Chapter 7. Crystalline Polymers

7.1 Background

Crystalline polymers ~ regular chain structure

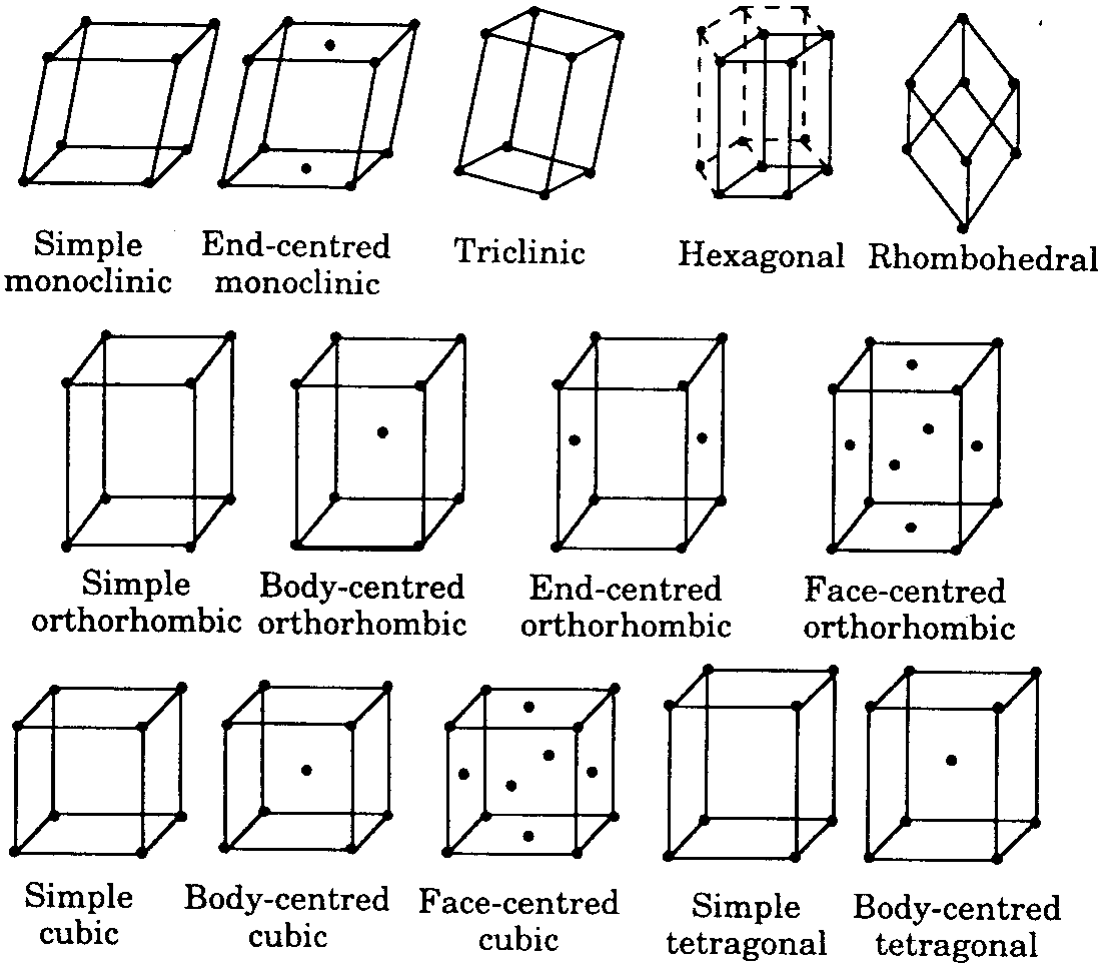
specific preferred chain conformation

* Crystal systems (7 groups)

Table 7.1 Crystal systems

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

* Unit cells of the 14 Bravais lattices



* Polyethylene crystal

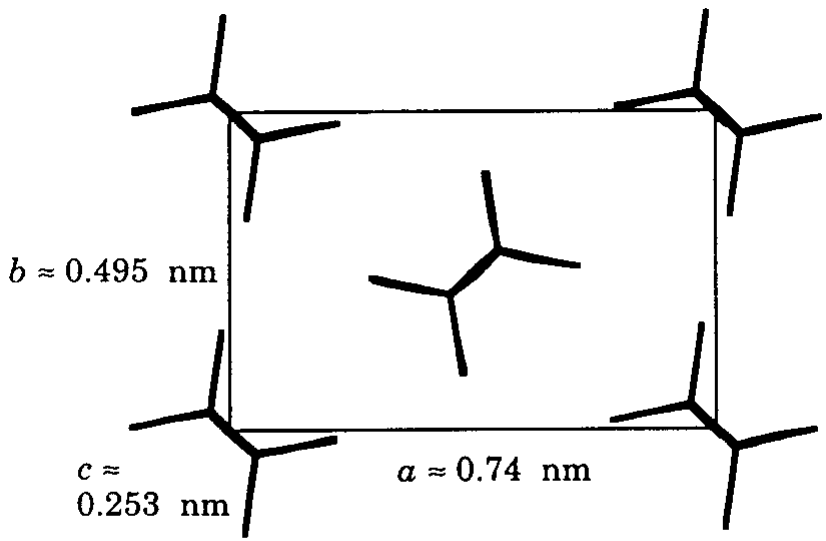


Figure 7.2 View along *c* (chain) axis of orthorhombic polyethylene crystal.

※ ***Crystal structure*** *(Miller indicies)* to denote **planes** and **directions**

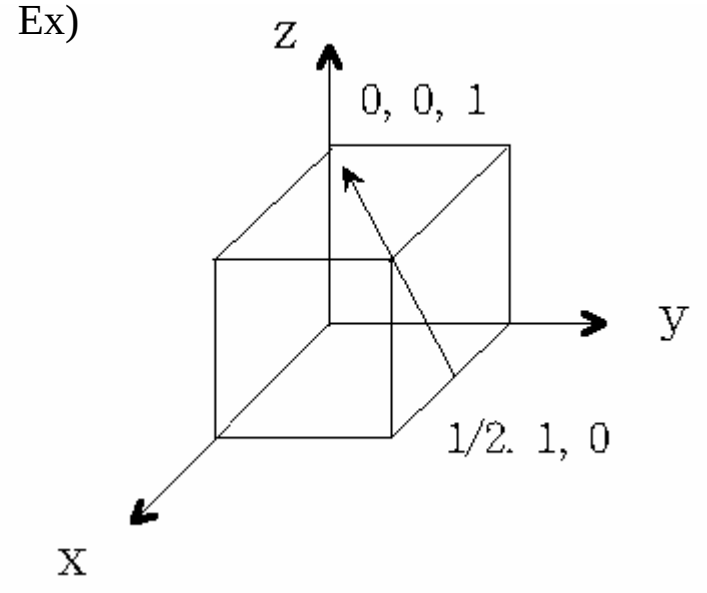
· **Directions**: ① Subtract the tail coordinates from the head coordinates

② Make the resulting number into lowest integer

[ ], < >

↘ a group of equivalent directions

Ex)



① 0-1/2, 0-1, 1-0 --> -1/2, -1, 1

② [-1, -2, 2] --> [$\bar{1}$ $\bar{2}$ 2]

< 1 1 0 > represents [1 1 0], [$\bar{1}$ $\bar{1}$ 0]

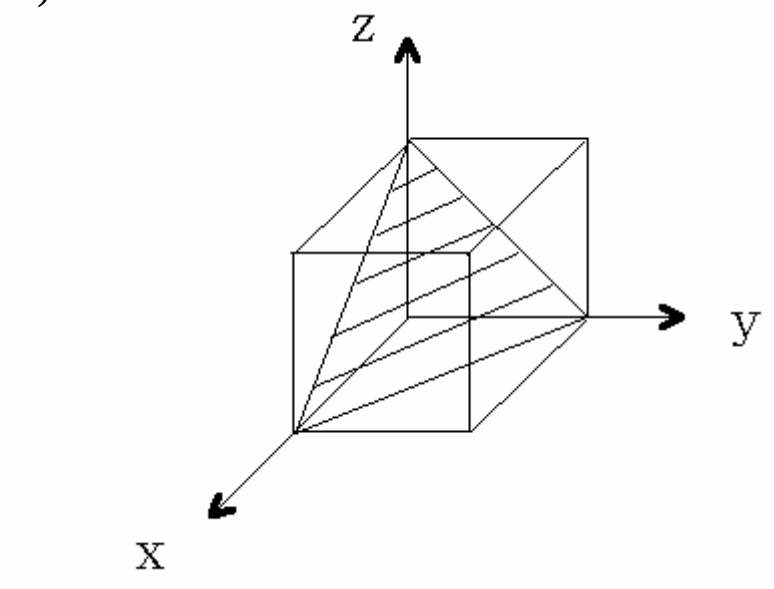
· **Planes**: ① Determine the points at which the plane intercepts the x, y, z coordinates

② Take the reciprocals of these intercepts

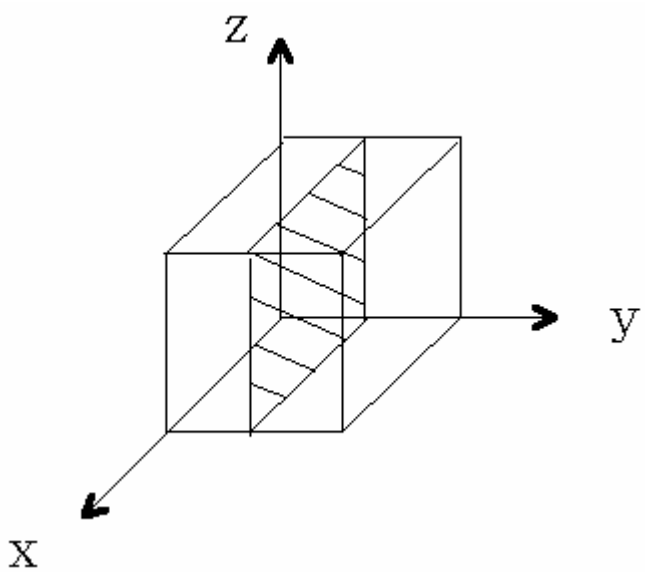
( ), { }

↘ a group of equivalent planes

Ex)



(1 1 1)



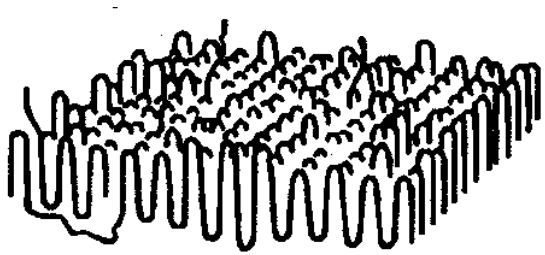
∞, 1/2, ∞ --> (0 2 0)

{ 1 0 0 } represents

(1 0 0), (0 1 0), (0 0 1),

($\bar{1}$ 0 0), (0 $\bar{1}$ 0), (0 0 $\bar{1}$)

7.2 Crystal lamella



From X-ray diffraction, polymers never crystallize to 100%.

. Fringed micelle crystal

. Folded chain crystal, 10nm thick

regular facets, chain direction perpendicular to the lamellar surface

- Examples for the case of *polyethylene*

  Single crystals of linear PE

  from dilute solutions in xylene

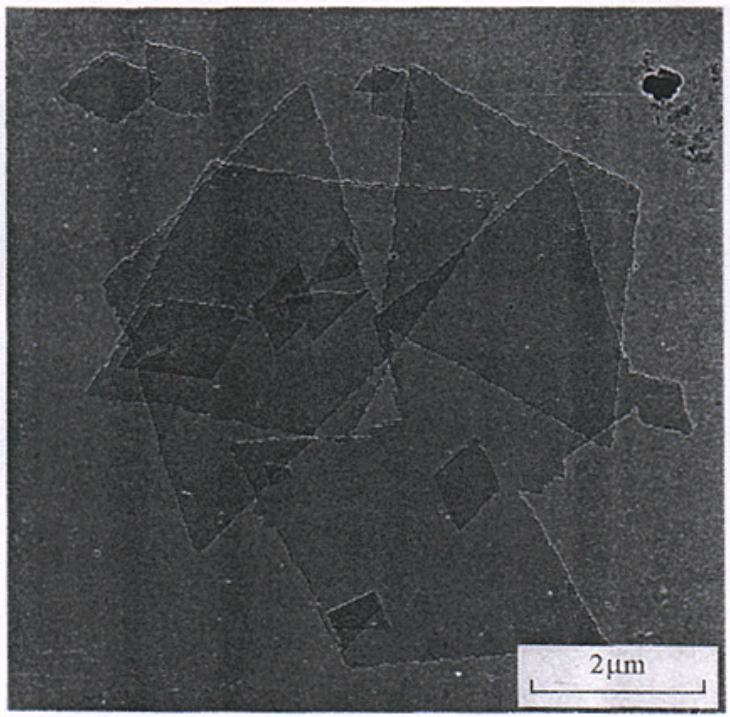


Figure 7.11 Single crystals of linear polyethylene (BP Rigidex 140 60) crystallized from dilute solution in xylene at 74°C. Transmission electron micrograph by A. M. Hodge and D. C. Bassett, University of Reading, Reading, UK.

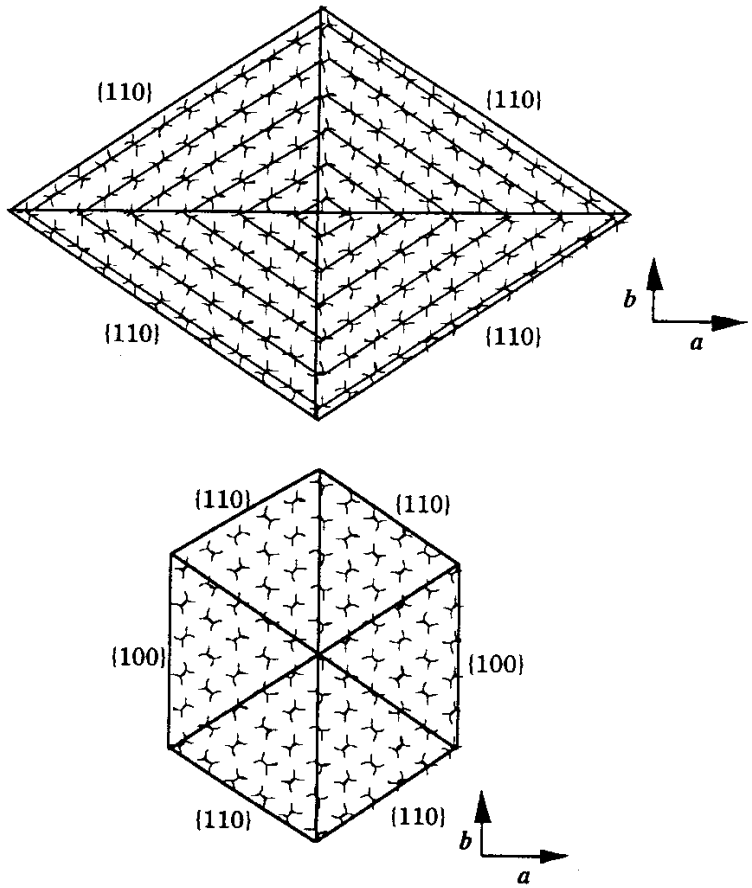


Figure 7.12 Sectorization of polyethylene single crystals. Upper crystal shows only {110} sectors whereas the lower also has {100} sectors.

Hollow pyramid shape --> chain axis ≠ normal of the lamella

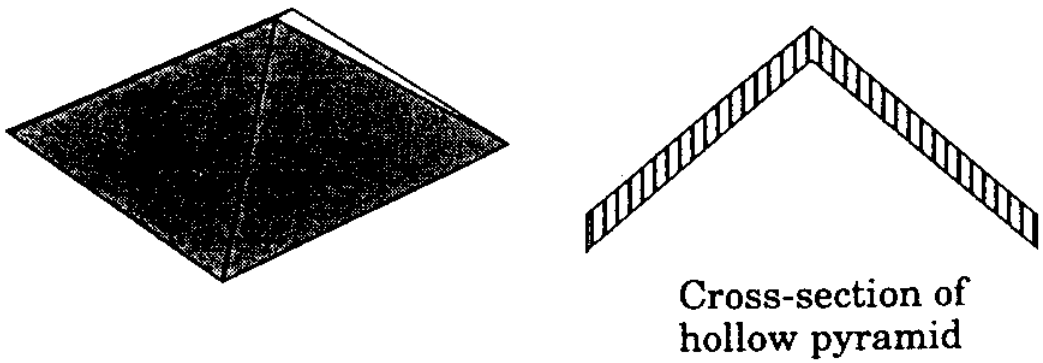


Figure 7.13 Pyramid-shaped single-crystal.

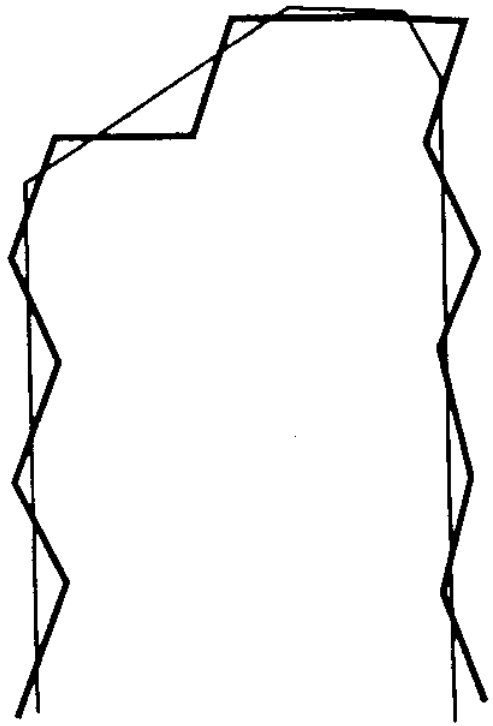
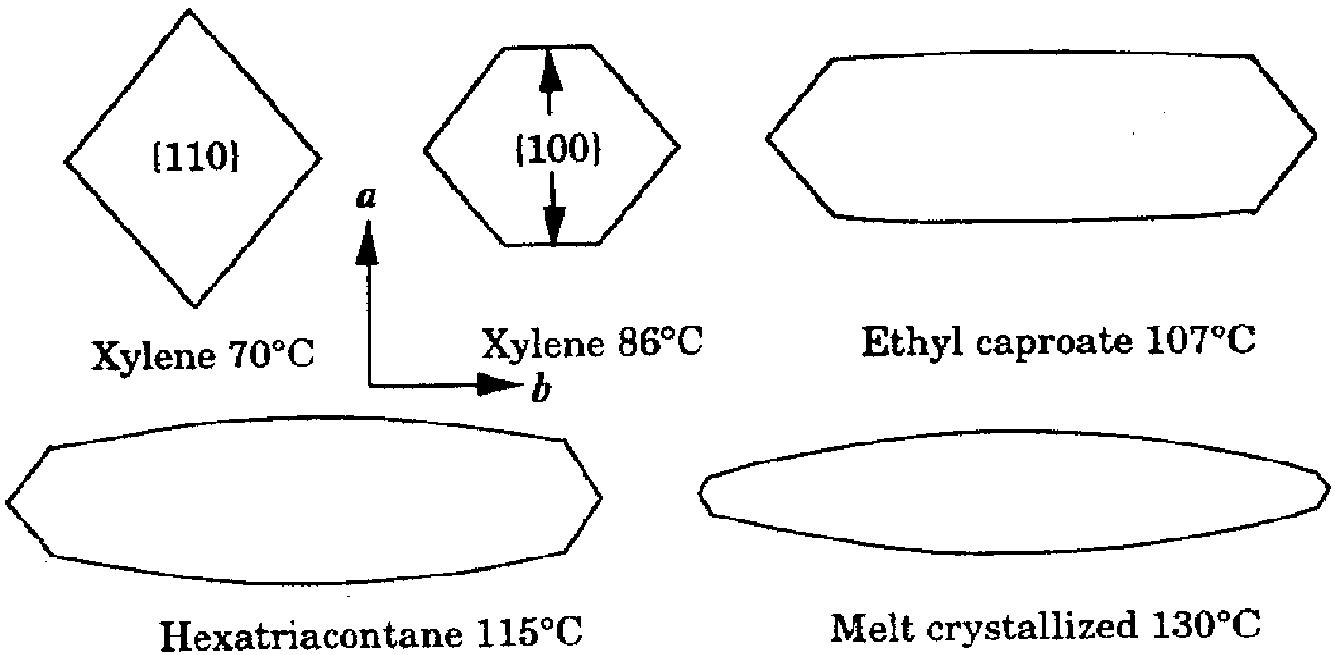


Figure 7.14 Crystallographic (110) fold in linear polyethylene. Note that the lamellar surface and the chain axis are not perpendicular to each other.



Lateral shape of crystals of linear polyethylene crystallized in dilute solutions

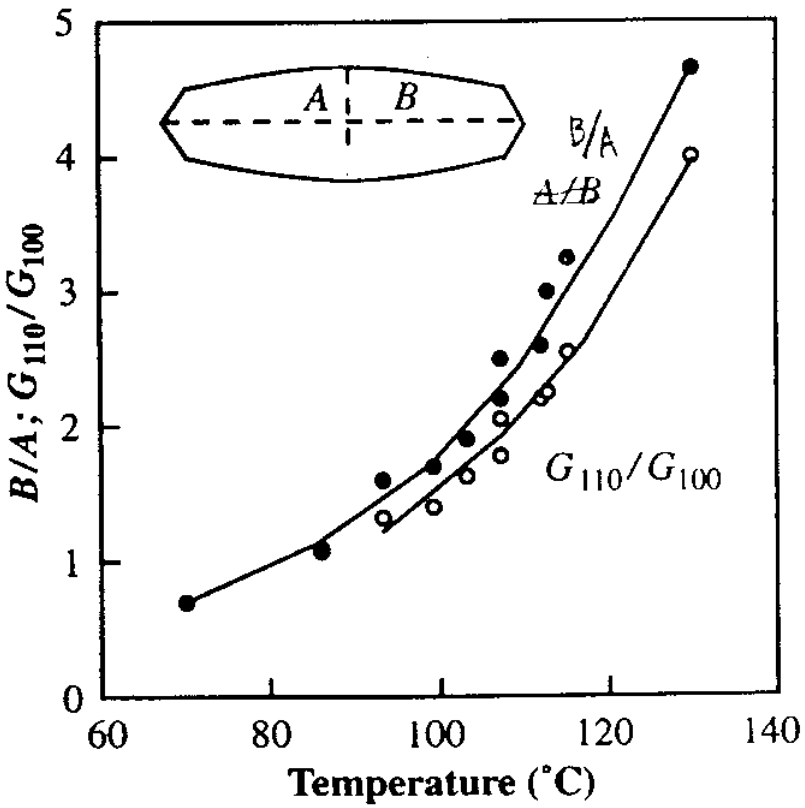
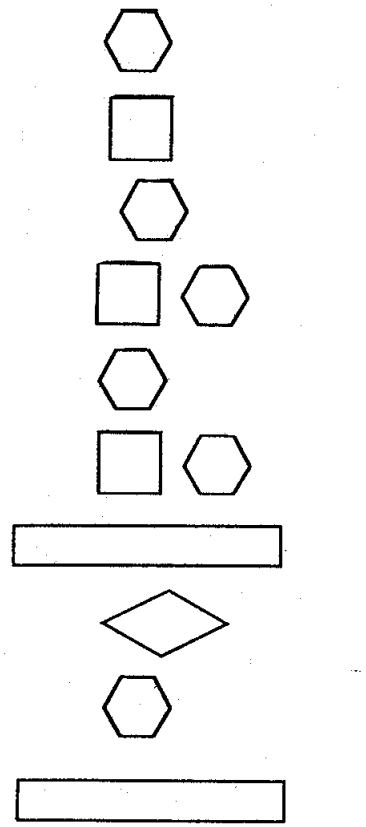


Figure 7.16 Lateral aspect ratio (B/A) and calculated ratio of the linear growth rates perpendicular to $\{110\}$ and $\{100\}$. Drawn after data from Organ and Keller (1985) and Bassett, Olley and Al Reheil (1988).

Table 7.2 Lateral shapes of solution-grown single crystals

Polymer	Shape/comments
Polyoxymethylene	Six-sided (hexagonal hollow pyramids)
Poly(4-methyl-1-pentene) (isotactic form)	Square-based hollow pyramid
Polytetrafluoroethylene	Irregular hexagonal lamellae
Poly(1-butene)	Square and hexagonal lamellae
Polystyrene (isotactic form)	Hexagonal lamellae
Poly(ethylene oxide)	Square and hexagonal lamellae
Poly(ethylene terephthalate)	Flat ribbons of 30 nm width to spindle-like lamellae
Polyamide 6	Lozenge-shaped lamellae
Polyamide 6,6	Irregular hexagonal lamellae and flat ribbons with H-binding plane parallel to the long direction of the ribbon
Polypropylene (isotactic form)	Lath-shaped lamellae



. thickness-to-width ratio : 0.01 - 0.001

· *Annealing* of monolayer single crystals (at high T)

--> crystal thickening & formation of holes

→ "thermodynamically more stable"

E of lateral surfaces : 15mJ/m^2

E of fold surfaces : 90mJ/m^2

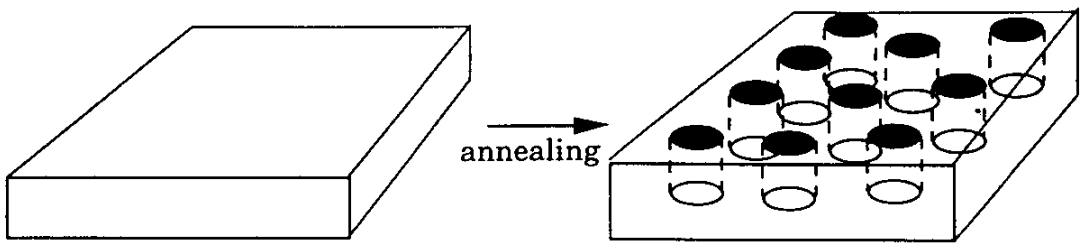


Figure 7.18 Annealing (heat treatment) of a solution-grown monolayer single crystal of polyethylene (schematic drawing).

. Melting point depends on heating rate. (m. p. ↓ with heating rate ↑)

Thin crystals thicken during heating. (thickness ∝ log(annealing time))

. At elevated pressure (4-6 kbar), thick (μm) crystal lamellae are formed.

· *Thompson-Gibbs* (TG) *equation*

<-- relating melting point and crystal thickness

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

: linear relationship between m.p. & 1/crystal thickness

where, T_m^0 : m. p. at equilibrium value (infinite crystal thickness)

σ : fold surface free energy

L_c : thickness of lamellar crystals

ρ_c : density of crystal phase

Δh^0 : heat of fusion

* Experimental techniques

TEM(transmission electron microscopy)

: Main technique to observe lamellar crystals

Can be viewed after shadowing with a heavy metal (e.g. Au or Pd/Pt)

Density difference between crystalline & amorphous components gives contrast

ex.) PE sample --> etching with chlorosulphonic acid

--> staining with uranyl acetate

(Uranium은 amorphous 성분에 선택적으로 착색)

Unsaturated polymers (ex. polybutadiene or polyisoprene)

--> are stained with OsO_4

↘ double bond에 착색, shrinkage의 문제

PS or PA are stained with RuO_4

Figure 7.24 Contrast from a stained section with crystals (low density, white areas) and amorphous domains (high density, heavier elements have been added, black areas).

XRD (X-ray diffraction)

: Provides information about the crystal thickness

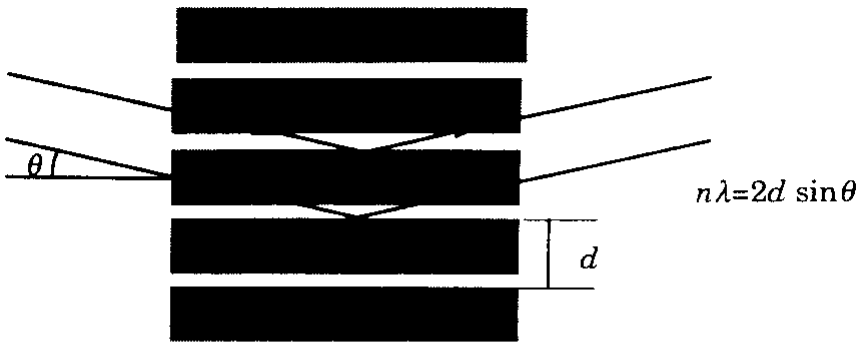


Figure 7.26 Small-angle diffraction from a stack of lamellar crystals (shaded areas) with the repeating distance (long period) *d*. The condition for constructive interference is expressed in the Bragg equation.

Bragg equation :

$$d = \frac{n\lambda}{2\sin\theta}$$

λ : X-ray wavelength

n : order of reflection

θ : angle between beam & planes

7.3 Crystal lamella stack

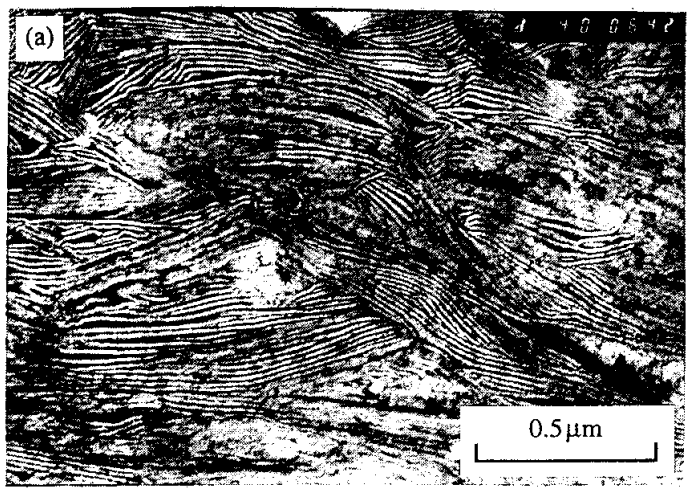
Crystal growth from the concentrated molten state

lamella stack --> almost parallel

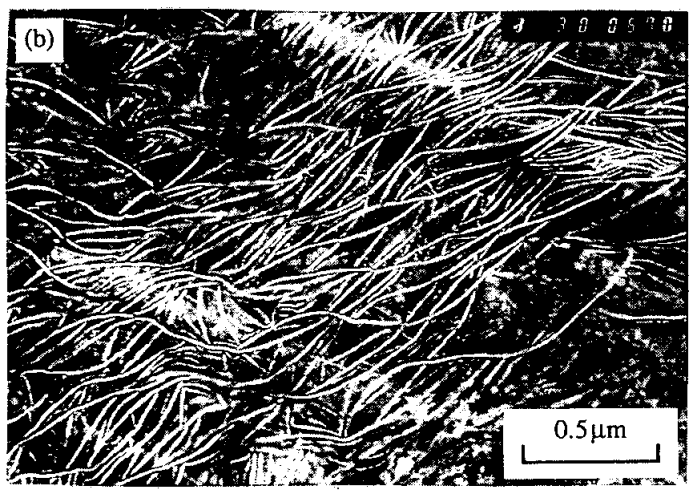
amorphous component between crystal lamellae

--> amorphous density is 10-20% lower than the crystal density

shape -- function of MW, chain branching, crystallization T



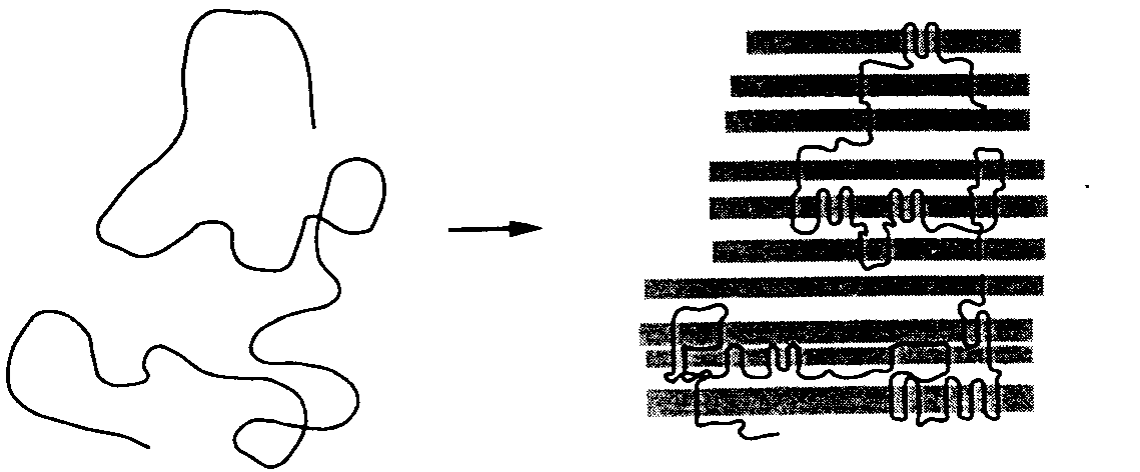
(a) linear polyethylene (HDPE)



(b) branched polyethylene (LDPE)

Change in conformation of a single chain on crystallization under rapid cooling

: about 90% of chain ends are located in the amorphous phase



Molecule in melt

Molecule in semicrystalline state

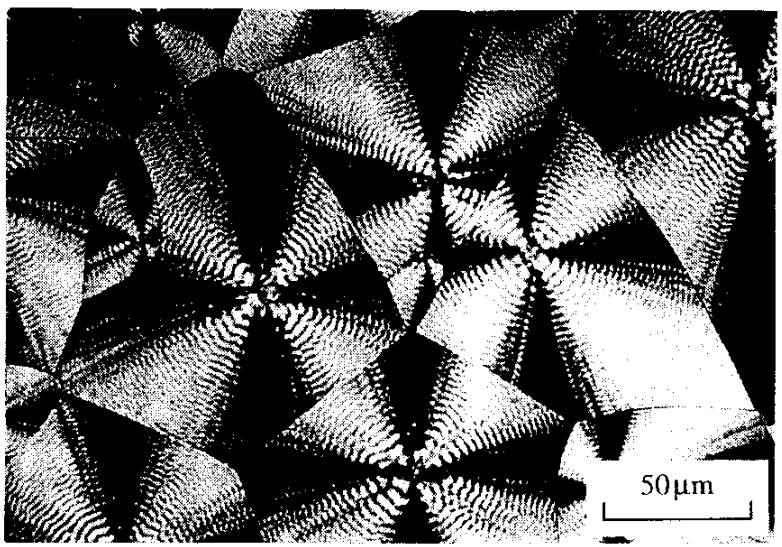
7.4 Supermolecular structure

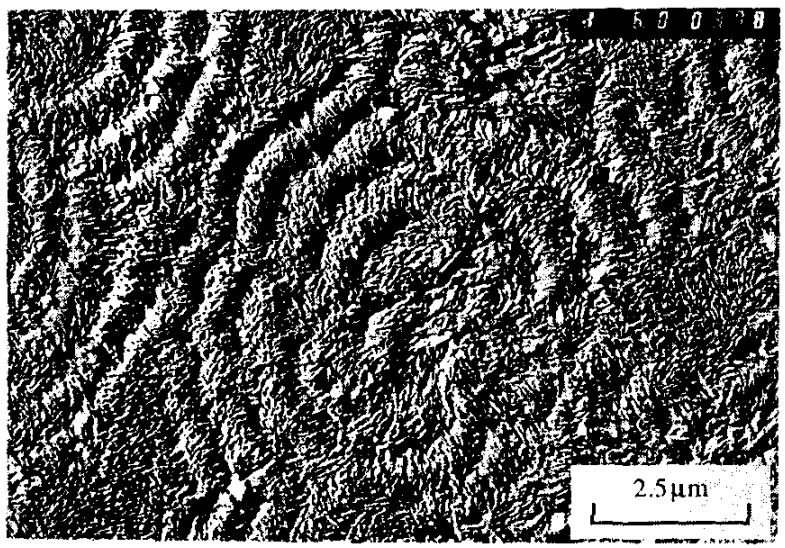
Size : 0.5 $\mu m \sim mm$

Spherulite (“ball” or “globe”) -- polycrystalline

Two refractive indicies : n_t (tangential) & n_r (radial)

$n_t > n_r$: negative spherulites (most polymers)





"*Crystallization induced by orientation*"

(or orientation-induced crystallization)

: shish-kebab morphology

(from solutions subjected to elongational flow)

- shish : a central group of highly oriented fibrils
- kebab : a great many grown lamellar crystals

Table 7.3 Supermolecular structures found in polyethylene

Superstructure	Internal structure	Molecular structure	Crystallization conditions
Axialites (sheaves)	Straight or roof-shaped lamellae	Low molar mass	High crystallization temperature
Banded spherulites	S- or C-shaped lamellae	Intermediate molar mass	Low crystallization temperature
Non-banded spherulites	Straight or weakly 'bent' lamellae	Intermediate molar mass	Intermediate crystallization temperature
Random lamellar structure	Randomly oriented lamellae, short and C-shaped	Very high molar mass	Formed at all temperatures
Shish-kebab structure	Fibrous core with lamellar overgrowth	Intermediate to high molar mass	Oriented crystallization from solution
Row-nucleated structure	Fibrous core with lamellar overgrowth	Intermediate to high molar mass	Oriented crystallization from the melt
Trans-crystalline structure	Columnar growing lamellae	–	Crystallization from a foreign or own nucleating surface