Outline

- Introduction
- Molecular Structure and Configurations
- Polymer's synthesis
- Molecular weight of polymers
- Crystallinity

Polymers

- You may think of polymers as being a relatively modern invention
  - however naturally occurring polymers have been used for thousands of years
  - wood, rubber, cotton, wool, leather, silk,.. etc
- Artificial polymers are, indeed, relatively recent and mostly date from after WWII
  - in many cases, the artificial material is both **...........** and **.............** than the natural alternative

Introduction to Polymers

styrofoam cups
contact lenses
rubber tires
telephone housings
epoxies
sandwich bags
soda bottles
rubber bands
computer keyboards
cables … etc

COMMERCIAL Polymers: used in large quantities for their lightweight, corrosion-resistance, and good formability.
- usually low strength and stiffness

ENGINEERING Polymers: improved strength and better elevated temperature properties.

in fact, just look around your, house, dorm or apartment room and you'll likely find plenty of examples of polymeric materials.

Polymers:
……………………..….., ………………… AND ………………

Types of Polymers

Thermoplastics:

- Soften on heating, can then be formed & shaped by viscous flow. Retain shape on cooling. Process can be repeated. (*Becomes plastic on heating*)
- Thermoplastics generally consist of very long carbon chains with side groups of H, O, N.. etc.

Thermosets

- Thermosetting plastics are formed/shaped then "Cured" or "Set" by a chemical reaction, permanently. ………… be remelted or reshaped by application of heat.
- Other side-groups O, N, H will be present.

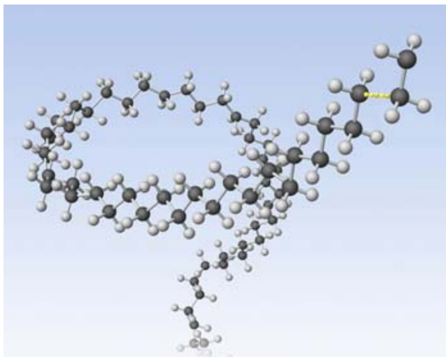
ELASTOMERS (Rubbers)

- Very large elastic deformations, when loaded, (which can be recovered on unloading) up to ……. elongation possible.

Molecular Structure and Configurations

Definition: A polymer is a molecule with a molecular weight on the order of several thousands g/mol.

- Polymers are usually ……………..…..-based and contain many individual repeat units, or "mers"; polymers consist of chains of carbon atoms
- Sometime called ………………… because of their huge size.



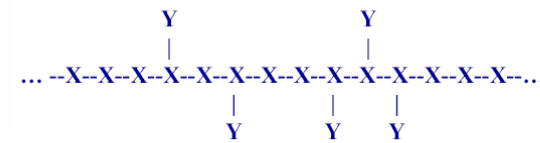
Molecular Configurations

Suppose our repeat unit is an "X" Then, a linear polymer based on "X" would look like the following:

… --X--X--X--X--X--X--X--X--X--X--X--X--…

where each "X" represents a "mer"

Sometimes, polymers contain functional side groups, called pendant groups:



We call the primary linear chain the "backbone"

Molecular Configurations

Homopolymers vs. co-polymers: If only one type of repeat unit is present, the polymer is called a ***homopolymer***. If a second monomer is also present in the chain, the resulting material is called a ***co-polymer***.

Model for a *homopolymer*:

--X--X--X--X--X--X--X--X--X--X--X—X

Model for an *alternating co-polymer*:

--X--W--X--W--X--W--X--W--X--W--X—W

Model for a *random co-polymer*:

--X--X--X--W--X--W--X--X--W--X--W—W

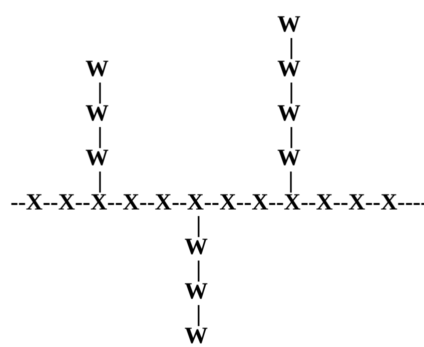
Model for a *block co-polymer*:

--X--X--X--X--X--X--X--X--W--W--W--W--W--W--

Molecular Configurations

Graft co-polymer: The resulting structure when chains of one type of monomer, say W, are grafted onto a backbone polymer chain of, say X.

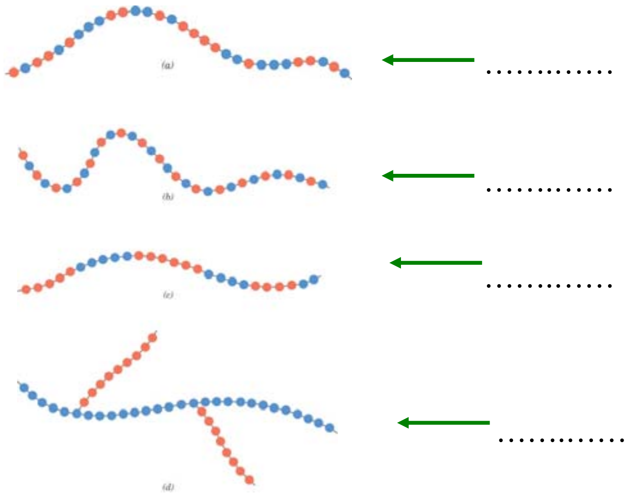
Model for a *graft co-polymer*:



Side branches like this tend to make a polymer …….. and ………..

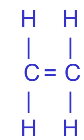
Molecular Configurations

Another conceptual representation of various co-polymers:



Molecular Structure: *Hydrocarbon Molecules*

- Hydrocarbons
  - hydrogen and carbon, bonded covalently
- Simplest are methane, ethane, propane, butane
  - C_nH_{2n+2}, the paraffin family
  - where each carbon shares an electron either with another carbon or with a hydrogen
- Alternatively, a carbon can share two electrons with another carbon atom
  - a double bond
  - hence ethylene, C_2H_4



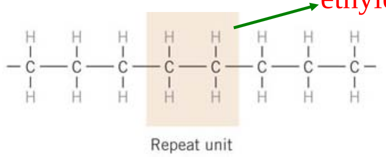
- And triple bonds are also possible
  - e.g. acetylene, C_2H_2 $H-C\equiv C-H$

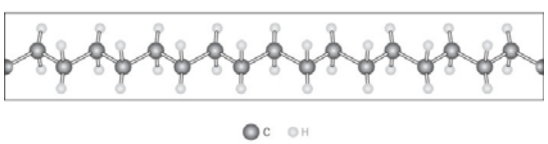
Structure of Polymers

Examples of "actual" monomers and their resulting polymers:

Polyethylene: (the mer unit is C_2H_4)

ethylene





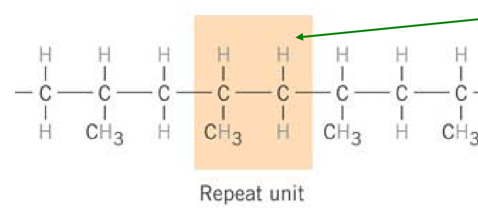
- Polyethylene is used for flexible bottles, toys, ice trays, and film wrapping materials.
- It is tough but possesses low strength.
- Trade names: Ethron, Fortiflex, Hi-fax, Rigidex, Zendel.

*This is an example of a linear chain ………………, where the "X" in our model is replaced by the **ethylene** group.*

Structure of Polymers

Polypropylene: (the mer unit is now C_3H_6)

propylene

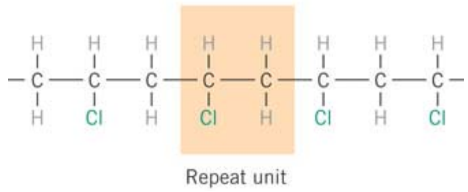


now, the repeat unit (or mer) is the propylene unit:

- Polypropylene is used for items such as: bottles, TV cabinets, luggage.
- It tends to be relatively ……… and …………………….
- It has the trade names Herculon, Meraklon, and Profax.

Structure of Polymers

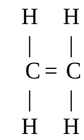
Polyvinyl chloride: (the mer unit is C_2H_3Cl)



- **Polyvinyl chloride** is a *very popular*, low cost ………. material
- It can be made ……….. by adding **plasticizers**.
- It is used as floor coverings, pipe, garden hose, electrical wire insulation, and earlier as phonograph records.
- Tradenames: PVC, Saran, Tygon, Darvic, Geon.

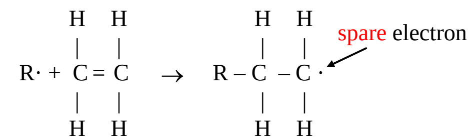
Synthesis of Polymers (Polymerization)

- **So how is a polymer formed from the monomer?**
- **Consider ethylene (a gas)**



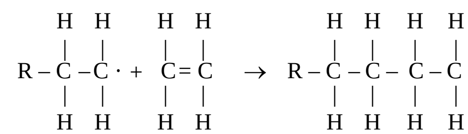
Note: the polymer which forms is polyethylene (solid at room temp)

- The reaction is initiated by an *initiator*, R·



The unsaturated double bond is broken to produce active sites, which then attract additional repeat unit to either end to produce a chain.

- The active (spare) electron is transferred to the end monomer, and **the molecule grows**



Synthesis of Polymers (Polymerization)

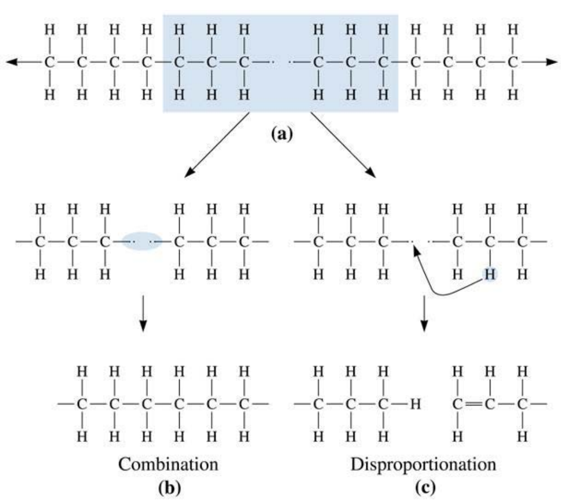
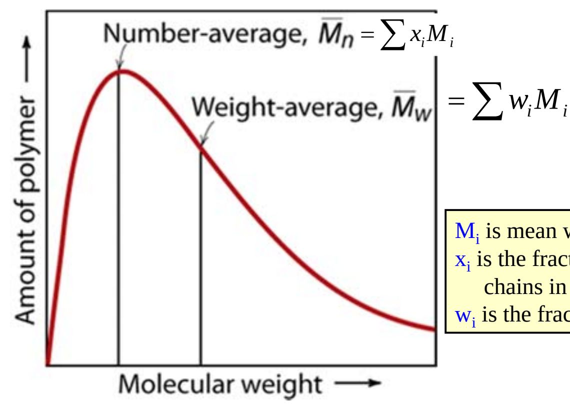


Figure 15.6 (The Science and Engineering of Materials – by D.R. Askeland and P.P. Phule)

Termination of polyethylene chain growth: (a) the active ends of two chains come into close proximity, (b) the two chains undergo combination and become one large chain, and (c) rearrangement of a hydrogen atom and creation of a double covalent bond by disproportionation cause termination of two chains.

Molecular Weight

- ***Since not all chains in a sample of material are the same length, and so there is a distribution of molecular weights***



M_i is mean weight in size range, i
x_i is the fraction of total number of chains in size range, i
w_i is the fraction of total weight in size range, i

Very large molecular weights are common for polymers

Molecular Weight

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

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

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

The mer molecular weight for a co-polymer can be determined by:

$$\overline{m} = \sum f_j m_j$$

f_j chain fraction of mer j
m_j molecular weight of mer j

• 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

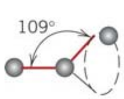
Example

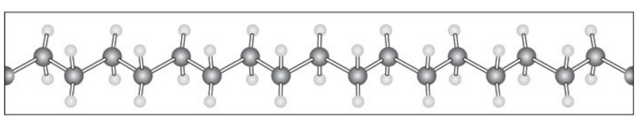
Below, molecular weight data for a polypropylene material are tabulated. Compute **(a)** the number-average molecular weight, **(b)** the weight-average molecular weight, **(c)** the number-average degree of polymerization, and **(d)** the weight-average degree of polymerization.

Molecular Weight Range (g/mol)	x_i	w_i	x_iM_i	w_iM_i
8,000–16,000	0.05	0.02	600	240
16,000–24,000	0.16	0.10	3200	2000
24,000–32,000	0.24	0.20	6720	5600
32,000–40,000	0.28	0.30	10,080	10,800
40,000–48,000	0.20	0.27	8800	11,880
48,000–56,000	0.07	0.11	3640	5720

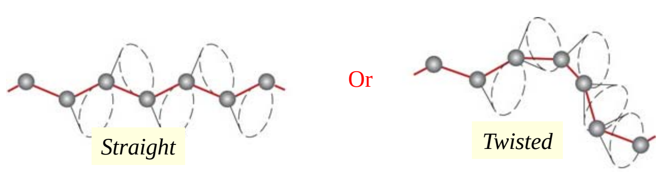
Molecular Shape

- ***If the positions of the atom were strictly determined, polymers would form straight chains***
  - *in fact, the 109° bond angle in polyethylene gives a cone of rotation around which the bond lies*





Because of this we can get:



Molecular Shape

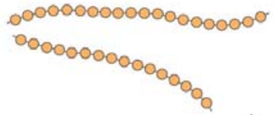
• **Hence the polymer chain can bend, twist, and kink into many shapes**

- *adjacent molecules can intertwine*
- *leading to the highly elastic nature of many polymers, such as rubber*

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

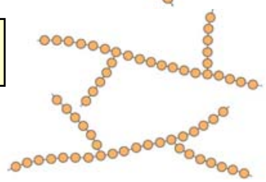
Molecular Structure

- **Linear polymers**
  - long, single, flexible chains with some van der Waals or hydrogen bonding

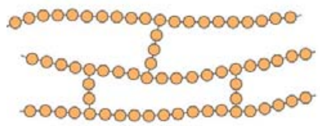


- **Branched polymers**

Chain packing efficiency is **reduced** compared to linear polymers (lower density)

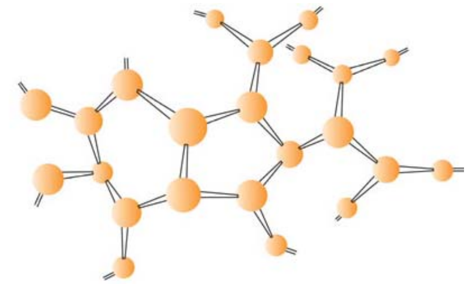


- **Cross-linked polymers**
  - cross linkage happens either during synthesis or in a separate process, typically involving addition of impurities which bond covalently
  - this is termed vulcanisation in rubber



Molecular Structure

Network polymers: 3D networks made from trifunctional mers. Examples: epoxies, phenolformaldehyde



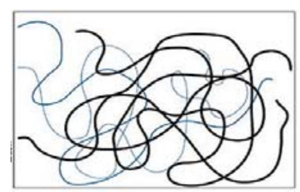
Note that these are …………… polymers

Classification of Polymers

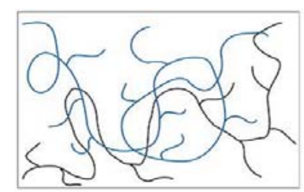
- Thermoplastics - Linear or branched polymers in which chains of molecules are not interconnected to one another.
- Thermosetting polymers - Polymers that are heavily cross-linked to produce a strong three dimensional network structure.
- Elastomers - These are polymers (thermoplastics or lightly cross-linked thermosets) that have an elastic deformation usually > 200% and can reach to 900%.

Note that branching can occur in any type of polymer (e.g., thermoplastics, thermosets, and elastomers).

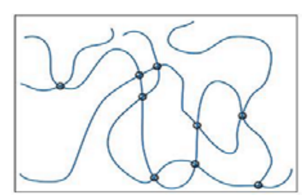
Classification of Polymers



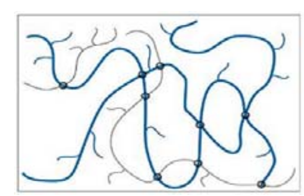
(a) Linear unbranched polymer: notice chains are not straight lines and not connected.



(b) Linear branched polymer: chains are not connected, however they have branches.



(c) Thermoset polymer without branching: chains are connected to one another by covalent bonds but they do not have branches



(d) Thermoset polymer that has branches and chains that are interconnected via covalent bonds

Crystallinity in Polymers

- Although it may at first seem surprising, Polymers can form crystal structures (*all we need is a repeating unit, which can be based on molecular chains rather than individual atoms*)
- Some parts of structure align during cooling to form crystalline regions. (Not like FCC + BCC metals - *chains align alongside each other*)
- Around CRYSTALLITES the AMORPHOUS regions occur (*next slide*).

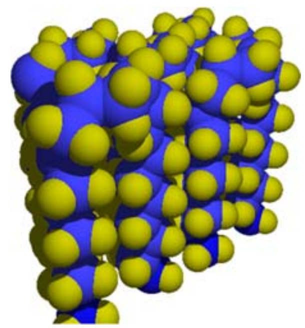
$$\%\ crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

Where:

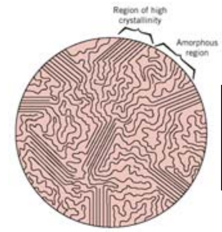
ρ_s = Density of sample

ρ_a = Density of the completely amorphous polymer

ρ_c = Density of the completely crystalline polymer



Crystallinity in Polymers



Most actual polymers contain both amorphous and crystalline regions, as shown above.

% crystallinity depends on several factors:

✓ Rate of cooling (……. cooling – ……. crystallinity)

✓ Chain configuration (…….. structures – …….. crystallinity)
(Copolymers – less crystallinity)

✓ Linear polymers form crystals more easily because the molecules can orient themselves readily

- Degree of Crystallinity ranges from 5 - 95%
- Higher % Crystallinity → higher strength

Next time:

Polymers to be continued