Chain Folding

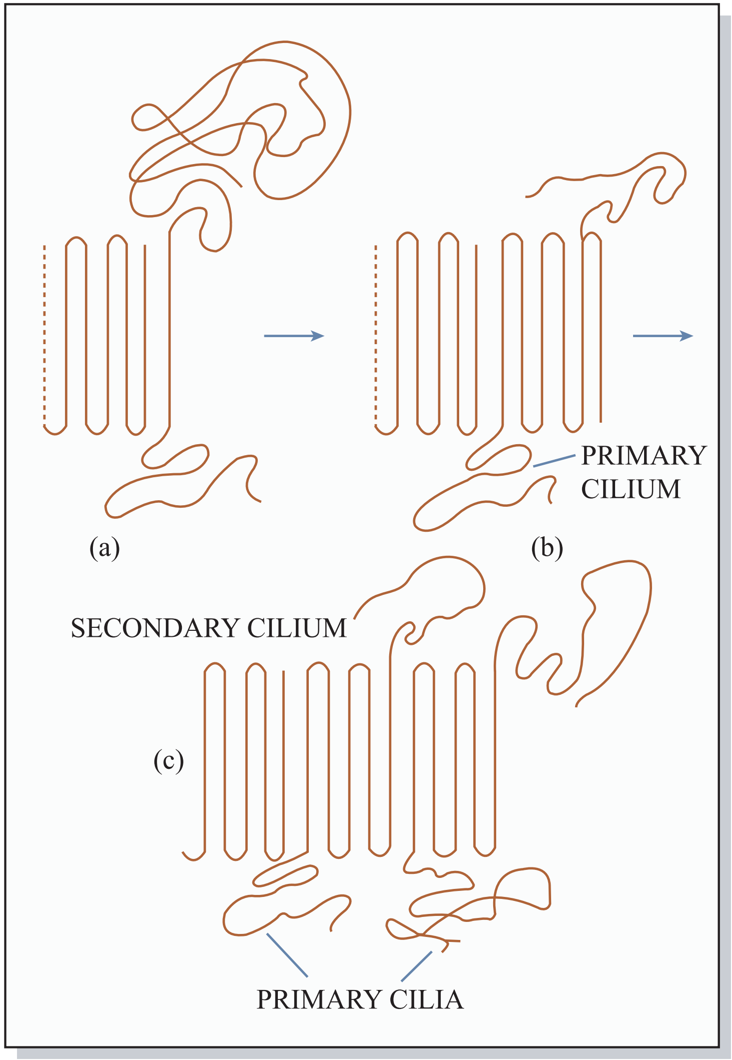
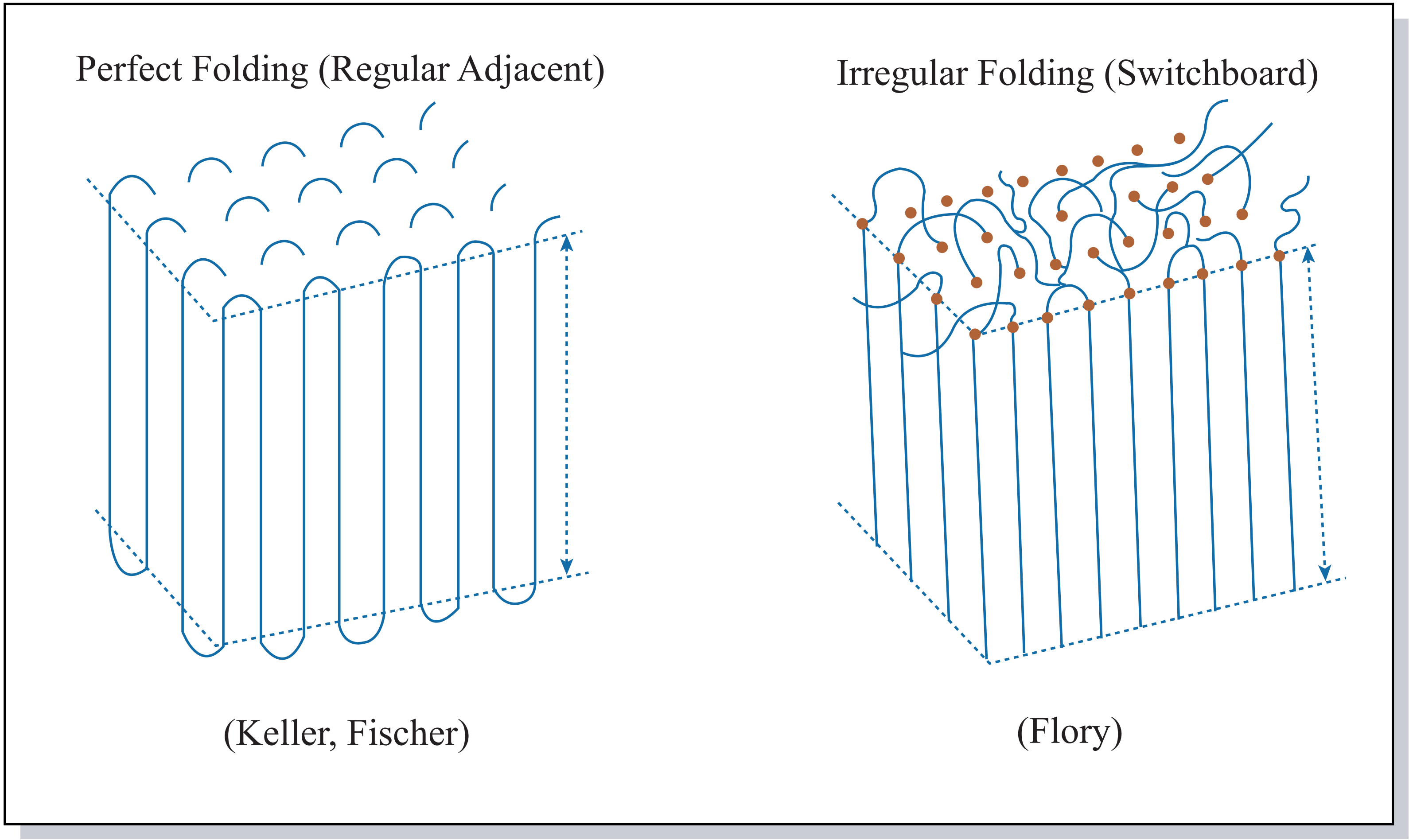


Figure by MIT OCW.

Chain Folding

Perfect vs Irregular



Perfect Folding (Regular Adjacent)

Irregular Folding (Switchboard)

(Keller, Fischer)

(Flory)

Figure by MIT OCW.

Orthorhombic Polyethylene Structure

(Bunn, 1953)

C4 H8

Image removed due to copyright restrictions.

Please see Fig. 1 in Keller, A. “Polymer Crystals.” *Reports on Progress in Physics* 31 (July 1968): 624-704.

a = 7.4Å
b = 4.93Å
c = 2.54Å

Regular adjacent

$$\rho_c = 1.0 \frac{g}{cm^3} \qquad \rho_a = 0.86 \frac{g}{cm^3}$$

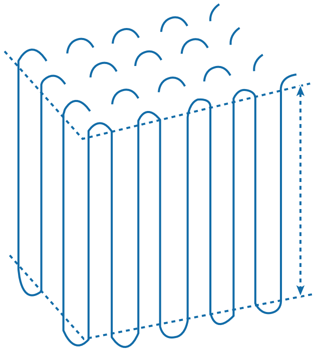
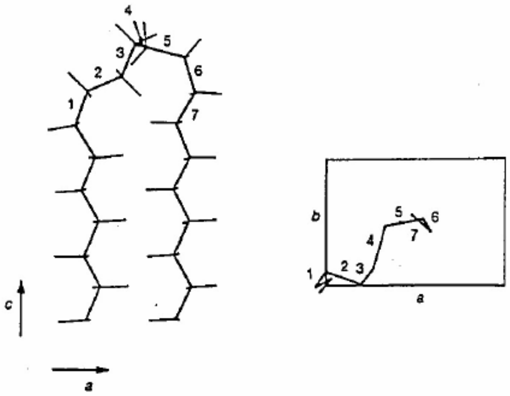


Figure by MIT OCW.



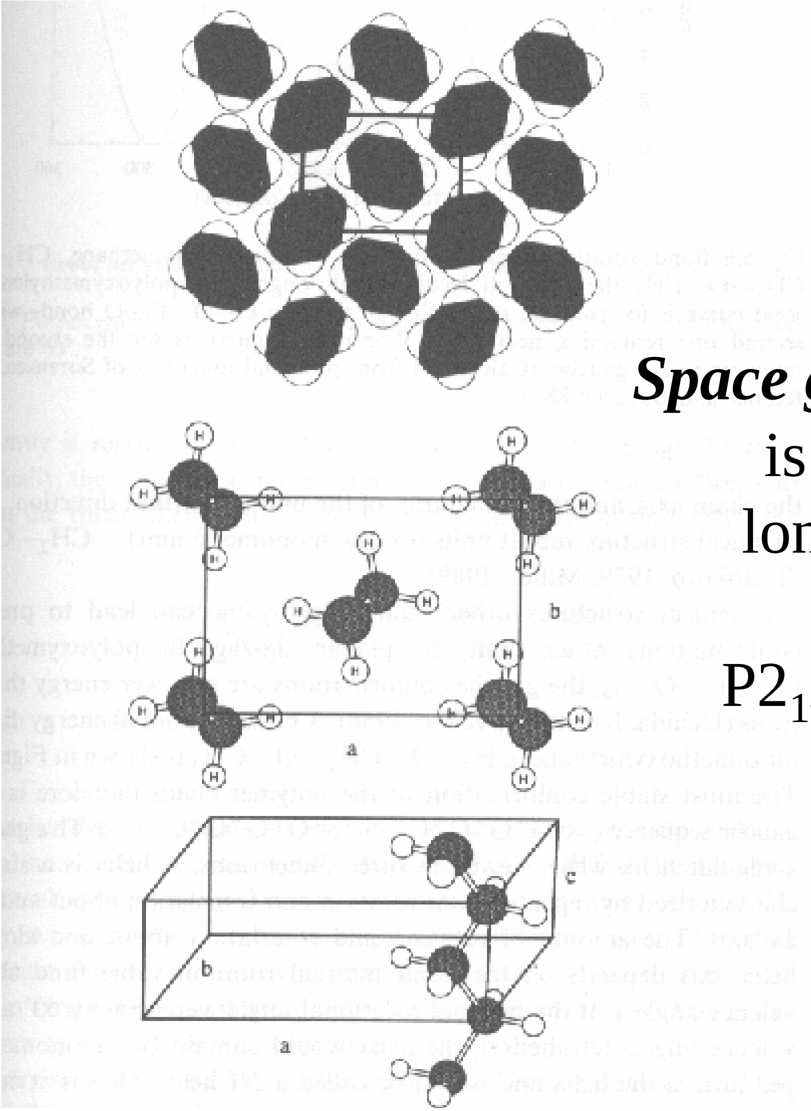
Polyethylene Crystal Packing

Orthorhombic unit cell.

a = 7.4 A

b = 4.93 A

c = 2.54 A



Space group of PE is $Pna2_1$; long form is $P2_1/n\ 2_1/a\ 2_1/m$

Single Crystals

Self Seeding Growth Method

- This method yields a uniform crystal preparation, all crystals are nucleated simultaneously at same T_c

1. Dissolve polymer in relatively poor solvent at high temperature
2. Cool: yielding complex crystal aggregates
3. Slowly reheat until dissolution first begins (T_s)
4. Cool quickly to desired T_c by adding fresh solvent at appropriate temperature
5. Crystallization takes place on relatively few nuclei which survived T_s treatment

Image removed due to copyright restrictions.

Please see Fig. 15 in Blundell, D. J., and Keller, A. “Nature of Self-seeding Polyethylene Crystal Nuclei.” *Journal of Macromolecular Science B* 2 (June 1968): 301-336.

POM Single Crystal

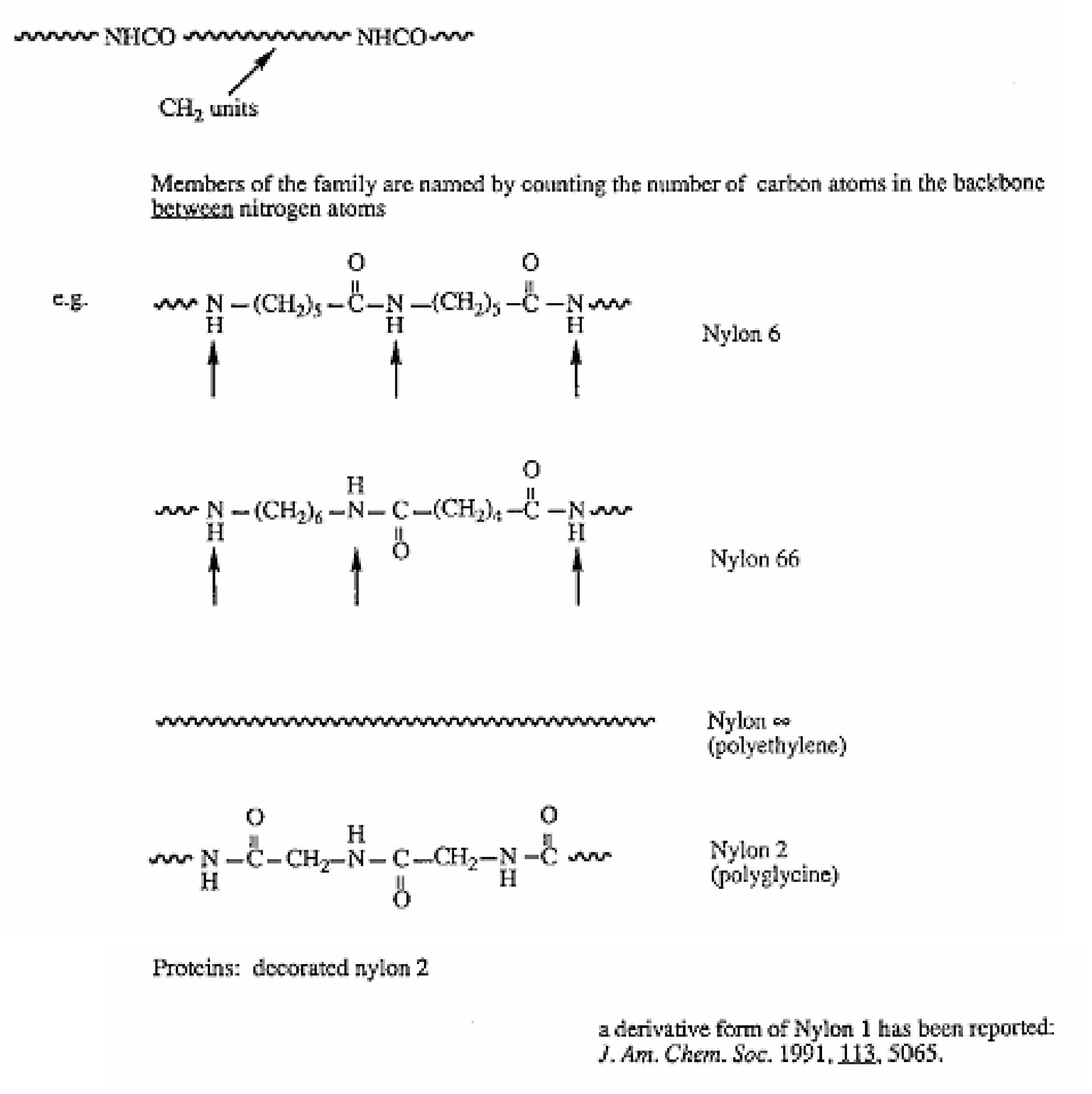
Image removed due to copyright restrictions.

Please see Fig. 4 in Wittmann, Jean Claude, and Lotz, Bernard. “Crystallization of Paraffins and Polyethylene from the ‘Vapour Phase’: a New Decorative Technique for Polymer Crystals.” *Die Makromolekulare Chemie, Rapid Communications* 3 (1982): 733-738.

And

Fig. 7b in Balik, C. M., et al. “Epitaxial Morphologies of Polyoxymethylene. I. Electron Microscopy.” *Journal of Polymer Science: Polymer Physics* 20 (1982): 2003-2016.

Polyamides (Nylons)



$\sim\sim\sim NHCO \sim\sim\sim\sim\sim\sim NHCO \sim\sim$

CH_2 units

Members of the family are named by counting the number of carbon atoms in the backbone <u>between</u> nitrogen atoms

e.g.

$\sim\underset{\underset{\uparrow}{H}}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\underset{\underset{\uparrow}{H}}{N}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-\underset{\underset{\uparrow}{H}}{N}\sim$ Nylon 6

$\sim\underset{\underset{\uparrow}{H}}{N}-(CH_2)_6-\overset{H}{\underset{\uparrow}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{\underset{\uparrow}{H}}{N}\sim$ Nylon 66

$\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim$ Nylon ∞ (polyethylene)

$\sim\underset{H}{N}-\overset{O}{\overset{\|}{C}}-CH_2-\overset{H}{N}-\underset{\underset{O}{\|}}{C}-CH_2-\underset{H}{N}-\overset{O}{\overset{\|}{C}}\sim$ Nylon 2 (polyglycine)

Proteins: decorated nylon 2

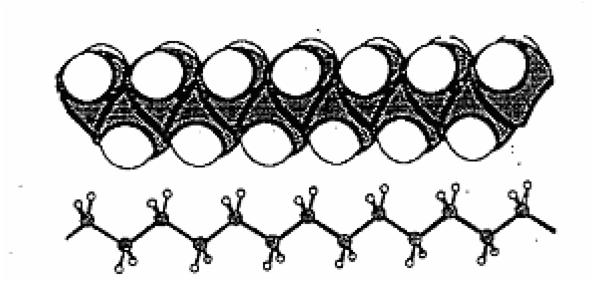
a derivative form of Nylon 1 has been reported: *J. Am. Chem. Soc.* 1991, <u>113</u>, 5065.

Nylon 6,6

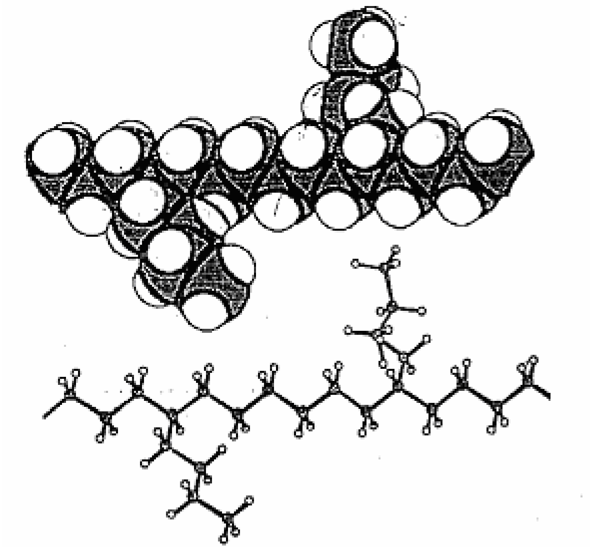
Image removed due to copyright restrictions.

Please see Fig. 13 in Bunn, C. W., and Garner, E. V. “The Crystal Structures of Two Polyamides (‘Nylons’).” *Proceedings of the Royal Society of London A* 189 (March 27, 1947): 39-68.

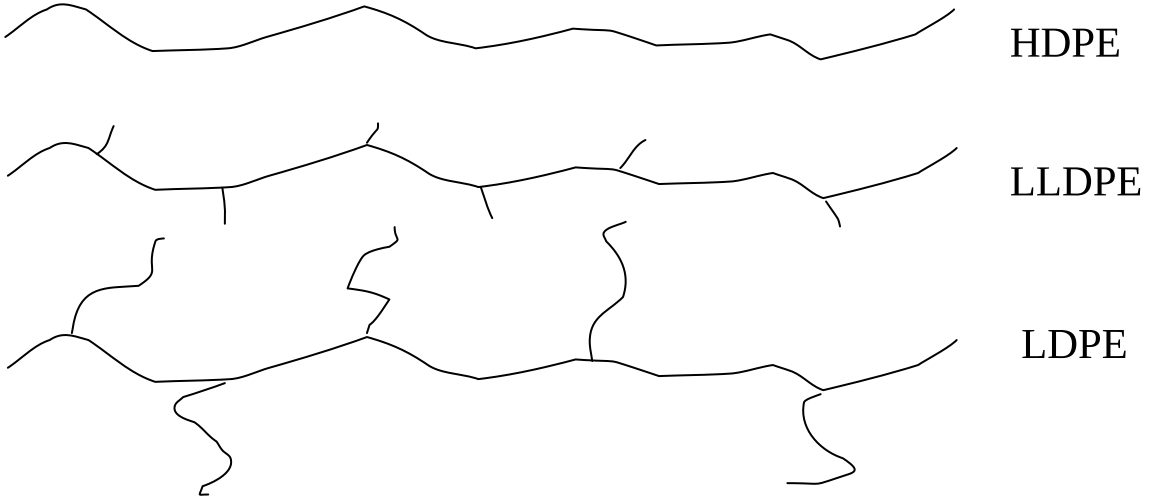
Linear and Branched Polyethylene



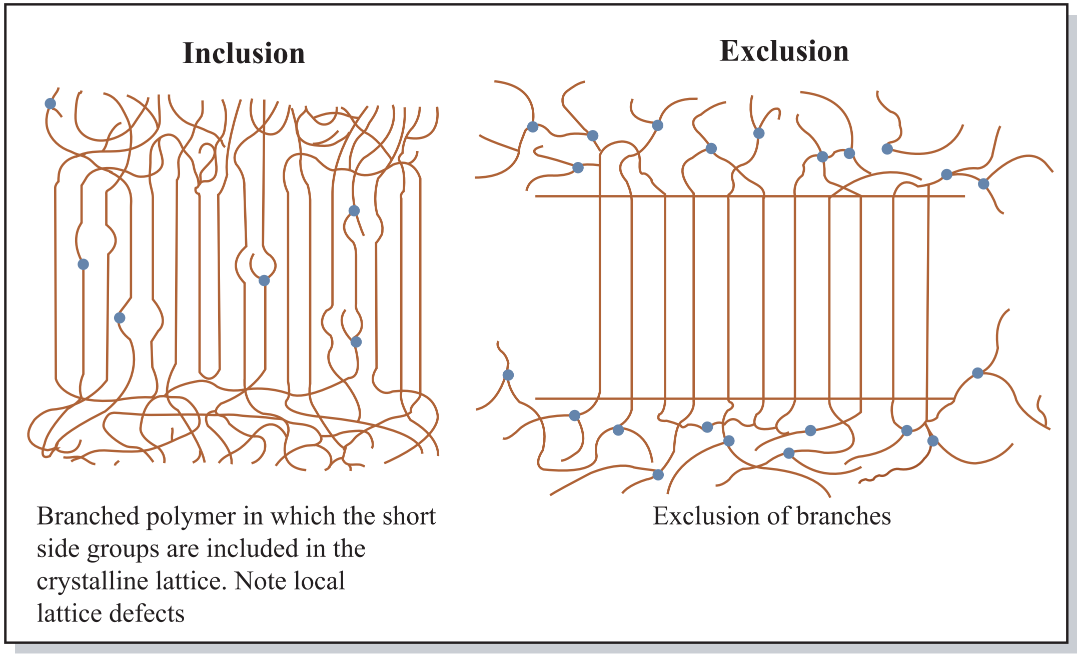
part of a linear PE



part of a branched PE



Crystallization of Branched Polymers



Branched polymer in which the short side groups are included in the crystalline lattice. Note local lattice defects

Exclusion of branches

Figure by MIT OCW.

Exclusion – Noncrystallographic species are rejected from crystal, requires slow crystallization rate.

Inclusion – Fast crystallization rates force incorporation of defects into the crystal creating a strained lattice.

$$\frac{1}{T_m(x)} - \frac{1}{T_m{}^o} = -\frac{R}{\Delta H}\ln(1-x)$$

x = mole % of noncrystallizable units (randomly distributed)

Hierarchical Structure of Semicrystalline Polymers

Spherulite radially twisted lamellae

Images removed due to copyright restrictions.

Please see, for example, http://www.doitpoms.ac.uk/tlplib/polymers/images/img015.gif

tie molecule

100um

5Å scale

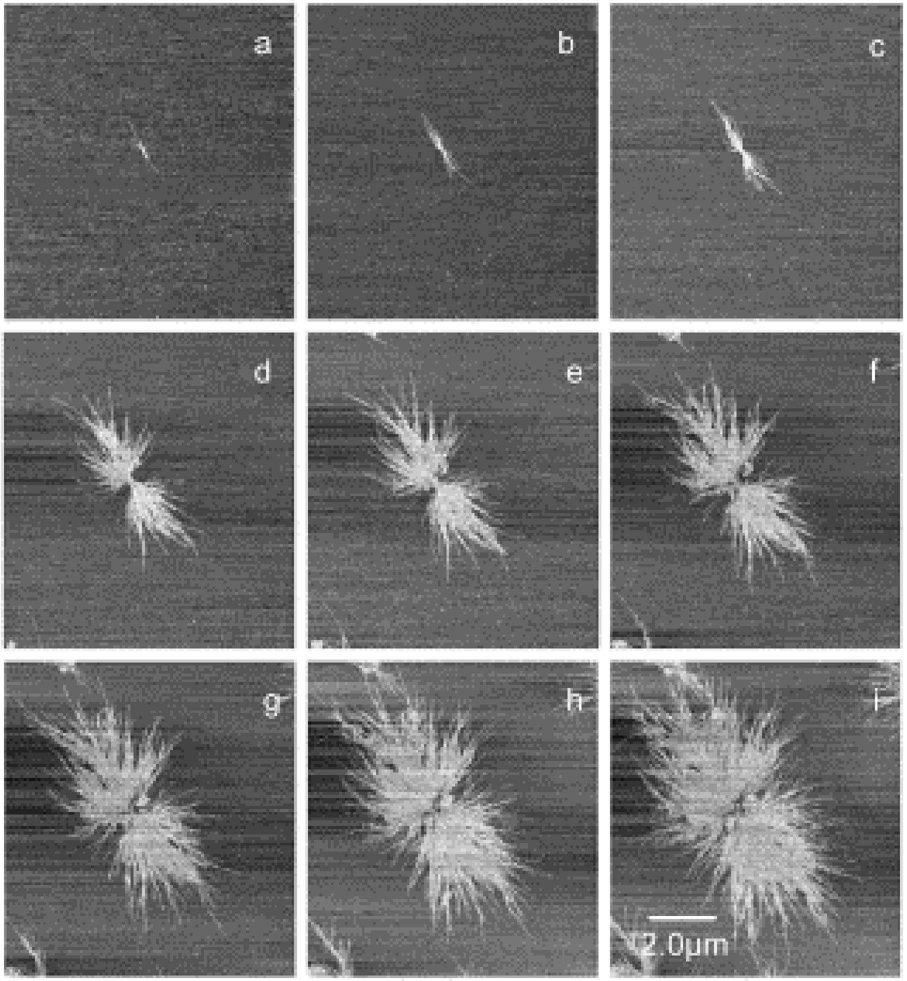
Unit cell

Skeletal lamellae

200Å

< 10um

Growth of Spherulites



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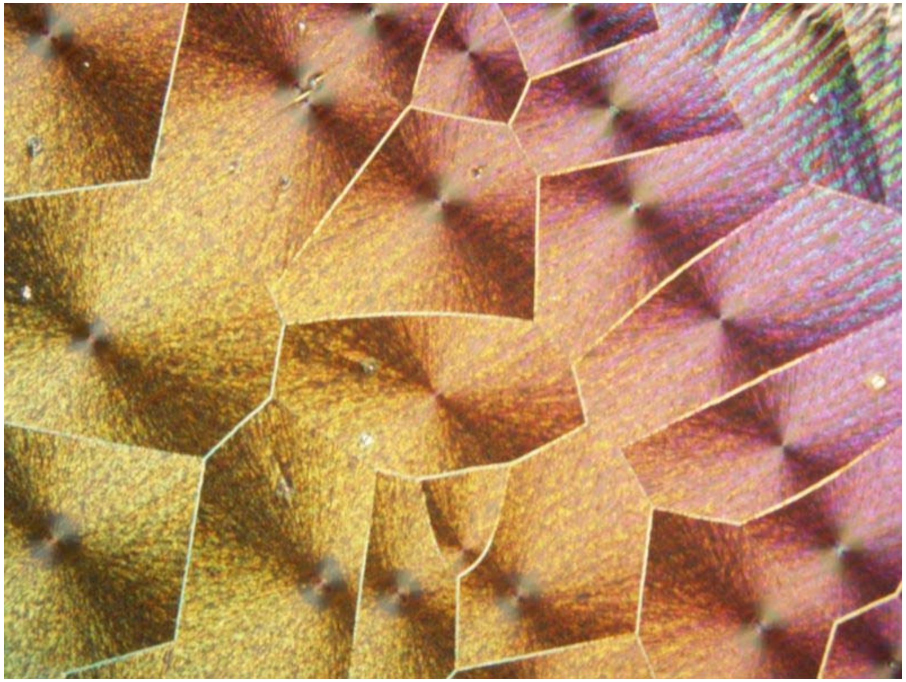
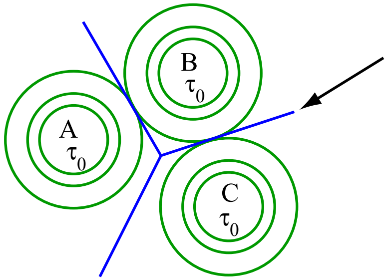


Image from Wikimedia Commons, http://commons.wikimedia.org

Spherulite Boundaries (2D)

(1) **Homogeneous nucleation** – All spherulites nucleate at the same time, τ_0 , growth fronts meet midway between centers along straight lines (straight boundaries). Morphology may be modeled by simply constructing perpendicular bisectors between centers (area in 2D) closest to a given point. This is called a Voronoi cell.



At subsequent times, B and C continue to impinge along this straight line

Figure by MIT OCW.

(2) **Sporadic, homogeneous nucleation** – times of nucleation (τ_1, $\tau_{2\ldots}$) are varied. Morphology consists of curved boundaries. Intersection of growth are hyperbolae (curved lines).

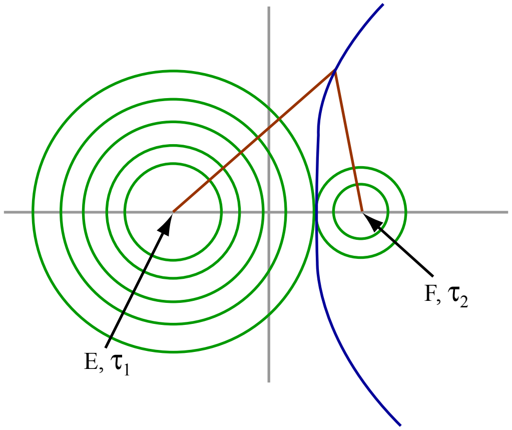


Figure by MIT OCW.

Definition: A hyperbola is the locus of points such that the difference of its distances from two fixed points (E,F) is a constant

Dissection of a Spherulite

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See Figure 6.5 in Allen, S. M., and E. L. Thomas. *The Structure of Materials.* New York, NY: J. Wiley & Sons, 1999.

Spherulite Microstructure

Lamellae – Unit Cell

Images removed due to copyright restrictions.

Please see, for example,
http://www.doitpoms.ac.uk/miclib/micrographs/large/000556.jpg

single chain
folded lamellae

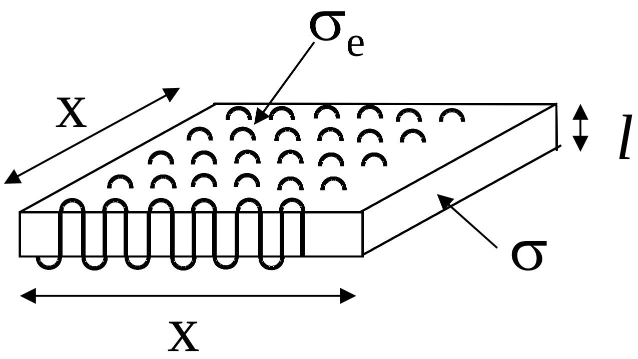
cis 1,4 polyisoprene (crystallizes at –12^{o}C)

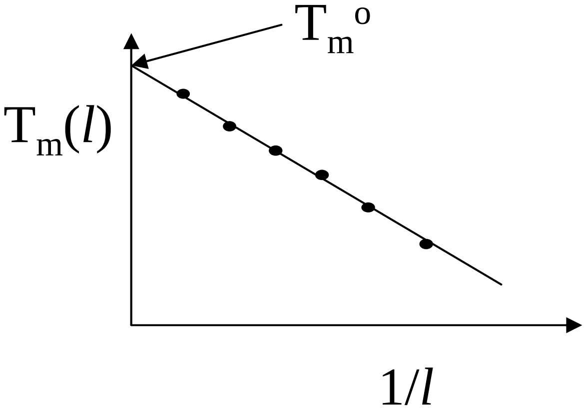
Spherulite Banding

Images removed due to copyright restrictions.

Please see, for example,
http://www.doitpoms.ac.uk/miclib/micrographs/large/000601.jpg
http://www.doitpoms.ac.uk/miclib/micrographs/large/000555.jpg

Melting Temperature of Chain Folded Crystals





l = fold thickness

T_m^o = equilibrium melting point for infinite thickness XL

$$\Delta g = \Delta h - T\Delta s$$

$T_m(l)$

at T_m^{o} $\quad$ $\Delta g = \Delta h - T_m{}^{o} \Delta s = 0$

$$\Delta g(T) = \Delta h(T) - T\Delta s(T)$$

$$= \Delta h(T) - T\frac{\Delta h(T)}{T_m{}^{o}}$$

$$\Delta g(T) = \Delta h(T)\left(1 - \frac{T}{T_m{}^{o}}\right) \cong \Delta h\left(\frac{T_m{}^{o} - T}{T_m{}^{o}}\right)$$

$$\Delta g_{12} = -\Delta g x^2 l + 2\sigma_e x^2 + 4\sigma x l$$

x >> *l* , neglect 4σx*l*

For a crystal of thickness *l*, with melting point $T_m(l)$:

$$\Delta g x^2 l = 2\sigma_e x^2$$

$$\Delta h\left(\frac{T_m{}^{o} - T}{T_m{}^{o}}\right) l = 2\sigma_e$$

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

Crystallization Rate

1. **Transport term**

$$e^{-E_D/k(T_c-T_g)} \qquad T_m - T_c = \Delta T = \text{under cooling}$$

E_D = **activation energy for diffusion**

- move crystallizable material to growth face
- remove noncrystallizable material from growth face

As T_g is approached, transport term severely limits crystallization

2. **Nucleation Term**

$$e^{-\left(\Delta\phi_2^*/kT_c\right)}$$

Secondary nucleation of polymer chains onto growth face

$$\Delta\phi_2^* \sim \frac{c}{\Delta T} \sim \frac{c}{T_m - T_c} \qquad \text{so,} \quad e^{-\left(\frac{c}{k(T_m-T_c)T_c}\right)}$$

As T_c approaches T_m, nucleation severely limits crystallization