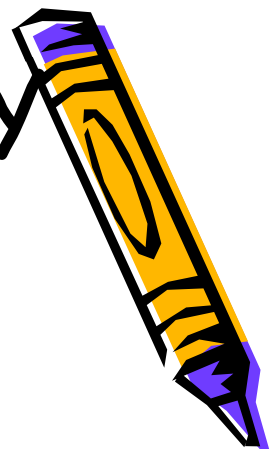# POLYMER CHEMISTRY

COURSE CONTENT

1.Introduction

2.Synthesis of polymer

Polymer Science

What is it ?

- The Science of Large Molecules
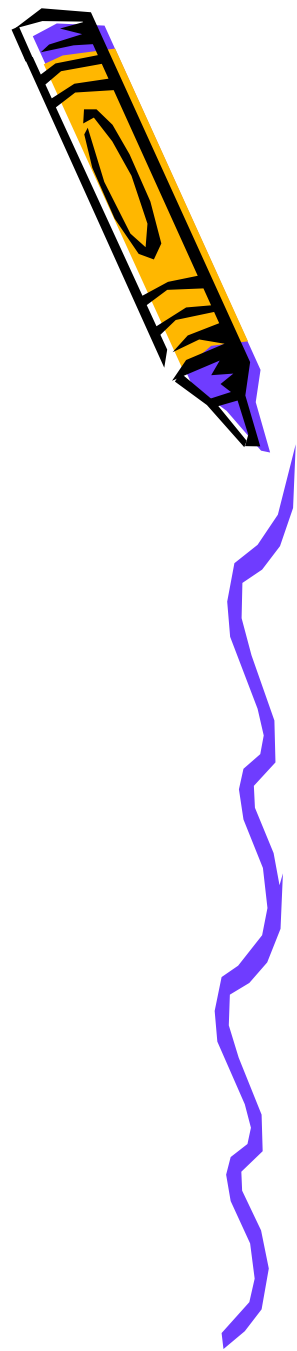
This includes

Synthesis

Characterization

Polymer Physics and Physical Chemistry

Polymer Engineering

Poly.........mer
many   units

$$-M-M-M-M-M-M-$$

or

$$-(M)_n-$$

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**
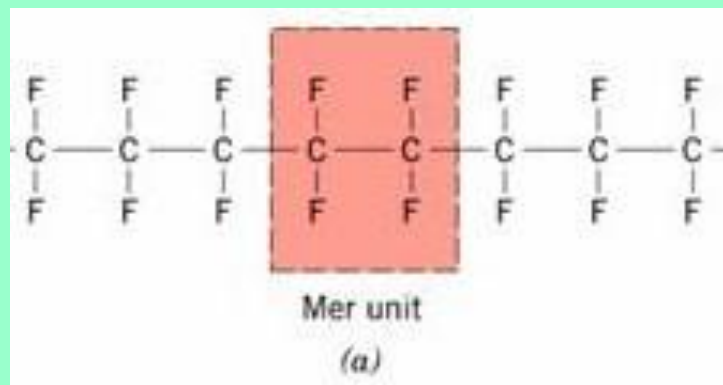
Chemistry of polymer molecules (I)
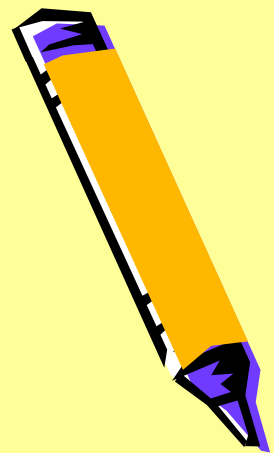
● Ethylene (C_2H_4) is a gas at room temp and pressure.

● Ethylene transforms to polyethylene (solid) by forming active mers through reactions with an initiator or catalytic radical (R.)
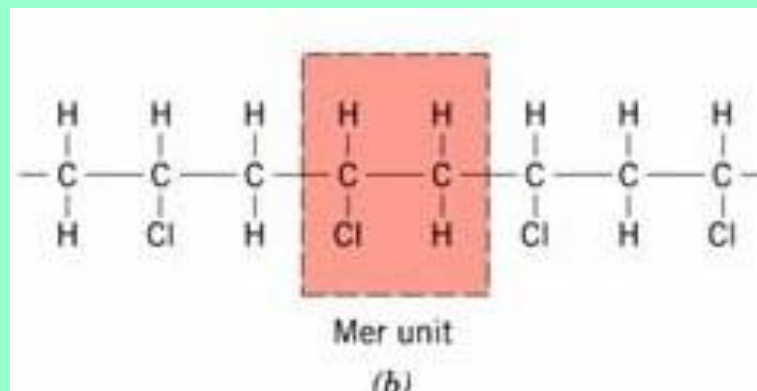
Ethylene   Polyethylene
$CH_2= CH_2$ $[-CH_2- CH_2-]n$
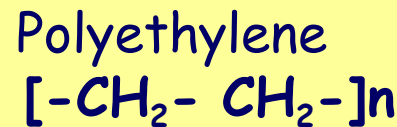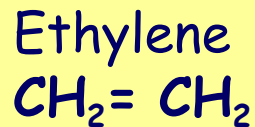
● Rapid propagation ~1000 mer units in 1-10 ms:

Chemistry of polymer molecules (II)
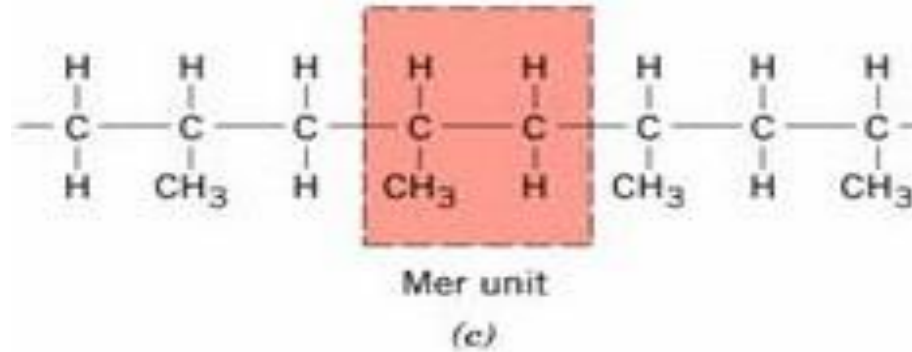

Mer unit
(a)
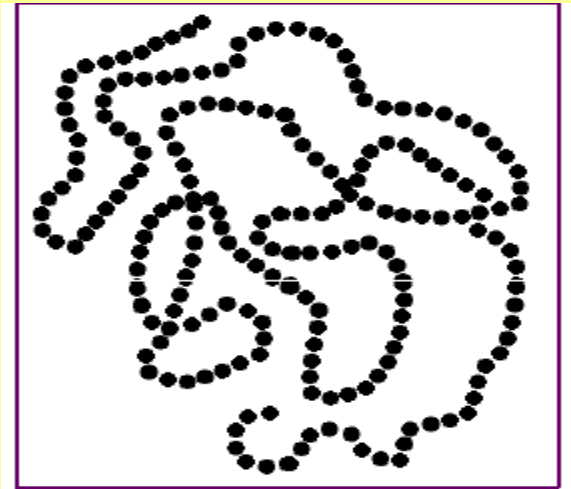
Replace hydrogen atoms in polyethylene: make polytetraflouroethylene (PTFE) – Teflon

Mer unit
(b)

Replace every fourth hydrogen atom in polyethylene with Cl atom: polyvinylchloride

Mer unit

(c)

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.
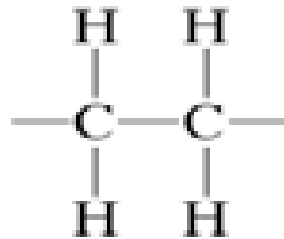
Polyethylene
(bifunctional)
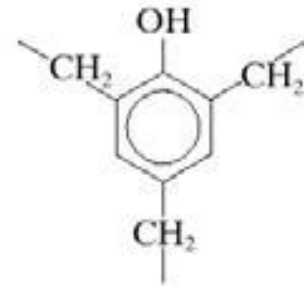
Phenol-formaldehyde
(trifunctional)

Molecular weight (I)

☐ F i n a l molecular weight (chainlength) 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**).
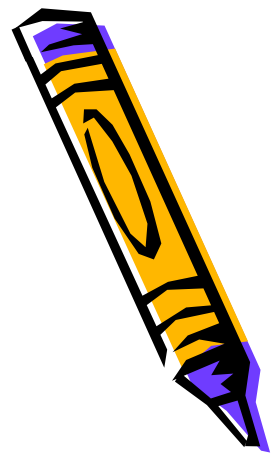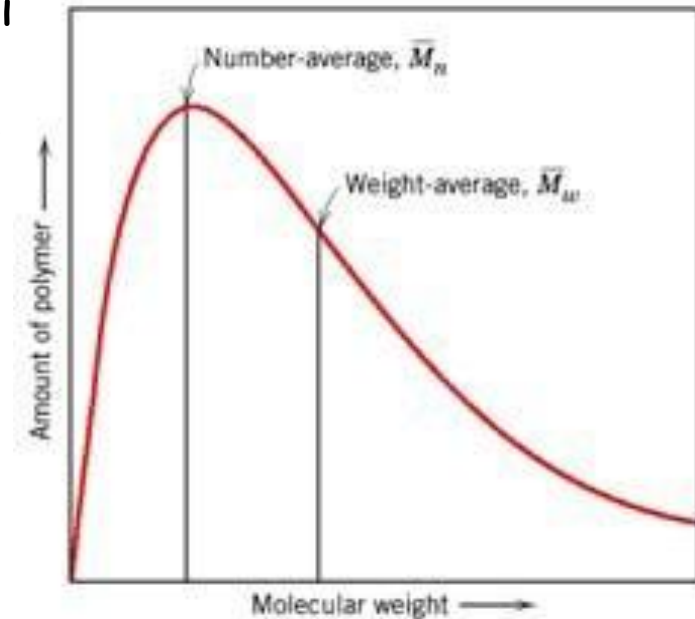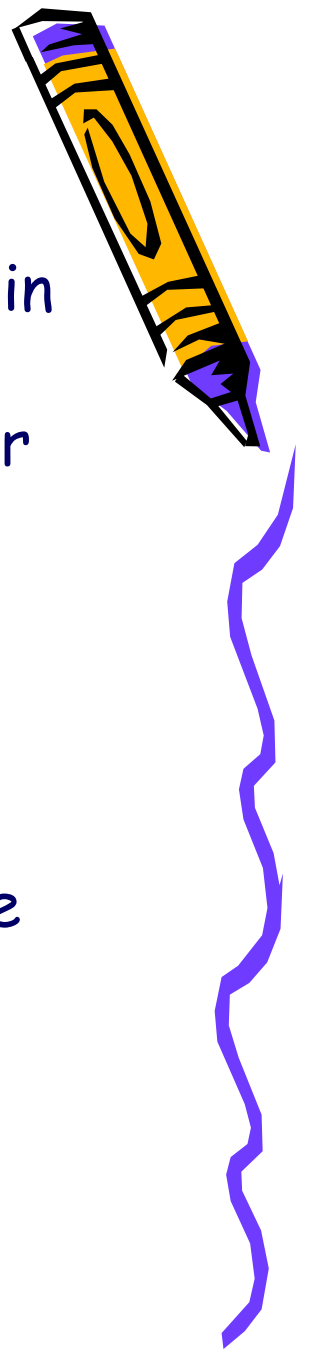
Number average:

$$\overline{M_n} = \Sigma x_i M_i$$

Weight average

$$M_w = \Sigma w_i M_i$$

- 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

Eg: If we started with 100 moles of monomers in a pot and polymerized these to give 5 moles of chains, then the average "length" of the chain, or degree of polymerization, would be **20**;

100 divided by 5.

If the weight of each unit in the chain were 100 units, the average molecular weight would be 20,000.

But this says nothing about the distribution. Do we have one chain 96 units long and 4 unreacted monomers, or chains of length 18,19,20,21 and 22 ? Or some other distribution ?

Also, what we have calculated is something called a **number average**, which is defined mathematically

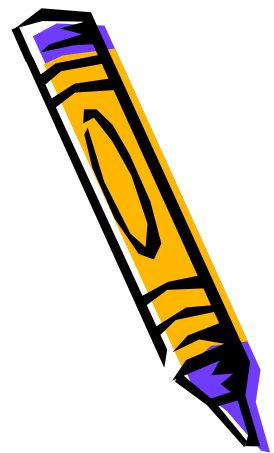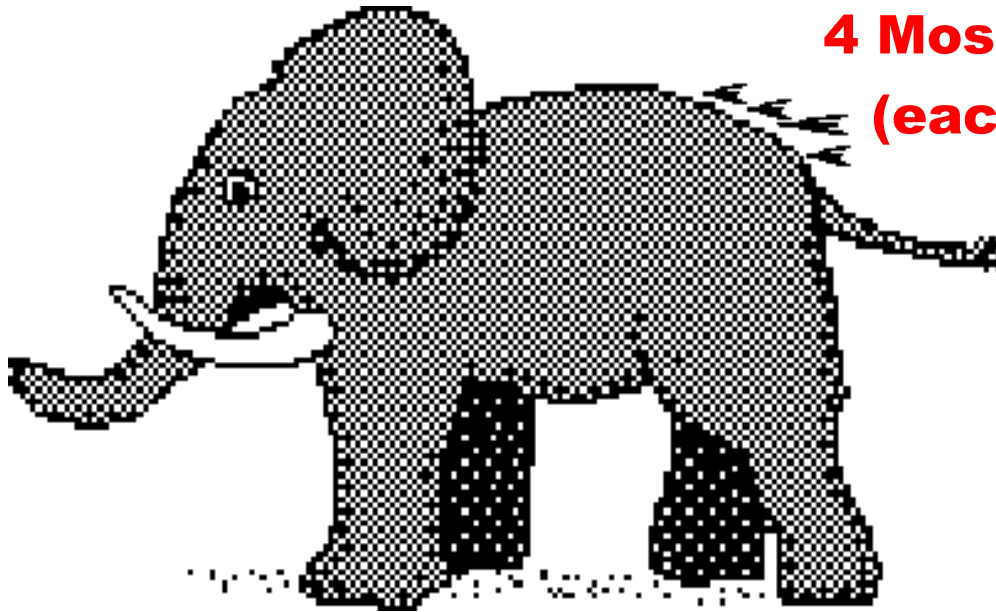$$\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x}$$
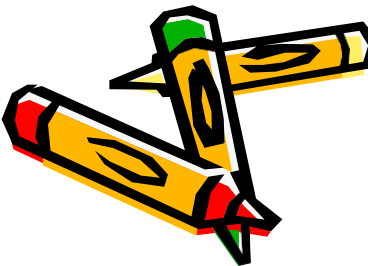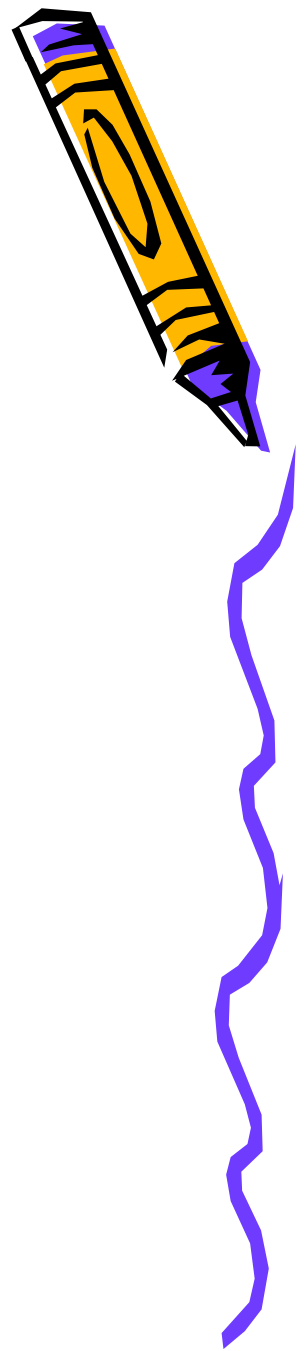
Behold an elephant with four mosquito's on its bum. If the elephant weighs 10,000 lbs., and the mosquito's 1 lb. each. What would be the average weight of each of the things or species present ?

10,000 lb Elephant

4 Mosquitos

(each weighing 1 lb)

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{[1 \times 10,000] + [4 \times 1]}{4 + 1} \sim 2,000$$
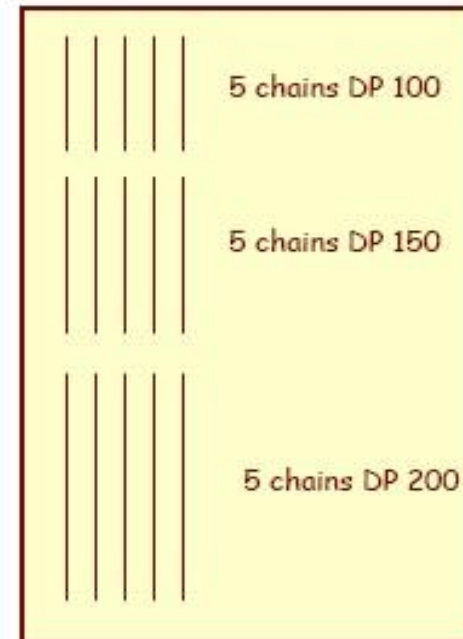
Molecular Weight - Definition of Number Average and Weight Average

Consider a sample with 5 (moles of) chains of "length" (degree of polymerization or DP) 100, (i.e. has 100 monomer units in the chain), 5 (moles of) chains of length 150 and 5 (moles of) chains of length 200.

For this simple example it should be easy to see that the average DP of the sample is 150.

If the molecular weight of each unit in the chain were 100, the number average molecular weight would then be 15,000.

5 chains DP 100

5 chains DP 150

5 chains DP 200

$$\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x}$$

Molecular Weight - Definition of Number Average and Weight Average

Here's how the equation works;

$$\overline{M_n} = \frac{\sum N_x M_x}{\sum N_x} = \frac{[5 \times 10{,}000] + [5 \times 15{,}000] + [5 \times 20{,}000]}{5 + 5 + 5}$$

$$= \frac{50{,}000 + 75{,}000 + 100{,}000}{15} = 15{,}000$$

What about weight average molecular weight?

Weight Average Molecular Weight

First recall the definition of weight average;

$$\overline{M_w} = \frac{\sum W_x M_x}{\sum W_x}$$

Now note that the total weight of species x present is just the molecular weight of each chain of type x multiplied by the number of chains of this type. Eg if there are 5 chains, each of weight 10,000, then w_x is 50,000;

$$W_x = N_x M_x$$

We can now substitute in the equation at the top to obtain a different form of the equation for weight average;

$$\overline{M_w} = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

Weight Average Molecular Weight

This gives us;

$$\overline{M_w} = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x} = \frac{5 \times 10,000^2 + 5 \times 15,000^2 + 5 \times 20,000^2}{5 \times 10,000 + 5 \times 15,000 + 5 \times 20,000} = 16,111$$

Note that the weight average is larger than the number average. This is always true, except in the case when all the chains are the same length (as in proteins, where the number and sequence of amino acids is specified by the cell's machinery). We call the ratio of the two averages the polydispersity of the system. It is a measure of the breadth of the distribution

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n} \geq 1$$

Molecular Weight of Polymers - What Average ?

We have seen that *average molecular weight* is not unique. It turns out that there are more than two ways to define an average. Look at the definitions of number and weight average again;

Number Average Molecular Weight

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x}$$

Weight Average Molecular Weight

$$\overline{M}_w = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

You can see that we can go from number to weight average by multiplying each of the terms inside the summations by M_x. Higher order averages can be constructed in the same way. Eg the z-average;

$$\overline{M}_z = \frac{\sum N_x M_x^3}{\sum N_x M_x^2}$$

The ratio's of these averages can be related to the moments of the distribution and tell us about its breadth and "skewedness"

Z-Average Molecular Weight (z stands for centrifuge. German *zentrifuge*)

$$M_z = \Sigma N_i M_i^3 / \Sigma N_i M_i^2 = \Sigma w_i M_i^2 / \Sigma w_i M_i$$

Viscosity-Average Molecular Weight

$$M_\eta = (\Sigma N_i M_i^{1+a} / \Sigma N_i M_i)^{1/a} = (\Sigma w_i M_i^a / \Sigma w_i M_i)^{1/a}$$

Mathematically, $M_n \leq M_w \leq M_z$, here the equality sign holds only for monodisperse polymers.

The ratios of different molecular weight averages M_w/M_n and M_z/M_w are often used as characteristics of polymer **polydispersity**.

For most polymers M_w/M_n: 1.5–2.5

For **monodisperse polymer**: $M_w/M_n = M_z/M_w = 1$

MOLE (NUMBER) AND WEIGHT DISTRIBUTIONS
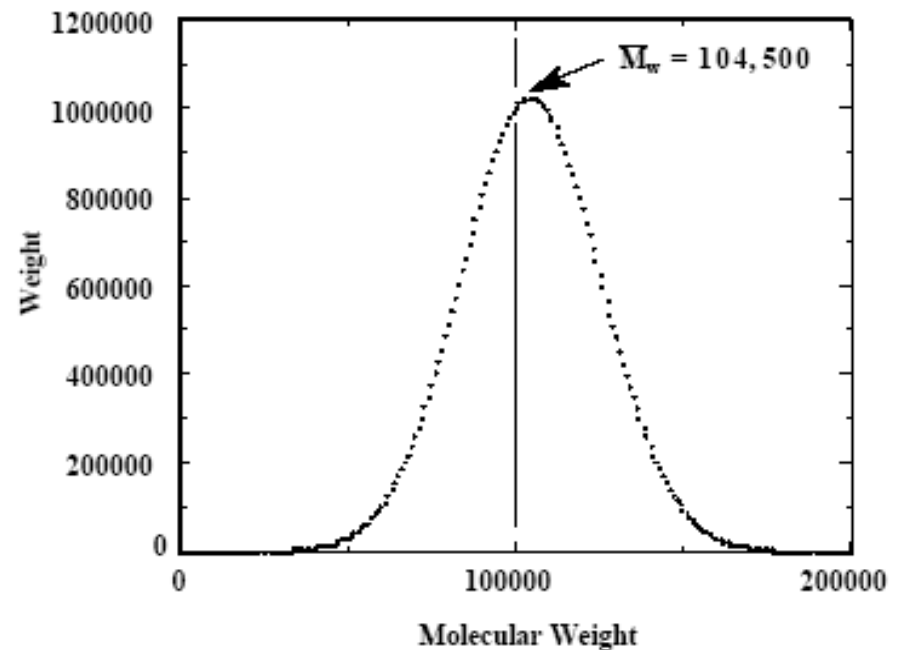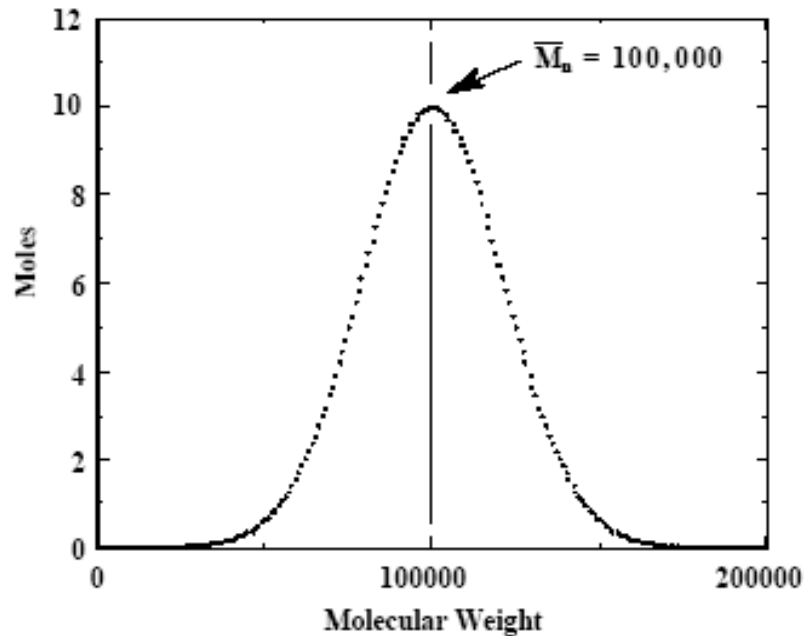
A *narrow* molecular weight distribution plotted
according to *number* (left) and *weight* (right)

Try it yourself

Calculate Mn (number average molecular weight), Mw (weight average molecular weight) and the polydispersity index for a polymer sample that contains the following mixture.

Weight(g)	Molecular wt
10.0	100000
20.0	50000
100.0	10000
50.0	70000

Mw= 36170, Mn =16077,

Polydispersity= 2.25
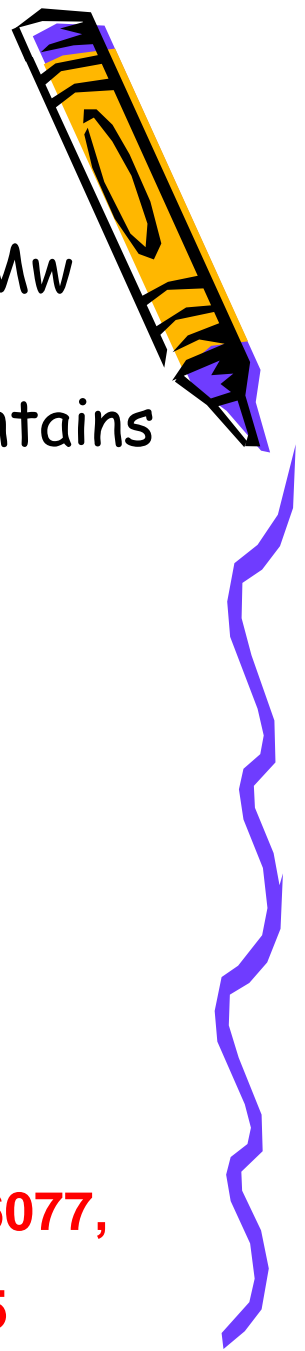
Molecular structure

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.
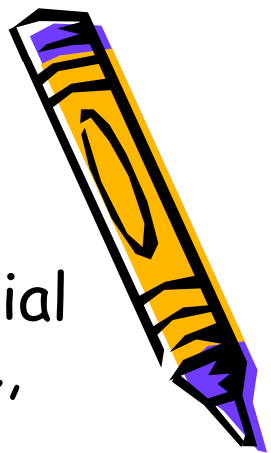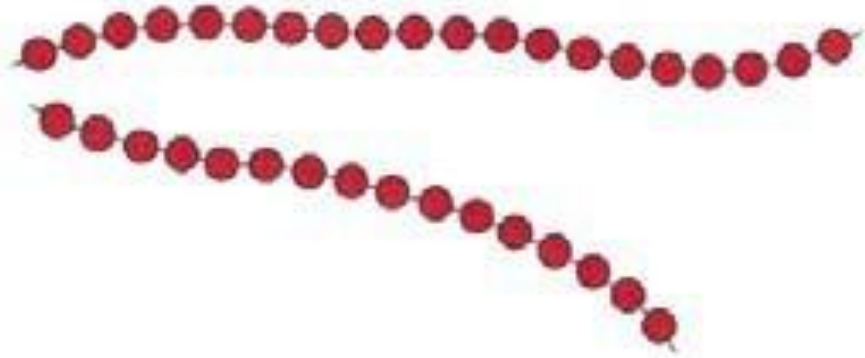
2. Branched polymers:

Chain packing efficiency is reduced compared to linear polymers - lower density
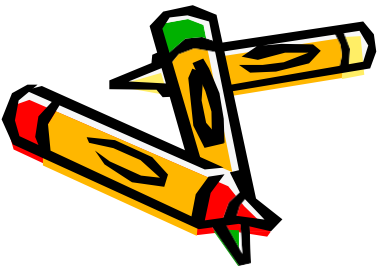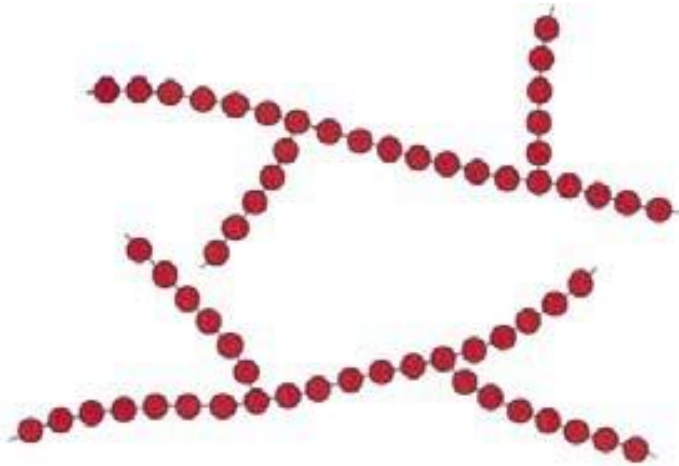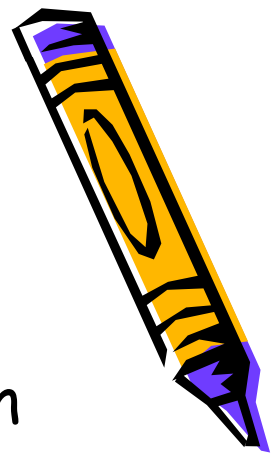
3. Cross-linked polymers:

Chains are connected by covalent bonds. Often achieved by adding atoms or molecules that form covalent links between chains.

Many rubbers have this structure.
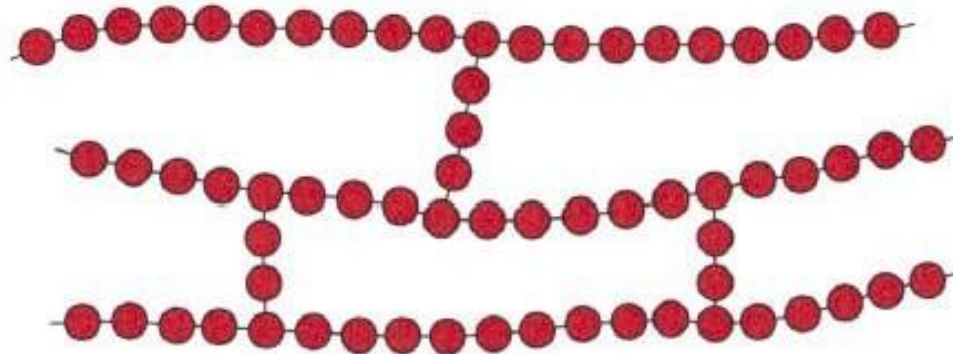
4. Network polymers

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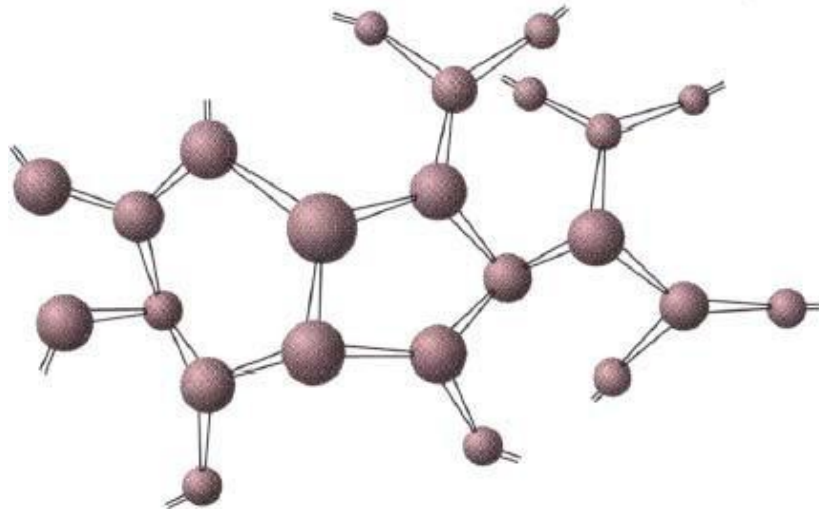
Copolymers

- When the two monomers are arranged in an alternating fashion, the polymer is called, of course, an *alternating copolymer*:

—A—B—A—B—A—B—A—B—A—B—A—B—A—B—
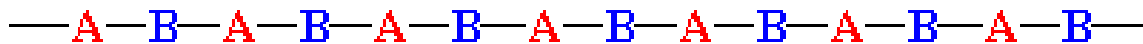
alternating copolymer

- In a *random copolymer*, the two monomers may follow in any order:

—A—A—B—A—B—B—A—B—A—A—B—B—B—A—
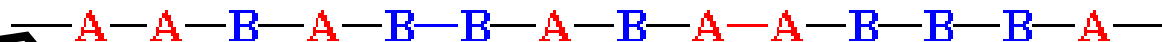
random copolymer
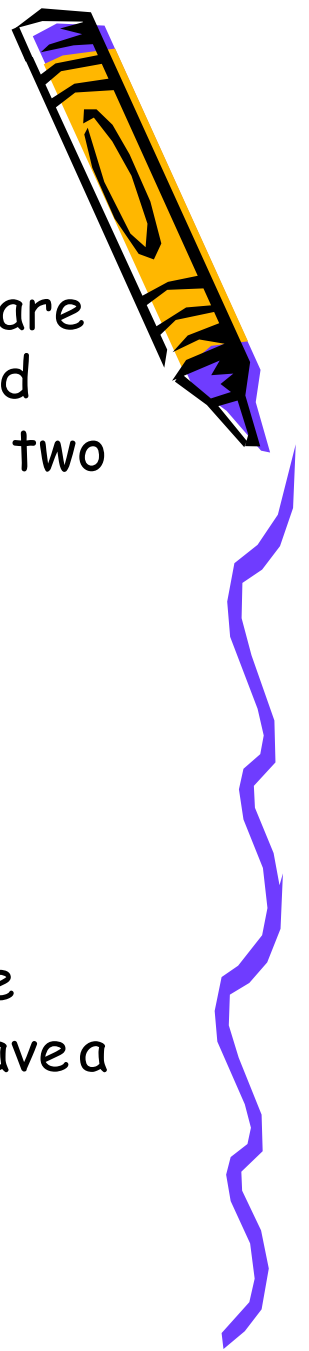
- In a **block copolymer**, all of one type of monomer are grouped together, and all of the other are grouped together. A block copolymer can be thought of as two homopolymers joined together at the ends:

$$—A—A—A—A—A—A—A—B—B—B—B—B—B—B—$$
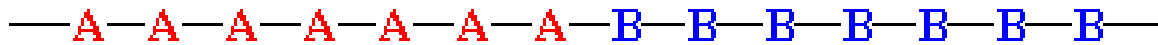
block copolymer

- When chains of a polymer made of monomer **B** are grafted onto a polymer chain of monomer **A** we have a **graft copolymer**:
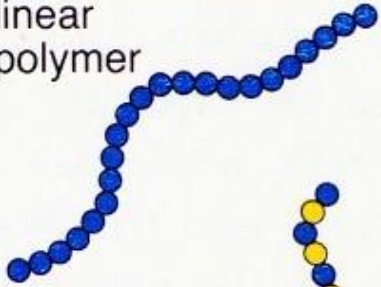
graft copolymer

Block and graft copolymers usually show properties characteristic of each of the constituent homopolymers. They also have some unique properties arising from the copolymerization.

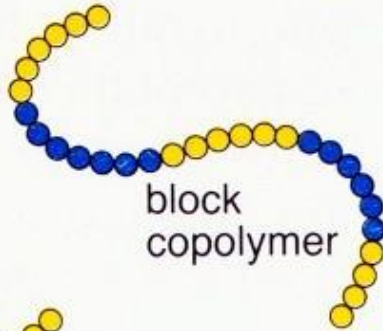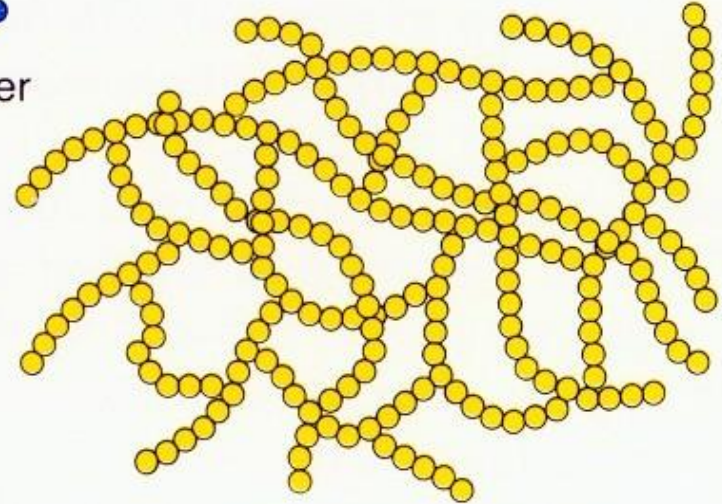# Different types of polymers
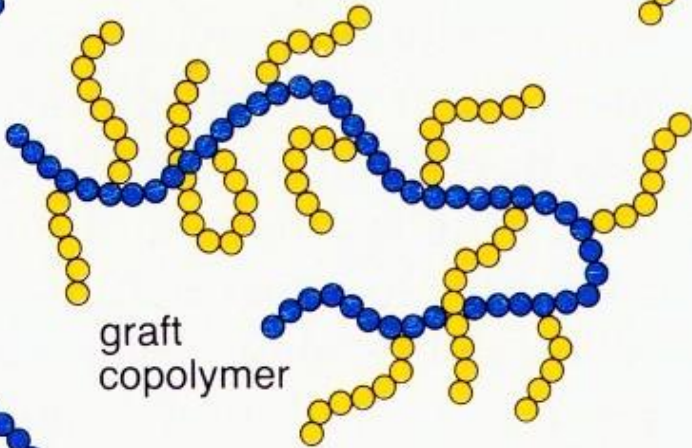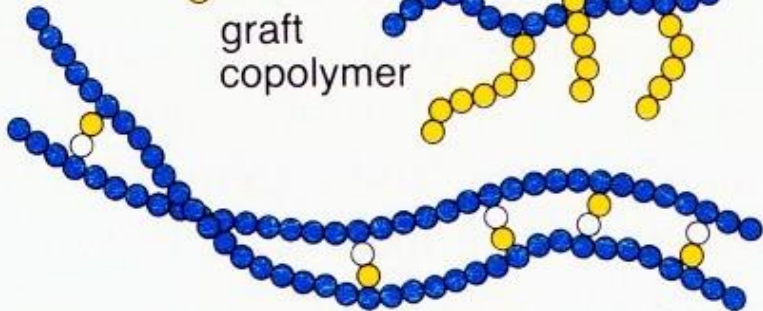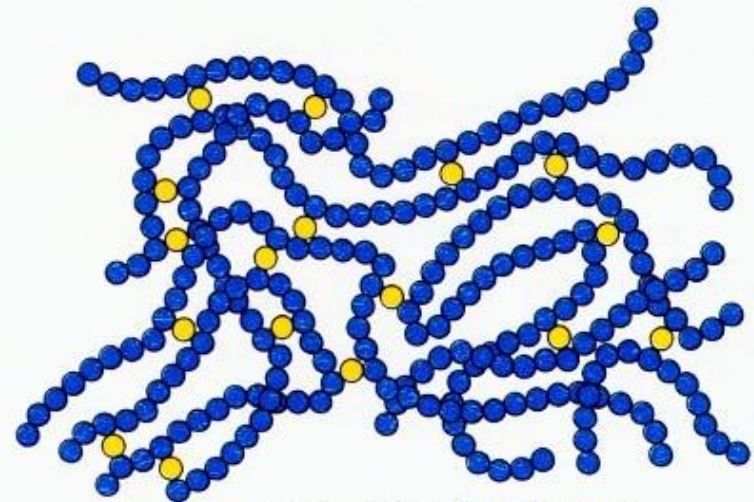
Linear polymers may be represented by a chain with two ends.

Linear chain does not imply "straight" molecules.

They can curl, twist or fold

Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points, and are characterized in terms of the number and size of the branches.
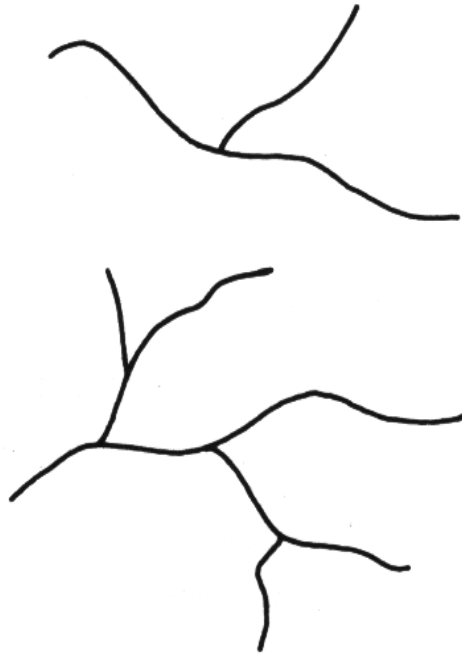Polymers with well-controlled modes of branching:
comblike polymers, star polymers, dendrimers, *etc*.

Network polymers have three-dimensional structures in which each chain is connected to all others, and are characterized by their crosslinking density or degree of crosslinking (number of **junction points** per unit volume).
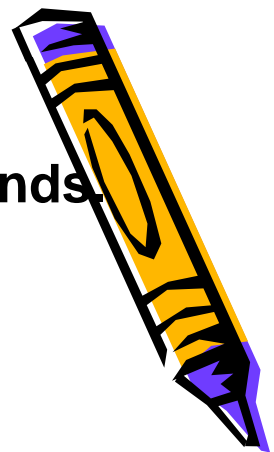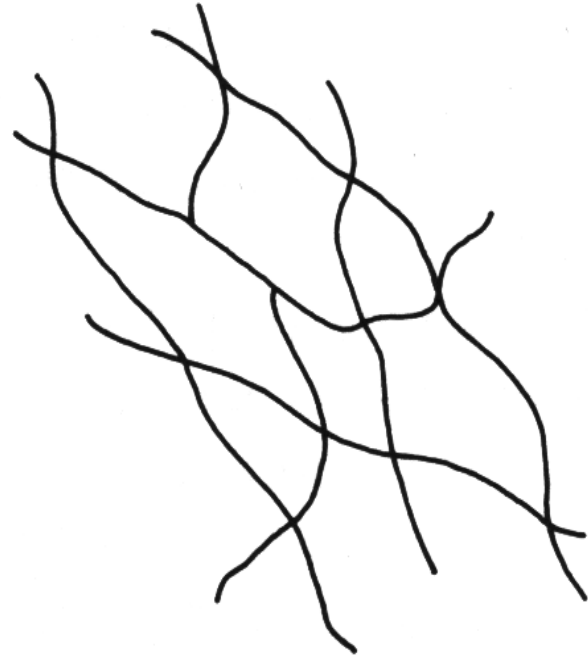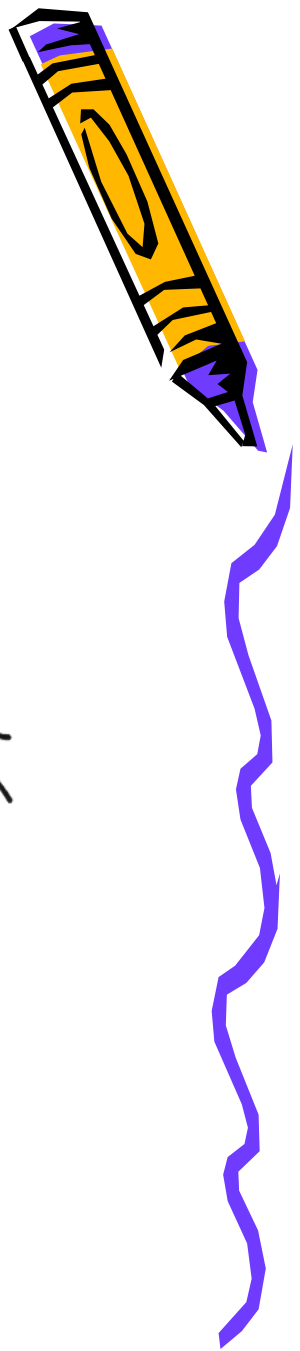
Linear   Branched   Network

Classification of Polymers

- **Thermosets**

- **Rigid materials and network polymers in which chain motion is greatly restricted by a high degree of crosslinking.**

- **Intractable once formed.**

- **Degrade rather than melt upon heating.**

- **Elastomers**

- **Crosslinked rubbery polymers that can be stretched easily to high extensions and which rapidly recover their original dimensions when the applied stress is released.**

- **Low crosslink density.**

- **Thermoplastics (plastics)**

- **Linear or branched polymers which can be melted upon the application of heat. (Largest proportion of the polymers used in industry.)**
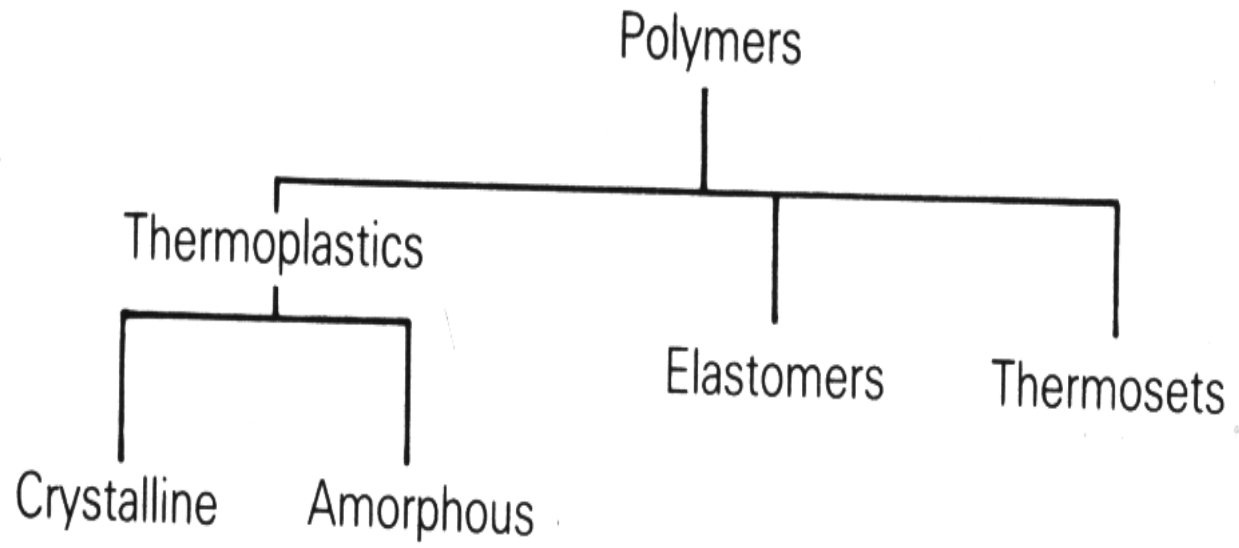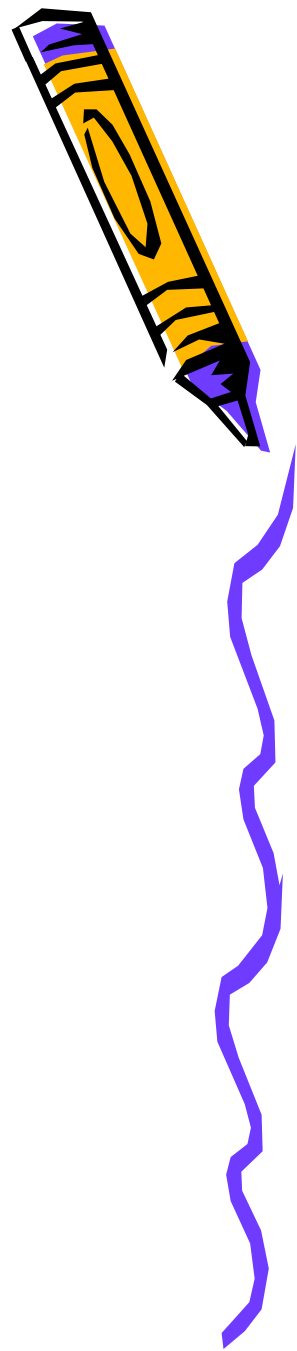
Fig. 1.2 *Classification of polymers.*

•**Crystalline polymers**

Invariably do not form perfect crystalline materials but instead are semicrystalline with both crystalline and amorphous regions.

**The crystalline phase of such polymers are characterized by their melting temperature (T_m).**

Amorphous polymers

Characterized by their glass transition temperature (T_g), the temperature at which they transform abruptly from the glass state (hard) to the rubbery state (soft). This transition corresponds to the onset of chain motion.
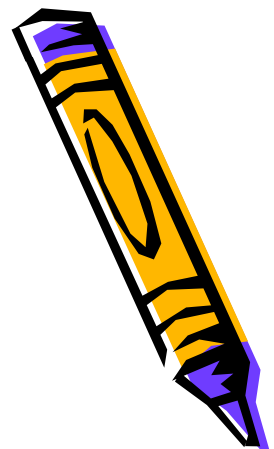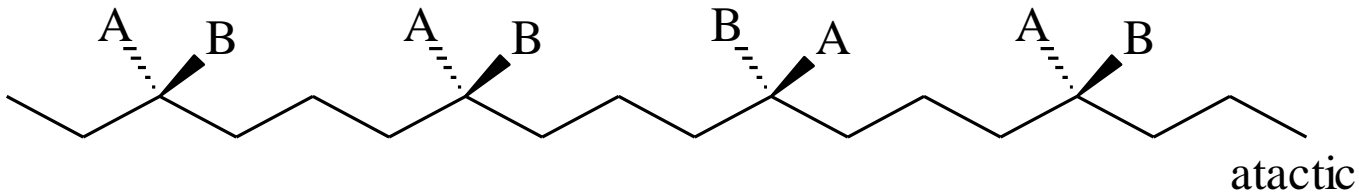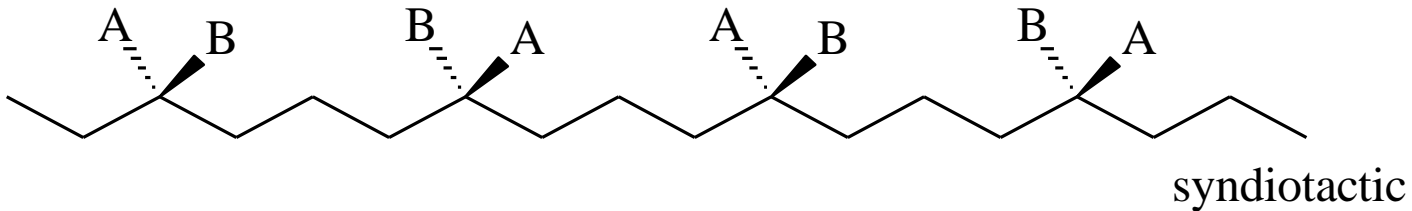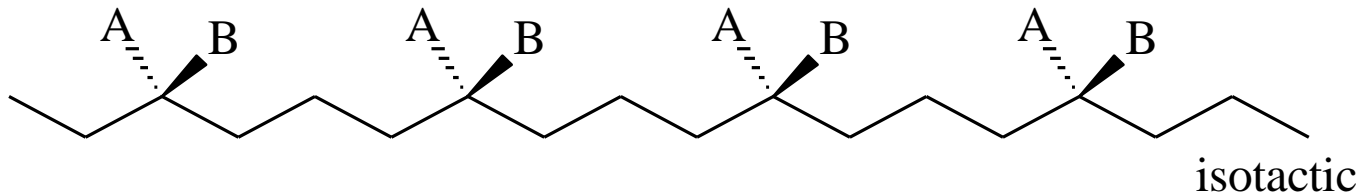
Stereochemistry

Geometrical isomers
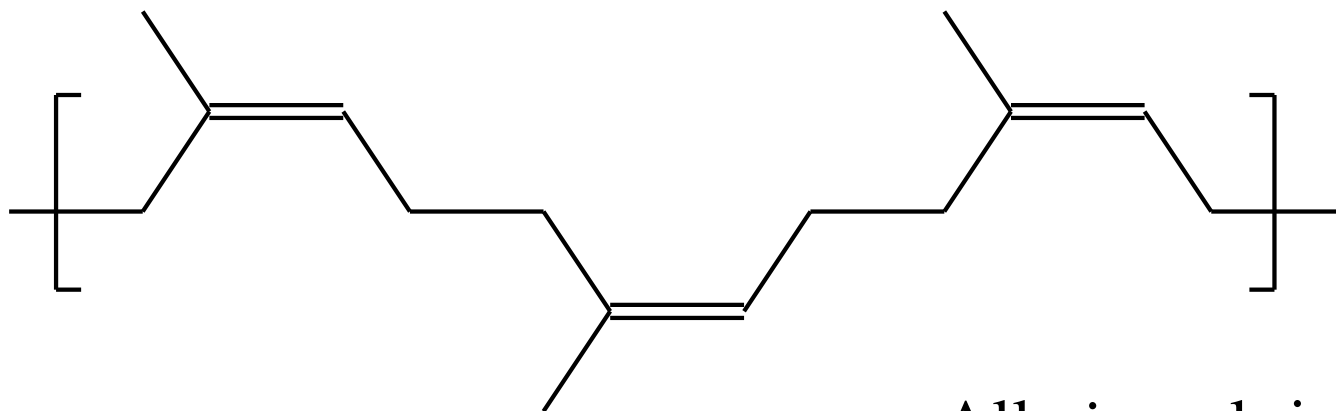
All *cis*-polyisoprene

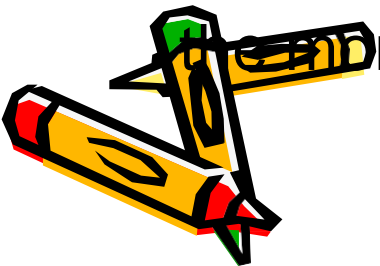# Configuration - atactic, isotactic, syndiotactic
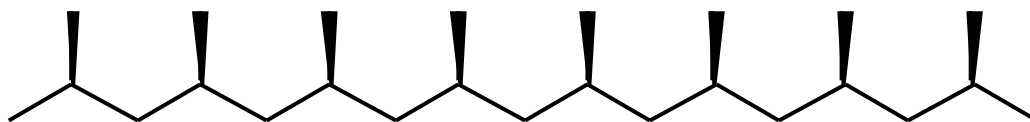

isotactic

syndiotactic

atactic

Isotactic polypropylene chain has ordered placement of the CH_3 groups. This type of arrangement lead to close molecular-chain packing and crystallinity

Syndiotactic polypropylene, the CH_3 groups are arrange regularly alternating the CH_3 molecules on either side of backbone of the chain, which lead toward a tougher, more dense crystalline structure.
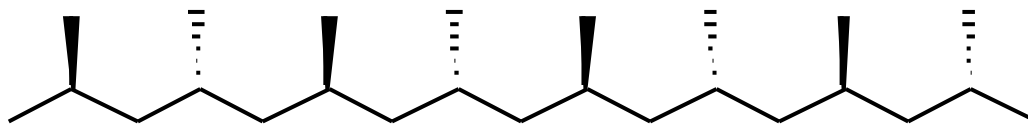
Atactic polypropylene is formed that has a random placement of the CH_3 groups. This random placement prevents chain packing and a noncrystalline polymer is formed. This polymer is soft, weak and less cloudy than the more crystalline isotactic and syndiotactic forms.
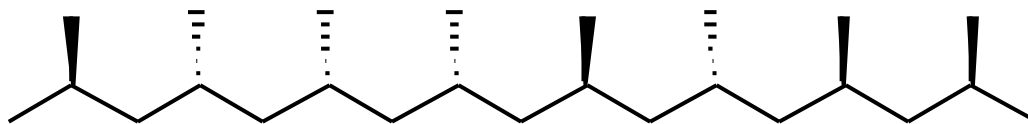
Stereochemistry and Polymer Properties
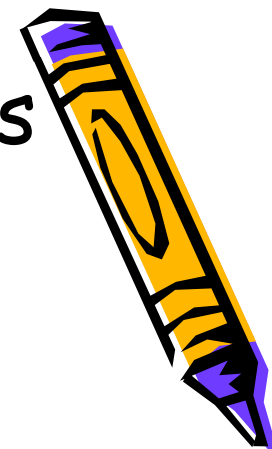
isotactic

syndiotactic

atactic

Isotactic: fabrics for carpets, automobile parts, battery casings, medicine bottles
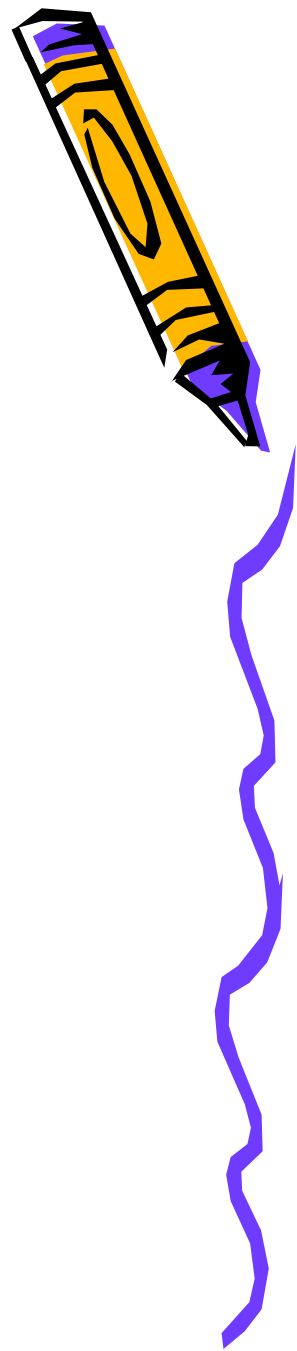
Syndiotactic: new applications are emerging

Atactic: soft, and not very useful

Try it

Draw the structure of atactic polystyrene and syndiotactic PMMA

Nomenclature

Source-based nomenclature **places the prefix *poly* before the name of the monomer, the monomer's name being contained within parentheses unless it is a simple single word [e.g., poly(methyl methacrylate) (PMMA), polyethylene (PE)].**

In structure-based nomenclature the prefix *poly* is followed in parentheses by words which describe the chemical structure of the repeat unit [e.g., poly(ethylene terephthalate) (PET)].

- **Polyesters:** $-(O\text{-}R\text{-}CO)_n-$ or $-(O\text{-}R\text{-}O\text{-}CO\text{-}R'\text{-}CO)_n-$

- e.g., **HO-R-OH + HOCO-R'-COOH (diol + diacid)**

- **Polycarbonates:** $-(O\text{-}R\text{-}O\text{-}CO)_n-$
- e.g., **HO-R-OH + $COCl_2$ (diol + phosgene)**

- **Polyamides:** $-(NH\text{-}R\text{-}CO)_n-$ or $-(NH\text{-}R\text{-}NH\text{-}CO\text{-}R'\text{-}CO)_n-$
  e.g., $NH_2\text{-}R\text{-}NH_2$ + **HOCO-R'-COOH (diamine + diacid)**

- **Polyurethanes:** $-(O\text{-}R\text{-}O\text{-}CO\text{-}NH\text{-}R'\text{-}NH\text{-}CO\text{-})_n-$
  e.g., **HO-R-OH + OCN-R'-NCO (diol + diisocyanate)**

- **Polyureas:** $-(NH\text{-}R\text{-}NH\text{-}CO\text{-}NH\text{-}R'\text{-}NH\text{-}CO\text{-})_n-$
  e.g., $NH_2\text{-}R\text{-}NH_2$ + **OCN-R'-NCO (diamine + diisocyanate)**
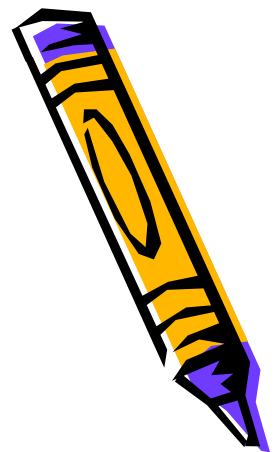
MOLECULAR MASS (WEIGHT)

WHY IS IT IMPORTANT ?

TENSILE
STRENGTH

MOL.WT.

MELT
VISCOSITY

MOL.WT.
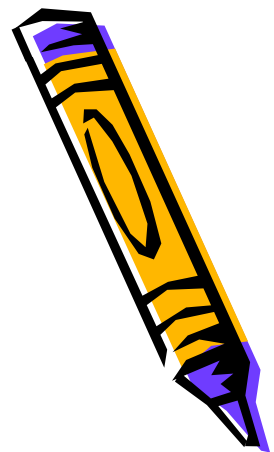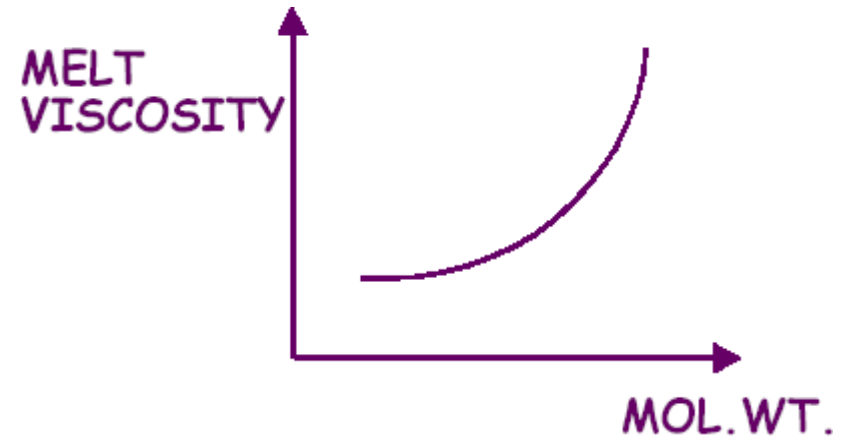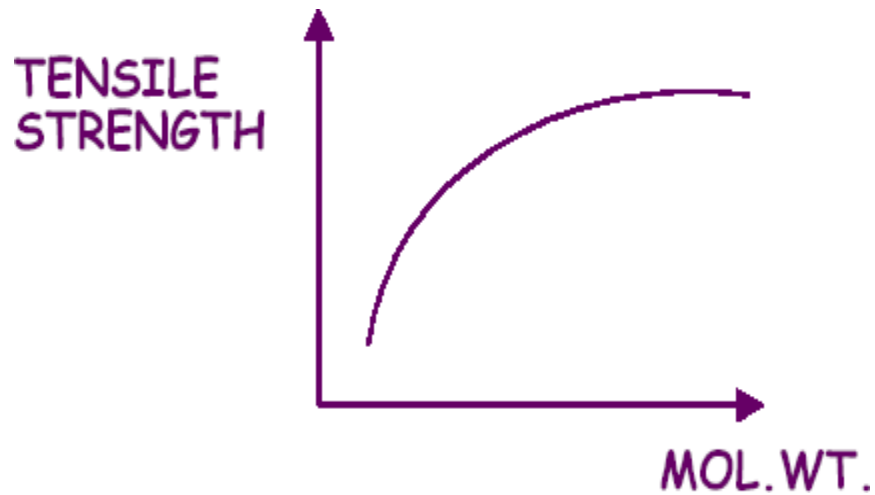
Beside structures molecular mass (weight) also effects the properties of polymer.

Molecular mass is defined as the sum of the ralative atomic masses of the constituent atoms of polymers.

The larger the molecular mass indicates longer chain length, thus has a profound effect on processing.

Increasing chain length may increase toughness, melt temperature, melt viscosity, creep and stress resistance.

It may lead to difficulty in processing, material costs and may cause polymer degradation.