

# Chapter 6. Crystalline State



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# Chapter 6. Crystalline State



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## 6.1. General Consideration

### 6.1.1. Crystalline state

- ❑ Most pure substances have a definite melting temperature below which the change from a random liquid structure to a well ordered, periodic crystalline structure can occur
  - this transformation is called *crystallization* (the reverse process : melting)
- ❑ Crystallization is also possible from solutions (the reverse process : dissolving)
- ❑ Only polymers with regular molecular chains are able to crystallize fast enough from a melt, notwithstanding the high viscosity. (Many polymers → glassy solids)
  
- ❑ Crystallization from a solution ~ the cooling rate & the rate of change in solubility  
~ polymers without side groups → crystallize fast
  
- ❑ *The crystalline state* : a state that diffracts X-rays and exhibits the 1st order transition  $T_m$ .
  - Polymer crystallines are never totally crystalline due to
    - ① their long chain nature
    - ② entanglements



# 6.1. General Consideration

## 6.1.2. Crystallinity

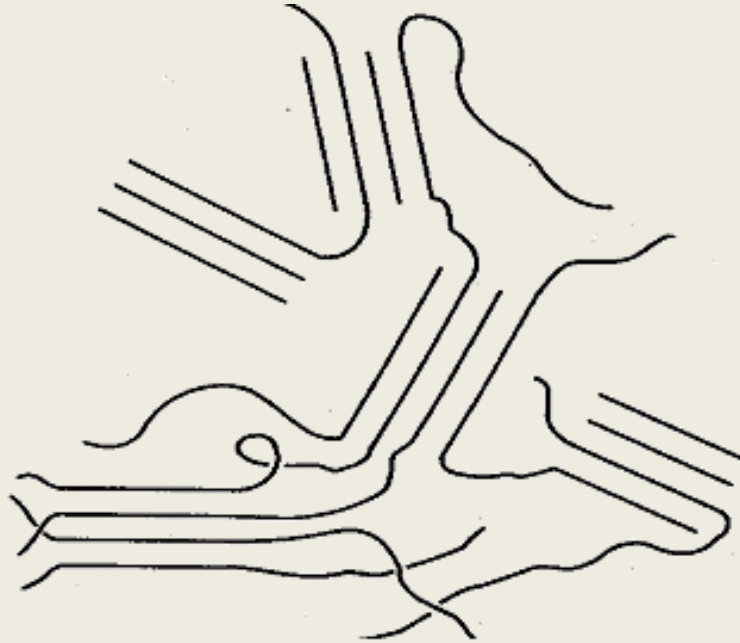
- ❖ Since polymers cannot be completely crystalline, the concept “*crystallinity*” has been introduced. → The meaning is still disputed.
- ❖ The original micellar theory of polymer crystallization  
: randomly distributed small crystallites + linked by intervening amorphous areas

Table 6.1 Definitions of crystallinity ( $x_c$ )

Based on	Definition
specific volume ( $v$ )	$x_c = \frac{v_a - v}{v_a - v_c}$
specific heat ( $c_p$ )	$x_c = \frac{c_p^a - c_p}{c_p^a - c_p^c}$
specific enthalpy ( $h$ )	$x_c = \frac{h_a - h}{h_a - h_c}$
specific enthalpy of fusion ( $\Delta h_m$ )	$x_c = \frac{\Delta h_m}{\Delta h_m^c}$
infrared mass extinction coefficient ( $\epsilon$ ) of characteristic vibrational mode	$x_c = \frac{\epsilon_\lambda}{\epsilon_\lambda^{(c)}} = 1 - \frac{\epsilon_\lambda}{\epsilon_\lambda^{(a)}}$
X-ray scattering intensity ( $I$ =area under selected peak)	$x_c = \frac{I_c}{I_c + I_a} \approx 1 - \frac{I_a}{(I_a)_{\text{melt}}}$
nuclear magnetic resonance	$\frac{x_c}{1 - x_c} = \frac{\text{area of broad component}}{\text{area of narrow component}}$



## 6.2.1. The Fringed Micelle Model (see Fig.6.9 p.257)



*Fig. 6.1 The fringed micelle model. Each chain meanders from crystallite to crystallite, binding the whole mass together.*



- ❑ In 1928, Hengstenberg and Mark estimated that the crystallites of ramie, a form of native cellulose. (*Z. Kristallogra.*, **69** (1928) 271)  
→ Their findings led to the fringed micelle model.
- ❑ The crystallites are about 100 Å long
  - The disordered regions separating the crystallites are amorphous.
  - The chains wander from the amorphous region through a crystallite, and black out into the amorphous region.
  - The chains are long enough to pass through several crystallites, finding them together.
- ❑ This model explains
  - The leathery behavior of ordinary polyethylene plastics.  
(The greater  $\sigma_t$  of PE over that of low MW hydrocarbon waxes was attributed to amorphous chains wandering from crystallite to crystallite holding them together by primary bonds.)
  - The flexible nature of fibers was explained similarly  
(The exact stiffness of the plastic or fiber was related to the degree of crystallinity, or fraction of the polymer that was crystallized.)



## 6.2. Structures of Crystalline Polymers

### 6.2.2. The Folded Chain Model

- Discovery of polymer single crystals from dilute solutions
  - : In 1957, Keller prepared single crystals of PE by precipitation from extremely dilute solutions of hot xylene
  - diamond shaped of the order of 100~200 Å thick
  - electron diffraction showed that the polymer chains in the crystal body were essentially perpendicular to the large, flat faces of the crystal.

*Polymer chain contour lengths of PE ~2000 Å*  
*thickness of the single crystals 110~140 Å*

- Keller concluded that the polymer molecules in the crystals had to be folded upon themselves.
- *The folded-chain model*



## 6.2. Structures of Crystalline Polymers

### 6.2.2. The Folded Chain Model (see Fig.6.10 p.259)

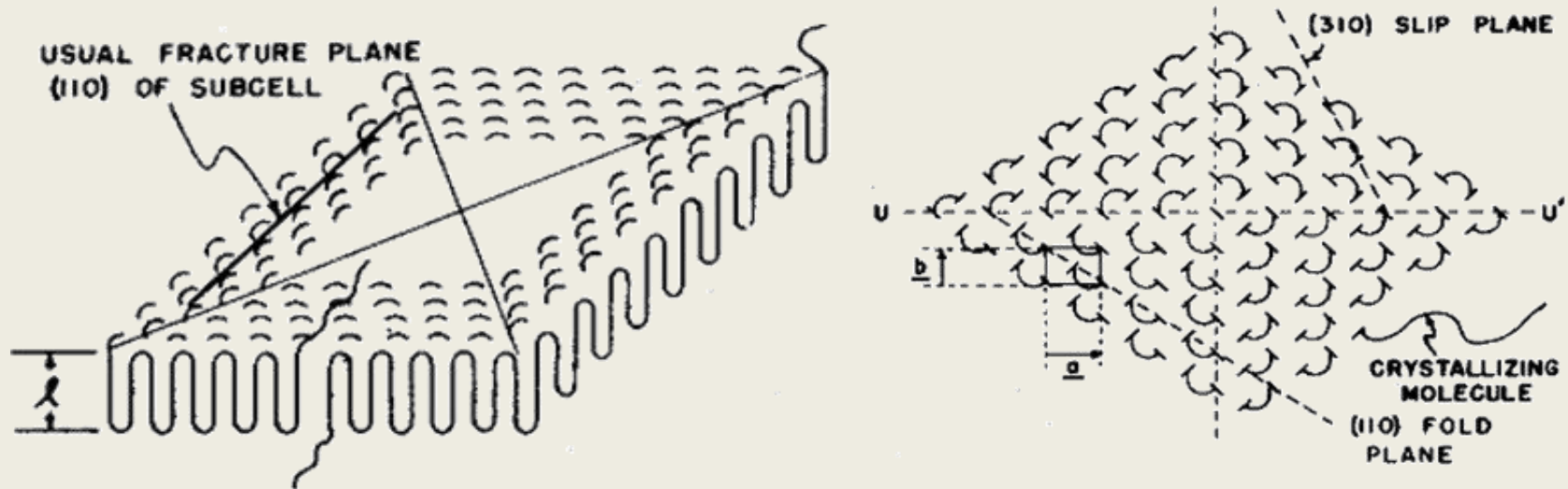


Fig. 6.2 Schematic view of a polyethylene single crystal exhibiting adjacent reentry. The orthorhombic subcell with dimensions  $a$  and  $b$ , typical of many  $n$ -paraffins, is illustrated in right

#### ✧ *The Switchboard Model*

the chains do not have a reentry into the lamellae by regular folding, but rather re enter more or randomly. → Discuss in 6.4.6





## 6.2. Structures of Crystalline Polymers

### 6.2.3. The Models of Polymer Crystallization

- ❖ The five main models of polymer crystallization:
  - a. The folded-chain model of a single crystal structure
  - b. The spontaneous, *spherulitic*, crystallization of flexible polymeric molecules under quasi-isotropic conditions
  - c. The *induced* crystallization of flexible polymeric chains in field of force, mainly by application of stress
  - d. The *extended chain* crystallization of *flexible* polymer molecules
  - e. The *extended chain* crystallization of *semi-rigid* polymer molecules



## 6.2. Structures of Crystalline Polymers

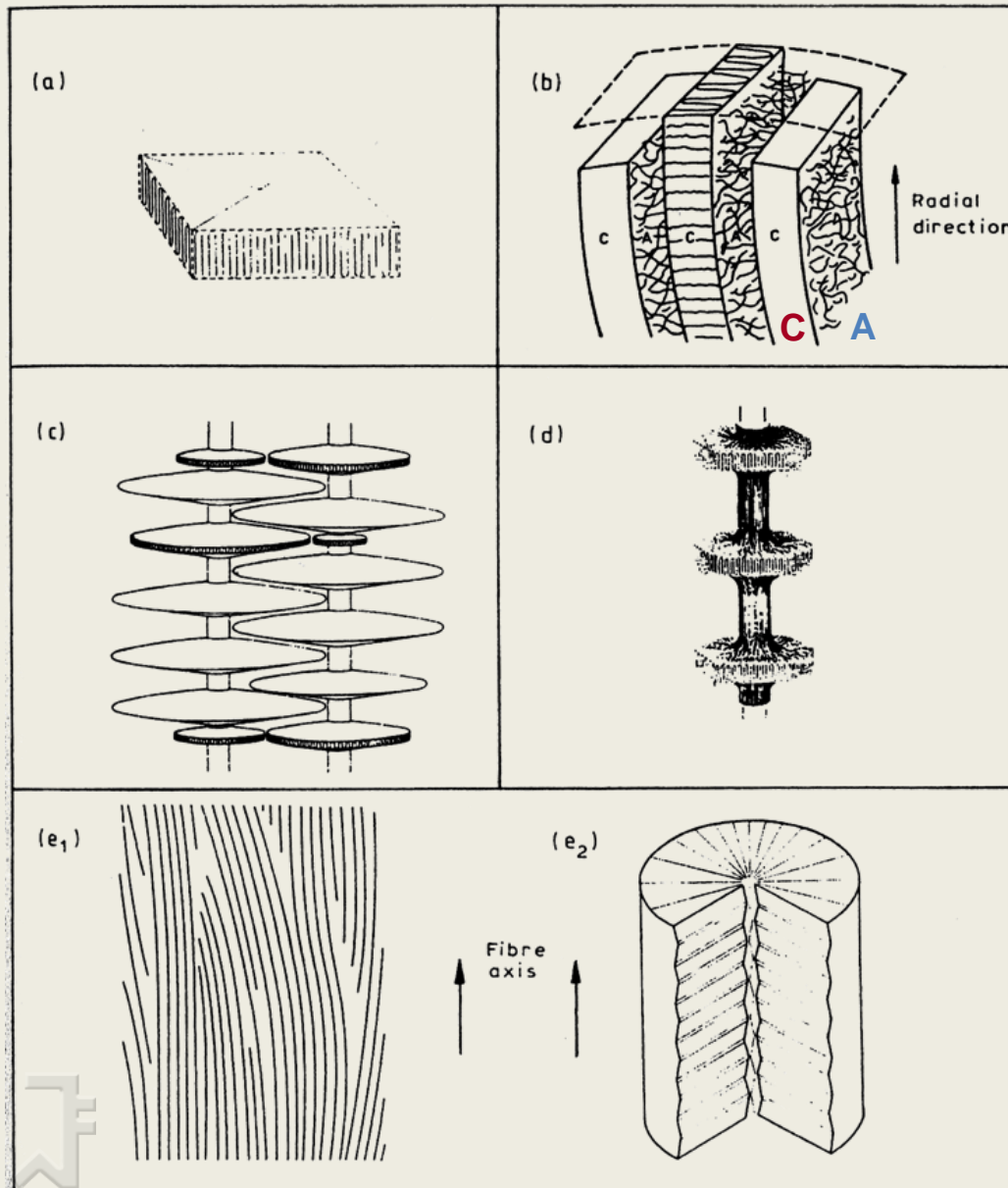
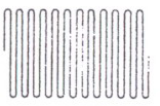

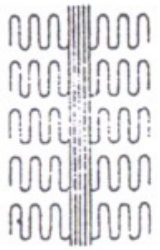


Fig. 6.3 Morphological models of some polymeric crystalline structures

- Model of a single crystal structure with macromolecules within the crystal (Keller, 1957)
- Model of part of a spherulite (Van Antwerpen, 1971)  
**A. Amorphous regions.**  
**C. Crystalline regions; lamellae of folded chains.**
- Model of high pressure crystallized polyethylene (Ward, 1985)
- Model of a shish kebab structure (Pennings et al., 1970)
- Model of paracrystalline structure of extended chains (aramid fiber).  
 e<sub>1</sub> lengthwise section (Northholt, 1984)  
 e<sub>2</sub> cross section (Dobb, 1985)

Table 6.2 Morphology of crystallites in polymers

Type of Polymer Chain	Conformation in Melt/Solution	Mode of Crystallization	Basic Substructure of crystallites	Micro-Structure		Illustration of characteristic features
				Conditions of Formation	Type	
Flexible	Random Coil	Free (spontaneous)	Lamellae made up of Folded Chains	Very dilute quiescent solution	Single Crystals	
				Quiescent Melt	Spherulites	
	Partly oriented or partly ordered (disentangled) Coils	Induced by Pressure, Flow, Stress, etc.	Hybrid structure made up of thin core of extended chains and matrix of Lamellae	Stirred very dilute solution	Shish Kebab Fibrils	
				Melt- or solution-spinning and drawing	Row nucleated Crystallites	
				Microfibrils of extended chains	Gel-spinning followed by ultradrawing	Extended Chain Microfibrils
	Rigid	Liquid Crystals of rigid rods	Mainly spontaneous	Microfibrils mad up of rigid rodlets	Solution-spinning with gas gap and drawing	Para-crystalline microfibrils

## 6.3. Spherulitic Crystallization of Polymers from the Melt

### 6.3.1. Spherulitic Morphology

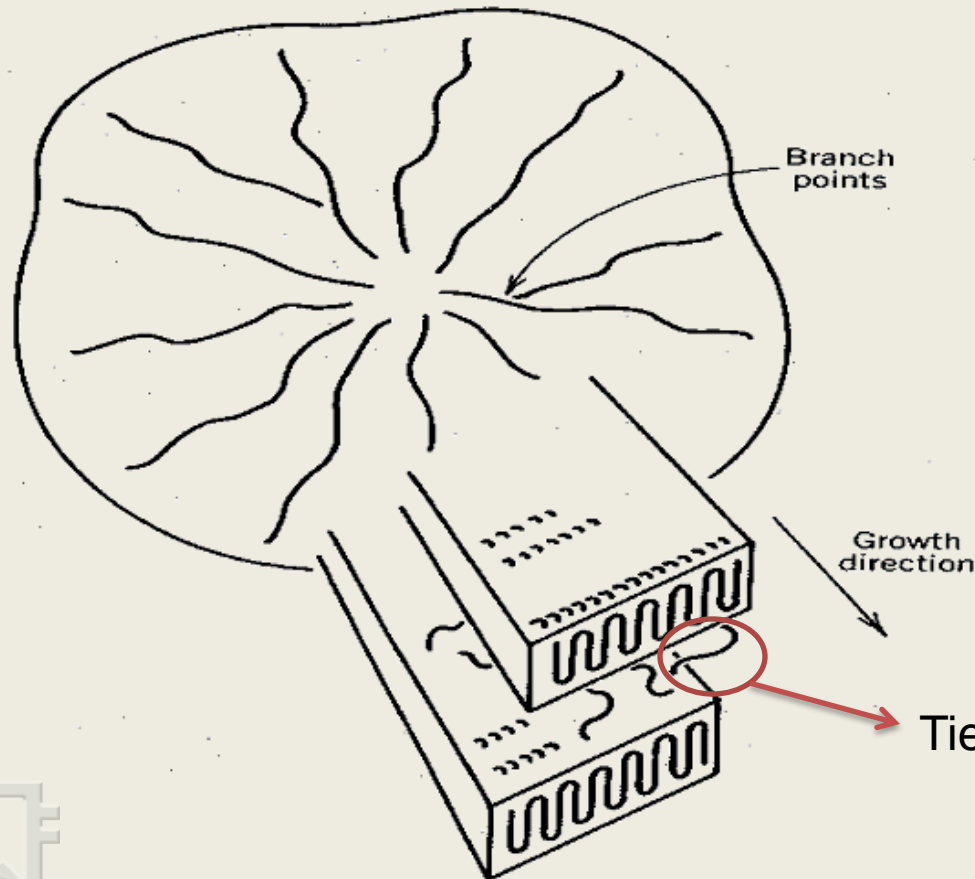
- When polymer samples are crystallized from the bulk, the most obvious of the observed structures are the spherulites (see Fig. 6.13. p.261)  
→ sphere-shaped crystalline structures that form in the bulk.



*Fig. 6.4 Spherulites of low-density polyethylene, observed through crossed polarizers. Note characteristic Maltese cross pattern.*

## 6.3. Spherulitic Crystallization of Polymers from the Melt

- How the lamellae are formed within the spherulite?  
→ each spherulite exhibits an extinction cross.  
= a Maltese cross



*Fig. 6.5 Model of spherulitic structure. Note growth directions and lamellar branch points. to fill space uniformly with crystalline material.*

*After J. D. Hoffman et al.*

Tie molecules → intercrystalline link  
→ effect on toughness

## 6.3. Spherulitic Crystallization of Polymers from the Melt

- ❑ This extinction is centered at the origin of the spherulite, and the arms of the cross are oriented parallel to the vibration directions of the microscope polarizer and analyzer.
  
- ❑ Usually the spherulites are really spherical in shape only during the initial stages of crystallization. During the latter stages of crystallization, the spherulites impinge on their neighbors.
  - nucleation
    - ┌ simultaneous : the boundaries between them are straight
    - └ at different times : the boundaries form hyperbolas.
  
  - X-ray & e<sup>-</sup> diffraction indicates that the c axis of the crystals is
    - ┌ normal to the radial direction of the spherulites.
    - └ perpendicular to the lamellae flat surfaces





## 6.3. Spherulitic Crystallization of Polymers from the Melt

### □ SALS (small angle light scattering)

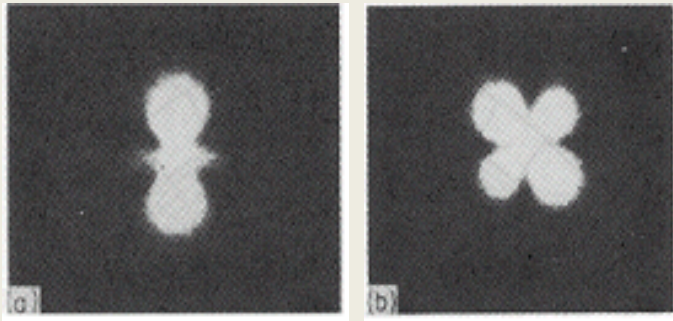
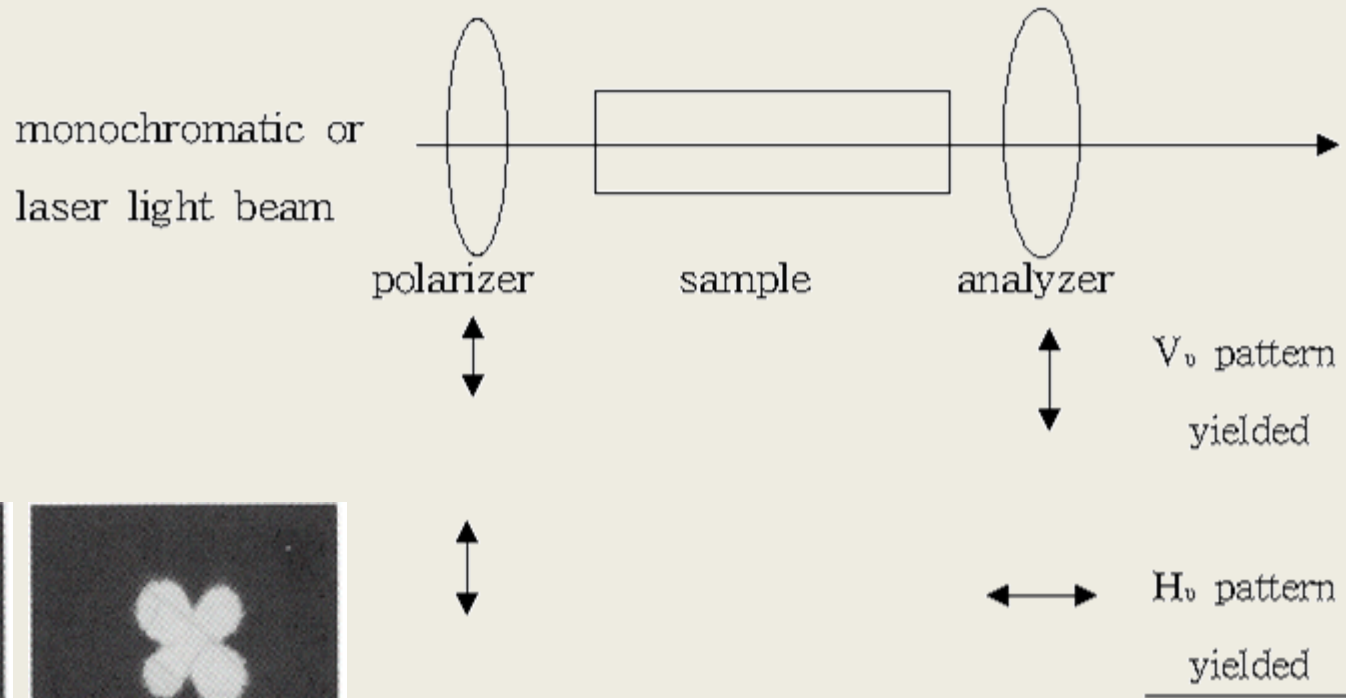


Fig.6.6 Different types of light-scattering patterns are obtained from spherulitic polyethylene using (a)  $V_v$  and (b)  $H_v$  polarization

(arise from the spherulitic structure of the polymer, which is optical anisotropic with the radial and tangential refractive indices being different)

## 6.3. Spherulitic Crystallization of Polymers from the Melt

- The scattering pattern can be used to calculate the size of the spherulites. i.e.

$$U_{\max} = \left( \frac{4\pi R}{\lambda} \right) \sin \frac{\theta_{\max}}{2} = 4.1$$

where  $U_{\max}$  : the intensity maximum occurring in the radial direction

$R$  : the radius of the spherulite

$\theta_{\max}$  : the angle at which the intensity maximum occurs

$\lambda$  : the wavelength

- ⇒ As the spherulites get larger, the maximum in intensity occurs at smaller angles.
- ⇒ Stein points out that in very rapidly crystallized polymers spherulites are often not observed.

- Mandelkern showed that the molecular structures become less ordered as the molecular weight is increased or the temperature of crystallization is decreased.





## 6.3. Spherulitic Crystallization of Polymers from the Melt

- In between the lamellar structures lies amorphous material.

The individual lamellae in the spherulites are bonded together by tie molecules, which lie partly in one crystallite and partly in another.

- **tie molecules :**

- ① sometimes in the form of intercrystalline links, which are long, threadlike crystalline structures with the c axis along their long dimension.
- ② important in the development of the great toughness characteristic of semicrystalline polymers.



## 6.3. Spherulitic Crystallization of Polymers from the Melt

### 6.3.2. Mechanism of Spherulite Formation (see Fig 6.19, p.266)

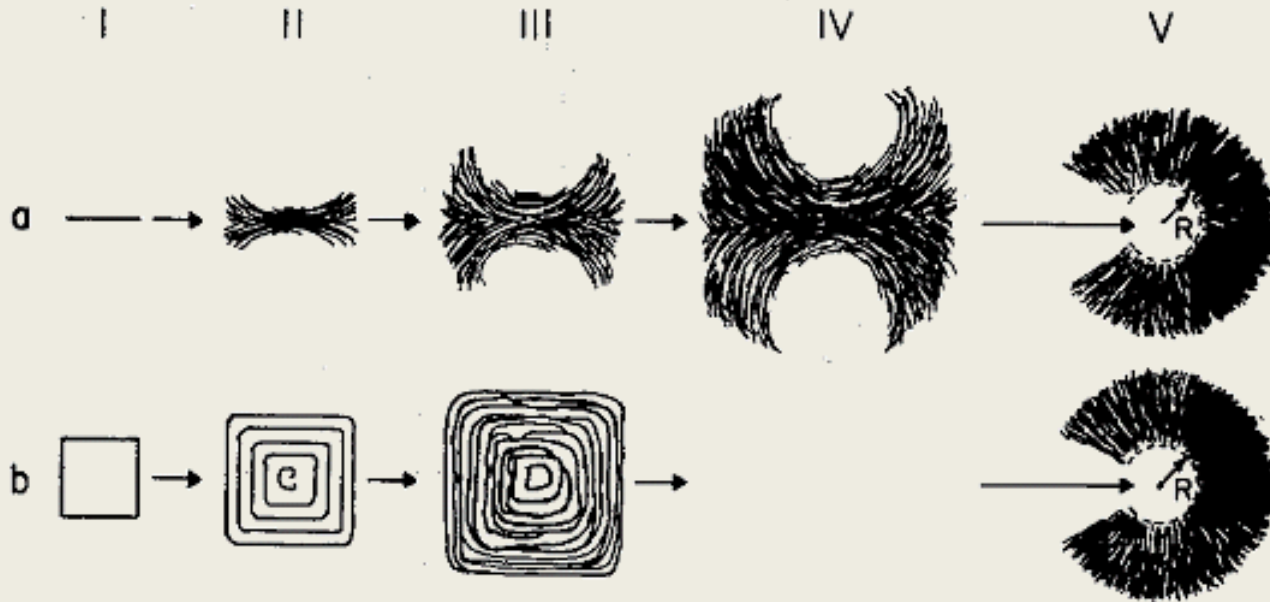


Fig. 6.7 Schematic development of a spherulite from a chain-folded precursor crystal Rows (a) and (b) represent, respectively, edge-on views of the evolution of the spherulite.

- On cooling from the melt

single crystal → sheaflike structure → spherulites  
(=axialite or hedrite)

## 6.3. Spherulitic Crystallization of Polymers from the Melt

### 6.3.3. Spherulites in Polymer Blends and Block Copolymers

- ❑ Miscible blend in one phase :  
if  $T_g$  of noncrystallizing polymer component  $< T_g$  of the crystallizing component, the spherulites will actually grow faster.
- ❑ Immiscible blend in two phases : On spherulite formation, the droplets, which are noncrystallizing, become ordered within the growing arms of the crystallizing component.
- ❑ Block copolymers form spherulites on a finer scale.



## 6.3. Spherulitic Crystallization of Polymers from the Melt

### 6.3.4. Percent Crystallinity in Polymers

❑ The reason why polymers fail to attain 100% crystallinity is kinetic, resulting from the inability of the polymer chains to completely disentangle and line up properly in a finite period of cooling or annealing.

❑ Experimental Methods to determine percent crystallinity.

① DSC : The heat of fusion per mole of crystalline material can be estimated independently by  $T_m$  depression.

② Density determination : (see Fig.6.8)

$$\% \text{ crystallinity} = \left[ \frac{D_{\text{exp}} - D_{\text{amorph.}}}{D_{100\% \text{ cryst.}} - D_{\text{amorph.}}} \right] \times 100$$

③ X-ray intensity  $\propto$  the No. of e-s involved and is thus proportional to the density  
- amorphous halo : broader due to the molecular disorder

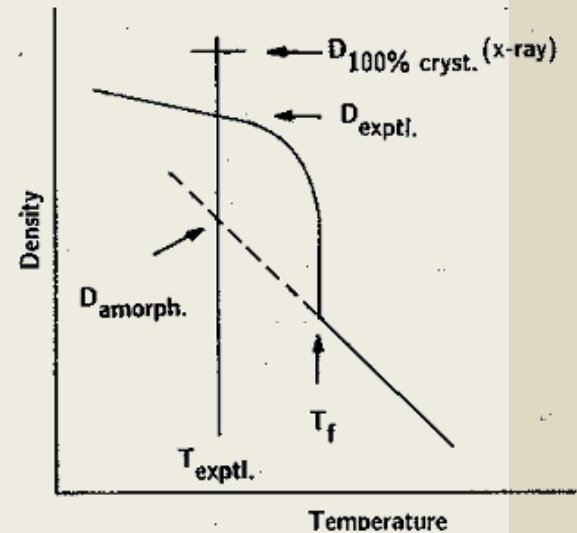


Fig. 6.8 The experimental determination of the extent of polymer crystallinity using the density method.

## 6.4. Kinetics of Crystallization

### 6.4.1. Experimental Observations of Crystallization Kinetics

- ① volume change on melting - dilatometry (Fig.6.25 p.272)

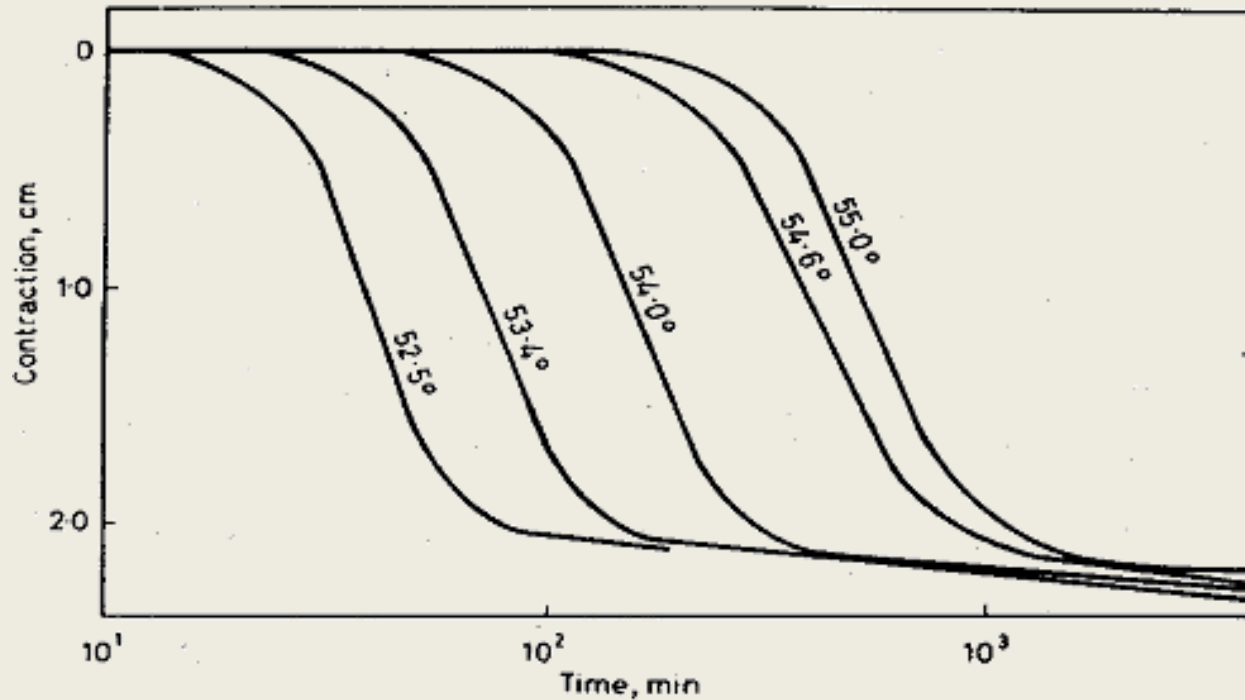


Fig. 6.9 Dilatometric crystallization isotherms for poly(ethylene oxide),  $M=20,000\text{g/mol}$ . The Avrami exponent  $n$  falls from 4.0 to 2.0 as crystallization proceeds.



## 6.4. Kinetics of Crystallization

- ② microscopy - by measuring the growth of the spherulites as a function of time. (Fig.6.26 p.272)

impurity concentration  $\uparrow$  the growth rate  $\downarrow$

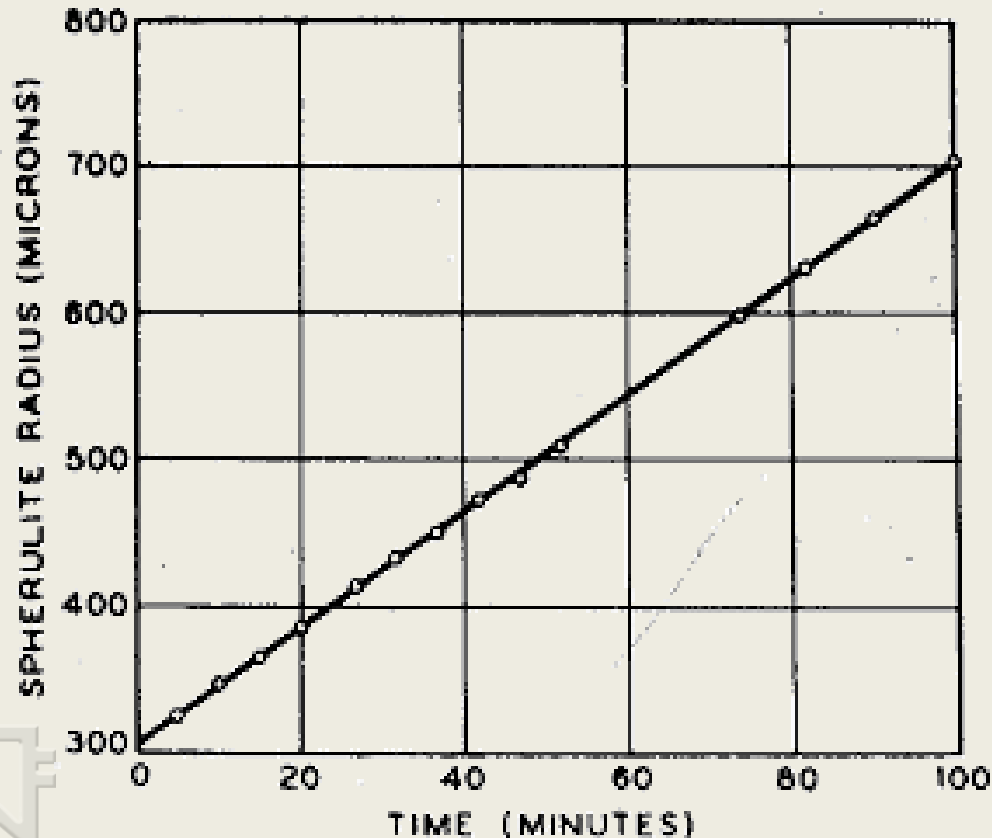


Fig. 6.10 Spherulite radius as a function of time, grown isothermally (at 125 °C) in a blend of 20% isotactic and 80% atactic ( $M=2600$ ) polypropylene. Note the linear behavior.

## 6.4. Kinetics of Crystallization

### 6.4.2. The Overall Rate of Crystallization

- : determined by two factors
- └ the formation rate of nuclei (above the critical size)
  - └ the growth rate of nuclei to final crystalline aggregate
- ❖ When a polymer cools down from the molten state, crystallization is very slow at first (*induction* period)
    - After an induction period, the process speeds up to a maximum rate
    - Slows down again as it approaches the final equilibrium state
  - ❖ The usual procedure in studying the rate of polymerization
    - : cooling the polymer quickly from the molten state → measure the development of crystallinity at constant temperature (isothermal crystallization)
  - ❖ Well-defined spherulites visible under a microscope
    - the rate of nuclei formation and growth into spherulites (in  $\mu\text{m}$  per min)



## 6.4. Kinetics of Crystallization

### 6.4.3. Nucleation and Growth

- ❖ The rate of crystallization (C) = Nucleability (N) • Transportability (T)  
“nucleation factor” “transport factor”  
→ valid as well for the primary nucleation in melt or solution, as for the growth of the crystallites
- ❖ The assumption of the general theory of phase transition by crystallization
  - In supercooled melts, fluctuations → leading to the formation of a new phase
  - Very small particles of the new phase → phase transformation (*nucleation*)  
→ The decrease in free energy » the increase in interfacial energy  
→ So, the possible growth of new particles ~ the ratio of surface area to volume.
  - *Critical size* : separating particles
    - └ whose free energy of formation increase
    - └ whose free energy of formation decrease
  - So, the small particles : redissolve and the larger ones : grow
  - A particle which has just the critical size acts as a *nucleus for growth*





## 6.4. Kinetics of Crystallization



### 6.4.4. Theories of Crystallization Kinetics

- ❑ Avrami : formulations for metallurgy were adapted to polymer science.
- ❑ Keith and Padden : provides a qualitative understanding of the rates of spherulitic growth.
- ❑ Hoffman : developed the kinetic nucleation theory of chain folding.

#### ***6.4.4.1. The Avrami Equation***

- ❑ Imagine raindrops falling in a puddle
  - raindrops strike the puddle surface at random points.
  - expanding circles of waves are the growth fronts of the spherulites.
  - the points of impact are the crystallite nuclei.



## 6.4. Kinetics of Crystallization

### 6.4.4.1. The Avrami Equation

- The probability  $P_x$  that a point P is crossed by x fronts of growing spherulites is given by an equation originally derived by Posson.

$$P_x = \frac{e^{-E} E^x}{x!} \quad \rightarrow \text{Appendix 6.1}$$

where E represents the average number of fronts of all such points in the system.

- The probability that P will not have been crossed by any of the fronts, and is still amorphous

$$\begin{aligned} P_0 &= e^{-E} \text{ (} E \text{ and } 0! \text{ are both unity)} \\ &= 1 - X_t \end{aligned}$$

$X_t$  : is the volume fraction of crystalline material  
i.e. the degree of crystallinity

- For low degrees of crystallinity  $X_t \cong E$  (by approximation)



## 6.4. Kinetics of Crystallization

- For the bulk crystallization of polymers  $X_t$  (in the exponent)  $\simeq V_t$  where  $V_t$  is the volume of crystallization material

$$1 - X_t = e^{-V_t}$$

- The problem now resides on the evaluation of  $V_t$ . There are two cases to be considered:

- (a) the nuclei are predetermined – the nuclei all develop at once on cooling the polymer to the temperature of crystallization
- (b) sporadic nucleation of the spheres.

- **For case (a),**

→  $L$  spherical nuclei, randomly placed, are considered to be growing at a constant rate,  $g$ .

The volume increase in crystallinity in the time period  $t$  to  $t+dt$  is

$$dV_t = 4\pi r^2 L dr \quad r : \text{radius of the spheres at time } t \text{ (i.e. } r = g t)$$

$$\therefore V_t = \int_0^1 4\pi g^2 t^2 L g dt = \frac{4}{3} \pi g^3 L t^3$$

## 6.4. Kinetics of Crystallization

□ **For case (b),**

- The No. of spherical nuclei is allowed to increase linearly with time at a rate  $l$ .
- Then spheres nucleated at time  $t_i$  will produce a volume increase of

$$dV_t = 4\pi g^2 (t - t_i)^2 l t g dt$$

$$V_t = \frac{2}{3} \pi g^3 l \pi t^4$$

To produce the familiar form of the Avrami equation:

$$1 - X_t = e^{-Zt^n}$$

→ Appendix 6.2

$$\ln(1 - X_t) = -Zt^n$$

where  $X_t$  : the fraction of material transform (into the spherulitic state) at time  $t$   
 $n$  : constant (an integer value depend on the mechanism of nucleation and on the form of crystal growth)

$Z$  and  $n$  are diagnostic of the crystallization mechanism. (ref. to Table 6.3)



## 6.4. Kinetics of Crystallization

Table 6.3 Constants  $n$  and  $Z$  of Avrami equation (Theoretical value)

Form of growth	Type of nucleation					
	Predetermined (constant number of nuclei per cm <sup>3</sup> )			Spontaneous (sporadic) (constant nucleation rate)		
	$n$	$Z$		$n$	$Z$	
Spherulitic (spheres)	3	$\frac{4}{3} \pi g^3 L$		4	$\frac{2}{3} \pi g^3 l$	
Discoid (Platelets) <sup>a</sup>	2	$\pi g^3 Ld$		3	$\frac{\pi}{3} g^2 ld$	
Fibrillar (rodlets) <sup>b</sup>	1	$\frac{1}{2} \pi g Ld^2$		2	$\frac{1}{4} \pi gld^2$	

<sup>a</sup> Constant thickness=  $d$

<sup>b</sup> Constant radius=  $d$



## 6.4. Kinetics of Crystallization

### 6.4.4.2. Keith-Padden Kinetics of Spherulitic Crystallization

- As the spherulites grow, the individual lamellae branch.
- Impurities, atactic components, become trapped in the interlamellar regions.

$$\delta = \frac{D}{G}$$

D : the diffusion coefficient for impurity in the melt

G : the radial growth rate of a spherulite.

$\delta$  : the lateral dimensions of the lamellae : dimension is that of length.

= a measure of the internal structure of the spherulite, or its coarseness.

- By logarithmic differentiation of above eqn.

$$\frac{1}{\delta} \left( \frac{d\delta}{dT} \right) = \frac{1}{D} \left( \frac{dD}{dT} \right) - \frac{1}{G} \left( \frac{dG}{dT} \right)$$

always (+)      (+) or (-)

: (+) means increase in coarseness the temperature is increased.

## 6.4. Kinetics of Crystallization

$$G = G_0 \exp\left(\frac{\Delta E}{RT}\right) \exp\left(\frac{-\Delta F^*}{RT}\right)$$

where  $\Delta F^*$  : the free  $\epsilon$  of formation of a surface nucleus of critical size

$\Delta E$  : the free  $\epsilon$  of activation for a chain crossing the barrier to the crystal.

i.e. Two competing processes

- ① the rate of molecular transport in the melt  $\uparrow$  as  $T \uparrow$
  - ② the rate of nucleation  $\downarrow$  as  $T \uparrow$
- According to Keith and Padden
    - diffusion is the controlling factor at low  $T$
    - the rate of nucleation dominates at higher  $T$
    - in between the growth rate passes through a maximum.

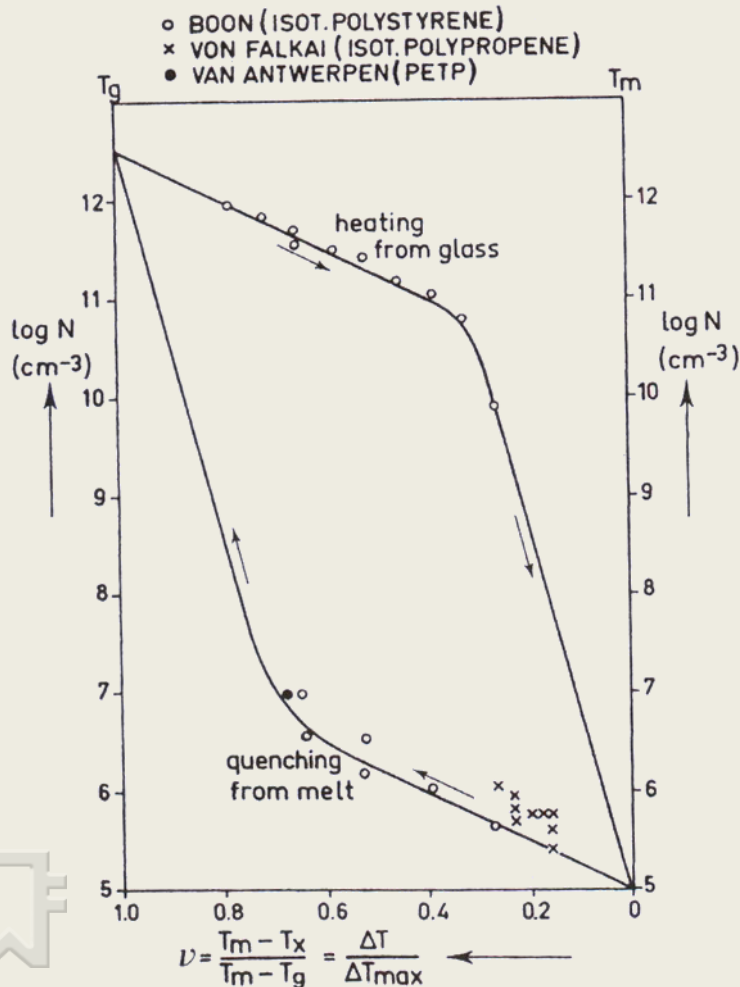


## 6.4. Kinetics of Crystallization

### 6.4.4.3. Hoffman's Nucleation Theory

❖ The number of nuclei  $N$  (=L at Avrami eqn.)

: low growth rate of isotactic polystyrene → the crystallization can be studied in the whole region from  $T_g$  to  $T_m$



: Boon (1968) determined the number of nuclei in the two extreme case

- starting from a superheated melt and quenching to the crystallization temp.
- starting from the solid state and heating to the crystallization temp.

Fig 6.11 Boon's data as a function of the dimensionless parameter  $v [= (T_m - T_x) / (T_m - T_g)]$ , the *relative undercooling*. In this master-form the graph also fits with the data of Von Flakai (1960) for isotactic polypropene and with those of Van Antwerpen (1972) on PETP.

$T_x$  : crystalline temperature



## 6.4. Kinetics of Crystallization

- ❖ For all crystallizing polymers, the number of nuclei will be following order of magnitude
  - starting from the melt and quenched to  $T_x$ :  $\sim 3 \times 10^6 \text{cm}^{-3}$
  - starting from the quenched solid state ( $T < T_g$ ) and heated to  $T_x$ :  $3 \times 10^{11} \text{cm}^{-3}$
  - $N$  will determine the maximum size of the spherulites after conversion of the whole melt into crystalline materials.

$$\frac{4}{3} \pi \bar{R}_{\max}^3 \cdot N = x_c$$

so that, if  $x_c \approx 1$

$$\bar{R}_{\max} \cdot N^{1/3} \approx 0.62$$

- ❖ Theoretical expression for the rate of nucleation

$$N' = N'_0 \cdot \underbrace{\exp(-E/RT)}_{\text{transport factor}} \cdot \underbrace{\exp(-\Delta G_n^*/kT)}_{\text{nucleation factor}}$$

where  $N'$  : rate of nucleation

$N'_0$  : is a constant for the zero-condition ( $E$  and  $\Delta G^*=0$ )

$E$  : activation energy of transport (self-diffusion)

$\Delta G_n^*$  : Gibbs free energy of formation of a nucleus of critical size

## 6.4. Kinetics of Crystallization

$$\Delta G_n^* / kT = \frac{32NA \cdot \gamma_{\parallel}^2 \cdot \gamma_{\perp} \cdot T_m^4}{RT (\Delta H_m)^2 T^2 (\Delta T)^2} \approx \frac{32NA \cdot \gamma_{\parallel}^2 \cdot \gamma_{\perp} \cdot T_m^2}{RT (\Delta H_m)^2 (\Delta T)^2}$$

For large undercooling      For small undercooling

$$E / RT = C_1 / R (C_2 + T - T_g)$$

- where  $\gamma_{\parallel}$  : free interfacial energy parallel to chain direction  
 $\gamma_{\perp}$  : free interfacial energy perpendicular to chain direction  
 $\Delta H_m$  : Heat of melting (fusion)  
 $\Delta T = T_m - T_x$  : =undercooling,  $T_x$  : crystalline temperature  
 $C_1$  : constant = 17.2 kJ/mol,  $C_2$  : constant = 51.6 K



## 6.4. Kinetics of Crystallization

❖ **The rate of growth** is very much dependent on the temperature of crystallization

- At  $T_m$  and  $T_g$ , its value is nearly zero
- In the intermediate region, a maximum ( $v_{\max}$ ) is observed at a temperature  $T_k$

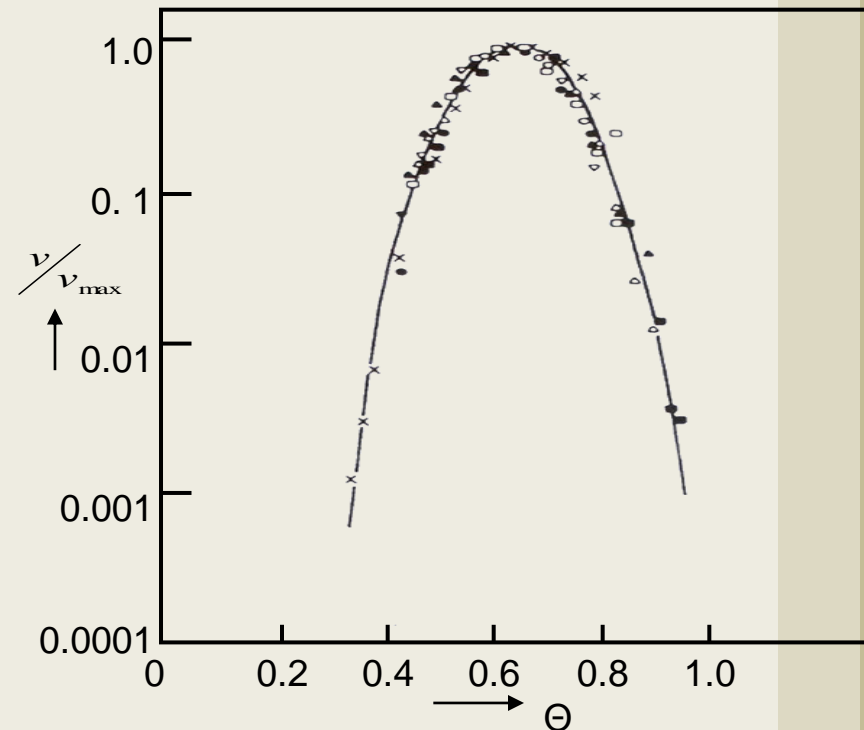
$$\Theta = \frac{T - T_\infty}{T_m - T_\infty} \quad \text{where } T_\infty \approx T_g - 50$$

$$T_k \approx 0.5(T_m + T_g)$$

❖ Theoretical expression for the rate of nucleation

$$v = v_0 \underbrace{\exp\left(-\frac{E_D}{RT}\right)}_{\text{Transport factor}} \underbrace{\exp\left(-\frac{W^*}{kT}\right)}_{\text{Work factor (surface nucleation factor)}}$$

Fig 6.12 Dimensionless master curve of the rate of growth, suggested by Gandica and Magill. (1972).  $\Theta \approx 0.635$



$E_D$  : the activation energy for the diffusive transport process at the interface

$W^*$  : the free energy of formation of a surface nucleus of critical size

$k$  : the Boltzmann constant ( $=R/N_A$ )

## 6.4. Kinetics of Crystallization

### ❖ Hoffman equation

$$\frac{E_D}{RT} = \frac{C_1'}{C_2 + (T - T_g)} \quad \text{WLF formulation} \quad \longrightarrow \quad \text{Appendix 6.3}$$

$$\frac{\Delta W^*}{kT} = \frac{4b_0\gamma_{\parallel}\gamma_{\perp}T_m}{k\Delta h_m T\Delta T} = \frac{C_3 T_m}{T(T_m - T)}$$

$b_0$ : thickness of the chain molecules

$\gamma_{\parallel}$ : free interfacial energy parallel to chain

$\gamma_{\perp}$ : free interfacial energy perpendicular to chain

$\Delta h_m$ : heat of melting per unit volume

$C_1' \approx 2060 \text{ K}$ ,  $C_2 \approx 51.6 \text{ K}$ ,  $C_3 \approx 265 \text{ K}$

- Hoffman supposed that  $E_D$  was not a constant, but that the diffusive transport in a melt could be described by a WLF function.

$$\frac{E_D}{RT} \approx \frac{C_1}{R(C_2 + T - T_g)}$$

- The final expression for the growth rate becomes

$$v \approx 10^7 \cdot \exp\left[-\frac{C_1 / R}{C_2 + (T - T_g)}\right] \exp\left[\frac{C_3 T_m}{T(T_m - T)}\right] \text{ nm/s}$$

## 6.4. Kinetics of Crystallization

### ❖ Mandelkern equation

: The WLF formulation (success in explaining the segmental mobility and flow properties of completely amorphous polymers) *is not applicable to the transport process involved in the growth of spherulites in melts of semicrystalline polymers.*

$$\frac{v}{v_0} = \exp\left[-\frac{E_D}{RT}\right] \exp\left[-\frac{C_3 T_m^0}{T(T_m^0 - T)}\right]$$

$v_0$ : universal constant for semicrystalline polymer  
 $\approx 10^{12}$  nm/s

$T_m^0$ : effective melting point

$E_D$ : constant in the undercooled melt

- Mandelkern determined activation energies for a series of polymers and found that  $E_D$  for different polymers increases monotonically with  $T_g$ .

$$\frac{E_D}{R} \approx 5.3 \times \frac{T_m^2}{T_m - T_g} \quad \longrightarrow \quad \text{See Table 6.4 and Fig 6.13}$$

- A semi-empirical expression for the growth rate

$$\log \frac{v}{v_0} \approx -\frac{1}{2.3} \frac{T_m}{T} \left\{ \frac{5.3 T_m}{T_m - T_g} + \frac{265}{T_m - T} \right\}$$

or

$$\log \frac{v}{v_0} \approx -2.3 \frac{T_m}{T} \left\{ \frac{T_m}{T_m - T_g} + \frac{50}{T_m - T} \right\}$$

where  $v_0 \approx 10^{12}$  nm/s

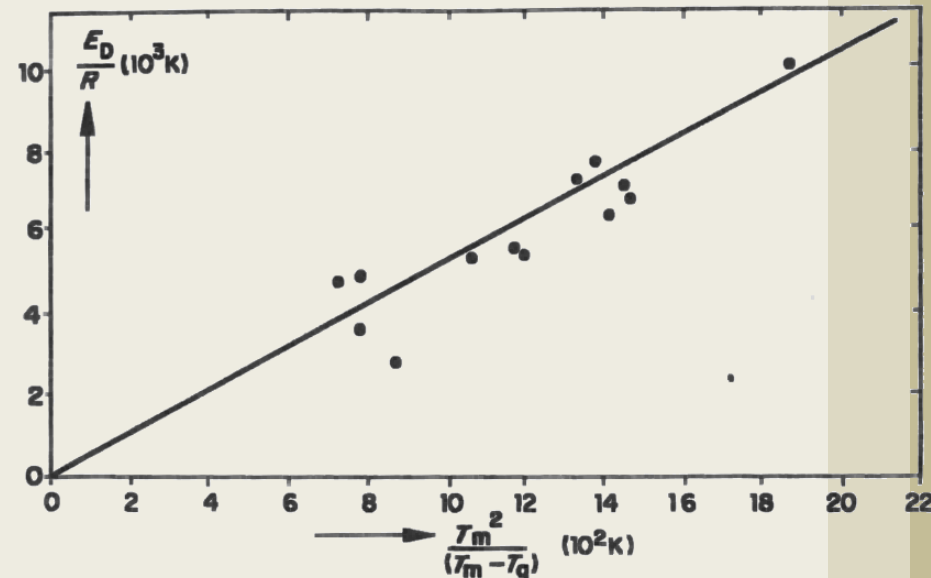
## 6.4. Kinetics of Crystallization

Table 6.4 Survey of Mandelkern's data on crystallization

Polymer	$T_m^0$ (K)	$T_m$ (K)	$E_D$ ( $10^3$ J/mol)	$T_g$ (K)
polyethylene	419	414	29.3	195
polypropylene	438	456	50.2	264
polybutene (isot.)	407	415	44.4	249
polystyrene (isot.)	527	513	84.6	373
poly(chlorotrifluoroethylene)	499	491	59.4	325
polyoxymethylene	456	456	41.0	191
poly(ethylene oxide)	347	339	23.0	206
poly(tetramethylene oxide)	462	453	56.1	193
poly(propylene oxide)	354	348	40.6	201
poly(decamethylene sebacate)	356	358	12.6	-
poly(decamethylene terephthalate)	418	411	46.5	268
nylon 6	505	502	56.5	330
nylon 5,6	541	531	61.1	318
nylon 6,6	553	540	64.5	330
nylon 9,6	529	515	56.9	-
nylon 6,10	516	499	53.6	323

$$\frac{E_D}{R} \approx 5.3 \times \frac{T_m^2}{T_m - T_g}$$

Fig 6.13 Correlation for the activation energy for transport.



## 6.4. Kinetics of Crystallization

❖ Steiner, Magill, van Antwerpen and van Krevelen

: at low to moderate molecular weights,  $v_0$  is dependent on the molecular weight

$$v_0 = a + b / M_n$$

: To obtain a universal correlation for the linear growth rate in the full temperature region between  $T_g$  and  $T_m$  → introduce the variables

$$\xi = T_m / T_x \quad \text{and} \quad \delta = T_g / T_m \quad \longrightarrow \quad \text{Hoffman eqn. and Mandelkern eqn.}$$

for  $T_x \geq T_k$

$$\log v = \log v_0 - 2.3 \frac{\xi}{1-\delta} - \frac{115}{T_m} \frac{\xi^2}{\xi-1}$$

For the higher temp. region  
: Mandelkern-type equation

for  $T_x \ll T_k$

$$\log v = \log v_0 - \frac{895\xi}{51.6\xi + T_m(1-\delta\xi)} - \frac{115}{T_m} \frac{\xi^2}{\xi-1}$$

For the lower temp. region  
: Hoffman-type equation

# 6.4. Kinetics of Crystallization

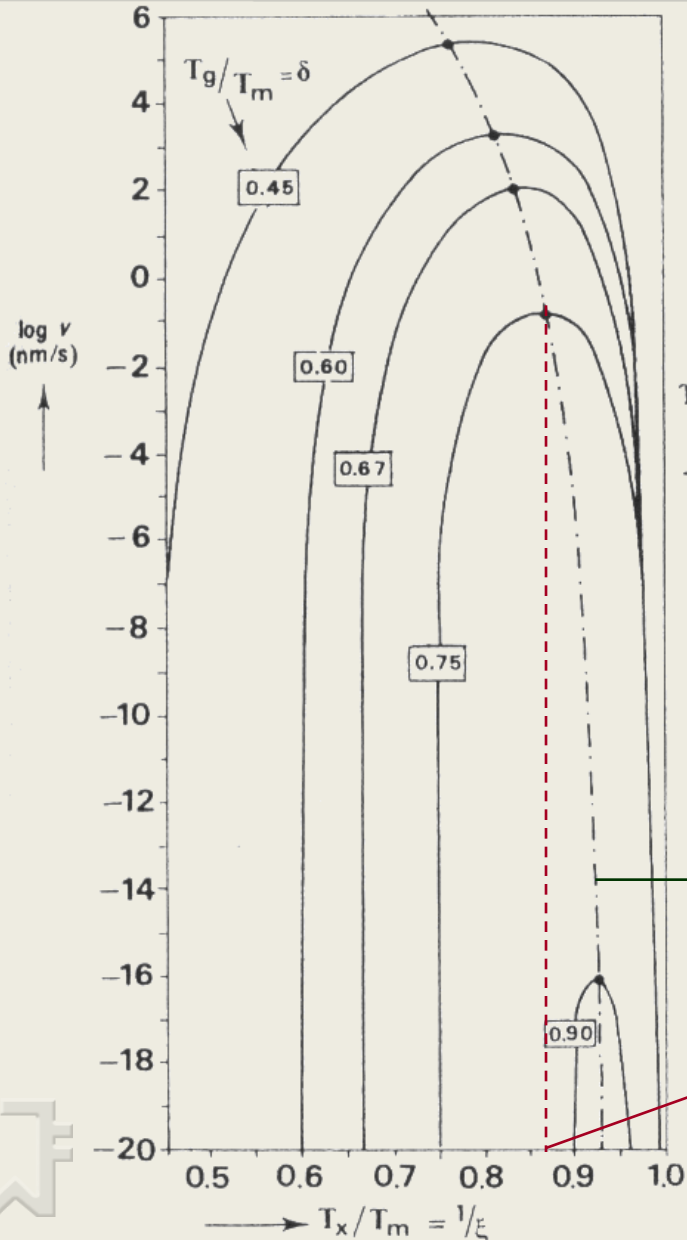


Fig 6.14 Master curve of the rate of growth of spherulites as a function of the dimensionless parameters  $T_x/T_m$  and  $T_g/T_m$  (van Krevelen 1978).

⇒ enables us to predict the value of  $v$  under experimental conditions for all normal polymers



Fig 6.15

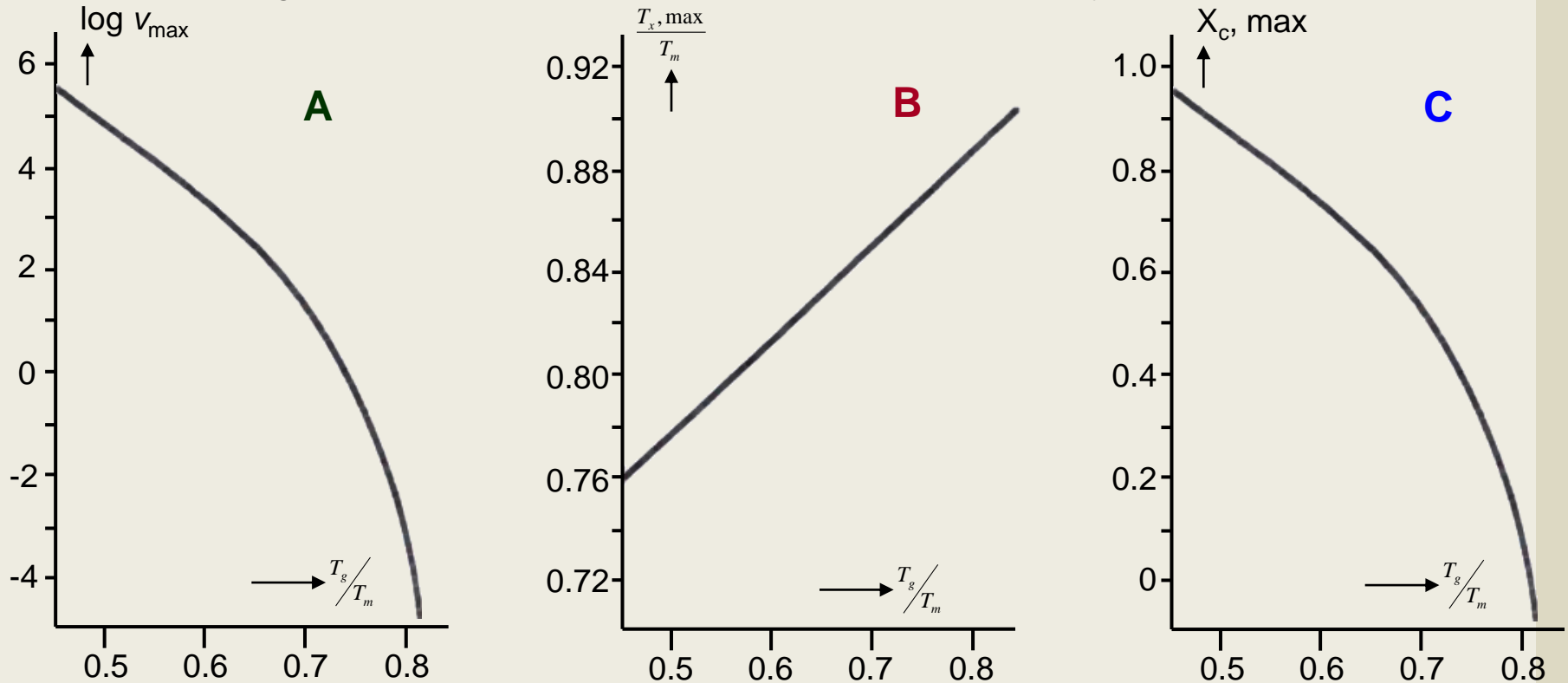
log  $v_{max}$  → Fig 6.15 (A)

$\frac{T_{x, max}}{T_m}$  → Fig 6.15 (B)



## 6.4. Kinetics of Crystallization

Fig 6.15 The three main parameters of spherulitic crystallization.



- A** : The maximum rate of spherulite growth is a function of the ratio  $T_g/T_m$ .
- B** : The temperature of maximum crystalline rate is also determined by  $T_g/T_m$ .
- C** : The attained degree of crystallization  $\sim$  the maximum rate of crystallization  $\sim T_g/T_m$



## 6.4. Kinetics of Crystallization

Table 6.5 Comparison of experimental and estimated (predicted) data in polymer crystallization

Polymer	$T_m$ (K)	$T_g/T_m$	$T_{x,max}/T_m$	$T_{x,max}(=T_k)$ (K)		$\log v_{max}$ (nms <sup>-1</sup> )		$x_{c,max}$	
	Exp.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
p-ethylene (linear)	414	0.475	0.77	-	319	4.92	5.1	0.80	0.80
p-(propene) (isot.)	445	0.575	0.805	-	350	2.5	3.6	0.63	0.66
p-(1-butene) (isot.)	380	0.63	0.825	-	318	2.2	2.9	0.50	0.55
p-(styrene) (isot.)	513	0.725	0.86	449	442	0.6	0.8	0.34	0.32
p-(chlorotrifluoro-ethylene)	500	0.62	0.834	-	418	2.65	2.9	0.70	0.57
p(isoprene)	300	0.67	0.84	248	254	-	1.9	0.45	0.47
p(methylene oxide)	400	0.54	0.79	-	318	3.5	4.2	-	0.72
p(ethylene oxide)	340	0.665	0.84	-	286	-	2.1	-	0.47
p(propylene oxide)	340	0.62	0.83	290	282	2.9	2.9	-	0.53
polycarbonate	545	0.745	0.87	-	482	-0.8	-0.7	0.25	0.21
p-(ethyleneterephthalate)	548	0.63	0.835	459	466	2.1	2.8	0.5	0.54
nylon 66	545	0.59	0.81	420	440	4.3	3.5	0.70	0.63
nylon 6	496	0.675	0.84	413	418	3.5	1.9	0.5	0.45

## 6.4. Kinetics of Crystallization

### 6.4.5. Practical Considerations

#### a. Influencing the spherulitic crystallization

- It is customary to define the overall rate of crystallization as the inverse of the time needed to attain one-half of the final crystallinity  $\rightarrow t_{1/2}^{-1}$

$$\ln(1 - X_t) = -Zt^n$$

$\downarrow X_t = 1/2$

$$t_{1/2}^{-1} = 1.8 \cdot L^{1/3} \cdot g \quad \longleftarrow \quad Z = (t_{1/2}^{-1})^n \cdot \ln 2 \quad + \text{Table 6.3} \quad Z = \frac{4}{3} \pi g^3 L$$

: The number of nuclei  $L$  is determined by the thermal program ( $3 \times 10^{6-11} \text{ cm}^{-3}$ )

: The rate of growth  $g$  depends on

- ① The ratio  $T/T_m$  ( $= 1/\xi$ )
- ② The ratio  $T_g/T_m$  ( $= \delta$ )
- ③ The absolute value of  $T_m$
- ④ The absolute value of  $v_0$

: A maximum growth rate at  $T_k \approx 0.825 T_m \rightarrow$  optimum temperature

- $T_g/T_m$  and  $T_m$  are determined by the constitution of the polymer and cannot be influenced by process parameters



## 6.4. Kinetics of Crystallization

- The practical way to influence the free crystallization of polymers
  - ① The right temp. program for an optimal nucleation
  - ② The optimum crystallization temp. for a rapid growth rate
  - ③ An optimal nucleation agent in order to increase the temperature-independent factor

### b. Properties of semicrystalline spherulitic polymers

- Plastic materials are brittle when they consist of large spherulites (Table 6.6)
  - The spherulities had better be as small as possible
  - N must be large and undercooling by quenching must be deep and fast
- The optimum conditions : quenching is followed by reheating to  $T_k$ , with thorough crystallization → vacuum-forming like processes

Table 6.6 Yields points of nylon 66

Spherulite size (d)	Yield stress $P_Y$	
	[ $\mu$ ]	10 <sup>6</sup> [N/m <sup>2</sup> ]
50	10,250	72
10	11,800	83
5	12,700	89
3	14,700	98

$$\frac{P_y}{P_{y,\max}} = 1 - 0.18 \log \frac{(\mu)}{0.35}$$



## 6.4. Kinetics of Crystallization

### 6.4.6. The reentry problem in lamellae

- The lamellae were assumed to be formed through regular adjacent reentry, although it was recognized that this was an oversimplification.
- The question of the molecular organization within polymer single crystals as well as the bulk state:  
*Switchboard model or folded-chain model?*
- Since the chain length far exceeds the thickness of the crystal, the chains must either reenter the crystal or go elsewhere.
- However, the relative merits of the switchboard model versus folded-chain model remained substantially unresolved for several years for lack of appropriate instrumentation.



## 6.4. Kinetics of Crystallization

### 6.4.6.1. Infrared Spectroscopy

- Beginning in 1968, Tasumi and Krimm undertook a series of experiments using a mixed crystal infrared spectroscopy technique.
- Solution - grown PE crystals : chain folding takes place with adjacent reentry along (110) planes. High probability for a molecule to fold back along itself on the next adjacent (110) plane.
- Melt crystallized PE : a much lower extent of adjacent reentry.

### 6.4.6.2. Carbon-13 NMR

- Favors a tight adjacent reentry fold model for single crystals.
- Three major regions
  - 1) the crystalline region
  - 2) interfacial region : reduces the requirements for chain folding.
  - 3) amorphous region



## 6.4. Kinetics of Crystallization

### 6.4.6.1. Small-Angle Neutron Scattering

- Single-Crystal Studies
  - : adjacent reentry does not correlate with experiment
  - alternative model by Yoon and Flory

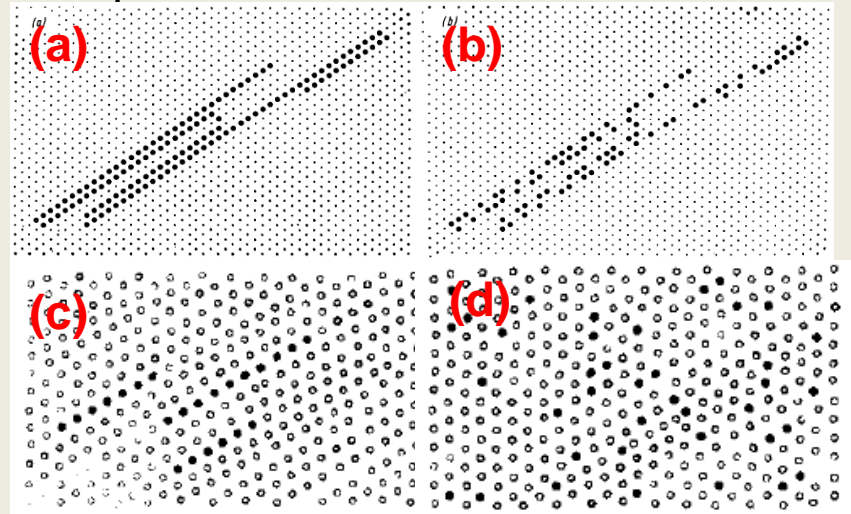
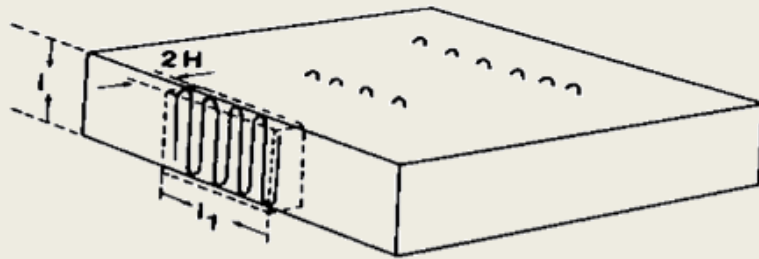


Fig. 6.16 Models of stem reentry for chain sequences in a lamellar-shaped crystal. (a) Regular reentry with superfolding; (b) partial nonadjacency (stem dilution) as required by closer matching of the experimental data in accord with Yoon and Flory; (c) adjacent stem positions without superfolding; (d) the switchboard model. All reentry is along the (110) plane; superfolding is along adjacent (110) planes. View is from the (001) plane, indicated by dots.

→ Appendix 6.4

## 6.4. Kinetics of Crystallization

### 6.4.6.1. Small-Angle Neutron Scattering

- Melt crystallized polymers
  - : switchboard model is more appropriate than nearby reentry.
    - i.e. adjacent reentry occurs much less than in solution crystallized polymers.
  - : Frank's Eqn. which describes the minimum conditions to prevent an anomalous density in the amorphous region.

$$\left(1 - P - \frac{2l}{L}\right) \cos \theta \leq \frac{3}{10}$$

where P: the probability of back folding  
 $\theta$ : the oblique angle  
l: the crystalline stem length  
L: the contour length of the chain

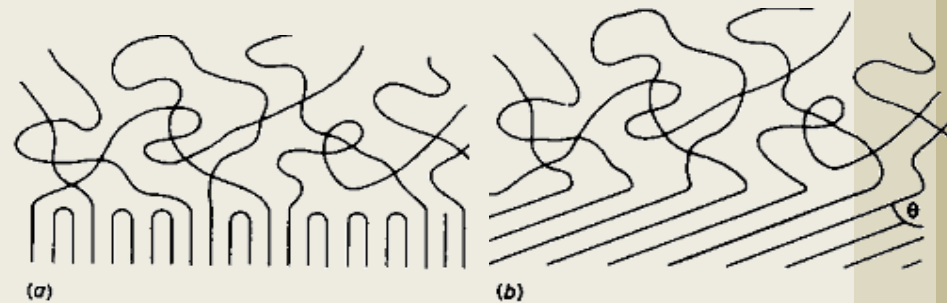


Fig. 6.17 Alternative resolutions of the density paradox  $(1-p-2l/L)\cos\theta < 3/10$ :  
(a) increased chain folding beyond critical value  
(b) oblique angle crystalline stems to reduce amorphous chain density at interface.

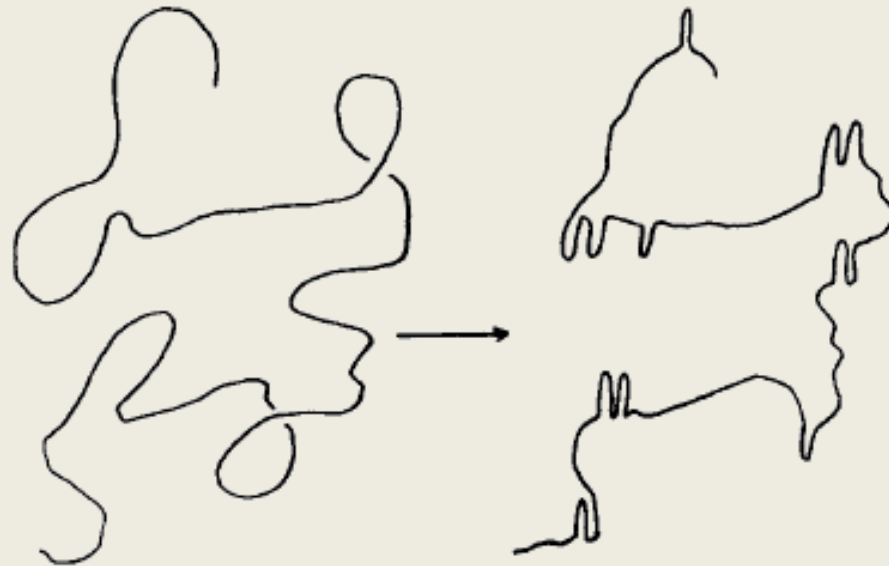


## 6.4. Kinetics of Crystallization

- The above findings led to two different models. i.e.
- *Solidification model*: Dettenmaier et al.  
: Crystallization occurred by a straightening out of short coil sequences without a long-range diffusion process.  
⇒ showed how  $R_g$  values could remain virtually unchanged during crystallization.
- *Variable cluster model*: Hoffman  
: has at least about 2/3 adjacent reentries.
  - ⇒ The fringed micelle model fails, because it predicts that the density of the amorphous polymer at both ends of the crystal will be higher than that of the crystal itself.
  - ⇒ In conclusion, For dilute - solution grown crystals a modified regular reentry model fits best, with the same molecule forming a new stem either after immediate reentry or after skipping over one or two nearest-neighbor sites. For melt-formed crystals, the concept of folded chains is considerably modified.



## 6.4. Kinetics of Crystallization



*Fig. 6.18. The variable cluster model, showing how a chain can crystallize from the melt with some folding and some amorphous portions, and retain, substantially, its original dimensions and its radius of gyration.*



# 6.5. Induced Crystallization of Flexible Polymeric Molecules by Pressure and Stress

## 6.5.1. Pressure-induced Crystallization

❖ The effect of high pressure on the crystallization process

① Enhancement of the formation of crystal modification with a dense packing : favorable for chain extension (Since extended chains have a denser packing than folded chains)

② Rise of the melting temperature : the change of melting temperature;

$$P - P^\circ = a \left[ \left( \frac{T_m}{T_m^\circ} \right)^c - 1 \right] \quad : \text{Simon equation}$$

where  $^\circ$  : the standard condition (atmosphere pressure)

③ The melting temp.  $\uparrow$   
 $\Rightarrow$  the fold length in crystal lamellae  $\uparrow$

- Pressure crystallization is a rather slow process : annealing times ~ several hours or even days
- Formation mechanism direct from the melt

: unfolding and lamella thickening at low temp. for long annealing times.

Fig 6.19

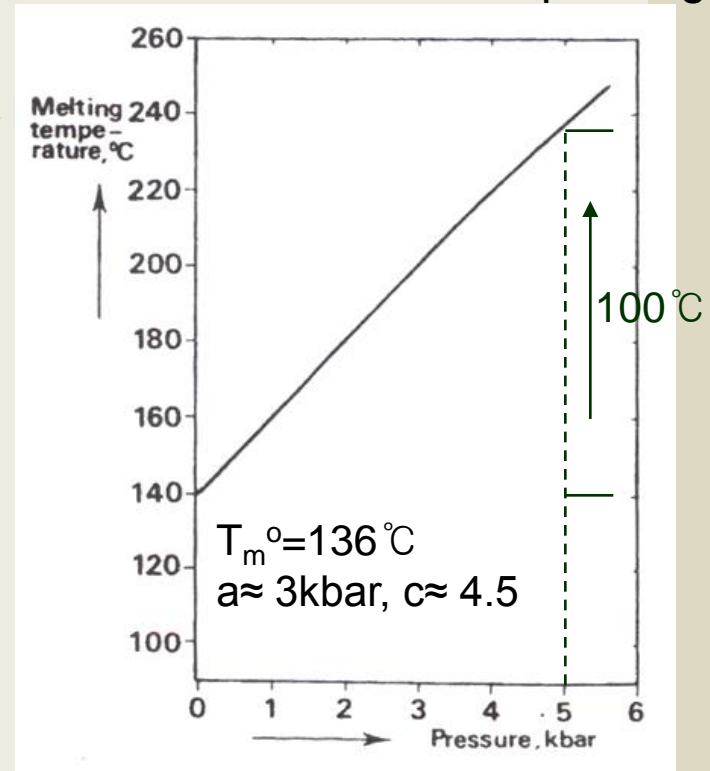


Fig 6.19 Melting temperature of polyethylene as a function of pressure (Osugi and Hara).

# 6.5. Induced Crystallization of Flexible Polymeric Molecules by Pressure and Stress

## ❖ Structure and high-pressure crystallization

- A relation between the tendency toward extended chain crystallization and the melting point dependence on pressure

$$\frac{dT_m}{dP} = T_m \frac{\Delta V_m}{\Delta H_m} = \kappa$$

$$P_{(>100nm)}^{\min} \approx 60\kappa^{-1}$$

-----  
 : The minimum pressure required to form extended chains > 10<sup>-7</sup>m in the crystal

Table 6.7 Correlation between  $\kappa$  and  $P_{(>100nm)}^{\min}$

polymer	$\kappa$ [K/kbar]	$P_{(>100nm)}^{\min}$ [kbar]
PE	25	~3
Nylon	15-40	~2 (?)
PCTFE	65	~1
PTFE	140	~0.3

- The disadvantage of pressure crystallization  
 : a quasi-isotropic brittle product ( ∴ randomly oriented crystallites without much interconnection)  
 → very poor mechanical properties!



# 6.5. Induced Crystallization of Flexible Polymeric Molecules by Pressure and Stress

## 6.5.2. Stress-induced Crystallization

### A. Axially oriented crystallization by drawing of spun filaments

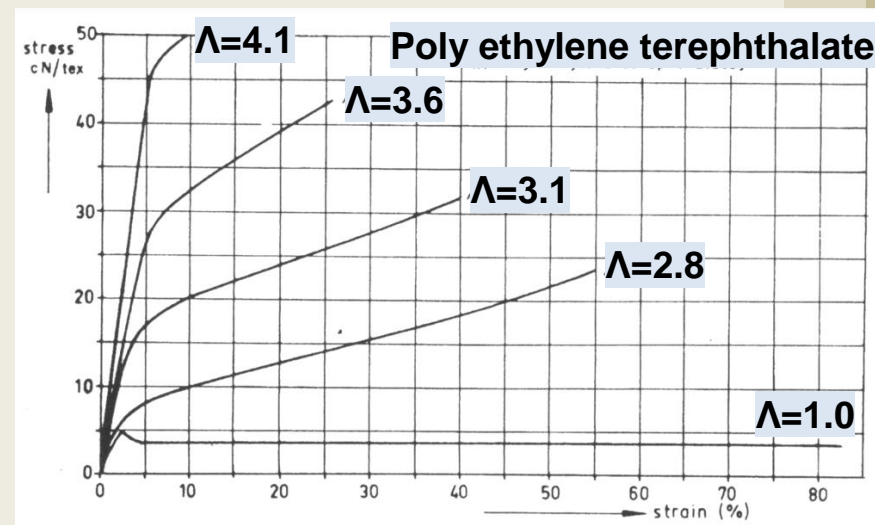
- If an isotropic polymer is subjected to an imposed external stress at a suitable temperature (usually above  $T_g$ )  $\rightarrow$  a structural rearrangement : *orientation*
- Semi-crystalline polymers  $\rightarrow$  drastic rearrangement : *stress-induced crystallization*
- By a drawing machine consists of two sets of rolls  $\rightarrow$  the filament becomes thinner abruptly over a short distance : *neck*  $\rightarrow$  almost completely reorganized
- Rapid cooling-down (under stress)  $\rightarrow$  the orientation is frozen in, combined with a very fast fibrillar crystallization

#### ❖ Properties

Table 6.8 Stretch series of PET yarns

	Draw ratio ( $\Lambda$ )				
	1	2.8	3.1	3.6	4.1
density ( $\rho$ ) (20 °C) (g/cm <sup>3</sup> )	1.338	1.369	1.378	1.380	1.381
crystallinity ( $x_c$ ) (%)	3	22	37	40	41
tensile strength ( $\sigma_{max}$ ) (cN/tex)	11.8	23.5	32.1	43.0	51.6
elongation at break (%)	-	55	39	27	11.5
Young's modulus ( $10^9$ N/m <sup>2</sup> )	2.6	7.8	11.5	14.9	18.0

Fig 6.20 Stress-strain diagram

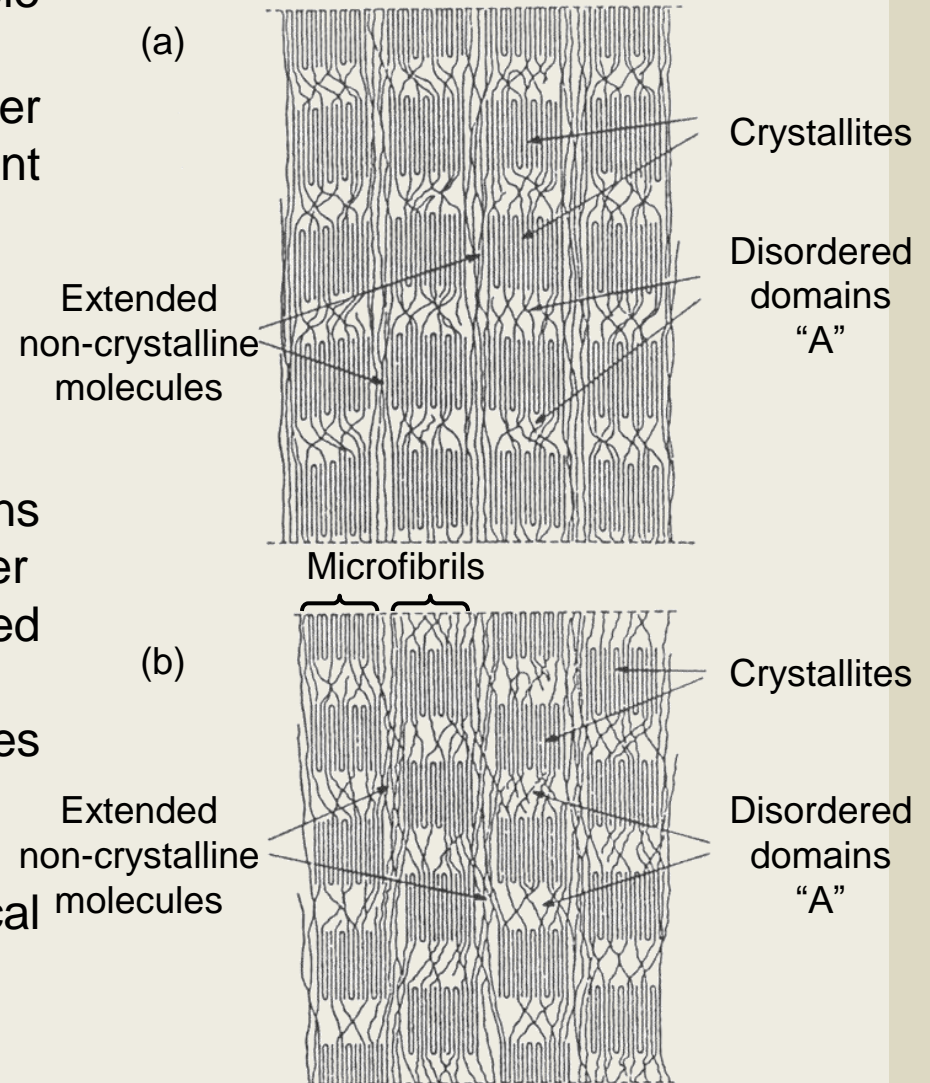


## 6.5. Induced Crystallization of Flexible Polymeric Molecules by Pressure and Stress

### ❖ Morphology

- An interesting model of the possible structure of semi-crystalline yarns : supposes that along the fibrils a number of extended “*tie molecules*” are present → responsible for the strength : at higher draw ratio, tie molecules ↑
- The concept of “*Tie molecules*” : introduced by Peterlin (1973) : part of chains or bundles of chains extending from one crystalline to another : constitute the core of the stretched filament in fibers : concentrate and distribute stresses throughout the materials → strength ↑ and brittleness ↓ → important for the mechanical properties of semi-crystalline polymers

Fig 6.21 Structure model of (a) nylon fibers; (b) PET fibers (fiber axis vertical) as suggested by *Prevorsek and Kwon*.

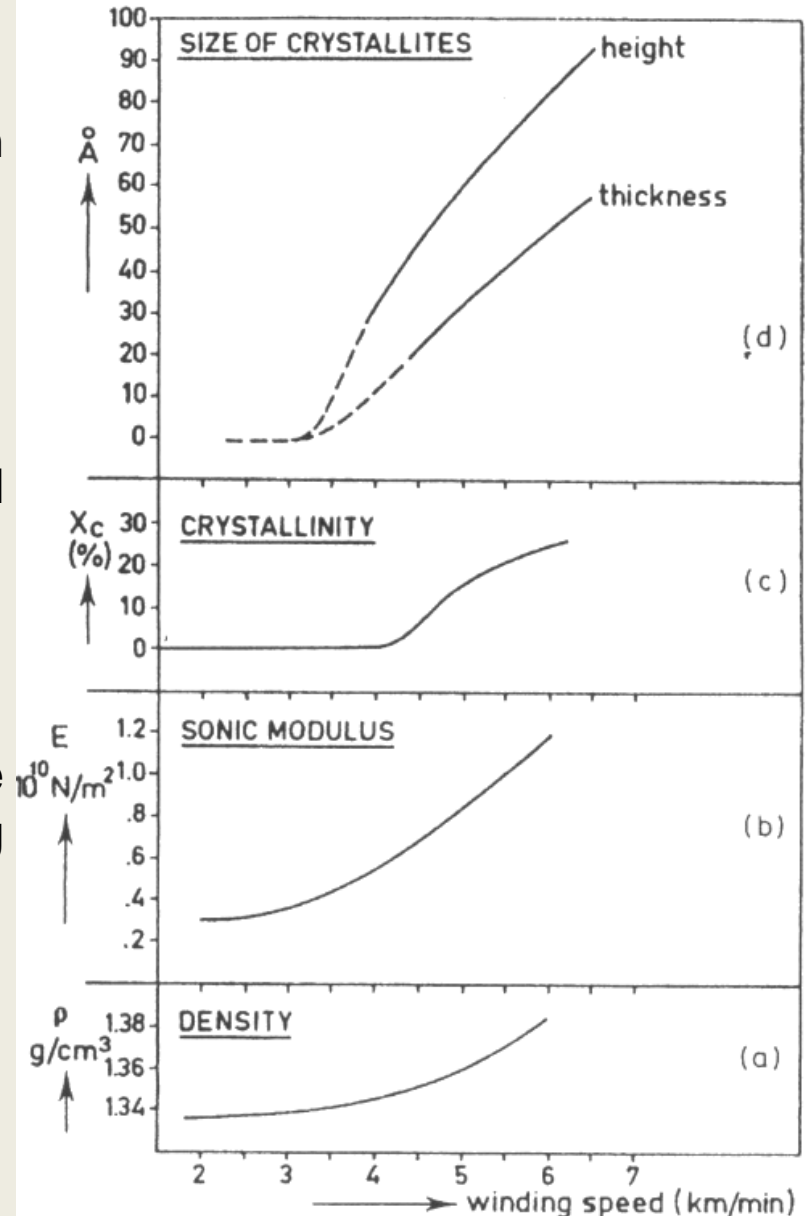


# 6.5. Induced Crystallization of Flexible Polymeric Molecules by Pressure and Stress

## B. Spinning with high-speed winding

- Physical structure of polymers dependent on the rate of extension during spinning (on the winding speed)
- Example of PET
  - at low winding speed  $<35$  m/s  $\rightarrow$  amorphous
  - at high speed  $>100$  m/s  $\rightarrow$  well-developed crystallites of closely packed molecules  $\rightarrow$  Fig 6.22
- The molar mass, the molar mass distribution, the temperature, pre-heating time of melt, the shape of the spinneret and the way of cooling  $\rightarrow$  also influence the crystalline structure

Fig 6.22 Physical constants of PET yarns wound at various speeds (Husman and Heuvel)



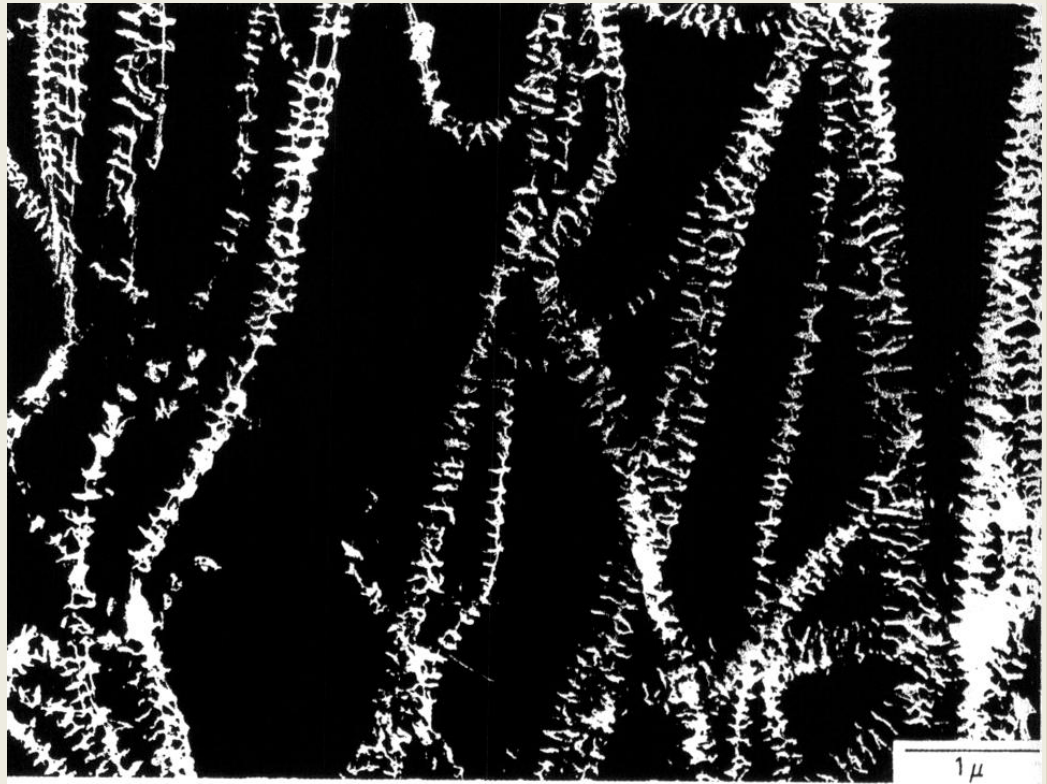


## 6.6. Extended Chain Crystallization of Flexible Polymer Chains

### 6.6.1. Gel-spinning

- Until 1970's, the theoretical modulus of polymer chains and the practical value → a substantial gap → bridged by the fibers made by extended chain crystallization
- *shish kebab structure*  
: Cooling the dilute solution of PE under continuous stirring → very fine fibers → a fine central core of extended CH<sub>2</sub> chains, with an outer sheath of folded chain .

*Fig 6.23 Electron micrograph of polyethylene "shish kebabs" (Pennings et al., 1970).*



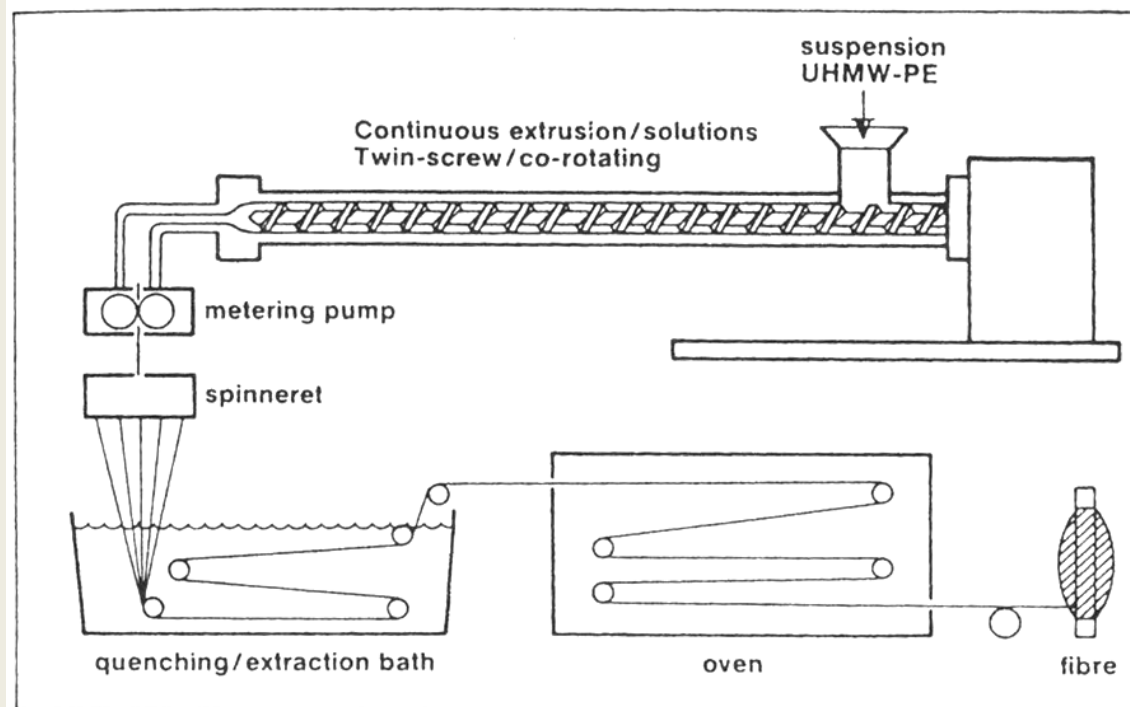


## 6.6. Extended Chain Crystallization of Flexible Polymer Chains

### ❖ Gel-spinning

- produced by spinning a dilute solution of very high MW PE into cold water → drying → drawing in a hot oven at about 120 °C
- Requirements for successful gel-spinning/ultra-drawing
  - a) very high MW ( $M_w > 10^6$ )
  - b) disentangled individual molecular coils (can easily be unfolded on drawing)

Fig 6.24 Experimental set-up for the continuous production of PE fibers.



# 6.6. Extended Chain Crystallization of Flexible Polymer Chains

❖ Some basic considerations

- For chain extension → a considerable stretching force to balance the entropic retracting force of the chains
- The extension time of the same order as the relaxation time of the chains ( $10^{-3}$  s)

$$\begin{aligned} \dot{\epsilon} \cdot \Theta &\approx 1 \text{ for tensile stretch} \\ \dot{\gamma} \cdot \Theta &\approx 1 \text{ for shear stretch} \end{aligned} \quad \left( \begin{array}{l} \dot{\epsilon} = \text{rate of elongation} \\ \dot{\gamma} = \text{rate of shear} \\ \Theta = \text{relaxation time} \end{array} \right)$$

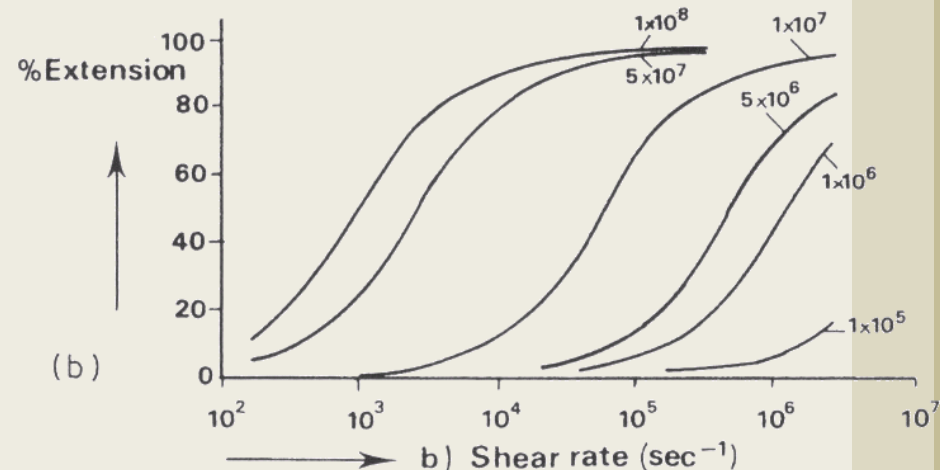
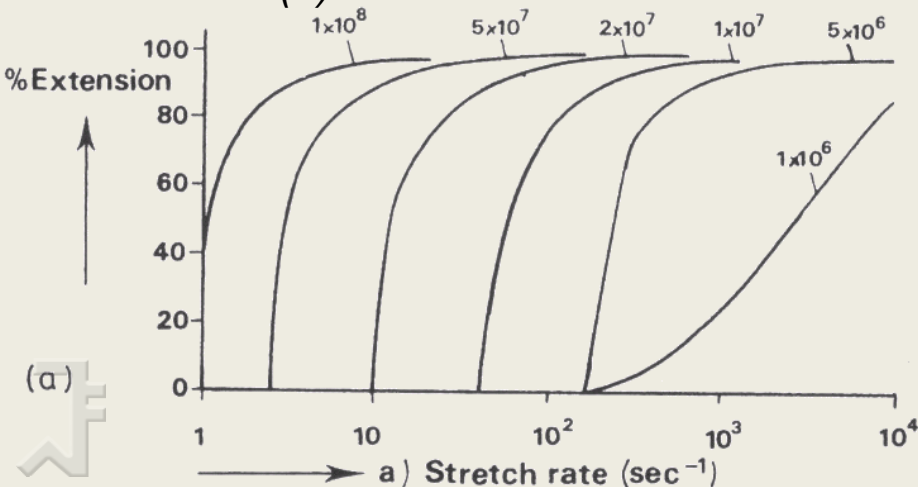
✧ The relaxation time (*Bueche*)

$$\Theta_0 = \frac{6}{n^2} \cdot \frac{\eta_0 \bar{M}}{\rho RT} \rightarrow \text{chain extension is a function of molecular weight}$$

Fig 6.25 Percentage extension by different deformations (for various molecular masses)

(a) a function of the stretch rate

(b) a function of the shear rate



# 6.6. Extended Chain Crystallization of Flexible Polymer Chains

## ❖ Properties of gel-spun yarns

- The difference in drawing behavior between conventional melt-extruded polymers and ultra-drawable gel-spun polymers
- Correlation between the initial concentration of the polymer in its solvent and the attainable draw ratio

$$\Lambda_{\max} = C\phi^{-1/2} \left( \begin{array}{l} C = \text{constant} \\ \phi = \text{polymer vol. fraction} \end{array} \right)$$

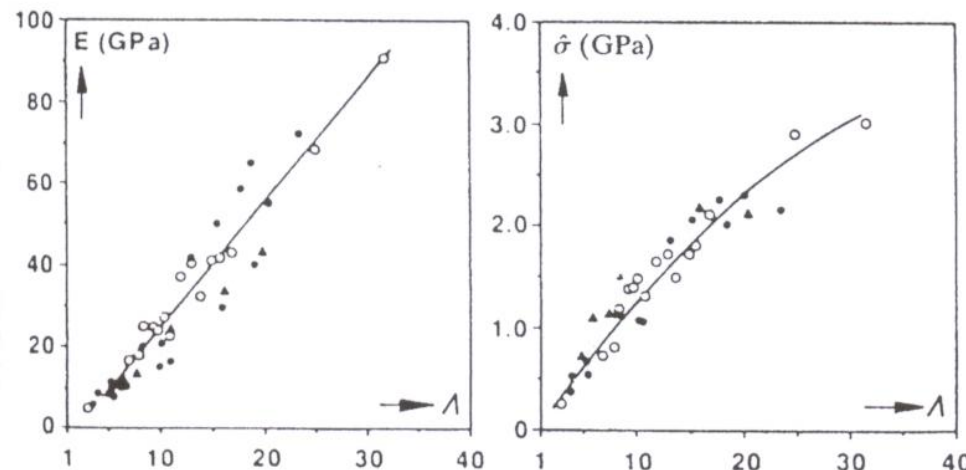
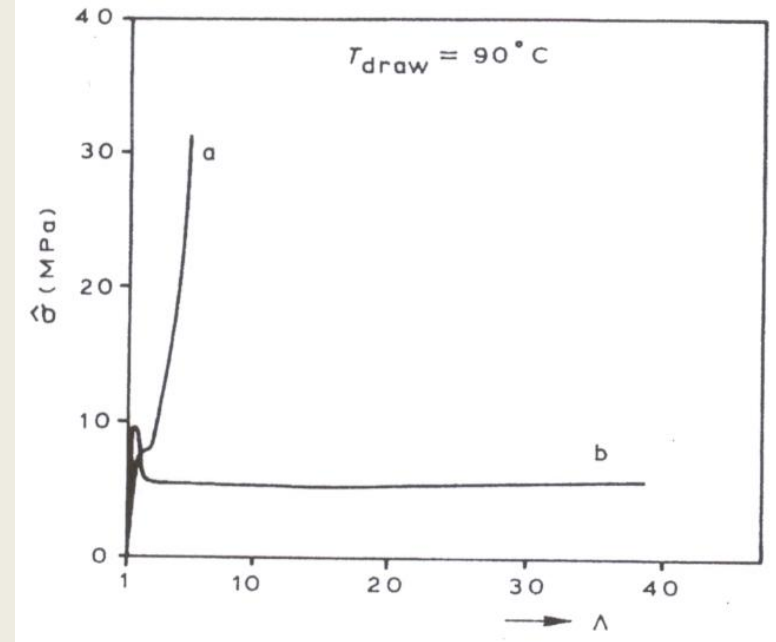
- Relationship between draw ratio, modulus and strength  
: Young's modulus  $\rightarrow$  linear function of draw ratio

$$E(\text{GPa}) = 2.85\Lambda_{\max}$$

- : Strength vs. modulus (well-known form)

$$\hat{\sigma} = 0.1E^{3/4}$$

Fig 6.26 Nominal stress  $\sigma$  vs. draw ratio (a) melt-crystallized; (b) solution-spun/extracted

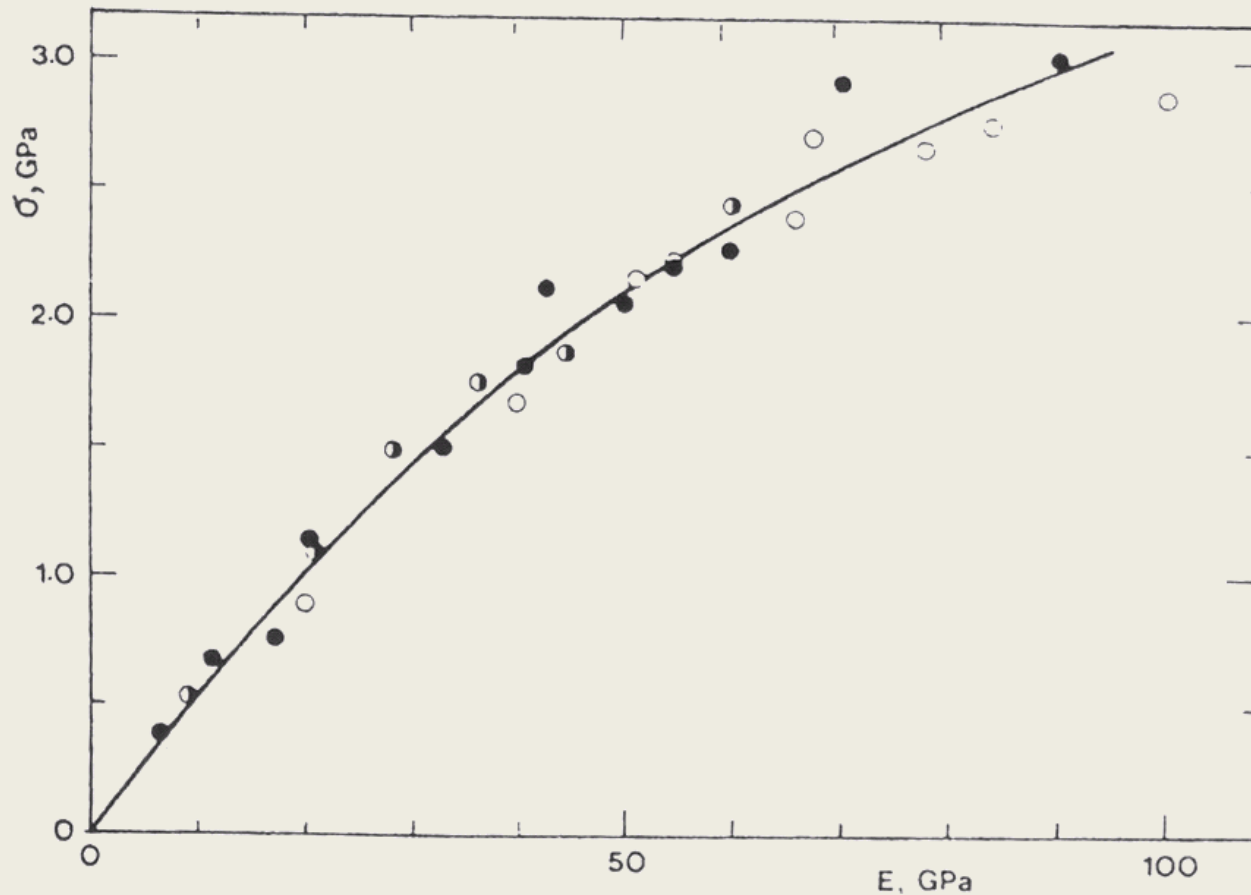


## 6.6. Extended Chain Crystallization of Flexible Polymer Chains



$$\hat{\sigma} = 0.1E^{3/4}$$

Fig 6.27 Tensile strength vs. Young's modulus for high MW PE ( $M_n=200 \times 10^3$ ,  $M_w=1.5 \times 10^6$ ): (○) surface grown (●) solution spun-drawn wet; (◐) solution spun/drawn dried



## 6.6. Extended Chain Crystallization of Flexible Polymer Chains



### ❖ Restrictions

- Heating above  $T_m$  for a short time ( $\sim 1$  min)  $\rightarrow$  ultra-drawability of gel-spun polymers destroys  $\rightarrow$  retract to folded chains  
 $\rightarrow$  use temperature is about  $40^\circ\text{C}$  below  $T_m$
- For ultra-drawing, polymer should have smooth chains without large side groups or H-bonded groups and with as few entanglement as possible
- For limited number of polymers, ultra-drawing has proved possible and successful : linear PE, PP, poly(oxymethylene), PVA and PAN



## 6.6. Extended Chain Crystallization of Flexible Polymer Chains



Table 6.9 Physical properties of para-crystalline fibers in comparison with other reinforcing materials

Properties		Paracrystalline fibers						Conventional spun/drawn fibers		Inorganic filaments	
		Aramid		Carbon		Arom. polyester	Gel-spun PE	PA-6	PETP	E-glass	Steel
		HM	HS	HM	HS						
Modulus E and E/ρ (specif.)	Tensile (GPa)	130	65	400	230	75	150-220	5-15	10-20	75	200
	Do, theor.* (GPa)	240	240	960	960	(250)	250	170	137	69-138	208
	Tensile (specific) (N/tex)	90	45	300	150	35	200	7	10	20	26
Strength σ and σ/ρ (specif.)	Tensile (GPa)	3.0	4	2.3	3.1	2.9	3.5	0.8	1	2.1	2.8
	Do., theor.* (GPa)	21	21	4	5.7	-	25	28	17	11	11
	Tenacity (N/tex)	2.1	2-3	1.2	2-3	2.1	3.5	0.8	0.75	0.8	0.35
	Compression (GPa)	0.25	0.3	1.5	2.5	-	-	0.7	0.1	0.5	2.4
	Do. (specific) (N/tex)	0.17	0.2	0.86	1.3	-	-	0.07	0.07	0.19	0.31
other Physical Properties	Density (g/cm <sup>3</sup> )	1.44	1.44	1.90	1.74	1.40	1.0	1.1	1.38	2.6	7.8
	Max. working temp. (°C)	200	250	600	500	150	60	120	120	350	300
	T <sub>m</sub> (°C)	480	480	3600	3600	305	135	220	260	700	1400
	T <sub>d</sub> (°C)	480	480	3600	3600	400	390	350	380	-	-
	brittleness (test result)	+	+	-	-	+	+	+	+	-	+

## 6.7. Extended Chain Crystallization of Rigid Macromolecules

- ❖ the para-para type aromatic polymers (ex. Aramid )
  - : theoretically high orientation in fiber form
  - : difficulty in melting and dissolution
  - Fortunately exhibit the unusual property to be able to form liquid crystalline under certain condition)
  - Details in next chapter (chapter 7)
- ❖ Properties
  - : theoretical expression for the modulus and the elastic stress-strain relation for aramid fibers

$$\frac{1}{E} = \frac{1}{e_c} + \frac{\langle \sin^2 \Phi_0 \rangle}{2g} \quad \varepsilon = \frac{\sigma}{e_c} + \frac{\langle \sin^2 \Phi_0 \rangle}{2} \left[ 1 - \exp \left( 1 - \frac{\sigma}{g} \right) \right]$$

$e_c$  = the chain modulus

$g$  = the modulus for shear between chains

$\langle \sin^2 \Phi_0 \rangle$  = initial orientation distribution parameter



## 6.8. Methods of Determining Crystal Structure

### 6.8.1. A Review of Crystal Structure

- The science of geometric crystallography  
: being concerned with the outward spatial arrangement of crystal planes and the geometric shape of crystals.  
→ Three fundamental laws

#### ❖ *Three fundamental laws*

##### (a) the law of constancy of interfacial angle

- For a given substance corresponding faces or planes that form the external surface of a crystal always intersect at a definite angle. This angle remains constant independent of the sizes of the individual faces.

##### (b) the law of rationality of indices

- For any crystal a set of three coordinate axes can be chosen such that all the faces of the crystal will either intercept these axes at definite distances from the origin or be parallel to some of the axes.
- Weiss indices = 1/ Miller indices

$$(ma : nb : pc) = \left( \frac{1}{m} a : \frac{1}{n} b : \frac{1}{p} c \right)$$



## 6.8. Methods of Determining Crystal Structure

### ❖ *Three fundamental laws*

#### (c) the law of symmetry

- All crystals of the same compound possess the same elements of symmetry.

#### ▪ Three Types of Symmetry

- ① a plane of symmetry : passes through the center of the crystal and divides it into two equal portions, each of which is the mirror image of the other.
- ② a line of symmetry : an imaginary line through the center of the crystal to appear unchanged two, three, four, or six times in  $360^\circ$  of revolution.
- ③ a center of symmetry : If every face has an identical atom at an equal distance on the opposite side of this center.



## 6.8. Methods of Determining Crystal Structure

### 6.8.2. X-ray Methods

▪ *Bragg's Law*  $2d \cdot \sin \theta = n\lambda$

: the intensity of the diffraction spot or line depends on

- ① the scattering power of the individual atoms, which in turn depends on the number of electrons in the atom.
- ② the arrangement of the atoms with regard to the crystal planes
- ③ the angle of reflection
- ④ the No. of crystallographically equivalent sets of planes contributing
- ⑤ the amplitude of the thermal vibrations of the atoms.

: Intensity & the positions are required to calculate the crystal lattice.

### 6.8.3. Electron Diffraction of Single Crystals

: provides a wealth of information about the very small, including a view of the actual crystal size and shape.



## 6.8. Methods of Determining Crystal Structure

### 6.8.4. IR Absorption

- ① IR Spectra of semicrystalline polymer include "crystallization-sensitive lands." - intensities of these lands vary with the degree of crystallinity.
- ② By measuring the polarized infrared spectra of oriented semicrystalline polymers, information about both the molecular and crystal structure can be obtained. Both uniaxially and biaxially oriented samples can be studied.
- ③ The regular arrangement of polymer molecules in a crystalline region can be treated theoretically, utilizing the symmetry properties of the chain or crystal. With the advent of modern computers, the normal modes of vibrations of crystalline polymers may be calculated and compared with experiment.
- ④ Deuteration of specific group yields information about the extent of the contribution of a given group to specific spectral lands. This aids in the assignment of the lands as well as the identification of lands owing to the crystalline and amorphous regions.



## 6.8. Methods of Determining Crystal Structure

### 6.8.5. Raman Spectra

- ① Since the selection rules for Raman and IR spectra are different, Raman spectra yield information complementary to the IR spectra.
  - For example, the S-S linkages in vulcanized rubber and the C=C bonds yield strong Raman spectra but are very weak or unobservable in IR spectra.
- ② Since the Raman spectrum is a scattering phenomenon, whereas the IR methods depends on transmission, small bulk, powdered, or turbid sample can be employed.
- ③ On analysis, the Raman spectra provide information equivalent to very low-frequency measurements, even lower than  $10\text{cm}^{-1}$ . Such low-frequency studies provide information on lattice vibrations.
- ④ Polarization measurements can be made on oriented samples.





# Keywords in Chapter 7

- Nematic, Smectic, Cholesteric, Discotic
  - First-order transitions in LC
- Lyotropic, Thermotropic, Mesogenic
  - $\chi_1$  for LC

