Chapter 6 Condensed States of Polymers

6.1 Polymer Melts and Glasses

6.2 Crystalline States of Polymers

6.2.1 Chain Conformations in Crystals

6.2.2 Basic Morphology of Polymer Crystals

6.2.3 Polymer Crystallization

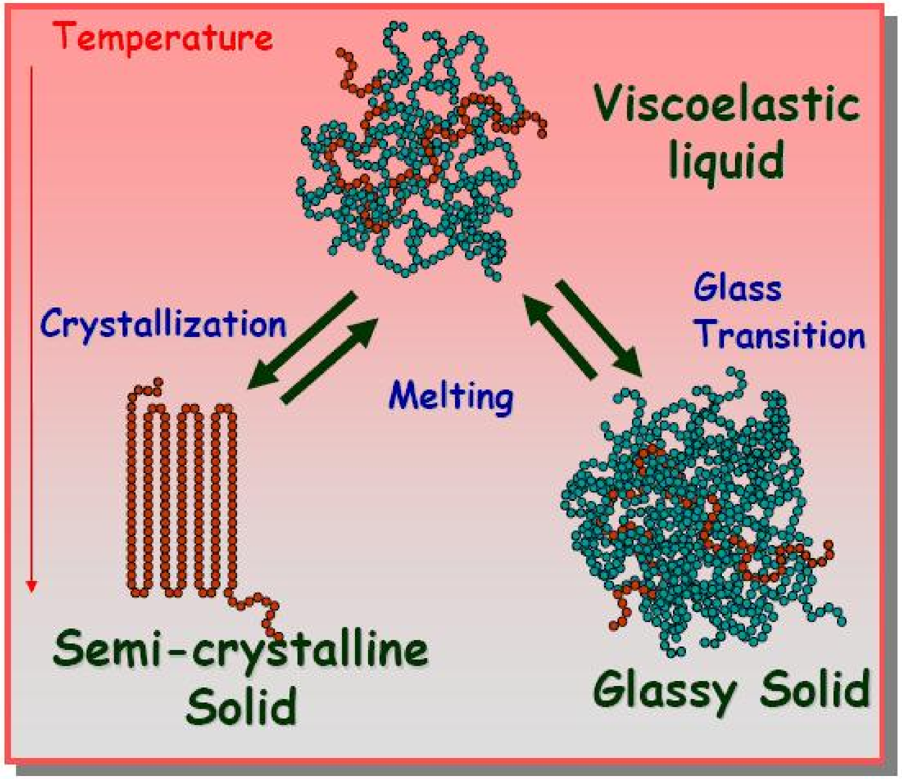
Models、Thermodynamics、Kinetics

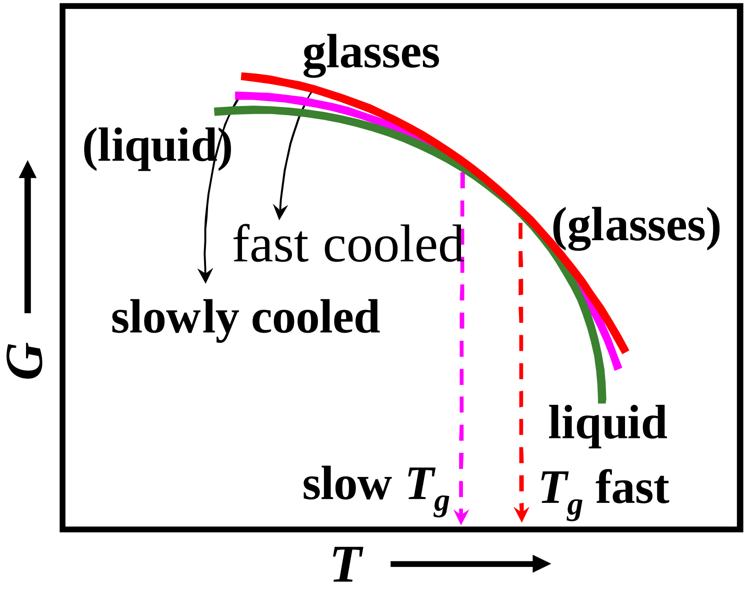
6.3 Oriented States of Polymers

6.4 Liquid Crystalline Polymers

6.1 Polymer Melts and Glasses

- The transition from melt to glass is called glass transition (玻璃化转变)
- The transition from melt to solid(crystal) is called solidification(crystallization)





- T_g: glass transition temperature (玻璃化转变温度)

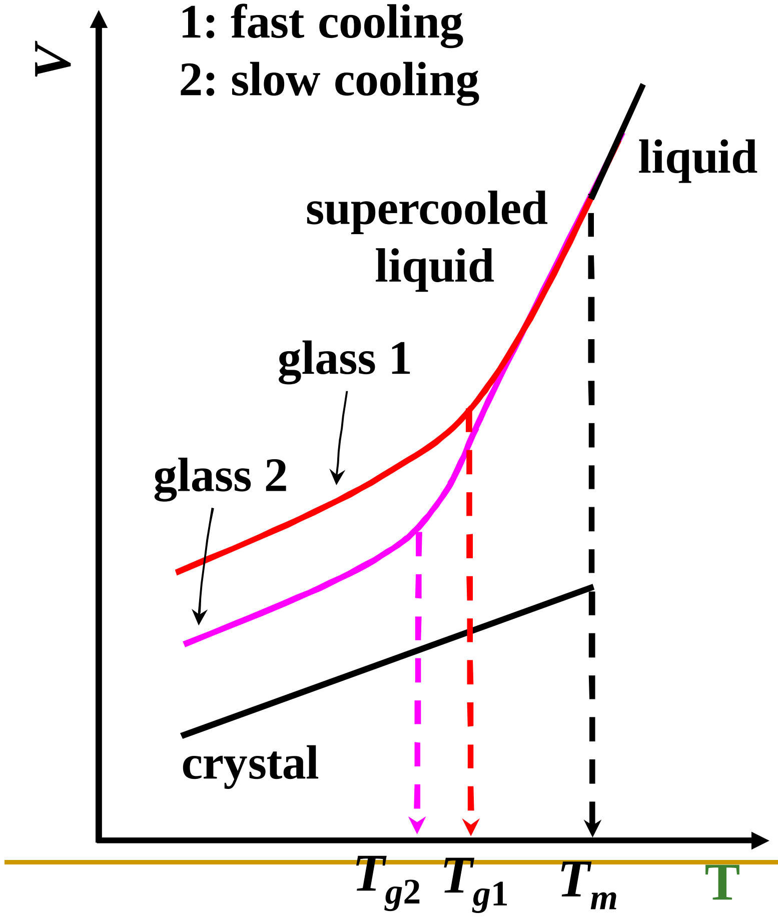
T_m: Melting point

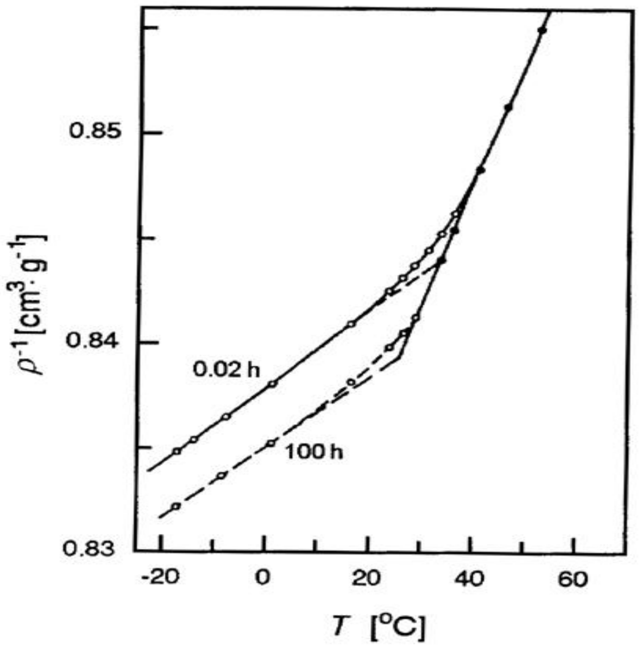
$\Delta T = T_m - T_c$: undercooling

$T_c < T_m$: crystallization temperature

Glass Transition as a Relaxation Process

- **Thermal history dependence of T_g**





Temperature dependence of the specific volume of PVA, measured during heating. Dilatometric (膨胀计法) results obtained after a quench to –20 °C, followed by 0.02 or 100 h of storage. (Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* **1966**, *3*, 394)

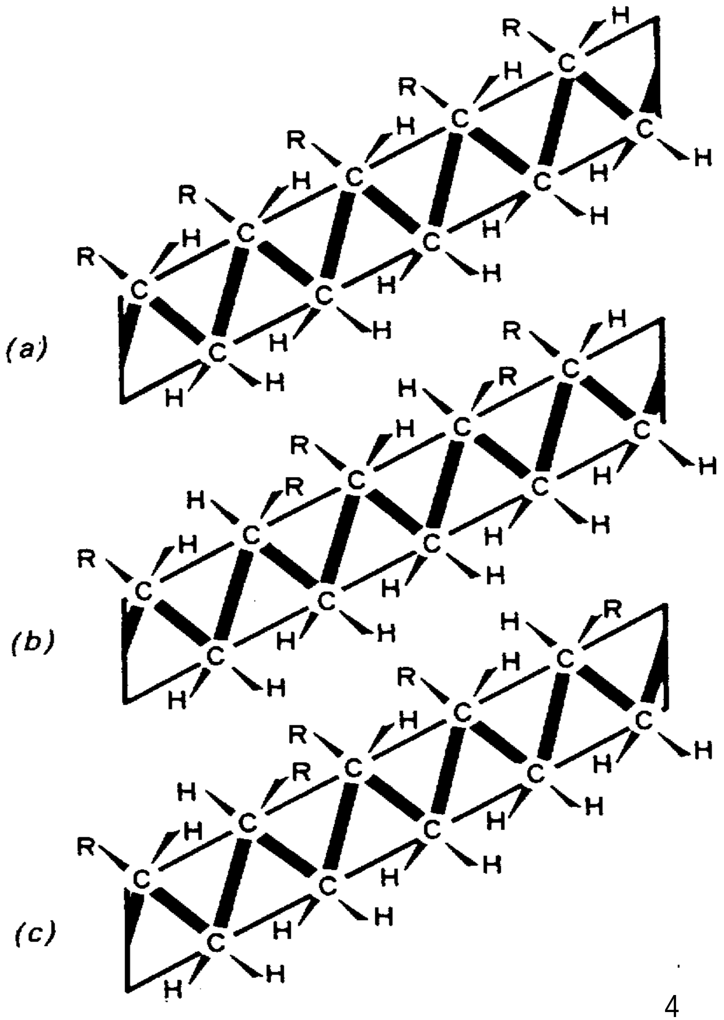
6.2 Polymer Crystallization

- **Requisites for polymer crystallization**
  - **Chemical regularity**
    - **Homopolymer**
    - **Copolymer**

      block copolymer

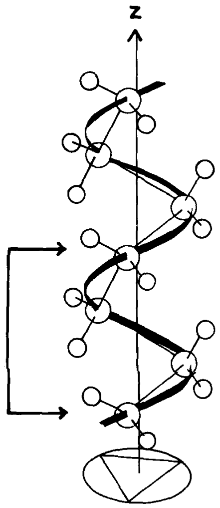
      random copolymer

  - **Stereoregularity (立构规整度)**
    - **Isotactic (等规)**
    - **Syndiotactic (间规)**
    - **Atactic (无规)**

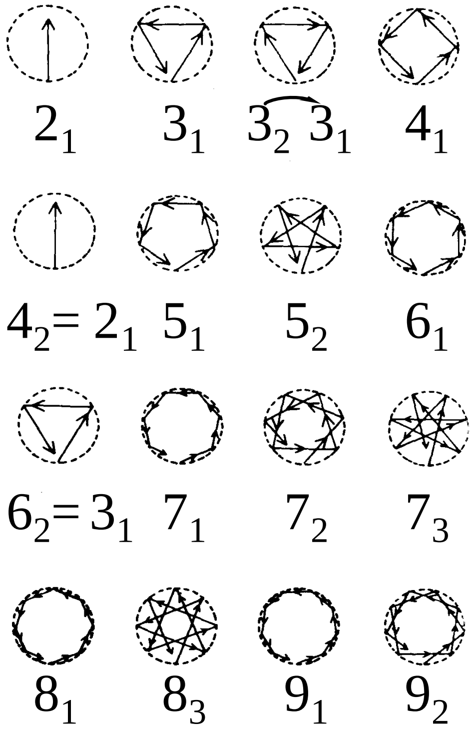


6.2.1 Chain Conformations in Crystals

Helix Conformations



$H3_1$



repeating unit $-CHCH_3-CH_2-CHCH_3-$

isotactic

Zig-zag Conformations

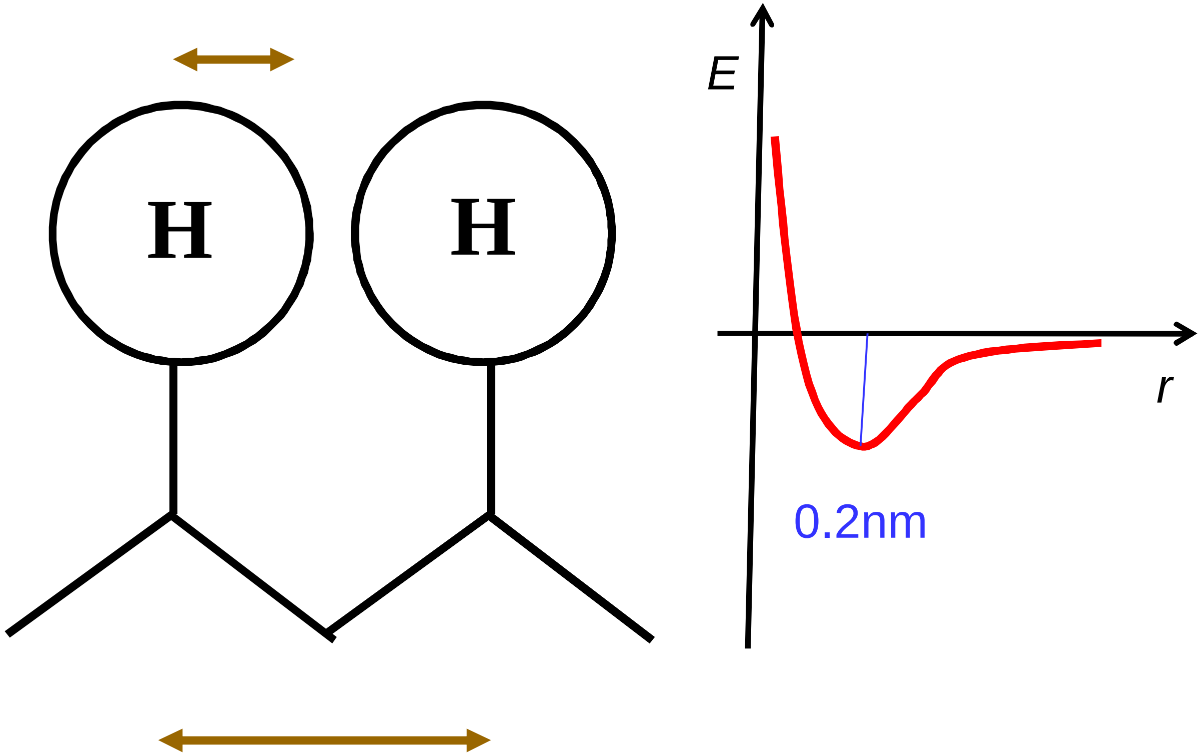
Hydrogen bonding

$H2_1$

syndiotactic

Why Helix ?

PE

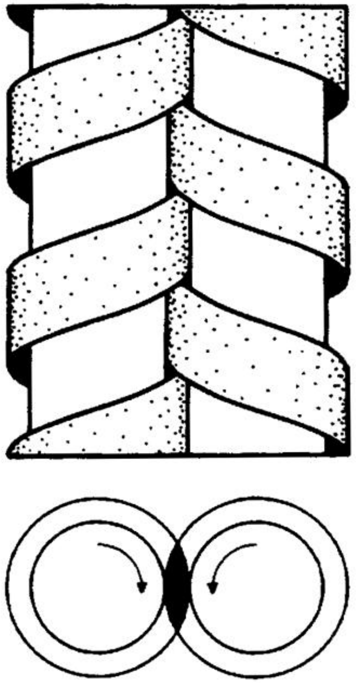


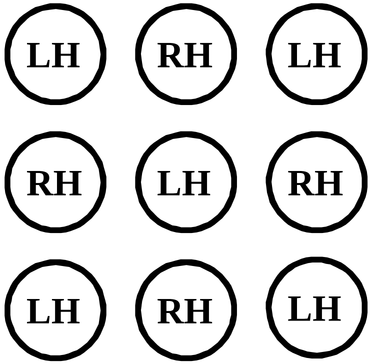
0.12 nm

0.25 nm

PP **CH_3: 0.2 nm**

Chain packing in crystal lattices

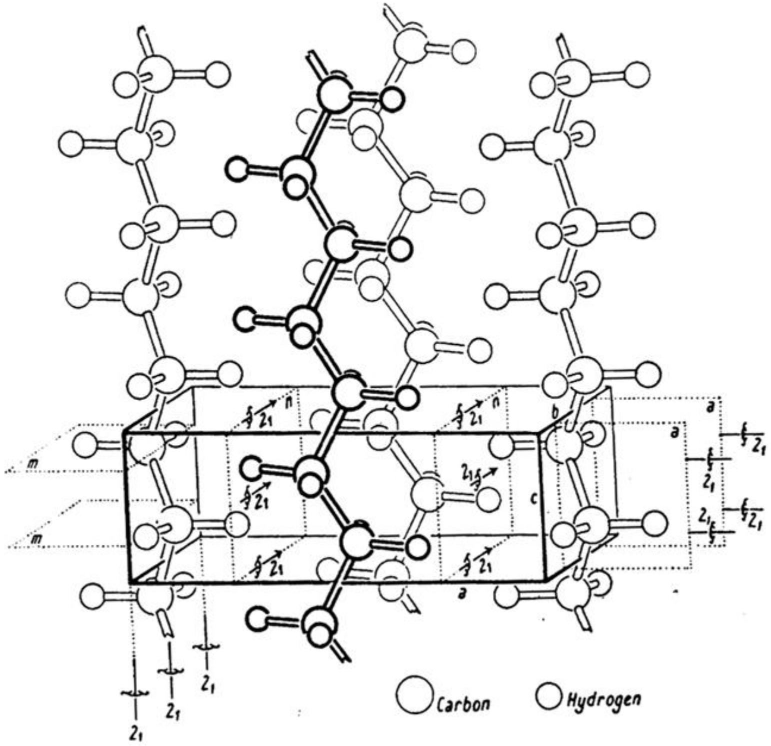




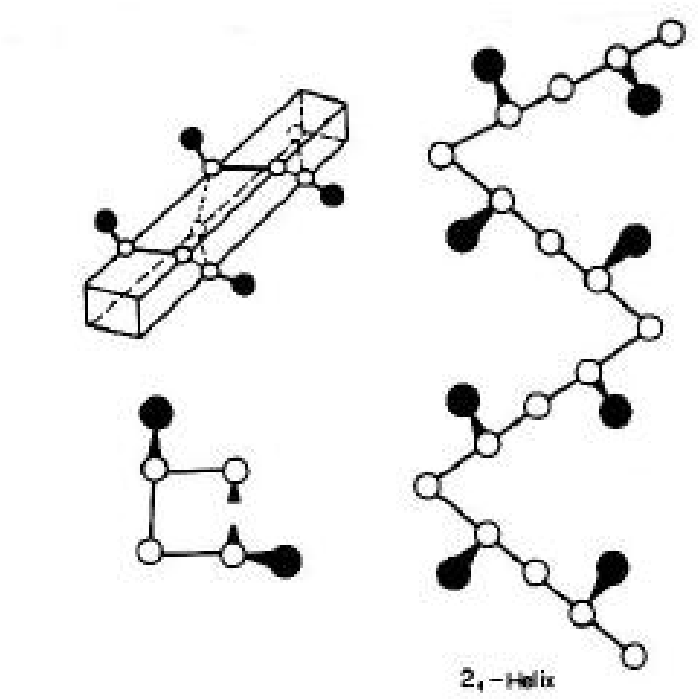
LH	RH	LH
RH	LH	RH
LH	RH	LH

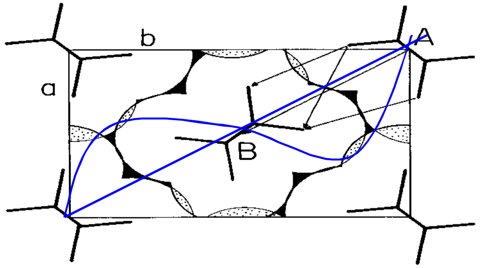
Chain packing in crystal lattices

PE

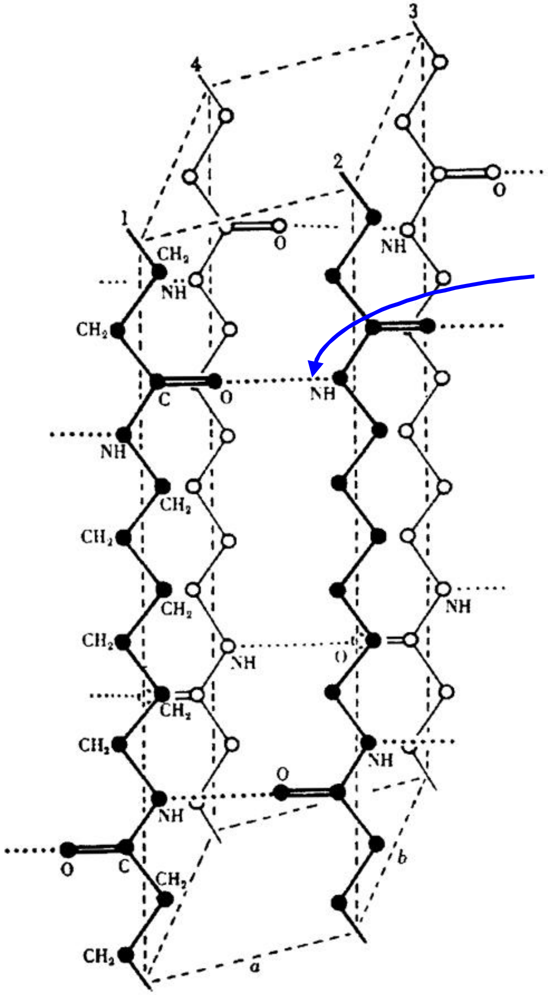


s-PP





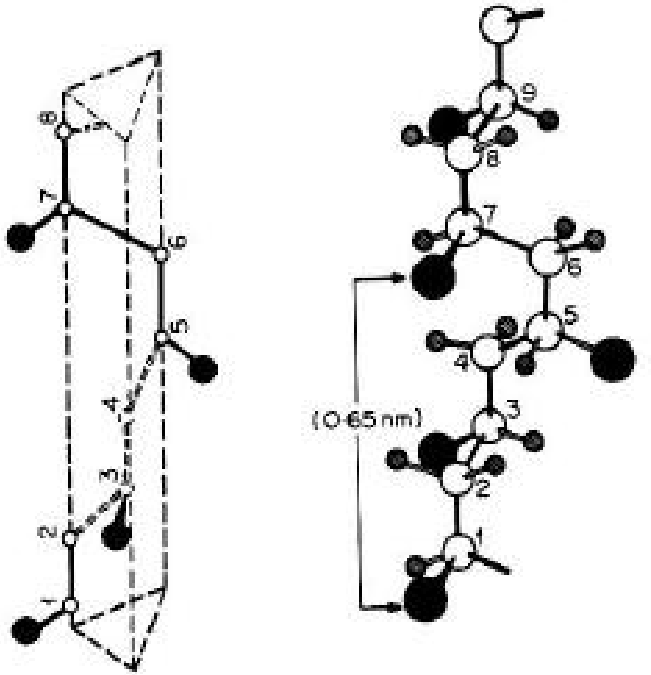
orthorhombic



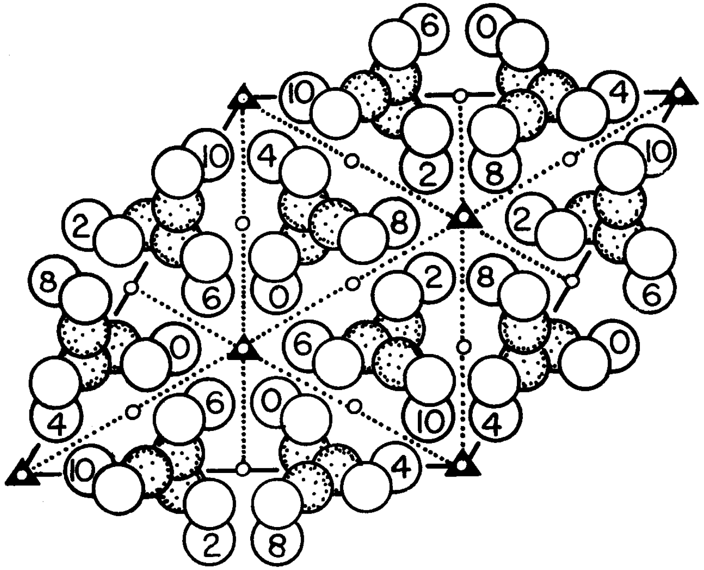
Hydrogen bonding

triclinic

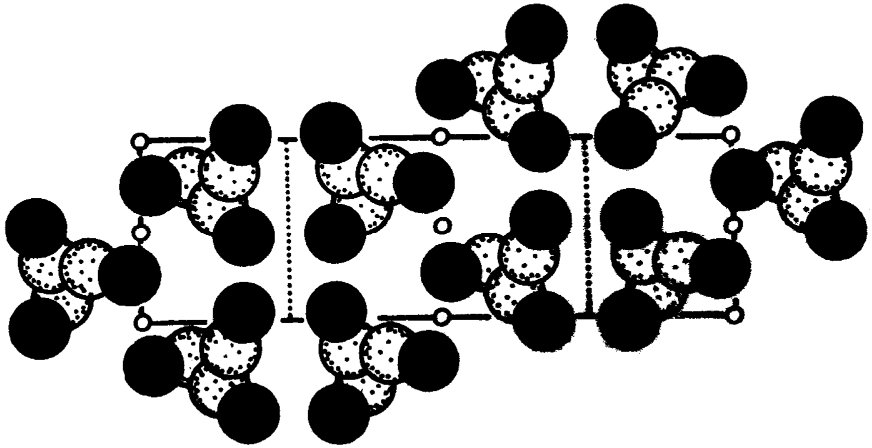
it-PP



i-Poly-1-butene



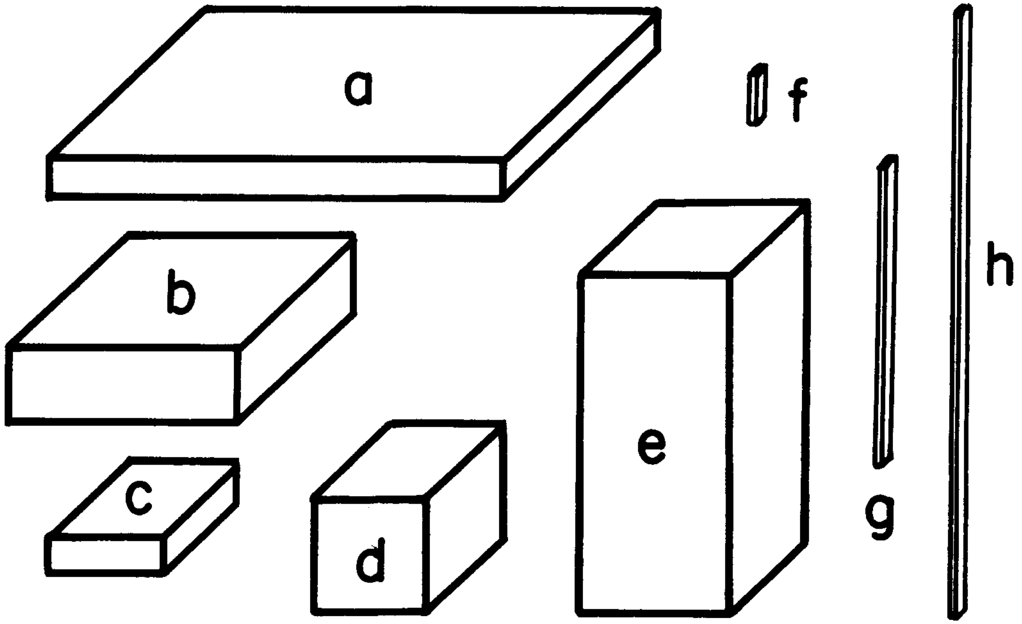
Trigonal



Monoclinic

6.2.2 Basic Morphology of Polymer Crystals

- **"Single crystals" have one lattice**
- **"Polycrystalline samples" are aggregates of many single crystals**

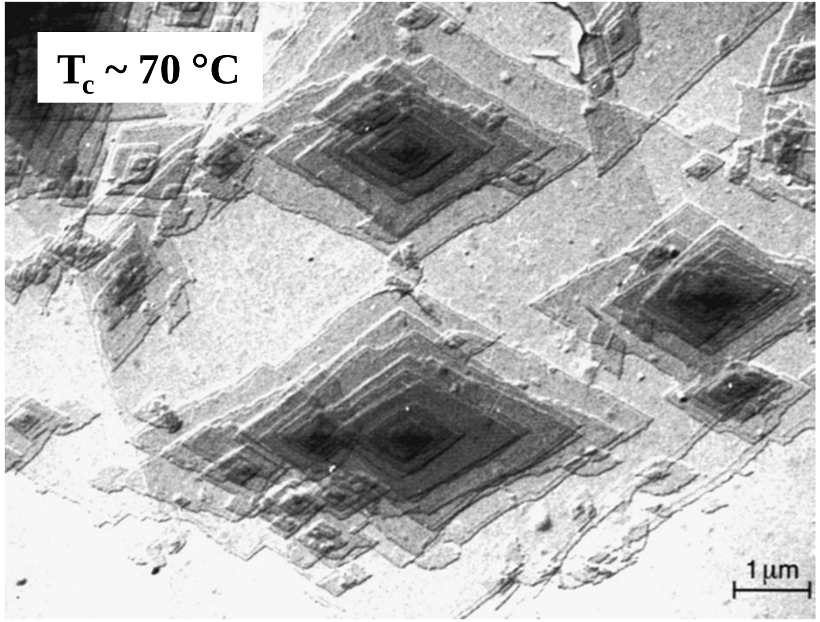


- **Crystal Habits:**
  - ***a: lamellar*** **(薄片状)**
    b: platy
    c: tabular
    d: isometric
    e: prismatic
    f: acicular
    g: needle-like
  - ***h: fibrous*** **(纤维状)**

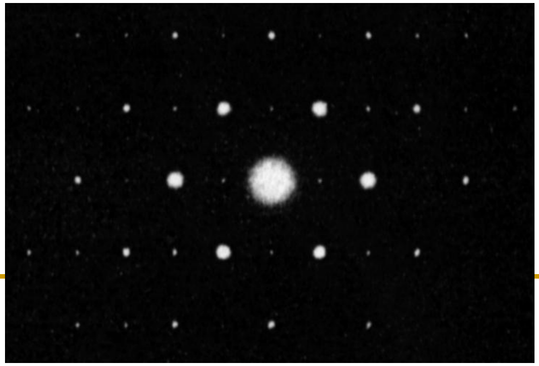
- **Macromolecular crystals are often lamellar or fibrous.**

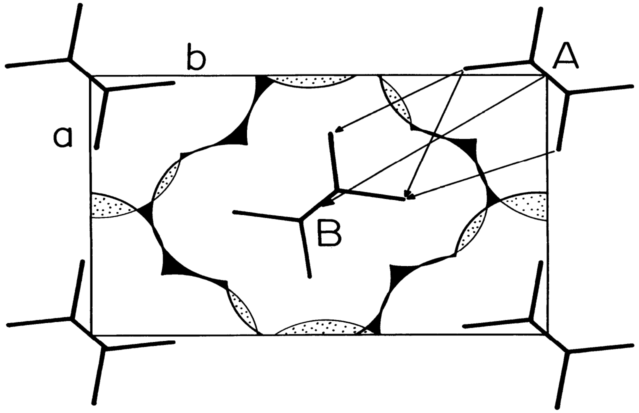
(1) Lamellae (片晶)Crystallized from Dilute Solution

- **Polyethylene (聚乙烯)**


T_c ~ 70 °C


T_c ~ 80 °C



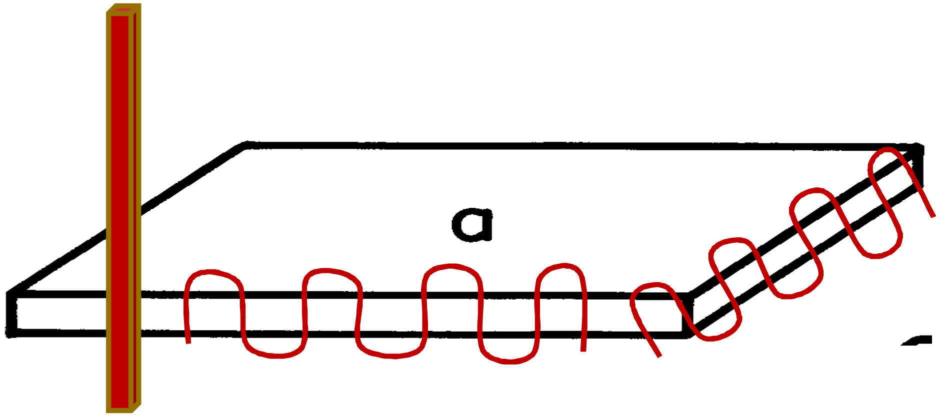


Orientations of polymer chains in lamellae

- PE chains are perpendicular to the lamellar surface.

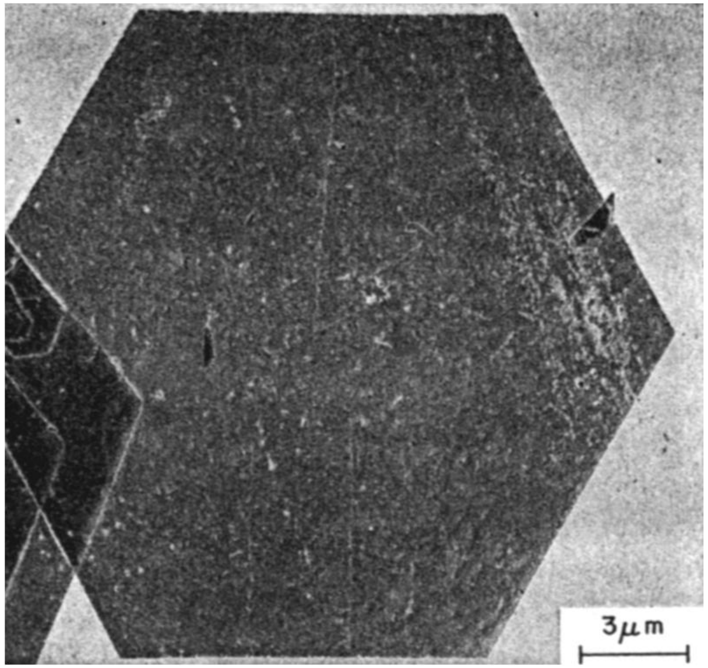
Note: the lamellar thickness is ~10 nm,

the chain length is > 1000 nm.

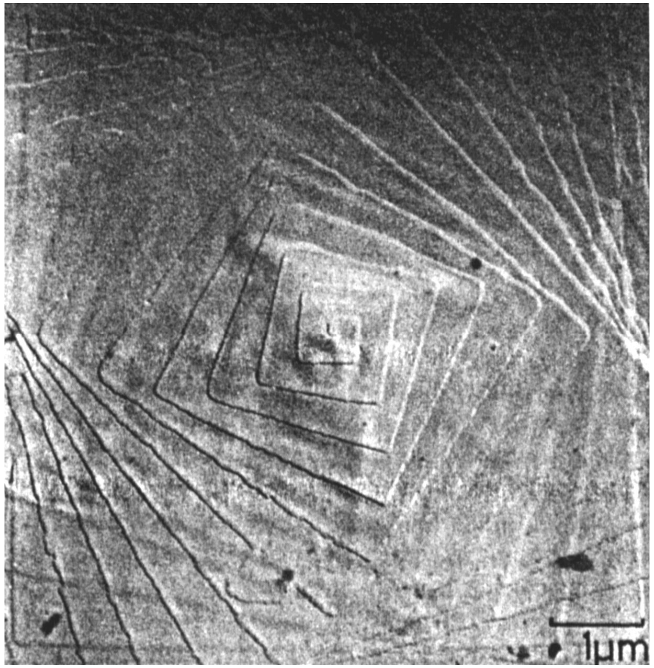


- PE chains must be folded back and forth within the lamella!

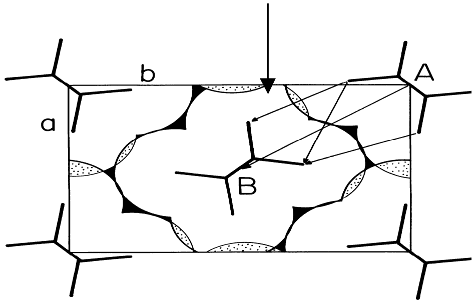
- **Polyoxymethylene (聚甲醛)**

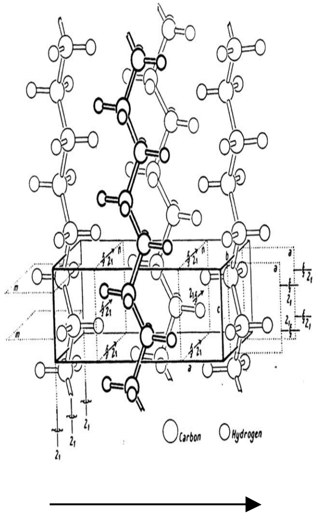


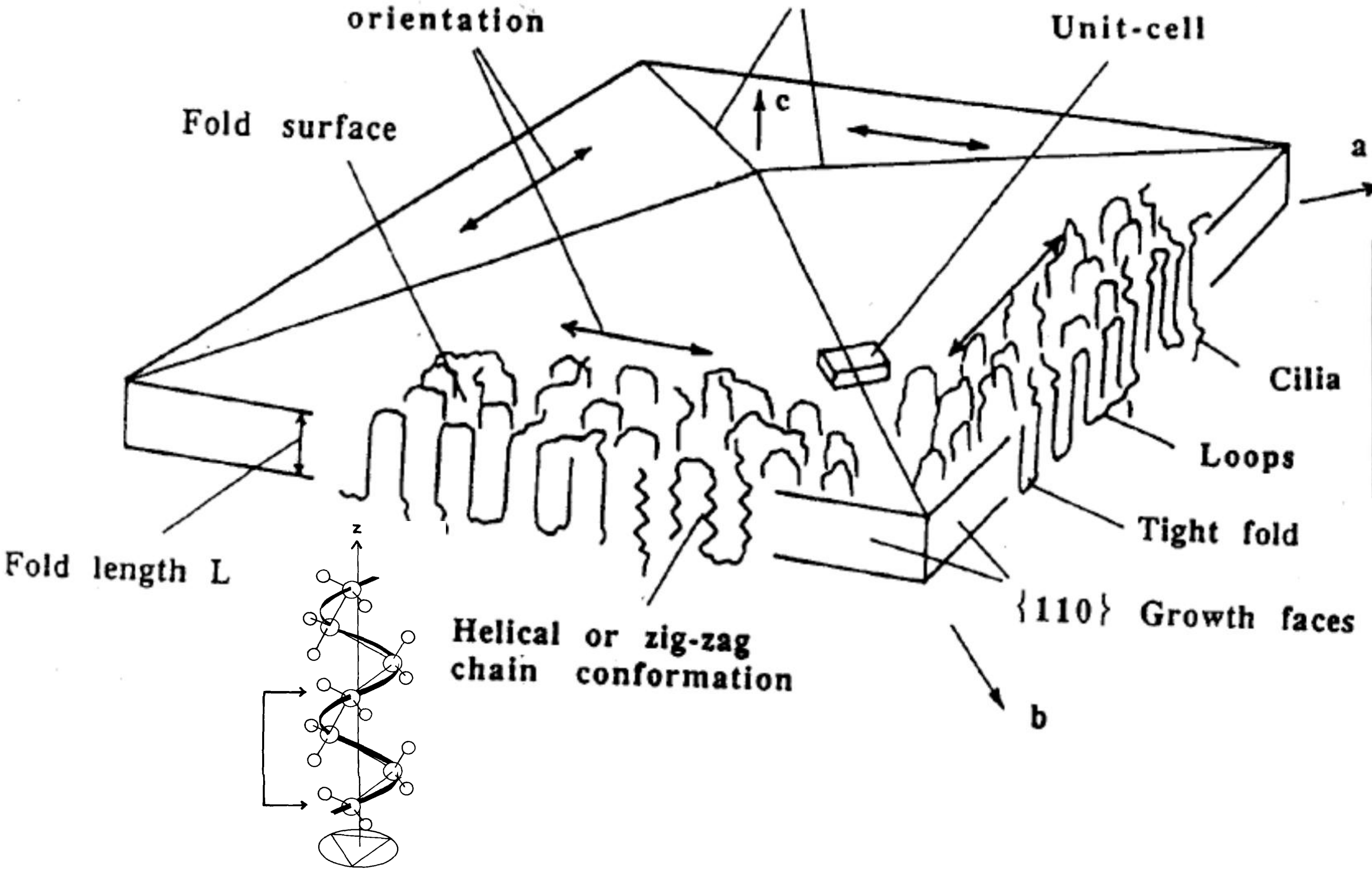
- **PEO(聚氧乙烯)-*b*-PS(聚苯乙烯) diblock copolymer**

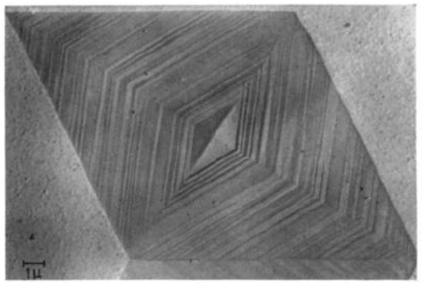


The Structure of Lamellae



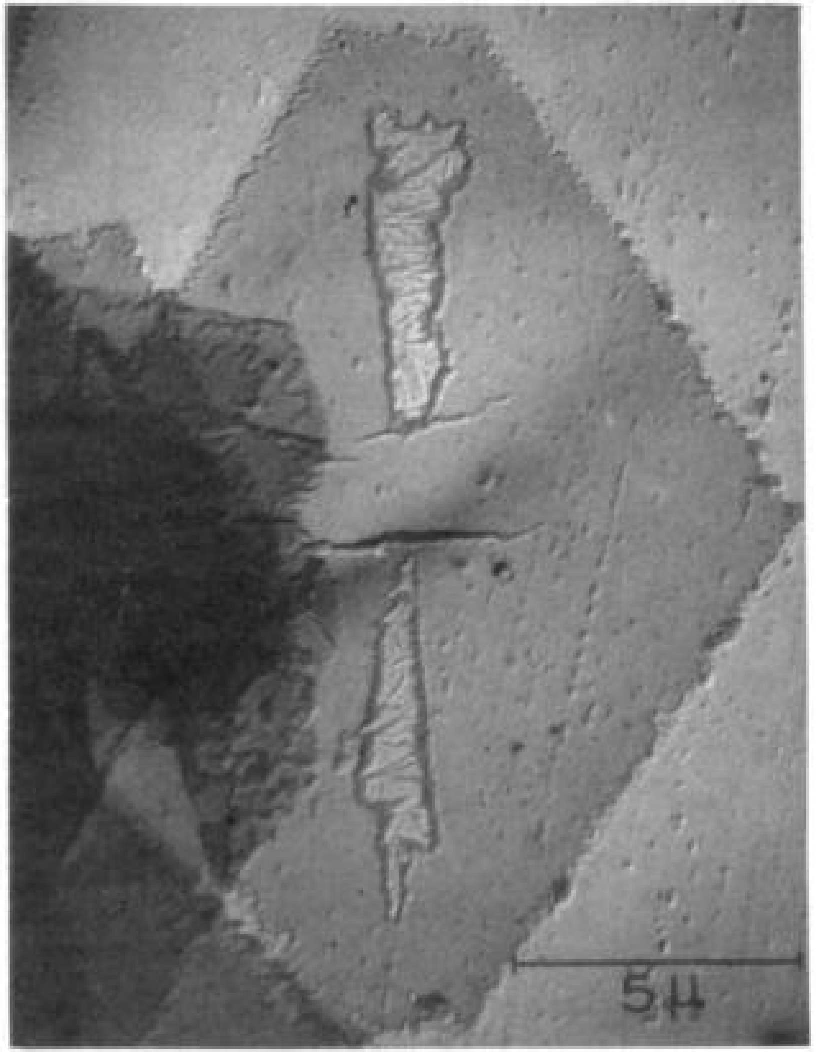


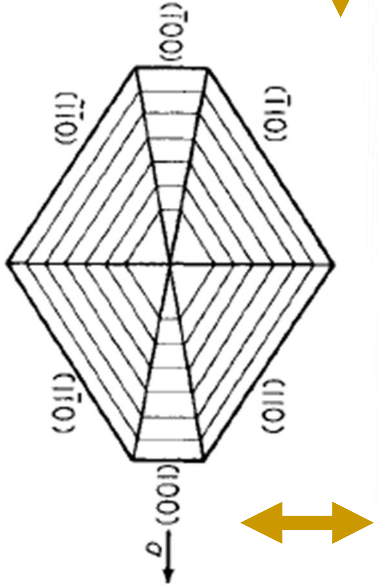


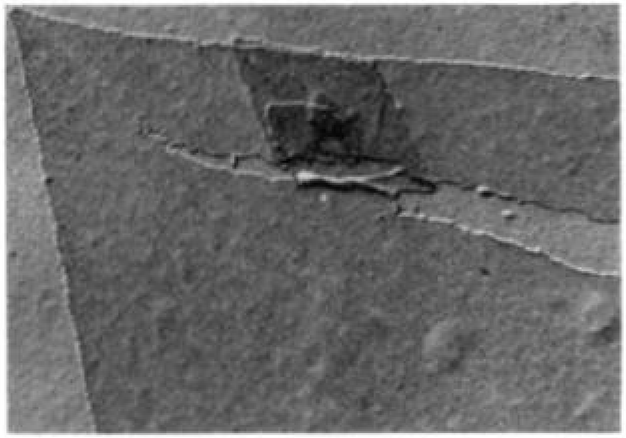


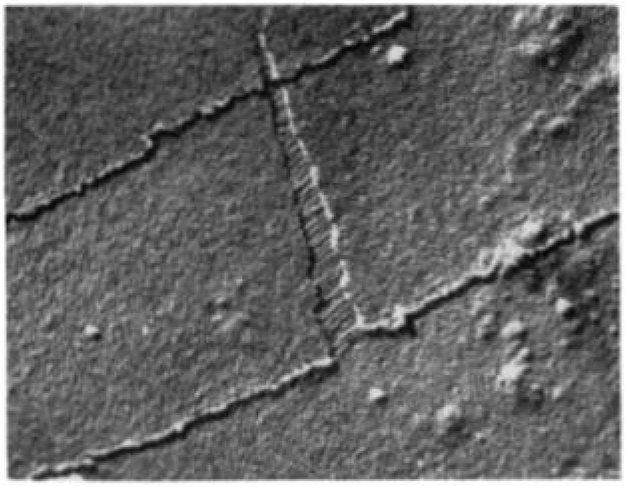
非平面
空锥形

Melting and Stretching of lamellae









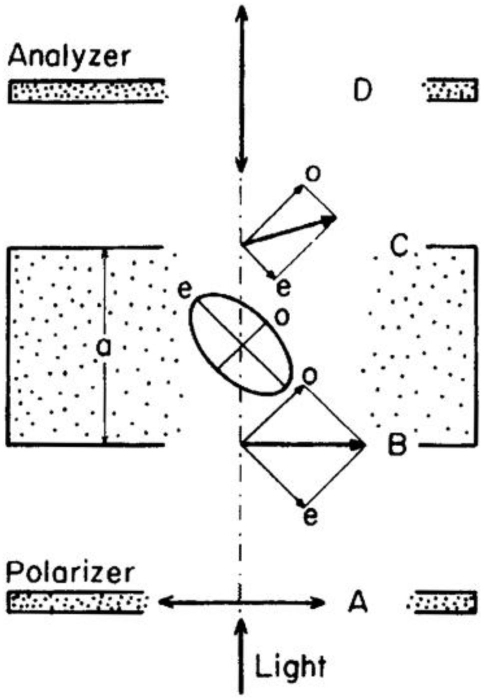
扇形化

Melting

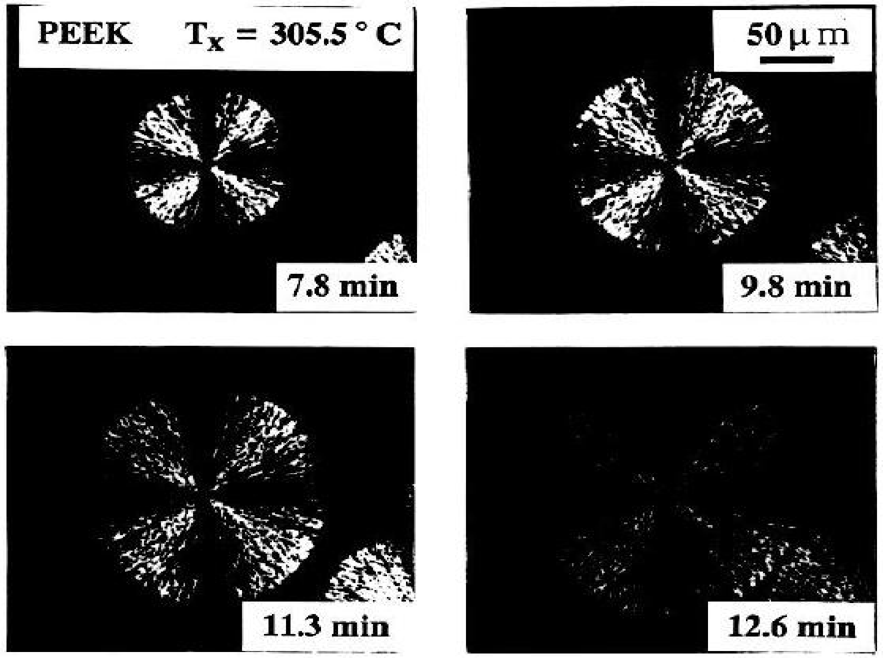
Stretching

(2) Lamellae Crystallized from Melt

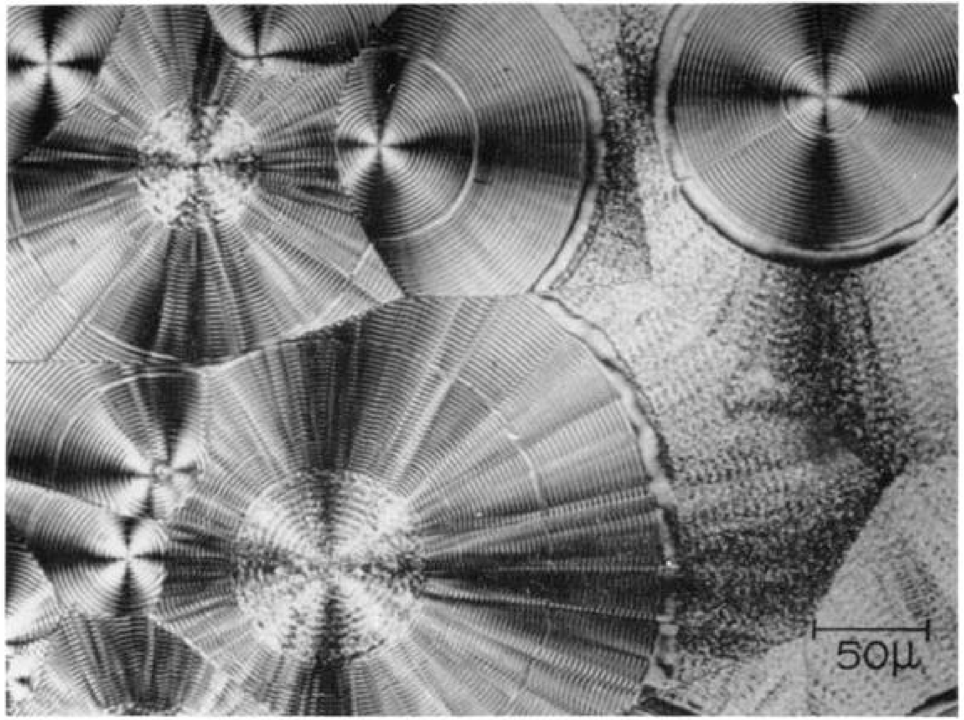
➢ Spherulites (球晶) of polymers

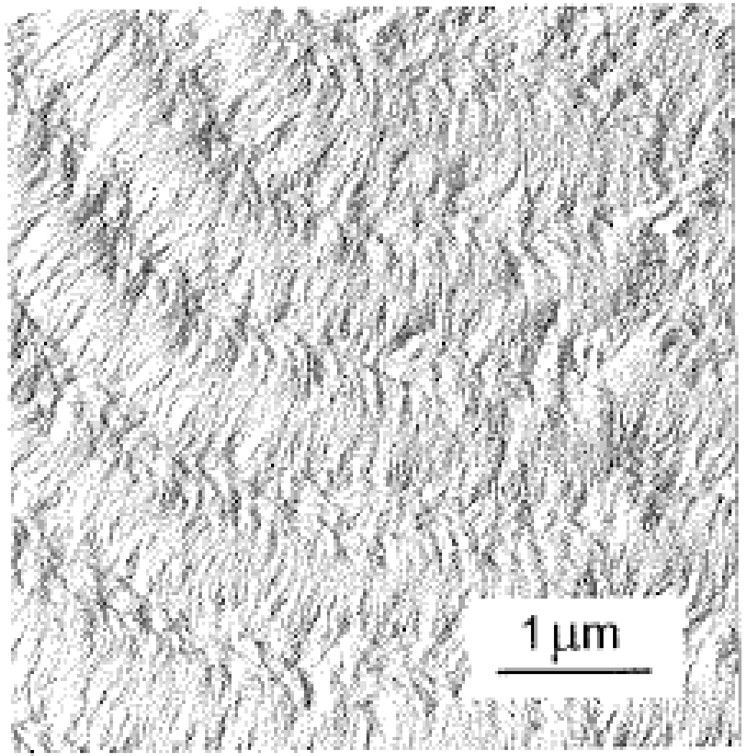


Under Polarized optical microscopy

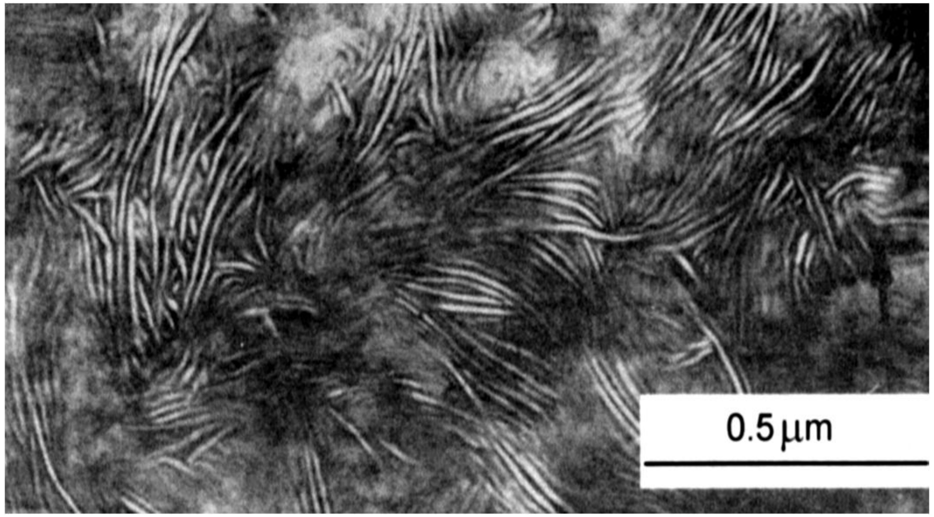


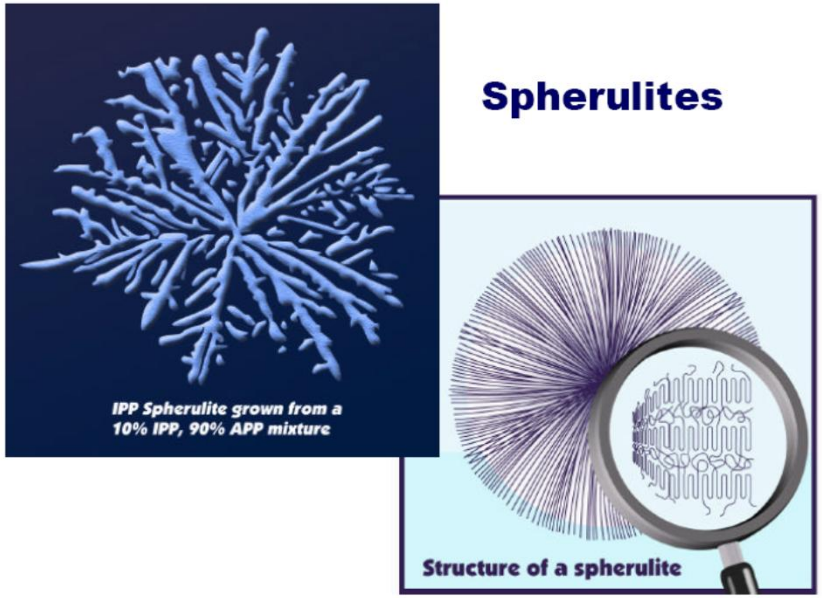
Banded spherulites (环带球晶)

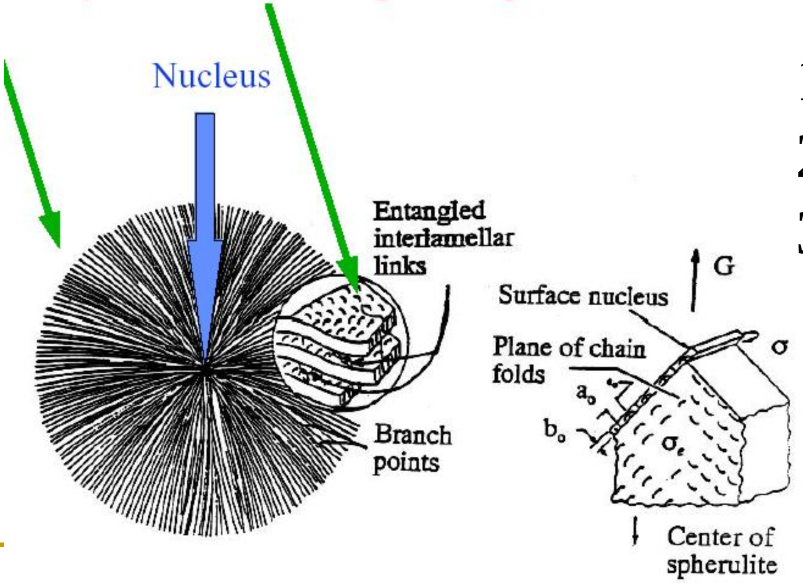




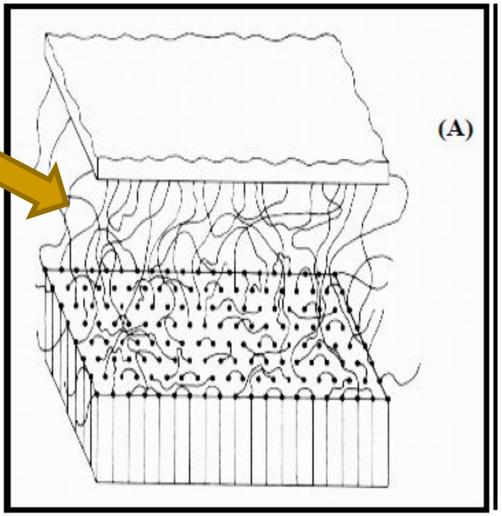
Lamellae in a spherulite



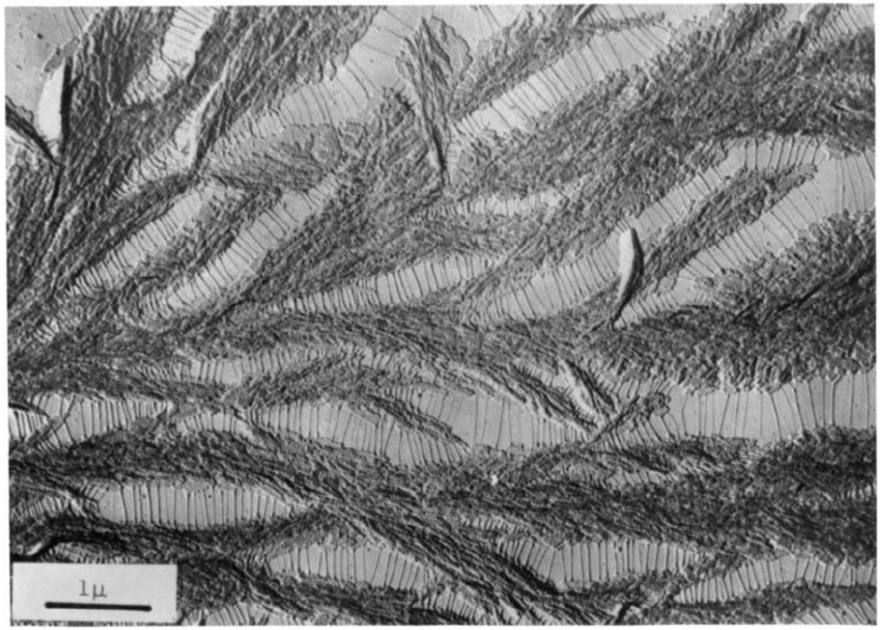


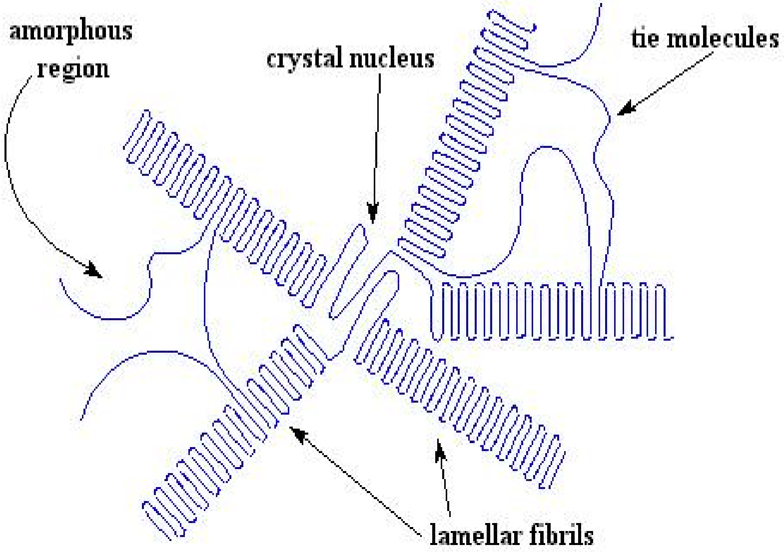


1. Lamellae
2. Tie Molecules
3. Amorphous

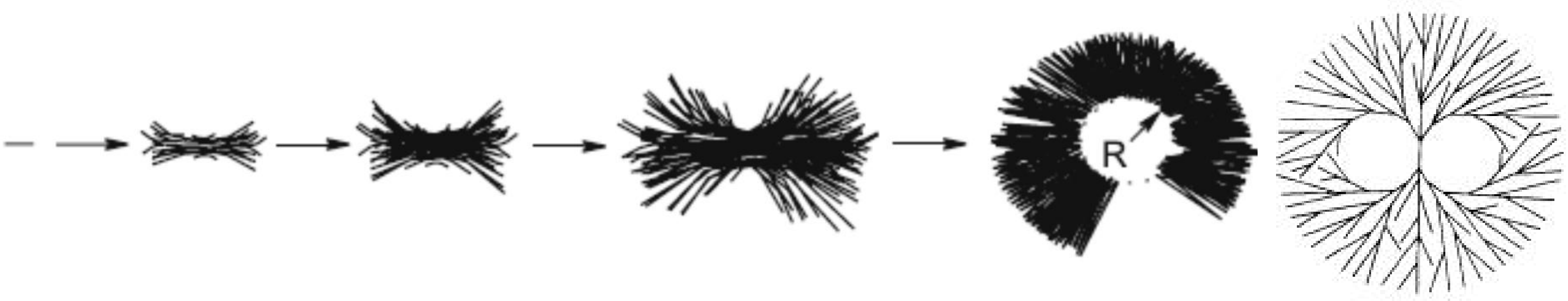


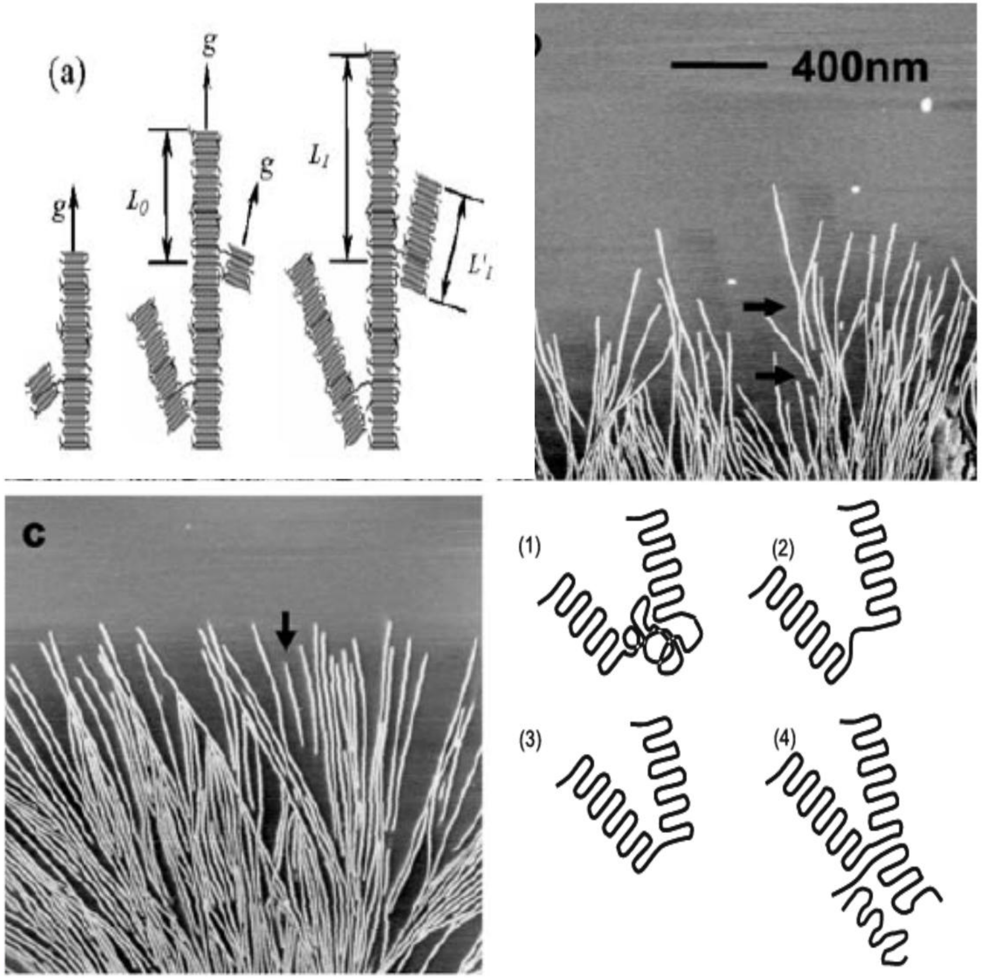
intercrystalline links in **spherulites**



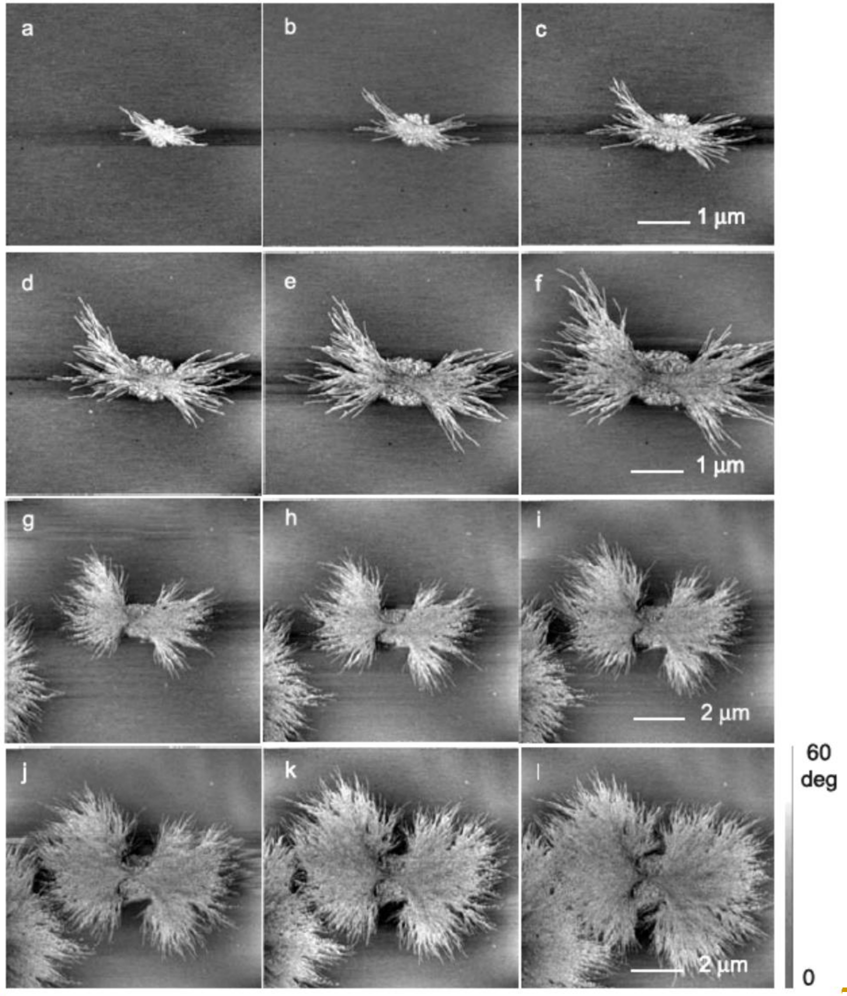


a polymer crystalline spherulite

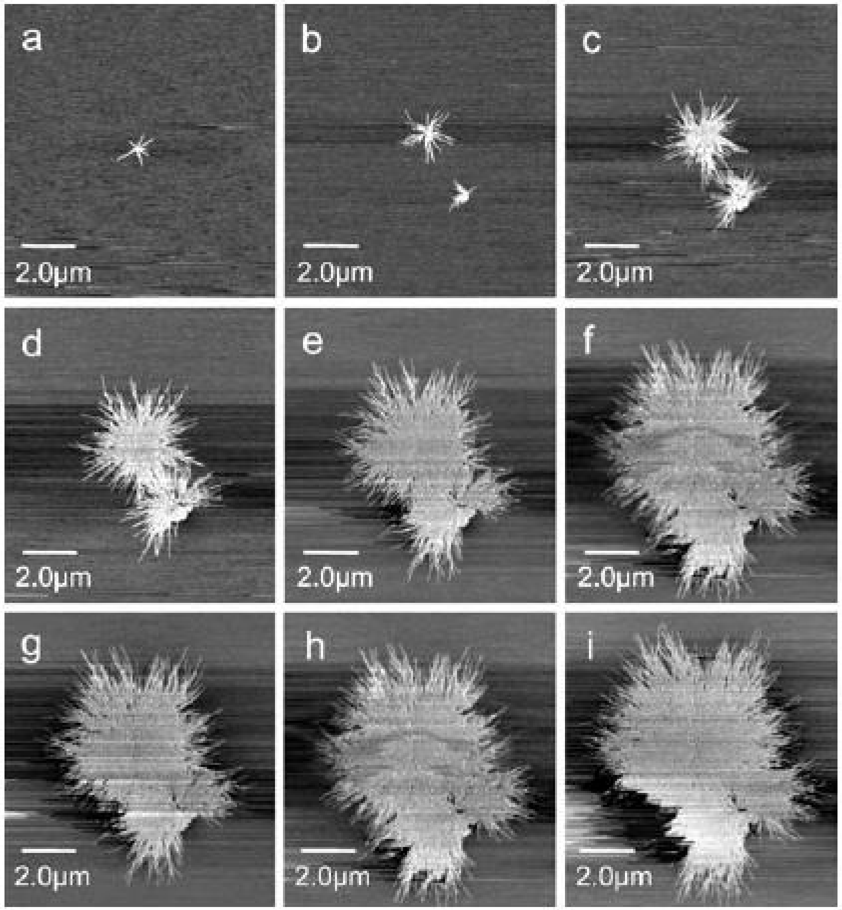

R


(a)
g
g
g
L0
L1
L'1
400nm
c
(1)
(2)
(3)
(4)

Growth of spherulites

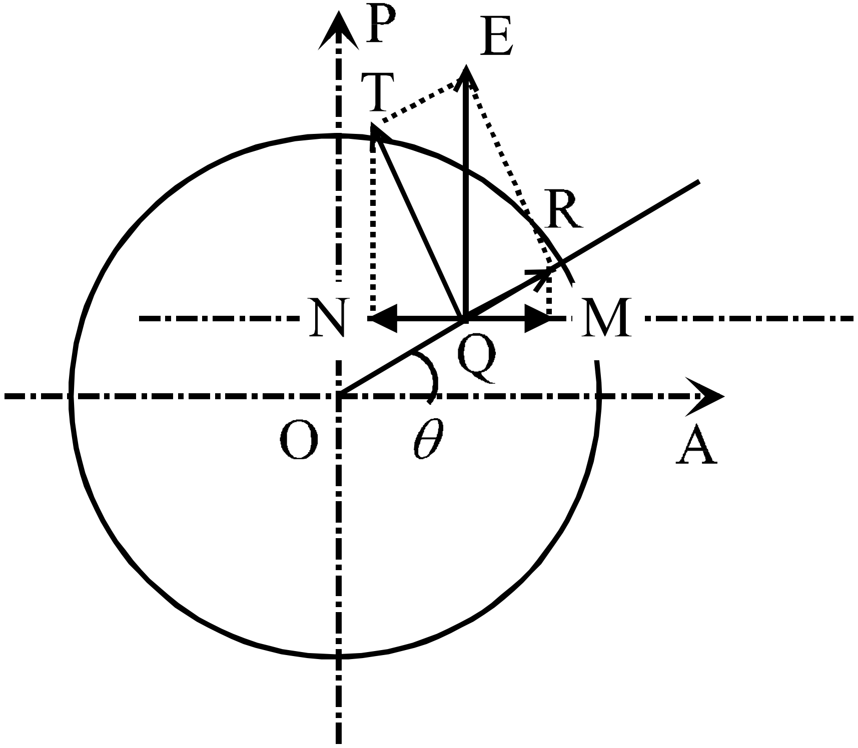


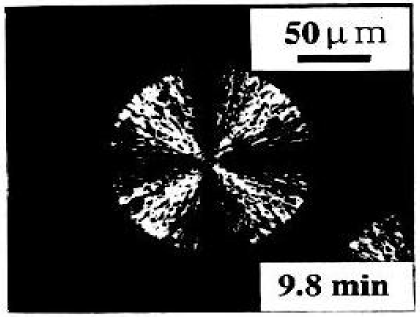
homogenously nucleated



heterogeneously nucleated

The mechanism of ***Maltese cross*** extinction pattern

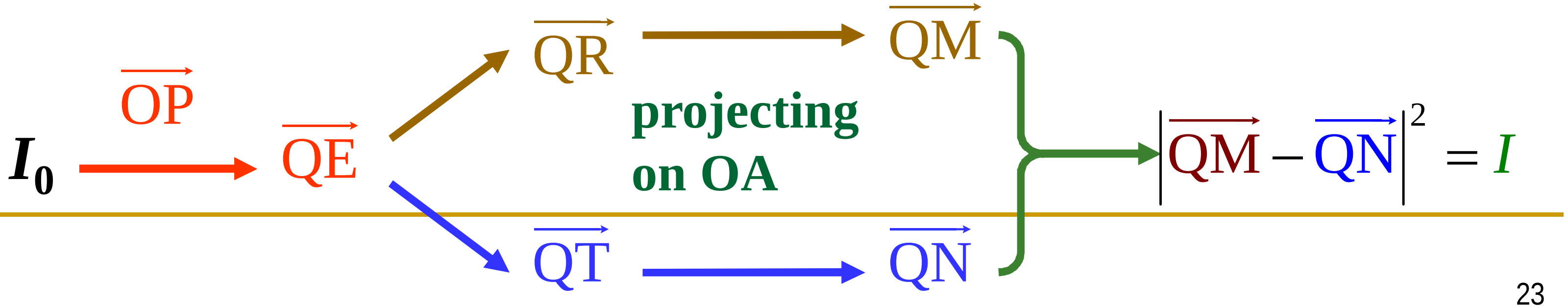




OP: Polarizer

OA: Analyzer

QE: Vector of polarized light



$I_0 \xrightarrow{\overrightarrow{OP}} \overrightarrow{QE}$

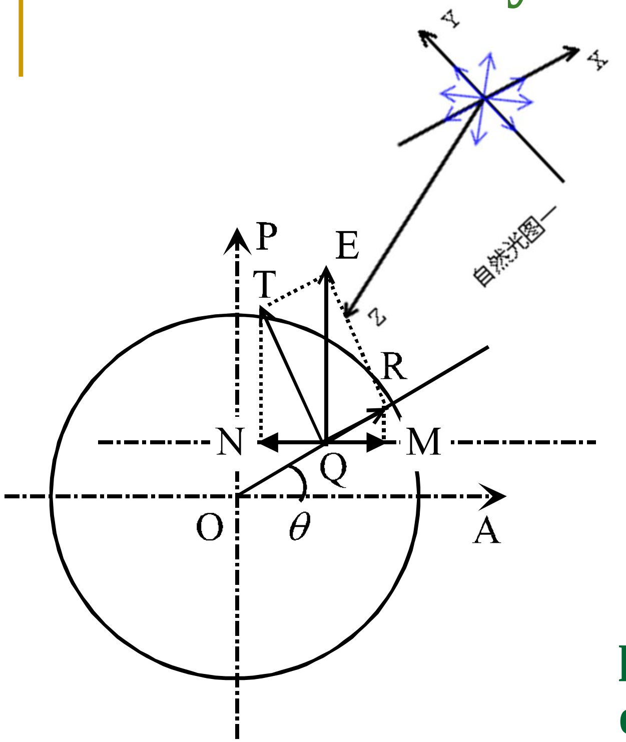
$\overrightarrow{QE} \rightarrow \overrightarrow{QR} \rightarrow \overrightarrow{QM}$

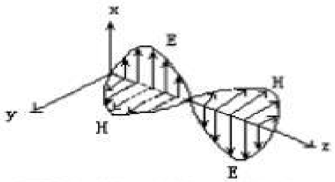
$\overrightarrow{QE} \rightarrow \overrightarrow{QT} \rightarrow \overrightarrow{QN}$

projecting on OA

$\left|\overrightarrow{QM} - \overrightarrow{QN}\right|^2 = I$

Theoretical analysis of ***Maltese cross*** extinction pattern





平面电磁波t时刻E、H分布示意

$$\overrightarrow{QE} = E_0 e^{i\omega t}$$

$$\overrightarrow{QR} = E_0 \sin\theta e^{i(\omega t \pm \delta)}$$

$$\delta \sim \frac{n_{//} - n_{\perp}}{\lambda}$$

$n_{//} > n_{\perp}$ positive spherulite

$n_{//} < n_{\perp}$ negative spherulite

$$\overrightarrow{QT} = E_0 \cos\theta e^{i\omega t}$$

projecting on OA

$$\left.\begin{array}{l} \overrightarrow{QM} = E_0 \sin\theta \cos\theta e^{i(\omega t \pm \delta)} \\ \\ \overrightarrow{QN} = E_0 \cos\theta \sin\theta e^{i\omega t} \end{array}\right\}$$

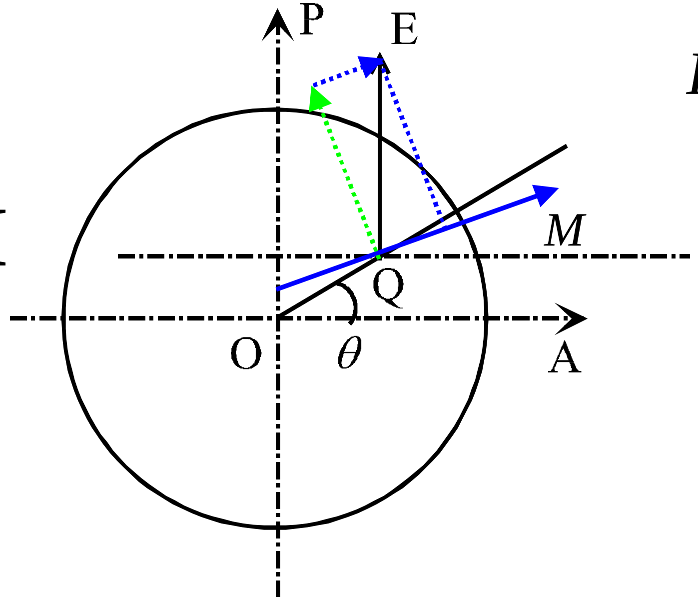
$$\overrightarrow{QM} - \overrightarrow{QN} = E_0 \sin\theta \cos\theta e^{i\omega t}\left(e^{\pm i\delta} - 1\right) = E_0 \frac{\sin 2\theta}{2} e^{i\omega t}\left(\cos\delta \pm i\sin\delta - 1\right)$$

$$= E_0 \frac{\sin 2\theta}{2} e^{i\omega t}\left(-2\sin^2\frac{\delta}{2} \pm i2\sin\frac{\delta}{2}\cos\frac{\delta}{2}\right) = -E_0 \sin 2\theta e^{i\omega t} \sin\frac{\delta}{2}\left(\sin\frac{\delta}{2} \mp i\cos\frac{\delta}{2}\right)$$

$$I = \left|\overrightarrow{QM} - \overrightarrow{QN}\right|^2 = E_0^2 \sin^2 2\theta \sin^2\frac{\delta}{2} \sim \left[E_0^2\left(n_{//} - n_{\perp}\right)^2 \sin^2 2\theta\right]/4$$

Relations of POM and SALS (small angle light scattering) on spherulites

POM



$$\vec{M} = n_{//}\left(\vec{E}\bullet\vec{n}\right)\vec{n} + n_{\perp}\left[\vec{E} - \left(\vec{E}\bullet\vec{n}\right)\vec{n}\right]$$

$$I \sim \left|\vec{M}\bullet\overrightarrow{OA}\right|^2$$

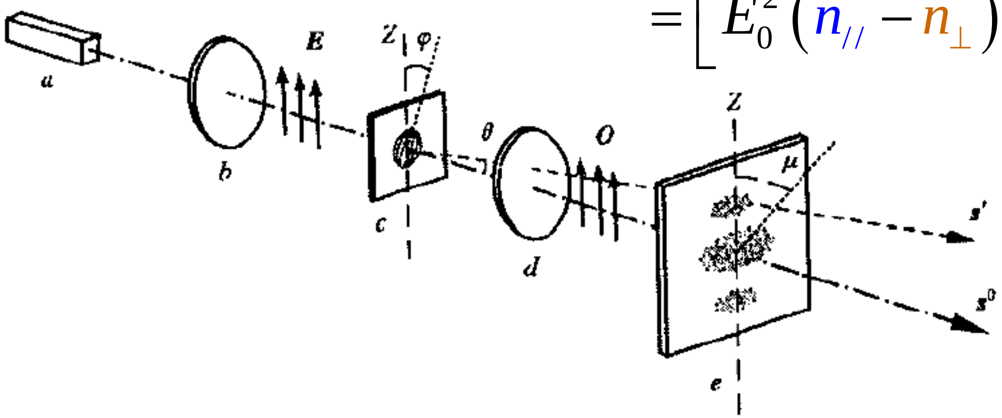
$$= \left|n_{//}\left(\vec{E}\bullet\vec{n}\right)\left(\vec{n}\bullet O\vec{A}\right) - n_{\perp}\left(\vec{E}\bullet\vec{n}\right)\left(\vec{n}\bullet O\vec{A}\right)\right|^2$$

$$= \left|\left(n_{//} - n_{\perp}\right)\left(\vec{E}\bullet\vec{n}\right)\left(\vec{n}\bullet O\vec{A}\right)\right|^2$$

$$= \left(n_{//} - n_{\perp}\right)^2\left[E_0\cos\left(\frac{\pi}{2} - \theta\right)\cos\theta\right]^2$$

$$= \left[E_0^2\left(n_{//} - n_{\perp}\right)^2\sin^2 2\theta\right]/4$$

SALS



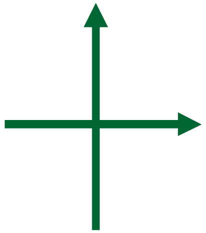
$$S\left(\mathbf{\vec{q}}\right) \sim \int\left(\vec{M}\bullet\overrightarrow{OA}\right)e^{i\mathbf{\vec{q}}\cdot\mathbf{\vec{r}}}\mathrm{d}\mathbf{\vec{r}}$$

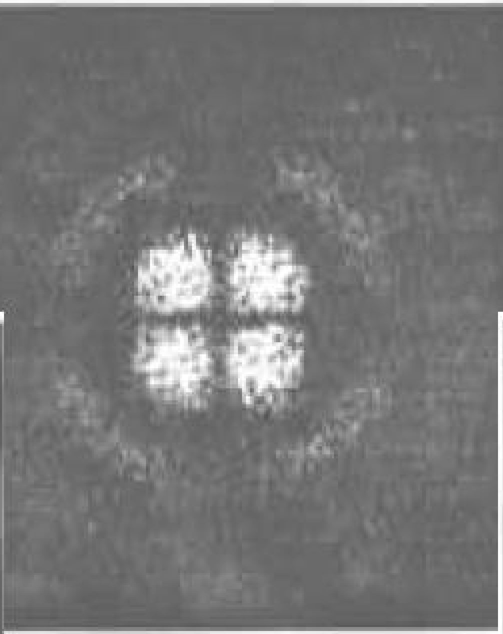
$$I\left(\vec{q}\right) = \left|S\left(\vec{q}\right)S^*\left(\vec{q}\right)\right|$$

SALS patterns of **spherulites: Stein Formula**

$$I_{\text{Hv}} = AV_0^2\left(\frac{3}{q^3}\right)^2\left[(\alpha_r-\alpha_t)\cos^2\frac{\theta}{2}\sin\mu\cos\mu\left(4\sin q - q\cos q - 3\text{Si}q\right)\right]^2$$

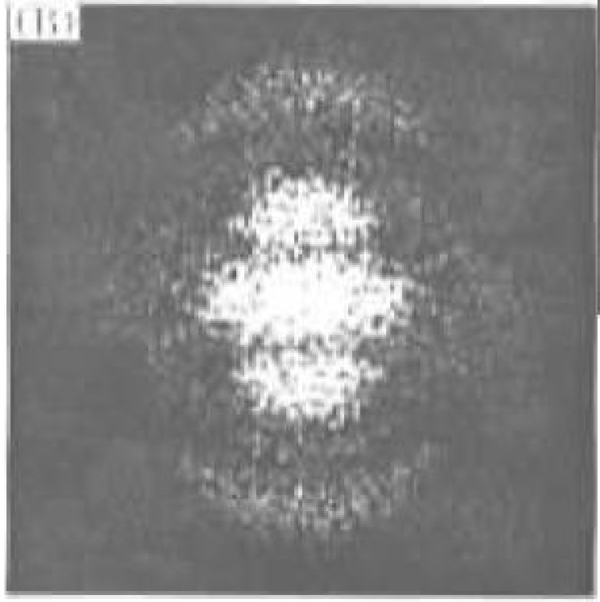
Hv





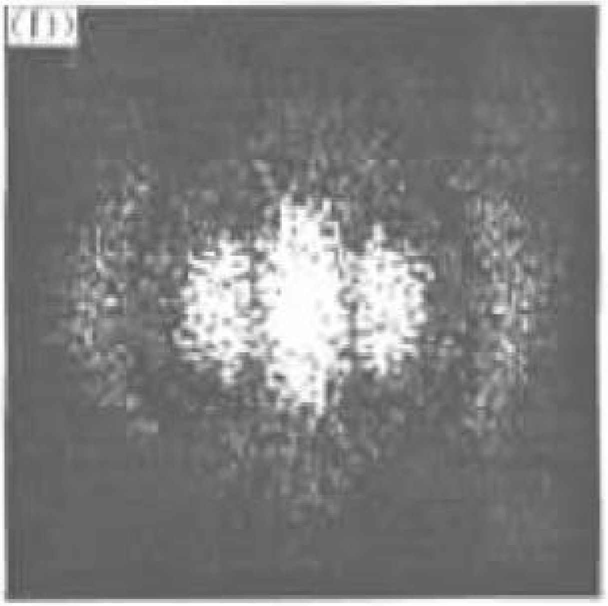
$$q = \frac{4\pi R}{\lambda}\sin\frac{\theta}{2} \qquad \text{Si}q = \int_0^U \frac{\sin x}{x}\,\mathrm{d}x$$

$$\boldsymbol{q_{\text{max}} \sim 1/R}$$



Positive spherulites

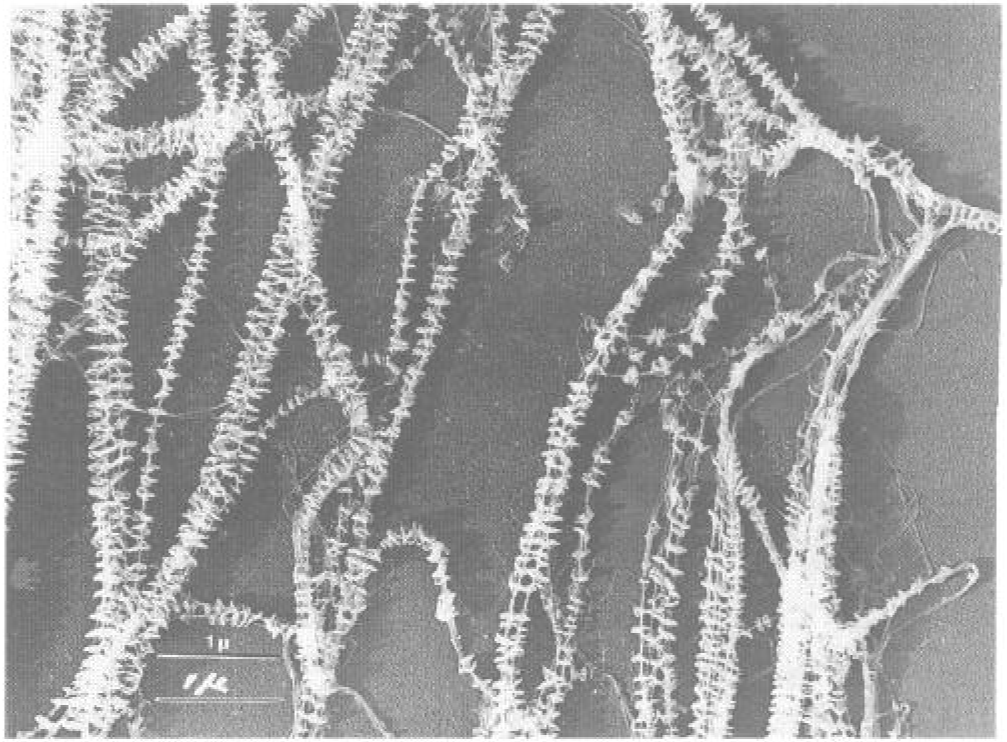
Vv

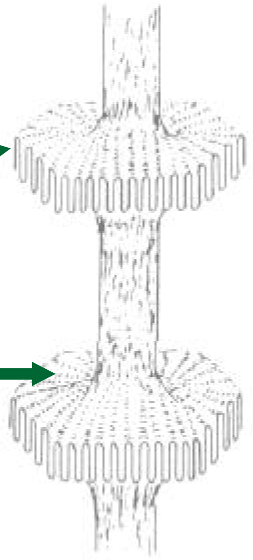


negative spherulites

$$I_{\text{Vv}} = AV_0^2\left(\frac{3}{q^3}\right)^2\left[(\alpha_t-\alpha_s)(2\sin q - q\cos q - \text{Si}q) + (\alpha_r-\alpha_s)(\text{Si}q - \sin q) + \frac{1}{\sqrt{AV_0}}\left(\frac{q^3}{3}\right)\frac{\cos\mu}{\sin\mu}\sqrt{I_{\text{Hv}}}\right]^2$$

(3) Formation of shish-kebab crystallite (串晶) under shear flow





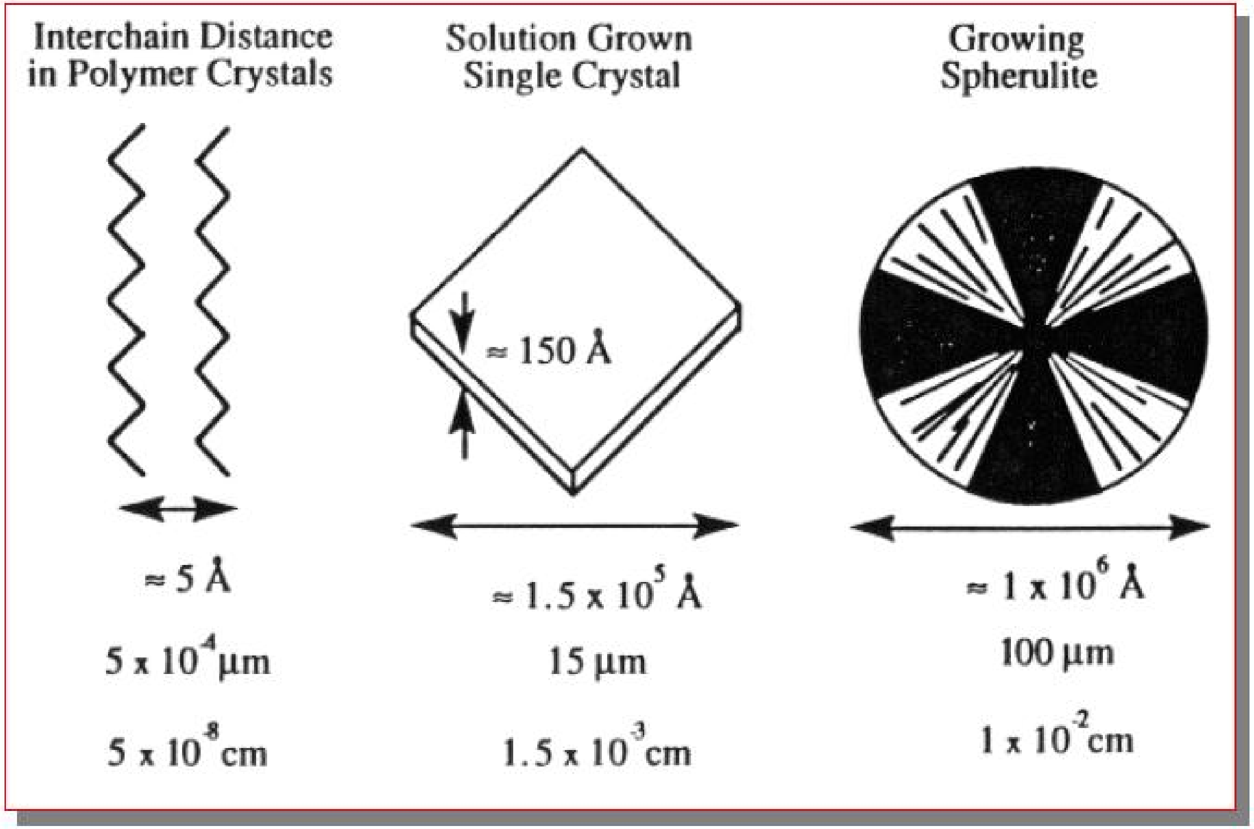
Folded chain

Extended chain

◆串晶由伸直链和折叠链组成

Lamallae & Spherulites

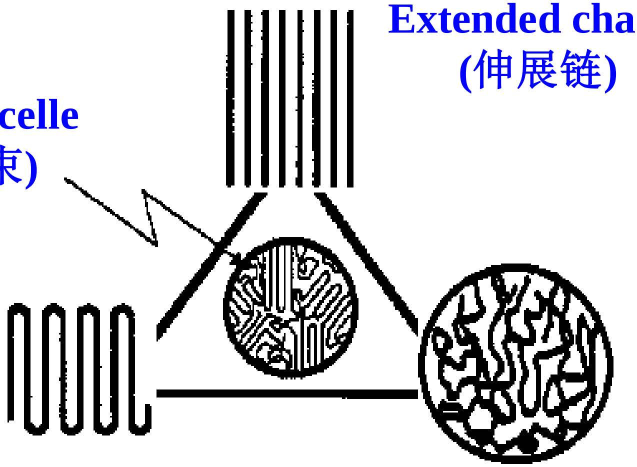
How Big Are They?



Interchain Distance in Polymer Crystals	Solution Grown Single Crystal	Growing Spherulite
≈ 5 Å	≈ 1.5×10^{5} Å	≈ 1×10^{6} Å
5×10^{-4} µm	15 µm	100 µm
5×10^{-8} cm	1.5×10^{-3} cm	1×10^{-2} cm

6.2.3 Polymer Crystallization

- **Macroconformations (巨构象):**



Extended chains
(伸展链)

Fringed micelle
(缨状微束)

Folded chains
(折叠链)

Random coils
(无规线团)

- **How do the polymer chains pack in the lamellar crystals?**

Crystallization

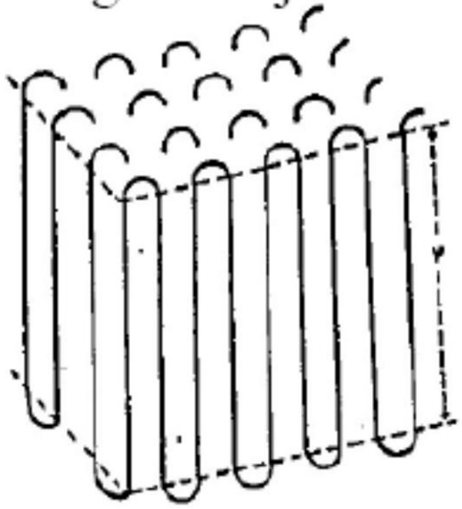
Random coil with the chain contour length (轮廓长度) longer than 1 μm

Lamella with the thickness of 5-50 nm and lateral size of microns.

6.2.3.1 Models

Perfect Folding

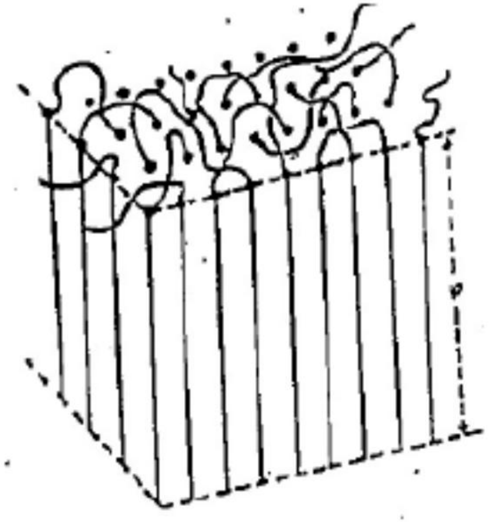
Regular adjacent



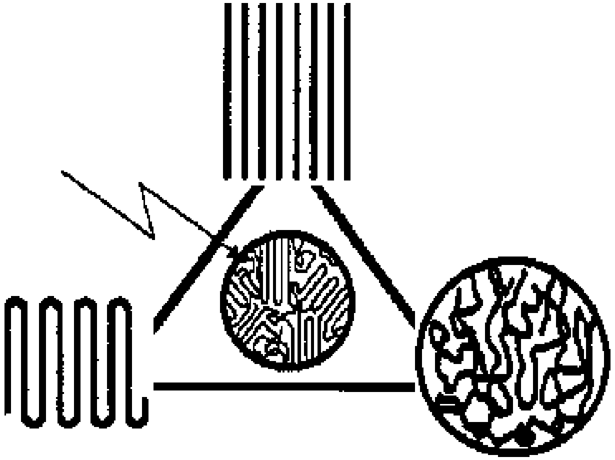
(Keller, Fischer)

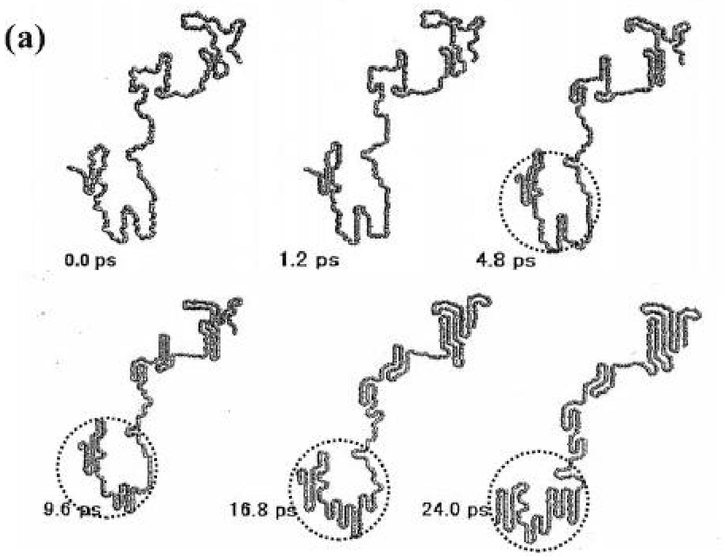
Irregular Folding

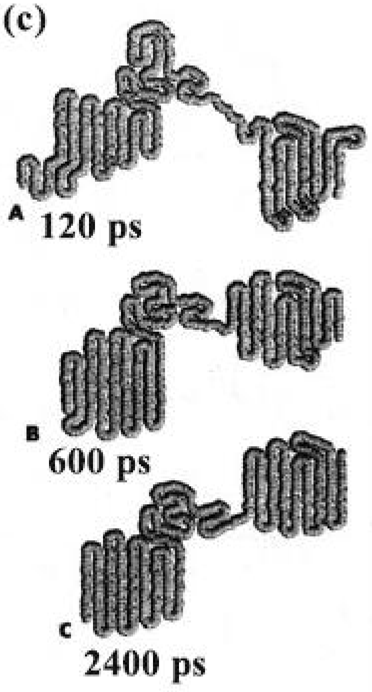
Switchboard



(Flory)

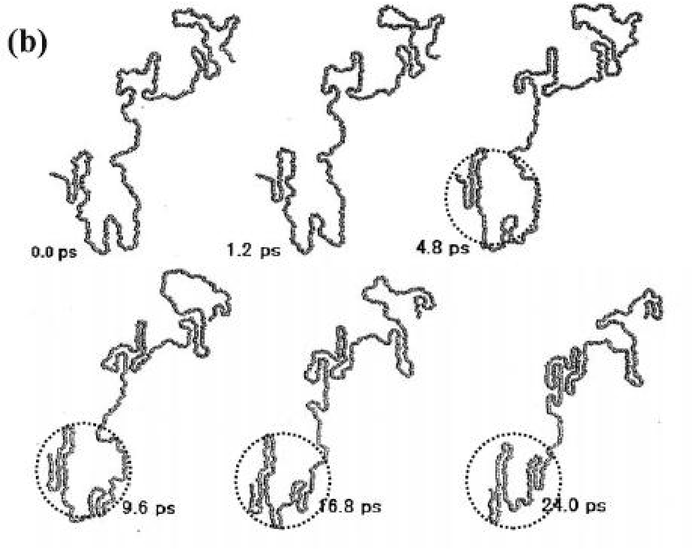


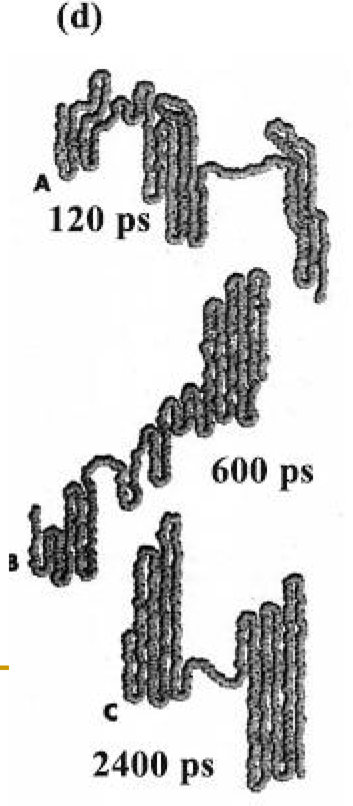




Yamamoto, T., Adv in Polym Sci, 191, 37(2005)

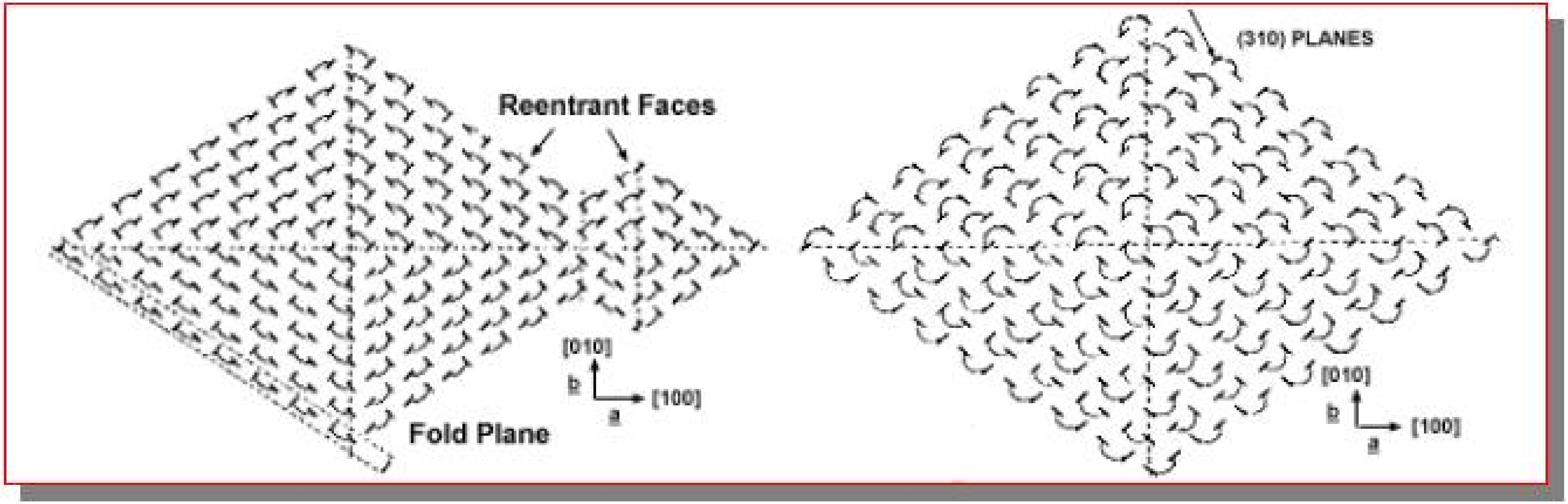
50K





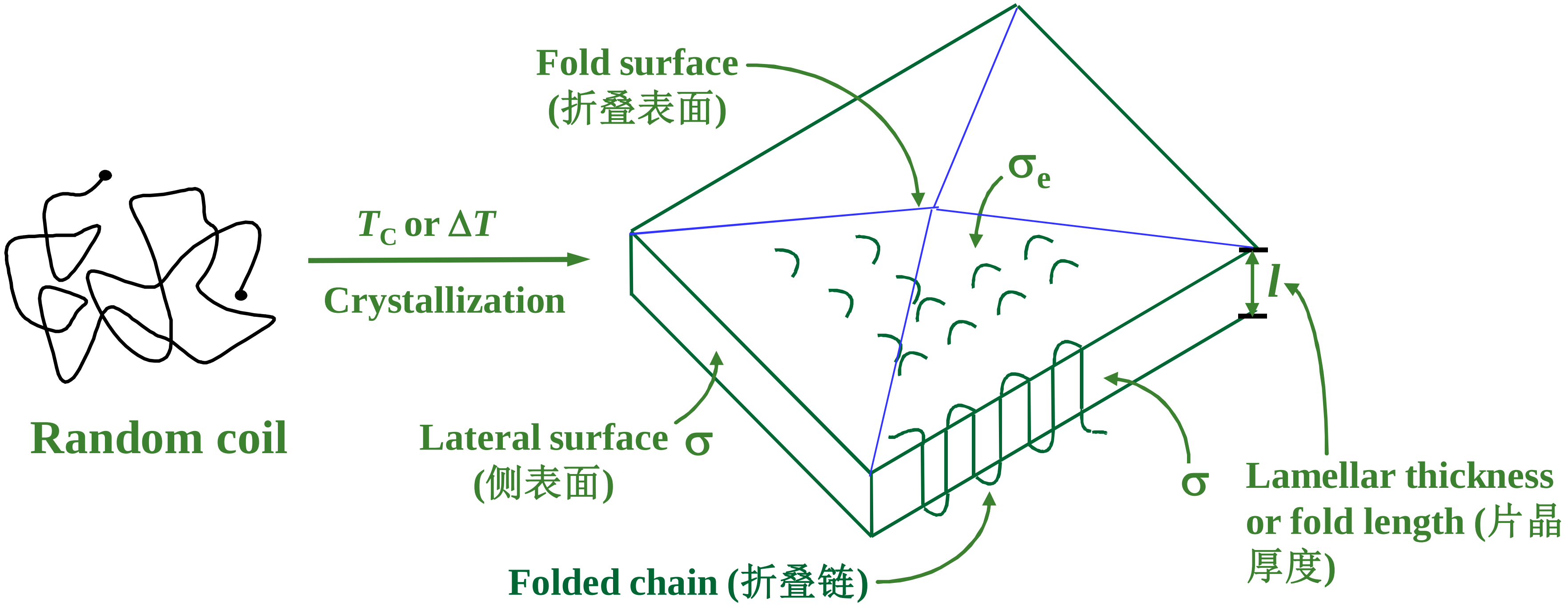
300K

Chain-Folded Lamellae of Polymers



Chain-Folded Lamellae of Polymers

- **Chain folding (链折叠) concept**



Random coil

T_C or ΔT

Crystallization

Fold surface (折叠表面)

σ_e

Lateral surface (侧表面) σ

l

σ

Lamellar thickness or fold length (片晶厚度)

Folded chain (折叠链)

Chain-folded Lamellae

T_C: crystallization temperature (结晶温度)

ΔT: supercooling (过冷度), $\Delta T = T_m^0 - T_C$

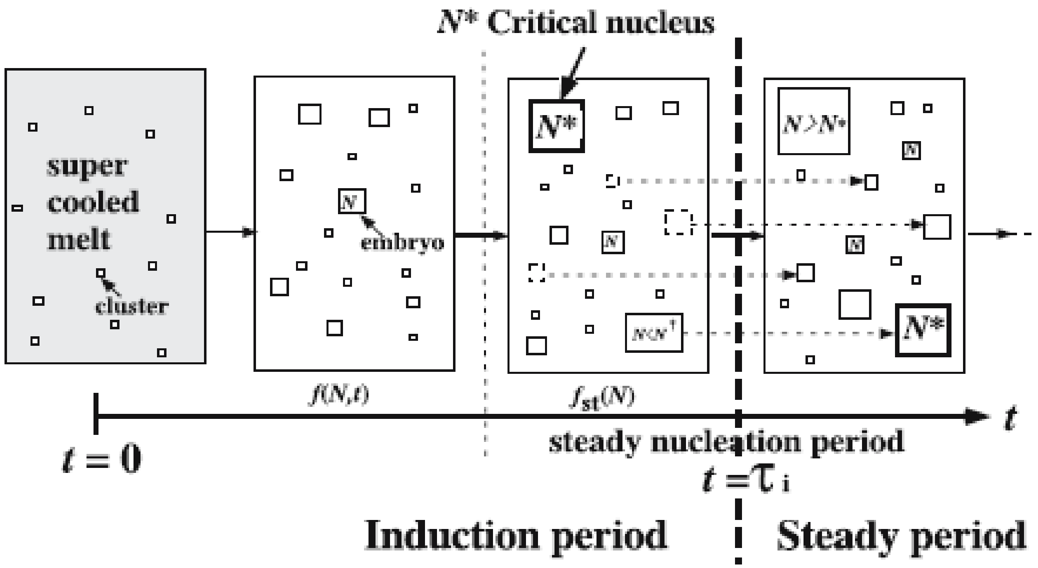
σ_e: fold surface free energy (折叠表面自由能)

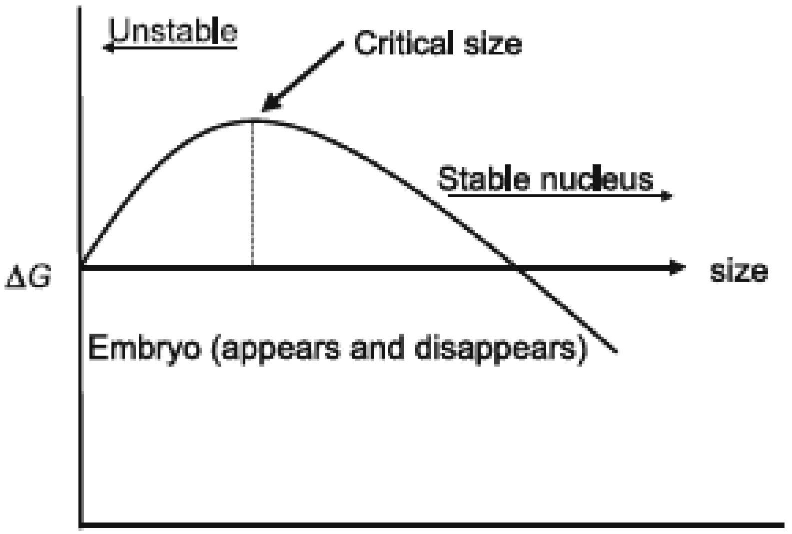
σ: lateral surface free energy (侧表面自由能), $\sigma_e \approx 10\sigma$

6.2.3.2 Process of Polymer Crystallization

Two steps: (1) Nucleation & (2) Linear Growth

- **(1) Nucleation (成核) process**



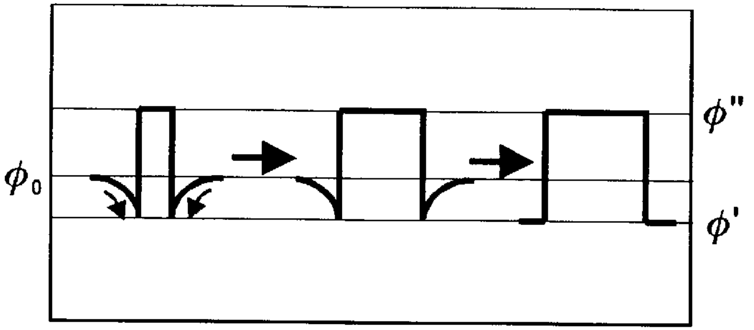


Schematic representation of the change in free energy as a function of size illustrating the nucleation process

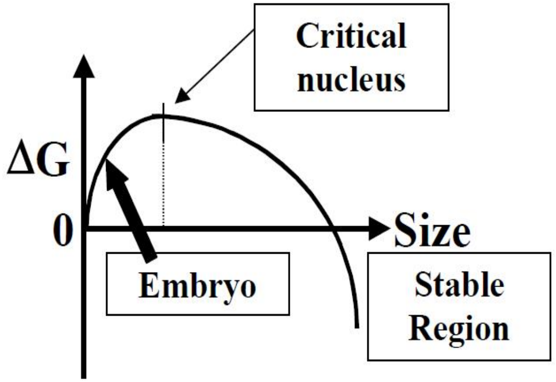
- **Homogeneous (均相) and heterogeneous (异相) nucleation**

Phase Separation Mechanisms

Nucleation and growth (成核生长) mechanism of Phase Separation

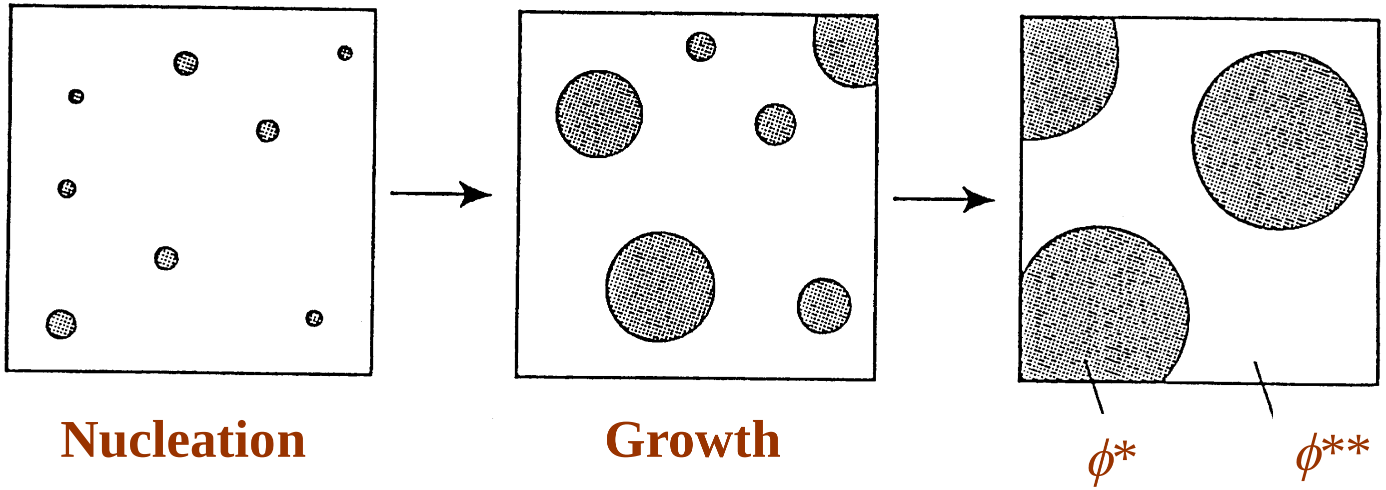


In metastable region, separation can proceed only by overcoming the barrier with a large fluctuation in composition.



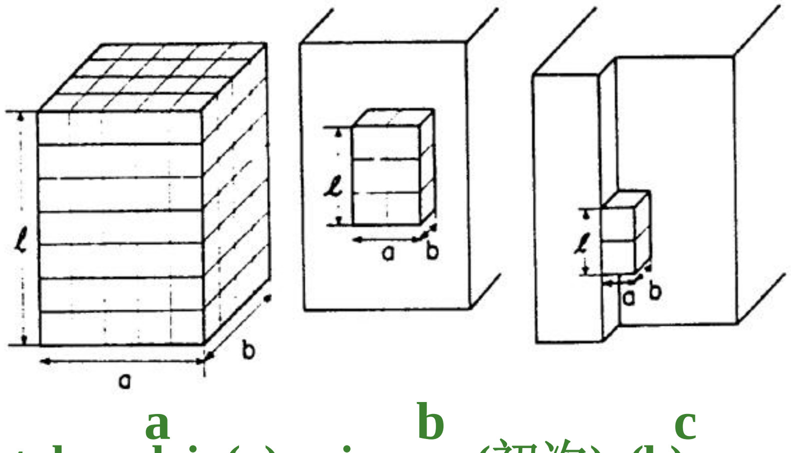
Nucleation barrier: $\Delta G(r) = -\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \sigma$ **with** $\Delta g = g(\phi_0) - g(\phi'')$

***r*: radius of the nuclear; *σ*: excess free energy per unit surface area.**



droplet-dispersed phase

(1) Nucleation (成核) process of Crystallization



Types of crystal nuclei. (a) primary (初次), (b) secondary (二次), (c) tertiary (三次) nucleus.

$$\Delta G = \Delta H - T\Delta S, \ \ \Delta G = G_{\text{crystal}} - G_{\text{melt}}$$

$$G_{\text{crystal}} = G_{\text{bulk}} + \Sigma A\sigma$$

A is the suface area and ΔG_f is the bulk free energy change.

$$\Delta G = G_{\text{bulk}} - G_{\text{melt}} + \Sigma A\sigma = \Delta G_f + \Sigma A\sigma$$

Classic Nucleation Theory - Estimate the critical nucleus size

For primary nucleus $\Delta G\left(T_c\right) = -a^2 l \Delta g_f\left(T_c\right) + 4al\sigma + 2a^2\sigma_e$

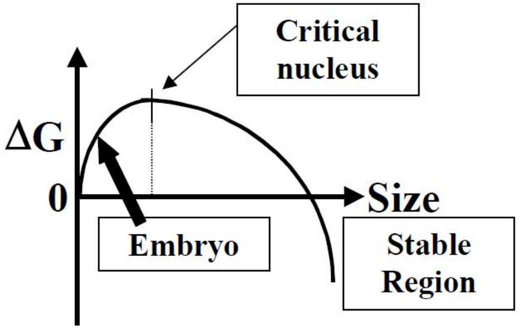
$$\partial\Delta G / \partial a = -2al\Delta g_f\left(T_c\right) + 4l\sigma + 4a\sigma_e = 0$$

$$\partial\Delta G / \partial l = -a^2\Delta g_f\left(T_c\right) + 4a\sigma = 0$$

$$\longrightarrow$$

$$l^* = 4\sigma_e / \Delta g_f\left(T_c\right)$$

$$a^* = 4\sigma / \Delta g_f\left(T_c\right)$$



$$\Delta g_f\left(T_m\right) = \Delta h_f - T_m \Delta s_f = 0 \qquad \boxed{\Delta s_f = \frac{\Delta h_f}{T_m}}$$

$$\Delta g_f\left(T_c\right) = \Delta h_f - T_c \Delta s_f = \Delta h_f \frac{\Delta T}{T_m}$$

$$l^* = \frac{4\sigma_e}{\Delta g_f} = \frac{4\sigma_e T_m}{\Delta h_f \Delta T} \qquad a^* = \frac{4\sigma T_m}{\Delta h_f \Delta T}$$

For secondary nucleus $\Delta G = -abl\Delta g_f + 2bl\sigma + 2ab\sigma_e$

$$\partial\Delta G / \partial a = 0$$

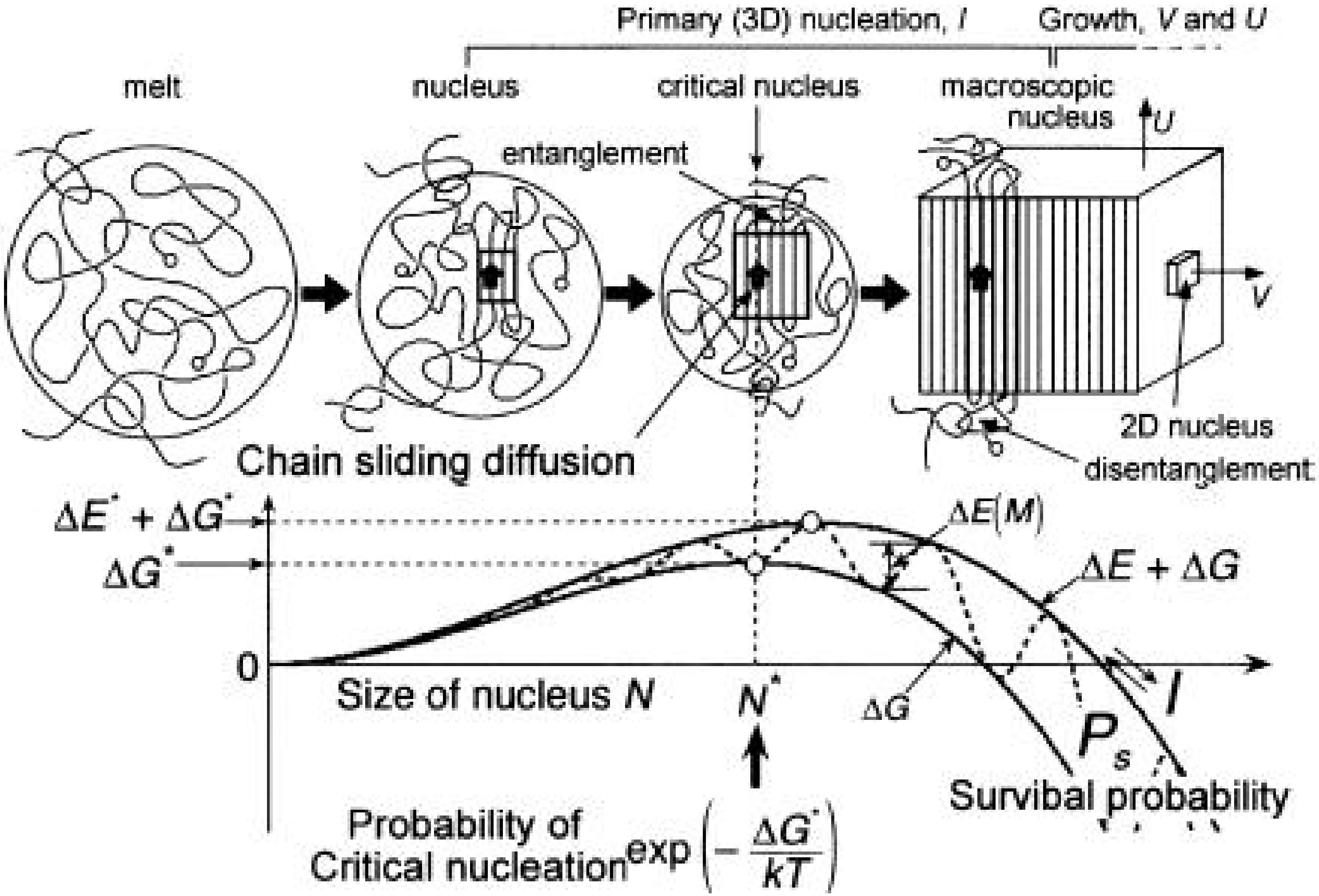
$$\partial\Delta G / \partial l = 0$$

$$\longrightarrow$$

$$l^* = \frac{2\sigma_e}{\Delta g_f} = \frac{2\sigma_e T_m}{\Delta h_f \Delta T} \qquad a^* = \frac{2\sigma}{\Delta g_f} = \frac{2\sigma T_m}{\Delta h_f \Delta T}$$

$$\Delta G_{II}^* = \frac{4b\sigma\sigma_e T_m}{\Delta h_f \Delta T} \qquad v_{II} \propto k \exp\left[-\frac{\Delta G^*}{k_B T}\right]$$

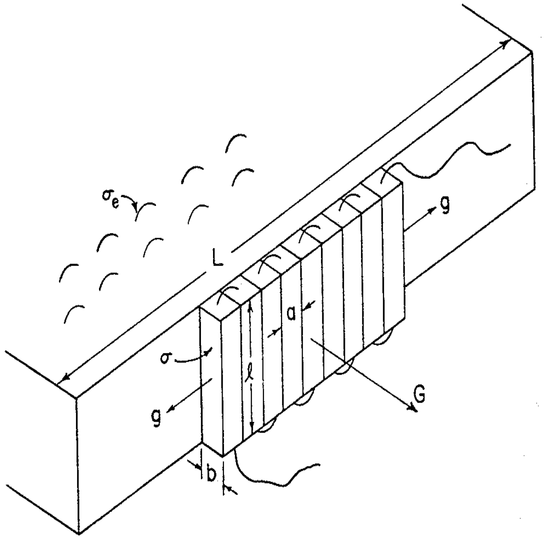
Chain sliding diffusion model of primary nucleation



Hikosaka, M., Adv in Polym Sci, 151, 137 (2005)

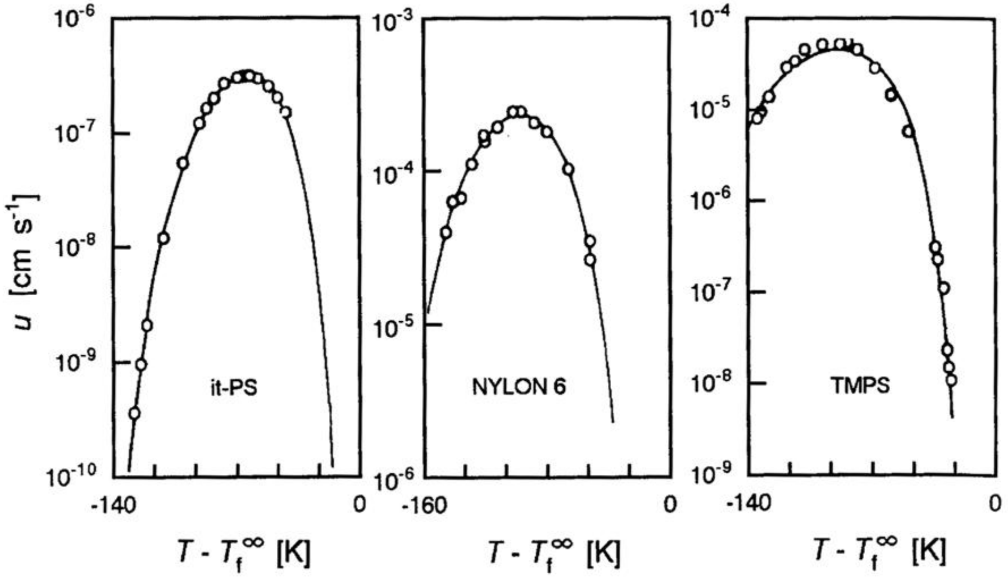
(2) Linear Growth of Polymer Crystallization

- **Surface nucleation on substrate with length L with a rate i**
- **Linear growth rate G: the growth rate of crystal perpendicular to the substrate**



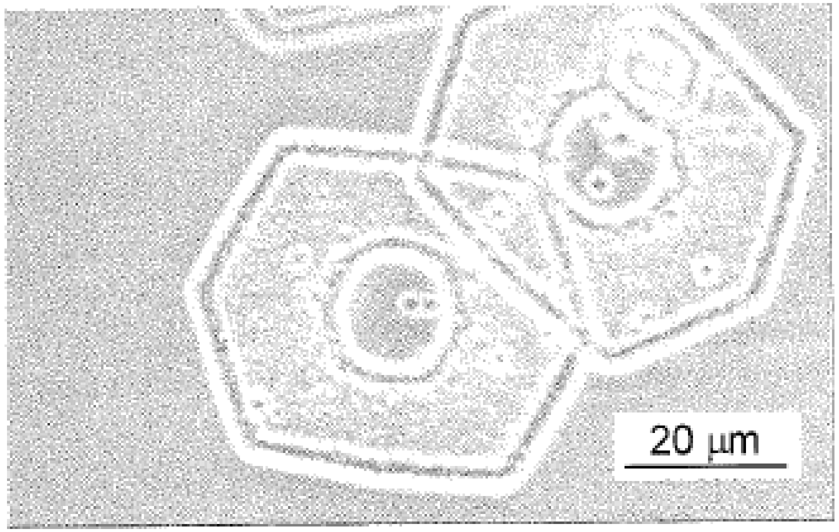
l: fold length; a: width of stem; b: thickness of the stem; g: substrate completion rate

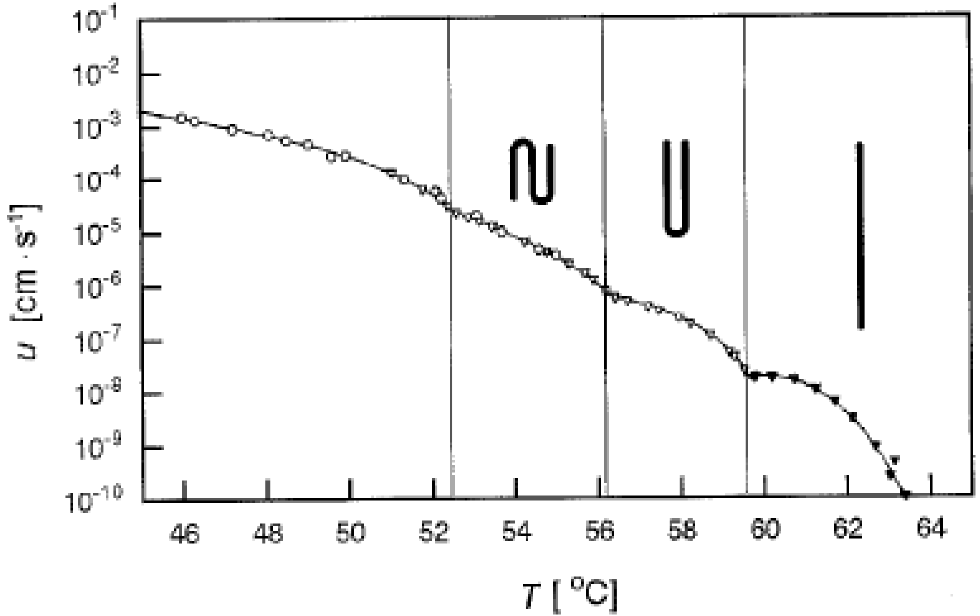
- **Temperature dependence of linear growth rate (线生长速度)**



Temperature dependence of the radial growth rate u of spherulites in isotactic polystyrene (*left*), polyamid 6 (*center*) and poly(tetramethl-p-silpheylene siloxane) (*right*). T_f^{∞}: equilibrium melting temperature.

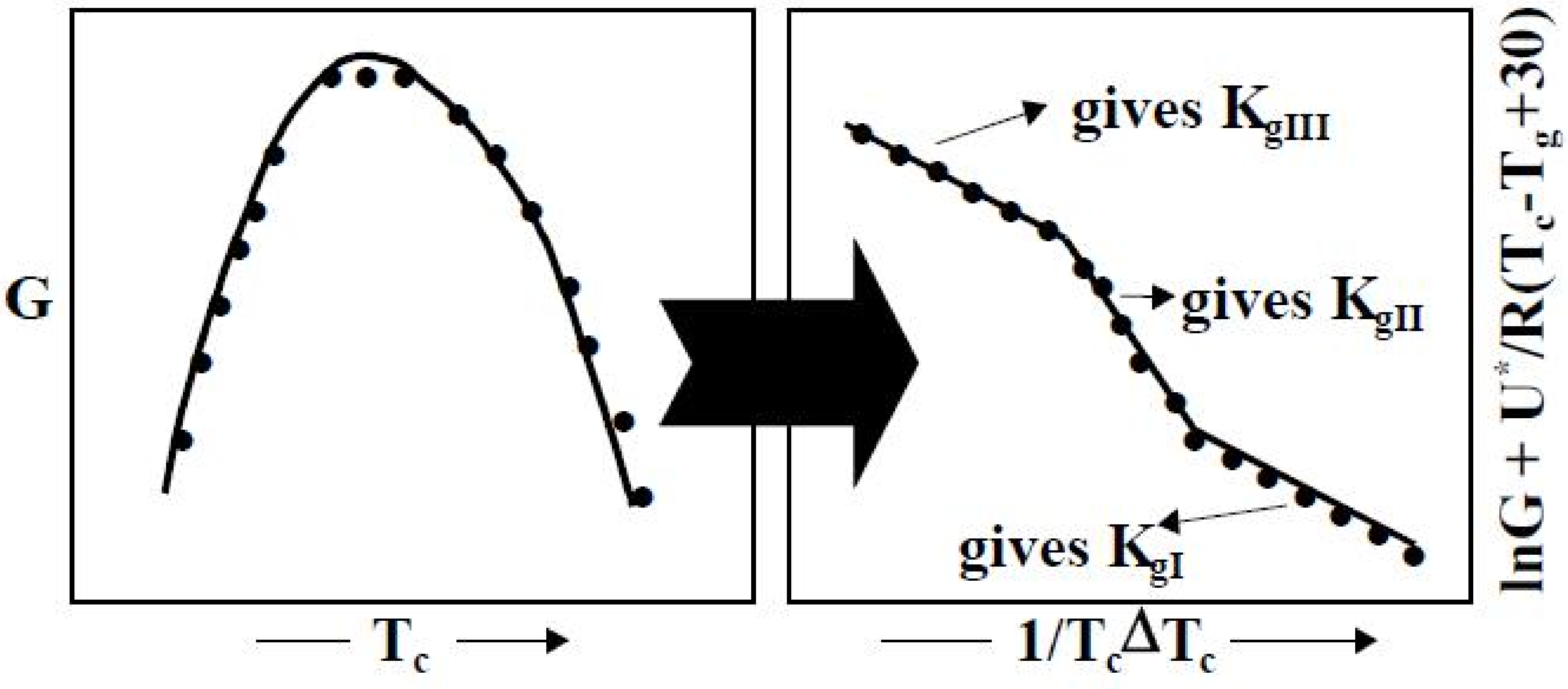
Crystal Growth Rate of PEO in melt





A.J. Kovacs, C. Straupe, and A. Gonthier. *J. Polym. Sci., Polym. Symp. Ed.*, 59:31, 1977

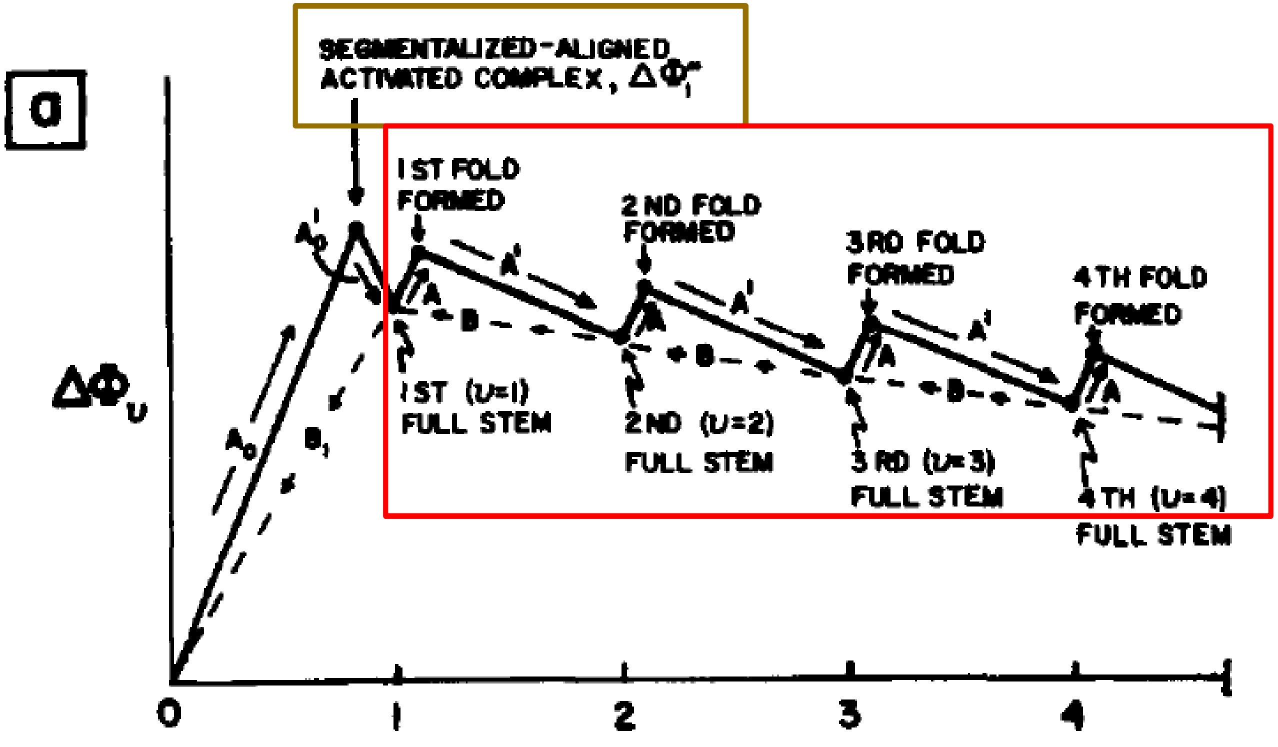
Regime I, II & III of Linear Growth

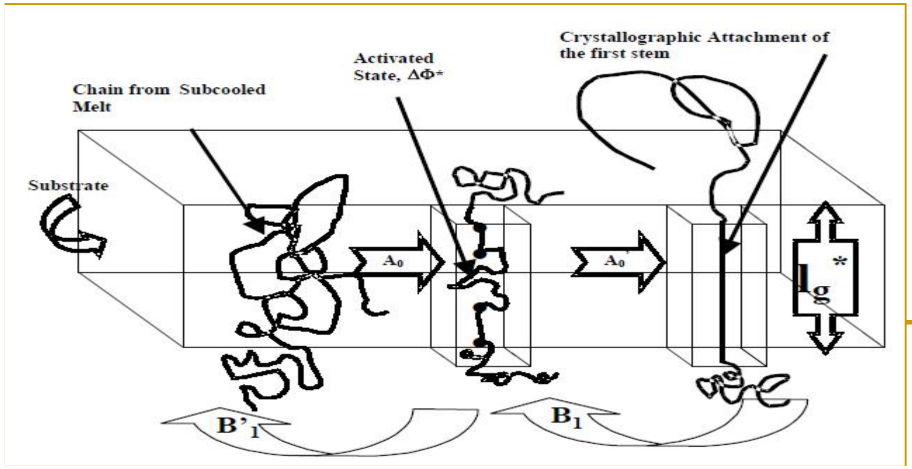


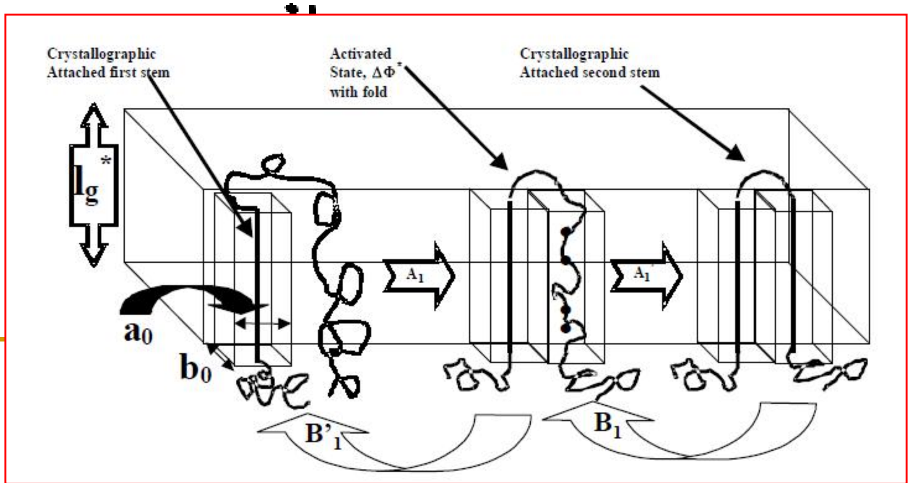
(3) Microscopic model - Lauritzen-Hoffman (LH) Theory

(1) Energy barrier for secondary nucleation

假定：
(1) 无序相是无规线团
(2) 链的扩散是蛇行的
(3) 解缠结比较快



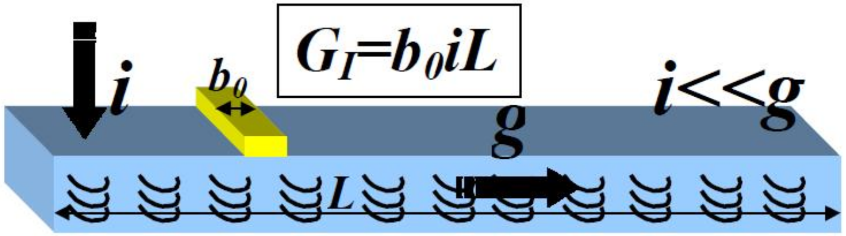


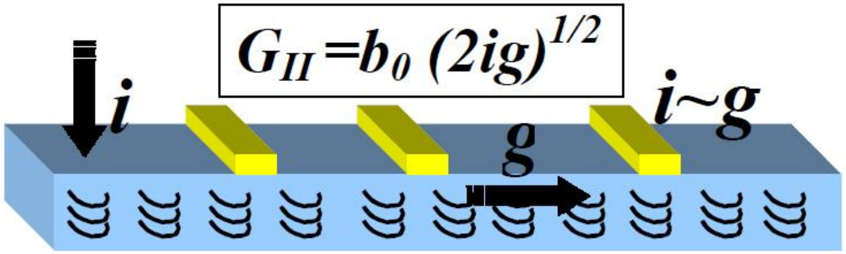


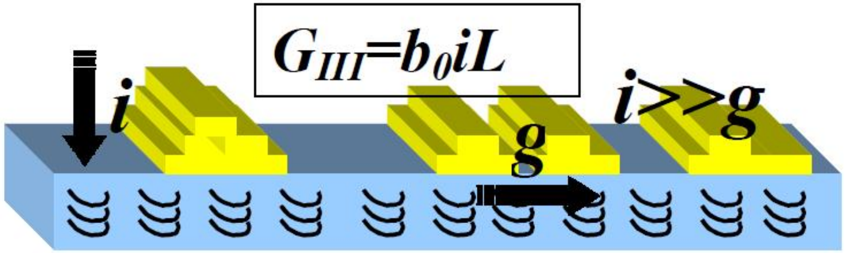
(3) Microscopic model - Lauritzen-Hoffman (LH) Theory

(2) Linear growth rate *G*

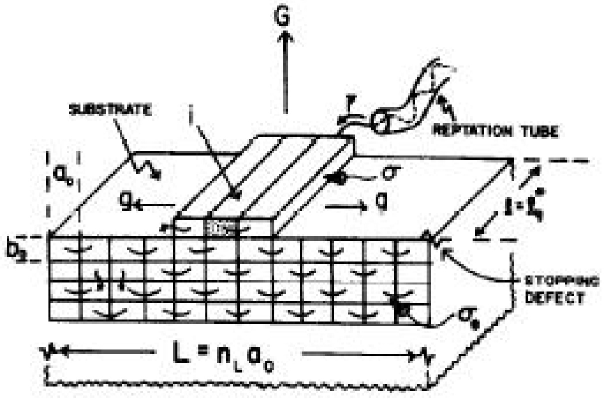
$$i = flux / L$$

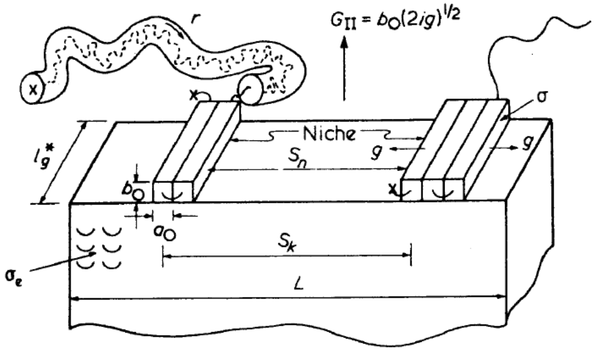






过冷度增加





Regime III: 真实加工过程的淬冷很短的侧向铺展，不超过几个链段，存在多种形式的链折叠

Hoffman, J. D., Polymer, 38(13), 3151(1997)

Experimental Evidence of regimes I, II, and III

$$i \propto \exp\left(-\frac{\Delta G^*}{k_B T}\right) \propto \exp\left(-\frac{1}{k_B T}\frac{4b\sigma\sigma_e T_m}{\Delta h_f \Delta T}\right)$$

$$G_\alpha = \left(\frac{C_\alpha}{n}\right)\exp\left(\frac{-Q_D^*}{k_B T}\right)\exp\left(-\frac{K_{g(\alpha)}}{k_B T \Delta T}\right)$$

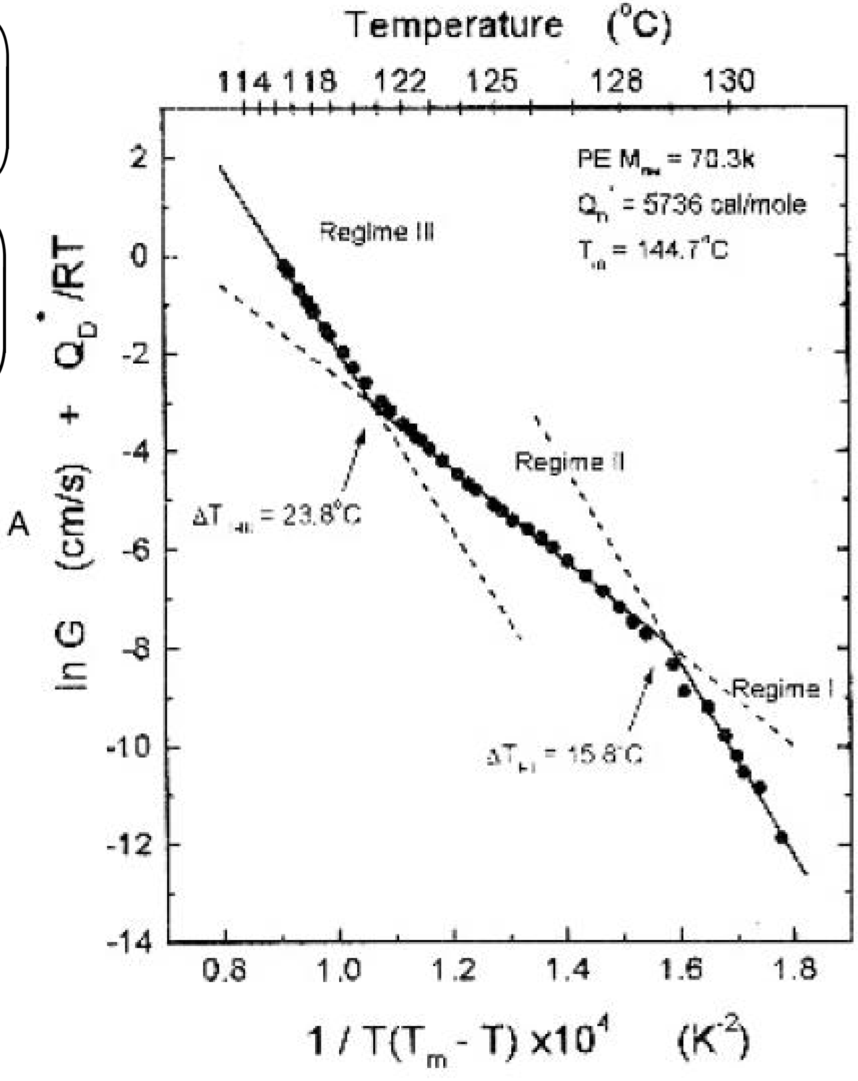
Q_D^* 蛇行活化能 $\alpha = I, II, III$

$K_{g(\alpha)}$ Regime α 的成核常数

$$K_{g(I)} = \frac{4b_0\sigma\sigma_e T_m}{\Delta h_f}$$ p.38

$$K_{g(II)} = \frac{2b_0\sigma\sigma_e T_m}{\Delta h_f}$$

$$K_{g(I)} = K_{g(III)} = 2K_{g(II)}$$



6.2.3.3 Overall Polymer Crystallization Rate

- **Definition of crystallinity (结晶度)**

  $w^c \equiv W_c/W_{total}$; $v^c \equiv V_c/V_{total}$

  w^c: weight fraction; v^c: volume fraction

  W: weights
  ρ: density (g/cm^3)
  v: specific volume (cm^3/g)＝1/ ρ

Total volume or density: $\frac{W}{\rho} = \frac{W_a}{\rho_a} + \frac{W_c}{\rho_c}$ or $\rho V = V_a\rho_a + V_c\rho_c$

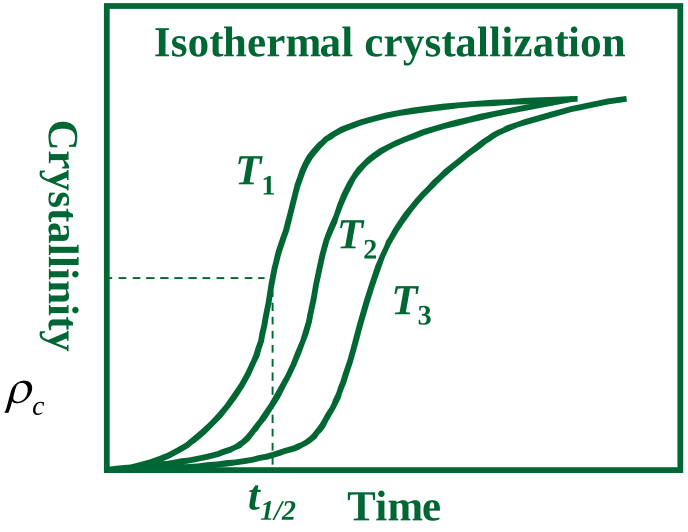
Crystallinity: $w^c = \frac{W_c}{W}$ or $v^c = \frac{V_c}{V}$

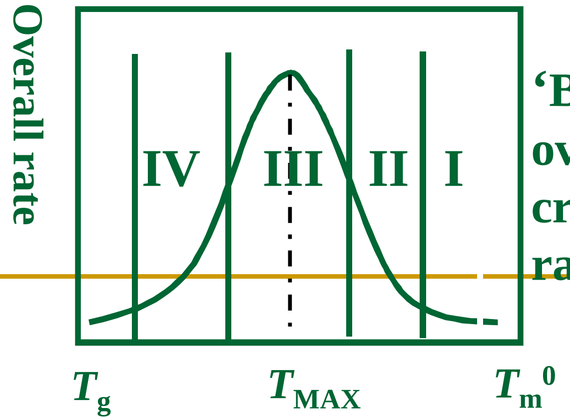
$$\frac{1}{\rho} = \frac{(1-w^c)}{\rho_a} + \frac{w^c}{\rho_c} \quad \text{or } \rho = \left(1-v^c\right)\rho_a + v^c\rho_c$$

$$w^c = \frac{\rho_c}{\rho}\,\frac{\rho-\rho_a}{\rho_c-\rho_a} = \frac{v_a - v}{v_a - v_c} \quad \text{or } v^c = \frac{\rho-\rho_a}{\rho_c-\rho_a}$$

usually $w^c = 0.7 \pm 0.2$

- **Overall crystallization rate (总结晶速度)**

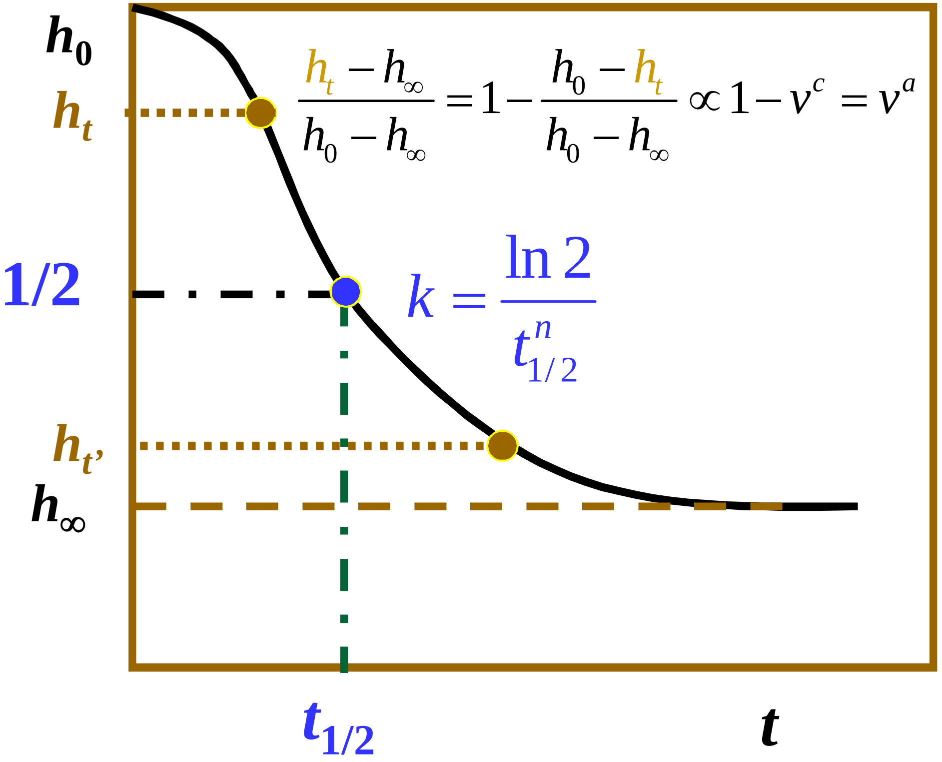




'Bell' curve of overall crystallization rate

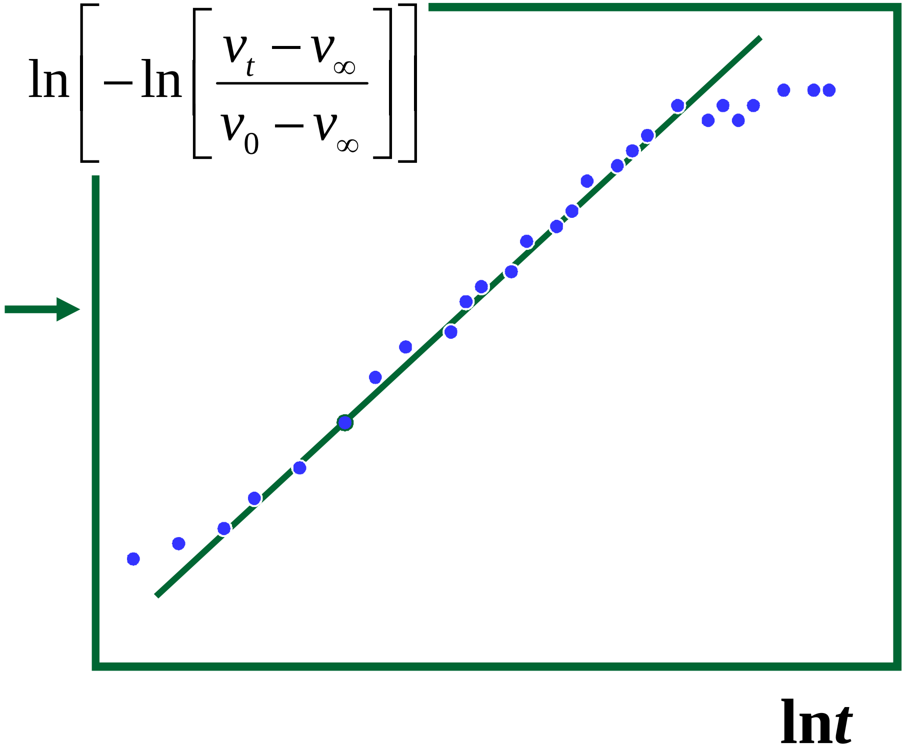
Overall Crystallization Kinetics

Dilatometric (膨胀计法) $v_t = 1/\rho_t \propto h_t$



$$\frac{h_t - h_\infty}{h_0 - h_\infty} = 1 - \frac{h_0 - h_t}{h_0 - h_\infty} \propto 1 - v^c = v^a$$

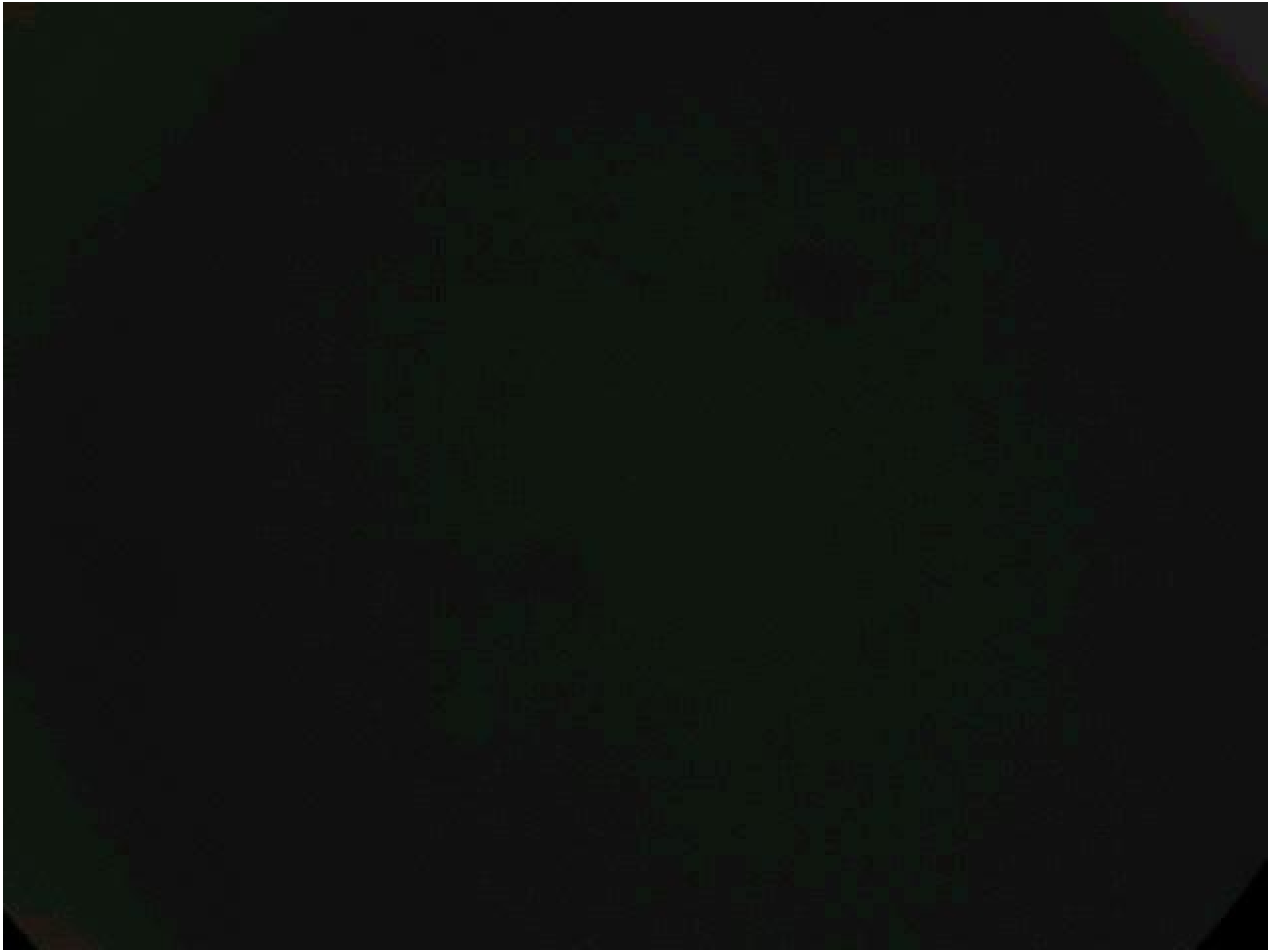
$$k = \frac{\ln 2}{t_{1/2}^n}$$



- **Avrami equation**

$$\frac{v_t - v_\infty}{v_0 - v_\infty} = e^{-kt^n} \quad \longrightarrow \quad \ln\left[-\ln\left[\frac{v_t - v_\infty}{v_0 - v_\infty}\right]\right] \sim \ln\left[-\ln\left(1 - v^c\right)\right]$$

$$= n \ln t + \ln k$$

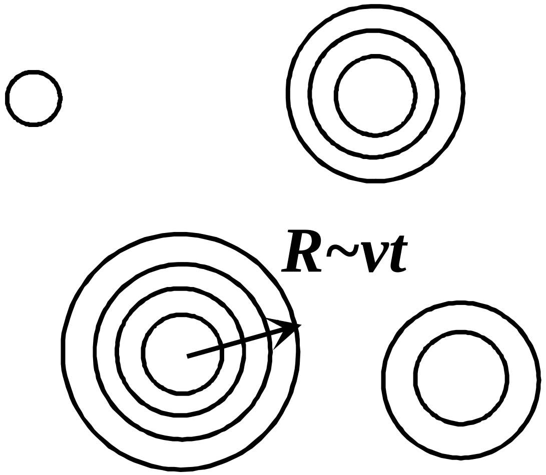


(1) Phenomenological models (唯象模型) of overall crystallization - based on classic nucleation theory

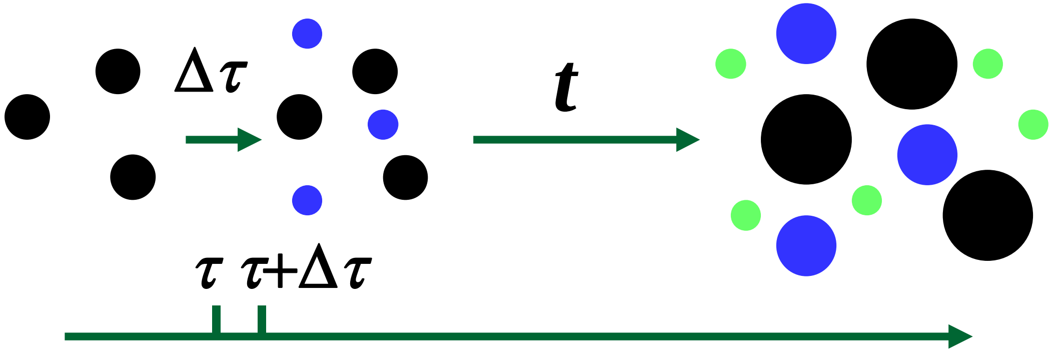
- (1) Free growth model

a. constant numbers of nucleus- heterogeneous

$$\boxed{v^c = \frac{V_{\text{crystal}}}{V_{\text{total}}} = \frac{\sum V_i}{V} = N\frac{4\pi}{3}(vt)^3}$$



b. new nucleus generated - homogeneous



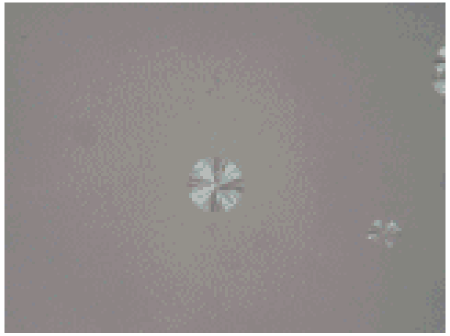
$\tau \to t$ $\quad I^*\Delta\tau\frac{4}{3}\pi\left[v(t-\tau)\right]^3$ **I* constant nucleation rate** $\quad I^*\Delta\tau$?

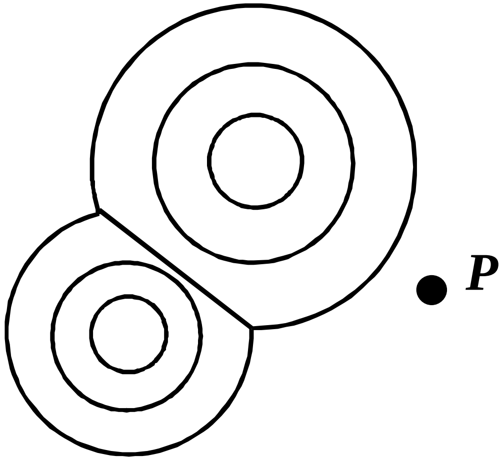
$0 \to t$ $\quad I^*\Delta\tau\frac{4}{3}\pi\left[v(t-0)\right]^3 + \cdots + I^*\Delta\tau\frac{4}{3}\pi\left[v(t-\tau)\right]^3 + \ldots + I^*\Delta\tau\frac{4}{3}\pi\left[v(t-\tau_i)\right]^3 \cdots$

$$\boxed{v^c = \sum_{\tau=0}^{t} I^*\frac{4}{3}\pi\left[v(t-\tau)\right]^3\Delta\tau} = \int_0^t I^*\frac{4}{3}\pi\left[v(t-\tau)\right]^3 \mathrm{d}\tau = I^*\pi v^3 t^4/3$$

(2) Phenomenological models of overall crystallization - based on classic nucleation theory –Avrami equation

- (2) Impingement model





Poisson’s (泊松) raindrop problem

If raindrops fall randomly on a pond creating expanding circular waves, what is the chance that the number of waves created by different raindrops which pass over a representative point *P* up to time *t* is exactly *n*?

solution : $P_n(t) = e^{-E}\left(E^n / n!\right)$ Poisson distribution

What is the chance that no wave reaches a given point *P* in space ? $\propto 1 - v^c$

$$P_0 = e^{-E} = 1 - v^c$$

E*(*t*): wave spreading area during *t $E(t) = \frac{\sum V_i(t)}{V}$

$$\left.\begin{array}{ll} \text{heterogeneous} & 1 - v^c = e^{-N 4\pi (vt)^3/3} \\ \text{homogeneous} & 1 - v^c = e^{-I^* \pi v^3 t^4/3} \end{array}\right\}$$

The Avrami equation for 3D

While *t* or *v* is very small $e^{-x} \approx 1 - x$

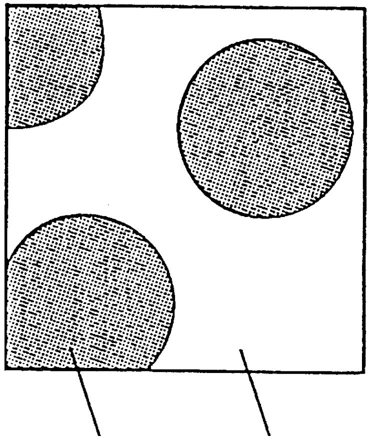
$$\boxed{v^c = E(t) =} \boxed{N \frac{4\pi}{3} (vt)^3} \text{ or } \boxed{I^* \pi v^3 t^4 / 3}$$

高分子结晶和高分子共混物分相的相似性

Phase Transition:

(1) Nucleation and Growth – **First-order phase transition**

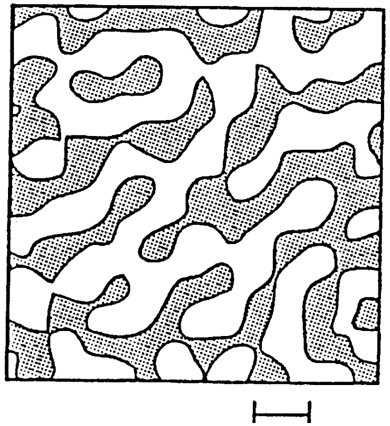
isotropic



anisotropic

(2) Spinodal Decomposition – **Second-order phase transition**

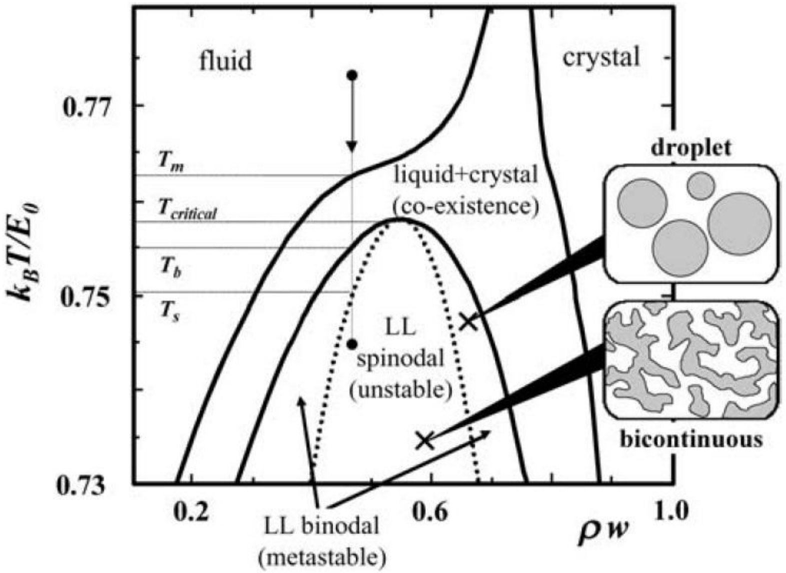
continuous phase transition



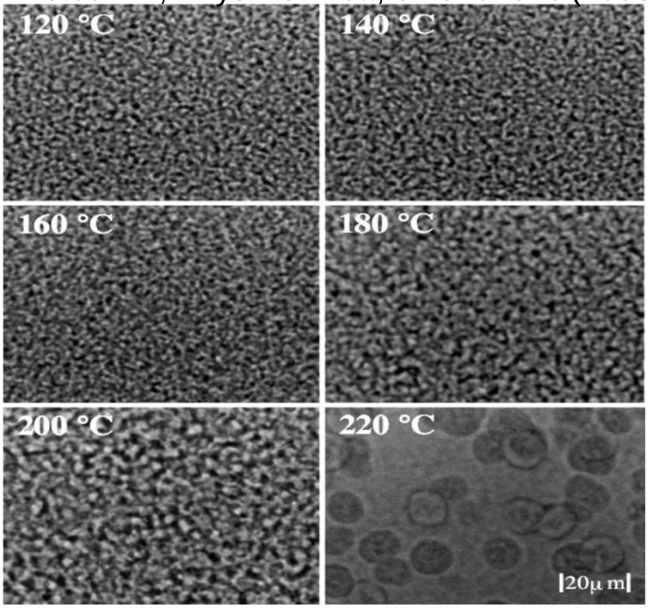
?

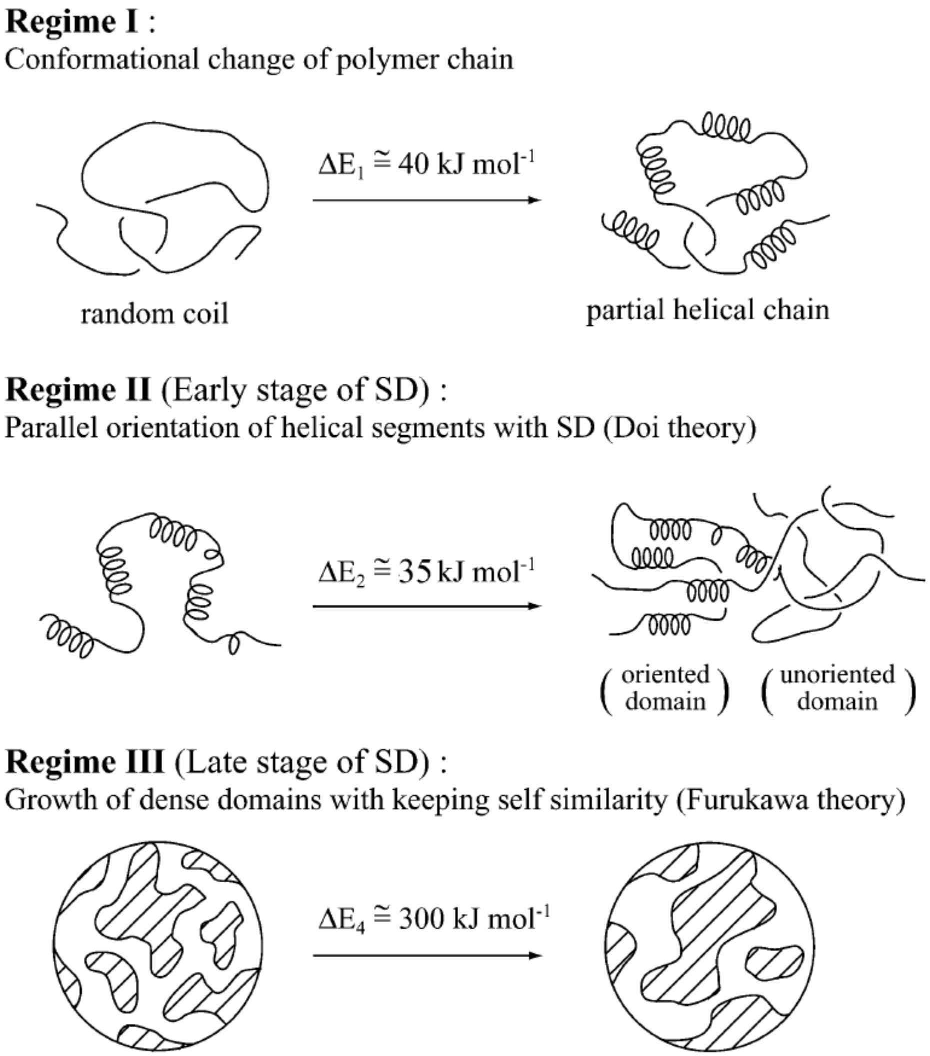
Two Phase Equilibrium

(3) Phenomenological models of overall crystallization - based on spinodal decomposition ?

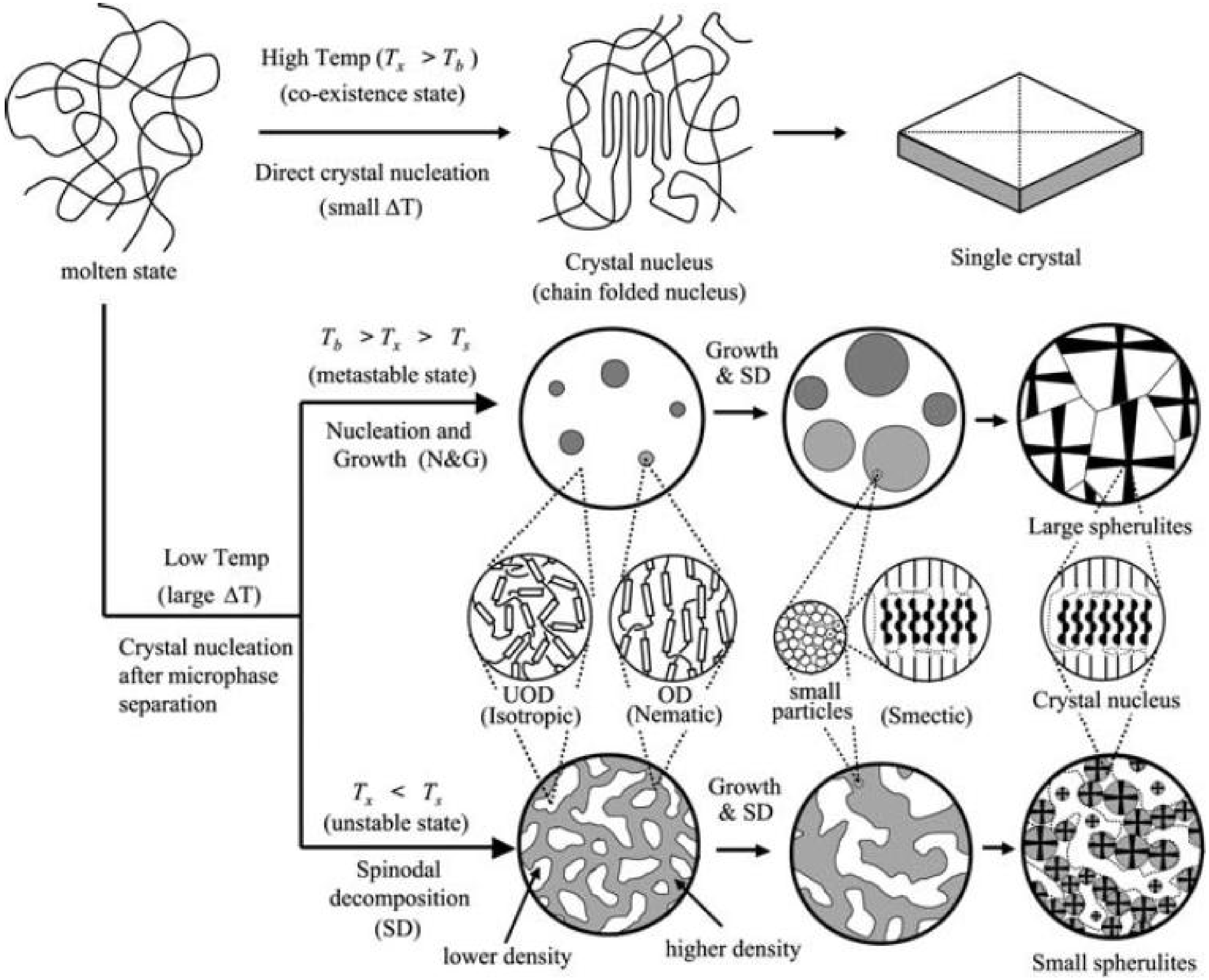


Olmsted PD, Phys Rev Lett, 81:373–376 (1998)

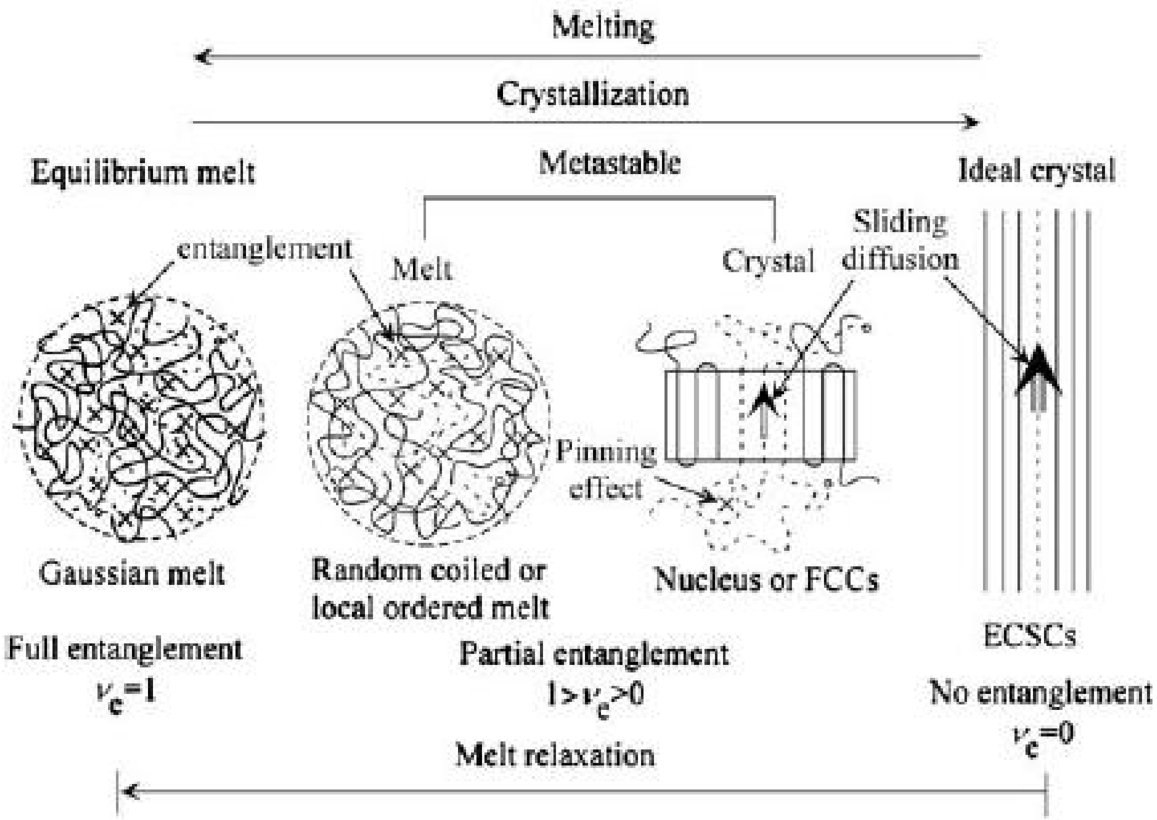


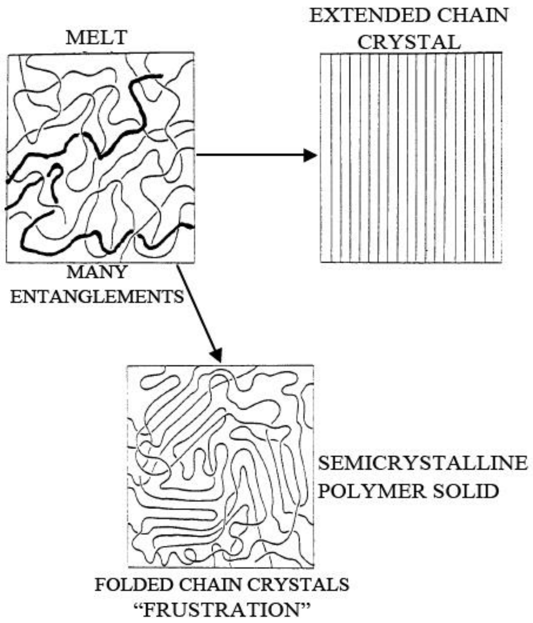


Kaji, K., Adv in Polym Sci, 191, 185 (2005)


molten state
High Temp ($T_x > T_b$)
(co-existence state)
Direct crystal nucleation
(small ΔT)
Crystal nucleus
(chain folded nucleus)
Single crystal
Low Temp
(large ΔT)
Crystal nucleation after microphase separation
$T_b > T_x > T_s$
(metastable state)
Nucleation and Growth (N&G)
Growth & SD
Large spherulites
UOD (Isotropic)
OD (Nematic)
small particles
(Smectic)
Crystal nucleus
$T_x < T_s$
(unstable state)
Spinodal decomposition (SD)
Growth & SD
lower density
higher density
Small spherulites

6.2.4 Thermodynamics of Crystallization:

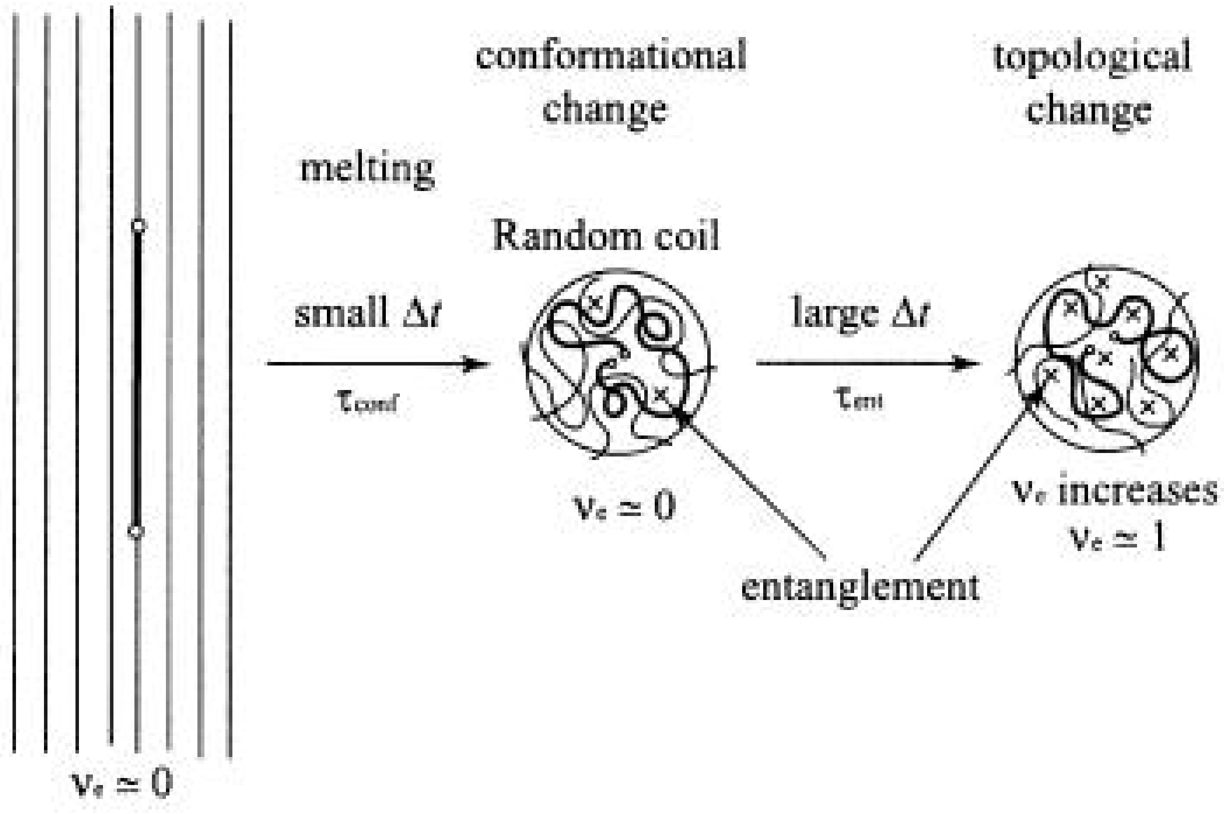


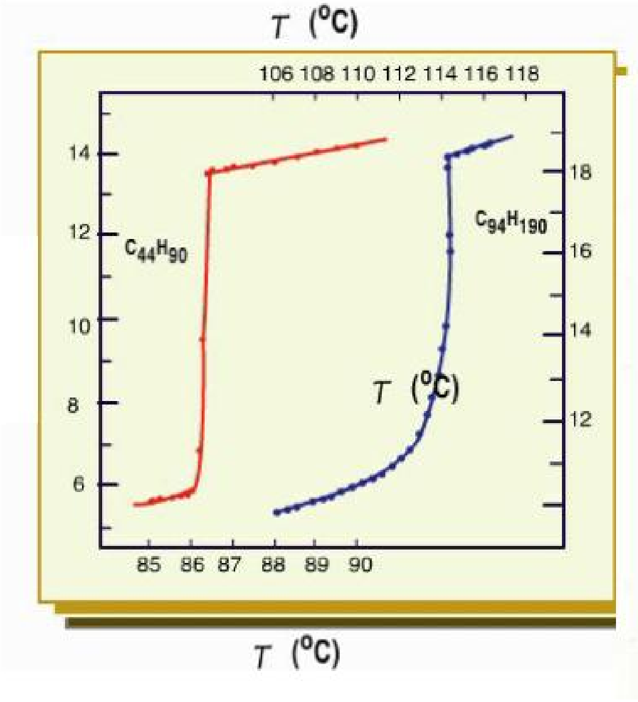


Equilibrium state

Actual state

1. Melting point of Lamellar Crystals



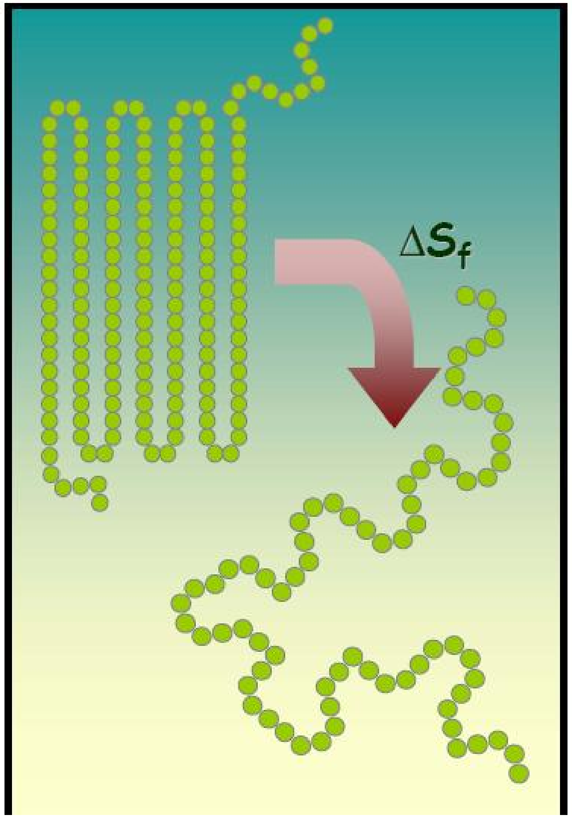


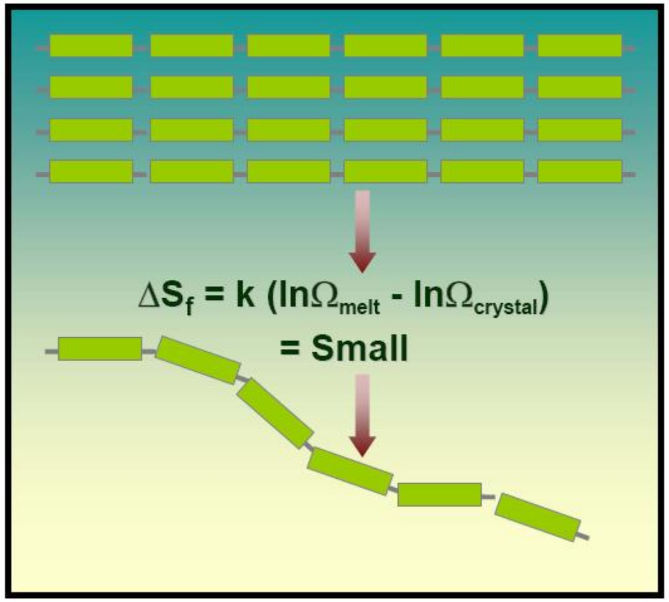
(1). Effects of Chain Structure on T_m

$$\Delta G_m = \Delta H_m - T_m \Delta S_m = 0 \Longrightarrow T_m = \left| \frac{\Delta H_m}{\Delta S_m} \right|$$

1) Symmetry and Asymmetry

2) Flexible and Rigid





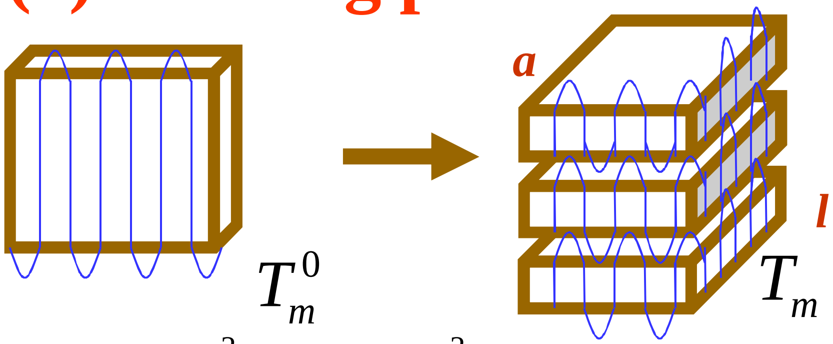
$$S = k \ln\Omega$$

$$\Delta S_f = k\,(\ln\Omega_{melt} - \ln\Omega_{crystal}) = Large$$

3) Molecular Interaction

Thermodynamics of Crystallization:

(2). Melting point of Lamellar Crystals



$$\Delta G = -a^2 l \Delta g_f + 2a^2\sigma_e + 4al\sigma$$

$$\Delta g_f\left(T_m^0\right) = \Delta h_f - T_m^0 \Delta s_f = 0 \rightarrow \boxed{\Delta s_f = \frac{\Delta h_f}{T_m^0}}$$

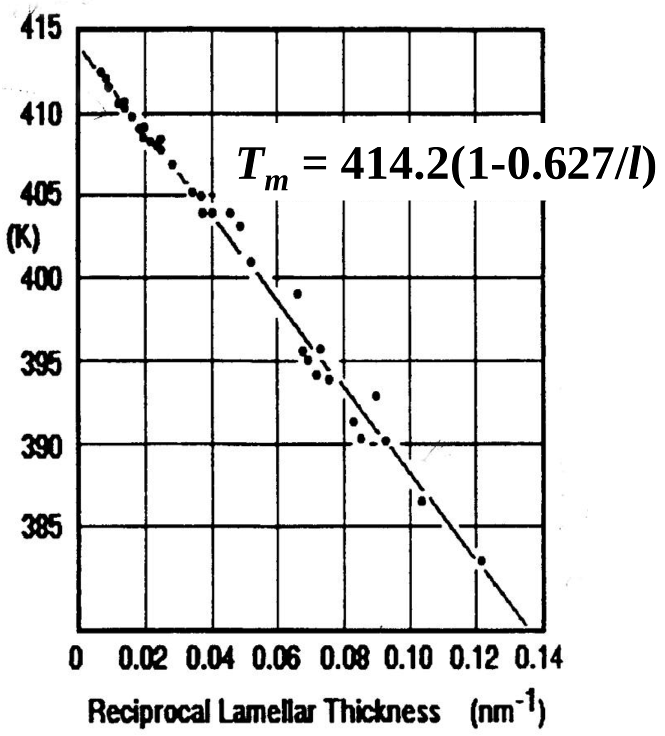
$$\Delta g_f\left(T_m\right) = \Delta h_f - T_m \Delta s_f = \Delta h_f \frac{T_m^0 - T_m}{T_m^0}$$

$\Delta G = 0 \qquad 4al\sigma \approx 0$ ⇨ **Lauritzen-Hoffman equation**

$$l = \frac{2\sigma_e T_m^0}{\Delta h\left(T_m^0 - T_m\right)} \qquad T_m = T_m^0\left(1 - \frac{2\sigma_e}{l\Delta h}\right)$$

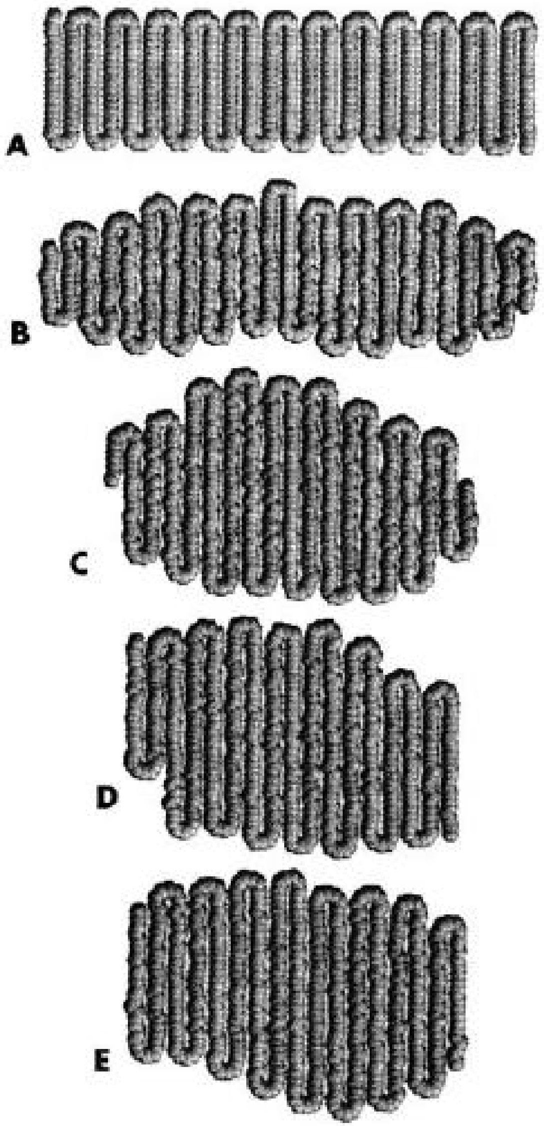
Similar to critical nucleus size

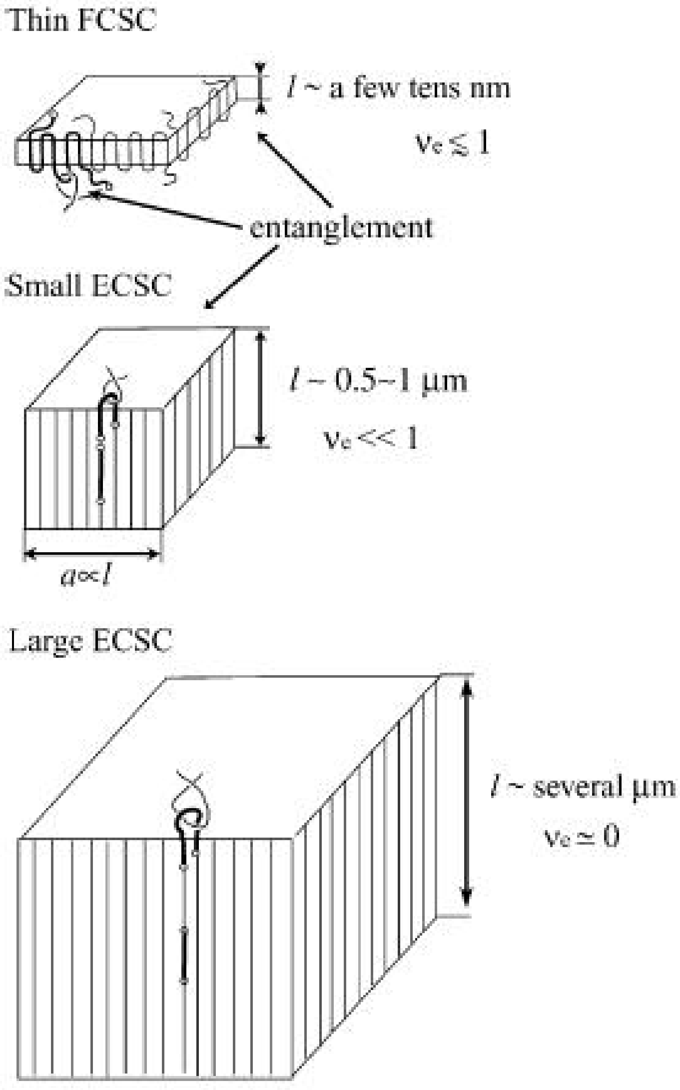
- **Gibbs-Thomson extrapolation**



Melting data for lamellar polyethylene grown from the melt and from solution

Typical molecular process of thickening in the thin lamella

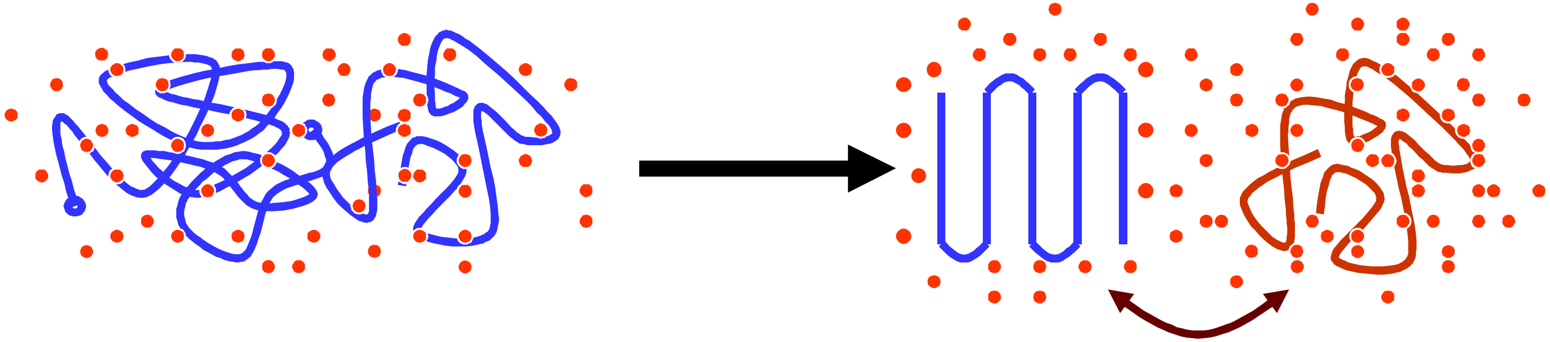




Thermodynamics of Crystallization:
(3). Melting point of Polymer mixture

Consider a system of Polymer/Impurity mixture:

Polymer is compatible with impurity but can’t co-crystallize with impurity



$$\mu_u^C - \mu_u^0 = \mu_u^I - \mu_u^0$$

Chemical Potential of crystallizable polymer in amorphous phase

$$\mu_2 - \mu_2^0 = RT\left[\ln\phi_2 - (x-1)\phi_1 + \chi x(1-\phi_2)^2\right]$$

Chemical Potential of one monomer unit of polymer in amorphous phase

$$\mu_u - \mu_u^0 = RT\left[\frac{\ln\phi_2}{x} - \left(1-\frac{1}{x}\right)\phi_1 + \chi(1-\phi_2)^2\right]$$

Effects of “Impurities” on T_m

Condition of Phase Equilibrium

$$\mu_u^I - \mu_u^0 = \mu_u^C - \mu_u^0$$

Superscript of *I*: Amorphous Phase ⟷ **Superscript of *C*: Crystalline Phase**

$$\begin{aligned}\mu_u^I - \mu_u^0 \\ = RT\left[\frac{\ln\phi_2}{x} - \left(1-\frac{1}{x}\right)\phi_1 + \chi\left(1-\phi_2\right)^2\right]\end{aligned}$$

⟷

$$T_m^0 = \frac{\Delta H_m}{\Delta S_m}$$

$$\Delta S_u = \frac{\Delta H_u}{T_m^0}$$

$$\begin{aligned}\mu_u^C - \mu_u^0 &= -\Delta G_u \\ &= -\left(\Delta H_u - T_m \Delta S_u\right) \\ &= -\Delta H_u\left(1-\frac{T_m}{T_m^0}\right)\end{aligned}$$

$$-\Delta H_u\left(1-\frac{T_m}{T_m^0}\right) = RT\left[\frac{\ln\phi_2}{x} - \left(1-\frac{1}{x}\right)\phi_1 + \chi\left(1-\phi_2\right)^2\right]$$

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u}\left[\frac{\ln\phi_2}{x} - \left(1-\frac{1}{x}\right)\phi_1 + \chi\left(1-\phi_2\right)^2\right]$$

Effects of "Impurities" on T_m

polymer/small molecule

$$\frac{1}{T_m}-\frac{1}{T_m^0}=-\frac{R}{\Delta H_u}\left[\frac{\ln\phi_2}{x}-\left(1-\frac{1}{x}\right)\phi_1+\chi\left(1-\phi_2\right)^2\right]$$

polymer/polymer

$$\frac{1}{T_m}-\frac{1}{T_m^0}=-\frac{R}{\Delta H_u}\left[\frac{\ln\phi_2}{x_2}-\left(\frac{1}{x_1}-\frac{1}{x_2}\right)\phi_1+\chi\left(1-\phi_2\right)^2\right]$$

For $x_2\to\infty$, $x_1=1$

Note: $-\phi_1-\frac{1}{2}\phi_1^2\approx\ln\left(1-\phi_1\right)=\ln\phi_2$

$$\frac{1}{T_m}-\frac{1}{T_m^0}=-\frac{R}{\Delta H_u}\left[-\phi_1+\chi\phi_1^2\right]=-\frac{R}{\Delta H_u}\left[-\phi_1-\frac{1}{2}\phi_1^2+\frac{1}{2}\phi_1^2+\chi\phi_1^2\right]\approx-\frac{R}{\Delta H_u}\ln\phi_2$$

For end-group effects: $\phi_1=2/N$, $\chi=0$

$$\frac{1}{T_m}-\frac{1}{T_m^0}=\frac{R}{\Delta H_u}\frac{2}{\overline{N}}$$

For polymer blends

$$\chi = \frac{A}{T} + B \qquad \frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R\chi}{\Delta H_u}\left(1-\phi_2\right)^2$$

Phase Diagram of Crystal / Amorphous Polymer Mixture

Liquid + Solid Phase Equilibrium

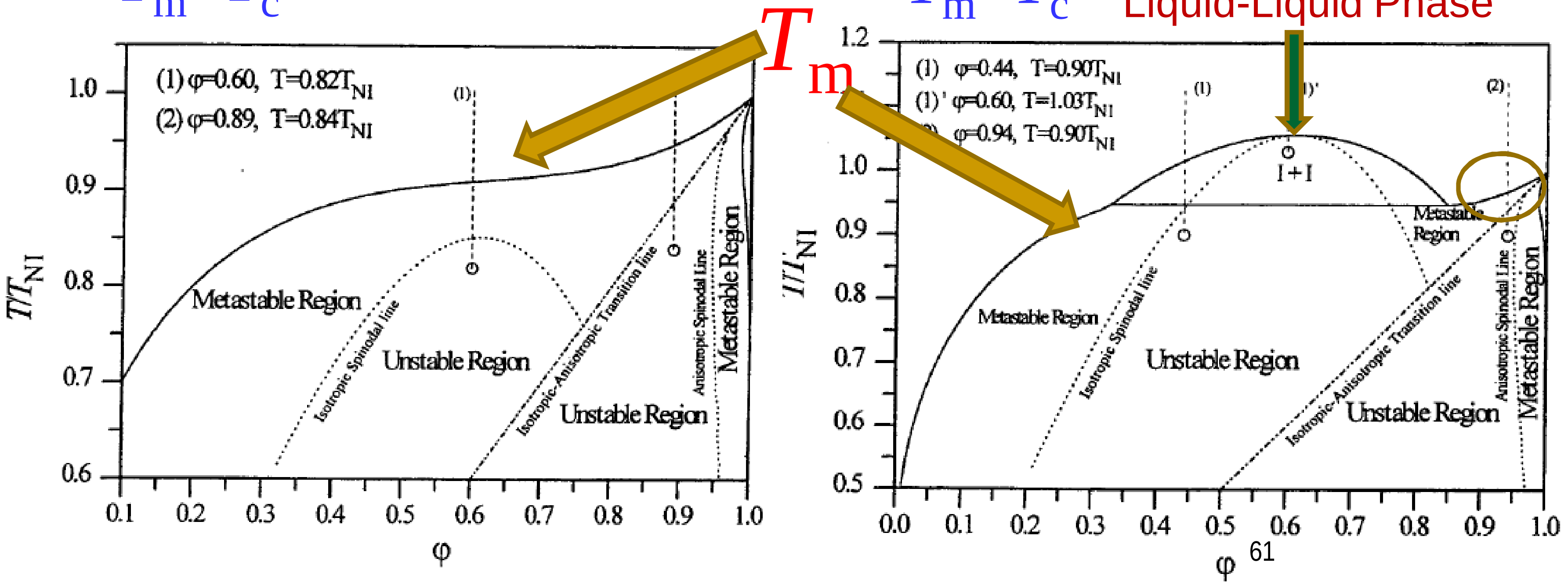
Crystallization *vs* Phase Separation ?

$$\chi_c = \frac{1}{2}\left(\frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}}\right)^2 \qquad \chi_c = \frac{A}{T_c} + B$$

$T_m > T_c$

$T_m < T_c$

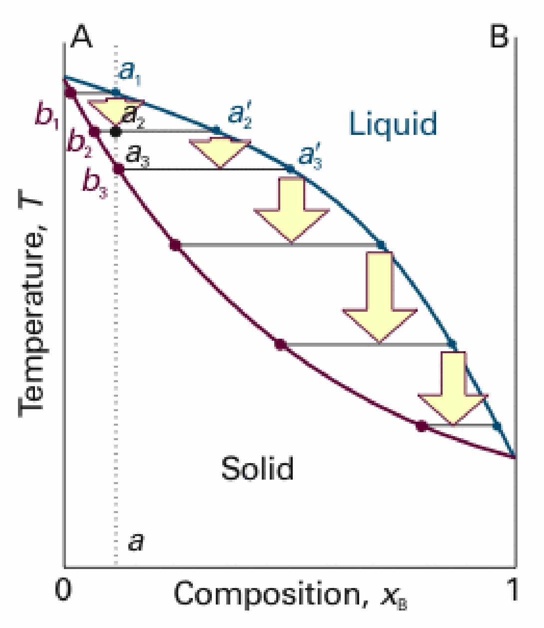
Phase Boundary of Liquid-Liquid Phase

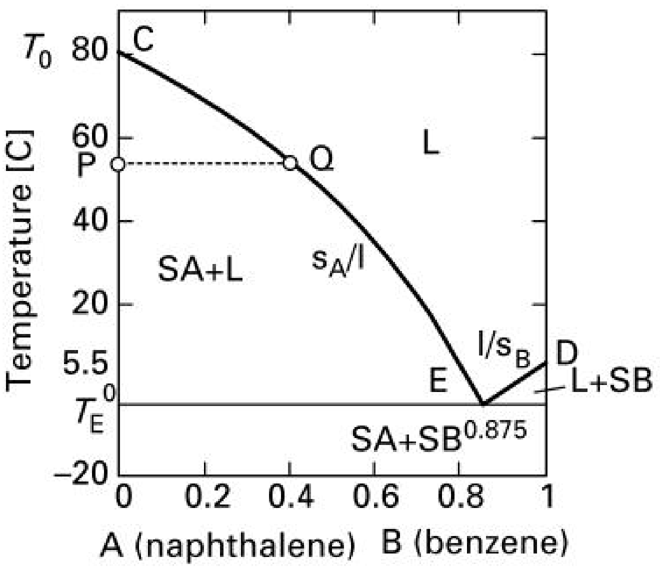


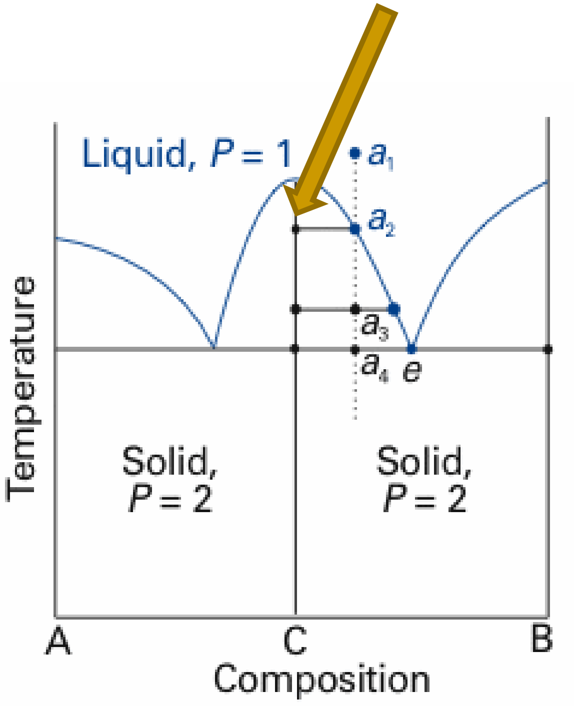
T_m

Typical Phase Diagram of Mixture III: Liquid-Solid & Solid-Solid

& Liquid-Liquid







There may exit Solid Phase in Polymer System

For copolymer

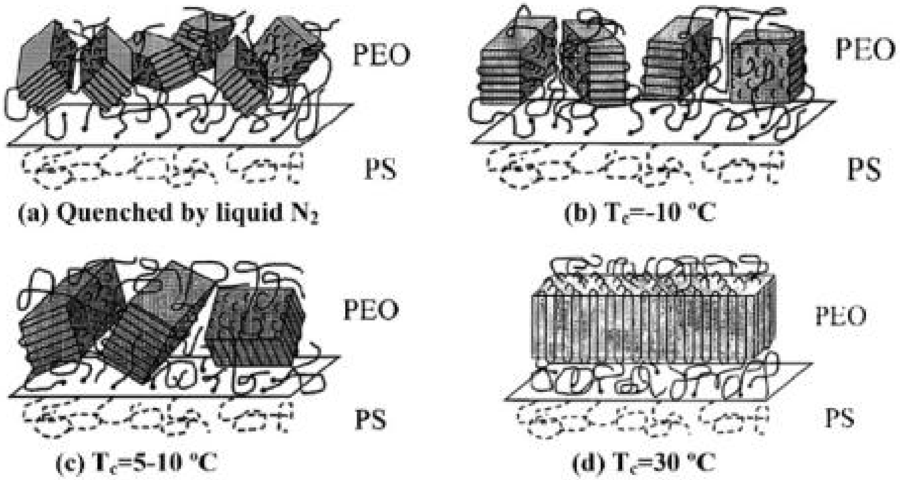
$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln P$$

***P*: Probability of crystalline unit with sequential connection**

alternating copolymer: $P << X_A$

Random copolmer: $P = X_A$

Block Copolymer: $P >> X_A \approx 1$



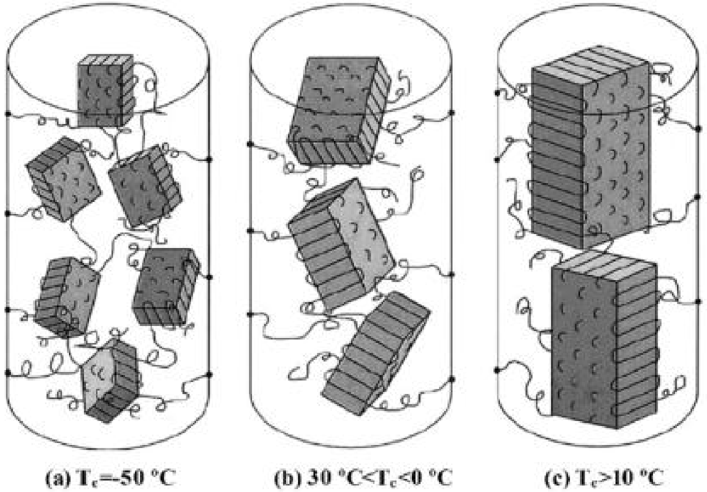
(a) Quenched by liquid N₂

(b) T_c=-10 °C

(c) T_c=5-10 °C

(d) T_c=30 °C

Crystallization of PEO-*b*-PS in Lamellae



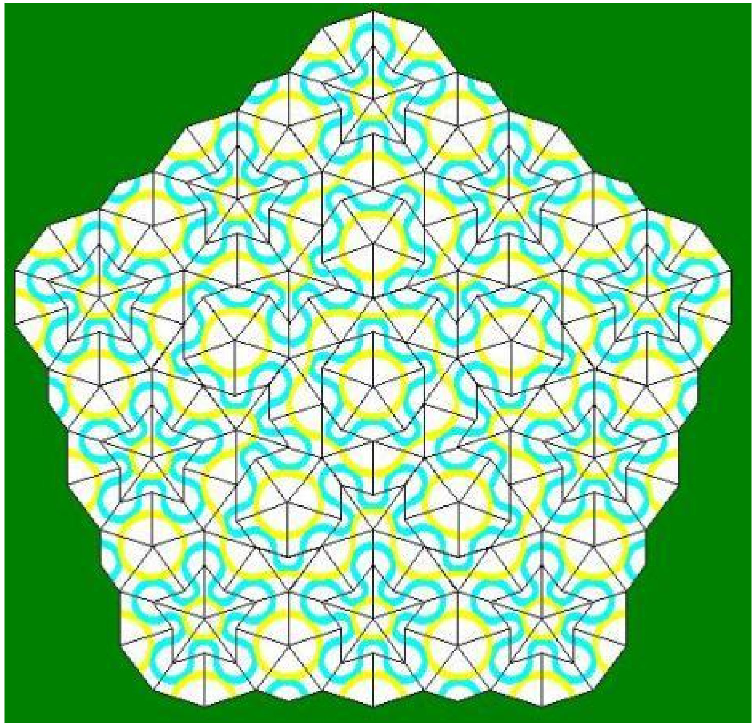
(a) T_c=-50 °C

(b) 30 °C<T_c<0 °C

(c) T_c>10 °C

Crystallization of PEO-*b*-PS in Columnar

Quasicrystal?

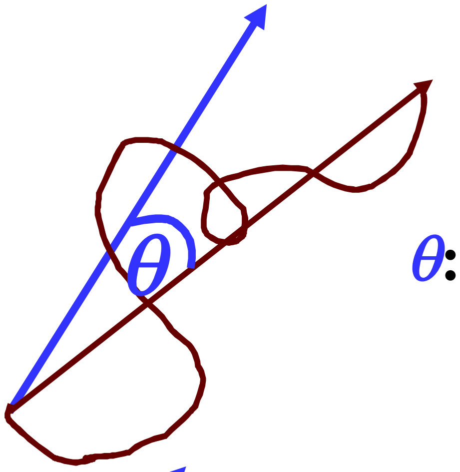


D. Shechtman, Nobel Prize 2011

Roge Penrose

6.3 Oriented States of Polymers

- Definition



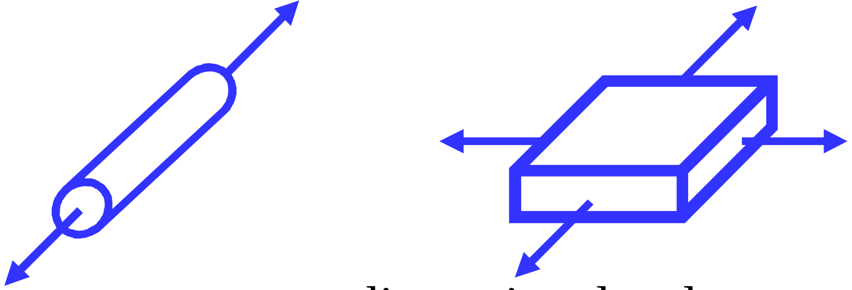
θ: 0~180 °

Applications

Fiber, BOPP, BOPET, BOPE, …

Orientation function

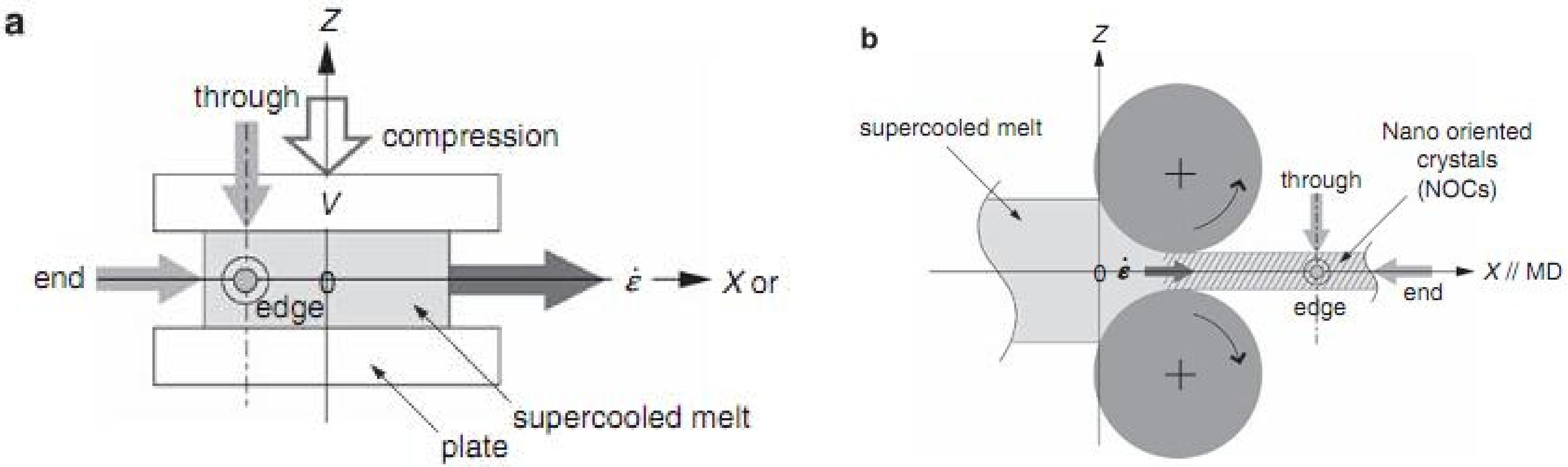
$$F = \frac{1}{2}\left(3\left\langle \cos^2\theta \right\rangle - 1\right)$$

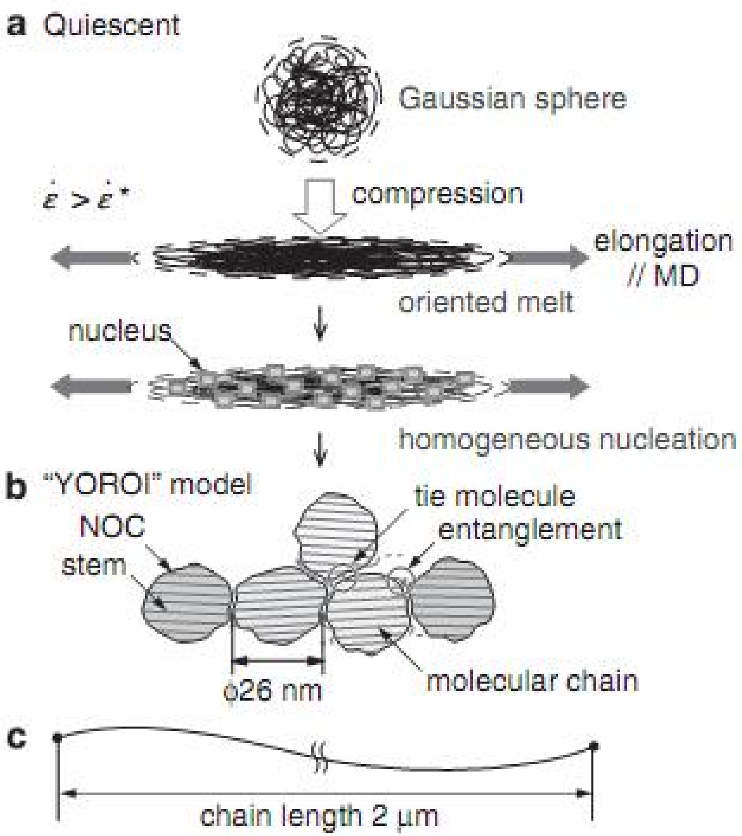


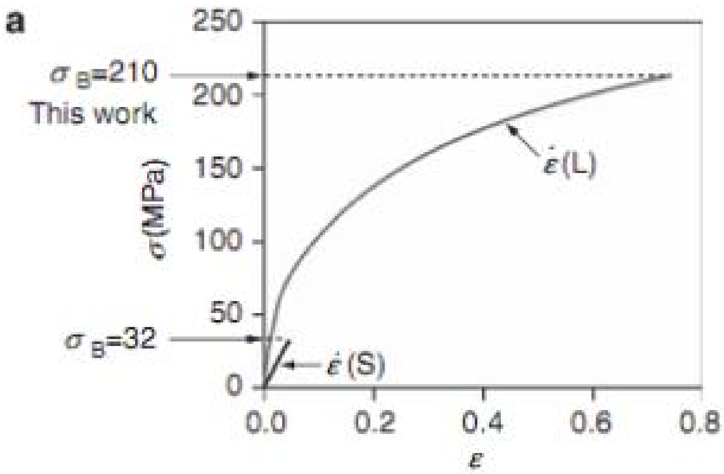
one or two dimensional order

	<cosθ>	<cos$^2\theta$>	*F*
fully oriented	**1**	**1**	**1**
fully disorder	**0**	**1/3**	**0**
perpendicular	**0**	**0**	**-1/2**

*i*PP 的固相加工技术


a
Z
through
compression
V
end
edge
0
ε̇
X or
supercooled melt
plate
b
Z
supercooled melt
Nano oriented
crystals
(NOCs)
through
0
ε̇
X // MD
end
edge



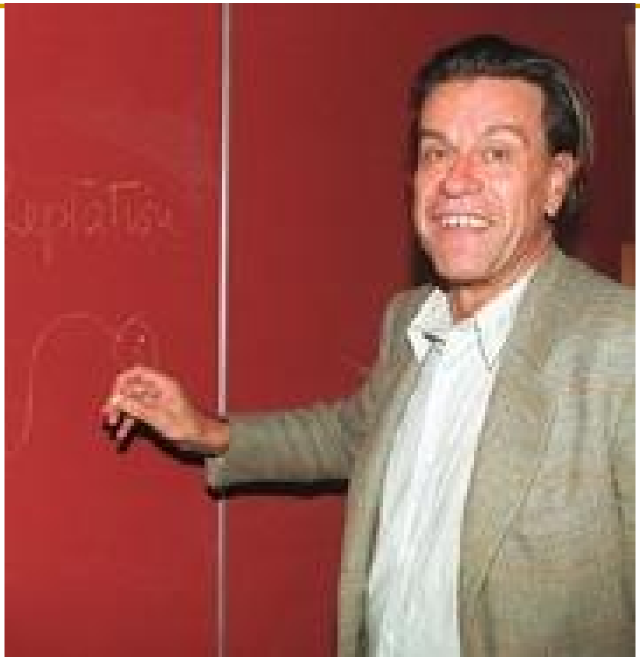


材料	断裂强度 (MPa)	密度 (g/cm^3)	比强度 (Mpa)	杨氏模量 (GPa)	透明性 (雾度)
固相加工iPP	230	0.94	244	4.1	0.9%
传统iPP	30-40	0.94	32-42	1.5-2	>50%
钢材	400-800	7.8	51-102	~200	~100%

6.4 Liquid Crystalline Polymers

- **States of matter:**
  - **Solids, liquids, and gases**
  - **“Liquid crystals” (LCs) represent a number of different states of matter in which the degree of molecular order lies intermediate between the perfect long-range positional and orientational order found in crystalline solid and the statistical long-range disorder found in an isotropic liquid. Phenomenologically, LCs exhibit both solid-like anisotropic features and liquid-like fluidity. On the basis of these characteristics, the term “mesomorphic phases” or “mesophases”, may be a more appropriate name than liquid crystals.**
- **“Liquid crystals stand between the isotropic liquid phase and the strongly organized solid state. Life stands between complete disorder, which is death, and complete rigidity, which is death again.”**

Dervichian D. G. *Mol. Cryst. Liq. Cryst.* **1977**, *40*, 19.



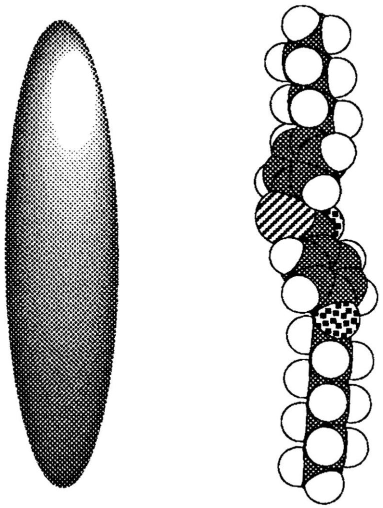
Pierre Gilles de Gennes (1932-2007.5.20)

- 法国科学院院士，早年从事中子散射和磁学研究，1961年始从事超导研究，1968年始研究液晶, 1971年任法国大学教授, 从事高分子物理研究，1980年从事界面研究，主要为润湿动力学，近年从事粘附物理化学（细胞粘附）和脑功能研究。Pierre-Gilles De Gennes教授首次阐明了从向列型液晶散射出的异常光现象，成功地将研究简单体系中有序现象的方法推广到高分子、液晶等复杂体系。他编撰的“液晶物理”，“高分子物理的标度定则”、“高分子动力学导论”、“软物质界面”是相关领域的权威著作。由于Pierre-Gilles De Gennes教授在多方面研究的重要建树，被誉为"当代牛顿"，他特别为液晶和聚合物这类物质的研究发展奠定了坚实的基础。1991年获诺贝尔物理奖。

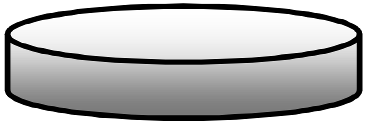
What are Liquid Crystals

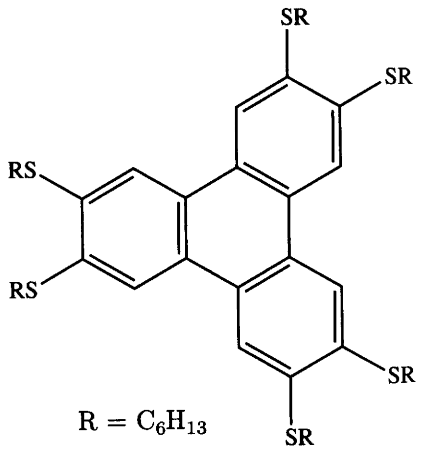
- **Anisotropic molecular shape of liquid crystals**

  - **Rod-like or ellipsoid-like**
  - **Plate-like or disk-like**



Space filling model of molecule 7S5





$R = C_6H_{13}$

- **Thermotropic liquid crystals (热致型液晶):**

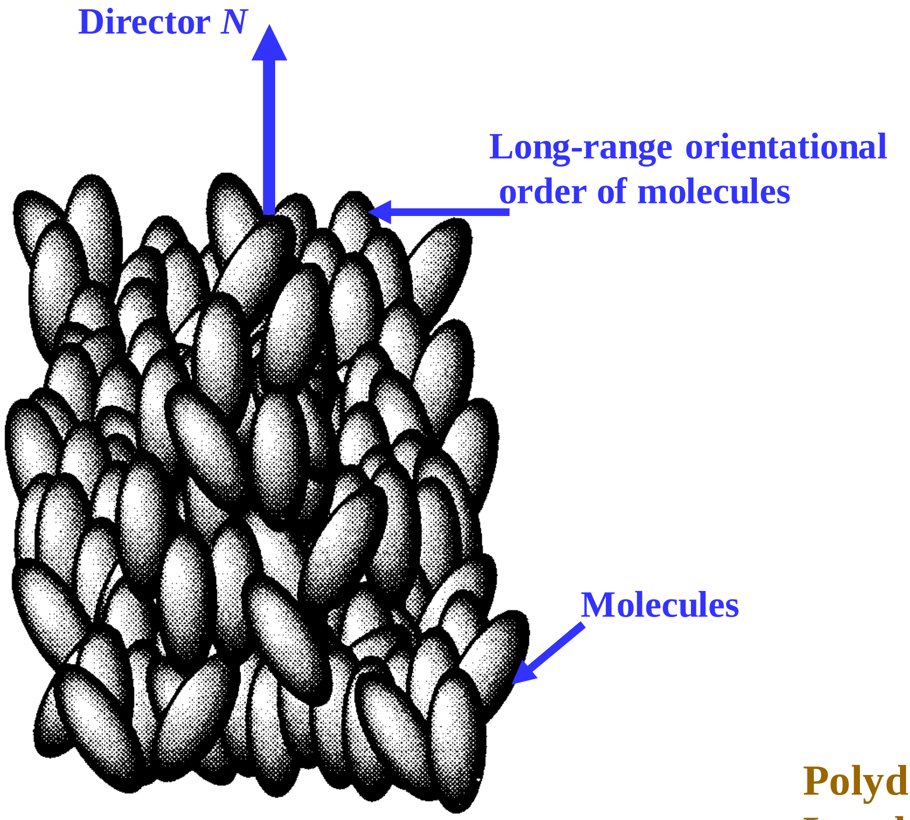
  The liquid crystal phases of pure substance are caused by temperature change.

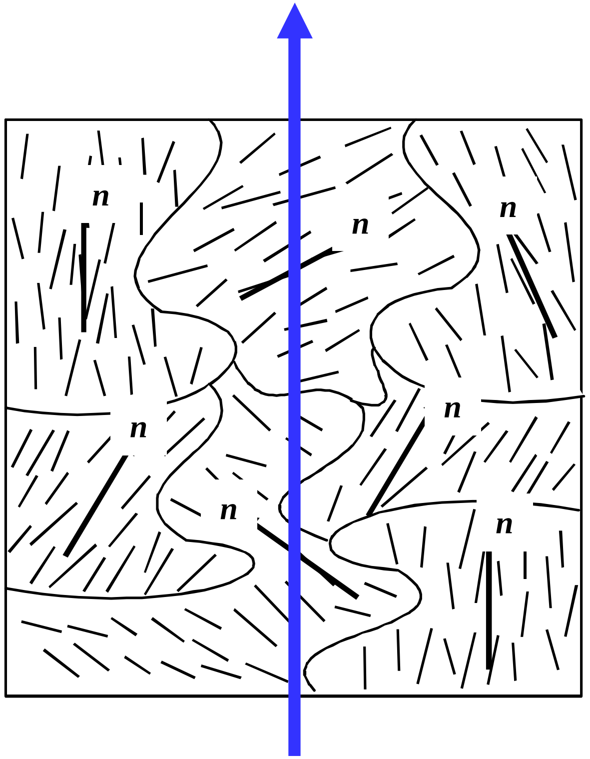
- **Lyotropic liquid crystals (溶致型液晶):**

  The liquid crystal phase is dependent on the concentration of one component in another.

Nematic Phase (向列相)

- **Molecular arrangement in a nematic phase**

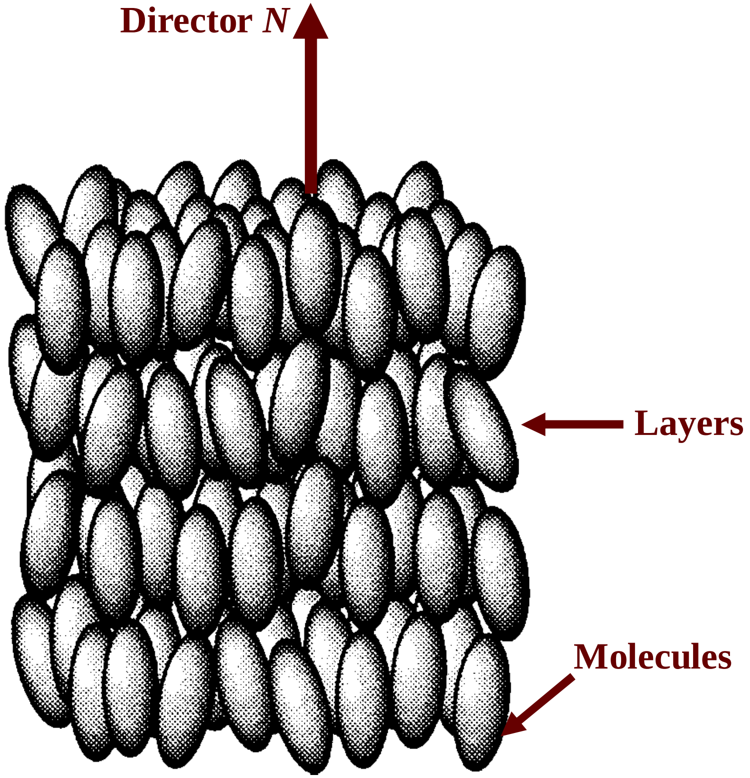




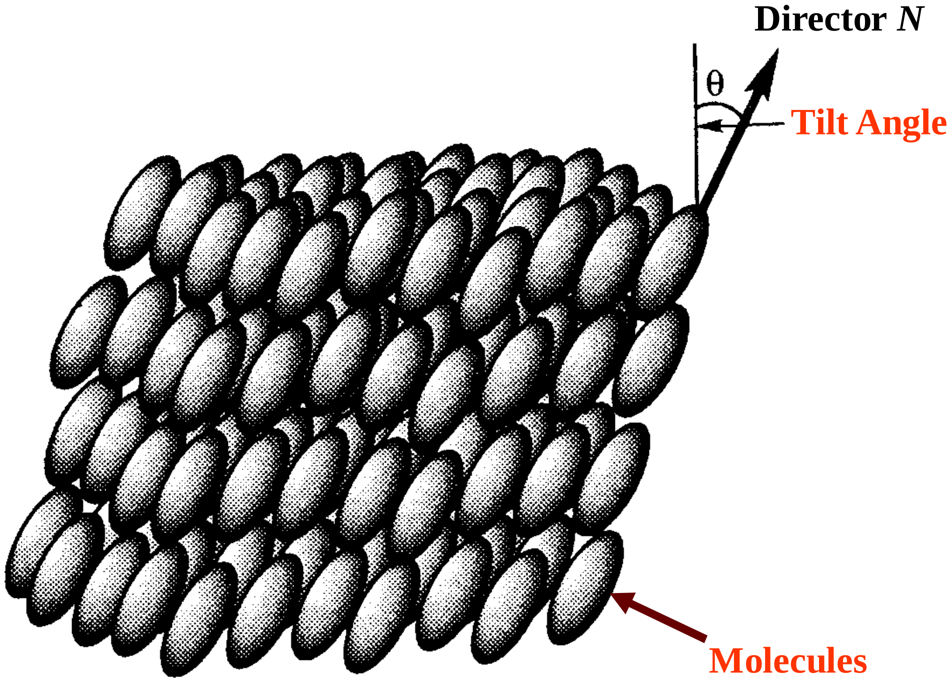
Polydomain structure in a nematic phase. Local directors are represented by *n*, and the global director is represented by *N*.

Smectic Phases (近晶相)

- **Layer structure in smectic phases**



Smectic A

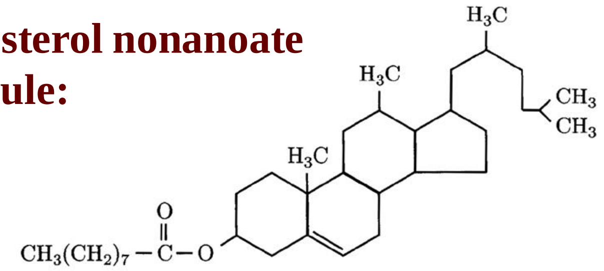


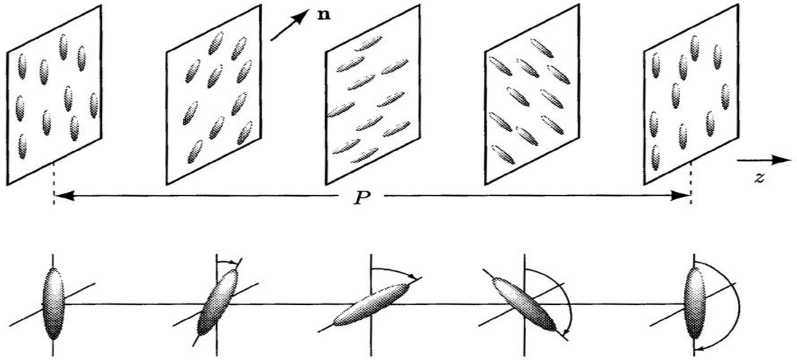
Smectic C

Liquid Crystal Phase of Chiral Molecules

- **Cholesteric phase (胆甾相) (chiral (手性) nematic phase)**

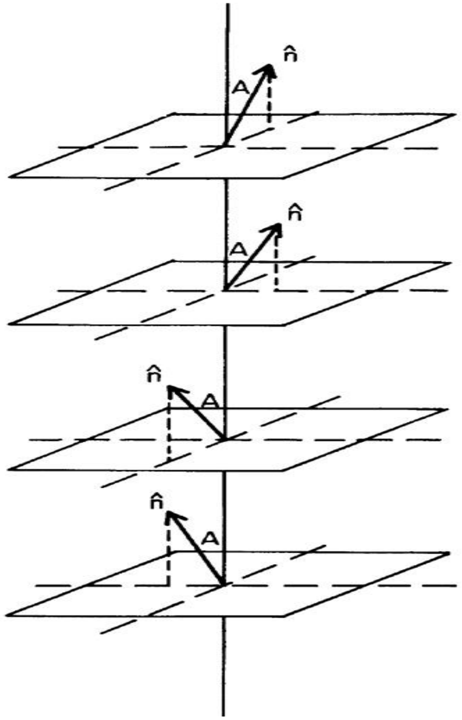
Cholesterol nonanoate molecule:





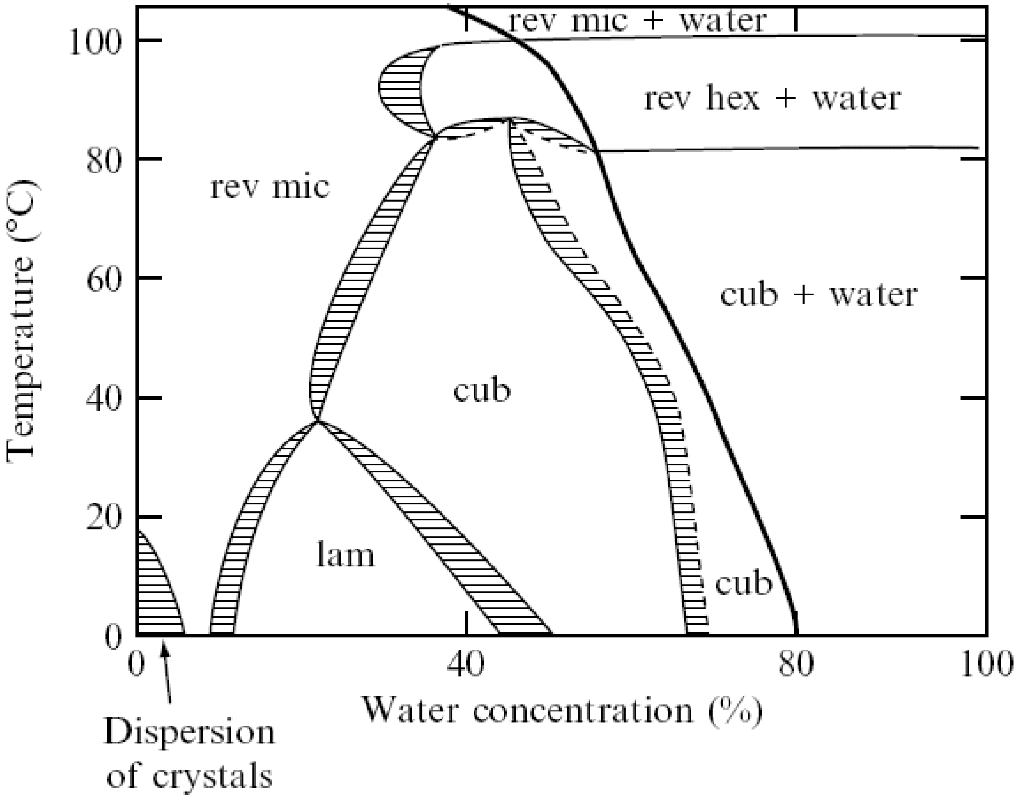
Molecules in the cholesteric phase. The director *n* rotates in a helical fashion. Because no physical quantities depend on the sign of *n*, the physical pitch of the cholesteric phase is *P* = π/k_0 rather than $2\pi/k_0$.

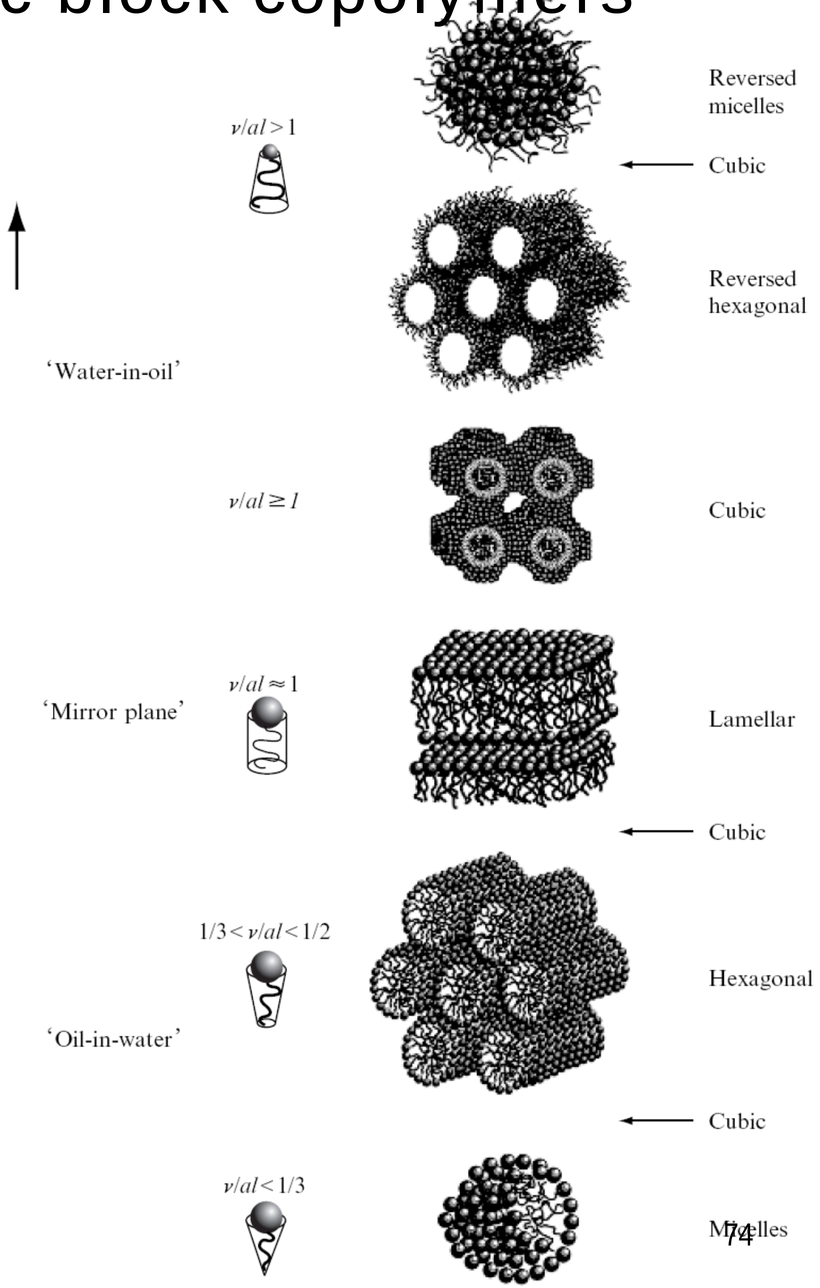
- **Chiral smectic phase**



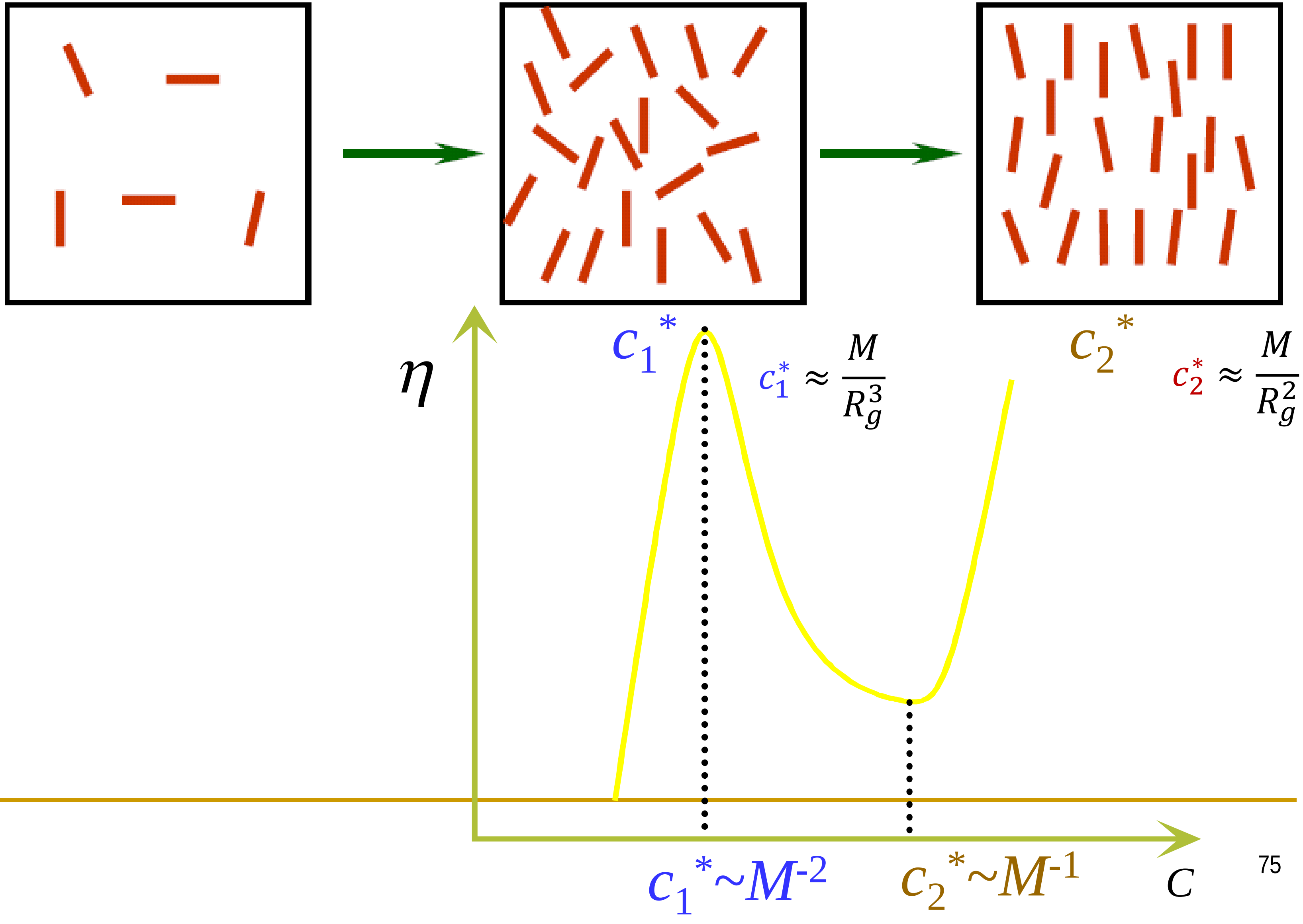
Structure of chiral smectic or smectic C* phase. The planes represent the smectic layers. The director always makes the same angle with the smectic planes, but the orientation of the director rotates about the line perpendicular to the planes in going from one layer to the next.

Lyotropic liquid crystals:
1) surfactants or amphiphilic block copolymers



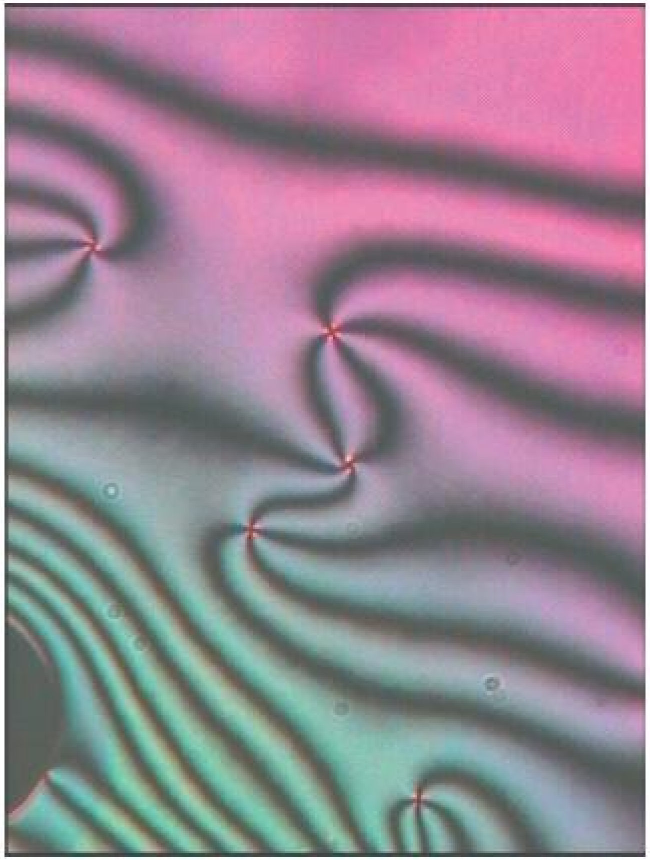


Lyotropic liquid crystals:
2) rigid-rod polymers

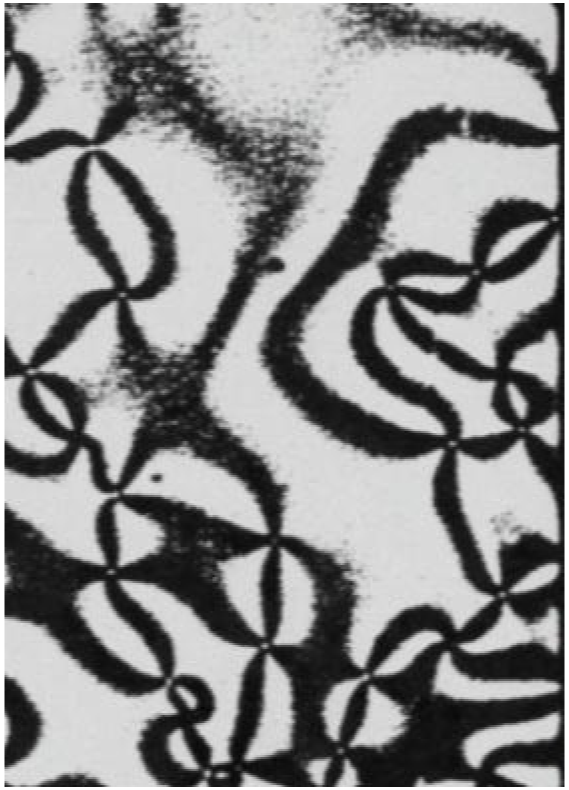


POM Used in the Study of LC Phases

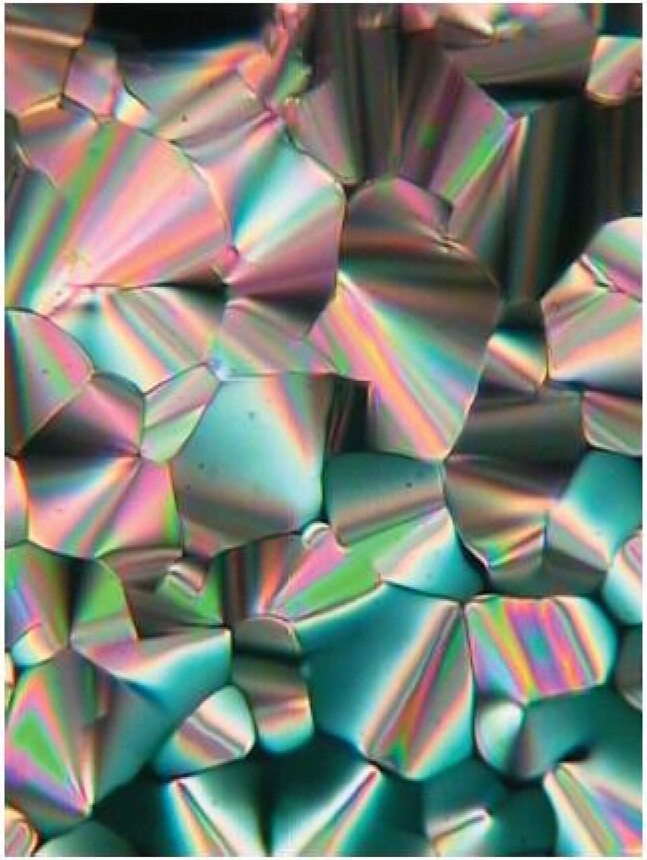
- **For different LC phases, the textures (织构) under POM are different**



Nematic: *schlieren* (纹影) texture

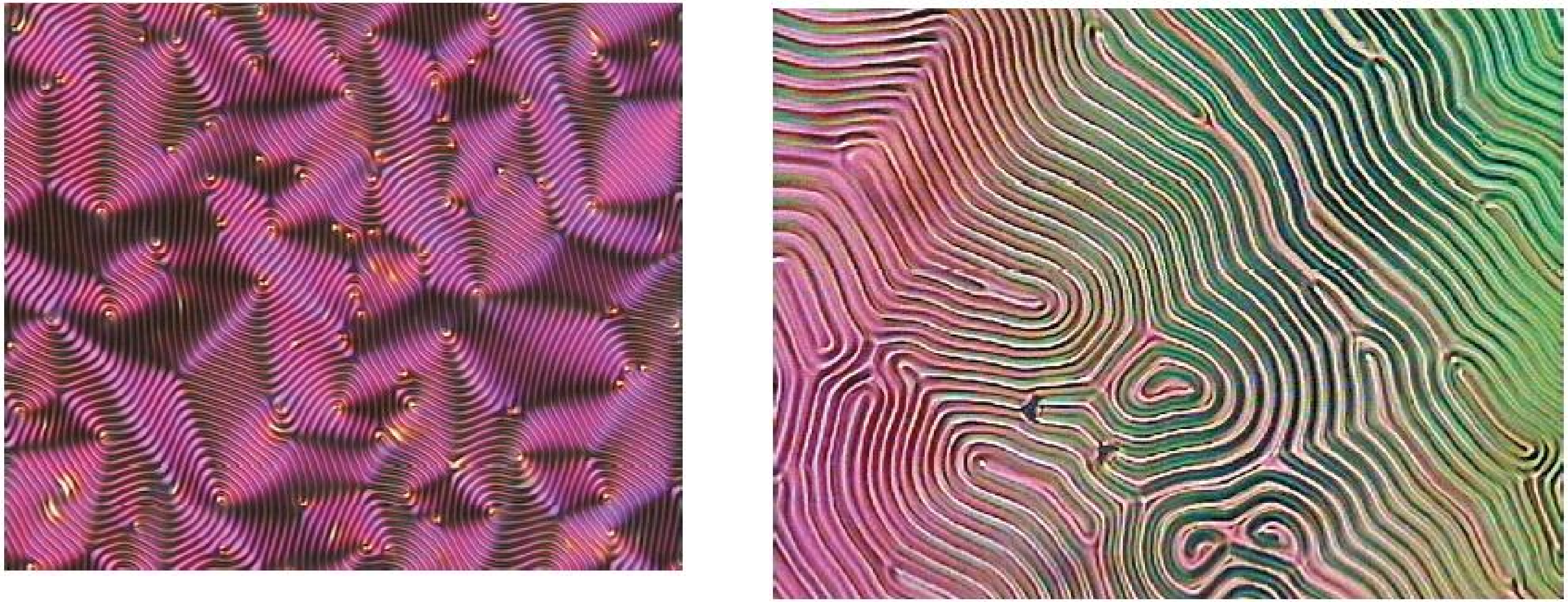


Semctic C: *schlieren* texture



Smectic A: focal-conic fan (焦锥扇形) texture

POM Used in the Study of LC Phases



Cholesteric (fingerprint) texture

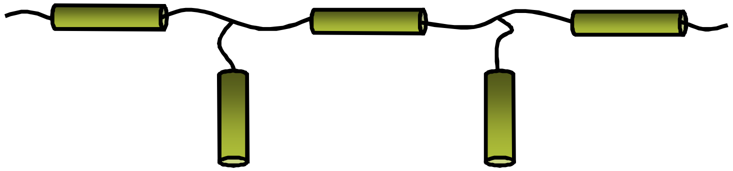
Liquid Crystalline Polymers

- **Common architectures for liquid crystalline polymers (LCPs): some examples**

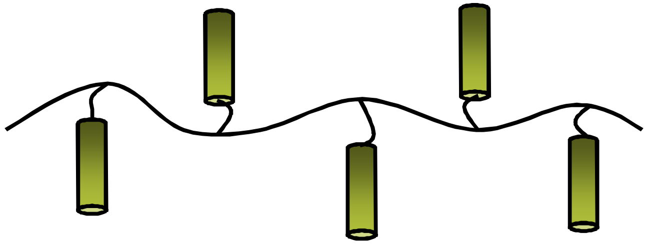
main-chain rigid-rod: lyotropic

main-chain with flexible spacers:

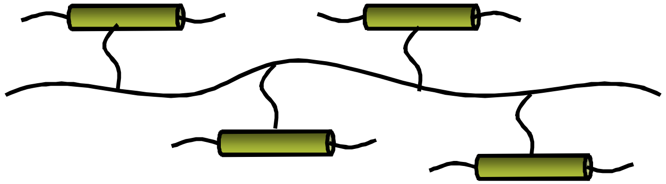
hybrid: combination of main-chain and side-chain:



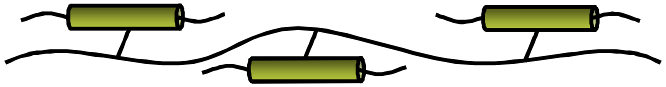
side-chain with terminal attachment:



side-chain with lateral attachment:



mesogen-jacketed LCP

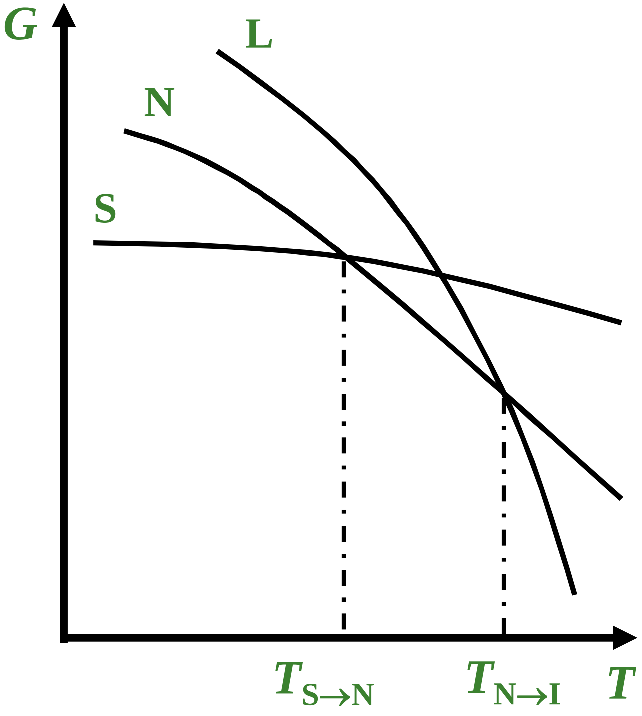


- **Applications:**

  Ultra-high-strength fibers: Kevlar®, Xydar®, Vectra®, Ultrax®
  membrane,
  Electro-optic (low molecular weight thermotropic LCs)……

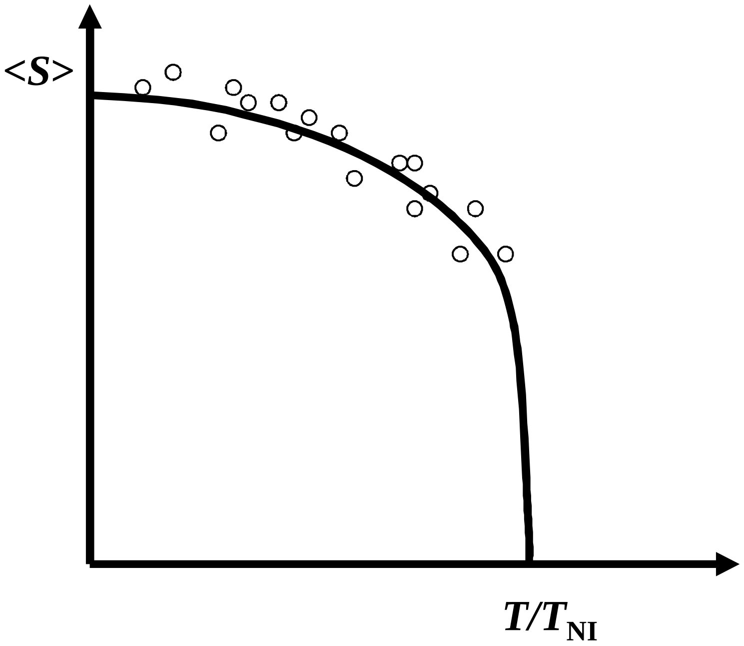
Thermodynamics of thermotropic liquid crystal transition

- ***G*-*T* diagram:**
  Gibbs free energy as function of temperature

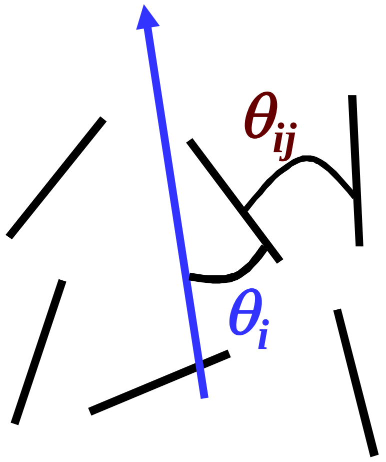


Order parameter(序参量)

$$\langle S\rangle = \frac{1}{2}\left(3\langle \cos^2\theta\rangle - 1\right)$$



Maier-Saupe Theory for LC Transition



Interaction Potential $U_{ij} = -\varepsilon_b(r)\, S(\cos\theta_{ij})$

$$U_i = -\sum_j \varepsilon_b(r) S(\cos\theta_{ij})$$

Mean-field Approximation

$$S(\cos\theta_i) = \frac{1}{2}\left(3\cos^2\theta_i - 1\right)$$

$$U_i = -\bar{\varepsilon}_b \langle S\rangle S(\cos\theta_i)$$

$$S(\cos\theta_{ij}) = \frac{1}{2}\left(3\cos^2\theta_{ij} - 1\right)$$

$$\langle S\rangle = \frac{\int S(\cos\theta_i)\, e^{(-U_i/kT)} \sin\theta_i d\theta_i}{\int e^{(-U_i/kT)} \sin\theta_i d\theta_i}$$

$$= \frac{\int S(\cos\theta) \exp\left(\frac{\bar{\varepsilon}_b}{kT}\langle S\rangle S(\cos\theta)\right) \sin\theta d\theta}{\int \exp\left(\frac{\bar{\varepsilon}_b}{kT}\langle S\rangle S(\cos\theta)\right) \sin\theta d\theta}$$

Self-consistence method $\varepsilon_b/kT_{\mathrm{NI}}=4.541$

Phase Transition Temp.

$\varepsilon_b/kT_{\mathrm{NI}}=4.541 \longrightarrow \boxed{T_{\mathrm{NI}}=4.541\varepsilon_b/k}$