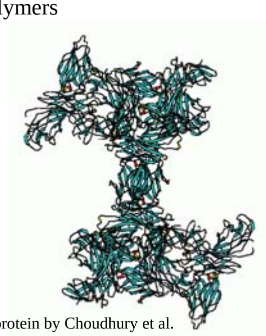
Chapter Outline: Polymer Structures

- Hydrocarbon and polymer molecules
- Chemistry of polymer molecules
- Molecular weight and shape
- Molecular structure and configurations
- Thermoplastic and thermosetting polymers
- Copolymers
- Polymer crystals and degree of crystallinity
- Defects and diffusion in polymers

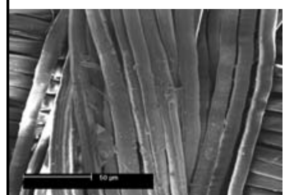
Optional reading: none



Chaperone/structural protein by Choudhury et al.

Polymers: Introduction

- **Polymers** – materials consisting of *polymer molecules* that consist of repeated chemical units (`mers') joined together, like beads on a string. Some polymer molecules contain hundreds or thousands of monomers and are often called *macromolecules*.
- Polymers may be **natural**, such as leather, rubber, cellulose or DNA, or **synthetic**, such as nylon or polyethylene.



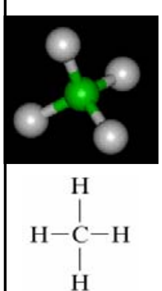
Silk fiber is produced by silk worms in a cocoon, to protect the silkworm while it metamorphoses in a moth.

Many of important current research problems and technological applications 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.

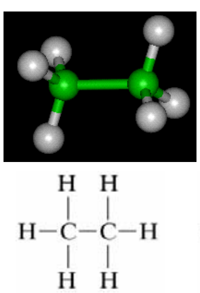
Hydrocarbon molecules (I)

- Most polymers are organic in their origin and are formed from hydrocarbon molecules
- Each C atom has four e^- that participate in bonds, each H atom has one bonding e^-

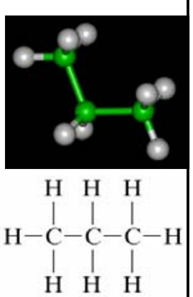
Examples of **saturated** (all bonds are single ones) hydrocarbon molecules:



Methane, CH_4



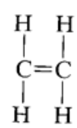
Ethane, C_2H_6



Propane, C_3H_8

Hydrocarbon molecules (II)

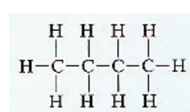
Double and triple bonds can exist between C atoms (sharing of two or three electron pairs). Molecules with double and triple bonds are called **unsaturated.** Unsaturated molecules are more reactive

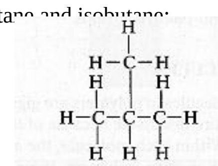


H-C≡C-H

Ethylene, C_2H_4 **Acetylene, C_2H_2**

Isomers are molecules that have the same composition (contain the same atoms) but have different atomic arrangement. An example is butane and isobutane:



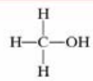
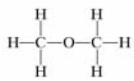
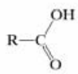
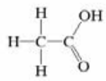
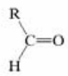
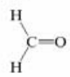
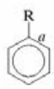
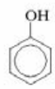


Butane → C_4H_{10} ← Isobutane

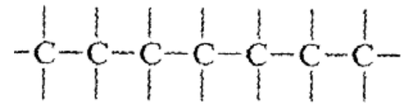
physical properties (e.g. boiling temperature) depend on the isomeric state

Hydrocarbon molecules (III)

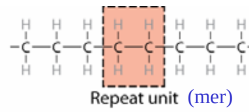
Many other organic groups can be involved in polymer molecules. In table below R represent a radical, an organic group of atoms that remains as a unit and maintains their identity during chemical reactions (e.g. CH_3, C_2H_5, C_6H_5)

Family	Characteristic Unit	Representative Compound	
Alcohols	R—OH		Methyl alcohol
Ethers	R—O—R'		Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

Polymer molecules

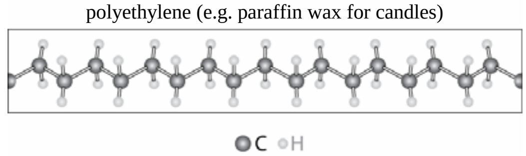


- Polymer molecules can be very large (macromolecules)
- Most polymers consist of long and flexible chains with a string of C atoms as a backbone
- Side-bonding of C atoms to H atoms or radicals
- Double bonds are possible in both chain and side bonds
- Repeat unit in a polymer chain ("unit cell") is a **mer**
- Small molecules from which polymer is synthesized is **monomer**. A single mer is sometimes also called a monomer.



(mer)

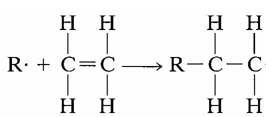
polyethylene (e.g. paraffin wax for candles)



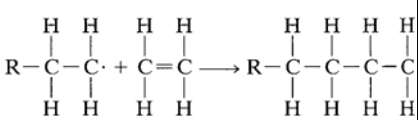
Chemistry of polymer molecules (I)

- Ethylene (C_2H_4) is a gas at room temp and pressure
- Ethylene transform to polyethylene (solid) by forming active mer through reaction with initiator or catalytic radical (R·)
- (·) denotes unpaired electron (active site)

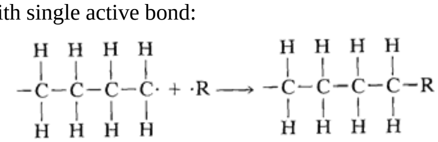
Polymerization:

1. Initiation reaction: 

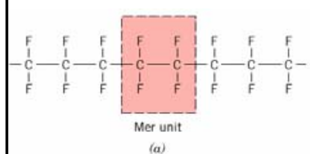
2. Rapid propagation ~1000 mer units in 1-10 ms:



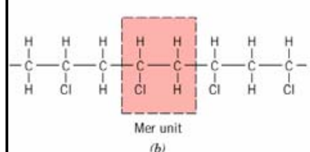
3. Termination when two active chain ends meet each other or active chain end meet with initiator or other species with single active bond:



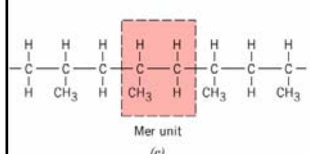
Chemistry of polymer molecules (II)



hydrogen atoms in polyethylene are replaced by fluorine: polytetraflouroethylene PTFE – Teflon



every fourth hydrogen atom in polyethylene is replaced with chlorine: poly(vinyl chloride) PVC

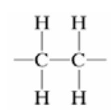


every fourth hydrogen atom in polyethylene is replaced with methyl group (CH_3): polyproplylene PP

More examples on pp. 539-540 of the textbook

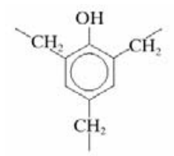
Chemistry of polymer molecules (III)

- When all 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



Polyethilene

(bifunctional)



Phenol-formaldehyde

(trifunctional)

Molecular weight

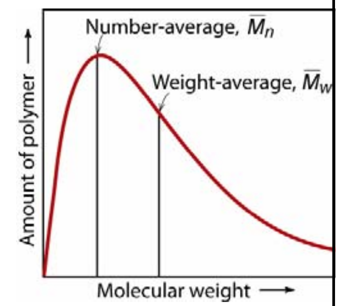
- The molecular weight (chain length) is controlled by the synthesis process: Relative rates of initiation, propagation, termination steps of polymerization
- Formation of macromolecules during polymerization results in a distribution of chain lengths and molecular weights
- The average molecular weight 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:

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



w_i is weight fraction of chains of length *i*
x_i is number fraction of chains of length *i*

Molecular weight: Example illustrating the difference between number-average and weight-average

student	weight mass (lb)
1	104
2	116
3	140
4	143
5	180
6	182
7	191
8	220
9	225
10	380

What is the average weight of students in this class:

a) Based on the number fraction of students in each mass range?

b) Based on the weight fraction of students in each mass range?

Solution:

The first step is to sort the students into weight ranges (let's use 40 lb ranges).

weight range	# of students N_i	mean weight M_i	number fraction x_i	weight fraction w_i
81-120	2	110	0.2	0.117
121-160	2	142	0.2	0.150
161-200	3	184	0.3	0.294
201-240	2	223	0.2	0.237
241-280	0	-	0	0.000
281-320	0	-	0	0.000
321-360	0	-	0	0.000
361-400	1	380	0.1	0.202

$\sum N_i = 10 \quad \sum N_i M_i = 1881 \quad x_i = N_i / \sum N_i \quad w_i = N_i M_i / \sum N_i M$

Molecular weight: Example illustrating the difference between number-average and weight-average

weight range	# of students N_i	mean weight M_i	number fraction x_i	weight fraction w_i
81-120	2	110	0.2	0.117
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$\sum N_i = 10 \quad \sum N_i M_i = 1881 \quad x_i = N_i / \sum N_i \quad w_i = N_i M_i / \sum N_i M_i$

$$\overline{M}_n = \sum x_i M_i = 0.2 \times 110 + 0.2 \times 142 + 0.3 \times 184 + 0.2 \times 223 + 0.1 \times 380 = 188\ lb$$

$$\overline{M}_w = \sum w_i M_i = 0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 + 0.237 \times 223 + 0.202 \times 380 = 218\ lb$$

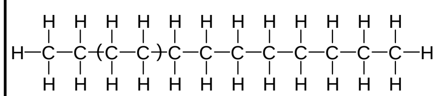
$$\overline{M}_w > \overline{M}_n$$

Degree of polymerization

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

$$DP = \frac{\overline{M}_n}{\overline{m}}$$

$\overline{m}$ is the average molecular weight of repeat unit
for copolymers it is calculated as $\overline{m} = \Sigma f_i m_i$
(f_i is fraction of mer i of molecular weight m_i)

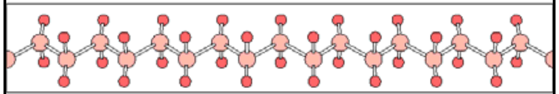


$DP = 6$

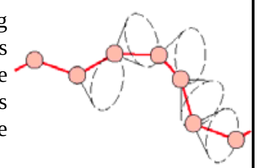
Properties of polymers depend on molecular weight

- 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 (sometimes called *high polymers*) have molecular weights of 10^4 - 10^7 g/mol

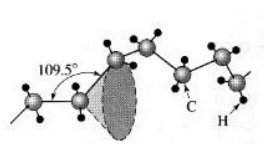
Molecular shape (conformation)

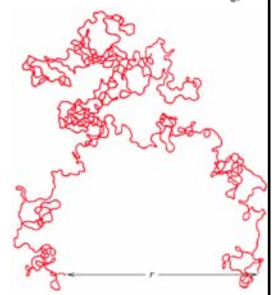


- The angle between the singly bonded carbon atoms is ~109° – carbon atoms form a zigzag pattern in a polymer molecule.
- Moreover, while maintaining the 109° angle between bonds polymer chains can rotate around single C-C bonds (double and triple bonds are very rigid).



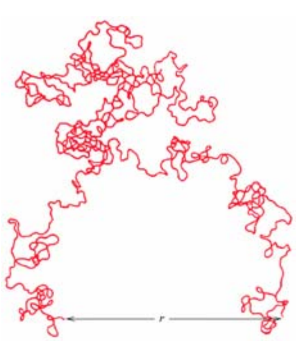
- Random kinks and coils lead to entanglement, like in the spaghetti structure:





Molecular shape (conformation)

- 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

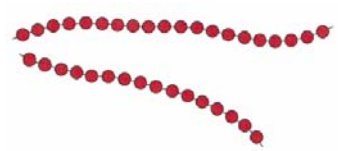


chain end-to-end distance, *r*

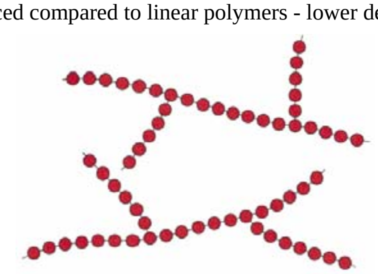
Molecular structure (I)

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.

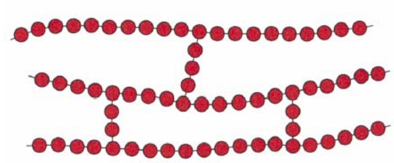


2 **Branched polymers**: Chain packing efficiency is reduced compared to linear polymers - lower density

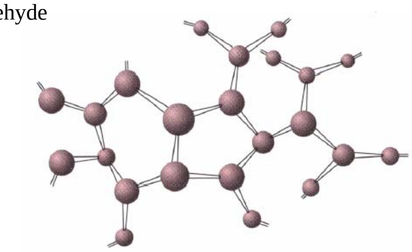


Molecular structure (II)

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.



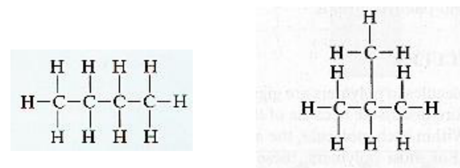
4 **Network polymers**: 3D networks made from trifunctional mers. Examples: epoxies, phenol-formaldehyde



Isomerism

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

Physical properties may depend on **isomeric state** (e.g. boiling temperature of normal butane is -0.5 °C, of isobutane -12.3 °C)



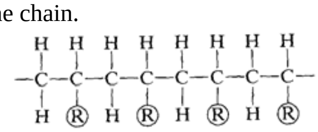
Butane → C_4H_{10} ← Isobutane

Two types of isomerism in polymers are possible: stereoisomerism and geometrical isomerism

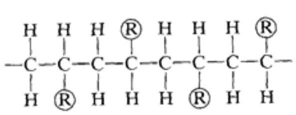
Stereoisomerism

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

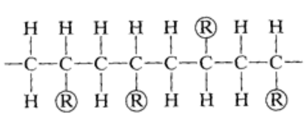
1 **Isotactic configuration:** all side groups R are on the same side of the chain.



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

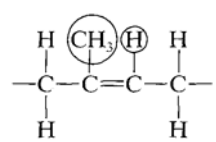


3 **Atactic configuration:** random orientations of groups R along the chain.

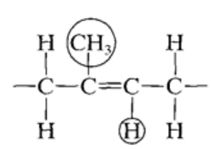


Geometrical isomerism

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).

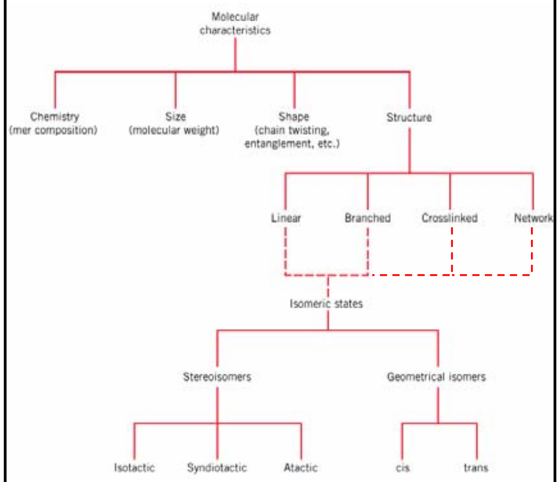


Cis-polyisoprene



Trans-polyisoprene

Size – Shape – Structure classification



Thermoplastic and thermosetting polymers

Depending on the response to temperature increase, two types of polymers can be distinguished:

(1) **Thermoplastic polymers:** soften and liquefy when heated, harden when cooled (reversible).

Molecular structure: linear or branched polymers, with secondary bonding holding the molecules together.

Easy to fabricate/reshape by application of heat and pressure

Examples: polyethylene, polystyrene, poly(vinyl chlodide).

(2) **Thermosetting polymers:** become permanently hard during their formation, do not soften upon heating.

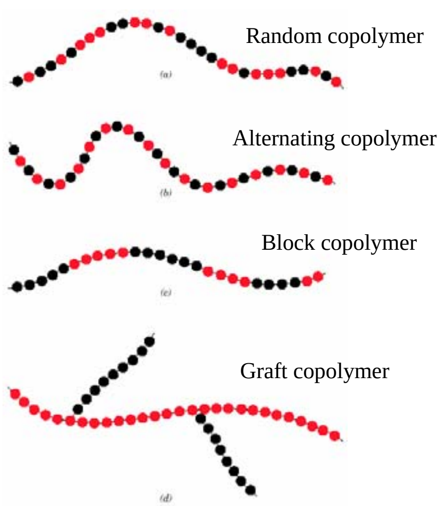
Molecular structure: network polymers with a large density of covalent crosslinks between molecular chains (typically, 10-50% of repeat units are crosslinked).

Harder and stronger than thermoplastics, have better dimensional and thermal stability.

Examples: vulcanized rubber, epoxies, phenolics, polyester resins.

Copolymers (composed of different mers)

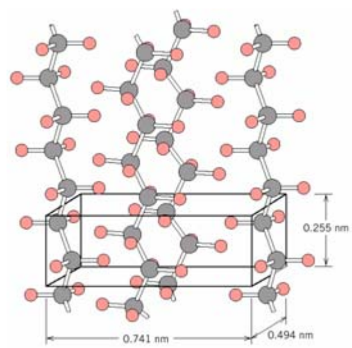
Copolymers, polymers with at least two different types of mers, can differ in the way the mers are arranged:



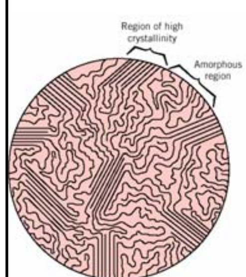
average molecular weight of repeat unit, $\overline{m} = \Sigma f_i m_i$, is used in calculation of the degree of polymerization of copolymers (f_i is fraction of mer i of molecular weight m_i)

Polymer Crystallinity (I)

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



Polyethylene



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

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 polymers is 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:

$$\% \quad \text{crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

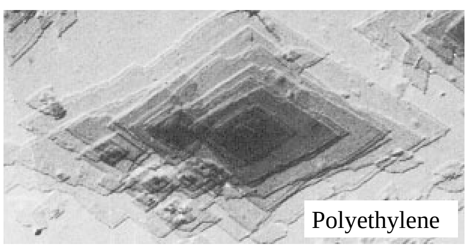
ρ_c: Density of perfect crystalline polymer

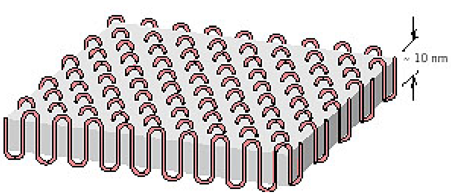
ρ_a: Density of completely amorphous polymer

ρ_s: Density of partially crystalline polymer that we are analyzing

Polymer Crystals (I)

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

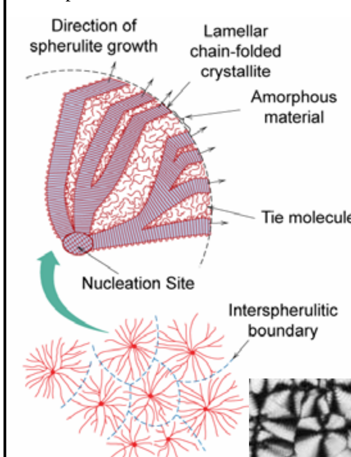




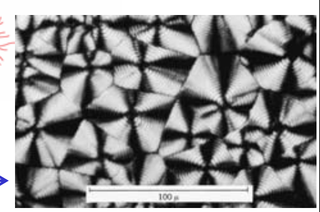
The average chain length can be much greater than the thickness of the crystallite

Polymer Crystals (II)

Spherulites: Aggregates of lamellar crystallites ~ 10 nm thick, separated by amorphous material. Aggregates are formed upon solidification from a melted state and are approximately spherical in shape.



Photomicrograph of spherulite structure of polyethylene →



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
- Degree of polymerization
- Graft copolymer
- Homopolymer
- Isomerism
- Isotactic configuration
- Linear polymer
- Macromolecule
- Mer, monomer
- Molecular chemistry
- Molecular structure
- Molecular weight
- Network polymer
- Polymer
- Polymer crystallinity
- Random copolymer
- Saturated
- Spherulite
- Stereoisomerism
- Trans (structure)
- Trifunctional mer

Five Bakers Dancing