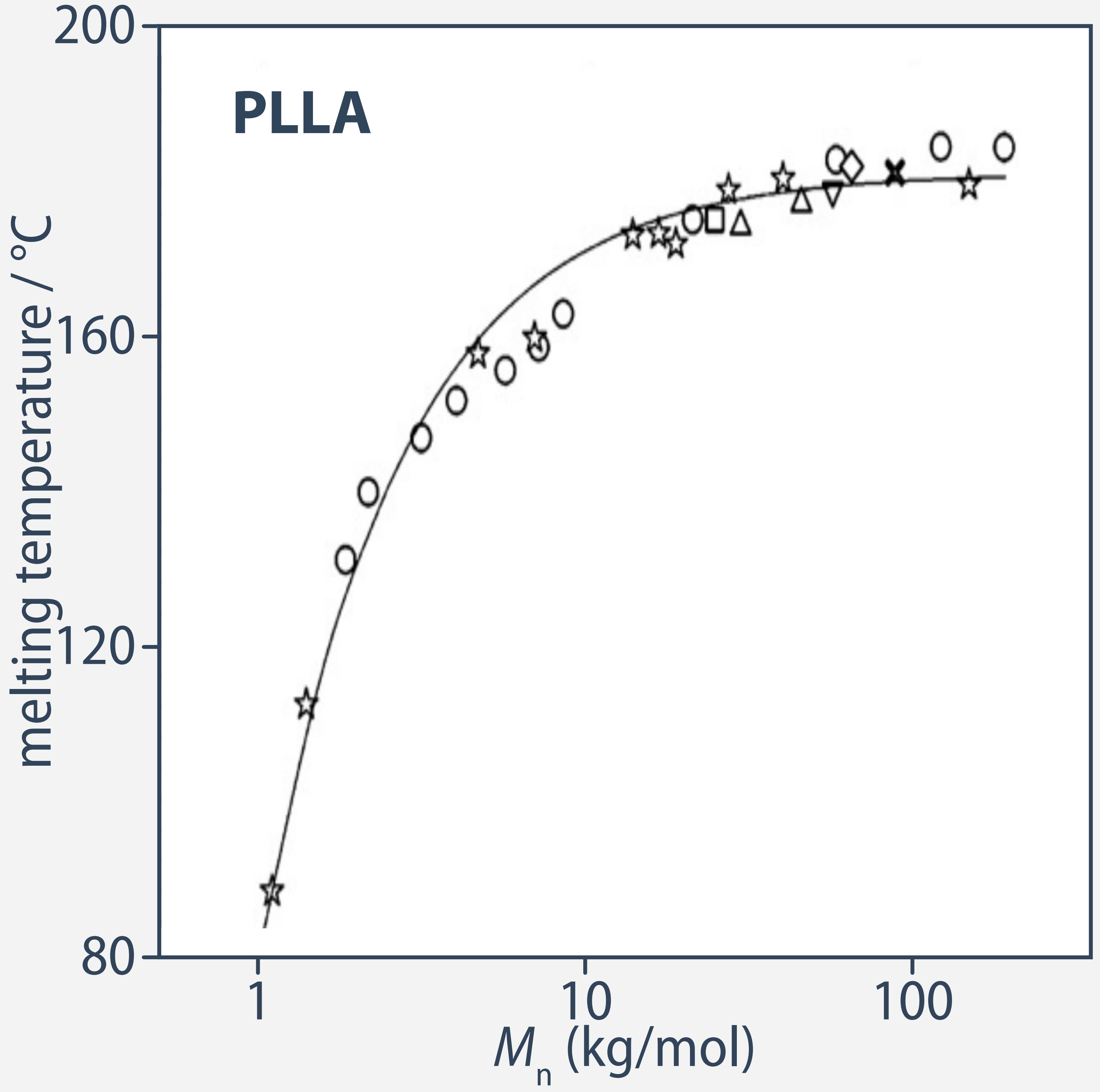
● unsymmetric repeating units

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

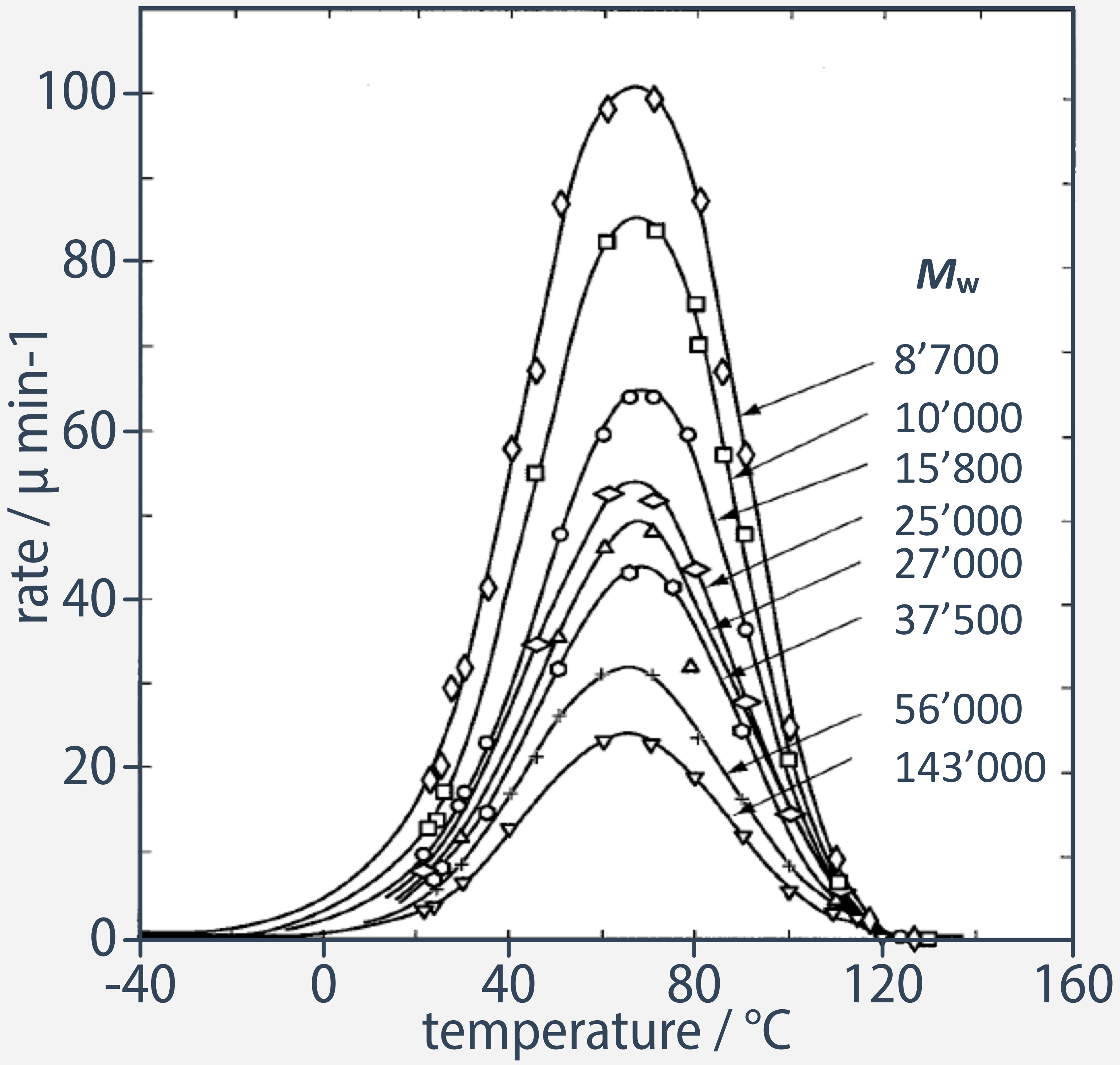
Molar Mass Dependence

- melting temperature increases with molar mass and approaches an asymptotic limit

melting temperatures



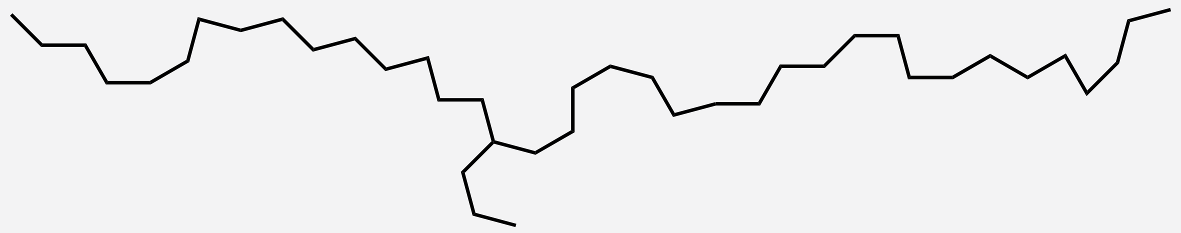
crystal growth rates



- **however, higher molar mass reduces chain mobility, making crystallisation progressively slower**

Branching

HDPE

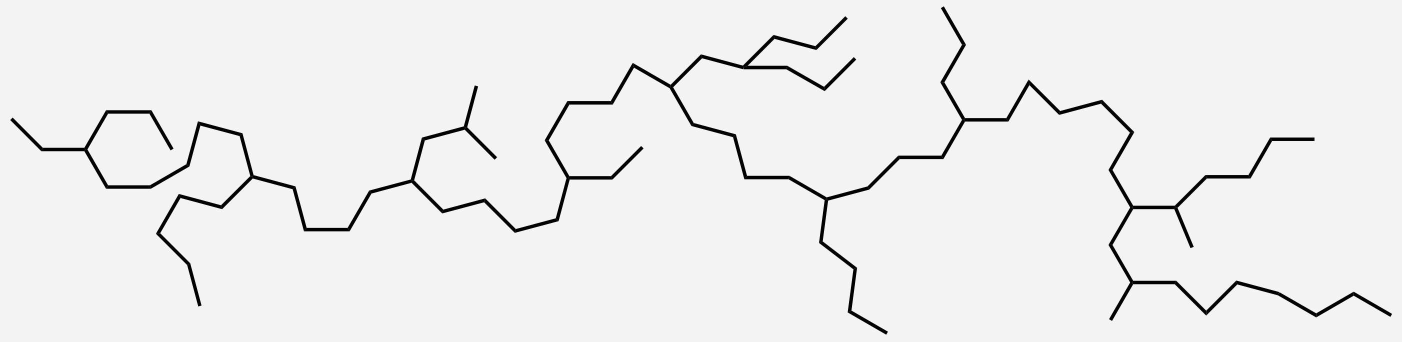


high-density polyethylene (HDPE)

structurally “regular” with few branching points (7/1000 carbons)

packs efficiently, high crystallinity, high density

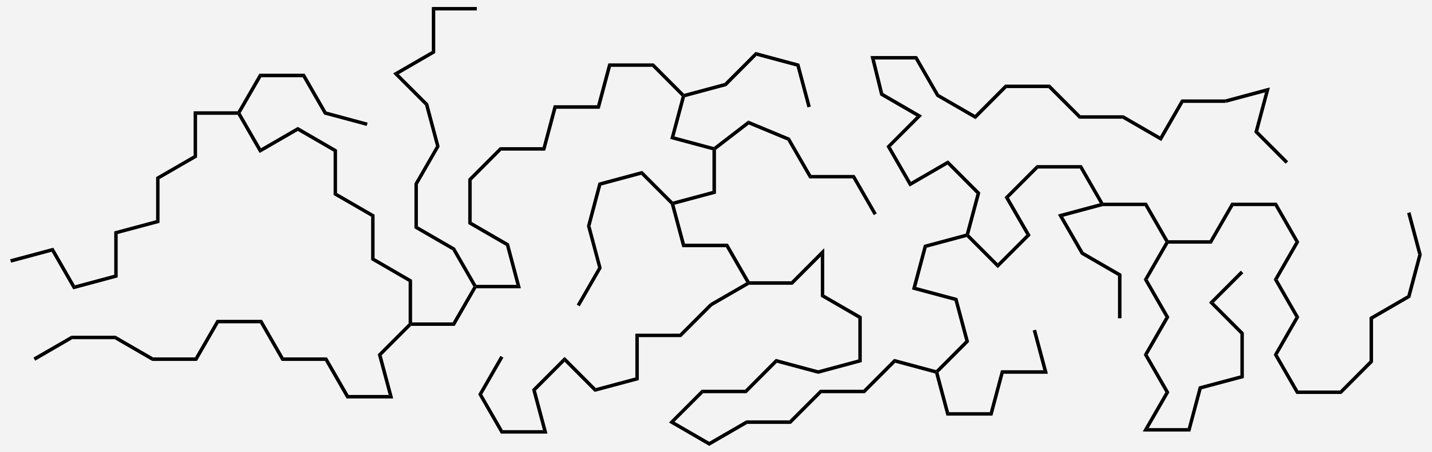
LLDPE



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

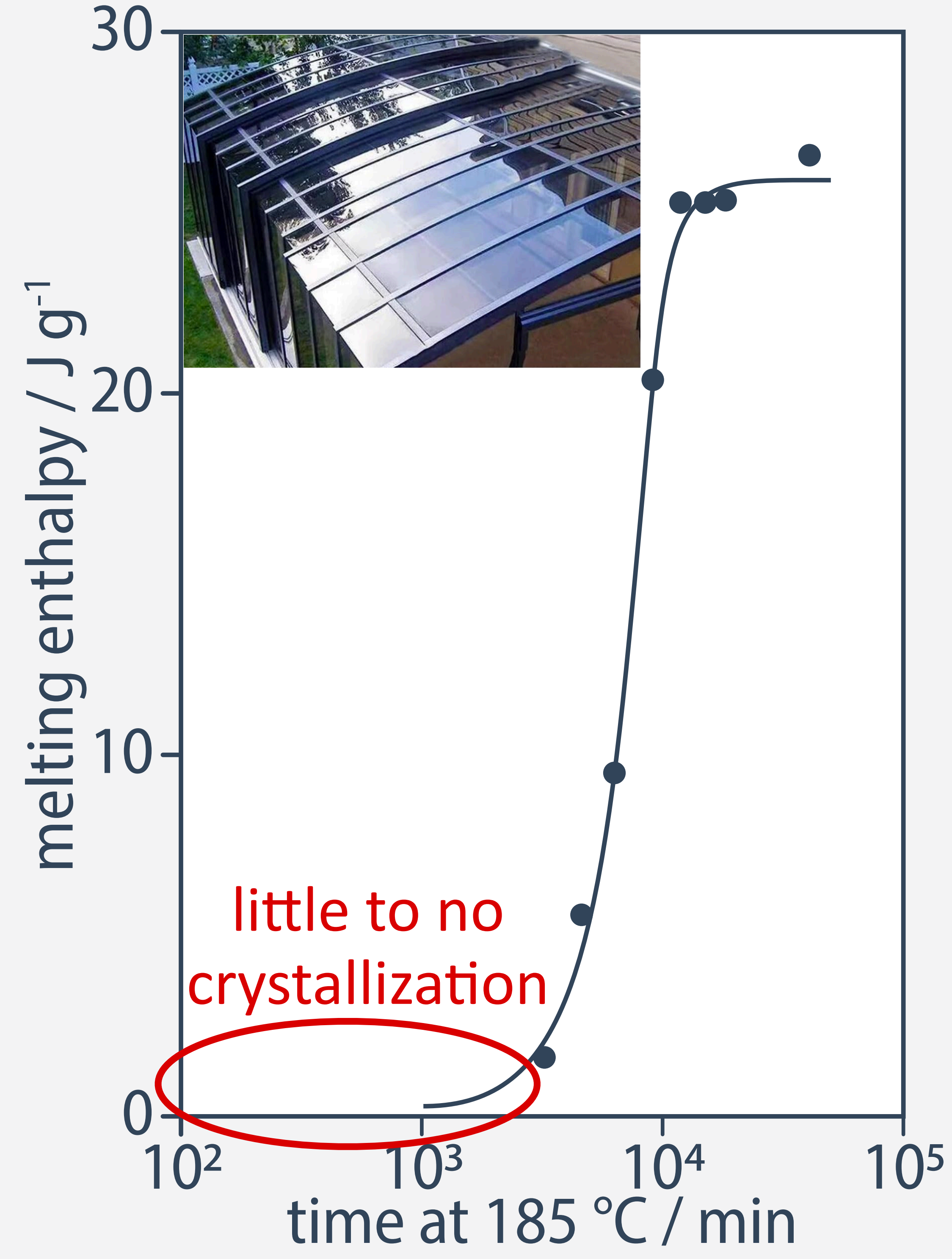
Property	HDPE	LLDPE	LDPE
melting point (°C)	130	120-130	110
degree of crystallinity (%)	80-90	60-70	30-50
density (g/mL)	0.94-0.97	0.92-0.94	0.92
tensile strength (MPa)	32	25	21

- **branching lowers crystallinity:** HDPE (crystalline) & LDPE (branched, less dense) separable based on density!

Time as Limiting Factor

polycarbonate

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

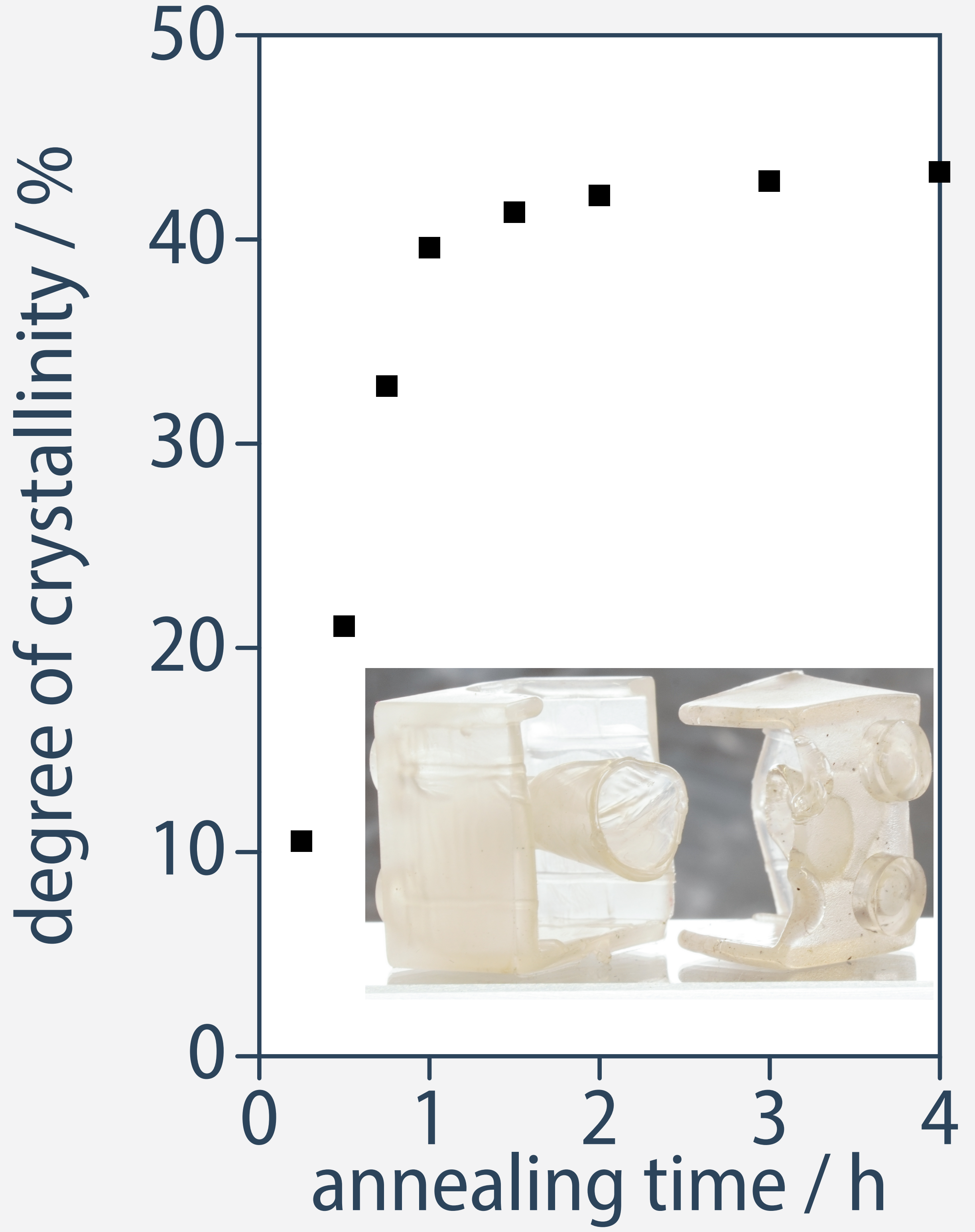


PET

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

aliphatic polyesters

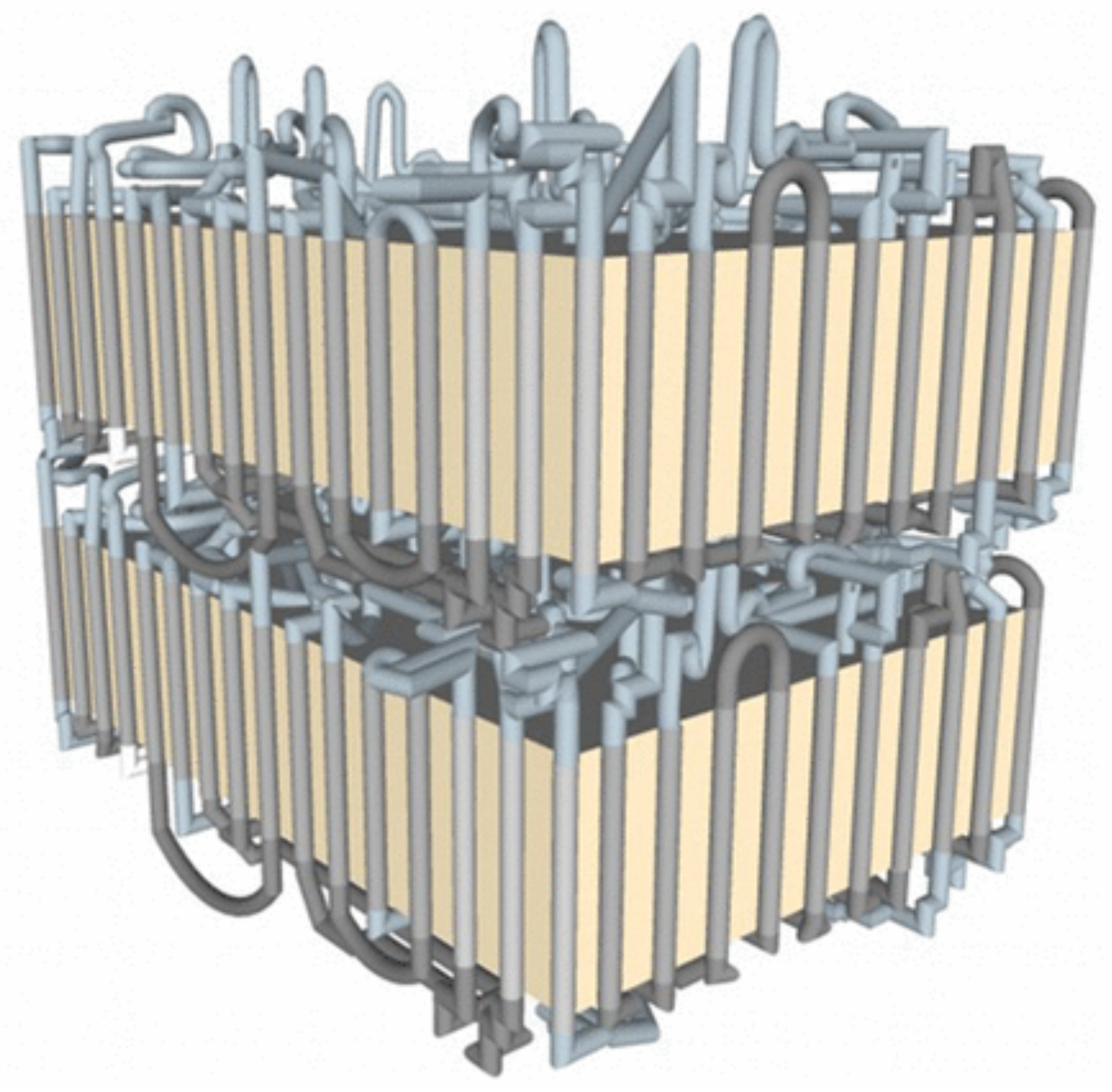
(T_g(PLLA) ≈ 60 °C, T_m(PLLA)≈ 160 °C)



- **suppressed polymer crystallization can be desirable for processing and performance**
- example: PC is ~0% crystalline, PET bottles (~30% crystalline) blown from fully amorphous preforms

Morphology of Semi-Crystalline Polymers

Semi-Crystalline Nature of Polymers



crystalline lamella

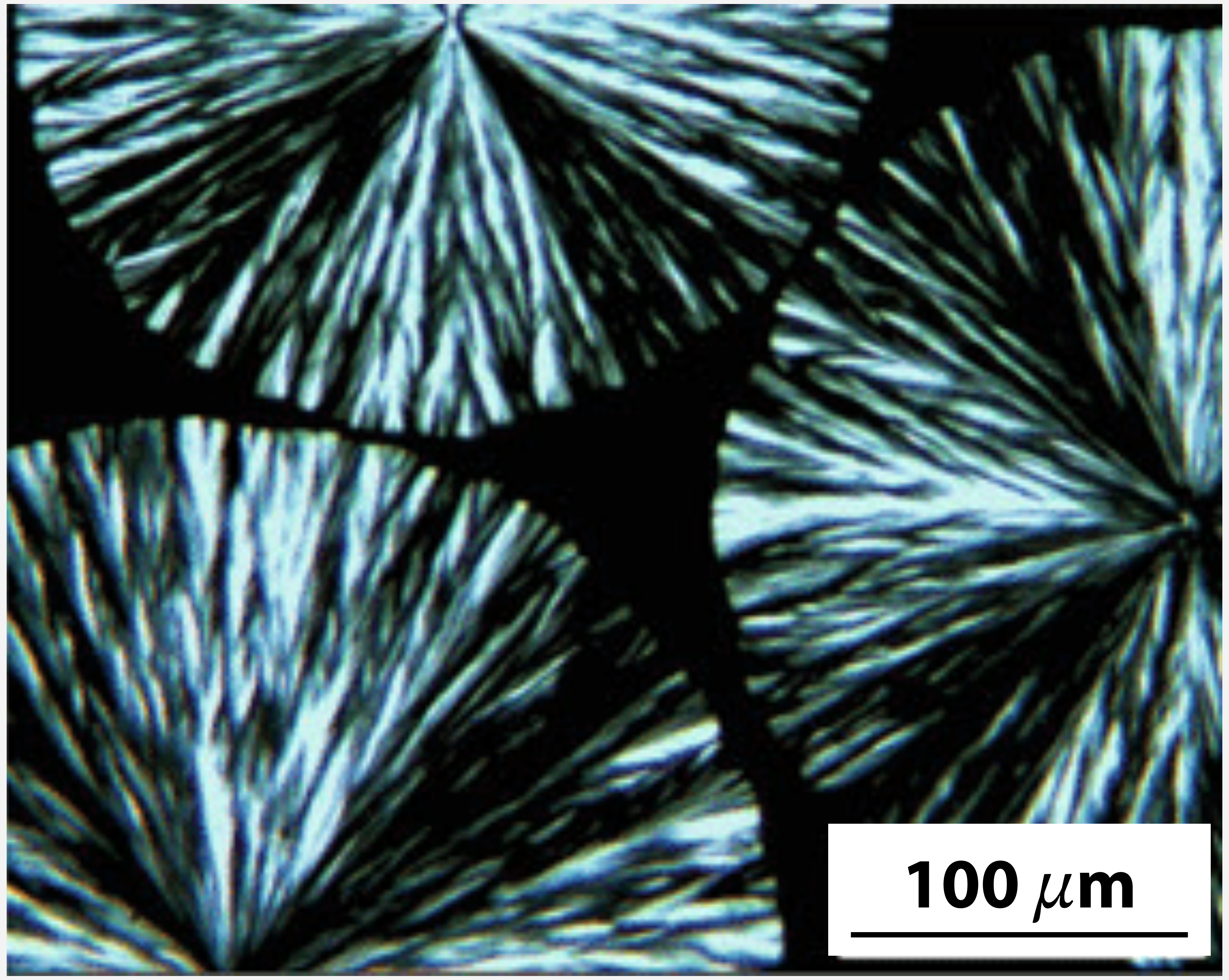
amorphous matrix

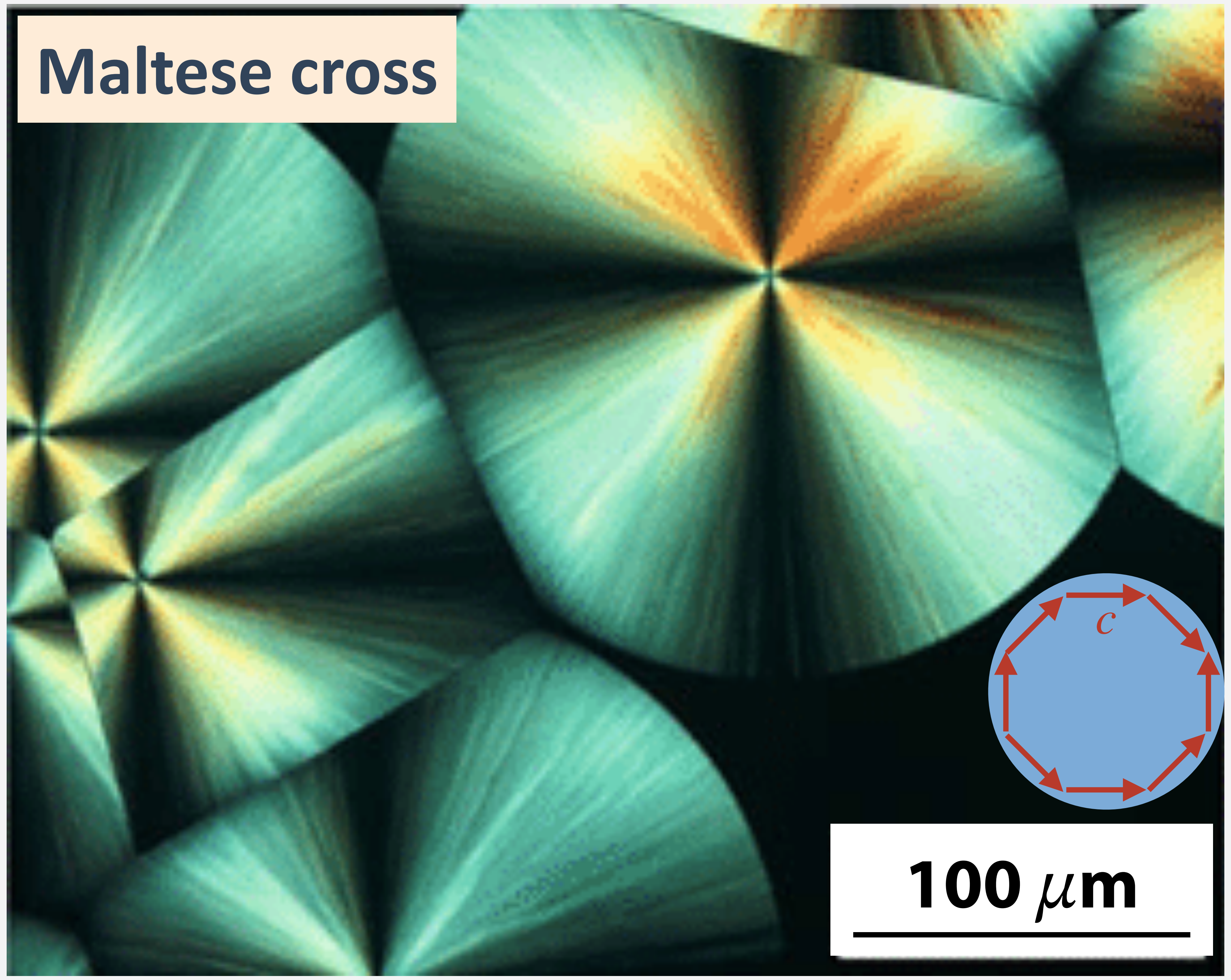
crystalline lamella

- **typical crystallinity: 30-60%, depending on polymer and processing**
- **remaining fraction is the amorphous matrix** (glassy, rubbery, or fluid depending on T_g and temperature)

Spherulites

- semicrystalline polymers usually solidify into spherulites (radially symmetric aggregates of lamellae and amorphous materials)

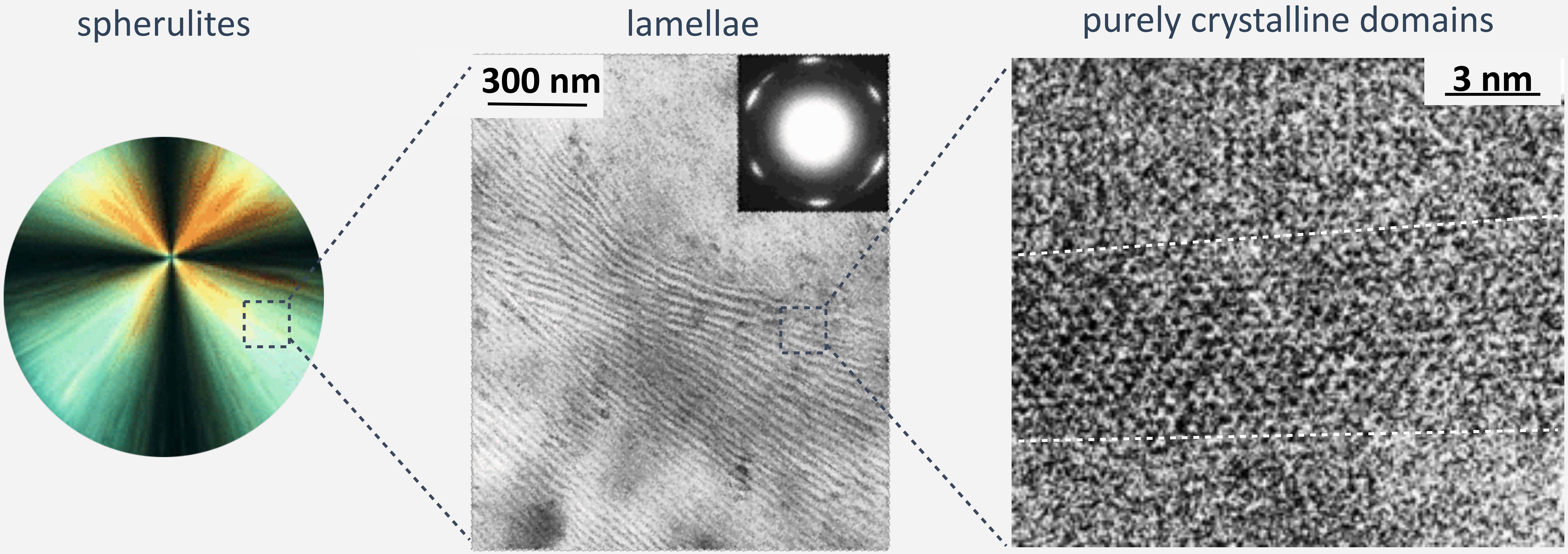




- **birefringence under polarised light reveals radial lamellae, chains (*c*-axis) oriented tangentially**
- **generally opaque due to scattering, though some partially crystalline materials remain transparent** (e.g. PET bottles that are approximately 30% crystalline)

Spherulite Structure

- **TEM shows lamellae in spherulites with diffraction patterns identical to polymeric single crystals**


spherulites

lamellae

purely crystalline domains

- **lamellae typically ~10 nm thick, separated by amorphous layers of comporable thickness**

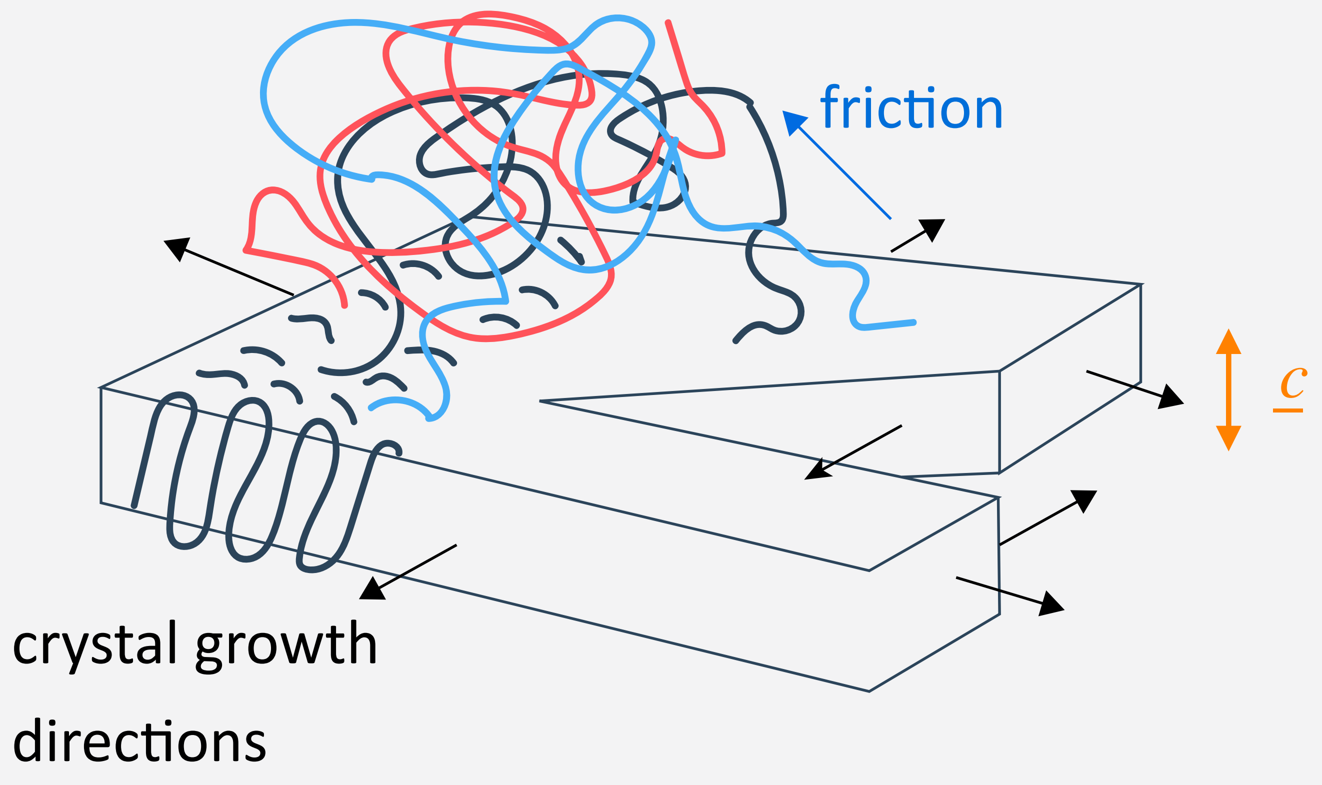
  (depending on degree of crystallinity)

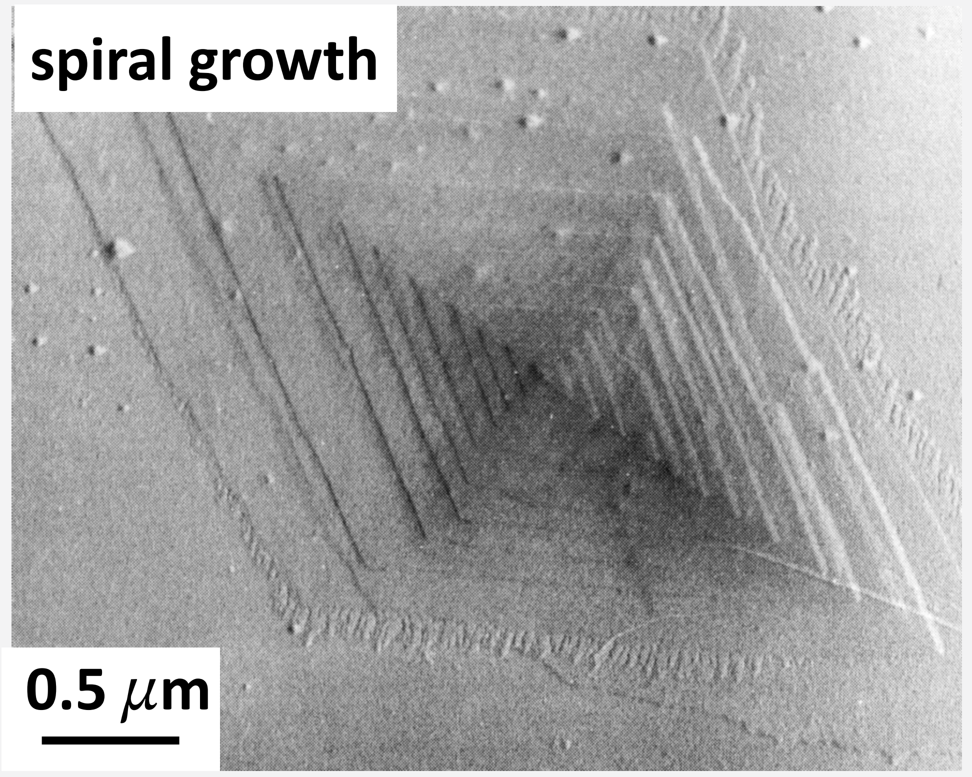
- **lamellae are stacked radially, producing the layered internal structure of the spherulite**

Origin of Spherulites

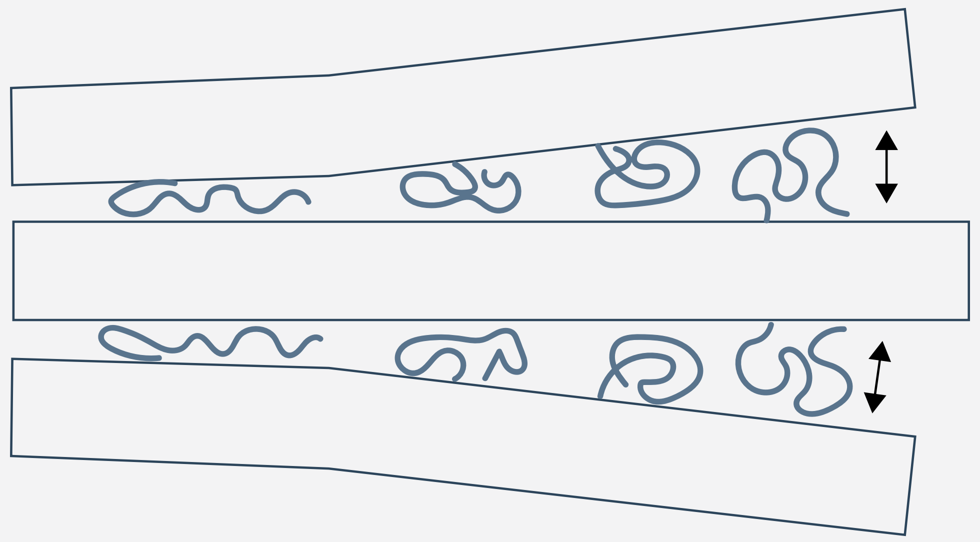
- growth stresses and interactions with entangled melt chains (low flexural rigidity of lamellae due to low thickness) lead to cracks and screw dislocations

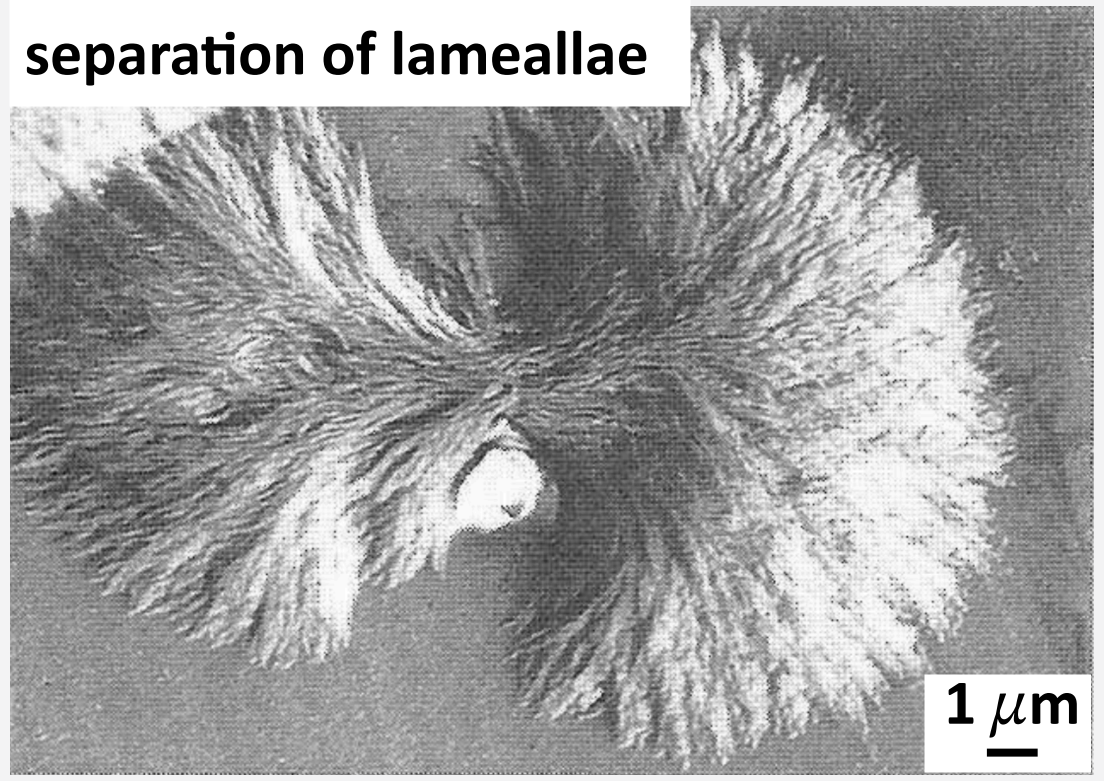
new growth direction



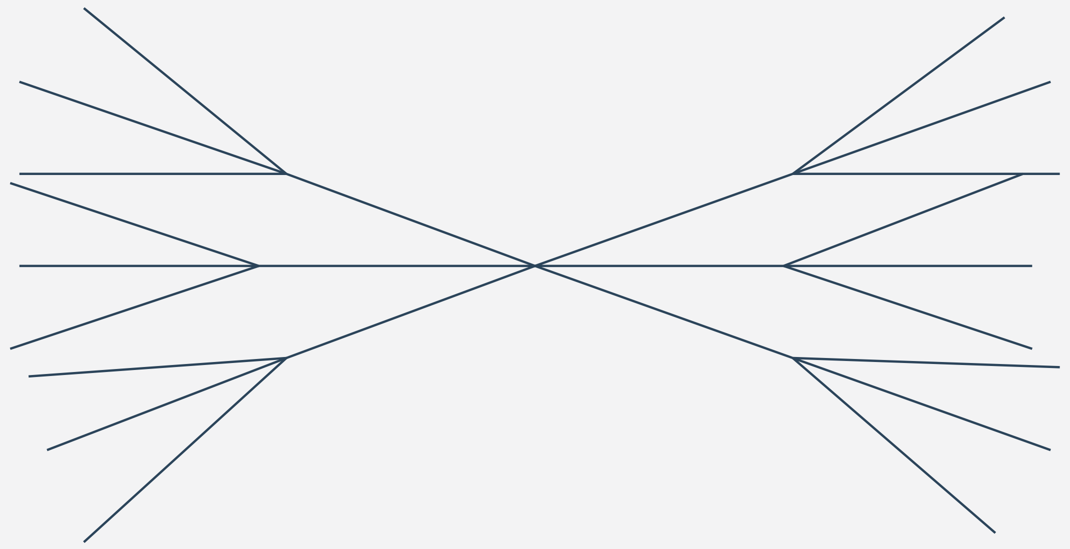


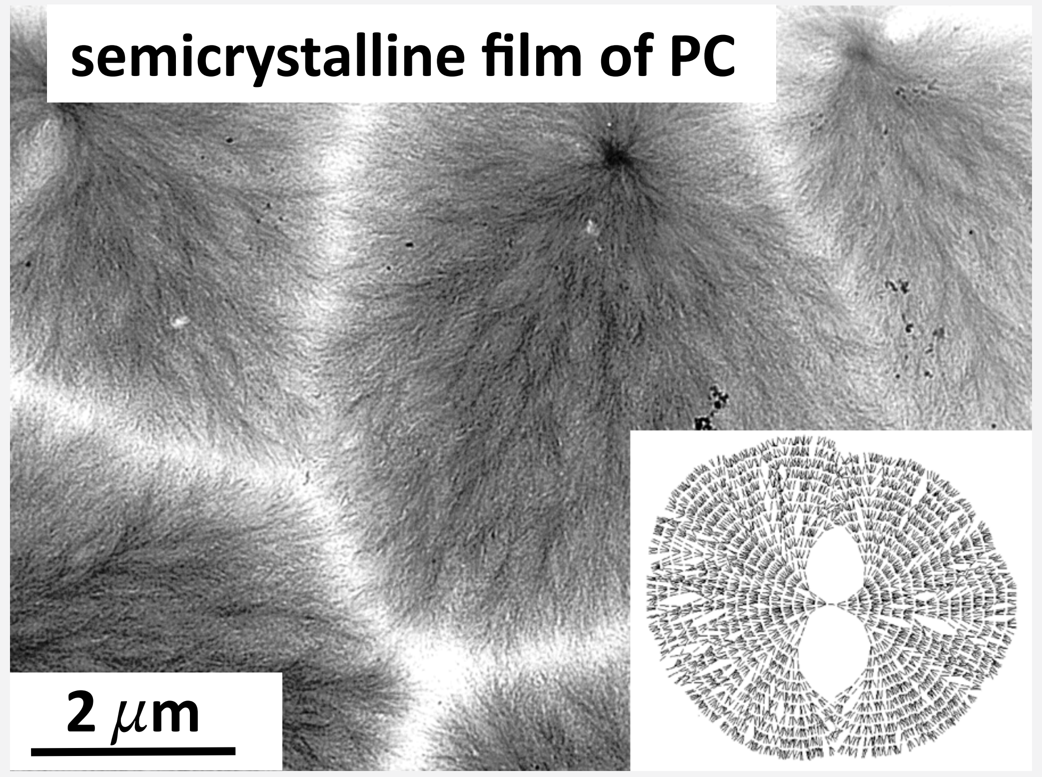
new growth direction





multiple dislocations

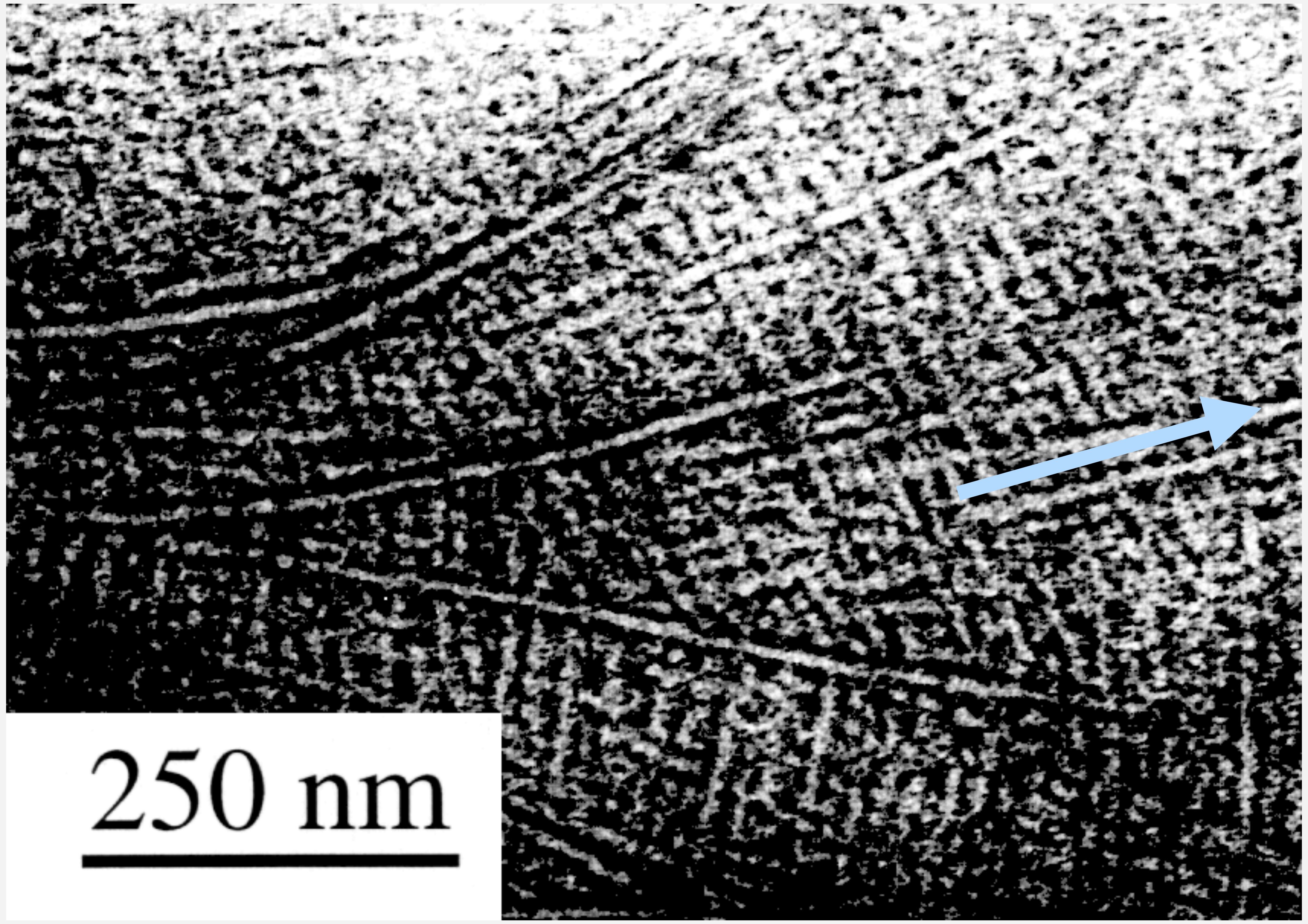




- **lamellae separated by amorphous layers, oriented radially from the nucleus outward**

Twinning

- commonly observed in commercial isotactic polypropylene (iPP)

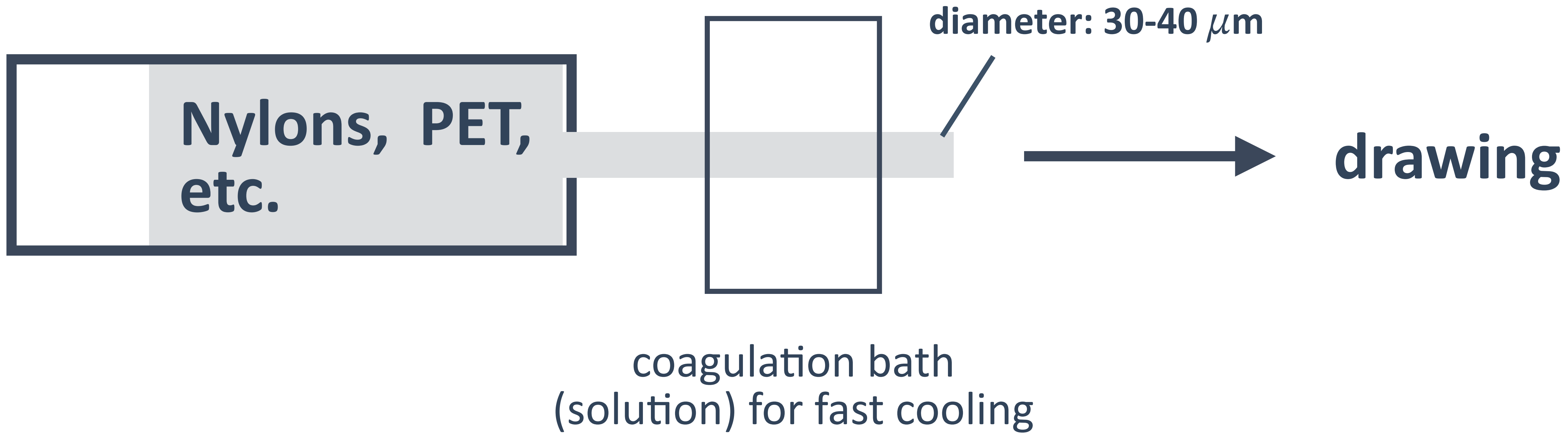


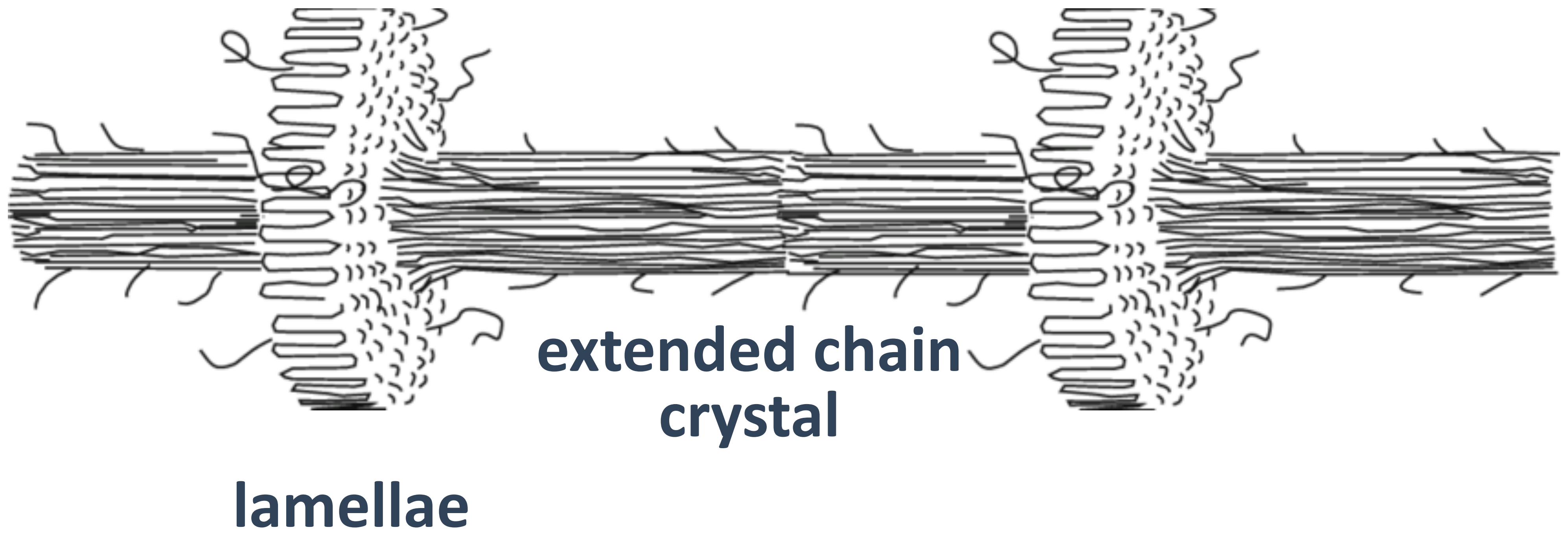
direction of the spherulitic radius

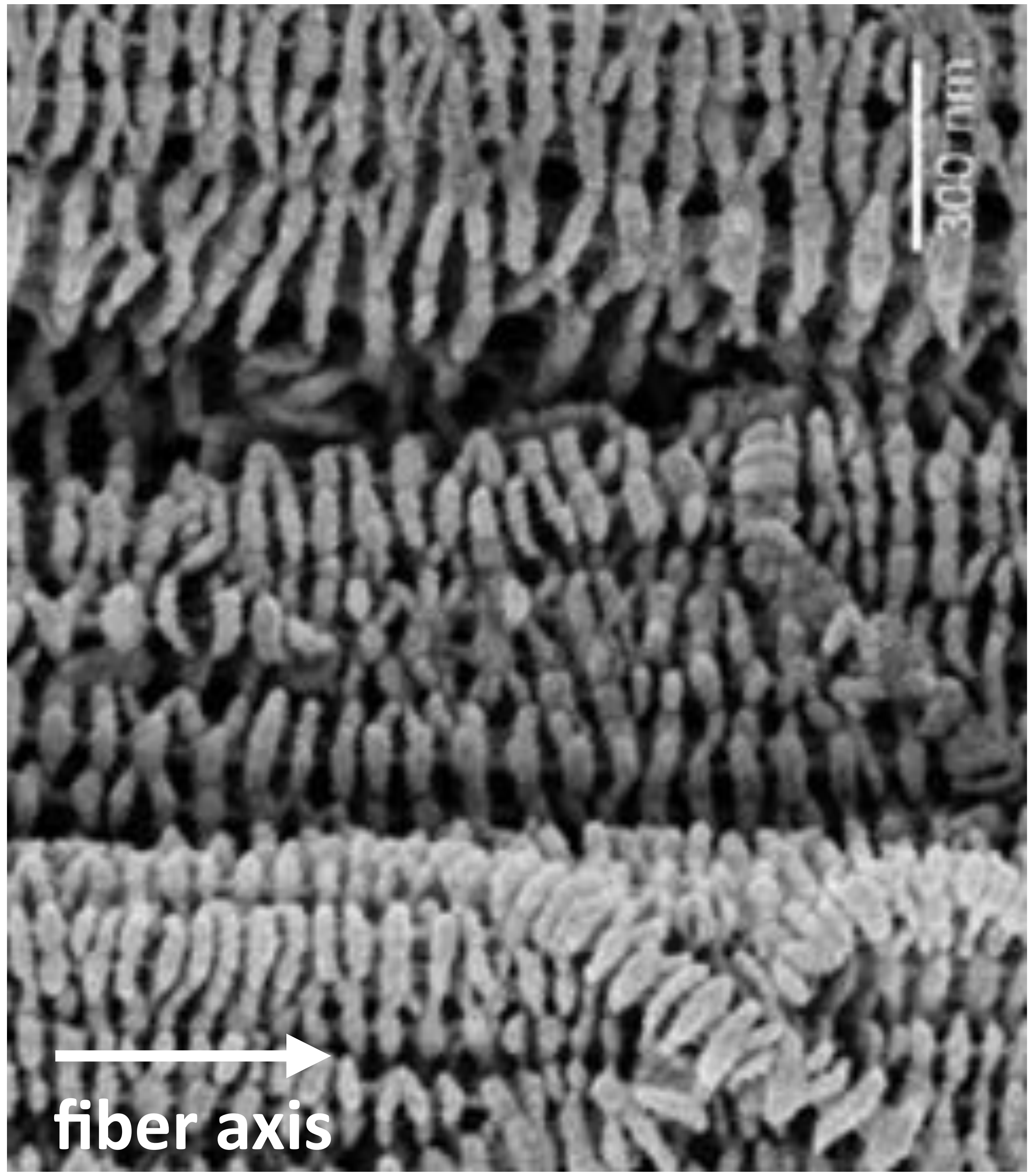
- **secondary lamellae nucleate nearly at right angles (~90°) to the primary lamellae**
- **attributed to defects in isotactic sequence regularity**

Shish-Kebab Structures

- in fibers, high shear stresses during processing align chains and generate **“shish-kebab” strutures**



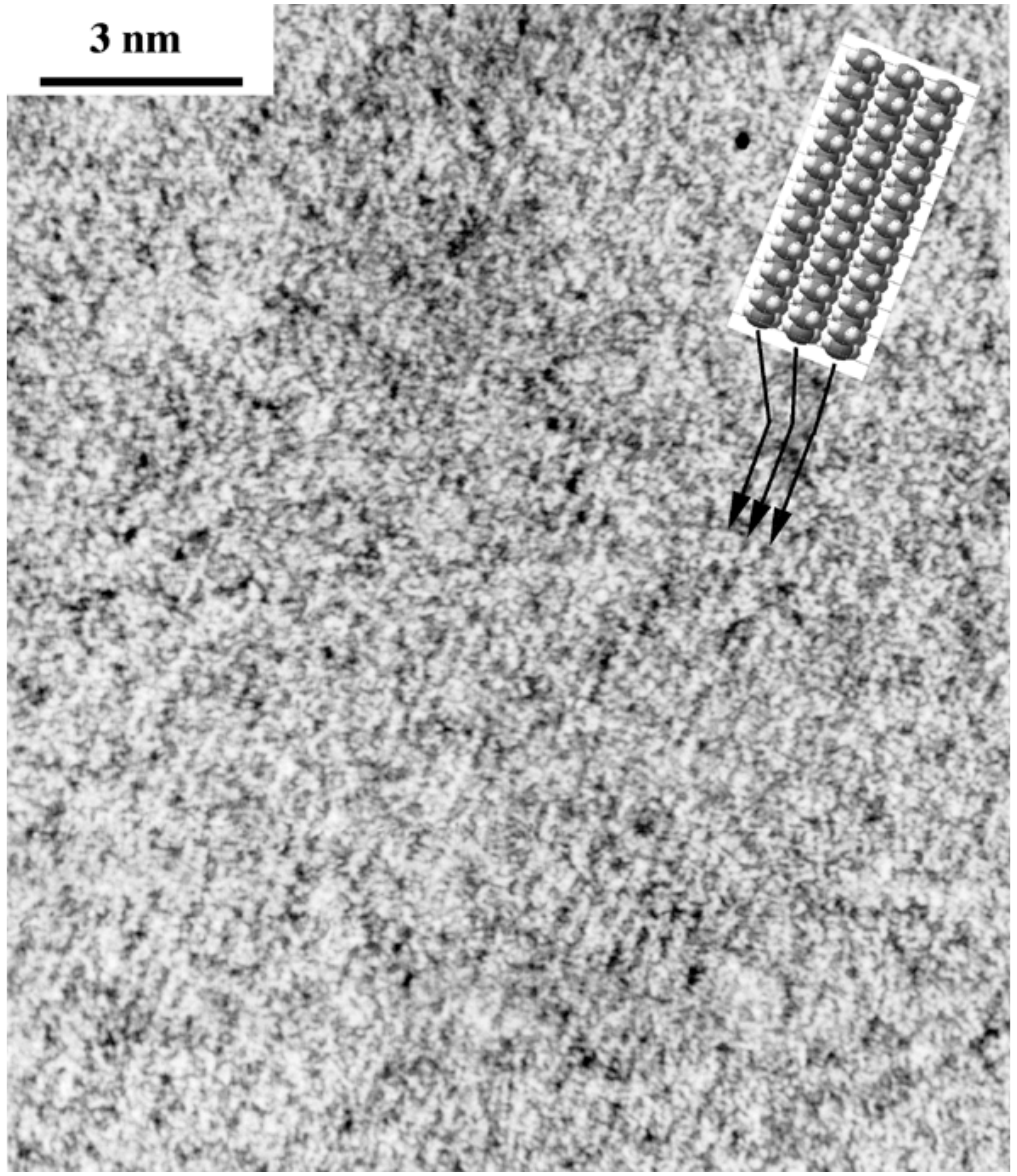




- **extended chain crystals** (“shish”) **act as nucleation sites for lamellae** (“kebabs”) **growing perpendicularly**

Ultrahigh Molecular Weight PE (UHMWPE)

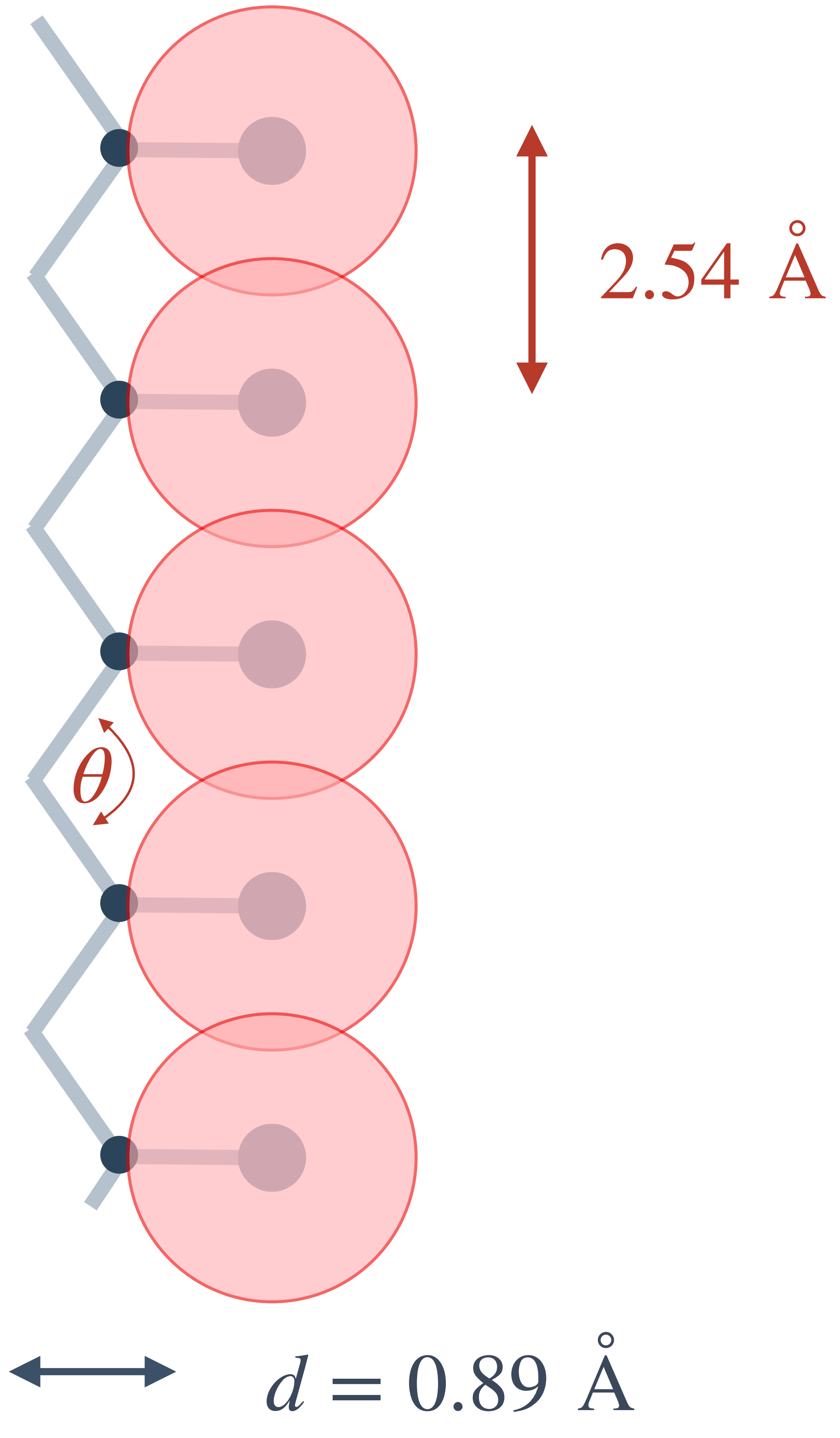
- UHMWPE fibers ($M_n \approx 3 \times 10^6$ g/mol) from dilute gels show extremely high orientation and crystallinity



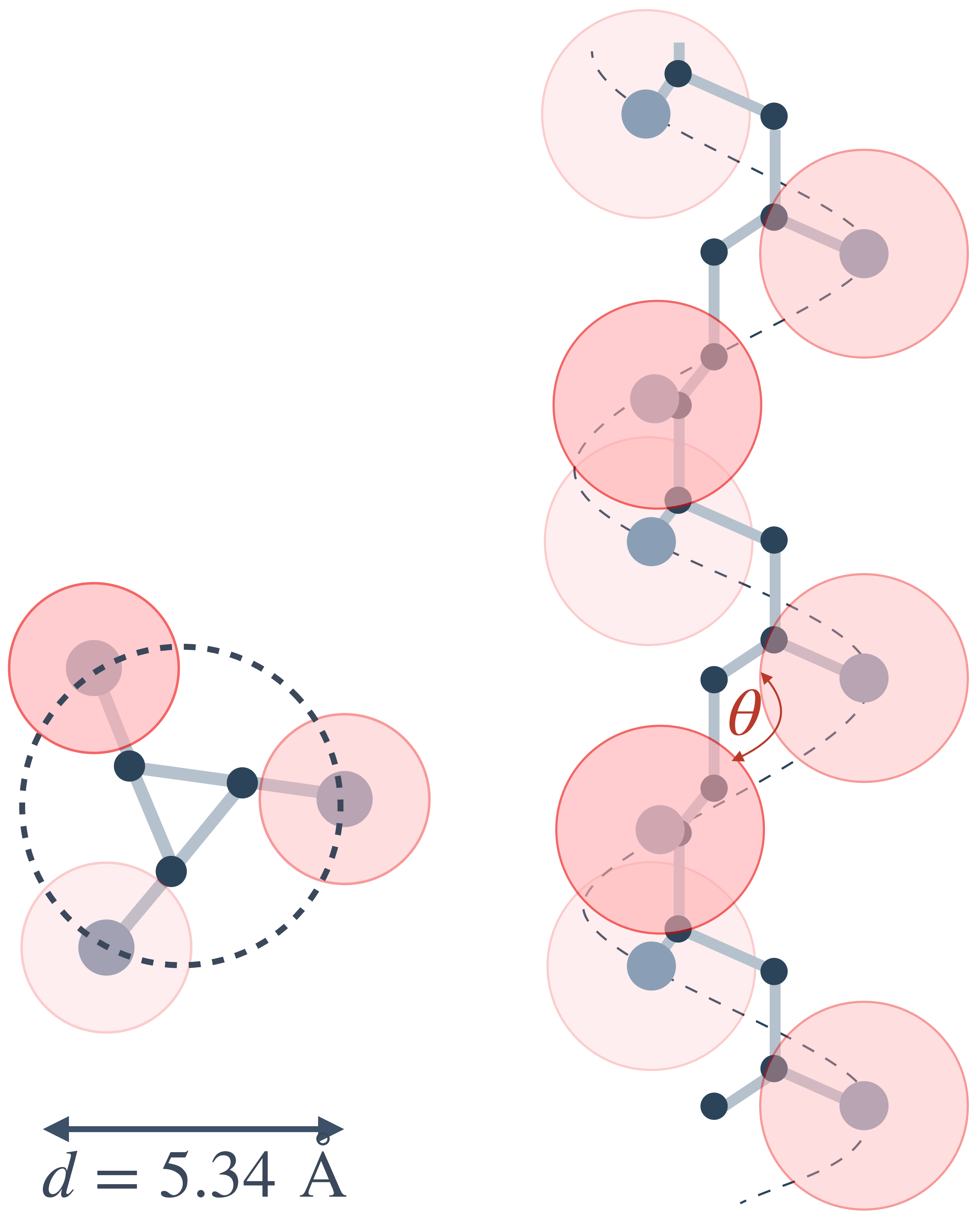
- **exhibit exceptional properties: stiffness *E* = 200 GPa, tensile strength up to 7 GPa**
  (comparable to inorganic high-performance fibers)

What about Ultrahigh Molecular Weight PP???

isotactic (i.e. PE)



isotactic (i.e. PP, PS)



Learning Outcome

- many polymers crystallize if chains are sufficiently regular, linear, and periodic
- single crystals form thin lamellae with chain folding. The fold surface energy reduces T_m compared to the ideal infinite crystal.
- crystallisation rate depends on supercooling: it peaks at intermediate temperature due to competition between nucleation and viscosity
- melt-crystallised polymers are semi-crystalline (often 30–60%) and form spherulites
- specific processing routes yield alternative morphologies: stacked lamellae (fibers) or extended chain crystals (UHMWPE).