Spherulite [球晶]

- spherical crystal formed from the melt
  - μm – mm in diameter
- spherulite formed in the film
  - observed under polarized optical microscope [POM]
  - Maltese cross pattern

lamella
spherulite
crystallite

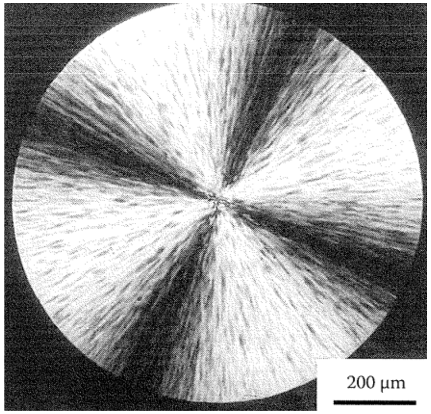
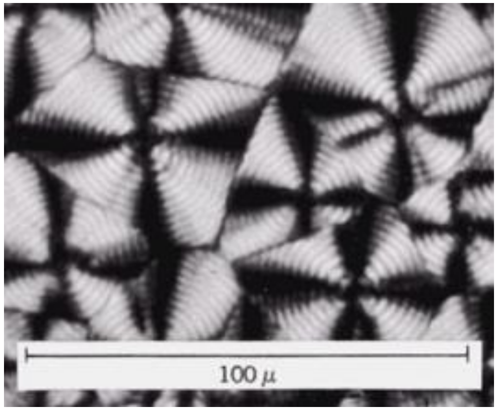
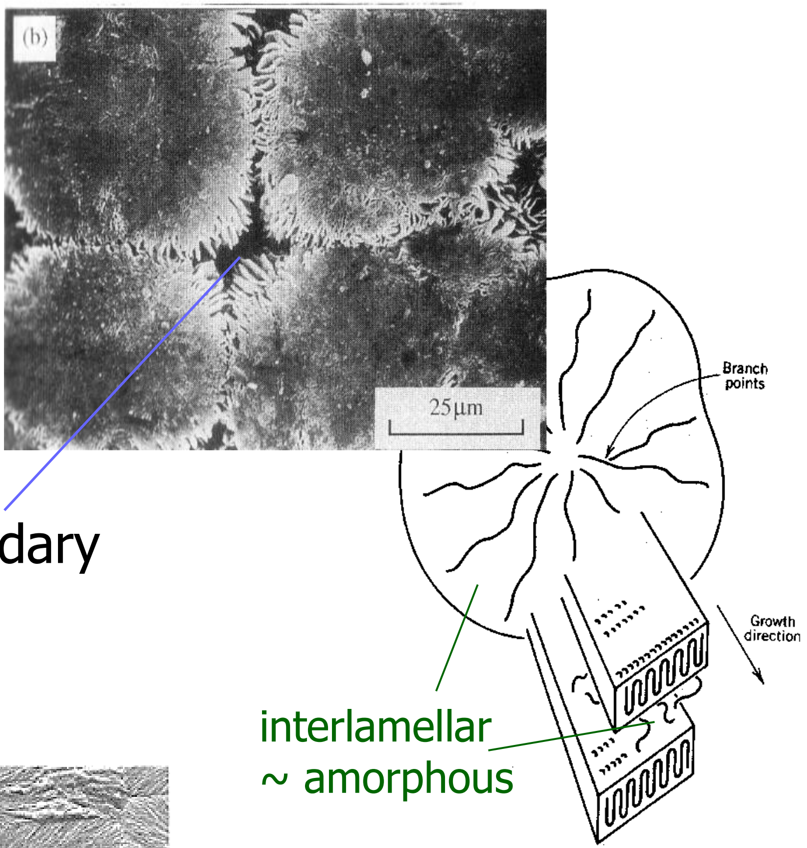


Fig 17.13
single spherulite of iPS

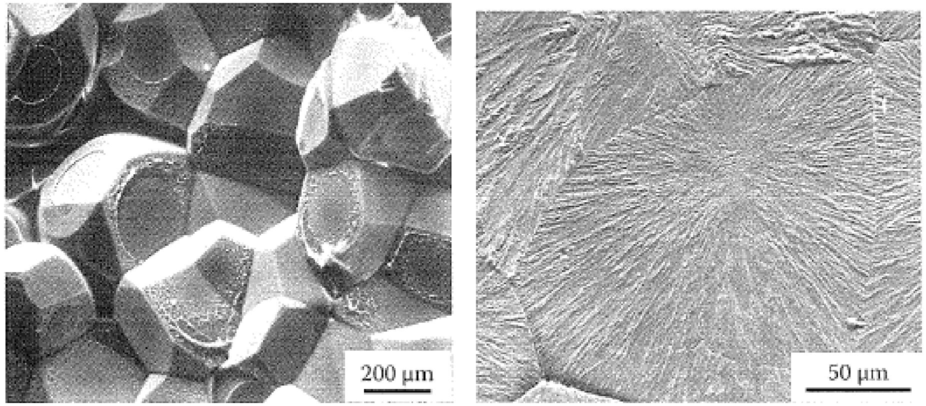


impinged spherulites

- spherulite formed in the bulk
  - radial growth of lamella
  - radius ⊥ c axis
  - molecular fractionation
    - high MW crystallize first
    - low MW subsidiary or repelled
  - low MW and impurities on the boundary
    - weak boundary → fracture



interlamellar
~ amorphous



ground and etched

Fig 17.14 p 414

- banded spherulite
  - lamellar twisting
    - why? not clear

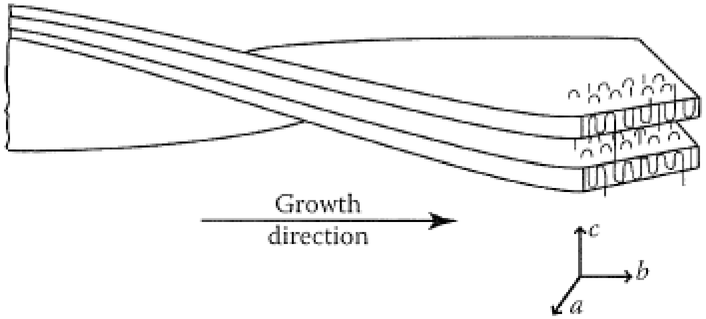
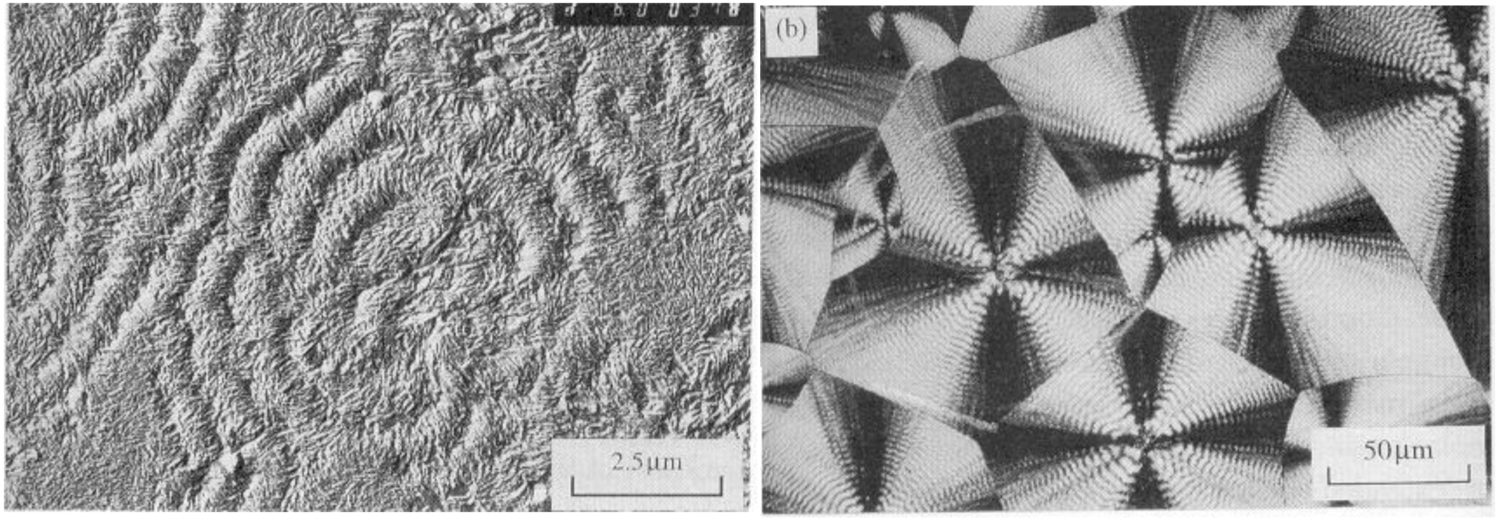


Fig 17.15 p 415



Lamella re-entry

- 2 models
  - adjacent re-entry
    - folded chain
  - random or switchboard re-entry
    - fringed micelle

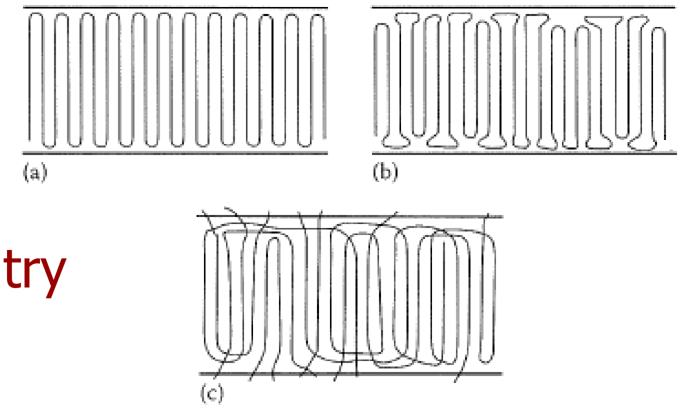
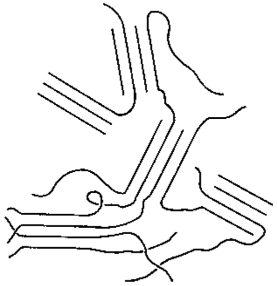
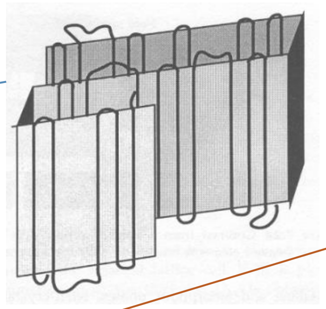


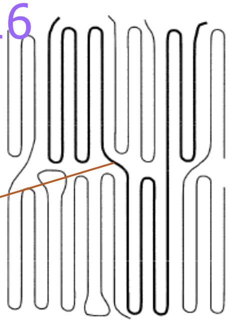
Fig 17.10

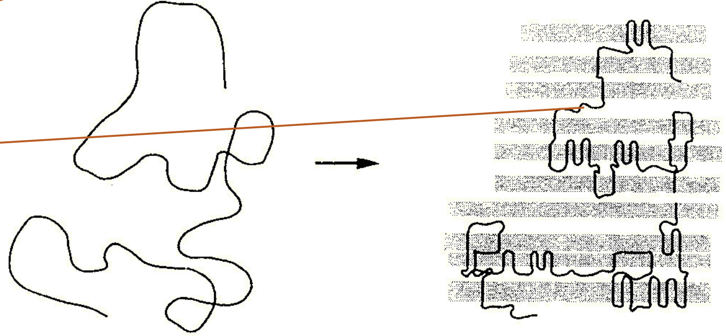


- SANS with mixed crystal
  - sol’n grown single crystal
    - $\langle r^2\rangle^{1/2} \propto M^{0.1}$
    - superfolding with 75% adjacent
  - melt-crystallized lamellae
    - $\langle r^2\rangle^{1/2} \propto M^{0.5}$
    - switchboard + some folding
    - ‘tie-molecule’
    - crystal + interface + amorphous

Fig 17.16



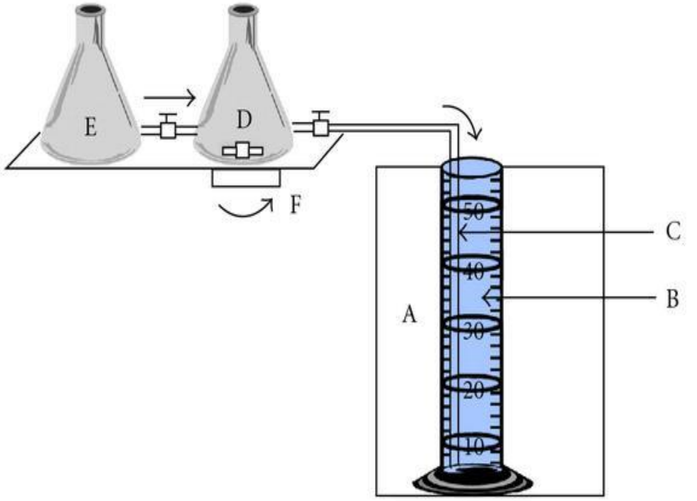




Crystallinity

- crystallinity = degree of crystallinity = % crystallinity
  - x_c = volume [weight] of Xtal / total volume [weight]
  - 30 – 70% for polymers
- measuring x_c
  - volumetric
    - density gradient column
    - dynamic density measurement

$$x_c = \frac{W_c}{W} = \frac{\rho_c V_c}{\rho V} = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right)$$



- ➢ ρ = density of sample
- ➢ ρ_c [x_c = 1] from unit cell
- ➢ ρ_a [x_c = 0] from quenched sample (for slow crystallizing like nylon) or extrapolation from melt (for fast like PE)

- measuring x_c (cont'd)
  - crystallographic ~ WAXS

$$x_c = \frac{A_c}{(A_a + A_c)}$$

    - A_a ~ area under amorphous halo
  - thermal ~ DSC
    - ΔH_m
  - spectroscopic
    - IR, raman ~ crystalline band
    - (solid-state) NMR

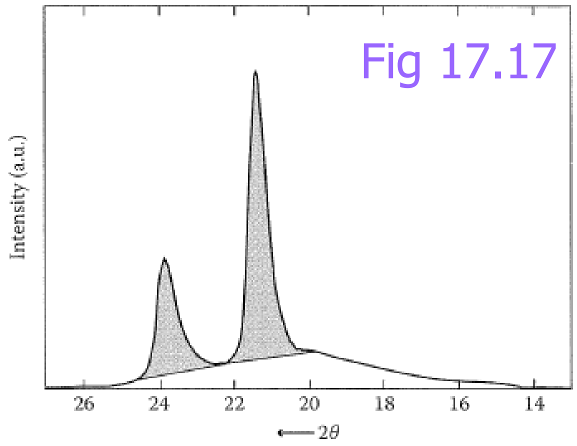
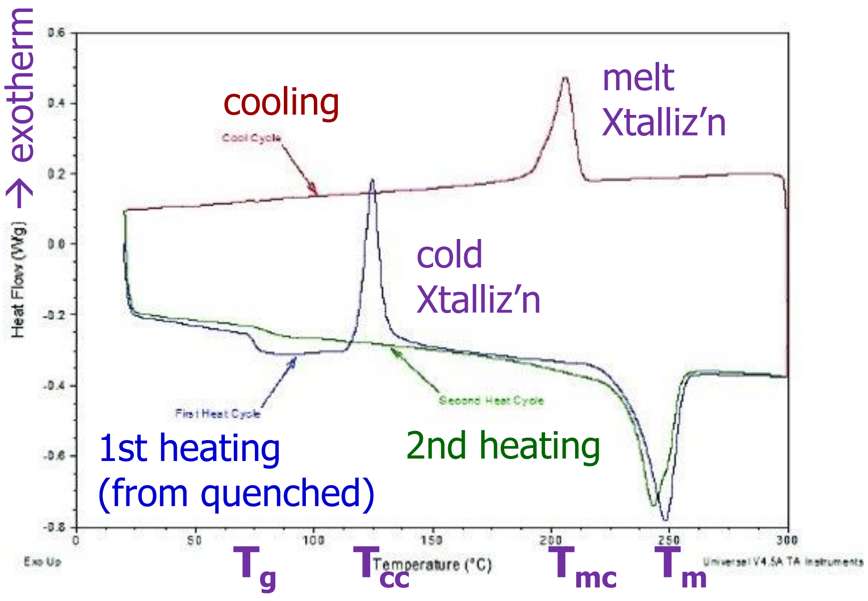
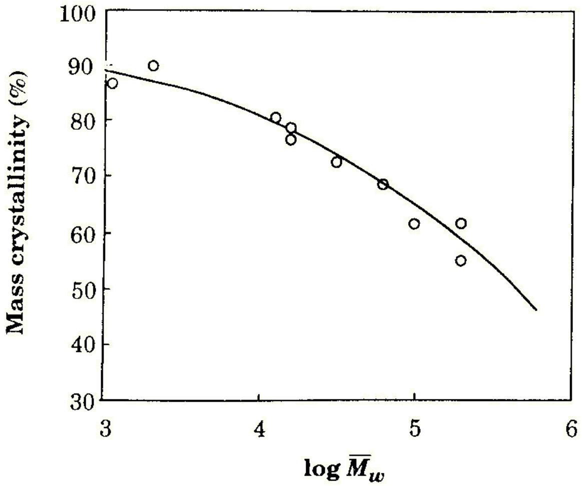


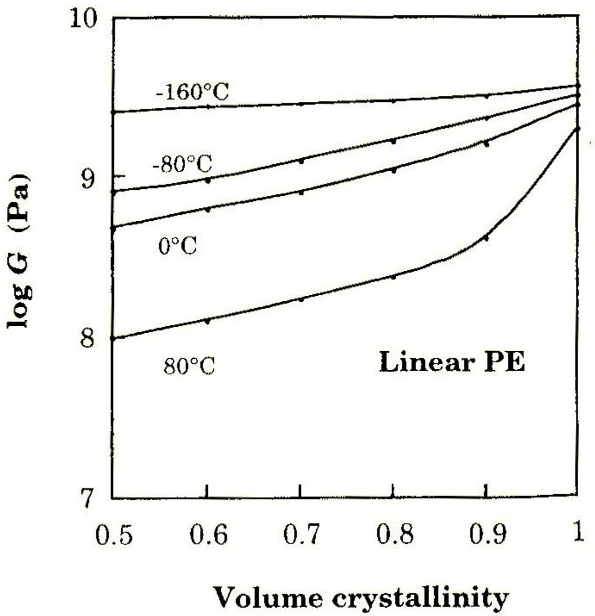
Fig 17.17



- ➢ x_c (WAXS) < x_c (DSC)
  - ➢ crystal + interface + amorphous

- x_c ↓ as
  - molar mass ↑
  - branches ↑
  - cooling rate ↑
- x_c and properties
  - stiffness [modulus E]
    - E ↑ with x_c ↑
      - E(crystal) > E(amorphous)
    - brittle if x_c too high
      - ← no interlamellar region
  - permeability
    - transport through amorphous only
  - weatherability
    - degradation a/o oxidation on amorphous





Lamellar thickness

- measured by μscopy or SAXS
- As T_c ↑ [ΔT ↓], thickness ↑
  - ΔT = degree of supercooling = $T_m - T_c$
  - for both of solution- and melt-grown
- As P_c ↑, thickness ↑
  - at high P, extended-chain crystal
    - μm-thick, brittle

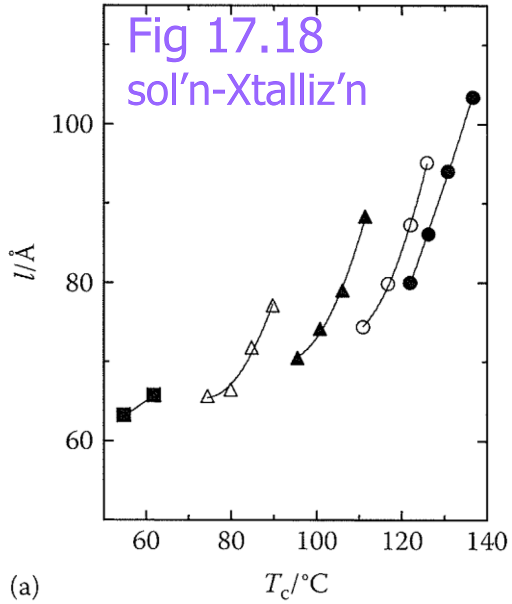


Fig 17.18

sol'n-Xtalliz'n

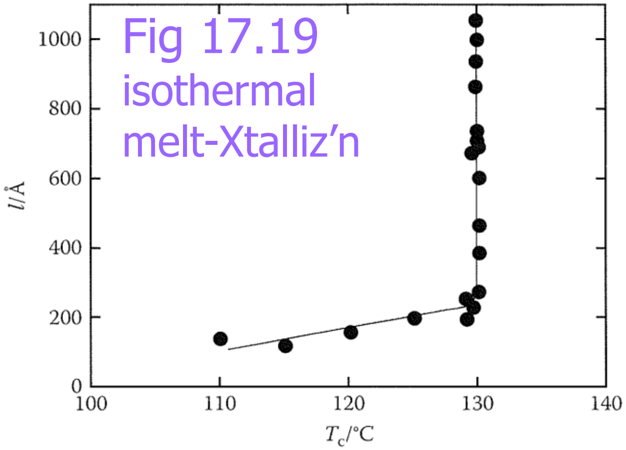
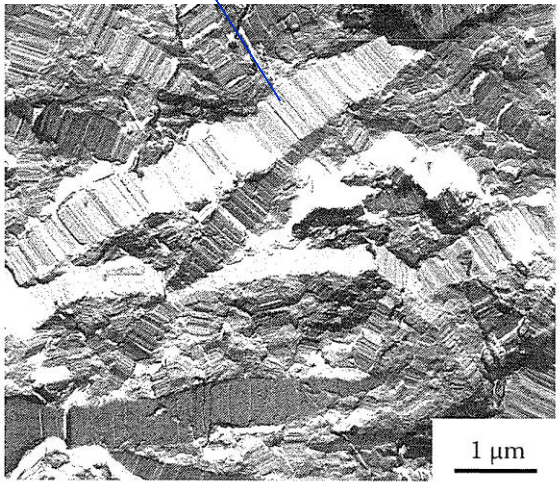


Fig 17.19

isothermal melt-Xtalliz'n

Fig 17.20

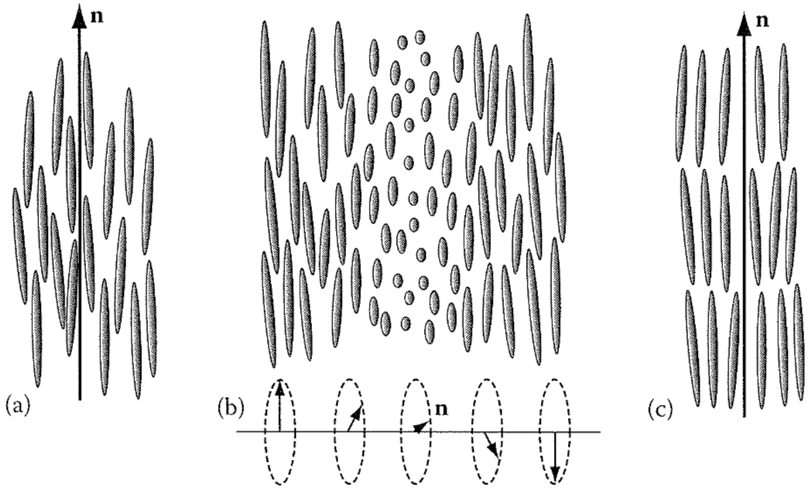
chain-extended crystal?



Liquid crystalline polymers

- LC state
  - 4th state of matter between solid and liquid
    - ordered but flow
  - with 1 or 2 dimensional order
    - amorphous ~ liquid ~ no order
    - crystalline ~ solid ~ order in 3 dimensions
- classes = nematic, cholesteric, or smectic

Fig 17.22



- polymer LC
  - main-chain or side chain LC
  - thermotropic or lyotropic LC

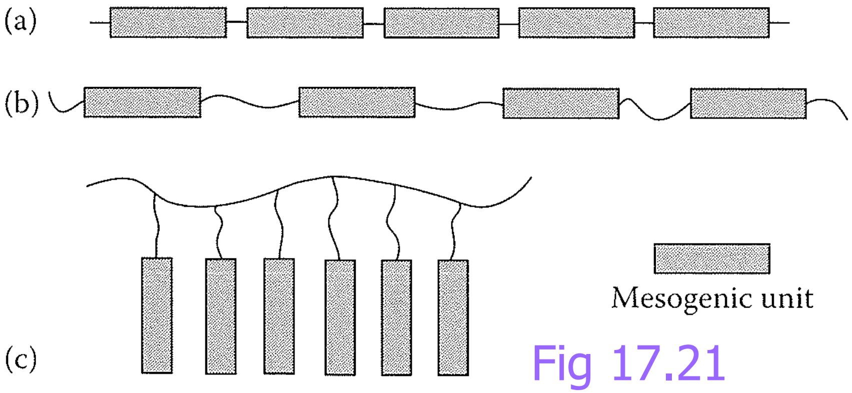


Fig 17.21

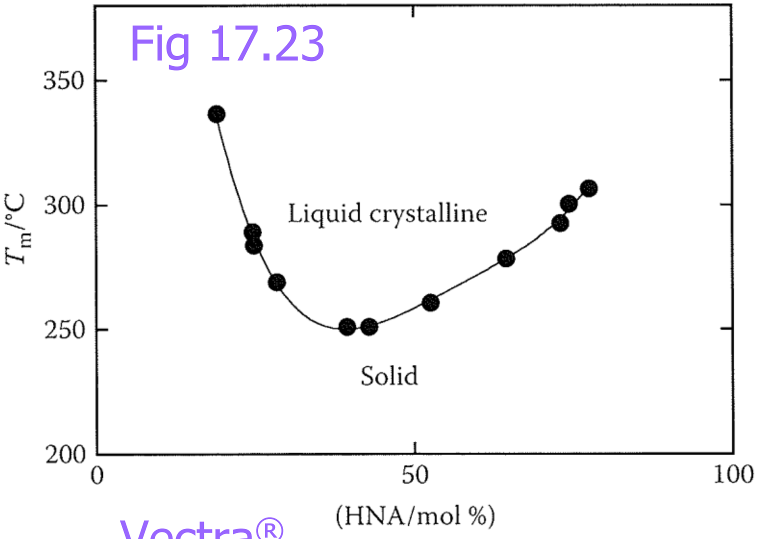
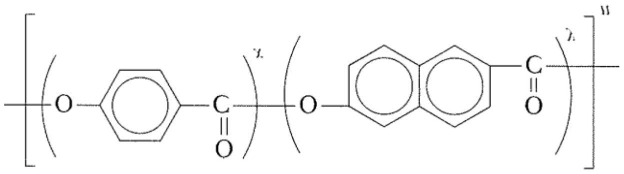
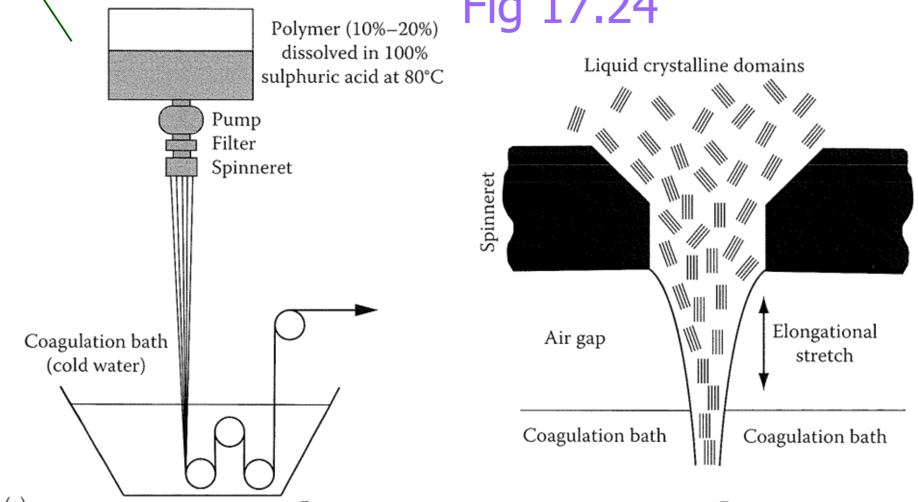


Fig 17.23

Vectra®

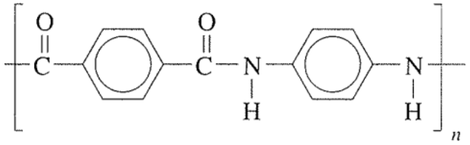




(a)

Fig 17.24

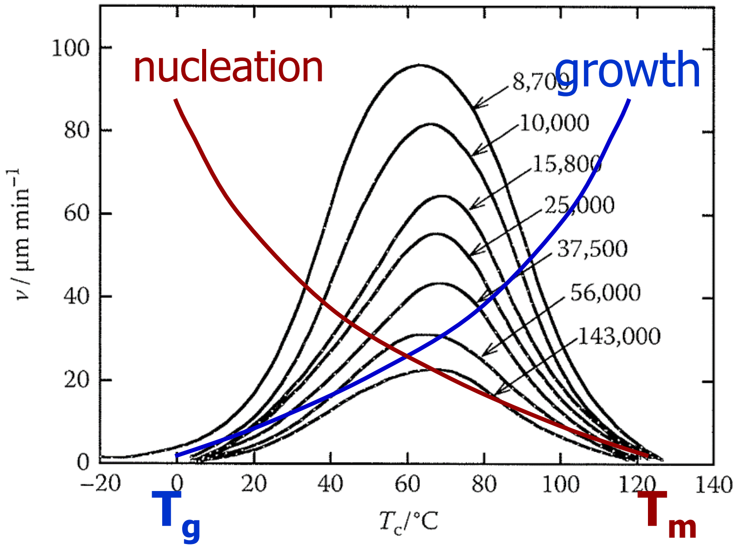
Kevlar®

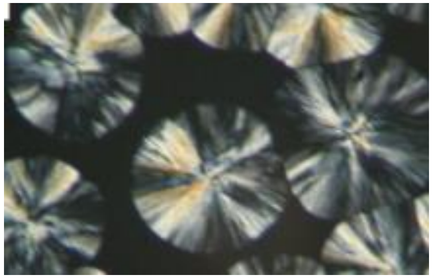


Crystallization

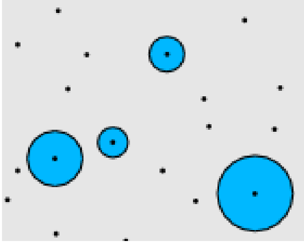
- crystallization by nucleation and growth
  - rate v = C exp[–K/T_c ($T_m{}^0$ – T_c)] exp[U/R(T_c – T_g)]
  - C ~ structural factor
    - chain regularity, flexibility, MM, --
  - nucleation
    - homogeneous < heterogeneous
    - thermodynamic ~ ΔT ~ zero at T_m
  - growth
    - diffusion of segment against viscosity
    - kinetic ~ increase with T ~ zero at T_g
- measurement of crystallization rate
  - dilatometry ~ dV/dt
  - microscopy ~ dr/dt

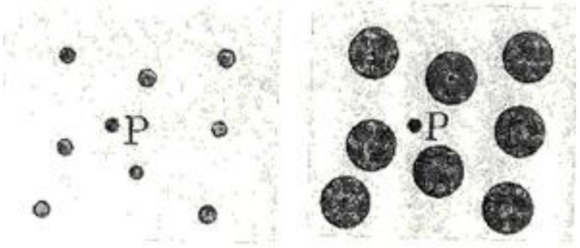
Fig 17.29





Crystallization kinetics





- Avrami equation ~ time-crystallinity relation
  - for general [any material] N-and-G crystallization
  - valid only for early stage of crystallization
  - useful for molding simulation
- mass of crystal $dW_S = \frac{4}{3}\pi v^3 t^3 \rho_S N W_0 \frac{dt}{\rho_L}$
  - radial growth → $r = vt$
  - N = # of nuclei formed/volume/dt
- crystallinity $x_c = \frac{W_S}{W_0} = \frac{\pi N v^3 \rho_S t^4}{3\rho_L}$
- amorphous $1 - x_c = \frac{W_L}{W_0} = 1 - \frac{\pi N v^3 \rho_S t^4}{3\rho_L} = \exp(-zt^4)$

$W_S + W_L = W_0$
S = spherulite, L = liquid

$e^{-x} = 1 - x$ for small x
→ valid for early stage only

- Avrami euation:

  $$1 - x_c = W_L / W_0 = \exp(-zt^n)$$

  - n = Avrami exponent
  - n = 4
    - for thermal [sporadic] nucleation
  - n = 3
    - for athermal [nucleation at once] nucleation
  - n = 2.5 (thermal) or 1.5 (athermal)
    - when diffusion (of impurity) controls
    - $dW_s \propto (vt^{1/2})^3$ not $(vt)^3$

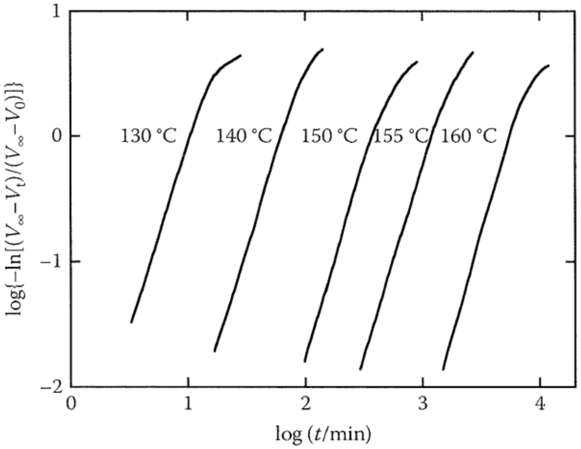
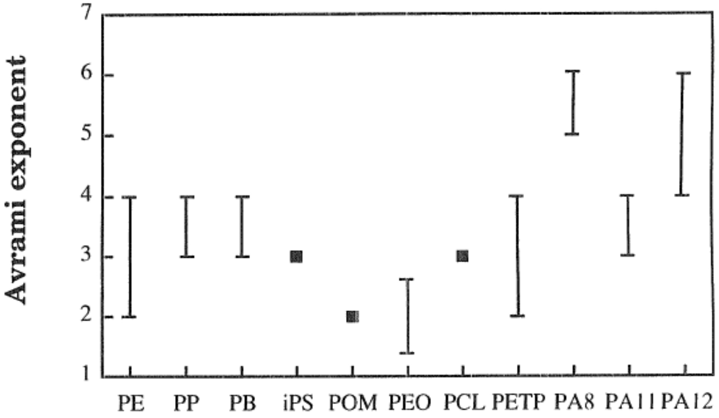


Fig 17.30 Avrami plot (using dilatometry)

$$\frac{W_L}{W_0} = \frac{V_t - V_\infty}{V_0 - V_\infty} = \exp(-zt^n)$$



Molecular mechanism of crystallization

- primary [1°] nucleation
  - surface vs volume energy
  - not popular (than 2° or 3°) ← 6 sides (> 4 or 2)
- Lauritzen-Hoffman theory
  - 2° nucleation and growth
  - (surface) free energy change
  - $\Delta G_n = \underbrace{2bl\gamma_s + 2nab\gamma_e}_{\text{surface}} - \underbrace{nabl\,\Delta G_V}_{\text{volume}}$

    (volume) ΔG for Xtalliz'n
  - growth direction depends on Temp

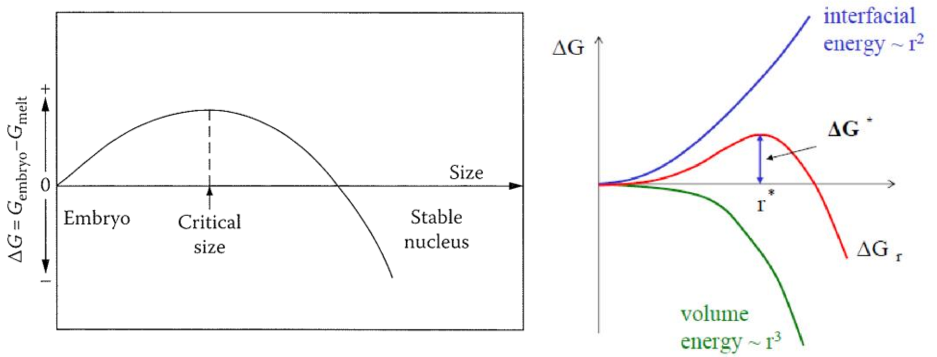
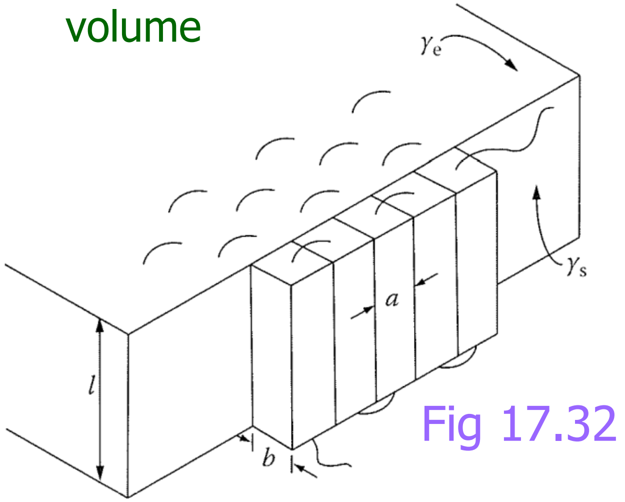


Fig 17.31



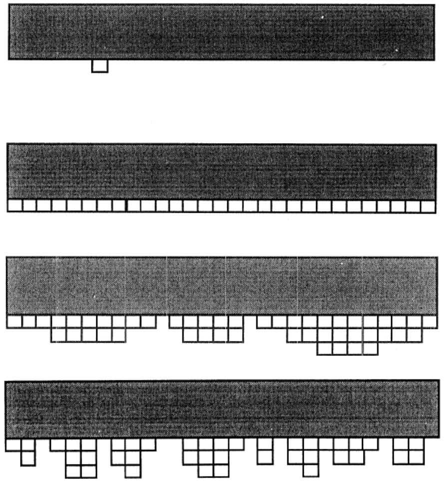


Fig 17.32

Equilibrium melting Temp T_m^0

= T_m of infinitely thick crystal (lamella) with infinite mol wt

= T_m of crystal with no surface (by L-H theory)

- ‘Polymer crystals are <u>not</u> in equilibrium.’

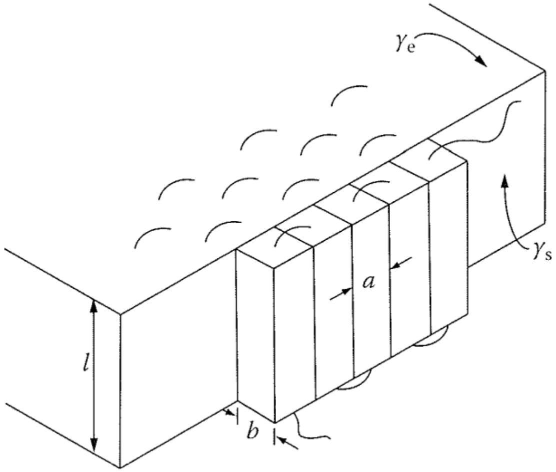
- $\Delta G_V = \Delta H_V - T_m^\circ \Delta S_V$
  - At equili, $\Delta G_v = 0$ → $\Delta S_V = \dfrac{\Delta H_V}{T_m^\circ}$
  - At $T_{(c)}$ below T_m^0, $\Delta G_V = \Delta H_V - \dfrac{T\,\Delta H_V}{T_m^\circ} = \dfrac{\Delta H_V \Delta T}{T_m^\circ}$

degree of supercooling
$\Delta T = T_m^0 - T_{(c)}$

- lamellar thickness
  - lamella stable when $\Delta G_n \le 0$

$$\Delta G_n = 2bl\gamma_s + 2nab\gamma_e - nabl\,\Delta G_V$$

0 ← large # of stems (n >> a, b, l)



- $\Delta G_n = 0$ → $\boldsymbol{l} = \dfrac{2\gamma_e T_m^\circ}{\Delta H_V \Delta T}$

predicts the exp’t of Fig 17.18
[T_c ↑ → ***l*** ↑] See sl #24

- estimation of T_m^0 ~ Hoffman-Weeks plot
  - for equilibrium [infinitely large, $l = \infty$] crystal

$$l = \frac{2\gamma_e T_m^\circ}{\Delta H_V \Delta T} \qquad T_m = T_m^\circ - \frac{2\gamma_e T_m^\circ}{l \Delta H_V}$$

    - $l = \infty \rightarrow \Delta T = 0 \rightarrow T_m^0 = T_c \rightarrow T_m = T_m^0$
    - $T_m = T_c$ → infinitely slow cooling → infinite time for Xtallization → infinitely large crystal
  - procedure
    - isothermal Xtallization at various Temp's
    - measuring T_m
    - plot T_m vs T_c, and extrapolate to $T_m = T_c$

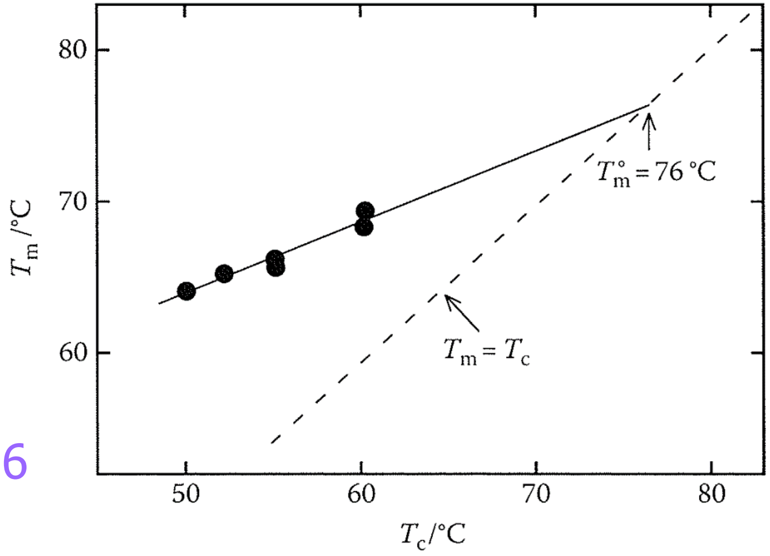
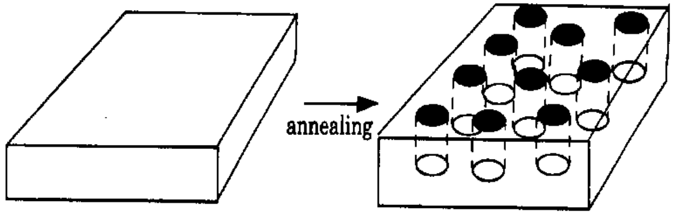


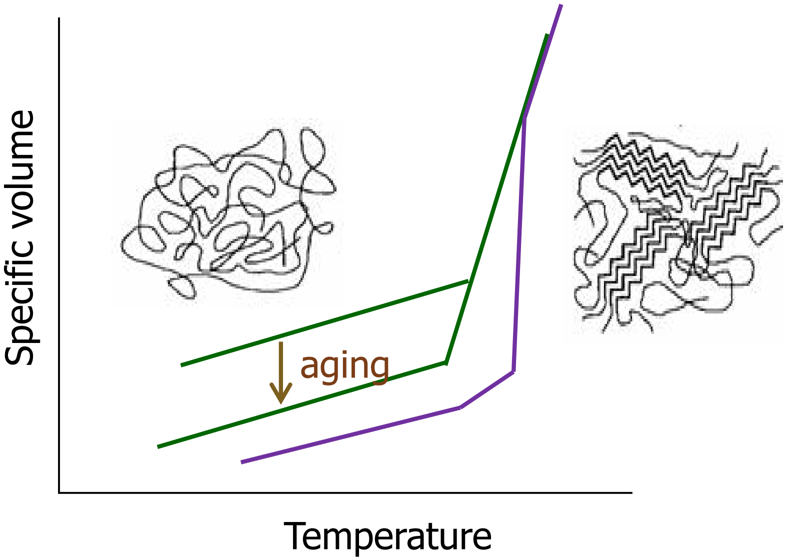
Fig 17.36

- annealing
  - heat treatment at $T_g < T < T_m$
  - by annealing
    - lamella thickening
      - to equilibrium [thick] Xtal ← lower energy fold plane [*trans*]
    - T_m ↑ (← thicker lamellar)
    - x_c ↑ (← segment mobility)
  - thickness ↑ with annealing time and Temp



Swiss cheese

- 'physical aging' at $T < T_g$
  - for amorphous polymers to equilibrium liquid



Factors affecting $T_m^{(0)}$

- structure
  - $\Delta G_V = \Delta H_V - T_m^{\circ}\Delta S_V$
  - $T_m^0 = \Delta H_{fusion} / \Delta S_{fusion}$
  - ΔS_f ~ (intra)chain flexibility
    - aromatic, side group, --
  - ΔH_f ~ interchain interaction
    - dispersion, polar, H-bond

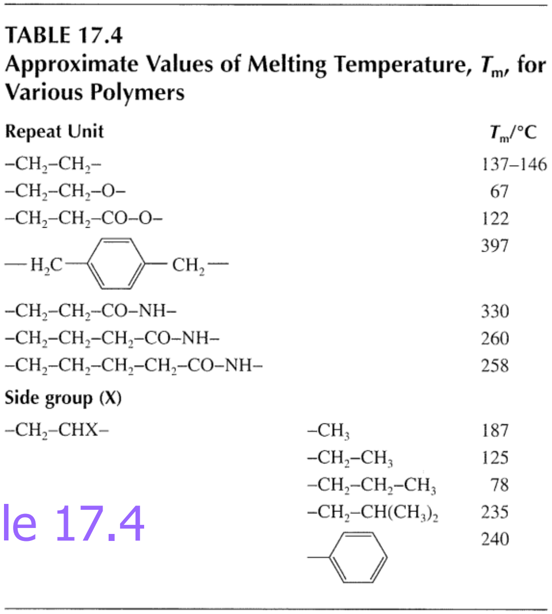
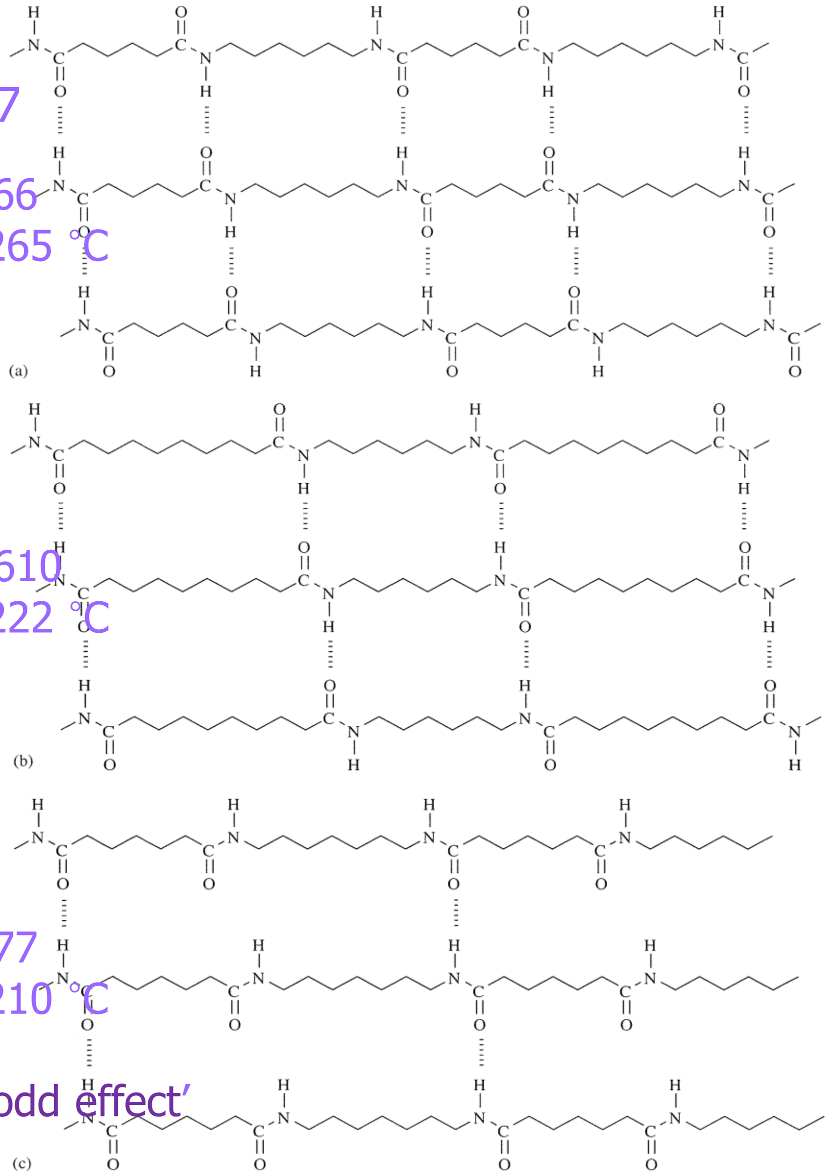


TABLE 17.4
Approximate Values of Melting Temperature, T_m, for Various Polymers

Repeat Unit		T_m/°C
$-CH_2-CH_2-$		137–146
$-CH_2-CH_2-O-$		67
$-CH_2-CH_2-CO-O-$		122
$-H_2C-$ ⌬ $-CH_2-$		397
$-CH_2-CH_2-CO-NH-$		330
$-CH_2-CH_2-CH_2-CO-NH-$		260
$-CH_2-CH_2-CH_2-CH_2-CO-NH-$		258
Side group (X)		
$-CH_2-CHX-$	$-CH_3$	187
	$-CH_2-CH_3$	125
	$-CH_2-CH_2-CH_3$	78
	$-CH_2-CH(CH_3)_2$	235
	⌬	240

Table 17.4

Fig 17.37



nylon 66
T_m = 265 °C

nylon 610
T_m = 222 °C

nylon 77
T_m = 210 °C

'even-odd effect'

- MM and branching
  - MM ↑ → chain ends [defect] ↓ → T_m ↑
    - increase levels off (just like T_g)
  - branching ↑ → branching point [defect] ↑ → T_m ↓
  - quantitative approach pp443 – 444
    - chain ends and branching point as impurity
    - $\Delta\mu \rightarrow \Delta G \rightarrow \Delta H - T\Delta S \rightarrow \Delta T_m$
    - not that quantitative ~ ignore
- copolymers (and blends)
  - random or alternating ~ no crystallization
  - block or graft (and blends) ~ T_m ↓
    - non-crystallizable comonomer (and 2nd polymer) is impurity

Relationship btw T_m and T_g

- T_g and T_m are correlated.

  ← the same factors (intra/inter)

- T_g = 0.5 – 0.8 T_m (in K)
  - 'two-thirds rule'

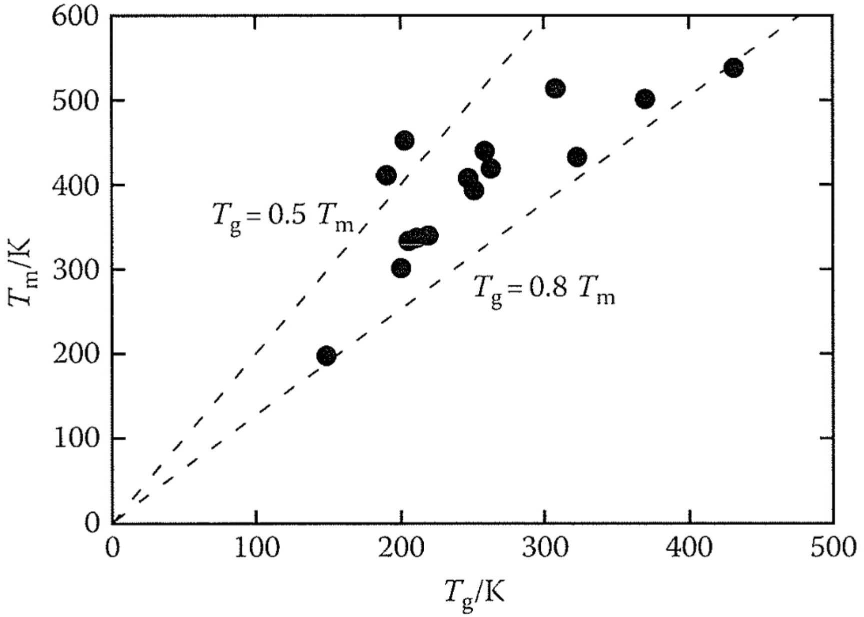


Fig 17.38 p 445

Crystallization and property

- degree of crystallinity
  - modulus, yield strength
- spherulite size
  - clarity, toughness
- property vs productivity
- processing condition

Fig 17.29