

M.Sc. IV Semester

Chemistry
Paper - IV (Polymers)

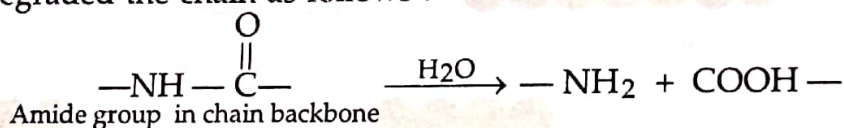
▶ POLYMER REACTIONS

A polymer molecule contains functional groups which are not very much different in behaviour from those of a simple organic molecule. On the basis of the chemical nature of the functional groups, they can undergo a variety of reactions and form a polymer structure with entirely new properties and applications. Because of this reason, various interesting reactions are available with polymer molecules. Some of them are discussed as :

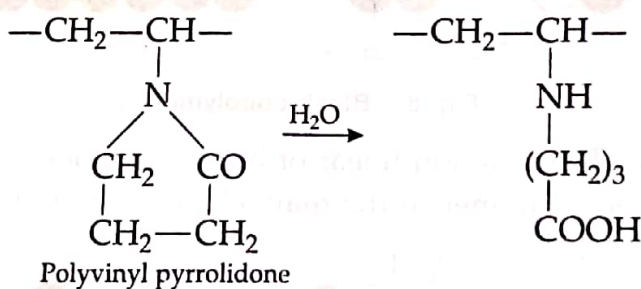
HYDROLYSIS

Hydrolysis proceeds in the presence of acids or alkalis. Polymers containing amide ester and acetal groups can be easily hydrolysed.

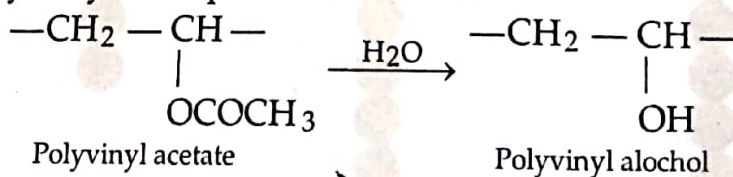
When these functional groups present in the backbone of the polymer chain, the hydrolysis degraded the chain as follows :



Contrary to this, when these groups are present in the side chain of the polymer molecule, hydrolysis causes only to a change of functional group and not any chain degradation as shown below :



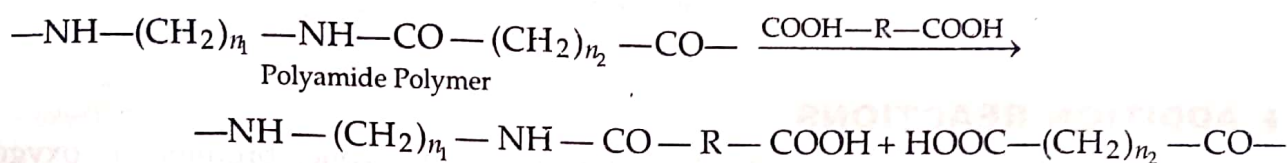
Another example of degradation of side chain is an polymer having ester linkage which can be easily hydrolysed in presence of an alkali as :



In hydrolysis reactions, the chemical composition of the polymer repeat unit is changed, but its degree of polymerisation remains same.

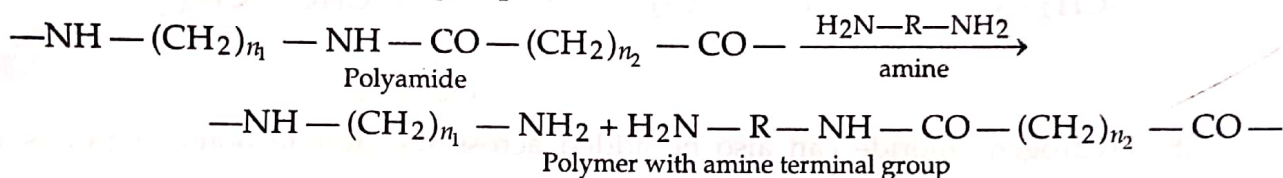
▶ ACIDOLYSIS

Acidolysis is the degradation of the molecule in presence of an acid. In polymers, the splitting of the bond of a high polymer weight polyamide takes place resulting into a low molecular acid as follows :



▶ AMINOLYSIS

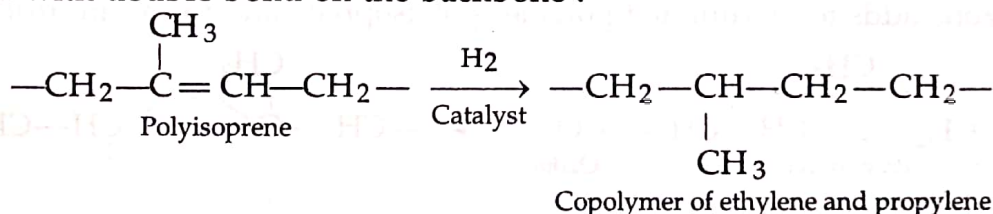
Aminolysis occurs in presence of an amine. This reaction is similar to acidolysis, where splitting of a high molecular weight polymer involves resulting into a low molecular weight polymer with an amine terminal group as follows :



▶ HYDROGENATION

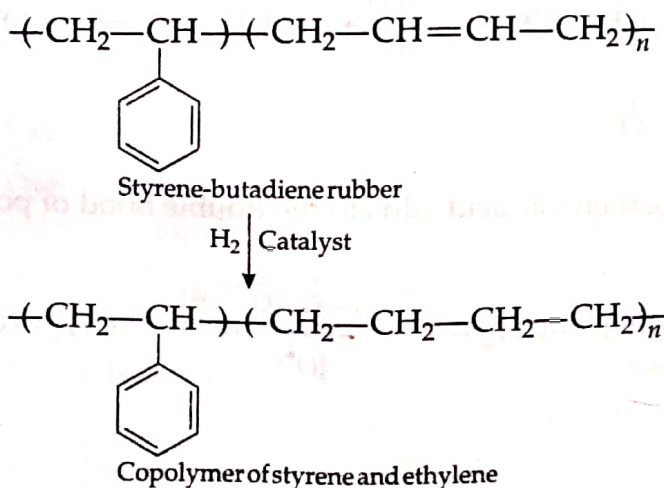
Hydrogenation is a property of unsaturated organic molecules. In the presence of a catalyst, hydrogen can be added in main chain of the polymer molecule as well as side groups of the polymer chain containing double bonds, as discussed below :

Polymer with double bond on the backbone :

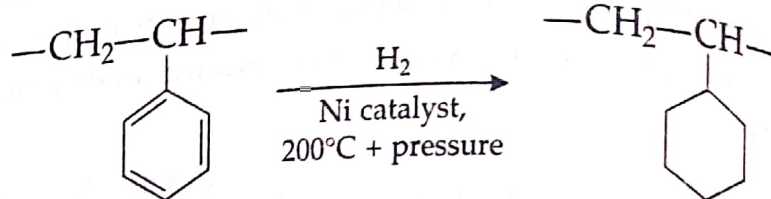


In polyisoprene, hydrogen is added on the backbone and forms a polymer resembling an alternating copolymer of ethylene and propylene.

In another example, copolymer styrene and ethylene is formed by the hydrogenation of Buna-S rubber.



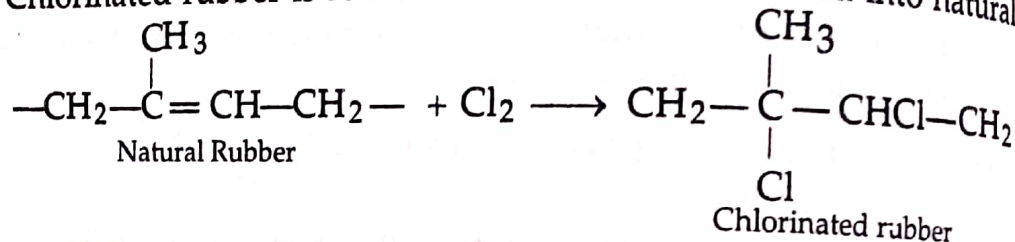
Polymer with double bond on the side chain group



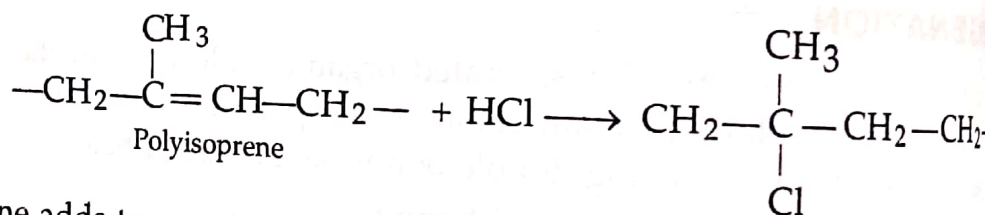
▶ ADDITION REACTIONS

Addition reactions of chlorine, hydrogen chloride, ozone, bromine on unsaturated polymer molecules are also found as :

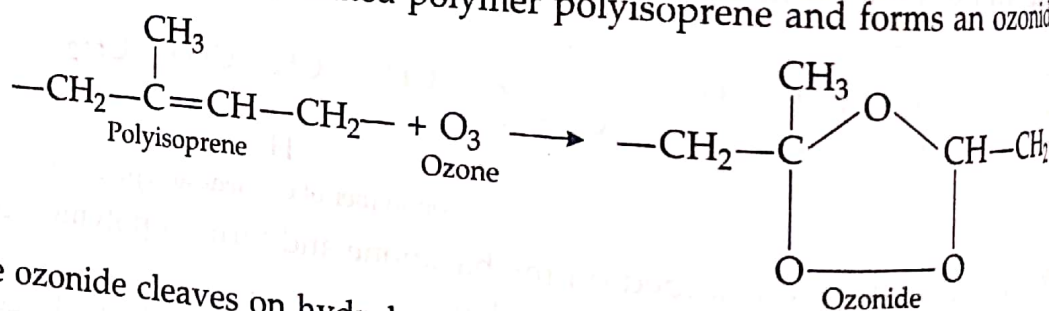
(a) Chlorinated rubber is formed when chlorine is added into natural rubber



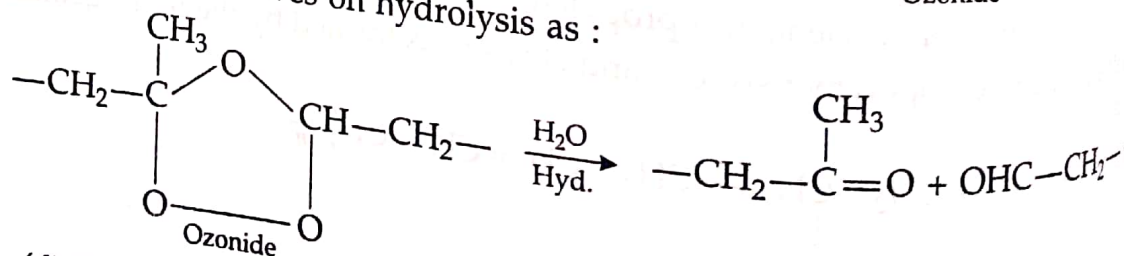
(b) Hydrogen chloride can also be added across the double bond of a molecule as :



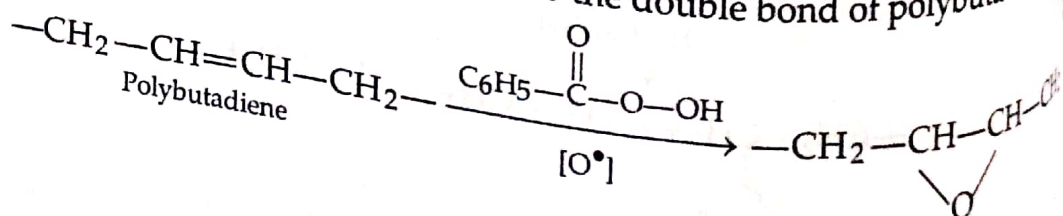
(c) Ozone adds to unsaturated polymer polyisoprene and forms an ozonide



The ozonide cleaves on hydrolysis as :

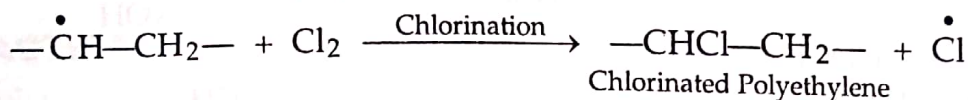
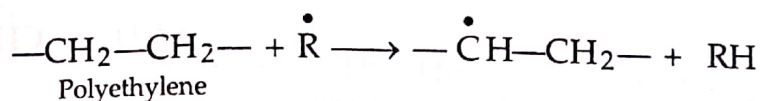


(d) Oxygen from perbenzoic acid adds to the double bond of polybutadiene as

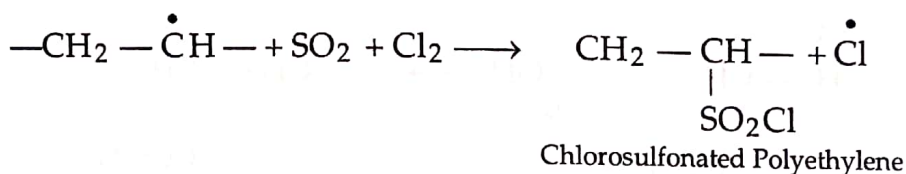
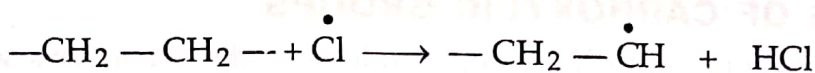


▶ SUBSTITUTION REACTIONS

Substitution reactions can be involved in saturated polymers through a radical chain process.



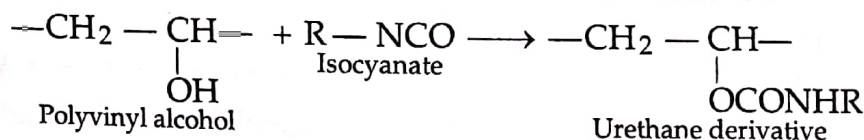
In another substitution reaction, chlorosulfonation of polyethylene can be carried out as follows :



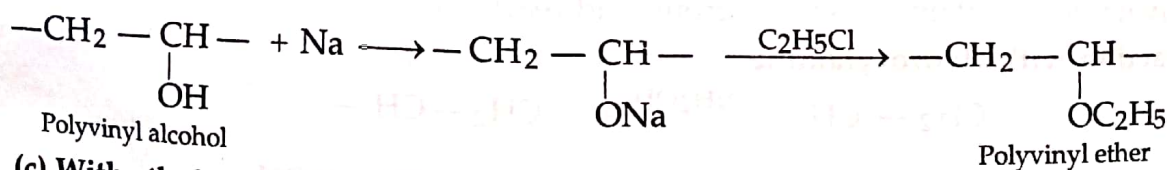
▶ REACTION OF HYDROXYL GROUPS

Polymer molecules, which consist of hydroxyl groups in their structure give following reactions :

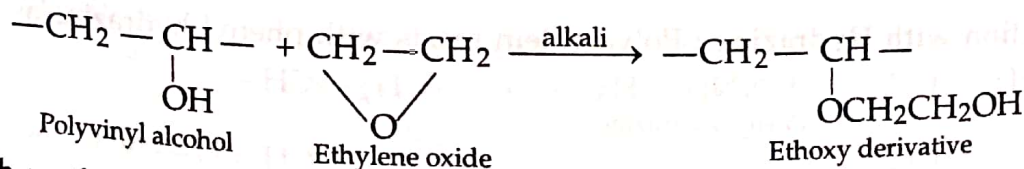
(a) **With Isocyanates** : Polymer molecule, containing hydroxyl group such as polyvinyl alcohol reacts with isocyanate and forms a derivative of urethane as :



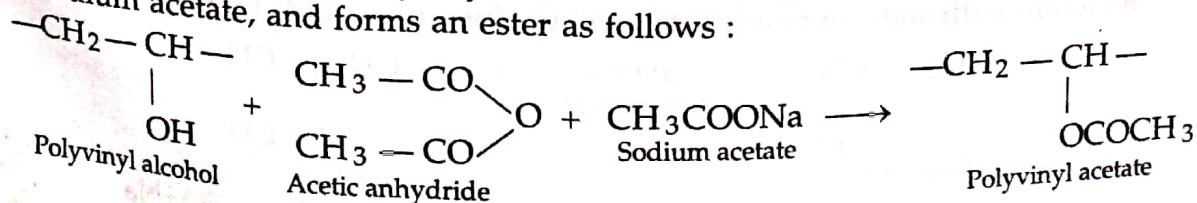
(b) **With metallic sodium** : Polymer polyvinyl alcohol can react with metallic sodium and forms a product. This product further reacts with alkyl halides and gives polyvinyl ether.



(c) **With ethylene oxide** : Polyvinyl alcohol can react with ethylene oxide in presence of an alkali as :

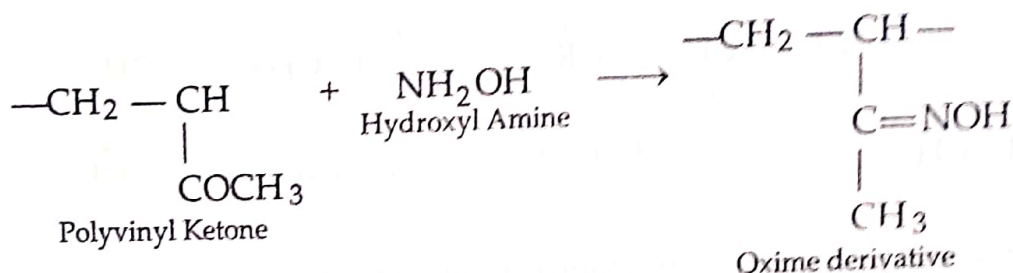


(d) **With acetic anhydride** : Polyvinyl alcohol can also react with acetic anhydride and anhydrous sodium acetate, and forms an ester as follows :



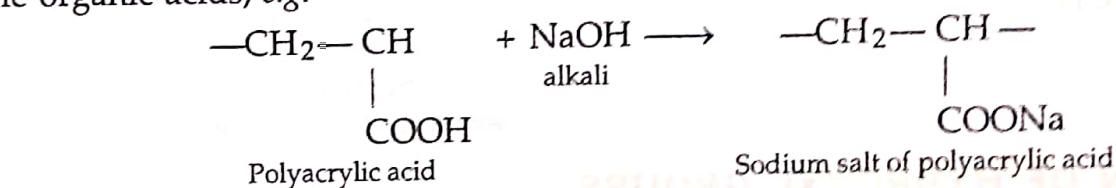
▶ REACTION OF KETONIC GROUPS

Polyvinyl ketone consists of a ketonic group and reacts with hydroxylamine as follows :

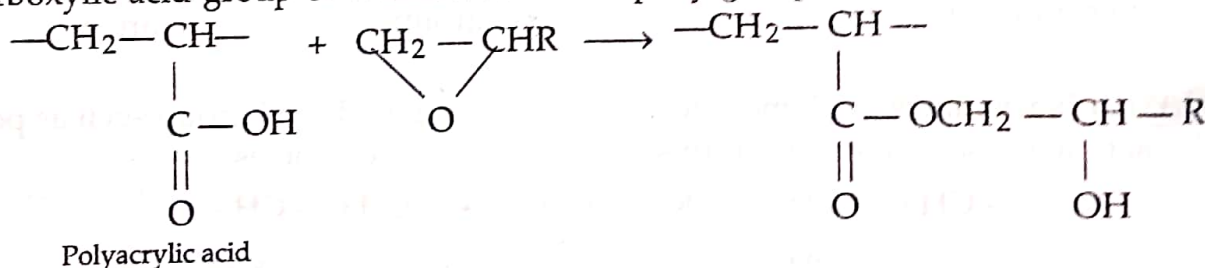


▶ REACTIONS OF CARBOXYLIC GROUPS

Polymer containing $-\text{COOH}$ groups undergoes those reactions which are found in simple organic acids, e.g.



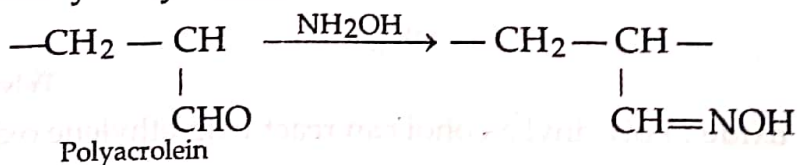
Carboxylic acid group can form ester with epoxy groups as :



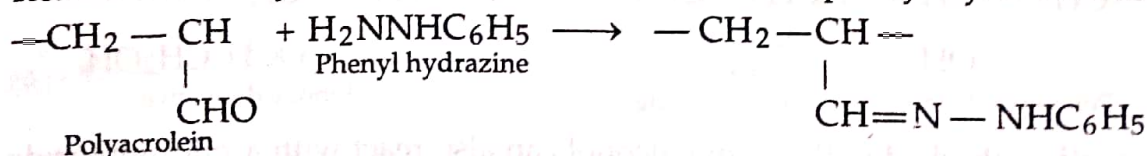
▶ REACTIONS OF ALDEHYDE GROUPS

Aldehyde groups of polymers react in similar way to that of a simple organic aldehyde. Polyacrolein contains aldehyde group and reacts as :

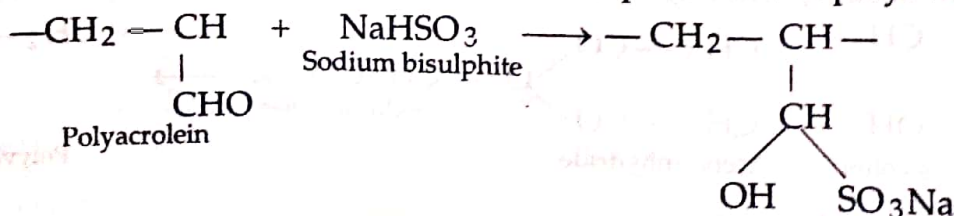
Reaction with Hydroxylamine



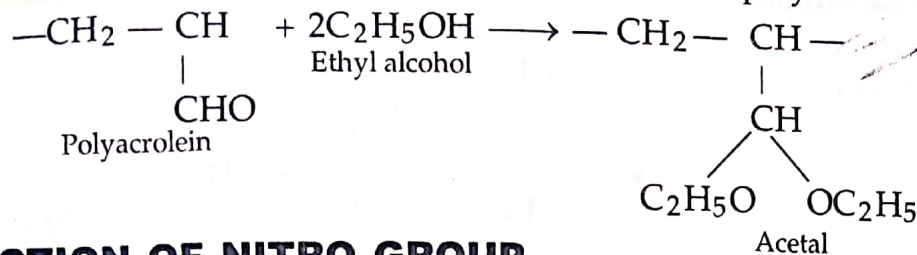
Reaction with Hydrazine : Polyacrolein reacts with phenyl hydrazine as :



Reaction with sodium bisulphite : Sodium bisulphite adds to polyacrolein as follows :

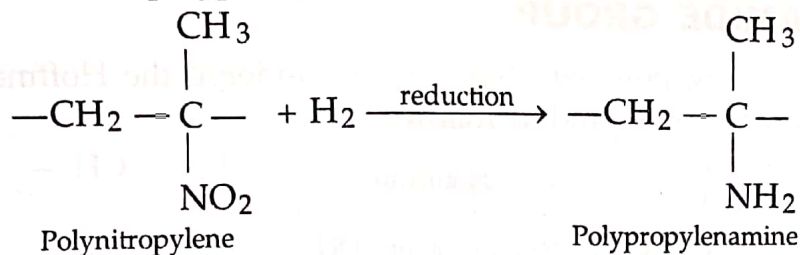


Reaction with alcohols : On treating with alcohol polyacrolein gives acetals :



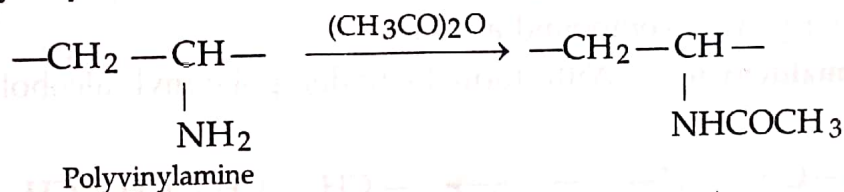
▶ REACTION OF NITRO GROUP

Polymer containing nitro group can be converted to amino group on reduction. Polynitro propylene forms polypropylenamine as follows :



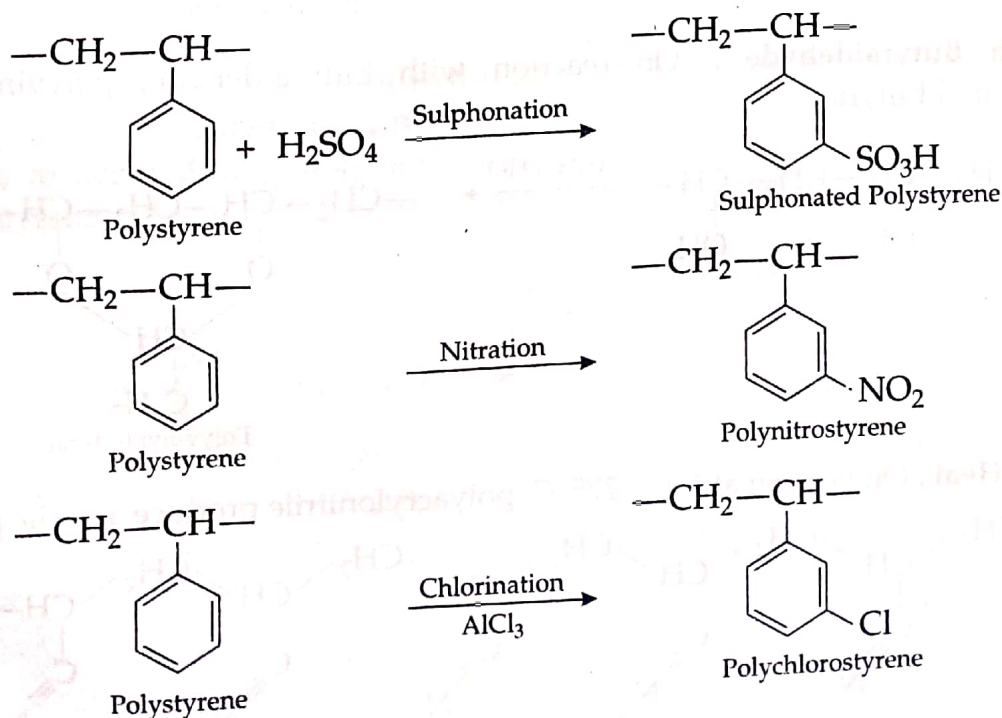
▶ REACTION OF AMINO GROUP

Polymer polyvinyl amine reacts with acetic anhydride and gives a modified polymer :

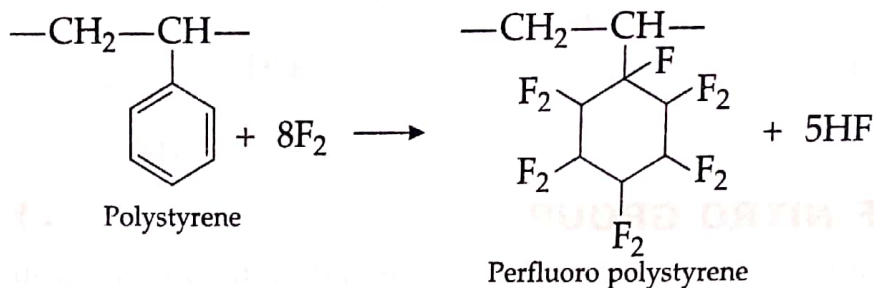


▶ REACTION OF AROMATIC RING

Polymers having aromatic rings, can undergo reactions characteristic to aromatic nucleus. The benzene nucleus of polystyrene shows various reactions of aromatic rings as :

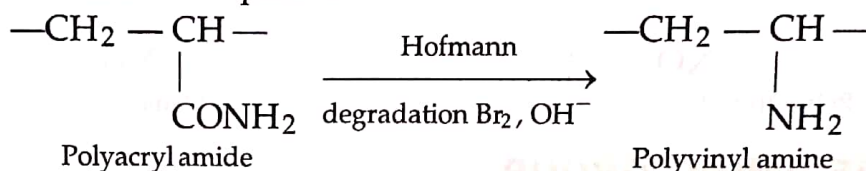


Polystyrene forms an important polymer perfluoropolystyrene by fluorination reaction :



▶ REACTION OF AMIDE GROUP

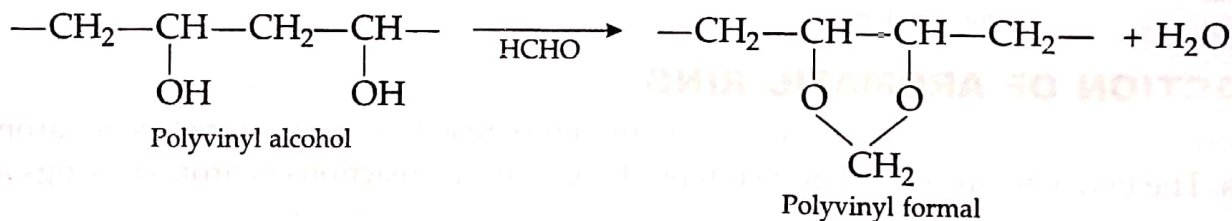
Amido group containing polymer molecule can undergo the Hoffmann degradation reaction and produce amino compound as follows :



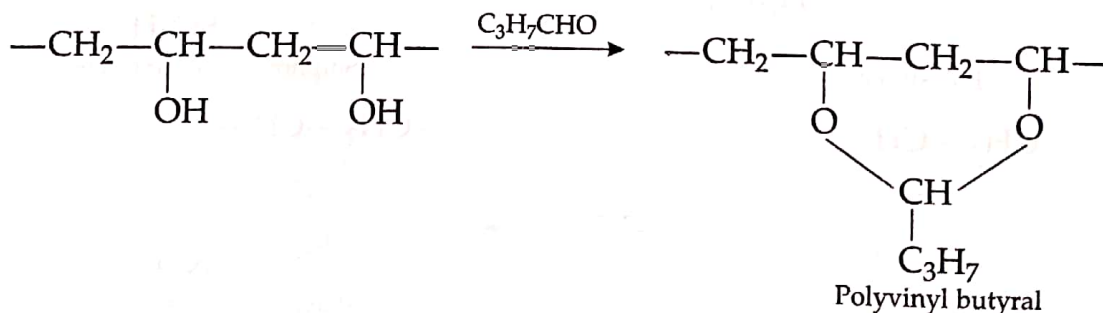
▶ CYCLISATION REACTION

Polymers can form cyclic compound as follows :

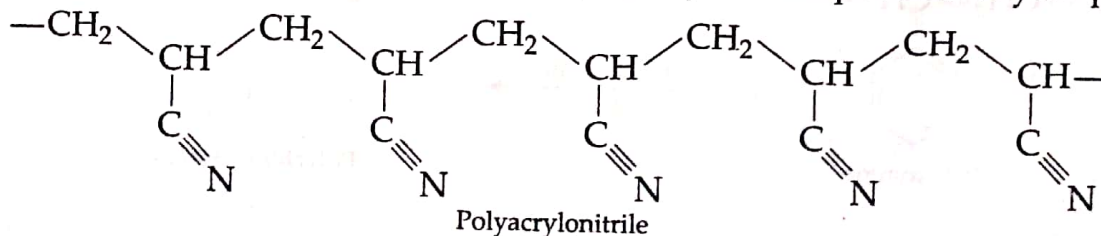
(a) **With Formaldehyde** : With formaldehyde, polyvinyl alcohol gives a cyclic compound as :

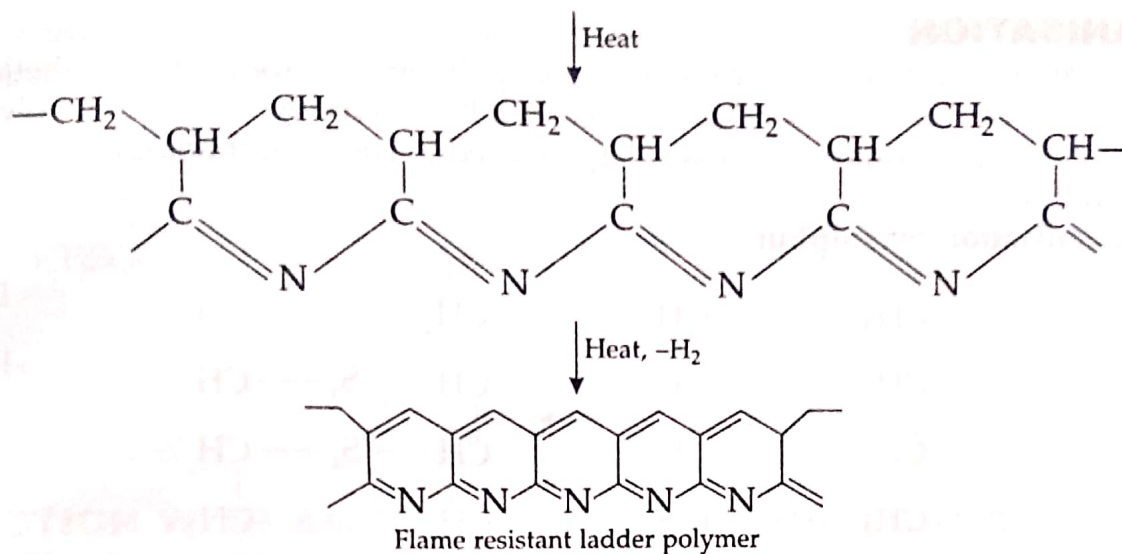


(b) **With Butyraldehyde** : On reaction with butyraldehyde, polyvinyl alcohol produce polyvinyl butyral.

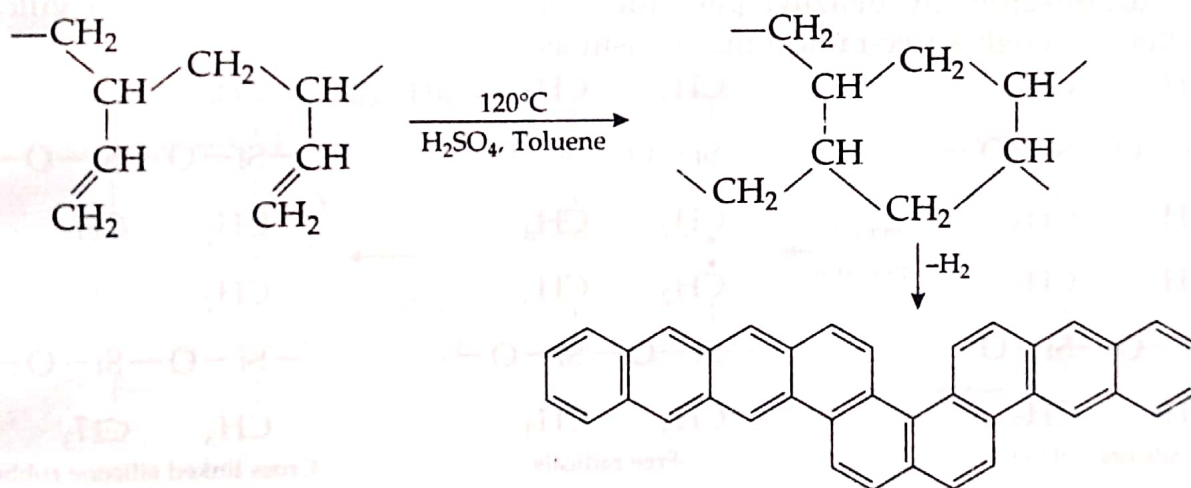


(c) **With Heat** : On heating at 160 – 275°C, polyacrylonitrile produce a cyclic polymer.



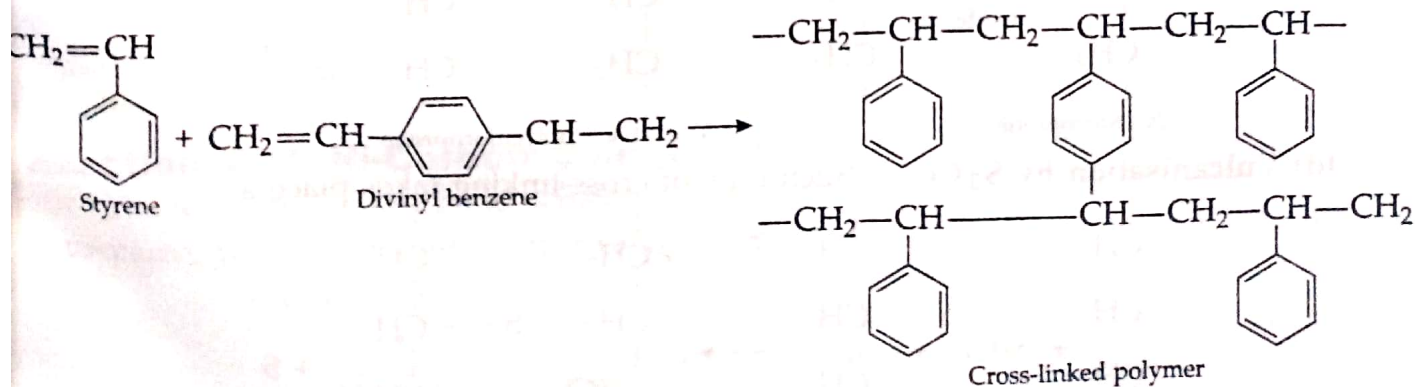


On heating in presence of an acid, polybutadiene gives a cyclic compound as follows :



CROSS-LINKING REACTIONS

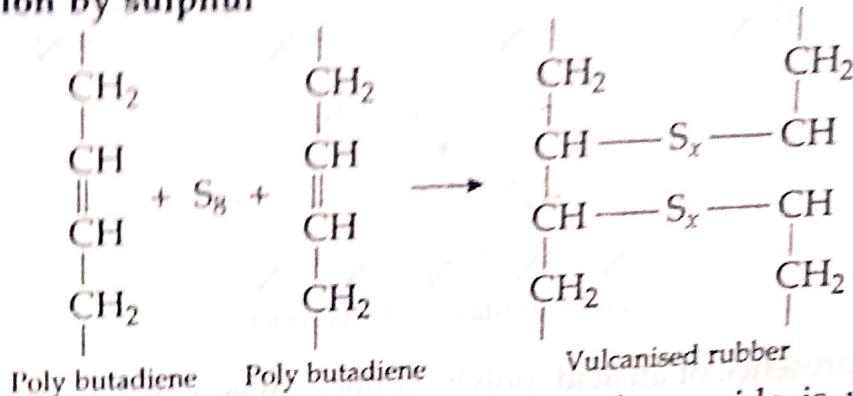
When bridge of a covalent bond or hydrogen bond is formed between linear polymer chains, leading to a three dimensional network is known as 'cross-linking'. Cross-linking could be made to occur during polymerisation. For example, a cross-linked polymer is formed when styrene polymerised with small amounts of divinyl benzene as :



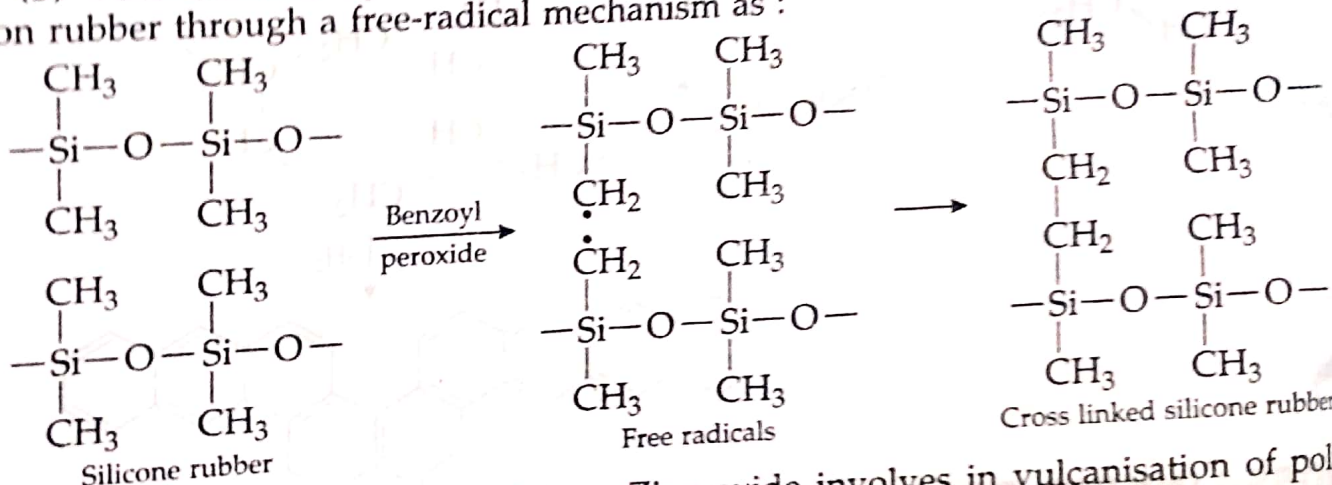
♦ VULCANISATION

Vulcanisation is a process of cross-linking of polymer in natural and synthetic rubber. It was discovered by *Goodyear* in 1839. He used sulphur molecule to crosslink polyisoprene in natural rubber. Vulcanisation process is largely used in rubber technology. This process involved as follows :

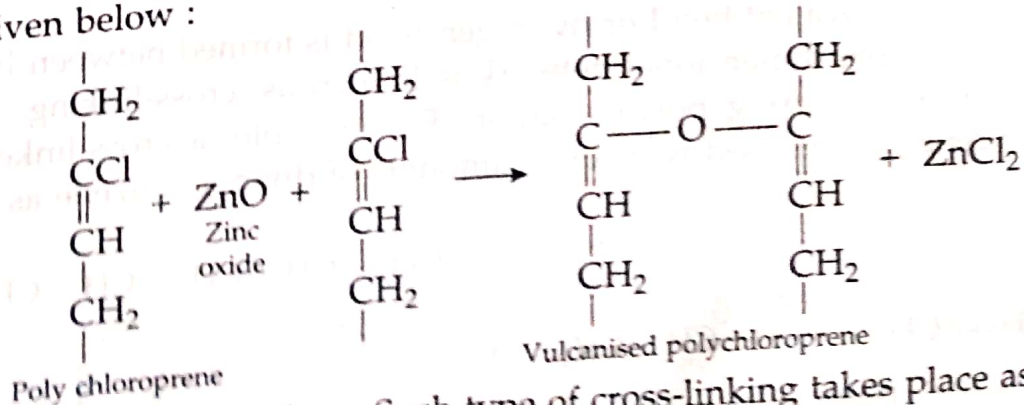
(a) Vulcanisation by sulphur



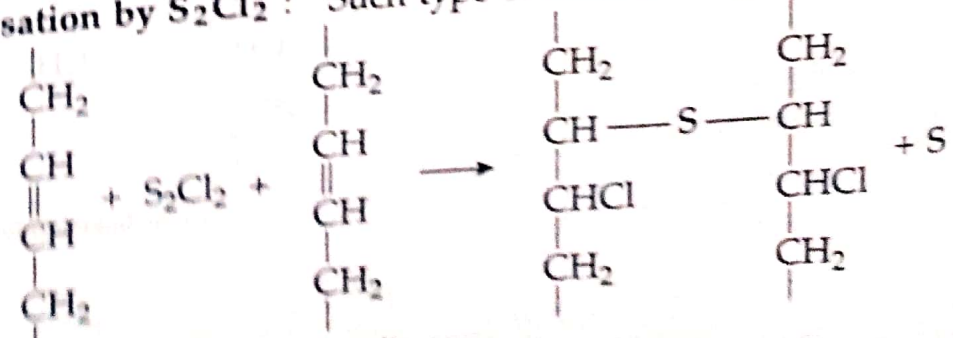
(b) Vulcanisation by benzoyl peroxide : Benzoyl peroxide is used to vulcanise silicon rubber through a free-radical mechanism as :



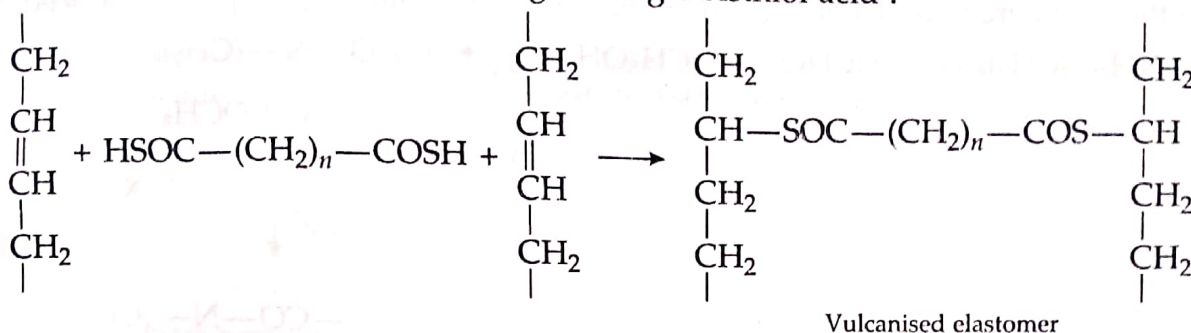
(c) Vulcanisation by zinc Oxide : Zinc oxide involves in vulcanisation of polymer molecule as given below :



(d) Vulcanisation by S₂Cl₂ : Such type of cross-linking takes place as :

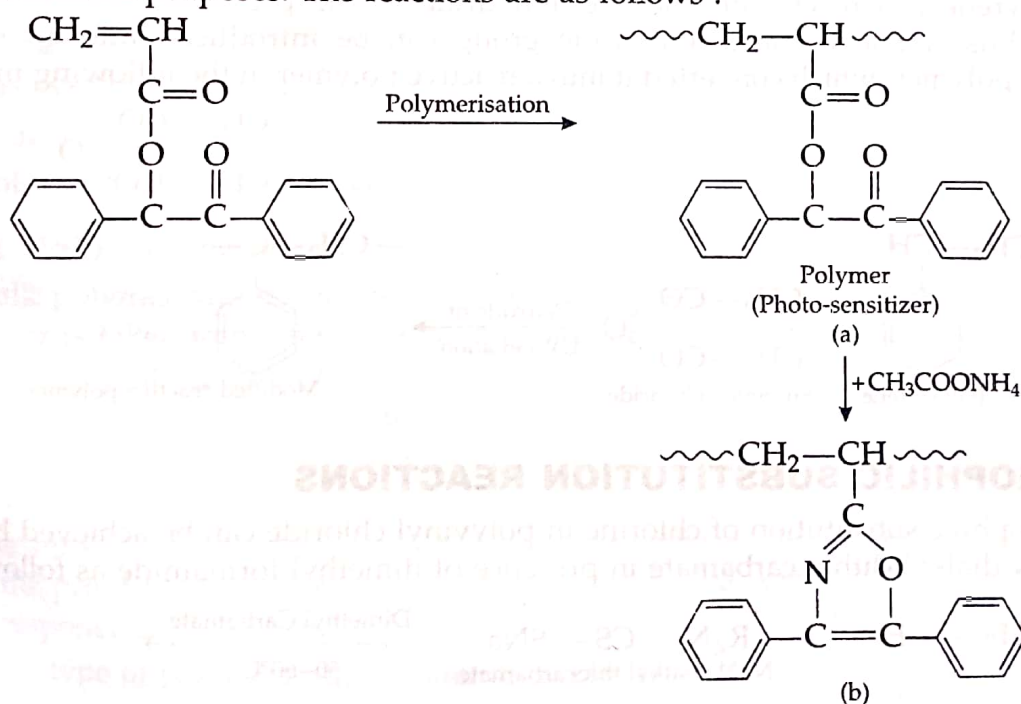


(e) **Vulcanisation by mercapto acid** : In this type of vulcanisation, the cross-linking is effected between two linear chains through a single bithiol acid :



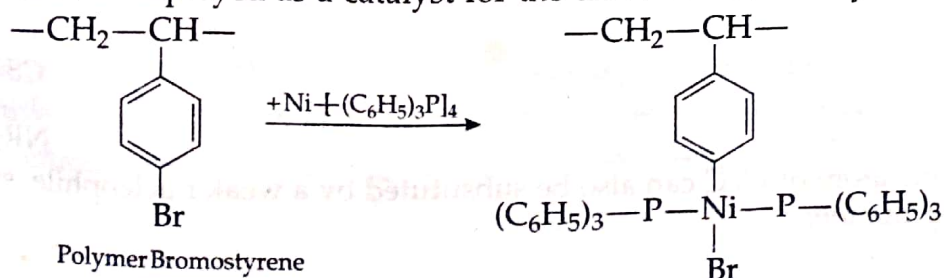
▶ REACTION WITH AMMONIUM ACETATE AND FORMATION OF PHOTOREACTIVE POLYMER

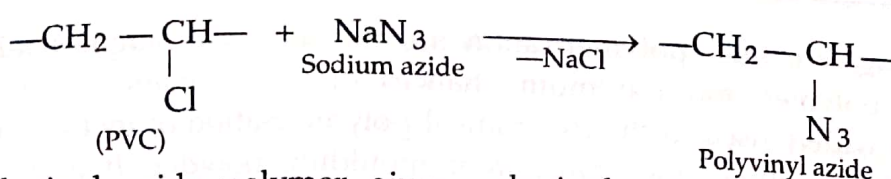
A photoreactive polymer has been synthesised by *M. Okawara* with ammonium acetate. This polymer contains a benzoin structure. Polymer (a) formed by this manner is a photosensitizer for photografting and photocross-linking, while polymer (b) is used for intense fluorescence purposes. The reactions are as follows :



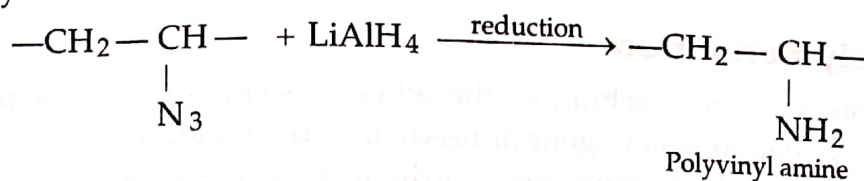
Reaction with Ni-Carbon Compound

The Ni-carbon sigma bond is incorporated in the polymer structure and a new polymer is prepared, which is employed as a catalyst for the dimerisation of ethylene as follows :





The polyvinyl azide polymer gives polyvinyl amine on reduction with lithium aluminium hydride :



▶ POLYMERISATION IN HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

Since the polymerisation is an exothermic reaction, commercially it must be carried out under conditions which allow careful control of temperature, pressure and catalyst. The polymerisation process may be carried out in two systems :

- (1) Homogeneous system (2) Heterogeneous system

(1) Homogeneous System

In this system, following types of polymerisation is possible :

- (a) Bulk Polymerisation (b) Solution Polymerisation
(c) Solution Polycondensation (d) Melt Polycondensation

(a) Bulk Polymerisation

In bulk polymerisation, the whole system remains in a homogeneous phase, because the monomer is taken in the liquid state, the initiator is dissolved in the monomer and the chain transfer agent (if used to control the molecular weight) is also dissolved in the monomer liquid. The reaction mixture is heated or exposed to a UV radiation source for initiating the polymerisation; and is kept on a rotatory shaker for proper mixing the mass and uniform heat transfer.

In the bulk polymerisation, only the initiator and the chain transfer agent is used, therefore, the product formed has a high degree of purity, *i.e.*, without any contamination of reactant components.

In such type of polymerisation, some disadvantages can be noticed :

- (i) As the polymerisation proceeds, the viscosity of the reaction medium increases and its mixing becomes very difficult; leading to products with highly broad molecular weight distribution.
- (ii) As the medium becomes viscous, the diffusibility of the growing polymer chain gets restricted.
- (iii) The probability of chain collision becomes less and termination causes difficulty.
- (iv) Active radical site gets accumulate and the rate of polymerisation increases.
- (v) Sometimes, the excessive heat due to exothermic reaction may lead to an explosion

The advantages of bulk polymerisation are the use of a simple equipment, direct recovery of the polymer and minimum chances of contamination. This technique of polymerisation is widely used in the free-radical polymerisation of methyl methacrylate or styrene to get cast sheetings and transparent moulding powder. It is also used to get polyvinyl chloride resin from vinyl chloride.

(b) Solution Polymerisation

In solution polymerisation technique, the whole system is in a homogeneous phase, because the monomer chain transfer agent (if used) and free-radical initiator are dissolved in an inert suitable solvent, while the ionic and coordination catalysts can either be dissolved or suspended in the solvent medium.

In this polymerisation technique, the temperature is easily controlled because of the fact that the monomers are dissolved in solvent and the upper limit of the whole system depends upon the boiling point of the solvent. Other advantage of this process is that the presence of inert solvent medium helps to control viscosity and promote a uniform heat transfer. Solution technique is used in industrial production of polyacrylonitrile by free-radical polymerisation and also polyisobutylene by cationic polymerisation. This technique is exclusively used in the production of block co-polymers.

This method suffers from some disadvantages :

- (i) The polymer produced is low average molecular weight and is always contaminated with traces of the solvent.
- (ii) The polymer formed will also have to be isolated from the solution either by precipitation in a non-solvent or by evaporation of the solvent.
- (iii) Moreover, difficulty also arises if the solvent is capable of acting as a chain transfer agent.

(c) Solution Polycondensation

In the solution polycondensation technique, all the reactants are dissolved in an inert solvent as a solution, therefore, the whole system is in a homogeneous phase.

In this method, the reaction can be carried out at low temperature during which mass and heat transfer processes are comparatively easier. The solvent can also help as an entrapping agent for the byproduct formed; hence the removal of the byproduct from the final product and solution becomes easy.

This technique is useful in the preparation of liquid polyester resin from the glycols and unsaturated dicarboxylic acid using high boiling aromatic hydrocarbon as solvent.

(d) Melt Polycondensation

The production of polyethylene terephthalate from dimethyl terephthalate and ethylene glycol, and nylon 66 are prepared by using melt polycondensation technique.

In this method, one of the monomers used is solid, which cannot decompose around its melting point. The reaction has to be carried out in an inert atmosphere of N_2 or CO_2 to avoid side reactions such as oxidation, decarboxylation, etc.

Sometimes, the reaction is carried out under reduced pressure to initiate the removal of the byproduct.

The major disadvantage of this technique is removal of the byproduct becomes extremely difficult because there is much increase in the viscosity of the medium.

The polymer formed is in molten state at the reaction temperature and it is important to isolate it from the reactor during hot condition, otherwise it will solidify inside the reactor and removal becomes very hard.

(2) Heterogeneous System

Heterogeneous system falls under two categories :

- (a) Suspension Polymerisation (b) Emulsion Polymerisation

(a) Suspension Polymerisation

Suspension polymerisation is a heterogeneous system, where polymerisation proceeds to 100% conversion and the product is obtained as spherical beads or pearls. For this reason, this technique is known as beads or pearl polymerisation.

By this technique only water-insoluble monomers can be polymerised. In the form of fine droplets, the monomer molecules are suspended in water and mixed with surface active agents and water-soluble protective colloids. During polymerisation process, stirring remains continue. The initiators are monomer soluble. The continuous aqueous phase separating the monomer droplets acts as an heat transfer medium and hence the exothermicity is quite under control.

This is an economical process because here water is taken as heat transfer medium. Isolation of the product is quite easy because this technique involves only filtration of the beads. The surface active agents and protective colloids are washed and removed by water-washing manner. The washed and dried polymer products can be used as such for moulding, coating and adhesive purposes.

By suspension polymerisation method, polyvinyl acetate beads, polystyrene beads and styrene-divinyl copolymer beads can be produced. A fairly narrow molecular weight product can be achieved by this technique.

(b) Emulsion Polymerisation

Emulsion polymerisation is a most widely used industrial technique. The monomers e.g., butadiene, chloroprene, vinyl acetate, vinyl chloride, acrylates and methacrylates, etc., are used to polymerised by this method. A very high molecular weight product can be achieved by this technique. In this system, the monomer is dispersed in the aqueous phase as a uniform emulsion, and the emulsion is stabilised by surfactants (*i.e.*, surface active agents), protective colloids and by certain buffers.

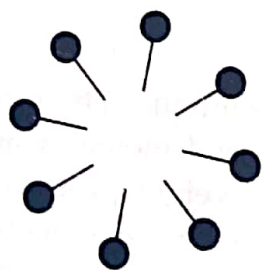
The surfactants used are of three types :

- (i) anionic surfactants which are alkali salts of fatty acids, and of aryl and alkyl sulphonic acids,

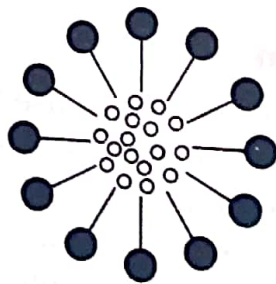
- (ii) cationic surfactants consist of alkyl ammonium halides and alkyl amine hydrochlorides, and
- (iii) non-ionic surfactants involve saccharose esters of fatty acids and alkyl glycosides. Surfactants have low solubility, therefore, they get completely dissolved only at low concentrations. If the concentration is beyond the prescribed limit, the excess amount of surfactants form a molecular aggregate which is called micelles.

The highest concentration at which all the molecules are in a dispersed state, or the concentration above which only micelle formation takes place called 'critical micelle concentration' (CMC). A few examples of surfactants with CMC values are as follows :

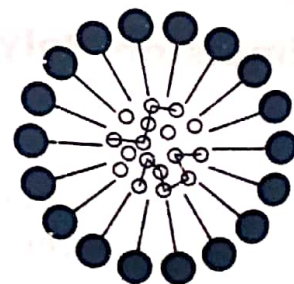
Surfactants	CMC (g/l)
Anionic	
$\text{CH}_3(\text{CH}_2)_6\text{COONa}$	6.5×10^1
$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$	5.6
$\text{CH}_3(\text{CH}_2)_7\text{OSO}_3\text{Na}$	3.0×10^1
$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$	2.6
$\text{CH}_3(\text{CH}_2)_5\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	9.8
$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$	4.0×10^{-1}
Cationic	
$\text{CH}_3(\text{CH}_2)_9\text{NH}_2 \cdot \text{HCl}$	8.5
$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2 \cdot \text{HCl}$	2.7
$\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_3)_3\text{Br}$	7.8×10^1
$\text{CH}_3(\text{CH}_2)_{11}\text{N}(\text{CH}_3)_3\text{Br}$	5.4
Non-ionic	
$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_{11}\text{O}_6$	7.3
$\text{C}_{12}\text{H}_{20}\text{O}_9(\text{C}_{16}\text{H}_{31}\text{O}_2)_2$	1.1×10^{-2}
$\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_{12}\text{H}_{21}\text{O}_{10}$	7.1×10^{-3}



Empty micelle



Monomer filled micelle



Monomer droplets and latex particles containing growing polymer chain

○ Monomer molecule in the polymer chain
● Surfactant molecule

Fig. 10.

The surfactant molecule consists of two parts (A) a long non-polar hydrocarbon chain, (B) a polar group as $-\text{SO}_3\text{Na}$, $-\text{COONa}$, $-\text{NBr}$, or NH_2HCl . In emulsifier molecule, the non-polar part attached with polar end, and form micelle. The hydrocarbon ends of all the emulsifier come close to each other at the interior and polar end align themselves outward. Emulsification can be achieved when the monomer is added and agitated. In the emulsion system, a monomer droplets and micelles are dispersed uniformly.

Emulsion systems generally utilise water soluble initiators such as persulfates or hydrogen peroxide. Redox initiators are also widely used in this system.

Polymerisation occurs at the surface layer of the micelle and proceeds inwards. When the monomer inside the micelle is consumed, more monomer diffuses into the micelle from the monomer droplets present in the aqueous phase. The chain growth remains continue till the another radical species enters and arrests the chain growth. The polymer chain thus agglomerate into fine particles and stabilised by the emulsifier layer of the micelle.

Monomer droplets in this system act only as a reservoir where from the monomer diffuses into micelles or polymer particles.

At the end of polymerisation, the polymer particles are found dispersed uniformly in the aqueous phase and stabilised by the emulsifier layer. This is a milky white dispersion medium which is often called 'latex'. The latex can be used as such for making water-soluble emulsion paints and adhesives, etc. Sometimes, the polymer is isolated from the latex by destabilising the emulsion, by spray drying or by freezing.

In this process, the rate of polymerisation is very high, because the polymerisation is proceeded at the micelles, where the surface/volume ratio is much large. Although, the number of radicals in a micelle is quite limited, even then the continuous supply of monomer molecules to the growing chain takes place, which causes the formation of a very high molecular weight polymer product.

POLYMERISATION