Chain Folding

(a) PRIMARY CILIUM
(b) SECONDARY CILIUM
(c) PRIMARY CILIA

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)

\[ a = 7.4\text{Å} \]
\[ b = 4.93\text{Å} \]
\[ c = 2.54\text{Å} \]

\[ \rho_c = 1.0 \frac{g}{cm^3} \]
\[ \rho_a = 0.86 \frac{g}{cm^3} \]

Regular adjacent

Figure by MIT OCW.
Polyethylene Crystal Packing

Orthorhombic unit cell.

\[ a = 7.4 \, \text{Å} \]
\[ b = 4.93 \, \text{Å} \]
\[ c = 2.54 \, \text{Å} \]

*Space group* of PE is Pna\(_2\)_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

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POM Single Crystal

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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

Polyamides (Nylons)

Members of the family are named by counting the number of carbon atoms in the backbone between nitrogen atoms.

For example:

Nylon 6:

\[
H \quad \overset{\text{O}}{\text{N}} \quad (\overset{\text{H}}{\text{CH}_2\_5}) \quad \text{\text{-}} \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{O}}{\text{N}} \quad (\overset{\text{H}}{\text{CH}_2\_5}) \quad \text{\text{-}} \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{H}}{\text{N}} \quad H
\]

Nylon 66:

\[
H \quad \overset{\text{O}}{\text{N}} \quad (\overset{\text{H}}{\text{CH}_2\_6}) \quad \text{\text{-}} \quad \overset{\text{H}}{\text{N}} \quad (\overset{\text{H}}{\text{CH}_2\_4}) \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{O}}{\text{N}} \quad H
\]

Nylon ∞ (polyethylene):

\[
\text{---------} \quad \text{---------} \quad \text{---------} \quad \text{---------}
\]

Nylon 2 (polyglycine):

\[
\overset{\text{O}}{\text{H}} \quad \text{\text{-}} \quad \overset{\text{O}}{\text{N}} \quad \text{\text{-}} \quad \overset{\text{H}}{\text{N}} \quad \text{\text{-}} \quad \overset{\text{O}}{\text{O}} \quad \text{\text{-}} \quad \overset{\text{H}}{\text{C}} \quad \overset{\text{O}}{\text{H}}
\]

Proteins: decorated nylon 2

A derivative form of Nylon 1 has been reported:

Nylon 6,6

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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

HDPE

LLDPE

LDPE
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

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

- **Skeletal lamellae**
  - 100um
  - 200Å

- **Unit cell**
  - 5Å scale
  - < 10um
Growth of Spherulites

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

Spherulite Boundaries (2D)

(1) Homogeneous nucleation – All spherulites nucleate at the same time, $\tau_0$, 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.

(2) Sporadic, homogeneous nucleation – times of nucleation ($\tau_1, \tau_2...$) are varied. Morphology consists of curved boundaries. Intersection of growth are hyperbolae (curved lines).

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

Figure by MIT OCW.
Dissection of a Spherulite

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Spherulite Microstructure
Lamellae – Unit Cell

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

cis 1,4 polyisoprene (crystallizes at –12°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

\[ l = \text{fold thickness} \]
\[ T_m^o = \text{equilibrium melting point for infinite thickness XL} \]

\[ \Delta g = \Delta h - T \Delta s \]
\( T_m(l) \)

at \( T_m^o \)

\[
\Delta g = \Delta h - T_m^o \Delta s = 0
\]

\[
\Delta g(T) = \Delta h(T) - T \Delta s(T) = \Delta h(T) - T \frac{\Delta h(T)}{T_m^o}
\]

\[
\Delta g(T) = \Delta h(T) \left( 1 - \frac{T}{T_m^o} \right) \approx \Delta h \left( \frac{T_m^o - T}{T_m^o} \right)
\]

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

\( x > \gg l \), neglect \( 4 \sigma xl \)

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

\[
\Delta g x^2 l = 2 \sigma_e x^2
\]

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

\[
T_m(l) = T_m^o \left( 1 - \frac{2 \sigma_e}{l \Delta h} \right)
\]
1. **Transport term**

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

\[ E_D = \text{activation energy for diffusion} \]
- 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

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

As \( T_c \) approaches \( T_m \), nucleation severely limits crystallization