
Text Books

- Engineering Chemistry, Jain P.C.; Jain M., Dhanpat Rai and Sons, Delhi, 17th Edn. 2015.
- Engineering chemistry, Wiley India Pvt. Ltd., 2nd Edn. 2014.

Reference Books

- Chemistry in Engineering and Technology, Kuriacose J.C.; Raja R. J., Vol. I/II McGraw Hill Education, 2001.
 - Materials Science for Engineering Students, Fischer T., Academic Press, London, 2009.
 - Fuel Science & Technology, James G Speight; Marcel Dekker, New York, 1990
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Syllabus

Module: Advanced materials and polymers: Advanced materials and polymers: Introduction, Definition, classification of polymers – based on origin, thermal behaviour, Polymerization reactions and applications, Tacticity. Functionality, Degree of polymerization, Co-polymerization – alternating, random, block and graft polymers. Mechanism of free radical polymerization and ionic polymerization. Mechanism of coordination polymerization, Condensation polymerization reactions, Glass transition temperature & factors affecting it. Molecular weight of polymers, Number average and weight average molecular weights, Numerical problems. Preparation, properties and applications of Polythene (LDPE and HDPE), Nylon(6:6, 6, 6:10, 11), PF resins and Polyester. Natural rubber, Processing of Natural Rubber, Vulcanization, Compounding of rubber; Synthetic Rubber: Buna-N, Buna-S. Composites, biomaterials, their properties and applications..

Module – Advanced Materials and Polymers

Module 1: Advanced materials and polymers: Introduction, Definition, classification of polymers – based on origin, thermal behaviour, Polymerization reactions and applications, Tacticity. Functionality, Degree of polymerization, Co-polymerization – alternating, random, block and graft polymers
Mechanism of free radical polymerization and ionic polymerization. Mechanism of coordination polymerization, Glass transition temperature & factors affecting it.
Molecular weight of polymers, Number average and weight average molecular weights, Numerical problems.
Preparation, properties and applications of Polythene (LDPE and HDPE), Nylon (6:6, 6, 6:10, 11), PF resins and Polyester. Natural rubber, Processing of Natural Rubber, Vulcanization, Compounding of rubber; Synthetic Rubber: Buna-N, Buna-S.
Composites and biomaterials: properties and applications

Development of civilization

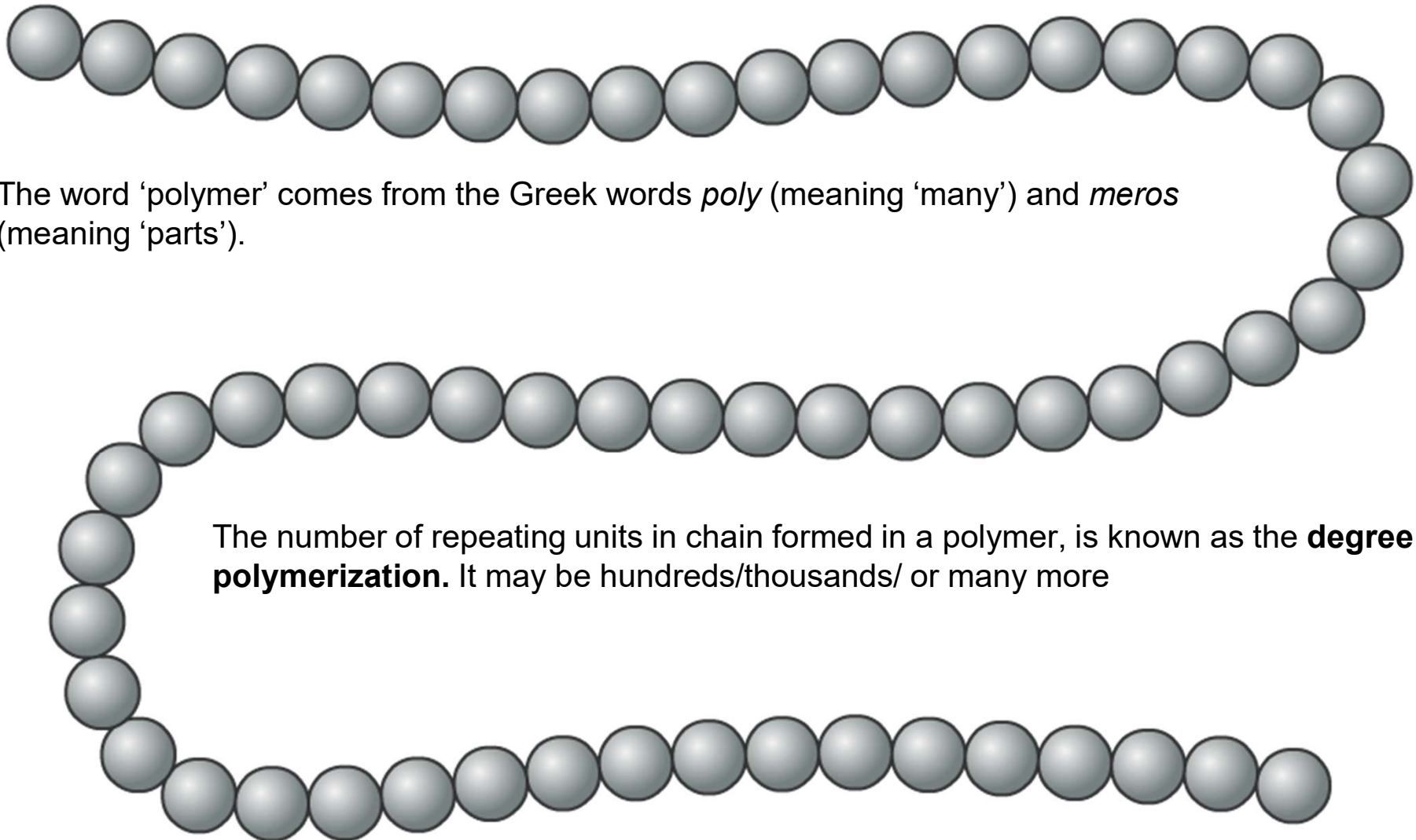
Stone age → Bronze age → Iron age → Polymer age

A world of polymer



What are polymers?

A **polymer** is a high molar mass molecular compound made up of many repeating chemical units (Monomers).



The process by which monomers are transformed into polymers is called *polymerization*.

Few Queries???

- What are some of the polymers that you encounter every day?
Sandwich bags, carpets, nylon stockings, stackable chairs, milk cartons, etc.
 - Why do different polymers have different properties?
They have different chemical compositions (different monomer units), different structures, different ways of being fabricated, etc.
 - Imagine samples of LDPE (sandwich bag, squeeze bottle) and HDPE (milk jug, grocery bag). What are some of the differences in the physical properties of these substances?
LDPE – more transparent, flexible, waxy
HDPE – more opaque, rigid, non-waxy
-

POLYMERS

DEFINITION:

The word *polymer* is derived from the two greek words

poly

and

mers

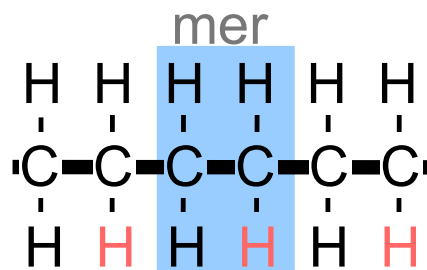


many

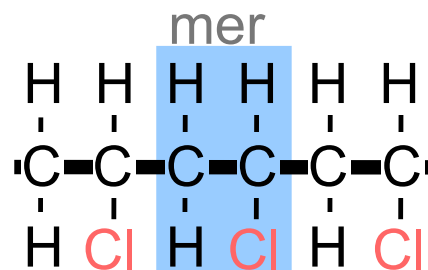


parts or units

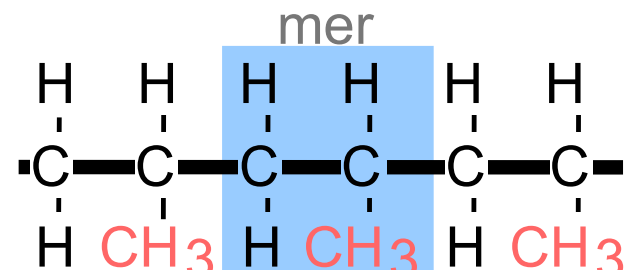
e.g.



Polyethylene (PE)



Polyvinyl chloride (PVC)

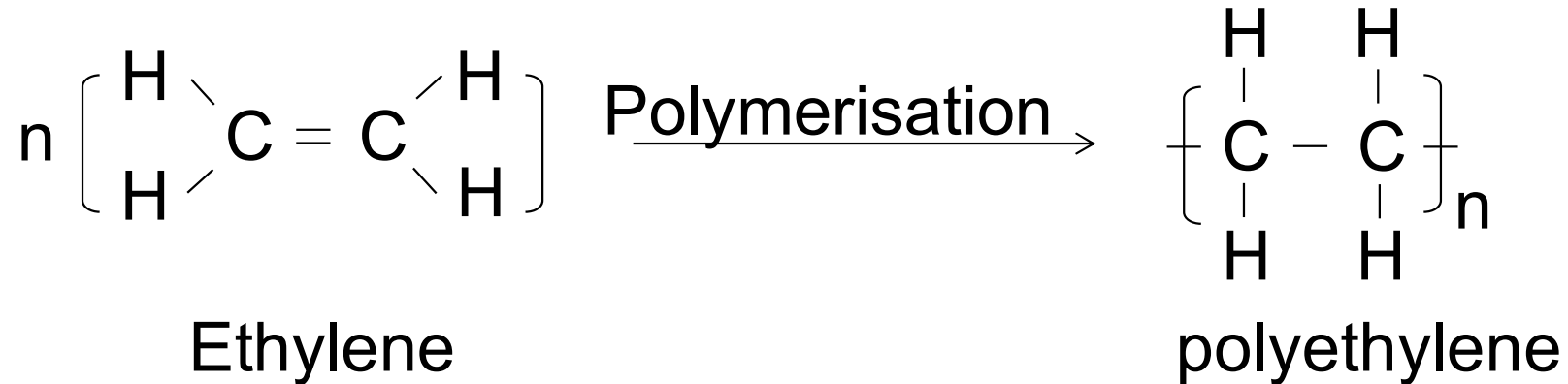


Polypropylene (PP)

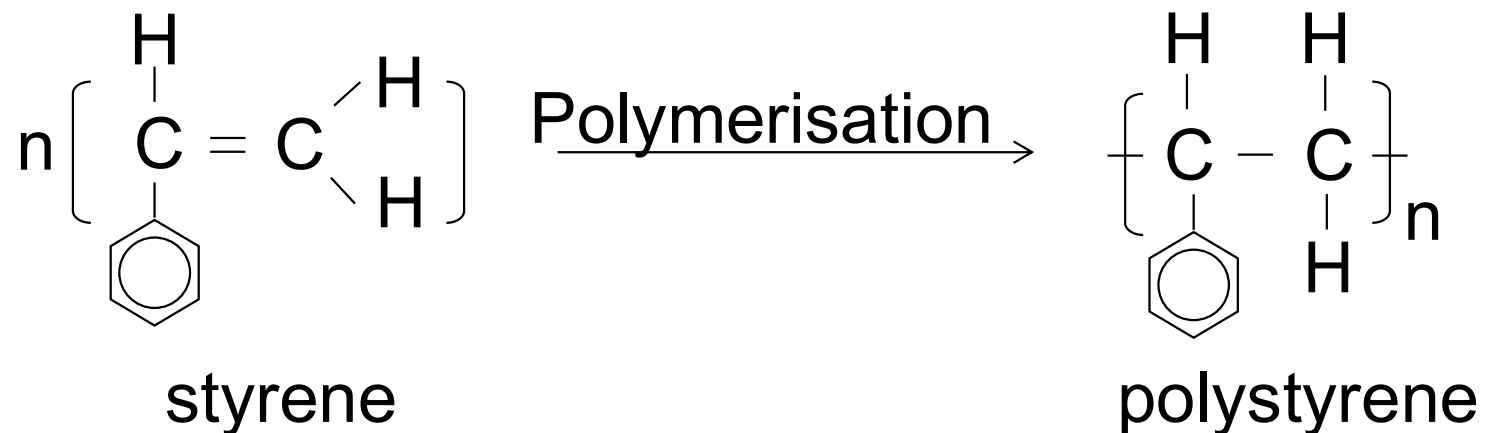
Polymers are macro molecules formed by linking smaller molecules repeatedly, called *monomers*.

Examples:

Polyethylene is formed by linking a large number of ethylene molecules



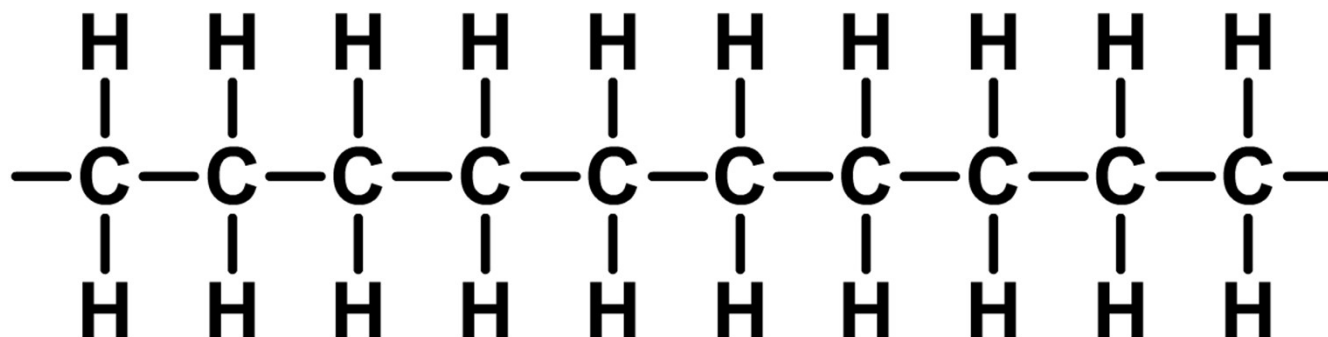
polystyrene is formed by linking styrene molecules



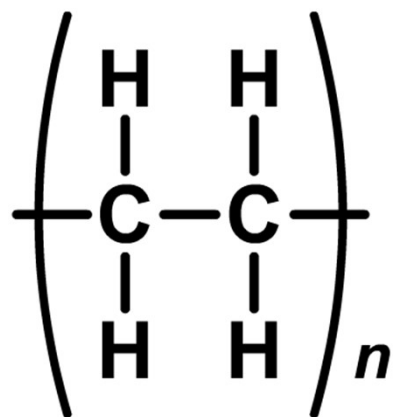
Drawing polymers – shorthand formulae

Polymers contain thousands of molecules, so how can their structures be easily drawn?

Part of the polymer molecule can be drawn:



A better way is to show a **shorthand formula**:



The '*n*' means that the polymer contains a very large number of the repeating unit shown in the brackets.

Degree of Polymerization

The main characteristic of polymer which determines the physical properties of polymer materials is defined as the degree of polymerization. A large molecule is made up of rings or chains of linked repeating subunits referred to as monomers called a polymer. The number of monomeric units present in a polymer is known as the degree of polymerization. They generally have high boiling and melting points.

$$\text{Degree of polymerization} = M_w/M_o$$

where M_w is the average molecular weight of the polymer and M_o is the molecular weight of the repeating unit or monomer.

How to calculate the degree of polymerization?

1. Write the chemical formula of the polymer.

For example, let us consider tetrafluoroethylene. Its chemical formula is written as -
(CF₂-CF₂)_n.

2. Evaluate the molecular weight.

To calculate the molecular weight follow the sequence below:

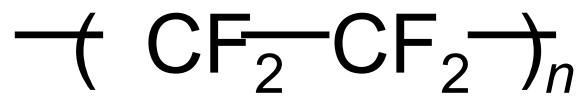
- Multiply the atomic mass of carbon element by the number of carbon atoms in the monomer
- Multiply the atomic mass of fluorine element by the number of fluorine atoms in the monomer
- Therefore, the molecular weight of tetrafluoroethylene is $12 \times 2 + 19 \times 4 = 100$.

3. Divide the molecular mass of the polymer by the molecular weight of the monomer.
For example, if the molecular mass of a polymer of tetrafluoroethylene is 1,20,000, then its degree of polymerization is calculated as

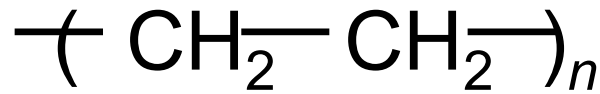
$$DP = M_w/M_o = 1,20,000 / 100 = 1,200.$$

Therefore, the degree of polymerization is 1,200.

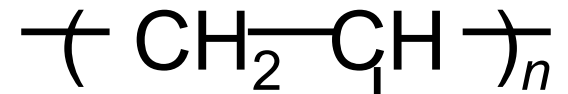
Homopolymer is a polymer made up of only one type of monomer



Teflon

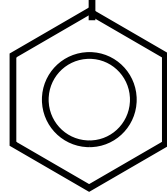
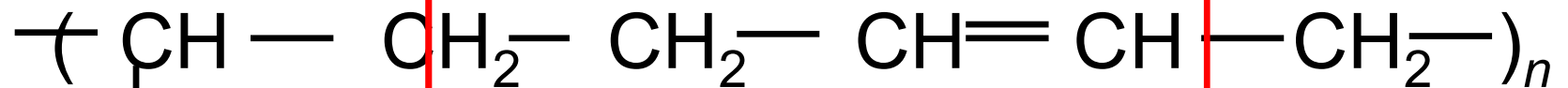


Polyethylene



PVC

Copolymer is a polymer made up of two or more monomers



Styrene-butadiene rubber

Copolymers

two or more monomers polymerized together



Alternating **A** and **B** alternate in polymer chain



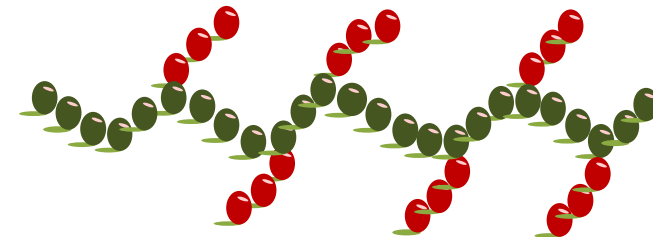
Block large blocks of **A** units alternate
with large blocks of **B** units



Random A and B randomly positioned along chain



Graft chains of **B** units grafted onto **A** backbone



Classification of Polymers:

1. Based on origin:

A. Natural Polymers

These occur in nature in plants and animals and are very essential for life. For e.g., proteins, nucleic acids, Starch, cellulose, protein, silk, wool and natural rubber are some natural polymers.

B. Synthetic Polymers

Synthetic polymers are man-made polymers which include fibers like teflon and dacron, synthetic rubbers, Polyethylene, Polystyrene, polyvinylchloride, nylon, polyester

2. based on polymerization reactions:

Based on the mode of polymerization, polymers are classified as:

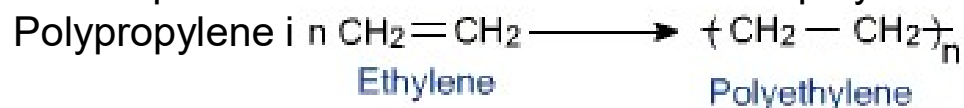
1. *Addition polymers*
 2. *condensation polymers*
-

Addition polymers

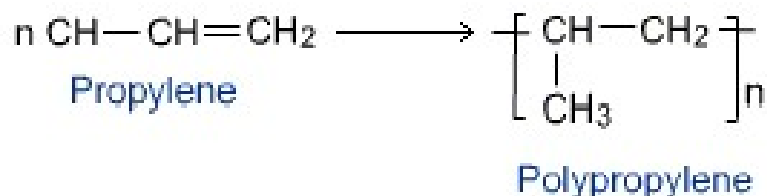
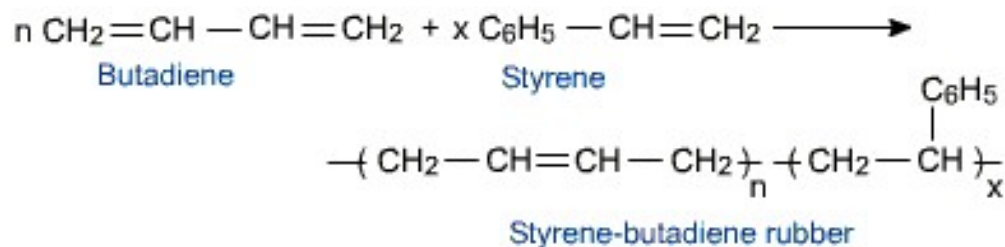
Addition polymers are formed when monomer units are separately added to form long chains without elimination of any by-product molecules. These polymers are formed by reactions between monomer molecules possessing multiple bonds.

Example: Ethylene undergoes polymerization to form polythene.

The empirical formula of the monomer and polymer are the same. Other examples:



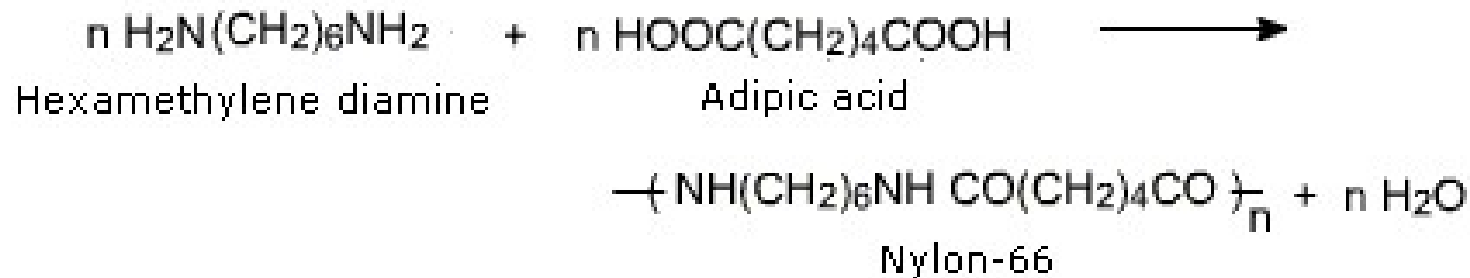
Styrene-butadiene rubber is an addition polymer formed by addition reactions between butadiene and styrene.



Condensation polymers

Condensation polymers are formed when the monomers containing active functional groups (generally two), which react together with the elimination of a small molecule like water, ammonia, alcohol etc.

Examples: Nylon-66, polyester, Bakelite etc. Nylon-66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:



3. Based on thermal behavior

The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.

Thermoplastics and Thermosets are the 2 categories.

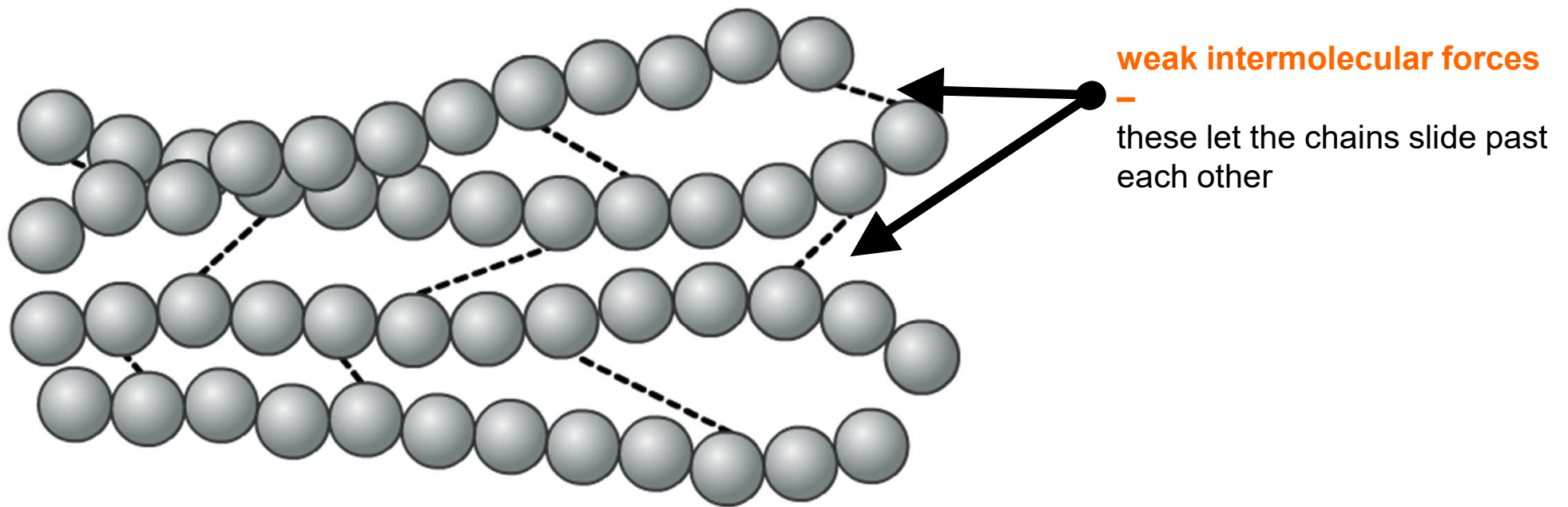
1. A **thermoplastic** is a polymer that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently. Thus thermoplastics can be moulded on heating. Most thermoplastics are high-molecular-weight polymers whose chains associate through weak Van der Waals forces (polyethylene); stronger dipole-dipole interactions and hydrogen bonding (nylon).

These polymers have no cross-linking between chains. Examples: Polyethylene, polystyrene etc.

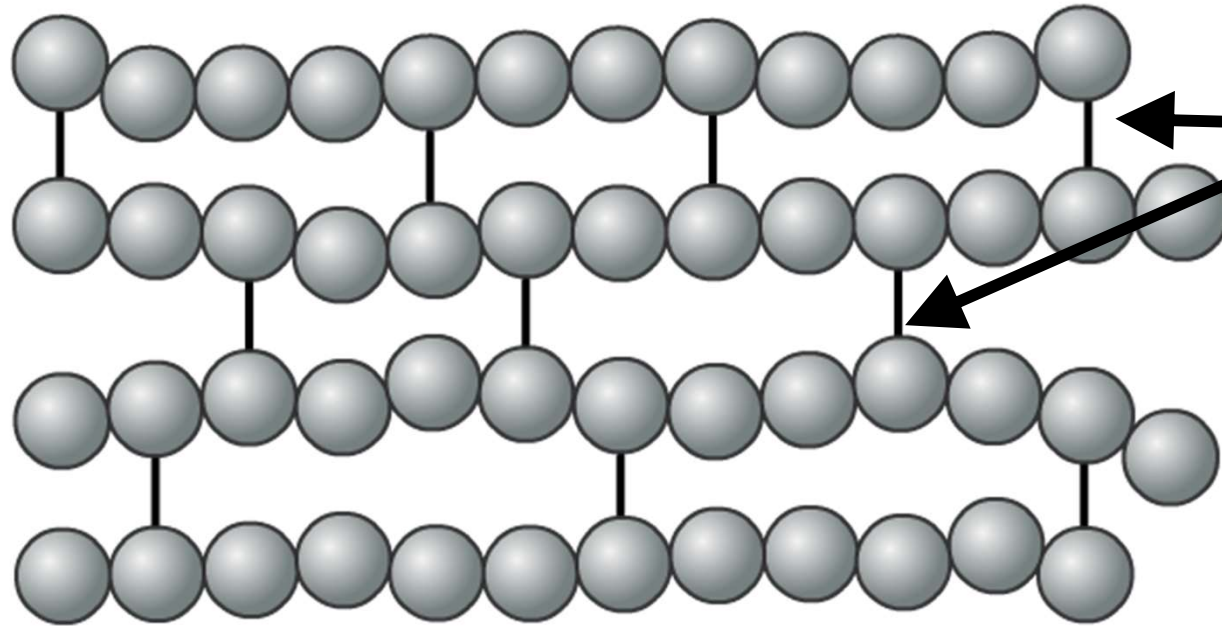
2. **Thermosetting** polymers

Thermosetting polymers made from relatively low molecular mass semi-fluid polymers which when heated in a mould forms an insoluble hard mass which is infusible. This is due to extensive crosslinks between the different polymer chains forming three dimensional network of bonds.

Example: Bakelite and melamine



Plastics made of these polymers are stretchy and have a low melting point. They are called **thermoplastic polymer**.



**strong intermolecular
forces
(cross-links) –**
these hold the chains firmly in
place

Plastics made of these polymers cannot be stretched, are rigid and have a high melting point. They are called **thermosetting** plastics (or 'thermosets').

4. Classification of polymers based on applications:

- 1. Elastomers:** a natural or synthetic polymer having elastic properties, e.g. rubber.
 - 2. Resins:** Resin is a natural or synthetic compound that begins in a highly viscous state and hardens with treatment. Eg. PF resins , epoxy resins
 - 3. Fibers:** a thread or filament from which a vegetable tissue, mineral substance, or textile is formed. Eg. Nylon
 - 4. Plastics :** Organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst eg. Bakelite, pvc.
-

Elastomers are viscoelastic polymers with long chains of molecules that are held together by weak forces. They can stretch to at least twice their length under low stress and return to their original shape when the stress is released.

Uses

Elastomers are used in many applications, including rubber bands and industrial seals.

Following are examples of elastomers with their applications:

Natural rubber: These are used in the automotive industry and in the manufacture of medical tubes, balloons, adhesives.

Polyurethanes: These are used in the textile industry for manufacturing elastic clothing like lycra.

Polybutadiene: These are used for providing wear resistance in wheels of vehicles.

Silicone: These are used in the manufacture of medical prostheses and lubricants as they have excellent chemical and thermal resistance.

Neoprene: These are used in the manufacture of wet-suits and in industrial belts.

Resins: Resin is a natural or synthetic compound that begins in a highly viscous state and hardens with treatment.
Eg. PF resins , epoxy resins

Structure

Polymers are large molecules made up of repeating structural units connected by covalent chemical bonds. Resins are viscous substances that are a subset of polymers.

Sources

Resins can be derived from both natural and synthetic sources. Synthetic resins are man-made polymers.

Uses

Epoxy: A coating material made from polymer resins and hardening chemicals that creates a rigid plastic-like surface.

Fibers: a thread or filament from which a vegetable tissue, mineral substance, or textile is formed. Eg. Nylon

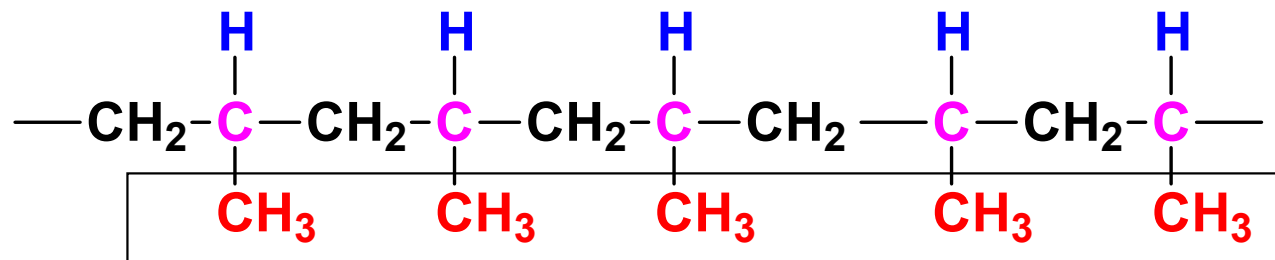
Fiber polymers have many properties, including:

- High strength-to-weight ratio
- Stiffness
- Resistance to corrosion, wear, impact, and fire

Plastics : Organic materials of high molecular weight, which can be moulded into any desired form, when subjected to heat and pressure in the presence of a catalyst eg. PVC.

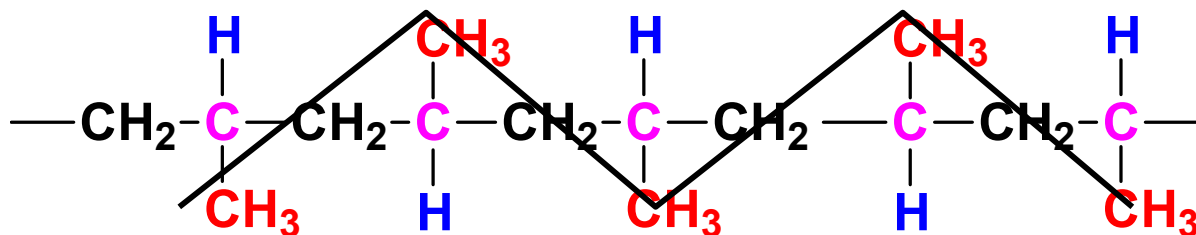
Tacticity- Plane representation of polypropylene polymer

1. Isotactic polymers



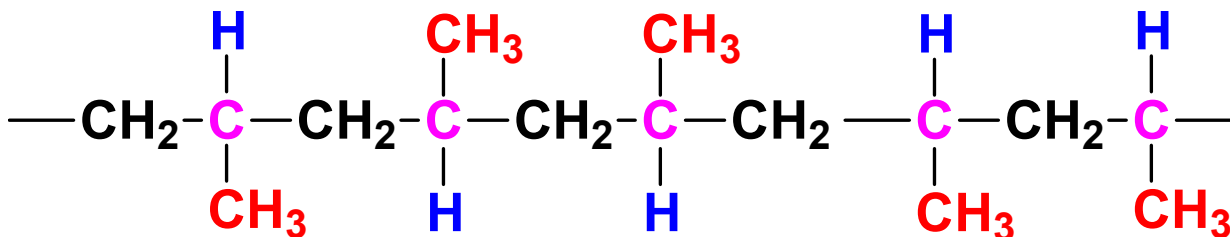
Functional groups on the same side of the main carbon skeleton

2. Syndiotactic polymers



Functional groups arranged in the alternate fashion of the main carbon skeleton

3. Atactic polymers



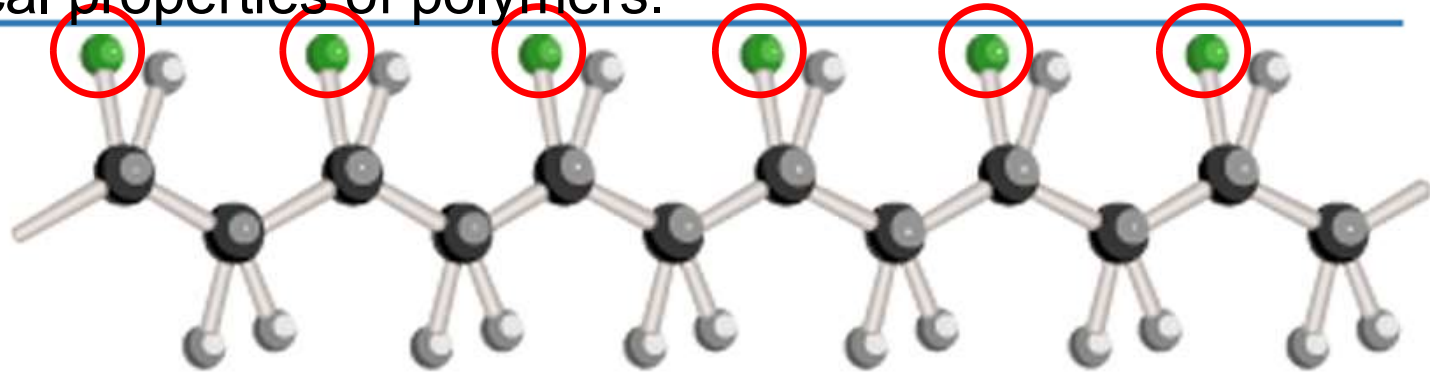
Functional groups arranged in a random manner around the main carbon skeleton

Tacticity : the orientation of monomeric units in a polymer molecule

It affects the physical properties of polymers.

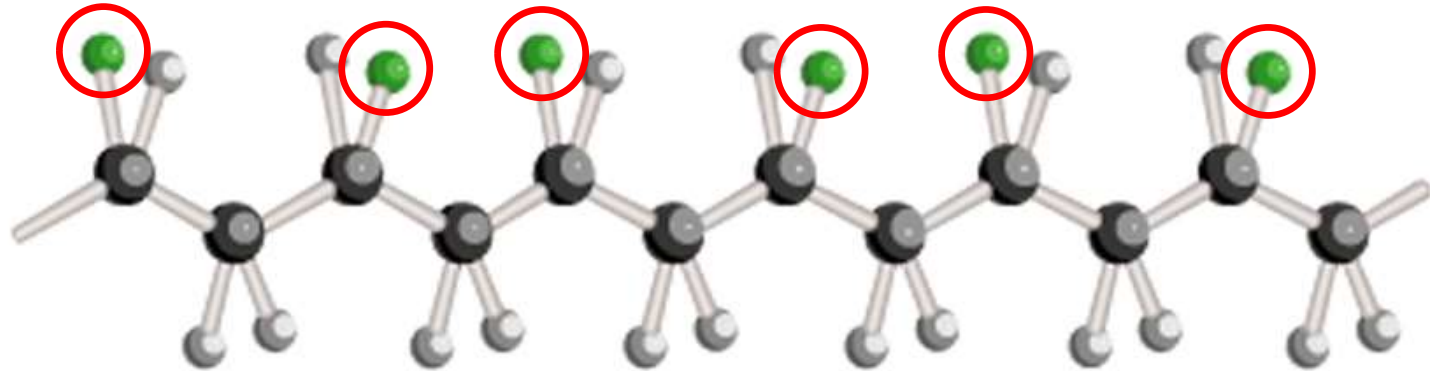
R groups on same
side of chain

Isotactic



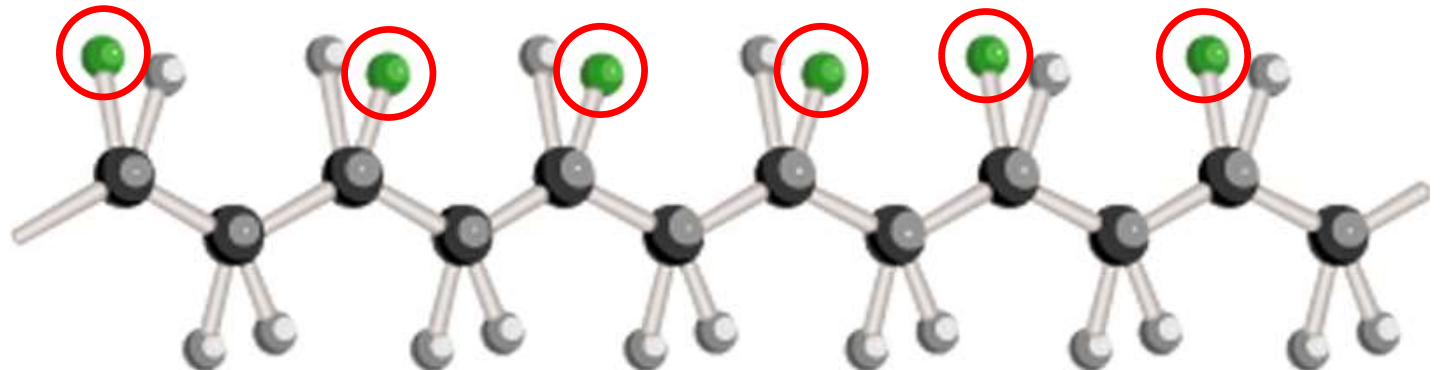
R groups alternate
from side to side

Syndiotactic



R groups disposed
at random

Atactic



Tacticity is a property of polymers that refers to the arrangement of pendant groups along a polymer's hydrocarbon chain.

isotactic



syndiotactic



atactic



Importance of tacticity

The practical importance of tacticity lies in its impact on the physical properties of a polymer. The regularity of the polymer's macromolecular structure determines whether it exhibits rigid, crystalline long-range order or flexible, amorphous long-range disorder. A clear understanding of a polymer's tacticity also aids in predicting its melting temperature, solubility in solvents, and mechanical properties.

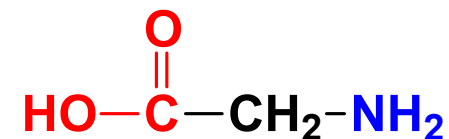
Functionality

The number of reactive sites present in a monomer is called functionality

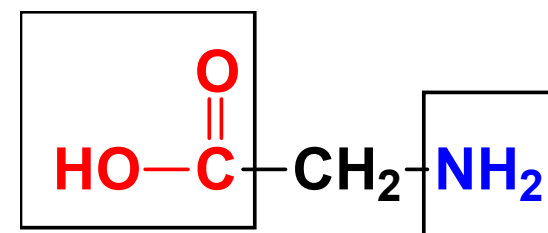
1.



Linear chain polymer is formed if the functionality of the monomer is only two (Bifunctional)

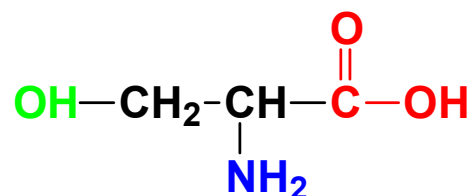
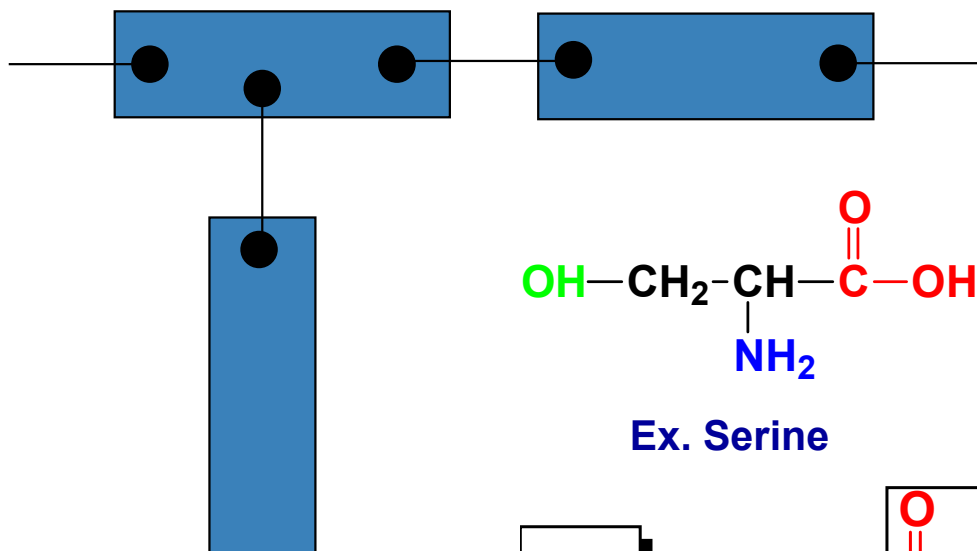


Ex. Glycine

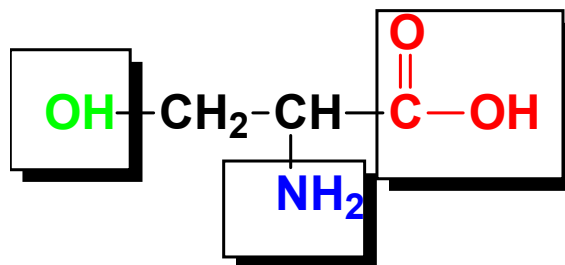


Glycine

2.



Ex. Serine



Cross linked chain polymer is formed if the functionality of the monomer is more than two (multifunctional)

Functionality

The number of bonding sites in a monomer is referred as its functionality

Bifunctional: eg. alkene

Trifunctional: eg. Monomethylsilicon trichloride (MeSiCl_3)

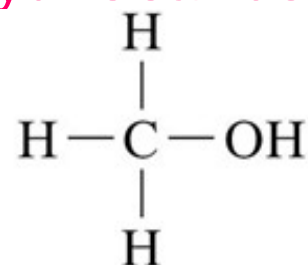
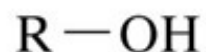
Polyfunctional: eg. Silicon tetrachloride (SiCl_4)

Functionality

the number of reactive sites or bonding sites

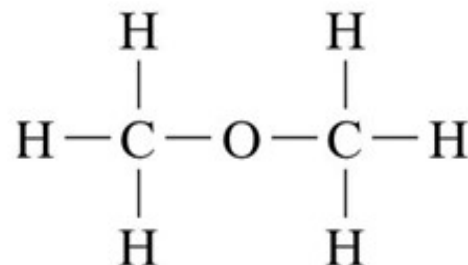
Some mono functional hydrocarbons

Alcohols



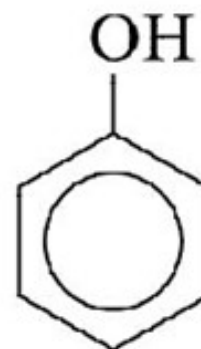
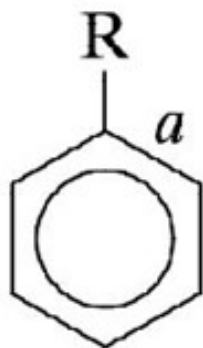
Methyl alcohol

Ethers



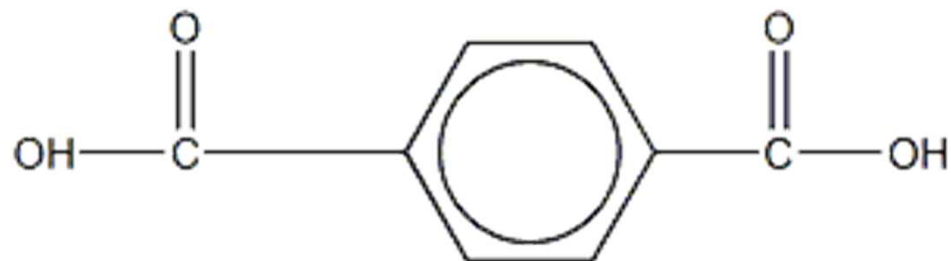
Dimethyl Ether

Aromatic
hydrocarbons

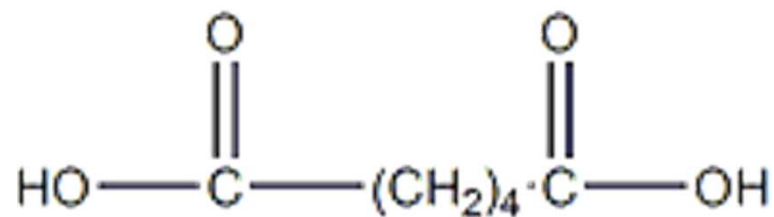


Phenol

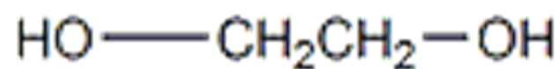
Some bi functional hydrocarbons



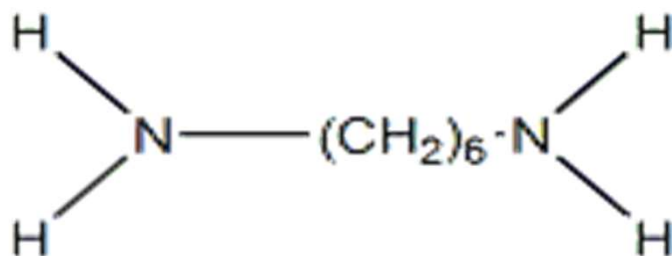
Terephthalic acid



adipic acid (hexanedioic acid)

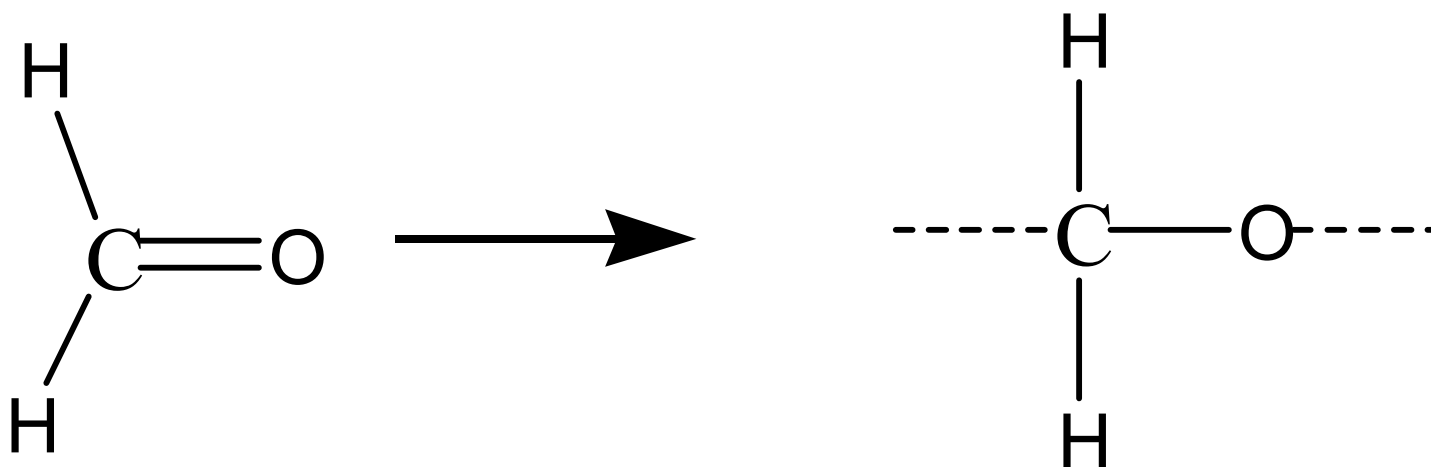
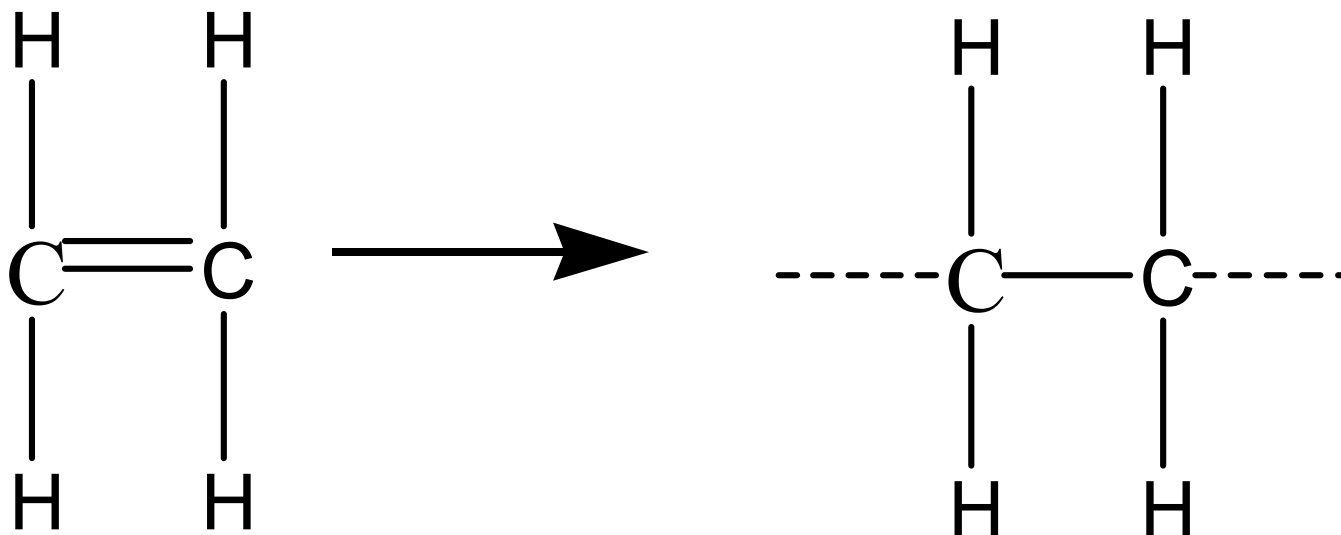


ethylene glycol



1,6-hexanediamine

Ethylene is considered to be bifunctional



General method of polymerization

Two major methods generally used for preparing polymers:

1. Addition polymerization
2. Condensation polymerization

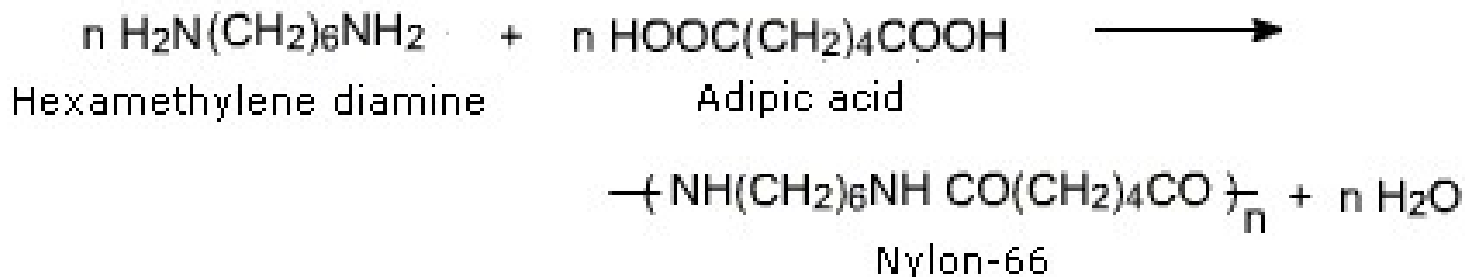
Addition Polymerization

It is a reaction that yields a product, which is an exact multiple of the original monomeric molecule. Such a monomeric molecule usually contains one or more double bonds, which by intermolecular rearrangement may make the molecule bifunctional. The addition polymerization reaction must be instigated by the application of heat, light, pressure or a catalyst for breaking down the double covalent bonds of monomers.

Condensation polymerization

May be defined as a reaction occurring between simple polar-group-containing monomers with the formation of polymer and elimination of small molecules like water, HCl etc.

Examples: Nylon-66, polyester, Bakelite etc. Nylon-66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:

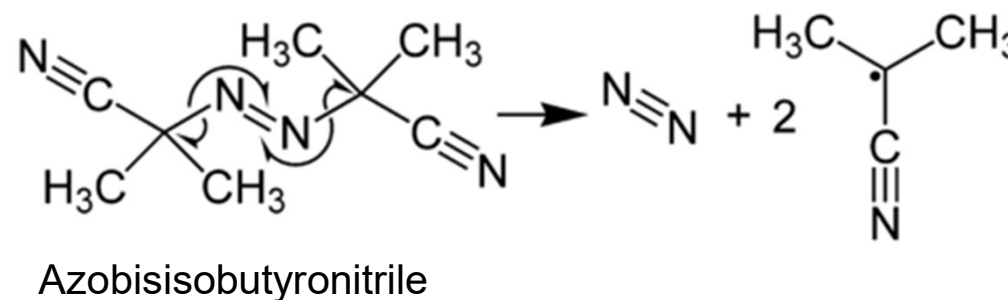
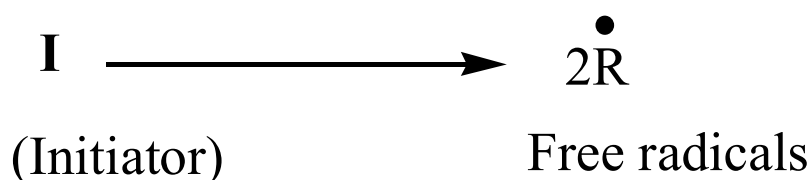


Mechanism of addition polymerization:

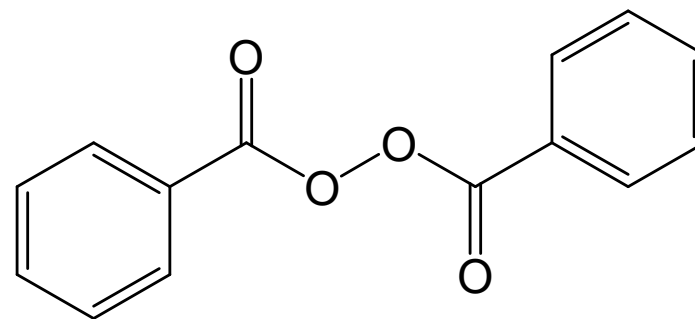
1. Free radical polymerization
2. Cationic polymerization
3. Anionic polymerization
4. Coordination polymerization or Ziegler-Natta polymerization

1. Free radical polymerization mechanism:

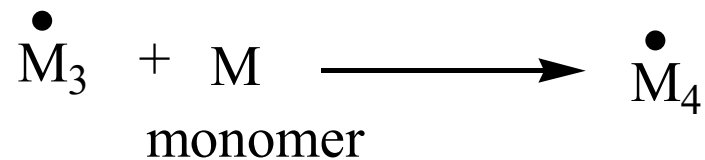
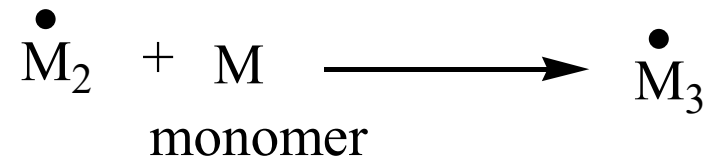
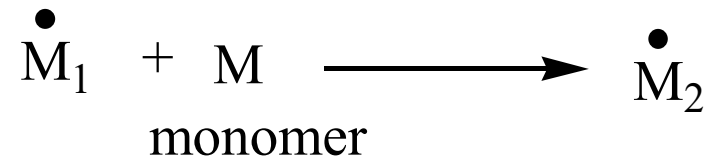
- (i) **Initiation step** is considered to involve two reactions. The first step is the production of free radicals by **homolytic dissociation** of an initiator to yield pair of radicals. (**benzoylperoxide**, **tert-butylperoxide**, **AIBN**)



The second part of the initiation steps involves the reaction of this radical with first monomer unit (M) to produce chain initiating species



(ii) Propagation step consists of the growth of M_1 free radical by successive reaction of large numbers of monomers molecules



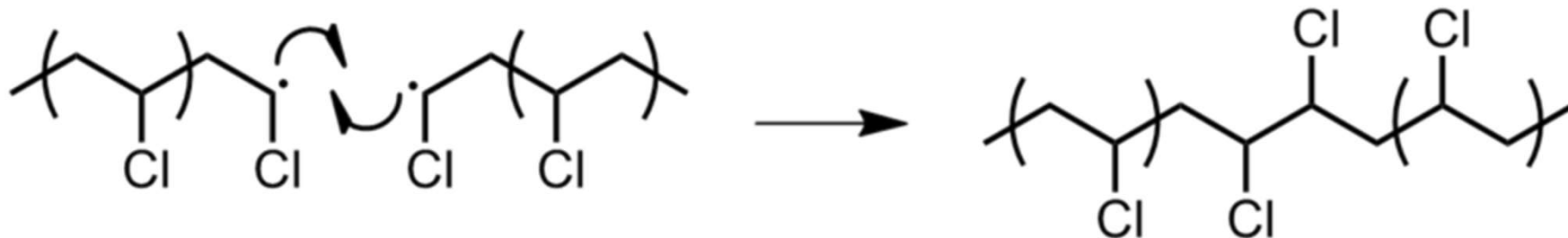
In general



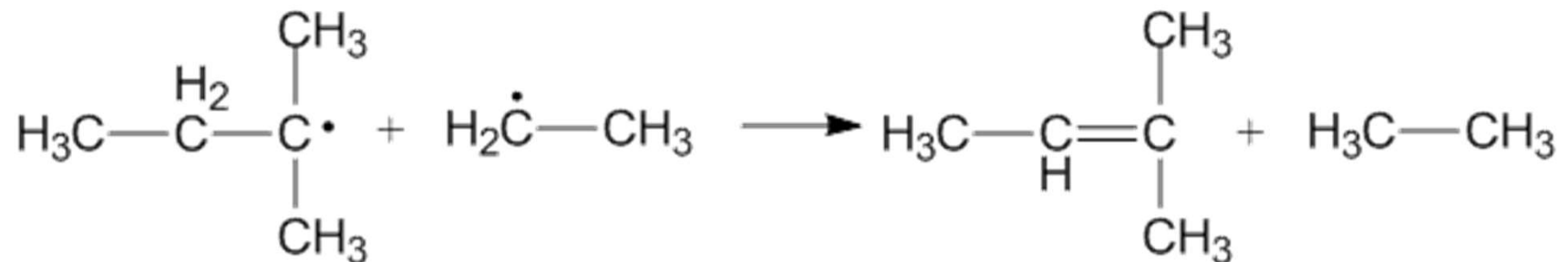
Termination steps

a) Termination by coupling

b) Termination by disproportionation



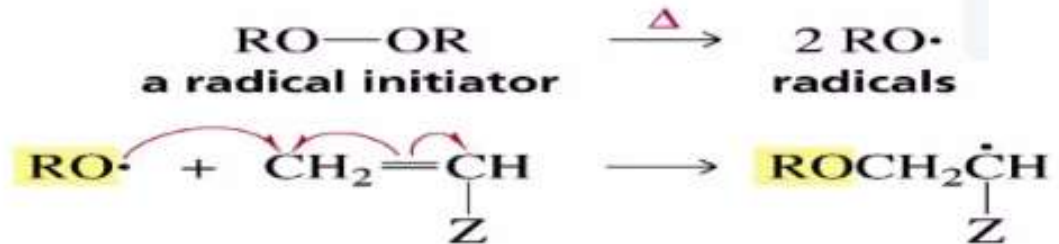
Termination by coupling



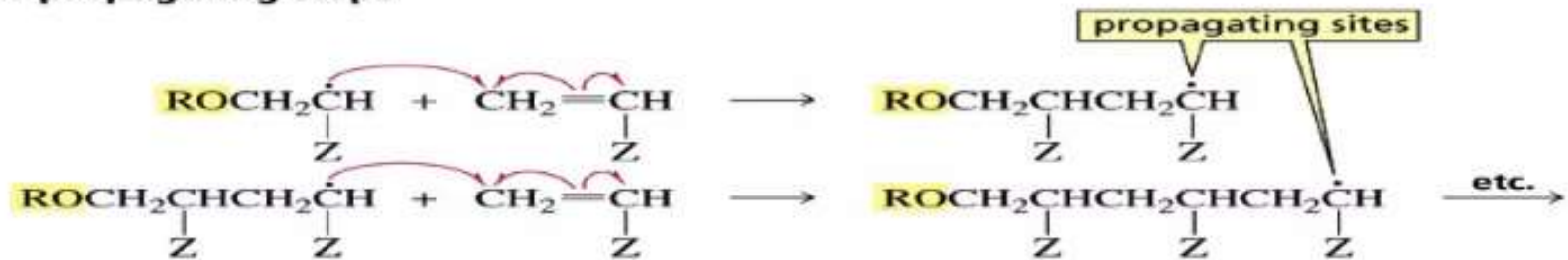
Termination by disproportionation

Free redical polymerization mechanism:

chain-initiating steps

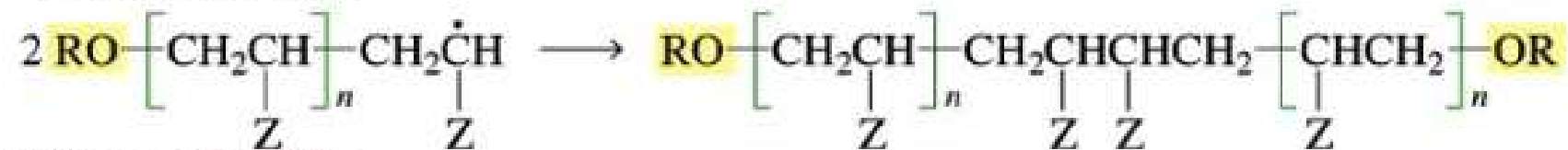


chain-propagating steps

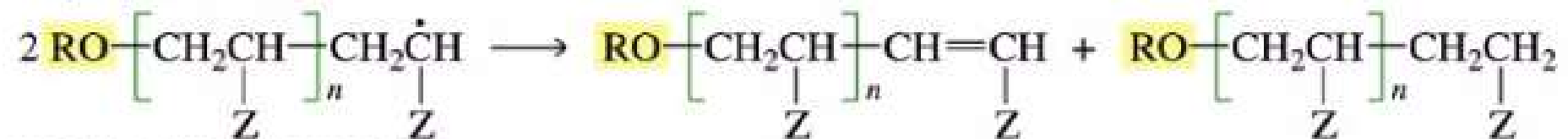


methods to terminate the chain

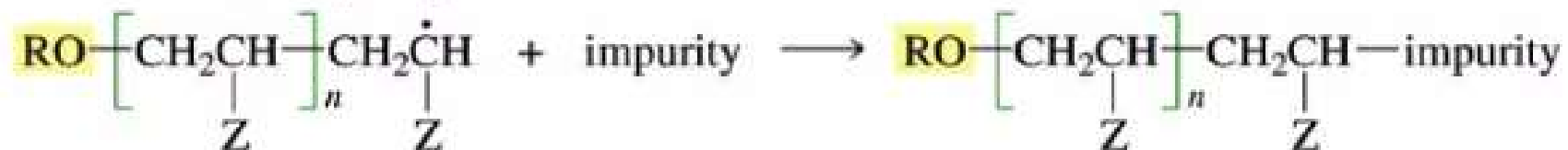
chain combination



disproportionation



reaction with an impurity



IONIC CHAIN POLYMERIZATION

Ionic polymerization is more complex than free-radical polymerization

Whereas free radical polymerization is non-specific, the type of ionic polymerization procedure and catalysts depend on the nature of the substituent (R) on the vinyl (ethenyl) monomer.

Cationic initiation is therefore usually limited to the polymerization of monomers where the R group is electron-donating. This helps stabilize the delocalization of the positive charge through the p orbitals of the double bond.

Anionic initiation, requires the R group to be electron withdrawing in order to promote the formation of a stable carbanion.

Using catalyst, not initiator

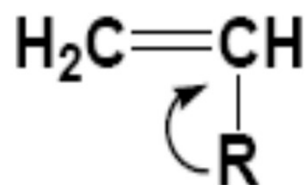
Highest reaction rate

Termination step is just disproportionation

Environment must be pure

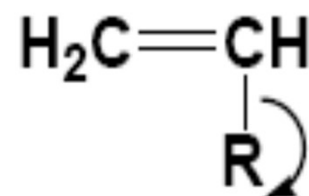
Ionic Polymerization

Cationic



R - Electron donating

Anionic



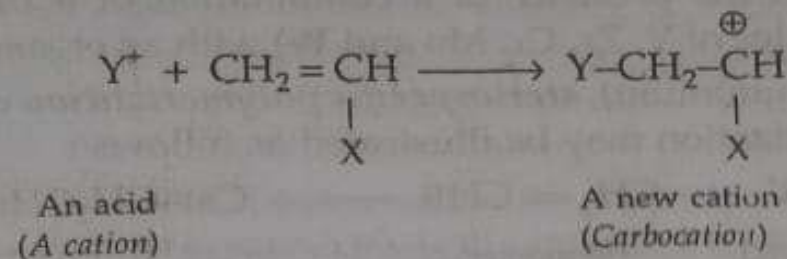
R - Electron withdrawing

2. Cationic Polymerization

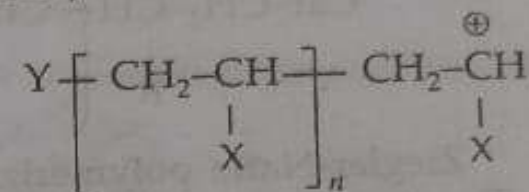
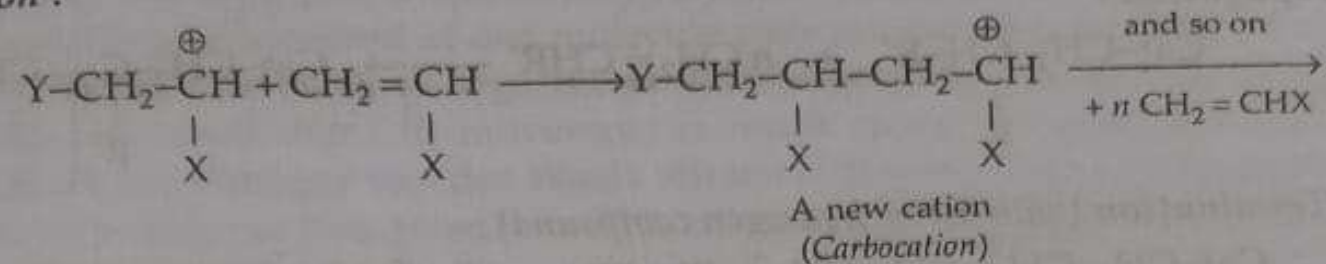
- Involves the polymerization of monomers that have strong electron-donating groups, eg, propylene etc.
 - typical initiators (catalysts) are compounds with electron acceptor properties eg. AlCl_3 , SnCl_4 , TiCl_4 , and BF_3
 - Steps of polymerization
 - i) Initiation : AlCl_3 initiates the reaction and carbocation is formed
 - ii) Propagation
 - iii) Termination
-

(2) Cationic mechanism of polymerization involves the following steps .

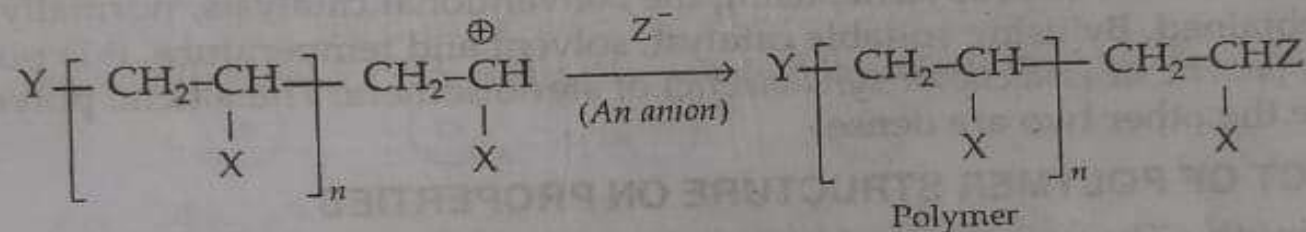
(i) Initiation :



(ii) Propagation :



(iii) Termination :



3. Anionic Polymerization

Involves the polymerization of monomers that have strong electron-withdrawing groups, eg, acrylonitrile, vinyl chloride, methyl methacrylate, etc.

typical catalyst include KNH_2 , n-BuLi , and Grignard reagents such as alkyl magnesium bromides

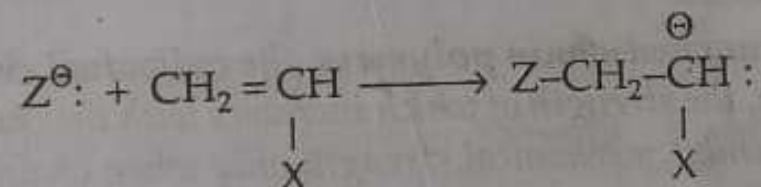
If the monomer has only a weak electron-withdrawing group then a strong base initiator is required, eg, butyllithium; for strong electron-withdrawing groups only a weak base initiator is required, eg, a Grignard reagent.

Steps of polymerization

- i) Initiation: KNH_2 initiates the reaction and carbanion is formed
 - ii) Propagation
 - iii) Termination
-

(3) Anionic mechanism of polymerization involves the following steps :

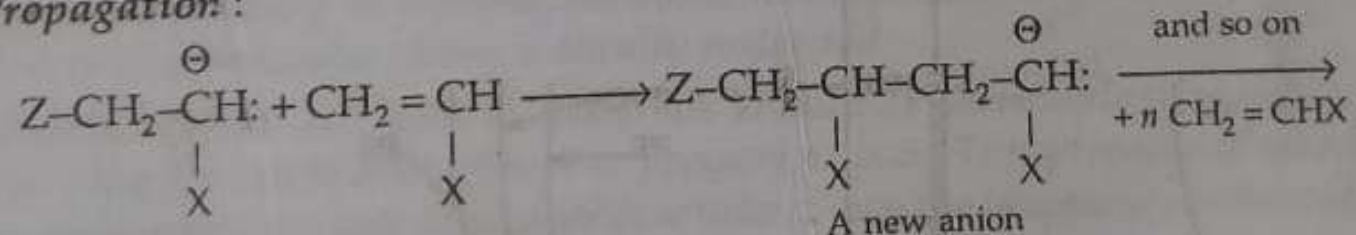
(i) **Initiation :**



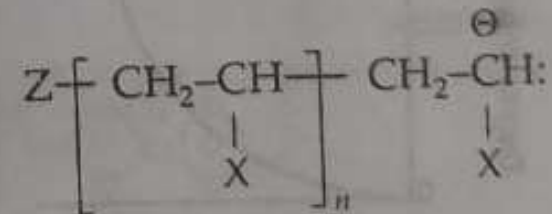
A base (An anion)

A new anion (Carbanion)

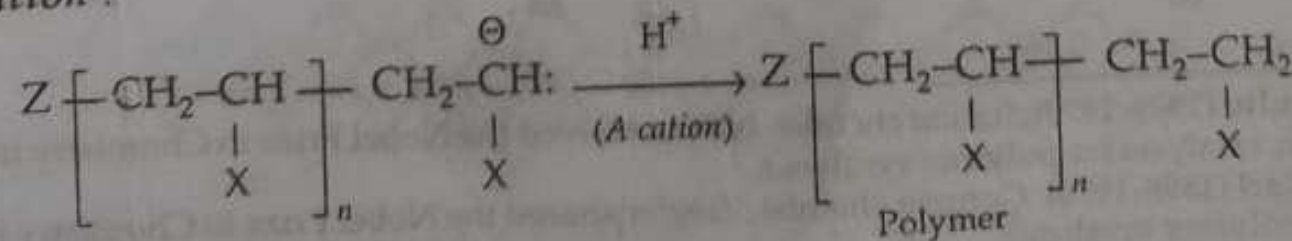
(ii) **Propagation :**



A new anion



(iii) **Termination :**



Polymer

Coordination polymerization (Ziegler-Natta catalysts)

Coordination polymerization is a form of addition polymerization in which monomer adds to a growing macromolecule through an organometallic active center.

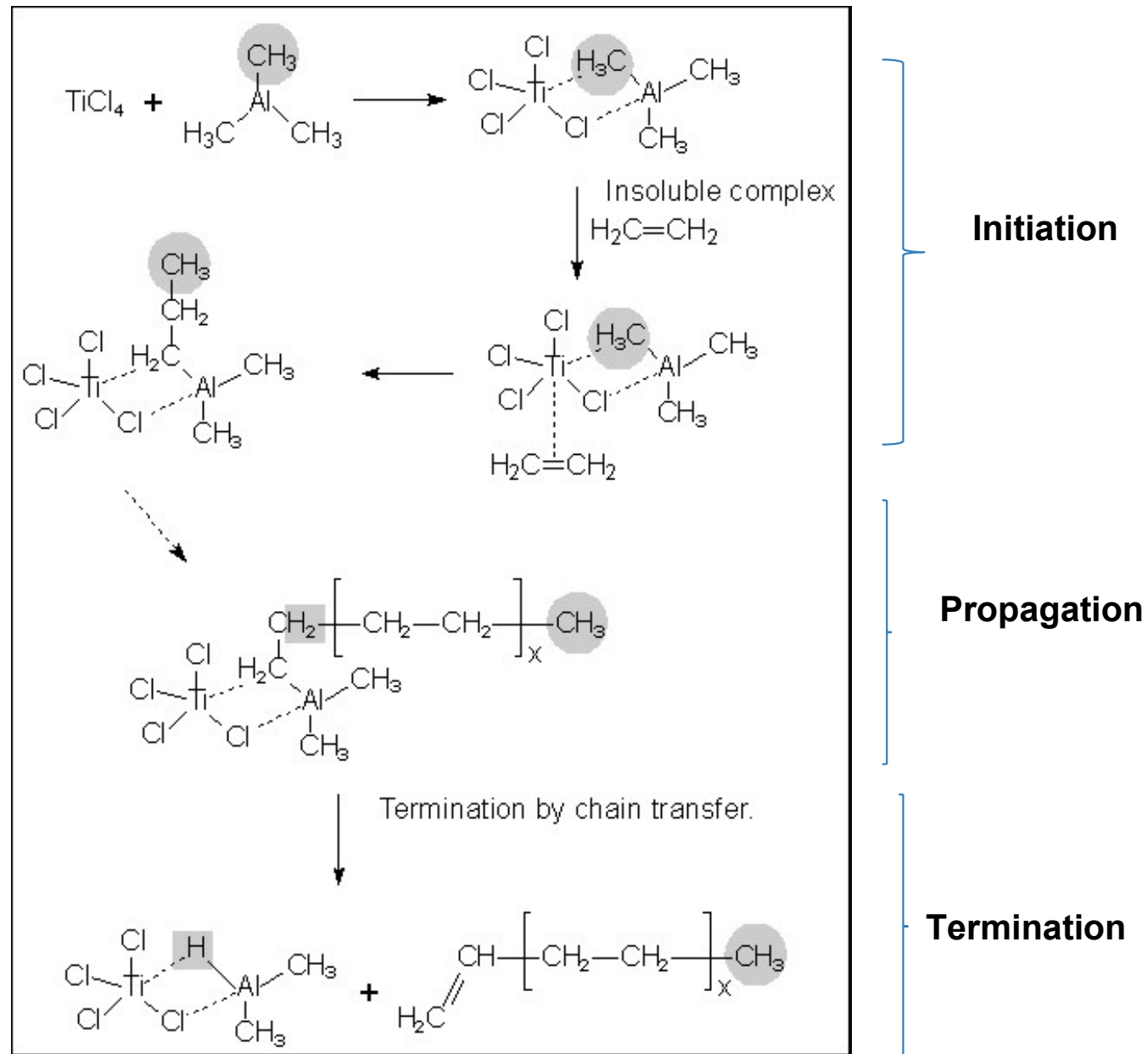
The development of this polymerization technique started in the 1950s with heterogeneous **Ziegler-Natta catalysts** based on **titanium tetrachloride** and an **aluminium co-catalyst ($\text{TiCl}_4 + \text{R}_3\text{Al}$)**

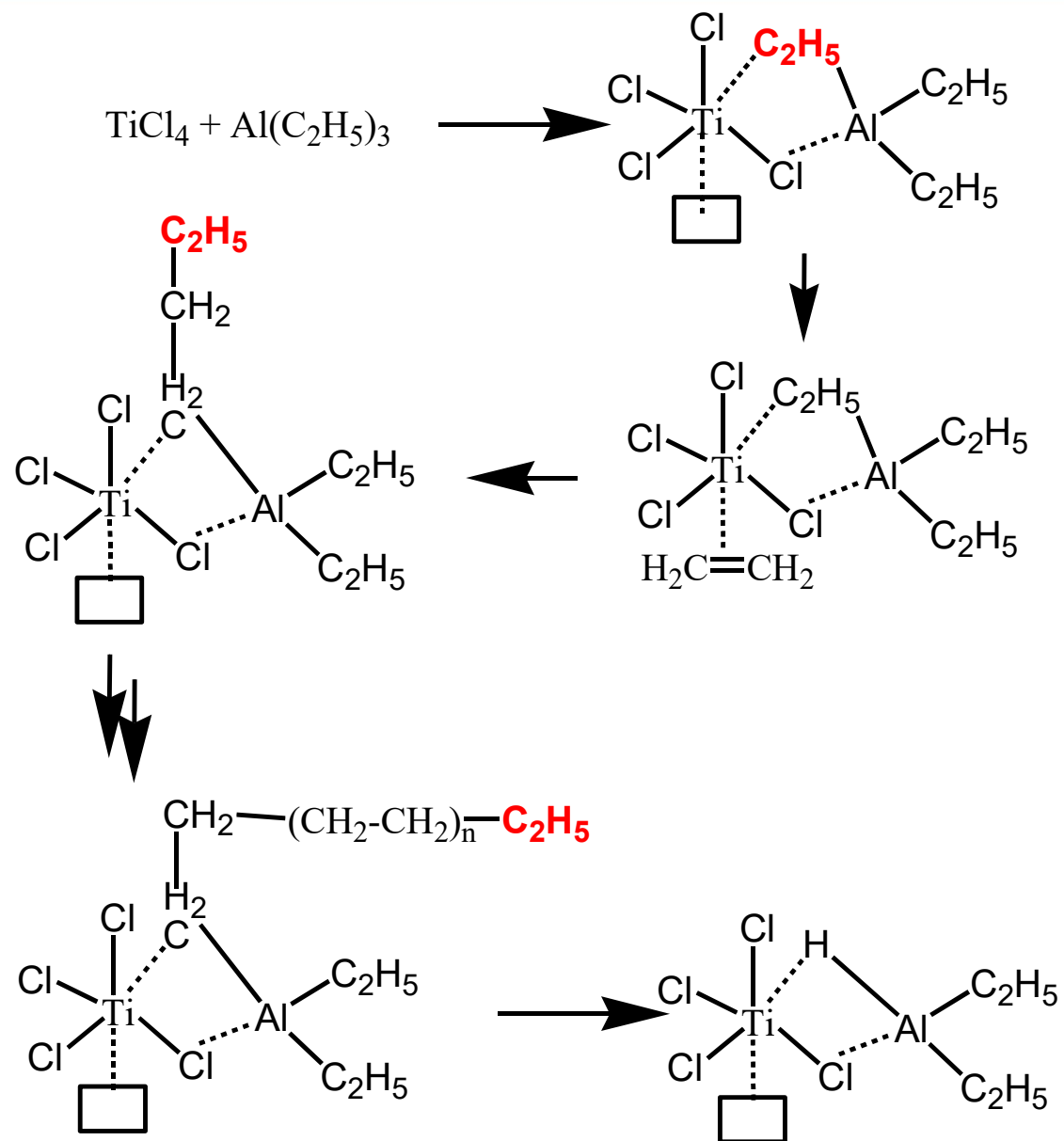
Coordination polymerization has a great impact on the physical properties of vinyl polymers such as polyethylene and polypropylene compared to the same polymers prepared by other techniques such as free radical polymerization.

The polymers tend to be linear and not branched and have much **higher molar mass**. Coordination type polymers are also stereoregular and can **be isotactic or syndiotactic** instead of just **atactic**. This tacticity introduces crystallinity in otherwise amorphous polymers.

From these differences in polymerization type the distinction originates between low-density polyethylene (LDPE), high-density polyethylene (HDPE) .

Mechanism: **Coordination polymerization**





CONDENSATION POLYMERIZATION

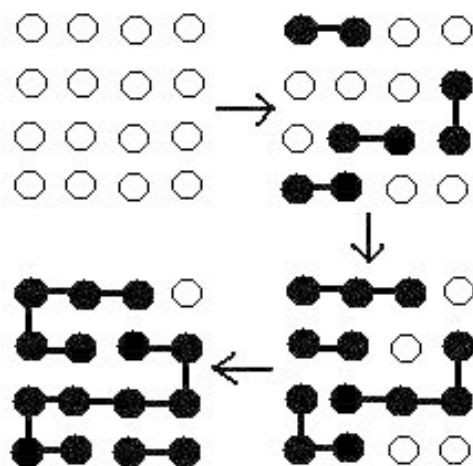
Minimum two functional groups required

Usually linear

Molecular weight increases slowly at low conversion

High extents of reaction are required to obtain high chain length

Step-growth polymerization refers to a type of polymerization mechanism in which bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers. Many naturally occurring and some synthetic polymers are produced by step-growth polymerization, e.g. polyesters polyamides, polyurethanes, etc. Due to the nature of the polymerization mechanism, a high extent of reaction is required to achieve high molecular weight. The easiest way to visualize the mechanism of a step-growth polymerization is a group of people reaching out to hold their hands to form a human chain — each person has two hands (= reactive sites). There also is the possibility to have more than two reactive sites on a monomer: In this case branched polymers are produced.



A generic representation of a step-growth polymerization. (Single white dots represent monomers and black chains represent oligomers and polymers)

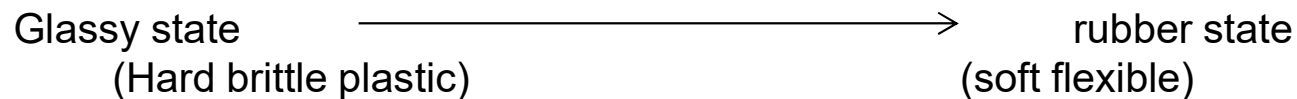
Differences between step-growth polymerization and chain-growth polymerization

Step-growth polymerization	Chain-growth polymerization
Growth throughout matrix	Growth by addition of monomer only at one end of chain
Rapid loss of monomer early in the reaction	Some monomer remains even at long reaction times
Same mechanism throughout	Different mechanisms operate at different stages of reaction (i.e. Initiation, propagation and termination)
Average molecular weight increases slowly at low conversion and high extents of reaction are required to obtain high chain length	Molar mass of backbone chain increases rapidly at early stage and remains approximately the same throughout the polymerization
Ends remain active (no termination)	Chains not active after termination
No initiator necessary	Initiator required

Glass transition temperature: (T_g)

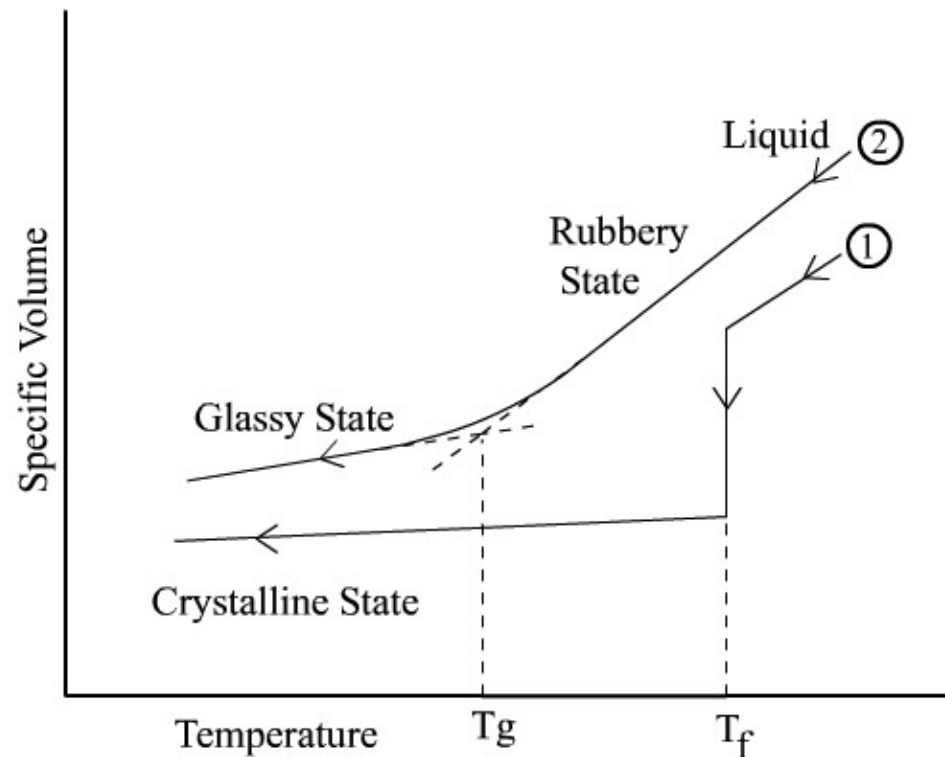
- At low temperatures, all amorphous polymers are stiff and glassy.
- On Warming, polymers soften in a characteristic temperature range known as the glass-rubber transition region.
- The glass transition temperature (T_g), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states.
- T_g constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured.

So, the *glass transition temperature* can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery.



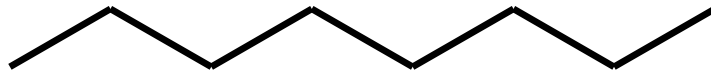
In the glassy state of the polymer, there is neither molecular motion nor segmental motion.

To become more quantitative about the characterization of the liquid-glass transition phenomenon and T_g , we note that on cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point, T_f . Instead, at the glass transition temperature, T_g , there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the figure below. Note that the intersections of the two straight line segments of curve (2) defines the quantity T_g .

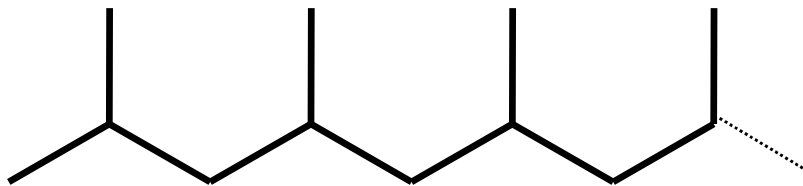


Factors affecting T_g

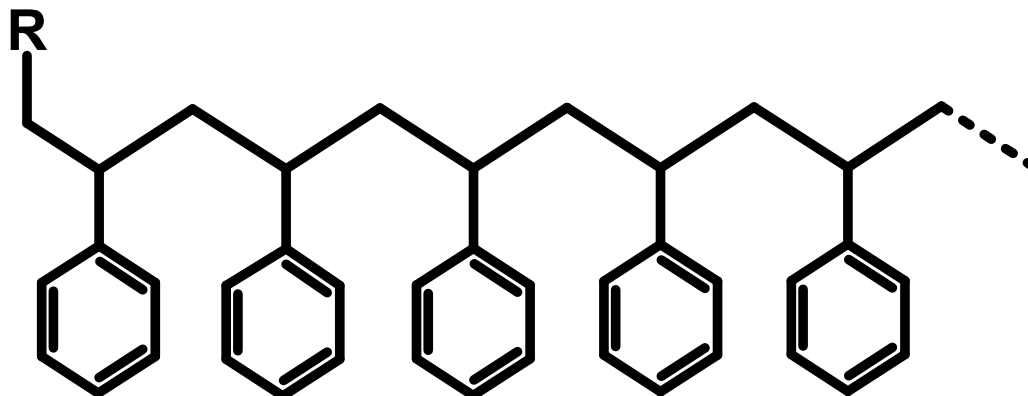
the bulky groups on chain, increases the Tg of the polymer



Polyethylene
T_g = -110 °C

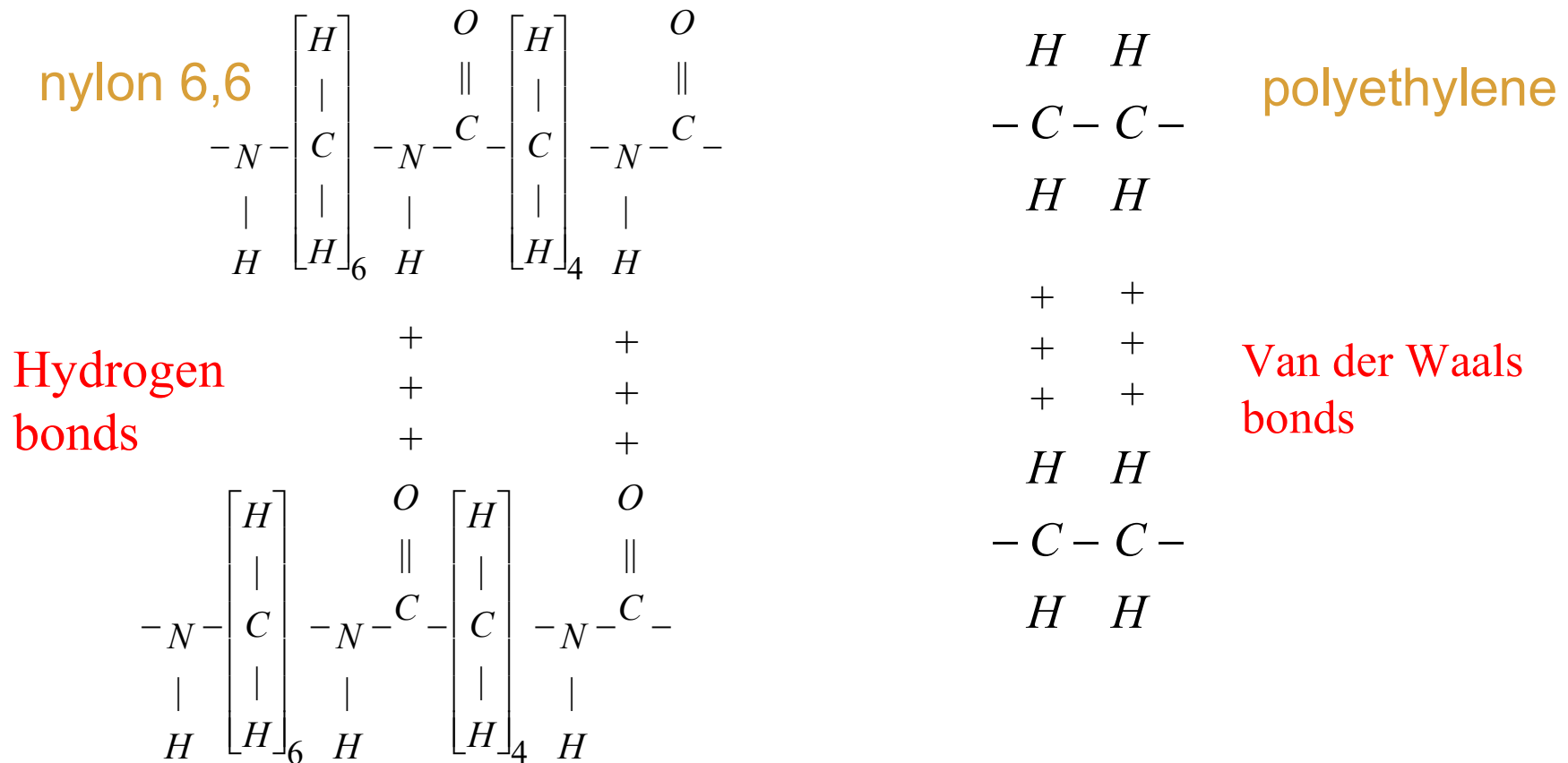


Polypropylene
T_g =



Polystyrene
T_g = 100 °C

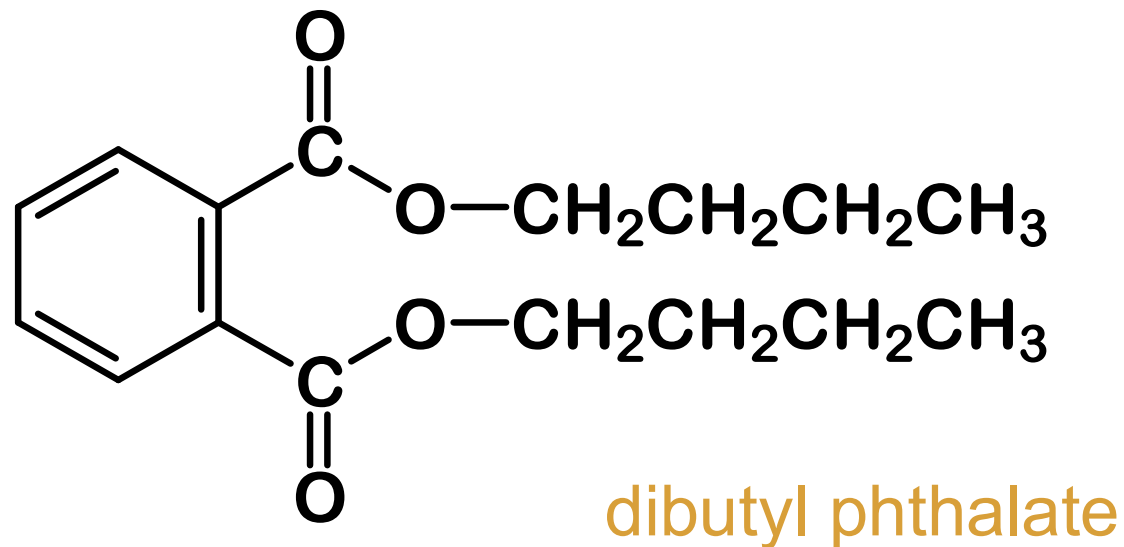
- e.g., the Tg of *nylon 6,6* (Tg = 50 °C) is higher than *PE* (Tg = -110 °C)



With H-bonds vs vdW bonds, nylon is expected to have (and does) higher T_g.

The presence of a **plasticizer** reduces the T_g of a polymer

The **plasticizers** are usually dialkyl phthalate esters, such as dibutyl phthalate, a high boiling liquid.



The plasticizer separates the individual polymer chains from one another. It acts as a lubricant which reduces the attractions between the polymer chains.

The Tg of a polymer is influenced by its molecular weight

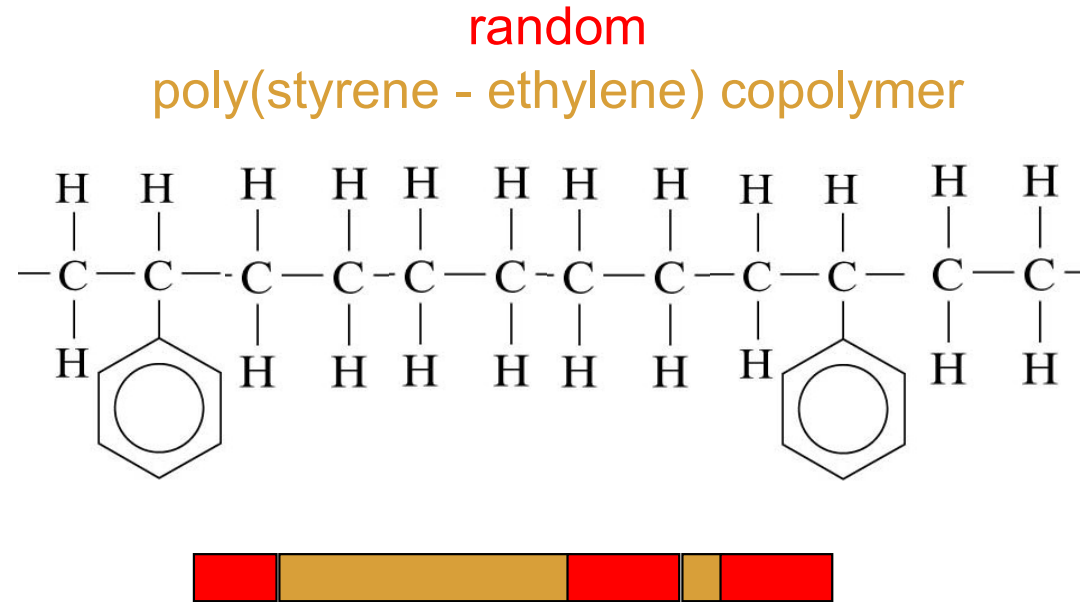
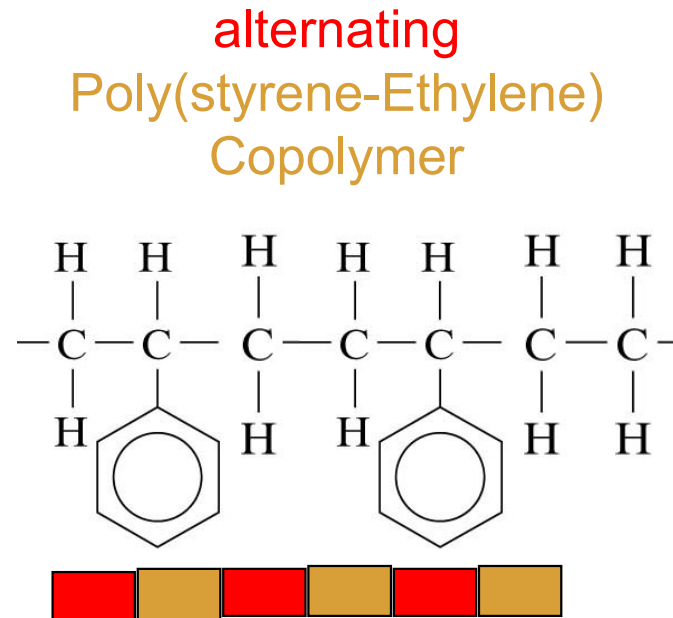
With increase in molecular mass, the Tg increases

e.g., PE (low M_w) -110 °C
 PE (high M_w) - 90 °C

Thus,

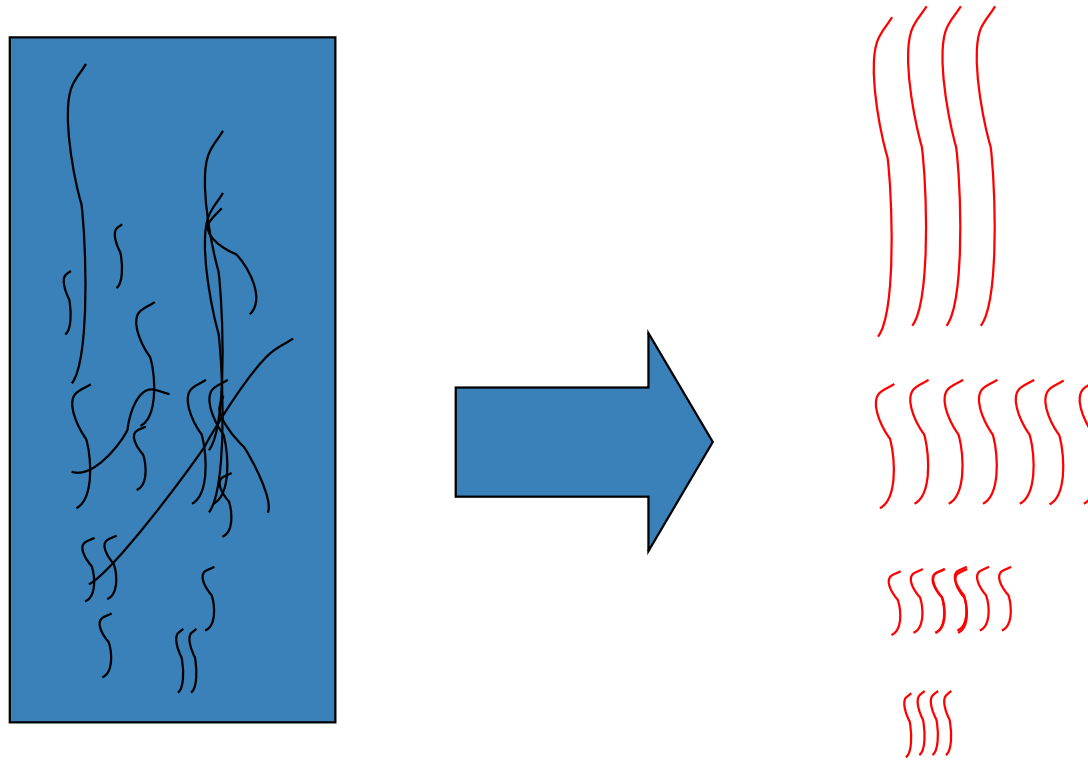
- 1) The presence of bulky side groups increase T_g .
 - 2) Polar side atoms or groups of atoms increase T_g .
 - 3) Double chain bonds and aromatic chain groups which tend to stiffen the molecular backbone increases T_g .
 - 4) Increase in the molecular weight also tends to raise the glass transition temperature.
 - 5) A small amount of branching will tend to lower T_g ; on the other hand , a high density of branches reduces chain mobility, and elevates glass transition temperature.
-

Which polymer more likely to crystallize? Can it be decided?



- Alternating co-polymer more likely to crystallize than random ones, as they are always more easily crystallized as the chains can align more easily.
-

Molecular Weight of Polymers



The molecular weight of a polymer can only be viewed statistically and expressed as some average of the Mol. Wt.s contributed by the individual molecules that make the sample

the molecular weight of a polymer can be expressed by two most and experimentally verifiable methods of averaging

(i) Number – average

(ii) weight – average

Number average molecular mass of a polymer can be defined as the total mass of all the molecules in a polymer sample divided by the total number of molecules present

The molecular mass of a polymer can use either *number fractions* or the *weight fractions* of the molecules present in the polymer

In computing the number average molecular mass of a polymer, we consider the number fractions

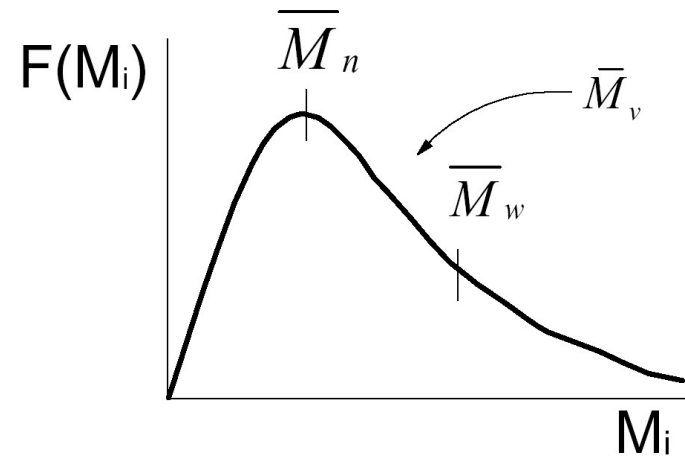
Polymers: Molecular Weight

N_i : no. of molecules with degree of polymerization of i

M_i : molecular weight of i

number average, \bar{M}_n

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$



- weight average, \bar{M}_w

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

The dispersity index, or formerly polydispersity index (PDI) = \bar{M}_w / \bar{M}_n

The number-average molecular mass (\overline{M}_n) is determined by the measurement of colligative properties such as

lowering of vapour pressure

osmotic pressure

depression in freezing point

elevation in boiling point

The weight-average molecular mass (\overline{M}_w) is determined by

light scattering

ultra-centrifugal techniques

Numerical

Consider a polymer sample containing 50 molecules of molecular weight 10000, 35 molecules of molecular weight 12000 and 15 molecules of molecular weight 14000. Determine **Number Average Molecular Weight** and **Weight Average Molecular Weight**. If the polymer is **polypropylene**, what will be the **degree of polymerization**?

$$\overline{M}_n = \frac{(50 \times 10000) + (35 \times 12000) + (15 \times 14000)}{(50 + 35 + 15)}$$

Ans. = 11,300 (Number Average Molecular Weight)

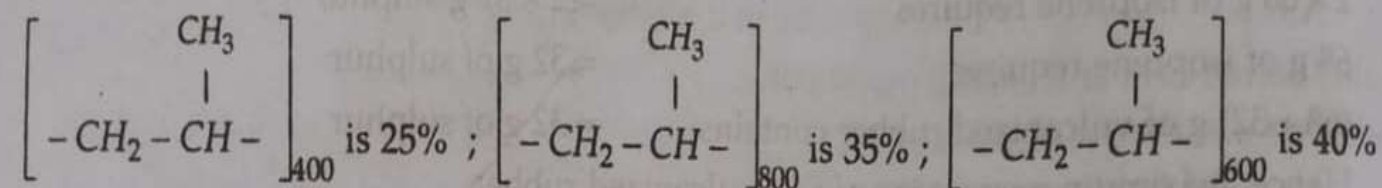
$$\overline{M}_w = \frac{50(10000)^2 + 35(12000)^2 + 15(14000)^2}{(50 \times 10000) + (35 \times 12000) + (15 \times 14000)}$$

Ans. = 11,486.7 (Weight Average Molecular Weight)

$$DP = \frac{\overline{M}_n}{\text{Molecular weight of monomer}}$$

Ans. = 269 (DP)

Example 8. Calculate the number average and weight average molecular masses of polypropylene polymer with the following composition :



Given that at. mass of C = 12 and H = 1.]

[VT, Aug. 2K]

Solution. Mol. mass of repeat unit, $-\text{CH}_2 - \text{CH}(\text{CH}_3) -$ is 42.

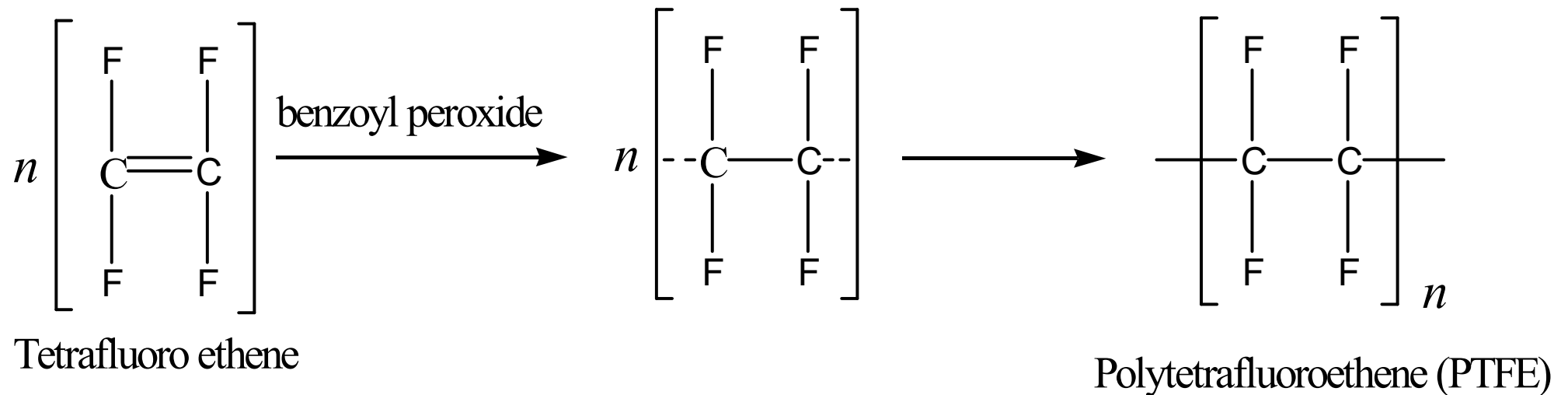
No. of repeat unit (n) in polymer	400 in I	800 in II	600 in III
Mol. mass (M_i) (= 42 n)	16,300	32,600	25,200
No. of molecules in 100	25	35	40

$$\therefore \overline{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{25 \times 16,300 + 35 \times 32,600 + 40 \times 25,200}{100} = 25,565$$

and
$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{25 (16,300)^2 + 35 (32,600)^2 + 40 (25,200)^2}{25 \times 16,300 + 35 \times 32,600 + 40 (25,200)}$$

$$= \frac{69,24045 \times 10^4}{25,56,500} = 27,084$$

Polytetrafluoroethylene (TEFLON) or FLUON (PTFE)



Properties of TEFLON:

- They are extreme tough, high softening point, exceptionally high chemical-resistances towards all chemicals, high density, waxy touch.
- It can be punched, machined and drilled

Uses

- As an insulating materials (for motors, transformers, cables, wires, fitting)
 - For making gaskets, packing, pump parts, tank, chemical-carrying pipe lines, tubing
 - For coating
 - In non-lubricating bearing and non-sticking stop-cocks.
-

Nylon:A man-made polymer

Nylon is used in clothes, shoes, jackets, belts, Tires, ropes and various accessories.



Polyamides are synthetic polymers, which have recurring amide groups. ***Nylons***, used mostly for making fibers, belong to ***polyamides***.

Nylon 6:6

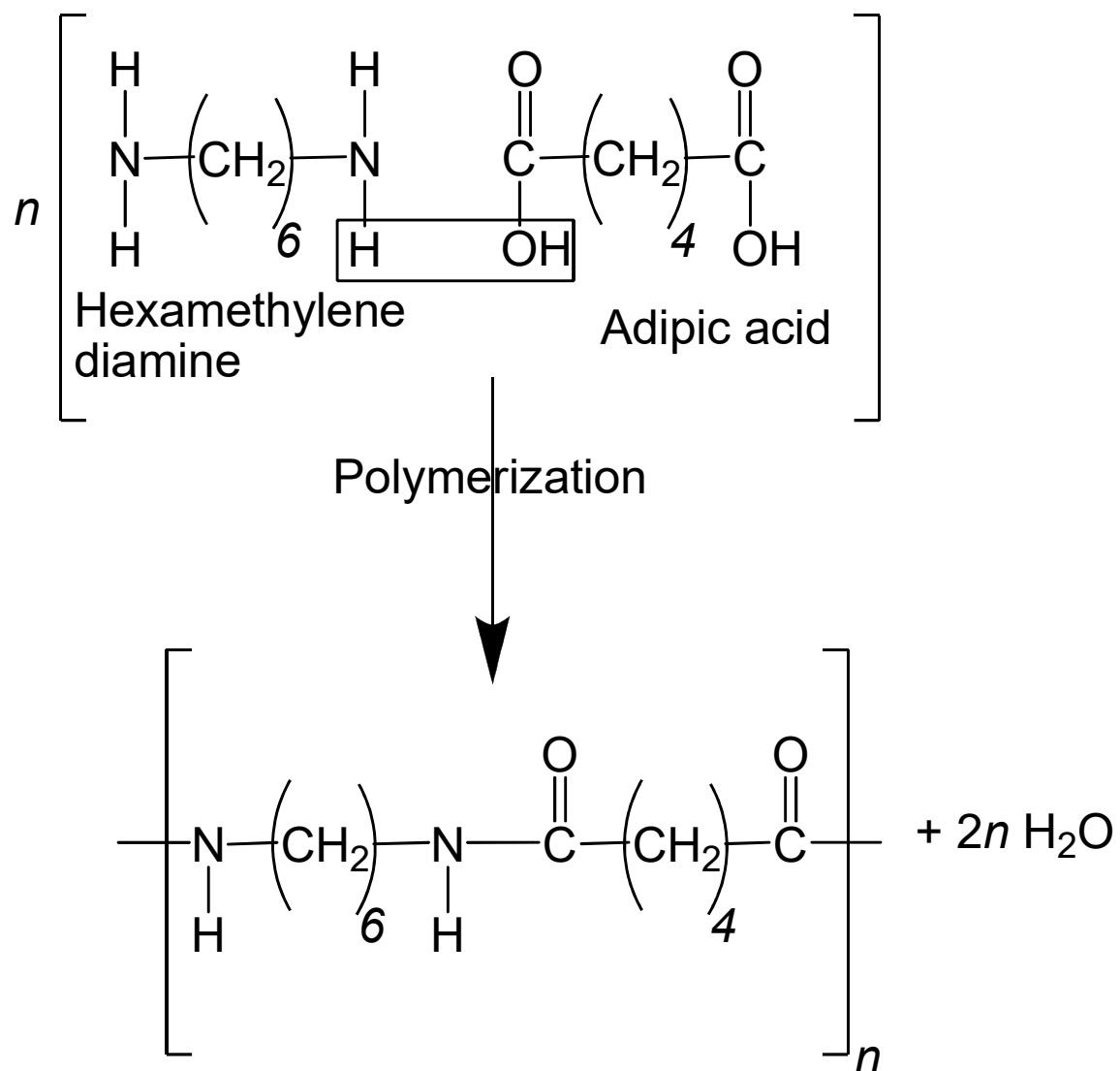
Nylon 6

Nylon 11

Nylon 6:10

Nylon 6:6

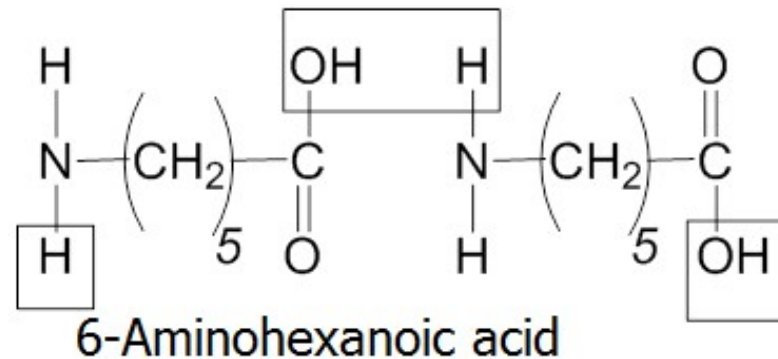
Nylon 6:6 is obtained by the polymerization of adipic acid with hexamethylene diamine.



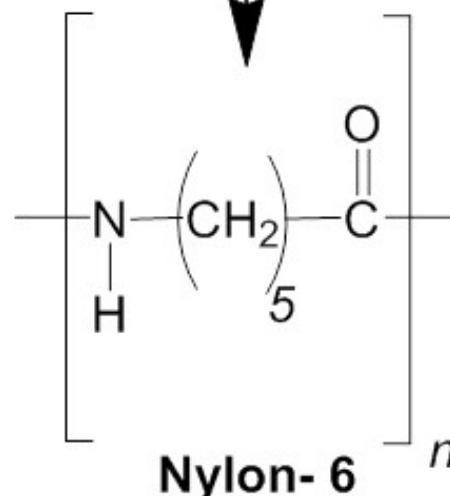
Nylon 6:6

Nylon 6: Nylon-6 is produced by the following two methods:

1. Self-condensation of 6-aminohexanoic acid (ϵ -aminocaproic acid)



Polymerization
 $-\text{H}_2\text{O}$

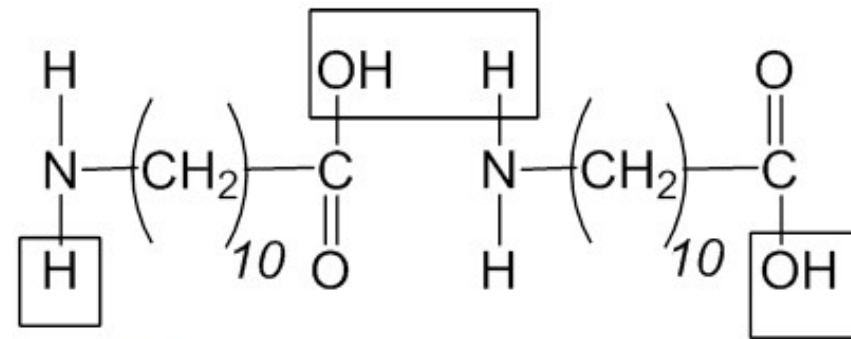


2. Ring opening polymerization of a caprolactum:



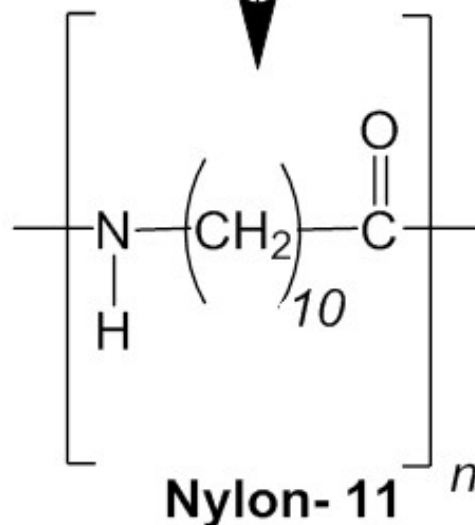
Nylon-11

Nylon-11 is made by self condensation of 11-aminoundecanoic acid.



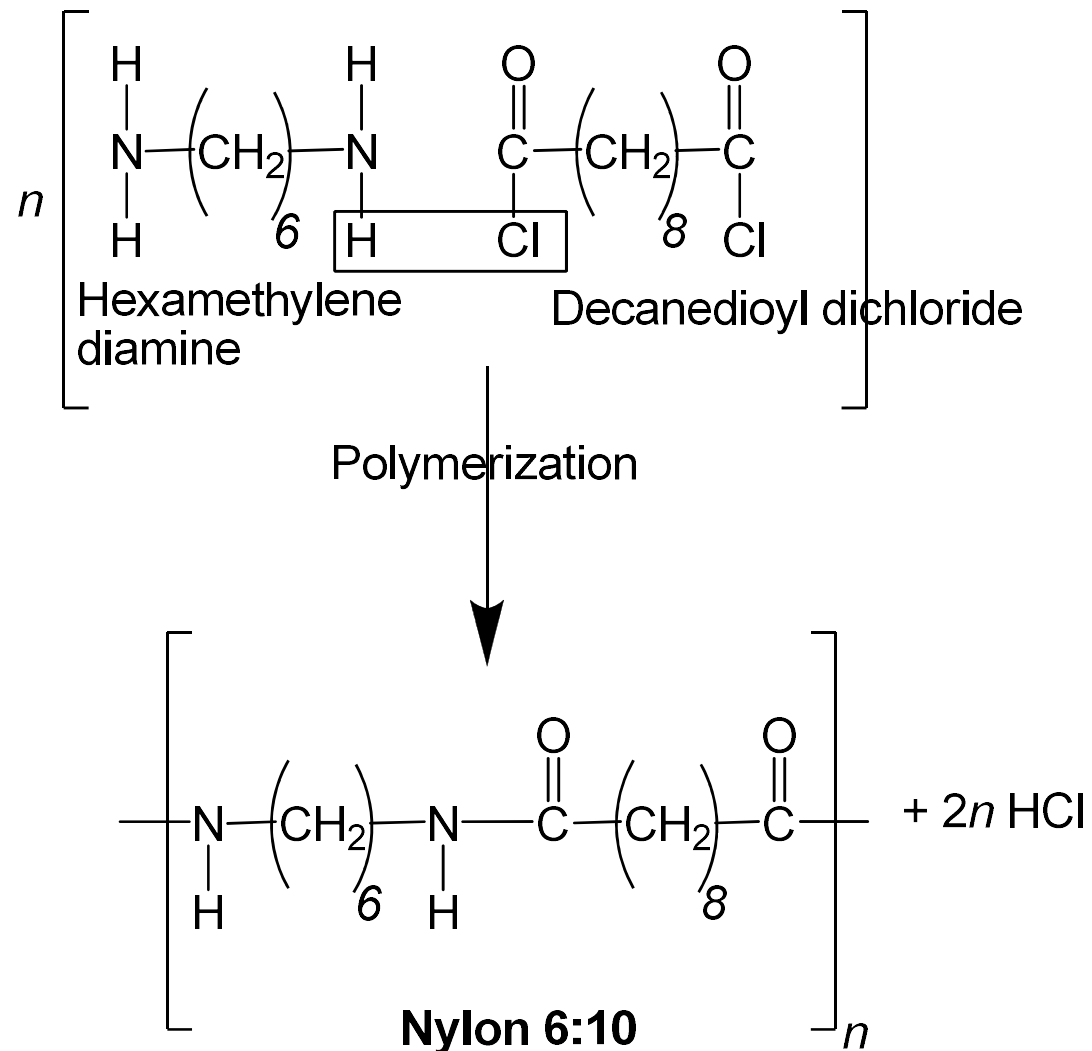
11-Amino undecanoic acid

Polymerization
-H₂O



Nylon 6:10

Nylon 6:10 is obtained by the polymerization of Decanedioyl dichloride with hexamethylene diamine.



Properties of Nylon:

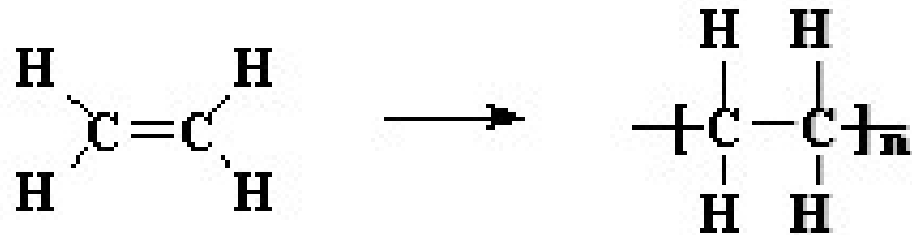
1. One of the very strong fibers. Extremely resistant to abrasion and flexing.
2. The specific gravity is 1.14 Very light, i.e., 80% of that of silk fibers, and 70% of that of cotton fibers.
3. Since nylon fibers absorb little water even though they are wetted., they dry fast and simple in laundering.
4. Excellent in elasticity and resistant to wrinkle.
5. Resistant to chemicals and oil. Non-attackable by sea water.
7. Non-attackable by molds and insects.

Uses:

1. Nylon-6:6 is primarily used for fibers, which find use in making socks, under-garments, dresses, carpets etc.
 2. Nylon -6 and nylon-11 are mainly used for moulding purposes for gears, bearings etc. Nylon bearing and gears work quietly without any lubrication.
 3. They are also used for making filaments for ropes, bristles for tooth brushes and films, tyre-cords etc.
-

Polyethylene (PE)

Polyethylene (PE) is obtained by polymerization of ethylene.



Properties:

- 1) Polyethylene is a rigid , waxy, white translucent, non polar material.
 - 2) Polyethylene exhibits considerable chemical resistance to strong acids, alkalis and salt solutions at room temperature.
 - 3) It is good insulator of electricity.
 - 4) It is swollen and permeable to most oils and solvents.
-

Low-density polyethylene (LDPE)

Low-density polyethylene (LDPE) is a linear polymer with branching. It is manufactured under high pressure (1000-3000 atm) and in the temperature range of 80-350°C using initiators such as benzoyl peroxide or oxygen.

Method: free radical polymerization.

Properties of LDPE

- 1) LDPE is defined by a density range of 0.910–0.925 g/cm³.
 - 2) It is not reactive at room temperatures, except by strong oxidizing agents, and some solvents cause swelling.
 - 3) It can withstand temperatures of 80 °C continuously and 95 °C for a short time.
 - 4) Made in translucent or opaque variations, it is quite flexible, and tough but breakable.
 - 5) LDPE has more branching than HDPE.
 - 6) Since its molecules are less tightly packed and less crystalline because of the side branches, its density is lower. LDPE contains the chemical elements carbon and hydrogen.
-

Uses of LDPE

LDPE is widely used for manufacturing various containers dispensing bottles, wash bottles, tubing, plastic bags for computer components, and various molded laboratory equipment. Its most common use is in plastic bags. Other products made from it include:

- 1) Trays and general purpose containers.
 - 2) Corrosion-resistant work surfaces.
 - 3) Parts that require flexibility, for which it serves very well
 - 4) Juice and milk cartons are made of liquid packaging board, a laminate of paperboard and LDPE (as the water-proof inner and outer layer), and often with a layer of aluminum foil (thus becoming aseptic packaging)
 - 5) Parts of computer hardware, such as hard disk drives, screen cards, and optical disc drives
-

High-density polyethylene (HDPE)

High-density polyethylene (HDPE) is a linear polymer with little or no branching. It is manufactured under low pressure (1000-3000 atm) and below 100°C using Ziegler Natta catalyst (Et_3Al and TiCl_4) by coordination polymerization or using metal oxide catalyst by Phillips process.

Properties of HDPE

- 1) HDPE is known for its large strength to density ratio.
 - 2) The mass density of high-density polyethylene can range from 0.941 to 0.97 g/cm³.
 - 3) Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving it stronger intermolecular forces and tensile strength than LDPE. The difference in strength exceeds the difference in density, giving HDPE a higher specific strength.
 - 4) It is also harder and more opaque and can withstand somewhat higher temperatures (120 °C/ 248 °F for short periods, 110 °C /230 °F continuously). High-density polyethylene, unlike polypropylene, cannot withstand normally required autoclaving conditions. The lack of branching is ensured by an appropriate choice of catalyst (e.g., Ziegler-Natta catalysts) and reaction conditions.
-

HDPE is resistant to many different solvents and has a wide variety of applications, including:

3-D printer filament

Banners

Bottle caps

Chemical resistant piping systems

Food storage containers

Fuel tanks for vehicles

Electrical and plumbing boxes

Folding chairs and tables

P – F Resins

These are formed by condensation polymerization and are thermosetting polymers

There are two important commercial PF resins: Novolacs and Resoles

Both **novolacs** and **resoles** are linear, low molecular weight, soluble and fusible prepolymers

The nature of the product formed depends largely on the molar ratio of phenol to formaldehyde and also on the nature of the catalyst

During moulding operations, these two undergo extensive branching leading to the formation of highly cross linked, insoluble, hard, rigid and infusible products

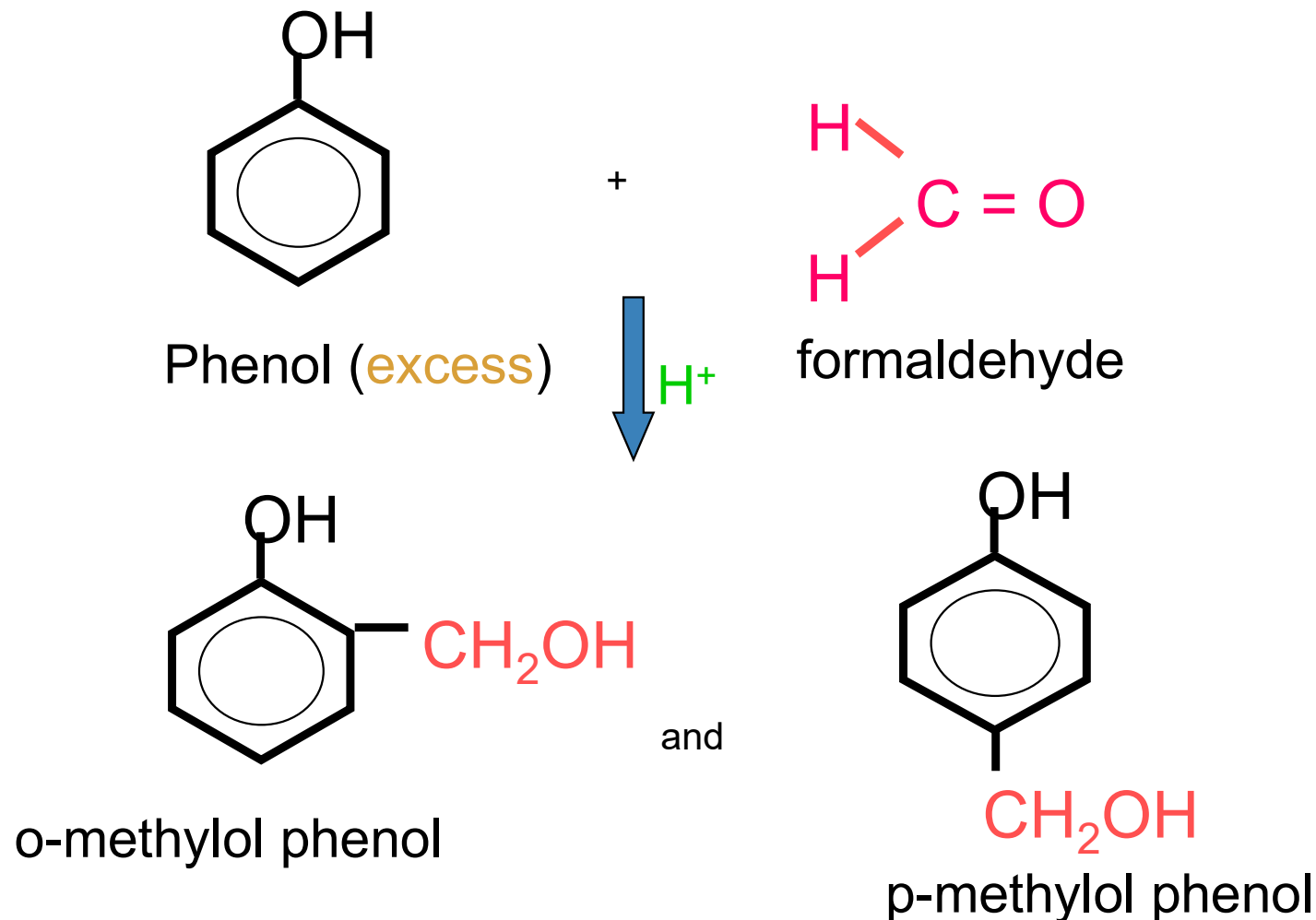
The phenol ring has three potential reactive sites while the formaldehyde has two reactive sites

The polycondensation reaction between these two are catalyzed by either acids or alkalies

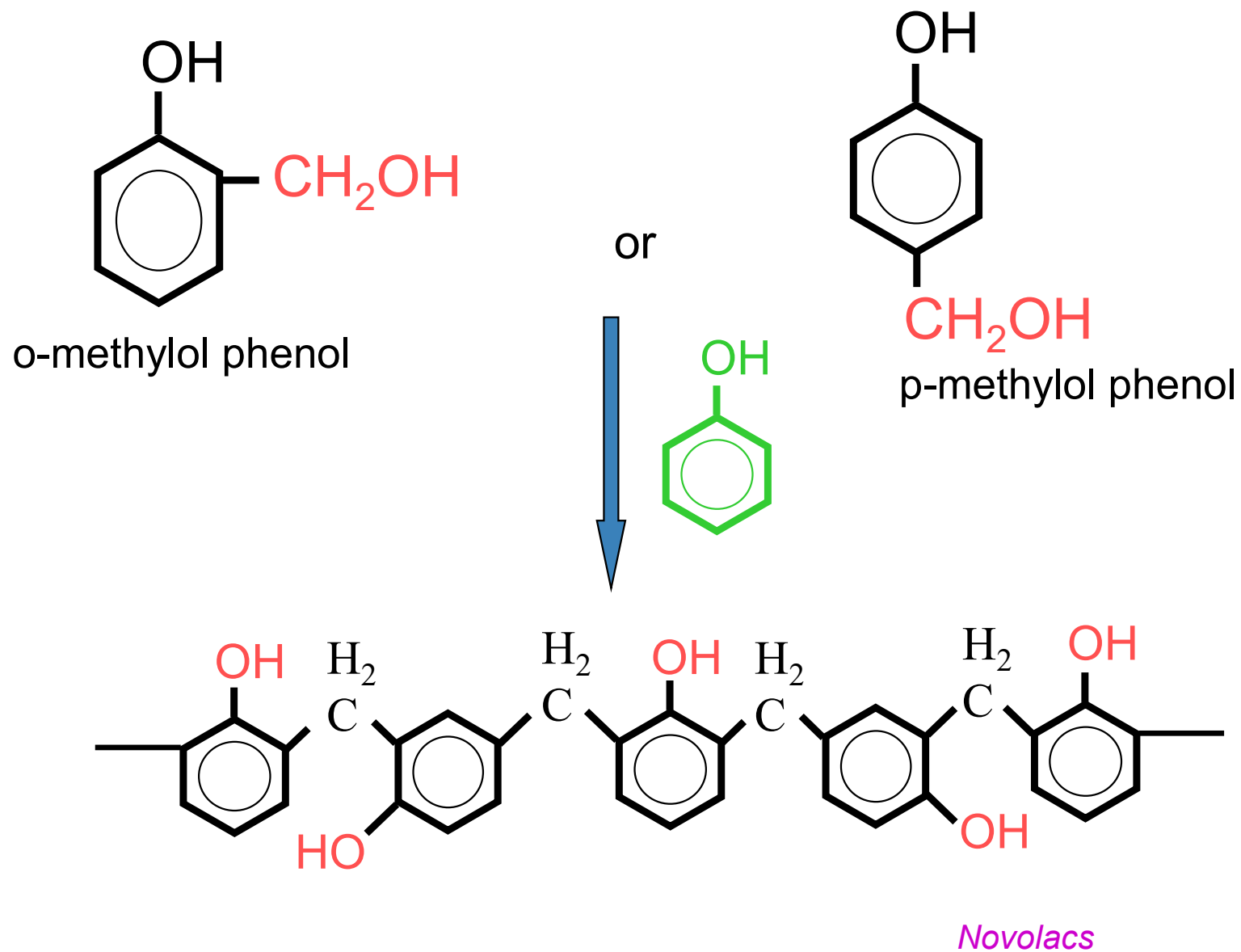
Novolacs

When P/F molar ratio is ~~is~~ > 1 and the catalyst used is an acid, low mol. wt. polymers formed are called **Novolacs**

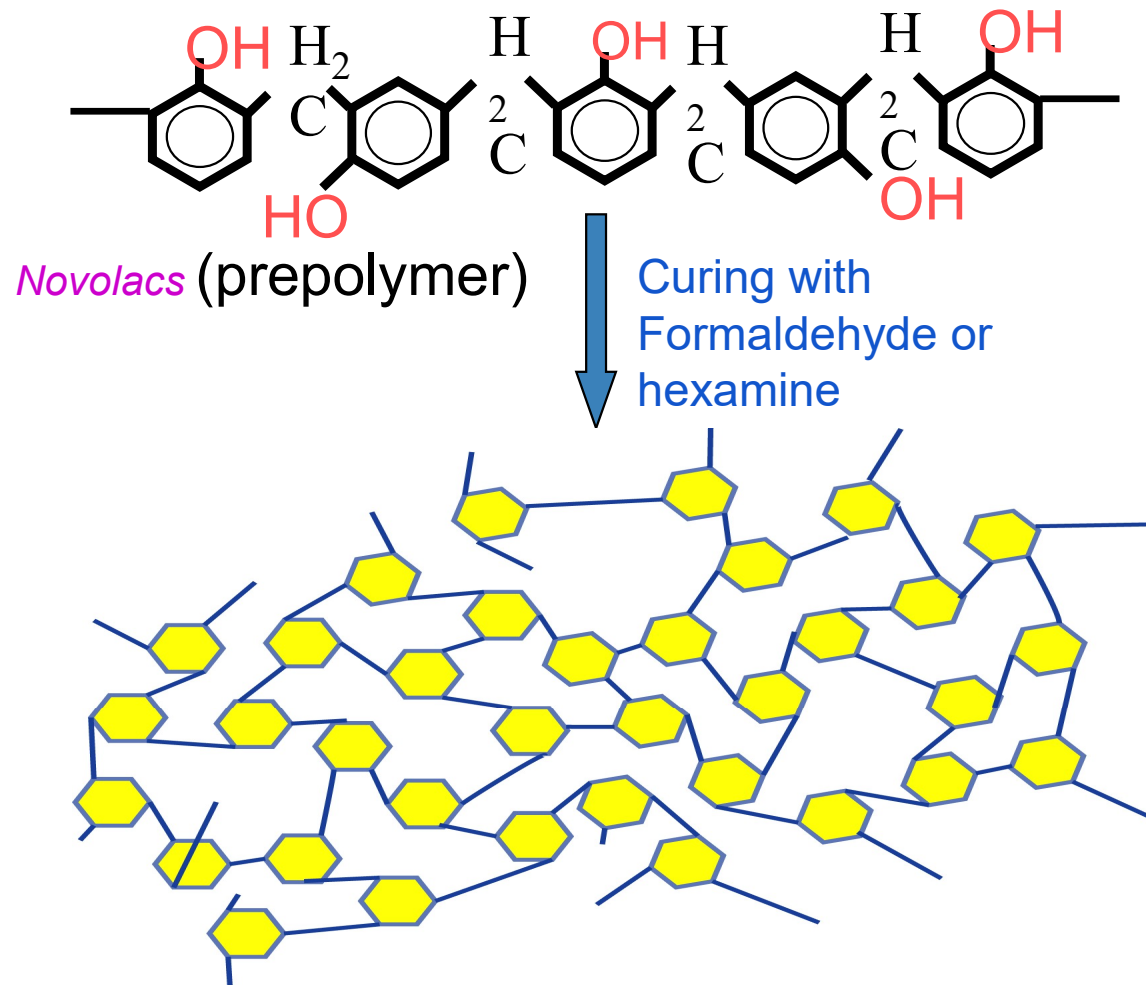
The first step in the reaction is the addition of formaldehyde to phenol to form *ortho* or *para* methylol phenols



These methylol phenols condense rapidly to form Novolacs



These novolacs are linear and low mol. wt. polymers. They are soluble and fusible. About 5 – 6 phenol rings per molecule are linked through methylene bridges. Since they contain no active methylol groups, they themselves do not undergo cross linking. However, when heated with formaldehyde or hexamine, they undergo extensive cross linking, resulting in the formation of infusible, insoluble, hard and rigid thermosetting product



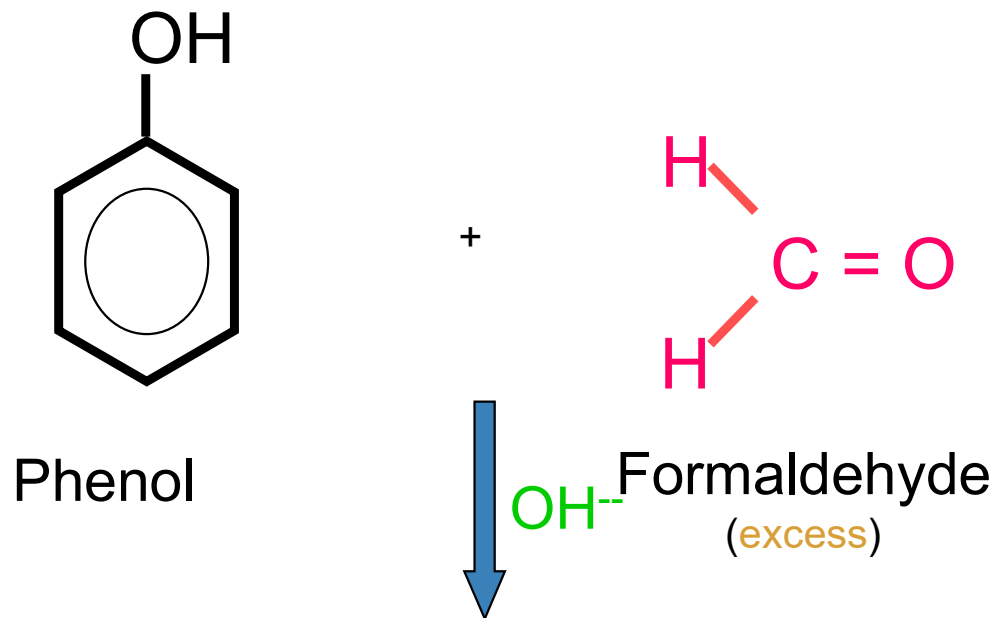
Resoles

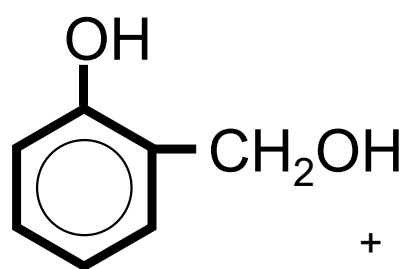
When the molar ratio of P/F is < 1 and the catalyst used is a base, the polymer formed are called Resoles

The first step in the reaction is the formation of mono, di and trimethylol phenols. They undergo condensation to form resoles

The resoles in which phenols are linked through methylene bridges are soluble and fusible

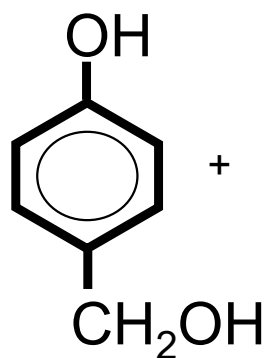
Since they contain alcoholic groups, further reaction during curing leads to cross linking, resulting in a network, infusible and insoluble product





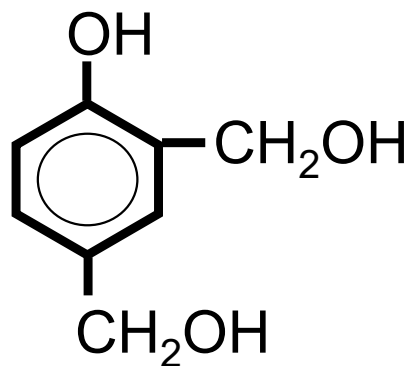
o-methylol phenol

+



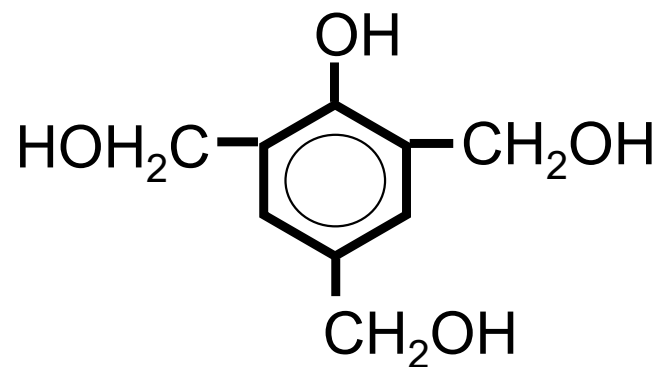
p-methylol phenol

+



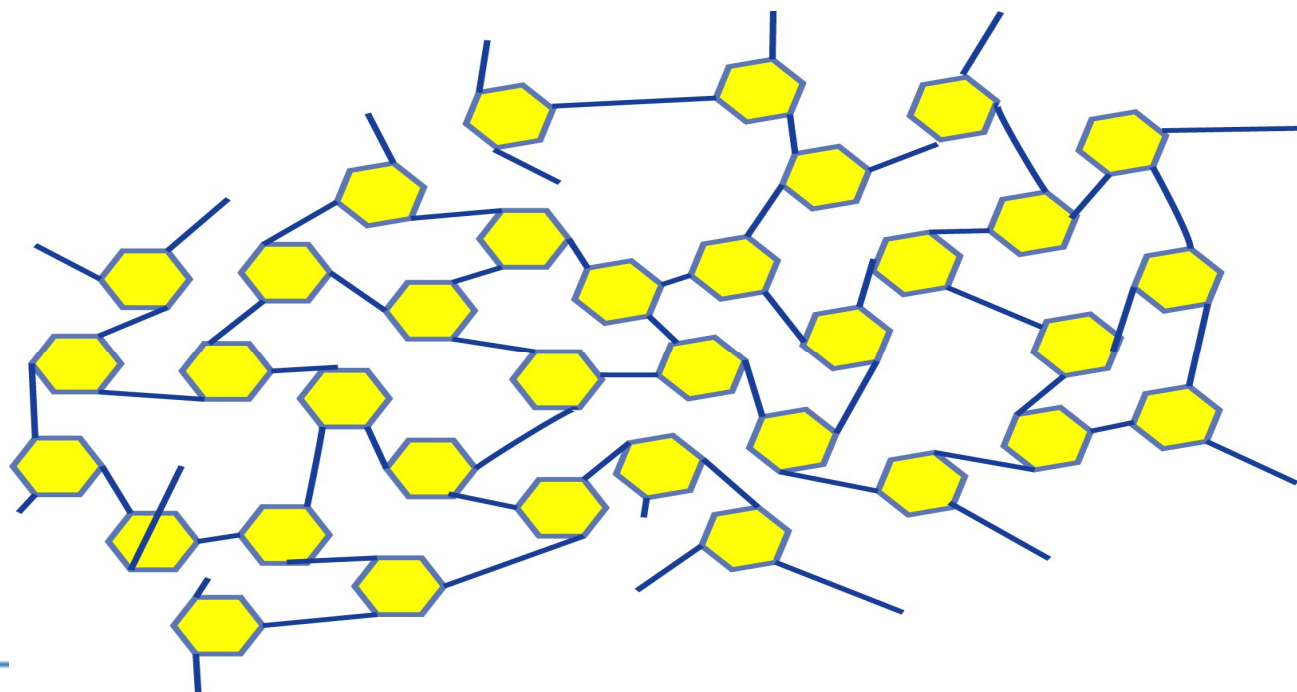
di-methylol phenol

+



tri-methylol phenol

↓
Curing



Properties of Bakelite:

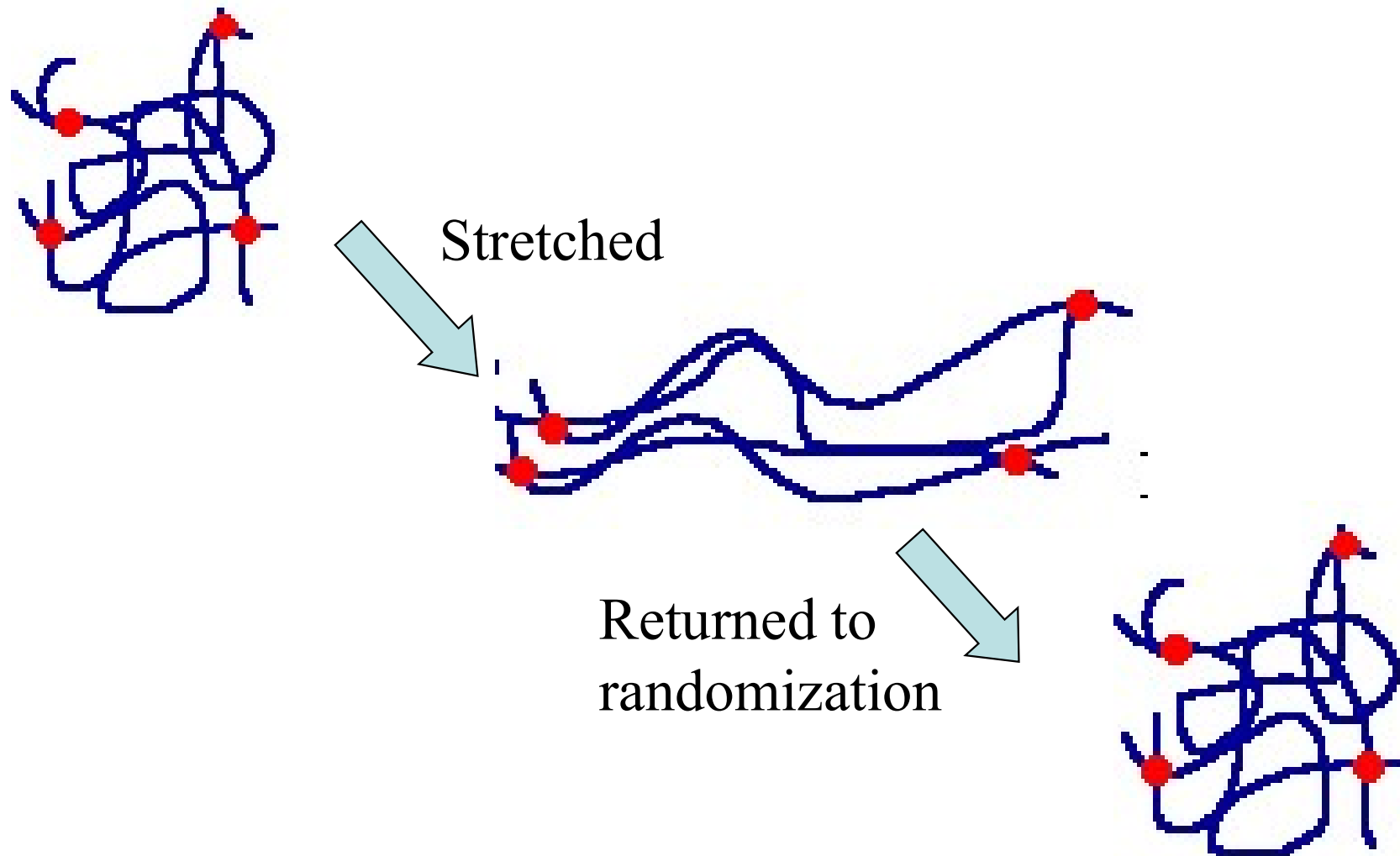
- They are rigid, hard, scratch-resistant, infusible, water resistant, insoluble solid.
- Resistant to non-oxidizing acids, salts and many organic solvents.
- They are attacked by alkalis
- They possess excellent electrical insulating character

Uses

- For making electric insulators parts like switches, plugs, switch board, heater-handles etc.
 - For making moulded articles like telephone parts, cabinets for radio and television.
 - For impregnating fabrics, woods and paper
 - As adhesives (binder) for grinding wheels.
 - In paints and varnish
 - As hydrogen exchanger resins in water softening
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ELASTOMERS

Elastomer is defined as a long chain polymer which under stress undergoes elongation by several times and regains its original shape when the stress is fully released



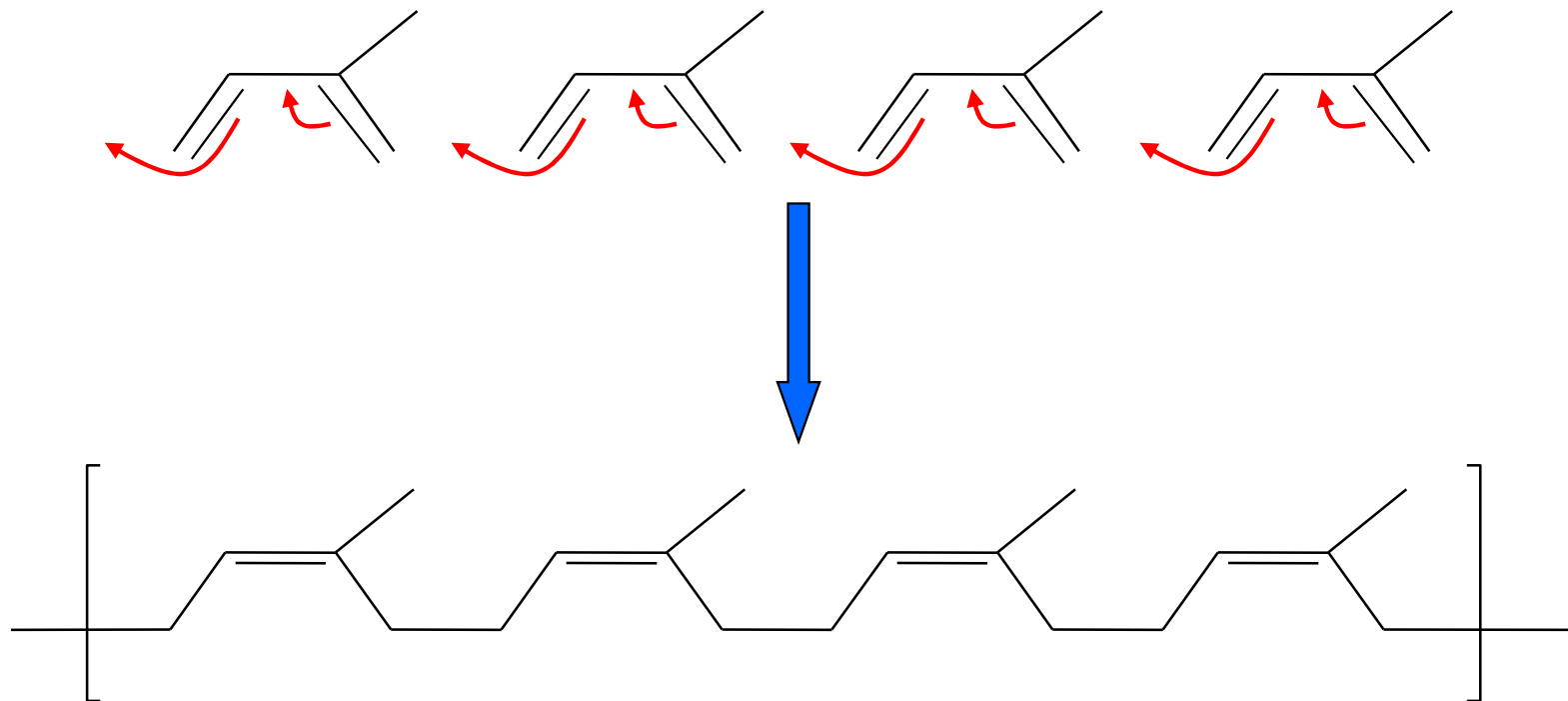
Natural rubber is obtained from the exudates of the rubber trees in the form of a milky colloidal solution called latex containing 25-45% of rubber dispersed in a watery medium with small amounts of protein and other materials. The latex is tapped by cutting through the bark of the tree and the liquid that comes out is collected in containers.

The latex is processed either by i) coagulation by acid or by heat and processed further or ii) mixed with compounding materials and precipitated directly from the solution.

Natural rubber is an addition polymer formed from the monomer called isoprene i.e., 2-methyl-1,3-butadiene

The average D.P. (n) of rubber is around 5000

Addition between molecules of isoprene takes place by 1,4 addition and one double bond shifts between 2nd and 3rd positions



Drawback of raw rubber

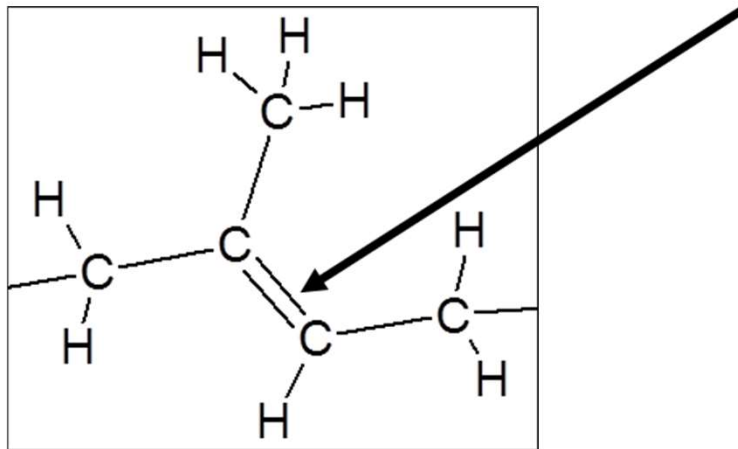
- It is plastic in nature: It becomes soft at high temperature and is too brittle at low temperature. So it can be used in temperature range between 10 to 60°C only
 - It is weak: tensile strength is only 200kg/cm²
 - It has large water absorption capacity
 - It is non-resistant to non-polar solvents like vegetable and mineral oil
 - It is attacked by oxidizing agent
 - It swells in organic solvent and gradually degrade
 - It has little durability
-

Vulcanization

Vulcanization is a process, through which elasticity of the rubbers increases and reduces plasticity by the formation of a crosslinked molecular network.

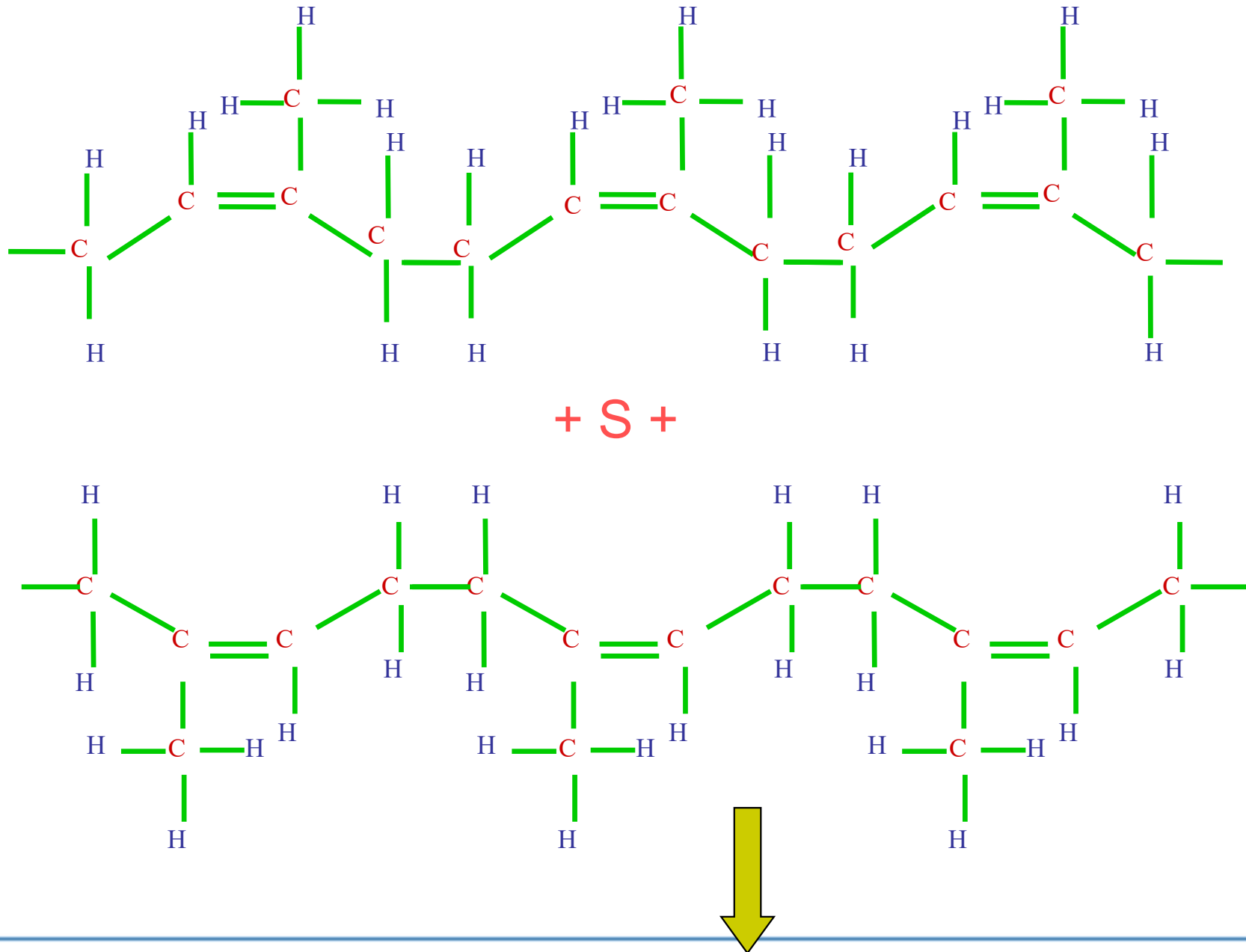
Vulcanization is done by heating the rubber with sulfur or other vulcanizing agents under pressure

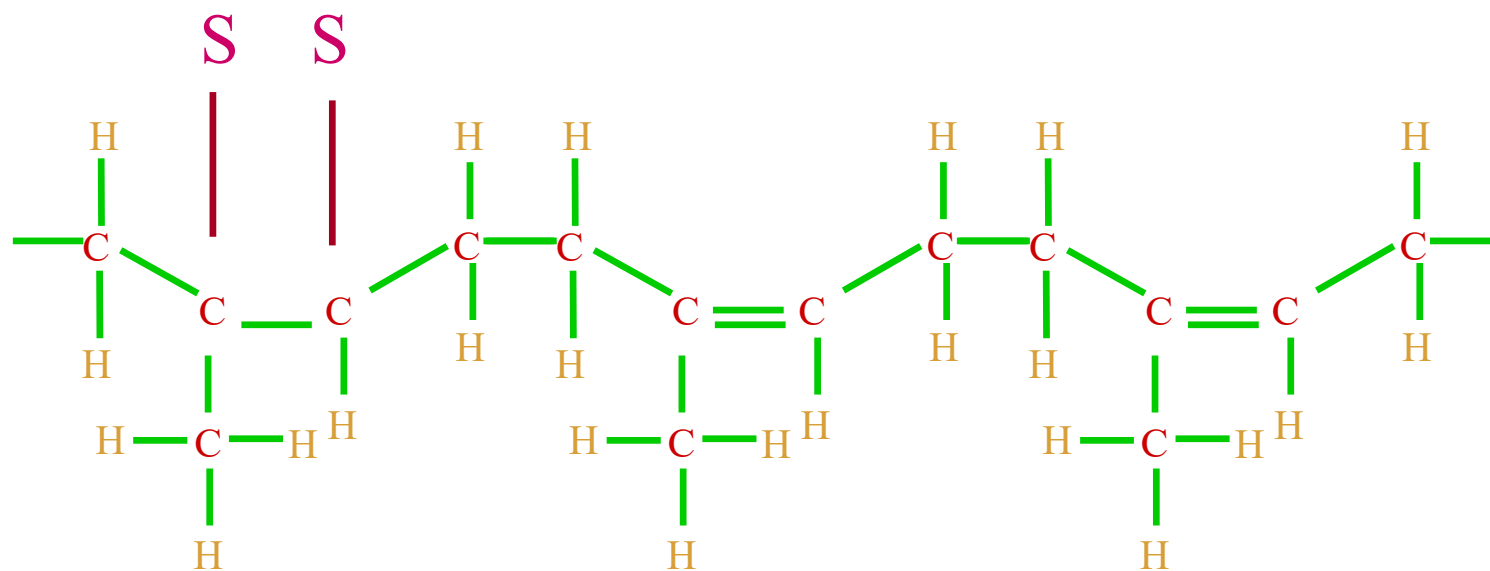
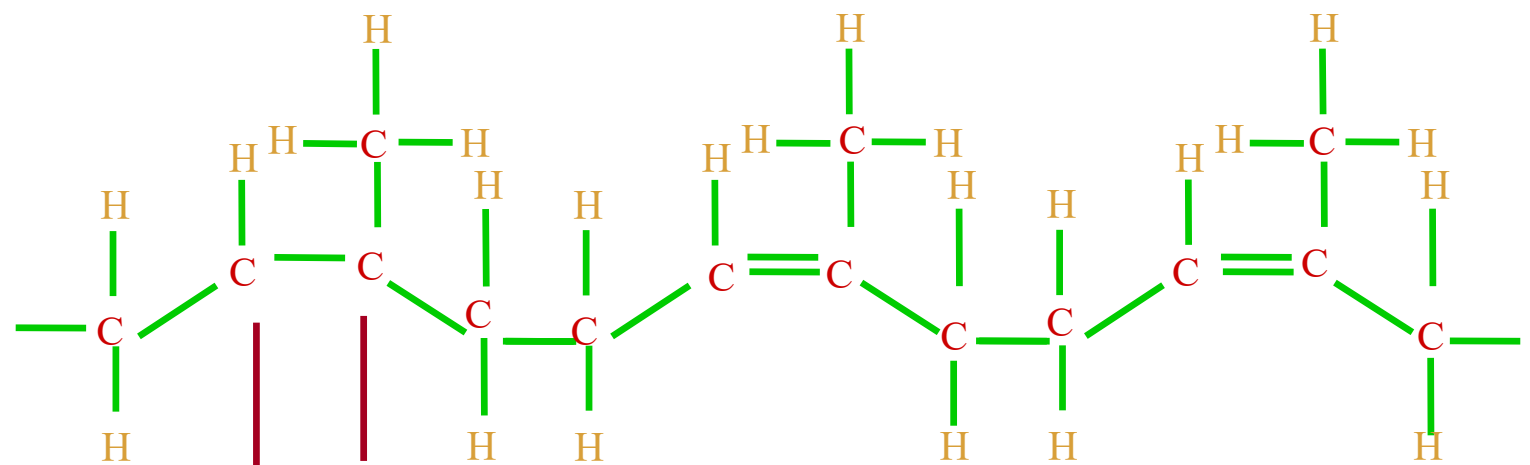
Sulphur attacks this double bond



Charles Goodyear (December 29, 1800 – July 1, 1860) was an American inventor who developed a process to vulcanize rubber in 1839—a method that he perfected while living and working in Springfield, Massachusetts in 1844, and for which he received patent number 3633 from the United States Patent Office.

e.g., a tyre rubber may contain 3 to 5% sulphur, but a battery case rubber may contain as much as 30% sulphur





Compounding of Rubber

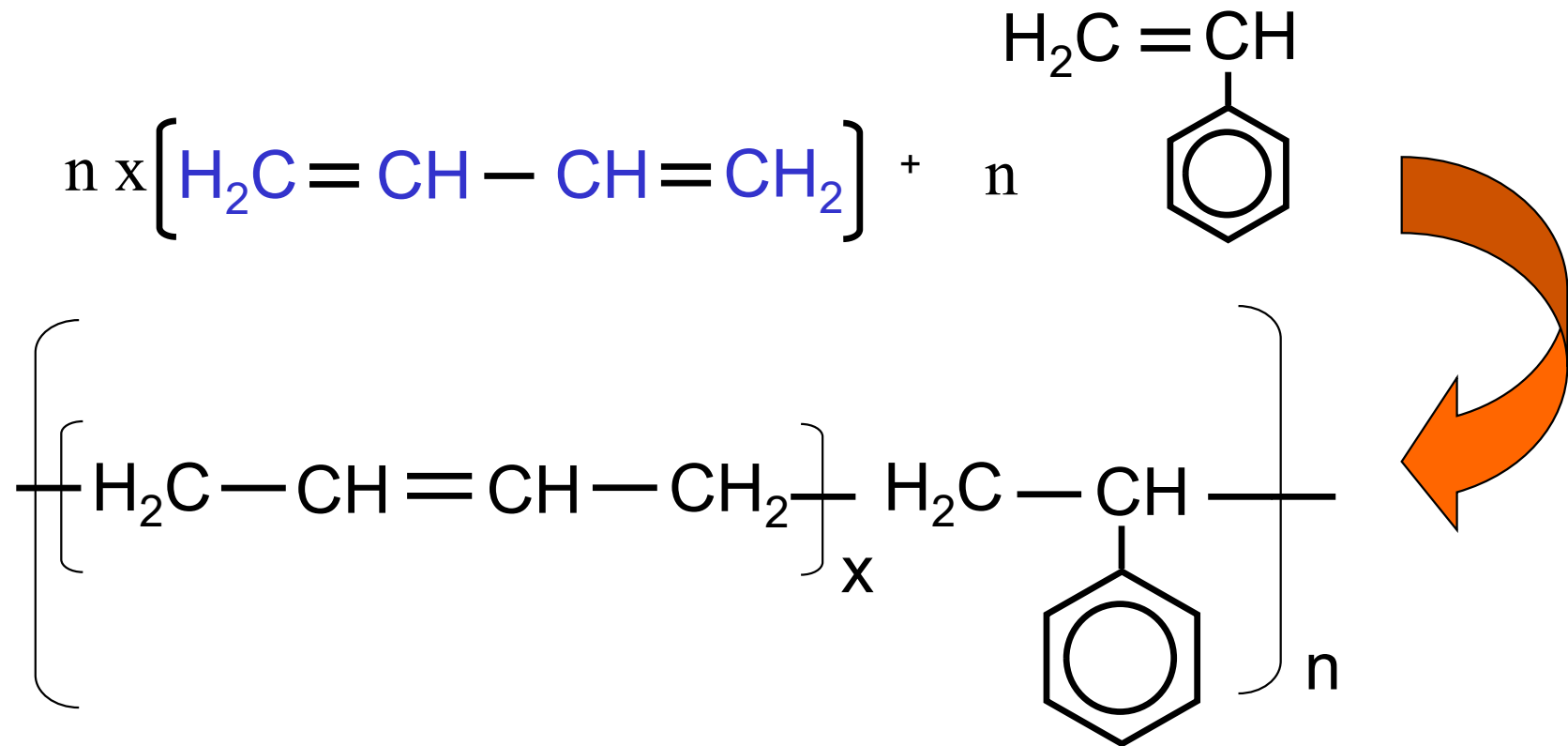
Compounding is mixing of the raw rubber (synthetic or natural) with other substances so as to impart the product specific properties suitable for particular job.

- (1) **Softener and plasticizers** are added to give the rubber greater tenacity and adhesion. For e.g. vegetable oil, waxes, stearic acid.
 - (2) **Vulcanizing agents**: sulfur, sulfur monochloride, benzoyl chloride etc.
 - (3) **Accelerators**: These materials drastically shorten the time required for vulcanization. 2-mercaptol, Benzothiazole etc.
 - (4) **Antioxidants**: Natural rubbers has a tendency to perish due to the oxidation. For this reason antioxidants are required, such as complex amine, phosphites etc.
 - (5) **Reinforcing fillers**: theses materials gives strength and rigidity to the rubber products. For e.g. CaCO_3 , ZnO etc.
 - (6) **Colouring agents**
-

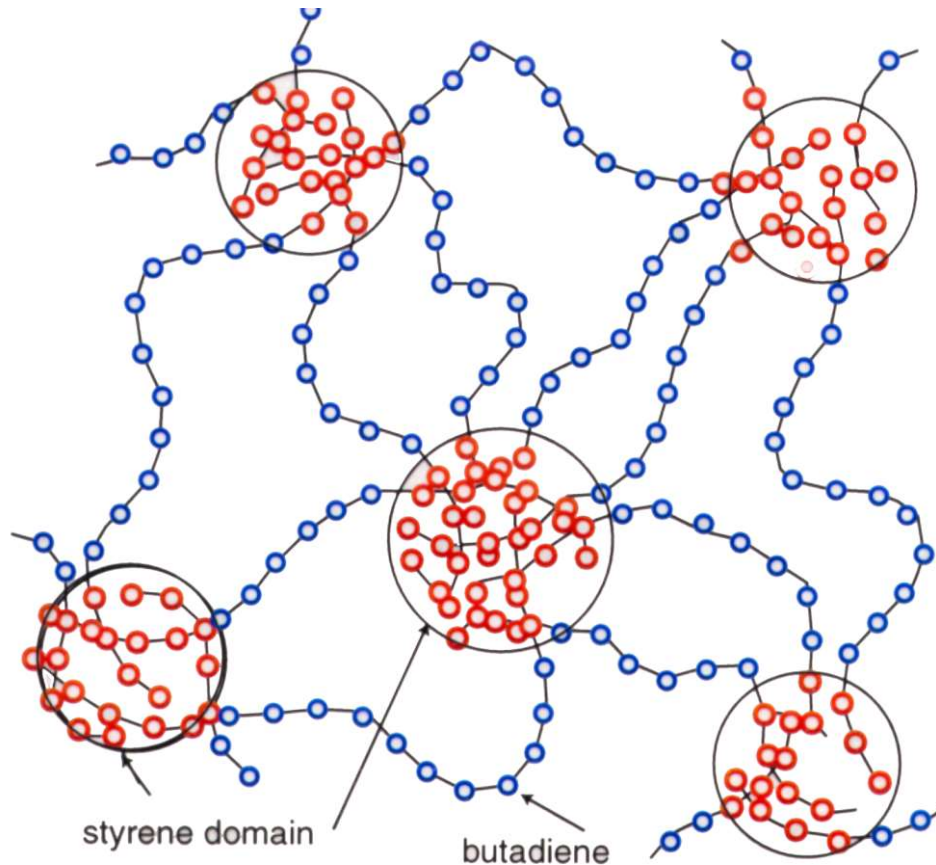
Styrene rubber (GR-S or Buna-S or SBR)

Preparation

This is produced by copolymerization of butadiene (about 75% by wt.) and styrene (about 25% by wt.)



Styrene-butadiene copolymer



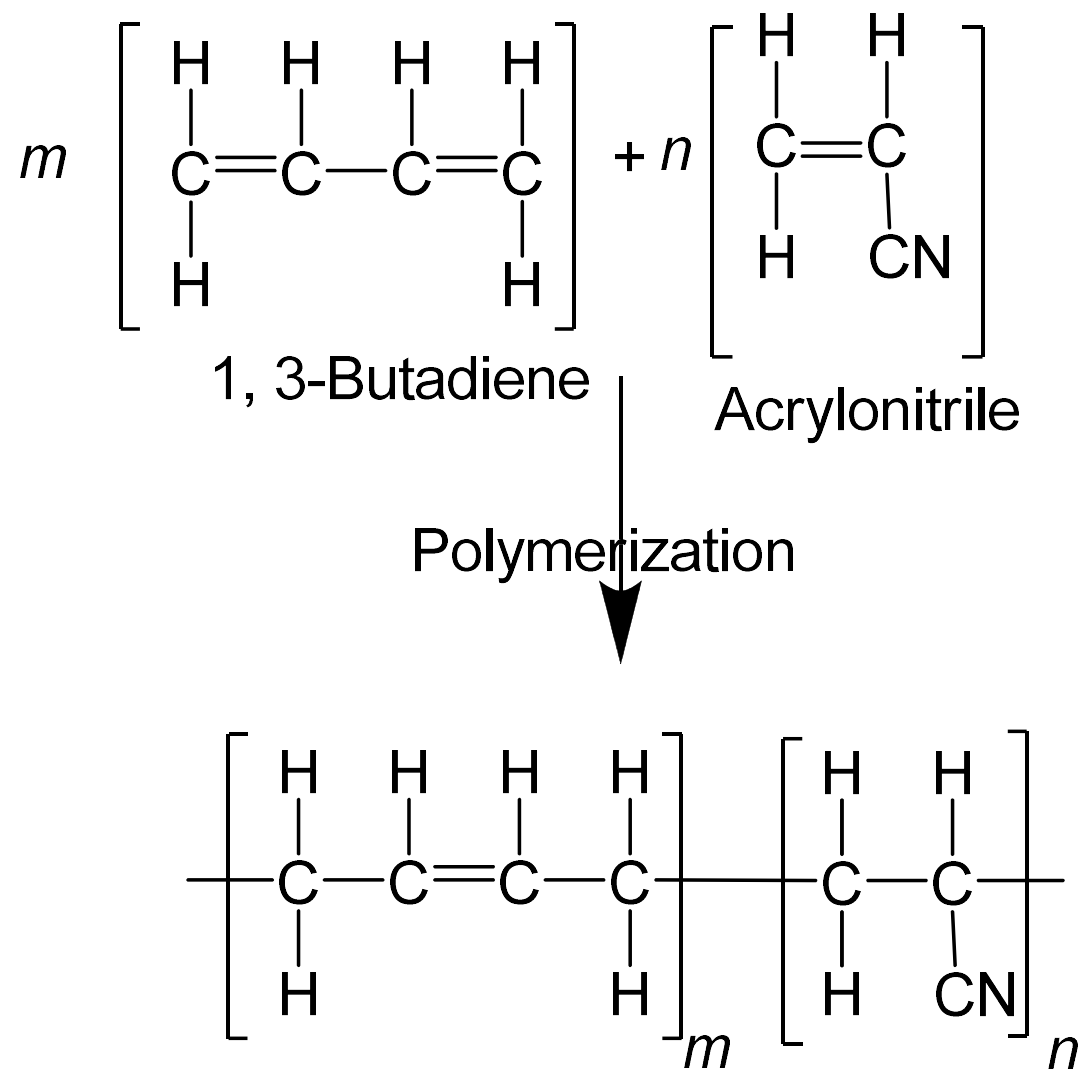
Styrene domains act as anchors or junctions

Butadienes provide flexible linkages

The desire to maximize the ways you can arrange the flexible links is what causes rubbers to return to given shapes

Buna-N(Nitrile rubber)

Buna –N is copolymer of butadiene and acrylonitrile rubber.



Nitrile rubber or Buna-N

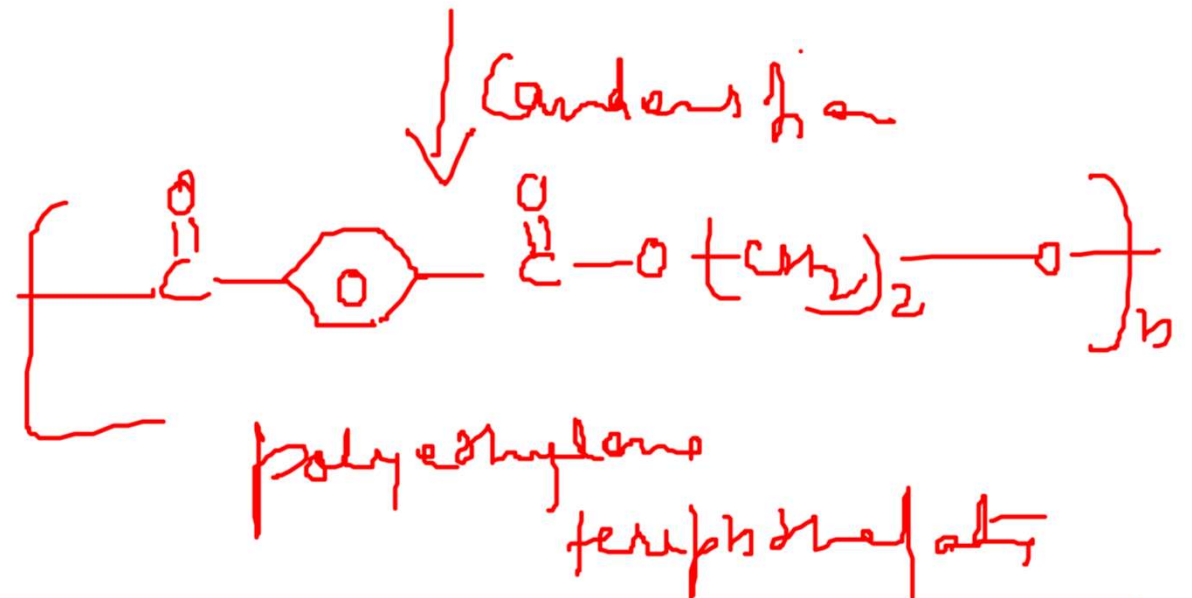
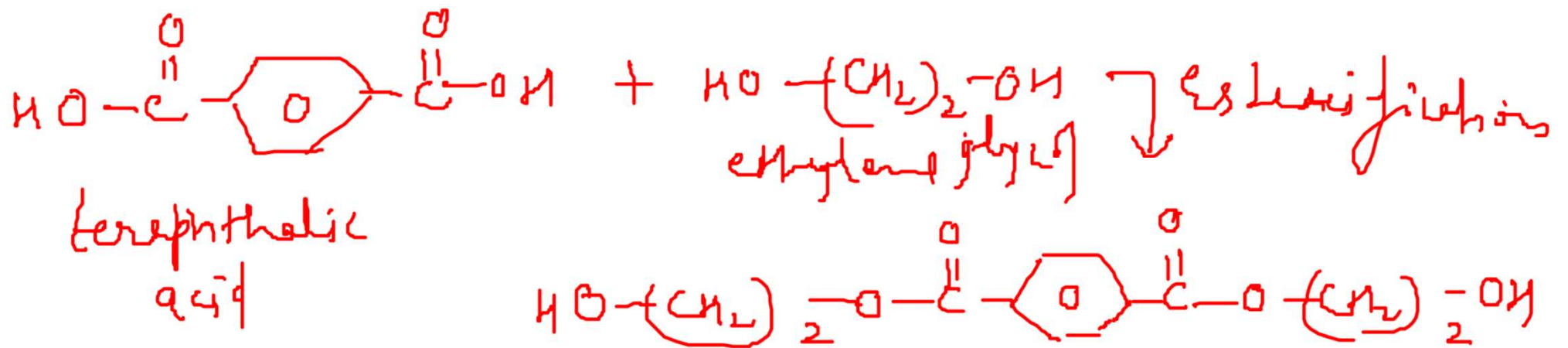
Properties of Buna-N

It possesses excellent resistance to heat, sunlight, oils, acids and salts, but less resistant to alkalis than natural rubber, because of presence of cyano (-CN) groups. As the proportion of acrylonitrile is increased, the resistance to acids, salts, oils, solvents increases but the low temperature resilience suffers. Vulcanized nitrile rubber is more resistant to heat and ageing than natural rubber.

Uses:

For making conveyer belts, high altitude aircraft components, tank lining, hoses, gaskets, printing rollers, adhesives, oil resistant foams and automobile parts.

Polyester -



Dalton

Properties:

1. PET can exist both in amorphous and semicrystalline form
2. It has high mechanical strength and dimension stability and is stable over temperature range of -40 °C to 100 °C.
3. It shows creep and abrasion resistance and good electrical insulating properties.
4. At room temperature, it is resistant to water, dilute acids, salts, aromatic and aliphatic hydrocarbons and alcohols.

Applications:

1. It is used for making video and audio tapes.
 2. It is commonly used in making clear bottles for foods and beverages.
 3. It is used to make films for shrink packaging.
 4. As an electrical insulator, it is used for making molds for electrical appliances.
 5. The synthetic fibers can be woven to make fabrics, upholstery, artificial grass etc.
 6. The fiber may be blended with wool and other natural fibers.
 7. The films may be combined with paper or other polymeric films to form multilayer materials.
 8. It can be used to produce injection molded articles, such as switches, valves etc.
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