

CHEMISTRY

Organic Polymer [Macromolecules]

By *Dr. B. C. Dixit.*

Definitions :

(a) Monomer : The individual small molecules from which the polymer is formed are known as monomers.

(b) Polymer : Polymers are macro molecules (giant) having high molecular weight and are made up of a great many simpler units – identical to each other or at least chemically similar – joined together in a regular way.

(c) Polymerization : The process by which the monomer molecules are linked together to form a bigger molecule (macro-) is called polymerization.

(d) Degree of polymerization : The number of repeating unit present in the polymer chain is called degree of polymerization (n).

(e) Plastics : When a polymer is shaped in to a hard and tough utility articles by the applications of heat and pressure then it is used as plastics. E.g. P.V.C. polymethyl methacrylate (P.M.M.A.), poly styrene etc. which can be extruded as a sheets or pipes.

(f) Fibers : Fibers are long, thin, thread like bits of material that are having great tensile (pulling) strength in the direction of the fiber. E.g. nylon, terylene, polyester etc.

(g) Elastomers : Elastomer possesses the high degree of elasticity that is characteristic of rubber. It can be greatly deformed and stretched up to eight

times of its original length and yet return to its original shape. E.g. natural rubber, synthetic rubber, silicon rubber.

(h) Co-polymer : Polymers which are made up of two or more different kind of monomers are known as copolymer e.g. styrene- butadiene copolymer.

(i) High polymers: Polymer which contains more than hundred monomers in their backbone is called high polymers.

(j) Initiator : Initiator is species which are responsible to initiate chain reaction by breaking down it self to form a free radical in presence of U.V. light or heating.

Classification of polymers :

Polymer can have different chemical structures, physical properties, mechanical behavior, thermal characteristics etc. and can be classified in different ways.

- (I) Natural and synthetic polymer.
- (II) Organic and inorganic polymer.
- (III) Thermoplastic and thermosetting polymers.
- (IV) Homochain and heterochain polymers.
- (v) Addition and condensation polymers.
- (vi) Homopolymers and copolymers.
- (vii) Fibers, plastics and elastomers.
- (viii) Linear, branched and cross-linked polymers.

(I) Natural and Synthetic Polymer:

Those polymers which are isolated from natural materials are called natural polymer. e.g. Cotton, silk, wool, and rubber.

Those polymer which are synthesized from low molecular weight compounds are called synthetic polymer. E.g. polyethylene, P.V.C., etc.

(II) Organic and Inorganic Polymer:

A polymer whose backbone chain is made up of carbon atom is known as organic polymer. A polymer whose backbone chain is made up of only inorganic molecules and not of carbon atom is known as inorganic polymers. E.g. Glass, silicone, rubber etc.

(III) Thermoplastic and Thermosetting Polymer:

Thermoplastic: Those polymer which soften on heating and molded or extruded in to required shapes and are used as plastics for the manufacturing of a wide range of articles. E.g. Polyethylene, polypropelene, P.V.C, polystyrene, etc.

The process of heating, reshaping and retaining the same on cooling can be repeated several times.

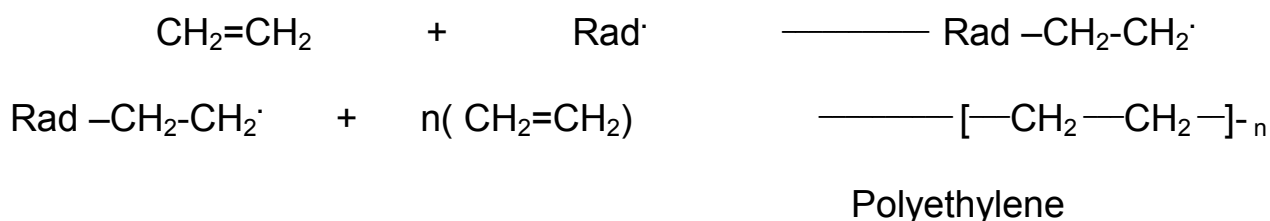
Thermosetting Polymers: A sample of such material is gigantic molecule and heating does not soften it, since softening would require breaking of covalent bond. Indeed, heating may causes formation of additional cross-links and make the material harder, for this reason space network polymer are called thermosetting polymer. Such polymers, upon heating sets into an infusible

mass and once sets can not be reshaped. E.g. Phenol-formaldehyde (Bakelite), Urea-formaldehyde (polyurethane) etc.

(v) Addition and Condensation polymerization:

Addition polymerization: It is also known as chain reaction polymerization.

There is series of reactions each of which consumes a reactive particle and produce another similar particle, each individual reaction thus depends upon the previous one. The reactive particles can be free radicals; cation or anion

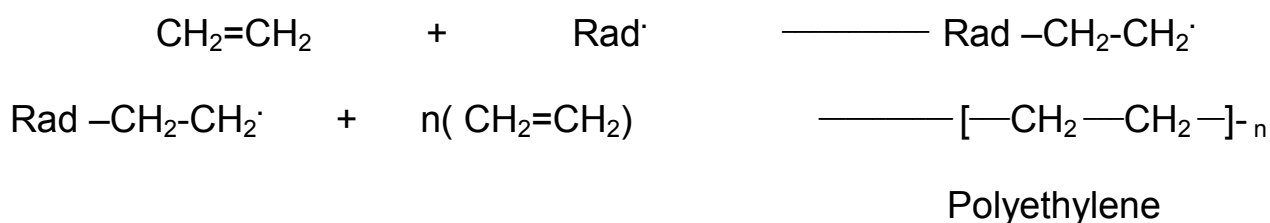


Polymers are formed in two general ways.

(A) Chain reaction polymerization. (Addition polymerization)

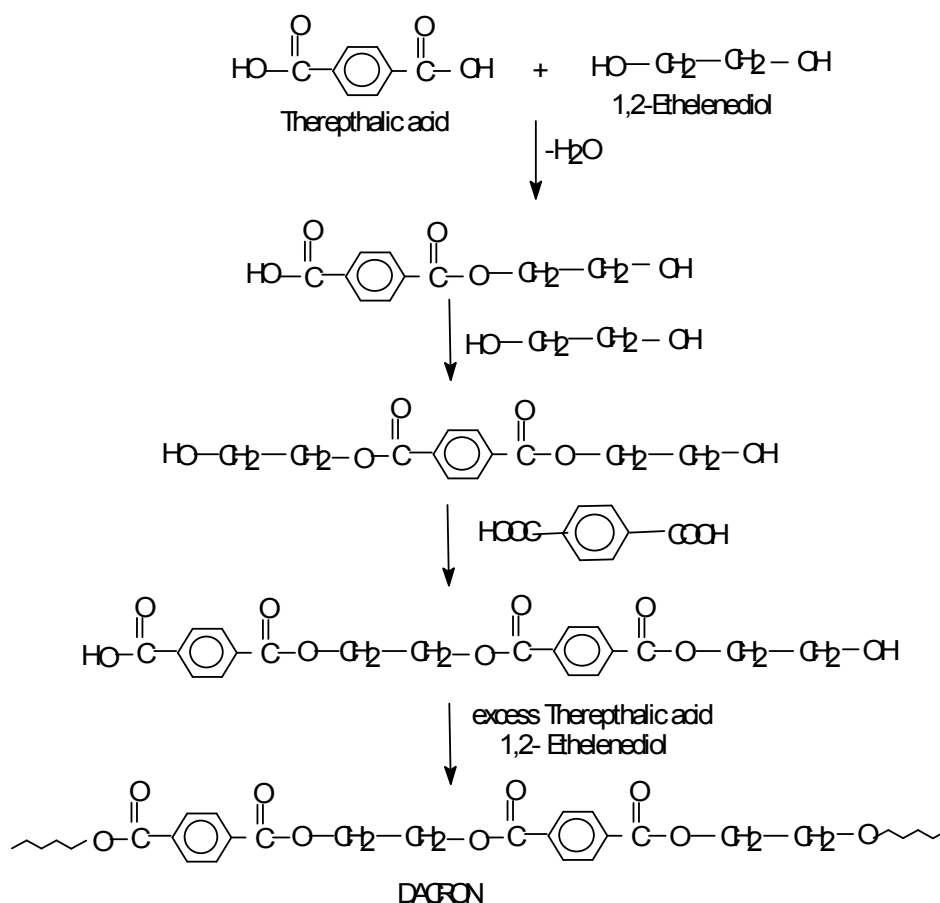
(B) Step reaction polymerization. (Condensation polymerization)

(a) Chain Reaction Polymerization: There is series of reactions each of which consumes a reactive particle and produce another similar particle, each individual reaction thus depends upon the previous one. The reactive particles can be free radicals; cation or anion



(b) Step Reaction Polymerization: There is a series of reactions each of which is essentially independent of the preceding one. Formation of polymer

take place because the monomer undergo reaction at more than one functional group. E.g. A diol reacts with a dicarboxylic acid to form an ester but each moiety of the simple ester still contain a group that can react to generate another ester linkage and hence a large molecule and so on.



(A) Chain Reaction Polymerization:

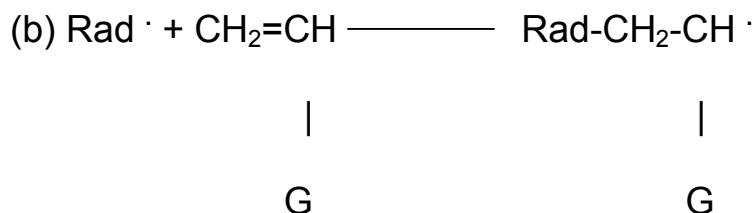
Que. Write Free radical Vinyl Polymerization by taking illustration of Acrylonitrile/V.C. /Styrene/MMA/etc.

Ans. There are a series of reactions. In which an initiator such as peroxide is added to monomer to form a bigger free radical. This bigger radical adds to another monomer (alkene) to generate a still larger radical and so on. And

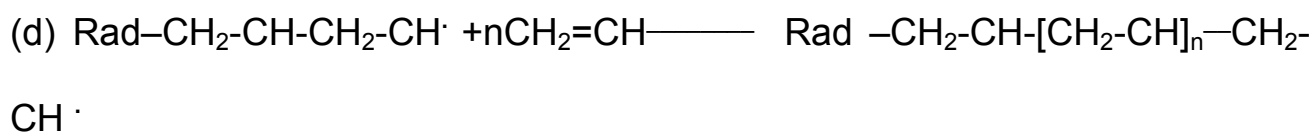
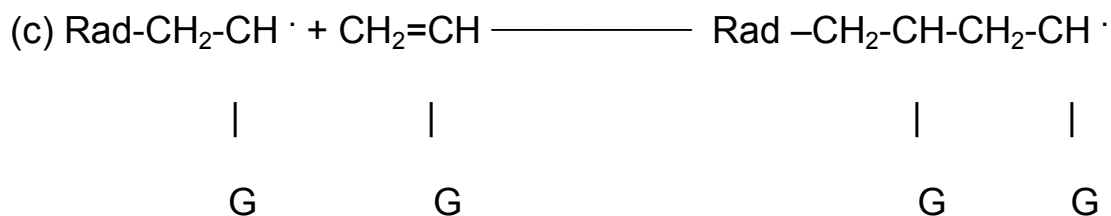
finally at the chain termination large molecule known as polymer is produced.

E.g. Polymerization of vinyl compound it proceeds via three steps.

(i) Chain initiating step: Free radical generated from initiator, adds to the double bond of monomer to form a new bigger free radical.



(ii) Chain propagation:

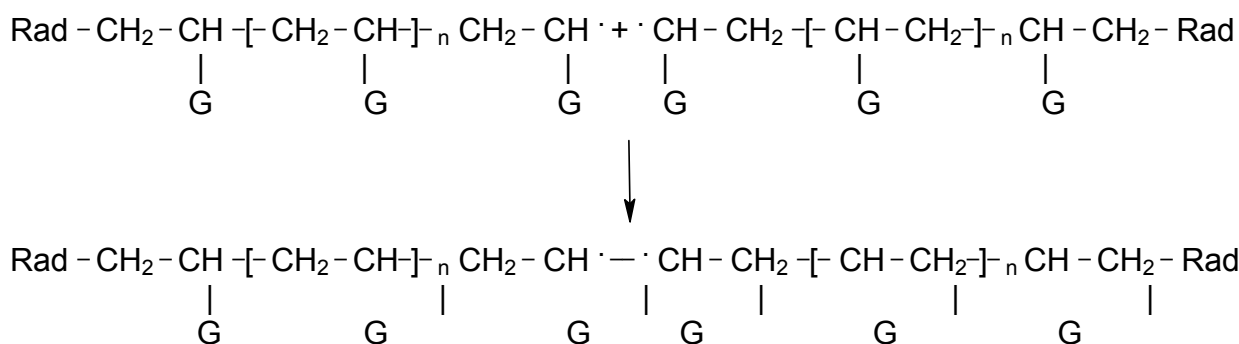


In the propagation step, radical combines with second monomer molecule. This forms a new radical and then after many similar repetition produce large radical. Thus in each step consumption of free radical is accompanied by the formation of new; bigger free radical.

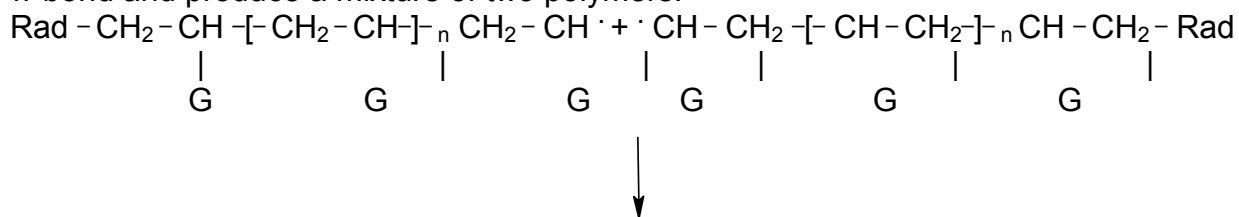
(iii) Chain Termination:

Reaction chain is terminated by combination or disproportionation of two free radicals.

(a) Combination the two radical may pair their odd electrons to produce a polymer.



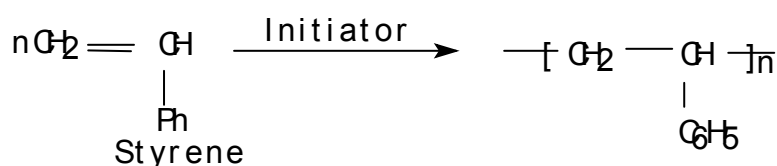
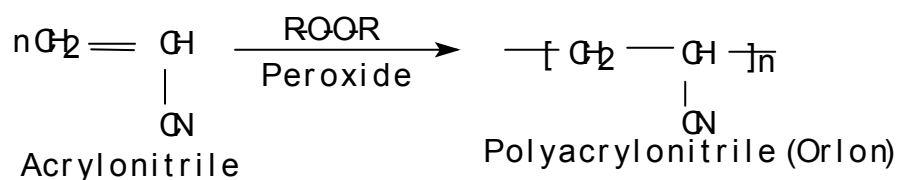
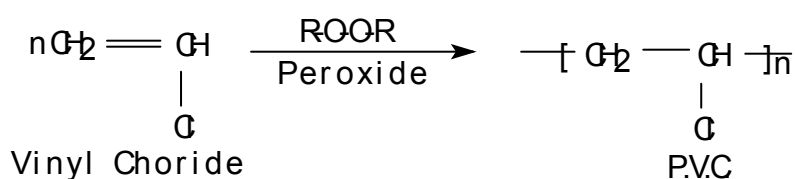
(b) The active site of one radical may strike on the second carbon in the chain of other radical. Here first one radical abstracts an H[·] from the other radical, which forms a π-bond and produce a mixture of two polymers.



Que. State and explain mechanism of Vinyl Polymerization.

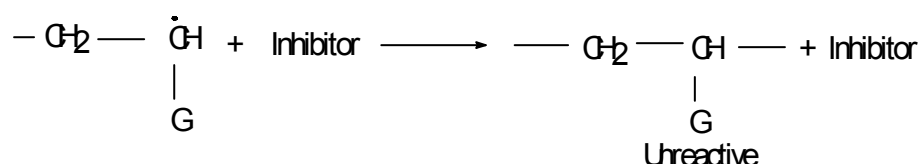
Ans. Free radical vinyl polymerization:

The polymerization of ethylene and substituted ethylene (i.e. styrene, acrylonitrile, vinyl chloride) are carried out using free radicals; which are generated in the presence of a small amount of an initiator such as peroxide. Here the reaction occurs at the doubly bonded carbons i.e. at the vinyl groups and hence is called vinyl polymerization. E.g.



Que. Give an account of Inhibitor:

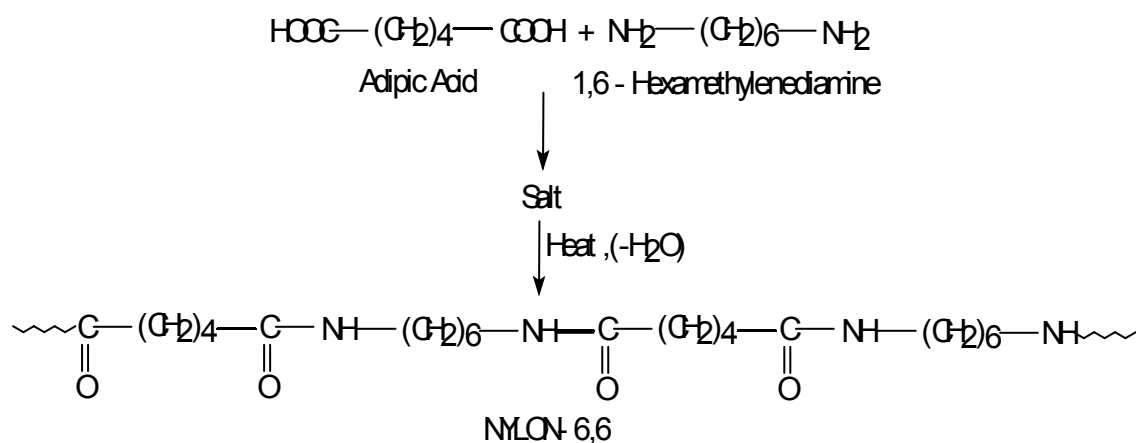
Ans. When compound such as phenols, quinones and some amines are added during polymerization process the growing free radical may react with such compound and therefore reaction chain is terminated, but no new one begun. Such compound is known as inhibitor.



Que. What are Nylons? Give Synthesis of NYLON-- 6,6 also give their uses .

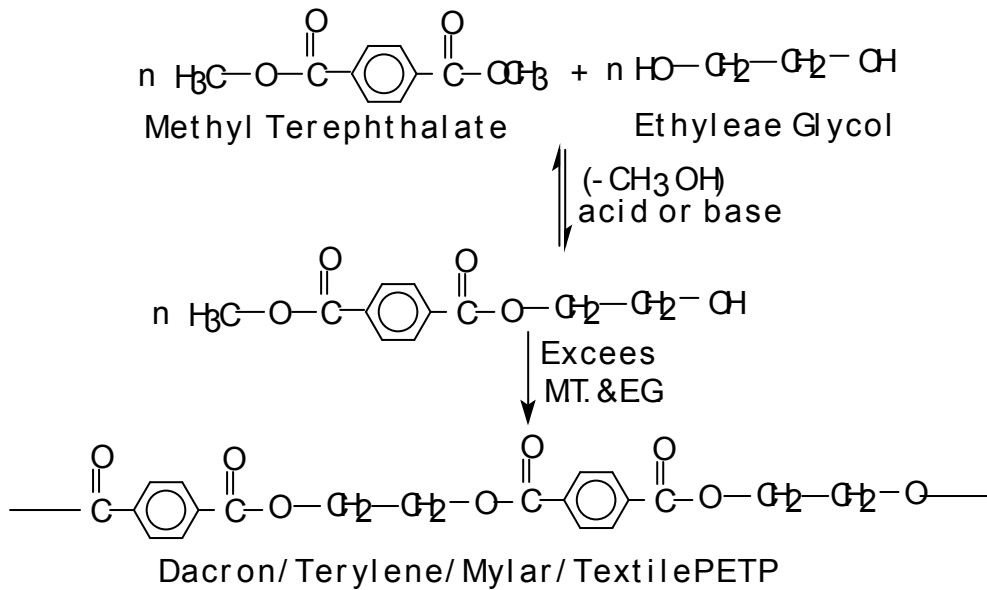
Ans. Step reaction Polymerization: When Carboxylic acid that contains more than one $-\text{COOH}$ group reacts with an amine that contains more than one $-\text{NH}_2$ group then the products are polyamides. Nylons are aliphatic polyamides. There are different types of nylons and are indicated by numbering systems. This numbers gives the number of carbon atom present in (first) the diamines and (second) in the dicarboxylic acid.

NYLON--6,6: It is prepared by the condensation between adipic acid and 1,6-hexanediamine.



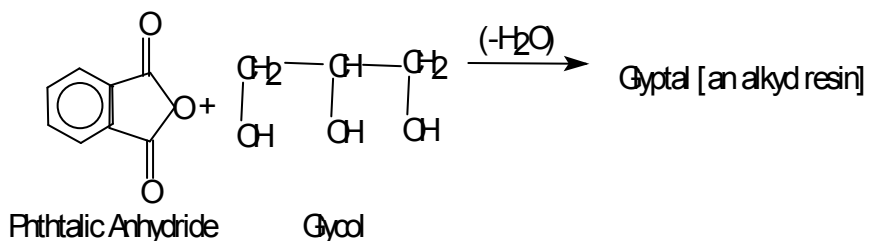
It is used as plastic as well as fiber. As a plastic it is used in gears and bearings. As a fiber it is used in tyres cord and rops.

POLYETHYLENE TEREPHTHALATE (PETP)(Terylene, Dacron): When Carboxylic acid or it's ester that contains more than one $-\text{COOH}$ group or $-\text{COOR}$ group reacts with diol then the products are,



They are used as fibers. It is commonly known as terylene. PETP is also used in films of magnetic recording tapes. The material in sheet form is also marketed as Malar.

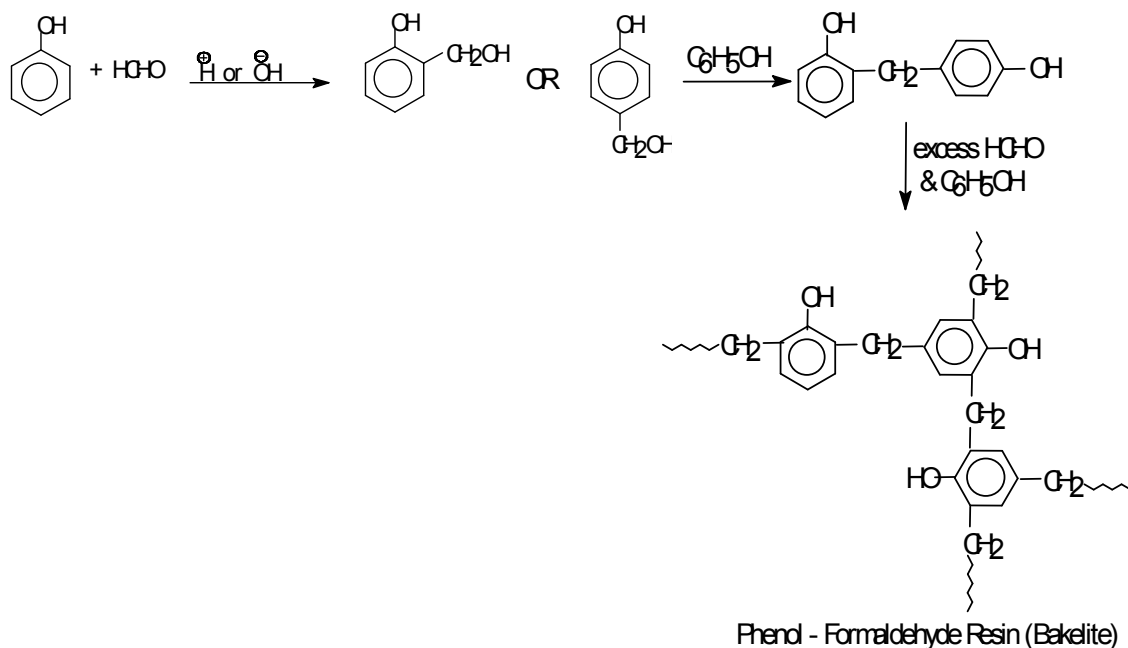
If each monomer molecule contains just two functional groups, growth can occur in only two directions and a linear polymer is obtained as in Dacron. But if a reaction can occur at more than two positions in a monomer, there is a formation of a highly cross-linked space network polymer as in glyptal, an alkyd resin.



Que. Discuss the Step Reaction Polymerization and explain by giving

illustration. Ans. Step reaction polymerization proceeds through a series of reaction in which two monomers each of which contains two functional groups are combined to produce high molecular weight substance and a small molecule like H_2O , HCl or CH_3OH .

Phenol - Formaldehyde (Bakelite) resins are formed by the polycondensation between phenol and formaldehyde. It can be catalysed by either acids or base.



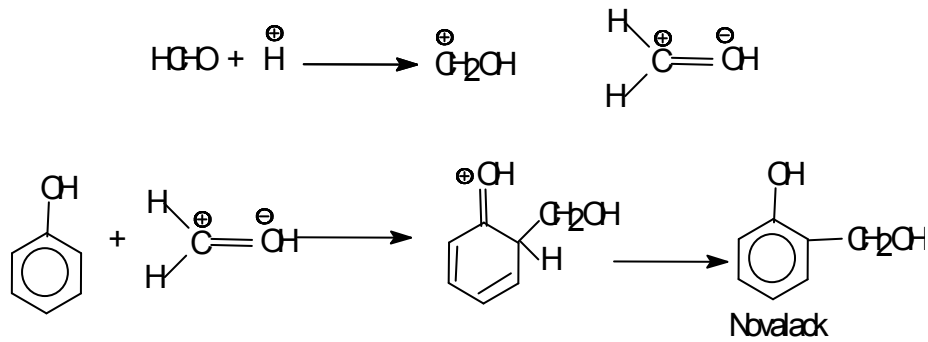
when phenol is treated with formaldehyde in presence of alkali or acid, there is obtained a high molecular weight Phenol – formaldehyde resin, in which many phenol resin are held together by $-CH_2$ groups. The stages involved in the formation of polymer seem to be the following. First phenol reacts with formaldehyde to form O- or P- hydroxymethylphenol. Hydroxymethylphenol then reacts with another molecule of phenol, with the loss of H_2O , to form a

compound in which two rings are joined by a $-\text{CH}_2$ link. This process is then continuous to yield a product of high molecular weight. Since three positions in each phenol molecule are susceptible to attack, the final product contains many cross links and hence has a rigid three-dimensional structure. It is thus a space network polymer.

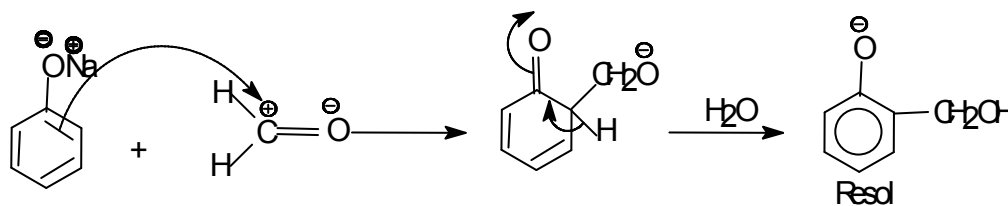
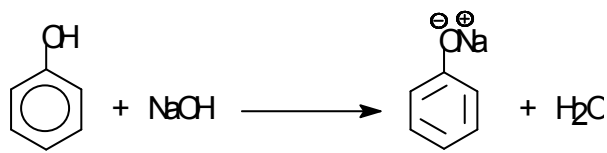
Mechanism Of Phenol Formaldehyde:

Phenol-Formaldehyde (PF) resins are formed by the polycondensation between phenol and formaldehyde. It is catalysed by either acid or base. It proceeds via electrophilic aromatic substitution. The first stage can be viewed as both electrophilic substitution on the ring by the electron deficient carbon of formaldehyde, and nucleophilic addition of the aromatic ring to the carbonyl group. Acid catalyzes reaction by protonating formaldehyde and increasing the electron deficiency of the carbonyl carbon. While base catalyzes reaction converting phenol into a more reactive phenoxide ion.

MECHANISM: (a) The acid catalysed reaction:

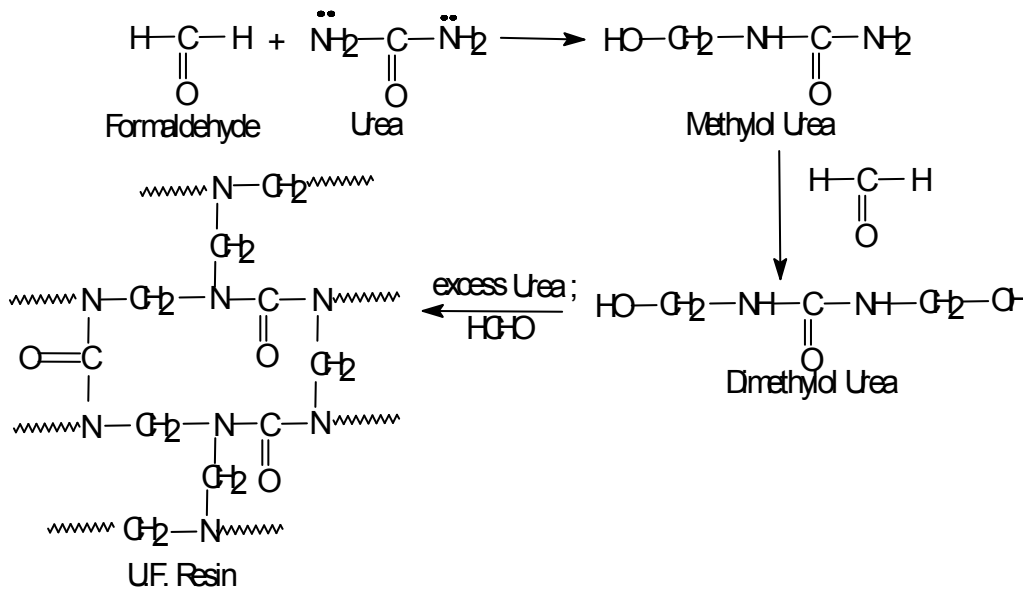


(b) Base catalysed reaction :



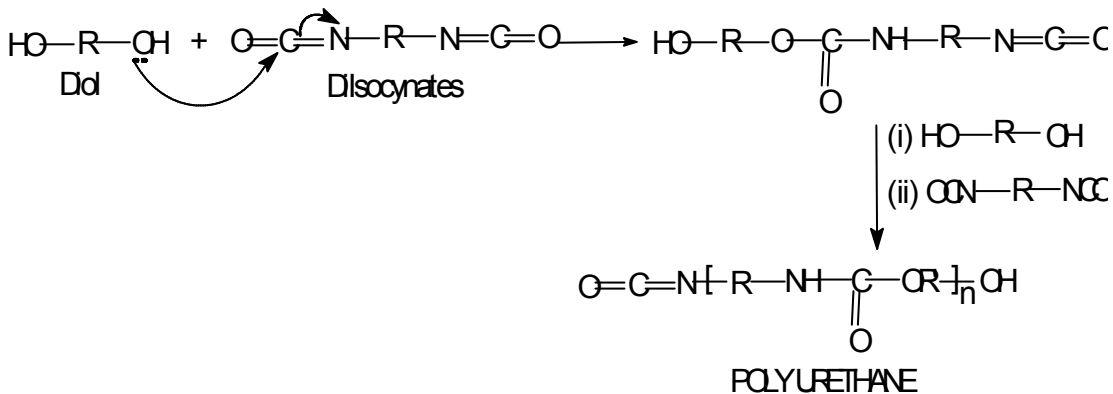
Urea – Formaldehyde Polymer:

When urea reacts with formaldehyde it produces methylol urea, dimethylol urea and so on. It is also step reaction polymerization. When excess urea and formaldehyde are there it will result in a three-dimensional space-network Urea formaldehyde polymer. It is highly important molded plastic. Also used in textile finishing.

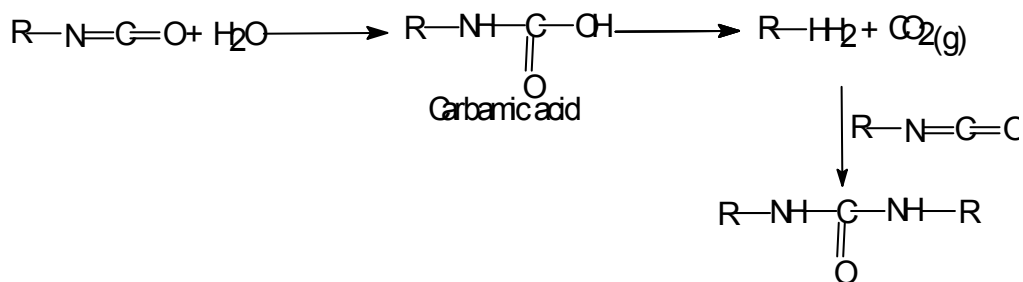


Polyurethane:

When dihydroxy alcohols reacts with diisocyanates will result in polyurethane are;

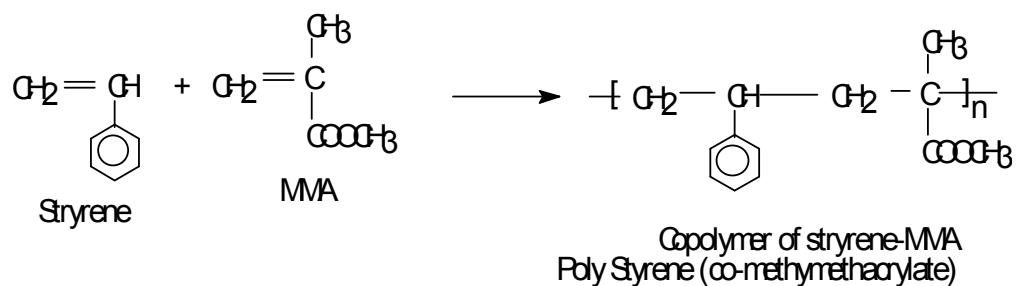
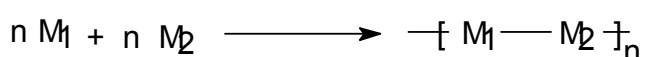


It is linear polymer and have a wide industrial application upon hydrolysis it gives polyurethane form.

**CO-POLYMERIZATION :**

Que. EXPLAIN BY GIVING AN ILLUSTRATION THE COPOLYMERIZATION OR DICUSS THE DIFFERENT PROPERTIES OF COPOLYMERS.

Ans. When a mixture of two or more different monomer is allowed to undergo polymerization, will results in to co-polymer. OR A polymer that contains two or more different kind of monomeric units in the same molecule are known as co-polymer. If the polymer is prepared from different type of monomers (M_1 & M_2) then the process is known as CO-POLYMERIZATION.



By the process of copolymerization the polymer can be made with different properties compare to homopolymerization. E.g. Polystyrene alone have a

good electric insulation properties and can be molded in to parts for radios, television sets and automobiles etc. But when styrene is copolymerized with 30% butadiene adds toughness to the polymer. Styrene with acrylonitrile with (20-30%) increase resistance to impact and to hydrocarbons(solvent). Styrene with maleic anhydride produce polymer which on hydrolysis becomes water soluble and is used as a dispersant and sizing agent. Styrene with 75% butadiene produce an elastomer .

Que. EXPLAIN THE TERM, CO-POLYMERIZATION. DISCUSS THE PROPERTIES OF CO-POLYMERS OBTAINED FROM STYRENE AND BUTADIENE, STYRENE AND MALEIC ANHYDRIDE. OR DISCUSS AND DEFINE COPOLYMERIZATION.

Que. GIVE THE CLASSIFICATION OF COPOLYMER IN DETAIL.

Ans. If two monomers M_1 & M_2 are polymerized together four arrangements are possible in the polymer structure.

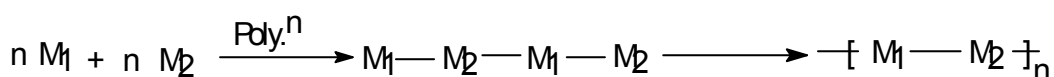
(i) Alternating copolymer.

(ii) Random copolymer

(iii) Block copolymer

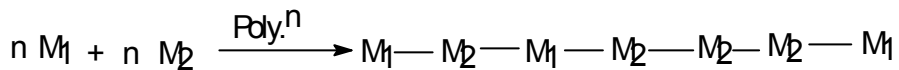
(iv) Graft copolymer

(i) Alternating copolymers : When the two monomer units alternatively in a linear fashion the product so obtained is called alternating copolymers.



e.g. Styrene and methacrylate.

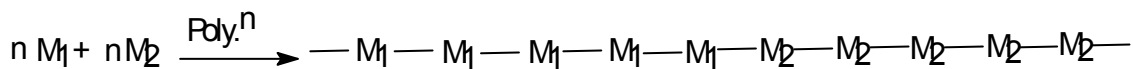
(ii) Random copolymer : When the two monomer are distributed randomly among the chain the product so obtain is called random copolymer.



e.g. Styrene and butadiene.

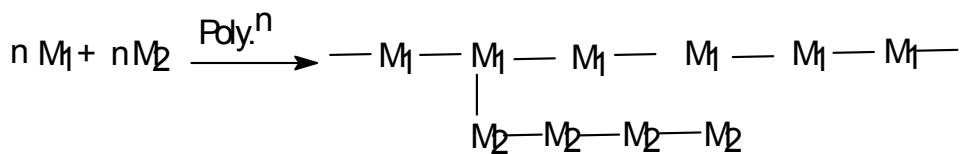
(iii) Block copolymer : When the two monomer get inited in a block made up of one monomer alternate with block of another is called block copolymer.

Here section made up of one monomer alternate with section of another.

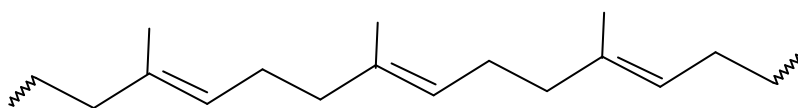


e.g. Ethylene oxide & Ethelene Terphthalate

(iv) Graft copolymer : A branch of one kind is grafted to a chain of another kind. The one monomer unit can be grafted (i.e. added in the form of branched chain) on the linear chain of a polymer molecules. Such branched polymer are known as graft copolymer



E.g. Natural rubber and acrylonitrite.



GUTTA PERCHA trans STEREOISOMER

Plastic: The molecular structure of plastics is of two general kinds. The linear and branched polymers may be more or less crystalline, and include some of the materials also used as fibers: nylon, e.g. They include the various polyalkenes we have mentioned: polyethylene, poly(vinyl chloride), polystyrene, etc. on heating, these polymers soften, and for this reason are called Thermoplastic. It is in this softened state that they can be molded or extruded.

Space-network polymers (or resins) are highly cross-linked to form a rigid but irregular three-dimensional structure, as in phenol-formaldehyde or urea-formaldehyde resins. A sample of such material is essentially one gigantic molecule; heating does not soften it, since softening would require breaking of covalent bonds. Indeed, heating may cause formation of additional cross-links and thus make the material harder; for this reason, these polymers are called Thermosetting polymers. This continuation of the polymerization process through heating is often coupled with the shaping of the product.