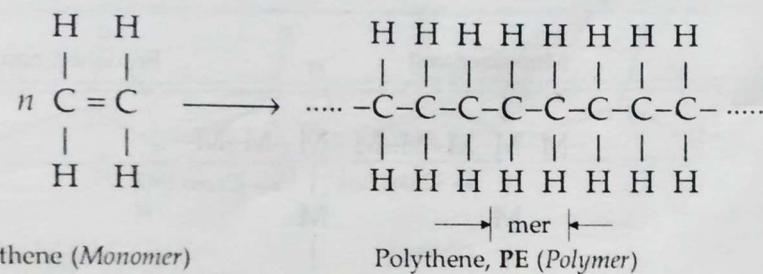


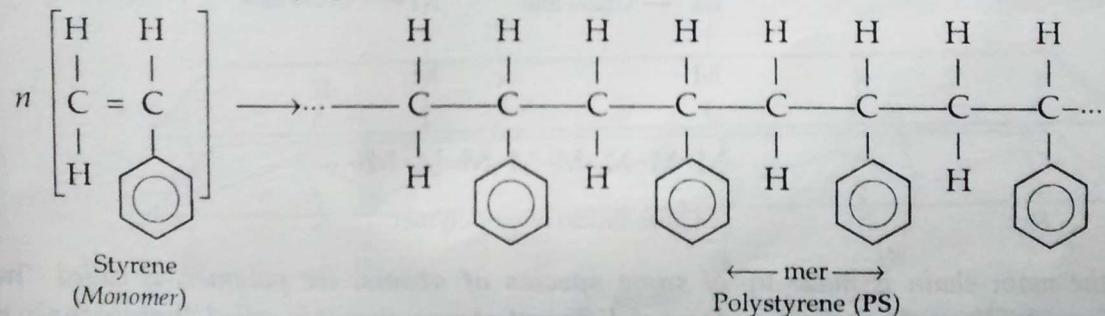
Unit – IV: Polymer Chemistry

Polymer, Polymerization & Degree of polymerization

Polymers* (Greek *poly* - many ; *mers* - units or parts) are 'macromolecules' (giant molecules of high molecular masses) built-up by the linking together of a large number of small molecules (called monomers). For example, polythene is a polymer formed by linking together of a large number of ethene (C_2H_4) molecules. Thus :



Thus, small molecules which combine with each other to form polymer molecules, are termed **monomers** ; and the "repeat unit" in a polymer is called **mer**. Thus :

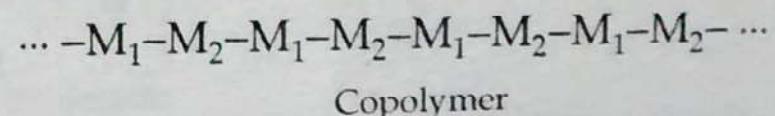
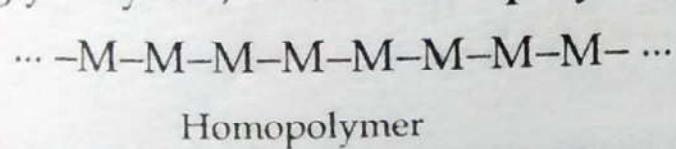


The number of repeating units (n) in chain formed in a polymer, is known as the "degree of polymerization" (DP). There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule. Most of the polymers, usually, fall into the 5,000–200,000 molecular mass range.

Nomenclature of Polymers

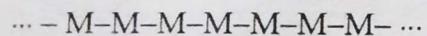
2 NOMENCLATURE OF POLYMERS

A polymer may consist of *identical monomers* or *monomers of different chemical structure* and accordingly they are, called **homopolymers** and **copolymers** respectively. Thus :

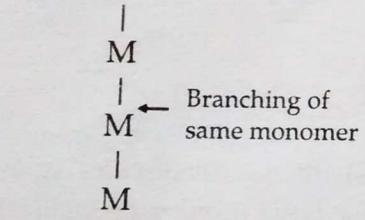
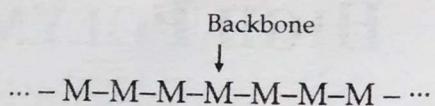


* STAUDINGER, Hermann (1881-1963). German chemist. One of the pioneers in polymer chemistry, Staudinger was awarded the Nobel Prize in Chemistry in 1953.

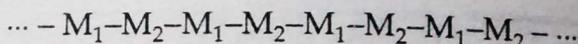
The monomeric unit in a polymer may be present in **linear, branched or cross-linked (three-dimensional) structure**. Thus :



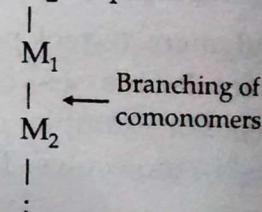
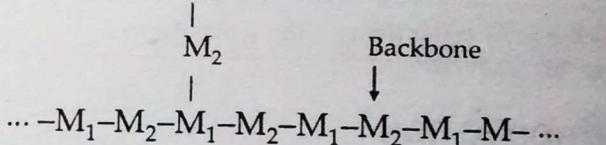
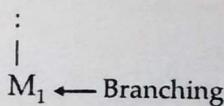
Linear homopolymer



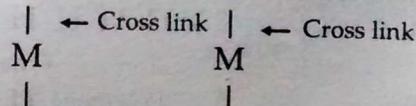
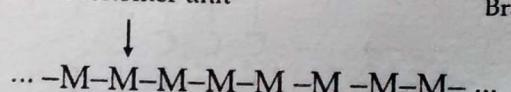
Branched chain homopolymer



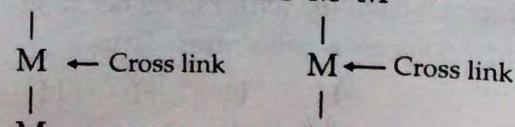
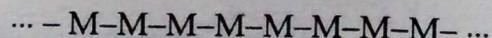
Linear copolymer

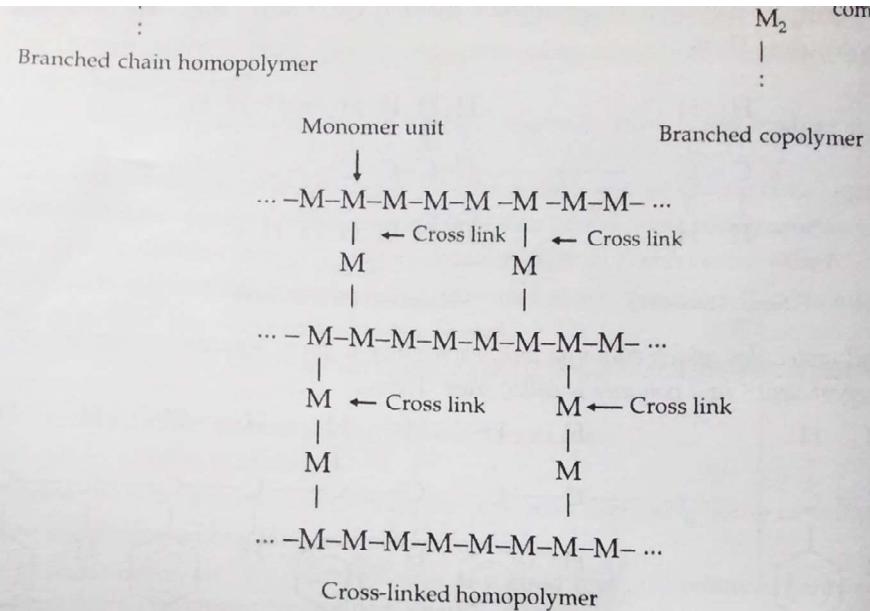


Monomer unit



Branched copolymer





If the main chain is made up of same species of atoms, the polymer, is called "homochain polymer", and if the main chain is made up of different atoms, then it is called "heterochain polymer". Thus :

Homochain polymer : ...-C-C-C-C-C-C-C-...

$$\cdots -C-C-C-C-C-C-C-\cdots$$

↑

Main chain

Heterochain polymer:

$$\cdots -C-C-O-C-C-O-C-C-O-C-C-O-\cdots$$

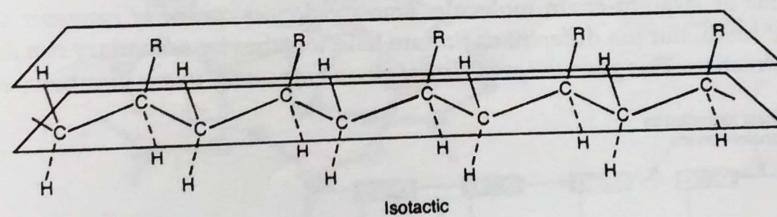
↑
Main chain

Graft copolymers are branched structures in which the monomer segments on the branches and the backbone differ. Thus :

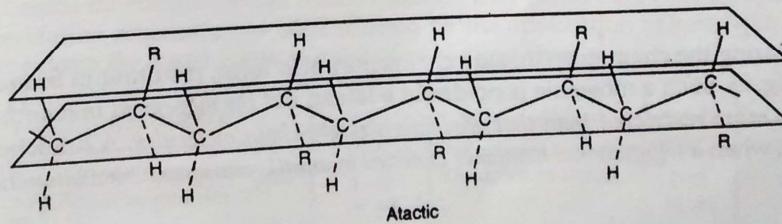
Graft copolymer : ... -M₁-M₁-M₁-M₁-M₁-M₁-M₁-M₁- ...

Tacticity : The orientation of monomeric units in a polymer molecule can take place in an orderly or disorderly fashion with respect to the main chain. The difference in configuration (tacticity) do affect their physical properties.

(i) The head-to-tail configuration, in which the functional groups are all on the same side of the chain, is called **isotactic polymer**, e.g.,



(ii) If the arrangement of functional groups are at random around the main chain, it is called atactic polymer, e.g., polypropylene.

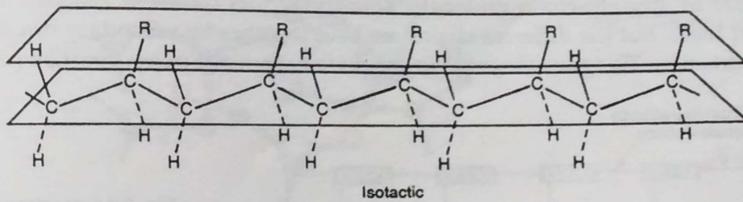


If the polymer is in alternating fashion, it is called 'syndiotactic' polymer.

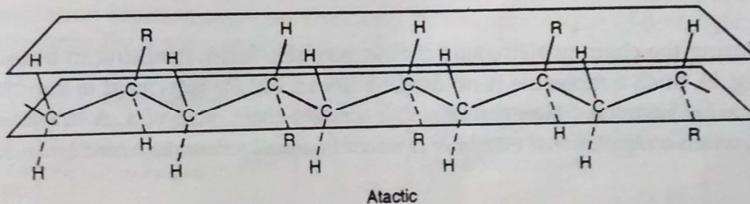


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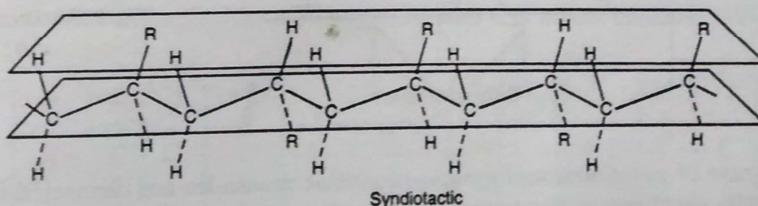
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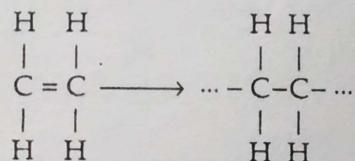


(iii) If the arrangement of side groups is in alternating fashion, it is called '**syndiotactic**' polymer, e.g., gutta percha.



3 FUNCTIONALITY

For a substance to act as a monomer, it must have *at least two reactive sites or bonding sites*. The number of bonding sites in a monomer, is referred to as its *functionalities*. In an olefin, the double bond can be considered as a site for two free valencies. When the double bond is broken, two single bonds become available for combination. Thus :



Thus, ethylene is considered to be *bifunctional*. Other reactive groups are *hydroxyl, acid, amino-acid, di-ol, polyalcohols, di-amino acids, di-acids, etc.*

(1) Depending upon the functionality of monomeric units, it is possible to obtain different types of structures. In case of a *bifunctional monomer*, two reactive groups attach side by side to each other forming a **linear or straight-chain molecule**. Linear molecules consist of monomer units linked by primary covalent bonds, but the different chains are held together by secondary van der Waals forces of molecular attraction. This gives the possibility of *chain movement* in one direction (see Fig 1).

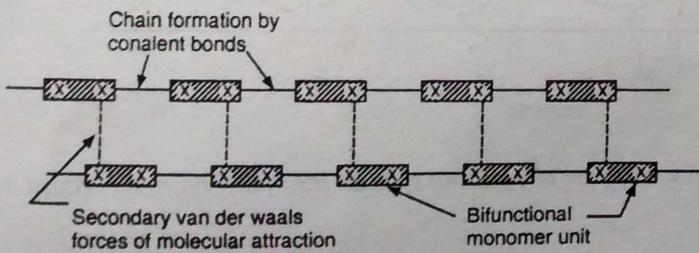


Fig. 1. Linear chain polymer from a bifunctional monomer.

(2) During the chain growth, side chains may also form, resulting in **branched-chain molecules** (see Fig. 2). Such a molecule is no doubt a linear, but the movement in branched-chain molecules is more restricted than that of simple straight-chain molecules. A branched-chain polymer

Molecular attraction. This gives the possibility of chain movement in one direction (see Fig 1).

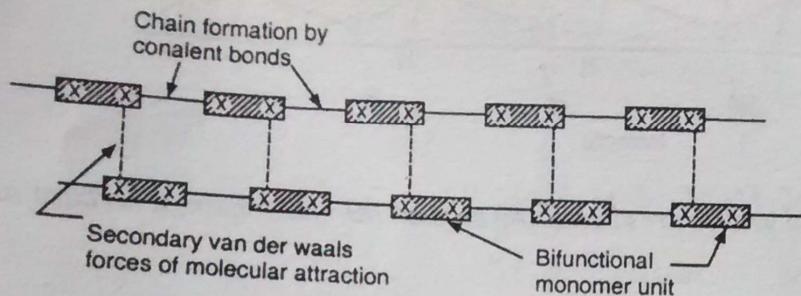


Fig. 1. Linear chain polymer from a bifunctional monomer.

(2) During the chain growth, side chains may also form, resulting in **branched-chain molecules** (see Fig. 2). Such a molecule is no doubt a linear, but the movement in branched-chain molecules is, generally, more restricted than that of simple straight-chain molecules. A branched-chain polymer also results, when a trifunctional monomer is mixed in small amounts with a bifunctional monomer and polymerized.

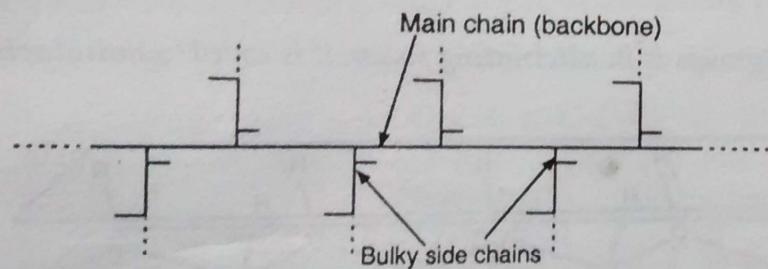


Fig. 2. Branched-chain polymer.

(3) In case of **polyfunctional groups**, monomer molecules are connected to each other by covalent bonds, resulting in the formation of a three-dimensional network. In such polymeric molecules, the movement of individual molecules is prevented by strong cross-links (see Fig. 3).

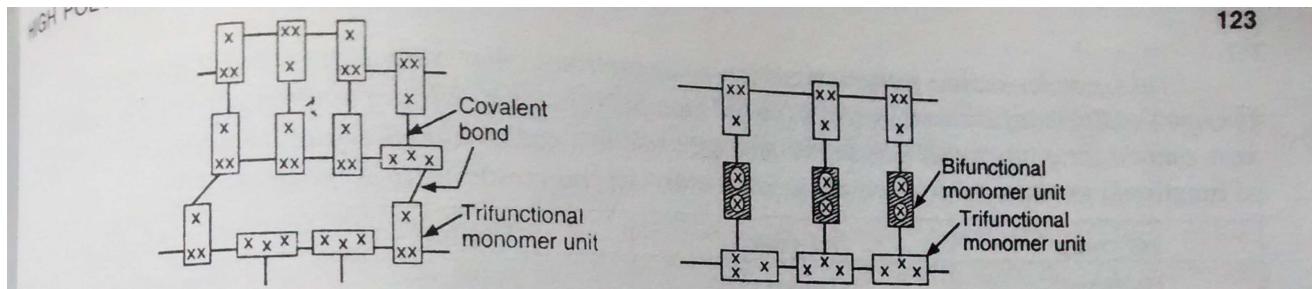


Fig. 3. Formation of a three-dimensional network polymer : (a) reaction of three-functional molecules, (b) reaction between two and three-functional molecules.

Note : A network polymer is formed only if one of its monomers is *trifunctional*.

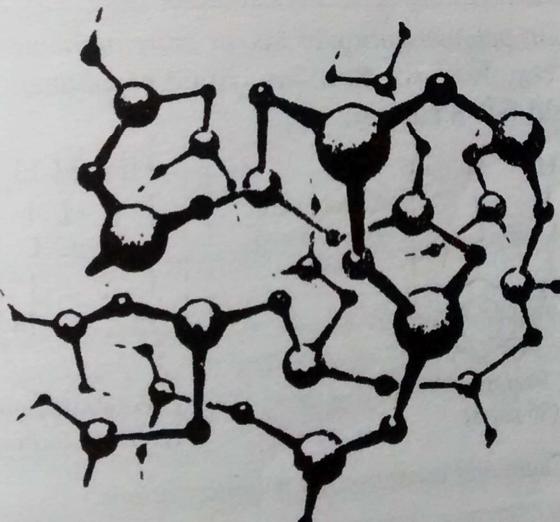
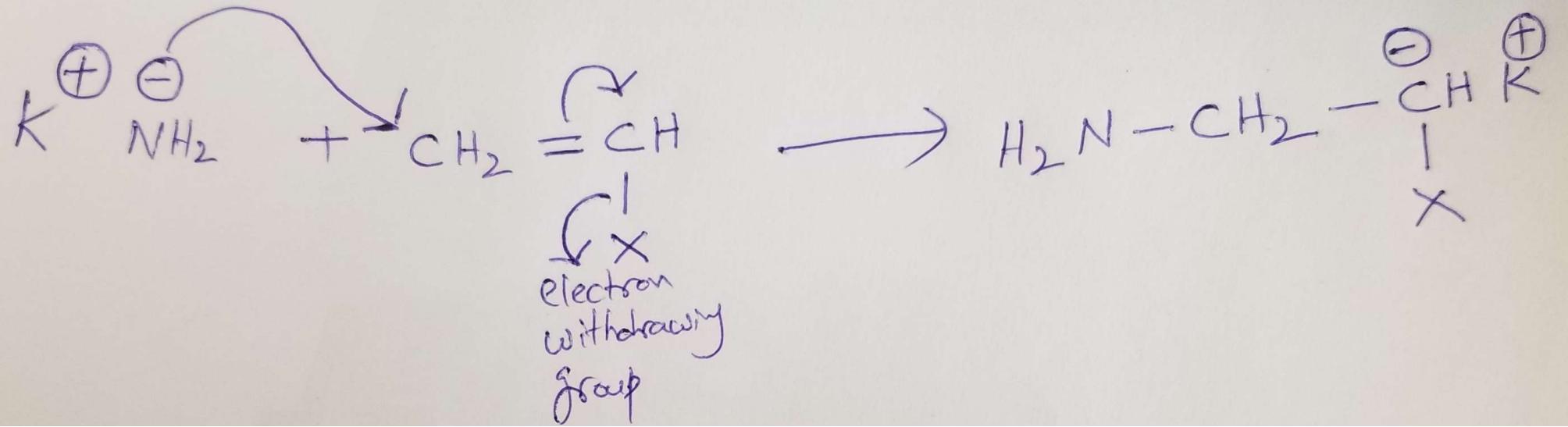


Fig. 4. Network polymer.

TYPES OF POLYMERIZATION

TYPES OF POLYMERIZATION

(1) **Addition or chain polymerization** is a reaction that yields a product, which is an exact



Introduction to polymerization techniques –
bulk, solution, suspension, and emulsion
polymerization.

POLYMERIZATION TECHNIQUES

1. Addition polymerization

- Bulk polymerization
- Solution polymerization
- Suspension polymerization
- Emulsion polymerization

1. Condensation polymerization

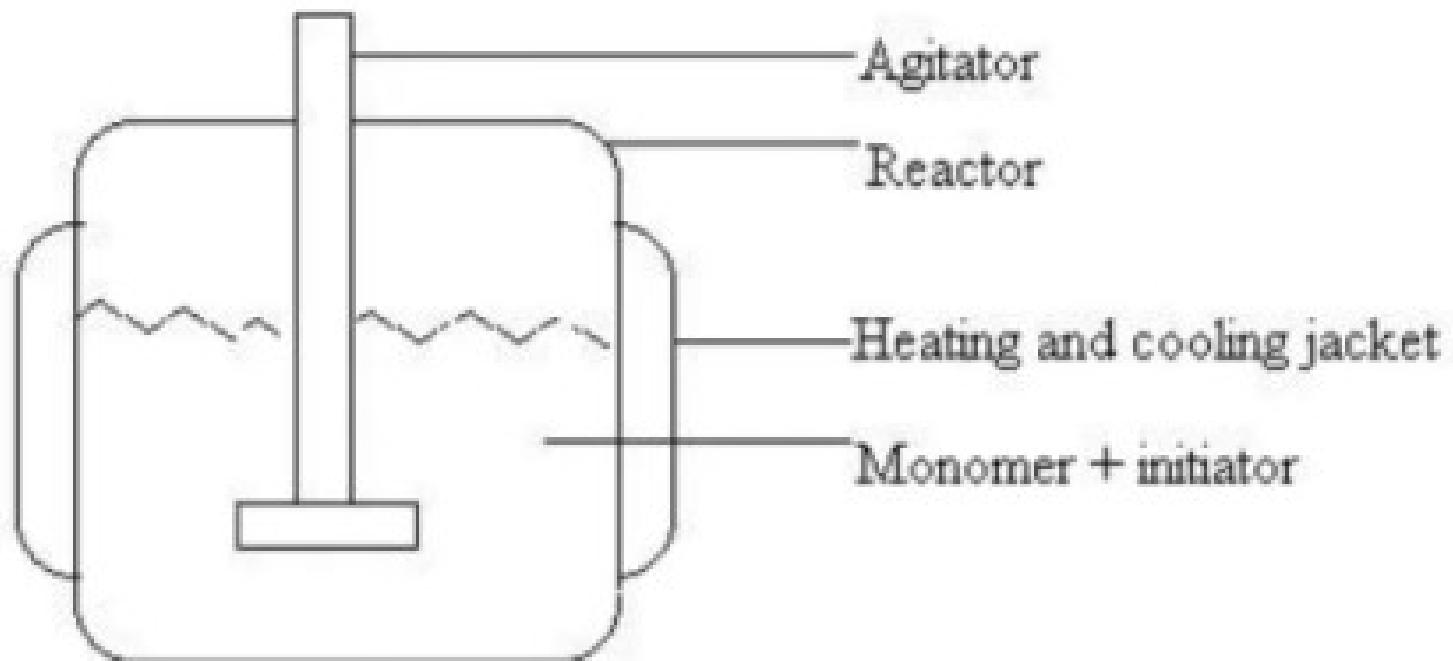
BULK POLYMERIZATION

- Mass or block polymerization: Polymerization of the **undiluted** monomer.
- carried out by adding a soluble initiator to pure monomer (in liquid state).
- The mixture is constantly agitated & heated to polymerization temperature.
- Once the reaction starts, heating is stopped as the reaction is exothermic.
- The heat generated is dissipated by circulating water jacket.
- Viscosity increases dramatically during conversion.



BULK POLYMERIZATION

- The method is used for the polymerization of liquid state monomers.
- It is usually adopted to produce polystyrene, polyvinyl chloride, polymethyl methacrylate and low density polyethylene.



Advantages

- The system is simple and requires thermal insulation.
- The polymer is obtained pure.
- Large castings may be prepared directly.
- Molecular weight distribution can be easily changed with the use of a chain transfer agent.

Disadvantages

- Heat transfer and mixing become difficult as the viscosity of reaction mass increases.
- Highly exothermic.
- The polymerization is obtained with a broad molecular weight distribution due to the high viscosity and lack of good heat transfer.
- Very low molecular weights are obtained.

SOLUTION POLYMERIZATION

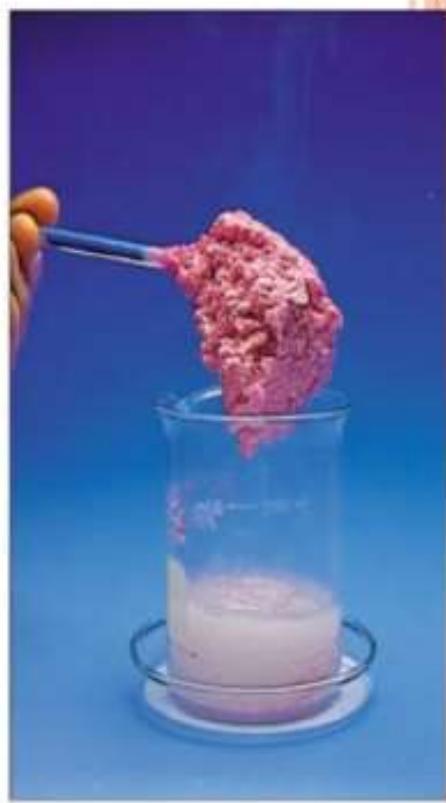
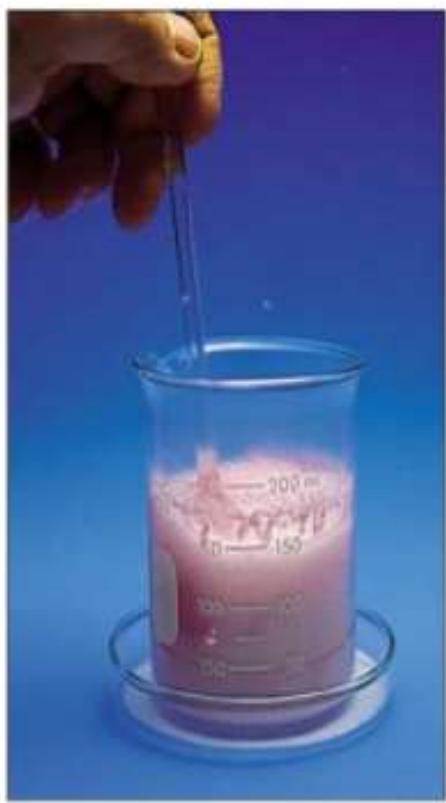
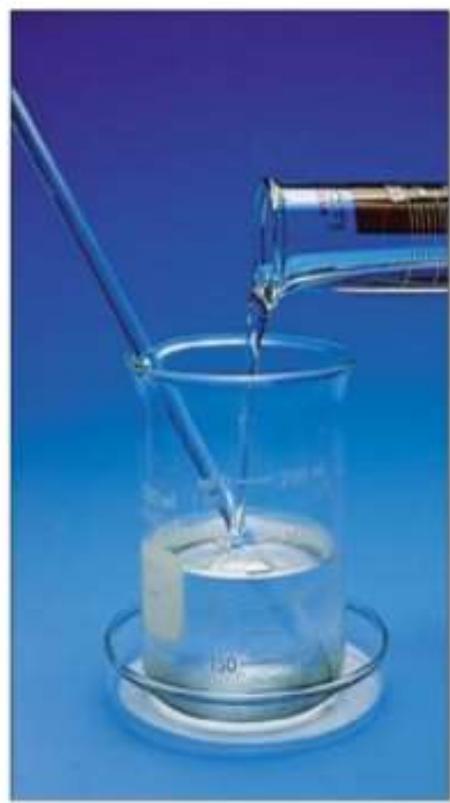
- Some disadvantages of bulk polymerization are eliminated in solution polymerization.
- Monomer along with initiator dissolved in solvent, formed polymer stays dissolved.
- The mixture is kept at polymerizaion temperature & constantly agitated.
- Depending on concentration of monomer the viscosity of solution does not increase.



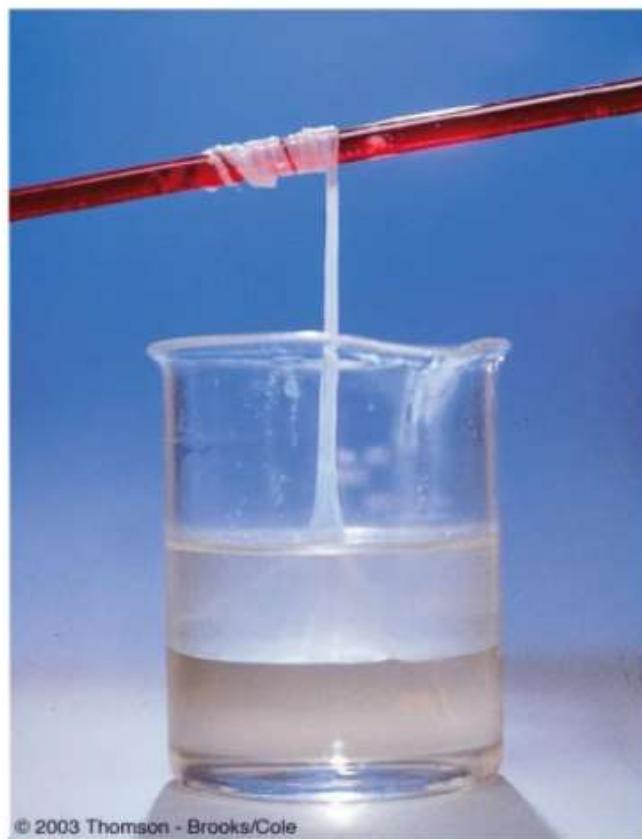
SOLUTION POLYMERIZATION

- After the reaction is over, the polymer is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent.
- Polymer so formed can be used for surface coating.
- It is used for the production of Polyacrylonitrile, PVC, Polyacrylic acid, Polyacrylamide, Polyvinyl alcohol, PMMA, Polybutadiene, etc





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Advantages

- The solvent acts as a diluent & helps in facilitating continuous transfer of heat of polymerization. Therefore temperature control is easy.
- The solvent allows easy stirring as it decreases the viscosity of reaction mixture.
- Solvent also facilitates the ease of removal of polymer from the reactor.
- Viscosity build up is negligible.



Disadvantages

- To get pure polymer, evaporation of solvent is required additional technology, so it is essential to separate & recover the solvent.
- The method is costly since it uses costly solvents.
- Polymers of high molecular weight polymers cannot be formed as the solvent molecules may act as chain terminators.
- The technique gives a smaller yield of polymer per reactor volume, as the solvent waste the reactor space.
- The purity of product is also not as high as that of bulk polymerization. Removal of last traces of solvent is difficult.

SUSPENSION POLYMERIZATION

- Liquid or dissolved *monomer suspended in liquid* phase like water.
- *Initiators used are monomer soluble* e.g. dibenzoyl peroxide.
- Thus, polymer is produced in heterogeneous medium.
- Initiator
- The size of monomer droplets is **50-200 μm** in diameter.
- The dispersion is maintained by continuous agitation and *the droplets are prevented to coalesce* (unite or merge) by *adding small quantity of stabilizers*.



SUSPENSION POLYMERIZATION

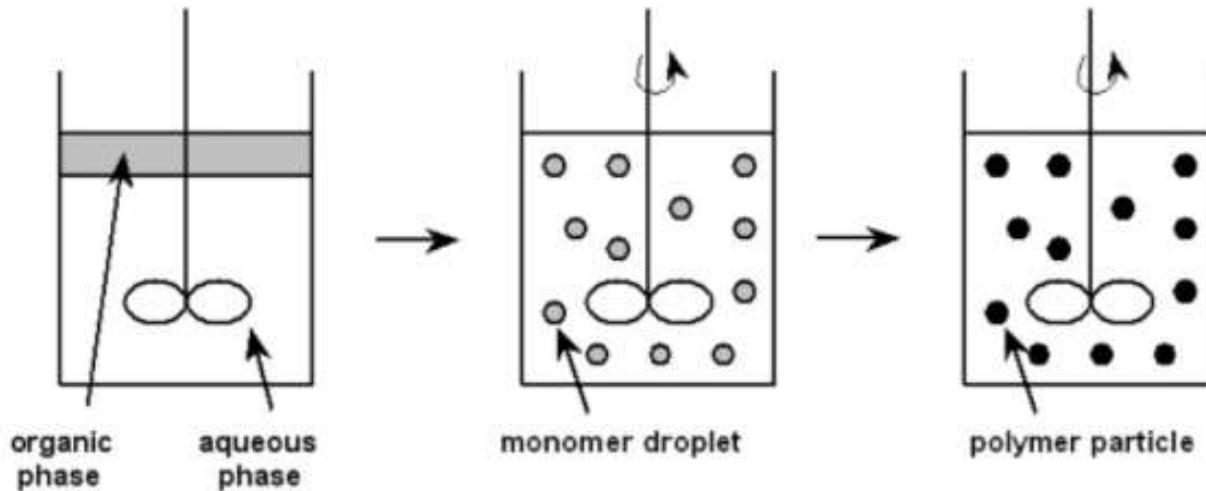
- The stabilizers used are **PVA, gelatin, cellulose** are used along with inorganic stabilizers such as **kaolin, magnesium silicate, aluminum hydroxide, calcium/magnesium phosphate**, etc if necessary.
- As it concerns with droplets, **each droplet is tiny bulk reactor**. The polymerization takes place **inside the droplet** & product formed being **insoluble in water**.
- The product separated out in the form of **spherical pearls or beads** of polymer.
- Hence the technique is also known as **Pearl polymerization / Granular polymerization / Bead polymerization**.

SUSPENSION POLYMERIZATION

- The products are small uniform spheres. They can be used directly for some applications as precursors of ion exchange resins otherwise they can be extruded & chopped to form larger, easily moulded pallets.
- They can be dissolved in a suitable medium for use as adhesives & coatings.
- This technique is used to form PVC, Polyvinyl acetate, Polystyrene, Styrene-divinyl benzene copolymer beads (used for ion exchange) etc.



SUSPENSION POLYMERIZATION



Advantages

- The process is comparatively cheap as it involves only water instead of solvents.
- Viscosity increase is negligible.
- Agitation & temperature control is easy.
- Product isolation is easy since the product is insoluble in water.

Disadvantages

- The method can be adopted only for water insoluble monomers.
- It is difficult to control polymer size.
- Polymer purity is low due to the presence of suspending & stabilizing additives that are difficult to remove completely.
- Suspension polymerization reaction is highly agitation sensitive.
- Larger volume of reactor is taken up by water.
- The method cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles.

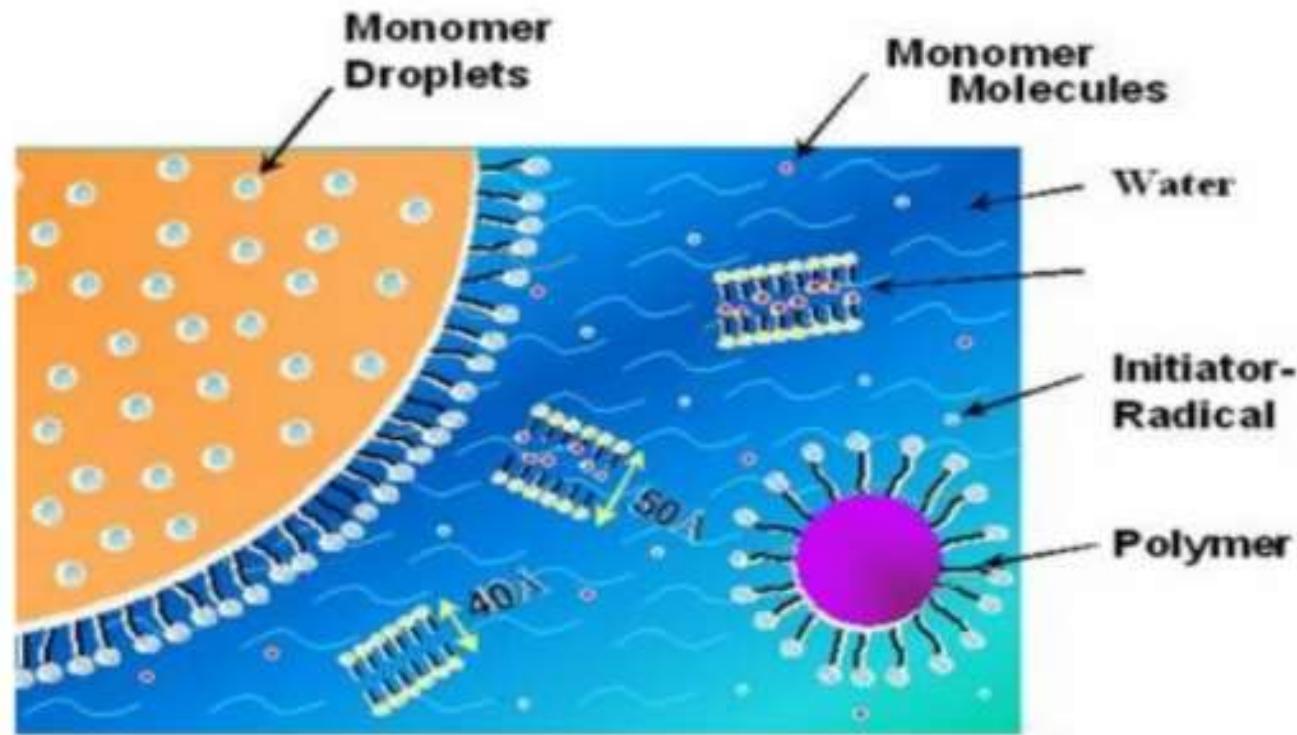
EMULSION POLYMERIZATION

- The technique is used for the production of large number of commercial plastics & elastomers.
- The system consists of water insoluble monomer, dispersion medium & emulsifying agents or surfactants (soaps and detergents) and a water soluble initiator (potassium persulphate / H_2O_2 , etc).
- The monomer is dispersed in the aqueous phase, not as a discrete droplets, but as a uniform emulsion.
- The size of monomer droplet is around 0.5 to 10 μm in diameter depending upon the polymerization temperature & rate of agitation.

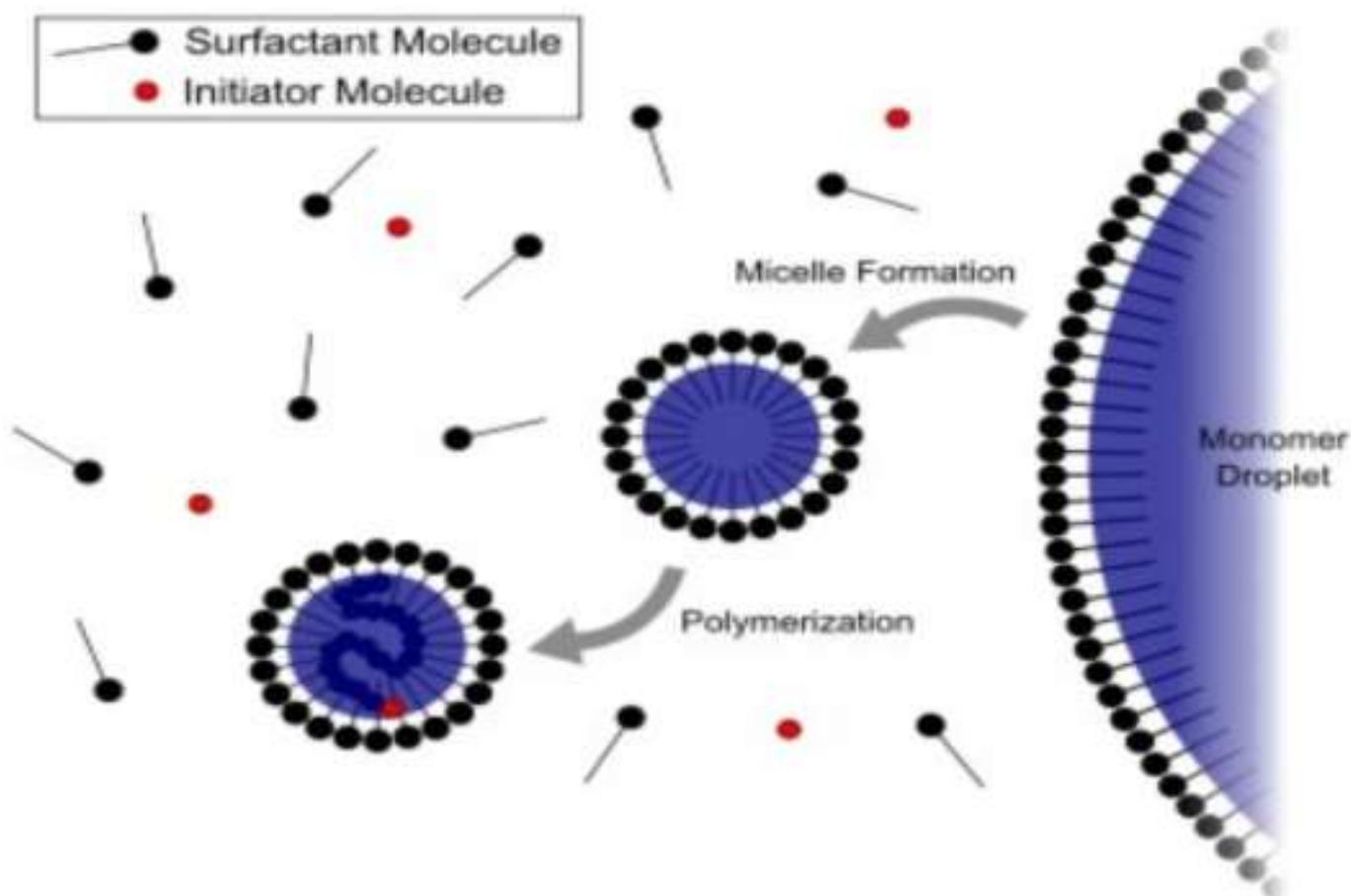
EMULSION POLYMERIZATION

- The emulsion of monomer in water is stabilized by a surfactant.
- A surfactant has a hydrophilic and hydrophobic end in its structure.
- When it is put into a water, the surfactant molecules gather together into aggregates called micelles.
- The hydrocarbon tails (hydrophobic) orient inwards & heads (hydrophilic) orient outwards into water.
- The monomer molecules diffuse from monomer droplets to water & from water to the hydrocarbon centre of micelles.

EMULSION POLYMERIZATION



EMULSION POLYMERIZATION



EMULSION POLYMERIZATION

- Water
- Monomer
- Surfactant

Examples:

- Synthetic rubber-styrene-butadiene (SBR), Polybutadiene, Polychloroprene.
- Plastics-PVC, polystyrene, Acrylonitrile-butadiene-styrene terpolymer (ABS).
- Dispersions-polyvinyl acetate, polyvinyl acetate copolymers, latexacrylic paint, Styrene-butadiene, VAE

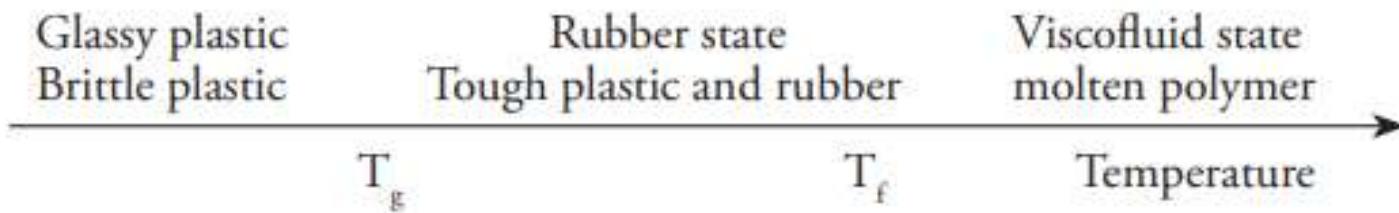
Advantages

- High molecular weight polymers
- fast polymerization rates.
- allows removal of heat from the system.
- viscosity remains close to that of water and is not dependent on molecular weight.
- The final product can be used as such ,does not need to be altered or processed

Disadvantages

- Surfactants and polymerization adjuvants -difficult to remove
- For dry (isolated) polymers, water removal is an energy-intensive process
- Designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.
- Can not be used for condensation, ionic or Ziegler-Natta polymerization.

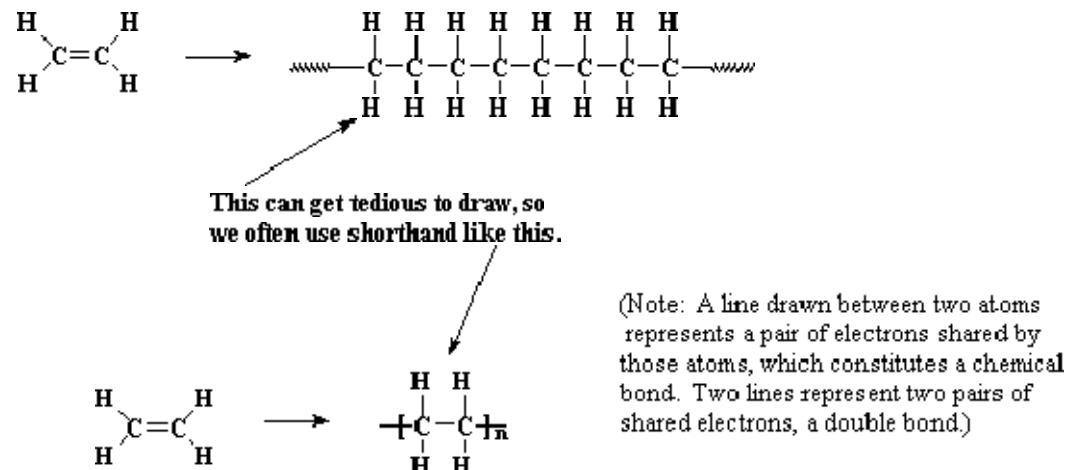
Glass transition temperature (T_g) is defined as the temperature below which an amorphous polymer (sometimes crystalline polymer) becomes hard, brittle and breaks like glass. Above this temperature it is soft, flexible and rubbery. The hard and the brittle state is called the glassy state because random arrangement of polymeric chains is similar to the random molecular arrangement found in glass. The soft, flexible state is the rubbery or viscoelastic state. On heating beyond T_g the polymer first changes into soft, flexible rubbery state and then converts into the highly viscous liquid and starts flowing. This is called as viscofluid state and the temperature at which this occurs is called the flow temperature T_f . as explained in Figure



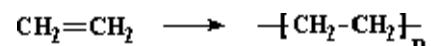
Some polymers are used to above T_g and some below. Hard plastics like polystyrene and poly methylmethacrylate are used below T_g, that is, in their glassy state. Rubbers, elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in their rubbery state when they are flexible. Some polymers like polycarbonate, although amorphous, are considered tough at temperatures well below their T_g. This behavior is because of the chemical bonds in polycarbonates rather than the arrangement of the polymeric chains. The above phenomenon can be explained considering the three states of matter solid, liquid and gas. Polymers however exist only in two phases solid and liquid because they decompose before reaching their boiling points. In a long chain of polymer molecule, some segments have freedom of movement while others do not. When such a polymer molecule is heated first there is internal mobility of the polymeric segments (called segmental mobility), and then the whole molecule starts moving (molecular mobility; segmental mobility can be compared with the audience standing in their position or stretching their arms while watching a movie, whereas molecular mobility is the moving out of the audience during intermission or after the movie). When segmental mobility comes into play the solid polymer acquires a soft and rubbery state. With the onset of molecular mobility the polymer changes into the liquid state.

Crystalline and amorphous structure of polymer, Degree of crystallinity, Types of polymer degradation-Chain-end

& Random degradation, Thermal Degradation, Mechanical Degradation, Ultrasonic wave Degradation, Photo degradation. Introduction, preparation and applications of bio-degradable polymers (PLA) and conducting polymers (PANI).



And when we're feeling really lazy we just draw it like this:



Amorphous vs. Crystalline Polymers.

Polymers are unlike other types of materials because of their high molecular weight. Molecular weight is the value used to express the size of a molecule. Water, for example, has a molecular weight of 18 atomic mass units. Polymers are much larger, with molecular weights ranging from tens of thousands up to several million atomic mass units. The sheer size of polymers has a great impact on their unique properties.

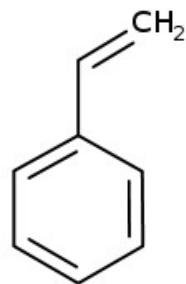
One important implication of polymer size is how atoms behave in different phase states. Smallermolecule compounds have three states of matter — solids, liquids and gases. The particles of a solid are packed closely together and have very little motion. The particles of a liquid, by comparison, are more loosely packed and slide more easily past one another. And the particles of a gas are very loosely packed and move about with great energy.

Large molecules, like polymers, behave differently because there are so many more atoms to interact with each other. **For example, polymers aren't thought of simply as solids — they are classified further into two types: amorphous and crystalline.** What's more, some polymeric solids can be both amorphous and crystalline at the same time. This surprising idea is particularly important to the study of polymers. In this article, we'll explain the difference between amorphous and crystalline polymers and provide some common examples of each.

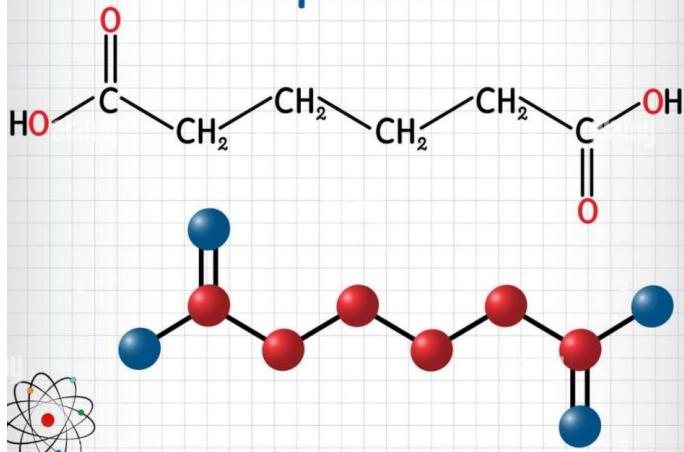
Examples of Amorphous and Crystalline Polymers

Although 100 percent and 0 percent crystallinity are rare, some polymers fall close to either extreme. Those that tend toward high crystallinity are rigid, have high melting points, and are less affected by solvent penetration. Those that tend toward high amorphousness are softer, have [glass transition temperatures](#), and are penetrated more by solvents than are their crystalline counterparts. Here are some examples, along with their key properties:

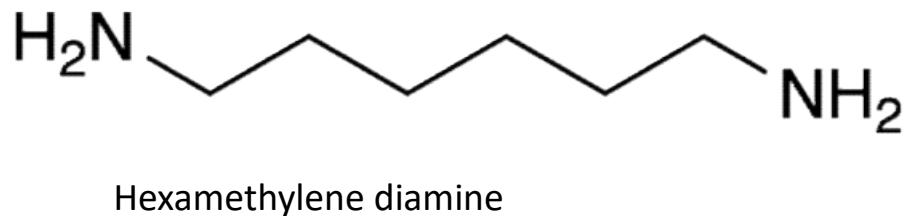
Examples of Amorphous and Crystalline Polymers



Adipic acid



Crystalline Polymers				
	Nylon	Polypropylene (Isotactic*)	Polyethylene	Polystyrene (Syndiotactic*)
Monomer(s):	adipic acid & hexamethylene diamine	propylene	ethylene	styrene
T _m :	260°C (500°F)	174°C (345°F)	137°C (279°F)	270°C (518°F)
Uses:	thermoplastics, fibers	thermoplastics, fibers	thermoplastics, fibers	thermoplastics
Polymerization:	acid catalyzed condensation polymerization	Ziegler-Natta polymerization	free radical chain polymerization	metallocene catalysis polymerization



Examples of Amorphous and Crystalline Polymers

Amorphous Polymers				
	<p>Polypropylene (Atactic*)</p>	<p>Poly(methyl methacrylate)</p>	<p>Polybutadiene</p>	<p>Polystyrene (Atactic*)</p>
Monomer(s):	propylene	methyl methacrylate	butadiene	styrene
T _g :	-17 °C (1.4 °F)	120 °C (248 °F)	-106 °C (-159 °F)	100 °C (212 °F)
Uses:	elastomers	thermoplastics	tires, belts, hoses, gaskets, and seals	thermoplastics
Polymerization:	Metallocene catalysis polymerization	free radical vinyl polymerization	Ziegler-Natta polymerization, free radical polymerization	free radical vinyl polymerization

Degree of Crystallinity

Most crystalline polymers have amorphous regions, which means crystalline polymers are never completely crystalline. Scientists often refer to a polymer's degree of crystallinity to describe where it sits along this spectrum. Crystallinity can range from 0 percent (entirely amorphous) to 100 percent (entirely crystalline), but most polymers fall somewhere between those extremes. Chain flexibility — both flexing along the entire chain and flexing in bonds between atoms — plays a big role in polymer crystal formation. **As chains flex and bend against each other, various attractive and repulsive forces affect how polymer chains arrange themselves, either more orderly or less orderly.** Degree of crystallinity is directly related to whether a polymer melts like a typical solid or whether it transitions between glassy and rubbery states. **Highly crystalline polymers have a more traditional melting point, so when they are heated, they reach a certain temperature at which the orderly arrangement of their long-chain structure transitions to a random and disorganized arrangement. This value is usually a specific number, designated as the melting point, or T_m .**

Amorphous solids don't melt suddenly when they're heated. Instead, they reach a range of temperatures over which the material becomes less glassy and more rubber-like or vice versa. As a result, amorphous polymers don't have a melting point — they have a glass transition temperature, or T_g . The glass transition temperature of a specific polymer may be listed as a single temperature, but this number is a representative value representing a range of temperatures.

To explain glass transition temperature in terms of molecular motion, we would say that, at temperatures below T_g , the amorphous polymer chains cannot rotate or move in space (the cooked spaghetti is frozen and cannot move). This produces the glassy state, which is hard, rigid, and brittle. When the temperature rises above T_g , the entangled chains can move (small portions of the spaghetti noodles can move around). This produces a rubbery state, when an amorphous polymer is soft and flexible.

Types of polymer degradation-

Chain-end & Random degradation, Thermal Degradation, Mechanical Degradation, Ultrasonic wave Degradation, Photo degradation.

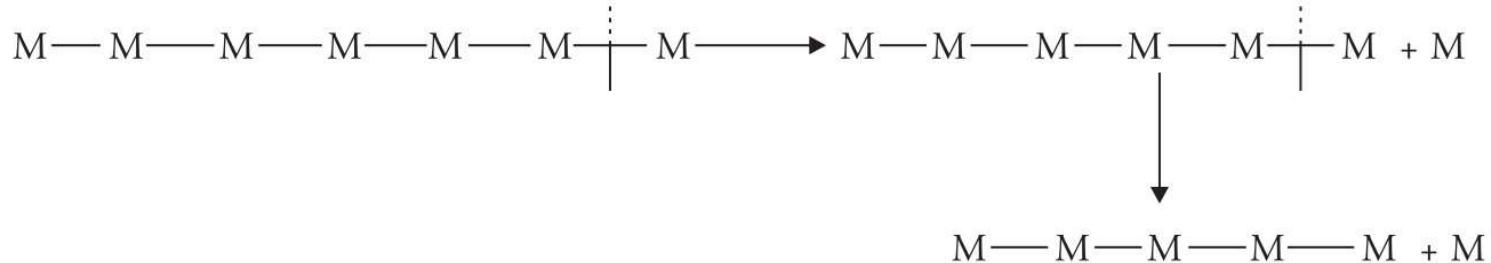
Degradation of Polymer

Conventionally, the term 'degradation' means reduction in the molecular weight of the polymer. A polymer suffers degradation or degeneration gradually. This effect is observed in day to day life also. We have seen that plastic objects tend to lose their lustre with time and they gradually fade away, lose their strength and break. Mechanical stress, radiation, oxygen and other environmental factors are generally responsible for the degradation of a polymer. Polymers also degrade during fabrication process when they are subjected to high temperatures.

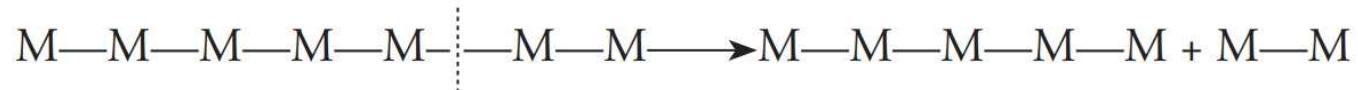
Types of polymer degradation

Polymer degradation is generally of two types.

- (i) **Chain end degradation** In this type, the degradation starts from the chain end releasing the monomeric units. This phenomenon is the reverse of chain propagation and is also termed as ‘depolymerisation’.



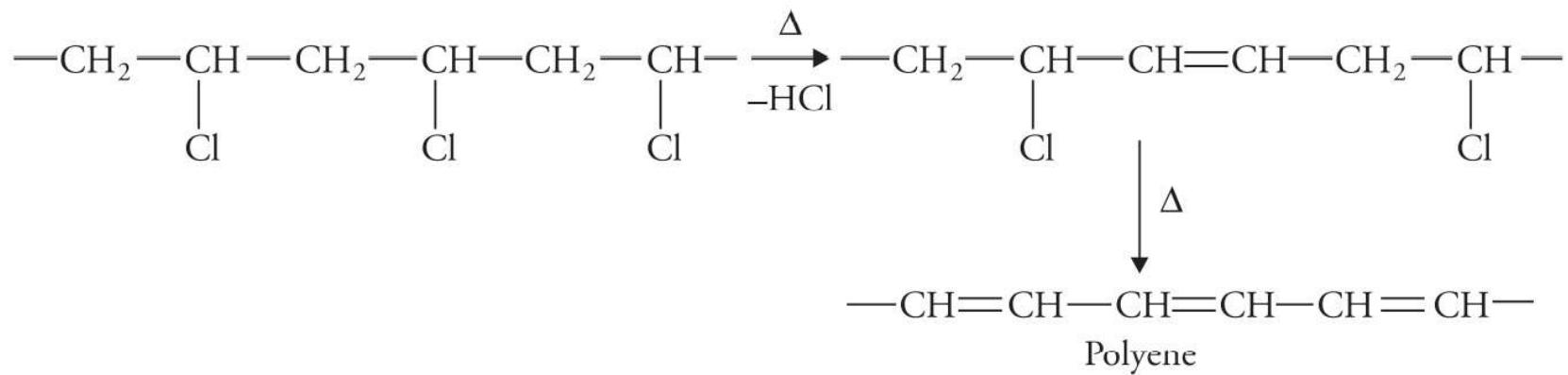
- (ii) **Random degradation** This type of degradation takes place from any point on the polymeric chain.



In this type, low molecular weight fragments are formed, but monomeric units are not released.

Types of polymer degradation

Thermal degradation Degradation under the influence of heat is termed as thermal degradation. Thermal degradation occurs by both chain end degradation, leading to the formation of monomer units, or by random degradation. Besides the above two types of degradation, non-chain scissions also occur, which involve the pendant (substituent) groups without affecting the main chain. For example, PVC degrades at about 200 °C releasing HCl. As a result of this degradation, the color of PVC changes from white to black.



Types of polymer degradation:

Photodegradation

Degradation by radiation It is brought about by ultraviolet or visible light. Also called photodegradation, it is responsible for the yellowing and gradual embrittlement of plastic material on storage. Ultraviolet or visible light causes 1,1-disubstituted polymers to degrade to monomers almost exclusively at room temperatures. Polymethylmethacrylate gives a quantitative yield of the monomer in the presence of ultraviolet rays. Generally, photostabilisers like 'salol' are added to protect the polymers from deteriorating in the presence of light.

Types of polymer degradation:

Mechanical degradation

Mechanical degradation Some polymers degrade under mechanical stress. Polystyrene dissolved in a solvent when stirred vigorously undergoes molecular degradation or fragmentation. Similarly, rubber on being subjected to mechanical stress called mastication undergoes chain scission, leading to the formation of low-molecular-weight fragments.

Polymers also undergo degradation by ultrasonic waves, X-rays, gamma rays, alpha rays, beta rays and other high-energy radiations.

Types of polymer degradation:

Oxidative degradation

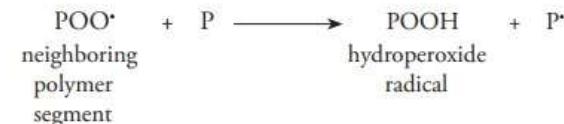
Oxidative degradation It leads to the hardening, discoloration and surface changes in the polymer. Saturated polymers degrade very slowly by oxygen, whereas unsaturated polymers are easily attacked by oxygen. It is believed that oxidative degradation proceeds by the formation of hydroperoxide radical, which is mainly responsible for chain incision.



P- represents the polymer chain.



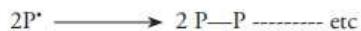
POO[•] abstracts hydrogen from the neighbouring polymer chain P and forms hydroperoxide radical.



The hydroperoxide leads to the formation of several new free radical sites.



The recombination of free radicals occurs leading to chain termination.



Introduction, preparation and applications of bio-degradable polymers (PLA) and conducting polymers (PANI).

Bio-degradable polymers: Ex. PLA (Polylactic acid)

Preparation:

Applications:

Conducting polymers: Ex. PANI (Polyaniline)

Preparation:

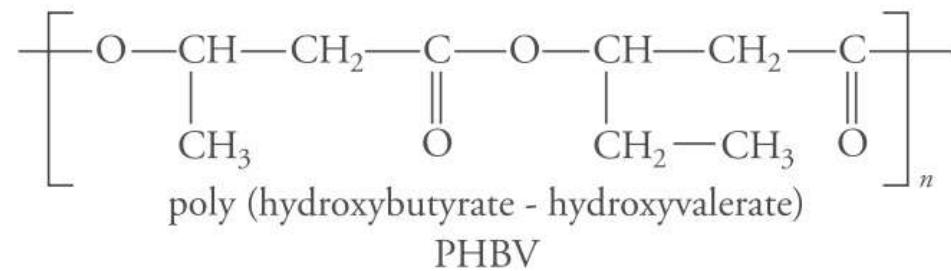
Applications:

Biodegradable polymers

Biodegradable polymers

Biodegradation is the degradation of a material by environmental factors such as sunlight, temperature changes or by the action of microbes (bacteria, fungi, etc.).

The use of biodegradable polymers is increasing day by day. Many natural polymers like rubber and cellulose are biodegradable. They degrade gradually by bacterial action. Biodegradable synthetic polymers are polyvinyl alcohol, hydroxyethylcellulose polymer, polycaprolactone, polylactic acid, hydroxybutyrate polymer, hydroxyvalerate polymer and poly(hydroxybutyrate hydroxyvalerate) (PHBV) a copolymer of hydroxybutyrate and hydroxyvalerate. PHBV is a biodegradable aliphatic polyester.



Applications

Biodegradable polymers find extensive use in the medical field. They are used commercially in tissue engineering and drug delivery field of biomedicine. Typical medical applications include the following.

Medical applications of Biodegradable polymers

- Use in orthopaedic fixation devices. Biodegradable polymers are used to join fractured bones. They provide the required strength to the bone and after the bone heals and can take the load, they harmlessly degrade over time. This prevents the patient from an additional operation for removal, as would be required if a metallic device was used.
- In controlled drug delivery, the polymer slowly degrades into smaller fragments releasing the drug gradually and in a controlled manner.
- It is used in dental devices, biodegradable vascular stents, biodegradable soft tissue anchors, etc. Biodegradable polymers are also being increasingly used in the manufacture of plastic bags, toys and other plastic products. These polymers gradually degrade in the environment (or in landfills) and leave the environment ‘greener’.

Conducting Polymers

Conducting Polymers

The use of polymers is increasing rapidly in our day to day life. Because of their light weight, corrosion resistance, easily workability, easy maintenance they are replacing metals in all walks of life. However, the drawback with polymers is that they do not conduct electricity. Research went on in this area and in 1977, three scientists Professor Alan-J. Heeger, Professor Alam. G Macdiarmid and Professor Hideki Shirakawa discovered that oxidation of polyacetylene with iodine results in 10^8 fold increase in its conductivity, that is, the conductivity of the doped polymer approaches the conductivity of one of the best conductors. The conductivity of doped ‘polyacetylene’ was found to be as high as 10^3 S cm^{-1} . This is comparable to the conductivity of copper on an equal weight basis. The three scientists received the Nobel prize in chemistry in the year 2000 for their discovery and the development of electrically conducting polymers.

After the above discovery, research continued in this field and a large number of electrically conducting polymers were discovered gradually. Some common conducting polymers are as follows.

Table 6.3 Common conducting polymers and their conductivity

Conducting polymer	Repeating unit	Dopant	Conductivity (S cm ⁻¹)
Polyaniline		HCl	200
Trans polyacetylene		I ₂ , Br ₂ , Li, Na, AsF ₅	10 ⁴
Polypyrrole		BF ₄ ⁻ , ClO ₄ ⁻ , tosylate	500–7500
Poly(p-phenylene)		AsF ₅ , Li, K	10 ³
Poly(p-phenylene vinylene)		AsF ₅	10 ⁴
Polythiophene		BF ₄ ⁻ , ClO ₄ ⁻ , tosylate, FeCl ₄ ⁻	10 ³

Classification of conducting polymers

Polymers that conduct electricity are called conducting polymers. They can be classified as follows.

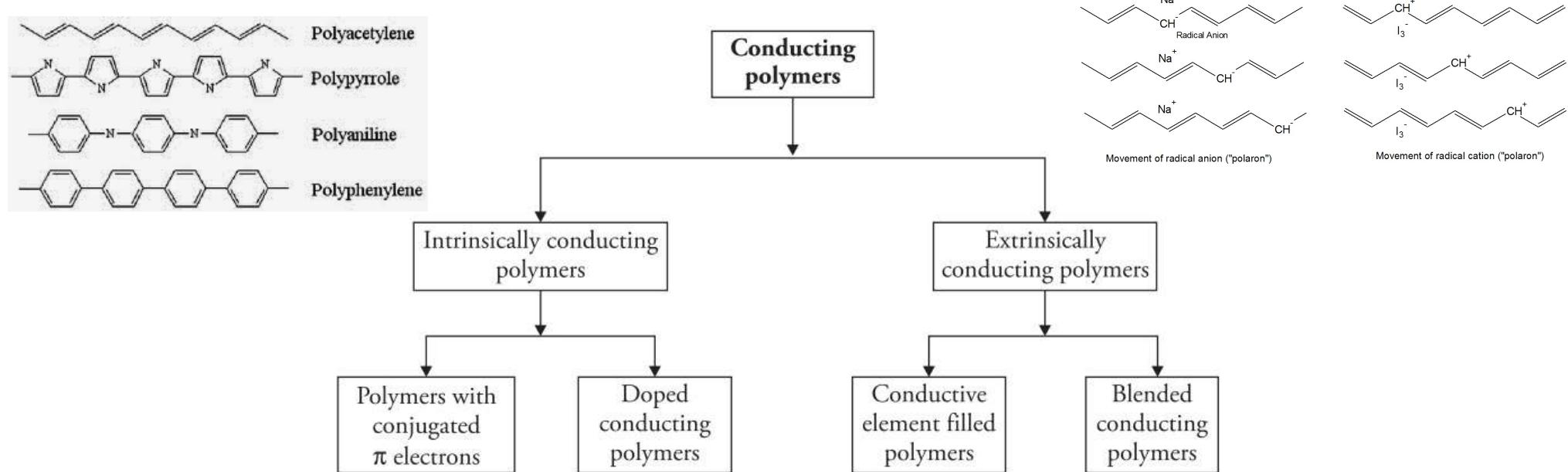


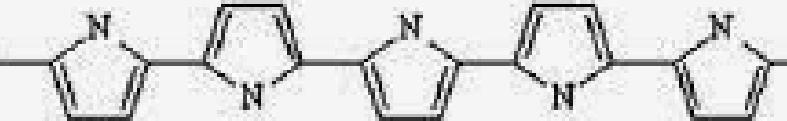
Figure 6.12 Classification of conducting polymers

Intrinsically conducting polymers

The conductance of these polymers is due to the extensive conjugation in their backbone. They are further of two types.



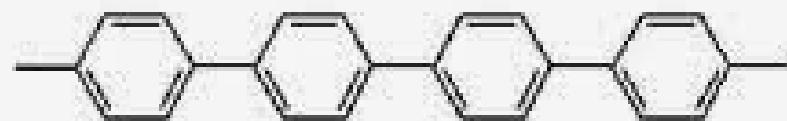
Polyacetylene



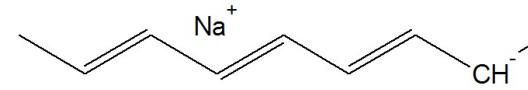
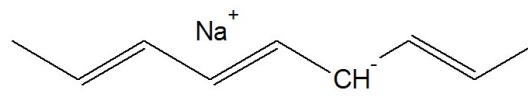
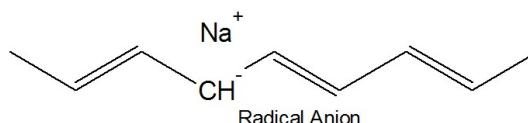
Polypyrrole



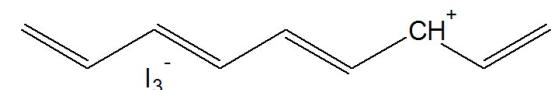
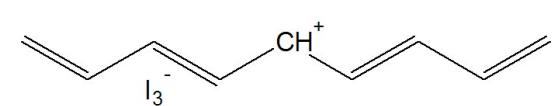
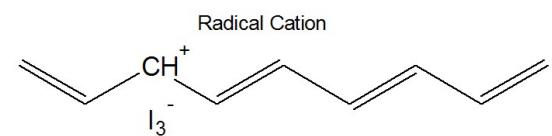
Polyaniline



Polyphenylene



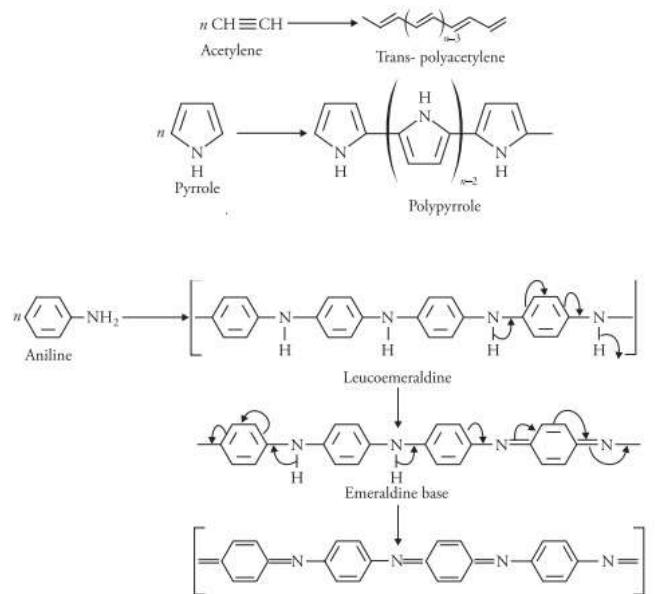
Movement of radical anion ("polaron")



Movement of radical cation ("polaron")

- (a) **Conjugated π -electron conducting polymers** The conductivity of these polymers is due to the presence of conjugated π -electrons. The conjugated π electrons are delocalised. In an electric field, the π electrons get excited and are transported through the solid polymeric material. However, the conductivity of these polymers is not sufficient for their use in various industrial applications.

Example

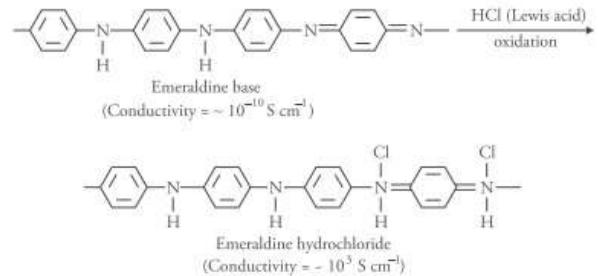


All the three forms of aniline conduct electricity. The conductivity of polyacetylene is $1.7 \times 10^{-9} \text{ S cm}^{-1}$ and that of polyaniline is $10^{-10} \text{ S cm}^{-1}$. The conductivity is greatly enhanced by doping.

- (b) **Doped conducting polymers** The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types.

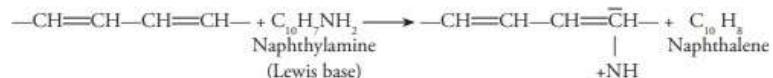
- (i) **p-type doping** When the polymer is treated with a Lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p-dopants are I_2 , FeCl_3 , Br_2 , AsF_5 , etc. For example,





Because of its conductivity it is also known as *synthetic metal*.

- (ii) **n-type doping** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, naphthylamine, etc. For example,



The conductivity of the above polymers depends on various factors.

- (i) **Length of conjugation of the polymeric chain** Greater the conjugation level, more will be the delocalised electrons and greater will be the conductivity.
- (ii) **Doping level** Conductivity increases with the increase in the amount of dopant.
- (iii) **Temperature** Contrary to metals, the conductivity of these polymers increases with the rise in temperature.

Extrinsically conducting polymers

The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

Conductive element-filled polymers When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises. Here the polymer acts as the binder of the conducting elements. However, addition of these elements affects tensile strength and impact strength of the polymer. This problem is overcome by blending a conventional polymer with a conducting polymer.

Blended conducting polymer Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties.

Applications of conducting polymers

Conducting polymers find use in electronics, solar cells, displays, illumination sources and microchips. Some of the major application areas are

- In rechargeable light weight batteries. These have perchlorate-doped polyacetylene-lithium system. These batteries are light in weight, leak-proof and small in size.
- Used in photovoltaic devices like in Al/polymer/Au photovoltaic cells.
- In telecommunication systems.
- Electrically conducting polyaniline is used for antistatic coatings, and also for producing ‘smart windows’. Polyaniline shows different colors in different oxidation states. Hence, its color changes in response to sunlight or temperature changes.
- They are also used in organic light-emitting diodes (OLEDs).
- In electronic devices such as transistors and diodes.

Antistatic coating: A material used with textiles, plastics, paper products, or wax polishes to reduce static-electrical charges by allowing the charge to leak off

*A smart glass or switchable glass (also called **smart window** or switchable window in those applications) is a glass or glazing whose light transmission properties are altered when voltage, light, or heat is applied.*