

Properties of Polymer

Why the Polymer Properties Important

Because the Polymer manufactured for
special article production (end use)



Thermal
,Rheologic
al,Mechan
ical,Trans
parant,Ch
emical
and etc...

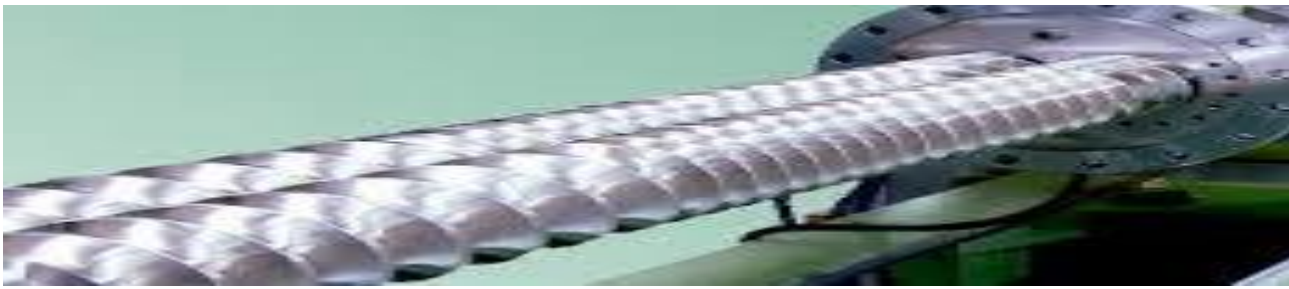
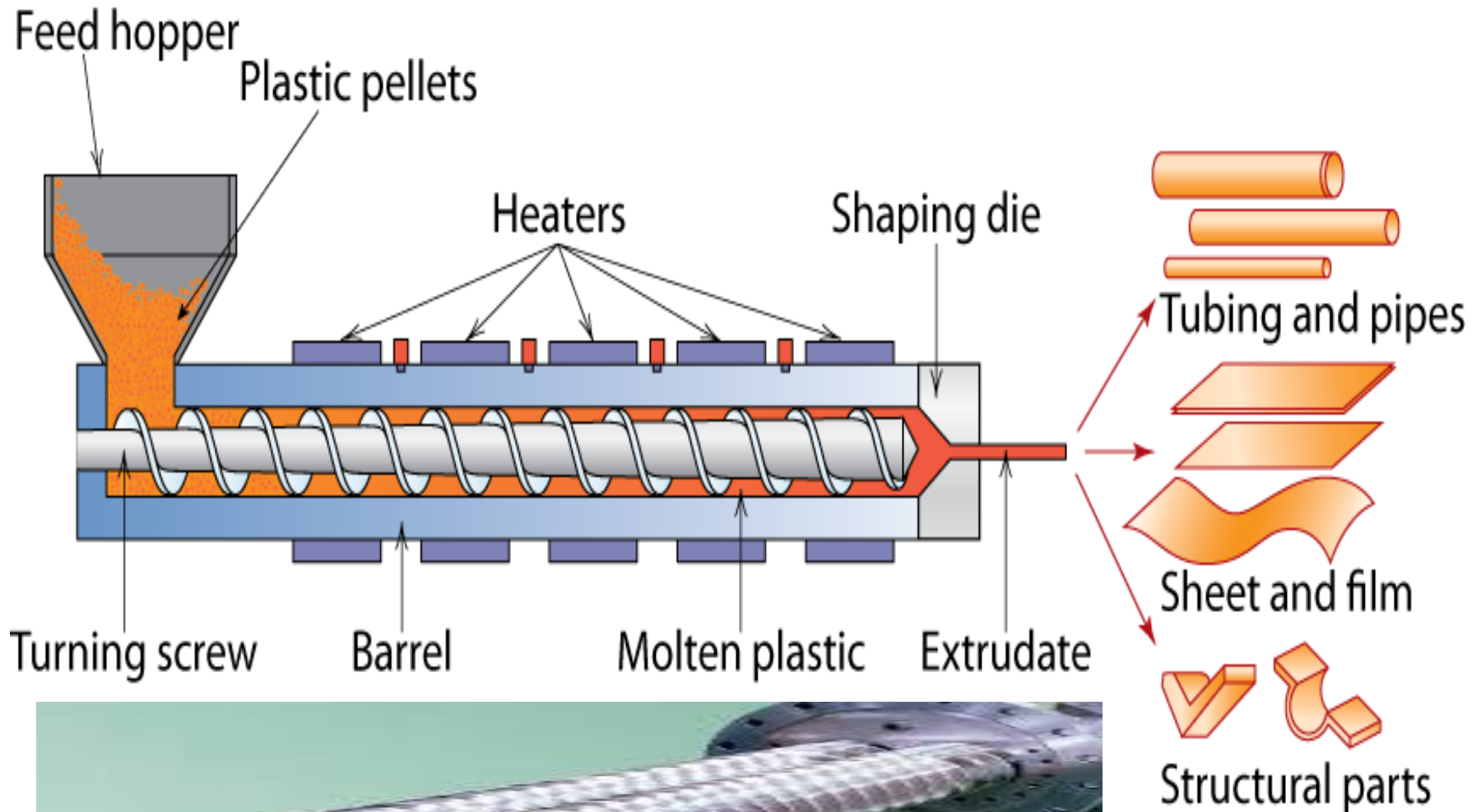
PROCESSING RHEOLOGICAL AND THERMAL PROPERTIES



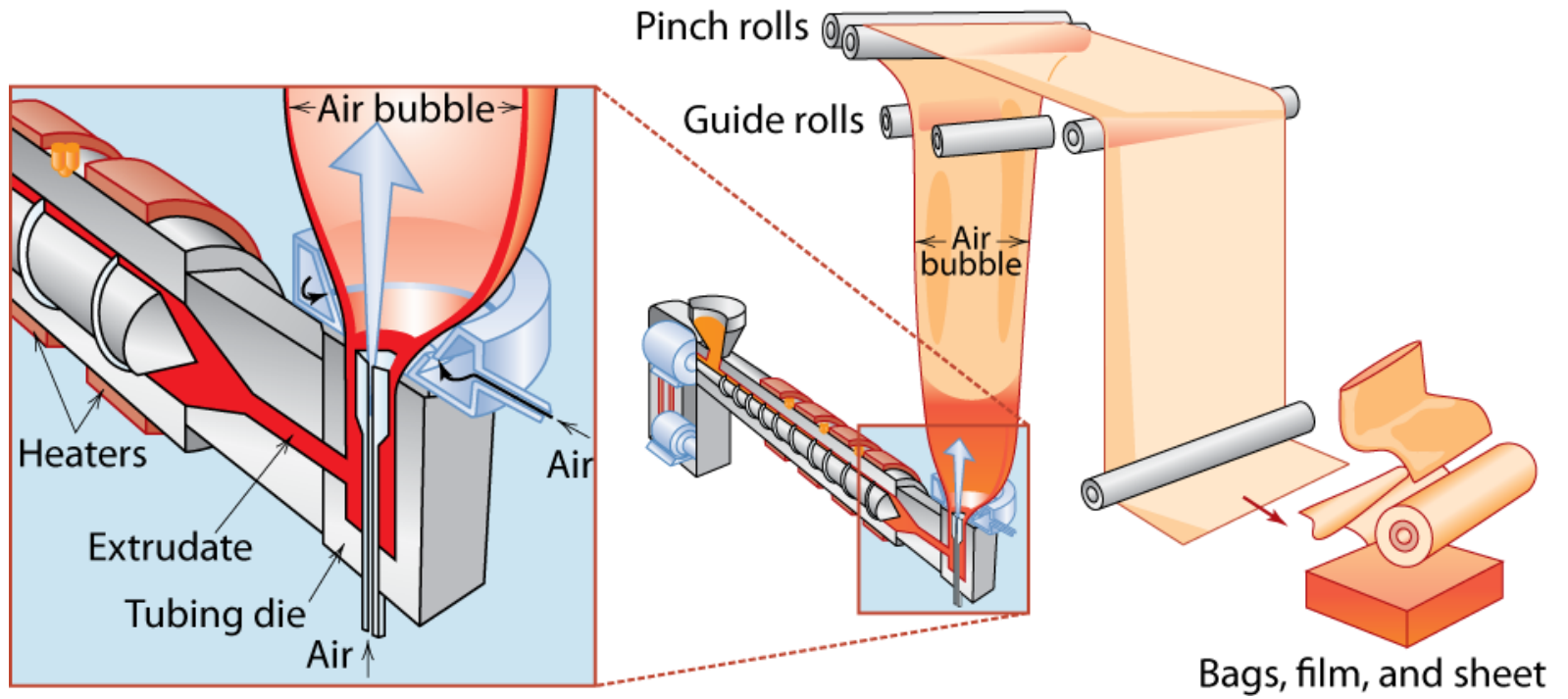
Thermal
mechanical,
Tansparant,
Electrical,In
sulation and
etc...



Processing Plastics – Extrusion



Blown-Film Extrusion



Polymers

Made up of chain molecules → long-range connections throughout material



In practice, mostly carbon atoms along length of the chain + various side-groups (e.g. -H, -Cl, -OH, -CH₃) attached to it at regular intervals

Polymer materials

High Density Polyethylene for storm water drainage system.

Replaces fired clay ceramics (brittle, difficult to make long sections, difficult to join) and cast iron (heavy, low corrosion resistance)

Also used in domestic plumbing, displacing copper (expensive)



Polymer materials

Kevlar for body armour.

Replaces iron (heavy, stiff)



General characteristics

Cheap

Tough

Lightweight: polyethylene density = 0.96 g cm^{-3}

Easy to shape

Flexible

Resistant to chemical attack

Thermally, electrically insulating

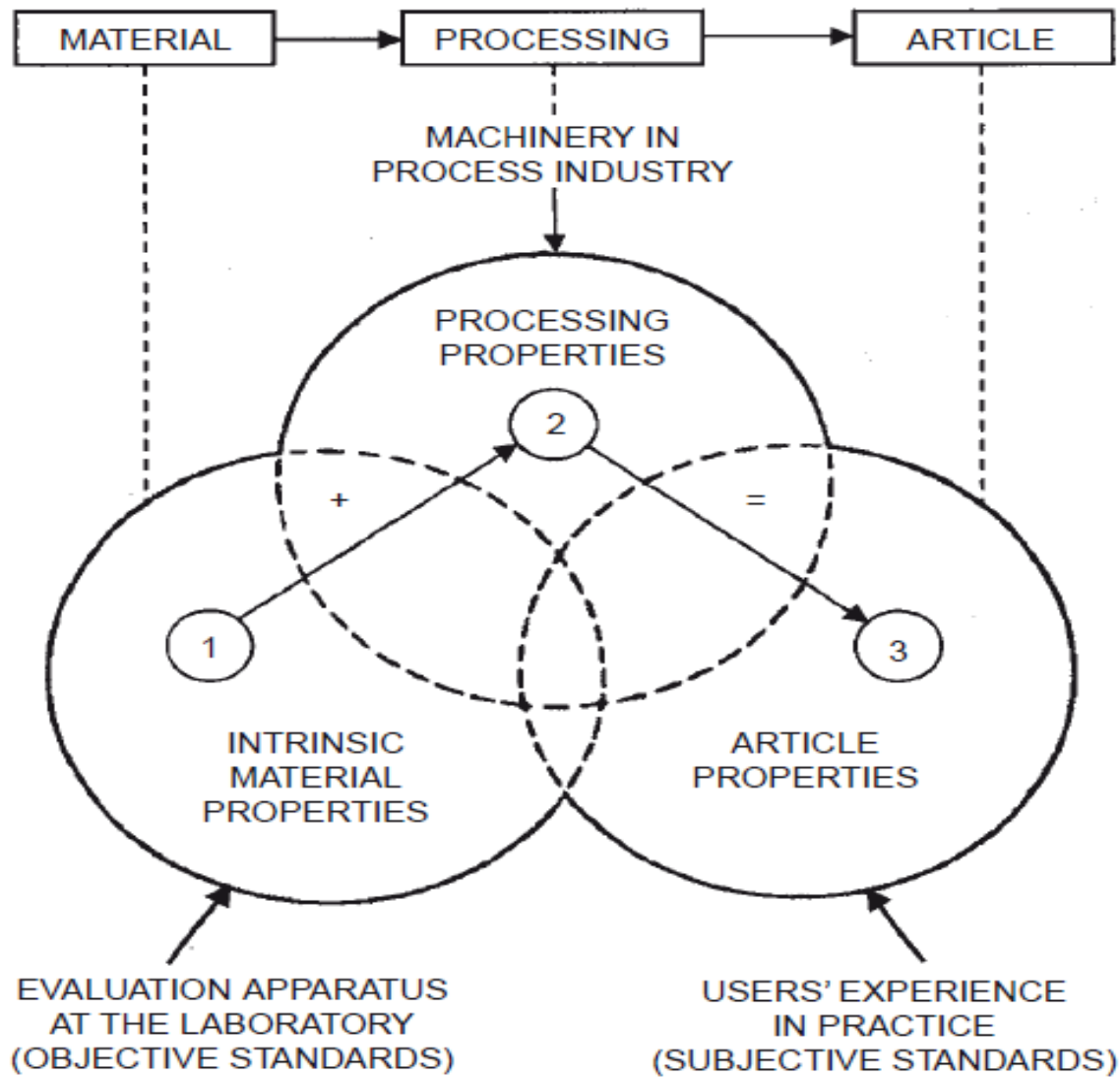
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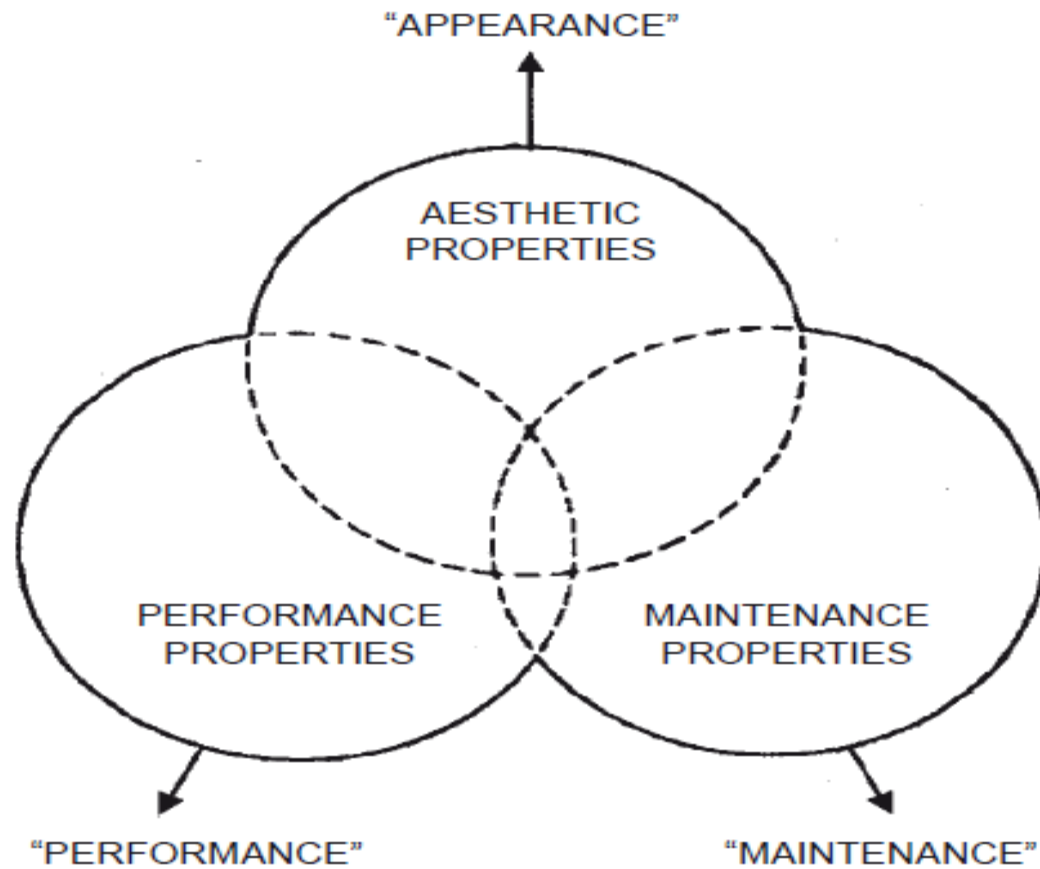
low stiffness / strength: E (polyethylene) = 1 GPa

limited temperature range: T_m (polyethylene) = 105°C

high coefficient of thermal expansivity: α (polyethylene) = $150 \times 10^{-6} \text{ K}^{-1}$

Degrade when exposed to UV light, oxygen





Properties of Polymer

Basic types of polymers

Basic Types of Polymers:

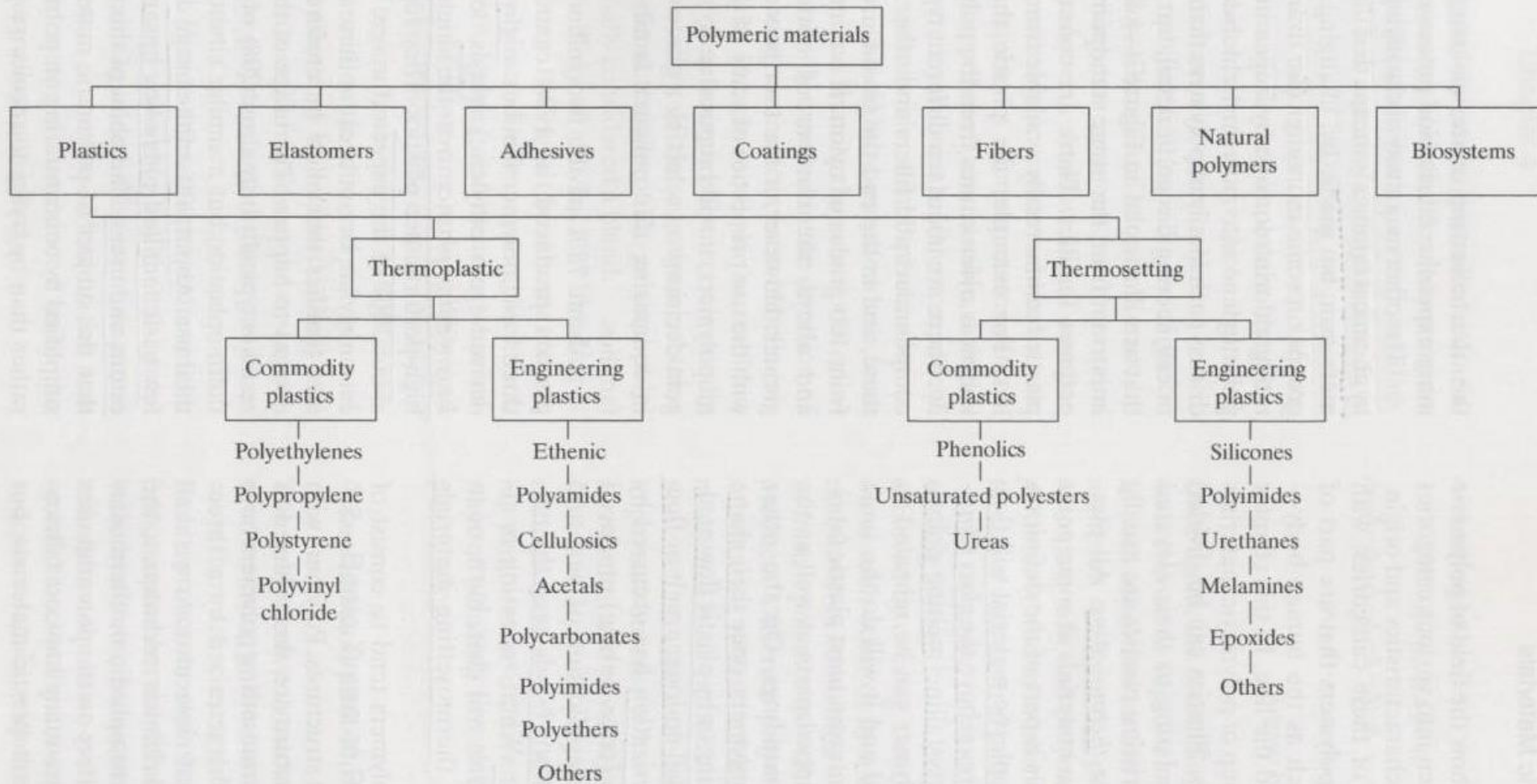


Figure 4-4

Main Categories of Polymers:

- **Plastics:**
 - **Thermoplastics** – can be remelted:
 - Engineered Thermoplastics
 - Commodity Thermoplastics
 - **Thermosetting Plastics** – can not be remelted
 - Engineered Thermosets
 - Commodity Thermosets
- **Elastomers:**
 - **Thermosets and thermoplastic!!**

Commodity Thermoplastics

- Commodity: Polyethylene (PE), Polystyrene (PS), Polypropylene (PP), Polyvinyl Chloride (PVC or vinyl) – 80% of all thermoplastics!!
- Also, Styrene Acrylonitrile (SAN) – the copolymer we tested in lab
- Flows at elevated temperatures.
- Has a glass transition temperature.
- Long polymer chains
- Can be remelted and recycled.

Engineering Thermoplastics

- Engineering Plastics: Polycarbonate (PC), Acrylonitrile-butadiene-styrene (ABS), Polyamide (Nylons, PA)
- Engineered plastics account for about 10% of all plastic usage.
- Generally have higher tensile strength and elongation than commodity plastics

Thermosetting Plastics

- Polyurethane, Phenolics, silicones, ureas
- Tend to be strong but brittle
- Molecules cross-linked
- Can not be remelted or reprocessed

Elastomers

- Butyl, natural rubber (polyisoprene), EPDM, neoprene, nitrile, etc..
- Characterized by high deformation (extremely flexible) – generally greater than 100%.
- Almost all are thermosetting with exception of TPE's

Properties of Polymer

Polymer structure

In essence there are only two really fundamental characteristics of polymers:

- 1- Their chemical structure and
- 2- Their molar mass distribution pattern.

The chemical structure (CS) of a polymer comprises:

- a. The nature of the repeating units
- b. The nature of the end groups
- c. The composition of possible branches and cross links
- d. The nature of defects in the structural sequence

Properties of Polymer

Polymer structure

The molecular weight distribution (MWD) or molar mass distribution (MMD)

informs us about the average molecular size and describes how regular (or irregular) the molecular size is. The MMD may vary greatly, depending on the method of synthesis of the polymer.

Properties of Polymer

These two fundamental characteristics, **CS** and **MMD**

determine all the properties of the polymer. In a direct way they determine the **cohesive forces**, the **packing density (and potential crystallinity)** and the **molecular mobility (with phase transitions)**.

In a more indirect way they control the **morphology** and the **relaxation phenomena**,
i.e. the **total behavior of the polymer**.

What Influence Polymer Properties ?

Various parameters affect the properties of a polymer e.g. the ability to form crystalline or amorphous phases, thermal stability and mechanical behaviour (strength, toughness). In general , polymer properties depend on:

1- Polymer size i.e. molar mass and chain length

2- Chemical composition as this determines the strength of intra- and inter-molecular forces

3- Polymer structure and architecture i.e. is the material composed of single chains or are the chains linked to form a network structure? And if there are single chains what is their architecture? Are they linear or branched?

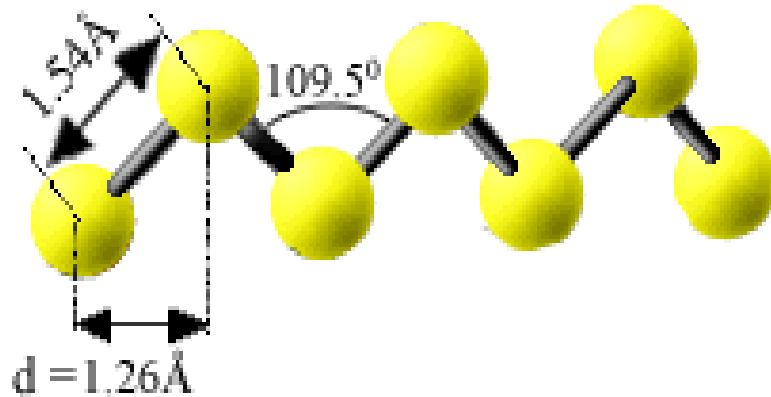
4- Polymer shape (degree of chain twisting and coiling, chain entanglements)

Size and Length of Polymer :-

The effect of chain length on properties is important .For that we must know how to estimate the size and length of a polymer molecule if we know its degree of polymerization n .

For example, let's consider a polyethylene chain with a degree of polymerization of 10^4 . The molar mass of this chain can be calculated from the molar mass of the repeat unit which is equal to 28 g mol^{-1} by considering the number of repeat units

$$M = 28 \text{ g mol}^{-1} \cdot 10^4 = 280,000 \text{ g mol}^{-1}$$



We can estimate the length of this chain if we imagine that the polymer backbone can be described by an all trans conformation as shown in the figure below (for simplicity the hydrogen atoms attached to the carbon atoms in the backbone are not shown).

As the chain is composed of a sequence of tetrahedral carbon atoms, the angle between the C-C bonds is 109.5° and the C-C distance equal to 1.54 \AA ($1\text{\AA} = 10^{-10} \text{ m}$). Thus the apparent distance d (in \AA) between two successive carbon atoms of the all trans chain is given by:

$$d = 1.54 \times \sin \frac{109.5^\circ}{2} = 1.26$$

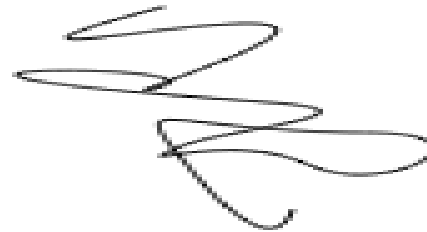
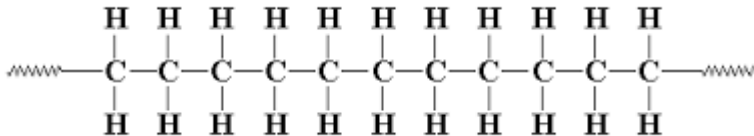
If we consider that there are 2 C atoms per polymer repeat unit, then the length of the polyethylene molecule with $n = 10^4$ in the zig-zag state is equal to $25,200 \text{ \AA}$ or 2.52 mm .

Polymer Structure and Architecture :-

The key feature of polymers is that they are very large molecules made up of long sequences of relatively simple chemical units.

Most polymeric materials can be thought as consisting of individual, although very large molecules. In some cases the polymer chains are made up of linear sequences

of **monomeric** units:

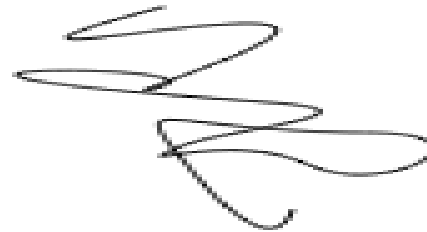
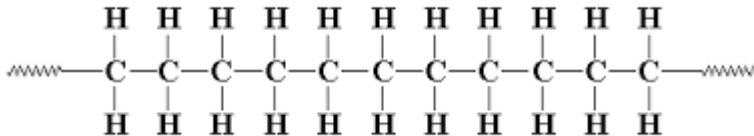


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of **monomeric** units:



but other types of chain architecture are possible and have been exploited commercially to tailor the properties of polymers.

For example, in **branched** polymers



long chains are joined to the backbone at various points along the main chain. The existence of branches and their lengths have a profound effect on the physical properties. Polyethylene (PE) can be commercialized in three main different forms: low density PE (**LDPE**), linear low density polyethylene (**LLDPE**) and high density polyethylene (**HDPE**). All these materials have the same chemical structure but differ in degree of branching.

Polyethylene

LDPE

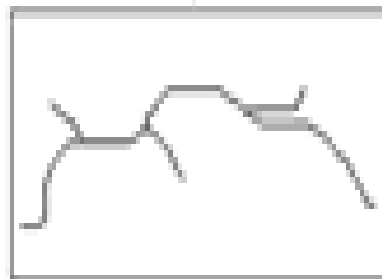


high-pressure radical
polymerization

60 branches per 1000 C atoms

*low density
polyethylene*

LLDPE

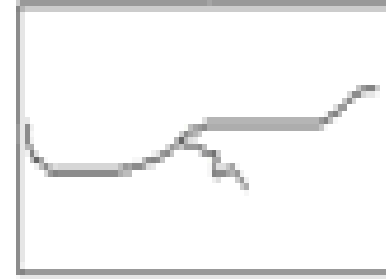


copolymerization of
ethylene and α -olefin

controlled branching

*linear low density
polyethylene*

HDPE



organometallic catalysts

7 branches per 1000 C atoms

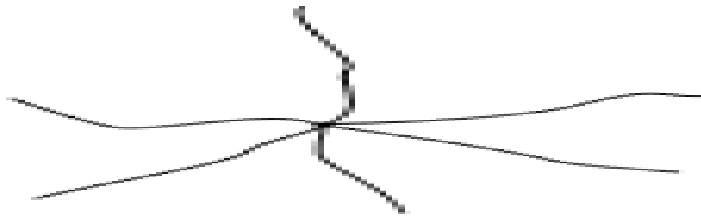
*high density
polyethylene*

The presence of even short branches affects the ability of the polymer to crystallize. As a consequence, as branching increases the melting temperature decreases and so does the density of the material, indicating that packing becomes less efficient. Some of the properties of **LDPE**, **LLDPE** and **HDPE** are summarized in the table below.

Branching also affects the mechanical properties of a material such as its tensile strength (which is defined as the ability of a material to withstand a tensile force).

<i>Property</i>	LDPE	LLDPE	HDPE
T_m (K)	383	393-403	>403
Density (g/cm^3)	0.92	0.92-0.94	0.94-0.97
Tensile Strength (MPa)	24	37	43

In addition, to linear and branched polymers, other types of chain architecture lead to materials with interesting physical properties. For example, **star polymers**



have found use as viscosity modifiers in motor oil. **Dendrimers** (from the Greek word **tree**)

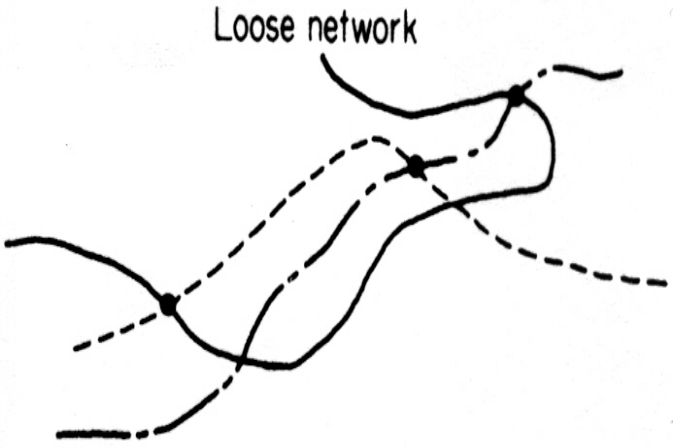


represent a new class of polymers with regularly branched structure.

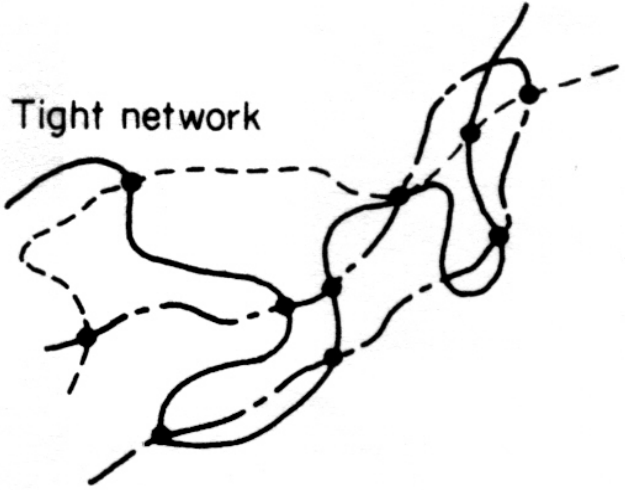
represent a new class of polymers with regularly branched structure

Networks

We represent chain architecture to materials that are composed of individual polymer molecules. However, it is also possible to link by covalent bonds linear or branched polymers forming network structures.

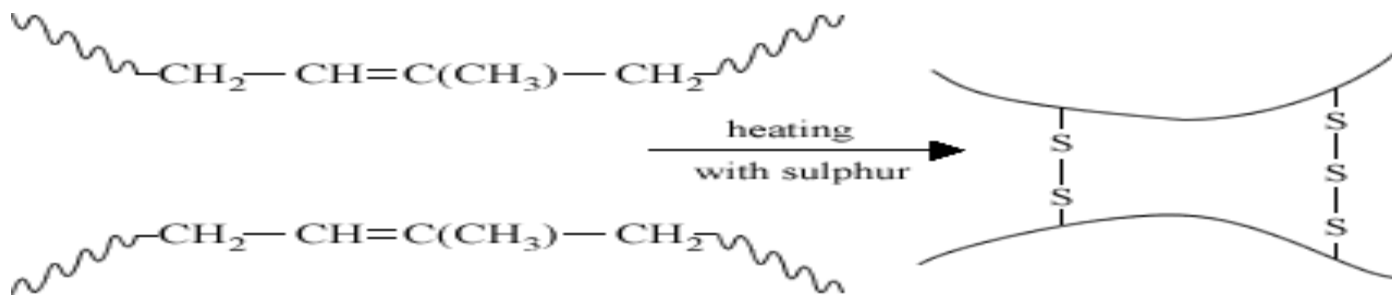


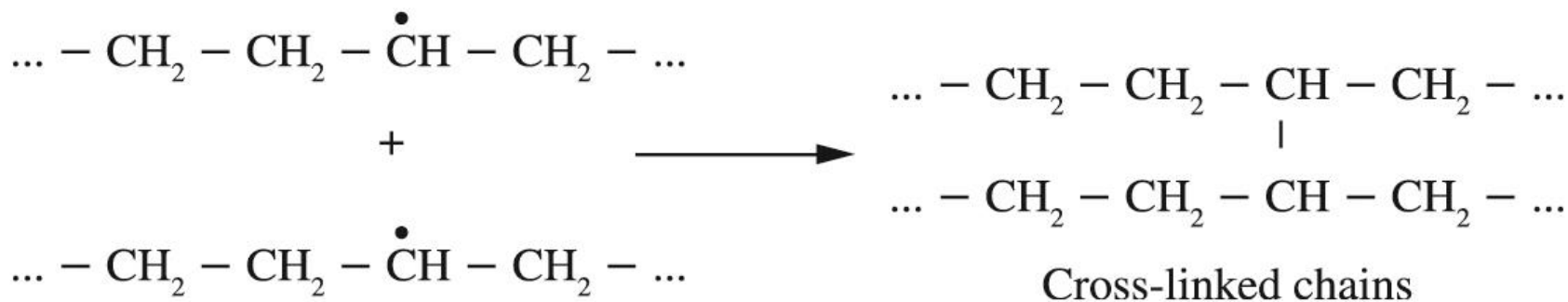
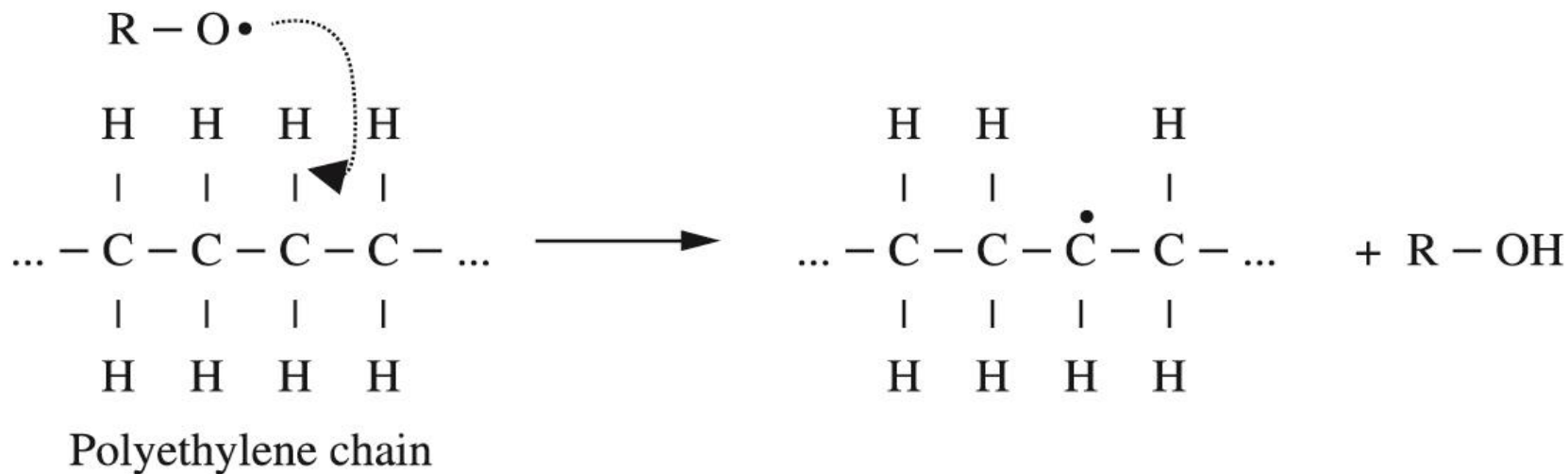
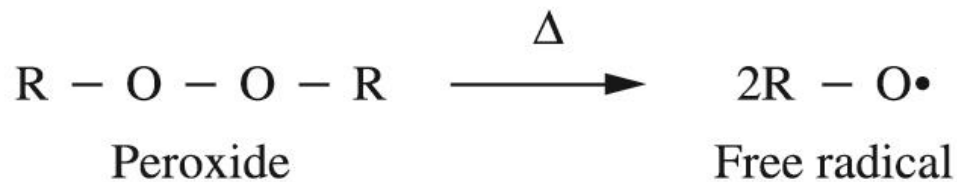
شبكة فضفاضة



شبكة ضيقة

The network is created in a **cross-linking process** which consists of forming short linkages of few covalent bonds between polymer chains. The process of "**vulcanisation**", discovered by *Charles Goodyear* in 1839 lead to considerable improvement in the properties of natural rubber (cis-1,4-polyisoprene):





Interaction and Molar Mass

The **polymers** was a **large molecules** and we have shown how to calculate their size and contour length from the degree of polymerization. In that case we have used a degree of polymerization of 10^4 . However, there exists a range of n values for which materials with identical chemical structure but different length will show similar physical and mechanical properties.

We may ask the question: how many **units** or **mers** are required for a high molecular weight material to be classified as a **polymer**? We will see that, for reasons that are stated below, we will never be able to define a precise molar mass range that is valid for all polymers. However, as a guideline, we can say that a **minimum of 20 to 30 units** is needed.

For low degrees of polymerization the term **oligomer** (from the Greek *oligo* = few) is used; it refers to low molecular weight polymers (ca. $n = 2$ to 20-30). Typically 100 to 1000 units are required for a large molecule to have polymeric properties *e.g.* good mechanical strength. This corresponds to molar mass values between 10,000 to 1,000,000 g mol^{-1} , reaching up to 10^7 g mol^{-1} for ultra-high molecular weight polyethylene (UHMWPE).

Interaction and Molar Mass

Let us consider once again polyethylene. The general structure may be indicated as:



If we now let n vary from 1 to very large values we are able to reproduce the homologous series of the alkanes. For $n=1$ we have **ethane**, for $n = 2$ we have **butane** and so on. At room temperature ethane is a gas. The table below shows how the physical state of the molecules changes for the alkane series as n increases.

$\text{---CH}_2\text{CH}_2\text{---}$	<i>Molar Mass</i>	<i>Physical State</i>
1	30	gas
6	170	liquid
35	1000	grease
140	4000	wax
250	7000	hard wax
430	>12000	resin

Interaction and Molar Mass

Only when n is large, will the molecule acquire the necessary mechanical strength to be regarded as polyethylene.

Although the interaction between two monomers is the same as that between two repeat unit, it is the cumulative effect of a large number of intermolecular interactions along the chain that is responsible for the properties of polymers (e.g. the change in physical state that is illustrated above).

The same consideration may be applied to other homologous series but there are important differences. **Vinyl polymers** obtained from chain growth polymerisation have high molar masses, typically in the range 100,000 to 1,000,000 g mol⁻¹ .

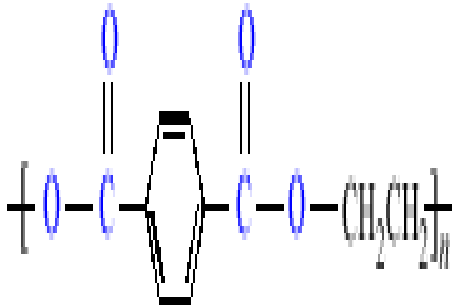
Interaction and Molar Mass

While lower values are obtained for polymers prepared by step-growth polymerisation *e.g.* polyesters and nylons, in the range 15,000 to 20,000. Although these differences are due to **limitations of the polymerisation process** used, it must be said that while a molar mass of 15,000 g mol⁻¹ for **polyethylene is too low to be useful in applications**, this is not true for the relatively **low molar masses of polyesters and nylons**.

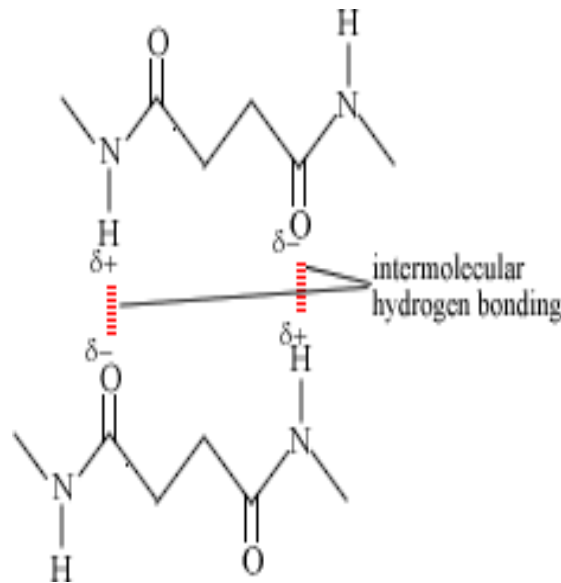
Obviously, the chemical structure plays an important role in determining the polymer properties. As for small molecules, it does not only influence the strength of the **intramolecular covalent bonds** and therefore thermal and photochemical stability of the compound but it also determines the nature of the **intermolecular bonding forces**. Since the strength of the intermolecular forces increases if polar groups are present, we expect that the minimum value of molar mass, M_c , required for a molecule to exhibit "*polymer properties*" will **decrease with increasing polarity in the molecule**.

Interaction and Molar Mass

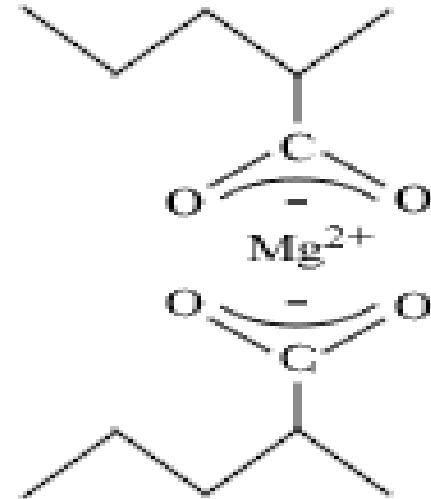
Depending on the chemical structure, polar forces, hydrogen bonding and ionic interactions may occur between molecules. In the example below, the strength of the intermolecular forces increase from left to right.



Polyester (PET)



aliphatic polyamides



ionomer

Conformation and Configuration :-

As for **small molecules**, the spatial arrangement of the atoms in space is fully specified if we know its **configuration** and **conformation**.

The term **configuration** refers to the arrangement of atoms which are fixed by the chemical bonds. **Configurations** cannot be interchanged without breaking some bonds and forming new ones.

For example, there are two possible configurations for small molecules with double bonds i.e. *cis* and *trans* isomers.

Similarly, polymers containing double bonds show *cis-trans* isomerism.

The term **conformation** refers to the three dimensional arrangement in space of the atoms that can be altered through rotation about single bonds.

In this case, no bond breaking is involved to interchange among different conformations

Configuration :-

For **polymeric materials**, two types of **configurational** isomers are of importance :

(a) **geometric isomers** e.g. *cis* and *trans*

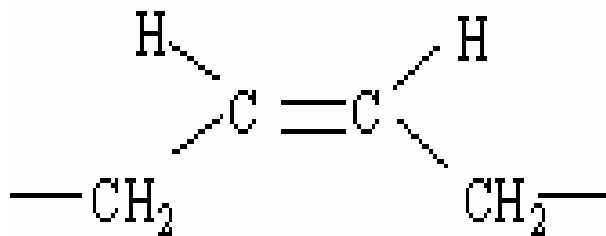
(b) **stereoisomers**

(a) **Geometric Isomerism**

The **polymerization** of **monomers** with two double bonds e.g. *butadiene* leads to polymer chains with a residual double bond per monomer unit. *Cis-trans* isomers are possible.

Two important polymers that show this type of isomerism are *1,4-polybutadiene* and *1,4-polyisoprene*.

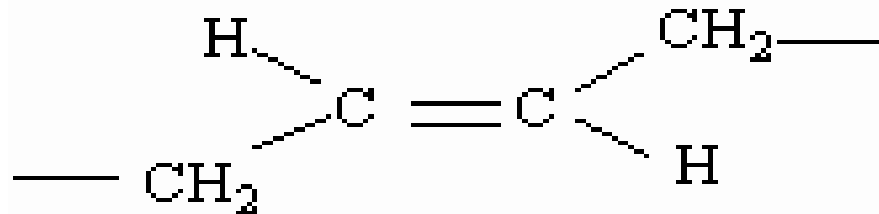
For **1,4-polybutadiene**, in the *cis* isomer



the two parts of the chains are on the same side with respect to the double bond

Configuration :-

whereas for the *trans* isomer they are placed on **opposite** sides.



The two isomers have **different physical properties**.

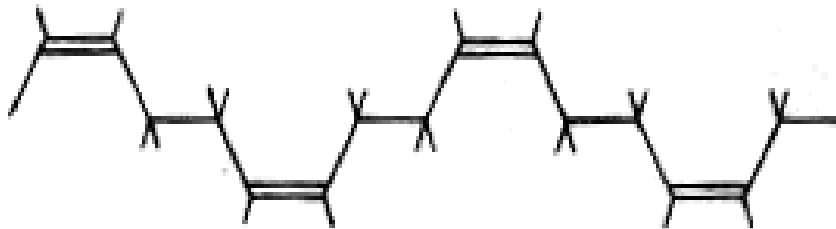
The regularity of the *trans* configuration makes this type of isomer more crystalline and this leads to a higher melting point compared to the *cis* configuration.

The *cis* configuration is less regular and therefore this polymer has not the same ability to arrange in crystalline structures.

Configuration :-



Trans



cis

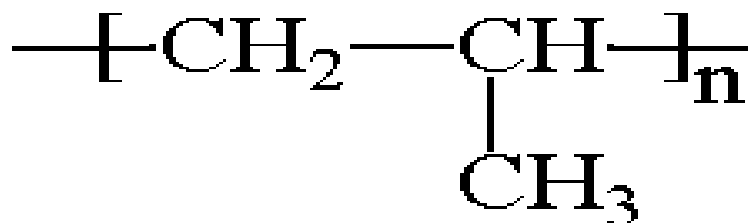
Configuration :-

(b) Tacticity and Stereoisomerism

If the polymer chains contain carbon atoms with two different substituents, then the C atom is **asymmetrical** as the two parts of the chains to which it is connected are unlikely to be the same *i.e.* they do not have the same number of monomer units.

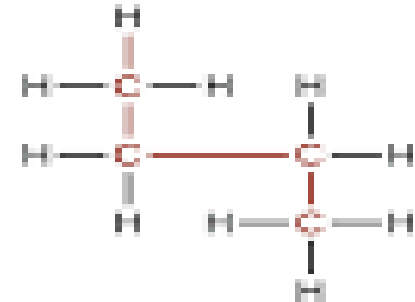
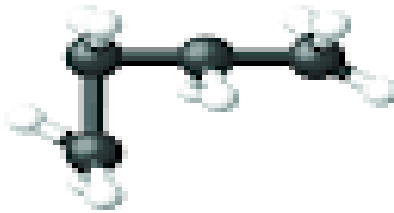
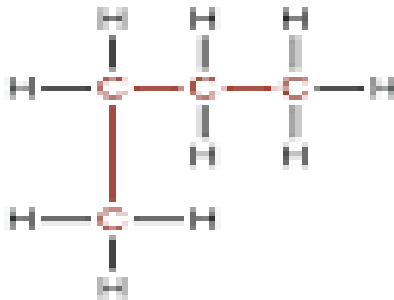
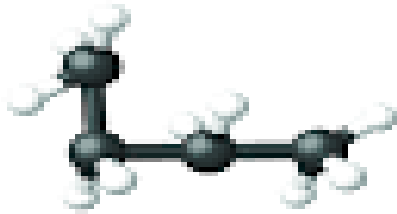
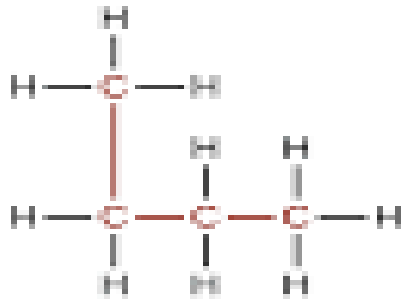
The C atom is said to be a stereogenic or **chiral** centre, while the molecule is **chiral** and its mirror image cannot be superimposed on the original structure without bond breaking.

This condition is satisfied for polypropylene



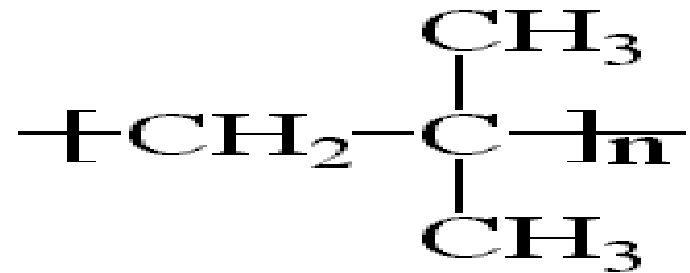
Configuration :-

Three different isomers for polypropylene



Configuration :-

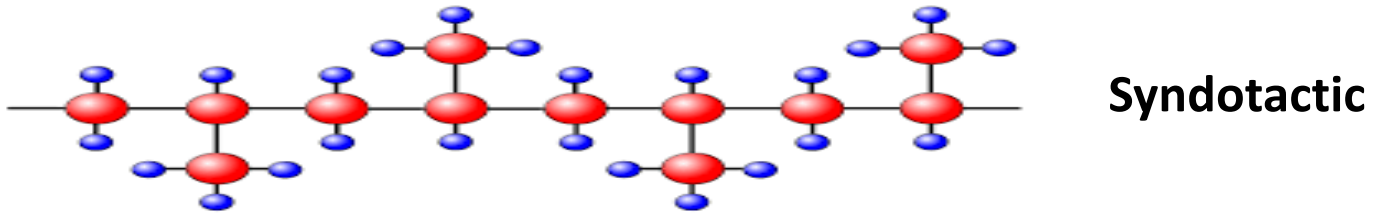
Other polymers such as polyethylene and polyisobutylene (PIB)



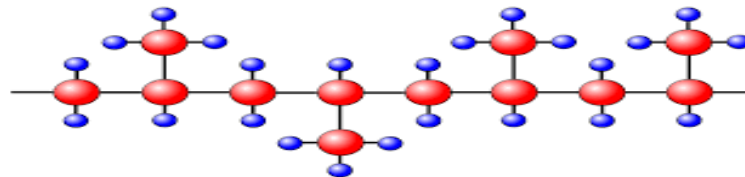
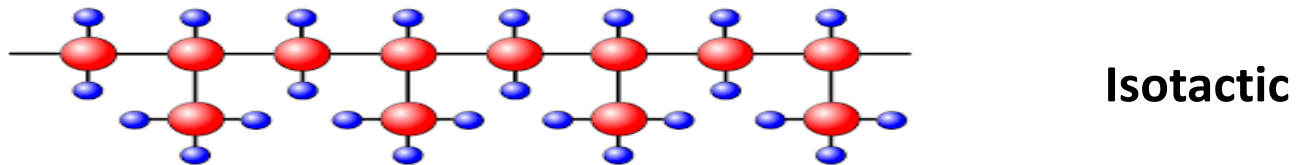
will not show stereoisomers as two identical substituents are attached to each carbon atom in the chain.

Configuration :-

The structure of the three stereoisomers is best illustrated by considering a polypropylene chain in the fully extended all trans conformation



Two ordered configurations are possible, the **isotactic** configuration ;



Configuration :-

Of the three stereoisomers, **atactic polypropylene** was the first to be synthesized.

This is because it is the atactic structure that is obtained by conventional polymerisation of the monomers when no optically active catalyst is used.

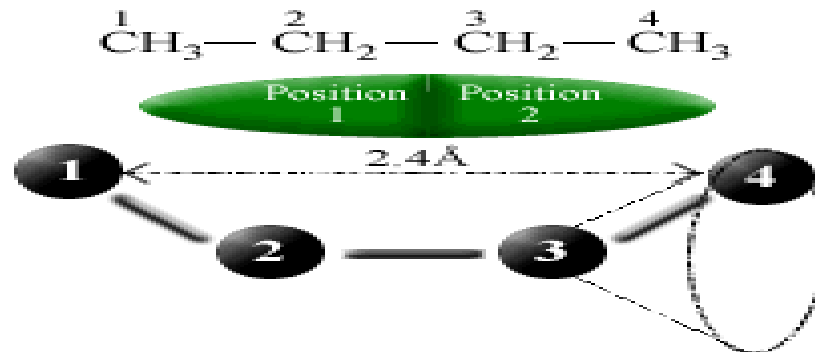
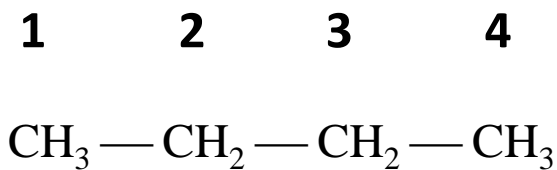
It was only when the Ziegler-Natta catalysts were introduced in the 1950's that the production of **stereoregular polymers** became possible.

It is interesting to note that **polypropylene** did not find any commercial use until the Ziegler-Natta catalysts became available. In fact the atactic structure that was originally produced leads to a viscous liquid at room temperature of limited use. Isotactic polypropylene instead is one of the most important commercial polymers

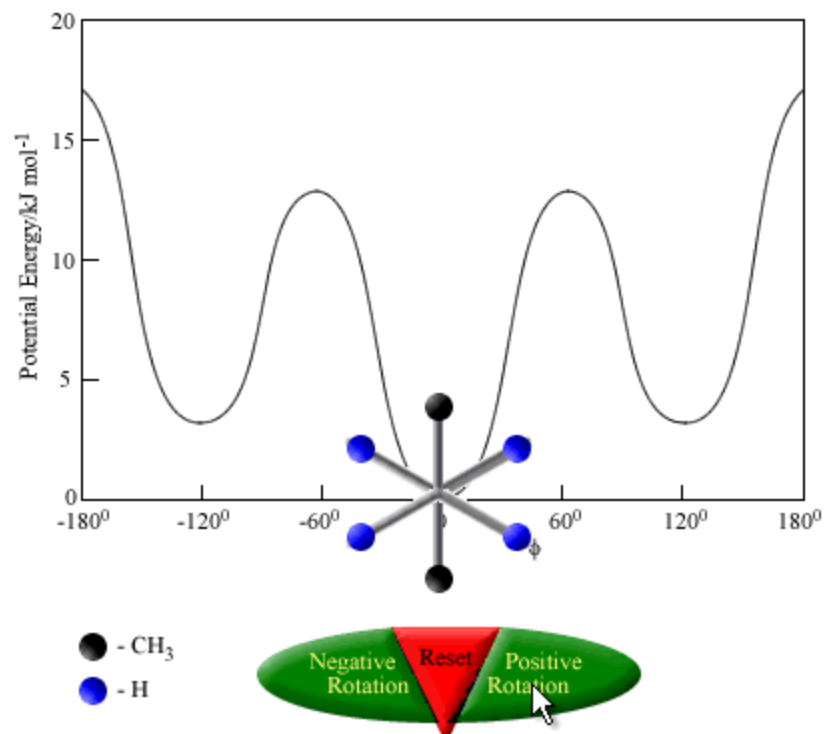
Conformation :-

In previous sections we have calculated the length of a fully extended polyethylene chain and later pointed out that this is not the most likely shape that a polymer chain will adopt in solution, in the melt or in the glassy state. The possibility of rotation about the C-C single bonds means that a polymer is capable of adopting a wide range of conformations.

We will illustrate this point by considering butane as an example



Conformation :-



Conformation :-

We can identify *three staggered* positions i.e. one **trans** and two **gauche** states corresponding to local minima of the potential energy curve. The two gauche states have higher energy than the trans as the two CH₃ groups are closer in space. The energy difference between trans and gauche states is 3.3 kJ mol⁻¹ and as a result the "staggered" or trans conformation is **the most favored** one. Obviously the eclipsed conformation is strongly unfavoured compared to the staggered positions as it corresponds to a maximum of the potential energy curve.

Similar considerations can be extended to longer molecules where we simply need to replace the methyl groups in n-butane with two portions of polymer chain i.e.

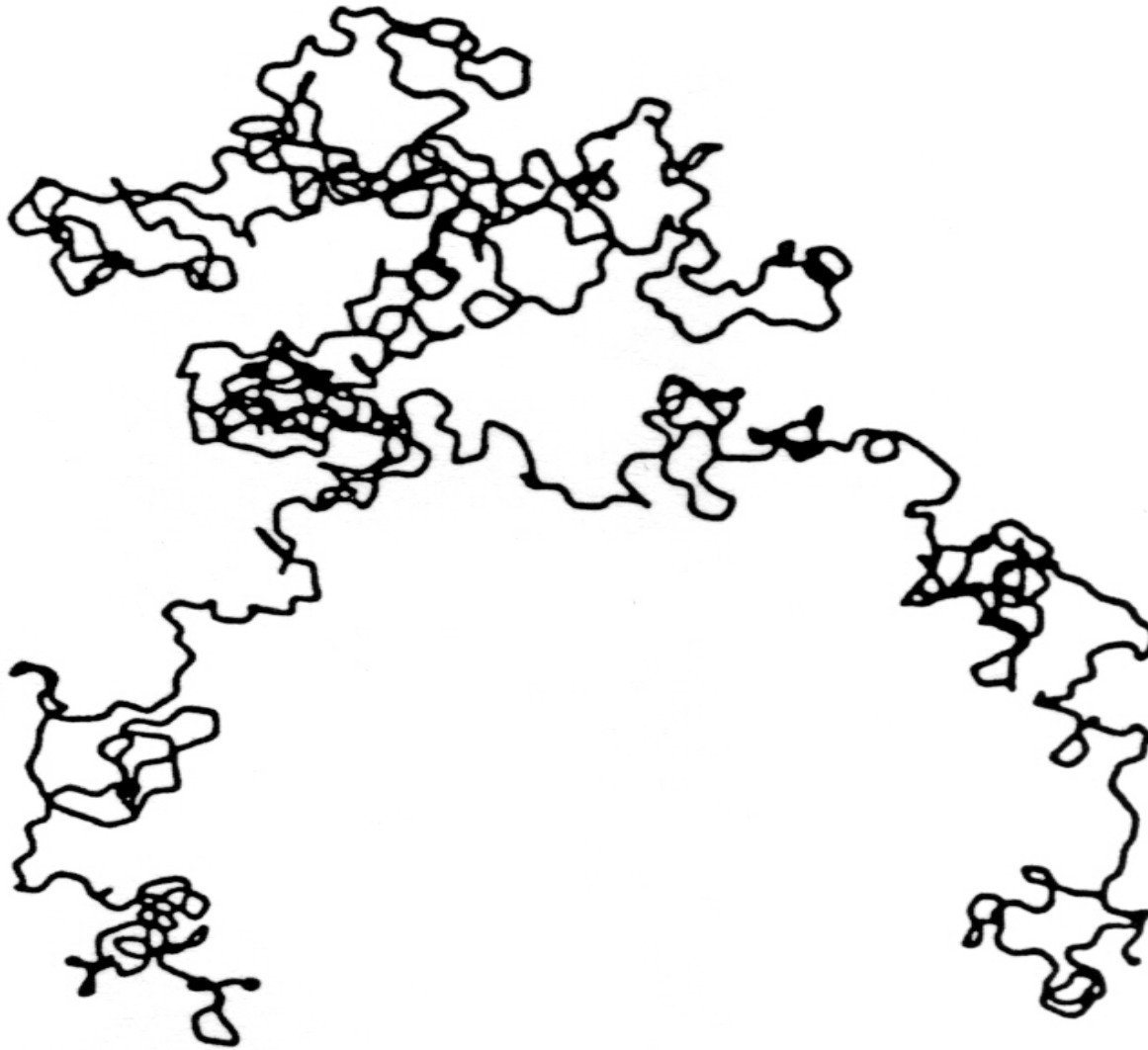
Conformation :-

$-(\text{CH}_2-\text{CH}_2)_n-$. Each successive linkage can assume one of three possible low energy conformations i.e. one *trans* and two *gauche*.

As the energy of the *trans* state is always lower compared to the energy of the two equivalent *gauche* positions, we may ask ourselves the question: *why does the chain not adopt the all trans extended conformation?*

We will see in later sections that a chain capable of crystallizing does adopt a very extended conformation (but the all *trans* state may not extend to the whole chain contour length). This is because in a **crystal**, the demand for regular packing favours highly ordered zig-zag shapes. However, in **solution** and in the **melt**, a chain will prefer to adopt a variety of different conformations to maximize the entropy.

Conformation :-



Conformation :-

shows a statistical conformation of a polyethylene chain made up of 1000 C-C bonds. This was generated by restricting the possible rotations around each bond to a set of six angular positions (differing by 60° and with the *trans* conformation given a value of zero).

Each of these six positions was considered to be equally probable and angle of rotation was determined by the throw of a dice.

The resulting chain is only one of an enormous number of possible conformations that a molecule may adopt, but it gives a typical representation of how a molecule will look. A conformation that is unlikely to occur (except for crystalline materials) is the all extended *trans* state that we considered at the beginning of the course.