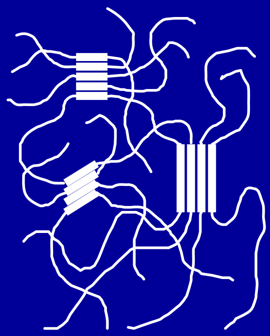
Chapter 6
Crystalline State

Contents

- Melting
- Crystal structure
- Semicrystalline structure
  - Models
  - Lamella & Spherulite
- Crystallinity
- Crystallization
- Lamella re-entry
- Melting point
- Annealing

1. Melting



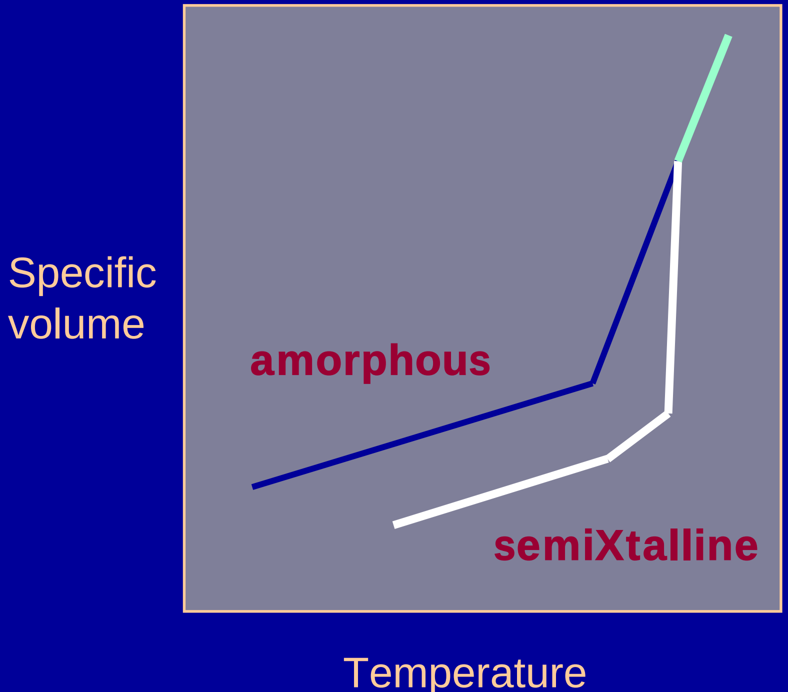
- semicrystalline = crystal + amorphous region
- melting = fusion of crystals
- Melting is a (true) 1st-order phase transition

  $(dG/dP)_T = V$

  $(dG/dT)_P = S$

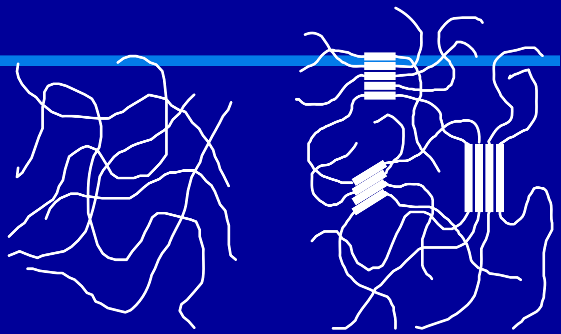
  $(d(G/T)/d(1/T)) = H$

  - ✓ V, S, H are discontinuous at T_m
- T_m measurement
  - Dilatometry (V) Fig 6.2
    - » on heating



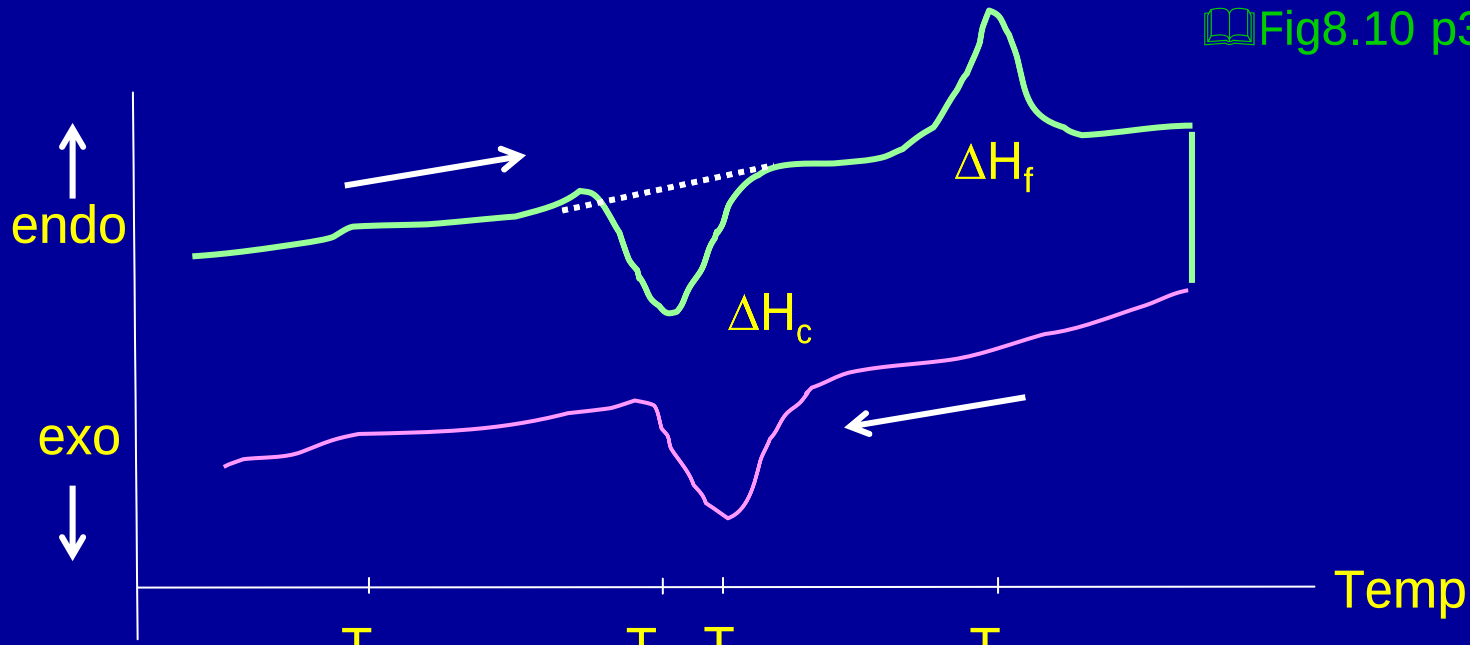
Melting (cont'd)

- T_m measurement (cont'd)
  - DSC (*H*)
    - » on heating
    - » crystallinity 🕮p244



🕮Fig6.3 p244

🕮Fig8.10 p369



Melting (cont'd)

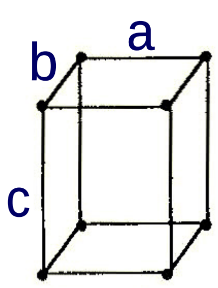
- T_m measurement (cont'd)
  - IR, microscopy, X-ray
    - conventional ~ snapshot ~ indirect and not popular
    - real-time ~ measurement possible

2. Crystal Chemistry

- (semi)crystalline = crystal + amorphous
- crystal = regular array of atoms
- unit cell = smallest volume of repeating structure
  - crystal system ~ shape of unit cell
  - Orthorhombic is popular for polymers

Table 7.1 Crystal systems

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



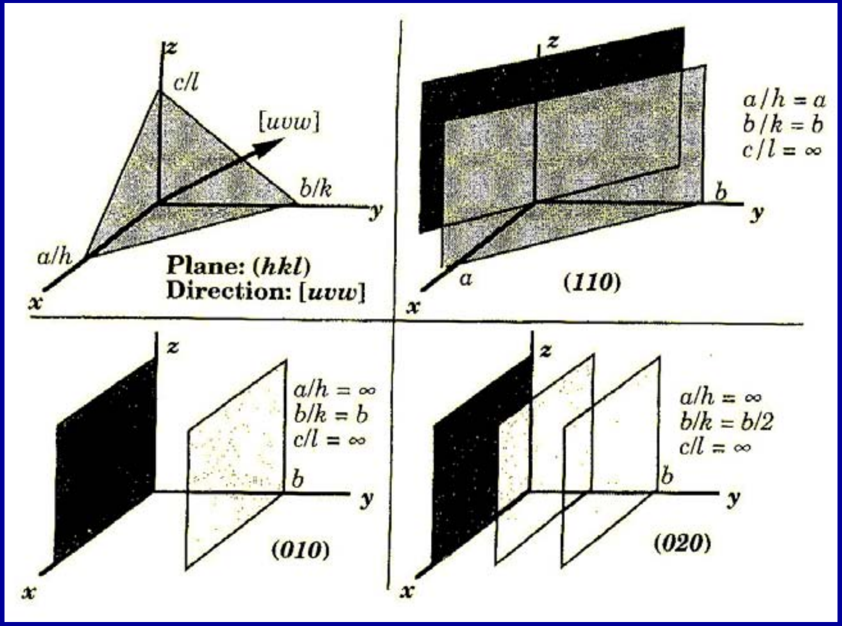
$\alpha = \angle bc$

$\beta = \angle ac$

$\gamma = \angle ab$

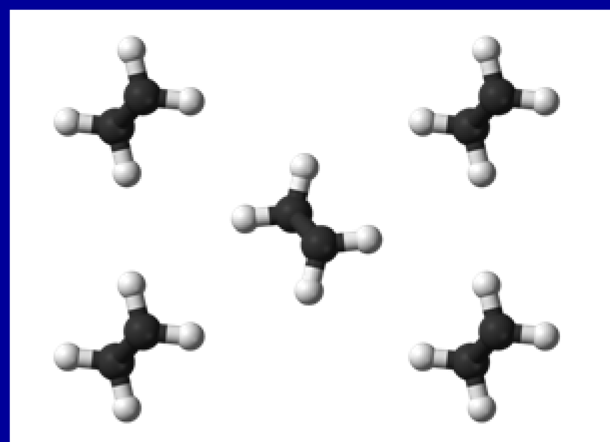
Crystal Chemistry (cont'd)

- observing crystal structure
  - X-Ray (WAXD) 🕮Fig 6.4 & 6.5(b)
  - ED, IR, Raman
- Miller index   See the supplement
  - The plane passing (*a/h, b/k, c/l*) is (*h k l*) plane.

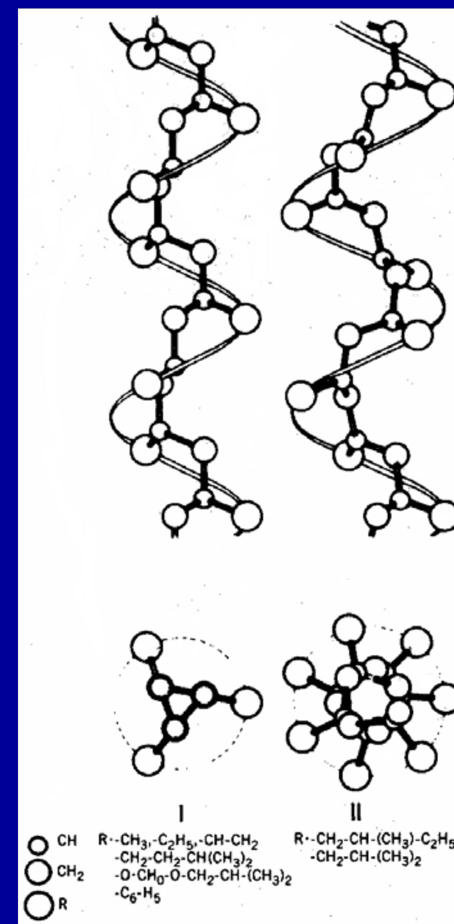


3. Crystallographic Structure of Polymers

- crystal(lographic) structure = unit cell structure
- Chains are of their preferred conformation given by RIS model. ← minimum energy 🕮p256 #2
  - Polyethylene; *tttttt*…; planar zigzag
    - » 🕮Fig 6.5



  - Isotactic polypropylene; *tgtg*…; 3_1 helix
    - » 🕮Fig 6.6, 6.7

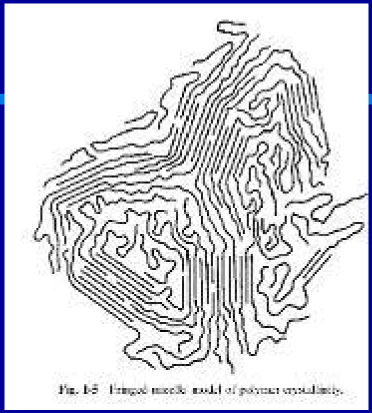


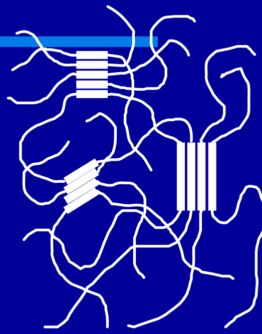
Crystal Structure (cont'd)

- Polyoxymethylene; *g+g+g+g+… or g-g-g-g-…*; 2_1 helix
- Nylon; hydrogen bonding; planar zigzag 🕮Fig 6.8

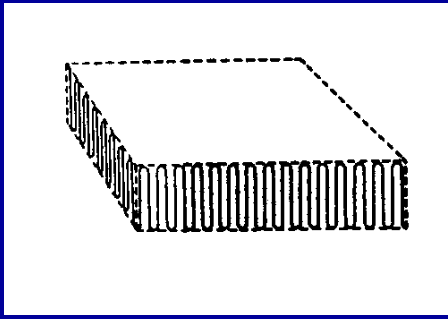
- orthogonal popular ← packing 🕮p256 #3
- anisotropic ← packing 🕮p256 #3
- polymorphic 🕮Table 6.2

4. Semicrystalline State



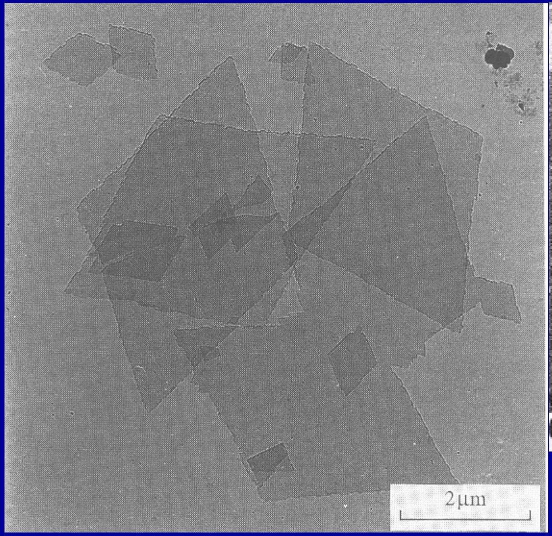


- Fringed micelle model 📖Fig 6.9
  - intuitive
  - A chain passes through crystallites.
  - 2-phase morphology (crystallites + amorphous)
- Folded chain model 📖Fig 6.10
  - Single crystal lamella from dilute solution 📖Fig 6.5(a)
  - Chains are perpendicular to lamella by ED
  - Chains got to be *folded*
  - 3-phase morphology (lamellae + interface + amorphous)
  - Lamella re-entry – adjacent or switchboard?

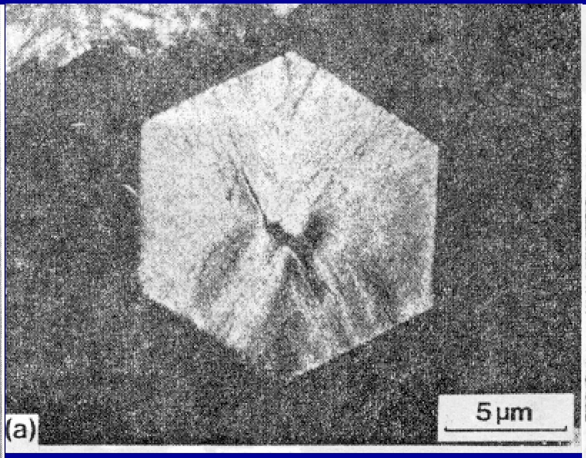


Lamella 1

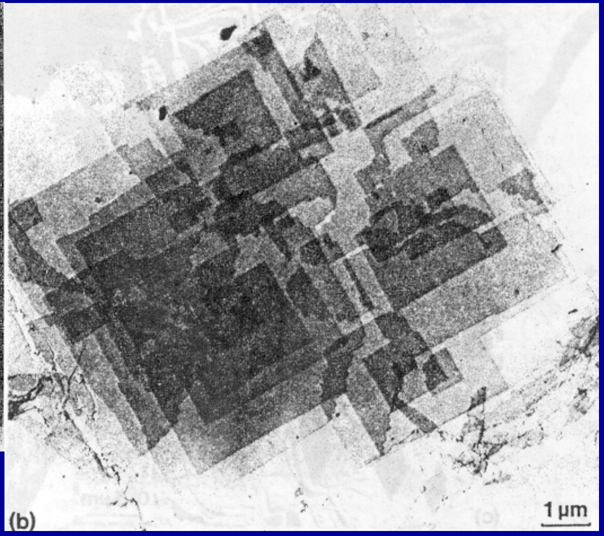
- Single crystal from solution
  Part of spherulite from melt
- Shape depends on crystal structure 📖Fig 6.11 vs 6.12



Polyethylene
(orthorhombic)



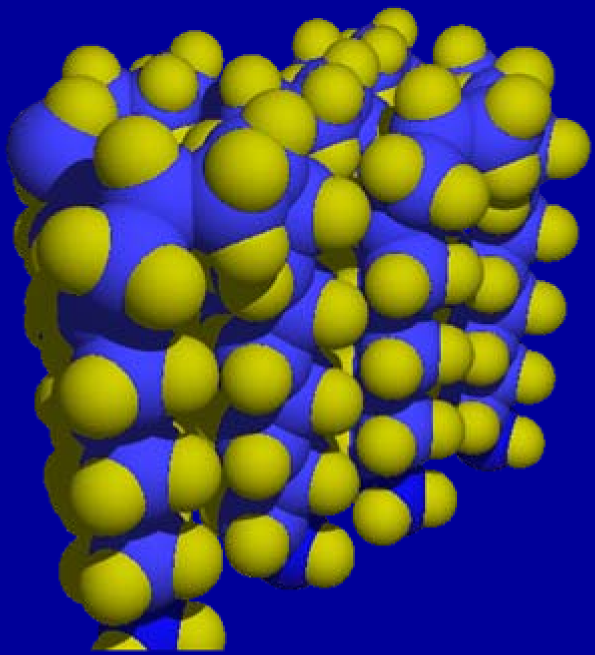
Polyoxymethylene
(hexagonal)

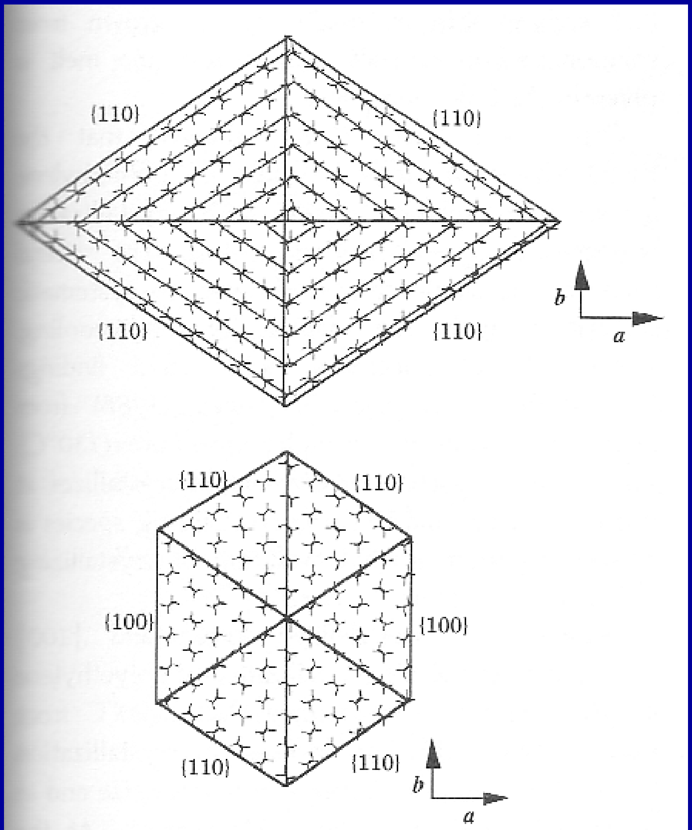


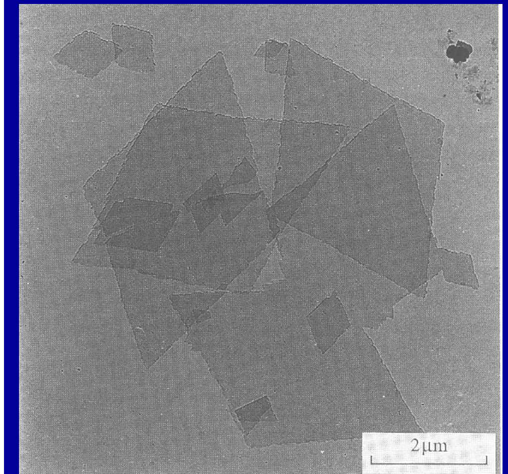
Poly-4-methyl-1-pentene
(tetragonal)

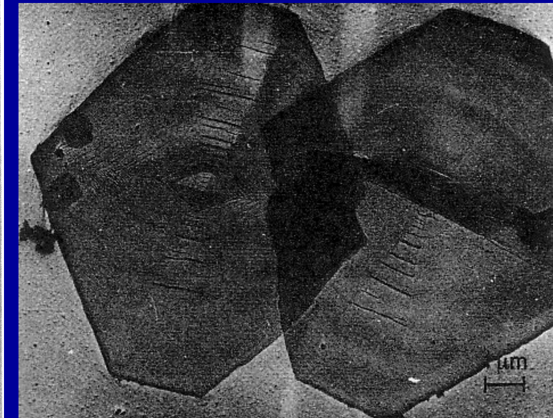
Lamella 2

- Growth
  - on [110] fold plane 📖Fig 6.10
  - on [110] and [100] plane



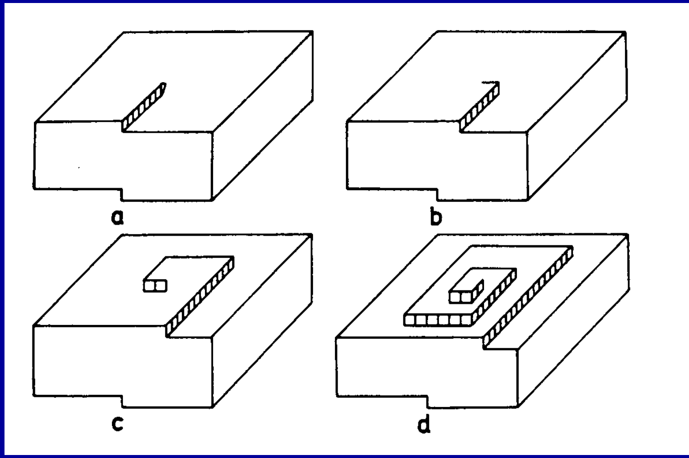


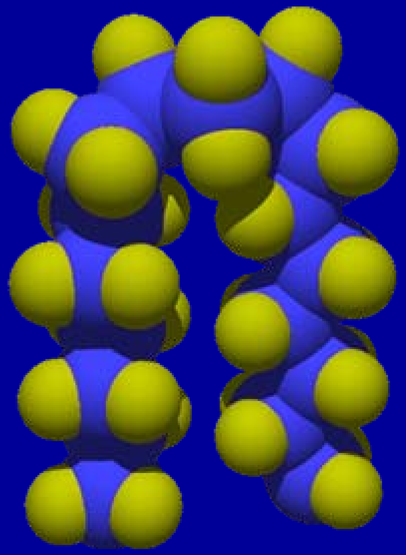


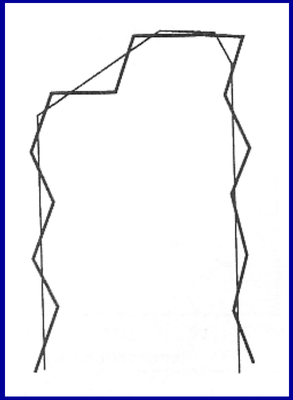


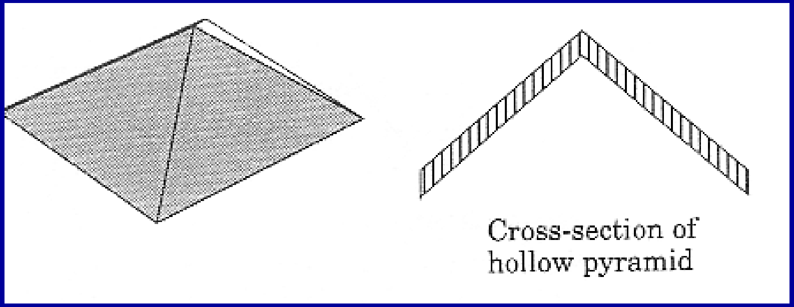
Lamella 3

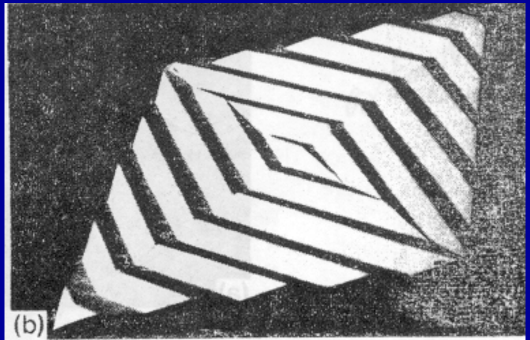
- Multi-layer lamella 📖Fig 6.11 & 6.12
  - Screw dislocation
- Hollow Pyramid
  - lattice mismatch

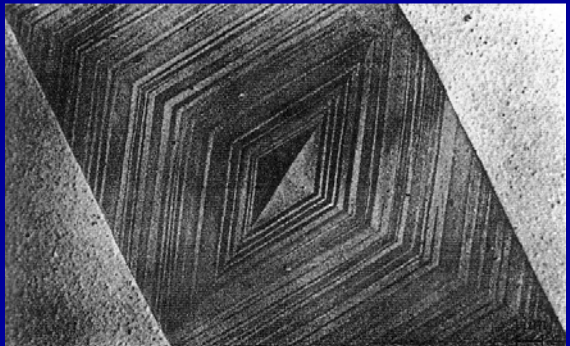






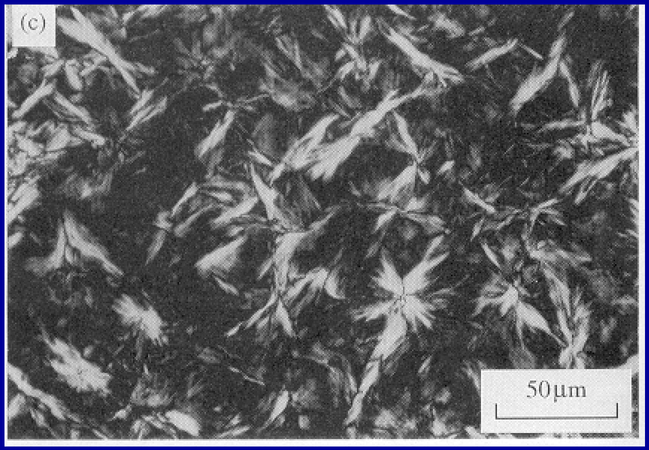


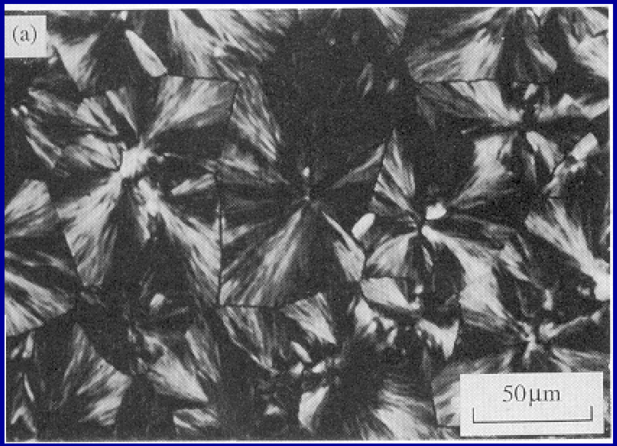


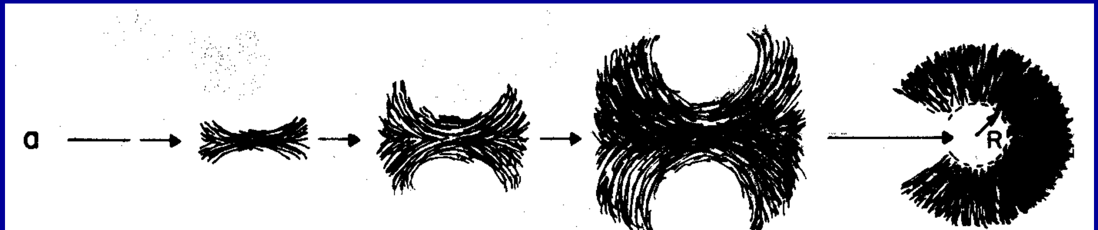


5. Spherulite

- from melt
- Melt crystallized
  - at high temperature – axialite (sheaf-like)
  - at low temperature – spherulite (dendritic growth)
- Axialite to spherulite 📖Fig 6.19

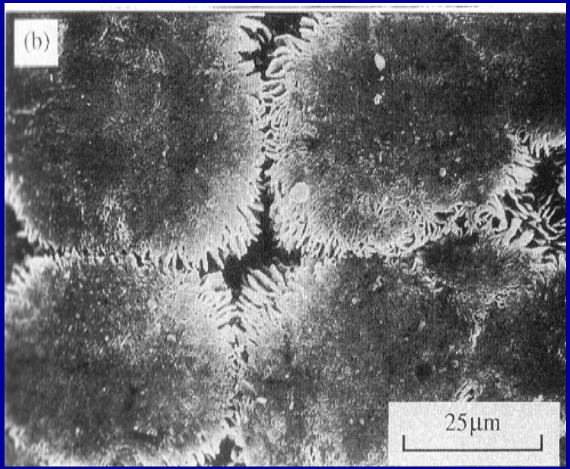






Spherulite (cont'd)

- Growing of lamellae from the center 📖Fig 6.17



- under POM ~ Maltese cross pattern 📖Fig 6.13

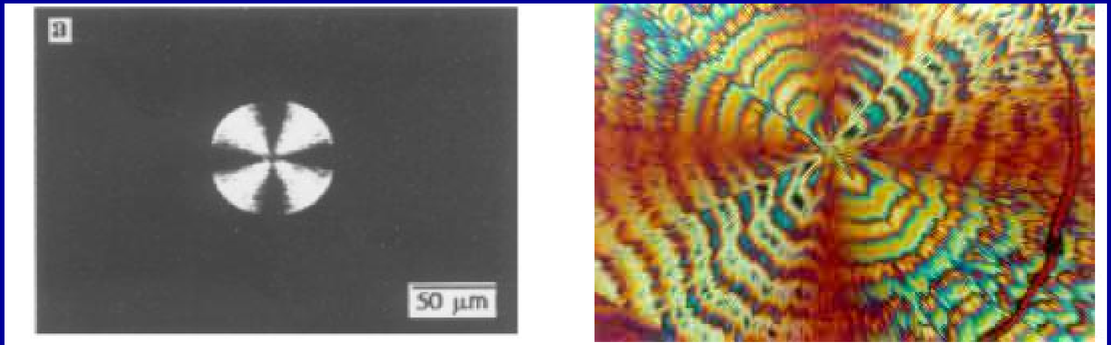
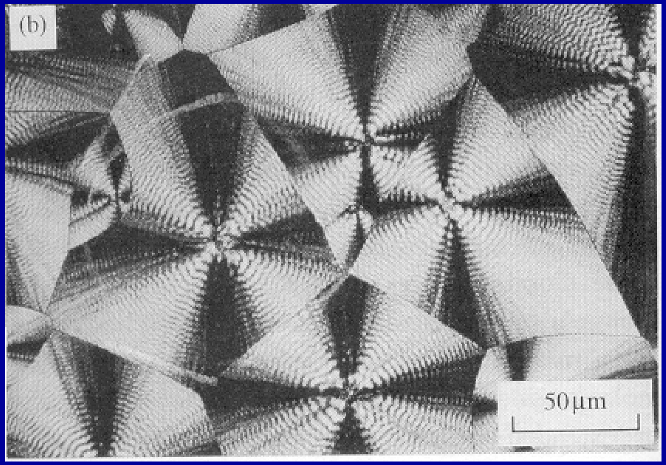


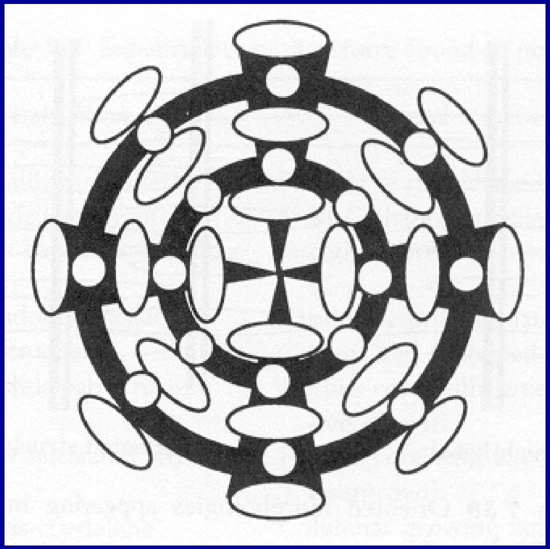
Figure 3. Micrographs of the same spherulite grown in two stages at different T_c: (a) after 16 hours at 140°C, (b) followed by 3 hours at 180°C.

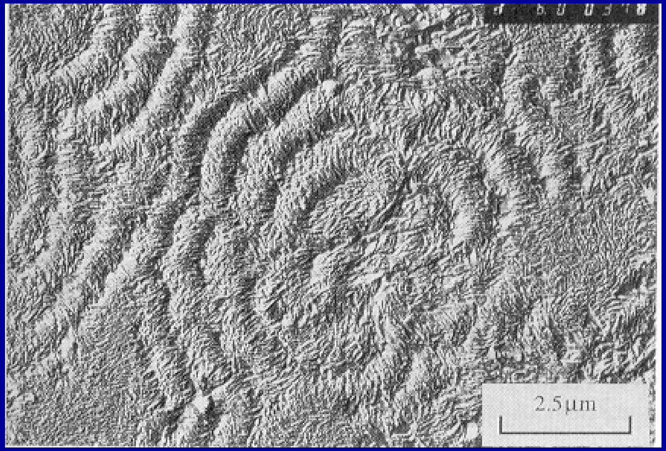
Banded spherulite

- lamellar twisting



📖Fig 6.22





Crystallinity

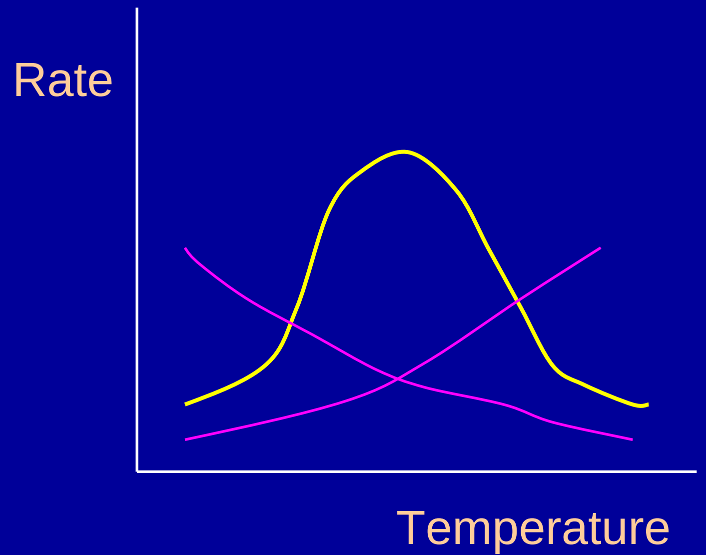
- Crystallinity = % crystallinity = degree of crystallinity
  - X_c = volume of Xtal / total volume = 30 ~ 70% for polymers
- X_c depends on
  - repeat unit structure X_c(PE) > X_c(PEster)
  - cooling rate
- Measuring X_c
  - Volumetric ~ density gradient column
  - Crystallographic ~ WAX
  - Thermal ~ DSC
  - Spectroscopic ~ IR

  - 100% crystal data ← unit cell structure, T_m depression
  - 100% amorphous data ← quenched sample, extrapolation from melt

Fig 6.24

6. Crystallization

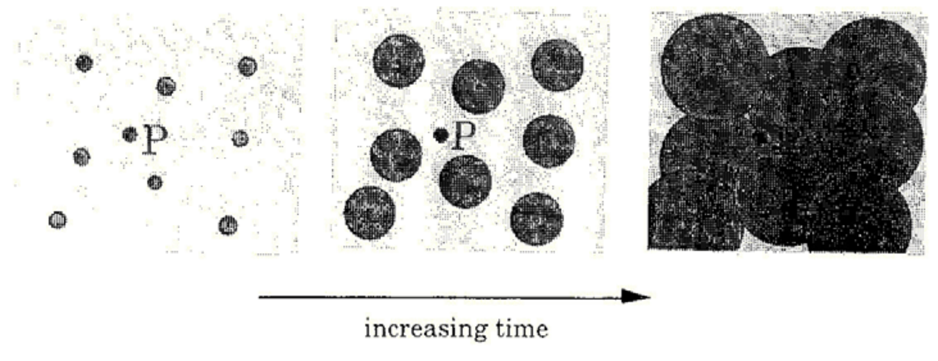
- Nucleation
  - at $T < T_m$
  - thermodynamic control
  - faster at large ΔT (= T_m - T)
- Growth
  - at $T > T_g$
  - diffusion (kinetic) control
  - faster at high T
    higher chain mobility and lower viscosity at large $T - T_g$



- 🕮Fig 6.27 (T or T-T_g)
- Measurement of Xtallization rate
  - dilatometry 🕮Fig 6.25
  - microscopy 🕮Fig 6.26

Theories of Crystallization Kinetics

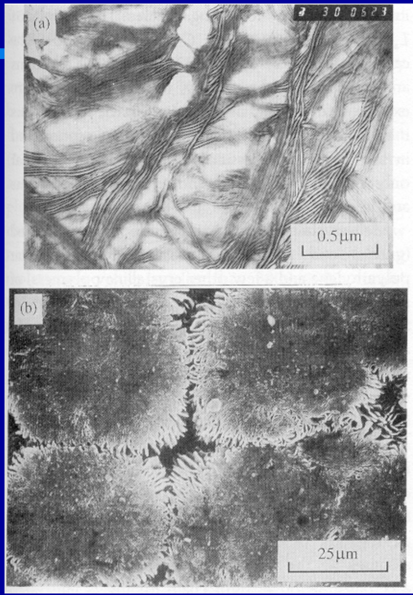
- Avrami equation ~ time-dependency



- $p_x = \exp(-E)\, E^x / x!$
  - » probability of P crossed by x fronts out of E fronts
- $p_0 = \exp(-E) = 1 - X_t = \exp(- Z\, t^{\,n})$ 📖Eqn (6.16)
- athermal (predetermined) N & G; $n = 3$
- thermal (sporadic) N & G; $n = 4$
- diffusion (of impurity) controlled; $n = 2.5$

📖Table 6.4, 6.5

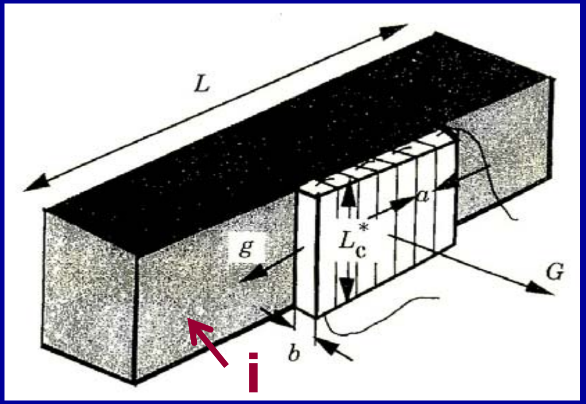
Theories of Crystallization Kinetics



- Keith-Padden theory ~ structure 📖Fig 6.28
  - δ = D / G (Diffusion of impurity / radial Growth)
    - ≈ δ ~ lateral dimension of lamellae
    - » small δ ~ coarse spherulites

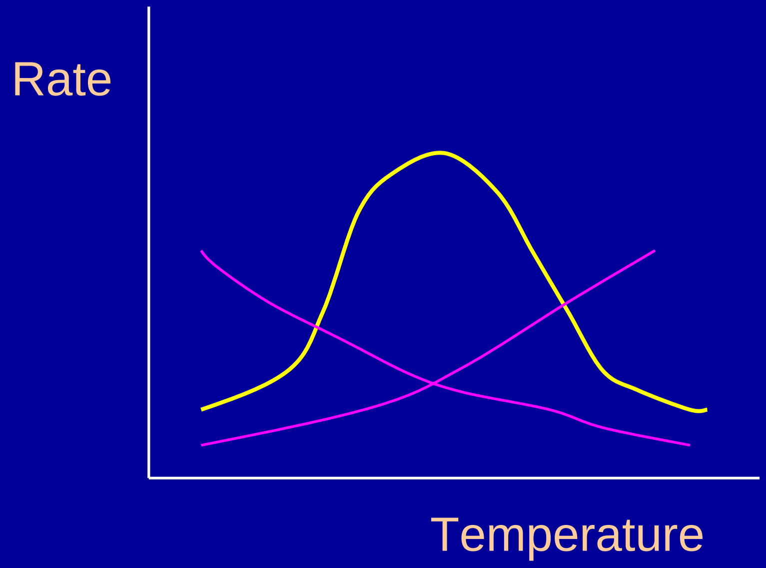
Hoffman

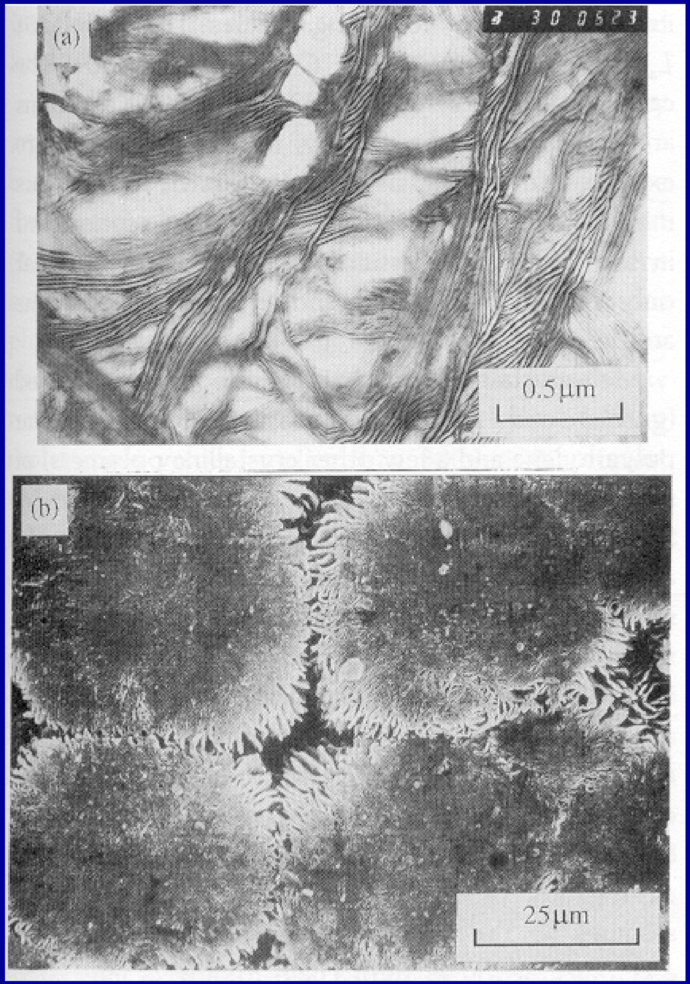
- Lauritzen-~~Hopffmann~~ theory ~ mechanism 📖Fig 6.30-31
  - three regimes of Xtallization 📖Fig 6.32
    - » Regime I ~ at high T, g >> i
      - ◆ axialite, adjacent reentry
    - » Regime II ~ at lower T, g < i, spherulite
    - » Regime III ~ at even lower T, g ~ i
      - ◆ random, switchboard



Crystallization and Property

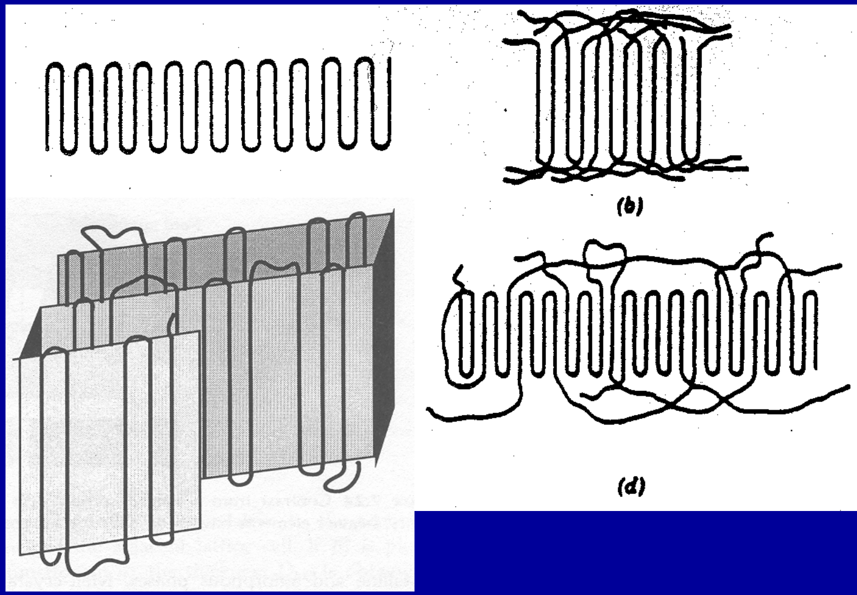
- Degree of crystallinity
  - modulus, yield strength
- Spherulite size
  - clarity, toughness
- Processing condition





7. Lamella Re-entry

- 2 models
  - Adjacent → folding
    - IR of mixed crystal
  - Switchboard → fringed micelle
    - etching experiment



- 4 models
  - Adjacent with superfolding 🕮Fig 6.34(a)
  - Adjacent without superfolding 🕮Fig 6.34(c)
  - Mixed or partial adjacent 🕮Fig 6.34(b)
  - Switchboard 🕮Fig 6.34(d)

Lamella Re-entry 2

- (sol'n grown) single crystal lamellae
  - super-folding for intermediate MW
    - $\langle r^2 \rangle^{1/2} \propto M^{0.1}$ by SANS
    - 75% adjacent
  - Mixed or partial non-adjacent for high MW
- Melt crystallized lamellae
  - Switchboard + some folding
  - $\langle r^2 \rangle^{1/2} \propto M^{0.5}$ by SANS
  - 3 phases
    - crystal + interface + amorphous

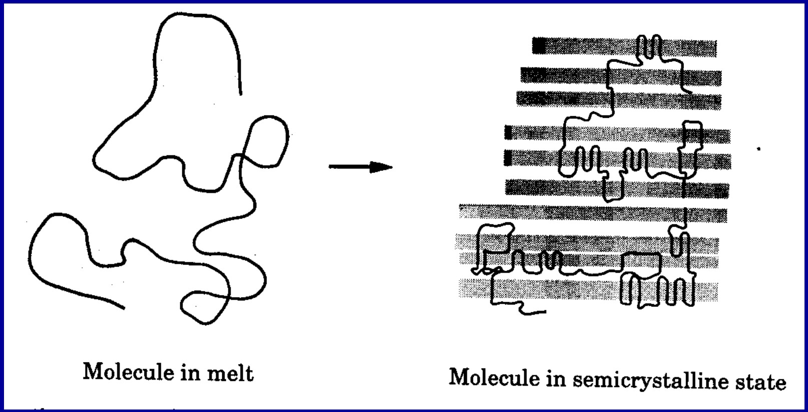


Fig 6.36

8. Melting Temperature

- $\Delta G_f = \Delta H_f - T\Delta S_f$
- At pure state, $T_m^0 = \Delta H_f^0 / \Delta S_f^0$
- Equilibrium melting temperature, T_m^0
  - for infinitely thick crystal (lamella)
  - for infinitely high molecular weight
- Melting point depression by impurity
  - Copolymer
  - Molecular weight
  - 2nd component (low MW or other polymer)
- T_m^0 measured by Hoffman-Weeks plot 📖Fig 6.40
  - isothermal crystallization at various T_c

9. Structure and T_m

- $T_m^0 = \Delta H_f^0 / \Delta S_f^0$
- ΔH_f ~ interchain interaction

  ΔS_f ~ chain flexibility
- Higher for more regular, rigid, closely-packed, and stronger interaction

  📖(6.54-56) p305-306
- T_g and T_m are correlated.

  $$T_g = (0.5 \sim 0.8)\, T_m \text{ (in K)}$$

Annealing

- At $T_g < T < T_m$
- Due to
  - activated internal mobility
  - promoted higher stability
- Results
  - Growth of crystalline region
    → increase in crystallinity
  - Increase in crystal perfection
    → increase in T_m
  - More stable structure
    → lamella thickening