## Chapter Outline: Polymer Structures

➢ Hydrocarbon and Polymer Molecules

➢ Chemistry of Polymer Molecules

➢ Molecular Weight and Shape

➢ Molecular Structure and Configurations

➢ Copolymers

➢ Polymer Crystals

Optional reading: none

Polymers: Introduction

➢ **Polymer** - a large molecule consisting of (at least five) repeated chemical units (`mers') joined together, like beads on a string. Polymers usually contain many more than five monomers, and some may contain hundreds or thousands of monomers in each chain.

➢ Polymers may be **natural**, such as cellulose or DNA, or **synthetic**, such as nylon or polyethylene.
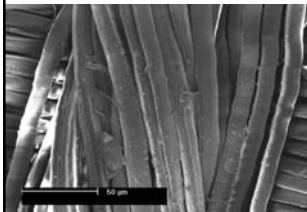

Silk fiber is produced by silk worms in a cocoon, to protect the silkworm while it metamorphoses in a moth.

Many of the most important current research problems involve polymers. Living organisms are mainly composed of polymerized amino acids (proteins) nucleic acids (RNA and DNA), and other *biopolymers*. The most powerful computers - our brains - are mostly just a complex polymer material soaking in salty water! We are just making first small steps towards understanding of biological systems.
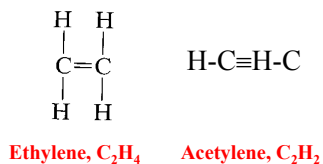
Hydrocarbon molecules (I)

➢ Most polymers are organic, and formed from hydrocarbon molecules

➢ Each C atom has four e⁻ that participate in bonds, each H atom has one bonding e⁻

Examples of **saturated** (all bonds are single ones) hydrocarbon molecules:

H	H H	H H H
H—C—H	H—C—C—H	H—C—C—C—H
H	H H	H H H

Methane, CH₄   **Ethane, C₂H₆**   **Propane, C₃H₈**
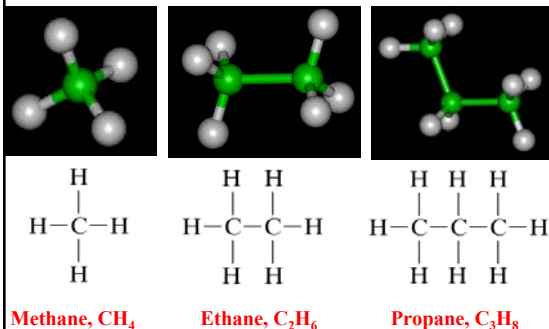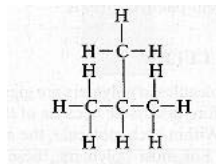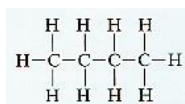

Hydrocarbon molecules (II)

Double and triple bonds can exist between C atoms (sharing of two or three electron pairs). These bonds are called **unsaturated bonds.** Unsaturated molecules are more reactive
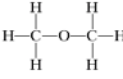
$$\begin{matrix} H & H \\ | & | \\ C = C \\ | & | \\ H & H \end{matrix} \qquad H\text{-}C\equiv H\text{-}C$$

Ethylene, C₂H₄   **Acetylene, C₂H₂**
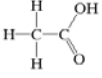
Isomers are molecules that contain the same atoms but in a different arrangement. An example is butane and isobutane:

$$H\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\text{—}H$$

Butane → C₄H₁₀ ← Isobutane

Hydrocarbon molecules (III)

Family	Characteristic Unit	Representative Compound	
Alcohols	R—OH	H—C(H)(H)—OH	Methyl alcohol
Ethers	R—O—R′	H—C(H)(H)—O—C(H)(H)—H	Dimethyl ether
Acids	R—C(OH)=O	H—C(H)(H)—C(OH)=O	Acetic acid
Aldehydes	R(H)C=O	H(H)C=O	Formaldehyde
Aromatic hydrocarbons	R—(benzene ring)	OH—(benzene ring)	Phenol

Many other organic groups can be involved in polymer molecules. In table above, R represents a radical, an organic group of atoms that remain as a unit and maintain their identity during chemical reactions (e.g. CH_3, C_2H_5, C_6H_5)
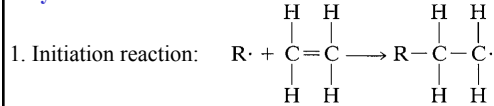

Polymer molecules
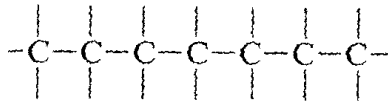
➤ Polymer molecules are very large: **macromolecules**

➤ Most polymers consist of long and flexible chains with a string of C atoms as a backbone.

➤ Side-bonding of C atoms to H atoms or radicals

➤ Double bonds are possible in both chain and side bonds

➤ A repeat unit in a polymer chain ("unit cell") is a **mer**

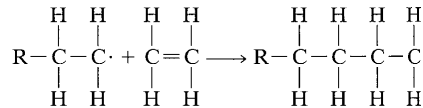➤ A single mer is called a **monomer**

Chemistry of polymer molecules (I)

➢ Ethylene (C_2H_4) is a gas at room temp and pressure

➢ Ethylene transforms to polyethylene (solid) by forming active mers through reactions with an initiator or catalytic radical (R·)

➢ (·) denotes unpaired electron (active site)

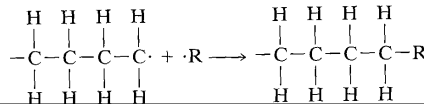**Polymerization:**

1. Initiation reaction:

$$R\cdot + \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \longrightarrow R - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\cdot$$

2. Rapid propagation ~1000 mer units in 1-10 ms:

$$R - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}}\cdot + \overset{H}{\underset{H}{C}} = \overset{H}{\underset{H}{C}} \longrightarrow R - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}}$$
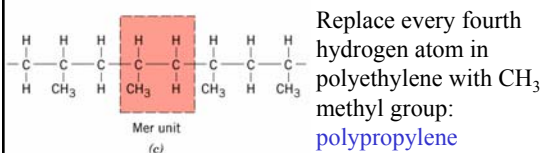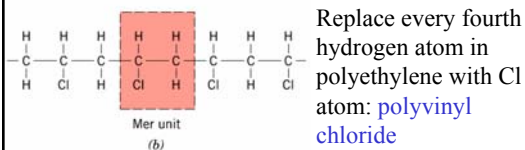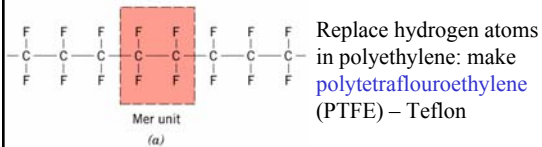
3. Termination: When two active chain ends meet each other or active chain ends meet with initiator or other species with single active bond:

$$-\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}}\cdot + \cdot R \longrightarrow -\overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - R$$

7

Chemistry of polymer molecules (II)

Replace hydrogen atoms in polyethylene: make polytetraflouroethylene (PTFE) – Teflon

Replace every fourth hydrogen atom in polyethylene with Cl atom: polyvinyl chloride

Replace every fourth hydrogen atom in polyethylene with CH_3 methyl group: polypropylene

Chemistry of polymer molecules (III)

➢ When all the mers are the same, the molecule is called a **homopolymer**

➢ When there is more than one type of mer present, the molecule is a **copolymer**

➢ Mer units that have 2 active bonds to connect with other mers are called **bifunctional**

➢ Mer units that have 3 active bonds to connect with other mers are called **trifunctional.** They form three-dimensional molecular network structures.
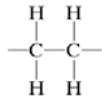
Polyethylene

(bifunctional)
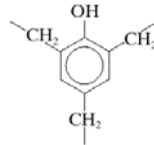
Phenol-formaldehyde

(trifunctional)

Molecular weight (I)

➢ Final molecular weight (chain length) is controlled by relative rates of initiation, propagation, termination steps of polymerization

➢ Formation of macromolecules during polymerization results in distribution of chain lengths and molecular weights

➢ The average molecular weight can be obtained by averaging the masses with the fraction of times they appear (**number-average molecular weight**) or with the mass fraction of the molecules (**weight-average molecular weight**).
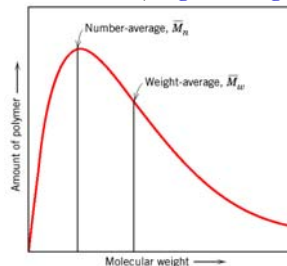
number-average:

$$\overline{M}_n = \sum x_i M_i$$

weight-average:

$$\overline{M}_w = \sum w_i M_i$$

M_i is the mean molecular weight of range i
w_i is weight fraction of chains of length i
x_i is number fraction of chains of length i

Molecular weight (II)

➢ Alternative way to express average polymer chain size is **degree of polymerization** - the average number of mer units in a chain:

number-average: weight-average:
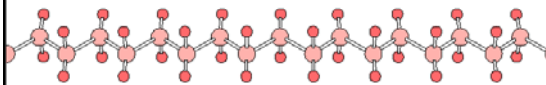
$$n_n = \frac{\overline{M}_n}{\overline{m}} \qquad\qquad n_w = \frac{\overline{M}_w}{\overline{m}}$$

$\overline{m}$ is the mer molecular weight

• Melting / softening temperatures increase with molecular weight (up to ~ 100,000 g/mol)

• At room temperature, short chain polymers (molar weight ~ 100 g/mol) are liquids or gases, intermediate length polymers (~ 1000 g/mol) are waxy solids, solid polymers have molecular weights of 10^4 - 10^7 g/mol
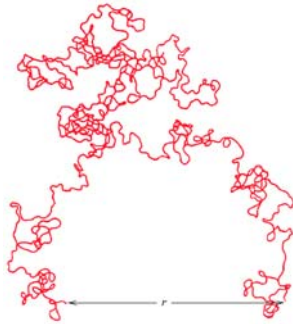
Molecular shape

➢ The angle between the singly bonded carbon atoms is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.

➢ Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).

➢ Random kinks and coils lead to entanglement, like in the spaghetti structure:
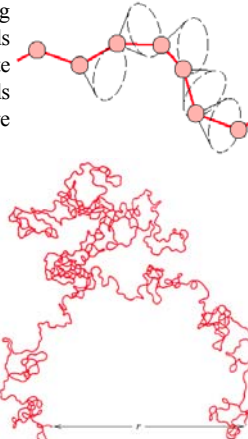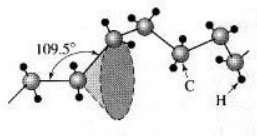
Molecular shape

➢ Molecular chains may thus bend, coil and kink
➢ Neighboring chains may intertwine and entangle
➢ Large elastic extensions of rubbers correspond to unraveling of these coiled chains
➢ Mechanical / thermal characteristics depend on the ability of chain segments to rotate

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Molecular structure

The physical characteristics of polymer material depend not only on molecular weight and shape, but also on molecular structure:

1 **Linear polymers**: Van der Waals bonding between chains. Examples: polyethylene, nylon.
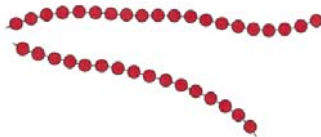
2 **Branched polymers**:   Chain packing efficiency is reduced compared to linear polymers - lower density

Molecular structure

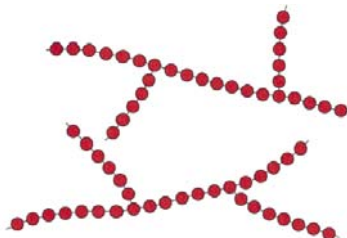**3** **Cross-linked polymers**: Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains. Many rubbers have this structure.
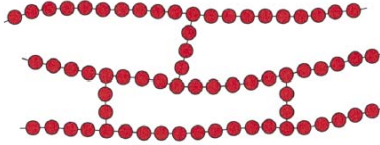
4 **Network polymers**: 3D networks made from trifunctional mers. Examples: epoxies, phenol-formaldehyde

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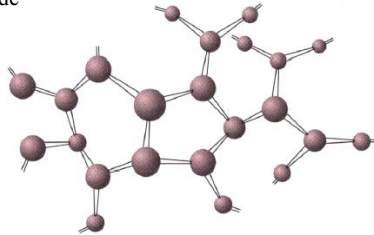
Isomerism

Isomerism: Hydrocarbon compounds with same composition may have different atomic compositions.

Physical properties may depend on **isomeric state** (e.g. boiling temperature of normal butane is -0.5 ^{o}C, of isobutane - 12.3 ^{o}C)
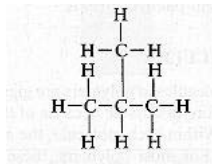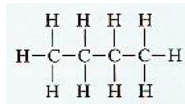
Butane → C_4H_{10} ← Isobutane

Two types of isomerism are possible: stereoisomerism and geometrical isomerism

Stereoisomerism

Stereoisomerism: atoms are linked together in the same order, but can have different spatial arrangement

1 **Isotactic configuration:** all side groups R are on the same side of the chain.

$$
\begin{array}{cccccccc}
H & H & H & H & H & H & H & H \\
| & | & | & | & | & | & | & | \\
-C & -C & -C & -C & -C & -C & -C & -C- \\
| & | & | & | & | & | & | & | \\
H & \textcircled{R} & H & \textcircled{R} & H & \textcircled{R} & H & \textcircled{R}
\end{array}
$$

2 **Syndiotactic configuration:** side groups R alternate sides of the chain.

$$
\begin{array}{cccccccc}
H & H & H & \textcircled{R} & H & H & H & \textcircled{R} \\
| & | & | & | & | & | & | & | \\
-C & -C & -C & -C & -C & -C & -C & -C- \\
| & | & | & | & | & | & | & | \\
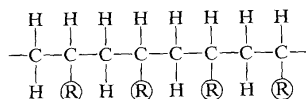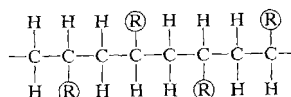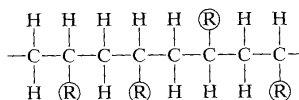H & \textcircled{R} & H & H & H & \textcircled{R} & H & H
\end{array}
$$

3 **Atactic configuration:** random orientations of groups R along the chain.

$$
\begin{array}{cccccccc}
H & H & H & H & H & \textcircled{R} & H & H \\
| & | & | & | & | & | & | & | \\
-C & -C & -C & -C & -C & -C & -C & -C- \\
| & | & | & | & | & | & | & | \\
H & \textcircled{R} & H & \textcircled{R} & H & H & H & \textcircled{R}
\end{array}
$$

Geometrical isomerism

Geometrical isomerism: consider two carbon atoms bonded by a double bond in a chain. H atom or radical R bonded to these two atoms can be on the same side of the chain (**cis** structure) or on opposite sides of the chain (**trans** structure).

$$
\begin{array}{cccc}
H & \textcircled{CH_3}\,\textcircled{H} & H \\
| & | \quad | & | \\
-C & -C = C & -C- \\
| & & | \\
H & & H
\end{array}
$$

Cis-polyisoprene

$$
\begin{array}{cccc}
H & \textcircled{CH_3} & H \\
| & | & | \\
-C & -C = C & -C- \\
| & | & | \\
H & \textcircled{H}\;H &
\end{array}
$$
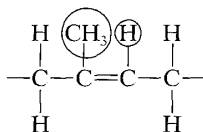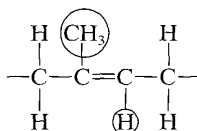
Trans-polyisoprene

Summary: Size – Shape -Structure

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                        Molecular
                     characteristics

    ┌─────────────┬─────────────┬─────────────┐
 Chemistry       Size        Shape        Structure
(mer composition) (molecular weight) (chain twisting,
                              entanglement, etc.)
                                        ┌──────┬──────┬──────┬──────┐
                                      Linear Branched Crosslinked Network
                                        └──────┘
                                        Isomeric states
                              ┌──────────────────┴──────────────────┐
                         Stereoisomers                      Geometrical isomers
                    ┌────────┼────────┐                   ┌────┴────┐
                 Isotactic Syndiotactic Atactic          cis      trans
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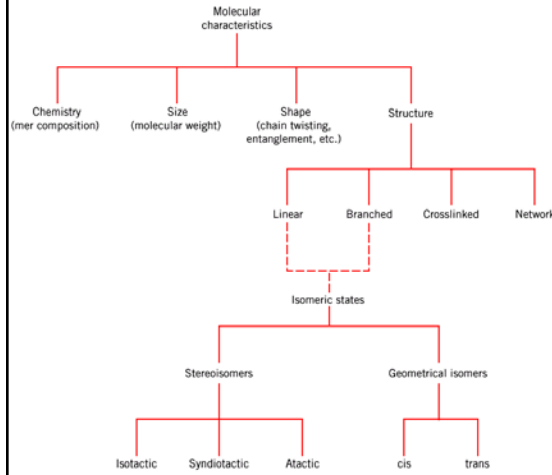

Copolymers (composed of different mers)

Copolymers, polymers with at least two different types of mers, can differ in the way the mers are arranged:

Random copolymer

(a)

Alternating copolymer

(b)

Block copolymer

(c)

Graft copolymer

(d)
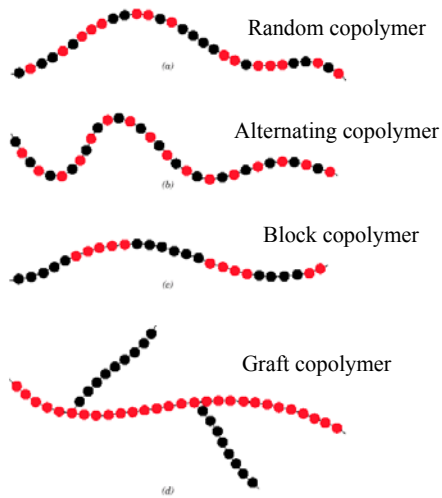
Synthetic rubbers are copolymers

Polymer Crystallinity (I)

Atomic arrangement in polymer crystals is more complex than in metals or ceramics (unit cells are typically large and complex).

0.255 nm

0.741 nm   0.494 nm

Polyethylene

C   H
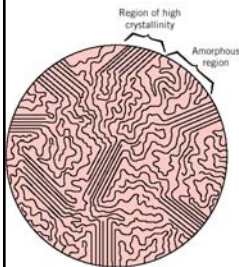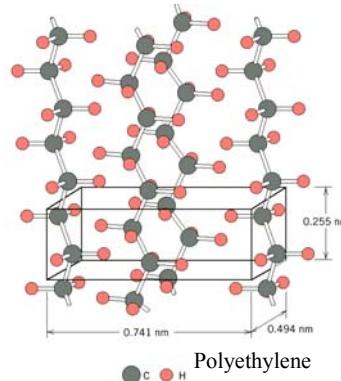
Polymer molecules are often partially crystalline (semi-crystalline), with crystalline regions dispersed within amorphous material.

Region of high crystallinity

Amorphous region

Polymer Crystallinity (II)

Degree of crystallinity is determined by:

➢ **Rate of cooling during solidification**: time is necessary for chains to move and align into a crystal structure

➢ **Mer complexity**: crystallization less likely in complex structures, simple polymers, such as polyethylene, crystallize relatively easily

➢ **Chain configuration**: linear polymers crystallize relatively easily, branches inhibit crystallization, network polymers almost completely amorphous, cross-linked polymers can be both crystalline and amorphous

➢ **Isomerism**: isotactic, syndiotactic polymers crystallize relatively easily - geometrical regularity allows chains to fit together, atactic difficult to crystallize

➢ **Copolymerism**: easier to crystallize if mer arrangements are more regular - alternating, block can crystallize more easily as compared to random and graft

More crystallinity: higher density, more strength, higher resistance to dissolution and softening by heating

Polymer Crystallinity (III)

Crystalline polymers are denser than amorphous polymers, so the degree of crystallinity can be obtained from the measurement of density:

$$\% \quad crystallin\,ity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$
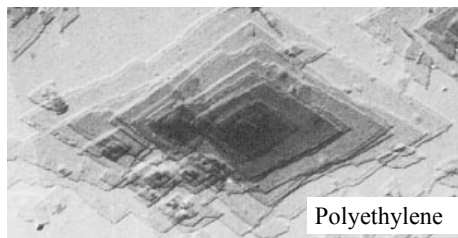
ρ_c: Density of perfect crystalline polymer

ρ_a: Density of completely amorphous polymer
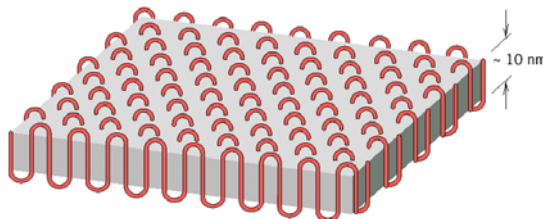
ρ_s: Density of partially crystalline polymer that we are analyzing

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Polymer Crystals

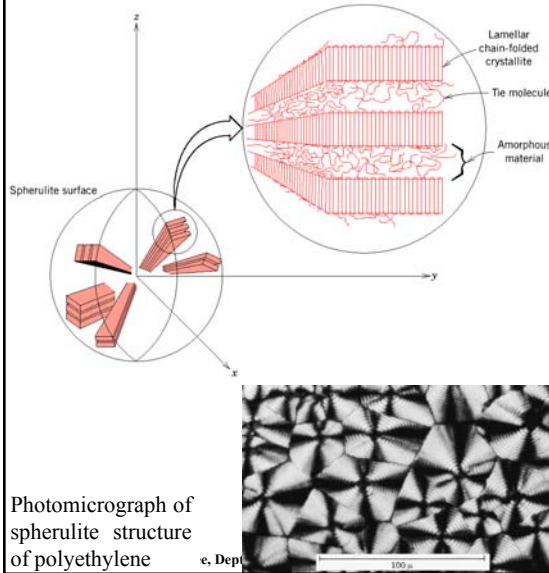Thin crystalline platelets grown from solution - chains fold back and forth: chain-folded model
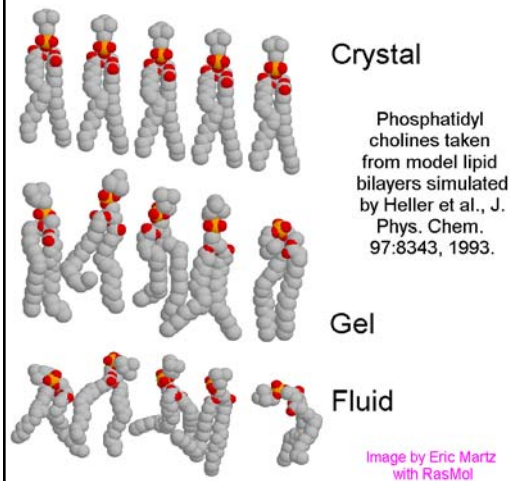

Polyethylene

~ 10 nm

The average chain length is much greater than the thickness of the crystallite
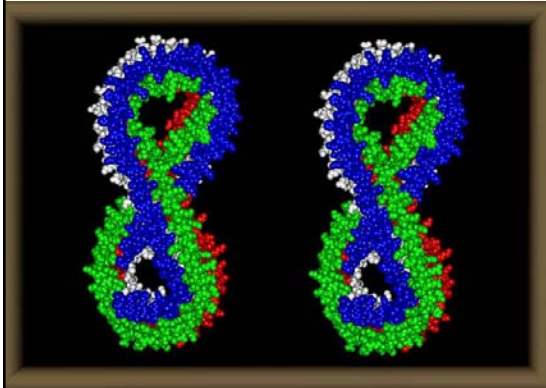
Polymer Crystals

Spherulites: Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates approximately spherical in shape.

Photomicrograph of spherulite structure of polyethylene

Five Bakers Dancing

Crystal

Phosphatidyl cholines taken from model lipid bilayers simulated by Heller et al., J. Phys. Chem. 97:8343, 1993.

Gel

Fluid

Image by Eric Martz with RasMol

Number Eighty Eight

HUMAN APOLIPOPROTEIN A-I.

Biopolymers can be complex… and nice

His bark is worse than his bite

CHAPERONE/STRUCTURAL PROTEIN

Authors: D. Choudhury, A. Thompson, A. Thompson, V. Stojanoff, S. Langerman, J. Pinkner, S. J. Hultgren, S. Knight

Summary

Make sure you understand language and concepts:

- Alternating copolymer
- Atactic configuration
- Bifunctional mer
- Block copolymer
- Branched polymer
- Chain-folded model
- Cis (structure)
- Copolymer
- Crosslinked polymer
- Crystallite
- Degree of polymerization
- Graft copolymer
- Homopolymer
- Isomerism
- Isotactic configuration
- Linear polymer
- Macromolecule

- Mer
- Molecular chemistry
- Molecular structure
- Molecular weight
- Monomer
- Network polymer
- Polymer
- Polymer crystallinity
- Random copolymer
- Saturated
- Spherulite
- Stereoisomerism
- Syndiotactic configuration
- Trans (structure)
- Trifunctional mer
- Unsaturated

Reading for next class:

Chapter 16: Characteristics, Applications, and Processing of Polymers

- Mechanical properties
    - Stress-Strain Behavior
    - Deformation of Semicrystalline Polymers
- Crystallization, Melting, Glass Transition
- Thermoplastic and Thermosetting Polymers
- Viscoelasticity
- Deformation and Elastomers
- Fracture of Polymers
- Polymerization
- Elastomers

Optional reading: 16.10, 16.12-16.14, 16.16-16.18