



# Kinetics and Mechanism of Polymerization

**Polymerization techniques :** The process of linking together of the monomers to form a polymer (macromolecule) may be called polymerisation. The physical aspects of polymerisation reactions decide whether the monomer is polymerised in its condensed or gaseous state, whether it is polymerised as such or along with other inert components such as solvents and non-solvent.

These varying physical conditions leads to different polymerisation techniques, as discussed as :

**1. Bulk polymerisation :** The monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer agent, whenever used to control the molecular weight is also dissolved in the monomer itself. Therefore, the whole system is in a homogeneous phase. The reaction mixture is heated or exposed to a radiation source for initiating the polymerisation. As the polymerisation proceeds, the viscosity of the medium increases and mixing becomes progressively difficult, leading to products with very broad molecular weight distribution.. Another disadvantage of bulk polymerisation is that as the medium gets viscous, the diffusibility of the growing polymer chain becomes restricted, the probability of chain collision becomes less and the rate of polymerisation increases enormously.

Bulk polymerisation is quite simple and the product obtained has a high purity. The polymer obtained can also be used as such since no isolation from other components is involved. The bulk polymerisation technique is used in free - radical polymerisation of methyl methacrylate or styrene to get transparent moulding powders and cast sheetings and also of vinyl chloride to get PVC resin.

**2. Solution polymerisation :** In solution polymerisation, the monomer is dissolved in a suitable inert solvent along with the chain transfer agent, whenever used. The free-radical initiator is also dissolved in the solvent medium, while the ionic and coordination catalysts can either be dissolved or suspended. The presence of the inert solvent medium helps to control the viscosity increase.

The main disadvantage of the solution polymerisation technique is that chain transfer to the solvent cannot be completely ruled out and hence, it is difficult to get very high molecular weight products.

By the use of solution technique, production of polyacrylonitrile by free-radical polymerisation and polyisobutylene by cationic polymerisation is carried out at industrial level. Block co-polymers are also made exclusively by this technique.

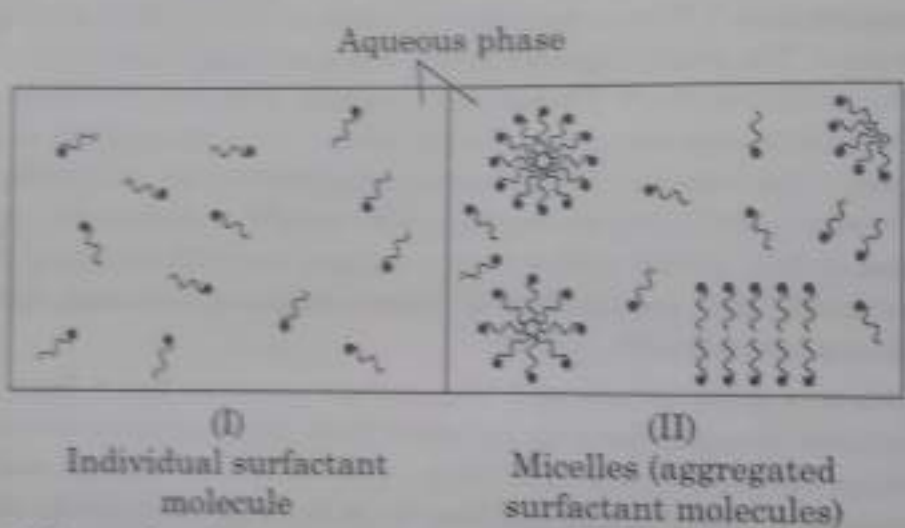
**3. Suspension polymerisation :** Only water-insoluble monomers can be polymerised by this technique. The monomer is suspended in water, in the form of fine droplets, which are stabilised and prevented from coalescing by using suitable water-soluble protective colloids, surface active agents and by stirring. The size of the monomer droplets formed depends on the monomer-to-water ratio, the type and concentration of the stabilising agents and also on the type and speed of agitation employed.

Expandable polystyrene beads (used for the preparation of polystyrene foams), styrene - divinyl benzene co-polymer beads (from which ion - exchange resins are made) and polyvinyl acetate beads are produced by the suspension technique using free radical initiators.

**4. Emulsion polymerisation :** Like suspension polymerisation, in emulsion polymerisation also, the monomer is dispersed in the aqueous medium not as discrete droplets, but as a uniform emulsion. The emulsion is stabilised by surfactants, protective colloids and also by certain buffers. The surfactants can be anionic, cationic or non-ionic. Surfactants lower the surface tension at the monomer-water interface and facilitate emulsification of the monomer in water.

Surfactants have low solubility so they are fully dissolved only at low concentrations. Beyond a particular concentration, the excess quantity does not get molecularly dispersed, but forms molecular aggregates known as 'micelles' and an equilibrium is set up between the dissolved surfactant molecules and the aggregated ones.

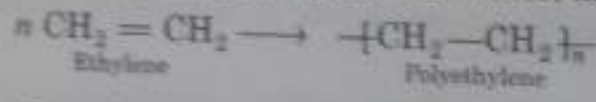
The highest concentration, where in all the molecules are in a dispersed state or the concentration beyond which only micelle formation is possible, is known as the **critical micelle concentration (CMC)**. The micelle formation of surfactant in aqueous phase can be represented as:



It is the most widely used technique at industrial level. By this technique, the monomers like vinyl chloride, chloroprene, Vinyl acetate, butadiene, acrylates and methacrylates are polymerised.

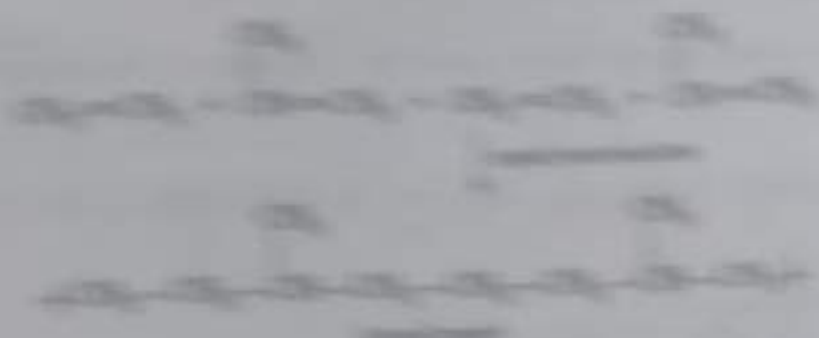
### Addition or Chain Growth Polymerisation

In addition polymerisation, large number of molecules of a compound are combine to form a polymer without involving loss of any small molecule like water, ammonia etc. *e.g.*,



Compounds having C=C bonds undergo addition polymerisation, so it is a characteristic reaction of alkene and its derivatives.

Some polymers are formed from one type of monomers are called **homopolymers** while some polymers are formed from two different types of monomers, are called **copolymers**. Polypropylene, polyethylene are the examples of homopolymers while nylon, decron, some vinyl polymers are the examples of copolymers. Specific properties of a homopolymer can be improved by copolymerisation process.



Handwritten text describing a chemical process or reaction.



**Allylic Polymerization**

Handwritten text explaining allylic polymerization, mentioning radical addition to the double bond.

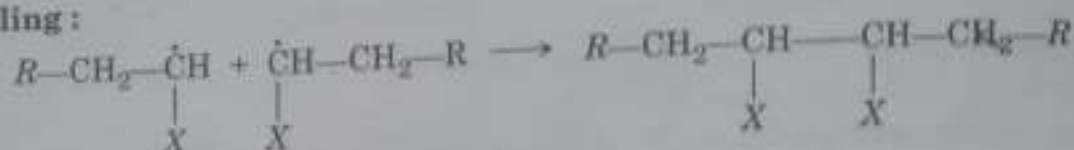


Handwritten text describing the mechanism of allylic polymerization, showing the movement of the radical.

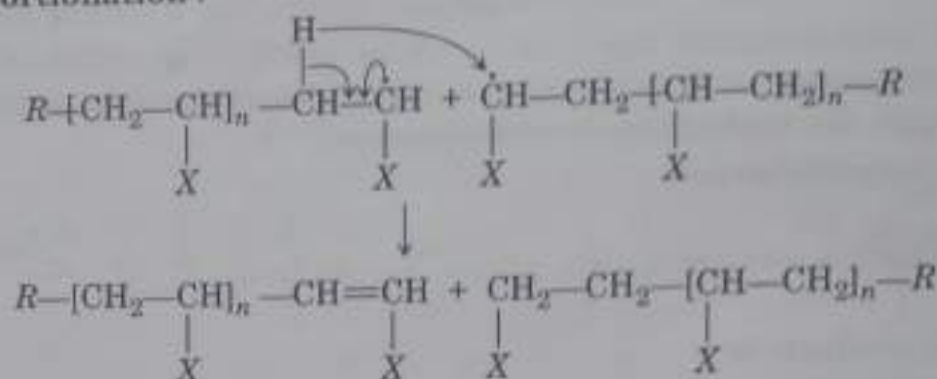


3. **Termination** : Termination takes place by coupling or disproportionation or by chain transfer processes.

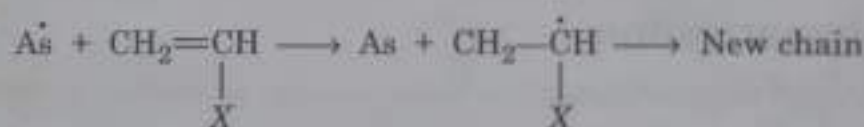
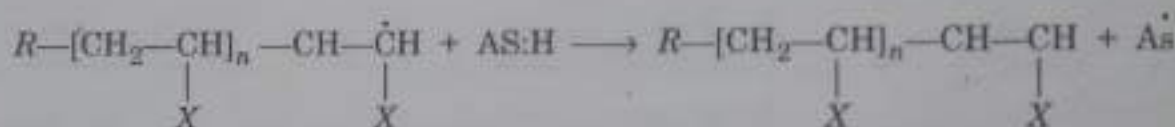
(i) **Coupling** :



(ii) **Disproportionation** :



(iii) **Chain transfer** : Due to the presence of impurities in the monomer, termination of growing polymer chain may occur by chain transfer reactions. A growing polymer radical abstracts an atom from chain transfer agent (AS : H) to terminate polymer chain and produce a new polymer chain.



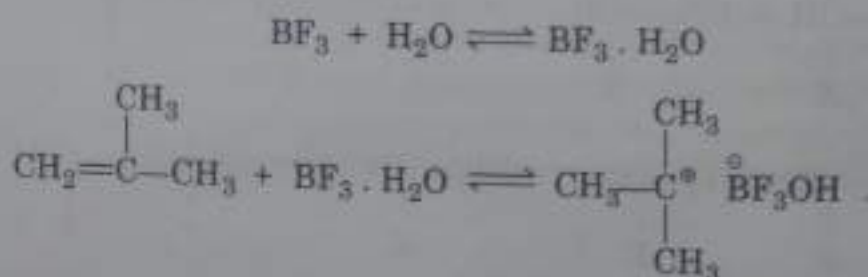
There are many substances which reduce the rate of reaction by terminating reaction chains. Such substances are called inhibitors or retarders. Phenols are commonly used as inhibitor or retarder.

### Ionic Vinyl Polymerisation

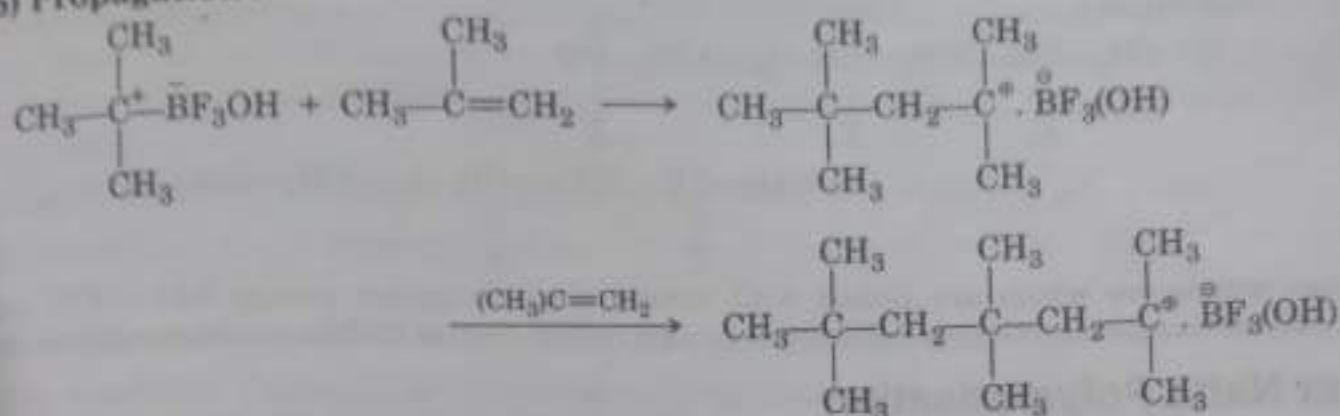
Vinyl monomers can be polymerised not only by free radicals but also by either anions or cations.

(i) **Cationic addition polymerisation** : In this polymerisation, carbocations act as chain carriers. These reactions are catalysed by halo acids, sulphuric acid and Lewis acids such as  $AlCl_3$ ,  $TiCl_4$ ,  $BF_3$ ,  $SnCl_4$  and other strong Lewis acids and involves positively charged carbocations as chain carriers. Monomers with electron releasing substituents such as alkoxy and phenyl groups undergo this type of polymerisation. The reaction takes place in three steps.

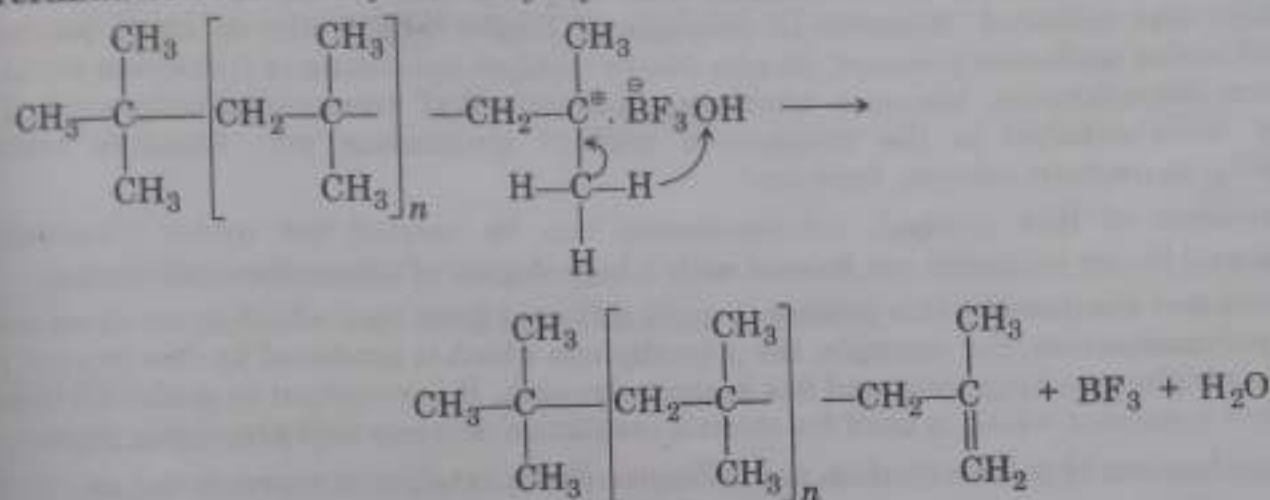
(a) **Initiation** :



(b) Propagation :



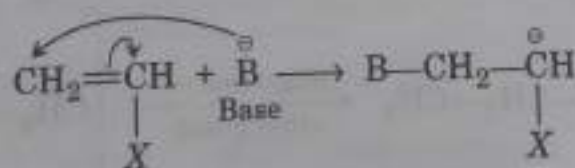
(c) Termination : It usually occurs by a proton transfer



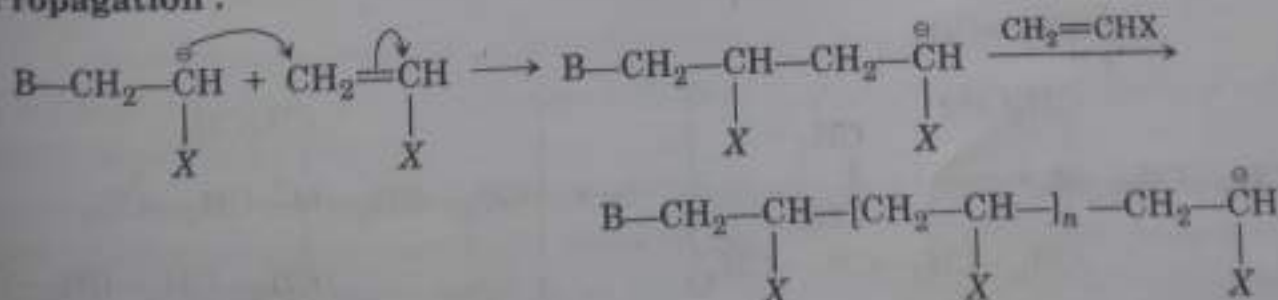
The speed of reaction is very fast even at low temperature e.g., the polymerisation of isobutylene gets completed at  $-100^\circ\text{C}$  in a few seconds.

(ii) **Anionic addition polymerisation** : In this polymerisation negatively charged carbanions are the chain carriers. Strong bases like alkali metal alkyls, alkali metal amides and Grignard reagents are used as catalysts in the reactions. The reaction takes place in three steps as :

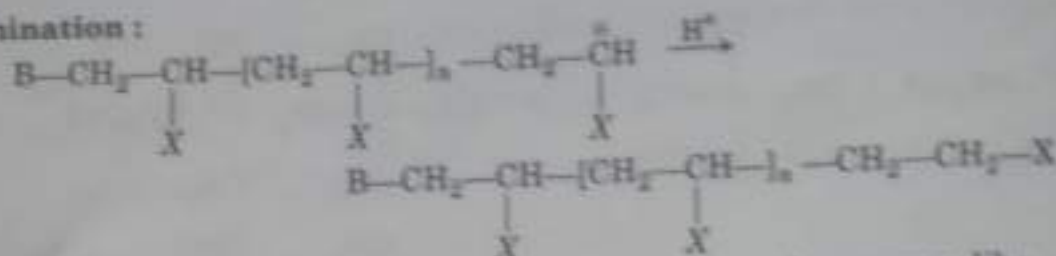
(a) Initiation :



(b) Propagation :



(c) Termination :



Those monomers which are linked with strong electronegative groups like  $-\text{CN}$  undergo anionic polymerisation reactions because such groups confer greater stability to intermediate anions.

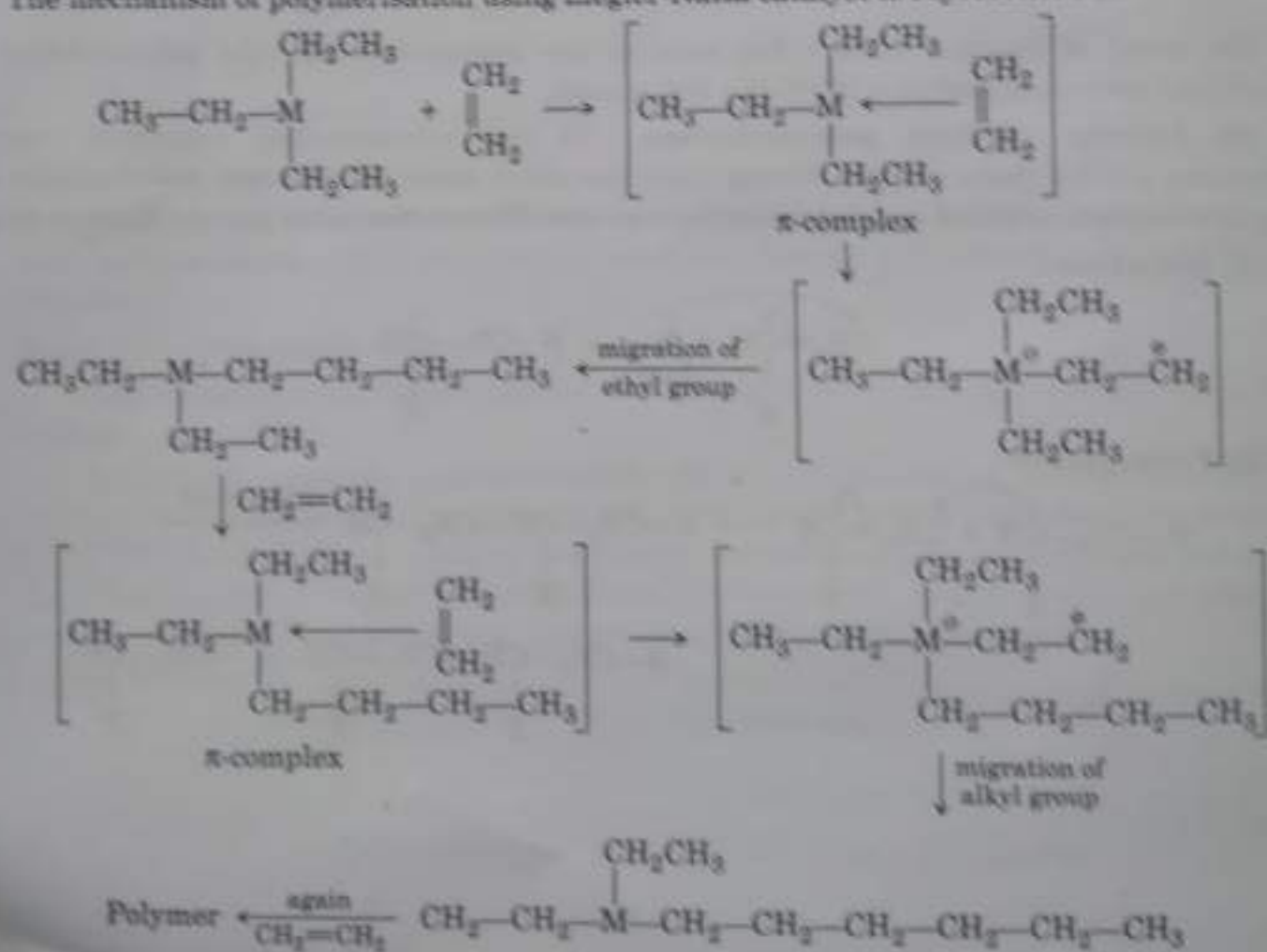
## Ziegler Natta Polymerisation

For the polymerisation of compounds like ethylene and propylene, high pressure and temperature was required. However in presence of Ziegler and Natta catalyst, polymerisation carried out under moderate pressure. Ziegler-Natta catalyst consisting of transition metal chloride as titanium tetrachloride, titanium trichloride and an alkyl ammonium compound. The most commonly used catalyst is the mixture of triethyl aluminium and titanium tetrachloride ( $\text{Et}_3\text{Al}-\text{TiCl}_4$ ) in an inert solvent, heptane.

In presence of this catalyst, polymerisation can be carried out under relatively milder conditions and linear polymers are formed with a high degree of stereochemical control.

The polymer obtained by this process is quite different from that which is obtained under high pressure polymerisation. For example, the polyethylene which is produced by this process is of high density, has higher melting point and has greater strength. It is resistant to acids and bases. It is a good electric insulator which is used for electric insulation of wires and preparing pipes.

The mechanism of polymerisation using Ziegler-Natta catalyst is represented as

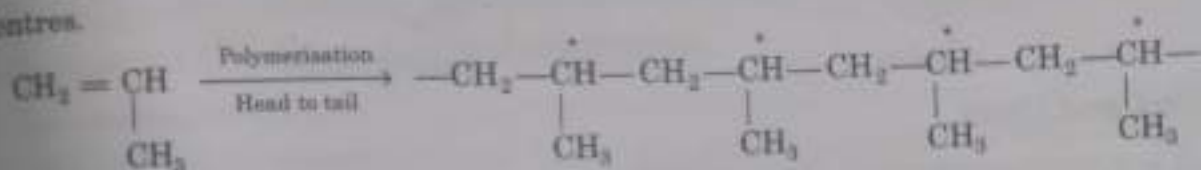


Such type of polymer is a straight chain polymer which differ from the polymer obtained by free radical process that has a branched structure. Another important characteristic of Ziegler Natta polymerisation is the stereochemical control over the way in which the monomer units enters the polymer chains.

Three different type of head to tail polymers are possible in vinyl polymerisation.

- (i) **Atactic** in which stereocentres are randomly disposed on either side of the stretched carbon chain.
- (ii) **Syndiotactic** in which configuration of stereocentre alternate regularly.
- (iii) **Isotactic** in which all the stereocentres have identical configuration.

For example, head to tail polymerisation of propylene produces a polymer in which every other atom is a stereocentre. Many physical properties of the propylene depend on the stereochemistry of these centres.



There are three arrangements of methyl group and hydrogen along the chain at stereocentres. These are atactic, syndiotactic and isotactic as discussed above.

### Vinyl Polymers

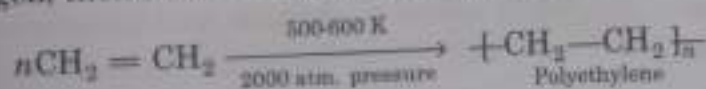
Some important vinyl polymers are :

(a) **Polythene** : It is an addition polymerisation and is of two types. Both types of polythene have widely different properties.

(i) Low density polyethylene (LDPE)

(ii) High density polyethylene (HDPE)

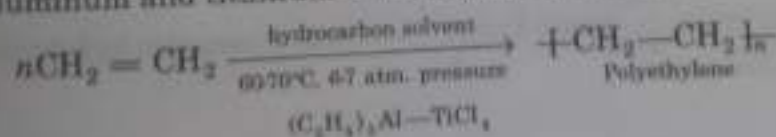
When pure ethylene is heated at 500-600 K and under a pressure of about 2000 atmosphere in presence of trace of oxygen, then **low density polyethylene** is obtained.



### Properties and Use

- (i) Such type of polymer is translucent, tough solid compound.
- (ii) It has insulating character so it is used cable insulation.
- (iii) It is a poor electrical conductor, chemical inert, tough and flexible plastic.
- (iv) It is used for packaging and in the manufacture of pipes, squeeze bottles and toys and is also used as a film.

When polymerisation of ethylene takes place by Ziegler-Natta process heating at comparatively low pressure and temperature, then **high density polyethene** is obtained. It is prepared by heating ethylene at 60-70°C temperature and 60-7 atm. pressure in a hydrocarbon solvent in presence of triethyl aluminum and titanium tetrachloride (catalyst)

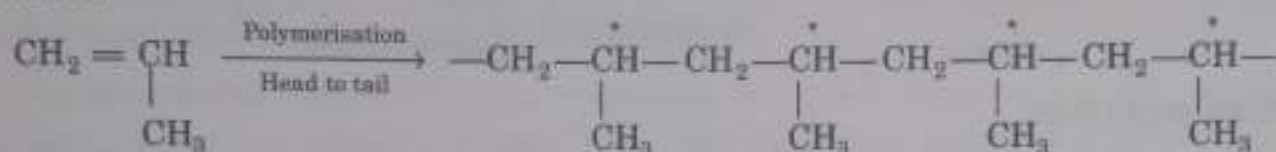


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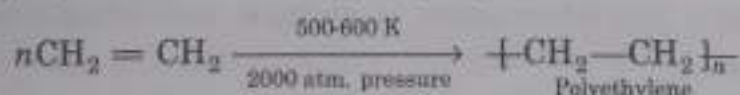
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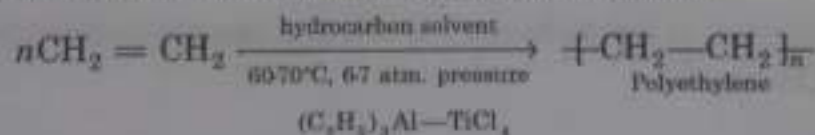
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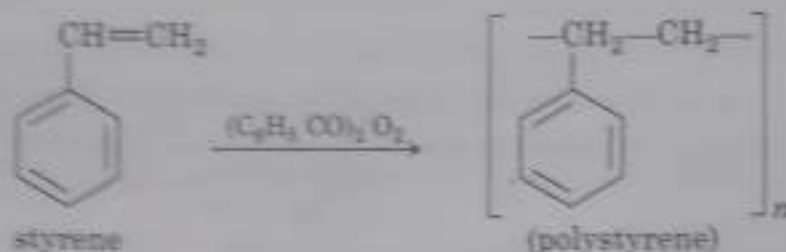




### Properties and Uses

- (i) HDPE is tougher and harder but chemically inert.
- (ii) It has more tensile strength than LDPE.
- (iii) It is mainly used in the manufacture of housewares such as buckets, pipes, dustbins, toys, bottles, containers, radio and television cabinets etc.

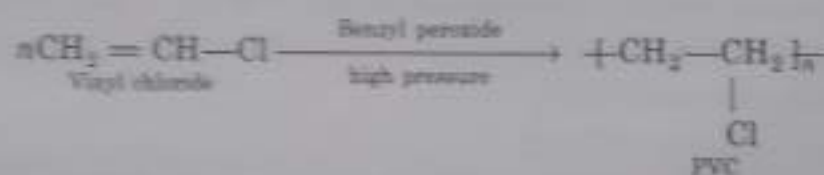
(b) **Polystyrene** : It is obtained by the polymerisation of styrene in presence of benzoyl peroxide.



### Properties and Uses

- (i) It is a white transparent thermoplastic.
- (ii) It is used in the manufacture of cosmetic bottles, food containers, combs, radio and television cabinets, tiles, plastic cups, packaging, toys and lead storage battery cases.

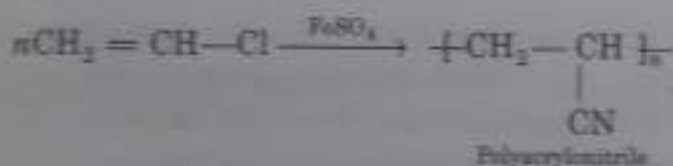
(c) **Polyvinyl chloride (PVC)** : Polymerisation of vinyl chloride in presence of benzoyl peroxide under high pressure give polyvinyl chloride polymer



### Properties and Uses

- (i) It is a thermoplastic and when esters of phthalic acid (plasticizer) is added, its plastic nature is increases.
- (ii) It is an electrical insulator.
- (iii) It is resistant to fire and chemicals.
- (iv) It is used for making rain coats, hand bags, vinyl floor covering sheets, gramophone records and electrical insulation coating on electrical cable.

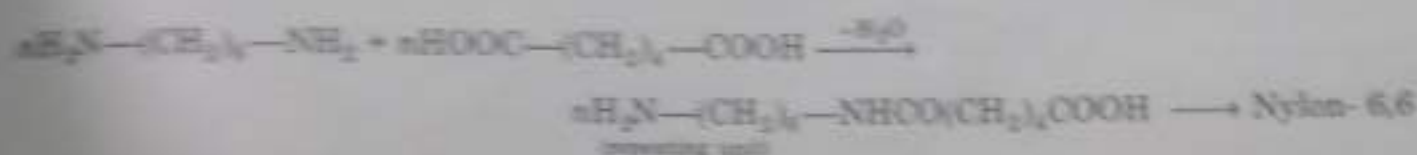
(d) **Polyacrylonitrile** : It is obtained by the polymerisation of acrylonitrile in presence of ferrous sulphate and hydrogen peroxide



It is also known as **acrylon**. It can be knitted or worn. It can also be blended with wool. It is used for clothes, carpets and blankets.

## Condensation Polymerisation or Step Growth Polymerisation

Intermolecular condensation between molecules containing two or more different functional groups i.e. between same or different monomers with the liberation of simple molecules like water, ammonia etc., from the reacting molecules is known as step growth polymerisation. For example, when condensation reaction between adipic acid and hexamethylene diamine takes place, Nylon-6,6 is formed.

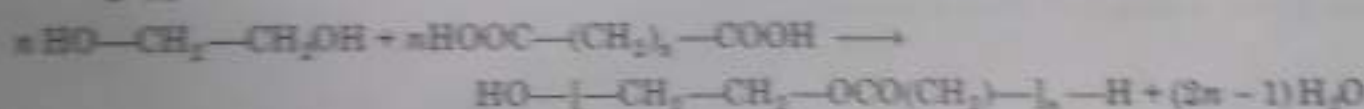


Nylon, terylene, bakelite etc. are some important condensation polymers.

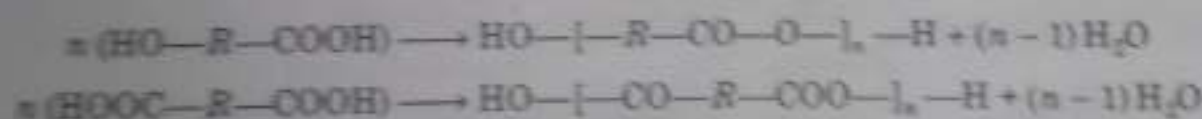
### Mechanism of Condensation Polymerisation

Two identical or different monomers condense with each other with or without elimination of molecules like water, alcohol to form a dimer. The dimer then condense with another molecule of monomer with the elimination of small molecule to form a trimer and progress goes on till a substance of high molecular weight is formed which is called as polymer. If both the reactants contain two functional group each then the reaction continues till the formation of a polymer.

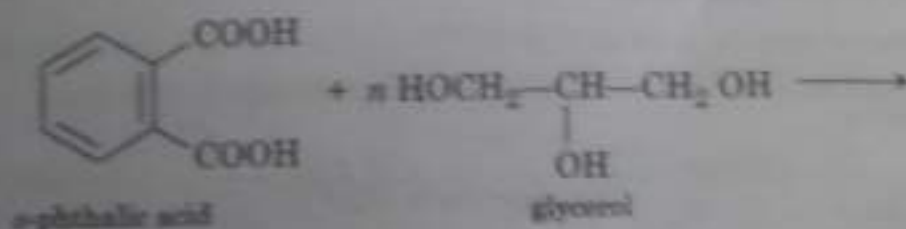
If  $n$  molecules of a dihydric alcohol condense with  $n$  molecules of a dibasic acid then a polymer of the following type is obtained.

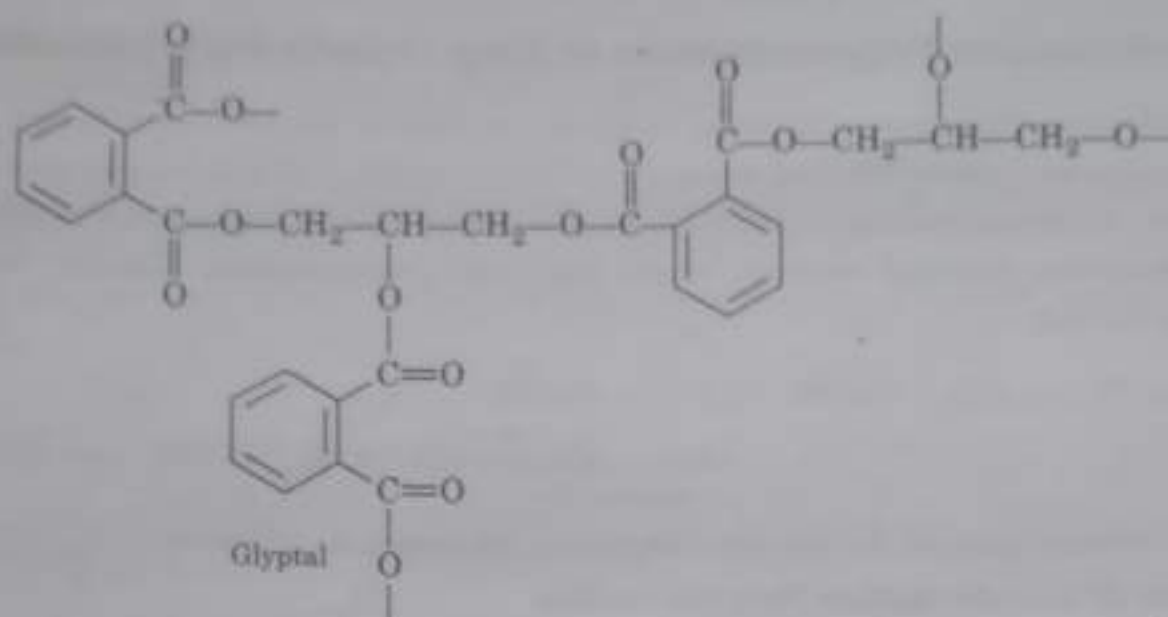


It is not necessary to use two different alcohol in condensation polymerisation. A monomer which has two functional groups can undergo condensation polymerisation, i.e., hydroxy acids and dibasic acids.



In this condensation polymerisation, elimination of some water molecules takes place and the polymer formed is always linear because it does not contain a third functional group for the continuity of the chain, but if both the reactants contain two or more functional groups then a three dimensional polymer will be formed. e.g., glycerol  $\text{HOCH}_2-\text{CHOH}-\text{CH}_2\text{OH}$  condenses with a dibasic acid like *o*-phthalic acid  $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$  to give glyptal (a thermosetting plastic)

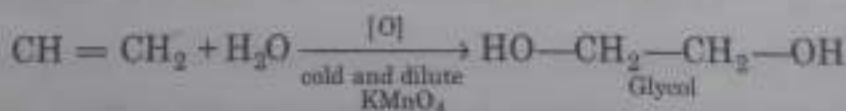
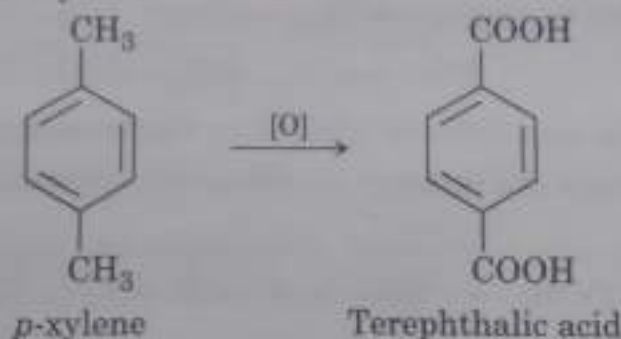




The condensation polymerisation reactions are applied in the manufacture of polymer of polyester and polyanhydrides (for nylons), polyamides (for terylene) polyurethans and silicone (for rubbers) urea-formaldehyde and phenol formaldehyde (for plastics.)

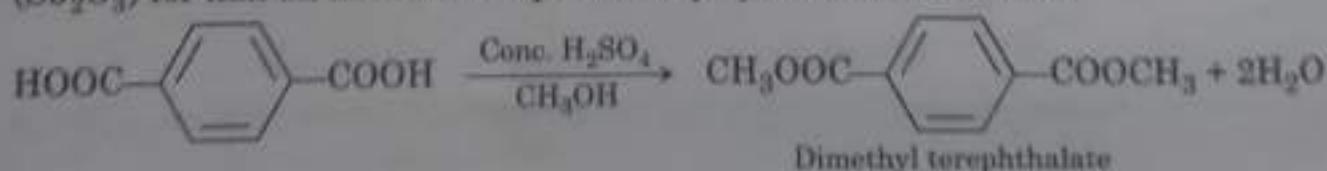
### Some Important Polymers

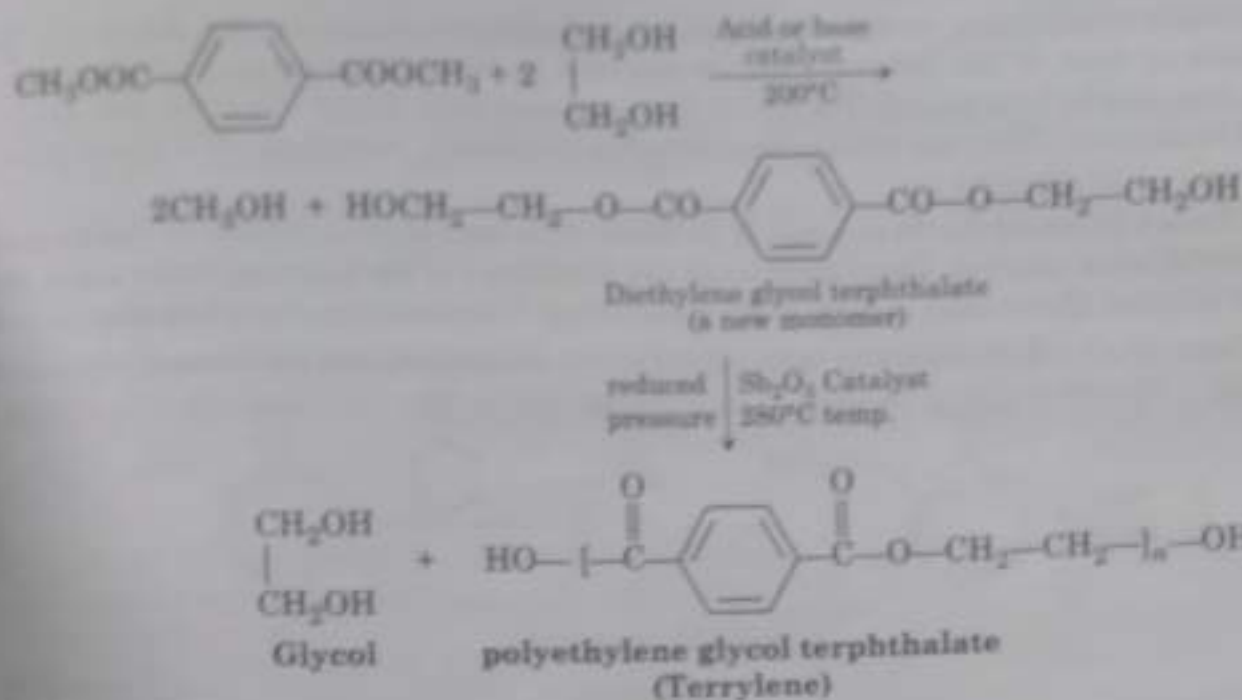
(a) **Polyesters** : Polyesters are the condensation polymers which are formed by the condensation reaction between polybasic acid and polyols. A typical polyester, terylene is prepared by the esterification of terephthalic acid with glycol. Terephthalic acid is obtained from *p*-xylene while glycol is obtained from ethylene.



*Synthesis of terylene is accomplished through two steps as :*

- (i) In this step first of all dimethyl ester of the acid is prepared, which is then treated with glycol at 250-260°C temperature in an inert atmosphere and gives diethylene glycol terephthalate (a new monomer).
- (ii) This monomer of step (i) is heated at 280°C under reduced pressure in presence of catalyst ( $\text{Sb}_2\text{O}_3$ ) for half an hour for completion of polymerisation reaction.

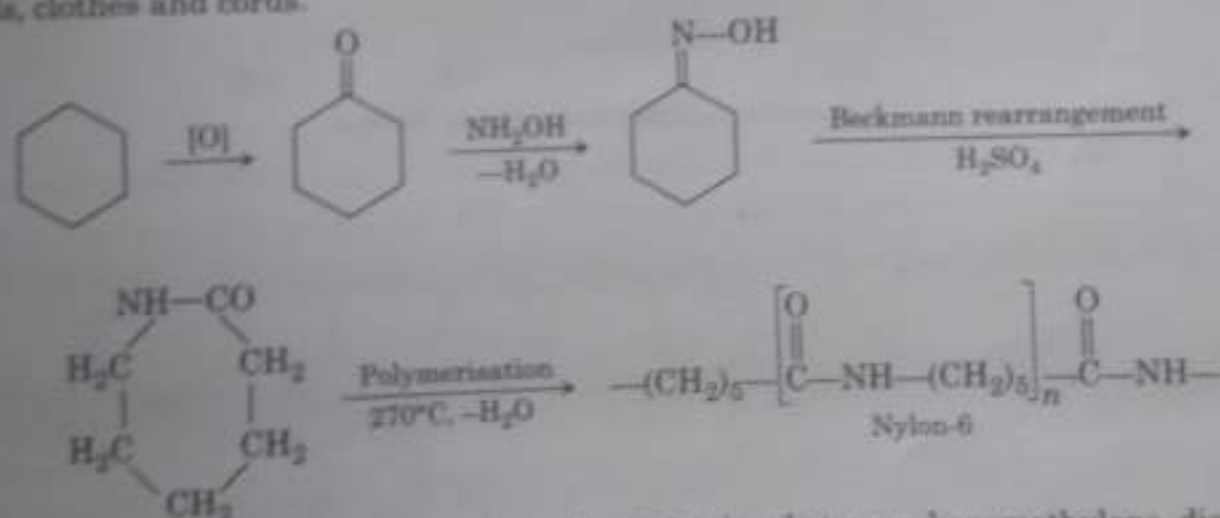




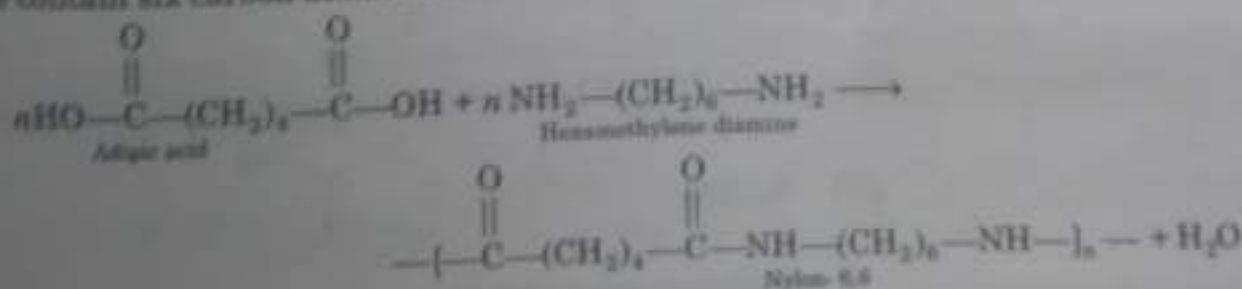
Terylene is converted into fibres for manufacture of textiles.

(b) **Polyamides (Nylon)** : Many polyamides have been prepared by heating diamines with dicarboxylic acids. Some common polyamides are Nylon-6, 6, Nylon -6 etc.

(i) **Nylon-6 or Perlen** : It is obtained by the polymerisation of caprolactam (Perlon - L) monomer. As this monomer contains six carbon atoms so it is called as Nylon-6. It is mainly used in tyre cords, clothes and cords.



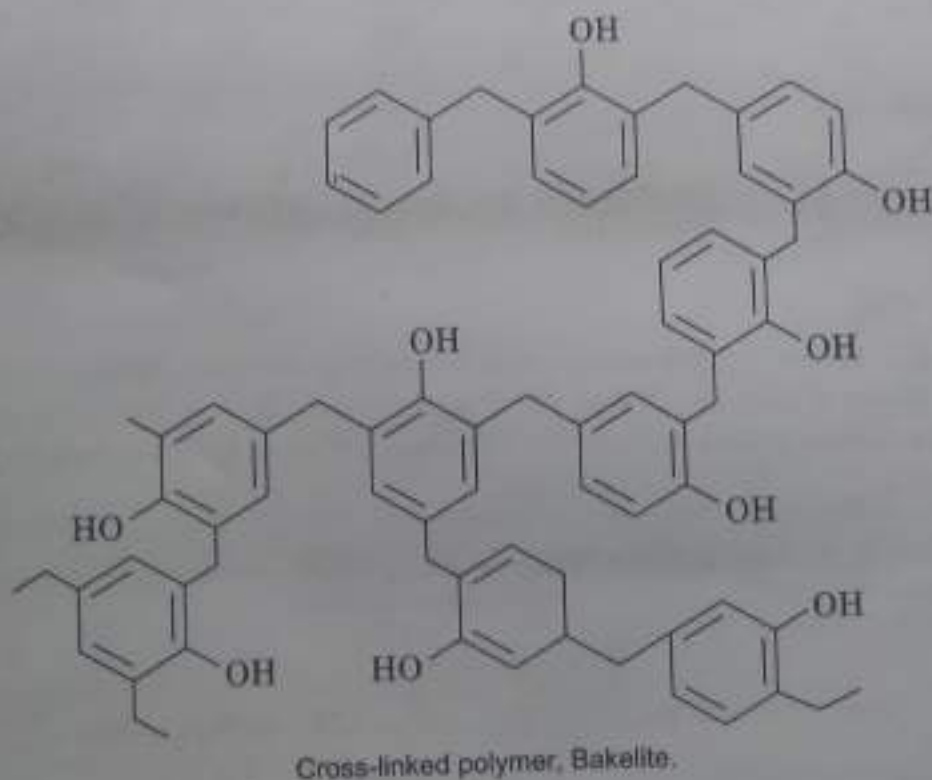
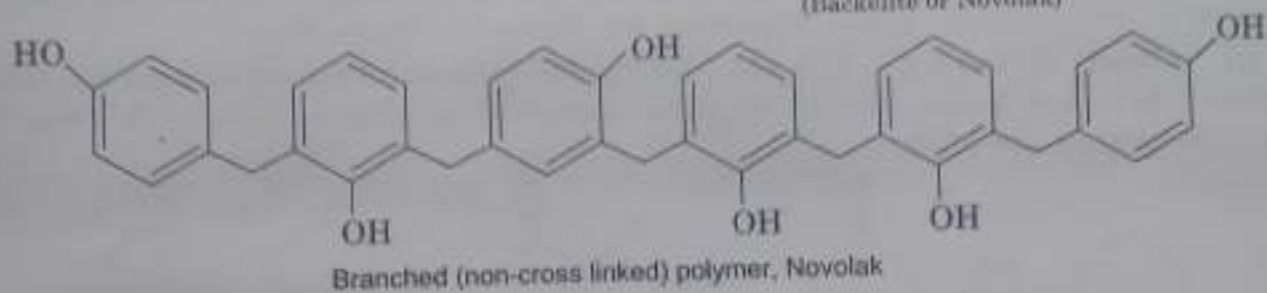
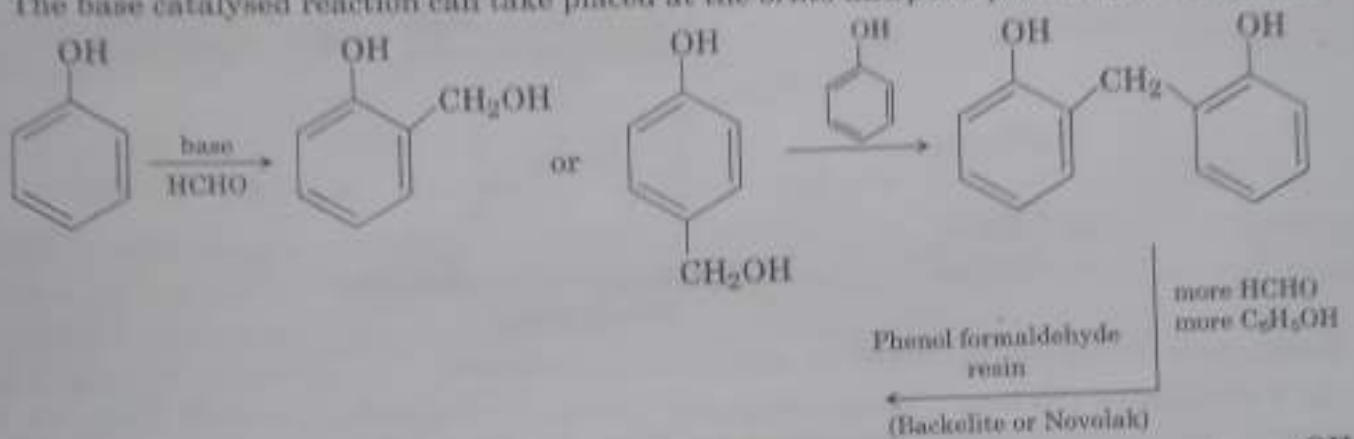
(ii) **Nylon 6,6** : When condensation polymerisation between hexamethylene diamine and adipic acid takes place, a polymer Nylon -6, 6 is obtained. Both adipic acid and hexamethylene diamine contain six carbon atoms each so the obtained polymer is called nylon - 6, 6.



Nylon-6, 6 is extremely strong, elastic, tough and abrasion resistant fibre. Its *m. p.* is 250°C. It is insoluble in most of the common organic solvents at room temperature but dissolves only in phenols, cresols and formic acid. The nylon fibres possess high tensile strength and are hard and resistant to abrasion. They are used in toothbrushes, bedsheets, thread etc. It is mixed with wool to prepare socks and sweaters.

(c) **Phenol formaldehyde resins** : It is obtained by the reaction of phenols and formaldehyde in presence of basic catalyst. Depending upon the conditions of the reaction either a low molecular branched polymer (**Novolak**) is formed or cross-linked thermosetting resin **bakelite** is produced.

The base catalysed reaction can take place at the *ortho* and *para* positions of the phenol.



These are used as solid primers and a used for the manufacture of electrical appliances such as insulators and plugs.

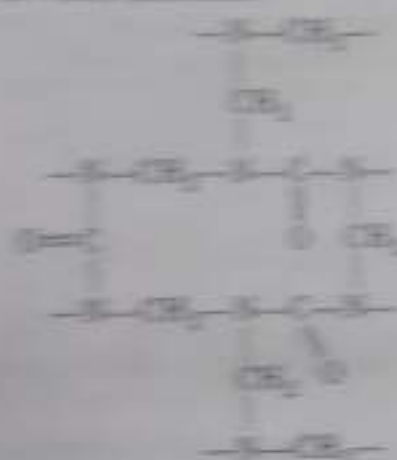
(b) **Unsaturated polyester resins** : These resins are important polymers produced by the reaction between unsat and benzaldehyde.



Condensation followed by cross-linking on heating produces crosslinking.



In polymerization, crosslinking gives a cross-linked three dimensional structure and insoluble resin by elimination of water molecule.

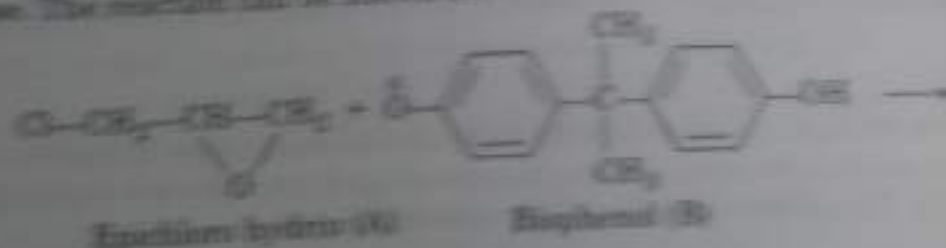


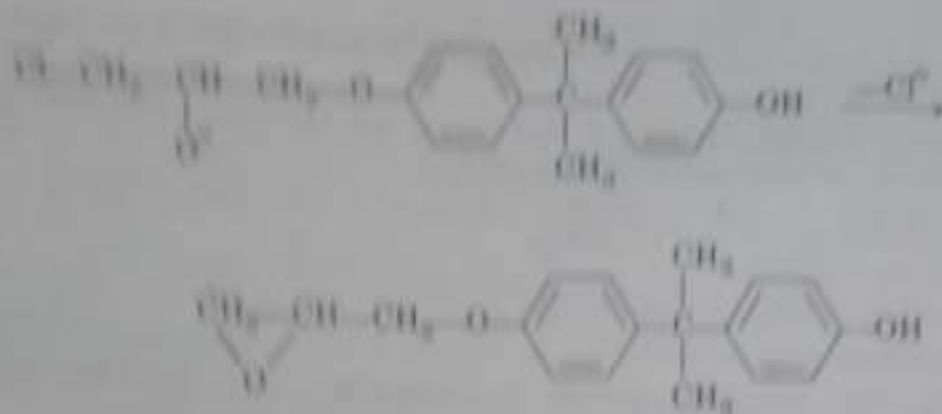
Unsaturated polyester resin (cross-linked three dimensional structure)

(c) **Epoxy resins** : The epoxy resins are produced by the reaction between an epoxide and a dihydroxy compound.



Most of the epoxy resins are made by the reaction of epichlorohydrin (E) with a bisphenol (B) in presence of a base. The reaction can be shown as:

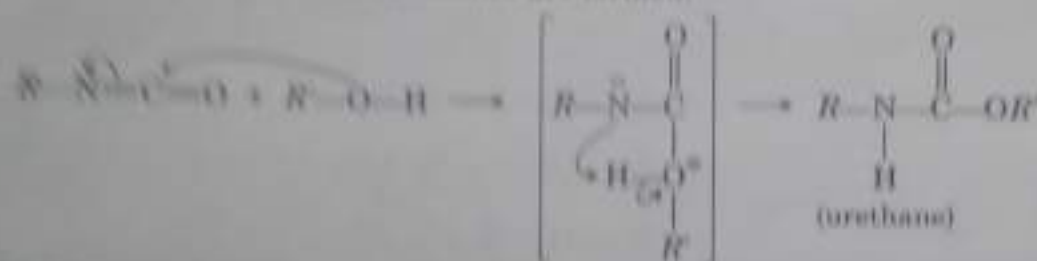




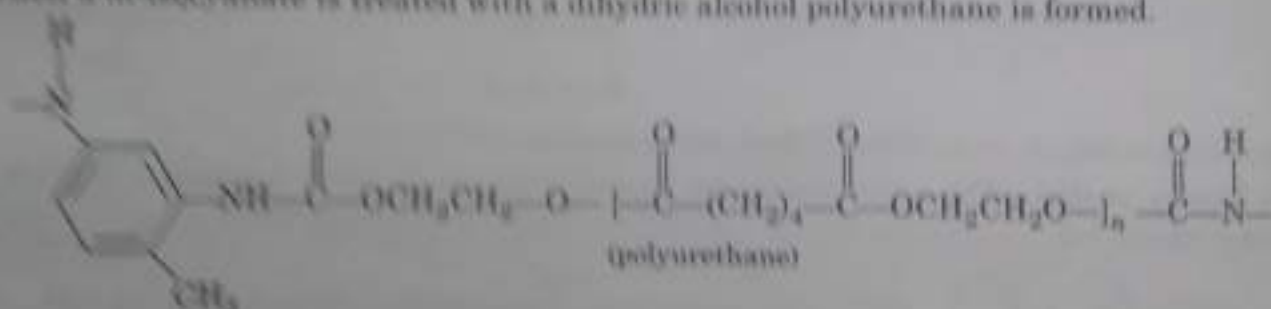
(An epoxy resin)

These polymers are soluble in water and are used in manufacture of electrical equipment, in insulating materials, for flooring and find wide range of application in cosmetics, pharmaceuticals and lubricants.

(ii) **Polyurethane** : When the compounds containing active hydrogen (as alcohols) add across the  $\text{N} = \text{C}$  double bond of isocyanates, urethanes are formed.



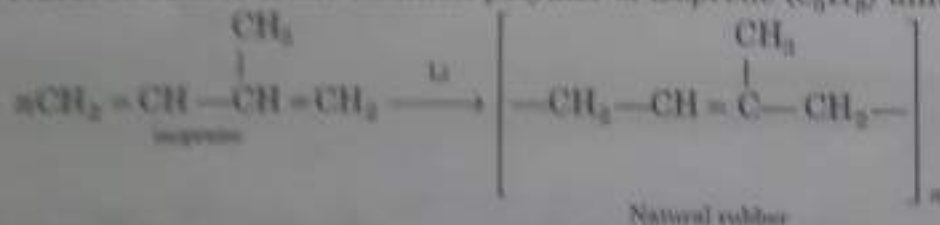
When a di-isocyanate is treated with a dihydric alcohol polyurethane is formed.



**Polyurethanes** are resistant to acid or alkaline. It is used in the development of foams which are used for household and office furnitures and automobile cushioning.

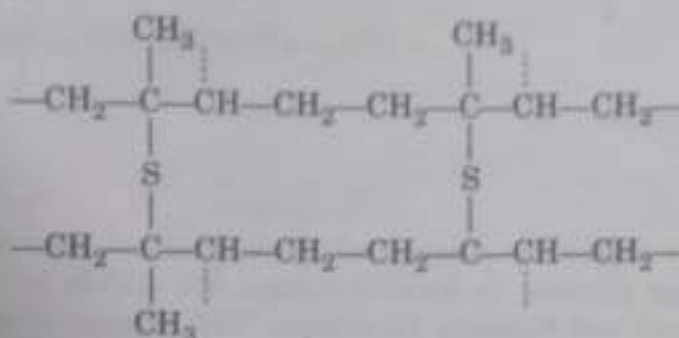
### Natural and Synthetic Rubber

**Natural rubber** is obtained from the tree *Hevea brailliensis*. The rubber is produced from a milky white colloidal latex. It has 30-40% rubber, 0.3% proteins, 0.25% sugar, 0.5% ashes and remaining water. Natural rubber is the addition-polymer of isoprene ( $\text{C}_5\text{H}_8$ ) units (approx. 10000)

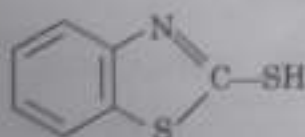
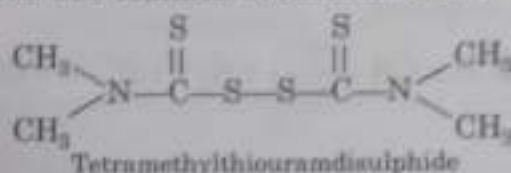
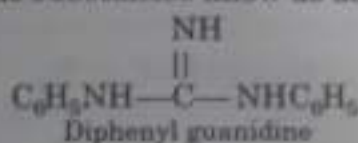


Natural rubber obtained as above is soft, sticky and gummy mass. It has low elasticity and low tensile strength, hence it is not used as such. In order to give strength and elasticity to it, cross links are introduced in it. This process is called **Vulcanisation**.

In Vulcanisation process, natural rubber is treated with sulphur under heat so to modify its properties. Sulphur reacts with the polymer molecule forming a cross linked network. Due to cross linking strength of the rubber increases. When vulcanised rubber is stretched then these isoprene units are also stretched but do not slip on one another. On removing stress, isoprene chains come back to their original state.



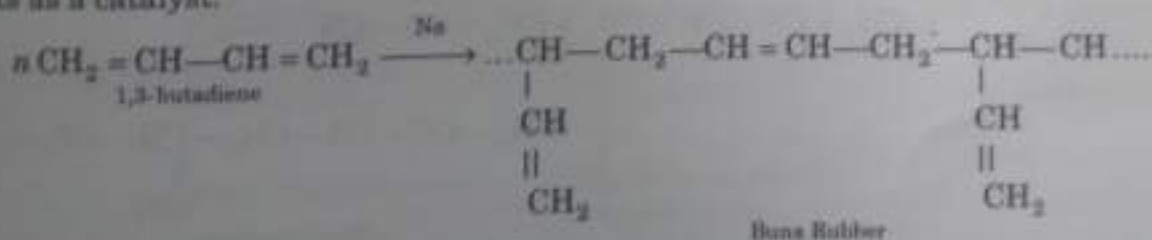
The vulcanisation process converts the natural rubber into either soft rubber (5% sulphur) or hard rubber (30-35% sulphur). The Vulcanisation process can be enhanced in the presence of certain organic substances known as accelerators. The common accelerators are :



Mercaptobenzo thiazole

**Synthetic rubbers :** Synthetic rubbers have been produced by the polymerisation of a large number of conjugated dienes like isoprene. Some important synthetic rubbers are given as :

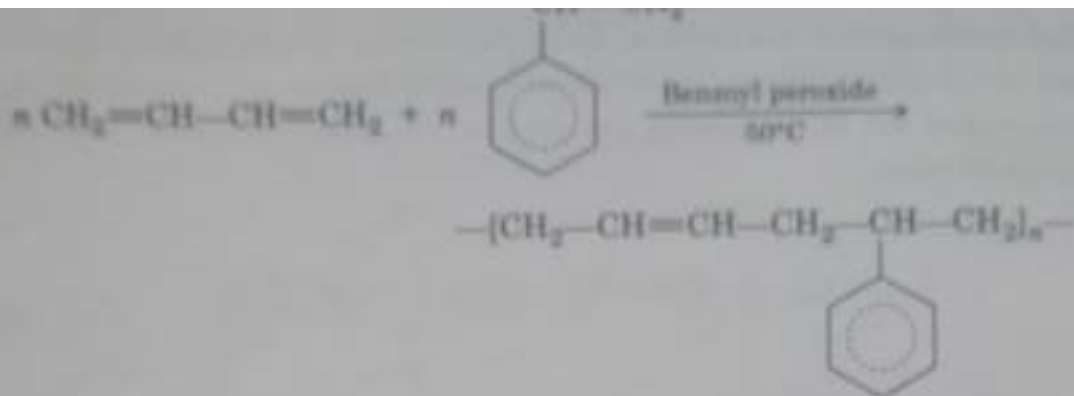
(1) **Buna Rubber :** It is prepared by the reaction of sodium with 1,3-butadiene. In this reaction sodium acts as a catalyst.



Buna rubber has properties similar to that of natural rubber but it is more precious than natural rubber.

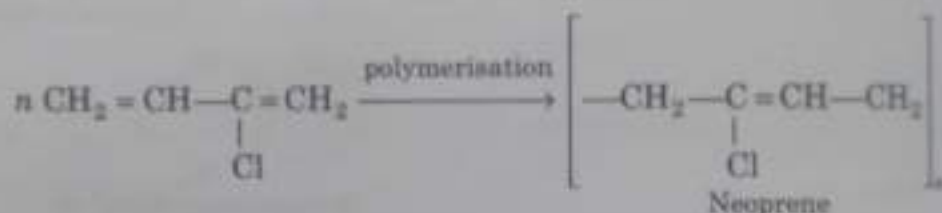
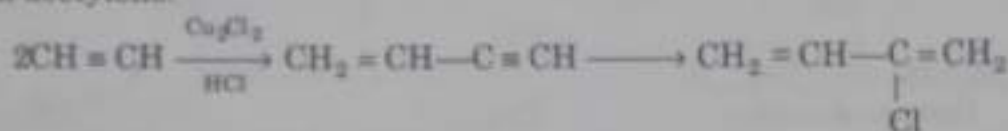
(2) **Buna-s-rubber, SBRC styrene-butadiene rubber :** It is a copolymer of 75% butadiene and 25% styrene. The polymerisation is carried out in presence of benzoyl peroxide catalyst at 50°C. This rubber has approx similar number of double bonds as natural rubber has.





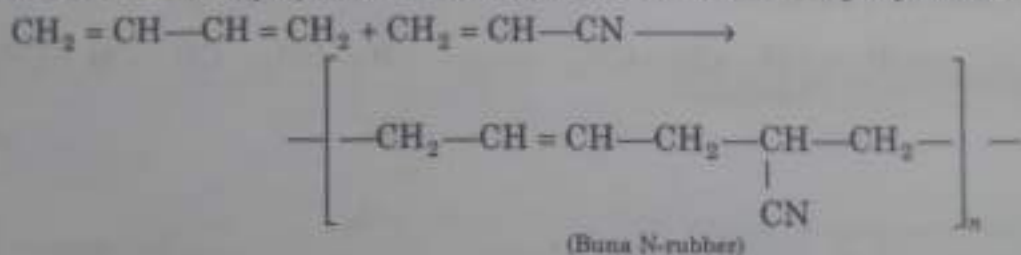
Since Buna-S polymer molecules possess ethylenic linkages they can also be vulcanised by sulphur to give cross-linked polymer. In Buna-S rubber, 'Bu' stands for butadiene, 'na' stands for sodium (polymerising agent) and S-stands for styrene. SBR is used in manufacturing tyre treads and mechanical rubber goods.

(3) **Neoprene** : This synthetic rubber is similar to natural rubber 2-chloro butadiene (chloroprene) on polymerisation gives neoprene. It is also called diprene. The monomer, chloroprene is prepared from acetylene.



Neoprene has similar properties to that of natural rubber. It is non-inflammable. It is inactive towards oil, hydrocarbon, light, air and heat. It is used in the manufacturing of refrigerator parts, automobile and used for insulation of electric wires.

(4) **Buna N (BNR) Rubber** : It is copolymer of 75% butadiene and 25% vinyl cyanide.



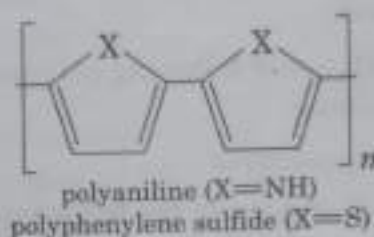
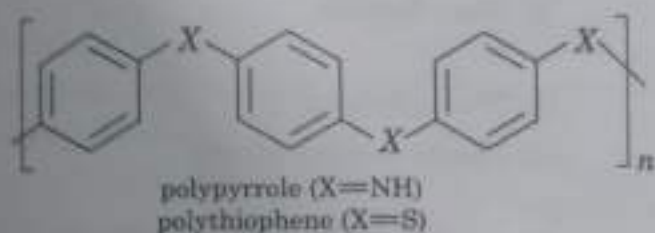
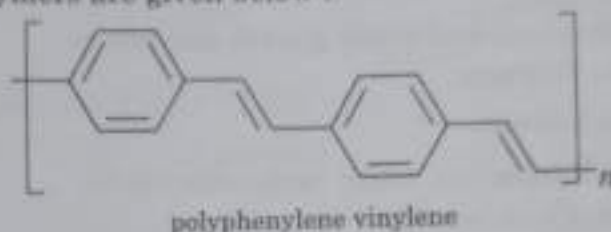
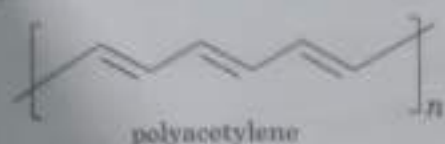
It is also known as perbunan. It is extra ordinarily resistant to oils, chemicals, aging and abrasion. It finds use in fuel tanks.

## Elementary idea of Organic conducting Polymers

Conductive polymer or intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semi-conductors. The main advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show

similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic-synthesis and by advanced dispersion techniques.

Chemical structures of some conductive polymers are given below :



Polyacetylene, polypyrrole, polyindole and polyaniline and their copolymers are the main class of conductive polymers. Poly (*p*-phenylene vinylene) (PPV) and its soluble derivatives are emerged as the prototypical electroluminescent semi conducting polymers. Today, poly (3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

Some organic conductive polymers according to their composition are given in the following table :

The main Chain contains	No hertero atom	Hetero atoms present	
		Nitrogen-containing	Sulphur-containing
Aromatic cycles	Poly (fluorene)s Polyphenylenes  Polypyrenes  Polyazulenes  Polynaphthalenes	The N is in the asromatic cycle : Poly (pyrrole)s (PPY) Poly carbazoles  Polyindoles  Polyazepines  The N is outside the aromatic cycle : polyanilines (PANI)	The sulphur is in the aromatic cycle : Poly (thiophene)s (PT) Poly (3, 4- ethylene dioxothiophene) (PEDOT)  The S is outside the aromatic cycle : Poly ( <i>p</i> -phenylene sulfide) (PPS)
Double bonds	poly (acetylene)s (PAC)		
Aromatic cycles and double bonds	poly ( <i>p</i> -phenylene vinylene) (PPV)		