Chapter 7

Semicrystalline State

Contents

- crystal structure
- lamella
- spherulite
- crystallinity

- crystallization ~ Chapter 8

Polymer crystallography

- (semi)crystalline = crystal + amorphous
- crystal = regular repeating 3-D array of atoms
- unit cell = smallest volume of repeating structure
  - depending on a, b, c, and α, β, γ

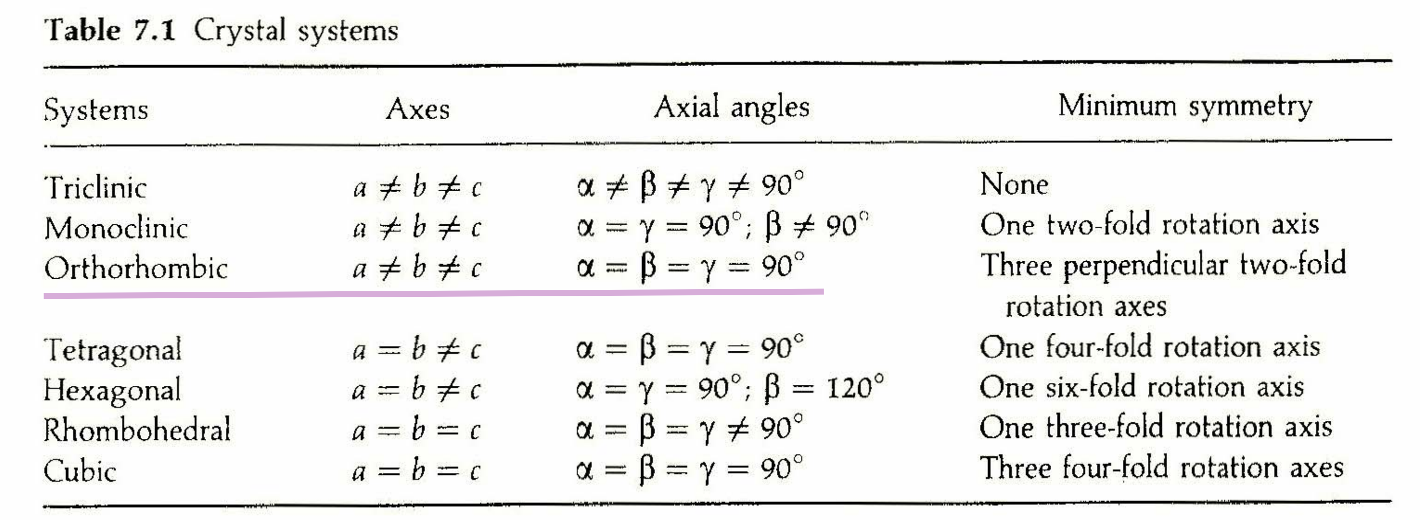
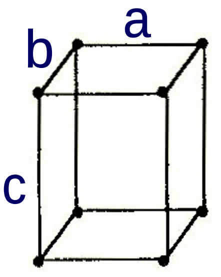


Table 7.1 Crystal systems

Systems	Axes	Axial angles	Minimum symmetry
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	None
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°$; $\beta \neq 90°$	One two-fold rotation axis
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Three perpendicular two-fold rotation axes
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	One four-fold rotation axis
Hexagonal	$a = b \neq c$	$\alpha = \gamma = 90°$; $\beta = 120°$	One six-fold rotation axis
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	One three-fold rotation axis
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Three four-fold rotation axes



$\alpha = \angle bc$

$\beta = \angle ac$

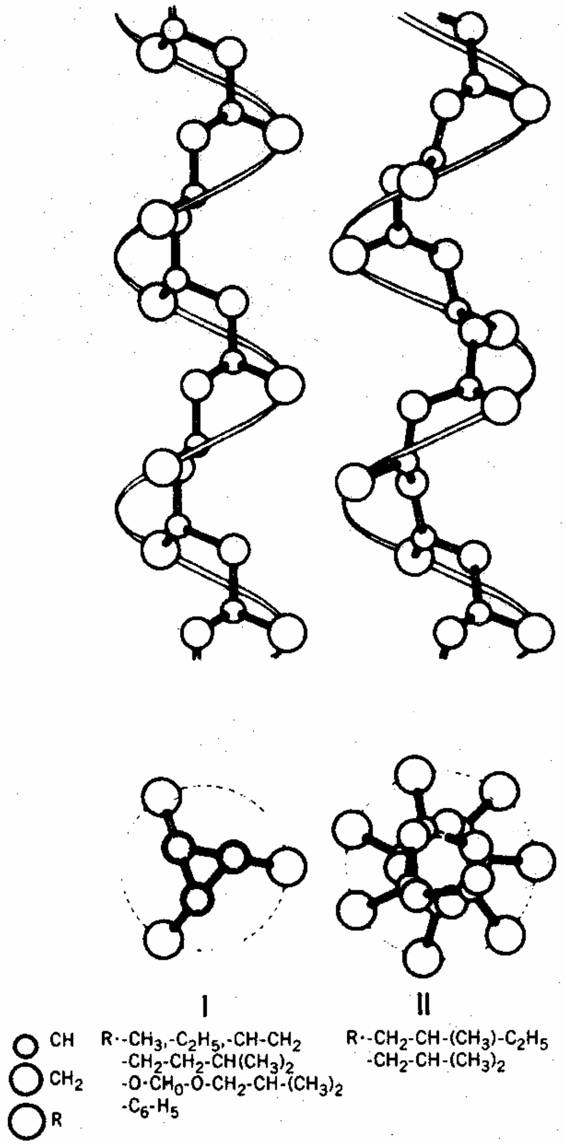
$\gamma = \angle ab$

- polymer crystal
  - monoclinic, orthorhombic (orthogonal) popular
  - c axis is chain axis

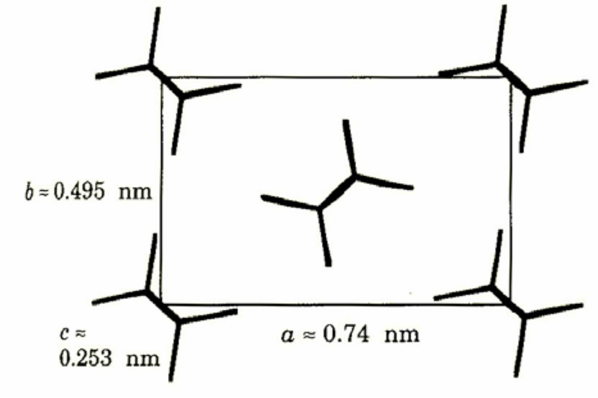
Polymer crystal

- Chains are of their preferred conformation given by RIS.
  - conformation of the lowest energy

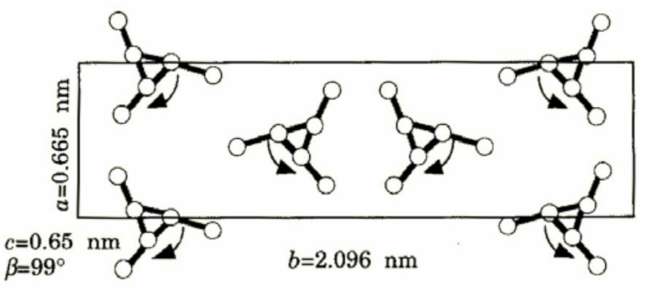
  - PE ~ TTTT--- → planar zigzag
  - POM ~ GGGG--- or G'G'G'G'--- → 2_1 helix
  - iPP ~ TGTG--- or TG'TG'--- → 3_1 helix
  - PVA, PVF ~ TTTT--- → planar zigzag
  - Nylon ~ hydrogen bonding → planar zigzag



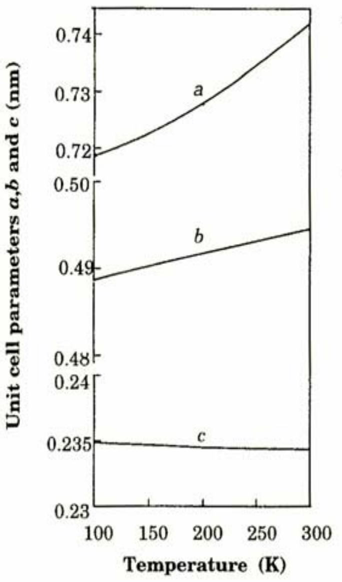
- Chains arranged to pack better.
  - planar zigzags
    - orthorhombic
    - not circular X-section
    - not very far from hexagonal

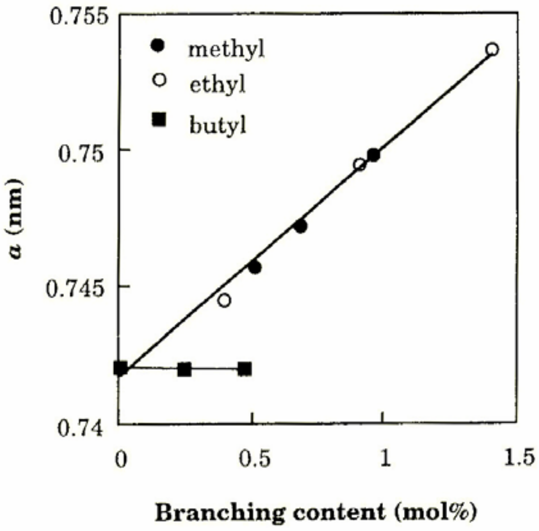


  - helices
    - iPP ~ left- and right-handed helices pairing
    - POM ~ left- and right-handed helices in different crystals



- anisotropic.
  - chain molecule
  - covalent bonding in c axis
  - E(c) >> E(a,b)
    - 300 >> 5 GPa for PE
    - E(Spectra®) ~ 60 GPa
  - birefringent



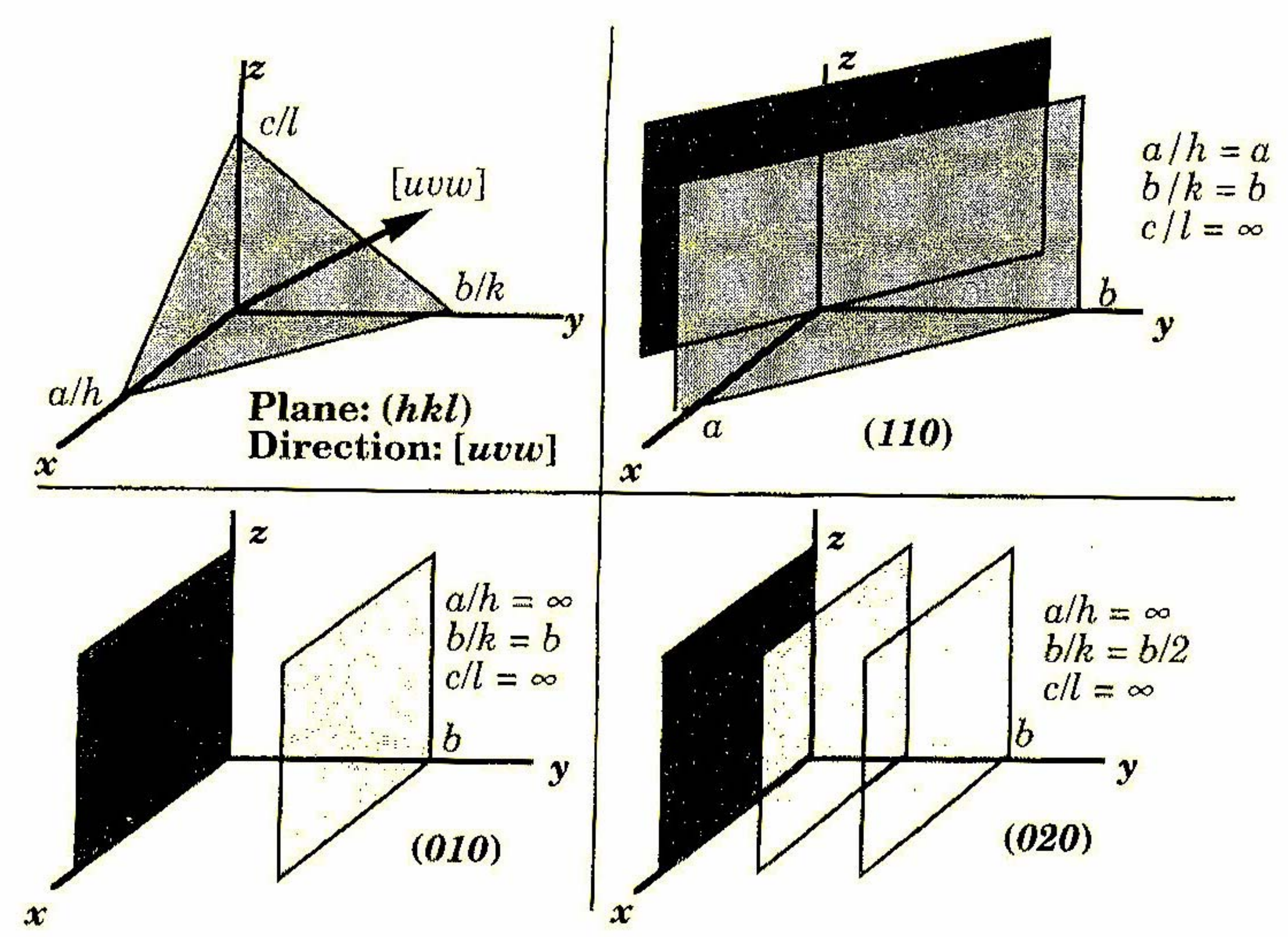


- polymorphic
  - depending on T and P

  - PE ~ orthogonal, monoclinic, hexagonal
  - iPP ~ α (monoclinic), β (hexagonal), γ (trigonal), smectic
    - different arrangement of left, right, up, and down

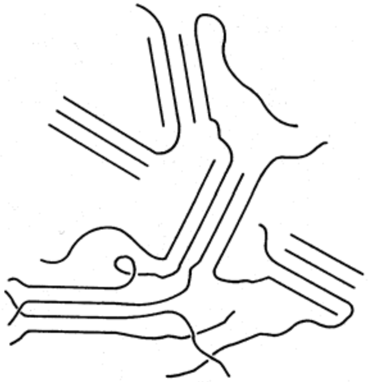
Miller index

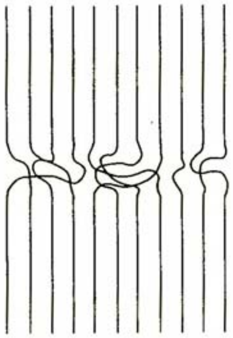
- The plane passing (a/h, b/k, c/l) is (hkl) plane.



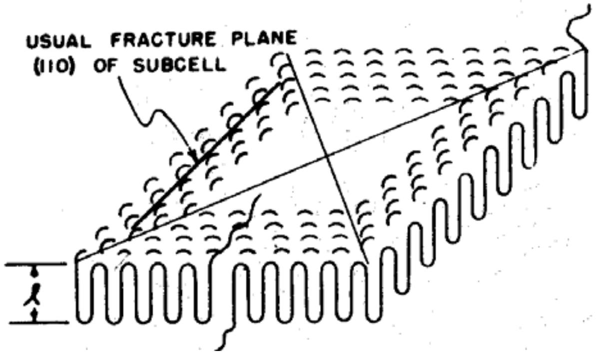
Semicrystalline state

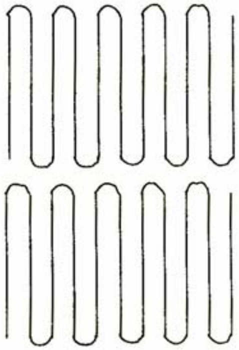
- fringed micelle model
  - intuitive and historical view
  - A chain passes through crystallites.
  - switchboard lamellar re-entry





- folded chain model
  - modern view
  - suggested in single crystal lamella from dilute solution
    - Chains are perpendicular to the surface of lamella of 10-nm thick.
    - Chains got to be folded.
  - adjacent lamellar re-entry

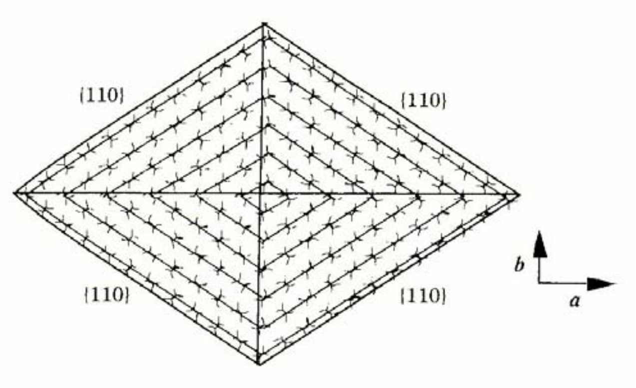


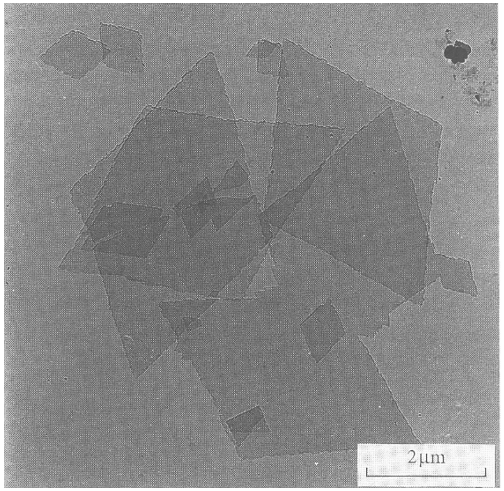


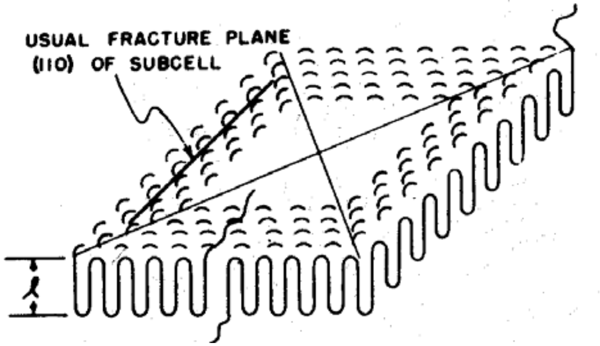
Lamella

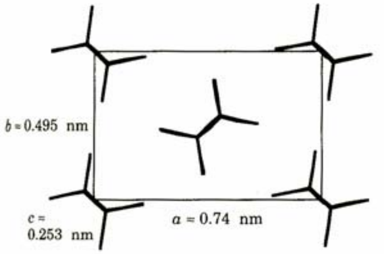
- formed as single crystal from solution or as part of spherulite from melt

- growth of PE lamella
  - on {110} fold plane

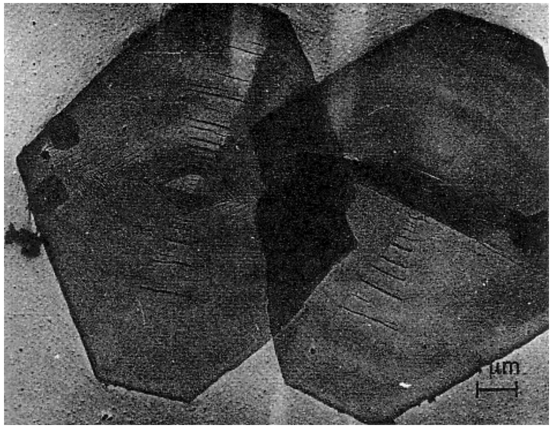


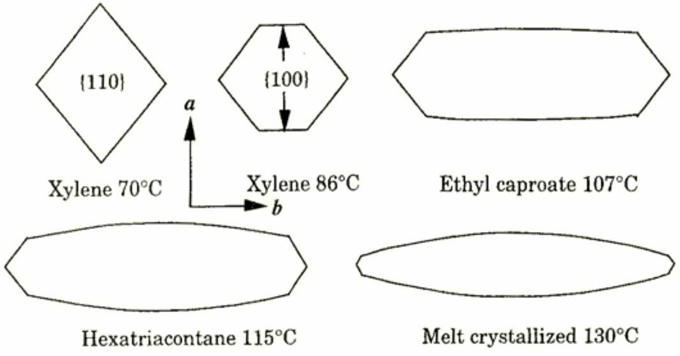


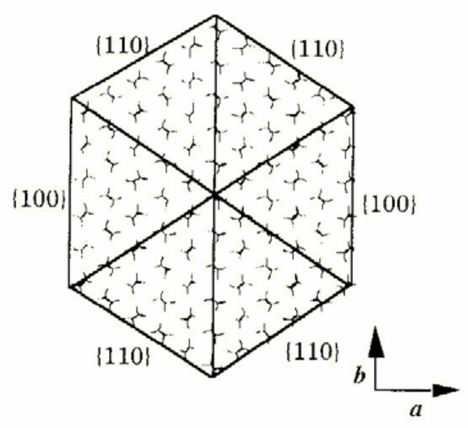


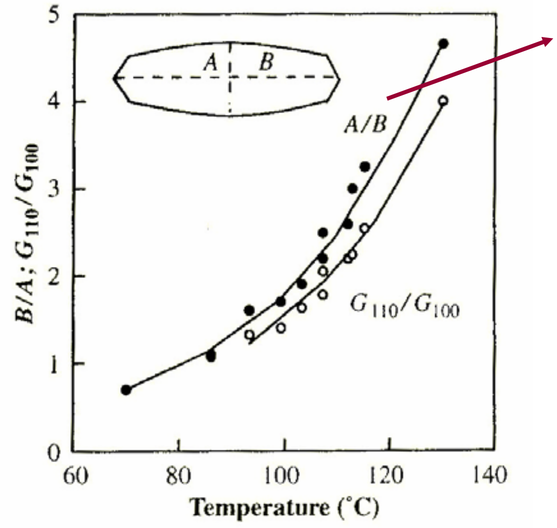


- growth of PE lamella (cont'd)
  - at higher temp ~ on {110} and {100} planes
    - crystals grown along {100} is of low T_m



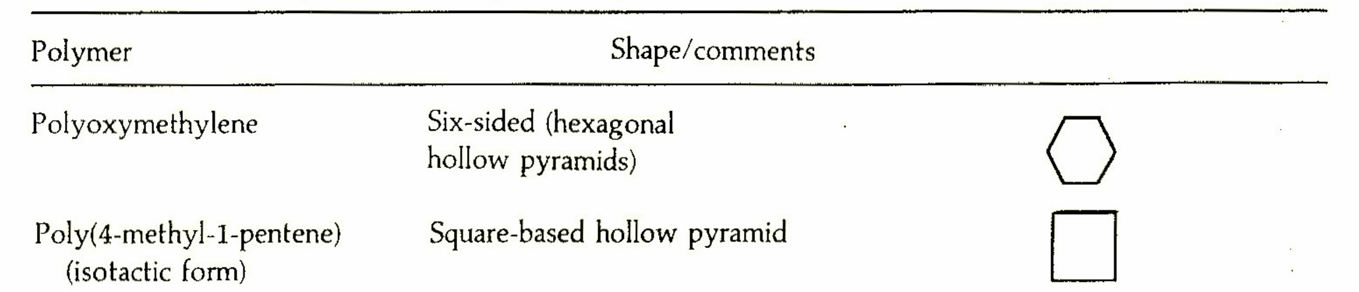




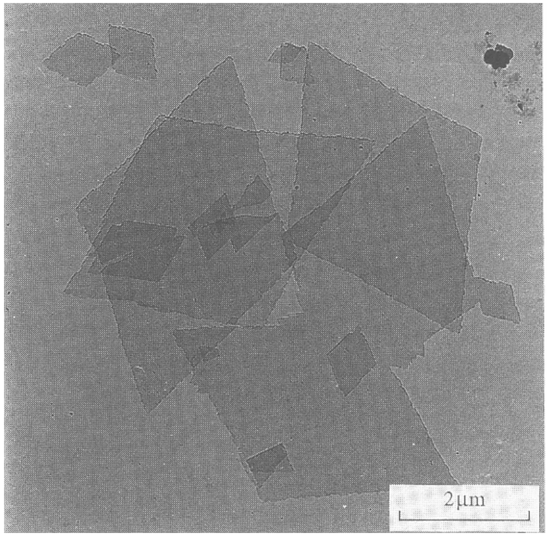


B/A

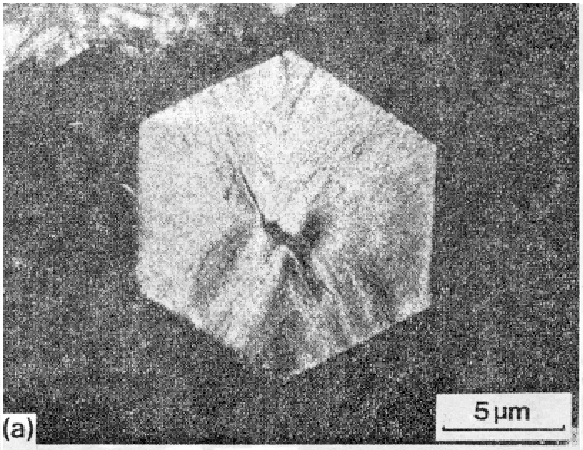
- shape of fold surface depends on crystal structure



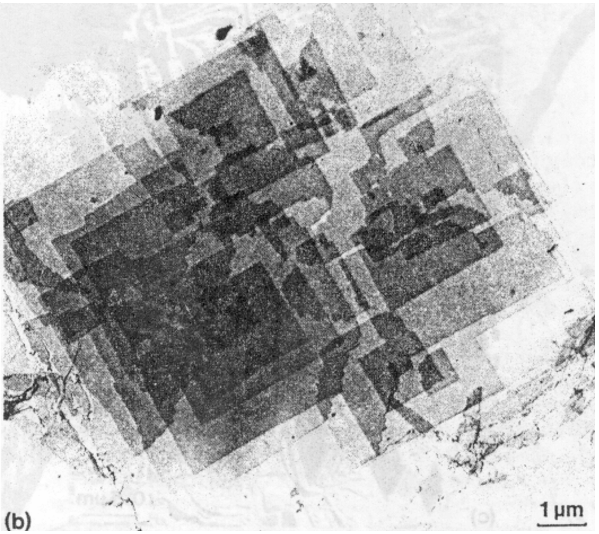
Polymer	Shape/comments	
Polyoxymethylene	Six-sided (hexagonal hollow pyramids)	⬡
Poly(4-methyl-1-pentene) (isotactic form)	Square-based hollow pyramid	□



PE
(orthorhombic)

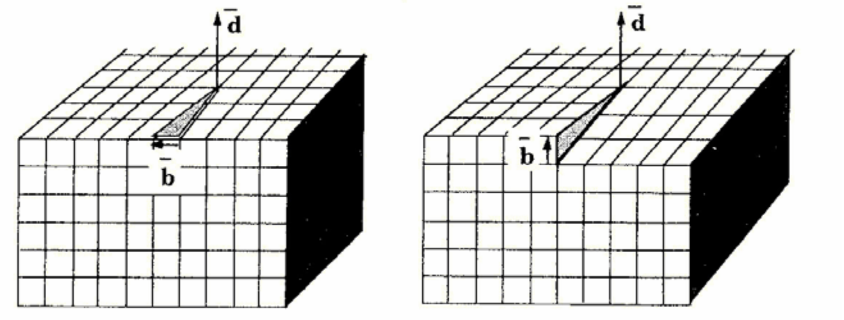


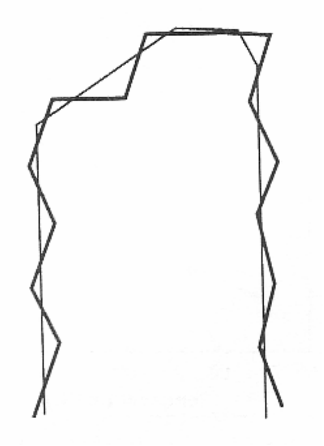
POM
(hexagonal)

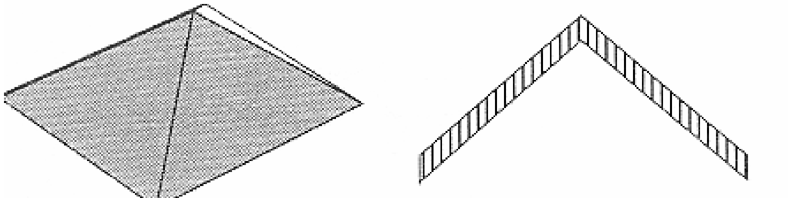


poly-4-methyl-1-pentene
(tetragonal)

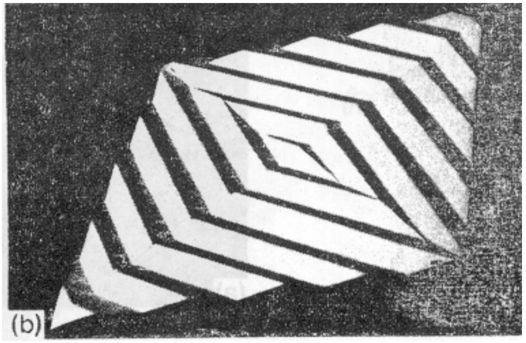
- multi-layer lamella
  - screw dislocation
- hollow pyramid
  - lattice mismatch

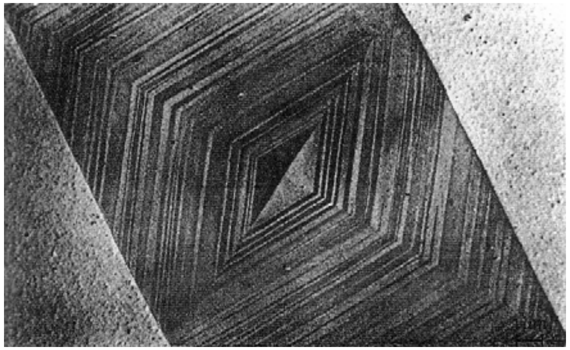






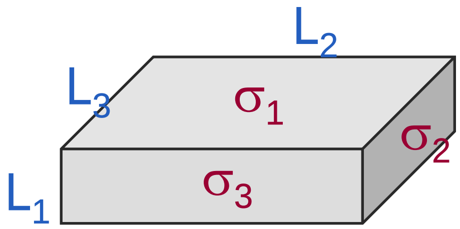
Cross-section of hollow pyramid





Lamellar thickness

- thickness/width ~ .01 - .001
- equilibrium crystal
  - dimension L_1, L_2, L_3
  - surface energy σ_1, σ_2, σ_3
  - free energy of crystal w/rt melt, ΔG



$$\Delta G = V\Delta g^0 + 2L_1L_2\sigma_3 + 2L_1L_3\sigma_2 + 2L_2L_3\sigma_1 \quad (7.7)$$

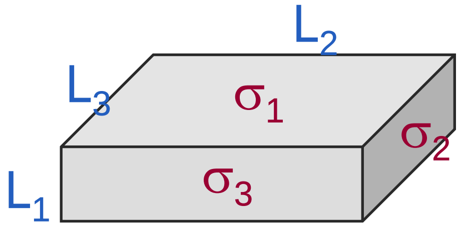
$$\Delta G = \underset{\substack{\uparrow \\ \text{free energy melting}}}{V\Delta g^0} + \underbrace{\frac{2V}{L_3}\cdot\sigma_3 + 2L_1L_3\sigma_2 + \frac{2V}{L_1}\cdot\sigma_1}_{\text{surface free energy of Xtal}} \quad (7.9) \quad \leftarrow L_2 = \frac{V}{L_1L_3} \leftarrow \text{const vol}$$

- for minimum free E of Xtal

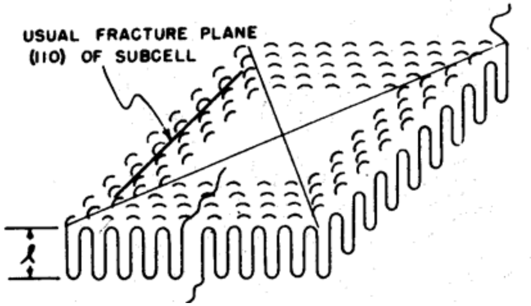
$$\frac{\partial(\Delta G)}{\partial L_1} = L_3\sigma_2 - \frac{V}{L_1^2}\sigma_1 = 0 \Rightarrow \frac{L_1}{\sigma_1} = \frac{L_2}{\sigma_2} \quad (7.10)$$

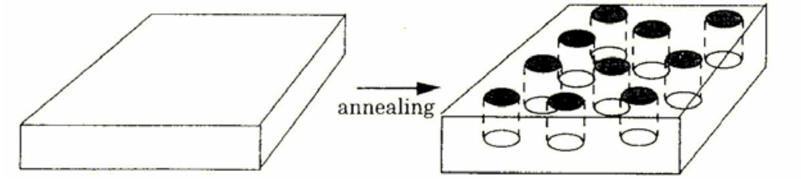
$$\frac{\partial(\Delta G)}{\partial L_3} = L_1\sigma_2 - \frac{V}{L_3^2}\sigma_3 = 0 \Rightarrow \frac{L_2}{\sigma_2} = \frac{L_3}{\sigma_3} \quad (7.11)$$

$$\frac{L_1}{\sigma_1} = \frac{L_2}{\sigma_2} = \frac{L_3}{\sigma_3} \qquad (7.12)$$



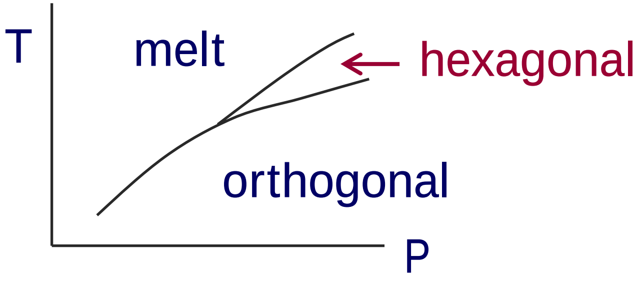
- σ_2, σ_3 ~ lateral surface
  - trans ~ lower energy ~ 15 mJ/m^2
- σ_1 ~ fold surface
  - gauche ~ higher energy ~ 90 mJ/m^2
- $\sigma_1 \approx 7\ \sigma_2$ or σ_3
- $L_1 \approx 7\ L_2$ or L_3 for equilibrium Xtal
- observed, $L_1 \approx (.01\text{-}.001)\ L_2$ or L_3
- Polymer crystals are not in equilibrium.
- thickening by ‘annealing’





‘Swiss cheese’

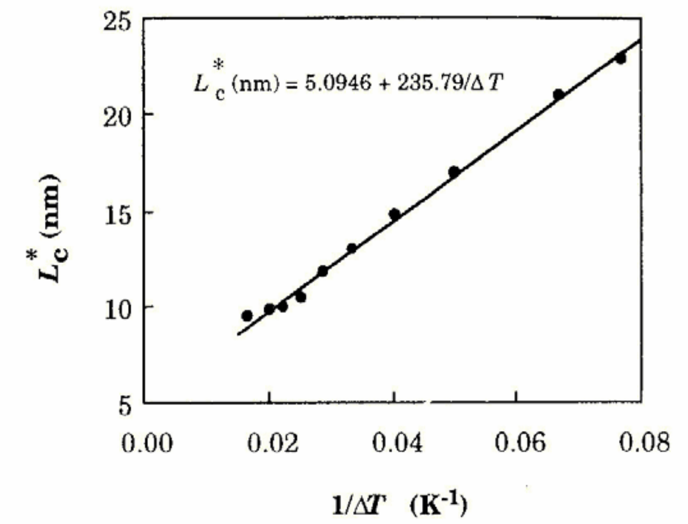
- annealing ~ heat treatment betw T_g and T_m
  - by annealing
    - L_1 increases
    - T_m increases
    - w_c (X_c) increases
  - L_1 increases with annealing time and Temp
    - L_1 vs log t linear
- thick crystal formed at high T and P
  - PE ~ μm-thick crystals at 5 kbar
  - extended-chain crystal with hexagonal array



- thickness dep on supercooling
  - Keller

$$L_c^* = \frac{C_1}{\Delta T} + \delta L \qquad (7.13)$$

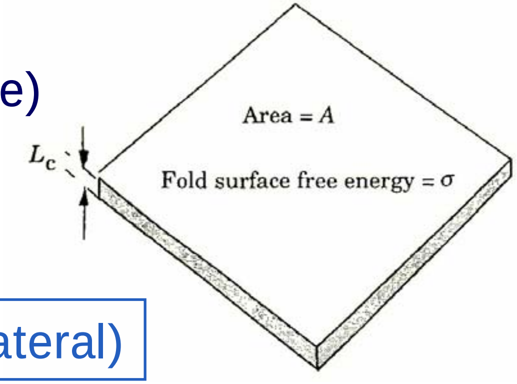
    - ΔT ~ supercooling ~ $T_m^0 - T_c$
    - T_m^0 ~ equili melting temp
      - T_m of perfect Xtal with M = ∞



  - Lauritzen-Hoffman

$$L_c^* = \frac{2\sigma T_m^0}{\Delta h^0 \rho_c \Delta T} + \delta L \qquad (7.14)$$

- thickness and T_m
  - Thompson-Gibbs eqn
  - free energy of melting, ΔG = ΔG(bulk) + ΔG(surface)



$$\Delta G = \Delta G^* + \sum_{i=1}^{n} A_i \sigma_i \qquad (7.15)$$

$$\Delta G = 0 \Rightarrow \Delta G^* = \sum_{i=1}^{n} A_i \sigma_i \approx 2\sigma A$$

A(fold) >> A(lateral)

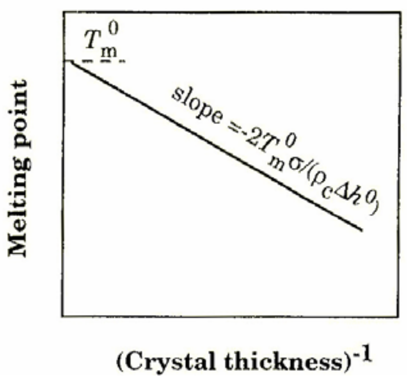
$$\Delta G^* = \Delta g^* A L_c \rho_c \qquad (7.17)$$

$$\Delta g^* = \Delta h^0 - T_m \Delta s^0 = \Delta h^0\left(1 - \frac{T_m}{T_m^0}\right) = \Delta h^0\left(\frac{T_m^0 - T_m}{T_m^0}\right)$$

at equili, $\Delta g^0 = 0$
$\Delta s^0 = \Delta h^0 / T_m^0$

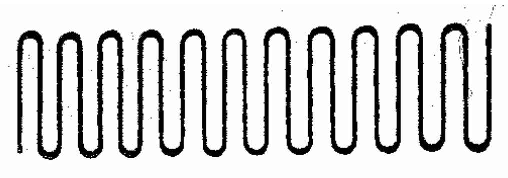
$$\Delta G^* = \Delta h^0 (T_m^0 - T_m) \frac{A L_c \rho_c}{T_m^0} \qquad (7.19)$$

$$T_m = T_m^0\left(1 - \frac{2\sigma}{L_c \rho_c \Delta h^0}\right) \qquad (7.21)$$

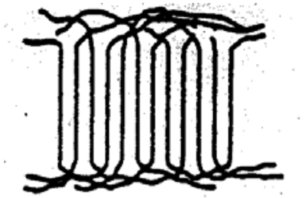


lamella re-entry

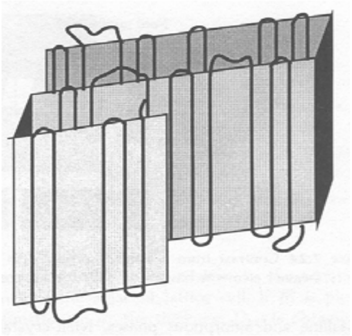
- 2 (original) models
  - adjacent reentry → folding
    - IR of mixed crystal



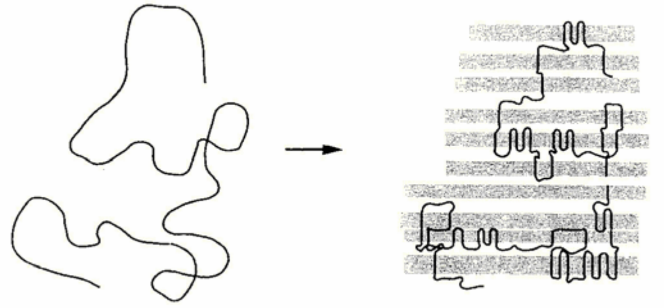
  - switchboard → fringed micelle
    - density, etching experiment



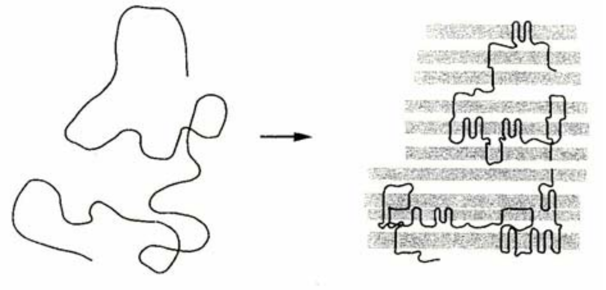
- (sol'n grown) single crystal lamellae
  - super-folding for intermediate MW
    - $<r^2>^{1/2} \propto M^{0.1}$ by SANS
    - 75% adjacent
  - mixed or partial non-adjacent for high MW



- melt crystallized lamellae
  - switchboard + some folding
  - $<r^2>^{1/2} \propto M^{0.5}$ by SANS
  - 3 phases
    - crystal + interface + amorphous

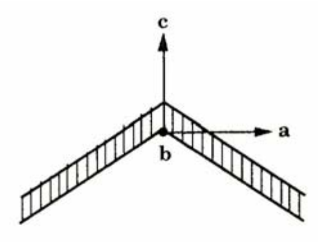


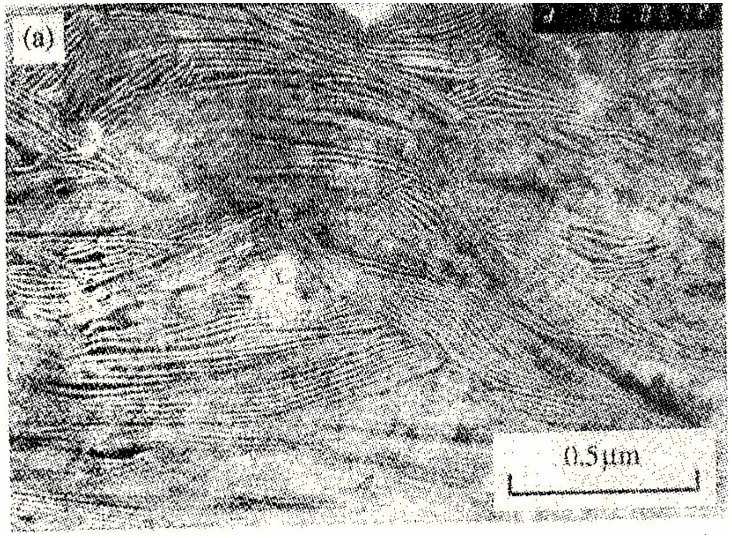
Lamella grown from melt



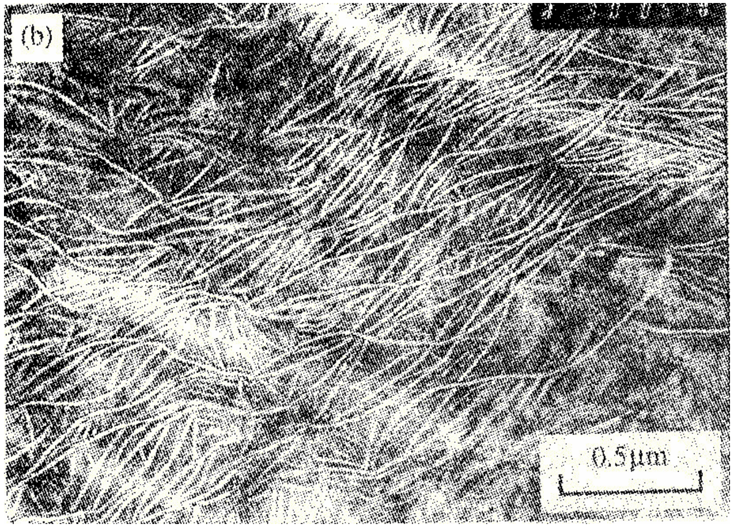
- crystallization from melt
    - in dilute solution ~ single chain
  - Many chains compete on crystal surface.
  - Chains are entangled.
  - Chain dimension preserved.
  - Local lamellar structure similar to that from solution.

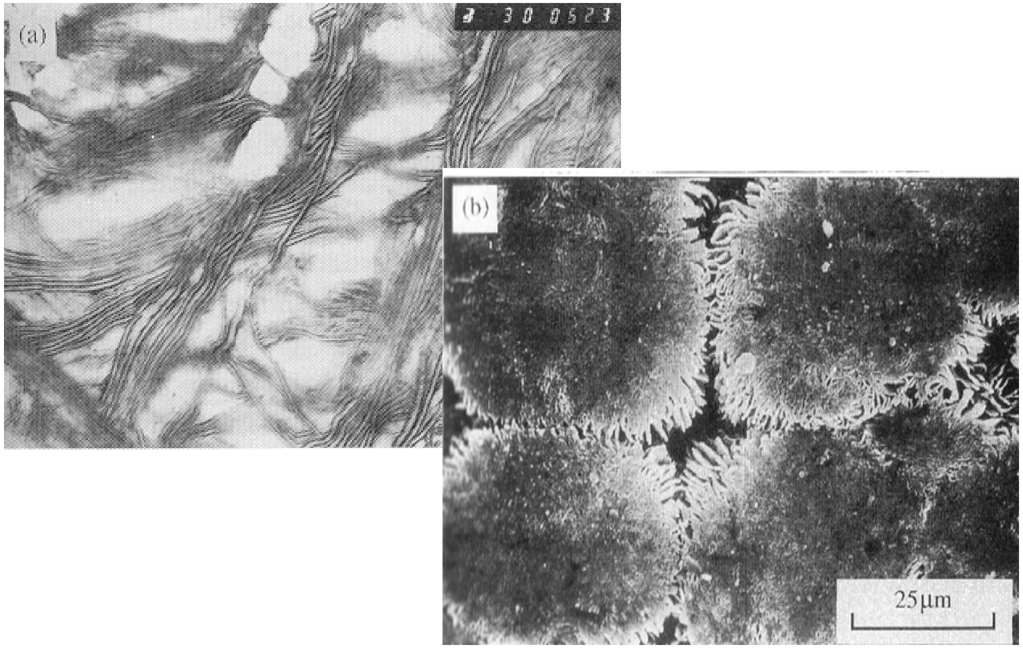
- lamellae stack
  - linear, low MW
    - large stack
    - straight or roof-shaped



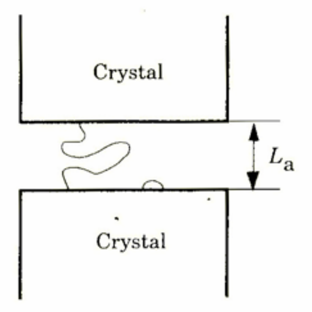


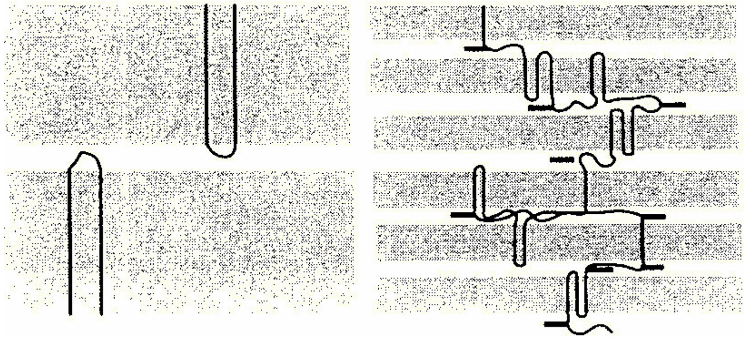
- branched, high MW
  - separated lamellae
    - defects (branches, low MW) between lamellae
    - linear, high MW crystallize first ~ ‘molecular fractionation’
  - C- or S-shaped
    - defects on the fold surface





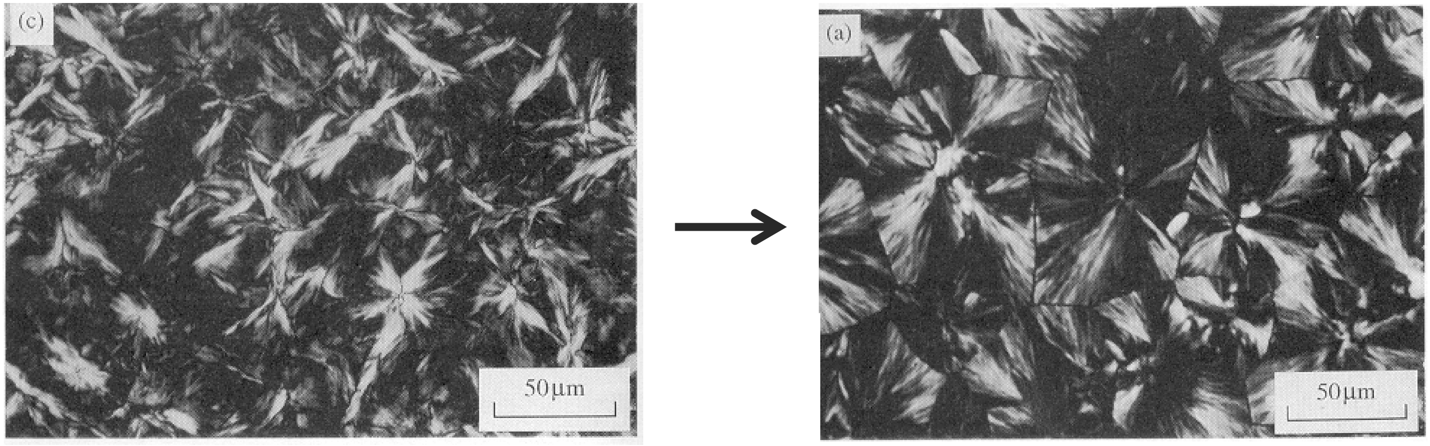
- tie-molecule
  - between lamellae
  - high MW
    - 90% of chain-end in amorphous
  - branches
    - branches longer than C2 in amorphous
  - can help strength and ductility

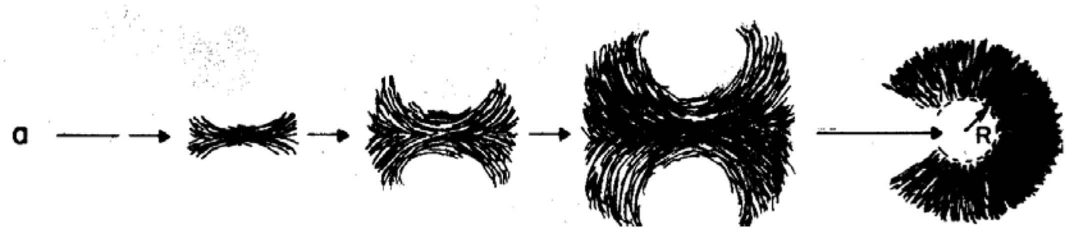




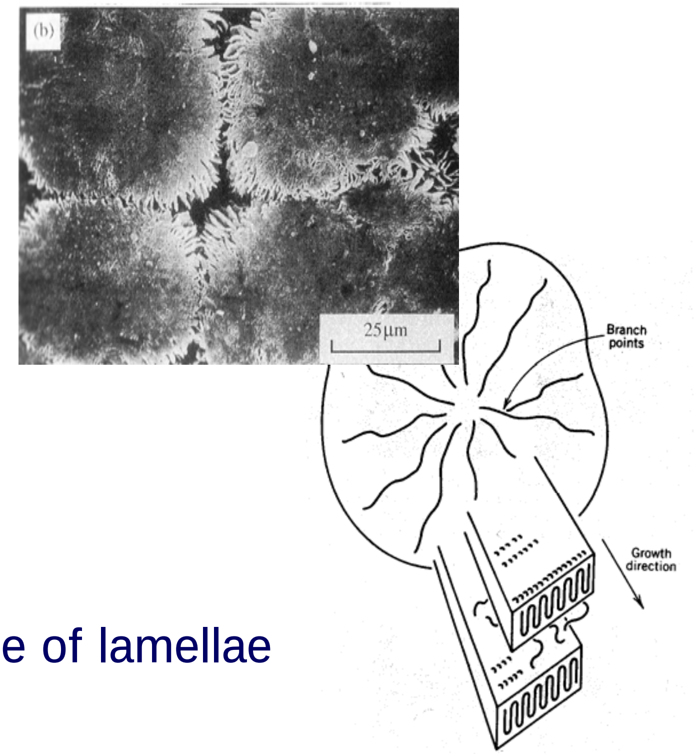
Spherulite

- spherical crystal from melt
  - µm – mm
- melt-crystallized
  - at high temperature → axialite (sheaf-like)
  - at low temperature → spherulite (dendritic growth)

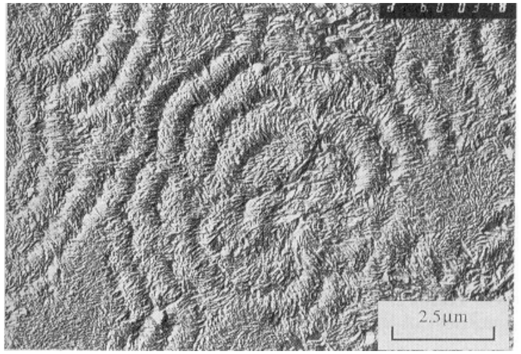


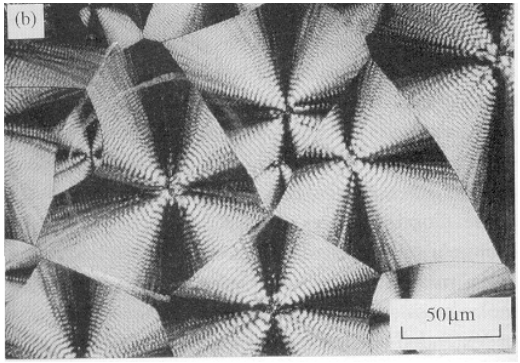


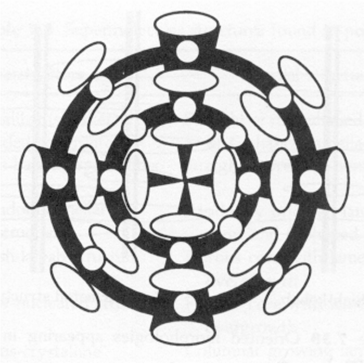
- radial growth
  - radius parallel to b axis
  - molecular fractionation
    - high MW first
    - low MW subsidiary or repelled



- banded spherulite
  - lamellar twisting
    - due to screw dislocation or curvature of lamellae





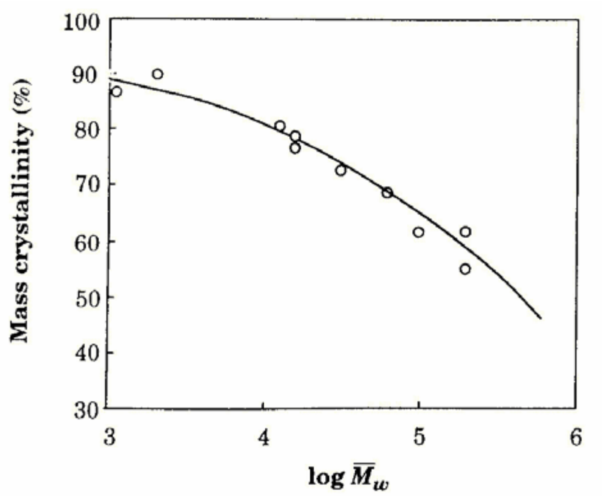


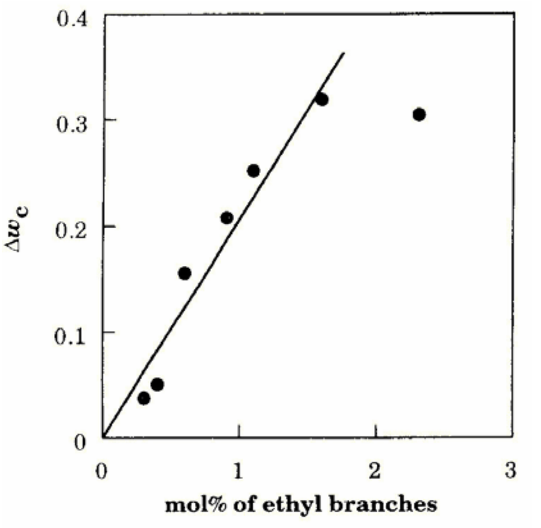
Crystallinity

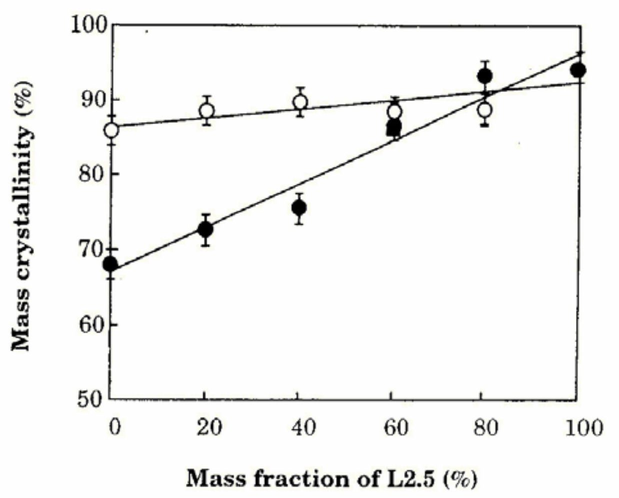
- crystallinity = degree of crystallinity = % crystallinity
  - X_c (w_c) = volume (weight) of Xtal / total volume (weight)
  - 30 ~ 70% for polymers

- measuring X_c
  - volumetric
    - density gradient column
    - dynamic density measurement
  - crystallographic ~ WAX
  - thermal ~ DSC
  - spectroscopic ~ IR, Raman
  - ➢ crystal + interface + amorphous
  - ➢ 100% crystal data ← unit cell structure
  - ➢ 100% amorphous data ← quenched sample, extrapolation from melt

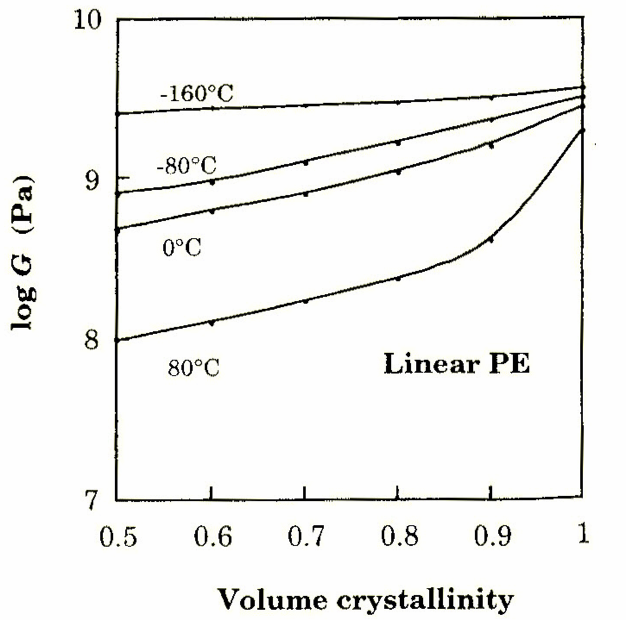
- X_c depends on
  - repeat unit structure
    - X_c(PE) > X_c(PEster)
  - MW
    - entanglements lowers X_c
  - branches
    - expansion of unit cell
    - decrease in X_c
  - thermal history
    - T_c
    - cooling rate

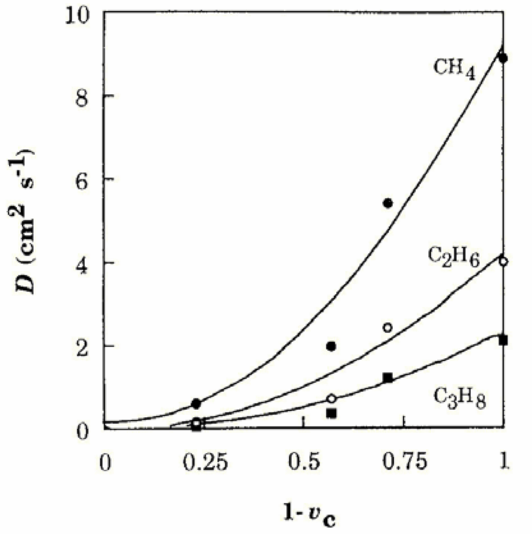






- X_c and properties
  - stiffness (modulus)
    - increases with increasing X_c
    - dep on temp (below or above T_g)
  - permeability
    - transport through amorphous only
  - weatherability
    - degradation, oxidation on amorphous



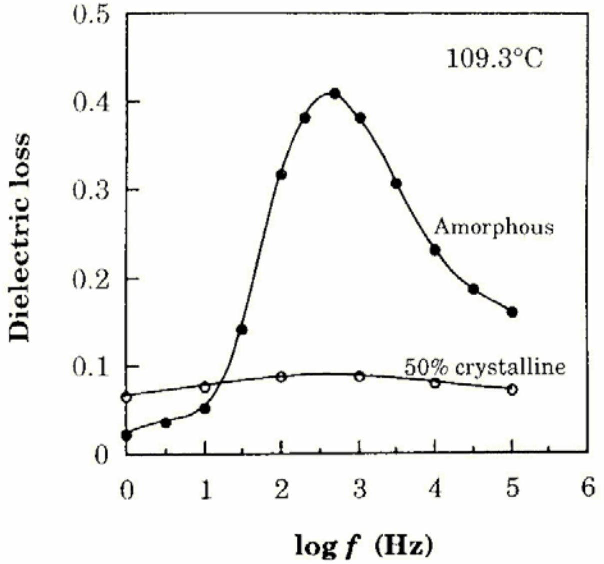


Relaxations in semiXtalline polymers

- complex
  - 2 (or 3) phases
  - X_c
  - orientation of Xtals

- secondary relaxations
  - in crystal, amorphous, or both
  - assigned through expt with varying X_c

- glass transition
  - only in amorphous
  - broader in semiXtalline
  - weak in high-X_c polymers



- crystalline relaxation
  - additional relaxation at above T_g
  - mechanical
    - sliding of lamellae
    - needs amorphous region
    - not found in single crystals
  - dielectric
    - twisting and c/2 translating of chain
    - found in single crystals
    - found in linear polymers with high X_c
      - in PE, iPP, POM
      - not in PET, PA
    - intensity proportional to lamellar thickness
    - peak temp Arrhenius dependent with $E_a \propto X_c$